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# STUDIES ON THE DESULPHURISATION REACTION

A THESIS

PRESENTED FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN THE

DEPARTMENT OF ORGANIC CHEMISTRY

OF THE

UNIVERSITY OF ADELAIDE.

by

PRADIT CHEUYCHIT, B.Sc., Dip.Ed.

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### Introduction

## CHAPTER II

### Experiments bearing on the mechanism of the desulphurisation reaction.

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# SUMMARY

Use of W-7 Raney nickel catalyst in the desulphurisation of 2,7-dihydrodibenzo[*c,e*]thiepin has been found to give the expected 2,2'-dimethylbiphenyl in 91% yield. Use of partially degassed Raney nickel (W-7J) catalyst gave a much smaller yield of 2,2'-dimethylbiphenyl but phenanthrene was isolated as additional product. The desulphurisation of thianthrene has been studied under varying conditions. Besides the expected dibenzothiophen, and biphenyl, triphenylene has been isolated in one experiment. In a series of experiments, 2,5-diphenyl-1,4-dithiin was desulphurised with W-7J Raney nickel to afford a mixture of sulphur-free products, believed to be 1,3-diphenylbuta-1,3-diene, and 1,3-diphenylcyclobutene in addition to the expected 2,4-diphenylthiophen. Characterization of these compounds is based on their chemical properties, infrared, ultraviolet, and proton magnetic resonance spectra. Desulphurisations of benzo[*b*]thiophen-3-carboxylic acid-1,1-dioxide with W-7 and W-7J, were found to give a mixture of phenylacetic acid and *dl*-hydratropic acid. The benzo[*b*]thiophen-3-carboxylic acid-1,1-dioxide with Aller Raney cobalt catalyst yielded a trace amount of benzo[*b*]thiophen-3-carboxylic acid together with phenylacetic acid and *dl*-hydratropic acid.

Desulphurisation of α-2-thienylbenzyl alcohols has been shown to proceed by two mechanisms. The first involves desulphurisation to the corresponding pentanol, which is then dehydrated to the

corresponding olefin; the second involves hydrogenolysis of the hydroxy group prior to or after removal of sulphur to give the saturated hydrocarbon. "Dimeric" products have also been found from these desulphurisations. In one instance, an undesulphurised dimeric product, namely, 9,9'-di-2"-thienyl-9,9'-bifluorenyl was isolated in addition to the expected 9-n-butylfluorene following the desulphurisation of 9-2'-thienylfluorene-9-ol.

The work described in this thesis is part of a more extensive investigation conducted by a number of other workers in this Department, but incorporates no material previously submitted for a degree in any University except where due reference has been made.

[redacted]

(P. Cheuychit).

# ACKNOWLEDGMENTS

I would like to express my deep gratitude for the advice and encouragement of Professor G.M. Badger and Dr. W.H.F. Sasse to whom this project owes its inception and whose wide knowledge was always at my disposal.

I should also like to thank Dr. R.A. Jones for the determination of the infrared spectra, Dr. T.M. Spotswood for the nuclear magnetic resonance spectra, and other members of this Department for helpful discussions.

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# CHAPTER 1

# INTRODUCTION

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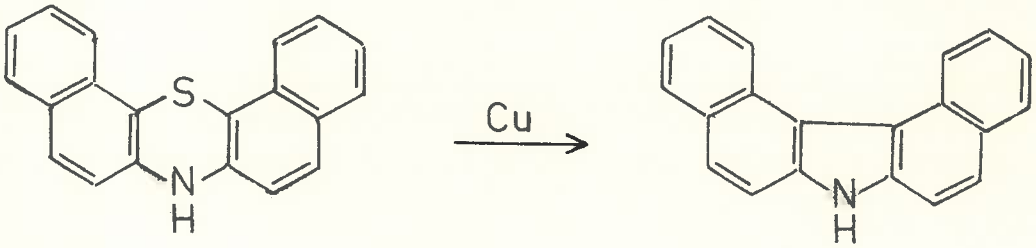
# INTRODUCTION

## (A) SURVEY OF THE DESULPHURISATION REACTION

The so-called "desulphurisation reaction" was first observed in 1886, when Ris synthesized 3,4,5,6-dibenzocarbazole (II) by heating the phenothiazine (I) with metallic copper.[1] The same reaction was later applied to the synthesis of 1,2-benzocarbazole,[2] and of carbazole itself.[3]



I

II

In 1940, Bougault, Cattelain and Chabrier[4] reported that in the presence of Raney nickel, a variety of both inorganic and organic sulphur compounds lose their sulphur under very mild conditions. With organic compounds the site of sulphur in the molecule was usually taken up by hydrogen. When a double bond was also present, hydrogenation of the double bond also occurred, (III).

$$Na_2S + NiH_n + H_2O \longrightarrow 2NaOH + (n/2+1)H_2 + NiS$$

$$HS.CH_2.CH_2.SH \longrightarrow CH_3.CH_3$$

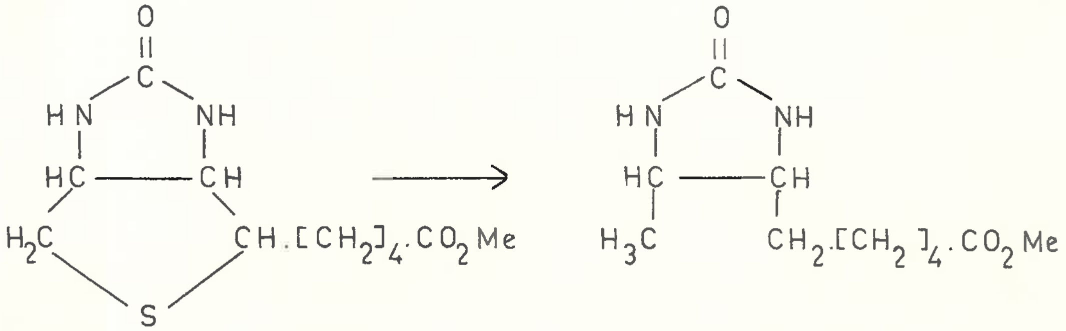
$$Ph.CH{:}C(SH).CO_2H \longrightarrow Ph.CH_2.CH_2.CO_2H$$

They also found that benzene containing thiophen and methylthiophen, after treatment with Raney nickel, gives a negative test with sulphuric acid and isatin and is sulphur-free. This method has become one of the most efficient laboratory techniques available for providing sulphur-free solvents.

The first remarkable success of the desulphurisation reaction was the elucidation of the structure of biotin (IV) in the year 1942.[5] This was made possible by the work of Mozingo, Wolf, Harris and Folkers[6] who showed that sulphides, sulphoxides, sulphones and disulphides undergo reductive cleavage when treated with Raney nickel catalyst.

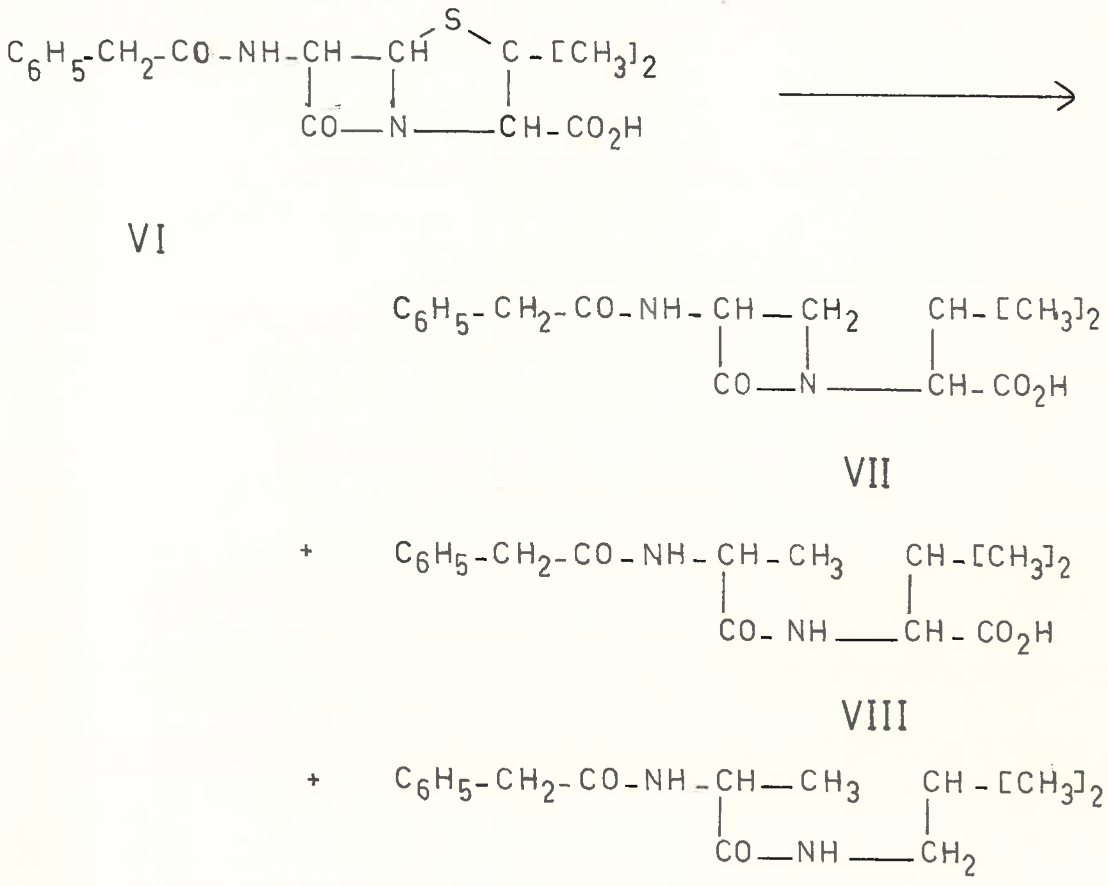
$$\begin{tikzcd}
R{-}S{-}R \arrow[dr] & & R{-}SO_2{-}R \arrow[dl] \\
& 2RH & \\
R{-}SO{-}R \arrow[ur] & & R{-}S{-}S{-}R \arrow[ul]
\end{tikzcd}$$

When the reaction was applied to biotin (IV), du Vigneaud *et al.*[5] obtained a desthio derivative (V), that was further degraded to a diaminopelargonic acid.



IV V

From this time onwards Raney nickel has been used successfully, and has become an everyday procedure in research on organo-sulphur compounds. While it has been used mainly for organic structural and synthetical problems,[7,8] it has also been applied to the quantitative determination of sulphur.[9,10,11] An outstanding example of the elucidation of an unusual organic structure is the desulphurisation of benzylpenicillin[12] which give dethiobenzylpenicillin, phenylacetyl-L-alanyl-D-valine, together with its decarboxylation product. The β-lactam ring, preserved in VII, served to provide evidence for the existence of such a structural feature in penicillin. Similar examples include the desulphurisations of ω,ω'-bimethionine,[13] streptomycin,[14] and oxytocin.[15]



$$C_6H_5\text{-}CH_2\text{-}CO\text{-}NH\text{-}\begin{array}{c}CH\\|\\CO\end{array}\!\!-\!\!\begin{array}{c}CH\\|\\N\end{array}\!\!\overset{S}{\frown}\!\!\begin{array}{c}C\text{-}[CH_3]_2\\|\\CH\text{-}CO_2H\end{array} \longrightarrow$$

VI

$$C_6H_5\text{-}CH_2\text{-}CO\text{-}NH\text{-}\begin{array}{c}CH\\|\\CO\end{array}\!\!-\!\!\begin{array}{c}CH_2\\|\\N\end{array}\!\!-\!\!\begin{array}{c}CH\text{-}[CH_3]_2\\|\\CH\text{-}CO_2H\end{array}$$

VII

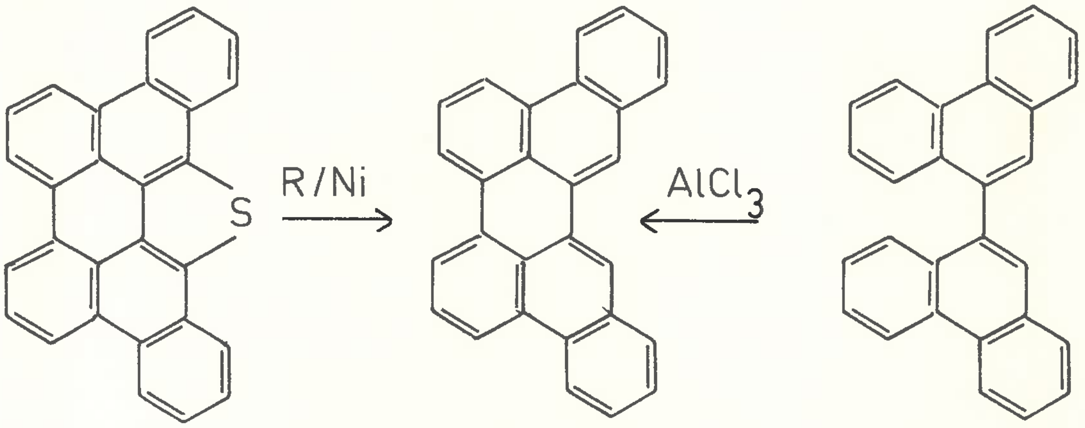
$$+\quad C_6H_5\text{-}CH_2\text{-}CO\text{-}NH\text{-}\begin{array}{c}CH\text{-}CH_3\\|\\CO\text{-}NH\end{array}\!\!-\!\!\begin{array}{c}CH\text{-}[CH_3]_2\\|\\CH\text{-}CO_2H\end{array}$$

VIII

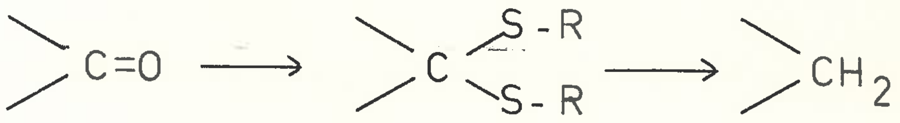
$$+\quad C_6H_5\text{-}CH_2\text{-}CO\text{-}NH\text{-}\begin{array}{c}CH\text{—}CH_3\\|\\CO\text{—}NH\end{array}\!\!-\!\!\begin{array}{c}CH\text{-}[CH_3]_2\\|\\CH_2\end{array}$$

IX

Desulphurisation of flavophen (X) with Raney nickel in boiling mesitylene yields 2,3-10,11-dibenzoperylene (XI), which is identical with the product obtained from 9,9'-diphenanthryl and aluminium chloride. This provided satisfactory evidence for the structure of the parent sulphur compound.[16]



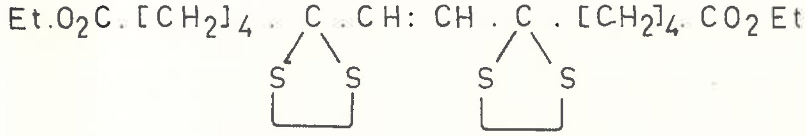
The successful applications of the desulphurisation reaction to structural problems were accompanied by the development of novel synthetical procedures which were based on the removal of sulphur from organic molecules by means of Raney nickel. Early work dealt with the transformation of certain groups. An important example of these is the conversion of a carbonyl group to a methylene group <u>via</u> a desulphurisation of the corresponding thioacetal or thioketal.[17]



$$>C{=}O \longrightarrow >C\begin{matrix}S-R\\S-R\end{matrix} \longrightarrow >CH_2$$

The first account of the desulphurisation of a thioacetal was published in 1944 by Wolfrom and Karabinos, who obtained, in good yields, toluene and <u>n</u>-heptane from the ethyl mercaptan derivatives of benzaldehyde and heptan-2-one respectively.[17] The method has since been employed mainly in steroid and in carbohydrate chemistry.[18-30] As the reaction can be carried out in almost neutral media, it has in many cases proved to be superior to the alternative methods of reduction which are associated with the names of Clemmensen and Wolff-Kishner.

In this way, treatment of the unsaturated dithioketal (XII) with W-4 Raney nickel in boiling ethanol gave diethyltetradecanedioate (XIII), but with deactivated Raney nickel, inseparable mixtures of saturated and unsaturated esters in different proportions, depending on refluxing time of the catalyst in acetone, were obtained.[31] In the same way, desulphurisation of (XIV) gave the normal product, without reduction of the nitrile group, in fairly good yield.[32]

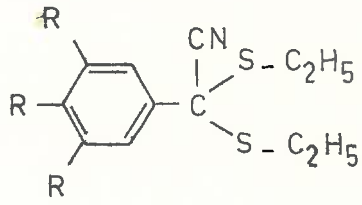


XII

$$\longrightarrow \quad Et.O_2C.[CH_2]_{12}.CO_2Et$$

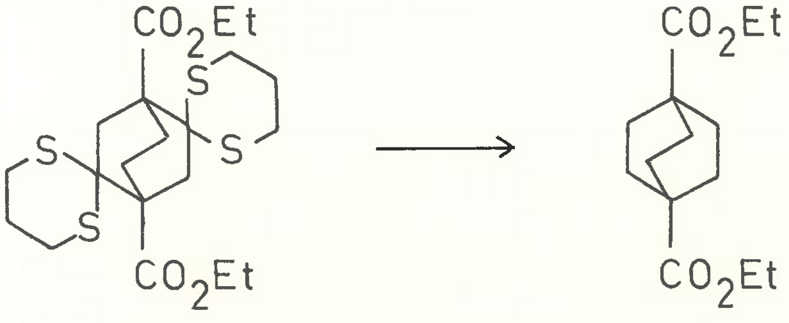
XIII

$$+ \quad Et.O_2C.[CH_2]_5.CH:CH.[CH_2]_5.CO_2Et$$



XIV

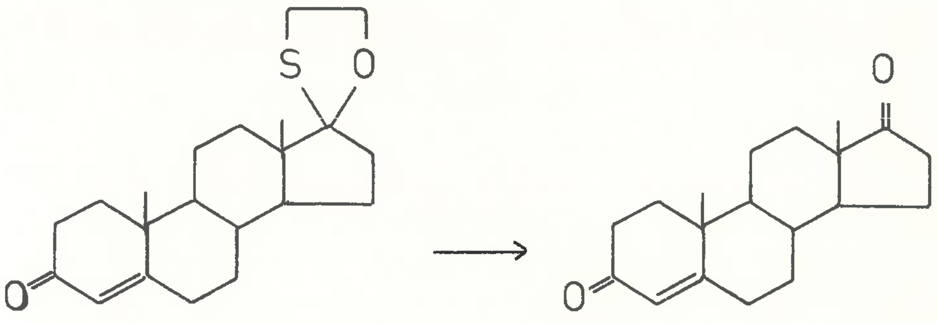
A special example is provided by the synthesis of dicarbethoxy-bicycloöctane (XVI) from (XV) in 70%,[33] and in 83% yield.[34] Several attempts to reduce the parent 2,5-diketone by the Wolff-Kishner and Clemmensen methods gave less than 15% of the expected diethyl bicyclo(2,2,2)octane-1,4-dicarboxylate.[33]



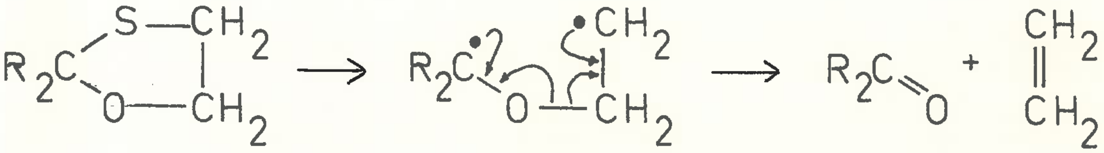
XV XVI

The literature is rich in examples of desulphurisations of dithioketals derived from heterocyclic compounds,[35-38] and carbocyclic compounds[39-45] including terpenes[46] and steroids.[47-71] These reactions have recently been reviewed.[72,73]

The desulphurisation of hemithioketals (e.g. XVII) has provided some interesting results.[24] In general the parent ketones were regenerated and the expected ethyl ethers were not observed. Desulphurisation of androst-4-ene-3,17-dione-17-ethylenehemithioketal afforded the original diketone (XVIII). This has been explained by assuming that the diketone might arise through the decomposition of an intermediate diradical to give ethylene as in the scheme (XIX ⟶ XXI),[24]

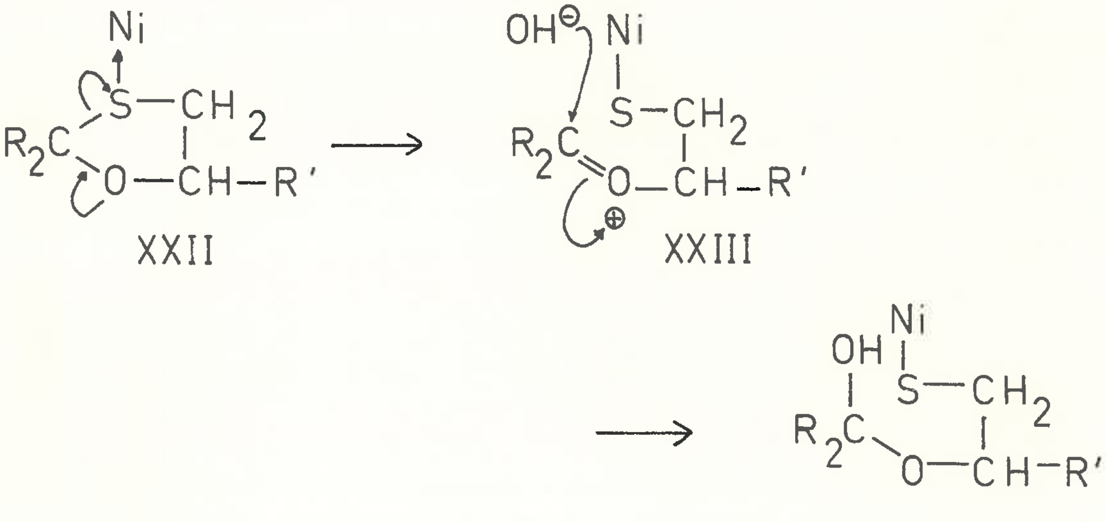


XVII XVIII

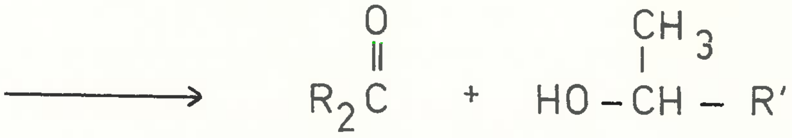


XIX XX XXI

However, subsequent work by Djerassi and his collaborators[25,28] suggested that oxygen may have been introduced from an outside source during the reaction. The mechanism (XXII → XXV) has been proposed by these authors for this reaction.



XXII XXIII XXIV



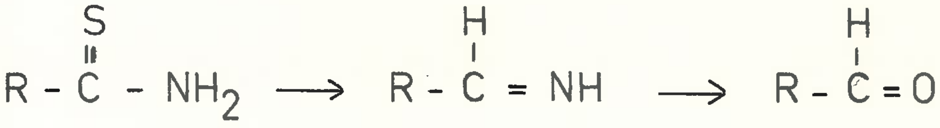
$$\longrightarrow \quad R_2\overset{\overset{\displaystyle O}{\|}}{C} \quad + \quad HO-\overset{\overset{\displaystyle CH_3}{|}}{C}H-R'$$

XXV

Various substituted thioamides have been converted to the corresponding substituted amines by means of Raney nickel.[74] A number of successful applications have been reported in recent years.[75-79]

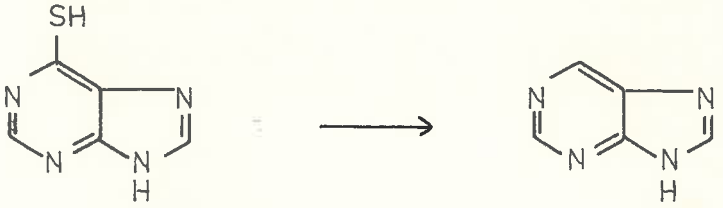
$$R-\overset{\overset{\displaystyle S}{\|}}{C}-NR'R'' \longrightarrow R-CH_2-NR'R''$$

With partially deactivated Raney nickel, the desulphurisation of simple or substituted amides or anilides affords aldehydes, supposedly by a two-step reaction.[23]

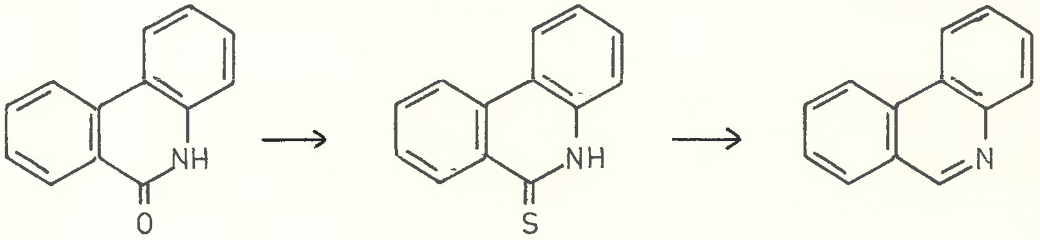


$$R-\overset{\overset{\displaystyle S}{\|}}{C}-NH_2 \longrightarrow R-\overset{\overset{\displaystyle H}{|}}{C}=NH \longrightarrow R-\overset{\overset{\displaystyle H}{|}}{C}=O$$

Generally the desulphurisation of thiols and thiones proceeds very readily by treatment with Raney nickel. The reactions range from relatively simple reductive desulphurisations, as in the early work of Bougault and his colleagues,[4] to more complex examples such as the transformation of 2-mercaptobenzothiazole which yields mixtures of various products.[80,81] The desulphurisation of 6-mercaptopurine (XXVI) which has been carried out in ethanolic ammonium hydroxide solution, or in boiling water, affords purine (XXVII) in good yield.[82] This example demonstrates a means for removing functional groups, especially in heterocyclic systems, by conversion to the thiol, followed by desulphurisation. In a similar fashion, reduction of phenanthridone (XXVIII) to phenanthridine (XXX) has been carried out *via* the phenanthridinethione (XXIX).[83,84]

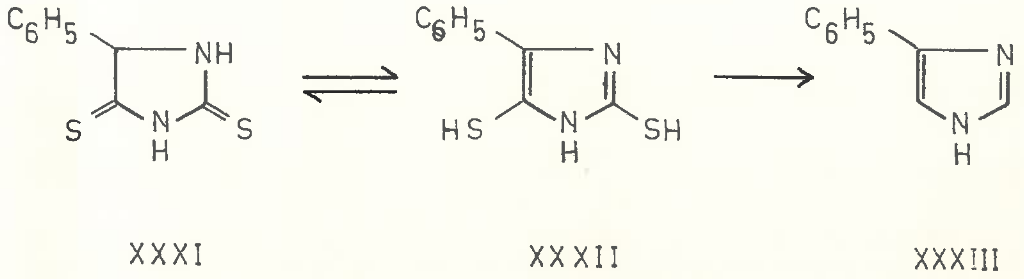


XXVI XXVII

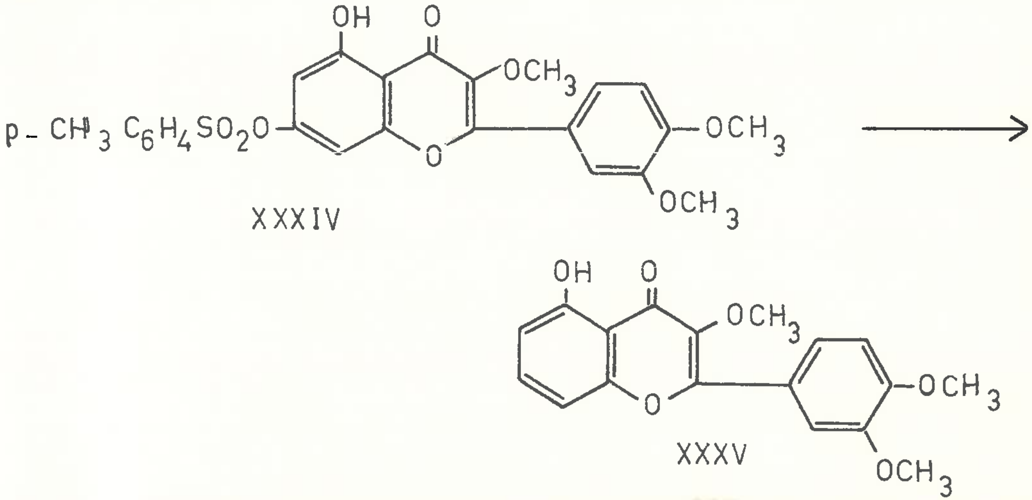


XXVIII XXIX XXX

Mercaptoquinazolines[85] and mercaptoimidazoles[86] have been similarly desulphurised. A great number of thiohydantoins, thiobarbituric acids and thiouracils, with one or more sulphur atoms attached directly to the aromatic ring have been desulphurised,[87-89] and these compounds are convenient starting materials for the synthesis of otherwise difficultly obtainable substances.[99-102] Thus imidazoles (XXXIII) can be prepared by removal of sulphur from thiohydantoins (XXXI).[103]



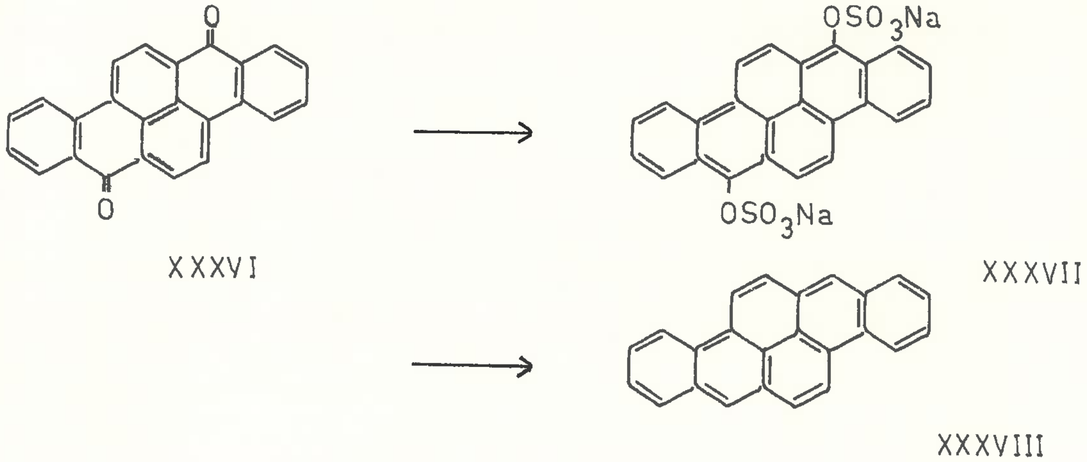
Closely related is the removal of phenolic hydroxy groups by the hydrogenolysis of the p-toluenesulphonates,[104] using either Raney nickel and hydrogen at room temperature and atmospheric pressure, or using ordinary desulphurisation conditions. Sometimes this has been found to result in the selective removal of one hydroxy group from a polyhydroxy compound.[105,106] This has been used to advantage in the synthesis of several flavones. The selective removal of the 7-hydroxy group from 5,7-dihydroxy-3,3',4'-trimethoxyflavone, for example, has been accomplished via the 7-tosyl derivative (XXXIV).[107]



XXXIV

XXXV

Venkataraman and his collaborators[108] have also developed a general method for the reduction of quinones to dihydroaromatic compounds by conversion to the sulphuric esters of the leuco forms, followed by desulphurisation using the method of Schwenk, Papa and Ginsberg. In this way the hydrogenolysis of the disulphuric acid ester of anthrahydroquinone and of Indanthrene Golden Yellow GK (3,4:8,9-dibenzopyrene-5,10-quinone) (XXXVI) yields the corresponding hydrogenated products, which on dehydrogenation furnish anthracene and 3,4:8,9-dibenzopyrene (XXXVIII) respectively.[108,109] Many other examples have also demonstrated the usefulness of this reduction route.[110]

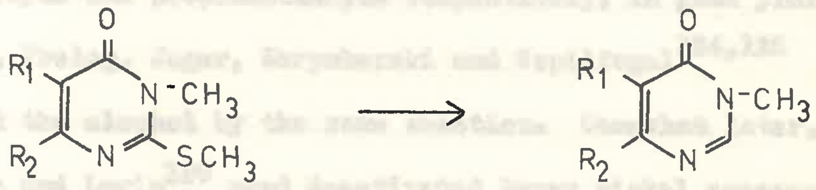


XXXVI

XXXVII

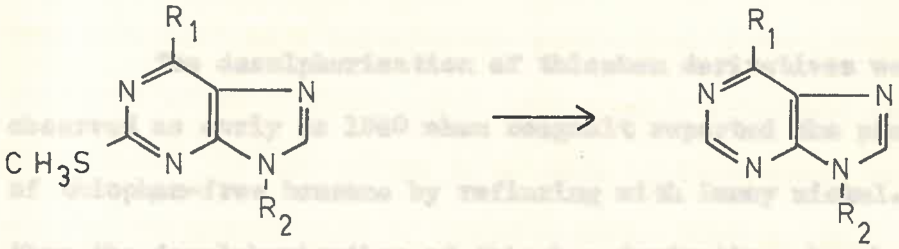
XXXVIII

The reductive desulphurisation of thioethers can sometimes be carried out selectively in the presence of other reducible groups. For example, some derivatives of 2-methylthio-3-methyl-4-oxodihydropyrimidine (XXXIX) have been desulphurised with Raney nickel without hydrogenation of the ring.[95]



XXXIX XL

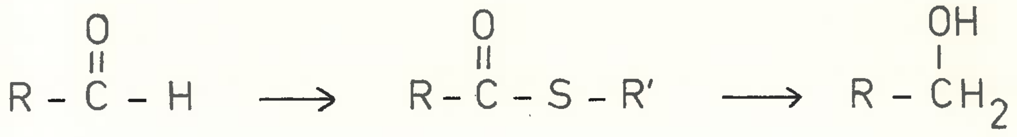
Many 2-methylthiopurine derivatives (XLI) have been desulphurised in the course of synthesizing some biologically interesting substances.[111-115]



XLI XLII

Raney nickel desulphurisations have been employed in the preparation of deoxy-sugars and some of their pyrimidine- or purineglycosides which are important in cancer research.[116-118] Studies of the desulphurisation of cyclic thioethers have also contributed to the knowledge of thioindigo chemistry.[119,120]

The desulphurisation of thiol esters produces either aldehydes[121] (which can be considered as the primary hydrogenolysis products) or alcohols, resulting from further reduction. This reaction was first described by Wolfrom and Karabinos[122,123] who transformed ethyl thiobenzoate and ethyl thiopropionate into benzaldehyde and propionaldehyde respectively, in good yield. However, Prelog, Jeger, Norymberski and Szpilfogel[124,125] obtained the alcohol by the same reaction. Somewhat later, Spero, McIntosh and Levin[126] used deactivated Raney nickel successfully to stop the reaction at the aldehyde stage.

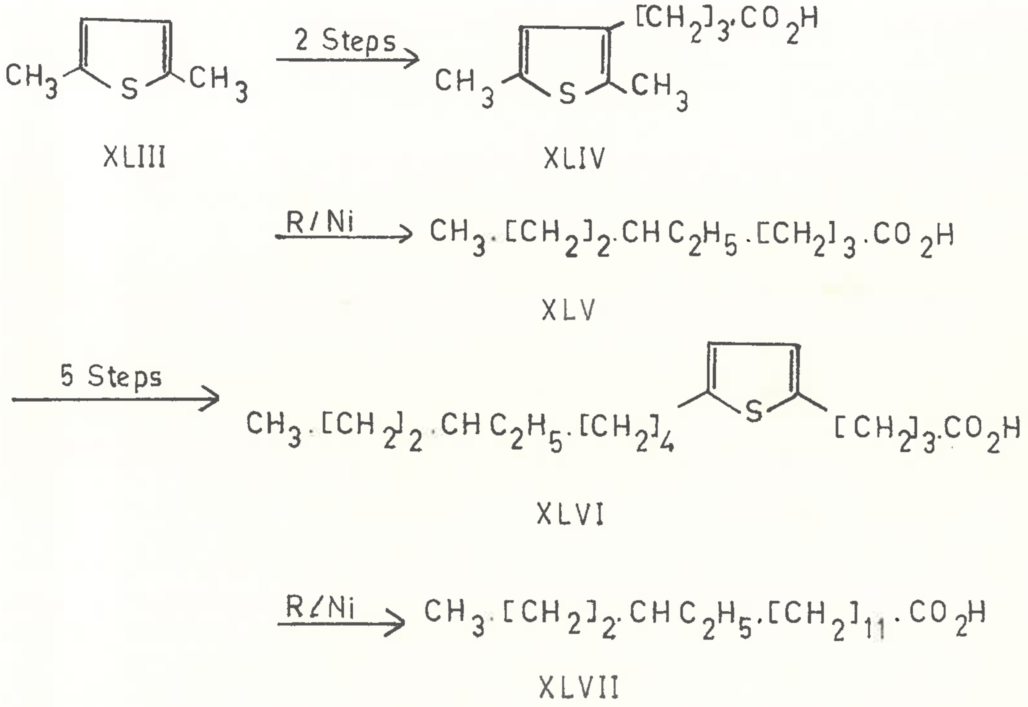


$$R-\overset{O}{\overset{\|}{C}}-H \longrightarrow R-\overset{O}{\overset{\|}{C}}-S-R' \longrightarrow R-\overset{OH}{\overset{|}{C}}H_2$$

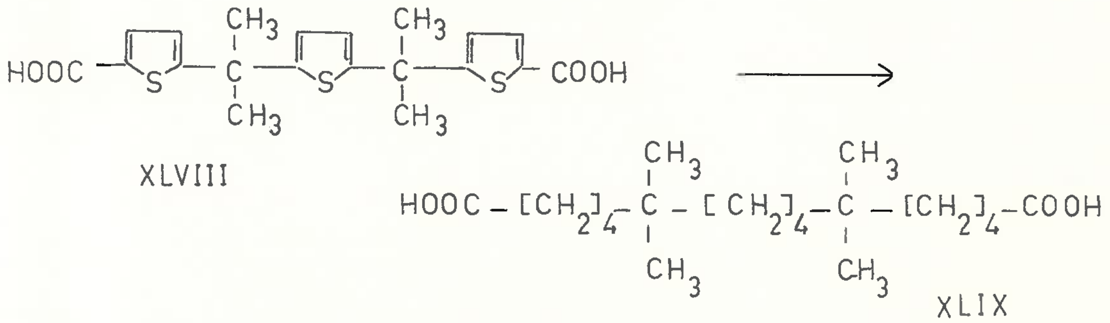
The desulphurisation of thiophen derivatives was first observed as early as 1940 when Bougault reported the preparation of thiophen-free benzene by refluxing with Raney nickel. Since then the desulphurisation of thiophen derivatives has been developed as a synthetical route to a variety of otherwise more difficultly accessible compounds. The desulphurisation of benzo[*b*]thiophen-2-carboxylic acid and benzo[*b*]thiophen-3-acetic acid was reported in the year 1948 by Blicke and Sheets,[127] and gave $\beta$-phenylpropionic acid and $\gamma$-phenylbutyric acid, respectively.

This drew attention to the advantages of this simple method for the confirmation of the structure of such thiophen derivatives. Papa, Schwenk and Ginsberg,[128] in 1949, desulphurised some acidic derivativesof thiophen by the gradual addition of nickel-aluminium alloy to the acid solution in alkali. They obtained heptan-3-one-1-carboxylic acid and 3-hydroxyheptane-1-carboxylic acid lactone by desulphurisation of β-(2-thenoyl)propionic acid; and several other thiophen derivatives were similarly desulphurised. From 1952, the desulphurisation of thiophen derivatives had its potentialities fully recognized. Among these, the studies of Badger, Buu-Hoï and Goldfarb and their groups are notable. Up to the present time, more than 200 thiophen-desulphurisations have been described.

The desulphurisation of acids derived from thiophen has been developed as a satisfactory synthetical method which allows the preparation of fatty acids from readily available starting materials.[8] It also serves as a means of lengthening carbon chains, and for the preparation of branched-chain fatty acids. Many of these are, of course, difficult to obtain by other methods. In this way, a great number of 2,5-disubstituted thiophens, carrying carboxyl groups in side chains, have been transformed into the corresponding aliphatic or aryl-aliphatic mono- or di-carboxylic acids. Several experimental variations have been reported. Thus, the preparation of 5-ethyloctanoic acid[129] (XLV) has been achieved by the desulphurisation of γ-(2,5-dimethyl-3-thienyl)butyric acid, which is readily prepared from 2,5-dimethylthiophen (XLIII). This branched-chain acid has itself been used as a starting point in a further synthesis to give 13-ethylhexadecanoic acid (XLVII).[129]

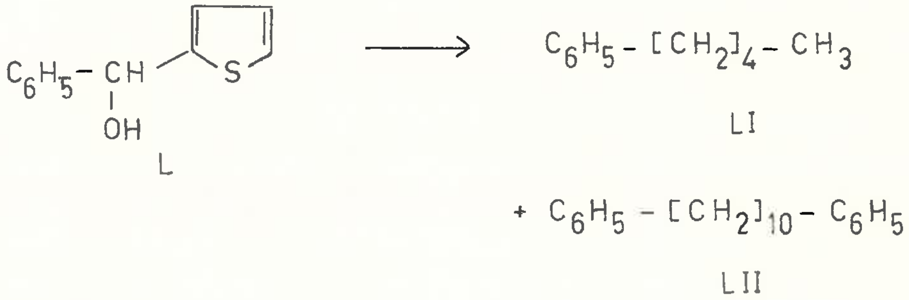


In the same way, 5-*t*-butylthiophen-2-carboxylic acid,[130] 5-ethylthiophen-2-carboxylic acid,[131] ω-(2-butyl-5-thenoyl)pelargonic acid,[132] γ-[2(β-methyl-*n*-decyl)thiophen]-5-butyric acid[133] have been converted into their corresponding sulphur-free acidic products. The reaction has been applied to many other acids, including dicarboxylic acids.[129,134,135a,b] Desulphurisation of (XLVIII), which affords 5,5,10,10-tetramethyl-*n*-tetradecane-1,14-dicarboxylic acids (XLIX) illustrates one of the applications.[135b]

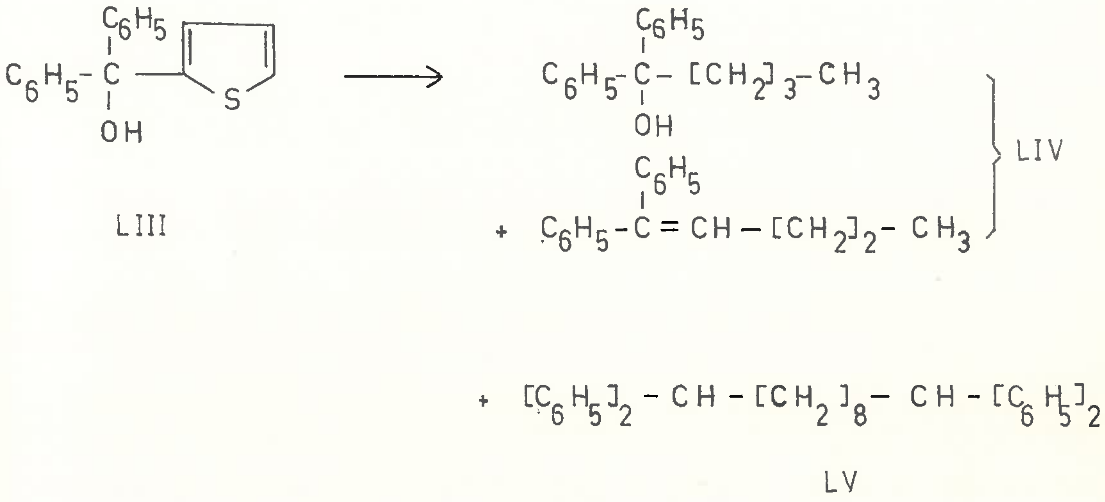


The method has also been extended to include the preparation of amino acids,[136] hydroxy acids,[137] aliphatic alcohols,[138] ethers,[139] and of acids labelled with tritium.[140] Apart from these synthetical applications, desulphurisation of non-acidic thiophen derivatives has been proved to be of value in structural determinations.[141,142]

As a further contribution to the synthetical applications of the desulphurisation reaction, the desulphurisation of several alcohols derived from thiophen has been studied in the present thesis. This method is complicated by the formation of several compounds (see detailed discussion in Chapter III). Thus desulphurisation of *α*-2-thienylbenzyl alcohol (L) gave 1-phenylpentane (LI) as the major product, together with some 1,10-diphenyldecane (LII).



On the other hand, the desulphurisation of diphenyl-2-thienylmethanol (LIII) gave a mixture containing both alcohol and olefin (LIV); a small amount of dimeric product, 1,1,10,10-tetraphenyldecane (LV) was also obtained.



(B) <u>THE NATURE OF RANEY NICKEL CATALYSTS</u>

In 1925, a patent covering a new method of preparation of a nickel catalyst was granted to Murray Raney.[143] The method which was well recognized as superior to the former 'nickel on kieselguhr', consisted of a treatment of a powdered Ni-Si alloy with aqueous alkali, from which a pyrophoric brownish nickel was obtained. Later investigation upon other alloys of nickel and alkali soluble metals, revealed that Ni-Al alloy was preferable.[144] Since then the catalyst which is prepared by this means has been known as Raney nickel catalyst. Today Raney nickel is one of the most commonly used and probably the most versatile catalyst known.[145] Some twenty or more different modifications of Raney nickel have been reported, and each has been prepared to suit a particular purpose in different types of reactions. These include hydrogenation of a variety of compounds,[145,146] desulphurisation,[8,72,73,106] dehalogenation,[147] _N_-alkylation of primary amines,[120,148] formation of heterocyclic biaryls,[149] etc.

A number of methods of processing the alloy to give the catalysts have been described in the literature.[cf.146a] The most common method of preparation of Raney nickel catalysts involves the addition of the alloy to an aqueous alkaline solution. By this means, catalysts of differing activities are obtained depending on the temperature and the other experimental variables. The original process recommended by Raney was first improved by Covert and Adkins.[150] This involved prolonging of the period of digestion of the alloy at 115°. The process was later further altered by Mozingo[151] by shortening and lowering the temperature of the digestion period. Adkins and Pavlic[152] introduced a classification for several Raney nickel catalysts using the designation W-1, W-2, W-3, W-4 for catalysts of increasing activities in hydrogenation. Adkins and Billica[153] later added the even more active W-5, W-6 and W-7 catalysts which are prepared by addition of Ni-Al alloy (50:50, W/W) to _ca._ 30% aqueous solution of sodium hydroxide at 50 ± 2°, with further digestion at the same temperature for 50 minutes. W-7 is washed only by decantation and therefore a considerable amount of alkali is retained, while W-5 is continually washed with distilled water until the washings are alkali-free. The loss of a great deal of hydrogen during the process of washing explains while W-5 is less active than W-7. W-6 is washed under a positive pressure of hydrogen, and this catalyst is more active than W-5 Raney nickel. The preparation of 'hydrogen-poor' or 'hydrogen-free' nickel was first described by Hauptmann and his colleagues.[154] Although many of the desulphurisations in the literature have been carried out with W-1 and W-2 Raney nickel, most of the work in this thesis has been performed with catalyst of W-5 - W-7 type, and with the partially degassed catalyst of Badger and Sasse.[149a] Other degassed catalysts have been described by Sasse,[149b] and Sasse and Whittle.[155]

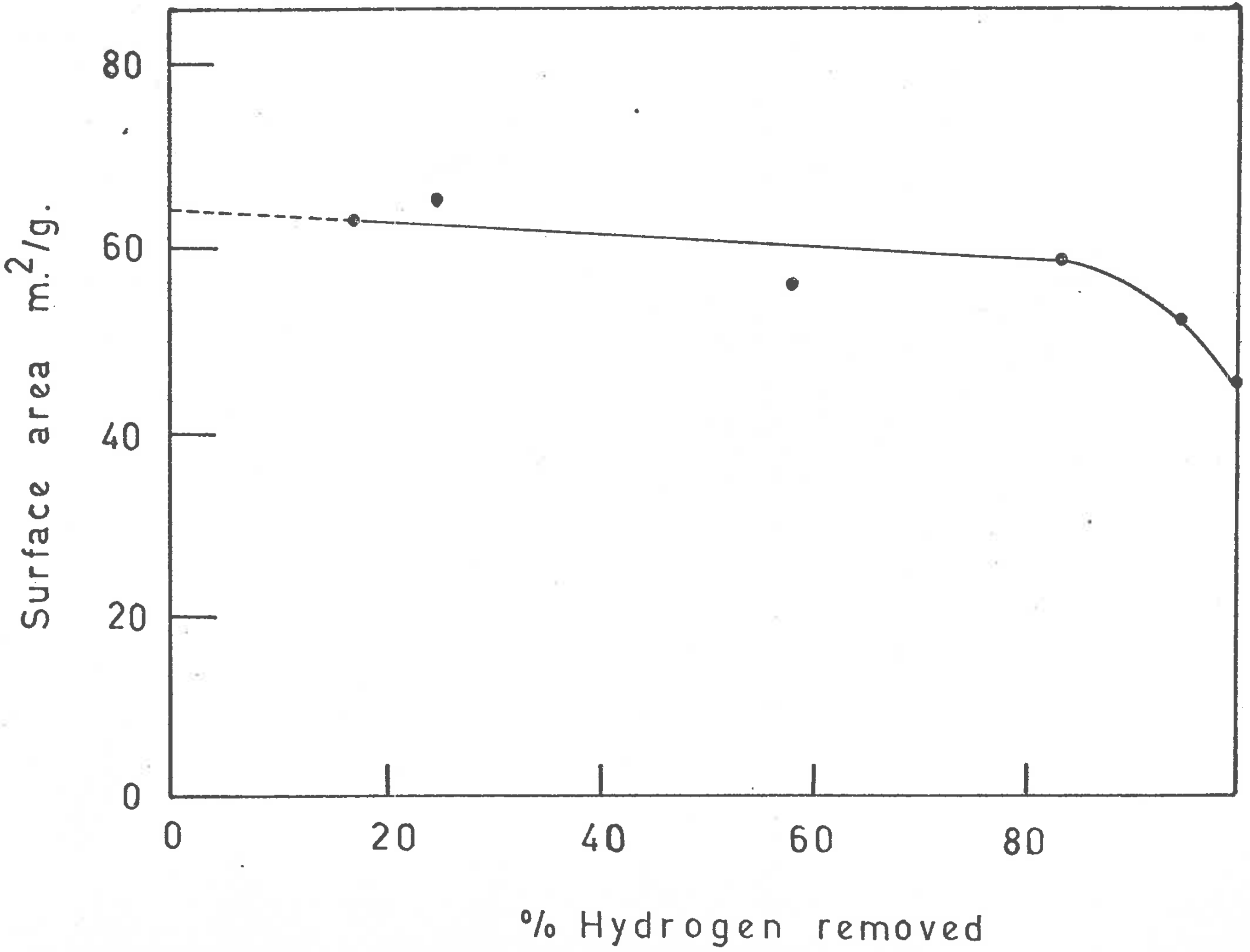
Pattison and Degering[156] have prepared a catalyst of Raney type from a Ni-Mg alloy. The inactive portion of the alloy is dissolved in acetic acid and the obtained nickel catalyst was found to be as active as the W-4 Raney nickel of Pavlic and Adkins and twice as active as the W-2 catalyst of Mozingo.

Preparation of Raney cobalt has been described by several authors.[157,158] Unlike Raney nickel, Raney cobalt is not normally pyrophoric unless warmed; but some samples prepared by the method of Billica and Adkins have been found to be pyrophoric. The preparation of an active copper catalyst has been described by Faucounau.[159] It is considerably weaker than nickel, but no systematic study has been carried out. Paul and Hilly[160] have described the preparation of Raney iron. Although it has been reported to hydrogenate triple bonds selectively to double bonds at pressures of 55-75 atmospheres, and temperature of 100-135°, Raney iron has found little application. Hauptmann[161] observed that strongly degassed Raney copper, Raney cobalt and Raney iron desulphurise organic compounds at elevated temperatures, but less effectively than Raney nickel.

There has been some disagreement in the literature concerning the nature of Raney nickel catalysts, and widely differing views have been expressed.[162,163,164,165] The Raney nickel catalysts, which are prepared by leaching Ni-Al alloys as previously mentioned consist mainly of nickel (*ca.* 77%), aluminium (1-3% as metal, 19.8-21% as oxide) and some sodium aluminate.[163,164,166,167] Like the other Raney metals, Raney nickel is essentially finely divided, crystalline particles, the size of which varies between 40-80 Å in diameter.[157] This is almost one-tenth of the size of the particles obtained from reduction of nickel oxide (400-1090 Å). Nickel can exist in both hexagonal and face-centred cubic close packed structures, but only the latter is catalytically active.[168] Both reduced[168] and Raney nickel[164] exist in the cubic form, but on heating at 170° for several days the cubic form rearranges to the hexagonal lattice.[169] The interatomic spacings in the face-centred cubic structure are 2.47 and 3.50 Å,[170] and only the latter has been found to be effective in the hydrogenation of ethylene.[170,171]

Raney nickel is porous in structure as a result of its mode of preparation; and the surface area is very large due to the pore distributions. The data obtained from chemisorption measurements at -195° for carbon monoxide on a W-6 Raney nickel catalyst degassed at 400°, as shown by Kokes and Emmett,[172] suggest that only about 20% of its surface consists of metallic nickel. The remainder is non-metallic and probably consists largely of alumina formed during the leaching process. The average pore diameter of the Raney nickel catalyst was reported to be 84 Å.[172] The surface area of Raney nickel has been given earlier as 100 m.$^2$/g.,[173] while Smith, Chadwell and Kirslis[163] have reported a value of 16.2 m.$^2$/g. as determined by palmitic acid adsorption. This decreases linearly with loss of hydrogen until about 70% is removed; then it decreases more rapidly. When all of the hydrogen has been removed, the surface area of the catalyst is about one-fifth of its original value.[163] However, in a more recent paper, Kokes and Emmett[164] have given the value for W-6 as 63 m.$^2$/g. which does not change with heat treatment below 350°. In addition, when W-6 Raney nickel was further heated to 500°, a loss of one-fourth of its area was observed. These results are in fair agreement with the value 87 m.$^2$/g. reported by Watt, Roper and Parker.[174] Kokes and Emmett[167] have also found that the

Fig. 1.- The variation in surface area of W-6 Raney nickel with loss of hydrogen; as determined by Kokes and Emmett.[167]



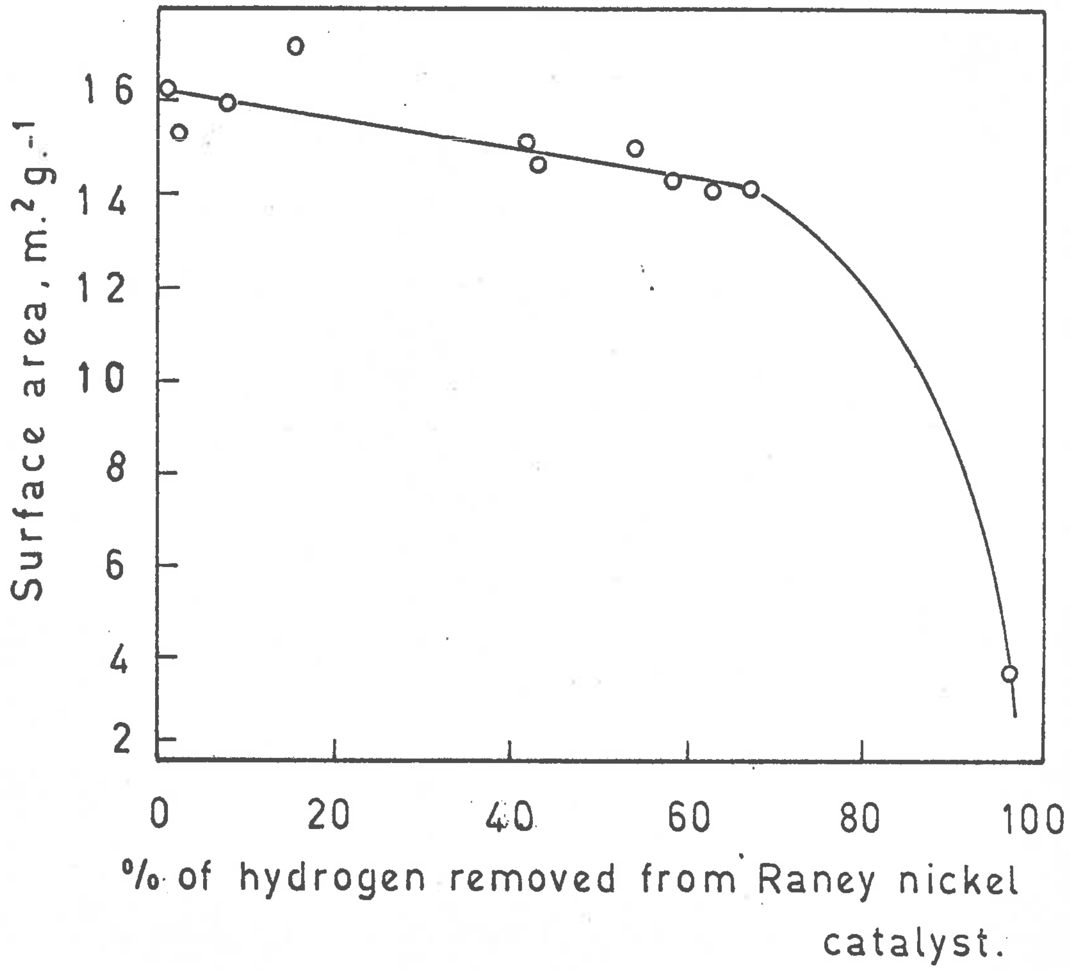


Fig.2.- Surface area of Raney nickel catalyst as a function of hydrogen content; as determined by Smith, Chadwell, and Kirslis![63]

surface area of the catalyst (W-6) remains essentially constant until about 85 to 95% of the hydrogen is removed which corresponds to a temperature of 300 to 400°. At higher temperatures the surface area falls off rapidly to *ca.* 45 m.$^2$/g.

To a first approximation, the density of Raney nickel increases linearly with the amount of hydrogen removed, but Kokes and Emmett reported that the density, found experimentally (5.5 g./c.c.), is much lower than would be expected (6.6-6.2 g./c.c., this has been corrected for the presence of alumina). This suggests that the catalyst has a highly defective structure.[164]

Undoubtedly, hydrogen is the most important component of Raney nickel besides nickel itself. Indeed, one of the most important features of Raney nickel is the quantity of hydrogen present, a quantity which is too great to be ascribable either to adsorption or to solution.[145,163,162] The amount and character of hydrogen in the catalyst has been the subject of some controversy. Some authors have described the catalytic material as a hydride of the formula $NiH_2$,[175] or a mixture of hydrides.[4] Freidlin and Ziminova,[162] reported the hydrogen content in Raney nickel to be 95.3 c.c./g. Although this value corresponds approximately to the formula $Ni_2H$, these authors do not consider the catalyst to be a hydride, but rather skeletal nickel promoted with hydrogen, part of which is adsorbed and part dissolved. They also found that the catalytic activity was lost when all hydrogen was removed, and it was difficult to replace dissolved hydrogen during a hydrogenation reaction. These facts prompted them to postulate that the loss of activity of the catalyst in the course of a hydrogenation is brought about by the destruction of active sites owing to loss of hydrogen and blocking.[176] Recently Csűrös and Petro[165] stated that the hydrogen content of Raney nickel depends on the conditions of preparation and showed that variations occurred even under identical conditions of preparation. These variations ranged from 180 to 300 c.c. in one c.c. of freshly prepared catalyst. This value is about one-half to one-third of the result obtained by Smith <u>et al</u>.,[163] who reported that freshly prepared catalyst of the W-6 type contain 92 to 157 c.c. of hydrogen per g. of catalyst; but is in fair agreement with the value, 45 to 100 c.c./g., found by Kokes and Emmett.[164] On storing, particularly under water, excess hydrogen is evolved and a stable state is reached, which is characterised by 72-81 c.c. of hydrogen per g.[164] Moreover, it has been suggested that a large part of the hydrogen lost during storage is the labile portion that can be removed from a fresh catalyst below 100 or 120°.[164]

As mentioned above, Smith <u>et al</u>.[163] observed that the surface area decreases more rapidly after about 70% of the hydrogen has been removed. If hydrogen is removed rapidly heat is evolved which sometimes results in an explosion of the catalyst.[149,154,161,177] Their explanation of these phenomena is based on the assumption that the hydrogen is in the form of atoms attached to the nickel in a metastable state.[163] If the desorption of the hydrogen occurs rapidly, the highly exothermic recombination of the hydrogen atoms becomes explosive. Similarly, Kokes and Emmett[164] showed that the evolution of hydrogen is an exothermic reaction. In order to explain how the hydrogen is held by the catalyst, they postulated that it is held in the nickel in the form of substitutional replacement of nickel atoms in the lattice. It does not appear to be present as adsorbed hydrogen, or as dissolved hydrogen; neither does it appear to be formed by the reaction of residual aluminium during the process of heating the sample to remove the hydrogen. The evidence, which is based on their extensive physico-chemical study is of some interest and may be summarized as follows.

(1) The density of the catalyst is much lower than would be expected. Their calculation suggests the presence of 30.4% lattice vacancies.

(2) 30.4% lattice vacancies calculated for the W-6 catalyst from the density data would correspond to 70 c.c. of hydrogen per g. of catalyst if each lattice vacancy is assumed to hold one hydrogen atom. By comparison the hydrogen evolved from the catalyst is about 100 c.c. per g. for the fresh catalyst and in the range 72-81 c.c. for the stable catalyst. This agrees well with the presence of 19.8% alumina.

(3) The surface area of the sample, 63 $m.^2/g.$, is much too small to permit the observed amounts of hydrogen to have been present

principally as adsorbed hydrogen (1.5 to 2 c.c. of hydrogen for chemical adsorption and 14.4 c.c., corresponding to nitrogen, for physical adsorption; compared with 72 and 100 c.c. of adsorbed hydrogen).

(4) Kokes and Emmett also showed that the evolution of hydrogen from the catalyst is an exothermic process. Apparently the desorption of a large amount of hydrogen from metal surfaces is generally an endothermic process. On this basis Kokes and Emmett ruled out surface adsorption as a major factor in retaining the hydrogen.

(5) The large amounts of hydrogen (72-100 c.c./g.) held by the catalyst cannot reasonably be interpreted as due to ordinary solution because the solubility of hydrogen in nickel accounts for only 0.01 c.c./g. at atmospheric pressure. A supersaturated solution is also unlikely because, at 400°/140 atm., the Raney nickel (degassed at 1200°) picks up only 50 c.c.[178] of hydrogen per g., or about half the amount it originally contained, while the true solubility at this temperature and pressure is only about 0.4 c.c./g. This agrees with the finding that when a Raney nickel catalyst is degassed, the alloy does not wholly anneal, but half of the lattice vacancies remain. Furthermore, the rate of hydrogen evolution from the catalyst is much slower than would be expected if it were merely dissolved in the nickel.

(6) The hydrogen evolved from the Raney nickel catalyst cannot be due to the reaction of water vapour with the residuel aluminium content of the catalyst because the alumina content in the final degassed catalyst is much less than would be expected.

Moreover, the specific magnetization of the W-6 Raney nickel catalyst, measured as a function of its hydrogen content, suggests that each hydrogen is, on the average, contributing one electron to the nickel.[164] On the basis of X-ray analysis Freidlin and his coworkers[179] suggest that the diffused X-ray interference lines which are frequently found may be due to the small size of the crystals (blocks of coherent scattering of X-rays), and due to distortions of the crystal lattice. In the process of formation of nickel crystals, hydrogen entering into the composition of the active centres is distributed not at intermodal points of the crystal lattice (i.e. does not form a solid solution with nickel), but at the boundary surfaces of crystals forming a particle of the Raney nickel powder. Owing to the small size of the crystals, the internal intercrystalline surface must be very large, so that, as already found, the amount of hydorgen bound to active centres of the catalyst must be very considerable. It is possible that the presence of such an intercrystalline layer of hydrogen (and also, probably, the presence of vacant spaces in the crystal lattice) prevents the crystallisation of Raney nickel even when the catalyst is heated.

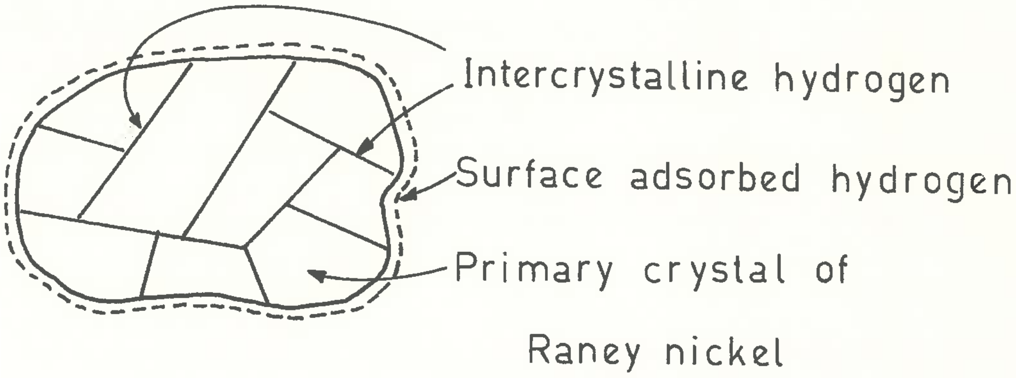


Fig. 3. - A particle of the Raney nickel powder, as suggested by Freidlin _et al._[179]

By comparison of the activity and crystal-size of Raney nickel heated at 300, 450 and 570°, Freidlin and his collaborators[179] found that there is no change in the activity after treatment at 300°, but that heating at 450° and 570° results in a reduction in activity by factors of 1.7 and 4 respectively. Heating of Raney nickel for 2 hr. at 450 and 570° results in an increase in crystal size by 1.7 and 2.1 times respectively. This points to the existence of a relationship between the physical structure and the activity of the catalyst. This relationship is confirmed by the behaviour of Raney nickel which is regenerated after being free from hydrogen by a chemical method and by complete restoration of the activity of such catalyst by treatment with hydrogen at 300°. However, if the catalyst is heated at higher temperatures (450 and 570°) and then treated with hydrogen, its activity is not completely restored owing to the change in physical structure.

Taylor and Weiss[180] explained the high activity of Raney nickel catalysts by the defect structure of its crystal lattice and the valence unsaturation of its atoms. Aubry,[181] stated that the activity of Raney nickel is due to adsorbed and absorbed hydrogen, and that the catalyst behaves as a reversible electrode to hydrogen. In the pH range from 5 to 14 Raney nickel follows potential changes in the same manner as a hydrogen electrode. Paul[182] associates the activity of this catalyst with the presence of residual metallic aluminium, while Ipatieff and Pines[166] associate it with the presence of alumina. Moreover, the catalyst contains sufficient hydrogen to lead some investigators to suggest that it is a compound of nickel and hydrogen.[4,175] However, Freidlin and his associates[182a,183] demonstrated that the hydrogen in Raney nickel is chemically heterogeneous whereas in a hydride, all the hydrogen atoms should be equivalent. They showed that part of the sorbed hydrogen enters into the composition of the active centres of the catalyst and, together with the nickel, determines the activity of the catalyst. It has been shown that the activity of these catalysts for the hydrogenation of benzene is a function of hydrogen content.[183] In addition removal of this hydrogen is accompanied by a decline in the catalytic activity.[162,163,183] On hydrogenating quinone, in turn, Sokolsky[184] found that removing up to 70% of bound hydrogen, almost no change occurs in activity, which then abruptly decreases on removal of more hydrogen.

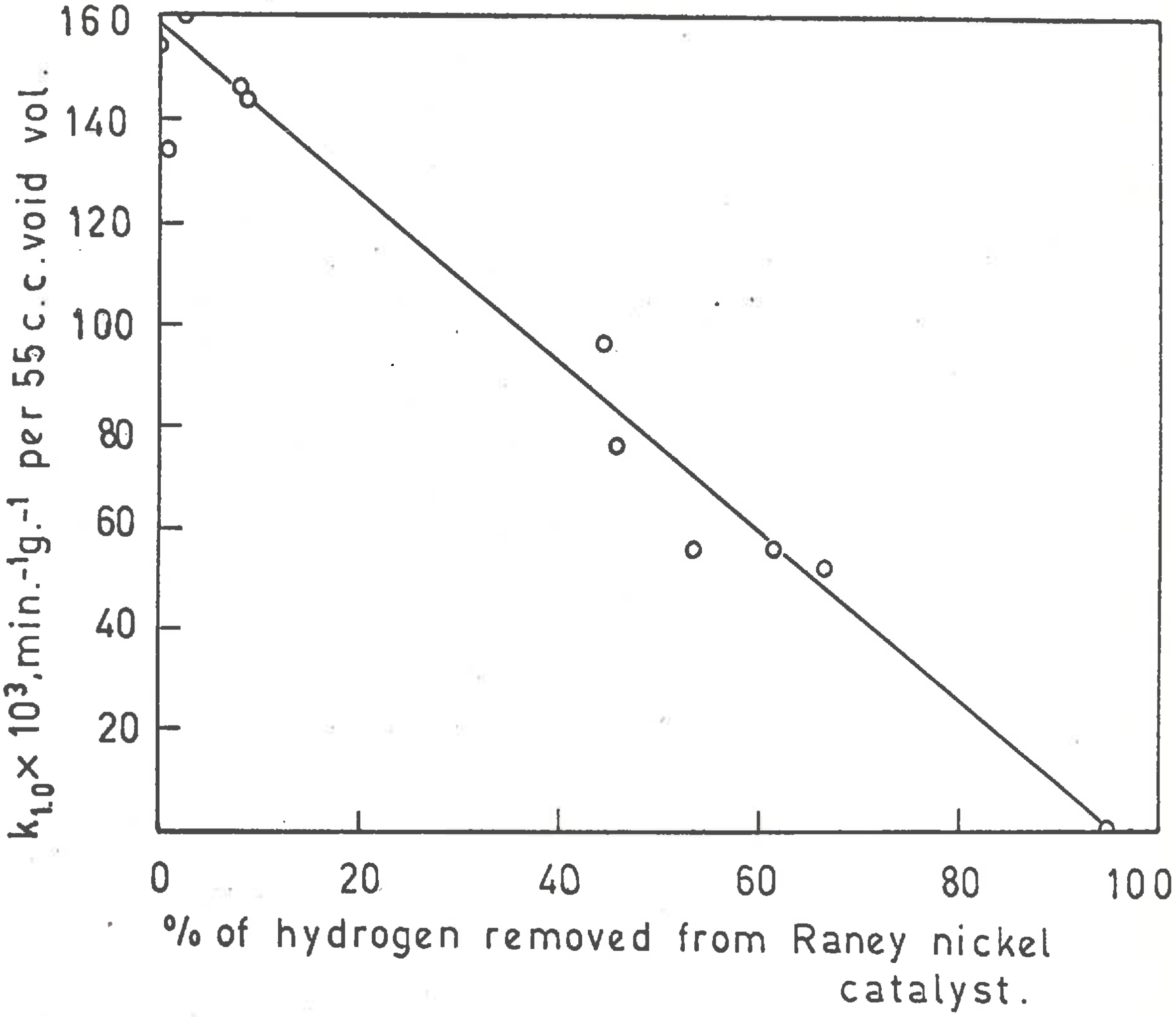


Fig. 4.- Catalytic activity of Raney nickel catalyst for the hydrogenation of benzene at 80° as a function of hydrogen content of the nickel; as determined by Smith, Chadwell, and Kirslis.[163]

During 1934-1948 Beeck and his coworkers[185] carried out their experiments on the study of the catalytic hydrogenation of ethylene over metallic films. They reached the conclusion that the activity of these metallic films for this reaction was apparently related to certain interatomic spacings in the metal. In 1950, Beeck[185d] pointed out that these results could also be interpreted on the basis of the per cent *d*-character of the various metals as defined by the theory of Pauling.[186] Thus Beeck and his coworkers suggested an electronic interpretation that suited their data equally as well as the geometric interpretation. Dowden[187] predicted that when enough copper was added to nickel to fill completely the *d*-band vacancies, one would probably destroy the catalytic activity of the nickel towards the hydrogenation. This prediction was beautifully confirmed[188] by Dowden and Reynolds. However, Best and Russell[189] pointed out later that the explanation for the alloy effect is not the same for all hydrogenation reactions. Furthermore,[190] Hall found that hydrogen added in the temperature range 100 to 300° acts as a promoter to the copper-nickel catalysts, but as an inhibitor for pure nickel. A theoretical explanation of these results is not yet available.

More recently, Kokes and Emmett,[167] who have previously suggested that the metallic phase of the catalyst is an atomic, substitutional, nickel-aluminium-hydrogen alloy wherein the hydrogen functions as copper in a copper-nickel alloy and contributes one electron per atom to the d-band of the nickel, have obtained results that throw additional light on the question of the action of alloying constituents on the activity of metallic catalysts. The results indicate that as the dissolved hydrogen content of the original Raney catalysts is gradually removed, the activity falls to a minimum and again increases as the last portion of the dissolved gas is removed from the nickel catalyst. It appears, then, that an important factor in determining the activity of alloy catalysts is the number of electrons per unit cell. This is substantiated by the fact that the activity for the copper-nickel and the nickel-hydrogen-aluminium systems are similar.

A comprehensive study of the behaviour of Raney nickel catalysts as a function of their hydrogen contents has been carried out independently and simultaneously by Csűrös and Petró.[165] These authors have found that the maximum catalytic activity of a given Raney nickel catalyst does not necessarily correspond to its maximum hydrogen content. In fact, the relationship between catalytic activity and hydrogen content depends markedly on the nature of the substrate. While some compounds appear to be extremely sensitive to the hydrogen content of the catalyst, the rate of hydrogenation of other compounds is less affected by small variations in the hydrogen content of the catalyst.

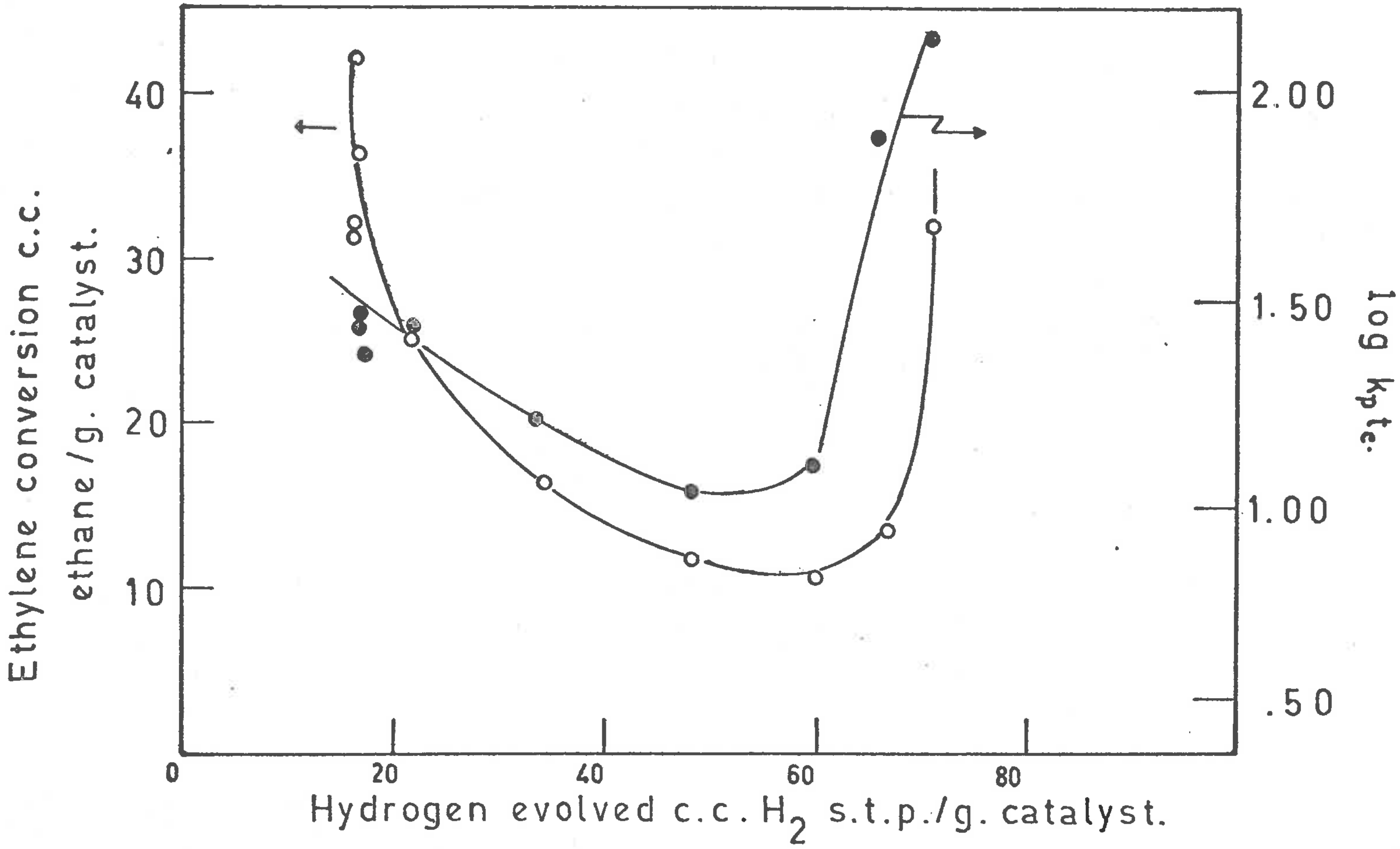


Fig. 5.- Activity of W-6 Raney nickel ethylene hydrogenation and parahydrogen conversion; as determined by Kokes and Emmett.[167]

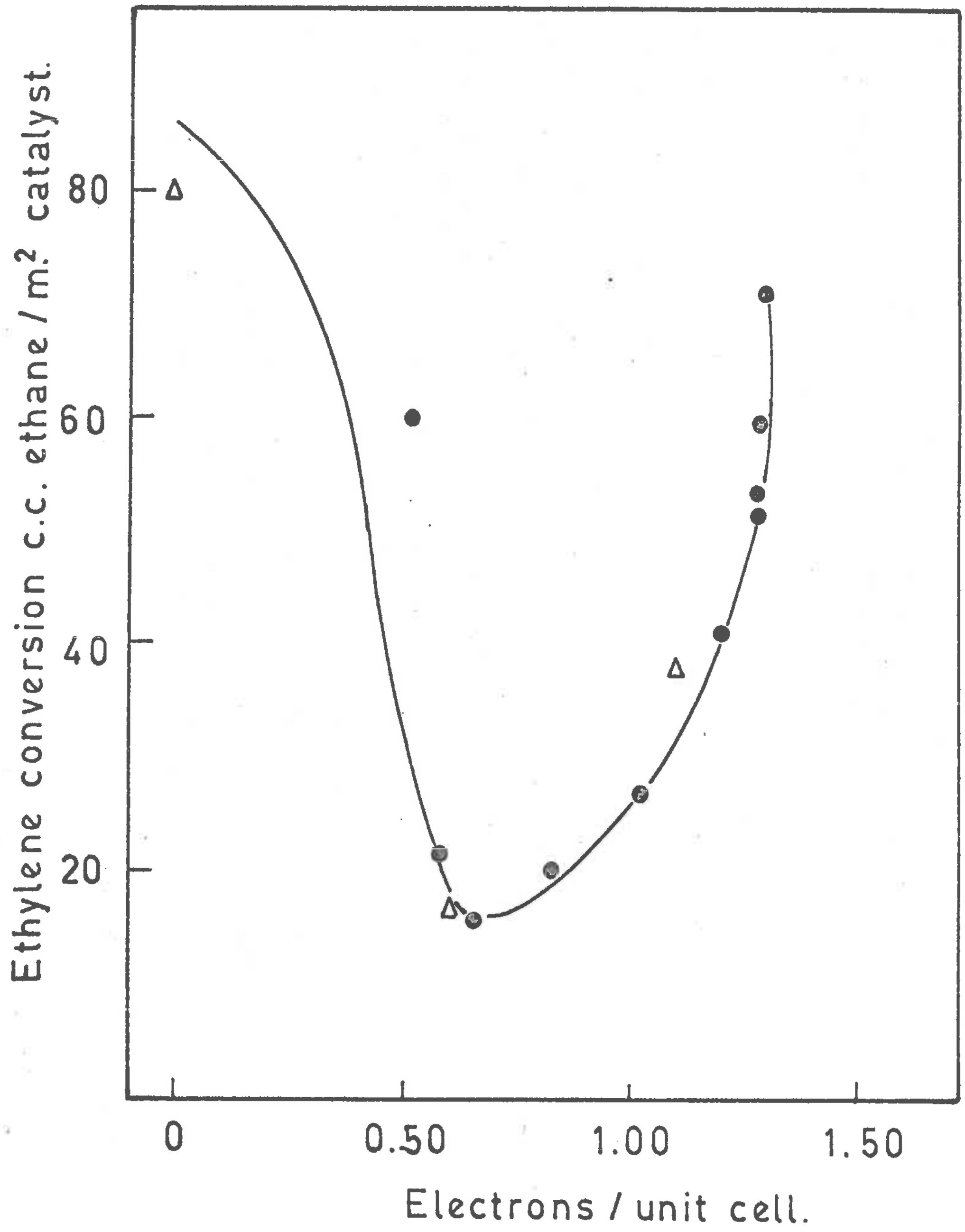
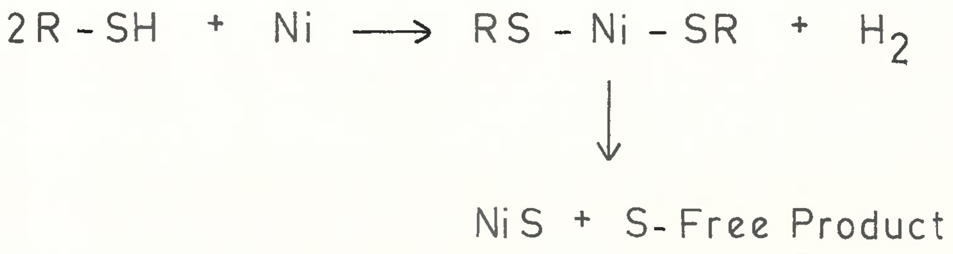


Fig. 6.- Activity per sq.m of surface area for the hydrogenation of ethylene over a Raney nickel catalyst and over a nickel-copper alloy as a function of the number of electrons added by alloying components per unit cell; as determined by Kokes and Emmett.[167]

## (c) MECHANISM OF THE DESULPHURISATION REACTION

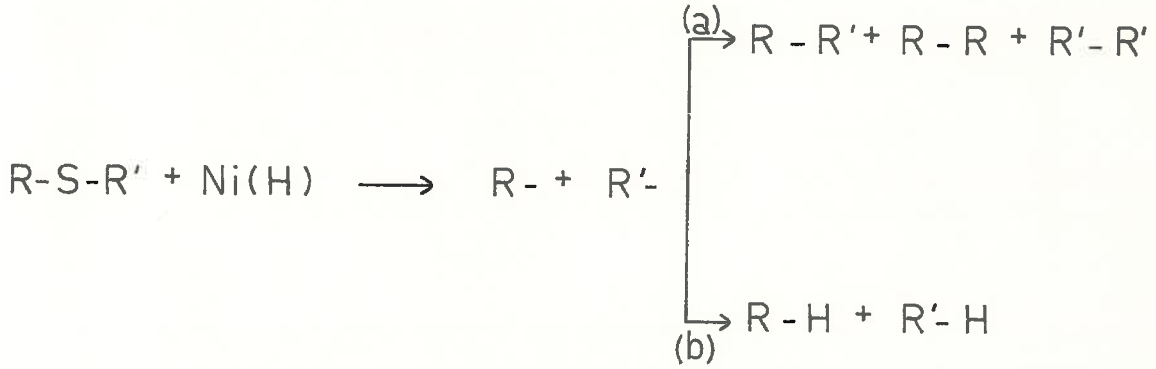
Bougault, Cattelain and Chabrier[4] have suggested that the initial step of desulphurisation involves the formation of nickel mercaptides, subsequent decomposition of which results in the production of nickel sulphide and a sulphur-free compound.



$$\begin{array}{lcl} 2R-SH + Ni & \longrightarrow & RS-Ni-SR + H_2 \\ & & \qquad\downarrow \\ & & NiS + S\text{-Free Product} \end{array}$$

Clearly, desulphurisation with Raney nickel is not a catalytic process and the nickel functions simply as a 'desulphurising agent'. However, since the activity of Raney nickel in catalytic hydrogenation, and its effectiveness in the desulphurisation reaction appear to be almost parallel, and both processes are thought to involve (as a first step) the adsorption of the substrate on the nickel surface, they are closely related to each other. The term 'Raney nickel catalyst in desulphurisations' is obviously indefensible.

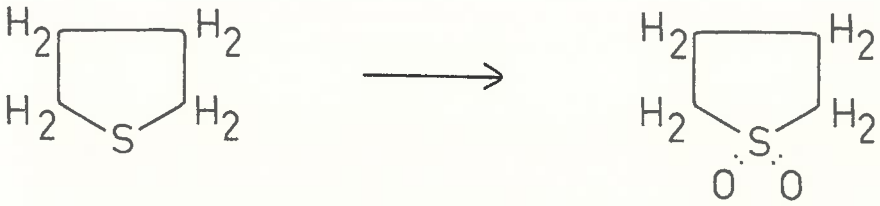
When Mozingo, Wolf, Harris and Folkers[6] discussed the mechanism of the desulphurisation reaction, they regarded the cleavage of the carbon-sulphur bonds under the influence of Raney nickel as the first step. Two possible routes leading to the formation of the products were then postulated as follows:



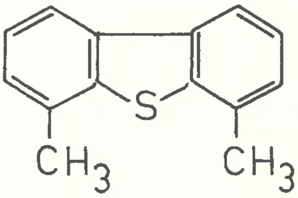
However, Mozingo and his collaborators did not find any evidence supporting route (a), and concluded that all free radicals resulting from rupture of the C-S bond combined with hydrogen derived from the nickel catalyst to give the observed products.

Wolfrom and Karabinos[17] expressed the belief that it is the hydrogen produced in the dehydrogenation of ethanol to acetaldehyde (isolated in the desulphurisation of certain thioketals which were carried out in ethanol solvent) that is utilized in the formation of the products. However, several experiments conducted by Bonner[191] showed that the hydrogen for reductive desulphurisation is provided by the hydrogen bound to the catalyst, and that the production of acetaldehyde from ethanol is simply a concurrent reaction.

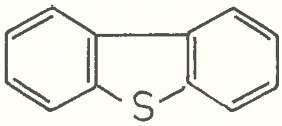
At present, there seems to be general agreement[154a,192-196] that the first step in the desulphurisation of bivalent sulphur derivatives involves the chemisorption of the sulphur atom, by means of its lone pair of electrons, onto the metal surface. This has been pointed out by Maxted, who also demonstrated that this chemisorption did not occur when both lone electron-pairs of the sulphur atom were already engaged in stable chemical bonds, as in the case of tetrahydrothiophen dioxide. Thus, toxicity towards the metal catalyst of tetrahydrothiophen can be readily eliminated by oxidising it to the corresponding sulphone.[197]



Apart from this, the specific affinity between the chemisorbed atom and the catalyst is of significance. For example, the action of 'hydrogen-free' or 'hydrogen-poor' nickel, on aromatic mercaptals, thioesters, and related compounds results in the isolation of diaryls,[196] arylsulphides,[184c] and stilbene,[198,199] while the same catalyst has very little effect on bromobenzene. Similarly, the degassed catalyst of Badger and Sasse, which afforded 2,2'-biaryls from pyridine and related bases in good yield, did not react to any extent with 3,5-dibromopyridine although it was found to have some effect on thiophen.[200] Moreover, some sulphur compounds which can be desulphurised smoothly by Raney cobalt are not affected by Raney tungsten.[201] These results indicate that the availability of at least one lone electron-pair, as well as the specific affinity of the chemisorbed element towards the metal catalyst, are important in the first step. If the chemisorption of the sulphur atom is sufficiently strong, it is thought that it causes a weakening of the carbon-sulphur bonds which will favour further chemical changes.[154a] This view is also supported by the observation that compounds in which the sulphur atom is flanked by bulky groups cannot be desulphurised.[135a,202-204] For example, 1,8-dimethyldibenzothiophen (LVI) has been found to be unaffected by Raney nickel,[202,203] while dibenzothiophen (LVII) affords biphenyl in 98% yield.[192]

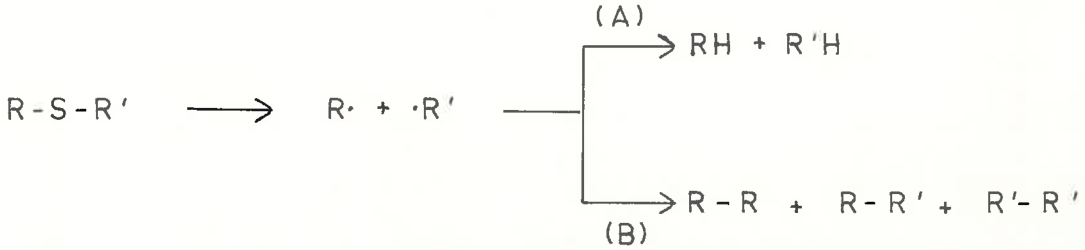


LVI



LVII

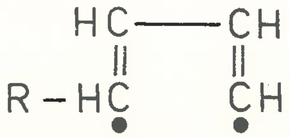
It was first suggested by Kenner, Lythgoe and Todd, and supported some years later by Hauptmann and his colleagues,[154c,e; 177b,196] Bonner,[194,195] and Badger and Sasse,[192] that the second step in the reaction involves a weakening of carbon-sulphur bonds. This results in homolytic splitting of one or both carbon-sulphur bonds, and gives rise to free radicals as intermediates. These radicals then react with hydrogen (route A) or with themselves (route B), depending on the particular environment, to give the observed products.



Both routes have been observed. The extent to which each reaction occurs depends *inter alia* on the quantity of hydrogen available. If sufficient amounts of active Raney nickel are used, the substitution of hydrogen for sulphur is usually preferred (route A). On the other hand, if a less active Raney nickel is used, dimerisation according to route B becomes noticeable. The experiments of Hauptmann[184a,177b,196] have shown that many aromatic sulphides, disulphides, thiol esters and thiols yield biphenyl derivatives when heated at 220° with degassed Raney nickel. On treatment at 140° with the same catalyst, diphenyldisulphide is converted to diphenylsulphide in 87% yield. Apparently, at this temperature the carbon-sulphur bonds remain intact for the most part, and the reaction is temperature-dependent. The isolation of mixed biaryls following the desulphurisation of a mixture of sulphides confirms the intermolecular character of the process, while the isolation of terphenyl from some reaction products provides valuable evidence for the homolytic process of the reaction described. Accordingly, it was found that the yield of dimeric materials is dependent on the hydrogen-content of the catalyst. Hauptmann's work with 'hydrogen-poor' and 'hydrogen-free' nickel firmly established route B in desulphurisation reaction.

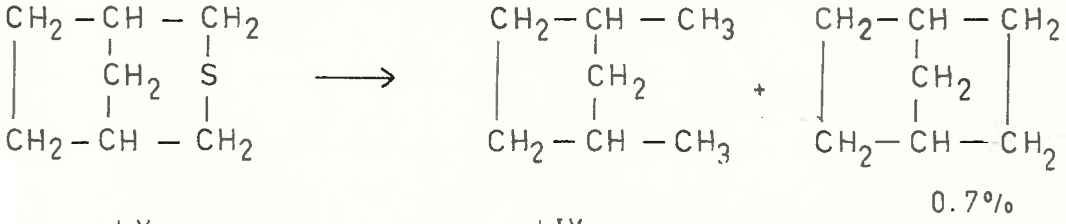
In this connection, it has always been understood that hydrogen does not take part in radical formation.[154a,191,192] However, in the desulphurisation of diphenyldisulphide by heating at 140° with Raney nickel, degassed at 200°, Hauptmann and his colleagues have isolated diphenylsulphide in addition to the other expected products. On the other hand, when Raney nickel, degassed at 100° (more hydrogen-content than the catalyst degassed at 200°) was applied in the similar reaction, the thioether was not isolated. These results prompted these authors to postulate that hydrogen does take part in the splitting of carbon-sulphur bonds, perhaps by displacing the diradicals from the sulphur.

Badger and Sasse[192] observed similar dimerisations during the course of the desulphurisation of thiophen derivatives. These observations also strongly supported a mechanism involving the formation of free radical intermediates. Thus desulphurisation of 2-acetylthiophen under certain conditions gave a little dodecane-2,11-dione in addition to the expected hexane-2-one; and some 1,8-dibenzoyloctane was obtained from 2-benzoylthiophen in addition to the expected valerophenone. In this connection, it has been found that the yield of dimeric product depends on the concentration of the thiophen derivative in the reaction mixture, the time of contact with the catalyst and its hydrogen content. In every case, the results are consistent with the view that the postulated intermediates must be diradicals with the uncoupled electrons at positions 2 and 5. It is noteworthy that when recombination occurs it invariably involves the union at the unsubstituted terminal carbon of the thiophen ring. Steric hindrance may be a factor here, making recombination at the substituted 2-position difficult or impossible; 2,5-disubstituted thiophens fail altogether to yield dimeric products. In view of these observations, Badger and Sasse have suggested that the desulphurisation mechanism involves a 2,5-diradical (LVIII), and that the dimerisation probably occurs while the diene system is still adsorbed on the catalyst surface.



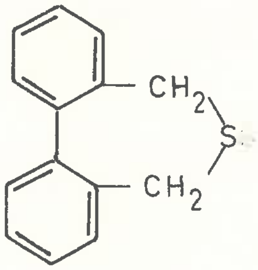
LVIII

Another example is provided by the production of bicyclo[2,2,1]heptane in addition to the expected 1,3-dimethylcyclopentane (LIX) from the desulphurisation of 6-thiabicyclo-octane (LX).[205] Badger[7] has suggested that this course of the reaction is compatible with a mechanism involving the recombination of free radicals after desulphurisation.

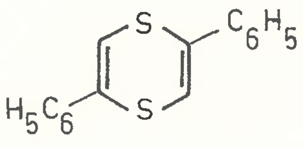


LX LIX

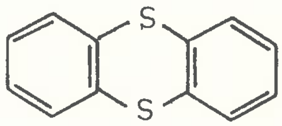
In this case, the internal cyclisation occurred in poor yield and, apparently, no attempt was made to improve the yield by suitable variation in the reaction conditions. As it may be expected that the yield of an internally cyclised product might be increased by employing a hydrogen-poor Raney nickel, a study of the desulphurisation of three suitable sulphur-compounds are described in this thesis. These compounds include 2,7-dihydrodibenzo[*c,e*]thiepin (LXI), 2,5-diphenyl-1,4-dithiin (LXII) and thianthrene (LXIII). The desulphurisation of (LXI), for example, may be expected to yield 2,2'-dimethylbiphenyl, 9,10-dihydrophenanthrene and phenanthrene.



LXI



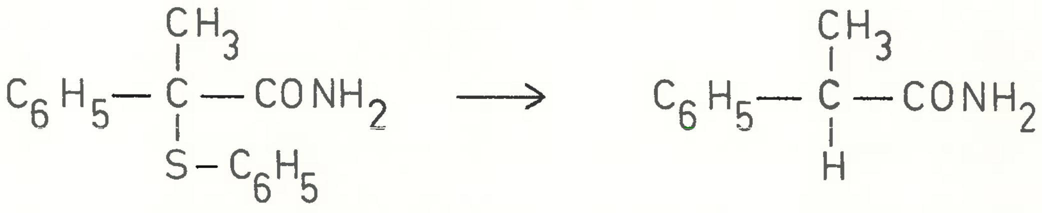
LXII



LXIII

An extended series of experiments on the course of desulphurisation of 2,5-diphenyl-1,4-dithiin has been conducted. These have been shown to give the expected 2,4-diphenylthiophen, together with a liquid of unknown structure. Although the results of analyses have pointed to the molecular formula of $C_{16}H_{14}$, the structure has not yet been established with certainty. The small amount of the product isolated from each experiment did not permit any extensive investigation; but the available evidence suggests that it is a mixture of diphenylcyclobutene and 1,3-diphenylbuta-1,3-diene. Similar results have been observed in the desulphurisation of thianthren. The expected dibenzothiophen and biphenyl were isolated. The isolation of these products, as has been mentioned, provides very strong evidence in support of the hypothesis that such intermediates occur in the desulphurisation (see Chapter II).

The occurrence of free radicals during the desulphurisation reaction was postulated by Bonner[194] to explain the result of a study in which he determined the stereochemical fate of an asymmetric centre adjacent to a sulphur atom during reductive desulphurisation with Raney nickel. For this purpose 2-phenyl-2-phenylmercaptopropionic acid was synthesized, and resolved into both enantiomorphs. The resolved acids were converted into their amides (LXIV), and subsequently subjected to desulphurisation. Both products (LXV) obtained were completely racemic, as would be expected in accordance with the known optical instability of free radicals.



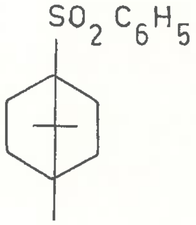
$$C_6H_5-C(CH_3)(S-C_6H_5)-CONH_2 \longrightarrow C_6H_5-C(CH_3)(H)-CONH_2$$

LXIV LXV

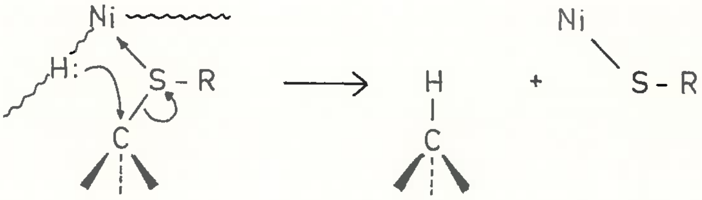
On the other hand, Djerassi and Grossman[206] found that when the asymmetric centre is separated from the sulphur atoms, then no such racemisation occurs. The desulphurisation of optically active 1,1-diphenyl-3-mercaptopropan-2-ol and its derivatives serve as illustrations.[206]

However the antipodal sulphones of optically active ethyl 2-phenyl-2-benzenesulphonylpropionate were desulphurised to give optically active ethyl 2-phenylpropionate with 90% retention of optical activity.[194] Although the relative configuration of the substrate and product obtained were not rigorously determined, inversion was indicated by the method of rotational trends. On the basis of these results, and others, Bonner advanced a concerted mechanism involving co-ordination between the catalyst surface and the oxygen atoms of the sulphone. The interaction between the adsorbed molecule and an adjacent adsorbed hydrogen atom results in breaking of the carbon-sulphur bond and simultaneous formation of an optically active reduction product.

In addition, van Tamelen and Grant[207] have recently demonstrated that, among the three possible sulphur-free intermediates [arising from the desulphurisation of phenyl-4-camphyl sulphone (LXVI)] which might be involved (carbanion, carbonium or free radicals), the carbanion is considered to be the least likely, and the carbonium ion also seems to be excluded. These results have been explained on the basis that the asymmetric centre in the system chosen cannot easily accommodate a positive charge. Moreover, the steric condition of the substrate does not allow the reaction to proceed with inversion of configuration. However, an $S_Ni$ mechanism (e.g. LXVII) (with hydride ion attacking at the carbon-bearing sulphur atom), promoted by the energetically favourable formation of nickel sulphide, has been considered possible.

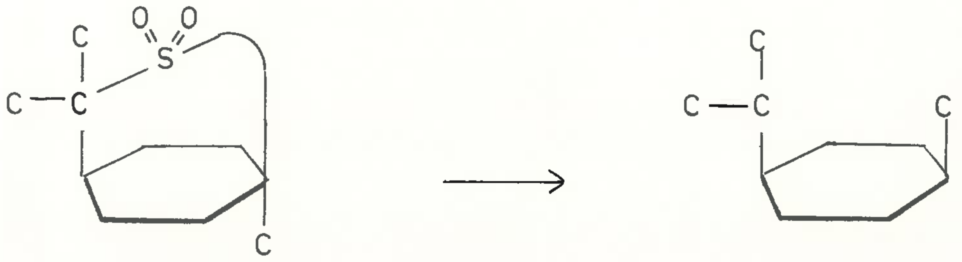


LXVI



LXVII

Nevertheless, the evidence is not incompatible with the current preference for the formation of radical intermediates. In contrast, work by Weitkamp[208] appears to be consistent with ionic mechanism. Thus, desulphurisation of 1,8-p-menthylene sulphone (LXVIII) with Raney nickel proceeds smoothly to give a good yield of *cis-p*-menthane (LXIX) with no trace of the *trans* isomer. Weitkamp has suggested that the inversion of configuration occurs by an $S_N2$ mechanism.



LXVIII LXIX

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# CHAPTER 2

## EXPERIMENTS BEARING ON THE MECHANISM OF THE DESULPHURISATION REACTION.

## A. THE DESULPHURISATION OF 2,7-DIHYDRODIBENZO[*c*,*e*]THIEPIN.

## B. THE DESULPHURISATION OF THIANTHREN, AND 2,5-DIPHENYL-1,4-DITHIIN.

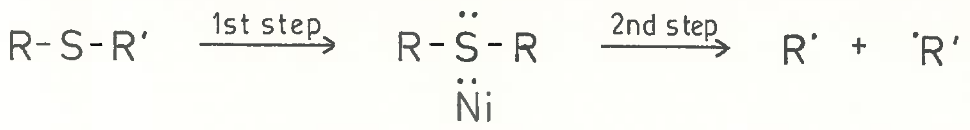
# C. THE DESULPHURISATION OF BENZO[*b*]THIOPHEN-3-CARBOXYLIC ACID-1,1-DIOXIDE

# EXPERIMENTS BEARING ON THE MECHANISM OF THE DESULPHURISATION REACTION

## (A) DESULPHURISATION OF 2,7-DIHYDRODIBENZO[c,e]THIEPIN.

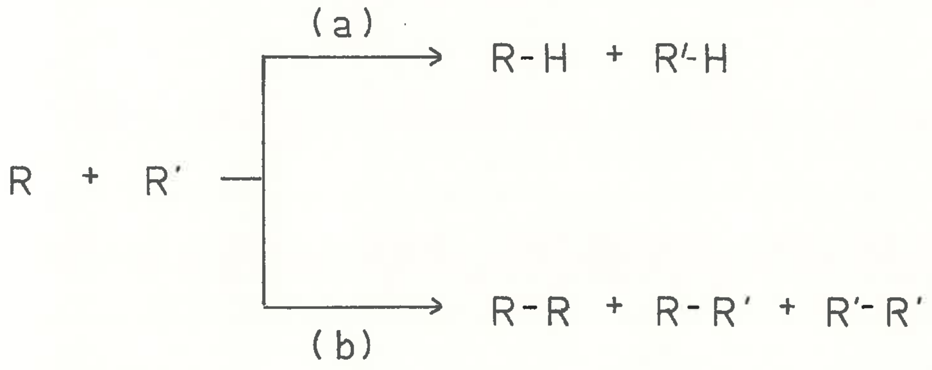
### INTRODUCTION

As previously mentioned, the initial step in any desulphurisation of bivalent sulphur compounds with Raney nickel is, almost certainly, chemisorption of the sulphur atom via its lone pair of electrons onto the metallic surface of the catalyst. This presumably results in a weakening of the carbon -sulphur bonds, thus permitting detachment of the free radicals in the second step.

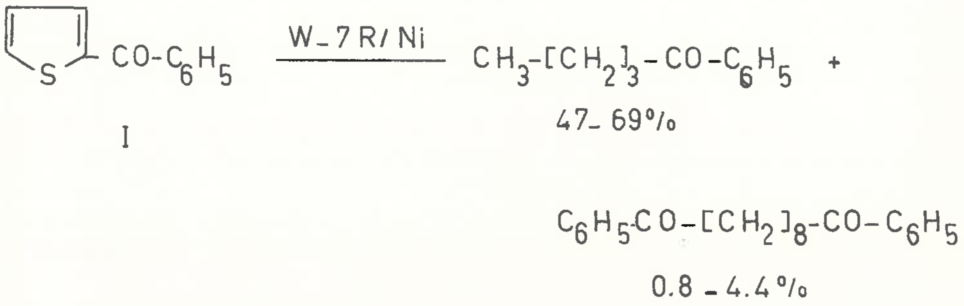


$$R-S-R' \xrightarrow{\text{1st step}} R-\underset{\overset{\cdot\cdot}{Ni}}{\overset{\cdot\cdot}{S}}-R \xrightarrow{\text{2nd step}} R^{\cdot} + {}^{\cdot}R'$$

The radicals formed are either hydrogenated to give the normal desulphurised product, or recombined (as an alternative reaction route) to give a dimeric product.

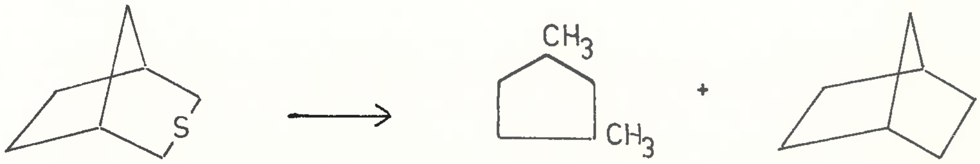


Badger and Sasse[1] have observed that the yield of dimeric product depends on the concentration of the substrate in the reaction mixture, the time of contact with the catalyst, and its hydrogen-content. Desulphurisation of 2-benzoylthiophen (I) may be cited as an example.



Moreover, the stereochemical course has been studied by Bonner.[2] The observation that desulphurisation of optically active α-phenyl-α-phenylthiopropionamide is accompanied by complete racemisation, is consistent with a free radical mechanism. Although these results support the view that desulphurisations over Raney nickel proceed via radical intermediates, the details of this mechanism have not yet been sufficiently proved. It is still possible that some dimerisation of thiophen derivatives may occur prior to desulphurisation (as in the case of 9,9'-di-2"-thienyl-9,9'-bifluorenyl which was isolated following the desulphurisation of 9,2'-thienylfluoren-9-ol, see Chapter III). Up to the present time there appears to be only two records in the literature of the detection of unsaturated compounds formed directly by the desulphurisation of thiophen derivatives.[3,77]

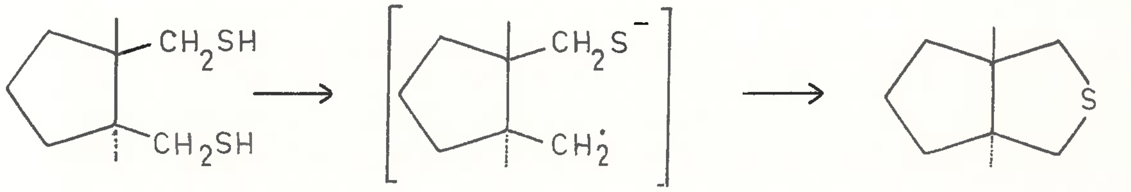
Additional evidence for the occurrence of such free radicals as intermediates in the desulphurisation reaction is provided by the formation of bicyclo[2,2,1]heptane (IV) in addition to the expected dimethylcyclopentane (III), in the reaction of 6-thiabicyclo-octane (II) with Raney nickel catalyst in ethanol. Clearly, intramolecular recombination of the intermediates diradical formed initially from (II) would account for the formation of the bicycloheptane.[4]



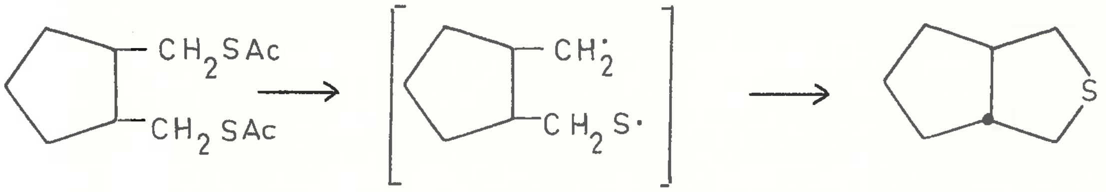
II III IV

This seems to be one of the few instances in the literature in which a cyclisation due to desulphurisation with Raney nickel has been reported. Although, the yield of the cyclisation product is so small (0.7%), it provides marked evidence for the occurrence of a diradical intermediate, the recombination of which is the only reasonable explanation for the production of the observed desulphurised compound. Moreover, it provides a new synthetic route by which cyclisation may proceed.

In this connection it should be noted that two similar cyclisations have been reported by Owen and Peto.[5,6] These authors found that the desulphurisation of both (V) and (VIII) afforded the same product (VII, X). They suggested that the desulphurisation of *trans*-1,2-bismercaptomethylcyclopentane (V) proceeds *via* the radical ion (VI) as intermediate. Subsequently Owen and Peto proposed that the closely related compound (VIII) yields the cyclised product (X) by way of the diradical intermediate (IX). The compound (VIII) was hydrolysed with aqueous alkali to give the corresponding dithiol prior to Raney nickel desulphurisation.[6] The contradiction existing in the postulation of the two intermediates (VI and IX) has not, however, been explained, and the yields have not been reported.



V VI VII

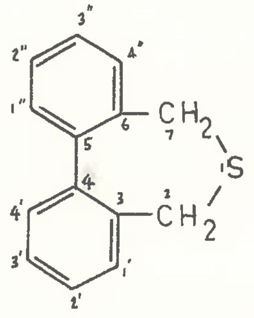


VIII IX X

Usually the product of internal cyclisation is obtained in poor yield; but it seemed conceivable that the proportion might be increased by employing hydrogen-poor Raney nickel, or Raney nickel of a deactivated type.

Although the idea of free radicals as intermediates in the desulphurisation reaction has had a largely independent and somewhat more recent development, the hypothesis has been supported by experiments involving racemisation, dimerisation and internal-cyclisation (intramolecular dimerisation).

Among these, the paucity of evidence on internal cyclisation is of interest. As an extension of this work on the desulphurisation, the synthesis of phenanthrene by the desulphurisation of 2,7-dihydrodibenzo[c,e]thiepin (XI) has therefore been attempted.



XI

( Numbering according to Truce & Emrick[7] )

The dihydrodibenzothiepin was first synthesized in 1956, by Truce and Emrick.[7] It was obtained in 93% yield by treatment of 2,2'-dibromodimethylbiphenyl with sodium sulphide in methanol.

Since the sulphur atom in the bridged biphenyl is separated from each of the benzene rings by one methylene group, the effect of any electronic or resonance interaction between the hetero-function and the aromatic system would be expected to be greatly reduced. The ultraviolet absorption spectrum of this compound[7] indicates that it shows less 1,1'-biphenylic conjugation than biphenyl itself, and very much less conjugation than the coplanar fluorene.[8]

2,7-Dihydrodibenzo[*c,e*]thiepin-1-dioxide-2',3"-dicarboxylic acid has been found to be resolvable. This finding suggests that in the presence of a sufficiently large bridging group (the sulphone group in this case) the two phenyl rings are no longer co-planar. As a result, this compound possesses molecular dissymmetry. Although the parent dihydrodibenzothiepin has not been resolved, inspection of a Fischer-Herschfelden-Taylor molecular model suggests that the presence of sulphur atom in this 2,2'-bridged biphenyl (XI) allows similar deviation from co-planarity.[7,cf.13] Dreiding model of the dihydrodibenzothiepin has been shown in Fig. I. This absence of co-planarity of the benzene rings is also clearly demonstrated by the difference in the ultraviolet spectrum of (XI) and biphenyl ($\lambda_{max.}$ of the dihydrodibenzothiepin, 245 mμ; $\lambda_{max.}$ biphenyl, 275 mμ).

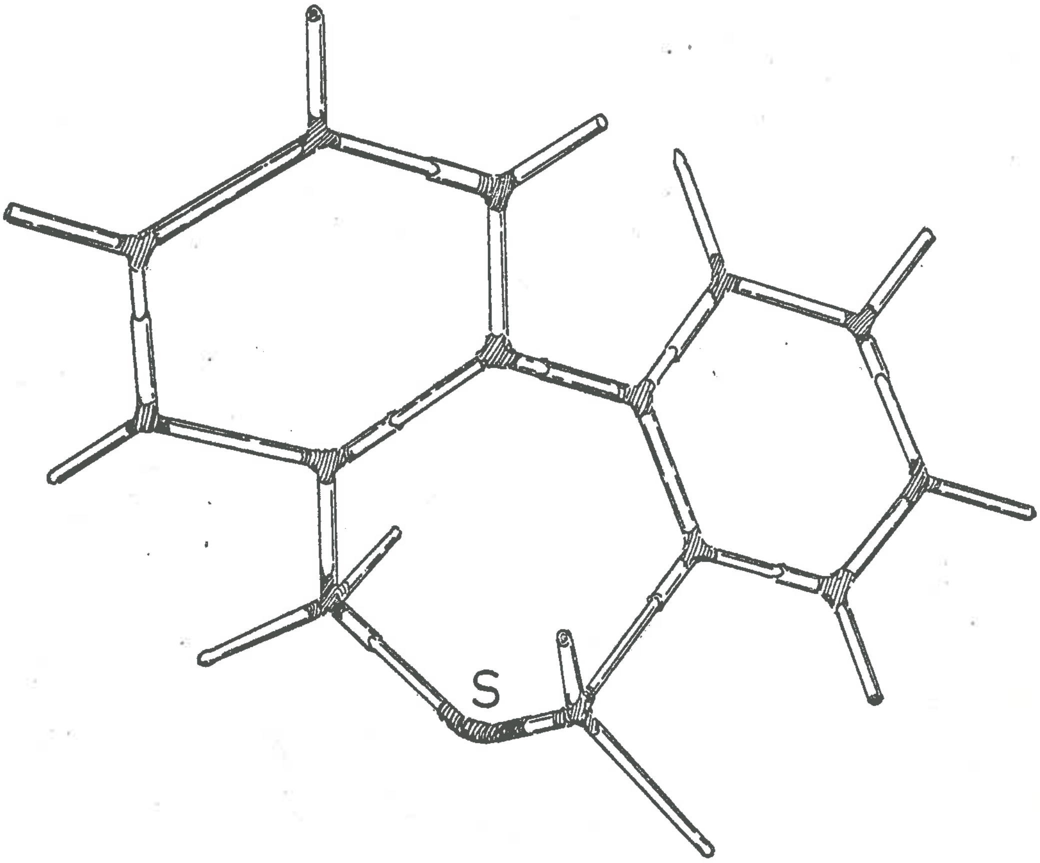
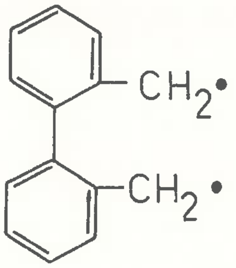


Fig.7,- A Dreiding Model of

2,7-Dihydrodibenzo[c,e]thiepin.

The above considerations led to the expectation that the removal of the sulphur atom from the hetero-ring in (XI) should occur under the influence of a deactivated Raney nickel catalyst. This is important as it has been found that only catalysts which contain large amounts of chemisorbed hydrogen are able to overcome the resonance stabilization and thus cause desulphurisation of polycyclic aromatic sulphur compounds such as dibenzothiophen.[1,9,10] It is also noteworthy that even thiophen itself has been reported to react explosively with W-7J Raney nickel catalyst (prepared according to Badger and Sasse[11]) and yet 88.5% of the starting material was recovered.[12] Although treatment of the used catalyst with mineral acid indicated that some desulphurisation had occurred, the amount of the starting material recovered showed that it resists desulphurisation.

Accordingly, it was thought that desulphurisation of the dihydrodibenzothiepin would be effected by a hydrogen-poor Raney nickel catalyst. The postulated intermediate is the diradical with uncoupled electrons at the terminal methylene groups (XII).



XII

Badger and Sasse[1] have expressed the view that the formation of dimeric product during desulphurisations probably takes place while the free radicals are still adsorbed on the catalyst surface. This suggestion is based on the observations that the dimeric products obtained from desulphurisations of thiophen derivatives always involves recombination at the 5-position of the diradical intermediates ($R-\underset{\bullet}{C}H=CH-CH=\underset{\bullet}{C}H$).

In the course of desulphurisation of the dihydrodibenzothiepin under the experimental conditions favouring the formation of dimeric product, the dimerisation would be expected to occur on the above hypothesis. Nevertheless, in view of the stereochemistry of (XI) it is unlikely that the dihydrodibenzothiepin would be adsorbed flat on the surface of the catalyst using the $\pi$-electrons of both benzene rings. In this sense, the dihydrodibenzothiepin differs from simple thiophen derivatives, which can presumably be adsorbed flat on the catalyst. This may explain the absence of detectable quantity of products formed by intermolecular dimerisation of the postulated diradical (XII). Steric hindrance of the phenyl rings may be another factor, preventing the recombination of two free radicals from two molecules of the substrate. On the other hand, after removal of the sulphur atom, the free rotation about the single bond joining the two phenyl rings would result in periodical overlapping of the two methylene groups. This would be expected to facilitate the sharing between the two unsaturated valent electrons, located at each carbon atom of the methylene groups.

In this respect, the 'interference value' between (1) methylene group and methylene group, (2) methylene group and hydrogen atom at the 6-position have been calculated according to the equation:[14]

$$I.V. = (d_A + d_B) - 2.90$$

The average distances from the nucleus of the carbon atoms of the phenyl ring to the centre of the substituent atom or group have been listed by Stanley and Adams.[15] In this thesis, the bond length of $C-CH_3$ is taken as the bond length of $C-CH_2'$.

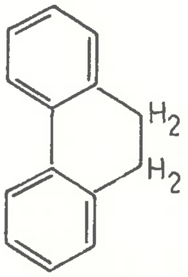
In the first case the interference value is,

$$(1.73 + 1.73) - 2.90 = +0.56 ;$$

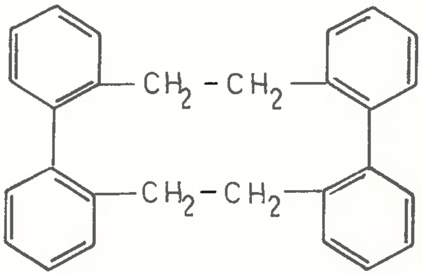
in the second

$$(1.73 + 0.94) - 2.90 = -0.23.$$

These results predict that steric interference in the postulated diradical would be expected to facilitate the formation of 9,10-dihydrophenanthrene (XIII) rather than 1,2-3,4-7,8-9,10-tetrabenzocyclododeca-1,3,7,9-tetraene (XIV) provided that the assumption of the formation of free radicals as intermediates in desulphurisation reaction is accepted. In order to test this hypothesis, the reaction of 2,7-dihydrodibenzo[*c,e*]thiepin with Raney nickel catalyst was carried out under various experimental conditions.



XIII



XIV

## RESULTS AND DISCUSSION

Reaction with W-7 Raney nickel catalyst for 30 min. gave the expected 2,2'-dimethylbiphenyl in 91% yield (determined pure). Although the amount of the residue, left after redistillation of the dimethylbiphenyl was too small to permit any further purification, its infrared spectrum was almost identical with the authentic specimen of 2,2'-dimethylbiphenyl. No evidence for the presence of sulphur was found.

The short reaction time is noteworthy. Obviously, this is not only because of the presence of intervening methylene groups which greatly decrease the resonance stabilization between the hetero-function and the aromatic rings, but also because of the activity and the high hydrogen-content of the catalyst.

All attempts to detect the dimeric material (XV) in the reaction mixture were unsuccessful. This failure may be related to the fact that this desulphurisation had been carried out in a relatively dilute solution (1.5 g. of the starting material per 100 c.c. of methanol), as it is known that the formation of intermolecular dimers occurs more readily in more concentrated solution.

The absence of this dimeric product also supports the belief that the molecules of the substrate were not adsorbed flat owing to the non-planarity of its structure. For the molecule, lying flat on the surface of the catalyst (using $\pi$ conjugation system of the aromatic rings), dimerisation would occur while the system is still adsorbed on the catalyst surface,[16] and this would be expected to increase the probability of intermolecular dimerisation.

Crystalline 9,10-dihydrophenanthrene (XIII) could not be isolated in this experiment. Although the formation of this product is thought to be favoured by the relatively low concentration of the starting material in the reaction mixture, it is clear that the large amount of hydrogen available in W-7 Raney nickel would cause hydrogenation of the intermediate diradicals (XII) before they could undergo intramolecular recombination.

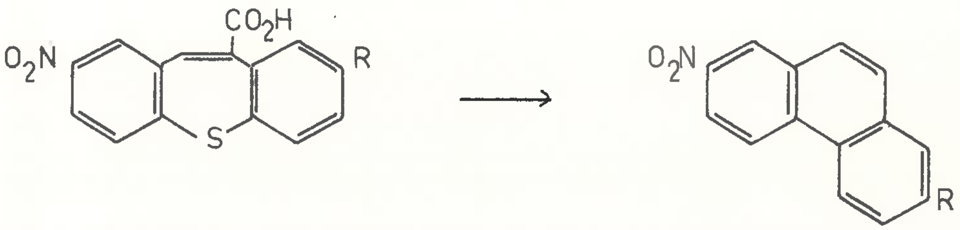
A second product which was isolated in small quantity was an aliphatic hydrocarbon which was identical in all respects with a sample of polymethylene [$(CH_2-)_x$] derived from the reaction of quinoline with Raney nickel.[16] No attempt was made to elucidate the structure of this compound.

Reaction of the dihydrodibenzothiepin with W-2 Raney nickel catalyst also gave 2,2'-dimethylbiphenyl and "polymethylene" in comparable yields; and 9,10-dihydrophenanthrene could not be detected. The reaction had been carried out under similar conditions to those mentioned above.

When the dihydrodibenzothiepin was treated with W-7J Raney nickel (a catalyst heated in vacuo at 100° to reduce its hydrogen-content), a much reduced yield of 2,2'-dimethylbiphenyl (29.8%) was obtained together with phenanthrene (not less than 50.6%). In addition, a mixture of 9,10-dihydrophenanthrene (?) and phenanthrene (0.69 g., ca. 0.8%) was isolated. All attempts to separate these two compounds seemed to result in dehydrogenation of the dihydro derivative.

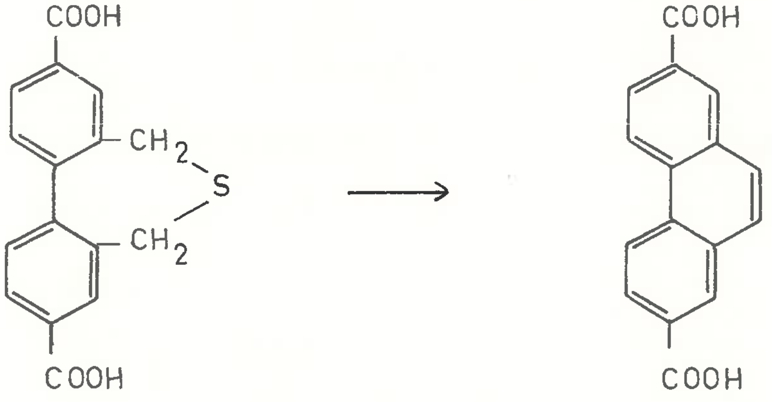
The relatively low yield of 2,2'-dimethylbiphenyl and the formation of phenanthrene (which is undoubtedly derived from 9,10-dihydrophenanthrene by dehydrogenation, either during the reaction or afterwards) in this experiment, are consistent with the view that the hydrogen-content of a catalyst determines the fate of the intermediate free radical (XI). Moreover, the formation of dihydrophenanthrene provides further evidence for the homolytic character of the desulphurisation reaction. Thus removal of sulphur atom first gives a diradical (XII), which, in the presence of an excess of hydrogen, is reduced to 2,2'-dimethylbiphenyl; but in its absence, the diradical is largely converted into dihydrophenanthrene and thence phenanthrene.

The synthesis of phenanthrene by the desulphurisation of dihydrodibenzothiepin with Raney nickel catalyst represents a new synthetical route which could be extended to other phenanthrene derivatives. It woul be noted that several derivatives of dibenzo[b.f.]thiepin have been reported to yield phenanthrene derivatives on the so-called 'extrusion of sulphur' by means of copper in a suitable solvent.[17,18] However, the yields are normally poor[17] and it seems that the only example which has been reported to give a moderately good yield (ca. 50%) is the preparation of 2-methyl-7-nitrophenanthrene (XVII, R=Me) by treatment of 8-methyl-2-nitrodibenzo[b,f]thiepin-10-carboxylic acid (XVI, R=Me) with copper bronze in pure quinoline.



XVI XVII

The preparation of phenanthroic acid derivatives by the desulphurisation of suitable derivatives of dihydrodibenzothiepin by Raney nickel catalyst may become a valuable alternative to the extrusion of sulphur from the benzothiepin derivatives in the presence of copper bronze, since the latter reactions are known to be accompanied by decarboxylation. For example, desulphurisation of 2,7-dihydrodibenzo[c,e]thiepin-2',3"-dicarboxylic acid (XVIII, numbering after Truce and Emrick[7]) with W-7J Raney nickel catalyst might be expected to afford phenanthrene-2,7-dicarboxylic acid (XIX) under similar conditions.



XVIII XIX

Prior to 1896, no method existed for the synthesis of phenanthrene derivatives, while phenanthrene itself had been prepared only under the extreme conditions of "hot tube" reactions. All phenanthrene syntheses, except the aromatic cyclodehydration introduced by Bradsher,[19] require drastic conditions such as dehydrogenation, or give ambiguous results. The Pschorr synthesis was later found to have wide application, but consisted of four separate reaction-steps: condensation, reduction, coupling and decarboxylation. Some difficulties arise as a result of side reactions. For example, reduction and/or hydroxylation may accompany coupling, and where the $\alpha$-phenyl nucleus of the cinnamic acid derivative is unsymmetrically substituted, two isomeric coupling products are possible.[20] Also, the decarboxylation step is often difficult. These complications limit the applications of the Pschorr synthesis. Moreover, the starting materials are not always readily available (i.e. expensive and usually obtained in poor yields).[20,21]

In this study, the parent compound, 2,7-dihydrodibenzo[_c_,_e_]thiepin, was obtained in nearly quantitative yield[7] by cyclisation of 2,2'-bisbromomethylbiphenyl[22] with sodium sulphide in methanol, illustrating the ease of forming seven-membered ring when the hetero-function is represented by sulphide. Provided that the other suitable derivatives of this parent compound could be successfully synthesised, desulphurisation would possibly lead to many interesting phenanthrene derivatives, probably including certain polycyclic hydrocarbons of interest in cancer research

# EXPERIMENTAL

**o-Iodotoluene** was obtained by the diazo reaction from *o*-toluidine in 70.2% yield. The method was adapted from the procedure, described in Vogel,[23] for the preparation of *p*-iodotoluene. Previous attempts to prepare *o*-iodotoluene by direct iodination according to Datta and Chatterjee[24] were unsuccessful owing to difficulties of separating the *ortho* and *para* isomers from the reaction products.

**2,2'-Dimethylbiphenyl** was prepared by the Ullman reaction[25] from *o*-iodotoluene and copper bronze. The reaction mixture (*ca.* 1:1, w/w) was heated under reflux for 3½ days with occasional and gentle shaking. The cooled mixture was filtered and the residue washed with hot benzene. Working up as usual gave the dimethylbiphenyl, at 130-2°/22 mm., in 70.5% yield (the method described by Hall, Lesslie and Turner[26] using activated copper bronze gave 65% yield).

**2,2'-Bisbromomethylbiphenyl** was obtained in 43.5% yield by bromination of 2,2'-dimethylbiphenyl according to the procedure of Hall, Lesslie and Turner,[26] as colourless prisms, m.p. 91-92° after recrystallisation from light petroleum (b.p. 60-80°) and decolourisation with activated charcoal (lit.[26] m.p. 91-93°).

*2,7-Dihydrodibenzo[c,e]thiepin* was prepared, according to Truce and Emrick,[7] by treatment of 2,2'-bisbromomethylbiphenyl with sodium sulphide in methanol. The 2,7-dihydrodibenzo[*c,e*]thiepin was obtained as prisms (from absolute ethanol and charcoal), m.p. 89-90° (lit. m.p. 89-90°), yield 92%.

*Raney nickel:* W-7 Raney nickel was prepared by the method of Billica and Adkins,[27] except that the catalyst was washed with methanol instead of ethanol.

W-2 Raney nickel was prepared as described by Ralph and Mozingo[28] and washed with a continuous stream of distilled water until neutral to litmus, then with methanol by decantation.

W-7J Raney nickel was prepared by the method of Badger and Sasse.[11]

All the catalysts used in each reaction were freshly prepared from 50:50 aluminium-nickel alloy (B.D.H.). Methanol and ethanol were purified by fractional distillation over sodium hydroxide.

*Desulphurisation with W-7 Raney nickel.* The dihydrodibenzothiepin (3 g.) was added to a suspension of W-7 Raney nickel (from 30 g. of alloy) in methanol (200 ml.) and the mixture refluxed for $\frac{1}{2}$ hr. The catalyst was collected on Celite, washed with hot methanol (3 x 100 ml.), and subsequently extracted with methanol (Soxhlet) overnight. The combined filtrates and extracts were evaporated and the residue taken up in ether, dried over anhydrous magnesium sulphate.

Distillation of the dried residue gave 2,2'-dimethylbiphenyl (2.35 g., 91%) and a yellow wax (0.063 g.). No impurity could be detected in the dimethylbiphenyl by gas-liquid chromatography (Griffin and George V.P.C. mark II), and the retention time was identical with that of an authentic specimen. Recrystallisation of the product from absolute ethanol (freezing mixture) gave the dimethylbiphenyl as prisms, m.p. 18° alone or admixed with an authentic specimen. The yellow waxy residue was not further purified. It infrared spectrum, however, was almost identical with that of an authentic specimen of 2,2'-dimethylbiphenyl.

*Desulphurisation with W-2 Raney nickel.*- The dihydrodibenzothiepin (10 g.) was added to a suspension of W-2 Raney nickel (from 150 g. of alloy) in methanol (600 ml.), and the mixture refluxed for 2 hr. After working up as before, the product was distilled, to give 2,2'-dimethylbiphenyl (7.08 g.) and a residue (0.72 g.). The latter was chromatographed on alumina (30 g.) in light petroleum (320 ml., b.p. 40-70°) and gave a further quantity of 2,2'-dimethylbiphenyl (0.42 g., total yield, 87.4%) and a colourless solid (0.008 g.), $\nu_{max}$ (in $CCl_4$) 2867 ($CH_2$), 2860 and 1450 $cm^{-1}$ ($C-CH_3$), which corresponded to those of a "polymethylene" (the sample was supplied by G.D.F. Jackson).

*Desulphurisation with W-7J Raney nickel.*- Xylene (sulphur-free; 200 ml.) was cautiously added from a separating funnel to the dry W-7J Raney nickel (from 125 g. of alloy, degassing time 4 hr.) in a vacuum. The dihydrodibenzothiepin (10 g.) in sulphur-free xylene (300 ml.) was then run in slowly, followed by more xylene (100 ml.). Traces of water were removed by azeotropic distillation with xylene until no moisture was detected in the distillate. The escaped amount of xylene was then replaced. The mixture was refluxed for 15 hr., and the catalyst was collected over Celite, washed with boiling xylene (2 x 50 ml.), and then extracted with xylene (Soxhlet) for 36 hr. Evaporation of the combined xylene filtrates and extracts, and distillation of the residue gave 2,2'-dimethylbiphenyl (2.56 g., 29.8%) and a brown residue (6.9 g.). Chromatography of the residue in hexene on alumina (260 g.) gave:

(a) a pale yellow wax (2.4 g.),

(b) plates, m.p. 92-94° (2.18 g.),

(c) prisms (1.31 g.),

(d) prisms (0.91 g.).

Fraction (a) was chromatographed on partially acetylated paper (prepared by the method of Spotswood[29] but with more sulphuric acid, 0.8 g. of 92% acid per l. of acetic anhydride), with ethanol-toluene-water (17:4:1 v/v). Under ultraviolet light (Chance OX7 U.V. Filter) two spots were seen: one showed blue fluorescence, the other violet. The spots were cut out and separately extracted into 95% ethanol. The extract from the violet-fluorescing area gave an absorption maximum at 252 mμ (Optica CF-4 Recording Spectrophotometer), identical with that given by phenanthrene[30] (which also had the same $R_F$ value, 0.4). The extract from the blue-fluorescing area gave an absorption maxima at 252 (phenanthrene) and 265 mμ (dihydrophenanthrene?).

Attempts to separate the phenanthrene and dihydrophenanthrene by column chromatography on partially acetylated cellulose (prepared according to Spotswood[32]) in ethanol-benzene-water (17:4:1, v/v) were unsuccessful. Pure phenanthrene (1.71 g.) was obtained, together with a mixture of phenanthrene and dihydrophenanthrene (0.69 g.). Attempted separation by picrate formation in ethanol (which was afterwards evaporated) and subsequent chromatography on alumina in hexane-benzene (1:1, v/v), also gave only phenanthrene(0.41 g.).

Recrystallisation of fraction (b) gave phenanthrene as colourless plates, m.p. and mixed m.p. 101°. Its picrate had m.p. 144° (lit. 144°), and its $R_F$ value was identical with that of an authentic specimen, (0.4). The total yield of pure phenanthrene isolated was 4.3 g., (50.6%).

Fraction (c) was chromatographed on partially acetylated paper. Two spots were obtained. The first (violet-fluorescing) was identified as phenanthrene (ultraviolet spectrum); the second (brown in ultraviolet light) had the same $R_F$ value as the dihydrodibenzothiepin and the general appearance of the ultraviolet spectra were the same. Sodium-fusion of the crude fraction gave a positive test for sulphur. The yield of phenanthrene in this fraction was not determined.

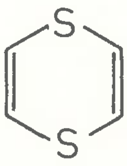
Recrystallisation of fraction (d) gave dihydrodibenzothiepin, m.p. and mixed m.p. 89-90°.

In another experiment, the reaction was carried out on the same scale and under almost the same conditions as above except that the degassing time of the catalyst was only 2 hr. (instead of 4 hr.) and the reaction time was prolonged to 24 hr. Under these conditions, the yield of 2,2'-dimethylbiphenyl was raised to 5.47 g. (66.39%) while the yield of phenanthrene was lowered to 1.9 g. (22.63%). A small amount of colourless solid (16 mg.), m.p. 59-60° after recrystallisation from ethanol, was isolated from the first fraction following chromatography on alumina in light petroleum (b.p. 40-60°). Its infrared spectrum (in $CCl_4$) showed maxima at 2959 ($CH_3$-), 2925 (-$CH_2$-), 2874 ($CH_3$-), 2853 (-$CH_2$-), 1476 (-$CH_2$-) and 1470 $cm^{-1}$ ($CH_3$-), corresponding to a "polymethylene". No unchanged starting material was recovered. Again, the attempts to separate the mixture of phenanthrene and dihydrophenanthrene failed.

## (B) DESULPHURISATION OF THIANTHREN, AND 2,5-DIPHENYL-1,4-DITHIIN

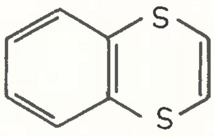
### INTRODUCTION

The parent sulphur compound, 1,4-dithiin (I) was first synthesized in the year 1953, by Parham, Wynberg, and Ramp.[33]

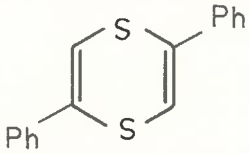


I

Although this compound is structurally related to γ-pyran and to 1,4-dihydropyrazine rather than to pyrazine, there is some tendency to cyclic conjugation in accordance with the known ability of sulphur to transmit conjugation.[34] As a result, benzo-1,4-dithiin (II)[33] and 2,5-diphenyl-1,4-dithiin (III)[35] exhibit some aromatic properties.



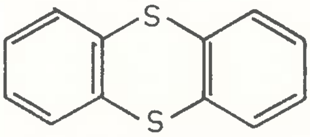
II



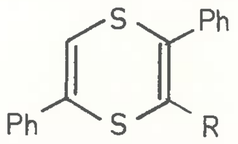
III

Thus, both compounds undergo a number of electrophilic substitution reactions.[36-38] Despite these aromatic properties, 1,4-dithiin cannot be regarded as truely aromatic in the usual sense of the word.[34] For example,[35] attempted acylation of the parent 1,4-dithiin by the Friedel-Crafts type reactions led to the formation of tars. The facile conversions of the compound to the corresponding monosulphilimine (84% yield) and disulphone (72% yield), and also facile polymerisation of 1,4-dithiin by action of Lewis acids have been reported. Moreover, X-ray diffraction data suggest that 1,4-dithiin exists in the so-called "boat" conformation, with the C-S-C bond angle of about 100° and with ethylenic hybridization of the double bonds.[35]

Although both 2,5-diphenyl-1,4-dithiin (III) and thianthren (IV) are derivatives of 1,4-dithiin, these two compounds differ from each other in certain respects. For example, thianthrens are thermally stable compounds,[37,38] but 2,5-diphenyl-1,4-dithiins of type (V; R = H, CHO, $NO_2$) are converted by heat, or by treatment with phosphorus oxychloride, into derivatives of thiophen.[39]



IV

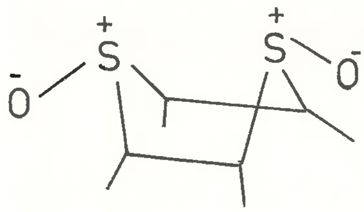


V

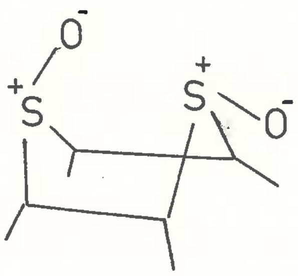
These two compounds, therefore, will be described separately.

## DESULPHURISATION OF THIANTHREN

Bergmann and Tschudnowsky[40] have previously found that thianthren has a dipole moment (1.7 e.s.u.; solvent benzene) and suggested that the central ring was folded about the line joining the two sulphur atoms. Bennett and Glasstone[41] have confirmed the order of magnitude of the moment (1.54 e.s.u., in carbon tetrachloride; and 1.47 e.s.u., in carbon disulphide) and interpreted the previous authors' statement as meaning that the molecule as a whole is folded about the S-S axis. This view has been confirmed by the crystal structure studies of Lynton and Cox,[42] who state that the plane of the benzene rings in the molecule of thianthren are inclined to one another at an angle of 128°. This folded nature of thianthren has been demonstrated also by the observation that thianthren dioxide exists in two isomeric forms. The α-isomer (VI) has an *anti-cis* structure; and the β-isomer (VII) has a *trans* configuration.[43]



VI



VII

In addition, the carbon-sulphur bonds in thianthren molecules have been found to have a length of 1.76 Å.[42] This value lies between the characteristic bond length of pure C-S bond (1.81 Å) and that of C=S bond (ca. 1.64 Å) indicating a certain amount of d$\pi$ conjugation. This finding is of interest, as Sutton[44] has pointed out that the sulphur atom could use d$\pi$ as well as p$\pi$ orbitals, and conjugation could therefore occur even though the molecule is not flat. The C-S-C bond angle[42] of 100° is the same as that found in 1,4-dithiin[45] and agrees well with the C-S-C bond angles in various non-cyclic compounds, so that this experimental evidence supports the view that folding of the molecule enables the sulphur atoms to retain its natural valency angle.

Removal of the sulphur atoms from a molecule of thianthren can occur either in two steps, or in one. If simultaneous loss of both sulphur atoms takes place, the diradical (VIII) should be formed. Depending on the conditions, (VIII) will react either with hydrogen or with other radicals; some of the possible products are shown in Fig. 9. If only one atom of sulphur is lost from a molecule of thianthren another series of products may be expected to be formed.[cf.46,47] Among these, the aromatic dibenzothiophen should be more resistant towards desulphurisation than any other possible sulphur-containing products (see Fig. 9).

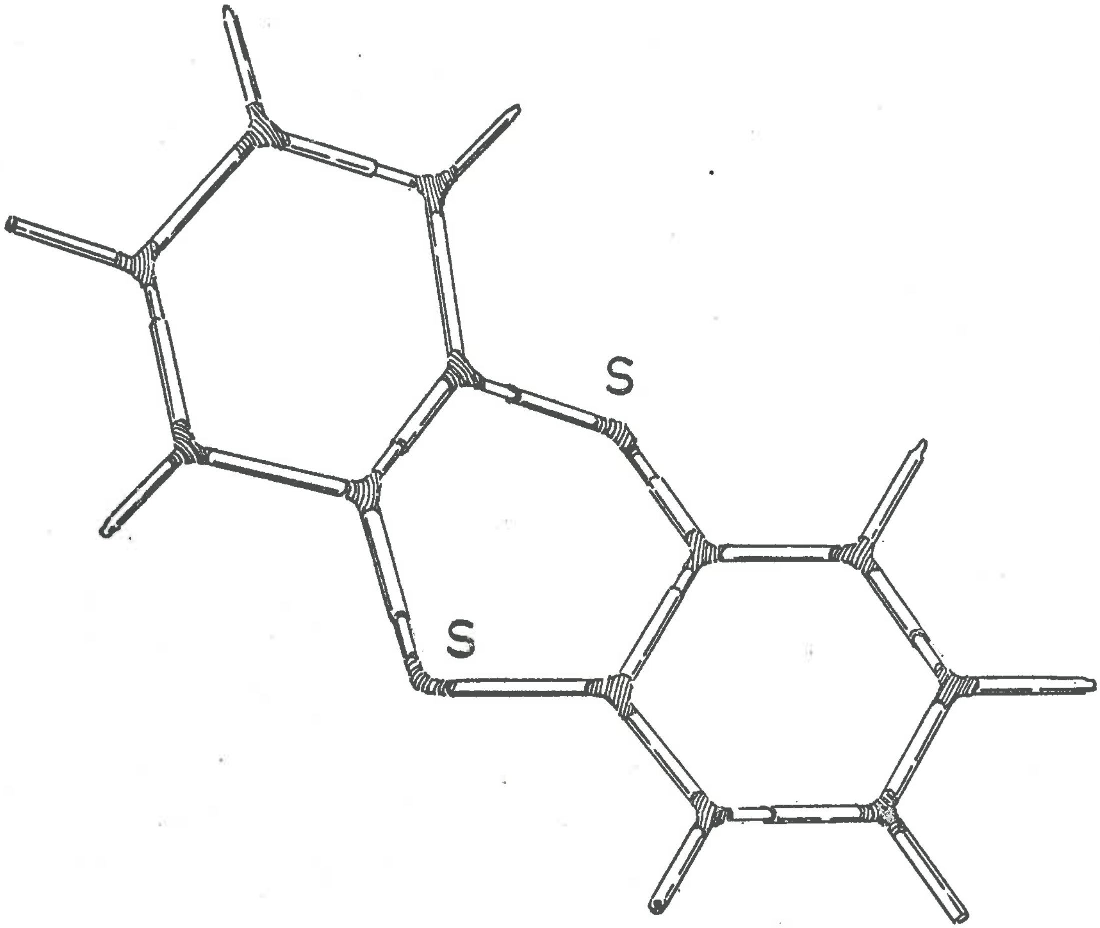


Fig. 8 .- A Dreiding Model of Thianthren.

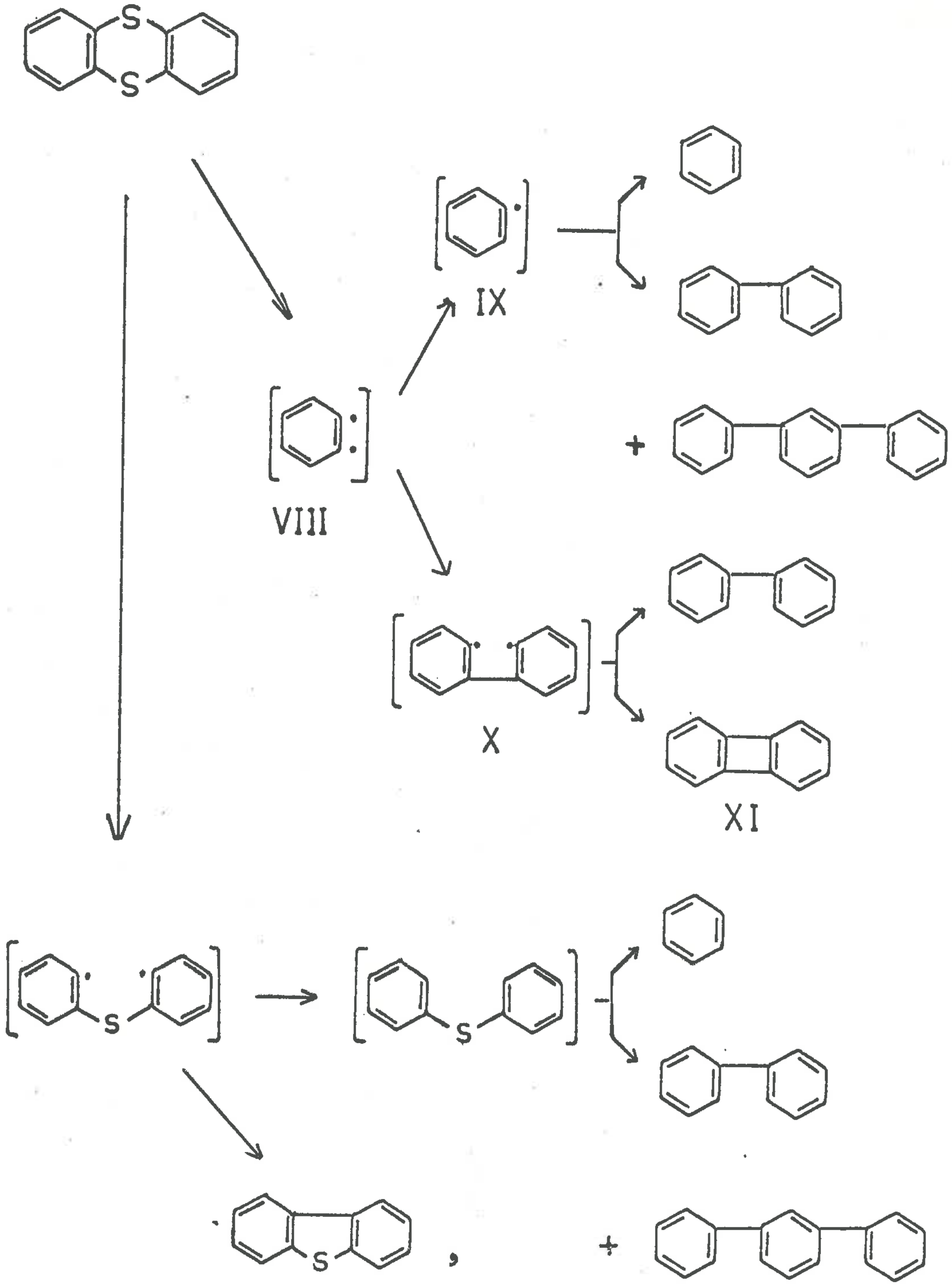


Fig. 9. - Some Theoretically Possible Products of the Desulphurisation of Thianthren.

The first attempts to desulphurise thianthren were carried out with copper powder. These reactions require temperatures as high as 300° and are commonly carried out in an atmosphere of hydrogen or carbon dioxide. Under these conditions thianthren [47, also cf. 48] is converted to dibenzothiophen but as much as 50% of the starting material has been recovered. This reaction is related to the conversion of phenothiazines to carbazoles.[49,50] More recently, Loudon and his colleagues applied this method for the extrusion of sulphur as a synthetic approach to derivatives of phenanthren,[17] and of phenanthridine.[51] Polycyclic thiazepines have been similarly converted to polycyclic aza-hydrocarbons.[52] It is noteworthy that most of the examples of the extrusion of sulphur involve a ring contraction, and they are generally accompanied by aromatisation. As far as the mechanism of this reaction is concerned, it has been reported that cupric sulphide is among the reaction products isolated.[49,50] However considerable evidence exists in the literature to support the view that the "extrusion of sulphur" produces elemental sulphur and that the cupric sulphide is the only result of subsequent reaction.[53-56] For example, the action of heat alone may extrude sulphur from certain compounds, causing aromatisation.[37,53-56] Hence it appears that the extrusion of sulphur is largely dependent on the overall molecular structure of the sulphur compound, and the transition metal (copper) plays only a subsidiary part.[57] In contrast, the desulphurisation with Raney nickel (see Introduction Chapter) must be regarded as reaction between the activated metal catalyst and the sulphur atom of the organo-sulphur compound. This reaction is, to a first approximation, independent of the remainder of the molecule.

Among the three possible methods which may be expected to effect desulphurisation of thianthren (extrusion of sulphur in the presence of copper, desulphurisation with hydrogen-rich Raney nickel catalyst, and desulphurisation with hydrogen-poor Raney nickel catalyst) it seemed that the use of a hydrogen-rich Raney nickel catalyst would be most effective. This view is supported by several observations which indicate that hydrogen may take part in the scission of carbon-sulphur bonds. For example, Badger, Kowanko, and Sasse have demonstrated that in desulphurisations with Raney cobalt and Raney iron, the presence of a hydrogen atmosphere significantly increased the percentage of sulphide undergoing reaction.[58] Hauptmann, Walter and Marino[46] also have observed that the desulphurisation of diphenylsulphide can be effected with a nickel catalyst which is essentially free of hydrogen, provided that the reaction temperature is sufficiently high. Similarly, di-1-naphthylsulphide[59a] which was not affected by a degassed Raney nickel at 64° was desulphurised at 140°. Evidently, hydrogen released from the interstitial positions in the metal promoted the reaction. Furthermore, the observation that, in general, hydrogenolytic desulphurisation does not occur with degassed Raney nickel catalysts under conditions, which reactions can proceed smoothly with active, hydrogen-rich Raney nickel, seems to point in this direction.[59b] Although a hydrogen rich Raney nickel catalyst should therefore be most effective in desulphurising thianthren, benzene would be expected to be the only product. On the other hand, a degassed Raney nickel catalyst was expected to favour the formation of at least some of the other products shown in Fig. 9. At this point it should be noted that Baker, Barton, and McOmie,[60] in one of their attempts to synthesize a derivative of the unsaturated four-membered ring compound (biphenylene, XI), have observed that thianthren was unaffected by treatment with a deactivated Raney nickel catalyst. Experimental details have not been reported.

In the present study, W-7J Raney nickel catalyst prepared according to Badger and Sasse,[11] and Raney nickel catalyst degassed at 340° were used to effect the desulphurisation of thianthren.

## RESULTS AND DISCUSSION

The first attempt to desulphurise thianthren with W-7J Raney nickel was carried out in toluene as solvent. In this way, 97.7% of the starting material was recovered and traces only of benzene (1.04%, if formed from thianthren) were detected. Since it is known that degassed Raney nickel catalyst brings about the dealkylation of the xylenes[61] it is not possible to state with certainty whether the benzene detected in this reaction mixture is derived from thianthren or from the solvent.

However, by analogy with results obtained from the other experiments carried out in the present study, it is thought that the benzene was derived by the demethylation of toluene rather than by hydrogenolytic desulphurisation of thianthren. For example, isolation of the aliphatic hydrocarbon believed to be "polymethylene" following desulphurisation of thianthren in mesitylene supports this view. Sasse[16] was the first to isolate this paraffin from the reaction of the quinolines with Raney nickel catalyst. The material observed in the present study was identical in all respects with that obtained by Sasse. He found that the compound has the melting point 59-60° and a characteristic infrared spectrum. Moreover, Jackson[61] recently reported the isolation of toluene and of benzene from the reaction products arising from the action of a mixture of isomeric xylene over degassed Raney nickel catalyst. In his study of the formation of indoles from o-alkylanilines and N-alkyl-o-alkylaniline by the action with W-7J degassed Raney nickel, he has pointed out that the compound $(CH_2)_x$ must arise from the side chain of the o-alkylaniline and not from the phenyl ring. These results lend support to the above hypothesis and the amount of the starting material, which was not recovered, lies well within the experimental error. This is also in agreement with the work of Baker, Barton and McOmie,[60] who observed, as mentioned earlier, that thianthren was unaffected by treatment with a deactivated Raney nickel catalyst.

Since the desulphurisation of thianthren with W-7J Raney nickel catalyst conducted in toluene resulted in recovering of most of the starting material, this prompted the author to attempt reactions at higher temperature than that of boiling toluene. At first it was considered that, owing to its high boiling point, methylnaphthalene might be a suitable solvent for such an experiment. However, any dealkylation would result in the formation of naphthalene, separation of which from the expected products of desulphurisation (e.g. biphenyl) seems to be particularly difficult. It was, therefore, planned to carry out the desulphurisation reaction at the melting point (158-159°) of the sulphur compound. By this means, no solvent would be needed, provided that sufficient thianthren was used to cover the pyrophoric catalyst. Nevertheless, in order to introduce the starting material to the degassed catalyst the thianthren had to be dissolved in a suitable solvent and the latter had to be removed subsequently. When dioxan was used for this purpose, explosions resulted in several experiments. The reason for these occurrences are not known, and work along these lines was abandoned. However, it is known that thiophen reacts explosively when added to a degassed Raney nickel catalyst without being diluted with a suitable solvent.[12]

Further attempts to desulphurise thianthren were carried out in diethyl phthalate as solvent. Although care was taken to wash the catalyst free of alkali, small quantity of ethyl benzoate and benzoic acid were formed in these experiments. That these products arose from reaction of diethyl phthalate with the "neutral" W-7J Raney nickel catalyst was shown by treating diethyl phthalate with this catalyst under the same conditions employed for the desulphurisation of thianthren. Under these conditions, ethyl benzoate, benzoic acid and phthalic acid were formed. Although phthalic acid was not among the products obtained in the desulphurisation of thianthren in the other experiment, it was probably present in the residue being saponified (see Experimental part). The formation of phthalic acid is undoubtedly due to hydrolysis by hydroxide ions which remained adsorbed on the catalyst even after prolonged washing with distilled water. Incidently, after washing the catalyst for about 5 hr. with distilled water the supernatant was found to be neutral to B.D.H. indicator papers.

Since it has been reported previously that ester groups are not affected by Raney nickel,[62] (also cf. Chapter III), the formation of benzoic acid, ethyl benzoate and phthalic acid from diethyl phthalate in the presence of degassed Raney nickel is of interest. It is thought that the high reaction temperature is possibly responsible for the release from the Raney nickel catalyst, of adsorbed hydroxide ions, which subsequently react with the solvent to form phthalate anions. It is not known how these anions are converted to phthalic acid, which is isolated from the basic reaction mixture without the addition of protic solvents. The formation of benzoic acid and ethyl benzoate from diethyl phthalate involves loss of carbon dioxide either from phthalic acid (or its anions) or from its monoester (or its anion). Reactions involving the decarboxylation of phthalic acid (or its anions) appears to have been observed previously only under more vigorous conditions than used in the present work. Thus, the decarboxylation of the calcium salt of phthalic acid[63] is known not to occur below 300°. Similarly Ipatiev and Philipov[64] have reported that diethyl phthalate gives rise to ethyl-*o*-toluate, carbon dioxide and methane when heated with hydrogen at 230° (100 atmospheres) in the presence of nickel oxide. Moreover, Schrader, and Wolter[65] observe the conversion of sodium phthalate to sodium benzoate and benzene by heating the phthalate salt with water under pressure.

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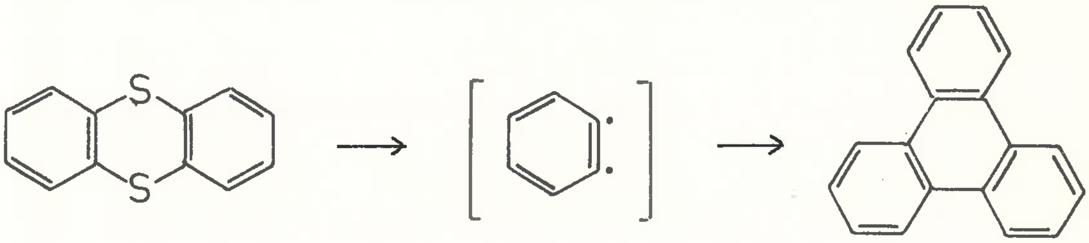
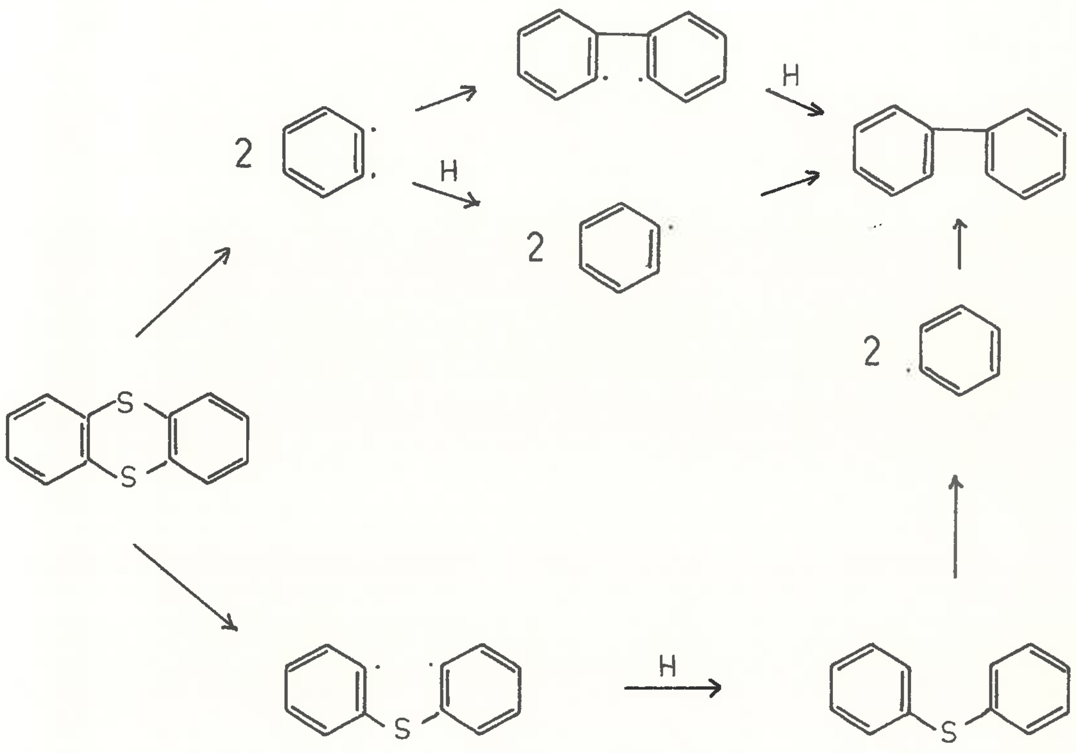
In view of these complications, another desulphurisation was carried out in mesitylene (b.p. 164-165°) with Raney nickel which had been degassed at 340°. Although more thianthren was recovered (74.6%), traces of another product, triphenylene were isolated. The isolation of this hydrocarbon in this reaction provides evidence for the view that the simultaneous loss of two sulphur atoms occurs at least occassionally giving rise to the formation of the diradical (VIII). It is not known whether such these diradical are identical with the benzyne intermediate which was first postulated by Wittig,[66] and studied by Roberts and his co-workers.[67] However, it is noteworthy that triphenylene is commonly observed in reactions involving benzyne.



It was thought that the yields of this interesting product might be increased by increasing the concentration of theanthren in mesitylene. Recovery of unchanged starting material in higher yields is consistent with the view that conjugation in the thianthren molecule (see p. 91) is apparently a factor resisting desulphurisation with a Raney nickel catalyst of a deactivated type. Finally, isolation of biphenyl (4.91%) suggests that the Raney nickel catalyst degassed at 340° still contains a certain quantity of adsorbed hydrogen which probably effect the scission of carbon-sulphur bonds and hydrogenation of the postulated radical as shown below.



## EXPERIMENTAL

### Desulphurisation of Thianthren

Ultraviolet Spectra.- These were determined in 95% ethanol on an Optica CF-4 recording spectrophotometer.

Infrared Spectra.- An infracord spectrophotometer, Perkin-Elmer, Model 137 was used throughout.

Gas-liquid Partition Chromatography.- A Griffin V.P.C. apparatus Mk. II was used with a 6 ft. column packed with Celite (60-80 mesh; coated with 15% (wt.) of ApiezonL), inlet pressure 29 mm., outlet pressure 8.7 mm., and a flow rate of 1 l./hr. of nitrogen. Standard mixtures were run wherever possible.

Paper Chromatography.- This was carried out on acetylated paper prepared according to the method of Spotswood;[29] but more sulphuric acid (0.8 g. of 92% acid per l. of acetic anhydride) was used.

Partially Acetylated Cellulose Powder.- Both for column and thin film chromatography the powder was prepared according to the method of Spotswood[32] except that 72% perchloric acid was used as a catalyst.

Preparation of Catalysts.- W-7J Raney nickel catalyst was prepared from nickel-aluminium alloy (50:50; B.D.H.) according to the procedure described by Badger and Sasse,[11] except that, in the third experiment (desulphurisation in diethylphthalate), for the washing process, the catalyst was washed (with gentle stirring) continuously with distilled water until washings were neutral to pH indicator paper (B.D.H.) (15 hr.). The degassing period, at 100°/12 mm. was also prolonged to 6 hr.

A Raney nickel catalyst degassed at 340° was prepared from nickel-aluminium alloy according to the method described for W-7J Raney nickel catalyst of Badger and Sasse except that the addition of alloy was carried out with external cooling (ice), and that the degassing procedure was altered as follows. The flask contents were kept at 80°/5 mm. (water bath) for 3 hr., and then at 100°/5 mm. for 2 hr. Then the flask was carefully heated to 220° (air bath), when the pressure was observed to rise up rapidly to *ca.* 10 mm. The flask was maintained at this temperature until the pressure fell to 5 mm. Finally, the catalyst was heated to 340° and kept at this temperature for 1 hr.

A Raney cobalt catalyst was prepared by the addition of cobalt-aluminium alloy (21 g., 30:70; Lights) to the vigorously stirred solution of sodium hydroxide (27 g.) in distilled water (100 c.c.). This was done as quickly as frothing allowed. After the addition had been completed the catalyst was digested at 100° for 1 hr.; then washed successively by decantation with distilled water (4 x 100 c.c.) and methanol (2 x 100 c.c.).

Preparation of Thianthren.- The compound was prepared from 2-aminodiphenyl sulphide and sodium xanthate by the method of Cullinane and Davies.[78]

Desulphurisation of Thianthren.-

(1) In toluene. Thianthren (12 g.) in sulphur-free toluene (800 c.c.) was cautiously added from a separating funnel to the dry W-7J Raney nickel catalyst (from 125 g. of alloy), while air was being excluded. The mixture was then refluxed under nitrogen for 6 hr. The catalyst was collected over Celite and subsequently extracted with toluene (Soxhlet) overnight. The filtrate and extract were combined and fractionally distilled through a jacketed column (2 x 60 cm.) packed with single turn glass helices. All the material boiling below 110.5° (reflux ratio *ca.* 1:10) was collected in one fraction (17.3 g.) and a second fraction, b.p. 110.5° (675 c.c.) was taken. Examination of the first fraction (dried over potassium hydroxide pellets) by gas-liquid partition chromatography showed the presence of benzene (0.09 g.; calculated from areas under peaks in comparison with those of standard mixtures). Benzene was not found in the second fraction. Concentration of the residue gave colourless needles (11.72 g.), which after crystallisation from light-petroleum (b.p. 60-70°) melted at 156-157°, alone and mixed with thianthren. Their infrared spectrum was identical with that of an authentic specimen of thianthren. The mother liquor was not further investigated.

(2) Without solvent. Pure dioxan (200 c.c.) was introduced into the flask containing the W-7J Raney nickel catalyst (from 125 g. of alloy) in the same manner as described previously. Next, thianthren (75 g.) was added to the suspension. Dioxan was then removed by distillation through a jacketed column packed with helices, while nitrogen was being passed through the system. During this time the temperature in the reaction flask was gradually increased but before the thianthren melted the mixture exploded. This occurred in four separate experiments.

(3) In diethyl phthalate. A mixture of thianthren (10 g.), diethyl phthalate (330 c.c.), and W-7J Raney nickel catalyst (from 125 g. of alloy) was refluxed at 200-230° for 60 hr. while nitrogen was being passed through the apparatus. The gas escaping from the condenser was passed through a trap cooled in solid carbon dioxide. The catalyst set to a solid mass, and green crystals were deposited on its surface. The solid was separated, washed repeatedly with hot diethyl phthalate (2 x 50 c.c.) and then extracted with hot absolute ethanol (Soxhlet) for 3 days. The combined filtrates and extracts were divided into two equal portions and worked up separately as follows:

Portion (a) was evaporated on a water bath to remove ethanol. Distillation of the yellow liquid residue under reduced pressure gave:

(i) a colourless liquid of pleasant smell, b.p. 50-60°/7 mm. (0.2 g.);

(ii) a colourless liquid of pleasant smell, b.p. 109-110°/7 mm. (0.19 g.);

(iii) colourless needles deposited along the wall of the condenser, b.p. 120-130°/7 mm., m.p. 114-115° (1.77 g.);

(iv) residue (*ca.* 200 c.c.), was recombined to the portion (b).

Examination of fraction (i) by gas-liquid partition chromatography of 100° gave two peaks, the retention times of which corresponded to ethanol and ethyl benzoate respectively. The infrared spectrum of the fraction shows all the peaks of a mixture of ethanol and ethyl benzoate. Fraction (ii) was identified as ethyl benzoate by comparison of its infrared spectrum with that of an authentic specimen. Fraction (iii) gave a negative test for the presence of sulphur (sodium-fusion). After recrystallisation of the fraction (light-petroleum, b.p. 60-80°), its melting point dropped from 114-115° to 107-108°. This suggested that fraction (iii) was a mixture. The infrared spectrum of this recrystallised material indicated the presence of a carboxylic acid. Extraction of this fraction by sodium bicarbonate yielded benzoic acid (0.91 g.), identical in all respects with that of an authentic specimen. No other acids could be detected. The resulting neutral fraction crystallised from light-petroleum (b.p. 30-45°) to give colourless needles m.p. 69-70.5° (0.145 g.), alone and mixed with an authentic specimen of biphenyl. Infrared and ultraviolet spectra also confirmed this identification.

Portion (b), which was recombined with the fraction (iv) above, was added dropwise to a stirred solution of potassium hydroxide (300 g.) in methanol (2500 c.c.) during $2\frac{1}{2}$ hr. at room temperature. After the addition was complete, stirring was continued for a further 6 hr. The precipitate of potassium phthalate was separated and subsequently extracted with ether (Soxhlet) for 20 hr. The filtrate was concentrated on a water bath and the residue was poured into distilled water (500 c.c.). It was then continuously extracted with ether for 24 hr. Both ethereal extracts were combined, washed with distilled water (5 x 500 c.c.), dried (anhydrous magnesium sulphate), and evaporated on a water bath. Distillation of the dark yellow residue (5.99 g.) in vacuo gave:

(i) colourless needles, b.p. 140-145°/21 mm. (2.35 g.), m.p. 61-63°;

(ii) light brown residue (2. 71 g.).

Recrystallisation of fraction (i) (light-petroleum, b.p. 60-80°) raised the melting point to 69-70.5° alone or admixed with an authentic specimen of biphenyl. This identity was also confirmed by its infrared and ultraviolet spectra. Thin film chromatography of the fraction (ii) on partially acetylated cellulose plate using the solvent system methanol-ether-water (4:4:1, v/v), gave three spots. Two of these were identical with the spots given by authentic specimens of biphenyl and dibenzothiophen respectively. The other spot ($R_F$ = 0.46) could not be identified and was not identical with the starting material. Fraction (ii) (1.6 g.) was chromatographed on a column of partially acetylated cellulose (*ca.* 80 g.) in ethanol-toluene-water (17:4:1, v/v) and 80 fractions (*ca.* 10 c.c. each) were collected. Fractions with identical ultraviolet spectra were combined and worked up to give:

(*a*) biphenyl (0.31 g.) (first eluate), identified as above;

(*b*) a mixture of biphenyl and dibenzothiophen (overlapping fractions); and

(*c*) dibenzothiophen (0.7 g.), m.p. and mixed m.p. 98-99°, identified by its picrate, m.p. and mixed m.p. 123-124° and also by comparison of its infrared spectrum with that of an authentic specimen.

The separation of the overlapping fractions of biphenyl and dibenzothiophen (combined with the light brown residue (ii), 1.2 g.) was attempted by chromatography on a Raney cobalt column, prepared according to the method described by Kowanko.[57] This resulted in isolation of the further amount of biphenyl (0.11 g.). The methanol extract of the catalyst (Soxhlet) was concentrated to a small volume, then added to water and continuously extracted with ether for 24 hr. In this way dibenzothiophen (0.12 g.) was obtained. The mother liquors were not examined.

The liquid collected in the trap (ca. 3 c.c.) was dried over potassium hydroxide pellets. The dried liquid was examined by gas-liquid partition chromatography and peaks corresponding to benzene and ethanol were obtained. The areas under peaks gave the yield of benzene (0.12 g.).

Attempted reaction of diethyl phthalate and neutral W-7J Raney nickel catalyst. The mixture of diethyl phthalate (95 c.c.) and the neutral W-7J Raney nickel catalyst (prepared from 30 g. of alloy) was refluxed at 190-235° under nitrogen for 3 days. The catalyst was separated, washed with pure benzene (2 x 50 c.c.) and then extracted with the same solvent (Soxhlet) for 12 hr. The combined filtrate and extracts (brown-green fluorescence under ultraviolet light) was evaporated on a water bath to remove benzene and traces of water. Redistillation of the residue gave:

(a) ethyl benzoate, b.p. 56-58°/0.55 mm. (21.9 g.) identified as above;

(b) benzoic acid, b.p. 120°/0.9 mm., m.p. 120.5° (8.2 g.), identified as above; further distillation *in vacuo* gave unreacted diethyl phthalate and

(c) dark brown residue (9.5 g.). This was poured into a solution of sodium bicarbonate and non-acidic matter was then extracted with ether. The bicarbonate extract was acidified and subsequently extracted continuously with ether overnight. The ethereal extract was dried and evaporated to give a residue (3.16 g.).

Chloroform extraction (Soxhlet) of the residue for 8 hr. gave benzoic acid (0.59 g.). A colourless solid residue (2.57 g.) remained in the thimble and was identified as phthalic acid by mixed m.p. and by its infrared spectrum in comparison with that of an authentic specimen. The total yield of benzoic acid isolated was 8.79 g. and of phthalic acid, 2.57 g.

(4) In mesitylene. Thianthren (10 g.) in redistilled mesitylene (400 g.) was added to Raney nickel catalyst (from 125 g. of alloy; degassed at 340°) as previously described, followed by more mesitylene (100 g.). The mixture was refluxed under oxygen-free nitrogen for 3 days. The catalyst was collected over Celite and subsequently extracted with sulphur-free benzene overnight (Soxhlet). Colourless needles separated from the filtrate on standing at room temperature and were collected. Recrystallisation from n-hexane gave colourless needles, m.p. 159° (4.55 g.), identified as thianthren by direct comparison. The mother liquors were combined with the benzene extract of the catalyst, and evaporated on a water bath to remove benzene and hexane. Mesitylene was distilled at 32-34°/1.8 mm., and a dark brown residue (4.5 g.) was obtained. Chromatography of the residue on a column of activated alumina (B.D.H.; 250 g.) in n-hexane and elution with the same solvent gave:

(a) a colourless wax, m.p. 59-60° (0.15 g.) after recrystallisation from absolute ethanol, identical (mixed m.p. and infrared spectra) with a "polymethylene" supplied by G.D.F. Jackson;[61]

(b) a mixture of biphenyl and dibenzothiophen (0.68 g.), as indicated by chromatography of the fraction on partially acetylated paper;

(c) a mixture of dibenzothiophen and thianthren (chromatography on acetylated paper) crystallisation of the mixture in n-hexane gave colourless prisms, m.p. 158° (2.7 g.), identical (mixed m.p. and infrared spectra) with thianthren; concentration of the mother liquor gave colourless needles, m.p. 98-99° (0.9 g.), identical in all respects with dibenzothiophen;

(d) thianthren (0.21 g.), identified by mixed m.p. and infrared spectrum;

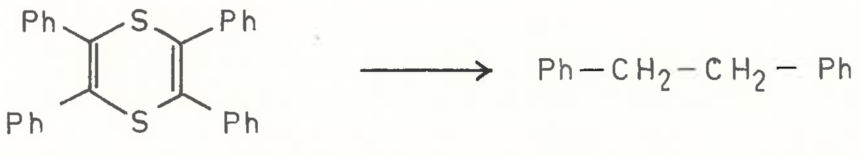
(e) a dark brown oil (0.2 g.) eluted with hexane-benzene (1:1, v/v). Recrystallisation (charcoal) from hexane-ethanol gave colourless needles m.p. 192° (7.0 mg.), $\lambda_{max.}$ (in 95% ethanol) at 248, 257, 272.5, 284, 300, 320, 326 and 332 mμ. This absorption corresponded to those given by triphenylene;[cf.79] and the melting point was not depressed by admixture with an authentic specimen[80] of this hydrocarbon. No other products were identified in the mother liquor.

An attempt was also made to separate the biphenyl and dibenzothiophen of fraction (b) by chromatography on a Raney cobalt column. This gave dibenzothiophen (0.14 g.) and biphenyl (0.35 g.). Recovery of starting material was 7.46 g. (74.6%); and the total yields of the products were dibenzothiophen 1.04 g. (12.2%), biphenyl (4.91%), and triphenylene (0.1%).

## DESULPHURISATION OF 2,5-DIPHENYL-1,4-DITHIIN

Johnson, Moran, and Kohmann[68] first synthesized this compound in 1889 by hydrolysis of 2-benzoylmethylmercapto-4-methyl-6-oxypyrimidine. The first attempts to desulphurise this compound were also carried out by the same authors; but these were unsuccessful and the compound was described as being extremely stable. Another synthesis of 2,5-diphenyl-1,4-dithiin is due to Groth,[69] who prepared phenacyl mercaptan and condensed it to give 2,5-diphenyl-1,4-dithiin; but no yield were given. In the present study, the dithiin was obtained in nearly quantitative yield by the acid hydrolysis of sodium phenacyl thiosulphate.[70]

A search of the literature revealed that several derivatives of 1,4-dithiin compound have been of interest in desulphurisation studies. Generally, these desulphurisation reactions were carried out with a large excess of Raney nickel catalyst (type was not reported) in ethanol solution during 2-5 hr. at reflux. These resulted in the replacement of sulphur by hydrogen, and hydrogenation of double bonds of the dithiin ring. The desulphurisation of 2,3,5,6-tetraphenyl-1,4-dithiin (XII) reported recently by Kirmse and Horner,[71] may be cited as an example.



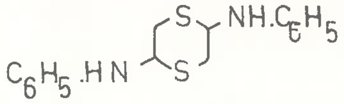
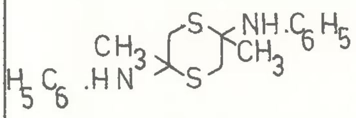
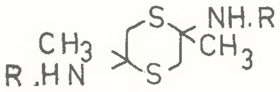
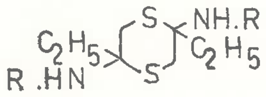
XII

78%

Dibenzyl was the only product observed in the above experiment and the other possible products e.g. tetraphenylthiophen, and stilbene, were not isolated. It is noteworthy that the same authors have obtained 2,3,4,5-tetraphenylthiophen in 87% yield from thermal decomposition of the 1,4-dithiin which was conducted in decalin.

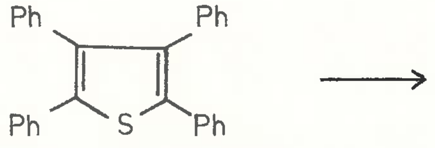
Some perhydro derivatives of 1,4-dithiins which have been desulphurised are assembled in Table 1.

TABLE 1

| Starting compound | Reaction product | Yield | Reference |
|---|---|---|---|
|  | $C_6H_5.NH.C_2H_5$ | - | 72 |
|  | $C_6H_5.NH.CH(CH_3)_2$ | 60 | 73 |
|  | $4-CH_3.C_6H_4.NHCH(CH_3)_2$ | 75 | 73 |
|  | $4-CH_3.C_6H_4.NH.CH(CH_3)C_2H_5$ | 65 | 74 |

R = $4-CH_3$

The desulphurisation of 2,3,4,5-tetraphenylthiophen (XIII) with W-7 Raney nickel catalyst in xylene has been reported by Badger, Christie, Pryke, and Sasse[75] to give 1,2,3,4-tetraphenylbutane (32.5%) together with dibenzyl (5%). These authors have found that the W-7 Raney nickel catalyst does not effect desulphurisation of the tetraphenylthiophen when the reaction is conducted in methanol-benzene.



$CH_2.Ph.CH_2.Ph.CH_2.Ph.CH_2.Ph$

$+ \quad Ph.CH_2.CH_2.Ph$

XIII

As mentioned earlier, X-ray diffraction data established the boat configuration for 1,4-dithiin.[35] In addition, inspection of a Dreiding model of 1,4-dithiin indicates that this conformation is the most preferred one; in particular, it is not possible to construct the chair conformation of this ring system. This being so, sulphur atoms in the same molecule could be adsorbed simultaneously onto the metal surface. Subsequently this could result in simultaneous removal of the two sulphur atoms and the production of the observed sulphur-free compound even under relatively mild conditions, as in the case of the tetraphenyl-1,4-dithiin (ethanol was used as a solvent), whereas the tetraphenylthiophen does resist desulphurisation (xylene, b.p. 138-142°, had to be used as a solvent).

Inspection of a Dreiding model of 2,5-diphenyl-1,4-dithiin (see Fig. 10, p. 118) also supports the view that the presence of both phenyl groups does not hinder such simultaneous adsorption of the two sulphur atoms. Nevertheless, the probability of adsorption through only one sulphur atom in the molecule cannot be excluded. If this is followed by desulphurisation, formation of 2,4-diphenylthiophen may be expected, provided that the Raney nickel catalyst used is of a degassed type and the conditions are not too vigorous.[cf.75]

In this respect, it should be noted that a certain number of reactions, which involve the conversion of 2,5-diphenyl-1,4-dithiin (III) into 2,4-diphenylthiophen or derivatives of 2,4-diphenylthiophen have been observed. For instances, treatment of (III) with dimethylformamide and phosphorus oxychloride (the Vilsmeier reaction) gave rise to 2-formyl-3,5-diphenylthiophen instead of the expected 2-formyl-3,6-diphenyl-1,4-dithiin.[39] The thermal aromatisation of (III) to give sulphur and 2,4-diphenylthiophen also has been reported. Moreover, the monosulphone of (III) has been shown to eleminate sulphur dioxide and give 2,4-diphenylthiophen.[39] In this connection, it was anticipated that the presence of a sulphone group would assist in the polarization of the double bonds of the ring system. The course of the reaction was represented as follows:

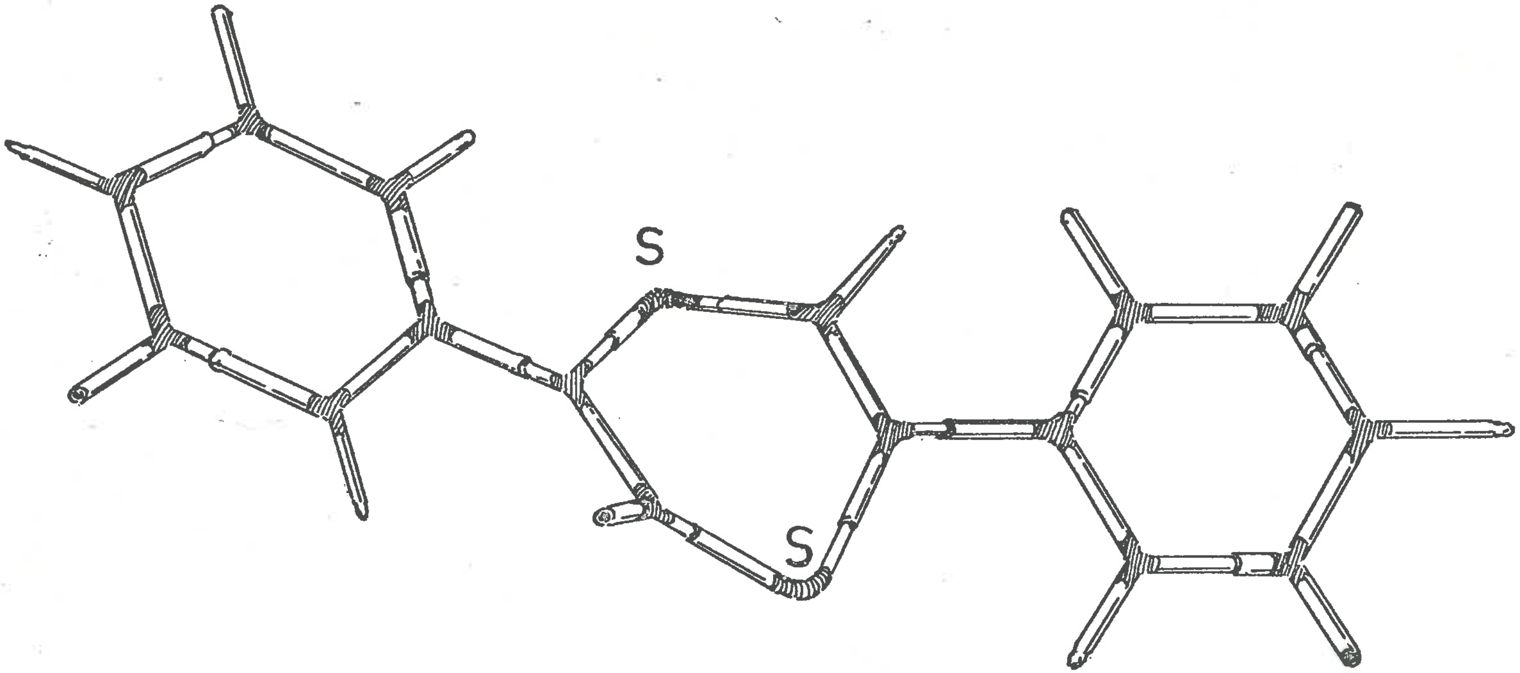
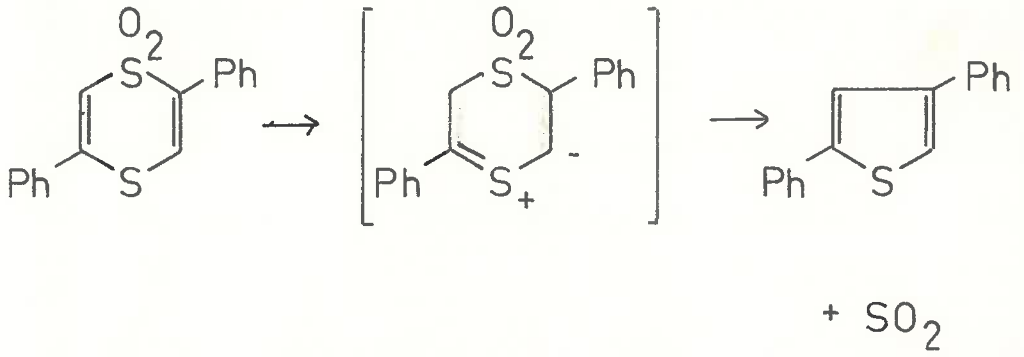
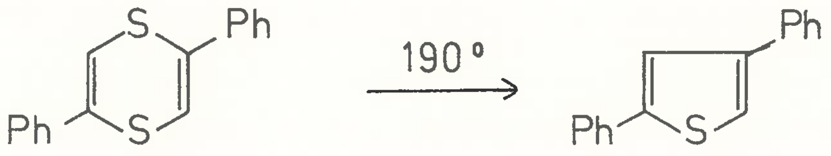


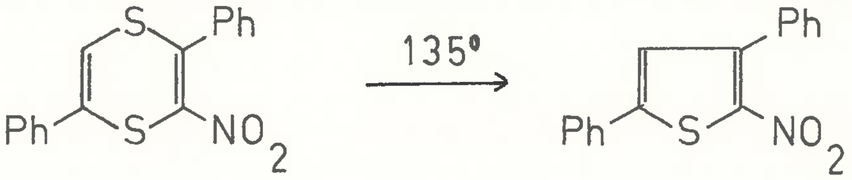
Fig. 10. - A Dreiding Model of 2,5-Diphenyl-1,4-dithiin.



Similarly the elimination of sulphur is facilitated by the presence of a polarising group on the dithiin ring. Thus, when 2,5-diphenyl-3-nitro-1,4-dithiin (XIV) was heated to 135°, Parham and Traynelis[37] found that a vigorous exothermic reaction occurred which resulted in the formation of 5-nitro-2,4-diphenylthiophen. Similarly, mere heating of (III) at 190° has been found to cause the extrusion of sulphur and the formation of 2,4-diphenylthiophen.[39]



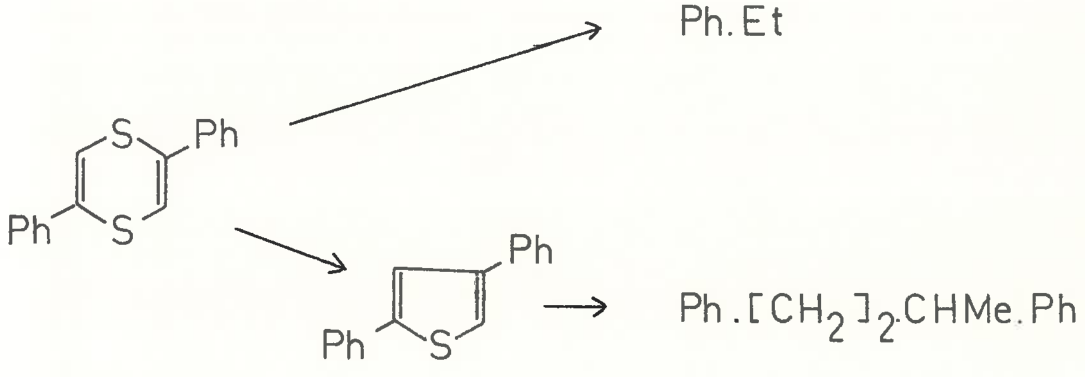
III



XIV

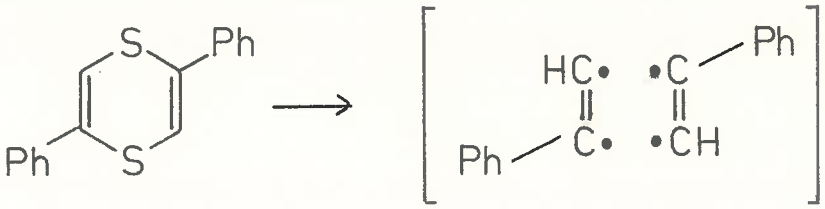
For the present purpose, it seemed, therefore, desirable to work at temperature below 135° in order to exclude any possibility of thermal aromatisation to give 2,4-diphenylthiophen.

As discussed earlier (see Chapter I, p. 42) many facts support the view that the hydrogen present in Raney nickel catalysts does take part in the homolytic splitting of carbon-sulphur bonds during desulphurisation reactions. In accordance with the observation of Kirmse and Horner, who obtained dibenzyl in 78% yield from desulphurisation of 2,3,5,6-tetraphenyl-1,4-dithiin, it would not be advisable to employ the most active Raney nickel catalysts to effect the desulphurisation of 2,5-diphenyl-1,4-dithiin. This is because whether the hydrogenation takes place prior to or after desulphurisation, the most likely product would be simply ethylbenzene and probably 1,3-diphenylbutane.



Therefore no experiments were carried out in the present thesis with more active Raney nickel catalyst such as W-5, W-6, or W-7. Instead, the action of the degassed W-7J Raney nickel catalyst on 2,5-diphenyl-1,4-dithiin was explored.

At the outset of this study there was no reason to assume that desulphurisation would take place to a large extent, but it was hoped that at least a small percentage of the dithiin might suffer simultaneous loss of both sulphur atom to yield the styryl-α,β-diradical (XV). If it is assumed that these diradicals are formed in a sufficiently large concentration to enable recombination to occur then a relatively large number of different products is theoretically possible. Obviously, if radicals containing one sulphur atom are included, the number of possible products becomes much larger still.



XV

Some of the theoretically possible products, which could arise from the above diradical, have been listed in Table 2.

TABLE 2

| No. | Possible product | Reaction |
|---|---|---|
| 1 | Styrene | Partial hydrogenation of the radical (XV) |

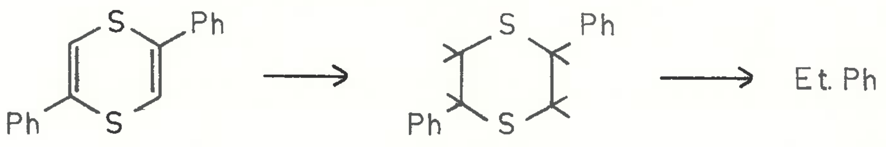
| | | |
|---|---|---|
| 2 | Polystyrene | Polymerisation of (1) |
| 3 | Ethylbenzene | Hydrogenation of the radical |
| 4 | Toluene | Hydrogenolysis of (3) |
| 5 | Benzene | Hydrogenolysis of (3) and (4) |
| 6 | 1,3-Diphenylbuta-1,3-diene[a] | Recombination of the free radicals |
| 7 | 1,3-Diphenylbutane | Hydrogenation of (6) |
| 8 | 1,4-Diphenylbuta-1,3-diene[b] | Recombination of the free radicals |
| 9 | 1,4-Diphenylbutane | Hydrogenation of (8) |
| 10 | 2,3-Diphenylbuta-1,3-diene | Recombination of the free radicals |
| 11 | 2,3-Diphenylbutane | Hydrogenation of (10) |
| 12 | 1,3-Diphenylcyclobutadiene | Recombination of the free radicals |
| 13 | 1,3-Diphenylcyclobutane | Hydrogenation of (12) |
| 14 | 1,3-Diphenylcyclobutene | Partial hydrogenation of (12)[c] |

[a] Two possible stereo-isomeric forms.

[b] Three known stereo-isomeric forms.

[c] Not the only possible pathway.

An alternative pathway for the desulphurisation of 2,5-diphenyl-1,4-dithiin could involve the hydrogenation of the ring system to give its perhydro derivative, followed by ready desulphurisation to give the ethylbenzene.



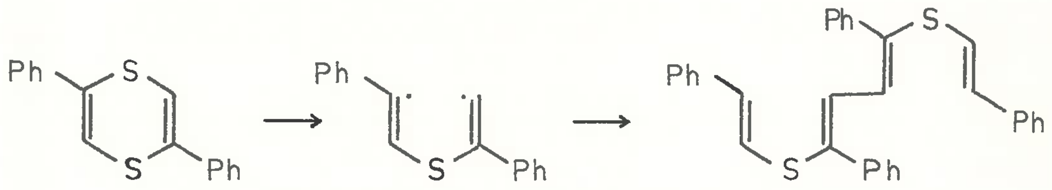
However, this pathway is not likely to be important as the Raney nickel used in these experiments was a degassed catalyst. The decreased hydrogen-content of this catalyst would be insufficient to effect, to any extent, the reduction of the relatively stable dithiin ring. Furthermore, chemisorption involving the $\pi$ electrons of the ethylenic double bond would probably not be able to compete successfully with the chemisorption *via* the sulphur atom.[76] This is because the hydrogenation of olefins is well known to be inhibited by the presence of sulphur compounds.[76]

Up to the present time, isolation of unsaturated materials from desulphurisation reactions with Raney nickel catalyst has been recorded in the literature only in a few cases. Among these, the desulphurisation of thionaphtheno [3,2-b] thionaphthen with a deactivated Raney nickel catalyst recently studied by Badger, Kowanko and Sasse,[77] has been found to give 17.5% yield of *trans*-stilbene. A few years earlier, Corson, Tiefenthal, Atwood, Heintzelman and Reilley[3] detected 10% of olefin, in addition to the expected saturated hydrocarbon, following the desulphurisation of 3-t-butylbenzo[*b*]thiophen. Although the authors did not isolate the olefin, its presence was inferred from the infrared spectra and from quantitative hydrogenation experiments.

## RESULTS AND DISCUSSION

2,5-Diphenyl-1,4-dithiin has been found to be one of the most interesting materials for the study of desulphurisation. The reaction was attempted in five separate experiments which were carried out under similar conditions. The diphenyl-1,4-dithiin, which was previously said[68] to be extremely stable to desulphurisation has been found to be smoothly desulphurised by the use of the W-7J Raney nickel catalyst. As described previously, this led to the production of many more interesting compounds than those expected from a catalyst of greater activity like the W-5, W-6, or W-7 Raney nickel (cf. the desulphurisation of 2,3,5,6-tetraphenyl-1,4-dithiin[71]). In spite of the relatively low yields of the desulphurisation products, which were usually difficult to work up, the compounds isolated were of worth-while interest.

Most of the experiments for the desulphurisation of the diphenyl-1,4-dithiin carried out in the present study were conducted in toluene (b.p. 110.5°) as solvent. The concentration of the sulphur compound in the reaction mixture was kept low (2%) to avoid any possible intermolecular dimerisation, supposing removal of one sulphur atom in a molecule could occur to any extent. In this connection, the desulphurisation reaction could proceed to give simple products only, e.g. (XVI) and (XVII) as shown below.



$$\longrightarrow \text{Ph.Et} + \text{Ph.[CH}_2]_4\text{.Ph} + \text{etc.}$$

XVI XVII

In synthesizing the starting material, following the procedure of Baker and Barkenbus,[70] it was found that the compound is susceptible to aerial oxidation. The reactions were therefore carried out under nitrogen, and to lessen the possibility of a photochemical effect towards the postulated styryl diradical (if formed), the reaction flask was well covered with photographic paper. The degassing times with the W-7J Raney nickel catalysts used in these experiments were prolonged (and varied from 4 to 16 hr.) in order to decrease their activity as much as possible. Owing to the possession of some aromatic properties,[35] which could account for its resistance to desulphurisation,[68] the desulphurisation times of the diphenyl-1,4-dithiin were also extended longer than usual. These ranged from *ca.* three to four days.

Since isolation of some of the products from the first experiments had drawn most attention to the study of their properties, the reaction conditions used initially were not altered in subsequent experiments. The limited amount of the starting material available, the lability of the products and the difficulties of purification of the small amounts of the liquid compounds, were other reasons why improvement of the yields of the desulphurised products were not attempted at this stage. It was found that variation of the degassing period of the catalyst (reduction from 6 to 4 hr. in the third experiment) resulted in the isolation of a different hydrocarbon product. It was therefore thought that desulphurisation of this sulphur compound should be carried out in several separate experiments, from which small yields of those labile material might be worked up and investigated in time before any change could take place.

As expected, a sulphur-containing compound, 2,4-diphenylthiophen was among the products from these desulphurisations. The yield, the average of five experiments, was 24.4%. The formation of this compound is consistent with the expectation that removal of one sulphur atom would be accompanied by aromatisation and gave rise to the more stable thiophen compound. It has been found that it is not possible to effect desulphurisation of 2,4-diphenylthiophen by the use of the W-7J Raney nickel catalyst. Refluxing of 2,4-diphenylthiophen over this catalyst in toluene for five days resulted in the recovery of the starting material in nearly 99% yield. The diphenylthiophen was, however, found to give 1,3-diphenylbutane in 45.9% yield when treated with W-7 Raney nickel catalyst in boiling xylene (b.p. 138-139°) for 6 hr. A similar result has also been reported recently by Saikachi and Hisano.[81]

In accordance with the previous observation, some by-products, believed to be formed from the solvent and the degassed catalyst (e.g. benzene and "polymethylene") were also obtained. As the isolation of these materials has been discussed earlier (see the desulphurisation of thianthren, and of 2,7-dihydrodibenzo[c,e]thiepin), these products will be not of interest in this discussion. It should be noted that a considerable amount of an intractable brown tar was also obtained in each experiment on the desulphurisation of 2,5-diphenyl-1,4-dithiin. This would account for the relatively low yields of the desulphurised products observed.

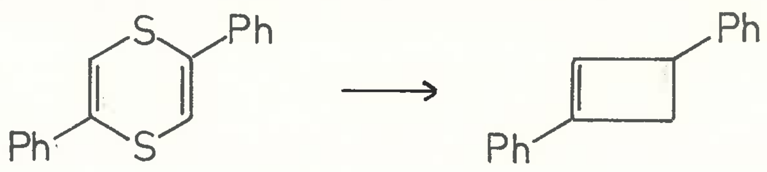
In the first experiment, in addition to 2,4-diphenylthiophen and a small amount of a complex mixture of 2,4-diphenylthiophen and 2,5-diphenyl-1,4-dithiin, a liquid hydrocarbon of a characteristic and pleasant smell was obtained. As it was eluted in a single fraction following chromatography of a crude residue, it was first thought to consist of only one compound. Microanalyses of the fraction suggested that the compound had an empirical formula of $C_{16}H_{14}$. The yield of the liquid based on this molecular formula was 11.7%. It was observed that the liquid, on standing at room temperature under diffuse daylight for ca. 12 hr. in a flask (stoppered), slowly crystallised to give colourless needles. The first m.p. observed was 89-91°, being raised to 96° by one recrystallisation; but further recrystallisation could not be attempted. The molecular weight determination of the solid (Rast) suggested a molecular weight of not more than 206 (calc. for $C_{16}H_{14}$). Addition of tetranitromethane to the liquid and to the solid showed that both were unsaturated hydrocarbons. The liquid and solid compounds showed almost identical ultraviolet spectra ( $\epsilon$ not determined), except for shoulders at 228 and 236 mμ which were absent from the spectrum of the liquid. The general shape of the spectra were somewhat similar to that of toluene ($\lambda_{max.}$ 256, 260, and 268 mμ. $\lambda_{min.}$ 228.5 mμ). The bathochromic shifts observed in the spectra of the products ($\lambda_{max.}$ 265, 280, 288, and 297, $\lambda_{min.}$ 242.5 mμ) suggested the presence of at least one conjugated double bond in a side chain of an aromatic ring. As the products were not identical with any of the known compounds having the formula $C_{16}H_{14}$, it was thought, at this stage, that the product was probably one of the stereoisomers of 1,3-diphenylbuta-1,3-diene (XVIII). However, the reported m.p. of the diphenylbuta-1,3-diene,[82] (for which the possible existence of the _cis_ and _trans_ forms has not yet been established) was 55°.

XVIII

The infrared spectrum of the liquid compound was found to be consistent with the structure (XVIII). The presence of a sharp and rather strong absorption band at 3077 $cm^{-1}$ characteristic of C-H stretching vibrations of $R_1R_2C=CH_2$ (3075-3095 $cm^{-1}$), together with another rather strong band at 906.8 $cm^{-1}$ not far from the position expected for the $CH_2$ out-of-plane deformation band of $R_1R_2C=CH_2$ (895-885 $cm^{-1}$)[83] were significant features. A band at 906.8 $cm^{-1}$ should be strong if the group $=CH_2$ is present. Strong bands at 1600, 1493, and at 1449 $cm^{-1}$ suggested phenyl-conjugated double bonds. A very strong band at 695, and medium bands at 1067, 1029, as well as four evenly spaced bands in the region 1942-1739 $cm^{-1}$ suggested the presence of only a mono-substituted phenyl group. The presence of a medium band at 961.5 $cm^{-1}$ suggested that one of the two double bonds could be <u>trans</u>.

However, these assignments were not entirely satisfactory, since the two sharp and strong bands at 2927 and 2857 $cm^{-1}$ apparently indicated the presence of a $-CH_2-$ group of an alkane (2926 and 2853 $cm^{-1}$ stretching frequencies). Moreover, a distinct band at 1667 $cm^{-1}$ (weak), which could indicate a non-conjugated double bond, was observed, together with a close band at 1686 $cm^{-1}$ (possibly an overtone of the substitution pattern of the band at 695 $cm^{-1}$ as in the case of a polystyrene spectrum). It is noteworthy that Sheppard and Sutherland[84] have observed that it is possible to differentiate between the double bond of the type

$R_1R_2C=CH_2$ and $R_1R_2C=CHR_3$ by the position of the peak (1655-1645 $cm^{-1}$ for the former and 1680-1670 $cm^{-1}$ for the latter). These two linkages can also be differentiated by the intensity in these regions, as the terminal double bond gives rise to a considerably more intense band than that given by a double bond included in a chain. This conclusion has been supported by Thompson and Whiffen,[85] and by McMurry and Thornton.[86] Furthermore, it was observed that each band of the four evenly spaced peaks (absorption patterns typical of a monosubstituted benzene derivative) was split. It was thought that this was probably accounted for by the two phenyl groups attached at different positions of the molecule, which would exhibit slightly the same substitution patterns but at slightly different frequencies rather than by overtones of the vinyl or substituted vinyl type absorptions,[83] (1856-1800 $cm^{-1}$ and 1800-1750 $cm^{-1}$). The splitting of these peaks as well as the frequencies characteristic for a $-CH_2-$ group, and for a non-conjugated double bond are compatible with the structure (XIX), namely 1,3-diphenylcyclobutene.



XIX

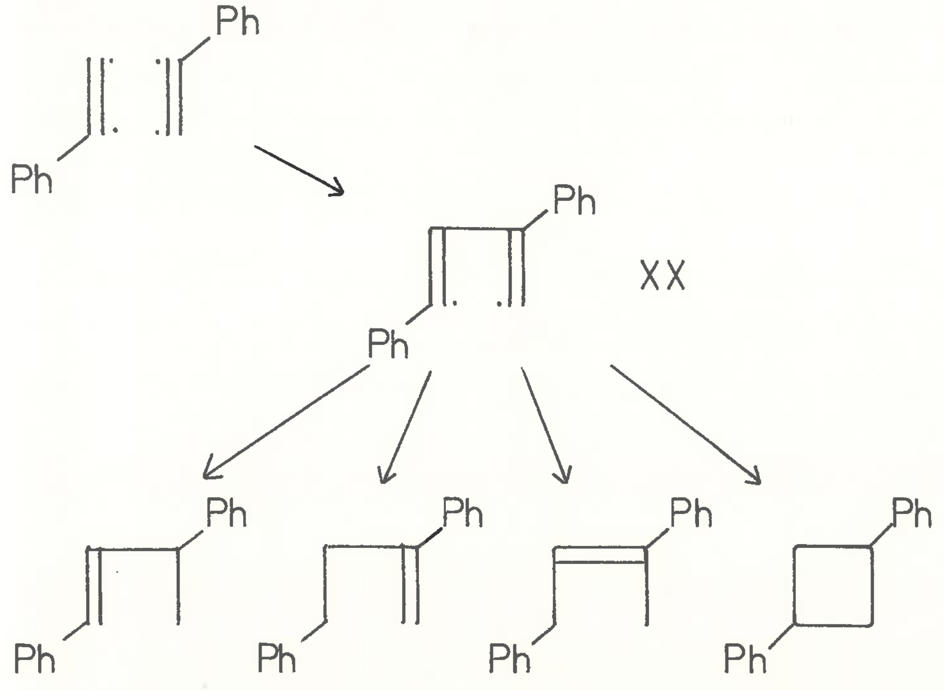
The discrepancy which existed in the preliminary assignments of the infrared spectrum of this liquid product, was difficult to understand. The small amount of the solid product permitted only the determination of its melting point, molecular weight, and the ultraviolet spectrum. These observations did not correspond to any of the known compounds having the formula $C_{16}H_{14}$, even the reported 1,3-diphenylbuta-1,3-diene.[82]

A liquid product isolated in the second experiment was found to have properties identical in all respects with those of the liquid from the previous experiment, and was obtained in 26.1% yield. Two analyses of the product were also in reasonable agreement with the formula $C_{16}H_{14}$. Its molecular weight, determined by the Rast method was 177 (calc. for $C_{16}H_{14}$, 206.3). This led to the conclusion that the molecular formula of the liquid was also $C_{16}H_{14}$. The p.m.r. spectrum ($CCl_4$) showed peaks at $\tau$ 7.13 (singlet) corresponding to methylene protons (alicyclic ?), $\tau$ 3.50 (singlet) for olefinic protons, and $\tau$ 2.89 (complex) for olefinic and aromatic protons. Impurity peaks were observed in the regions $\tau$ 8.78, $\tau$ 7.8-7.27, and $\tau$ 6.26-6.09. It was thought that the presence of these peaks were due to isomers of the "not yet known" liquid product, the lability of which might be responsible for their occurrence, or alternatively that, they were given by reaction products having the same molecular formula.

Quantitative determination of the double bonds in the liquid compound was first attempted by epoxidation[87] with monoperphthalic acid. Three experiments were conducted under varying conditions but oxidation did not occur. The alternative perbenzoic acid was not tried as an epoxidising agent because the experiment had to be carried out on such a small scale due to the limited quantity of the starting material available. It is well known that the advantage of monoperphthalic acid over perbenzoic acid is the greater stability of the former.[88,89] Since the process required great accuracy, monoperphthalic acid was, therefore, the reagent of choice for a small scale experiment.

The third desulphurisation of the 2,5-diphenyl-1,4-dithiin led to the isolation of the other liquid product, analysis of which suggested the formula $C_{16}H_{16}$. This was confirmed by microhydrogenation (using palladium-charcoal as catalyst in ethanol at room temperature and pressure), 1 mole of hydrogen being absorbed. The hydrogenation product was spectroscopically identical (infrared) with that of an authentic specimen of 1,3-diphenylbutane.

The formation of this hydrocarbon ($C_{16}H_{16}$) suggested that the intermediate must be (XX). This could be formed by the combination of two of the postulated styryl-$\alpha,\beta$-diradicals. (If the combination occurred while the system was still adsorbed on the surface of the metal catalyst[1]). This being so, the hydrocarbon could correspond to any of the following structures (XXI-XXIV).



XX

XXI XXII XXIII XXIV

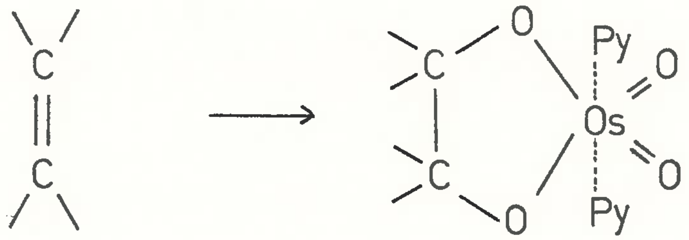
Examination of the infrared spectrum of the liquid $C_{16}H_{16}$ suggested that the structure (XXII) was unlikely even though the weak band at 909.1 cm$^{-1}$ was present. Although this band could indicate $CH_2$ out-of-plane deformation of a vinylic double bond (915-905 cm$^{-1}$)[83] such a band should be strong. Moreover, the absence of the band near 990 cm$^{-1}$, which is connected with the hydrogen deformation mode of the $-CH=C-$ structure,[90] and which usually accompanies the former (909.1 cm$^{-1}$), suggested that the compound did not contain a vinyl type double bond. The absence of bands in the region 3095-3075 cm$^{-1}$ and at 895-885 cm$^{-1}$ are also strong indications that the compound is not a disubstituted ethylene ($R_1R_2C=CH_2$). However, at this stage a disubstituted ethylene of the type $R_1CH=CHR_2$ could not be excluded because of the presence of a band (medium) at 965.4 $cm^{-1}$ (*trans*) possibly due to hydrogen atoms out of the plane of the double bond, and because of the presence of a band at 687.3 $cm.^{-1}$ (possibly *cis*-); but these correlations are not certain.[83] The presence of two strong bands at 2976 and 2882 $cm^{-1}$, characteristic for the stretching frequencies of the $CH_3$ group, not only rules out structures (XXII) and (XXIV), but also supports the suggestion that either (XXI) or (XXIII) is possible. However, it should be noted that bands at 924.1 and 965.4 $cm^{-1}$ could only be assigned to two $CH_2$ rocking frequencies of the cyclobutane structure.[91-93] The week band at 823.4 and a very strong band in the region 788-749.2 $cm^{-1}$ (the latter if due to the combined peaks of out-of-plane deformations arising from olefinic C-H[86] and from aromatic C-H[83]) are significant features suggesting a tri-substituted ethylene (XXIII). The weak band at 1372 $cm^{-1}$ could be assigned to an in-plane $=CH-$ deformation vibration of (XXIII). The position of this band agrees with that observed very recently by Parkhurst, Rodin, and Silverstein,[94] who isolated the *cis*- and *trans*- forms of 1,3-diphenylbut-2-ene together with 2,4-diphenylbut-1-ene and others from the so-called "styrene dimer fraction" obtained by refluxing styrene with a small amount of sulphur. This band was absent in the infrared spectrum of the 2,4-diphenylbut-1-ene, reported by the same authors. On the basis of these observations, it seems that the most likely structure to satisfy the above assignments is (XXIII). A contradiction existed (e.g. bands at 966.4 and 687.3 $cm^{-1}$) but these were thought to be due to impurities.

Periodate-permanganate oxidation of the liquid on a small scale resulted in the isolation of a black residue (acid fraction) in which phenylacetic acid was detected by paper chromatography, together with a yellow wax (neutral fraction) from which acetyophenone was isolated as its 2,4-dinitrophenylhydrazone. These compounds were undoubtedly formed by oxidative degradation of (XXIII).

It is noteworthy that increasing the time of the degassing period (7½ hr.) of the W-7J Raney nickel catalyst used for the fourth desulphurisation of the diphenyl-1,4-dithiin resulted in the ready isolation of the liquid $C_{16}H_{14}$ once again. The catalyst used in the third experiment was degassed at 100°/12 mm., for only 4 hr., while in the first and the second experiments the degassing period was 8 and 6 hr. respectively; this suggested that the W-7J Raney nickel catalyst requires, at least 6 hr., under these conditions, to reduce its hydrogen content to give minimum activity.

Quantitative determination of the double bonds of the liquid $C_{16}H_{14}$ was again attempted by microhydrogenation using several different kinds of catalyst. It was surprising to find that hydrogenation could not be effected by the use of a platinum on charcoal catalyst, but palladium on charcoal was effective. The consumption of hydrogen was 73.66% of the theoretical amount required for 1 double bond. The limited quantity of the material did not permit further investigation. The use of platinum dioxide, and platinum dioxide-platinum, in the other two experiments, led to the hydrogenation of the aromatic rings. However, no conclusion could be reached in either experiment as the hydrogen uptake was, in both cases, very close to 7.5 double bonds rather than 7 or 8. The infrared spectrum of the product from experiment no. 2 (see Table 6 in the experimental part) was not conclusive owing to aerial oxidation.

It was later thought that in addition to the oxidative degradation processes, such as osmium tetroxide catalysed periodate oxidation,[95] periodate-permanganate oxidation,[96] and ozonisation, as well as hydrogenation, all of which seemed to be difficult in the present case, there was another procedure namely "the addition of osmium tetroxide"[97] which might be more satisfactory. It is well known that osmium tetroxide reacts readily with ethylenic double bonds to form organo-osmium compounds which in the presence of a tertiary base, such as pyridine, to give an osmate ester complex (XXV) as follows:-



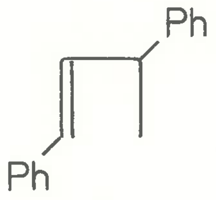
XXV

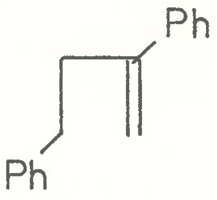
These complexes (XXV) are generally crystalline brown compounds and may often be isolated in almost theoretical yield.[97] This was found, in the present study, to be one of the most convenient methods for the estimation of the number of double bonds in a compound, specially when a small amount only of the material was available. However, experiments carried out with the liquid $C_{16}H_{14}$ and with an authentic stilbene, gave complexes for which the carbon analyses were too high, due to the presence of osmium (see Experimental part) and it was found that only the hydrogen figures were reliable. In this connection, the result obtained from the liquid indicated that it contained two double bonds. It should be noted, however, that the hydrogen value for the one double bond differs by only 0.5%.

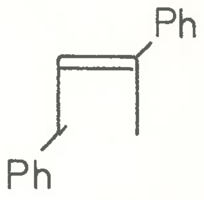
At this stage it had been realized that the liquid products obtained from the above four experiments were all mixtures of isomers of compounds possessing the formula $C_{16}H_{14}$. As many contradictions existed in the above investigations (e.g. infrared spectral assignments, determination of the number of double bonds, impurity peaks in the p.m.r. spectrum) the liquid was examined by vapour-phase chromatography. This revealed that at least three components, corresponding to the peaks at the retention times of 8.4, 11.1 and 18.05 min. respectively, were present. Other minor peaks, probably corresponding to impurities, were also detected.

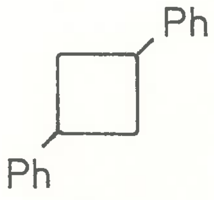
The liquid product (4.85 g.) from the fifth experiment (which was performed on about 5 times the scale of the second) was separated by preparative gas chromatography into four fractions, which were collected in trap 1 (6.0 mg.), trap 3 (0.46 g.), trap 5 (0.48 g.), and trap 7 (0.37 g.) of a Megachrom apparatus. Owing to its small amount, the liquid in trap 1 was examined only by infrared spectroscopy. The spectrum showed the typical pattern of a monosubstituted benzene compound, peaks corresponding to a phenyl-conjugated double bond, substituted benzene, and aliphatic C-H stretching frequencies.

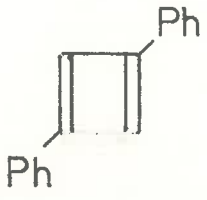
As the products collected in each trap were not sufficient to effect satisfactory purification for analytical purposes, no definite conclusion about their molecular formulae could be drawn. However, in accordance with the previous experiments it was reasonable to assume that the sulphur-free products possess the formula range from $C_{16}H_{14}$ to $C_{16}H_{16}$. The degassing period of the W-7J Raney nickel catalyst used in this experiment was extended up to 16 hr. (nearly 3 times longer than previous experiments), and this makes the former formula ($C_{16}H_{14}$) preferable to the latter ($C_{16}H_{16}$). As has been discussed, the theoretically possible structures of $C_{16}H_{16}$ might be any one of (XXI-XXIV); and of $C_{16}H_{14}$ might be either (XVIII) or (XIX); or both.

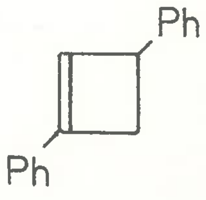

XXI


XXII


XXIII


XXIV


XVIII


XIX

The infrared spectrum of the liquid from trap 3 gave a rather sharp and strong band at 3040 cm$^{-1}$ as an indication of a characteristic -CH- stretching frequency of a double bond (possibly *cis*- CH=CH-). This assignment is associated with the band at 963.6 cm$^{-1}$ which was too weak to be indicative of a *trans*,[83] and a medium intensity band at 1406 cm$^{-1}$ which is assigned to a CH in-plane deformation of a *cis*-disubstituted ethylene.[98] The strong band at 923.2 cm$^{-1}$ was not very far from the expected for out-of-plane deformation of an asymmetric di-substituted ethylene ($R_1R_2C=CH_2$, 895-885 cm$^{-1}$) for it is known that conjugation with an olefinic group raises this frequency.[99] The weak band at 1686 cm$^{-1}$ is more likely to be an overtone of the CH out-of-plane deformation of the band at 698.3 cm$^{-1}$ (monosubstituted benzene), as well as of the bands at 1029 and 1073 cm$^{-1}$, rather than a non-conjugated C=C stretching vibration (cf. the polystyrene spectrum). However, the splitting of the band at 1686 $cm^{-1}$ together with the presence of a band at 3012 $cm^{-1}$ may be due to the conjugation of double bonds in its molecule. Bands at 1600, 1493, and 1445 $cm^{-1}$ correspond to phenyl conjugated double bonds, while bands at 1073 and 1029 $cm^{-1}$ may be expected from a mono-substituted benzene. The presence of a weak band at 2899 $cm^{-1}$, believed to be a characteristic of CH (tertiary) stretching frequency (2890 ± 10),[100] suggests that the compound possesses the formula (XVIII) in agreement with the above assignments. The absence of CH stretching frequencies in the regions 2962 and 2872 $cm^{-1}$ ± 10, together with 2926 and 2853 $cm^{-1}$ ± 10, rules out the structures (XXI-XXIV) and also structure (XIX). It is also noteworthy that the infrared, ultraviolet and proton magnetic resonance spectra of both _cis_ and _trans_ forms of 1,3-diphenylbut-2-ene (XXIII) and 2,4-diphenylbut-1-ene (XXII), reported recently by Parkhurst, Rodin, and Silverstein are not identical with those of any hydrocarbon isolated in this experiment.

The ultraviolet spectrum of the liquid compound shows a general shape similar to that of _cis-cis_-1,4-diphenylbuta-1,3-diene ($\lambda_{max.}$ 299 mμ), but with a shift towards shorter wavelength ($\lambda_{max.}$ (223 mμ).

Although, in one experiment the liquid on microhydrogenation absorbed one mole of hydrogen, in agreement with structure (XXVI),

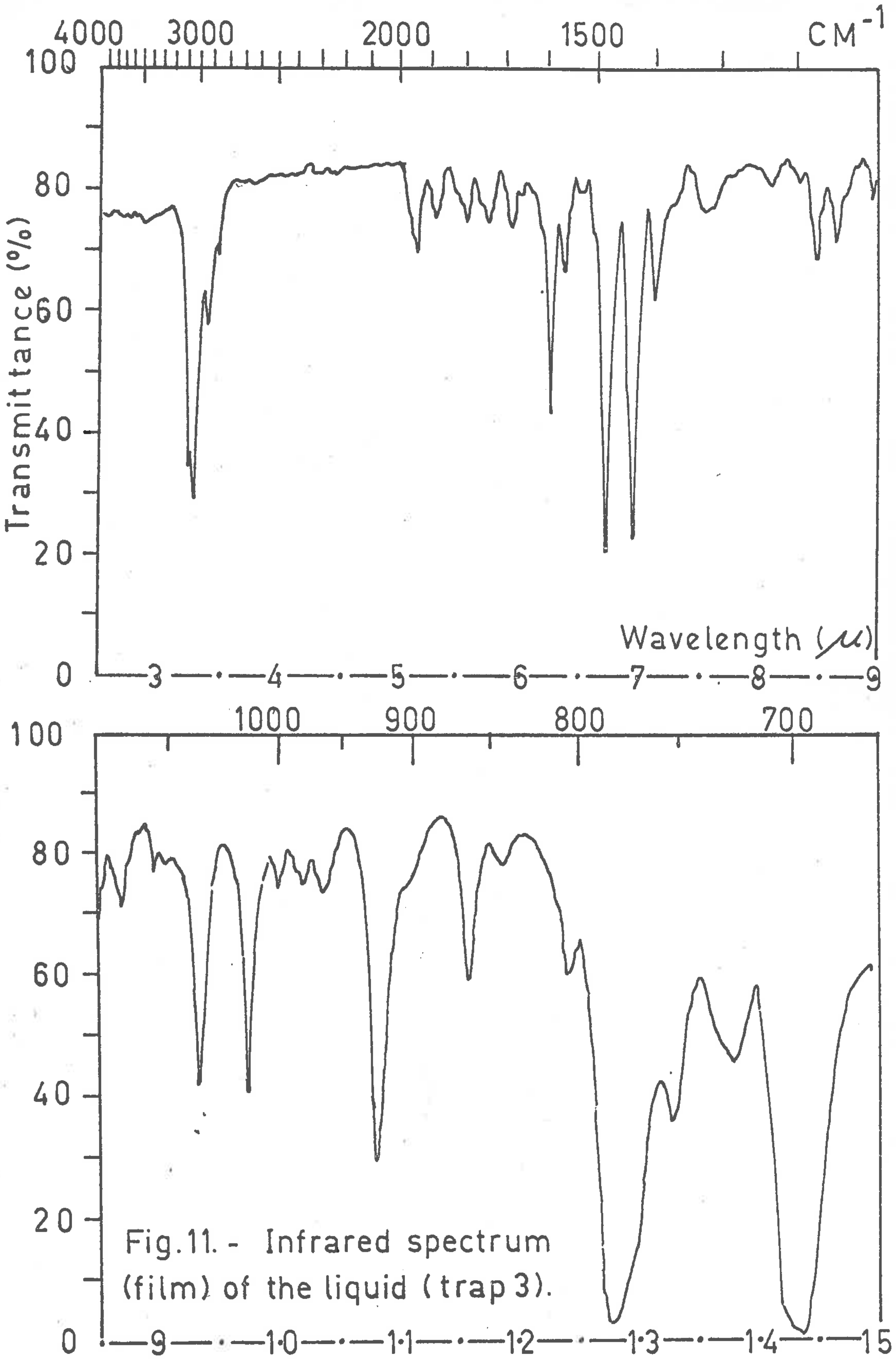


Fig. 11. - Infrared spectrum (film) of the liquid (trap 3).

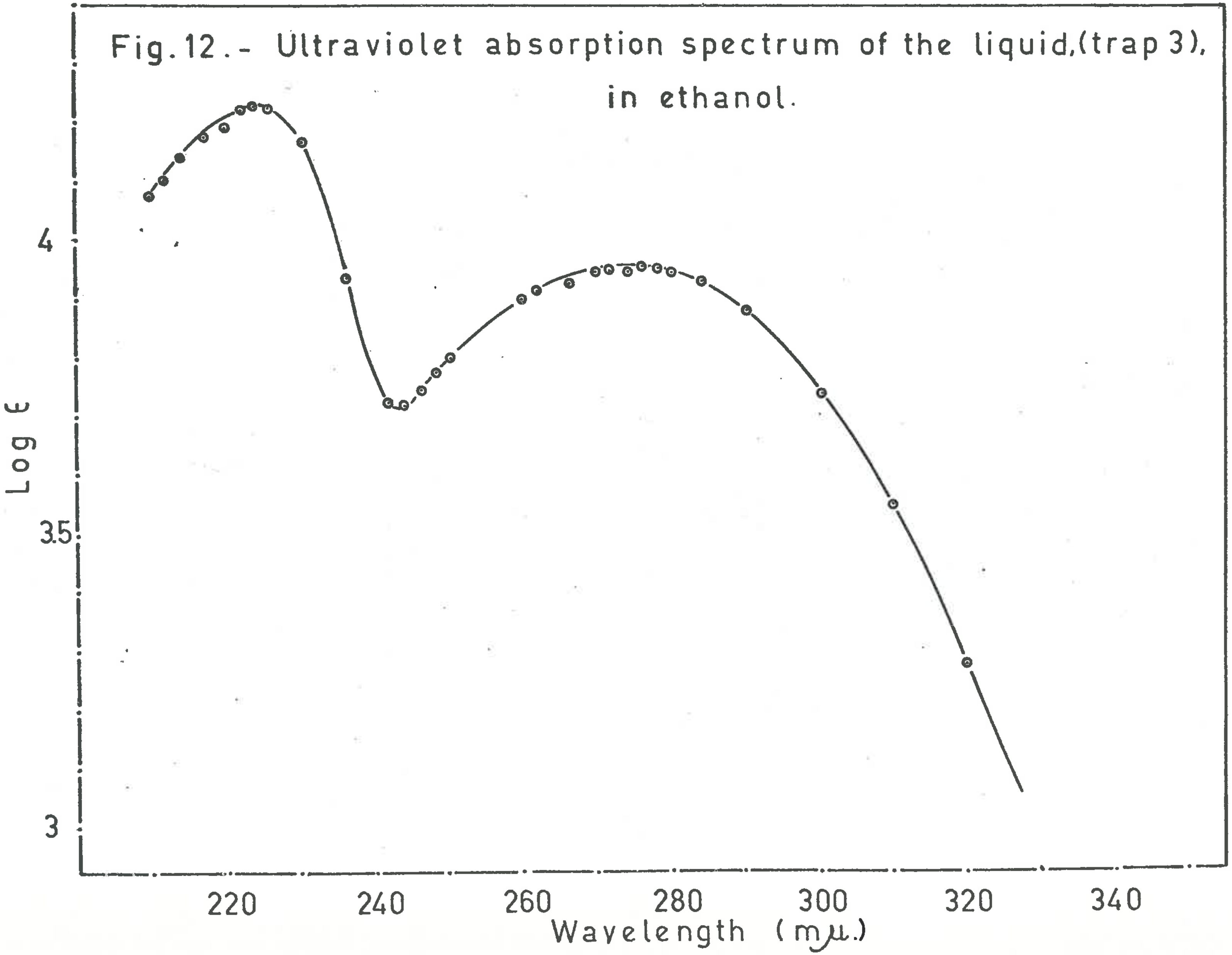


Fig. 12.- Ultraviolet absorption spectrum of the liquid,(trap 3), in ethanol.

the amount of the material available precluded accurate work. Thus, the result of this experiment and the assignment of the infrared spectrum, which favoured structure (XXVII), did not agree. However the discussion of its proton magnetic resonance will be based on these two structures (XXVI, and XXVII),(see next page).

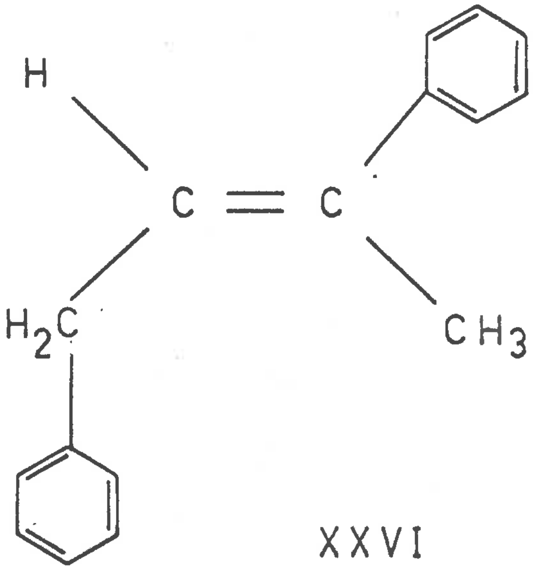
Since the proton magnetic resonance spectrum did not exhibit any signals at *ca.* $\tau$ 6–8, structure (XXVI) was ruled out,[101] in agreement with the infrared spectrum. The figures of the proton magnetic resonance spectrum are summarised in Table 3.

TABLE 3

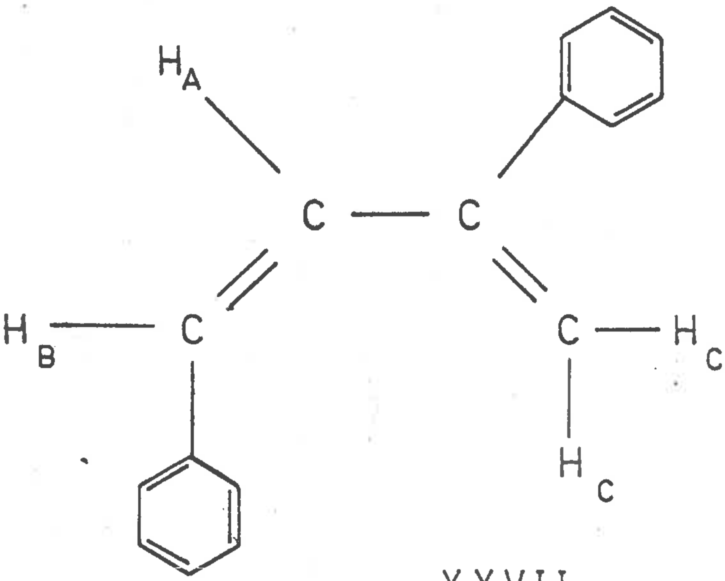
The proton magnetic resonance spectrum of the liquid (trap 3)

| $\tau$ (p.p.m.) | Appearance | Proton count | Assignment |
|---|---|---|---|
| 3.45 | singlet | 2 | olefinic |
| 3.04 | complex | 12 | olefinic + aromatic |
| 2.99 | | | |
| 2.87 | | | |
| 2.77 | | | |

Proton (A) and (B). Chemical shifts of these protons would be expected to be similar to *cis*-stilbene and hence[102] might be expected to have $\tau$ value in the region 3.51. This could account for the 2 protons having $\tau$ 3.45.



XXVI

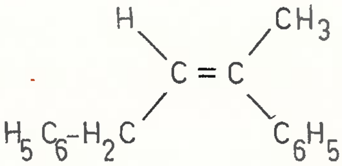
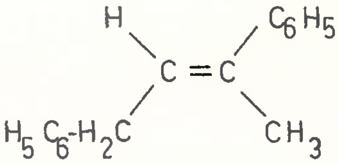


XXVII

Proton (C). The peaks at τ values 3.04 and 2.99 seem to be low[101] (5.46-2.99) but in view of the high conjugation in this molecule (lower τ value) this is not surprising. The low τ value could also be accounted for by the deshielding effect of the adjacent benzene ring. It is well known that a benzene ring and a double bond are effective in deshielding an adjacent proton.

Since no significant signals occurred at τ 9.78-6.45, the range in which methylene protons are reported to absorb,[101] the cyclobutene structure was ruled out.

It should also be noted that minor peaks were observed in the proton magnetic resonance spectrum of the product, but the integration curve indicated that these peaks arise from a minor component of a mixture. The τ values were very similar to those of the following compounds.[94]

| Minor peaks given by Compounds from Trap 3 |  |  |
|---|---|---|
| τ | τ | τ |
| 7.76 | 7.93 | 7.88 |
| 6.82 | 6.74 | 6.50 |
| 4.57 | 4.42 | 4.08 |
| 2.85 | 2.85,2.83 | 2.85 |

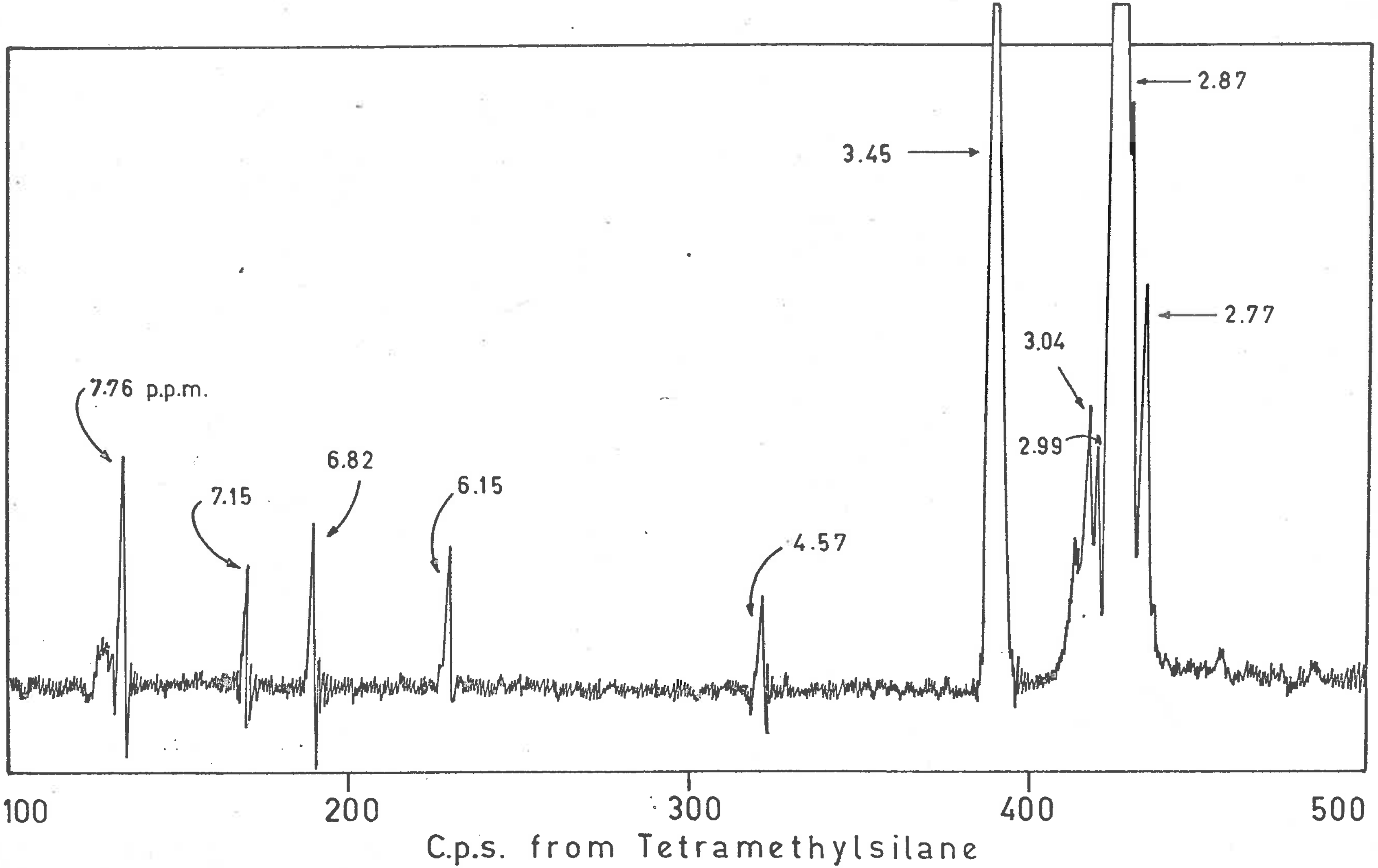


Fig.13.- Proton magnetic resonance spectrum of the liquid (trap 3) in $CCl_4$, taken at 60 mc./sec. and expressed in units of τ

Other supplementary peaks were observed at $\tau$ 7.15, and 6.15, but the intensities were even smaller.

The evidence available from the infrared, ultraviolet and proton magnetic resonance spectra prompts the author to regard the liquid compound from trap 3 as the <u>cis</u>-form of 1,3-diphenylbuta-1,3-diene.

This compound has been observed to be labile in light. The "as yet unidentified", colourless crystals formed by slow crystallisation of the liquid compound melt at 123-124°, which does not correspond to any of the known 1,3-diphenylbuta-1,3-diene dimers. Their ultraviolet spectrum differs from that of the liquid in having three separate maxima, with a general shape similar to that of <u>trans</u>-<u>trans</u>-1,4-diphenylbuta-1,3-diene. As the crystals were available only in small amount, no further investigations could be attempted.

The infrared spectrum of the compound from trap 5 (solid m.p. 61-62°) showed a CH stretching frequency at 3040 cm$^{-1}$ corresponding to a double bond, and at 3030 cm$^{-1}$ for the aromatic =CH stretching mode. The medium band at 2899 cm$^{-1}$ suggested the CH (tertiary) stretching frequency as in the spectrum of the liquid from trap 3. The four evenly-spaced peaks typical of a mono-substituted benzene compound were clearly split. This could be due to slightly different frequencies of the substitution pattern of two unequal phenyl rings. The weak band at 1664 cm$^{-1}$ is not far from the position expected for <u>trans</u>-olefinic compounds as quoted by Sheppard and Simpson[98] (1673 $cm^{-1}$). However, the expected *trans* ethylenic double bond peak at the region 990-965 $cm^{-1}$ is present as only a weak band at 961.5 $cm^{-1}$ together with another similar band at 988.3 $cm^{-1}$. Bands at 1603, 1567, 1493, 1441, 1068, 1026 and at 698 $cm^{-1}$ may be assigned to the presence of benzene rings as described before. A strong band at 913.8 $cm^{-1}$ would be expected for the out-of-plane deformation of an asymmetric di-substituted ethylene ($R_1R_2C=CH_2$) as in the previous case (trap 3). A strong indication for the presence of such an ethylenic double bond was a band at 1300 $cm^{-1}$.

The ultraviolet spectrum of the solid compound showed a fine structure different from that of the liquid from trap 3. The two separate maxima at 279.5 and 296.5 with a middle small peak at 288 mμ exhibited a general shape similar to that of the compound $C_{16}H_{24}$ obtained in the previous experiments. It is noteworthy that Pinckard, Wille and Zechmeister[103] have observed that the spectrum of *trans-trans*-1,4-diphenylbuta-1,3-diene shows definite fine structure while the two other isomers are characterized by smooth curves, which are rather similar in this respect. Furthermore, these authors have pointed out that most of the since known poly-*cis*-lycopenes showed a very limited fine structure in their ultraviolet spectra when compared to those of all trans-forms. The solid absorbed two moles of hydrogen, confirming the presence of two double bonds. Moreover, the infrared spectrum ~~of the~~ of the hydrogenation product has been found to be superimposable with that of the hydrogenation product from trap 3 and with that of an authentic specimen of 1,3-diphenylbutane.

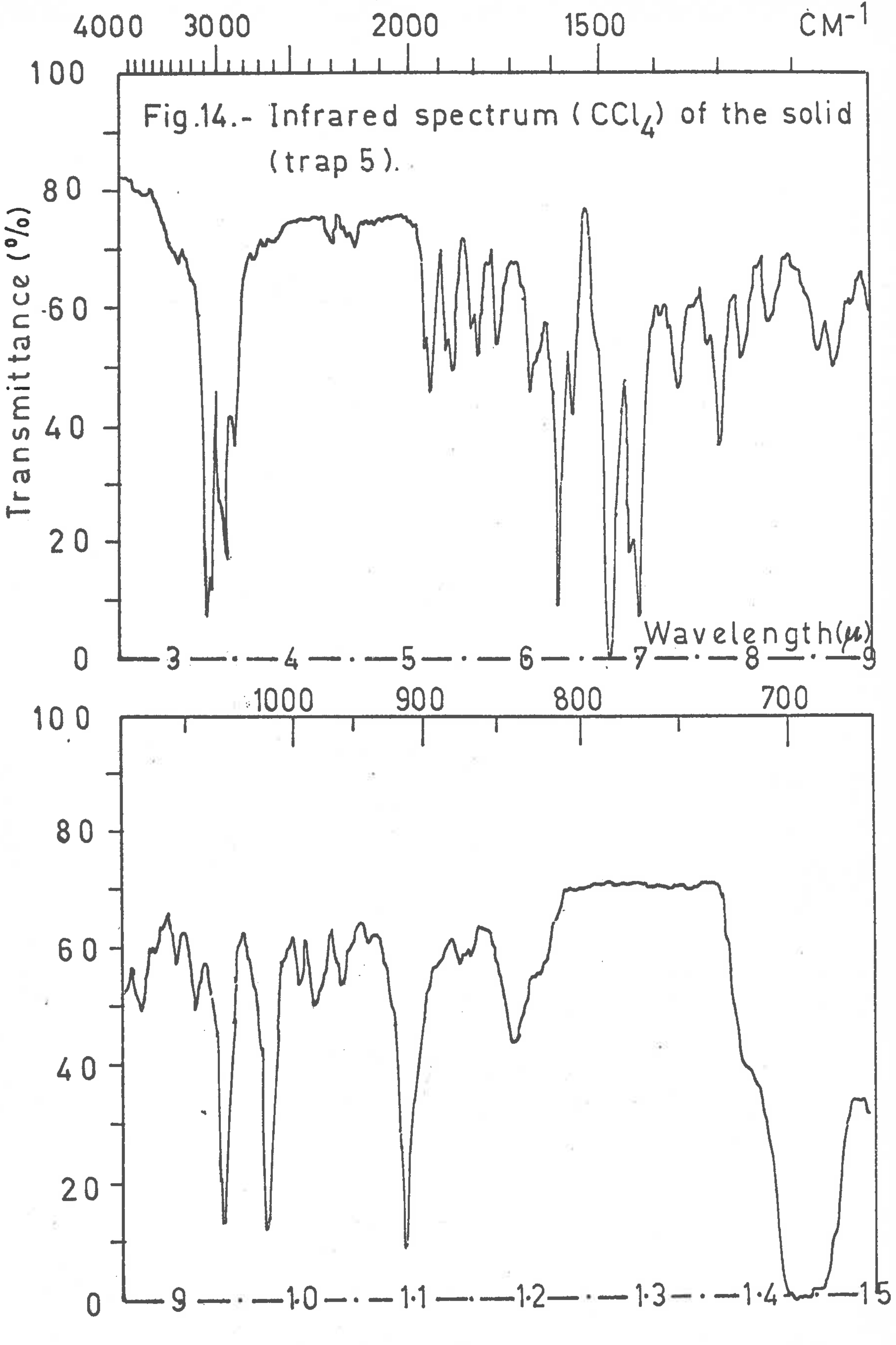


Fig.14.- Infrared spectrum ( $CCl_4$) of the solid (trap 5).

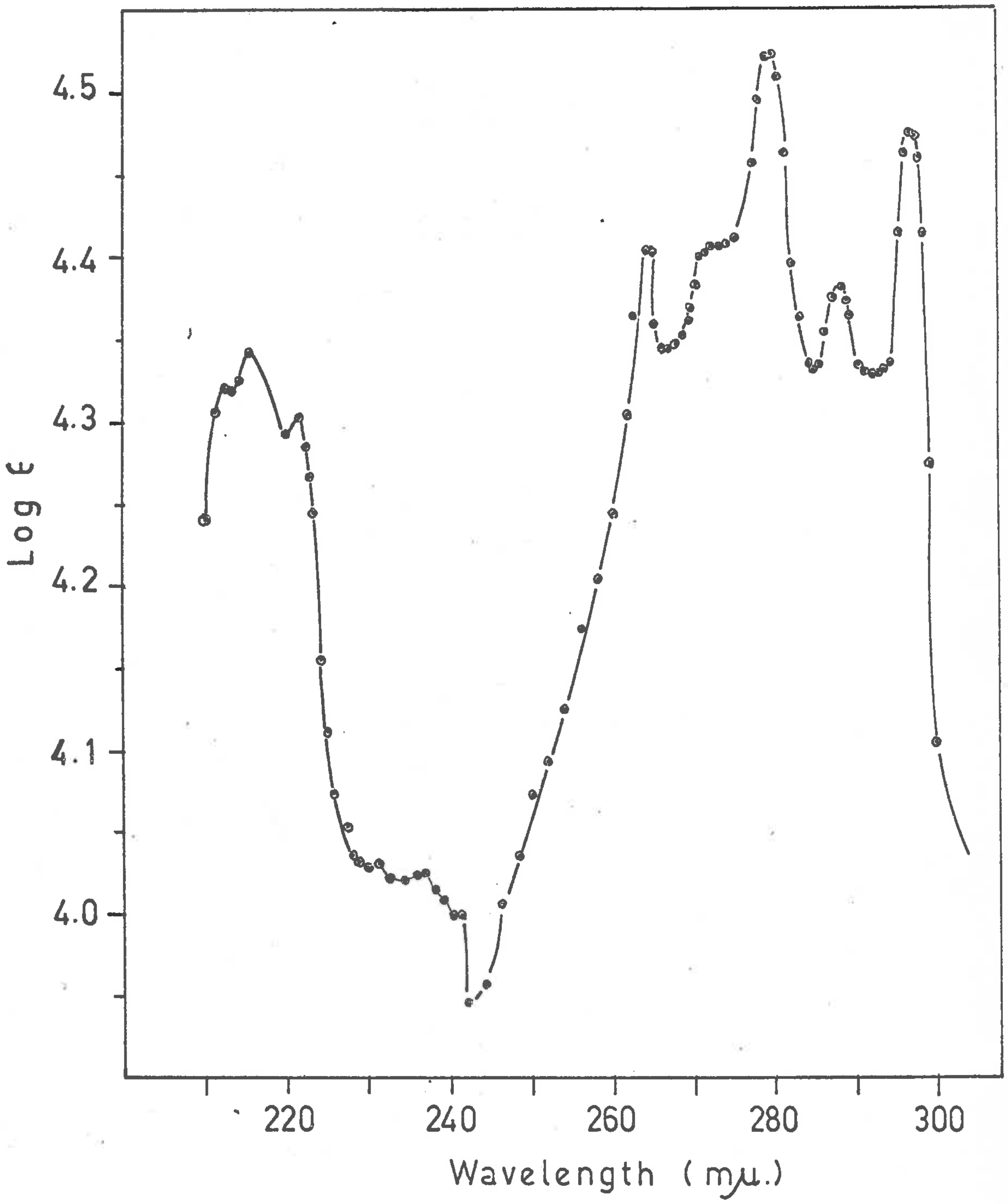


Fig. 15.- Ultraviolet absorption spectrum of the solid (trap 5), in ethanol.

The proton magnetic resonance of this compound showed only one extremely complex peak. It is concluded that this compound can only be diphenylbuta-1,3-diene. The absence of methyl proton absorption is especially noteworthy. The complex peaks must be due to combined absorption of olefinic and aromatic protons. The shifts of the vinylic protons to lower field could be readily explained by the deshielding effect of the olefinic double bonds and the aromatic nuclei. In view of its low τ values (*trans*-stilbene absorb in the region τ 3.0) and in accordance with the previous assignment of the liquid from trap 3, it is, therefore, thought that this compound must be regarded as *trans*-1,3-diphenylbuta-1,3-diene. The figures of the proton magnetic resonance spectrum of this compound are assembled in Table 4.

TABLE 4

The proton magnetic resonance spectrum of the solid (trap 5)

| τ (p.p.m.) | Appearance | Assignment |
|---|---|---|
| 2.765 | complex | olefinic + aromatic |
| 2.72 | | |
| 2.65 | | |
| 2.63 | | |
| 2.57 | | |
| 2.53 | | |
| 2.47 | | |
| 2.41 | | |

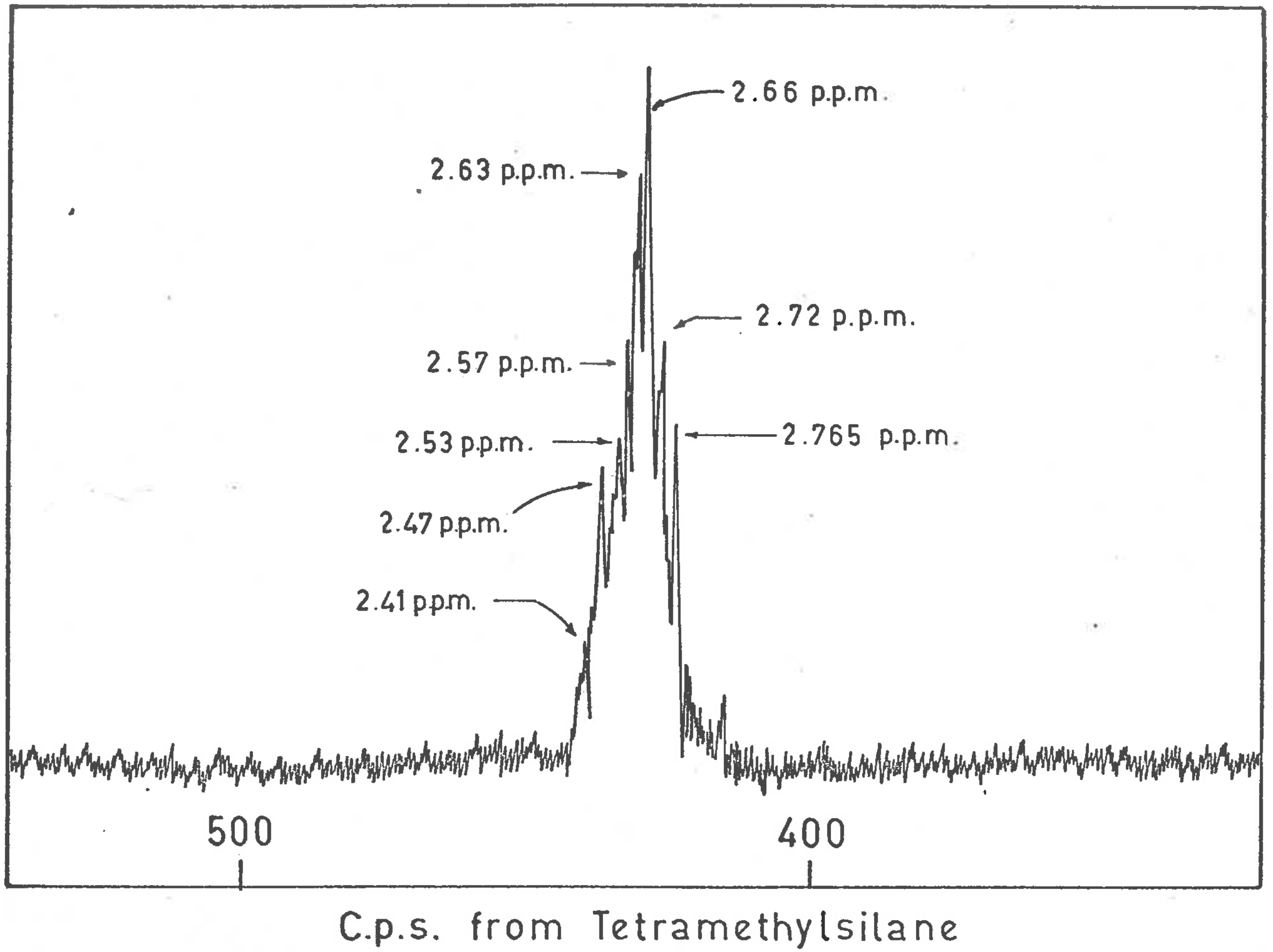
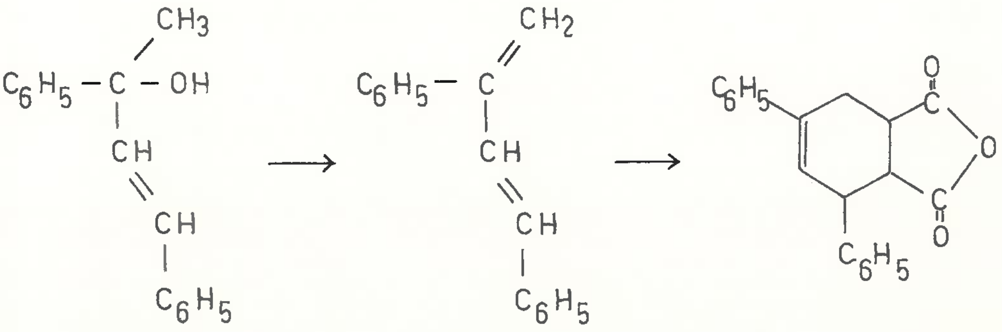


Fig. 16.- Proton magnetic resonance spectrum of the solid (trap 5) in $CCl_4$, taken at 60 mc./sec. and expressed in units of $\tau$

Attempts to prepare the maleic anhydride adduct of the solid were unsuccessful. This could be due to difficulties arising from the small scale experiment (10.4 mg. of the starting material), and probably from its labile nature.

A search of the literature showed that many attempts have been made to synthesize 1,3-diphenylbuta-1,3-diene by many workers. The only report which claims isolation of this compound was that of Dombrovskii[82] in 1956. The compound was prepared by reaction of 2-phenylbuta-1,3-diene with benzenediazonium chloride. Yields and experimental details, however, were not given. The isolation of 1,3-diphenylbuta-1,3-diene, m.p. 55°, was confirmed by the formation of its maleic anhydride adduct, m.p. 154°. Whitby and Gallay[104] were the first to report that the addition of benzalacetophenone to methylmagnesium iodide at -10° gave a 70% yield of a compound, m.p. 167°, which possessed the composition and molecular weight of 1,3-diphenylbuta-1,3-diene dimer. However, repetition of this procedure by other workers[105] has been reported to give a 60% yield of the 1,4-addition product (1,3-diphenylbut-1-one) and 27% of 4-benzoyl-1,3,5-triphenylhexa-1,3-diene; none of the dimeric material could be isolated. These products are in accord with those obtained from benzalacetophenone and methylmagnesium bromide as observed by Kharasch and Sayles.[106] Reaction of benzalacetone with phenyllithium was carried out by Cope, Wick and Fawcett[107] to give trans-1,3-diphenylbut-1-ene-3-ol

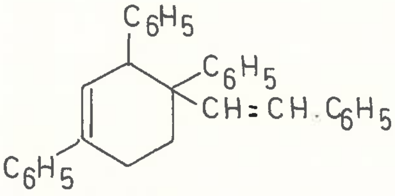
(XXVIII), but the dehydration product polymerized readily and it was not possible to isolate the expected diene. However, Cope and co-workers obtained the adduct (XXIX) by heating a mixture of the alcohol (XXVIII), iodine, and maleic anhydride in toluene. The adduct had a melting point range of 142.2-149°, indicating (as postulated by the authors) that is was a mixture of stereoisomers.



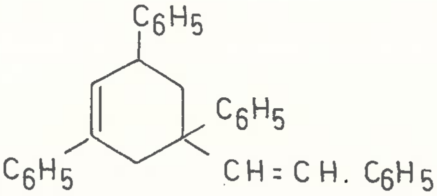
XXVIII XXIX

Surprisingly, shortly after the report of Dombrovskii, two independent groups, Jacobs, and Goodrow,[105] also Herz, and Lewis[108] reinvestigated the above observations and their papers were presented only one month apart. The first group demonstrated that dehydration of *trans*-1,3-diphenylbut-1-ene-3-ol under a variety of conditions resulted in a "dimer I", m.p. 137-138°, a "dimer II", m.p. 125-126° (unidentified) and other polymeric material (a yellow oil). Herz and Lewis reported that both 1,3-diphenylbut-2-ene-1-ol and 1,3-diphenylbut-1-ene-3-ol, on dehydration under various conditions gave a hydrocarbon $(C_{16}H_{14})_2$, m.p. 136-137° together with the other unidentified isomeric materials. Addition of maleic anhydride to the reaction mixture, both prior to or after dehydration, led to the isolation of the adduct, m.p. 158-159° which was identical with that obtained by Cope and his co-workers (XXIX).

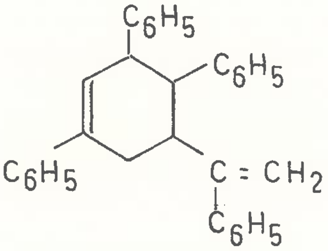
Four Diels-Alder dimers of trans-1,3-diphenylbuta-1,3-diene are theoretically possible (as would be expected from its dimerisation) and are shown below (XXX-XXXIII). Both groups came to the same conclusion, namely that the "dimerI" of Jacobs and Goodrow, and the hydrocarbon, m.p. 136-137° isolated by Herz and Lewis, corresponded to (XXX).



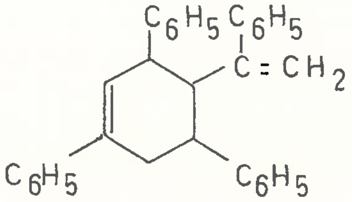
XXX



XXXI



XXXII



XXXIII

Herz and Lewis have found that the molecular weight of the dimer, as determined by ebullioscopic method in methyl ethyl ketone, to be 426 (calc. for $C_{32}H_{28}$, 412). Curiously, the molecular weight as determined by the Rast method was 215 (calc. for $C_{16}H_{14}$, 206). These authors have stated that Fiesselmann and Ribka[109] reported an analogous result for the dimer of 2-phenylacrylophenone. Nevertheless, both the liquid $C_{16}H_{14}$ from the trap 3 and the solid compound from the trap 5, observed in the present study have nothing (e.g. melting point, infrared and ultraviolet spectra) in common with the above-mentioned dimer.

Attempts to synthesise 1,3-diphenylbuta-1,3-diene were also reported by Staggs[110] in his paper "An attempted synthesis of 1,3-diphenyl-1,3-butadiene." The starting material, 2,4-diphenylbut-3-ene-1-ol, was prepared by lithium aluminium hydride reduction of methyl-2,4-diphenyl-3-butenoate. Purification of the product by saponification of the unchanged ester in the reaction mixture resulted in dehydration of the alcohol, but only a low yield of the "dimer I" was isolated. Attempts to pyrolyse the 3,5-dinitrobenzoate of 2,4-diphenylbut-3-ene-1-ol gave neither the diene nor its dimer.

The solid, m.p. 123-124°, isolated in the present study was thought to be probably one of unknown dimers of 1,3-diphenylbuta-1,3-diene. As will be shown later, it was identical (mixed m.p. and the ultraviolet spectrum) with the solid compound obtained from the product (collected in the trap 7), which was believed to be 1,3-diphenylcyclobutene. While this product has aroused a new interest in the preparation of small ring compounds by a desulphurisation reaction route, the chemistry of 1,3-diphenylbuta-1,3-diene invites wide interest. More conclusive evidence is required in order to support the above postulations.

Examination of the infrared spectrum of the liquid from the trap 7 showed peaks similar to that of the solid compound from the trap 5 in the region 1400-4000 $cm^{-1}$. The strong bands at 2924 and 2857 $cm^{-1}$ indicate the presence of $CH_2$ groups. The absorption at 3049 $cm^{-1}$ may be ascribed to C-H stretching vibration of an ethylenic double bond as it is not far from the region 3040-3010 $cm^{-1}$. Four evenly spaced peaks typical of those given by monosubstituted benzene derivatives, as well as bands at 1600, 1493, 1447, 1070, 1029 and 694.4 $cm^{-1}$ may be assigned to the presence of the benzene rings as has been discussed above. The medium band at 1429 and a broad peak at 838 $cm^{-1}$ provide evidence for the presence of a tri-substituted ethylene (a CH in-plane and out-of-plane deformations respectively). The band at 1645 $cm^{-1}$ which corresponds to C=C stretching vibration seems low for a non-conjugated double bond (1680-1620 $cm^{-1}$), but with aromatic conjugation, this is not surprising. It is known[83] that when a double bond is conjugated with an aromatic ring the C=C frequency shifts to lower frequency (but generally less than that occurring with full aliphatic conjugation). Moreover the shoulder which appears at 1580 $cm^{-1}$ is a positive indication of conjugation of a double bond (1587-1575 $cm^{-1}$ as pointed out by Randall _et al._[111]) with the aromatic ring. It is noteworthy that Wiberg and Nist[112] have recently demonstrated that a cyclobutene shows C=C stretching frequency at 1566 $cm^{-1}$. However, in association with the assignments from the proton magnetic resonance spectrum which indicate that this compound is 1,3-diphenylcyclobutene, the appearance of the strong band at 963.6 cm.$^{-1}$ (*trans* ethylenic double bond) is not understandable.

The ultraviolet spectrum of this hydrocarbon, shows peaks ($\lambda_{max}$ and log$\epsilon$ ; 253, 4.02; 293, 3.19; and $\lambda_{min}$ 225 m$\mu$, 3.67) and is similar to that of the "dimer m.p. 136-137$^{\circ}$" reported by Herz and Lewis[108] ($\lambda_{max}$ and log $\epsilon$ ; 253, 4.56; 294, 3.19; and $\lambda_{min}$ 226 m$\mu$, 4.12) and indicative of a slightly modified styrene chromophore. The position of the principal maximum and the high extinction coefficient suggests that the double bond is present as a styryl function. Moreover, a comparison with the spectrum of *trans*-1,3-diphenylbut-1-ene which displays maxima at 294 (log$\epsilon$ 3.100), 286 (log$\epsilon$ 3.240), and 253 m$\mu$ (log$\epsilon$ 4.250) supports the view that the compound contains the 1,3-diphenylbut-1-ene system (the spectrum of the liquid also shows a shoulder at 283, log $\epsilon$ 3.29).

At this stage,on the basis of the above evidence, the structure of the liquid hydrocarbon in the trap 7 may be regarded as 1,3-diphenylcyclobutene. The presence of one double bond in the molecule was confirmed by microhydrogenation. The volume of the hydrogen absorbed was 99.98% of the theoretical amount. The hydrogenation product was susceptible to aerial-oxidation as can be seen from the weak band in the region of a carbonyl absorption frequencies (1727 cm$^{-1}$) in its infrared spectrum and its colour

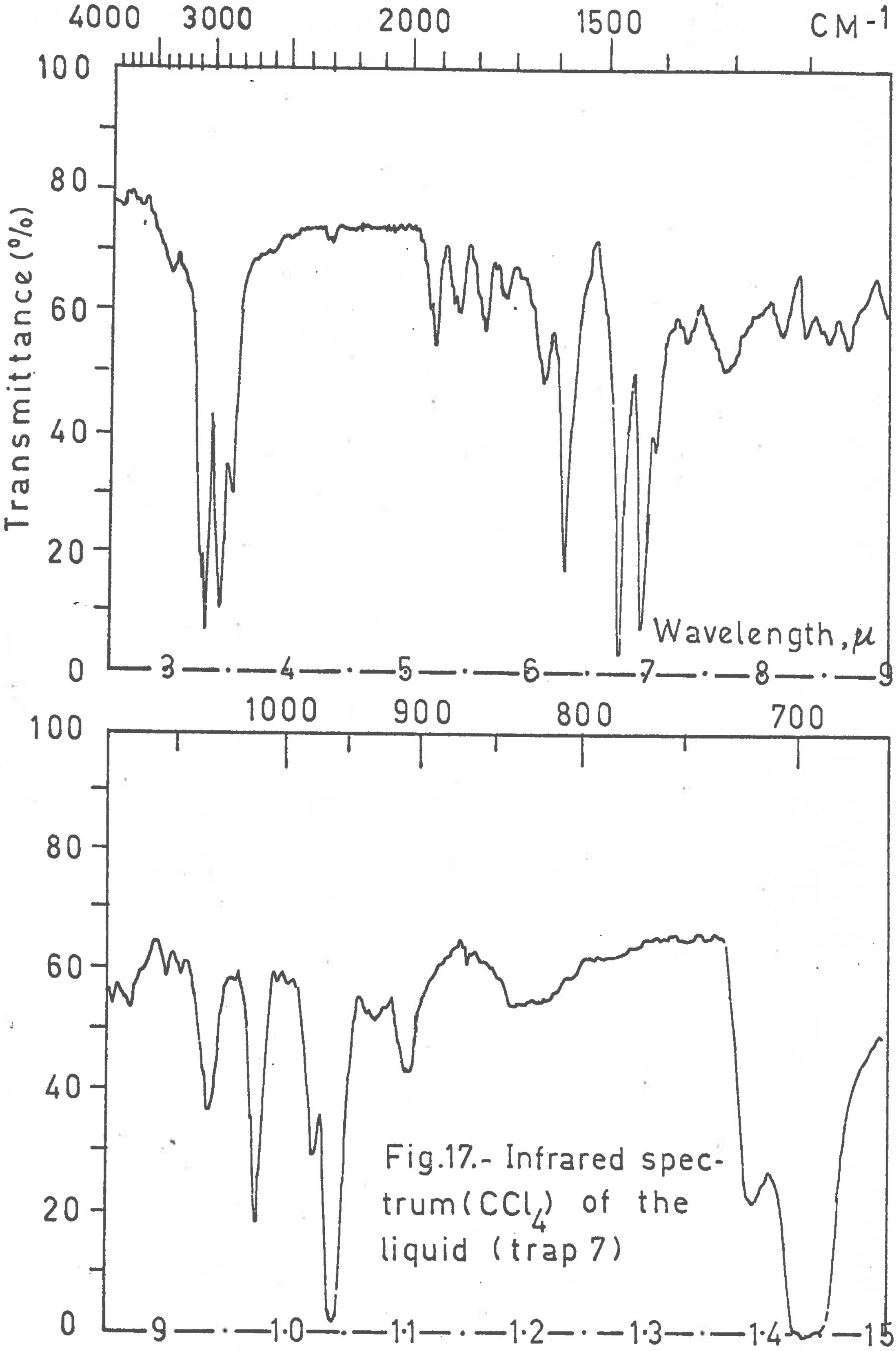


Fig.17.- Infrared spectrum ($CCl_4$) of the liquid (trap 7)

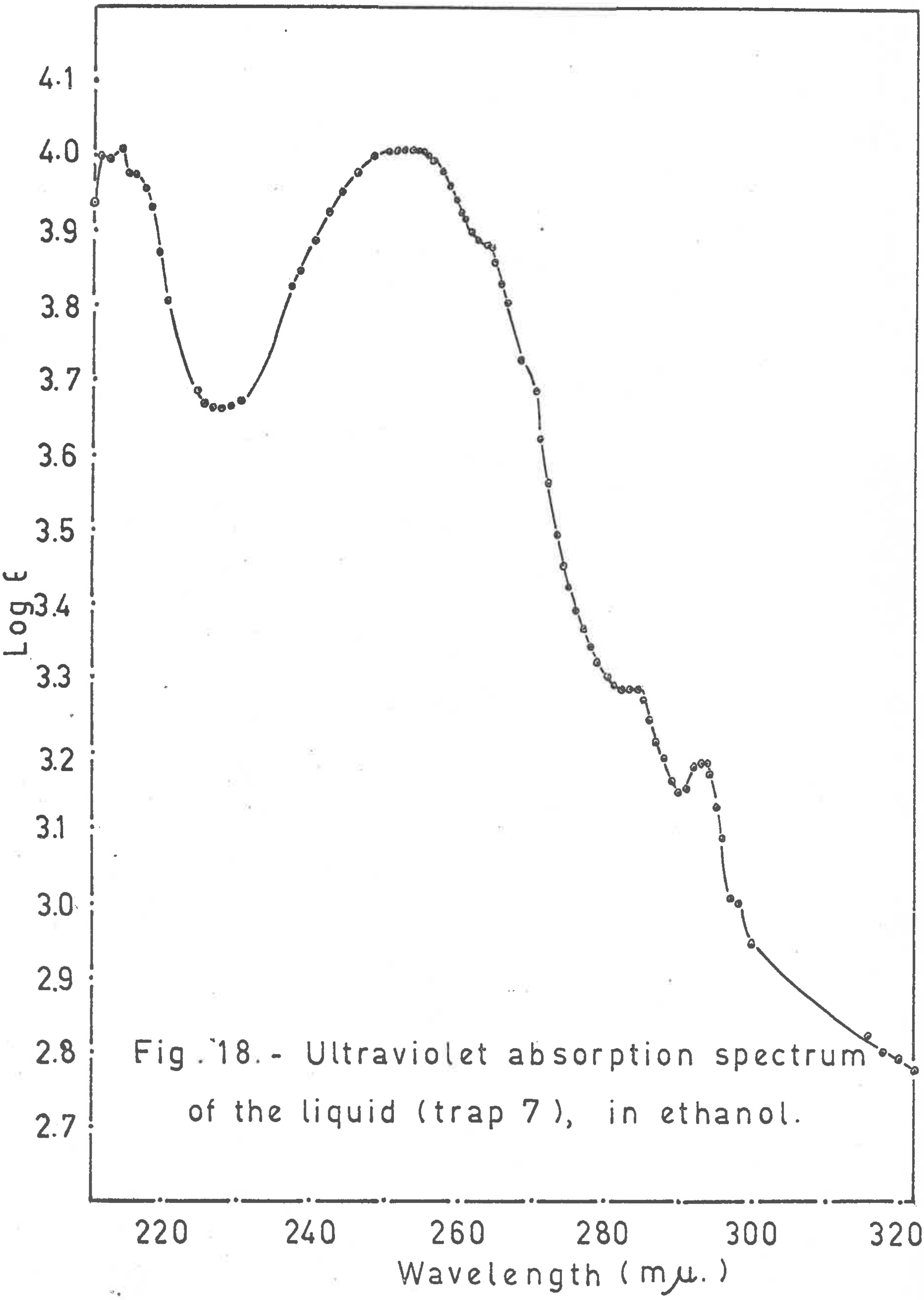


Fig. 18. - Ultraviolet absorption spectrum of the liquid (trap 7), in ethanol.

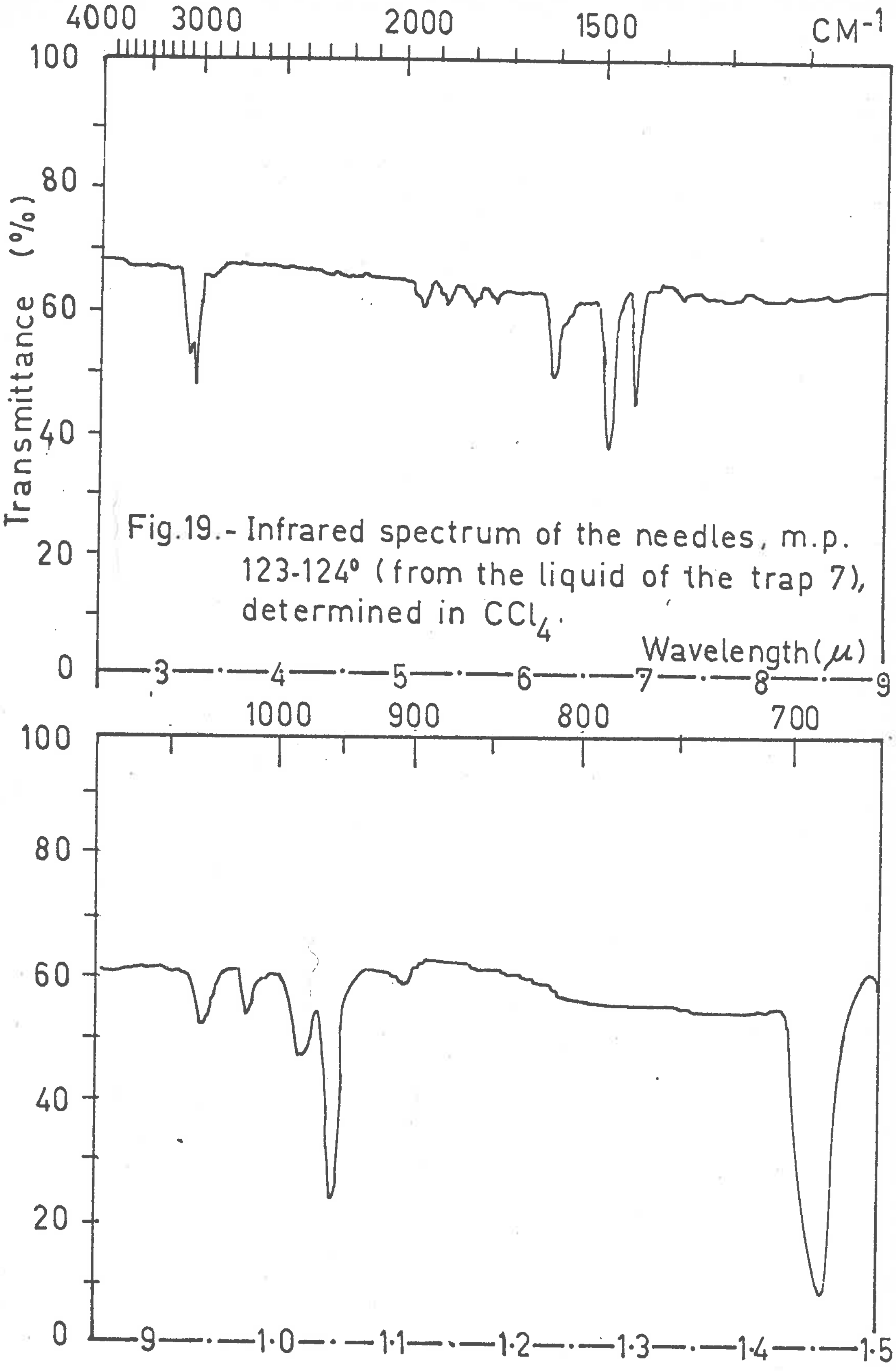


Fig.19.- Infrared spectrum of the needles, m.p. 123-124° (from the liquid of the trap 7), determined in $CCl_4$.

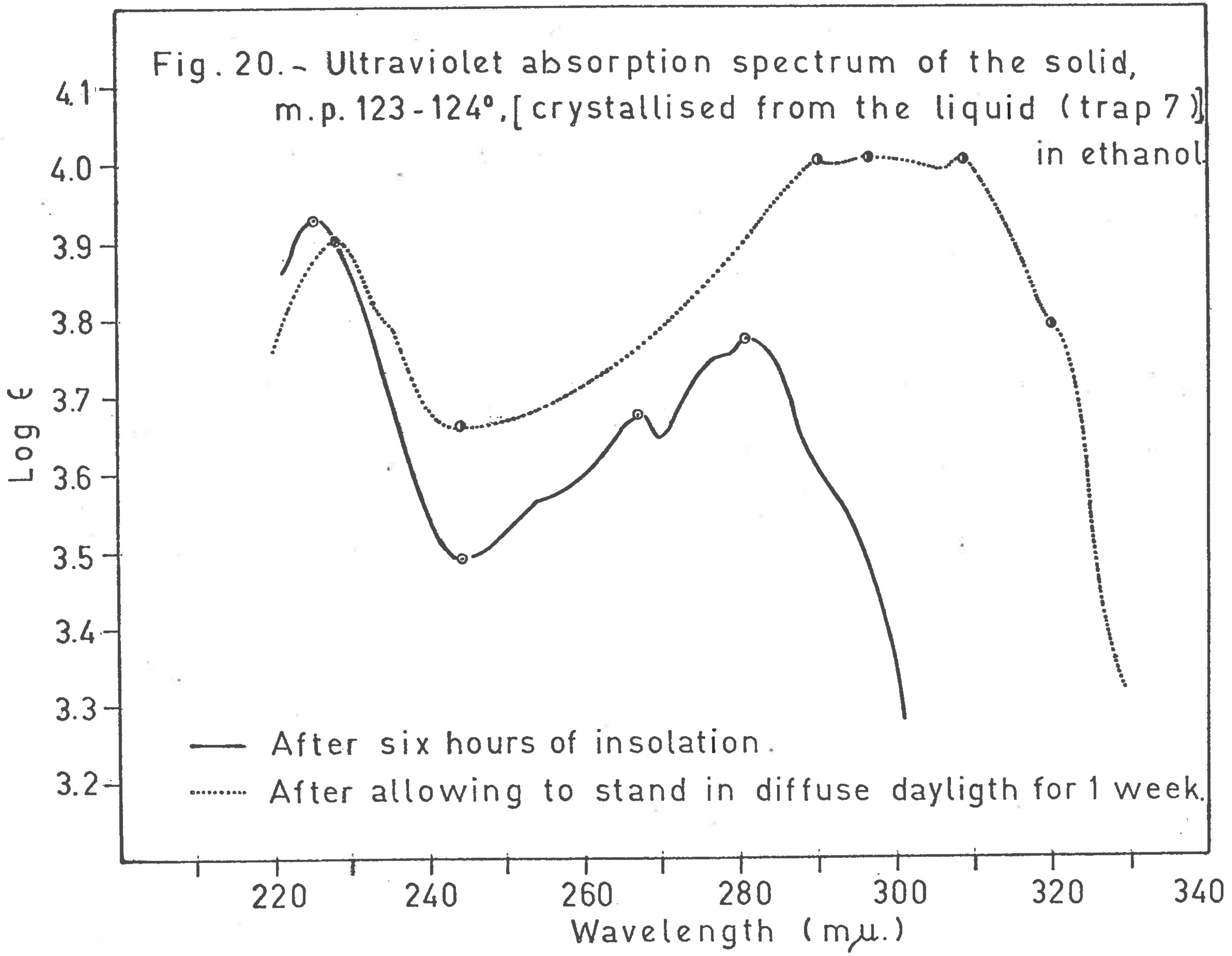
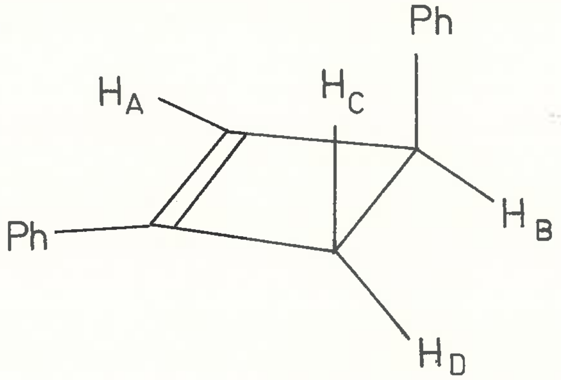


Fig. 20.- Ultraviolet absorption spectrum of the solid, m.p. 123-124°, [crystallised from the liquid (trap 7)] in ethanol.

(yellowish) which was distinguishable from the other hydrogenation products of the compounds from the other traps. However, besides those expected for the presence of monosubstituted benzene rings and phenyl conjugated double bonds, the presence of the band at 909.1 cm$^{-1}$ is remarkable for the assignment in correlation with the other substituted cyclobutane.[85] Blank microhydrogenation of an authentic trans-trans-1,4-diphenylbuta-1,3-diene was also attempted and 2 moles of hydrogen (99.27% of the theoretical amount) were taken up. The hydrogenation proceeded smoothly, and gave rise to the expected 1,4-diphenylbutane.

The structure of the liquid product (trap 7) as suggested by the proton magnetic resonance spectrum is as follows:



The figures of the proton magnetic resonance spectrum of this liquid product are summarised in Table 5.

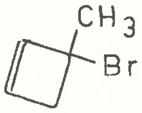
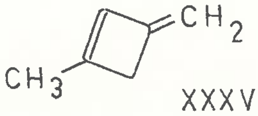
## TABLE 6

| τ<br>(p.p.m.) | Splitting<br>(c.p.s.) | Appearance | Proton Count | Assignment |
|---|---|---|---|---|
| 8.49 | 2.8 | complex | 1 | $H_C$ |
| 8.45 | | | | |
| 8.39 | | | | |
| 8.34 | 4.4 | | | |
| 8.26 | | | | |
| 7.54 | | complex | 1 | $H_D$ |
| 7.41 | 2.4 | | | |
| 7.37 | | | | |
| 7.32 | | | | |
| 6.585 | 5.0<br>2.4 | triplet | 1 | $H_B$ |
| 6.55 | | | | |
| 6.50 | | | | |
| 3.71 | | doublet | 1 | $H_A$ |
| 2.86 | | doublet | 10 | aromatic |

### Proton $H_A$.

This can be rationalized in the following manner: aromatic protons absorb at τ 2.86. The vinylic hydrogen is unique and is assigned to the peak at τ 3.71 (chemical shift 377.43 c.p.s.).

Other cyclobutene compounds have vinylic protons with similar chemical shift, e.g.

| No. | Compound | Chemical Shift | $\tau$ | Ref. |
|---|---|---|---|---|
| 1. |  XXXIV | 355<br>295 | 4.08<br>5.08 | 113 |
| 2. |  XXXV | 387.15 | 3.55 | 114 |

The lower $\tau$ value in the compound (XXXV) and in the cyclobutene structure suggested above can be accounted for by the deshielding effect of the adjacent olefinic group in the former and the benzene ring in the latter.

### Proton $H_C$ and $H_D$

These protons would be expected to have similar but not identical $\tau$ values due to the proximity of phenyl rings. Since $H_C$ is much closer to the phenyl ring, the following assignments are made.

$H_C$ $\tau$ = 8.39 (96.810 c.p.s.)
$H_D$ $\tau$ = 7.41 (155.424 c.p.s.)

These values are comparable with other methylene protons in cyclobutene rings reported in the literature[113,114] ( $\tau$ 6.97, shift 182; and $\tau$ 6.90, shift 195.74 c.p.s. respectively).

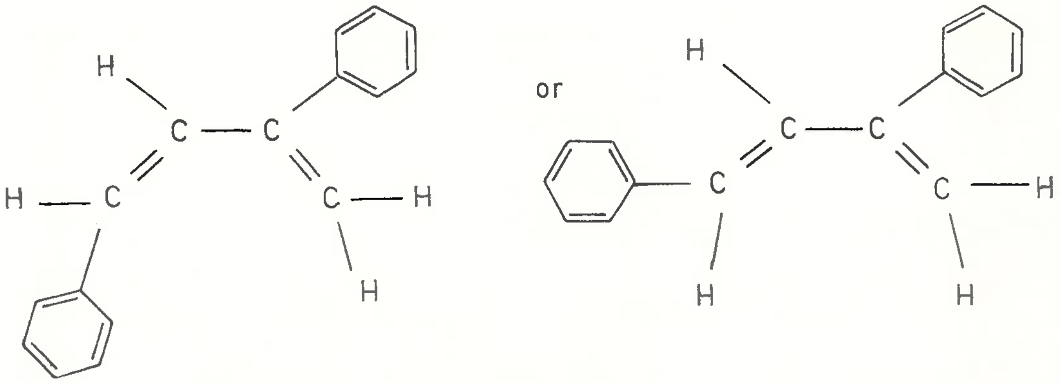
A determination of the coupling constants (splitting) arising from a coupling of $H_B$ with $H_C$ and $H_D$ enables a specific assignment of these protons to the above $\tau$ values. A relatively large J value would be expected to arise from the coupling of $H_B$ and $H_C$ due to their *trans*-conformation. Hence the peak with $\tau$ value 8.39 was assigned to $H_C$ and the J value equal to 4.44 (J of $H_B$ = 2.395, 4.97 c.p.s.).

On the other hand, the coupling of $H_B$ and $H_D$ would be expected to give rise to a much smaller coupling constant, this being similar to a coupling of an axial proton with adjacent equatorial proton in cyclohexane (J. *ca.* 3 c.p.s.). This was observed and the peak with $\tau$ 7.37 was assigned to $H_D$ (J = 2.404 c.p.s.).

### Proton $H_B$

There is only one proton in the molecule which could give rise to a triplet peak and this is the proton $H_B$. The peak with $\tau$ 6.55, therefore, is assigned to this proton.

As can be seen from this discussion, the p.m.r. spectrum can readily be interpreted for the compound with the above structure. It is not possible to rationalize this spectrum if the compound was assumed to have the other possible structures, either



The liquid believed to be 1,3-diphenylcyclobutene on exposure to diffuse sunlight crystallised to give needles, m.p. 123-124° which were found to be identical (mixed m.p. and ultraviolet spectra) with that obtained from the liquid of trap 3 under similar conditions. The infrared spectrum of the needles was identical with that of the solid compound, m.p. 96° (not pure) obtained in the previous experiments, but the ultraviolet spectrum was not. This may be due to the photochemically labile nature of the product. It is interesting that its infrared spectrum, which is essentially different from that of the original liquid, was found to be almost the same as that of *trans-trans*-1,4-diphenylbuta-1,3-diene except for variations in the region 11-12 $\mu$ (see Experimental part). Its structure is still unknown; the small amount of the compound did not permit further investigation.

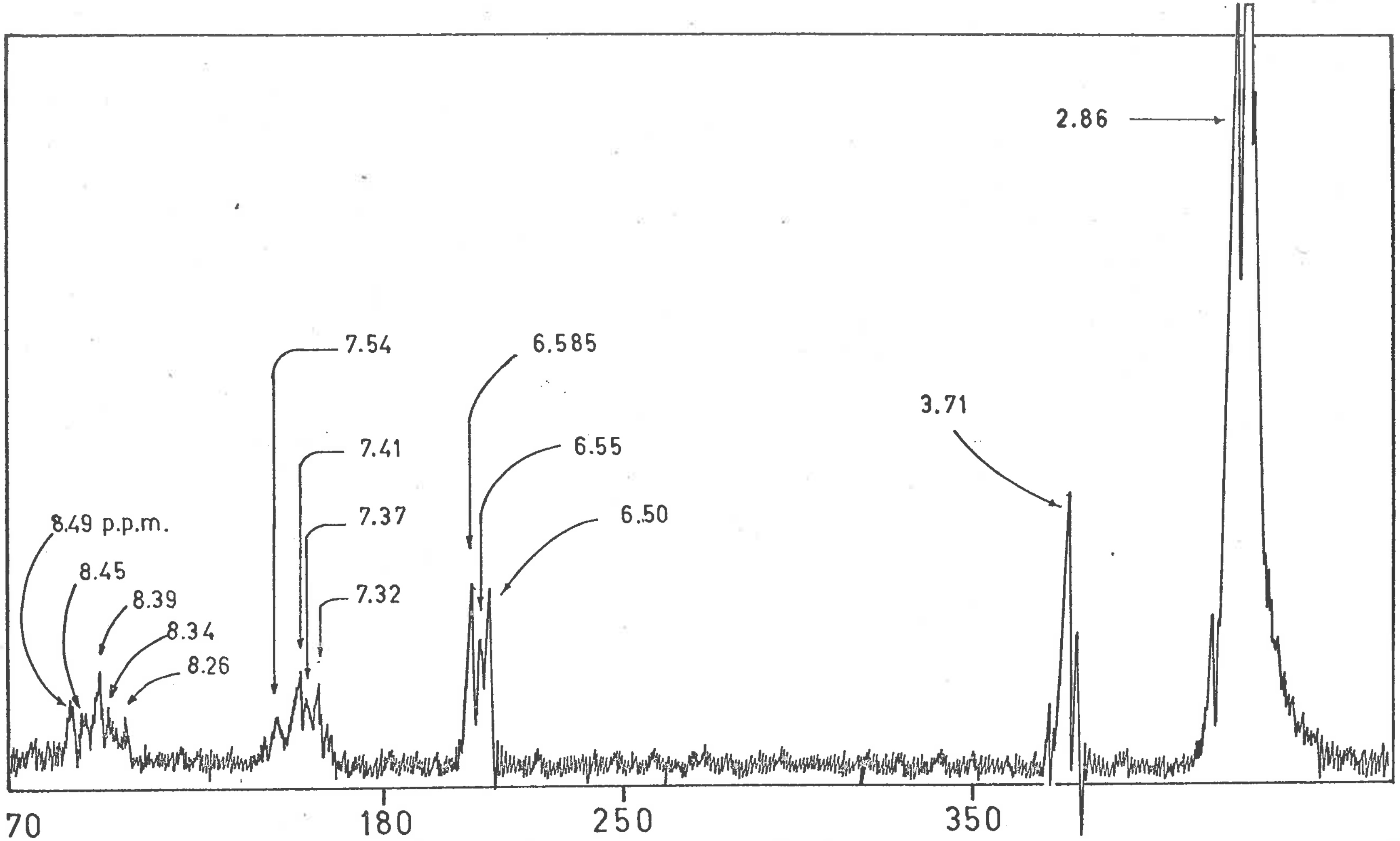


FIG. 21.- PROTON MAGNETIC RESONANCE SPECTRUM OF THE LIQUID (TRAP 7) IN $CCl_4$, TAKEN AT 60 MC./SEC. AND EXPRESSED IN UNITS OF $\tau$

In no experiment on the desulphurisation of 2,5-diphenyl-1,4-dithiin with W-7J Raney nickel catalyst, was the "expected" ethylbenzene isolated, despite the utmost care. 1,3-Diphenylbuta-1,3-diene and 1,3-diphenylcyclobutane must surely arise from a combination of two of the postulated styryl-$\alpha,\beta$-diradicals prior to hydrogenation. Furthermore, attempted reactions of styrene with W-7J Raney nickel catalyst, which was conducted under the similar conditions with those of the desulphurisation reactions of 2,5-diphenyl-1,4-dithiin, have been found to give ethylbenzene and polystyrene. On the other hand, reaction of phenylacetylene over the W-7J Raney nickel catalyst yielded no ethylbenzene but polystyrene and some of the intractable brown tar.

## EXPERIMENTAL

Ultraviolet Spectra.- These were measured in 95% ethanol solutions with an Optica CF-4 recording spectrophotometer, and with a Hilger Uvispek spectrophotometer.

Infrared Spectra.- These were examined with the Infracord spectrophotometer, Perkin-Elmer, Model 137, or Grubb-Parsons DB 1 spectrophotometer using sodium chloride optics.

Proton Magnetic Resonance Spectra.- These were determined with a Varian Associates high resolution nuclear magnetic resonance spectrometer model D.P. 60.

I am grateful to Dr. T.M. Spotswood for these spectra.

Melting Points.- These were determined by a melting-point microscopic apparatus (Ernst Leitz, Wetzlar).

Microanalyses.- These were performed by the Australian Microanalytical Service, C.S.I.R.O., Melbourne.

Gas-liquid Partition Chromatography.- Unless indicated otherwise, analyses involving gas chromatography were carried out using a Griffin V.P.C. apparatus Mark II, with a 6 ft. column packed with Celite (40-60 mesh; coated with 15% Apiezon L.). By comparison of the areas under peaks, the approximate compositions of a number of mixtures were obtained. Standard mixtures were run wherever possible.

For preparative work, a Beckman Megachrom instrument was used, with eight 6 ft. columns packed with C-22 Firebrick (42-60 mesh; coated with 35% Apiezon J.).

Preparation of the Catalysts.- W-7 and W-7J Raney nickel catalysts were prepared as previously described (see p. 83). The catalyst was freshly prepared for each experiment.

Preparation of 2,5-diphenyl-1,4-dithiin.- The material used in the first four experiments was obtained commercially (Eastman Organic Chemicals Distillation Products Industries; Rochester 3, New York). It was recrystallised from absolute ethanol. In the last experiment, the diphenyl-1,4-dithiin was obtained in 84% yield as bright yellow plates, m.p. 116-117° (lit.[70] m.p. 115-117°) following protonation of the intermediate phenacyl mercaptan, according to the method given by Baker and Barkenbus,[70] except that phenacyl bromide was used instead of phenacyl chloride. In this preparation it was observed that using bone-charcoal during the recrystallisation of the product (as described in the literature) reduced the yield (reported to be 74%), probably by aerial oxidation of the sulphur compound, and the mother liquors become much darker in colour. Long exposure to air and light or suction filtration also darkened the colour of the crystals. The phenomenon was also observed on the commercial sample.

Preparation of 2,4-Diphenylthiophen.- This was obtained in 66.3% yield from the pyrolysis of 2,5-diphenyl-1,4-dithiin according to the method of Parham and Traynelis,[39] except that purification of the product was accomplished by formation of the picrate, separation and subsequent dissociation of the picrate in benzene on the short column of activated alumina. Elution with benzene-light petroleum (b.p. 50-60°)(1:4,; v/v) gave colourless plates, m.p. 123-124° (lit.[115] m.p. 122.5°). Its picrate had m.p. 133-134° (lit.[116] m.p. 133.1-133.6°).

Desulphurisation.- General Procedure. Unless otherwise stated, the desulphurisation with W-7J Raney nickel catalyst was performed as follows: sulphur-free toluene was cautiously added from a separating funnel to the dry W-7J Raney nickel catalyst *in vacuo*. The solution of sulphur compound in toluene (sulphur-free) was then run in slowly, followed by more toluene, and air admitted. A trace of water was removed by azeotropic distillation with toluene until none could be detected in the distillate, the same amount of toluene then being replaced. The mixture was refluxed under dry, oxygen-free nitrogen gas with the trap (dry ice in ethanol) attached to the top of the reflux condenser. The catalyst was collected on Celite and subsequently extracted with toluene (Soxhlet) overnight. The liquid collected in the trap, the filtrate, and the extract, were combined, and the solvent removed. Fractional distillation of the solvent was accomplished through a jacketed column (2 x 60 cm.) packed with glass helices and fitted with a variable take-off total condensation head (reflux ratio ca. 1:10). The various fractions were examined qualitatively and quantitatively by gas-liquid partition chromatography. The residue was chromatographed on a column of alumina (B.D.H.) in light-petroleum (except where otherwise indicated, b.p. 52-58° was used).

Wherever possible (e.g. the reaction flask, the chromatography column) the reaction products were protected from light by black photographic paper.

Methanol and ethanol were purified by distillation over potassium hydroxide.

## Desulphurisation of 2,4-diphenylthiophen.

(1) With W-7J Raney nickel catalyst. 2,4-Diphenylthiophen (4.8 g.) in dry sulphur-free toluene (350 c.c.) was refluxed with W-7J Raney nickel catalyst (from 125 g. of alloy, degassing period 6 hr.) for 5 days. Working up as described above gave starting material (4.75 g.; 98.96%), identified by m.p., mixed m.p., picrate (m.p. and mixed m.p.), and by comparison of its infrared spectrum with that of the authentic sample. No other product except benzene (yield not determined) could be detected by gas chromatography of the solvent.

(2) *With W-7 Raney nickel catalyst.* The mixture of 2,4-diphenylthiophen (4.7 g.) in sulphur-free xylene (to make the total volume *ca.* 250 c.c.) and W-7 Raney nickel catalyst (from 62.5 g. of alloy; previously washed five times with methanol and then five times with sulphur-free xylene) was distilled on a heating mantle to remove traces of water until the distillate was water-free. More dry xylene was then added to the mixture (to make up the original volume) which was then refluxed for 6 hr. The catalyst was separated on Celite followed by extraction with xylene (Soxhlet) overnight. Fractional distillation of the combined filtrate and extract gave:

(*a*) a liquid, b.p. 134-138° (61.98 g.);

(*b*) xylene, b.p. 138-139° (*ca.* 500 c.c.); and

(*c*) a yellow residue (6.55 g.).

Examination of the fraction (*a*) by gas-liquid chromatography on a 6ft. column packed with Celite (60-80 mesh; coated with 10% Gum Rubber SE 30) at 86°, inlet pressure 29.5, outlet pressure 7.3 mm., and with nitrogen flow of 1.05 l./hr., showed the presence of a small amount of benzene and toluene (identification based on retention time only; yield not determined). No other product could be isolated by further gas chromatography of the fraction using a Beckman Megachrom instrument with nitrogen as a carrier gas, an inlet pressure of 8 lb. and an outlet pressure of 2 lb., the following retention times were observed at detector temperature

195°: trap 1, toluene (8.5 min.); trap 3, *m*-xylene (15 min.); trap 5, benzene (2 min.); trap 7, *p*-xylene (7.5 min.). These were characterized by their infrared spectra.[117]

Fraction (*b*) was identified as a mixture of xylene isomers by comparison of its infrared spectrum with that of authentic specimens. No other components could be detected by gas chromatography.

Fraction (*c*) was chromatographed on an alumina column in light-petroleum (b.p. 50-60°). Elution with the same solvent gave: (i) a colourless liquid (1.92 g.); (ii) colourless plates, m.p. 121-122° (2.5 g.), after recrystallisation from absolute ethanol.

Redistillation of fraction (i) *in vacuo* three times gave a colourless liquid of constant refractive index ($n_D^{20}$ 1.5527). This was identified as 1,3-diphenylbutane (reported[118] $n_D^{20}$ 1.5522). Its infrared spectrum was found to be identical in every respect with that reported in the literature.[119] The ultraviolet spectrum showed: $\lambda_{max.}$ 253 ($\epsilon$ 324.882), $\lambda_{min.}$ 234 ($\epsilon$ 219.98).

Found : C, 91.6; H, 8.5%; M, 202 (Rast).

Calc. for $C_{16}H_{18}$: C, 91.4; H, 8.6%; M, 210.3.

The melting point of the plates from (ii) was not depressed when admixed with 2,4-diphenylthiophen. Comparison of the infrared spectra, and the m.p. and mixed m.p. of the picrates, also confirmed the identity. The total yield of the diphenylbutane was 45.91% and the starting material recovered was 53.19%.

### Desulphurisation of 2,5-diphenyl-1,4-dithiin.

Experiment (1). The mixture of the diphenyl-1,4-dithiin (8.0 g.) in toluene (400 c.c.) and W-7J Raney nickel catalyst (from 125 g. of alloy; degassing period at 100°/12 mm., 8 hr.) was refluxed for 65 hr. The solvent was removed from the combined filtrates and extracts by evaporation under nitrogen at 14-15°/15 mm., and a red-brown residue (8.0 g.) was obtained. Fractional distillation of the removed solvent gave a fraction boiling below 110.5° (15 c.c.), and a fraction boiling at 110.5° (ca. 600 c.c.). Gas-liquid chromatography of the first fraction showed the presence of benzene (yield was not calculated) but no other product was detected.

Chromatography of the red-brown residue (8.0 g.) on a column of alumina (250 g.) gave 3 fractions on elution with light-petroleum:

(a) a colourless liquid of pleasant smell (0.72 g.);

(b) colourless plates, m.p. 123-124°, after several recrystallisations from absolute ethanol, (2.21 g.);

(c) yellow prisms, m.p. 128-129° after recrystallisation from absolute ethanol (0.09 g.). Further elution with benzene-light petroleum (b.p. 50-60°) (1:4, v/v) gave

(d) an intractable brown tar (2.25 g.).

Redistillation *in vacuo* of the fraction (*a*) at 170° (bath)/0.1 mm., gave a colourless liquid (0.35 g.). Analysis of the product suggested the empirical formula $C_{16}H_{14}$, but it was not identical with any of the known compounds having this formula.

Found: C, 93.0; H, 7.3.

$C_{16}H_{14}$ requires: C, 93.2; H, 6.8%.

Its infrared spectrum (carbon tetrachloride) showed bands at 3077 (C=C), 3030 (aromatic CH), 2927 and 2857 ($CH_2$), four evenly spaced peaks in the region 1942-1739 (each with splitting except at 1739) and a strong band at 695 (monosubstituted aromatic), 1600 (benzene), 1443 ($CH_2$), 1449 (benzene), 1493 (benzene), 1307 (*cis*-CH=CH), 1067 (benzene), 1029 (benzene), 1667 (isolated double bond ?), 961.5 (*trans*-double bond), 862.1 (unassigned), 922.3 (unassigned), 906.9 $cm^{-1}$ ($CH=CH_2$); and 906.8 $cm^{-1}$ ($R_1R_2C=CH_2$). Its ultraviolet spectrum showed $\lambda_{max.}$ 265, 280, 288, 297; with shoulders at 258 and 272 mμ: $\lambda_{min.}$ 243; ( $\epsilon$ , not determined).

The product on standing in an unsealed container under ordinary daylight, slowly crystallised to give colourless needles, m.p. 89-91° (5.0 mg.). The mother liquor, after a month, had turned yellow. Examination of the yellow liquid by infrared spectroscopy, showed bands almost identical with the original liquid $C_{16}H_{14}$ except that bands at 3509 (CH), 1721 (CO), 1698 (CO of aryl acid), and

814.6 cm$^{-1}$ (origin uncertain) were observed in addition. The absorption at OH stretching vibrations was characteristic of a carboxylic acid (a broad absorption peak).

Recrystallisation of the needles from light-petroleum (b.p. 50-60°) raised the melting point to 96°. The ultraviolet spectrum of this compound showed peaks almost identical with those of the liquid product except for shoulders at 228 and 236 mμ, which did not appear in the spectrum of the liquid. Both liquid and solid products gave an intense yellow colour with tetranitromethane, providing more evidence for the presence of a non-aromatic double bond. An alternative possible, 1,3-diphenylcyclobutene is still unknown. The small amount of the solid product did not permit any further purification. Its molecular weight, determined by the Rast method, was 148 (calc. for $C_{16}H_{14}$, 206.3).

Fraction (*b*) was identified as 2,4-diphenylthiophen by m.p., mixed m.p., by comparison of its infrared spectrum with that of the authentic specimen, and by picrate formation, m.p. and mixed m.p. 133-134° (lit.[116] m.p. 133.1-133.6°).

Found: C, 81.4; H, 5.3; S, 13.4%; M, 210 (Rast).
Calc. for $C_{16}H_{12}S$: C, 81.3; H, 5.1; S, 13.6%; M, 236.3.

The infrared spectrum of fraction (*c*) was found to be superimposable with that of the complex[39] (m.p. 128-129°) obtained by the recrystallisation of an equimolecular mixture of 2,5-diphenyl-1,4-dithiin (m.p. 117-118°) and 2,4-diphenylthiophen (m.p. 122-123°)

from ethyl acetate. The product also caused no depression in melting point when mixed with the complex.

Fraction (d) was not investigated. The total yield of the hydrocarbon $C_{16}H_{14}$ was 11.7%, and of 2,4-diphenylthiophen was 31.25%.

Experiment (2). The mixture of 2,5-diphenyl-1,4-dithiin (12 g.), toluene (600 c.c.) and W-7J Raney nickel catalyst (from 125 g. of alloy, degassing period 6 hr.) was refluxed for 4 days. After seperation and subsequent extraction of the catalyst as described above, the combined filtrates and extracts was subjected to careful fractional distillation (reflux ratio 1:18) under nitrogen atmosphere and the fractions collected were examined by gas-liquid chromatography. No other products were detected except benzene (11.72 g., calculated from areas under peaks). The dark brown residue (6.8 g.) was chromatographed in light-petroleum on deactivated alumina (160 g.). From the light-petroleum eluate, the following were obtained:

(a) a colourless waxy solid (0.20 g.), m.p. 59-60° after recrystallisations from absolute ethanol; the mixed m.p. with the sample of "polymethylene" was not depressed and their infrared spectra were identical.

(b) a colourless liquid (1.41 g.); and

(c) 2,4-diphenylthiophen (2.47 g.), characterized as before.

A tarry residue (2.45 g.) was eluted with benzene-light petroleum (b.p. 50-60°) (1:2; v/v), but this could not be identified.

The liquid product (b) boiled at 173° (bath)/0.7 mm. and possessed the same characteristic smell as had been observed in the first experiment. The infrared and ultraviolet spectra were both found to be identical in every respect with those of the liquid $C_{16}H_{14}$ obtained previously. The analyses were also in reasonable agreement.

Found: C, 93.0; H, 7.15
93.1; 6.9%; M, 177 (Rast).
$C_{16}H_{14}$ requires: C, 93.2; H, 6.8%; M, 206.3.

Upon standing the product slowly solidified to give colourless flat needles, m.p. 92-93° (7 mg.), not depressed when admixed with the solid hydrocarbon from the above experiment, and their ultraviolet spectra were identical. The compound was readily soluble in light-petroleum (b.p. 30-45°), chloroform, and carbon tetrachloride and very difficult to crystallise (small scale). Investigation of the infrared spectrum indicated that this solid product was not the same compound as the original liquid (see Fig. 22 and 23). The following absorption bands were observed: 3030 (aromatic C-H), 2967 (C-H), 1942-1739 (four evenly spaced peaks, typical patterns of monosubstituted aromatic), 1603 (benzene), 1493 (benzene), 1449 (benzene), 1441 ($CH_2$), 1304 (unassigned), 1198 (unassigned), 1067 (benzene), 1024 (benzene), 961.5 (trans-ethylenic double bond), 913.8 ($CH=CH_2$) and a strong band at 695 $cm^{-1}$ (mono substituted benzene ring).

The p.m.r. spectrum ($CCl_4$) of the liquid compound showed peaks (singlet) at $\tau$ 7.13 (methylene protons); singlet at $\tau$ 3.50 (olefinic protons); and a complex region at $\tau$ 2.89 (olefinic + aromatic). The areas under the peaks were not determined. Peaks due to impurities were also observed at 73.44, 131.82-163.63, and at 224.02-234.54 c.p.s. respectively.

The total yield of the liquid $C_{16}H_{14}$ was 26.14% and of 2,4-diphenylthiophen was 23.37%.

Epoxidation of the liquid $C_{16}H_{14}$ by monoperphthalic acid.

Monoperphthalic acid was prepared by treatment of phthalic anhydride with strongly alkaline hydrogen peroxide at -10° according to the method described by Böhme.[120] Titrations of the acid (5 c.c.) in excess potassium iodide solution with standard sodium thiosulphate (0.08231 N., 33.05 c.c.) revealed that the concentration of the acid was 0.2136 N. The volume read, each time, was the average of at least three titrations. The standard solution of sodium thiosulphate was obtained by dissolving sodium thiosulphate (B.D.H., 396.69 mg.) in carbon dioxide-free distilled water (the volume made up to 500 c.c.). This was standardised with an acidified solution (diluted sulphuric acid) of iodide-free potassium iodate (0.06 N., 20 c.c.) in an excess of potassium iodide, using starch

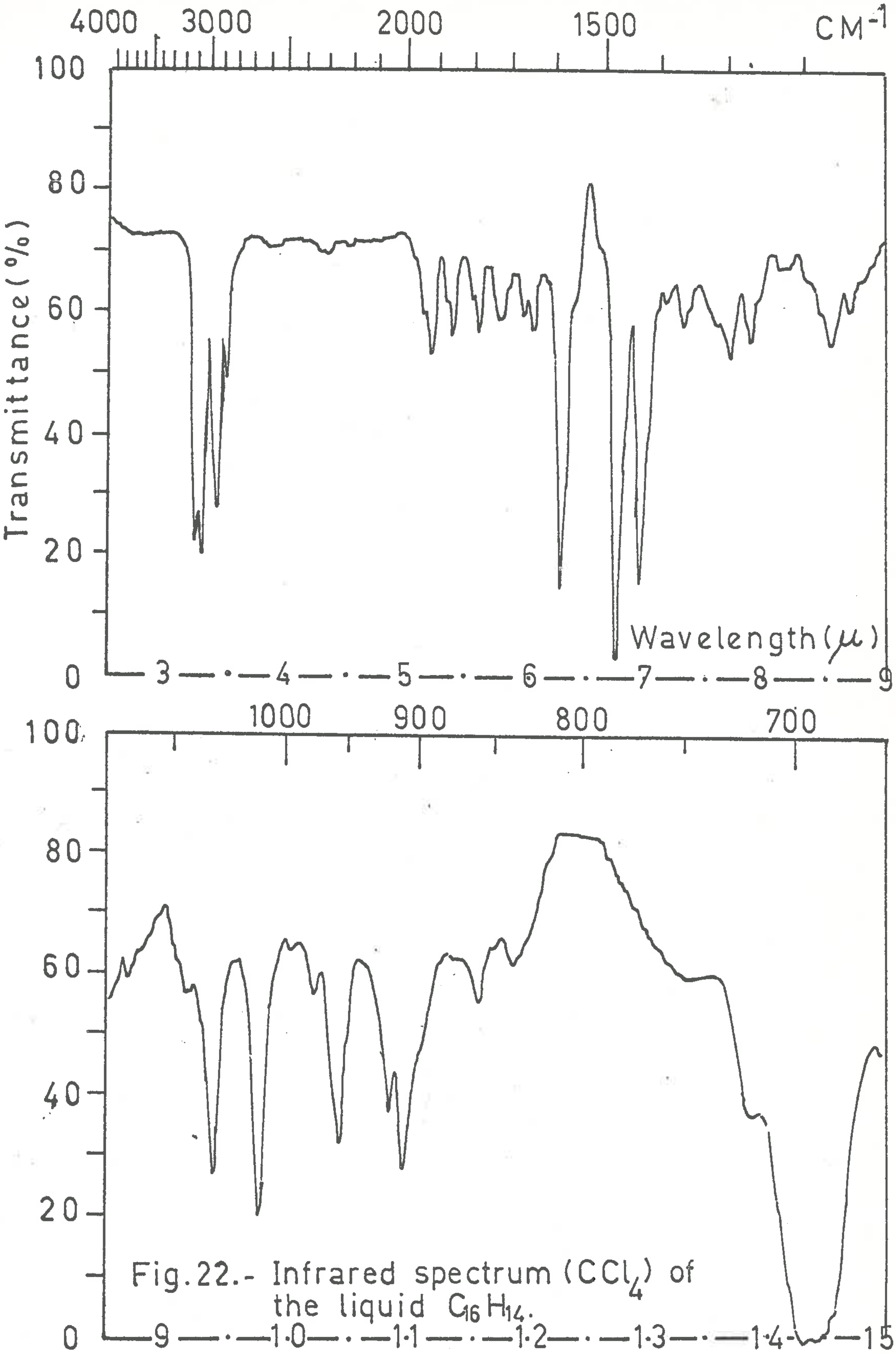


Fig.22.- Infrared spectrum ($CCl_4$) of the liquid $C_{16}H_{14}$.

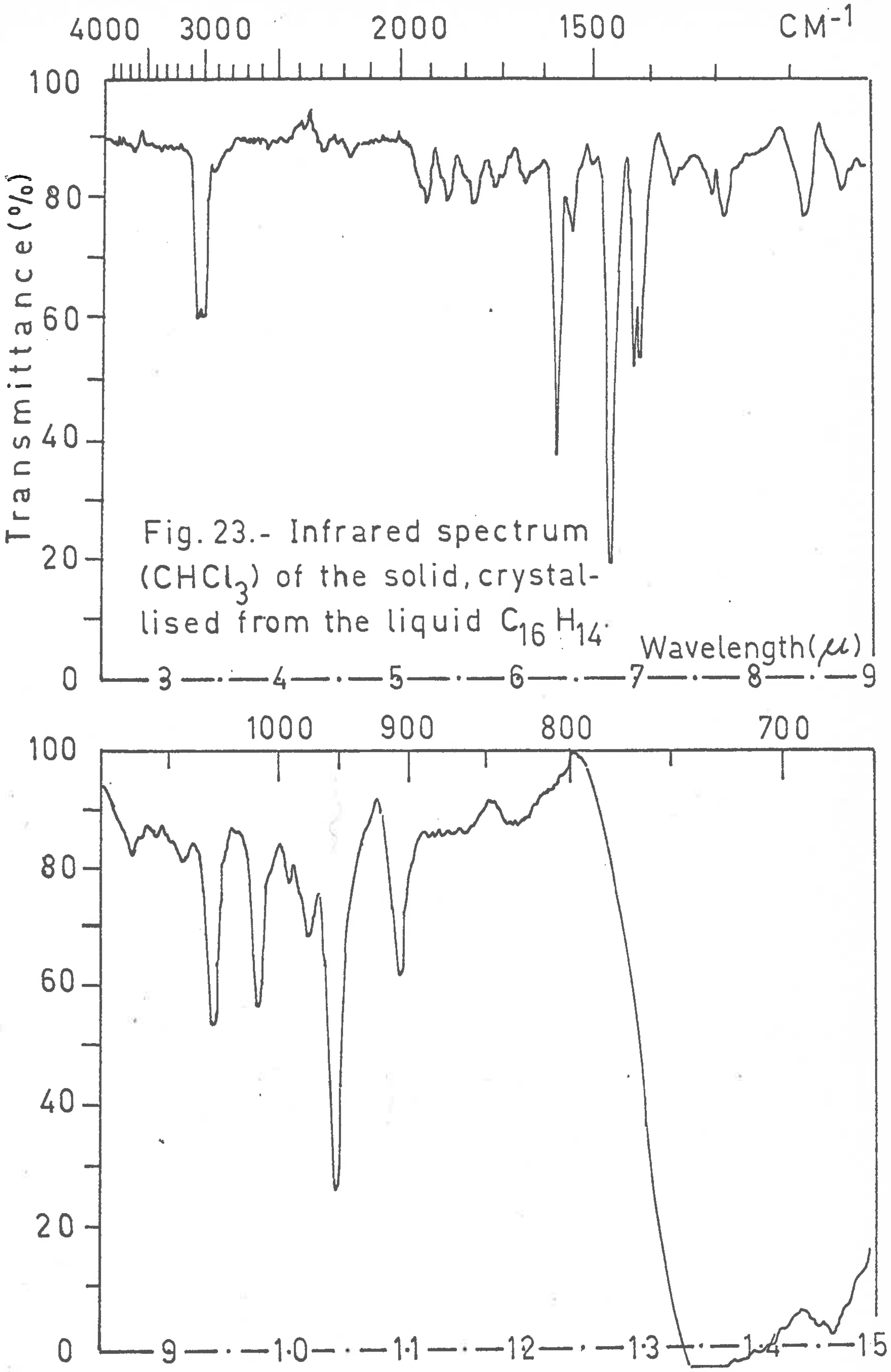


Fig. 23.- Infrared spectrum ($CHCl_3$) of the solid, crystallised from the liquid $C_{16}H_{14}$.

indicator. The volume required for the solution of sodium thiosulphate (30.95 c.c.) showed that its concentration was 0.03231 N.

The liquid $C_{16}H_{14}$ (23.1 mg.) was dissolved in cold dry ether (15 c.c.) at -10°. An excess of monoperphthalic acid (3 c.c.; 0.00065 g.eq.) previously cooled to -10° was added to the ethereal solution. The mixture was allowed to stand in a refrigerator, for five days and then made up to 25 c.c. with cold ether. An aliquot (1/5) was treated with potassium iodide solution (20%, 2 c.c.) and allowed to stand for 10 min. After acidification with dil. $H_2SO_4$ acid, the liberated iodine was titrated with a sodium thiosulphate solution (second preparation 0.03249 N., 4 c.c.). This accounts for 0.00065 g.eq. of the acid.

Blank titrations of the monoperphthalic acid solution (3 x 5 c.c.) were run simultaneously with the standard solution of sodium thiosulphate (0.03249 N.). The average volume of the thiosulphate solution required (32.8 c.c.) revealed that the concentration of the acid was 0.2131 N.

The ethereal solution of the mixture of the monoperphthalic acid and the liquid $C_{16}H_{14}$ was, therefore, left at room temperature for a further 12 hr., and for 60 hr. Examination of aliquots after each time by the same procedure as described above showed that no oxidation of the liquid $C_{16}H_{14}$ had taken place.

*Experiment (3).* The mixture of 2,5-diphenyl-1,4-dithiin (10 g.), toluene (500 c.c.), and W-7J Raney nickel catalyst (from 125 g. of alloy, degassing period at 100°/15 mm., 4 hr.) was refluxed for 75 hr. The catalyst was filtered off and subsequently extracted as mentioned previously. Fractional distillation of the combined filtrates and extracts gave a fraction boiling below 110° (38.75 g.) and another fraction boiling at 110° (*ca.* 1000 g.); these were examined by gas-liquid chromatography. The first fraction showed the presence of benzene (8.1 g., retention time 1.75 min.) and toluene (retention time 2.9 min.), but the second fraction showed the presence of toluene only. The dark brown residue (5.6 g.) was chromatographed on a column of activated alumina (150 g.) in light-petroleum (b.p. 53-66°). Elution with the same solvent gave:

(*a*) a colourless waxy solid m.p. 59-60° after recrystallisation from ethanol, (0.54 g.) which was identical with the "polymethylene" previously mentioned;

(*b*) a colourless liquid (0.66 g.); and

(*c*) 2,4-diphenylthiophen as colourless plates (1.94 g.) identified as before.

Fraction (*b*) was redistilled *in vacuo* to give a colourless liquid, b.p. 140° (bath)/0.1 mm., (0.38 g.). The infrared spectrum of the liquid (film) showed bands (s = strong, m = medium, w = weak) at 3030, m., (aromatic C-H); 2976, s., and 2882, s., ($CH_3$); 2817, m., (unassigned); four evenly spaced peaks between 1940-1730 (absorption patterns typical of monosubstituted aromatic), 1681, w., (unassigned); 1656, w., (double bond); 1595 (benzene); 1486 (benzene), 1445 (benzene), 1372 (trisubstituted ethylene); 1259 (unassigned), 1196 (unassigned); 1064 (benzene); 1024 (benzene); 965.4, m., (unassigned), 924.1, m., (unassigned), 909.1 (double bond); 823.4, w., (trisubstituted ethylene); and strong bands at 699.5,687.3, and 769.2 $cm^{-1}$ (monosubstituted benzene). This was not identical with that of the liquid product $C_{16}H_{14}$ obtained in the previous experiment. Addition of tetranitromethane to the compound gave an intense yellow colour as a confirmatory test for the presence of unsaturation.

Found: C, 92.55; H, 7.4.

$C_{16}H_{16}$ requires: C, 92.3; H, 7.7%

The total yield of the liquid $C_{16}H_{16}$ was 6.51%, and of 2,4-diphenylthiophen was 22.02%.

Microhydrogenation of the liquid $C_{16}H_{16}$. The liquid $C_{16}H_{16}$ (24.7 mg.) was introduced into the suspension of palladium-charcoal catalyst (4.0mg.) in ethanol (9 c.c.) which had been initially saturated with hydrogen at room temperature and pressure (17°, 761 mm.). The system was shaken for 3½ hr. The hydrogen was rapidly taken up in the first 15 min. (2.75 c.c., 96.8% of the theoretical amount for one double bond) after which no more hydrogen

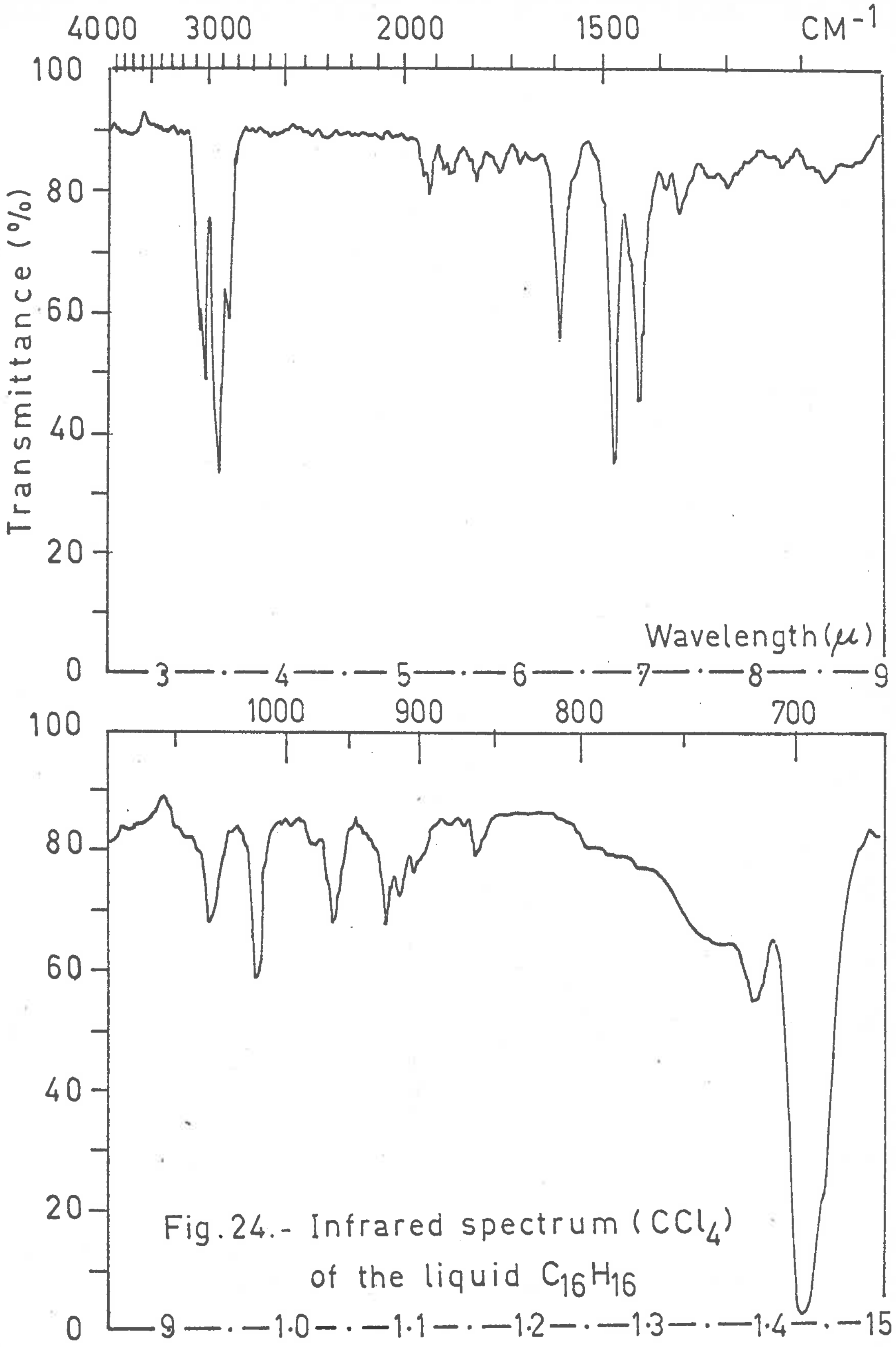


Fig. 24.- Infrared spectrum ($CCl_4$) of the liquid $C_{16}H_{16}$

was absorbed. The catalyst was collected and washed with hot ethanol (2 x 10 c.c.). The filtrate was evaporated to a small volume and carbon tetrachloride (spectroscopically pure, ca. 40 c.c.) added. Traces of water and ethanol were then removed by azeotropic distillation with carbon tetrachloride, and the residue concentrated (to ca. 1 c.c.). Examination of the infrared spectrum of the product showed that it was identical with that of 1,3-diphenylbutane in every respect.

### Periodate - permanganate oxidation of the liquid $C_{16}H_{16}$.

This was adapted from the procedure described by Lemieux and Rudloff.[96] All chemical reagents used were of Analar grade (B.D.H.). Solvents were further purified by standard methods. Evaporation of solvents was accomplished using a stream of nitrogen.

The liquid $C_{16}H_{16}$ (96.088 mg., 0.5 mM) in dioxane (100 c.c.) was added to a mixture of sodium meta periodate (834.21 mg., 3.9 mM) and an aqueous solution of potassium permanganate (1 c.c., 0.1 M) then allowed to stand at room temperature for 2 days. The reaction was stopped by adding with cooling a solution of sulphuric acid (10 c.c., 10%) and enough sodium bisulphite to reduce all periodate, iodate and iodine, to iodide. The reaction mixture, after addition of three times its volume of distilled water, was extracted, continuously with ether for 3 days. The ethereal extract was carefully evaporated to a small volume, then washed thoroughly with a saturated solution of sodium bicarbonate (3 x 25 c.c.). The combined washings, after acidification (10% hydrochloric acid), was again extracted continuously with ether for 3 days. Both acid and neutral fractions were worked up as usual to give respectively:

(a) a black residue (118.3 mg.); and

(b) a yellow wax (146.8 mg.).

The residue (a) was spotted on paper (Whatman No. I) and developed by descent using the n-butanol-ammonia (15 N), (1:1, v/v) as solvent. Spraying with universal indicator showed a spot at $R_f$ 0.36 corresponding to phenylacetic acid (run on the same chromatogram). Further paper chromatography of the residue in n-butanol-ammonium carbonate buffer, using methyl red as indicator, also gave a spot ($R_f$ = 0.41) corresponding to phenylacetic acid.

The 2,4-dinitrophenylhydrazone [from 100 mg. of fraction (b)] in chloroform (25 c.c.) was run onto the top of a column of bentonite (B.D.H., 14 g.) and kieselguhr (acid-washed, B.D.H., 4 g.), prepared according to the procedure of Elvidge and Whalley.[121] As the chromatogram developed, an orange-yellow band appeared, and unchanged reagent remained firmly adsorbed on the top of the column. No further bands were observed on further elution with ethanol-chloroform (250 c.c.; 1:19, v/v). Two fractions were collected as follows:

(i) orange solid, m.p. 234-236° (60.6 mg.); and

(ii) orange solid, m.p. 236-237° (77.2 mg.).

The mixed m.p. of both fractions showed no depression. This compound was identified as the 2,4-dinitrophenylhydrazone of acetophenone by mixed m.p. and identity of their infrared spectra with that of an authentic specimen.

Experiment (4) The mixture of 2,5-diphenyl-1,4-dithiin (11 g), toluene (550 c.c.) and W-7J Raney nickel catalyst (from 125 g. of alloy), degassing period $7\frac{1}{2}$ hours) was refluxed for 3 days. Working up as above gave:

(a) benzene (9.1 g.);

(b) "polymethylene" (0.15 g.);

(c) a colourless liquid (1.09 g.); and

(d) 2,4-diphenylthiophen as colourless plates (2.53 g.).

All known products were detected, (a); or isolated, (b) and (d); as previously described. A colourless liquid, (c), boiled at 90-91°/0.02 mm. The infrared and ultraviolet spectra of the liquid were found to be identical in all respects with those of the liquid $C_{16}H_{14}$, obtained in the first two experiments.

Found: C, 92.8; H, 7.2.

$C_{16}H_{14}$ requires: C, 93.2; H, 6.8%.

The liquid was examined by gas-liquid chromatography on a 6 ft. column packed with Celite (62-80 mesh; coated with 15% Apiezon L) at 240°, inlet pressure 37, outlet pressure 5.5 mm., and with nitrogen flow of 1.1 l./hr. Three different peaks at the retention times of 6.4, 11.1, and 18.05 min. respectively were observed.

Attempted microhydrogenation of the liquid $C_{16}H_{14}$. Four different kinds of catalyst were used to effect hydrogenation of the liquid $C_{16}H_{14}$. Unless otherwise stated, the hydrogenations were carried out in a Towers microhydrogenator at atmospheric temperature and pressure in ethanol (volume of mixture made up to 10 c.c.) while the flasks were being shaken at 315 ± 35 vibrations per min. The system was degassed and filled with hydrogen 6 times, and the catalyst was saturated with hydrogen (30 min.), then equilibrated before the substrate was introduced. After completion of a run, the catalyst was collected and washed thoroughly with the same solvent (hot). The combined filtrate and washings were evaporated on a boiling water bath and carbon tetrachloride (*ca.* 50 c.c.) added to the residue. Traces of water and ethanol (or acetic acid) were removed by azeotropic distillation with carbon tetrachloride until the residue was concentrated to *ca.* 1 c.c., then taken up for infrared spectroscopic examination. All distillations were carried out under nitrogen, but even so, most of the residues obtained were yellow.

The infrared spectrum of the residue, obtained from experiment No. 1 (see Table 3) was found to be superimposable with that of the starting material. This confirmed that, using platinum-charcoal as catalyst, no hydrogenation had occurred. The infrared spectrum of the residue of experiment No. 2 showed peaks at 2886, s., (C-H); 2813, m., (unassigned); 1733, w., ($C = O$);

1698, m., (C=O); 1449, m., ($-CH_2-$); 1370, w., ($C-CH_3$), 1312, w., (unassigned); 1282, m., (alkyl ketone ?); 1028 and 934.6, v.w., (cyclohexane); and 711.9 $cm^{-1}$ (unassigned). The residue from experiment No. 4 absorbed at 3067, sh., (unassigned), 3030, m., (aromatic CH); 2924, v.s., and 2849, s., ($-CH_2-$); 1934, w. and split, 1706, w., 1786, w., 1733, m., and 1706, m. and split, and a strong band at 699.3 (absorption patterns typical of monosubstituted aromatic); 1606, m., (benzene); 1493, m., (benzene); 1456, sh., ($-CH_2-$); 1449 (benzene); 1370, w., (unassigned); 1258, m., (unassigned); two broad peaks at 1093 and 1029, each with split, (benzene); 903.0, w., ($-CH_2-$ in cyclobutane ?)[91] and a broad peak at 816.5 $cm^{-1}$ (unassigned).

### Attempted preparation of the osmic ester of the liquid $C_{16}H_{14}$.

Chloroform was purified by stirring with concentrated sulphuric acid in a separating funnel for 20 min. (twice) followed by washing with distilled water, a dilute solution of sodium hydroxide and then with several changes of distilled water. The dried chloroform (anhydrous calcium chloride) was distilled through a jacketed column (as described on page 172, reflux ratio 15:1) and the distillate (fraction b.p. 61-62°, stored in a filled brown bottle) was used for the preparation of the standard solution and the reaction mixture within 24 hr. Pyridine was purified by refluxing with potassium permanganate for 6 hr. followed by distillation over potassium

## TABLE 6

### Microhydrogenation of the liquid $C_{16}H_{14}$ from the fourth experiment.

| No. | Wt. of the substrate (mg.) | Catalyst | Wt. of the catalyst (mg.) | Solvent | Temp. and Press. (°C, mm.) | Time (hr.) | Vol. of hydrogen absorbed (c.c.) | Vol., theoretically absorbed, of hydrogen | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | 1 d.b. | 2 d.b. |
| 1 | 11.0 | Pt/C | 5.8 | Ethanol | 16°/755 | $3^1/_3$ | - | 1.27 | 2.54 |
| 2 | 28.8 | $PtO_2$ | 17.0 | Acetic acid[a] | 18°/750 | $3\frac{1}{2}$ | 25.33[b] | 3.38 | 6.76 |
| 3[c] | 10.0 | $PtO_2/Pt$ | - | Acetic acid | 0°/760 | - | 8.141 | 1.087 | 2.175 |
| 4 | 19.65 | Pd/C | 5.2 | Ethanol | 16°/764 | $1\frac{1}{2}$ | 1.65 | 2.24 | 4.49 |

[a] Glacial acetic acid (B.D.H., Analar) was further purified by refluxing over ferrous sulphate crystals for 2 hr. and then redistilled.

[b] After ca. 5 c.c. of hydrogen was consumed each time, shaking of the flasks was stopped; more hydrogen from the cylinder was added and the system readjusted as quickly as possible. Reactions were continued until no more hydrogen was absorbed.

[c] This was performed by the Australian Microanalytical Service, C.S.I.R.O., Melbourne.

hydroxide pellets. Pure benzene was obtained commercially (Fluka) and was further redistilled and sodium-dried.

A standard solution was prepared by dissolving osmium tetroxide (B.D.H., 1 g. ampule) in pure benzene at 23° (volume making up to 25 c.c.). The solution was kept in a well-stoppered dark brown bottle wrapped with photographic paper.

The hydrocarbon-osmium tetroxide-pyridine complex (from 20.4 mg. of the liquid $C_{16}H_{14}$, 31.27 mg. of pyridine, 1.235 c.c. of the standard solution) was prepared according to the procedure described by Cook and Schoental.[122] The mixture became red-brown in colour in *ca.* 1 min. and slowly deposited a jelly-like mass. After standing for a further 1 hr. at room temperature the clear solution deposited no more precipitate. However the reaction mixture, on standing overnight in the dark, reverted to a suspension, from which the precipitate could not be separated by filtration. The osmic ester complex was collected by centrifugation and the clear solution was decanted. The centrifugate was added with pure benzene (3 x 3 c.c.) followed by stirring, centrifuging and decanting respectively. The brown-grey precipitate was dried in a vacuum over phosphorus pentoxide for 6 hr. and amounted to 100.5 mg. (98.72%). Attempts to recrystallise the complex from benzene, chloroform-pyridine (10:1, v/v) and light-petroleum (b.p. 50-56°) were unsuccessful.

Found: C, 49.9;* H, 3.4.

$C_{16}H_{14}.2OsO_4.4Py.$ requires: C, 41.9; H, 3.3.

$C_{16}H_{14}.OsO_4.2Py.$ requires: C, 50.6; H, 3.9%.

( * unreliable value due to the interference of osmium oxides in the absorption tube).

Attempted preparation of the osmic ester of an authentic stilbene.

Stilbene was obtained commerically (Fluka) and further purified by recrystallisation from ethanol. The plates m.p. 124° were used. The solvents and reagents were also purified as described above.

A solution of the purified hydrocarbon (20 mg.) in benzene (0.2 c.c.) was treated with the standard solution of osmium tetroxide in benzene (0.705 c.c., 1 g./25 c.c. concentration) and pyridine (17.554 g.) at room temperature. The red-brown micro-crystalline complex appeared suddenly. After further standing for ½ hr., the decanted clear solution deposited no more precipitate. The crystals (64.8 mg., 98.63%) were collected by centrifugation and purified as above. Attempts to recrystallise the complex by dissolving in chloroform-pyridine (25:1, v/v) followed by concentration on a hot plate, and addition of light-petroleum (b.p. 50-56°), were unsuccessful.

Found: $C$, 62.7;* $H$, 4.3.

$C$, 62.3;* $H$, 4.3.

$C_{14}H_{12}.OsO_4.2Py$. requires: $C$, 48.6; $H$, 3.7%.

(* unreliable value due to the interference of osmium oxide in the absorption tube).

In this experiment, the total yield of the liquid $C_{16}H_{14}$ was 12.38%, and of 2,4-diphenylthiophen was 26.11%.

Experiment (5). The 2,5-diphenyl-1,4-dithiin (60 g.) in toluene (3 l.) was introduced into the W-7J Raney nickel catalyst (prepared from 625 g. of alloy, degassing time 16 hr.) and the mixture refluxed for 4 days. Working up as previously described gave:

(a) benzene (yield not determined) identified by gas-liquid chromatography (based on retention time only);

(b) "polymethylene" (1.37 g.), identified as above;

(c) a yellowish liquid (4.85 g.);

(d) 2,4-diphenylthiophen as colourless plates, m.p. 122-123° (10.16 g.), identified as above; and

(e) a considerable amount of tarry residue (not eluted from the chromatography column).

The colourless liquid of (c), (4.5 g.) which gave a negative test for sulphur; after one distillation to remove a coloured solid residue, it was subjected to a Megachrom separation using helium as carrier gas, an inlet pressure of 8 lb. and an outlet pressure of 2 lb. The following products were obtained at 240° (yields and retention times in parentheses): trap 1, a trace of a colourless liquid (6 mg., 16 min.); trap 3, a colourless liquid with a trace of yellow impurity (476.8 mg., 20.5 min.); trap 5, colourless flat needles (476.9 mg., 32.15 min.), m.p. 61-62° after recrystallisation from light-petroleum (b.p. 30-45°); trap 7, a yellowish liquid (371.2 mg., 40.5 min.). All the liquid products were further purified by molecular distillation (three times) and colourless liquids were obtained in every case.

The infrared spectrum of the liquid from trap 1 (film) showed bands at: 3077 (unassigned), 3030 (aromatic C-H), 2941 (C-H), 2857 (C-H), 4 peaks between 1931-1739 and strong bands at 737.4 and 696.9 (absorption patterns typical of monosubstituted aromatic), 1600 (benzene), 1490 (benzene), 1447 (benzene), 1073 (benzene), 1029 (benzene), 745.2 (unassigned), and 786.8 cm$^{-1}$ (C=C ?). No further information could be drawn from this spectrum (all bands were relatively week), and no further investigation was attempted.

The infrared spectrum of the liquid from trap 3 (film) showed bands at: 3040, s., ($CH=CH_2$); 3012, s., (splitting of the former band); 2899, w., (C-H); 2883, sh., (unassigned), four evenly spaced peaks, each with a splitting, between 1949-1751 and bands at 7519, v.s., and 698.3, v.s., (monosubstituted aromatics); 1686, w., (C = C ?); 1600, m., (benzene); 1575, w., (benzene); 1493, s., (benzene); 1445, s., (benzene); 1406, m., ($R_1CH=CHR_2$); 1325, w., (*cis* - CH = CH ?); 1181, m., (unassigned); 1153, m., (unassigned); 1073, s., (monosubstituted aromatic); 1029, s., (monosubstituted aromatic); 990.1, w., (unassigned); 980.4, w., (unassigned); 963.6, w., (unassigned); 923.2, s., (unassigned); 862.1, m., (unassigned) and bands at 843.1, w., 805.2, m., 780.0, m., 723.5 $cm^{-1}$ (all unassigned). The liquid, after standing at room temperature under nitrogen and in the absence of light for 1 week, was found to give the same infrared spectrum. The ultraviolet spectrum showed a broad absorption curve with $\lambda_{\text{min.}}$ 244 ($\epsilon$ 5376.28), $\lambda_{\text{max.}}$ 223 ($\epsilon$ 17439.77) and 276 m$\mu$ ($\epsilon$ 9207.57). The molecular weight (calc. for $C_{16}H_{14}$, 206.27) was 179, determined by the Rast method. The liquid was exposed to ordinary daylight for 3 days, and partially crystallised to give colourless needles (3.0 mg.), m.p. 123-124° after recrystallisation from carbon tetrachloride. The ultraviolet spectrum of the needles in ethanol, after having been left for several days, showed $\lambda_{\text{max.}}$ ($\epsilon$ not determined) 229.17; 296.66, 309.17, with a shoulder at 235.83, 320 and $\lambda_{\text{min.}}$ 243.3 m$\mu$. Both the liquid and solid product gave an intense yellow colour with tetranitromethane.

TABLE 7

Proton magnetic resonance spectrum of the liquid (trap 3)

| Shift c/s | $\tau$ p.p.m. | Appearance | Proton count | Assignment |
|---|---|---|---|---|
| 392.86 | 3.45 | singlet | 2 | olefinic |

| | | | | |
|---|---|---|---|---|
| 417.86 | 3.04 | complex | 12 | olefinic + aromatic |
| 420.536 | 2.99 | | | |
| 427.68 | 2.87* | | | |
| 433.94 | 2.77 | | | |

*main peak

Microhydrogenation of the liquid product (trap 3). The liquid (17.47 mg.) was hydrogenated in a Towers microhydrogenator, using palladium-charcoal catalyst (5.5 mg.) in ethanol (10 c.c.) and the product was worked up as described previously. The hydrogen was rapidly taken up in the first hour (1.86 c.c. at 23°, 765 mm., 102.94% of the theoretical amount for 1 double bond) after which no absorption was observed for 1½ hr. The infrared spectrum of the hydrogenation product (carbon tetrachloride) showed bands at 3058, m., (unassigned); 3030, s., (aromatic C-H); 2924, s., (-$CH_2$-); 2857, m., (-$CH_2$-); four evenly spaced peaks, each with splitting, between 1916-1706 and band at 699.3, s., with a shoulder at 719.4 (absorption patterns typical of monosubstituted aromatic); 1595, s., (benzene); 1488, s., (benzene); 1443, s., (benzene); 1060, m., (monosubstituted aromatic); 1029, m., (monosubstituted aromatic); 904.6, w., (unassigned).

The infrared spectrum of the needles from trap 5 (carbon tetrachloride) showed bands at 3040, s., (-CH=CH-); 3030, s., (aromatic C-H); 2899, s., (C-H); 2833, m., (unassigned); four evenly spaced peaks, each with splitting, between 1938-1742 and strong peaks at 1068, 1026, 698 respectively (monosubstituted aromatic); 1664, m., (terminal double bond ?); 1603, 1493, 1441 all strong peaks (benzene); 1300, m., ($R_1R_2C=CH_2$); 1172, 1152, 1096 all weak bands (monosubstituted aromatic); 1364, 1269, 1233 all weak bands (unassigned); and a strong peak at 913.8 cm$^{-1}$ together with a weak peak at 988.3 cm$^{-1}$ ($\geq C=CH_2$). The ultraviolet spectrum of the compound showed $\lambda_{max.}$ ($\epsilon$ in parentheses) at 212 (21120.42), 215 (22074.53), 221 (20122.95), 264-266 (25153.68), 279.5 (35523.79), 288 (24156.21), 296.5 (30357.89) with shoulder at 272-274 (25587.37) and $\lambda_{min.}$ at 242 m$\mu$ (8760.42). Addition of tetranitromethane to the needles gave an intense yellow colour. The colourless needles gradually turned pale pink on standing at room temperature for 1 week. The molecular weight (calc. for $C_{16}H_{14}$, 206.27) was 156, determined by the Rast method.

TABLE 8

Proton magnetic resonance spectrum of the solid (needles)(trap 5)

| Shift c/s | $\tau$ p.p.m. | Appearance | Proton Count | Assignment |
|---|---|---|---|---|
| 434.13 | 2.765 | | | |
| 436.90 | 2.72 | | | |
| 440.59 | 2.66 * | | | |

| | | | |
|---|---|---|---|
| 442.43 | 2.63 | complex | olefinic + aromatic |
| 445.20 | 2.57 | | |
| 447.97 | 2.53 | | |
| 451.66 | 2.47 | | |
| 455.35 | 2.41 | | |

* main peak

<u>Attempted addition of maleic anhydride to the solid from trap 5.</u> A solution of the solid (10.4 mg.) in benzene (0.5 c.c.) and freshly sublimed maleic anhydride (5.0 mg.) was refluxed for 12 hr. The solvent was removed under reduced pressure and the starting material recovered (m.p. and mixed m.p.). Further attempts tbe prepare the maleic anhydride adduct of this compound, using xylene as solvent, and without solvent (same scale) were unsuccessful.

<u>Microhydrogenation of the solid product (trap 5).</u> The solid (18.4 mg.) in ethanol (10 c.c.) was hydrogenated in the presence of palladium charcoal catalyst (6.0 mg.), using a Towers micro-hydrogenator, and the product worked up, as described above. The compound took up hydrogen rapidly in the first 10 min. (5.15 c.c., at $23^{\circ}$, 763 mm.; 119.21% of the theoretical amount required for 2 double bonds). Since the quantity available of the purified solid product was too small, further investigation on hydrogenation could not be attempted. The infrared spectrum of the hydrogenation product, however, was identical in every respect with that of the hydrogenation product of the liquid from the trap 3.

The infrared spectrum (film) of the liquid from the trap 7 showed bands at: 3049, s., (C=C ?); 3030, s., (aromatic C-H); 2924, s., and 2857, m., ($-CH_2-$); four evenly spaced peaks between 1923-1724, each with splitting (absorption patterns typical of monosubstituted aromatic); 1645, m., (double bond); 1600, s., (benzene); 1580, sh., (double-bond conjugation with aromatic ring); 1493, s., (benzene); 1447, s., (benzene; 1429, m., ( $>C=CH-$); 1314, w., (unassigned); 1236, w., (unassigned); three peaks between 1235-1176, w., (unassigned); 1151, w., (monosubstituted aromatic); 1070, m., (monosubstituted aromatic); 1029, s., (benzene); 963.6, s., (<u>trans</u>-double bond ?); 838, w., ($R_1R_2C=CHR_3$); 910.1, w., (unassigned); and 719.4, s., together with 694.4 $cm^{-1}$, s., (monosubstituted aromatic). The ultraviolet spectrum of the fraction showed a broad absorption peak with $\lambda_{max.}$ mμ ($\epsilon$ in parentheses) at 253 (10396.56) and shoulders at 263 (7692.81), 270 (4538.44), 283 (1957.0); with a peak at 293 (1567.87) and $\lambda_{min.}$ at 225 (4725.12). The molecular weight (calc. for $C_{16}H_{14}$ 206.27) was 195, determined by the Rast method. Addition of tetranitromethane to the liquid gave an intense yellow colour. The liquid was allowed to stand under nitrogen in the absence of light for one week and was found to be unchanged (infrared spectrum); but on exposure to ordinary daylight for 12 hr. the liquid partially crystallised to give colourless needles. The crystals (8.0 mg.) were collected and washed with light petroleum (redistilled, b.p. 30-45°). The dry needles, m.p. 123-124°, did not depress when mixed with the needles obtained from the liquid of trap 3. Their ultraviolet spectra were identical. The needles sublimed at 110-120°/5 mm. to give colourless plates, m.p. 152.5-153°. This was identified as *trans,trans*-1,4-diphenylbuta-1,3-diene by melting point, mixed melting point, and by comparison of its ultraviolet spectrum with that of an authentic specimen. The infrared spectrum of the needles (m.p. 123-124°) was almost the same as that of *trans,trans*-1,4-diphenylbuta1,3-diene, except in the 11-12 $\mu$ region. The compound gave a strong absorption band at 962.6 and medium absorption at 987.4 together with a weak absorption at 905.2 whereas the authentic *trans,trans*-1,4-diphenylbuta1,3-diene gave a strong band at 990.1 with a shoulder at 980 and a weak absorption band at 910.2 cm$^{-1}$ respectively. The needles (0.39 mg.) were dissolved in 97% ethanol (to make up 50 c.c.) and allowed to stand in sunlight for 6 hr. The ultraviolet spectrum of the solution showed bands at ($\epsilon$ in parentheses) $\lambda_{max.}$ 225 (8504.08), 267 (4701.02), 281 (7401.02) and a shoulder at 292 ($\epsilon$ not determined), with a $\lambda_{min.}$ at 244 m$\mu$ (3142.81). The same solution after allowing to stand in diffuse daylight for 1 week exhibited absorption bands at $\lambda_{max.}$ 228 (8055.1), 297 (11409.21), 309 (10247.16) with shoulders at 235 ($\epsilon$ not determined), 290 (10511.26), 320 (6153.58) and a $\lambda_{min.}$ 244 m$\mu$ (4621.78). On leaving in the absence of light for 1½ months, the ultraviolet spectrum (of the original needles) was essentially unchanged ($\lambda_{max.}$ 228.3, 296.6, 309.2, with shoulders at 236.2, 280, 320 and $\lambda_{min.}$ 243.3 mμ), and its melting point (123-124°) remained constant.

Microhydrogenation of the liquid from trap 7. The liquid (9.17 mg.) was hydrogenated and the product worked up as previously described, using palladium charcoal catalyst (5.35 mg.) and ethanol (9 c.c.) as solvent. The hydrogen was taken up steadily in the first 33 min. (0.99 c.c.) then slowly for a further 15 min. (0.07 c.c., at 23.5°, 758 mm.) after which no absorption was observed for 2 hr. This was 99.98% of the theoretical amount required for 1 double bond. The infrared spectrum of the product (yellowish) in carbon tetrachloride showed bands at 3049, m., (unassigned); 3030, m., (aromatic C-H); 2924, s., and 2849, s., ($CH_2$); four peaks between 1942-1757 (absorption pattern typical of monosubstituted aromatic) the last of which was a little stronger than usual at the region 1727 (combined with CO) and split; 1600, m., (benzene); 1493, s., (benzene); 1449, s., (benzene); 1374, w., (unassigned); 1261, s., (unassigned); broad peaks at 1096 and 1030 (monosubstituted aromatic); 909.1, w., (substituted cyclobutane); 867.3, w., (unassigned); 814.6, w., (unassigned); 719.4 and 700.4, s., (monosubstituted aromatic).

*Attempted microhydrogenation of authentic trans,trans-1,4-diphenylbuta-1,3-diene.* The diphenylbutadiene (17.49 mg.) was hydrogenated, using palladium-charcoal catalyst (6.8 mg.) in ethanol (10 c.c.), and the product worked up in the same manner as previously mentioned. The compound took up hydrogen smoothly during the first 10 min. (3.71 c.c. at 25.8°, 765 mm.) then slowly for a further 30 min. (0.35 c.c.) after which no more hydrogen was absorbed (1½ hr. observation). This was 99.27% of the theoretical amount required for the hydrogenation of two double bonds. The infrared spectrum of the product (colourless) in carbon tetrachloride was identical in every respect with the reported for 1,4-diphenylbutane.[123]

In this experiment, the total yield of the liquid compound was 10.52% (based on the formula $C_{16}H_{14}$ only), and of 2,4-diphenylthiophen was 19.23%.

## TABLE 9

### Proton magnetic resonance spectrum of the liquid (trap 7)

| Shift c.p.s. | τ p.p.m. | Splitting c.p.s. | Appearance | Proton Count | Assignment |
|---|---|---|---|---|---|
| 90.339 | 8.49 | 2.8 | complex | 1 | $H_C$ |
| 93.113 | 8.45 | | | | |
| 96.810 | 8.39 * | | | | |
| 99.584 | 8.34 | 4.4 | | | |
| 104.0265 | 8.26 | | | | |

| | | | | | | |
|---|---|---|---|---|---|---|
| 147.658 | 7.54 | | | complex | 1 | $H_D$ |
| 155.424 | 7.41* | 2.4 | | | | |
| 157.8275 | 7.37 | | | | | |
| 160.601 | 7.32* | | | | | |
| 204.867 | 6.585* | 2.4 | 5.0 | triplet | 1 | $H_B$ |
| 207.2616 | 6.55 | | | | | |
| 209.8404 | 6.50* | | | | | |
| 377.430 | 3.71 | | | doublet | 1 | $H_A$ |
| 428.17 | 2.86 | | | doublet | 10 | aromatic |

* main peak

<u>Attempted reaction of styrene and W-7J Raney nickel catalyst.</u> The mixture of redistilled styrene (25 g.), toluene (500 c.c.), and W-7J Raney nickel catalyst (from 125 g. of alloy) was refluxed under the atmosphere of nitrogen and in the absence of light for 18 hr. The catalyst was separated on Celite, washed with toluene and then extracted (Soxhlet) with the same solvent overnight. Fractional distillation of the combined filtrates and extracts under nitrogen gave:

(a) a colourless liquid, b.p. 108-110° (25.3 g.)

(b) a colourless liquid, b.p. 110-110.5° (430 g.)

(c) a viscous brown residue (*ca.* 100 c.c.).

Examination of the fraction (a) (dried over potassium hydroxide pellets) by gas chromatography at 104° showed peaks corresponding to toluene and benzene, while fraction (b) exhibited a peak corresponding to toluene only. Fraction (c) was redistilled to give

(i) a colourless liquid, b.p. 112-115° (39.2 g.);

(ii) a colourless liquid, b.p. 39°/80 mm. (21.9 g.);

(iii) a colourless liquid, b.p. 62°/78 mm. (2.4 g.).

Fraction (i) and (ii) showed three peaks (gas-chromatography at 104°) corresponding to toluene (retention time 3.1 min.), ethylbenzene (retention time 6.0 min.), and styrene (retention time 8.4 min.) respectively. The residue (60.7 g.) was identified as polystyrene by comparison of its infrared spectrum with that of an authentic specimen.

Attempted reaction of phenylacetylene and W-7J Raney nickel catalyst. The mixture of redistilled phenylacetylene (20 g.), toluene (400 c.c.) and the W-7J Raney nickel catalyst (from 125 g. of alloy) was refluxed under nitrogen and in the absence of light for 40 hr. Working up as above gave:

(a) a colourless liquid, b.p. 108-110° (57.3 g.);

this was dried over potassium hydroxide pellets;

(b) a colourless liquid, b.p. 110° (453 g.);

(c) a viscous brown residue (89.2 g.).

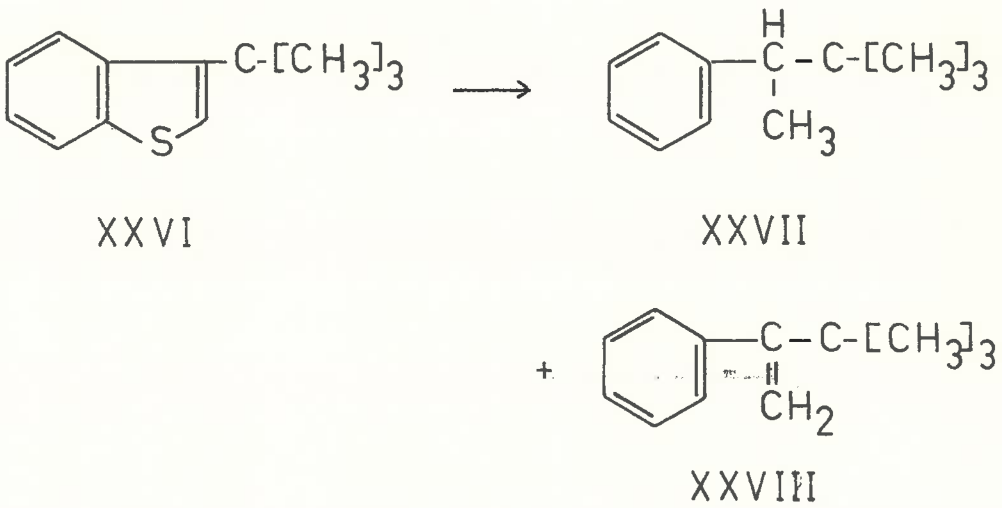
Fraction (a) and (b) were examined by gas chromatography at 100°. Both fractions showed peaks corresponding to benzene (retention time 3.5 min.) and toluene (retention time 6.4 min.). No other products were detected.

Redistillation of the residue at 200° (bath)/0.5 min. resulted in sudden formation to the solid mass of the residue and no liquid was distilled over except small amounts of colourless crystals sublimed through the condenser and then disappeared. The infrared spectrum of the residue (nujol mull) was identical with that of a polystyrene (Perkin-Elmer). The brown solid was not further investigated.

## (c) DESULPHURISATION OF BENZO[b]THIOPHEN-3-CARBOXYLIC ACID-1,1-DIOXIDE

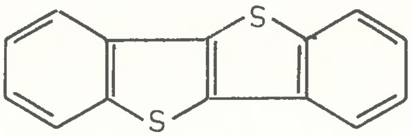
### INTRODUCTION

It has been reported, in 1956 by Corson, Tiefenthal, Atwood, Heintzelman, and Reilly,[3] that the desulphurisation of 3-t-butylbenzo[b]thiophen (XXXVI) gave rise to the expected hydrocarbon (XXXVII) together with about 10% of the corresponding olefin (XXXVIII). The latter, although, was not isolated and the presence of the compound was inferred only by its infrared spectrum, the finding is still of considerable interest. This suggests that the desulphurisation reaction may be employed as a possible synthetic route to lead to many relatively inaccessible unsaturated compounds.



The reaction also indicates that the desulphurisation of thiophens can occur without prior hydrogenation of the hetero ring as is the case with dibenzothiophen.[124]

Some years later, Badger, Kowanko, and Sasse[77] obtained similar results in the desulphurisation of thionaphtheno[3,2-b] thionaphthen (XXXIX). The compound, on desulphurisation with the W-7 Raney nickel catalyst (as well as with W-7 Raney nickel catalysts aged for 3 months and 18 months, respectively) has been shown to give bibenzyl as the only product. With poisoned and degassed Raney nickel catalysts, trans-stilbene was obtained together with bibenzyl, 2-phenylbenzo[b]thiophen, and starting material.

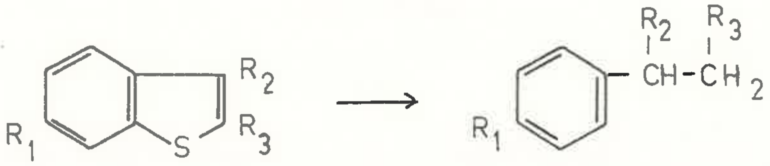


XXXIX

Although 1,2,3,4-tetraphenylcyclobutane had previously been reported[125] as one of the reactions products, these authors[77] failed to isolate it. They therefore suggested that the compound was chemisorbed on the nickel surface in a "more or less" perpendicular fashion. The reaction was then thought to proceed by removal of the sulphur to give a diradical with subsequent hydrogenation to the observed product.[77]

However, most of the sporadic examples of benzo[<u>b</u>]thiophens desulphurisation appearing in the literature have been found to give rise to the corresponding saturated sulphur-free compounds. Some of them are listed in Table 10.

TABLE 10

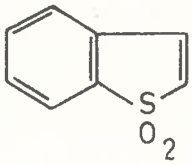


| $R_1$ | $R_2$ | $R_3$ | Yield % | Reference |
|---|---|---|---|---|
| $CH_3O$ | H | $C_6H_5$ | - | 126 |
| H | H | $4\text{-}CH_3OC_6H_4$ | - | 126 |
| H | $CH_3$ | $CO_2H$ | - | 127 |
| H | $CH_3$ | $CONH_2$ | 86 | 127 |
| H | $CO_2H$ | $CH_3$ | - | 127 |
| H | $CH_3$ | $CO.NH.CH_3$ | - | 127 |
| H | $CO.NH.CH_3$ | $CH_3$ | - | 127 |
| $CH_3O$ | H | $CO_2H$ | 97 | 128 |
| H | H | $CH(CH_3).CO_2H$ | - | 129 |

As mentioned earlier in this thesis, many observations indicate that sulphone derivatives appear to be more resistant to desulphurisation than the corresponding sulphides or sulphoxides.

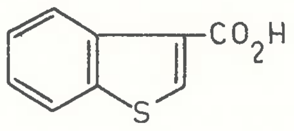
The desulphurisation of tetrahydrothiopyran sulphone[4] and limonene sulphone[130] may be cited as examples. The reaction of sulphone desulphurisation has been postulated to proceed via an ionic mechanism[2,130] and Bonner suggested initial adsorption of the sulphone group on the nickel surface through the oxygen of the sulphone function. This is followed by the interaction with an adjacent hydrogen atom causing the cleavage of the carbon-sulphur bonds thus completing the desulphurisation reaction.[2]

In this connection, it is noteworthy that Davies, Porter and Wilmshurst[131] stated that benzo[b]thiophen-1,1-dioxide (XL) resisted desulphurisation with "one specimen" of Raney nickel, but with a more reactive nickel all the sulphone was apparently reduced. Unfortunately these authors could not identify the oily products.



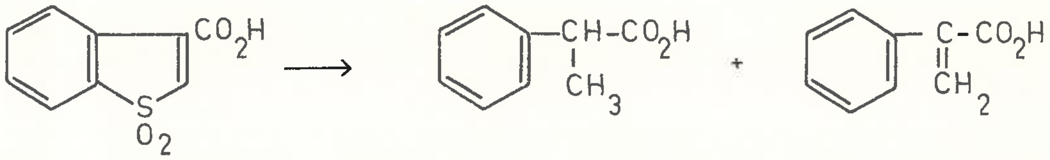
XL

Desulphurisation of benzo[b]thiophen-3-carboxylic acid (XLI),[9] and of benzo[b]thiophen-3-acetic acid,[132] however, have been reported to give hydratropic acid (93% yield) and β-phenylbutyric acid (98% yield) respectively.



XLI

It seems, therefore, of interest to investigate desulphurisation of benzo[b]thiophen-3-carboxylic acid-1,1-dioxide (XLII). Firstly, if the reaction could give rise to the corresponding unsaturated sulphur-free acid (atropic acid in this case) (XLIII) it would open up a new synthesis not only for atropic acid but possibly also for other aryl derivatives of olefinic carboxylic acids. Furthermore, it may be expected that identification of the product derived from these reactions might shed some light on the mechanism of the desulphurisation of sulphones.



XLII

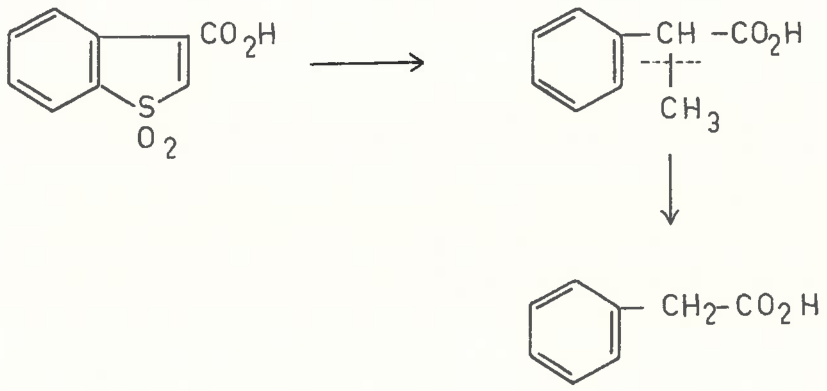
XLIII

## RESULTS AND DISCUSSION

A comparative study of the desulphurisation of diphenyl sulphide, diphenyl sulphoxide, and diphenylsulphone, which was undertaken in the present work, showed that the sulphone is most resistant to the desulphurisation. These reactions were carried out under identical conditions (e.g. scale, temperature, and time of reaction) and the products were worked up in the same way. The catalysts used were prepared simultaneously but separately from alloy obtained from the same container. The recovery of the starting material from the desulphurisations of the sulphides, sulphoxide, and sulphone were 60.75, 64.75, and 93.00% while the yields of benzene as determined by gas chromatography were 39.28, 34.68 and 4.21%, respectively. This finding is consistent with previous observations reported by other workers.[4,130]

Benzo[b]thiophen-3-carboxylic acid-1,1-dioxide, was first prepared by Crook and Davies[133] in 1937, but no yields were given. The sulphone is obtained by oxidation of the parent acid with hydrogen peroxide in acetic acid. In the present work it was found that this reaction required considerable care as on two occassions the reaction mixture decomposed explosively. When properly controlled, this compound was obtained in 56% yield (pure product).

The desulphurisation of benzo[*b*]thiophen-3-carboxylic acid-1,1-dioxide with W-7 Raney nickel gave a trace of phenylacetic acid in addition to the expected α-phenylpropionic acid (*dl*-hydratropic acid). The production of the former is believed to have arisen by the dealkylation of the latter (cf. p. 97-98). However, "polymethylene" was not detected in this desulphurisation, probably due to the small scale of the reaction.

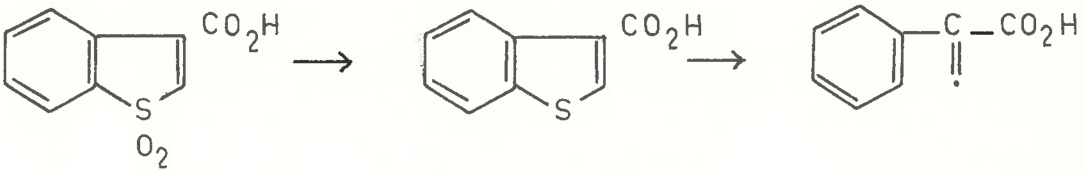


The desulphurisation of the benzo[*b*]thiophen-3-carboxylic acid-1,1-dioxide with W-7J Raney nickel gave a smaller yield of the mixture together with decomposed material which could not be identified. However, it is not likely that the decomposed products have arisen from the unsaturated α-phenylacrylic acid (atropic acid). It is known that atropic acid when heated with water dimerises to yield isatropic and diatropic acids (which are probably related to atropic acid in the same way as the truxillic acids to cinnamic acid)[134,135] but these are stable compounds.

Several attempts had been made to separate phenylacetic acid from hydratropic acid by chromatography on a column of cellulose in butanol-ammonia but these experiments were unsuccessful as was the attempt to use chromatography on ordinary papers with the same solvent system. The difficulties encountered with the paper chromatography arose from the small amount of the mixture which could be put on the papers, although a large number of papers (15 x 60 cm.) was employed in these experiments. The contamination of the separated material with n-butanol was another factor which made the purification of the compound difficult. Since complete evaporation of n-butanol under reduced pressure (rotatory evaporator) required a long period of time (18 hr. or more) and since the product which was present in trace amount mostly disappeared, the separation of butanol from the acids was effected by extraction with ether of an aqueous solution of the sodium salts of the acids. By this means, the use of preparative paper chromatography proved satisfactory but still the separated acids could not be isolated pure and could be identified only by their infrared spectra.

The use of Aller Raney cobalt[136] in the desulphurisation of the acid sulphone resulted in isolation of a mixture of five acids. The reaction was conducted under nitrogen and no decomposed material was isolated from the reaction mixture. A satisfactory separation of these acids was achieved by chromatography on a column of buffered silica gel. Besides phenylacetic acid and *dl*-hydratropic acid, the starting material and benzo[*b*]thiophen-3-carboxylic acid together with an unidentified acid were isolated from the column without any overlap. The isolation of benzo[*b*]thiophen-3-carboxylic acid is significant as it supports the assumption that adsorption of the sulphone on the surface of the catalyst occurs *via* the oxygen atoms of the sulphone function. In this particular case, cleavage of sulphur-oxygen bonds rise to the observed sulphur compound. This appears to be the first case of the removal of the oxygen atom of the sulphone group to give the corresponding sulphide. This may suggest that deoxygenation is the first step in the desulphurisation of sulphones. However this finding is not compatible with the previous postulation made by Bonner[2] who stated that sulphones are not desulphurised *via* intermediate sulphide.

The isolation of an unidentified material, m.p. 130-131°, is of interest. However several attempts to purify the compound were unsuccessful and the nature of this compound remained obscure. It was first thought that this compound could be an unsaturated dimeric material arising from the recombination of two free radicals (XLIV). Nevertheless, this was not consistent with the findings of Badger and Sasse,[1] who postulated that steric hindrance may prevent the combination of two free radicals from two molecules of 3-acetylbenzo[*b*]thiophen, for no dimeric product was observed from the desulphurisation of such compound.



The small amount of this compound available did not permit further investigation.

## EXPERIMENTAL

*General*.- Ultraviolet and infrared spectra were determined as previously described. Analyses involving gas chromatography were carried out as before (see p. 113), with inlet pressure 42.8 mm., outlet pressure 12.8 mm. and nitrogen flow of 1.2 l./hr.

*Catalysts*.- W-7 and W-7J Raney nickel catalyst were prepared by the same methods as mentioned in the previous work of this thesis (see p. 53). Raney cobalt catalyst was obtained according to the procedure of Aller,[136] using cobalt-aluminium alloy (50:50, Fluka). The catalysts were freshly prepared for every experiment. In desulphurisations of the acid both Raney nickel and Raney cobalt catalysts were washed by decantations with distilled water (ten times) and then with a sodium bicarbonate solution (ten times).

*Diphenyl Sulphide*.- This was obtained commercially (Fluka A.G. Chemische Fabrik Buchs S.G.).

*Diphenyl Sulphoxide*.- The sulphoxide was prepared by oxidation of the sulphide with hydrogen peroxide (restandardised, 282·825 g./l, M & B) in glacial acetic acid (redistilled over chromic oxide, B.D.H., Analar) at room temperature, according to the indications of Rheinboldt and Giesbrecht.[137] This was obtained as colourless needles (91.01% yield), m.p. 69-70° (lit.[137] m.p. 69.6-70.4°) after recrystallisation from light-petroleum (b.p. 50-60°) and then from ethanol.

*Diphenyl Sulphone*.- The sulphone was obtained by oxidation of the sulphide with hydrogen peroxide (100 Vol. oxygen, M & B) in glacial acetic acid (as above), according to the procedure of Mikeska, Farinacci, and Bogert.[138] The reaction, was carried out at 95° for 2½ hr. then left overnight, gave colourless prisms (90.7% yield), m.p. 123-124° (lit.[138] m.p. 124°).

*3-Bromobenzo[b]thiophen*.- A solution of bromine (121.7 g.) in chloroform (300 c.c.) was added dropwise to a stirred solution of benzo[b]thiophen (101.42 g., B.D.H.) in chloroform (300 c.c.) at room temperature according to the method of Komppa[139] during 8 hr. The reaction mixture was stirred overnight. The dark brown residue was washed with distilled water (3 x 500 c.c.) and dried over anhydrous sodium sulphate (three times). The solvent was removed on a water bath under reduced pressure and the residue redistilled to give a yellow oil (159.79 g., 98.7%). Further purification of the oil *in vacuo* at 98°/0.3 mm. gave a colourless 3-bromobenzo[b]thiophen (149.46 g.; 92.23%), $n_D^{27.5}$ 1.6610.

*Benzo[b]thiophen-3-carboxylic acid*.- This was obtained in 75.66% yield from the Grignard reaction of 3-bromobenzo[b]thiophen (145 g.), methyl iodide (192.19 g.), magnesium turnings (53.51 g.), sodium-dried ether (600 c.c.), and dry ice (200 g.) according to the method of Crook and Davies.[133] The product, after recrystallisation from benzene, was obtained as colourless fine needles, m.p. 176.5-177.5° (lit.[133] m.p. 174-175°).

Benzo[b]thiophen-3-carboxylic acid-1,1-dioxide.- This was prepared in six separate experiments according to the indications of Crook and Davies[133] except that the reaction mixture was kept at room temperature for 3 days instead of 2 days before being worked up. The scale used in each preparation was as follows: benzo[b]thiophen-3-carboxylic acid (15 g.), hydrogen peroxide (100 Vol. oxygen, M & B, 112.5 c.c.), distilled water (75 c.c.), glacial acetic acid (B.D.H., Analar, 300 c.c.). The yield, average of 5 experiments, was 56.2%. The product was obtained as big-long yellow needles (ca. 2-3 cm. long) m.p. 218-219° (lit.[133] m.p. 218°) after recrystallisation from distilled water. In the process of working up it was observed that separation of deposited clusters of yellow prisms from the reaction mixture prior to evaporation of the solvent was preferable. The mother liquor was then concentrated under reduced pressure on a water bath but with great care not to allow a decrease of its total volume below ca. 50 c.c. Release of pressure also should be gentle and with precaution since this might lead to an uncontrollable decomposition of the sulphone or even a violent explosion.

*Desulphurisation of Diphenyl Sulphide*.- A solution of diphenyl sulphide (redistilled, 4.0 g.) in methanol was added through a reflux condenser to a suspension of W-7 Raney nickel catalyst (from 6.0 g. of alloy) in methanol (to make up the total volume of the reaction mixture to 250 c.c.). The gasses escaping through the condenser were passed through a trap which was cooled by a mixture of dry ice and ethanol. After 70 min. of refluxing on a water bath, the catalyst was collected on Celite and washed with methanol (3 x 25 c.c.). Careful fractional distillation of the combined filtrates and the liquid collected in the trap through a jacketed column (cf. p. 115) gave:

(*a*) a colourless liquid, b.p. 63-65° (24.22 c.c.);

(*b*) a colourless liquid, b.p. 65° (11.8 c.c.); and

(*c*) a residue (*ca.* 285 c.c.).

Examination of (*a*) by gas chromatography at 82° showed peaks corresponding to benzene and methanol at the retention times of 4.25 and 1.3 min. respectively. Experiments with authentic mixtures of benzene and methanol revealed that the benzene present amounted to 1.51 c.c. (1.32 g.). No traces of benzene were detected in (*b*).

Concentration of (*c*) on a water bath gave a further residue (oil) which was redistilled at 185°/1.3 mm. to give a colourless liquid identified as diphenyl sulphide (2.43 g.) by comparison with the authentic specimen. The yield of the unchanged sulphide was 60.75% and of benzene was 39.28%.

*Desulphurisation of Diphenyl Sulphoxide*.- The sulphoxide (4.0 g.) was desulphurised with the W-7 Raney nickel catalyst (from 5.0 g. of alloy) under the same conditions as described above in every respect. When worked up in the same manner diphenyl sulphoxide (2.59 g., 64.75%) was obtained as colourless needles m.p. 69-70° after recrystallisation from light-petroleum (b.p. 50-60°), identified by comparison (mixed m.p., infrared spectra) with an authentic specimen; benzene (1.22 c.c., 1.07 g., 34.63%) was detected as above.

*Desulphurisation of Diphenyl Sulphone*.- The sulphone (4.0 g.) and W-7 Raney nickel catalyst (from 5.0 g. of alloy) in methanol (to make the total volume 250 c.c.) was refluxed under the same conditions as mentioned above. The reaction mixture was worked up as before except that the residue was concentrated on a water bath (instead of redistilled) and the crystals separated. Recrystallisation of the product in ethanol gave diphenyl sulphone as colourless prisms (3.72 g., 93.00%) m.p. 123-124°, identified by comparison with an authentic specimen. The amount of benzene detected in the same manner as above was .075 c.c. (0.06 g., 4.21%).

*Desulphurisation of benzo[b]thiophen-3-carboxylic acid-1,1-dioxide*.-

(a) *With W-7 Raney nickel catalyst*. A mixture of the acid (5.0 g.) and W-7 Raney nickel catalyst (from 125 g. of alloy) in a solution of sodium bicarbonate (total volume *ca.* 300 c.c.) was refluxed for 3 hr. The catalyst was filtered off (Celite) and washed with a solution of sodium bicarbonate (3 x 150 c.c.). The combined filtrates were evaporated on a water bath under reduced pressure and the residue acidified with hydrochloric acid (20%). The acid was taken up by alcohol-free ether. Evaporation of the dry solvent (anhydrous magnesium sulphate) on a water bath gave a yellow oil (3.37 g.). On standing, the liquid partially crystallised. The crystals were collected (1.12 g.) and subsequently recrystallised from ethanol-free chloroform. Colourless needles (0.6 g.), m.p. 219-220° were obtained and the presence of sulphur was found by sodium fusion test. The compound was characterized as the starting material by mixed melting point, comparison of the infrared spectra, and paper chromatography (Whatman paper No. 1) using solvent system n-butanol-ammonia (1.5 N.; 1:1, v/v; $R_F$ 0.42). The mother liquor (oil) was chromatograph on paper (conditions as above). Development by descent produced two spots which were made visible by spraying with *p*-bromocresol purple. These corresponded to phenylacetic acid ($R_F$ 0.41, small spots) and *dl*-hydratropic acid ($R_F$ 0.56, big spot, kindly supplied by J.E. Goodrich) respectively. Both authentic specimens of the acids were also run on the same chromatogram. Redistillation of the oil at 115-116°/0.6 mm. gave a colourless liquid (1.074 g.) by examination of the liquid by paper chromatography showed that it was still a mixture of phenylacetic acid and dl-hydratropic acid. The infrared spectrum of the mixture, however, was identical with that of a mixture of authentic specimens of these two compounds. The residue (0.6 g.) was not further examined.

(b) With W-7J Raney nickel catalyst. The acid (5.0 g.), dissolved in sodium bicarbonate solution (to make a total volume up to ca. 500 c.c.) was introduced to the W-7J Raney nickel catalyst (from 125 g. of alloy), and the mixture was then refluxed for 36 hr. Working up as above gave a brown oil residue (2.56 g.), after evaporation of ether. This was found to turn black on standing for 24 hr. Redistillation of the black oil *in vacuo* gave a colourless liquid (1.76 g.) at 165° (bath)/0.2 mm. This was characterized as a mixture of phenylacetic acid and dl-hydratropic acid by the methods described above. The residue (0.8 g.) could not be further purified. Attempts to separate phenylacetic acid from dl-hydratropic acid by partition chromatography on a column of cellulose in n-butanol-ammonia were unsuccessful as was preparative paper chromatography on ordinary paper. However preparative paper chromatography on Whatman 3 mm. paper (n-butanol-ammonia; conditions as before) led to the separation of both acids of which was detected by infrared spectroscopy. However, they could not be isolated. The procedure carried out was as follows.

The liquid mixture was applied in a thin streak by means of a capillary tube (three times) along a straight line instead of spotted as usual for ordinary paper chromatography. Development by ascent (n-butanol-ammonia) required 3½ days. The paper was allowed to dry (air) in a hood and two small narrow strips were then cut off vertically at the left and right ends of the paper. The strips were examined by spraying with a universal indicator and the locations of the two separated acids were marked. By bringing back the two strips to their original positions at both ends of the paper the invisible parts of separated acids were located and subsequently cut off. These were separately extracted with distilled water (Soxhlet) for 24 hr. The aqueous extracts were then separately extracted (continuously) with alcohol-free ether for 36 hr. to remove butanol. Both aqueous extracts were evaporated under reduced pressure and residues being acidified (20% hydrochloric acid). The acids were taken up in carbon tetrachloride, evaporated (traces of water being removed by azeotropic distillation with carbon tetrachloride) and examined by infrared spectroscopy. These were found to be identical in every respect with those of authentic specimens of phenylacetic acid and dl-hydratropic acid respectively. The residues obtained from evaporation of carbon tetrachloride were not further purified.

(c) *With Aller Raney cobalt catalyst.* A mixture of benzo[*b*]thiophen-3-carboxylic acid-1,1-dioxide (3.0 g.), Aller Raney cobalt catalyst[136] (from 80 g. of alloy) and aqueous sodium bicarbonate (*ca.* 200 c.c.) was refluxed for 6 hr. under nitrogen. The catalyst was separated and washed with hot sodium bicarbonate solution (5 x 75 c.c.). The combined filtrates were concentrated on a water bath under reduced pressure and in an atmosphere of nitrogen. The residue after acidification (20% hydrochloric acid) was extracted with alcohol-free ether. The dry solvent (anhydrous calcium sulphate) was removed under nitrogen and a light-brown residue (partially crystallized, 2.15 g.) was obtained. Examination of the residue by paper chromatography (butanol-ammonia; conditions as above) showed spots at $R_F$ : 0.40 (phenylacetic acid); 0.56 (*dl*-hydratropic acid ); 0.64 (benzo[*b*]thiophen-3-carboxylic acid); 0.43 (benzo[*b*]thiophen-3-carboxylic acid-1,1-dioxide); and 0.27 (unidentified).

### *Attempted separation of acid-products, from the desulphurisation of benzo[b]thiophen-3-carboxylic acid-1,1-dioxide with Aller Raney cobalt, by partition chromatography on a column of buffered silica gel.*

The procedure described below was adapted from Barber, and Clingman,[140] and from Bulen, Varner, and Burrell.[141] I am grateful to Dr. G.E. Gream for helpful discussions.

All reagents used were of "Analar" grade (B.D.H.). Freshly boiled distilled water (to remove carbon dioxide) was used throughout the experiment. The silica acid (M.B., prepared for chromatography) was slurried with distilled water about 15 times and the fine particles were discarded prior to each sedimentation. The silicic acid was then dried in the oven at 120° for 30 hr.

Prepared silicic acid (100 g.) was mixed thoroughly with sulphuric acid (0.5 N., 80 c.c.). The mixture (4-5 g. each time) was poured into the tube (half filled with chloroform) followed by repeated pressing with a glass rod until all of the column was well packed. The acid mixture (from 2.0 g. of the residue) in sulphuric acid (0.5 N., 10 c.c.) was mixed thoroughly with dry silica gel (20 g.) and then transferred to the top of the column with precautions to prevent trapping of air bubbles. The top of the column was then leveled and protected with a plug of glass wool.

The column was eluted by gradient elution with n-butanol in chloroform. Fractions were collected (9-10 c.c. each) at the rate of 0.5 c.c./min. Each fifth fraction was examined by paper chromatography (conditions as described) and appropriate fractions were combined and worked up in the customary way. The schedule was used as follows.

(a) Chloroform (270 c.c.); this gave dl-hydratropic acid (0.96 g.), identical in all respects with an authentic specimen. No acid was detected on further elution with chloroform (210 c.c.).

(b) Chloroform (200 c.c.); colourless needles (0.05 g.) were obtained from these combined fractions. They were characterized as phenylacetic acid by mixed m.p. and comparison of the infrared spectrum with that of the authentic acid.

(c) n-Butanol-chloroform (5:95, v/v; 540 c.c.); this gave colourless labile prisms (0.21 g.), m.p. 130-131°. Attempts to purify the compound by recrystallisation in the following solvents led to partial decomposition: chloroform, dioxan, dioxan-n-hexane, hexane, toluene, xylene, sodium carbonate solution followed by acidification, and water. The compound could be identified. Sodium fusion test showed the absence of sulphur. The ultraviolet spectrum of the product showed $\lambda_{max.}$ at 269, 277 with shoulders at 224 and 263 mμ; $\lambda_{min.}$ at 244 mμ.

(d) n-Butanol-chloroform (10:90, v/v; 150 c.c.), colourless needles (0.010 g.) were isolated and were identified as benzo[b]thiophen-3-carboxylic acid by m.p., mixed m.p. and paper chromatography.

(e) n-Butanol-chloroform (10:90, v/v; 200 c.c.), yellowish needles (0.021 g.) were obtained and were identified as starting material by comparison with an authentic sample (mixed m.p. and infrared spectra).

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# CHAPTER 3

## THE DESULPHURISATION OF SOME SECONDARY AND TERTIARY ALCOHOLS DERIVED FROM THIOPHEN.

# THE DESULPHURISATION OF SOME SECONDARY AND TERTIARY ALCOHOLS DERIVED FROM THIOPHEN.

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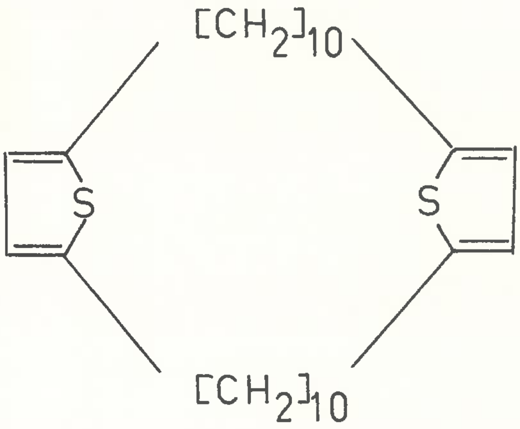
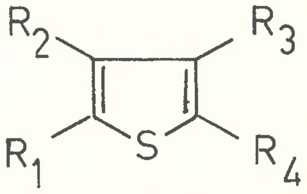
## INTRODUCTION

Earlier in this thesis, it has been shown that sulphur in an aromatic nucleus could be removed by hydrogenolysis like sulphur in aliphatic carbon compounds. This was first demonstrated by Bougault et al.,[1] who, in 1940, reported the preparation of thiophen-free benzene, and methylthiophen-free toluene by treatment of ordinary benzene or toluene by Raney nickel. However, the desulphurisation of thiophen derivatives did not receive much attention until 1948, when Blicke and Sheets[2] studied the desulphurisation of benzo[b]thiophen-2-carboxylic acid and benzo[b]thiophen-3-acetic acid (see p. 211, Chapter II). These experiments were carried out mainly in order to elucidate the structure of such thiophen derivatives. A year later, Papa, Schwenk, and Ginsberg[3] carried out the desulphurisation of several acidic derivatives of thiophen with nickel-aluminium alloy in alkaline solution and obtained the corresponding sulphur-free acid. Since then, the desulphurisation of thiophen derivatives has received wide attention as a synthetic route to a variety of compounds. For instances, desulphurisation of suitably substituted derivatives of thiophen has been shown to provide a convenient route for the preparation of many long chain fatty acids,[4,5] and many branched-chain acids are more accessible by this route than by any other (see also p. 14-17, Chapter I). Dicarboxylic acids, keto-acids, hydroxy-acids, amino-acids, and a few hydrocarbons, ketones, and alcohols have been prepared by modification of the method.[4,6]

The desulphurisation of thiophen hydrocarbons usually does not present any difficulty. As an example, the cyclic compound (I) which on Raney nickel desulphurisation gave cyclooctacosane[7] may be cited. The thiophen derivatives (II) which were desulphurised with Raney nickel in ethanol, dioxan, or toluene have been reported to give the corresponding saturated branched-chain aliphatic hydrocarbons.[8]

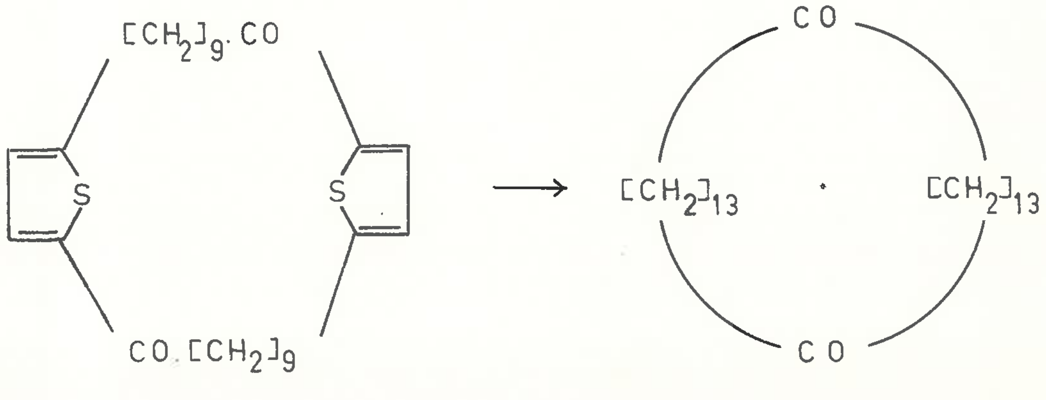


I

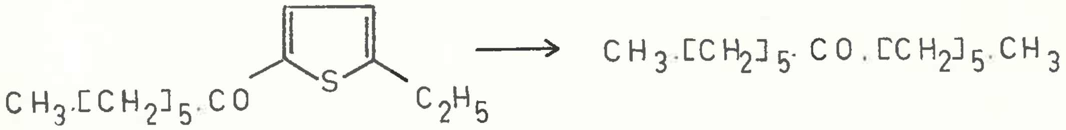


II

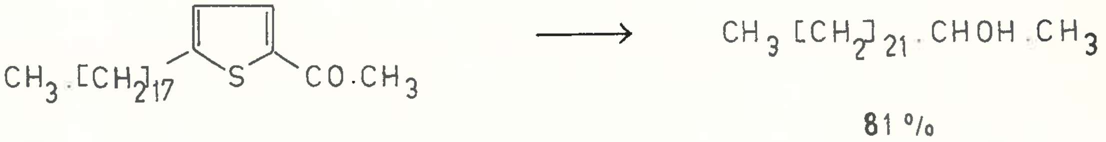
Similarly, thiophen ketones have been desulphurised with Raney nickel in ethanol, benzene, dioxan, or acetone to the corresponding saturated aliphatic ketones,[7,4] e.g.



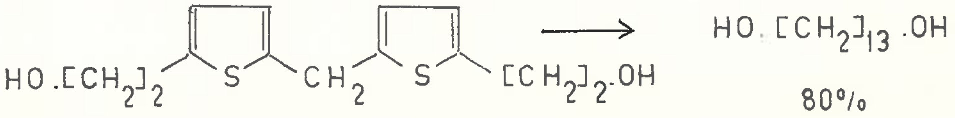
III



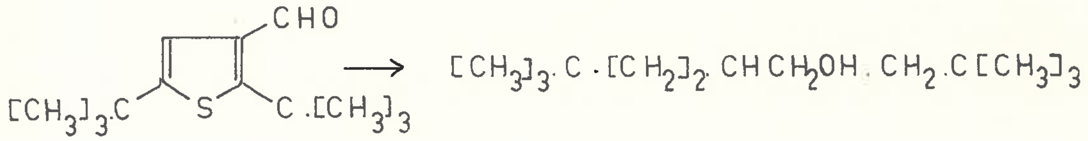
However, it has been observed, in some instances, that desulphurisation of thiophen ketones lead to the formation of the corresponding saturated aliphatic alcohols.[6c,6f,9] It is thought that the weight ratio of the compound to Raney nickel catalyst is the factor determining the extent of reduction of the carbonyl groups.[10] Thus the desulphurisation of the ketone (III) was carried out using the weight ratio of the compound: Raney nickel about 1:3. The synthesis of long chain and branched-chain aliphatic alcohols have similarly been achieved.[11,12] Saturated alcohols have also been obtained by the desulphurisation of thiophen aldehydes.[6f.,13] Desulphurisation of (IV),[6c] (V),[11] and (VI)[6f] may be cited as examples.



IV



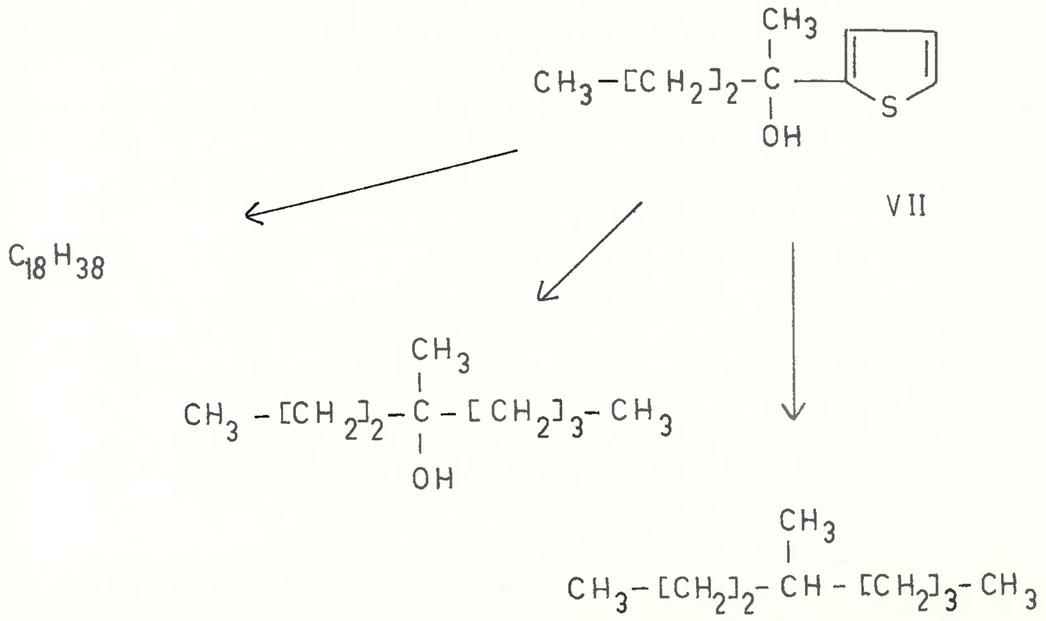
V



VI

It should be noted here again that the formation of dimeric products during the desulphurisation of thiophen derivatives have been observed and several examples could be cited[4,14] (see p. 42-43). Thus, the desulphurisation of thiophen-2-carboxylic acid gave n-valeric acid and sebacic acid; and γ-2-thienylbutyric acid gave octanoic acid and hexadecane-1,16-dioic acid.[14]

These examples may suffice to demonstrate the versatility of the desulphurisation of substituted thiophen as a synthetic route to a wide variety of aliphatic compounds. In spite of these potentialities, the desulphurisation of alcohols derived from thiophen has been reported only in a few instances; most of the compounds concerned are primary alcohols.[11,12] To the author's knowledge, only one paper dealing with the desulphurisation of secondary and tertiary alcohol derived from thiophen appeared in the literature before the present study was undertaken. In this paper, Wynberg and Logothetis[6c] report the preparation of $\alpha,\alpha$, 2-thienylmethyl-n-butyl alcohol from the Grignard reaction of n-butyl-2-thienyl ketone and methylmagnesium iodide but the oily product obtained was described as somewhat unstable alcohol (VII). They divided the oil into three parts, the first of which was redistilled to give a material, the boiling point of which was higher than that of the expected product. This on desulphurisation with a Raney nickel catalyst yielded the "dimeric product" $C_{18}H_{38}$ which was not identified. The second part of (VII), which was immediately subjected to desulphurisation reaction with a Raney nickel catalyst, gave a colourless oil. This was characterized as 4-methyloctan-4-ol. The other part was treated with oxalic acid and the purified product was immediately desulphurised to give a saturated hydrocarbon, 4-methyloctane. However, characterization of these products were based on their boiling points and refractive indices only.

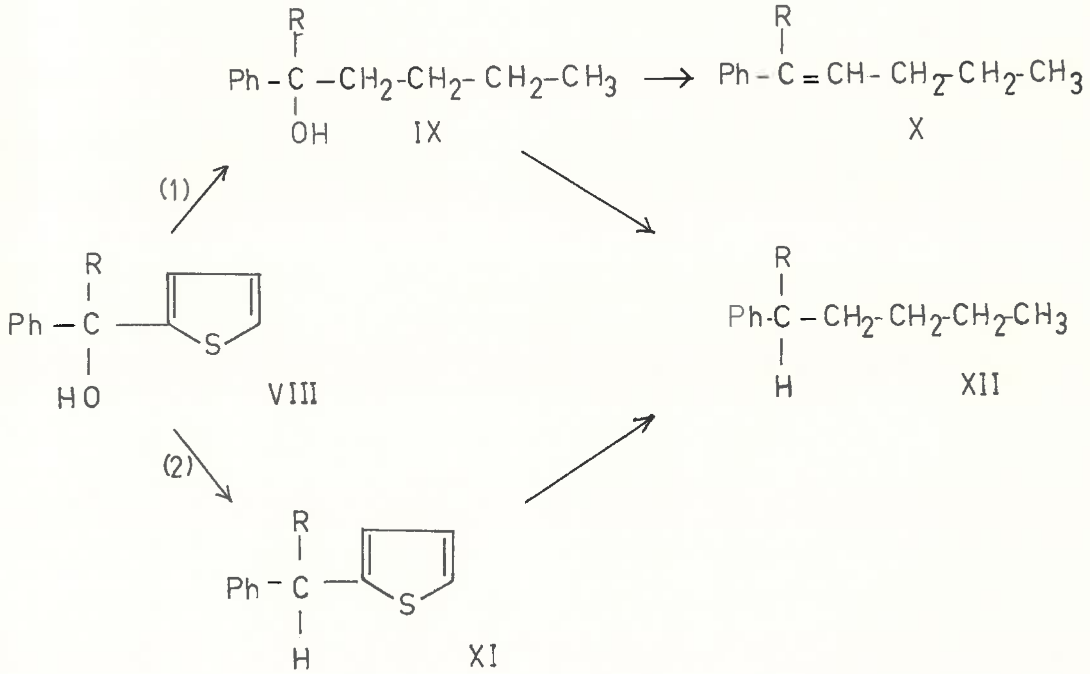


VII

In order to examine further the synthetic applications of the desulphurisation reaction, several $\alpha$-2-thienylbenzyl alcohols and related compounds have now been desulphurised. These reactions were effected in benzene or methanol with W-7 Raney nickel.

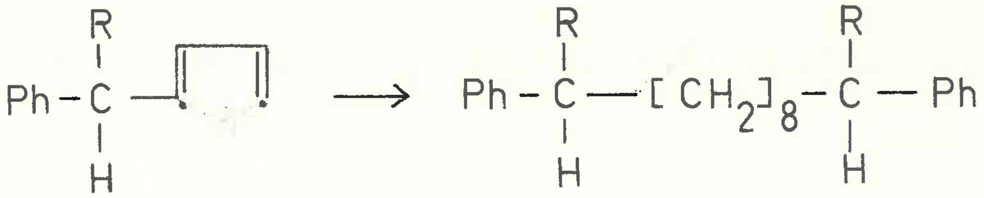
## RESULTS AND DISCUSSION

In accordance with the work described above, desulphurisation of α-2-thienylbenzyl alcohol (VIII) might be expected to give the alkanols (IX), which could suffer ready dehydration to the olefins (X). It is known that dehydration of some tertiary alcohols takes place readily during distillation *in vacuo*.[15] On the other hand, hydrogenolysis of the hydroxy group to give compound (XI) may also be expected, in analogy with the previous observations made by Bonner and his co-workers.[16] This would give the saturated hydrocarbon (XII) on desulphurisation. Similarly, the alcohols (IX) would be expected to suffer some hydrogenolysis to the saturated compounds (XII).



The results obtained in the present investigation indicate that both mechanisms must operate, but in varying degree. Intractable mixtures of alcohol (IX), olefin (X), and saturated hydrocarbon (XII) were sometimes formed, and these were worked up by dehydration and reduction to give the saturated compound.

It now seems to be well established that desulphurisations of organo-sulphur compounds, except that of sulphones, proceed by a radical mechanism. As pointed out previously "dimerisation" of such intermediate radicals (rather than their hydrogenation) has been demonstrated in a few cases.[14,17] Dimerisation of the intermediate radical expected from the action of Raney nickel on the 2-benzylthiophene (XI) would give the hydrocarbons (XIII), and it is significant that compounds of this type were observed among some of the reaction products. In analogy with the present results, it seems beyond doubt that the unidentified material $C_{18}H_{38}$ obtained by Wynberg and Logothetis would likewisely correspond to 4,13-dimethylhexadecane.



XIII

The same hydrocarbon (XIII) could also be formed by dimerisation of the radical intermediate from the action of Raney nickel on the sulphur atom in the alcohol (VIII). Removal of both hydroxy groups in the corresponding dimer by hydrogenolysis would give rise to the observed dimeric product. Since no unsaturated dimers were observed in the present work, dehydration is considered unlikely. However, olefins of the type (X) are believed to be isolated in some cases (identification based on analyses only), this postulate, therefore, does not preclude the possibility of such dehydration in monomeric compounds.

Since an attempt to recrystallise diphenyl-2-thienylmethanol (VIII, R = Ph) resulted in the formation of the corresponding ethyl ether presumably by the action of the ethanol solvent, all the desulphurisation reactions of the alcohols derived from thiophen described below, therefore, have been conducted in benzene.

Desulphurisation of $\alpha$-2-thienylbenzyl alcohol (VIII; R = H) gave 1-phenylpentane (XII; R = H) as a major product (58.06%), together with some 1,10-diphenyldecane (XIII; R = H) (17.67%). No alcohol (IX) or olefin (X) was detected among the products, and it seems, therefore, that reaction proceeded entirely by the second mechanism.

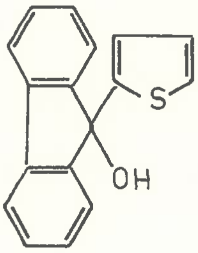
Desulphurisation of $\alpha$-methyl-$\alpha$-2-thienylbenzyl alcohol (VIII; R = Me) proceeded similarly as above, giving 2-phenylhexane (XII; R = Me) (62.46%), but in this case no dimeric product (XIII) could be isolated. This may be caused by the fact that this experiment was carried out on a smaller scale and in a higher dilution than the other experiments described here.

On the other hand, the desulphurisation of diphenyl-2-thienylmethanol (VIII; R = Ph) gave a mixture containing both alcohol and olefin and probably the saturated hydrocarbon as well. Since the mixture could not be separated, it was treated with iodine and subsequently hydrogenated to give 1,1-diphenylpentane (XII; R = Ph). The presence of the unsaturated product (X; R = Ph) was confirmed by the isolation of 1,1-diphenylpent-1-ene from methanol extracts of the catalyst. A small amount of dimeric product, 1,1,10,10-tetraphenyldecane (XIII; R = Ph) (4.03%) was also obtained. The yield of the saturated monomeric hydrocarbon was not determined.

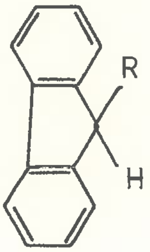
The desulphurisation of αα-di-2-thienylbenzyl alcohol (VIII; R = $C_4H_3S$) gave a mixture of alcohol and olefin which was completely dehydrated to give 5-phenylnon-4-ene (X; R = $Bu^n$) (16.0%). It is interesting that no saturated compound (XII; R = $Bu^n$) was found, while the dimeric product 5,14-diphenyloctadecane (XIII; R = $Bu^n$) was isolated (6.38%). This suggests that the reaction probably proceeded mostly by the first mechanism. Two further products were isolated. The first is provisionally regarded as 5-phenyloctadecane; the second was characterized as biphenyl (17.01%). The production of these two compounds is of some interest as it evidently means that phenyl radicals were liberated at some stage in the desulphurisation of the alcohol. However, it should be noted that the starting material, $\alpha\alpha$-di-2-thienylbenzylalcohol, in this desulphurisation reaction was prepared from the Grignard reaction between ethyl benzoate and 2-thienylmagnesium bromide in ether-benzene. Owing to its extreme lability (easily decomposed by light, air and heat), the alcohol was not isolated and the reaction was carried out in a dark room. The desulphurisation was accomplished by addition of the Raney nickel in benzene to the Grignard mixture and the suspension was then gently refluxed on a warm water bath in the absence of light under oxygen-free nitrogen. Nevertheless, the biphenyl was not derived from any unchanged ethyl benzoate in the reaction mixture, as this compound was recovered unchanged following treatment with W-7 Raney nickel in boiling benzene. It is also noteworthy that the desulphurisation of $\alpha\alpha$-di-2-thienylbenzyl alcohol with a very large excess of Raney nickel gave biphenyl in 70% yield.

Desulphurisation of $\alpha$-1-naphthyl-$\alpha$-2-thienylbenzyl alcohol (VIII; $R = C_{10}H_7$), which is also very unstable, gave only the saturated product 1,1'-naphthyl-1-phenylpentane (XII; $R = C_{10}H_7$) in 70.09% yield. Neither the alcohol nore the olefin was observed. A high boiling fraction proved to be intractable and appeared to consist mainly of decomposed material containing sulphur. No dimeric product (XII) was isolated.

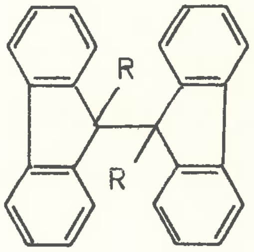
Finally, the desulphurisation of 9-2'-thienylfluoren-9-ol (XIV) gave 9-n-butylfluorene (XV; R = $Bu^n$) (69.82%), and 9,9'-di-2"-thienyl-9,9'-bifluorenyl (XVI; R = $C_4H_3S$) (4.86%), together with small amounts of other unidentified products. The isolation of (XV) and (XVI) suggests that in this reaction hydrogenolysis of the hydroxy groups proceeded desulphurisation of the thiophen nucleus. Moreover, the isolation of the dimer (XVI) is probably the first instance of a desulphurisation reaction in which dimerisation occurs prior to desulphurisation.



XIV



XV



XVI

In the preceding discussion, it has been assumed that the saturated compounds (XII) were formed from the alcohols (VIII) by way of either (XI) or (IX), that is, by hydrogenolysis of the hydroxy group. A small proportion of the saturated compound could conceivably arise by dehydration of the alcohol (IX) in the reaction mixture, followed by subsequent hydrogenation of the resulting olefin (X). The alcohols (IX) are certainly dehydrated when heated with a trace of iodine (this has been achieved in several instances); but it seems very unlikely that these alcohols (IX) would be dehydrated during treatment with alkaline Raney nickel. It is much more reasonable to suppose that the olefins are formed by dehydration of the alcohols during the process of working up, which involves a high-temperature distillation. Nevertheless it is also noteworthy that treatment of the alcohol, 2-phenylhexan-2-ol with 20% sulphuric acid and fused potassium bisulphate for two hours, or with fused zinc chloride and acetic anhydride for four hours, or with a trace of iodine for eight hours as reported by Crawford, Saeger, and Warneke[18] always gave rise to a mixture of the expected unsaturated hydrocarbon and the unchanged alcohol. This compound was described by these authors as being unusually resistant to dehydration. As this alcohol is the expected product from the desulphurisation of $\alpha$-methyl-$\alpha$-2-thienylbenzyl alcohol and could not be isolated, it is, thought that the observed product, 2-phenylhexane arose from either hydrogenolysis of the hydroxy group or probably dehydration during reaction followed by hydrogenation in the presence of the catalyst. However, repetition of the work of these authors in the present thesis from a reaction of this alcohol with iodine for 30 hr. resulted in the isolation of 2-phenylhex-2-ene (correct analyses). In this case dehydration of 2-phenylhex-2-ol (if formed) would be unlikely during working up since no unsaturated hydrocarbon was isolated. In view of the above discussion, the production of 2-phenylhexane following the desulphurisation of $\alpha$-methyl-$\alpha$-2-

thienylbenzyl alcohol is probably more readily explained by the second mechanism (p. 245) rather than the first. The variation in the amount of olefin formed also supports the view that these alcohols (IX) are not intermediates (at least, not to any significant extent) in the formation of the saturated hydrocarbons (XII).

It has also been confirmed in two instances that the alcohols do, in fact, undergo hydrogenolysis on treatment with Raney nickel in boiling methanol. In this way 2-phenylhexan-2-ol gave 2-phenylhexane; and 5-phenylnonan-5-ol gave 5-phenylnonane.

# EXPERIMENTAL

Ultraviolet and Infrared Spectra.- These were carried out as previously mentioned (p.169).

Raney Nickel.- W-7 Raney nickel was prepared by the usual method, except that methanol was used instead of ethanol in the washing process, and centrifugation was replaced by simple decantation. For desulphurisation in benzene the Raney nickel was washed three time with distilled water, ten times with methanol (redistilled over potassium hydroxide), and finally, ten times with sulphur-free benzene. The Raney nickel was freshly prepared for every desulphurisation.

Preparation of 2-Bromothiophen.- This was obtained in 77% yield by refluxing thiophen with N-bromosuccinimide according to the method of Buu-Hoi.

Preparation of $\alpha$-2-Thienylbenzyl Alcohol.- Freshly redistilled benzaldehyde (10.61 g.) in anhydrous sulphur-free benzene (20 c.c.) was added dropwise to a boiling Grignard solution from 2-bromothiophen (18.75 g.) and magnesium (2.64 g.) in sodium-dried ether. Benzene (20 c.c.) was then added and refluxing continued for 1 hr. After recrystallisation of the product from benzene-light petroleum (b.p. 60-90°), $\alpha$-2-thienylbenzyl alcohol (14.31 g., 75.3%) formed needles, m.p. 56-57° (lit.[20] 57-58°).

**Desulphurisation of α-2-Thienylbenzyl Alcohol.**- A mixture of the alcohol (9.0 g.) and W-7 Raney nickel (from 125 g. of alloy) in sulphur-free benzene (200 c.c.) was stirred and refluxed for 3 hr. The catalyst was collected, washed with pure benzene (2 x 25 c.c.), and then extracted with benzene (Soxhlet) for 3 days. The combined filtrates and extracts were evaporated, and the residue was distilled, to give:

(a) an oil, b.p. 94°/9 mm. (4.07 g.);

(b) an oil, b.p. 140°/1 mm. (1.23 g.); and

(c) a residue (0.02 g.).

Fraction (a) was identified as 1-phenylpentane by comparison of its infrared spectrum with that of an authentic specimen.

Found: C, 89.4; H, 10.7.

Calc. for $C_{11}H_{16}$ : C, 89.1; H, 10.9%.

Redistillation of fraction (b) gave 1,10-diphenyldecane as an oil, $n_D^{15}$ 1.5318 (lit.,[21] $n_D^{20}$ 1.5281), which crystallised on cooling to give prisms, m.p. 15-16° (lit.,[21,22] 12°, 17.5°).

Found: C, 89.3; H, 10.0.

Calc. for $C_{22}H_{30}$: C, 89.7; H, 10.3%.

The alternative possible structure, namely, 5,6-diphenyldecane, is reported[23] to have m.p. 50°. The residue (c) was not examined.

The yield of the saturated product, 1-phenylpentane was 58-06% and of the dimeric hydrocarbon, 1.10-diphenyldecane was 17.67%.

**Preparation of $\alpha$-Methyl-$\alpha$-2-thienylbenzyl Alcohol.-** A solution of 2-acetylthiophen (12.6 g.) in anhydrous benzene was added to a Grignard solution from freshly redistilled bromobenzene (18.06 g.) in anhydrous ether. The resulting alcohol (VII; R = Me) (19.17 g., 94.4%) had m.p. 50° (lit.[24] m.p. 50°).

**Desulphurisation of $\alpha$-Methyl-$\alpha$-2-thienylbenzyl Alcohol.-** W-7 Raney nickel (from 62.5 g. of alloy) was added to a solution of this alcohol (5.0 g.) in sulphur-free benzene (100 c.c.), and the mixture stirred and refluxed for 32 hr. Evaporation of the combined filtrates and distillation of the product gave:

(a) an oil, b.p. 110-112°/12 mm. (0.12 g.);

(b) an oil, b.p. 112-116°/12 mm. (2.965 g.); and

(c) a residue (0.012 g.).

Fraction (a) and (b) gave almost identical infrared spectra, and bands characteristic for OH and C = C groups could not be observed. Nevertheless, to ensure complete removal of any alcoholic or unsaturated product, fraction (b) was redistilled over a crystal of iodine and the distillate treated with hydrogen (800 lb./ in.$^2$) and platinum-charcoal in absolute ethanol (50 c.c.) at 70° for 6 hr. Redistillation gave 2-phenylhexane (1.61 g.) as an oil, b.p. 101-102°/5 mm., $n_D^{26}$ 1.4912 (lit.,[25] $n_D^{15}$ 1.4920).

Found: C, 89.0; H, 11.0.

Calc. for $C_{12}H_{18}$ : C, 88.8; H, 11.2%.

Its infrared spectrum was identical with that given by an authentic specimen of 2-phenylhexane in every respect. Attempts to crystallise the residue (c) were unsuccessful.

*Dehydration of 2-Phenylhexan-2-ol.*- 2-Phenylhexan-2-ol was prepared in 84% yield from acetophenone and n-butylmagnesium bromide. Dehydration was effected by refluxing the alcohol (5.0 g.) with a trace of iodine for 30 hr.[18] The product was washed with aqueous sodium hydrogen sulphite and extracted in ether, the ether solution dried and evaporated and the residue distilled, to give 2-phenylhex-2-ene, b.p. 62-63°/0.7 mm. (4.235 g., 94.23%), $n_D^{17.5}$ 1.5258 (lit.,[26] $n_D^{20}$ 1.5200).

Found: C, 89.5; H, 10.1.

Calc. for $C_{12}H_{16}$ : C, 89.9; H, 10.1%.

However, the product was still contaminated with traces of starting material as indicated by the presence of week bands at 3650 (OH stretching) and 1150 $cm^{-1}$ (OH deformation).

*Hydrogenolysis of 2-Phenylhexan-2-ol.*- A mixture of 2-phenylhexan-2-ol (5.0 g.), W-7 Raney nickel (from 62.5 g. of alloy), and methanol (to bring the total volume up to 80 c.c.) was refluxed for 3 hr. The catalyst was collected on Celite and washed with methanol (3 x 50 cm.). The combined filtrates were poured into water, the product was extracted into ether, the ether solution dried and evaporated, and the residue distilled. The

2-phenylhexane obtained had b.p. 93-94°/1 mm. (3.9 g., 85.70%), $n_D^{17.5}$ 1.4862 (lit.,[25] 1.4920).

Found: C, 89.1; H, 11.3.

Calc. for $C_{12}H_{18}$: C, 88.8; H, 11.2%.

Its infrared spectrum was identical with that given by an authentic specimen.

Preparation of Diphenyl-2-thienylmethanol.- Recrystallised benzophenone (18.2 g.) in anhydrous benzene was added to the Grignard solution from 2-bromothiophen (18.75 g.) in anhydrous ether. Recrystallisation of the product from benzene-light petroleum (b.p. 30-40°) gave diphenyl-2-thienylmethanol as light brown prisms, m.p. 128° (23.6 g., 88.3%) (lit.,[27] m.p. 129-130°). However, recrystallisation of the alcohol from absolute ethanol (charcoal) resulted in isolation of its corresponding ethyl ether, m.p. 83.5-84.5°. No hydroxy band was observed in its infrared spectrum.

Found: C, 77.3; H, 6.3; O, 5.6; S, 10.7.

$C_{19}H_{19}OS$ requires: C, 77.3; H, 6.4; O, 5.4; S, 10.85%.

Desulphurisation of Diphenyl-2-thienylmethanol.- W-7 Raney nickel (from 125 g. of alloy) was added to the above alcohol (6.0 g.) in sulphur-free benzene (60 c.c.), and the mixture stirred and refluxed for 1 hr. The catalyst was collected and washed with pure benzene (2 x 60 c.c.), the combined filtrates were evaporated, and the product distilled to give:

(a) an oil, b.p. 108-110°/15 mm. (0.38 g.);

(b) an oil, b.p. 110-112°/15 mm. (3.44 g.); and

(c) a fluorescing yellow-green residue (1.0 g.).

Fraction (a) and (b) gave identical infrared spectra, having a weak OH band at 3660 cm$^{-1}$. They also decolourised bromine in carbon tetrachloride, and potassium permanganate in acetone; and they both gave a deep yellow solution when added to tetranitromethane. The product was accordingly treated to remove any alcohol and unsaturated material. Fraction (b) was refluxed for 0.5 hr. with a trace of iodine, and the product treated with hydrogen (800 lb./in.$^2$) and platinum-charcoal in absolute ethanol at 50-60°. The resulting 1,1-diphenylpentane was obtained as an oil, b.p. 180°/12 mm., $n_D^{25}$ 1.5480 (lit.,[15] $n_D^{20}$ 1.5511).

Found: C, 91.3; H, 9.1.

Calc. for $C_{17}H_{20}$: C, 91.0; H, 9.0%.

Light petroleum (b.p. 30-40°) was added to the residue (c); concentration gave colourless needles (0.27 g.), m.p. 90-91°. Recrystallisation from n-hexane gave 1,1,10,10-tetraphenyldecane as needles, m.p. 90-91°.

Found: C, 91.2; H, 8.6%; M (Rast), 494, 468.

$C_{34}H_{38}$ requires: C, 91.4; H, 8.6%; M, 446.6.

The theoretically alternative structure, 5,5,6,6-tetraphenyldecane is reported[28] to have m.p. 62-63° (air) or 68-70°

(nitrogen). Concentration of the mother liquors gave a further quantity (0.40 g.) of 1,1-diphenylpentane, $n_D^{20}$ 1.5505, having an infrared spectrum identical with that of the material above.

Found: C, 91.0; H, 8.9.

Calc. for $C_{17}H_{20}$: C, 91.0; H, 9.0%.

Extraction of the catalyst with benzene in a Soxhlet for 48 hr. gave a further fraction (d) (0.15 g.), and subsequent extraction with methanol gave an additional fraction (e) (0.15 g.). Fraction (d) was redistilled at 200° (bath)/8 mm., to give an oil (mainly 1,1-diphenylpent-1-ene ?).

Found: C, 92.0; H, 8.5.

Calc. for $C_{17}H_{18}$: C, 91.8; H, 8.2%.

Similar distillation of fraction (e) gave an oil (Found: C, 91.2; H, 8.3%).

Preparation of $\alpha\alpha$-Di-2-thienylbenzyl Alcohol.- Preliminery experiments showed that this alcohol is extremely unstable in the presence of light and air or on strong refluxing. The following experiment was therefore carried out in a dark room, and reaction mixtures were covered with an atmosphere of dry oxygen-free nitrogen.

Ethylbenzoate (7.5 g.) in anhydrous sulphur-free benzene (40 c.c.) was added dropwise to a Grignard solution prepared from freshly distilled 2-bromothiophen (18.75 g.) and magnesium (2.64 g.) in anhydrous ether (70 c.c.). Gentle warming was required during the addition, and when this was complete the mixture was gently refluxed for a further 3 hr. The complex was not decomposed and was subjected to the desulphurisation reaction as below.

*Desulphurisation of αα-Di-2-thienylbenzyl Alcohol (Grignard Complex).*- W-7 Raney nickel (from 125 g. of alloy) was then added to the cooled mixture (above), which was made up to *ca.* 250 c.c. with pure benzene. The mixture was then stirred and refluxed for 12 hr., and tested for completeness of desulphurisation (by withdrawing a small amount of mixture and exposing it to light and air: when reaction was incomplete, the mixture became rapidly dark violet). More Raney nickel (from 125 g. of alloy) was added if required, and refluxing continued for 4 hr. The catalyst was collected on Celite and washed with sulphur-free benzene (3 x 50 c.c.), and the combined filtrates were evaporated, and the residue was distilled, to give:

(*a*) a forerun, b.p. 158-160°/ 9 mm. (0.11 g.);

(*b*) a colourless liquid, b.p. 160-164°/9 mm. (3.23 g.);

(*c*) a colourless liquid, b.p. 180°(bath)/0.5 mm. (0.12 g.); and

(*d*) a dark violet residue (1.35 g.) (which, after chromatography on alumina in hexane and subsequent distillation, gave a yellow oil, b.p. 174-175°/0.2 mm. (1.2 g.)).

Extraction of the catalyst with benzene (Soxhlet) for 96 hr. and evaporation gave a further fraction,

(e) which, after recrystallisation from absolute ethanol, yielded plates, m.p. 69-70° (2.62 g.).

Subsequent extraction of the catalyst with methanol for 48 hr. and evaporation gave,

(f) colourless crystals (11.9 g.) (which were obtained from chromatography of the crude extracts (ca. 27 g.) on alumina in hexane, the crystals did not melt and left a colourless residue on ignition).

The infrared spectrum of fraction (a) showed strong absorption of frequencies corresponding to C-H stretching vibrations in methyl, methylene, and phenyl groups. No absorption was observed above 3100 cm$^{-1}$, indicating the absence of a hydroxy group.

The infrared spectrum of fraction (b) showed a band at 1603 (conjugated C = C), and a weak band at 3650 cm$^{-1}$ (OH group). In addition, it showed absorptions at 2962 and 2874 ($CH_3$), and between 1940 and 1740 cm$^{-1}$ (monosubstituted aromatic). The liquid decolourised bromine in carbon tetrachloride, and potassium permanganate in acetone. It was redistilled in the presence of a trace of iodine and the resulting 5-phenylnon-4-ene was obtained as an oil, b.p. 80-82°/0.6 mm., $n_D^{15}$ 1.4985 (lit.,[29] 1.5012).

Found: C, 89.4; H, 10.7.

Calc. for $C_{15}H_{22}$: C, 89.0; H, 11.0%.

Its infrared spectrum was identical with that of an authentic specimen. The yield of 5-phenylnon-4-ene was 16.0%.

Fraction (c) showed, on examination with the infrared spectroscopy, strong absorption at 3030 (aromatic C-H), at 2874 (aliphatic C-H), at 1595 $cm^{-1}$ (C = C), and bands between 1942 and 1740 $cm^{-1}$ typical of monosubstituted benzene derivatives. It seems likely that this is 5-phenyloctadecane (?).

Found: C, 88.4; H, 10.8.

$C_{24}H_{36}$ requires: C, 88.8; H, 11.2%.

Fraction (d) was again distilled, to give 5,14-diphenyloctadecane, b.p. 180-182°/0.25 mm., $n_D^{23}$ 1.5150.

Found: C, 88.65; H, 11.0%; M (Rast), 395.

$C_{30}H_{46}$ requires: C, 88.6; H, 11.4%; M, 406.6.

The alternative possible product, namely, 1,1,2,2-tetra-n-butyl-1,2-diphenylethane, is reported[30] to have m.p. 63°. The yield of 5,14-diphenyloctadecane was 6.38%.

Fraction (e) was again recrystallised, to give biphenyl as plates, m.p. and mixed m.p. 69-70°. The infrared and ultraviolet spectra of the plates were also identical in every respect with those of the authentica specimen. The yield of this product was 17.01%.

The residue obtained from the ignition test of fraction (f) was found the presence of magnesium. The sodium fusion test of the crystals showed the presence of bromide ions. The compound was readily soluble in water. It seems likely that this product is magnesium ethoxy bromide formed during the Grignard reaction of the starting material.

Repetition of this desulphurisation, with an increased amount of Raney nickel (from 450 g. of alloy) which was added to a reaction mixture in one lot, gave biphenyl in 70% yield, and no liquid product was isolated.

Dehydration of 5-Phenylnonan-5-ol.- The alcohol, b.p. 165-166°/6 mm., was obtained in 82.1% yield by Petrov's method.[31] It was refluxed with a trace of iodine for 0.5 hr., giving 5-phenylnon-4-ene, b.p. 142-145°/13 mm. (4.27 g.), $\nu_{max}$ 3040 (C = C), 3030 (aromatic CH), 2967 ($CH_3$ stretching), 2857 ($CH_2$ stretching), 1597 (conjugated C = C), and a pattern of bands between 1942 and 1740 $cm^{-1}$ (monosubstituted benzene).

Found: C, 89.0; H, 10.6.

Calc. for $C_{15}H_{22}$: C, 89.0; H, 11.0%.

Hydrogenolysis of 5-Phenylnonan-5-ol.- This alcohol (2.0 g.) and W-7 Raney nickel (from 30 g. of alloy) in methanol (25 c.c.) were refluxed for 1½ hr. The resulting 5-phenylnonane (1.5 g.) had b.p. 100°/3.5 mm., $n_D^{18}$ 1.4851 (lit.,[29] 1.4874).

Found: C, 88.1; H, 11.7.

Calc. for $C_{15}H_{14}$: C, 88.2; H, 11.8%.

*Attempted Reaction of Ethyl Benzoate with W-7 Raney Nickel.*– A mixture of ethyl benzoate (5.0 g.) and W-7 Raney nickel (from 55 g. of alloy) in sulphur-free benzene (100 c.c.) was refluxed with stirring for 4 hr. The catalyst was separated on Celite and subsequently extracted with benzene (Soxhlet) overnight. Evaporation of the combined filtrates and extracts gave a residue which was distilled at 87°/10 mm. to give the unchanged ethyl benzoate (4.61 g., 92.2%). No other product could be isolated from the residue (0.12 g.).

*Preparation of 1-Naphthoyl Chloride.*– 1-Bromonaphthalene was obtained in 72.5% yield according to the method of Clarke and Brethen.[30] This was subjected to the Grignard reaction by the method of Gilman, St. John, and Schulze[31] to give 1-naphthoic acid in 71.2% yield. The mixture of dried 1-naphthoic acid (25 g.), redistilled thionylchloride (30 g.) and anhydrous benzene (100 c.c.) was refluxed for 1 hr. The excess of thionyl chloride and benzene were removed by distillation and the residue was distilled to give 1-naphthoyl chloride (24.81 g., 89.61%) at 115°/0.5 mm. as colourless liquid.

*Preparation of 1-Naphthyl Phenyl Ketone.*– 1-Naphthoyl chloride (24.61 g.) was added to the mixture of finely powdered aluminium chloride (19.09 g.) in anhydrous benzene (300 c.c.) in the usual manner of Friedel-Crafts ketone synthesis. Working up in the customary way gave 1-naphthyl phenyl ketone at 154°/1.2 mm., m.p. 75.5° (lit.[37] m.p. 75.5°), (20.45 g., 67.8%).

Preparation of α-1-Naphthyl-α-2-thienylbenzyl Alcohol.- The following procedure for preparation of this alcohol was superior to that of Minnis.[34] 1-Naphthyl phenyl ketone (23.2 g.) in anhydrous benzene (150 c.c.) was added during 2 hr. to a Grignard solution prepared from 2-bromothiophen (18.75 g.) in anhydrous ether. Decomposition was effected under nitrogen with 20% aqueous ammonium chloride. The ether-benzene layer was washed, dried and evaporated under reduced pressure in nitrogen. The residue crystallised from benzene under nitrogen, to give prisms, m.p. 134.5-135° (27.1 g., 85.8%) (lit.[34] 131°).

Desulphurisation of α-1-Naphthyl-α-2-thienylbenzyl Alcohol.- W-7 Raney nickel (from 125 g. of alloy) was added to this alcohol (25 g.) in sulphur-free benzene (150 c.c.), and the mixture stirred and refluxed for 4 hr. The catalyst was collected on Celite and extracted (Soxhlet) with benzene overnight. The combined filtrates and extracts were evaporated and the residue was distilled, to give:

(a) a yellow viscous oil, b.p. 137°/0.05 mm., $n_D^{16.5}$ 1.6108 (15.19 g.); and

(b) a dark violet residue (5.67 g.).

The infrared spectrum of fraction (a) showed no OH band, but bands at 2967 ($CH_3$ stretching) and 3030 $cm^{-1}$ (aromatic CH stretching) were found. It is, therefore, 1,1'-naphthyl-1-phenylpentane.

Found: C, 91.6; H, 8.6%; M (Rest), 262

$C_{21}H_{22}$ requires: C, 91.9; H, 8.1%; M, 274.4.

No pure product was obtained on chromatography of fraction (b).

Preparation of 9-2'-Thienylfluoren-9-ol.- In Minnis's procedure[34] for preparation of this fluorenol, 2-bromothiophen was substituted for 2-iodothiophen, and filtration and washing were omitted. In the present study, attempts to recrystallise the product without decomposition were unsuccessful. The desulphurisation of this alcohol was effected by its magnesium complex.

Desulphurisation of 9-2'-Thienylfluoren-9-ol. (Grignard Complex).- W-7 Raney nickel (from 250 g. of alloy) was added to a suspension of the magnesium complex of the alcohol (prepared from fluorenone, 2-bromothiophen, and magnesium, on a 0.1 molar scale) in ether-benzene, and sulphur-free benzene was added to bring the volume up to 400 c.c. The stirred mixture was refluxed under dry oxygen-free nitrogen for 3½ hr. A test showed that desulphurisation was incomplete (red colour), so a further quantity of Raney nickel (from 125 g. of alloy) was added and refluxing continued for 5 hr. The catalyst was collected, washed with benzene (2 x 50 c.c.), and extracted successively with benzene and methanol, each for 2 days. The combined filtrates and extracts were evaporated and the residue was distilled, to give

(a) a yellow viscous oil, b.p. 120°/0.2 mm. (15.62 g.); and

(b) a residue (3.0 g.)

Redistillation of fraction (a) gave 9-butylfluorene, b.p. 121-122°/0.2 mm., $n_D^{16.5}$ 1.5908 (lit.,[35] $n_D^{20}$ 1.5950).

Found: C, 91.3; H, 8.3%; M (Rast), 214.

Calc. for $C_{17}H_{18}$: C, 91.8; H, 8.2%; M, 222.

Satisfactory analyses could not be obtained owing to the rapid oxidation of this material. Its ultraviolet absorption spectrum in 95% ethanol showed maxima at 267.5, 292, and 304 mμ; and was similar to that of 9-methylfuorene ($\lambda_{max.}$ 263, 280, 300 mμ).[36]

Distillation of fraction (b) gave (c) an intense yellow oil, b.p. 146-147°/1.2 mm. (0.27 g.), and (d) a red residue.

Fraction (c) crystallised, and recrystallised from light petroleum (b.p. 60-90°) gave colourless needles, m.p. 115-116° (21 mg.). This product did not form a picrate; it was not identical with fluorene and was not identified. Concentration of the mother-liquors gave two further unidentified products: one with m.p. 195-196° (2 mg.); the other as prisms, m.p. 127.5-128.5° (37.5 mg.).

Fraction (d) was chromatographed on alumina in hexane and eluted with hexane-benzene. Recrystallisation from toluene gave 9,9'-di-2''-thienyl-9,9'-bifluorenyl as needles, m.p. 269-270° (0.24 g.).

Found: C, 82.3; H, 5.1; S, 12.7.

$C_{34}H_{24}S_2$ requires: C, 82.2; H, 4.9; S, 12.9%.

The yield of 9-n-butylfluorene was 69.82% and of 9,9'-di-2''-thienyl-9,9'-bifluorenyl was 4.86%.

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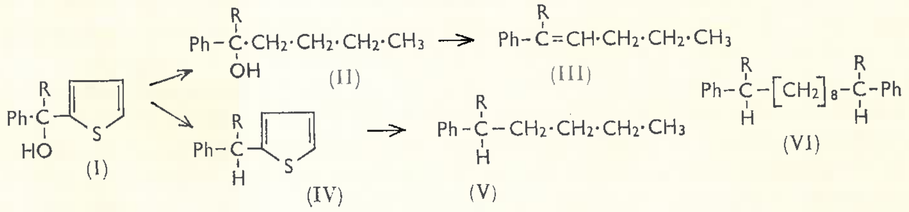
# **624.** *Synthetical Applications of Activated Metal Catalysts. Part XIII.** *The Desulphurisation of Alcohols Derived from Thiophen.*

By G. M. Badger, P. Cheuychit, and W. H. F. Sasse.

Desulphurisation of α-2-thienylbenzyl alcohols (I) has been shown to proceed by two mechanisms. The first involves desulphurisation to the pentanol (II) which is then dehydrated to the olefin (III); the second involves hydrogenolysis of the hydroxyl group in (I) or (II), and desulphurisation to give the saturated hydrocarbon (V). " Dimeric " products (VI) have also been found.

Desulphurisation of suitably substituted acidic derivatives of thiophen has been shown to provide a convenient route for the preparation of many long-chain fatty acids;[1, 2] and many branched-chain acids are more accessible by this route than by any other. Dicarboxylic acids, keto-acids, hydroxy-acids, amino-acids, and a few ketones, alcohols, and hydrocarbons have been prepared by modifications of the method.[1, 3] In order to examine further the synthetical applications of the desulphurisation reaction, several α-2-thienylbenzyl alcohols and related compounds have now been desulphurised. These reactions were effected in benzene or methanol with W-7 Raney nickel.

Desulphurisation of α-2-thienylbenzyl alcohols (I) might be expected to give the alkanols (II), which could suffer ready dehydration to the olefins (III). On the other hand, hydrogenolysis of the hydroxy-group to give compounds (IV) would also be expected, and on desulphurisation these would give the saturated hydrocarbons (V). Similarly, the alcohols (II) would be expected to undergo some hydrogenolysis to the saturated compounds (V). The results obtained in the present investigation indicate that both mechanisms must operate, but in varying degree. Intractable mixtures of alcohol (II), olefin (III), and saturated compound (V) were sometimes formed, and these were worked up by dehydration and reduction to give the saturated compound.



It now seems to be established that desulphurisations over Raney nickel proceed by a radical mechanism, and in a few cases the " dimerisation " of such intermediate radicals (rather than their hydrogenation) has been demonstrated.[4] Dimerisation of the intermediate radical expected from the action of Raney nickel on the 2-benzylthiophens (IV) would give the hydrocarbons (VI), and it is significant that compounds of this type were observed among some of the reaction products. The same hydrocarbons (VI) could also be formed by dimerisation of the radical intermediate from the action of Raney nickel on the sulphur atom in the alcohol (I), followed by removal of the hydroxyl group by hydrogenolysis. Unsaturated dimeric products were not observed in the present work.

Desulphurisation of α-2-thienylbenzyl alcohol (I; R = H) gave 1-phenylpentane (V; R = H) as the major product, together with some 1,10-diphenyldecane (VI; R = H). No alcohol (II) or olefin (III) was detected among the products, and it seems, therefore, that reaction proceeded entirely by the second mechanism. Desulphurisation of α-methyl-

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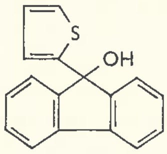
* Part XII, *J.*, 1961, 1347.

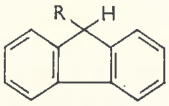
α-2-thienylbenzyl alcohol (I; R = Me) proceeded similarly, to give 2-phenylhexane (V; R = Me), but in this case no dimeric product (VI) could be isolated. On the other hand, the desulphurisation of diphenyl-2-thienylmethanol (I; R = Ph) gave a mixture containing both alcohol and olefin, and as this mixture could not be separated it was completely dehydrated and then hydrogenated, to give 1,1-diphenylpentane (V; R = Ph); extraction of the catalyst gave an oil which gave correct analyses for 1,1-diphenylpent-1-ene; a small amount of dimeric product, 1,1,10,10-tetraphenyldecane (VI; R = Ph) was also isolated.

The desulphurisation of αα-di-2-thienylbenzyl alcohol (I; R = $C_4H_3S$) gave a mixture of alcohol and olefin which was completely dehydrated to give 5-phenylnon-4-ene (III; R = Bu$^n$). No saturated compound (V) was found, but the dimeric product 5,14-diphenyloctadecane (VI; R = Bu$^n$) was isolated. Two further compounds were also obtained. The first is provisionally regarded as 5-phenyloctadecane; the second was characterised as biphenyl. This isolation of biphenyl is of some interest as it evidently means that phenyl radicals were liberated at some stage in the desulphurisation of the alcohol. The biphenyl was not derived from any unchanged ethyl benzoate in the reaction mixture, as this compound was recovered unchanged following treatment with W-7 Raney nickel in boiling benzene. It is also noteworthy that the desulphurisation of αα-di-2-thienylbenzyl alcohol with a very large excess of Raney nickel gave biphenyl in 70% yield.

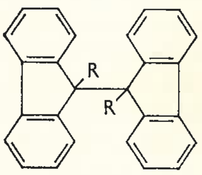
Desulphurisation of α-1-naphthyl-α-2-thienylbenzyl alcohol (I; R = $C_{10}H_7$) gave the saturated compound, 1-1′-naphthyl-1-phenylpentane (V; R = $C_{10}H_7$), and no alcohol or olefin could be found. The high-boiling fraction proved to be intractable, and no dimeric product (VI) was isolated.



(VII)



(VIII)



(IX)

Finally, the desulphurisation of 9-2′-thienylfluoren-9-ol (VII) gave 9-n-butylfluorene (VIII; R = Bu$^n$), presumably by hydrogenolysis of the hydroxyl group followed by desulphurisation. This view is also supported by the isolation of some undesulphurised dimeric product, namely, 9,9′-di-2″-thienyl-9,9′-bifluorenyl (IX; R = $C_4H_3S$).

In the preceding discussion, it has been assumed that the saturated compounds (V) were formed from the alcohols (I) by way of either (IV) or (II), that is, by hydrogenolysis of the hydroxyl group. A small proportion of the saturated compound could conceivably arise by dehydration of the alcohol (II) in the reaction mixture, followed by subsequent hydrogenation of the resulting olefin (III). The alcohols (II) are certainly dehydrated when heated with a trace of iodine (this has been achieved in several instances); but it seems very unlikely that these alcohols (II) would be dehydrated during treatment with alkaline Raney nickel. It is much more reasonable to suppose that the olefins are formed by dehydration of the alcohols during the working-up, which involves a high-temperature distillation. The variation in the amount of olefin formed also supports the view that these products are not intermediates (at least, not to any significant extent) in the formation of the saturated hydrocarbons (V).

It has also been confirmed in two instances that the alcohols do, in fact, undergo hydrogenolysis on treatment with Raney nickel and boiling methanol. In this way 2-phenylhexan-2-ol gave 2-phenylhexane; and 5-phenylnonan-5-ol gave 5-phenylnonane.

## EXPERIMENTAL

*Raney Nickel.*—W-7 Raney nickel was prepared by the usual method, except that methanol was used instead of ethanol in the washing process, and centrifigation was replaced by simple decantation. For desulphurisations in benzene the Raney nickel was washed three times with distilled water, ten times with methanol (redistilled over potassium hydroxide), and, finally, ten times with sulphur-free benzene. The Raney nickel was freshly prepared for every desulphurisation.

*Desulphurisation of α-2-Thienylbenzyl Alcohol.*—Freshly redistilled benzaldehyde (10·61 g.) in anhydrous sulphur-free benzene (20 ml.) was added dropwise to a boiling Grignard solution from 2-bromothiophen[5] (18·75 g.) and magnesium (2·64 g.) in anhydrous ether. Benzene (20 ml.) was then added and refluxing continued for 1 hr. After recrystallisation of the product from benzene–light petroleum (b. p. 60—90°) α-2-thienylbenzyl alcohol (14·31 g., 75·3%) formed needles, m. p. 56—57° (lit.,[6] 57—58°). A mixture of this product (9·0 g.) and W-7 Raney nickel (from 125 g. of alloy) in sulphur-free benzene (200 ml.) was stirred and refluxed for 3 hr. The catalyst was collected, washed with pure benzene (2 × 25 ml.), and then extracted with benzene (Soxhlet) for 3 days. The combined filtrates and extracts were evaporated, and the residue was distilled, to give (*a*) an oil, b. p. 94°/9 mm. (4·07 g.), (*b*) an oil, b. p. 140°/1 mm. (1·23 g.), and (*c*) a residue (0·02 g.). Fraction (*a*) was identified as 1-phenylpentane by comparison of its infrared spectrum with that of an authentic specimen (Found: C, 89·4; H, 10·7. Calc. for $C_{11}H_{16}$: C, 89·1; H, 10·9%). Redistillation of fraction (*b*) gave 1,10-diphenyldecane as an oil, $n_D^{15}$ 1·5318 (lit.,[7] $n_D^{20}$ 1·5281), which crystallised on cooling to give prisms, m. p. 15—16° (lit.,[7, 8] 12°, 17·5°) (Found: C, 89·3; H, 10·0. Calc. for $C_{22}H_{30}$: C, 89·7; H, 10·3%). The alternative possible structure, namely, 5,6-diphenyldecane, is reported[9] to have m. p. 80°. The residue (*c*) was not examined.

*Desulphurisation of α-Methyl-α-2-thienylbenzyl Alcohol.*—A solution of 2-acetylthiophen (12·6 g.) in anhydrous benzene was added to a Grignard solution from freshly redistilled bromobenzene (18·06 g.) in anhydrous ether. The resulting alcohol (I; R = Me) (19·17 g., 94·4%) had m. p. 50° (lit.,[10] 50°).

W-7 Raney nickel (from 62·5 g. of alloy) was added to a solution of this alcohol (5·0 g.) in sulphur-free benzene (100 ml.), and the mixture stirred and refluxed for 4 hr. The catalyst was collected on Celite and extracted with methanol (Soxhlet) for 32 hr. Evaporation of the combined filtrates and distillation of the product gave (*a*) an oil, b. p. 110—112°/12 mm. (0·12 g.), (*b*) an oil, b. p. 112—116°/12 mm. (2·965 g.), and (*c*) a residue (0·012 g.). Fractions (*a*) and (*b*) gave almost identical infrared spectra, and bands characteristic for OH and C=C groups could not be observed. Nevertheless, to ensure complete removal of any alcoholic or unsaturated product, fraction (*b*) (2 g.) was redistilled over a crystal of iodine and the distillate treated with hydrogen (800 lb./in.$^2$) and platinum–charcoal in absolute ethanol (50 ml.) at 70° for 6 hr. Redistillation gave 2-phenylhexane (1·61 g.) as an oil, b. p. 101—102°/5 mm., $n_D^{26}$ 1·4912 (lit.,[11] $n_D^{15}$ 1·4920) (Found: C, 89·0; H, 11·0. Calc. for $C_{12}H_{18}$: C, 88·8; H, 11·2%). Its infrared spectrum was identical with that given by an authentic specimen. Attempts to crystallise the residue (*c*) were unsuccessful.

*Dehydration of 2-Phenylhexan-2-ol.*—2-Phenylhexan-2-ol was prepared in 84% yield from acetophenone and n-butylmagnesium bromide. Dehydration was effected by refluxing the alcohol (5 g.) with a trace of iodine for 30 hr.[12] The product was washed with aqueous sodium hydrogen sulphite and extracted in ether, the ether solution dried and evaporated, and the residue distilled, to give 2-phenylhex-2-ene, b. p. 62—63°/0·7 mm. (4·235 g.), $n_D^{17·5}$ 1·5258 (lit.,[13] $n_D^{20}$ 1·5200) (Found: C, 89·6; H, 10·1. Calc. for $C_{12}H_{16}$: C, 89·9; H, 10·1%). However, the product was still contaminated with traces of starting material as indicated by the presence of weak bands at 3650 (OH stretching) and 1150 cm.$^{-1}$ (OH deformation).

*Hydrogenolysis of 2-Phenylhexan-2-ol.*—A mixture of 2-phenylhexan-2-ol (5·0 g.), W-7 Raney nickel (from 62·5 g. of alloy), and methanol (to make total volume 80 ml.) was refluxed for 3 hr. The catalyst was collected on Celite and washed with methanol (3 × 50 ml.). The combined filtrates were poured into water, the product was extracted into ether, the ether solution dried and evaporated, and the residue distilled. The 2-phenylhexane obtained had b. p. 93—94°/1 mm. (3·9 g.), $n_D^{17·5}$ 1·4862 (lit.,[11] $n_D^{15}$ 1·4920) (Found: C, 89·1; H, 11·3. Calc. for $C_{12}H_{18}$: C, 88·8; H, 11·2%). Its infrared spectrum was identical with that given by an authentic specimen.

*Desulphurisation of Diphenyl-2-thienylmethanol.*—Recrystallised benzophenone (18·2 g.) in anhydrous benzene was added to the Grignard solution from 2-bromothiophen (18·75 g.) in anhydrous ether. Recrystallisation of the product from benzene–light petroleum (b. p. 30—40°) gave diphenyl-2-thienylmethanol as light brown prisms, m. p. 128° (23·6 g., 88·3%) (lit.,[14] 129—130°).

W-7 Raney nickel (from 125 g. of alloy) was added to the above alcohol (8 g.) in sulphur-free benzene (80 ml.), and the mixture stirred and refluxed for 1 hr. The catalyst was collected and washed with pure benzene (2 × 50 ml.), the combined filtrates were evaporated, and the product distilled to give (*a*) an oil, b. p. 108—110°/15 mm. (0·38 g.), (*b*) an oil, b. p. 110—112°/15 mm. (3·44 g.), and (*c*) a residue fluorescing yellow-green (1·0 g.). Fractions (*a*) and (*b*) gave identical infrared spectra, having a weak OH band at 3650 cm.$^{-1}$. They also decolorised bromine in carbon tetrachloride, and potassium permanganate in acetone; and they both gave a deep yellow solution when added to tetranitromethane. The product was accordingly treated to remove any alcohol and unsaturated material. Fraction (*b*) was refluxed for 0·5 hr. with a trace of iodine, and the product treated with hydrogen (800 lb./in.$^2$) and platinum–charcoal in absolute ethanol at 50—60°. The resulting 1,1-diphenylpentane was obtained as an oil, b. p. 180°/12 mm., $n_D^{25}$ 1·5480 (lit.,[15] $n_D^{20}$ 1·5511) (Found: C, 91·3; H, 9·1. Calc. for $C_{17}H_{20}$: C, 91·0; H, 9·0%).

Light petroleum (b. p. 30—40°) was added to the residue (*c*); concentration gave colourless needles (0·27 g.), m. p. 90—91°. Recrystallisation from n-hexane gave 1,1,10,10-*tetraphenyldecane* as needles, m. p. 90—91° [Found: C, 91·2; H, 8·6%; *M* (Rast), 494, 468. $C_{34}H_{38}$ requires C, 91·4; H, 8·6%; *M*, 446·6]. The theoretically alternative structure, 5,5,6,6-tetraphenyldecane, is reported[16] to have m. p. 62—63° (air) or 68—70° (nitrogen). Concentration of the mother-liquors gave a further quantity (0·40 g.) of 1,1-diphenylpentane, $n_D^{20}$ 1·5505, having an infrared spectrum identical with that of the material above (Found: C, 91·0; H, 8·9%).

Extraction of the catalyst with benzene in a Soxhlet for 48 hr. gave a further fraction (*d*) (0·15 g.), and subsequent extraction with methanol gave an additional fraction (*e*) (0·15 g.). Fraction (*d*) was redistilled at 8 mm. (bath-temperature 200°), to give an oil (mainly 1,1-diphenylpent-1-ene?) (Found: C, 92·0; H, 8·5. Calc. for $C_{17}H_{18}$: C, 91·8; H, 8·2%); similar distillation of fraction (*e*) gave an oil (Found: C, 91·2; H, 8·3%).

*Desulphurisation of αα-Di-2-thienylbenzyl Alcohol.*—Preliminary experiments showed that this alcohol is extremely unstable in the presence of light and air. The following experiment was therefore carried out in a dark room, and all reaction mixtures were covered with an atmosphere of dry oxygen-free nitrogen.

Ethyl benzoate (7·5 g.) in anhydrous sulphur-free benzene (40 ml.) was added dropwise to a Grignard solution prepared from freshly distilled 2-bromothiophen (18·75 g.) and magnesium (2·64 g.) in anhydrous ether (70 ml.). Gentle warming was required during the addition, and when this was complete the mixture was refluxed for 3 hr. W-7 Raney nickel (from 250 g. of alloy) was then added to the cooled mixture, which was made up to *ca.* 250 ml. with pure benzene. The mixture was then stirred and refluxed for 12 hr., and tested for completeness of desulphurisation (by withdrawing a small amount of mixture and exposing it to light and air: when reaction was incomplete, the mixture rapidly became dark violet). More Raney nickel (from 125 g. of alloy) was added if required, and refluxing continued for 4 hr. The catalyst was collected on Celite and washed with sulphur-free benzene (3 × 50 ml.), and the combined filtrates were evaporated, and the residue was distilled, to give a forerun (*a*), b. p. 158—160°/9 mm. (0·11 g.), fraction (*b*), b. p. 160—164°/9 mm. (3·23 g.), fraction (*c*) [which was distilled at a bath temperature of 160° and 0·5 mm. to give an oil (0·12 g.)], and a dark violet residue (*d*) (1·35 g.) [which, after chromatography on alumina in hexane and subsequent distillation, gave a yellow oil, b. p. 174—175°/0·2 mm. (1·2 g.)]. Extraction of the catalyst with benzene (Soxhlet) and evaporation gave a further fraction (*e*) which, after recrystallisation from absolute ethanol, yielded plates, m. p. 69—70° (2·62 g.). The infrared spectrum of fraction (*a*) showed strong absorption at frequencies corresponding to C–H stretching vibrations in methyl, methylene, and phenyl groups. No absorption was observed above 3100 cm.$^{-1}$, indicating the absence of a hydroxyl group.

Fraction (*b*) decolorised bromine in carbon tetrachloride, and potassium permanganate in acetone. Its infrared spectrum showed a band at 1603 (conjugated C=C), and a weak band at 3650 cm.$^{-1}$ (OH group). In addition, it showed absorption at 2874 ($CH_2$), and between 1940 and 1740 cm.$^{-1}$ (monosubstituted aromatic). It was redistilled in the presence of a trace of iodine and the resulting 5-phenylnon-4-ene was obtained as an oil, b. p. 80—82°/0·6 mm., $n_D^{15}$ 1·4985 (lit.,[17] 1·5012) (Found: C, 89·4; H, 10·7. Calc. for $C_{15}H_{22}$: C, 89·0; H, 11·0%). Its infrared spectrum was identical with that of an authentic specimen.

The infrared spectrum of fraction (*c*) showed strong absorption at 3030 (aromatic CH), at 2874 (aliphatic CH), at 1595 cm.$^{-1}$ (C=C), and bands between 1942 and 1740 cm.$^{-1}$ typical of monosubstituted benzene derivatives. It seems likely that this is *5-phenyloctadecane* (?) (Found: C, 88·4; 10·8. $C_{24}H_{36}$ requires C, 88·8; H, 11·2%).

Fraction (*d*) was again distilled, to give *5,14-diphenyloctadecane*, b. p. 180—182°/0·25 mm., $n_D^{23}$ 1·5150 [Found: C, 88·65; H, 11·0%; *M* (Rast), 395. $C_{30}H_{46}$ requires C, 88·6; H, 11·4%; *M*, 406·6]. The alternative possible product, namely, 1,1,2,2-tetra-n-butyl-1,2-diphenylethane, is reported [18] to have m. p. 63°.

Fraction (*e*) was again recrystallised, to give biphenyl as plates, m. p. and mixed m. p. 69—70°, with the authentic infrared and ultraviolet spectra.

Repetition of this desulphurisation, with an increased amount of Raney nickel (from 450 g. of alloy), gave biphenyl in 70% yield, and no liquid product was isolated.

*Dehydration of 5-Phenylnonan-5-ol.*—The alcohol, b. p. 165—166°/6 mm., was obtained in 82·1% yield by Petrov's method.[19] It was refluxed with a trace of iodine for 0·5 hr., giving 5-phenylnon-4-ene, b. p. 142—145°/13 mm. (4·27 g.), $\nu_{max.}$ 3040 (C=C), 3030 (aromatic CH), 2967 ($CH_3$ stretching), 2857 ($CH_2$ stretching), 1597 (conjugated C=C), and a pattern of bands between 1942 and 1740 cm.$^{-1}$ (monosubstituted benzene) (Found: C, 89·0; H, 10·6. Calc. for $C_{15}H_{22}$: C, 89·0; H, 11·0%).

*Hydrogenolysis of 5-Phenylnonan-5-ol.*—This alcohol (2·0 g.) and W-7 Raney nickel (from 30 g. of alloy) in methanol (25 ml.) were refluxed for $1\frac{1}{2}$ hr. The resulting 5-phenylnonane (1·5 g.) had b. p. 100°/3·5 mm., $n_D^{18}$ 1·4851 (lit.,[17] 1·4874) (Found: C, 88·1; H, 11·7. Calc. for $C_{15}H_{24}$: C, 88·2; H, 11·8%).

*Desulphurisation of 9-2′-Thienylfluoren-9-ol.*—In Minnis's procedure [20] for preparation of this fluorenol, 2-bromothiophen was substituted for 2-iodothiophen, and filtration and washing were omitted. In our hands, attempts to recrystallise the product without decomposition were unsuccessful and the following procedure was adopted.

W-7 Raney nickel (from 250 g. of alloy) was added to a suspension of the magnesium complex of the alcohol (prepared from fluorenone, 2-bromothiophen, and magnesium, on a 0·1-molar scale) in ether–benzene, and sulphur-free benzene was added to bring the volume up to 400 ml. The stirred mixture was refluxed under dry oxygen-free nitrogen for $3\frac{1}{2}$ hr. A test showed that desulphurisation was incomplete (red colour), so a further quantity of Raney nickel (from 125 g. of alloy) was added and refluxing continued for 5 hr. The catalyst was collected, washed with benzene (2 × 50 ml.), and extracted (Soxhlet) successively with benzene and methanol, each for 2 days. The combined filtrates and extracts were evaporated and the residue was distilled, to give (*a*) a yellow viscous oil, b. p. 120°/0·2 mm. (15·52 g.), and (*b*) a residue (3·0 g.).

Redistillation of fraction (*a*) gave 9-butylfluorene, b. p. 121—122°/0·2 mm., $n_D^{16·5}$ 1·5908 (lit.,[21] $n_D^{20}$ 1·5950) [Found: C, 91·2; H, 8·3%; *M* (Rast), 214. Calc. for $C_{17}H_{18}$: C, 91·8; H, 8·2%; *M*, 222]. Satisfactory analyses could not be obtained owing to the rapid oxidation of this material. Its ultraviolet absorption spectrum in 95% ethanol showed maxima at 267·5, 292, and 304 mμ, and was similar to that of 9-methylfluorene ($\nu_{max.}$ 263, 290, 300 mμ).[22]

Distillation of fraction (*b*) gave (*c*) an intense yellow oil, b. p. 146—147°/1·2 mm. (0·27 g.), and (*d*) a red residue. Fraction (*c*) crystallised, and recrystallisation from light petroleum (b. p. 60—90°) gave colourless needles, m. p. 115—116° (21 mg.). This product did not form a picrate; it was not identical with fluorene and was not identified. Concentration of the mother-liquors gave two further unidentified products: one with m. p. 195—196° (2 mg.); the other as prisms, m. p. 127·5—128·5° (37·5 mg.).

Fraction (*d*) was chromatographed on alumina in hexane and eluted with hexane–benzene. Recrystallisation from toluene gave 9,9′-di-2″*-thienyl*)9,9′*-bifluorenyl* as needles, m. p. 269—270° (0·24 g.) (Found: C, 82·3; H, 5·1; S, 12·7. $C_{34}H_{24}S_2$ requires C, 82·2; H, 4·9; S, 12·9%).

*Desulphurisation of α-1-Naphthyl-α-2-thienylbenzyl Alcohol.*—The following procedure for preparation of this alcohol was superior to that of Minnis.[20] 1-Naphthyl phenyl ketone [23] (23·2 g.) in anhydrous benzene (150 ml.) was added during 2 hr. to a Grignard solution prepared from 2-bromothiophen (18·75 g.) in anhydrous ether. Decomposition was effected under nitrogen with 20% aqueous ammonium chloride. The ether–benzene layer was washed, dried, and evaporated under reduced pressure in nitrogen. The residue crystallised from benzene under nitrogen, to give prisms, m. p. 134·5—135° (27·1 g., 85·8%) (lit.,[20] 131°).

W-7 Raney nickel (from 125 g. of alloy) was added to this alcohol (25 g.) in sulphur-free benzene (150 ml.), and the mixture stirred and refluxed for 4 hr. The catalyst was collected on Celite and extracted (Soxhlet) with benzene overnight. The combined filtrates and extracts were evaporated and the residue was distilled, to give (*a*) a yellow viscous oil, b. p. 137°/0·05 mm., $n_D^{16\cdot5}$ 1·6108 (15·19 g.), and (*b*) a dark violet residue (5·67 g.). The infrared spectrum of fraction (*a*) showed no OH band, but bands at 2967 ($CH_3$ stretching) and 3030 cm.$^{-1}$ (aromatic CH stretching) were found. It is, therefore, 1-1′-*naphthyl*-1-*phenylpentane* [Found: C, 91·6; H, 8·6%; *M* (Rast), 262. $C_{21}H_{22}$ requires C, 91·9; H, 8·1%; *M*, 274·4]. No pure product was obtained on chromatography of fraction (*b*).

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UNIVERSITY OF ADELAIDE, SOUTH AUSTRALIA.

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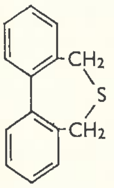
# **625.** *Synthetical Applications of Activated Metal Catalysts. Part XIV.* The Desulphurisation of* 2,7-*Dihydrodibenzo*[c, e]*thiepin.*

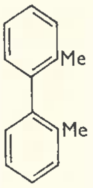
By G. M. BADGER, P. CHEUYCHIT, and W. H. F. SASSE.

THE formation of free radicals as intermediates in the desulphurisation of organosulphur compounds over Raney nickel has been postulated on many occasions.[1] Experimental support has been provided by the work of Hauptmann and his co-workers using hydrogen-free nickel,[2] by the formation of " dimeric " products during the desulphurisation of some thiophen derivatives,[3] by the formation of some bicycloheptane in addition to the expected 1,3-dimethylcyclopentane following desulphurisation of 6-thiabicyclo-octane,[4] and by the observation that desulphurisation of optically active α-phenyl-α-phenylthiopropionamide is accompanied by complete racemisation.[5] As a further contribution to this study the desulphurisation of 2,7-dihydrodibenzo[*c, e*]thiepin (I) has been examined, with a hydrogen-rich catalyst (W-7 Raney nickel), a hydrogen-deficient catalyst (W-7J Raney nickel), and a catalyst of medium activity (W-2 Raney nickel).

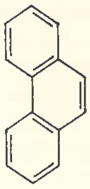
Use of W-7 Raney nickel gave the expected 2,2′-dimethylbiphenyl (II) in excellent yield. Use of neutral W-2 Raney nickel also gave this product, together with a trace of a compound believed to be a paraffin. Use of a Raney nickel which had been heated in a vacuum to reduce the hydrogen content (W-7J Raney nickel), however, gave a much smaller yield of the expected 2,2′-dimethylbiphenyl together with phenanthrene (III) and a dihydrophenanthrene (?) (not obtained pure; all purification processes seemed to result in some dehydrogenation to phenanthrene).



(I)



(II)


(III)

The isolation of phenanthrene is consistent with the view that the removal of the sulphur atom gives first a diradical. In the presence of an excess of hydrogen this is reduced to 2,2′-dimethylbiphenyl; but in its absence this diradical is largely converted into dihydrophenanthrene and thence phenanthrene. The steric arrangement of the diradical facilitates this cyclisation.

*Experimental.*—2,7-*Dihydrodibenzo*[c, e]*thiepin.* 2,2′-Dimethylbiphenyl[6] was prepared by the Ullmann reaction from *o*-iodotoluene, and brominated to give 2,2′-bisbromomethylbiphenyl.[7] Treatment with sodium sulphide, by the method of Truce and Emrick,[8] gave 2,7-dihydrodibenzo[*c, e*]thiepin as prisms (from absolute ethanol), m. p. 89—90° (lit.,[8] 89—90°).

*Raney nickel.* W-7 Raney nickel was prepared by the method of Billica and Adkins,[9] except that the catalyst was washed with methanol instead of ethanol. W-2 Raney nickel was prepared as described by Ralph and Mozingo[10] and washed with a continuous stream of distilled water until neutral to litmus, then with methanol by decantation. W-7J Raney nickel was prepared by the method of Badger and Sasse.[11]

*Desulphurisation with W-7 Raney nickel.* The dihydrodibenzothiepin (3 g.) was added to a suspension of W-7 Raney nickel (from 30 g. of alloy) in methanol (200 ml.), and the mixture refluxed for ½ hr. The catalyst was collected with Celite, washed with hot methanol (3 × 100 ml.), and extracted with methanol (Soxhlet) overnight. The combined filtrates and extracts were evaporated. Distillation of the dried residue gave 2,2′-dimethylbiphenyl (2·35 g., 91%) and a yellow wax (0·063 g.). No impurity could be detected in the dimethylbiphenyl by gas-

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* Part XIII, preceding paper.

liquid chromatography (Griffin and George VPC mark II), and the retention time was identical with that of an authentic specimen. Recrystallisation of the product from absolute ethanol (freezing mixture) gave the dimethylbiphenyl as prisms, m. p. and mixed m. p. 18°.

*Desulphurisation with W-2 Raney nickel.*—The dihydrodibenzothiepin (10 g.) was added to a suspension of W-2 Raney nickel (from 150 g. of alloy) in methanol (600 ml.), and the mixture refluxed for 2 hr. After working up as before, the product was distilled, to give 2,2′-dimethylbiphenyl (7·08 g.) and a residue (0·72 g.). The latter was chromatographed on alumina in light petroleum (b. p. 40—70°) and gave a further quantity of 2,2′-dimethylbiphenyl (0·42 g., total yield, 87·4%) and a colourless solid (0·008 g.), $\nu_{max.}$ (in $CCl_4$) 2867 ($CH_2$), 2860 and 1450 cm.$^{-1}$ ($C$-$CH_3$).

*Desulphurisation with W-7J Raney nickel.* Xylene (sulphur-free; 200 ml.) was cautiously added from a separating funnel to the dry W-7J Raney nickel (from 125 g. of alloy) in a vacuum. The dihydrodibenzothiepin (10 g.) in sulphur-free xylene (300 ml.) was then run in slowly, followed by more xylene (100 ml.). The mixture was refluxed for 15 hr., and the catalyst was collected over Celite, washed with boiling xylene (2 × 50 ml.), and then extracted with xylene (Soxhlet) for 36 hr. Evaporation of the combined xylene filtrates and extracts, and distillation, gave 2,2′-dimethylbiphenyl (2·56 g., 29·8%) and a brown residue (6·9 g.). Chromatography of the residue in hexane on alumina gave (*a*) a pale yellow wax (2·4 g.), (*b*) plates, m. p. 92—94° (2·18 g.), (*c*) prisms (1·37 g.), and (*d*) prisms (0·91 g.).

Fraction (*a*) was chromatographed on partially acetylated paper (prepared by the method of Spotswood [12]), with ethanol–toluene–water (17 : 4 : 1 v/v). Under ultraviolet light two spots were seen: one showed blue fluorescence, the other violet. The spots were cut out and separately extracted into 95% ethanol. The extract from the violet-fluorescing area gave an absorption maximum at 252 mμ, identical with that given by phenanthrene [13] (which also had the same $R_F$ value). The extract from the blue-fluorescing area gave absorption maxima at 252 (phenanthrene) and 265 mμ (dihydrophenanthrene ?).[14] Attempts to separate the phenanthrene and dihydrophenanthrene by column chromatography on acetylated cellulose were unsuccessful, as was attempted separation by picrate formation. Recrystallisation of fraction (*b*) gave phenanthrene, m. p. and mixed m. p. 101°. Its picrate had m. p. 144° (lit., 144°), and its $R_F$ value was identical with that of an authentic specimen.

Fraction (*c*) was chromatographed on partially acetylated paper. Two spots were obtained. The first (violet-fluorescing) was identified as phenanthrene (ultraviolet spectrum); the second (brown in ultraviolet light) had the same $R_F$ value as the dihydrodibenzothiepin and the general appearance of the ultraviolet spectra was the same. Sodium-fusion of the crude fraction gave a positive test for sulphur.

Recrystallisation of fraction (*d*) gave dihydrodibenzothiepin, m. p. and mixed m. p. 89—90°.

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UNIVERSITY OF ADELAIDE, SOUTH AUSTRALIA.

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