THE FREE-RADICAL SUBSTITUTION OF FERROCENE AND THE STABILITY OF FERROCENYLMETHYL RADICAL

A thesis presented for the degree of Doctor of Philosophy

in

The University of Adelaide

by

G. G. Vickery, B.Sc.(Hons)

Department of Organic Chemistry, 1971.

CONTENTS

Statement

The work described in this thesis incorporates no material previously submitted for a degree in any University, except where due reference has been made.

(G. G. Vickery)

Acknowledgements

I wish to thank Professor A. L. J. Beckwith for his guidance and encouragement throughout this work.

I also thank both academic and technical staff members and colleagues who have helped me.

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Summary

The electron transfer between ferrocene and triphenylmethyl tetrafluoroborate has been shown to be moderately fast, and to be completely independent of the subsequent substitution of ferrocene.

Methyl-, isopropyl-, benzyl-, and phenyl-ferrocene have been mono-benzoylated by free-radical and electrophilic methods. For a particular ferrocene the isomer distributions of the products in both methods have been found to be identical. It was concluded that free-radical substitution of ferrocenium ion and electrophilic substitution of ferrocene pass through a common transition state. Some benzoylferrocenes which are inaccessible by electrophilic substitution may be synthesized by the free-radical route; the synthesis of p-benzoylferrocene in moderate yields was achieved.

The reaction of ferrocenium ion with alkyl radicals generated from triorganotin hydrides and alkyl halides was investigated. A value of c. 7×10^5 l. $mol^{-1}s^{-1}$ at 25^oC was derived for the rate constant for ferrocenium ion substitution by alkyl radicals.

The stability of ferrocenylmethyl radical has been investigated by studying the products obtained from the one-electron reductions of a series of alkyl(ferrocenylmethyl) quaternary ammonium salts. The stability of this radical is intermediate between that of benzyl and t-butyl radicals. A method of synthesizing ferrocenylmethylamines from ferrocenylmethanol and amines has been explored, and shown to depend upon the pH of the solution, and on the nature of the amine.

CHAPTER I.

INTRODUCTION

INTRODUCTION

Preamble

When Lavoisier[1] introduced the term "radical" in 1789 he could not have forseen the variety of meanings that this term would take or the volume of work devoted to the structure and reactions of radicals.

The first indication of the existence of free radicals as we now understand them is contained in Gomberg's work with "hexaphenylethanes" and triphenylmethyl radicals.[2] The initial proposals were received sceptically. Not until the tetraethyllead experiments[3] of Paneth and Hofeditz in 1929, was the existence of free radicals, as unstable intermediates in the gas-phase, generally recognised. Although extension of this concept to solution reactions was advanced at about this time, acceptance was slow. The work of Kharasch[4] led towards an understanding of the nature and course of free-radical reactions. Subsequent work has expanded knowledge of the scope and subtlety of these reactions so that they now form an important part of organic chemistry. Currently, a simple definition of a free radical is[5] "an atom or group of atoms with an unpaired elctron".

The following introduction consists of an elementary account of free-radical chemistry, followed by some salient features of ferrocene chemistry.

Unimolecular Radical Reactions

1. Rearrangement.

The simplest free-radical reaction is unimolecular rearrangement. Because of more favourable alternative reaction paths, free radicals usually do not rearrange at ordinary temperatures to the same extent as do carbonium ions.[6] However, rearrangement may be a frequently occurring phenomenon under some conditions,[7] especially at high temperatures.

There is little evidence for the 1,2- hydrogen shift, the simplest rearrangement. However, hydrogen shifts to more remote radical centres have been observed; the Barton-type rearrangement of long-chain hypochlorites to give δ-chloroalcohols is a 1,5- hydrogen shift from carbon to oxygen.[8]

1,2- Aryl shifts were first reported by Kharasch[9] and have been reviewed.[10] Aldehyde decarbonylation in the presence of t-butyl peroxide gives the most intensively studied rearrangement of this type.

2. Fragmentation.

Fragmentation can be illustrated by the well-known β-scission of t-butoxy radical[11] to give acetone and methyl radical (Scheme 1).

$$(CH_3)_3CO\cdot \longrightarrow CH_3COCH_3 + \cdot CH_3 \qquad \text{Scheme 1}$$

Bimolecular Radical Reactions

Disproportionation and dimerization are examples of bimolecular reactions of radicals with radicals.

$$2(C_6H_5C_6H_6)\cdot \longrightarrow C_6H_5C_6H_7 + C_6H_5C_6H_5 \quad \text{disproportionation}$$
$$2(C_6H_5C_6H_6)\cdot \longrightarrow (C_6H_5C_6H_6)_2 \quad \text{dimerization}$$

Scheme 2

Bimolecular reactions with one-electron-transfer agents are important; the ferrous-catalyzed reaction of hydroperoxides is an example[10] (Scheme 3).

$$\begin{array}{lll} Fe^{2+} + ROOH \longrightarrow Fe^{3+} + OH^- + RO\cdot & & \\ & & \text{Scheme 3} \\ Fe^{2+} + RO\cdot \longrightarrow Fe^{3+} + RO^- & & \end{array}$$

Reaction of free radicals with molecules may involve abstraction or addition.

1. Abstraction

Peripheral monovalent atoms such as hydrogen or halogen are usually involved in abstraction processes. Hydrogen abstractions in the gas phase[12,13] and in solution[13,14] have been the subject of reviews. Rates of hydrogen abstraction are influenced by polar factors and the strengths of bonds broken and formed. No satisfactory method has been found for quantifying polar effects although radical reactions with a series of aromatic compounds have been shown to obey Hammett relations.[13] Some limited equations have been derived[15] to relate the activation energies of radical reactions to bond strengths, and hence to heats of reaction; however, any one relationship will not even cover both alkanes and alkenes. Also, because the tunnel effect is important in hydrogen transfer, experimental values of the activation energy may be lower than anticipated for movement over the potential surface.

One of the best understood complex chain reactions involving hydrogen and halogen abstractions is the reduction of alkyl (and aryl) halides with organotin hydrides. This reaction is well-documented and has been reviewed.[16-18] Reduction can be represented by the following processes (Scheme 4);

Initiation $\longrightarrow$ $R\cdot$

Propagation

$R\cdot + R'_3SnH \longrightarrow RH + R'_3Sn\cdot$

$R'_3Sn\cdot + RX \longrightarrow R'_3SnX + R\cdot$

Termination

$$R\cdot + R\cdot \longrightarrow R_2$$

$$R\cdot + R'_3Sn\cdot \longrightarrow R'_3SnR$$

$$R'_3Sn\cdot + R'_3Sn\cdot \longrightarrow R'_3SnSnR'_3$$

Scheme 4

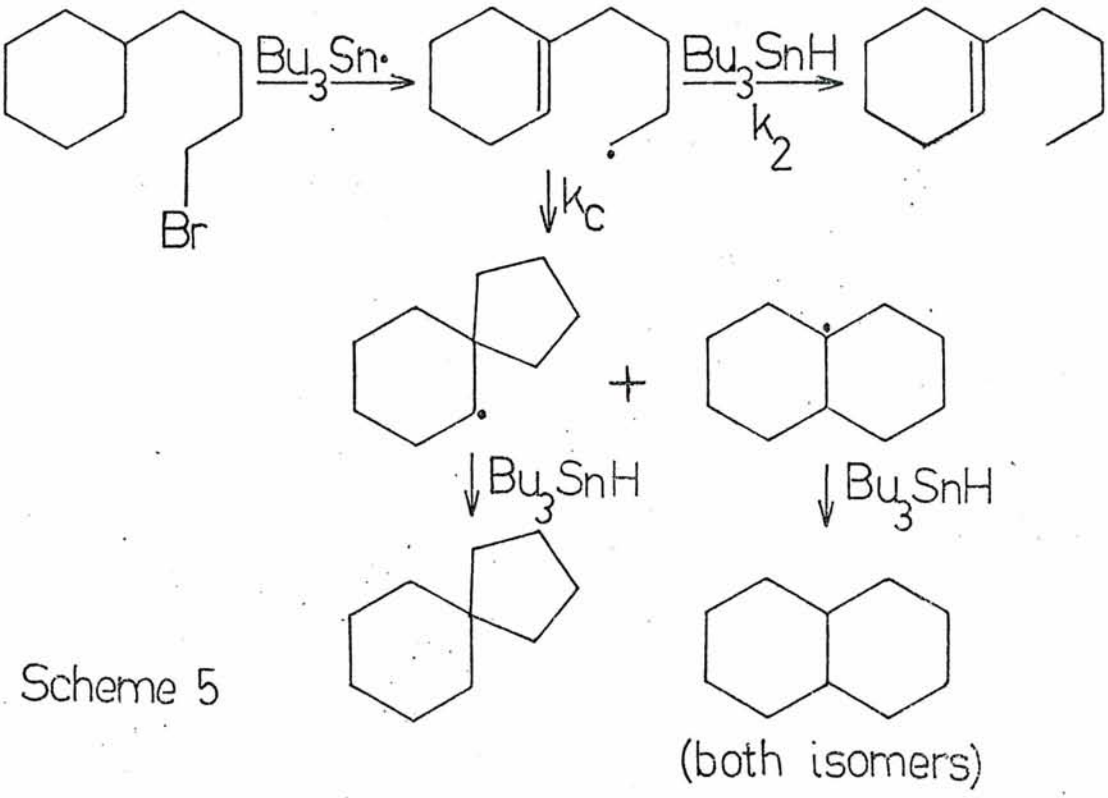
The propagation processes are simple abstractions. Kuivila[19] and others[20] have shown that the reactivity of an alkyl halide with a tin hydride increases in the order $RF < RCl < RBr < RI$, and for a particular halogen the reactivity order is primary<secondary<tertiary halide. Carlsson and Ingold[21] have determined absolute rate constants for the reduction by using the rotating sector method. Of particular interest for the following work (see II.3.) are the absolute values shown in Table 1. For a particular comparable group of reactions the variation in absolute values is at most only several powers of 10; for instance, triphenyltin hydride is only c. ten times more reactive than trimethyltin hydride. Hydrogen-atom abstraction from tin hydride shows an increase in the order t-butyl<cyclohexyl< methyl radical, and bromine atom is abstracted more readily than is chlorine atom by a particular tin hydride.

TABLE I

Absolute Rate Constants for Radical-Molecule Reactions in Cyclohexane at 25° (ref.[21])

Reaction	$k(l.mol^{-1}s^{-1})$
t-Bu· +Ph_3SnH	$3.1X10^6$
t-Bu· +n-Bu_3SnH	$7{\cdot}4X10^5$
t-Bu· +Me_3SnH	$2{\cdot}9X10^5$
C_6H_{11}· +n-Bu_3SnH	$1{\cdot}2X10^6$
Me· +n-Bu_3SnH	$5{\cdot}8X10^6$
n-Bu_3Sn· +t-BuCl	$1{\cdot}6X10^4$
n-Bu_3Sn· +$C_6H_{11}Br$	$2{\cdot}2X10^7$
n-Bu_3Sn· +t-BuBr	$8{\cdot}5X10^7$

By combining the absolute rate constants with the results obtained by other authors, approximate estimates of rate constants for a number of reactions were made.[21] For example, by judicious choice of an absolute value for k_2, the rate constant, k_c, for cyclization of the 4-(1-cyclohexenyl)-butyl radical[22] was calculated to be c. $4X10^4$ mol $l^{-1}s^{-1}$ (Scheme 5).



Scheme 5

Similarly, by setting up an appropriate competitive system, an approximate rate constant for the free-radical substitution of ferrocenium ion* could be determined (see II.3.).

2. Addition to Double Bonds.

Di- and tri-alkyltin hydrides add to olefins and acetylenes when catalyzed by free radicals and heated to moderate temperatures.[23,24] The reaction usually does not occur with

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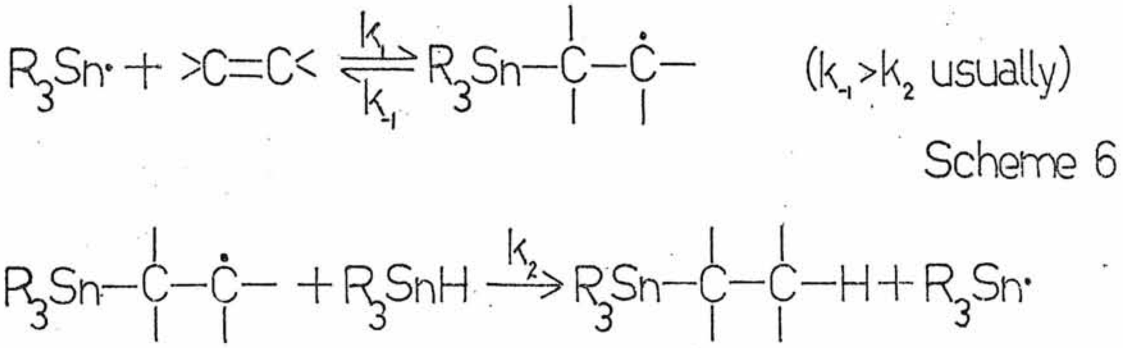
* From 1967 (*Chem.Abstr.*, 1967, 66.) this term replaced the previously used " ferricinium ion."

internal olefins, and is reversible.[23]



$$R_3Sn\cdot + {>}C{=}C{<} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_3Sn{-}\overset{|}{\underset{|}{C}}{-}\overset{\bullet}{\underset{|}{C}}{-}$$

(k₋₁>k₂ usually)

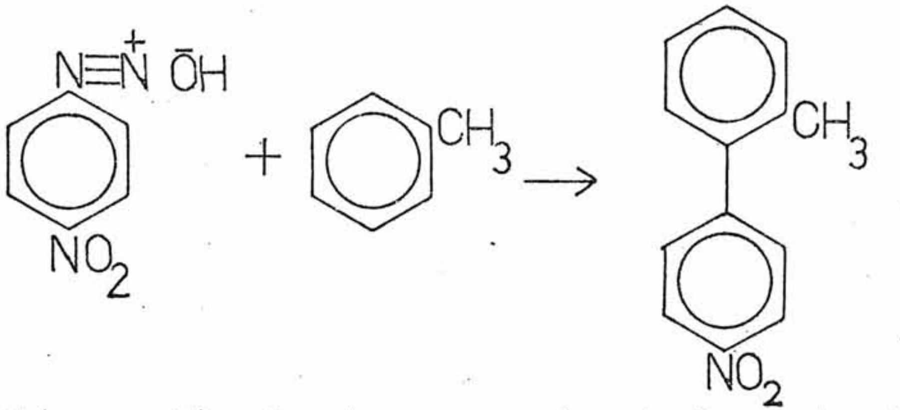
Scheme 6

$$R_3Sn{-}\overset{|}{\underset{|}{C}}{-}\overset{\bullet}{\underset{|}{C}}{-} + R_3SnH \xrightarrow{k_2} R_3Sn{-}\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}}{-}H + R_3Sn\cdot$$

The stability of the addition-produced radical will determine k and k_{-1}. Addition reactions are usually radical chains, affected markedly by light, oxygen, peroxides, and inhibitors, and, for a given set of experimental conditions, the yields of desired products will be determined by rates of initiation, propagation, and termination.[25] Complicating factors may include polymerization and allylic radical formation.

3. Arylation of Aromatic Compounds.

Of more relevance to this thesis (see II.3.) are free-radical arylations of aromatic compounds. The earliest example[26,33] is the fragmentation of p-nitrobenzene-diazonium hydroxide in the presence of toluene to give the appropriate product (Scheme 7).


Scheme 7

This reaction has been comprehensively reviewed.[27]

(a) Sources of aryl radicals

A number of reactions have been developed as sources of aryl radicals in solution. Among these are the decomposition of acylnitrosoamines,[28,33] and phenylazotriphenylmethane.[29] The most widely studied[27] sources of aryl radicals are diaroyl peroxides, which decompose via aroyloxy radicals. The reaction is relatively clean and the products easily isolated, enabling fundamental mechanistic work. The simplified reaction scheme is shown (Scheme 8).

$$(ArCO_2)_2 + C_6H_5R \longrightarrow ArC_6H_4R + ArCO_2H + CO_2$$

Scheme 8

Yields are significantly increased by oxygen[27] or catalytic amounts of nitro compounds.[30] Fragmentations also assumed to pass through the aroyloxy radical include those of phenyliodosobenzoate and silver iodide dibenzoate[31] (Scheme 9). Photochemical methods have been used to generate

$$\mathrm{PhI(OCOPh)_2 \longrightarrow PhI + 2PhCO_2\cdot \longrightarrow 2Ph\cdot + CO_2}$$

$$\mathrm{AgI(OCOPh)_2 \longrightarrow AgI + 2PhCO_2\cdot \longrightarrow 2Ph\cdot + CO_2}$$

Scheme 9

phenyl radicals from compounds with appropriately low bond strenths - usually aryl halides or organometallics.

(b) Mechanism of arylation.

Detailed mechanistic investigations of free-radical arylation of aromatic compounds have been facilitated by modern techniques, especially spectroscopy and vapour-phase chromatography. The main steps involved in fragmentation and arylation by aroyl peroxides are shown[32] in Scheme 10. The steps in Scheme 2 are part of this sequence.

$$\mathrm{(PhCO_2)_2 \longrightarrow 2PhCOO\cdot \longrightarrow 2Ph\cdot + 2CO_2}$$

$$\mathrm{Ph\cdot + C_6H_6 \longrightarrow (PhC_6H_6)\cdot}$$

$$\mathrm{(PhC_6H_6)\cdot \longrightarrow PhC_6H_5 + H\cdot}$$

$$\mathrm{PhC_6H_7 \longrightarrow PhC_6H_5 + 2H\cdot} \qquad \text{Dehydrogenation}$$

$$\mathrm{(PhC_6H_6)_2 \longrightarrow Ph(C_6H_4)_2Ph + 4H\cdot}$$

Scheme 10.

Benzoic acid is a major byproduct, and side-reactions may be important under certain conditions.

Intensive investigation of a few arylation reactions has established that certain isomer distributions are characteristic of homolytic substitutions. If a new reaction gives this same orientation of isomers, then it follows that the reaction path is closely similar to those thoroughly investigated. Substitution patterns, however, are modified by polar and steric influences in the attacking radical. For example, nitro- and chloro-phenyl have electrophilic character and *meta*-tolyl and *para*-tolyl radicals have nucleophilic character.[33]

4. Relative Reactivities

An elegant procedure for determining the relative reactivities of unsaturated compounds towards free radicals has been developed by Zwarc.[34] A dilute solution of acetyl peroxide and hydrocarbon in isooctane is maintained at the appropriate temperature. The peroxide fragments to give methyl radicals, which then either abstract hydrogen atoms from the solvent or add to the unsaturated hydrocarbon (Scheme 11). The decrease in methane formation is a measure of hydrocarbon reactivity relative to solvent.

$$(CH_3COO)_2 \longrightarrow 2CH_3\cdot + 2CO_2$$

$$CH_3\cdot + SH \longrightarrow CH_4 + S\cdot$$

$$S\cdot \longrightarrow \text{Products}$$

$$CH_3\cdot + ArH \longrightarrow ArCH_3 + H\cdot$$

\- Scheme 11

The results have been correlated with hydrocarbon localization energies and good correspondence observed[34] (see Table 2). Some criticisms have been made of predictions based upon such correlations.[13]

TABLE 2

Some Correlations of Methyl Affinities with Localization Energies (ref.34).

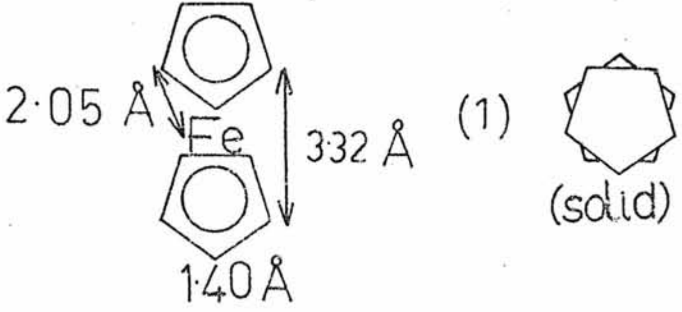
Hydrocarbon	Relative Methyl Affinity per Reactive Position at 85°	Lowest Localization Energy
Benzene	1.0	2.54
Biphenyl	7.5	2.38
Naphthalene	33.0	2.30
Phenanthrene	40.5	2.30
Pyrene	187	2.19
Anthracene	2460	2.01
Tetracene	13900	1.93

The establishment of a reactivity series (Table 2) tentatively enables the reactivity of any appropriate compound to be compared with all of those listed in the table after a single competitive reaction. For example, in the presence of benzenediazonium salts, anthracene and ferrocenium ion give phenylated anthracenes and ferrocenes in moderate yields.[35] Thus, ferrocenium ion and anthracene are of approximately equal reactivity towards free-radical attack, and ferrocenium ion reactivity can be compared with the reactivity of other hydrocarbons. However, because experimental ferrocenium ion concentrations were not determined, the results are very approximate. An investigation of alternative methods of determining ferrocenium ion reactivity forms part of this thesis (see II.3).

Ferrocene

1. General

Ferrocene (dicyclopentadienyliron) was first prepared unexpectedly by Kealy and Pauson[36,37] in 1951. Synthesis now usually consists of treating a solution of cyclopentadiene in diethylamine with anhydrous ferric or ferrous chloride.[38] The compound was deduced to have an aromatic sandwich structure, antiprismatic in the solid state (1), with the cyclopentadienyl rings freely rotating about the central iron atom in solution.[39]



More than 60 elements are known to form compounds with cyclopentadiene, and cyclopentadienyl-transition metal complexes have been extensively studied. The preparation, properties, and chemistry of ferrocene and analogues have been the subject of numerous reviews, see e.g.[40-44] Cyclopentadienyl compounds may be arbitrarily divided into three classes: salt-like compounds, true organometallic compounds (e.g. ferrocene), and intermediate complexes. The neutral organometallic species have been called metallocenes, and the cationic species resulting from loss of one electron, metallocenium ions.

Considerable interest has been shown[40] in the bonding between the cyclopentadienyl rings and the iron atom of ferrocene. The octahedral complex-ligand field treatment and the molecular orbital approach[45] have points of agreement and divergence. The M.O. approach satisfactorily explains aromaticity and the stability of α-carbonium ions. This description[41] suggests that there is one delocalized covalent bond from each cyclopentadienyl ring to the central iron atom, leaving 4 π-electrons in each ring unassociated with bonding to iron. A molecular orbital between the plane of the two rings is also described (and designated h_{ag} or e_{2g} by different workers[41])*. In particular,

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* This is described as the E_{2g} molecular orbital in ref.[40]

this has been invoked to explain α-ferrocenyl carbonium ion stability.[40]

2. Substitution.

Ferrocene can react as an aromatic compound; Friedel-Crafts acylation was the first observed manifestation of this property.[39] Oxidation of the iron atom often intervenes in reactions with electrophiles. The iron atom may be considered to exist in the Fe^{II} oxidation state in ferrocene and, with a polarographic half-wave potential of -0.31V (versus S.C.E. in 90% EtOH), is readily oxidized to the Fe^{III} state of ferrocenium ion electrolytically and photolytically, and by ferric salts, nitric and sulphuric acids, and similar oxidizing agents.[40] Thus, attempts to nitrate or halogenate ferrocene directly gave ferrocenium ion, a water-soluble, blue-green salt with a formal positive charge. Similarly, attempts to acylate ferrocene with p-nitrobenzoyl chloride, chloroacetyl chloride, and similar reagents gave ferrocenium salts instead of expected products.[46,47]

Acylation is usually[40] carried out with aluminium trichloride and acyl halide in dichloromethane, chloroform, or carbon disulphide. Ferrocene and the 9-position of anthracene have approximately the same reactivity, and even mono-acylferrocenes are readily transformed into di-acylferrocenes (Table 3).

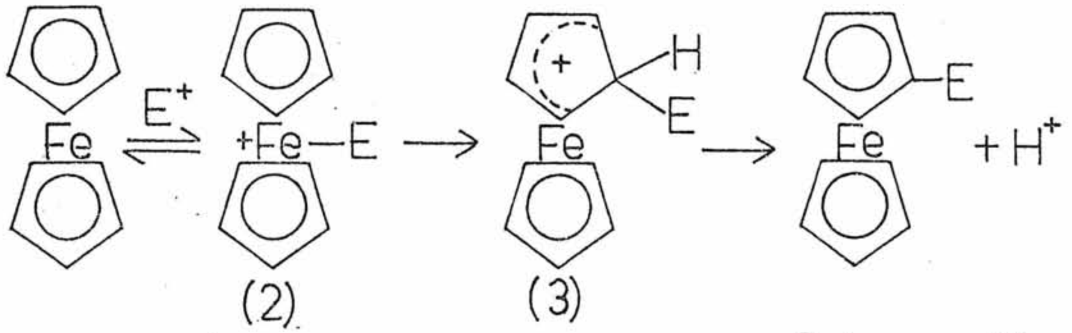
TABLE 3.

Relative Reactivity of Aromatic Compounds (for Acylation)

Compound	Relative Reactivity
Benzene	1
Acetylferrocene	$1.9X10^2$
Mesitylene	$2.9X10^3$
Pentamethylbenzene	$1.3X10^4$
Ferrocene	$3.3X10^6$

Mild catalysts e.g. phosphoric acid, boron trifluoride, and acylating agents e.g. acid anhydrides, have been used to prevent diacylation.[42] Because polyalkylation occurs readily, alkylferrocenes are prepared from alkylcyclopentadienes or by reduction of acylferrocenes.[48]

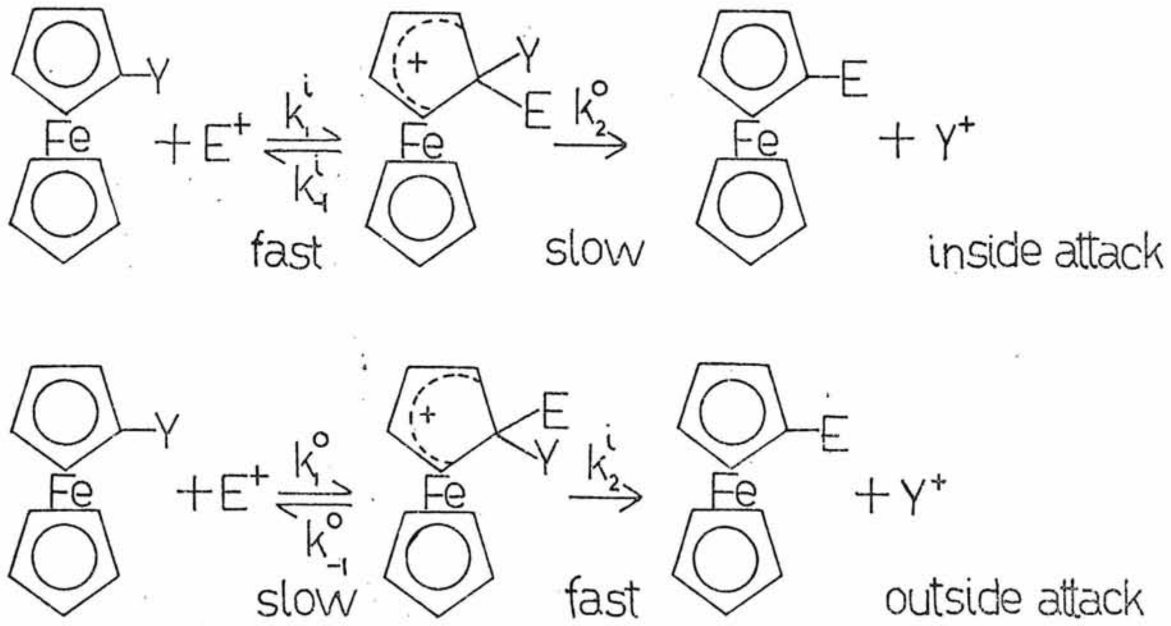
The mechanism of electrophilic substitution has been studied thoroughly. The early consensus favoured the formation of a charge-transfer complex as part of the substitution mechanism.[40] ((2), Scheme 12).



Scheme 12

The highest-energy, filled molecular orbital would be involved in bonding in the complex. Protonation of metallocenes at the metal atom[49] lends support to the hypothesis of complex formation, although there is little direct evidence for the formation of (2) when E^+ is not H^+.

More recently, Rosenblum and Abbate[50] have concluded from acylation studies that the iron atom does not necessarily participate directly in the substitution as shown in Scheme 12. Similar views have been expressed by Mangravite and Traylor.[51] They postulated the "inside-outside relationship" assuming that the metal complex (2) (if it exists) is the counterpart of the π-complex in benzenoid substitution and is not significant in the proposed mechanism (Scheme 13).



Scheme 13

Detailed analysis of σ^+ substituent parameters and solvolytic data showed that when E^+ is more electrophilic than Y, outside attack occurs, and when E^+ is less electrophilic than Y, inside attack occurs. General features of metallocene chemistry could be explained with this relationship. For example, the solvolytic reactivity order of α-metallocenylmethylacetates is osmocene>ruthenocene>ferrocene, while acylation reactivity order is osmocene<ruthenocene<ferrocene. This can be rationalized by assuming that solvolysis occurs by inside attack and acylation by outside attack.

Marr and Webster[52] showed that in protodesilylations, (Scheme 14) parallel changes occurredin the kinetic behaviour of trimethylsilylated ferrocenes and benzenes when reaction conditions were changed. The experimental results were explained by assuming that reaction mechanisms

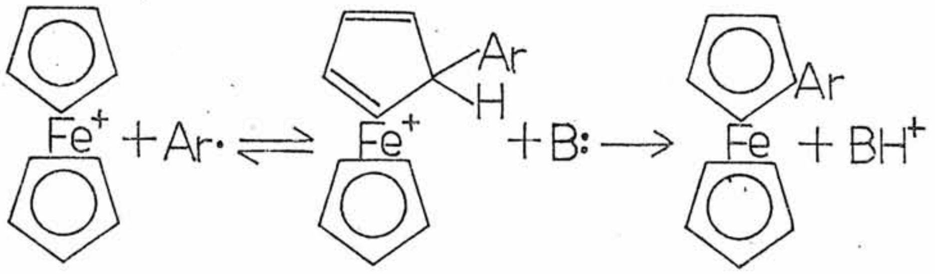
$$R^1SiMe_3 + R^2OH \xrightarrow{H^+} R^2OSiMe_3 + R^1H \qquad \text{Scheme 14}$$

for benzenes and ferrocenes were closely similar. The rate-determining step was assumed to be the formation of a σ-complex (3).

Compared with the large body of work concerned with electrophilic attack, free-radical substitution of ferrocenium ion has received little attention. Arylations with arenediazonium salts have been studied most intensively, and the features of this reaction have been rationalized.[40] If ferrocene and an arenediazonium salt are mixed in an organic solvent an arylated product results. Alternatively, an aqueous ferrocenium salt solution may be used, but a small quantity of ferrocene is necessary[53] for reaction to occur. Little *etal*.[54] proposed the mechanism shown in Scheme 15 for the reaction. However, Rosenblum[55] has suggested that some sort of iron-bound complex (4) could be envisaged.

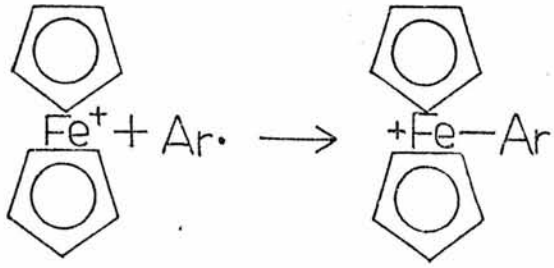
$FcH + ArN_2^+ \longrightarrow FcAr + N_2 + H^+$ overall reaction

$FcH + ArN_2^+ \longrightarrow FcH^+ + Ar\cdot$ ($Fc- \equiv C_5H_5FeC_5H_4-$)



Scheme 15

In view of the recent work on electrophilic substitution,[50-52] (4) may be unnecessary. Scheme 15 adequately explains the features of ferrocene arylation, and work by Beckwith and Leydon[56] and others[53-55] has dissipated most of the early



(4)

Scheme 16

mechanistic ambiguity. Ferrocenium ion has been cited as the reactive species in substitutions by radicals generated from phenylazotriphenylmethane,[57] hydrazines and silver oxide,[58] azobisisobutyronitrile,[56] and benzoyl peroxide and toluene.[56] Mechanisms similar to that shown in Scheme 15 have been proposed. Ferrocene has been conclusively shown to resist radical substitution,[56-58] and such a substitution would theoretically be unlikely.[40] A recent report[59] indicated that ultraviolet irradiation of ferrocene in haloalkane solvents gave substituted ferrocenes in appreciable yields. Irradiation of ferrocenium solutions did not give substituted products. The authors suggested that the reaction was not free-radical but that an electron-transfer mechanism was operating.

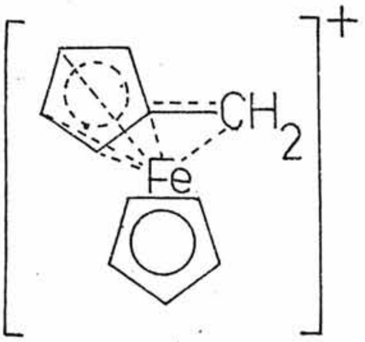
The transition state suggested by Little etal.[54] for free-radical substitution (Scheme 15) is structurally identical with those postulated for electrophilic substitution (Schemes 12 and 13). This transition state could also apply to electron-transfer between ferrocene and triphenylmethyl carbonium ion.[60] An investigation of the apparent similarity of mechanism could be of great interest, being potentially the first example of a common route for free-radical and electrophilic substitution. Part of this thesis is an investigation of the proposed similarity of mechanism (see

II.1,2a).

3. Stability of α-ferrocenyl carbonium ion and radical. Participation of non-bonding e_{2g} metal orbital electrons has been an explanation[61,62] of the exceptional stability of α-metallocenyl carbonium ions. This stability is of a similar order to that of α-methoxymethyl or triphenylmethyl carbonium ions. The ease with which α-hydroxyferrocenylalkyl compounds undergo acid-catalyzed dehydration and etherification, and the reactivity of alkenylmetallocenes towards acid addition, have been attributed to the stability of the carbonium ion.[40]

Recent work has indicated that carbonium ion stabilization was most probably due to a type of σ-π conjugation and not to direct participation of e_{2g} electrons. This work included studies on the resonance stabilization of phenylferrocene during isotopic hydrogen exchange,[63] solvolyses of ferrocenylmethyl chlorides,[64] and the "inside-outside relationship".[51] Other workers have shown that in solvolysis of α-ferrocenylmethyl p-toluenesulphonates, participation of interannular electrons is more effective than that of extraannular electrons.[65]

However, stabilization by σ-π hyperconjugation has been criticized in a review by Cais,[66] and Mossbauer studies of the ferrocenylmethyl* carbonium ion[67] have indicated that in concentrated sulphuric acid at 137K, structure (5) is in accord with the spectral data.



(5)

More recent work[68,69] using a "Hammett-Deno type indicator acidity study" (involving examination of ultraviolet and visible spectra of acid solutions of ferrocenylmethylcarbinols and carbonium ions) has given results which question the relevance of kinetic evidence when determining the structure of the α-ferrocenyl carbonium ion. Thermodynamic stability of the carbonium ion was suggested to be several powers of 10 greater than kinetically indicated.[68] Compared with the neutral molecule, reorganization of bonding and structure is probably involved, i.e. structure (5)

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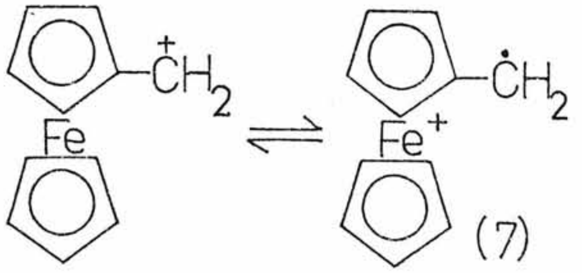
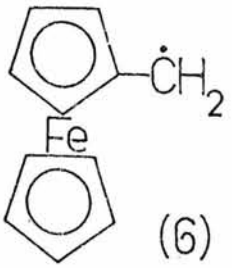
* Ferrocenylmethyl will be used throughout to denote $C_5H_5FeC_5H_4CH_2$.

is feasible. Rosenblum and Feinberg[70] have concluded from n.m.r. studies of α-ferrocenyl carbonium ions that distortion (5) may not necessarily occur but that some molecular deformation or charge redistribution probably takes place. Hill and Richards[71] had originally suggested a similar deformation, but they doubted that a definite molecular distortion would lead to increased stabilization. However, it seems that simple e_{2g} electron participation or σ-π hyperconjugation in undistorted α-ferrocenyl carbonium ion does not adequately explain the exceptional stability of this ion.

Despite thorough investigation of the ferrocenylmethyl carbonium ion, very little notice has been taken of the ferrocenylmethyl radical, (6). Formation of diferrocenylethane in acid solutions of ferrocene and formaldehyde has been attributed [72] to dimerization of the radical cation (7)

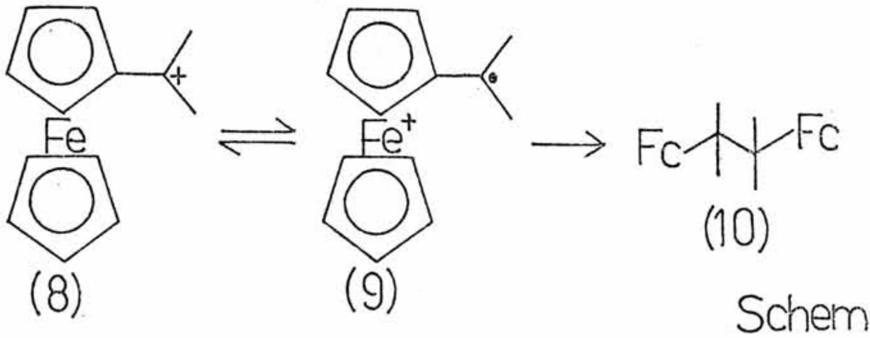


Scheme 17



(6)

formed from the carbonium ion (Scheme 17). Similarly, the formation of 2,3-diferrocenyl-2,3-dimethylbutane, (10), in acid solution was claimed[73] to arise by dimerization of the analogous radical cation (9), (Scheme 18). Re-investigation[74] of this reaction showed that (10) was <u>not</u> formed and that (8) was stable under the conditions used. Dimers were formed by alkylation of isopropenylferrocene with carbonium ion (8) during work-up.[74]



Scheme 18

Few direct investigations of ferrocenylmethyl-radical stability have been reported. Russian workers[75] have treated quaternary ammonium salts (11) with simple Grignard reagents and cobaltous chloride. The products presumably arose by fragmentation of the intermediate. When R=benzyl,

$$\underset{(11)}{\mathrm{FcCH_2{-}\overset{+}{N}(CH_3)_2R\ I^-}} \longrightarrow \left[\mathrm{FcCH_2\overset{\bullet}{N}(CH_3)_2R}\right] \longrightarrow \text{products}$$

(ferrocenylmethyl)dimethylamine and benzyl-radical products were isolated, indicating that benzyl is more stable than ferrocenylmethyl radical. When R=ferrocenylmethyl, methylferrocene was isolated. Slocum's preparation of methylferrocene[76] by reduction of a quatemary ammonium salt (11; R=Me) gave 1,2-diferrocenylethane, also indicative of ferrocenylmethyl-radical existence.

Attempts to prepare the pinacol FcC(OH)PhC(OH)PhFc, by photolysis of benzoylferrocene,[77] gave starting material only, probably because of difficulty in forming the α-ferrocenyl-radical intermediate. An e.s.r. study of the radical anion derived from benzoylferrocene[78] showed that the unpaired electron was delocalized predominantly onto the phenyl ring.

Because of the paucity of data concerning ferrocenylmethyl· radical stability, an investigation was undertaken and forms part of this thesis (see III, 3).

CHAPTER II

THE FREE-RADICAL SUBSTITUTION OF FERROCENIUM ION

II. 1. A kinetic investigation of the electron-transfer between ferrocene and triphenylmethyl carbonium ion

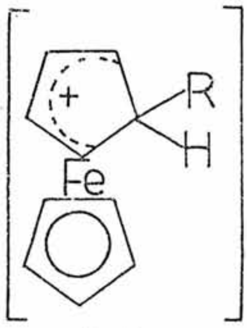
II. 2a. Comparative isomer distributions after free-radical and electrophilic substitutions of substituted ferrocenes

2b. The free-radical synthesis of some benzoylferrocenes

II. 3. The reactivity of ferrocenium ion

II.1 Kinetic Investigations of Electron Transfer Between Ferrocene and Trityl Carbonium ion.

The transition state for free-radical subsitution of ferrocenium ion has been represented as (12),[54] and that for electrophilic substitution of ferrocene as (13).[40] Unstable intermediates in the two reactions have been represented as (14) and (2) respectively.[55,40]



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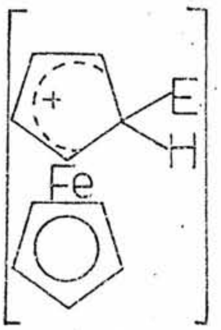

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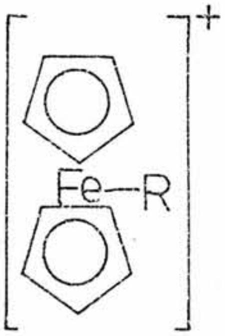

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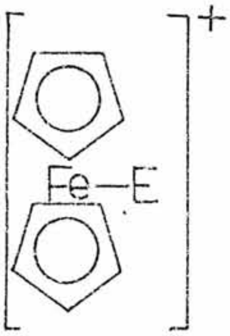
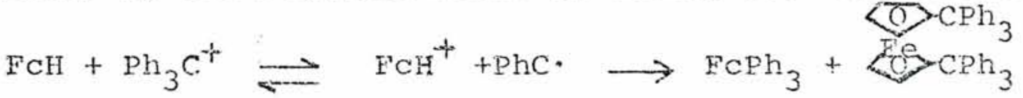


(2)

Structures (12) and (13), and (14) and (2) (if (14) and (2) are necessary) may be indistinguishable mechanistically and representationally, i.e. both substitution pathways may pass through a common transition state or unstable intermediate.

Pauson and co-workers[79] have suggested that triphenyl-methyl (trityl) tetrafluoroborate reacts with ferrocene in dichloromethane by the sequence shown in Scheme 19. The electron-



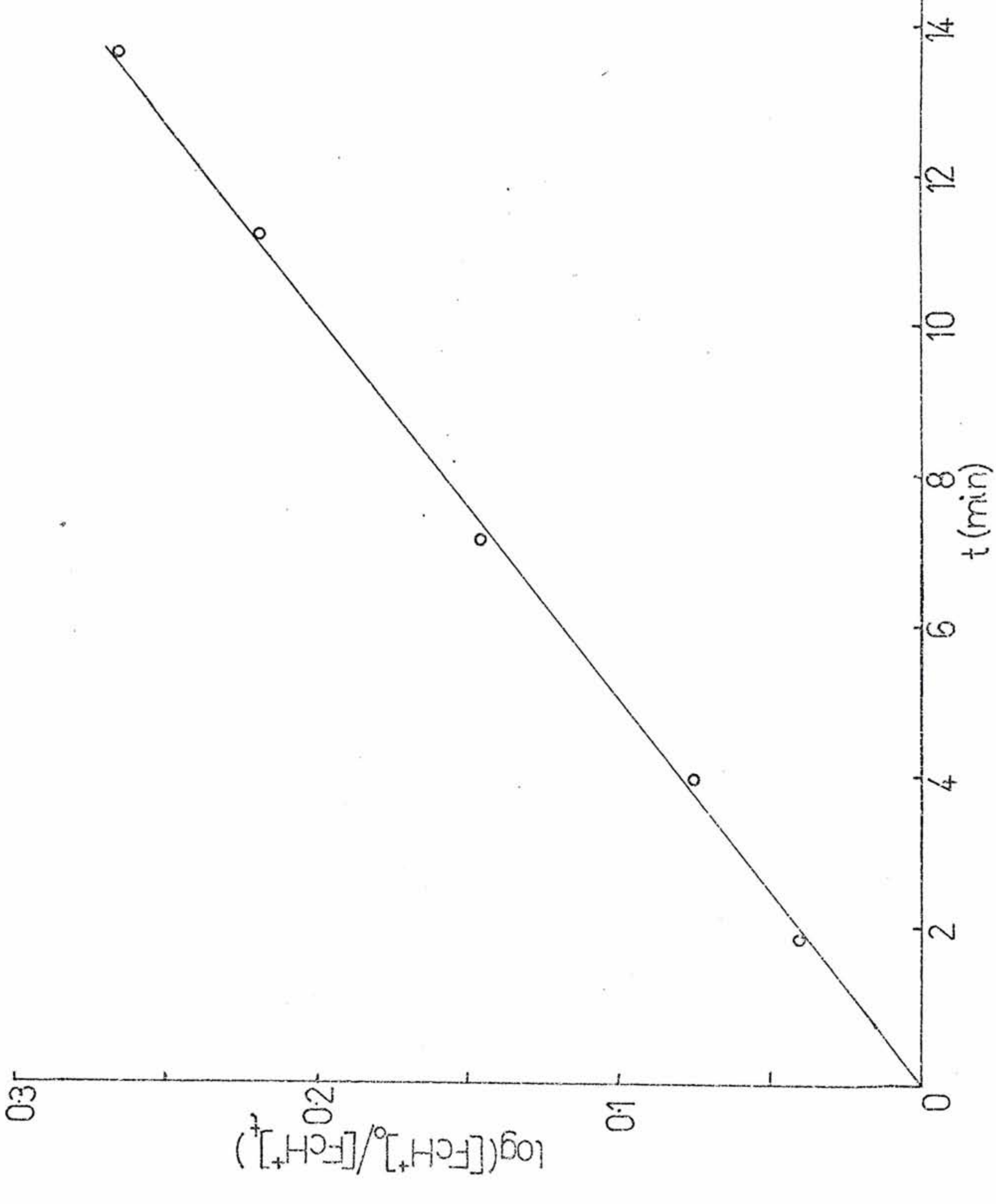
$$FcH + Ph_3C^+ \rightleftharpoons FcH^+ + PhC\cdot \longrightarrow FcPh_3 + \overset{\text{CPh}_3}{\text{Fe}}\,\text{CPh}_3$$

Scheme 19.

transfer equilibrium had previously been postulated by Hawthorne[60] to explain the formation of di-(trityl) peroxide and ferrocenium ion in aerobic nitromethane solutions of trityl chloride and ferrocene. The transition state for electron-transfer could be identical with that suggested to be common for free-radical and electrophilic substitution.[57] If this is the case, then it is no longer meaningful to distinguish mechanistically between these substitutions.

The ferrocene - trityl carbonium ion system was used for an investigation of the inter-related reactions. Ferrocenium ion concentrations can be conveniently measured by monitoring the visible absorbance at 610nm. After preliminary trials, acetone was used as solvent. Solutions of ferrocenium ion in acetone slowly decompose to give ferric and ferrous salts, ferrocene, traces of other ferrocenes, and unidentified oils. Other workers have shown that ferrocenium ion is readily cleaved by chelating agents[80] and has a relatively low activation energy for hydrolytic decomposition (36 kcal mol^{-1}).[81] A first-order rate plot for ferrocenium ion decomposition was drawn and the rate constant calculated (Fig.1) to be $7.5X10^{-4}$ S^{-1} at 22°C, which is negligible when compared with the electron-transfer rate constants.

Fig. 1:- Decomposition of ferrocenium ion in acetone



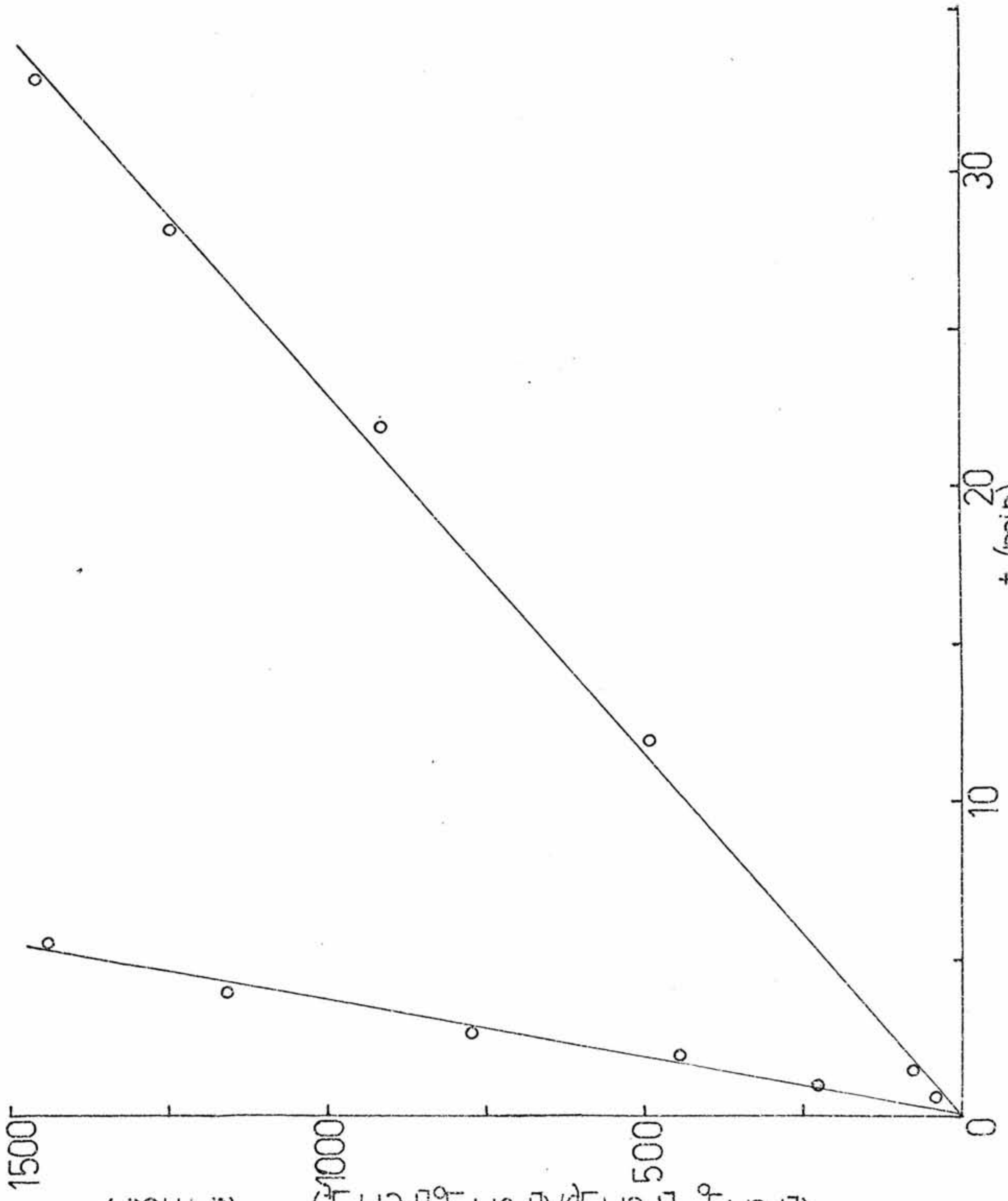
The rate of ferrocenium ion decomposition was approximately halved in the presence of equimolar ferrocene, but equimolar trityl tetrafluoroborate had little effect.

Rate constants for the electron-transfer (Scheme 20) were determined with 4 or 5×10^{-3}M solutions of ferrocene and trityl tetrafluoroborate in acetone. The solutions were made up separately under nitrogen and then quickly transferred to a glass cell, stoppered, and the spectrum monitored at 610nm. Although precautions were taken, complete exclusion of atmospheric oxygen would probably not be achieved by the method used. Limiting k values for the electron-transfer were 0.73 l. $\mathrm{mol^{-1}s^{-1}}$ (at 21°C) and 6.3 l. $\mathrm{mol^{-1}s^{-1}}$ (at 22°C) (see Fig.2).

$$\mathrm{FcH + Ph_3C^+\ BF_4^-} \rightleftharpoons \mathrm{FcH^+ + Ph_3C\cdot + BF_4^-} \qquad \text{Scheme 20}$$

The results varied with each solvent batch and this variation can be attributed to interaction of trityl tetrafluoroborate with solvent. The potential of the ferrocene-ferrocenium couple is independent of solvent,[82] but ionization of trityl chloride depends on the method of solvent purification.[83] At the low concentrations at which these experiments were conducted ($\underline{c}4 \times 10^{-3}$M) minor amounts of water, oxygen, or other impurities would vary kinetic results appreciably.

Fig. 2.- Electron-transfer for $FcH-Ph_3C^+$ in acetone



From the k values, it appears that electron transfer, although moderately fast, possibly involves a loosely bound complex. Alternatively, electron transfer could occur by an "outer sphere" mechanism (which does not require formation of new chemical bonds in the activated complex).[84] However, the ferrocene-ferrocenium electron exchange, which is typical of this class of mechanism, has a k value of 10^6 l. $mol^{-1}s^{-1}$ at -65 to -75°C.[84] The data reported in this thesis also indicate that K is large, electron transfer going to completion. This is expected, as the overall oxidation potential for forward reaction (Scheme 20) is 0.62V (conventional determination[53,85]) or 0.67V (polarographic determination[40,86]).

If transition states for substitution and electron-transfer were identical, tritylferrocene formation would be expected to closely parallel ferrocenium ion appearance. In the extreme case, ferrocenium ion would not form, the reaction following the course shown in Scheme 21.

$$FcH + Ph_3C^+ \rightleftharpoons [FcHCPh_3]^+ \longrightarrow FcCPh_3 + H^+ \qquad \text{Scheme 21}$$

This extreme case was not observed. In small-scale spectrophotometric rate-determinations, traces of atmospheric oxygen could seriously upset equilibrium by forming di(trityl) peroxide from trityl radical. A large-scale reaction with ferrocene and trityl tetrafluoroborate in acetic acid at room temperature under nitrogen gave, after quenching, ferrocenium ion in 16% yield. Only a trace of tritylferrocene could be detected. Ferrocene-tritylmethanol mixtures in acetone did not form ferrocenium ion or tritylferrocene; however, in acetic acid the characteristic blue colour slowly appeared, and after three days complete conversion into ferrocenium ion was observed. This reaction presumably follows the route shown (Scheme 22).

$$\mathrm{Ph_3COH + AcOH \rightleftharpoons Ph_3C^+ + H_2O + AcO^- \overset{FcH}{\rightleftharpoons} Ph_3C^{\bullet} + FcH^+}$$

Reversal of the reaction in Scheme 20 occurred only when tritylferrocene was refluxed in trifluoroacetic acid with the passage of a steady stream of oxygen. Ferrocenium ion was formed in 2.3% yield (spectroscopic estimate). Examination of the reduced products (t.l.c.) showed that ferrocene was present.

Overall, the results show that a ready electron-transfer occurred. But, because tritylferrocene formation is apparently irreversible under the reaction conditions in acetone, concomitant formation of tritylferrocene and ferrocenium ion would be expected if transition states for substitution and electron-transfer were identical. This was not the case. Beckwith and Leydon,[57] and Pauson et al.[79] have reported the rapid formation of blue ferrocenium ion as ferrocene reacts with trityl carbonium ion. However, solutions were heated for 24 and 15 hr., respectively, before tritylferrocene was isolated. Electron-transfer was clearly a separate process from product formation.

II 2a Comparative Isomer Distribution in Free-Radical and Electrophilic Substitutions of Substituted Ferrocenes.

Comparison of the isomer distributions from parallel electrophilic and free-radical substitutions of suitable monosubstituted ferrocenes is one way of studying the proposed[57] identity of substitution transition-states. If this proposal is accurate then substitution patterns should be conditioned only by the relative stabilities of the isomeric σ-complexes.

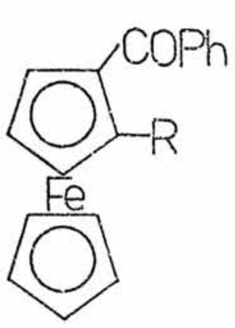
Some aspects of ferrocene acylation have been discussed in the Introduction. Electrophilic carbonium ions are the substituting intermediates in Friedel-Crafts acylations with benzoyl chloride-aluminium chloride. A comprehensive review[87] of the Friedel-Crafts reaction, after discussing all of the conflicting data, suggested that the benzoylonium ion $PhC\equiv O^+$ is the effective intermediate in benzoylation, although the acid halide-catalyst oxonium complex is also present.

Abstraction of hydrogen from aldehydes to give acyl radicals[14] provides a convenient source of benzoyl radicals *in situ* (Scheme 23). This is despite the fact that the benzaldehyde C-H bond is relatively unreactive in free-radical reactions.[14] The reaction mixtures used for the work reported here were considered not to contain other sources of abstractable hydrogen atoms.

$$\mathrm{FcR} + \mathrm{Fe}^{3+} \longrightarrow \mathrm{FcR}^{+} + \mathrm{Fe}^{2+}$$
$$\mathrm{Bu^tOOH} + \mathrm{Fe}^{2+} \longrightarrow \mathrm{Bu^tO\cdot} + \mathrm{OH}^{-} + \mathrm{Fe}^{3+}$$
$$\mathrm{Bu^tO\cdot} + \mathrm{PhCHO} \longrightarrow \mathrm{Bu^tOH} + \mathrm{Ph\dot{C}O}$$
$$\mathrm{Ph\dot{C}O} + \mathrm{FcR}^{+} \longrightarrow \text{products} \qquad \text{Scheme 23}$$

For example, in experiments with methylferrocene, 1,2-diferrocenylethane was not observed. Thus the relatively low reactivity of benzaldehyde towards hydrogen abstraction is unimportant in Scheme 23. t-Butyl hydroperoxide in the presence of ferrous ions was found to be the most successful room temperature initiator. t-Butyl perbenzoate was used in preliminary experiments but gave tarry products.

Because of free-rotation of the cyclopentadienyl rings about the iron atom in solution, monobenzoylation of a substituted ferrocene can give three products. These are the 1,2- and 1,3-homoannular compounds, (15) and (16) respectively, and the 1,1'- heteroannular compound (17). A variety of methods have been used to characterize the isomers. The i.r. "9,10 μ rule"[40] distinguishes between homo- and hetero-annular disubstituted ferrocenes. Homoannular ferrocenes have two strong i.r. absorptions at *c.* 9 and 10 μ. Heteroannular (1,1') ferrocenes do not have these absorptions. It has also been suggested[95] that i.r. absorptions may serve to define the structures of homoannularly-disubstituted ferrocenes, a 1,3- structure exhibiting two bands near 11μ, and the 1,2-isomer only one.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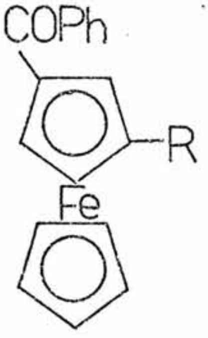
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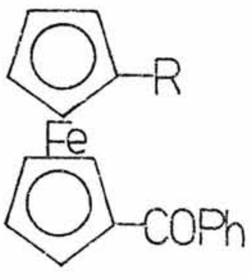
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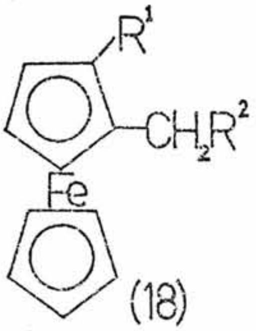
(18)

R^1 various
R^2 N<, S<, O< etc.

However, close examination of a number of acetyl-alkylferrocenes has cast doubt upon this latter generalization.[88]

N.m.r. spectroscopy has been used to distinguish between homoannularly-disubstituted ferrocenes.[88-90] Other workers[91] have studied 1,2-disubstituted ferrocenes with complex substituents, e.g. (18), and have concluded that the assignment of structures to homoannular ferrocenes on the basis of the chemical shifts of α-methylene protons is fraught with difficulty. But, despite this, when R^2=alkyl and R^1=acyl in (18), consistent structural assignments have been made.[88-90] The chromatographic elution order of the isomers has been used[88] as a rough identity tool; only one exception to the order of $1,2 > 1,1' > 1,3$ isomers is known.[89]

An independent synthesis of one of the disubstituted products in this work has been carried out to enable unambiguous assignments of structure.* Using the well-known specific 2-lithiation of (dimethylamino)methylferrocene[92] (19), 1-benzoyl-2-methylferrocene (22) was synthesized (Scheme 24). A similar unambiguous synthesis of 1,2-dimethylferrocene was reported[93] after the

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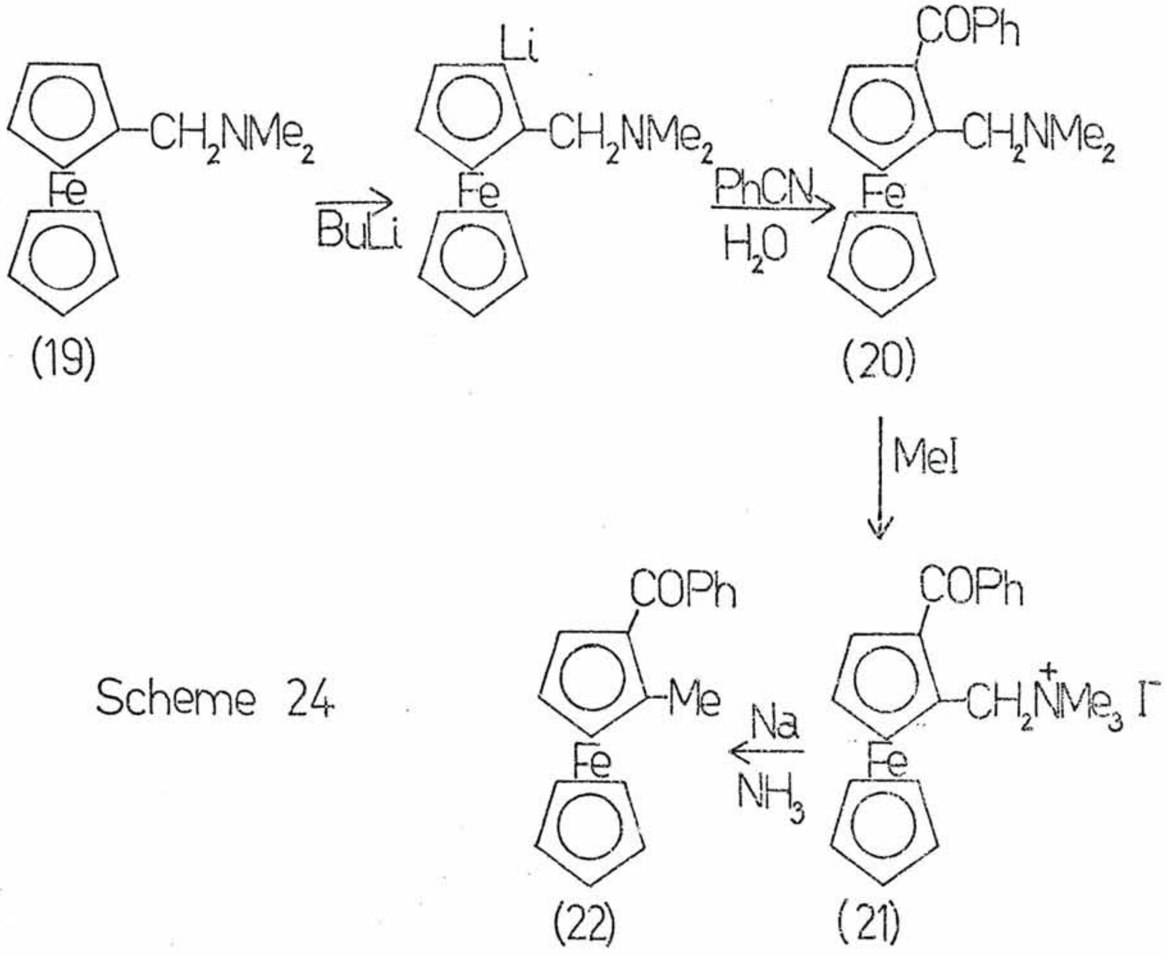
* Even if structural assignments are incorrect, the conclusions of this study are still valid because relative isomer distributions were examined, irrespective of structure.

completion of this synthesis of 1-benzoyl-2-methylferrocene.



Scheme 24

(Dimethylamino)methylferrocene (19) was converted into the known[92] 2-(dimethylaminomethyl)ferrocenylphenone (20). Formation of the methiodide (21), and subsequent sodium-ammonia reduction, gave the 1,2-disubstituted product (22). The structures of other disubstituted compounds discussed in this section were assigned after a comparison of R_f values and n.m.r.

spectra with those of (22). With the isomeric benzoylmethylferrocenes, the methyl resonance of the 1,2-isomer is shifted furthest downfield from the methyl resonance in the n.m.r. spectrum of methylferrocene. The methyl resonance in 1-benzoyl-1′-methylferrocene would be shifted downfield least with respect to the methyl resonance of methylferrocene. The position of the methyl resonance of the 1,3-isomer would be intermediate between those of the other two isomers.

A suitable method for determining the absolute yields of products had to be devised to enable the study of comparative isomer distributions. Other workers have used column chromatography to separate isomeric products, but with only limited success.[94,95] For example, to separate 2g of mixture, 3 kg of alumina and 9-week elution times have been used, and decomposition was extensive.[94] N.m.r.[90] and vapour phase chromatography (v.p.c.)[40,88] methods have been used to a limited extent in determining yields. In this work, trial experiments with chromatography on alumina columns led to extensive decomposition of the substrates, and either quantitive v.p.c. or n.m.r. methods were used for isomer estimations.

A number of ferrocenes with electron-donating and -withdrawing substituents were chosen for study. Simple molecular-orbital calculations[95,96] of transition-state localization energies for electrophilic substitution predict a higher reactivity at the 2-position for both electron-donating and -withdrawing substituents. Early experimental results[40] indicated that the 2-position was not activated by alkyl substituents but was activated by the phenyl substituent. These results were confirmed by a thorough investigation and review of relative site-reactivity values[89] (some of these values are reproduced in Table 4). All alkyl substituents are activating, with 3-position activation dominant. Strongly deactivating substituents such

TABLE 4

Relative site-reactivity values for electrophilic substitution of substituted ferrocenes (from ref.[89] and references therein).

Values were recalculated to make 1′-position=1. A, electrophilic acetylation; B, aminomethylation.

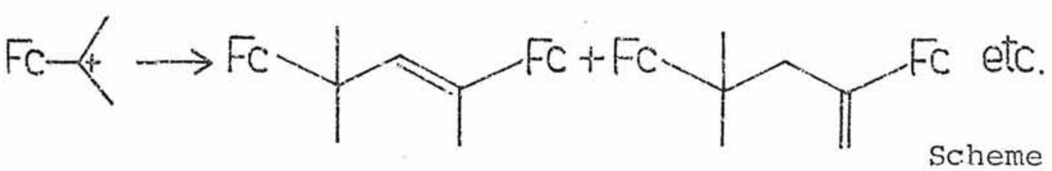
Substituent	Reaction	Site-Reactivity Values 2	 3	 1′
Me	A	1.2	1.6	1
Me	B	2.6	6.7	1
Et	A	1.4	4.2	1
		0.85	1.9	1
Pr^i	A	0.59	2.4	1
Bu^t	A	0.3	3.3	1
Ph	A	0.72	0.53	1

TABLE 4 (Cont.)

Substituent	Reaction	Site-Reactivity Values 2	3	1′
p-MeOPh	A	1.15	0.59	1
MeO	B	3.7	2.3	1
MeS	B	2.4	1.7	1

as methoxycarbonyl, cyano, bromo, chloro, acetyl, acetamido, urethano, or phthalimide gave only 1,1′-products. Phenylferrocene was weakly deactivating, but gave the three isomeric products. Methoxy- and methylsulphide-ferrocene could not be acetylated to give meaningful results.[96] The anomalous activity of the 2-position towards aminomethylation was attributed to ortho effects.

Methyl-, ethyl-, isopropyl-, t-butyl-, benzyl-, phenyl-, isopropenyl-, and benzoyl-ferrocenes were intended for use in this work. However, 1,1′- and 1,3-benzoylethylferrocenes were not quite resolved by v.p.c. analysis, and t-butylferrocene was very impure when prepared by literature methods.[97] Benzoylferrocene gave only a small yield of product under the free-radical conditions, probably because of decomposition of benzoylferrocenium ion. Isopropenylferrocene gave more than three benzoylated products under Friedel-Crafts conditions. A recent report[74] indicated that sulphuric acid solutions of isopropenylferrocene gave a number of alkylated products which were thought to form in dilute acid during workup (Scheme 25). Since Friedel-Crafts acylation solutions are acidic, similar dimerizations presumably occurred.



Scheme 25

The results of successful experiments are recorded in Table 5. Stirring and heating times were sometimes varied to increase low yields of products, but no concerted attempt was made to maximize all yields. In some experiments, up to 25% of the starting ferrocene could not be accounted for after workup. This can perhaps be explained by the known[98] decomposition of ferrocene in the presence of aluminium trichloride, and by decomposition of ferrocenium ion in solution (see II.1.). Materials and workup procedures were standardized for each substituted ferrocene. Progressively milder reaction conditions were used, most of the later experiments being performed at room temperature.

TABLE 5

Benzoylation of Four Monosubstituted Ferrocenes

Compounds	Friedel-Crafts								
	FcR Recov. (%)	FcR Conv. (%)	FcR Total (%)	Isomer as % of products 1,2	1,1′	1,3	Site Reactivity 1,2	1,1′	1,3
Me	52.3	35.4	87.7	14	47	39	0.74	1	2.08
	29	59.4	88.4	14	46	40	0.76	1	2.18
Pr^i	45	30	75	14	48	38	0.73	1	1.98
	40	34	74	14	48	37	0.73	1	1.93
CH_2Ph	45.6	52.7	98.3	25	50	25	1.25	1	1.25
	47.5	43	90.5	26	48	26	1.36	1	1.36
Ph[a]	50.7	25.8	76.5	21	$\overbrace{\quad 79 \quad}$				
[a]	61.2	23.3	84.5	18	$\overbrace{\quad 82 \quad}$				
[b]	54	21	75	21	54.5	24.5	0.96	1	0.89

[a] Estimated by preparative t.l.c.

[b] Estimated by n.m.r. method

TABLE 5

Benzoylation of Four Monosubstituted Ferrocenes

	Free-Radical								
Compound	FcR Recov. (%)	FcR Conv. (%)	FcR Total (%)	Isomer as % of products			Site Reactivity		
				1,2	1,1′	1,3	1,2	1,1′	1,3
Me	68	9.8	78	13	47	40	0.7	1	2.15
	55	21.5	76.5	10	51	40	0.5	1	1.96
Pr^i	71	12	83	7	56	37	0.31	1	1.65
		17		10	54	36	0.46	1	1.67
CH_2Ph	76.2	17.6	93.8	22	50.5	27.5	1.1	1	1.36
	57.6	27.9	85.5	25.5	48	26	1.36	1	1.36
CH_2Ph	With benzene-diazonium salt								
b				28	48	24	1.46	1	1.25
Ph^a	81	17.2	98.2	17.6	$\overbrace{82.4}$				
b	65			17	57	26	0.75	1	1.14
a	64	28	92.8						

a Estimated by preparative t.l.c.

b Estimated by n.m.r. method

Relative Isomer Distributions in Methylferrocene

Friedel-Crafts benzoylation of methylferrocene was conducted in dichloromethane with aluminium trichloride - benzoyl chloride as the source of benzoylonium ions. Free-radical benzoylation was conducted in benzaldehyde with ferric chloride as the oxidant of methylferrocene. The fragmentation of t-butyl hydroperoxide was catalyzed by ferrous ions, and subsequent hydrogen-abstraction from benzaldehyde (Scheme 23) gave benzoyl radicals which then substituted methylferrocene. Isomer distributions were determined by v.p.c. analysis. Retention-time (FFAP stationary phase) and chromatographic-elution orders (t.l.c., silicagel; column chromatography, neutral alumina) were identical, as has previously been noted for acetylalkylferrocenes.[88] Average relative site-reactivities* are shown in Figure 3. Absolute conversion of methylferrocene to benzoylated products was low, the yields of 1-benzoyl-2-methylferrocene from the free-radical reactions being only 1.3 and 2.1%. A small error in estimating the yield of one product would alter site-reactivity values appreciably.

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* Relative site-reactivities are determined as follows: the absolute yield of a disubstituted product is divided by the number of sites available for that product, the resulting ratio for the 1,1′-compound given the value 1.0 and the other site ratios are given proportional values.

Friedel-Crafts benzoylation Free-radical benzoylation

Methylferrocene

Friedel-Crafts benzoylation Free-radical benzoylation

Isopropyl-ferrocene

Figure 3.— Relative site-reactivities of methyl- and isopropyl- ferrocene for Friedel-Crafts and free-radical benzoylations.

However, the results compare favorably with those reported by Schloegl et al.[90] who estimated site-reactivities for Friedel-Crafts benzoylation (by n.m.r.) to be 0.9, 1.0, and 2.0 for the 2-, 1′- and 3-positions, respectively.

A trial Friedel-Crafts reaction in refluxing chloroform showed that neither solvent nor reaction temperature was significant in determining site reactivities. V.p.c. integration ratios for 1,1′ and 1,3-benzoylmethylferrocene were very close to those values obtained from experiments performed in dichloromethane at lower temperatures. An experiment performed under the usual free-radical conditions, but without the addition of peroxide, did not give appreciable yields of benzoylated products.

Relative Isomer Distribution in Isopropylferrocene

The reactions with isopropylferrocene were carried out in a manner similar to those with methylferrocene. The results are shown in Figure 3. The v.p.c. retention-times paralleled the chromatographic elution-order as for benzoylmethylferrocenes. Absolute yields of benzoylated products were low under free-radical conditions, only 0.8 and 1.7% of 1-benzoyl-2-isopropyl being formed in the two experiments reported here.

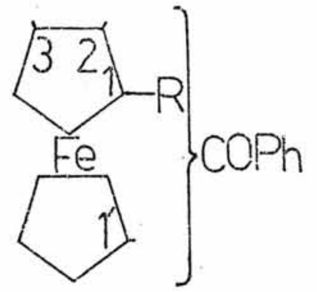
Relative site-reactivities reported for Friedel-Crafts acetylation of ispropylferrocene are given in Table 4.[89] Despite differing reaction conditions, reagents, and isolation procedures, there is fair agreement between the values reported in Table 4 and those shown in Figure 3 for free-radical and electrophilic benzoylations. The 2- and 3-positions of 1,1′-diisopropylferrocene have site-reactivity values for acetylation of 1.0 and 4.3 respectively,[99] emphasising the difference in substitution behaviour between mono- and di-substituted ferrocenes.

Relative Isomer Distribution in Benzylferrocene

The isomeric benzoylbenzylferrocenes could not be satisfactorily resolved by v.p.c. analysis. However, the isomers were separated, and structures were assigned, by comparing the chromatographic elution order and n.m.r. spectra with those of benzoylmethylferrocenes.

Site-reactivity values were then determined by n.m.r. spectroscopy using the α-methylene resonances; α-hydrogen resonances for benzoylisopropyl-, benzoylbenzyl- and benzoylmethyl-ferrocenes are shown in Table 6. Site-reactivities are shown in Figure 4.

TABLE 6

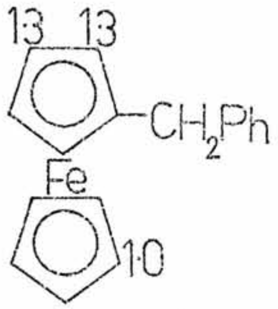


δ-Values for ferrocenyl α-position protons in disubstituted ferrocenes

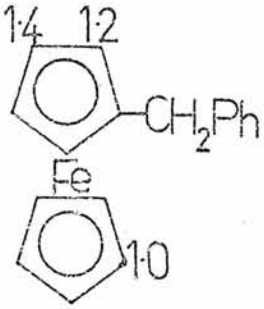
	δ (p.p.m.)		
R	2	3	1′
Me	2.26	2.04	1.83
Pr^i	3.4-4.05	2.5-3.13	2.15-2.9
CH_2Ph	4.27	3.68	3.53

The site-reactivity order contrasts with that for methyl- and isopropyl-ferrocene (Fig. 3) in that the 2- and 3-positions have approximately equal site-reactivity values in benzylferrocene.

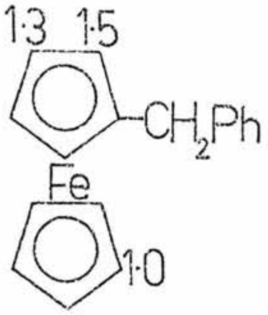
Rationalization of the observed reactivities in benzylferrocene is aided by reference to an e.p.r. study of the *benzoylferrocene* radical anion.[78] This study showed that free spin in the radical anion was delocalized mainly into the phenyl ring; phenyl was interpreted to be less electron-releasing than ferrocenyl.[78] By analogy, the phenyl ring in benzylferrocene will be relatively electron-attracting compared with the ferrocenyl ring and, overall, the benzyl substituent would be expected to be electron-attracting i.e. deactivating.



Friedel-Crafts
benzoylation

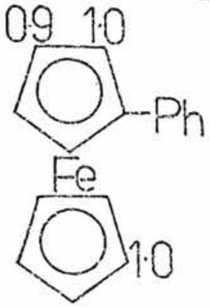


Free-radical
benzoylation

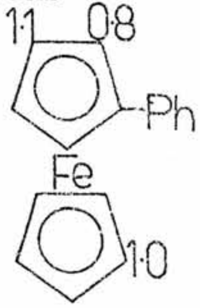


Free-radical
phenylation

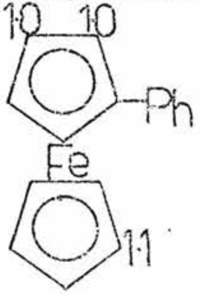
Benzylferrocene



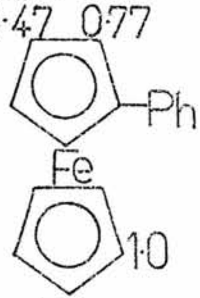
Friedel-Crafts
benzoylation



Free-radical
benzoylation



ref.[94]



ref.[95]

Literature values for Friedel-Crafts acetylation

Figure 4.—Relative site reactivities of benzyl- and phenylferrocene for Friedel-Crafts and free-radical substitutions.

The phenyl group in phenylferrocene is reported to be weakly deactivating,[95] and the 3-position of phenylferrocene is relatively deactivated when compared with the 2-position. Therefore, relative deactivation of the 3-position in benzylferrocene would be expected. Experimentally, the 2 and 3-positions showed approximately equal reactivity (See Fig.4 and Table 5).

In a separate experiment, benzylferrocene was phenylated with phenyl radicals generated from benzenediazonium sulphate. N.m.r. analysis of the products indicated that site-reactivity values for phenylation were similar to those obtained from free-radical benzoylation (see Fig. 4 and Table 5). The difference between site-reactivities determined for benzoyl and phenyl radical substitution could be a function of the different electrophilicities of these radicals. However, the homolytic substitution-pattern is not affected markedly by the difference in substituting radicals. Homolytic substitution-patterns are not restricted to benzoyl radicals only.

Relative Isomer Distribution in Phenylferrocene.

The isomeric benzoylphenylferrocenes could not be resolved by v.p.c. analysis. The n.m.r. spectrum of a mixture of the compounds did not exhibit distinctive resonances which could be assigned to the expected isomeric products. Preparative t.l.c. was used to separate 1,2-benzoylphenylferrocene from a mixture of 1,1′- and 1,3-isomers.* The ratio of 1,2-isomer to (1,1′ + 1,3)-isomers is shown in Table 5.

Benzoylferrocenes can be reduced quantitatively to benzylferrocenes with aluminium trichloride - lithium aluminium hydride mixtures.[46] The reduction of a mixture of benzoylphenylferrocenes by this method, followed by quantitative v.p.c. analysis of the products, gave integration ratios of (1,1′-isomer)/(1,3-isomer) = 2.23 and 2.26 for Friedel-Crafts and free-radical benzoylations, respectively. The structures of the benzylphenylferrocenes were assigned on the basis† of n.m.r. data for the ferrocenyl α-methylene protons (Table 7). This data was analogous to that for benzoylated methyl-, isopropyl-, and benzyl-ferrocenes (Table 6). The relative yields and site-reactivity values were determined by first separating benzoylated products from phenylferrocene by preparative t.l.c.

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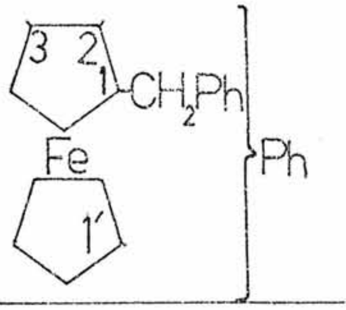
* The structures were initially assigned on the basis of R_f values from t.l.c. on silica gel, assuming that R_f values are in the order 1,2>1,1′>1,3.

† The isomer assigned the 1,2-structure had the shortest R_t by v.p.c. on FFAP.

TABLE 7



δ-Values for ferrocenyl α-methylene protons

	2	3	1′
δ	3.86	3.63	3.37

The benzoylated products were reduced[46] and the isomer proportions were then estimated by n.m.r. The ratio of 1,2- to (1,1′ + 1,3)-isomers is similar to that estimated by isolation without reduction (Table 5).

The site-reactivity values are similar for free-radical and electrophilic benzoylations. However, there is a definite difference between results obtained by the two methods. Also, the phenyl group does not appear to be markedly deactivating for either reaction. Site - reactivity values for acetylation, determined by Rosenblum,[94,95] are shown in Figure 4. The variation in these values was attributed to slight differences in acetylation conditions and product-isolation procedures; 1,1′- and 1,3-acetylphenylferrocenes were not separated successfully and relative yields were determined indirectly.[94,95] The site-reactivities for free-radical and electrophilic benzoylations can therefore be considered to be in accord, when compared with the scatter of results obtained for the two reported electrophilic acetylations.[94,95]

Conclusions

The values for site-reactivity determined for the four substituted ferrocenes are similar in free-radical and electrophilic benzoylations. The values by both routes for methyl- and benzyl-ferrocene are in good agreement, and the values for isopropyl and phenylferrocene are in fair agreement (see Figs. 3 and 4). For isopropyl- and phenyl-ferrocene the difference between site-reactivity values determined for the two routes is smaller than the reported difference between site-reactivity values for two different Friedel-Crafts acetylation procedures with phenylferrocene.[94,95] Electrophilic acetylation and aminomethylation of methylferrocene also gave widely different electrophilic site-reactivity values.[89]

In all cases the site-reactivities by both routes are roughly comparable with the site-reactivities for the acetylations of methyl-, isopropyl-, and phenylferrocene quoted in Table 4.[89] Within experimental error, values were found to be independant of variations in individual reaction conditions. Free-radical phenylation of benzylferrocene gave site-reactivity values similar to those for benzoylation; obviously site-reactivities did not vary markedly for these two substituting species.

The formation of similar isomer-distribution patterns has been assumed to indicate close similarity in key mechanistic steps for comparable reactions.[33] Thus, because of the similarity of isomer distributions for electrophilic substitution of ferrocene and free-radical substitution of ferrocenium ion, these two reactions may be considered to be mechanistically indistinguishable under some circumstances.

II 2b Free-radical Synthesis of some Benzoylferrocenes

The blue charge-transfer complexes formed during electrophilic acylation of ferrocene,[40] and the charge-transfer excitations observed[100] in alkyl halide solutions,[100] indicate that electron transfer from ferrocene is possible under Friedel-Crafts conditions. The absence of appreciable quantities of ferrocenium salts after work-up of most electrophilic reactions, and the work reported in II.1, indicate that electron transfer is separate from product formation. Electron transfer is dominant when R in RCOCl is strongly electron- attracting i.e. when $R = \underline{p}\text{-}NO_2C_6H_4$.[46,47] In some instances when transfer readily occurred, electrophilic substitution was not observed.

Repetition of the reaction of p-nitrobenzoyl chloride-aluminium trichloride with ferrocene in dichloromethane confirmed the results previously obtained [46] (See Table 8). p-Nitrobenzophenone was isolated in low yield when a slight excess of acylating agent was present in benzene solution, but not when ferrocene was in excess. p-Nitrobenzoylferrocene cannot be synthesized by the Friedel-Crafts reaction, and m-nitrobenzoylferrocene is formed in only 2.5% yield.[46] However, p-nitrobenzoyl radical and ferrocenium ion, in dichloromethane or benzene, gave small yields of p-nitrobenzoylferrocene (up to 11%). Free-radical substitutions were carried out basically according to the generalized Scheme 23. However, conditions were varied in some experiments and the results are tabulated (see Table 8). Moderate yields of m-nitro- and p-chloro-benzoylferrocene were also prepared by this method.

The experiments recorded in Table 8 ii and v were aimed at investigating the conditions necessary for free-radical synthesis of benzoylferrocenes. (The application of statistical design in organic synthesis[150b] could prove useful in a more thorough investigation of this synthesis). Ferric chloride facilitated the reaction by oxidizing ferrocene to ferrocenium ion, and then, as ferrous ions, by catalyzing peroxide fragmentation which leads to p-nitrobenzoyl radical production. Excessiv t-butyl hydroperoxide (see experiment ii(d)) caused extensive

TABLE 8

Preparation of Benzoylferrocenes

Reaction	Ferrocene mmol	Ferric Chloride mmol	t-Butyl Hydroperoxide mmol	Substituted Benzaldehyde mmol	Solvent and Conditions*	Ferrocene Recovered (%)	Benzoyl-ferrocene (%)
i	Friedel-Crafts Conditions						
(a)	10				CH_2Cl_2 reflux	79	–
(b)	10				C_6H_6 reflux	85	–
(c)	10				C_6H_6 reflux	89	
(d)	10	10			CH_2Cl_2 reflux	96	
ii	p-Nitrobenzoylferrocene						
(a)	10	5	20	65	C_6H_6 reflux 90 min.	56	2
(b)	10	10	20	50	C_6H_6 R.T. 30 min.	67	6.7
(c)	10	–	20	32	C_6H_6 reflux 30 min.	65	5.3
(d)	10	10	80	20	C_6H_6 reflux 30 min.	14	5.3
(e)	10	10	10	20	C_6H_6 reflux 30 min.	70	6.8
(f)†	10	10	20	20	C_6H_6 reflux 30 min.	63	4.4
(g)	10	10	20	32	C_6H_6 reflux 30 min.	61	11.3
(h)	10	10	20	32	EtOAc reflux 30 min.	76	1.3
(i)	10	10	20	30	Me_2CO reflux 1 hr.	77	1.7
(j)	10	10	20	32	CH_2Cl_2 reflux 1 hr.	64	10.2
(k)‡	10	10	20	30	CH_2Cl_2 reflux 2 hr.	38	1.5
iii	O-Nitrobenzoylferrocene						
	10	10	20	32	C_6H_6 reflux 2 hr.	75	–
iv	m-Nitrobenzoylferrocene						
	10	10	20	32	C_6H_6 reflux 2 hr.	68	15
v	p-Chlorobenzoylferrocene						
(a)	10	10	20	30	DMF 80° 30 min.	50	1
(b)	10	10	20	30	CH_2Cl_2 reflux 30 min.	82	14.5

* Times exclude room-temperature addition of peroxide over 30 min.

† Benzoic acid (30mmol) added.

‡ Aluminium trichloride (30mmol) added.

decomposition. Benzoic acid was added in one experiment in the hope of neutralizing hydroxide (Scheme 23) and preventing the attack of this agent on ferrocenium ion;[80,81] apparently the overall reaction is not as simple as that shown in Scheme 23, because the yield of substituted product decreased in the presence of benzoic acid.

It is interesting that the yield of benzoylferrocenes was low when solvents containing the carbonyl group were used i.e. ethyl acetate, acetone, and DMF, in experiments ii(h), ii(i) and v(a) in Table 8, respectively. The radical initiator could perhaps interact with solvent instead of abstracting the relatively slowly-abstracted benzaldehyde hydrogen atom.[14] Alternatively, benzoyl radical could be stabilized in the polar solvent. This experimental behaviour contrasts markedly with that observed for alkyl radicals, and reported in section II.3. (Presumably in the work reported in II.3, ethyl acetate solvent allowed an increase in ferrocenium ion concentrations, and hence an increase in product yields, without noticeably affecting alkyl radicals).

Electron-transfer is independent of free-radical substitution (see II,1), but in some systems, substituted products are formed after electron transfer,[57,79] and, if generated in the presence of ferrocenium ion, p-nitrobenzoyl radical can give the substituted product. Thus, electron-transfer products in electrophilic acylation media may be prevented from reacting by the formation of complexes. When excess aluminium chloride was added to the free-radical reaction (Table 8, experiment ii(k)), p-nitrobenzoylferrocene was still isolated, although the yield of this product was reduced. Unsuccessful attempts were made to isolate a ferrocenium complex similar to $\left[(C_{10}H_{11}Fe)^+(AlCl_4)^-\right]_n$ isolated by Rosenblum.[101] Precipitations from HCl-saturated solutions of ferrocenium salt appeared to give only the salt. Because ferrocenium ion is formed in attempted electrophilic acylation reactions, electron-transfer must take place, and free-radical substitution should occur (see II.2a). Thus, despite unsuccessful attempts to isolate such a complex, ferrocenium ion and $AlCl_4^-$ must complex in the solvent cage subsequent to electron-transfer. A perhaps fortuitous feature of electron-transfer is that approximately one-half of the ferrocene is converted to ferrocenium ion after attempted Freidel-Crafts syntheses.[46,47] The work reported in II.1 and II.2a gives a framework which enables rationalization of the non-isolation of substituted products from attempted electrophilic substitutions.

Having established that free-radical and electrophilic substitutions follow parallel courses, the success of free-radical acylation in the synthesis of previously inaccessible products illustrates the utility of approaching some syntheses from the free-radical side of the reaction pair.

II. 3. The Reactivity of Ferrocenium Ion.

Competitive experiments have shown that ferrocenium ion and anthracene are of comparable reactivity in free-radical reactions.[35] Unfortunately, the values for localization energies or free valence have not been calculated for ferrocenium ion. The publication of accurate rate constants for the reactions of tin hydrides with alkyl halides,[21] has enabled the reactivity of ferrocenium ion to be determined by another method. If an alkyl halide is allowed to react competitively with a triorganotin hydride in the presence of ferrocenium ion, the relative proportions of the alkane and alkylferrocene products give a measure of the absolute rate of substitution of ferrocenium ion (see the Introduction for a brief discussion of the reactions of triorganotin hydrides).

The overall reaction scheme would be;

$$\begin{aligned}
&\mathrm{In{\cdot}} + \mathrm{R'_3SnH} &&\longrightarrow \mathrm{R'_3Sn{\cdot}} + \mathrm{InH}\\
&\mathrm{R'_3Sn{\cdot}} + \mathrm{RX} &&\longrightarrow \mathrm{R'_3SnX} + \mathrm{R{\cdot}}\\
&\mathrm{R{\cdot}} + \mathrm{R'_3SnH} &&\longrightarrow \mathrm{R'_3Sn{\cdot}} + \mathrm{RH}\\
&\mathrm{R{\cdot}} + \mathrm{FcH^+} &&\rightleftharpoons [\mathrm{RFcH}]^+ \longrightarrow \mathrm{RFc} + \mathrm{H^+} \qquad \text{Scheme 26.}
\end{aligned}$$

A number of assumptions were made. These were that the last and second-last equations in Scheme 26 were strictly comparable mechanistically; the overall reaction scheme did not include any other, complicating, steps; the rate of substitution of FcH^+ was assumed to be the same for all R.

Mixtures of ferric chloride and ferrocene were used to give ferrocenium ion solutions. Ferrocenium tetrafluoroborate and similar salts were not sufficiently soluble in benzene etc. to be useful sources of ferrocenium ion.

Metal halides and oxides are reduced to the elemental metals by triethyltin hydride.[153] In particular, ferric oxide (Fe_2O_3) is reduced to elemental iron under relatively mild conditions.[153] Therefore it is possible that ferrocenium ion could be reduced by the organotin hydride. However, in benzene, ethyl acetate, or methyl acetate, not all of the ferrocene is in the ferrocenium form at any moment so that some of the ferric salt is always present. The ferric ions would be reduced by the hydride more readily than would ferrocenium ion. In some cases an orange-red precipitate (of Fe?) was observed at the end of the reaction. When making up experimental solutions, the tin hydride was always added after ferrocene and ferric chloride in an attempt to forestall the reduction of the ferric salt. Unfortunately, because peroxides were used as initiators in many experiments (see Scheme 23 for an example of initiation by peroxides) it is difficult to tell whether the reduction of the ferric and ferrocenium cations is important in these experiments. However, alkylferrocenes were isolated when azobisisobutyronitrile was used as the initiator, indicating that if reduction of the cations by tin hydride does occur it does not prevent substitution. Some tin hydride was recovered from almost every reaction, although in most cases this was very impure. Thiophenol is a better hydrogen donor than tin hydrides;[16] and a comprehensive study of the reactions of thiophenol and ferrocenium ion in the presence of free-radical initiators could be pertinent. It is worth noting that 3-hydroxybutan-2-one has been oxidized to 2,3-butanedione by ferrocenium ion in 50% aqueous ethanol;[101] presumably the ferrocenium ion was reduced.

The $R_3Sn\cdot$ radical could conceivably substitute ferrocenium cation, but such substitution products were not isolated in the experiments reported here. The reduction of alkyl halides by organotin hydrides is known[16] to occur more readily than addition to double bonds.

The choice of a suitable initiator and alkyl halide for the investigation of the reaction sequence shown in Scheme 26 required numerous preliminary experiments. Because the chain process would be interrupted by substitution of the ferrocenium cation, one molar equivalent of initiator was used in most instances. The intense absorption of ferrocenium-ferric solutions in the 320-410nm region precluded the use of the usual[21] photochemical initiation with bis-azo compounds. Thermal initiation by azobisisobutyronitrile, in an attempt to synthesise benzoylferrocenes by an alternative route to that reported in II. 2b, gave inconclusive results (Table 9, i (a)-(c)). However, experiments (Table 9, (ii)-(v)) with azobisisobutyronitrile(ABIBN) as initiator in the presence of methyl iodide or cyclohexyl, t-butyl, or benzyl bromides gave more satisfactory results.

When ferrocenium ion, tributyltin hydride, benzyl bromide, and ABIBN were refluxed in ethyl acetate (Table 9 (v)(b)), benzylferrocene and dibenzylferrocene*were isolated in moderate yield

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* After several recrystallizations, the m.p. of this product was less than that previously observed for 1,1'-dibenzylferrocene.[40] V.p.c. traces of di-t-butylferrocene and dicyclohexylferrocene formed in other experiments indicated that at least two, and probably three, partially resolved products were present. The results in II.2a suggest that three disubstituted isomers would form, with the 1,1'-isomer predominating.

Table 9 Substitution of Ferrocenium Ion by Alkyl Radicals.

Expt	FcH mmol	$FeCl_3$ mmol	Bu_3SnH mmol	RX mmol	Initiator mmol	Solvent	FcH (%)	FcR (%)	Other Products (%)
(i) (a)	10	10	1	$\underline{p}NO_2PhCOCl$ 1	-	C_6H_6 reflux 24 hr	83	3.6 (of halide)	Not isolated
(b)	6	6	1	1	ABIBN 1	C_6H_6 reflux 4 days	50	20 (of halide)	$FcC(CN)Me_2$,14;FcCN,10.
(c)	4	4	2	2	ABIBN 2	C_6H_6 reflux 3 days	56	1.5 (of halide)	$FcC(CN)Me_2$,8;FcCn,12.5 Bu_3SnH,26.
(ii) (a)	4	4	4	MeI 4	ABIBN 4	C_6H_6 reflux 37 hr	96	n.d.	$FcC(CN)Me_2$,FcCN,trace; Bu_3SnH^a 37; $(Me_2CCN)_2$59
(b)	20	20	4	MeI 4	ABIBN 4	C_6H_6 reflux 80 hr	85	$\underline{c}$.½ (of halide)	Not isolated
(iii)	4	4	4	$C_6H_{11}Br$ 4	ABIBN 4	C_6H_6 reflux 5 hr	98	FcR$\underline{c}$. 1 $FcR_2\underline{c}$. ½	$FcC(CN)Me_2$, trace; $(Me_2CCN)_2$,61;Bu_3SnH,76
(iv)	4	4	4	Bu^tBr 4	ABIBN 4	EtOAc reflux 21 hr	86	FcR $\underline{c}$. 7 $FcR_2\underline{c}$. 2	$FcC(CN)Me_2$,FcCN,trace; Bu_3SnH,46; $(Me_2CCN)_2$,32
(v) (a)	4	4	4	$PhCH_2Br$ 4	ABIBN 6	C_6H_6 reflux 26 hr	39	FcR 14 FcR_2 6	$FcC(CN)Me_2$ 4; $(Me_2CCN)_2$ Bu_3SnH 71.
(b)	4	4	4	4	ABIBN 4	EtOAc reflux 23 hr	80 (impure)	FcR 18 FcR_2 2	$FcC(CN)Me_2$3; $(Me_2CCN)_2$2 Bu_3SnH 18.
(c)	4	4	-	4	ABIBN 4	EtOAc reflux 23 hr	83	-	$FcC(CN)Me_2$4; $(Me_2CCN)_2$5 red oil.
(d)	10	10	-	10	-	EtOAc reflux 8 hr	92	-	-
(vi) (a)	10	10	-	$PhCH_2Br$ 10	$(PhCO_2)_2$10	EtOAc reflux 7 hr	44	9	Unidentified ferrocene brown oils.
(b)	10	10	10	10	$(PhCO_2)_2$10	C_6H_6 reflux 15 hr	34	8	Unidentified ferrocene brown oils.
(c)	-	-	-	10	$(PhCO_2)_2$10	C_6H_6 reflux 78 hr	-	-	$(PhCH_2)_2$ 14 by v.p.c.

Expt	FcH mmol	$FeCl_3$ mmol	Bu_3SnH mmol	RX mmol	Initiator	Solvent	FcH (%)	FcR (%)	Other Products (%)
(d)	10	10	-	-	$(PhCO_2)_2$ 10	C_6H_6 20 hr	51	-	Not isolated
(vii) (a)	10	10	10	$PhCH_2Br$ 10	$Bu^tOOCOPh$ 10	EtOAc reflux 69 hr	52	8	Not separated
(b)	10	10	-	10	$Bu^tOOCOPh$ 10	EtOAc reflux 69 hr	54	10	$PhCO_2H$ impure
(viii) (a)	10	-	10	$PhCH_2Br$ 10	Bu^tOOH 10	C_6H_6 reflux 49 hr	85	-	Unidentified oils
(b)	4	4	4	4	Bu^tOOH 4	C_6H_6 reflux 25 hr	54	5	Unidentified oils
(c)	10	10	-	10	Bu^tOOH 10	C_6H_6 reflux 22 hr	6	2	Tars
(d)	10	10	-	10	Bu^tOOH 10	EtOAc reflux 18 hr	64	7	FcCOPh trace
(e)	10	10	-	10	Bu^tOOH 10	EtOAc room temp. 7 days	83	-	Not isolated
(f)	10	10	10	10	Bu^tOOH 10	EtOAc room temp. 67 hr	71	6	Not isolated
(g)	10	10	-	10	Bu^tOOH 10	C_6H_{12} room temp. 19 hr	72	-	Not isolated
(h)	10	10	10	10	Bu^tOOH 10	C_6H_{12} room temp. 20 hr	80	trace	Not isolated
Semiquantitative Reactions									
(b)	5	5	5	$PhCH_2Br$ 5	Bu^tCOH 5	MeOAc 25^o 24 hr	61	4	FcCOPh 4 $PhCH_3$ <2% $(PhCH_2)_2$ trace
(c)	5	5	Ph_3SnH 5	5	Bu^tOOH 5	MeOAc 25^o 24 hr	65	5	Ph_3SnBr 41 $PhCH_3$ <2% $(PhCH_2)_2$ trace
(d)	-	$FeSO_4$ 10	10	10	Bu^tOOH 20	MeOAc 25^o 7 days	-	-	Toluene 8%

[a] In this and subsequent experiments, the Bu_3SnH recovered also contained Bu_3Sn halide and small amounts of other compounds.

(18 and 2% respectively). Small amounts of 2 cyano-2-ferrocenylpropane and cyanoferrocene were detected; the first was formed by substitution of ferrocenium ion by 2-cyanopropyl radicals produced by thermal homolysis of the initiator. The formation of cyanoferrocene is somewhat surprising. Hydrogen cyanide may be produced by simple ionic elimination from ABIBN or tetramethylsuccinonitrile. Cyanide ion could then be reduced by ferric chloride to cyanide radical which could substitute ferrocenium ion (see ref.[40] for a discussion of this substitution). Benzoylferrocene was also isolated in small yield. Benzylferrocene is known to be oxidized into benzoylferrocene during chromatography on alumina.[102] Tetramethylsuccinonitrile was formed by the dimerization of 2-cyanopropyl radicals. Blank reactions were performed without stannane (v(c)), or stannane and initiator (v(d)), and benzylferrocene was not isolated.

Ethyl acetate and benzene were used as solvents and only minor variations in the products obtained in these two solvents were observed (v(a),(b)). In benzene, the yield of dibenzylferrocene was relatively higher. This observation may merely be fortuitous; the amount of ferrocene recovered from this particular reaction was low. However, ferrocenium ion is not very soluble in benzene, and benzylferrocene once formed, may be oxidized, by electron-transfer, into benzylferrocenium ion. The relative concentration of ferrocenium ion would be lowered. Dibenzylferrocene could thus be formed in higher yield in benzene. Because ferrocenium ion is relatively soluble in ethyl acetate, benzylferrocenium ion would always be in low concentration when compared with the ferrocenium ion. The quantity of tin hydride recovered from reactions in ethyl acetate is lower than from reactions in benzene. Presumably tin hydride slowly reduces the ethyl acetate solvent.

The reactions were allowed to proceed for somewhat arbitrary periods of time. However, these were similar enough to allow approximate comparisons of the results to be made.

t-Butylferrocenes were formed in small yield (*c.*7% mono-, and *c.*2%di-substituted products) from a reaction using t-butyl bromide (Table 9 (iv)). Cyclohexylferrocenes were formed in even smaller yield (*c.* 1% mono-, and *c.*½% di-substituted products) from the reaction using cyclohexyl bromide (Table 9, (iii)). Only a trace of methylferrocene could be detected after one reaction using methyl iodide (Table 9, (ii)). The rates of hydrogen abstraction from tin hydride increase in the order t-butyl<cyclohexyl<methyl[21] and, as would be expected, the

yields of alkylferrocenes are the reverse of this order. Because very little mono- and di-cyclohexylferrocenes are formed and the benzylferrocenes are formed in moderate yield, ferrocenium ion appears to compete with tin hydride for alkyl radicals at a rate intermediate between the rates of reaction of tin hydride with cyclohexly and benzyl radicals. Thus, the rate of substitution of ferrocenium ion appears to be approximately of the order of the rate of hydrogen abstraction from tributyltin hydride by t-butyl radical.

Further investigations were aimed at finding a suitable room-temperature initiator for the benzyl bromide - tin hydride - ferrocenium ion reaction. Initiators which gave alkylated ferrocenes when tin hydride was absent were not investigated further. Benzoyl peroxide gave a violently exothermic reaction when it was added to a mixture of the other reagents; small yields of benzylferrocene were isolated when tin hydride was not present (Table9(v)(b)). Unidentified ferrocenes and brown oils were also isolated. Pausacker[103] noted that ferrocene and benzoyl peroxide gave ferric benzoate after an exothermic reaction, and benzoyl peroxide is known[154] to react with triorganotin hydrides to give esters of the type $RCO_2SnR'_3$ etc. t-Butyl perbenzoate also gave benzylferrocene when tin hydride was absent (Table 9 (vii) (b)), as did t-butyl hydroperoxide, but with extensive tar-formation and decomposition (Table 9,(viii)(c)). Neither benzoyl peroxide or t-butyl perbenzoate was investigated further, although t-butyl perbenzoate may have been a suitable initiator at room temperature.

When t-butyl hydroperoxide was used at room temperature in ethyl acetate without tributyltin hydride being present (Table 9,(viii)(e)), benzylferrocene was not isolated. The yields of benzylferrocene were low when tributyltin hydride *was* present (e.g. *c*. 6% after 67 hr, Table 9,(viii)(f)), however, a somewhat more detailed investigation of this reaction was attempted.

Although rate constants for the reduction of alkyl halides with triorganotin hydrides were determined[21] in cyclohexane at 25°C, methyl acetate was used in the following experiments. Other workers[104-105] have shown that there is little variation in the results obtained from competitive tin hydride reductions in different solvents . A preliminary experiment in cyclohexane (Table 9, (viii)(g)) did not give benzylferrocene.

When tributyltin hydride, benzyl bromide, ferrocenium ion, and t-butyl hydroperoxide were allowed to react for 24 hr in methyl acetate at 25°C, small amounts of benzyl- and benzoyl-ferrocene were isolated, the total yield being *c*.8%. V.p.c. analysis detected a trace of bibenzyl, but toluene appeared to be absent. Tests of the analytical procedure indicated that toluene could be detected down to c.2% yield. When tributyltin hydride, ferrous sulphate, benzyl bromide, and t-butyl hydroperoxide were allowed to stand in methyl acetate for seven days at 25°C, toluene (8%, by v.p.c.) was detected.

When tributyltin hydride was replaced by triphenlytin hydride in a reaction with ferrocenium ion, benzylferrocene (5%) and triphenyltin bromide (41%) were isolated. A trace of bibenzyl was detected by v.p.c. analysis.

An approximate value of the rate constant for substitution of the ferrocenium ion can be computed from the above results to be c. $4X10^5$ l. $mol^{-1}s^{-1}$ (assuming $FcCH_2Ph:CH_3Ph$ 4:1, and k 10^5 l. $mol^{-1}s^{-1}$ for $PhCH_2\cdot + Bu_3SnH \longrightarrow PhCH_3 + Bu_3Sn\cdot$) or c. $1X10^6$ l. $mol.^{-1}s^{-1}$ (assuming $FcCH_2Ph:CH_3Ph$ 5:2, and k $4X10^5$ l. mol^{-1} s^{-1} for $PhCH_2\cdot + Ph_3SnH \longrightarrow PhCH_3 + Ph_3Sn\cdot$). The values were obtained by assuming that toluene was formed in not quite detectable amounts and that rate constants for the tin hydride-benzyl radical reaction can be extrapolated from the data of Carlsson and Ingold.[21]

Of course there are a number of serious objections to the method of obtaining these values. They are:

(1) the rate constants for hydrogen abstraction from triorganotin hydrides by benzyl radicals have not been accurately estimated.

(2) The concentrations of ferrocenium ion vary markedly during experiments. In the presence of t-butyl hydroperoxide and ferric chloride, the ferrocenium ion concentration approximately doubled during the period of consumption of peroxide.

(3) Although triphenyltin bromide was isolated in 41% yield in one experiment, benzylferrocene was isolated in only 5%, a trace of bibenzyl was detected, and toluene was absent. Benzyl radicals could be oxidized to give unobserved products and tars, or free radical polymerization could occur.

(4) The chromatographic separation, on alumina, of the reaction mixtures containing ferrocenes gave benzoylferrocene, making the estimation of yields difficult.

(5) The substitution of ferrocenium ion by benzyl radical is not strictly comparable with radical-tin hydride reactions.

However, the preliminary assertion that the substitution rate would be roughly of the order of the rate of hydrogen abstraction from tributyltin hydride by the t-butyl radical, ($7.4\mathrm{X}10^5$ $\mathrm{l.mol}^{-1}\mathrm{s}^{-1}$) is confirmed by the rate constants from the somewhat more rigorously conducted experiments (c. $4\mathrm{X}10^5$ $\mathrm{l.mol}^{-1}\mathrm{s}^{-1}$ or c. $1\mathrm{X}10^6$ $\mathrm{l.mol}^{-1}\mathrm{s}^{-1}$). The decreasing yields of alkylated ferrocenes from reactions with benzyl, t-butyl, cyclohexyl, and methyl halides (in that order) is what is expected after a consideration of the values of the rate constants[21] for the reactions of alkyl radicals with triorganotin hydrides.

The large value of the rate constant for the free-radical alkylation of ferrocenium ion shows that the ion is a good radical-scavenger. Hydroquinone would probably not inhibit the substitution of ferrocenium ion by free-radicals.

To illustrate the radical-scavenging ability of ferrocenium ion, t-butyl hydroperoxide, phenylthiol, and ferrocenium ion were refluxed together and phenylthioferrocene was formed in small yield (3%), despite the electrophilicity of phenylthio radical. (Generally, thiyl radicals do not substitute aromatic rings that are less reactive than anthracene.) No attempt was made to maximize the yield from this reaction. However, this is a feasible one-step synthesis of various thioferrocenes which have commercial possibilities as fuel additives etc.[106] A literature route[42] to these compounds, albeit in fair yield (c. 40% from FcHgCl), requires at least four steps. An alternative free-radical route to thioferrocenes could involve the interception, by ferrocenium ion, of organothio radicals generated from disulphides and organotin hydrides.[107] The rate-controlling step in this chain reaction is the fast (c. $1X10^6$ $l.mol^{-1}s^{-1}$)attack of tributyltin radicals on disulphides, suggesting that interception by ferrocenium ion may be too slow to complete effectively. However, judicious choice of disulphide, tin hydride, and reaction conditions could favour the formation of thioferrocenes.

Phenylations with diazonium salts are another example of the reactivity of ferrocenium ion in free-radical substitutions. By analogy with the reasoning about electrophilic substitution (see Introduction), complexes bound to iron have been postulated for free-radical phenylations;[54] however, this complication is probably unnecessary.

When free-radical phenylation was carried out in acetone or acetic acid in the presence of benzyl bromide, phenylferrocenes were formed in fair yield and small amounts of benzyl-

TABLE 10.

Phenylations of Ferrocene at Room Temperature

Ferrocene (mmol)	PhN_2BF_4 (mmol)	$PhCH_2Br$ (mmol)	Solvent	Products
10	10	10	Me_2CO	FcH 62%; FcPh 14%; $FcCH_2Ph$ some (c. 1%)
10[a]	10	10	Me_2CO	FcH 41%; FcPh 26%; $FcPh_2$ 2.3%; $FcCH_2Ph$ some.
10	10	10	HOAc	FcH 27%; FcPh 29%; $FcPh_2$ 4%; $FcCH_2Ph$ some.
10	10	10	Pr^iOH	FcH 85%; FcPh c. 3%; $FcCH_2Ph$ c. 3%.
10	10	-	Pr^iOH	FcH 70%; FcPh 8%
10[b]	10	10	Me_2CO	FcH 63%; FcPh 13% $FcCH_2Ph$ nil

[a] As ferroceniumtetrafluoroborate.

[b] p-Hydroquinone, 40 mmol, added.

ferrocene were detected (Table 10). However, if the reaction was performed in isopropyl alcohol the yield of phenylferrocenes was greatly reduced, while that of benzylferrocene was not. In the presence of hydroquinone, benzylferrocene was not detected. These observations can be best rationalized by assuming that isopropyl alcohol and hydroquinone act in different ways. The first step in the reaction is:

$$FcH + PhN_2^+ \longrightarrow FcH^+ + Ph\cdot + N_2 \qquad (27)$$

Phenyl radical can then react with the radical-scavenger, ferrocenium ion:

$$FcH^+ + Ph\cdot \xrightarrow{B:} FcPh + BH^+ \qquad (28)$$

or with benzyl bromide to form the stable benzyl radical:

$$Ph\cdot + PhCH_2Br \longrightarrow PhCH_2\cdot + PhBr \qquad (29)$$

Benzyl radical can then be scavenged by ferrocenium ion, but the efficiency of scavenging of phenyl radicals by ferrocenium ion limits the extent of (29). If an iron-bound complex between the diazonium and ferrocene was a necessary precursor to the substitution of ferrocene, isopropyl alcohol would not be likely to depress the yield of phenylferrocene relative to that of benzylferrocene.

Isopropyl alcohol could react with a large proportion of the phenyl radicals to give $Me_2\dot{C}OH$ radicals. This radical is a powerful reducing agent[156] and Scheme 30 is feasible. Therefore, in isopropyl alcohol the relative amount of benzyl radi-

$$PhCH_2Br + Me_2\dot{C}OH \longrightarrow PhCH_2\cdot + Me_2CO + H^+ + Br^- \qquad \text{Scheme 30}$$

cal available to substitute ferrocenium ion may be greater than when isopropyl alcohol is absent. The total yield of substituted ferrocenes is lower in the alcohol than in acetone or acetic acid. This may be caused by both the consumption of phenyl radicals and by the reduction of ferrocenium ion as shown in Scheme 31. The relative concentration of ferrocenium ion available for substitution by benzyl and phenyl radicals

$$FcH^+ + Me_2\dot{C}OH \longrightarrow FcH + H^+ + Me_2CO \qquad \text{Scheme 31}$$

would thus be lowered.

When ferrocenium ion and hydroquinone compete, ferrocenium ion is obviously substituted by phenyl radicals faster than hydroquinone can effectively remove them (just as hydroquinone has no effect on the two-step organotin hydride-organic halide reduction[21]), so the yield of phenylferrocene is unaffected. However, hydroquinone may effectively compete with the phenyl radical-benzyl bromide reaction, completely suppressing benzylferrocene formation.

CHAPTER III

THE STABILITY OF FERROCENYL-METHYL RADICAL

III.1. Preamble
III.2. Preparation of materials
III.3. Investigation of stability,-reductions

III.1. Preamble

When one considers the amount of work concerned with the properties and stability of the α-ferrocenylcarbonium ion, the relative lack of interest in the ferrocenylmethyl radical is surprizing. Pauson and Watts[108] have suggested that the stability of the intermediate ferrocenylmethyl radical determined the products they obtained from some reactions of ferrocenecarbaldehyde. The dimeric products isolated from the Clemmensen reduction of benzoylferrocene require the intermediacy of α-ferrocenyl radicals.[109] Perevalova and Ustynyuk[75] have reduced a number of quaternary ammonium salts with cobaltous chloride and Grignard reagents and they concluded that ferrocenylmethyl radical was less stable than benzyl radical. The ferrocenylmethyl radical has been suggested as an intermediate in the formation of methylferrocene and 1,2-diferrocenylethane from (ferrocenylmethyl)trimethylammonium iodide.[76] Incidentally, the Stevens rearrangement of quaternary ammonium salts has been shown by chemically-induced dynamic nuclear polarization[110] and by product studies[111] to occur by a radical-pair mechanism.

Ferrocenylmethyl radical would be expected to be relatively unstable when compared with benzyl or similar radicals. The delocalization of an extra odd-electron onto ferrocene is forbidden on theoretical grounds,[40] ferrocene is decomposed in lithium-ethylamine reducing solutions, and the free spin on the benzoylferrocene radical anion is delocalized into the phenyl moiety.[78] Although the stability of the α-ferrocenyl carbonium ion has been attributed to the involvement of iron electrons, the mechanism of this stabilization is still a matter of dispute (see the Introduction). Therefore, it is difficult to draw analogies with the carbonium ion to suggest specifically how the ferrocenylmethyl radical is stabilized or destabilized, although resonance structures could be drawn.

Preliminary investigations of the stability of ferrocenylmethyl radical involved four different experimental approaches. These were:

(1) The attempted dimerization of acetylferrocene by photochemical means to give the pinacol, 2,3-diferrocenylbutan-2,3-diol. This pinacol was not obtained. Weliky and Gould[77] had previously attempted to dimerize benzoylferrocene by photochemical means to give the corresponding pinacol, but were equally unsuccessful. However, the reductive dimerization was successful with the same alkyl Grignard-cobaltous chloride reducing agent as was used[75] in the reduction of ferrocenyl quat-

ernary ammonium salts.

(2) The reaction of ferrocenylmethyl chloride with an organotin hydride to give ferrocenylmethyl radicals in a competitive situation was considered feasible. Paradoxically, a a preliminary experiment gave methylferrocene (from ferrocenylmethyl chloride) without the formation of toluene (from benzyl chloride), suggesting that ferrocenylmethyl was more stable than benzyl radical. However, tin hydrides readily transfer hydride under conditions which preclude hydrogen-atom transfer by a radical-chain mechanism.[112] The stability and ease of formation of ferrocenylmethyl carbonium ion could well facilitate hydride transfer to give methylferrocene by a non-radical path.

(3) An attempted synthesis of ferrocenylmethyl chloroformate was unsuccessful. This compound, if prepared, was to be the basis for competitive studies with organotin hydrides[104] (scheme 32):

$$R^1CH_2OCOCl + R^2_3Sn\cdot \rightleftharpoons R^1CH_2OCO\cdot + R^2_3SnCl$$

$$R^1CH_2OCO\cdot \longrightarrow R^1CH_2\cdot + CO_2$$

Scheme 32

However, alkyl chloroformates may be sources of free cations,[113] so great care would have to be taken in assessing the results. Thus, the attempted synthesis was not pursued when preliminary work was unsuccessful.

(4) The addition of tributyltin hydride to the double bond of

isopropenylferrocene was attempted but the addition product was not readily formed. This is not surprising as olefins are activated by electronegative substituents for these additions.[16] Two unstable oily products with n.m.r. and mass spectral features similar to those expected were isolated. Tar formation was extensive.

After the unsuccessful approaches mentioned above, a further experimental investigation was undertaken. A number of ferrocenylmethyl quaternary ammonium salts were prepared and then reduced, and the products from the reduction were identified. This approach was intended to allow an examination of the relative stability of the fragments formed by one-electron reduction. Some of the salts were easy to prepare, but the adaptation of a known synthetic route was necessary to prepare some of the precursor amines. The scope of this synthetic route was explored. Unfortunately, the salts prepared from these amines were not as useful for the reductions as had been hoped.

The synthesis of the amines and quaternary salts will be discussed in the next section.

III.2. The Preparation of Materials

Amines

Recently it has been reported that the hydroxyl group in ferrocenylmethanols can be displaced by N,N,N',N',- tetramethyl-diaminomethane,[114] malonic acid diethyl esters,[115] and aniline.[116] The ease of replacement of the hydroxyl group has been attributed to the greater nucleophilic character of the replacing groups and the inherent stability of the ferrocenylmethyl carbonium ion. More extensive synthetic use has been made of the leaving group of (ferrocenylmethyl) trimethylammonium iodide.[42] However, the lack of recorded experimental detail available when the displacing agent was amine,[117] and the low yields of product obtained in preliminary experiments in this work (22% of N-t-butyl(ferrocenylmethyl)amine) led to an attempt to modify the hitherto unsuccessful displacement of hydroxyl by aliphatic amines.[116]

Obviously, if the pH of a reaction solution is lowered, protonation of the hydroxyl group will potentially facilitate the S_N-type displacement by amines (Scheme 33):

$$FcCH_2OH_2^+ + \text{Amine} \rightleftharpoons FcCH_2\text{Amine}^+ + H_2O \qquad \text{Scheme 33}$$

Table 11 lists the results of displacement experiments,

TABLE 11.

The Preparation of (Ferrocenylmethyl)amines from Ferrocenylmethanol

All mixtures were refluxed for 12 hr

Amine	Solvent	pH	Products
Bu^tNH_2	H_2O		Starting material recovered
Bu^tNH_2	H_2O, trace HOAc		Starting material recovered
Bu^tNH_2	H_2O, excess HOAc		N-t-butyl(ferrocenylmethyl)-amine 75%
Bu^tNH_2	H_2O, excessHOAc	5.2	quantitative
$C_5H_{10}NH$	H_2O, excessHOAc	5.1	N-(ferrocenylmethyl)piperidine 97%
$C_6H_{11}NH_2$	H_2O, excessHOAc	5.0	N-cyclohexyl(ferrocenylmethyl)-amine 89%
$PhCH_2NH_2$	H_2O, excessHOAc	4.9	N-(ferrocenylmethyl)benzylamine 92%
$PhNH_2$	H_2O, MeOH	8.8	N-(ferrocenylmethyl)aniline 95%
$PhNH_2$	H_2O, MeOH, excess HOAc	4.3	N-(ferrocenylmethyl)aniline 50% ferrocenylmethyl methyl ether 1
p-$NO_2C_6H_4NH_2$	H_2O, MeOH	9.6	N-(ferrocenylmethyl)-*p*-nitroaniline 84%
p-$MeOC_6H_4NH_2$	H_2O, MeOH	9.7	N-(ferrocenylmethyl)-*p*-methoxyaniline 70%
NH_2CONH_2	H_2O	7.2	N-(ferrocenylmethyl)urea 33%

showing that t-butylamine, piperidine, cyclohexylamine, and benzylamine form the corresponding (ferrocenylmethyl)amines in excellent yields when the pH of the solution was adjusted to c. 5 by the addition of acetic acid. In Table 12 are given the

TABLE 12.

The Preparation of N-(Ferrocenylmethyl)piperidine at Various pH Values

Solvent	pH[a]	Conditions	Products
H_2O,MeOH	7.8	ambient temp	none observed
H_2O	7.9	reflux overnight	traces only
H_2O	6.5	reflux overnight	N-(ferrocenylmethyl)piperidine 60%
H_2O,MeOH	7.8	reflux overnight	ferrocenylmethyl methyl ether trac
H_2O,MeOH	8.1	reflux 72 hr	N-(ferrocenylmethyl)piperidine 22% ferrocenylmethyl methyl ether 5%
H_2O,MeOH	7.2	reflux 6 hr	traces only
H_2O,MeOH	3.8	reflux overnight	N-(ferrocenylmethyl)piperidine 23% ferrocenylmethyl methyl ether 62%
H_2O,MeOH	3.4	ambient temp24hr	ferrocenium salts
H_2O,MeOH	0.6	ambient 6 hr	di(ferrocenylmethyl) ether 67%
H_2O	1.3	reflux overnight	tars

[a] Buffer solutions were made as in: Vogel,A.I.,"Quantitative Inorganic Analysis." p.1162.(Longmans:London 1961); or Fieser,

results of varying the reaction conditions for the reaction between ferrocenylmethanol and piperidine. Above pH 7, N-(ferrocenylmethyl)piperidine was formed only after prolonged heating. At c. pH 4 methanol competed favourably with piperidine, probably because protonation effectively removed the free amine from the solution. At values of pH<4 tars and ferrocenium salts were formed, and di(ferrocenylmethyl)ether was formed in good yield in one experiment. A literature[118] synthesis of di(ferrocenylmethyl)ether consists of refluxing ferrocenylmethanol in dilute aqueous acetic acid.

Aniline, p-nitroaniline, p-methoxyaniline, and urea all gave good yields of amines at high pH values without acetic acid (Table 11). If acid was added to the reaction with aniline, a small amount of ferrocenylmethyl methyl ether was also formed by attack of the methanol solvent.

Because triphenylmethanol and aniline readily form p-(triphenylmethyl)aniline in the presence of acetic acid [119] and trityl cation has a stability similar to that of ferrocenylmethyl

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L.F., and Fieser,M., "Reagents of Organic Synthesis." (Wiley: New York 1967). The pH values of 0.6 and 1.3 were achieved by the addition of dilute aqueous hydrochloric acid cation,[40] the structures of the (ferrocenylmethyl)anilines are potentially ambiguous. However, a double reduction of p-nitrobenzoylferrocene, first with lithium aluminium hydride-aluminium trichloride, and then with hydrazine and platinum in ethanol (Scheme 34), gave p-(ferrocenylmethyl)aniline m.p.105-107°, with physical data distinctively different from that of N-(ferrocenylmethyl)aniline m.p.84-85°.

$$\text{p-}NO_2C_6H_4COFc \xrightarrow{LiAlH_4-AlCl_3} \text{p-}NO_2C_6H_4CH_2Fc$$

$$\text{p-}NO_2C_6H_4CH_2Fc \xrightarrow{NH_2NH_2-Pt} \text{p-}NH_2C_6H_4CH_2Fc$$

Scheme 34

Aniline did not displace the methoxy group from ferrocenylmethyl ether on prolonged heating at pH 8, and methanol did not displace piperidyl from N-(ferrocenylmethyl)piperidine when they were heated together. When ferrocenylmethanol and aqueous aniline were heated with cyclohexylamine or t-butylamine (in the absence of acetic acid), only N-(ferrocenylmethyl)aniline was isolated.

The probable mechanism for the preparation of the amines is (Scheme 35):

$$FcCH_2OH + H^+ \rightleftharpoons FcCH_2OH_2{}^+$$

$$RR'NH + H^+ \rightleftharpoons RR'NH_2{}^+$$

$$FcFH_2OH_2{}^+ + RR'NH \longrightarrow FcCH_2\overset{+}{N}RR'H + H_2O$$

Scheme 35

This suggests that the strongest bases (although predominantly in the protonated form) would displace the protonated hydroxyl most readily. This is true below pH 7, with good yields of ferrocenylmethylamines from the strong bases cyclohexylamine, t-butylamine, piperidine, and benzylamine. The last two bases have been incorrectly described by Marr et al.[115] as "weaker bases than aniline." A relatively poor yield of N-(ferrocenylmethyl)aniline was isolated with the weak base aniline at pH value <7. Methanol, a very weak base, competed effectively with amines at pH<4, presumably because the free amine was largely removed by the protonation equilibrium.

Harder to account for is the high nucleophililicty apparently displayed by anilines. Despite being classified as weaker bases and nucleophiles than aliphatic amines,[120] the anilines gave good yields of N-(ferrocenylmethyl)anilines at c.pH 9. (It should be noted at this stage that recent work has indicated that the traditional inductive model for the electronic effects of alkyl groups needs to be modified extensively to include solvents effects etc. when considering such properties as basicity.[157]) However, the results reported here can possibly be accounted for with the aid of Pearson's hard and soft acid and base concept.[121] Ferrocenylmethanol can be considered a soft acid, and it will react rapidly with soft bases e.g. anilines, diethyl malonate,[115] but not with harder bases e.g. t-butylamine, piperidine, etc. At low pH values, protonated ferrocenylmethanol (or ferrocenylmethyl cation) is a harder acid and reacts readily with t-butylamine, piperidine, etc. Because the pH of aqueous solutions of urea was relatively low (7.2), the hard acid form of the alcohol was present, allowing only low yields of product from the reaction with this soft base.

An alternative quantitative description of the reaction between ferrocenylmethanol and amines can be constructed. (Assuming that the same mechanism is applicable to all amines.) The acid-base equilibria are

$$\mathrm{FcCH_2OH} + \mathrm{H^+} \rightleftharpoons \mathrm{FcCH_2OH_2}^+ \qquad K_1$$

$$\mathrm{RNH_2} + \mathrm{H^+} \rightleftharpoons \mathrm{RNH_3}^+ \qquad K_2$$

$$\text{and} \quad \frac{K_1}{K_2} = \frac{[\mathrm{FcCH_2OH_2}^+][\mathrm{RNH_2}]}{[\mathrm{FcCH_2OH}][\mathrm{RNH_3}^+]}$$

The rate of substitution of ferrocenylmethanol is $k[\mathrm{RNH_2}].[\mathrm{FcCH_2OH_2}^+]$ and at a fixed pH the weaker bases would be expected to give the fastest rate of substitution. The reaction would be subject to general acid catalysis. However, this argument ignores changes in the rate constant k. This could be expected to vary proportionately with the strength of an individual base. If this is the case then the two effects would tend to cancel each other, and no conclusions can be drawn. In the absence of detailed kinetic data, the results appear to be more in accord with the operation of two catalysis mechanisms. At low pH values it would appear that for the strong bases (piperidine, t-butylamine, etc.), specific hydronium-ion catalysis takes place. This is supported by the observation that the reaction appears to depend on the pH and not on the media in solution. Consistent results were obtained for the reaction of piperidine with ferrocenylmethanol with various acids present (see Table 12) and for the reactions with a variety of other aliphatic amines (Table 11). However, whether acid or base catalysis applies to the reaction of anilines and urea with ferrocenylmethanol at high pH is open to conjecture. Certainly the substitutions by these nucleophiles do not depend simply on the pH of solution.

N-Cyclohexyl(ferrocenylmethyl)amine was also synthesized via the appropriate Schiff's base (imine). Ferrocenecarbaldehyde and cyclohexylamine, on prolonged standing, gave the imine, and this was catalytically hydrogenated over platinum to give N-cyclohexylferrocenylmethylamine in moderate yield.

N-Methyl-N-t-butyl(ferrocenylmethyl)amine was not isolated in good yield by the procedure with ferrocenylmethanol, acetic acid, and N-methyl-t-butylamine, although the crude base-fraction appeared to contain some of the ferrocenylmethylamine. The synthetic method of choice consisted of treating ferrocenylmethyl chloride (from ferrocenylmethanol and dry dydrogen chloride under anhydrous conditions) with an excess of N-methyl-t-butylamine. Initially, only a 27% yield of the purified ferrocenylmethylamine was obtained, but subsequent large-scale experiments gave yields of 67% and 72%.

Quaternary ammonium salts

Ethyl(ferrocenylmethyl)dimethylammonium iodide, (ferrocenylmethyl)isopropyldimethylammonium iodide, allyl(ferrocenylmethyl)dimethylammonium bromide, and benzyl(ferrocenylmethyl)-dimethylammonium bromide were readily synthesized by treating (dimethylamino)methylferrocene with an excess of the appropriate alkyl halide in benzene and then filtering off the product. However, neither the t-butyl- nor the cyclohexyl-ammonium salt was preparable by this method, whether the bromide, iodide, or tosyl derivatives were used as N-alkylating agents.

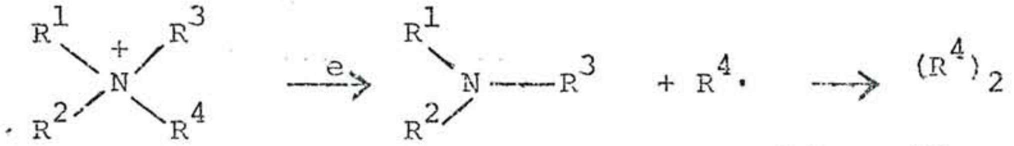
Treatment of N-t-butyl- and Ncyclohexyl-(ferrocenylmethyl)-amines (described in the previous section) with an excess of methyl iodide allowed the monomethylated quaternary ammonium iodides to be isolated in good yields. The n.m.r. spectral resonances for these compounds were not as easily assigned as those for the other ammonium salts. Possibly the very low solubility in $CDCl_3$ had some effect. Satisfactory analytical results were obtained. N-t-Butyl-N-methyl(ferrocenylmethyl)-amine was converted into the methiodide by treatment with an excess of methyl iodide; this salt gave satisfactory physical data.

N.m.r. spectal characteristics of quaternary ammonium salts were interesting. By analogy with the fully interpreted spectrum of (ferrocenylmethyl)trimethylammonium iodide,[122] all quaternary salts gave a singlet at δ c. 5.0 for the methylene protons, a triplet at c. 4.6, J 2Hz, for the 2,5-ferrocene protons, and a triplet (J 2Hz) superimposed on a singlet at c. 4.3, for the 3,4 and the C_5H_5 protons.

The difficulty experienced in preparing some of the quaternary ammonium salts is not surprising in view of the fragmentations reported when N-(ferrocenylmethyl)anilines were treated with methyl iodide under a variety of conditions.[123] In alcohols and acetonitrile the quaternary salts were not isolated. Decomposition products of these salts were obtained.

III.3. Investigations of Stability-Reductions.

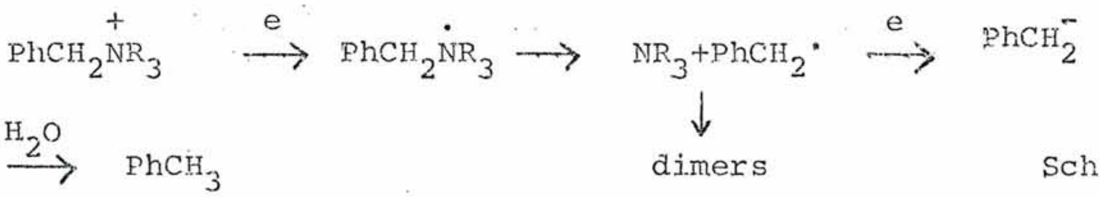
In 1960 Ross, Finkelstein, and Petersen[124] showed that cathodic reduction of quaternary ammonium salts in dimethylacetamide or dimethylformamide gave the dimers of free radicals formed by one-electron transfer (Scheme 36):



Scheme 36.

In all cases, the products were those expected from cleavage to give the most stable radical. The yields of dimerized products ranged from 6-35%. Subsequently, a detailed polarographic analysis of the reductions of quaternary ammonium hydrox-ides[125] confirmed the results and conclusions obtained with the simpler experimental apparatus.[124] (The straightforward regulation of the total current or voltage is usually inadequate in maintaining the controlled potential at the working-electrode interface which is usually required to control product formation.) Polarographically the quaternary ammonium salts were difficult to handle, and the coincidence of the results from the two investigations indicates that there is probably only one practicable route for the cathodic reduction of quaternary ammonium salts.

A further study[126] of the electroreduction confirmed its relative simplicity, but the mechanistic scheme proposed was of dubious value. In 1968 Utley[127] suggested a simplified scheme for the electroreductive formation of toluene and bibenzyl (Scheme 37):



$$PhCH_2\overset{+}{N}R_3 \xrightarrow{e} PhCH_2\overset{\cdot}{N}R_3 \longrightarrow \underset{\substack{\downarrow \\ \text{dimers}}}{NR_3+PhCH_2^{\cdot}} \xrightarrow{e} PhCH_2^{-} \xrightarrow{H_2O} PhCH_3$$

Scheme 37

This scheme is similar to that proposed by Perevalova _et al._[75] for the reduction of ferrocenylmethyl quaternary ammonium salts by cobaltous chloride-Grignard reagents.

The apparatus of Ross _et al._[124], with a cathode of aluminium foil and an anode of platinum in the same compartment, was initially used in this work. A trial reduction of benzyltrimethylammonium bromide in DMF gave bibenzyl (28%); toluene was detected by v.p.c. analysis. Nitrogen was bubbled through the electrolysis solution and then into ethereal methyl iodide and trimethylamine was trapped as tetramethylammonium iodide. (Ferrocenylmethyl)trimethylammonium nitrate in DMF gave methylferrocene (29%), 1,2-diferrocenylethane (2%), and crude tetramethylammonium iodide (57%) by the same method. However, electrolysis of benzyl(ferrocenylmethyl)dimethylammonium bromide in DMF or water gave products consistent with the formation of benzyl and ferrocenylmethyl radicals. Extensive decomposition of the salt, and the cathode itself, occurred during electrolysis in aqueous media.

The preparation of nitrates for electrolyses proved difficult. However, a trial reduction with separated anode and cathode compartments connected by a salt bridge was successful. The apparatus is shown in Figure 5 and it was used in all subsequent electrolyses (see Table 13). To facilitate the reductions, a mercury-pool cathode was used (mercury has an overpotential of 0.78Vin 1N H_2SO_4). Because of the simplicity of the electrolytic reduction, controlled-potential electrolysis was considered unnecessary. The applied voltage was usually maintained at 30V. No attempt was made to measure the quantity of electricity by coulometry because the efficiencies for reductions of quaternary salts are low (c.30%) and variable (20-50% range).[125] DMF was the solvent of choice because it extends the range of available working potentials, but the results obtained were similar in acetonitrile and water. Supporting

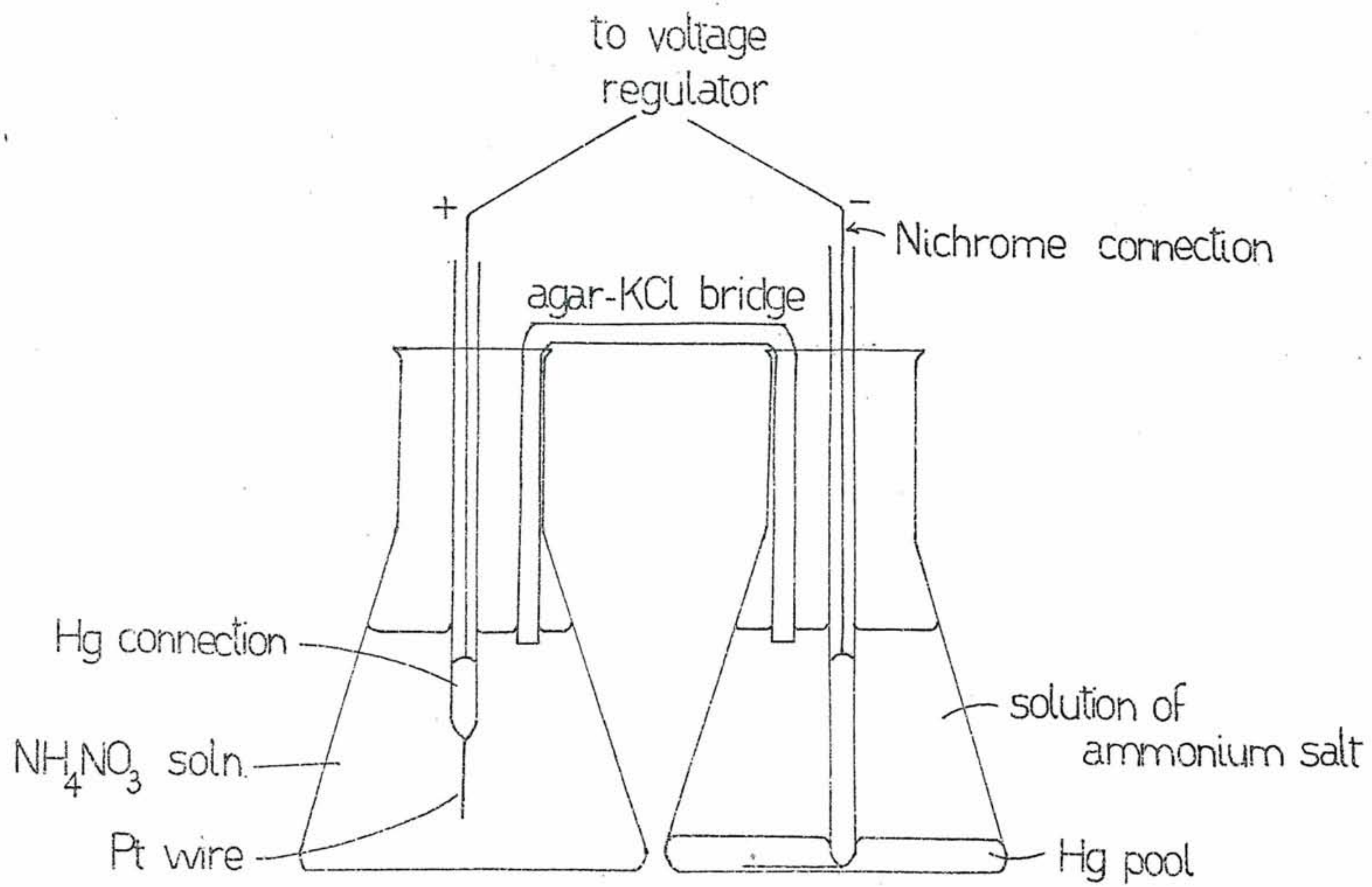

to voltage regulator
+
−
Nichrome connection
agar-KCl bridge
Hg connection
NH_4NO_3 soln.
Pt wire
solution of ammonium salt
Hg pool

Fig. 5.

TABLE 13.

The Reduction of Quaternary Ammonium Salts.

E, electrolysis; S, sodium-liquid-ammonia reduction; all, allyl; Fc, ferrocenyl($C_5H_5FeC_5H_4$)

Quaternary Salt	Amount (g)	Method	Solvent	Products
$FcCH_2\overset{+}{N}Me_3\ I^-$	3.9	E	H_2O 150 ml	MeFc 14.3%
$FcCH_2\overset{+}{N}Me_2Et\ I^-$	3.0	E	DMF 200ml	MeFc 10%, $FcCH_2CH_2Fc$ trace
$FcCH_2\overset{+}{N}Me_2Pr^i\ I^-$	2.1	E	DMF 200ml	MeFc 19%, $FcCH_2CH_2Fc$ trace
$FcCH_2\overset{+}{N}HMeC_6H_{11}\ I^-$	1.1	E	DMF 200ml	MeFc 18%, base decomposed during chromatography to give FcCHO(10mg).
"	0.4	S	NH_3 30ml	MeFc 15%, $FcCH_2CH_2Fc$ trace
$FcCH_2\overset{+}{N}HMeBu^t\ I^-$	0.5	E	DMF 150 ml	MeFc, $FcCH_2NHBu^t$.
	0.7	E	H_2O 150ml	MeFc, $FcCH_2NHBu^t$.
$FcCH_2\overset{+}{N}Me_2Bu^t\ I^-$	0.5	E	DMF 100ml	MeFc 10%, $FcCH_2CH_2Fc$ trace, $(PhCH_2)_2$ trace, ? $FcCH_2NMe_2$ 7%(impure)
	0.2	S	NH_3-THF 1:1 60ml	MeFc,18%, $FcCH_2CH_2Fc$ trace.
	0.25	S	NH_3 20ml	MeFc 21%, $FcCH_2CH_2Fc$ 7% ferrocene bases (small amounts)
	1.0	S	NH_3 50ml	MeFc 32%, $FcCH_2CH_2Fc$ 10%, $FcCH_2NMe_2$ 2%.

Table 13 (cont.)

Quaternary Salt	Amount (g)	Method	Solvent	Products
$FcCH_2\overset{+}{N}Me_2$ all Br^-	1.0	E	DMF 150ml	MeFc 3%
	1.2	S	NH_3 70ml	MeFc 18%, $FcCH_2CH_2Fc$ 3%.
$FcCH_2\overset{+}{N}Me_2CH_2Ph$ Br^-	4.1	E	DMF 200ml	$FcCH_2NMe_2$ 55% (crude) MeFc 1%.
	4.1	E	CH_3CN 200ml	$FcCH_2NMe_2$ 19%, MeFc <½% $PhCH_3$ detected.

electrolytes were not used because they can influence the formation of products.[128] Because the current was very low (c. 0.05A) and the salt bridges needed regular replacement, the solutions did not become noticeably hotter during electrolyses. The results are shown in Table 13. No attempt was made to maximize the yields of products. Only the ferrocene products were examined in detail.

Confirmation of the reduction-fragmentation pathway was sought by using Slocum's method[76] of reducing quaternary ammonium salts with sodium-liquid ammonia. In explaining the formation of methylferrocene from (ferrocenylmethyl)trimethylammonium iodide, Slocum postulated a one-electron transfer to the salt, followed by fragmentation. The expected Steven's rearrangement did not occur, but as mentioned previously, even this rearrangement takes place by a diradical route.[110,111] The results of various reductions with sodium-liquid ammonia are given in Table 13. The maximization of yields was not attempted.

(Ferrocenylmethyl)trimethylammonium iodide, ethyl(ferrocenylmethyl)dimethylammonium iodide, and (ferrocenylmethyl)isopropyldimethylammonium iodide all gave appreciable yields of methylferrocene after electrolytic reduction. The N-cyclohexyl(ferrocenylmethyl)amine methiodide salt also gave methylferrocene by electrolysis and reduction with sodium-liquid ammonia. However, this salt and N-t-butyl(ferrocenylmethyl)-amine methiodide were readily cleaved in aqueous basic solution (e.g. 5% potassium carbonate) to give the parent amine, i.e. demethiodidation occurred. The aqueous electrolysis solutions became basic enough to cause this cleavage and aqueous basic solutions were employed in work-up procedures used for electrolyses in non-aqueous media.

t-Butyl(ferrocenylmethyl)dimethylammonium iodide gave predominantly methylferrocene (10%) and 1,2-diferrocenylethane by electrolysis, but an appreciable quantity of (dimethylamino)-methylferrocene (7%) was also isolated, albeit very impure. A small amount of (dimethylamino)methylferrocene (2%) was isolated from one of the reductions with sodium-ammonia (see Table 13) although in the particular reduction, methylferrocene predominated (32%). The results discussed so far indicate that ferrocenylmethyl radical is more stable than methyl, ethyl, isopropyl, and t-butyl radicals but that the stability is comparable with that of the last radical. Benzyl(ferrocenylmethyl)-dimethylammonium bromide gave predominantly (dimethylamino)-methylferrocene.

The results clearly indicate that ferrocenylmethyl radical is less stable than benzyl radical and accord well with the order of stability of the radicals being methyl$\leq$ethyl$<$isopropyl$<$t-butyl$\ll$ferrocenylmethyl$<$benzyl.

The reduction of allyl(ferrocenylmethyl)dimethylammonium bromide by both methods gave results which contradicted the order of radical stabilities given above. Methylferrocene was isolated in both instances and (dimethylamino)methylferrocene was not detected.

It is attractive to suggest that reduction of the allyl salt is a special case and should be considered separately from the other reductions. Olefinic compounds are reduced at the cathode and this reaction is well-documented (see e.g. ref[128]). Relative to ferrocene, the allyl part of the quaternary cation would be attracted to the mercury-solvent interface, perhaps modifying the properties of the ion (by weakening the N-CH_2Fc bond relative to the CH_2CHCH_2-N bond). This could allow electron-transfer and subsequent fragmentation to favour the formation of the ferrocenylmethyl radical. Alternatively, reduction may involve two-electron transfer and the formation of carbanions. However, all previous workers[124-127] have suggested that if carbanions are formed, the process consists of single-electron transfer, followed by fragmentation and then by carbanion formation.

An effect also has to be invoked to explain the results of reduction by sodium-liquid ammonia. The reducing solution is analogous to a cathode, and solvation of the allyl moiety could again modify the bond strengths and hence the radicals formed. While superficially adequate, the above reasoning ignores the fact that the benzyl salt gives explicable products while the allyl salt does not. Both salts would be expected to behave similarly because the allyl and benzyl radicals have similar stabilities. Any postulated effects must apply to both reductions and be specific for the allyl salt. Perevalova and Ustynyuk[75] noted that the reduction of the allyl(ferrocenylmethyl)dimethylammonium salt with cobaltous chloride-ethyl Grignard was anomalous. They suggested that the cleavage of this salt was probably of a heterolytic nature. Also, the reductive coupling of activated olefins is known to be encouraged by the presence of quaternary ammonium ions (see ref.[127]) However, the ions were not reduced under the experimental conditions.

The stability of the ferrocenylmethyl radical is less than that for benzyl radical and is approximately of the order of the stability of the t-butyl radical under the experimental conditions used for these investigations. It is difficult to conceive the nature of the ferrocenylmethyl radical. Little guidance can be gained by a consideration of the ferrocenylmethyl carbonium ion. The stabilization of this ion has been described as "either the consequence of very different molecular deformations or derived from a charge distribution and metal-ring bonding interactions which are significantly different in the ion compared with uncharged derivatives."[70] Somewhat simplistic contributing structures could be drawn for the radical. However, it must be remembered that the extra odd-electron would go into an antibonding orbital according to the M.O. descriptions of ferrocene. Thus, there would be little likelihood of significant stabilization of the ferrocenylmethyl radical by delocalization of the electron into the ferrocenyl moiety. The radical may be stabilized by some type of limited hyperconjugation similar to that suggested by Ware and Traylor for the ferrocenylmethyl carbonium ion.[64]

Very recently it has been reported[160] that photolysis of α-ferrocenyl ethers gives rise to products which can only be ascribed as coming from both the α-ferrocenyl carbonium ion and radical.[160] This somewhat surprising result suggests that there is still much to be learned about the behaviour and formation of the α-ferrocenyl carboniun ion and radical.

CHAPTER IV

EXPERIMENTAL

General

IV.1.	Kinetic Investigations
IV.2a	Comparative Isomer Distributions
2b	The synthesis of Benzoylferrocenes
IV.3.	The Reactivity of Ferrocenium Ion
IV.4.	Preliminary Experiments for Studies of Stability
IV.5.	The Preparation of Amines and Quaternary Salts
IV.6.	The reductions of Quaternary Ammonium Salts

IV Experimental General

Detail of materials and equipment used frequently are given here.

Column chromatography was carried out on Spence alumina neutralized as follows: alumina (500g) was covered with ethyl acetate (c.600ml) and set aside for 24 hr., then it was filtered, washed with distilled water (c.1l.) and methanol (c.200ml), and dried at the pump. The alumina was then activated by heating for 12 hr. at 400° in a muffle furnace.

Thin layer chromatography (t.l.c.) was carried out on glass plates (6cm by 20 cm) covered with Merck Kieselgel HF_{254} to a depth of 0.5mm. Preparative t.l.c. was carried out on glass plates (20cm by 20cm) covered to a depth of 2mm with a 1:1 mixture of Merck Kieselget HF_{254} and Kieselgel G. Quantitative and qualitative vapour phase chromatography (v.p.c.) were conducted on a Perkin-Elmer 800 gas chromatograph using a nitrogen gas flow of c. 30ml/min. The following stationary phases in stainless steel columns were used: A, 5% SE30, 6ft. by 1/8in.; B, 5% Apiezon 6ft. by 1/8in.; C, 5% FFAP 6ft. by 1/8in.; D, 2% FFAP 10ft. by 1/8in.; E, 1% FFAP 20ft. by 1/8in. F, 5% Carbowax, 10ft. by 1/8in. A Perkin-Elmer 194B printing integrator was used for quantitative determinations. Preparative v.p.c. was performed on a Aerograph Autoprep A70.

Melting points were determined in capillaries on a Gallenkamp melting point apparatus and were uncorrected. Microanalyses were done by the Australian Micranalytical Service, Melbourne.

Infrared spectra (i.r.) were recorded on a Unicam SP200 and ultraviolet-visible spectra were recorded on a Perkin-Elmer 137 spectrophotometer. Nuclear magnetic resonance spectra (n.m.r.) were measured on a Varian T60 spectrometer operating at 60 MHZ using $CDCl_3$ or CCl_4 solutions with TMS (0.00) internal standard. Each signal is described in terms of chemical shift in p.p.m., intensity, multiplicity (br, broad; s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet) coupling constant in Hz, and assignment. Mass spectra were recorded using a Hitachi Perkin-Elmer RMU6D double-focusing mass spectrometer. pH values were determined with a Pye Electronics pH meter, using a single glass-calomel electrode. Ferrocene was a commercial specimen from the Ethyl Corporation, recrystallized once from methanol.

All organic extracts were dried over magnesium sulphate, or, for compounds containing nitrogen, sodium sulphate. Light petroleum was that fraction with b.p. 56-64°.

IV. 1 Kinetic Investigations

Materials

Ferrocenium tetrafluoroborate[129] and trityl tetrafluoroborate[130] were prepared by literature methods. Attempts to prepare and use "hexaphenylethane"[131] as a source of trityl radicals were initially unsuccessful and its synthesis was not pursued. It has recently been shown that Gomberg's "hexaphenylethane" does not have the expected structure but is an isomer.[132] This does not affect the results reported here.

Acetone was refluxed over $KMnO_4$ and fractionated onto "Drierite". The fraction with b.p. 56-57° was filtered onto P_2O_5 and then fractionated into dry containers. The fraction with b.p. 56.5° was stored in securely stoppered flasks in the dark.

Dimethylformamide (DMF) was fractionated and the fraction with b.p. 152-154° was dried over calcium chloride, filtered, and fractionated onto calcium hydride. When bubbles were no longer evolved, a further fractionation was carried out, the fraction with b.p. 153-154° was collected and stored over calcium hydride.

Titanous chloride was a commercial sample.

Kinetics of Ferrocenium Ion Decomposition

(i) Ferrocenium tetrafluoroborate ($5X10^{-3}M$) was allowed to stand in water, nitromethane, DMF, and acetone. Ferrocenium ion decomposition (monitored at 610 nm) appeared to be slowest in acetone and DMF.

(ii) Ferrocenium tetrafluoroborate ($5X10^{-3}M$) was allowed to stand in freshly distilled DMF and in freshly distilled acetone (3X20ml of each). Aliquots (3ml) were withdrawn at c.2 hr. intervals and were monitored at 610 nm. First-order rate constants were calculated and k values averaged. These were $7.5X10^{-4}s^{-1}$ at 23°C for acetone solutions and $1.0X10^{-3}s^{-1}$ at 22°C for DMF solutions.

(iii) A mixture of ferrocenium tetrafluoroborate ($5X10^{-3}M$) and ferrocene ($5X10^{-3}M$) was allowed to stand in acetone, and decomposition was monitored by checking the absorption at 610 nm. First-order rate constants were calculated to be c. $3.5X10^{-4}s^{-1}$ at 23°C.

Ferrocenium tetrafluoroborate ($5X10^{-3}M$) and trityl tetrafluoroborate ($5X10^{-3}$) in acetone (the same batch as above) were allowe to stand under a nitrogen atmosphere while the decomposition was monitored (at 610 nm). Rate constants were calculated as before and found to be c. $7X10^{-4}s^{-1}$ at $23^{o}C$.

A control solution of ferrocenium tetrafluoroborate ($5X10^{-3}M$) in acetone was monitored at 610 nm simultaneously with the previous two solutions, (k $7X10^{-4}$ s^{-1}).

Decomposition Products from Ferrocenium Ion

(i) Ferrocenium tetrafluoroborate (0.8g) was kept in acetone (30ml) for 23 days. The precipitate, which was collected by filtration, gave positive tests for ferrous and ferric ions. The filtrate was evaporated, and ether (20ml) and water (50ml) were added. The ethereal layer was separated, washed with saturated ferric chloride in 6N aqueous sulphuric acid (2X30ml), and the aqueous layers separated, combined, and treated with titanous chloride. After extracting the reduced aqueous solution with ether (2X30ml), the ether was dried and evaporated to give ferrocene (0.21g, 26%). The original ethereal extract contained five products by t.l.c. Column chromatography gave small amounts of unidentified brown oils.

The original aqueous fraction was treated with titanous chloride and extracted with ether (2X30ml). The ethereal extracts were dried and evaporated to give ferrocene (0.16g, 20%).

(ii) Ferrocene (0.1g) and trityl tetrafluoroborate (0.175g) were stirred in acetone (50ml) under nitrogen. The solution changed rapidly to the dichroic blue colour of a ferrocenium salt which intensified steadily. After 50 hr. the mixture was worked up as in (i). Ferrous and ferric ion tests were positive. A number of brown oils were separated with similar t.l.c. properties to those in (i). Ferrocene (0.03g, 30%) and tritylferrocene (0.08g, 4%) were identified by comparison with authentic samples. Initial filtration of the reaction solution gave, besides ferric and ferrous salts, a white solid (0.014g) which was recrystallized from dichloromethane - light petroleum as white needles m.p. 178-179° (lit.[133] ditrityl peroxide 183°).

(iii) Ferrocene (1g) was stirred in acetone (50ml) for 62 hr. Decomposition products were not detected.

(iv) Ferrocene (0.93g) and tritylmethanol (1.3g) were stirred in acetone (50ml) under nitrogen for 96 hr. Ferrocenium ion was not detected (visible spectroscopy). An identical solution was stirred in acetic acid for 96 hr and complete conversion to ferrocenium ion was observed.

Kinetics of Electron Transfer

(i) Residual water in the solvent sample was determined graphically by examining the hydrolysis of trityl tetrafluoroborate with a series of u.v. spectra.

(ii) Kinetic runs. - Reaction solutions 4 or 5×10^{-3}M in ferrocene and trityl tetrafluoroborate were made up separately in acetone, using a nitrogen-filled dry box. The solutions were quickly mixed, transferred to a u.v. cell, tightly stoppered and the spectrum was monitored at 610 nm with the aid of a Perkin-Elmer 220-0177 time drive attachment. This procedure was standardised and the hydrolysis of trityl salt was considered when making up solutions.

After a typical experiment, $\frac{[FcH_o] - [FcH_t]}{[FcH_o][FcH_t]}$ was plotted against time, assuming $[FcH] = [\text{trityl tetrafluoroborate}]$. The line of best fit was drawn through the points. Because values of k where found to vary by a factor of 10, the two extreme values are given, and the plots are reproduced in Chapter II.1.

Reversibility of Reaction

(i) Tritylferrocene (0.18g) was heated under reflux in trifluoroacetic acid (10ml) for 2 hr. with the passage of a slow stream of oxygen. An aliquot (0.2ml) was diluted with trifluoroacetic acid (3ml) and ferrocenium ion concentration was determined to be c.0.004g/10ml of original solution. The 610nm absorbance appeared as a shoulder on a stronger absorbance at 650 nm attributed to tritylferrocenium ion. Water (10ml), and titanous chloride solution (10ml) were added serially to the reaction mixture. Extraction with ether (20ml) and t.l.c. examination of the organic layer indicated the presence of tritylferrocene and ferrocene.

(ii) Experiment (i) was repeated with the passage of a slow stream of nitrogen in place of oxygen. Ferrocene was not detected by t.l.c. or by visible spectroscopy (as ferrocenium ion).

(iii) Tritylferrocene (0.2g) was stirred in acetic acid overnight. Ferrocenium ion and ferrocene could not be detected by visible spectroscopy and t.l.c. examination, respectively.

(iv) Tritylferrocene (0.04g) and ferric chloride (0.04g) were allowed to stand in acetone (30ml). Spectroscopic examination after 30 min. and 3 hr. revealed the absence of ferrocenium ion. T.l.c. examination of a reduced aliquot showed that ferrocene was absent.

Acetic Acid Reaction

Trityl tetrafluoroborate (0.7g) was stirred in acetic acid (15ml) under nitrogen, while ferrocene (0.4g) in acetic acid (20ml) was added. The mixture was then stirred under nitrogen for a further 30 min. The solution rapidly turned green. Water (30ml) was added, giving a yellow precipitate, 1ml was withdrawn and made up to 10ml in acetone. The ferrocenium concentration was found to be 16% of ferrocene present (visible spectroscopy).

The remaining reaction solution was quickly poured into aqueous sodium carbonate (53g in 200ml), made slightly acidic (aqueous acetic acid), and then reduced with titanous chloride solution. Ether extraction (2X100ml) followed by drying and evaporation of the solvent gave a crude product (0.888g). Preparative t.l.c. gave ferrocene (0.35g) and tritylferrocene (trace).

IV 2a Comparative Isomer Distributions

Materials

Dichloromethane was twice dried over calcium chloride, filtered, and distilled. The fraction with b.p. 40-41° was collected in dry containers which were sealed and stored in the dark.

Benzaldehyde was fractionated twice at water pump pressure, then once at atmospheric pressure. The fraction with b.p.179-180° was collected in dry nitrogen-flushed containers which were tightly stoppered and stored in the dark.

Benzoyl chloride and aluminium trichloride were commercial samples purified by literature methods,[140] and p-nitrobenzaldehyde and p-nitrobenzoyl chloride were recrystallized once before use. Commercial samples of peroxides were used without purification. t-Butyl-hydroperoxide was 70% pure,[133] and was used as such.

The following ferrocenes were prepared by literature methods and are given in the format: compound m.p. (lit. m.p.).

Methylferrocene,[76] 33-34° (lit.[76] 34-35°); isopropenylferrocene,[134] 76-77° (lit.[134] 77°); acetylferrocene,[135] 84-85° (lit.[135] 85-86°); ethylferrocene,[136] liquid[136]; benzoylferrocene[137] 106-107° (lit.[137] 108°); benzylferrocene,[46] 74-75° (lit.[46] 74-75°); phenylferrocene,[138] 112-113° (lit.[138] 114-115°) dimethylaminomethylferrocene,[139] liquid[139]; 1,2-diferrocenylethane,[72] 177-179° (lit. [72] 183-188°).

Isopropylferrocene was prepared by catalytic hydrogenation of isopropenylferrocene (2g) over platinum in ethyl acetate for 24 hr. Filtration and evaporation of the filtrate gave crude isopropylferrocene (2.1g) which was purified by chromatography on alumina.

t-Butylferrocene was prepared by the method of Benkeser and Bach,[97] but was very impure (v.p.c.). Small amounts of t-butyl- and di-t-butyl-ferrocene were separated by preparative v.p.c. on a stationary phase of 20% SE 30. However, the detector repeatedly became contaminated, and only very small injections could be put onto the column.

The Reaction of Ferrocene with t-Butyl Perbenzoate

(i) To stirred ferrocene (2g) in benzaldehyde (60ml) under nitrogen was added t-butyl perbenzoate (2.4g) over 15 min. The solution darkened rapidly. After heating at 130° for 13 hr. the solution was poured into water (200ml), reduced with titanous chloride solution, and extracted with ether (2X50ml). After drying, ether and most of the benzaldehyde were evaporated under reduced pressure. Benzoylferrocene was detected by t.l.c. and estimated by u.v. to be present in 54% yield (1.7g).

(ii) An identical reaction was carried out with the addition of ferric chloride (3.5g). The solution darkened rapidly. Benzoylferrocene (0.3g,10%) was detected by u.v., and the yield was estimated by this method.

Reaction of Benzoylferrocene with t-Butyl Perbenzoate

(i) t-Butyl perbenzoate (1.2g) was slowly added with stirring to benzoylferrocene (1g) in benzaldehyde (40ml). The mixture was heated at 110° under nitrogen for 24hr. A rapid darkening of the solution was observed. The mixture was poured into water (200ml) and reduced with titanous chloride. The mixture was then extracted with ether (3X50ml) and the extract dried and evaporated under reduced pressure. A trace of 1,1′-dibenzoylferrocene was detected by t.l.c. Tar formation was extensive.

(ii) Experiment (i) was repeated with heating for 4 days. A trace of 1,1′-dibenzoylferrocene was detected.

Friedel-Crafts Reaction of Benzoylferrocene.

Benzoylferrocene (1.45g) was added with stirring to benzoyl chloride (1.4g) and aluminium trichloride (1.4g) in dichloromethane (30ml) protected from moisture. The solution rapidly turned blue. After being refluxed for 24 hr. the solution was tipped into sodium carbonate (100ml of 10% solution) and stirred for 1 hr. The mixture was then extracted with chloroform (2X100ml) and the extract dried and evaporated. Separation by preparative t.l.c. gave benzoylferrocene (0.15g, 10%) and 1,1-dibenzoylferrocene (1.1g, 56%). Tar formation was noted.

Reaction of Methylferrocene with t-Butyl Perbenzoate

t-Butyl perbenzoate (0.22g) was added with stirring to methylferrocene (0.2g) in benzaldehyde (0.22g). The solution was maintained at 110° for 9 hr. under nitrogen, then benzaldehyde was distilled off under reduced pressure. The crude residue was reduced with titanous chloride solution, extracted with ether (2X20ml), and the extracts washed with dilute sodium carbonate (20ml of 10% solution) and dried. The solvent was evaporated and the residue made up to 25ml in ethyl acetate. For the following v.p.c. analyses 1 µl samples were injected, the peak responses were triangulated and cut out, and these were then weighed. With column A, recorder responses were observed for solvent, ferrocene, and two peaks attributed to benzoylmethylferrocenes; the second peak was partially split into two peaks which were poorly resolved. Results for v.p.c. analyses were (column temperature, weight of first peak:

weight of second partially split peak): 225°, 4.34; 228°, 4.9; 230°, 4.1; 235°, 7.3; 250°, 6.6.

Friedel-Crafts Reaction of Methylferrocene

Methylferrocene (0.2g) was added to stirred benzoyl chloride (0.14g) and aluminium trichlordie (0.14g) in dichloromethane (20ml) with protection from moisture. The mixture rapidly became blue. After stirring at room temperature for 6 hr., the solution was poured into 10% sodium carbonate (100ml). The mixture was extracted with chloroform (2X50ml) and the extract was dried and evaporated. The residue was made up to 25ml in ethyl acetate and analysed by v.p.c. as described in the previous experiment. Results of v.p.c. analyses: 225°, 4.1; 228°, 4.9; 230°, 4.2; 235°, 7.4; 250°, 6.9.

Preparation of Benzoylmethylferrocenes

Methylferrocene (1g) was added to stirred benzoyl chloride (0.8g) and aluminium trichloride (0.8g) in dichloromethane (30ml) with protection from moisture. After being refluxed for 6 hr., the solution was poured into 10% aqueous sodium carbonate (100ml). The mixture then was extracted with chloroform (2X100ml) and the extract was dried and evaporated.

Preparative t.l.c. of the crude material (1.43g) gave methylferrocene (0.39g) and benzoylmethylferrocenes (0.93g). Repeated preparative t.l.c. in light petroleum-ether (3:1) gave three products: that with high R_f was 1-benzoyl-2-methylferrocene (o.031g), a red solid m.p. 88-90° (lit.[90] 87-89°), n.m.r. identical with that reported,[90] M^+ at m/e 304; that with intermediate R_f was 1-benzoyl-1'-methylferrocene (0.033g), a red oil which did not crystallize, n.m.r. identical with that reported,[90] M^+ m/e 304; that with low R_f was, 1-benzoyl-3-methylferrocene (0.028g), a red oil which did not crystallize, n.m.r. identical with that reported,[90] M^+ at m/e 304. Extensive decomposition occurred during chromatography. V.p.c. analysis (column D,220°) showed that the three products were homogeneous.

Friedel-Crafts Reaction of Methylferrocene - Accurate Isomer Analysis

(i) Methylferrocene (0.94g) was added with stirring to benzoyl chloride (0.7g) and aluminium trichloride (0.67g) in dichloromethane (40ml). After 2 hr., the solution was tipped into 10% aqueous sodium carbonate (100ml). The mixture was then extracted with chloroform (3X100ml) and the extract was dried and evaporated. The residue was chromatographed on neutral alumina (50g) to give methylferrocene (0.48g) m.p. 33-34° (lit.[76] 34-35°), and benzoylmethylferrocenes (0.40g). An accurately weighed portion of this mixture (0.160g) was made up in ethyl acetate (25ml) and phenylferrocene (internal standard,[141] o.0486g) was added. Quantitative v.p.c. analysis (column D, 220°) gave, in order of increasing retention times: 1,2-isomer, 23 min (0.057g); 1,1′-isomer, 28.5 min (0.187g); 1,3-isomer, 30 min (0.154g).

Accurately weighed samples of internal standard (c. 5mg) and authentic isomer (c. 2-10mg) were dissolved in ethyl acetate (c. 5ml) or hexane (c. 5ml). Samples of the solutions were injected onto the appropriate v.p.c. column under identical conditions to those used for product analysis, and peak areas were determined by integration. (Peak integration of isomer)/(peak integration of standard) was plotted against (weight of isomer)/(weight of standard) to enable absolute yields of isomers to be calculated. Each unknown mixture was run at least five times and the values were averaged. Retention time values for most compounds varied with column age because column stationary phases were used near their thermal limits. Retention times quoted are thus approximate only.

(ii) Experiment (i) was repeated with modifications. Methylferrocene (0.48g) was added with stirring to benzoyl chloride

(0.37g) and aluminium trichloride (0.36g) in dichloromethane (20ml) which was refluxed for 1 hr. Phenylferrocene (internal standard, 0.0423g) was added before the work-up procedure, and the crude product was made up to 25ml in ethyl acetate without chromatography on alumina. Quantitative v.p.c. analysis (column D, 220°) gave: 1,2-isomer (0.059g); 1,1'-isomer (0.214g); 1,3-isomer (0.164g). Preparative t.l.c. after evaporation of ethyl acetate gave methylferrocene 0.141g.

(iii) Reaction in chloroform. - Methylferrocene (0.1g) was added with stirring to benzoyl chloride (0.07g) and aluminium trichloride (0.07g) in chloroform (60ml). The mixture was refluxed for 18 hr. under nitrogen then poured into water and reduced with the addition of titanous chloride solution. The mixture was then extracted with chloroform (2X50ml) and the extract was dried and evaporated. V.p.c. analysis (column D, 220°) of the residue dissolved in ethyl acetate (5ml) showed that the 1,1'-:1,3-isomer ratio was 1.2 in agreement with the results of experiments (i) and (ii).

Free-radical Reactions of Methylferrocene

(i) Trial reaction. - Methylferrocene (0.40g) was added with stirring to ferric chloride (0.28g) in benzaldehyde (50ml). The solution was stirred for 20 hr. under nitrogen, then poured into saturated aqueous sodium metabisulphite solution,[140] and the mixture was allowed to stand for 1 hr. The mixture was filtered (sinter) and the precipitate was washed thoroughly with chloroform (3X100ml). The aqueous filtrate was extracted with the chloroform washings and the extracts were dried. After evaporation of the solvent, the residue was separated by preparative t.l.c. into methylferrocene (0.31g, 89%) and benzoylmethylferrocenes (traces only).

(ii) Accurate isomer analysis. - t-Butyl hydroperoxide (0.28g) was added dropwise to a stirred solution of methylferrocene (0.48g) and ferric chloride (0.39g) in benzaldehyde (40ml). The mixture was heated at 40° for 48 hr. under nitrogen, then cooled and poured into saturated sodium meta-bisulphite. Phenylferrocene (internal standard, 0.0517g) was added. After 1 hr. the mixture was filtered, the precipitate was washed with chloroform (3X100ml), and the aqueous filtrate was extracted with the chloroform washings. The extracts were dried and evaporated and the crude product was made up to 25ml in ethyl acetate. Quantitative v.p.c. analysis (column D, 220°) gave: 1,2-isomer (0.0092g); 1,1′-isomer (0.032g); 1,3-isomer (0.027g). An unidentified product was observed with R_t similar to that of phenylferrocene. Evaporation of ethyl acetate followed by preparative t.l.c. gave methylferrocene (0.33g) and a yellow oil (0.017g). This oil was not oxidized by excess aqueous ferric chloride. Preliminary examination (i.r., mass spectrum, n.m.r.) indicated that the oil contained benzyl benzoate.

(iii) Accurate isomer analysis. - t-Butyl hydroperoxide (o.2g) was added with stirring to methylferrocene (0.2g) and ferric chloride (0.14g) in benzaldehyde (20ml). The mixture was heated at 40° for 30 hr under nitrogen and worked up as in (ii), adding phenylferrocene (internal standard 0.0212g) as before.

Quantitative v.p.c. analysis (column D, 220°) gave: 1,2-isomer (0.0064g); 1,1'-isomer (0.033g); 1,3-isomer (0.026g). The non-ferrocene compound was again present. Evaporation of the ethyl acetate, followed by preparative t.l.c. gave methylferrocene (0.11g), and yellow oil (0.006g). 1,2-Diferrocenylethane was not detected (t.l.c. analysis).

Synthesis of 1-Benzoyl-2-methylferrocene

2-(Dimethylaminomethyl)-ferrocenylphenone (20) was prepared by the method of Slocum, Rockett, and Hauser[92] using dimethylaminomethylferrocene (4.9g) in ether (20ml), a commercial sample of 20% n-butyl lithium (16ml), and benzonitrile (4.5g). After chromatography, the resultant red oil was dissolved in benzene (20ml) and treated with an excess of methyl iodide (c.5ml). The precipitate (21; 3.1g) was collected and reduced by the method of Slocum.[76]

Crude methiodide (3g) was covered with ammonia (150ml) and sodium (5g) was quickly added. After stirring for 5 min., ammonium chloride (12g) was added, this was followed by water (300ml) and the solution was stirred for 6 hr. The mixture was extracted with ether (2X100ml) and the extract was dried and evaporated. The red oily residue was chromatographed on alumina (100g) to give a red solid which was identified as 1-benzoyl-2-methylferrocene (22; 0.35g) which crystallized as red needles from hexane m.p. 93-95° (lit.[90] 87-89°) mixed m.p. 90-91° on admixture with a sample from Friedel-Crafts benzoylation of methylferrocene (Found: C, 71.0; H, 5.6. $C_{18}H_{16}FeO$ requires C, 71.1; H, 5.3%). The n.m.r. spectrum was identical with that reported;[90] mass spectrum: M^+ at m/e 304.

Friedel-Crafts Reaction of Ethylferrocene.

Ethylferrocene (2.14g) was added with stirring to benzoyl chloride (1.4g) and aluminium chloride (1.4g) in dichloromethane at room temperature. The solution rapidly turned blue.

After the usual work-up procedure, ethylferrocene (0.7g, 33%) and benzoylethylferrocenes (1.92g) were isolated. Repeated chromatography of the benzoylethylferrocenes on alumina gave two products. V.p.c. analysis of the higher R_f product (column A, 200°, 210°, 220°, 230°, 240°, 250°) indicated that it was homogeneous. V.p.c. analysis of the lower R_f product (column A, 200°, 210°, 220°, 230°, 240°, 250°; column B, 200°, 250°; column C, 220°, 230°, 250°; column F, 200°, 220°) indicated that it contained two compounds which were not completely resolved. Chromatography of this second fraction (0.52g) on neutral alumina (300g) with protection from light gave the starting mixture after eluting for 6 days with light petroleum-ether (200:1).

Preparation of Benzoylisopropylferrocenes

Isopropylferrocene (0.23g) was added with stirring to benzoyl chloride (0.14g) and aluminium trichloride (0.20g) in dichloromethane (30ml) protected from moisture. The mixture rapidly turned blue. After being stirred for 2 hr. at room temperature, the mixture was worked up in the same manner as for benzoylmethylferrocenes. Repeated preparative t.l.c. in light petroleum-ether (19:1) gave three products: that with high R_f was 1-benzoyl-2-isopropylferrocene (0.017g), a red oil. I.r.

($CHCl_3$):1695(CO),1105, 1005 cm^{-1} (homoannular substitution; n.m.r. δ (CCl_4):7.2-8.0(5H, m, benzoyl hydrogens), 4.36 (1H,m, H 5 relative to benzoyl), 4.26(1H,m,H 4 relative to benzoyl), 4.2(1H,m,H 3), 4.05 (5H,s, C_5H_5), 3.4-4.05 (1H, septet, J 6½, CH), 0.95-1.45(6H,dd,J 22 J' 6½, 2Me); mass spectrum: M^+ at m/e 332. The product with intermediate R_f value was 1-benzoyl-1'- isopropylferrocene, a red oil (0.021g). I.r. ($CHCl_3$): 1705 cm^{-1}(CO); n.m.r. δ(CCl_4): 7.1-8.0 (5H, m, benzoyl), 4.75 (2H,t,J 2, H2,5 relative to benzoyl) 4.35(2H, t,J 2, H3), 3.97 (4H, s, Pr^i-substituted ring), 2.15-2.9(1H, septet, J 7, CH), 1.03-H6 (6H,d, J 7, 2Me); mass spectrum: M^+ at m/e 332. The low R_f product was 1-benzoyl-3-isopropylferrocene, a red oil (0.017g). I.r. ($CHCl_3$): 1690(CO),1110, 1010 cm^{-1} (homoannular substitution); n.m.r. δ (CCl_4): 7.23-8.0 (5H,m, benzoyl), 4.72(2H,t,J 2, H2,5 relative to benzoyl), 4.32(1H,t, J 2, H4 relative to benzoyl), 4.07(5H,s, unsubstituted ring), 2.50-3.13(1H, septet, J 6, CH), 1.08-1.16(6H, broad d, J 9, 2Me); mass spectrum: M^+ at m/e 332. All compounds were homogeneous by v.p.c. (column D,210^o).

Friedel-Crafts Reaction of Isopropylferrocene - Accurate Isomer Analysis.

(i) Isopropylferrocene (0.16g) was added with stirring to benzoyl chloride (0.1g) and aluminium trichloride (0.1g) in dichloromethane (20ml) protected from moisture. A blue colour rapidly appeared. The mixture was refluxed for 2 hr. and then worked up in the usual way. Phenylferrocene was added (internal standard, 0.0241g) and the oily mixture was made up to 10ml with hexane. Quantitative v.p.c. analysis (column D, 130^{o} programmed at 40^{o} min^{-1} to 210^{o} after 14 min) gave: isopropylferrocene 0.0723g; 1,2-isomer 0.0096g; 1,1′-isomer 0.0323g; 1,3-isomer 0.0258g.

(ii) Repetition of experiment (i) gave: isopropylferrocene (0.0638g); 1,2-isomer (0.0112g); 1,1′-isomer (0.0378g); 1,3-isomer (0.0292g).

Free-radical Reaction of Isopropylferrocene- Accurate Isomer Analysis

(i) t-Butyl hydroperoxide (0.08g) was added dropwise to a stirred solution of isopropylferrocene (0.16g) and ferric chloride (0.06g) in benzaldehyde (20ml). The mixture was heated at 40^{o} for 2 hr. under nitrogen, then it was poured into an excess of aqueous saturated sodium metabisulphite and phenlyferrocene (internal standard, 0.0108g) was added. After the usual work-up procedure the oily material was made up to 10ml in hexane. Quantitative v.p.c. analysis (column D, 130^{o} raised to 210^{o} at 40^{o} min^{-1} after 14 min) gave: isopropylferrocene (0.114g); 1,2-isomer (0.0019g); 1,1′-isomer (0.016g); 1,3-isomer (0.0103g).

(ii) Duplication of experiment (i) gave: 1,2-isomer (0.0039g); 1,1′-isomer (0.0214g); 1,3-isomer (0.0144g).

Friedel-Crafts Reaction of Isopropenylferrocene

Isopropenylferrocene (0.266g) was added with stirring to benzoyl chloride (0.14g) and aluminium trichloride (0.14g) in dichloromethane (20ml) protected from moisture. The mixture rapidly turned blue-green. After being refluxed for 2 hr. the mixture was poured into aqueous sodium carbonate (100ml) and extracted with chloroform (2X100ml). Titanous chloride solution was then added to the aqueous layer to reduce the blue ferrocenium salts which were still present. After further extraction with chloroform (2X50ml), the extracts were combined, dried, and the solvent evaporated. Preparative t.l.c. indicated that a complex mixture of at least six benzoylated ferrocenes had been formed.

Preparation of Benzoylbenzylferrocenes.

Benzylferrocene (0.28g) was added with stirring to benzoyl chloride (0.14g) and aluminium trichloride (0.14g) in dichloromethane (20ml) protected from moisture. A blue colour rapidly appeared. After stirring for 2 hr at room temperature, the mixture was worked up as for benzoylmethylferrocenes.

Repeated preparative t.l.c. in light petroleum-ether (4:1) gave three products: that with high R_f was 1-benzoyl-2-benzylferrocene (0.048g), a red solid m.p. 110-111^o (hexane)(Found: C, 75.8; H, 5.5. $C_{24}H_{20}FeO$ requires C, 75.8; H, 5.3%). I.R. ($CHCl_3$): 1690 (CO), 1110, 1005 cms^{-1} (homoannula substitution); n.m.r. δ (CCl_4): 7.15-7.9 (5H, m, benzoyl), 7.1 (5H, s, benzyl aromatic protons), 4.1-4.55 (3H, m, substituted ring hydrogens), 4.27 (2H, s, CH_2), 4.05 (5H, s, unsubstituted ring hydrogens); mass spectrum: M^+ at m/e 380. The product with intermediate R_f was 1-benzoyl-1'-benzylferrocene, a red oil (0.027g)(Found: C, 76.1; H,5.8. $C_{24}H_{20}FeO$ requires C, 75.8; H,5.3%). I.r. ($CHCl_3$): 1690 cm^{-1} (CO); n.m.r. δ (CCl_4): 7.2-8.0 (5H, m, benzoyl), 7.15 (5H, s, benzyl ArH), 4.8 (2H, t, J 1½, H 2,5 relative to benzoyl), 4.4 (2H, t, j 1½, H 3,4 relative to benzoyl), 4.05(4H, s, benzyl-substituted ring hydrogens), 3.53 (2H, s, CH_2); mass spectrum: M^+ m/e 380. The product with low R_f was 1-benzoyl-3-benzylferrocene, a red oil (0.021g). (Found: C, 75.7; H, 5.6. $C_{24}H_{20}FeO$ requires Cm 75.8; H,5.3%)

I.r. ($CHCl_3$): 1700(CO), 1105, 1010 cm^{-1} (homoannular substitution); n.m.r. δ (CCl_4): 7.2-8.0 (5H, m, benzoyl), 7.15 (5H, s, benzyl ArH), 4.78(2H, t, J 1½, H 2,5 relative to benzoyl), 4.38 (1H, t, J 1½, H 4 relative to benzoyl), 4.05 (5H, s, unsubstituted ring), 3.68 (2H, s, CH_2); mass spectrum: M^+ at m/e 380. All compounds were homogeneous by v.p.c. (column F, 250°), but extensive tailing of v.p.c. peak traces was observed under all conditions.

Friedel-Crafts Reaction of Benzylferrocene - Accurate Isomer Analysis

(i) Benyzlferrocene (0.552g) was added with stirring to benzoyl chloride (0.28g) and aluminium trichloride (0.28g) in dichloromethane (20ml) protected from moisture. The solution rapidly turned blue. After being refluxed for 1 hr, the mixture was treated with the usual work-up procedure. A single rapid separation by preparative t.l.c. in light petroleum-ether 1:3 gave: benzylferrocene (0.251g) m.p. 74-75° (lit.[46] 74-75°); 1-benzoyl-2-benzylferrocene(0.095g); and a mixture of 1,1′- and 1,3-benzoylbenzylferrocenes (0.288g), estimated, by integration of the methylene resonances in the n.m.r. spectrum, to contain 2/3 of the 1,1′-isomer and 1/3 of the 1,3-isomer.

(ii) Experiment (i) was repeated on one-half scale with stirring at room temperature for 24 hr. After the usual work-up procedure, rapid separation by preparative t.l.c. gave benzylferrocene (0.131g), 1-benzoyl-2-benzylferrocene (0.042g), and a mixture of 1,1'- and 1,3-isomers (0.121g). The mixture was estimated (by integration of the methylene resonances in the n.m.r. spectrum) to contain $\frac{25}{38}$ of the 1,1'-isomer and $\frac{13}{38}$ of the 1,3-isomer.

Free-Radical Reaction of Benzylferrocene - Accurate Isomer Analysis

(i) t-Butyl hydroperoxide (0.26g) was added with stirring to benzylferrocene (0.552g) and ferric chloride (0.33g) in benzaldehyde (20ml) under nitrogen. After heating at 40° for 1 hr, the mixture was poured into an excess of saturated aqueous sodium metabisulphite and then worked up by the usual procedure. Preparative t.l.c. gave benzylferrocene (0.421g), 1-benzoyl-2-benzylferrocene (0.025g), and a mixture of 1,1'- and 1,3-isomers (0.11g). This mixture was estimated, by integration of the methylene resonances in the n.m.r. spectrum, to contain $\frac{20}{31}$ of the 1,1'-isomer and $\frac{11}{31}$ of the 1,3-isomer.

(ii) Experiment (i) was repeated but with the addition of a little more t-butyl hydroperoxide (0.32g total). Product isolation similar to that in (i) gave benzylferrocene (0.323g), 1-benzoyl-2-benzylferrocene (0.054g), and a mixture of 1,1' and

1,3-isomers (0.158g), estimated by integration of the methylene resonances in the n.m.r. to contain $\frac{31}{48}$ of the 1,1′-isomer and $\frac{17}{48}$ of the 1,3-isomer.

Preparation of Benzoylphenylferrocenes

Phenylferrocene (0.52g) was added with stirring to benzoyl chloride (0.28g) and aluminium trichloride (0.28g) in dichloromethane protected from moisture. A blue colour rapidly appeared After being refluxed for 2 hr, the mixture was worked up by the procedure used for benzoylmethylferrocenes. Qualitative v.p.c. analysis (columns D, E, F) was unsuccessful, peak traces tailing badly. Preparative t.l.c. of a portion of the crude mixture gave three products: that with high R_f was 1-benzoyl-2-phenylferrocene, a red semi-solid (distilled 135°/0.1mm) (Found: C, 75.8; H,5.2. $C_{23}H_{18}FeO$ requires C,75.4; H, 5.0%). I.r. ($CHCl_3$): 1680 (CO), 1100, 1005 cm^{-1} (homoannular substitution); n.m.r. δ (CCl_4): 7.05-8.0 (10 H, m, benzoyl + phenyl), 4.72 (2H, t, J 2, H 3,4 relative to benzoyl), 4.5 (1H, t, J 2, H 5 relative to benzoyl), 4.2 (5H, s, unsubstituted ring); mass spectrum: M^+ at m/e 366. A mixture of 1,1′- and 1,3-isomers was isolated (Found: C, 74.9; H,5.2%). N.m.r. δ (CCl_4) 7.0-8.0 (10H, m, benzoyl + phenyl), 4.0-5.4 (8H, m, ferrocene hydrogens).

Reduction of Benzoylphenylferrocenes

(i) A portion of the crude product from the previous experiment was reduced by the method of Tyurin *et al.*[46]

Benzoylphenylferrocenes (0.1g) in dry ether (5ml) were added to a stirred suspension of lithium aluminium hydride (0.038g) and aluminium trichloride (0.133g) in dry ether (20ml). After 1 hr, ethyl acetate (5ml) was added dropwise, followed by water (10ml). The organic layer was then separated, washed with 10% sodium carbonate (20ml), and dried. The solvent was then evaporated and the residue (0.11g) made up to 10ml in hexane. V.p.c. analysis (column E, 210^{o}) indicated that (in order of increasing R_t), phenylferrocene (20min), 1-benzyl-2-phenylferrocene (65 min), 1-benzyl-1-phenylferrocene (78 min), and 1$'$-benzyl-3-phenylferrocene (82 min) were present. T.l.c. examination gave only one spot for the benzylphenylferrocenes.

(ii) Reduction of 1-benzoyl-2-phenylferrocene (0.03g) as in (i) gave a yellow oil identified as 1-benzyl-2-phenylferrocene (Found: C, 78.4; H, 5.8. $C_{23}H_{20}FeO$ requires C, 78.4, H,5.7%). I.r. ($CHCl_3$): 1105, 1005 cm^{-1} (homoannular substitution); n.m.r. $\delta(CCl_4)$: 7.0-7.6 (10H, m, benzyl + phenyl), 4.35 (1H, t, J 2, H 5 relative to phenyl), 4.07 (2H, m, H 3,4 relative to phenyl), 3.98 (5H, s, unsubstituted ring), 3.86 (2H, s,

CH_2). Mass spectrum: M^+ at m/e 352.

(iii) Reduction of a portion of the 1,1′- and i,3-isomer mixture as in (i) gave a yellow oil. (Found: C,78.4; H,6.0. $C_{23}H_{20}FeO$ requires C, 78.4; H,5.7%). I.r. ($CHCl_3$): 1110, 1005 cm^{-1} (homoannular substitution). N.m.r.δ(CCl_4): 6.8-7.5 (10H, m, benzyl+phenyl), 3.75-4.62 (8H,m,ferrocene protons), 3.67 (2/3H, s, CH_2 of 1,3-isomer), 3.37 ($\frac{4}{3}$H, s, CH_2 of 1,1′-isomer); mass spectrum: M^+ at m/e 354.

Friedel-Crafts Reaction of Phenylferrocene - Accurate Isomer Analysis

(i) Phenylferrocene (0.26g) was added with stirring to a mixture of benzoyl chloride (0.14g) and aluminium trichloride (0.14g) in dichloromethane (20ml),protected from moisture. A blue colour rapidly appeared. After stirring for 1 hr, followed by the usual work-up procedure, the mixture was separated quickly by preparative t.l.c. to give phenylferrocene (0.136g), 1-benzoyl-2-phenylferrocene (0.020g), and a mixture of 1,1′- and 1,3-isomers (0.0745g). Reduction of this mixture by the method of Tyurin <u>et al</u>.[46] and v.p.c. analysis (column E, 210°) of the resulting yellow oil dissolved in hexane (5ml), gave a peak integration ratio for (1,1′-isomer)/(1,3-isomer) of 2.23 (three injections, close range of values).

(ii) Experiment (i) was repeated to give phenylferrocene (0.16g) 1-benzoyl-2-phenylferrocene (0.015g) and a mixture of 1,1′- and 1,3-isomers (0.07g).

(iii) Experiment (i) was repeated to give phenylferrocene (0.14g) and benzoylphenylferrocenes (0.077g). This mixture was reduced by the method of Tyurin <u>et al</u>.[46] and estimated by integration of the methylene resonances in the n.m.r. spectrum to contain 1,2-isomer 21%, 1,1′-isomer 54.5%, and 1,3-isomer 24.5%.

Free-Radical Reaction of Phenylferrocene - Accurate Isomer Analysis

(i) t-Butyl hydroperoxide (0.13g) was added with stirring to phenylferrocene (0.26g) and ferric chloride (0.17g) in benzaldehyde (20ml). After stirring at room temperature for 1 hr, under nitrogen, the usual work-up procedure was followed by rapid preparative t.l.c. to give phenylferrocene (0.21g) and benzoylphenylferrocenes (0.063g). Reduction of the benzoylphenylferrocenes by the method of Tyurin[46] was followed by quantitative v.p.c. (column E, 210°) of the reduced mixture dissolved in hexane (5ml). The integration ratio of the peaks for the 1,1′-isomer and 1,3-isomer was 2.26 (four injections, wide range of values).

(ii) Experiment (i) was repeated to give phenylferrocene (0.168g) 1-benzoyl-2-phenylferrocene (0.018g), and a mixture of the 1,1'- and 1,3-isomers (0.087g).

(iii) Experiment (i) was repeated to give phenylferrocene (0.17g) and benzoylphenylferrocenes contaminated with a little benzaldehyde. The benzoylphenylferrocene mixture was reduced and estimated by integration of the methylene resonances in the n.m.r spectrum to contain 1,2-isomer 17%, 1,1'-isomer 57%, and 1,3-isomer 26%.

<u>Phenylation of Benzylferrocene</u>

Benzylferrocene was phenylated by a modified literature method.[13] Benzendiazonium sulphate (from aniline, 0.1g) was added with stirring to benzylferrocene (0.276g) in acetic acid (7ml). The solution darkened rapidly. After stirring at room temperature for 3½ hr under nitrogen, the mixture was poured into an excess of aqueous sodium metabisulphite. The solution was then extracted with chloroform (2X50ml) and the extracts washed with 10% sodium carbonate (2X100ml) and dried. The solvent was evaporated and the yellow oil (0.195g) was dissolved in hexane (5ml). T.l.c. indicated that benzylferrocene and benzylphenylferrocenes were present. Qualititative v.p.c. (column

E, 210°) indicated that the 1,2-, 1,1′- and 1,3- isomers were present. N.m.r. analysis (by integration of methylene resonances) showed that the mixture contained the 1,2-isomer 28%, 1,1′-isomer 48%, and 1,3-isomer 24% (as percentages of benzylphenylferrocenes).

IV 2b Synthesis of Benzoylferrocenes

i Attempted Friedel-Crafts Synthesis of p-Nitrobenzoylferrocene

(a) Ferrocene (1.86g) was added with stirring to p-nitrobenzoyl chloride (1.86g) and aluminium trichloride (1.4g) in dichloromethane (30ml) under nitrogen. The mixture was refluxed for 2 hr, then poured into water (100ml), and extracted with chloroform (2X100ml). The extracts were then combined, dried, evaporated, and chromatographed on alumina (100g) to give ferrocene (0.81g).

The aqueous solution was treated with an excess of titanous chloride and extracted with chloroform (2X100ml). The chloroform extracts were then combined, dried, evaporated, and chromatographed on alumina (100g) to give ferrocene (0.68g). p-Nitrobenzoylferrocene and p-nitrobenzaldehyde were not detected.

(b) Experiment (a) was repeated in benzene solvent (30ml) with heating at 60° for 2 hr under nitrogen. From the organic (unoxidized) fraction ferrocene (0.98g) and p-nitrobenzophenone (0.036g) m.p.138-139° (lit.[140] 138°) were isolated. Ferrocene (0.60g) was isolated from the aqueous (oxidized) fraction.

(c) Repetition of (b) with p-nitrobenzoyl chloride (0.93g) and aluminium trichloride (0.70g) gave ferrocene (1.06g) from the organic (unoxidized) fraction. p-Nitrobenzophenone was not detected. Ferrocene (0.72g) was isolated from the aqueous (oxidized) fraction.

(d) Experiment (a) was repeated but with ferric chloride (1.65g) in place of aluminium trichloride. Ferrocene (1.08g) was isolated from the organic (unoxidized) fraction and from the aqueous (oxidized) fraction (0.58g).

ii Free-Radical Synthesis of p-Nitrobenzoylferrocene

(a) t-Butyl hydroperoxide (2.6g) was added dropwise over 30 min to a stirred mixture of ferrocene (1.86g), ferric chloride (0.82g), and p-nitrobenzaldehyde (10g) in benzene (35ml). The mixture was refluxed for 90 min under nitrogen, then tipped into saturated aqueous sodium metabisulphite solution (250ml) and allowed to stand with occasional swirling for 1 hr. The precipitate was filtered, washed with hexane (2X100ml) and chloroform (3X100ml), and the chloroform washings were then used to extract the aqueous filtrate. The organic fractions were combined, dried, and chromatographed on alumina (100g). Elution with hexane gave ferrocene (1.04g) and then elution with hexane-ether 1:1 gave p-nitrobenzoylferrocene (0.07g) which crystallized from hexane-ether as purple-red needles m.p.144-146° (Found: C, 61.0; H, 4.0; N, 4.2. $C_{17}H_{13}FeNO_3$ requires C, 60.9; H, 3.9; N, 4.2%). I.r. ($CHCl_3$) 1680 cm^{-1} (CO); n.m.r. δ ($CDCl_3$): 8.1-8.25 (2H, d, J 9, benzoyl H 3,5) 7.75-7.9 (2H, d, J 9, benzoyl H 2,6), 4.7-4.75 (2H, t, J 1½, H 2,5 relative to benzoyl), 4.45-4.55 (2H, t, J 1½, H 3,4), 4.1(4H, s, unsubstituted ring); mass spectrum: M^+ at m/e 335.

Experiments (b)-(k) were performed in similar fashion to (a) and the results are tabulated in Table 8. From experiment (b), two unidentified non-ferrocene products were isolated. The first as white flakes m.p. 112-114° (hexane)(0.11g), the second as yellow crystals m.p. 92-94° (ether-hexane)(0.07g). From experiments (g), (h), and (j) small amounts (0.09g, 0.04g, and 0.02g) of unidentified material were isolated.

In experiment (d) t-butyl hydroperoxide was added over 1 hr. In (f) benzoic acid (2.5g) was added, and in (h) aluminium trichloride (4.1g) was added.

iii Attempted Synthesis of o-Nitrobenzoylferrocene

Ferrocene (1.86g), ferric chloride (1.65g), and *o*-nitrobenzaldehyde (5g) were stirred in benzene (30ml) during the addition of t-butyl-hydroperoxide (2.5g) over 30 min. After stirring under nitrogen for 1 hr, product isolation gave ferrocene (1.4g) only.

iv Synthesis of m-Nitrobenzoylferrocene

Ferrocene (1.86g), ferric chloride (1.65g), and *m*-nitrobenzaldehyde (5g) were stirred in benzene (30ml) during the addition of t-butyl hydroperoxide (2.5g) over 30min. After refluxing for 2 hr under nitrogen, product isolation gave ferrocene (1.26g) and *m*-nitrobenzoylferrocene (0.44g), m.p. 142-144° (ether-hexane)(lit.[46] m.p.139-140°).

Synthesis of p-Chlorobenzoylferrocene

(a) Ferrocene (1.86g), ferric chloride (1.65g), and *p*-chlorobenzaldehyde (4.2g) were stirred in dimethylformamide (30ml) during the addition of t-butyl hydroperoxide (2.5g) over 30 min. After heating at 80° for 30 min under nitrogen, product isolation gave ferrocene (0.94g) and *p*-chlorobenzoylferrocene (0.03g).

(b) Experiment (a) was repeated in dichloromethane solvent (30ml), the mixture being refluxed for 30 min. The usual work-up procedure gave ferrocene (1.53g) and p-chlorobenzoylferrocene (0.47g) m.p. 199-120° from hexane-ether (lit.[46] m.p. 121-122°).

Attempted Isolation of Ferrocenium Complex

(a) Ferrocene (0.93g) and ferric chloride (0.85g) were dissolved in dichloromethane (50ml). Aluminium trichloride (0.75g) in dichloromethane (30ml) was added and the mixture was stirred for 2 hr with protection from atmospheric moisture. Excess hexane (300ml) was added, and filtration gave a blue precipitate identical with authentic ferrocenium tetrachloroferrate.

(b) A solution of ferrocenium tetrafluoroborate (1.2g) in dichloromethane (50ml) was treated with aluminium trichloride (0.8g) in dichloromethane (50ml) saturated with dry hydrogen chloride. After stirring for 2 hr, addition of hexane (300ml) and filtration gave a product identical with authentic ferrocenium tetrafluoroborate.

IV 3 Reactivity of Ferrocenium Ion

Materials

Solvents were fractionally distilled thrice, halides were commercial samples, fractionated twice and stored under nitrogen in the dark. Tri-n-butyltin hydride and triphenyltin hydride were prepared by the method of Kuivila.[143] Cyclohexyl- and dicyclohexyl- ferrocene were prepared by the method of Vishnyakova *et al.*,[144] and purified by preparative v.p.c.

(i) Ferrocenium Ion with Tri-n-butyltin Hydride and p-Nitrobenzoyl~~ferrocene~~ chloride

(a) Ferrocene (1.86g), ferric chloride (1.65g), tri-n-butyltin hydride (0.33g) and *p*-nitrobenzoyl chloride (0.19g) were refluxed under nitrogen in benzene (20ml) for 24 hr. The mixture was poured into water (200ml), treated with excess titanous chloride, and extracted with chloroform (2X100ml). The extracts were dried and evaporated, and the mixture dissolved in hexane (50ml). V.p.c. analysis (columnC, 190°) showed that tributyltin hydride was present. *p*-Nitrobenzaldehyde was not detected. The hexane was evaporated and the solid residue was chromatographed on alumina (200g). Elution with light petroleum gave ferrocene (1.54g), and with light petroleum-ether (3:1) gave *p*-nitrobenzoylferrocene (0.011g).

(b) A mixture of ferrocene (1.12g), ferric chloride (0.99g), tributyltin hydride (0.33g), *p*-nitrobenzoyl chloride (0.186g), and azobisisobutyronitrile (ABIBN)(0.164g) in benzene (20ml) was refluxed under nitrogen for 4 days. The work-up procedure as in (a) was followed by v.p.c. analysis (column C, 190°). Tributyltin hydride and a trace of p-nitrobenzaldehyde were detected.

Chromatography on alumina (200g) gave ferrocene (0.56g), 2-cyano-2-ferrocenylpropane, which was identical with an authentic specimen (0.035g), cyanoferrocene, m.p. and mixed m.p. 95-98° (0.022g), and p-nitrobenzoylferrocene (0.067g).

(c) A mixture of ferrocene (0.74g), ferric chloride (0.66g), tributyltin hydride (0.58g) p-nitrobenzoyl chloride (0.37g), and ABIBN (0.323g) in benzene (20ml) was refluxed under nitrogen for 3 days. The isolation of products as in (b) gave ferrocene (0.41g), 2-cyano-2-ferrocenylpropane (0.041g), cyanoferrocene (0.053g), p-nitrobenzoylferrocene (0.01g), and tin hydride (0.15g). The products were identified by comparison with authentic samples.

(ii) Ferrocenium ion with tin hydride and methyl iodide

(a) A mixture of ferrocene (0.74g), ferric chloride (0.66g), methyl iodide (0.57g), tributyltin hydride (1.16g), and ABIBN (0.65g) in benzene (15ml) was refluxed under nitrogen for 37 hr. The solution was cooled then poured into an excess of titanous chloride and extracted with chloroform (2X100ml).

The extracts were dried, the solvent was evaporated, and the mixture was chromatographed on alumina (60g). Ferrocene (0.72g) was isolated after elution with hexane. V.p.c. analysis of the crude product (column A, 150°) did not detect methylferrocene (ferrocene and methylferrocene elute from alumina together). Small amounts of 2-cyano-2-ferrocenylpropane (0.013g) and cyanoferrocene (0.008g) were isolated after elution with hexane-ether. "Tin hydride" (0.43g) and tetramethylsuccinonitrile (0.32g) m.p. 170-172° (both identified by comparison with authentic samples) were also isolated after elution with hexane-ether mixtures. Tin hydride is eluted after tetramethyl succinonitrile on alumina, but has a higher R_f on silica gel (t.l.c.). In this and subsequent experiments the "tin hydride" that was recovered also contained tributyltin halide and other products (v.p.c. analysis).

(b) A mixture of ferrocene (3.72g), ferric chloride (3.30g), tributyltin hydride (1.17g), ABIBN (0.65g), and methyliodide (0.57g) in benzene (40ml) was refluxed for 80 hr under nitrogen. The isolation of products gave crude ferrocene (3.16g) containing a trace of methylferrocene ($<\frac{1}{2}\%$ of iodide) by v.p.c. analysis (column A,150°). No attempt was made to isolate any other products.

(iii) Ferrocenium ion with tin hydride and cyclohexyl bromide

A mixture of ferrocene (0.74g), ferric chloride (0.66g), cyclohexyl bromide (0.65g), tributyltin hydride (1.16g), and ABIBN (0.65g) in benzene (10ml) was refluxed under nitrogen for 5 hr. The mixture was tipped into an excess of aqueous titanous chloride and extracted with chloroform (2X100ml). The extracts were dried, the solvent was evaporated, and the residue was chromatographed on alumina (100g). Elution with hexane gave cyclohexyl bromide (0.06g) (v.p.c. analysis, column C, 110^{o}) and crude ferrocene (0.73g). V.p.c. analysis (column C, 160^{o}) of the ferrocene fraction indicated that cyclohexylferrocene and dicyclohexylferrocenes (c. 1% and ½% respectively) were present. The identity of these compounds was confirmed by comparison of R_t values with those of authentic samples (columns A and C). Tetramethylsuccinonitrile (0.33g) and tin hydride (0.88g) were eluted as increasing proportions of ether were added to the hexane eluant. A trace of 2-cyano-2-ferrocenylpropane was identified by t.l.c. comparison with an authentic sample.

(iv) Ferrocenium ion with tin hydride and t-butyl bromide.

A mixture of ferrocene (0.74g), ferric chloride (0.66g), t-butyl bromide (0.55g), tin hydride (1.16g), and ABIBN (0.65g) in ethyl acetate (15ml) was refluxed under nitrogen for 21 hr. The odour of hydrogen cyanide was detected as work-up was begun. The isolation of products gave crude ferrocene (0.73g), 2-cyano-2-ferrocenylpropane (0.009g), cyanoferrocene (0.007g), tetramethylsuccinonitrile (0.056g), and tin hydride (0.53g). V.p.c. analysis (column A, 160°) of the crude ferrocene sample indicated that t-butylferrocene and di-t-butylferrocenes were present (C. 7% and 2% respectively).

(v) Ferrocenium ion with benzyl bromide and tin hydride

(a) A mixture of ferrocene (0.74g), ferric chloride (0.66g), ben 1 bromide (0.68g), tributyltin hydride (1.164g), and ABIBN (0.97g) in benzene (10ml) was refluxed under nitrogen for 26 hr. Product isolation gave; ferrocene (0.29g); benzylferrocene (0.16g) m.p. 72-74° (lit.[46] 74.5-75.5°); dibenzylferrocenes (0.08g) m.p. 96-99° (hexaneX3) (lit.[145] 103-105°), i.r., weak bands at 1100, 1005 cm^{-1}, mass spectrum, M^+ at m/e 366; and 2-cyano-2-ferrocenylpropane (0.040g). Tetramethylsuccinonitrile (0.25g) and tin hydride (0.82g) were also isolated, the former was identified by comparison with an authentic sample, but tin hydride was very impure by v.p.c. (column A, 140°). A small amount of unidentified red oil containing benzoylferrocene (identified by t.l.c. comparison) was also isolated.

(b) A mixture of ferrocene (0.74g), ferric chloride (0.66g), benzyl bromide (0.68g), tributyltin hydride (1.16g), and ABIBN (0.65g) in ethyl acetate (15ml) was refluxed under nitrogen for 23 hr. The isolation of products in the usual way gave: crude ferrocene (0.64g); benzylferrocene (0.19g) m.p. 72-74°; dibenzylferrocenes (0.031g); 2-cyano-2-ferrocenylpropane (0.03g) and cyanoferrocene (trace). Tetramethylsuccinonitrile (0.107g) and impure tin hydride (0.213g) were also isolated, the latter was coloured pink with benzoylferrocene (trace).

(c) A mixture of ferrocene (0.74g), ferric chloride (0.66g), benzyl bromide (0.68g), and ABIBN (0.65g) in ethyl acetate (15ml) was refluxed for 23 hr under nitrogen. The odour of hydrogen cyanide was noted as work-up was begun. The isolation of products gave ferrocene (0.61g), 2-cyano-2-ferrocenylpropane (0.05g), tetramethylsuccinonitrile (0.27g), and an unidentified viscous reddish oil which did not crystallize.

(d) A mixture of ferrocene (1.86g), ferric chloride (1.65g), and benzyl bromide (1.71g) in ethyl acetate (15ml) was refluxed for 8 hr under nitrogen. The usual work-up procedure gave ferrocene (1.67g).

A sample of benzylferrocene (0.20g) was treated under indentical conditions to those above and 90% (0.18g) of this was recovered.

(vi) Ferrocenium ion with benzyl bromide and benzoyl peroxide

(a) A mixture of ferrocene (1.86g), ferric chloride (1.65g), benzyl bromide (1.7g), and benzoyl peroxide (2.42g) was stirred in ethyl acetate (15ml) under nitrogen. As the peroxide was added dropwise an exothermic reaction began. After this reaction had subsided, the mixture was refluxed for 7 hr. The isolation of products gave ferrocene (0.82g), benzylferrocene (0.24g), an unidentified brownish-yellow product m.p.114-117° (0.11g), and brown oils (total 0.973g). Biphenyl (trace) was detected (v.p.c., column D, 150°).

(b) Experiment (a) was repeated with tributyltin hydride (2.92g) present. Ferrocene (0.64g), benzylferrocene (0.23g) an unidentified product (0.10g), and brown oily mixtures containing tin hydride (total 2.65g) were isolated.

(c) Benzyl bromide (1.71g) and benzoyl peroxide (2.42g) were refluxed in benzene (30ml) for 78hr under nitrogen. Quantitative v.p.c. analysis (column D, 80° programming to 150°) of the crude reaction mixture showed that bibenzyl (0.13g) was present; it was identified by v.p.c. comparison with an authentic sample (columns A and D).

(d) A mixture of ferrocene (1.86g), ferric chloride (1.65g), and benzoyl peroxide (2.42.g) in benzene (20ml) was refluxed for 20 hr under nitrogren. The isolation of ferrocene - containing materials gave only ferrocene (0.95g). Repetition of this experiment in ethyl acetate gave only ferrocene (1.17g). The non-ferrocene organic material was not examined.

(vii) Ferrocenium ion with t-butyl perbenzoate and benzyl bromide.

(a) A mixture of ferrocene (1.86g), ferric chloride (1.65g), benzoyl bromide (1.71g), tributyltin hydride (2.92g), and t-butyl perbenzoate (1.94g) in ethyl acetate was refluxed for 69 hr under nitrogen. The mixture was cooled, poured into an excess of acidified aqueous ferric chloride solution (200ml), and extracted with ether (2X100ml). The ethereal extracts were washed with water (3X100ml), the aqueous washings were combined with the aqueous ferric chloride fraction and then treated with an excess of titanous chloride solution. The aqueous solution was extracted with chloroform (4X100ml) and the chloroform and ether extracts were dried separately.

After evaporation of the chloroform the residue was chromatographed on alumina (100g) to give ferrocene (0.97g), benzylferrocene (0.24g) m.p. 71-73°, and a trace of dibenzylferrocene.

The ether was evaporated and chromatography of the oily residue on alumina (120g) gave benzyl bromide contaminated with tin hydride, a mixture of these compounds, and tin hydride contaminated with benzyl bromide (total 3.12g). Both compounds were identified by v.p.c. comparisons (column B, 130°) with authentic compounds. A number of unidentified oils were also present.

(b) A mixture of ferrocene (1.86g), ferric chloride (1.65g), benzyl bromide (1.71g), and t-butyl perbenzoate (1.94g) in ethyl acetate was refluxed for 69 hr under nitrogen. The isolation of products as in (a) gave ferrocene (1.01g) and benzylferrocene (0.27g). Extensive decomposition of the ferrocene-containing material during chromatography coloured the alumina green.

The crude non-ferrocene material (2.0g) contained benzoic acid contaminated with benzyl bromide. A small sample crystallized from water had a m.p. 118-120° (lit.[140] 121°) and liberated carbon dioxide from aqueous sodium bicarbonate.

(viii) Ferrocenium ion with benzyl bromide and t-butyl hydroperoxide.

(a) A mixture of ferrocene (1.86g), benzyl bromide (1.71g), and tributyltin hydride (2.92g) was stirred in benzene (15ml) under nitrogen during the addition of t-butyl hydroperoxide (1.3g of 70%) over 1 hr. After refluxing for 41 hr, the usual work-up procedure ((vii)(a)) gave ferrocene (1.59g). The ethereal organic fraction gave ferrocene (c. 0.2g) and an unidentified oily mixture (3g).

(b) A mixture of ferrocene (0.75g), ferric chloride (0.67g), benzyl bromide (0.68g), and tributyltin hydride (1.17g) was stirred in benzene (15ml) under nitrogen during the slow addition of t-butyl hydroperoxide (0.52g of 70%). The mixture was refluxed for 25½ hr. The isolation of products in the usual way (see vii(a)) gave ferrocene (0.40g), benzylferrocene (0.05g), and dibenzylferrocene (trace). The ethereal organic fraction gave an unidentified mixture of red oily materials (1.57g).

(c) A mixture of ferrocene (1.86g), ferric chloride (1.65g), and benzyl bromide (1.71g) in benzene (15ml) was treated as in (b) with t-butyl hydroperoxide (1.3g of 70%) to give an extremely tarry mixture. This was separated with difficulty into ferrocene (0.11g) and benzylferrocene (0.06g) by preparative t.l.c.

(d) A mixture of ferrocene (1.86g), ferric chloride (1.65g), and benzyl bromide (1.71g) was stirred in ethyl acetate (15ml) under nitrogen during the addition of t-butyl peroxide (1.3g of 70%). The mixture was then refluxed for 18 hr. The usual work-up procedure gave ferrocene (1.19g), benzylferrocene (0.21g) and a trace of benzoylferrocene (t.l.c. identification). The non-ferrocene organic materials were not examined.

(e) Experiment (d) was repeated without heating. The mixture was allowed to stand for 7 days at ambient temperature. The isolation of products gave ferrocene only (1.46g).

(f) Ferrocene (1.86g) was treated at room temperature for 67 hr as in (e) but in the presence of tributyltin hydride (2.92g). A mild exotherm was noted as t-butyl hydroperoxide (1.3g of 70%) was added. The usual work-up procedure and chromatography on alumina gave ferrocene (1.33g) and benzylferrocene (0.17g).

(g) A mixture of ferrocene (1.86g), ferric chloride (1.65g), and benzyl bromide (1.71g), was stirred in cyclohexane (15ml) under nitrogen during the slow addition of t-butyl hydroperoxide (1.3g of 70%). After stirring at room temperature for

19 hr, ferrocene (1.33g) was isolated by the usual method.

(h) Ferrocene (1.86g) was treated as in (g) but with tributyltin hydride (2.91g) present. After stirring at room temperature for 20 hr, ferrocene (1.49g) and benzylferrocene (trace) were isolated.

Absolute rates of Substitution of Ferrocenium Ion

(a) Ferrocenium ion concentrations. - Two identical solutions of ferrocene (0.93g) and ferric chloride (0.85g) in methyl acetate (20ml) were thermostated at 25° under an atmosphere of nitrogen. t-Butyl hydroperoxide (0.65g of 70%) was added dropwise to one, and then both were kept overnight at 25°. Ferrocenium ion concentration (spectroscopic estimation) was c. twice as great in the solution to which hydroperoxide had been added.

(b) Ferrocenium ion with tributyltin hydride. - Ferrocene (0.93g), ferric chloride (0.83g), benzyl bromide (0.86g), and tributyltin hydride (1.46g) were stirred in methyl acetate (30ml) at 25° under an atmosphere of nitrogen. t-Butyl hydroperoxide (0.65g of 70%) was added dropwise over 1 hr, then the mixture was kept at 25° for 24hr. A sample (10ml) of the mixture was withdrawn and filtered, and subjected to v.p.c. analysis (column F, 25°); toluene was not detected. t-Butylbenzene (0.008g) was added to the sample and the solvent was then evaporated under reduced pressure at room temperature. V.p.c. analysis (column F, 25°) of the residue did not detect toluene. Trials with t-butylbenzene-toluene mixtures in methyl acetate showed that toluene could be detected at concentrations as low as 15mg/35ml (i.e. c. 2.5% yield from the reaction above).

Analysis (visible spectroscopy) of the reaction solution showed that 58.5% (0.52g) of ferrocene existed as ferrocenium ion after 24 hr.

The sample and the reaction mixture were recombined and treated in the usual way (see (vii)(a)) to give ferrocene (0.57g) and benzylferrocene (0.055g). Careful stripping of decomposition products from the alumina column and preparative t.l.c. of these gave benzoylferrocene (0.051g). Only the hexane eluate from the chromatography of the non-ferrocene organic materials on alumina was examined by v.p.c. (column F, 80°; column C, 100°). A trace of bibenzyl was present.

(c) Ferrocenium ion with triphenyltin hydride. - Experiment (b) was repeated with triphenyltin hydride (1.75g) in place of tributyltin hydride. The ferrocenium ion concentration was estimated (visible spectroscopy) to be 37% (0.34g). of the total ferrocene after 24 hr. Toluene could not be detected by v.p.c. analysis. The isolation of products (see vii(a)) followed by preparative t.l.c. gave ferrocene (0.60g) and benzylferrocene (0.07g). A trace of bibenzyl was detected and triphenyltin bromide (0.87g) m.p. 113-115° (lit.[146] 119-121°) was isolated.

(d) <u>Blank reaction.</u> - Benzyl bromide (1.72g), tributyltin hydride (2.92g), ferrous sulphate (1.52g), and t-butyl hydroperoxide (1.80g) were allowed to stand in methyl acetate (40ml) under nitrogen, with occasional swirling, for 1 week. The ferrous sulphate turned yellow. V.p.c. analysis (column F, 25°) of the methyl acetate solution showed that toluene was present. t-Butylbenzene was added and the toluene concentration was estimated by v.p.c. (column F, 25° programming to 80°) to be 0.073g/40ml.

<u>Ferrocenium ion with phenylthiol and t-butyl hydroperoxide</u>

A mixture of ferrocene (1.86g), ferric chloride (1.65g), and phenylthiol (4.4g) in methyl acetate (30ml) was refluxed under nitrogen, during the slow addition of t-butyl hydroperoxide (2.6g of 70%). After 2 hr the mixture was cooled, and separated (see (vii) (a)) into ferrocene and non-ferrocene fractions. Chromatography of the ferrocene sample on alumina gave three main fractions. The first fraction contained only ferrocene, the second contained ferrocene and a yellow compound with slightly lower R_f value by t.l.c., and the third fraction contained pink material. An n.m.r. spectral examination of the second fraction showed that phenyl protons were present. Preparative t.l.c. gave an impure compound (0.078g) identified by n.m.r.[106] as phenylthio-ferrocene m.p. 105-107° (lit.[106] 111.5-112°).

An n.m.r. examination of the third fraction showed that phenyl protons were absent.

Ferrocene phenylations

(a) A mixture of ferrocene (1.86g), benzyl bromide (1.71g), and phenyldiazonoum tetrafluoroborate (1.92g) was stirred in acetone (20ml) under nitrogen for 1 hr at ambient temperature. The mixture turned dark green-blue and heat and gas were evolved. The mixture was tipped into an excess of aqueous ferric chloride solution and extracted with ether (2X100ml). The aqueous extract was treated with titanous chloride, then it was extracted with chloroform, dried, and chromatographed on alumina (70g). Ferrocene (1.16g) was eluted first, followed by phenylferrocene contaminated with benzylferrocene. Crystallization from hexane gave phenylferrocene (0.37g) m.p. 111-113° (lit.[138] 114-115°). V.p.c. examination of the mother liquor from the crystallization of phenylferrocene (column D, 200°)

showed that they contained c. 80% phenylferrocene and 20% benzylferrocene. The crystalline phenylferrocene contained only a trace of benzylferrocene.

(b) Repetition of (a), but with ferrocenium tetrafluoroborate (2.8g) in place of ferrocene, gave ferrocene (0.76g), phenylferrocene (0.48g), and diphenylferrocene (0.08g) m.p. 152-153° (hexane (lit.[138] 154-155°). V.p.c. analysis (column D, 200°) showed that benzylferrocene was present in the mother liquors as in (a).

(c) Repetition of (a) with acetic acid (20ml) as solvent and using the work-up procedure described in (a), gave ferrocene (0.50g), phenylferrocene (0.75g), and diphenylferrocene (0.13g). V.p.c. analysis indicated that benzylferrocene was present as before.

(d) Repetition of (a) with isopropyl alcohol (20ml) and acetone (10ml) as solvents gave, after the usual work-up procedure, ferrocene (1.58g) and a mixture of phenyl- and benzyl-ferrocene (0.16g), m.p. 85-105°. V.p.c. analysis (column D, 200°) showed that approximately equal amounts of the two ferrocenes were present.

(e) Repetition of (d) without benzyl bromide gave ferrocene (1.30g) and phenylferrocene (0.24g).

(f) Repetition of (a) with *p*-dihydroquinone (4.4g) present, gave ferrocene (1.18g) and phenylferrocene (0.34g). V.p.c. examination showed that benzylferrocene was absent.

IV. 4. Preliminary Experiments for Studies of Stability

An Attempted photochemical synthesis of 2,3-diferrocenylbutan-2,3-diol

Acetylferrocene (0.20g) in isopropyl alcohol (200ml) was allowed to stand in a quartzflask under nitrogen in direct sunlight. After 1 month, only acetylferrocene was detected by t.l.c. After being filtered the solvent was evaporated and the residue was chromatographed on alumina (10g). Acetylferrocene (0.07g) was recovered.

Ferrocenylmethyl and benzyl chloride with tributyltin hydride

Ferrocenylmethyl chloride was prepared by the method of Tidwell and Traylor.[147]

Benzyl chloride (0.12g), ferrocenylmethyl chloride (0.24g), tributyltin hydride (0.23g), and ABIBN (0.02g) were heated at 50° in benzene (10ml), under nitrogen, for 64 hr. V.p.c. examination of the solution (column F, 25°) did not detect toluene. After work-up in the usual way (IV.3.(vi)(a)), and chromatography on alumina (10g), methylferrocene (0.06g) and ferrocenylmethanol (0.13g) were isolated.

Attempted synthesis of ferrocenylmethyl chloroformate.

The synthesis was attempted by Farthing's method.[148] Ferrocenylmethanol (1g) in benzene (20ml) was cooled in dry-ice-acetone while phosgene (commercial sample, unpurified) was slowly bubbled through the solution. After 1 hr the weight of the solution had increased by c. 1g, and dry nitrogen was then bubbled through the mixture at room temperature for 6 hr. The remaining benzene was evaporated, leaving a green residue which gave only weak carbonyl absorptions in the i.r. Strong hydroxyl absorptions were observed. Variations of this attempted synthesis did not give the required product in good yield.

Attempted addition of tributyltin hydride to isopropenylferrocen

A mixture of isopropenylferrocene (0.90g), tributyltin hydride (1.16g), and ABIBN (0.03g) in benzene (10ml) was refluxed under nitrogen for 24 hr. The reaction mixture was separated into ferrocenes and non-ferrocenes, and t.l.c. separation of the ferrocene fraction gave three products. One of these was isopropylferrocene (comparison with authentic sample); the other two products had n.m.r. spectra with multiplets centred at δ 1.0 and 4.0 (alkyl and ferrocene hydrogens respectively) which had integration ratios of c. 4:1. Mass spectra gave groups of peaks centred at m/e 516. However, both samples decomposed readily, and were obtained in low yield. ar formation was extensive.

IV. 5. The Preparation of Amines and Quaternary Salts

Amines

(i) (Ferrocenylmethyl)trimethylammonium iodide (2.2g) and aqueous t-butylamine (20ml) were heated under reflux for 12 hr. The mixture was cooled, and then it was poured into water (100ml) and extracted with light petroleum (3X100ml). After drying, the solvent was evaporated to give crude N-t-butyl(ferrocenylmethyl)amine (0.35g, 22%) m.p. 60-62^{o} (hexane) (Found: C, 66.1, H, 7.9. $C_{15}H_{21}FeN$ requires C, 66.4; H, 7.8%). N.m.r. (CCl_4): δ 4.2-3.9(9H, m, ferrocenyl), 3.9 (1H, br.s, NH?), 3.3 (2H, s, Fc$C\underline{H}_2$), 1.1 (9H, s, Bu^t). Mass spectrum: M^+ at m/e 271. $C_{15}H_{21}FeN$ requires m/e 271.

(ii) Ferrocenylmethanol (0.9g) in aqueous t-butylamine (20ml) was refluxed for 12 hr. A sample was extracted with light petroleum, and t.l.c. examination of the extract showed that

N-t-butyl(ferrocenylmethyl)-amine was absent.

(iii) Ferrocenylmethanol (0.9g), aqueous t-butylamine (20ml), and acetic acid (0.5ml) were refluxed for 12 hr. T.l.c. indicated that the required amine was not present.

(iv) A mixture of ferrocenylmethanol (0.9g), t-butylamine (20ml), and an excess of acetic acid (20ml) was refluxed for 12 hr. After cooling, the mixture was poured into 5% aqueous acetic acid (200ml), and extracted with light petroleum (2X50ml) The aqueous solution was basified with sodium carbonate and then re-extracted with light petroleum (2X100ml). When this latter fraction was dried and the solvent evaporated, crude N-t-butyl-(ferrocenylmethyl)amine was isolated (0.84g, 75%) m.p. 58-61°.

N-(Ferrocenylmethyl)piperidine

(i) A mixture of (ferrocenylmethyl)trimethylammonium iodide (0.5g), piperidine (2ml), and water (10ml) was refluxed for 6hr. After cooling, the mixture was extracted with light petroleum (2X20ml), the organic extracts were dried and the solvent was evaporated to give oily material. This crystallized from hexane as yellow flakes (0.19g, 53%) of N-(ferrocenylmethyl)-piperidine m.p. 86-87° (lit.[149] 84-85.5°). N.m.r. (CCl_4): δ 4.0 (9H, s, ferrocenyl protons), 3.2 (2H, s, $FcC\underline{H}_2$), 2.2 and 1.4 (10H, 2m, piperidine protons).

(ii) A mixture of ferrocenylmethanol (0.46g), piperidine (3ml), and aqueous acetic acid (18ml) (solution pH 5.1) was refluxed for 12 hr. After cooling, the mixture was poured into water (100ml), and extracted with light petroleum (2X50ml). The aqueous solution was basified with excess sodium carbonate, and re-extracted with light petroleum (2X100ml). This second extract was dried and the solvent was evaporated to give crude N-(ferrocenylmethyl)piperidine (0.58g, 97%) m.p. 81-83°.

N-(Ferrocenylmethyl)benzylamine

(i) A mixture of (ferrocenylmethyl)trimethylammonium iodide (0.5g) and benzylamine (2ml) in water (10ml) was refluxed overnight. After cooling, the mixture was extracted with light petroleum (2X50ml) and the organic extracts were dried and the solventevaporated. The oily residue contain two compounds (t.l.c.).

(ii) A mixture of ferrocenylmethanol (0.4g), benzylamine (3ml), and acetic acid (4ml) in water (10ml) was refluxed for 12 hr. The basic and neutral organic fractions were separated as before the neutral fraction contained starting material (0.03g). Crude N-(ferrocenylmethyl)benzylamine (0.52g, 92%) was obtained as a yellow viscous oil, which was not further purified (Found: C, 71.0; H, 6.4; N, 4.6. $C_{18}H_{19}FeN$ requires C, 70.8; H, 6.3;

N, 4.6%). N.m.r. (CCl_4): δ 7.1 (5H, s , Ph), 4.2-3.9 (9H, m, ferrocenyl protons), 3.8 (2H, s, $FcC\underline{H}_2$), 1.3 (1H, br.s, NH). Mass spectrum: M^+ at m/e 305. $C_{18}H_{19}FeN$ requires m/e 305.

N-(Ferrocenylmethyl)aniline

(i) A mixture of (ferrocenylmethyl)trimethylammonium iodide (0.5g) and aniline (2ml) in water (10ml) was refluxed for 6 hr. After cooling and the usual work-up procedure, an oily material (0.2g) was obtained. This was not further purified.

(ii) Ferrocenylmethanol (0.5g), aniline (2ml), methanol (15ml), and water (20ml) were refluxed for 12 hr. The solution had pH 8.8 before heating. After the usual isolation of products, crude N-(ferrocenylmethyl)aniline (0.63g, 95%) was obtained as yellow crystals m.p. 84-85° (lit.[150] 85-86°). I.r. (Nujol): 3450 cm^{-1} (NH); n.m.r. (CCl_4): δ 7.2-6.4 (5H, m, Ph), 4.3-4.0 (9H, m, ferrocenyl protons), 3.9 (2H, s, $FcC\underline{H}_2$), 3.5 (1H, br.s, NH). The β-naphthol derivative gave a green precipitate — presumably a ferrocenium salt.

A trace of ferrocenylmethanol was isolated from the neutral fraction.

(iii) A mixture of ferrocenylmethanol (0.5g), aniline (2ml), methanol (15ml), and acetic acid (5ml) was refluxed in water

(20ml) for 12 hr. The solution had pH 4.3 before heating. N(-Ferrocenylmethyl)aniline (0.34g, 50%), ferrocenylmethanol (0.08g), and ferrocenylmethyl methyl ether (0.08g, 15%) were isolated. T.l.c. indicated that traces of other products were present.

N-(Ferrocenylmethyl)-p-nitroaniline

A mixture of ferrocenylmethanol (0.1g), p-nitroaniline (2g), and methanol (5ml) was refluxed for 12 hr in water (10ml). The solution had pH 9.6 before heating. After the usual work-up procedure, preparative t.l.c. gave N-(ferrocenylmethyl)-p-nitroaniline (0.14g, 84%) m.p.148-150° (hexane) (Found: C, 60.5; H, 4.8; N, 8.2. $C_{17}H_{16}FeN_2O_2$ requires C, 60.7; H, 4.8; N, 8.6%). N.m.r. (CCl_4): δ 8.16 (2H, d, J 9, Ph), 6.16 (2H, d, J 9, Ph), 4.6 (1H, br. s, NH), 4.3-4.0 (11H, br.m, with s at 4.2, ferrocenylmethyl protons). Mass spectrum: M^+ at m/e 336. $C_{17}H_{16}FeN_2O_2$ requires m/e 336.

N-(Ferrocenylmethyl)-p-methoxyaniline

Ferrocenylmethanol (0.1g) and p-methoxyaniline (0.25g, freshly recrystallized) were treated as in the previous experiment. After the work-up procedure, two products were isolated by preparative t.l.c.; the yellow oil with lower R_f was identified as N-(ferrocenylmethyl)-p-methoxyaniline (0.10g, 70%)

(Found: C, 67.0; H, 5.0; N, 4.4. $C_{18}H_{19}FeNO$ requires C, 67.3; H, 6.0; N, 4.4%). N.m.r. (CCl_4): δ 6.9-6.4 (4H, q ,Ph), 4.2-4.0(9H, m, ferrocenyl protons), 3.9(2H, s, CH_2), 3.7(3H, s, OMe), and 3.4(1H, s, NH). Mass spectrum: M^+ at m/e 321. $C_{18}H_{19}FeNO$ requires m/e 321. The other product (0.03g), with R_f similar to that of ferrocenylmethyl methyl ether, decomposed when purification was attempted.

N-(Ferrocenylmethyl)urea

Ferrocenylmethanol (0.14g) and urea (2g), were heated in refluxing water (20ml) for 20 hr. The solution had pH 7.2 before heating. Work-up in the usual fashion gave ferrocenylmethanol (0.05g), and N-(ferrocenylmethyl)urea (0.08g, 33%) as yellow crystals m.p. 163-164° ($CHCl_3$)(Found: C, 55.8; H, 5.4; N, 10.6. $C_{12}H_{14}FeN_2O$ requires C, 55.8; H, 5.5; N, 10.8%). I.r. (Nujol) 3400s, 3200sh, 3100w (NH); 1680s cm^{-1} (CO). N.m.r. (CCl_4): δ 4.4-4.0 (11H, m with 9H s, $FcCH_2$), 2.2 (1H, br. s, NH?), 1.6 (2H, br.s, NH_2?). Mass spectrum: M^+ at m/e 258. $C_{12}H_{14}FeN_2O$ requires m/e 258. A number of unidentified products were present in small yield.

Preparation of p-(Ferrocenylmethyl)aniline.

p-Nitrobenzoylferrocene (0.10g) was mixed with 1:1 lithium aluminium hydride (0.08g) — aluminium trichloride (0.27g) in dry ether (10ml). The mixture was allowed to stand overnight at room temperature. Ethyl acetate (5ml) was added dropwise and then water (30ml) was added and the organic layer was separated. The organic layer was washed with water (3X20 ml), 10% sodium carbonate (3X20ml), and water (20ml), and then dried. The organic solvent was evaporated and the crude residue was dissolved in ethanol (5ml) and added to a mixture of hydrazine (0.2g) and platinum oxide (0.05g) in ethanol (10ml). After 12 hr, the mixture was filtered, and the ethanol was evaporated. The oily residue was purified by chromatography on alumina (5g) to give a yellow product m.p. 105-107°, which blackened slowly on exposure to air. N.m.r. (CCl_4): δ7.0-6.3 (4H, q, J 13, J′ 4, Ph), 3.9 (9H, two s, ferrocenyl protons), 3.5 (2H, s, CH_2), 3.3 (2H, br. s, NH_2?). Mass spectrum: M^+ at m/e 291. $C_{17}H_{17}FeN$ requires m/e 291. The splitting pattern was similar to that for $FcCH_2Ph$ (See Appendix).

Reactions at Various pH Values

Piperidine (0.2g) and ferrocenylmethanol (0.1g) were added to different buffer solutions in water (10ml) and the pH was measured. Some of the solutions were allowed to stand at room temperature and others were heated under reflux. After 12 hours they were worked up in the usual way. The pH values, measured immediately before work-up, did not vary more than 0.4 units from the initially-recorded values. The results of various reactions are shown in Table 12.

Blank Reactions

(i) A mixture of ferrocenylmethyl methyl ether (0.1g) and aniline (0.5g) in water (10ml) was refluxed for 12 hr (pH 8.1). After work-up in the usual way, the ether was regained almost quantitatively.

(ii) A mixture of N-(ferrocenylmethyl)piperidine (0.1g), aqueous methanol (15ml), and acetic acid (5ml) was heated under reflux for 12 hr (pH5.0). The amine was recovered unchanged.

Competitive Aminations

(i) A mixture of ferrocenylmethanol (0.1g), aniline (2g), and aqueous t-butylamine (10ml) was refluxed overnight (pH 11.1 at beginning). After the usual work-up procedure, the ferrocene bases were isolated, and examined by n.m.r. This indicated that N-t-butyl(ferrocenylmethyl)amine was absent and that the "bases" were mainly N-(ferrocenylmethyl)aniline.

(ii) A mixture of ferrocenylmethanol (0.1g), aniline (2g), cyclohexylamine (2g), and water (10ml) was heated under reflux, An n.m.r. examination of the ferrocene bases showed that N-cylcohexyl(ferrocenylmethyl)amine was absent.

<u>Synthesis of N-cyclohexyl(ferrocenylmethyl)amine</u> (Schiff's Base Method)

Ferrocenecarbaldehyde was prepared by a Vilsmeier-Haack Reaction.[40]

Aldehyde (2.14g) and cyclohexylamine (3g) were allowed to stand in dry ethanol (5ml) for 2 days. The precipitated orange-red imine (2.5g, 85%) was crystallized from light petroleum, m.p. 106-107° (mixed mp. with ferrocenecarbaldehyde 50-60°) (Found: C, 69.4; H, 7.2; N, 4.7. $C_{17}H_{21}FeN$ requires C, 69.3; H, 7.2; N, 4.7%). N.m.r. (CCl_4): δ 4.5(2H, m, ferrocenyl protons), 4.2 (2H, m, ferrocenyl protons), 4.0(5H, s, ferrocenyl protons), 3.0 (1H, br. s, CH), 1.6(11H, br.m, C_6H_{11}). Mass spectrum: M^+ at <u>m/e</u> 295. $C_{17}H_{21}FeN$ requires <u>m/e</u> 295. The imine (2.4g) and platinum oxide (0.2g, Adam's catalyst), in ethyl acetate (30ml), were stirred under hydrogen until the calculated volume of H_2 (183ml) had been absorbed. After filtration and evaporation of the solvent, N-cyclohexyl(ferrocenylmethyl)amine (1.3g, 56%) was obtained as orange flakes m.p. 35-37° (hexane) (Found: C, 68.6; H, 8.0; N, 4.7. $C_{17}H_{23}Fe N$ requires C, 68.6; H, 7.7; N, 4.7%). N.m.r. (CCl_4): δ 4.1(9H, m, ferrocenyl), 3.5(2H, s, CH_2), 2.4(1H, br. s, NH?), 1.7 and 1.2(11H, two br. m, C_6H_{11}). Mass spectrum: M^+ at <u>m/e</u> 297. $C_{17}H_{23}FeN$ requires <u>m/e</u> 297. The amine was also prepared by the ferrocenylmethanol - acetic acid method in 89% yield.

N-t-Butyl-N-methyl(ferrocenylmethyl)amine

N-Methyl-t-butylamine was prepared by the methods of Heath and Mattocks,[151a] or Meiners *et al.*[151b]

(i) A mixture of the amine (2.3g), ferrocenylmethanol (0.5g), acetic acid (3ml), water (40ml), and methanol (10ml) was refluxed overnight (initial pH5.2). After the usual work-up procedure, ferrocenylmethyl methyl ether (0.44g) and a small amount of ferrocene base were isolated. An n.m.r. spectrum of the base showed some similarities to that of the amine from (v); peaks (CCl_4) at δ 4.1-4.0, 3.4-3.3, 2.0, 1.3-1.0.

(ii) The above experiment was repeated without methanol. A much larger base fraction was obtained, and this was combined with that from (i). Benzene (10ml), and methyl iodide (3ml) were added. A small amount of methiodide (20mg) was collected.

(iii) A mixture of (ferrocenylmethyl)trimethylammonium iodide (2.5g), N-methyl-t-butylamine (3g), acetic acid (4ml), and water (50ml) was refluxed for 3 hr (initial pH 4.6). The solution slowly turned green. After the usual work-up procedure, ferrocenylmethanol (0.8g) and methylferrocene (0.04g) were isolated.

(iv) A mixture of ferrocenylmethanol (0.1g), N-methyl-t-butylamine (1g), acetic acid (1.5ml), in acetone (20ml) was brought to pH 6.5 with solid sodium hydrogen carbonate. The mixture was refluxed for 12 hr. The usual work-up procedure gave di-(ferrocenylmethyl) ether (0.06g) m.p. 132-133° (lit.[118] 134-136°), and an unidentified product which slowly decomposed. Starting material (0.03g) was also recovered.

(v) Ferrocenylmethanol (0.2g) in ether (50ml), over calcium chloride (5g), was treated with a slow stream of dry HCl (Kipp's apparatus) for 3 hr.[147] The ether was carefully evaporated under reduced pressure, and then light petroleum (10ml), solid dry sodium hydrogen carbonate, and N-methyl-t-butylamine (2g) were added, in that order. The mixture was allowed to stand overnight. After being filtered off the filter-cake was washed with ether (2X50ml) and ethyl acetate (2X50ml). The organic filtrates were combined, dried, and evaporated. The usual separation procedure gave N-t-butyl-N-methyl(ferrocenylmethyl)amine as a yellow oil (0.044g, 26%)(Found: C, 66.9; H, 8.1; N, 5.3. $C_{16}H_{23}FeN$ requires C, 67.3; H, 8.1; N, 4.9%). N.m.r. (CCl_4): δ 4.1-4.0(9H, m and s, ferrocenyl), 3.3(2H, s, CH_2), 2.0(3H, S, Me), 1.1(9H, S, Bu^t). Mass spectrum: M^+ at *m/e* 285. $C_{16}H_{23}FeN$ requires *m/e* 285. Di(ferrocenylmethyl) ether (0.012g, 7%) and ferrocenylmethanol (0.012g, 6%), were also recovered.

Subsequent experiments gave (yields as % of ferrocenylmethanol): amine 67 and 72%, ether 11 and 5%, and ferrocenylmethanol 12 and 13%.

Quaternary Ammonium Salts

(Ferrocenylmethyl)trimethylammonium Salts.-

(Dimethylamino)methylferrocene was treated with an excess of methyl iodide, in benzene at room temperature, to give the methiodide salt m.p. 216-218° dec. (lit.[152] m.p. 220°). The n.m.r. spectrum was as reported.[122] Quantitative addition of silver nitrate, by the method of Vogel,[155] gave the nitrate which was recrystallized from isopropanol-ether m.p. 173° dec.

Readily-formed salts. - Ethyl(ferrocenylmethyl)dimethylammonium iodide, (ferrocenylmethyl)isopropyldimethylammonium iodide, allyl(ferrocenylmethyl)di-methylammonium bromide, and benzyl-(ferrocenylmethyl)dimethylammonium bromide were all prepared by treating (dimethylamino)methylferrocene with an excess of the appropriate alkyl halide in benzene. After allowing to stand, the salts were collected by filtration, and then dried. The following physical data were recorded; *ethyl(ferrocenylmethyl)dimethylammonium iodide* m.p. 178-180° dec. (lit.[152] 185-188°dec); n.m.r. ($CDCl_3$): δ 4.9 (2H, s, Fc$C\underline{H}_2$), 4.6 (2H, t, J 2, ferrocenyl H2,5), 4.3(7H, t and s, J 2, H3,4 and C_5H_5), 3.6(2H, q, J 15, J$'$3, NCH_2), 3.1(6H, s, 2NMe), 1.4(3H, t, J 7, Me).

(Ferrocenylmethyl)isopropyldimethylammonium iodide m.p 170-174° dec. (lit.[152] 179-181°); n.mr. ($CDCl_3$): δ 4.9(2H, s, Fc$C\underline{H}_2$), 4.6(2H, t, J 2, H2,5), 4.3(7H, t and s, J 2, H3,4 and C_5H_5), 3.8(1H, m, CH), 3.1(6H, s, 2NMe), 1.5(6H, d, J 7, CMe_2)

Allyl(ferrocenylmethyl)dimethylammonium bromide m.p. 180-181° dec. (lit.[152] 183-185°); n.mr. ($CDCl_3$): δ 6.0(3H, br. m, allyl), 4.9(2H, S, Fc$C\underline{H}_2$), 4.6 (2H, t, J 2, H2,5), 4.3(7H, t and s, J 2 H3,4 and C_5H_5), 3.2(6H, s, 2NMe).

Benzyl(ferrocenylmethyl)dimethylammonium bromide m.p. 168-170° dec. (lit.[152] 180-182°)(Found:C,57.6; H,5.8; N,3.3. Calc. for $C_{20}H_{24}BrFeN$: C,58.0, H,5.8, N,3.4%). N.m.r. ($CDCl_3$): δ 8.0-7.0(5H, m, Ph), 5.0(2H, S, Fc$C\underline{H}_2$), 4.6(2H, t, J 2, H 2,5), 4.3 (9H, br.m, H 3,4, C_5H_5, and Ph$C\underline{H}_2$), 3.0(6H, s, 2NMe).

Preparation of Cyclohexyl(ferrocenylmethyl)ammonium Salt.

(i) (Dimethylamino)methylferrocene did not give the required salt (by n.m.r. spectral examination) when treated with cyclohexyl bromide or iodide, or cyclohexyl p-toluenesulphonate.

(ii) N-Cyclohexyl(ferrocenylmethyl)amine (1.3g, prepared previously) was treated with an excess of methyl iodide in benzene for 12 hr. The salt (1.7g, 88%) was collected by filtratration as a yellow crystalline solid m.p. 184° dec. (Found: H, 6.0; N, 3.2. $C_{18}H_{26}FeNI$ requires H, 5.7; N, 2.8%). N.m.r. ($CDCl_3$): δ 6.8(1H, br.s, NH?),5.0(2H, s, $FcC\underline{H}_2$), 4.6 (2H, t, J 2, H 2,5), 4.4 (7H, t and s, J 2, H 3,4 and C_5H_5), 4.0(1H, m, CH), 3.1(3H, S, NMe), 2.4-1.4(10H, br.m, C_6H_{10}).

Preparation of t-Butyl(ferrocenylmethyl)ammonium Salts

(i) (Dimethylamino)methylferrocene did not give the required salt (by n.m.r. spectral examination) when treated with an excess of t-butyl bromide or iodide.

(ii) N-t-Butyl(ferrocenylmethyl)amine (0.5g, prepared previously) was treated with excess methyl iodide in benzene for 12 hr. The salt (0.6g) was collected as a yellow crystalline solid m.p. 152° dec. (Found: C, 46.3; H, 5.9; N, 3.1. $C_{16}H_{24}FeNI$ requires C, 46.5; H, 5.9, N, 3.4%). N.m.r. ($CDCl_3$): δ 6.1 (1H, br.s, NH?), 4.9(2H, s, $FcC\underline{H}_2$), 4.6(2H, t, J 2, H 2,5), 4.3(7H, s?, H 3,4 and C_5H_5), 3.0(3H, s, NMe), 1.7(9H, s, Bu^t).

(iii) A mixture of ferrocenylmethanol (0.4g), acetic acid (2ml), N,N-dimethyl-t-butylamine[151] (2g), and water (20ml) was refluxed overnight. The solution was cooled, and then neutralized with sodium carbonate. Potassium iodide (2g) was added, and the solution was extracted with ether (3X100ml). The solvent was evaporated, and the residue was chromatographed on alumina to give starting material (0.11g), and di(ferrocenylmethyl) ether (0.17g). Extraction of the aqueous solution with chloroform (2X100ml) did not give ferrocene salts.

(iv) N-t-Butyl(ferrocenylmethyl)amine (0.3g) was heated in an excess of methanolic methyl iodide for 72 hr in the presence of solid sodium carbonate (0.3g). After cooling, and treatment with ascorbic acid, the solution was evaporated, and the dry cake was dissolved in water and extracted with chloroform (3X100ml). The extracts were dried, and the chloroform was evaporated. An n.m.r. spectral examination revealed little of the desired product.

(v) N-t-Butyl-N-methyl(ferrocenylmethyl)amine (0.5g, prepared previously) was treated with an excess of methyl iodide in benzene for 12 hr, to give the yellow crystalline salt m.p. 170° (dec.)(Found: C,48.6; H,6.1; N,3.1 $C_{17}H_{26}FeNI$ requires C, 47.8; H, 6.1; N, 3.3%). N.m.r. ($CDCl_3$): δ 4.9(2H, s, FcC$\underline{H}_2$), 4.6(2H, t, J 2, H 2,5), 4.3(7H, s?. H 3,4 and C_5H_5), 2.9 (6H, S, 2NMe), 1.6(9H, s, Bu^t).

IV. 6. The Reductions of Quaternary Ammonium Salts

Exploratory Reductions - Electrolysis of Benzyltrimethylammonium Bromide

A solution (200ml of 0.25M) of the salt in dry DMF was placed in a 500-ml conical flask surrounded by an ice-salt bath. An aluminium cathode and a platinum wire anode were connected to a voltage regulator (built by Organic Chemistry department technical staff) which was plugged into the mains power supply. A steady stream of nitrogen was bubbled through the solution, and was then passed through a cooled ethereal solution of methyl iodide. The potential reading was maintained at 30 V and the current was *c.* 0.5 A. After 20 hr. the reduction mixture was poured into water, and the aqueous mixture was extracted with ether (2X100ml). The ether was dried, and a small sample was examined by v.p.c. analysis (column F, 25°). Toluene was present. The ether was evaporated to give crude bibenzyl (1.64g 28%) m.p. 53° (lit.[140] 52-53°).

Filtration of the ethereal methyl iodide solution gave white, finely crystalline, tetramethylammonium iodide (0.20g, 2%) m.p.$>$240° (lit.[140] $>$230°).

Electrolysis of (Ferrocenylmethyl)trimethylammonium Nitrate

A solution (100ml of 0.15M) of the salt in dry DMF was electrolysed, as above, for 28hr. The potential reading was maintained at 30 V and the current was c. 0.2 A. After the work-up procedure, methylferrocene (0.86g, 29%) mp. 33-34°, 1,2-diferrocenylethane (0.074g, 2%) m.p.177-178° (lit.[76] 183-188°), and an unidentified oily material (0.04g), were isolated. Crude tetramethylammonium iodide (1.71g, 57%) was isolated from the ethereal methyl iodide solution, as a yellow solid.

Electrolysis of Benzyl(ferrocenylmethyl)dimethylammonium Bromide

(i) A solution of the salt (200ml of 0.104M) in DMF was electrolysed for 20 hr in the presence of sodium metabisulphite (5g). The potential reading was maintained at 30 V and the current was *c*. 0.3 A. Extensive tar formation was noted, especially at the anode. The mixture was tipped into water (300ml), and extracted with ether (2X100ml) and light petroleum (2X100ml), and the organic extracts were separated into basic and neutral fractions. The neutral fraction was chromatographed on alumina to give methylferrocene (0.19g, 5%), 1,2-diferrocenylethane (0.04g, 1%), and bibenzyl (impure, *c*. 0.2g, rechromatographed to give 0.12g, 6%). A small amount (0.04g, 1%) of impure N,N-dimethylbenzylamine, and a larger quantity (0.72g, 14%) of impure (dimethylamino)methylferrocene, were isolated and identified by v.p.c. comparisons (column F, 150°) with authentic samples.

(ii) The salt (0.83g) in DMF (20ml) was allowed to stand in the presence of sodium metabisulphite (1g) for 20 hr, without electrolysis. After the work-up procedure, traces of decomposition products were detected by t.l.c.

(iii) A solution of the salt (200ml of 0.05M), in water, was electrolysed for 9hr in the presence of sodium metabisulphite. The potential reading was maintained at 8 V and the current was *c*. 0.25 A. Extensive foaming occurred, the mixture blackened, and the aluminium cathode partially dissolved. After the usual work-up procedure, a diverse mixture of products (t.l.c. examination) was present in small yield. Extensive tar formation was noticed.

(iv) The salt (400ml of 0.05M) was dissolved in water in a 500ml conical flask which was connected by a folded 30 cm filter paper, saturated with aqueous potassium chloride, to a 500 ml conical flask containing potassium chloride (40g) in water 400ml The anode was a platinum wire, and the cathode (placed in the ferrocenylmethyl salt solution) was a mercury pool (80ml) connected with a platinum wire to the voltage regulator. After electrolysis at 30 V and 0.1 A for 2 hr, methylferrocene and N,N-dimethylbenzylamine were detected (t.l.c.).

Reductions of Quaternary Ammonium Salts.

(i) Electrolyses

The apparatus shown in III.3 Figure 5, was used for all of the following electrolytic reductions. The anode was a platinum wire, and ammonium nitrate (10g in 200ml of water) was used as the anode electrolyte. A mercury pool cathode (250g) was used, and the appropriate (ferrocenylmethyl)ammonium salt was dissolved in the appropriate solvent (usually DMF) and added to the cathode compartment. The mercury pool was connected by a bent platinum wire to the voltage regulator. Salt bridges were made up in the minimum length of ¼ in. o.d. glass tubing. They consisted of potassium chloride (30g, A.R.), and agar-agar (3g), in water (100ml) which was gently heated until solution. This solution was poured into the inverted glass tubing, and allowed to cool and solidify.

The potential readings were usually maintained at 30 V to ensure a reasonable current flow, which was indicated by bubbles at the anode. Aqueous solutions were kept at lower readings. When DMF solutions were electrolysed, salt bridges were changed frequently.

Work-up procedure. - The solution was decanted carefully from the mercury cathode, and the mercury pool was washed several times with water which was added to the decanted solution (500ml of water used). The aqueous solution was extracted with ether

(5X100ml), and the combined ethereal extracts were extracted with 2% aqueous acetic acid (4X100ml). An excess of solid sodium carbonate was added to the aqueous acidic extracts. The basified solution was then extracted with ether (3X100ml), and these extracts were combined, dried, and evaporated. The amines present were identified by v.p.c. analysis (column F, 150°).

The 500ml ethereal fraction was extracted with ferric chloride solution (200ml of 6N H_2SO_4) saturated with ferric chloride), and then washed with water (2X100ml). The ferric solution and the aqueous washings were combined. The ethereal fraction was washed with 5% sodium carbonate (2X100ml), and it was then dried, and concentrated carefully at room temperature. The presence of toluene was detected by v.p.c. analysis (column F, 25°) of the concentrated residue.

The combined ferric solution was reduced with an excess of titanous sulphate and then it was extracted with ether (3X100ml). The ether extracts were washed with 5% sodium carbonate (2X100ml) and then dried. The ether was evaporated and the residue was separated by preparative t.l.c.

The results of electrolytic reductions are shown in Table 13.

(a) Electrolysis of t-Butyl(ferrocenylmethyl)ammonium Iodide

The salt (0.7g) in water ((150ml) was electrolysed in the usual way. (The solution had pH 5.5 at the beginning of electrolysis). A yellow precipitate slowly formed. (The solution had pH 12.0 at the end of electrolysis). T.l.c. examination indicated that N-t-butyl-(ferrocenylmethyl)amine was the major constituent of the precipitate. Small amounts of methylferrocene and 1,2-diferrocenylethane were also present. After the usual work-up procedure, small amounts of bases were isolated, and were characterized by v.p.c. comparison with authentic samples.

The salt (0.5g) was dissolved in DMF (30ml) and the solution was divided into two. Each fraction was worked up as for the electrolyses, except that 5% aqueous sodium bicarbonate(pH7.9) was used to make the solution basic in one instance, and 5% aqueous potassium carbonate (pH10.6) was used in the other. N-t-Butyl(ferrocenylmethyl)amine m.p.58-61^{o} (hexane), no m.p. depression on admixture with an authentic sample, was isolated from the procedure in which potassium carbonatewas used. This was <u>not</u> isolated by the other procedure.

(b) Electrolysis of Cyclohexyl(ferrocenylmethyl)methylammonium Iodide

The salt (1.1g) in DMF (200ml) was electrolysed and worked up in the usual way. N-Cyclohexyl(ferrocenylmethyl)amine was present in the base-containing fraction (0.5g), but chromatography on neutral alumina (20g) gave only ferrocenecarbaaldehyde (0.01g). Decomposition was extensive. Treatment of the salt with 5% aqueous potassium carbonate as in (a) above, gave the parent amine.

(c) Blank Reaction

Benzyl(ferrocenylmethyl)dimethylammonium bromide (0.6g) in water (30ml) was allowed to stand over a mercury pool(10ml) with potassium hydroxide (0.7g) present. After 3 days, the work-up procedure as for the electrolyses did not reveal appreciable quantities of products.

(ii) Sodium-Liquid Ammonia Reductions

Slocum's method[76] for the reduction of (ferrocenylmethyl)trimethylammonium iodide was followed. After the ammonia had been evaporated and water had been added, the products were separated by the method used to separate the electrolysis mixtures. Because these reductions were on a small scale, the work-up procedure was scaled down appropriately. Results of the various reductions are included in Table 13.

(a) Blank Reaction

N-Cyclohexyl(ferrocenylmethyl)amine (0.2g) was allowed to stand in liquid ammonia for 15 min. The solution was then worked up in the usual way, but 5% aqueous sodium bicarbonate was used to make the solution basic. Reduction products were not detected.

APPENDIX

APPENDIX - THE MASS SPECTRA OF FERROCENES

All mass spectra were recorded at 70 eV on a Hitachi Perkin-Elmer RMU6D double-focusing mass spectrometer. Only peaks $\geqslant 4\%$ are reported here.

1. Monosubstituted Ferrocenes

Methylferrocene, isopropylferrocene, and isopropenylferrocene all had M^+ as the base peak, and exhibited strong peaks for $(FeCp)^+$ (121), $(FeC_6H_6)^+$ (134), and Fe^+ (56). Alkylferrocenes have been investigated thoroughly,[158] but only very broad generalizations have been made about their fragmentation patterns.[159]

p-Nitrobenzoylferrocene had M^+ as the base peak and an almost featureless spectrum; the loss of NO_2 to give $(FcCOPh)^+$ (289, loss substantiated by a metastable at m/e 249) being the only spectral aspect worthy of comment.

Mass spectrometry afforded a decisive method of distinguishing between the structural isomers p-(ferrocenylmethyl)aniline and N-(ferrocenylmethyl)aniline. p-(Ferrocenylmethyl)aniline had a spectrum almost identical with that of benzylferrocene: the base peak was M^+, with fragmentation from M^+ with the loss of

CpH(66) and PhH(78), and fragmentation from $(M - 68)^+$ with loss of Fe(56). All of these fragmentations were substantiated by metastable peaks. Peaks other than M^+ and $(M+1)^+$ were $<15\%$. N-(Ferrocenylmethyl)aniline had a typical (ferrocenylmethyl)-amine fragmentation pattern: the base peak was $(FcCH_2)^+$(199), with a strong $(FeCp)^+$ (121, 43%) peak, and with a metastable at m/e 74 to substantiate the 199-C_6H_6 fragmentation.

N-(Ferrocenylmethyl)-p-nitroaniline, N-(ferrocenylmethyl)-p-methoxyaniline, N-t-butyl(ferrocenylmethyl)amine, N-(ferrocenylmethyl)-piperindine, N-benzyl(ferrocenylmethyl)amine, N-cyclohexyl(ferrocenylmethyl)amine, and N-t-butyl-N-methyl (ferrocenylmethyl)amine all gave strong $(FcCH_2)^+$ peaks (199, usually the base peak). Fragmentation from $(FcCH_2)^+$ to $(FeCp)^+$ (121) was substantiated by metastable peaks. N-Benzyl(ferrocenylmethyl)amine had M^+ as the base peak, and N-(ferrocenylmethyl)-p-nitroaniline had m/e 138 as the base peak. Both of these compounds had prominent $(FcCH_2)^+$ (199) and $(FeCp)^+$ peaks. N-(Ferrocenylmethyl)urea also had prominent $(FcCH_2)^+$ and $(FeCp)^+$ peaks, but with a base peak at $(M-HNCO)^+$ (215), M^+ being only 8% of this. Di(ferrocenylmethyl)ether also had $(FcCH_2)^+$ as the base peak and a prominent $(FeCP)^+$ peak. Ferrocenecarbaldehyde cyclohexylimine gave a similar pattern, but with M^+ as the base peak, and $(FcCH_2)^+$ and $(FeCp)^+$ were present in an otherwise featureless pattern.

Monosubstituted Ferrocenes - Mass spectra

Methylferrocene: m/e 201(25% of base peak), 200(100,M$^+$), 199 (11), 198(13), 135(11), 134(76), 132(7), 122(10), 121(14), 100 (7), 95(11), 94(8), 81(13), 79(13), 77(10), 57(10), 56(89), 54 (7). Metastable peaks at 121, 90, 57, 24.

Isopropylferrocene: m/e 229(18% of base peak), 228(100,M$^+$), 227(5), 226(20), 214(13), 213(75), 212(18), 211(5), 199(3), 186(6), 162(4), 160(3), 147(9), 135(4), 134(6),122(9), 121(42), 119(3), 96(4), 95(5), 94(4), 91(6), 84(4), 81(4), 71(5), 57(8), 56(21). Metastable peaks at 199, 173.5, 162, 122, 111, 101, 68.5. Doubly-charged ions at 114.5, 106.5, 105.5, 99.5, 84.5-76.5.

Isopropenylferrocene: m/e 227 (19% of base peak), 226(100,M$^+$), 186(5), 158(3), 153(3), 134(6), 121(21), 113(4), 95(4), 81(4), 56(14). Metastable peaks at 222, 220, 218, 197, 173, 153, 79. Doubly-charged ions at 114.5 - 110.5, 99.5, 90.5, 89.5, 82.5-75.5.

p-Nitrobenzoylferrocene: m/e 336(24%), 335(100,M$^+$), 333(9), 305(5), 290(9), 289(36), 260(7), 205(6), 203(6), 197(5), 141(6), 139(11), 132(6), 129(6), 121(18), 94(5), 56(11). Metastable at 277, 249, 235, 203, 168, 144.

Di(ferrocenylmethyl)ether: m/e 415(20%), 414(66,M^+), 413(4), 412(10), 270(15), 258(6), 216(10), 214(6), 200(24), 199(24), 197(9), 196(12), 193(13), 186(29), 138(13), 121(45), 56(32). Metastables 219, 161, 144, 96, 73. Doubly-charged ions 206.5, 207.5.

Benzylferrocene: m/e 277(23%), 276(100,M^+), 275(8), 274(10), 211(6), 210(5), 208(12) 198(5), 184(5), 153(12), 152(13), 133 (7), 121(10), 56(12). Metastables at 206, 160, 142, 111. Doubly-charged ions at 138.5, 137.5.

p-(Ferrocenylmethyl)aniline: m/e 292(23%),291(100,M^+), 290(14), 289(9), 226(5), 225(4), 223(8), 213(5), 211(4), 199(3), 183(7), 182(5),170(6), 169(13), 168(14), 167(15), 121(10), 115(10), 106 (13), 69(8), 56(7),. Metastables 259, 193, 174, 156, 136, 125. Doubly-charged ions at 146.5-144.5, 91.5-89.5, 83.5, 78.5.

N-(Ferrocenylmethyl)aniline: m/e 292(11%), 291(49,M^+), 290(4), 289(6), 200(18), 199(100,base peak), 198(4), 197(8), 168(5), 148(5), 122(5), 121(43), 93(8), 81(3), 78(5), 77(6), 69(8), 65(5), 56(14). Metastables at 243, 136, 99, 74. Doubly-charged ions at 243.5, 146.5-144.5.

N-(Ferrocenylmethyl)-p-nitroaniline: m/e 337(9%), 336(38,M^+), 335(3), 334(13), 304(4), 200(13), 199(76), 197(6), 186(4), 167(3), 139(10), 138(100), 122(7),121(12), 119(4), 108(29), 92(42), 80(12), 78(4), 66(8), 65(54), 64(7), 63(9), 56(6). Metastables at 248, 227, 214, 186, 118, 73. Doubly-charged ions at 168.5, 167.5.

<u>N-(Ferrocenylmethyl)-p-methoxyaniline:</u> <u>m/e</u> 322(4), 321(18,M^+), 320(3), 319(8), 228(5), 200(18), 199(100), 197(7), 134(4), 123(8), 122(5), 121(33), 119(4), 108(9),56(2). Metastables at 259, 175, 124, 95, 74. Doubly-charged ions 161.5, 160.5, 159.5.

<u>N-t-Butyl(ferrocenylmethyl)amine:</u> <u>m/e</u> 272(15%), 271(69,M^+), 270(6), 269(8), 214(27), 200(18), 199(100), 197(7), 187(7), 186(23), 178(14), 149(16), 148(7), 128(18), 122(11), 121(44), 119(4), 78(7), 69(7),56(6). Metastables at 240, 170, 163, 137, 108, 73. Doubly-charged ions at 128.5, 127.5, 99.5, 98.5.

<u>N-(Ferrocenylmethyl)piperidine:</u> <u>m/e</u> 284(19%), 283(87,M^+), 282(17), 281(8), 215(6),204(13), 201(17), 200(100), 199(97) 198(8), 197(7), 186(19), 134(15), 122(18), 121(57), 98(8), 97(8), 84(9), 78(7), 69(12), 56(18), 55(11). Metastables at 127, 90, 73. Doubly-charged ions at 141.5, 127.5, 114.5, 113.5, 100.5, 99.5, 98.5.

N-Benzyl(ferrocenylmethyl)amine: m/e 306(25%), 305(100,M$^+$), 304(7), 303(13), 239(9),238(30), 226(8), 225(7), 214(9), 213 (22), 212(42), 201(8), 200(53), 199(46), 198(5), 186(14), 161 (7), 160(6), 152(10), 148(18), 147(10), 146(8), 134(9), 122 (6), 121(45), 107(13), 106(22), 92(8), 91(27), 79(8),78(7), 77 (8), 56(18). Metastables at 131, 90, 78, 73. Doubly-charged ions 152.5, 113.5, 99.5, 98.5.

N-(Ferrocenylmethyl)urea: m/e 259(3%), 258(8,M$^+$), 257(2), 256(3), 242(5), 241(30), 216(17), 215(100), 214(15), 213 (13), 200(9), 199(17), 186(15), 163(33), 150(10), 149(30), 148(9), 138(5), 137(52), 136(6), 135(7), 129(10), 123(7), 122(20),121 (38), 120(6), 111(7), 109(8), 105(8), 97(18), 95(16), 93(14), 85(13), 83(20),81(35), 78(18), 73(17), 71(16), 69(69), 57(30), 56(25), 55(28). Doubly-charged ions 107.5, 106.5, 99.5.

N-Cyclohexyl(ferrocenylmethyl)amine: m/e 298(27%), 297(74,M$^+$), 296(13), 295(11), 218(6), 214(9), 201(7), 200(46), 199(100), 198(5), 197(8), 186(15), 151(5), 149(12), 134(10), 127(24), 122(10), 121(42), 99(20), 78(9), 57(11), 56(98), 55(11). Metastables at 160, 134, 90. Doubly-charged ions at 148.5, 127.5, 126.5, 100.5, 99.5, 98.5.

Ferrocenecarbaldehyde cyclohexylimine: m/e 296(23%), 295(100,M$^+$ 294(11), 293(11), 252(5), 213(13), 212(12), 199(19), 186(14), (148(7), 129(6), 122(5), 121(30), 56(8). Metastable peaks at 244, 178, 165, 153, 148, 134. Doubly-charged ions 126.5, 119.5, 113.5, 112.5, 99.5.

2. Disubstituted Ferrocenes

M$^+$ was the base peak in all cases. Although it has been claimed[158] that the relative intensity of the peak for (FeCp)$^+$ may serve as an indicator of ring substitution-patterns, the spectra reported here do not support this claim. The (FeCp)$^+$ peak appeared in all spectra with similar relative instensities. The peaks at (M-65)$^+$ and (M-66)$^+$ were better indicators of substitution-patterns. They were present in all of the 1,2- and 1,3- disubstituted compounds (although often in only 2 or 4
3%) and absent in the 1,1'-disubstituted compounds. The (M-94)$^+$ peak(M$^+$ - CpH - CO?) was also prominent in 1,2- and 1,3- isomers when compared with the 1,1'-isomers.

After considering a mass spectrum and the i.r. data for the dibenzylferrocene isolated from the ferrocenium ion - tin hydride experiments (e.g. IV.3v(a)), this was presumed to be predominantly the 1,1'-isomer.

<u>1,2-Benzoylmethylferrocene:</u> m/e 305(25%), 304(100, M$^+$), 302 (9), 210(6), 208(9), 200(6), 199(35), 198(8), 154(7), 153(11),

152(13), 133(8), 121(14), 56(14). Metastables 271, 249, 238, 186, 152, 130, 112.

1,3-Benzoylmethylferrocene: m/e 305(25%), 304(100,M^+), 302(8), 206(12), 199(12), 149(40), 133(9), 121(12), 105(14), 91(26), 77(11), 56(8). Metastables 250, 238, 199, 186, 152, 130, 107. Doubly-charged peaks 152.5, 151.5.

1,1'-Benzoylmethylferrocene: 305(21%), 304(100,M^+), 302(6), 290(8), 279(26), 199(21), 198(10), 167(14), 150(12), 149(98), 121(14), 113(28), 105(21), 83(17), 71(54), 69(37), 67(12), 57(34), 56(28). Metastables at 278, 198, 130, 112, 100. Doubly charged peaks 152.5, 151.5.

1,2-Benzoylisopropylferrocene: m/e 333(27%), 332(100,M^+), 330(8), 317(10),262(7), 237(9), 228(12), 227(67), 199(6), 198(14 165(11), 149(14), 133(8), 121(21), 105(39), 91(6), 77(19), 71(9), 69(9), 57(11), 56(11). Metastables 317, 303, 262, 237, 227, 212, 198, 166, 155. Doubly-charged peaks 166.5, 165.5.

1,3-Benzoylisopropylferrocene: m/e 333(27%), 332(100,M^+), 317(11) 227(9), 212(12), 211(11), 198(7), 165(6), 121(14), 105(16), 77(10), 69(6), 57(8), 56(6). Metastables at 303, 155, 142, 119. Doubly-charged peaks 166.5, 165.5.

1,1'-Benzoylisopropylferrocene: m/e 333(27%),332(100,M^+), 300(10), 228(6), 227(33), 226(8), 212(23), 199(4), 198(14), 197(7), 186(6), 149(12), 141(9), 133(15), 121(9), 105(18), 91(5), 56(7). Metastables 303, 227, 211, 198, 166, 155, 142, 119.

1,2-Benzoylphenylferrocene: *m/e* 368(27%), 367(100,M^+), 365(8), 302(4), 215(11), 139(6), 133(3), 121(7), 105(8), 77(5), 56(6). Metastables 312, 271, 248, 228, 203, 188, 171. Doubly-charged ions at 183.5, 182.5.

1,2-Benzoylbenzylferrocene: *m/e* 381(32%), 380(100,M^+), 378 (8), 314(12), 286(20), 275(9), 274(40), 241(4), 230(4), 229 (7), 228(13), 215(5), 208(6), 198(6), 153(12), 152(18), 151 (7), 133(6), 121(13), 105(23), 77(18), 56(14). Metastables at 347, 261, 199, 111. Doubly-charged ions at 190.5, 151.5, 150.5.

1,3-Benzoylbenzylferrocene: *m/e* 381(29%), 380(100,M^+), 378 (9), 275(17), 228(6), 208(5), 198(4), 153(9), 152(9), 133(5), 121(12), 105(18), 91(5), 86(10), 84(16), 77(14), 56(7). Metastables 260, 246, 199, 184. Doubly-charged ions 190.5, 189.5, 151.5.

1,1'-Benzoylbenzylferrocene: *m/e* 381(31%), 380(100,M^+), 378 (8), 276(10), 275(44), 274(6), 273(5), 211(6), 198(12), 197

(5), 196(6), 153(12), 152(9), 141(7), 133(14), 121(11), 115 (6), 105(18), 77(10), 69(6), 57(6), 56(9). Metastables 246, 199, 172, 11. Doubly-charged ions at 190.5, 189.5, 151.5.

Dibenzylferrocene: *m/e* 367(32%), 366(100,M^+), 364(9), 275(14), 212(7), 211(8), 208(6), 155(5), 153(12), 152(8), 133(9), 121 (10), 56(8). Metastables at 271, 246, 225, 207, 152, 122, 112. Doubly-charged ions at 183.5, 143.5.

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