

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF BRANDEIS UNIVERSITY, WALTHAM 54, MASS.]

## The Chemistry and Structure of Ferrocene. VIII. Interannular Resonance and the Mechanism of Electrophilic Substitution

BY M. ROSENBLUM, J. O. SANTER<sup>1</sup> AND W. GLENN HOWELLS

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Certain anomalous features of Friedel-Crafts acetylation reactions involving ferrocene are shown to be due to protonation of the metal atom. The relative rates of acetylation of ferrocene and acetylferrocene, compared with an assigned rate of 1.0 for benzene, were found to be  $3.3 \times 10^6$  and  $1.9 \times 10^2$ , respectively. The large interannular deactivation due to the acyl function cannot be accounted for in terms of inductive or direct electrostatic field effects. While these results imply effective interannular electronic transmission, the ultraviolet absorption spectra of a number of arylferrocenes fail to reveal any pronounced coupling of heteroannularly disposed groups. These apparently conflicting findings are reconciled in terms of a general mechanism for electrophilic substitution in which the metal atom is the primary site for electrophilic attack. The energetics and stereochemistry of these reactions and the comparative reactivities of the iron group metallocenes are considered. Certain broader implications of this theory are discussed.

### Introduction

In two earlier papers the general problem of intramolecular electronic effects in substituted ferrocenes was considered.<sup>2</sup> The present paper is concerned with the mechanism by which transmission is apparently effected, through the metal atom, from a substituent in one ring to positions in the second. Although the operation of such interactions in ferrocene derivatives has long been apparent, their precise character has remained obscure. Among the very early examples of this phenomenon is the resistance of 1,2-diacetylferrocene<sup>3a</sup> to further acylation<sup>3b</sup> and of ferrocene to diformylation with excess N-methylformanilide and phosphorus oxychloride.<sup>4</sup> More recently, Little and Eisenhorn have reported similar observations in the aluminum chloride-catalyzed acylation of ferrocene with carbamyl chloride and N,N-diphenylcarbamyl chloride.<sup>5</sup> Nesmeyanov and Reutov have also noted that ferrocenoic acid is not sulfonated with sulfur trioxide in dioxane, while ferrocene itself readily gives ferrocenesulfonic acid under these conditions.<sup>6</sup> Normally, with more electrophilic reagents such as acid halides or anhydrides and Lewis acids, heteroannular diacylation can readily be effected. Yet even here, appreciable deactivation of the unsubstituted ring in the monoacyl intermediate might be inferred from the fact that minor but significant amounts of homoannular products have been detected in two such reactions which have been carefully examined.<sup>3,7</sup>

More recently some success has been achieved in extending free energy correlations of the Hammett type to acid dissociation constants<sup>8</sup> and to rates of esterification of heteroannularly substituted ferrocenoic acids.<sup>9</sup> Unfortunately, these correlations provide little information regarding possible interannular resonance interactions since the observed effects must derive considerable contribution from inductive as well as from electrostatic field effects.<sup>10,11</sup>

(1) Taken in part from a dissertation submitted by J. O. Santer in partial fulfillment of the requirements for the Ph.D. degree, June, 1960.

(2) M. Rosenblum, *J. Am. Chem. Soc.*, **81**, 4530 (1959); M. Rosenblum and W. G. Howells, *ibid.*, **84**, 1167 (1962).

(3) (a) J. H. Richards and T. J. Curphey, *Chem. Ind. (London)*, 1456 (1956); (b) M. Rosenblum and R. B. Woodward, *J. Am. Chem. Soc.*, **80**, 5443 (1958).

(4) M. Rosenblum, *Chem. Ind. (London)*, 72 (1957); P. J. Graham, *et al.*, *J. Am. Chem. Soc.*, **79**, 3416 (1957); G. D. Broadhead, J. M. Osgerby and P. L. Pauson, *J. Chem. Soc.*, 650 (1958).

(5) W. F. Little and R. Eisenhorn, *J. Am. Chem. Soc.*, **82**, 1577 (1960).

(6) A. N. Nesmeyanov and O. A. Reutov, *Doklady Akad. Nauk S.S.S.R.*, **115**, 518 (1957).

(7) P. L. Pauson, *Quart. Rev. (London)*, **9**, 391 (1955).

(8) A. N. Nesmeyanov and O. A. Reutov, *Izvest. Akad. Nauk S.S.S.R.*, 926 (1959); W. F. Little and R. Eisenhorn, *J. Org. Chem.*, **26**, 3609 (1961).

(9) W. F. Little and R. Eisenhorn, *J. Am. Chem. Soc.*, **83**, 4936 (1961).

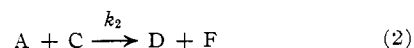
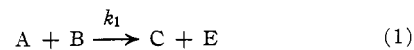
(10) The importance of such effects has been adequately demonstrated for *m*- and *p*-substituted benzoic acid [J. N. Sarmousakis, *J. Chem. Phys.*, **12**, 277 (1944), and F. H. Westheimer, *J. Am. Chem. Soc.*, **61**, 1977 (1939)] and for 4-substituted bicyclo(2.2.2)octane-1-carboxylic acids [J. D. Roberts

Our purpose in these investigations was twofold. We wished firstly to obtain a more quantitative measure of interannular interactions in those situations where such interactions might be expected to be large. Secondly we sought to examine the general question of resonance interactions by an independent means, through a study of the ultraviolet spectra of suitably chosen derivatives.

### Results

In order to obtain a more quantitative measure of interannular transmission effects, we undertook a study of the comparative reactivities of ferrocene and acetylferrocene toward Friedel-Crafts acetylation.

Owing to the very great reactivity of ferrocene, direct kinetic determination of its rate of acetylation was not possible. Since, in any event, our primary interest was in the relative rather than in the absolute rates of reaction of ferrocene and acetylferrocene, we turned to the direct determination of this ratio. McMillan has recently shown that rate constant ratios for competitive consecutive second-order irreversible processes of the form



may be calculated from the expression

$$K \ln \beta = \ln [\beta + (1 - K)\gamma] \quad (3)$$

where  $K = k_2/k_1$  and  $\beta$  and  $\gamma$  are the reduced concentrations,  $B/B_0$  and  $C/B_0$ , respectively.<sup>12</sup>

The essential irreversibility of these Friedel-Crafts acetylation reactions was demonstrated by treating acetylferrocene, or a mixture of diacetylferrocene and ferrocene, with aluminum chloride and hydrogen

and W. T. Moreland, *ibid.*, **75**, 2167 (1953)]. The general problem of transmission of polar effects has recently been discussed [M. J. S. Dewar and P. J. Grisdale, *ibid.*, **84**, 3539, 3541, 3546, 3549 (1962)].

For ferrocene-1,1'-dicarboxylic acid, the ratio of first to second ionization constants is very adequately accounted for in terms of the electrostatic model of Kirkwood and Westheimer [*J. Chem. Phys.*, **6**, 506 (1938)]; M. Rosenblum, Thesis, Harvard Univ., 1953].

(11) It is important to note that the application of free energy correlations of this type to ferrocene derivatives may be complicated by the relatively unrestricted rotational motion of the rings. As a consequence, the time average distance separating the substituents may not in all cases be independent of the nature of the functional groups. The anomalous rate of esterification of 1'- $\alpha$ -hydroxybenzylferrocenoic acid (ref. 9) and of the acid dissociation constants of 1'-carbomethoxy- and 1'-sulfonamidoferrocenoic acids (ref. 6) may have their origins in direct substituent interactions.

It is not difficult, in any event, to imagine how inductive effects may be transmitted from one ring to the second since resonance or inductive interactions between a substituent and the ring to which it is bonded are well documented (ref. 2) and rather facile polarization of metal ring bonds involving d-orbitals is to be expected. A much better criterion for direct interannular resonance effects, employing this approach would be a duality of  $\sigma$ -constants for substituents whose interactions with a particular functional group might be large.

(12) W. G. McMillan, *J. Am. Chem. Soc.*, **79**, 4838 (1957).

chloride under conditions similar to those employed in the acylation reactions. In none of these experiments was any disproportionation observed, and the recovery of products was good.

The acetylation or benzoylation of benzene and toluene under conditions of reaction similar to those employed in our own studies has been shown to be second order, first order in the aromatic and first order in acyl halide-aluminum chloride complex.<sup>13</sup> The reasonable assumption of identity in kinetic form was made in our studies.

A series of initial experiments employing equimolar quantities of ferrocene, aluminum chloride and acetyl chloride in methylene chloride were carried out and the products separated chromatographically on alumina. Although the two major products anticipated, mono- and diacetylferrocene, are readily separated from one another and from starting material by these procedures, no trace of diacylated products was obtained in any of these experiments.<sup>14</sup> These results served to confirm an appreciable interannular deactivation, but the magnitude of the effect clearly precluded this experimental approach.

During the course of these investigations we noted that the balance of reaction products could be profoundly altered by the use of aluminum chloride in excess of ferrocene and the acid halide.<sup>15</sup> Thus, when equimolar quantities of ferrocene and acetyl chloride in methylene chloride were treated with two molar equivalents of aluminum chloride, considerable quantities of 1,1'-diacetylferrocene was formed. Broadhead, Osgerby and Pauson, who had earlier made qualitatively similar observations, ascribed these results to an inhomogeneity of the reaction medium.<sup>4</sup> However, a careful examination of the reaction solution did not reveal a liquid-liquid or a solid-liquid inhomogeneity. Further experiments established that not only was the apparent ratio of rates ( $k_2/k_1$ ) altered under these conditions, but that this ratio was a function of the extent of reaction, increasing as the reaction proceeded to completion. These results are summarized in Table I (experiments 1 and 2).

TABLE I

Expt. <sup>a</sup>	Reaction time, min.	Mole % acetyl chloride consumed	Mole % material recovered	Acetylferrocene, g.	Diacetylferrocene, g.	$k_2/k_1$ (apparent) <sup>g</sup>
1 <sup>b</sup>	150	72.6	72	0.090	0.480	10.9
2 <sup>c</sup>	12	62.5	86	0.546	0.131	0.45
3 <sup>d</sup>	150	84.0	85	1.034	None	0
4 <sup>e</sup>	150	22.8	87	0.120	0.095	6.8
5 <sup>f</sup>	150	92.1	91	0.660	0.290	0.40

<sup>a</sup> All reactions were carried out at 0°, in methylene chloride, employing one gram of ferrocene and a mole ratio of AlCl<sub>3</sub>:AcCl:ferrocene of 2:1.2:1. <sup>b</sup> Average of three runs. <sup>c</sup> Average of two runs. <sup>d</sup> Reaction run under conditions of tenfold dilution. <sup>e</sup> Solution saturated with hydrogen chloride prior to addition of reactants; average of two runs. <sup>f</sup> Magnesium amalgam added prior to addition of reactants. <sup>g</sup> Calculated from eq. 3.

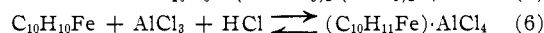
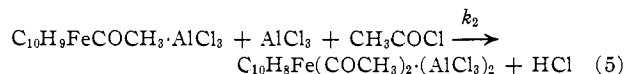
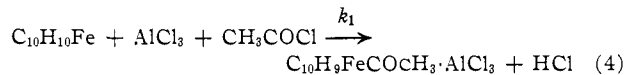
Although changes in kinetic order for Friedel-Crafts acylation reactions in the presence of an excess of catalyst or acylating complex have been noted previously,<sup>13</sup> such a pronounced effect on one, but not on the other, of the two rate constants is exceptional. The observations are, however, readily accommodated by assuming that, in the presence of free aluminum chloride, the hydrogen chloride generated in the first

(13) H. C. Brown, G. Marino and L. Stock, *J. Am. Chem. Soc.*, **81**, 3310 (1959); F. R. Jensen, G. Marino and H. C. Brown, *ibid.*, **81**, 3303 (1959).

(14) For similar observations, cf. M. Rausch, M. Vogel and H. Rosenberg, *J. Org. Chem.*, **22**, 903 (1957).

(15) The results which follow have been described briefly in a previous communication: M. Rosenblum and J. O. Santer, *J. Am. Chem. Soc.*, **81**, 5517 (1959).

step (eq. 4) forms a stable, soluble and non-acylable complex with ferrocene, which effectively removes the ferrocene from the competition reaction (eq. 6). Two immediate implications of this hypothesis are readily susceptible to experimental examination. First, the



acetylferrocene-aluminum chloride complex generated in the first step (eq. 4) must be largely undissociated. This is easily verified by treatment of either acetylferrocene or benzoylferrocene with a molar equivalent of aluminum chloride and acetyl chloride. Under these conditions, no diacetylferrocene is formed. Second, the implied solubility of the complex is readily demonstrated. Addition of hydrogen chloride to a methylene chloride solution of ferrocene containing a suspension of aluminum chloride, results in rapid dissolution of the aluminum chloride and the formation of a clear orange solution.

It was of interest to subject the proposed mechanism to further, more definitive, experimental test. The stoichiometry of the complex formation step is such that its equilibrium concentration must be strongly reduced on dilution. The results obtained by carrying out the Friedel-Crafts acylation reaction under conditions of tenfold dilution are summarized in expt. 3 of Table I. As expected, the reaction under these conditions returns to "normalcy" and essentially no diacylated products are formed. If complex formation is now facilitated by the introduction of dry hydrogen chloride at the beginning of reaction, relatively little total acylation should occur, but nevertheless the apparent ratio of rate constants should be high. Both of these predictions are fulfilled, as seen by the results obtained in expt. 4 of Table I. If, on the other hand, measures are taken to remove the hydrogen chloride generated in the reaction, precisely the contrary results must ensue. That this is indeed so is demonstrated by the results of expt. 5 in which amalgamated magnesium was added to the reaction solution.

Finally, the complex was isolated as a pale green solid, dec. 125°, by the addition of ligroin to its methylene chloride solutions. Its analysis corresponds to the empirical formula  $(\text{C}_{10}\text{H}_{10}\text{Fe} \cdot \text{HAlCl}_4)_n$ . Decomposition of the complex results in the regeneration of ferrocene, accompanied by the small amounts of ferricenium cation, to which impurity the salt owes its green color. Its thermal stability is illustrated by the fact that it is not decomposed by heating at 100° under reduced pressure, conditions under which ferrocene itself readily sublimates. The ultraviolet and visible spectra of the complex, of ferricenium perchlorate and of ferrocene are reproduced for comparison (Fig. 1.). (The long wave length absorption at 630 m $\mu$  in the complex arises from minor contamination with the ferricenium cation, estimated to be approximately 7%.)

The question as to the site of proton bonding in the complex was ultimately resolved by examining the n.m.r. spectrum of ferrocene in boron trifluoride hydrate in which medium it is completely protonated. In sharp contrast to benzenoid aromatics, which form  $\sigma$ -complexes under these conditions,<sup>16</sup> the only de-

(16) C. MacLean, J. H. van der Waals and E. L. Mackor, *Mol. Phys.*, **1**, 247 (1958); G. A. Olah, A. E. Pavlath and J. A. Olah, *J. Am. Chem. Soc.*, **80**, 6540 (1958); G. A. Olah and S. J. Kuhn, *ibid.*, **80**, 6535 (1958); **82**, 6541 (1960).

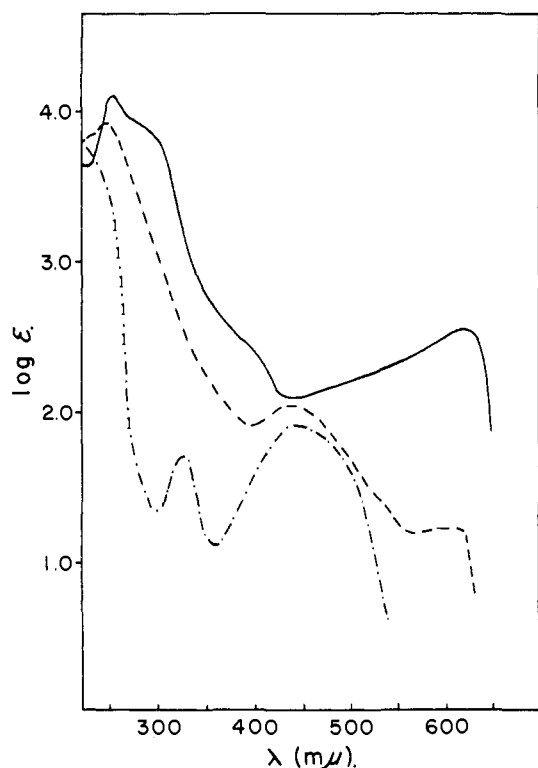
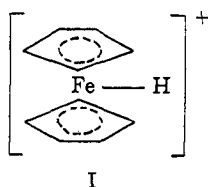


Fig. 1.—Spectra of ferrocene in 95% ethanol, - · - · -;  $(C_{10}H_{11}-Fe \cdot AlCl_4)_n$  in methylene chloride, - - - - -; ferricenium perchlorate in water, ———.

tectable cationic species is that in which the proton is bonded directly to the metal atom (I).<sup>17</sup>



**Competitive Acetylation.**—Since direct determination of the rate constant ratio for the acetylation of ferrocene and acetylferrocene was not feasible, we sought instead to measure their relative reactivities through a sequence of competition reactions. The results of these studies, in which ferrocene competed with pentamethylbenzene, pentamethylbenzene with mesitylene and mesitylene with acetylferrocene, are summarized in Table II. Reactivities are given in terms of an assigned unit reactivity for benzene, employing the relative rate for mesitylene given by Brown and Marino.<sup>18</sup> Although these competition reactions were not carried out under conditions identical with those employed by Brown and Marino, the data are nevertheless compatible as evidenced by the correspondence in the rate ratio found for pentamethylbenzene/mesitylene (4.66), with that determined by Brown and Marino (4.52).<sup>18</sup>

Owing to the great difference in reactivities of ferrocene and pentamethylbenzene and the inherent difficulties in the analytical procedure, the accuracy of the determinations is not great and the present results must be considered as only semiquantitative.<sup>19</sup>

(17) T. J. Curphey, J. O. Santer, M. Rosenblum and J. H. Richards, *J. Am. Chem. Soc.*, **82**, 5249 (1960). Similar observations have been made for protonated bis-cyclopentadienyrrhenium hydride; M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 3916 (1958).

(18) G. Marino and H. C. Brown, *J. Am. Chem. Soc.*, **81**, 5929 (1959).

(19) Cf. T. S. Lee, "Techniques of Organic Chemistry," Vol. VIII, Interscience Publishers, Inc., New York, N. Y., 1953, p. 110, for a discussion of this problem.

TABLE II  
RELATIVE RATES OF ACETYLATION OF AROMATICS IN METHYLENE CHLORIDE AT 0°

Compound	Rate
Benzene	1.0
Acetylferrocene	$1.9 \times 10^2$
Mesitylene	$2.92 \times 10^3$
Pentamethylbenzene	$1.34 \times 10^4$
Ferrocene	$3.3 \times 10^6$

Nevertheless the very great reactivity of ferrocene and the pronounced interannular deactivating effect of the acyl substituent in acetylferrocene is apparent.<sup>20</sup> Correcting for statistical factors, each of the positions in ferrocene is almost four orders of magnitude more reactive than comparable sites in acetylferrocene.

It is important to note that the observed deactivation is not attributable to a direct dipolar field effect, since *p*-nitrophenylferrocene, in which the electron-withdrawing function is rigidly held at a considerable distance from the reaction site, is relatively inert to Friedel-Crafts acetylation.<sup>21a</sup> Indeed, so resistant is this substance that it may be heated for prolonged periods in benzoyl chloride solution in the presence of aluminum chloride without apparent acylation.<sup>21b</sup>

While these results would appear to suggest rather effective resonance coupling between ring  $\pi$ -orbitals, such an inference is at variance with the electronic absorption spectra of substituted ferrocenes.<sup>22</sup> The arylferrocenes are substances particularly well suited for the detection of such interactions, since appreciable electronic coupling, as for example between heteroannularly disposed aryl substituents, would be expected to lead to pronounced spectral changes. Moreover, the preparation of several isomeric homoannularly substituted diarylferrocenes makes it possible to compare the spectra of these substances, in which conjugation of aryl groups is more clearly permissible, with their heteroannular isomers.

The absorption spectra of these substances are characterized by two bands of relatively high intensity between 220 and 330  $m\mu$ , and two others of considerably lower intensity, near 460 and 335  $m\mu$ .<sup>23</sup> The latter peak, which is clearly defined in ferrocene itself, is frequently obscured by the more intense shorter wavelength band in certain of the arylferrocenes.

Although substitution of the benzene ring by *p*-substituents of increasing electronegativity results in a bathochromic shift for all of these bands, that near 460  $m\mu$  is much less sensitive to these structural

TABLE III  
ULTRAVIOLET ABSORPTION MAXIMA OF MONOARYLFERROCENES

Substituent	Absorption peaks, $m\mu$ , and molar extinctions <sup>a</sup>			
Phenyl-	238(17,600)	278(10,600)	310 <sup>b</sup>	447(330)
<i>p</i> -Chlorophenyl-	243(18,150)	281(13,800)	315 <sup>b</sup>	450(346)
<i>p</i> -Methoxyphenyl	243(18,000)	282(14,500)	...	454(307)
<i>p</i> -Acetylphenyl-	266(9,850)	304(16,280)	376(2290)	466(1130)
<i>p</i> -Nitrophenyl-	280 <sup>b</sup>	326(13,000)	397(2640)	503(2580)

<sup>a</sup> All spectra were determined in 95% ethanol. <sup>b</sup> The peak appears as an inflection and its extinction coefficient and position cannot be accurately determined.

(20) Strictly speaking, it is the complexed acyl substituent which is the deactivating group, since the carbonyl function strongly binds aluminum chloride.

(21) (a) A. N. Nesmeyanov, *et al.*, *Izvest. Akad. Nauk S.S.S.R.*, 638 (1957); (b) unpublished observations with R. Fajer.

(22) Similar observations have recently been made by R. T. Lundquist and M. Cais, *J. Org. Chem.*, **27**, 1167 (1962).

(23) In ferrocene itself, these two peaks occur as shoulders near 230 and 260  $m\mu$  on a high intensity band at 203  $m\mu$  [D. R. Scott and R. S. Becker, *J. Chem. Phys.*, **35**, 516 (1961)]. These authors also report the presence of a shoulder at 528  $m\mu$ , assigned to a singlet-triplet transition corresponding to the absorption at 324  $m\mu$ . A fifth peak near 200  $m\mu$  may be present as well, but in general spectra were not recorded below 220  $m\mu$ .

TABLE IV  
 ULTRAVIOLET ABSORPTION MAXIMA OF DIARYLFERROCENES

Substituents and orientation	Absorption peaks, $m\mu$ , and molar extinctions <sup>a</sup>			
	Phenyl			
1,1'	239(24,700)	281(16,500)	335 <sup>b</sup>	453(569)
1,2	238(21,800)	263(11,800) <sup>c</sup>	320(1780) <sup>c</sup>	446(297)
1,3	248(28,200)	275(14,300) <sup>c</sup>	355(2620) <sup>c</sup>	465(498)
	<i>p</i> -Methoxyphenyl			
1,1'	244(25,000)	279(20,400)	340 <sup>b</sup>	454(536)
1,2	247(25,100)	275(15,000) <sup>c</sup>	330 <sup>b</sup>	450(307)
1,3	255(37,300)	300 <sup>b</sup>	340 <sup>b</sup>	465(488)
	<i>p</i> -Acetylphenyl			
1,1'	286(30,000)	308(19,000) <sup>b</sup>	390(4220)	465(2000) <sup>b</sup>
1,2	264(21,600)	291(25,500)	363(3440)	460(1540)
1,3	300(31,000)		407(7520)	480(2630) <sup>c</sup>
	<i>p</i> -Methoxyphenyl- <i>p</i> -nitrophenyl			
1,1'		284(14,600)	325(8980)	410(1820) <sup>c</sup>
1,2	230(17,000) <sup>c</sup>	280(12,600)	310 <sup>b</sup>	400(2040) <sup>c</sup>
1,3	240(22,000)	290(18,300)	350(10,600)	405(4000) <sup>b</sup>
	$\Sigma^d$	283(21,600)	323(14,800)	400(2700)

<sup>a</sup> All spectra were determined in 95% ethanol. <sup>b</sup> The peak appears as an inflection and its extinction coefficient and position cannot be accurately determined. <sup>c</sup> The peak appears as a flat shoulder and its position cannot be accurately determined. <sup>d</sup> Composite of *p*-methoxyphenylferrocene and *p*-nitrophenylferrocene.

changes. Thus, the difference in transition energies between phenylferrocene and *p*-nitrophenylferrocene is approximately 2600  $\text{cm}^{-1}$  for this long wave length peak, but is more than twice this for all of the short wave length bands. These points are illustrated by the spectral data for the monoarylferrocenes and isomeric diarylferrocenes, summarized in Tables III and IV.

The assignment of the 440  $m\mu$  band in ferrocene to a d-d type transition would appear plausible, but it seems likely that some mixing of ring orbitals in this transition must be assumed to account for the moderate effect of substituents on the band position.<sup>23</sup> The remaining peaks probably represent charge-transfer type transitions between the metal atom and either non-bonding or anti-bonding orbitals on the cyclopentadienyl rings. The bathochromic shift observed on increasing the electronegativity on the substituent corresponds to charge-transfer from the metal to the ligands. In accord with this conclusion, the energy associated with these transitions exhibits a reasonable correlation with the chemical oxidation potential of the arylferrocenes.<sup>24</sup> The assignment by Dahl and Ballhausen<sup>25</sup> of the 440  $m\mu$  band in ferrocene as a symmetry-forbidden ( $e_{2g} \rightarrow e^*_{2g}$ ) transition and of the remaining bands to symmetry allowed and forbidden ( $e_{2g} \rightarrow e_{2u}$ ) transitions is consistent with the observed spectral behavior. The first of these transitions involves electronic excitation from a weakly bonding orbital essentially localized on the metal atom ( $3d \pm 2$ ) to an anti-bonding molecular orbital in which ring orbitals make significant contributions, while in the latter transitions the excitation is to an unmixed non-bonding ring orbital.

The absence of conjugation between aryl substituents in 1,1'-disubstituted ferrocenes is suggested by a comparison of their spectra with the spectrum of their monoaryl analogs. Such a correspondence is illustrated in Fig. 2, 3, 4 and 5 for phenyl-,<sup>26</sup> *p*-chlorophenyl-,<sup>26</sup> *p*-methoxyphenyl-<sup>27</sup> and *p*-acetylphenylferrocenes.<sup>27</sup> By contrast, the 1,3-homoannular diaryl-

ferrocenes exhibit spectra which differ significantly from those of the mono- and 1,1'-disubstituted derivatives, especially in the region below 350  $m\mu$ . In the 1,2-diarylferrocenes, the two benzenoid substituents cannot

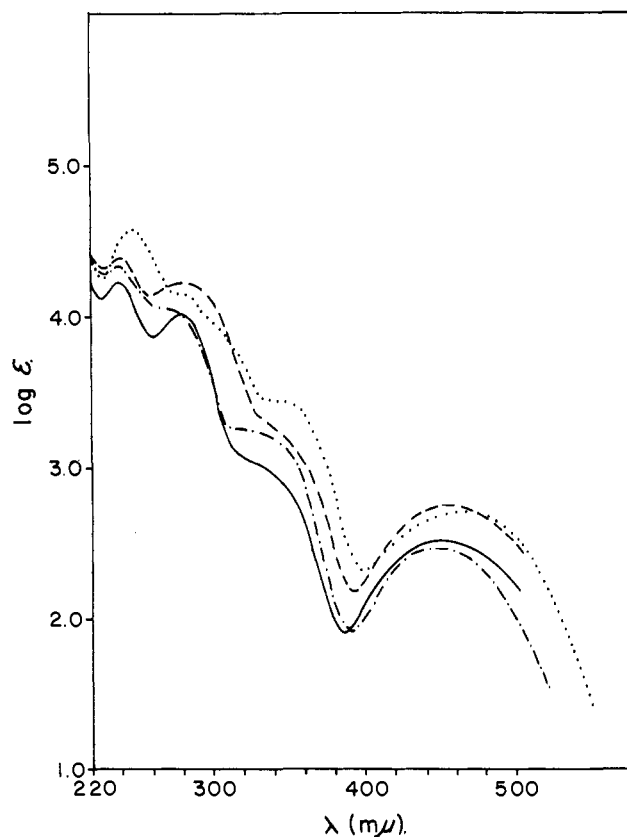


Fig. 2.—Spectra of phenylferrocene, —, and isomeric diarylferrocenes: 1,1'-isomer, - - - -; 1,2-isomer, - · - · -; 1,3-isomer, · · · · · (in 95% ethanol).

simultaneously attain a position of coplanarity with the ferrocene ring to which they are bonded. The hypsochromic shift and relatively smaller increase in intensity of the band at 280  $m\mu$  compared with that near 240  $m\mu$  is typical of situations in which structural factors

(24) J. G. Mason and M. Rosenblum, *J. Am. Chem. Soc.*, **82**, 4206 (1960).

(25) J. P. Dahl and C. J. Ballhausen, *Mat. Fys. Medd. Dan. Vid. Selsk.*, **33**, 5 (1962).

(26) V. Weinmayr, *J. Am. Chem. Soc.*, **77**, 3012 (1955).

(27) M. Rosenblum, W. G. Howells, A. K. Banerjee and C. Bennett, *ibid.*, **84**, 2726 (1962).

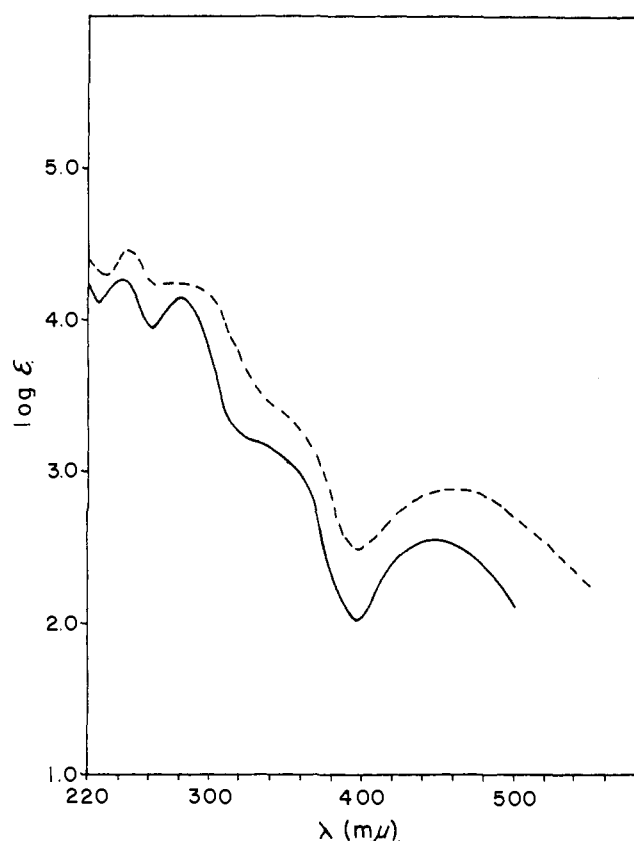


Fig. 3.—Spectra of *p*-chlorophenylferrocene, —, and 1,1'-bis-*p*-chlorophenylferrocene, - - - - (in 95% ethanol).

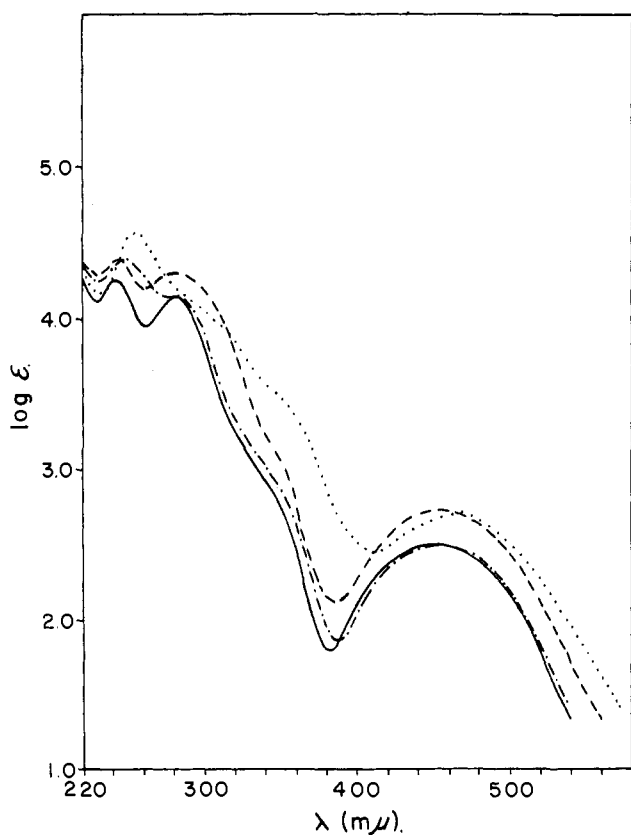


Fig. 4.—Spectra of *p*-methoxyphenylferrocene, —, and isomeric bis-*p*-methoxyphenylferrocenes: 1,1'-isomer, - - - -; 1,2-isomer, - · - · -; 1,3-isomer, · · · · (in 95% ethanol).

prevent maximal conjugation of normally coupled chromophores. A similar decrease in intensity of this

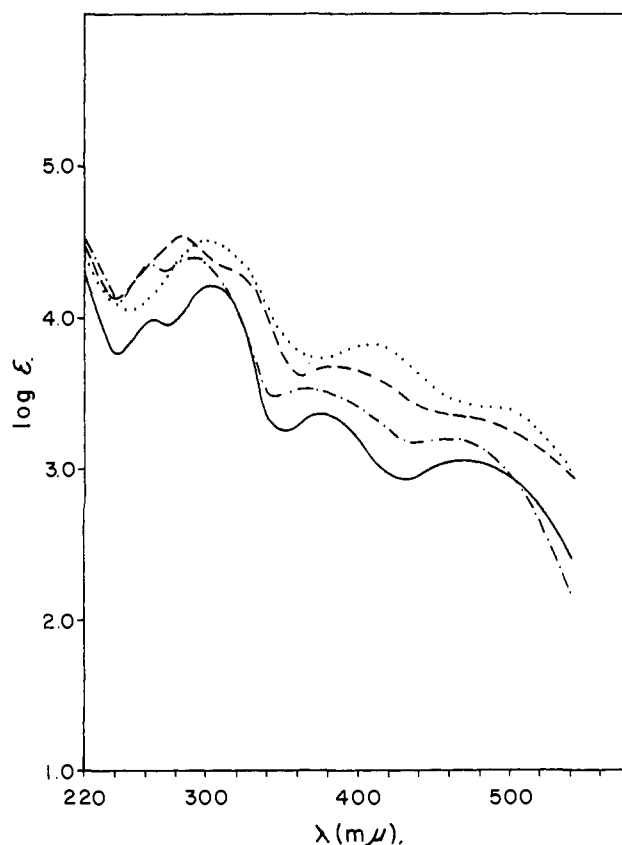


Fig. 5.—Spectra of *p*-acetylphenylferrocene, —, and isomeric bis-*p*-acetylphenylferrocenes: 1,1'-isomer, - - - -; 1,2-isomer, - · - · -; 1,3-isomer, · · · · (in 95% ethanol).

band has been noted for certain bridged acylferrocenes in which the geometry of the bridge prevents effective conjugation of the carbonyl group with the cyclopentadienyl ring.<sup>28</sup> These observations suggest that at least one and possibly both of the high intensity peaks which occur in this region of the spectrum are associated with electronic transitions involving the benzenoid substituents.

As a further test of these ideas we prepared structurally isomeric diarylferrocenes in which the two benzene rings bear electronically complimentary *p*-substituents. The spectra for one such series, the isomeric *p*-nitrophenyl-*p*-methoxyphenylferrocenes, are reproduced in Fig. 6.<sup>29</sup> We may note first the essential correspondence of peaks in the heteroannular isomer with arylferrocenes in general. This is to be contrasted with the appearance of an additional peak near 240 mμ in the spectra of the two homoannular isomers.

A final and particularly striking demonstration of the electronic isolation of heteroannular substituents may be made by comparing the spectrum of the unsymmetrical heteroannular diarylferrocene with that derived by summing the spectra of *p*-nitrophenylferrocene and *p*-methoxyphenylferrocene (Fig. 7). Not only are the band maxima of the diaryl derivative closely reproduced in the composite, but the general appearance of the curve is as well. This circumstance can hardly be fortuitous since a similar additive correspondence holds for the spectra of 1-*p*-nitrophenyl-1'-*p*-cyclohexanecarboxamidophenylferrocene, 1-acetyl-1'-phenylferrocene and 1-acetyl-1'-*p*-methoxyphenylferrocene.

(28) K. L. Rinehart and R. J. Curby, *J. Am. Chem. Soc.*, **79**, 3290 (1957); M. Rosenblum, A. K. Banerjee, N. Danieli, R. W. Fish and V. Schlatter, *ibid.*, **85**, 317 (1963).

(29) The assignment of structure to these and other diarylferrocenes is based on their infrared (ref. 27) and n.m.r. spectra and will be discussed in a separate paper.

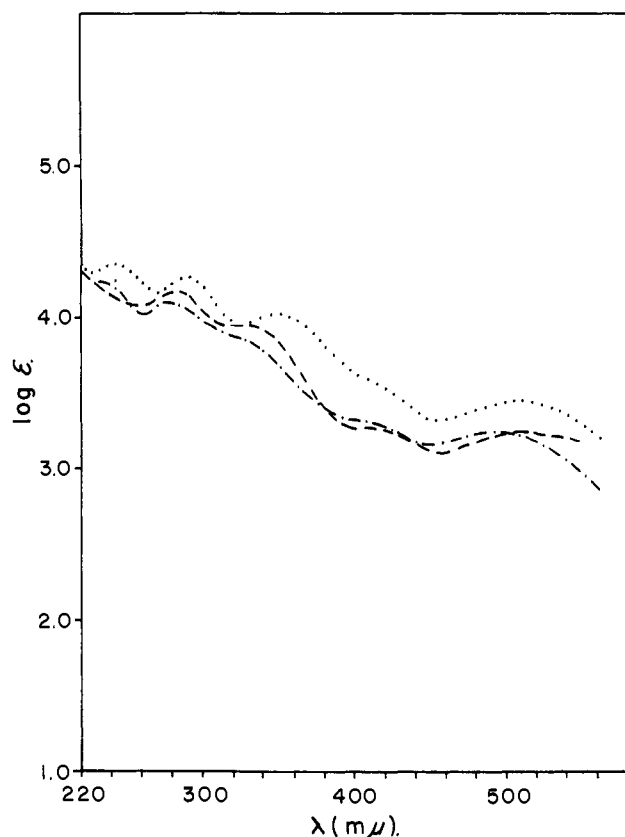


Fig. 6.—Spectra of isomeric *p*-methoxyphenyl-*p*-nitrophenylferrocenes: 1,1'-isomer, - - - -; 1,2-isomer, - · - · -; 1,3-isomer, · · · · (in 95% ethanol).

### Discussion

These apparently discordant observations find a satisfactory and general explanation in terms of a mechanism for electrophilic substitution which assigns a fundamental role to the metal atom.<sup>17,30</sup> While the several recent and most detailed molecular orbital treatments of ferrocene differ in detail, they are generally in accord in assigning the highest filled orbitals to the degenerate  $e_{2g}$  ( $3d \pm 2$ ) levels<sup>25,31</sup> (Fig. 8b). It would therefore be anticipated that the primary site of electrophilic attack would be initially localized upon electrons in these orbitals. Furthermore these electrons are essentially non-bonding, so that their participation in coordinate bonding with the electrophile would not greatly diminish the over-all bonding within the molecule. Sufficient presumptive evidence is at hand to identify these electrons as the primary "chemical electrons" of the metallocenes. Thus the duality of reaction paths observed with a variety of electrophiles (ring substitution or oxidation) implies that a common intermediate is involved whose fate is largely dependent upon the electron affinity of the electrophile. Those of relatively high electron affinity such as  $\text{NO}_2^+$ ,  $\text{NO}^+$  and the halogens promote electron transfer, while those such as  $\text{RCO}^+$  or  $\text{RSO}_2^+$  follow primarily an alternate course leading to ring substitution. The protonation of ferrocene at the metal provides the clearest evidence for the accessibility of these electrons and for their identification as the primary site of electrophilic attack. We have already noted that the reactions en-

(30) The first suggestion that the metal atom might play a role in these reactions was made by J. H. Richards, Abstracts of the 135th National Meeting of the American Chemical Society, April, 1959, p. 86-O.

(31) G. Wilkinson and F. A. Cotton, in "Progress in Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1959, p. 1; J. W. Richardson in "Organometallic Chemistry," Reinhold Publishing Corp., New York, N. Y., 1960, p. 1; E. M. Shustorovich and M. E. Dyatkina, *Doklady Akad. Nauk S.S.S.R.*, **128**, 1234 (1959).

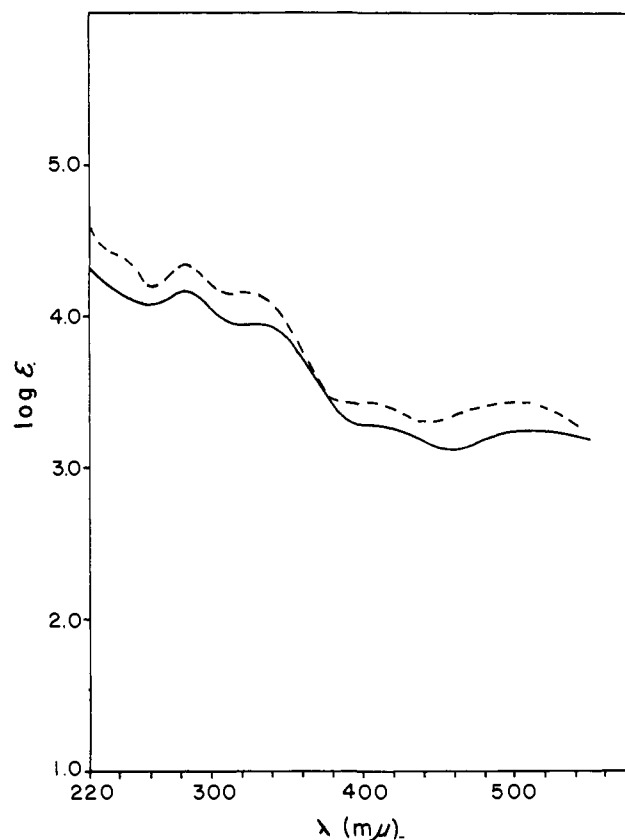


Fig. 7.—Spectra of 1-*p*-methoxyphenyl-1'-*p*-nitrophenylferrocene, —, and composite of *p*-methoxyphenylferrocene and *p*-nitrophenylferrocene, - · - · -.

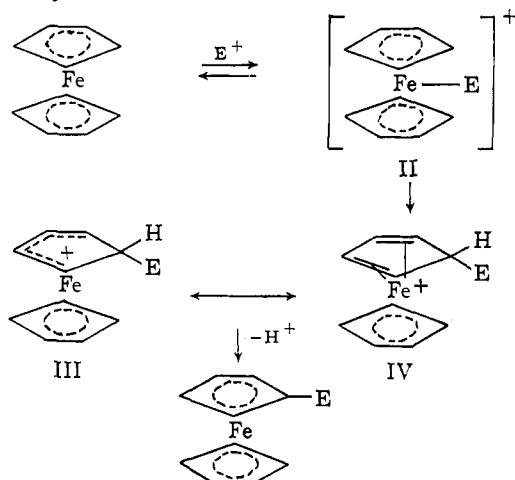
countered with aryldiazonium salts are best interpreted in terms of such an intermediate.<sup>27</sup> It remains now to consider in detail the course of events following this stage, which lead to ring substitution. Briefly, these may be pictured as an internal rearrangement of the electrophile leading to the endocyclic  $\sigma$ -complex III, and finally expulsion of a proton.<sup>32</sup>

**Primary Energy Barrier.**—We consider first that the rate-determining step for electrophilic substitution is the rearrangement of intermediate II to III. However, the over-all rate of reaction will of necessity be affected by the position of the prior equilibrium step leading to II. For electrophiles of comparable electron affinity, the equilibrium concentration of this intermediate is determined by the ionization potential of the  $e_{2g}$  electrons which is, as a consequence of inductive effects transmitted through the bonding orbitals, sensitive to the nature and degree of ring substitution.<sup>33</sup> Such sensitivity is amply supported by the increase in oxidation potential and corresponding decrease in reactivity of ferrocenes substituted by electron-withdrawing substituents.<sup>2</sup> The subsequent rearrangement of the  $\delta$ -complex II to the  $\sigma$ -complex III, in the rate-determining step, results in a partial transfer of charge to the ring undergoing substitution, and hence the activation energy pertaining to this step is again largely dependent upon the type of substituent(s) in the ring undergoing substitution. It is important to note that any significant contribution from resonance form IV in the  $\sigma$ -complex must moderate the normally anticipated effect of electron-withdrawing substituents in reducing

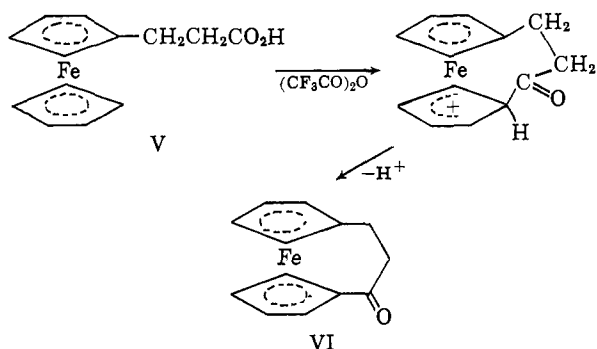
(32) A very similar mechanism has recently been proposed by A. Sorokin and G. A. Domrachev, *Trudy Po Khimii Khimicheskoi Tekhnologii*, **4**, 665 (1961).

(33) The correlation of these oxidation potentials with  $\sigma$  rather than  $\sigma^+$  [ref. 26; G. L. K. Hoh, W. E. McEwen and J. Kleinberg, *J. Am. Chem. Soc.*, **83**, 3949 (1961)], suggests the absence of appreciable overlap of  $e_{2g}$  orbitals with ring orbitals.

the reactivity of the ring. Thus, the formation of small, but significant, amounts of 1,2-diacetylferrocene in the Friedel-Crafts acetylation of acetylferrocene may be due primarily to such charge delocalization rather than to inductive deactivation of the unsubstituted ring by the acyl substituent.



This mechanism obviously requires that electrophilic substitution proceed preferentially in an endocyclic sense. That such a reaction path is at least sterically permissible, if not energetically preferred, is clearly evidenced by the facile cyclization of  $\beta$ -ferrocenylpropionic acid (V) to  $\alpha$ -keto-1,1'-trimethyleneferrocene (VI).<sup>28</sup> Formulation of this reaction in terms of an exocyclic bridging unit in the intermediate can be excluded on structural grounds.



**Steric Factors.**—An explanation for the low degree of steric control manifest in the acetylation of methyl-, ethyl- and isopropylferrocenes has been sought in the larger angle of meeting of adjacent substituents in a five-membered aromatic ring compared with benzenoid rings.<sup>34</sup> While these arguments would appear plausible, they are somewhat more difficult to apply to arylation, isobutyrylation<sup>35</sup> and pivaloylation<sup>35</sup> reactions in which a similarly low steric factor is manifest. On the other hand, these observations find an agreeable accommodation in terms of the rate-determining formation of intermediate (III  $\leftrightarrow$  IV), in which the incoming group is tetrahedrally bound to the reaction site.

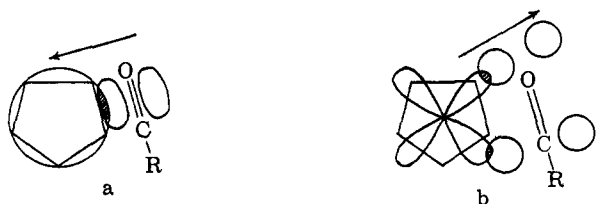


Fig. 8

(34) K. L. Rinehart, K. L. Motz and S. Moon, *J. Am. Chem. Soc.*, **79**, 2749 (1957).

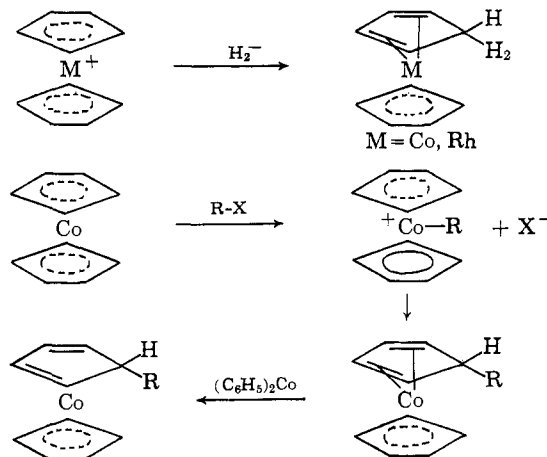
(35) Unpublished work with G. L. K. Hoh.

The comparatively lower reactivity of ferrocene in Friedel-Crafts alkylation reactions<sup>36</sup> may be related to the greater steric hindrance which a planar alkyl carbonium ion, compared with the linear acylium ion or aryldiazonium cation, may experience in its primary interaction with the metal orbitals (Fig. 8).<sup>37</sup>

**Comparative Reactivity of Metallocenes.**—A qualitative determination of the reactivities of the iron group metallocenes in Friedel-Crafts acylation has recently been made by Rausch, Fischer and Grubert.<sup>38</sup> It is significant that the order found: ferrocene > ruthenocene > osmocene, parallels the relative basicities<sup>17</sup> of these substances and their oxidation potentials,<sup>39</sup> both of which latter properties are associated with a reaction at the metal atom. These considerations suggest that the primary factor determining the Friedel-Crafts reactivity sequence is the position of the equilibrium involving formation of the  $\delta$ -complex II.

Quite a different order has been observed for the rates of SN1 solvolysis of methylmetallocenylcarbinol acetates,<sup>40</sup> the rates of addition of acetic acid and hydrazoic acid to vinylmetallocenes,<sup>41</sup> and for the strength of intramolecular metal hydrogen bonds in metallocenylalkylcarbinols.<sup>40,42</sup> For these processes the order is: osmocene > ruthenocene > ferrocene. It seems likely that the reversal in sequence is related to the intramolecular nature of the interaction in these latter processes. In such circumstances the interacting centers may not be capable of attaining their energetically preferred minimum separation so that the energy associated with these processes would be largely determined by the extent of overlap with the metal  $nd \pm 2$  orbital.

We believe that the mechanism proposed for the electrophilic substitution of ferrocene and its congeners possesses a generality considerably greater than is im-



(36) A. N. Nesmeyanov and J. S. Kochetkova, *Doklady Akad. Nauk S.S.S.R.*, **109**, 543 (1956); **114**, 800 (1957); **117**, 92 (1957); E. W. Neuse and D. S. Triphan, *J. Am. Chem. Soc.*, **84**, 1850 (1962).

(37) Competing oxidation of ferrocene under certain conditions of alkylation appears to be a complicating factor in these reactions. See for example, V. Weinmayr, *ibid.*, **77**, 3009 (1955), and P. L. Pauson, *Quart. Rev. (London)*, **9**, 391 (1955).

(38) M. D. Rausch, E. O. Fischer and H. Grubert, *J. Am. Chem. Soc.*, **82**, 76 (1960); C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **22**, 482 (1957).

(39) T. Kuwana, D. E. Bublitz and G. Hoh, *J. Am. Chem. Soc.*, **82**, 5811 (1960). Both ruthenocene and osmocene have oxidation potentials greater than that of ferrocene (+0.307). The relative oxidation potentials of ruthenocene and osmocene are not as easily assessed since their apparent potentials lie close to one another (ruthenocene, +0.693; osmocene, +0.633) and are apparently not reversible. It may be significant, however, that the potential for ruthenocene represents a two-electron oxidation, whereas the potentials determined for osmocene and ferrocene correspond to a one-electron transfer.

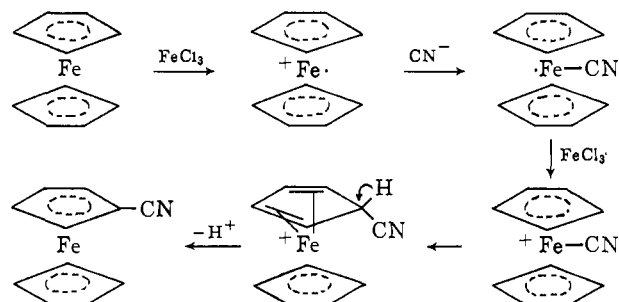
(40) E. A. Hill and J. H. Richards, *ibid.*, **83**, 3840 (1961).

(41) G. R. Buell, W. E. McEwen and J. Kleinberg, *ibid.*, **84**, 40 (1962).

(42) D. W. Triphan and R. Bacskai, *ibid.*, **82**, 5010 (1960).

plied by the present restricted context. Thus, the reduction of cobaltocenium and rhodocenium ions by complex hydrides apparently proceeds by initial hydride attack at the metal atom, as has been pointed out.<sup>43</sup> Furthermore the reaction of cobaltocene with alkyl halides<sup>43</sup> may be formulated in terms of similar intermediates. In all of these processes, the tendency of the complex to attain the stable electronic configuration  $(12) 2a'_g(3d_0)^4e_{2g}(3d \pm 2)$  is evident.

The recently reported preparation of cyanoferrrocene from ferricenium salts and hydrogen cyanide<sup>44</sup> may be similarly accounted for.



It is important to note that when this reaction is carried out on monosubstituted ferrocenes, the substituent exercises a directive effect paralleling that observed in normal electrophilic substitutions. Similar pseudo-nucleophilic substitution reactions of ferricenium salts may be possible and, moreover, both electrophilic and nucleophilic substitution of other olefin-metal complexes may be quite general.

Viewed in these terms, the electrophilic substitution reactions of ferrocene can no longer be interpreted in terms of the explicit aromaticity of the cyclopentadienyl rings, but constitute a more general phenomenon associated in large measure with the metal atom.

### Experimental

**Irreversibility of the Acetylation Reaction.**—In the first experiment acetylferrocene (1.82 g., 8 mmoles) and aluminum chloride (2.14 g., 16 mmoles) were added to 150 ml. of dry methylene chloride. The mixture was stirred at 0° for 4.5 hours and was then decomposed by addition of ice-water. The aqueous layer was removed, extracted three times with ether, and the ether extracts were combined with the methylene chloride solution. The organic solution was washed to neutrality and dried over magnesium sulfate. Evaporation of solvent gave 1.81 g. of solid material. Chromatographic purification on 80 g. of alumina (Woelm, neutral, Grade II) gave 1.72 g. of acetylferrocene, m.p. 84–87°, as the single product.

The addition of dry hydrogen chloride to the reaction mixture did not alter the result, although the recovery of acetyl ferrocene fell to 66%. In the second reaction, ferrocene (0.059 g., 0.32 mmole), 1,1'-diacetylferrocene (0.087 g., 0.32 mmole) and aluminum chloride (0.090 g., 0.67 mmole) were added to 150 ml. of dry methylene chloride. After stirring at 0° for 4.5 hr. hours, the mixture was decomposed with ice and worked up as in the previous experiment. Chromatographic purification of the crude product on 70 g. of alumina gave 0.042 g. of ferrocene, and 0.053 g. of 1,1'-diacetylferrocene as the sole products.

**Stability of the Acylferrocene-Aluminum Chloride Complex.**—Benzoylferrocene (0.355 g., 1.22 mmoles) and aluminum chloride (0.154 g., 1.16 mmoles) were added to 100 ml. of ice-cooled dry methylene chloride maintained in a nitrogen atmosphere. Acetyl chloride (0.196 g., 2.5 mmoles), dissolved in 30 ml. of the same solvent was added dropwise to this solution over a period of 30 minutes. Reaction was allowed to continue for a period of 4 hours while the stirred solution was allowed to come to room temperature. The mixture was then decomposed with ice-water, worked up in the usual fashion, and the crude product was chromatographed on 130 g. of alumina, using benzene as eluent. Only one band developed, and this gave benzoylferrocene (0.347 g.), m.p. 107–109°.

A similar reaction with acetylferrocene, aluminum chloride and acetyl chloride gave only starting material.

**Acetylation of Ferrocene under Conditions for Competitive-consecutive Acylation.**—The experiments were performed under essentially identical conditions of temperature, concentration, time of addition of the acetyl chloride-aluminum chloride complex, and reaction time. In a typical run, ferrocene (1.00 g., 5.4 mmoles) and aluminum chloride (0.720 g., 5.4 mmoles) were added to 100 ml. of dry methylene chloride maintained in a nitrogen atmosphere. The solution was cooled in an ice-bath and stirred while a solution of aluminum chloride (0.720 g., 5.4 mmoles) and acetyl chloride (0.500 g., 6.37 mmoles) in dry methylene chloride, was added dropwise over a period of 10 minutes. The reaction was allowed to proceed at 0° for an additional 2.5 hours and was then interrupted by the addition of ice. The blue aqueous layer, containing dissolved ferricenium salts, was separated, treated with sodium bisulfite, and extracted with ether. The combined ether extract was washed with sodium carbonate solution, then with water to neutrality, and was finally dried over magnesium sulfate. On evaporation of solvent, crystalline ferrocene was obtained. In each of the experiments, the amounts of ferrocene recovered from the ferricenium salt solutions was less than 100 mg.

The methylene chloride solution was worked up in the same manner and the crude product was chromatographed on 200 g. of alumina (Merck, acid-washed, 2% water added) using benzene as eluent. Separation of unreacted ferrocene was rapid, after which elution was continued with 5% solutions of chloroform in benzene, until separation and collection of mono- and diacetylferrocene was complete.

In the experiment in which magnesium amalgam was used, the amalgam was prepared by grinding 0.25 g. of magnesium turnings with excess mercury, and this was added to the reaction mixture prior to addition of the acetyl chloride-aluminum chloride complex.

In the experiment carried out in the presence of excess hydrogen chloride, the anhydrous gas was bubbled through the reaction mixture for 30 minutes before addition of the acylating solution, and for a further 15 minutes following.

In the reaction carried out under conditions of high dilution, the solution of aluminum chloride-acetyl chloride was added over a period of 30 minutes to 1,000 ml. of methylene chloride solution containing ferrocene and aluminum chloride.

**Examination of the Reaction Solution for Inhomogeneity.**—Ferrocene (1.00 g., 5.37 mmoles) was dissolved in 200 ml. of dry methylene chloride. The solution was stirred magnetically at 0° while aluminum chloride (0.720 g., 5.40 mmoles) and acetyl chloride (0.420 g., 5.35 mmoles), dissolved in 50 ml. of methylene chloride, were added rapidly. The time of addition was noted. Stirring was continued for 1 minute, and then interrupted for 2 minutes to allow for settling. Aliquots of 1.0 ml. each were withdrawn from the extreme upper and lower layers of the dark purple solution. These were transferred separately to flasks containing 10.0 ml. of standard 0.92 *N* sodium hydroxide solution, and the solutions were back titrated with standard 0.424 *N* hydrochloric acid solutions, using phenolphthalein as indicator. The procedure was repeated again after 15 minutes and 110 minutes of reaction. The volume of standard acid solution required for neutralization remained essentially constant (13.2–13.8 ml.) for all aliquots.

The experiment was repeated using acetylferrocene instead of ferrocene, and again no significant variation in acid content of the solution aliquots was detected.

In a third experiment, acetylferrocene (0.500 g., 2.19 mmoles) and aluminum chloride (0.596 g., 4.47 mmoles) were added to 140 ml. of dry methylene chloride and the solution stirred at 0° in a nitrogen atmosphere. After 1 hour, 1.0-ml. aliquots were withdrawn as before and titrated. The neutralization equivalents were identical.

To test for the possible presence of a solid phase in the deeply colored solution, a typical reaction solution containing ferrocene (0.412 g., 2.22 mmoles), aluminum chloride (0.593 g., 4.44 mmoles) and acetyl chloride (0.173 g., 2.2 mmoles) was filtered, in a nitrogen atmosphere, after 1 hour of reaction through a sintered glass plate. Only a small amount (*ca.* 20 mg.) of a colorless granular material, probably aluminum oxide, was collected.

**Isolation of the Complex Salt.**—Ferrocene (2.009 g., 10.9 mmoles) and aluminum chloride (1.402 g., 10.5 mmoles) were added in a nitrogen atmosphere to 100 ml. of dry methylene chloride in a three-necked flask fitted at the bottom with a sintered glass disk and stopcock. Dry hydrogen chloride was passed in for 30 minutes and then the volume of solution was reduced to 50 ml. by sweeping with dry nitrogen. The complex was then precipitated by adding 100 ml. of dry ligroin. The complex was collected, washed thoroughly with ligroin and dried by flushing with nitrogen. The olive-green precipitate decomposed at 125° (sealed tube).

*Anal.* Calcd. for  $(C_{10}H_{10}Fe \cdot HAAlCl_4)_n$ : ferrocene, 52.5; Al, 7.6; neut. equiv., 89. Found: ferrocene, 54.0; Al, 8.1; neut. equiv., 86.

(43) M. L. H. Green, L. Pratt and G. Wilkinson, *J. Chem. Soc.*, 3753 (1959).

(44) A. N. Nesmeyanov, E. P. Perevalova and L. P. Yuryeva, *Ber.*, **93**, 2729 (1960).



**Competitive Acetylation Reactions.**—All experiments were carried out under similar conditions. The acetyl chloride-aluminum chloride complex, dissolved in dry methylene chloride, was added dropwise to a stirred methylene chloride solution of the competing compounds. All reactions were carried out at 0° in a nitrogen atmosphere. In those reactions in which acetylferrocene was a competitor, an equivalent of aluminum chloride was added to the reaction mixture prior to the addition of the acetylating reagent. The molar equivalent of acetylating reagent never exceeded, and was generally equivalent to, that of the competitor present in lesser amount. The reactions were terminated by addition of ice-water, and the solutions worked up as previously described. Reaction products were separated chromatographically on 350–650 g. of Merck, acid-washed alumina (2% water added).

**Reaction of *p*-Methoxyphenylferrocene with Diazotized *p*-Nitroaniline.**—An ice-cold aqueous solution of diazotized *p*-nitroaniline, prepared from 6.9 g. (0.05 mole) of the amine, was added with stirring to an aqueous solution of *p*-methoxyphenylferricium chloride (4.0 g., 0.014 mole). Reaction was then allowed to proceed at 0° for 20 hours. An aqueous solution of sodium bisulfite was then added and the solution was extracted repeatedly with ether. The combined ether extract was washed to neutrality, dried over magnesium sulfate and filtered. A solution of ferric chloride (2.3 g., 0.016 mole) in ether was then added and the resulting ferricium salts were extracted into water. The combined aqueous extract was treated with bisulfite, extracted with ether and the ether extracts combined, washed to neutrality and dried over magnesium sulfate. After removal of solvent, the residue was chromatographed on 1 kg. of Merck acid-washed alumina employing low boiling petroleum ether as eluent. Several bands developed.

The first gave 37 mg. of 4-methoxy-2(4'-nitrophenyl)-phenylferrocene as red crystals, m.p. 158–159°. The compound exhibits a second crystalline form, m.p. 178–180°.

*Anal.* Calcd. for C<sub>23</sub>H<sub>19</sub>NO<sub>3</sub>Fe: C, 66.83; H, 4.60; N, 3.38. Found: C, 66.78; H, 4.64; N, 3.27.

A second band gave 177 mg. of a purple oil which crystallized after 9 months. Fractional crystallization of this material, using petroleum ether gave 150 mg. of 1-*p*-methoxyphenyl-2-*p*-nitrophenylferrocene as purple crystals, m.p. 146–148°.

*Anal.* Calcd. for C<sub>23</sub>H<sub>19</sub>NO<sub>3</sub>Fe: C, 66.83; H, 4.60; N, 3.38. Found: C, 67.0; H, 4.9; N, 3.5.

In addition, 2 mg. of 4-methoxy-3(4'-nitrophenyl)-phenylferrocene, m.p. 210–212°, was obtained. Additional material was obtained in a second experiment.

*Anal.* Calcd. for C<sub>23</sub>H<sub>19</sub>NO<sub>3</sub>Fe: C, 66.83; H, 4.60; N, 3.38. Found: C, 67.03; H, 4.62; N, 3.57.

A third band gave 217 mg. of 1-*p*-methoxyphenyl-1'-*p*-nitrophenylferrocene as purple plates, m.p. 214–216° (from ether).

*Anal.* Calcd. for C<sub>23</sub>H<sub>19</sub>NO<sub>3</sub>Fe: C, 66.82; H, 4.60; N, 3.38. Found: C, 66.82; H, 4.54; N, 3.62.

The fourth band gave 12 mg. of 1-*p*-methoxyphenyl-1'-*x*-bis-*p*-nitrophenylferrocene, m.p. 165.5–167.5°.

*Anal.* Calcd. for C<sub>29</sub>H<sub>22</sub>N<sub>2</sub>O<sub>6</sub>Fe: C, 65.19; H, 4.12; N, 5.19; Found: C, 65.09; H, 4.12; N, 5.23.

In a second experiment employing *p*-methoxyphenylferrocene rather than its ferricium salt, the remaining isomer, 9 mg. of 1-*p*-methoxyphenyl-3-*p*-nitrophenylferrocene, m.p. 193–195°, was isolated from a small band following the 1,1'-isomer.

*Anal.* Calcd. for C<sub>23</sub>H<sub>19</sub>NO<sub>3</sub>Fe: C, 66.83; H, 4.60. Found: C, 66.43; H, 4.91.

**Acknowledgment.**—This research was supported by a grant [RG-5978] from the National Institutes of Health, Public Health Service. We are indebted to Professor M. Cais for making a copy of his paper (ref. 22) available to us prior to publication.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS, AUSTIN 12, TEX.]

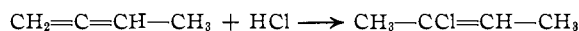
## Hydroboration of Allenes

BY DEVADAS DEVAPRABHAKARA<sup>1</sup> AND PETE D. GARDNER

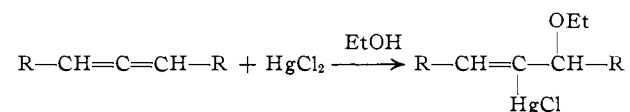
RECEIVED DECEMBER 20, 1962

The hydroboration of 1,2-cyclononadiene followed by oxidation of the intermediate organoborane afforded cyclononane and smaller amounts of cyclononanol and cyclononene. 1,2-Cyclodecadiene and 1,2,6-cyclononatriene behaved similarly. From the former was obtained principally cyclodecanone; the latter gave mainly cyclononene-6-one. It is concluded that the attack of diborane on the allene linkage occurs primarily at the central carbon atom.

Factors which determine the course of addition of unsymmetrical addenda to allenes are not at all understood. Hydrogen chloride, for example, adds to most allenes with placement of the chlorine atom at the central atom of the three-atom unsaturation, *e.g.*,<sup>2,3</sup>



Mercuric chloride, on the other hand, adds with mercury bonding to the central atom of the three.<sup>4</sup> This reaction probably proceeds through a carbonium ion intermediate. The present report is concerned with



the addition of diborane, a reagent well known as an electrophile<sup>5</sup> which adds through a four-center transition state.

The reaction of 1,2-cyclononadiene with diborane (generated *in situ*<sup>6</sup>) followed by an oxidative work-up employing hydrogen peroxide and sodium hydroxide

afforded mainly cyclononane. A smaller amount of cyclononanol and *cis*-cyclononene was also obtained. These results suggest that the principal organoborane, tris-1-cyclononenylborane, is that formed from attack of boron at the central carbon atom of the allene linkage. It is the organoborane which would be formed by hydroboration of cyclononyne.<sup>7</sup> The formation of cyclononene is best interpreted as evidence for the competitive formation of tris-3-cyclononenylborane. This, by analogy with the facile hydrolysis of triallylborane,<sup>8</sup> would be expected to give rise to cyclononene under the experimental conditions employed. There exists ample evidence that other types of organoboranes are not hydrolyzed rapidly at room temperature.<sup>9</sup> The formation of cyclononanol is expected once it is recognized that the principal organoborane in the mixture is tris-1-cyclononenylborane. The dihydroboration of acetylenes affords (*via* an organoborane analogous to the nonenylborane involved here) the corresponding alcohol.<sup>7</sup> Cyclononanol would therefore appear to be the result of over-hydroboration. The mechanism suggested<sup>7</sup> for this interesting reduction seems quite reasonable.

Data presented thus far are summarized as

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