ORGANIC AND BIOLOGICAL CHEMISTRY

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The Structure and Chemistry of Ferrocene. V. Intraannular Electronic Effects

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A series of mono- and 1,1'-diarylferrocenes have been acetylated under Friedel–Crafts conditions, and relative site reactivities have been determined from the proportion of isomers formed. The 2-position in the arylferrocenes studied is more reactive than is the 3-position, but in general aryl substituents inductively deactivate the ferrocene ring to which they are bonded. In agreement with the experimental results, molecular orbital calculation of localization energies predicts a higher reactivity for the 2-position in those derivatives substituted by electron donor groups. The theory also predicts higher reactivity at the 2-position in derivatives bearing an electron-withdrawing substituent.

Introduction

Notwithstanding the very considerable research efforts devoted during the past ten years to the study of the chemistry of ferrocene, the nature of electronic transmission within and across the aromatic rings is as yet incompletely understood. Theoretical treatments of such interactions are largely complicated by uncertainties regarding the detailed electronic structure of ferrocene.[2] The studies reported herein were undertaken with the intent of experimentally defining the character of intraannular electronic interactions and of providing thereby information relevant to the theoretical analysis.

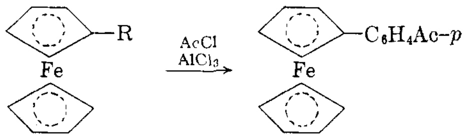
Previous studies concerned with intraannular directive effects have for the most part been confined to substitution of alkylferrocenes wherein steric rather than electronic factors largely determine the course of reaction.[3] These considerations prompted us to initiate a study of the phenylferrocenes and of *p*-substituted phenylferrocenes. In such derivatives, variation of the *p*-substituent affords a means of examining inductive and resonance effects of the aryl group which are to a first approximation free of steric complications.

In the previous paper the ratios of isomers formed in the Friedel-Crafts acetylation of phenylferrocene and of 1,1'-diphenylferrocene were reported.[4] The present paper extends these observations to the *p*-methoxyphenyl- and *p*-bromophenylferrocenes.

Results

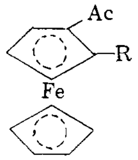
In these, as in the earlier studies, the arylferrocenes were subjected to Friedel-Crafts acetylation in the presence of aluminum chloride and under standard conditions of temperature, time and molar proportions of reactants. In general acylation proceeds under mild conditions with a variety of ferrocene derivatives and affords respectable yields of readily characterizable products. Moreover, the reaction is essentially irreversible under the experimental conditions employed,[5] thus fulfilling a fundamental prerequisite for these studies.

Separation of isomeric ketonic products was in general conveniently achieved by chromatography on Merck alumina (approximately Brockmann activity grade 1) employing ether as eluent. This technique represents a distinct improvement over former procedures, in which grade 2 alumina and solvents of lower polarity had been used for the separation of closely related ferrocene derivatives. The extended periods of elution necessitated under these circumstances resulted in partial decomposition of the products on the alumina column and further losses attending their isolation from relatively dilute solutions. Although the present technique also required the use of relatively large quantities of alumina, separation of components was generally complete within several hours, and the total recovery of product was in all cases excellent.[6]



Ia, R = C_6H_5
b, R = p-$CH_3OC_6H_4$
c, R = C_2H_5

II



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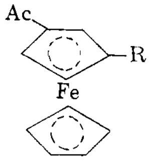

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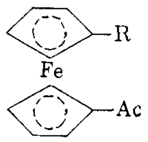

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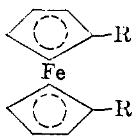
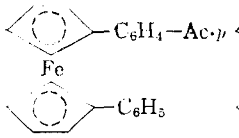
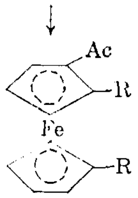


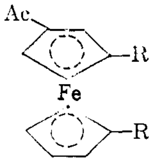
VIa, R = C_6H_5
b, R = p-$CH_3OC_6H_4$
c, R = p-BrC_6H_4



VII



VIII



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[1] Taken in part from a dissertation submitted by W. G. H. in partial fulfillment of the requirements for the Ph.D. degree, June, 1961.

[2] F. A. Cotton and G. Wilkinson in "Progress in Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1959, p. 85.

[3] (a) M. Rosenblum and R. B. Woodward, *J. Am. Chem. Soc.*, **80**, 5443 (1958); (b) K. L. Rinehart, K. L. Motz and S. Moon, *ibid.*, **79**, 2749 (1957); (c) A. N. Nesmeyanov and N. A. Volkenau, *Doklady Akad Nauk S.S.S.R.*, **111**, 605 (1956).

[4] M. Rosenblum, *J. Am. Chem. Soc.*, **81**, 4530 (1959).

[5] M. Rosenblum and J. O. Santer, *ibid.*, **81**, 5517 (1959).

[6] Vapor phase chromatographic analysis of the mixture of ferrocene derivatives reported herein has not yet been possible.

However, separation of isomers IVa from Va and IVb from Vb, derived from the acetylation of phenylferrocene (Ia) and *p*-methoxyphenylferrocene (Ib), respectively, could not be achieved even under these conditions. The proportions of these isomers were calculated as before[4] from their combined weights, the weight of the corresponding isomers IIIa or IIIb and the ratios of compounds VIIIa to IXa and VIIIb to IXb.

The improved chromatographic technique for analysis of reaction mixtures prompted us to reexamine the acetylation of phenylferrocene and of 1,1′-diphenylferrocene with a view toward improving the accuracy of the results reported previously.[4] The present results, although differing somewhat from those obtained earlier,[7] serve nonetheless to amplify and secure the conclusion deduced in the previous communication.

Site reactivities for 1,1′-diphenylferrocene (VIa), 1,1′-bis-*p*-methoxyphenylferrocene (VIb) and 1,1′-bis-*p*-bromophenylferrocene (VIc) are given in Table I. These are calculated from the proportion of ketonic isomers formed, and are corrected for statistical factors. For each of these arylferrocenes the reactivity of the 3-position in the ferrocene ring is taken as an internal standard and assigned unit reactivity. Similar data, derived from Friedel–Crafts acetylation of phenylferrocene (Ia) and *p*-methoxyphenylferrocene (Ib), are recorded in Table II. For purposes of qualitative comparison, the previously reported site reactivities in ethylferrocene (Ic)[3a] are included in this table. For these ferrocene derivatives, each position within the unsubstituted cyclopentadienyl ring is taken as an internal standard and assigned unit reactivity.

TABLE I

RELATIVE SITE REACTIVITIES IN 1,1′-DIARYLFERROCENES

Ferrocene	Site reactivities *p*-Position	 2-Position	 3-Position
1,1′-Diphenyl-[a]	0.50[c]	1.65	1.00
1,1′-Bis-*p*-methoxyphenyl-[b]	...	1.95	1.00
1,1′-Bis-*p*-bromophenyl-[a]	...	1.11	1.00

Data are an average of two experiments. [b] Data are an average of five experiments. [c] Experimental value is probably high.

TABLE II

RELATIVE SITE REACTIVITIES IN MONOARYLFERROCENES

Ferrocene	Site reactivities *p*-Position	 1′-Position	 2-Position	 3-Position
Phenyl-[a]	0.23[b]	1.00	0.77	0.47
p-Methoxyphenyl-[a]	...	1.00	1.16	0.60
Ethyl-[c]	...	1.00	1.4	4.2

[a] Data are an average of two experiments. [b] Experimental value is probably high. [c] Ref. 3a.

A series of competitive acetylation reactions of ferrocene with 1,1′-bis-*p*-bromophenylferrocene[8] and of 1,1′-bis-*p*-bromophenylferrocene with 1,1′-diphenylferrocene was carried out under conditions essentially identical with those employed for the site reactivity studies. The data derived from these experiments together with those of Table I permit the reactivities of each of the nonequivalent ring sites in these diarylferrocenes to be calculated with respect to an assigned unit reactivity for each of the positions in ferrocene itself. These results are summarized in Table III.

TABLE III

SITE REACTIVITIES IN DIARYLFERROCENES COMPARED WITH FERROCENE[a]

Ferrocene	Site reactivities *p*-Position	 2-Position	 3-Position
1,1′-Diphenyl-	0.22[b]	0.71	0.43
1,1′-Bis-*p*-bromophenyl-	...	0.33	0.30

[a] Each position in ferrocene is assigned unit reactivity. [b] Calculated value is probably high.

The material balance for all experiments was in excess of 80 mole per cent. and normally exceeded 90 mole per cent. Experiments were generally run in duplicate with the exception of the acetylation of 1,1′-bis-*p*-methoxyphenylferrocene (VIb) which was repeated five times. The standard deviation of the datum is estimated to be ±5%, except for the reactivities of the *p*-positions in phenylferrocene (Ia) and in 1,1′-diphenylferrocene (VIa), which are greater owing to the relatively low proportion of ketonic product derived from substitution at the *p*-position in these substances. Moreover, the site reactivities recorded for these positions are probably high since the figures were calculated using the weights of relatively impure material.

Structural assignments for the acetyl-arylferrocenes were made on the basis of comparisons of the infrared spectra of these substances with those of the acetyl-phenylferrocenes of established structure.[4] The infrared peaks relevant to these correlations are summarized in Table IV. The present data allow a further extension of those generalizations, initially derived from an examination of the spectra of isomeric acetyl-alkylferrocenes and acetyl-phenylferrocenes, to the acetyl-arylferrocenes reported herein. In particular, the spectra of ferrocene derivatives which possess the grouping

TABLE IV

STRUCTURALLY SIGNIFICANT INFRARED ABSORPTION PEAKS OF ARYLFERROCENES[a]

Ferrocene	Absorption peak, μ			
Phenyl-	11.27	...	...	...
p-Methoxyphenyl-	11.26	...	...	...
2-Acetyl-1-phenyl-	...	...	...	10.96
2-Acetyl-1-*p*-methoxyphenyl-	...	...	...	10.95
2-Acetyl-1,1′-diphenyl-	11.28	...	...	10.97
2-Acetyl-1,1′-bis-*p*-methoxyphenyl-	11.26	...	...	10.94
2-Acetyl-1,1′-bis-*p*-bromophenyl-	11.28	...	...	10.94
3-Acetyl-1-phenyl-	...	11.17	11.05	...
3-Acetyl-1,1′-diphenyl-	11.30	11.15	11.05	...
3-Acetyl-1,1′-bis-*p*-methoxyphenyl-	11.28	11.13	11.03	...
3-Acetyl-1,1′-bis-*p*-bromophenyl-	11.31	11.16	11.03	...

[a] All spectra were determined in chloroform solution.

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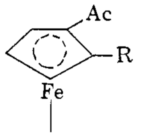
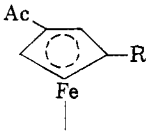
(7) The two series of experiments are not strictly comparable since the experimental conditions employed in each, although similar, were not identical.

(8) Difficulties encountered in the separation of products precluded the competition of ferrocene directly with 1,1′-diphenylferrocene.

illustrated by partial structure X (R = alkyl or aryl) exhibit absorption near 10.90 μ, while those in which the substituents are 1,3 disposed as in XI possess two peaks in this region between 10.8 and 11.2 μ.[9] A more detailed analysis of the spectral regularities of these ferrocene derivatives has been given elsewhere.[4,10]



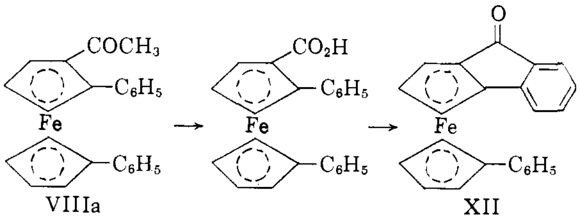
X

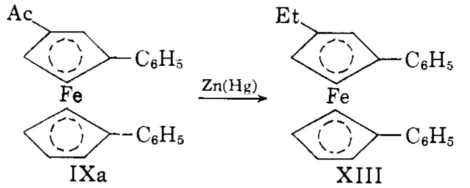


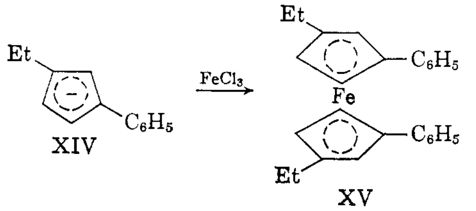
XI

Rinehart, Motz and Moon[3b] earlier drew attention to the utility of bands in this region of the spectrum in defining the disposition of alkyl groups in polyalkylferrocenes. More recently, Nesmeyanov and Kazitsyna have suggested a correlation between the structures of these ferrocene derivatives and a peak near 7.8 μ.[11]

The assignment of structures to the acetyl-1,1′-diphenylferrocenes VIIIa and IXa, and thence to isomers IIIa and IVa, rested in part upon the conversion of VIIIa to the tetracyclic ketone XII.[4]







Further evidence supporting assignments for this series of compounds has now been obtained by Clemmensen reduction of IXa to the corresponding 3-ethyl-1,1′-diphenylferrocene (XIII), and comparison of its infrared spectrum with that of 1,1′-diethyl-3,3′-diphenylferrocene (XV) prepared earlier from 1-ethyl-3-phenylcyclopentadiene (XIV). As required by the structural assignments and the spectral additivity principle,[10] the infrared spectrum of XIII is a composite of the spectra of XV[12] and of 1,1′-diphenylferrocene.

Discussion

For benzenoid and aliphatic systems, the electronegativity of a phenyl substituent compared with hydrogen is well established.[13] These electronegativity relationships are unquestionably maintained and are probably augmented in the phenylferrocenes as a consequence of ground state resonance interactions. The latter inference is supported by a comparison of the position of carbonyl absorption of acetylferrocene (5.97 μ) with that of acetophenone (5.93 μ), and of the pK_a of ferrocenoic acid (6.72)[14] with that of benzoic acid (6.62).[14] Perhaps the best evidence for the pronounced electronegativity of the aryl group in these ferrocene derivatives may be derived from a comparison of the dipole moments of *p*-chlorobiphenyl (1.66 D.)[15a] and *p*-chlorophenylferrocene (2.09 D.),[4] of the pK_b's of *m*-ferrocenylaniline (9.85),[15b] *p*-ferrocenylaniline (9.66)[15b] and aniline (10.14),[15b] and of the pK_a's of phenol (11.33)[15b] and *p*-ferrocenylphenol (11.79).[15b]

The lower reactivity of 1,1′-diphenylferrocene compared with ferrocene (Table III) and of the phenyl substituted ring compared with the unsubstituted ring in phenylferrocene (Table II) illustrates the deactivating effect of the phenyl substituent. The extent to which this deactivation may be transmitted, in monoarylferrocenes, to the unsubstituted ring is not known at present. For 1,1′-bis-*p*-bromophenylferrocene, a further decrease in the reactivity of the ferrocene ring is observed, as a consequence of the increase in the gross electronegativity of the aryl substituent. The effect of the aromatic substituent on the reactivity of the ferrocene nucleus in these substances is not unlike that of halogen in the halobenzenes, except that in the former instance ground state resonance interactions as well as inductive withdrawal of electrons appear to contribute to the lower reactivity of the substituted ferrocene ring.

For the monoarylferrocenes, the difference in reactivity between those sites in the unsubstituted

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[9] K. Schlögl and H. Seiler [*Tetrahedron Letters*, **7**, 4 (1960)] have recently applied these correlations in assigning structures to formyl- and acyl-1,1′-trimethyleneferrocenes.

[10] M. Rosenblum, *Chemistry & Industry*, 953 (1958).

[11] A. N. Nesmeyanov and L. A. Kazitsyna, *Doklady Akad. Nauk S.S.S.R.*, **125**, 1037 (1959). This correlation would appear to be of doubtful validity since the structures of two of the three derivatives which failed to exhibit absorption at 7.8 μ, and which were accordingly assigned a 1,2-disubstituted structure, have since been shown to be monosubstituted ferrocenes [K. L. Rinehart, G. J. Michejda and P. A. Kittle, *J. Am. Chem. Soc.*, **81**, 3162 (1959)]. The third substance, 1,2-tetramethyleneferrocene, was the only cyclic derivative examined and in this respect alone is structurally distinct from all the others cited. The spectral region near 7.8 μ is, in any event, not particularly well suited for this type of structural correlation since the region is normally rich in absorptions characteristic of a wide variety of groupings.

[12] The preparation of this compound will be reported in a separate note.

[13] P. B. D. de la Mare and M. Hassan, *J. Chem. Soc.*, 3004 (1957); H. C. Brown, Y. Okamoto and T. Inukai, *J. Am. Chem. Soc.*, **80**, 4964 (1958); N. N. Lichtin and H. P. Leftin, *ibid.*, **74**, 4207 (1952). For a general treatment of polar substituent constants, including the phenyl group, *cf.* R. W. Taft, Jr., in "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 556.

[14] M. Rosenblum, Thesis, Harvard University, 1953. These determinations were carried out in 2:1 (by volume) ethanol-water solution. R. A. Benkeser, D. Goggin and G. Schroll, *J. Am. Chem. Soc.*, **76**, 4025 (1954), have reported values of 6.78 and 6.32 for the pKa of ferrocenoic and benzoic acids, respectively, under the same conditions.

[15] (a) J. W. Smith, "Electric Dipole Moments," Butterworths Scientific Publications, London, 1955, p. 221; (b) A. N. Nesmeyanov, E. G. Perevalova and R. V. Golovnya, *Doklady Akad. Nauk S.S.S.R.*, **103**, 81 (1955).

and those in the substituted ferrocene rings, manifest in phenylferrocene, are diminished in *p*-methoxyphenylferrocene as a consequence of a reduction in the electronegativity of the aryl substituent and of enhanced resonance stabilization by the methoxyl group of processes involving homoannular substitution.[16] The data summarized in Table II illustrate these points.

With regard to the central problem of intraannular electronic effects, the data summarized in Table I leave little doubt but that resonance stabilization of the transition states pertaining to substitution at the 2- and 3-positions ring is not identical. Furthermore, the difference in resonance stabilization must be somewhat greater than is suggested merely by the ratio of isomers formed in the acetylation reactions, since both inductive as well as steric factors militate against substitution at the 2-position in these derivatives. The latter factor, although clearly less important than in benzenoid derivatives, cannot be entirely neglected.[17]

These findings correspond quite closely with those reported by Knox, Pauson and Tiers for the aminomethylation of 1,1′-bis-methylthioferrocene.[18] The ratio of 2- to 3-isomer was found to be approximately 1.9:1. Similarly, competition experiments involving the dithio derivative and ferrocene revealed a somewhat greater reactivity for the parent compound. To some extent the interpretation of these results is complicated by the presence of the sulfur atom which may facilitate substitution at the 2-position through interaction with the electrophile. Evidence for the operation of such a mechanism in promoting *ortho* nitration in anisole and related aromatic ethers has recently been provided by Norman and Rodda.[19]

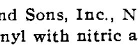
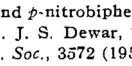
The simple LCAO approximation first introduced by Wheland[20] for the calculation of transition state π-electron localization energies[21] has generally been successful in accounting for the pattern of substitution in benzene derivatives. These calculations ascribe a greater reactivity to the *o*-compared with the *p*-position for electrophilic substitution of benzene derivatives bearing either electron-withdrawing or donor groups.[22] While these relative reactivities are in fact observed for benzene derivatives bearing *meta*-directing groups,[23a] the order is normally reversed for benzene derivatives substituted by donor groups.[23b] For these latter derivatives, the low observed *o:p* ratios have generally been attributed to steric factors. From this point of view, the comparatively minor interference from steric effects observed in the substitution of ferrocene derivatives makes these systems especially advantageous ones for checking the theoretical calculations.

Localization energies for electrophilic substitution of ferrocene derivatives bearing electron-withdrawing or electron-donor groups have been calculated using the method of Wheland[20] and the further approximations introduced by Roberts and Streitwieser,[22] in which the substituent types are generalized in terms of an anionic or cationic carbon center. These energies, given in terms of the negative resonance integral β, are summarized in Table V.[24] Following the treatment of Wheland,[20] the non-orthogonality integral S between adjacent carbon atoms has been taken as 0.25.

As a model for the ferrocene ring under consideration, we have taken a substituted cyclopentadienyl radical.[25] This treatment is in accord with the molecular orbital description of Moffitt[26] and of Dunitz and Orgel[27] in which primary metal to ring bonding is derived from essentially a single delocalized covalent electron pair bond.

TABLE V

LOCALIZATION ENERGIES ($-\beta$)

Model	2-Position	3-Position
	1.149	1.356
	1.685	1.734

As seen from the data, the calculations, in agreement with the experimentally determined order of reactivities, predict higher reactivity for those

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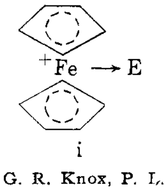
(16) Evidence in support of this latter derivation, which implies a low degree of effective resonance coupling between the ferrocene rings, will be considered in a subsequent paper.

(17) The low degree of steric control exerted by substituents on the ferrocene nucleus may have its origin in the larger angle of meeting of adjacent substituents in ferrocene derivatives compared with their benzenoid analogs.[2b] However, such differences may in part be the consequence of the operation of a mechanism for electrophilic substitution fundamentally distinct from that which pertains to substitution of benzenoid systems. Thus, were substitution to take place by initial attack of the electrophile on an available metal d-orbital, ring substitution might then proceed by rearrangement of the d-orbital complex (i) to an endocyclic σ-complex (ii). Under such circumstances, C–E bond formation might be appreciably developed at an early stage in the rearrangement process.



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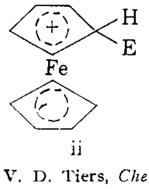

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(18) G. R. Knox, P. L. Pauson and G. V. D. Tiers, *Chemistry & Industry*, 1046 (1959).

(19) R. O. C. Norman and G. K. Rodda, *Proc. Chem. Soc.*, 423 (1961).

(20) G. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

(21) R. D. Brown, *Quart. Revs.*, **6**, 63 (1952).

(22) (a) M. J. S. Dewar, *J. Chem. Soc.*, 463 (1949); (b) M. J. S. Dewar, *J. Am. Chem. Soc.*, **74**, 3357 (1952); (c) J. D. Roberts and A. Streitwieser, Jr., *ibid.*, **74**, 4723 (1952).

(23) (a) For a general discussion of this problem *cf.* G. S. Hammond and M. F. Hawthorne in "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 176. (b) Nitration of biphenyl with nitric acid in acetic anhydride solution is reported to give *o*- and *p*-nitrobiphenyl isomers in a ratio significantly greater than 2:1; M. J. S. Dewar, T. Mole, D. S. Urch and E. W. T. Warford, *J. Chem. Soc.*, 3572 (1956); O. Simamura and Y. Mizuno, *Bull. Chem. Soc. Japan*, **30**, 196 (1957). For additional examples of similar substitution reaction in which the *o:p* ratio of products exceeds two, *cf.* P. B. D. de la Mare and J. H. Ridd, "Aromatic Substitution," Academic Press, Inc., New York, N. Y., 1959.

(24) The coulombic integral term α is not included in the table since it is identical for all of the reactions being considered.

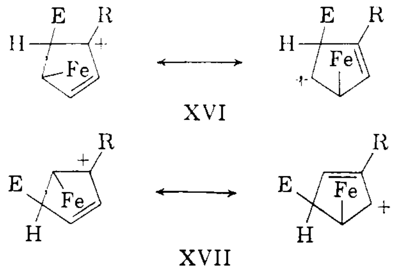
(25) The results remain essentially the same if instead a cyclopentadienyl anion is considered. For electrophilic substitution of derivatives bearing a donor group, the activated complexes for the two substitution paths (*cf.* Fig. 1) differ only in the number of electrons present in the zero energy non-bonding molecular orbital associated with each transition state. Hence the difference in localization energies of the two reaction paths is not affected by our choice of models. This is not the case with derivatives bearing an electron-deficient substituent, where the difference in localization energies is increased, but the relative stabilities of the transition states are unaltered.

(26) W. Moffitt, *J. Am. Chem. Soc.*, **76**, 5386 (1954).

(27) J. D. Dunitz and L. E. Orgel, *Nature*, **171**, 121 (1953); *J. Chem. Phys.*, **23**, 954 (1955).

positions adjacent to the substituent in ferrocene derivatives bearing a potential electron donor group. The difference in localization energy calculated for non-equivalent sites, although somewhat larger than might be estimated simply from the proportion of ketonic isomers formed, is nevertheless of the correct order of magnitude. The calculations are not capable of taking steric effects into account, nor have electronegativity parameters been introduced.[20,22a] It is clear, however, that each of these factors would be expected to retard substitution at sites adjacent to the substituent.

It is of interest to note that a descriptive resonance treatment, in which the primary covalent iron to ring bond is formalized in terms of a position variable single bond, gives qualitatively the same answer, predicting greater stabilization of transition states for electrophilic substitution involving the 2-position, when the orienting substituent is an electron donor group.[14] Two such resonance forms depicting the charge distribution in the transition states or intermediates associated with the separate substitution processes are shown in Fig. 1. In all, six such resonance forms may be written for each substitution path. Provided all of these resonance forms are equally important, the essential difference between the sets lies in the greater localization of charge at the site bearing the orienting substituent which is implied for substitution at the 2-position, since in two of the canonical forms belonging to this set, the charge may be written on the carbon bearing the substituent whereas only one such form may be written in the second set.



XVI

XVII

Fig. 1

For electrophilic substitution of ferrocene derivatives bearing electron-withdrawing groups, the molecular orbital calculations (Table V) again predict a somewhat greater reactivity for the 2-position, although the inclusion in the calculations of electronegativity parameters for the substituent might lead to a reversal in this order for substituents having a high electron affinity.[22a] By contrast, the descriptive resonance treatment suggests that for ferrocene derivatives of this general type, the 3-position is invariably the more reactive. Unfortunately, sufficient data for assessing the accuracy of these analyses are not yet available. Diacetylation of ferrocene does afford a small amount of 1,2-diacetylferrocene accompanying the major product, 1,1′-diacetylferrocene.[14,28] However, the very low yield of this isomer and the fact that normally 1,3-disubstituted ferrocenes are quite difficult to separate from their 1,1′-isomers preclude our drawing any certain conclusions from these experiments.

The present experimental results as well as the theoretical calculations imply a close analogy between *o*- and *p*-positions in benzenoid aromatics and the 2- and 3-positions, respectively, in ferrocene derivatives, at least for those substances bearing electron donor groups.[3b] Whether this analogy is complete and may be extended to ferrocene derivatives substituted by electron deficient groups, remains to be demonstrated.

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Experimental[29]

Friedel–Crafts Acetylation of Arylferrocenes.—The general procedure outlined below was employed for the acetylation of the following ferrocene derivatives: phenylferrocene (Ia), *p*-methoxyphenylferrocene (Ib), 1,1′-diphenylferrocene (VIa), 1,1′-bis-*p*-methoxyphenylferrocene (VIb) and 1,1′-bis-*p*-bromophenylferrocene (VIc). This same procedure was followed in competitive acetylation reactions involving ferrocene with 1,1′-bis-*p*-bromophenylferrocene and 1,1′-diphenylferrocene with 1,1′-bis-*p*-bromophenylferrocene.

The compound or equimolar mixture of compounds to be acetylated was dissolved in a mixture of 15 ml. of dry methylene chloride and 15 ml. of acetyl chloride contained in a 100-ml. single necked round-bottom flask, fitted with a dropping funnel and calcium chloride drying tube. The solution was cooled in an ice-bath and stirred magnetically while a molar equivalent of aluminum chloride in 15 ml. of acetyl chloride was added dropwise over a period of 15 minutes. The reaction was allowed to proceed at 0° for 1 hour and was then poured into a separatory funnel containing sodium bisulfite dissolved in 100 ml. of saturated sodium chloride solution. After extraction, the organic phase was withdrawn and the aqueous phase was repeatedly extracted with ether until the ether extracts were colorless. The organic solutions were combined, washed first with a dilute solution of sodium hydroxide saturated with sodium chloride until the *p*H of the aqueous wash was 8, then with saturated sodium chloride solution to neutrality. After drying over magnesium sulfate, the drying reagent was filtered off and washed with anhydrous ether until colorless. The organic solution was concentrated to a volume of about 10 ml. and this was placed on an alumina column prepared from 1 kg. of Merck acid-washed alumina. Elution was carried out with anhydrous ether. The separate fractions, each derived from discrete bands, were collected and solvent was removed on the steam-bath until the volume of solution was reduced to about 10 ml. These solutions were then transferred to tared weighing tubes, and the final volume of ether was allowed to evaporate overnight. The products and recovered starting materials were then pumped down to constant weight. With the exception of 2-acetyl-1,1′-bis-*p*-methoxyphenylferrocene (VIIIb) and 2-acetyl-1,1′-diphenylferrocene (VIIIa), all of the ketones were crystalline solids. The non-crystalline products were rechromatographed once on a short alumina column using anhydrous ether as eluent and the weight of product determined as above. Crystalline derivatives obtained directly from the chromatographic column generally melted

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(28) J. H. Richards and T. J. Curphey, *Chemistry & Industry*, 1456 (1956).

(29) All melting points were determined using a Fisher–Johns micro melting point apparatus, and are uncorrected. Analyses were performed at the microanalytical laboratory of the Massachusetts Institute of Technology, Cambridge, Mass., at the Schwarzkopf Microanalytical Laboratory, N. Y., N. Y., and by Dr. C. K. Fitz, Needham Heights, Mass.

5° lower than the analytical samples and over a range of 4–5°. The infrared spectra of all compounds isolated by the procedure described were identical with those of the analytical samples.

The following acetylferrocenes which have not previously been reported were isolated and characterized.

2-Acetyl-1,1′-bis-methoxyphenylferrocene was an oil. It was purified for analysis by chromatography on alumina employing ether as eluent.

Anal. Calcd. for $C_{26}H_{24}O_3Fe$: C, 70.9; H, 5.4. Found: C, 71.2, 70.5; H, 5.6, 5.6.

Its 2,4-dinitrophenylhydrazone melted at 158–159°

Anal. Calcd. for $C_{32}H_{28}O_6N_4Fe$: C, 61.9; H, 4.5; N, 9.0. Found: C, 62.5; H, 4.5; N, 9.2.

3-Acetyl-1,1′-bis-*p*-methoxyphenylferrocene was recrystallized for analysis from cyclohexane to give red block-shaped crystals, m.p. 147–148°.

Anal. Calcd. for $C_{26}H_{24}O_3Fe$: C, 70.9; H, 5.4. Found: C, 70.8; H, 5.5.

2-Acetyl-1,1′-bis-*p*-bromophenylferrocene.—Recrystallization of this compound from Skellysolve B gave red crystals, m.p. 126.5–127.5°.

Anal. Calcd. for $C_{24}H_{18}OBr_2Fe$: C, 53.53; H, 3.35. Found: C, 53.71; H, 3.55.

3-Acetyl-1,1′-bis-*p*-bromophenylferrocene was recrystallized from Skellysolve B to give red crystals, m.p. 145–147°.

Anal. Calcd. for $C_{24}H_{18}OBr_2Fe$: C, 53.53; H, 3.35. Found: C, 53.9; H, 3.2.

1-Acetyl-1′-*p*-methoxyphenylferrocene was recrystallized for analysis from low boiling petroleum ether (38–52°) to give orange-red plates, m.p. 97–98°.

Anal. Calcd. for $C_{19}H_{18}O_2Fe$: C, 68.3; H, 5.4. Found: C, 68.7; H, 5.3.

2-Acetyl-1-*p*-methoxyphenylferrocene was recrystallized from Skellysolve B as an orange microcrystalline powder, m.p. 137–139°.

Anal. Calcd. for $C_{19}H_{18}O_2Fe$: C, 68.3; H, 5.4. Found: C, 68.7; H, 5.5.

Clemmensen Reduction of 3-Acetyl-1,1′-diphenylferrocene.—The ketone (240 mg., 0.63 mmole) was dissolved in 30 ml. of glacial acetic acid, and to this solution was added amalgamated zinc, prepared from 414 mg. of zinc dust (0.64 mmole), and 1 ml. of concentrated hydrochloric acid. The reaction mixture was stirred magnetically and heated at 100° for a period of 30 minutes, then cooled and poured into a saturated solution of sodium chloride containing sodium bisulfite. The aqueous acid solution was extracted several times with ether until these extracts were colorless. The extracts were combined, washed twice with saturated sodium chloride solution, then once with sodium carbonate solution to a *p*H of 8, and finally with saturated sodium chloride to neutrality. The ether solution was dried over magnesium sulfate, drying reagent was filtered off, and the organic solution was concentrated to a volume of about 5 ml. Chromatographic purification of this material on 30 g. of alumina employing ether as eluent afforded 100 mg. of unreacted ketone and 100 mg. of 3-ethyl-1,1′-diphenylferrocene (XIII). An analytical sample, m.p. 88–90°, was prepared by rechromatographing the above material twice on short alumina columns employing petroleum ether (b.p. 20–40°) as eluent.

Anal. Calcd. for $C_{24}H_{22}Fe$: C, 78.7; H, 6.0. Found: C, 78.8; H, 5.8.

Calculations.—The quantities used in the calculations have their usual definitions[30]: $S = \int \phi_i \phi_j d\tau$, with the value of the overlap integral taken as 0.25 for adjacent 2p-orbitals $\alpha = \int \phi_i H \phi_i d\tau$; $\gamma = \int \phi_i H \phi_j d\tau$; $\beta = \gamma - S\alpha$. The overlap and resonance integrals between non-adjacent 2p-orbitals, were neglected.

The secular equation for the substituted ferrocene ring, formalized in terms of the models shown in Table V, is identical to that for fulvene. The 6 × 6 matrix, which may be factored by symmetry into one 2 × 2 and one 4 × 4 matrix, gives the molecular orbital energy levels shown in Table VI (column 1). The figures are in agreement with those calculated earlier by Pullman, Berthier and Pullman.[31]

The matrices corresponding to the secular equations for transition states, or intermediates represented by partial structures XVI and XVII are, respectively

$$\begin{matrix} A & B & 0 & 0 & 0 \\ B & A & B & 0 & 0 \\ 0 & B & A & B & 0 \\ 0 & 0 & B & A & B \\ 0 & 0 & 0 & B & A \end{matrix} \qquad \begin{matrix} A & B & 0 & 0 & 0 \\ B & A & B & 0 & B \\ 0 & B & A & B & 0 \\ 0 & 0 & B & A & 0 \\ 0 & B & 0 & 0 & A \end{matrix}$$

where: $A = \alpha - E$; $B = \beta + S\alpha - SE$.

The roots of the secular equations are given in Table VI, and these are symmetric with respect to a non-bonding molecular orbital. Localization energies were calculated in the usual fashion.[20,21]

TABLE VI

ENERGY LEVELS

Ground state	Activated complex (XVI)	Activated complex (XVII)
1.383	1.208	1.263
0.800	0.800	0.642
.535	.000	.000
− .271	− .800	− .642
−2.717	−1.208	−1.263
−3.479		

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[30] G. W. Wheland, *J. Am. Chem. Soc.*, **63**, 2025 (1941).

[31] A. Pullman, G. Berthier and B. Pullman, *Bull. soc. chim. France*, 1097 (1950).

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The Formation of Carbon–Metal Bonds

BY RAYMOND E. DESSY, WILLIAM L. BUDDE[1] AND CAROL WOODRUFF

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The reaction of monosubstituted acetylenes, $R'C{\equiv}CH$, with M_2HgX_4 and $RHgX$, leading to $(R'C{\equiv}C)_2Hg$ and $RHgC{\equiv}CR'$ has been investigated kinetically, and a four-center transition state postulated for all reactions involved. This confirms earlier suggestions made concerning the transition state for cleavage of R_2Hg compounds with HX, and suggests that the stereochemical consequences of SE2 reactions in organomercury systems are as yet unknown.

In a previous publication in this series[2] the mechanism of the cleavage of C–Hg bonds by acids was discussed in detail. In summary, it was concluded that in the cleavage of C–Hg bonds by halogen acids a four-center mechanism was in operation, involving simultaneous attack by electrophilic proton and nucleophilic halide ion. The mechanism of this reaction is of some importance since

$$\begin{array}{ccc} C & \cdots & Hg \\ \vdots & & \vdots \\ H & \cdots & X \end{array}$$

in recent years evidence concerning the stereochemical outcome of SE reactions has been derived from systems of the type C*–Hg– being cleaved

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[1] Diamond Alkali Co. Predoctoral Fellow.

[2] R. E. Dessy and J. Kim *J. Am. Chem. Soc.*, **83**, 1167 (1961).