The phosphite was oxidized by method B, and the product subjected to molecular distillation at $10^{-5}$ mm. and a bath temperature of 65°. The product crystallized on the cold finger of the distillation apparatus; the yield was 61%. The highest melting point obtained was 49–51°. However, the solid rapidly deliquesced on exposure to the atmosphere, and dissolved in water to give an acidic solution; the material is thus extraordinarily unstable to moisture. The principal infrared bands were located at 3.31, 3.40, 3.46, 6.68, 6.79, 6.88, 7.25, 7.32, 7.69, 8.25, 9.45(shoulder), 9.67, 9.83, 10.79, 11.48(broad) and 11.90(broad) $\mu$. A sample was resublimed for analysis, performed by S. M. Nagy, M. I. T.

*Anal.* Calcd. for $C_9H_{11}PO_4$: C, 50.23; H, 5.42; P, 14.47. Found: C, 50.00; H, 5.46; P, 14.56.

**Triphenyl Phosphate.**—Triphenyl phosphite was oxidized by method A. The excess $N_2O_4$ was removed under vacuum, and the product, dissolved in methylene chloride, was filtered through a short column of activated alumina in order to remove a colored impurity. The yield of triphenyl phosphate, melting at 49–51°, was 84%.

**Triphenyl Phosphine Oxide.**—Triphenyl phosphine (Eastman Kodak Co.) was oxidized by method A. Removal of the solvent gave 99% of triphenylphosphine oxide, m.p. 155–156° (reported[16] 153°); $N_2O$ was identified in the gaseous product by infrared measurements, as reported above.

**Acknowledgments.**—The authors wish to express their appreciation to the National Science Foundation for a grant in support of this work. They also wish to thank Prof. K. B. Wiberg for obtaining the mass spectra of the gaseous reduction products, and Prof. L. Field and Dr. D. Samuel for helpful discussions.

[16] G. Kosolapoff, THIS JOURNAL, **64**, 2982 (1942).

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[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORIES OF HARVARD UNIVERSITY]

# The Structure and Chemistry of Ferrocene. III. Evidence Pertaining to the Ring Rotational Barrier

BY MYRON ROSENBLUM[1,2] AND R. B. WOODWARD

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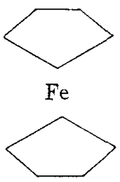
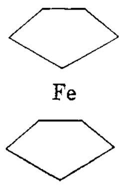
Certain early evidence, on the basis of which it had been concluded that the carbocyclic rings in the ferrocene molecule are essentially free rotating, is summarized. Both the number and structural type of acetylethylferrocene isomers formed in the acetylation of ethylferrocene are shown to be inconsistent with the assumption of a rigid ferrocene system. Partial catalytic reduction of 1,1′-diacetylferrocene leads to the formation of an acetylethylferrocene identical with the heteroannularly substituted acetylethylferrocene derived from acetylation of ethylferrocene. This result is interpretable only in terms of a free rotating ferrocene model.

Ferrocene has been the subject of two previous communications from this Laboratory.[3,4] In the first of these, evidence was presented on the basis of which structure I or II was advanced for ferrocene. The validity of this suggestion subsequently was confirmed by X-ray crystallographic studies,[5-7] the results of which unequivocally established the antiprismatic formulation (I) for ferrocene in the crystalline state.



I



II

Notwithstanding the high degree of formal unsaturation implied by such a structure, ferrocene does not exhibit properties characteristic of polyolefinic substances. Thus, its failure to undergo a Diels–Alder addition with maleic anhydride and its resistance to catalytic reduction led to the view that the substance must possess a high order of resonance stabilization. The subsequent demonstration that ferrocene entered into a normal Friedel–Crafts substitution reaction with a variety of acyl halides not only accorded well with this hypothesis, but opened up an entirely new field of research, the fertility of which is attested by the ever growing number and variety of ferrocene derivatives which have since taken their place in chemical literature.[8] Some early observations concerning the preparation and properties of several acylated ferrocenes and of substances derived from these were recorded briefly in our second communication.[4] In the present report, evidence pertaining to the question of the ring rotational barrier in ferrocene is adduced.

It must be noted that the conclusions regarding the rotational barrier in ferrocene, derived some time ago[2] and reported herein, have in the intervening years been amply confirmed in the synthetic work of Pauson[9] and in the dipole moment studies of Richmond and Freiser.[10] They are, moreover,

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[1] (a) National Institutes of Health predoctoral fellow 1952–1953. (b) Department of Chemistry, Brandeis University, Waltham 54, Mass.

[2] Abstracted in part from the Ph.D. thesis of M. Rosenblum, Harvard University, August, 1953. In 1955, Pauson (*Quart. Revs.*, **9**, 391 (1955), briefly outlined our experimental results and the conclusions derived therefrom. More recently, Struchkov (*Zhur. Obshch. Khim.*, **27**, 2039 (1957) has discussed in some detail the question of the rotational barrier in ferrocene and the effect of ring substitution on this potential barrier, citing the chemical evidence referred to by Pauson for certain of the conclusions deduced.

[3] G. Wilkinson, M. Rosenblum, M. C. Whiting and R. B. Woodward, THIS JOURNAL, **74**, 2125 (1952).

[4] R. B. Woodward, M. Rosenblum and M. C. Whiting, *ibid.*, **74**, 3458 (1952).

[5] J. D. Dunitz and L. E. Orgel, *Nature*, **171**, 121 (1953).

[6] P. F. Eiland and R. Pepinsky, THIS JOURNAL, **74**, 4971 (1952).

[7] E. O. Fischer and W. Pfab, *Z. Naturforschung*, **7B**, 377 (1952).

[8] The number of such publication is so large and their present proliferation so great that it is impossible to summarize these here. The interested reader is, however, referred to the very excellent review article by Pauson (ref. 2) for an early account of progress in this field.

[9] P. L. Pauson, THIS JOURNAL, **76**, 2187 (1954); *cf.* also P. L. Pauson, ref. 2, p. 400.

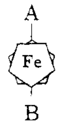
[10] H. H. Richmond and H. Freiser, THIS JOURNAL, **77**, 2022 (1955).

in accord with the conclusions of Moffitt,[11] of Dunitz and Orgel[12] and of Jaffé[13] derived from molecular orbital treatments of the ferrocene molecule.[14]

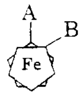
Acetylation of ferrocene in the presence of an excess of acetyl chloride and aluminum chloride leads to the formation of two isomeric diacetylferrocenes.[2] Of these, the predominant product, m.p. 130°, was assigned a structure in which the acetyl functions were distributed between the two ferrocene rings,[4] on the basis of the assumption that the acylated ring of the intermediate monoacetylferrocene should be considerably more resistant to further acylation than the second unsubstituted ring. This structural formulation has since been confirmed by the work of Nesmeyanov, *et al.*,[15] in which it was shown that high pressure reduction of this substance yielded ethylcyclopentane, but no cyclopentane or diethylcyclopentane. Struchkov[16] has also reported preliminary data from X-ray studies in support of the assigned structure.

The second diacetyl isomer, m.p. 96°, is formed in a ratio of approximately 1:60 to the higher melting derivative, and is separable from it only by careful chromatographic purification. The elucidation of its structure was of central importance with regard to the question of the rotational barrier in ferrocene. It is clear that were the rings in the ferrocene molecule rigidly fixed with respect to one another, then this substance as well as the predominant diacetyl derivative should most reasonably be formulated in terms of one of the three heteroannularly disubstituted structures IIIa, IVa and Va, since again, diacetylation of ferrocene would be expected to proceed more readily in such a manner as to lead to a distribution of the deactivating groups between the two rings.

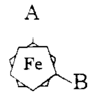
By contrast, if the rings are assumed to be essentially free rotating at normal temperatures in all but the crystalline state, only one heteroannularly disubstituted derivative is possible, and hence the choice of structures for the low melting diacetyl derivative is then necessarily confined to one of the two homoannularly disubstituted forms VIa and VIIa.



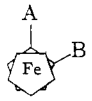
IIIa, A = B = Ac
b, A ≠ B
c, A = Ac,
B = Et



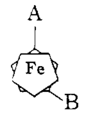
IVa, A = B = Ac
b, A ≠ B



Va, A = B = Ac
b, A ≠ B



VIa, A = B = Ac
b, A ≠ B
c, A = Ac, B = Et



VIIa, A = B = Ac
b, A ≠ B
c, A = Ac, B = Et

In the elucidation of the structure of the latter isomer, certain aspects of the infrared spectra of ferrocene and its derivatives proved to be singularly useful. We observed that a large variety of monosubstituted ferrocenes all exhibited the two medium intensity absorption bands near 9 and 10 μ, present in the spectrum of ferrocene,[17] while disubstituted ferrocene derivatives to which a heteroannular structure might reasonably be assigned,[18] uniformly failed to exhibit these peaks. On the basis of these observations, the following empirical generalization was set forth[2]: *Ferrocene derivatives, in which at least one ring remains unsubstituted, exhibit absorption in the infrared near 9 or 10 μ, while those derivatives in which both rings are either singly or multiply substituted do not exhibit such absorption.*[19]

The spectrum of the low melting diacetylferrocene isomer was found to exhibit two moderately intense absorption peaks at 9.02 and 9.96 μ. Thus, provided that the empirical generalization set forth above is valid for this substance, the presence of an unsubstituted ring was indicated. Hence we concluded that this isomer must possess either structure VIa or VIIa, and that the ferrocene molecule was therefore best described in terms of a free rotating model.

Although, at the conclusion of our researches, the available evidence did not allow an unambiguous choice between structures VIa and VIIa for this isomer, the recently demonstrated oxidation of the substance to a diacid which readily formed an anhydride now establishes its structure as 1,2-diacetylferrocene (VIa).[20]

**Study of Isomer Numbers.**—In order to adduce further evidence relevant to the problem of the rotational barrier in ferrocene, a study of the number of isomeric ferrocenes of the type $FeC_{10}H_8AB$ capable of existence was undertaken.

The total number of such isomeric disubstituted

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[11] W. Moffitt, THIS JOURNAL, **76**, 3386 (1954).

[12] J. D. Dunitz and L. E. Orgel, *J. Chem. Phys.*, **23**, 954 (1955).

[13] H. H. Jaffé, *ibid.*, **21**, 156 (1953).

[14] Since the completion of the manuscript additional evidence has been reported by Rinehart, Motz and Moon (ref. 24), and by Benson and Linsey, THIS JOURNAL, **79**, 5471 (1957).

[15] A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya, T. V. Nikitina and N. A. Simoukova, *Izvest Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk*, 739 (1956).

[16] Y. T. Struchkov, *Doklady Akad. Nauk. S.S.S.R.*, **110**, 67 (1957).

[17] E. R. Lippincott and R. D. Nelson, *J. Chem. Phys.*, **21**, 1307 (1953); THIS JOURNAL, **77**, 4990 (1955); *Spectrochim. Acta*, **10**, 307 (1958).

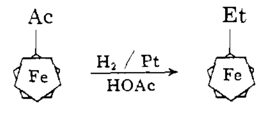
[18] These latter derivatives are substances derived from the higher melting, predominant diacetylferrocene isomer through chemical transformations involving one or both of its acetyl functions, as well as the large variety of diacylated ferrocenes formed as the predominant products in Friedel–Crafts reactions. For the reasons stated above, such substances may with confidence be assigned a heteroannularly disubstituted structure, regardless whether a rigid or non-rigid ferrocene model be adopted.

[19] While either the absence or presence of both of these peaks appears to be a dependable guide in structural elucidation, it must be pointed out that the latter criterion may, in some cases, prove unreliable, since it is possible that for certain heteroannularly substituted ferrocene derivatives the substituents alone or in combination may themselves possess absorption bands at these wave lengths. Rinehart, *et al.*, THIS JOURNAL, **79**, 3420 (1957), have noted the occurrence of bands at 9.00 and 9.94 μ in the spectrum of 1,1′-ferrocene-diacetodithiomorpholide. To our knowledge this compound represents the only ferrocene derivative thus far reported for which the above rule is inapplicable. For other references to and examples of this empirical generalization *cf.* P. L. Pauson (ref. 9); Rinehart, *et al.*, (above); G. R. Knox and P. L. Pauson, *J. Chem. Soc.*, 692 (1958); and A. N. Nesmeyanov, *Doklady Akad. Nauk S.S.S.R.*, **117**, 433 (1957).

[20] J. H. Richards and T. J. Curphy, *Chemistry & Industry*, 1456 (1956). On the basis of certain theoretical considerations we had tentatively assigned the structure of 1,3-diacetylferrocene to this substance (ref. 2).

ferrocenes predicted on the basis of a rigid ferrocene model is five (IIIb, IVb, Vb, VIb and VIIb), while for a free rotating ferrocene system the number of such isomers is reduced to three (IIIb = IVb = Vb, VIb and VIIb).

When monoethylferrocene (IX), prepared by catalytic reduction of monoacetylferrocene (VIII), was treated with aluminum chloride and one equivalent of acetyl chloride, and the resulting complex mixture subjected to careful chromatographic separation, three isomeric acetylethylferrocenes were isolated.[21]



VIII IX

Of these substances, isomers A and C each possess absorption in the infrared near 9 and 10$\mu$, while isomer B does not.[22] Thus, not only is the total number of isomeric acetylethylferrocenes formed in the above reaction consistent with that predicted on the basis of the free rotating model, but the number belonging to each structural class conforms as well. Isomer B must possess the heteroannular 1,1′-disubstituted structure IIIc, while isomers A and C may each be assigned one of the two remaining homoannular structures VIc and VIIc.

In the assignment of structures to acetylethylferrocene isomers A and C, we considered the probability that, as in the electrophilic substitution of alkylbenzenes, the course of homoannular acylation of ethylferrocene was more likely to be determined by steric factors than by an unequal activation of the carbon centers resulting from the small inductive or hyperconjugative effect of the alkyl group.[23] On the basis of these considerations the predominant C isomer was tentatively assigned the 1,3-disubstituted structure VIIc and the A isomer the 1,2-disubstituted structure VIc.[2]

These conclusions receive considerable support in the work of Rinehart, Motz and Moon,[24] who recently recorded the preparation of the isomeric acetyl-1,1′-dimethyl- and acetyl-1,1′-diisopropylferrocenes by acylation of the corresponding 1,1′-dialkylferrocenes. The structural assignments of the former isomers were confirmed by reduction of each to the trialkylferrocenes and comparison of the infrared spectra of these with that of an independently synthesized 1,1′-diethyl-2,2′-dimethylferrocene, while the structures of the latter isomers were deduced by comparison of their properties with those of the acetyl-1,1′-dimethylferrocene isomers. The ratio of 2-acetyl- to 3-acetyl-1,1′-dialkylferrocenes reported by these workers, together with the proportion of 1,2- to 1,3-acetylethylferrocene isomers obtained in this investigation, are summarized in Table I.

TABLE I

RATIO OF ISOMERIC ACETYLALKYLFERROCENES FORMED DURING ACETYLATION OF ALKYLFERROCENES

| Alkylated ferrocene | Ratio of 2:3 acetylalkyl isomers |
|---|---|
| 1,1′-Dimethylferrocene | 1:2.3[a] |
| Ethylferrocene | 1:3.0 |
| 1,1′-Diisopropylferrocene | 1:4.3[a] |

[a] Ref. 24.

From the above data it is clear that the ratio of 1,2- to 1,3-acetylethylferrocene isomers formed in the acetylation of ethylferrocene follows the ratios of the similarly constituted acetyldialkylferrocene isomers. Moreover, the continuous decrease in the ratio of 2- to 3-acetylalkylferrocene isomers, as the size of the homoannularly substituted alkyl group is increased, is consistent with the view that steric factors largely determine the course of acylation. As pointed out by Rinehart, *et al.*,[24] the magnitude of such steric control is necessarily less in the ferrocene system than it is for benzenoid aromatics, owing to the larger projected angle of meeting of two adjacent substituents and the consequent reduction in overlap of van der Waals radii in the former case.

From the amounts in which the three acetylethylferrocenes are formed (1,1′:1,2:1,3 = 1.0: 0.55:1.7) the partial rate factors for acylation at each of the three non-equivalent positions in ethylferrocene may be calculated employing the method of Ingold.[25]

Assigning a value of unity to the partial rate factor pertaining to acetylation at each of the carbon centers in the unsubstituted ring of ethylferrocene, the calculated values of the partial rate factors associated with acylation at positions 2 and 3 in the alkylated ring are 1.4 and 4.2, respectively.

The larger values for each of the partial rate factors pertaining to homoannular acylation relative to heteroannular acylation reflect the increased reactivity of the alkylated ring as compared with the unsubstituted ring, a result entirely in accord with experience in benzenoid systems.[26]

The above structural assignments for acetylethylferrocene isomers A, B, and C are further supported by a comparison of their ultraviolet absorption maxima with that of acetylferrocene and with those of the acetyl-1,1′-dialkylferrocenes prepared by Rinehart.[24] Table II summarizes these data.

Those derivatives, in which the acyl and alkyl groups occupy adjacent positions on the same ring, exhibit maxima identical in position with, but of greater intensity than, those of acetylferrocene. By contrast, the maxima of all the 1,3-disubstituted

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[21] A. N. Nesmeyanov and N. A. Vol'kenau, *Doklady Akad. Nauk, S.S.S.R.*, **111**, 605 (1956), have reported the acetylation of monoethylferrocene employing the silico-anhydride of acetic acid in the presence of stannic chloride. However these authors isolated only two isomeric acetylethylferrocenes, which they characterized as semicarbazones.

[22] The isomers have been designated, in the initial discussion, alphabetically in the order in which they emerge from the chromatographic column employed to effect their separation.

[23] *Cf.* C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 256–260; G. S. Hammond and M. E. Hawthorne in "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956; Groggins and Nagel, *Ind. Eng. Chem.*, **26**, 1313 (1934); D. T. Mowry, M. Renoll and W. F. Huber, THIS JOURNAL, **68**, 1105 (1946); C. F. H. Allen in "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 3.

[24] K. L. Rinehart, K. L. Motz and S. Moon, THIS JOURNAL, **79**, 2749 (1957).

[25] C. K. Ingold, *J. Chem. Soc.*, 2918 (1927).

[26] *Cf.* C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 243–248; and W. S. Johnson, in "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1944, Vol. II, p. 119.

TABLE II

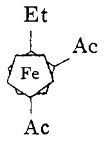
ULTRAVIOLET ABSORPTION MAXIMA OF THE ACETYLALKYLFERROCENES

| | $\lambda_{max}$, $m\mu^a$ | $E_{max}$ | $\lambda_{max}$, $m\mu^a$ | $E_{max}$ |
|---|---|---|---|---|
| Acetylferrocene | 225 | 14,600(16,500)[b] | 268 | 5400(6500)[b] |
| 1-Acetyl-1′-ethyl- | 228 | 15,100 | 270 | 5800 |
| 1-Acetyl-2-ethyl- | 225 | 18,600 | 268 | 7100 |
| 2-Acetyl-1,1′-dimethyl-[b] | 227 | 18,600 | 271 | 6800 |
| 2-Acetyl-1,1′-diisopropyl-[b] | 226 | 18,200 | 271 | 6700 |
| 1-Ethyl-3-acetyl- | 230 | 15,100 | 272 | 6500 |
| 3-Acetyl-1,1′-dimethyl-[b] | 232 | 15,800 | 274 | 6600 |
| 3-Acetyl-1,1′-diisopropyl-[b] | 231 | 15,600 | 273 | 6700 |

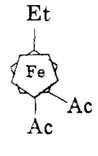
[a] Spectra were taken in 95% ethanol solution. [b] Ref. 24.

isomers are displaced to distinctly longer wave length, although the molar extinctions of these bands remain approximately equal to those of acetylferrocene. The small average displacements of 2 mμ evidenced in the maxima of the dialkylated acetylferrocenes, relative to the corresponding monoethylacetyl derivatives, may be ascribed to the bathochromic effect of the second alkyl group substituted at the 1′-position. This influence of a 1′-alkyl substituent on the absorption maxima of the acetylferrocenes, which is most clearly demonstrated by a comparison of the data for acetylferrocene with that of 1-acetyl-1′-ethylferrocene, strongly suggests some degree of electronic coupling between the heteroannularly distributed chromophores.

Additional evidence consistent with the hypothesis of a free rotating ferrocene system has been obtained in a study of the number of isomeric diacetylferrocenes which are formed when ethylferrocene is treated with two equivalents of acetyl chloride. Under these conditions, only two such isomers are formed, as predicted on the basis of a free rotating ferrocene model. By contrast, a total of ten isomeric diacetylethylferrocenes (excluding homoannularly diacetylated derivatives) would be capable of existence were the carbocyclic rings of ferrocene rigidly fixed with respect to one another. These two diacetylethylferrocenes have not been fully characterized, although their constitution cannot be in doubt. As with the two homoannular acetylethylferrocenes, assignment of structure to these substances may be made on the basis of their relative yields. Diacetylethylferrocene-B, m.p. 34–37°, is formed in a ratio of approximately 2.4:1 to the A isomer. Accordingly the A isomer may be assigned structure X and the B isomer structure XI.



X



XI

Rinehart[24] recently has recorded the infrared absorption peaks in the region of 10 to 11μ exhibited by the isomeric acetyldimethyl- and acetyldiisopropylferrocenes, on the basis of which certain general structural correlations were proposed. A comparison of the infrared absorption bands of these substances with those reported herein makes it possible to set forth certain more specific correlations which encompass not only the monoacetyldialkylferrocenes, but the monoacetylalkyl- and the diacetylmonoalkylferrocenes as well. Data relevant to these generalizations are presented in Table III.

TABLE III

INFRARED ABSORPTION SPECTRA OF ACETYLATED FERROCENES

| Acetylated ferrocene | Absorption peaks, μ | | | | | |
|---|---|---|---|---|---|---|
| Monoacetyl-[a] | 11.19 | ... | ... | 9.96 | 9.01 | 8.98 |
| 1,1′-Diacetyl-[a] | 11.19 | ... | ... | .. | .. | 8.95 |
| 1,2-Diacetyl-[a] | ... | ... | 10.90 | 9.96 | 9.02 | 8.98 |
| 1-Acetyl-2-ethyl-[b] | ... | ... | 10.87 | 9.96 | 9.01 | .. |
| 1-Acetyl-3-ethyl-[b] | ... | 11.10 | 10.88 | 9.96 | 9.01 | .. |
| 1-Acetyl-1′-ethyl-[b] | 11.20 | 11.04 | ... | .. | .. | 8.96 |
| 1,1′-Diacetyl-2-ethyl-[b] | 11.18 | ... | 10.83 | .. | .. | 8.95 |
| 1,1′-Diacetyl-3-ethyl-[b] | 11.21 | 11.10 | 10.88 | .. | .. | 8.96 |
| 1,1′-Dimethyl-2-acetyl-[c] | ... | ... | 10.81 | .. | .. | .. |
| 1,1′-Diisopropyl-2-acetyl-[c] | ... | ... | 10.81 | .. | 9.04 | .. |
| 1,1′-Dimethyl-3-acetyl-[c] | ... | 11.10 | 10.82 | .. | .. | .. |
| 1,1′-Diisopropyl-3-acetyl-[c] | ... | 11.05 | 10.82 | .. | 9.03 | .. |
| 1,1′-Diethyl-[d] | ... | 11.04 | ... | .. | .. | .. |
| Ethyl-[d] | ... | 11.04 | ... | 9.97 | 9.03 | .. |
| 1-Acetyl-1′-chlorocarbonyl-[b,e] | 11.20 | ... | ... | .. | .. | 8.98 |
| 1-Acetyl-1′-carbomethoxy-[a,e] | 11.20 | ... | ... | .. | .. | 8.95 |

[a] Spectrum determined in $CHCl_3$ solution. [b] Spectrum determined in $CCl_4$ solution. [c] Spectrum determined at liquid smear; ref. 24. [d] Spectrum determined in $CS_2$ solution. [e] Ref. 2.

We may note firstly the occurrence of the two peaks near 9.95 and 9.00μ in the spectra of all those ferrocene derivatives possessing an unsubstituted ring, and the absence of these bands for those compounds in which both rings are either mono- or disubstituted. In addition, the bands at 8.96 and 11.20μ, apparently characteristic of the acetyl function, are present only in spectra of those acyl derivatives in which the ring bearing the acyl function is unencumbered by alkyl groups. (In the spectrum of the homoannularly disubstituted 1,2-diacetylferrocene the band at 8.96μ is present, but that at 11.20μ is absent.) Those derivatives possessing both an alkyl and an acetyl group on the same ring are identified by the presence of absorption near 10.87μ. Within this group of homoannularly substituted acetylalkylferrocenes the 1,3-isomer may be distinguished from the 1,2-derivatives by the absorption band at 11.05μ, present in the infrared spectra of the 1,3-disubstituted isomers only. It is of interest to note that 1,2-diacetylferrocene also exhibits absorption near 10.87μ, but not at 11.05μ. The presence of absorption at 11.04μ in the spectrum of 1-acetyl-1′-ethylferrocene is reasonably attributed to an unmodified ethyl chromophore, as is evidenced by the fact that both mono- and diethylferrocene exhibit such absorption.[27]

Of some interest and potential utility in structural elucidation is the relationship between the structures of isomeric acetylalkylferrocenes and their adsorbabilities on the alumina column used to effect their separation. Thus, of the three isomeric monoacetylmonoethylferrocenes, the order

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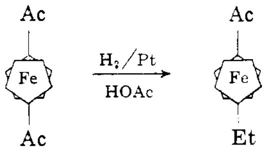
(27) NOTE ADDED IN PROOF.—Since the completion of this manuscript these generalizations have been extended successfully to include the acetylphenylferrocene isomers; *cf.* M. Rosenblum, *Chemistry and Industry*, 953 (1958).

of increasing adsorbability is given by: 1-acetyl-2-ethylferrocene < 1-acetyl-1′-ethylferrocene < 1-acetyl-3-ethylferrocene. Qualitatively the difference in adsorbability between the 1,2-isomer and both the 1,1′- and 1,3-isomers is greater than that between the latter two isomers themselves. The order as well as the qualitative difference in adsorbabilities exhibited by these substances is moreover maintained for the isomeric diacetylmonoethylferrocenes. Thus, on chromatography, 1,1′-diacetyl-2-ethylferrocene (X) precedes and is relatively easily separable from 1,1′-diacetyl-3-ethylferrocene (XI). This observed regularity is by no means confined to the above substances, but appears to apply equally well to those isomeric monoacetyldialkylferrocenes recently prepared by Rinehart.[24]

**Interannular Electronic Effects.**—Partial reduction of 1,1′-diacetylferrocene (IIIa) over a platinum catalyst affords an acetylalkylferrocene identical with the heteroannularly substituted acetylethylferrocene obtained by acetylation of ethylferrocene.



IIIa IIIc

This result is explicable only in terms of a free rotating ferrocene model. Were the ferrocene molecule to be a rigid one, then the formation of only one of the three possible heteroannularly diacetylated derivatives requires the corollary assumption that the acyl group in the intermediate monoacetylferrocene exerts a powerful directive influence over the course of subsequent electrophilic attack. Under these circumstances, the relative orientation of the two acyl functions in 1,1′-diacetylferrocene must be distinct from the relative disposition of the substituents in the heteroannularly disubstituted acetylethylferrocene, since these substances are derived through acylation of monosubstituted ferrocenes in each of which the substituents should manifest different directive effects.

On the other hand, interpretation of the experimental results on the basis of a non-rigid ferrocene model requires only the assumption that an acyl function present on one of the ferrocene rings inhibits further acylation within the same ring, but that such deactivation is not equivalent for all positions within that ring. The experimental facts neither require nor can they exclude the existence of interannular directive forces, since determination of such effects requires that the two centers involved (that which bears the directing group and the second at which reaction occurs) maintain a defined spatial relationship with respect to one another subsequent to as well as during chemical reaction.

Although interannular directive effects are therefore not amenable to experimental detection in a free rotating ferrocene system, certain observations strongly suggest the operation of general interannular forces, ascribable to either field effects or to specific resonance interactions between the rings. Thus, 1,2-diacetylferrocene resists further acetylation in the presence of a large excess of acetyl chloride and aluminum chloride, although it possesses an unsubstituted ring. The observation that formylation of ferrocene with excess N-methylformanilide and phosphorus oxychloride does not proceed beyond the introduction of one aldehyde group,[28] would also appear to be significant.

Work, now in progress and directed toward the elucidation of the nature, magnitude and possible directional properties of these interannular forces, will be reported subsequently.

## Experimental[29]

**1,1′-Diacetylferrocene (IIIa).**—Ferrocene (30 g., 0.162 mole), dissolved in 100 cc. of dry methylene chloride, was added over a period of 15 minutes to a stirred mixture of aluminum chloride (53 g., 0.40 mole) and acetyl chloride (32 cc., 0.45 mole) in 200 cc. of dry methylene chloride. The reaction, carried out in an atmosphere of dry nitrogen to avoid oxidation of ferrocene, proceeded readily at room temperature, with immediate evolution of hydrogen chloride and the formation of an intensely violet solution. The mixture was stirred at room temperature for two hours, then cooled, decomposed with ice and filtered from alumina. The alumina was washed with chloroform until colorless. The separated aqueous phase was extracted several times with chloroform and these extracts, combined with the main body of organic solution, were washed to neutrality. The pale blue color of the aqueous solution suggested little oxidation of ferrocene. The deep red organic solution was set on the steam-bath and dried by distilling solvent until the volume of solution was approximately 200 cc. At this point 100 cc. of cyclohexane was added, and the solution was again concentrated to a volume of 200 cc. On slow cooling, large ruby-red rectangular plates of 1,1′-diacetylferrocene deposited (24.4 g.), m.p. 127.5–128.5°. The second crop after one recrystallization weighed 7.0 g., m.p. 127.5–128.5°. An analytical sample of this substance melted at 130–131°.[4]

1,1′-Diacetylferrocene is slightly soluble in ether, cyclohexane and water, very soluble in chloroform, carbon tetrachloride and ethyl acetate.

The compound dissolves readily in strong mineral acids to give intensely colored violet solutions, from which it can be recovered unchanged by dilution and extraction with chloroform.

The oxime, prepared by treatment of a methanolic solution of the ketone with a solution of hydroxylamine hydrochloride in methanol, was crystallized once from this solvent. The substance is an orange powder, dec. 200°.[4]

**Isolation of 1,2-Diacetylferrocene (VIa) and Monoacetylferrocene (VIII).**—The mother liquor from crop 2 above was treated in the following manner. Solvent was removed *in vacuo*, and the dark viscous oil was taken up in a small volume of benzene and chromatographed on 300 g. of alumina. (Many ferrocene derivatives darken at the alumina surface on exposure to diffuse sunlight, and hence all chromatograms were protected from the light by wrapping the column with aluminum foil.)

Elution was carried out initially with benzene, during the course of which four main bands appeared on the column. After development, these bands were eluted with mixtures of benzene and ether. The first band yielded 0.10 g. of product, m.p. 120–140°, which on recrystallization from cyclohexane gave ferrocene, identified by mixed m.p. Band 2 gave 1.9 g. of partially crystalline material which,

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(28) M. Rosenblum, *Chemistry & Industry*, 72 (1957); G. D. Broadhead, J. M. Osgerby and P. L. Pauson, *J. Chem. Soc.*, 650 (1958); P. J. Graham, R. V. Lindsey, G. W. Parshal, M. L. Peterson and G. M. Whitman, THIS JOURNAL, **79**, 3416 (1957).

(29) All melting points were determined using a Fisher–Johns or Kofler micro melting point apparatus, and are uncorrected. Infrared spectra were taken with a Baird double beam recording spectrophotometer, model B. Ultraviolet absorption spectra were determined with the aid of a Beckman quartz spectrophotometer, model DU, and were taken in 95% ethanol solution unless otherwise noted. Analyses were performed at the microanalytical laboratory of the Massachusetts Institute of Technology.

after recrystallization from cyclohexane and then petroleum ether, afforded 0.82 g. of orange needles, m.p. 83–85°, undepressed on admixture with monoacetylferrocene prepared by reaction of equimolar quantities of ferrocene and acetyl chloride (yield of monoacetylferrocene 2.4%).

The product (2.6 g.) obtained from elution of band 4 was recrystallized from chloroform–cyclohexane to give 1.8 g. of 1,1′-diacetylferrocene, m.p. 128.5–129.5° (total yield of 1,1′-diacetylferrocene, 33.2 g., 76%).

The product (1.1 g., m.p. 86–92°) derived from band 3 was taken up in 20 cc. of benzene and rechromatographed on 100 g. of alumina. A forerun of dark gum was obtained. Succeeding fractions 2 through 5 gave, after recrystallization from ether, a total of 0.521 g. of 1,2-diacetylferrocene, m.p. 96–97° (yield of this product, 1.2%).[30]

*Anal.* Calcd. for $C_{14}H_{14}O_2Fe$: C, 62.25; H, 5.22. Found: C, 62.28; H, 5.10.

**Catalytic Reduction of Monoacetylferrocene (VIII). Monoethylferrocene (IX).**—Monoacetylferrocene (4.5 g., 0.02 mole), dissolved in 30 cc. of glacial acetic acid, was added to a suspension of 300 mg. of reduced platinum oxide catalyst in 20 cc. of the same solvent. The mixture was stirred in an atmosphere of hydrogen, at room temperature, for a period of 70 hours, at the end of which time 994 cc. of hydrogen had been taken up (100%, based on a theoretical uptake of 2 moles of hydrogen per mole of ketone). The deep amber solution was filtered by suction, in an atmosphere of nitrogen, directly into 300 cc. of water containing sufficient sodium carbonate to neutralize the acetic acid. The aqueous solution was then extracted twice with 100-cc. portions of ether, and these were combined, washed to neutrality and dried. Removal of solvent left 4.3 g. of mobile, amber colored oil, possessing a mild camphoraceous odor. An infrared spectrum of this product revealed the presence of small amounts of partially reduced and unreduced material. Purification was effected by dissolving the crude product in a small volume of petroleum ether and chromatographing on 200 g. of alumina. On elution with petroleum ether, monoethylferrocene separated easily from alcoholic and ketonic contaminants. The product was distilled at 121–123° (10 mm.) (yield 3.28 g. (77%), $n^{20}D$ 1.6012.[31] Monoethylferrocene undergoes slow decomposition in air and may also be photosensitive.

*Anal.* Calcd. for $C_{12}H_{14}Fe$: C, 67.32; H, 6.59. Found: C, 67.44; H, 6.56.

**Acetylation of Monoethylferrocene. 1-Acetyl-2-ethylferrocene (VIc), 1-Acetyl-1′-ethylferrocene (IIIc) and 1-Acetyl-3-ethylferrocene (VIIc).**—A solution of 100 g. (0.013 mole) of acetyl chloride and 1.60 g. (0.12 mole) of aluminum chloride, dissolved in 20 cc. of methylene chloride (previously dried over Drierite), was added dropwise over a period of 1.5 hours to a stirred solution of 2.14 g. (0.01 mole) of monoethylferrocene in 30 cc. of dry methylene chloride. The reaction was continued at room temperature in an atmosphere of dry nitrogen for an additional 1.5 hours, and was then cooled and decomposed with ice and water. The blue-green aqueous phase was separated and extracted once with ether. The combined organic solutions were washed to neutrality and dried. Removal of solvent *in vacuo* left 2.50 g. of a dark red oil.

The crude product was taken up in benzene and chromatographed on 600 g. of alumina. Three main zones appeared on continued elution with benzene, a small orange band preceding a second and much broader orange zone and a sharp red-orange band which showed some fractionation, but whose movement was very much slower than either of the others. Monoethylferrocene, whose color on the column can barely be detected due to its high dilution, was collected in fraction zero, and identified by its infrared spectrum. Altogether twenty-one fractions were taken.

Fractions 1 through 3, weighing 0.256 g., gave 0.143 g. of 1-acetyl-2-ethylferrocene as orange crystals, m.p. 42.5–44.5°, after several recrystallizations from petroleum ether.

*Anal.* Calcd. for $C_{14}H_{16}OFe$: C, 65.65; H, 6.30. Found: C, 65.56; H, 6.35.

Fractions 6 through 9 afforded a total of 0.782 g. of red oil. These fractions, crystallized separately at low temperatures from petroleum ether, gave 0.428 g. of 1-acetyl-1′-ethylferrocene as long, fine orange needles, m.p. 11–12°. An analytical sample of this substance melted at 12.5–13.2°.

*Anal.* Calcd. for $C_{14}H_{16}OFe$: C, 65.65; H, 6.30. Found: C, 65.50; H, 6.61.

From a portion of fraction 8 above, a 2,4-dinitrophenylhydrazone derivative was prepared, which after two recrystallizations from ethyl acetate–ethanol gave 9 mg. of blue-black, square faced rods, m.p. 177.5–178.5°.

Fractions 12 through 20 were recombined and crystallized at low temperatures from petroleum ether to give 268 mg. of product, m.p. 8.6–10.8°. This was recrystallized again in low yield for analysis to give 70 mg. of 1-acetyl-3-ethylferrocene as fine orange needles, m.p. 11.6–12.6°.

*Anal.* Calcd. for $C_{14}H_{16}OFe$: C, 65.65; H, 6.30. Found: C, 64.93; H, 6.33.

A mixture of 1-acetyl-1′-ethylferrocene and 1-acetyl-3-ethylferrocene melted below 3°.

The 2,4-dinitrophenylhydrazone was prepared from a portion of the analytical sample of 1-acetyl-3-ethylferrocene above and recrystallized from ethyl acetate–ethanol as dark purple rods, m.p. 179–180°.

*Anal.* Calcd. for $C_{20}H_{20}N_4O_4Fe$: C, 55.06; H, 4.62; N, 12.84. Found: C, 55.09; H, 4.81; N, 12.89.

A mixed m.p. of this dinitrophenylhydrazone with that prepared from 1-acetyl-1′-ethylferrocene gave a depression of 30° (m.p. 149–159°).

The essential homogeneity of fractions 12 through 20 was established by rechromatographing the mother liquors obtained from crystallization of these combined fractions. The mother liquors, containing approximately 250 mg. of product, were taken up in a small volume of petroleum ether and placed on a 25-g. alumina column. A total of 9 fractions were collected. The crystalline products derived from fractions 4 (0.019 g., m.p. 10.4–11.6°) and 9 (0.033 g., m.p. 11.6–12.6°) were found to be identical by mixed m.p. (10.2–11.8°).

Fractions 7, 8 and 9 were combined and a 2,4-dinitrophenylhydrazone derivative was prepared. This derivative was identical by mixed m.p. with the derivative prepared from authentic 1-acetyl-3-ethylferrocene.

**Partial Reduction of 1,1′-Diacetylferrocene. 1-Acetyl-1′-ethylferrocene (IIIc).**—A solution of 2.0 g. of 1,1′-diacetylferrocene in 20 cc. of glacial acetic acid was added to a suspension of 100 mg. of prereduced platinum oxide in 10 cc. of the same solvent. The mixture was stirred at room temperature in an atmosphere of hydrogen until the uptake of hydrogen was half of that required for complete reduction to diethylferrocene. The solution was then suction filtered, in an atmosphere of nitrogen, directly into 200 cc. of water containing 40 g. of sodium carbonate. The basic aqueous solution was extracted several times with ether, and the combined ether extracts were then washed to neutrality and dried over anhydrous sodium sulfate. Removal of solvent *in vacuo* left a partially crystalline red oil, which was taken up in 25 cc. of benzene and placed on a 200-g. alumina column.

On elution with benzene, five bands developed. Band 1, containing diethylferrocene, passed rapidly down the column and separated easily from the other color zones

The second band, a broad orange zone, yielded 0.379 g. of red oil, which upon crystallization from petroleum ether at low temperatures gave 0.201 g. of fine orange needles, m.p. 11.0–12.5°, mixed m.p. with 1-acetyl-1′-ethylferrocene, obtained previously by acetylation of monoethylferrocene, 11.0–12.5°.

A dinitrophenylhydrazone was prepared from this product and recrystallized twice from ethyl acetate–ethanol to give square faced, blue-black rods, m.p. 179–180°. Its mixed m.p. with the dinitrophenylhydrazone of 1-acetyl-1′-ethylferrocene was 179–180°.

The remaining three, relatively slow moving bands were removed manually from the column, and the alumina extracted with chloroform.

The product derived from band 3 could not be crystallized.

Band 4 yielded, after two crystallizations from cyclohexane, 0.275 g. of product, m.p. 125.5–128°, identical with 1,1′-diacetylferrocene.

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[30] This substance was first isolated in these laboratories by Dr. M. C. Whiting.

[31] A. N. Nesmeyanov and N. A. Vol'kenau, *Doklady Akad. Nauk, S.S.S.R.*, **107**, 262 (1956), give b.p. 108–109° (5.5 mm.) and $n^{20.5}D$ 1.6017, for the compound prepared by Clemmensen reduction of monoacetylferrocene.

The product obtained from band 5 consisted of alcohol and glycol components and resisted attempts at crystallization.

**Resistance of 1,2-Diacetylferrocene (VIa) to Further Acetylation. A. Room Temperature Reaction.**—A solution containing 0.90 cc. (0.113 mole) of acetyl chloride and 1.10 g. (8.3 mmoles) of aluminum chloride in 10 cc. of methylene chloride (dried over Drierite) was prepared and filtered through glass wool into the reaction vessel. The solution was stirred at room temperature in an atmosphere of dry nitrogen while 0.070 g. (0.26 mmole) of 1,2-diacetylferrocene dissolved in 10 cc. of dry methylene chloride was added over a period of 15 minutes. After stirring at room temperature for four hours, the intensely violet solution was cooled and decomposed with water. The aqueous phase was separated, extracted with ether until colorless, and the combined organic solutions were washed to neutrality and dried. Removal of solvent *in vacuo* left 0.111 g. of partially crystalline material. This was taken up in a small volume of benzene and chromatographed on 10 g. of alumina. After developing the chromatogram by elution with benzene, the alumina was withdrawn from the column, and the broad orange band was cut away from resinous material at the top of the column and extracted thoroughly with chloroform. Removal of chloroform *in vacuo* left 60 mg. of product, m.p. 84–94°, which after one recrystallization from ether–petroleum ether yielded 45 mg. of material, m.p. 95–97°, identical by mixed melting point with 1,2-diacetylferrocene. From the mother liquors, after several recrystallizations, an additional 3 mg. of 1,2-diacetylferrocene was recovered.

**B. Reaction at 40°.**—1,2-Diacetylferrocene (0.135 g., 0.5 mmole) dissolved in 10 cc. of dry methylene chloride was added to a stirred suspension containing 0.70 g. of aluminum chloride and 0.30 cc. of acetyl chloride in 20 cc. of the same solvent. No evolution of hydrogen chloride was evident either on mixing the reactants or during the subsequent two hours when the mixture was stirred at room temperature. At the end of this period an additional 0.70 g. of aluminum chloride and 0.30 cc. of acetyl chloride were added and the reaction mixture was warmed on the steam-bath for 1.25 hours. During this period hydrogen chloride was evolved slowly. When 8.6 cc. of 0.1 *N* sodium hydroxide solution had been titrated by the emergent gas, the reaction was cooled, decomposed with ice and filtered from alumina. The aqueous solution was separated, washed several times with chloroform, and the combined organic solutions were washed to neutrality and dried. Solvent was removed *in vacuo*, leaving a dark red gum. The crude product was taken up in benzene and chromatographed on 25 g. of alumina. Of the three bands which appeared on the column, the first was eluted with 5% chloroform–benzene, the second with 20% chloroform–benzene, and the third with 50% chloroform–benzene.

Fraction 1 was recrystallized twice from ether–petroleum ether to give 21 mg. of product, m.p. 96.5–98.0°, identical with 1,2-diacetylferrocene by mixed melting point. Neither fraction 2 nor 3 could be crystallized; the spectra of both of these possessed bands at 9.00 and 9.95 μ in the infrared.

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[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE, THE WEIZMANN INSTITUTE OF SCIENCE]

# Reactions of Active Methylene Compounds in Pyridine Solution. I. The Ionic Autoxidation of Fluorene and its Derivatives[1]

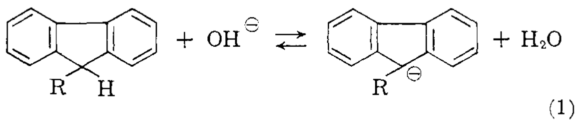
BY YAÏR SPRINZAK

RECEIVED APRIL 7, 1958

Fluorenes are oxidized smoothly by oxygen to fluorenones in pyridine solution and in the presence of benzyltrimethylammonium hydroxide. 9-Alkylfluorenes give 9-hydroperoxy-9-alkylfluorenes and 9-alkylfluorenols. This high reactivity is attributed to the presence of appreciable concentration of carbanions, recognizable by the color of their solutions. The reaction provides a convenient method for the preparation in high yields of oxygen compounds belonging to the above three classes. Low temperature oxidation of 2,3-diphenylindene affords 2,3-diphenylindone and a tertiary hydroperoxide, identified as 1-hydroperoxy-1,2-diphenylindene.

The present work was undertaken following the observation that substituted fluorenes, such as 2-nitro and 2,7-dibromofluorene, are oxidized by silver acetate in pyridine solution, at ordinary temperatures, to yield polymeric substances.[1] This reactivity was attributed to an increased ionizability of the hydrogen atoms at the 9-position of the fluorene molecule both owing to the presence of appropriate substituents and to the influence of the medium. It was therefore anticipated that a strong base, such as the hydroxide ion, might, in the same solvent, produce carbanions in appreciable concentration from fluorene and its derivatives.

Thus, when benzyltrimethylammonium hydroxide (Triton B), an alkali-like compound remarkable for its solubility in non-hydroxylic solvents, is added to a solution of fluorene in pyridine, an orange-yellow color develops. The color fades gradually with the addition of a foreign solvent (*e. g.*, water, alcohol, benzene, heptane), but reappears when sufficient pyridine is subsequently added to the mixture. It is assumed that the appearance of color is indicative of an ionization process wherein colored fluoryl ions are formed (eq. 1, R = H), and that the fading of the color brought about by changing the composition of the medium represents a reversal of the process.[2]



(1)

The faculty of developing a color under the action of Triton B in pyridine appears to be shared by all hydrocarbons of the cyclopentadiene series in which at least one hydrogen atom of the active methylene group is present. Thus, 1,2,3,4-tetraphenylcyclopentadiene, 2,3-diphenylindene and 9-ethylfluorene form reddish solutions, while indene

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(1) Presented in part at the XIVth International Congress of Pure and Applied Chemistry, Zurich, July 1955; Congress Handbook, p. 66.

(2) While it is felt that the bulk of the observations here reported provide substantial support for this assumption, experiments are in progress with a view to obtaining more direct evidence as to the presence of carbanions under the prescribed conditions as distinct from related systems (*e.g.*, a solution of fluorene in alcoholic sodium hydroxide) where the formation of carbanions is generally postulated to account for chemical reactions (see A. Alexander, "Principles of Organic Ionic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 123 ff.).