point while stirring at high speed. When the contents were at 100°, 3.0 g. of ferrocene was added and gradual heating resumed, using a protective helium atmosphere. Careful visual examination indicated no appreciable reaction until the temperature had reached *ca.* 190° at which time the lithium surface appeared to darken slightly and the presence of iron particles could be discerned by testing with a magnet. Heating was resumed and the temperature raised to 220° over a 10-minute period and then the mixture was allowed to cool. By this time the lithium particles were very much darker and *ca.* 0.1 g. of magnetic black precipitate had settled to the bottom of the flask. After rinsing with solvent, the Fe-coated lithium sand adhered readily to the magnet. In the absence of lithium at these temperatures and in contact with air, no evidence of degradation could be observed.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Organic Chemistry of Ferrocene. I. The Acetylation of Dialkylferrocenes[1]

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Acetylation of 1,1'-dimethylferrocene gives a 7 to 3 ratio of the 3- or β-acetyldialkylferrocene to the 2- or α-acetyl isomer, while the ratio of the corresponding acetyldiisopropyl isomers obtained from acetylation of 1,1'-diisopropylferrocene is 9 to 2. The isomeric acetyldialkylferrocenes have been isolated, characterized by infrared and ultraviolet spectra and converted by oxidation to the corresponding carboxylic acids and by reduction to the corresponding alkyl derivatives. Dissociation constants of the isomeric dimethylferrocenecarboxylic acids and infrared spectra of the isomeric ethyldimethylferrocenes have been presented and discussed.

Since the initial report in 1951 of the isolation of ferrocene[2,3] and the discovery that the compound is, in many respects, an aromatic system,[4] there have been numerous chemical confirmations of the similarity of its chemistry to that of the classical benzenoid compounds and, indeed, the name ferrocene was chosen to indicate the compound's aromatic character.[4] Thus, for example, ferrocene may be acylated,[4,5] sulfonated,[5,6] metalated[7,8] and arylated by other aromatic nuclei.[7,9–12] On the other hand, in its resistance to alkylation[5,13] and its behavior toward oxidizing media[14] ferrocene shows marked differences from benzene. The present study has been undertaken as part of a general investigation of substituted ferrocenes and to investigate to what extent the normal directive effects of alkyl groups[15] are observed in the ferrocene system.

For this purpose the acylation reaction is particularly well adapted since it has been studied extensively in benzenoid systems and found to be highly selective in substitution at ring positions.[16] Further, acylation of ferrocenes leads to little or no degradation of the ring system and often gives products in high yields.[5,17] Previous investigations of acylations have shown similarities between ferrocene and benzene in that acylation may be accomplished under conditions employed for benzene[4,5] and also in that the presence of one acyl group on the ferrocene nucleus strongly deactivates the substituted ring toward further acylation[4,18] and to a certain extent deactivates the other ring as well.[5,13,18] By contrast, the presence of an alkyl group might be expected to activate somewhat the substituted ring toward acylation.[19]

In the present study the compounds investigated have been the 1,1'-dialkylferrocenes,[20] in which each ring bears a substituent alkyl group. Both 1,1'-dimethyl- (Ia) and 1,1'-diisopropyl-ferrocene (Ib) have been examined in order to observe the differing effects of the methyl and isopropyl substituents and the response of acylation of the system toward increasing steric bulk on the rings.

Acetylation of either of these compounds can give substitution in the 2- or 3- (α- or β-)[21] positions. If care is taken to prevent disubstitution, only two isomers are formed, 2-acetyl- (IIa,b) and 3-acetyl-1,1'-dialkylferrocenes (IIIa,b); measurement of the proportion of the two isomers leads to

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(1) Presented in part at the 129th Meeting of the American Chemical Society, Dallas, Texas, April 8 to 13, 1956; see Abstracts of Papers, p. 12-N.

(2) T. J. Kealy and P. L. Pauson, *Nature*, **168**, 1039 (1951).

(3) S. A. Miller, J. A. Tebboth and J. F. Tremaine, *J. Chem. Soc.*, 632 (1952).

(4) R. B. Woodward, M. Rosenblum and M. C. Whiting, THIS JOURNAL, **74**, 3458 (1952).

(5) V. Weinmayr, *ibid.*, **77**, 3009 (1955).

(6) A. N. Nesmeyanov, XIVth International Congress of Pure and Applied Chemistry, Zurich, July 21–27, 1955; *cf.* Abstracts of Papers, p. 193.

(7) A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and O. A. Nesmeyanova, *Doklady Akad. Nauk SSSR*, **97**, 459 (1954).

(8) R. A. Benkeser, D. Goggin and G. Schroll, THIS JOURNAL, **76**, 4025 (1954).

(9) A. N. Nesmeyanov, E. G. Perevalova and R. V. Golovnya, *Doklady Akad. Nauk SSSR*, **99**, 539 (1954).

(10) A. N. Nesmeyanov, E. G. Perevalova, R. V. Golovnya and L. S. Shilovtseva, *ibid.*, **102**, 535 (1955).

(11) G. D. Broadhead and P. L. Pauson, *J. Chem. Soc.*, 367 (1955).

(12) V. Weinmayr, THIS JOURNAL, **77**, 3012 (1955).

(13) P. L. Pauson, *Quart. Revs.*, **9**, 391 (1955).

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

(15) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 236.

(16) R. C. Fuson, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 333; H. C. Brown and W. H. Bonner, THIS JOURNAL, **76**, 605 (1954); R. Pajeau, *Bull. soc. chim. France*, 544 (1946).

(17) R. Riemschneider and D. Helm, *Chem. Ber.*, **89**, 155 (1956).

(18) M. Rosenblum, Ph.D. Thesis, Harvard University, August, 1953.

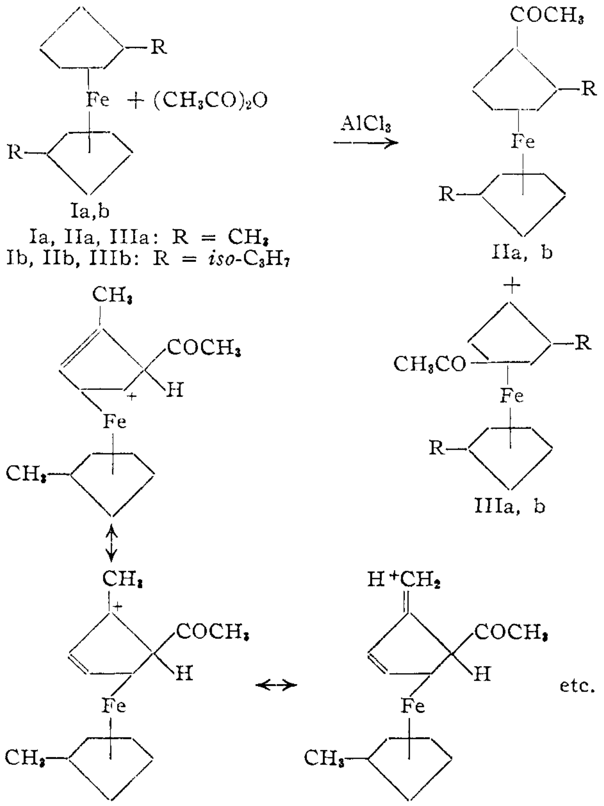
(19) Reference 15, pp. 245–256.

(20) K. L. Rinehart, Jr., Sung Moon and K. L. Motz, in preparation.

(21) The α–β nomenclature commonly employed in heterocyclic and condensed ring aromatic compounds seems preferable to any system based on an *ortho–meta–para* scheme. Confusion arises in the five-membered ring series since electronically there are probably two "*para*" positions and no "*meta*" position (*cf.* below).

an indication of directive influences in the ring.[22]

Influences favoring one or the other of the two isomers may be described as steric or electronic in nature. On purely steric grounds formation of the 3- or β-acetyl isomer is favored, especially from the acetylation of diisopropylferrocene. Electronic effects are more difficultly predictable. The inductive effect of an alkyl substituent should favor the formation of the 2- or α-acetyl isomer since this effect diminishes with increasing distance from the substituent. Hyperconjugative interaction of the alkyl group with the ring might be expected to enhance the reactivity of both positions, however, since acylation transition states of the usual type[23] in which the positive charge is delocalized about the ring may be pictured for substitution at either ring position.[24]



Ia,b

Ia, IIa, IIIa: R = CH_3
Ib, IIb, IIIb: R = iso-C_3H_7

IIa, b

IIIa, b

A greater number of such hypothetical delocalized forms may be drawn for hyperconjugation of the acylation transition state at a position alpha to the alkyl group, but, of course, the number of such forms says nothing for the stability or relative contribution of each.[25] From the above discussion no predictions may be made with certainty, but since the various electronic and steric influences are complex and to an extent oppose one another, it might be expected that a mixture of the two isomeric products should be formed in which neither isomer strongly predominates.

Both diisopropyl- and dimethyl-ferrocene were acetylated with acetic anhydride employing an aluminum chloride catalyst. To inhibit the formation of diacetyl products, only one-half mole of anhydride was employed per mole of ferrocene and the anhydride was added slowly to the ferrocene solution. The mixture of products was separated chromatographically, whereby the dialkylferrocene was recovered readily, while the two isomeric acetyldialkylferrocenes were separated with greater difficulty. The relative proportions of the two isomers formed from dimethyl- and diisopropylferrocene are summarized in Table I. These proportions were calculated from the ultraviolet spectra of mixtures of the two compounds and, as a check, for the diisopropylferrocene acetylation, also from the weights of the two isomers obtained from chromatographic fractions; agreement between the two methods is good.

TABLE I

PROPORTIONS OF ISOMERIC ACETYLDIALKYLFERROCENES FORMED

Dialkylferrocene acetylated[a]	Proportion of isomers, % α-[a]	β-[a]
1,1′-Dimethyl-	30[b]	70[b]
1,1′-Diisopropyl-	19[b]	81[b]
1,1′-Diisopropyl-	17[c]	83[c]

[a] α = 2-acetyldialkylferrocene (IIa,b). β- = 3-acetyldialkylferrocene (IIIa,b). [b] Composition estimated from ultraviolet spectra. [c] Composition estimated from weights of chromatographed isomers.

In the acetylation of dimethylferrocene there is little selectivity between the two positions and, while 3-acetyl-1,1′-dimethylferrocene is formed in somewhat greater amount, it nevertheless accounts for only 70% of the product and the 2-acetyl isomer for 30%. There is somewhat greater selectivity in the acetylation of diisopropylferrocene; here the β-isomer is formed in larger amount (82%) than with the methyl analog, while substitution of the α-position, hindered sterically, occurs to the ex-

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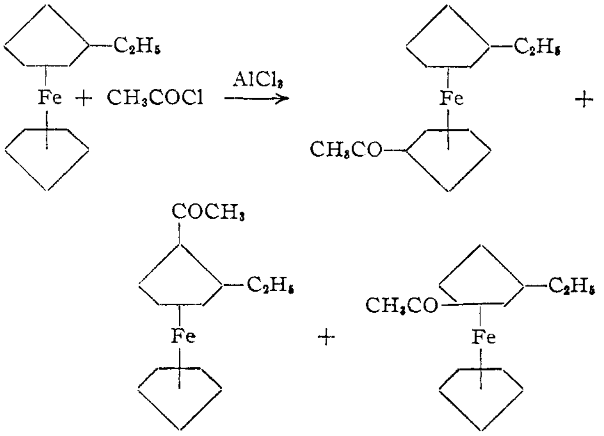
[22] It may be noted that Rosenblum[18] earlier acetylated monoethylferrocene and obtained the expected three isomers, although he did not assign definite structures to the two homoannular compounds. The present 1,1′-dialkyl system has the virtue of simplicity in that it allows the isolation and study of directive effects on substitution in the same ring uncomplicated by those exerted on substitution in the other ring.



[23] J. W. Baker, "Hyperconjugation," Oxford University Press, London, 1952, p. 48.

[24] It is on this basis that the α- and β-positions seem to resemble more closely the o- and p-positions of benzene, while no true m-position exists.

[25] On the basis of an approximate molecular orbital treatment of substituted ferrocenes, Richards has predicted the formation of a somewhat higher proportion of the α-isomer for both electron-donating and electron-withdrawing substituents [J. H. Richards, private communication].

tent of only 18%. This is rather a surprisingly small difference in light of the considerably greater bulk of the isopropyl group.[26] However, the bond angles of the 5-membered ring are much less conducive to steric crowding than those of benzene, as may be seen from Fig. 1, where van der Waals radii[28] have been drawn. Thus there is less interaction between adjacent substituents on the ring. This conclusion is supported by the ultraviolet spectra of the acetyl isomers and the dissociation constants of the corresponding isomeric acids presented below. The formation of the two isomers in similar amounts is consistent with the treatment of competing electronic effects outlined above. In summary, it may be stated that there is little selectivity between acylation at one or the other position of the ferrocene ring and that steric effects are not as important as in the benzene analogs, where acetylation of toluene gives nearly exclusively *p*-substitution,[29] although electronic factors presumably favor *o*-substitution also.[19]

As a further comparison between the ferrocene and benzene systems the physical properties of substituted ferrocenes are of interest. In Table II are presented maxima from the ultraviolet spectra of the isomeric acetyl-dialkylferrocenes, together with those of the isomeric methylacetophenones for comparison. Both series of compounds have strong conjugated ketonic absorption; for phenyl ketones this is near 245 mμ, while for ferrocenyl ketones there are two bands, near 230 and 270 mμ.

TABLE II

ULTRAVIOLET ABSORPTION MAXIMA OF FERROCENYL AND PHENYL KETONES

Ketone	λ_{max}, mμ[a]	ϵ_{max}[a]
Acetylferrocene	226	16,500 (14,600)[b]
	269	6,500 (5,400)[b]
2-Acetyl-1,1′-dimethylferrocene	227	18,600
	271	6,800
3-Acetyl-1,1′-dimethylferrocene	232	15,800
	274	6,600
2-Acetyl-1,1′-diisopropylferrocene	226	18,200
	271	6,700
3-Acetyl-1,1′-diisopropylferrocene	231	15,600
	273	6,700
Acetophenone	242	12,000 (12,800)[c]
o-Methylacetophenone	243	9,500 (8,850)[c]
m-Methylacetophenone	247	11,300
p-Methylacetophenone	252	15,800 (15,100)[c]

[a] Spectra determined in 95% ethanol. [b] Ref. 18. [c] Ref. 30.

Of particular interest is the striking difference between the effect of alkyl substituents on the spectra of the two systems. Methyl substitution in the *p*-position of acetophenone increases both the wave length of maximum absorption and the extinction coefficient. A *m*-methyl substituent shifts the maximum to somewhat longer wave lengths but has little effect on the extinction coefficient. An *o*-substituent, on the other hand, does not shift the wave length of the peak at all from that of acetophenone but leads to a sharp decrease in the extinction coefficient. This behavior of *o*-methylacetophenone generally has been considered to be due to steric interaction between the acetyl group and the adjacent methyl and hydrogen,[28,30] and Braude has interpreted the effect more specifically as due to a decrease in the population of rotational conformations suitable for transition to the excited state responsible for the 245 mμ maximum.[31]

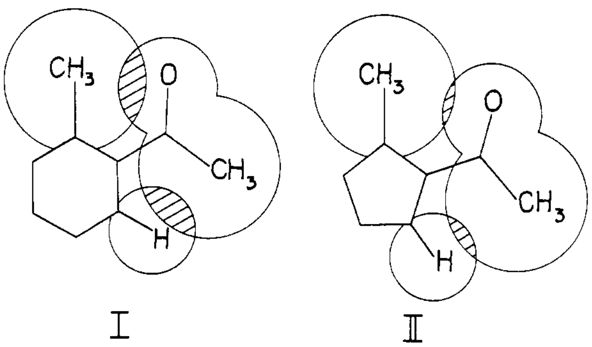


Fig. 1.—Overlap of van der Waals radii between acetyl and adjacent groups in substituted aromatic ketones: I, *o*-methylacetophenone; II, 2-acetyl-1,1′-dimethylferrocene.

In the dialkylferrocenyl ketones the β-isomer shows a slight bathochromic shift and an extinction coefficient little different from that of acetylferrocene. In these properties it resembles *m*-methylacetophenone. However, the α-isomer shows strikingly different behavior from that of *o*-methylacetophenone. Although the peak wave length remains the same as that of acetylferrocene, the coefficient is higher than that of the unsubstituted ketone, rather than lower. Thus in these ultraviolet spectra, as in the acylation isomer ratios, steric effects are not so important as in the corresponding benzene compounds (*cf.* Fig. 1). This is further confirmed by the spectra of the diisopropyl ketones, which are nearly identical to those of the corresponding dimethyl isomers.[32]

Stronger absorption by the α-isomer must be due to electronic influences and may be attributed either to a strong inductive effect or to better hyperconjugative stabilization of the excited state in the α-isomer than in the β-analog (*cf.* above). The longer wave length absorption by the β-isomer is due probably to the greater length of the chromophoric system.

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(26) An attempt was made to direct acetylation more stereospecifically by employing nitrobenzene as a solvent[27]; however, oxidation to the blue-green, water-soluble ferricinium cation was the predominant reaction under these conditions.

(27) G. Baddeley, *J. Chem. Soc.*, S99 (1949).

(28) M. T. O'Shaughnessy and W. H. Rodebush, THIS JOURNAL, **62**, 2906 (1940).

(29) R. Adams and C. R. Noller, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 111.

(30) R. B. Turner and D. M. Voitle, THIS JOURNAL, **73**, 1403 (1951).

(31) For reviews, *cf.* (a) E. A. Braude in "Determination of Organic Structures by Physical Methods," E. A. Braude and F. C. Nachod, eds., Academic Press, Inc., New York, N. Y., 1955, pp. 172–174; (b) E. A. Braude, *Experientia*, **11**, 457 (1955); E. A. Braude and E. S. Waight in "Progress in Stereochemistry," Vol. I, W. Klyne, ed., Academic Press, Inc., New York, N. Y., pp. 144–148.

(32) Although the ultraviolet spectrum of *o*-isopropylacetophenone appears not to have been recorded, it should have a lower extinction coefficient than that of *o*-methylacetophenone since 2,4,6-triisopropylacetophenone has λ_{max} (shoulder) 244 mμ, ϵ_{max} 2,000, while 2,4,6-trimethylacetophenone has λ_{max} 247 mμ, ϵ_{max} 3,500 (ref. 28).

Infrared spectral bands of the ferrocenyl ketones are presented in Table III, again with those of the methyl acetophenones for comparison. From this Table it may be seen that the carbonyl stretching band of the ferrocenyl compounds falls near 1665 cm.$^{-1}$ for all isomers, at a somewhat longer wave length than that of the phenyl analogs. However, there are other characteristic bands which differ for α- and β-isomers but which for each positional isomer occur near the same position for both the dimethyl and diisopropyl compounds. Thus, the aromatic ketone band in the 1300–1250 cm.$^{-1}$ region occurs at lower frequency for the α-substituted compounds than for acetylferrocene itself but at higher frequency for the β-isomer. The spectra of corresponding alkyl acetophenones show a similar shift to higher frequencies for *m*- and *p*-substitution, lower for *o*-. In addition to the ketonic bands there are also bands in the 1000–900 cm.$^{-1}$ region, which has been shown to be highly useful for the characterization of isomeric polyalkylferrocenes.[20] In this region, too, both the dimethyl and diisopropyl compounds show similar bands for each of the positional isomers.

TABLE III

INFRARED BANDS OF FERROCENYL AND PHENYL KETONES

Ketone	ν, cm.$^{-1a}$		
Acetylferrocene	1661	1285	896, 965
2-Acetyl-1,1′-dimethylferrocene	1667	1275	925, 930
3-Acetyl-1,1′-dimethylferrocene	1666	1299	901, 924 940, 966
2-Acetyl-1,1′-diisopropylferrocene	1666	1269	925, 930
3-Acetyl-1,1′-diisopropylferrocene	1666	1280 1285	905, 924 937, 969
Acetophenone	1683	1269	690, 761
o-Methylacetophenone	1682	1254	721, 759
m-Methylacetophenone	1684	1279	690, 786
p-Methylacetophenone	1681	1271	816

[a] Determined as liquid smears or mulls.

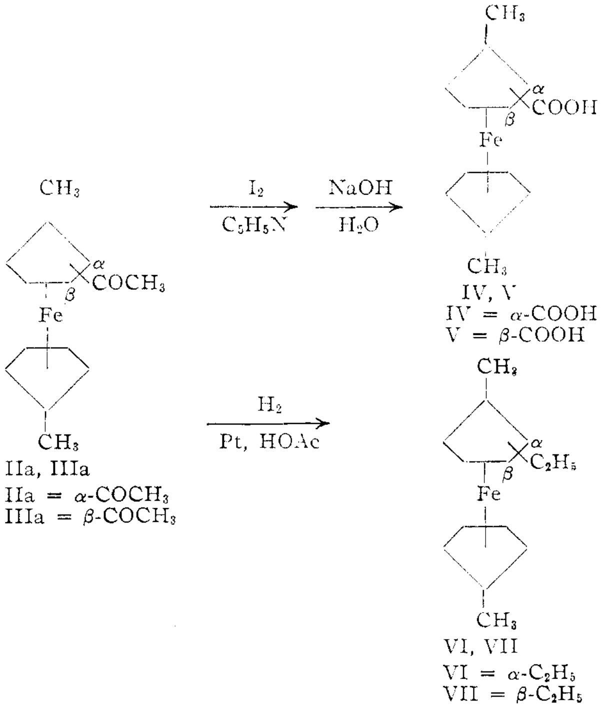
Each of the isomeric acetyldimethylferrocenes (IIa, IIIa) was oxidized by the modified iodoform procedure of Weinmayr[5] to the corresponding carboxylic acid (IV, V). Dissociation constants of the two acids and that of ferrocenecarboxylic acid are presented in Table IV, with those of benzoic and the toluic acids for comparison.

TABLE IV

DISSOCIATION CONSTANTS OF FERROCENE AND BENZENE CARBOXYLIC ACIDS

Acid	*p*Ka′	Solvent
Ferrocenecarboxylic acid	4.4^a 7.3^a 7.26^b	Water 66% DMF 66% ethanol
1,1′-Dimethyl-2-ferrocenecarboxylic acid	5.4^a 8.15^a	Water 66% DMF
1,1′-Dimethyl-3-ferrocenecarboxylic acid	4.7^a 7.5^a	Water 66% DMF
Benzoic acid	4.20^c 7.38^b	Water 66% ethanol
o-Toluic acid	3.91^c	Water
m-Toluic acid	4.24^d	Water
p-Toluic acid	4.34^d	Water

[a] Determined in *ca.* 3×10^{-3} *M* solution. No correction has been applied for the small effect of ionic strength at this low concentration. Aqueous determinations were effected by back-titration of the potassium salts. [b] Ref. 18. [c] J. F. J. Dippy, *Chem. Revs.*, **25**, 151 (1939). [d] G. Briegleb and A. Bieber, *Z. Elektrochem.*, **55**, 250 (1951).



IIa, IIIa

IIa = α-COCH$_3$

IIIa = β-COCH$_3$

IV, V

IV = α-COOH

V = β-COOH

VI, VII

VI = α-C$_2$H$_5$

VII = β-C$_2$H$_5$

Here, as in the ultraviolet spectra of the ketones, the behavior of substituted ferrocenes is considerably different from that of the benzene analogs. While both *m*- and *p*-toluic acids are somewhat weaker acids than benzoic, *o*-toluic acid is stronger than the parent acid (*cf.* Table IV). The anomalous behavior of the *o*-isomer has been attributed by Brown[33] to steric interference toward conjugation between the carboxyl and ring.[34] However, *both* the 2- and 3-methyl-substituted ferrocene acids have lower dissociation constants than the unsubstituted acid, and the α-acid is the weakest of the three. The dissociation constants, then, as the ultraviolet spectra and isomer distribution ratios, support a view of the ferrocene system as being less affected (or at least affected differently) by steric factors than benzene. Electronic factors, either inductive or hyperconjugative, favoring greater electron release by the α-methyl, are probably responsible for the considerably lower dissociation constant of 1,1′-dimethyl-2-ferrocenecarboxylic acid, although an alternative explanation attributing the differences in dissociation constants to decreased solvation of the carboxylate anion[34,35] cannot be ruled out.

(33) H. C. Brown, D. H. McDaniel and O. Häfliger in ref. 31a, p. 603.

(34) Steric interference toward solvation of the carboxylate ion has been discussed by Newman[35] as an opposing effect which serves to lower the dissociation constants of *o*-substituted acids. No attempt is made in the present work to distinguish between the two effects. The principal point to be made is that the ferrocene and the benzene systems sometimes behave differently and that in the present case, the difference is probably due to the steric requirements of the two systems.

(35) H. L. Goering, T. Rubin and M. S. Newman, THIS JOURNAL, **76**, 787 (1954).

The decreased proportion of one isomer formed on acetylation of diisopropylferrocene (as compared to the amount formed on acetylation of dimethylferrocene) argues strongly for the formulation of that as the sterically less favored isomer and thus the α-compound. In addition, the structures assigned to the two isomers have been confirmed by hydrogenation of both acetyldimethylferrocenes (IIa, IIIa) to the corresponding ethyldimethylferrocenes (VI and VII) and comparison of the infrared spectra of the two compounds to those of independently synthesized alkylferrocenes.[20]

The 1000–900 cm.$^{-1}$ region has been shown to contain characteristic bands for the identification of alkyl-substituted ferrocenes.[20] In Table V are presented bands from that region found in the spectra of the present hydrogenation products and those of two previously known polyalkyl ferrocenes, together with other significant bands useful in distinguishing between the two ethyldimethyl isomers.

TABLE V

INFRARED BANDS OF ALKYL FERROCENES

Substituted ferrocene	ν cm.$^{-1a}$								
1,1′-Dimethyl-[b]			812	836	854		923 929		
2,2′-Diethyl-1,1′-dimethyl[b]	694	790	809	823		870		952 967	1207
2-Ethyl-1,1′-dimethyl-	693	790	807	823	850	870	926	949 969	1205
3-Ethyl-1,1′-dimethyl-		790	805 815	840	850		917 926	944	

[a] Determined as liquid smears. [b] Ref. 20.

Thus, 1,1′-dimethylferrocene has a single band in the 1000–900 cm.$^{-1}$ region, near 925 cm.$^{-1}$, while 2,2′-diethyl-1,1′-dimethylferrocene has two bands, at 965 and 950 cm.$^{-1}$. The 2-ethyl-1,1′-dimethylferrocene obtained on reduction of 2-acetyl-1,1′-dimethylferrocene should, then, have a band near 925 cm.$^{-1}$ characteristic of the monosubstituted ring and bands at 965 and 950 cm.$^{-1}$ characteristic of the α-disubstituted ring. As may be seen from Table V, this is indeed the case. The isomeric 3-ethyl compound has no bands at 965 and 950 cm.$^{-1}$, though it has one at 926 cm.$^{-1}$ for the methyl-substituted ring and bands at 917 and 944 cm.$^{-1}$, apparently characteristic of a 1,3-methylethyl disubstituted ring. Similarly, other bands present in the spectrum of 2-ethyl-1,1′-dimethylferrocene (*e.g.*, at 693, 870 and 1205 cm.$^{-1}$), and absent from that of the 3-ethyl- analog are found in the spectrum of 2,2′-diethyl-1,1′-dimethylferrocene.

Experimental[36]

Acetylation of dimethylferrocene was effected with acetic anhydride and aluminum chloride in the usual Friedel–Crafts manner. A mixture of 20.4 g. of 1,1′-dimethylferrocene[20] and 14.6 g. of aluminum chloride in 300 ml. of methylene chloride was cooled in an ice-bath, and 4.72 ml. of acetic anhydride in 25 ml. of methylene chloride was added during 3 hr. The reaction mixture was allowed to stand for 1 hr. at room temperature and was then poured over ice. After the organic phase had been separated and washed, methylene chloride was removed under reduced pressure and the residue was transferred to an alumina column 25-mm. × 120-cm.

After the column had been developed with benzene, the lower yellow band, containing recovered dimethylferrocene, was eluted with *n*-pentane. The upper orange band of acetylated isomers was eluted rapidly with hexane containing 5% methanol and concentrated to give 9.3 g. (72%) of a mixture of acetyldimethylferrocenes. The oil was distilled rapidly under high vacuum; the distillate had λ_{max} 229 mμ, ϵ_{max} 16,400, ϵ_{227} 16,300. From this spectrum and those of the two pure isomers given below the mixture may be estimated to consist of approximately 70% of the 3-acetyl isomer and 30% of the corresponding 2-acetyl isomer. The infrared spectrum of the distilled mixture was identical with that of the oil before distillation.

The orange oil was re-chromatographed in benzene on the same column to give two major fractions and an intermediate portion. The first fraction was concentrated to a red oil, which could be crystallized from *n*-pentane at Dry Ice–acetone temperatures to red crystals of **2-acetyl-1,1′-dimethylferrocene**, m.p. 15–16°. The ultraviolet spectrum of a distilled sample had λ_{max} 227 mμ, ϵ_{max} 17,600.

Anal. Calcd. for $C_{14}H_{16}FeO$: C, 65.65; H, 6.30; Fe, 21.80.[37] Found: C, 66.30; H, 6.65; Fe, 22.01.

The second fraction on concentration also yielded a red oil, which crystallized on standing to orange needles of **3-acetyl-1,1′-dimethylferrocene**, m.p. 48.4–48.6°. The ultraviolet spectrum had λ_{max} 232 mμ, ϵ_{max} 15,800, ϵ_{227} 15,300.

Anal. Calcd. for $C_{14}H_{16}FeO$: C, 65.65; H, 6.30; Fe, 21.80. Found: C, 65.33; H, 6.35; Fe, 22.13.

1,1′-Dimethylferrocene-2-carboxylic acid was prepared by a modification of the procedure of Weinmayr.[5,38] A mixture of 1.0 g. of 2-acetyl-1,1′-dimethylferrocene, 2 ml. of pyridine and 1.1 g. of iodine was agitated for 12 hr. at room temperature, then for 90 min. in a boiling water-bath. The mixture was diluted with aqueous 0.6 *N* sodium hydroxide and stirred for 24 hr. at room temperature, then for 1 hr. on the steam-bath. The mixture was filtered and acidified with glacial acetic acid to precipitate 185 mg. (18%) of 1,1′-dimethylferrocene-2-carboxylic acid. The crude material was dissolved in ether, filtered free of insoluble impurities, extracted into sodium carbonate solution, reprecipitated with hydrochloric acid and finally recrystallized from ether; m.p. 118–118.5° dec.

Anal. Calcd. for $C_{13}H_{14}FeO_2$: C, 60.49; H, 5.43; Fe, 21.64. Found: C, 60.34; H, 5.39; Fe, 21.68.

Potentiometric titration of the acid showed the apparent molecular weight[39] to be 256 ± 5 (theoretical is 260) and yielded the following dissociation constants: pK_a' 8.15 ± 0.05 (66% dimethylformamide, 34% water), pK_a' 5.4 ± 0.1 (water).

1,1′-Dimethylferrocene-3-carboxylic acid was prepared by the same procedure employed for the corresponding 2-carboxylic acid. The yield of crude acid was 373 mg. (37%), and the recrystallized acid had m.p. 106–106.5° dec., apparent molecular weight 258 ± 15, pK_a' 7.5 ± 0.1 (66% DMF), pK_a' 4.7 ± 0.1 (water).

Anal. Calcd. for $C_{13}H_{14}FeO_2$: C, 60.49; H, 5.43; Fe, 21.64. Found: C, 60.44; H, 5.55; Fe, 21.70.

2-Ethyl-1,1′-dimethylferrocene was prepared by reduction of 2-acetyl-1,1′-dimethylferrocene over platinum oxide

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[36] Melting points and boiling points are uncorrected. Fractional distillations were through a 3-ft. Nester whirling band column. Ultraviolet spectra were determined in 95% ethanol in a Beckman model DU spectrophotometer, employing calibrated quartz cells. We are indebted to Mr. Jozsef Nemeth, Mrs. Maria Benassi and Mrs. Ruby Ju for microanalyses and to Mr. James Brader and Mrs. Louise Griffing for infrared spectra. The spectra were obtained for solids in Nujol mulls, for liquids as smears, with a recording Perkin–Elmer infrared spectrophotometer, model 21.

[37] Iron was determined (by J. Nemeth) by the general ashing technique (A. Steyermark, "Quantitative Organic Microanalysis." The Blakiston Co., New York, N. Y., 1951, p. 47), employing sulfuric acid and micro-size samples, ignited to 950°. The ferric oxide residue was weighed to constancy and corrected for surface moisture (previously established for a reliable sample) by deducting 1.5% of its weight.

[38] V. Weinmayr, U. S. Patent 2,683,157 (1954); *C. A.*, **49**, 10364a (1955).

[39] Uncertainty in values of the neutralization equivalents is due to the very small samples available for titration (*e.g.*, sample weight, 2.58 ± 0.05 mg.; volume of titrant, 0.0050 ± 0.0002 ml.).

in a Parr bomb. Hydrogenation, effected in glacial acetic acid under 3.5 atm. pressure, was essentially complete after 24 hr. at room temperature. The product was dissolved in pentane, washed with sodium bicarbonate and separated from ketonic and alcoholic material by chromatography on an alumina column. Concentration of the pentane eluates gave the yellow-brown, liquid 2-ethyl-1,1′-dimethylferrocene.

Anal. Calcd. for $C_{14}H_{18}Fe$: C, 69.44; H, 7.49. Found: C, 69.78; H, 7.79.

3-Ethyl-1,1′-dimethylferrocene was prepared and purified by the procedure described above for the corresponding 2-ethyl isomer.

Anal. Calcd. for $C_{14}H_{18}Fe$: C, 69.44; H, 7.49. Found: C, 69.57; H, 7.76.

Acetylation of 1,1′-diisopropylferrocene was effected by the method described above for acetylation of the corresponding dimethylferrocene. To an ice-cold mixture of 8.75 g. of diisopropylferrocene[20] and 4.86 g. of aluminum chloride in 100 ml. of methylene chloride was added during 1 hr. 1.65 g. of acetic anhydride in 25 ml. of methylene chloride. The resulting mixture was stirred overnight at room temperature and poured over ice. After work-up the concentrated dark brown organic liquid was chromatographed on a 25-mm. × 120-cm. alumina column to give 3.6 g. (41%) of recovered diisopropylferrocene and a total of 4.54 g. (45%) of the isomeric acetyldiisopropylferrocenes, contained in seven fractions. From the weights of the individual fractions it was estimated that the monoacetyl compounds consisted of 17% of the 2-acetyl isomer and 83% of the 3-acetyl analog.

2-Acetyl-1,1′-diisopropylferrocene, obtained from an early chromatography fraction, was purified by distillation and had b.p. 120–125° (0.4 mm.), λ_{max} 226 mμ, ϵ_{max} 18,200, ϵ_{225} 18,000.

Anal. Calcd. for $C_{18}H_{24}FeO$: C, 69.21; H, 7.75. Found: C, 69.53; H, 7.73.

3-Acetyl-1,1′-diisopropylferrocene, obtained from a later chromatographic fraction and purified by distillation, had b.p. 150–155° (1.3 mm.), λ_{max} 231 mμ, ϵ_{max} 15,600, ϵ_{225} 14,300.

Anal. Calcd. for $C_{18}H_{24}FeO$: C, 69.21; H, 7.75. Found: C, 67.58; H, 7.78.

In a second run the above procedure was followed except that the aluminum chloride (1.63 g.) and acetic anhydride (0.572 g.) were added together in 10 ml. of methylene chloride to the diisopropylferrocene (3.0 g.) in 30 ml. of methylene chloride. From the chromatogram 0.65 g. (23%) of diisopropylferrocene was recovered. The acetylated material was removed in one band and distilled to give 0.85 g. (25%) of mixed isomers, b.p. 120–133° (0.8 mm.), λ_{max} 232 mμ, ϵ_{max} 15,500, ϵ_{225} 15,000. From these spectral data and those above for the two pure isomers the proportion of the 2-acetyl compound may be estimated to be 19%, that of the 3-acetyl compound 81%.

Acetylferrocene[40] was prepared by the procedure described above for the acetylation of dimethylferrocene. From 18.6 g. of ferrocene, 14.7 g. of aluminum chloride and 4.73 ml. acetic anhydride there was obtained after chromatography 7.4 g. (65%) of crude acetylferrocene. This material was recrystallized from benzene to give long red needles, m.p. 86–87°, λ_{max} 226 mμ, ϵ_{max} 16,500 (lit. m.p. 85–86°,[5] λ_{max} 225 mμ,[18] ϵ_{max} 14,600[18]).

Ferrocenecarboxylic acid was prepared by the procedure described above for the dimethylferrocenecarboxylic acids, except that the terminal heating of the aqueous sodium hydroxide solution was omitted.[5,33] From 1.0 g. of acetylferrocene there was obtained 0.35 g. (35%) of ferrocenecarboxylic acid, which was recrystallized from chloroform to give crystals which decomposed at 208.5°.[41] Potentiometric titration gave the apparent molecular weight as 250 ± 15 (theoretical is 232) and pK_a' 7.3 ± 0.1 (66% DMF), pK_a' 4.4 ± 0.1 (water) [lit.[18] pK_a' 7.26 (66% ethanol)].

Acetophenone was fractionally distilled; a center cut had b.p. 97–97.5° (14 mm.), $n^{25}{}_D$ 1.5314, λ_{max} 242 mμ, ϵ_{max} 12,000 [lit. b.p. 85.5–86.5° (16 mm.),[30] $n^{20}{}_D$ 1.5338,[42] λ_{max} 242 mμ[30], ϵ_{max} 12,800[30]].

o-**Methylacetophenone**[40] was prepared in 60% yield from the cadmium alkyl reaction from *o*-bromotoluene and acetyl chloride by the method of Cason.[43,44] The fractionally distilled product had b.p. 87–88° (11 mm.), $n^{25}{}_D$ 1.5299, λ_{max} 243 mμ, ϵ_{max} 9,500 [lit. b.p. 93–94° (16 mm.),[30] $n^{20}{}_D$ 1.5320,[42] λ_{max} 243 mμ,[30] ϵ_{max} 8,850[30]].

m-**Methylacetophenone**[40] was prepared from *m*-bromotoluene and acetyl chloride in 45% yield by the same procedure employed for the preparation of *o*-methylacetophenone. The twice fractionally distilled product had b.p. 97–98° (15 mm.), $n^{25}{}_D$ 1.5285, λ_{max} 247 mμ, ϵ_{max} 11,300 [lit.[42] b.p. 109° (12 mm.), $n^{20}{}_D$ 1.5306].

p-**Methylacetophenone** was fractionally redistilled; a center cut had b.p. 99–100° (12 mm.), $n^{25}{}_D$ 1.5317, λ_{max} 252 mμ, ϵ_{max} 15,800 [lit. b.p. 94–95° (12 mm.)[30], $n^{20}{}_D$ 1.5342,[42] λ_{max} 252 mμ[30], ϵ_{max} 15,100[30]].

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(40) We are indebted to Messrs. P. E. Sokol, K. D. Berlin and J. R. Larson for the preparation of these compounds.

(41) Further purification, either by recrystallization from ether or by dissolving in base and reprecipitating with acid, did not alter the melting point behavior, as the pale orange needles still decomposed below 210° and the decomposition point depended upon the rate of heating. Rosenblum[18] has reported decomposition at 210° and Nesmeyanov[7] over the range 195–205°, while Weinmayr[6] gave m.p. 225–230° for this compound.

(42) K. von Auwers, *Ann.*, **408**, 212 (1915).

(43) J. Cason, THIS JOURNAL, **68**, 2078 (1946).

(44) J. Cason and F. S. Prout, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1954, p. 601.