The Use of NMR Spectroscopy as a Structural Probe in Ferrocene Chemistry[1)]

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(Received August 30, 1963)

Electrophilic substitution reactions in the ferrocene systems give rise, in most instances, to complex isomeric mixtures,[2)] such that separation and structural characterization often constitute a perplexing problem. Several methods have been employed for structure determination, of which the most generally useful has proved to be infrared spectroscopy. In particular, the "9, 10μ" Rule[3)] has been an invaluable aid for distinguishing between homoannularly- and heteroannularly-substituted ferrocene derivatives.

Classic methods of structure proof involving either independent syntheses[2)] or degradative (e. g., bromination,[4)] forced catalytic hydrogenation[4,5)] and chemical reduction[6)]) schemes appear to be limited to mono- or symmetrically-substituted ferrocene types. Unequivocal syntheses are hampered by the relative inaccessibility of the appropriately substituted cyclopentadiene (except in the simplest cases),[7)] whereas degradative methods frequently bring about mixtures of substituted cyclopentadienes and cyclopentanes, the structures of which are also frequently unestablished.

Relative yield data[8)] and arguments based on analogy to the benzenoid analogs[9)] have also been offered as evidence in support of structures. Another proposal of practical use has been advanced[10)] that the relative adsorbabilities of disubstituted ferrocenes on the alumina column provided to effect their separation constitute a useful primary indication of structure. Thus, it has been found that, for a variety of alkyl- and arylferrocenes, the order of the elution of isomers from an alumina column is $1,2>1,1'>1,3$.

Ultraviolet spectroscopic data have been

[1)] This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under Contract No. A. F. 49(638)—297. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2)] P. L. Pauson, "Organometallic Chemistry," Ed. by H. Zeiss, Reinhold Publishing Corp., New York, N. Y. (1961).

[3)] a) M. Rosenblum, *Chem. & Ind.*, **1958**, 953; b) M. Rosenblum and R. B. Woodward, *J. Am. Chem. Soc.*, **80**, 5443 (1958).

[4)] A. N. Nesmeyanov, E. G. Perevalova and O. A. Nesmeyanova, *Doklady Akad. Nauk. SSSR*, **100**, 1099 (1955).

[5)] A. N. Nesmeyanov et al., *Izvest. Akad. Nauk. SSSR Otdel. Khim. Nauk.*, 749 (1956).

[6)] D. S. Trifan and L. Nicholas, *J. Am. Chem. Soc.*, **79**, 2746 (1957).

[7)] For example, the symmetrical structure of dibenzoylferrocene was confirmed by conversion to dibenzhydrylferrocene (addition of phenyl Grignard reagent followed by reduction of the tertiary carbinol). The properties of the latter were identical to those of the material prepared from benzhydrylcyclopentadiene, cf. B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, **1956**, 3030.

[8)] K. L. Rinehart, Jr., K. L. Motz and S. Moon, *J. Am. Chem. Soc.*, **79**, 2749 (1957).

[9)] C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **21**, 382 (1956).

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

employed[8,11] to distinguish between homoannular isomers; the absorption for the 2-isomer is more intense, but it appears at a shorter wavelength than that of the 3-isomer.

Recently, it has been suggested that infrared absorptions may serve to define the structures of homoannularly-disubstituted ferrocene derivatives;[12] a 1,3-structure exhibits two bands in the region between 10.8 and 11.2 μ, whereas the 1,2-isomer possesses only one band, near 10.9 μ.

It can be seen from Table VIII,[13] however, that it is difficult to distinguish between the 1,2 and 1,3-structures of the acylalkyl series by a simple application of this generalization.

Another attempted correlation,[14] in which the infrared absorption at 7.80 μ was said to be characteristic of a 1,3-disposition of groups, has been questioned recently.[15] It will be noted from Table VIII that the 1,1′ compounds, as well as several of the 1,2-types, show absorption very near 7.80 μ.

In many cases, a judicious combination of all these methods has been employed.[11] However, relatively little use has been made of NMR spectroscopy to distinguish between various structural types.[16]

It is the purpose of this paper to report that NMR spectroscopy can provide an unequivocal and universal probe for determining the structure of many substituted ferrocenes.

Results and Discussion

In connection with another study[17] we have had occasion to acylate the homologous series of alkylferrocenes. The isomeric acetylmethyl- and acetylethyl-derivatives are known, whereas the isopropyl- and *t*-butyl-derivatives have not yet been reported. Each of these compounds could be conveniently prepared by a modification of the mild acylation procedure described by Hauser and Lindsay.[18] The resulting isomeric acetylalkylferrocenes were separated by column chromatography (Merck neutral alumina). For the methyl, ethyl and isopropyl-derivatives, the course of the separation was conveniently followed by vapor phase chromatographic analysis.[19]

Incomplete resolution of the vapor chromatogram for the mixture of 1,1′- and 1,3-acetyl-*t*-butylferrocenes required that a different criterion of purity be employed (cf. Experimental). Interestingly, the order of the increasing retention times (VPC) of isomers within a given set parallels the order of increasing adsorbability on the alumina column initially employed for their separation, i.e., 1,2-<1,1′< 1,3-acetylalkylferrocene.

A preliminary determination of the chemical shifts[20] for a variety of monosubstituted ferrocenes revealed that the 2- (or 5-) and 3- (or 4-) protons[21] were shielded only slightly by alkyl substituents (ca. 0.09∼0.14 p.p.m. relative to ferrocene), whereas electron-withdrawing substituents (e.g., acetyl, carbomethoxy) displayed a pronounced deshielding effect. These results are analogous to those already described for the benzenoids.[22]

For the homoannular acetylalkylferrocenes, there is one "ortho" proton (relative to the acetyl group) for the 1,2-isomer, whereas for the 1,3-structure there are two such positions. It was reasoned qualitatively that if any small shielding effects imposed by alkyl groups were outweighed by the more substantial deshielding effect caused by electronegative functions, NMR spectroscopy should provide a useful probe for elucidating homoannular positional isomers. That this indeed proved to be the case is convincingly demonstrated by the data in Table I. (See also the N.M.R. illustrations.)

All 1-acetyl-1′-alkylferrocenes exhibit similar patterns for the ring protons.[23] When the

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[11] K. L. Rinehart, Jr., D. E. Bublitz and D. H. Gustafson, ibid., **85**, 970 (1963).

[12] M. Rosenblum and W. G. Howells, ibid., **84**, 1167 (1962).

[13] This table summarizes all the characteristic infrared absorption bands for the acylalkylferrocenes we have prepared and characterized.

[14] A. N. Nesmeyanov, L. A. Kazitsyna, B. V. Lokshin and V. D. Vil'chevskaya, *Doklady Akad. Nauk. SSSR*, **125**, 1037 (1959).

[15] Ref. 12 and E. W. Neuse and D. S. Trifan, *J. Am. Chem. Soc.*, **85**, 1952 (1963).

[16] K. L. Rinehart et al. (*J. Am. Chem. Soc.*, **82**, 4111 (1960).) made use of this method, as did M. Rosenblum et al. (*J. Am. Chem. Soc.*, **85**, 316 (1963).), to study the conformation of alkyl-bridged ferrocenes. Apparently the only use of NMR to distinguish between homoannularly-substituted isomers is the recent report by Rinehart and his coworkers, which was contemporaneous with our preliminary communication. [R. A. Benkeser, Y. Nagai and J. Hooz, This Bulletin, **36**, 482 (1963).].

[17] R. A. Benkeser, Y. Nagai and J. Hooz, *J. Am. Chem. Soc.*, to be prepared.

[18] C. R. Hauser and J. K. Lindsay, *J. Org. Chem.*, **22**, 482 (1957).

[19] There is relatively little mention in the literature of the use of VPC for ferrocene compounds. Perhaps the reason for such an aversion resides in the fact that ferrocene and many of its derivatives are solids. That such a view is unwarranted is clearly demonstrated by the successful analysis of numerous ferrocene compounds in our laboratory.

[20] The nuclear magnetic resonance spectra were determined in a carbon tetrachloride solution employing a Varian A-60 spectrometer. Tetramethylsilane served as an internal standard. Chemical shifts are reported to the estimated center of a singlet or multiplet. Peak areas were determined by electronic integration.

[21] The 2- (or 5-) and 3- (or 4-) protons represent the positions "ortho" and "meta" to the substituent. In the discussion of the spectra of acetylalkylferrocenes presented below, the acetyl group is assigned position one.

[22] L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, New York, N. Y. (1959).

TABLE I. CHEMICAL SHIFTS FOR THE RING PROTONS OF SUBSTITUTED FERROCENES[1,2]

Substituent	*a*[3]	*b*[4]	*c*[5]	*d*[6]
H (ferrocene)	—	—	5.94	—
Me	—	—	6.01(7)	6.06(2)
Et	—	—	5.99(5)	6.03(4)
i-Pr	—	—	5.98(5)	6.04(4)
t-Bu	—	—	5.98(5)	6.08(4)
Ac (acetyl)	5.33(2)	5.64(2)	5.88(5)	—
1-Ac-1′-Me	5.42(2)	5.70(2)	—	6.01(4)
1-Ac-2-Me	5.56(1)	5.72(1); 5.82(1)	5.95(5)	—
1-Ac-3-Me	5.40(2)	5.69(1)	5.92(5)	—
1-Ac-1′-Et	5.41(2)	5.69(2)	—	5.99(4)
1-Ac-2-Et	5.53(1)	5.69(1); 5.79(1)	5.93(5)	—
1-Ac-3-Et	5.37(2)	5.69(1)	5.91(5)	—
1-Ac-1′-*i*-Pr	5.39(2)	5.66(2)	—	5.98(4)
1-Ac-2-*i*-Pr	5.51(1)	5.64(1); 5.76(1)	5.92(5)	—
1-Ac-3-*i*-Pr	5.41(2)	5.71(1)	5.91(5)	—
1-Ac-1′-*t*-Bu	5.32(2)	5.61(2)	—	5.98(4)
1-Ac-2-*t*-Bu	5.46(1)	5.71(1); 5.79(1)	5.85(5)	—
1-Ac-3-*t*-Bu	5.43(2)	5.72(1)	5.90(5)	—

1) The data listed are "tau" values, using tetramethylsilane as an internal standard.
2) The values in parentheses are relative intensities. All measurements were made on a Varian A-60 analytical spectrometer.
3) Column "*a*" values refer to the H in the 2- and 5-position relative to the acetyl group.
4) Column "*b*" values refer to the H in the 3- and 4-position relative to the acetyl group.
5) Column "*c*" values refer to the H on an unsubstituted ring.
6) Column "*d*" values refer to the H on an alkylated ring.

spectrum of acetyl- and the appropriate alkylferrocene is inspected, it may be seen that the only reasonable assignment for the ring protons of 1, 1′-isomers is to ascribe the two low-field resonances (each of an intensity of two) to the acetylated ring. The lower resonance (column a, Table I) is due to 2- and 5-H (relative to the acetyl group), and the higher field triplet, to 3- and 4-H. Within this set, the alkylated ring protons possess chemical shifts that are only slightly different from the alkylated ring protons of the parent alkylferrocene.

Unsubstituted ring protons of all 1-acetyl-2-alkylferrocenes are singlets, exhibiting a deshielding order from methyl (5.95 tau) through *t*-butyl (5.85 tau). Of greater interest to the present investigation, however, was the appearance of the disubstituted ring protons as three complex peaks, indicating three non-equivalent protons. The most deshielded multiplet (column a, Table I) was reasonably assigned to 5-H, by analogy with acetylferrocene itself. The high-field multiplet (column b, Table I, higher entries) was assigned to 3-H by inspection of the alkylated ring protons of the parent alkylferrocene, whereas the mid-field multiplet (the lower of the two tau values in column b, Table I) was assigned to 4-H. The general appearance of three complex peaks of the intensity 1 : 1 : 1[24] was in itself diagnostic of a 1, 2-disubstituted ferrocene, bearing an alkyl and an electronegative moiety.

Furthermore, clinching evidence in support of these assignments is provided by the model have space compound, 1, 2-(α-ketotetramethylene)-ferrocene.[25] Infrared absorptions at 9 and 10 μ eliminate the possibility of the 1, 1′-structure, and a 1, 3-disposition is seemingly impossible on structural grounds. The NMR spectrum showed three peaks[26] on the low-field side of the unsubstituted ring (intensities 1 : 1 : 1); this is in complete agreement with the above assignments for the 1-acetyl-2-alkylferrocenes. In this instance, any structural assignments based upon only infrared generalizations might prove ambiguous, as will be shown later (Table VIII).

The 1, 3-structures presented an entirely different NMR pattern. The spectra of all

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23) We are concerned here only with ring proton spectra. The alkyl groups behaved normally, although it should be mentioned that the gem-dimethyl groups of the 1-acetyl-2-isopropylferrocene displayed two nonequivalent methyl groups, each split into a doublet by the methine hydrogen.

24) Alternatively, since the shoulders of the 3-H multiplets were frequenly hidden under the wings of the 4-H multiplet, one may consider the intensities as 1 : 2 (in order of increased shielding). The difference in chemical shifts between 5-H and 4-H was greater than that between 4-H and 3-H (see in particular the 1-acetyl-2-*t*-butyl entry).

25) K. L. Rinehart, Jr., et al., *J. Am. Chem. Soc.*, **84**, 3263 (1962).

26) The tau values obtained in a carbon tetrachloride solution are 5.28 (5-H), 5.60 (4-H), 5.66 (3-H), 5.88 (unsubstituted ring protons), and 7.68 (-CH_2-).

1, 3-isomers displayed two peaks on the low field side of the respective unsubstituted ring in the ratio of 2 : 1. (The peak of intensity 2 was in all cases more deshielded than the intensity 1 peak.) Each peak appeared as an unresolved multiplet. In these isomers there are two unsubstituted positions adjacent to an acetyl group, the other position being adjacent only to an alkyl function. There can be little doubt, therefore, that the peaks of intensity 2 correspond to the two protons (2-H and 5-H) adjacent to the acetyl group. The somewhat higher-field peak (intensity 1) is due to 4-H. The latter proton for each 1, 3-isomer possesses a chemical shift not widely different from the 4-H of the corresponding 1, 2-isomer.

These structural assignments receive further support from the trend of the chemical shifts of the α-protons of the alkyl groups attached to the ferrocene ring (see Table II). It may be seen from the table that the frequencies for the α-protons of the 1, 1′-isomers are only slightly different from those of the respective parent hydrocarbons.

TABLE II. CHEMICAL SHIFTS FOR α-PROTONS[1] OF ALKYL GROUPS ON FERROCENE RINGS[2–4]

Substituent	α-H(Me)	α-H(Et)	α-H(*i*-Pr)
R (alkyl)	8.04	7.71	7.41
1-Ac-1′-R	8.09	7.73	7.43
1-Ac-2-R	7.67	7.28	6.59
1-Ac-3-R	7.97	7.62	7.34

1) The α-protons referred to in this table are those located on the carbon atom of the alkyl group which is attached to the ferrocene ring.
2) The data listed are " tau " values, using tetramethylsilane as an internal standard. A Varian A-60 analytical spectrometer was used for all the measurements.
3) Ac in the table refers to the acetyl group.
4) The spectra of all the compounds listed in this table, as well as all those in Table I, were obtained in a solvent of carbon tetrachloride.

For the homoannularly-substituted acetylmethylferrocenes, the α-proton of one isomer is deshielded 0.37 p. p. m., whereas that of the other is deshielded 0.07 p. p. m. (relative to methylferrocene). Consequently, due to the shielding effect on the α-protons induced by their proximity to the acetyl group, the former isomer must possess the 1, 2-, and the latter, the 1, 3-structure.

The same trends are manifest for the homoannularly-substituted acetylethyl- and acetylisopropylferrocenes, the largest deshielding (relative to the corresponding alkylferrocene) occurring for the 1, 2-isomer.

Interestingly enough, it was observed that the chemical shifts for ring protons of those acetylalkylferrocenes could be calculated with a reasonable degree of accuracy (average deviation : 0.04 p. p. m.) employing a simple additivity relationship[27] akin to that developed by Shoolery[28] for acyclic systems.

Shielding constants, measuring the effect of a substituent at a given position (in a given solvent),[29] are tallied relative to the chemical shift for the ring protons of ferrocene itself in Table III.

It is evident from Table I that an acetyl group deshields " ortho " hydrogens by -0.61 p.p.m. and " meta " hydrogens by -0.30 p.p.m. The alkylated ring protons of isopropylferrocene appear as a singlet at 6.04 tau, so that an isopropyl group shields both " ortho " and " meta " hydrogens by $+0.10$ p.p.m. A set of shielding constants calculated in this manner appears in Table III. Using these values, a chemical shift for the ring protons of an acetyl-isopropylferrocene may be calculated. For example, the 5-H resonance of the 1, 3-isomer is obtained from: $5.94+(-0.61+0.10)=5.43$ tau (versus 5.41 tau, observed). Tables IV to VII list predicted and observed tau values for the ring protons in the acetylalkylferrocenes,

TABLE III. SHIELDING CONSTANTS (p.p.m.)

Group	2-Position	3-Position	1′-Position
Me	+0.12	+0.07	+0.07
Et	+0.09	+0.09	+0.05
i-Pr	+0.10	+0.10	+0.04
t-Bu	+0.14	+0.14	+0.04
Ac	−0.61	−0.30	−0.06
CO_2Me[a]	−0.66	−0.21	−0.07

a) Carbomethoxyferrocene absorbs at 5.28 tau (2- and 5-H) ; 5.73 tau (3- and 4-H) and 5.87 tau (the unsubstituted ring protons).

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[27] A simple additivity rule was also observed for various alkylcarbomethoxy and alkyldicarbomethoxyferrocenes, the NMR spectra of which will be described later.

[28] Ref. 22, p. 59.

[29] The simple additivity observed and the conclusions drawn are to be considered limited to carbon tetrachloride solutions. NMR spectra of acetylalkylferrocenes were also determined in benzene solvent, which proved far less satisfactory than carbon tetrachloride. In general, chemical shifts were higher in benzene. The spectra of all the 1, 3-isomers possessed the 2 : 1 intensities of substituted ring protons already noted in carbon tetrachloride. However, the greater differential shielding (in benzene) caused an overlap of 4-H and 5-H for the 1, 2-isomes when R= *i*-Pr and *t*-Bu; consequently, the 1, 2-structure also displayed a 2 : 1 intensity relationship in the region of interest, which could lead to ambiguity. For this reason, carbon tetrachloride is the preferred solvent. Since the proton frequencies are solvent-dependent, no general conclusions regarding the additivity of substituent effects may as yet be drawn. It is not unreasonable, however, to employ shielding constants characteristic of substituents in a given solvent as a first approximation. This approach has been used by Taft et al. (*J. Am. Chem. Soc.*, **85**, 709 (1963).) to determine substituent constants in a study of the NMR spectra of meta-substituted fluorobenzenes.

TABLE IV. COMPARISON OF PREDICTED AND OBSERVED τ-VALUES FOR RING PROTONS OF 1-ACETYL-2- and -3-ALKYLFERROCENES AND 1,1′-DICARBOMETHOXY-2- AND 3-ALKYLFERROCENES

Compound	2-Proton		3-Proton		4-Proton		5-Proton	
	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
1-Ac-2-Me	—	—	5.76	5.82	5.71	5.72	5.40	5.56
1-Ac-3-Me	5.45	5.40	—	—	5.76	5.69	5.40	5.40
1-Ac-2-Et	—	—	5.73	5.79	5.73	5.69	5.42	5.53
1-Ac-3-Et	5.42	5.37	—	—	5.73	5.69	5.42	5.37
1-Ac-2-*i*-Pr	—	—	5.74	5.76	5.74	5.64	5.43	5.51
1-Ac-3-*i*-Pr	5.43	5.41	—	—	5.74	5.71	5.43	5.41
1-Ac-2-*t*-Bu	—	—	5.78	5.79	5.78	5.71	5.47	5.46
1-Ac-3-*t*-Bu	5.47	5.43	—	—	5.78	5.72	5.47	5.43
2-Me-1,1′-DCM[a)]	—	—	5.78	5.74	5.73	5.74	5.28	5.35
3-Me-1,1′-DCM[b)]	5.33	5.31	—	—	5.78	5.74	5.28	5.31
2-Et-1,1′-DCM	—	—	5.75	5.78	5.75	5.78	5.30	5.33
3-Et-1,1′-DCM	5.30	5.30	—	—	5.75	5.74	5.30	5.30
3-*i*-Pr-1,1′-DCM	5.31	5.35	—	—	5.76	5.76	5.31	5.35
3-*t*-Bu-1,1′-DCM	5.35	5.31	—	—	5.80	5.75	5.35	5.31

a) DCM = dicarbomethoxy

b) Sample calculation: $\tau(2)=5.94+[\sigma(\text{2-CM})+\sigma(\text{2-Me})+\sigma(\text{h-CM})]=5.94+[-0.66+0.12-0.07]=5.94-0.61=5.33$. In all the dicarbomethoxy compounds the effect of the heteroannular carbomethoxy group is taken into account.

TABLE V. PREDICTED AND OBSERVED τ-VALUES FOR HOMOANNULAR-SUBSTITUTED ACETYLALKYLFERROCENES[a)]

Compound	1′-Proton	
	Calcd.	Obs.
1-Ac-2-Me	5.95	5.95
1-Ac-3-Me	5.95	5.92
1-Ac-2-Et	5.93	5.93
1-Ac-3-Et	5.93	5.91
1-Ac-2-*i*-Pr	5.92	5.92
1-Ac-3-*i*-Pr	5.92	5.91
1-Ac-2-*t*-Bu	5.92	5.85
1-Ac-3-*t*-Bu	5.92	5.90

a) For these compounds, all protons of the unsubstituted ring appear as a singlet and are simply designated as 1′-.

and in several 1,1′-dicarbomethoxy-2- and 3-alkylferrocenes.[30)]

This very simple but valuable method of prediction should serve as a useful guide for the elucidation of many other ferrocene derivatives.

Summary

All of the acetylalkylferrocenes have been synthesized and obtained in a highly pure state. The infrared and NMR spectrum of each of these compounds has been determined, and the results tabulated.

It has been shown that NMR spectroscopy provides a convenient tool in elucidating the structure of substituted ferrocenes. It is particularly useful in distinguishing between 1,2- and 1,3-disubstituted structures, a situation where infrared has its greatest limitations.

A series of shielding constants has been developed for a variety of ferrocene substituents. These enable one to predict with considerable precision the chemical shifts of a variety of protons bonded to the ferrocene nucleus.

Experimental

Alkylferrocenes.—These materials were prepared by procedures described elsewhere.[31)]

Acetylferrocene.—This was prepared following the directions of Hauser and Lindsay,[18)] with the exception that boron fluoride-etherate was used instead of the boron fluoride-ethyl acetate complex.

Acetylation of Alkylferrocenes.—The acetylation procedure was identical for all alkylferrocenes. A solution of 0.05 mol. of the appropriate alkylferrocene and 10.2 g. (0.1 mol.) of acetic anhydride in 100 ml. of methylene chloride was cooled to 0°C. To this solution was added 21.3 g. (0.15 mol.) of boron fluoride-etherate with stirring. A nitrogen sweep was employed throughout. The mixture was stirred at 0°C for 30 min. and at room temperature for 2 hr. The contents of the flask were decomposed with water and extracted with methylene chloride. The organic layer was dried over calcium chloride. The residue obtained after removal of

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30) The observed values for the latter compounds are taken from the Ph. D. thesis of J. L. Bach, Purdue University, June, 1963.

31) R. A. Benkeser and J. L. Bach, *J. Am. Chem. Soc.*, **85** (1963), in press.

32) E. A. Hill and J. H. Richards. ibid., **83**, 4216 (1961).

Table VI. Predicted and observed τ-values for the alkyl- and acetyl rings of 1-acetyl-1′-alkylferrocenes

Compound	Alkyl ring protons		Acetyl ring protons			
			2=5		3=4	
	Calcd.	Obs.	Calcd.	Obs.	Calcd.	Obs.
1-Ac-1′-Me	6.00[a]	6.01	5.40	5.42	5.71	5.70
1-Ac-1′-Et	5.97	5.99	5.38	5.41	5.69	5.69
1-Ac-1′-*i*-Pr	5.98	5.98	5.37	5.39	5.68	5.66
1-Ac-1′-*t*-Bu	6.02	5.98	5.37	5.32	5.68	5.61

a) The H atoms in the 2-position were used in this calculation.

Table VII. Predicted and observed τ-values for 1, 1′-dicarbomethoxy-2- and 3-alkylferrocenes

Compound	2′-Proton		3′-Proton	
	Calcd.	Obs.	Calcd.	Obs.
2-Me-1, 1′-DCM[a]	5.28	5.35	5.73	5.74
3-Me-1, 1′-DCM	5.28	5.31	5.73	5.74
2-Et-1, 1′-DCM	5.26	5.33	5.71	5.78
3-Et-1, 1′-DCM	5.26	5.30	5.71	5.74
3-*i*-Pr-1, 1′-DCM	5.25	5.35	5.70	5.76
3-*t*-Bu-1, 1′-DCM	5.25	5.31	5.70	5.75

a) DCM=dicarbomethoxy

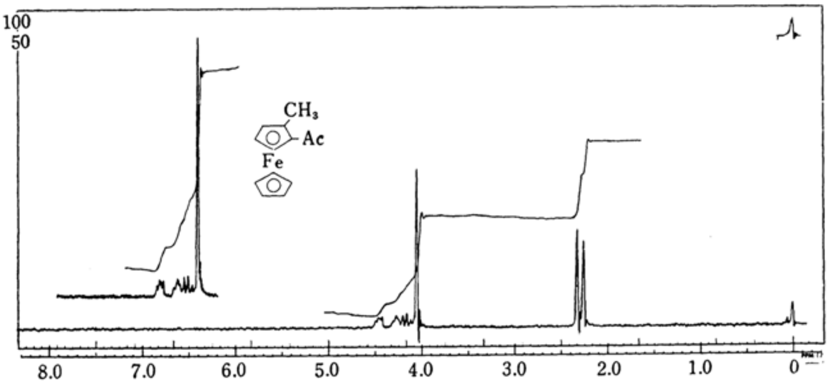

Fig. 1.

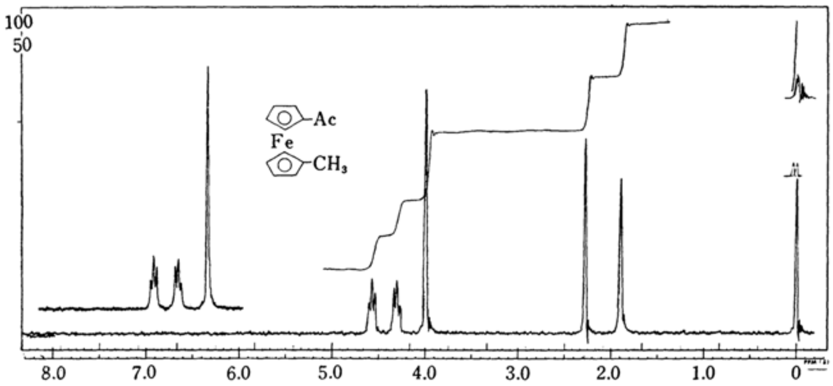

Fig. 2.

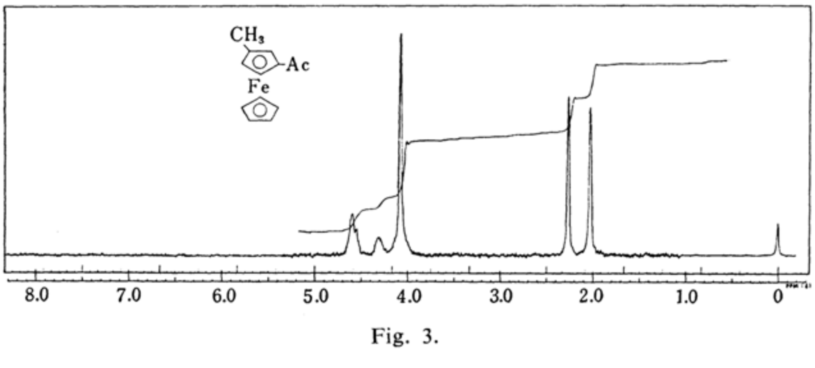

Fig. 3.

TABLE VIII. THE INFRARED SPECTRA OF ACYLFERROCENES (μ)[a, b]

Substituent	Characteristic absorptions[c, d]					
Ac	11.19(s)	—	9.96(s)	9.01(s)	8.98(s)	7.81(s)
1-Ac-1′-Me	11.23(m)	10.85(m)	—	—	8.96(m)	7.82(s)
1-Ac-2-Me	11.17(w)	10.72(s)	9.96(s)	9.05(s)	—	7.85(s)
1-Ac-3-Me	11.05(m)	10.69(w)	9.95(s)	9.05(s)	—	7.70(s)
1-Ac-1′-Et	11.20(m)	11.02(m)	—	—	8.97(s)	7.82(s)
1-Ac-2-Et	11.21(w)	10.80(s)	9.98(s)	9.04(s)	—	7.87(s)
1-Ac-3-Et	11.10(s)	10.88(m)	9.97(s)	9.04(s)	—	7.75(s)
1-Ac-1′-*i*-Pr	11.20(s)	10.86(m)	—	—	8.97(s)	7.82(s)
1-Ac-2-*i*-Pr	—	10.77(s)	9.96(s)	9.02(s)	—	7.90(s)
1-Ac-3-*i*-Pr	11.10(s)	10.70(m)	9.96(s)	9.03(s)	—	7.80(s)
1-Ac-1′-*t*-Bu	11.20(s)	11.00(s)	—	—	8.97(s)	7.85(s)
1-Ac-2-*t*-Bu	11.25(w)	10.83(s)	9.95(s)	9.01(s)	—	8.02(s)
1-Ac-3-*t*-Bu	11.11(s)	10.83(w)	9.95(s)	9.05(s)	—	8.05(s)
1,2-(α-Ketotetramethylene)	11.22(m)	—	9.96(s)	9.02(s)	—	7.80(s)

a) Spectra of crystalline materials were determined as Nujol mulls, those of liquids, as capillary films. A Perkin-Elmer Model 221 spectrophotometer was used.

b) s = strong, m = medium, w = weak

c) Rosenblum's correlations (Ref. 12) hold with a slight modification. Actually, in most cases, both the 1,2- and 1,3-isomers exhibit two bands in the region between 10.7 and 11.25 μ. It may be said, however, that for these bands a stronger absorption appears at a shorter wavelength with the 1,2-structure, while with a 1,3-disposition a more intense peak lies at a higher wavelength. An exceptional case is 1,2-(α-ketotetramethylene)-ferrocene.

d) The "9, 10 μ" rule holds in every case.

the solvent was chromatographed on an alumina (Merck, neutral grade) column.

The development and elution of methylacetyl-isomers were carried out with pentane-ether mixtures (approximately 1 : 1 by volume). A faster moving band was separated from the major band. The first compound eluted was 1-acetyl-2-methylferrocene (1.34 g.) (m. p. 62.5～63.5°C) (lit.[32]) 62.2～63.2°C).

Found: C, 64.82; H, 5.77; Fe, 23.39. Calcd. for $C_{13}H_{14}OFe$: C, 64.49; H, 5.83; Fe, 23.07%.

The second isomer eluted from the column was 1-acetyl-1′-methylferrocene (2.74 g.) (m. p. 42～43°C) (lit.[32]) 42.7～43.2°C). Found: C, 64.45; H, 5.75; Fe, 23.30%.

The third isomer eluted from the column was 1-acetyl-3-methylferrocene (1.16 g.) (m. p. 61.5°C) (lit.[32]) 57.5～61.5°C). Found: C, 64.54; H, 6.00; Fe, 23.30%.

The ethylacetyl-isomers were separated in the same manner as above. The first compound eluted was 1-acetyl-2-ethylferrocene (0.94 g.) (m. p. 44.5°C) (lit.[3b]) 42.5～44.5°C).

The second isomer eluted from the column was 1-acetyl-1′-ethylferrocene (1.59 g.) (b. p. 128°C/0.2 mmHg) (lit.[3b]) m. p. 12.5～13.2°C).

Found: C, 65.97; H, 6.24; Fe, 21.56. Calcd. for $C_{14}H_{16}OFe$: C, 65.65; H, 6.30; Fe, 21.80%.

The third isomer eluted from the column was 1-acetyl-3-ethylferrocene (0.55 g.) (b. p. 144°C/0.8 mmHg) (lit.[3b]) m. p. 11.6～12.6°C). Found: C, 66.13; H, 6.69; Fe, 22.19%.

The separation of the isomeric acetyl-isopropylferrocenes was more laborious than that of the methyl- or ethyl-acetyl analogs. Using a pentane-ether (ca. 9 : 1 by volume) mixture, a faster-moving band could be separated from the major broad band. The first compound eluted was 1-acetyl-2-isopropylferrocene (1.03 g.) (b. p. 145°C/1 mmHg).

Found: C, 67.21; H, 7.00; Fe, 21.10. Calcd. for $C_{15}H_{18}OFe$: C, 66.69; H, 6.71; Fe, 20.67%.

Elution was continued using a pentane-ether mixture, gradually enriching the ether content. The major band became broader than it was at the beginning, but no discrete bands were formed. Thus, ten fractions of ca. 100 ml. each were taken. The separation was conveniently checked by VPC (F and M Model 500 vapor fractometer; DEGS column; 15 feet × 1/4 inch; 215°, at a flow rate of helium of 60 ml./min.). From the first two cuts 1-acetyl-1′-isopropylferrocene (2.04 g.) was obtained (b. p. 146°C/1 mmHg.). Found: C, 66.60; H, 6.25; Fe, 20.43%.

From fractions 9 and 10 1-acetyl-3-isopropylferrocene (0.99 g.) was obtained (b. p. 143°C/1 mmHg). Found: C, 66.81; H, 6.61; Fe, 20.90%.

The separation of the *t*-butylacetylferrocenes (1,1′- and 1,3-isomers) was accomplished only with great difficulty. Elution with pentane-ether mixtures (ca. 9 : 1 by volume), gradually enriching the ether content, developed a discrete, faster-moving band, followed by a broad and unresolved major band. The first compound eluted was 1-acetyl-2-*t*-butylferrocene (0.38 g.) (m. p. 99～100°C).

Found: C, 67.83; H, 7.19; Fe, 19.55. Calcd. for $C_{16}H_{20}OFe$: C, 67.62; H, 7.09; Fe, 19.65%.

No discrete separation of the major band could be effected. A total of ten fractions were taken of ca. 100 ml. each. The course of the separation in this instance could not be followed by vapor phase chromatographic analysis, since a wide variety of column materials proved ineffective in separating the 1,1′- and 1,3-isomers. A method based on infrared spectroscopy was employed. Earlier fractions were characteristically devoid of the "9, 10μ" absorption bands. This indicated the presence of 1,1'-disubstituted products. Although these fractions did possess strong absorption bands at 7.85 and 8.97 μ, they had no absorption at 8.0 μ.[33] The first four fractions were combined and rechromatographed in the same manner. From the latter first fraction 1-acetyl-1'-*t*-butylferrocene (1.22 g.) was isolated (b. p. 144°C/3 mmHg). Found: C, 67.15; H, 7.02; Fe, 19.99%.

The middle fractions of the original chromatograph possessed an infrared absorption at 7.85 μ, but a band started appearing at 8.0 μ. The "9, 10 μ" bands also started appearing, with the 9 μ band possessing a shoulder on the low wavelength side. The last fractions taken indicated the total disappearance of the 7.8 μ band, but a strong absorption at 8.05 μ. The "9,10 μ" bands appeared at 9.05 and 9.95 μ respectively. In this manner there was obtained 3.09 g. of 1-acetyl-3-*t*-butylferrocene, melting at 83.5~84.5°C. Found: C, 67.77; H, 7.00; Fe, 19.59%.

1,2-(α-Ketotetramethylene)-ferrocene. — This compound was prepared according to the directions of Rinehart and his coworkers[25] (m. p. 86~87°C) (lit.[25] 87.5~88.5°C).

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[33] The correlation of 10.8 and 11.2 μ bands for a 1,3-disposition of substituents[12] could not be employed since the 1,1'-structure absorbs in this region.