The Importance of NMR in Determining Structure and Electrical Effects in Substituted Ferrocenes[1]

By Robert A. BENKESER, Yoichiro NAGAI and John HOOZ

(Received December 24, 1962)

The determination of the structure of polysubstituted ferrocenes has proved to be a vexing problem. Classic methods of structure proof based upon unequivocal syntheses or degradations are not often feasible in the case of substituted ferrocenes. The ferrocene moiety is quite stable, and, while degradation of the molecule is possible, generally rather drastic conditions must be employed[2]. The result is usually a mixture of products which contains substituted cyclopentadienes and cyclopentanes, the structures of which are also frequently in doubt. Likewise the unequivocal synthesis

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 H on an alkylated ring.

---

[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] A. N. Nesmeyanov, E. G. Perevalova and R. V. Galovnya, *Bull. Acad. Sci. U. S. S. R., Div. Chem. Sci.*, 749 (1956); D. S. Trifan and L. Nicholas, *J. Am. Chem. Soc.*, 79, 2746 (1957).

of a polysubstituted ferrocene is not easily accomplished. Isomeric mixtures are almost invariably encountered which are difficult and tedious to separate³⁾.

As a result of the synthetic problems associated with structure proofs in this field, considerable reliance has been placed upon infrared spectroscopy⁴⁾ for determining the structure of substituted ferrocenes. While infrared is extremely useful in determining the structure of certain ferrocene compounds, there is considerable need for a more unequivocal and universal structural probe. It is the purpose of this paper to report that NMR spectroscopy will provide such a probe in many instances.

Table I lists the chemical shifts and relative intensities for the ring protons of seventeen substituted ferrocene compounds. It is immediately apparent from this table that the structure of the mono-, as well as the disubstituted ferrocenes (1, 1'- as well as 1, 2- and 1, 3-) are clearly pinpointed by the chemical shifts of the ring protons. In addition to establishing the ferrocene structures, the values in Table I can be used also as a measure of the electrical effects of substituent groups at various positions in the ferrocene ring system, a topic of considerable current interest⁵⁾.

TABLE II. CHEMICAL SHIFTS FOR α-PROTONS¹⁾ OF ALKYL GROUPS ON FERROCENE RINGS²⁻⁴⁾

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 in Table I were obtained in a solvent of carbon tetrachloride.

The structural assignments for the acetylalkylferrocenes listed in Table I are further supported by the trend of the chemical shifts for the α-protons of the various alkyl groups attached to the ferrocene ring (see Table II).

Thus the α-protons in 1-acetyl-1'-alkylferrocenes are at higher field than the 1, 3-isomers. The latter, in turn, are at higher field than the 1, 2-isomers. This trend can be rationalized in terms of the shielding effect on the α-protons induced by their proximity to the electron withdrawing acetyl group.

Department of Chemistry
Purdue University
W. Lafayette, Ind.
U. S. A.

---

3) Indicative of the problems in this area is a recent article (M. Rosenblum, *J. Am. Chem. Soc.*, **81**, 4530 (1959)) which reports the relative adsorbabilities of certain isomeric disubstituted ferrocenes on alumina. This was offered (and rightly so) as a useful primary indication of structure.

4) M. Rosenblum, *Chem. & Ind.*, **1958**, 953; *J. Am. Chem. Soc.*, **81**, 4530 (1959); K. L. Rinehart, K. L. Motz and S. Moon, ibid., **79**, 2749 (1957).

5) A. N. Nesmeyanov and O. A. Reutov, *Doklady Akad. Nauk., S. S. S. R.*, **115**, 518 (1957); W. F. Little and R. Eisenthal, *J. Org. Chem.*, **26**, 3609 (1961); *J. Am. Chem. Soc.*, **83**, 4936 (1961); M. Rosenblum and W. G. Howells, ibid., **84**, 1167 (1962).