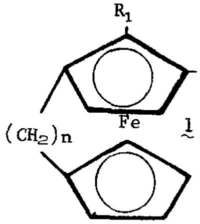
Tetrahedron Letters No. 19, pp. 1593-1594, 1970. Pergamon Press. Printed in Great Britain.

FERROCENOPHANES: NMR SPECTRA[1] OF MONOACYLFERROCENOPHANES

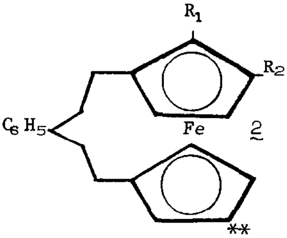
George J. Gauthier[2], Jack A. Winstead and A. D. Brown, Jr.
The Frank J. Seiler Research Laboratory
Office of Aerospace Research
USAF Academy, Colorado 80840

(Received in USA 9 February 1970; received in UK for publication 19 March 1970)

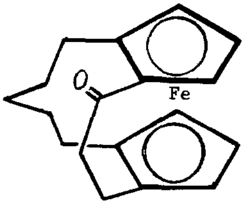
We recently prepared a series of monoacylferrocenophanes[3] **1** and **2** for further syntheses and have noted some interesting and useful features of the NMR spectra of these compounds which others apparently have not considered. Two regions of the NMR spectrum help to indicate the position of an acyl group with respect to the interannular bridge. In **1a** - **1h** only two monoacyl derivatives exist for each value of n because of conformational mobility of the unsubstituted bridge. These acyl groups can be adjacent (α) to the bridge or one ring position removed (β). In **2**, the phenyl group causes the bridge to assume a stable preferred conformation so that two α- and two β-isomers exist[3].



1



2



3

Cmpd	n	R_1*	R_2*	Cmpd	n	R_1	R_2
1a[4]	3	Ac	H	**1e**[3]	4	Ac	H
1b[4]	3	H	Ac	**1f**[3]	4	H	Ac
1c[3]	3	Cin	H	**1g**[3]	5	Ac	H
1d[3]	3	H	Cin	**1h**[3]	5	H	Ac

2a[3]; R_1 = Ac, R_2 = H
b[3]; R_1 = H, R_2 = Ac

An acyl group α to the bridge causes the single bridge proton nearest the acyl group to be deshielded by approximately 0.8 ppm. A β-acyl group exerts no discernable effect on the bridge protons. An example of portions of representative spectra are shown in figure 1. The deshielded bridge proton appears as a poorly defined (60 MHz) or fairly well defined (100MHz)

---

* Ac = CH_3CO; Cin = $C_6H_5CH{=}CH{-}CO$

** We report two compounds although four isomers are formed. We have experienced considerable difficulty in purifying two of these isomers; cf. ref 3.

set of four doublets near 7 τ , consistent with coupling of the one proton with its non-equivalent geminal and two vicinal neighbors. This multiplet integrates for one proton and accordingly the signal for the other bridge protons is broadened and reduced in intensity. For example in 1a, $J_{gem} \simeq 13.5$ Hz, $J_{vic_1} \simeq 7$ Hz, and $J_{vic_2} \simeq 3$ Hz. We have observed this effect in α-acyl derivatives in which the carbonyl group is free to assume a position parallel to the cyclopentadienyl ring but not in those in which this freedom does not exist, e. g., 3[5]. Using this information one is able to distinguish easily α,α', α,β', and β,β' substitution patterns in diacylferrocenophanes.

A somewhat less reliable but still useful feature of the spectra of 1c and 1d, which we have observed to apply also to diacyl derivatives of [3]ferrocenophane is the structure of the AB doublets of the cinnamoyl group. The center of this signal was found to occur at slightly higher field for α- than for β-cinnamoyl substituents. Further, the total separation of the outer signals of the two doublets is greater (63-65Hz) than is the separation (60-62 Hz) for the α isomer.

While the position of a single acyl group relative to the bridge in ferrocenophanes can be determined simply by observing the order in which the isomers are eluted in purification by column chromatography[4], (α before β), no such rules exist for assigning structures to diacyl derivatives. Thus, the peculiarities observed in the NMR spectra of monoacylferrocenophanes have been of considerable assistance to us in assigning structures to a series of diacylferrocenophanes which will be reported soon.

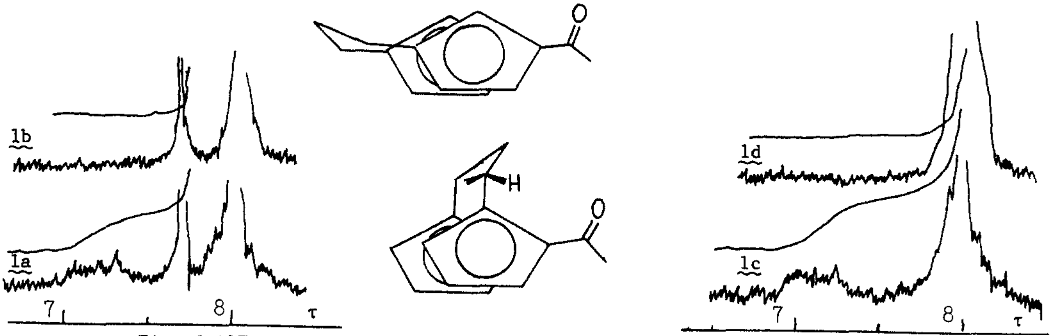


Fig. 1 NMR Spectra of Representative α- and β-Monoacylferrocenophanes

REFERENCES

1. Spectra taken in $CDCl_3$ solution using tetramethylsilane as internal standard.
2. Present address: Pfizer (Chas.) and Company, Inc., Groton, Connecticut.
3. While this note was being prepared T. H. Barr, E. S. Bolton, H. L. Lentzner and W. E. Watts, Tetrahedron 25, 5245 (1969), reported the preparation of 1c - 1h, 2a and 2b.
4. K. L. Rinehart, Jr., D. E. Bublitz and D. H. Gustafson, J. Amer. Chem. Soc., 85, 970 (1963).
5. One of a series of doubly-bridged ferrocenophanes recently prepared and will be reported in a subsequent communication.