# Protonation of Ferrocenylethylenes: Nuclear Magnetic Resonance Spectra of Some α-Ferrocenyl Carbonium Ions[1]

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DURING the last ten years a considerable amount of experimental evidence has been gathered in support of the thesis that α-ferrocenyl carbonium ions are particularly stable[2,3] and recently it has been reported that the n.m.r. spectra of such carbonium ions can be observed by examination of strong acid solutions of the appropriate secondary alcohols.[4] We report that the protonation of ferrocenylethylenes (I) by strong acids leads to solutions of ions which are stable for several days and give well-resolved n.m.r. spectra. These spectra can best be interpreted as those due to α-ferrocenyl carbonium

TABLE

| Ion | Solvent | Alkyl substituent | Unsub. ring | $H^2$ and $H^5$ | $H^3$ and $H^4$ | Carbinyl proton |
|---|---|---|---|---|---|---|
| (IIa) | $H_2SO_4$ | 128 d<br>$J$ = 6·8 c./sec. | 295 s | 260 bs<br>295 bs | 362 bs<br>371 bs | 413 q.<br>$J$ = 6·8 c./sec. |
| (IIb) | $H_2SO_4$ | 79 d<br>89 d } $J$ = 6·8 c./sec.<br>154 m<br>Isopropyl group | 304 s | 261 bs<br>296 bs | 368 bs<br>374 bs | 415 d<br>$J$ = 8·6 c./sec. |
| (IIc) | $H_2SO_4$ | 120 s | 274 s | 279 t | 360 t | — |
|  | $CF_3{\cdot}CO_2H^a$ | 94 s | 248 s | 254 t | 334 t | — |
| (IId) | $CF_3{\cdot}CO_2H^a$ | 36 (bt)<br>105 (bq) } $J$ = 7·7 c./sec.<br>Ethyl group<br>87·5 s | 243 s | 246 bs | 327 bs | — |

Spectra measured on a Perkin-Elmer R10, 60 Mc./sec. n.m.r. spectrometer. Absorptions measured in c./sec. downfield from external $Me_4Si$

s = singlet, bs = broad singlet, d = doublet, t = triplet, m = multiplet.

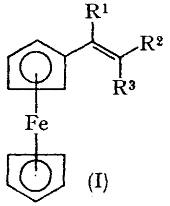
In spectrum (IId), due to the asymmetry of the carbinyl carbon, the ethyl group has additional coupling thus deforming the triplet (bt) and quartet (bq).

[a] Solvent shift in trifluoroacetic acid appears to be about 25 c./sec. upfield.

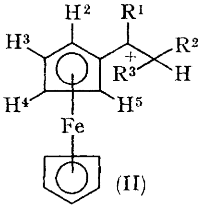
ions. It is well-known that weak acids, *e.g.*, acetic acid, will add to ferrocenylethylenes to yield α-acetoxy-derivatives,[5] but reactions with strong acids have not been reported. Our results are tabulated.

The protonation of four olefins has been studied. (Ia) and (Ib) lead to the formation of secondary ions (IIa and IIb) while (Ic) and (Id) yield tertiary ions (IIc and IId). The spectra of some secondary ions have been reported recently by Richards *et al.*,[4] and our results are in agreement with their figures. Cais[2] states that a decrease in the separation of the absorptions due to $H^{2,5}$ and $H^{3,4}$ in the substituted ring, should result from the presence of substituents which are electron releasing and this, in fact, is shown to be the case in α-ferrocenyl ions with phenyl substituents.[4] A similar trend is also seen in our data. The separation of the absorptions due to $H^{2,5}$ and $H^{3,4}$, measured between the centres of each pair of absorptions, for ions (IIa) and (IIb) are 89 and 92 c./sec., respectively, while the presence of an additional alkyl substituent in ions (IIc) and (IId) reduces the separation to 81 c./sec. Further examination of the results shows that in the spectra of secondary ions the four protons of the substituted ring appear as four separate absorptions, while in the spectra of tertiary ions the protons appear as two absorptions. In particular, in the tertiary ion (IIc) these absorptions show up as two well resolved triplets which are compatible with an $A_2B_2$ spectrum.[6]

To account for this difference between tertiary and secondary ions it is necessary to consider the canonical structures (A and B) suggested to explain the stability of α-ferrocenyl ions. In both structures rotation of the alkyl substituent is hindered either by overlap of the carbonium ion orbital with the π-system of the ring (A) or by orbital overlap, with the iron atom (B). The result is the production of an asymmetric ion when $R^1$ and $R^2$ are different. In the secondary ion ($R^1$ = H, $R^2$ = Me) this effect will result in a

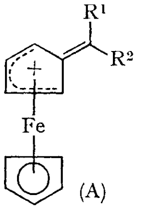


(I)

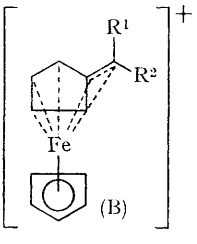


(II)

a; $R^1 = R^2 = R^3 = H$
b; $R^1 = H, R^2 = R^3 = Me$
c; $R^1 = Me, R^2 = R^3 = H$
d; $R^1 = R^2 = Me, R^3 = H$



(A)



(B)

difference in the relative shielding of the ring protons and will be greater for the $H^2$ and $H^5$ protons. This is shown by a separation of 35 c./sec. of the two absorptions due to these protons whereas with protons $H^3$ and $H^4$ the separation is only 9 c./sec. With the symmetrical ion (IIc), no separation of these absorptions is seen as mentioned above. The asymmetry of the ion has further experimental proof from a consideration of the spectrum of (IIb) where the isopropyl substituent shows up as a double doublet and not as a doublet.†

Another important difference in the spectra is the position of the absorption of the unsubstituted ring. In the spectra of the secondary ions the absorption is at 295—304 c./sec., whereas in the tertiary ions the absorption occurs at 274 c./sec.

This work represents a novel approach to the production of α-ferrocenyl carbonium ion for n.m.r. study and appears to be applicable to many ferrocene systems including stilbene analogues and bridged olefins.

(*Received, June 22nd,* 1967; *Com.* 632)

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† A well established phenomenon of substituents attached to an asymmetric molecule.

[1] Part I of the series in "Studies on Ferrocene Derivatives".
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[5] G. R. Buell, W. E. McEwan, and J. Kleinberg, *Tetrahedron Letters*, 1959, 16.
[6] see J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Resonance Spectroscopy", Pergamon Oxford, 1965.

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