

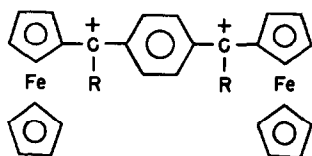
DIRECT OBSERVATION OF A 1,1'-di- α -FERROCENYL CARBONIUM ION

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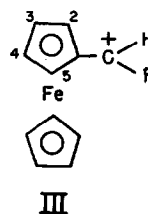
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(Received in USA 19 April 1967)

Carbonium ions generated alpha to the ferrocene group are exceptionally stable. This has been demonstrated by the ready dehydration of 1-ferrocenylethanol to vinyl ferrocene,¹ by the ease of addition of weak acids (such as acetic acid and hydrogen azide) to vinyl ferrocene,² by the extremely rapid solvolysis rates of methylferrocenylcarbonyl acetates,^{3,4} and by the isolation of stable carbonium ion salts.⁵ Dicarbonium ion salts containing ferrocene have recently been reported by Cais and Eisenstadt, (see structures I and II),⁶ but these salts contain only one charged carbon atom adjacent to each ferrocene nucleus. α -Ferrocenylcarbonium ions have been directly observed in concentrated sulfuric acid.⁷ The ions reported are summarized by III a-1.^{7,8}



I. R=H
II. R=C₆H₆



R= a, CH₃; b, CH(CH₃)₂; c, C(CH₃)₃;
d, C₆H₆; e, p-CNC₆H₄;
f, p-CH₃C₆H₄; g, p-CH₃OC₆H₄;
h, p-CH₃O₂C-C₆H₄;
i, m-CH₃C₆H₄; j, m-CH₃OC₆H₄;
k, o-CH₃C₆H₄; l, o-CH₃OC₆H₄.

We now report the direct observation of 1,1'-di- α -ferrocenyl-carbonium ion IV in $\text{FSO}_3\text{H-SbF}_5$, using a method which has been described previously.⁹ 1,1'-(1-Methyl-1-hydroxyethyl) ferrocene was dissolved into pentane and this dilute solution was added to rapidly stirred 10% SbF_5 -90% FSO_3H at -60°C .¹⁰ The dicarbonium ion (structure IV) was instantly formed, and its nmr spectrum (obtained on a Varian A60 spectrometer equipped with a V6040 temperature controller and a V6031-B probe) is shown in Fig. 1. The methyl protons are a singlet at -3.20 ppm (area of 12). This compares favorably with the methyl protons of the diphenyl carbonium ion (-3.60 ppm)¹¹ and of the trimethylcarbonium ion (-3.83 ppm).⁹ The ring hydrogens appear as two singlets at -6.59 ppm (area of 4) and -7.25 ppm (area of 4), but conclusive assignment of these bands to the 3-4 and 2-5 hydrogens must be tentative until deuterium labeling experiments are performed. These ring hydrogen peaks are shifted 2.4 and 3.1 ppm downfield from the ring hydrogen bands of the unionized alcohol.

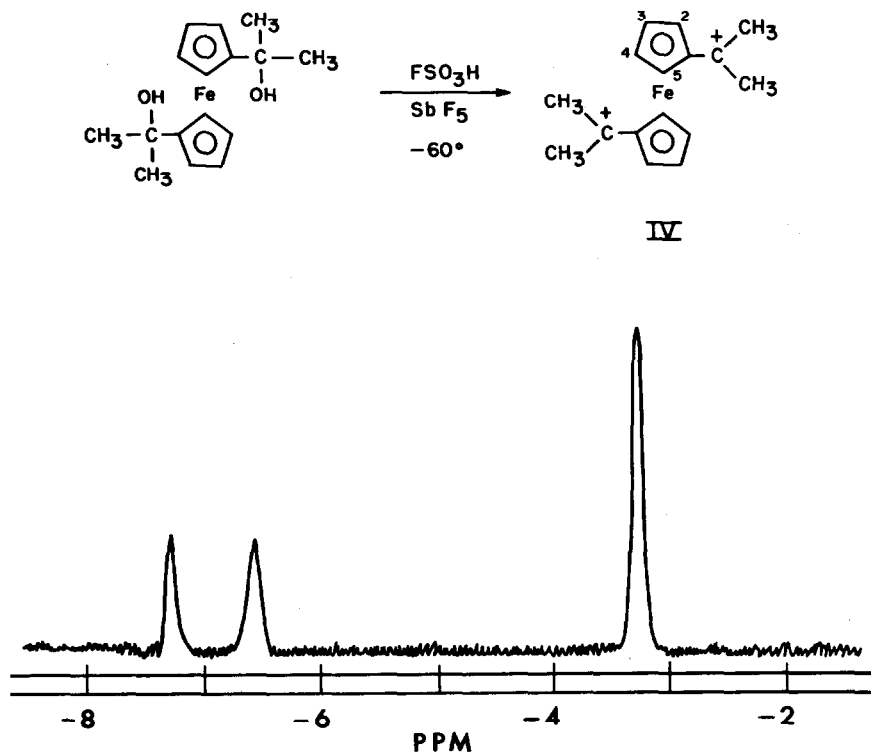
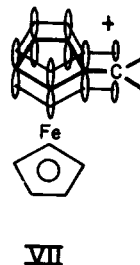
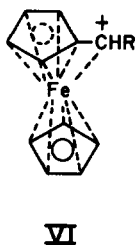
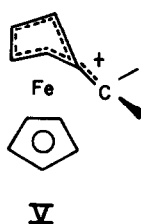


Fig. 1. NMR Spectrum of 1,1'-(1-methylethyl)-ferrocenyl-di- α Carbonium Ion in $\text{FSO}_3\text{H-SbF}_5$ at -30°

Interestingly, Cais⁸ reports that the four ring protons, H²-H⁵, of the substituted cyclopentadienyl rings of mono- α -ferrocenyl ions III a-1 appear in the nmr spectrum as four bands, one pair at fields 70-100 cps higher than the second pair. The high field pair were assigned to hydrogens at 2 and 5 while the low field pair were assigned to hydrogens at 3 and 4.⁸ Although the 2 and 5 hydrogens are nearer the positive charge, Cais proposed that shifts of the iron and the attached ring (as in structure VI) occurred which brought the hydrogens at 2 and 5 more under the influence of the shielding magnetic anisotropy of the ring. This shielding accounted for the high field position of the 2 and 5 hydrogens.⁸ This participation has been formulated as due to tilting of the ring (structure V), and shifting of the substituted ring relative to the rest of the molecule (structure VI).^{4,8,12} Ware and Traylor¹³ have concluded that neighboring group participation by the nonbonding Fe electrons is insignificant in comparison with resonance stabilization of the charged center by the ring (see VII).

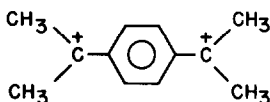


The structure of dicarbonium ion IV cannot be definitively assigned to any of these three models even if the -7.25 and -6.59 ppm band could be assigned with assurance to the 3-4 and 2-5 hydrogens. Cais⁸ pointed out that electron releasing groups, by supplying an electron flow towards the carbonyl carbon, should reduce the shift of the metal atom towards the charged center, and this reduction is reflected by a smaller degree of shielding of the hydrogens at 2 and 5 than of those at 3 and 4. Thus, the $\Delta\nu$ between these sets of hydrogens in ions III a-1 varied from 100 to 70 cps as electron donation increased. Electron-withdrawing groups should increase this $\Delta\nu$. In di-ion IV where a second very strongly electron-withdrawing group (the 1' cation center) has been added, the $\Delta\nu$ has been drastically reduced (to 38 cps) instead of increased. This, however, is not necessarily in contrast to the Cais model.¹⁴

If the low field band at -7.25 ppm is assigned to the 3 and 4 hydrogens, the smaller $\Delta\nu$ between 3-4 and 2-5 hydrogens in the dication is not unexpected because shifting of both rings to allow greater overlap of the charged center with iron is probably less favorable than in the monocations. In the dication such shifting requires the iron must bond with two charged carbons, not one, and the centers of charge density must be moved closer together. On this basis, the resonance stabilization model (VII) should be more important in dication IV than in monocations III a-1. Since ring shifting might be less important in IV than in III a-1, the 2 and 5 hydrogens of IV would be less shielded by the iron magnetic anisotropy, accounting for the smaller $\Delta\nu$ observed.

Solutions of IV were hydrolyzed as previously described¹⁵ and the precursor dialcohol was recovered in 48% yield, with the remainder consisting of polymeric products formed during hydrolysis. Ion IV was stable at temperatures of -30°C for over 24 hours and could be observed at 0°C; at room temperature, the ion was unstable and could not be observed.

The generation and stability of ion IV reflects that electronic effects are not strongly transmitted from one ring to the other in ferrocene. Under these same conditions, dication VIII was not formed. Some transmission of electronic effects is reflected by the much greater stability of mono- α -ferrocenylcarbonium ions which can be observed at 40°C in FSO₃H-SbF₅.



VIII

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