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cis- and *trans-*Tricarbonyl(π-pentadienyl)iron cations and their stereospecific interconversion

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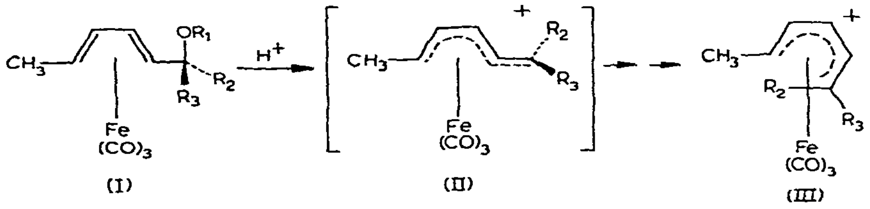
Tricarbonyl(*trans*-π-pentadienyl)iron cations (II) were originally proposed by Mahler and Pettit[1] as intermediates in the formation of the corresponding *cis* cations (III) from *trans*-dienol complexes (I, R_1 = H).



Clinton and Lillya have described the positive evidence for intervention of *trans-* ions as intermediates in the solvolysis of complexed dienyl esters (I, R_1 = 3,5-dinitrobenzoyl)[2].

In an attempt to observe *trans* cations (II) by NMR spectroscopy we have studied complexed secondary dienols in strongly acidic media at low temperatures. In every case addition of a small excess of FSO_3H to a $SO_2/CDCl_3$ solution of a dienol at −78° gave a red solution which changed to yellow in a few seconds. Immediate examination of the yellow solutions by NMR revealed only *cis* cations.

In the 5-methyl-3,5-heptadien-2-ol series the *ψ-exo* (IV)[3]★★, and the *ψ-endo* (V)[3]★★, isomers are converted stereospecifically to isomeric *cis* cations which have *syn,syn* (VI) and *syn,anti* (VII) structures respectively. Sorensen and Jablonski have observed similar conversions in the 3,5-heptadien-2-ol system[4]. Solutions of VI and VII were stable for at least 1 hour at −70°, and raising the temperature to −30° did not cause detectable interconversion. Full NMR assignments for VI and VII are given in Fig.1. The spectrum of VI-perchlorate in acetone-d_6 differs in some respects from that in $FSO_3H/SO_2/CDCl_3$ but is reproduced instead because its sharpness allows analysis of spin–spin splitting patterns★★★.

★Alfred P. Sloan Foundation Fellow, 1969–1971.

★★Spectral and chromatographic data as well as method of synthesis are uniquely consistent with structures IV and V[6].

★★★The large chemical shift difference between the *anti* hydrogens (H_2 and H_6) is unexpected and could be caused, in part, by asymmetric iron–carbon bonding.

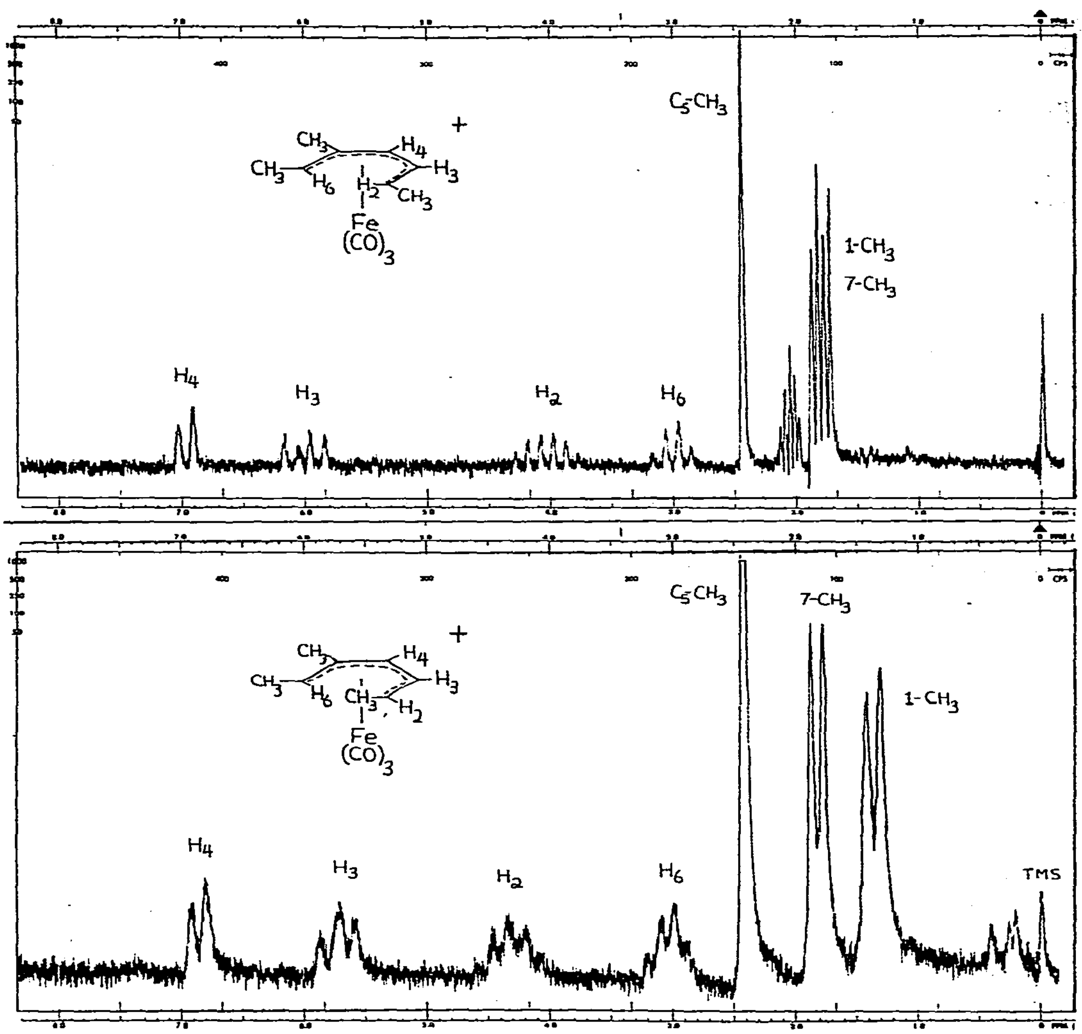
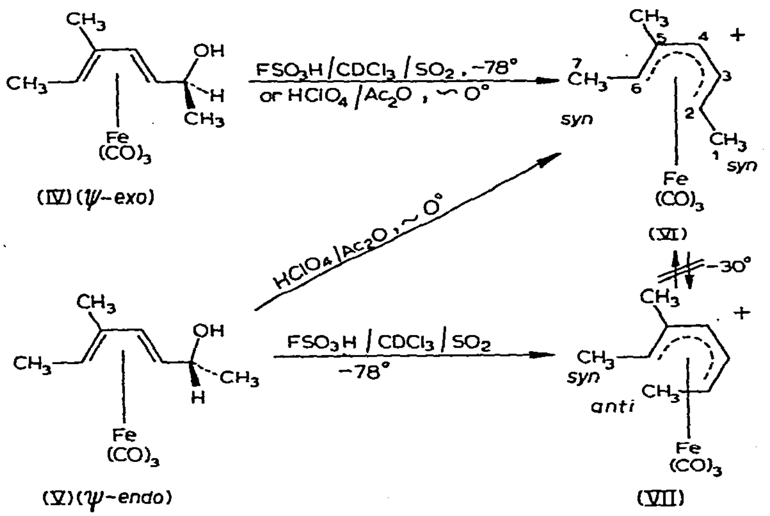


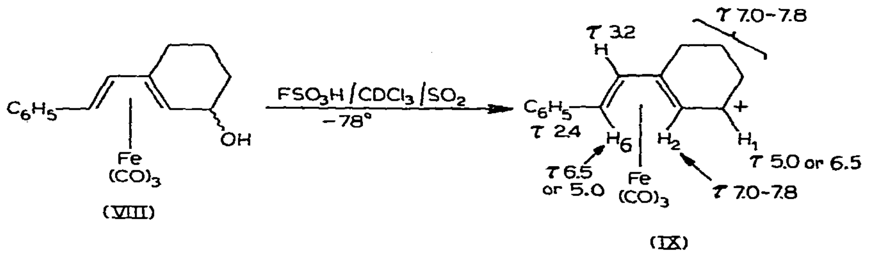
Fig.1. Above - NMR spectrum of cation VI as the perchlorate in acetone-d_6 (multiplet near τ 2.06 is acetone-d_5). Coupling constants are $J_{12} = J_{67} = 6$ Hz, $J_{23} = 12$ Hz, $J_{34} = 7$ Hz. Below - NMR spectrum of cation VII as the fluorosulfonate in $SO_2/CDCl_3$ at $-50°$ (signals immediately below TMS are caused by impurities). Coupling constants are $J_{23} = 9$ Hz, $J_{34} = 7$ Hz, $J_{67} = 6$ Hz.

In VII H_2 appears in the lower field region (τ 5.65) characteristic of *syn* not *anti* hydrogens, and the unusual shielding of the 1-methyl (τ 8.6) is in accord with an *anti* configuration. In contrast to VI where $J_{23} = 12$ Hz is consistent with *trans* vicinal coupling, the J_{23} value of 9 Hz in VII is characteristic of *cis* vicinal coupling[5] and strongly supports the *syn,anti* structure. These conversions are consistent with the Mahler–Pettit mechanism[1] (II → III) which features retention of configuration about the C_2–C_3 bond.



Treatment of either alcohol with perchloric acid and acetic anhydride at room temperature gave VI as an isolable perchlorate, the apparent product of thermodynamic control[1]. Quenching of either VI or VII in aqueous sodium bicarbonate at ca. 0° gave only *ψ-exo* alcohol (IV). Conversion of VII to IV may involve isomerization of the initial *ψ-endo* product, V to IV★ or isomerization of VII directly to the *syn,syn* ion (VI) at the relatively high quenching temperature[4].

To avoid loss of *trans* cation by its rapid rearrangement to *cis* we studied the cyclic dienol complexes VIII★★. Treatment of a $CDCl_3/SO_2$ solution of either *exo* or *endo* alcohol at −78° with a small excess of FSO_3H gave red-black solutions which exhibited identical NMR spectra. The signals, which are broad enough to obscure fine structure, were assigned as shown in IX.



The spectrum is virtually identical to that of the corresponding protonated ketone except that it exhibits an extra one-hydrogen signal at τ 5.0 which was assigned to H_1 or H_6. Assignment of H_2 as part of the τ 7.0–7.8 multiplet agrees with assignments of Sorensen and Jablonski

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★Since *ψ-endo* alcohols isomerize slowly even in dilute aqueous HCl[7] isomerization would have to occur before mixing is complete.

★★Prepared by D.E. Kuhn. All analytical data are satisfactory who have observed a *trans* cation which exhibits an NMR signal at τ 7.60 for the corresponding hydrogen[4]. Quenching of these solutions in aqueous bicarbonate gave mixtures which contained neither starting alcohol according to TLC analysis.

ACKNOWLEDGEMENTS

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