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Preliminary communication

6,7-Benzobicyclo[3.2.2]nonadienyliron tricarbonyl tetrafluoroborate

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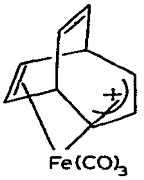
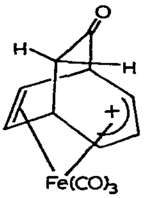
We have recently prepared some cationic iron complexes of the bicyclo[3.2.2]-system[1], I and II together with a novel Wagner–Meerwein type shift in the system.



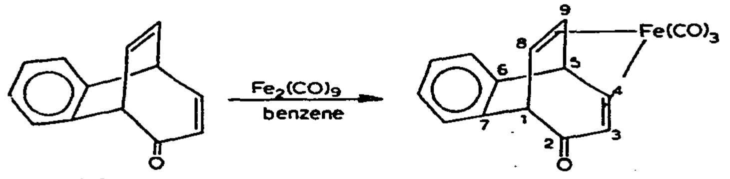
(I)



(II)

We now wish to report the preparation of benzobicyclo[3.2.2]nonadienyliron tricarbonyl tetrafluoroborate, III, and determination of its molecular structure in solution.

Treatment of IV[2] with $Fe_2(CO)_9$ in benzene solution afforded the keto complex V in quantitative yield, which was further purified by crystallization from hexane* m.p. 171–175° (decomp.) IR (hexane) 2050, 1990, 1975 cm^{-1} (CO absorptions) 1660 cm^{-1} (carbonyl). τ (in $CDCl_3$ with TMS as internal reference): The aromatic protons appear as A_2B_2 pattern centered at 2.81, the vinyl protons H_8, H_9 and H_4 give rise to a multiplet spread together with one proton at the bridgehead, H_1, between 5.7–6.4. The second bridgehead proton, H_5, shows triplet ($J_{12} \approx J_{18}$ = 8.0 Hz) and the vinyl proton α to the keto group, H_3, appears as double doublet at 7.49. ($J_{3,4}$ = 8.0 Hz, $J_{1,3}$ = 1.5 Hz). $J_{3,4}$ in the parent ketone IV is rather larger (= 11.5 Hz)[2].



(IV) (V)

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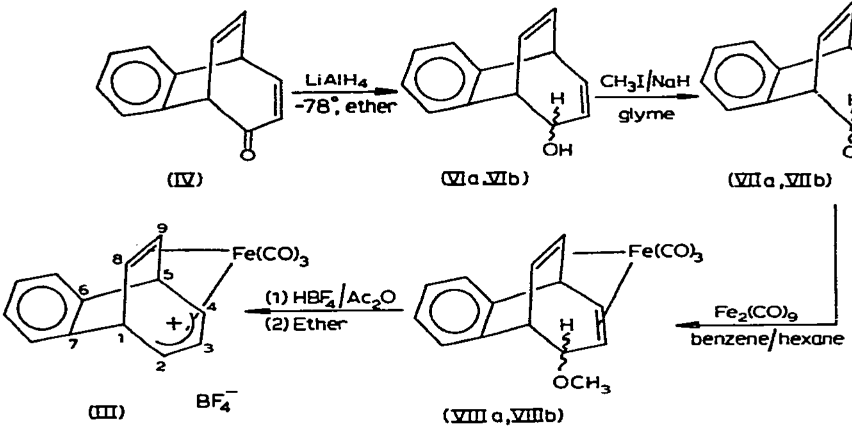
*All new compounds gave satisfactory analysis and/or mass spectra. Structures were assigned on the basis of chemical and spectral data.

Attempts to reduce V with lithium aluminium hydride (ether, −78°) left the complex untouched. On the other hand, $NaBH_4$ in ethanol or lithium aluminium hydride in ether at 0° caused disengagement of the metal to give the uncomplexed alcohols VI (a, m.p. 92–93°; b, m.p. 110–112°) identical with those obtained by direct reduction ($LiAlH_4$, ether, −80°) of the ketone IV. Steric hindrance probably plays a dominant role in inhibiting the hydride attack on the carbonyl group in V.

Methylation[3] of VIa and VIb provided the corresponding methoxy derivatives VII[★,★★] (a, m.p. 53–54°; b, oil).

Treatment of each of the isomeric 4-methoxybenzobicyclononatriene (VIIa and VIIb) with $Fe_2(CO)_9$ in hexane–benzene solution gave the iron tricarbonyl complexes VIIIa and VIIIb which were purified by basic alumina column chromatography and characterized by their IR and NMR spectra[★,★★★] VIII (a, oil; b, m.p. 78–79°). IR in hexane VIIIa: 2025, 1965, 1950 cm^{-1}; b: 2040, 1987, 1960 cm^{-1} (CO absorptions).



Treatment of either complex VIIIa or VIIIb with HBF_4 in acetic anhydride, followed by ether addition, led to the precipitation and isolation of a fine yellow powder, which, after recrystallization from acetonitrile gave yellow plates which decomposed above 230°. The latter was assigned as the structure of the cationic complex III on the basis of an analysis of its NMR spectrum (in CD_3CN with TMS as internal reference). The bridgehead protons H_1 and H_5 at τ5.75 overlap with the central allylic proton, H_3, which couples to H_2 and H_4 absorb as a triplet ($J_{1,2} = J_{2,3} = 7.5$ Hz) at τ5.02. The complexed vinyl protons

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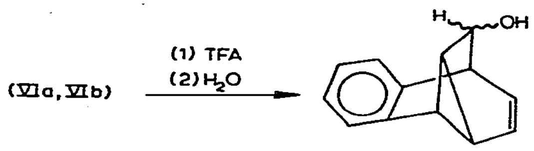
[★] Attempts to make stereochemical assignments of the epimeric hydroxy and methoxy derivatives by NMR techniques (solvent dependency, shift reagents like Eu complexes) were unsuccessful.

[★★] When this communication was being prepared, a report on the bicyclo[3.2.2]nona-2,6,8-triene system appeared, where some of our uncomplexed compounds were described[4]. The data (mainly on the methyl ethers VII) are in good agreement with our own, albeit no unequivocal stereochemical assignment is, in our opinion possible.

[★★★] Treatment of the methoxy ethers VIIIa and VIIIb with $Fe_2(CO)_9$ resulted in better yields of iron tricarbonyl complexes than treatment with the corresponding alcohols VIa and VIb. The latter, in this case, give rise to considerable amounts of V.

(H_8, H_9) appear as a multiplet at 5.23. The aromatic protons show a sharp singlet at 2.71. On the other hand, quenching the trifluoroacetic acid solution of the two isomeric alcohols VIa and VIb in ice water, gave only 6,7-benzo-9-barbaralol, IX★.



(IX)

ACKNOWLEDGEMENTS

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REFERENCES

1 A. Eisenstadt and S. Winstein, *Tetrahedron Letters*, (1970) 4603.
2 J. Ciabattoni, J.E. Crowly and A.S. Kende, *J. Amer. Chem. Soc.*, 89 (1967) 2778.
3 U.E. Diner, F. Sweet and R.K. Brown, *Canad. J. Chem.*, 44 (1966) 1591.
4 T. Tsuji, H. Ishitobi and H. Tanida, *Bull. Chem. Soc. Japan*, 44 (1971) 2447.
5 R.E. Leone and P.V.R. Schleyer, *Angew. Chem. Int. Ed. Engl.*, 9 (1970) 860, and references cited therein.

★Similar rearrangement processes have been exhibited by the parent cation, bicyclo[3.2.2]nonan-3,6,8-trienyl cation[5].