Tetrahedron Letters No.52, pp. 4603-4606, 1970. Pergamon Press. Printed in Great Britain.

A NOVEL ROUTE TO SOME TRICARBONYLIRON BICYCLO[3.2.2]NONADIENYL TETRAFLUOROBORATES.

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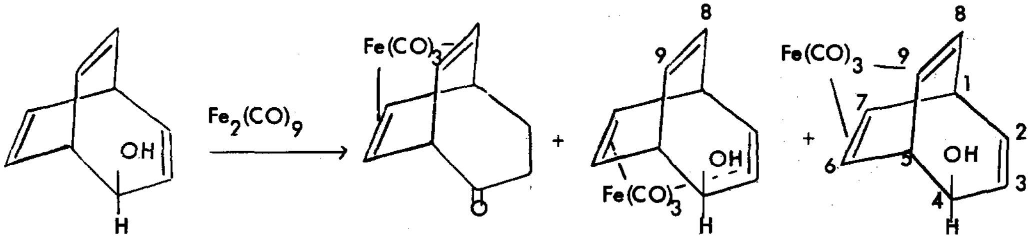
(Received in UK 21 September 1970; accepted for publication 14 October 1970)

The structure of the bicycloaromatic[3] bicyclo[3.2.2]nonatrienyl anions has received considerable attention recently.[4,5] On the other hand, the cationic species of the same structure seems to be an unstable intermediate or transition state between interconverting barbaralyl cations[6,7,8]. In this communication, we wish to report the preparation of some cationic iron complexes of the bicyclo[3.2.2] system[9]. One of the routes to these complexes involves what in organometallic chemistry is an apparently unprecedented, but nevertheless easily rationalized, Wagner-Meerwein type shift.

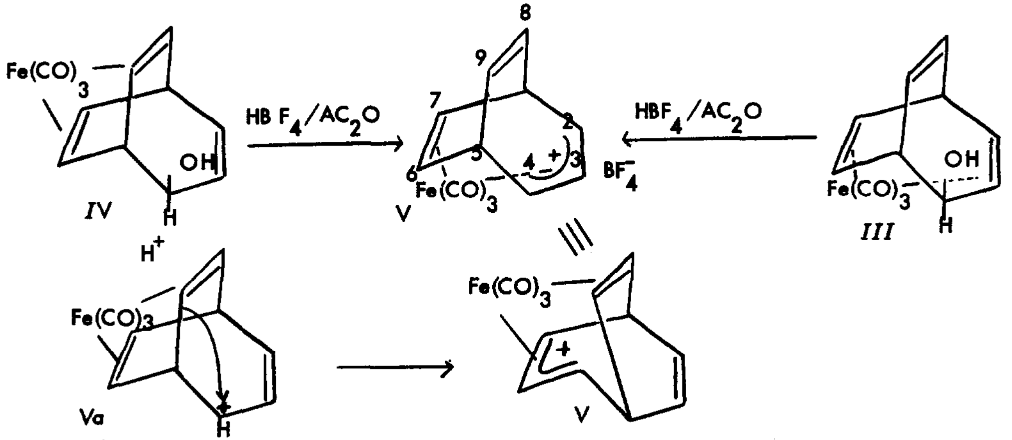
The reaction of bicyclo[3.2.2]nona-2,6,8-trien-4-ol[6] (I) with $Fe_2(CO)_9$ in hexane-benzene solution afforded three isomeric complexes (II, III, IV), which were separated by column chromatography and identified from their ir and nmr spectra[10,11]



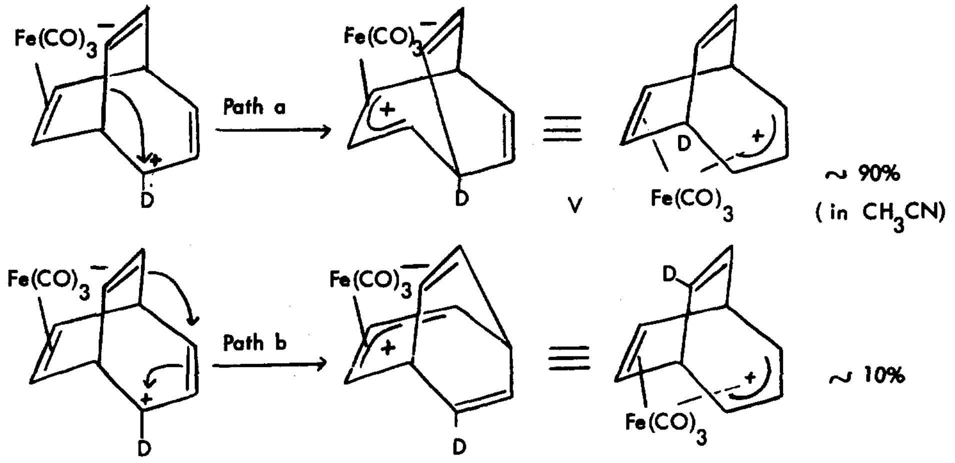
I *II* 8% *III* 10% *IV* 52%

Treatment of III 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, appeared as yellow, hexagonal crystals, mp 180°(d). The identification of the cationic complex as the expected V followed directly from the nmr spectrum (see below and Fig 1). Interestingly, similar acidic treatment of IV also resulted in the formation of V, apparently via a 1,2 carbon shift (Wagner-Meerwein process).

The nmr spectrum of V (Fig 1) shows the bridgehead protons, H_1 and H_5, as seven lines at τ6.30. The outer protons of the allylic portion, H_2 and H_4, absorb as a triplet ($J_{1,2}= J_{2,3}=7.5$ Hz) at τ5.12. *The central allylic proton, H_3, appears as a triplet of triplets (small long-range coupling to H_1 and H_5* as well as normal coupling to H_2 and H_4 at τ5.65. The complexed vinyl protons (H_6, H_7) and the free vinyl protons (H_8, H_9) both show multiplets at τ5.36 and τ3.6,[13] respectively.

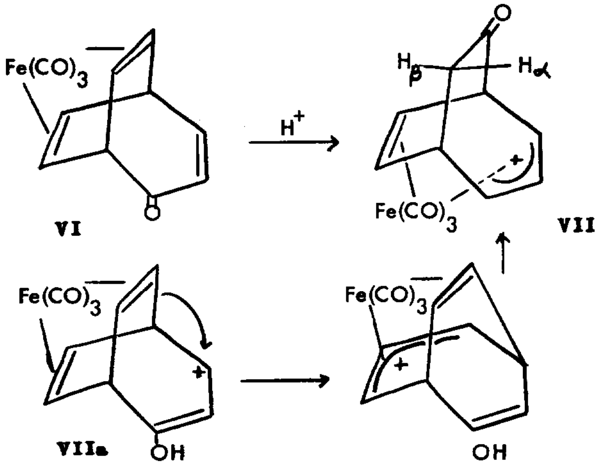


The Wagner-Meerwein type process which led to the transformation of IV into V could occur in two distinctly different ways. The first (path a) is a 1,2 shift of the neighboring 5,9 or equivalently, 5,6 bond. The second (path b) is the 1,2 shift of the 1,8 or 1,7 bond, along with allylic rearrangement.



As indicated in the diagrams, appropriate deuterium labeling could differentiate these two pathways. Indeed, when V was generated from IV-d$_1$-4,[14] the nmr spectrum (Fig.2) showed ca.90% of the deuterium had gone into the bridgehead position (path a), while only ca.10% of the label appeared in the unbound vinyl position (path b). This shows a roughly 1 kcal preference for the direct rearrangement which does not involve the allylic double bond.

Another instance of Wagner-Meerwein type isomerization occurred upon protonation of VI,[15] obtained as a product from the reaction of bicyclo[3.2.2]-nonatrienone with $Fe_2(CO)_9$. Thus, when the orange-red solution of VI in CH_2Cl_2 was extracted into conc. H_2SO_4 at room temperature, a yellow solution resulted, the nmr of which was only consistent with VII[16,17].



VI VII VIIa

At 100 MHz, the three allylic protons (H_2,H_3,H_4) were separated into three triplets. H_4(τ4.94)[18] appeared as a triplet ($J_{3,4}$=$J_{4,5}$=7.0Hz), broadened by long-range couplings. Irradiation of H_5(τ6.36) collapsed the H_4 resonance to a doublet, and the C_9 methylene protons to an AB quartet ($|J_{9\alpha,9\beta}|$ = 20 Hz). Of H_9 (τ 7.24, proton syn to allylic system) and $H_{9\beta}$(τ7.49), only the latter was coupled to H_5($J_{5,9\beta}$ =4.5 Hz)[19]. The central allylic proton, H_3, occurred as a triplet at τ5.20 ($J_{3,4}$=$J_{2,3}$=7.0 Hz); this could be reduced to a broadened doublet by irradiating H_4. H_2, τ5.48, partially overlapped the broad triplet due to H_6 and H_7 (bound vinyls) which was centered at τ5.61. The other bridgehead proton, H_1, resonated as a multiplet at τ5.97.

While it was obvious that the iron-complexed allylic (or homopentadienylic) cation, V, would be far more stable than the uncomplexed allylic ion, Va[21] (thus facilitating the observed rearrangement), it was not a priori obvious that the hydroxyallylic ion, VIIa, would be less stable than the iron-complexed allylic ion, VII.

In conclusion, the chemistry of the iron-complexed bicyclo[3.2.2]-nonatrienyl cation is in marked contrast to that of the free ion, where rearrangement to the barbaralyl cation is predominant[6,7,8].

ACKNOWLEDGMENT

We are indebted to Dr. Philip Warner for invaluable aid in the preparation of this manuscript. We are also grateful to Dr. David Harris and Dr. C.D. Poulter for their assistance in obtaining the 100 MHz mnr spectra and to Dr. D. Harris for helpful criticism of this manuscript.

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8. (a) P. Ahlberg, D.L. Hrris and S. Winstein, ibid., 92, 2146 (2970); (b) P. Ahlberg, D. Harris, J. Grutzner and S. Winstein, ibid., 92, 3478 (1970); (c) J. Grutzner and S. Winstein, ibid., 92, 3186 (1970).

9. The analogous tricarbonyliron bicyclo[3.2.1]octadienyl tetrafluoroborate has been reported: M. Margulis, L. Schiff and M. Rosenblum, ibid., 87, 3269 (1965).

10. All new compounds gave satisfactory C, H analyses and/or mass spectra.

11. (a) Data for I: mp 83-84°; ir 1976, 2045 cm^{-1} (CO absorptions), 1709 cm^{-1} (carbonyl); (b) Data for III: mp 56-57°; ir 1972, 2038 cm^{-1} (CO absorptions), 3595 cm^{-1} (OH-the absence of intra-molecular Fe-HO bonding indicated III was the exo isomer, as shown); nmr unbound vinyl protons (H_8, H_9) appeared as a 6 line symmetrical multiplet centered at 3.68; (c) Data for IV: mp 92-93°; ir 1969, 2037 cm^{-1} (CO absorptions), 3571 cm^{-1} (OH); nmr unbound vinyl protons (H_2, H_3) appeared as an AB pair centered at 4.17 ($J_{2,3}$ = 11.5 Hz), split further due to couplings with H_1 and H_4. The nmr spectrum of the corresponding ketone,[12] where $J_{3,4}$ was eliminated, served to further corroborate the assignments.

12. R. Aumann and S. Winstein, unpublished results.

13. The virtual identity in chemical shift of the unbound vinyl protons (H_8, H_9) in III and V indicates that the charge in V is not delocalized into the free double bond.

14. IV-d_1-4, where the deuteron replaced H_4, was obtained as yellow needles, mp 89°, via $LiAlD_4$ reduction of bicyclo[3.2.2]nonatrienone (to give I-d_1-4), followed by reaction with $Fe_2(CO)_9$.

15. VI was first prepared, in These Laboratories, by Dr. R. Aumann, unpublished results.

16. Of course, we cannot be sure whether or not the ketone moiety is also protonated, since exchange with the solvent would eliminate any peak due to a protonated ketone in this medium; however, this is a minor point which has no bearing on the results reported herein.

17. No signals corresponding to the ion with a bridgehead hydroxyl (1,2-shift of the 5,6 or 5-9 bond) could be seen in the nmr spectrum.

18. CH_2Cl_2, taken as τ4.70, was used as the internal standard.

19. This is in accord with theoretical predictions[20] made based upon examination of models.

20. M. Karplus, J. Chem. Phys., 30, 11 (1950).

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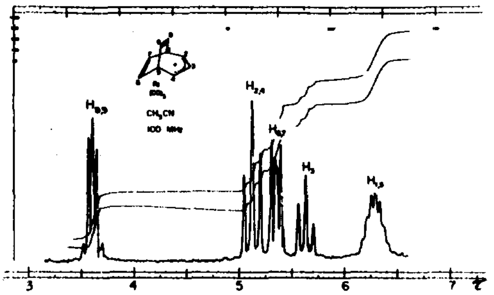

Figure 1.

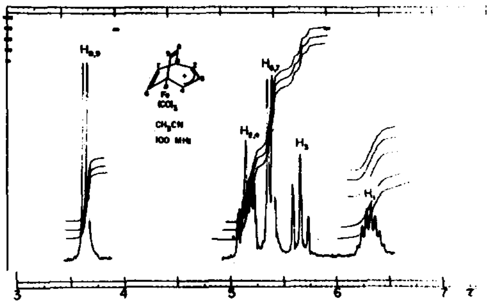

Figure 2.