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Preliminary communication

ANOMALOUS BEHAVIOR OF AN ALLYL ALCOHOL IN REACTION WITH IRON PENTACARBONYL

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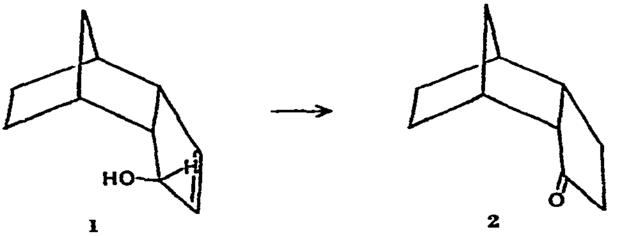
Summary

[(6,7,8,9-η)-Bicyclo[3.2.2]nona-2,6,8-trien-4-ol]tricarbonyliron (6) rearranges in the presence of $Fe(CO)_5$ to [(2,3,6,7-η)-bicyclo[3.2.2]nona-2,6,8-trien-4-one]tricarbonyliron (7); rather than [(6,7,8,9-η)-bicyclo-[3.2.2]nona-6,8-dien-2-one]tricarbonyliron (9), the product expected on the basis of known organoiron chemistry and previously proposed mechanisms. The starting material 6 is stable in the absence of $Fe(CO)_5$, which leads to the conclusion that some iron-containing species derived from $Fe(CO)_5$ is responsible for bringing about rearrangement. Since the usual mechanism for iron carbonyl-induced rearrangement in olefins cannot be operating here, a mechanism involving an ion pair with $[HFe(CO)_4]^-$ is suggested.

That allyl alcohols rearrange to saturated aldehydes and ketones upon treatment with one of a variety of iron carbonyl reagents is well known. *endo*-β—5-Hydroxytricyclo[5.2.1.0^{2,6}]dec-3-ene (1), for example, has been shown to yield the corresponding saturated ketone 2 [1], while the acyclic labelled alcohol 3 provided 1-propanal with deuterium distribution as indicated in structure 4 [2]. Observations such as these have led to a generally accepted mechanistic proposal for rearrangements which involves intermediary of a π-allyl hydridoiron tricarbonyl species 5; unambiguous proof for such an intermediate continues to elude interested investigators [3].

Some of our most recent results possibly reflect on this problem. We therefore wish to report an anomalous reaction of an allyl alcohol with iron pentacarbonyl, in which the product is an α,β-unsaturated ketone instead of the saturated ketone expected on the basis of previous observations recorded in the literature.



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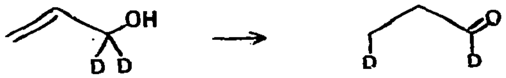

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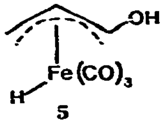

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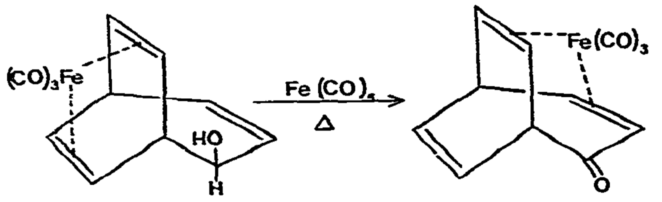
When [(6,7,8,9,η)-bicyclo[3.2.2]nona-2,6,8-trien-4-ol] tricarbonyliron (6) [4] was heated in refluxing heptane for 10 h under N_2 with a molar equivalent of $Fe(CO)_5$, a new complex of m.p. 180—181°C was obtained, as the only isolable material besides starting material, in about 70% yield, whose structure we have unequivocally assigned as that of [(2,3,6,7-η)-bicyclo[3.2.2]nona-2,6,8-trien-4-one] tricarbonyliron (7)* on the basis of its single crystal X-ray analysis. The complex 6 was found to be stable under identical reaction conditions in the absence of iron pentacarbonyl. It appears, therefore, that the reaction, formally an oxidation of an allyl alcohol, is brought about by $Fe(CO)_5$. It is likely that the transformation of 6 to 7 proceeds through intermediacy of 8, since 8 rearranges to 7 at refluxing heptane temperature whether or not $Fe(CO)_5$ is present. The isomerization proceeds more rapidly in the presence of $Fe(CO)_5$, but nonetheless proceeds at an appreciable rate in its absence. This transformation is currently under investigation, and is the subject of an upcoming report. Finally, the uncomplexed bicyclo[3.2.2]nona-2,6,8-trien-4-ol fails to rearrange to any significant extent under the reactions conditions which bring about 6→7 reaction, that is, under reflux in heptane for 10 h. At higher temperature (refluxing octane) some saturated ketone is produced from uncomplexed 6, but the reaction is very slow**.



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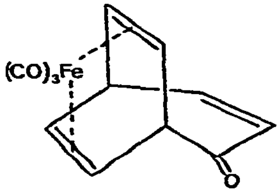

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*New compounds reported here gave satisfactory elemental analyses and spectral data. Compound 7, m.p. 180—181°C, IR ($CHCl_3$) 2060, 1990 and 1660 cm^{-1}; NMR ($CDCl_3$) δ 6.35 (br quartet, 2H); 3.60 (complex band, 5H) and 2.46 (br doublet, 1H) ppm. Compound 8, m.p. 116.5—117°C, IR (CCl_4) 2048, 1975, and 1670 cm^{-1}; NMR ($CDCl_3$) δ 6.93 (doublet of doublets, 1H), 6.15 (br doublet, 1H), 4.45 (br multiplet, 2H), 3.55 (br triplet, 2H), and 3.02 (br triplet, 2H) ppm.

**The reason that no 7 is produced during synthesis of starting material 6 apparently involves differences in reaction conditions, i.e., refluxing hexane for 1 h for synthesis and refluxing heptane for 10 h for 6→7 transformation.

Triclinic crystals of 7 belong to space group $P1(C_i^1)$, with two discrete molecules of composition $(C_9H_8O)Fe(CO)_3$ occupying the general positions in a unit cell of dimensions a 6.809(3), b 13.199(6), c 7.090(3) Å, α 110.26(5), β 114.30(5), γ 94.31(5)°. The structure was solved by the heavy-atom method. Full-matrix least squares refinement of atomic positional and thermal parameters (anisotropic, Fe, C, O; isotropic H) has reduced R to 0.062 over 1470 statistically significant $[I > 2.0\sigma(I)]$ reflections [5]. Measurements were made on an Enraf-Nonius CAD-3 automated diffractometer (Ni-filtered Cu-K_α radiation, λ 1.5418 Å; θ—2θ scans).

A view of the atomic arrangement of 7 is shown in Fig. 1. The iron atom coordination is distorted trigonal bipyramidal with C(1′), C(2′), and the midpoint of the C(2)—C(3) bond defining the equatorial plane, while C(3′) and the midpoint of the C(6)—C(7) bond occupy axial sites. The axial F—C(carbonyl) bond (1.758(8) Å) is slightly shorter than the mean of the two equatorial lengths (1.795(7) Å). The distinctly different lengths of the three C=C reflect the extent of their involvement with the iron atom. Thus, the uncoordinated C(8)—C(9) bond (1.319(9) Å lies close to the normal C=C length [6] (1.337(6) Å), the axially coordinated C(6)—C(7) bond (1.357(9) Å) which is *trans* to the strongest Fe—C(carbonyl) bond is only slightly longer than normal, and the strongly coordinated equatorial C(2)—C(3) bond (1.415(8) Å) is distinctly increased over the uncoordinated value. Some distances not shown in Fig. 1 are: Fe—C(3) 2.104, Fe—C(2) 2.118, Fe—C(6) 2.241, Fe—C(7) 2.171 Å. Angles (σ 0.3°) at the iron atom are: C(1′)—Fe—C(2′) 102.3, C(1′)—Fe—C(3′) 98.3, C(1′)—Fe—M(2,3) 117.9, C(1′)—Fe—M(6,7) 101.7, C(2′)—Fe—C(3′) 89.7, C(2′)—Fe—M(2,3) 139.6, C(2′)—Fe—M(6,7) 91.5, C(3′)—Fe—M(2,3) 88.6, C(3′)—Fe—M(6,7) 159.2, M(2,3)—Fe—M(6,7) 77.2°, where M(2,3) and M(6,7) are the midpoints of the C(2)—C(3) and C(6)—C(7) bonds, respectively.

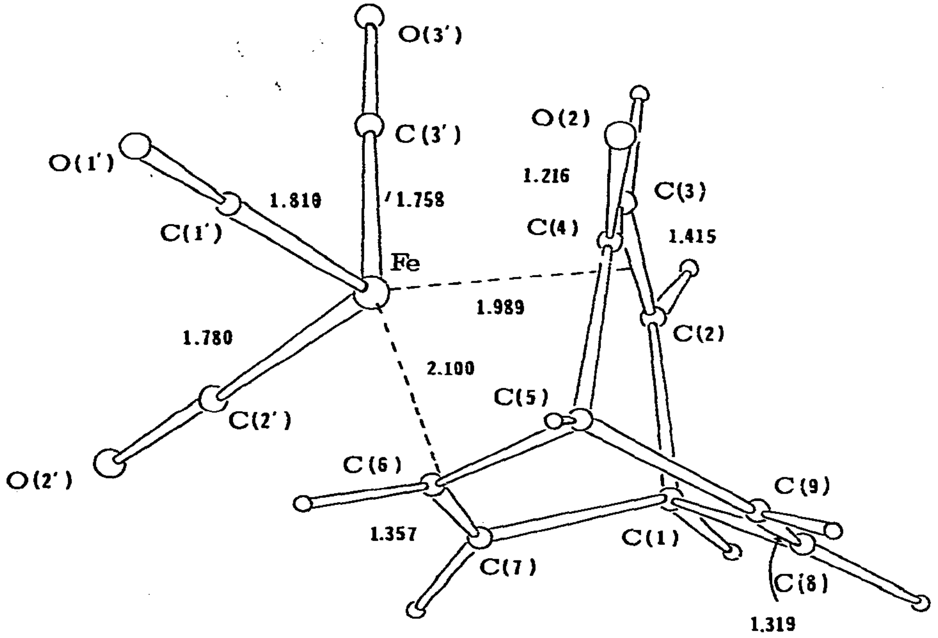
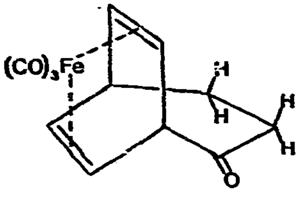


Fig. 1. Atomic arrangement and some bond lengths (σ 0.006—0.009 Å) in $(C_9H_8O)Fe(CO)_3$; small circles denote hydrogen atoms.

It is difficult to provide a convincing explanation for the observation reported here in terms of known organoiron carbonyl chemistry, and on the basis of currently accepted mechanisms for the interaction between iron carbonyl species and olefinic systems. The π-allylhydridoiron tricarbonyl mechanism described briefly above, which must proceed through intermediacy of **5**, has no application here, since the ultimate result of such a process should have been the saturated ketone complex **9** rather than **8** (or **7**). While the $Fe(CO)_3$ moiety in **6** is a prerequisite for the reaction we have observed (uncomplexed alcohol does not react under these conditions), it does not appear to be taking part in the reaction in a direct manner. The inescapable conclusion, it seems, would be that the reaction must be brought about by action of an extramolecular iron species on a system which has been rendered susceptible to this action by the presence of the previously attached $Fe(CO)_3$ unit.



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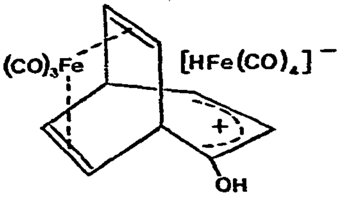

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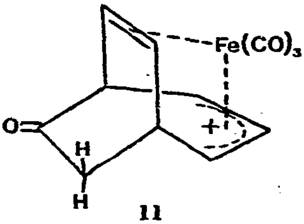

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In an earlier report [3], we had suggested the possibility that the species directly responsible for observed 1,3-H shifts is $Fe(CO)_4$, a molecule of fleeting existence [7] produced thermally from $Fe(CO)_5$, and the process through which the migration occurs involves hydride abstraction to form $(allyl)^+[HFe(CO)_4]^-$, rather than π-complexation such as that represented by **5**. While more evidence is needed before we can propose such a mechanism, this sequence of events is nicely adaptable to the present problem where the π-allylhydridoiron tricarbonyl mechanism is not. Iron tetracarbonyl can be envisioned as abstracting an allylic hydride to produce the intermediate cationic species **10**. It is not unreasonable to suppose that **10** is a sufficiently strong acid to protonate $[HFe(CO)_4]^-$, thereby bringing about formation of **8** and the volatile, unstable $H_2Fe(CO)_4$ [8].

The cationic species **10** should be attainable by protonation of the ketone **8**, a study which has been undertaken some time ago [4]. Under conditions employed in that work, Wagner—Meerwein rearrangement leading to the cationic complex **11** was observed. In our own work, we have not yet found evidence for such a rearrangement having taken place. It would not be particularly surprising that, under reaction conditions which we have employed, viz. heptane as solvent and elevated temperatures, rearrangement of **10** might not be competitive with hydroxyl proton transfer to the nearby $[HFe(CO)_4]^-$, since even in more polar solvents such as tetrahydrofuran it has been shown that this anion remains extensively associated with its counterion [9]. We are continuing our investigations in these and related systems, especially toward the determination of the nature of the inorganic products of the reaction we have reported here and toward determination of the validity of our mechanistic suggestions.*

Acknowledgements

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References

1 F.G. Cowherd and J.L. Rosenberg, J. Amer. Chem. Soc., 91 (1969) 2157
2 F.G. Cowherd, W.T. Hendrix, and J.L. Rosenberg, J. Chem. Soc., Chem. Commun., (1968) 97.
3 A brief discussion of this problem is given in J.C. Barborak, L.W. Dasher, A.T. McPhail, J.B. Nichols, and K.D. Onan, Inorg. Chem., 17 (1978) 2936.
4 A. Eisenstadt and S. Winstein, Tetrahedron Lett., (1970) 4603.
5 For more complete details see ref. 3.
6 International Tables for X-ray Crystallography, Vol. III, Kynoch Press, Birmingham, England, 1968.
7 B. Davies, A. McNeish, M. Poliakoff and J.J. Turner, J. Amer. Chem. Soc., 99 (1977) 7573.
8 (a) W. Hieber and H. Vetter, Z. Anorg. Allgem. Chem., (1933) 212, 145;
(b) H.W. Sternberg, R. Markby, and I. Wender, J. Amer. Chem. Soc., 79 (1957) 6116.
9 (a) M. Darensbourg, H. Barros, and C. Borman, J. Amer. Chem. Soc., 99 (1977) 1647.
(b) M.Y. Darensbourg, D.J. Darensbourg, and H.L.C. Barros, Inorg. Chem., 17 (1978) 297.

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*A referee has suggested the possibility of oxidative addition of $Fe(CO)_4$ to the O—H bond of our complexed alcohol 6, followed by β-elimination to produce the α,β-unsaturated ketone 8 and $H_2Fe(CO)_4$. We consider this proposal to be a viable alternative to our mechanism, and it bears further scrutiny in our continuing work.