Mechanism of the Rearrangement of Allyl Alcohol with Iron Pentacarbonyl: Evidence for a π-Allyl-Hydroirontricarbonyl Complex

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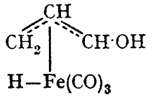
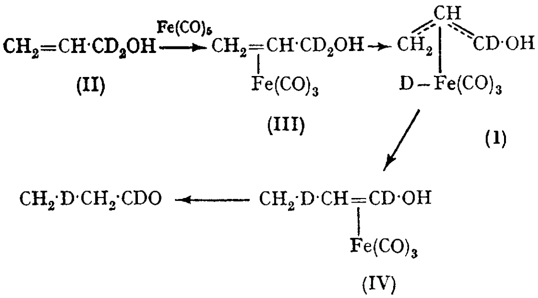
THE isomerization of allyl alcohol to propionaldehyde by reaction with $Fe(CO)_4$ has been reported by Emerson and Pettit, and a possible mechanism involving the intermediacy of a π-allyl-hydroirontricarbonyl complex (I) was proposed.[1] The same mechanism was also considered by Manuel to explain the rearrangement of mono-olefins when heated with iron carbonyls.[2] An alternate pathway involving an internal 1,3-hydrogen shift has been suggested in the rearrangement of both allyl alcohol[3] and allyl benzene[4] with $HCo(CO)_4$. We report evidence which, for the first time, strongly supports the involvement of a π-allyl-hydroirontricarbonyl complex (I) in the rearrangement of allyl alcohol by $Fe(CO)_5$.

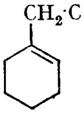
Rearrangement of [1,1-$^2H_2$]allyl alcohol (II) with $Fe(CO)_5$ produced propionaldehyde with deuterium appearing in the methyl but *not* in the methylene group, within the limits of the n.m.r. measurement.† The intergrated n.m.r. spectrum of the propionaldehyde showed a methyl to methylene proton ratio of 1·01 : 1·00, averaged over eight integrations. Furthermore, *both* the methyl and methylene proton resonances exhibited the expected triplet fine structure, showing the presence of only two protons per carbon atom. Additionally, the presence of the deuterium on the methyl could be seen from the geminal D–H coupling as the triplet was split distinctly into further individual triplets with $J_{\text{H-D}}$ = 2·02 ± 0·01 c./sec. The expected, negligible (less than 2%), aldehydic proton resonance arose from the fact that (II) showed a barely detectable trace of α-protons.†

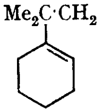
Our data are clearly consistent with the mechanism shown in equation (1), which requires that deuterium be found in the methyl but not in the methylene group of the propionaldehyde. It would appear also that the enol complex (IV) is converted directly into products, or at least no significant equilibrium exists between (IV) and (III) *via* the π-allyl complex.‡ If such an equilibrium did exist, a significant amount of aldehydic proton would be expected in the propionaldehyde. Our data failed to indicate this.

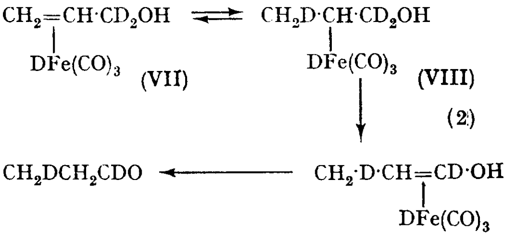
The reactions of 2-(1-cyclohexenyl)ethanol (V) and 2-methyl-2-(1-cyclohexenyl)propanol (VI) with $Fe(CO)_5$ provide further evidence for the occurrence of 1,3-hydrogen shifts in the rearrangement. If a route analogous to equation (1) is to be operative then each of the carbon atoms between the double bond and the carbinol group must possess at least one hydrogen atom. Compound (V) fulfills this requirement while (VI) does not. We have found that while (V) readily undergoes isomerization to the corresponding aldehyde no aldehyde is formed from (VI),[5] although some double bond rearrangement does occur.


(I)


(1)


(V)


(VI)


(2)

While our findings can adequately be explained by involvement of a π-allylhydroirontricarbonyl complex an alternative mechanism, which has been proposed to explain olefin isomerizations with iron carbonyls should be mentioned.[2] This involves formation, at some stage, of a metal carbonyl hydride–olefin π-complex (VII) in equilibrium with a σ-alkyl metal compound (VIII) as shown in equation (2). For this route to be operative with our deuteriated allyl alcohol a completely stereoselective transfer of deuterium to the terminal carbon atom in the transformation of (VII) into (VIII) would be required to avoid the incorporation of deuterium into the methylene group of the propionaldehyde. Cramer and Lindsey have reported a similar mechanism for the $DFe(CO)_4^-$-catalysed rearrangement of 1-butene.[6] These workers found however, that the major process leading to rearrangement was best explained by a transfer of deuterium to the 2-position of the 1-butene with resultant formation of a primary iron alkyl. Their findings would then seem to rule out such a mechanism in explaining our results with allyl alcohol and $Fe(CO)_5$.

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† N.m.r. spectra were taken at 60 Mc. sec. The integrated spectrum of (II) was in excellent agreement with the formulation indicated. The $LiAlD_4$ used in the preparation of (II) had a reported deuterium purity of 99%.

‡ Since the rearrangement will occur with less than stoicheiometric amounts of $Fe(CO)_5$, presumably the enol complex (IV) may react with another mole of allyl alcohol to regenerate (III).

Compound (II) was prepared by $LiAlD_4$ reduction of the Diels–Alder product of anthracene and ethyl acrylate followed by pyrolysis of the adduct at 350—400°. This circuitous method was found to be necessary in order to obtain reasonable yields of the desired alcohol. The rearrangement was performed by heating a solution of 0·28 moles of $Fe(CO)_5$ and 0·20 moles of allyl alcohol under reflux.§ A condenser heated to 55° allowed the passage of the priopionaldehyde into a cold trap as soon as it was formed. In this manner yields up to 60% were obtained.

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§ Although not necessary to induce rearrangement, larger quantities of $Fe(CO)_5$ simplified the experimental procedures.

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[2] T. A. Manuel, *J. Org. Chem.*, 1962, **27**, 3941.

[3] R. W. Goetz and M. Orchin, *J. Amer. Chem. Soc.*, 1963, **85**, 1549.

[4] L. Roos and M. Orchin, *J. Amer. Chem. Soc.*, 1965, **87**, 5502.

[5] Alcohols other than α,β-unsaturated ones have been shown to undergo rearrangement to the corresponding aldehydes and ketones) R. Damico and J. T. Logan, *J. Org. Chem.*, 1967, **32**, 2356; unpublished work in this laboratory).

[6] R. Cramer and R. V. Lindsey, jun., *J. Amer. Chem. Soc.*, 1966, **88**, 3534.