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THE ISOMERISATION OF OCTENES CATALYSED BY PHOSPHINE COMPLEXES OF IRIDIUM(III)

By R.S. Coffey,
Imperial Chemical Industries Limited
Heavy Organic Chemicals Division
Billingham
Co. Durham

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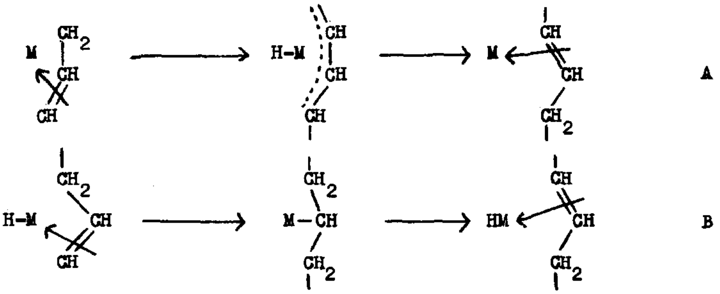
Recently papers have appeared describing the isomerisation of olefins catalysed by transition metal salts and complexes. In two of the proposed mechanisms, the "hydrido-π-allyl" (1) (scheme A) and the "hydrido-alkyl" (2) (scheme B) transition metal hydrides are key intermediates.



A third mechanism which does not involve a metal hydride has been suggested by Davies (3) for the isomerisation of octenes catalysed by palladium salts. The evidence for metal hydrides in isomerisation reactions is not always convincing and to obtain better evidence the reactions of octene-1 with a series of tertiary phosphine-iridium(III) complexes has been studied. For this work the octene-1 was purified from traces of oxygen containing impurities by passing it down an alumina column followed by distillation under nitrogen.

When a benzene solution containing octene-1 (1.1M) and the yellow hydride complex $[IrHCl_2(PEt_2Ph)_3]$ (8.4×10^{-3}M) is heated at 80-85° the octene-1 is rapidly converted to a mixture of isomers. Periodic v.p.c. analysis of the solution shows that the isomerisation is stepwise and that the octene-1 has almost disappeared after 30 min. A similar reaction using trans-$[IrH_3(PPh_3)_3]$ also causes rapid isomerisation of octene-1 and the isomerisation is inhibited by the addition of free triphenylphosphine (3×10^{-2}M) to the solution. The hydrides can be recovered from the reactions unchanged or as different geometrical isomers. On heating solutions of $[IrCl_3P_3]$ ($P = PEt_3$, PBu_3 or PEt_2Ph) in octene-1 at 120° almost no isomerisation is observed but on heating these solutions in sealed tubes at 160-170° much octene-2 and a little octene-3 is formed. The complexes can be recovered analytically pure by distilling off the olefins. If a solution of $[IrCl_3(PEt_3)_3]$ in octene-1, which has not been purified as described above, is heated at 120°, rapid isomerisation of the olefin occurs and a good yield of $[IrHCl_2(PEt_3)_3]$ is obtained, presumably from reaction with the oxygen containing impurities (4).

These results suggest that a preformed iridium hydride assists the olefin isomerisation but is not necessarily essential. The inhibition by free phosphine and the recovery of starting complexes suggest that the initial step is replacement of a phosphine by an octene-1 group according to the following equation:-

$$IrH_3(PPh_3)_3 + C_8H_{16} \rightleftharpoons IrH_3(PPh_3)_2(C_8H_{16}) + PPh_3$$

The hydride ligand which has a high trans effect(5) will assist this. To see if the hydride ligand reacts with the olefin the reaction of $[IrD_3(PPh_3)_3]$ with octene-1 has been studied. The initial rate of isomerisation of octene-1 is much slower with the deuteride than with the hydride and during the reaction the $[IrD_3(PPh_3)_3]$ is converted to $[IrH_3(PPh_3)_3]$. As a solution of $[IrD_3(PPh_3)_3]$ in benzene is stable to exchange of hydrogen for deuterium under these conditions, it is concluded that the metal-hydrogen bond takes part in the olefin isomerisation but there is as yet insufficient evidence in this work to differentiate between the "hydrido-π-allyl" and "hydrido-alkyl" routes. While this work was in progress Dr. B.L. Shaw and Mr. J.K. Nicholson of Leeds University have been studying independently the reaction of similar complexes with cyclo-octadienes. The author is grateful to them for valuable discussions.

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