Catalysis of the Transfer of Hydrogen from Propan-2-ol to αβ-Unsaturated Ketones by Organoiridium Compounds. A Carbon–Iridium Compound Containing a Chelate Keto-group

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THE effectiveness of iridium-containing catalysts for the reduction in solution of unhindered cyclohexanones to axial alcohols has been reported.[1] Further experiments show that a hydride, $HIrCl_2(Me_2SO)_3$, m.p. 184—186°, ν 2175 cm.$^{-1}$ is produced in 40% yield when a solution of the acid, $H[IrCl_4(Me_2SO)_2]2Me_2SO$, m.p. 165—170°, in propan-2-ol† is boiled for 4 hr. The hydride (0·05 mol.) catalyses the reduction of 4-t-butylcyclohexanone (1 mol.) by boiling propan-2-ol, a 77 : 23 ratio of axial : equatorial alcohols being formed (using the acid a 78 : 22 ratio was obtained[1]).

The acid, m.p. 165—170°, catalyses (or, see below, provides a catalyst for) the transfer of hydrogen from propan-2-ol to the carbon–carbon double bond in benzylideneacetophenone (chalcone) and related compounds. The following results were obtained using a 6 : 1 weight ratio (16—20 : 1 mol. ratio) of unsaturated ketone : iridium acid in boiling propan-2-ol.

$$\mathrm{PhCO{\cdot}CH{=}CHPh} \xrightarrow{\text{12 hr.}} \mathrm{PhCO{\cdot}CH_2{\cdot}CH_2Ph} \quad (95\%)$$

$$\mathrm{Me_3C{\cdot}CO{\cdot}CH{=}CHPh} \xrightarrow{\text{12 hr.}} \mathrm{Me_3C{\cdot}CO{\cdot}CH_2{\cdot}CH_2Ph} \quad (90\%)$$

$$\mathrm{PhCO(CH{=}CH)_2Ph} \xrightarrow{\text{24 hr.}} \mathrm{PhCO{\cdot}[CH_2]_4{\cdot}Ph} \quad (75\%)$$

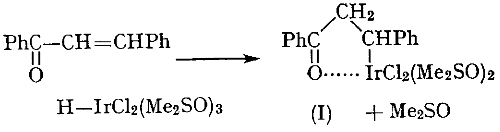
$$\mathrm{(PhCH{=}CH)_2CO} \xrightarrow{\text{12 hr.}} \mathrm{(PhCH_2{\cdot}CH_2)_2CO} \quad (65\%)$$

With a trace of acid (hydrochloric acid) present in solution, the hydride, $HIrCl_2(Me_2SO)_3$, is also effective as a catalyst for the chalcone–propan-2-ol reaction. (The iridium acid probably functions *via* conversion into this hydride). Using the hydride more than 300 mol. of chalcone can be converted into dihydrochalcone per atom of iridium present in solution.

Small amounts of a crystalline compound, m.p. 208—212°, were isolated from some of the chalcone–propan-2-ol reactions. Better yields (40—50%) of the product were obtained from reaction between chalcone (1—2 mol.) and the hydride (1 mol.) in propan-2-ol (or benzene) at 73° for 4 hr. This compound, having the composition $C_{19}H_{19}Cl_2IrO_3S_2$, is formed according to the equation:

$$\mathrm{PhCH{=}CHCOPh + HIrCl_2(Me_2SO)_3 \rightarrow (C_{15}H_{13}O)IrCl_2(Me_2SO)_2 + Me_2SO}$$

Spectroscopic evidence (i.r. and n.m.r.) is consistent with the cyclic structure (I) for the compound:



The stereochemistry and the finer structural details of the compound have been revealed by the *X*-ray studies reported in the following Communication.

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† Throughout this paper, propan-2-ol refers to the alcohol containing between 1 and 2% of water.

[1] Y. M. Y. Haddad, H. B. Henbest, J. Husbands, and T. R. B. Mitchell, *Proc. Chem. Soc.*, 1964, 361.