A Catalyst for the Homogeneous Hydrogenation of Aldehydes Under Mild Conditions

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RECENTLY it has been found that many complexes of transition metals are catalysts for the homogeneous hydrogenation of carbon–carbon multiple bonds under ambient conditions (see refs. quoted in reference 1). However, these complexes do not appear to catalyse the homogeneous hydrogenation of aldehydes to alcohols under similar mild conditions and indeed $[RhCl(PPh_3)_3]$, one of the most active and convenient catalysts for the hydrogenation of olefins,[1,2] conjugated and non-conjugated diolefins[2] and acetylenes,[1,2] is deactivated by aldehydes with which it reacts to give the catalytically non-active complex $[RhClCO(PPh_3)_2]$.[1,2] We now report that the complex[3,4] $[IrH_3(PPh_3)_3]$ is a catalyst for the homogeneous hydrogenation of aldehydes and some olefins at 50° and 1 atmos. pressure. A solution of $[IrH_3(PPh_3)_3]$ (5×10^{-3}M) in acetic acid catalyses the hydrogenation of n-butyraldehyde (0·56 M) to n-butanol at 50° and 1 atmos. of H_2 at an initial rate of 0·34 mole. $l.^{-1}hr.^{-1}$. Hydrogenation is virtually quantitative within 4 hr. and after distilling off the organic liquids the residual catalyst can be used again with identical results. Preliminary work shows the reaction is first order in both catalyst and aldehyde concentration and is very dependent on the solvent. No hydrogenation occurs in neat aldehyde or in toluene, but on adding acetic acid gas uptake begins.

Under similar conditions octenes are not reduced but the activated olefins acrylic acid and methyl acrylate are hydrogenated to propionic acid and methyl propionate, respectively, at a rate of approx. 0·1 mol. $l.^{-1}$ $hr.^{-1}$.

The reaction of $[IrH_3(PPh_3)_3]$ with acetic acid has been reported to give $[IrH_2O{\cdot}OC{\cdot}CH_3(PPh_3)_3]$,[5] but we find that a mixture of products is formed. A similar mixture of iridium hydrido-acetates is obtained from the hydrogenation experiments, and as these have similar catalytic activity to the starting material and are also inactive in toluene, we assume they are the true hydrogenation catalysts.

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