Solvent Transfer Hydrogenation of αβ-Unsaturated Aldehydes to the Unsaturated Alcohols Catalysed by Hydridoiridium Sulphoxide Complexes

By BRIAN R. JAMES* and ROBERT H. MORRIS

(*Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada* V6T 1W5)

Summary The unusual selective hydrogenation of αβ-unsaturated aldehydes to the unsaturated alcohols has been accomplished catalytically under mild conditions using the iridium complex $HIrCl_2(Me_2SO)_3$ in propan-2-ol, the solvent being the source of hydrogen.

THE catalytic hydrogenation of the olefinic bond in αβ-unsaturated carbonyl compounds is readily accomplished using transition metal complexes.[1] To accomplish the selective hydrogenation of the carbonyl function [*e.g.*, reaction (1)] is more difficult, and to our knowledge only one efficient metal complex catalyst has been discovered, a $[RhCl(CO)_2]_2$–tertiary amine system operating under hydroformylation conditions.[2] During development of the use of

$$RCH{=}CHCHO \xrightarrow{H_2} RCH{=}CHCH_2OH \qquad (1)$$

chiral sulphoxide ligands for catalytic asymmetric synthesis,[3] we have found that Henbest's catalyst system[4] [$HIrCl_2(Me_2SO)_3$–propan-2-ol–aqueous acid], at 80 °C under a nitrogen atmosphere, converts αβ-unsaturated aldehydes selectively into the unsaturated alcohol (see Table); the source of hydrogen is the alcohol solvent which is converted into acetone. With cinnamaldehyde at 90% conversion, there is essentially no reduction of the olefinic bond; cinnamyl alcohol is formed in high yields but, depending on the water content, up to 12% by-products (including ethers[5]) were detected.

TABLE. Hydrogenation of αβ-unsaturated aldehydes[a]

Substrate	Time/min for 90% conversion	At 90% conversion[b] % Unsat. alcohol	% Sat. aldehyde	% Sat. alcohol
Cinnamaldehyde	80 (or <15[c])	78[d]	Trace	0
α-Methylcinnamaldehyde	250	90	0	0
Crotonaldehyde	50	85	5	Trace

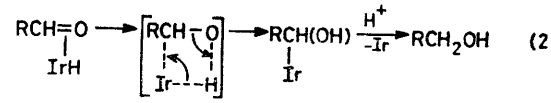
[a] 0·25M Substrate, *in situ* 10^{-2}M Ir, in propan-2-ol–water (30 : 1 v/v) at 80 °C under N_2. [b] Hydrogenation monitored by g.l.c. and n.m.r.; percentages refer to total substrate (reduced plus unchanged). The cinnamyl alcohols can be recovered by evaporation of the solvent followed by chromatography of the residue on alumina. [c] Using 10^{-2}M $HIrCl_2(Me_2SO)_3$, 10^{-2}M aqueous HCl, 30 : 1 v/v propan-2-ol–water. [d] About 12% by-products; at 300 : 1 v/v propan-2-ol–water, the amount of cinnamyl alcohol was 85% with 5% by-products; at 10 : 1 v/v, the hydrogenation was completely inhibited.

α-Methyl cinnamaldehyde at the same 90% conversion gives the unsaturated alcohol with 100% selectivity. Crotonaldehyde, less hindered at the olefinic bond, still gives *trans* but-2-en-1-ol with >90% selectivity at 90% conversion. The maximum selectivities achieved for these three substrates using the rhodium systems were 90, 87, and 50%, respectively.[2]

Our initial studies used an *in situ* catalyst preformed by warming *trans*-$[H(Me_2SO)_2][IrCl_4(Me_2SO)_2]$ in wet propan-2-ol for 2 h, which gives a mixture of isomers of $HIrCl_2(Me_2SO)_3$.[4] Use of an isolated white complex† with *trans* chlorides and meridional sulphur-bonded[6] sulphoxides [τ(Ir–H) 28·86 (1H, s), 6·45 (12H, s), and 6·30 (6H, s); ν(SO) 1134, 1110 cm^{-1}; ν(Ir–H) 2180 cm^{-1}; ν(Ir–Cl) 302 cm^{-1}] shortened reaction times considerably (Table). At higher water concentrations (<10 : 1 v/v propan-2-ol–water), the hydrogen transfer reactions were strongly inhibited, and we attribute this to the decomposition of the catalyst complex which rapidly turned yellow in the presence of moisture.

Gullotti *et al.*,[7] using *in situ* sulphoxide catalysts formed from $IrCl_3.3H_2O$, had used long reaction times (72 h) and had noted reduction of the olefinic bond as well as the carbonyl group with unsaturated aldehyde substrates. With our system further reduction of cinnamyl alcohol and the but-2-en-1-ol to the saturated alcohols was relatively slow; α-methylcinnamyl alcohol showed no reduction even after 20 h.

The reasons for the preferential reduction of the carbonyl unit are not too clear, since the same catalyst system effects the hydrogenation of the olefinic bond in αβ-unsaturated ketones[8] and also, but more slowly, the reduction of saturated cyclohexanones to the alcohols.[5] Steric factors could favour reduction of the aldehyde group compared with a ketone group but, since catalysts with phosphine-type ligands invariably reduce the olefinic bond in αβ-unsaturated aldehydes whether using H_2 gas or a hydrogen donor solvent,[1,2,9] we favour electronic arguments. A more acidic co-ordinated hydrogen, compared to corresponding phosphine complexes,[4] could favour reaction (2). Reduction of aldehydes is usually considered to be enhanced with



(2)

† The $HIrCl_2(Me_2SO)_3$ complex was synthesized by addition of HCl to $[IrCl(C_8H_{14})_2]_2$ (A. van der Ent and A. L. Onderdelinden, *Inorg. Synth.*, 1973, **14**, 92) in CH_2Cl_2–Me_2SO. The spectroscopic data do not correspond to those reported by Haddad *et al.* (ref. 4) for some isomers of $HIrCl_2(Me_2SO)_3$; however, no details of the ^1H n.m.r. spectrum in the sulphoxide region were given, and it is difficult to discuss the differences quantitatively.

increasing hydridic character *via* addition of the metal hydride in the reverse direction to that shown in reaction (2), but both modes of addition seem feasible.[10]

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