

Hydrogenation of α,β -Unsaturated Aldehydes and Ketones to the Unsaturated Alcohols catalysed by Hydrido-iridium Phosphine Complexes

E. Farnetti, M. Pesce, J. Kašpar, R. Spogliarich, and M. Graziani

Dipartimento di Scienze Chimiche, Università di Trieste, Piazzale Europa 1, 34127 Trieste, Italy

Unusual selective hydrogenation of cinnamaldehyde and benzylideneacetone to the corresponding unsaturated alcohols is catalysed by $[\text{H}_2\text{Ir}(\text{phosphine})_4]^+$ complexes in toluene; use of a chiral phosphine gives a 7.4% enantiomeric excess of (S)-(-)-1-phenylbut-1-en-3-ol.

Reduction of a carbonyl function is often an important step in organic synthesis, especially if it can be performed in the presence of other reducible groups. Catalytic hydrogenation of α,β -unsaturated aldehydes or ketones to the corresponding unsaturated alcohols is still an open problem and, whereas a few examples of catalytic aldehyde reduction are known,¹ highly selective catalytic hydrogenation of the carbonyl group in α,β -unsaturated ketones to our knowledge has not been reported so far.

We found that benzylideneacetone ($\text{PhCH}=\text{CHCOMe}$) is hydrogenated in toluene in the presence of a catalyst prepared *in situ* by treating $[\text{Ir}(\text{cod})(\text{OMe})]_2$ (cod = cyclo-octa-1,5-diene) with PEt_2Ph or PEtPh_2 . Both activity and selectivity depend on the P/Ir ratio. When a twofold excess of phosphine is used, the carbon-carbon double bond is quickly reduced to give the corresponding saturated ketone and saturated alcohol. On increasing the P/Ir ratio, reduction of the carbon-carbon double bond is depressed, the reaction

Table 1. Hydrogenation of α,β -unsaturated carbonyl compounds.^a

Run	Procatalyst	P/Ir	% Conversion (h)	% Unsaturated alcohol	% Saturated ketone	% Saturated alcohol
Substrate: $\text{PhCH}=\text{CHCOMe}$						
1	$[\text{Ir}(\text{cod})(\text{OMe})]_2 + \text{PEt}_2\text{Ph}$	2	93(5)	—	83	10
2	"	10	97(48)	90	5	2
3	"	10 ^b	32(144)	13	18	1
4	$[\text{Ir}(\text{PEt}_2\text{Ph})_4]^+$		96(70)	91	4	1
5	<i>cis</i> - $[\text{H}_2\text{Ir}(\text{PEt}_2\text{Ph})_4]^+$		92(28)	81	7	4
6	$[\text{Ir}(\text{cod})(\text{OMe})]_2 + \text{PEtPh}_2$	10	99(10)	96	2	1
7	"	10 ^b	98(70)	96	2	—
Substrate: $\text{PhCH}=\text{CHCHO}$						
8	$[\text{Ir}(\text{cod})(\text{OMe})]_2 + \text{PEt}_2\text{Ph}$	10	98(7)	97	—	1
9	"	10 ^b	97(7)	96	—	1
10	$[\text{Ir}(\text{PEt}_2\text{Ph})_4]^+$		99(28)	98	—	1
11	<i>cis</i> - $[\text{H}_2\text{Ir}(\text{PEt}_2\text{Ph})_4]^+$		95(22)	94	—	1

^a Reaction conditions: $[\text{Ir}] = 4 \times 10^{-4} \text{ M}$, substrate/Ir = 500, solvent toluene, H_2 pressure 30 atm, temperature 100 °C. Reactions were performed in a 190 ml autoclave using 75 ml of solvent. ^b Solvent propan-2-ol.

becomes much slower, the carbonyl group is selectively reduced, and 1-phenylbut-1-en-3-ol is obtained with 93–97% selectivity (see Table 1, runs 2, 6). Other phosphines behave in a similar way, but as a general trend more sterically demanding phosphines need larger excess of ligand to reach high selectivity; for example PEtPh_2 (cone angle,² $\theta = 140^\circ$), (*S*)-(+)- $\text{PPh}_2(\text{CH}_2\text{CHMeCH}_2\text{Me})$ ($\theta = 145^\circ$), and PPh_2Pr^i ($\theta = 150^\circ$) require a P/Ir ratio of 5, 8, and 10 respectively to achieve selectivity greater than 95%. Moreover when the above mentioned optically active phosphine is used (P/Ir = 10), (*S*)-(–)-1-phenylbut-1-en-3-ol is obtained in 91% yield, with an enantiomeric excess of 7.4%.

Recently Brouckova *et al.* have also reported that in the hydrogenation of cinnamaldehyde to hydridocinnamyl alcohol catalysed by ruthenium complexes an increase of selectivity and a decrease of catalytic activity are observed when an excess of diphos ($\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$) is used.³

From the experiments performed using a catalyst prepared *in situ* it appears that a large excess of phosphine is needed to depress carbon–carbon double bond reduction and hence to obtain high selectivity in carbonyl group hydrogenation. We prepared $[\text{Ir}(\text{PEt}_2\text{Ph})_4]^+$ and *cis*- $[\text{H}_2\text{Ir}(\text{PEt}_2\text{Ph})_4]^+$ ⁴ which also forms on addition of H_2 to a toluene solution of

$[\text{Ir}(\text{PEt}_2\text{Ph})_4]^+$, as we observe by monitoring the ^1H and ^{31}P n.m.r. spectra. Both these complexes catalyse the hydrogenation of benzylideneacetone to the corresponding unsaturated alcohol in high yields (see Table 1).

Cinnamaldehyde is also reduced to the unsaturated alcohol; the hydrogenation is faster than that of benzylideneacetone and the selectivity was very close to 100%.

This work was supported by University of Trieste and Progetto Finalizzato Chimica Fine e Secondaria, C.N.R. (Rome).

Received, 16th December 1985; Com. 1759

References

- 1 T. Mizoroki, K. Seki, S. Meguri, and A. Ozaki, *Bull. Chem. Soc. Jpn.*, 1977, **50**, 2148; B. R. James and R. H. Morris, *J. Chem. Soc., Chem. Commun.*, 1978, 929; E. Farnetti, F. Vinzi, and G. Mestroni, *J. Mol. Catal.*, 1984, **24**, 147; M. Visintin, R. Spogliarich, J. Kaspar, and M. Graziani, *J. Mol. Catal.*, 1985, **32**, 349.
- 2 C. A. Tolman, *Chem. Rev.*, 1977, **77**, 3.
- 3 Z. Brouckova, M. Czakova, and M. Capka, *J. Mol. Catal.*, 1985, **30**, 241.
- 4 L. M. Haines and E. Singleton, *J. Chem. Soc., Dalton Trans.*, 1972, 1891.