

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

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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	Pro catalyst	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%.

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