

PHOSPHINERHODIUM COMPLEXES AS HOMOGENEOUS CATALYSTS

XII *. ASYMMETRIC HYDROGENATION OF ARYL KETONES WITH HIGH ENANTIOSELECTIVITY

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Summary

The enantioselectivity of catalysts obtained in situ from $[\text{Rh}(\text{nbd})\text{Cl}]_2$, (+)-DIOP and triethyl amine for the hydrogenation of aryl ketones is significantly increased if benzene is used as a solvent. Optical yields of 55–84% were achieved at 50°C and 70 bar H_2 .

The asymmetric hydrogenation of simple ketones with phosphinerhodium complexes as catalysts usually occur with low efficiency; the rates and enantioselectivities which can be achieved with ionic [1–6] or in situ [6–10] catalysts are rather low. Recently we reported on in situ catalysts modified with triethyl amine which show significantly higher catalytic activity [11]. The best optical yield obtained with such catalyst was 53%, which was obtained with acetophenone as the substrate.

We have now found that the solvent has a dramatic influence on the enantioselectivity of this modified catalysts with benzene in place of the methanol used earlier, the optical yield in the hydrogenation of acetophenone was increased to 80%, and with other aromatic ketones optical yields above 50% were achieved. The results are summarized in Table 1.

No aliphatic ketones are included in Table 1 because with these substrates rates and optical yields were both very low, if measurable at all. In the light of the rather good results obtained with aromatic ketones, two conclusions regarding the mechanism of the catalytic reaction seem to be justified. First, that the rate determining step of the catalytic cycle may be nucleophilic attack of the rhodium hydride complex on the carbonyl group, and second, that an interac-

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TABLE 1
EXPERIMENTAL DETAILS AND RESULTS

Ketone	Et ₃ N/Rh	Reaction time (h)	Chemical yield (%) ^a	Optical yield (%)
Acetophenone	1.5	6	42	72 ^b
Acetophenone	2	6	64	80 ^b
Acetophenone	5	6	73	75 ^b
Acetophenone	5	6	95	68 ^b , 66 ^c
Acetophenone	20	6	98	37 ^b
2-methyl acetophenone	2	20	100	77 ^c
4-methyl acetophenone	2	20	65	61 ^c
4-methyl acetophenone	5	6	28	55 ^c
4-ethyl acetophenone	5	13	79	58 ^c
Benzyl methyl ketone	5	6	22	5 ^b
Methyl α -naphthyl ketone	2	4	100	82 ^b , 81 ^c
Methyl α -naphthyl ketone	5	4	100	84 ^b , 83 ^c
Methyl α -naphthyl ketone	10	6	87	69 ^b , 68 ^c
Methyl β -naphthyl ketone	5	13	100	62 ^c

^a Reaction conditions: 50°C, 70 bar H₂, 10 mmol ketone, 0.05 mmol Rh, 0.055 mmol (+)DIOP in 2.8 ml benzene. ^b Determined by measurement of optical rotation. ^c Determined by the NMR shift technique (in CS₂, room temperature; $n(\text{Eu}(\text{facam})_3)/n(\text{CH}_3\text{CH}(\text{OH})\text{R}) = 0.15-0.2$; $\Delta\Delta\delta(\text{CH}) \sim 0.2$ ppm, CH₃-decoupling).

tion between the aromatic rings of the ketone and those of the chiral DIOP ligand may be mainly responsible for the enantiotopic face discriminating complexation of the carbonyl group to the rhodium atom necessary for asymmetric induction. The relative positions of the carbonyl group and the aromatic ring in the ketone molecule are obviously critical for good enantioselectivity, as shown by the poor optical yield obtained with benzyl methyl ketone.

³¹P NMR spectroscopic studies are under way to investigate these proposals.

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