Journal of Organometallic Chemistry, 252 (1983) C60—C62
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

ASYMMETRIC HYDROGENATION OF α-β UNSATURATED KETONES WITH CHIRAL PHOSPHINECOBALT CARBONYL CATALYSTS

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(Received May 4th, 1983)

Summary

The hydrogenation of α-β unsaturated ketones with $Co_2(CO)_6[PPh_2\text{-Neomenthyl}]_2$ as catalyst gives optically active ketones with optical yields of 1.4—16%.

The asymmetric hydrogenation of prochiral olefins has been an especially active field of research since the pioneer work of Horner and Knowles [1]. Very commonly rhodium catalysts containing chiral phosphines have been used [2]. Our recent efforts have focused on using cheaper and more readily available catalysts which by chiral modification might also induce asymmetric synthesis. Unfortunately, all attempts to catalyze asymmetric hydrogenation of prochiral dienes with a modified arenechromium tricarbonyl system failed. It was found impossible to bring any chiral center into the catalytic cycle in this case [3]. We now report successes obtained with the chiral phosphine-modified cobalt carbonyl complexes. This system catalyses the asymmetric hydrogenation of α-β unsaturated ketones to optically active ketones. Optical yields in the range 1.4 to 16% have been obtained.

Surprisingly, in spite of the potential industrial applications, there are very few reports of asymmetric syntheses involving cobalt carbonyl catalysts [4], and to our knowledge previous hydrogenation attempts with dicobalt octacarbonyl complexes substituted by chiral phosphines were unsuccessful [5]. One of the main reasons for the striking difference from the effectiveness of rhodium catalysts is probably the greater ease of isomerization in the case of cobalt. Hydrogenation of optically active natural dienes catalysed by $Co_2(CO)_6[P(Bu)_3]_2$ (1) illustrates this [6]; thus (−)α-phellandrene and (−)-limonene were rapidly hydrogenated to give a mixture of Δ_1 and Δ_3 menthenes (80°C, 15 h, 30 atm of

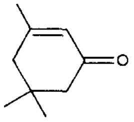
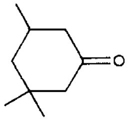
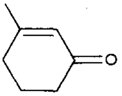
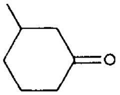
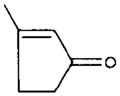
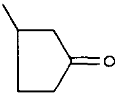
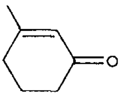
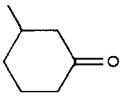
H_2, benzene, 50/1 substrate/catalyst) (and traces of menthane), there was not significant selectivity, the ratio between Δ_1 and Δ_3 menthenes being very close to unity in both cases. Moreover, the two reduced olefins showed no detectable optical activity between 590—350 μ. Thus isomerization of the menthenes was faster than hydrogenation of the diene. Since chiral dienes gave racemic mixtures and simple olefins were found to be difficult to hydrogenate, we decided to investigate the hydrogenation of a series of α-β unsaturated ketones.

To establish whether the configurational stability of the substrates were maintained, (+)-pulegone ($(\alpha)_D^{25}$ +22° (neat)) was first examined; the reduction yielded about 65% of menthone and 35% of isomenthone (110°C, 18 h, 30 atm of H_2, benzene, 50/1 substrate/catalyst). Using the reported optical rotations of the pure ketones [7], the value of $[\alpha]_D$ for the ratio of the two isomers obtained from the hydrogenation is approximately +12°. The recovered mixtures had $[\alpha]_D^{25}$ +11.5° indicating that no significant racemization had occurred.

Once the configurational stability of the compounds under hydrogenation had been established, asymmetric hydrogenations of prochiral cyclohexenones were undertaken. The results, shown in Table 1, are remarkable in a number of re-

TABLE 1

CATALYTIC HYDROGENATION USING $Co_2(CO)_6(PR_3)_2$ IN BENZENE[a]

PR_3	Substrate	Product (Configuration)	$[\alpha]_{334}$ (optical purity)	Yield (%)
PPh_2-Neomenthyl[b]		(S) 	+3.9° (16%)[d]	80
PPh_2-Neomenthyl		(S) 	−42° (10%)	40
PPh_2-Neomenthyl		(S) 	−30° (1.4%)	52
(−)-Diop[c]			−	36

[a] 30 atm H_2, 100°C, 50/1 substrate/catalyst. [b] $[\alpha]_D^{25}$ +87° (CH_2Cl_2). [c] The $Co_2(CO)_8$ (−)-Diop (1/2) catalytic system was obtained by adding both compounds in the solution before hydrogenation; (−)-Diop: $[\alpha]_D^{25}$ −12° ($CHCl_3$). [d] Based on the reported maximum rotation $[\alpha]_{334}$ +24° [9].

spects. First, although the results are of a preliminary nature and consequently show modest optical yields, hydrogenation of isophorone gave a 16% asymmetric synthesis using 2, $Co_2(CO)_6[P(Ph_2)Neomenthyl]_2$ $[\alpha]_D^{25} = +41$. Second, (−)-Diop a bidentate phosphine, which probably does not form a chelate ring around the cobalt, caused insignificant induction. Third, 2-methyl-2-cyclohexen-1 one was unreactive under these conditions with $Co_2(CO)_6[P(Bu)_3]_2$. Finally 3-methyl-2-cyclopenten-1-one gave 3-methylcyclopentanone with a very low optical yield (1.4%). Both reduction and asymmetric induction seem very sensitive to steric effects, and changing the nature of the substrate and the phosphine should provide some insight into the mechanism of the hydrogenation [8]. This is currently under investigation.

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