Journal of Organometallic Chemistry, 232 (1982) C17—C18
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

PHOSPHINORHODIUM COMPLEXES AS HOMOGENEOUS CATALYSTS

XIII*. ENANTIOSELECTIVE HYDROGENATION OF AMINOALKYL ARYL KETONES WITH A RHODIUM—DIOP CATALYTIC SYSTEM

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(Received February 26th, 1982)

Summary

The catalyst formed in situ from $[Rh(NBD)Cl]_2$ + DIOP catalyses the hydrogenation of α-(*N*,*N*-dialkylamino)alkyl aryl ketones to give enantioselectivities of up to 95%.

It is well known that the enantiomers of β-amino-α-phenylethanol derivatives show different biological activities, but only a few attempts have been reported to prepare these substances by asymmetric homogeneous catalytic hydrogenation of the corresponding prochiral aminoketones with phosphinorhodium complexes as catalyst [2—4].

We have previously found that use of a catalyst prepared in situ from $[Rh(NBD)Cl]_2$ and DIOP** and modified with tertiary amines can lead to good (55—84%) optical yields in the hydrogenation of aryl ketones in benzene solution [1]. We now extended this method to the asymmetric hydrogenation of (*N*,*N*-dialkylamino)alkyl aryl ketones and our results are summarized in Table 1.

As can be seen from the results, asymmetric hydrogenation of α-(*N*,*N*-dialkylamino)alkyl aryl ketones, with the catalytic system described yields the corresponding alcohols with high optical purity (87—95%). Addition of a tertiary amine to the catalytic system has no effect in this case because the substrate is itself a tertiary amine.

*For Part XII. see ref. 1. Some results of this work were presented at the 10th Intern. Conf. Organometal. Chem., Toronto, 9—14 August 1981. Abstracts p. 257.

**NBD = norbornadiene, DIOP = 2,3-*O*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)-butane [5].

0022-328X/82/0000—0000/$02.75

TABLE 1

RESULTS OF ASYMMETRIC HYDROGENATION OF (*N,N*-DIALKYLAMINO)ALKYL ARYL KETONES

Ketone	Et_3N/Rh	Chemical yield (%) [a]	Sign of rotation	Optical yield (%) [b]
α-NEt_2-acetophenone	—	70	(+)	93
α-NEt_2-acetophenone	5	63	(+)	91
α-$N(Bu^n)_2$-acetophenone	—	52	(+)	90
α-$N(CH_2)_5$-acetophenone	—	19	(+)	88
α-NEt_2-*p*-Me-acetophenone	—	68	(+)	91
α-NEt_2-*p*-Et-acetophenone	—	39	(+)	90
α-NEt_2-*p*-Pr^i-acetophenone	—	29	(+)	87
α-NEt_2-2-acetonaphthone	—	93	(+)	95
α-NEt_2-propiophenone	—	2		—
α-NEt_2-propiophenone	5	3		—
β-NEt_2-propiophenone	—	β-elimination		
β-$N(CH_2)_5$-propiophenone	—	β-elimination		
p-NMe_2-acetophenone	—	0		—
p-NMe_2-acetophenone	5	0		—
Acetophenone	5 [c]	4		—

[a] Reaction conditions: 50°C, 70 bar H_2, 20 h; 10 mmol ketone, 0.05 mmol Rh, 0.055 mmol (+)DIOP in 2.8 ml benzene. [b] Measured by the NMR shift technique (in CS_2, room temperature, in presence of Eu(facam)$_3$). All values are accurate to ±5%. [c] Et_2NPh instead of Et_3N.

The efficiency of the system is rather sensitive to minor changes in substrate structure. Even one methyl group α to the keto group strongly lowers the rate of hydrogenation. Hydrogenation of β-(*N,N*-dialkylamino)alkyl aryl ketones could not be achieved, because of β-elimination and formation of vinyl ketones which were saturated and in part further reduced to the corresponding secondary alcohols. The catalyst is inactive for the hydrogenation of alkyl *p*-(*N,N*-dimethylamino) aryl ketones, probably because of blocking by the aromatic amino group. This assumption was confirmed by the unsuccessful attempt to hydrogenate acetophenone using Et_2NPh instead of Et_3N as the modifying agent.

The high enantioselectivities achieved with α-(*N,N*-dialkylamino)alkyl aryl ketones are thought to be due to the simultaneous coordination of the nitrogen and oxygen atoms of the substrate to the central atom of the catalyst, thereby leading to a more rigid structure of the intermediate complex. A similar effect is responsible for the high optical yields achieved in hydrogenation of *N*-acylamino cinnamic acid derivatives [6,7].

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