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TRANSFORMATION OF ORGANIC COMPOUNDS IN THE PRESENCE OF METAL COMPLEXES

II *. REDUCTION OF ALKYL-SUBSTITUTED CYCLOHEXANONES VIA HYDROGEN-TRANSFER REACTIONS CATALYSED BY RHODIUM(I) COMPLEXES

K. FELFÖLDI, I. KAPOCSI and M. BARTÓK

Department of Organic Chemistry, József Attila University, Szeged (Hungary)

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Summary

Catalyst systems prepared in situ from bidentate phosphines ($Ph_2P(CH_2)_nPPh_2$, where $n = 1$–4) and from $[Rh(COD)Cl]_2$ proved to be active in the transfer hydrogenation of alkylcyclohexanones (alkyl = 2-Me, 4-Me, 4-t-Bu, *cis*-2,6-Me_2). With the exception of 4-methylcyclohexanone, which gave a *cis*/*trans*-cyclohexanol ratio of ~ 1, mainly *cis* alcohols were formed, their amounts increasing in proportion to the value of *n*. No reduction occurred in the case of 2-t-butyl- and 2,6-di-t-butyl-cyclohexanones.

Introduction

Numerous rhodium and iridium complexes containing various ligands are known to catalyse the transfer hydrogenation of ketones in the presence of isopropanol [1]. The stereochemistry of the hydrogenation depends considerably on the metal complex used, and on the bulk and position of the alkyl groups on the ring. The main product from 2-methylcyclohexanone is the *cis* alcohol [2], whereas from 4-alkylcyclohexanones, depending on the metal complex, either the *cis* [3,4] or the *trans* [3,4] alcohol is predominantly formed.

It was recently reported that the transfer hydrogenation of 4-t-butylcyclohexanone in isopropanol, in the presence of KOH, with complexes of the type $[Rh(diene)P_2]^+$ ($P_2 = Ph_2P(CH_2)_nPPh_2$, $n = 2$–4) gives a mixture of *cis*- and *trans*-4-t-butylcyclohexanol containing 69–76% *trans* isomer, the activity of the catalyst depending on the value of *n* [5].

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* For Part I see ref. 7.

Results and discussion

Our experimental results revealed that catalyst systems prepared in situ from $[Rh(COD)Cl]_2$ and bidentate phosphines are active in the transfer hydrogenation of alkyl-substituted cyclohexanones under conditions similar to those used for the cationic complexes (Tables 1 and 2). Whereas the cationic complexes yielded more of the *trans* isomer [5], we found that under certain conditions a *cis*/*trans* alcohol ratio > 1. The increase of n resulted in a larger amount of the *cis* isomer. Formation of the *cis* isomer was similarly favoured by increasing the bulk of the substituent (t-Bu in place of Me), and by the approach of the alkyl group to the carbonyl group (2-Me in place of 4-Me).

α-Substituents cause steric hindrance and therefore decrease the rate of the reaction. The presence of the bulky alkyl groups in 2-t-butyl- and *cis*-2,6-di-t-butylcyclohexanone inhibited the reduction completely.

Experimental

The ketones were from Fluka, the bidentate phosphine ligands ($Ph_2P(CH_2)_nPPh_2$, $n = 1$–4) were from Ventron, and $[Rh(COD)Cl]_2$ was made according to ref. 6. Gas chromatographic studies were carried out on a Chrom 4 apparatus: 3.6 m 5%

TABLE 1

REDUCTION OF 4-ALKYL-SUBSTITUTED CYCLOHEXANONES WITH RHODIUM(I) COMPLEXES PREPARED IN SITU FROM $[Rh(COD)Cl]_2$ [a]

Phosphine [b]	4-Methyl			4-t-Butyl		
	Time (h)	Conversion (%)	*cis*-Isomer (%)	Time (h)	Conversion (%)	*cis*-Isomer (%)
DPM	1	99	38	1.2	100	45
DPE	0.5	100	46	0.7	100	57
DPP	0.5	97	46	0.5	100	60
DPB	0.5	93	52	0.7	100	61

[a] Reactions were carried out in refluxing i-PrOH (5 ml) under nitrogen. $[Rh(CO)Cl]_2$ concentration was 1×10^{-5} *M*; $[P]/[Rh] = 2$, $[KOH]/[Rh] = 10$, $[substrate]/[catalyst] = 250$. [b] $PPh_2(CH_2)_nPPh_2$, DPM: $n = 1$, DPE: $n = 2$, DPP: $n = 3$, DPB: $n = 4$.

TABLE 2

REDUCTION OF α-ALKYL-SUBSTITUTED CYCLOHEXANONES WITH RHODIUM(I) COMPLEXES PREPARED IN SITU FROM $[Rh(COD)Cl]_2$ [a]

Phosphine	2-Methyl			*cis*-2,6-Dimethyl		
	Time (h)	Conversion (%)	*cis*-Isomer (%)	Time (h)	Conversion (%)	*cis*-Isomer (%)
DPM	5	56	52	5	52	78
DPE	5	58	77	5	67	81
DPD	5	60	80	5	51	93
DPB	5	60	85	5	63	95

[a] Reactions were carried out as reported in Table 1.

Carbowax 20/Chromosorb P column, flame ionization detector, nitrogen carrier gas. A Digint 34 μ integrator was used for quantitative evaluation.

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