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TRANSFORMATION OF ORGANIC COMPOUNDS IN THE PRESENCE OF METAL COMPLEXES

III *. TRANSFER HYDROGENATION OF ALKYLCYCLOHEXANONES. EFFECT OF PHOSPHINE BASICITY ON STEREOSELECTIVITY

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Summary

The transfer hydrogenation of 2- and 4-alkylcyclohexanones (alkyl = Me or t-Bu) was studied in alkaline i-PrOH with catalyst systems prepared in situ from $[Rh(COD)Cl]_2$ + phosphine (Ph_3P, Bu_3P). The stereoselectivity depends on the basicity of the phosphine and on the bulk and position of the alkyl substituent.

Introduction

Numerous rhodium(I) complexes are known to catalyse the transfer hydrogenation of ketones in alkaline i-PrOH [1]. The rapid study of the effects of the ligands on the hydrogenation is made possible by application of catalyst systems prepared in situ from $[Rh(diene)Cl]_2$ and the ligands. It was recently reported that the stereoselectivity of direct hydrogenation of 4-t-Bu-cyclohexanone with rhodium complexes produced in situ depends to a considerable extent on the basicity of the phosphine and on the use of a basic additive (Et_3N) [2].

Results and discussion

The transfer hydrogenation of 2- and 4-alkylcyclohexanones was studied with $[Rh(COD)Cl]_2$ + phosphine catalyst systems in alkaline i-PrOH (Tables 1–3). It was found that the stereoselectivity is influenced considerably by the basicity of the phosphine and by the position of the alkyl group.

From 2-alkylcyclohexanones, the *cis* alcohol (containing the thermodynamically less stable axial OH group) was the main product in the case of either PPh_3 or the

* For Part II see ref. 5.

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TABLE 1

RELATIVE AMOUNT OF *cis*-ALKYLCYCLOHEXANOLS IN THE TRANSFER HYDROGENATION OF CYCLOHEXANONES BY Rh CATALYST PREPARED IN SITU FROM $[Rh(COD)Cl]_2$ AND PHOSPHINES [a]

Cyclohexanone	Phosphine	Time (h)	Conversion (%)	*cis*-Isomer [b] (%)
2-Me	PPh_3	0.6	100	85
	PBu_3	0.5	95	83
2-t-Bu	PPh_3	1.6	91	86
	PBu_3	1.6	88	81
4-Me	PPh_3	0.3	100	63
	PBu_3	0.5	100	46
4-t-Bu	PPh_3	0.2	100	72
	PBu_3	0.5	100	44
cis-2,6-Me_2	PPh_3	0.9	100	98
	PBu_3	1.5	85	92

[a] Reactions were carried out in refluxing i-PrOH (5 ml) under nitrogen. $[Rh(COD)Cl]_2$ concentration was 1×10^{-5} *M*; [KOH]/[Rh] = 10, [P]/[Rh] = 2. [b] By GLC.

more basic PBu_3, with only slight differences in the two cases. The quantity of *cis* isomer formed from the 4-alkylcyclohexanones was decreased appreciably, however, if the more basic PBu_3 was applied (Table 1). This indicates that the substituent near the carbonyl group in the 2-alkylcyclohexanones exerts a predominant effect on the stereochemical course of the reaction, whereas with the more distant 4-alkyl substituent the main factors influencing the stereochemistry are the structural properties of the complex.

A study was made of the effect of the phosphine/Rh ratio in the case of PPh_3: increasing the amount of phosphine decreases the activity of the catalyst mainly in the case of 2-t-Bu-cyclohexanone, but its selectivity is only slightly enhanced (Table 2).

TABLE 2

EFFECT OF [P]/[Rh] ON THE STEREOSELECTIVITY IN THE TRANSFER HYDROGENATION OF CYCLOHEXANONES BY IN SITU PREPARED Rh CATALYST [a]

Cyclohexanone	Phosphine	[P]/[Rh]	Time (h)	Conversion (%)	*cis*-Isomer (%)
2-Me	PPh_3	2	0.6	100	85
		3	2.5	96	91
		4	5.0	91	92
2-t-Bu	PPh_3	2	1.6	91	86
		3	4.0	24	92
		4	5.0	15	98
4-Me	PPh_3	2	0.3	100	63
		3	0.6	90	65
		4	0.8	89	67
4-t-Bu	PPh_3	2	0.2	100	72
		3	0.3	100	72
		4	0.7	100	78

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

TABLE 3

CHANGE OF THE *cis*-ALKYLCYCLOHEXANOLS WITH TIME IN THE TRANSFER HYDROGENATION OF CYCLOHEXANONES BY IN SITU PREPARED Rh CATALYST [a]

Cyclohexanone	Phosphine	Time (h)	Conversion (%)	*cis*-Isomer (%)
4-Me	PPh_3	0.1	80	69
		0.5	100	67
		1.0	100	65
		2.3	100	63
4-Me	PBu_3	0.2	75	47
		1.2	100	44
		3.3	100	40
4-t-Bu	PPh_3	0.1	60	78
		0.2	80	72
		1.0	100	70
2-t-Bu	PBu_3	0.3	34	87
		1.0	67	83
		1.6	88	82

[a] Reactions were carried out as in Table 1; [P]/[Rh] = 2.

In some cases, the *cis/trans* product ratio displayed a tendency to decrease as the reaction time advanced (Table 3).

Experimental

Experiments were performed similarly as in ref. 3. The compounds used were from Fluka; $[Rh(COD)Cl]_2$ was prepared according to ref. 4. Reactions were followed by gas chromatograph on a Chrom 4 apparatus: 5% Carbowax 20M/Chromosorb P column, flame ionization detector, nitrogen carrier gas. Quantitative evaluations were carried out with a Digint 34 μ integrator.

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