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RHODIUM-PHOSPHINE COMPLEXES AS HOMOGENEOUS CATALYSTS

IV *. HOMOGENEOUS CATALYTIC HYDRODEHALOGENATION OF ORGANIC HALIDES BY MOLECULAR HYDROGEN

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Summary

Rhodium-phosphine complexes formed in situ from bis(1,5-hexadienechlororhodium), tertiary phosphines, and amines, catalyse the hydrodehalogenation of alkyl and aryl halides. Catalysts containing PPh_3 and with a P/Rh ratio of 1.1/1 are the most active; water increases the rate of the reaction.

Introduction

The heterogeneous catalytic hydrodehalogenation of organic halides by molecular hydrogen is a well known and industrially used reaction [2], but to our knowledge there has been only one report on homogeneous catalysis of this reaction [3]. However, there have been reports of homogeneous hydrodehalogenation using organic compounds such as alcohols [4] or amines [5] as hydrogen donors. We report below results on hydrodehalogenation with dihydrogen using rhodium-phosphine complexes obtained "in situ" from $[Rh(Hex)Cl]_2$ (Hex = 1,5-hexadiene) and PPh_3 as catalysts.

Results and discussion

The dark homogeneous solution obtained from $[Rh(Hex)Cl]_2$, triphenylphosphine, triethylamine and benzyl chloride (1/4.4/200/200) in benzene/methanol (1/1) was found to absorb dihydrogen at 50°C, and toluene was detected by GLC as the sole reaction product:

$$PhCH_2Cl + H_2 \xrightarrow[Et_3N]{[Rh]} PhCH_3 + Et_3N \cdot HCl$$

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* For part III see ref. 1.

Experiments under a variety of conditions revealed that the rate could be significantly increased by lowering the phosphine/rhodium ratio to 1.1/1, and by using a two phase *p*-xylene/water solvent system. Use of the somewhat stronger base diethylamine instead of triethylamine as HCl acceptor increased the rate, whereas tributylphosphine or $Ph_2PCH_2CH_2PPh_2$ gave less active catalysts than triphenylphosphine. The results of these experiments are shown in Table 1.

The catalytic system found to be most effective, viz. 1 Rh + 1.1 $PPh_3/Et_2NH/$*p*-xylene + H_2O, was succesfully used for the hydrodehalogenation of several organic halogen compounds such as alkyl and aryl halides, α-chlorocarboxylic esters and various benzyl and benzylidene halides. Alkyl halides were found to be the least reactive, and compounds with activated halogens, such as benzyl halides and α-chlorocarboxylic esters, the most reactive. Within the simple alkyl and aryl halides the reactivity order was $I > Br > Cl$, but benzyl iodide was, surprisingly, unreactive. Generally no significant difference was found between the aliphatic and aromatic compounds. Table 2 lists some representative data.

In most cases 100% conversion based on hydrogen consumption was easily achieved, which means a turnover number of 100 for the catalytically-active rhodium complex. The catalyst was generally still active at this point, and addition of new substrate restarted the H_2 absorption. By repeatedly adding additional benzyl chloride, a turnover number of 400 was reached in one experiment without deactivation of the catalyst, although the rate gradually diminished.

The yield of hydrogenated product determined by GLC amounted to 60—90%. No dimeric products or other by-products were detected. With substrates containing 2 or 3 halogen atoms the partially dehalogenated intermediates were found in samples taken during the reaction. For example after the consumption of 0.5 mol H_2 for 1 mol of CCl_4, the reaction product contained 1.1% CH_3Cl, 5.8% CH_2Cl_2, 22.3% $CHCl_3$ and 70.4% CCl_4, and a small amount of methane could be detected in the gas above the reaction mixture.

The remarkable low P/Rh ratio (the usual "Wilkinson-type" rhodium-phosphine catalysts require at least 2 phosphorus donor atoms per rhodium [6]) and the very dark brown colour of the clear homogeneous solutions suggest that our catalysts is rather different from the generally used rhodium(I)-phosphine complexes derived from $Rh(PPh_3)_3Cl$. Lowering the P/Rh ratio below 1/1 results in the visible precipitation of rhodium. The hydrogenolysis is also catalysed by this rhodium precipitate, as shown by a relatively rapid H_2 consumption, but this heterogeneous catalytic reaction is practically completely inhibited by adding 1.1 mol of PPh_3 per rhodium to the reaction mixture after formation of the precipitate. This dramatic difference between the effect of PPh_3 added before or after the start of hydrogenation clearly shows the existence of two different types of catalysts: the homogeneous species, which needs the presence of 1 PPh_3 per rhodium, and the heterogeneous species, which is inhibited by PPh_3.

Experiments to clarify the structure of the homogeneous catalytic system and its application to other reactions are in progress.

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TABLE 1

HYDRODEHALOGENATION OF BENZYL CHLORIDE [a]. EFFECT OF REACTION CONDITIONS

Solvent	Base	Phosphine	P/Rh	$t_{0,5}$(min) [b]	ITO [c]	Conversion (%) [d]
Benzene	Et_3N	PPh_3	2,2/1	—	0,05	—
Benzene/MeOH (1/1)	Et_3N	PPh_3	2,2/1	260	0,7	73
Benzene/MeOH (1/1)	Et_3N	PPh_3	1,1/1	60	2,5	76
Benzene/H_2O (1/1)	Et_3N	PPh_3	1,1/1	50	2,8	78
p-Xylene/H_2O (1/1)	Et_3N	PPh_3	1,1/1	20	3,8	81
p-Xylene/H_2O (1/1)	Et_2NH	PPh_3	1,1/1	15	5,1	88
p-Xylene/H_2O (1/1)	Et_2NH	PPh_3	2,2/1	230	0,4	70
p-Xylene/H_2O (1/1)	NaOH	PPh_3	1,1/1	26	4,5	86
p-Xylene/H_2O (1/1)	Et_2NH	PBu_3	1,1/1	50	1,3	71
p-Xylene/H_2O (1/1)	Et_2NH	$Ph_2PCH_2CH_2PPh_2$	1,1/1	20	3,8	83
p-Xylene/H_2O (1/1)	Et_2NH	—	—	—	4,0 [e]	—
p-Xylene/H_2O (1/1)	Et_2NH	PPh_3	1,1/1	—	0,3 [f]	—

[a] 0,025 mmol $[Rh(Hex)Cl]_2$, 5,0 mmol benzyl chloride, 5,0 mmol base, 12 ml solvent, 50°C and 1 bar H_2. [b] Time necessary for the consumption of 2,5 mmol H_2 (50% conversion or turnover number 50). [c] ITO = initial turnover (mol H_2/mol Rh min^{-1}). [d] As determined by GLC. All experiments were run until H_2 absorption reached 5,0 mmol. [e] Rhodium metal precipitated from the solution. [f] After adding PPh_3 to e).

TABLE 2

HYDRODEHALOGENATION OF VARIOUS ORGANIC HALIDES [a]

Halide	$t_{0,5}$(min) [b]	ITO [c]	Conversion [d] (%)	Halide	$t_{0,5}$(min) [b]	ITO [c]	Conversion [d] (%)
Benzyl chloride	15	5,1	88 [e]	1-Chloropentane		no reaction	
Benzyl bromide	16	4,5	63 [e]	1-Bromopentane	200	0,6	67 [e]
Benzyl iodide	110	2,8	70 [e]	3-Bromopentane	140	0.7	65 [e]
Benzylidene dichloride	140	5,3	—	1-Iodopentane	50	2,8	73 [e]
Benzylidene dibromide	170	4,8	—	Cyclohexylchloride	800	0,3	20 [f]
Chlorobenzene	400	0,1	32 [f]	Cyclohexyliodide	22	3,4	72 [e]
Bromobenzene	210	0,6	68 [e]	$ClCH_2COOEt$	11	8,9	84 [e]
Iodobenzene	55	2,3	82 [e]	$Cl_3CCOOEt$	290	4,8	—

[a] 0.025 mmol $[Rh(Hex)Cl]_2$, 5.0 mmol organic halogen compound, 5.0 mmol Et_2NH, 6 ml *p*-xylene, 6 ml H_2O, 50°C and 1 bar H_2. [b] Time necessary for the consumption of 2.5 mmol H_2 per 5.0 mmol organic halogen (50% conversion or turnover numbers of 50, 100 or 150 depending on the number of halogen atoms in the substrate). [c] Initial turnover (mol H_2/mol Rh min^{-1}). [d] As determined by GLC. [e] Reaction run until complete conversion of organic halide. [f] Reaction stopped before complete conversion of organic halide.

Experimental

General procedure

11.0 mg (0.025 mmol) $[Rh(Hex)Cl]_2$ and 14.4 mg (0.055 mmol) PPh_3 were dissolved at 50°C in 6 ml of *p*-xylene under H_2 in a thermostatted flask connected to a thermostatted gas burette equipped with a magnetic stirrer and a silicone rubber cap. When solution was complete, 6 ml water and 0.52 ml (5.0 mmol) Et_2NH were added and the catalyst was prehydrogenated for 30 min. The substrate (5.0 mmol) was then added with a syringe, and the reaction was monitored by measuring the hydrogen consumption. The product was analyzed by GLC.

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