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NEW CATALYTIC SYSTEM FOR THE HYDROGENATION OF KETONES *

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Summary

Alcohols are produced in high yield by hydrogenation of several aliphatic and aromatic ketones with rhodium complexes as catalysts in the presence of strong alkali.

Introduction

Few examples of the homogeneous hydrogenation of ketones to alcohols are known and most of them are based on the use of cationic complexes of formula $[RhH_2(PR_3)_2L_2]^+$ [1], involving basic tertiary phosphines [2], chiral phosphines [3,4] or phosphines bound to an insoluble resin [5].

During studies of the activation of molecular hydrogen by transition metal complexes [6,7] we have found new, very effective catalytic systems, able to promote the hydrogenation of several ketones. In the case of acetone we recognised a new reaction mechanism involving the addition of hydrogen to the enol form of the substrate, contrasting with the behaviour of previously reported catalysts which promote direct interaction of the carbonyl double bond with hydrogen [2].

Results and discussion

Recently we found that some monophosphino complexes of iridium [7] and rhodium [10] catalyse the hydrogenation of the carbon—carbon double bond of several olefins, but do not show any catalytic activity toward the carbon—oxygen double bond of aldehydes, ketones and esters in neutral or acid solution. However, in the presence of strong alkali the complexes $RhCl(C_8H_{12})PPh_3$ and $Rh_2H_2Cl_2(C_8H_{12})(PPh_3)_2$ readily promote the hydrogenation of acetone. The

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best results were obtained using the hydrido complex, whereas low reaction rates were observed with $RhCl(C_8H_{12})PPh_3$. Operating at 20°C and 1 atm of H_2, we obtained the highest rate of H_2 uptake (12 ml min^{-1}) using $Rh_2H_2Cl_2(C_8H_{12})(PPh_3)_2$ (10 mg) dissolved in pure acetone (2 ml) in the presence of a few drops of 30% NaOH. At the end of the reaction, isopropanol was detected by GLC (ca. 99%). During the reaction a dark powder, which does not contain rhodium metal, slowly separated from the solution; it was not characterised owing to difficulties encountered in its manipulation.

Under similar conditions other aliphatic ketones, such as butan-2-one and pentan-3-one, were also hydrogenated but with a lower and not well reproducible rate (0.2—2 ml H_2 min^{-1}), while benzophenone was not reduced.

An improved homogeneous system giving better and more reproducible hydrogenation rates with several aliphatic and aromatic ketones is obtained when the above reported rhodium complexes are pretreated with a stoichiometric amount of $NaBH_4$ in toluene and methanol. In this case we obtained dark and very reactive solutions which in the presence of strong alkali catalyse the hydrogenation of a number of ketones, as shown in Table 1. The reduction of benzophenone is the first example of hydrogenation of an aromatic ketone by use of a homogeneous catalyst (in fact the Osborn-type catalysts are inactive in this case [2]).

A mechanistic study of the reduction of acetone was carried out using isotopically labelled reagents; the same results were obtained with non-reduced or pre-reduced catalysts.

Starting from CH_3COCH_3, D_2, NaOH and H_2O, the NMR spectrum of the isopropanol produced showed a complex absorbance (doublet plus unresolved triplet) at τ 8.9 ppm (CH_3), a very weak and broad resonance at τ 6.1 ppm (CH) and a broad singlet at τ 4.6 ppm (OH). Using CD_3COCD_3, H_2, NaOD and D_2O, the NMR of the isopropanol showed two strong absorptions, one at τ 8.9 ppm (complex, 1H) and the second at τ 6.1 ppm (broad singlet, 1H) and a weaker absorption at τ 4.9 ppm (doublet, 0.3H).

These data show that: (1) most of the absorbed gas is incorporated at the terminal and central carbon atoms in equal abundance; (2) an isotopic exchange between the gas, the water and the alcoholic hydroxyl also occurs. A slow isotopic exchange between D_2O and H_2 in the presence of NaOD and catalysed by $Rh_2H_2Cl_2(C_8H_{12})(PPh_3)_2$, was in fact directly observed.

TABLE 1

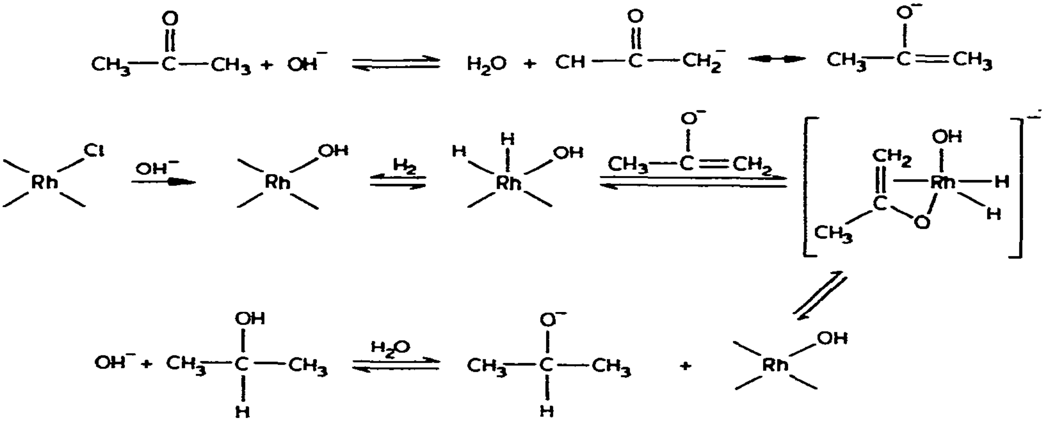
HYDROGENATION OF KETONES [a]

Ketone	Yield (%)	Rate (ml H_2 min^{-1})
Acetone [c]	>98 [b]	10.0
Hexan-2-one [d]	>98 [b]	4.0
Pentan-3-one [d]	>98 [b]	3.4
Acetophenone [d]	96 [b]	2.5
Benzophenone [d]	>98 [e]	2.5
Adamantan-2-one [d]	>98 [e]	4.0

[a] 2 ml of reacting solution plus solid KOH (ca. 50 mg). Catalyst concentration 9.8×10^{-3} *M* ($RhCl(C_8H_{12})PPh_3$ pre-reduced with $NaBH_4$). [b] Based on GLC determination of the formed alcohol. [c] 6.8 *M* in toluene. [d] 1.5 *M* in toluene and ethanol (10 : 1). [e] Based on IR estimation of the formed alcohol.

The results obtained in the hydrogenation of acetone can be interpreted in terms of the mechanism shown in Scheme 1. The existence of a hydroxo complex of rhodium as an active intermediate is supported by the observation that (a) treatment of $RhCl(C_8H_{12})(PPh_3)$ with strong alkali and hydrogen gives a dark product which do not contain chlorine; (b) the latter product is active in the hydrogenation of ketones only in the presence of OH^- and (c) the replacement of OH^- by CH_3O^- or other strong bases, leads to inactive systems.

SCHEME 1



For other ketones we have no evidence for the mechanism of the hydrogenation. Non enolisable ketones, such as adamantanone and benzophenone, can be hydrogenated by a direct attack of hydrogen on the C=O bond. However, the need for use of alkali also for these substrates and the observation of a large H—D scrambling in the aromatic protons of benzophenone during the deuteration to Ph_2CDOD indicate more complicated pathways.

It is of interest that only complexes containing triphenylphosphine in a ratio 1 : 1 with the rhodium are active catalysts in the presence of alkali. Complexes containing more phosphine, as $RhCl(PPh_3)_3$ [12] $Rh_2Cl_2(PPh_3)_4$ [12] $[Rh(C_8H_{12})(PPh_3)_2]BPh_4$ [13] and non-containing phosphine, as $Rh_2Cl_2(C_8H_{12})_2$ [14] and $Rh_2Cl_2(C_8H_{14})$ [15] are inactive under our conditions.

Experimental

IR spectra were recorded on a Perkin—Elmer 577 instrument and PMR spectra on a Varian HA 100 instrument. GLC analyses were carried out with a Hewlett—Packard 5750 apparatus using a flame detector and nitrogen as the carrier gas. Acetone/isopropanol were separated with Carbowax 400 (10%) on a Chrom. P. column (3 m × 1/8"); hexan-2-one/hexan-2-ol, pentane-3-one/pentan-3-ol, acetophenone/1-phenylethanol with DEGS (15%) on Chrom. P. column (4.5 m × 1/8"). Benzophenone/diphenylmethanol and adamantan-2-one/adamanton-2-ol were determined by IR analysis.

Preparation of the complex $Rh_2H_2Cl_2(C_8H_{12})(PPh_3)_2C_6H_5CH_3$

A solution of $RhCl(C_8H_{12})PPh_3$ [9] (1 g) in toluene (10 ml) was stirred at

90°C under H_2 (1 atm) for 3 h. Cooling to room temperature gave yellow crystals. Found: C, 60.99; H, 5.15; Cl, 7.10; P, 6.54. $C_{51}H_{52}Cl_2P_2Rh_2$ calcd.: C, 61.03; H, 5.22; Cl, 7.06; P, 6.17%. The IR spectrum (ν(Rh—H) at 2105 and 2135 cm^{-1}) and the chemical properties of this complex are very similar to those of the analogous iridium complex, for which the structure was derived from spectroscopic data [6] and confirmed by X-ray diffraction studies [11].

Hydrogenation of ketones

The reactions of hydrogen and different substrates were carried out using a thermostatted Pyrex apparatus (~10 ml) connected to a gas burette (10 ml) containing H_2 on Hg. The temperature was 25°C and the hydrogen pressure was 1.2—1 atm. The pre-reduction of $RhCl(C_8H_{12})PPh_3$ was carried out in the reaction cell by dissolving the complex (5—10 mg) in toluene (1 ml) and adding two molar equivalents of ethanolic $NaBH_4$. After stirring for a few minutes the solvents were evaporated under reduced pressure.

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