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Homogeneous Catalytic Hydrogenation of Unsaturated Aldehydes to form Saturated Aldehydes

By F. H. Jardine and G. Wilkinson, Inorganic Chemistry Laboratories, Imperial College, London S.W.7

The homogeneous catalytic hydrogenation system for olefins based on the use of tris(triphenylphosphine)chlororhodium has been extended to the specific reduction of the unsaturated carbon-carbon bond in propenal, but-2enal, and trans-2-methylpent-2-enal, resulting in the corresponding saturated aldehydes. The method would appear to be of general utility for such reductions.

It has been shown that the complex tris(triphenylphosphosphine)chlororhodium dissociates in benzene solution and that the *cis*-dihydrido species, $RhCl(H_2)(PPh_3)_2$, formed reversibly on exposure to molecular hydrogen, is a very effective catalyst for the hydrogenation of olefinic and acetylenic hydrocarbons at 25° and pressures of 1 atm. hydrogen.^{1,2} Since the reaction appears to be specific for unsaturated carbon-carbon linkages and the catalyst is not affected by a variety of other functional groups, a potentially useful application is the reduction of unsaturated aldehydes to saturated aldehydes. A non-catalytic reduction using a metal hydrido-complex involves the attack of hydridotetracarbonylcobalt, $HCo(CO)_4$, in excess, on propenal to give propanal and a little propanol.³

The main difficulty in such an application is to eliminate, or at least substantially reduce, the decarbonylation reaction^{2,4} of aldehydes with the solvated solution species, RhCl(PPh₃)₂, which yields the complex trans-RhCl(CO)(PPh₃)₂. By so removing the solvated species, which is in equilibrium with the catalytically active ¹ J. A. Osborn, G. Wilkinson, and J. F. Young, Chem. Comm., 1965, 17.

cis-dihydrido-species, the hydrogenation system is effectively destroyed since the carbonyl complex cannot function as an activator for molecular hydrogen under mild conditions.² This loss can be minimised by employing fairly dilute solutions (<0.2M) of unsaturated aldehydes and by adding the aldehyde to the hydrogenated catalyst solution under an atmosphere of hydrogen. Thus in 0.15_M solution in benzene at 25° using 60 cm. hydrogen pressure and with a catalyst concentration *ca*. 10⁻³ molar, propenal can be rapidly reduced; indeed the initial uptake of hydrogen may be so rapid that the characteristic pale yellow of the *cis*-dihydrido-species² in solution is not evident due to limitation of the rate of stirring in of hydrogen. But-2-enal and trans-2-methylpent-2-enal are reduced more slowly, presumably because the less favourable stereochemistry about the C=C bond operates adversely in the co-ordinative olefin activation step² on the *cis*-dihydrido-species. Hence, for these aldehydes, the rate of hydrogenation compared to the rate of the aldehyde decarbonylation poisoning reaction is lower than that for propenal, and the ratio

270

² J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, J. Chem. Soc. (A), 1966, 1711.

 ³ R. W. Goetz and M. Orchin, J. Org. Chem., 1962, 27, 3698;
 J. Amer. Chem. Soc., 1963, 85, 2782.
 ⁴ J. Tsuji and K. Ohno, Tetrahedron Letters, 1965, 3969.

271

of the catalyst to aldehyde concentration must be increased for more effective reduction, e.g., 5×10^{-3} M catalyst and 0.15M aldehyde.

The reaction products were studied by gas-liquid chromatography (g.l.c.) and, in agreement with the volumes of hydrogen absorbed, complete reduction of the olefinic function of the unsaturated aldehyde was confirmed. However, using high detector sensitivity, it was found that in the propanal there was a small quantity, less than 5% of the total reduced product, of propanol; no allyl alcohol was detected. The hydrogenation of the other unsaturated aldehydes also gave a similar low yield of the saturated alcohol.

A practical difficulty is the separation of the product aldehyde from rather dilute benzene solution. A preparative g.l.c. column could be employed, but we have used the classical method of recovery by washing the solution with aqueous sodium hydrogen sulphite, since there are no interfering reactions with either the residual catalyst or the carbonyl complex present in the benzene solution.

Because of this difficulty we have made several attemps to increase the utility of the process by altering the conditions so that more concentrated solutions of the unsaturated aldehydes may be reduced.

The temperature cannot be raised with profit since not only is the rate of the hydrogenation reaction increased but the rate of the decarbonylation reaction is similarly increased. It is not practical to replace the chloro-complex by the corresponding bromo- or iodocomplexes, $RhX(PPh_3)_3$, (X = Br or I), as their greater rates of hydrogenation are more than offset by their much greater rates of carbonyl extraction.⁵ The quantity of catalyst that can be added to the solution is also limited by its low solubility, and its dimerisation at high concentrations.² A practical limit in the above low-pressure experiments is about 5×10^{-3} M. Some advantage is gained by increasing the hydrogen pressure. Experiments have shown that the catalyst concentration can be greatly increased when higher hydrogen pressures are employed. The higher hydrogen pressure increases the rate of hydrogenation during the lifetime of the catalyst and may also prolong the lifetime of the catalyst by supressing the decarbonylation reaction. As a result more aldehyde may be reduced by a given quantity of catalyst. At hydrogen pressures of ca. 55 atm. we found that a 1.55m solution of but-2-enal could be reduced by a 9.4×10^{-3} M solution of the catalyst. However, the yield of saturated alcohol was also increased to 18.5%. This additional reduction may be due to the activation of hydrogen by the carbonyl complex trans-RhCl(CO)(PPh₃)₂. Experiments using the pure carbonyl complex have shown that trans-2-methylpent-2-enal is completely reduced to 2-methylpentanol at 80 atm. hydrogen pressure and 80°.

Other catalysts that have been tested have not proved to be very effective in bringing about the reduction to saturated aldehydes. When trans-IrCl(CO)(PPh₃)₂ is used to catalyse the addition of hydrogen to but-2-enal in benzene at 40° under 70 atm. of hydrogen, reduction is slow and only ca. 1% conversion is achieved after 24 hr. If this catalyst is used in toluene at 40° under 70 cm. of hydrogen for three days, very slow reduction takes place and approximately equal quantities of butanol and butanal are formed in ca. 2% yield. The ruthenium complex, RuCl₂(PPh₃)₃, fails to hydrogenate unsaturated aldehydes; using benzene as solvent no hydrogen uptake at 1 atm. and 25° was observed. This contrasts with its ready catalysis of the addition of

EXPERIMENTAL

The apparatus used and the preparation of tris(triphenylphosphine)chlororhodium(1) have been described.²

hydrogen to acyclic olefins under similar conditions.⁶

A Perkin-Elmer F.11 gas chromatograph fitted with a flame ionisation detector and a 1 m. $\times \frac{1}{8}$ in. Carbowax column was used to determine the products. The column temperature was set at an appropriate value for each aldehyde.

Hydrogen (British Oxygen Co.) was passed through an Engelhard "Deoxo" catalyst tube before admission to the vacuum system. Benzene (AnalaR) was dried over sodium; all other chemicals were of reagent quality.

Propenal (Kodak Ltd.) was distilled under nitrogen, using a short fractionating column, to free it from polymeric material and inhibitor. The fraction coming over between $52-53^{\circ}$ was collected and used immediately. But-2-enal (B.D.H. Ltd.) was similarly purified, the fraction coming over between $101-102^{\circ}$ was collected and used immediately. *Trans*-2-methylpent-2-enal (kindly provided by Dr. B. Saville of the British Rubber Producers Research Association, Welwyn Garden City) was not distilled but was scrubbed with dry nitrogen before addition to the benzene solution of the catalyst.

Procedure.— Tris(triphenylphosphine)chlororhodium(1) (0·2 g.; 2·16 mmoles) was dissolved in de-aerated benzene (75 ml.) under hydrogen at 25° and 70 cm. pressure. But-2-enal (1·5 ml.; 18·3 mmoles) was added to the vigorously stirred solution and the hydrogen uptake was measured. After 16 hr., 19·1 mmoles of hydrogen was absorbed. The solution was washed with saturated sodium hydrogen sulphite (3 × 10 ml.) containing some solid sodium metabisulphite, each portion being left in contact with the benzene for *ca*. 1 hr. The aqueous layers and solid were combined, neutralised with solid sodium hydrogen carbonate, and the solution extracted with diethyl ether (3 × 10 ml.). After drying over sodium sulphate, removal of solvent left butanal (1·0 ml.; 11·2 mmoles, 61·2% yield).

Experiments at high gas pressures were carried out in stainless steel autoclaves which were flushed with hydrogen before admission of hydrogen to the working pressure. In the experiments using the carbonyl complexes $MCl(CO)(PPh_3)_2$ (M = Rh or Ir) a 50 ml. autoclave was charged with the catalyst (0.2 g.), benzene (20 ml.), and the aldehyde (5 ml.). Using RhCl(PPh_3)_2 the autoclave (25 ml.) was charged with the catalyst (0.1 g.), benzene (10 ml.), and aldehyde (1.5 ml.) in a small glass ampoule fitted with a break seal, and was then pressured to 70 atm. with hydrogen. The ampoule was broken on shaking by a steel bolt.

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⁵ M. C. Baird and G. Wilkinson, unpublished results.
⁶ D. Evans, J. A. Osborn, F. H. Jardine, and G. Wilkinson, *Nature*, 1965, 208, 1203.