Stereoselective Homogeneous Hydrogenation of Arenes to Cyclohexanes Catalysed by $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$[†]

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Summary $[Rh(\eta^5\text{-}C_5Me_5)Cl_2]_2$ catalyses the hydrogenation of benzene and a variety of substituted benzenes to the appropriate cyclohexanes under homogeneous conditions (50 °C, 50 atm) in the presence of base (Et_3N); the reaction is highly stereoselective and all-*cis* isomers are the chief products.

WHILE very many examples of the hydrogenation of olefins and dienes catalysed by homogeneous complexes are known,[1] few complexes have been found to catalyse arene hydrogenation homogeneously and those that do are rapidly deactivated or have a limited range.[2] The readily prepared and air stable di-μ-chlorodichlorobis(pentamethylcyclopentadienylrhodium) (I)[3] is a catalyst for olefin hydrogenation at ambient temperature and pressure[4] and we here report that it is also an effective catalyst for arene hydrogenation at 50 °C and 15—50 atm of H_2. No detectable amounts of metal were formed under these conditions; this was confirmed by light-scattering experiments.

For the hydrogenation of benzene to cyclohexane the following points have been established but it should be emphasised that the conditions have not yet been optimised either for these reactions or for the others described.

(i) Base is required as a co-catalyst and at least 15 equiv. of Et_3N per mole of (I) were used. Kinetic studies of alkene hydrogenation using (I) indicate that heterolytic cleavage of hydrogen occurs and that the role of the base is to tie up the HCl generated and so promote the formation of rhodium-hydrido species.[5] Base is assumed to play a similar role in arene hydrogenation.

(ii) The reaction proceeds best in weakly co-ordinating polar media and propan-2-ol was used as solvent for most experiments.

(iii) The rate of reaction varies linearly with H_2-pressure, increases with catalyst concentration up to a point where H_2-absorption appears to become rate-limiting, and increases with temperature.

TABLE. Hydrogenation of substituted benzenes[a]

Compound	Products[b]
Styrene	Ethylbenzene (97%), ethylcyclohexane (3%)
Phenylacetylene	Styrene (7%)
Anisole	Methoxycyclohexane (6%), methoxycyclohexene (19%)
Phenol	Cyclohexene (0·5%), cyclohexanone (1%)
Methyl benzoate	Toluene (8%), methyl cyclohexanoate (75%)
Acetophenone	Methyl cyclohexyl ketone (100%)
Benzophenone	Cyclohexyl phenyl ketone (15%), dicyclohexyl ketone (50%), dicyclohexylmethanol (10%)
NN′-Dimethylaniline	*NN′*-Dimethylcyclohexylamine (73%)
Nitrobenzene	Aniline (96%), cyclohexane (4%)
Fluorobenzene	Fluorocyclohexane (14%), cyclohexane (38%)
Chlorobenzene	Cyclohexane (1%), benzene (0·5%)
Bromobenzene	Cyclohexane (10%)
Iodobenzene	Cyclohexane (2%), benzene (3%)

[a] Conditions: complex (I) (0·05 mmol), Et_2N (0·2 ml, 1·5 mmol) propan-2-ol (18 ml), substrate (2 ml), 50 °C, 50 atm, 36 h.
[b] Products and percentages [relative to benzene (100%)] were estimated by g.c.–mass spectrometry.

[†] No reprints available.

(iv) No cyclohexadienes or cyclohexene could be detected in the products even when the reactions had not gone to completion.

(v) $[^2H_6]$Benzene was hydrogenated to $[^2H_6]$cyclohexane; a sample containing 85 ± 4% $C_6{}^2H_6$ gave cyclohexane containing 75 ± 4% $C_6{}^2H_6{}^1H_6$ while the isotopic constitution of the $[^2H_6]$benzene which had not reacted was unchanged. This indicates that only a little $^2H/^1H$ exchange occurs during the hydrogenation.

Reactions were normally carried out at 50 °C and 50 atm for 36 h using 20 ml of reaction mixture containing catalyst (0·05 mmol), arene (22·5 mmol), and Et_3N (1·48 mmol). Under these conditions in propan-2-ol, benzene was reduced to cyclohexane in the presence of (I) and a turnover of 225 benzene molecules per rhodium was achieved; when benzene itself was the solvent the turnover number rose to over 400 molecules of benzene per rhodium. The complexes $[Rh(C_5Me_5)Br_2]_2$, $[Rh(C_5Me_5)(OAc)_2.H_2O]_n$, and $[\{Rh(C_5Me_5)\}_2HCl_3]$ all showed similar activity but the iridium analogues were significantly less active catalysts; $[Rh(PPh_3)_3Cl]$ only showed 3% of the activity of (I) and $[Co(C_5Me_5)I_2]_2$ was inactive and decomposed.

High stereospecificity for all-*cis* hydrogenation was observed. *o*-Xylene gave *cis*- and *trans*-1,2-dimethylcyclohexanes in a 6·2 : 1 ratio, *m*-xylene gave 1,3-dimethylcyclohexanes (*cis* : *trans*, 3·8 : 1), and *p*-xylene gave 1,4-dimethylcyclohexanes (*cis* : *trans*, 2 : 1).‡ By comparison with benzene, the following amounts of substituted cyclohexanes were obtained from substituted benzenes, indicating that the substituents do exercise some steric hindrance towards the reaction: $C_6H_6 \approx C_6H_5Me \approx$ *o*-, *m*-, and *p*-$C_6H_4Me_2$ (100%) > C_6H_5Et (60%) > $C_6H_5Bu^t$ (45%) > 1,3,5-$C_6H_3Me_3$ (35%) > $C_6H_5Bu^s$ (25%).

Preliminary studies show the catalyst system to tolerate at least some functionalities on the arene (Table); thus, while substrates containing unprotected -OH or -CO_2H groups were hydrogenated only to a very small degree or not at all, aryl-ethers, -esters, -ketones, and *NN'*-dimethylaniline were all reduced. Hydrogenolysis of the functional group occurred for methyl benzoate and for the halogenobenzenes; nitrobenzene was reduced to aniline and some hydrogenolysis again occurred.

Anthracene was reduced to tetrahydroanthracene (70%), octahydroanthracene (two isomers, 15 and 7%), and perhydroanthracene (3%).

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‡ Identified and determined by ^{13}C n.m.r. spectroscopy and g.c.–mass spectrometry.

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