Mechanisms of Hydrogenation. Part X.[1] Homogeneous Hydrogenolysis of Organic Halides and Hydrogenation of the Carbonyl, Epoxy-, and Nitro-groups

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The catalyst formed from trichlorotris(pyridine)rhodium with sodium borohydride in dimethylformamide is shown to be effective for the homogeneous hydrogenolysis of the carbon–halogen bond, R–X, where R = benzyl, allyl, aryl, or –CO–C< but not alkyl, and X = Cl or Br. Vicinal dihalides have also been hydrogenolysed. The stereochemistry of halogen displacement is consistent with a free-radical mechanism.

The carbonyl groups in acetophenone, benzophenone, and benzoin have been hydrogenated with this catalyst system, and styrene oxide gives 2-phenylethanol. Examples of hydrogenation of nitro-groups ($RNO_2 \longrightarrow RNH_2$; R = aryl or cyclohexyl) are reported.

THE catalyst system $RhCl_3py_3$–$NaBH_4$ in dimethylformamide (DMF) has been shown to be highly active for catalytic homogeneous hydrogenation and to reproduce many of the properties of heterogeneous catalysis.[1] We were interested to discover whether this soluble catalyst would also catalyse hydrogenolysis of the carbon–halogen, benzyl-OR, or allyl-OR bond (R = H, COR', *etc.*) as observed with various transition metals.

The system $RhCl_3py_3$–$NaBH_4$–H_2 in dimethylformamide did not hydrogenolyse bromocyclohexane, but proved very effective with benzyl halides, α-halogeno-ketones, α-halogeno-esters, and a range of aryl halides.

In olefin hydrogenation with this catalyst we found evidence [2] that hydrogen transfer rather than olefin co-ordination is rate-limiting. Hydrogen transfer appeared to be rate-limiting also in the hydrogenolysis of benzyl chloride. The rate of reaction was found proportional to the catalyst concentration [Table (a)], and not much affected by the benzyl halide concentration [Table (b)] or by alkyl substitution on the benzylic carbon atom [Table (c)]. The rate differences in (c) are much smaller

(a) $PhCH_2Cl$ (70mM in DMF)

$[RhCl_3py_3]$/mM:	4·3	8·6	12·8	17·0
H_2(ml min^{-1}):	0·85	2·4	3·7	4·3

(b) $RhCl_3py_3$–$NaBH_4$ (8·6mM in DMF)

$[PhCH_2Cl]$/mM:	70	140	270	540	1080
H_2(ml min^{-1}):	2·3	2·4	2·7	3·2	3·2

(c) $RhCl_3py_3$–$NaBH_4$ (36mM in DMF), halide (180mM)
H_2 uptake: $PhCH_2Cl$ 4·5, $PhCHMeCl$ 3·0, $PhCHMe_2Cl$ 2·7 ml min^{-1}

than for first- or second-order nucleophilic displacement,[3] but comparable to the relative rates of heterogeneous hydrogenolysis of $PhCH_2$·OH and $PhCMe_2$·OH at palladium.[4]

Benzyl bromide underwent hydrogenolysis more slowly than benzyl chloride (3·2 and 4·0 ml min^{-1}, respectively). This suggests that the halogen enters the reaction complex and that the greater π-acceptor property of Br in comparison with Cl retards hydrogen transfer.

Toluene was shown (g.l.c., n.m.r.) to be the only product of hydrogenolysis, and toluene was obtained also from benzyl acetate, and more rapidly from benzyl monochloroacetate, but benzyl alcohol, and di- and triphenylmethanol proved resistant to hydrogenolysis. Thus, as in the heterogeneous reaction,[4] the polarity of the displaced groups is important.

In no case did we detect hydrogenolysis by $RhCl_3py_3$–$NaBH_4$ in the absence of hydrogen, nor was there evidence for heterogeneous catalysis; the reactions were always examined for any deposition of rhodium metal.

In respect of mechanism the stereochemistry of hydrogenolysis should be informative. In seeking suitable instances where the stereochemistry could be determined we showed that hydrogenolysis is catalysed for halogen displacement from ethyl bromoacetate, methyl 2-chloro-2-phenyl-ethanoate and -propanoate, *endo*-3-bromocamphor, and 2-halogeno-3-oxo-steroids.

(—)-2-Chloro-2-phenylpropanoic acid [5] and its methyl ester were hydrogenolysed without difficulty, to give, however, almost totally racemic 2-phenylpropanoic acid or methyl ester. Since (—)-2-phenylpropanoic acid proved optically stable in the presence of the catalyst and hydrogen we infer that hydrogenolysis is initiated by halogen abstraction by rhodium, which releases an organic residue free to undergo co-ordination and hydrogen addition from either side.

2α-Bromo-2β-methylcholestan-3-one [6] on hydrogenolysis showed some stereoselectivity in giving 2α- and 2β-methylcholestan-2-one in a ratio of *ca.* 1 : 3. However, the reaction is evidently not stereospecific. The product ratio is the same as was observed for heterogeneous hydrogenolysis of the same bromide.[7] We infer that this reflects the steric requirements for 2α- and 2β-hydrogen addition and is not a mechanistic consequence of the catalytic process.

Camphor exhibits well known steric preferences in its reactions, *viz.* in reduction of the carbonyl group, with

[1] P. Abley, I. Jardine, and F. J. McQuillin, *J. Chem. Soc.* (*C*), 1971, 840.

[2] I. Jardine and F. J. McQuillin, *Chem. Comm.*, 1969, 502.

[3] S. Winstein, E. Grunwald, and H. W. Jones, *J. Amer. Chem. Soc.*, 1951, **73**, 2700; E. D. Hughes, C. K. Ingold, and A. D. Scott, *J. Chem. Soc.*, 1937, 1201; A. Streitweiser, *Chem. Rev.*, 1956, 607.

[4] A. M. Khan, F. J. McQuillin, and I. Jardine, *J. Chem. Soc.* (*C*), 1967, 136.

[5] E. L. Eliel and J. P. Freeman, *J. Amer. Chem. Soc.*, 1952, **74**, 923.

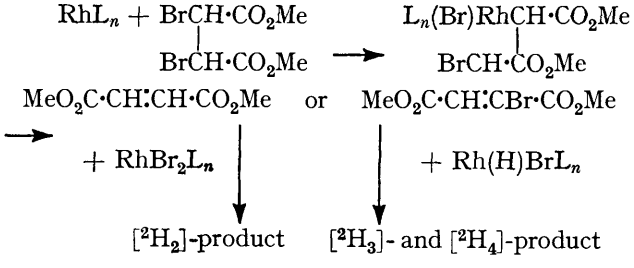
[6] Y. Mazur and F. Sondheimer, *J. Amer. Chem. Soc.*, 1958, **80**, 5220; *cf.* C. Djerassi, N. Finch, R. C. Cookson, and C. W. Bird, *ibid.*, 1960, **82**, 5488.

[7] D. A. Denton, F. J. McQuillin, and P. L. Simpson, *J. Chem. Soc.*, 1964, 5535.

predominantly *endo*-hydrogen addition,[8] and in protonation of the enol, with predominantly *exo*-hydrogen uptake.[9] 3-*endo*-Bromocamphor was reduced with $RhCl_3py_3$–$NaBD_4$ in deuterium. This gave a [^{2}H]camphor which with lithium aluminium hydride afforded a [$^2H_1$]-bornan-2-ol showing a clear n.m.r. doublet at τ 6·44 (J 8·2 Hz). This is as expected for a 3-*exo*-deuteriobornanol,[10] and although the presence of some *endo*-deuterio-product cannot be excluded it is apparent that *endo*-halogen removal results in *exo*-deuterium addition. 3-[$^2H_2$]Camphor showed no loss of deuterium when shaken with the catalyst for 20 h in hydrogen, *i.e.* there is no evidence for rearrangement of hydrogen substituents after hydrogenolysis.

Taken together, these three instances show that the mechanism of hydrogenolysis imposes no set steric course of displacement, the stereochemistry of the product being determined by the requirements of the substance under study. This is most consistent with halogen removal to give an organic radical and precedent is found in the reaction [11] of variously substituted organic halides with $[Co(CN)_5]^{3-}$. We also note that whereas $RhCl_3py_3$–$NaBH_4$-catalysed hydrogenolysis of benzyl and triphenylmethyl chlorides give only toluene and triphenylmethane, hydrogenolysis of chlorodiphenylmethane gives *sym*-tetraphenylethane as well as diphenylmethane. The analogy with the reactions of $[Co(CN)_5]^{3-}$ is reinforced by the report that hydrogenolysis of (+)-1-bromo-2,2-diphenylcyclopropanecarboxylic acid with $[Co(CN)_5]^{3-}$ in hydrogen gives racemic 2,2-diphenylcyclopropanecarboxylic acid.[12] Also it now appears that oxidative addition of organic halides to IrCl(CO)$(PMe_3)_2$ occurs non-stereospecifically.[13] We infer that halide hydrogenolysis by the $RhCl_3py_3$–$NaBH_4$ catalyst is similar in mechanism.

Hydrogenolysis of 1,2-dihalides was examined with dimethyl *meso*-2,3-dibromosuccinate and *meso*-1,2-dibromo-1,2-diphenylethane in deuterium. The reactions were rapid, and gave dimethyl [^{2}H]succinate of isotope composition: $^2H_0$ 0, $^2H_1$ 4·3, $^2H_2$ 29·0, $^2H_3$ 53·0, $^2H_4$ 10·0%, and [^{2}H]bibenzyl of composition: $^2H_0$ 5, $^2H_1$ 30, $^2H_2$ 55, $^2H_3$ 8, $^2H_4$ 1·9%, respectively. It appears that halogen displacement is stepwise and the significant amount of [$^2H_3$]- and [$^2H_4$]-products suggests a sequence of elimination steps, *via* a rhodium–carbon intermediate, *e.g.*



[8] H. C. Brown and J. Muzzio, *J. Amer. Chem. Soc.*, 1966, **88**, 2811.

[9] T. T. Tidwell, *J. Amer. Chem. Soc.*, 1970, **92**, 1448; P. von R. Schleyer, *ibid.*, 1967, **89**, 701; S. P. Jindal, S. S. Sohoni, and T. T. Tidwell, *Tetrahedron Letters*, 1971, 779.

Vicinal dihalides are known to undergo elimination [14] to form olefins in the presence of $[Co(CN)_5]^{3-}$ or Cr^{2+}, and we have earlier drawn attention to instances of elimination in heterogeneous hydrogenation catalysis.[7]

As an example of an allylic halide we examined cinnamyl bromide, which with $RhCl_3py_3$–$NaBH_4$–H_2 gave 1-phenylpropane and 1-bromo-3-phenyl propane (4 : 1 by n.m.r. analysis). With only 1 mol. equiv. uptake of hydrogen the product comprised 1-phenylpropene, 1-phenylpropane, and 1-bromo-3-phenylpropane (52 : 25 : 22 by n.m.r.), *i.e.* hydrogenolysis of the C–Br bond is rapid relative to olefin hydrogenation.

If hydrogenolysis of the carbon–halogen bond is a homolytic process, aryl halides would be expected to react. This was verified for chloro- and bromo-benzene, and for a series *p*-BrC_6H_4X (X = NH_2, OMe, CO_2Me). Chlorobenzene reacted more rapidly than bromobenzene, and methyl 4-bromobenzoate more rapidly than 4-bromoanisole. No biphenyl derivatives were detected, *i.e.* the aryl intermediate is rapidly reduced. Some measure of hydrogen abstraction from the DMF solvent is possible, but in view of the high deuterium incorporation in experiments with deuterium, hydrogen transfer within an aryl–rhodium hydride complex seems to be the main process.

The level of reactivity observed with the catalyst system suggested that hydrogenation of carbonyl and epoxy-groups should be possible. Cyclohexanone, however, proved completely resistant to hydrogenation; this also shows that the borohydride used to reduce the complex is inactive in carbonyl reduction. Rhodium perchlorate, chosen as offering a potentially more cationic complex, with $NaBH_4$ in DMF also failed to catalyse this hydrogenation, although it proved highly active towards oct-1-ene. However, $RhCl_3py_3$–$NaBH_4$–H_2 proved effective with aryl ketones (acetophenone, benzophenone, and benzoin). No reduction was observed in the absence of hydrogen (n.m.r. examination of recovered ketone). However, benzoin gave *meso*- and (±)-hydrobenzoin (85 : 15 by n.m.r. analysis) in proportions very similar to those observed for borohydride reduction in DMF (86 : 14), *i.e.* the steric requirements of the two reagents are not very dissimilar.

The relatively few reported examples of homogeneous hydrogenation of the carbonyl group include the conversion of benzil into benzoin, catalysed [15] by $[Co(CN)_5]^{3-}$,

[10] A. F. Thomas, R. A. Schneider, and J. Meinwald, *J. Amer. Chem. Soc.*, 1967, **89**, 68.

[11] J. Halpern and J. P. Maher, *J. Amer. Chem. Soc.*, 1964, **86**, 2311; P. B. Chock, and J. Halpern, *ibid.*, 1969, **91**, 582; J. Halpern and P. E. Phelan, *ibid.*, 1972, **94**, 1881.

[12] J. Kwiatek and J. K. Seyler, A.C.S. Adv. Chem. Series, 1968, vol. 70, p. 207.

[13] J. S. Bradley, D. E. Connor, D. Dolphin, J. A. Labinger, and J. A. Osborn, *J. Amer. Chem. Soc.*, 1972, **94**, 4043; F. R. Jensen and B. Knickel, *ibid.*, 1971, **93**, 6339; R. G. Pearson and W. R. Muir, *ibid.*, 1970, **92**, 5519.

[14] J. Halpern and J. P. Maher, *J. Amer. Chem. Soc.*, 1965, **87**, 5361; W. C. Kray and C. E. Castro, *ibid.*, 1964, **86**, 4603.

[15] J. Kwiatek, I. L. Mador, and J. K. Seyler, *J. Amer. Chem. Soc.*, 1962, **84**, 304; M. Murakani, R. Kwai, and K. Suzaki, *J. Chem. Soc. Japan*, 1963, **84**, 669.

and reductions of a small number of aliphatic ketones [16] using $[RhH_2(PPhMe_2)_2]^+$.

We have already reported instances of homogeneous hydrogenation of the C=N bond and of the nitro-group.[1] However, we have been unable to effect hydrogenation of acetophenone oxime. Nitrocyclohexane, on the other hand, absorbed 3 mol. equiv. of hydrogen to give cyclohexylamine. In the case of 2-nitro-1-phenylprop-1-ene and 1-(3,4-dimethoxyphenyl)-2-nitroethene, however, only the olefinic bond could be hydrogenated, as has been observed [17] for similar hydrogenations catalysed by $RhCl(PPh_3)_3$. Nitro-aromatic compounds reacted more readily: nitrobenzene, *p*-nitrotoluene, and *p*-nitrobenzoic acid could be slowly hydrogenated to the corresponding amines. After uptake of 1 mol. equiv. of hydrogen 4-nitrobenzyl chloride gave 4-nitrotoluene, which was further hydrogenated to *p*-toluidine. 4-Dimethylaminonitrosobenzene was readily hydrogenated to 4-dimethylaminoaniline.

Styrene oxide could be hydrogenated to 2-phenylethanol. This reaction has previously been observed [15] in the presence of $[Co(CN)_5]^{3-}$, and we note that the epoxy-group is also cleaved by cobaloxime.[18]

Taken together with the previously reported examples of homogeneous hydrogenation the present results disclose a very close similarity to the phenomena of heterogeneous hydrogenation catalysis. The failure of the homogeneous system to effect hydrogenolysis of benzyl alcohols draws attention to the importance of available electron density, or electron promotion energy. This factor is underlined also in heterogeneous catalysis by a variety of observations. Acidity is inhibitory of the heterogeneous hydrogenolysis of organic halides. This has been attributed [7] to surface protonation reducing the catalyst electron density. We suggest that the observed increase in the amount of steric inversion in hydrogenolysis of benzyl ethers with increasing palladium content of the catalyst [19] is also a reflection of increasing surface electron density.

EXPERIMENTAL

Hydrogenations were followed by observing hydrogen uptake at constant pressure in a differential form of apparatus.

The catalyst was prepared [1] from recrystallised $RhCl_3py_3$ and sodium borohydride, which was recrystallised from diethylene glycol dimethyl ether.[20] The combination of $RhCl_3py_3$ with $NaBH_4$ (*ca.* 1 equiv.) in DMF was equilibrated with hydrogen before use.

Benzylic Halides.—Rate data are quoted in the Discussion section. The products (toluene, ethylbenzene, isopropylbenzene) were identified by g.l.c. and n.m.r. comparison with authentic materials.

The benzyl derivatives $PhCH_2X$ (X = HO, Cl, Br, OAc, or $O{\cdot}CO{\cdot}CH_2Cl$) were hydrogenated at a concentration of 150mM in DMF with the 8·5mM-catalyst. For X = HO no toluene was detected; for the remainder, reaction was essentially complete and toluene was recognised by g.l.c. and n.m.r. Diphenylmethyl chloride was recovered unchanged after being stirred in DMF for 49 h, but with the catalyst and hydrogen gave 1,1,2,2-tetraphenylethane, m.p. 210°, *m/e* 332, τ 2·68 and 5·22, and diphenylmethane, m.p. 24°, τ 2·89 and 6·08. Chlorotriphenylmethane similarly gave triphenylmethane, m.p. 91°, identical (t.l.c., n.m.r.) with an authentic sample.

(−)-2-*Chloro*-2-*phenylpropanoic Acid.*—(*a*) (−)-2-Hydroxy-2-phenylpropanoic acid ($[\alpha]_D$ −37·2) was obtained [21] by resolution of the racemate with (+)-1-amino-1-phenylethane. The derived chloro-acid ($[\alpha]_D$ −24·8°), made by treatment with thionyl chloride, was esterified with diazomethane to give methyl (−)-2-chloro-2-phenylpropanoate,[5] b.p. 125° at 11 mmHg, $[\alpha]_D$ −4·5°.

(*b*) (−)-2-Chloro-2-phenylpropanoic acid (166 mg) and $RhCl_3py_3$–$NaBH_4$ (170 mg) in DMF (10 ml) absorbed 1 mol. equiv. of hydrogen in 3·5 h. The product, isolated in light petroleum, showed $[\alpha]_D$ −0·13°, τ 2·70, 6·31 (q, *J* 8 Hz), and 8·54 (d, *J* 8 Hz); 2-phenylpropanoic acid [22] shows $[\alpha]_D$ ±92·5°.

(*c*) Methyl (−)-2-chloro-2-phenylpropanoate (173 mg) with the catalyst (270 mg) in DMF (10 ml) absorbed 1 mol. equiv. of hydrogen to give methyl 2-phenylpropanoate, b.p. 105—115° at 14 mmHg, τ 2·75, 6·4, and 8·56 (d, *J* 7 Hz), $[\alpha]_D$ +0·1° (lit.,[23] $[\alpha]_D$ +86°).

(*d*) (−)-2-Phenylpropanoic acid (50 mg) of $[\alpha]_D$ −62° with the catalyst (100 mg) in DMF (10 ml) under hydrogen for 25 h gave an acid of $[\alpha]_D$ −60·3°.

3-endo-*Bromocamphor.*—(*a*) 3-*endo*-Bromocamphor with the catalyst in DMF in hydrogen gave camphor, identified by t.l.c., n.m.r., and *m/e* (152) (the doublet τ 5·40 of *endo*-bromocamphor was completely absent).

(*b*) A mixture of $RhCl_3py_3$ (145 mg) and $NaBD_4$ (13 mg) in DMF (10 ml) was shaken in deuterium; the system was evacuated and re-equilibrated twice with deuterium. 3-*endo*-Bromocamphor (150 mg) was added and 14 ml of deuterium was absorbed in 15 min. The product, isolated by t.l.c. on silica gel in benzene, gave a [^{2}H]camphor which with lithium aluminium hydride in ether gave [^{2}H]bornan-2-ol, τ 9·0, 9·13, 9·17, 8·2—9·0, 6·44 (d, *J* 8·2 Hz), $^2H_0$ 26, $^2H_1$ 65, $^2H_2$ 8% (mass spectroscopy).

(*c*) [^{2}H]Camphor [9] (140 mg) ($^2H_0$ 8·6, $^2H_1$ 70·2, $^2H_2$ 21·2%), kept with $RhCl_3py_3$–$NaBH_4$ (160 mg) in DMF under hydrogen for 20 h, showed on recovery $^2H_0$ 2, $^2H_1$ 72·7, $^2H_2$ 23·7.

Halogenoketo-steroids.—(a) 2α-Bromocholestan-3-one (150 mg) with the catalyst (76 mg) in DMF (10 ml) absorbed 1 mol. equiv. of hydrogen in 10 min, to give 5α-cholestan-3-one, m.p. 125°, which was pure by t.l.c. (silica gel in benzene).

(*b*) 2α-Chlorocholestan-3-one similarly gave a product of m.p. 126°.

(*c*) 2α-Bromolanost-8-en-3-one (100 mg), treated similarly, gave lanost-8-en-3-one, m.p. 118°, shown to be pure by t.l.c.

(*d*) 2α-Bromo-2β-methylcholestan-3-one [6] similarly gave a

[16] J. A. Osborn and R. R. Schrock, *Chem. Comm.*, 1970, 567.
[17] D. W. Cooke, S. K. Gupta, R. E. Harmon, and J. Schoolenberg, *J. Org. Chem.*, 1969, **34**, 3684.
[18] F. R. Jensen, V. Madan, and D. H. Buchanan, *J. Amer. Chem. Soc.*, 1970, **92**, 1414.
[19] S. Mitsui and S. Imaizumi, *Bull. Chem. Soc. Japan*, 1963, **36**, 855.
[20] H. C. Brown, E. J. Mead, and B. C. Subba Rao, *J. Amer. Chem. Soc.*, 1955, **77**, 6209.
[21] L. Smith, *J. prakt. Chem.*, 1911, **84**, 731.
[22] W. A. Bonner, G. A. Casaletto, and J. A. Zderic, *J. Amer. Chem. Soc.*, 1952, **74**, 5086; W. A. Bonner and J. A. Zderic, *ibid.*, 1956, **78**, 3218.
[23] C. L. Arcus and J. Kenyon, *J. Chem. Soc.*, 1939, 916.

product showing two components, R_F 0·56 and 0·86 (t.l.c. on silica gel in benzene [7]). Preparative t.l.c. separated the 2α- and 2β-methylcholestan-3-ones, each *m/e* 400, in a ratio of 1 : 3.

1,2-*Dibromides*.—(*a*) Dimethyl *meso*-2,3-dibromosuccinate (210 mg) with $RhCl_3py_3$–$NaBD_4$ (300 mg) absorbed 30 ml of deuterium in 6 min. The dimethyl [^{2}H]succinate product, b.p. 80—100° at 10 mmHg, τ 6·31 and 7·45, showed $^2H_0$ 0, $^2H_1$ 4·3, $^2H_2$ 29·0, $^2H_3$ 53·0, $^2H_4$ 10·0%, and fragment ions *m/e* 115—120 and 87—92, indicating the absence of deuterium in the CO_2Me groups.

(*b*) *meso*-1,2-Dibromo-1,2-diphenylethane treated similarly gave a [^{2}H]bibenzyl, m.p. 52°, τ 2·83 and 7·11, $^2H_0$ 5, $^2H_1$ 30, $^2H_2$ 55, $^2H_3$ 8, $^2H_4$ 1·9%.

Cinnamyl Bromide.—The bromide (250 mg) with the catalyst (70 mg) in DMF (10 ml) absorbed 45 ml of hydrogen to give a product showing τ 2·67, 6·7, 7·41, and 7·85 ($PhCH_2{\cdot}CH_2{\cdot}CH_2Br$) and 2·81, 7·41, 8·32, and 9·06 ($PhCH_2{\cdot}CH_2{\cdot}CH_3$). After uptake of only 31 ml of H_2 (1 mol. equiv.) cinnamyl bromide (268 mg) gave a product showing additional n.m.r. signals: τ 3·70 and 8·14 (d, *J* 6 Hz) due to $PhCH{:}CH{\cdot}CH_3$.

Aryl Halides.—(*a*) Bromobenzene (230 mg) with the catalyst (37 mg) in DMF (10 ml) absorbed 23 ml of H_2 in 72 h. The product (examined by g.l.c., t.l.c., and n.m.r.) contained benzene but no biphenyl.

(*b*) Chlorobenzene (168 mg) similarly absorbed 18 ml of H_2 in 13 h.

(*c*) 4-Bromoaniline (265 mg) similarly absorbed 40 ml of H_2 in 18 h. Aniline was identified in the product by g.l.c. and t.l.c. Benzidine was absent.

(*d*) Methyl 4-bromobenzoate (190 mg) absorbed 18 ml of H_2 in 16 h to give methyl benzoate, identified by t.l.c. and n.m.r. signals (τ 1·87, 1·96, 2·02, 2·48, 2·58, and 6·11).

(*e*) 4-Bromoanisole (168 mg) absorbed 16 ml of H_2 in 90 h to give anisole, τ 2·59, 2·72, 2·82, 3·07, 3·34, and 6·25.

Nitro-compounds.—(*a*) Nitrocyclohexane (204 mg) with the catalyst (200 mg) in DMF (10 ml) absorbed 100 ml of H_2 in 17 h to give cyclohexylamine, identified by t.l.c. and conversion into *N*-cyclohexylbenzamide, m.p. 148°.

(*b*) Nitrobenzene (171 mg) similarly absorbed 94 ml of H_2 in 12 h to give aniline, identified by n.m.r. and as acetanilide, m.p. 112°.

(*c*) 4-Nitrobenzoic acid (190 mg) similarly absorbed 67 ml of H_2 in 6 h to give 4-aminobenzoic acid, τ 2·11 (d), 3·19 (d), and 4·2, and thence 4-acetamidobenzoic acid, m.p. 253°.

(*d*) 4-Nitrotoluene gave *p*-toluidine, τ 3·03 (d), 3·43 (d), 6·6, and 7·78, and thence 4-acetamidotoluene, m.p. 145°.

(*e*) 4-Nitrobenzyl chloride or bromide could be hydrogenated to *p*-toluidine. After 1 mol. equiv. uptake 4-nitrobenzyl chloride gave a product containing 4-nitrobenzyl chloride (18%), 4-nitrotoluene (76%), and *p*-toluidine (6%) (n.m.r. analysis).

(*f*) 4-Dimethylaminonitrosobenzene gave 4-dimethylaminoaniline, m.p. 38°, τ 3·24, 6·61, and 7·17.

(*g*) 1-(3,4-Dimethoxyphenyl)-2-nitroethene (392 mg) with the catalyst (68 mg) absorbed 43 ml of H_2 in 0·5 h to give a liquid product, *m/e* 211 ($C_{10}H_{13}NO_2$), τ 3·21 (3H), 5·41 (t, 2H), 6·16 (s, 6H), and 6·76 (t, 2H) which with $LiAlH_4$ in ether gave 1-amino-2-(3,4-dimethoxyphenyl)ethane, identical with an authentic sample (n.m.r. comparison).

(*h*) 2-Nitro-1-phenylpropene similarly gave 2-nitro-1-phenylpropane, *m/e* 165, τ 2·78 (5H), 5·34 (1H), 6·9 (2H), and 8·52 (3H).

Ketones.—(*a*) $RhCl_3$ (2 g) in water (25 ml) with an excess of Na_2CO_3 gave a yellow solid which was filtered off and redissolved in $HClO_4$ (60%; 2 ml); the solution was evaporated. The residual red solid in DMF (8 ml) with $NaBH_4$ (37 mg) gave a brown solution (centrifuged) which catalysed very rapid hydrogenation of oct-1-ene, but failed for cyclohexanone.

(*b*) Benzophenone (210 mg) with $RhCl_3py_3$–$NaBH_4$ (60 mg) in DMF (10 ml) absorbed 56 ml of H_2 in 4 days to give diphenylmethanol, τ 2·83, 4·55, and 6·5, and a trace of benzophenone. In the absence of hydrogen under the same conditions no diphenylmethanol was detected (n.m.r.) after 4 days.

(*c*) Acetophenone similarly gave 1-phenylethanol, τ 2·73, 5·27, 6·0, and 8·65.

(*d*) Benzoin (250 mg) similarly absorbed 23 ml of H_2 in 21 h (to give a deep green solution), yielding hydrobenzoin: *meso* (τ 5·2) 85, (±) (τ 5·31) 15%.

Styrene Oxide.—The epoxide (300 mg) with $RhCl_3py_3$–$NaBH_4$ (75 mg) absorbed 56 ml of H_2 in 3 h to give 2-phenylethanol, τ 2·83, 6·15, 6·36, and 7·29.

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