# *Hydrogenation and Hydrogenolysis. II*(1). *Selective Hydrogenation of Benzyl Alcohol, Methylphenylcarbinol and Benzohydrol to the Corresponding Saturated Carbinols*

By Shigeo NISHIMURA

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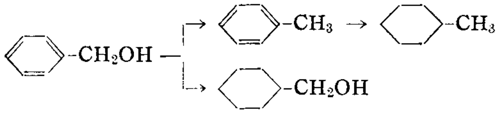
Benzyl alcohol may be catalytically reduced either to methylcyclohexane through toluene, absorbing 4 mol. of hydrogen, or to cyclohexylcarbinol, absorbing 3 mol. of hydrogen:



Under mild conditions the two reactions compete, the former usually predominating.

The palladium catalyst in the presence of a trace of a mineral acid is preferred

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1) Part I of this series: S. Nishimura and K. Mori, This Bulletin, **32**, 103 (1959).

TABLE I. MOLES OF HYDROGEN ABSORBED BY BENZYL ALCOHOL IN THE PRESENCE OF PLATINUM OXIDE-PLATINUM BLACK

| Solvent | Catalyst g. | Compound, g. | | |
|---|---|---|---|---|
| | | Benzyl alcohol (0.541) | Methylphenyl carbinol (0.611) | Benzohydrol (0.533) |
| EtOH, 30 cc.+HCl, 2 drops | 0.2 | 3.96 | 3.98 | 7.04 |
| AcOH 30 cc. | 〃 | 3.95 | 3.87 | 6.73 |
| EtOH, 30 cc.+AcOH, 0.2 cc. | 〃 | 3.47 | | |
| 〃 +AcOH, 0.1 cc. | 〃 | 3.29 | | |
| 〃 +AcOH, 0.03 cc. | 0.1 | 3.16 | | |
| 〃 +AcOH, 0.02 cc. | 0.2 | 3.10 | 3.08 | 6.10 |

TABLE II. HYDROGENATION OF PHENYLCARBINOLS TO CYCLOHEXYLCARBINOLS IN THE PRESENCE OF PLATINUM OXIDE-PLATINUM BLACK

| Compound | Amount g. | Solvent | Catalyst g. | Time hr. | Moles of $H_2$ absorbed mol./mol. | Product |
|---|---|---|---|---|---|---|
| Benzyl alcohol | 3.24 | EtOH, 30 cc.+ AcOH, 0.05 cc. | 1.0 | 7 | 3.06 | Cyclohexylcarbinol (88%), (106~107°C/ 52 mm.), $n_D^{25}$ 1.4622 |
| Methylphenyl-carbinol | 3.66 | 〃 | 〃 | 6 | 3.07 | Cyclohexylmethyl-carbinol (86%), (91~92°C/21 mm.), $n_D^{20}$ 1.4656 |
| Benzohydrol | 3.68 | 〃 | 〃 | 9 | 6.10 | Dicyclohexylcarbinol (89%), (160~161°C/ 22 mm.), (62~63°C) |

for the selective reduction of benzyl alcohol to toluene because of its high activity for the hydrogenolysis and of its low activity for the hydrogenation of the benzene nucleus. Adkins et al. carried out this hydrogenation, using various preparations of nickel-on-kieselguhr catalysts, but the highest yield of cyclohexylcarbinol was only 34%[2]. With Raney nickel toluene is obtained as the main product along with less than 20% of cyclohexylcarbinol[3-6].

With the platinum oxide catalyst, methylcyclohexane was the main product in the presence of a trace of hydrochloric acid or in acetic acid as indicated by the moles of hydrogen absorbed (Table I).

From the results reported previously[1], it was expected that benzyl alcohol could be quantitatively hydrogenated with platinum oxide to cyclohexylcarbinol best in neutral ethanolic solution, but under this condition benzyl alcohol absorbed practically no hydrogen. However, it was found that addition of acetic acid causes the absorption of hydrogen, and that the hydrogen absorption decreases with the decrease of the added acetic acid with no great depression of the rate of hydrogenation, until 3 mol. is absorbed in the presence of the trace of acetic acid, the results being summarized in Table I with those obtained with methylphenylcarbinol and benzohydrol. Thus, in the presence of a very small amount of acetic acid, the phenylcarbinols can be hydrogenated without difficulty to give nearly quantitative yields of the corresponding saturated carbinols[7] (Table II). Triphenylcarbinol was reduced only very slowly and the hydrogenation could not be completed.

With platinized Raney nickel, which is an excellent catalyst for the selective hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol and of cinnamyl alcohol to 3-phenyl-1-propanol[1], benzyl alcohol gave only a 20% yield of cyclohexylcarbinol.

All the hydrogenations, except those with platinized Raney nickel (100°C, 70 atm.), were carried out at the ordinary temperature and pressure. The substance to be hydrogenated was added after

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2) H. Adkins and L. W. Covert, *J. Phys. Chem.*, **35**, 1684 (1931).

3) Hilly, *Bull. soc. chim.*, [5], **7**, 371 (1940).

4) L. Palfray, ibid., [5], **7**, 407 (1940).

5) B. Gauthier, *Ann. chim.*, [11], **20**, 647 (1945).

6) N. S. Tikhomirova-Sidrova, *Zhur. Obshchei Khim.*, **25**, 1504 (1955); *Chem. Abstr.*, **50**, 4825*h* (1956).

7) Under similar conditions cholest-4-en-3-ols can be hydrogenated to cholestan-3-ols almost quantitatively: C. W. Shoppee et al., *J. Chem. Soc.*, **1957**, 3107.

platinum oxide had been shaken with hydrogen for about thirty minutes(8).

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*Department of Chemistry*
*Faculty of Science*
*The University of Tokyo*
*Hongo, Tokyo*

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8) Freshly reduced platinum oxide-platinum black often catalyzes the hydrogenolysis even in neutral solution, but loses completely such activity after being shaken with hydrogen for about thirty minutes. The activity is recovered by the addition of a trace of hydrochloric acid. This is probably caused by platinum nitrate or basic nitrates remaining in traces in platinum oxide, which may liberate nitric acid when reduced with hydrogen, but, when the resulting material is shaken with hydrogen once again, the nitric acid is reduced to ammonia and the catalyst loses the activity for the hydrogenolysis.