Hydrogenation and Hydrogenolysis. VII.¹⁾ Selective Hydrogenation of Aromatic Compounds Containing C-O Linkages Liable to Hydrogenolysis with a Rhodium-Platinum **Oxide under High Pressures**

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In a series of previous papers¹⁻⁴, it was shown that (3:1) or (7:3) rhodium-platinum oxide of Adams' type is not only a highly active catalyst in hydrogenation of various organic compounds, but also very effective for the selective hydrogenation of the compounds having C-O linkages liable to hydrogenolysis⁵⁾. It was also shown that the rhodium-platinum oxides containing 70 to 90% of rhodium by the weight of the metal are even more active and selective than pure rhodium oxide⁶). Subsequently, the use of the rhodium-platinum oxide under high pressures of hydrogen was found to be extremely effective in hydrogenation of various aromatic compounds⁷.

This paper describes the high pressure hydrogenation of aromatic compounds containing C-O linkages susceptible to hydrogenolysis with (7:3) rhodium-platinum oxide and acetic acid as solvent. As is seen from Table I, most hydrogenations proceed rapidly at room temperature and 100 to 150 kg./cm² of hydrogen accompanied with only slight hydrogenolysis.

¹⁾ Part VI of this series: S. Nishimura and K. Mori, This Bulletin, 36, 318 (1963).

²⁾ S. Nishimura, ibid., 33, 566 (1960).

S. Nishimura, T. Onoda and A. Nakamura, ibid., 33, 3) 1356 (1960).

⁴⁾ S. Nishimura, ibid., 34, 32 (1961).
5) Recently, two years after our first publication on this subject²⁾, Stocker, J. Org. Chem., 27, 2288 (1962), reported the substantially same results in the hydrogenation of α -substituted benzyl alcohols and benzyl ethers with 5% rhodium-on-alumina and at 3 to 4 atmospheres of hydrogen.

⁶⁾ S. Nishimura, This Bulletin, 34, 1544 (1961).

⁷⁾ S. Nishimura and H. Taguchi, ibid., 35, 1625 (1962).

 TABLE I.
 CATALYTIC HYDROGENATION OF AROMATIC COMPOUNDS CONTAINING C-O LINKAGES

 LIABLE TO HYDROGENOLYSIS WITH (7:3)RHODIUM-PLATINUM OXIDE

Compound	Amount g.	Catalyst g.	Solvent AcOH ml.	°C ℃	H ₂ press. kg./cm ²	Time min.	% Product isolated
Phenol	9.41	0.05	30	23	128~ 99	9	91 Cyclohexanol ^a)
Anisole	10.8	0.05	30	20	150~112	6	91 Cyclohexyl methyl ether ^{b)}
Phenyl ether	17.0	0.10	50	22	125~ 87	28	{ 71 Cyclohexyl ether ^c) 10 Cyclohexanol
Phenyl ether	8.51	0.20	30	18	1.0	240	{ 51 Cyclohexyl ether ^c) 22 Cyclohexanol
<i>p</i> -Hydroxybenzoic acid	13.8	0.10	50	20	140~110	25	 82 4-Hydroxycyclo- hexane-1-carboxy- lic acids⁴) 10 Cyclohexane- carboxylic acid⁹)
<i>p</i> -Hydroxybenzoic acid	13.8	0.30	50	19	1.0	480	 65 4-Hydroxycyclo- hexane-1-carboxy- lic acids⁽⁵⁾ 23 Cyclohexane- carboxylic acid⁽⁶⁾
Benzyl acetate	15.0	0.05	15*	25	133~108	15	62 Hexahydrobenzyl acetate ^{g)}
Benzyl acetate	15.0	0.20	50	26	1.0	210	21 Hexahydrobenzyl acetate ^{g)}
Acetophenone	12.0	0.05	30	21	150~115	35	86 Cyclohexylmethyl- carbinol ^{b)}
Acetophenone	12.0	0.20	50	25	1.0	210	80 Cyclohexylmethyl- carbinol ^h)
Benzophenone	9.11	0.05	30	21	148~110	220	93 Dicyclohexyl- carbinol ¹
Benzyl ether	9.91	0.10**	30	23	154~123	77	83 Cyclohexylmethyl ether ^j
1-Naphthol	7.21	0.10	50	18	138~110	120	90 1-Decalols ^k)
2-Naphthol	7.21	0.10	50	18	142~103	150	90 2-Decalols ¹)
Furfuryl alcohol	9.81	0.05	0.5 + EtOH, 50	23	125~100	8	88 Tetrahydrofurfuryl alcohol ^m

* With 50 ml. of acetic acid, the yield of hexahydrobenzyl acetate was 50%.

** The catalyst was added in two portions.

a) B. p. 159.0~159.5°C; n_{19}^{19} 1.4647. b) B. p. 131°C; n_{16}^{15} 1.4363. c) B. p. 119°C/22 mmHg; n_{12}^{25} 1.4690. d) M. p. 142~145°C; m. p. after recrystallization twice from chloroform, 149.0~150.5°C: Reported m. p. of the cis isomer, 152°C [N. L. Edison, J. Soc. Chem. Ind., 53, 138T (1934)]. e) B. p. 127°C/20 mmHg; m. p. 30~31°C. f) M. p. 128~135°C. g) B. p. 89°C/22 mmHg; n_{12}^{25} 1.4430. h) B. p. 90°C/22 mmHg; n_{19}^{15} 1.4652. i) B. p. 156~157°C/20 mmHg; m. p. 60~62°C. j) B. p. 150~151°C/22 mmHg; n_{12}^{20} 1.4703. k) B. p. 126~129°C/20 mmHg; m. p. 86~62°C. j) B. p. 150~151°C/22 mmHg; n_{12}^{20} 1.4703. k) B. p. 126~129°C/22 mmHg; m. p. 84~88°C; m. p. after recrystallization twice from petroleum benzinc, 89.0~90.5°C: Reported m. p. of cis-cis-1-decalol, 93°C [W. Hückel et al., Ann., 502, 99 (1933)]. l) B. p. 133°C/22 mmHg; m. p. 87~94°C; m. p. after recrystallization twice from petroleum benzine, 103~104°C: Reported m. p. of cis-cis-2-decalol, 105°C [W. Hückel et al., Ann., 451, 109 (1927)]. m) B. p. 75~76°C/19 mmHg; n_{21}^{20} 1.4482.

In four compounds in Table I (phenyl ether, p-hydroxybenzoic acid, benzyl acetate and acetophenone) which are all liable to hydrogenolysis with great ease, hydrogenations were carried out also at atmospheric pressure and the results compared with those at high pressures (see Table I). In all the cases the proportion of hydrogenolysis at high pressures decreased to about a half of that at atmospheric pressure, and better yields of the corresponding saturated compounds were obtained at high pressures. Under these conditions, phenol, anisole, acetophenone, benzophenone, benzyl

ether, 1- and 2-naphthols, and furfuryl alcohol gave in quantitative or nearly quantitative yields the corresponding saturated alcohols or ethers. Benzyl acetate, where the most extensive hydrogenolysis occurred of the compounds investigated, gave a 62% yield of hexahydrobenzyl acetate. At high pressure *p*-hydroxybenzoic acid gave not only 4-hydroxycyclohexane-1-carboxylic acids in a better yield, but also of a higher melting point than at atmospheric pressure, probably the cis isomer being produced more predominantly at high pressure. 1- and 2-Naphthols also gave the

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products of melting points not so much lower than those of the corresponding *cis-cis*-decalols. In both cases almost pure cis-cis isomer was obtained in about 50 to 60% yield by recrystallization of the product twice from petroleum benzine⁸. Thus, the results show that the high pressure hydrogenation of aromatic compounds with (7:3)rhodium-platinum oxide is a very effective synthetic method where it is desired to avoid the hydrogenolysis concerning C-O linkages. The described method will also be useful for the synthesis of cis compounds by hydrogenation of substituted aromatic compounds⁹.

Experimental

Catalyst.—(7:3) Rhodium-platinum oxide was prepared as described previously⁶).

Hydrogenation.—Hydrogenation was carried out in a 200 ml. autoclave equipped with a magnetic stirrer. The stirrer was driven at the speed of 1000 to 1500 r. p. m.

Isolation of Product.—The hydrogenation product was separated from acetic acid by neutralization with aqueous sodium hydroxide followed by extraction with ether or by distillation at reduced pressure. The product was then distilled at atmospheric or reduced pressure except in case of phydroxybenzoic acid. In this case, after most of 4-hydroxycyclohexane-1-carboxylic acids was removed as solid, cyclohexanecarboxylic acid was steamdistilled from the residue. Evaporation of water from the residual solution gave a further portion of the hydroxy acid. When the hydrogenation was quantitative, the yield of the product after distillation was usually about 90%.

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⁸⁾ Cf. W. G. Dauben et al., J. Am. Chem. Soc., 74, 5206 (1952); 76, 4420 (1954).

⁹⁾ o- and p-Xylenes also give better yields of cis-1, 2and cis-1, 4-dimethylcyclohexanes, respectively, in hydrogenation with (7:3)rhodium-platinum oxide at high pressure than at atmospheric pressure or with platinum oxide (S. Nishimura, to be published).