The Selective Nuclear Hydrogenation of Benzyl-type Alcohols. On the Effect of the Solvent

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It has been well known that the aromatic nuclear catalytic hydrogenation of benzyl-type oxygen compounds is accompanied by the hydrogenolysis of carbon-oxygen linkage.[1] In recent years, studies concerning the selective nuclear hydrogenation have been described by many investigators. Especially, Nishimura[2] reported that the catalytic hydrogenation of benzyl alcohol (I) by means of Adams' platinum oxide catalyst gave cyclohexylcarbinol (II) in a high yield of 88% at ordinary temperature and pressure in ethanol containing a trace of glacial acetic acid. However, no report on the effect of the solvent has been made.

In order to prepare 1, 4-dihydroxymethylcyclohexane (III), an important intermediate of synthetic fiber,[3] we studied the selective nuclear hydrogenation of *p*-xylylene glycol (IV), which had not yet been described. Since IV has two carbon-oxygen linkages susceptible to hydrogenolysis, the hydrogenation of IV to III seemed to be more difficult than that of I to II.

We now wish to report that we have been able to synthesize compound III in an almost quantitative yield at ordinary temperature and high hydrogen pressure in *t*-butanol containing a trace of glacial acetic acid by the use of Adams' platinum oxide catalyst.

It has been found that alcohols used as solvents strongly influence the selectivity of the nuclear hydrogenation of benzyl-type alcohols. The selectivity increases in the following order of the solvent alcohols: prim-<sec-<tert-alcohol. This effect of solvents may be caused by some affinity between the solvent and the catalyst. Supposing that there exist active centers of nuclear hydrogenation and of hydrogenolysis on the surface of the

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[1] W. H. Hartung and R. Simonoff, "Organic Reactions," 7, 263 (1953).

[2] S. Nishimura, This Bulletin, 32, 1155 (1959).

[3] E. V. Martin, *Textile Research Journal*, 32, 619 (1962).

TABLE I. CATALYTIC HYDROGENATION OF *p*-XYLYLENE GLYCOL AND BENZYL ALCOHOL

No.	Compound g.	Solvent ml.	Organic acids added ml.	Catalyst g.	Temp. °C	H_2 press. kg./cm²	Time min.	H_2 up-take %	Conversion* %	Selectivity* %
1	*p*-Xylylene glycol 7.0	EtOH 70	AcOH 1.15	PtO_2 0.35	28	20~10	75	80.7	100	63.8
2	*p*-Xylylene glycol 7.0	EtOH 70	AcOH 1.15	PtO_2 0.35	28	20~10	20	28.7	30.0	62.3
3	*p*-Xylylene glycol 7.0	EtOH 70	AcOH 1.15	PtO_2 0.35	25	96~90	90	29.0**	30.0	81.0
4	*p*-Xylylene glycol 7.0	EtOH 70	AcOH 1.15	PtO_2 0.35	50	20~10	50	79.0	100	51.0
5	*p*-Xylylene glycol 7.0	EtOH 70	AcOH 1.15	(7:3) Pt-Pt 0.35	27	20~10	45	20.8**	24.8	
6	*p*-Xylylcne glycol 7.0	*iso*-PrOH 70	AcOH 1.15	PtO_2 0.35	25	20~10	120	80.0	100	70.5
7	*p*-Xylylene glycol 7.0	Dioxane 70	AcOH 1.15	PtO_2 0.35	24	20~10	135	41.7**	44.9	75.0
8	*p*-Xylylene glycol 7.0	*t*-BuOH 70	AcOH 1.15	PtO_2 0.35	25	20~10	120	98.0	100	89.5
9	*p*-Xylylene glycol 7.0	*t*-BuOH 70	AcOH 1.15	PtO_2 0.35	29	95~70	75	91.9	100	97.9
10	*p*-Xylylene glycol 7.0	*t*-BuOH 70	AcOH 1.15	(10:1) Pt-Rh 0.35	29	20~10	120	28.8	22.6	
11	*p*-Xylylene glycol 7.0	*t*-BuOH 70	AcCH 1.15	(10:1) Pt-Pd 0.35	27	20~10	120	27.6**	32.8	70.0
12	*p*-Xylylene glycol 7.0	*t*-BuOH 70	$EtCO_2H$ 1.35	PtO_2 0.35	26	20~10	120	ca. 12.0**	ca. 10.0	ca. 90.0
13	*p*-Xylylene glycol 7.0	*t*-BuOH 70	MeCH(OH) CO_2H 1.57	PtO_2 0.35	27	20~10	180	88.6	100	50.5
14	Benzyl alcohol 7.0	MeOH 70	AcOH 1.15	PtO_2 0.35	22	20~10	90	18.5**	10.7	42.0
16	Benzyl alcohol 7.0	EtOH 70	AcOH 1.15	PtO_2 0.35	27	20~10	210	45.0**	45.5	69.0
16	Benzyl alcohol 7.0	*n*-BuOH 70	AcOH 1.15	PtO_2 0.35	25	20~10	210	48.5**	43.0	71.0
17	Benzyl alcohol 7.0	*s*-BuOH 70	AcOH 1.15	PtO_2 0.35	22	20~10	90	30.3**	21.5	74.0
18	Benyzl alcohol 7.0	*t*-BuOH 70	AcOH 1.15	PtO_2 0.35	26	20~10	270	101.0	100	98.5
19	Benzyl alcohol 7.0	*t*-AmOH 70	AcOH 1.15	PtO_2 0.35	25	20~10	210	99.3	100	97.0

TABTE II. CATALYTIC HYDROGENATION OF *p*-XYLYLENE GLYCOL DIACETATE

Compound g.	Solvent ml.	Catalyst g.	Temp. °C	H_2 press. kg./cm²	Time min.	H_2 up-take %	Conversion %*	Selectivity %*
7.0	EtOH 70	PtO_2 0.35	25	20~10	45	107	100	0
7.0	EtOH 70	PtO_2 0.35	25	80~70	30	106	100	0
7.0	EtOH 70	(7 : 3) Rh-Pt 0.35	25	20~10	20	105	100	0
7.0	EtOH 70	(7 : 3) Rh-Pt 0.35	25	80~70	4	121	100	Trace
7.0	*t*-BuOH 70	PtO_2 0.35	25	20~10	20	103	100	Trace

* Analytical value by gas chromatogram. (The ratio of cis- to trans-form of III obtained in the experiment No. 1 was about 7 to 3.)

** Hydrogen up-take became extremely slow and almost stopped at these points.

catalyst, the larger the electron density of the oxygen atom of an alcohol the stronger may be the poisoning with the alcohol which occurs on the active centers of hydrogenolysis, which are supposed to be of an electrophilic character. Therefore, the nuclear hydrogenation is considered to occur selectively.

The experimental data on the hydrogenation of I and IV are shown in Table I. Hydrogenations were carried out in a magnetic, mechanically-stirred autoclave (600 r. p. m.) made of SUS-32 stainless steel.

Runs No. 1 and No. 2, the conversion rates of which were 30 and 100% respectively, show no difference in selectivity, so it seems that subreactions are concurrent.

In tests using various alcohols as solvents, the initial rate of hydrogen absorption in the hydrogenation of IV decreased in the following order; prim->sec->tert-alcohol (cf. Fig. 1).

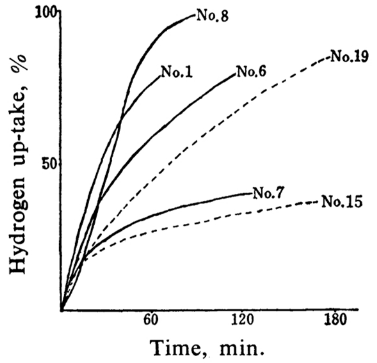

Fig. 1. Effect of solvent on the rate of hydrogen absorption.
Full lines ; hydrogenation of IV
Broken lines ; hydrogenation of IV

However, the absorption rates of primary and secondary alcohols show a tendency to decrease after the hydrogen absorption goes over 30~40% of the theoretical amount. On the contrary, no such tendency was observed in *t*-butanol. The selectivity of the nuclear hydrogenation diminished in the order: tert->sec->prim-alcohol. Dioxane seemed to make the selectivity higher than primary alcohol, but hydrogen absorption was very slow at the initial stage, and it soon stopped entirely. In the case of I, where the reaction was slower than in the case of IV, the solvent effect was similar to that in the case of IV, and II was obtained in a quantitative yield by the use of *t*-alcohols as the solvent.

The effects of hydrogen pressure on the hydrogenation of IV were studied in about 15 kg./cm^2 and 90 kg./cm^2. The selectivity was higher at the higher pressure, when either ethanol or *t*-butanol was used as the solvent. In *t*-butanol, the initial rate of hydrogen up-take at the higher pressure was about twice as great as that at the lower pressure, while in ethanol, under the increased hydrogen pressure, the hydrogen up-take was slower and stopped when less than 30% of the theoretical amount.

In the hydrogenation of IV with platinum-rhodium catalysts of the Adams type, the reaction proceeded slowly, both in ethanol and in *t*-butanol, and it stopped halfway (Nos. 5 and 10)*. An analogous result was obtained with the use of a platinum-palladium catalyst of the Adams type (No. 11). On adding 30% of II to I at the starting of a repeated test of No. 14, no hydrogen absorption occurred. When the influence of added organic acids was investigated in *t*-butanol, acetic acid was bound to be the most effective. When a weaker acid was added, the rate of hydrogen absorption was extremely slow; when a stronger acid was added it was fast, but the selectivity was lower (Nos. 8, 12 and 13). Thus, it is necessary to add a proper organic acid in order to accelerate the hydrogenation without inviting hydrogenolysis.

The hydrogenation of IV with palladium, palladium-carbon or nickel on a kieselguhr catalyst gave no III; with Raney nickel (W-2), it gave just a trace of III.

p-Xylylene glycol diacetate (V) more easily underwent hydrogenolysis than IV, and its aromatic nucleus was scarcely be hydrogenated without inviting an extensive hydrogenolysis, as Table II shows.

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* S. Nishimura (Rh, Pt(3:1))4) and J. H. Stocker (Rh)5) have observed similar phenomenon in the hydrogenation of benzyl alcohol.

4) S. Nishimura, This Bulletin, **34**, 32 (1961).

5) J. H. Stocker, *J. Org. Chem.*, **27**, 2288 (1962).