

## Different Behavior between Pt and Pd Catalysts in the Hydrogenolysis of Cyclohexanediones and Hydroxycyclohexanones

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Hydrogenolysis reactions of cyclohexanediones, hydroxycyclohexanones, and some related alicyclic ketones were studied over Pt, Pd, Ir, and Rh catalysts at atmospheric hydrogen pressure in *t*-butyl alcohol as a solvent. Pt and Pd had high catalytic activities for the hydrogenolysis of carbon-oxygen bonds. However, Ir and Rh scarcely had any activity unless 1,3-cyclohexanedione and 3-hydroxycyclohexanone were involved. The mechanisms of the hydrogenolysis differed with Pt and Pd. In the hydrogenation of 4-methoxycyclohexanone, Pt afforded cyclohexyl methyl ether as the hydrogenolysis product; while Pd afforded cyclohexanone, which was then hydrogenated to cyclohexanol. Thus Pt cleaved the carbon-oxygen double bond, and Pd cleaved the carbon-oxygen single bond. Deuterolysis of cyclohexanone and 4-methoxycyclohexanone on Pt gave mainly *d*<sub>2</sub> species of cyclohexane and cyclohexyl methyl ether as the hydrogenolysis products. This indicated that the carbon-oxygen double bonds were directly cleaved to yield methylene groups on Pt. Almost of all 3-hydroxycyclohexanone was hydrogenolyzed to cyclohexanone on Pd; whereas cyclohexanone as well as cyclohexanol was not hydrogenolyzed at all. In the case of Pd, the carbon-oxygen single bond was cleaved when it was activated by formation of  $\pi$ -oxoallyl adsorbed species on the catalyst at the carbon-oxygen double bond. © 1984 Academic Press, Inc.

### INTRODUCTION

Usually a carbonyl group is catalytically hydrogenated to the corresponding alcohol without hydrogenolysis. Exceptionally a carbonyl group adjacent to an aromatic nucleus is readily hydrogenolyzed on Pd catalyst (1), because a benzyl alcohol is produced by the hydrogenation of the carbonyl group and the alcohol is easily hydrogenolyzed. Similarly an allyl alcohol is effectively hydrogenolyzed on Pd catalyst (2).

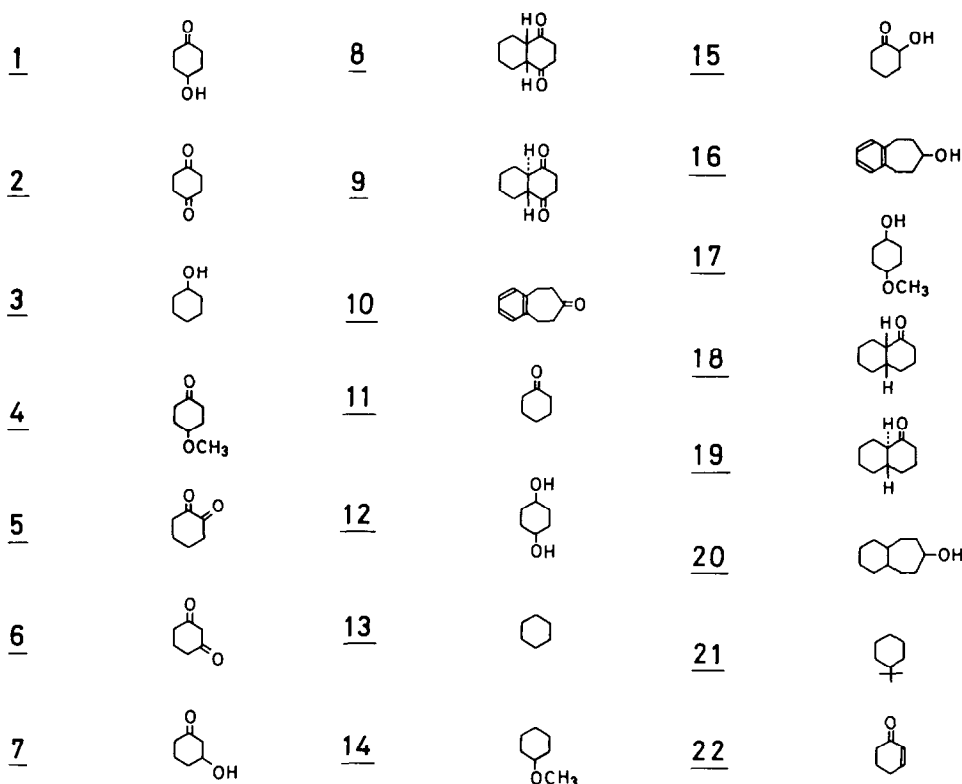
1,3-Diketones have been reported to be hydrogenolyzed under certain reaction conditions (3). Hydrogenolyses of 1,4- and 1,5-diketones have rarely been reported (4). Indeed it has been reported that 4-hydroxycyclohexanone (1) was synthetically obtained by catalytic hydrogenation of 1,4-cyclohexanedione (2) over Ru-on-silica gel (5). However, we have found that more

than half of 2 was hydrogenolyzed to cyclohexanol (3) on unsupported Pt catalyst at 30°C in *t*-butyl alcohol at atmospheric hydrogen pressure (6). An appreciable amount of 2 was hydrogenolyzed on unsupported Pd catalyst also.

Some factors affecting the hydrogenolysis are reported: the structure of the substrate, the amount of catalyst, the kind of solvent, additive agent, reaction conditions, and so on (7). In this paper the mechanisms of the hydrogenolysis are studied and will be discussed based not only on the structure of the substrates but also on the different behavior between Pt and Pd catalysts.

In order to decide the cleaved bonds in the hydrogenolysis of 2, 1 and 4-methoxycyclohexanone (4) were allowed to react. Then 1,2-cyclohexanedione (5), 1,3-cyclohexanedione (6), 3-hydroxycyclohexanone (7), *cis*- and *trans*-1,4-dioxoperhydro-naphthalene (8 and 9, respectively), and

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4,5-benzocycloheptanone (**10**) were allowed to react in order to investigate the scope of the hydrogenolysis and to determine the mechanism of the hydrogenolysis on each catalyst. For Pt catalyst, deuterolyses of cyclohexanone (**11**) and **4** were examined.

#### EXPERIMENTAL

##### Materials

Ketones **5** and **11** were commercial products and distilled just before use.

3-Hydroxyketone **7** was prepared as follows (**8**): 1,3-Cyclohexanedione was partially acetylated with acetyl chloride to form 3-hydroxycyclohexyl acetate. Chromic acid oxidation of this product gave 3-acetoxycyclohexanone, which was then hydrolyzed to **7**: bp 100°C/1.5 mmHg (lit. bp 95°C/1 mmHg).

4-Hydroxyketone **1** was prepared in the following way (**9**): 4-Hydroxycyclohexyl benzoate was prepared by partial esterifica-

tion of 1,4-cyclohexanediol (**12**) with benzoyl chloride. Chromic acid oxidation of this product followed by saponification with sodium hydroxide gave **1**: bp 99°C/1.3 mmHg (lit. bp 97–98°C/0.5 mmHg (**9**), 83–85°C/0.6 mmHg (**10**)).

Methoxyketone **4** was prepared (**11**) by hydrogenation of 4-hydroxyanisole over Raney Ni, followed by chromic acid oxidation: bp 89°C/19 mmHg (lit. bp. 81–83°C/11 mmHg (**11**), 84–85°C/14 mmHg (**12**)).

1,3-Dione **6** was prepared (**13**) by partial hydrogenation of resorcinol with Raney Ni: mp 103–104°C (lit. mp 103–104°C (**13**), 104.5°C (**14**)).

1,4-Dione **2** was a commercial product and was recrystallized from *t*-butyl alcohol.

*trans*-Dioxonaphthalene **9** was prepared as follows (**15**): 1,4-Naphthoquinone was hydrogenated with 5% Rh-on-charcoal to yield *cis*-rich 1,4-dihydroxyperhydronaphthalenes. It was oxidized with chromic acid to the corresponding diketones, and then

converted to the pure *trans* form by heating it in an acetic anhydride solution. The product was purified by recrystallization from *n*-hexane and acetone successively: mp 120–121.5°C (lit. mp 120.5–121.5°C (15), 121°C (16)).

*cis*-Dioxonaphthalene **8** was prepared in the following way (17): *cis*-1,4-Dioxo-5,8-dihydronaphthalene was obtained by condensation of *p*-benzoquinone with 1,3-butadiene. Then the olefinic bonds of the condensation product were hydrogenated with 5% Pd-on-charcoal. The product was purified by recrystallization from a *n*-hexane-*t*-butyl alcohol solution: mp 53°C (lit. mp 52.5–53°C (16), 49–50°C (18)).

Cycloheptanone **10** was prepared as follows (19): Di-*t*-butyl 4,5-benzooctanedioate was obtained by condensation of *o*-xylene dibromide with lithio-*t*-butyl acetate. Cyclization of the ester with sodium hydroxide followed by decarboxylation yielded the ketone: mp 42°C (lit. mp 41–42°C).

*t*-Butyl alcohol and *t*-butyl alcohol-*OD* (Merck Sharp & Dohme, Canada Limited, 99 atm% *D*) were commercial products and were used without further purifications.

Hydrogen (99.99999%) and deuterium (Showa Denko Limited, 99.5 atm% *D*) were used as obtained.

All the metal catalysts used were in the form of black fine powders, which were prepared by precipitation of the metal oxides from chloride solution followed by hydrogenation of the oxides (20).

### Procedures

To a glass reaction vessel (10 ml) a weighed catalyst sample (about 200 mg for Pd, about 20 mg for the others; catalyst amounts had no influence on the selectivity for hydrogenolysis) and *t*-butyl alcohol (5 ml) were added. Then the reaction vessel was flushed several times with hydrogen and charged with it. The temperature was maintained at 30°C and the hydrogen pressure at atmospheric. After shaking the reaction vessel for 20 min in order to prereduce the catalyst, the reaction was started by ad-

dition of the ketone (2.5 mmol) followed by shaking the reaction vessel. The reaction mixture was sampled at appropriate time intervals and kept at –196°C before analysis.

Deuterolyses of **4** and **11** were made using *t*-butyl alcohol-*OD* and deuterium. The cyclohexane (**13**) and cyclohexyl methyl ether (**14**) produced were isolated using a gas chromatograph.

### Analysis

All the reaction products were identified with authentic samples obtained commercially or synthetically. Reaction mixtures were analyzed by means of a gas chromatograph equipped with a polyethylene glycol 20,000 column. For the analysis of mono- and dihydroxyperhydronaphthalenes, a polyethylene glycol 4000 column was used (21).

A mass spectrometer was used for the analysis of deuterolyzed products. The deuterium distribution in the product was obtained after the correction of the mass spectra for the natural abundance of <sup>13</sup>C and for ion fragmentation (22).

## RESULTS AND DISCUSSION

### Selectivity for Hydrogenolysis

Selectivity for hydrogenolysis was defined as the ratio of hydrogenolyzed molecules against the total molecules reacted. According to this definition, the selectivity for hydrogenolysis stands for the ratio of cleaved carbon–oxygen bonds, both carbon–oxygen single bonds (C–O) and double bonds (C=O), relative to all the carbon–oxygen bonds reacted, unless two or more hydrogenolyses took place on one molecule.

The selectivity for hydrogenolysis thus defined was varied in the course of the reactions in two cases: the hydrogenolyses of **5** and **10** on Pt. The selectivities increased markedly in the latter half stage of the reactions. The reaction profile of **5** on Pt is shown in Fig. 1. It can be seen from this figure that the hydrogenation proceeded

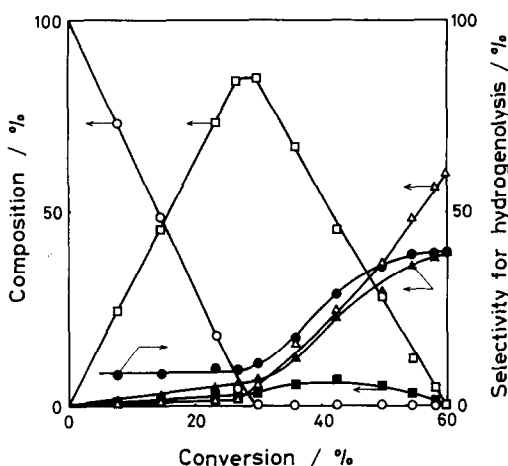


FIG. 1. Hydrogenolysis of **5** over Pt; **5** (○), **15** (□), 1,2-cyclohexanediol (△), **11** (■), **3** (▲), and selectivity for hydrogenolysis (●).

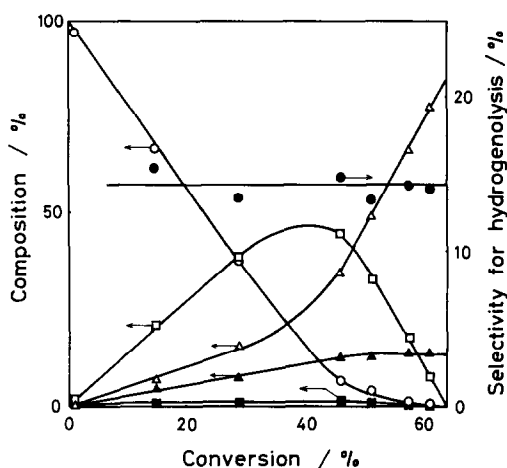


FIG. 2. Hydrogenolysis of **5** over Ir; **5** (○), **15** (□), 1,2-cyclohexanediol (△), **11** (■), **3** (▲), and selectivity for hydrogenolysis (●).

stepwise yielding the intermediate, 2-hydroxycyclohexanone (**15**), almost quantitatively and that the intermediate was also hydrogenolyzed in considerable amounts. Similarly 4,5-benzocycloheptanol (**16**), the hydrogenation intermediate of **10**, was formed almost quantitatively and then hydrogenolyzed with Pt considerably.

In the other cases, the selectivity was not varied in the course of the reactions as exemplified in Fig. 2. The selectivity for hydrogenolysis did not change in the course of the reaction, unless the reaction proceeded stepwise yielding the intermediate in an appreciable amount and the intermediate was

hydrogenolyzed to some extent.

In this paper, conversion was defined as the percentage of the consumed hydrogen relative to the amount of hydrogen necessary for complete hydrogenolysis of the carbonyl groups to the corresponding methylene groups and water. If no hydrogenolysis occurs, the reaction stops at 50% conversion in the cases of aliphatic ketones.

#### Hydrogenolysis of 1,4-Cyclohexanedione (**2**) on Pt

1,4-Dione **2** was allowed to react on a Pt catalyst under atmospheric hydrogen pres-

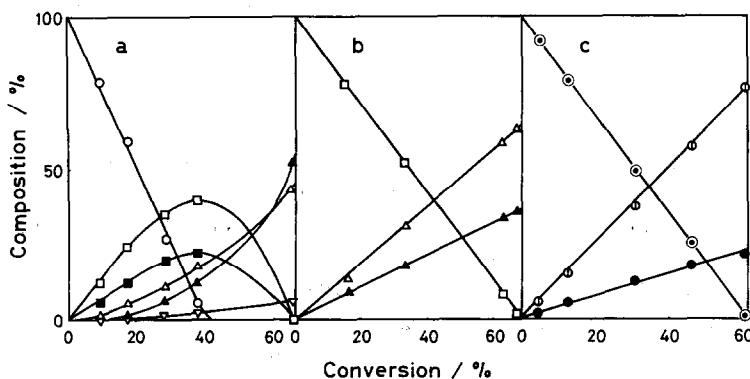


FIG. 3. Reaction profiles of **2** (a), **1** (b), and **4** (c) over Pt; **2** (○), **1** (□), **12** (△), **11** (■), **3** (▲), **13** (▽), **4** (○), **17** (◊), and **14** (●).

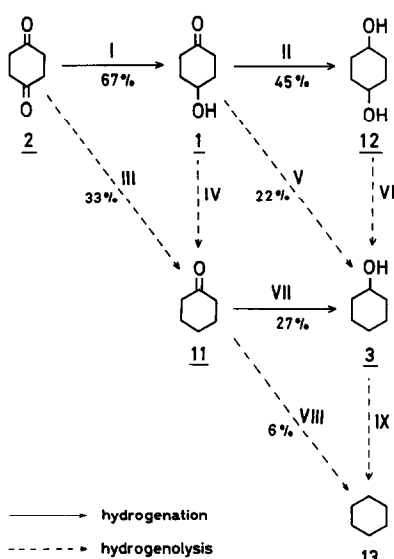


FIG. 4. Reaction scheme of 2 over Pt.

sure at 30°C. The reaction profile is represented in Fig. 3a. More than half of 2 was hydrogenolyzed to 3 in the final stage of the reaction. Cyclohexanone 11 was produced in about a maximum 22% yield. In addition, 1 was formed at about a maximum 40% yield. These two ketones, 1 and 11, could be converted into 3 by hydrogenolysis or hydrogenation, respectively (steps V and

VII in Fig. 4). To examine the whole reaction pathway in detail, 1, the hydrogenation intermediate of the reaction, was allowed to react and the reaction profile is represented in Fig. 3b. This figure shows that 3 was directly formed from 1 (step V in Fig. 4), though the extent of hydrogenolysis decreased somewhat. The Pt catalyst hydrogenolyzed the C=O group to a methylene group. Methoxyketone 4 was allowed to react under the same reaction conditions to confirm this result. As shown in Fig. 3c, only 14 was obtained as the hydrogenolysis product (step I in Fig. 5), though the extent of hydrogenolysis decreased further. Formation of 3 was not detected. Thus there was no possibility that the hydrogenolysis took place by cleavage of the C–O bond of 1 to yield 11, which was immediately hydrogenated to 3 without desorption from the catalyst surface.

Hydrogenolysis profile of 2 was roughly estimated as discussed below: Figure 3a shows that the amount of 11 produced from 2 (step III in Fig. 4) was about half that of 1 (step I in Fig. 4) in the early stage of the reaction. On the other hand, about 18% of

TABLE I  
Selectivity for Hydrogenolysis<sup>a</sup>

Substrate	Catalyst			
	Pt	Pd	Ir	Rh
11	18.0	1.5	0.7	1.2
5	39.4 <sup>b</sup>	1.5 <sup>c</sup>	14.2	1.3
6	75.8	34.6	59.3	11.6
7	73.8	94.7	83.7	10.9
2	53.6	22.4	0.3	0.3
1	35.5	7.7	0.2	0.2
4	22.5	3.2	0.3	0.3
8	7.8	2.5	0.4	0.9
9	5.9	0.4	0.3	0.2
10	23.0 <sup>d</sup>	0.7	0.1	0.1

<sup>a</sup> Percentage of hydrogenolysis at the final stage of the reaction.

<sup>b</sup> In the early stage of the reaction the value was 9.8%.

<sup>c</sup> The reaction stopped when 5 had been consumed.

<sup>d</sup> In the early stage of the reaction the value was 9.1%.

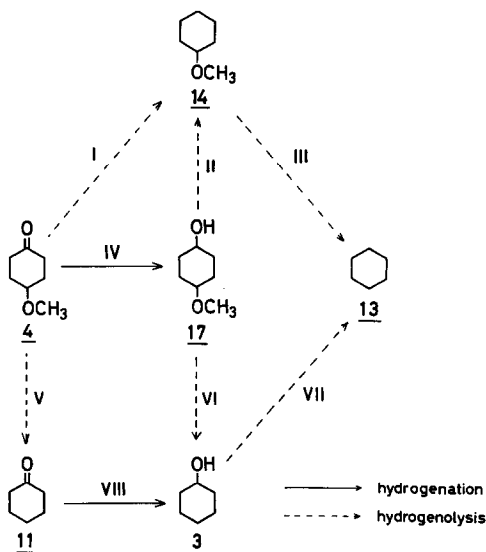


FIG. 5. Reaction scheme of 4.

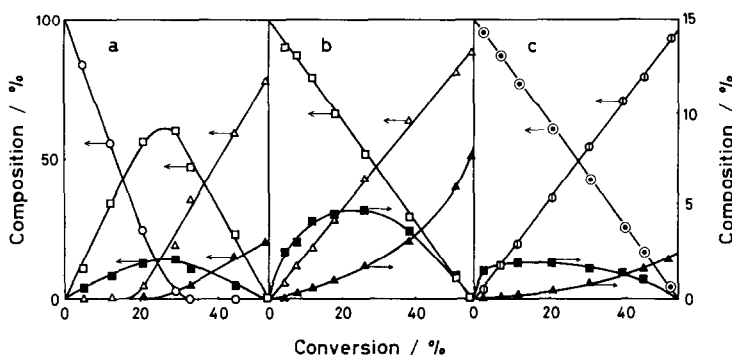


FIG. 6. Reaction profiles of **2** (a), **1** (b), and **4** (c) over Pd; **2** (○), **1** (□), **12** (△), **11** (■), **3** (▲), **4** (⊙), and **17** (⊕).

**11** was hydrogenolyzed to **13** (step VIII in Fig. 4, see Table 1). Figure 3b shows that about one-third of **1** was hydrogenolyzed to **3** (step V in Fig. 4). The C–O bonds of **12**, **3**, 4-methoxycyclohexanol (**17**), and **14** were confirmed not to be hydrogenolyzed under the same reaction conditions (steps VI and IX in Fig. 4 and steps II, III, VI, and VII in Fig. 5). Consequently as Fig. 4 shows, about 27% of **2** was hydrogenolyzed to **3** by way of **11** (steps III and VII in Fig. 4) and about 22% by way of **1** (steps I and V in Fig. 4). About 6% of **2** was hydrogenolyzed to **13** by way of **11** (steps III and VIII in Fig. 4). Total hydrogenolysis percentage of **2** estimated in this way accords with that observed (see Table 1).

#### Hydrogenolysis of 1,4-Cyclohexanedione (**2**) on Pd

1,4-Dione **2** was allowed to react on a Pd catalyst under atmospheric hydrogen pressure at 30°C. As Fig. 6a shows, about 22% of the diketone was hydrogenolyzed to **3** in the final stage of the reaction. To determine the hydrogenolysis pathway of the reaction, **1** was subjected to reaction. As shown in Fig. 6b, the reaction profile on Pd was quite different from that on Pt shown in Fig. 3b. A considerable amount of **11** was produced as a hydrogenolysis product in the middle stage of the reaction (step IV in Fig. 7). In the final stage of the reaction, **3** was produced by hydrogenation of **11** (step VII in Fig. 7); the maximum amount of **11** pro-

duced was comparable to that of **3** in the final stage of the reaction. The hydrogenolysis occurred in the step of the formation of **11** from **1** (step IV in Fig. 7). Pd cleaved the C–O bond of the molecule. To confirm this result, **4** was allowed to react in the same way. As Fig. 6c shows, **11**, which was then hydrogenated to **3**, was obtained as the hydrogenolysis product (steps V and VIII in Fig. 5), and the formation of **14** was not detected in this reaction. This indicates that the C–O bond of **4** was cleaved by Pd. The C–O bonds of **12**, **3**, and **17** were confirmed not to be hydrogenolyzed into C–H

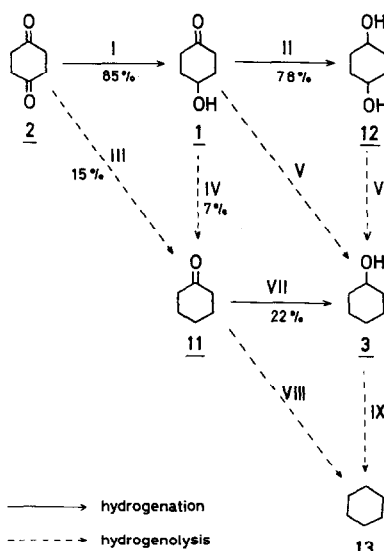


FIG. 7. Reaction scheme of **2** over Pd.

groups under the same reaction conditions (steps II, VI, and VII in Fig. 5 and steps VI and IX in Fig. 7). Consequently, the C–O bond was cleaved by Pd in the presence of the carbonyl group in the same molecule.

The production of **3** from **2** was roughly estimated as discussed below: Figure 6a shows that **2** was converted to **11** directly in about 15% selectivity (step III in Fig. 7) and to **1** in about 85% selectivity (step I in Fig. 7) in the early stage of the reaction. Figure 6b shows that about 8% of **1** was hydrogenolyzed to **3** by way of **11** (steps IV and VII in Fig. 7). Consequently as Fig. 7 shows, about 15% of **2** was hydrogenolyzed to **3** by way of **11** (steps III and VII in Fig. 7), and about 7% by way of **1** and **11** successively (steps I, IV, and VII in Fig. 7). Total hydrogenolysis percentage of **2** estimated in this way accords with that observed (see Table 1).

#### Hydrogenolysis on Pt

To investigate the scope of the hydrogenolysis, the other cyclohexanediones and the related carbonyl compounds were allowed to react. The selectivity values for the hydrogenolysis are presented in Table 1. This table shows that about 18% of unsubstituted **11** was hydrogenolyzed to **13**. However, the extent was not as large as that of **2**, **1**, or **4**. The extent of hydrogenolysis increased by introduction of a carbonyl, hydroxyl, or methoxy group at the 4-position of the ring of **11**.

Table 1 shows that the selectivities for hydrogenolysis of **6** and **7** were high on Pt as in the cases of the other catalysts. Only a small amount of **5** was hydrogenolyzed. Compound **15** could not be isolated in a pure form because of the tendency to form dimerized acetal (**23**). However, the selectivity for hydrogenolysis of **5** in the final stage suggests that the hydrogenation intermediate, **15**, was hydrogenolyzed in about 33% selectivity.

Table 1 also shows that the selectivities for hydrogenolysis of **8** and **9** on Pt were not as large as that of **2**. The selectivity values of *cis*- and *trans*-1-oxoperhydronaphthalenes (**18** and **19**, respectively) were less than 1% on Pt. Lower selectivity for hydrogenolysis of **9** than that of **8** indicates that rigidity of the 1,4-cyclohexanedione ring did not favor the hydrogenolysis.

As seen above, the carbonyl group of **11** was hydrogenolyzed to some extent without the aid of other functional groups on Pt, though the selectivity for hydrogenolysis increased when a group containing oxygen was introduced and decreased when an alicyclic ring was introduced. The mechanism of hydrogenolysis on Pt should be considered on one carbonyl group essentially. Three capable pathways were considered here (Fig. 8): (a) One is the direct cleavage of the carbonyl group to a methylene group. (b) Another consists of the formation of vinyl alcohol followed by hydrogenolysis of the hydroxyl group (**24**). (c) The other con-

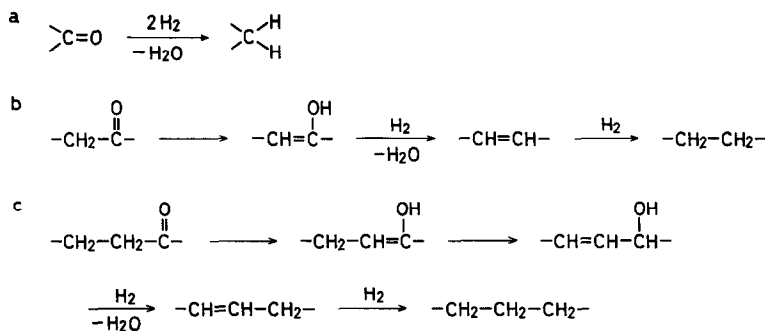


FIG. 8. Reaction scheme for carbonyl hydrogenolysis. (a) Direct cleavage, (b) by way of vinyl alcohol, (c) by way of allyl alcohol.

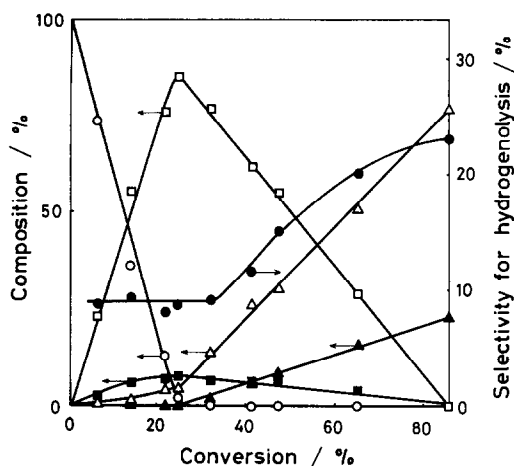


Fig. 9. Hydrogenolysis of **10** over Pt; **10** (○), **16** (□), **20** (△), benzocycloheptane (■), bicyclo[5.4.0]undecane (▲), and selectivity for hydrogenolysis (●).

sists of the formation of allyl alcohol by migration of the vinyl alcohol followed by hydrogenolysis of the hydroxyl group, for it has been reported that the olefinic double bond could migrate on Pt catalyst (25), that an allyl alcohol was susceptible to hydrogenolysis (2), and that deuterated cyclohexanones containing more than five deuterium atoms were recovered in the deuteration of 4-*t*-butylcyclohexanone (26), 2-methylcyclohexanone (27), and 2-ethylcyclohexanone (28).

To determine the mechanism, **10** was allowed to react and the result is represented in Fig. 9. In the first half of the reaction, benzocycloheptane was obtained as the hydrogenolysis product in only about 9% selectivity, which was less than that of **11**. The allyl alcohol, 4,5-benzocyclohept-2-enol, produced from **10** would be stabilized by the benzene ring attached (Fig. 10). If the hydrogenolysis occurred by way of the allyl alcohol, **10** should be hydrogenolyzed in larger selectivity. Consequently, there

was little possibility of case (c), and cases (a) and (b) remained.

The hydrogenation of **10** proceeded stepwise as shown in Fig. 9. The intermediate alcohol **16** was produced almost quantitatively and then it was hydrogenated to 4-bicyclo[5.4.0]undecanol (**20**). The selectivity for hydrogenolysis of this reaction remained about 9% until **10** had been consumed and then increased up to about 23% at the end of the reaction. The hydrogenolysis product was bicyclo[5.4.0]undecane at the end of the reaction. Saturated alcohol **20** was no longer hydrogenolyzed. Hydrogenations of aromatic compounds form olefin intermediates (29). Migration of olefinic double bonds is observed on Pt catalyst (25). Allylic oxygen compounds are known to be susceptible to hydrogenolysis (2). Hence the higher selectivity for hydrogenolysis of **10** in the final stage was attributed to the hydrogenolysis of the allyl alcohol which was produced in the course of hydrogenation of the aromatic ring in **16**.

#### Deuterolysis of Cyclohexanone on Pt

Deuterolysis of **11** and **4** was carried out. The selectivity for deuterolysis of each ketone was the same as that for hydrogenolysis. Deuterium distributions of the deuterolyzed products, **13** and **14**, are listed in Table 2. As can be seen from this table, species- $d_2$  was the main product of each reaction. The carbonyl groups were found to be directly converted to the methylene groups (case (a)). This occurs because three deuterium atoms should be introduced into the product when the carbonyl group was hydrogenolyzed by way of vinyl alcohol (case (b)): one by hydrogenolysis of the hydroxyl group and two by hydrogenation of the olefinic bond. For the sake of comparison, the deuterium distribution of the hydrogenoly-

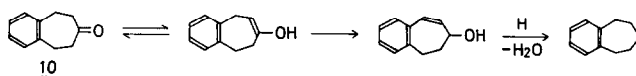


Fig. 10. Hydrogenolysis of **10** by way of allyl alcohol.



TABLE 2  
Isotope Distribution of Deuterolyzed Product with Pt<sup>a</sup>

Product	Percentage of each isotopic species													$D_m$
	$d_0$	$d_1$	$d_2$	$d_3$	$d_4$	$d_5$	$d_6$	$d_7$	$d_8$	$d_9$	$d_{10}$	$d_{11}$	$d_{12}$	
<b>13</b>	1.3	12.7	48.9	17.0	8.0	4.0	2.4	1.7	1.1	0.8	0.7	0.7	0.6	2.78
<b>14</b>	0.5	9.7	66.2	15.9	5.2	1.6	0.6	0.2						2.28
<b>21<sup>a</sup></b>	4.0	11.7	22.1	26.8	20.0	11.3	4.0	0.2						2.98

<sup>a</sup> Deuterolyzed product of enol ether (30).

sis product of an enol ether is also presented in the same table as *t*-butylcyclohexane (**21**), which was produced by deuterolysis of 4-*t*-butyl-1-cyclohexenyl methyl ether (30). Apparently species- $d_3$  was the main product of this reaction. In addition, the deuterium distribution of this product was essentially different from that of **13** and **14**.

Consequently, hydrogenolysis of the carbonyl group on Pt catalyst did not occur by way of vinyl alcohol (case (b)) but by direct cleavage to the methylene group (case (a)).

#### Hydrogenolysis on Pd

To investigate the mechanism of hydrogenolysis on Pd, the other cyclohexanediones and the related ketones were allowed to react. The results are summarized in Table 1. On hydrogenation of **11** with Pd, there was little hydrogenolysis product. This indicates that a certain functional group was required on the ring of **11** for hydrogenolysis.

Cycloheptanone **10** was scarcely hydrogenolyzed. This indicates that the hydrogenolysis did not occur by way of allyl alcohol on Pd catalyst (case (c)).

Only a small amount of **5** was hydrogenolyzed. This reaction ceased when **5** had been consumed. 2-Hydroxyketone **15** produced or its dimerized acetal (**23**) retarded the activity of the Pd catalyst. On the other hand, **6** was hydrogenolyzed in about 35% selectivity. 3-Hydroxyketone **7** was hydrogenolyzed in as much as 95% selectivity.

The hydrogenolysis products of **7** were **11**

and 2-cyclohexenone (**22**) in the early stage of the reaction. The former was produced 10 times as much as the latter. The principal pathway of the hydrogenolysis was reductive cleavage of the hydroxyl group, though there was a little contribution of dehydration-hydrogenation pathway. In the hydrogenation of **6**, the formation of **22** was negligible. In the hydrogenation of **1** and **2**, the dehydration products, **22** and 3-cyclohexenone, were not detected.

It has been reported that a  $\pi$ -oxoallyl adsorbed species (Fig. 11a) was formed when an aliphatic carbonyl group was adsorbed on Pd catalyst (27, 31). It has also been reported that Pd was the best catalyst for hydrogenolysis of allyl and benzyl alcohols (1, 2). The hydrogenolysis of **7** proceeded in the following way as shown in Fig. 11b: First, the carbonyl group was adsorbed on the Pd catalyst forming a  $\pi$ -oxoallyl adsorbed species, and then the activated vicinal hydroxyl group was hydrogenolyzed by Pd. In this way, Pd cleaved the C-O bond with the aid of the carbonyl group. In the case of **6**, **7** must first be formed in order to follow above scheme. Further, a considerable amount of **6** must exist in the enol form, 3-hydroxy-2-cyclohexenone, under the reaction conditions (32). Therefore the selectivity for hydrogenolysis of **6** was smaller than that of **7**.

In the case of **1** an extension of the adsorbed  $\pi$ -bond is necessary to locate the hydroxyl group at the vicinal position. Consequently the selectivity for hydrogenolysis was smaller than that of **7**. For **5** and **15**, the

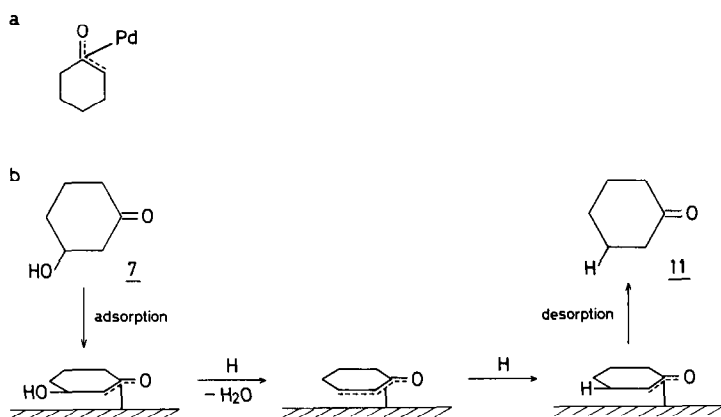


FIG. 11.  $\pi$ -Oxoallyl adsorbed species of **11** (a) and hydrogenolysis of **7** by way of the species (b).

carbonyl and hydroxyl groups are not on a suitable position for hydrogenolysis.

Selectivity values for the hydrogenolysis of **8** and **9** on Pd are also seen in Table 1. The values were smaller than that of the corresponding cyclohexanedione **2**. The selectivities for hydrogenolysis of **18** and **19** were less than 1% on Pd. Introduction of alicyclic rings on the ring of **2** or **11** hindered the hydrogenolyses as in the case of Pt. Hydrogenolysis was very susceptible to steric hindrance. This result is consistent with the general concept that carbonyl compounds are hydrogenated to the corresponding alcohols without hydrogenolysis in the practical synthetic field. The selectivity for hydrogenolysis of **8** was greater than that of **9**. Two carbonyl groups of **8** could contact the catalyst surface at the same time by changing the conformation; whereas those of **9** could not because of the rigid ring structure of the molecule. A suitable conformation was required for the hydrogenolysis.

#### Hydrogenolysis on Ir and Rh

Except for **5**, **6**, and **7** little hydrogenolysis occurred on Ir and Rh catalysts. Ir was somewhat more active for hydrogenolysis than Rh. On Ru and Os catalysts, the selectivities for hydrogenolysis of **2** were less than 1%. Thus the hydrogenolysis of **2** was characteristic of Pt and Pd.

An appreciable extent of hydrogenolysis of **7** and **6**, which produces **7** on partial hydrogenation, could be attributed to the allyl alcohol structure of the molecule. In this structure, the hydroxyl group is known to be susceptible to hydrogenolysis (3).

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