

## Stereochemistry and Mechanism of the Catalytic Hydrogenation of Methylcyclohexenols

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Four methylcyclohexenols were hydrogenated over several transition metal catalysts. The isomeric distributions of the products obtained over Raney Ni were different from those obtained over Pd or Pt catalysts and the adsorption of the substrate on the catalyst is considered to be rate determining in the hydrogenation on this catalyst.

### INTRODUCTION

We have investigated the directive effect of the hydroxyl group on the stereochemistry of the products in the hydrogenation of olefinic alcohols (1-3). When Raney Ni is used as the catalyst the product which is obtained by the hydrogen addition from the same side as the hydroxyl group is more favored than the alternative. It may be that the interaction of the hydroxyl group with the catalyst (anchor effect (4)) participates in the determination of the product distribution.

Siegel and Smith reported that the rate determining step of the hydrogenation of dialkylcyclohexenes over Pt catalysts at an atmospheric pressure and room temperature is the hydrogen transfer to the adsorbed species (5) and that over Pd it is the hydrogen transfer to the half-hydrogenated intermediate (6). In order to study the stereochemistry and the mechanism of the hydrogenation of olefinic alcohols and the effects of the hydroxyl group on the product distribution, methylcyclohexenols were prepared and were hydrogenated over several transition metal catalysts.

### EXPERIMENTAL METHODS

*Materials.* All methylcyclohexenols (3-methyl-2-cyclohexenol(I) (b.p. 80°C/15

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mm) (7), 2-methyl-2-cyclohexenol(II) (b.p. 80°C/20 mm) (8), 4-methyl-3-cyclohexenol(III) (b.p. 91-93°C/26 mm) (9), and 3-methyl-3-cyclohexenol(IV) (b.p. 80°C/14 mm) were obtained by LiAlH<sub>4</sub> reduction of corresponding cyclohexenones (3-methyl-2-cyclohexenone, 2-methyl-2-cyclohexenone, 4-methyl-3-cyclohexenone and 3-methyl-3-cyclohexenone (10)) prepared as described earlier. W-5 Raney Ni (11), Pd-carbon (12) and PdO (13) were prepared as described earlier. Reduced Ni was prepared by the reduction of NiO which was obtained from Ni(NO<sub>3</sub>)<sub>2</sub> in hydrogen atmosphere at 290°C. PtO<sub>2</sub> was purchased from Wako Pure Chemical Co., Tokyo, Japan. Pt-black was prepared by the hydrogen reduction of PtO<sub>2</sub> and was washed well with distilled water. Rh-carbon was purchased from Nippon Engelhard Co., Tokyo, Japan.

*Procedures.* A 1/400 mole of methylcyclohexenol, catalyst and 5 ml of ethanol were stirred with hydrogen at an atmospheric pressure and room temperature. After the reduction was over the catalyst was removed by the centrifugal method and the mixture was analyzed by gas chromatography. Hitachi F-6 or K-53 gas chromatograph equipped with flame ionization detector was used with Infotronics digital integrator. The products were analyzed on

a 45 m × 0.25 mm Goley column of PEG 400 at 90°C.

## RESULTS AND DISCUSSION

The experimental results are listed in Table 1. Detailed product analysis showed that the distribution of epimeric alcohols hardly changed during the hydrogenation. It was also checked that after the reaction was completed the distribution of epimeric alcohols did not change under the hydrogenation condition employed in the present study. The hydrogenolyzed products were obtained over all catalysts used in the present study, even though only in a few percent over freshly prepared Raney Ni. The observation that 1-methylcyclohexene was found in the course of the hydrogenation suggests that methylcyclohexane is the secondary product which is derived by the hydrogenation of

primarily obtained methylcyclohexene from methylcyclohexenols. Three typical cases are shown in Figs. 1, 2 and 3.

In the Pd catalyzed hydrogenation the more thermodynamically stable of the two possible products was favored. Siegel and Smith reported that since the rate determining step of the hydrogenation of cycloalkenes over Pd catalyst is the hydrogen transfer to the half-hydrogenated intermediate, the preceding reactants and intermediates tend to become equilibrated with one another. If the transition states for the postulated rate determining step resembles the preceding intermediates (the half-hydrogenated states), then the configuration of the main saturated isomer may be predicted also. A consideration of substituted cyclohexanols supplies a rationale for these results. Since the stability of the carbon-metal bond is usually in the order,

TABLE I  
HYDROGENATION OF METHYLCYCLOHEXENOLS IN ETHANOL

Substrate					
Catalyst <sup>a</sup>	(I)	(II)	(III)	(IV)	
Product composition ( <i>cis</i> %)					
Pd-carbon	76	30	45	76	60 <sup>e</sup>
PdO	75	26	—	—	—
Pd-black	75	29	—	—	—
PtO <sub>2</sub>	55	66	67	71	—
Pt-black	67	69	76	67	70 <sup>e</sup>
Rh-carbon	51	45	47	47	—
Raney Ni-A <sup>b</sup>	19	30	48	50	25 <sup>e</sup>
Raney Ni-B <sup>c</sup>	13	—	38	42	—
Raney Ni (acetone treated)	6	—	26	30	—
Reduced Ni	6	—	34	46	—
Equilibrium	77 <sup>d</sup>	16 <sup>d</sup>	31.5 <sup>d</sup>	77 <sup>d</sup>	57 <sup>f</sup>

<sup>a</sup> Weight of catalyst (mg): Raney Ni, 1000; reduced Ni, 2000; Pd-carbon, 20; PdO, 20; PtO<sub>2</sub>, 10; Pt-black, 7; Rh-carbon, 20.

<sup>b</sup> Freshly prepared.

<sup>c</sup> Aged for 7 days.

<sup>d</sup> E. L. Eliel and R. S. Ro, *J. Amer. Chem. Soc.* **79**, 5992 (1957).

<sup>e</sup> Ref. (2).

<sup>f</sup> R. G. Haber and B. Fuchs, *Tetrahedron Lett.* 1447 (1966).

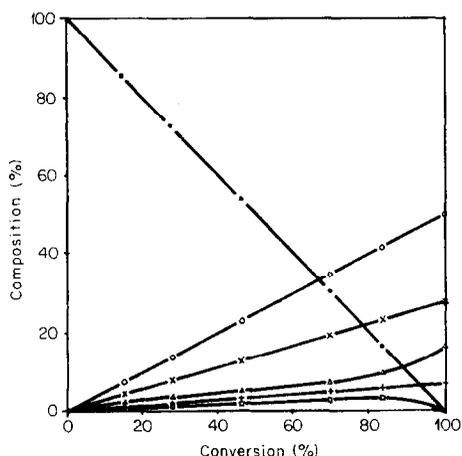


FIG. 1. Hydrogenation of 2-methyl-2-cyclohexenol over  $PtO_2$ . ● 2-Methyl-2-cyclohexenol; ○ *cis* 2-Methylcyclohexanol; × *trans* 2-Methylcyclohexanol; + 2-Methylcyclohexanone; □ 1-Methylcyclohexene; △ Methylcyclohexane.

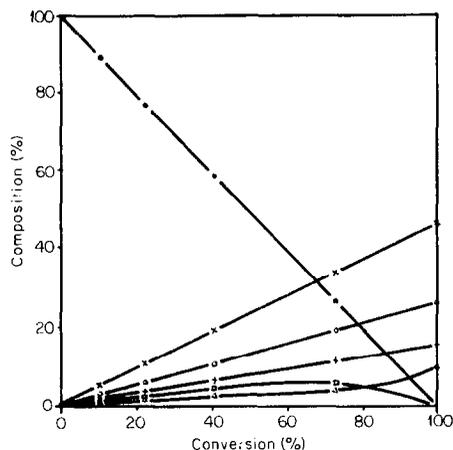


FIG. 3. Hydrogenation of 2-methyl-2-cyclohexenol over Pd-carbon. ● 2-Methyl-2-cyclohexenol; ○ *cis* 2-Methylcyclohexanol; × *trans* 2-Methylcyclohexanol; + 2-Methylcyclohexanone; □ 1-Methylcyclohexene; △ Methylcyclohexane.

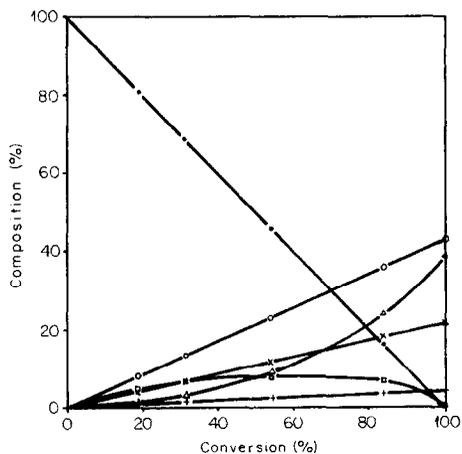
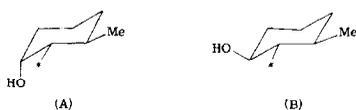


FIG. 2. Hydrogenation of 2-methyl-2-cyclohexenol over Pt-black. ● 2-Methyl-2-cyclohexenol; ○ *cis* 2-Methylcyclohexanol; × *trans* 2-Methylcyclohexanol; + 2-Methylcyclohexanone; □ 1-Methylcyclohexene; △ Methylcyclohexane.

primary > secondary > tertiary (14), the carbon-metal bond forms with less-substituted carbon atom in the half-hydrogenated intermediate. Thus the half-hydrogenated intermediates in the hydrogenation of I are as follows:



The structure A leads to the *trans* isomer, while the *cis* isomer is obtained from B. Of these two isomers A has a much higher energy and is less likely, while B has lower energy and is more favored. Similarly, the half-hydrogenated intermediates of other substrates used in the present study are supposed as 4c ~ 4h (Fig. 4). The *cis* products will be obtained from 4c, 4f and 4g, while 4d, 4e and 4h should yield the *trans* products.

The *cis* alcohol was favored during Pt catalyzed hydrogenation. The rate determining step of the hydrogenation of olefins over this catalyst is the hydrogen transfer to the adsorbed species (5). The rate determining step of the hydrogenation of ole-

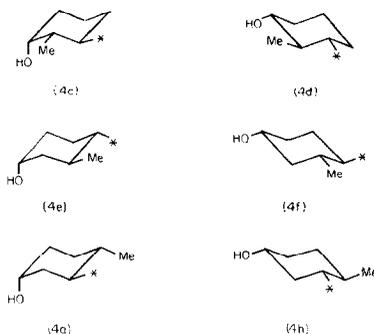


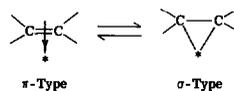
FIGURE 4

finic alcohols thus appears to be the same reaction step as that of olefins.

The hydrogenation of allylic alcohols such as I and II over freshly prepared Raney Ni gave preferably the trans products probably obtained by the hydrogen attack from the same side as the hydroxyl group. Almost equal amounts of the cis and the trans product were obtained from homo-allylic alcohols such as III and IV over freshly prepared catalyst. When aged Raney Ni which was stored in ethanol at room temperature for 7 days, the catalyst treated with acetone or reduced Ni were used, the trans isomers were more favored from all substrates. These are different from those over Pt or Pd catalysts similar to the case of the hydrogenation of 3-methyl-2-cyclopentenol (Table 1) (2) and suggest that the rate determining step of this reaction may be the adsorption of the substrate on the catalyst. Although simple hydrogen addition is generally dominant in the hydrogenation of allylic alcohols over Raney Ni, small amounts of hydrogenolyzed products (hydrocarbons) were also obtained. The double bond migration was also observed in the hydrogenation of alkylmethylenecyclohexanes (15), disubstituted cyclopentenes (16) and dimethylcyclohexenes (17).

If adsorption of the substrate on the catalyst is rate determining over Raney Ni, taking account of the results that the hydrogenation occurred accompanying the double bond migration and the hydrogenolysis which are considered to proceed via  $\pi$ -allylic adsorbed species, two types of adsorbed states are imagined (15); one the  $\pi$ -type and the other the  $\sigma$ -type. The former is assumed to be the adsorption in which  $\pi$ -electrons of the double bond are donated to the vacant  $d$ -orbitals of the metal and the filled metal  $d$ -orbitals are donated to the anti-bonding  $\pi$ -orbitals of the olefin. Then the  $\pi$ -type adsorbed species may convert to the alternative adsorbed species on the catalyst surface

forming a  $\sigma$ -bonded three membered ring in which electrons from two  $\sigma$ -orbitals of the metal are paired with  $sp^3$  electrons of carbon by the extreme back donation. These species can be illustrated as follows:



As a consequence, a possible reaction course of the hydrogenation is shown in Fig. 5 (a case of I is schematized). At first stage the substrate I is adsorbed on the catalyst surface to form  $\pi$ -type adsorbed species, two types of which are expected (2a and 2b). The  $\pi$ -type adsorbed species then subsequently convert to  $\sigma$ -type ones, 2'a and 2'b whose structures are assumed to contain a three membered ring including a metal atom. The adsorbed species, 2'a and 2'b are hydrogenolyzed by the adsorbed hydrogen on the catalyst surface to form the half-hydrogenated species (4a and 4b) through the transition states, 3a and 3b. The second hydrogen transfers to the

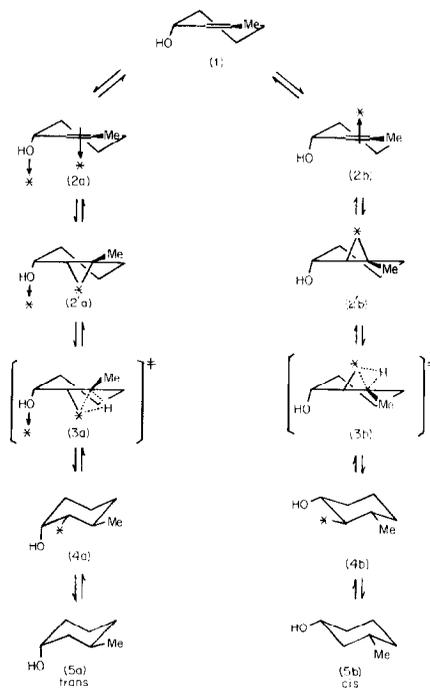
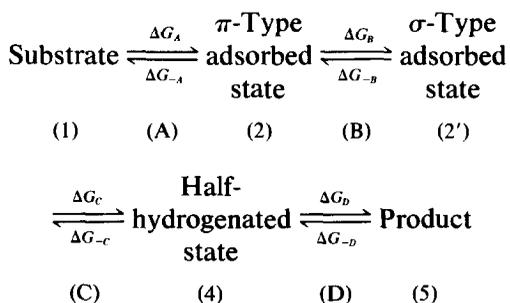


FIGURE 5

half-hydrogenated species and the epimeric products, 5a and 5b, will be obtained.

In the adsorbed states, 2a and 2'a, the hydroxyl group is directed toward the catalyst surface and the anchor effect as well as the catalyst hindrance should be considered. The hydrogenation results from allylic cyclohexenols (I and II) indicate that Ni has strong affinity for negative atom such as oxygen (2) and the anchor effect is more effective than the catalyst hindrance to determine the product distribution, namely the trans product is favored, though homoallylic cyclohexenols (III and IV) gave no stereoselectivity on the freshly prepared catalyst. Since the hydroxyl group of 2-cyclohexenols takes preferably pseudo-axial orientation (18,19) the adsorption of that functional group on the catalyst (anchor effect) is considered to be easy (20). In contrast, the hydroxyl group of the homo-allylic cyclohexenols takes mainly equatorial orientation. Less anchor effect, therefore, is operative.

The stereoselectivity of the products obtained using aged Raney Ni was better than that using freshly prepared one. Similar trends were also observed in the hydrogenation of methylenecyclohexanes (15) and alkylcyclohexanones (21). If we assume some free energy of activation difference between these two types of adsorbed states, the formation of adsorbed species is consistent with two consecutive elementary reactions:



(i) if  $\Delta G_B$  and  $\Delta G_{-B}$  are nearly zero, a resonance hybrid between these two ad-

sorbed species is assumed. (ii) If  $\Delta G_B$  and  $\Delta G_{-B}$  are sufficiently small compared to  $\Delta G_{-A}$  and  $\Delta G_C$ , these two adsorbed species are in equilibrium. (iii) If  $\Delta G_A$  or  $\Delta G_B$  is larger than those of any other elementary reaction step, one of these two reaction steps will be rate determining. It is not necessary to imagine the presence of two types of adsorbed species in two cases (i) and (ii). Since in the case of Raney Ni hydrogenation the rate determining step appears to be the adsorption of the substrate on the catalyst, the third case can be applied. Two observations can be made: (i) the fraction of the hydrogenolyzed product was less over the fresh catalyst than for those aged or treated with acetone (for instance, in the hydrogenation of I over Raney Ni treated with acetone 26% of hydrogenolyzed product was obtained, though only a few percent over freshly prepared catalyst) and (ii) during the hydrogenation of olefins some double bond migration occurred even on the freshly prepared Raney Ni, but relatively more double bond migration seemed to occur on the catalyst aged or treated with acetone. Presumably, there are two different processes in this reaction, viz (Fig. 6), and the more reaction via  $\pi$ -allylic adsorbed species occurs over the catalyst aged or treated with acetone as a by-pass route (15).

In case of the hydrogenation of homo-allylic cyclohexenols, the increase in the stereoselectivity over Raney Ni aged or treated with acetone is similar to the case of allylic cyclohexenols and may be due to the participation of the adsorption of the hydroxyl group on the catalyst. The double bond migration is also considered to take part in the change of the product distribution. These allylic cyclohexenols probably form more stable adsorbed species than homo-allylic ones due to the conformational orientation of the hydroxyl group to be adsorbed on the catalyst. The formation of hydrocarbons, even though in

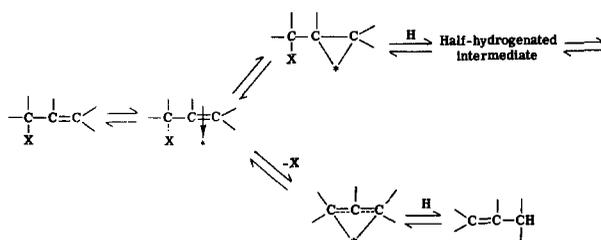


FIG. 6. X = H or OH.

very small amounts, supports the double bond migration to form allylic cyclohexenols.

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