

## Stereochemistry and Mechanism of the Catalytic Hydrogenation of Dimethylcyclohexenes

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Received August 9, 1974

Dimethylcyclohexenes were hydrogenated over several transition metal catalysts. The Pd catalyzed hydrogenation gave always more stable of the two possible products, while the *cis* products were favored over Pt catalyst. In the hydrogenation over Raney Ni the amount of less stable of the two possible products increased with an increase of the aging period of the catalyst. The mechanism of the reaction is discussed in terms of the modified Horiuti-Polanyi mechanism.

### INTRODUCTION

We have previously pointed out that the stereochemistry of the hydrogenation of substituted methylenecycloalkanes (1,2), cycloalkanones (2,3) and disubstituted cyclopentenes (4) depends on the chemical and steric structure of the substrate, catalyst and reaction conditions. We have also suggested that in the Raney Ni catalyzed hydrogenation the adsorption of the substrate on the catalyst is rate determining according to the stereochemical results of the hydrogenation of methylcyclohexenols (5).

In order to confirm the mechanism of the hydrogenation, some dimethylcyclohexenes were hydrogenated over various kinds of transition metal catalysts, though some of these had been investigated by several workers (6-10). The stereochemical results are discussed on the basis of the modified Horiuti-Polanyi mechanism (1).

### EXPERIMENTAL METHODS

**Materials.** 1,2-Dimethylcyclohexene(I) (bp 137°C) (9), 2,3-dimethylcyclohexene(II) (bp 134°C) (9), 1,3-dimethylcyclohexene(III) (bp 122°C) (7) and 1,4-dimethylcyclohexene(V) (bp 127°C) (7)

were prepared as described earlier. 2,4-Dimethylcyclohexene(IV) (bp 128°C) was prepared by the dehydration of 1,3-dimethylcyclohexanol in concd H<sub>2</sub>SO<sub>4</sub> and acetic acid (1:7), followed by the purification with preparative gas chromatography. All compounds were also checked by gas chromatography and NMR and ir spectra. 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. 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. Rh-carbon was purchased from Nippon Engelhard Co., Tokyo, Japan.

**Procedures.** A 1 mmol sample of dimethylcyclohexene, catalyst and 5 ml of ethanol were stirred with hydrogen at an ordinary pressure and room temperature. After the reaction was over the catalyst was removed by the centrifugal method and the mixture was analyzed by gas chromatography. Hitachi F-6 and K-53 gas chromatographs equipped with flame ionization detector were used with Infotronics digital integrator. The products were ana-

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lyzed on a 45 m × 0.25 mm Goley column of PEG 400 at 40°C.

### RESULTS AND DISCUSSION

A possible reaction course of the hydrogenation is shown in Fig. 1 on the basis of the modified Horiuti-Polanyi mecha-

nism and the hydrogenation results are summarized in Table 1.

The Pd catalyzed hydrogenation gave preferably the *trans* products from I, II and V, and the *cis* from III and IV. Since the rate determining step of the hydrogenation over Pd catalyst is the hydrogen

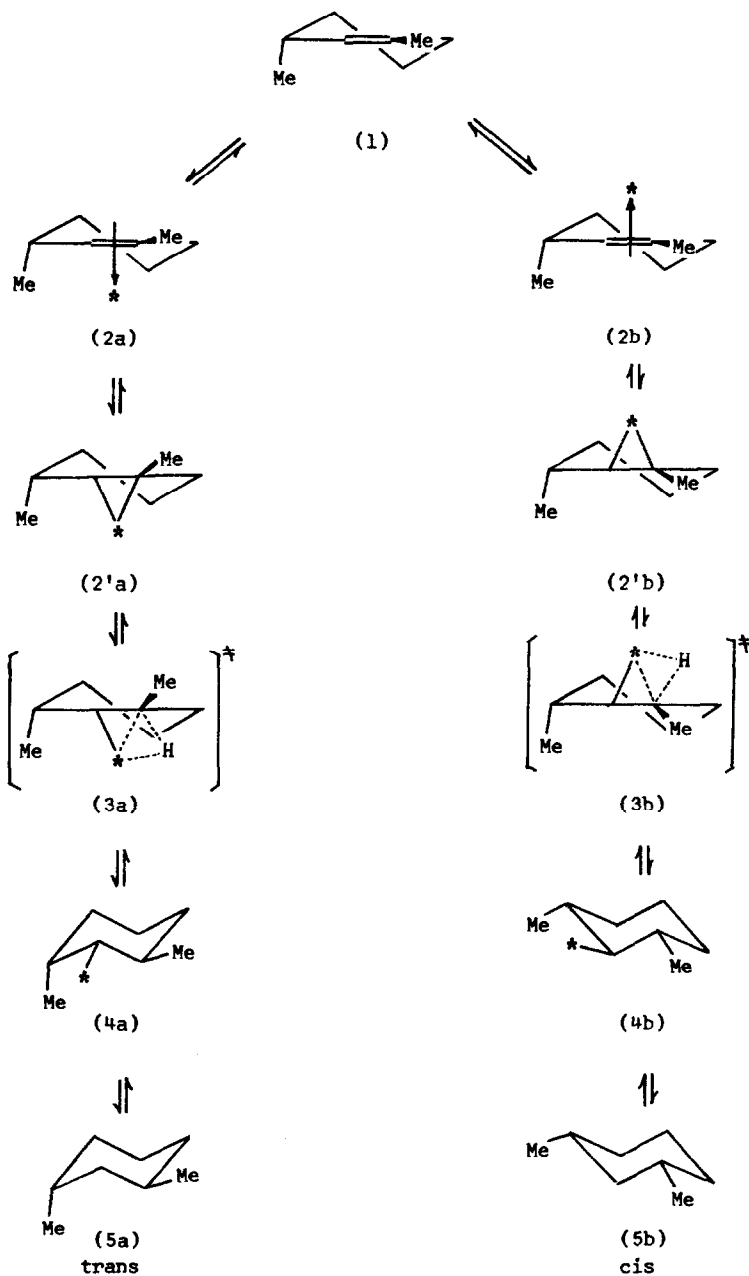
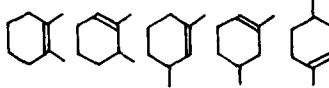


FIGURE 1.

TABLE 1  
 HYDROGENATION OF DIMETHYLCYCLOHEXENES  
 IN ETHANOL

Substrate					
	I	II	III	IV	V
Catalyst <sup>a</sup>	Product composition ( <i>cis</i> %)				
Pd-carbon	— <sup>f</sup>	— <sup>h</sup>	82	81	27 <sup>l</sup>
PdO	27	27	81	82	—
Pd-black	24	24	80	80	—
PtO <sub>2</sub>	81 <sup>g</sup>	67 <sup>i</sup>	72 <sup>j</sup>	59 <sup>k</sup>	57 <sup>m</sup>
Pt-black	77	67	74	50	62
Rh-carbon	66	60	74	49	57
Raney Ni-A <sup>b</sup>	49	50	71	65	48
Raney Ni-B <sup>c</sup>	55	58	62	63	58
Raney Ni-C <sup>d</sup>	66	64	50	34	56
Raney Ni-D <sup>e</sup>	—	—	44	41	70
Acetone treated					
Raney Ni	—	—	52	—	—
Reduced Ni	69	71	64	56	61

<sup>a</sup> Weight of catalyst (mg). Raney Ni, 300; reduced Ni, 2000; Pd-carbon, 20; PdO, 10; 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> Aged for 2 wks.

<sup>e</sup> Aged for 1 mo.

<sup>f</sup> 25% over Pd-Al<sub>2</sub>O<sub>3</sub> in acetic acid, Ref. (6).

<sup>g</sup> 82% in acetic acid, Ref. (9).

<sup>h</sup> 24% over Pd-Al<sub>2</sub>O<sub>3</sub> in acetic acid, Ref. (6).

<sup>i</sup> 77% in acetic acid, Ref. (10).

<sup>j</sup> 74% in acetic acid, Ref. (7).

<sup>k</sup> 49% in acetic acid, Ref. (10).

<sup>l</sup> 28% in acetic acid, Ref. (8).

<sup>m</sup> 56% in acetic acid, Ref. (10).

transfer to the half-hydrogenated intermediate (6), the favored formation of thermodynamically more stable of the two possible products, therefore, is quite reasonable.

The results obtained in the hydrogenation over Pt catalyst are in good agreement with those reported by Siegel and Smith (6,9,10) and Sauvage, Baker and Hussey (7,8). The *cis/trans* ratio of the hydrogenation of I was larger than that of II. Such a difference in the stereoselectivity infers that although the double bond migration occurred to a limited extent, I, even it is

tetrasubstituted olefin which is less reactive, was hydrogenated as such as Siegel and Smith suggested (6).

We suggested that the rate determining step of the Raney Ni hydrogenation is the adsorption of the substrate on the catalyst. If the catalyst hindrance by the methyl group at the tetrahedral carbon atom is operative the *cis* product is expected. The experimental results indicate that III and IV gave preferably the *cis* products, while almost equal amounts of the *cis* and the *trans* products were obtained from I, II and V in the hydrogenation over freshly prepared Raney Ni.

During the hydrogenation the double bond migration was observed especially over Raney Ni treated with acetone (Table 2). If the adsorption of the substrate on the catalyst is rate determining the hydrogenation of I was expected to give exclusively the *cis* product, but similar ratio to that from II was obtained. Taking account of these isomeric distributions of the products, the double bond migration which we have observed in the hydrogenation of methylenecycloalkanes (1,2) and cyclopentenes (4) as well as dimethylcyclohexenes

 TABLE 2  
 HYDROGENATION OF DIMETHYLCYCLOHEXENES  
 OVER RANEY Ni<sup>a</sup>

Substrate	Catalyst	Composition of resulting mixture (%)			
		Saturated Product	Original	Olefins isomerized cyclohexene	<i>exo</i> -Cyclic
I	A <sup>b</sup>	49	50	1	0
II	A	50	47	3	0
III	A	100	0	Tr <sup>c</sup>	0
	C <sup>c</sup>	59	37	4	0
	D <sup>d</sup>	76	22	2	Tr
	Acetone treated	14	81	5	0
	Reduced Ni	56	39	5	0
IV	A	91	8	1	0
	C	46	45	3	6
	Reduced Ni	66	31	3	0

<sup>a</sup> *endo*-Cyclic disubstituted olefins could not be found in the resulting mixture.

<sup>b</sup> Freshly prepared.

<sup>c</sup> Aged for 2 wk.

<sup>d</sup> Aged for 1 mo.

<sup>e</sup> Trace.

should be taken into consideration. Since tetrasubstituted double bond is less reactive than the others, the double bond migration occurs to some extent to form II and 2-methylmethylenecyclohexane. As a consequence, the isomeric distribution of the products from I became similar to that from II. In the hydrogenation of II the increase in the aging period of Raney Ni which was stored in ethanol at room temperature increased the amount of the *cis* product, though no appreciable stereoselectivity was observed over freshly prepared catalyst. On the other hand, the hydrogenation of III and IV, the amount of the *cis* products decreased and the *trans* products were favored on aged Raney Ni. If the stereochemistry of the products is attributed only to the catalyst hindrance of the methyl group at the tetrahedral carbon atom, the amounts of the *cis* products should be favored. These results infer that the catalyst hindrance of the methyl group of cyclohexene is not the dominant factor to determine the product distribution.

Presumably, the double bond migration occurs to form the mixture of cyclohexenes and methylenecyclohexane (Fig. 2) during the hydrogenation and the hydrogen transfer from the catalyst surface to the *exo*-cyclic double bond is far faster than that to the *endo*-cyclic trisubstituted one. The hydrogenation, therefore, may proceed to a considerable extent via methylenecyclohexane as in the pathway (scheme 1) especially on aged Raney Ni. The observation that the isomeric distribution of the products from all substrates over the aged catalyst were similar, but not exactly the same, as those of corre-

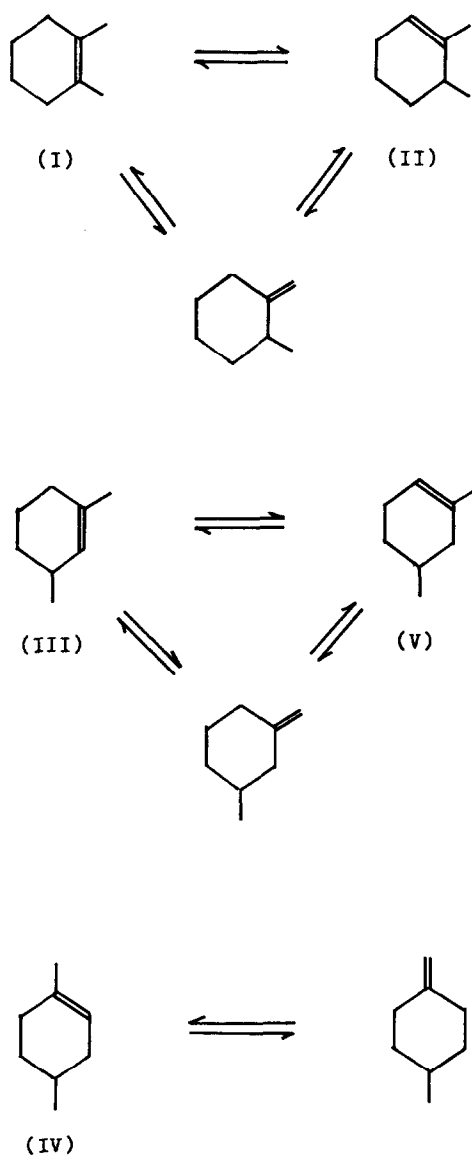
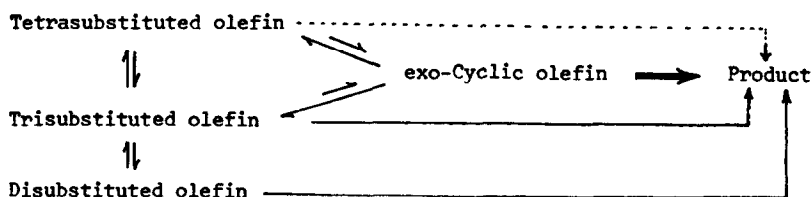





FIGURE 2.



SCHEME 1

TABLE 3  
HYDROGENATION OF  
METHYLMETHYLENECYCLOHEXANES<sup>a</sup>

Substrate	Product composition (cis %)		
			
Catalyst			
Raney Ni, freshly prepared	60	50	45
aged for 2 wk	63	18	8

<sup>a</sup> In ethanol, Ref. (1).

sponding 2-methyl-, 3-methyl- and 4-methyl-methylenecyclohexane (Table 3) supports the above reaction pathway. The results of the Raney Ni hydrogenation infer that contrast to the Pt catalyzed reaction the tetrasubstituted olefins seems hardly to proceed over Raney Ni especially over the catalyst aged or treated with acetone, but the double bond migration occurs in advance of the hydrogenation. Such a difference is attributed to the affinity of the metal for the olefinic double bond. The Pt is classified as soft acid compared to Ni (14).

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