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Stereochemistry and Mechanism of the Hydrogenation of Dialkyl Cyclohexenes

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In order to investigate the steric effect of the substituents to determine the product distribution, disubstituted cyclohexenes were hydrogenated over several transition metal catalysts. Some cyclohexenes which have two large substituents at the vicinal carbon atoms, at least one of which is trigonal, were not hydrogenated over Raney Ni at all but were hydrogenated over Pt catalyst under our experimental conditions. Presumably, the stereoselectivity depends on the competitive operation of the torsional angle strain and the catalyst hindrance with substituents. In the hydrogenation over Pd catalyst, thermodynamically more stable products were dominant at the standard condition but at high substrate to catalyst ratio the less stable products were slightly preferred. No appreciable stereoselectivity was observed in the hydrogenation of 1,4-disubstituted cyclohexenes.

INTRODUCTION

The hydrogenation of 1,2- and 2,3-dimethylcyclohexene gave similar distributions of isomeric products depending on the kind of catalysts at atmospheric pressure and room temperature (*1–3*). The hydrogenation over Pd catalyst for which the hydrogen transfer to the half-hydrogenated intermediate is product controlling gave preferably the *trans* products (*1*). The *cis* products were favoured on Pt catalyst, where the product controlling step is the hydrogen transfer to the adsorbed species (*2*). The adsorption of the substrate on the catalyst is assumed to be product controlling on Raney Ni catalyst (*4*). Almost equal amounts of the *cis* and the *trans* products were obtained on the freshly prepared Raney Ni, while the amounts of the *cis* products increased if the catalyst was aged in ethanol at room temperature. In order to investigate the effects of the substituent on the stereochemistry of the hydrogenation of cyclohexenes, several disubstituted cyclohexenes were prepared and were hydrogenated over transition metal catalysts.

EXPERIMENTAL METHODS

Materials. Olefinic compounds other than 1-methyl-4-isopropylcyclohexene were prepared by Grignard reaction on the corresponding substituted cyclohexanones, followed by dehydration. The preparative methods are tabulated in Table 1. 1-Methyl-4-isopropylcyclohexene was obtained by the hydrogenation of D-limonene over Raney Ni which was aged for 8 months in ethanol at room temperature, bp 68–70°C/20 mm. The purity of 1-methyl-4-isopropylcyclohexene was 98.5%. Impurities were 0.3% of starting material, 0.5% of *cis* and 0.4% of *trans*-1-isopropyl-4-methylcyclohexane, and 0.3% of 1-isopropyl-4-methylcyclohexene. All compounds were checked by gas chromatography and ir and NMR spectra. W-5 Raney Ni (*5*), and Pd-carbon (*6*) were prepared as described earlier. PtO_2 was purchased from Wako Pure Chemical Co.,

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TABLE 1
PREPARATION OF OLEFINIC COMPOUNDS

Olefin	Starting material (cyclohexanone)	Grignard reagent	Dehydrating reagent	Method of separation	Melting point or boiling point
I[a]	2-*t*-Butyl-	CH_3MgI	I_2 (distillation)	glc	—
II					—
V			$POCl_3$ (pyridine)		—
XI					—
III[b]	2-Phenyl-	$C_6H_{11}MgCl$	$POCl_3$ (pyridine)	Aluminum column chromatography (Hexane)	bp 110–113°C/0.1 mm
IV[c]	2-Cyclohexyl-	C_6H_5MgBr	$POCl_3$ (pyridine)	glc	mp 36.5°C
VII	4-Ethyl-	CH_3MgI	P_2O_5	—	bp 58–60°C/23 mm
IX	4-*t*-Butyl-	CH_3MgI	P_2O_5	—	bp 75–78°C/17 mm
X	4-Methyl-	$C_6H_{11}MgCl$	H_2SO_4–AcOH	—	bp 117–118°C/11 mm
XII	2-Phenyl-	CH_3MgI	—[d]	Aluminum column chromatography (Hexane)	mp 56°C

[a] The dehydration of 1-methyl-2-*t*-butylcyclohexanol by distillation with I_2 catalyst gave mainly I and II which might form by the double bond migration. The dehydration with $POCl_3$ in pyridine gave mainly V and XI.

[b] The prepared III contained about 30% of 1-cyclohexyl-2-phenylcyclohexene. Since the stereochemical results of the hydrogenation of 1-cyclohexyl-2-phenylcyclohexene showed exclusive formation of *cis* 1-cyclohexyl-2-phenylcyclohexane (*21*), the isomeric distribution of the hydrogenation product of III was estimated.

[c] 1-Phenyl-2-cyclohexylcyclohexanol which was prepared by the Grignard reaction of 2-cyclohexylcyclohexanone with C_6H_5MgBr was hydrogenated to give 1,2-dicyclohexylcyclohexanol over Raney Ni at high temperature and high hydrogen pressure.

[d] 1-Methyl-2-phenylcyclohexyl acetate (acetylation of parent cyclohexanol with Ac_2O in pyridine for 25 days) was heated on crashed glass. The distillate contained 60% of XII.

Tokyo, Japan. Pt-black was prepared by the hydrogen reduction of PtO_2 and was washed well with distilled water. Rh-carbon was purchased from Nippon Engelhard Co., Tokyo, Japan.

Catalytic hydrogenation. The following general procedure was used. A 1/1000 mol of substrate and a known amount of catalyst in the solvent were stirred with hydrogen at an ordinary temperature. After the reaction the catalyst was removed by centrifugation and the solution was analyzed by gas chromatography.

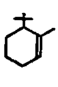
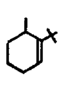
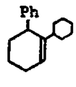
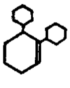
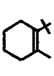
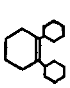
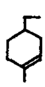
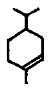
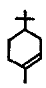
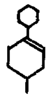
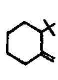
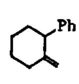
Quantitative analyses. The analyses were performed on a 15 m × 0.25 mm or 45 m × 0.25 mm Goley column of PEG 4000 or a 45 m × 0.25 mm Goley column of PEG 400 using a Hitachi K-53 or F-6 gas chromatograph equipped with a flame ionization detector and with an Infotronics digital integrator.

RESULTS AND DISCUSSION

The results obtained in the hydrogenation are summarized in Table 2.

Raney Ni. In the hydrogenation of 2-methyl-3-*t*-butylcyclohexene (I), the amount of the *cis* product was 93–94%, while only 6–13% of the *cis* product was obtained from 2-*t*-butyl-3-methylcyclohexene (II). We suggested that the factors determining the isomeric distribution of the products operate in the formation of σ-type adsorbed species from π-type ones (*7*). Two stereochemical factors are supposed to determine the distribution of two stereoisomeric adsorbed

TABLE 2
THE HYDROGENATION OF DISUBSTITUTED CYCLOHEXENES AND METHYLENECYCLOHEXANES[a]

Substrate[b]												
	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	(IX)	(X)	(XI)	(XII)
Catalyst[c]	Products (*cis* %)											
Raney Ni[d]	94	6	x[f]	x	49	x	48	46	44	56	85	44
Raney Ni[e]	93	13	—	—	54	—	58	56	48	—	86	—
PtO_2	94	6	18	28	—	42	52	46	41	63	90	81
Pt-black	95	7	24	25	100	42	54	48	40	65	80	86
Rh-carbon	94	14	—	—	80	—	54	51	44	—	81	—
Pd-carbon	59[g]	6	13	4	56[g]	4	28	29	17	20	71	50

[a] In ethanol.

[b] 1/1000 mol.

[c] Weight of catalyst (mg). Raney Ni, 1000; PtO_2, 10; Pt-black, 7; Rh-carbon, 20; Pd-carbon, 20, unless otherwise indicated.

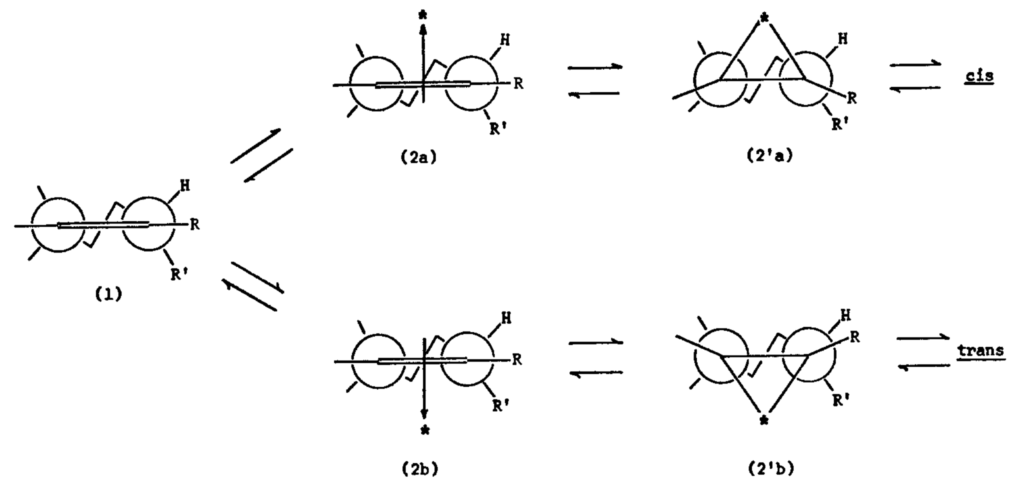
[d] Freshly prepared.

[e] Aged for 7 days.

[f] No hydrogenation occurred.

[g] Pd-carbon, 5 mg.

species; one is the steric interaction of the catalyst with the allylic substituent and the other is the torsional angle strain between the allylic substituent and the substituent on the adjacent vinylic carbon atom. It has been reported previously by several investigators that the allylic strain in the cyclohexene ring (the strain between the substituent at the allylic position and that at vicinal vinylic carbon atom) is relatively large forcing the allylic substituent to take a pseudoaxial orientation. Garbisch reported that the *t*-butyl group of 2-phenyl-3-*t*-butylcyclohexene preferably takes the pseudoaxial (*8*). Hanaya showed that the pseudoaxial hydroxyl group of 2-cyclohexenol is preferred (*9*). Senda *et al.* (*10,11*) reported that the hydroxyl group of 2-cyclohexenol exists in a distribution of 84.0 ± 2.3% of pseudoaxial orientation and 16.0 ± 2.3% of pseudoequatorial, and 2-methyl-2-cyclohexenol in a distribution of 93.8 ± 3.7% of pseudoaxial and 6.2 ± 3.7% of pseudoequatorial. If the allylic substituent of I and II preferably takes the pseudoaxial orientation, the results obtained in the hydrogenation of these compounds indicate that the catalyst hindrance with the methyl group at the allylic position is small enough that the torsional angle strain with the *t*-butyl group becomes dominant in determining the distribution of the two stereoisomeric adsorbed species. In going from the π-type adsorbed species (2a in Scheme 1) to the corresponding σ-type (2′a), the *t*-butyl group at the 2 position (*R*) is bent toward the same side as the methyl group at the 3 position (*R*′) and the dihedral angle is decreased, increasing the torsional angle energy contribution to the transition state. In contrast, in going from the alternative π-type adsorbed species (2b) to the corresponding σ-type one (2′b), the *t*-butyl group at the 2 position (*R*) is bent toward the opposite side of the methyl group (*R*′) at the 3 position and the dihedral angle is increased. Thus, the torsional angle energy contribution to the transition state decreases (Scheme 1). The observation that the hydrogenation of 2,3-dimethylcyclohexene gave almost equal amounts of *cis* and *trans* isomers also suggests that the catalyst hindrance with the allylic methyl group and the torsional angle strain between the vicinal methyl group operate competitively to determine the product distribution (*3*).



On the other hand, the catalyst hindrance with the bulky *t*-butyl group at the allylic position is dominant over the torsional angle strain between 2-methyl and 3-*t*-butyl group. As a consequence, the *cis* product became favored in the hydrogenation of I. The hydrogenation of 1-methyl-2-*t*-butylcyclohexene (V) gave almost equal amounts of *cis* and *trans* isomers. Since a tetrasubstituted double bond is so much less reactive, double bond migrations of 1,2-disubstituted cyclohexenes are expected to form 2,3-disubstituted cyclohexenes and methylenecyclohexanes during the hydrogenation (*1–3*). Therefore, the distribution of the isomeric products from V was in between those from I, II, and 2-*t*-butylmethylenecyclohexane (XI), the hydrogenation of which gave 85–86% of the *cis* product.

The hydrogenation of 2-cyclohexyl-3-phenyl- (III) and 2,3-dicyclohexylcyclohexene (IV) hardly occurred under the reaction conditions employed. This may mean that catalyst hindrance with the allylic substituent is so large that no adsorbed species is formed. Alternatively, assuming that adsorbed species are formed, the torsional angle strain between the allylic substituent and the substituent at the adjacent vinylic carbon atom is so large in the transition state that the reaction hardly proceeds with the *cis* forming pathway more hindered than the *trans*. 1,2-Dicyclohexylcyclohexene (VI) was not hydrogenated at all under the reaction conditions employed. If 1,2-disubstituted cyclohexenes are adsorbed on the catalyst to form three-membered σ-type adsorbed species, the eclipsing strain between two substituents on the vicinal vinylic carbon atoms is assumed to increase compared to the parent cyclohexenes because the carbon atoms carrying the substituents rehybridize from sp^2 to sp^3. If these two substituents are large (the case of VI) the increased eclipsing strain may prevent the molecule from being adsorbed on the catalyst. Although double bond migration of VI could form 2,3-disubstituted cyclohexene (IV) and 1-cyclohexylidene-2-cyclohexylcyclohexane, these olefinic compounds are hydrogenated with great difficulty as mentioned earlier.

The hydrogenation of 1,4-disubstituted cyclohexenes; 1-methyl-4-ethyl- (VII), 1-methyl-4-isopropyl- (VIII), 1-methyl-4-*t*-butyl- (IX), and 1-cyclohexyl-4-methylcyclohexene (X) gave no stereoselectivity, especially on the freshly prepared catalyst. On the aged catalyst which was stored in ethanol at room temperature for 7 days, the amounts of the *cis* products increased slightly. This shows that the effects of the substituents did not appear on the freshly prepared catalyst but slightly observed on the aged one. Detailed product analysis showed that during the course of the reaction, migration of the double bond occurred to form other isomeric cyclohexenes especially on the aged catalyst (Table 3). Methylenecyclohexanes which were not detected are supposed to form during the hydrogenation. The *cis* product was favored in the hydrogenation of 4-methylmethylenecyclohexane over the aged catalyst. This result supports our previous postulate that the double bond migration occurs *via* π-allylic adsorbed species as a bypass route (*12*).

Pt catalyst. The hydrogenation of III and IV did not proceed over Raney Ni but was hydrogenated to give 18–24 and 25–28% of the *cis* products over Pt catalyst, respectively. There are two characteristic features on Pt: (i) Pt is expected to have a strong affinity for the olefinic double bond because of being classified as soft acid compared to Ni; (ii) the hydrogenation over Pt may be less sensitive to the catalyst hindrance because the metallic bond radius of Pt is larger than that of Ni. Therefore, these substrates (III and IV) may form the adsorbed species and the hydrogenation occurs subsequently, contrary to the case over Raney Ni. The hydrogenation of V showed that the substrate is adsorbed on the catalyst, and the hydrogen transfers subsequently to give exclusively the *cis* product.

Siegel and Smith proposed that the product controlling step of the Pt catalyzed hydrogenation is the hydrogen transfer from the catalyst to the adsorbed species under 1 atm pressure of hydrogen and room temperature. Comparison of the stereochemical results in the hydrogenation over Pt catalyst with those over Raney Ni (except in the case of V) suggests that the distribution of the stereoisomeric half-hydrogenated species which may be similar to that of the products reflects the initial distribution of the corresponding adsorbed species.

The transition state of the product controlling step is considered to be reactant-

TABLE 3

HYDROGENATION OF 1-METHYL-4-ALKYLCYCLOHEXENES OVER RANEY NI[a]

Substituent	Catalyst	Reaction time (hr)	Composition of resulting mixture (%)		
				Cyclohexene	
			Cyclohexane	Original	Isomerized (1-alkyl-4-methyl-)
Isopropyl	A[b]	1	91	7	2
	B[c]	2	26	72	2
t-Butyl	A	1	81	14	5
	B	2	21	65	14

[a] In ethanol.

[b] Freshly prepared.

[c] Aged for 7 days.

like in the Pt catalyzed hydrogenation of six-membered cyclic olefins, whereas product-like in that of five-membered ones by taking into account the hydrogenation results of cycloalkenes (*7*), methylenecycloalkanes (*12,13*), and cycloalkanones (*13,14*) together with the stereochemical results of $LiAlH_4$ reduction of cycloalkanones (*15,16*).

Since the double bond migration of VI may occur to form IV and 1-cyclohexylidene-2-cyclohexylcyclohexane, it is reasonable for VI to give only 42% of the *cis* isomer.

The hydrogenation of 1,4-disubstituted cyclohexenes did not show any stereoselectivity.

Pd catalyst. The Pd catalyzed hydrogenation gave preferably the *trans* products. Taking into account the following factors suggested by Siegel and Smith that (i) the product controlling step of the hydrogenation over Pd catalyst is the hydrogen transfer to the half-hydrogenated intermediate, so that the preceding reactants and intermediates should tend to become equilibrated with one another; (ii) the carbon–metal bond forms with the less substituted sp^2 carbon atom; (iii) the metal is the largest substituent among others in the cyclohexane ring; (iv) the transition state for the postulated product controlling step resembles the preceding intermediate (half-hydrogenated state); the thermodynamical stability between two epimeric half-hydrogenated intermediates determines the distribution of the corresponding products. Thus, the favored formation of the thermodynamically more stable of the two possible products is quite reasonable.

In the hydrogenation of I and V the amount of the *cis* isomer was slightly larger than that of the *trans*. In these cases the weight of Pd carbon was ca. $1/40$ of the substrate, compared to ca. $1/10$ in other cases. It has been suggested that the stereoselectivity of the hydrogenation is controlled by the quantity of the Pd catalyst (*12,17*). House *et al.* (*17*) reported that the stereoselectivity of the hydrogenation is controlled by the quantity of the Pd catalyst. Augustine also reported that when a large amount of catalyst was used, the amount of hydrogen available is spread over a large surface area, decreasing the probability of interaction with the reactant. This permits equilibration between the *cis* and the *trans* half-hydrogenated states or the *cis* and the *trans* adsorbed species, thus resulting in decreased stereoselectivity of the reaction (*18*). When a large reactant to catalyst ratio is employed, the hydrogen transfer to the adsorbed species is relatively easy. The product controlling step[2] of the hydrogenation of olefin with Pd catalyst is not the hydrogen transfer to the half-hydrogenated species but the adsorption of the substrate on the catalyst as with Raney Ni or the hydrogen transfer to the adsorbed species as with Pt catalyst. Therefore, the thermodynamically more stable of the two possible products was no longer the major product in the hydrogenation of I and V.

Rh catalyst. The stereoselectivity of Rh catalyzed hydrogenation has remained obscure, sometimes it is intermediate between Ni and Pt, and sometimes it is close to Ni or Pt. These observation infer that both elementary reaction steps, the adsorption of the substrate on the catalyst and the hydrogenation transfer to the adsorbed species, influence the stereochemistry of the isomeric products.

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[2] Siegel reported that in the case of the hydrogenation of 1-methyl-4-*t*-butylcyclohexene, the stereoisomeric products ratio was changed depending on the hydrogen pressure. He concluded that this is because the product controlling step (*19*) [rate-limiting step (*20*)] can be altered by varying the hydrogen pressure.

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