Epoxide Rearrangement II.[†] Isomerization of 1-Methylcyclohexene Oxide over Solid Acids and Bases

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The reaction of 1-methylcyclohexene oxide over solid acids and bases at 108 °C was found to give five main products, 2-methylcyclohexanone (III), 1-methylcyclohexanol (IV), 2-methyl-2-cyclohexene-1-one (V), 2-methyl-enecyclohexanol (VIa), and 2-methyl-2-cyclohexene-1-ol (VIb), with a small amount of 1-methylcyclohexene (I) and unidentified compound (II). The ketone (III) was formed predominantly over zeolite, SiO_2-Al_2O_3, H_2SO_4/SiO_2, $AlCl_3$, and BBr_3, while the allyl alcohol (VI) was given by Al_2O_3 and TiO_2. HCl/SiO_2 and solid H_3PO_4 calcined at 400—900°C gave both products, III and VI, in the same amounts, though the latter calcined at 200—300 °C formed almost 100% ketone. Solid lithium perchlorate was surprisingly active for the formation of ketone, but other metal perchlorates and lithium salts were quite inactive. Alkaline earth metal oxides and $NaOH$/SiO_2 were almost inactive. The catalytic activity and selectivity as well as the reaction path and mechanism are briefly discussed mainly in connection with acid-base property of solid catalysts.

Since Cope and Tiffany[1] observed an unusual base-catalyzed rearrangement of cyclooctatetraene oxide, much work has been done on the rearrangements of both cycloalkene oxide and open-chain oxide with strong bases, usually lithium dialkylamide.[2–6] The isomerization reactions of various epoxides with Lewis acid catalysts such as BF_3,[7,8] $ZnBr_2$,[9] $MgCl_2$,[10] and solid acid catalyst, Al_2O_3[11,12] have also been investigated.

Recently, Imanaka et al.[13,14] have studied the activity and selectivity of several solid acids and bases for the isomerization of propylene oxide. However, no work has been reported on the isomerization of epoxides other than propylene oxide and ethylethylene oxide[15,16] over solid acids or bases.

Cyclohexene oxide, one of the simplest cycloalkene oxides, seems suitable to study the selectivity and activity of solid acid or base catalysts and the effect of ring structure on the reaction. However, the reaction rate was extremely slow even over SiO_2-Al_2O_3. Thus, 1-methylcyclohexene oxide was chosen, because the reaction rate was much faster due to the electronic effect of methyl group and the selectivity for the formation of allyl alcohol with exo- or endo-double bond can be investigated.

In the present work, the activity and selectivity of several solid acids and bases and some salt catalysts for the isomerization of 1-methylcyclohexene oxide have been studied in a heterogeneous solid-liquid system.

Experimental

Catalysts and Materials.   1-Methylcyclohexene oxide, supplied from Takasago Perfumery Co., was fractionally distilled to purify to more than 98% and toluene, a guaranteed reagent, used as a solvent was redistilled over sodium metal.

The zeolite H–F9 was prepared from zeolite F-9, supplied from Tekkosha Co., by a conventional ion-exchange method using NH_4Cl and by calcining at 500° C. Al_2O_3

was KAT6 of Nishio Chemical Co. and SiO_2-Al_2O_3 was N631(L) (Al_2O_3; 15 wt. %) of Nikki Chemical Co. Both catalysts were calcined at 500 °C. H_2SO_4/SiO_2 was prepared as follows: 10 g of granular silica gel (White, Kanto Chemical Co.) was immersed in 12 ml of 0.5 M H_2SO_4, evaporated, dried and then calcined at 150 °C. HCl/SiO_2 was prepared by the same method. TiO_2 was prepared by the hydrolysis of titanium tetrachloride with 28% ammonia water at pH=9.4, followed by washing the precipitate, drying at 110 °C for 14 hr and calcining at 500 °C for 3 hr. ZnO was prepared by the hydrolysis of zinc nitrate with 28% ammonia water similarly as in the case of TiO_2.

Anhydrous $AlCl_3$ and BBr_3 were guaranteed reagents of Wako Pure Chemical Co. Solid phosphoric acid was N501 of Nikki Chemical Co. $LiClO_4 \cdot 3H_2O$, a guaranteed reagent of Nakarai Chemical Co., was used without any pretreatment. $LiClO_4$, $KClO_4$, $LiCl$, and $LiNO_3$, guaranteed reagents of Nakarai Chemicals Co., and $NaClO_4$ and Li_3PO_4, reagents of Wako Pure Chemical Co., were dried at 120 °C for 3 days. $NaOH$/SiO_2 was prepared by following the procedure of Malinowski and Czczepanska[17]: 10 g of granular silica gel was immersed in 12 ml of 1 M NaOH, dried and calcined at 500 °C. CaO and MgO were prepared by calcining their hydroxides in air at 550 °C or by calcining further the oxide *in vacuo* (10^{-4}—10^{-5} mmHg) in quartz tubes at 600 °C for 2 hr and at 640 °C for 3 hr, respectively. All the catalysts prepared were stored in sealed ampoules.

Procedure and Analysis of Products.   In general, the reaction was carried out in the presence of toluene as a solvent at 108 °C for 2 hr. A mixture of 0.5 ml of the epoxide, 2.5 ml of toluene, and about 0.3 g of catalyst below 100 mesh was stirred in a reaction vessel by a magnetic stirrer, At appropriate time intervals, a small amount of the sample was taken out by a 1 ml syringe, separated from catalyst and analyzed by a gas chromatograph with a hydrogen-flame detector using a 3 m column of polyethylene glycol 20 M on celite 545 SK (150 °C; N_2, 0.9 kg/cm²). For the separation of two allyl alcohols, a 45 m capillary column of Ucon LB–550–X (100 °C; N_2, 1.2 kg/cm²) was used. The yields of products were calculated from VPC peak areas (uncorrected).

In the experiment where $AlCl_3$ was used as a catalyst, 0.5 g of the catalyst was added into a mixture containing 0.5 ml of the epoxide and 2.5 ml of toluene with vigorous stirring at room temperature and the reaction was continued for 15 min. Then, the reaction mixture was poured into

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50 ml of 5% hydrochloric acid. The organic layer was separated, washed with water twice and then dried over anhydrous calcium chloride. In the case of BBr_3, 0.3 ml of BBr_3 was poured into the same reaction mixture cooled in ice and the reaction was continued for 10 min. The subsequent procedure was the same as in the case of $AlCl_3$.

The reactions catalyzed by MgO and CaO calcined *in vacuo* were carried out by the procedure of Ohnishi and Tanabe.[18] The catalyst prepared *in vacuo* was introduced into an evacuated and sealed reaction vessel through a breakable joint to prevent the contact with air. Then, the reaction was followed by the general procedure.

The main reaction products, III–VI, were isolated by a column chromatograph on silica gel eluted with petroleum ether–diethyl ether (1 : 1) and analyzed by NMR and IR. Compound III was easily identified as 2-methylcyclohexanone by its IR spectrum and by glc comparison with the authentic sample; IR (neat): 2940, 2860, 1710, 1445, 1370—1330, 1310, 1210, 1120, 860, 810, and 720 cm⁻¹. Compound IV was identified as 1-methylcyclohexanol by IR and NMR; IR (neat): 3400—3200, 2950—2850, 1450, 1370, 1320, 1050, 1020, and 380 cm⁻¹; NMR (δ): 3.4 (s, 1H, OH), 1.7— 1.1 (m, 10H, CH_2) and 1.0 ppm (s, 3H, CH_3). Compound V was recognized as 2-methyl-2-cyclohexene-1-one by its IR and by glc comparison with the authentic sample; IR (neat): 3500—3300, 2594, 2586, 2660, 1450, 1360, 1180, 1110, 1020, and 900 cm⁻¹. Compound VI was revealed to be a mixture of two allylic alcohols by its glc analysis with a capillary Golay column, IR, and NMR; IR (neat): 3180, 990 cm⁻¹ assigned to hydroxyl group and 890 cm⁻¹ to methylene group; NMR (δ): 5.1—5.3 ppm assigned to olefinic protons. The mixture is considered to consist of 2-methyl-2-cyclohexene-1-ol and 2-methylenecyclohexanol in view of mechanistic considerations. The hydrogenated compound of VI was identical in glc, IR and NMR spectra to those of the synthesized and hydrogenated compound of 2-methyl-2-cyclohexene-1-ol and identified to be 2-methyl-cyclohexanol. Both allylic alcohols were synthesized as follows in order to identify compound VI in glc.

(1) *2-Methyl-2-cyclohexene-1-ol.* 1-Methylcyclohexene (1.0 g) was oxidized with $Hg(OCOCH_3)_2$ (3.2 g) in 10 ml CH_3COOH at 80 °C for 2 hr to form 1-acetoxy-2-methyl-2-cyclohexene (0.90 g): bp 85 °C/15 mmHg, which was hydrolyzed with $NaOH-CH_3OH$ to yield its allyl alcohol (0.5 g): bp 90 °C/18 mmHg; IR (neat); 3180, 990 cm⁻¹ (-OH); NMR (δ): 5.4 (t, 1H, C=CH), 4.1 (s, 1H, OH), 3.8 (t, 1H, CHOH), and 1.7 ppm (s, 3H, C=CCH_3), which were identical with the literature values.[19] This sample showed the second peak of compound VI in glc.

(2) *2-Methylenecyclohexanol.* Methylenecyclohexane (0.5 g) synthesized by Wittig reaction from cyclohexanone, $(C_6H_5)_3PCH_3Br$ and BuLi[20] was oxidized with SeO_2 (1.1 g) in 8 ml AcOH and 2 ml Ac_2O at 60 °C for 2 hr, followed by the saponification with aqueous NaOH to give its allyl alcohol (75 mg); IR (neat): 3170, 995 cm⁻¹ (-OH) and 890 cm⁻¹ (CH_2=C); NMR (δ): 5.3 (s, 2H, CH_2=C), 4.1 (s, 1H, OH), and 3.8 ppm (t, 1H, CHOH), which were identical with the literature values.[21] This sample gave the first peak of compound VI in glc.

Results and Discussion

The reaction of 1-methylcyclohexene oxide over solid acids and bases gave five main products, 2-methylcyclohexanone (III), 1-methylcyclohexanol (IV), 2-methyl-2-cyclohexene-1-one (V), 2-methylenecyclohexanol (VIa), and 2-methyl-2-cyclohexene-1-ol

(VIb), with a small amount of 1-methylcyclohexene (I) and unidentified compound (II).

(III)   (IV)   (V)   (VIa)   (VIb)
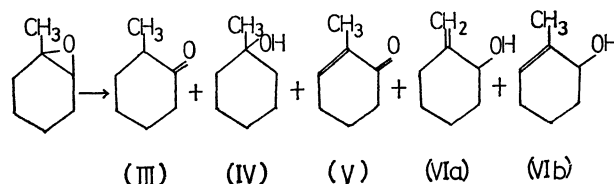
II was possibly the dehydrated diene-compound of VI, because cyclohexene oxide also rearranged under the same reaction conditions with extended periods to yield a small amount of cyclohexene and 1,3-cyclohexadiene, presumably formed by the dehydration of cyclohexenol. Their RRT (Relative Retention Time) in GLC was quite close to that between I and II.[22]

The relation between the yields of the products and reaction time is shown in Fig. 1, where the catalyst was solid H_3PO_4 calcined at 900 °C. The yields of III and VI increased almost parallel with each other during the course of reaction. The similar time-variation of the products was also observed in the case of TiO_2. This suggests that they are not intermediate species for each other. Since other products, IV and V, are presumably formed by hydrogenation and dehydrogenation of the starting epoxide, respectively, these two materials can not be intermediate species for III or VI formation. Consequently, it seems likely that ketone and allyl alcohol are formed by different mechanisms. However, there is a report implying the possibility of the carbonyl compound formation from the corresponding allyl alcohol on the base-induced conversion of epoxides.[5] This possibility seems to be very small, judging from the product distribution during the course of reaction in the present work.

Table 1 shows the catalytic activity and selectivity of several solid acid catalysts in 2 hr at 108 °C, and those of solid H_3PO_4 calcined at different temperatures are given in Table 2. The products are mainly divided into two categories, ketone (III) and allyl alcohol (VI). The former was formed predominantly
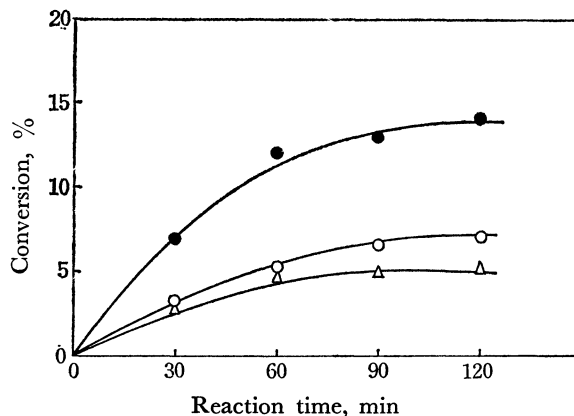
Fig. 1. Isomerization of 1-methylcyclohexene oxide over solid phosphoric acid calcined at 900 °C.
Reaction temp.: 108 °C, (-●-) Total conversion, (-○-) Allyl alcohol (VI), (-△-) ketone (III).

TABLE 1. CATALYTIC ACTIVITY AND SELECTIVITY OF SOLID ACID CATALYST FOR
ISOMERIZATION OF 1-METHYLCYCLOHEXENE OXIDE AT 108 °C

Catalysts	Amount of catalyst (g)	Conversion (%)	Products (%)[d]					
			I	II	III	IV	V	VI (a,[e] b[f])
Zeolite H-F9[a]	0.343	35.8		1.7	23.2	0.6	0.9	8.6 (6.7, 1.9)
SiO₂-Al₂O₃[a]	0.473	42.3			42.3			
Al₂O₃	0.340	90.4	trace	2.4	5.6	4.8	2.4	74.6(51.1, 23.5)
Al₂O₃[b]	0.340	75.2			4.2	trace		69.6
H₂SO₄/SiO₂	0.413	100.0	0.8		99.2			
H₂SO₄/SiO₂[b]	0.413	98.4	0.8		97.6			
HCl/SiO₂	0.453	37.1	0.6		18.0			14.5 (3.9, 10.6)
TiO₂	0.435	27.3		0.2	2.0		0.2	24.9(13,9, 11.0)
ZnO	0.190	2.4						2.4
AlCl₃[c]	0.5	95.5	1.4	1.0	79.6	1.7	3.1	1.9
BBr₃[e]	0.3(ml)	93.4	3.6	28.3	31.3	3.0	1.0	2.0

a) A mixture of 1 ml of the epoxide and 5 ml of toluene was reacted at 100 °C.   b) Reaction time: 30 min. c) The reactions were carried out at room temperature for 15 min in a heterogeneous state and at 0 °C for 10 min in a homogeneous state for AlCl₃ and BBr₃, respectively. Both catalysts gave several small peaks of unexpected and unidentified compounds in glg. d) See text. e) 2-methylenecyclohexanol. f) 2-methyl-2-cyclohexene-1-ol.

TABLE 2. CATALYTIC ACTIVITY AND SELECTIVITY OF SOLID PHOSPHORIC ACID
FOR ISOMERIZATION OF 1-METHYLCYCLOHEXENE OXIDE AT 108 °C

Temperature of calcination (°C)	Amount of catalyst (g)	Conversion (%)	Products (%)[b]					
			I	II	III	IV	V	VI (a, b)
200	0.440	98.0	0.5		96.8		trace	
200[a]	0.440	78.8	0.5	0.6	76.2			
300	0.370	87.7		1.2	86.5			
300[a]	0.370	85.1			57.9	8.1		17.6(12.8, 4.8)
400[c]	0.508	45.2		4.7	19.7		0.9	17.5 (9.2, 8.3)
900	0.380	12.4			5.3			7.2 (4.4, 2.8)

a) Reaction time: 30 min. b) See text. c) A mixture of 1 ml of the epoxide and 5 ml of toluene reacted at 100 °C.

over zeolite, SiO₂-Al₂O₃, H₂SO₄/SiO₂, AlCl₃, BBr₃ and solid H₃PO₄ calcined at 200 and 300 °C, while the latter was given by Al₂O₃ and TiO₂. HCl/SiO₂ and solid H₃PO₄ calcined at 400 and 900 °C gave both products in the same amounts, though their catalytic activities were not high. It is especially interesting that SiO₂-Al₂O₃, H₂SO₄/SiO₂ and low-temperature calcined solid H₃PO₄, which are known to have strong acid sites,[23,24] formed almost 100% ketone, whereas Al₂O₃ and TiO₂ gave more than 80% of allyl alcohol.

AlCl₃ and BBr₃, which are typical Lewis acid catalysts, showed the almost similar selectivity for ketone to those of H₂SO₄/SiO₂ and solid H₃PO₄ calcined at low temperature, which are Brönsted acids. Accordingly, it is considered that the selectivity does not depend on the type of acid sites, Brönsted and Lewis acids. BBr₃ produced a large amount of the unidentified compound (II) and many products other than those listed in the table, probably owing to its very high acid strength.[25]

A number of authors have reported that ketone is formed from epoxides with various acid catalysts; for example, from p-menthene and d-limonene oxide with ZnBr₂,[26] 2,3-butene oxide with BF₃-etherate,[27] d-limonene oxide with CH₃COOH,[28] propylene oxide

over zeolite.[29] Our observations also substantiate the ketone formation with acid catalysts.

The pronounced activity of Al₂O₃ for the allyl alcohol formation was quite similar to Nigam and Levi's results,[30] where limonene and α-pinene oxides isomerized to the corresponding α, β-unsaturated alcohols, the yields being increased in order of acidic< neutral<basic alumina. Okamoto et al. have investigated the isomerization of propylene oxide over SiO₂-MgO catalysts using a pulse reactor and concluded that allyl alcohol was formed by acid-base bifunctional catalysts, where the oxygen of the epoxide was adsorbed on an acidic site and β-hydrogen on a basic site and that even very weak acid site was favorable for its formation.[14] Taking into account both observations, our results of Al₂O₃ could be explained by the bifunctional mechanism. The same mechanism seems to operate over TiO₂, since it has basic sites[31] as well as acidic sites.[32] The catalytic activities of solid H₃PO₄ calcined at various temperatures correlate well with their acidities, which are 4.5 mmol/g for 250 °C, 1.6 for 400, and 0.4 for 980 at pKₐ=1.5.[24] The formation of allyl alcohol over the catalyst calcined at high temperature suggests that basic sites appear on the surface and the reaction takes place by acid-base bifunctional mechanism,

Table 3. Catalytic activity and selectivity of solid metal perchlorates, lithium salts and solid base catalysts for isomerization of 1-methylcyclohexene oxide at 108 °C

Catalysts	Amount of catalyst (g)	Conversion (%)	Products (%)[d]					
			I	II	III	IV	V	VI
LiClO$_4$·3H$_2$O	0.301	75.7		0.5	70.3			
LiClO$_4$·3H$_2$O[a]	0.301	86.9		0.7	80.3			
LiClO$_4$	0.290	87.3	0.5	0.3	86.5			
LiClO$_4$[b]	0.290	86.7	0.4	0.6	85.7			
KClO$_4$	0.383	1.6			1.1		0.2	
NaClO$_4$	0.656	8.4		0.6	5.5			2.3
Li$_3$PO$_4$	0.351	2.9			1.8			1.1
LiCl	0.327	2.2			0.6			0.8
LiNO$_3$	0.355	2.4			0.4			0.3
NaOH/SiO$_2$	0.365	2.8		0.2	1.3		trace	1.2
CaO	0.270	2.8		0.2	1.5	1.1		
MgO	0.238	2.3		trace	1.3	0.9		
CaO[c]		0						
MgO[c]		0						

a) Reaction time: 15 min.   b) Rection time: 30 min.   c) Calcined *in vacuo.*   d) See text.

In allyl alcohol formation, VIa generally exceeded VIb. This seems to be caused by the competition between primary and secondary proton abstraction. The preference for primary proton abstraction is due to the more enhanced acidity of primary hydrogen by the electronic effect and the preferred geometry,*i.e.*, less strain of cyclohexane ring containing the exo-double bond. The similar observations were demonstrated by Rickborn and Thummel,[5,6] in which the relative rates of proton abstraction were in order of primary>secondary> tertiary in the rearrangement of both cycloalkene and open-chain oxides catalyzed by a strong base, lithium diethylamide. Only in the case of HCl/SiO$_2$, VIb exceeded VIa against the above rule. This is probably due to the absence of appropriate basic sites on the catalyst.

Table 3 shows the catalytic activity and selectivity of solid metal perchlorates, lithium salts and solid base catalysts. Solid lithium perchlorate was surprisingly active for the formation of ketone, but other metal perchlorates and lithium salts were quite inactive. The high polarisability of lithium cation, the smallest cation of alkali metals, combined with perchlorate ion in which negative charge is dispersed seems to be necessary as the active sites for the rearrangement. Another reason for the high activity of LiClO$_4$ is considered to be the partial dissolution of the catalyst or its complex with the epoxide. Rickborn and Gerkin[33] reported that lithium perchlorate partially dissolved in benzene solution of epoxides gave rise to the rapid rearrangement. They obtained 80% of 2-methyl-cyclohexanone from 1-methylcyclohexene oxide over LiClO$_4$ in agreement with our findings. They also found that 1,2-dimethylcyclohexene oxide gave 91—98% of 1-acetyl-1-methylcyclopentane and 2—9% of 2,2-dimethylcyclohexanone,[33] which were formed with the same amount in the HClO$_4$-catalyzed pinacolone rearrangement.[34] In both reactions, the product formation can be best interpreted by assuming a planar carbonium ion intermediate. Thus, the cyclo-

hexanone products from 1-methyl- and 1,2-dimethyl-cyclohexene oxide are considered to be formed by a process which allows the development of a planar carbonium ion at the cleaved tertiary center.
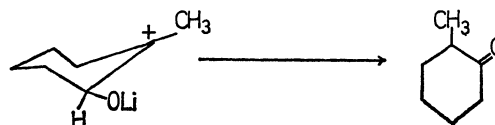
Sodium-silica gel, calcium and magnesium oxides calcined in air, which have basic characters,[17,35] were almost inactive for this reaction. The alkaline earth metal oxides calcined *in vacuo,* which were found recently to show strong basic character and high catalytic activity for the isomerizations of 1-butene to 2-butenes and α-pinene to β-pinene,[18,36,37] were not active at all at the mild reaction condition in the present work. However, a small amount of ketone was formed over these basic catalysts calcined in air. The formation of ketone may be due to the weak interaction between the alkaline earth metals as soft acids and the oxygen atom of the reactant as reported by Matsumoto *et al.*[38] Since MgO was active for the isomerization of propylene oxide at 260—270 °C in a gas phase,[14] the experiment at more severe condition is being planned in order to clarify the activity difference for different epoxides.

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