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Epoxide Rearrangement. IV.[1] Isomerization of Cyclohexene and 1-Methylcyclohexene Oxides over Solid Acids and Bases in Gas Phase

Kazushi Arata, Kiyoshi Kato, and Kozo Tanabe*
Hokkaido University of Education, 1-2 Hachiman-cho, Hakodate 040
**Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060*

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Synopsis. A large amount of diene compounds was found to form in the isomerizations of cyclohexene and 1-methylcyclohexene oxides catalyzed by solid acids and bases in gas phase. The catalysts which were quite inactive in liquid phase showed unexpectedly high activities in gas phase, indicating the different catalytic actions.

We have recently studied the isomerization of 1-methylcyclohexene oxide catalyzed by solid acids and bases in a heterogeneous solid-liquid system and observed the markedly different selectivities which depended on the type of catalysts.[1-3] In order to elucidate the electronic and steric effects of methyl group of the oxide on the reactivity and selectivity, the isomerization of cyclohexene oxide together with 1-methylcyclohexene oxide was studied in a solid-gas system in the present work, since the reaction rate of cyclohexene oxide was extremely low in a solid-liquid system.[3] The catalytic action of solid acids and bases in a solid-gas system was also compared with that in a solid-liquid system.

Experimental

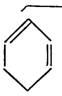
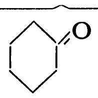
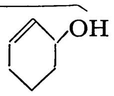
Catalysts and Materials. Cyclohexene and 1-methylcyclohexene oxides, supplied from Takasago Perfumery Co., were fractionally distilled to purify to more than 98%. $NiSO_4$ and $FeSO_4$ were prepared by calcining their heptahydrates (G. R.). Al_2O_3, KAT6 of Nishio Chemical Co., was calcined at 500 °C. TiO_2, $TiO_2 \cdot ZrO_2$, ZrO_2, and ZnO were prepared by thermal decompositions of H_4TiO_4, $H_4TiO_4 \cdot Zr(OH)_4$, $Zr(OH)_4$ and $Zn(OH)_2$, respectively, which were produced by the same procedure as that described previously.[1,3] The preparations of $LiClO_4$ and $NaOH/SiO_2$ were also followed by the previous experiment.[3] CaO and MgO were prepared by calcining their hydroxides at 550 °C. All the catalysts were heat-treated in air and stored in sealed ampoules until use.

Procedures. The isomerization of oxides was carried out at 150 °C in a conventional pulse reactor in N_2 carrier. The catalysts (40 mg, 100—200 mesh) were heat-treated again in the reactor at their preparation temperatures in air for 3 hr before reaction. The amount of reactant injected was 0.3—0.4 μl. The products were analyzed and identified by gc comparison with the authentic samples using a 3 m column of 20% polyethylene glycol 20 M on Celite 545 SK (150 °C; N_2, 27 cc/min; FID).

Results and Discussion

The catalytic activity and selectivity for the isomerization of cyclohexene oxide are summarized in Table 1. The main products were cyclohexanone, cyclohexenol and 1,3-cyclohexadiene. Cyclohexanol and cyclohexenone, which are formed by hydrogenation and dehydrogenation of cyclohexene oxide, respectively, were almost negligible or not produced at all, though those corresponding compounds were considerably produced in the rearrangement of 1-methylcyclohexene oxide in the heterogeneous liquid phase.[1-3]

Table 1. Catalytic activity and selectivity for isomerization of cyclohexene oxide

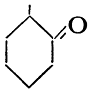
Catalyst[a]	Conversion %	Products (%)[b]		
				
$NiSO_4$ (250 °C)	58.9	42.0	7.2	7.2
$NiSO_4$ (400 °C)	25.8	11.5	3.3	7.5
$FeSO_4$ (200 °C)	24.5	8.5	2.7	8.6
$FeSO_4$ (400 °C)	49.1	25.6	6.3	13.0
Al_2O_3	79.1	56.4	9.1	9.2
TiO_2	36.8	21.8	2.2	8.2
TiO_2-ZrO_2[c]	59.5	43.7	2.2	9.0
ZrO_2	22.4	5.2	2.0	8.3
ZnO (400 °C)	18.7	5.5	1.5	7.0
$LiClO_4$ (150 °C)	16.0	4.3	1.5	6.4
$NaOH/SiO_2$	18.7	5.1	1.5	6.7
MgO (550 °C)	19.3	5.2	1.8	7.4

a) Calcined at 500 °C unless noted. b) About 3% of an unidentified compound was found right before the epoxide in glc in every reaction. c) Molar ratio = 1 : 1.

The relative activities of $NiSO_4$, Al_2O_3, TiO_2, TiO_2–ZrO_2 and ZrO_2 were similar to those for 1-methylcyclohexene oxide in a liquid phase;[1-3] namely, (1) the activities were higher when calcined at low temperature for $NiSO_4$ and at high temperature for $FeSO_4$, (2) the activity of Al_2O_3 was highest, which gave the outstanding activity for the allyl alcohol formation in the liquid phase reaction, and (3) the activity of TiO_2–ZrO_2 was higher than that of TiO_2 or ZrO_2 due to its higher acidity created by combining both oxides.

Comparatively high activities were shown by ZnO, $NaOH/SiO_2$ and MgO, which were quite inactive in our previous work,[3] where it was considered that basic catalysts such as $NaOH/SiO_2$,[4] CaO and MgO[5] did not cause the rearrangement of 1-methylcyclohexene oxide. ZnO and CaO showed unexpectedly high activities for 1-methylcyclohexene oxide (Table 2). These high activities in the present investigation are considered to be due to the different reaction condi-

Table 2. Catalytic activity and selectivity for isomerization of 1-methylcyclohexene oxide

Catalyst$^{a)}$	Conversion %	Products (%)$^{b)}$		
		Dienes		Allyl$^{c)}$ alcohols
$NiSO_4$ (250 °C)	72.4	35.2	35.2	0
Al_2O_3	74.2	44.8	27.3	0
TiO_2	62.9	32.1	12.6	16.3
TiO_2-$ZrO_2$$^{d)}$	71.3	43.3	15.3	7.0
ZrO_2	46.2	12.9	14.4	15.0
ZnO (400 °C)	45.0	12.0	16.5	14.3
CaO (550 °C)	43.6	11.0	14.9	15.5

a) Calcined at 500 °C unless noted. b) The amounts of 1-methylcyclohexanol and 2-methyl-2-cyclohexene-1-one produced in the liquid phase reaction were almost negligible. c) 2-Methyl-2-cyclohexene-1-ol and 2-methylenecyclohexanol. d) Molar ratio=1 : 1.

tions; 40 °C higher in reaction temperature, absence of solvent and gas phase.

The activity of $LiClO_4$, which was surprisingly active for the formation of ketone in the liquid phase reaction,$^{3)}$ was relatively low. The fact seems to support our previous conclusion that the high activity of $LiClO_4$ in a solid-liquid system is due to the partial dissolution of the catalyst or the complex formation with the epoxide.$^{3)}$

The most unexpected observation was the formation of a large amount of the diene compound, 1,3-cyclohexadiene, which was probably formed by the dehydration of cyclohexenol, though the amounts of the corresponding dienes were almost negligible in the liquid phase reaction.$^{1-3)}$ Since there is a report that cyclohexene oxide is pyrolyzed to form cyclohexanone and cyclohexenol with the negligible amount of 1,3-cyclohexadiene at 407—467 °C,$^{6)}$ the readsorption of cyclohexenol on the catalyst surface is supposed to cause the dehydration. This interpretation is also supported from another experimental fact that the conversion of cyclohexenol into 1,3-cyclohexadiene was 80% over $NiSO_4$ (400 °C) under the present reaction conditions.

The similar conversion to dienes was also observed for the isomerization of 1-methylcyclohexene oxide as shown in Table 2. The dienes were not identified by comparison with the authentic samples, but the identification is unquestionable from the quite similar selectivities to those of cyclohexene oxide and the additional experimental results: that is, (1) allyl alcohols (a mixture of 2-methylenecyclohexanol and 2-methyl-2-cyclohexene-1-ol in 1 : 1.5) converted into their dienes over $NiSO_4$ (250 °C) in almost 100% under th esame reaction conditions, (2) the oxide isomerized to form 18.8% of dienes, 11.9% of ketone and 25.5% of allyl alcohols over TiO_2 (500 °C, 23 mg) in faster carrier gas (twice as fast as the flow rate in general runs), indicating the decrease of dienes from allyl alcohols and (3) relative retention time in glc between the oxide and dienes was quite close to that in the case of cyclohexene oxide.

There have not been reports concerning the considerable diene formation by the catalyzed isomerization of epoxides, with the exception of the 1,3-cycloheptadiene formation from cycloheptene oxide catalyzed by lithium diethylamide.$^{7)}$ The conversion of propylene$^{8,9)}$ and ethylethylene oxides$^{10,11)}$ over solid acids or bases in gas phase were also not reported to yield their dienes.

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