Isomerization of Cyclooctene and Cyclododecene Oxides Catalyzed by Solid Acids and Bases[1)]

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(Received April 4, 1994)

Synopsis. The title reactions were carried out over seven catalysts. From cyclooctene oxide a large amount of 7-octenal was formed together with 3-cycloocten-1-ol over SiO_2–Al_2O_3 and SiO_2–TiO_2, 3-cycloocten-1-ol over solid H_3PO_4, and cyclooctanone over $FeSO_4$. Most catalysts except for $NiSO_4$, Al_2O_3, and TiO_2–ZrO_2 produced 1,3-cyclododecadiene, cyclododecanone, and 2-cyclododecen-1-ol uniformly from cyclododecene oxide. Allylic alcohols were preferentially given by Al_2O_3 and TiO_2–ZrO_2.

Products formed by rearrangement of epoxide compounds provide useful intermediates in organic syntheses, and some of them are valuable as raw materials in the chemical industry. Many studies on the catalytic rearrangement of the epoxides have been made.[2)] The reactions which have been used frequently are homogeneous with acid or base catalysts such as BF_3, $MgBr_2$, *t*-BuOK, or lithium dialkylamides. The heterogeneous reaction over solid catalysts was also investigated.

Arata and co-workers have investigated isomerizations of several epoxides catalyzed by solid acids and bases such as alumina and silica gel in a heterogeneous system.[2)] Most of the epoxides studied were cyclic alkene oxides with methyl group on the oxirane ring such as 1-methylcyclohexene oxide, *d*-limonene oxide, 2- and 3-carene oxides, and α-pinene oxide; for isomerization of the oxides tertiary carbonium ion intermediates were formed by adsorbtion of the oxygen on acid sites of the catalyst surface followed by cleavage of the oxygen bond.

As for other cyclic oxides, cyclohexene oxide (**1**) was studied in order to see how catalytic activity and selectivity differ in comparison with those for an oxide containing a methyl group on the oxirane ring; main products through secondary carbonium ion intermediates on acid sites were 1,3-cyclohexadiene (**2**), cyclohexanone (**3**), and 2-cyclohexen-1-ol (**4**) together with some minor products, cyclohexanol (**5**) and 2-cyclohexen-1-one (**6**) (Scheme 1).[3)]

As a series of studies on the rearrangement of epoxides over heterogeneous acid and base catalysts, cyclic alkene oxides have been limited to a six-membered ring. We have now carried out the reactions of cyclooctene and cyclododecene oxides in order to examine change in the catalytic action due to the effects of eight- and twelve-membered rings.

Studies on rearrangement of the above oxides have been made in the homogeneous system. Reaction of cyclooctene oxide with magnesium bromide-diethyl ether gave a mixture of cycloheptanecarbaldehyde, cyclooctanone, 1,4-epoxycyclooctane, hexahydro-*o*-tolualdehyde, and others.[4)] The oxide was also transformed mainly into *endo-cis*-bicyclo[3.3.0]octan-2-ol, a bicyclic alcohol, when refluxed in benzene with $LiNEt_2$ and in ether with $LiN(i\text{-}Pr)_2$, basic catalysis.[5,6)] The reaction of epoxides with diethylaluminum dialkylamide constitutes a synthetic method for the preparation of allylic alcohols; diethylaluminum 2,2,6,6-tetramethylpiperidide, prepared in situ from diethylaluminum chloride and lithium 2,2,6,6-tetramethylpiperidide, converted cyclododecene oxide into 2-cyclododecen-1-ol.[7,8)]

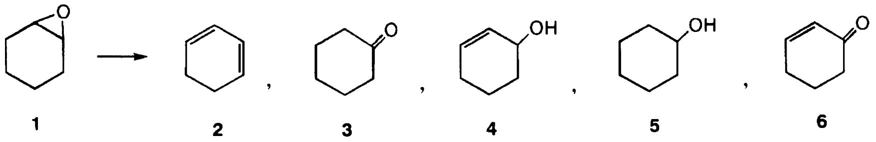
Experimental

Cyclooctene and cyclododecene oxides (Aldrich Chemical Co.) were more than 99% pure, and toluene (guaranteed reagent) used as solvent was purified by distillation over sodium metal.

Reaction Procedure. A mixture of 0.5 g of the epoxide, 2.5 cm^3 of toluene, and 0.2—0.4 g of catalyst ground to over 100 mesh was stirred in a reaction vessel with a magnetic stirrer. At appropriate time intervals, a small amount of the sample was taken out with a 1 cm^3 syringe, separated from the catalyst by centrifugation, and analyzed with a gas-liquid chromatograph using a 1 m column of PEG 20M. Yields based on the epoxide were calculated from GLC peak areas.

Catalysts. $FeSO_4$ (Kanto Chemical Co.) and $NiSO_4$ (Wako Pure Chemicals Ltd.) were prepared by calcining their hydrates at 500 and 350 °C, respectively. Al_2O_3 (KAT6, Nishio Chemical Co.) and SiO_2–Al_2O_3 (N361L, Nikki Chemical Co.) were subjected to heat-treatment at 500 °C. Solid phosphoric acid (N501, Nikki Chemical Co.) was calcined at 300 °C. Procedures for the preparation of SiO_2–TiO_2 (molar ratio=1 : 1) are described in the literature.[9)] TiO_2–ZrO_2 (molar ratio=1 : 1) was prepared by thermal decomposition at 500 °C of H_4TiO_4–$Zr(OH)_4$, coprecipitated by heating a mixed aqueous solution of titanium tetrachloride, zirconium (IV) dichloride oxide, and an excess amount of urea on a boiling water bath, followed by thorough washing of the precipitate with distilled water until no chloride ion was detected in the filtrate, and drying in air at 110 °C. All the catalysts were powdered over 100 mesh, calcined in Pyrex glass tubes in air for 3 h, and sealed in ampoules, while being hot, until use to avoid humidity.

Identification of Products. Catalytic activities of various solid acids and bases and the product distributions are given in Tables 1 and 2. The reaction products are given in the order of elution on a GLC PEG 20M column. Products were isolated from the isomerized mixture using a preparative GLC column (100×0.6 cm, packed with PEG 20M) and identified by their IR, NMR, and MS spectra:



Scheme 1.

Table 1. Catalytic Activity and Selectivity of Solid Acids and Bases for Isomerization of Cyclooctene Oxide at 108 °C

Catalyst	Reaction time/h	Conversion %	Selectivity/% II	III	IV	V	VI
SiO_2–Al_2O_3	0.5	100	39	9	16	22	
SiO_2–TiO_2	0.5	61	30	7	15	33	6
Solid H_3PO_4	10 min	43	6	7	12	49	5
$FeSO_4$	2	60	4	19	43	16	13
$NiSO_4$	6	8	6	17	31	11	22
Al_2O_3	6	40		5	10	10	62
TiO_2–ZrO_2	6	20		2	8	15	67

Table 2. Isomerization of Cyclododecene Oxide at 108 °C

Catalyst	Reaction time/h	Conversion %	Selectivity/% VIII	IX	X
SiO_2–Al_2O_3	10 min	100	24	32	37
SiO_2–TiO_2	1.5	97	57	12	26
Solid H_3PO_4	15 min	89	23	11	49
$FeSO_4$	7	38	29	22	48
$NiSO_4$	16	17	69		27
Al_2O_3	8	22	7		93
TiO_2–ZrO_2	4	74	18		82

MS being obtained by combined gas chromatography–mass spectrometry at 70 eV of ionization voltage.

II was identified as 7-octenal; IR (KBr) 3070, 2925, 2850, 1705 (–CHO), 1635 (C=C), 905 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ= 1.13—1.72 (m, 6H, 3×CH_2), 1.96—2.09 (m, 2H, CH_2C=C), 2.36 (dt, J=1.7, 7.6 Hz, 2H, C$\underline{H}_2$CHO), 4.89—5.08 (m, 2H, CH_2=C), 5.61—6.01 (m, 1H, C$\underline{H}$=CH_2), 9.76 (t, J=1.7 Hz, 1H, CHO); MS m/z 126 (M^+), 98 (M^+-CO), 82 (bp).

III was identified as cycloheptanecarbaldehyde; IR (KBr) 2940, 2860, 1700 (–CHO), 1450 cm^{-1}; ^{1}H NMR (CCl_4) δ= 1.40—1.82 (m, 12H, 6×CH_2), 2.26—2.43 (m, 1H, C$\underline{H}$CHO), 9.95 (br s, 1H, CHO); MS m/z 126 (M^+), 98, 97, 82 (bp).

IV was identified as cyclooctanone; IR (KBr) 2960, 2900, 1700 cm^{-1} ($\rangle$CO); ^{1}H NMR (CCl_4) δ=1.40—1.63 (m, 6H, 3×CH_2), 1.62—1.98 (m, 4H, 2×CH_2), 2.23—2.39 (m, 4H, 2×CH_2CO); MS m/z 126 (M^+), 98 (bp).

V was identified as 3-cycloocten-1-ol by IR, MS, NMR of ^{1}H, ^{13}C, and ^{1}H–^{1}H COSY;[10,11] IR (KBr) 3419 (–OH), 2927, 1654, 1466 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.29—1.99 (m, 6H, 3×CH_2), 2.04—2.33 (m, 2H, CH_2C=C), 2.34—2.39 (m, 2H, CH_2C=C), 3.77—3.86 (m, 1H, C$\underline{H}$–OH), 5.59—5.77 (m, 2H, CH=CH); ^{13}C NMR ($CDCl_3$) δ=21.31 (C_7), 25.81 (C_5), 28.40 (C_6), 34.09 (C_2), 35.17 (C_8), 72.20 (C_1), 125.97 (C_3), 132.26 (C_4); MS m/z 126 (M^+), 108 (M^+-H_2O), 97, 83 (bp). The H–H COSY spectrum revealed the connectivity among various signals due to protons by reading the cross peaks, from which structure **V** was assembled. In order to confirm position of the double bond, 3rd or 4th position, 3-cycloocten-1-ol and 4-cycloocten-1-ol were differently synthesized; the monoepoxidation of 1,3-cyclooctadiene and 1,5-cyclooctadiene was performed with m-chloroperbenzoic acid followed by reduction with $LiAlH_4$ to give 3- and 4-cycloocten-1-ol, respectively. The NMR spectra of ^{1}H, ^{13}C, and H–H COSY for the former alcohol agreed with those of **V**.

VI was identified as 2-cycloocten-1-ol; IR (KBr) 3340 (–OH), 3030, 1645 (C=C), 1445, 1050, 990 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.34—1.68 (m, 8H, 4×CH_2), 1.90 (m, 1H, OH), 2.04—2.21 (m, 2H, CH_2–C=C), 4.62—4.68 (m, 1H, C$\underline{H}$–OH), 5.50—5.64 (m, 2H, CH=CH); MS m/z 126 (M^+), 108 (M^+-H_2O), 97, 83 (bp).

VIII was identified as 1,3-cyclododecadiene; IR (KBr) 3000 (CH=C), 2920, 1460, 1440, 980, 950 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.24—1.61 (m, 12H, 6×CH_2), 2.02—2.14 (m, 4H, 2×CH_2C=C), 5.21—5.75 (m, 2H, CH=CH), 6.00—6.25 (m, 2H, CH=CH); MS m/z 164 (M^+), 150, 136, 67 (bp), 41.

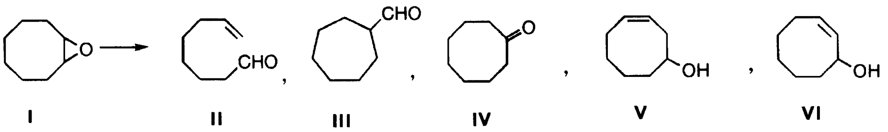
IX was identified as cyclododecanone by comparing its gas-chromatographic retention time and mass spectrum with those of the commercially authentic sample (Tokyo Kasei Kogyo Co.).

X was identified as 2-cyclododecen-1-ol; IR (KBr) 3350 (–OH), 1450, 985 cm^{-1}; ^{1}H NMR (CCl_4) δ=1.20—1.72 (m, 16H, 8×CH_2), 1.99—2.18 (m, 2H, CH_2C=C), 2.30—2.42 (m, 1H, OH), 3.58—3.72 (m, 1H, C$\underline{H}$–OH), 5.24—5.23 (m, 2H, CH=CH); MS m/z 182 (M^+), 123, 109, 97, 82, 55, 41 (bp).

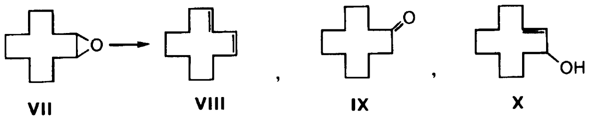
Results and Discussion

The reaction of cyclooctene oxide (**I**) catalyzed by solid acids and bases gave 7-octenal (**II**), cycloheptanecarbaldehyde (**III**), cyclooctanone (**IV**), 3-cycloocten-1-ol (**V**), and 2-cycloocten-1-ol (**VI**) (Scheme 2). Cyclododecene oxide (**VII**) was converted into 1,3-cyclododecadiene (**VIII**), cyclododecanone (**IX**), and 2-cyclododecen-1-ol (**X**) (Scheme 3). Some catalysts (SiO_2–Al_2O_3 and Solid H_3PO_4) formed other products, but no detailed analysis was performed because of minor products.

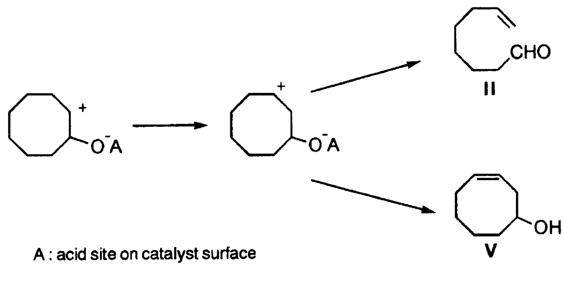
The compounds formed from cyclododecene oxide were similar to those from cyclohexene oxide (**1**), though no substance corresponding to **5** and **6**, produced by a hydrogen transfer from **6** to **5**, was found. On the other hand, the products from cyclooctene oxide were greatly different; the formation of **II**, **III**, and **V**, whose corresponding materials were not found for the oxides of **1** and **VII**, could be characterized by the property of eight-membered ring. In particular, this is the first case where a open-chained, olefinic aldehyde, **II**, is formed from cyclic oxides, together with an alcohol with a double bond at 3-position, **V**. No diene was also detected for **I**.



Scheme 2.



Scheme 3.



Scheme 4.

The catalytic activity and selectivity of several solid acid and base catalysts are shown in Tables 1 and 2. Catalysts were chosen from those studied in isomerizations of cyclohexene oxide and other oxides on the basis of their activities and selectivities;[2,3] the catalysts in the tables are shown in order of decrease of the surface acidity together with increase of the basicity. The time of reaction was so selected that appropriate conversion levels could be achieved. Although the reaction of cyclohexene oxide required a much longer reaction time for the formation of secondary carbonium ions by cleavage of carbon–oxygen bond than the case of formation of tertiary carbonium ions on carbon atoms bearing methyl groups, the present reactions were carried out in shorter time than that of **1**, the reactivities being intermediate between the above ones.

A large amount of **II** was formed together with **V** over SiO_2–Al_2O_3 and SiO_2–TiO_2, **V** over solid H_3PO_4, **IV** over $FeSO_4$, and **VIII** over SiO_2–TiO_2. $NiSO_4$ formed all products uniformly from **I**. For **VII** most catalysts except $NiSO_4$, Al_2O_3, and TiO_2–ZrO_2 formed three species of the products almost equally.

Allylic alcohols (**VI** and **X**) were preferentially given by Al_2O_3 and TiO_2–ZrO_2, in particular for **X** 93 and 82%, respectively, in selectivity. TiO_2–ZrO_2 has both acidic and basic sites to act as an acid-base bifunctional catalyst.[3,12] Epoxide opening to allylic alcohols can be explained in terms of the bifunctional character of TiO_2–ZrO_2; an oxygen atom of the oxide adsorbs on an acidic site of the catalyst, while a hydrogen atom of methylene group on a basic site of the catalyst surface, and both the opening of the epoxide ring and the hydrogen abstraction take place simultaneously to form the allyl alcohol. From the above point of view Al_2O_3 has also the bifunctional character.

As for the formation of carbonyl compounds (ketone and aldehyde), it can be explained by the formation of a carbonium ion intermediate via the breaking of oxygen bond adsorbed on an acid site followed by rearrangement to ketones, **IV** and **IX**, or to a ring-contracted aldehyde, **III**.

The preferential formation of **II** and **V** was observed over SiO_2–Al_2O_3 and SiO_2–TiO_2. These catalysts are known to have strong acid sites on their surface.[13,14] The yields of all products from cyclooctene oxide increased almost parallel to each other during the course of reaction. Thus, the reaction seems to occur in the following parallel and consecutive steps via the migration of a carbonium ion intermediate to form **II** and **V** (Scheme 4).

A large amount of diene **VIII** was formed in the case of **VII**. The diene formation was interpreted by the dehydration of allylic alcohol **4** for **1**.[3] Time-variation of the products for **VII** showed the yields of all products to be parallel each other. Thus, the dehydration mechanism through readsorption of the hydroxyl group of **X** is not known.

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