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Isomerization of Carvomenthene Oxide over Solid Acids and Bases[1)]

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The reaction of carvomethene oxide (a mixture of *cis*- and *trans*-forms) over solid acids and bases gives *trans*- and *cis*-1-methyl-3-isopropyl-1-cyclopentanecarbaldehyde (III), carvomenthone (IV), 1(7)-*p*-menthen-2-ol of *trans*-(V) and *cis*-form and carvotanacetol of *trans*-(VI) and *cis*-form. A large amount of III was formed together with IV over SiO_2–Al_2O_3, SiO_2–TiO_2 and zeolite H-F9. $LiClO_4$, H_2SO_4/SiO_2, $FeSO_4$, and solid H_3PO_4 gave preferentially IV, while TiO_2–ZrO_2 formed mainly V and VI. With respect to aluminas, carbonyl compounds (III and IV) were predominantly formed over Al_2O_3D, while allylic alcohols (V and VI) were preferentially given by Al_2O_3 A and B.

Several workers have studied the isomerization reaction of terpene epoxides such as α-pinene, limonene, carvomenthene, and caryophyllene oxides,[2)] some products being valuable as raw material for perfume, flavor cosmetic and pharmaceutical materials. Settine and his co-workers found that, in the case of carvomenthene oxide, the oxide in the presence of zinc bromide rearranges with ring contraction to 1-methyl-3-isopropyl-1-cyclopentanecarbaldehyde and methyl (3-isopropylcyclopentyl) ketone, undergoing isomerization to carvomenthone.[3)] Eschinasi reported that the rearrangement of the oxide in the presence of a catalytic amount of aluminum isopropoxide is utilizable for selective preparation of allylic alcohols (carvotanacetol and 1(7)-*p*-menthen-2-ol) in high yields.[4)]

Previous studies disclosed that the isomerization of *d*-limonene oxide catalyzed by solid acids and bases shows strikingly different selectivity depending on the type of catalyst.[5)] Since the studies on the isomerization of carvomenthene oxide were performed in a homogeneous system, the oxide in the present experiment has been isomerized over solid acid and base catalysts under heterogeneous conditions.

Experimental

Carvomenthene oxide (Takasago Perfumery Co., a 1: 1 mixture of *cis*- and *trans*-forms, purity 97%) and toluene of guaranteed grade were used. The latter was purified by distillation over sodium metal.

Standard Reaction Procedure. The reaction was carried out in the presence of toluene as a solvent at 80 °C for 75 min. A mixture of 0.5 ml of the epoxide, 2.5 ml of toluene, and about 0.3 g of catalyst ground to below 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 ml syringe, separated from the catalyst by centrifugation, and analyzed with a gas-liquid chromatograph with a TCD detector using a 3 m column of 20% polyethylene glycol 20 M on Celite 545 SK (150 °C; He, 1.0 kg/cm^2). For the separation of two peaks of III, a 45-m capillary column of Ucon LB-550-X (112 °C; N_2, 2.0 kg/cm^2) was used. The yields of products were based on the unreacted epoxide and calculated by measurement of GLC peak areas (uncorrected.)

Catalysts. SiO_2–Al_2O_3 [N361(L)(Al_2O_3; 15 wt%) of Nikki Chemical Co.] was calcined at 500 °C. SiO_2–TiO_2 (molar ratio= 1: 1) was prepared by coprecipitation of a mixed solution of ethyl orthosilicate and titanium tetrachloride with aqueous ammonia. The precipitate was aged over a water bath for 1 h, washed with distilled water until no chloride ion was detected, dried at 100 °C for 20 h and calcined at 500 °C. Zeolite H-F9 was prepared from zeolite F-9 (Tekkosha Co.,) by a conventional ion-exchange method using NH_4Cl and by calcination at 500 °C. $LiClO_4 \cdot 3H_2O$ (guaranteed grade, Nakarai Chemical Co.) was dried at 120 °C for 3 days. H_2SO_4/SiO_2 was prepared as follows. 10 g of granular silica gel was immersed in 12 ml of 0.5 M H_2SO_4, evaporated, dried and then calcined at 150 °C. $FeSO_4$ and $NiSO_4$ were prepared by calcining their heptahydrates (guaranteed grade) at 600 and 350 °C, respectively. Solid phosphoric acid, N501 (Nikki Chemical Co.) was calcined at 400 °C. TiO_2–ZrO_2 (molar ratio= 1: 1) was prepared by thermal decomposition at 500 °C of H_4TiO_4–$Zr(OH)_4$, precipitated by heating a mixed aqueous solution of titanium tetrachloride, zirconium oxychloride and an excess amount of urea on a boiling water bath, followed by thorough washing of the precipitate with distilled water until no chloride ions were detected in the filtrate, and drying in air at 110 °C. ThO_2 was prepared by thermal decomposition at 500 °C of $Th(OH)_4$, precipitated by hydrolysis of $Th(NO_3)_4$ with 28% ammonia. Al_2O_3 A (KAT 6, Nishio Chemical Co.) was subjected to heat-treatment at 500 °C. Al_2O_3 B, C, and D, *viz.*, Albes FF, Albes FE, and Albes C (Showa Tansan Kaisha, Ltd.) were calcined at 500 °C before use. All the catalysts were heat-treated in the air for 3 h and stored in sealed ampoules.

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 (Table 1) on a GLC PEG 20 M column at 150 °C. Product IV, a mixture of V and VI, and VII, was isolated from the isomerized mixture catalyzed by solid H_3PO_4 by column chromatography using silica gel and eluting with petroleum ether–diethyl ether (1: 1). IV was identified as carvomenthone by its IR, NMR, and MS:** IR (neat): 1710 cm^{-1} ketone, 1380, 1360 cm^{-1}, isopropyl;[6)] NMR (δ): 1.8—1.1 (m, 6H, CH_2), 0.8—1.0 ppm (m, 9H, CH_3–); MS: important ions at *m/e* 154 (M^+), 111 (100%), 55 (70%), 41 (43%), 83 (27%) (Lit,[6)]: 154 (M^+), 111 (100%) 55 (51%), 41 (33%), 83 (23%)). VII was identified as carvotanacetol by its IR, NMR, and MS:** IR (neat): 1385, 1370 cm^{-1} isopropyl, 1060, 1035 cm^{-1} secondary alcohol, 915 cm^{-1} vinyl; NMR (δ): 5.5 (t, 1H, C=CH), 4.2 (s, 1H, OH), 1.8 (s, 3H, C=CCH_3), 0.9 ppm (d, 6H, C$(CH_3)_2$); MS: important ions at *m/e* 154 (M^+), 84 (100%), 82 (83%), 43 (67%), 93 (65%), 69 (63%), (lit,[7)]:

** Obtained by combined gas chromatography-mass spectrometry, Hitachi RM50GC, using a 2-m column of PEG 20-M at 70 eV of ionization voltage.

Table 1. ISOMERIZATION OF CARVOMENTHENE OXIDE OVER VARIOUS SOLID ACID AND BASE CATALYSTS AT 80 °C FOR 75 min

Catalyst	Catalyst amount g	Total conversion %	Products (%)					
			II	III (a, b)	IV	V	VI	VII+VIII
SiO_2–Al_2O_3[a]	0.46	100	3	50 (41, 9)	40			
SiO_2–Al_2O_3[b]	0.46	100	4	60	32			
SiO_2–TiO_2	0.39	100	8	70 (36, 34)	22			
SiO_2–TiO_2[c]	0.39	100	7	68	22			
Zeolite H-F9[d]	0.29	100	1	50 (29, 21)	38	4		1
$LiClO_4$	0.38	97	3	12 (8, 4)	77			1
H_2SO_4/SiO_2	0.25	54	3	6	37	1	2	2
H_2SO_4/SiO_2[b]	0.25	19	1	3	10	1	1	1
$FeSO_4$	0.25	98	1	19 (15, 4)	61	4	5	5
$FeSO_4$[b]	0.25	84	1	20	45	4	6	4
$NiSO_4$	0.32	44		9	13	12	5	4
$NiSO_4$[b]	0.32	28	0.5	5	9	5	3	2
Solid H_3PO_4[e]	1.09	100		24 (15, 9)	41	10	11	11
TiO_2–ZrO_2	0.39	59	1	6	4	16	22	7
TiO_2–ZrO_2[b]	0.39	28		4	2	6	12	2
ThO_2	0.29	3						

a) Temperature, 70 °C; time, 1 h. b) Time, 10 min. c) Time, 25 min. d) Mixture of 1 ml epoxide and 5 ml toluene reacted at 100 °C for 1 h. e) Mixture of 5.5 ml epoxide and 30 ml toluene reacted at 100 °C for 1 h.

Table 2. ISOMERIZATION OF CARVOMENTHENE OXIDE OVER ALUMINAS AT 80 °C FOR 75 min

Catalyst	Catalyst amount g	Total conversion %	Products (%)					
			II	III (a, b)	IV	V	VI	VII+VIII
Al_2O_3 A[a]	0.22	31		4	2	12	4	6
Al_2O_3 B	0.22	66		15 (10, 5)	7	21	9	10
Al_2O_3 C	0.32	65		24 (17, 7)	16	9	10	
Al_2O_3 C[b]	0.32	43		15	12	5	7	
Al_2O_3 D	0.17	100	2	33 (25, 8)	45	4	6	6
Al_2O_3 D[c]	0.17	100	2	36	43	3	8	7

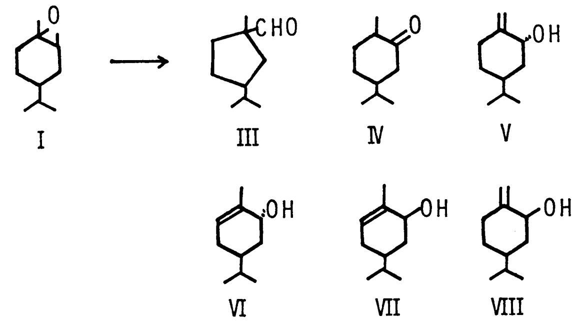
a) Temperature, 70 °C. b) Time, 25 min. c) Time, 10 min.

154 (M^+), 82 (100%), 84 (88%), 43 (75%), 69 (72%)). A mixture of V and VI was revealed to consist of 1(7)-*p*-menthen-2-ol and carvotanacetol by IR, NMR, and MS: IR (neat): 1380, 1370 cm^{-1} isopropyl, 1070, 1050, 1030 cm^{-1} secondary alcohol, 900 cm^{-1} methylene;[7] NMR (δ): 5.5 (C=CH), 4.8 ($C=CH_2$), 4.4 and 4.1 (OH), 1.8 ($C=CCH_3$), 0.85 ppm ($C(CH_3)_2$); MS of V: 154 (M^+), 82 (100%), 111 (91%), 93 (83%), 55 (80%), 41 (80%), 43 (70%); MS of VI: 154 (M^+), 84 (100%), 82 (78%), 43 (73%), 93 (71%) [Lit,[7]: *trans*-1(7)-*p*-menthen-2-ol: 154 (M^+), 111 (100%), 93 (95%), 55 (84%), 82 (83%), 43 (80%)]. V, VI, and VII were recognized to be *trans*-1(7)-*p*-menthen-2-ol, *trans*- and *cis*-carvotanacetol, respectively, from the following experimental results: (1) the mass spectra of VI and VII are identical, indicating the *cis-trans* relationship, (2) the GLC column gives the elution order of *trans-exo*-carveol, *trans-endo*-carveol, *cis-endo*-carveol and *cis-exo*-carveol for the isomerized products of *d*-limonene oxide.[5] The same order of elution was also obtained on a Carbowax 20 M column for the allylic alcohols selectively prepared from *d*-limonene and carvomenthene oxides by aluminum isopropoxide. Nearly the same isomeric ratio was observed in both reactions.[4] The catalytic selectivity of the present catalysts (Tables 1 and 2) is also analogous to that expected from the results in the case of *d*-limonene oxide.[5]

For the identification of III, a mixture of *cis*- and *trans*-carvomenthene oxide (50 g) was reacted with 5 g of Davison silica-alumina (W. R. Grace Company, Grade 160) at 70—150 °C with vigorous stirring, a sufficient amount of III for analysis being obtained. The two compounds (IIIa and IIIb), bp 76 °C/10 mmHg could not be separated on a 61 cm Nester-Faust spinning band column. However, the mixture showed NMR and IR spectra in line with the structure of *cis*- and *trans*-1-methyl-3-isopropyl-1-cyclopentanecarbaldehyde. The mass spectra of the two compounds were identical. IR (neat): 1715 cm^{-1} aldehyde, 1377, 1357, 934 cm^{-1} isopropyl; NMR (δ): 9.36 (s, 1H, CHO), 2.3—1.2 (m, 6H, $>CH_2$), 1.13 (s, 3H, $-CH_3$), 0.89 ppm (d, 6H, $C(CH_3)_2$; MS: seven most intense peaks at *m/e*, 154 (M^+), 69, 55, 41, 83, 43, 125, 57 for IIIa and IIIb.

Results and Discussion

The reaction products of carvomenthene oxide (*cis* and *trans* in a 1: 1 ratio) (I) catalyzed by solid acids and bases were 1-methyl-3-isopropyl-1-cyclopentanecarbaldehyde (III), carvomenthone (IV), *trans*-1(7)-*p*-menthen-2-ol (V), *trans*-carvotanacetol (VI), *cis*-carvotanacetol (VII) and unidentified compound (II).



The products are given in the order of elution on a GLC column. II is the first eluted compound of the products, *i.e.*, immediately after toluene as a solvent. It might be a diene formed by the dehydration of the allylic alcohols, since cymene formation was observed in the rearrangement of *d*-limonene oxide.[5] The mass spectrum of II was not identical with that of cymene, 1,3-*p*-menthadiene or 1,4-*p*-menthadiene. Thus II is considered to be a compound with double bonds in other positions.

A minor compound observed immediately after VII in GLC is supposed to be *cis*-1(7)-*p*-menthen-2-ol (VIII) from the elution order of four allylic alcohols produced from carvomenthene and *d*-limonene oxide (see Experimental). No detailed analysis was performed, it being a minor product. Since VII and VIII were not separated satisfactorily, summation of their percentage is given in Tables 1 and 2.

III consists of two compounds, *cis*- and *trans*-form. The aldehyde was identified by Settine and McDaniel from the reaction of zinc bromide with carvomenthene oxide.[8] However, they made no mention of using a mixture of *cis*- and *trans*-oxides or the kind of aldehyde obtained (*cis*-, *trans*- or the mixture). In our case, two aldehydes were neither separated nor identified spectroscopically, but IIIa, eluted earlier, and IIIb are considered to be *trans*- and *cis*-forms, respectively, from the view point that *trans*-forms of allylic alcohols and ketones in the rearrangement of *d*-limonen[5] and carvomenthene[4] oxides were eluted earlier in high yields on a GLC column. The formation of IIIa is shown to predominate over the catalysts used in this investigation. From the product distribution, *trans*-oxide seems to be more reactive than *cis*-one (Tables 1 and 2). Similar observations were reported in the case of *d*-limonene oxide.[5b] The higher reactivity of *trans*-oxides was also observed by Eschinasi for the rearrangement of limonene and menthene oxides catalyzed by aluminum isopropoxide.[4] A large amount of ring-contracted aldehydes (III) was formed together with ketone (IV) over SiO_2–Al_2O_3, SiO_2–TiO_2, and zeolite H-F9, the selectivity for the carbonyl compounds (III+IV) being 90%. SiO_2–Al_2O_3 and SiO_2–TiO_2 are known to have exceedingly strong acid sites on their surfaces, *viz.*, 0.34 mmol/g at $H_0=-8.2$ for SiO_2–Al_2O_3[9] and the analogous acidic properties for SiO_2–TiO_2.[10] Thus, the remarkable activity for isomerization as well as high selectivity for the carbonyl formation of these catalysts can be explained by the formation of a tertiary carbonium ion intermediate *via* the breaking of α-bond of oxygen adsorbed on the strong acid sites.

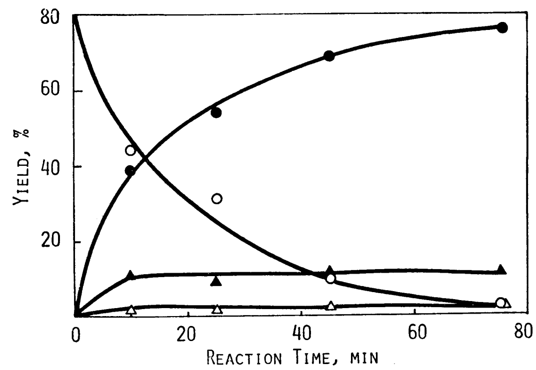
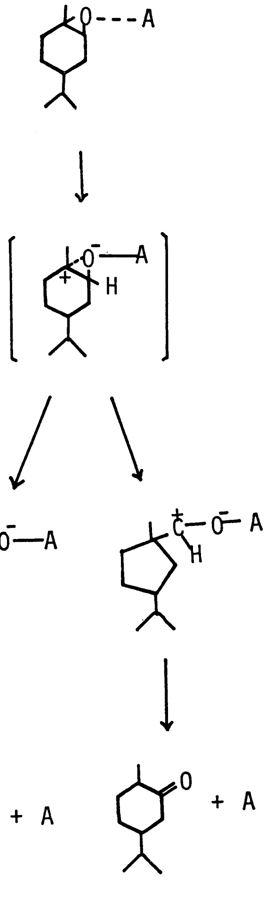


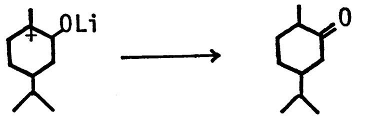
Fig. 1. Isomerization of carvomenthene oxide over $LiClO_4$ at 80 °C.
I (○), II (△), III (▲), IV (●).

The reaction mechanism for the preferential formation of carbonyl compounds is illustrated as follows.



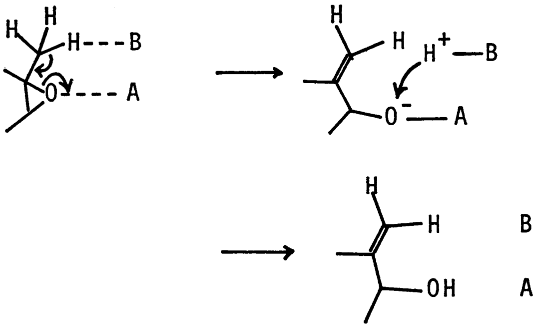
A: acid site on catalyst surface, protonic (Brönsted) or Lewis acid.

Lithium perchlorate, H_2SO_4/SiO_2 and $FeSO_4$ gave preferentially ketone (IV). The high activity of $LiClO_4$ for the ketone formation is similar to the observation of Rickborn and Gerkin that 80% of 2-methylcyclohexanone is formed from 1-methylcyclohexene oxide over $LiClO_4$.[11] The relation of the product distribution *vs.* reaction time over $LiClO_4$ is shown in Fig. 1. The yield of ketone increases remarkably following almost first-order reaction kinetics with respect to oxide concentration. Since the partial dissolution of the catalyst was observed, Li^+ is considered to be catalytically significant. The ketone formation over $LiClO_4$ is interpreted by a process *via* tertiary carbonium ion produced with Li^+, as was shown by Rickborn and Gerkin.



Sulfuric acid mounted on silica gel gave only a small amount of II which was formed by the dehydration of carvomenthene oxide, though it gave a large amount of *p*-cymene formed by dehydration in the case of *d*-limonene oxide. The difference might be due to high stability of *p*-cymene. The preferential formation of ketone (IV) was observed over H_2SO_4/SiO_2, $FeSO_4$, $NiSO_4$, and solid phosphoric acid. The tertiary carbonium ion formed by the breaking of α-bond of oxygen adsorbed on strong acid sites of SiO_2–Al_2O_3 and SiO_2–TiO_2 should be strong enough to be attached to the 3-position of cyclohexane ring to form a five-membered ring, while the carbonium ion formed by relatively weak acid sites[12] on H_2SO_4/SiO_2, $FeSO_4$, $NiSO_4$ or solid phosphoric acid does not seem to be so. A hydrogen at the 2-position of ring seems to migrate as a hydride ion to the cleaved tertiary center, 1-position, during the course of formation of a weak carbonium ion, probably a partially ionized cation.

Titania-zirconia shows a remarkable activity for the allylic alcohol formation. TiO_2–ZrO_2 is known to have both acidic acid basic sites, acting as an acid-base bifunctional catalyst.[13] Epoxide opening to allylic alcohols can be illustrated in terms of the bifunctional character of TiO_2–ZrO_2 as follows.



B: basic site.

In the formation of allylic alcohols over TiO_2–ZrO_2, VI exceeded V. According to electronic considerations, the preferential formation of V is expected due to the more enhanced acidity of primary hydrogen. Such observations were reported by Eschinasi; isomerization of menthene oxide catalyzed by aluminum isopropoxide gives 70% of V and 30% of VI.[4] From the above acid-base bifunctional mechanism, the acidic and basic properties of TiO_2–ZrO_2 seem to be quite specific.

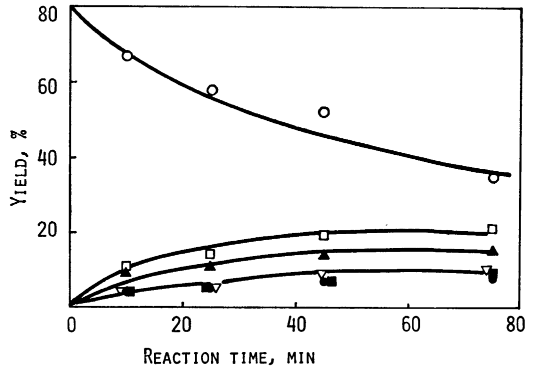


Fig. 2. Isomerization of carvomenthene oxide over Al_2O_3 B at 80 °C.
I (○), III (▲), IV (●), V (□), VI (■), VII+VIII (▽).

Thorium oxide, which is known to produce selectively 1-alkene in the dehydration of secondary alcohol,[14,15] is almost inactive in the reaction of carvomenthene oxide. This catalyst would become active at higher reaction temperature.

It is of interest that the selectivity of aluminas differs a great deal with the type of alumina (Table 2). Carbonyl compounds (III) and (IV) were predominantly formed over Al_2O_3 D, the yield being about 80%. Allylic alcohols (V) and (VI) were preferentially given by Al_2O_3 A and B. It is remarkable that Al_2O_3 D is extremely active for the isomerization. Thus, Al_2O_3 A and B are expected to have both acidic and basic sites, while Al_2O_3 D is expected to have high acidity on its surface. In this respect Al_2O_3 C falls into the intermediate category of acid-base property. An example of time-variation of the products is shown in Fig. 2, where the catalyst is Al_2O_3 B. The yields of all products increase almost parallel to each other during the course of reaction. A similar time-variation of product was observed over other catalysts, suggesting that they are not precursors of each other and that there is little possibility of interconversion after the formation.

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