

Isomerization of Caryophyllene Oxide Catalyzed by Solid Acids and Bases

Kazushi ARATA,* Kiyoharu HAYANO,[†] and Haruhisa SHIRAHAMA^{††}

Department of Science, Hokkaido University of Education, Hachiman-cho, Hakodate 040

[†] Chemistry Laboratory, Hokkaido University of Education, Ainosato, Sapporo 002^{††} Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received July 9, 1992)

The reaction of caryophyllene oxide over eleven catalysts of solid acids and bases gave 4,5-dihydrocaryophyllen-5-one (**III**), (1*R*, 5*S*, 8*R*, 9*R*)-4,4,8-trimethyltricyclo[6.3.1.0^{1,5}]dodeca-2-en-9-ol (**IV**), (2*S*, 5*R*, 9*R*)-caryophylla-1(12),8(15)-dien-9-ol (**V**), (2*S*, 5*R*, 9*R*)-caryophylla-1(12),7-dien-9-ol (**VI**), and (2*S*, 5*R*, 9*S*)-caryophylla-1(12)-7-dien-9-ol (**VII**). A large amount of **III** was formed together with **IV** over FeSO₄ and Zr(SO₄)₂. Allylic alcohols (**V**, **VI**, and **VII**) were preferentially given by Al₂O₃-**II** and TiO₂-ZrO₂ in >74% selectivity: 96% on TiO₂-ZrO₂. Other catalysts formed three to five species of the products uniformly.

Alumina and silica gel are industrially important as catalysts, especially in the petrochemical processes. Much of the use to which these materials are put in the laboratory is in the chromatographic separation of compounds, and it was during such an application that an interesting reaction was observed. While working on the isolation and purification of humulene epoxide, which is naturally found in an essential oil, it was observed that considerable loss of the epoxide occurred during contact with active Al₂O₃ by conversion of the oxide to alcohols;^{1,2} the alcohols were identified on the basis of spectral data.^{3,4} Similarly, caryophyllene oxide underwent a characteristic isomerization to alcohols during column chromatography on alumina.

The catalytic action of active Al₂O₃ on caryophyllene oxide was investigated somewhat in detail.⁵ It was found that exposure of the epoxide to active Al₂O₃ in petroleum ether resulted in its transformation to a mixture of three alcohols, which were assigned to the following structures (Scheme 1).

Arata and Tanabe have systematically investigated isomerizations of several terpene epoxides catalyzed by solid acids and bases such as alumina and silica gel in a heterogeneous system. They chose the reactions of *d*-limonene oxide,^{6–8} 2- and 3-carene oxides,^{9,10} and α -pinene oxide.¹¹ The isomerization of carvomenthene oxide (**1**) was also studied by referring to observations on the reaction of *d*-limonene oxide.¹² The products were 1-methyl-3-isopropylcyclopentane-1-carbaldehyde (**2**), carvomenthone (**3**), 1(7)-*p*-menthen-2-ol (**4**), and carvotanacetol (**5**); in case of *d*-limonene oxide the isomerization occurred to form a compound containing an exo-double bond in a 5-membered ring and one with an endo-double bond in a 6-membered ring by a shift of the double bond of isopropenyl group (Scheme 2).⁶

A large amount of **2** was formed together with **3** over SiO₂-Al₂O₃, SiO₂-TiO₂, and zeolite, the selectivity for the both compounds being 90%, while TiO₂-ZrO₂ and Al₂O₃ formed mainly allylic alcohols, **4** and **5**, the selectivity for both being over 70%.¹² The preferential formation of ketone **3** was also observed over FeSO₄, NiSO₄, and solid phosphoric acid.

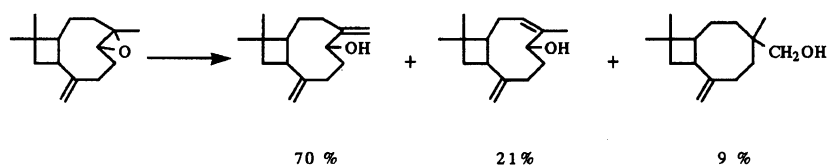
As part of a series on dealing with the rearrangement of epoxides over heterogeneous acid and base catalysts, studies on terpene oxides have been limited to compounds with the carbon number of 10. Since only alumina among solid acids and bases has been investigated for the isomerization of caryophyllene epoxide, we have now carried out the reaction of caryophyllene oxide with the carbon number of 15 over several solid acids and bases in order to examine the change in catalytic action due to the effects of a large molecule and a four-membered ring as a substituent group.

Experimental

Preparation of Caryophyllene Oxide. To a solution of 4.35 g (21.3 mmol) of 97% pure caryophyllene, supplied by Takasago Perfumery Co., in 50 ml of CH₂Cl₂ chilled in an ice bath was added *m*-chloroperbenzoic acid (4.9 g, 75%). The reactants were kept at ca. 5°C for 5 h until no peracid remained. The reaction mixture was washed twice with an aqueous NaOH solution (1 mol m⁻³), twice with water, and dried over MgSO₄. Removal of solvent left 3.8 g (81%) of a colorless viscous oil. Recrystallization of the crude product from 5 cm³ of methanol yielded 2.1 g of large colorless crystals with a ratio of 4 : 1 of **I** : **II** referring to the literature.¹³

Standard Reaction Procedure. A mixture of 0.5 g of the epoxide, 2.5 cm³ of toluene (purified by distillation over sodium metal) as a solvent, 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 cm³ syringe, separated from the catalyst by centrifugation, and analyzed with a gas-liquid chromatograph using a 1 m column of Reoplex 400 (140°C). Yields based on the epoxide were calculated from GLC peak areas.

Catalysts. FeSO₄ (Kanto Chemical Co.), NiSO₄ (Wako Pure Chemicals Ltd.), and Ti(SO₄)₂ (Nakarai Chemicals Ltd.) were prepared by calcining their hydrates at 500, 350, and 625°C respectively. Al₂O₃-**I** (KAT6, Nishio Chemical Co.), Al₂O₃-**II** (Woelm B-Super 1, West Germany), and SiO₂-Al₂O₃ (N361L, Nikki Chemical Co.) were subjected to heat-treatment at 500°C. SiO₂-TiO₂ (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

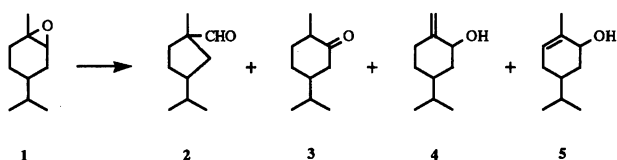


Scheme 1.

Table 1. Catalytic Activity and Selectivity of Solid Acids and Bases for Isomerization of Caryophyllene Oxide

	Catalyst	Reaction temp/°C	Reaction time/h	Conversion %	Selectivity/%					
					III	IV	V	VI	VII	Σ
1	FeSO ₄	100	3	64	46	23	8	9	9	95
2	NiSO ₄	100	3	57	23	8	32	25	9	97
3	Ti(SO ₄) ₂	RT	3	68	27	26	25	18	4	100
4	Zr(SO ₄) ₂	RT	3	74	46	15	22	12		95
5	Al ₂ O ₃ -I	90	3	67	20	10	27	21	6	84
6	Al ₂ O ₃ -II	90	3	36	19	7	43	22	9	100
7	SiO ₂ -Al ₂ O ₃	RT	1	26	21	22	26	27		96
8	SiO ₂ -TiO ₂	RT	1	30	17	12	39	27	2	97
9	TiO ₂ -ZrO ₂	70	2	45	3		41	35	20	99
10	SO ₄ /ZrO ₂	0	3	90	30	10	17	7		64
11	SO ₄ /TiO ₂	0	2	52	23	27	26	17	2	95

RT: Room temperature



Scheme 2.

h, washed with distilled water until no chloride ion was detected, dried at 100°C for 20 h and calcined at 500°C. TiO₂-ZrO₂ (molar ratio=1:1) was prepared by thermal decomposition at 500°C of H₄TiO₄-Zr(OH)₄, coprecipitated by adding aqueous ammonia into a mixed aqueous solution of titanium tetrachloride and zirconium(IV) dichloride oxide, 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. SO₄/ZrO₂ and SO₄/TiO₂ were prepared by treating hydroxides (2 g) of Zr and Ti with 0.5 mol m⁻³ H₂SO₄ (30 cm³) on a filter-paper followed by drying and calcining at 650 and 525°C, respectively. Zirconium hydroxide was obtained by hydrolyzing zirconium(IV) dichloride oxide with ammonia solution, washing the precipitate and drying it at 100°C. Titanium hydroxide was obtained by dissolving titanium(IV) isopropoxide in dilute nitric acid, hydrolyzing with ammonia and drying at 100°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. Zr(SO₄)₂ was prepared by calcining its hydrate (Mitsuwa Chemical Co.) in a crucible at 725°C for 3 h followed by powdering over 100 mesh, heating in a Pyrex glass tube at 500°C for 1 h, and sealing: melting point of Pyrex glass being in the vicinity of 700°C.

Identification of Products. Catalytic activities of

various solid acids and bases and the product distributions are given in Table 1. The reaction products are given in the order of elution on a GLC Reoplex 400 column. Products V, VI, and VII were isolated from the isomerized mixture using a preparative GLC column (100×0.6 cm, packed with Reoplex 400) and identified by their IR, ¹H NMR, and MS spectra: MS being obtained by combined gas chromatography-mass spectrometry at 20 eV of ionization voltage. The spectra of IR, NMR, and MS for V, VI, and VII were in agreement with those of the literatures.^{14,15)}

V was identified as (2*S*, 5*R*, 9*R*)-caryophylla-1(12),8(15)-dien-9-ol:^{14,15)} IR 3400 cm⁻¹ (alcohol), 3080, 1640, 890 cm⁻¹ (C=CH₂); ¹H NMR δ=1.0 (s, 6H, C(CH₃)₂), 3.9–4.1 (m, 1H, -CH(OH)-), 4.78 (bs, 2H, C=CH₂(C-3)), 4.96 and 5.05 (bs, 2H, C=CH₂(C-7)); MS important ions at *m/z*, 220 (M⁺, 2%), 136 (100%), 69 (48%), 93 (26%), 109 (24%), 91 (21%), (lit,¹⁵⁾ 220 (M⁺), 136 (100%), 69 (65%), 91(40%), 79 (40%), 109 (30%). The IR, NMR, and mass spectra of VI showed it to be (2*S*, 5*R*, 9*R*)-caryophylla-1(12),7-dien-9-ol^{14,15)} [IR 3360 cm⁻¹ (-OH), 3080, 1640, 890 cm⁻¹ (exocyclic double bond); ¹H NMR δ=1.00 and 0.98 (2s, 6H, C(CH₃)₂), 1.7 (bs, 3H, C=C-CH₃), 4.4 (m, 1H, -CH(OH)-), 4.8 (bs, 2H, C=CH₂), 5.3 (m, 1H, C=CH-); MS 220 (M⁺, 8%), 93 (100%), 109 (97%), 107 (85%), 81 (75%), 105 (68%), 69 (68%), (lit,¹⁵⁾ 220 (M⁺), 41 (100%), 93 (70%), 69 (65%), 105 (60%), 55 (60%), 136 (48%)]. VII was identified as (2*S*, 5*R*, 9*S*)-caryophylla-1(12)-7-dien-9-ol:^{14,15)} IR 3350 cm⁻¹ (-OH), 3090, 1630 cm⁻¹ (exocyclic double bond); ¹H NMR δ=0.96 and 1.01 (2s, 6H, C(CH₃)₂), 1.63 (bs, 3H, C=C-CH₃), 4.46 (m, 1H, -CH(OH)-), 4.7 (m, 2H, C=CH₂), 5.5 (m, 1H, C=CH-); MS 220 (M⁺, 15%), 93 (100%), 109 (82%), 81 (73%), 69 (65%), 121 (60%), 55 (50%), (lit,¹⁵⁾ 220 (M⁺), 41 (100%), 93 (80%), 69 (61%), 79 (64%), 109 (60%), 121 (42%).

III was identified as dihydrocaryophyllen-5-one¹⁶⁾ by its

IR, NMR, and MS: IR: 1720 cm^{-1} (C=O), 3080, 1640, 895 cm^{-1} (C=CH₂), 1380 cm^{-1} (C(CH₃)₂); ¹H NMR δ =0.92 and 0.97 (2s, 6H, C(CH₃)₂), 1.06 (d, 3H, J =4.5 Hz, -CH-CH₃), 4.88 and 4.89 (2s, 2H, C=CH₂); MS 220 (M^+ , 19%), 96 (100%), 138 (72%), 82 (67%), 109 (60%), 69 (60%), 79 (57%).

IV was identified as (1*R*, 5*S*, 8*R*, 9*R*)-4,4,8-trimethylbicyclo[6,3,1,0^{1,5}]dodeca-2-en-9-ol by IR, MS, NMR of ¹H (400 MHz), ¹³C (100 MHz), ¹³C INEPT, ¹H-¹H COSY (280 MHz), and C-H COSY (250 MHz) [IR 3500–3100 cm^{-1} ; MS main peaks at m/z , 220 (M^+ , 6%), 161 (100%), 187 (38%), 205 (25%), 162 (18%), 105 (11%), 119 (10%), 93 (10%); ¹H NMR δ =0.96 (s, 6H, C(CH₃)₂), 0.99 (d, 1H, J =9.3 Hz), 1.07 (s, 3H, C-CH₃), 1.13 (dd, 1H, J =3.5, 9.6 Hz), 1.18 (dd, 1H, J =4.4, 10.0 Hz), 1.39 (ddd, 1H, J =2.3, 4.2, 10.0 Hz), 1.44 (d, 1H, J =9.3 Hz), 1.50 (m, 2H), 1.63 (ddd, 1H, J =1.4, 3.5, 9.6 Hz), 1.74 (dt, 1H, J =3.5, 9.6 Hz), 2.06 (ddt, 1H, J =2.0, 3.5, 9.6 Hz), 3.35 (bs, 1H, >CH-OH), 5.27 (d, 1H, J =6.1 Hz, -CH=CH-), and 5.37 (d, 1H, J =6.1 Hz, -CH=CH-); ¹³C NMR δ =21.1 (t), 24.8 (q), 27.3 (t), 28.2 (q), 32.6 (q), 33.4 (t), 33.6 (t), 34.1 (s), 35.4 (t), 47.7 (s), 49.5 (d), 49.7 (s, >CH-O-), 74.1 (d, >CH-OH), 135.8 (d, -CH=CH-), and 138.3 (d, -CH=CH-); HRMS Calcd for C₁₅H₂₄O: M , 220.3540. Found: m/z 220.3543].

Every peak of ¹³C NMR spectrum was characterized by the observation in INEPT conditions (delay time=3/4*J*) as shown in Fig. 1, and consequently, the presence of following groups was confirmed: -CH₃×3, >CH₂×5, ≡CH×4, and ≡C-×3. The H-H COSY spectrum (Fig. 2) revealed the connectivity among various signals due to protons by reading the cross peaks, and the C-H COSY spectrum (Fig. 2) showed that most peaks of ¹H NMR were assigned to the particular peak of ¹³C NMR spectrum by picking out the cross peaks. Analysis of these two COSY spectra demonstrated the presence of following partial structures,

■-CH₃×3, ■-CH₂-CH₂-CH(OH)-■, ■-CH-CH₂-CH₂-■, ■-CH₂-■, and $\begin{array}{c} \blacksquare \\ \diagup \quad \diagdown \\ \text{H} \quad \text{C}=\text{C} \quad \text{H} \\ \diagdown \quad \diagup \\ \blacksquare \end{array}$ (■ shows a tertiary carbon), from which structure **IV** was assembled.

Results and Discussion

The monoepoxidation of caryophyllene with peracid at the ice cold temperature gives two trans epoxides of **I** and **II** in the ratio 4:1.¹⁴ The mixture, caryophyllene oxides, was transformed into mainly five materials in contact with solid acids and bases. The products were isolated and identified by their IR, NMR, and MS spectra to be 4,5-dihydrocaryophyllen-5-one (**III**), (1*R*, 5*S*, 8*R*, 9*R*)-4,4,8-trimethyltricyclo[6.3.1.0^{1,5}]dodeca-2-en-9-ol (**IV**), (2*S*, 5*R*, 9*R*)-caryophylla-1(12),8(15)-dien-9-ol (**V**), (2*S*, 5*R*, 9*R*)-caryophylla-1(12),7-dien-9-ol (**VI**), and (2*S*, 5*R*, 9*S*)-caryophylla-1(12)-7-dien-9-ol (**VII**). Some catalysts (Al₂O₃-**I** and SO₄/ZrO₂) formed other products, but no detailed analysis was performed because of minor products (Scheme 3).

The catalytic activity and selectivity of several solid acid and base catalysts are shown in Table 1. Catalysts were chosen from those studied in isomerizations of α -pinene and carvomenthene oxides on the basis of

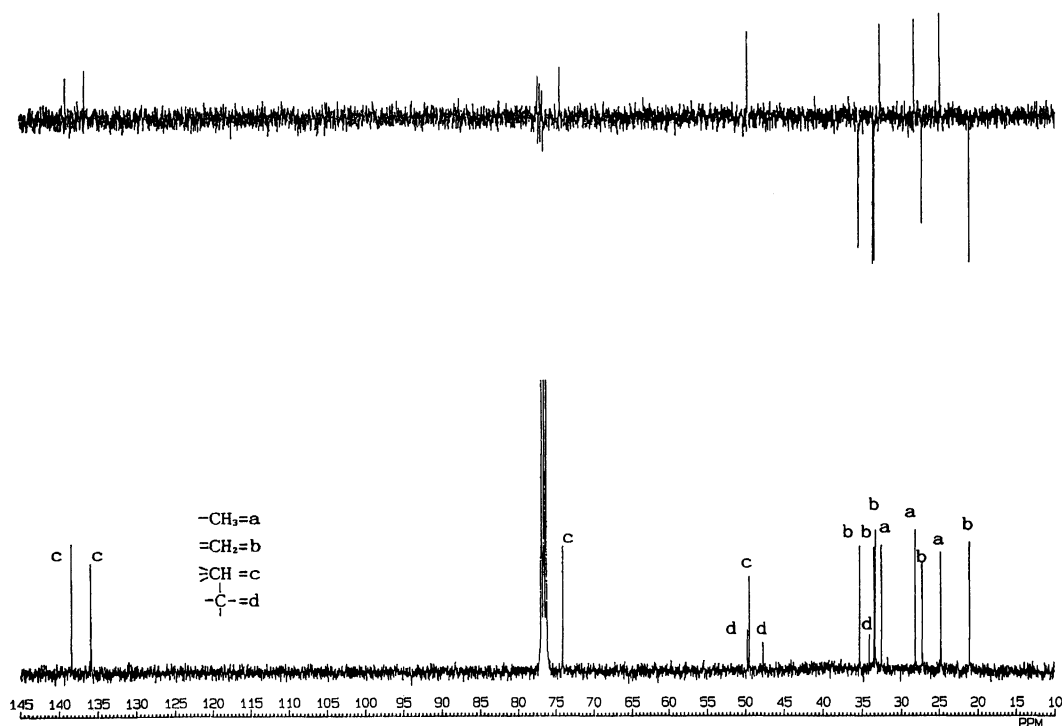
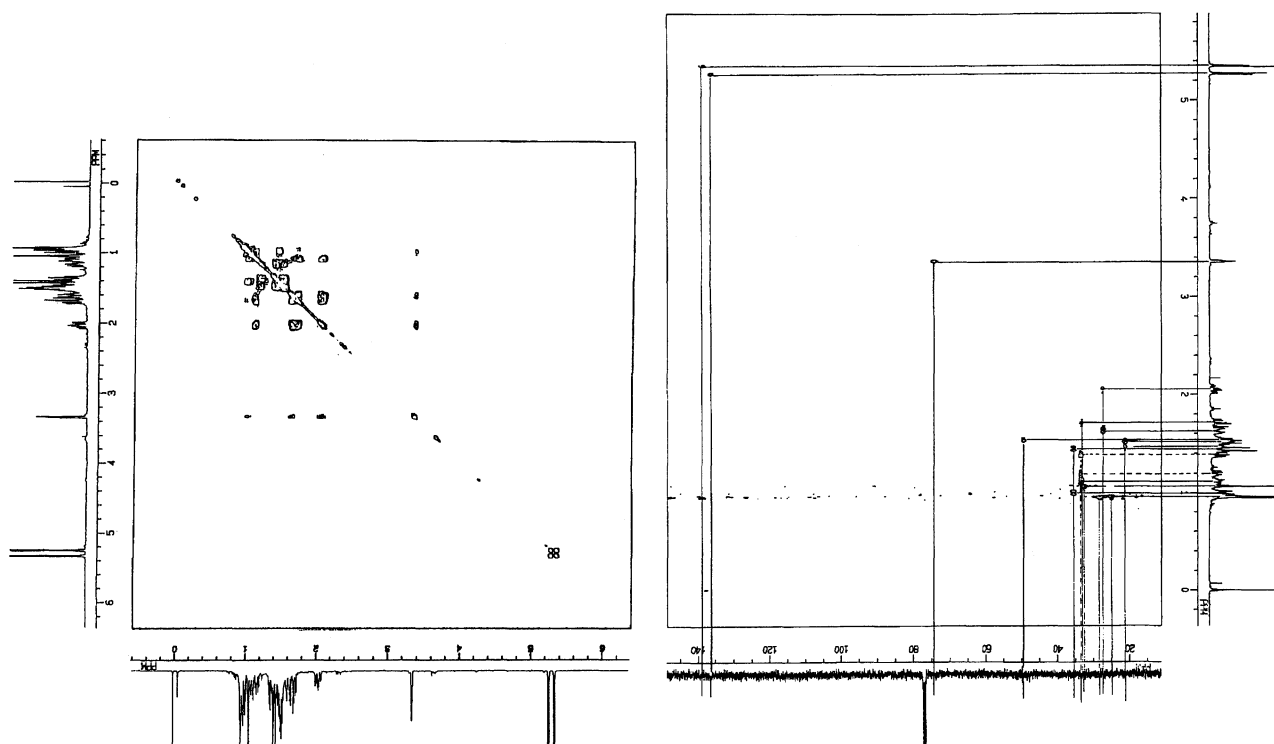
their activities and selectivities.^{11,12} The reactions were carried out at different temperatures from 0 to 100°C according to their catalytic activities. As for temperatures of heat treatment for the catalysts, calcination at 350°C for NiSO₄, 625°C for Ti(SO₄)₂, and 725°C for Zr(SO₄)₂ gives the highest surface acidity,^{17,18} that for FeSO₄ being 700°C.¹⁹ Activation at 500°C is a usual temperature for the metal oxides of solid acids.

A large amount of **III** was formed together with **IV** over FeSO₄ and Zr(SO₄)₂, the selectivity for **III** and **IV** being more than 60%. Allylic alcohols (**V**, **VI**, and **VII**) were given by NiSO₄, Al₂O₃-**II**, SiO₂-TiO₂, and TiO₂-ZrO₂, the selectivity for those being higher than 60%: in particular 96% on TiO₂-ZrO₂. In the case of carvomenthene oxide with a 6-membered ring SiO₂-Al₂O₃ and SiO₂-TiO₂ formed preferentially carbonyl compounds (aldehyde and ketone), but those catalysts gave large amounts of allyl alcohols in addition to ketone for the present oxide, the selectivity for **V**, **VI**, and **VII** being 53 and 68% for SiO₂-Al₂O₃ and SiO₂-TiO₂, respectively. All of the catalysts gave rather considerable yields of the alcohols, in this respect the selectivity for carbonyls or allylic alcohols being lower than that for carvomenthene or *d*-limonene oxide.

The preferential formation of ketone (**III**) was observed over FeSO₄ and Zr(SO₄)₂. It can be explained by the formation of a tertiary carbonium ion intermediate via the breaking of α -bond of oxygen adsorbed on an acid site followed by the migration of a hydrogen as a hydride ion to the cleaved tertiary center. An alcohol compound (**IV**) was formed in place of ring-contracted aldehydes observed on carvomenthene and *d*-limonene oxides. It is due to the large cyclic structure of epoxide with a four-membered ring and a double bond. Aqueous acid hydration of the epoxide suggests the isomerization to **IV**,^{20,21} though the systematic isomerization reaction in a homogeneous system is not found in the literature.

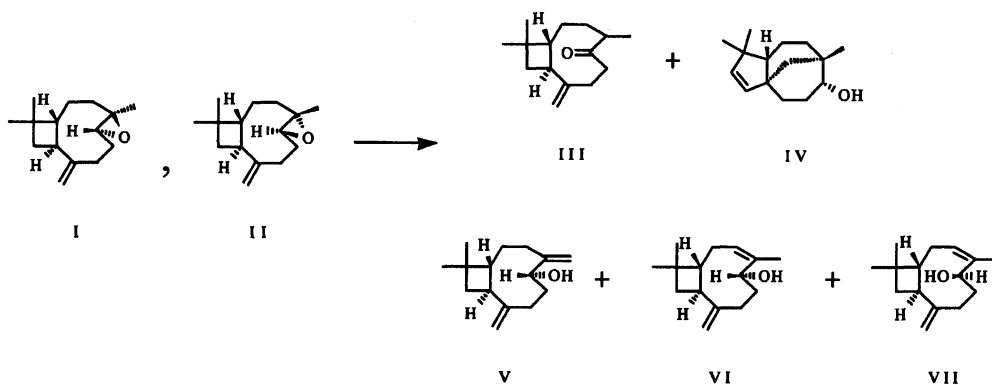
Titania-zirconia and Al₂O₃-**II** show remarkable activities for the allylic alcohol formation. TiO₂-ZrO₂ has both acidic and basic sites to act as an acid-base bifunctional catalyst.²² Epoxide opening to allylic alcohols can be explained in terms of the bifunctional character of TiO₂-ZrO₂; an oxygen atom of the oxide adsorbs on an acidic site of the catalyst, while a hydrogen atom of the methyl or methylene group on a basic site of the catalyst surface, and both the opening of the epoxide ring and the hydrogen abstraction from the methyl or methylene group take place simultaneously to form the allyl alcohol. From the above point of view Al₂O₃-**II** seems to have the bifunctional character more strongly than Al₂O₃-**I**. In the formation of allylic alcohols, **V** exceeded **VI** over most of the catalysts. The preferential formation of **V** is expected due to the more enhanced acidity of primary hydrogen.

It can be concluded from steric character of the allylic alcohols formed on the acid-base bifunctional catalyst

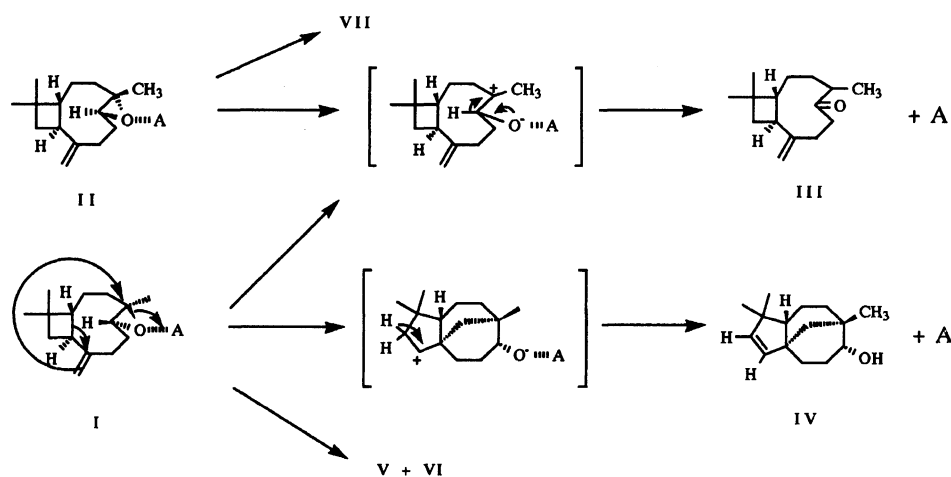
Fig. 1. ^{13}C INEPT spectrum of IV.Fig. 2. ^1H - ^1H COSY and ^{13}C - ^1H COSY spectra of IV.

that V and VI are produced from epoxide I, and VII from II. It is sufficient to understand that III is formed from both I and II judging from a large amount of III formed over FeSO_4 and $\text{Zr}(\text{SO}_4)_2$. It is not clear at

the present stage from which epoxide IV is produced, but the probable formation of IV from I can be interpreted by taking into account the total amount (75%) of selectivity IV, V, and VI over $\text{SiO}_2\text{-Al}_2\text{O}_3$. Thus,

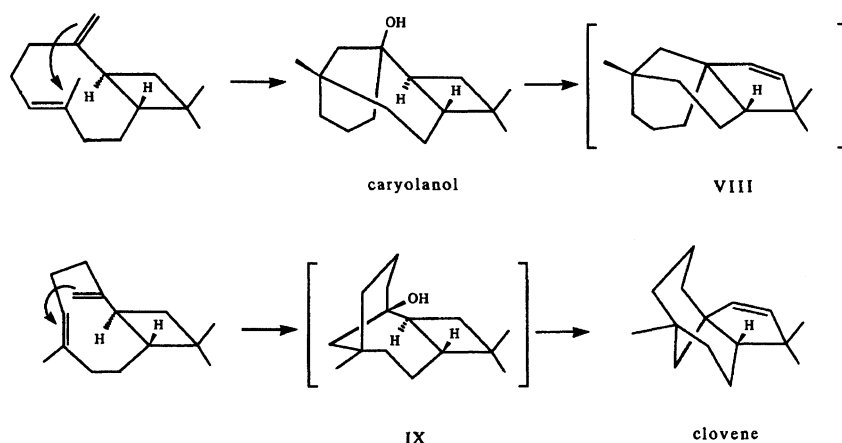


Scheme 3.



A : acid site on catalyst surface.

Scheme 4.

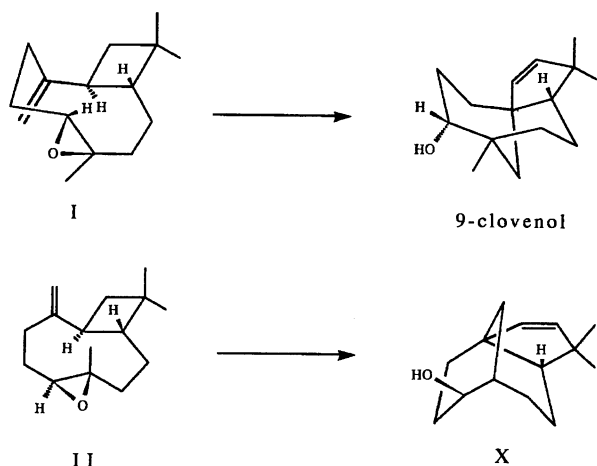


Scheme 5.

the reaction mechanism for the formation of IV from epoxide I in addition to III from epoxide I and II is illustrated as follows (Scheme 4).

It is well known that caryophyllene is converted into clovene and caryolanol on the treatment with mineral acid. Stereochemistry of the reaction was beautifully

analyzed by Nickon et al. (Scheme 5).²³⁾ The analysis could be reasonably applied to the present reaction, that is, major (I) and minor (II) epoxides (almost 75% and 25%)^{13,24)} could give 9-clovenol and X, respectively (Scheme 6). In the present experiments, only IV was obtained, and it is difficult to determine if the prod-



Scheme 6.

uct **IV** coincides with 9-clovenol or **X** by the spectral analysis so far. However, as shown in Scheme 5 major conformer of caryophyllene, which corresponds to **I**, is always converted into clovene, minor one (**II**) into caryolanol; **VIII** and **IX** have never been derived yet. Furthermore, survey of the product percentage in every experiment shown in Table 1 seems to suggest that **IV** is probably derived from **I** instead of **II**; **IV** is namely 9-clovenol.²⁵ Scheme 4 is plausibly rationalized along these inferences.

Solid superacids with an acid strength higher than that of 100% H_2SO_4 are obtained by adsorbing sulfate ion onto hydroxides or amorphous oxides of Zr and Ti followed by calcination in air at temperatures above 500°C; the highest acid strength can be given by calcination at 650 and 525°C for the Zr and Ti materials, respectively.^{26,27} Since the acid strength of them is too strong, the reactions were carried out at 0°C. The results showed low selectivities, four of the products, **III**–**VI**, being uniformly formed.

References

- 1) I. C. Nigam and L. Levi, *Can. J. Chem.*, **41**, 1726 (1963).
- 2) A. S. Gupta and S. Dev., *J. Chromatogr.*, **12**, 189 (1963).
- 3) I. C. Nigam and L. Levi, *J. Org. Chem.*, **29**, 2803 (1964).
- 4) N. P. Damodaran and S. Dev, *Tetrahedron Lett.*, **1963**, 1941.
- 5) S. Dev, *J. Sci. Ind. Res.*, **31**, 60 (1972).
- 6) K. Arata, S. Akutagawa, and K. Tanabe, *J. Catal.*, **41**, 173 (1976).
- 7) K. Arata, H. Takahashi, and K. Tanabe, *Rocz. Chem.*, **50**, 2101 (1976).
- 8) K. Arata and K. Tanabe, *Chem. Lett.*, **1976**, 321.
- 9) K. Arata, J. O. Bledsoe, Jr., and K. Tanabe, *Tetrahedron Lett.*, **1976**, 3861.
- 10) K. Arata, J. O. Bledsoe, Jr., and K. Tanabe, *J. Org. Chem.*, **43**, 1660 (1978).
- 11) K. Arata and K. Tanabe, *Chem. Lett.*, **1979**, 1017.
- 12) K. Arata, S. Akutagawa, and K. Tanabe, *Bull. Chem. Soc. Jpn.*, **51**, 2289 (1978).
- 13) E. W. Warnhoff and V. Srinivasan, *Can. J. Chem.*, **51**, 3955 (1973).
- 14) C. J. Mussinan, B. D. Mookherjee, M. H. Vock, J. F. Vinals, J. Kiwara, and F. L. Schmitt, U.S. Patent 4229599 (1980).
- 15) K. H. Schulte-Elte and G. Ohloff, *Helv. Chim. Acta*, **51**, 494 (1968).
- 16) A. Dupta and S. Dev, *Tetrahedron*, **27**, 635 (1971).
- 17) K. Tanabe, "Solid Acids and Bases," Kodansha, Tokyo (1970), pp. 82–83.
- 18) K. Arata, M. Hino, and N. Yamagata, *Bull. Chem. Soc. Jpn.*, **63**, 244 (1990).
- 19) K. Arata and M. Hino, *Bull. Chem. Soc. Jpn.*, **53**, 535 (1980).
- 20) A. Aebi, D. H. R. Barton, and A. S. Lindsey, *J. Chem. Soc.*, **1953**, 3124.
- 21) A. W. Lutz and E. B. Reid, *J. Chem. Soc.*, **1954**, 2265.
- 22) K. Arata, S. Akutagawa, and K. Tanabe, *Bull. Chem. Soc. Jpn.*, **49**, 390 (1976).
- 23) A. Nickon, F. Y. Edamura, T. Iwadare, K. Matsuo, F. J. McGuire, and J. S. Roberts, *J. Am. Chem. Soc.*, **90**, 4196 (1968).
- 24) H. Shirahama, E. Ohsawa, B. R. Chabra, T. Shimokawa, T. Yokono, T. Kanaiwa, T. Amiya, and T. Matsumoto, *Tetrahedron Lett.*, **22**, 1527 (1981).
- 25) This compound has not been reported so far.
- 26) K. Arata and M. Hino, *Mater. Chem. Phys.*, **26**, 213 (1990).
- 27) K. Arata, *Adv. Catal.*, **37**, 165 (1990).