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ISOMERIZATION OF 2- AND 3-CARENE OXIDES OVER SOLID ACIDS AND BASES[1)]

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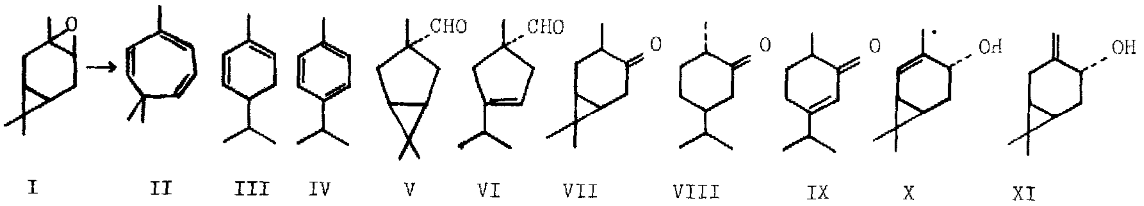
3-Carene oxide isomerized preferentially to carbonyl compounds over SiO_2-Al_2O_3, Al_2O_3 I, and $FeSO_4$ or to allylic alcohols over Al_2O_3 II and TiO_2-ZrO_2 with retention of its three-membered ring, while 2-carene oxide rearranged predominantly to the ring-opened alcohol, the selectivity over TiO_2-ZrO_2 being 100%.

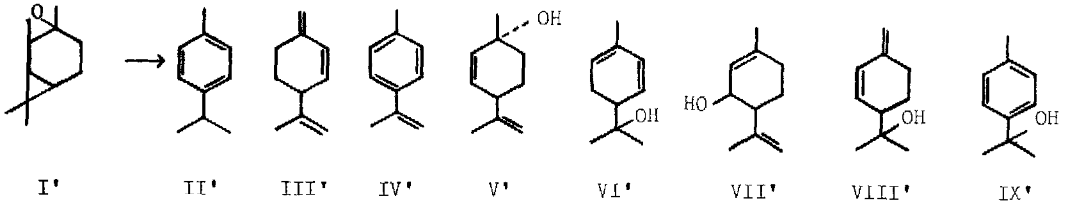
We have recently reported some work on the isomerization of cycloalkene oxides catalyzed by solid acids and bases, where markedly different selectivities were observed depending on the type of catalysts.[2-4)] In order to examine the change in catalytic action due to the effect of the three-membered ring as a substituent group, we have studied the isomerization of 2- and 3-carene oxides over several solid acid and base catalysts.

The reaction was carried out in the presence of toluene at 80°C. A mixture of 0.5 ml of the epoxide (more than 96% pure), 2.5 ml of toluene (purified by distilling over sodium metal) and 0.1-0.4 g of a catalyst below 100 mesh was stirred. The reaction products, separated from the catalyst, were analyzed by gas chromatography with a 3 m column of PEG 20 M on Celite 545 SK.[5)]

SiO_2-Al_2O_3, Al_2O_3 I and Al_2O_3 II were N631(L) (Al_2O_3; 15%) of Nikki Chemical Co., Albes C of Showa Tansan Kaisha LTD. and KAT 6 of Nishio Chemical Co., respectively and calcined in air at 500°C for 3 hr. H_2SO_4/SiO_2 was prepared by immersing 10 g of granular silica gel (white, Knato Chemical Co.) in 12 ml of 1 N H_2SO_4, evaporating, drying and calcining at 150°C. $FeSO_4$ was prepared by calcining its heptahydrate, guaranteed reagent of Knato Chemical Co., in air at 700°C for 3 hr. TiO_2-ZrO_2 (molar ratio = 1:1) was prepared by thermal decomposition of H_4TiO_4-$Zr(OH)_4$ in air at 500°C for 3 hr. The H_4TiO_4-$Zr(OH)_4$ was precipitated by heating a mixed aqueous solution of titanium tetrachloride, zirconium oxychloride and an excess amount of urea on a boiling water bath and washed thoroughly to remove adherent chloride ion. CaO was prepared by calcining $Ca(OH)_2$ at 550°C for 3 hr.

The reaction products of 3-carene oxide (I) were 3,7,7-trimethyltropilidene (II), 1,5,8(9)-p-menthatriene (III), p-cymene (IV), 3,6,6-trimethylbicyclo [3,1,0] hexane-3-carboxaldehyde (V), 1-methyl-1-formyl-3-isopropyl-3-cyclopentene (VI), caranone (VII), isocaranone (VIII), carvenone (IX), trans-2-carene-4-ol (X), trans-3(10)-carene-4-ol (XI) and unidentified products.





Those of 2-carene oxide (I') were p-cymene (II'), 1(7), 2,8(9)-p-menthatriene (III'), α,p-dimethylstyrene (IV'), <u>cis</u>-2,8(9)-p-menthadiene-1-ol (V'), α -phellandrene-8-ol (VI'), <u>cis</u>- and <u>trans</u>-1,8 (9)-p-menthadiene-3-ol (VII'), β-phellandrene-8-ol (VIII'), p-cymene-8-ol (IX') and unidentified products.[6)]

Table 1. Isomerization of 3-Carene Oxide at 80°C for 75 minutes

Catalyst	Catalyst amount g	Conversion	Selectivity (%) II	III	IV	V	VI	VII	VIII	IX	X	XI	Others
SiO_2-Al_2O_3[a)]	0.16	100	1	2	9	52	1	11	14		1		10
H_2SO_4/SiO_2	0.24	100	2		24		15	10	4	23			23
Al_2O_3 I	0.22	70	10	5	4	46		3	13		6	12	1
$FeSO_4$	0.32	95		2	4	23		4	36	2	3	7	17
Al_2O_3 II	0.27	37	4	1	1	17		3	3		15	54	1
TiO_2-ZrO_2[b)]	0.24	61	12	10	2	11		1	2		41	19	2

a) in 10 min. b) at 90°C.

Table 1 shows the catalytic activity and selectivity for the isomerization of 3-carene oxide. The main products were carbonyl compounds (V, VII, and VIII) and allylic alcohols (X and XI) with a three membered ring except for the case of H_2SO_4/SiO_2, which gave a large amount of IV, VI and IX, probably owing to its large amount of Brönsted acid. The carbonyl compounds were predominantly formed over SiO_2-Al_2O_3, Al_2O_3 I and $FeSO_4$, while the allylic alcohols were preferentially formed Al_2O_3 II and TiO_2-ZrO_2, their selectivities being more than 60%. SiO_2-Al_2O_3 is extremely active

Table 2. **Isomerization** of **2**-Carene Oxide at 80°C for 10 min.

Catalyst	Catalyst amount	Conversion	Selectivity (%)								
	g		II'	III'	IV'	V'	VI'	VII'	VIII'	IX'	Others
SiO_2-Al_2O_3 [a)]	0.13	100	43	6	7		5				28
Al_2O_3 I	0.12	54	21			43	4	3	4		20
$FeSO_4$ [a)]	0.24	45	24	1		45	5				24
$FeSO_4$ [a,b,c)]	0.21	4									
Al_2O_3 II	0.30	53	14	3		36	7	8			31
TiO_2-ZrO_2 [a)]	0.20	77	11		2	75	4	2		3	
TiO_2-ZrO_2 [d)]	0.25	20				100					
CaO [a,c)]	0.10	2									

a) A mixture of 0.25 ml of the epoxide and 1.25 ml of toluene was used.
b) Calcined at 900°C. c) for 75 min. d) at 30°C for 1 hr.

for the isomerization. In our previous paper,[2)] it was concluded that the preferential formati of carbonyl compounds was given by strong acid on the catalyst surface. As for the allylic alcohol formation, X was predominantly formed over TiO_2-ZrO_2, while XI over Al_2O_3 II. It is inferred on the basis of our previous conclusion about the allylic alcohol formation by an acid-base bifunctional mechanism[2)] that the choice of the X or XI formation depends on the different properties of acidic and basic sites on the catalyst surface.

The catalytic activity and selectivity for the isomerization of 2-carene oxide is shown in Table 2. The epoxide used was a mixture of 2- and 3-carene oxides (4:1), but the yields of II, V, VII and VIII, which were supposedly formed from 3-carene oxide, are excluded from the Table. However, the conversion of 3-carene oxide was quite low except the case of SiO_2-Al_2O_3 under the present reaction conditions. The reactivity was exceedingly high in comparison with that of 3-carene oxide. However, $FeSO_4$ calcined at 900°C **or** CaO, which has a **basic character**[7)] was almost inactive. It can be seen that all the products were the three-membered ring-opened ones, in contrast to the observations in the case of 3-carene oxide. The formation of allylic alcohols with the hydroxyl group rearranged to the 3 or 8 position was also observed. A large amount of II' andV' was formed. In particular, TiO_2-ZrO_2 showed 75% selectivity for the formation of V'. This catalyst gave even 100% of V' at 30°C. It is significant that the breaking of (C-3)-O bond of oxygen is much more favorable with 3-carene oxide, while the (C-2)-O bond is broken with 2-carene oxide suggesting cyclopropyl participation in the latter case.

References

1) Epoxide Rearrangement IX. Part VIII: Ref. 4.

2) K. Arata, S. Akutagawa, and K. Tanabe, Bull.Chem.Soc.Japan, 48, 1097 (1975); ibid. 49, 390 (1976); J.Catal., 41, 173 (1976).

3) K. Arata, H. Takahashi, and K. Tanabe, to be published.

4) T. Yamada, K. Arata, M. Itoh, H. Hattori, and K. Tanabe, to be published.

5) All compounds identified showed satisfactory spectral data (IR, NMR, MS). Compounds III, IV, IX, II', III', IV', V', VI', VII', VIII' and IX' were identified by comparing them with authentic materials from the Glidden-Durkee research laboratories. The rest were identified using spectral data reported in the following references: R. L. Settine and C. McDaniel, J.Org.Chem., 32, 2910 (1967); V. S. Joshi, N. P. Damodaran and Sukh Dev, Tetrahedron Letters, 24, 5817 (1968); and V. S. Joshi, N. P. Damodaran and Sukh Dev, Tetrahedron Letters, 27, 475 (1971).

6) Opening of the three-membered carbocyclic ring can occur, especially with 3-Carene Oxide, to give m-menthane derivatives, and these products also often have identical elution times by gas chromatography as the corresponding p-menthane derivative.

7) T. Iizuka, H. Hattori, Y. Ohno, J. Sohma, and K. Tanabe, J.Catal., 22, 130 (1971).