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ISOMERIZATION OF d-LIMONENE OXIDE OVER ALUMINAS[1)]

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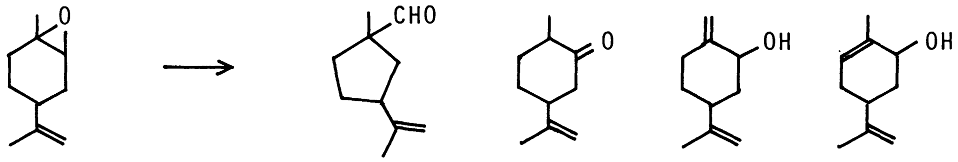
The title reaction was carried out over five different aluminas. One of them formed predominantly carbonyl compounds, while two gave more than 80 % allyl alcohols. Others produced both products.

We have recently studied the isomerizations of cycloalkene oxides catalyzed by several solid acids and bases, whose catalytic activity and selectivity were of much interest.[2,3)] Since the metal oxides prepared by different methods were found to show different catalytic actions,[4,5)] we have examined the catalytic activity and selectivity of several commercially available aluminas together with a prepared alumina for the isomerization of d-limonene oxide.

Al_2O_3 I (amorphous, surface area 50 m^2/g) was prepared by hydrolysis of its sulfate with ammonia water, followed by washing thoroughly, drying and calcining. Al_2O_3 II, III and IV were Albes C (fibrillar alumina of Beohmite, 100 m^2/g), Albes FE (fibrous powder containing no sodium, 120 m^2/g) and Albes FF (fibrous fine particle with samll bulk density, 300 m^2/g), respectively, supplied from Showa Tansan Kaisha, Ltd. Al_2O_3 V (Gibbsite, 220 m^2/g) was KAT 6 of Nishio Chemical Co. All the catalysts were heat-treated in air at 500°C for 3 hr and stored in sealed ampoules until use. The reaction was carried out in the presence of toluene at 90°C for 1 hr. A mixture of 0.5 ml of the epoxide (a mixture of cis- and trans-forms in 1:1, more than 97 % pure), 2.5 ml of toluene (purified by distilling over sodium metal) and 0.2-0.3 g of the catalyst less than 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.[2)]

The reaction products of d-limonene oxide (I) were 1-methyl-3-isopropenyl-cyclopentyl-1-carboxaldehyde (II), dihydrocarvone (III), exo-carveol (IV) and endo-carveol (V).



I II III IV V

Table 1. Isomerization of d-Limonene Oxide over Aluminas at 90°C for 1 hr

Catalyst	Catalyst amount, g	Conversion %	Selectivity (%) a)			
			II	III	IV	V
Al_2O_3 I c)	0.29	15		57 (1.5)	10 b)	33 b)
Al_2O_3 II	0.20	98	23	52 (0.7)	8 (2.3)	14 (3.7)
Al_2O_3 II d)	0.10	31		21 (1.0)	17 (4.9)	59 (6.0)
Al_2O_3 III	0.29	24		42 (1.4)	23 (6.9)	33 (14.8)
Al_2O_3 IV	0.22	29		18 (1.2)	61 (3.9)	21 b)
Al_2O_3 V	0.30	45		12 (0.9)	65 (2.8)	22 (3.3)
Al_2O_3 V d)	0.25	8		14 (1.7)	47 (4.3)	32 b)

a) numerals in parentheses are relative ratios of trans against cis,
b) trans only, c) carried out at 110°C for 2 hr, d) calcined at 950°C for 3 hr.

As shown in Table 1, carbonyl compounds (II and III) were predominantly formed over Al_2O_3 II, the yield being 75 %, while allyl alcohols (IV and V) were preferentially given by Al_2O_3 II calcined at high temperature, Al_2O_3 IV and V. In particular, Al_2O_3 IV and V showed more than 80 % selectivity for the formation of allyl alcohols. Al_2O_3 I and III gave almost the same amount of both products. It is remarkable that Al_2O_3 II is extremely active for the isomerization. Since the preferential formation of carbonyl compounds was concluded to be given by strong acid on the catalyst surface such as SiO_2-Al_2O_3,2) this alumina is considered to have quite strong acid sites on the surface. On the other hand, it is inferred from our previous explanation about the allyl alcohol formation by an acid-base bifunctional mechanism,2,3) that Al_2O_3 IV and V have both acidic and basic sites effective to produce allyl alcohols. In this regard, Al_2O_3 I and III fall into the intermediate category of acid-base property. The striking formation of allyl alcohols over Al_2O_3 II calcined at 950°C suggests that acidic sites on the surface was decreased by calcining at high temperature, resulting in the bifunctional catalytic action. As for the allyl alcohol formation, IV was predominantly formed over Al_2O_3 IV and V, while V over Al_2O_3 I, II and III. The much preferential formation of trans-form of allyl alcohols was observed, in contrast to the observations in the case of ketone.

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