

Isomerizations of Citronellal to Isopulegol and Geraniol to
Linalool Catalyzed by Solid Acids and Bases

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Citronellal was isomerized to isopulegol over $\text{SiO}_2\text{-Al}_2\text{O}_3$, $\text{TiO}_2\text{-ZrO}_2$, FeSO_4 , NiSO_4 , $\text{Ti}(\text{SO}_4)_2$, $\text{Zr}(\text{SO}_4)_2$, and Al_2O_3 , with the selectivity higher than 91%. Geraniol was also isomerized mainly to linalool over $\text{SiO}_2\text{-Al}_2\text{O}_3$ and those four metal sulfates, and the selectivity on $\text{SiO}_2\text{-Al}_2\text{O}_3$ and FeSO_4 was higher than 81%.

Some products isomerized from terpene compounds are valuable as raw materials for perfume, flavor cosmetic, and pharmaceutical materials and also provide useful intermediates for the synthetic organic chemicals. The isomerization of monoterpenes such as linalool, terpineol, and geraniol has been carried out with oxalic acid, H_2SO_4 , AlCl_3 , $\text{BF}_3\cdot\text{ether}$, and HFSO_3 in the homogeneous catalytic reaction; their selectivities were, however, exceedingly low, for instance geraniol being rearranged to twenty-three products containing α -terpineol as a main product with oxalic acid.¹⁻⁴) Recently, we reported on isomerization reactions of various epoxide compounds over heterogeneous acid and base catalysts; the results showed markedly different selectivities according to the type of catalyst used.⁵) Thus, we examined solid acids and bases in the isomerizations of citronellal and geraniol, and several catalysts were found to show quite high selectivities.

The reaction was carried out with stirring a mixture of 0.5 ml of citronellal (Tokyo Kasei Kogyo Co.) or geraniol (Wako Pure Chemical Ind.), 2.5 ml of toluene as a solvent and 0.25 g of catalyst. The products separated from the catalyst were analyzed by gas chromatography with a 2 m column of PEG 20 M (140 °C) for citronellal and a 1 m column of Reoplex 400 (120 °C) for geraniol. The products isolated from the reaction mixture were identified by comparison of MS, IR, and NMR spectra with reference materials.

The catalysts were prepared as follows. $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-1}$ (Shokubai Kasei Kogyo Ltd., 13% Al_2O_3) and $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-2}$ [N361(L)(Al_2O_3 : 15%) of Nikki Chemical Co.] were calcined at 500 °C. $\text{TiO}_2\text{-ZrO}_2\text{-1}$ and -2 were prepared by thermal decomposition at 500 °C of $\text{H}_4\text{TiO}_4\text{-Zr}(\text{OH})_4$ (molar ratio=1:1), precipitated by adding aqueous ammonia to a mixed aqueous solution of $\text{Ti}(\text{i-pr})_4\text{-ZrO}(\text{NO}_3)_2$ and of $\text{TiCl}_4\text{-ZrOCl}_2$, respectively, followed by thorough washing of the precipitate with water and drying. NiSO_4 , FeSO_4 , $\text{Ti}(\text{SO}_4)_2$, and $\text{Zr}(\text{SO}_4)_2$ were prepared by calcining their hydrates at 350, 500, 625, and 700 °C, respectively. Al_2O_3 was obtained by calcining a reference catalyst (JRC-ALO-2), supplied from Catalysis Society of Japan, at 500 °C. CaO was prepared by calcination at 550 °C of $\text{Ca}(\text{OH})_2$.

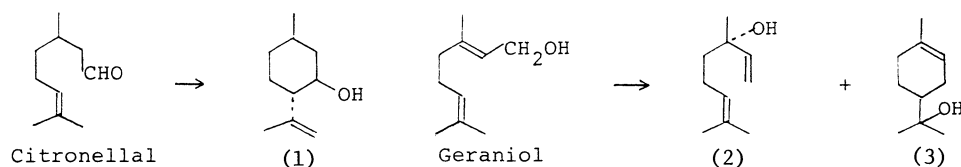
Table 1. Isomerizations of citronellal and geraniol over solid acids and bases

Catalyst	Reaction of citronellal				Reaction of geraniol			
	React. temp/°C	React. time/h	Conv. %	Select./% (1)	React. temp/°C	React. time/h	Conv. %	Select./% (2) (3)
SiO ₂ -Al ₂ O ₃ -1	RT ^{a)}	0.5	91	94	50	2	28	86 6
-2	RT	0.5	91	93	70	0.5	76	47 8
TiO ₂ -ZrO ₂ -1	70	2	37	91	100	2	5	0 0
-2	70	2	20	91	100	2	2	0 0
FeSO ₄	70	2	65	95	80	1	40	81 6
NiSO ₄	70	2	79	95	80	1	61	51 7
Ti(SO ₄) ₂	RT	2	78	96	50	2	60	53 5
Zr(SO ₄) ₂	RT	2	96	95	50	1	62	57 24
Al ₂ O ₃	70	2	90	91	100	2	0	0 0
CaO	100	3	3	0	90	2	0	0 0

a) Room temperature.

All the catalysts ground to below 100 mesh were calcined in glass ampoules in air for 3 h and sealed to store.

The products were isopulegol (1) from citronellal, and linalool (2) and α -terpineol (3) from geraniol; large amounts of hydrocarbons, probably formed



by the dehydration of 3, were produced according to types of catalysts and/or reaction conditions for the latter.

The catalytic activity and selectivity are shown in Table 1. The reactions were carried out at temperatures from room temperature to 100 °C according to their catalytic activities. Citronellal was converted into 1 with 91-96% selectivity, an useful intermediate for the synthesis of *l*-menthol, over the acidic catalysts.⁶⁻⁸⁾ Geraniol was isomerized predominantly to 2 over SiO₂-Al₂O₃ and four metal sulfates, the selectivity on SiO₂-Al₂O₃ and FeSO₄ being higher than 81%. It is considered that geraniol is converted into 2 and 3 by an acid-catalyzed mechanism on the catalyst surface, but the reaction was not brought about even at 100 °C over TiO₂-ZrO₂, which is one of the catalysts with the highest surface acidity and whose acid strength is close to that of SiO₂-Al₂O₃,⁶⁾ Al₂O₃ being also inactive. TiO₂-ZrO₂ and Al₂O₃ are known to have both acidic and basic characters or acid-base bifunctional catalysts.⁶⁾ So, the basic property seems to inhibit the reaction. CaO, which has basic character, was inactive for both reactions.⁶⁾

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