Cyclization of Citronellal to Isopulegol by Cu-Cr and Cu-Cr-Mn Catalysts

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Isopulegol is usually prepared by heating⁽¹⁾ citronellal with or without silica gel,⁽²⁾ active carbon,⁽³⁾ or boric acid.⁽⁴⁾

In their studies of the catalytic dehydrogenation of geraniol, the present authors found that Cu-Cr-Mn also catalyzes the cyclization of citronellal to isopulegol. In this paper, the results of the catalysis of Raney Nickel, Ni-diatomaceous earth, Cu-Cr, and Cu-Cr-Mn, and the effect of the hydrogen treatment of the catalysts on the cyclization, will be presented. Cu-Cr and Cu-Cr-Mn, without any hydrogen treatment, were found to be good catalysts for this reaction.

Experimental

Materials. Citronellal was prepared from citronellal oil (made in Formosa) by the known method.⁽⁵⁾ The catalysts used here were supplied by the Nikki Chem. Co., Ltd. Raney Nickel was pretreated with alkali. Cu-Cr N202, Cu-Cr-Mn N203, and Nickel-diatomaceous earth N111, treated or untreated, were used.

The Procedure of the Cyclization of Citronellal. In the case of a catalyst pretreated with hydrogen, a 0.5 g portion of it placed at the bottom of a 300 *ml* flask equipped with an air-tight stirrer, a reflux condenser, a gas outlet tube with a rubber stopper, and a

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1) V. Grignard and J. Doeuvre, *Compt. rend.*, **190**, 1164 (1930).

2) H. B. Glass, U. S. Pat. 2117414 (1936).

3) S. Kimura, *Mem. Coll. Sci. Kyoto. Imp. Univ.*, **10**, 330 (1935).

4) S. Katsura, O. Okuda and A. Komatsu, Japanese Pat. 8875 (1957).

5) A. Lewinson, *Perfumery and Essential Oil Record*, **14**, 360 (1923).

two-necked glass tube with a thermometer, and then a glass inlet-tube reaching to the bottom of the flask was fitted on. The flask was immersed in an oil bath at 150—170°C. The hydrogen was passed through the catalyst at a rate of 200 m*l*/min for 1.5 hr, and then it was replaced by nitrogen at the same flow rate for 0.5 hr. Then citronellal (50 g, 0.23 m) was put into the flask, and the flask was kept at 160—200(±1)°C with stirring under a nitrogen flow. In a case without a catalyst or with a catalyst not treated with hydrogen, citronellal was put into a flask which had previously been filled with nitrogen, and the flask was kept at 205°C by means of an oil bath and allowed to react much as has been described above for 5 to 7 hr under a nitrogen atmosphere.

When the reaction was complete, the reacting mixture was cooled to room temperature, and 150 m*l* of ether was added to it. After the catalyst had been removed by filtration, the ethereal solution was washed with an aqueous solution of sodium carbonate, and then with water, and dehydrated over sodium sulfate. After evaporation, an oily product was obtained.

Determination of the Composition of the Product by Gas Chromatography. Each sample (0.05 m*l*) was taken by a mycrosyringe from the reactor through the rubber stopper and analyzed by a gas chromatograph, Kotaki GU-21, under the following conditions: column temperature, 150°C; split temperature 250°C; carrier gas, helium; inlet pressure, 0.8 kg/cm^2; flow rate, 26 m*l*/min; sensitivity, 8 mV; chart speed, 0.5 cm/min. The column was of stainless steel and was 3 mm in diameter and 3 m long, packed with Diabase A, 80—60 mesh, coated by an acetone solution of Hyprose SP 80. The accuracy of the analysis was estimated to be ±1% (the product obtained at 200°C for 5 to 7 hr was analyzed for the fraction; bp 72—110°C/4 mmHg).

The standard materials used for the analysis were: (1) citronellal (the same as the starting material); (2) citronellol (from the ABRAC Co., Ltd.; bp 100°C/6 mmHg, n_D^{30} 1.4639, d_{30}^{30} 0.8572); (3) isopulegol (from Tokyo Kasei, Inc.); a mixture of 20% neo-isopulegol; 75% isopulegol; and 5% iso-isopulegol (by gas chromatographic analysis; bp 74—78°C/6 mmHg, n_D^{30} 1.4679), and (4) pulegone (from Tokyo Kasei, Inc.; bp 98°C 6 mmHg, n_D^{30} 1.4880, d_{30}^{30} 0.9731, $[\alpha]_D^{25}$ +20°).

Separation of Isopulegol. The cyclization product (154 g) which was obtained under the conditions (Run 4) shown in Table 1 was treated with 400 m*l* of a 35% sodium hydrogen sulfite solution at 40°C for 3 hr. The reaction mixture was then cooled to room temperature and extracted with 300 m*l* of benzene. The benzene layer was washed with an aqueous sodium carbonate solution and with water, and then dried over sodium sulfate. Upon the removal of the benzene, the oily product was distilled *in vacuo* to give a fraction of bp 72—90°C/4 mmHg (124 g), together with the residue (9.2 g); the former was found to be a mixture of 1.8% pulegone and 98.2% isopulegol isomers (20.2% neo-iso, 70% iso, and 8.0% iso-isopulegol); while the latter exhibited no peak in its gas chromatogram. From the aqueous sodium hydrogen sulfite solution, 12 g of citronellal used recovered.

Results and Discussion

The results obtained at 200°C are given in Table 1. Table 1 shows that, among the catalysts used here, Raney Nickel and Ni-diatomaceous earth were ineffective. The Cu-Cr and Cu-Cr-Mn catalysts, without hydrogen treatment, gave higher cyclization yields. The latter catalyst (Run 4) was most useful; the yield with it was 80% of the theoretical value. Using the Cu-Cr-Mn catalyst, further studies were then undertaken at 160°C, 180°C, and 200(±1)°C. Figure 1 and Table 2 show some of these results. In Table 2, the results obtained without a catalyst are also given. From these results, the rate of reaction was found to be first order with respect to the concentration of citronellal (see Table 2). The activation energies for the catalytic and non-catalytic reactions were

TABLE 1. CATALYZED AND THERMAL CYCLIZATION OF CITRONELLAL

Run	Catalyst		Reaction temperature °C	Reaction time hr	Conversion of citronellal into each product (% theor.)								
	Amount (wt% of citronellal)	Treatment with H_2			Citronellal	Unknown	Neo-isopulegol	Iso pulegole	Iso-isopulegol	Pulegone	Citronellal	Distillation residue	Cyclization* yield, %
1	Cu-Cr 0.5	+	200	5	12.5	1.8	15.3	48.9	6.2	3.7	3.6	4.4	74
2	Cu-Cr-Mn 0.5	+	200	6	9.0	4.7	14.2	49.4	6.5	4.3	3.9	4.0	74
3	Cu-Cr 1.0	−	200	6	11.7	0	16.6	52.7	6.3	2.7	0	5.9	78
4	Cu-Cr-Mn 1.0	−	200	7	9.3	0	16.3	56.0	6.3	1.4	0	5.9	80
5	Ni-Diatomaceous earth 0.5	+	200—205	5	16.7	0	14.1	46.0	5.7	2.8	2.6	8.5	69
6	Raney Ni 0.5		200—205	6	7.1	1.2	13.5	50.8	5.5	4.3	5.6	7.9	72
7	None		200	6	13.5	2.6	17.8	48.3	4.8	0	0	9.6	71

* Cyclization yield; a combined yield (%) of isopulegol isomers and pulegone.

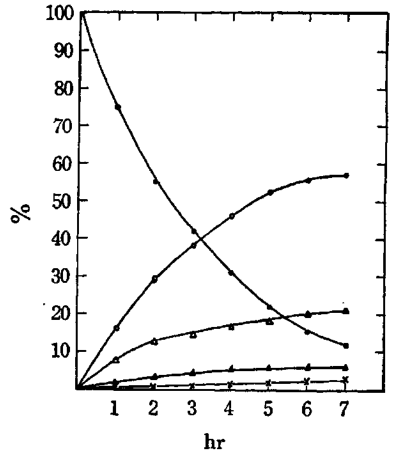

Fig. 1. The composition of reacting mixture *vs.* reaction time, using Cu-Cr-Mn catalyst (1 wt%) without H_2 pretreatment; reaction temperature 200°C; ● citronellal, ○ isopulegol, △ neo-isopulegol, ▲ iso-isopulegol, × pulegone.

estimated to be 17.2 kcal/mol and 20.4 kcal/mol, respectively.

Table 2. Rate constant K and activation energy E

Reaction temperature °C	K^*, sec^{-1} $\times 10^5$	
	Cu-Cr-Mn (1% by weight) without H_2 treatment	Thermal reaction without catalyst
200	10.3	8.14
180	4.01	3.41
160	1.37	1.19
Activation energy obtained from Arhenius plots E	17.2 kcal/mol	20.4 kcal/mol

* $K = 1/t \cdot \log(100/(100-X))$

X: Weight percent of remaining citronellal

It has become obvious that the Cu-Cr and Cu-Cr-Mn catalysts without hydrogen treatment have a catalytic activity for the cyclization. The reaction process with the Cu-Cr-Mn catalyst without hydrogen treatment may proceed according to the thermal isomerization mechanism already proposed by Ohloff.6)

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6) G. Ohloff, *Tetrahedron Letters*, **1960**, No. 11, 11—14 (1960).