SHORT COMMUNICATIONS

Formation of Myrcene in the Sodium-catalyzed Oligomerization of Isoprene[1]

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Recently investigations[2] have been carried out on the metal complex-catalyzed oligomerization of isoprene. However, no information was obtained on the formation of myrcene (I) (7-methyl-3-methylene-1,6-octadiene), a very important monoterpene occurring in nature, directly from isoprene.

We have investigated the sodium-catalyzed polymerization of isoprene already reported,[3,4] under improved conditions, and found that the oligomers contained significant amounts of myrcene(I) and 6-isopropenyl-9-methyl-3-methylene-1,8-decadiene (II).

Isoprene reacted smoothly with sodium metal in benzene solution and the oligomers were obtained (Table 1). For example, isoprene (15 g) in benzene (20 m*l*) was allowed to react with lumps of sodium (0.5 g, about 1.5 mm cubes) at 40°C for 5 hr with stirring in a pressure bottle. The reaction mixture was then cooled and treated with 15 m*l* ethanol to decompose sodium and organosodium compounds. Distillation of the reaction products gave C_{10} fraction (0.7 g) at 55—60°C/15 mmHg, C_{15} fraction (0.3 g) at 60—63°C/1.0 mmHg and the residue[5] (0.7 g). The first fraction was found to contain 85% of I and the second 76% of II by IR, NMR, and mass spectrometry after gas chromatographic fractionation.[6]

TABLE 1. THE REACTIONS OF ISOPRENE WITH SODIUM

Isoprene (g)	Solvent	(m*l*)	Na (g)	Temp (°C)	Time (hr)	Fractions (g)		
						C_{10}	C_{15}	Residue
15	C_6H_6	20	0.5	40	5	0.7	0.3	0.8
10	C_6H_6	30	0.4	40	5	0.2	t[a]	0.9
20	C_6H_6	20	2.0	40	5	0.6	0.3	1.7
15	C_6H_6	20	0.5	40	10	0.9	0.3	3.3
20	C_6H_6	20	1.0	50	6	t[a]	—	4.6
15	Et_2O	20	0.5	40	3	—	—	12.5[b]
15	THF	20	0.5	40	1.5	—	—	13.0[b]

a) t; trace. b) Distillation was impossible.

Myrcene (I):[7] Mass; *m/e* 136 (M^+). IR (cm^{-1}); 1650, 1600, 990, 910, 890, 825. NMR (CCl_4); δ, 4.80—6.50 (4H, m, $-CH=CH_2$ and $-\overset{|}{C}=CH-$), 4.90 (2H, broad-s, $-\overset{|}{C}=CH_2$), 2.03—2.30 (4H, m, $=\overset{|}{C}-CH_2-CH_2-\overset{|}{C}=$), 1.65 (3H, s, $CH_3\overset{|}{C}=$), 1.57 (3H, s, $CH_3\overset{|}{C}=$).

6-Isopropenyl-9-methyl-3-methylene-1,8-decadiene (II): Mass; *m/e* 204 (M^+). IR (cm^{-1}); 1650, 1600, 990, 910, 890, 835. NMR (CCl_4); δ, 4.82—6.50 (4H, m, $-CH=CH_2$ and $-\overset{|}{C}=CH-$), 4.88 (2H, broad-s, $-\overset{|}{C}=CH_2$), 4.65 (2H, broad-s, $-\overset{|}{C}=CH_2$), 1.80—2.50 (5H, m, $-CH_2-\overset{|}{C}=$ and $-CH-\overset{|}{C}=$), 1.60 (9H, broad-s, $CH_3C=$), 1.20—1.52 (2H, m, $-CH_2-$).

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[1] Syntheses of Terpenoids by Telomerization. VII. Part VI; T. Katagiri, K. Takabe, K. Ono, and J. Tanaka, *Nippon Kagaku Zasshi*, **92**, 811 (1971).

[2] a) C. W. Bird, "Transition Metal Intermediate in Organic Synthesis", Logos Press, London, (1967), p. 30. b) A. Misono, Y. Uchida, K. Furuhata, S. Yoshida, This Bulletin, **42**, 1383, 2303 (1969); S. Watanabe, K. Suga, H. Kikuchi, *Aust. J. Chem.*, **23**, 385 (1970); Y. Uchida, K. Furuhata, H. Ishikawa, This Bulletin, **44**, 1118 (1971).

[3] The sodium catalyzed polymerization of isoprene in tetrahydrofuran has been known to form mainly 1,4- and 3,4-polymers. [A. V. Tobolsky, C. E. Rogers, *J. Polym. Sci.*, **40**, 73 (1959).]

[4] It has been reported by Suga that the reactions of isoprene with lithium- or sodium-naphthalene gave the linear dimers of isoprene (dimethyloctadienes and trimethylheptadiene). [K. Suga, S. Watanabe, This Bulletin, **40**, 1257 (1967); S. Watanabe, K. Suga, T. Fujita, *Synthesis*, **7**, 375 (1971).]

[5] The residue was a very viscous fluid and considered to be a mixture of 1,4- and 3,4-bonded higher oligomers of isoprene by IR. [IR(cm^{-1}); 885, 835.]

[6] Glc conditions; Apiezon L, 0.5 mmϕ × 90 m, 110°C for C_{10} fraction and 150°C for C_{15} fraction.

[7] The data of I agreed completely with those of authentic myrcene.