Synthesis of 1, 8(9)-p-Menthadien-10-yl-carbinol

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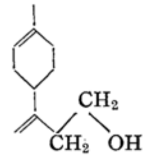
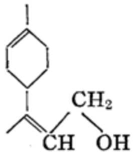
The addition of formaldehyde to olefines is known as Prins reaction[1]. For the first time Ladenberg[2] discovered that formaldehyde can be added to terpenes and Kriewitz[3] researched this reaction with β-pinene. Lombard[4] obtained alcohol (IV) from *d*-limonene, using zinc chloride as a catalyst. The present authors investigated the addition reaction of *d*-limonene and formaldehyde, and prepared a limonenylcarbinol in high yields (30%), the structure of which was proved to be 1,8(9)-*p*-menthadien-10-yl-carbinol (III).

d-Limonene(I) and paraformaldehyde(II) scarcely reacted at all when the mixture was agitated in the presence of zinc chloride for 3 hr. at about 80°C; neither aluminum chloride nor ferric chloride in place of zinc chloride gave good results. When a mixture of one mol. each of I and II was heated for 12 hr. at 200∼220°C in a sealed tube, a yellow viscous oil was obtained (yield, 11%). It gave a phenylurethan, m. p. 54∼55°C, which was analyzed as the phenylurethan derived from an alcohol, $C_{11}H_{18}O$. As this procedure did not give satisfactory yields, a mixture of I, II and acetic anhydride was heated in an autoclave, and a limonenylcarbinyl acetate was obtained in a yield of 30%. The use of 0.5 mol. or more of acetic anhydride per one mol. of I, the reaction temperature 180∼190°C, and the reaction time 4∼5 hr., gave the best result. A limonenylcarbinol was prepared by the saponification of the acetate. The acetate could not be saponified by the action of 20% aqueous or alcoholic potassium hydroxide at 100°C, but the carbinol was produced almost quantitatively by heating the acetate with 20% aqueous potassium hydroxide for 3∼4 hr. at 180∼190°C in an autoclave. The carbinol is a colorless liquid and it smells like cineol. The analysis of its phenylurethan, m. p. 56∼57°C, indicated that the alcohol was a limonenylcarbinol. The velocity of esterification of phenylacetic acid with the carbinol showed that the carbinol was a primary alcohol.

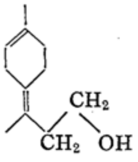
In the addition of formaldehyde to terpenes or other compounds[5], formaldehyde adds usually at an end methylene group[6] or an active methylene group[9] adjacent to a double bond. Thus it is considered that the limonenylcarbinol possesses one of structures III, IV, V, VI and VII.



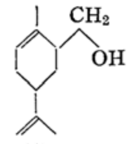
III



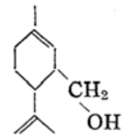
IV



V



VI



VII

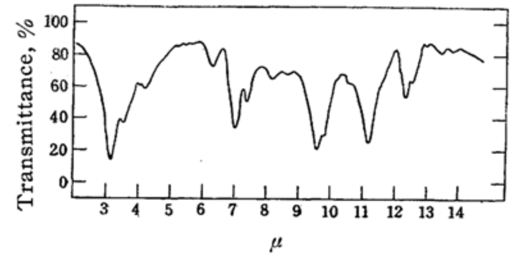


Fig. 1. The infrared absorption spectrum of the limonenylcarbinol (III).

The infrared absorption spectrum (Fig. 1) indicates the presence of a primary alcohol group (absorption peak at $9.6\,\mu$) and an end methylene group (strong band at $11.25\,\mu$), which excludes IV and V.

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[1] H. J. Prins, *Proc. Acad. Sci. Amsterdam*, **22**, 51 (1919), *J. Chem. Soc.*, **118**, 42 (1920).

[2] A. Ladenberg, *Ber.*, **31**, 289 (1898).

[3] O. Kriewitz, ibid., **32**, 57 (1899).

[4] R. Lombard, *Bull. soc. chim. France*, No. **10**, C 24 (1953), No. **11**, C 1216 (1954).

[5] E. E. Swissmann and R. A. Mode, *J. Am. Chem. Soc.*, **79**, 3447 (1957).

[6] For example, β-pinene[7], 8(9)-*p*-menthene[4] and methylenecyclohexene[8].

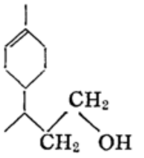
[7] J. P. Bain, *J. Am. Chem. Soc.*, **68**, 638 (1946).

[8] E. Arundale and L. A. Mikeska, *Chem. Revs.*, **51**, 505 (1952).

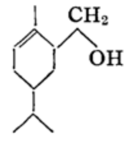
[9] For example, carvomenthene[10].

[10] H. Yonetani and H. Yamabe, *Reports of Camphor Chemists' Society* (*Shono Gijitsu Kyokai Kogi*), **20**, 109 (1955).

The optical activity ($[\alpha]_D^{10}$ +37.2) also makes V improbable. Formula III was concluded from the comparison of the infrared spectrum of the product (VIII), prepared by catalytic hydrogenation of the end methylene group of the carbinol, with that of 1(2)-*p*-menthen-6-yl-carbinol (IX) which was prepared from 1(2)-*p*-menthene and paraformaldehyde. The 1(2)-*p*-menthen-6-yl-carbinol (IX) showed remarkable doublet absorption peaks[11] at 7.2 μ (1390 cm^{-1}) and 7.3 μ (1370 cm^{-1}), and medium absorption peaks at 8.55 μ (1170 cm^{-1}) and 9.05 μ (1150 cm^{-1})[12] owing to an isopropyl radical (Fig. 2). On the other hand, the hydrogenation product from the limonenylcarbinol gave the strong single band of a methyl group at 7.25 μ, but no absorptions of an isopropyl group at 8.55 μ and 9.05 μ (Fig. 3). These results suggest the structure of 1,8(9)-*p*-menthadien-10-yl-carbinol (III) for the limonenylcarbinol.



VIII



IX

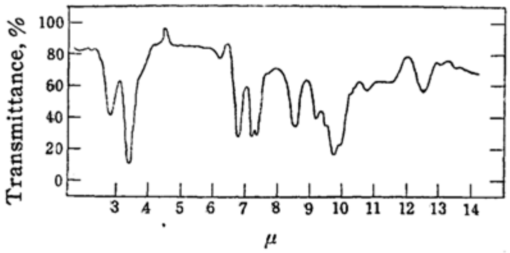


Fig. 2. The infrared absorption spectrum of 1(2)-*p*-menthen-6-yl-carbinol (IX).

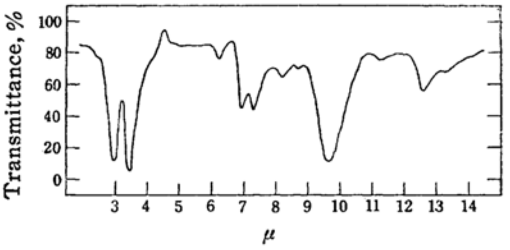


Fig. 3. The infrared absorption spectrum of 1(2)-*p*-menthen-10-yl-carbinol (VIII).

Experimental

***d*-Limonene (I)**.—Commercial *d*-limonene was distilled with a rectifying column. B. p. 64~65°C/15 mmHg; d_4^{15} 0.8494; n_D^{15} 1.4756; $[\alpha]_D^{10}$ +113°.

Reaction in a Sealed Tube.—A mixture of 20 g. (0.15 mol.) of I, 4.5 g. (0.15 mol.) of II and 10 g. of ethanol was sealed in a hard glass tube, and heated at 200~220°C for 12 hr. in an electric furnace. The reaction mixture was poured into water and extracted with ether, and the ethereal solution was washed with water and dried over anhydrous sodium sulfate. By fractional distillation, 14 g. of I and 2.8 g. of the limonenylcarbinol were obtained. B. p. 102~105°C/4 mmHg; d_4^{8} 0.9612; n_D^{12} 1.5069. Yield, 11%.

Phenylurethan.—It was prepared as usual and recrystallized from methanol. Colorless needles, m. p. 54~55°C.

Anal. Found: N, 4.79; Calcd. for $C_{18}H_{23}O_2N$: N, 4.91%.

Limonenylcarbinyl Acetate (1,8(9)-*p*-Menthadien-10-yl-carbinyl Acetate).—A mixture of 45.3 g. (0.333 mol.) of I, 10 g. (0.333 mol.) of II and 20 g. (0.196 mol.) of acetic anhydride was heated at 180~190°C for 4~5 hr. in an autoclave. The reaction mixture was washed with water and dried over anhydrous sodium sulfate. Fractional distillation gave 20.5 g. of the crude acetate. B. p. 96~106°C/4 mmHg Yield, 29.6%. It was redistilled for characterization. B. p. 103~107°C/5 mmHg; d_4^{28} 0.9618; n_D^{28} 1.4790; molecular refraction 61.38 (Calcd. for $C_{11}H_{17}O\cdot COCH_3$, F_2, 60.75).

Limonenylcarbinol (1,8(9)-*p*-Menthadien-10-yl-carbinol).—A mixture of 13 g. of the crude acetate and 6 g. of potassium hydroxide (20% aq. solution) was heated at 180°C for 4 hr. in an autoclave. After cooling, the reaction mixture was extracted with ether, and the extracts were washed with water and dried over anhydrous sodium sulfate. Fractional distillation gave 10 g. of the limonenylcarbinol in a yield of 96%. B. p. 102~106°C/4 mmHg; d_4^{17} 0.9603; n_D^{17} 1.5020; molecular refraction 51.04 (Calcd. for $C_{10}H_{15}CH_2OH$, F_2, 51.39) $[\alpha]_D^{10}$ +37.2.

Phenylurethan.—It was prepared as usual and recrystallized from methanol. Colorless needles, m. p. 56~57°C.

Anal. Found: N, 4.86. Calcd. for $C_{18}H_{23}O_2N$: N, 4.91%.

Velocity of Esterification of Phenylacetic Acid with the Limonenylcarbinol.—The nature of the hydroxyl group of the limonenylcarbinol was determined by Murahashi's method[13]. A small amount of the carbinol was heated with phenylacetic acid at 150°C for an hour in a sealed glass tube. The initial rate of esterification in an hour was found 63% showing the carbinol is a primary alcohol.

1(2)-*p*-Menthen-10-yl-carbinol (VIII).—In methanol solution 3.93 g. of the limonenylcarbinol was hydrogenated with Pd-$BaSO_4$ containing 3%

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[11] It was reported that the doublet absorption peaks of the isopropyl group are at 1362 cm^{-1} and 1378 cm^{-1}.

[12] H. L. McMurry and V. Thornton, *Anal. Chem.*, **24**, 318 (1952).

[13] E. Funakubo, "Identification of Organic Compounds, I" (Yuki Kagobutsu Kakuninho I), Yokendo, Tokyo (1951), p. 11.

Pd, and absorbed 583 cc. of hydrogen (760 mmHg, 20°C) to give 3.0 g. of VIII. B. p. 100～103°C/4.5 mmHg; n_D^{13} 1.4923.

***d*-Limonene Hydrochloride**[14,15].—In a 200 cc. three-necked flask equipped with a mechanical stirrer, a thermometer and a gas inlet tube, 100 g. of I was placed. The flask was cooled to −5°C in an ice-salt freezing mixture. Anhydrous hydrogen chloride was passed into the solution for 2 hr. The reaction mixture turned deep purple in color and sticky. It was washed with water, dried over anhydrous sodium sulfate and fractionally distilled to give a fraction of b.p. 65～68°C/4 mmHg. By redistillation 84 g. of *d*-limonene hydrochloride was obtained. B. p. 73～75°C/5 mmHg; n_D^{12} 1.4850.

1(2)-*p*-Menthene[14,16]. — Sodium (40 g.) was added gradually in an hour to a mixture of 40 g. of *d*-limonene hydrochloride and 200 g. of absolute ethanol with ice cooling. After sodium ethylate was decomposed with water, the product was extracted with ether and the ethereal solution was washed with water and dried over anhydrous sodium sulfate. By fractional distillation, 22 g. of 1(2)-*p*-menthene was obtained. B. p. 50～54°C/3.5 mmHg; n_D^{12} 1.4766.

1(2)-*p*-Menthen-6-yl-carbinol (IX). — To a mixture of 12 g. of 1(2)-*p*-menthene, 3 g. of II, 17 g. of 95% acetic acid and 4 g. of ether, cooled to −2°C, a mixture of 7 g. of 95% acetic acid and 2.5 g. of 98% sulfuric acid was added, and the mixture was agitated for 5 hr. After being allowed to stand overnight, it was extracted with ether and the ethereal solution was washed with aqueous sodium bicarbonate and with water, dried over anhydrous sodium sulfate, and fractionally distilled to give 3 g. af 1(2)-*p*-menthen-6-yl-carbinyl acetate. B. p. 90～100°C/4 mmHg; n_D^{6} 1.4860.

A mixture of 3 g. of the acetate, 4 g. of potassium hydroxide, 40 cc. of methanol and 1 cc. of water, was refluxed on a warm water bath for 3 hr. The product was extracted with ether, and the ethereal solution was washed with water and dried over anhydrous sodium sulfate. Evaporation of the ether and fractional distillation gave 2 g. of the carbinol (IX). B. p. 95～97°C/3 mmHg; n_D^{9} 1.4896.

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[14] F. W. Semmler, *Ber.*, **36**, 1036 (1903).
[15] H. Katsuragi, *Koryo*, No. **24**, 25 (1953).
[16] F. W. Semmler, *Ber.*, **40**, 2959 (1907).