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The Action of Boron Trifluoride Etherate on *l*-Menthol

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The reaction of menthol with sulfuric acid has been reported by Wagner,[1] who detected *p*-menthane and alkane, bp 178.0—180.0°C/13 mmHg, in the reaction product. Aizawa *et al.*[2] have reported that the reaction of menthyl chloride with anhydrous aluminum chloride resulted in the formation of *p*-menthane, a dimer ($C_{20}H_{36}$), 1-*p*-menthene and 3-*p*-menthene via the menthyl cation. In this work, *l*-menthol was reacted with an equimolar amount of boron trifluoride etherate at 80°C for 45 min. A light-yellow oil separated as an upper layer; it consisted of a low-boiling part and a high-boiling part. Six components were isolated from the low-boiling part by preparative gas chromatography, and one component from the high-boiling part by column chromatography.

(a) Low-boiling Component. Component (1), 3-isobutyl-1-methylcyclopentane: The molecular formula is found to be $C_{10}H_{20}$ from the mass spectrum (parent peak M^+, *m/e* 140, Fig. 1). The IR and NMR spectra showed the bands at 1384, 1368, and 1169 cm^{-1} associated with a branched dimethyl group and the signals corresponding to three methyl groups (9H) between 0.80 and 1.00 ppm (Fig. 2). This component is a saturated mono-cyclic hydrocarbon which differs from *o*-, *m*- and *p*-menthane in its IR and NMR spectra. The main peaks of *m/e* 97, 83, 69, 55, and 41 in the mass spectrum can be well explained as those of 3-isobutyl-1-methylcyclopentane, which has not previously been reported.

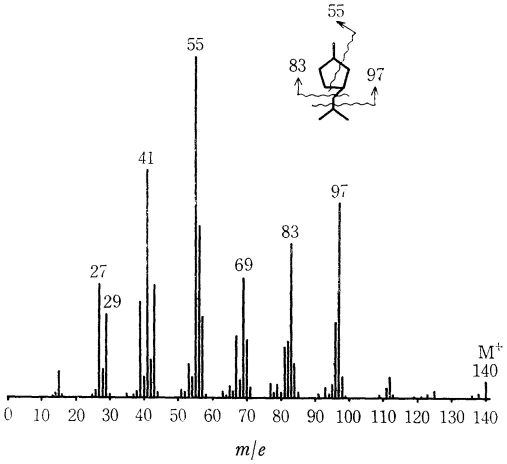

Fig. 1. Mass spectrum of 3-isobutyl-1-methylcyclopentane.

Component (2): The molecular formula is found to be $C_{10}H_{18}$ from the mass spectrum (parent peak M^+, *m/e* 138). The IR spectrum showed the bands at 1386, 1370, and 1167 cm^{-1} associated with a branched dimethyl group. The compo-

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[1] G. Wagner, *Ber.*, **27**, 1636 (1894).

[2] F. Aizawa, M. Arai and M. Yamaguchi, *Nippon Kagaku Zasshi*, **90**, 497 (1969).

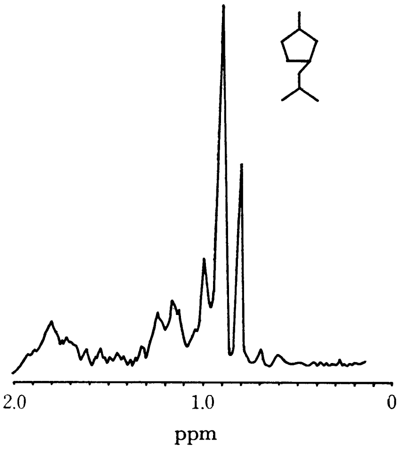


Fig. 2. NMR spectrum of 3-isobutyl-1-methylcyclopentane.

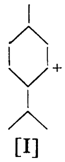
nent (2) seems to have been found to be a mixture of two compounds through careful gas chromatography using Carbowax 6000 as a stationary phase. When this component was hydrogenated in the presence of platinum oxide, it absorbed one mole of hydrogen and changed to 3-isobutyl-1-methylcyclopentane. Judging from the base peak of *m/e* 81 in the mass spectrum, this component seems to be an unsaturated five-membered ring compound having the same carbon skeleton as 3-isobutyl-1-methylcyclopentane.

Components (3), (4), (5) and (6) were identified as *trans-p*-menthane, *cis-p*-menthane, 3-*p*-menthene, and 1-*p*-menthene respectively by comparing them with authentic specimens by gas chromatography or by comparing their IR spectra and also by the preparation of nitrosochloride.

(b) High-boiling Component. A colorless and rather viscous oil was isolated from the high-boiling part by elution chromatography. The molecular formula is found to be $C_{20}H_{38}$ from the mass spectrum (parent peak M^+, *m/e* 278). Peaks at *m/e* 139 corresponding to a half of the molecular weight of this component and at *m/e* 235 ($M^+ - C_3H_7$) appeared in the mass spectrum. It was suggested that this compound was bis-menthyl.

The reaction of boron trifluoride etherate with *l*-menthol was carried out under various conditions (Experiment (1), temp. 25°C, reaction period 30 days; (2) temp. 60°C, reaction period 6.5 hr; (3) temp. 80°C, reaction period 45 min). The contents of C_{10}- and C_{20}-hydrocarbons identified in Experiment (3) were as follows: 3-isobutyl-1-methylcyclopentane 2%, 3-isobutyl-1-methylcyclopentene 1%, *trans-p*-menthane 9%, *cis-p*-menthane 2%, 3-*p*-menthene 10%, 1-*p*-menthene 2%, $C_{20}H_{38}$ 30%.

trans-p-Menthane was produced in a large quantity at room temperature (25°C), but the amount of 3-*p*-menthene increased with a rise in the reaction temperature. Also, C_{20}-hydrocarbon was



[I]

obtained in a large quantity in every experiment. It seems that 3-isobutyl-1-methylcyclopentane and 3-isobutyl-1-methylcyclopentene were formed through a ring contraction of the cation [I]. It is interesting that 3-isobutyl-1-methylcyclopentane and 3-isobutyl-1-methylcyclopentene were produced from *l*-menthol by ring contraction; these two compounds have not yet been reported.

Experimental

1. Sample. *l*-Menthol: mp 42.5—43.5°C, $[\alpha]_D^{25}$ −46.7° (in ether), phenylurethane, mp 111.0—111.5°C. The sample exhibited only one peak on gas chromatography with either Carbowax 6000 and Neopentyl glycol succinate. Neoiso-menthol which shows the same retention value at *l*-menthol, could not be detected on the basis of the IR spectrum (lack of bands, 795 and 629 cm^{-1} characteristic of the neoiso-isomer).

Boron trifluoride etherate: Commercially-available boron trifluoride ehterate (BF_3 47%) of the first grade was used.

2 Identification of the Reaction Product. Three hundred grams of *l*-menthol and 300 m*l* of boron trifluoride etherate were reacted at 80°C for 45 min; 260 g of the oil were thus obtained from the upper layer. The oil, washed with a saturated aqueous solution of sodium carbonate and water, was distilled under reduced pressure to 7 fractions. Six components were isolated from fractions (1) to (4) by preparative gas chromatography using Carbowax 6000 at 65°C.

Component (1), 3-isobutyl-1-methylcyclopentane: The component corresponding to the peak (1) on gas chromatography was a colorless oil with petroleum-like smell. The mass and NMR spectra are shown in in Figs. 1 and 2.

Component (2): This was a colorless oil with a petroleum-like smell; it corresponded to the peak (2). This oil was shown to be a mixture of two compounds by gas chromatography, but the two compounds could not be separated. When 0.5 g of the oil was hydrogenated on platinum oxide, it absorbed one molar equivalent of hydrogen and changed into 3-isobutyl-1-methylcyclopentane.

Components (3), (4), (5), and (6) were identified by the following measurements and by the preparation of derivatives. Their IR and GLC were compared with those of authentic specimens.

Component (3): *trans-p*-menthane, mol wt, 139 (Rast), Elementary analysis: $C_{10}H_{20}$, IR, GLC

Component (4): *cis-p*-menthane, IR, GLC

Component (5): 3-*p*-menthene, IR, GLC, nitrosochloride

Component (6): 1-*p*-menthene, IR, GLC, nitrosochloride

High-boiling component: The oil was isolated from the fraction (6) by passing *n*-hexane through a silica gel column. The component showed a spot of R_f 0.88

on thin-layer chromatography. Bp 145.0—145.5°C/5 mmHg, d_4^{25} 0.8829, n_D^{25} 1.4820, mol wt, 278 (mass spectrum); elementary analysis, $C_{20}H_{38}$. This component seemed, on the basis of the IR and NMR spectra, to be a saturated hydrocarbon with two separated C_6-rings and an isopropyl group.

Gas chromatography. A Shimadzu GC-2 apparatus equipped with a thermal conductivity detector was used. Carrier gas, helium; flow rate, 60 m*l*/min. For hydrocarbon analysis, Celite 545 (60—80 mesh) coated with Carbowax 6000 (30%) was used at 65°C.

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