Summary

1. The volatile oil of *Sarothra gentianoides* L. consists largely of liquid acyclic hydrocarbons, of which at least 20% is *n*-nonane, a compound which has not hitherto been found in nature.

2. In addition to *n*-nonane, there is evidence of the presence of the following: a low-boiling optically active olefin (probably an octene), unidentified terpenes and sesquiterpenes, α-terpineol, geraniol, traces of phenols, aldehydes and ketones, caproic acid and a caprylic ester.

NEW YORK, N. Y.

RECEIVED JUNE 5, 1933
PUBLISHED OCTOBER 6, 1933

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE AND THE MALLINCKRODT CHEMICAL WORKS]

Preparation and Dehydration of 4,4-Dimethylpentanol-2 (Methylneopentylcarbinol)

BY FRANK C. WHITMORE AND AUGUST H. HOMEYER[1]

The dehydration of dimethylneopentylcarbinol[2] and of methylethylneopentylcarbinol[3] gives olefins without rearrangement and with dehydration chiefly from the smaller groups. The neopentyl group shows little tendency to supply the proton in the dehydrations. The acid splitting of a C–C linkage in certain olefins having a neopentyl group attached to the ethylenic carbon has been observed.[4] Methyl neopentyl ketone reacts with sodium hypobromite as if it enolized exclusively from the methyl group.[5] Moreover, neopentylethylene adds hydrogen bromide entirely contrary to Markownikoff's rule.[6] In a further study of the neopentyl group, methylneopentylcarbinol has been prepared and dehydrated. Contrary to expectation the dehydration took place mainly from the neopentyl rather than the methyl group, the chief product being 4,4-dimethylpentene-2. No product of any rearrangement was detected.

4,4-Dimethylpentene-2 has been reported by Favorsky and Alexeeva[7,8] who gave its boiling point as 84–86°. Edgar, Calingaert and Marker[9] found that dehydration of 4,4-dimethylpentanol-3 gave a mixture of 4,4-dimethylpentene-2 and rearranged olefins. Boord and Schurman[10] pre-

---

[1] Mallinckrodt Research Fellow.

[2] Unpublished results, Whitmore and Wrenn.

[3] Whitmore and Laughlin, This Journal, **55**, 3732 (1933).

[4] Whitmore and Stahly, *ibid.*, **55**, 4153 (1933).

[5] Homeyer, Whitmore and Wallingford, *ibid.*, **55**, 4209 (1933).

[6] Unpublished results, Whitmore and Homeyer.

[7] Favorsky and Alexeeva, *J. Russ. Phys.-Chem. Soc.*, **50**, 557–570 (1918).

[8] Favorsky and Alexeeva, *C. A.*, **18**, 1466 (1924); *Chem. Zentr.*, III, 998 (1923).

[9] Edgar, Calingaert and Marker, This Journal, **51**, 1487 (1929).

[10] Boord and Schurman, Paper before the Division of Organic Chemistry, American Chemical Society, Washington, D. C., March 28, 1933.

pared 4,4-dimethylpentene-2 by dehydration of 4,4-dimethylpentanol-3 by the methyl xanthate method.

Experimental

Preparation of 4,4-Dimethylpentanol-2.—A total of 746 g. of 4,4-dimethylpentanone-2 was reduced[11] in twelve runs in moist benzene solution with sodium. The product was distilled through an 85 × 2.1 cm. packed column.[12] The fore-run from each distillation was used in the next reduction. The yield was 548 g., 72%; b. p. 137–137.5° (736 mm.); n_D^{20} 1.4188; d_4^{20} 0.8115; MR. found 36.12, calcd. 36.17.

The residue was 176 g. corresponding to 23% of the original ketone. Distillation through a 70 × 1 cm. indented column showed it to be the pinacol, 2,2,4,5,7,7-hexamethyl-octanediol-4,5: b. p. 98–100° (2–3 mm.); m. p. 34–36°. It crystallized very slowly; the index of refraction taken soon after distillation was n_D^{20} 1.461. *Anal.* Calcd. for $C_{14}H_{30}O_2$: C, 73.0; H, 13.1. Found: C, 72.6; H, 13.4. The rearrangement of this pinacol is being studied.

Derivatives of 4,4-Dimethylpentanol-2.—α-Naphthyl urethan, from petroleum ether, m. p. 86.5–87°. 3,5-Dinitrobenzoate, from dilute alcohol, m. p. 95.2–95.7°. The carbamate was prepared by converting the carbinol to the chloroformic ester with phosgene and then treating it with aqueous ammonia; m. p. 71°. *Anal.* Calcd. for $C_8H_{17}O_2N$: N, 8.81. Found: N, 8.82. The acetate distilled at 92–92.5° (90 mm.); n_D^{20} 1.4071; d_4^{20} 0.8563; MR. found 45.44, calcd. 45.30. The *tert*-butyl acetate distilled at 92–94° (7–8 mm.), n_D^{20} 1.4195. Chloral mono-(methylneopentylcarbinyl)-acetal was prepared by adding 12 g. of pure methylneopentylcarbinol to 16 g. of Eastman anhydrous chloral. An exothermic reaction occurred. On the following day the product was washed with three 50-cc. portions of water and dried over calcium chloride. The product was a colorless oil, heavier than water, n_D^{20} 1.459. Distillation was not attempted.

Dehydration of 4,4-Dimethylpentanol-2.—Two hundred and fifteen grams of the carbinol was mixed with 5.5 cc. of 100% sulfuric acid. The mixture was added to the distilling flask in 40–50 g. portions and dehydrated by distilling through a 91 × 1.4 cm. packed column.[12] Distillation was regulated by controlling the rate of heating and take-off so that the head temperature did not exceed 80°. Twenty-three cc. of water was separated from the distillate. The product was washed with sodium bicarbonate solution, dried over 5 g. of potassium carbonate and fractionated through the 91 × 1.4 cm. column at 739 mm. using a reflux ratio of 10:1.

Fraction	B. p., °C.	n_D^{20}	d_4^{20}	Wt., g.	MR. found
1	74–75.3	1.3970	0.6885	41	34.31
2	75.3–75.6	1.3970	.6892	65	34.28
3	75.6–76.2	1.3981	.6903	42	34.31

The yield of olefins was 148 g. or 82%. The residue was 36 g., consisting chiefly of the unchanged carbinol. The calculated molecular refraction of the heptenes is 34.06 (Eisenlohr's values). Similar results were obtained in another experiment.

4,4-Dimethylpentene-1, b. p. 72.35° (760 mm.), n_D^{20} 1.3911, has been prepared in this Laboratory.[6] We are indebted to C. E. Boord for the properties of 4,4-dimethylpentene-2, b. p. 76.0–76.1° (760 mm.), n_D^{20} 1.3986. From the refractive indexes it is estimated that the olefin mixture contained 82% of 4,4-dimethylpentene-2 and 18% of 4,4-dimethylpentene-1.

---

[11] Whitmore and Krueger, THIS JOURNAL, **55**, 1531 (1933).

[12] Whitmore and Lux, *ibid.*, **54**, 3451 (1932).

Ozonolysis.—Analysis of the olefin mixture by ozonolysis[13] was difficult because the ozonide was dangerously explosive. Decomposition by a boiling suspension of zinc dust was accompanied with foaming.

Formaldehyde was identified by the resorcinol–sulfuric acid test, by the Rimini-Schryver[14] test, and by its condensation product with dimethyldihydroresorcinol,[15] m. p. 185–187°. The yield of formaldehyde as determined by iodimetric titration was 5.6%.

Acetaldehyde was isolated to the extent of 25.4% as acetaldehyde–ammonia, m. p. 90°. It was also identified by the Leys test.[16]

The oil isolated from ozonolysis of 58 g. of olefin amounted to 35 g. It contained both aldehydes and acids and separation even by repeated fractionation was not satisfactory. The aldehydes were oxidized to acids by excess alkaline potassium permanganate. The acids were separated as well as possible by several distillations and converted to the amides. Trimethylacetamide, m. p. 154–155°, was obtained after four crystallizations from ethyl acetate by adding petroleum ether. The mixed melting point with a known sample showed no depression. *Tert*-butylacetamide was not obtained pure. After repeated crystallizations it melted at 124–125° and a mixture with a known sample, m. p. 131°, melted at 126–127°. A mixture of *tert*-butyl acetamide (7.5 mg.) with trimethylacetamide (5.0 mg.) melted at 123–125°.

A search for acetone in the aqueous products of ozonolysis by attempting to obtain its dibenzylidene derivatives failed. The method was checked successfully with a known 3% solution of acetone.

Summary

Reduction of methyl neopentyl ketone in moist benzene solution with sodium gave 4,4-dimethylpentanol-2 (72% yield) and 2,2,4,5,7,7-hexamethyloctanediol-4,5. Dehydration of the carbinol gave 4,4-dimethylpentene-2 and 4,4-dimethylpentene-1 in the ratio 4.5:1.

STATE COLLEGE, PENNSYLVANIA
SAINT LOUIS, MISSOURI
RECEIVED JUNE 5, 1933
PUBLISHED OCTOBER 6, 1933

---

(13) Whitmore and Church, THIS JOURNAL, **54**, 3712 (1932).

(14) Schryver, *J. Chem. Soc.*, **98** ii, 334 (1910).

(15) Weinberger, *Ind. Eng. Chem., Anal. Ed.*, **3**, 365 (1931).

(16) Leys, *J. pharm. chim.*, [6] **22**, 107 (1905); *Bull. soc. chim.*, [3] **33**, 1316 (1905); *Chem. Zentr* II, 855 (1905).