

barium methylate 1.8 g. of the D-mannosan was isolated as prisms upon crystallization from a 3:1 mixture of ethyl alcohol and ethyl acetate. The yield, phenylmannoside to mannosan, was 57%. The product was identified as D-mannosan<1,5> β <1,6> by its rotation of -127.4° in water (*c.* 1.6), and its m. p. of 210° , in agreement with the data of Knauf, Hann and Hudson.⁷ The melting point was not depressed when the substance was mixed with an authentic sample of D-mannosan<1,5> β <1,6>.

DIVISION OF CHEMISTRY
NATIONAL INSTITUTE OF HEALTH
BETHESDA, MARYLAND

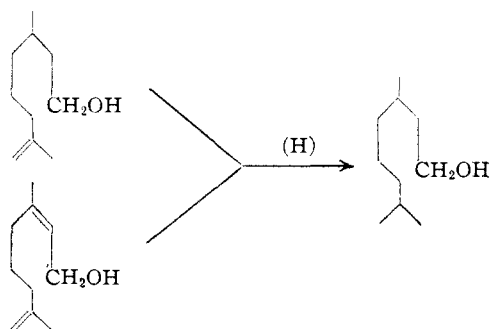
RECEIVED MAY 11, 1942

3,7-Dimethyloctene-2

BY SAMUEL NATELSON, SIDNEY P. GOTTFRIED AND
SEYMOUR KORNBLAU

The diterpenes of the citronellol and geraniol family are of interest in the possible synthesis of cholesterol and related products such as the anti-rachitic vitamin. They possess the side chain of cholesterol and two extra carbon atoms.

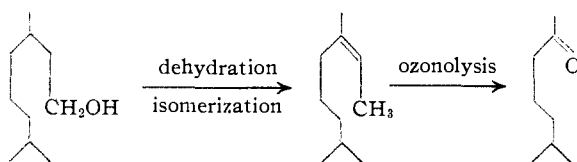
As a preliminary study citronellol and geraniol were reduced catalytically to 3,7-dimethyloctanol-1.



Methods for dehydrating large amounts of this material were studied. After some experimentation it was found that the 3,7-dimethyloctanol-1 could be dehydrated readily in a catalytic chamber with a small amount of phosphorus pentoxide at a temperature above 180° . The distillate was found to be different from that reported by Braun and Teffert for 3,7-dimethyloctene-1.¹ Elementary analysis showed it to be isomeric with 3,7-dimethyloctene-1. That the product had one double bond was shown by its iodine number and titration with benzoyl hydrogen peroxide. The oxide derivative was isolated.

The main product of the reaction after ozonolysis was found to be methyl isohexyl ketone. This was identified by the preparation of the semicarbazone and elementary analysis of the ketone and semicarbazone. This product could only have

been formed if the double bond had shifted, during the process, from the terminal position to the tertiary position.



The fore-runnings of the fractionation of the unsaturated hydrocarbon, b. p. $159-162^\circ$, were ozonized to get an idea of its composition. The product of ozonolysis was found to consist mainly of methyl isohexyl ketone. In addition, an appreciable amount of product after ozonolysis was found to boil at a higher temperature than the methyl isohexyl ketone and a residue was observed. This higher boiling fraction was not obtained on ozonizing the main fraction; b. p. $162-163^\circ$. This higher boiling fraction was not identified.

Experimental

Dimethyloctanol-1.—The dimethyloctanol was prepared by reduction of geraniol with a platinum oxide catalyst in the standard reducing machine at three atmospheres. It was also prepared by reduction with Raney nickel at 100° at twenty atmospheres,² b. p. $113-114^\circ$ (7 mm.); d^{20} 0.8362; n_D^{20} 1.4433.

3,7-Dimethyloctene-2.—Twenty grams of phosphorus pentoxide was placed in a Claisen distilling flask, fitted with a dropping funnel leading to the bottom and a thermometer. The flask was placed in an oil-bath so that the bulb of the flask was completely immersed. The side arm was attached to an air condenser. The temperature of the oil-bath was raised to $200-210^\circ$ and 20 cc. of the dimethyloctanol was added slowly; 1000 g. of dimethyloctanol was then added drop by drop at the same rate that the decylene and water distilled over. The distillate came over between $160-180^\circ$ and was transferred to a separatory funnel and the lower water layer removed. The oily layer was washed with dilute bicarbonate, then water and finally dried over anhydrous sodium sulfate. On distillation 810 g. of a product boiling from $159-163^\circ$ was obtained. On fractionation with a Vigreux column (2 ft.) 600 g. of a product boiling from $162-163^\circ$ (761 mm.) was obtained; b. p. $162-163^\circ$; d^{24} 0.7501; n_D^{25} 1.4258. *Anal.* Calcd.: C, 85.63; H, 14.37; iodine no., 181.3. Found: C, 85.77; H, 14.42; iodine number, 191.

Methyl Isohexyl Ketone.—3-5% ozone was passed through a mixture of 20 g. of 3,7-dimethyloctene-2 with 30 cc. glacial acetic acid until a test sample did not decolorize bromine in carbon tetrachloride. The mixture was then dissolved in 150 cc. of ether, and 20 g. of zinc dust was added. The mixture was cooled in an ice and salt bath, 20 cc. of water was added slowly with vigorous stirring. Stirring was continued until a test with potassium iodide

(1) Braun and Teffert, *Ber.*, **62**, 235-241 (1929).

(2) Dimethyloctanol is commercially available. The authors are grateful to Dr. Arthur Wendt of Seeley and Co., New York, N. Y., for large samples of this material.

paper showed no presence of peroxides. The mixture was diluted with a large volume of water. The ether layer was separated and washed once with water. The ether was evaporated and the residue was dissolved in an equal volume of petroleum ether. Fifty cc. of saturated sodium bisulfite solution was added and the mixture was shaken on a shaking machine for two hours. The bisulfite addition product was washed well with petroleum ether, transferred to a separatory funnel and well shaken with 200 cc. of 10% sodium carbonate solution until all the solid material dissolved. The mixture was extracted with petroleum ether. The petroleum ether layer was dried and the solution was fractionated, collecting the material from 168-171°; yield 9 g.; d^{20}_D 0.8149; n^{20}_D 1.4150. *Anal.* Calcd.: C, 74.98; H, 12.59. Found: C, 74.60; H, 12.54.

Methyl Isohexyl Ketone Semicarbazone.—One gram of the ketone was dissolved in 5 cc. of alcohol and floated on 5 cc. of a solution containing 1 g. of semicarbazide hydrochloride and 1 g. of sodium acetate. The tube was heated to 60° and the contents rapidly mixed. On cooling, a heavy crystalline precipitate of the semicarbazone was obtained and filtered off. The product was recrystallized from dilute alcohol; m. p. 146-147°. *Anal.* Calcd.: C, 58.35; H, 10.34. Found: C, 58.38; H, 10.00.

3,7-Dimethyloctene-2 Oxide.—0.33 mole of benzoyl hydrogen peroxide in 635 cc. of chloroform was added slowly to 40 g. of the hydrocarbon at 0°, and the mixture was allowed to stand overnight at 0°. Titration showed that 0.30 mole of the benzoyl hydrogen peroxide had been used (one double bond). The solution was washed with dilute sodium carbonate, dried over anhydrous potassium carbonate. The chloroform was recovered and the residue was distilled; yield 40 g. of a product boiling from 179-183°; d^{23}_D 0.8183; n^{26}_D 1.4290.

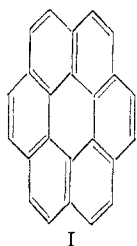
PEDIATRIC RESEARCH LABORATORY
JEWISH HOSPITAL OF BROOKLYN
BROOKLYN, N. Y.

RECEIVED MARCH 3, 1942

The Ultraviolet Absorption Spectra of Coronene

BY JOHN W. PATTERSON

Coronene, I, is the simplest hydrocarbon in which benzene rings completely surround a central aromatic nucleus. It is the most symmet-



rical of the more complex aromatic hydrocarbons and as such its absorption spectrum is of particular interest.

The sample, which was kindly furnished by Dr. Newman¹ was a synthetic preparation of greater

(1) Newman, *THIS JOURNAL*, **62**, 1683 (1940).

TABLE I

POSITIONS	AND INTENSITIES OF BANDS IN CORONENE		
Fresnels, f.	Wave number, cm. ⁻¹	Wave length, m μ	Extinction, log ₁₀ E molar
697	23,200	431	2.23
710	23,600	422	2.15
730	24,300	411	2.60
743	24,700	404	2.50
770	25,600	389	2.50
785	26,100	382	2.49
795	26,400	377	2.49
844	28,000	355	3.00
863	28,700	347	4.06
880	29,300	441	4.74
895	29,800	335	4.21
920	30,600	326	4.35
950	31,600	316	4.40
985	32,800	305	5.44
1002	33,400	299	4.98
1025	34,100	293	4.87
1065	35,400	282	4.29

purity than has hitherto been available. In making the ultraviolet absorption measurements, it was necessary to use chloroform as a solvent,

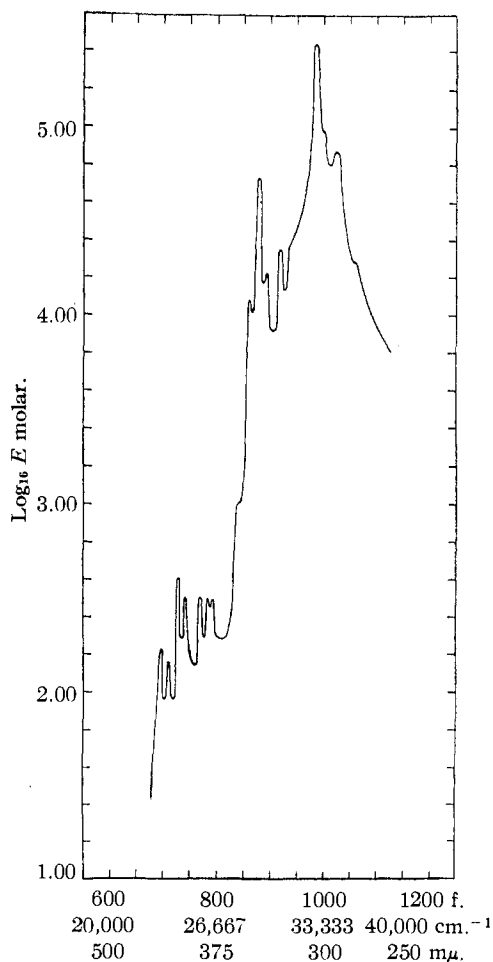


Fig. 1.—Ultraviolet absorption spectra of coronene.