ated polymers had molecular weights of not more than 2000–4000.

In the same way, the polymer produced by boron fluoride was fractionated in acetone solution. Nearly colorless polymers (gummy at room temperature) were obtained in 20–25% yield.

The polymerization of N-methylpropylenimine in the presence of triisobutylaluminum failed, while triethylaluminum at 80° in the atmosphere of nitrogen gave 10–20% conversion in one month.

In other experiments, copper phenyl[11] and silver phenyl[12] were used as possible catalysts for the polymerization of N-methylpropylenimine. However, the compounds showed practically no effect on polymerization other than to turn the monomer suspensions dark brown or black.

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[11] R. Reich, *Compt. rend.*, **177**, 322 (1923).

[12] E. Krause and B. Wendt, *Ber.*, **56**, 2064 (1923).

PHILADELPHIA 4, PENNA.

[CONTRIBUTION FROM THE TRUBEK LABORATORIES]

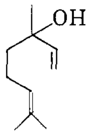
The Structure of the Alcohol Obtained by the Hydration of Myrcene

BY WILLIAM J. HOULIHAN,[1] JOSEPH LEVY AND JOSEF MAYER

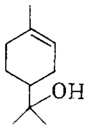
RECEIVED JANUARY 15, 1959

Evidence is brought forward that myrcenol is most likely 3-methylene-7-methyl-1-octen-7-ol. Tetrahydromyrcenol has been shown by synthesis to be identical with DL-2,6-dimethyl-2-octanol.

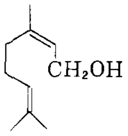
The alcohol, $C_{10}H_{18}O$, obtained by the sulfuric acid-catalyzed addition of acetic acid to myrcene (I) and subsequent hydrolysis of the intermediate ester, has been the subject of investigation by a number of workers.[2–6] Power and Kleber,[2] the first of these, concluded that this alcohol was identical with linalool. Barbier,[3] however, maintained that the alcohol was not linalool but a new isomeric alcohol called myrcenol. From a study of the products from dichromate oxidation he incorrectly assigned structure[7] IX to myrcenol.



IX



X



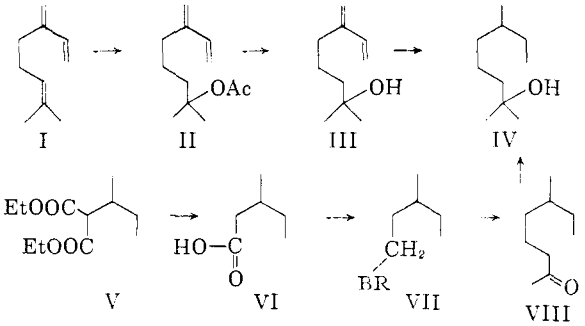
XI

A reinvestigation of the alcohol by Semmler[4b,c] and co-workers led them to conclude that myrcenol was not a single alcohol but a mixture of linalool and α-terpineol (X). However, Enklaar[5] isolated a phenylurethane from myrcenol that differed from that of linalool, α-terpineol or the isomeric geraniol (XI), thereby indicating that myrcenol was a distinct alcohol of unknown structure. Recently, Milas[6] in a patent states that the acid-catalyzed addition of acetic acid to myrcene furnishes a mixture of the acetates of linalool and geraniol.

Since myrcenyl acetate has value as an odorant it became of interest to determine the structure of this substance. We wish to present evidence that myrcenol is 3-methylene-7-methyl-1-octen-7-ol (III).

The treatment of myrcene with a cold acetic-sulfuric acid mixture gave an acetate fraction in *ca.* 25% yield. Careful distillation of this material gave a monoacetate of composition $C_{12}H_{20}O_2$. The ultraviolet spectrum of this compound was identical with the spectrum of myrcene. Saponification of the acetate with ethanolic sodium hydroxide afforded an alcohol, $C_{10}H_{18}O$, in 75% yield. Its ultraviolet spectrum also exhibited the same characteristic myrcene curve. The infrared spectrum showed a band at 8.35 μ which can be assigned[8] to a tertiary C–O absorption. The treatment of this alcohol with active manganese dioxide under controlled conditions failed to furnish an aldehyde or ketone. Geraniol (XI) under identical conditions gave a 69% yield of citral. On the basis of the above physical and chemical information the structure of the $C_{10}H_{18}O$ alcohol, myrcenol, can best be represented by III and that of myrcenyl acetate as II.

The gross skeleton of myrcenol was established by catalytic reduction to tetrahydromyrcenol which was identical with DL-2,6-diethyl-2-octanol (IV).



The synthesis of IV was accomplished by starting with diethyl *sec*-butyl malonate (V). The saponification and decarboxylation of this compound gave DL-3-methylpentanoic acid (VI). Lithium aluminum hydride reduction of VI gave

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[1] Department of Chemistry, Seton Hall University, South Orange, N. J.

[2] Power and Kleber, *Pharm. Rundschau* (*N. Y.*), **13**, 60 (1895).

[3] P. Barbier, *Bull. soc. chim. France*, [III] **25**, 688 (1901).

[4] (a) O. Tiemann and F. W. Semmler, *Ber.*, **28**, 2126 (1895); (b) F. W. Semmler, *ibid.*, **34**, 3128 (1901); (c) F. W. Semmler and E. W. Mayer, *ibid.*, **44**, 2009 (1911).

[5] P. Enklaar, *Rec. trav. chim.*, **26**, 167 (1907).

[6] N. A. Milas, U. S. Patent 2,467,330, April 12, 1949.

[7] This structure has been rigorously proved (by synthesis) to be the correct structure for linalool; *cf.* L. Ruzicka and P. Fornasir, *Helv. Chim. Acta*, **2**, 182 (1919).

[8] The C–O absorption band for *t*-butyl alcohol is reported as 8.3 μ; *cf.* H. H. Zeiss and M. Tsutsui, THIS JOURNAL, **75**, 897 (1953).

DL-3-methylpentanol which was converted to DL-1-bromo-3-methylpentane (VII) by treatment with a hydrobromic–sulfuric acid mixture. The alkylation of ethyl acetoacetate with VII gave a keto-ester that was not isolated but saponified and decarboxylated to DL-6-methyl-2-octanone (VIII). The reaction of this ketone with methylmagnesium iodide under standard Grignard conditions gave DL-2,6-dimethyl-2-octanol (IV). The infrared spectrum of IV was identical with that of tetrahydromyrcenol. A phenylurethan obtained from IV also failed to depress the phenylurethane obtained from tetrahydromyrcenol.

Experimental[9,10]

Myrcene (I).—The myrcene used below came from two sources.

A. Thermal Isomerization of β-Pinene.—This material was obtained from the Glidden Co., Naval Stores Division, Jacksonville 1, Fla. It is reported by Glidden to have a myrcene content of 75% with the remainder mainly limonene and unisomerized β-pinene. Distillation gave material of b.p. 165–169°, $n^{20}\mathrm{D}$ 1.4727, $d^{20}{}_{20}$ 0.8017, $\lambda_{\max}^{\mathrm{EtOH}}$ 225 mμ (ε 11, 850), $[\alpha]^{25}\mathrm{D}$ −13° (1 dm., liquid). The values reported[11,12] for pure myrcene are b.p. 65° (20 mm.), 64–65° (14.0 mm.), $n^{20}\mathrm{D}$ 1.4697, 1.4700, $d^{20}{}_{4}$ 0.7905, 0.79303; $\lambda_{\max}^{\mathrm{iso}}$ 225 (17,038), 225 (21,100).

B. Dehydration of DL-Linalool.[13]—The procedure of Arbusow[14] and Abranow was followed.

From DL-linalool (325 g., 2.11 moles) there was obtained 178 g. (41%) of myrcene, b.p. 67–68° (18.0 mm.), $n^{20}\mathrm{D}$ 1.4700, $d^{20}{}_{20}$ 0.7940; $\lambda_{\max}^{\mathrm{EtOH}}$ 225 mμ (ε 16,065). The infrared spectrum showed bands at 5.57, 6.08, 6.23, 10.09 and 11.23 μ.

The maleic acid adduct had m.p. 123–124° (petr. ether); lit.[15] gives m.p. 124–125°.

Addition of Acetic Acid to Myrcene. General Procedure.—A solution of myrcene (136 g., 1.0 mole), acetic acid (408 g., 6.8 moles) and hydroquinone (1.0 g.) was cooled to an internal temperature of *ca.* 10°. Concd. sulfuric acid (3 g.) was added with stirring in *ca.* 15 min. The solution turned pale red during the addition. The mixture was stirred an additional 7 hr., the temperature being maintained at 10 ± 5°. Sodium acetate (6 g.) was then added and the mixture distilled.

A. (Myrcene) from β-Pinene. From 1360 g. (10 moles) there was obtained 410 g. of acetate fraction, b.p. 86–90° (3.0 mm.), $n^{20}\mathrm{D}$ 1.4600–1.4662. Distillation under a nitrogen atmosphere gave (wt., g.; b.p. at 2.0 mm.; $n^{20}\mathrm{D}$; $\tau_{\max}^{\mathrm{EtoH}}$ 225 mμ): (1) 9.4, 74.2–77.4°, 1.4620; (2) 174.7, 77.4–77.5°, 1.4594–1.4595, 10, 195; (3) 112.6, 77.5–77.8°, 1.4595–1.4600, 10, 235; (4) 65.0, 77.8–79.3°, 1.4601–1.4604, 10, 200; and (5) 41.0, 79.3–82.0°, 1.4632–1.4646, 3, 815.

Fraction 3 (19.7 g., 0.10 mole) in toluene (50 ml.) was treated with maleic anhydride (9.8 g., 0.10 mole) and allowed to stand overnight at room temperature. Distillation gave (1) 6.0 g. of b.p. 68–70° (0.4 mm.), $n^{20}\mathrm{D}$ 1.4682, and (2) 21 g. of myrcenyl acetate–maleic anhydride adduct, b.p. 168–178° (0.6 mm.; dec.), $n^{20}\mathrm{D}$ 1.4960. Fraction 1 was found by infrared to be identical with α-terpinyl acetate, b.p. 93–94° (5.0 mm.), $n^{20}\mathrm{D}$ 1.4693.

Several other attempts[16] to separate the α-terpinyl acetate (by distillation) also failed.

B. (Myrcene) from DL-Linalool.—From 136 g. (1.0 mole) there was obtained 29.5 g. of acetate fraction, b.p. 116–120° (22.0 mm.), $n^{20}\mathrm{D}$ 1.4602. Distillation gave 21.5 g. of myrcenyl acetate, b.p. 116–118° (22.0 mm.), $n^{20}\mathrm{D}$ 1.4590, $d^{20}{}_{20}$ 0.9309, $\tau_{\max}^{\mathrm{EtOH}}$ 225 mμ (ε 15, 100); infrared (liquid) gave characteristic bands at 5.78, 6.08, 6.23 and 11.17 μ. This material was used in the following experiments.

Myrcenol (III).—A solution of myrcenyl acetate (9.8 g., 0.05 mole), ethanol (95%, 89 ml.) and sodium hydroxide (4 g., 0.1 mole) was refluxed under a nitrogen atmosphere for 5 hr. After cooling to room temperature water (150 ml.) was added and the organic layer separated. The water layer was washed with hexane (15 ml.) and the combined organic layers dried with magnesium sulfate. Distillation gave 6.0 g. (78%) of myrcenol, b.p. 105–6° (15 mm.), $n^{20}\mathrm{D}$ 1.4490, $d^{20}{}_{20}$ 0.9025, $\tau_{\max}^{\mathrm{EtOH}}$ 225 mμ (ε 15,500), infrared (film) 2.95, 5.55, 6.10, 6.26, 8.35, 10.10 and 11.05–11.20 μ.

Several unsuccessful attempts were made to obtain a phenylurethane.

Manganese Dioxide Oxidations.—A slurry of active manganese dioxide (2.0 g.), myrcenol (0.4 g.) and dry heptane (20 ml.) was stirred at room temperature for *ca.* 3 hr. The oxide was filtered off and washed with heptane (20 ml.). The combined heptane fractions were allowed to evaporate and the residue taken up in ethanol (5 ml.) and treated with 2,4-dinitrophenylhydrazine reagent[17] (20 ml.). No precipitate was obtained. In a similar experiment geraniol gave a 68% yield of citral 2,4-dinitrophenylhydrazone. Linalool under the above conditions also failed to give any carbonyl material.

DL-3-Methylpentanoic Acid (VI).—The procedure of Adams[18] and Marvel was followed. From diethyl *sec*-butyl malonate[19] (434 g., 2.0 moles) there was obtained 98 g. (42%) of DL-3-methylpentanoic acid, b.p. 194–197°, $n^{20}\mathrm{D}$ 1.4160, $d^{20}{}_{20}$ 0.9284; *MR* obsd. 31.26, calcd. 31.56; lit.[20] b.p. 197.5–198.4°.

DL-3-Methylpentanol.—To a freshly prepared slurry of lithium aluminum hydride (38 g., 1.0 moles) in ether (650 ml.) was added with stirring in 5 hr. a solution of DL-3-methylpentanoic acid (127 g., 1.1 moles) and ether (250 ml.). The reaction was allowed to stand overnight at room temperature. Ethyl acetate (50 ml.) was added followed by 8% sulfuric acid until a clean separation of salts occurred. The salts were filtered off and digested twice with ether (100 ml.). The combined ether layers were dried, filtered and distilled through an 8-in. packed column. There was obtained 75 g. (67%) of DL-3-methylpentanol, b.p. 156–159°, $n^{20}\mathrm{D}$ 1.4169, $d^{20}{}_{20}$ 0.8402; *MR* obsd. 30.65, calcd. 31.45, lit.[21] reports for DL-, b.p. 152.3–153°. This showed the characteristic hydroxyl band at 2.98 μ.

DL-1-Bromo-3-methylpentane (VII).—To a solution of 48% hydrobromic acid (92 g., 0.55 moles) and concd. sulfuric acid (25 g.) there was added with stirring (in 0.5 hr.) DL-3-methylpentanol (51 g., 0.5 mole). The mixture was stirred and refluxed for 3 hr. and then allowed to stand overnight at room temperature. The organic layer was separated and washed successively with water (100 ml.), concd. sulfuric acid (50 ml.) and satd. sodium bicarbonate until neutral to litmus. The crude bromide was dried with calcium chloride, filtered, and then distilled through a 6-in. packed column. There was obtained 40 g. (49%) of DL-1-bromo-3-methylpentane or b.p. 148–149°, $n^{20}\mathrm{D}$ 1.4496, $d^{20}{}_{20}$ 1.1711; *MR* obsd. 37.80, calcd. 37.69.

DL-6-Methyl-2-octanone (VIII).—Ethyl acetoacetate (43 g., 0.33 mole) was added rapidly to a solution of sodium (7.7 g., 0.33 g.-at.) in absolute ethanol (150 ml.). The solution was brought to reflux and DL-1-bromo-3-methylpentane (41 g., 0.25 mole) added in 1 hr. The reaction mixture was refluxed an additional 6 hr. and then allowed to stand overnight at room temperature. The bulk of the alcohol was removed and to the residue was added 5% sodium hydroxide (250 ml.). The mixture was refluxed 2 hr., cooled to *ca.* 25° and then treated carefully (foaming) with 50% sulfuric acid (25 ml.). Steam distillation gave 21 g. of crude ketone that furnished on fractionation 19.9 g. (57.5%) of DL-6-methyl-

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(9) All melting points are uncorrected.

(10) The microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, 56-19 37th Av., Woodside 77, N. Y.

(11) R. T. O'Connor and L. A. Goldblatt, *Anal. Chem.*, **26**, 1726 (1954).

(12) G. Ohloff, *Ber.*, **90**, 1554 (1957).

(13) Obtained from Hoffmann La Roche and Co., Nutley, N. J.

(14) B. A. Arbusow and W. S. Abranow, *Ber.*, **67**, 1942 (1934).

(15) L. A. Goldblatt and S. Palkin, THIS JOURNAL, **63**, 3517 (1941).

(16) Attempts to remove the terpineol impurities by distillation of the alcohol or tetrahydromyrcenol also failed. The authors wish to thank Dr. William C. Meluch and Mr. Rudolph Weber for carrying out this work.

(17) R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 3rd ed., p. 171.

(18) R. Adams and C. S. Marvel, THIS JOURNAL, **42**, 316 (1920).

(19) Prepared according to the procedure of C. S. Marvel in "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., p. 495.

(20) S. C. J. Olivier, *Rec. trav. chim.*, **55**, 1027 (1937).

(21) H. Bohnsack, *Ber.*, **74B**, 1575 (1941).

2-octanone,[22] b.p. 61–62° (7 mm.), n^{20}_D 1.4230, d^{20}_{20} 0.8328; *MR* obsd. 43.61, *calcd.* 43.81. A characteristic carbonyl band at 5.82 μ was shown in the infrared spectrum by this material.

The product gave a yellow 2,4-dinitrophenylhydrazone, m.p. 61.8–62.3° (ethanol), and a semicarbazone, m.p. 131.5–132.5° (ethanol).

DL-2,6-Dimethyl-2-octanol (IV). (A) Grignard Reaction on DL-6-Methyl-2-octanone.—A Grignard reagent was prepared from methyl iodide (14.2 g., 0.1 moles) and magnesium shavings, (3.65 g., 0.15 moles) in ether (200 ml.). With stirring added DL-6-methyl-2-octanone (10 g., 0.07 mole) in ether (50 ml.) over 1 hr. Stirred an additional 2 hrs. and then added satd. ammonium chloride until a clean separation of salts occurred. The salts were filtered and washed with ether (50 ml.). The combined ether layers were dried, filtered and distilled. There was obtained 7.0 g. (62.4%) of DL-2,6-dimethyl-2-octanol,[23] b.p. 75–76° (7.0 mm.), n^{20}_D 1.4336, d^{20}_{20} 0.8273; *MR* obsd. 49.57, calcd. 49.93. A characteristic hydroxyl band at 2.96 μ in the infrared spectrum was shown by this product.

Anal. Calcd. for $C_{10}H_{22}O$: C, 75.83; H, 13.92. Found: C, 75.32; H, 13.61.

There was obtained a phenylurethane of m.p. 84.0–85.0° (petr. ether).

Anal. Calcd. for $C_{16}H_{27}NO_2$: C, 73.60; H, 9.81; N. 5.29. Found: C, 73.61; H, 9.24; N, 5.61.

B. Reduction of Myrcenol.—Myrcenol (15.4 g., 0.10 mole) in absolute ethanol (70 ml.) was hydrogenated in the presence of 5% platinum–charcoal catalyst (0.5 g.) at room temperature and 3 atm. After the hydrogen uptake had ceased (2.5 hr., 98% theory) the catalyst was filtered off and the filtrate distilled through the modified Podbielniak column. There was obtained 13.4 g. (85%) of tetrahydromyrcenol, b.p. 83° (12.0 mm.), n^{20}_D 1.4332, d^{20}_{20} 0.8275. The infrared spectrum was identical with the spectrum of authentic DL-2,6-dimethyl-2-octanol. A phenylurethane, m.p. 83.5–84.5°, failed to depress a sample of authentic DL-2,6-dimethyl-2-octanol phenylurethan.

Acknowledgments.—The authors wish to express their appreciation to Dr. David Davidson of Brooklyn College for valuable discussions during the course of this work. We are also grateful to Mr. Erwin Sommer of our analytical department for infrared and ultraviolet determinations.

East Rutherford, N. J.

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[22] Sutherland has obtained a partially active 6-methyl-2-octanone b.p. 70–71° (10 mm.), n^{25}_D 1.420, d^{25}_4 0.822, $[\alpha]_D$ +1.4° (not optically pure) by the ozonolysis of partially active 2,6-dimethyloctene-1. He also reports a 2,4-dinitrophenylhydrazone, m.p. 61–62°, and semicarbazone, m.p. 130.5–131.5°. The above constants and the derivatives are in excellent agreement with the DL-isomer in this work. M. D. Sutherland, This Journal, **75**, 5945 (1953).

[23] Sutherland, *cf.* ref. 22, has reported a partially active 2,6-dimethyl-2-octanol. This alcohol was obtained from a chloride prepared from 2,6-dimethyl-2-octene, $[\alpha]^{25}_D$ +2.44°. He reports b.p. 80.5° (10 mm.), n^{25}_D 1.4220, d^{25}_4 0.8023, phenylurethan, m.p. 83–83.5°.

[Contribution from the Noyes Chemical Laboratory, University of Illinois]

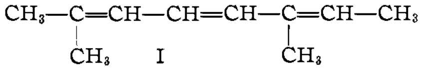
Polyalloöcimene[1]

By C. S. Marvel, P. E. Kiener[2] and E. D. Vessel

Received March 27, 1959

Alloöcimene has been polymerized to a linear soluble polymer by use of triisobutylaluminum–titanium tetrachloride catalyst. The tentative structure and some properties of the polymer are discussed.

The recent note by Jones[3] describing the acid-catalyzed cyclopolymerization of alloöcimene (2,6-dimethyl-2,4,6-octatriene) (I) has prompted us to report work which has been done in this Laboratory on the polymerization of this triene by a triiosbutylaluminum–titanium tetrachloride catalyst system. In view of the published work on this catalyst system,[4] it is surprising that such a substituted triene can be converted to a high polymer with this catalyst.



$$CH_3-\underset{CH_3}{C}=CH-CH=CH-\underset{CH_3}{C}=CH-CH_3$$

I

Alloöcimene which has been distilled over sodium in a nitrogen atmosphere readily polymerizes in heptane solution containing a catalyst prepared from a solution of three moles of triisobutylaluminum to one mole of titanium chloride. The polymerization goes best at about −15° and yields a white, fibrous, soluble polymer melting over the range of 120-154° which has an inherent viscosity of 1.0-1.2. The polymer is sensitive to oxygen, but if stablized with a little phenyl-β-naphthlyamine it can be stored for as much as a year without change as evidenced by the infrared spectrum.

Titration of the polymer with perbenzoic acid has demonstrated that two double bonds remain in the polymer for each ten carbon recurring units. The infrared spectrum shows strong bands at 970-965 cm.$^{-1}$ which are characteristic of *trans*-olefins and also at 1660-1650 cm.$^{-1}$ which are characteristic of double bonds. The ultraviolet spectrum of the polymer shows a λ_{max} at 245 mμ with an extinction coefficient of 5549. This λ_{max} is somewhat higher than would be expected for a simple conjugated system of double bonds which usually shows a λ_{max} of 232. The low extinction coefficient supports the view that this conjugated structure does not occur in every recurring unit.

Pyrolysis of a sample of the polymer by heating it to 205–210° gave about a 70% yield of alloöcimene which was identified by its infrared absorption spectrum.

Ozonolysis of the polymer gave 57-58% of the theoretical yield of acetone and 22% of the theoretical yield of glyoxal based on a C_{10} recurring unit. There was also obtained a low molecular weight polyaldehyde (inherent viscosity 0.05) corresponding to the composition (C_5H_8O). The yield of acetone is such that it seems probable the isopropylidene group is not affected by the polymerization.

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[1] This is a partial report of work done under contract with three Utilization Research and Development Divisions, Agricultural Research Service, U. S. Department of Agriculture, and authorized by the Research and Marketing Act. The contract was supervised by Dr. J. C. Cowan of the Northern Division.

[2] Fellow, Fundacion Creole, Caracas, Venezuela.

[3] J. F. Jones, *J. Pclymer Sci.*, **33**, 513 (1958).

[4] For a review, see J. K. Stille, *Chem. Revs.*, **58**, 550 (1958).