

1,9-dichlorononane via the dinitrile melted at 110°, and a mixed melting point showed no depression.

To a solution of 222 mg. of 11,12-dihydroxystearic acid, m. p. 93–94°, prepared from vaccenic acid, in 15 ml. of alcohol was added a solution of 182 mg. of periodic acid in 15 ml. of water. The solution was stirred up at room temperature for twenty minutes, then diluted with 150 ml. of water, and thoroughly extracted with ether. The ether solution was worked up as described above, and *n*-heptaldehyde semicarbazone was obtained. The yield of heptaldehyde was 58%. The sodium bisulfite addition product of the aldehyde acid fragment was precipitated as before, and was obtained in 52% yield. This product was unfortunately lost before it could be further examined.

Summary

cis-11-Octadecenoic and *trans*-11-octadecenoic (vaccenic) acids have been synthesized in good yield by condensation of 1-octyne with 1-chloro-9-iodonane, conversion of the resulting 1-chloro-10-heptadecyne, via the nitrile, to the acid, and partial hydrogenation of the acetylenic bond. The above synthesis yielded only the *cis* form which was isomerized to the *trans* form with selenium.

MADISON, WISCONSIN

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF MARYLAND]

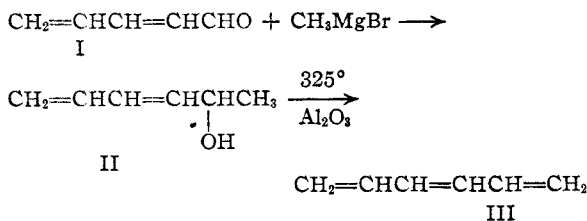
1,3,5-Hexatriene

By G. FORREST WOODS AND LOUIS H. SCHWARTZMAN¹

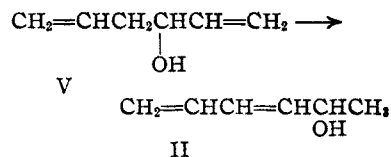
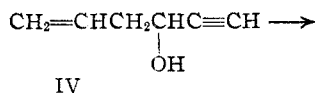
As Farmer and co-workers indicate,² 1,3,5-hexatriene is still of interest, inasmuch as (1) it is the simplest conjugated triene, and (2) its structure predicts two geometrical isomers, the *cis* form being the open chain analog of benzene.

1,3,5-Hexatriene has been prepared by (1) pyrolysis of *s*-divinylglycol diformate,³ (2) condensation of allyl chloride with sodamide,⁴ (3) phthalic anhydride dehydration of 1,5-hexadiene-3-ol⁵ and (4) debromination of 3,4-dibromohexadiene-1,5 with zinc.² The product in method (3) contained cyclohexadiene, and the purification of the substance seems to have been incomplete in all cases.^{3,5,6}

2,4-Pentadienal⁷ is an excellent starting material for the preparation of 1,3,5-hexatriene, as shown by the following reactions



Heilbron, *et al.*,⁸ prepared (II) by rearrangement of propenylvinylcarbinol (V), a partial reduction product of propenylethynylcarbinol (IV)



We made 1,3-hexadien-5-ol (II) as shown and its properties agree excellently with those reported by Heilbron, *et al.*,⁸ who identified it by reduction to the saturated alcohol, oxidation of the saturated alcohol to hexanone-2 and comparison with known samples.

Catalytic dehydration at reduced pressures of the 1,3-hexadien-5-ol over alumina in a nitrogen atmosphere gave a 60% yield of the hydrocarbon boiling at 79–80° and crystallizing on cooling below –12°; it absorbed three moles of hydrogen with Adams catalyst at room temperature and pressure. Crystallization of the unsaturated hydrocarbon at low temperature is an important step, since it assures good purification and gives a single sharp melting substance, apparently one of the geometric isomers. Van Romburgh and Mueller³ also obtained 1,3,5-hexatriene in solid state (m. p. –11°) by converting the impure hexatriene to pure dibromide, and debrominating it with zinc in boiling alcohol (*cf.* Farmer, *et al.*²). Table I contains collected data of various investigators for ready comparison. The refractive indices show wide variations; only Farmer, *et al.*, have reported analyses previously and their values fit more closely the formula C₆H₁₀ than C₆H₈.

The dipole moment⁹ of 1,3,5-hexatriene in benzene is 0.2D. If an atomic polarization value larger than 5% of the electronic polarization is assumed, then this small value might indicate a zero dipole moment, but an examination of models of both *cis* and *trans* forms shows that neither should have a zero moment. Thus this measurement gives no convincing evidence on geometrical structure.

(9) The authors are indebted to Prof. W. J. Svirbely for aid both in the determination of the dielectric constant and in the interpretation of this measurement.

- (1) National Institute of Health Predoctorate Research Fellow.
- (2) Farmer, Laroia, Switz and Thorp, *J. Chem. Soc.*, 2937 (1927).
- (3) Van Romburgh, *ibid.*, 90, 130 (1906); *Verslag. K. Akad. Wetenschappen*, 8, 568 (1905); 22, 1044 (1914).
- (4) Kharasch and Sternfeld, *THIS JOURNAL*, 61, 2320 (1939).
- (5) Butz, *et al.*, *J. Org. Chem.*, 5, 178 (1940); Butz and Butz, *ibid.*, 7, 199 (1942).
- (6) Butz, *THIS JOURNAL*, 64, 1978 (1942).
- (7) Woods and Sanders, *ibid.*, 69, 2927 (1947).
- (8) Heilbron, Jones, McCombie and Weedon, *J. Chem. Soc.*, 84 (1945).

TABLE I
 PHYSICAL CONSTANTS REPORTED FOR 1,3,5-HEXATRIENE

Investigator	B. p., °C.	M. p., °C.	n_D^{20}	d_4^{20}	Analyses, %	
					C(89.94)	H(10.06)
Farmer, <i>et al.</i>	78.5	1.4577 ²⁰	0.7175 ²⁰	88.5	11.6
Butz, Butz and Gaddis	80-82	1.4924 ¹⁸	.7754 ²⁰
Van Romburgh and Van Dorssen	78.5-80	1.49856 ¹⁰	.7565 ¹⁰
Van Romburgh and Mueller	80-80.5	-11	1.517 ¹⁴	.740 ¹⁴
Kharasch and Sternfeld	78-80	1.4330 ²⁰	.7182 ²⁰
Present work	79.5-80	-11.7	1.5035 ²⁸	.7338 ²²	90.07	10.52

Our 1,3,5-hexatriene readily forms a solid dibromide and solid adduct with maleic anhydride, both with properties in agreement with Farmer, *et al.*² We have determined ultraviolet absorption and infrared spectra of our 1,3,5-hexatriene, as shown in Figs. 1 and 2.

Experimental

Preparation of 1,3-Hexadien-5-ol (II).—Pentadienal was prepared in yields of 53% by the method of Woods and Sanders.⁷ Pentadienal (33.5 g., 0.41 mole) in 50 ml. of anhydrous ether was added slowly to an ethereal solution of methylmagnesium bromide from 15 g. of magnesium and 58 g. of methyl bromide. The Grignard addition complex was decomposed with aqueous ammonium chloride. The ether layer was separated, washed with water, and dried over magnesium sulfate. After removal of the drying agent, the solution was distilled under reduced pressure; 1,3-hexadien-5-ol (30 g., 75%) b. p. 65-65.5° (20 mm.), n_D^{20} 1.4829.

The α -naphthylurethan of 1,3-hexadien-5-ol was prepared in the usual manner. Recrystallization of the solid from petroleum ether (30-60°) yielded white crystals melting at 85.5-86.0°. Heilbron, *et al.*,⁸ reported m. p. 86° for this substance. *Anal.* Calcd. for $C_{17}H_{17}NO_2$: C, 76.31; H, 6.41. Found: C, 76.45; H, 6.15.

1,3-Hexadien-5-ol (10 g.) in ethyl alcohol (100 ml.) was hydrogenated with Raney nickel at room temperature and atmospheric pressure to hexanol-2 (7.3 g.) distilling at 136-137°. This product (7.3 g.) was oxidized in a solution of 46.5 g. of potassium dichromate, 62 g. of concd. sulfuric acid and 210 ml. of water, and steam distilled. Methyl *n*-butyl ketone was salted out of the steam distillate with sodium chloride, extracted with ether, the extract dried over magnesium sulfate and distilled. A portion of the methyl *n*-butyl ketone was converted to the semicarbazone melting at 123.5-124° after recrystallization from ethyl alcohol-water, and gave no depression in a mixed melting point determination with an authentic sample of methyl *n*-butyl ketone semicarbazone. *Anal.* Calcd. for $C_7H_{15}N_3O$: C, 53.47; H, 9.62. Found: C, 53.76; H, 9.45. Another portion of the above ketone was converted into the 2,4-dinitrophenylhydrazone which upon recrystallization from ethyl alcohol yielded orange crystals melting at 106-107°; no depression was observed in a mixed melting point determination with an authentic sample. *Anal.* Calcd. for $C_{12}H_{15}N_4O_4$: C, 51.42; H, 5.75. Found: C, 51.13; H, 5.61.

1,3,5-Hexatriene (III).—1,3-Hexadien-5-ol (35.8 g., 0.38 mole) was catalytically dehydrated in a stream of nitrogen under reduced pressure (0.1 mm.) over alumina (8-12 mesh) at 325-350°. The products were condensed in two traps cooled in Dry Ice-baths; on warming, the solid condensate liquified. The water layer was partially removed with a dropper and the remaining mixture dried with calcium oxide. Distillation of this material at atmospheric pressure in a nitrogen atmosphere in the presence of calcium oxide yielded 1,3,5-hexatriene (18 g., 64%) boiling at 79-80° and crystallizing readily on chilling below -12°.

The 1,3,5-hexatriene was partially frozen to a slurry by use of a Dry Ice-acetone-bath, the supernatant liquid

removed with an aspirator filter stick and this process repeated until a liquid of constant freezing point was obtained: f. p. -11.7°, n_D^{20} 1.5035, d_4^{22} 0.7338. Hexatriene so prepared was used for the subsequent physical measurements.

Analyses were difficult to obtain due to high volatility and other peculiar characteristics. *Anal.* Calcd. for C_6H_8 : C, 89.94; H, 10.06. Found: C, 90.07; H, 10.52.

1,3,5-Hexatriene (0.65 g., 0.0081 mole) in 50 ml. of absolute ethyl alcohol was hydrogenated at atmospheric pressure and room temperature with Adams catalyst (0.01 g.). The theoretical amount of hydrogen calculated for three ethylenic bonds was absorbed in approximately one and a quarter hours.

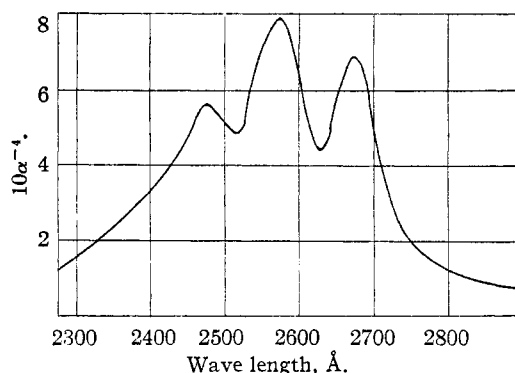
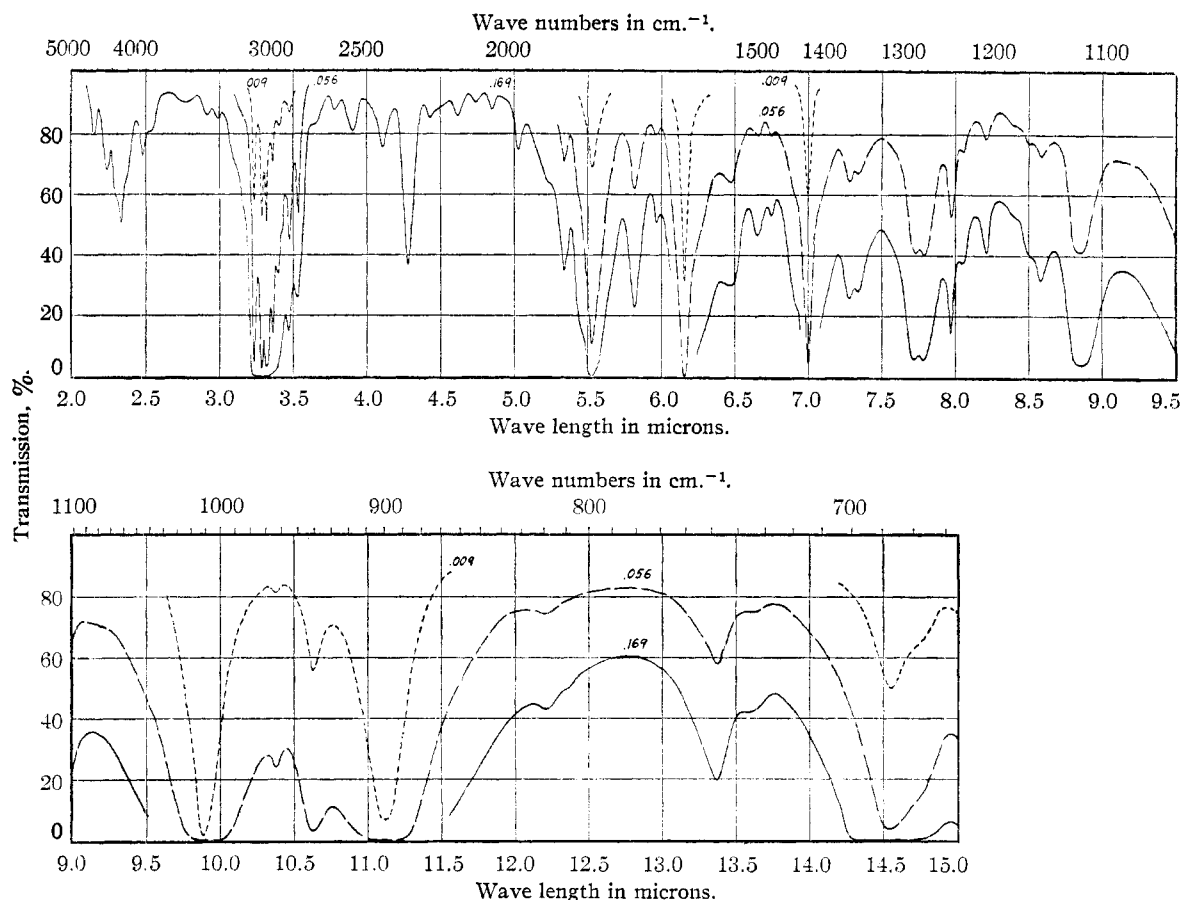


Fig. 1.—Ultraviolet absorption spectra of 1,3,5-hexatriene.¹⁰

1,6-Dibromohexadiene-2,4.—1,3,5-Hexatriene (3 g.) was dissolved in 10 ml. of chloroform and cooled to about 5°. To this solution was added slowly 6 g. of bromine dissolved in 25 ml. of chloroform, the temperature at no time exceeding 13°. After bromination, the solvent was removed under reduced pressure and a yellowish brown liquid was obtained, which on distillation at 2 mm. pressure yielded two substances: (1) a liquid (forerun) which turned black with time, and (2) a liquid (b. p. 105-115° (2 mm.)) which solidified on standing. The solid was recrystallized several times from ether-petroleum ether and gave very hard, long, white needles, m. p. 85-86°, agreeing very closely with Farmer's² 1,6-dibromohexadiene-2,4.

Maleic Anhydride Adduct of Hexatriene.—Freshly sublimed maleic anhydride (2.5 g., 0.025 mole) was mixed with 2.0 g. of 1,3,5-hexatriene (0.025 mole) in 10 ml. of benzene, allowed to stand for forty-eight hours and then refluxed on a steam-bath for six hours. The benzene was removed under reduced pressure and the adduct distilled (140° (0.5 mm.)). A drop of the distillate chilled and agitated in petroleum ether (30-60°) gave a mass of white crystals which were used to seed the rest of the distillate. The white crystals, after recrystallization from petroleum ether (30-60°) and filtration in the cold, melted at 50.5°.

(10) Kovner, C. A., 37, 1652 (1943); 39, 3204 (1945); Bailey and Tuck, *J. Chem. Soc.*, 93, 1909 (1908); Price and Walsh, *Proc. Roy. Soc. London*, 185A, 182 (1946).

Fig. 2.—Infrared spectra of 1,3,5-hexatriene.¹¹

These crystals turn into a yellow oil on standing in air. Farmer and Warren¹² reported a melting point of 51.5° for this substance. *Anal.* Calcd. for $C_{10}H_{10}O_3$: C, 67.43; H, 5.66. Found: C, 67.39; H, 5.97.

The heat of vaporization of 1,3,5-hexatriene was found to be 61.4 cal./g. by the closed manometer technique. The surface tension was measured by the capillary rise method and found to be 23.12 dynes/cm. at 20.2°; water Δh = 8.91 cm. at 21.4–21.6°; benzene Δh = 4.0 cm. at 22.5°; 1,3,5-hexatriene Δh = 3.85 cm. at 20.2–20.4°. The heterodyne beat method gave a dipole moment of 0.2 D in benzene at 36.80°, assuming the atomic polarization to be 5% of the electronic polarization.

Ultraviolet absorption spectra were measured with a Beckmann quartz spectrophotometer in carefully purified cyclohexane.¹³ The concentration necessary to resolve the

fine structure was 4.4×10^{-5} mole/liter, and maximum absorption coefficients are: 0.680×10^5 at 2675 Å.; 0.790×10^5 at 2575 Å.; 0.560×10^5 at 2475 Å.

Summary

1,3-Hexadiene-5-ol has been prepared by the reaction of pentadienal with methylmagnesium bromide and dehydrated over alumina catalyst to 1,3,5-hexatriene, which was purified by low temperature crystallization. Its boiling and freezing points, surface tension, heat of vaporization, dipole moment, refractive index, ultraviolet and infrared absorption spectra are reported.

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(11) This spectrum was kindly determined for us by Dr. Don C. Smith, of the Naval Research Laboratories.

(12) Farmer and Warren, *J. Chem. Soc.*, **135**, 908 (1929).

(13) Arnold Weissberger, "Physical Methods of Organic Chemis-

try," Interscience Publishers, New York, N. Y., 1946, Vol. II, pp. 766–777.