TABLE III

ENTROPIES AND ENTHALPIES OF ACTIVATION FOR ELIMINATIONS FROM Y-$C_6H_4$-$CH_2CH_2$-X

| Y | X | T, °C.[a] | $H‡$, kcal./mole[b] | $S‡$, cal./mole, °C.[c] |
|---|---|---|---|---|
| H | Cl | 70 | 23.2 | −5.6 |
| *p*-Cl | Cl | 70 | 22.4 | −4.8 |
| *m*-Br | Cl | 70 | 23.0 | −1.1 |
| H | F | 70 | 25.3 | −5.4 |
| *p*-Cl | F | 70 | 25.8 | −2.5 |
| *m*-Br | F | 70 | 25.5 | −1.2 |
| H | Br | 45 | 20.4[d] | −6.8[d] |

[a] Midpoint of the temperature range of the data. [b] Calculated from the slope (method of least squares) of a log *k* *vs.* $1/T$ plot and the equation $H‡ = E_a - RT$. [c] Calculated from the intercept of a log *k* *vs.* $1/T$ plot. [d] Ref. 4.

neously with elimination. The approximate yields of β-phenylethyl ether were for the fluoride 1%, and for the chloride, 3%. These values compare closely to the amounts of substitution occurring with the bromides and iodides and show that, despite the acidity of the benzyl hydrogen being removed, the $E_2$ and $S_N2$ reactions change in an analogous way as the nature of the halogen-leaving group changes.

**Acknowledgment.**—We wish to thank Miss Carol Jean Schultz for technical assistance.

## Experimental

**Preparation of β-Arylethyl Fluorides.**—The arylethyl tosylates were heated with an excess of potassium fluoride in diethylene glycol.[11] As a typical example, β-phenylethyl tosylate (5.0 g., 0.04 mole) and potassium fluoride dihydrate (11.2 g., 0.12 mole) were dissolved in 25 ml. of diethylene glycol and stirred at 100° for 20 hours. At the end of this time the initially heterogeneous system had become homogeneous. The solution was cooled and poured into 100 ml. of water and extracted with pentane. After washing and drying the extracts, the pentane was carefully removed and the product distilled.

**β-Phenylethyl fluoride:** 51% yield, b.p. 55–56° (12 mm.). *Anal.* Calcd. for $C_8H_9F$: C, 77.4; H, 7.30. Found: C, 77.5; H, 7.29.

**β-(*p*-Chlorophenyl)-ethyl fluoride:** 43% yield, b.p. 79–80° (9 mm.). *Anal.* Calcd. for $C_8H_8ClF$: C, 60.58; H, 5.08; Cl, 22.36. Found: C, 60.88; H, 5.13; Cl, 22.08.

**β-(*m*-Bromophenyl)-ethyl fluoride:** 45% yield, b.p. 80–81° (4 mm.) An insufficient amount of this compound was available for purification of an analytical sample. Gas phase chromatographic analysis showed it to be greater than 99% pure and the rate constants were calculated from experimental infinity points.

**Preparation of β-Arylethyl Chlorides.**—Arylethyl tosylates were heated with a 4:1 molar excess of lithium chloride in diethylene glycol in a procedure analogous to that for the preparation of the arylethyl fluorides.

**β-Phenylethyl chloride:** 69% yield, b.p. 81–83° (14 mm.) (lit.[9] b.p. 83–84° (14 mm.)).

**β-(*p*-Chlorophenyl)-ethyl chloride:** 41% yield, b.p. 82–83° (3 mm.) (lit.[12] b.p. 133° (35 mm.)).

**β-(*m*-Bromophenyl)-ethyl chloride:** 56% yield, b.p. 80–81° (1 mm.) An insufficient amount of this compound was available for purification of an analytical sample. Gas phase chromatographic analysis showed it to be greater than 99% pure and the rate constants were determined from experimental infinity points.

**Kinetic Measurements.**—Reactions were carried out in ampules of 10-ml. capacity each of which contained a 5-ml. sample. The samples were pipetted at 30° and appropriate corrections for volume expansion at a higher temperature were made in the calculations of rates.

The reactions were followed acidimetrically and olefin determinations were made spectrophotometrically.

Olefin determinations were made on the unsubstituted chloride and fluoride by gas phase chromatography technique.

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(12) G. Baddeley and G. M. Bennett, *J. Chem. Soc.*, 1820 (1935).

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[CONTRIBUTION FROM ROHM & HAAS CO.]

# A New Preparation of 1,3,5-Hexatriene and the Separation of its Geometrical Isomers

BY JESSE C. H. HWA, PETER L. DE BENNEVILLE AND HOMER J. SIMS

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Mixtures of *cis*- and *trans*-1,3,5-hexatriene were prepared from bromohexadienes by quaternization followed by Hofmann elimination. The separation of isomers has been carried out, and physical, spectral and chemical properties of the *cis* isomer determined for the first time. The *cis* isomer was shown to be obtained only in trace amounts by previously reported pyrolytic methods.

Recent descriptions of the preparation of 1,3,5-hexatriene[1,2] have presented more consistent and complete data on its properties than have many other past reports.[3] These recent preparations have both been characterized as the *trans* isomer.[2,4] In only one case[3c] has a definite claim been made of the preparation of the *cis* isomer. In our work, a new method of preparation of 1,3,5-hexatriene was developed, and from the hydrocarbon we have separated what we believe to be the pure *cis* and *trans* isomers. Our data do not agree with that given in this previous reference to the *cis* isomer.

We have prepared 1,3,5-hexatriene (I) by a Hofmann elimination under much milder conditions than those described in previous publications, from 1,5-hexadien-3-ol (II), according to the reaction scheme illustrated by the formula diagram. The lower temperature used in this synthesis has allowed the preparation of I containing substantial proportions of both isomers and completely free of cyclohexadiene. This is in contrast to most pyrolytic methods.[2]

The synthesis was most easily carried out without purification of intermediates to give I in 60%

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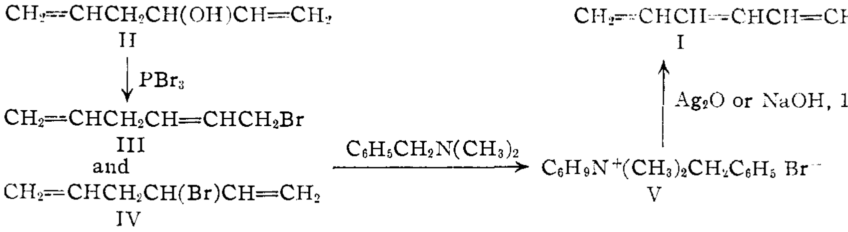
(1) (a) G. Woods and L. Schwartzman, THIS JOURNAL, **70**, 3394 (1948); (b) G. Woods, N. Bolgiano and D. Duggan, *ibid.*, **77**, 1800 (1957).

(2) K. Alder and H. von Brachel, *Ann.*, **608**, 208 (1957).

(3) (a) Ou Kiun-Houo, *Ann. chim.*, **13**, 175 (1940); (b) A. Klebanskii, L. Popov and N. Tsukarman, *J. Gen. Chem. U. S. S. R.*, **16**, 2083 (1946); (c) E. Farmer, B. Laroia, T. Switz and J. Thorpe, *J. Chem. Soc.*, 2937 (1927); (d) P. Van Romburgh and W. van Dorssen, *ibid.*, **90**, 130 (1906); (e) M. Kharasch and E. Sternfeld, THIS JOURNAL, **61**, 2320 (1939); (f) L. Butz and A. Gaddis, *J. Org. Chem.*, **5**, 178 (1940).

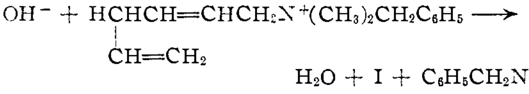
(4) E. Lippincott, C. White and J. Sibilia, THIS JOURNAL, **80**, 2926 (1958).



over-all yield. However, the three intermediates have been isolated and identified and used separately in subsequent steps. 1,5-Hexadien-3-ol[3f] (II) and phosphorus tribromide in the presence of a trace of hydrobromic acid gave a 60–65% yield of a mixture of 1-bromo-2,5-hexadiene (III) and 3-bromo-1,5-hexadiene (IV). The bromides III and IV which were produced in about 3:2 ratio, were easily separated by fractionation.[5] The infrared spectrum of III corresponded to published data, except that the doublet at 1638 and 1656 cm.$^{-1}$ was more clearly resolved.[6] The infrared spectrum of IV showed $CH_2$ out-of-plane deformation at 920 cm.$^{-1}$ and vinyl CH at 987 cm.$^{-1}$, but no absorption which would correspond to *trans*-CH=CH—, a single —C=C— band at 1614 cm.$^{-1}$ and no absorption corresponding to a methyl group.

From both III and IV, and from the crude mixture of bromohexadienes, a pure, crystalline, quaternary salt, formulated as benzyldimethyl-2,5-hexadienylammonium bromide (V), was obtained by reaction with benzyldimethylamine. This salt, whose spectrum taken in potassium bromide showed the two absorption bands at 1637 and 1661 cm.$^{-1}$ found in III, is so formulated from this spectrum and by analogy with closely-related reactions.[7] Its formation from IV by allylic rearrangement is an additional example of abnormal S$_N$2′ substitution. Ou Kiun-Houo[6] reported that only 2,5-hexadienyl acetate was obtained by the treatment of mixed III and IV with sodium acetate.

The quaternary salt V was converted to the hydroxide by treatment of the bromide with moist silver oxide, and this was decomposed by steam distillation to yield 1,3,5-hexatriene, b.p. 81.5–82°, $n^{25}_D$ 1.5073, and benzyldimethylamine. This reaction would occur through 1,4-conjugate elimination.[8]



$$OH^- + H\underset{\displaystyle CH{=}CH_2}{C}HCH{=}CHCH_2N^+(CH_3)_2CH_2C_6H_5 \longrightarrow H_2O + I + C_6H_5CH_2N(CH_3)_2$$

More conveniently, the reaction could be carried out by the addition of an aqueous solution of the crude quaternary salt to boiling sodium hydroxide solution, and isolation of hexatriene from the distillate.

An alternative source of III for the preparation was the bromination of biallyl with N-bromosuccinimide.[6b] The bromide obtained gave a spectrum identical with III obtained from the hexadienol II. It is interesting that the same sequence of reactions could be carried out in low yield with sorbyl alcohol, through sorbyl bromide, in this case requiring 1,6-conjugate elimination to give hexatriene.

The hexatriene from the sorbyl alcohol route gave an infrared spectrum identical with that published by Woods and Schwartzman[1a] (*trans* isomer). The infrared spectrum of the analytically pure material from II, however, showed additional bands at 815, 989 and 1452 cm.$^{-1}$. Since no bands were present which could be ascribed to an allene structure, it was assumed that the additional bands were due to the presence of *cis* and *trans* isomers. The difference in behavior of the hexadienyl bromides has not been cleared up.

When the hexatriene derived from II was subjected to gas chromatography, two peaks were observed, located close together and in a peak height ratio of 7 (first peak):3(second peak). The ratio of these peaks was essentially the same regardless of whether III, IV or the crude dibromide mixture was used as the intermediate, although there was some difference in over-all yield. By freezing and fractional melting it was possible to isolate one of the two compounds in the pure state. This material, b.p. 80–80.5°, $n^{25}_D$ 1.5088, showed only a single peak by gas chromatography, corresponding to the first peak originally obtained. Its infrared spectrum (Fig. 1A) corresponded closely to the published spectra for *trans*-1,3,5-hexatriene.[1,4] When it was treated with bromine, it gave the reported 1,6-dibromo-2,4-hexadiene, m.p. 85–86°.[3c,7b]

When the mixed hexatrienes were combined with maleic anhydride in ether and the ether solution was chromatographed at daily intervals, it was noted that the peak due to the *trans* isomer slowly disappeared, as this isomer was removed by a Diels–Alder reaction,[9] while the other peak remained unchanged. After five days, none of the *trans* isomer remained. The experiment was repeated in the absence of ether, and after two days, the unreacted hydrocarbon was removed and carefully fractionated. Pure *cis*-1,3,5-hexatriene, b.p. 82–83°, $n^{25}D$ 1.5042, showing only one peak by gas chromatography, was isolated. When Courtauld models of the two hexatriene isomers are made, it is seen that although it is easy to orient the *trans* isomer properly for Diels–Alder addition, the *cis* isomer cannot be so oriented. In general, 1-substituted *cis*-butadienes do not undergo Diels–Alder addition at room temperature.[10] No product could be isolated from the attempted reaction of the *cis* isomer with maleic anhydride at refluxing ether temperature.

When the *cis* isomer was treated with bromine, there was obtained the identical 1,6-dibromo-2,4-hexadiene that was obtained from the *trans* isomer. When an ether solution of the *cis* isomer was treated with a crystal of iodine, and chromatographed,

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(5) Ou Kiun-Houo, *Compt. rend.*, **208**, 50 (1939), reports a "desmotropic mixture" was obtained on distillation.

(6) (a) M. Lora-Tamayo, F. Martin-Panzio and R. Ossorio, *J. Chem. Soc.*, 1418 (1950); (b) L. Bateman, J. Cunneen, J. Fabian and H. Koch, *ibid.*, 936 (1950).

(7) W. Young, I. Webb and H. Goering, THIS JOURNAL, **73**, 1076 (1951); W. Young, R. Clement and C. Shih, *ibid.*, **77**, 3061 (1955).

(8) S. Cristol, W. Barasch and C. Tieman, *ibid.*, **77**, 583 (1955).

(9) E. Farmer and F. Warren, *J. Chem. Soc.*, 897 (1929).

(10) K. Alder, *Ann.*, **571**, 157 (1951).

formation of the *trans* isomer was noticed within 30 minutes, and after 24 hours, the isomerization was practically complete. Both isomers polymerized to waxy solids on standing at room temperature, but this occurred very much more rapidly with the *cis* form, within a few days. The pure isomers could be satisfactorily stored at Dry Ice temperatures. From various observations, *cis*-1,3,5-hexatriene appears to be very much more stable in solution.

The infrared spectrum of *cis*-1,3,5-hexatriene (Fig. 1C) showed features which were unexpected, but which can be ascribed to the high degree of conjugation, and probably symmetry in its conformational structure. There was only one band, at 1621 cm.$^{-1}$, which could be properly assigned to asymmetrical —C=C— stretching. The *cis* out-of-plane deformation could be assigned to a band at 818 cm.$^{-1}$, a position which is unusually high in wave numbers, but not unreasonable in view of the conjugation.[11] The $CH_2$ bending frequency was displaced with relation to the *trans* isomer to 1451 cm.$^{-1}$, and the vinyl CH out-of-plane deformation was displaced to 987 cm.$^{-1}$. Thus the mixed isomers showed absorption bands in pairs characteristic of each isomer at, respectively, for *trans* and *cis*, 1429 and 1451, 1011 and 987, and 941 and 818 cm.$^{-1}$ (Fig. 1B).

If one proportionates the values for $n^{25}$D found in these two isomeric hexatrienes with that found for the mixture, the latter is shown to contain 32.6% *cis* isomer and 67.4% *trans* isomer. This agrees with the approximate 3:7 ratio of peak heights in the gas chromatograms. As a further confirmation, and to provide more physical data, extinction coefficients were measured in the ultraviolet at 245, 255 and 265 mμ, where both isomers showed absorption. The data obtained in isoöctane, using a Beckman DK-1 spectrophotometer, are given in Table I, along with the calculated values for the mixture using the ratio of isomers obtained from the refractive indices. These data are consistent with the proposed ratio of isomers.

TABLE I

$\epsilon_{max} \times 10^{-4}$ IN ISOÖCTANE FOR 1,3,5-HEXATRIENES

| | | | Mixture | |
|---|---|---|---|---|
| mμ | *cis* | *trans* | Found | Calcd. |
| 245 | 2.9 | 3.6 | 3.5 | 3.4 |
| 255 | 4.1 | 5.3 | 4.8 | 4.9 |
| 265 | 3.0 | 4.4 | 3.9 | 3.9 |

The pyrolysis of 1,5-hexadien-3-ol was also briefly investigated, with the use of gas chromatography to study the products. Upon pyrolysis over alumina at 325–350°, two fractions were obtained boiling at 80–81°. Gas chromatography of these fractions showed only trace amounts of *cis*-hexatriene, and the *trans*-hexatriene followed peaks, which, by comparison with mixtures of authentic cyclohexadiene and 1,3,5-hexatriene (mixed isomers), undoubtedly were due to the presence of substantial amounts of cyclohexadiene.

**Acknowledgments.**—Mrs. Helen Parseghian aided in obtaining the ultraviolet spectra, and in some of the preparations. Mr. Luther Clement obtained and interpreted the infrared curves. Mr. W. A. Fleming, Mr. E. R. Mowry and Miss Rita Cerruti aided in some of the preparative work. Analyses were carried out under the supervision of Mr. Clyde Nash.

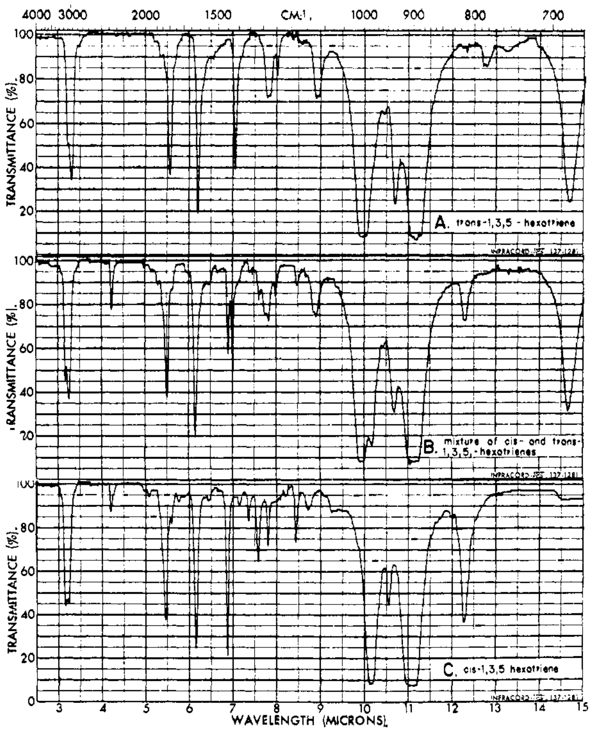

Fig. 1.—Infrared spectra of 1,3,5-hexatriene isomers.

## Experimental

Gas chromatograms were obtained using a tube packed with 30–60 mesh Chromosorb, containing 30% β,β′-oxydipropionitrile as the liquid phase, and heated at 80°. The carrier gas was helium. Infrared curves were taken on the Perkin–Elmer model 21 and Infracord spectrophotometers. A 0.026-mm. cell was used to scan 1,3,5-hexatriene.

**1-Bromo-2,5-hexadiene (III) and 3-Bromo-1,5-hexadiene (IV).**—1,5-Hexadien-3-ol[3f] (II, b.p. 79–79.5° (98 mm.), $n^{20}$D 1.4471, 120 g., 1.22 moles) was added dropwise during 3 hours to phosphorus tribromide (138 g., 0.51 mole) containing 3 drops of 48% hydrogen bromide, with cooling to maintain a temperature of 10–15°. After standing overnight at room temperature, the organic layer was separated, washed with water and 5% sodium bicarbonate solution, and dried over anhydrous magnesium sulfate to yield 180 g. (92%) of the crude mixed bromides. A portion (93 g.) was distilled through a 40-cm. spinning band (platinum) column; IV (22 g.) distilled at 52–56° (35 mm.), $n^{25}$D 1.4828; III (34 g.) distilled at 68–70° (35 mm.), $n^{25}$D 1.4960. Six grams of a small forerun and intermediate cuts, which may be accounted as product, were obtained; the residue was 23 g.; total distilled product, 62 g. (61%).

*Anal.* Calcd. for $C_6H_9Br$: C, 44.8; H, 5.6; Br, 49.6. Found: for III, C, 45.1; H, 5.9; Br, 49.9. For IV, C, 45.2; H, 5.9; Br, 49.2.

**Benzyldimethyl-2,5-hexadienylammonium Bromide (V).**—A solution of the crude bromohexadiene mixture (81 g., from 0.55 mole of II), benzyldimethylamine (82 g., 0.6 mole) and 0.2 g. of hydroquinone in dry toluene (900 ml.) was heated for 3 hours at 55° under a nitrogen atmosphere. After the mixture had stood for several hours at room temperature, the crystalline quaternary salt was removed by filtration, washed with benzene and dried. The yield was 91 g. (56%). A portion was recrystallized from ethanol-ethyl acetate mixture, m.p. 124–125°. The identical compound was obtained from pure IV in 66% yield, and from

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[11] L. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd Ed., Methuen & Co., Ltd., London, 1958, p. 48.

pure III in 90% yield. Infrared spectra of each of these preparations were identical. Mixture melting points showed no depression.

*Anal.* Calcd. for $C_{15}H_{22}BrN$: C, 61.1; H, 7.5; Br, 27.1; N, 4.8. Found: C, 61.1; H, 7.6; Br, 26.9; N, 4.6.

**1,3,5-Hexatriene (I). From V.**—A solution of V (81 g., 0.27 mole) in water (500 ml.) was treated in portions with freshly prepared moist silver oxide, until the brown color of the oxide persisted. The mixture was separated by filtration, and the precipitate was washed with water (100 ml.). The aqueous solution was straight-lead distilled in the presence of 0.2 g. of hydroquinone, in a nitrogen atmosphere. The distillation was continued until no more oil came over. The upper layer of distillate was separated, washed with three 60-ml. portions of cold 2 *N* hydrochloric acid, then with water, and dried over anhydrous magnesium sulfate, to yield 16 g. (73%) of I, b.p. 80°.

**From IV.**—A solution of benzyldimethylamine (27 g., 0.2 mole) and hydroquinone (0.04 g.) in water (150 ml.) was heated to 50°, and IV (32.2 g., 0.2 mole) was added dropwise over 1.5 hours. After 4 hours of additional heating, a small amount of unreacted amine was removed by applying a 25-mm. vacuum to the flask and steam distilling. The clear solution (130 ml.) was then added dropwise over a 3-hour period to boiling aqueous sodium hydroxide solution (32 g. of NaOH in 160 ml. of water) in a flask fitted with distillation condenser, and a receiver cooled in a Dry Ice–acetone-bath. When the distillate no longer contained oil, the oil layer was separated, washed with 100 ml. of 2 *N* hydrochloric acid, and then with water to yield 9.3 g. (58%) of mixed hexatrienes. Analysis of this product by gas chromatography gave two peaks in the ratio of 3:7 for the *cis* and *trans* isomers.

**From III.**—An identical procedure gave 14 g. (87%), showing the same ratio of peaks in the gas chromatogram.

**From Crude Bromohexadienes.**—Using the same procedure, the yield of mixed hexatrienes was 64% (assuming the starting bromides to be pure) in the same ratio, $n^{26}\mathrm{D}$ 1.5079. A sample of the hexatriene prepared in this way was dried over anhydrous magnesium sulfate, and distilled through a 40-cm. spinning band column to give the standard sample of mixed 1,3,5-hexatrienes, boiling at 81.5–82°, $n^{25}\mathrm{D}$ 1.5073, which was used for infrared and ultraviolet studies.

**From Biallyl.**—1-Bromo-2,5-hexadiene (III) was prepared from biallyl[12] by the method of Karrer and Ringli,[13] with the omission of light radiation; b.p. 52–58° (16 mm.), $n^{20}\mathrm{D}$ 1.4993. The infrared spectrum was identical with that of III obtained from II; III was converted to V in 90% yield, and V to I in 73% yield by methods already described.

**From Sorbyl Bromide.**—Sorbyl alcohol,[14] b.p. 94° (30 mm.), $n^{20}\mathrm{D}$ 1.4937, was converted to crude sorbyl bromide[15] by reaction with phosphorus tribromide, b.p. 58° (15 mm.) to 69° (20 mm.). The crude sorbyl bromide (37 g., 0.23 mole) was combined with benzyldimethylamine (37 g., 0.27 mole) in toluene (200 ml.), and the mixture was heated at 50° for 3 hours. The toluene was decanted from the quaternary salt, which was dissolved in water (500 ml.). The solution was steam distilled under diminished pressure at 50° until it was clear. To the cold solution was added a chilled solution of sodium hydroxide (30 g.) in water (100 ml.). The mixture was boiled in a nitrogen atmosphere, and the oil which collected in the distillate was separated, washed twice with 2 *N* hydrochloric acid, and then with water, and distilled. There was obtained 2.0 g. (5%) of I, identical in infrared spectrum with the previously published spectrum.[1a]

**Isolation of Pure *trans*-1,3,5-Hexatriene.**—A fritted-glass funnel of 1-inch diameter was arranged so that it, and the filter flask to which it was connected, could be surrounded by a Dry Ice–acetone-bath, while applying a vacuum. A piece of filter paper was placed in the funnel. An 8-g. sample of mixed hexatriene isomers, prepared from crude bromohexadienes, was frozen solid and transferred quickly to the funnel. A gentle suction was applied, and the solid was broken up and pressed against the filter paper to squeeze out liquid. The temperature of the bath, originally at −30 to −40°, was allowed to rise to −20 to −25°, and then to −15 to −20°, the process being repeated each time until no more liquid appeared to come through the funnel. The 2-g. residue was transferred from the funnel, allowed to melt, dried over a little anhydrous magnesium sulfate, and distilled through the spinning band column to give the pure *trans* isomer, b.p. 80–80.5°, $n^{25}\mathrm{D}$ 1.5088. The gas chromatogram showed only one peak. The filtrate showed equal parts of *cis* and *trans* isomers.

**Isolation of Pure *cis*-1,3,5-Hexatriene.**—To the mixed isomers of hexatriene (16 g., 0.2 mole) was added, over a 2-hour period, solid maleic anhydride (30 g., 0.3 mole) in small portions. A slight heat evolution was observed. After standing for 48 hours, unreacted hexatriene was removed by applying water aspirator vacuum, and collected in a Dry Ice-cooled trap. It was dried over anhydrous magnesium sulfate, and fractionated through a 40-cm. spinning band column. The product (1.4 g.) was collected at 82–83°, $n^{25}\mathrm{D}$ 1.5042.[16] Only the single *cis*-1,3,5-hexatriene peak was present in the gas chromatogram. Isomerization of the *cis* to the *trans* isomer was observed by dissolving it in ether, adding a crystal of iodine, and following the conversion by the known peaks in gas chromatography.

*Anal.* Calcd. for $C_6H_8$: C, 89.9; H, 10.1. Found: C, 90.2; H, 9.9.

**1,6-Dibromo-2,4-hexadiene.**—A solution of 0.4 g. of *trans*-I in 10 ml. of carbon tetrachloride was treated with 0.8 g. of bromine in 10 ml. of the same solvent. The solvent was evaporated and the residue recrystallized from petroleum ether, to give 0.25 g., m.p. 85–86°. From 0.2 g. of *cis*-I, in the same way, there was obtained 0.1 g., m.p. 85–87°. Mixture melting points showed no depression, and infrared spectra (Nujol mull) were identical.

*Anal.* Calcd. for $C_6H_8Br_2$: C, 30.0; H, 3.4; Br, 66.6. Found: C, 30.0; H, 3.6; Br, 66.8.

**Pyrolysis of 1,5-Hexadien-3-ol (II).**—A 1 × 30-inch vertical column was used. It was packed with 8–12 mesh alumina, heated to 325–350°, and II (49 g., 0.5 mole) was added dropwise over 45 minutes, while the pyrolysate was trapped in a Dry Ice-cooled receiver. The exit from the receiver was attached to a water aspirator. The oil (29 g.) was dried over anhydrous magnesium sulfate and distilled through the spinning band column to give 2.4 g. of forerun, 3.15 g., b.p. 80°, and 2.6 g., b.p. 80–81°. The remainder (19 g.) was probably unchanged alcohol. Authentic cyclohexadiene[17] was combined with the mixed isomers of I to give a standard for gas chromatography. Cyclohexadiene, eluted first, was present to the extent of 37% in the forerun, 64% in the first cut and 65% in the second. *trans*-I, eluting closely thereafter as a shoulder, was present to the extent of 15, 25 and 18% in these respective cuts. *cis*-I was present only in traces. An unknown low-boiling constituent constituted the remainder.

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(12) A. Turk and H. Chaman, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1953, p. 121.

(13) P. Karrer and W. Ringli, *Helv. Chim. Acta*, **30**, 863, 1771 (1947).

(14) R. Nystrom and W. Brown, THIS JOURNAL, **69**, 1197, 2548 (1947).

(15) M. Jacobson, *ibid.*, **77**, 2461 (1955).

(16) Recent values for $n^{25}\mathrm{D}$ for *cis*-, *trans*- and *cis–trans* mixtures are 1.5058, 1.5091 and 1.5082, respectively. These products were isolated by distillation at 5 mm. at room temperature into a Dry-Ice cooled receiver and are believed to be free of polymer, which probably caused the lower values given in the text.

(17) C. Grob, H. Kny and A. Gagneux, *Helv. Chim. Acta*, **40**, 130 (1957).