[CONTRIBUTION FROM THE CHEMISTRY LABORATORY, UNIVERSITY OF MARYLAND]

Dimethyl-1,3,5-hexatrienes

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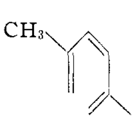
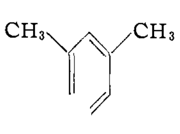
A study of the preparation and chemistry of some dimethyl-1,3,5-hexatrienes has been made. The trienes appear to undergo an internal Diels–Alder reaction leading to cyclohexadienes.

We have been interested in the synthesis and properties of the 1,3,5-hexatrienes, and have reported the parent hydrocarbon,[2a] nitro-,[2b] phenyl-,[2c] vinyl-[2d] and the methylhexatrienes.[2e] This paper is a report on some disubstituted 1,3,5-hexatrienes; in particular, the dimethyl-1,3,5-hexatrienes I, II and III.



I



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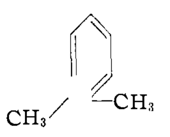

III

2,5-Dimethyl-1,3,5-hexatriene (I, or its other geometrical isomer) was prepared by the two-step process: (1) hydrogenation of 2,5-dimethyl-3-hexyne-2,5-diol and (2) catalytic dehydration of the ethylenic diol. The catalytic dehydration was an intricate process from which several products could be obtained dependent on the temperature of dehydration (Fig. 1). Dehydration at lower temperatures afforded 2,5-dimethyl-1,3-hexadien-5-ol (V) in rather poor yields. This substance, the ultraviolet absorption spectrum of which was typical of a conjugated diene, absorbed two moles of hydrogen. The product of hydrogenation was identical with a synthetic sample of 2,5-dimethyl-2-hexanol. The low yields in this first stage of dehydration are due to the fact that most of the enediol IV survives the dehydration.

Dehydration of the enediol IV or of the dienol V at a higher temperature led to the desired triene I. At still higher temperatures the product of cyclization, the dimethylcyclohexadiene VI (the double bond structure of which has not been established) is obtained. In practice the problem becomes one of separation of the triene from the dimethylcyclohexadiene. 2,5-Dimethyl-1,3,5-hexatriene, a solid just below room temperature, was isolated by crystallization. The properties of this material are in excellent accord with those reported by Kharasch.[3] The structure of the dimethylcyclohexadiene was established except for the double bond location by (1) conversion by aromatization (or better disproportionation) to *p*-xylene (and dimethylcyclohexane) and (2) by the formation of a Diels–Alder adduct with maleic anhydride which absorbed quantitatively but one mole of hydrogen.

The Diels–Alder adduct of dimethylhexatriene VII, Fig. 2, was used in an unsuccessful attempt to prepare 1,2,3,5-benzenetetracarboxylic acid.

The aromatization of VII concurrently leads to saturation of the isopropenyl side chain; this was also observed in the corresponding adduct from 1,3,5-hexatriene. The oxidation of VIII led to IX, the lactone, instead of the tetracarboxylic acid. This same oxidation of the *i*-propyl group was observed by Alder and Rickert[4] in the oxidation of 3-isopropyl-6-methylphthalic acid.

The dimethylcyclohexadiene VI could be obtained not only from the enediol IV, but also from the dienol V and from 2,5-dimethylhexatriene (I) by passage through the alumina catalyst heated to 500°. Actually this cyclization can be looked upon as an internal Diels–Alder reaction of the triene.

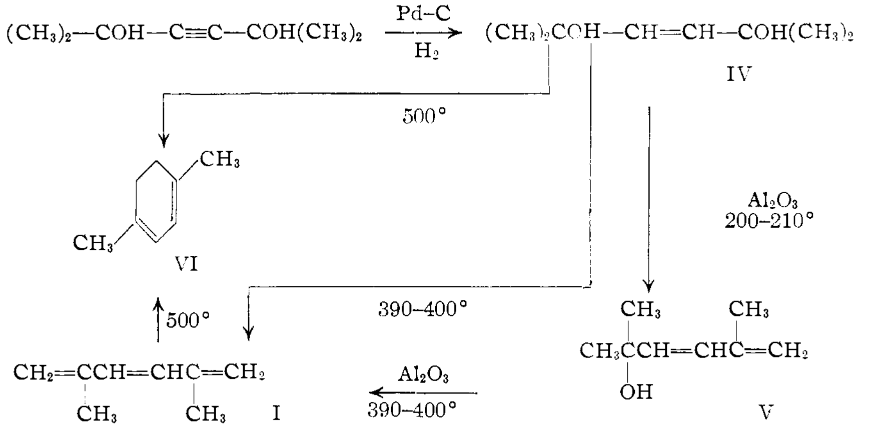

Fig. 1.—Catalytic dehydration scheme of 2,5-dimethyl-3-hexene-2,5-diol.

Attempts to obtain 2,4-dimethyl-1,3,5-hexatriene (II) were based on the dehydration by different

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(1) Monsanto Chemical Fellow.

(2) (a) G. F. Woods and L. H. Schwartzman, THIS JOURNAL, **70**, 3394 (1948); (b) G. F. Woods and N. C. Bolgiano and D. E. Duggan, *ibid.*, **77**, 1800 (1955); (c) G. F. Woods and S. C. Temin, *ibid.*, **72**, 139 (1950); (d) G. F. Woods and L. H. Schwartzman, *ibid.*, **71**, 1396 (1949); (e) G. F. Woods and H. Fleischacker, *ibid.*, **78**, 3436 (1956).

(3) M. S. Kharasch, W. Nudenberg and E. Sternfeld, *ibid.*, **62**, 2034 (1940).

(4) K. Alder and H. F. Rickert, *Ber.*, **70B**, 1364 (1937).

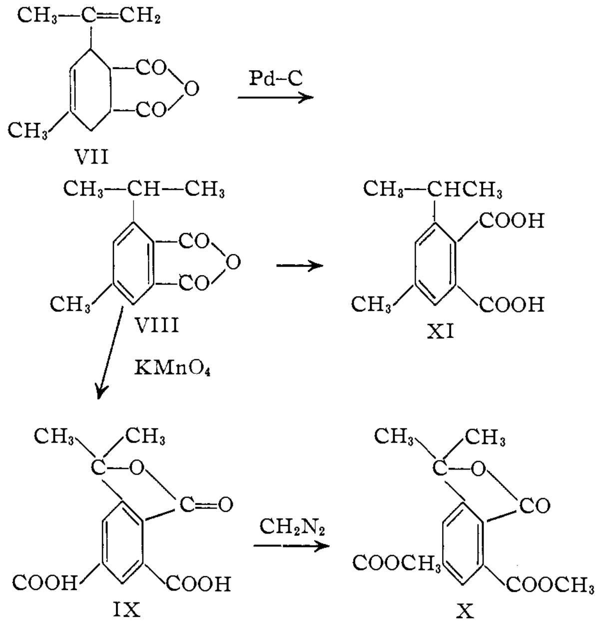

Fig. 2.—Conversions of the Diels–Alder adduct of 2,5-dimethyl-1,3,5-hexatriene.

means of 2,4-dimethyl-1,5-hexadiene-4-ol. This alcohol was prepared by the addition of methyl vinyl ketone to the Grignard reagent obtained from 3-chloro-2-methylpropene. The extinction coefficient of the dienol obtained from the above Grignard addition in the 220–280 mμ region was too low for existence of conjugate unsaturation; the alcohol also quantitatively absorbed two moles of hydrogen and the properties of the product of reduction were in excellent accord with those reported for 2,4-dimethyl-4-hexanol. Dehydration of the dienol with alumina under conditions adequate to cause loss of water led to the formation of 1,3-dimethylcyclohexadiene. (The position of the unsaturation was not determined.) The same results were obtained if dehydration was effected with phosphorus pentoxide or iodine. From dehydration with *p*-toluenesulfonic acid or acetic anhydride a product was obtained which, although considerable dimethylcyclohexadiene was present, contained substantial amounts of 2,4-dimethyl-1,3,5-hexatriene. This conclusion is based on the shape of the ultraviolet absorption curve of the dehydration product in that there were present three well-defined peaks of a triene. Purification or separation of the triene could not be accomplished by either distillation or crystallization.

The structure of the 2,4-dimethylcyclohexadiene obtained in the above dehydrations was established by its maleic anhydride adduct, a liquid, which could be converted to a solid diacid. This diacid upon quantitative hydrogenation absorbed one mole of hydrogen. The cyclic diene was converted to a mixture of *m*-xylene and 1,3-dimethylcyclohexane by heating over palladium-on-carbon. The presence of *m*-xylene was demonstrated by its ultraviolet absorption and by nitration to 2,4,6-trinitro-1,3-dimethylbenzene.

In view of the difficulties in obtaining and handling the different trienes it seemed desirable to check the preparation of 1,6-dimethyl-1,3,5-hexatriene. As reported by Kuhn and Grundemann,[5] 2,4-hexadienal was added to ethylmagnesium chloride and 2,4-octadien-6-ol was obtained. That no allylic rearrangement had occurred in the octadienol was established by reduction to 3-octanol. This substance and its acid phthalate derivative were compared with an authentic sample and its derivative. Dehydration of 2,4-octadien-6-ol with alumina provided the earlier reported solid substance which has been described as 1,6-dimethyl-1,3,5-hexatriene. This substance, however, degenerates so rapidly, with the formation of a tacky solid insoluble in the common organic solvents, that a satisfactory characterization of it could not be made. A small sample was dissolved in petroleum ether immediately after recrystallization and its ultraviolet absorption curve was determined. The typical triple peak of a triene was obtained but this does not distinguish between 1,6-dimethyl-1,3,5-hexatriene and the possible 1-ethyl-1,3,5-hexatriene.

The cyclization of 1-phenyl-1,2,5-dimethyl-, 2,4-dimethyl- and the three different methylhexatrienes to phenyl-, 1,4-dimethyl-, 1,3-dimethyl- and methylcyclohexadiene, respectively, may be looked upon as an internal Diels–Alder reaction. It would therefore be expected that cyclization followed by aromatization of 1,6-dimethyl-1,3,5-hexatriene would yield *o*-xylene while 1-ethyl-1,3,5-hexatriene would yield ethylbenzene. Experimentally, it was found that dehydration of 2,4-octadien-6-ol at 450–500° followed by treatment with palladium-on-carbon yielded a mixture of *o*-xylene and ethylbenzene as first evidenced by the ultraviolet absorption spectra. The positive proof rested in the oxidation of the aromatized mixture which provided both benzoic acid (from ethylbenzene) and phthalic acid. These results indicate that the dehydration of the octadienol either provided a mixture of 1,6-dimethylhexatriene and 1-ethylhexatriene, or that the cyclization of 1,6-dimethylhexatriene can occur in more than one way.

To extend the generality of the cyclization the parent triene, 1,3,5-hexatriene and its precursor, 2,4-hexadien-1-ol, were passed over alumina at 450–500°. Cyclohexadiene was the product isolated (b.p. 79–82°); the ultraviolet absorption curve of the product was devoid of fine structure ($E_{\max}$ (226 mμ) 2.7×10^3). Disproportionation of the cyclohexadiene with palladium-on-carbon led to a mixture of benzene and cyclohexane, but the ultraviolet absorption spectra clearly indicated the presence of a surviving diene which was destroyed by very mild conditions of hydrogenation. This substance is possibly a methylcyclopentadiene. The material, after mild hydrogenation, had an ultraviolet absorption spectrum identical with that of benzene.

Experimental

Dehydration of 2,5-Dimethyl-3-hexene-2,5-diol.—2,5-Dimethyl-3-hexyne-2,5-diol[6] (285 g., 2 moles) dissolved in absolute ethanol to give a volume of 1040 ml. was hydro-

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[5] R. Kuhn and C. Grundemann, *Ber.*, **71B**, 442 (1938).

[6] This material was kindly provided by the Air Reduction Chemical Co., New York, N. Y.

genated with palladium–carbon catalyst (1 g., 10%) at 1200 p.s.i. and room temperature. This pressure of hydrogen was the calculated amount for the conversion of the acetylenic link to the ethylenic link. The time for hydrogenation (Δp 1200 lb.) was approximately three minutes. The solution was filtered and the solvent removed by distillation under reduced pressure and the residue recrystallized from carbon tetrachloride. The material[7] (271 g., 94%) obtained melted at 61–65°.

Anal. Calcd. for $C_8H_{16}O_2$: C, 66.62; H, 11.18. Found: C, 66.63; H, 10.96.

The above hydrogenated product (90 g.) was distilled in a nitrogen atmosphere under reduced pressure (20 mm.) through a Pyrex column packed with 8–12 mesh alumina maintained between 210–225°. The product, collected in a receiver cooled by Dry Ice, was dried and distilled. Redistillation of the lower boiling fraction at room temperature yielded 8.4 g. (11%) of 2,5-dimethyl-1,3-hexadien-5-ol, b.p. 145–147°, $n^{25}\mathrm{D}$ 1.451. The ultraviolet absorption spectrum of this material was devoid of fine structure $E_{\max}$ (218 mμ) 2.3×10^4.

Anal. Calcd. for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 75.93; H, 11.36.

Hydrogenation at room temperature and atmospheric pressure with palladium-on-carbon absorbed 94% of the hydrogen calculated for saturation of two ethylenic links. The product of hydrogenation, 2,5-dimethyl-2-hexanol boiled at 147–149°, $n^{26}\mathrm{D}$ 1.419, $d^{29}{}_4$ 0.808 (literature[8] b.p. 150–153°, $d^{11.4}{}_4$ 0.115, $n^{11.4}\mathrm{D}$ 1.4243). An authentic sample of this material prepared by the Grignard reaction had the same physical constants.

If the above dehydration was effected in the same manner except that the temperature of the column was maintained at 390–400° but using either the dienol or enediol, a mixture of 2,5-dimethyl-1,3,5-hexatriene and 1,4-dimethylcyclohexadiene was obtained, b.p. 45–49° (31 mm.), $n^{28}\mathrm{D}$ 1.482. This product was chilled in a Dry Ice-bath and the crystalline material collected. Redistillation of the solid material after drying provided 2,5-dimethyl-1,3,5-hexatriene (50% recovery), b.p. 43–44° (25 mm.), m.p. −9°, $n^{25}\mathrm{D}$ 1.5106, $d^{29}{}_4$ 0.776; lit.[3] b.p. 90.2° (200 mm.), 58° (51 mm.), m.p. −9°, $n^{20}\mathrm{D}$ 1.5122, $d^{20}{}_4$ 0.7822. The ultraviolet spectrum of this material is identical with that reported by Kharasch[3] *et al.*

If 2,5-dimethyl-3-hexene-2,5-diol, 2,5-dimethyl-1,3-hexadien-5-ol or 2,5-dimethyl-1,3,5-hexatriene was passed through the column heated to approximately 500°, 1,4-dimethylcyclohexadiene was obtained which boiled at 130–131°, $n^{31}\mathrm{D}$ 1.472 (yield 80–90%). The ultraviolet absorption spectrum shows that a very small amount of the triene has survived.

Anal. Calcd. for C_8H_{12}: C, 88.89; H, 11.11. Found: C, 88.66; H, 11.24.

Aromatization of 1,4-Dimethylcyclohexadiene.—1,4-Dimethylcyclohexadiene (9 g.) was added dropwise through a condenser to a flask which contained 1 g. of palladium-on-carbon (10%) and which was heated by immersion in an oil-bath (200°). Reflux was maintained for an additional two hours after addition. The mixture was distilled and the colorless distillate was crystallized from an equal volume of petroleum ether (30–40°). A 25% yield of *p*-xylene was obtained which was identical with an authentic sample.

Treatment of 2,5-dimethyl-1,3,5-hexatriene in the above manner led almost entirely to polymerization (but a very small amount of *p*-xylene could be isolated).

5-Methyl-3-isopropylphthalic Anhydride (VIII).—A 70% yield of the Diels–Alder adduct of 2,5-dimethyl-1,3,5-hexatriene with maleic anhydride was obtained using Kharasch's[3] procedure, m.p. 117–118° (lit.[3] 115–116°).

A small amount of the adduct was dissolved in dilute aqueous potassium hydroxide. The resulting solution was extracted with ether, decolorized with charcoal, filtered, acidified with hydrochloric acid, and chilled. The precipitate was recrystallized from hot water to yield the dicarboxylic acid, m.p. 151–155° dec.

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.01; H, 7.03.

The original Diels–Alder adduct was heated under reflux with a small amount of palladium-on-carbon until gas evolution ceased and the product was distilled. Recrystallization of the distillate from petroleum ether yielded (60%) white crystalline 5-methyl-3-isopropylphthalic anhydride, m.p. 81–82°.

Anal. Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.93. Found: C, 70.56; H, 5.72.

The acid was obtained by treatment of the anhydride with dilute potassium hydroxide followed by acidification with hydrochloric acid of the alkaline solution. Recrystallization from water–ethanol yielded 5-methyl-3-isopropylphthalic acid (XI), m.p. 169–170° dec.

Anal. Calcd. for $C_{12}H_{14}O_4$: C, 64.85; H, 6.35. Found: C, 65.03; H, 6.19.

Oxidation of 5-Methyl-3-isopropylphthalic Anhydride.—The anhydride VIII was oxidized in the usual manner with potassium permanganate; the filtrate was acidified with hydrochloric acid. The precipitate was isolated, dried and recrystallized from benzene–dioxane. 3,3-Dimethyl-5,7-dicarboxyphthalide (IX) (yield 50%) melted at 273–275°.

Anal. Calcd. for $C_{12}H_{10}O_6$: C, 57.60; H, 4.03. Found: C, 57.69; H, 3.99.

Treatment of the phthalide (0.051 g.) with diazomethane in ether yielded the dimethyl ester X which was recrystallized from methanol–water (0.013 g.), m.p. 165–166°.

Anal. Calcd. for $C_{14}H_{14}O_6$: C, 60.43; H, 5.07. Found: C, 60.42; H, 5.32.

Diels–Alder Adduct of 1,4-Dimethylcyclohexadiene.—Equimolar quantities of maleic anhydride (4.9 g.) and 1,4-dimethylcyclohexadiene (VI) (5.4 g.) were added to 10 ml. of benzene. The mixture was first cooled until the original reaction subsided and was subsequently heated under reflux for 2.5 hours. The solvent was removed under reduced pressure and the product distilled, b.p. 115–118° (0.1 mm.). Recrystallization of the product first from ether–petroleum ether and then from petroleum ether (60–80°) yielded (51%) the adduct, m.p. 52–54°.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 69.92; H, 6.94.

Attempts to obtain the dicarboxylic acid were unsuccessful. Although the anhydride would react and dissolve in dilute alkali, the product isolated after acidification melted at the melting point of the anhydride and analysis of the material resulted in essentially the above figures.

Quantitative hydrogenation of the anhydride in petroleum ether (60–90°) (previously treated with Raney nickel) with palladium-on-carbon at room temperature and atmospheric pressure resulted in a 102% uptake of hydrogen calculated for one ethylenic link. After removal of the catalyst and chilling, the product precipitated and was recrystallized from petroleum ether, m.p. 62–63°.

Anal. Calcd. for $C_{12}H_{16}O_3$: C, 69.21; H, 7.75. Found: C, 69.67; H, 7.81.

Conversion of the anhydride to the acid was accomplished by treatment with dilute alkali followed by acidification; m.p. 134–137° dec. It is this material which provided the analysis below, for recrystallization from hot water resulted in anhydride formation.

Anal. Calcd. for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.85; H, 7.67.

Preparation of 2,4-Dimethyl-1,5-hexadien-4-ol.—The Grignard reagent of 3-chloro-2-methylpropene (150 g., 1.66 moles) was prepared with magnesium powder (85 g., 3.5 moles). The chloro compound dissolved in 2.5 l. of ether was added dropwise with vigorous stirring to the magnesium powder in 1 l. of ether. The Grignard solution was pumped by gas pressure through glass wool into a 5-l. flask. Washing of the unreacted magnesium required a further 0.5 l. of ether. To the combined ether filtrates was added with stirring methyl vinyl ketone (70 g.) dissolved in 100 ml. of ether. The reaction mixture was poured into chopped ice and ammonium chloride. 2,4-Dimethyl-1,5-hexadien-4-ol (86 g., 69%) was isolated in the usual manner, b.p. 46–47° (10 mm.), $n^{26}\mathrm{D}$ 1.449, $d^{25}{}_4$ 0.854.

Anal. Calcd. for $C_8H_{14}O$: C, 76.13; H, 11.18. Found: C, 76.43; H, 10.97.

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(7) The attempts to assign a geometrical structure to this substance have been unsuccessful: J. Salkind, *Ber.*, **56**, 187 (1923), and THIS JOURNAL, **63**, 2282 (1941); J. R. Johnson and O. H. Johnson, *ibid.*, **62**, 2615 (1940); and **63**, 2282 (1941); H. Bourguel and R. Rambaud, *Bull. soc. chim.*, [4] **47**, 173 (1930).

(8) V. Grignard, *Chem. Zentr.*, **72**, **II**, 623 (1901).

Quantitative hydrogenation of this material in methanol with palladium-on-carbon at room temperature and atmospheric pressure resulted in a 99% hydrogen uptake calculated for two ethylenic links. Removal of the alcohol and distillation of the product yielded 2,4-dimethyl-4-hexanol, b.p. 152–153°, $n^{26}D$ 1.423, d^{25}_4 0.827 (lit.[9] b.p. 151–153°, $n^{18}D$ 1.4286, d_{15} 0.830).

Dehydration of 2,4-Dimethyl-1,5-hexadien-5-ol.—The dienol (3 to 5 g.) was mixed with a small amount of *p*-toluenesulfonic acid and placed in a small distilling flask. The flask fitted for distillation was immersed in an oil-bath heated to 180°. The pressure was adjusted so that the temperature of the distilling vapor was about 90°. The product was again distilled from a second amount of *p*-toluenesulfonic acid; yield 1.5–3 g., $n^{25}D$ 1.463. The ultraviolet absorption curve of this material has the typical peaks of a triene at 256, 266 and 277 mμ. The absorption curves and the value of the refractive index show that the concentration of triene is fairly low. Attempts to isolate or to concentrate the triene were unsuccessful. Much the same results were obtained if acetic anhydride was used in place of *p*-toluenesulfonic acid. No triene was obtained if the dehydration reagent was phosphorus pentoxide or phosphoric acid.

Dehydration of 2,4-dimethyl-1,5-hexadien-4-ol with alumina from 250 to 500° did not lead to the formation of the desired 2,4-dimethyl-1,3,5-hexatriene, but rather to a 1,3-dimethylcyclohexadiene. The refractive index of the dehydration product varied from 1.468 to 1.479, b.p. 30° (12 mm.), 52–53° (50 mm.), yield 50–65%.

Anal. Calcd. for C_8H_{12}: C, 88.89; H, 11.11. Found: C, 89.02; H, 10.95.

Attempts to hydrogenate this material were unsuccessful and erratic, the hydrogen uptake was 67% or considerably less.

The ultraviolet absorption curve of material dehydrated at 480° with alumina was typical of a conjugated diene; the curve was devoid of fine structure, E_{max} (235 mμ) 1.3 × 10^4.

Dehydrogenation of this material with palladium-on-carbon resulted in a liquid (a mixture of *m*-xylene and 1,3-dimethylcyclohexane) the ultraviolet absorption spectrum of which was identical with that of an authentic sample of *m*-xylene. On the basis of calculations using E_{max} the mixture was approximately 60% *m*-xylene.

The aromatized mixture was treated with fuming nitric acid and concd. sulfuric acid to obtain yellow 2,4,6-trinitro-*m*-xylene, m.p. 181–182° (no depression on admixture with an authentic sample[10]).

Diels–Alder Adduct of 1,3-Dimethylcyclohexadiene.—An equimolar mixture of the 1,3-dimethylcyclohexadiene (3.24 g.) and maleic anhydride (2.94 g.) in 5 ml. of benzene was refluxed for 24 hours. After removal of benzene the Diels–Alder adduct was distilled, b.p. 165 (0.1 mm.). The distillate could not be induced to crystallize.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84. Found: C, 70.38; H, 6.83.

The anhydride was opened to the dicarboxylic acid with aqueous potassium hydroxide followed by acidification with hydrochloric acid. The product precipitated as a gum which solidified on standing. Several treatments with potassium hydroxide and hydrochloric acid (adjusted to a *p*H of 1) and finally washing with cold water provided a solid dicarboxylic acid, m.p. 132–133°.

Anal. Calcd. for $C_{12}H_{16}O_4$: C, 64.27; H, 7.19. Found: C, 64.42; H, 7.06.

The above Diels–Alder adduct and the resulting dicarboxylic acid are probably mixtures, for although the cyclohexadiene is a 1,3-dimethylcyclohexadiene, more than one assignment of position for the conjugated diene is possible. Further, there is possibility of geometrical isomerism of the adduct diacid.

Quantitative hydrogenation as described earlier of the above acid in the presence of a slight excess of aqueous potassium hydroxide resulted in a 100% hydrogen uptake calculated for one ethylenic link. Filtration of the catalyst and acidification in the cold (*p*H of 1) gave the white crystalline diacid, m.p. 124–125° dec.

Anal. Calcd. for $C_{12}H_{18}O_4$: C, 63.70; H, 8.02. Found: C, 63.85; H, 7.81.

Attempts to recrystallize this material from different solvents led to a viscous oil, probably the anhydride.

Dehydration of 2,4-Octadien-6-ol.—2,4-Octadien-6-ol was prepared according to the procedure of Kuhn and Grundemann[5] from 2,4-hexadienal and the ethyl Grignard reagent. The product, b.p. 88–89° (15 mm.), 68–69° (3 mm.), $n^{26}D$ 1.487, corresponded with that reported by the above workers.

To determine that no allylic shift had occurred, the dienol was quantitatively hydrogenated with palladium-on-carbon at room temperature and atmospheric pressure (89% uptake for two ethylenic links) and the product identified as 3-octanol, b.p. 172–174°, $n^{26}D$ 1.421, d^{25}_4 0.8223. These values are in excellent accord with those reported in the literature.[11] The acid phthalate[11] of the saturated alcohol melted at 61° (no depression on admixture with an authentic sample).

2,4-Octadien-6-ol was dehydrated over alumina at 300–310° in the manner described earlier. The liquid product after drying with magnesium sulfate was distilled, b.p. 40° (10 mm.), $n^{26}D$ 1.526, yield 15 g. from 20 g. of alcohol. The liquid was fairly stable but chilling provided a solid which underwent polymerization so rapidly that a satisfactory melting point could not be obtained. The material recrystallized from petroleum ether (35–40°), if allowed to dry, became very tacky; if sucked dry and melted the m.p. was slightly above room temperature. Analysis indicated the rate at which oxygen was absorbed.

Anal. Calcd. for C_8H_{12}: C, 88.89; H, 11.11. Found: C, 85.88; H, 10.51.

The ultraviolet spectrum of this material obtained immediately upon recrystallization (without drying) was determined: *E* (253 mμ) 3.0 × 10^4, *E* (262.5 mμ) 4.1 × 10^4 and *E* (273 mμ) 3.3 × 10^4.

2,4-Octadien-6-ol (10 g.) was dehydrated over alumina at a pressure of 1.0 mm. and a temperature of 490–500°. The product (5.4 g.) was liquid, b.p. 49–53° (50 mm.), $n^{27}D$ 1.482.

Anal. Calcd. for C_8H_{12}: C, 88.89; H, 11.11. Found: C, 88.90; H, 10.97.

This is a substituted cyclohexadiene the ultraviolet curve of which is without fine structure; E_{max} (234 mμ) 1.0 × 10^4.

Aromatization of this material with palladium-on-carbon as described earlier provided (75% yield) a colorless liquid the ultraviolet absorption spectrum of which was identical with neither *o*-xylene nor ethylbenzene but appeared to be a mixture of the two.

Oxidation of the aromatized product (1.0 g.) was accomplished in the usual manner with potassium permanganate and potassium hydroxide. After removal of manganese dioxide and decolorization with sodium thiosulfate, the aqueous solution was extracted with ether and acidified. The acidified solution was extracted several times with ether. The ether was partially evaporated and a small quantity of phthalic acid crystallized, m.p. 202–206°. Evaporation of the ether solution to dryness left a solid residue which was shaken with a mixture of 2 ml. of chloroform and 3 ml. of water. The undissolved solid melted at 206–208°. The chloroform layer was evaporated to dryness and the residue recrystallized from a small amount of water to yield benzoic acid (0.5 g.), m.p. 118–120° (no depression on admixture with benzoic acid). There was no depression of the m.p. of the phthalic acid upon admixture with an authentic sample. The yield of phthalic acid was less than 0.1 g.

Benzene from 2,4-Hexadien-1-ol or from 1,3,5-Hexatriene.—Either the alcohol or the triene was passed through the alumina column heated to 490 or 500° at 20 mm. in a nitrogen atmosphere. The product after drying was distilled, m.p. 79–82°, approximately 80–90% yield. This liquid was disproportionated with palladium-on-carbon as described above and distilled. The distillate was hydrogenated at atmospheric pressure and room temperature with palladium. The catalyst was filtered and the filtrate distilled, b.p. 78–81°. The ultraviolet spectrum of this material was identical with that of benzene and indicated a concentration of benzene of 50%.

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(9) F. Bodroux and F. Taboury, *Compt. rend.*, **148**, 1675 (1909).

(10) S. S. Voris and P. E. Spoerri, THIS JOURNAL, **60**, 935 (1938).

(11) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **103**, 1944 (1913).