TABLE VIII

MAJOR INFRARED ABSORPTION PEAKS FOR SOME SAMPLES OF POLYPROPYLENE OXIDE AND RELATED COMPOUNDS

Propylene oxide		Polypropylene oxide 2f[a]		Polypropylene oxide 1025[b]		Dimethyldioxane	
ν, cm.$^{-1}$	% tr.	ν, cm.$^{-1}$	% tr.	ν, cm.$^{-1}$	% tr.	ν, cm.$^{-1}$	% tr.
3000	5	3480	77	3400	76	2960	61
1500	21	3360	79	2880	47	2850	63
1450	11	2900	17			1715	88
1405	6	1450	40	1450	72	1465	79
1375	21	1375	19	1370	58	1405	83
1270	9	1345	40	1340	72	1385	73
1147	21	1300	42	1295	76	1350	82
1135	23	1260	56	1260	79	1275	87
						1155	57
1105	15	1080–1120	5	1098	21	1125	58
1023	7	1050	42	1050	75	1085	59
						1035	64
948	7	910	45	910	79	950	73
895	25	867	70			933	72
820–40	7					845	83
747	14						

[a] The sample of polypropylene oxide hydroxylated by treatment with hydrogen peroxide was virtually identical except for stronger absorption at 3450 cm.$^{-1}$ (65% transmission).

[b] Note that the relative intensity of the hydroxyl band (3400 cm.$^{-1}$) is greater in this material, in agreement with analytical titration data. The spectrum was unchanged after γ-ray irradiation.

then placed in the refrigerator overnight after which time the excess peroxide was decomposed using aqueous sodium metabisulfite. The polymer was then taken up in ether and neutralized with 20% sodium hydroxide. An excess of 40 ml. of 20% sodium hydroxide was added and the solution was refluxed for two hours to saponify any formate esters present. The organic portion was again taken up in 300 ml. of ether and shaken with ion exchange resin to neutralize any base carried over. The ether solution was evaporated to a low volume and then taken up in dry benzene and filtered in an effort to break the emulsion which had been formed. The benzene solution was then evaporated to a temperature of 165° at a pressure of 0.7 mm., yielding 27.5 g. (55% of starting weight) of polymeric material. Bromine analysis indicated the complete absence of unsaturation and the hydroxyl equivalent per gram of polymer was found by phthalation to have risen to 1.02 × 10^{-3}. The reduced viscosity had fallen, however, to 0.0805.

Treatment of this hydroxylated polymer with 1,5-naphthalene diisocyanate produced an insoluble gel, in contrast to the original polymer, which increased in viscosity but did not become insoluble.

PHILADELPHIA, PENNA.

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

Methyl-1,3,5-hexatrienes

BY HERMAN FLEISCHACKER AND G. FORREST WOODS

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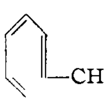
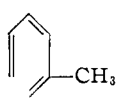
Methods of synthesis of 1-, 2- and 3-methyl-1,3,5-hexatrienes have been studied. The 1-, 2- and 3-methylhexatrienes give Diels–Alder adducts with maleic anhydride. The trienes undergo cyclization to methylcyclohexadienes by what is probably an internal Diels–Alder reaction. The methylcyclohexadienes were partially differentiated from the isomeric trienes by (1) reaction with maleic anhydride and (2) by aromatization.

The study of the conjugated trienes by this Laboratory has now been extended[1] from 1,3,5-hexatriene, the simplest of the conjugated trienes, to the monosubstituted hexatrienes, 1-, 2- and 3-methylhexatrienes, the particular isomers of which (I, II and III) are considered as the open chain analogs of toluene.


I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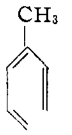
III

I, or one of its isomers, was readily prepared by the following reaction sequence: (1) addition of the methyl Grignard reagent to 2,4-hexadienal to give 2,4-heptadien-6-ol; (2) catalytic dehydration of the alcohol in the vapor phase with alumina. 1-Methylhexatriene[2] is a low melting solid (m.p. 22°) which undergoes polymerization rapidly in the solid state. It is, however, surprisingly stable in the liquid state, showing no marked deterioration upon standing for a period of several years in the absence of special precautions. A second isomeric substance is present in the catalytic dehydration product of the dienol. We first believed this substance was another geometrical isomer of 1-methyl-1,3,5-hexatriene but it was subsequently shown to be a methylcyclohexadiene (IV). The proportion of the methylcyclohexadiene increases with increasing temperature of dehydration. Further, passing 1-methyl-1,3,5-hexatriene over alumina at elevated temperatures converted it to methylcyclohexadiene.

These two substances were distinguished from each other by ultraviolet absorption spectra (Table I), hydrogenation experiments and the Diels–Alder adducts with maleic anhydride. The latter reaction with 1-methyl-1,3,5-hexatriene was interesting, for the addition of the anhydride apparently occurred across the triene at both the 1,4- and 3,6-positions. This fact was established by dehydrogenation of the adduct, and oxidation with permanganate to yield the tricarboxylic acid IX and tetracarboxylic acid X, Fig. 1. The tricarboxylic acid was isolated by extraction with ether (the tetra-

(1) G. F. Woods and L. H. Schwartzman, THIS JOURNAL, **70**, 3394 (1948); **71**, 1396 (1949); G. F. Woods and S. C. Temin, *ibid.*, **72**, 139 (1950); G. F. Woods, N. C. Bolgiano and D. E. Duggan, *ibid.*, **77**, 1800 (1955).

(2) C. J. Enklar (*C.A.*, **7**, 1169, 1704 (1913)) reported on the dehydration of 2,6-heptadien-4-ol with potassium hydrogen sulfate. He obtained a low melting (−14.5°) hydrocarbon (no other data were given), which he states is possibly 1,3,5-heptatriene. K. H. Ou (*Ann. Chim.*, **13**, 175 (1940)) dehydrated 1,5-heptadien-4-ol at 170° with sodium hydrogen sulfate deposited on pumice. A hydrocarbon was obtained described as "possibly 1,3,5-heptatriene." He reports a boiling point of 100–102° and n^{22}D 1.4798.

carboxylic acid was not extracted by this procedure). If the isolation of acids themselves was not attempted but the total oxidation material after aromatization was converted to the respective esters *via* the silver salt and the esters recrystallized, the tetramethyl ester of 1,2,3,4-benzenetetracarboxylic acid (X) was isolated.

3-Methyl-1,3,5-hexatriene[3] was obtained by the following sequence: (1) addition of allylmagnesium chloride to methyl vinyl ketone; (2) dehydration of the unsaturated alcohol 3-methyl-1,5-hexadien-3-ol (which was established to be free of any ketonic product by identification of the product of quantitative hydrogenation). Dehydration was carried out (A) catalytically over alumina and (B) by flash distillation from phosphorus pentoxide. Method A gave the much higher yield of product but of lower purity (ϵ 18,100) than method B (ϵ 21,400). This latter product absorbed 96.5% of the theoretical amount of hydrogen to saturate three double bonds. We consider the triene prepared by method B to be fairly pure although it is undoubtedly contaminated with a methylcyclohexadiene.

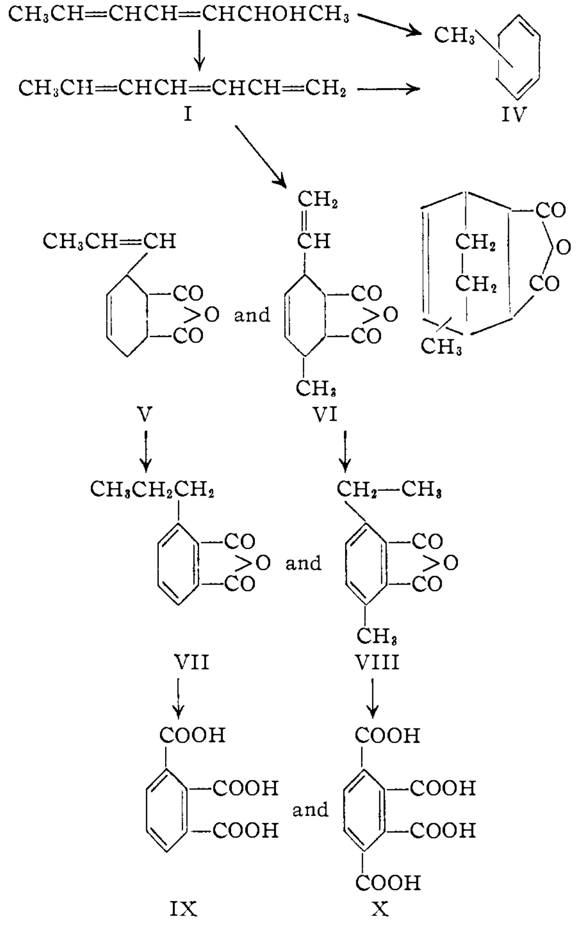

Fig. 1.—Preparation and reactions of 1-methyl-1,3,5-hexatriene

The chemistry of this sytem is comparable to that of 1-methyl-1,3,5-hexatriene. Dehydration of 3-methyl-1,5-hexadien-3-ol at more elevated temperatures led to increasing amounts of methylcyclohexadiene; passage of the triene over the catalyst at elevated temperatures also resulted in cyclization. 3-Methyl-1,3,5-hexatriene formed a Diels–Alder adduct with maleic anhydride. Although the adduct was a liquid (two adducts are possible because of 1,4-addition or 3,6-addition) the resulting acidic product was a solid which was purified by recrystallization. This solid absorbed the theoretical amount of hydrogen to saturate two ethylenic links. The methylcyclohexadiene from cyclization also formed a Diels–Alder adduct which absorbed but one equivalent of hydrogen.

The preparation of 2-methyl-1,3,5-hexatriene[4] was not entirely satisfactory. It was prepared by the dehydration of 2-methyl-1,5-hexadien-3-ol, which was the product of the reaction between allylmagnesium bromide and methacrolein. The dehydration of the alcohol was attempted catalytically with alumina and, although the triene was obviously present as evidenced by the ultraviolet absorption curve, the product contained predominately methylcyclohexadiene. Dehydration of 2-methyl-1,5-hexadien-3-ol was attempted with a number of reagents. The most successful was phosphorus pentoxide, since 2-methyl-1,3,5-hexatriene of high purity was obtained. The yield however was very low.

This methylhexatriene behaved as the other trienes in that it formed a Diels–Alder adduct which quantitatively absorbed two moles of hydrogen; it could be cyclized to a methylcyclohexadiene—indeed the cyclized product predominated upon vapor phase catalytic dehydration. The methylcyclohexadiene obtained in this manner formed a Diels–Alder product which quantitatively absorbed one mole of hydrogen.

The values for the ultraviolet absorption curves of the three methylhexatrienes are given in Table I. All the trienes that have been prepared possess a characteristic three peak curve the central one of which has the greatest extinction coefficient while the blue peak is the smallest.

TABLE I

ULTRAVIOLET ABSORPTION CHARACTERISTICS OF THE METHYL-1,3,5-HEXATRIENES (IN ISOÖCTANE)

1-Methyl		2-Methyl		3-Methyl	
λ, mμ	$\epsilon \times 10^{-3}$	λ, mμ	$\epsilon \times 10^{-3}$	λ, mμ	$\epsilon \times 10^{-3}$
247.5	34.2	248.0	20.2	253.0	15.5
257.5	46.8	257.5	26.5	262.5	21.4
267.5	38.1	267.5	21.4	272.5	16.5

If cyclization of the trienes occurs by an internal Diels–Alder[5] reaction, then the methylcyclohexa-

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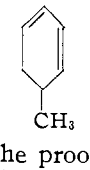
[3] K. H. Ou, ref. 2, dehydrated 3-methyl-1,5-hexadien-4-ol with sodium acid sulfate on pumice to yield probably impure 3-methyl-1,3,5-hexatriene.

[4] I. N. Nazarov and L. B. Fisher, *C.A.*, **38**, 4596 (1944), dehydrated 2-methyl-3,5-hexadien-2-ol with potassium acid sulfate or with acetyl chloride in pyridene to obtain impure 2-methyl-1,3,5-hexatriene. E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 2007 (1950), dehydrated the same alcohol as Nazarov and Fisher with dilute sulfuric acid or by distillation at reduced pressure from potassium hydrogen sulfate.

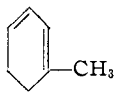
[5] The possibility of an internal Diels–Alder reaction in conjugated trienes has been recognized (K. Alder and M. Schumacher, Anwendungen der Dien-Synthese für die Erforschung von Naturstoffen in "Progress in the Chemistry of Organic Natural Products," Springer Verlag, Wien, 1953, page 10). Such a reaction has been postulated assuming intermediate trienes to account for observed cyclizations (H. Pines and J. Ryer, THIS JOURNAL, **77**, 4372 (1955); E. D. Parker and L. A. Goldblatt, *ibid.*, **72**, 2151 (1950)).

dienes that would be obtained from the methylhexatrienes could be predicted as shown

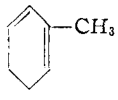
1-methyl-



2-methyl-



3-methyl-



The proof that methylcyclohexadienes were the products of cyclization of the three methylhexatrienes rests on the facts that: (1) each reacted with maleic anhydride to yield a product with one remaining double bond (established by hydrogenation); (2) aromatization of each cyclohexadiene yielded toluene, as indicated by the ultraviolet absorption spectrum of the aromatized mixture, and oxidation of this mixture resulted in benzoic acid. The ultraviolet absorption spectrum for each of the methylcyclohexadienes was characterized by the absence of fine structure and a much lower extinction coefficient than the precursor triene. The position of $\epsilon_{\max}$ could not be determined exactly since small amounts of triene which had survived the cyclization procedure were generally present.

Little can be said about the geometrical isomerism of the methyl-1,3,5-hexatrienes. Of the four geometrical isomers of 1-methylhexatriene one form only was obtained; the fact that it can be cyclized to a methylcyclohexadiene has no stereochemical meaning since the conditions of cyclization were such that *cis–trans* isomerization during the process is conceivable. The other two methylhexatrienes, 2-methyl and 3-methyl-, which are capable of being *cis* or *trans* were liquids and could not be crystallized or rigorously purified. It would appear that the three substances probably had the same configuration on the basis of the almost identical ultraviolet spectra. In fact, all the trienes we have prepared have essentially the same characteristic three peak ultraviolet absorption spectrum.

Experimental

1-Methyl-1,3,5-hexatriene.—2,4-Hexadienal[6] (144 g., 1.5 moles) dissolved in 1 l. of dry ether was added slowly to a methylmagnesium bromide solution prepared from 400 g. of methyl bromide. The addition complex was decomposed with ammonium chloride. The product was isolated in the usual manner. 3,5-Heptadien-2-ol[7] (153 g., 95%) was obtained, b.p. 51–52° (7 mm.), n^{26}_{D} 1.487. Reduction of the dienol provided 2-heptanol. This and the 3,5-dinitrobenzoate derivative[8] were identical with authentic samples.

Catalytic dehydration under reduced pressure of 3,5-heptadien-2-ol (20–40 mm.) and in a nitrogen atmosphere was accomplished by the use of 8–14 mesh activated alumina. The alumina was contained in a horizontal column of Pyrex glass which was heated to 325–350° by means of two electrical heating elements composed of resistance wire wound around the column. The dehydration product was collected in a flask which was cooled by immersion in a Dry Ice bath. The product was warmed to room temperature and most of the water layer was removed by means of an eye dropper. The remainder was distilled after drying over calcium oxide and the fraction boiling at 22–26° (14 mm.) was collected. This material was added to petroleum ether (30–40°) and chilled. The crystalline material was isolated by suction filtration. Redistillation of the melted solid provided 1-methyl-1,3,5-hexatriene, b.p. 114–115° (760 mm.), n^{28}_{D} 1.5239, m.p. 21–22°. The over-all yield on 50–60 g. runs was 40–50%.

Anal. Calcd. for C_7H_{10}: C, 89.30; H, 10.70. Found: C, 89.41; H, 10.70.

1-Methyl-1,3,5-hexatriene (2.4 g., 0.025 mole), dissolved in 100 ml. of ethanol, was hydrogenated at atmospheric pressure and room temperature. Palladium-on-carbon (10%, 0.1 g.) was the catalyst. In less than two hours 1775 ml. of hydrogen was absorbed (98%).

Diels–Alder Reaction of 1-Methyl-1,3,5-hexatriene with Maleic Anhydride.—A mixture of triene (25 g., 0.27 mole) and 24 g. of maleic anhydride was allowed to stand for 12 hours. The yellow glass (V and VI) which had formed and which could not be induced to crystallize was distilled yielding 36 g. (78%), b.p. 118–121° (1 mm.).

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.30. Found: C, 68.63; H, 6.19.

Hydrogenation of this material (2.33 g., 0.012 mole) in ethanol with palladium-on-carbon at atmospheric pressure and room temperature led to the absorption of 575 ml. of hydrogen (98% uptake for two moles).

If the Diels–Alder adduct was added to water with which concd. potassium hydroxide was mixed slowly until complete solubility was obtained and then adjusted to a *p*H of 5, a precipitate was formed. Recrystallization of the precipitate yielded a mixture of the dicarboxylic acids from the Diels–Alder adduct. This mixture melted (dec.) at 190° after recrystallization from ether.

Anal. Calcd. for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 63.01; H, 6.68.

Aromatization of the Diels–Alder Product from 1-Methyl-1,3,5-hexatriene.—The above Diels–Alder adduct (20 g.) was added dropwise to a flask which was heated to 220° and which contained 1 g. of 10% palladium-on-charcoal. Heating was continued after the addition until hydrogen evolution had ceased (detected by a bubble counter). Distillation of this material directly from the catalyst at reduced pressure (20 mm.) provided a mixture (8.1 g., 39%) of the aromatized anhydrides (VII and VIII) which could be crystallized from petroleum ether, m.p. 72–75°.

Anal. Calcd. for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30. Found: C, 69.71; H, 5.12.

Oxidation of the above in the usual manner with potassium permanganate and potassium hydroxide was accomplished. The acidified medium was extracted continuously with ether for 18 hours. On concentration of the ether solution 6.2 g. (from 8.5 g. of the mixture of anhydrides VII and VIII) of benzene-1,2,3-tricarboxylic acid was obtained which upon recrystallization melted at 190°. This, and its trimethyl ester prepared by the silver salt method, gave no depression with authentic samples.

If the original permanganate oxidation medium was acidified with nitric acid and silver nitrate added, a precipitate of silver salts occurred. The dried silver salts were refluxed in 100 ml. of benzene containing 48 g. of methyl iodide for 12 hours. After filtration, the filtrate was concentrated to a small volume and chilled. Upon cooling, white, crystalline methyl ester of 1,2,3,4-benzenetetracarboxylic acid precipitated (0.5 g.) which was recrystallized from methanol, m.p. 132–133° (no mixed m.p. with authentic sample). This material turns purple upon exposure to light as observed previously.[9]

Preparation of Methylcyclohexadiene (IV).—Redistillation of the petroleum ether solution recovered from the crystallization of 1-methyl-1,3,5-hexatriene provided a liquid boiling at 102–115°. The refractive index of samples increased from 1.48 to 1.52 of this liquid with increasing temperature of distillation; the lower boiling material is predominantly the methylcyclohexadiene (IV).

It was prepared in purer state by (A) the dehydration of 3,5-heptadien-2-ol over alumina heated at 500° (from 20 g. (0.18 mole) of alcohol 10.2 g. (61%) of methylcyclohexadiene); or (B) passage of methyl-1,3,5-hexatriene over the catalyst under the same conditions (yield 74%).

The methylcyclohexadiene boiled at 108° (atmospheric pressure), n^{28}_{D} 1.474, ϵ_{259} 3,300; this material will absorb oxygen upon exposure to air. Redistillation of this latter material has led several times to violent decomposition.

Anal. Calcd. for C_7H_{10}: C, 89.30; H, 10.70. Found: C, 89.61; H, 10.40.

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(6) This material was kindly provided by the Carbide and Carbon Chemicals Co.

(7) E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2085 (1951), give b.p. of 78° (20 mm.), n^{21}_{D} 1.4897, for this substance.

(8) G. B. Malone and E. E. Reid, THIS JOURNAL, **51**, 3424 (1929).

(9) L. I. Smith and E. J. Carlson, THIS JOURNAL, **61**, 288 (1939).

Diels–Alder Adduct of Methylcyclohexadiene (IV) with Maleic Anhydride.—Methylcyclohexadiene (6.1 g., 0.06 mole) was mixed with maleic anhydride (5.9 g., 0.06 mole). The reaction mixture, which became quite warm, was cooled until the vigorous reaction had ended and then was heated at 120° for one hour. The reaction mixture was stirred with aqueous potassium hydroxide and extracted with ether. The aqueous layer was acidified and extracted with ether. Distillation of the ether layer after drying provided 4.8 g. (42%) of the Diels–Alder adduct, b.p. 133–136° (1 mm.), n^{28}_{D} 1.504. In this process the anhydride which had been opened was obtained by dehydration of the dicarboxylic acid.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.30. Found: C, 68.63; H, 6.22.

A sample (0.72 g.) of the above anhydride was hydrogenated in ethanol at atmospheric pressure and room temperature with palladium-on-carbon catalyst. In 30 minutes the hydrogenation had ceased and 97 ml. (104% for saturation of one ethylenic link) of hydrogen had been absorbed.

Aromatization of the methylcyclohexadiene in the usual manner with palladium catalyst was effected. The ultraviolet spectrum of the product distilled directly from the catalyst was not quite identical with that of toluene. Hydrogenation with palladium at room temperature and atmospheric pressure absorbed too small an amount of hydrogen to report, but the ultraviolet absorption spectrum of the material distilled from the catalyst was identical with that of toluene.

Oxidation of 2.0 g. of the aromatized mixture with potassium permanganate in the usual manner provided 0.9 g. of benzoic acid which was identical with an authentic sample.

3-Methyl-1,3,5-hexatriene.—3-Methyl-1,3,5-hexatriene was prepared[10] by the dehydration of 3-methyl-1,5-hexadien-3-ol. This alcohol was obtained in 70% yield from the reaction of methyl vinyl ketone and allyl Grignard reagent; b.p. 137° (760 mm.), n^{22}_{D} 1.446. Hydrogenation of this dienol at atmospheric pressure and room temperature absorbed 102% of hydrogen calculated for two ethylenic links. The properties of the product, 3-methyl-3-hexanol, were identical with those of an authentic sample,[11] b.p. 140°, n^{20}_{D} 1.423.

Dehydration of 3-methyl-1,5-hexadien-3-ol over alumina, as described above, at 350° provided material whose ultraviolet spectrum had the typical three peaks ($\epsilon_{\max}$ 18,100), n^{26}_{D} 1.491.

If the alcohol (10 ml.) was added to phosphorus pentoxide (20 g.) an exothermic reaction occurred the heat of which was sufficient to distil the resulting product at 20 mm. After redistillation, 3-methyl-1,3,5-hexatriene[12] (app. 2 g.) was obtained boiling at 28° (25 mm.), n^{28}_{D} 1.492, $\epsilon_{262.5}$ 21,400.

Anal. Calcd. for C_7H_{10}: C, 89.20; H, 10.70. Found: C, 89.48; H, 10.71.

3-Methyl-1,3,5-hexatriene (1.19 g.) dissolved in 95% ethanol in the presence of palladium-on-carbon absorbed 780 ml. of hydrogen (96.5% for three ethylenic links) at atmospheric pressure and room temperature.

A Diels–Alder adduct was formed (which was a glass) upon allowing the triene to stand at room temperature with an equimolar quantity of maleic anhydride. The glass was treated with dilute potassium hydroxide and the aqueous layer extracted with ether. Upon careful acidification of the aqueous layer with hydrochloric acid a precipitate was formed, which was recrystallized from water–ethanol, m.p. 138°.

Anal. Calcd. for $C_{11}H_{14}O_4$: C, 62.85; H, 6.71. Found: C, 63.05; H, 6.77.

Quantitative hydrogenation at 750 mm. and at 26° with palladium-on-carbon of the dicarboxylic acid (0.18 g.) led to the absorption of 45 ml. of hydrogen (105% for two ethylenic links).

As in the case of 1,3,5-heptatriene, this system also underwent cyclization. Passage of the alcohol 3-methyl-1,5-hexadien-5-ol over alumina at 490–500° yielded a methylcyclohexadiene (56% yield, b.p. 26° (20 mm.), n^{28}_{D} 1.466).

Anal. Calcd. for C_7H_{10}: C, 89.30; H, 10.70. Found: C, 89.22; H, 10.46.

Hydrogenation of this material in a quantitative manner provided erratic results. But dehydrogenation of this material (more accurately described as disproportionation) with palladium-on-carbon gave a liquid product the ultraviolet absorption spectrum of which was identical with that of toluene. Oxidation of the material in the manner described above with potassium permanganate yielded benzoic acid.

The methylcyclohexadiene reacted with maleic anhydride in benzene with heating under reflux conditions for 8 hours. After removal of the solvent the product was distilled, b.p. 120° (0.1 mm.). It could not be induced to crystallize and the free acid, after opening the anhydride link with alkali, apparently reformed the anhydride. A solid could not be obtained.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.30. Found: C, 68.46; H, 6.36.

Upon quantitative hydrogenation in the usual manner (palladium-on-carbon) the Diels–Alder adduct absorbed 109% of hydrogen to saturate one ethylenic link.

2-Methyl-1,3,5-hexatriene.—The Grignard reaction was used in the usual manner with allyl bromide and methacrolein to prepare 2-methyl-1,5-hexadien-3-ol (74% yield), b.p. 144–145° (760 mm.), n^{26}_{D} 1.449.

Anal. Calcd. for $C_7H_{12}O$: C, 74.94; H, 10.78. Found: C, 75.15; H, 10.81.

Hydrogenation of a sample of this alcohol (palladium-on-carbon), which absorbed two moles of hydrogen, provided 2-methyl-3-hexanol (b.p. 140–141.5° (760 mm.) and n^{28}_{D} 1.414) which was identical with an authentic sample.[13]

Dehydration of 2-methyl-1,5-hexadien-3-ol catalytically over alumina from 300 up to 500° provided hydrocarbon material (much alcohol survived dehydration below the lower temperature) the refractive index of which was approximately 1.45. The ultraviolet spectrum of this material was essentially that of a diene although the triple peak of a triene in certain instances could still be discerned; $\epsilon_{\max}$ was 8700 or less.

Dehydration of the dienol with phosphorus pentoxide as described above provided in poor yield (10–25%) 2-methyl-1,3,5-hexatriene which, upon passing through a small absorption column packed with alumina and redistillation, boiled at 27° (14 mm.), n^{26}_{D} 1.491. Braude and Timmons[4] reported b.p. of 48–52° (52 mm.), n^{16}_{D} 1.5127; Nazarov and Fisher[4] reported b.p. of 42° (60 mm.), n^{20}_{D} 1.5051.

By means of the procedure described above, this triene formed a Diels–Alder adduct with maleic anhydride which was a liquid, b.p. 140–141° (0.1 mm.).

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.30. Found: C, 68.52; H, 5.98.

It could not be induced to crystallize nor could a solid dicarboxylic acid be obtained upon dissolving in alkali and reacidifying with hydrochloric acid.

The anhydride (0.18 g.) absorbed 43.4 ml. of hydrogen (96% of theory for two ethylenic links) at 22° and atmospheric pressure.

As before the dienol upon dehydration at higher temperatures underwent cyclization to form a methylcyclohexadiene (61%) b.p. 31–32° (20 mm.), n^{28}_{D} 1.460.

Anal. Calcd. for C_7H_{10}: C, 89.30; H, 10.70. Found: C, 89.60; H, 10.48.

Disproportionation of this material led to toluene on the basis of its ultraviolet spectrum; the oxidation of this mixture after disproportionation resulted in benzoic acid.

The Diels–Alder adduct of the methylcyclohexadiene was a liquid (b.p. 124–5° (0.8 mm.), n^{28}_{D} 1.503) and could not be made to crystallize nor could a solid dicarboxylic acid be obtained.

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.30. Found: C, 68.45; H, 6.09.

Quantitative hydrogenation of this material (0.71 g.), as before, absorbed 94.0 ml. of hydrogen at 22° and atmospheric pressure (105% of theory to saturate one ethylenic link).

COLLEGE PARK, MARYLAND

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(10) K. Zeile and H. Meyer, *Ber.*, **82**, 267 (1949).

(11) F. C. Whitmore and D. E. Badertscher, THIS JOURNAL, **55**, 4160 (1933), and E. J. Sokoloff, *J. prakt. Chem.*, **39**, 430 (1889).

(12) K. H. Ou (ref. 2) reports a boiling point of 92–94° (760) and n^{21}_{D} 1.4950. He had treated the Grignard reagent of crotonyl bromide with acrolein. The product, 3-methyl-1,5-hexadien-4-ol, was dehydrated with sodium bisulfate.

(13) R. H. Pickard and J. Kenyon, *J. Chem. Soc.*, **101**, 620 (1912).