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A Synthesis of Conjugated Polyenes: 1,3,5-Hexatriene and 1,3,5,7-Octatetraene

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A SYNTHESIS OF CONJUGATED POLYENES: 1,3,5-HEXATRIENE AND 1,3,5,7-OCTATETRAENE

By

Louis Herbert Schwartzman

Thesis submitted to the Faculty of the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy

1949

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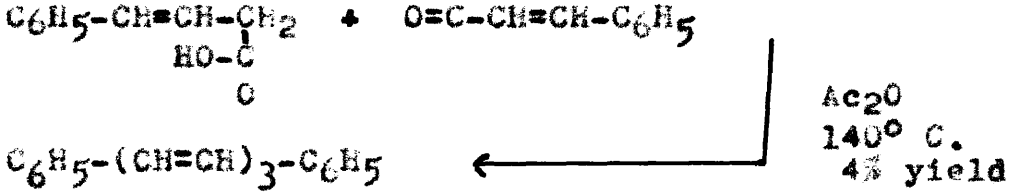
HISTORICAL

The importance of conjugated polyenes has been recognized because of the relation of these substances to many natural products and also to the problems of theoretical organic chemistry. The emphasis of the work contained in this thesis pertains specifically to the synthesis and properties, physical and chemical, of 1,3,5-hexatriene, $CH_2=CH-CH=CH-CH=CH_2$, and 1,3,5,7-octatetraene, $CH_2=CH-CH=CH-CH=CH-CH=CH_2$; and therefore no attempt has been made to review the status of the many carotenoid substances found in nature.

A review of the syntheses of polyenes reveals that certain general procedures have been developed, and that a number of specific reactions have been used.

One general method is the condensation of an α,β-unsaturated aldehyde with another compound, containing an active methyl or methylene structure, such as malonic acid.

In this manner 1,6-diphenylhexatriene was prepared[1] by the condensation of phenyl isocrotonic acid with cinnamaldehyde in the presence of acetic anhydride.



Condensation of 5-phenylpentadienal with succinic acid in the presence of lead oxide using a mixture of glacial acetic acid and acetic anhydride produced 1,12-diphenyldodecahexaene

in good yields[2].

$$2C_6H_5\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CHO + HOOC\text{-}CH_2\text{-}CH_2\text{-}COOH \xrightarrow[HAc\ Ac_2O]{PbO} C_6H_5\text{-}(CH{=}CH)_2\text{-}CH{=}C(COOH)\text{-}C(COOH){=}CH\text{-}(CH{=}CH)_2\text{-}C_6H_5 \longrightarrow C_6H_5\text{-}(CH{=}CH)_6\text{-}C_6H_5$$

Dihydromuccic acid, $HOOC\text{-}CH_2CH{=}CH\text{-}CH_2\text{-}COOH$, was used[2], in place of succinic acid, with cinnamaldehyde and 5-phenylpentadienal for the synthesis of $C_6H_5\text{-}(CH{=}CH)_5\text{-}C_6H_5$ and $C_6H_5\text{-}(CH{=}CH)_7\text{-}C_6H_5$ respectively.

Kuhn and Wallenfels[3] obtained 11-phenylundecapentaenal, $C_6H_5\text{-}(CH{=}CH)_5\text{-}CHO$, and 15-phenylpentadecaheptaenal, $C_6H_5\text{-}(CH{=}CH)_7\text{-}CHO$, by the condensation of cinnamaldehyde with crotonaldehyde in the presence of piperidine acetate.

$$C_6H_5\text{-}CH{=}CH\text{-}CHO + CH_3\text{-}CH{=}CH\text{-}CHO \xrightarrow[acetate]{piperidine} C_6H_5(CH{=}CH)_7\text{-}CHO + C_6H_5\text{-}(CH{=}CH)_5\text{-}CHO$$

Kuhn[4], by using a modification of the Knoevenagel condensation, synthesized the compounds $CH_3\text{-}(CH{=}CH)_n\text{-}CHO$ where n=1,2,3,4,5,7,9 and $CH_3\text{-}(CH{=}CH)_n\text{-}COOH$ where n=1,2,3,4,5,6,8. The reaction consisted of a condensation of an aliphatic aldehyde with another molecule of the same aldehyde or of another aldehyde in the presence of piperidine acetate as a catalyst.

$$CH_3\text{-}CH{=}CH\text{-}CHO + CH_3\text{-}CH{=}CH\text{-}CHO \xrightarrow[acetate]{piperidine} CH_3\text{-}(CH{=}CH)_3\text{-}CHO$$

$$CH_3\text{-}CHO + CH_3\text{-}CH{=}CH\text{-}CHO \xrightarrow[acetate]{piperidine} CH_3\text{-}(CH{=}CH)_2\text{-}CHO$$

The condensation of furfural[5,6] and acetaldehyde or crotonaldehyde in the presence of piperidine acetate has been used to prepare polyenes of the type  -$(CH=CH)_n$-CHO, where n=1,2,3,4,5,6,7.

All these conjugated polyenic aldehydes react with malonic acid in pyridine whereby the carboxylic acids[4] with one more double bond are obtained.

$$CH_3\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CHO + CH_2(COOH)_2 \xrightarrow{\text{Pyridine}} CH_3\text{-}(CH{=}CH)_3\text{-}CH{=}C(COOH)_2$$

$$CH_3(CH{=}CH)_4COOH \xleftarrow[-CO_2]{\text{heat}} CH_3\text{-}(CH{=}CH)_3\text{-}CH{=}C(COOH)_2$$

Wittig and Kethur[7], using a similar condensation of an unsaturated aldehyde with a compound containing an active methylene group, cyano-acetic acid, prepared the corresponding cyano unsaturated acid. The acid was then decarboxylated to the nitrile and a Stephan reduction on the nitrile afforded the polyene aldehyde.

$$C_6H_5\text{-}CH{=}CH\text{-}CH{=}CH\text{-}CHO + N{\equiv}C\text{-}CH_2COOH \longrightarrow C_6H_5\text{-}(CH{=}CH)_2\text{-}CH{=}C(CN)(COOH)$$

$$C_6H_5\text{-}(CH{=}CH)_2\text{-}CH{=}C(CN)(COOH) \xrightarrow{\text{Cu, heat, } -CO_2} C_6H_5(CH{=}CH)_3\text{-}C{\equiv}N$$

$$C_6H_5(CH{=}CH)_3\text{-}CHO \xleftarrow[HCl]{SnCl_2} C_6H_5(CH{=}CH)_3\text{-}C{\equiv}N$$

Another excellent general method of synthesizing polyenes was developed by Kuhn and co-workers[8]. The oxygen atom of the polyene aldehydes, just like that of the simple aldehydes, can be replaced by an atom of sulphur by the action of hydrogen sulfide under suitable conditions.

Similarly, the preparation of selenoaldehydes by the action of hydrogen selenide is also possible. The removal of sulphur or selenium by copper, various reducing agents, or amines such as piperidine leads to the polyene compounds.

$$C_6H_5\text{-}(CH{=}CH)_5\text{-}CHO \xrightarrow[H_2Se]{H_2S} C_6H_5\text{-}(CH{=}CH)_5\text{-}CH{=}S \downarrow C_6H_5\text{-}(CH{=}CH)_1\text{-}C_6H_5$$

Condensation of the polyene monocarboxylic esters, the synthesis of which was discussed earlier, with potassium ethoxide and oxalic ester yield the corresponding oxalo-polyene carboxylic esters.[9] Pyridine is a necessary catalyst in the case of higher esters. The oxaloesters so obtained were acetylated with acetic anhydride and these enol-acetates were reduced with aluminum amalgam. In accordance with Thiele's hypothesis, which deals with a partial residual valence at the ends of a conjugated system, the molecule adds two hydrogen atoms at the ends of the conjugated system. Finally, treatment with alcohol and sodium hydroxide subsequently yielded the polyene dicarboxylic acid. Kuhn and Grundman[9] prepared the compounds $HOOC\text{-}(CH{=}CH)_n\text{-}COOH$ where n=1,2,3,4,5,7 in this manner.

$$ROOC\text{-}COOR + CH_3\text{-}(CH{=}CH)_n\text{-}COOR \xrightarrow[KOEt]{\text{pyridine}} ROOC\text{-}\underset{\underset{O}{\|}}{C}\text{-}CH_2\text{-}(CH{=}CH)_n\text{-}COOR$$

$$ROOC\text{-}COAc{=}CH\text{-}(CH{=}CH)_n\text{-}COOR \xleftarrow{Ac_2O} ROOC\text{-}COH{=}CH\text{-}(CH{=}CH)_n\text{-}COOR$$

$$\downarrow Al.hg$$

$$ROOC\text{-}CHOAc\text{-}(CH{=}CH)_n\text{-}CH_2\text{-}COOR \xrightarrow{ROH + NAOH} ROOC\text{-}(CH{=}CH)_{n+1}\text{-}COOR$$

The preparation of tetradecaheptaene-1,14-dicarboxylic acid (n=7) did not follow as well[9]; aluminum amalgam reduction of the enol-acetate yielded $ROOC-CH_2-(CH=CH)_6-CH_2-COOR$, and this compound had to be dehydrogenated to the polyene dicarboxylic ester by the action of atmospheric oxygen in the presence of alkali, a reaction developed by Kuhn[10].

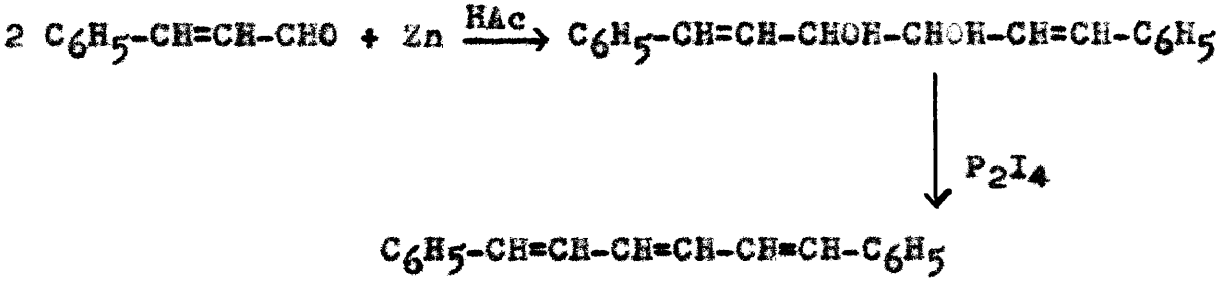
Alpha keto esters have been prepared as shown below by the condensation of oxalic ester with the appropriate unsaturated esters. These products upon hydrolysis and oxidation with hydrogen peroxide[9] yielded polyene dicarboxylic acids of the series $HOOC-CH_2(CH=CH)_n-COOH$ where n= 1,2,3,4.

$$ROOC-COOR + CH_3-(CH=CH)_n-COOR \xrightarrow{KOEt} ROOC-\underset{\underset{O}{\|}}{C}-CH_2(CH=CH)_n-COOR$$

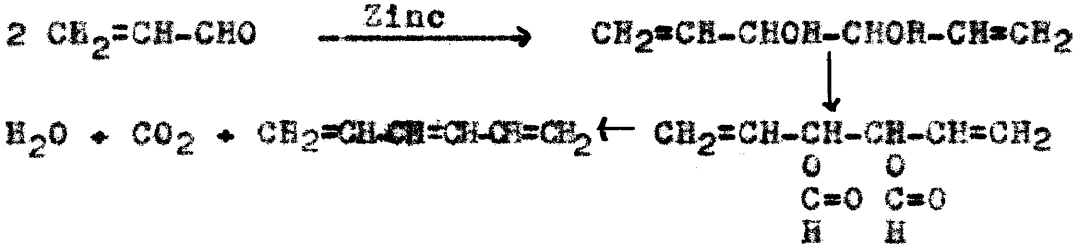
$$HOOC-CH_2-(CH=CH)_n-COOH \xleftarrow[(2)\ H_2O_2]{(1)\ \text{Hydrolysis}}$$

The dehydroxylation of glycols has been used successfully as another method of preparing polyenes.

Dihydrocinnamoin was prepared by a bimolecular reduction of cinnamaldehyde over zinc or aluminum amalgam, and when this compound was subsequently dehydroxylated with phosphorous diiodide, 1,6-diphenylhexatriene[2] was produced in yields approaching theoretical.



This same method was used for a preparation of 1,3,5-hexatriene. Griner[11] showed that the bimolecular reduction of acrolein yielded s-divinylethylene glycol. This substance was then esterified to the diformate, the pyrolysis of which produced 1,3,5-hexatriene[12].



An alternate means of converting the glycol, CH_2=CH-CHOH-CHOHCH=CH_2, to hexatriene was developed by Farmer and co-workers[13,14]. Their method consisted of the conversion of the glycol to the dibromide, which compound was then dehalogenated by treatment with zinc. The following equations (Fig. 1), outline this procedure and include the subsequent work of this group on hexatriene.

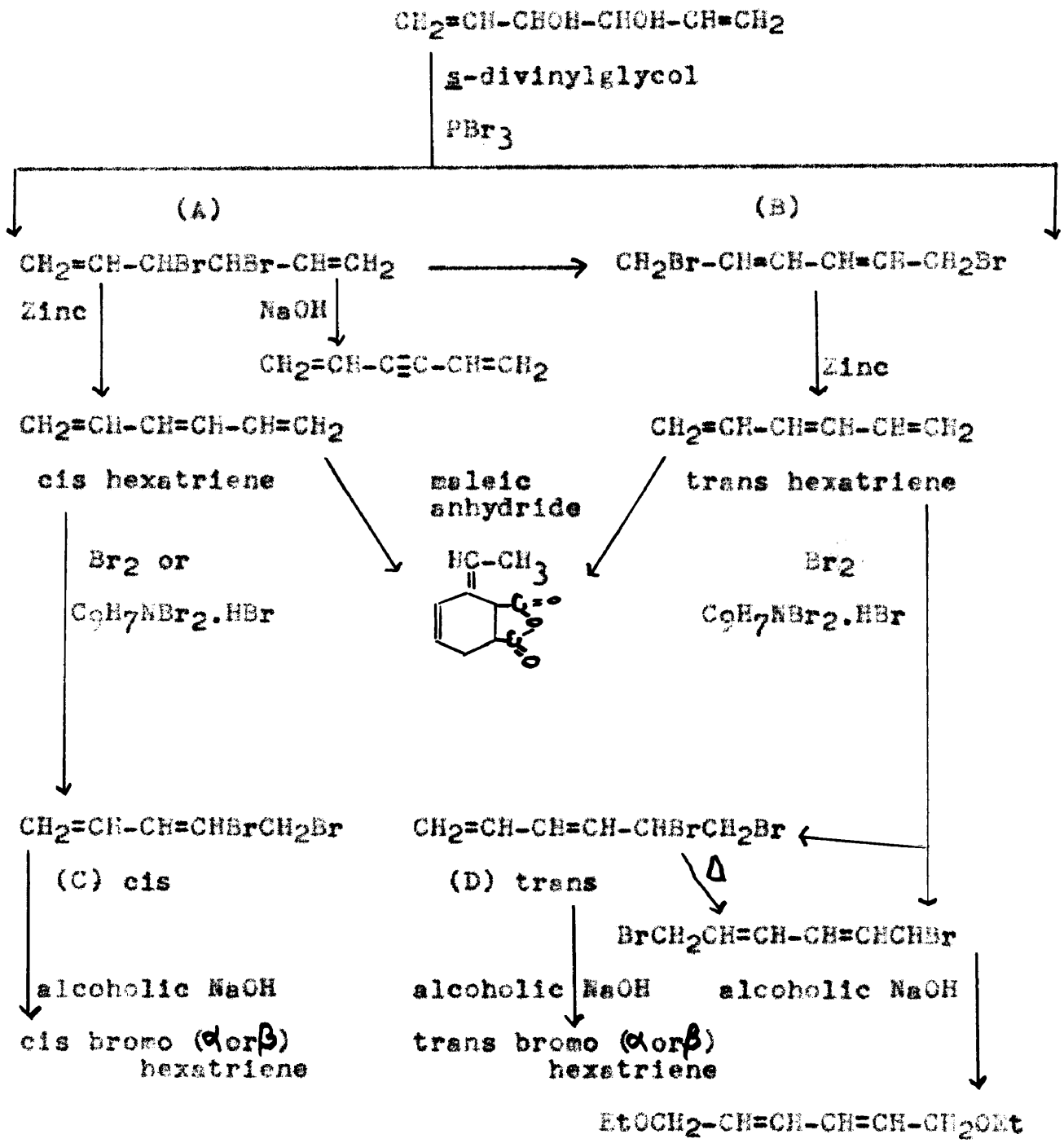
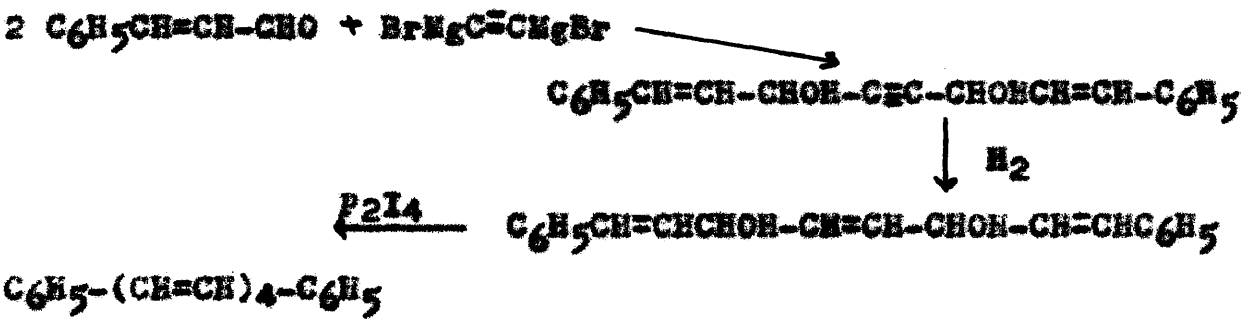
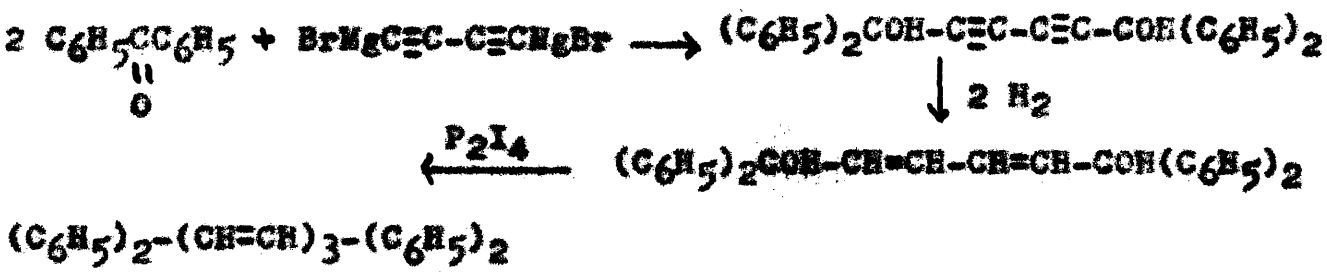


Fig. 1 Summary of Farmer's Work on Hexatriene

Dehydroxylation of 1,2-1,4 or 1,6 glycols by phosphorus diiodide has been used also by Kuhn and co-workers[2] for the preparation of many polyenic compounds. The 1,4 glycols were obtained by condensation of polyene aldehydes with acetylene dimagnesiumbromide [15] and subsequent partial hydrogenation in the following manner:



The 1,6 glycols were obtained in a similar way with diacetylene dimagnesiumbromide[15].



Probably the most generally used procedure of preparing polyenes has been the dehydration of an appropriately unsaturated alcohol (i.e., two or more double ethylenic links in the alcohol). In practice, the alcohol may not have been isolated.

The Reformatsky reaction[16], a reaction of an α-bromo ester with an aldehyde or a ketone in the presence of zinc, has been used very successfully for this purpose.

Crotonylidene acetone reacts with bromoacetic ester in the presence of zinc to give 3-methyloctatrienoic acid[17].

$$CH_3-CH=CH-CH=CH-\underset{\underset{O}{\|}}{C}-CH_3 + BrCH_2COOR \xrightarrow{Zinc}$$

$$CH_3-CH=CH-CH=CH-C(CH_3)=CHCOOH$$

Similarly cinnamalacetone reacts with bromoacetic ester to give 3-methyl-7-phenylheptatrienoic acid and 6-methyl-3, 5-heptadien-2-one reacts with bromoacetic ester to give 3,7-dimethyloctatrienoic acid[17].

Fischer and Lowenberg[18] prepared allocimene by the Reformatsky reaction. They reacted 6-methyl-3,5-heptadiene-2-one with α-bromopropionic ester.

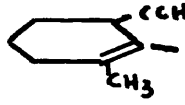
$$(CH_3)_2-C=CH-CH=CH-\underset{\underset{O}{\|}}{C}-CH_3 + BrCH(CH_3)COOC_2H_5 \xrightarrow{ZINC}$$

$$(CH_3)_2-C=CH-CH=CH-COH(CH_3)CH(CH_3)COOC_2H_5$$

$$(CH_3)_2-C=CH-CH=CH-C(CH_3)=CH-CH_3$$

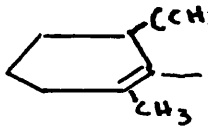
Allocimene

In an attempt to prepare compounds similar to vitamin A, Heilbron and co-workers[19] used the Reformatsky reaction. Their work is summarized by the equations below.



$$CH=C(CH_3)-CH=CH-CHO + BrCH_2COOC_2H_5 \xrightarrow{Zinc,53\%}$$

$$R-CH=C(CH_3)-CH=CH-CHOH-CH_2COOC_2H_5$$



$$CH=C(CH_3)(CH=CH)_2COOEt$$

The Grignard reaction which is an exceedingly useful tool in organic synthetic work finds great utility in the preparation of unseturated alcohols.

The reaction of the unsaturated aldehyde, 11-phenyl-unadecapentaenal, with benzylmagnesium chloride yields an alcohol which is dehydrated to the conjugated polyene, 1,12-diphenyldodecahexaene[3]:

$$C_6H_5\text{-}(CH{=}CH)_5\text{-}CHO + C_6H_5CH_2MgCl \longrightarrow C_6H_5\text{-}(CH{=}CH)_5\text{-}CHOH\text{-}CH_2\text{-}C_6H_5$$

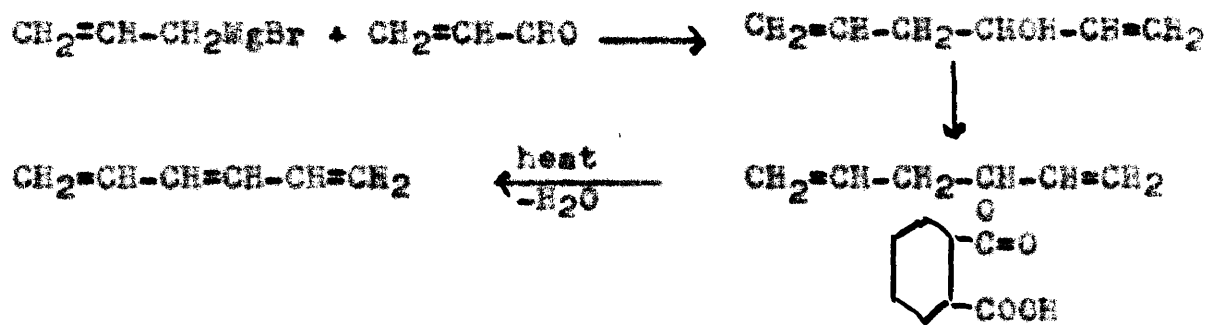
$$C_6H_5\text{-}(CH{=}CH)_5\text{-}CHOH\text{-}CH_2\text{-}C_6H_5 \xrightarrow{-H_2O} C_6H_5\text{-}(CH{=}CH)_6\text{-}C_6H_5$$

The polyene aldehydes discussed earlier react normally with alkylmagnesium halide, forming the corresponding carbinols, which are dehydrated by a 1-2% solution of p-toluene sulphonic acid in other to give the aliphatic polyene hydrocarbons. Kuhn and Grundman[20] prepared the compounds $CH_3\text{-}(CH{=}CH)_n\text{-}CH_3$ where n=1,2,3,4,6 in this manner.

$$CH_3\text{-}(CH{=}CH)_2\text{-}CHO + C_2H_5MgBr \longrightarrow CH_3\text{-}(CH{=}CH)_2\text{-}CHOH\text{-}C_2H_5$$

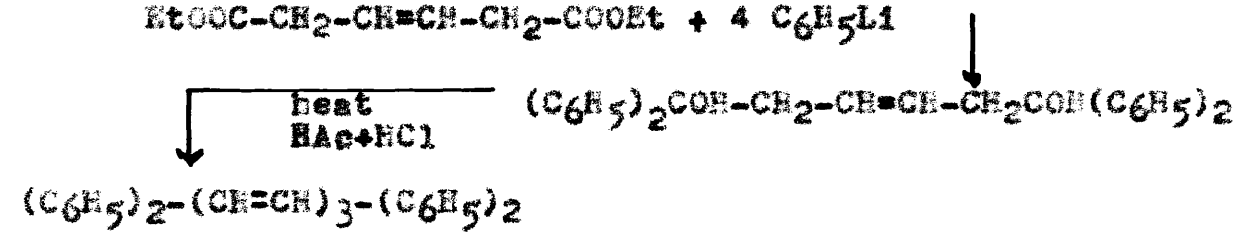
$$CH_3\text{-}(CH{=}CH)_2\text{-}CHOH\text{-}C_2H_5 \xrightarrow{Et_2O + H^+} CH_3\text{-}(CH{=}CH)_3\text{-}CH_3$$

Butz and coworkers[21] have used this procedure for the preparation of hexatriene. Their method consisted of the dehydration of 1,5-hexadien-3-ol. This alcohol had been prepared by the reaction of allylmagnesium bromide with acrolein. The dehydration was accomplished in a manner similar to the diformate pyrolysis method of van Romburgh[12], although the ester was the half-phthalate of 1,5-hexadien-3-ol.



The dehydration of 1,5-hexadiene-3-ol to hexatriene was reported in yields up to 70%. However, upon reaction with maleic anhydride this hydrocarbon sample gave two derivatives[22]; one proved to be identical with that obtained by Farmer and Warren[14], and the other proved to be identical to that obtained upon reacting maleic anhydride with cylco-hexadiene.

Phenyllithium[23] has been reacted with the diethyl ester of dihydromuconic acid to give tetraphenylhexatriene.



The use of zinc and cadmium alkyls has also been reported for the synthesis of polyenes, but the use of these reagents in this field is very limited[17].

An interesting and specific, as well as restricted, mode of synthesis was reported by Kharasch and co-workers[24] for the preparation of 1,3,5-hexatriene and 2,5-dimethyl-hexatriene-1,3,5 involving a bimolecular dehydrohalogenation from the appropriate allyl chloride with sodamide.

$$2\ CH_2{=}CH{-}CH_2Cl + 2\ NaNH_2 \longrightarrow CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$$

$$2\ CH_2{=}C(CH_3){-}CH_2Cl + 2\ NaNH_2 \longrightarrow CH_2{=}C(CH_3){-}CH{=}CH{-}C(CH_3){=}CH_2$$

Kharasch says that,[25,26] "Halides of weakly electronegative radicals will condense when treated with sodamide in liquid ammonia if there is a hydrogen atom on the carbon atom to which the halogen is attached". He implies that since the electronegativity of the allyl radical would be decreased by substituents on the alpha carbon atom and only very little affected by substituents on the beta carbon atom, this general method should apply to the preparation of many substituted hexatrienes.

In this method, there was the probability that the conversion of allyl chloride to hexatriene proceeded through the intermediate formation of a chlorohexadiene.

$$CH_2{=}CH{-}CH_2Cl + NaNH_2 + ClCH_2{-}CH{=}CH_2 \longrightarrow CH_2{=}CH{-}CH_2{-}CHCl{-}CH{=}CH_2$$

This possibility was investigated by Kharasch and coworkers[27]. It was shown two molecular equivalents of allyl chloride did react in the presence of one molecular equivalent of sodamide to give a chlorohexadiene. However, chlorohexadiene when reacted with another equivalent of sodamide failed to give hexatriene, but instead gave 1-butadienyl-2-vinyl cyclohexene-3.

The general reaction was repeated with beta-methyl allyl chloride and gave a 2,5-dimethyl hexadiene, which on further treatment was converted to 2,5-dimethyl hexatriene.

Recently, selective hydrogenation of acetylenic compounds

has been used as a method of preparation of hexatriene. Divinylacetylene was partially hydrogenated over a palladium-barium sulfate catalyst at room temperature and atmospheric pressure until one molar equivalent of hydrogen was absorbed. The hexatriene fraction, an unspecified amount, was reported to yield a dibromide[13] and a maleic anhydride adduct[14].

$$CH_2=CH-C\equiv C-CH=CH_2 \xrightarrow[Pd\text{-}BaSO_4\ catalyst]{H_2} CH_2=CH-CH=CH-CH=CH_2$$

In a similar manner, 1,3-hexadien-5-yne was selectively hydrogenated to hexatriene[28].

$$CH\equiv C-CH=CH-CH=CH_2 \xrightarrow{H_2} CH_2=CH-CH=CH-CH=CH_2$$

Very little is known of the cyclic polyenes with the obvious exception of benzene. The chemistry of benzene is too well known and too extensive for any inclusion here; and no instance of the preparation of cyclobutadiene has been reported.

However, Wilstätter[29a,29b] reported the preparation of cyclooctatetraene by the following method. Psuedopelletierine, a bicyclic ketone, is reduced and dehydrated to N-methyl granatenine. This latter substance is converted to α-des-dimethyl granatenine, by a Hofman exhaustive methylation, which upon another exhaustive methylation leads to cyclo-octatriene. Bromination of cyclooctatriene leads to a dibromide, which is not isolated due to its instability; however, subsequent reaction with dimethylamine produces 1,6-bis-(dimethylamino)-2,4-cyclooctadiene, in good yields. Another Hofman exhaustive methylation on the 1,6-bis-(dimethylamino)-2,4-cyclooctadiene liberates cyclooctatetraene.

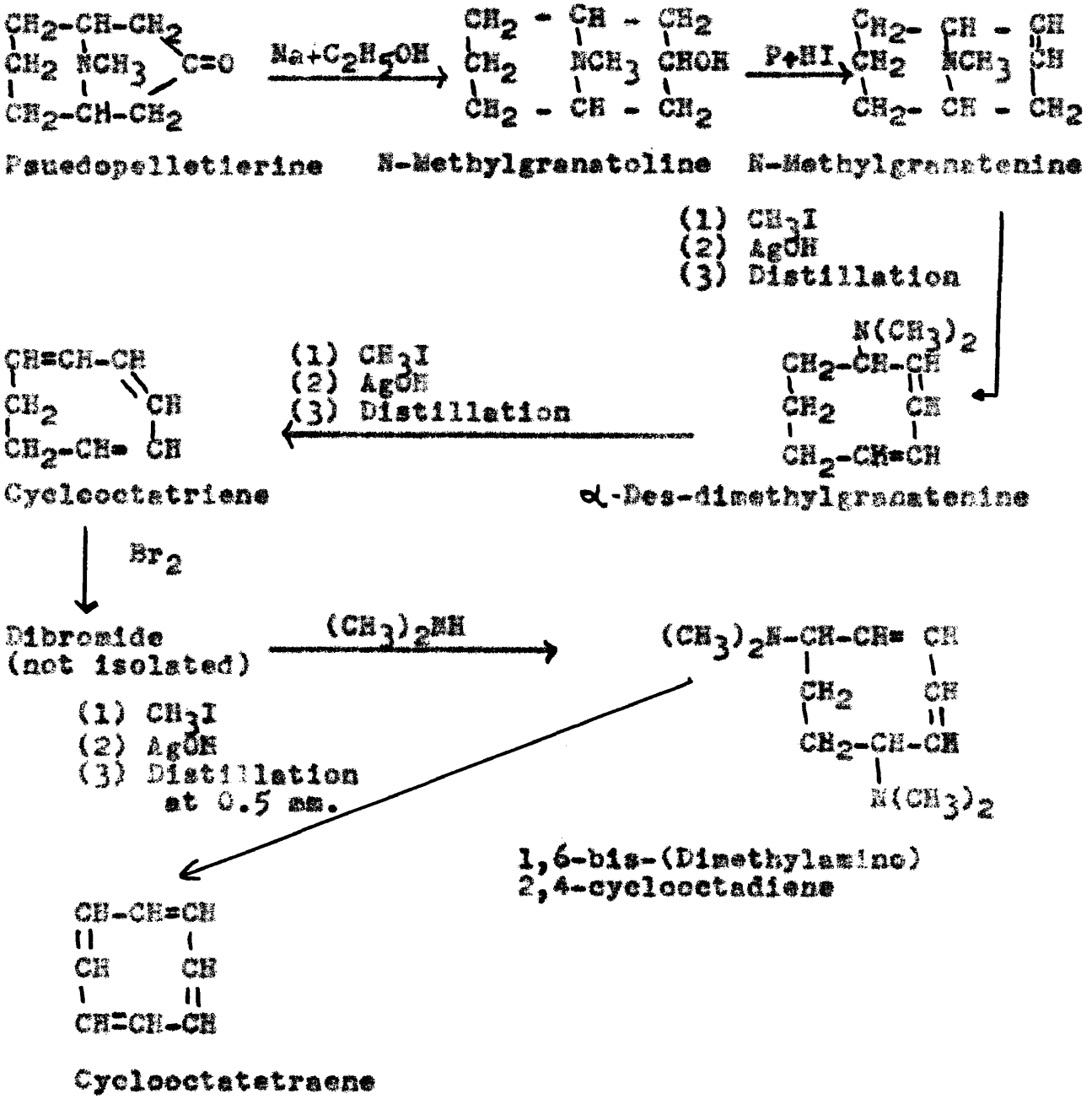
Figure 2 shows the Willstatter synthesis of 1,3,5,7-cyclooctatetraene.

The 1,3,5,7-cyclooctatetraene so prepared is a light yellow liquid, $n_D^{25} = 1.5342$, melting point -27, boiling point 142. It reacts with maleic anhydride, is reduced quantitatively to cyclooctane, decolorizes cold permanganate and bromine solutions, adds hydrogen bromide, and rearranges easily when in a slightly impure condition to a more stable product.

The properties of the cyclooctatetraene cited above are so contrary to what earlier had been expected of a completely conjugated ring system on the basis of previous concepts such as "aromaticity" that the authenticity of the work was doubted for a number of years[30]. The product had a marked similarity to styrene, in fact, recently it has been proven by infra-red absorption spectra that styrene was an impurity. Catalytic dehydrogenation of cyclooctene at 425-445 yielded styrene. Finally, the most marked criticism was proof that application of the Hofman exhaustive methylation procedures to diaminobutanes yielded ethyl acetylene and methyl allene in addition to the conjugated 1,3-butadiene.

However, the modern concepts of electronic interpretations and structural theories of organic chemistry have rationalized the apparent anomalies fairly well. Benzene, cyclohexatriene, has complete conjugation in a ring system, but it also has the additional feature that its structure

Figure 2- Willstatter's Synthesis of 1,3,5,7-Cyclooctatetraene



is planar without strain. The two major resonating forms, the Kekule models, are of equal energy states and therefore the resonance energy is large. However, although the resonance energy of the planar cyclooctatetraene model is large, since the two Kekule forms have the same energy content, the energy content of planar cyclooctatetraene is higher, in a corresponding sense to benzene, because of the energy of strain in the bond angles in being planar. Therefore, cyclooctatetraene should be expected to show properties which are apparently divergent, in degree, from the more stable molecule of benzene.

In 1940, while W. J. Reppe[31] and his associates were trying to make glycol from acetylene and ethylene oxide, they discovered that they had produced cyclooctatetraene and some of its homologues.

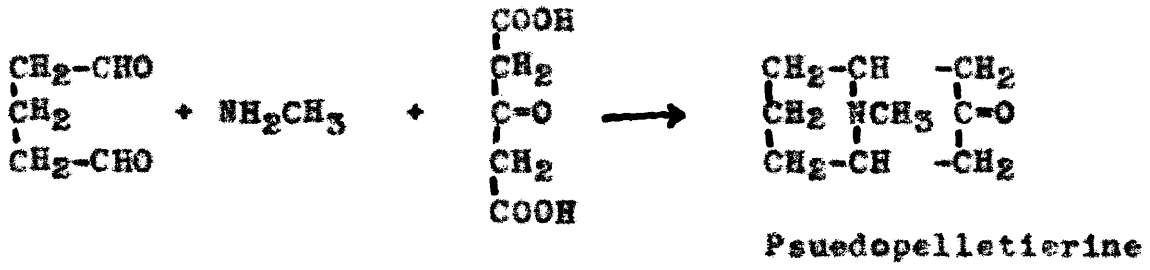
A solvent, tetrahydrofuran, containing nickelous cyanide, $Ni(CN)_2$, as a catalyst, was freed of oxygen with nitrogen and heated to 60-80, under a nitrogen pressure of five atmospheres. Acetylene under twenty to twenty-five atmospheres was then admitted at intervals, polymerization as an exothermic reaction beginning at once. The pressure was kept between five and ten atmospheres by acetylene additions during the thirty or so hours, during which the reaction continued before exhaustion of the catalyst. Nickel salts and cuprene formed during the reaction and settled out.

The tetrahydrofuran solution was filtered off and evaporated.

The first fraction was C_8H_8, cyclooctatetraene, having a boiling point of 142-143 at 760 mm pressure. The yield was 90%.

If the temperature was maintained at 80, cyclooctatetraene was the principal product, the yields being as high as 90% based on the acetylene used. At 90, the reaction mixture would consist of 98% cyclooctatetraene, but above 90, there was very little of the cyclooctatetraene formed, but somewhat more of the cyclodecapentaene and cyclododecahexaene were formed.

Development of the catalytic synthesis of cyclooctatetraene from acetylene by Reppe renewed interest in Wilstatter.s synthesis. Therefore, Cope and Overberger[32] decided to check Wilstatter's synthesis and also to check the properties of their cyclooctatetraene against those of the cyclooctatetraene as prepared by Reppe. The only modification that Cope used in the synthesis of cyclooctatetraene was the preparation of psuedopelletierine from glutaraldehyde, methylamine, and acetone-dicarboxylic acid instead of using the naturally occuring compound.

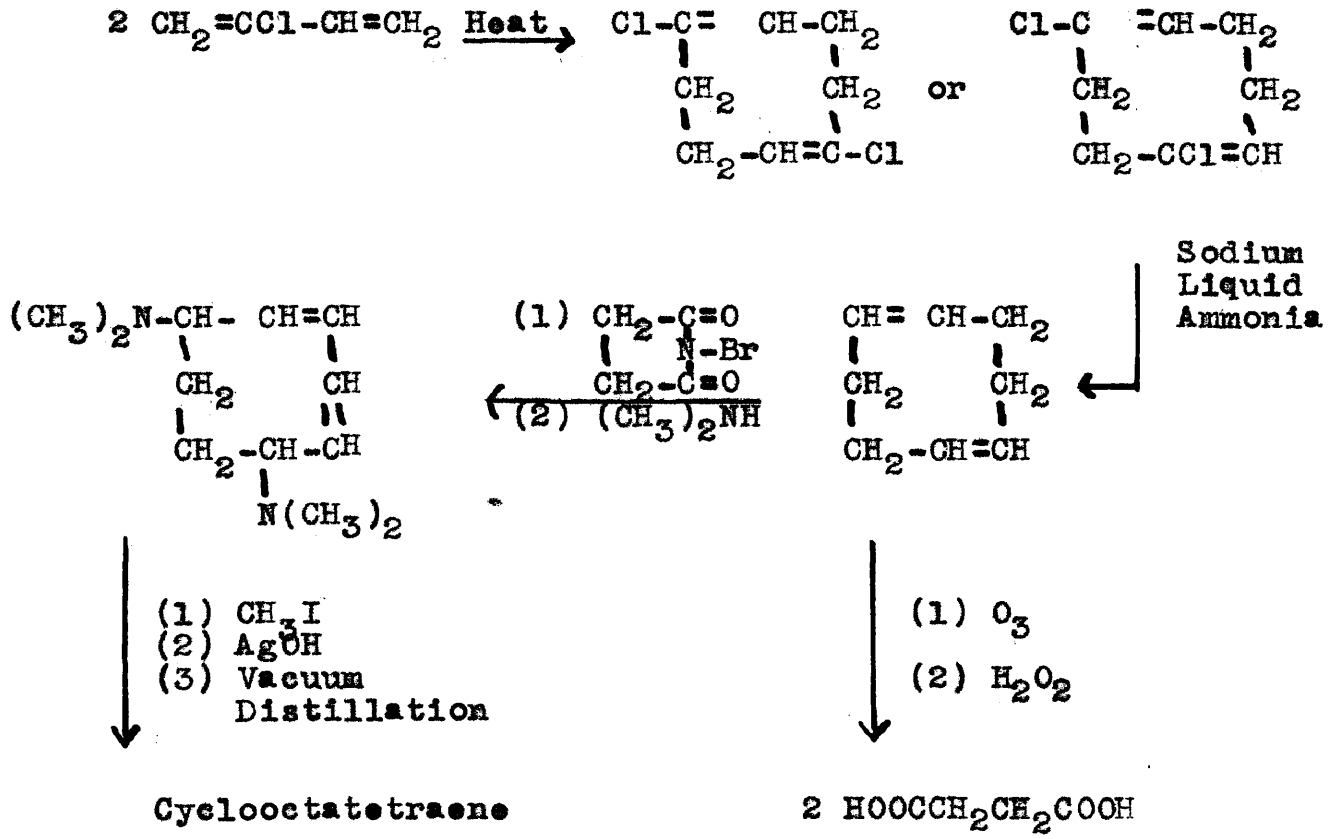


Psuedopelletierine

The cyclooctatetraene prepared by Cope was identical to that prepared by Reppe. The melting point was -5.8 to -5.4 and did not depress the melting point of cyclooctatetraene synthesized from acetylene. The melting point observed for the cyclooctatetraene is of interest, because Willstatter and Heidelberger[29b] had reported a freezing point of about -27 for their product, which was purified by vacuum distillation without fractionation. The maleic anhydride adduct obtained from the cyclooctatetraene from the two sources were identical. Both samples of cyclooctatetraene had practically identical ultra-violet and infra-red absorption spectra.

Cope and Bailey[33] recently worked out a new synthesis of cyclooctadiene from chloroprene. Chloroprene was converted into a mixture of dimers in the presence of phenothiazine as a polymerization inhibitor. The dimer, an eight membered ring compound which was identified by hydrogenation to cyclooctane, was separated from the six membered ring dimers by fractional distillation. The eight membered ring dimer was then dehalogenated with sodium in liquid ammonia to 1,5-cyclooctadiene; the structure of 1,5-cyclooctadiene was established by ozonization followed by hydrogen peroxide oxidation to succinic acid. 1,5-Cyclooctadiene reacted with two molar equivalents of N-bromosuccinimide in the presence of benzoyl peroxide to give a dibromo compound, which was not isolated, but instead was treated directly with an excess of dimethylamine. In this

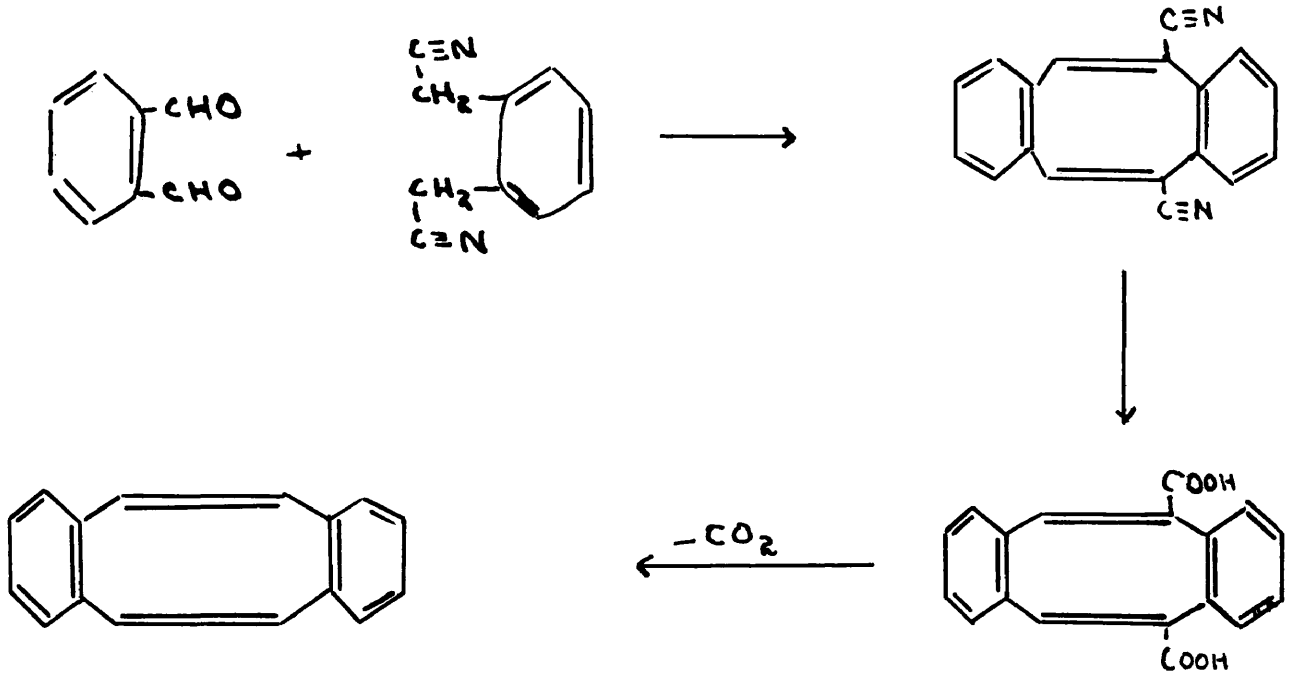
way a bis-(dimethylamino)-cyclooctadiene was obtained in an over-all yield of 34%. A Hofman exhaustive methylation of the quaternary iodide gave a 15.5% yield of cyclooctatetraene. The infra-red and ultra-violet absorption spectra of this sample indicates an 8% impurity of styrene, presumably formed by rearrangement during the decomposition of the quaternary base.



The Raman spectra of 1,3,5,7-cyclooctatetraene prepared by Reppe and sent to this country, was studied by Lippincott and Lord[34]. They stated that the spectrum shows that the material is not any substance, for example, styrene, for which Raman data are available. It was also noted that the

spectrum shows a strong carbon-carbon double bond frequency which would indicate that the double bond is not drastically affected by resonance, in contradistinction to the situation in benzene and to the argument of resonance energy in cyclooctatetraene. The molecule contains no acetylenic, methylene, or methyl groups nor a benzene ring with side groups or rings, and all the hydrogen atoms are equivalent.

Fieser and Pechet[35], in an attempt to elucidate the character of the cyclooctatetraene ring prepared 1,2,5,6-dibenzcyclooctatetraene. o-Phthaldehyde was condensed with o-phenylenediacetonitrile in the presence of sodium ethoxide. A white substance having the composition of the expected 3,8-dicyano-1,2,5,6-dibenzcyclooctatetraene was isolated in moderate yield. This compound on hydrolysis with sulfuric acid yielded the half amide of the dibasic acid and further treatment gave the diacid. Decarboxylation of the dibasic acid was poor, but nevertheless some 1,2,5,6-dibenzcyclooctatetraene was obtained. It is a colorless solid which melts at 107-108, decolorizes cold permanganate and bromine solutions, and in the presence of a catalyst absorbs two moles of hydrogen to give a hydrocarbon that did not depress the melting point of an authentic sample of 5-dibenzcyclooctadiene.



The chemical reactivity of the s-dibenz derivative of cyclooctatetraene indicates that the eight membered conjugated ring system does not have the stability or show the reactions characteristic of benzenoid substances.

DISCUSSION

The purpose of this research was to have been a continuation of the work of Sanders[36] on the reactions of Grignard reagents with 2,4-pentadienal. However, it soon became apparent that we had in our hands an excellent tool for the preparation of 1,3,5-hexatriene and 1,3,5,7-octatetraene.

The reaction of RMgX with unsaturated conjugated aldehydes may proceed either by 1,2 addition, 1,4 addition, or 1,6 addition.

1,2 Addition

CH_2=CH-CH=CH-CHO + RMgX ⟶ CH_2=CH-CH=CH-CHOH-R

1,4 Addition

CH_2=CH-CH=CH-CHO + RMgX ⟶ CH_2=CH-CHR-CH_2-CHO

1,6 Addition

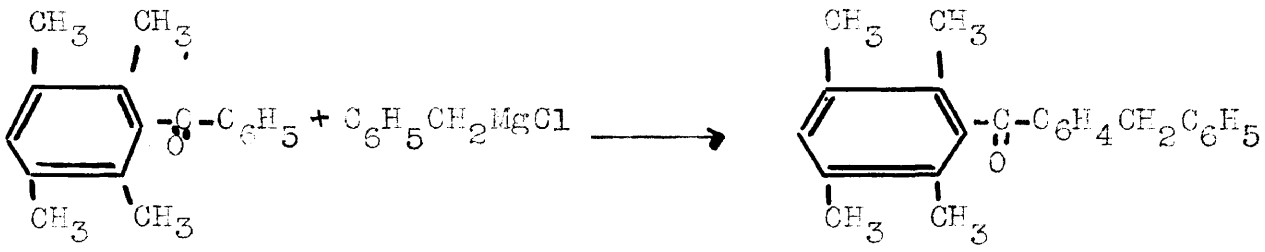
CH_2=CH-CH=CH-CHO + RMgX ⟶ RCH_2-CH=CH-CH_2-CHO

V. Grignard[37] reacted a series of alkylmagnesium halides on unsaturated aldehydes, and the products were all carbinols, indicating normal 1,2 addition.

Kohler[38] found no products other than 1,2 addition products upon reacting cinnamaldehyde and α-bromocinnamaldehyde with phenylmagnesium bromide. He also reacted acrolein with ethylmagnesium bromide and phenylmagnesium bromide and obtained 1,2 addition products exclusively. However, Kohler and co-workers[39] had shown definitely that

Grignard reagents could add 1,4 to α,β-unsaturated ketones .

Fuson and McKusick[40] have reported an instance of a 1,6 addition of a Grignard reagent to an unsaturated ketone. They reacted benzylmagnesium chloride with benzoyldurene and obtained para alkylation or 1,6 addition.



Stevens[41] undertook an ambitious program to determine to what extent, if any, 1,4 addition takes place when various Grignard reagents react with crotonaldehyde. The following chart is a tabulation of his results.

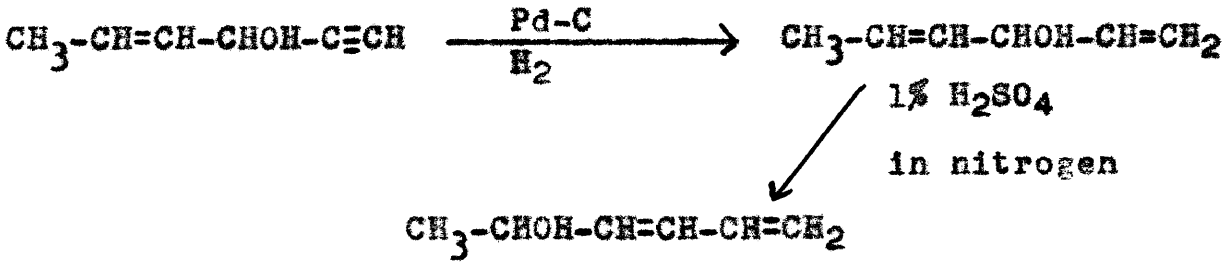
Grignard reagent	%Carbinol	% Aldehyde	% Complex products	Ratio of Aldehyde to Carbinol
C_6H_5	90	0.1	7.1	.0011
C_2H_5	70.3	0.1	11.4	.0014
C_3H_7	78.3	trace	7.6	.001
Allyl	-	trace	-	.001
Isopropyl	46.5	0.3	34.1	.007
t-Butyl	30.6	20.3	39.3	0.6
t-Amyl	16.3	22.6	45.7	1.4

The reason for the abnormal mode of addition of t-butyl and t-amyl magnesium halides is undoubtedly a difference in the reaction velocities of 1,2 and 1,4 addition, but the

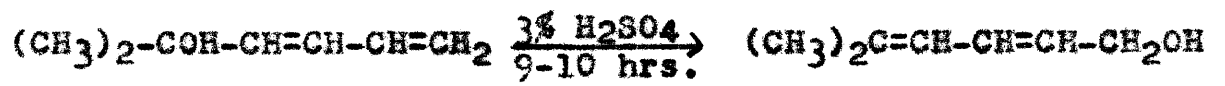
underlying causes for these different velocities are not clear. Steric hindrance seems to be an inadequate explanation as it fails to show why phenylmagnesium bromide, which contains a group that ordinarily presents more steric hindrance to addition to the carbonyl group than the methyl or ethyl radicals, always yields more 1,2 addition to α,β - unsaturated ketones than methyl or ethyl magnesium bromide. The best answer is that these differences in reaction velocity of 1,2 and 1,4 addition are due mainly to the differences in the individual chemical character or polarity of the organic radical of the Grignard reagent.

In addition to the mode of addition of the Grignard reagent to 2,4-pentadienal, there is always the possibility of subsequent rearrangement.

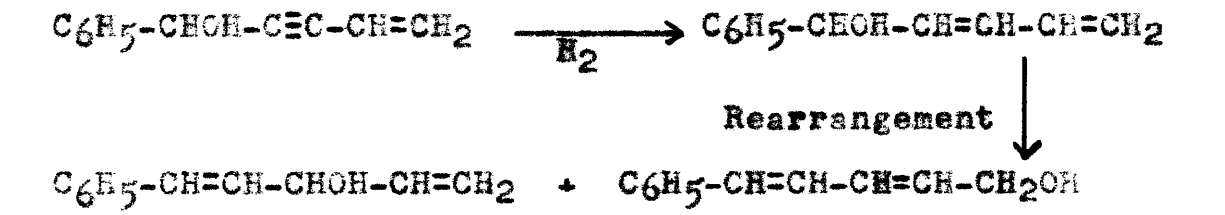
Propenyl-ethynyl carbinol was prepared by Heilbron[42] by the reaction of crotonaldehyde with acetylenemagnesium bromide; subsequent partial hydrogenation over a palladium-charcoal catalyst produced 1,4-hexadien-3-ol in good yields. When the 1,4-hexadien-3-ol was shaken for two hours in an atmosphere of nitrogen with a 1% solution of sulfuric acid, it rearranged to produce 1,3-hexadien-5-ol in yields of 80%. The 1,3-hexadien-5-ol so obtained boiled at 67-68 at 26 mm, n_D^{19}=1.4810, and gave a crystalline α-naphthyl urethane melting at 86.5-87.5.



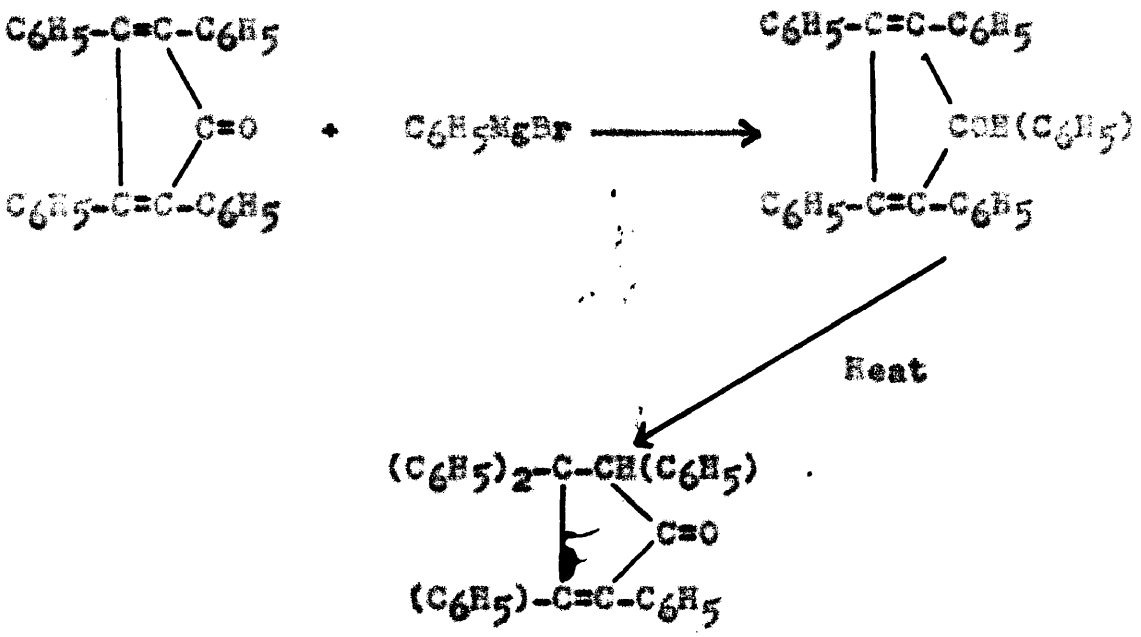
Other similar rearrangements are those reported by Nazrov and Fisher[43], and Zalkind and Kulikov[44]. Nazrov and Fisher obtained 5-methyl-2,4-hexadien-1-ol when 5-methyl-1,3-hexadien-5-ol was shaken in a 3% sulfuric acid solution for nine hours.



Zalkind and Kulikov partially reduced 1-phenyl-2-yne-4-ene-pentanol-1 to the phenyl-butadienyl-carbinol which rearranged to give a mixture of 1-phenyl-1,4-pentadien-3-ol and 1-phenyl-1,3-pentadien-5-ol.

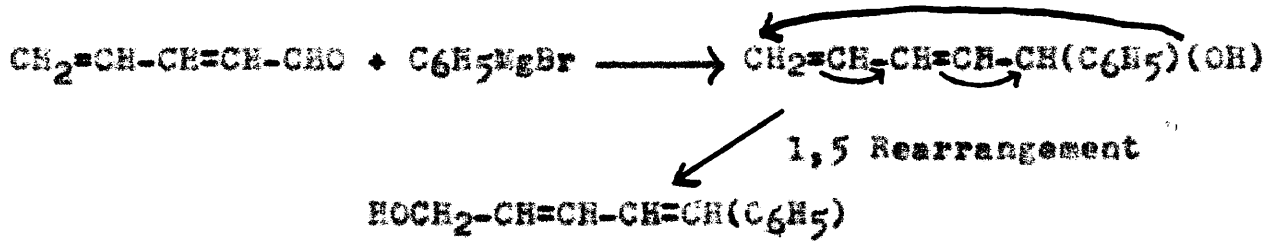


The action of phenylmagnesium bromide upon tetraphenyl-cyclopentadienone liberates either a carbinol formed by 1,2 addition to the carbonyl group, or a ketone, resulting from 1,4 addition to the α,β -unsaturated carbonyl system. Furthermore, the carbinol is converted into the ketone upon heating.



Allen and Van Allan[45] accounted for this isomerization by assuming that there had been a 1,3 rearrangement of the phenyl radical from the carbon atom of the original carbonyl group to one in the beta position of the unsaturated system. The evidence for such a change was the production of benzophenone upon oxidation of the isomerized ketone.

Phenylmagnesium bromide reacts with 2,4-pentadienal to yield 5-phenyl-2,4-pentadien-1-ol[36]. Since there were very few instances of rearrangements in skeletal structure during catalytic hydrogenation under mild conditions, it was concluded that the reaction between phenylmagnesium bromide and 2,4-pentadienal yielded 1-phenyl-2,4-pentadienol-1 and that this product immediately underwent a double allylic rearrangement of the hydroxyl group to produce the 5-phenyl-2,4-pentadien-1-ol.



2,4-Pentadienal was prepared according to the method of Woods and Sanders[46] from 2-ethoxy-Δ^3-dihydropyrane in 54% yields. Methylmagnesium bromide reacted vigorously with pentadienal and after the complex was decomposed with a saturated aqueous solution of ammonium chloride, a carbinol was obtained which boiled at 65-65.5°C at 20 mm in a nitrogen atmosphere. This carbinol, which was proved later to be 1,3-hexadien-5-ol, was produced in 81% yields and reacted with α-naphthylisocyanate to give a white, crystalline urethane melting at 85.5-86°C in excellent agreement with that reported by Heilbron[42].

That the addition of the methylmagnesium bromide to pentadienal had been a normal 1,2 addition to the carbonyl group was proved further by reduction of 1,3-hexadien-5-ol to the known hexanol-2, boiling point 136-137. The hexanol-2 prepared in this manner did not form satisfactory derivatives with α-naphthylisocyanate or with 3,5-dinitrobenzoyl chloride and so it was then oxidized with potassium dichromate and sulfuric acid to yield the known hexanone-2, boiling at 45-46 at 20 mm.

$$CH_3MgBr + CH_2{=}CH{-}CH{=}CH{-}CHO \longrightarrow CH_2{=}CH{-}CH{=}CH{-}CHOH{-}CH_3$$

$$\downarrow \text{Raney-nickel } H_2$$

$$CH_3CH_2CH_2CH_2{-}\overset{O}{\overset{\|}{C}}{-}CH_3 \xleftarrow{K_2Cr_2O_7+H_2SO_4} CH_3{-}CH_2{-}CH_2{-}CH_2{-}CHOH{-}CH_3$$

The hexanone-2 formed a white, crystalline semicarbazone melting at 123.5-124° and an orange 2,4-dinitrophenylhydrazone melting at 106-107. Mixed melting points taken with derivatives of an authentic sample of hexanone-2 showed no depression.

1,3-Hexadien-5-ol was found to undergo very smoothly, and in good yields, a catalytic dehydration when passed in the vapor state over alumina.

$$CH_2{=}CH{-}CH{=}CH{-}CHOH{-}CH_3 \xrightarrow[\text{Heat } 325\text{-}350]{Al_2O_3} CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$$

The products of this dehydration separated into two layers, one of which was water. Appropriate isolation of the organic material yielded 1,3,5-hexatriene. It was observed that the product was easily converted to a solid upon modest cooling. In this manner, a procedure of purification involving crystallization was developed which led to a pure product. It was material of this quality which was used in the determination of the properties of our sample of 1,3,5-hexatriene. These results are included in Figure 3 in which the results of previous workers are given.

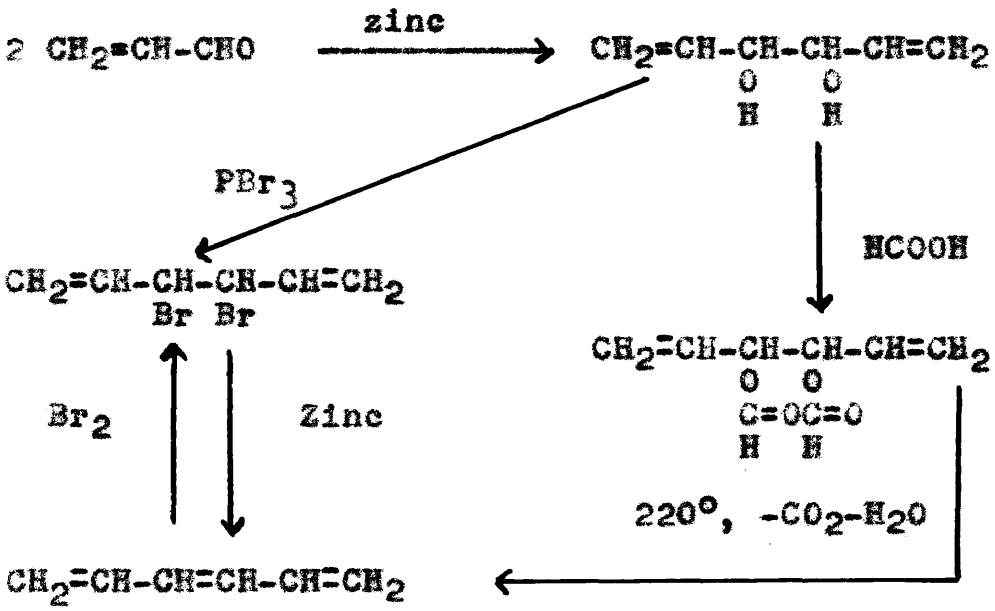
Van Romburgh and van Dorssen[12] were the first to report a preparation of 1,3,5-hexatriene. They prepared g-divinyl

Investigator	Boiling Point	Melting Point	Index of Refraction	Density	*Molar Refraction 28.51	Analyses C=89.94 H=10.06	
1. vanRomburgh and van Dorssen	78.5-80	-	1.49856^{10}	0.7565^{10}	31.07	-	-
2. van Romburgh and Mueller	80-80.5	-11	1.517^{14}	0.740^{14}	32.76	-	-
3. Farmer et al	78.5	-	1.4577^{20}	0.7175^{20}	30.45	88.5	11.6
4. Butz, Butz and Gaddis	80-82	-	1.4924^{18}	0.7754^{20}	30.00	-	-
5. Kharasch and Sternfeld	76-80	-	1.4330^{20}	0.7182^{20}	28.93	-	-
6. Klebanskii, Popov, and Tsukerman	77.5-78.5	-	$1.4866^{13.5}$	0.7756^{15}	29.69	-	-
7. This Work	79.5-80	-11.7	1.5035^{28}	0.7338^{22}	32.30	90.07	10.52

* These molar refractions were calculated using the data as reported by the various investigators.

Figure 3. Collected data of the various investigations on hexatriene.

glycol by the bimolecular reduction of acrolein over zinc and this was esterified to the diformate; pyrolysis of the g-divinylglycol diformate led to the formation of carbon dioxide and a hydrocarbon fraction, hexatriene, boiling at 78-81 at atmospheric pressure. This compound absorbed one mole of bromine to give a solid which was identical with that made by Griner[11] from treatment of g-divinylglycol with phosphorous tribromide. The equations of van Romburgh are given below:



The homogeneity of this sample of hexatriene is certainly open to question, since the only proof of structure was bromination and hydrogenation. No melting point or elemental analyses were reported.

van Romburgh seems to have been aware of this non-homogeneity of the hexatriene fraction. So with Mueller[47] he attempted to prepare a pure sample of 1,3,5-hexatriene by treating the impure hydrocarbon fraction with bromine

to form the dibromide and then debrominating this substance with zinc. This more pure sample of 1,3,5-hexatriene melted at -11°C and the physical properties reported agree very closely to the physical properties of our sample of hexatriene .

However, here again no analyses were reported on the hexatriene or derivatives of hexatriene.

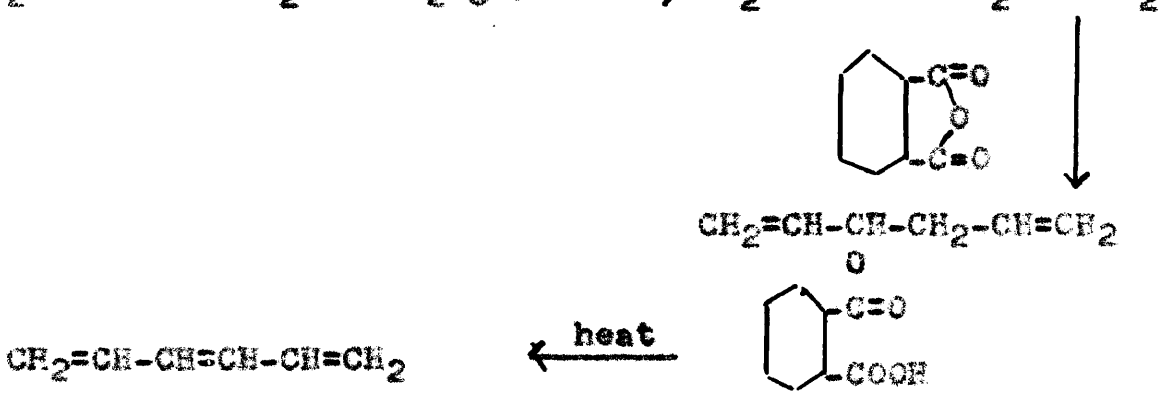
Farmer and co-workers[13,14] in making a comprehensive study of polyenes repeated all the previous work of van Romburgh[12,47] and also added a great deal to the chemistry of hexatriene.

Farmer obtained two dibromides, A and B, from the treatment of phosphorous tribromide on g-divinylglycol (see Figure 1, page 7). Of these, Farmer claims that the solid dibromide B, was the compound used by van Romburgh for regenerating hexatriene and that its configuration is trans. The cis hexatriene, Farmer reports, is prepared by the debromination of liquid dibromide, A.

More will be said of Farmer's work later, but in reviewing the physical properties of hexatriene reported by the various workers it is necessary to observe that Farmer tried to ascertain with which isomer of hexatriene he was working, but all efforts failed. Undoubtedly the two samples of hexatriene had different physical constants (see Figure 3 for van Romburgh and van Dorssen and Farmer) but nevertheless the questionable purity of these samples invalidates the constants. Farmer did succeed in obtaining an analysis for his sample of "cis" hexatriene. However

in obtaining this hexatriene, Farmer debrominated the liquid dibromide, A, in boiling methyl alcohol with zinc and under these conditions zinc is a reducing agent. On careful examination of Farmer's work, it becomes apparent that the analysis, C=88.5, H=11.6, corresponds more closely to that required for a formula C_6H_{10}, hexadiene, C=87.73, H=12.27, than for the formula C_6H_8, hexatriene, C=89.94, H=10.06.

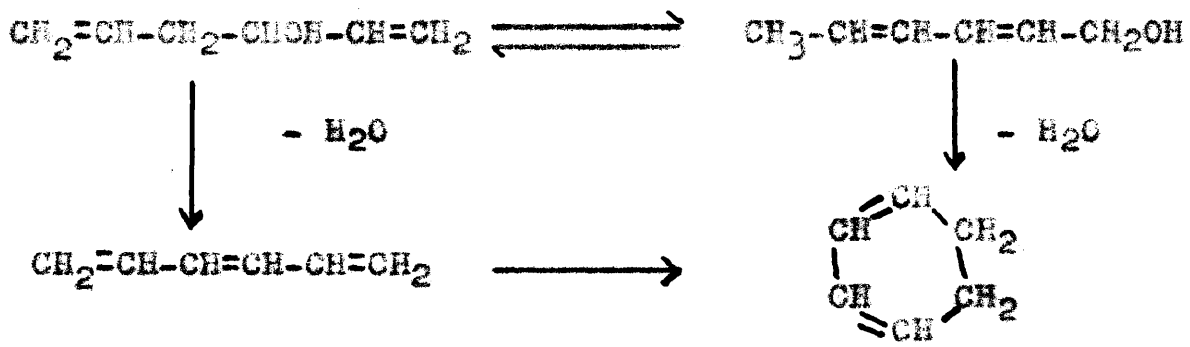
1,5-Hexadien-3-ol prepared from acrolein and allylmagnesium bromide was the substance used by Butz[21] for a preparation of 1,3,5-hexatriene. The method consisted of the pyrolysis of the half phthalate of 1,5-hexadien-3-ol:



The hydrocarbon fraction obtained in this way reacted with maleic anhydride to give the adduct of hexatriene as prepared by Farmer and Warren[14], but also yielded 25% of the adduct of 1,3-cyclohexadiene. On further investigation of the purity of his hexatriene fraction, Butz[22] showed that 1,3-cyclohexadiene was a known impurity. The Diels-Alder adduct of 1,4-naphthoquinone with 1,3-cyclohexadiene was prepared from the hexatriene fraction as well as from an authentic

sample of 1,3-cyclohexadiene, and the mixed melting point of the two showed no depression. Although variable amounts of 1,3-cyclohexadiene are formed by varying this procedure, at no time was 1,3-cyclohexadiene eliminated as an impurity.

Butz stated the possibility that 1,5-hexadien-3-ol during the dehydration reaction, rearranged to the 2,4-hexadien-1-ol which might then undergo a cyclodehydration to 1,3-cyclohexadiene or that the hexatriene was cyclized at the temperature of its formation.



Kharasch and Sternfeld[24] report a novel preparation of hexatriene. Two equivalents of allyl chloride were reacted with two equivalents of sodamide to give a 30% yield of a hydrocarbon fraction, which Kharasch designates as hexatriene.

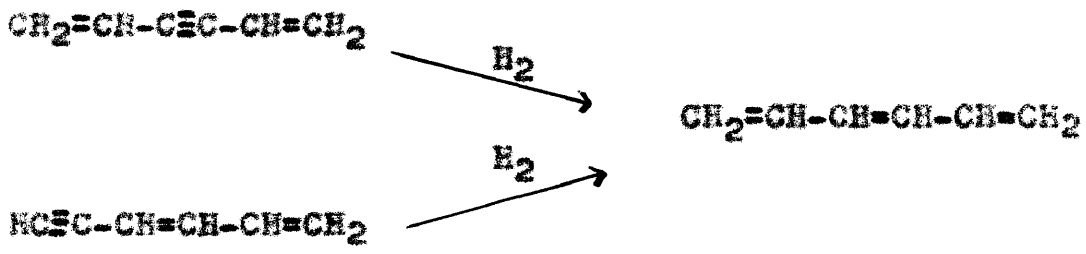
$$2\ CH_2{=}CH{-}CH_2Cl + 2NaNH_2 \longrightarrow CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$$

The physical properties reported for this sample definitely do not conform to those reported by the various other workers. The molar refraction of Kharasch's sample shows essentially no exaltation (28.5 as against 28.9), in spite of the fact that some exaltation should be expected for an aliphatic conjugated system such as hexatriene. It

is most unfortunate that Kharasch has reported no analytical data for his sample of hexatriene or for any derivatives of his product.

The physical properties reported by Kharasch for his hexatriene, along with other information from other sources such as infra-red data of the Diels-Alder adduct of hexatriene with maleic anhydride[27] and ultra-violet data[52] of his hexatriene, seems to indicate that the original substance was largely contaminated with hexadiene.

Klebanskii, Popov, and Tsukeiman[28] prepared their sample of 1,3,5-hexatriene by the selective partial hydrogenation of both divinylacetylene, $CH_2=CH-C\equiv C-CH=CH_2$ and ethynlbivinyl, $CH\equiv C-CH=CH-CH=CH_2$.



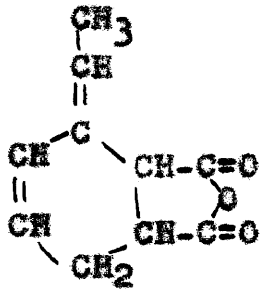
The physical constants reported by these workers for their hydrocarbon sample are not in accord with those reported by the other investigators. However, the fact that no elemental analyses were reported for the hydrocarbon fraction or for derivatives of this hydrocarbon fraction is the real criticism of this work.

Summarizing this work by the various investigators, it is obvious that a discordance exists, and it is unfortunate that a more careful examination by each group of workers

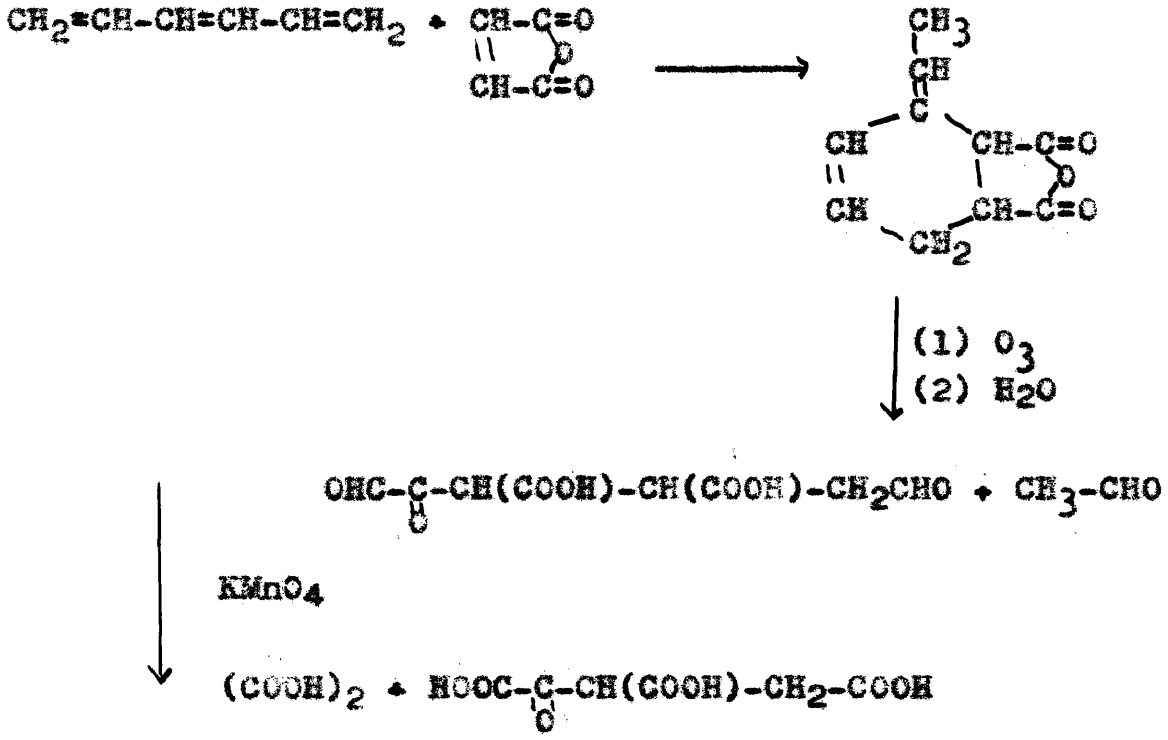
was not made. The discrepancies may be explicable on several bases. We are inclined to the idea that the variations in refractive indices, molar refractions, and densities lie either in geometrical isomerism or more likely in the purity or identity of samples.

Our sample of hexatriene was quantitatively hydrogenated at room temperature and atmospheric pressure with a platinum oxide catalyst and it absorbed the theoretical amount of hydrogen calculated for three ethylenic bonds.

Our sample of hexatriene also formed a Diels-Alder adduct. Maleic anhydride was refluxed with 1,3,5-hexatriene in anhydrous benzene, and after the solvent was removed under reduced pressure, the adduct was distilled at 140 C at 2 mm. The distillate on chilling and agitation in petroleum-ether yielded a mass of white crystals which melted at 50-50.5 C.

Shortly after the initial experiments of Diels and Alder, Farmer and Warren[14] reacted hexatriene with maleic anhydride. The hexatriene, which Farmer designates as trans, reacted almost quantitatively to produce a white crystalline anhydride which melted at 51.5 C. This substance was assigned as the 1-ethylidene- Δ^5-tetrahydrophthalic anhydride,  instead of the vinyl

compound on the following grounds. Degradation by ozonolysis yields acetaldehyde and a very strongly enolic aldehyde. The latter breaks down progressively on treatment with alkaline potassium permanganate, apparently owing to the successive formation and decomposition of keto succinic (or hydroxy maleic) acids to yield oxalic acid as the main product.



The hexatriene which Farmer designates as cis, also combines additively with maleic anhydride. The anhydrides formed in each case are identical.

However, Kharasch[27] argues that the structure of maleic anhydride adduct of hexatriene is the vinyl and not the ethylidene compound as Farmer contends. According to Kharasch, the infra-red spectroscopic data of the adduct shows very little evidance for conjugated carbon-carbon double bonds.

It should be noted that Kharasch's interpretations are based on his sample of hexatriene.

Our sample of hexatriene was brominated in carbon tetrachloride with one equivalent of bromine. After removal of the solvent under reduced pressure, the dibromide mixture was distilled at 2 mm. Two substances were obtained; one, a liquid forerun, turned black with time, and two, a liquid, boiled at 103-115°C and solidified on standing. Several recrystallizations from petroleum ether produced a dibromo compound, which was a very hard, long, white crystal, melting at 85-86°C. In spite of the rigors of purification, the solid dibromide evolved hydrogen bromide with time and turned into a solid black mass.

On repeating Griner's[11] and van Romburgh's[12,47] work, Farmer obtained two dibromides, (A) and (B), from the treatment of phosphorous tribromide on g-divinylglycol (see Figure 1). Of these, the solid (B) was the compound utilized by van Romburgh for regenerating hexatriene, while (A), an impure liquid dibromide, undoubtedly suffered progressive conversion into the positional isomeride (B). Griner had observed that the solid dibromide gave a diethoxyhexadiene with sodium ethoxide. Farmer hydrogenated this diethoxyhexadiene to the saturated compound, and by usual methods, converted the saturated substance into the diiodohexane, dicyanohexane, and a dibasic acid which proved to be suberic acid, indicating to Farmer that the substituents at each stage occupied the 1,6 positions. Farmer cites this

as evidence that van Romburgh was dealing with the 1,6-dibromohexadiene, however, he only casually agrees "that the change of substituent position during the transformation with sodium ethoxide is not entirely out of the question".

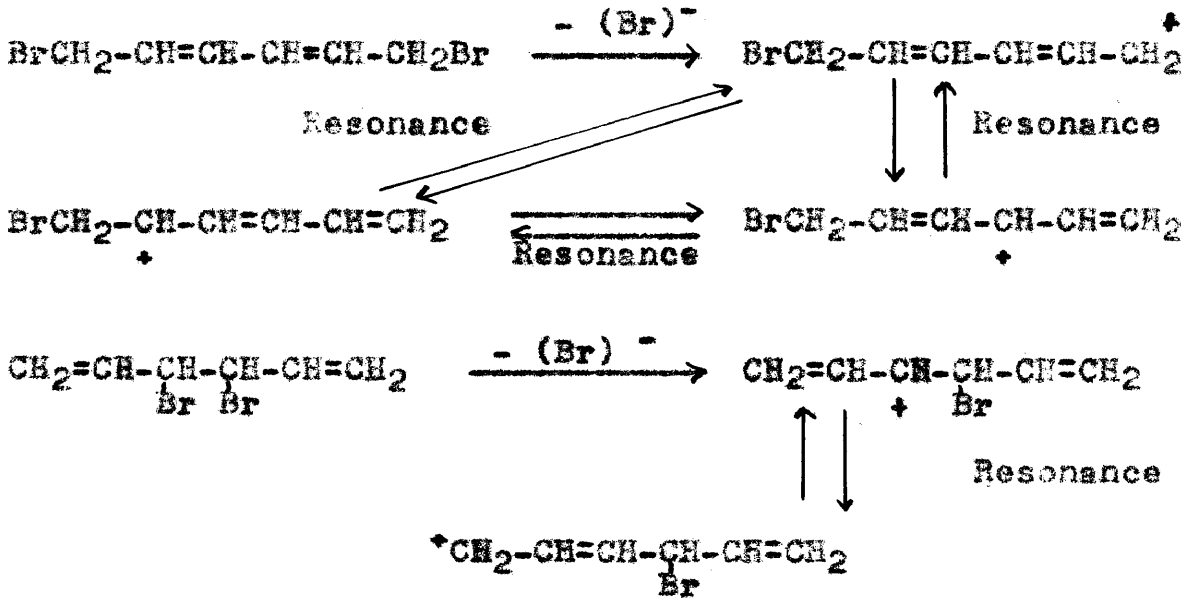
The chemistry of the bromination of hexatriene is intelligible on the basis of a bromine migration in a conjugated system, but although it is clear that a terminal additive product is by no means the necessary outcome of primary additive reaction, and although it may be demonstrable that a terminal product may arise merely by an isomerization of a different additive form, there is as yet no certainty that it may not also arise as a primary 1,6 addition.

The different chemical behavior of the two prepared hexatrienes, one giving a solid dibromide, the other giving liquid dibromides, was discovered at a very early stage by Farmer, but trustworthy evidence as to which was the trans and which the cis form was difficult to secure. A series of oxidations undertaken in the hope of retaining the $\gamma\delta$-carbon atoms in recognizable products such as maleic or tartaric acid proved fruitless. Attention was therefore centered on the dibromides, (A), (B), and (C), structural discrimination between which represented the apparent approach towards the elucidation of the chemistry of hexatriene. Of the dibromides of hexatriene which demand consideration, there are the geometrical, stereo, and positional isomerides. Here again in assignment of configurational formulae, direct oxidation methods had to be

abandoned; some thirty oxidations of the various dibromides were carried out and yielded little useful data.

According to Farmer,[13,14] 1,3,5-hexatriene adds bromine at the 1,2-1,6-or 3,4 positions, and an attachment at the 1,4 positions appears to be unfavored. With maleic anhydride, there is exclusive attachment at the 1,4 carbon atoms, and the selection of the second point of reaction seems connected with the strong tendency towards the formation of rings containing six members.

Farmer claims that the cis hexatriene is made by the debromination of 3,4-dibromohexadiene with zinc, while the trans is made from the 1,6-dibromohexadiene (see Figure 1). His attempts to prove these configurations are not satisfactory, since on the debromination step, the polarization of the molecule may well change the entire configuration.



In an attempt to find a convenient method to separate the geometrical isomers of the diphenyl polyenes as synthesized by Kuhn and co-workers[2], Zechmeister and LeRosen[48] evolved

some interesting facts. According to the available evidence, a strong accumulation of double bonds does not exclude the occurrence of cis-trans isomerism. That the higher diphenyl polyenes are known only in one spatial form is due to the inadequacy of the preparative methods. X-ray studies of Hengstenberg and H Kuhn[49] of the preparations of Kuhn and Winterstein[2] indicate all trans forms in the case of the 1,6-diphenylhexatriene and of the 1,8-diphenyloctatetraene.

In contrast, the existence of a great number of stereoisomers has been demonstrated for naturally occuring polyenes, the carotenoids. For example, fourteen stereoisomeric lycopenes, $C_{40}H_{56}$, have been reported, and one of them, prolycopene, containing four or five cis double bonds, has been isolated from natural sources[48].

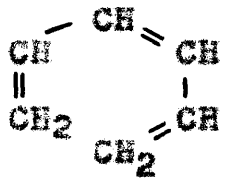
Chromatographically, the all trans configuration of 1,8-diphenyloctatetraene yields a single zone, showing an intense yellow fluorescence in ultra-violet light[48]. However, on refluxing this section in a benzene solution after elution, or on irradiation, or treatment with iodine, or if the crystals are melted for a short time, subsequent chromatography yields three well defined fluorescing zones in each case.

All diphenyloctatetraenes containing cis double bonds are labile. Their solutions when kept at room temperature contain a gradually increasing quantity of the all trans form as shown by the ultra-violet spectra and by chromatography.

Attempts to crystallize individual cis compounds, contained in chromatographic zones, using the ordinary methods

of elution and isolation gave only crystals of the trans isomer. Combustion analyses of some isomerized, chromatographed, and reconverted samples proved that no other change but a spatial shift within the molecule had taken place.

1,3,5-Hexatriene is capable of existence as isomers since the central double bond allows for geometrical isomerism.



cis

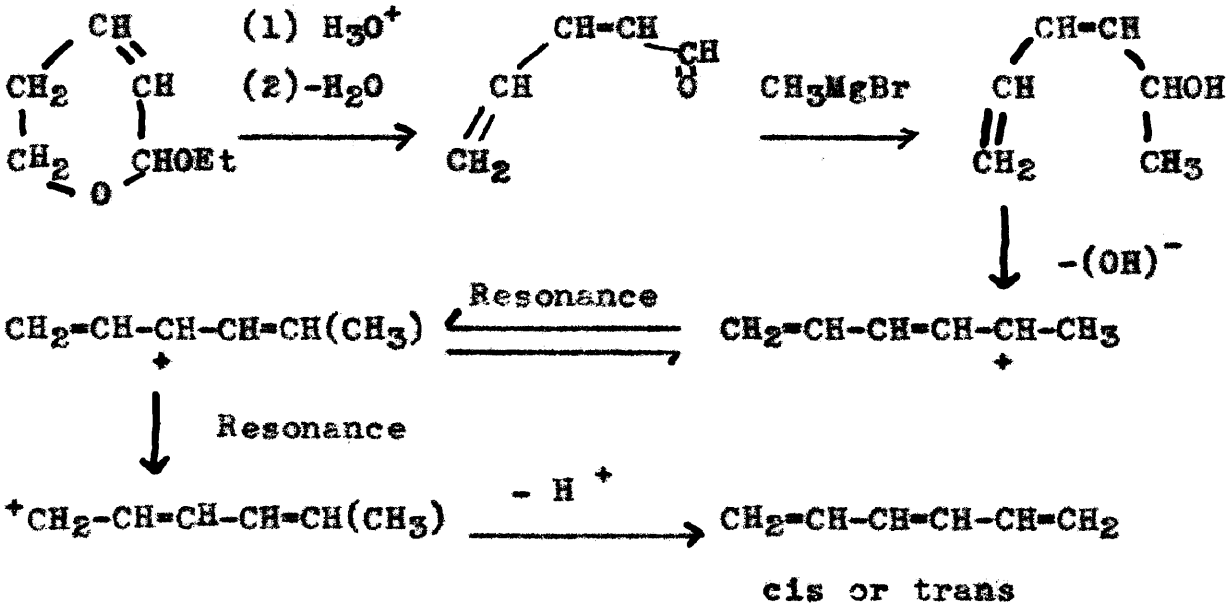


trans

The cis configuration is the open chain analog of benzene, and so much work has been done on various samples of hexatriene in attempting to prove configuration.

In our preparation of 1,3,5-hexatriene, 2-ethoxy-Δ^3-dihydropyrene is the starting material. Since this is a cyclic acetal, if the subsequent hydrolysis and dehydration should lead to a cis configuration of the central double bond in 2,4-pentadienal, then the reaction of metylmagnesium bromide with pentadienal should in no way alter the cis configuration of the resulting 1,3-hexadien-5-ol. For the above reasons, early in the research we were led to believe our sample of hexatriene to be of the cis configuration. However, after a more deliberate study of the problem, it became apparent that even if the 2,4-pentadienal were the cis form, the dehydration of the cis-1,3-hexadien-5-ol would lead to a carbonium ion which could resonate between several possible

structures and consequently could lead to isomerization and loss of configurational identity.



In an effort to elucidate the configurational structure of our sample of hexatriene, the dipole moment was taken. The value obtained by the heterodyne beat method is 0.29 Debye units.

If the structure of hexatriene could be represented as below,



where R designates a vinyl group, it seemed possible to be able to differentiate between the cis and trans forms, as is done in the case of the cis and trans dichloroethylenes. However, an additional complicating factor is present in

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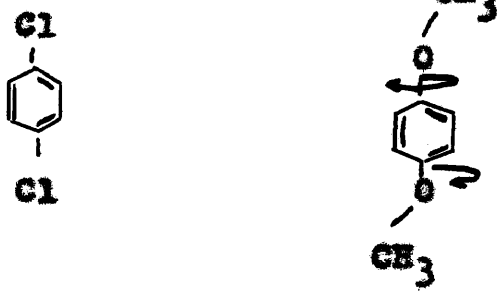
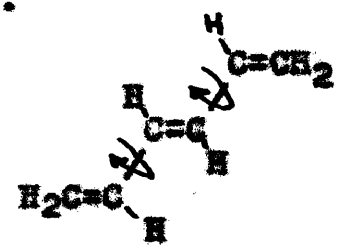
The author is indebted to Dr. John Lander for aid both in the determination of the dielectric constant and in the interpretation of this measurement.

the case of hexatriene. In the case of p-dichlorobenzene, the dipole moment is zero, due to the axis of symmetry of the molecule, but in the case of p-dimethoxybenzene, the substituents are not axially symmetrical, and the dipole moment is not zero.



Similarly in the case of hexatriene, due to the axial disymmetry of the substituent groups, the moment of even the trans form should not be zero.



Also, the value of 0.29 Debye units was obtained by assuming the atomic polarization to be 5% of the electronic polarization. If a value of 10% of the electronic polarization was assumed for the atomic polarization, the dipole might well be approaching zero. Therefore, no conclusion could be made from the dipole moment regarding the cis-trans isomerism of 1,3,5-hexatriene.

Therefore, we conclude that we have prepared a pure isomer of hexatriene, however, on the basis of the present knowledge at hand, we are not able to assign either a cis or a trans configuration to the sample.

The heat of vaporisation of our sample of hexatriene was found to be 61.4 cal/g by the closed manometer method, and the surface tension was found to be 23.1 dynes/cm at 20.2 C by the capillary rise method.

Baly and Tuck[50] were the first to report an ultra-violet absorption spectrum of hexatriene. Although, they failed to report their source of hexatriene, it seems that it had been prepared according to the method of van Romburgh and van Dorssen[12], since this was the only synthesis of hexatriene reported as of that date. This sample of hexatriene, which was admittedly impure, showed only general absorption at about 3300 cm^{-1}(3030$\mathring{A}$).

Macbeth and Stewart[51] in a study of the effect of unsaturation and conjugation on ultra-violet spectra, compared the spectra of dimethylacetylene, benzene, and hexatriene. However, they used the absorption spectrum of hexatriene as reported by Baly and Tuck[50], and so the conclusions at which they arrived are necessarily erroneous.

Hexatriene, prepared by the method of Kharasch and Sternfeld[24], when subjected to ultra-violet radiation, shows an absorption with a pattern of bands in the region 2520-2100 $\mathring{A}$. These spectra indicated that at least two types of molecular species were present and also that certain anomalies existed. Certain intensities appeared relatively more strongly in the earlier spectra obtained with the freshly prepared material than in the photographs taken at a later date. It was claimed that this "may in part be due to a more volatile

impurity such as a partially hydrogenated hexatriene which was eventually pumped off."[52]

In a series of quantum mechanical calculations, Kovner[53,54] determined that the wave length of maximum absorption of hexatriene would be at 2570 A.

Figure 4 is the ultra-violet absorption spectrum of our sample of hexatriene. This was taken with a Beckman quarts spectrophotometer. Cyclohexane, specially purified, was the solvent used and it transmitted ultra-violet light down to 2160 A. Since hexatriene is such a strong absorber, the concentration found necessary to resolve the fine structure was 4.4×10^{-5} moles/liter. The maximum absorption coefficients found for this solution were 0.68×10^5 at 2675 A, 0.79×10^5 at 2575 A, and 0.56×10^5 at 2475 A.

It is very interesting to note that the wave length of the maximum absorption coefficient, 2575 A, is almost exactly that calculated by Kovner. The curve has a definite similarity to the ultra-violet absorption curve of liquid benzene (Figure 5), but the hexatriene curve is displaced towards the visible. Also, the ultra-violet absorption spectrum of 2,5-dimethylhexatriene is characterized by three intense, narrow absorption bands at 2720 A, 2620 A, and 2520 A. These bands are associated with the presence of three conjugated carbon-carbon double bonds in a chain type aliphatic compound[28]. Although, our maxima for hexatriene are not displaced quite as far to the visible as those for 2,5-dimethylhexatriene, nevertheless, the increment of wave length

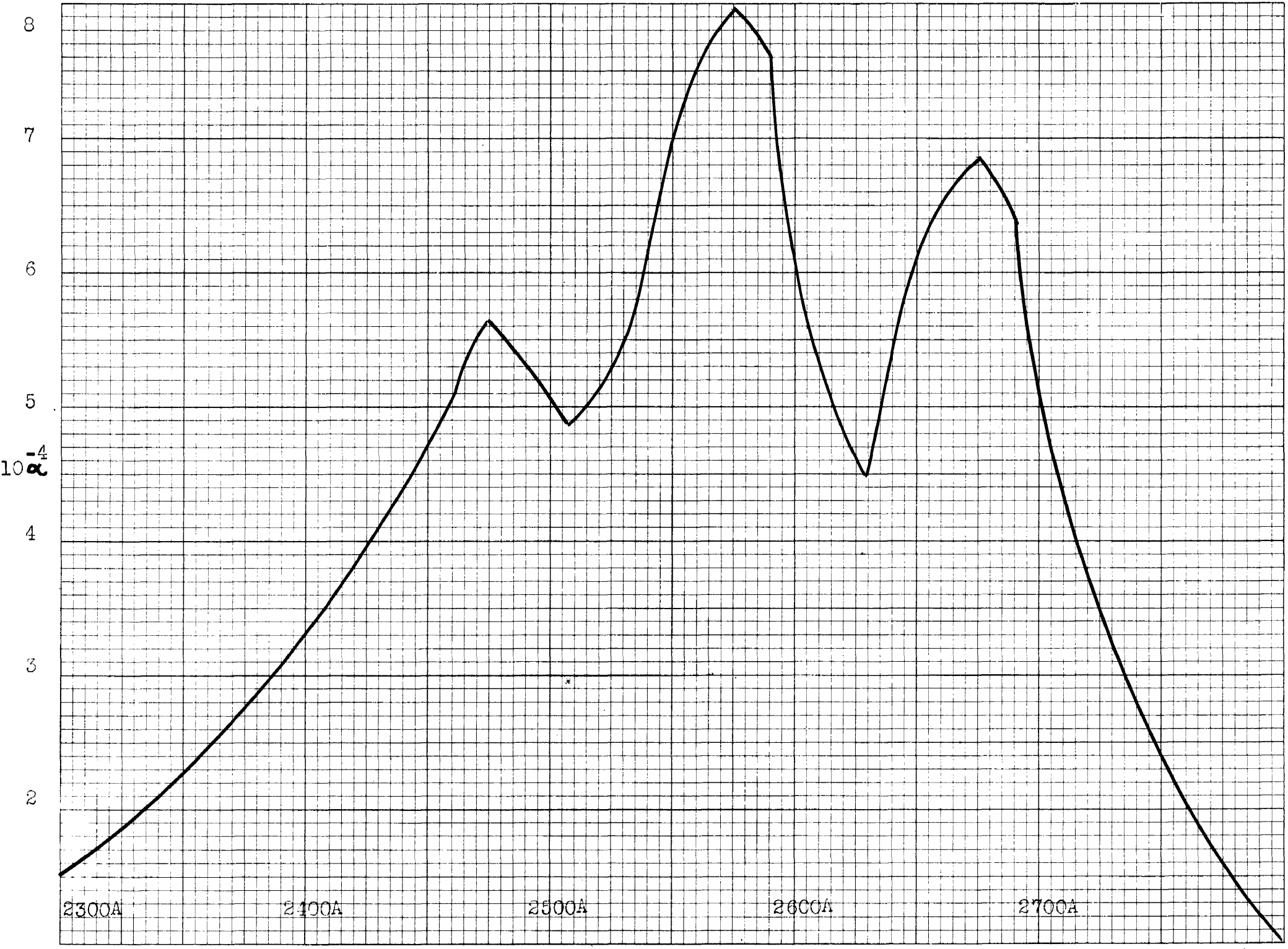


Fig.4- Ultra-violet Absorption Spectrum of 1,3,5-Hexatriene (molar absorption versus wave length)

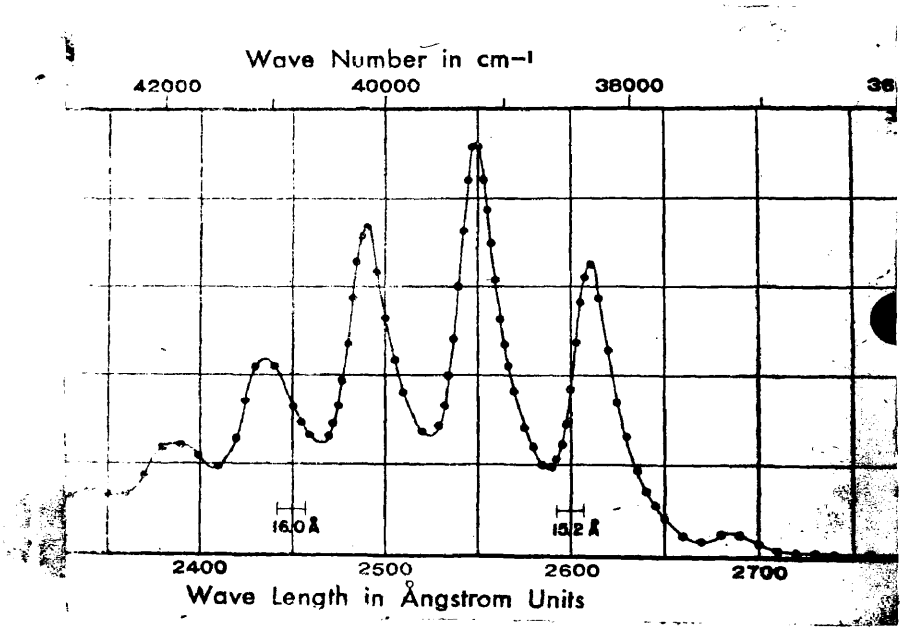
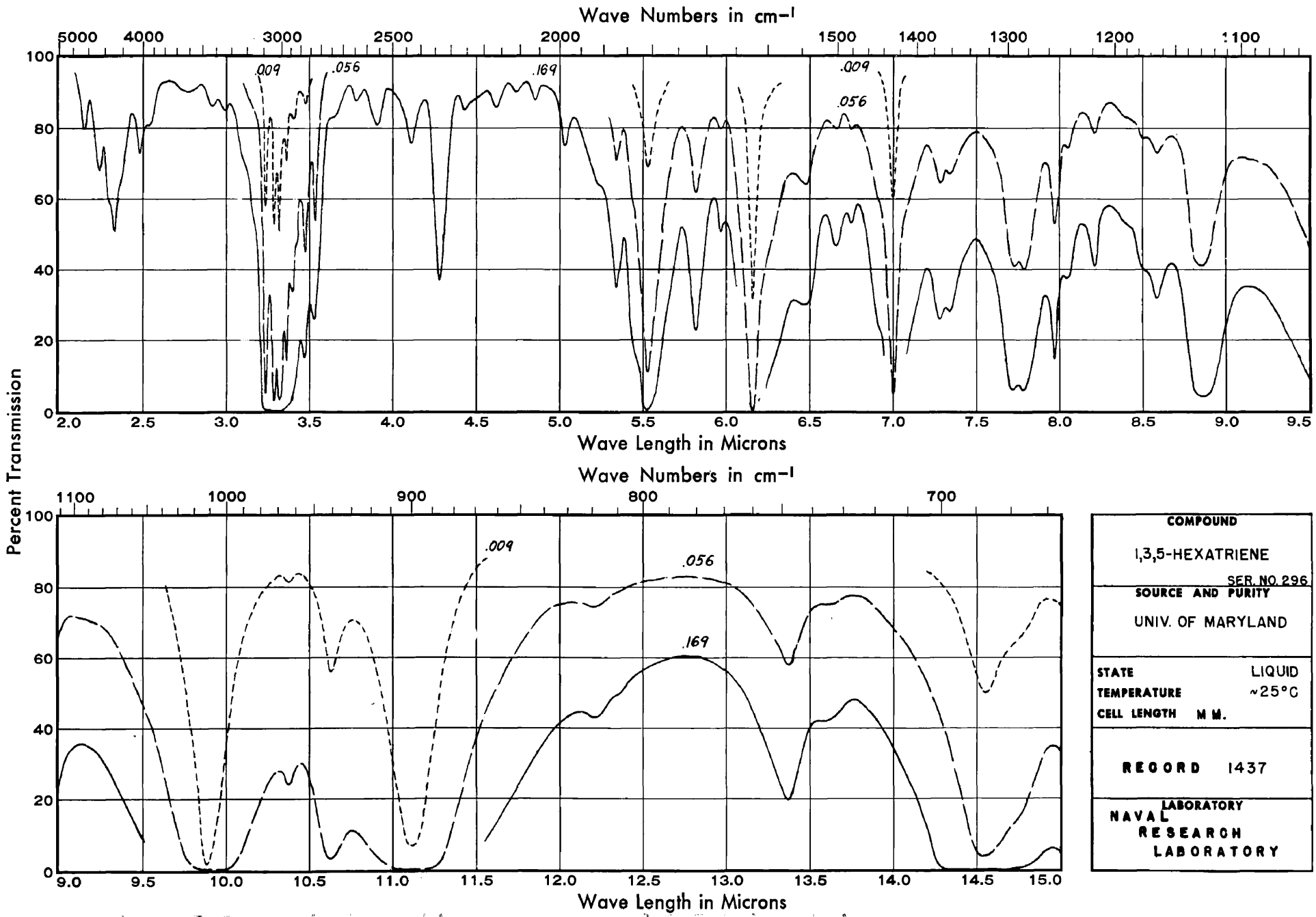


Fig.5-Ultra-violet Absorption Spectrum of Benzene

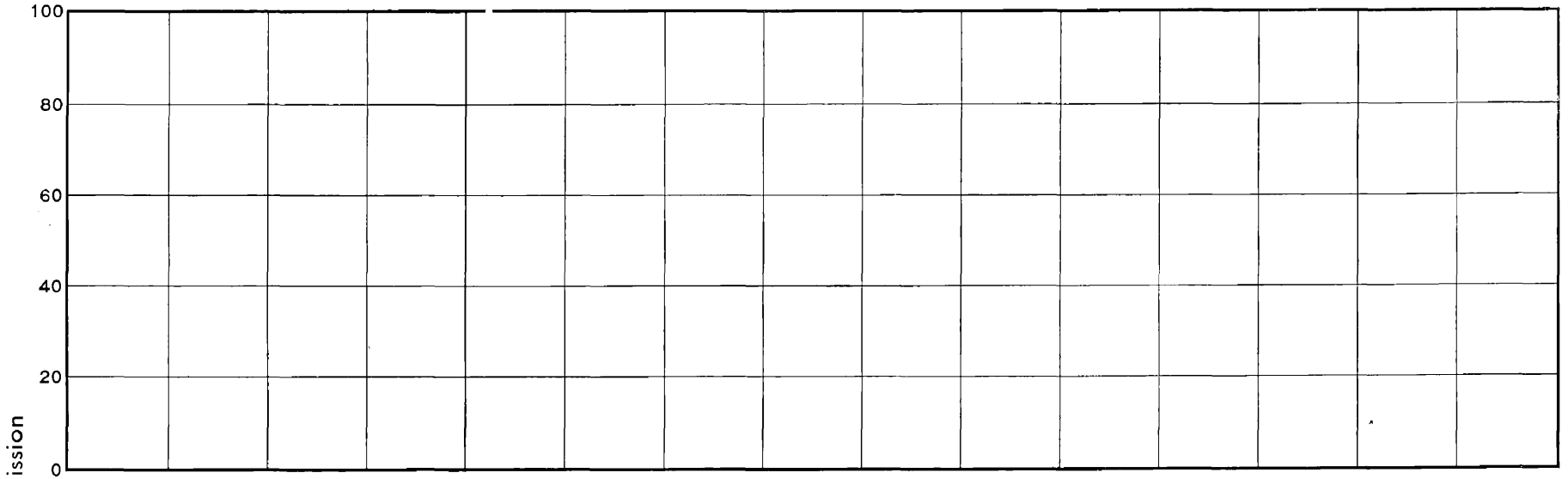
between maxima are very similar (1000 A) in both cases.

The infra-red absorption spectrum of hexatriene is shown in figure 6. The group of maxima from 3.235 to 3.536 microns (3091-2828 cm^{-1}) are characteristic of the "C-H stretching" vibration. Atomic forces between a carbon and a hydrogen atom are a function of these two atoms alone; the presence of C-H linkages in a molecule will cause at least two infra-red absorptions which are practically independent of the atomic constitution of the rest of the molecule[55]. A study of hundreds of molecules containing C-H linkages has shown an absorption around 2900 cm^{-1}, "C-H stretching," and another around 1450 cm^{-1}, "C-H bending." For hexatriene, the "C-H bending" vibration is at 1429 cm^{-1}. Aliphatic carbon-carbon double bond linkages occur between 1660 and 1600 cm^{-1}. However, these bands usually occur between 1660 and 1640 cm^{-1} when the bond is not conjugated. When the bond is conjugated with an aromatic unsaturation, the frequency drops to 1625 cm^{-1}, whereas, if full aliphatic conjugation occurs, the frequency is nearer 1600 cm^{-1}. This band for hexatriene is at 1623 cm^{-1}. The terminal group, $H_2C{=}CHR$, has an overtone band near 1800 cm^{-1} and a fundamental at 900 cm^{-1}; for hexatriene, these bands appear at 1810 and 899 cm^{-1}.

Dr. Donald C. Smith of the Naval Research Laboratories, who kindly ran the infra-red spectra for us, claims that this sample of hexatriene was at least 99.9% pure, or that to the limit of the spectroscopic method, the sample has no known impurities such as benzene, cyclohexadiene, C≡C bonding, etc

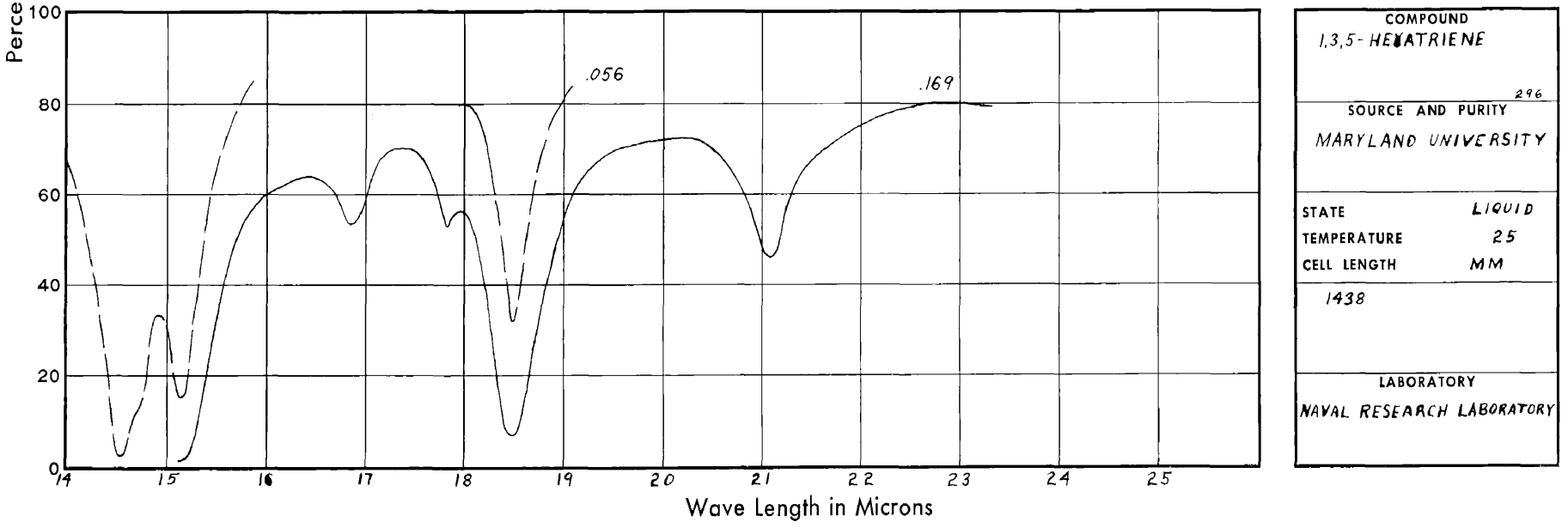

Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
.009
.056
.169
.009
.056
Percent Transmission
100 80 60 40 20 0
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Wave Numbers in cm⁻¹
1100 1000 900 800 700
.009
.056
.169
100 80 60 40 20 0
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
COMPOUND
1,3,5-HEXATRIENE
SER. NO. 296
SOURCE AND PURITY
UNIV. OF MARYLAND
STATE LIQUID
TEMPERATURE ~25°C
CELL LENGTH M M.
RECORD 1437
LABORATORY
NAVAL RESEARCH LABORATORY

Wave Numbers in cm^{-1}



Wave Length in Microns

Wave Numbers in cm^{-1}



Wave Length in Microns

COMPOUND	1,3,5-HEXATRIENE
	296
SOURCE AND PURITY	MARYLAND UNIVERSITY
STATE	LIQUID
TEMPERATURE	25
CELL LENGTH	MM
	1438
LABORATORY	NAVAL RESEARCH LABORATORY

The solution of the synthesis of hexatriene ended our interest in the reaction of 2,4-pentadienal with methylmagnesium bromide. It was apparent that essentially the same reaction using allylmagnesium bromide in place of methylmagnesium bromide might possibly furnish an intermediate in the synthesis of 1,3,5,7-octatetraene. Such was found to be the case.

The reaction of allylmagnesium bromide with 2,4-pentadienal had the same inherent difficulties as the reaction of methylmagnesium bromide with pentadienal. The possibility of 1,2-1,4 or 1,6 addition was always present as well as the possibility of the allylic rearrangements. However, since Stevens[42] had shown that the allyl radical reacted quite similarly to the methyl radical to give normal 1,2 addition and since the methylmagnesium bromide had reacted normally with pentadienal, the normal 1,2 addition of allylmagnesium bromide to pentadienal to give 1,3,7-octatrien-5-ol was anticipated.

$$CH_2{=}CH{-}CH{=}CH{-}CHO + CH_2{=}CH{-}CH_2MgBr \rightarrow CH_2{=}CH{-}CH{=}CH{-}CHOH{-}CH_2{-}CH{=}CH_2$$

In order to prepare allylmagnesium bromide in good yields, many precautions must be followed in addition to the usual procedures followed for most ordinary Grignard reagents[56]. When 0.5 mole of allylbromide in 285 ml. of anhydrous ether was added to three molar equivalents of #30 mesh magnesium in 100 ml of anhydrous ether with rapid agitation during a period of two hours, the yield of

allylmagnesium bromide was 90.3%. The yield is materially decreased by a decrease in the quantity of ether, and when magnesium turnings were used, the yield was 79%. Increasing the time for the addition of the allylbromide to the powdered magnesium to three hours gave a 91.9% yield and four hours produced a 93.6% yield.

The excess powdered magnesium was a handicap, since the decomposition of the Grignard complex by an acid even as mild as the ammonium ion presented conditions for a possible reduction of the octatrienol. Therefore, the allylmagnesium bromide was pumped away from the excess magnesium by means of a filter stick and dry nitrogen.

The carbinol product, obtained from the reaction of allylmagnesium bromide with pentadienal, boiled at 70-71 at 6 mm, n_D^{22}= 1.4931, and was obtained in yields of 90%. This carbinol was proven to be 1,3,7-octatrien-5-ol in the following manner. All attempts to make derivatives of 1,3,7-octatrien-5-ol by reaction with p-nitroisocyanate, β-naphthylisocyanate, α-naphthylisocyanate, phenylisocyanate, and 3,5-dinitrobenzoyl chloride failed. Therefore, the octatrienol was hydrogenated at room temperature, and octanol-4, boiling at 79 C at 20 mm, was obtained.

Octanol-4 reacted smoothly with α-naphthylisocyanate to produce a white crystalline urethane melting at 61-63 C.

An authentic sample of octanol-4 was prepared by reacting n-butyraldehyde with n-butylmagnesiumbromide. The α-naphthyl urethane of this authentic sample of octanol-4

did not depress the melting point of the derivative as prepared above.

Octanol-4 was oxidized with potassium dichromate and sulfuric acid. Steam distillation of this mixture produced octanone-4, which boiled at 164-168 C. The octanone-4 obtained in this manner reacted with 2,4-dinitrophenylhydrazine reagent to yield a red oil, and so it was not used for characterization. However, the octanone-4 reacted with an aqueous solution of semicarbazide hydrochloride and potassium acetate to produce a white semicarbazone which melted at 95-97 C and did not depress the melting point of an authentic sample of the semicarbazone of octanone-4.

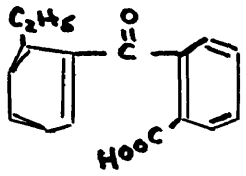
The catalytic dehydration of 1,3,7-octatrien-5-ol to 1,3,5,7-octatetraene was carried out in the same type of apparatus that was used for the preparation of hexatriene (see Figure 10). However, the first receiver was immersed in a calcium chloride-ice bath and the second was immersed in a Dry Ice-acetone bath. The temperature of the first thermometer was maintained at 210-220 C and that of the second thermometer was maintained at 275-280 C. The dehydration was accomplished by distilling the octatrienol into the aluminum oxide at about 25 mm in an atmosphere of nitrogen. The product, which was a solid at the temperature of the calcium chloride-ice bath, was a two layer liquid system at room temperature. The yellow top layer, which was the hydrocarbon fraction, was readily separated from the water layer and distilled at 57-60 C at 20 mm. The distillate solidified

in the receiver and after several recrystallizations from petroleum-ether, a faintly yellowish white crystalline solid was obtained. This solid absorbs atmospheric oxygen extremely rapidly and explodes upon long exposure to air. The decomposition products, after the explosion, had a characteristic acrolein-like (or formaldehyde) odor and gave a red 2,4-dinitrophenylhydrazone. The solid octatetraene also polymerizes readily when exposed to air or heat, and this white fluffy polymere is extremely insoluble in most organic solvents. However, octatetraene is stable if stored in solvents such as petroleum-ether or ether.

Since 1,3,5,7-octatetraene is so unstable to atmospheric oxygen and heat, precautions must be observed to insure purity of the sample. In order to get an analytical sample, the solid octatetraene was recrystallized several times from petroleum-ether and filtered and dried in an atmosphere of nitrogen.

Attempts to obtain a melting point on the solid octatetraene in air proved futile, as polymerization preceeded melting. In order to circumvent this difficulty, a micro melting point was attempted in a sublimation apparatus of a Kofler hot stage microscope. The apparatus containing the 1,3,5,7-octatetraene was evacuated, and then nitrogen was slowly circulated through the apparatus. In this manner, the octatetraene was observed to sublime at 47-50 C, but a satisfactory melting point has not been obtained.

Original attempts to hydrogenate octatetraene to n-octane were done on the impure hydrocarbon fraction. The hydrocarbon was reduced in the presence of a copper-chromium oxide catalyst at 2000 pounds pressure and 200 C. After completion of the hydrogenation, a colorless hydrocarbon fraction was obtained which boiled at 127-135 C. Oxidation of a sample of this hydrocarbon fraction with alkaline potassium permanganate and subsequent neutralization with hydrochloric acid produced a white crystalline solid. This solid melted at 122 C, and did not depress the melting point of an authentic sample of benzoic acid.

Another representative sample of the hydrocarbon fraction obtained from the hydrogenation of the octatetraene fraction was reacted with phthalic anhydride and anhydrous aluminum chloride. The white solid produced from this reaction melted at 122 C in good agreement with the melting point reported in the literature for the o-benzoyl benzoic acid derivative of ethylbenzene, 

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The oxidation and Friedel-Craft experiments proved conclusively that the hydrogenated hydrocarbon of the octatetraene fraction contained large amounts of ethylbenzene. Therefore, it became imperative to determine whether ethylbenzene was formed during the dehydration of the octatrienol or during the hydrogenation reaction.

Many samples of the octatetraene fractions obtained by the catalytic dehydration of octatrienol were oxidized with alkaline potassium permanganate and in no case was any benzoic acid produced. Therefore, the ethylbenzene was not formed during the dehydration reaction.

Then an alcoholic solution of octatetraene was refluxed for six hours with some palladium-charcoal catalyst. After removal of the catalyst, oxidation of the filtrate with alkaline permanganate failed to produce any benzoic acid. Therefore, the octatetraene is not cyclized to styrene or ethylbenzene on the surface of a catalyst such as palladium-charcoal.

Finally, a pure sample of solid octatetraene was hydrogenated over a palladium-charcoal catalyst at room temperature. The hydrogenation slowed down before the theoretical amount of hydrogen was absorbed and so the catalyst was removed by filtration and the hydrogenation continued to completion with a platinum oxide catalyst. Distillation of the product yielded a sweet smelling hydrocarbon boiling at 126-128 C at atmospheric pressure, n_D^{30}= 1.4001 and d_4^{25}= 0.714. The literature values for n-octane are: b.p. 125-126, d_4^{20} = 0.703, n_D^{20}= 1.3976.

Therefore, we assume that the ethylbenzene was formed from octatetraene by the drastic hydrogenation conditions of 2000 pounds pressure at 200 C over a copper-chromium oxide catalyst.

In a probing experiment, a small amount of octatetraene was brominated in cold petroleum-ether. The solution absorbed bromine rapidly and a white crystalline product was precipitated which melted at 123-125 C. In spite of the instability of this compound, a sufficiently good analysis was obtained which indicated that the white solid was a tetrabromide of octatetraene. We do not feel that a structure could be written for this tetrabromide until further work has been done.

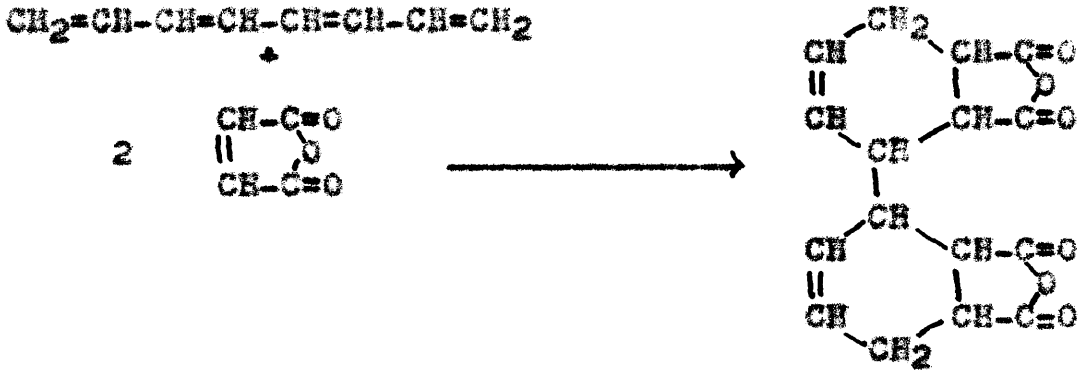
An anhydrous benzene solution of octatetraene reacted with maleic anhydride in an atmosphere of nitrogen to produce a white crystalline solid melting at 238-242 C with decomposition. Elemental analyses, and neutral equivalent determinations indicated an adduct containing two molecules of maleic anhydride. A "di-adduct" could possess any of several structures one of which would be a diphenyltetracarboxylic acid derivative depending on which ethylenic links had been involved. Therefore, we write:

$$C_8H_{10} + 2\ C_4H_2O_3 \longrightarrow C_{16}H_{14}O_6$$

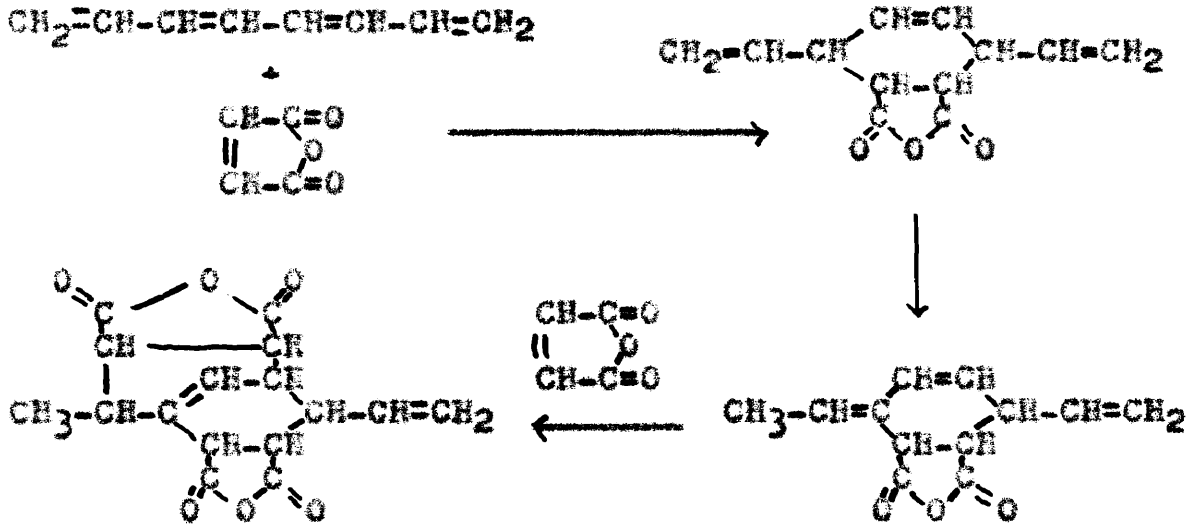
which would be a di-anhydride. We argued that we would proceed on the basis that the actual adduct was the diphenyl derivative and thus prove this structure. However, as will be seen later, we were unable to attain this objective.

Kuhn and Jauregg[57] ran a number of Diels-Alder reactions with 1,8-diphenyloctatetraene and maleic anhydride, and in every case, they found the diaddition product formed with the exclusion of the monoaddition compound.

The fact that the diaddition product of octatetraene with maleic anhydride was obtained proves that our eight carbon unsaturated hydrocarbon either had three or four double bonds.



or

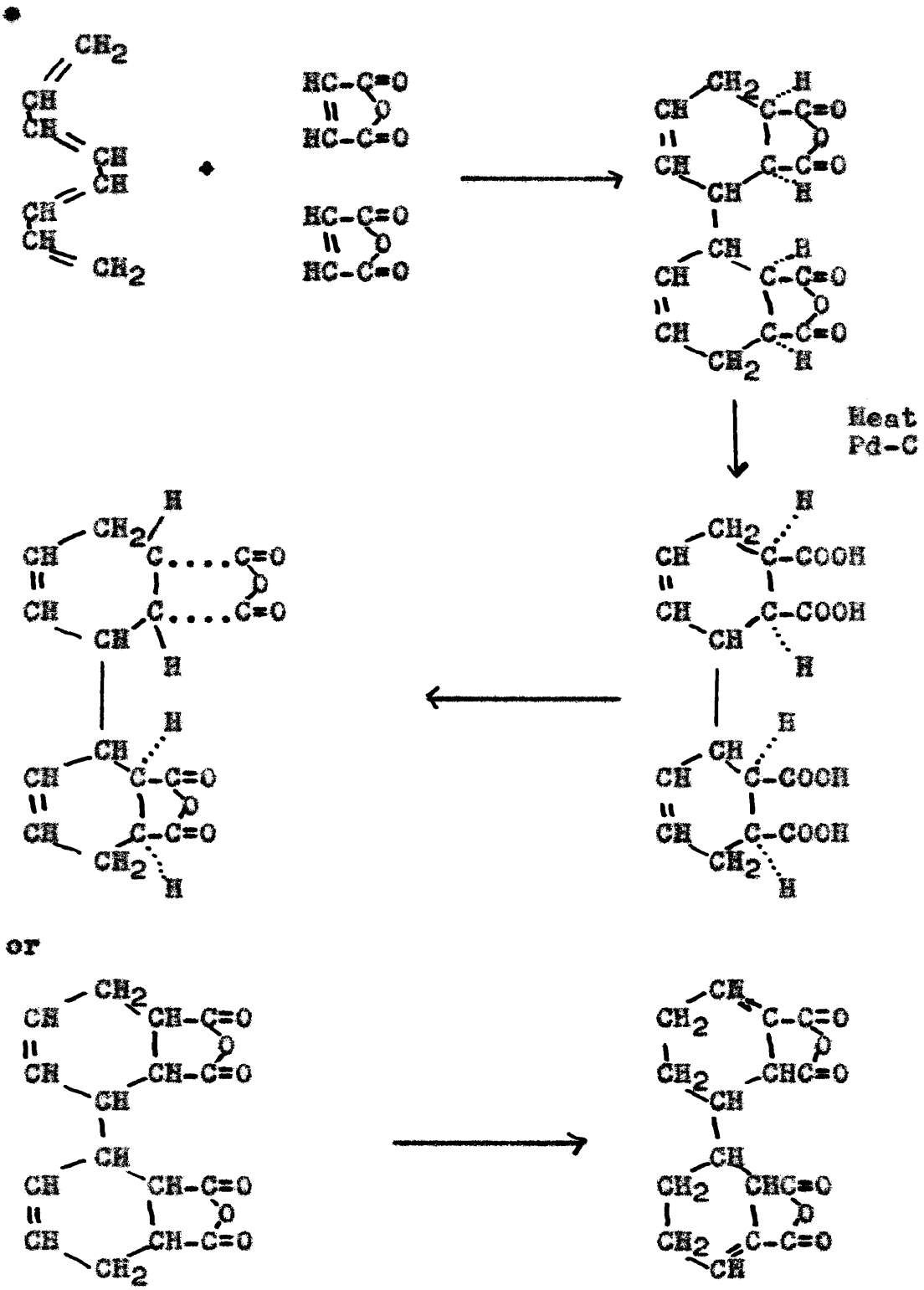


Therefore, in order to prove that the Diels-Alder product was really that of octatetraene, the adduct was quantitatively hydrogenated over a palladium-charcoal catalyst at atmospheric pressure and room temperature. The theoretical amount of hydrogen calculated for two double bonds was absorbed, proving conclusively that the eight carbon

unsaturated hydrocarbon, contained four double bonds and that the diaddition product with maleic anhydride contained two double bonds.

Attempts to dehydrogenate the maleic anhydride adduct of octatetraene to the completely aromatic diphenyl compound proved futile. Dehydrogenating reagents tried were sulfur[58], platinum oxide [59,60,61,62], palladium-charcoal[59,60,61,62], and chloranil[63,64].

Although we were unable to obtain the aromatized product, a white crystalline compound melting at 267-269 C was produced after refluxing the maleic anhydride adduct with p-cymene and palladium-charcoal. This substance melts about thirty-five degrees higher than the original adduct, but nevertheless, both yield the same analysis. The supposition here is that the dianhydride of $\Delta^{5,5'}$-octahydrodiphenyl-2,3-2',3'-tetracarboxylic acid has isomerized in one of the following ways.



* Dotted lines indicate that the attached atom is behind the plane of the paper; solid lines indicate that the attached atom is in front of the plane of the paper.

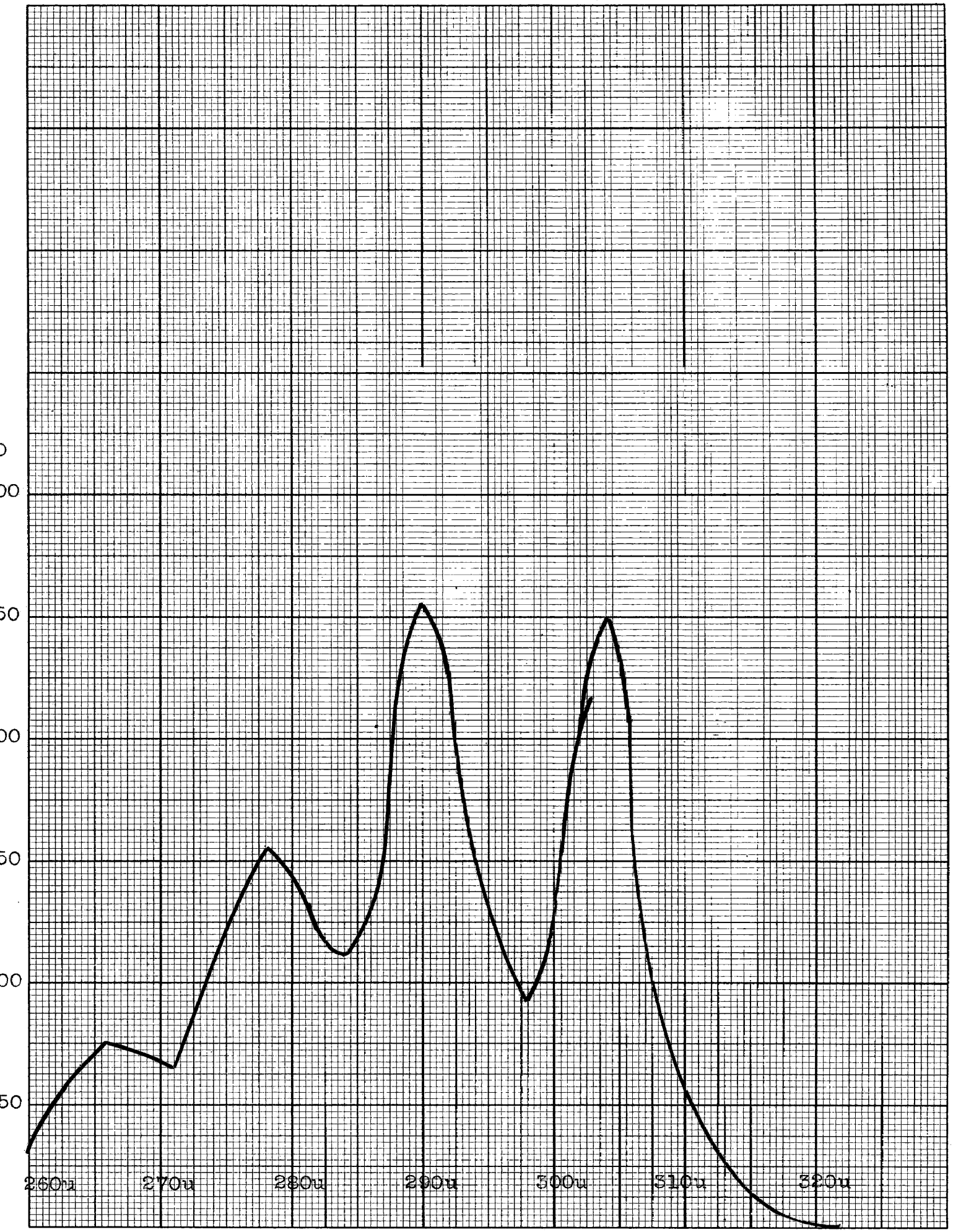


Fig.7- Ultra-violet Absorption Spectrum of 1,3,5,7-Octatetraene

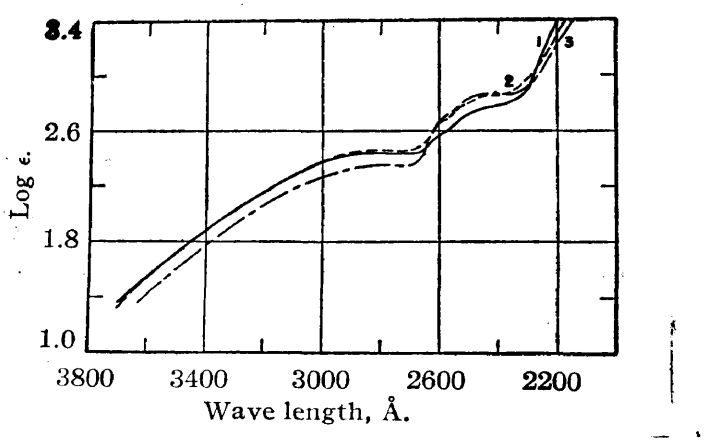


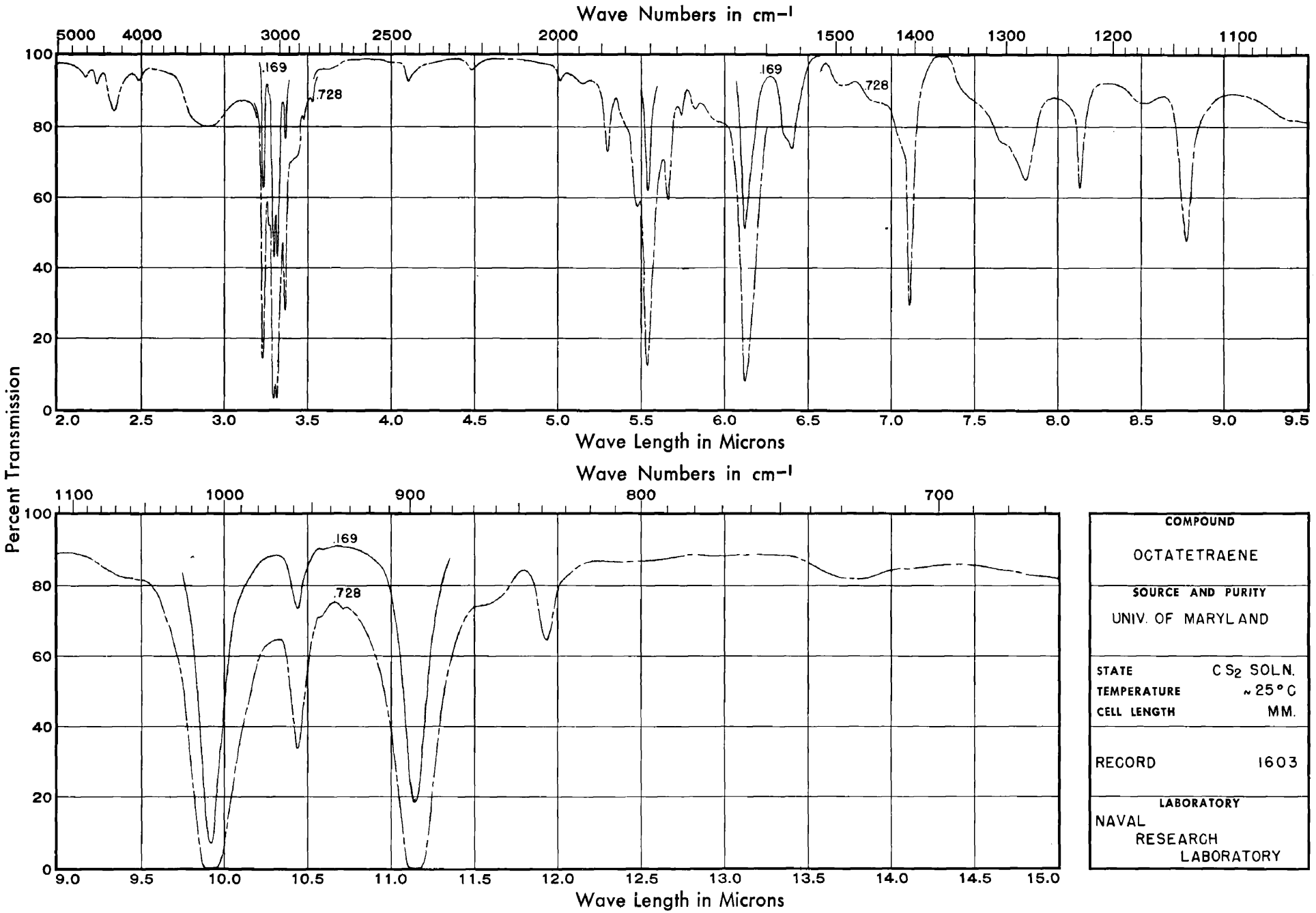
Fig.8-Ultra-violet Absorption Spectra of 1,3,5,7-Cyclooctatetraene

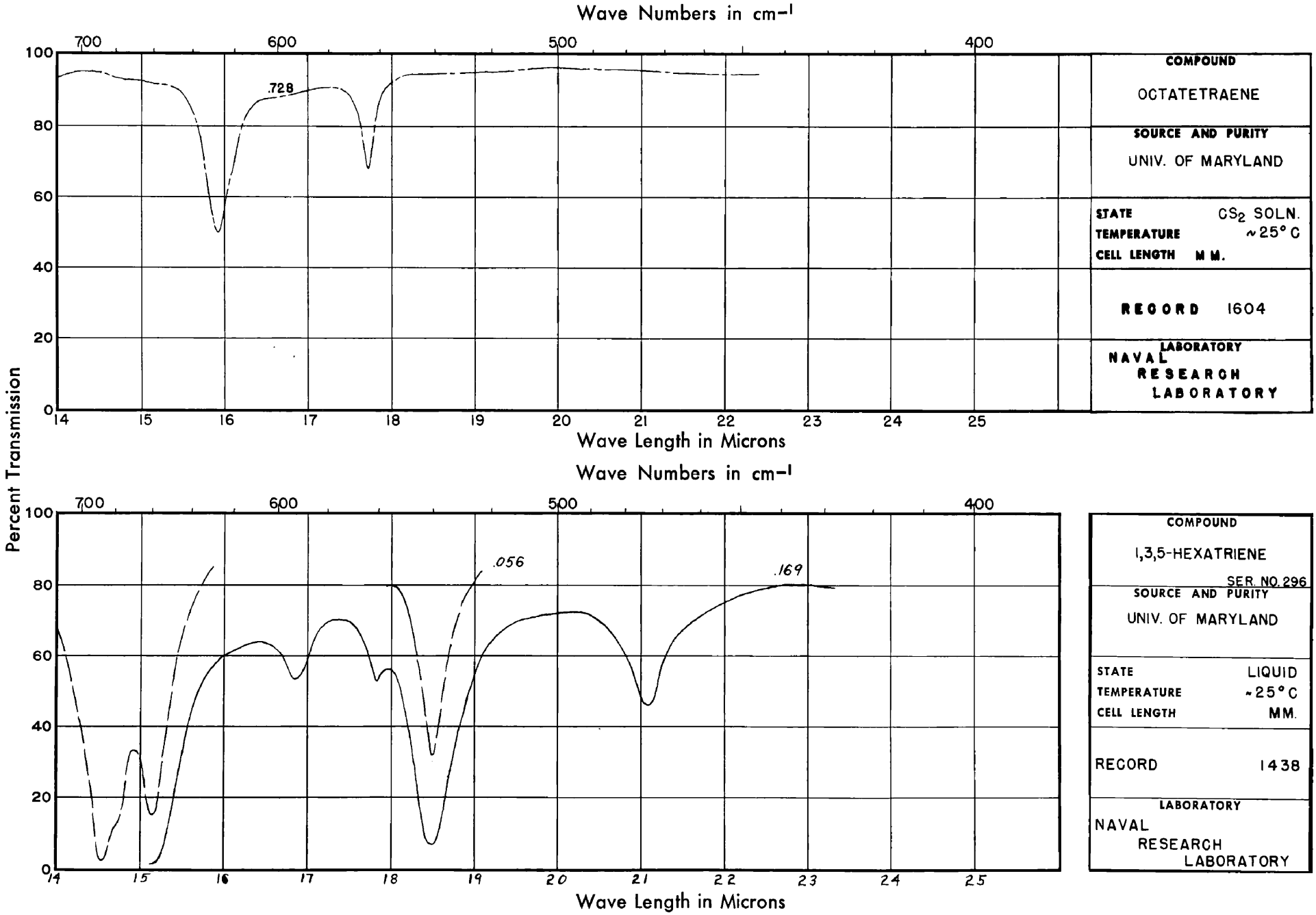
Figure 7 is a qualitative ultra-violet absorption spectrum of what we believe was our most pure sample of 1,3,5,7-octatetraene. Since octatetraene is so unstable to atmospheric oxygen, weighing the octatetraene in order to make a solution of a definite concentration would not be advisable, and therefore, we were unable to evaluate the various extinction coefficients.

The spectrum is nevertheless very valuable. For instance, the absorption is very similar to that of hexatriene, but it is displaced toward longer wave lengths. This displacement toward the visible is similar to that of the analogous series of 1,6-diphenylhexatriene and 1,8-diphenyloctatetraene. Figure 8 is the ultra-violet absorption spectrum of cyclo-octatetraene[32].

Since octatetraene has not been reported prior to this work, no comparisons can be made. However, Kovner[54] in a series of complicated quantum mechanical calculations obtained the value of the wave length of the maximum absorption for 1,3,5,7-octatetraene as 3117 A. Our spectrum shows four maxima at 2680 A, 2780 A, 2900 A, and 3040 A for 1,3,5,7-octatetraene.

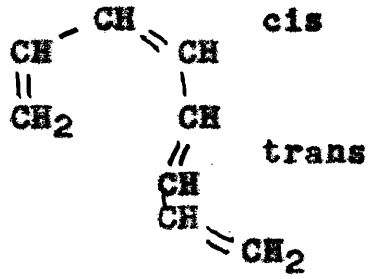
Figure 9 is a qualitative infra-red absorption spectrum of 1,3,5,7-octatetraene. A solution of the octatetraene in purified carbon disulphide was used for this determination. The striking similarity of this curve to the infra-red spectrum of hexatriene is very interesting. Needless to say, the two curves should be quite similar in all functional

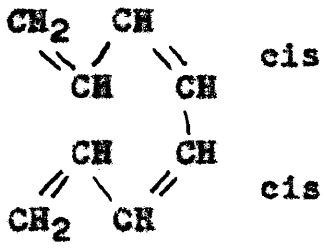

Wave Numbers in cm⁻¹
5000 4000 3000 2500 2000 1500 1400 1300 1200 1100
100 80 60 40 20 0
Percent Transmission
.169
.728
.169
.728
2.0 2.5 3.0 3.5 4.0 4.5 5.0 5.5 6.0 6.5 7.0 7.5 8.0 8.5 9.0 9.5
Wave Length in Microns
Wave Numbers in cm⁻¹
1100 1000 900 800 700
100 80 60 40 20 0
.169
.728
9.0 9.5 10.0 10.5 11.0 11.5 12.0 12.5 13.0 13.5 14.0 14.5 15.0
Wave Length in Microns
COMPOUND
OCTATETRAENE
SOURCE AND PURITY
UNIV. OF MARYLAND
STATE CS2 SOLN.
TEMPERATURE ~25°C
CELL LENGTH MM.
RECORD 1603
LABORATORY
NAVAL RESEARCH LABORATORY


Wave Numbers in cm⁻¹
700
600
500
400
100
80
60
40
20
0
.728
14
15
16
17
18
19
20
21
22
23
24
25
Wave Length in Microns
COMPOUND
OCTATETRAENE
SOURCE AND PURITY
UNIV. OF MARYLAND
STATE CS2 SOLN.
TEMPERATURE ~25° C
CELL LENGTH M M.
RECORD 1604
LABORATORY
NAVAL RESEARCH LABORATORY
Wave Numbers in cm⁻¹
Percent Transmission
.056
.169
Wave Length in Microns
COMPOUND
1,3,5-HEXATRIENE
SER. NO. 296
SOURCE AND PURITY
UNIV. OF MARYLAND
STATE LIQUID
TEMPERATURE ~25° C
CELL LENGTH MM.
RECORD 1438
LABORATORY
NAVAL RESEARCH LABORATORY

respects such as C-H stretching, C-H bending, CH_2 terminal, C=C, etc., and the variations should and do appear in the region of the harmonics and degeneracies which reflect the interactions of the whole molecule.

We are aware of the three possible geometrical isomerides of 1,3,5,7-octatetraene,







but in light of the inherent difficulties of assigning configuration to hexatriene, we realized we could not assign any geometrical structure to our material, although we do believe that again we most likely had a single isomer in view of our mode of isolation and purification.

EXPERIMENTAL

2-Ethoxy-Δ^3-dihydropyrane - The procedure used for the bromination of 2,3-dihydropyrane was a modification of that described by Paul[65]. A 2-liter, 3-neck flask was equipped with a dropping funnel, an efficient stirrer and a low range thermometer (immersed in the reaction mixture). Into this flask was added a solution of 340 g. of 2,3-dihydropyrane (4 moles) in 100 ml of dry carbon tetrachloride. The dihydropyrane solution was cooled to -35 to -60°C by means of a Dry Ice - acetone bath. A bromine solution (640 g, 4 moles) in 200 ml of carbon tetrachloride was added from the dropping funnel at such a rate that the temperature of the contents of the flask did not rise above -50°C. The bromine solution was added until decolorization was no longer evident and then a slight amount of dihydropyrane was added to destroy the excess bromine. The solvent was removed on a steam bath under reduced pressure. Care was taken that the solvent was removed at the lowest possible temperature, otherwise much of the 2,3-dibromotetrahydropyrane decomposed with the evolution of hydrogen bromide.

To two liters of well-cooled anhydrous alcohol, which had been saturated with dry ammonia, was cautiously added with stirring the 2,3-dibromotetrahydropyrane. After a few minutes, precipitation of ammonium bromide occurred. In this reaction it is important that an excess of ammonia be

maintained in the reaction mixture since traces of hydrogen bromide will decompose the product.

After one hour or longer at room temperature, the reaction mixture was filtered and the ammonium bromide was obtained in a nearly quantitative yield.

The filtrate of 2-ethoxy-3-bromo-tetrahydropyrane was then cautiously added to a cooled solution of 560 g. of potassium hydroxide (10 moles) in two liters of 95% alcohol. The mixture was then refluxed for ten hours, while removing the alcohol. About 3.5 liters of alcohol was removed in this manner. The residue was then diluted with water to remove the alcohol and extracted with peroxide-free ether and the extract was dried over anhydrous magnesium sulfate for twenty four hours. The ether was removed under reduced pressure and then sodium ethoxide - alcohol solution was added. The distillation was then continued under reduced pressure. More sodium ethoxide was added to the distillate and after two hours of refluxing the mixture was again distilled. The 2-ethoxy-Δ^3-dihydropyrane boiled at 153-5° at atmospheric pressure; yield 225 g. (44%), n_D^{25}= 1.4475.

2,4 Pentadienal. This procedure was described by Woods and Sanders[47]. To a solution of 80 ml of 85% phosphoric acid in 400 ml of distilled water was added with stirring, 80.4 g. of 2-ethoxy-Δ^3-dihydropyrane. There was no noticeable rise in temperature upon the addition of the dihydropyrane acetal. Within a few minutes, a homogeneous solution was obtained. This solution was added dropwise to a solution of 80 ml of

85% phosphoric acid in 400 ml of water which was already undergoing steam distillation. Steam distillation was discontinued when the distillate no longer gave the characteristic odor of 2,4-pentadienal or no longer gave a semicarbazone with a semicarbazide solution prepared from 12 g. of anhydrous potassium acetate plus 2 g. of semicarbazide hydrochloride added to 100 ml of water.

The steam distillate was repeatedly extracted with peroxide-free ether after sodium chloride had been added The extractions were continued until the water layer no longer gave a test for 2,4-pentadienal with semicarbazide solution as prepared above. After drying over anhydrous magnesium sulfate for twenty-four hours, the solvent was removed under reduced pressure and the residue was rapidly fractionally distilled. The condenser was cooled by circulating ice-water, the receiver was cooled in a Dry Ice-acetone bath and the heating was done with hot water. 2,4-Pentadienal was distilled at the pressure of 20 mm in a nitrogen atmosphere which was found to be most satisfactory, the yield was 27.8 g. (54%) boiling at 37-40°C, n_D^{25}= 1.5163, d_4^{25}= 0.894.

2,4-Pentadienal is almost colorless and possesses a marked acrolein-like odor and is strongly lachrymatory.

1,3-Hexadien-5-ol. Methylmagnesium bromide was prepared in the usual manner by adding 58 g. of gaseous methyl bromide (0.612 moles) to 15 g. of magnesium (0.616 moles) in 100 ml of anhydrous ether. A solution of 27.8 g. of 2,4-pentadienal dissolved in 200 ml of dry ether was added slowly with constant

stirring to the cooled solution of methylmagnesium bromide. The reaction was vigorous. After the addition, the mixture was stirred for an additional half hour and finally was decomposed with a saturated aqueous solution of ammonium chloride. The ether extract was washed several times with sodium bicarbonate and water, and then dried over anhydrous magnesium sulfate. The drying reagent was removed by filtration, and the ether extract distilled under reduced pressure. The 1,3-hexadien-5-ol distilled at 65-65.5 C in a nitrogen atmosphere at 20 mm. The yield was 27 g. (81%), $n_D^{30} = 1.4829$. Heilbron[42] reports the following physical constants for 1,3-hexadien-5-ol: b.p. 67-68 C at 26 mm, and $n_D^{19} = 1.4910$.

<u>α-Naphthyl Urethane of 1,3-Hexadien-5-ol</u>. A mixture of 1,3-hexadien-5-ol (0.5 g) and α-naphthylisocyanate (0.86 g.) was heated on a hot plate until a reaction ensued. The reaction was continued at this temperature until the mixture no longer had the strong lachrymatory odor of the α-naphthylisocyanate. The mixture was then cooled in an ice-bath, and a gummy mass was obtained. Treatment of this gummy mass with boiling petroleum-ether (30-60) dissolved most of the urethane. The solution, filtered from the residue, deposited crystals on cooling. Repeated recrystallization of this material yielded the white α-naphthyl urethane of 1,3-hexadien-5-ol melting at 85.5-86°C. Heilbron et al[42] reported a melting point of 86°C for this substance. Analysis: Calculated for $C_{17}H_{17}NO_2$: C, 76.31; H, 6.41. Found: C, 76.45; H, 6.15.

Conversion of 1,3-Hexadien-5-ol to Hexanone-2. Freshly distilled 1,3-hexadien-5-ol (10 g.) was hydrogenated with Raney-nickel at room temperature and atmospheric pressure. The amount of hydrogen absorbed was 93% of the theoretical value calculated for two double bonds. The catalyst was removed by filteration and the alcoholic filtrate distilled. Hexanol-2 (7.3 g., 70%) distilled at 136-137°C.

Potassium dichromate (46.5 g.) was mixed in the cold with concentrated sulfuric acid (62 g.) and water (210 g.). Hexanol-2 (7.3 g.) was added dropwise, with mechanical stirring, so that the temperature did not rise above 50 C. After completion of the addition, the mixture was stirred for an additional thirty minutes. The mixture was then steam distilled. The distillate, saturated with sodium chloride, was extracted with ether. The ether extract, dried over anhydrous magnesium sulfate, was distilled after removal of the solvent under reduced pressure. Hexanone-2 boiled at 45-46 at 26 mm, n^{27}_{D}= 1.3985.

Semicarbazone of Hexanone-2. A solution of 0.5 g. of semicarbazide hydrochloride and 1.5 g. of sodium acetate in 30 ml of water containing 0.4 g. of the previous product (hexanone-2) was warmed on a steam bath. The semicarbazone crystallized almost immediately. The white crystals were recrystallized from alcohol-water mixtures, and after drying, gave a melting point of 123.5-124 C. The semicarbazone of an authentic sample of hexanone-2 prepared in the above manner yielded no depression in mixed melting point. Analysis:

Calculated for $C_7H_{15}N_3O$: C, 53.47; H, 9.62. Found: C, 53.76; H, 9.45.

2,4-Dinitrophenylhydrazone of Hexanone-2. A sample of the ketone (1 g.) obtained by the oxidation of the reduction product of 1,3-hexadien-5-ol was added to a solution of 2,4-dinitrophenylhydrazine (2 g.) in alcohol (75 ml) which contained concentrated hydrochloric acid (1 ml). Immediate precipitation of the orange 2,4-dinitrophenylhydrazone was observed. The reaction mixture was heated on the hot plate for ten minutes after which time it was cooled and filtered. There was obtained almost a quantitative yield of the orange 2,4-dinitrophenylhydrazone of hexanone-2. After several recrystallizations from absolute alcohol, the compound melted at 106-107°C and did not depress the melting point of an authentic sample of the 2,4-dinitrophenylhydrazone of hexanone-2. Analysis: Calculated for $C_{12}H_{16}N_4O_4$: C, 51.42; H, 5.75. Found: C, 51.13; H, 5.61.

1,3,5-Hexatriene. 1,3,5-Hexatriene was obtained from the catalytic dehydration of 1,3-hexadien-5-ol; the apparatus used was that pictured in Figure 10. The column, which was heated by two separate electrical heating elements, was filled with a #12 mesh aluminum oxide. By means of variacs attached to the heating elements, a temperature range of 325-350 was obtained; these temperatures were produced by a setting of 50 volts on the first heating element and a setting of 60 volts on the second heating element. 1,3-Hexadien-5-ol (35.8 g.) was distilled into the aluminum oxide packed column at

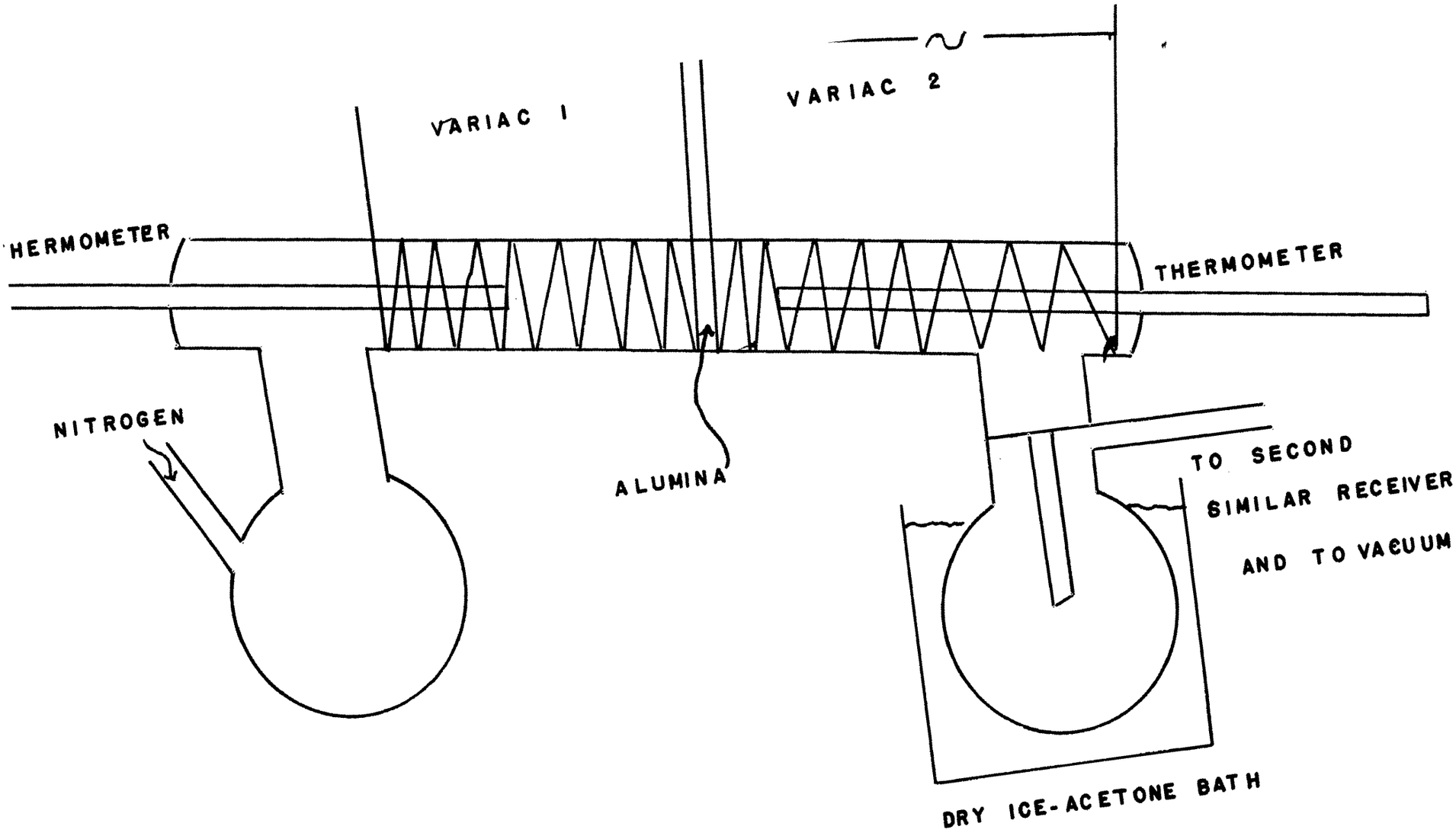


FIG.10. - CATALYTIC DEHYDRATION APPARATUS

1 mm under an atmosphere of nitrogen. The dehydration reaction proceeded in about one hour. The product, which was collected almost exclusively in the first receiver, was a solid in the Dry Ice-acetone bath, but on warming gave a two layer liquid system. The top layer was a yellow liquid and the bottom layer was water. The major portion of the water layer was removed with an eye dropper and the complete desiccation was accomplished by the addition of a small amount of anhydrous calcium oxide. After a short time, the liquid was filtered from the drying reagent and distilled under an atmosphere of nitrogen from over a small amount of anhydrous calcium oxide which had been added. The major fraction, 1,3,5-hexatriene (18.8 g, 64%) was obtained boiling at 79.0-79.6 C with an Anshutz thermometer which had been calibrated against boiling benzene. This hexatriene was a colorless liquid, which readily froze at temperatures below -12 C. This convenient freezing point became an exceedingly useful tool for the further purification of hexatriene. The fraction boiling at 79.0-79.6°C was then chilled in a Dry Ice-acetone bath and when the liquid was about three-fourths slurry, the supernatant liquid was filtered away by means of vacuum with a sintered glass filter stick. This procedure was continued until a sample was obtained with a sharp melting point. Hexatriene of this quality of purity was used for the subsequent physical measurements. The density at 22 C is 0.7338 and $n_D^{28} = 1.5035$.

The elemental analysis of hexatriene was extremely difficult to obtain. We are inclined to attribute this difficulty to the properties of this substance, i.e., the low heat of vaporization, the low flash point, and the relatively high heat of combustion. However, by using a closed bulb, containing the hexatriene, which was broken inside the combustion tube and by using a very low flame, an excellent analysis was obtained. Analysis: Calculated for C_6H_8: C, 89.94; H, 10.06. Found: C, 90.07; 89.51; H, 10.52, 10.15. It seems pertinent to add here that of the various workers in this field, only Farmer[13] reported an analysis for hexatriene and as was indicated on page 33, his values correspond more closely to the formula C_6H_{10} than to C_6H_8.

Hydrogenation of 1,3,5-Hexatriene. Hexatriene (.65 g., 0.0081 mole) in 50 ml of absolute alcohol was hydrogenated at 764 mm at 32°C with 0.01 g. of Adams' catalyst. The theoretical amount of hydrogen calculated for three ethylenic bonds was absorbed in approximately one and a quarter hours. See Figure 11 for a plot of volume of hydrogen absorbed versus time.

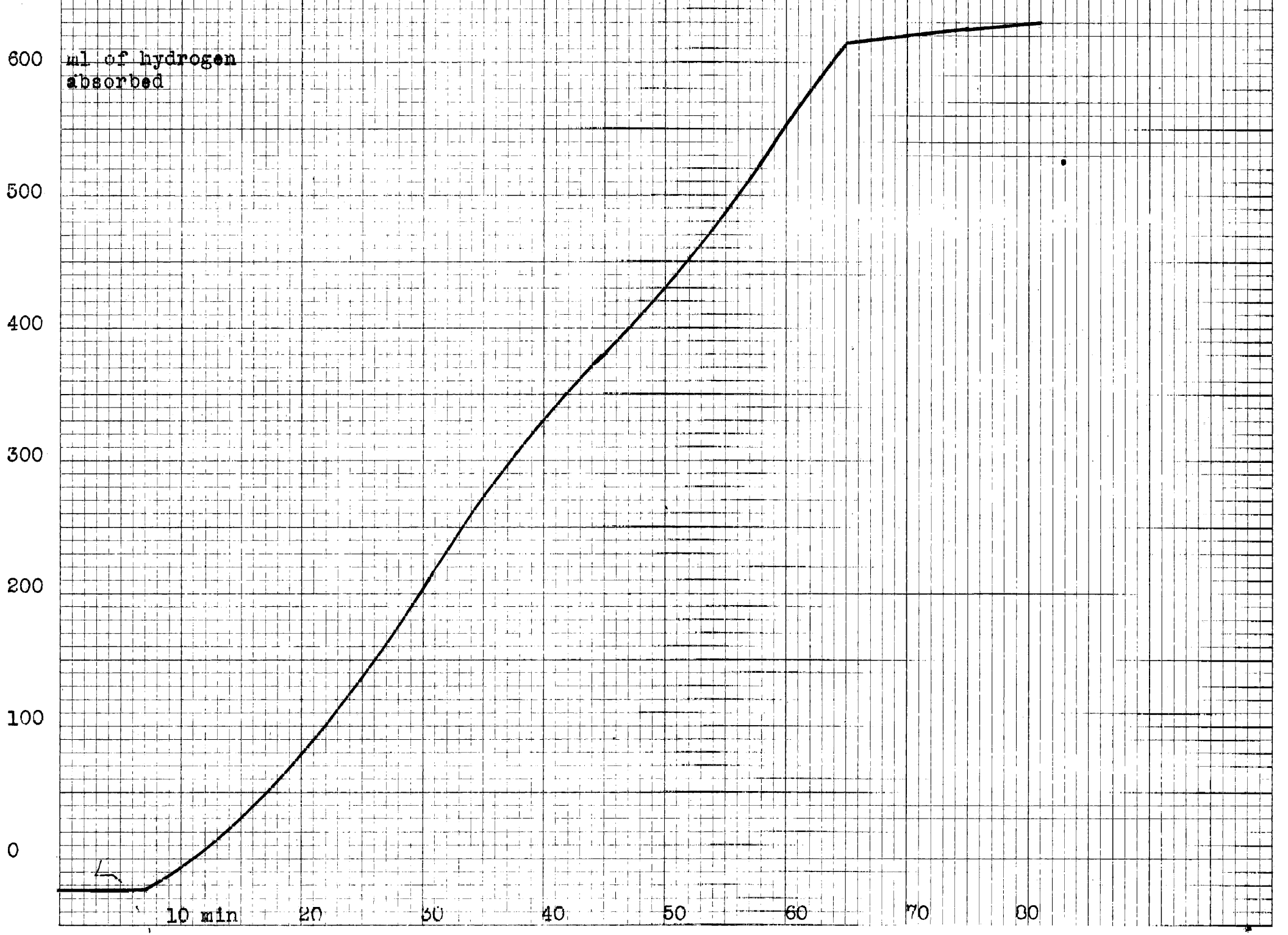


Fig.11- Quantitative Hydrogenation of 1,3,5-Hexatriene

Time (min)	Vol (ml)	Time	Vol
0	-25	37	290
1	-25	38	305
2	-25	39	315
3	-25	40	325
4	-25	41	337
5	-25	42	350
6	-25	43	360
7	-25	44	365
8	-15	45	376
9	-15	46	390
10	-5	47	400
11	-2	48	410
12	0	49	422
13	10	50	430
14	20	51	440
15	25	52	453
16	32	53	465
17	45	54	475
18	55	55	487
19	65	56	497
20	75	57	510
21	80	58	520
22	95	59	537
23	105	60	no reading
24	120	61	562
25	130	62	575
26	145	63	587
27	155	64	600
28	175	65	610
29	195	66	615
30	210	67	615
31	225	68	615
32	no reading	69	615
33	no reading	70	620
34	240	72	620
35	260	74	623
36	273	81	626

Freezing Point Determination of 1,3,5-Hexatriene. A sample of the hexatriene purified as above was placed in a test tube which was sealed at the top with a low temperature thermometer and a mechanical stirrer. This whole system was enclosed in another test tube which in turn was placed in a Dewar flask. The freezing mixture used was a Dry Ice-

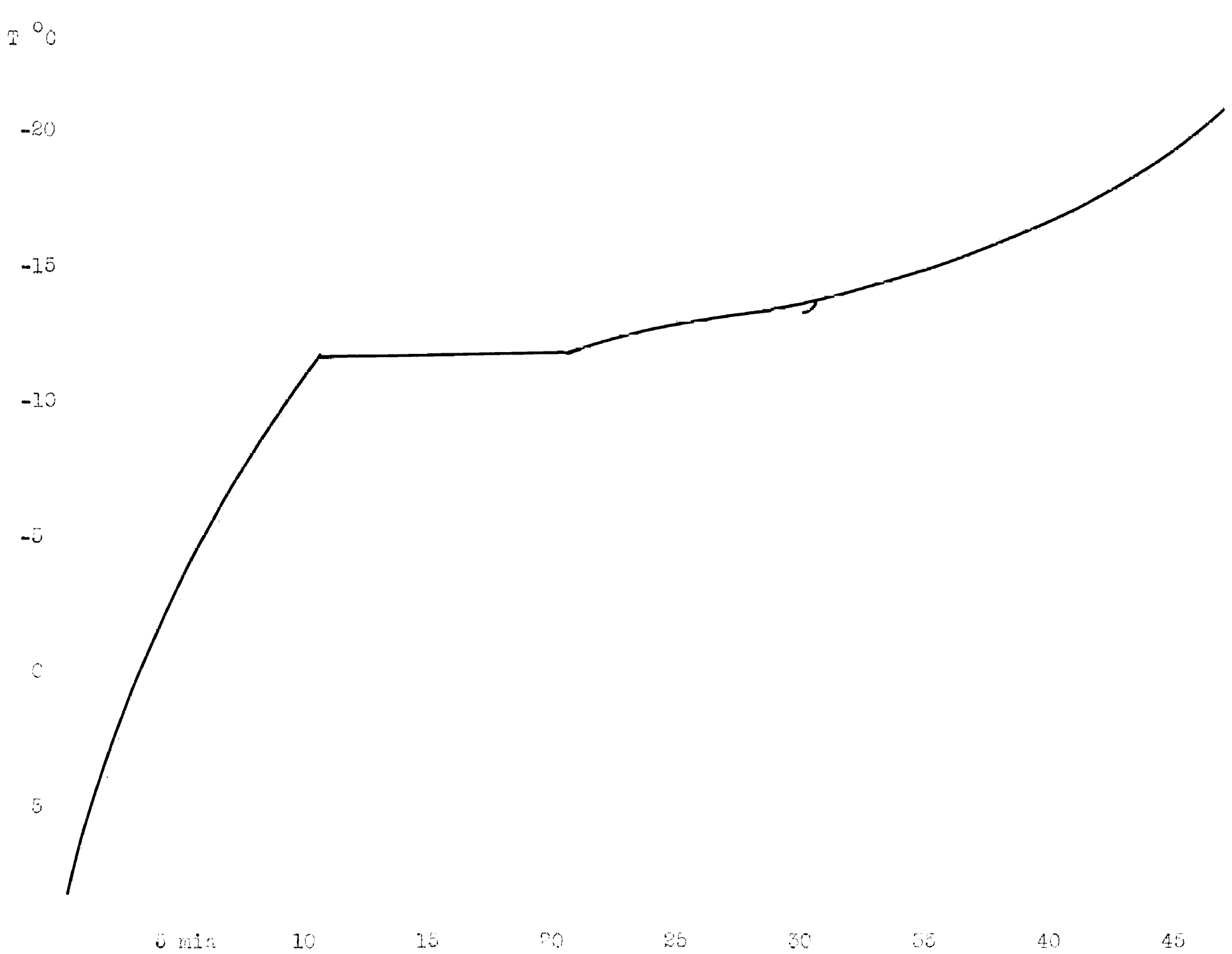


Fig.12-Freezing Point Determination of 1,3,5-Hexatriene

acetone bath. Temperature readings obtained at half minute intervals are plotted in Figure 12. A freezing point of -11.7 to -12.1 was selected from this curve. The solid, on warming slowly after freezing, melted and the temperature remained at -11.7 for several minutes.

Time	Temperature	Time	Temperature
0	9.7	20	-12.3
½	8.0	20½	-12.5
1	6.4	21	-12.5
1½	4.9	21½	-12.5
2	3.7	22	-12.5
2½	2.4	22½	-12.6
3	1.2	23	-12.7
3½	0.2	23½	-12.8
4	-0.9	24	-12.9
4½	-1.9	24½	-13.1
5	-2.8	25	-13.2
5½	-3.8	25½	-13.2
6	-4.8	26	-13.2
6½	-5.6	26½	-13.3
7	-6.5	27	-13.5
7½	-7.5	27½	-13.5
8	-8.3	28	-13.6
8½	-9.0	28½	-13.8
9	-9.5	29	-13.9
9½	-10.2	29½	-13.9
10	-11.o	30	-14.0
10½	-11.7	31	-14.1
11	-11.6	32	-14.2
11½	-11.5	33	-14.5
12	-11.6	34	-14.8
12½	-11.7	35	-15.1
13	-11.7	36	-15.6
13½	-11.8	37	-16.0
14	-11.8	38	-16.3
14½	-11.9	39	-16.6
15	-12.0	40	-17.1
15½	-12.0	41	-17.8
16	-12.0	42	-18.1
16½	-12.1	43	-18.5
17	-12.1	44	-19.2
17½	-12.1	45	-20.0
18	-12.1	46	-21.0
18½	-12.1		
19	-12.1		
19½	-12.3		

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 at 140°C at 2 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 C. These crystals turn into a yellow oil in standing in air. Farmer and Warren[14] reported a melting point of 51.5 for this substance. Analysis: Calculated for $C_{10}H_{10}O_3$: C, 67.43; H, 5.66. Found: C, 67.39 H, 5.97.

The Dibromide of 1,3,5-Hexatriene. Hexatriene (3 g) was dissolved in 10 ml of chloroform and cooled to about 5°. To this solution, bromine (6 g) dissolved in 25 ml of chloroform, was added slowly, 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° at 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's[13] 1,6-dibromo-hexadiene-2,4.

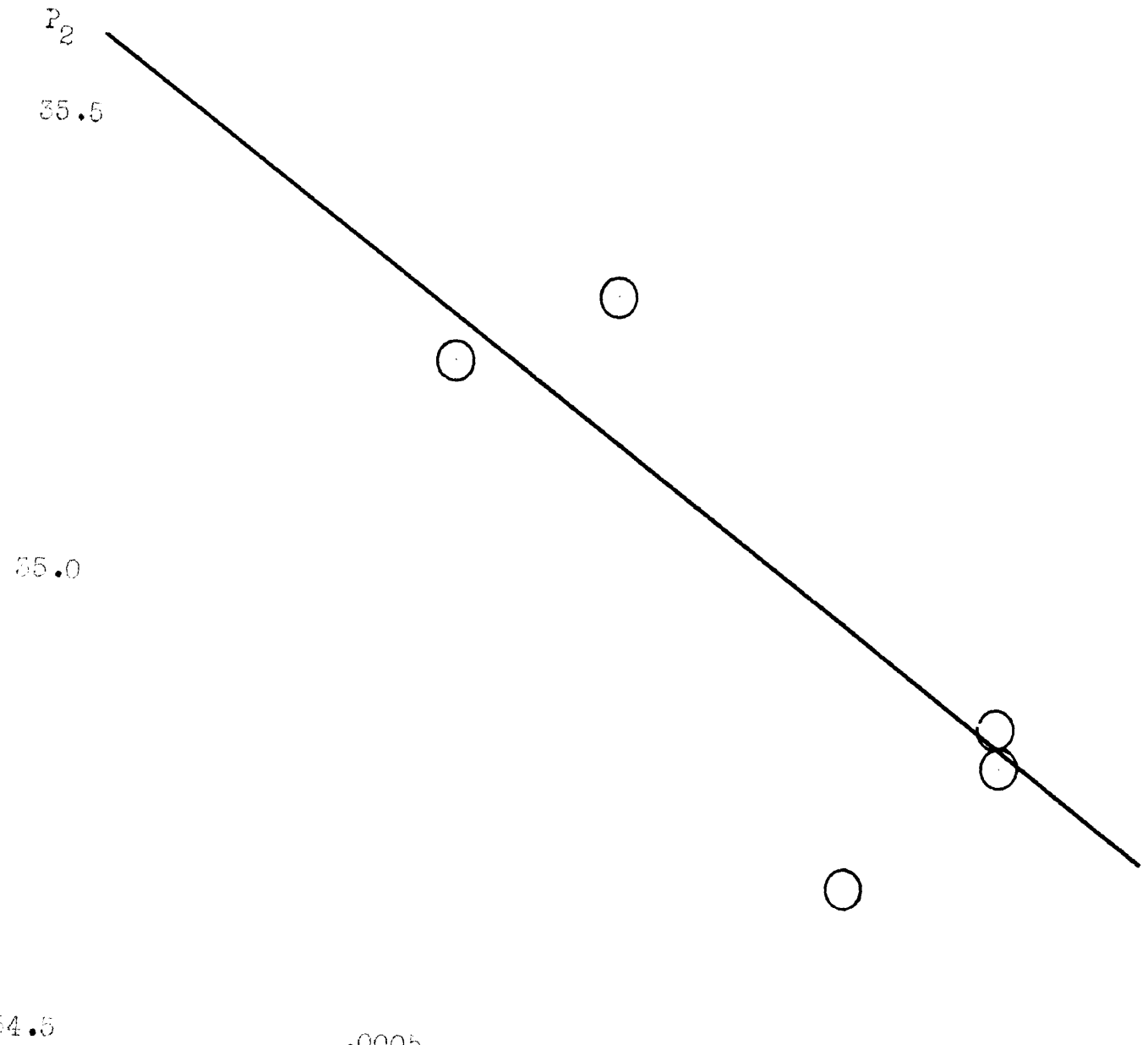


Fig.13-Polarization of Hexatriene-Benzene Solutions versus Concentration

Dipole Moment of 1,3,5-Hexatriene. The dipole moment of hexatriene was taken in purified benzene by the "heterodyne beat method."[66]

	Weight of solution	Mole fraction of hexatriene x 10^3	Density of sol.	Dial reading	Dielectric constant	P_{12}	P_2
1.	87.0825	0	*.85976	13.904	2.24620	26.6624	35.6
2.	87.5888	.563573	.85880	13.910	2.24717	26.7108	35.26
3.	87.7964	.792824	.858509	13.913	2.24766	26.7312	35.34
4.	88.1483	1.179013	.85776	13.914	2.24782	26.7573	34.71
5.	88.3399	1.388034	.85742	13.917	2.24830	26.7766	34.89
6.	88.3505	1.399571	*.857412	13.917	2.24830	26.7769	34.85

* measured values, other values obtained by plot of density versus concentration.

Molecular weight of benzene = 78.107

Molecular weight of hexatriene= 80.124

Temperature = 36.80 C.

Index of refraction of hexatriene at 28 = 1.5035

Density of hexatriene at 28= 0.7331

$$P_E = \frac{n^2-1}{n^2+2} \frac{M}{d} = 32.3357$$

$$P_E + P_A = P_E + .05\, P_E = 1.05\, P_E = 33.9525$$

$$P_1 = \frac{e_1 - 1}{e_1 + 2} \times M_1/d_1$$

$$P_{12} = \frac{e_{12} - 1}{e_{12} + 2} \times (M_1N_1 + M_2N_2)/d_{12}$$

$$P_2 = \frac{P_{12} - P_1N_1}{N_2}$$

P_2^{∞} was obtained by extrapolation to infinite dilution of the plot of P_2 versus concentration, $P_2^{\infty} = 35.6$ (see Figure 13)

$$\mu = 0.01273\, ([P_2^{\infty} - (P_E + P_A)]T)^{\frac{1}{2}}$$

$\mu = 0.29$ Debye units

However, if we assume $P_A = 10\%\ P_E$, then $\mu = 0$.

Subscript 1 applies to the benzene, subscript 2 applies to the hexatriene.

n= index of refraction

e= dielectric constant

M= molecular weight

N= mole fraction

d= density

P_E= electronic polarization

P_A= atomic polarization

μ= permanent dipole moment

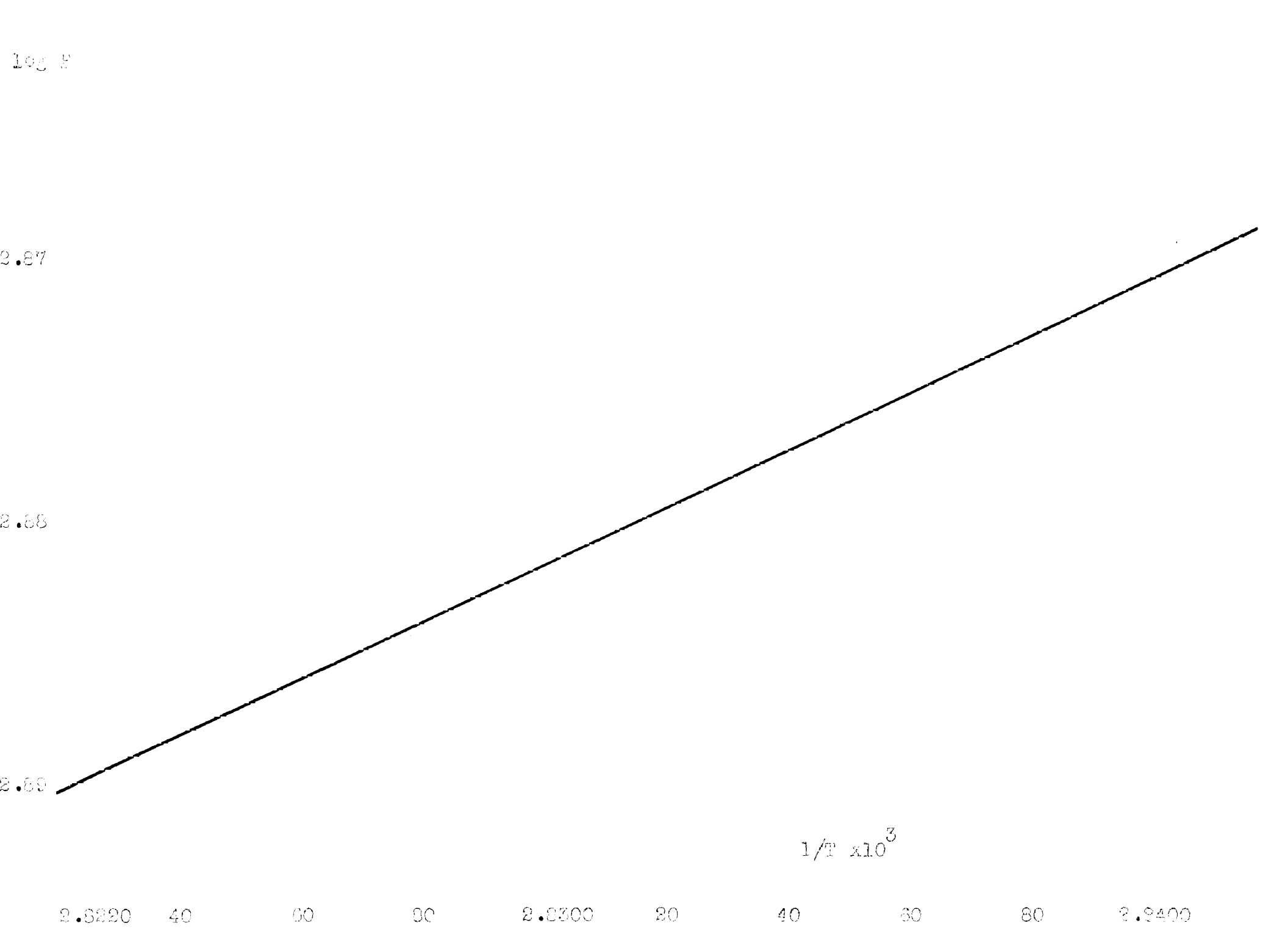


Fig.14- Curve for the Heat of Vaporization of 1,3,5-Pentatriene

The Heat of Vaporization of 1,3,5-Hexatriene. The apparatus for this experiment was as follows: a mercury filled U-tube which acted as a manometer, a measuring stick, a Beckmann thermometer, an Anshutz thermometer, a mechanical stirrer, and a water thermostat.

Several drops of purified hexatriene were placed above the mercury in the closed end of the manometer by merely tilting the manometer on its side and inserting the liquid, by means of a thin capillary tube, down to the U-bend of the manometer. Only a slight amount of liquid is necessary to provide for a liquid-vapor equilibrium at all times. The thermostat was then heated by means of a Bunsen burner and the following readings were taken.

Atmospheric Pressure = 763 mm

P (closed, cm)	P (open, cm)	P (mm)	Beckmann Thermometer	Anshutz Thermometer
88.9	91.6	736	5.06	78.6
89.1	91.4	740	4.78	78.9
89.5	90.9	749	4.28	79.4
89.7	90.7	753	3.95	79.6
89.9	90.5	757	3.77	78.8
90.0	90.4	759	3.63	80.0
90.2	90.3	762	3.38	80.2
90.3	90.2	764	3.23	80.4
90.4	90.1	766	3.11	80.5
90.5	90.0	768	2.95	80.6
90.6	89.9	770	2.84	80.8
90.7	89.8	772	2.67	81.0
90.8	89.7	774	2.52	81.2
90.9	89.6	776	2.40	81.2

These readings were plotted as log P versus 1/T, where T is absolute temperature, in Figure 14. The slope of the line so obtained is 1.07 x 10^3.

$\Delta H = 2.303 \frac{R \, d \log P}{d \, 1/T}$

$\Delta H = (1.99)(2.303)(\text{slope})$

$\text{Slope} = \frac{d \log P}{d \, 1/T} = \frac{2.88900 - 2.87400}{.0028370 - .0028230} = 1.07 \times 10^3$

$\Delta H = (1.99)(2.303)(1.07 \times 10^3) = 4.91$ Kcal/mole

ΔH for 1,3,5-Hexatriene is 61.4 cal/g.

Surface Tension of 1,3,5-Hexatriene. The surface tension was determined using the capillary rise method, measuring the rise by means of a cathetometer. The apparatus used was a small test tube, with a side arm for suction, into which was inserted a long capillary tube. The whole apparatus was mounted into a thermostated water bath. The liquid sample was inserted into the test tube and after temperature equilibrium had been established a reading was taken; then the liquid was pulled out of the capillary tube by suction and the liquid again allowed to reach equilibrium, at which time another reading was taken. In this manner the capillary rise was measured for benzene, water and hexatriene; with the values of the surface tension as reported in the International Critical Tables for benzene and water a value for the surface tension of hexatriene was calculated.

Benzene at 22.5°C

Literature value for benzene is 28.96 dyne/cm for 22.5°C.

h_o	h
13.75	9.75
13.75	9.75

$\Delta h = 4.00$ cm

$r = \frac{2\gamma}{hdg} = \frac{2(28.96)}{(4.00)(980.1)(.879)} = 0.0168$ cm

Water at 21.4 - 21.6°C

Literature value for water is 72.52 dyne/cm at 21.5°C.

ho	h.	Δ h
13.48	22.35	8.87
13.46	22.38	8.92
13.40	22.35	8.94

Δh=8.91 cm

$$r = \frac{2\gamma}{hdg} = \frac{(2)(72.52)}{(8.91)(.99791)(980.1)} = .0166 \text{ cm}$$

Hexatriene at 20.2 - 20.4°C

ho	h.	Δ h
17.69	13.82	3.87
17.68	13.84	3.84
17.69	13.85	3.84

Δh=3.85 cm

γ = 1/2 h dgr

γ = 1/2 (3.85)(.73384)(980.1)(.0167)

γ = 23.1 dynes/cm

Therefore using the radius of the capillary, r, as .0167 cm the surface tension of hexatriene at 20.2 - 20.4°C is 23.1 dynes/cm.

Ultra-violet Absorption Spectrum of 1,3,5-Hexatriene.

Cyclohexane, the solvent, was purified by stirring with portions of cold concentrated sulfuric acid until the sulfuric acid layer showed no discoloration. The cyclohexane layer was washed with saturated solution of sodium bicarbonate and then with water. The cyclohexane was then dried with anhydrous calcium sulfate for forty-eight hours, filtered from the drying reagent, sodium added to the filtrate and the mixture distilled through a Widmer column. Cyclohexane, purified in this manner, boiled at 79.5-80 at atmospheric pressure and it was transparent down to 216 mu.

A Beckman quartz spectrophotometer was used to measure the ultra-violet absorption spectrum. Quartz cells, 1.000 cm thick, were used. The concentration found necessary to resolve the fine structure of hexatriene was 4.4×10^{-5} moles/liter.

Figure 4 is a plot of α, the molar absorption coefficient, versus λ, the wave length in millimicrons.

$$I = I' e^{-cl\alpha}$$

$$\alpha = \frac{2.3}{cl} \log \frac{I'}{I} = \frac{2.3}{4.4 \times 10^{-5}} (\log 100 - \log I)$$

λ, mu	% Transmission	$\alpha \times 10^{-5}$	λ, mu	% Transmission	$\alpha \times 10^{-5}$
227.6	59.7	.117	260	6.82	.609
230	52.2	.147	260.5	8.29	.565
235	38.5	.217	261	9.70	.530
240	24.6	.318	262	11.8	.485
242	22.3	.341	262.5	12.7	.469
245	13.6	.453	263	13.7	.451
246	11.2	.495	264	12.2	.475
247	9.59	.533	265	9.95	.547
247.5	8.49	.560	266	7.09	.600
248	8.62	.556	267	5.40	.662
249	9.11	.544	267.5	5.00	.680
250	10.02	.522	268	5.07	.676
251	11.1	.499	269	6.6	.618
251.5	10.85	.504	269.5	7.55	.587
252	11.1	.499	270	9.66	.530
252.5	10.38	.514	270.5	12.5	.471
253	10.17	.518	271	16.2	.414
254	8.48	.561	272	24.1	.323
254.5	6.58	.618	273	33.0	.252
255	6.05	.636	275	48.8	.163
256	4.29	.714	280	64.9	.098
257	3.50	.760	285	69.2	.084
257.5	3.08	.790	290	72.9	.072
258	3.72	.746			
259	4.65	.696			

Infra-red Absorption Spectrum of 1,3,5-hexatriene. The infra-red absorption spectrum of a pure liquid sample of hexatriene was kindly run by Dr. Donald C. Smith of the Naval Research Laboratories.

The rock salt absorption cells used were 0.009 mm, 0.056 mm., and 0.169 mm. thick.

Figure 6 is a plot of the wave length, or wave number, versus percent transmission.

The following is a summary of the maximum absorption points in microns, μ, and wave number, cm^{-1}.

	(μ)	(cm^{-1})		(μ)	(cm^{-1})
	2.15	4650		5.53	1810
	2.24	4460		5.72	1750
	2.33	4290		5.97	1675
	2.48	4030		6.16	1623
ca.	2.76	3620	ca.	6.47	1546
	2.92	3420		6.66	1502
	2.99	3340		6.75	1481
	3.235	3091		7.00	1429
	3.290	3040		7.28	1374
	3.320	3012		7.34	1362
	3.364	2973		7.73	1294
	3.398	2943		7.97	1255
	3.475	2878		8.05	1242
	3.536	2828		8.21	1218
	3.78	2645		8.58	1166
	3.91	2560	ca.	8.85	1130
	4.11	2435		9.89	1011
	4.28	2335		10.38	963
	4.43	2255		10.63	941
	4.62	2165		11.12	899
	4.74	2110	ca.	12.22	818
	4.85	2060		13.37	748
	5.03	1990		14.55	687
	5.34	1875			

<u>1,3,7-Octatrien-5-ol</u>. The procedure for the preparation of the allyl Grignard reagent was essentially that used by Gilman[56]. Finely powdered magnesium (45 g.) in anhydrous ether (100 ml) was placed in a clean, dry, 1 liter, three-neck flask. Allyl bromide (80 g) in anhydrous ether (425 ml) was added over a period of three hours. The mixture was allowed to react at room temperature during this addition.

The ether solution of allyl magnesium bromide was then purged with nitrogen away from the excess magnesium into another 1 liter, 3- neck flask. Pentadienal (41 g) in anhydrous ether (100 ml) was then added dropwise to a chilled solution of the allylmagnesium bromide. After the addition, the mixture was stirred for an additional fifteen minutes at room temperature. The Grignard addition complex was then decomposed with a saturated aqueous solution of ammonium chloride. The ether layer was separated, washed with sodium bicarbonate and water, and dried over anhydrous magnesium sulfate for twenty-four hours. The solvent was removed under reduced pressure and the octatrienol distilled at reduced pressure in a nitrogen atmosphere, boiling point 70-71 at 6 mm, 80 at 13 mm, $n_D^{22} = 1.4931$. The yield was 55 g of 1,3,7-octatrien-5-ol or 90%. Analysis: Calculated for $C_8H_{12}O$: C, 77.37; H, 9.74. Found: C, 77.35; H, 9.84.

Octanol-4. Freshly distilled 1,3,7-octatrien-5-ol (4 g) was hydrogenated with Raney-nickel at room temperature and atmospheric pressure. Ninety-one percent of the theoretical amount of hydrogen calculated for three double bonds was absorbed in approximately thirty minutes. The alcoholic solution was filtered from the catalyst and distilled under reduced pressure. Octanol-4 (3.8 g) boiled at 79 C at 20 mm, $n_D^{24} = 1.3890$. Literature values for octanol-4 are: boiling point 79 C at 16 mm, $n_D^{24} = 1.3898$.

An authentic sample of octanol-4 was prepared by the addition of n-butyraldehyde to n-butylmagnesium bromide.

n-Butylbromide (30 g) in anhydrous ether (50 ml) was added slowly to magnesium (5.9 g) in anhydrous ether (50 ml). After all of the magnesium reacted, n-butyraldehyde (15.8 g) in anhydrous ether (30 ml) was added slowly dropwise. The mixture was then refluxed for an additional thirty minutes and then decomposed with a dilute solution of sulfuric acid. The ether layer was washed with a sodium bicarbonate solution, with water, and finally dried over anhydrous magnesium sulfate. The drying agent was removed by filtration and the octanol-4 distilled. (b.p. 70-71°C at 10 mm).

α-Naphthyl Urethane of Octanol-4. Octanol-4 (1 g) was added to α-naphthyl-isocyanate (1.3 g) and the mixture was heated for several minutes on a hot plate. The heating was discontinued when the lachrymatory odor of the α-naphthyl-isocyanate was no longer evident. After cooling, the addition of a 10 ml of petroleum-ether (90-100) precipitated a floculent white solid. The white urethane after recrystallization five times from petroleum-ether (30-60) melted at 60-61 C. The α-naphthylurethane prepared from an authentic sample of octanol-4 also melted at 61-63 and a mixed sample melted at 60-62. Analysis: Calculated for $C_{9}H_{25}N\ O_2$: C, 76.22; H, 8.42. Found: C, 76.21; H, 8.22.

Octanone-4. Potassium dichromate (31.4 g) was mixed in the cold with concentrated sulfuric acid (42 g) and water (200 ml). With mechanical stirring, octanol-4 (6.9 g) was added dropwise so that the temperature did not rise above 50°C. After completion of the addition, the mixture was

stirred for an additional thirty minutes. The mixture was then steam distilled and the distillate was saturated with sodium chloride and extracted with ether. The ether extract was dried over anhydrous magnesium sulfate and the solvent removed under reduced pressure. Octanone-4 boiled at 164-168°C, yield 3 g.

Semicarbazone of Octanone-4. A semicarbazide test solution was made by mixing 2 g of semicarbazide hydrochloride with 12 g of anhydrous potassium acetate and 100 ml of water. Twenty-five milliliters of this test solution was added to 0.3 g of octanone-4 and the mixture was heated on a hot plate. The semicarbazone was slow forming, but after thirty minutes on the shaking machine, a white crystalline solid precipitated. After several recrystallizations from methyl alcohol-water mixtures, the white semicarbazone melted at 95-97 and gave no depression with an authentic sample of the semicarbazone of octanone-4. Analysis: Calculated for $C_9H_9N_3O$: C, 58.35; H, 10.34. Found: C, 58.42; H, 10.09.

1,3,5,7-Octatetraene. The apparatus used for the catalytic dehydration of 1,3,7-octatrien-5-ol to 1,3,5,7-octatetraene is the same as that used for the preparation of 1,3,5-hexatriene and is pictured in Figure 10. However, the first receiver was cooled by a calcium chloride-ice bath, while the second receiver was cooled by a Dry Ice-Acetone bath. A few crystals of hydroquinone was added to each receiver and to the distilling pot to diminish the possibility of polymerization. The first heating element was regulated

for 210-220°C by setting the variac at 50 volts and the second heating element was regulated at 275-280°C by setting the second variac at 53 volts. Octatrien-5-ol was distilled into the aluminum oxide packed column at 25 mm under a nitrogen atmosphere. During the dehydration the temperature of each thermometer rose 30° and the variacs had to be shut off intermittently. The product, which was collected exclusively in the first receiver, was a two layer liquid system at room temperature. The top layer, a yellow liquid, was separated from the water layer, dried with anhydrous calcium oxide, and distilled in a nitrogen atmosphere. It boiled at 57-60°C at 20 mm and solidified in the receiver. The crystalline solid was dissolved in petroleum-ether (20-40), and recrystallized by means of a Dry-Ice acetone bath. After several recrystallizations from petroleum-ether (20-40), a slightly yellowish white crystalline material was obtained. This material was set aside to air dry and it exploded. The explosion products, which had definite acrolein-like odors, were dissolved in alcohol and upon addition of an acid solution of 2,4-dinitrophenylhydrazine gave a red 2,4-dinitrophenylhydrazone.

Octatrien-5-ol (22 g) was dehydrated to give 58.5% of solid 1,3,5,7-octatetraene (11 g) which was obtained by recrystallization from petroleum-ether (20-40) in a nitrogen atmosphere.

A sample of the octatetraene was recrystallized two additional times and then dried of the solvent (20-40 petroleum-ether) by means of vacuum aspiration in a drying pistol, and this sample was used for the analysis. Earlier attempts to get an analysis proved futile, due to rapid

absorption of oxygen, which invariably led to an explosion. In order to get a satisfactory analysis, the sample was placed in a constricted chamber through which was passed pure nitrogen. The sample was slowly sublimed out of the chamber and into the combustion tube where it was mixed with pure oxygen. After the entire sample of octatetraene was carbonized, then pure oxygen was passed into the constricted chamber and the remaining carbon was oxidized. Analysis: Calculated for C_8H_{10}: C, 90.51; H, 9.49. Found: C, 89.75; H, 9.77.

All early attempts to determine a melting point on 1,3, 5,7-octatetraene proved futile due to the rapid polymerization under the influence of heat and atmospheric oxygen and resort had to be made to a micro melting point technic. A Kofler hot stage was set up on a microscope stage and a small sample of octatetraene was placed in the vacuum sublimation apparatus. The sublimation apparatus was then evacuated by means of a water aspirator and then a slow stream of nitrogen was admitted into the sublimation chamber. Under these conditions octatetraene did not melt but it did sublime at about 47-50°C.

Attempt at Oxygen Absorption by Octatetraene. One-tenth of a gram of freshly recrystallized octatetraene was placed in 20 ml of petroleum-ether (20-40) and the mixture shaken in the quantitative hydrogenation apparatus at atmospheric pressure and room temperature in an atmosphere of air. After thirty minutes no oxygen was absorbed and the mixture was poured into a petre dish; the solvent evaporated slowly to give beautiful crystals of octatetraene, which sublimed readily.

Attempted Hydrogenation of Octatetraene. The entire liquid product from the dehydration of 22.7 g of octatrien-5-ol was hydrogenated over copper-chromium oxide catalyst at 2000 pounds and 200°C. A 500 pound pressure drop was observed, but due to the impurity of the starting material, a theoretical pressure drop could not be calculated. The product was extracted with ether, dried with anhydrous calcium chloride and distilled at atmospheric pressure.

Fraction 1	b.p. up to 127°C	
Fraction 2	b.p. 127-130	$n_D^{R.T}$ = 1.4667
Fraction 3	b.p. 129-131	$n_D^{R.T}$ = 1.4702
Fraction 4	b.p. 133-135	$n_D^{R.T}$ = 1.4812

One gram of fraction 3 was refluxed with 4 g of potassium permanganate in 80 ml of water with 3 ml of ten percent sodium hydroxide for two hours. The excess permanganate was destroyed with sodium bisulfite and the solution filtered. Neutralization with concentrated hydrochloric acid to the chilled alkaline solution gave a copious white precipitate. On recrystallization from hot water, this compound melted at 120-122 C and gave no depression with an authentic sample of benzoic acid.

One gram of fraction 3 was mixed in 25 ml of carbon disulfide with 1.4 g of phthalic anhydride and the mixture was immersed in an ice bath. Five grams of anhydrous aluminum chloride was then added portion wise so that the reaction did not get too vigorous. The reaction mixture was then refluxed for thirty minutes and the complex was decomposed with ice water and hydrochloric acid. Recrystallization of the gummy white solid from alcohol-water gave

beautiful white crystals melting at 122 C. The literature reports the o-benzoyl benzoic acid derivative of ethylbenzene melting at 122°.

Therefore fraction 3 consisted mainly of ethyl benzene.

Oxidation of Octatetraene. One gram of crude product from the dehydration of octatrien-5-ol was refluxed for ninety minutes with 4 g of potassium permanganate in 80 ml of water with 1 g of potassium hydroxide. The oxidation took place rapidly with a vigorous evolution of carbon dioxide. The reaction mixture was filtered and since an oily layer remained, and additional 1 g of permanganate was added and the mixture was then refluxed for another hour. The excess permanganate was destroyed with sodium bisulfite and the resulting solution was filtered, cooled, and acidified. After two days in the ice box, no precipitate was present.

This experiment was done several times on various samples of crude and pure octatetraene and at no time was any benzoic acid observed.

Attempt at Cyclization of Octatetraene. About 3 g of freshly recrystallized octatetraene was dissolved in 60 ml of absolute ethyl alcohol and 1 g of 5% palladium-charcoal catalyst was added to this solution. This mixture was refluxed for three hours and then most of the alcohol was distilled off at atmospheric pressure. The residue was filtered from the catalyst, flushed with water, and extracted with ether. On cooling the dried ether extract with a dry-ice-acetone bath, a copious precipitate of octatetraene resulted.

One gram of the residue after ether evaporation was oxidized with 4 g of potassium permanganate and 1 g of potassium hydroxide in 80 ml of water. After destroying the excess permanganate with sodium bisulfite, filtering, cooling and neutralizing with concentrated hydrochloric acid, no precipitate appeared after several days.

n-Octane-Octatetraene (4.5 g) in glacial acetic acid (60 ml) was hydrogenated with a 5% palladium - charcoal catalyst. After the hydrogenation had slowed down, the catalyst was filtered off, fresh platinum oxide was added and the hydrogenation continued to completion. The acetic acid solution was then chilled and neutralized with sodium hydroxide. The resulting sweet smelling oily layer was extracted with ether, and the ether extract dried with sodium and distilled from sodium. The n-octane distilled at 126-128°C at atmospheric pressure, $n_D^{30} = 1.4001$, $d_4^{25} = 0.714$.

Bromination of Octatetraene - In a probing experiment, a small amount of solid octatetraene dissolved in petroleum ether (80-100) was brominated in the cold. The solution absorbed bromine quickly and a white crystalline product was precipitated. After several recrystallizations from acetone-water mixtures, it melted at 123-5°C. This compound is not very stable and evolves hydrogen bromide rather readily. Analysis: Calculated for $C_8H_{10}Br_4$: C, 22.56; H, 2.35. Found: C, 23.75; H, 2.78.

Maleic Anhydride Diadduct of Octatetraene. Five grams of maleic anhydride, freshly recrystallized from chloroform, was added to a solution of 2.5 g. of octatetraene in 50 ml of dry benzene. This mixture was refluxed on a steam

bath in a nitrogen atmosphere for six hours. Almost immediately, a white solid was precipitated from the benzene solution, and this precipitate became more copious as the reaction proceeded. The white solid, 4.5 g, was filtered from the solution and on evaporation of the benzene filtrate and addition of alcohol, an additional 0.25 g of solid was obtained. The yield was 4.75 g or 67%. After several recrystallizations from acetic acid, the white solid melted at 238-242 with decomposition. Analysis: Calculated for $C_{16}H_{14}O_6$: C, 63.57; H, 4.67. Found: C, 63.44, 63.32; H, 4.92, 4.78.

Neutral Equivalent of the Adduct.- The maleic anhydride adduct of octatetraene (0.0584 g) was dissolved in 30.13 ml of 0.1135 N NaOH. This solution was then titrated with 0.1041 N HCl using a Fisher electro-titrimeter. The end point was reached at 25.07 ml of hydrochloric acid. Neutral Equivalent: Calculated 75 ± 1; Found 73.

Tetracarboxylic Acid of the Maleic Anhydride Adduct of Octatetraene. On refluxing a small amount of the maleic anhydride adduct of octatetraene in moist xylene there was obtained a white crystalline material. After several recrystallizations from acetone-xylene mixtures, the white crystalline solid melted at 247-250. Analysis: Calculated for $C_{16}H_{18}O_8$; C, 56.80; H, 5.36. Found: C, 56.45; H, 5.41.

Hydrogenation of the Diels-Alder Adduct of Octatetraene. The maleic anhydride diadduct of octatetraene (0.92 g) in glacial acetic acid was hydrogenated quantitatively over a 5% palladium-charcoal catalyst at room temperature and atmospheric pressure. The theoretical volume of hydrogen for

two double bonds was absorbed in thirty minutes. The product was heated on a hot plate and filtered from the catalyst. After recrystallization several times from acetone-water mixtures, the white solid melted at 260-261 C. Analysis: Calculated for $C_{16}H_{18}O_6.2H_2O$: C, 56.13; H, 6.47. Found: C, 56.24, 56.34; H, 6.58, 6.67.

Attempts to Dehydrogenate the Maleic Anhydride Adduct of Octatetraene.

a) Two grams of the maleic anhydride diadduct of Octatetraene was intimately mixed with 1 g of 5% palladium-charcoal catalyst and the mixture was refluxed for six hours in boiling p-cymene.[59-62] The hot solution was then filtered from the catalyst and the p-cymene filtrate was then distilled under reduced pressure; no product was obtained from the filtrate.

The catalyst residue was then refluxed with acetone and filtered while hot. On concentrating the acetone filtrate, a white crystalline substance was obtained. After several recrystallizations from glacial acetic acid, the substance, which proved to be an isomer of the Diels-Alder Adduct of Octatetraene, melted at 267-8 C. This compound was also capable of being recrystallized from acetone or xylene and in each case a melting point of 267-8 C was observed. Analysis: Calculated for $C_{16}H_{14}O_6$: C, 63.57; H, 4.67. Found: C, 63.37; H, 4.76.

b) One gram of the maleic anhydride diadduct of octatetraene was mixed thoroughly with 0.25 g of sulphur.[58] The mixture

was heated with a small open flame until a vigorous reaction ensued. A black gummy mass was obtained from this reaction and it was not possible to purify this mass by vacuum sublimation. The mixture was then crystallized from acetic acid-acetone, but sulfur was the only product which could be isolated.

c) A half gram of the maleic anhydride diadduct of octatetraene was mixed thoroughly with 0.2 g of platinum oxide. This mixture was then heated cautiously in a sand bath. When the temperature of the sand bath rose to about 225-240°C a rapid reaction set in and the reaction mixture exploded.

d) Chloranil was prepared according to the method of Gallott[67] in 96% yields.

One gram of the tetracarboxylic acid of the maleic anhydride diadduct of octatetraene and 3.6 g of chloranil was refluxed in xylene for four hours.[63,64] The solid which appeared in reaction mixture was filtered and washed with ether. It was then crystallized from a acetone-xylene mixture and after several treatments with charcoal, a white crystalline solid melting at 247-250°C was obtained. Analysis: Calculated for $C_{16}H_{18}O_8$: C, 56.80; H, 5.36. Found: C, 56.45; H, 5.41.

Ultra-violet Absorption Spectrum of 1,3,5,7-Octatetraene. Purified cyclohexane which transmitted down to 216 mu was used as the solvent. Quartz cells, 1.000 cm thick, were used in a Beckman quartz spectrophotometer. It was not possible to run a quantitative absorption spectrum, since the octatetraene, being such a strong absorber, would necessarily

have to be in very dilute solutions, and if weighed in air, pure octatetraene would probably be contaminated with oxidized and polymerized products. Therefore, the curve plotted in Figure 7 is a qualitative plot of wave length versus optical density (log I'/I)

λ(mu)	% Transmission	Optical Density	λ(mu)	% Transmission	Optical Density
260	93.8	.028	290	55.9	.253
262	91.8	.043	291	57.5	.240
264	88.4	.054	292	59.4	.226
266	86.2	.064	294	66.2	.178
268	84.5	.073	296	76.0	.119
269	85.2	.069	297	80.1	.096
270	85.2	.069	298	80.8	.093
271	86.1	.064	299	80.1	.096
272	84.8	.072	300	76.0	.119
274	80.2	.096	302	63.9	.195
276	74.2	.129	303	60.8	.216
277	72.4	.140	304	56.5	.248
278	69.9	.155	305	60.0	.220
279	71.0	.148	306	61.9	.208
280	71.0	.148	308	75.8	.120
282	75.4	.122	310	87.9	.056
284	77.2	.112	312	94.0	.026
286	74.0	.126	314	96.9	.014
288	63.8	.196	316	98.0	.008
289	60.4	.219	318	99.0	.005
			320	99.3	.003
			322	100	0

Infra-red Absorption Spectrum of Octatetraene. The infra-red absorption spectra of 1,3,5,7-octatetraene was kindly done by Dr. Donald C. Smith of the Naval Research Laboratories.

Since we were more interested in getting a curve for the pure octatetraene than getting absorption coefficients of an impure sample, no attempt was made to weigh out the octatetraene. The octatetraene was recrystallized five times from petroleum-ether (20-40) in an atmosphere of nitrogen. It was then put into 10 ml each of purified carbon disulfide

and carbon tetrachloride. The rock salt absorption cells, which were used, were 0.169 mm and 0.728 mm thick.

Figure 9 is a plot of percent transmission versus wave length in microns or in cm^{-1}.

The positions of the absorption maxima are given below:

λ, Microns	λ, Microns	λ, Microns
2.15	3.53	7.8
2.24	4.11	8.1
2.33	4.48	8.75
2.48	5.01	9.9
2.9	5.34	10.4
3.25	5.53	11.15
3.29	5.65	11.9
3.32	6.1	15.95
3.36	6.4	17.7
3.48	7.1	

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ABSTRACT

Louis H. Schwartzman, Doctor of Philosophy, 1949.

B.A. The Johns Hopkins University

Title of Thesis: "A Synthesis of Conjugated Polyenes; 1,3,5-hexatriene and 1,3,5,7-Octatetraene."

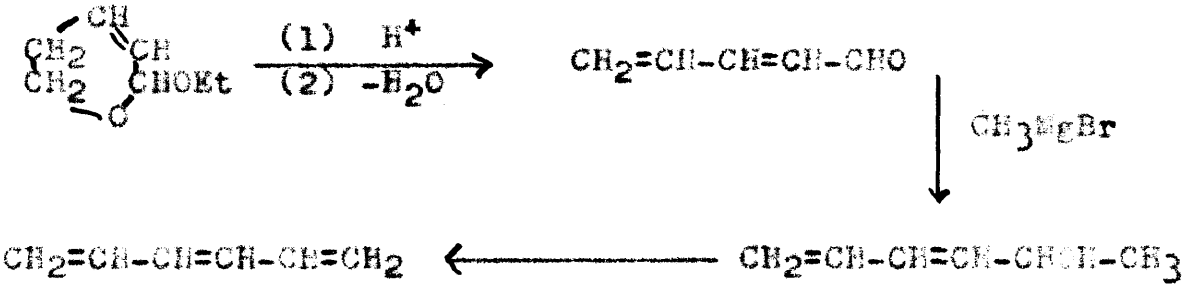
Thesis directed by Dr. G. Forrest Woods

Pages in thesis 105 Words in abstract: 208

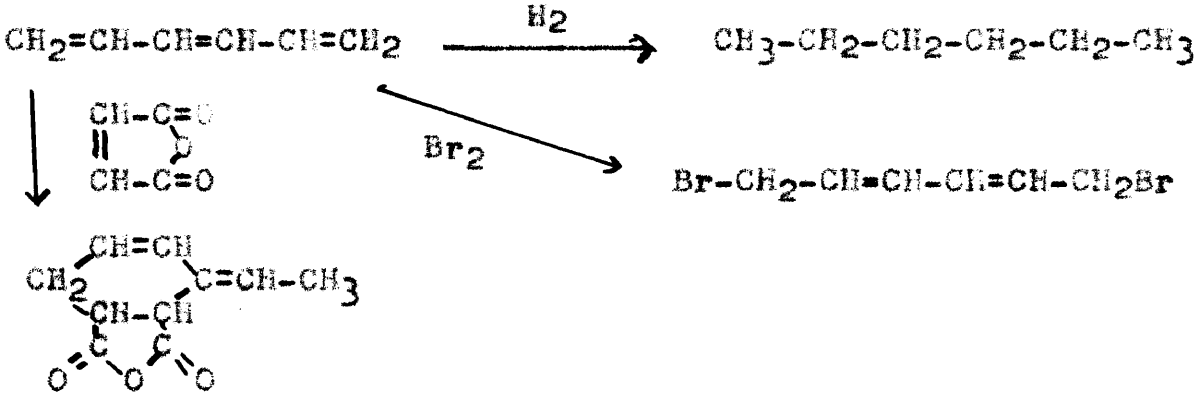
Major: Organic Chemistry

Minors: Physical Chemistry and Inorganic Chemistry

1,3,5-Hexatriene was prepared in good yields. 2-Ethoxy-Δ^3-dihydropyrane was hydrolyzed and dehydrated to produce 2,4-pentadienal. Methylmagnesium bromide reacted normally with 2,4-pentadienal to yield 1,3-hexadien-5-ol in excellent yields. This latter substance was identified and hydrogenated to hexanol-2, and then oxidized to hexanone-2. Catalytic dehydration of 1,3-hexadien-5-ol in a nitrogen atmosphere at reduced pressures produced good yields of 1,3,5-hexatriene. Purification afforded a sharp melting, pure isomer for which no geometrical configuration has been assigned.



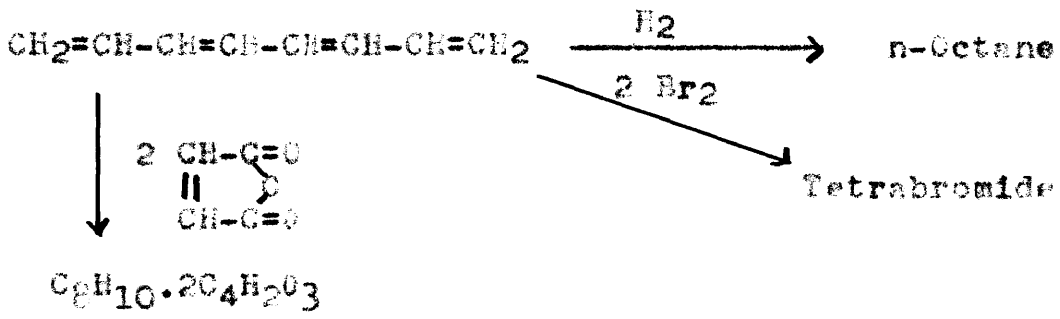
Chemically, the hexatriene was identified by reactions with bromine, hydrogen, and maleic anhydride.



Physical measurements such as freezing point, heat of vaporization, surface tension, dipole moment, ultraviolet absorption spectrum, and infra-red absorption spectrum were determined on 1,3,5-hexatriene.

1,3,5,7-Octatetraene was synthesized by a method similar to that for hexatriene. Allylmagnesium bromide reacted normally 2,4-pentadienal to produce 1,3,7-octatrien-5-ol in excellent yields. 1,3,7-Octatrien-5-ol was identified by reduction to the known octanol-4 and then oxidation to the known octanone-4 and identification of the derivatives thereof. Catalytic dehydration of octatrienol in a nitrogen atmosphere at reduced pressures produced 1,3,5,7-octatetraene. Purification was accomplished by recrystallization of the highly reactive solid octatetraene from petroleum-ether.

Reactions of octatetraene with bromine, hydrogen, and maleic anhydride amply identified the product.



Ultra-violet and infra-red absorption spectra were obtained on purified octatetraene in cyclohexane and carbon disulphide respectively.

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