column; evaporation of solvent at reduced pressure gave 3.7 g. (34%) of colorless prisms, m.p. 264–267°. Recrystallization from hexane gave a constant melting point of 266–267.5° (lit.,[5] m.p., 267–268°).

Anal. Calcd. for $C_{32}H_{24}$: C, 94.08; H, 5.92. Found: C, 94.22, 93.97; H, 5.97, 6.02.

The dark, resinous, ethanol-insoluble material (approximately 7.5 g.) could not be crystallized from common solvents and was only slightly soluble in dimethylformamide and dimethyl sulfoxide. Its infrared spectrum (Nujol mull) was extremely simple, showing bands characteristics of *o*-disubstituted benzene (746), olefin (1624), and both *cis*- and *trans*-1,2-disubstituted olefins (685, 1305, and 968 cm.$^{-1}$).[13,15] Oxidation of a 1.1-g. sample of the resin with excess potassium permanganate led to the formation of phthalic acid (1.4 g.).

Reduction of I.—A solution of 1.0 g. of I in dimethylformamide was hydrogenated over palladium. After the catalyst was removed by filtration, the colorless product was isolated by precipitation with water. Repeated recrystallization from benzene gave 0.72 g. of 1,2,5,6,9,10,13,14-tetrabenzocyclohexadeca-1,5,9,13-tetraene (VI), m.p. 204–205° (lit.[5] m.p. 205°). This material was identical in all respects (mixture melting point, ultraviolet and infrared spectra) to an authentic sample of VI.

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Synthesis of 1,3,5-Hexatriene

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A new and convenient synthesis of 1,3,5-hexatriene is described.

1,3,5-Hexatriene (I) has been previously synthesized *via* the pyrolysis of the diformate ester of 1,5-hexadien-3,4-diol,[4] condensation of allyl chloride with sodamide,[5] dehydration of 1,5-hexadien-3-ol with phthalic anhydride,[6] debromination of 3,4-dibromo-1,5-hexadiene,[7] and the vapor phase dehydration of 1,3-hexadien-5-ol[8,9] and 2,4-hexadien-1-ol.[10] Kiun-Houo[11] attempted to synthesize I by vapor phase dehydration of 1,5-hexadien-3-ol but obtained only resins. Prevost and Bidon[12] dehydrated 1,4-hexadien-3-ol in an attempt to synthesize I but obtained 1,3-cyclohexadiene. In most cases the yields were low and the purity questionable. In other cases the sample was purified[4,8] but no spectroscopically pure material was isolated.

Recently, Hwa, de Benneville, and Sims[13] prepared I by the quaternization of isomeric bromohexadienes followed by Hofmann elimination. This work gave two hydrocarbon fractions which were identified as *cis* and *trans* isomers of I. This was the first authentic sample of the *cis* isomer of I to be isolated.

We have synthesized I from easily available starting materials, *via* a four-step reaction, involving the synthesis of 4-hexen-1-yn-3-ol (II) from sodium acetylide and crotonaldehyde. Reduction of the en-yn-ol to the corresponding 1,4-hexadien-3-ol (III) and vapor phase dehydration over alumina gave I in an over-all yield of *ca.* 60%, *i.e.*

$$\mathrm{Na{-}C{\equiv}CH + CH_3{-}CH{=}CH{-}CHO \xrightarrow[-80^\circ]{NH_3} CH_3{-}CH{=}CH{-}CHONa{-}C{\equiv}CH} \qquad (1)$$

$$\mathrm{CH_3{-}CH{=}CH{-}CHONa{-}C{\equiv}CH + NH_4Cl \longrightarrow \underset{(II)}{CH_3{-}CH{=}CH{-}CHOH{-}C{\equiv}CH} + NaCl + NH_3} \qquad (2)$$

$$\mathrm{CH_3{-}CH{=}CH{-}CHOH{-}C{\equiv}CH + H_2 \xrightarrow{Pd} \underset{(III)}{CH_3{-}CH{=}CH{-}CHOH{-}CH{=}CH_2}} \qquad (3)$$

$$\mathrm{CH_3{-}CH{=}CH{-}CHOH{-}CH{=}CH_2 \xrightarrow[300^\circ]{alumina} \underset{(I)}{CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2} + H_2O} \qquad (4)$$

Compound I was purified by crystallization from methanol. It had a freezing temperature of −8.46°. The calculated purity was 98.8% based upon an estimated freezing temperature for pure I of −8.06° (method of Taylor and Rossini[14]). A cryoscopic constant of 2.9 mole per cent/degree and cyclohexene as an impurity were used in obtaining this

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estimated freezing temperature. Mass spectrometry and gas chromatography indicated a purity of at least 99%. The molar extinction coefficient (ϵ) of our product in the ultraviolet region was 34,000 at 247 mμ, 48,000 at 256 mμ, and 40,600 at 267 mμ. The infrared spectrum was identical to that reported by Woods and Schwartzman for a product that Lippincott, White, and Sibilia[15] later concluded to be *trans* isomer of I. This conclusion is also in agreement with the work of Hwa, de Benneville, and Sims.[13] The available evidence indicates that our product is the *trans* isomer of I.

It is probable that dehydration of any of the isomeric hexadienols would give I. There are six isomers of a hexadienol and of these, three have previously been dehydrated to I.[6,8–11] Dehydration of one of these, 2,4-hexadien-1-ol, must have involved a rearrangement to give the final product. A rearrangement also occurs in the dehydration of the isomers 1,4-hexadien-3-ol and 2,5-hexadien-1-ol, which we dehydrated to I.

The first step in the dehydration of the hexadienols to I is postulated to be the irreversible formation of a carbonium ion. The final results can then be explained by assuming the rearrangement of the carbonium ion to the same intermediate in the dehydration of all the isomeric hexadienols. Elimination of a proton would give I.

When the dehydration of III was carried out at such a rate that only 50–70% of the hexadienol was dehydrated, none of the other isomeric hexadienols could be detected in the unchanged product. This was considered to be evidence for the irreversible formation of a carbonium ion intermediate.

The preparation of II from crotonaldehyde has been previously reported[16–18] in yields ranging from 46 to 75% and under varying conditions. In this research, we have investigated the effect of the following variables: temperature, concentration, time of reaction, purity of reagents, method of formation of the sodium acetylide, speed of stirring, the rate of addition of the reagents, and the effect of light on the reactions. Our yields ranged from 55 to 77% depending on the conditions. It was established that reaction temperature and the purity of the reagents had the greatest effect. The effect of the other variables was either low or undeterminable. Our best yields (72–77%) were obtained at −80°, with a concentration of 2.5 moles of sodium acetylide per liter of liquid ammonia, where the equipment was thoroughly dry and the reagents were highly purified. Traces of water had a marked effect on lowering the yield. The reaction rate was quite fast, the reaction being essentially complete in a few minutes. When lithium acetylide was substituted for sodium acetylide, yields were moderately increased.

The selective reduction of II to III was previously reported by Heilbron.[19] The yield was given as 90%, but purity was not stated.

Considerable effort was spent by us in obtaining a catalyst which was 99+% selective for this reduction. It was found that platinum was completely unselective, 5% palladium-on-carbon was 92% selective, 5% palladium-on-calcium carbonate was 96–98% selective, and a 5% palladium-on-calcium carbonate poisoned with 40% by weight of lead acetate was 99+% selective.

The vapor phase dehydration of III to I was accomplished in 90% yields. Some of the variables studied were temperature, contact time, catalyst composition, catalyst surface area, and pressure. All of these variables influence the yield and purity of the I. The best conditions for the dehydration over an alumina catalyst were 300–325°, with a contact time of 0.2 second at 30-mm. pressure. Increasing the temperature, decreased the yield of I, and increased the yield of 1,3-cyclohexadiene. Dehydration of II over an 87% silica–13% alumina catalyst gave a lower yield of I than was obtainable with alumina. It was noted that the higher the surface area of the catalyst, the lower the temperature and the shorter the contact time required for optimum yields of 1,3,5-hexatriene.

Analysis of the crude I by gas chromatography and by mass spectrometry indicated that the major impurities were 1,3-cyclohexadiene and benzene.

Experimental

4-Hexen-1-yn-3-ol (II).—Liquid ammonia (500 ml.) was collected in a 1-l., four-neck, round-bottom flask, equipped with a dropping funnel and Dry Ice–cooled condenser. The flask was cooled to −80° and sodium (23 g., 1.0 g.-atom) was added concurrently with a stream of acetylene at such a rate that the characteristic blue color did not form. The acetylene was purified by passing it through Dry Ice–cooled traps, sulfuric acid, Drierite, and activated carbon towers before use. Crotonaldehyde (70 g., 1.0 mole) was added over a 1-hr. period, the reaction mixture was stirred at −80° for 4 hr., and decomposed by the slow addition of ammonium chloride (58 g., 1.1 moles). The openings in the reaction flask were covered with sheets of cellophane held with rubber bands. The ammonia was allowed to evaporate at room temperature. The solid residue was filtered from the liquid product. This solid material was washed with ethyl ether (3 × 250 ml.) and the organic liquids combined and distilled to yield II (76 g., 79%), b.p. 77–79°/30 mm., $n^{25}\text{D}$ 1.4630.

Anal. Calcd. for C_6H_8O: hydrogen no., 3.0. Found: hydrogen no., 2.99, 3.03.

The reported physical constants[18] are b.p. 74–75°/30 mm., $n^{21}\text{D}$ 1.4645.

When the reaction temperature was increased to −35° from −80°, the yield of II decreased from 76% to 55%. The addition of 0.5% water to the crotonaldehyde lowered the yield of product to 62%. Substitution of lithium acetylide for the sodium acetylide increased average yields by 5%.

1,4-Hexadien-3-ol (III).—II (96 g., 1.0 mole was reduced in an autoclave with hydrogen at 25 p.s.i.g. and 20° using 2 g. of catalyst which was 5% palladium-on-calcium carbon-

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ate poisoned with 40% by weight of lead acetate.[20] The temperature was controlled by means of a cooling coil. After the theoretical amount of hydrogen was absorbed, the reaction mixture was filtered and distilled through a Todd column at a 10:1 reflux ratio to yield III (92 g., 94%), b.p. 70–71°/40 mm., n^{25}D 1.4512. Heilbron[19] reported b.p. 86–87°/100 mm., n^{19}D 1.4052.

Anal. Calcd. for $C_8H_{10}O$: hydrogen no., 2.0. Found: hydrogen no., 1.99, 2.00.

1,3,5-Hexatriene (I).—A Pyrex tube (29 mm. i.d.) was packed with alumina for a length of 10 in. (Harshaw Chemical Co. 0104T—surface area, 80 sq. m./g.). A preheat zone of 6 in. of glass beads was used and a thermocouple well (4 mm. o.d.) was placed in the center of the tube before the catalyst was added. The exit line from the system was through a Dry Ice–cooled trap to a vacuum pump which was set to maintain a pressure of 30 mm. The catalyst was dried at 400° before use by passing a stream of nitrogen through the system. III (98 g., 1.0 mole) was distilled into the evacuated system over a period of 1 hr. The temperature in the catalyst zone was maintained at 300–315°. The products condensed in the Dry Ice–cooled trap were melted, the water separated and the organic layer distilled at 30 mm. and 0°. Only I (92–95% pure) distilled and the unchanged hexadienol remained in the distillation pot. The yield of I was 75% per pass and was 90–95% ultimate.

Crude I was recrystallized four times from methanol at −80°, washed with water, dried over magnesium sulfate, and flash distilled at 30 mm. into a Dry Ice–cooled trap, to give a product with a freezing temperature of −8.46°.

At a dehydration temperature of 350° over alumina at 30 mm. pressure, the yield of I was 70%, 50% at 400°, and 37% at 425°. Varying the contact time from 0.2 sec. to 1.5 sec. at 300° and 75 mm. pressure had essentially no effect on yield of product. Dehydration at reduced pressure gave a higher purity crude product than dehydration at atmospheric pressure. Comparable purities of the crude were 90% at 30 mm. pressure and 60% at 750 mm. pressure. Comparison of a silica–alumina catalyst (Davison Chemical—87% silica + 13% alumina) with an alumina catalyst indicated a preference for alumina. The silica–alumina gave a low purity crude product, 26% to 72%, whereas a crude of 90% purity was obtained with an alumina catalyst under optimum conditions.

Alternate Preparation of I. Dehydration of 2,5-Hexadien-1-ol.—The intermediate 5-hexen-2-yn-1-ol was prepared from propargyl alcohol and allyl chloride by the method of Kurtz[21]; yield 47%, b.p. 71–77°/11 mm., n^{22}D 1.4770.

Anal. Calcd. for C_6H_8O: hydrogen no., 3.0. Found: hydrogen no., 2.94.

5-Hexen-2-yn-1-ol (165 g., 1.72 moles) was hydrogenated at room temperature over a catalyst consisting of 5% palladium-on-calcium carbonate poisoned with 40% by weight of lead acetate.[20] Before hydrogenation, it was necessary to treat the 5-hexen-3-yn-1-ol with sponge nickel (2 g.) at room temperature to remove an impurity which markedly slowed hydrogenation. The hydrogenate was filtered and distilled to yield 2,5-hexadien-1-ol (157 g., 93%), b.p. 76–78°/25 mm., n^{22}D 1.4615 and a residue (10 g.).

Anal. Calcd. for $C_6H_{10}O$: hydrogen no., 2.0. Found: hydrogen no., 1.98, 2.0.

The 2,5-hexadien-1-ol was dehydrated to I over alumina in a manner similar to that which we have described for dehydration of III. The yield of crude I from 98 g. (1.0 mole) of 2,5-hexadien-1-ol was 45.5 g. Recycling of unchanged hexadienol gave an ultimate yield of 69% of a product which had purity of 80 mole %.

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Carbonyl and Thiocarbonyl Compounds. VII.[1a] A New Method for the Direct Synthesis of Ethylene Sulfides

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The ethylene sulfides, epithiotetraphenylethane, II, epithiobidiphenyleneethane, III, dispiro(xanthene-9,2′-thiirane-3′,9″-xanthene), IVa, and dispiro(thioxanthene-9,2′-thiirane-3′,9″-thioxanthene), IVb, are directly synthesized, in excellent yields, by the reaction of elemental sulfur with the corresponding diazoalkanes. A reaction mechanism, based on the formation of a biradical, is suggested. The reaction of 9-diazoxanthene with thioketones and of thiofluorenone with diazoalkanes is described.

The successful application of ethylene sulfides in industry and biology directed the attention of various investigators to study the chemistry of this group of compounds. Various aromatic and heterocyclic ethylene sulfides are now usually prepared by the reaction of diazoalkanes with thioketones[2] according to scheme A. However, the instability of some of these thioketones, such as thiofluorenone, and the difficulty of their preparation, limits the general usefulness of this method.

In the present investigation, the authors have found that symmetrical ethylene sulfides of the general formula I can be directly produced by the

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