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Acetylene Polymers and their Derivatives. XIII. The Action of Chlorine on Divinylacetylene

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Scarcely any information has been recorded concerning the behavior of multiply conjugated enyne systems in reactions of addition. A system of this kind is found in divinylacetylene, which has been made available through discoveries described in the first paper of this series.[1] In its reaction with thio-*p*-cresol only the ethylenic bonds of divinylacetylene are involved.[2] Chlorine behaves in a different manner. Reaction proceeds very rapidly, and a point of apparent saturation is reached when six atoms of chlorine have been absorbed. The product then consists of a crystalline, volatile hexachloride ($C_6H_6Cl_6$), and a pale yellow, very viscous sirup which also has the composition $C_6H_6Cl_6$. The sirup is not volatile and it has a higher molecular weight than that required by the simple formula. The crystalline hexachloride resists chlorination, ozonization and oxidation by hot nitric acid; and the action of alkaline permanganate leads to total destruction. Nevertheless, there can be no doubt that its structure is correctly represented by the formula hexachloro-1,2,3,4,5,6-hexene-3 (IV), and a study of the di- and tetrachlorides throws some light on the mechanism by which it is formed.

The di- and the tetrachlorides are both liquids, and they are not easily obtained in good yields since the application of as little as one mole of chlorine converts part of the reacting divinylacetylene to the hexachlorides. It appears on the other hand that only one dichloride and one tetrachloride are produced: the same tetrachloride is obtained by the chlorination of either divinylacetylene or its dichloride; and chlorination of the tetrachloride yields the hexachloride (IV) already referred to.

The dichloride still contains an open straight chain of six carbon atoms, since it can be hydrogenated to *n*-hexane. Oxidation with permanganate yields as the only identifiable product, chloroacetic acid; hence one of the chlorines is contained in the grouping $ClCH_2C{=}$ and there is no terminal CH_3 group. The other chlorine is attached to a doubly bonded carbon, since the action of boiling aqueous sodium carbonate liberates only one chloride ion per molecule of the compound. The only reasonable structure for the dichloride consistent with these facts is dichloro-1,4-hexatriene-2,3,5 (II).

I. $CH_2{=}CH{-}C{\equiv}C{-}CH{=}CH_2$
II. $ClCH_2{-}CH{=}C{=}CCl{-}CH{=}CH_2$
III. $ClCH_2{-}CH{=}CCl{-}CCl{=}CH{-}CH_2Cl$
IV. $ClCH_2{-}CHCl{-}CCl{=}CCl{-}CHCl{-}CH_2Cl$

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(1) Nieuwland, Calcott, Downing and Carter, THIS JOURNAL, **53**, 4197 (1931).

(2) Carothers, *ibid.*, **55**, 2008 (1933).

IIa. $ClCH_2—CHCl—C\equiv C—CH=CH_2$
IIb. $ClCH_2CH=C=C=CH—CH_2Cl$
IIIa. $ClCH_2—CH=C=CCl—CHCl—CH_2Cl$
IIIb. $ClCH_2—CH=CCl—CCl_2—CH=CH_2$
IVa. $ClCH_2—CHCl—CCl_2—CCl=CH—CH_2Cl$

V. $CH_2=CH—CCl=CCl—CH=CH_2$
VI. $CH_2=CH—CCl=C=C=CH_2$
VII. $ClCH_2—CH=CH—CCl_2—CH=CH_2$
VIII. $CH_2=C=CCl—CCl=CH—CH_2Cl$
IX. $CH_2=C=CCl—CCl=C=CH_2$

The tetrachloride of divinylacetylene when oxidized with potassium permanganate also yields as the only identifiable product chloroacetic acid, and hydrolysis with aqueous sodium carbonate shows that two of the chlorine atoms are reactive and the other two inactive. This behavior indicates that it has the structure tetrachloro-1,3,4,6-hexadiene-2,4 (III).

Formally, the relation between the three chlorides and the parent hydrocarbon is that each member of the series is derived from the preceding one by a process of 1,4 addition. It is impossible to demonstrate conclusively that they actually originate by this mechanism. Addition either 1,2 or 1,6 followed by an α,γ shift would lead to the same result. The dichloride (II) might arise thus from IIa or IIb, the tetrachloride from IIIa or IIIb and the hexachloride from IVa.

However, this dual mechanism appears highly improbable since it provides no visible reason for the fact that the observed products are without exception compounds that would result from their precursors by a process of 1,4 addition. There are moreover other independent facts to indicate that 1,4 addition may be a favorite mode of reaction for enyne compounds. Thus the action of hydrogen chloride on vinylacetylene yields chloro-4-butadiene-1,2, $CH_2=C=CH—CH_2Cl$,[3] and this must be a primary product since in the rearranged halide, $CH_2=CCl—CH=CH_2$, the chlorine is attached to a doubly bonded carbon where its mobility is lost. It is perhaps significant in this connection also that the dichloride (II) of divinylacetylene shows no tendency to rearrange into the completely conjugated triene (V) under experimental conditions that might be expected to favor especially such a transformation.

When the dichloride (II) is treated with alcoholic potash it rapidly loses one molecule of hydrogen chloride. The terminal chlorine and its adjacent hydrogen are involved in this reaction, and the product has the structure chloro-3-hexatetraene-1,3,4,5 (VI). When hydrogenated it is converted into *n*-hexane, and oxidation yields oxalic acid.

In the presence of cuprous chloride the dichloride (II) absorbs one molecule of hydrogen chloride from aqueous hydrochloric acid. In the

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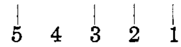
(3) Carothers, Berchet, and Collins, THIS JOURNAL, **54**, 4066 (1932).

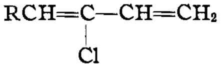
resulting trichloro compound all three of the chlorines are reactive toward aqueous sodium carbonate. It is therefore the central double bond bearing the inactive chlorine atom of the dichloride which disappears, and the trichloro compound must have the structure trichloro-1,4,4-hexadiene-2,5 (VII). When oxidized it yields chloroacetic acid.

The tetrachloride (III) of divinylacetylene also loses hydrogen chloride when treated with alcoholic potash and yields a trichloro and a dichloro compound. In this case only two positions are available for the loss of hydrogen chloride, namely, the 1,2 and 5,6. The trichloro compound must therefore be trichloro-1,3,4-hexatriene-2,4,5 (VIII) and the dichloro compound must be dichloro-3,4-hexatetraene-1,2,4,5 (IX).

The chloro compounds described above furnish several novel and unusual examples of triad systems potentially capable of allylic rearrangement. One rather striking anomaly that appears in this connection has already been referred to. In the dichloride, II, the terminal chlorine atom shows no tendency to undergo a shift to the γ position, in spite of the fact that such a shift would result in a completely conjugated triene. It is true that the γ carbon is at the center of a pair of twinned double bonds, but this in itself cannot be responsible for the absence of a tendency to rearrange since precisely the same configuration is found in chloro-4-butadiene-1,2, $CH_2=C=CH-CH_2Cl$, which undergoes the α,γ transposition with great facility. In the trichloro hexadiene, VII, also, a triad shift of one of the central chlorines would bring the double bonds into the conjugated configuration. No special attempts have been made to bring about rearrangement in this case, but it has not been observed to occur spontaneously. The absence of spontaneous rearrangements in the compounds III and VIII is not surprising, since a shift of the mobile chlorine atom in these compounds would destroy the conjugation of the double bonds.

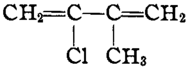
Four of the chloro compounds described above (II, VI, VIII and IX) exhibit a structural feature that has, so far as we are aware, not been exemplified in any compounds described hitherto. They contain a pair of conjugated double bonds and at least one of the pair is the first member of a series of two or more contiguous double bonds, thus,  $-\underset{\underset{5}{|}}{C}=\underset{4}{C}=\underset{\underset{3}{|}}{C}-\underset{\underset{2}{|}}{C}=\underset{\underset{1}{|}}{C}-$. The question arises, can the carbon atom bearing the twinned double bonds function as one of the ends of the conjugated system? The behavior of the dichloride II toward chlorine provides an affirmative answer to this question. The chlorine here almost certainly adds 1,4 to produce the tetrachloride, III. On the other hand, the addition of hydrogen chloride to the dichloride apparently involves only the 3 and 4 positions. The trichloro compound obtained (VII) is the compound that would be produced by 3,4 addition, and it is not likely that it arises by 1,4 addition followed by an allylic transposition, because the product, $ClCH_2-CH=CH-CCl=CH-CH_2Cl$, which would be formed by 1,4 addition, is precisely analogous to dichloro-1,3-butene-2, $CH_3-CCl=CH-CH_2Cl$, and deliberate attempts to rearrange this compound have given negative results.[4]

With two exceptions (IV and VII) all of the above described chloro compounds contain at least one pair of conjugated double bonds. Nevertheless, none of them reacts either with naphthoquinone or with maleic anhydride at 100°. This failure cannot be ascribed to the fact that in several cases the conjugated system terminates in a series of contiguous double bonds, since, as has already been pointed out above, this arrangement does not preclude 1,4 addition; moreover, this arrangement is not present in the tetrachloride III which also fails to react. Similar failures have been reported before. Thus, X, XI and XII all react very smoothly with naphthoquinone[5] but XIII and XIV do not.[6] It is evident that the diene reaction can be regarded as diagnostic only if it leads to positive results; comparatively trivial substitutions sometimes cause it to fail.



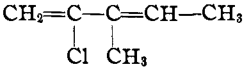
$RCH{=}\underset{Cl}{C}{-}CH{=}CH_2$

(R = H, CH_3, C_2H_5, C_4H_9, or C_7H_{15})
(X)



$CH_2{=}\underset{Cl}{C}{-}\underset{CH_3}{C}{=}CH_2$

(XI)

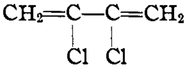


$CH_2{=}\underset{Cl}{C}{-}\underset{CH_3}{C}{=}CH{-}CH_3$

(XII)

$ClCH=CH-CH=CH_2$

(XIII)



$CH_2{=}\underset{Cl}{C}{-}\underset{Cl}{C}{=}CH_2$

(XIV)

Substitution similarly has a profound influence on the tendency of dienes to polymerize. Of the above described chloro compounds only the dichlorotetraene (IX) shows any great tendency to polymerize spontaneously. In the course of twenty-four hours at the ordinary conditions it was converted into a dark brown, hard, brittle resin. The dichloride II polymerized very slowly on standing, and after three months it was a viscous sirup. The polymerization was greatly accelerated by increased pressure. At 6000 atmospheres and 25° it was changed in twenty-three hours to a yellow, elastic, plastic mass. The chloro-3-hexatetraene-1,3,4,5 at 6000 atmospheres and 25° was changed in twenty hours to a hard coke-like mass. Pressure was not applied to the other compounds, but none of them showed any signs of polymerizing when allowed to stand for several weeks. We are indebted to Dr. H. W. Starkweather for the experiments at high pressure.

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[4] Unpublished results.

[5] Carothers and Coffman, THIS JOURNAL, **54**, 4071 (1932); Jacobson and Carothers, *ibid.*, **55**, 1624 (1933).

[6] Carothers and Berchet, *ibid.*, **55**, 2004 (1933).

Experimental Part

Preparation and Proof of Structure of Dichloro-1,4-hexatriene-2,3,5 (II)

Preparation of Dichloro-1,4-hexatriene-2,3,5 by Chlorination of Divinylacetylene.—Chlorine was passed into a solution of 400 g. (5 moles) of divinylacetylene in 300 g. of dry carbon tetrachloride at −50°. During five hours, 436 g. (6.1 moles) of chlorine was absorbed. Fractionation of the reaction product gave 191 g. (1.28 moles) of dichloro-1,4-hexatriene-2,3,5 boiling at 45–50° (3 mm.) (25% of the theoretical amount). Continued distillation of the residue yielded 57 g. of higher boiling material (b. p. 50–115° (3 mm.)) which was a mixture of the tetrachloro and hexachloro derivatives. The remainder consisted of undistillable material.

A chlorination similar to that described above was carried out by allowing only 332 g. (4.67 moles) of chlorine to be absorbed during five hours at −50°. There was obtained 145 g. (0.97 mole) of the dichloro derivative (19% of the theoretical amount) and 61 g. of tetrachloro-1,3,4,6-hexadiene-2,4. Chlorination of divinylacetylene at 0° (mole for mole) in carbon tetrachloride gave the dichloride in 20% yield.

The properties of dichloro-1,4-hexatriene-2,3,5 are: colorless mobile liquid with a sharp characteristic odor; b. p. 38° at 1 mm., 45–46° at 3 mm.; d_4^{20} 1.1807; n_D^{20} 1.5195; M_R calcd. 38.24; M_R found, 38.34. On standing it very slowly polymerized, and after three months it had changed to a viscous sirup.

The same compound was obtained in very small yield by the action of aqueous hypochlorous acid on divinylacetylene.

Anal. Calcd. for $C_6H_6Cl_2$: C, 48.35; H, 4.03; Cl, 47.62; mol. wt., 149. Found: C, 47.88; H, 4.00; Cl, 47.59; mol. wt. 155.

Reduction of Dichloro-1,4-hexatriene-2,3,5- to *n*-Hexane.—The dichloro compound (25 g., 0.168 mole) in 50 cc. of ethyl acetate (with 0.16 g. PtO_2) absorbed 0.484 mole of hydrogen during three hours (calcd. 0.672 moles). A large amount of hydrogen chloride was formed during the reduction. The filtered ethyl acetate solution was fractionated, and the fraction boiling at 50–75° was collected and allowed to stand over aqueous alkali until saponification of the ester was complete. The water insoluble layer was then separated and further dried over solid alkali. There was obtained 8 g. of *n*-hexane, b. p. 69–70°; d_4^{20} 0.677; n_D^{20} 1.3812. There was also obtained 15 g. of higher boiling material (b. p. range 30–80° at 21 mm.) from which no constant boiling fraction was received.

The Reactivity of the Halogens in Dichloro-1,4-hexatriene-2,3,5. Hydrolysis by Sodium Carbonate.—The dichloro compound (50 g., 0.333 mole) was refluxed with agitation during eight hours with 300 cc. of water containing 72 g. (0.67 mole) of sodium carbonate. Analysis of the aqueous solution showed that 0.281 mole of sodium chloride was formed. Hence only one active halogen atom is present in $C_6H_6Cl_2$. The hydrolysis product was a soft, sticky resin.

Permanganate Oxidation of Dichloro-1,4-hexatriene-2,3,5 to Chloroacetic Acid.—The dichloro compound 50 g. (0.33 mole) completely reduced 300 g. of potassium permanganate added with agitation in small portions to the aqueous solution (200 cc.) during three hours at 35–40°. Sulfur dioxide was passed into the reaction mixture; the manganese dioxide was filtered, and repeatedly washed. Continuous ether extraction of the strongly acidified aqueous solution gave 15 g. of acidic material, which was identified as chloroacetic acid, b. p. 61 to 63° at 2 mm.; m. p. 58–59°.

To complete the identification the chloroacetic acid was converted, through its chloride, into phenylglycocoll anilide, which showed the correct melting point and mixed melting point.

Chlorination of Dichloro-1,4-hexatriene-2,3,5 to Tetrachloro-1,3,4,6-hexadiene-2,4.—Chlorine was passed into 100 g. (0.67 mole) of $C_6H_6Cl_2$ in 54 g. of carbon tetrachloride at 5 to 10° until 42 g. (1.18 moles) of chlorine was absorbed. Fractionation of the product gave 10 g. of tetrachloro-1,3,4,6-hexadiene-2,4; b. p. 85 to 92° at 3 mm.; d_4^{20} 1.4902; n_D^{20} 1.5458. Part of the original dichloro compound (21 g.) was recovered. The remainder of the product consisted of higher boiling residue. The tetrachloro derivative is further described below.

Preparation and Proof of Structure of Chloro-3-hexatetraene-1,3,4,5 (VI)

Chloro-3-hexatetraene-1,3,4,5 Obtained by the Action of Alcoholic Alkali on Dichloro-1,4-hexatriene-2,3,5.—The dichloro compound (105 g., 0.67 mole) freshly distilled was added during one and one-half hours to a solution of 43 g. of potassium hydroxide (15% excess) in 200 cc. of absolute methanol with vigorous agitation at 10–15°. Stirring was continued at 15° during two hours. The insoluble potassium chloride was filtered off, washed with methanol, and dried. The yield of potassium chloride was 47 g. (94% of the theoretical amount). The methanol filtrate was poured into 500 cc. of water, and the water-insoluble material separated and dried. The yield of crude material was 74 g.

The pure chloro-3-hexatetraene-1,3,4,5 was obtained as a colorless liquid; b. p. 127° at 760 mm. (with decomposition), 82° at 163 mm., 55° at 54 mm.; d_4^{20} 0.9997; n_D^{20} 1.5280; M_R calcd., 32.91; M_R found, 34.64.

The same compound was obtained by the action of sodium methylate (in absolute methanol) on dichloro-1,4-hexatriene-2,3,5.

Anal. Calcd. for C_6H_5Cl: C, 64.02; H, 4.45; Cl, 31.53; mol. wt.. 112.5. Found: C, 63.99; H, 4.61; Cl, 31.61; mol. wt. (cryoscopic in benzene), 110.

Reduction of Chloro-3-hexatetraene-1,3,4,5 to *n*-Hexane.—The chloro compound (13 g.) absorbed 87% (0.403 mole) of the theoretical amount of hydrogen (catalyst 0.15 g. of PtO_2) in 25 cc. of ethyl acetate during three hours. A large amount of hydrogen chloride was formed. The ethyl acetate solution was distilled and the distillate up to 80° was collected and allowed to stand over aqueous alkali during four hours. The unsaponifiable material was separated and allowed to stand over solid potassium hydroxide during fifteen hours. There was obtained 2 g. of *n*-hexane, b. p. 64–70°; d_4^{20} 0.691; n_D^{20} 1.3766. A small amount of high boiling residue was obtained but not identified.

Permanganate Oxidation of Chloro-3-hexatetraene-1,3,4,5 to Oxalic Acid.—The oxidation was made by adding in small portions 224 g. of potassium permanganate to a vigorously agitated, aqueous solution (200 cc.) of 80 g. of potassium carbonate and 21 g. of chloro-3-hexatetraene-1,3,4,5 at 35–45°. After ten hours the solution was decolorized with sulfur dioxide and the manganese dioxide filtered and repeatedly washed. The combined filtrates were strongly acidified with sulfuric acid, while the reaction mixture was cooled in an ice-bath. Continuous ether extraction of the acidified aqueous solution during fifteen hours gave 15 g. of oxalic acid dihydrate (calcd. 25 g.). The acid melted at 101° (copper block).

Neutral equivalent. Subs., 0.2916 g. Required 41.10 cc. of 0.1117 *N* NaOH. Calcd. for $H_2C_2O_4 \cdot 2H_2O$; neutral equivalent, 63.0. Found: 63.5.

Preparation and Proof of Structure of Trichloro-1,4,4-hexadiene-2,5 (VII)

Addition of Hydrogen Chloride to Dichloro-1,4-hexatriene-2,3,5.—Dichloro-1,4-hexatriene-2,3 5 (75 g., 0.5 mole) was shaken during twelve hours at 27° with 30 g. of cuprous chloride and 75 cc. of hydrochloric acid (sp. gr. 1.18). The water insoluble layer was separated, washed and dried. Fractionation gave 20 g. of the original dichloro compound and 28 g. of trichloro-1,4,4-hexadiene-2,5, which boiled at 100–103° at 4 mm.; d_4^{20} 1.3036; n_D^{20} 1.5585; M_R calcd. 43.58; M_R found, 45.88.

Anal. Calcd. for $C_6H_7Cl_3$: C, 38.83; H, 3.78; Cl, 57.39; mol. wt., 185.5. Found: C, 38.87; H, 3.83; Cl, 57.38; mol. wt. (cryoscopic in benzene), 185.

Permanganate Oxidation of Trichloro-1,4,4-hexadiene-2,5 to Chloroacetic Acid.—The trichloro compound (18 g.) reduced 84 g. of potassium permanganate (added in small portions with vigorous agitation) in alkaline solution during four hours at 30–40°. The filtrates obtained after separating and washing the manganese dioxide were acidified and subjected to continuous ether extraction during fifteen hours. From the ether extract there was obtained 10 g. of chloroacetic acid, which boiled at 65–68° at 4 mm. and melted at 58–59°. It was further identified by conversion through its acid chloride into chloroacetanilide, which showed the correct melting point, 134–135°.

The Reactivity of the Halogens in Trichloro-1,4,4-hexadiene-2,5. Hydrolysis by Sodium Carbonate.—The trichloro compound (5.81 g., 0.0313 mole) was refluxed during seven hours with agitation in 110 cc. of water containing 8.6 g. of sodium carbonate. Analysis of the aqueous solution showed that 0.0763 mole of sodium chloride was formed. Therefore three active halogen atoms were present.

Preparation and Proof of Structure of Tetrachloro-1,3,4,6-hexadiene-2,4 (III)

Chlorination of Divinylacetylene to Obtain Tetrachloro-1,3,4,6-hexadiene-2,4.—Chlorine was passed into divinylacetylene (234 g., 3 moles) at −40 to −50° with vigorous agitation. During five and one-half hours 340 g. (4.8 moles) of chlorine was absorbed, corresponding to 80% chlorination to the tetrachloro derivative. Considerable loss of hydrogen chloride occurred. Distillation gave 119 g. of crude dichloro-1,4-hexatriene-2,3,5 and 96 g. of very crude tetrachloro derivative. Fractionation of 160 g. of the crude tetrachloro derivative (b. p. 50–120° at 3 mm.) gave 50 g. of tetrachloro-1,3,4,6-hexadiene-2,4 boiling at 84–89° at 2 mm.; d_4^{20} 1.4013; n_D^{20} 1.5465; M_R calcd., 48.43; M_R found, 49.71.

Anal. Calcd. for $C_6H_6Cl_4$: C, 32.76; H, 2.73; Cl, 64.51; mol. wt., 220. Found: C, 32.80; H, 2.49; Cl, 63.76; mol. wt. (cryoscopic in benzene), 222.

Permanganate Oxidation of Tetrachloro-1,3,4,6-hexadiene-2,4 to Chloroacetic Acid.—The tetrachloro derivative (58 g.) completely reduced 220 g. of potassium permanganate (added in small portions with vigorous agitation) during five hours at 35–40°. The filtrate obtained after separating and washing the manganese dioxide was strongly acidified and subjected to continuous ether extraction during fifteen hours. The ether extract gave 20 g. of chloroacetic acid which boiled at 64–66° at 3 mm. and melted at 58–59° after recrystallization from petroleum ether.

The Reactivity of the Halogens in Tetrachloro-1,3,4,6-hexadiene-2,4. Hydrolysis by Sodium Carbonate.—The tetrachloro compound (5 g., 0.0228 mole) was refluxed during eight hours with agitation in 100 cc. of water containing 7 g. (0.066 mole) of sodium carbonate. Analysis of the aqueous solution showed that 0.0414 mole of sodium chloride was formed. Therefore two active halogen atoms are present in the tetrachloride.

The Chlorination of Tetrachloro-1,3,4,6-hexadiene-2,4 to Hexachloro-1,2,3,4,5,6-hexene-3 (IV).—Chlorine was passed into 27 g. (0.12 mole) of tetrachloro-1,3,4,6-hexadiene-2,4, during eight hours at 60–70°. The product was distilled and from the portion boiling at 95–115° at 2 mm. was obtained 8 g. of pure hexachloro-1,2,3,4,5,6-hexene-3 which melted at 57 to 58° after two crystallizations from petroleum ether; yield, 23%. The remainder of the product was a viscous liquid not further investigated. The hexachloride is described in more detail below.

The Behavior of Tetrachloro-1,3,4,6-hexadiene-2,4 with Alcoholic Alkali. Trichloro-1,3,4-hexatriene-2,4,5 (VIII) and Dichloro-3,4,-hexatetraene-1,2,4,5 (IX)

The tetrachloro compound (75 g., 0.34 mole) was added during two hours to a solution of 44 g. of potassium hydroxide (15% excess) in 200 cc. of absolute methanol with vigorous agitation at 10–15°. The reaction was allowed to proceed for one hour after which the potassium chloride was filtered off (KCl, 36 g. or 48%). The methanol filtrate was poured into water, and the water-insoluble layer was separated, dried and distilled. From the crude material (50 g.) two fractions were obtained; one was trichloro-1,3,4-hexatriene-2,4,5 (25 g.) which boiled at 50° at 1 mm.; d_4^{20} 1.3132; n_D^{20} 1.5517; M_R calcd. 43.11; M_R found, 44.61. The other was dichloro-3,4-hexatetraene-1,2,4,5 (5 g.) which boiled at 38–40° at 8 mm.; d_4^{20} 1.1819; n_D^{20} 1.5456; M_R calcd. 37.77; M_R found, 39.41.

Trichloro-1,3,4-hexatriene-2,4,5.—*Anal.* Calcd. for $C_6H_5Cl_3$: C, 39.26; H, 2.73; Cl, 58.01; mol. wt., 183.4. Found: C, 39.70; H, 2.75; Cl, 57.52; mol. wt. (cryoscopic in benzene), 190.

Dichloro-3,4-hexatetraene-1,2,4,5.—*Anal.* Calcd. for $C_6H_4Cl_2$: Cl, 48.27. Found: Cl, 48.60, 48.32.[7]

The Chlorination of Divinylacetylene at 60–70° to Obtain Hexachloro-1,2,3,4,5,6-hexene-3 (IV).—Divinylacetylene (100 g., 1.28 moles) in 160 g. of carbon tetrachloride absorbed 197 g. (2.8 moles) of chlorine during twelve hours. Distillation of the product gave 30 g. (10% of the theoretical amount) of the hexachloride, which boiled at 110 to 112° at 2 mm. After recrystallization from petroleum ether the white crystals melted at 58 to 59°. The major part (150 g.) of the product from this reaction was an almost colorless, viscous sirup. This is described in more detail below.

Hexachloro-1,2,3,4,5,6-hexene-3 is not attacked by ozone or by hot nitric acid, and the action of alkaline permanganate leads to total destruction. It fails to chlorinate further even at elevated temperatures in the presence of light.

Anal. Calcd. for $C_6H_6Cl_6$: C, 24.76; H, 2.06; Cl, 73.16. Found: C, 25.14; H, 2.18; Cl, 73.37.

The viscous sirup that formed the major part of the product of the above-described reaction was obtained as a residue which remained after the removal of the hexachloro-1,2,3,4,5,6-hexene-3 by distillation. This material could not be distilled even at 185° at a pressure of 2 mm. although it darkened rapidly and showed a tendency to liberate hydrogen chloride under these conditions. Its chlorine content was generally 1–3% less than that of the pure hexachloride, and like the latter it showed no tendency to absorb more chlorine even at elevated temperature. This sirup probably results from the coupling together of two or more of the six-carbon atom chains at some stage of the chlorination.

Molecular weight determinations were made on two specimens of the sirup both of which contained a considerable proportion of the dissolved hexachloride. The values obtained were (a) Cl, 68.90%; mol. wt. (cryoscopic in benzene), 360; (b) Cl, 72.90%; mol. wt., 370.

Summary

Divinylacetylene reacts with chlorine to form a liquid dichloride and tetrachloride, a crystalline hexachloride, and a sirupy product having approximately the composition of the hexachloride but a higher molecular weight. The three monomeric products are each formed from their precursors by 1,4 addition and they have the formulas dichloro-1,4-hexatriene-2,3,5; tetrachloro-1,3,4,6-hexadiene-2,4; and hexachloro-1,2,3,4,-5,6-hexene-3. The following transformation products of these compounds are described: chloro-3-hexatetraene-1,3,4,5; trichloro-1,4,4-hexadiene-2,5; trichloro-1,3,4-hexatriene-2,4,5; and dichloro-3,4-hexatetraene-1,2,4,5.

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[7] The analyst found great difficulty in the proper combustion of this compound. The carbon percentage was usually lower and the hydrogen percentage higher than the theoretical amounts.