

Acetylene Polymers and their Derivatives. XIV. The Dihydrochloride of Divinylacetylene

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The addition of thio-*p*-cresol¹ to divinylacetylene² involves only the terminal ethylenic linkage. Chlorine on the other hand reacts by 1,4 addition to yield first a dichloride and then successively a tetra- and a hexachloride.³ Study of the action of hydrogen chloride on divinylacetylene has furnished further information concerning the behavior of this multiply conjugated enyne system.

Divinylacetylene reacts fairly rapidly when shaken with aqueous hydrochloric acid at room temperature. As in the case of vinylacetylene,⁴ the reaction is considerably accelerated by cuprous chloride. On the other hand, the same product is obtained whether cuprous chloride is present or not. Under ordinary conditions a point of apparent saturation is reached when two molecules of hydrogen chloride have been absorbed. The first step in the reaction undoubtedly involves the formation of a monohydrochloride, but apparently this reacts more readily than the parent hydrocarbon. Consequently the chief product is dihydrochloride even when a deficiency of hydrochloric acid is used. The monohydrochloride is produced in poor yields, and it is so difficult to separate from the unchanged hydrocarbon that it has not yet been obtained in a state of purity.

Purification of the dihydrochloride to constant composition requires rather sharp fractionation, and the boiling range (80 to 82° at 17 mm.) is wide enough to suggest the presence of geometrical isomers. Only one chlorine atom of the dihydrochloride is reactive. When heated with naphthoquinone or maleic anhydride the only evidence of reaction is the formation of a small amount of dark gummy material. However, as has already been pointed out,³ negative results in the Diels-Alder reaction are of no value in the demonstration of structure, since many 1,3-dienes fail to react. The compound is stable. It shows no tendency to polymerize spontaneously, but a sample that had been submitted to a pressure of 6000 atmospheres for ninety-three hours at 49° was changed to a dark, somewhat elastic and only slightly plastic mass. When heated with sodium acetate in acetic acid it yields a monoacetate, and the second chlorine atom remains unaffected. Similarly the action of methyl alcoholic potash results in a monomethyl ether. When oxidized with permanganate the dihydrochloride yields acetic acid and chloroacetic acid.

(1) Carothers, *THIS JOURNAL*, **55**, 2008 (1933).

(2) Nieuwland, Calcott, Downing and Carter, *ibid.*, **53**, 4197 (1931).

(3) Coffman and Carothers, *ibid.*, **55**, 2040 (1933).

(4) Carothers, Berchet and Collins, *ibid.*, **54**, 4066 (1932).

These facts furnish a basis for a discussion of its structure. We assume that the hydrogen atoms of the hydrocarbon retain their original positions during reaction, and the results of oxidation then indicate that the dihydrochloride contains the residues $\text{CH}_3\text{—CH}=\overset{\text{C}}{\text{—}}$ and $\text{ClCH}_2\text{—CH}_2=\overset{\text{C}}{\text{—}}$. Hence the chain has the formula $\text{CH}_3\text{—CH}=\overset{\text{C}}{\text{—}}\overset{\text{C}}{\text{—}}\text{CH}=\text{CH}_2\text{Cl}$. Only a hydrogen atom and a chlorine atom remain to be accounted for, and one of these must be attached to the third carbon atom and the other to the fourth carbon atom. No direct experimental method is available for a decision between these two alternatives, but a satisfactory conclusion can be reached by a consideration of the probable mechanism of the reaction. In the following chart the two alternative formulas, dichloro-1,3-hexadiene-2,4 and dichloro-1,4-hexadiene-2,4 are designated as A and B, respectively; the positions of the hydrocarbon chain are marked with the numbers 1 to 6; and the H and Cl of the addendum are called *a* and *b*, respectively. Addition at the first stage may be 1,2, 3,4, 1,4, or 1,6 and it must bring the chlorine atom to position 1 or position 3 (or 4). The formulas I to IV therefore include all the reasonable possibilities for the monohydrochloride. For further reaction the possibilities are

ADDITION OF HYDROGEN CHLORIDE TO DIVINYLACETYLENE						
No.	Mode of addition	Monohydrochloride produced	Mode of addition	Dihydrochloride produced		
I	1a, 4b	$\text{CH}_3\text{—CH}=\overset{\text{C}}{\text{—}}\text{CCl}=\overset{\text{C}}{\text{—}}\text{CH}=\text{CH}_2$	3a, 6b	$\text{CH}_3\text{—CH}=\overset{\text{C}}{\text{—}}\text{CH}=\overset{\text{C}}{\text{—}}\text{CCl}=\overset{\text{C}}{\text{—}}\text{CH}=\text{CH}_2\text{Cl}$	A	
II	4a, 1b	$\text{CH}_2\text{Cl—CH}=\overset{\text{C}}{\text{—}}\text{C}=\overset{\text{C}}{\text{—}}\text{CH}=\text{CH}=\text{CH}_2$	6a, 3b	$\text{ClCH}_2\text{—CH}=\overset{\text{C}}{\text{—}}\text{CH}=\overset{\text{C}}{\text{—}}\text{CCl}=\overset{\text{C}}{\text{—}}\text{CH}=\text{CH}=\text{CH}_2$	A	
III	3a, 4b	$\text{CH}_3=\overset{\text{C}}{\text{—}}\text{CH}=\overset{\text{C}}{\text{—}}\text{CCl}=\overset{\text{C}}{\text{—}}\text{CH}=\text{CH}_2$	1a, 6b	$\text{CH}_3\text{—CH}=\overset{\text{C}}{\text{—}}\text{CH}=\overset{\text{C}}{\text{—}}\text{CCl}=\overset{\text{C}}{\text{—}}\text{CH}=\text{CH}_2\text{Cl}$	A	
			6a, 1b	$\text{ClCH}_2\text{—CH}=\overset{\text{C}}{\text{—}}\text{CH}=\overset{\text{C}}{\text{—}}\text{CCl}=\overset{\text{C}}{\text{—}}\text{CH}=\text{CH}_2$	B	
IV	1a, 6b	$\text{CH}_3\text{—CH}=\overset{\text{C}}{\text{—}}\text{C}=\overset{\text{C}}{\text{—}}\text{CH}=\text{CH}_2\text{Cl}$	3a, 4b	$\text{CH}_3\text{—CH}=\overset{\text{C}}{\text{—}}\text{CH}=\overset{\text{C}}{\text{—}}\text{CCl}=\overset{\text{C}}{\text{—}}\text{CH}=\text{CH}_2\text{Cl}$	A	
			4a, 3b	$\text{CH}_3\text{—CH}=\overset{\text{C}}{\text{—}}\text{CCl}=\overset{\text{C}}{\text{—}}\text{CH}=\text{CH}=\text{CH}_2\text{Cl}$	B	
		I by 1,4 addition (3a, 6b) gives A		III by 1,6 addition (6a, 1b) gives B		
		II by 1,4 addition (6a, 3b) gives A		IV by 1,2 addition (3a, 4b) gives A		
		III by 1,6 addition (1a, 6b) gives A		IV by 1,2 addition (4a, 3b) gives B		

Thus of the six pairs of reactions that might lead to A or B, four lead to A and only two to B, and probability is two to one in favor of A as the formula of the dihydrochloride. Further than this, however, there are good reasons for rejecting both III and IV as possibilities. Evidence of 1,6 addition in the reactions of divinylacetylene has never been observed, nor of 1,2 addition at the acetylenic linkage of either vinylacetylene or divinylacetylene. Moreover, 1,2 addition followed by 1,6 addition and 1,6 addition followed by 1,2 addition both appear inherently improbable. The addition of chlorine to divinylacetylene proceeds 1,4: $\text{CH}_2=\text{CH}—\text{C}\equiv\text{C}—\text{CH}=\text{CH}_2 \rightarrow \text{CH}_2\text{Cl}—\text{CH}=\text{C}=\text{CCl}—\text{CH}=\text{CH}_2$; ³ and the primary step in the action of hydrogen chloride on vinylacetylene is 1,4 addition: $\text{CH}\equiv\text{C}—\text{CH}=\text{CH}_2 \rightarrow \text{CH}_2=\text{C}=\text{CH}—\text{CH}_2\text{Cl}$. ⁴ It seems certain therefore that the dihydrochloride of divinylacetylene is dichloro-

1,3-hexadiene-2,4 (A) and the mechanism by which it is formed is most probably represented by II.

Experimental Part

The Addition of Hydrogen Chloride to Divinylacetylene in the Presence of Cuprous Chloride.—Divinylacetylene (80 g.) was shaken at either 0° or room temperature during one hour with 1.5 liters of 12 *N* hydrochloric acid containing 300 g. of cuprous chloride. The reaction mixture was then subjected to steam distillation. By this process 80 g. of crude dihydrochloride was obtained (53% of the theoretical amount). Fractionation of 241 g. of material (b. p. 70–80° at 11 mm.) through an efficient column gave 170 g. of analytically pure dichloro-1,3-hexadiene-2,4 which boiled at 80–82° at 17 mm.; n_D^{20} 1.1456; n_D^{20} 1.5271; M_R calcd. 38.70; M_R found, 40.42.

Anal. (Carius). Subs., 0.1201 g.; AgCl, 0.2305 g. Calcd. for $C_6H_8Cl_2$: Cl, 46.99. Found: Cl, 47.47.

The Addition of Hydrogen Chloride to Divinylacetylene in the Presence of Calcium Chloride.—Six pressure bottles each containing 150 cc. of hydrochloric acid (sp. gr. 1.187), 30 g. of anhydrous calcium chloride and 80 g. of divinylacetylene were shaken at 25° during one hundred and ten hours. The water-insoluble layer was separated, washed with aqueous sodium carbonate and dried. Distillation gave 242 g. of material boiling above 50° at 70 mm.

Fractionation through an efficient column gave 94 g. of material boiling at 50–60° at 52 mm., and 60 g. of dichloro-1,3-hexadiene-2,4 which boiled at 80–82° at 17 mm. The residue weighed 60 g. The yield of dihydrochloride was 6.8% of the theoretical amount.

Repeated fractionation of the low boiling material (b. p. 50–60° at 52 mm.) failed to give a product having the composition of the monohydrochloride of divinylacetylene (C_6H_7Cl). The chlorine analysis of the samples collected was always less than the theoretical amount for the monohydrochloride, indicating that hydrocarbon material was present.

The Permanganate Oxidation of Dichloro-1,3-hexadiene-2,4 to Obtain Acetic and Chloroacetic Acids.—An analytically pure sample of the dihydrochloride (100 g.) was introduced into an aqueous solution (400 cc.) containing 46 g. of potassium carbonate. Potassium permanganate (486 g.) was added in small amounts during five hours with continuous agitation. The solution was decolorized with sulfur dioxide and the manganese dioxide filtered and washed. The combined filtrates were acidified with 100 cc. of concentrated sulfuric acid and the solution subjected to continuous ether extraction during fifteen hours. The ethereal extract was dried and the ether removed by evaporation. The acidic residue gave by fractionation 15 g. of acid boiling at 105–120° (Fract. C) and 10 g. of acid boiling at 62.5° at 3 mm. (Fract. A).

The determination of the Duclaux values of Fract. C indicated that acetic acid was the material under examination. The Duclaux values observed are 7.3, 6.7, 7.4, compared to 6.8, 7.1, and 7.4 for acetic acid, 3.95, 4.40, 4.55, for formic acid, and 11.9, 11.7, 11.3, for propionic acid. The identification of Fract. C was completed by the preparation of *p*-acet-toluidide, which showed the correct melting point and mixed melting point (149 to 150°). Fraction A was similarly identified as chloroacetic acid by conversion to chloroacetanilide, which showed the correct melting point and mixed melting point (134 to 135°).

The Action of Alcoholic Potash on Dichloro-1,3-hexadiene-2,4. Preparation of Methoxy-1-chloro-3-hexadiene-2,4.—Dichloro-1,3-hexadiene-2,4 (65 g.) in 200 cc. of absolute methanol containing 38 g. of potassium hydroxide was refluxed with vigorous agitation. Filtration of the reaction mixture gave 30 g. of dry potassium chloride

(calcd. 34 g.). Aqueous dilution of the alcohol solution was followed by separation of the water-insoluble layer which was dried and fractionated. There was obtained 20 g. of low boiling material and 21 g. of the methyl ether which boiled at 88–92° at 30 mm.; n_D^{20} 1.4928; d_4^{20} 1.0239; M_R calcd. 40.10; M_R found, 41.57.

Anal. Calcd. for $C_7H_{11}ClO$: C, 57.35; H, 7.51. Found: C, 56.91; H, 7.74.

Action of Sodium Acetate on Dichloro-1,3-hexadiene-2,4. Preparation of Acetoxy-1-chloro-3-hexadiene-2,4.⁵—One hundred grams of the dichloro compound, 100 g. of fused sodium acetate, and 300 cc. of glacial acetic acid were refluxed together for four hours. The acetic acid was neutralized with 20% sodium hydroxide and the mixture was extracted with ether. The ether extract was dried with calcium chloride, and then distilled. Three fractionations gave 55 g. of colorless liquid boiling at 84 to 85° at 3 mm.; d_4^{20} 1.0915; n_D^{20} 1.4890; M_R calcd., 44.61; M_R found, 46.14.

Anal. Calcd. for $C_8H_{11}O_2Cl$: Cl, 20.31. Found: 20.58, 20.78.

Summary

The action of aqueous hydrochloric acid on divinylacetylene yields a dihydrochloride. The compound is oxidized by permanganate with the formation of acetic acid and chloroacetic acid, and this fact together with a consideration of the probable mechanism of its formation, indicates that it has the structure dichloro-1,3-hexadiene-2,4 and that it results from two successive acts of 1,4 addition. When treated with sodium acetate its reactive (terminal) chlorine is replaced by acetoxy, and the action of methyl alcoholic potash similarly leads to the formation of a methyl ether.

(5) We are indebted to Dr. W. F. Talbot for this experiment.

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The Preparation of Amines by Catalytic Hydrogenation of Derivatives of Aldehydes and Ketones

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The preparation of amines through the hydrogenation of reaction products of aldehydes or ketones with ammonia or a substituted ammonia has attracted attention for several years. For example, the catalytic hydrogenation of oximes should be a practical process for the preparation of amines. There have been a number of papers bearing on this transformation, among which the following may be noted. Mailhe used nickel for a vapor phase hydrogenation and obtained a variety of products. Wassiljew by the use of two to four times as much nickel as oxime obtained in the liquid phase small quantities of amines which he did not isolate but determined as the platinum or gold derivatives. Mignonac has several patents on the hydrogenation of oximes over nickel. Hartung used palladium for the hydrogenation of oximes in a hydrochloric acid solution