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ACETYLENE POLYMERS AND THEIR DERIVATIVES. III. THE ADDITION OF HYDROGEN CHLORIDE TO VINYLACETYLENE

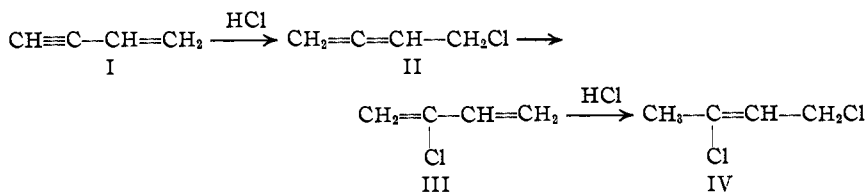
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Vinylacetylene (I) constitutes the simplest possible example of a conjugated enine system. Recorded information concerning the addition reactions of such systems is exceedingly meager. It has already been reported¹ that chloroprene (chloro-2-butadiene-1,3, III) can be obtained by the addition of (aqueous) hydrogen chloride to vinylacetylene, and the present paper is concerned with a further description of the mechanism of this reaction and the nature of the products to which it leads.

It is shown that the initial step consists in 1,4 addition, and the primary product thus formed is chloro-4-butadiene-1,2, (II) (b. p. 88°), a new compound of rather unusual structure and curious properties. Under certain conditions this chloro-4-butadiene-1,2 can be isolated as the major reaction product, but it readily undergoes an isomerization involving migration of the chlorine atom and a shift of a double bond. Chloroprene (b. p. 59.4°) is formed thus, and the transformation occurs with such facility in the presence of hydrogen chloride that chloroprene always constitutes a part of the reaction product. Certain salts reinforce the catalytic effect of hydrogen chloride on this transformation, and when cuprous chloride is present no chloro-4-butadiene-1,2 is found in the reaction product. When sufficient amounts of hydrogen chloride are present the reaction proceeds further with the formation of dichloro-2,4-butene-2 (IV).



Influence of Conditions on the Reaction.—The reaction between vinylacetylene and hydrogen chloride is conveniently carried out in the following manner. Fifty grams of vinylacetylene and 175 cc. of concentrated hydrochloric acid (about 2.2 moles of hydrochloric acid) are placed in a pressure bottle, and the bottle is shaken to promote contact between the aqueous and the hydrocarbon layers. After the completion of the reaction the oily layer is separated, dried, mixed with a small amount of an anti-oxidant such as catechol or pyrogallol, and distilled *in vacuo* through an efficient column. Data from a very large number of experiments of this

¹ Carothers, Williams, Collins and Kirby, *THIS JOURNAL*, 53, 4203 (1931).

type are available. Owing to the fact that in most cases neither the temperature nor the speed of shaking was precisely controlled these data cannot be used as a basis for a quantitative description of reaction velocities; nevertheless, they give a clear idea of relative rates.

In a typical experiment of the kind described above, about 43% of the vinylacetylene was utilized in seven hours, and analysis of the reaction product yielded chloro-4-butadiene-1,2 and chloroprene in the ratio 2.2:1.

In general this ratio is diminished by increase in the temperature, concentration of hydrogen chloride, or time of contact; and the proportion of the chloro-4-butadiene-1,2 in the product is less the more completely the vinylacetylene is utilized. This fact demonstrates that part at least of the chloroprene is formed by the isomerization of the chloro-4-butadiene-1,2 during the course of the reaction, and it seems reasonable to conclude that all of it is formed by this demonstrated mechanism.

The reaction is considerably accelerated by the presence of certain salts. Thus when 25 g. of calcium chloride is present in the reaction mixture the time required to obtain 40% conversion is decreased by about one-half, but the ratio of the two isomeric chlorobutadienes present in the reaction product at a given percentage conversion remains practically unaffected. Cuprous chloride is a much more powerful catalyst. When 25 g. of this salt is present in the reaction mixture, about 90% of the vinylacetylene reacts in four hours at 20°. In this case the product consists for the most part of chloroprene, and no chloro-4-butadiene-1,2 is present. It is, however, not necessary to assume that the cuprous chloride directs the reaction so that addition occurs at the acetylenic linkage. Separate experiments show that cuprous chloride reinforces the catalytic effect of hydrogen chloride on the isomerization of chloro-4-butadiene-1,2 and this effect seems adequate to explain the absence of chloro-4-butadiene-1,2 in the reaction product.

Chloroprene reacts further with hydrogen chloride to produce dichloro-2,4-butene-2. This reaction is also catalyzed by cuprous chloride, and the relative velocities are such that any conditions of concentration, temperature, and time of contact that suffice to convert all of a given sample of vinylacetylene result in the formation of a certain amount of the dichlorobutene. The following experiment is illustrative. Fifty grams of vinylacetylene, 175 cc. of concentrated hydrochloric acid, 25 g. of cuprous chloride, and 10 g. of ammonium chloride were placed in each of forty bottles. The bottles were gently shaken in a bath at 20° for four hours and then allowed to stand for twelve hours at 0°. The contents of all the bottles were combined and the mixture was steam distilled *in vacuo* into a receiver placed at the bottom of a 2-meter jacketed, carborundum-packed column provided with a dephlegmator and a second receiver each cooled to -80°. The pressure was kept at about 150 mm. until all of the unchanged vinyl-

acetylene had collected in the second receiver, and the pressure was then gradually reduced to 10 mm. until all of the chloroprene had collected in the second receiver. The dichlorobutene remained in the first receiver. The yields were: unchanged vinylacetylene, 115 g.; chloroprene, 2862 g.; dichlorobutene, 117 g. In mole percentages these values are 5.7, 84.2, and 2.5, respectively. The deficit amounting to 7.6 mole per cent. was mostly comprised in intermediate fractions. When this deficit is distributed proportionately among the three major fractions, the percentage yields become: unreacted vinylacetylene, 6.1%; chloroprene, 91.2%; dichlorobutene, 2.7%. The corresponding figures for the calculated yields based upon unrecovered vinylacetylene are chloroprene, 97%, and dichlorobutene, 3%. Further experiments indicate that the conditions of this experiment lie very close to the optimum for the conversion of vinylacetylene to chloroprene in a batch process: a higher ratio of chloroprene to dichlorobutene can be obtained only by utilizing a smaller proportion of the applied vinylacetylene, and a more complete utilization of the vinylacetylene results in a larger proportion of dichlorobutene.

The Properties of Chloro-4-butadiene-1,2 and the Proof of its Structure.—Chloro-4-butadiene-1,2 is a colorless liquid boiling at 87.7 to 88.1°. It is only slightly soluble in water but miscible with most of the common organic solvents. It has a peculiar, sharp odor. Some other properties are: n_D^{20} 1.4775; d_4^{20} 0.9891; M_R calcd., 24.61; M_R found, 25.30.

Anal. Calcd. for C_4H_5Cl : C, 54.23; H, 5.64; Cl, 40.11. Found: C, 55.04, 55.11; H, 5.70, 5.90; Cl, 39.75, 40.03.

Its chlorine atom is exceedingly reactive. When mixed with alcoholic silver nitrate it rapidly yields a copious precipitate of silver chloride. This fact in itself indicates that the compound is not a 1,3-diene, since in such a structure the chlorine atom would, of necessity, be attached to a doubly bonded carbon. Furthermore, the compound does not react with maleic anhydride or with naphthoquinone. It is not a true acetylenic compound either since it does not yield any derivative with ammoniacal cuprous chloride. When treated with ozone it yields formaldehyde and (after oxidation with potassium permanganate) chloroacetic acid. The compound has also been directly oxidized with potassium permanganate. The only product obtained was chloroacetic acid. Acetic acid and oxalic acid were absent. This behavior demonstrates the presence of the groups $CH_2=$ and $=CH-CH_2Cl$, and the compound must therefore have the structure chloro-4-butadiene-1,2. This structure is further confirmed by the fact that under the action of cold concentrated sulfuric acid, chloro-4-butadiene-1,2 is readily converted into chloro-4-butanone-2.²

The transformation of chloro-4-butadiene-1,2 into chloroprene exempli-

² Cf. Gustavson and Demjanoff, *J. prakt. Chem.*, [2] **38**, 201 (1888); Bouis, *Ann. chim.*, [10] **9**, 402 (1928).

fies a type of reaction that is common to many substituted allyl halides. Such halides (*e. g.*, $\text{CH}_3\text{CHXCH}=\text{CH}_2$ or $\text{CH}_3\text{CH}=\text{CHCH}_2\text{X}$) arise quite generally by the addition of halogens or hydrogen halides to 1,3-dienes, and in these cases the possibility of isomerization frequently makes it difficult or impossible to determine whether the primary product is the result of 1,2 or 1,4 addition. Chloro-4-butadiene-1,2, however, differs from other allyl halides: the α,γ shift brings the adjacent double bonds into the more stable conjugated configuration and the chlorine atom becomes attached to a doubly bonded carbon where its mobility is lost. A reversal of the isomerization is therefore impossible, and chloro-4-butadiene-1,2 cannot be other than a primary product of the addition of hydrogen chloride to vinylacetylene.

The transformation of chloro-4-butadiene-1,2 into chloroprene has been observed under a variety of conditions: by the action of powdered potassium hydroxide, by the action of hot quinoline (140–150°), by the action of heat (290°) in the presence of silica gel, and by the action of hot dilute hydrochloric acid.³ However, the isomerization occurred most smoothly and rapidly in the presence of hydrochloric acid containing cuprous chloride. Fifty grams of chloro-4-butadiene-1,2 was refluxed for three and one-half hours with 20 g. of cuprous chloride in 100 cc. of 18% hydrochloric acid. The oily layer was decanted, dried and distilled. The entire specimen except for a small amount of undistillable residue came over between 59 and 63° and the distillate was pure chloroprene. When the chloro-4-butadiene-1,2 was similarly treated with aqueous cuprous chloride alone it was recovered unchanged.

Chloro-4-butadiene-1,2 unlike its isomer chloroprene shows no tendency to polymerize. It can be distilled unchanged at ordinary pressure, and specimens stored under the ordinary laboratory conditions for many months remain unaltered. It undergoes no change even when submitted to a pressure of 6000 atmospheres for forty-five hours at 50°.⁴

Experimental Part

Oxidation of Chloro-4-butadiene-1,2.—To a mixture of 30 g. of chloro-4-butadiene-1,2 with 250 cc. of water containing a little sodium carbonate was added in small portions with constant stirring 214 g. of potassium permanganate. The mixture was filtered, the filtrate acidified and continuously extracted with ether for several hours. The ether solution on distillation gave a liquid boiling at 185° which solidified on cooling. This was chloroacetic acid, identified by its melting point, neutralization equivalent (found, 96; calcd., 94.5) and transformation into chloroacetamide, *m. p.* 119°. No acetic or oxalic acid was found.

Ozonization of Chloro-4-butadiene-1,2.—A solution of 20 g. of chloro-4-butadiene-1,2 in 20 cc. of chloroform was treated with ozone for twelve hours at 0°. The solvent and the unchanged material were evaporated *in vacuo* and the remaining ozonide

³ We are indebted to Dr. D. D. Coffman for some of these observations.

⁴ We are indebted to Dr. H. W. Starkweather for this observation.

was decomposed with water. Formaldehyde was detected in the aqueous solution by its strong odor and the formation of methylene-di- β -naphthol; white needles melting at 204° (corr.).

Chloroacetaldehyde was not detected directly. The aqueous solution was treated gradually with 50 g. of potassium permanganate, the excess permanganate destroyed with sulfur dioxide, and the filtrate extracted with ether. Distillation of the ether solution left a residue which crystallized on cooling. This product was chloroacetic acid, identified by its melting point and neutralization equivalent.

Hydration of Chloro-4-butadiene-1,2.—Into 250 cc. of concentrated sulfuric acid 88.5 g. of chloro-4-butadiene-1,2 was added dropwise with stirring, the temperature being maintained at -5 to 3° . The dark reaction product was poured onto cracked ice, partly neutralized with sodium carbonate and extracted with ether. The ethereal solution was washed, dried and distilled, yielding 58 g. of crude chloro-4-butanone-2, b. p. 110 – 123° . On redistillation it boiled at 120 to 122° at 760 mm.

Anal. Calcd. for C_4H_7OCl : C, 45.07; H, 6.57; Cl, 33.33. Found: C, 45.42, 45.42; H, 6.81, 6.47; Cl, 32.26, 32.42.

When treated with phenylhydrazine it gave a derivative having the correct melting point (77°) and analysis for phenylmethylpyrazoline.⁵

Anal. Calcd. for $C_{10}H_{12}N_2$: C, 75.00; H, 7.50; N, 17.50. Found: C, 74.32; H, 7.60; N, 17.10.

Dichloro-2,4-butene-2.—This material is obtained as a by-product in the preparation of chloroprene and it is readily prepared in quantity by shaking vinylacetylene with an excess (4 moles) of hydrochloric acid containing cuprous chloride. It is a colorless liquid having a characteristic odor; other properties are: boiling point 127 – 129° at 756 mm., 61 – 63° at 70 mm., 53 to 54° at 50 mm., d_4^{20} 1.1591, n_D^{20} 1.47239, n_c^{20} 1.46988, n_F^{20} 1.48187, M_R calcd. 29.94, M_R found 30.27.

Anal. Calcd. for $C_4H_6Cl_2$: C, 38.40; H, 4.80; Cl, 56.80. Found: C, 38.53; H, 4.87; Cl, 56.90.

The proof of the structure of this compound will be presented in a future paper dealing with its reactions.

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Summary

The results of experiments on the action of aqueous hydrogen chloride on vinylacetylene are described. The initial step consists in 1,4 addition and the primary product is chloro-4-butadiene-1,2. This readily undergoes isomerization, yielding chloroprene, which always constitutes a part of the reaction product. When cuprous chloride is present in the reaction mixture the isomerization proceeds more rapidly and no chloro-4-butadiene-1,2 is found in the reaction product. When sufficient hydrogen chloride is present the reaction proceeds further, yielding dichloro-2,4-butene-2.

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⁵ Maire, *Bull. soc. chim.*, [4] 3, 272 (1908).