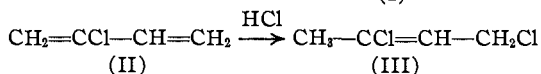
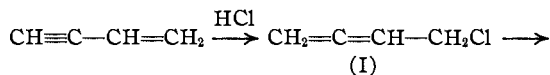


[CONTRIBUTION NO. 114 FROM THE EXPERIMENTAL STATION OF E. I. DU PONT DE NEMOURS & COMPANY]

Acetylene Polymers and their Derivatives. X. The Chlorination of the Hydrochlorides of Vinylacetylene

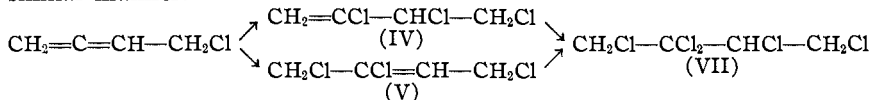
BY WALLACE H. CAROTHERS AND GERARD J. BERCHET

The action of hydrogen chloride on vinylacetylene gives rise to the two monohydrochlorides, chloro-4-butadiene-1,2 (I) and chloroprene (II), and the dihydrochloride, dichloro-2,4-butene-2 (III).¹



All of these compounds react rapidly with chlorine and we now record some observations on the products to which they lead.

Chloro-4-butadiene-1,2 in a series of experiments was chlorinated under various conditions and the combined distillable product was redistilled through an efficient column. Most of the material segregated into two fractions, one boiling at 40 to 41° at 10 mm. and the other at 64 to 65° at 10 mm. Each had the composition C₄H₅Cl₃. The lower boiling compound on oxidation with permanganate yielded α,β-dichloropropionic acid as the only recognizable product, and was thus identified as trichloro-1,2,3-butene-3 (IV). The higher boiling compound when similarly oxidized yielded only chloroacetic acid. The compound was therefore trichloro-1,3,4-butene-2 (V). The two compounds evidently arise by the addition of chlorine at the interior and the terminal members of the pair of contiguous double bonds. Other allenes have been observed to behave in a similar manner.²



Further experiments showed that although the two trichlorobutenes were the principal products when one mole of chlorine was added to chloro-4-butadiene-1,2, the ratio in which they were formed varied considerably with the conditions used. At 40 to 50° the 1,3,4-compound predominated, at -60 to -70° the 1,2,3-compound. Saturation of chloro-4-butadiene-1,2 with chlorine led to a compound having the composition C₄H₅Cl₅. In view of its origin it may be assigned the formula pentachloro-1,2,3,3,4-butane (VII).

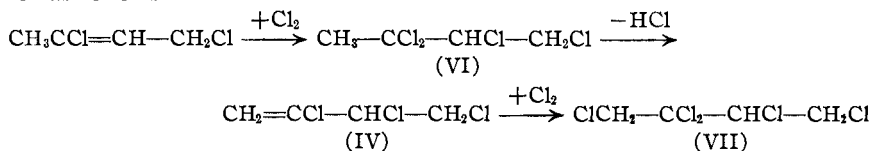
In all of the chlorinations of chloro-4-butadiene-1,2 a considerable fraction (up to about 20% of the total product) consisted of undistillable ma-

(1) Carothers, Berchet and Collins, *THIS JOURNAL*, **54**, 4086 (1932).

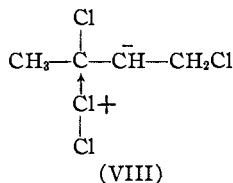
(2) Bouis, *Ann. chim.*, [10] **9**, 451 (1928).

terial. In the chlorination of chloroprene (1 mole : 1 mole) the proportion of undistillable product was still greater (up to about 50%). The distillable product formed either at 40 to 50° or at -60 to -70° was a difficultly separable mixture, but the principal fraction (25 to 30% of the total product) was closely similar in its physical properties to the compound already identified as trichloro-1,3,4-butene-2. This obviously might arise from chloroprene by a process of 1,4 addition.

The chlorination of dichloro-2,4-butene-2 leads to the formation of trichloro-1,2,3-butene-3 (IV), tetrachloro-1,2,3,3-butane (VI) and pentachloro-1,2,3,3,4-butane (VII). This series of products might be accounted for as follows



The isolated tetrachlorobutane however is a stable compound, that is, it shows no tendency to lose hydrogen chloride spontaneously. Moreover, a very curious feature of the reaction lies in the fact that at elevated temperature (*e. g.*, 40 to 60°) very little hydrogen chloride is evolved and the predominating product is the tetrachlorobutane; at low temperatures (*e. g.*, -60 to -70°), on the other hand, hydrogen chloride is formed in copious amounts, and the predominating product is the trichlorobutene or the pentachlorobutane, depending upon the amount of chlorine applied. It appears therefore that the trichlorobutene does not originate from the tetrachlorobutane as such, but that both of these compounds arise from a common prior intermediate. Such an intermediate might be VIII, which would be formed by the addition of the chlorine molecule at the deficient carbon in the active form of the double bond.³ Rearrangement of this intermediate would lead directly to tetrachlorobutane; loss of hydrogen chloride followed by rearrangement would lead to trichlorobutene. A sufficient difference in the temperature coefficients of the primary processes would account for the observed facts.



The above statements in regard to the influence of temperature on the chlorination of dichloro-2,4-butene-2 are illustrated by the following experiments.

One mole (125 g.) of the dichlorobutene in a flask cooled with a slush of solid carbon dioxide and acetone was treated with chlorine gas until 1.33 moles of chlorine had been absorbed. The mixture was allowed to warm up while a slow stream of air was passed through it to remove dissolved

(3) Carothers, *THIS JOURNAL*, **46**, 2227 (1924). Evidence that chlorinations involve primarily attack by the chlorine molecule has been presented by Soper and Smith, *J. Chem. Soc.*, 1582 (1926).

gases. During this operation there was a sudden and very copious evolution of hydrogen chloride. The loss in weight corresponded with the evolution of 0.9 mole of hydrogen chloride. The hydrogen chloride collected and titrated was only 0.73 mole, but some was lost owing to the suddenness of the evolution. Distillation of the mixture gave

Trichloro-1,2,3-butene-3	0.440 mole
Tetrachloro-1,2,3,3-butane	0.089 mole
Pentachloro-1,2,3,3,4-butane	0.198 mole

The rest (0.273 mole) was contained in intermediate fractions and residue; the latter comprised 10.3% of the total product. If the losses are distributed proportionately among the three chief fractions, the percentage yields of these are

Trichlorobutene 60.6% Tetrachlorobutane 12.2% Pentachlorobutane 27.2%

Since in the formation of the pentachloro compound the trichloro compound is a necessary intermediate, 88% of the dichlorobutene was converted to the trichlorobutene, and only 12.2% to the tetrachlorobutane.

One mole (250 g.) of the dichlorobutene was chlorinated at ordinary temperature, the rate being controlled so that the temperature of the mixture was between 45 and 60°. The increase in weight corresponded with the absorption of 0.61 mole of chlorine, and at the same time 0.36 mole of hydrogen chloride was liberated. Distillation of the mixture gave

Trichloro-1,2,3-butene-3	0.207 mole
Tetrachloro-1,2,3,3-butane	0.343 mole
Pentachloro-1,2,3,3,4-butane	0.100 mole

Chlorination in this case was incomplete and there was considerable loss in residue and intermediate fractions, but the data show that the yield of tetrachlorobutane was greater than the combined yields of the trichloro and the pentachloro compounds. Further experiments showed that by careful adjustment of the amount of chlorine applied at low temperatures the isolated yield of trichloro-1,2,3-butene-3 could be raised to 80%, while at high temperatures the yield did not exceed 25%.

Oxidation of Trichloro-1,2,3-butene-3.—Twenty grams of the compound was stirred with 200 cc. of water while 70 g. of potassium permanganate was added in portions. The alkaline solution was filtered, treated with sulfur dioxide, filtered, acidified and continuously extracted with ether for nine hours. Evaporation of the ethereal solution gave 8.5 g. of acidic oil which distilled at 125° at 25 mm. It was identified as α , β -dichloropropionic acid by its melting point (49–50°) and its neutralization equivalent (calcd., 143; found, 141.1).

Oxidation of Trichloro-1,3,4-butene-2.—Oxidation of this compound under the same conditions as those described above gave chloroacetic acid as the only product. It was identified by its melting point (63°), mixed melting point and neutralization equivalent (calcd., 94.5; found, 95.1).

TABLE I
 CHLORINATION PRODUCTS

Structural formula	Name	B. p., °C.	Mm.	n_D^{20}	n_D^{20}	M _R	
						Calcd.	Found
IV	Trichloro-1,2,3-butene-3	40-41	10	1.3430	1.4944	34.78	34.72
V	Trichloro-1,3,4-butene-2	64-65	10	1.3843	1.5175	34.78	34.89
VI	Tetrachloro-1,2,3,3-butane	90 55-57	32 10	1.4204	1.4958	40.14	40.25
VII	Pentachloro-1,2,3,3,4-butane	85	10	1.5543	1.5157	45.01	44.77
Anal.							
	Empirical formula	C	Calcd. H	Cl	C	Found H	Cl
IV	C ₄ H ₅ Cl ₃	30.09	3.13	66.77	29.95	3.30	66.34
V	C ₄ H ₅ Cl ₃	30.09	3.13	66.77	29.09	3.01	67.33
VI	C ₄ H ₅ Cl ₃			72.40			71.83
VII	C ₄ H ₅ Cl ₅	20.82	2.16	77.00	21.22	2.36	77.05

Summary

Chlorination of chloro-4-butadiene-1,2 gives mixtures of trichloro-1,2,3-butene-3 and trichloro-1,3,4-butene-2 which react further to produce pentachloro-1,2,3,3,4-butane. The chlorination of chloroprene (chloro-2-butadiene-1,3) gives considerable amounts of trichloro-1,3,4-butene-2. The chlorination of dichloro-2,4-butene-2 at 40 to 60° proceeds with little loss of hydrogen chloride, and the product formed in largest amount is tetrachloro-1,2,3,3-butane. At low temperatures (-60 to -70°) large amounts of hydrogen chloride are liberated during the chlorination, and the principal products are trichloro-1,2,3-butene-3 and pentachloro-1,2,3,3,4-butane.

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