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Abstract

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Chlorination of Diacetylene

Synthesis of Hexachlorobutadiene-1,3

(Presented by Academician A. V. Topchiev, August 2, 1957)

The halogenation reaction of diacetylene has been well studied using the addition of bromine as an example (⁀1). As regards chlorination, there are no corresponding data in the literature.

In the present communication we describe a method developed by us for the chlorination of diacetylene in carbon tetrachloride medium at a temperature from −30 to −25°. The reaction proceeded with the formation of liquid and crystalline 1,1,2,3,4,4-hexachlorobutene-2. The geometrical isomers of 1,1,2,3,4,4-hexachlorobutene-2, liquid and crystalline, were reported by Müller and Höttger (⁀2). These isomers were isolated by them in the study of halogen compounds of the butane series formed as by-products in the production of trichloroethylene. The authors indicated that hexachlorobutenes do not react with chlorine and bromine.

We succeeded in carrying out the further chlorination of hexachlorobutenes with liquid chlorine under pressure and under ultraviolet irradiation. Under conditions of a large excess of chlorine (4-8 and more moles) we did not observe chlorinolysis and obtained octachlorobutane in quantitative yield. Subsequent dehydrochlorination of octachlorobutane led to the synthesis of hexachlorobutadiene-1,3—a product possessing a number of valuable technical properties. There are patent indications (⁀3) for a method of obtaining hexachlorobutadiene on the basis of octachlorobutane (obtained from other starting materials by a more multistage route). In another application (⁀4), a continuous process is recommended for preparing hexachlorobutadiene on the basis of hexachlorobutene and chlorine. Syntheses of hexachlorobutadiene from heptachlorobutene have been described (^{5,}6). It is obtained by chlorination of polychloropentanes at high temperature and normal pressure (⁀7).

It should be noted that, in the patent, the elimination of HCl from octachlorobutane was recommended to be carried out by boiling with alcoholic alkali. We became convinced that this considerably contaminated the hexachlorobutadiene with side reaction products, since under the indicated conditions it is not inert. Indeed, quite recently it was shown (⁀8) that hexachlorobutadiene, on boiling with alcoholic alkalis, enters into reaction, replacing chlorine by an alkoxy group with the formation of perchlorinated vinyl and ortho esters. We therefore carried out the elimination of HCl from octachlorobutane with aqueous-alcoholic alkali at a temperature not above 30°.

Experimental Part

Diacetylene was obtained by a known procedure, somewhat modified in our laboratory and described in detail earlier (^9).

1. **Chlorination of diacetylene** was carried out in an apparatus with a mechanical stirrer. Into 100 ml of carbon tetrachloride, cooled to −50°, dry chlorine was passed until the required gain in weight was obtained (calculated ···

with a 2-3-fold excess of it). Diacetylene from the trap was blown with an even stream of nitrogen into the reaction flask with vigorous stirring of the whole mass. During 5-6 hr the experimental temperature was maintained at from −30 to −25°, and the mixture was left overnight under cooling. After removal of chlorine and solvent, the reaction mass was separated by suction on a glass filter into a liquid and a crystalline portion. The results of several experiments are given below (Table 1).

Table 1

Chlorination of diacetylene

Experiment no.	Diacetylene, g	Chlorine, g/mol per 1 g/mol diacetylene	Yield of reaction products, %, crystalline	Yield of reaction products, %, liquid	Yield of reaction products, %, total	Note
4	6	3.1	63	19	82	Total duration of the experiments 25-30 hr.
8	5.6	2.7	56.5	23.8	80.3	Total duration of the experiments 25-30 hr.

Experiment no.	Diacetylene, g	Chlorine, g/mol per 1 g/mol diacetylene	Yield of reaction products, %, crystalline	Yield of reaction products, %, liquid	Yield of reaction products, %, total	Note
10	6.6	4.2	60.3	18.7	79	Total duration of the experiments 25–30 hr.
13	6.8	3.4	47.6	25.2	72.8	Total duration of the experiments 25–30 hr.
16	5.7	4.1	58.5	15	73.5	Total duration of the experiments 25–30 hr.

As is evident from the data in Table 1, the total yield of the reaction products fluctuates within the range 73–80%, and there is no direct dependence on the initial chlorine concentration. The yields of the crystalline and liquid portions also fluctuate (15–25%). This is understandable if one bears in mind that the crystalline isomer is sufficiently soluble in the liquid.

Experiment 4. The experimental conditions and product yields are given in Table 1. After removal of chlorine and solvent from the reaction mass, 28 g of a white crystalline product remained. Suction on a glass filter gave 19.9 g of dry crystals and 6 g of an oily liquid. After one crystallization from boiling ethanol the crystals melted at 78° and, by analysis, corresponded to hexachlorobutene-2.

Found, %: C 18.69; 18.55; H 1.00; 0.92; Cl 80.39; 80.49
$C_4H_2Cl_6$. Calculated, %: C 18.28; H 0.77; Cl 80.95

Literature data (^{2}): m.p. 80°. On storage of the liquid portion, a small additional amount of crystalline isomer was deposited. The liquid portions from all experiments were combined, fractionated in vacuo, and subjected to further chlorination (see Sec. 2b). Usually a broad fraction of 82-90°/4 mm was used.

2. Synthesis of octachlorobutane. A weighed portion of hexachlorobutene dissolved in carbon tetrachloride was placed in an ampoule with a constriction. After the required amount of chlorine had been taken up (a 4-8-molar excess), the ampoule was sealed. The contents of the ampoules were carefully mixed, and the ampoules, in a horizontal position, were irradiated with a quartz lamp (20–25 hr). After completion of the reaction (3–4 days), the ampoules were opened while frozen; the excess chlorine was evaporated, and the reaction mass was transferred to a distillation apparatus to remove residues of chlorine and solvent.

a) **Chlorination of crystalline 1,1,2,3,4,4-hexachlorobutene-2.** Experiment 14. 25 g of hexachlorobutene (m.p. 78°) in 100 ml of CCl_4 and 65 g of liquid chlorine were sealed in an ampoule. The weight of the crystalline reaction product was 32 g. After the first crystallization from boiling alcohol, 25 g of a substance with m.p. 79.5° was isolated. A mixed sample with the initial hexachlorobutene melted at 52–55°, i.e., showed a sharp depression; as analysis showed, the synthesized substance corresponded to octachlorobutane.

Found, %: C 14.14; 14.08; H 0.69; 0.49; Cl 85.42; 85.23
$C_4H_2Cl_8$. Calculated, %: C 14.40; H 0.60; Cl 85.00

Literature data ([3]): m.p. 81°. From the mother liquor of the first crystallization a further 4 g of crystals with m.p. 79° were isolated, which gave no depression on melting with the main product. Thus, 29 g (91% of theoretical) of crystalline octachlorobutane was isolated.

b) Chlorination of liquid 1,1,2,3,4,4-hexachlorobutene-2. Experiment 30. 15 g of the liquid isomer (b.p. 82-90°/4 mm) in 50 ml of CCl_4 and 31 g of liquid chlorine were sealed in an ampoule. The gain in weight of the reaction mass was 4 g. After two crystallizations from hot alcohol, 13.9 g (76% of theoretical) of a crystalline substance with m.p. 79° was isolated; it gave no depression of the melting point with authentic octachlorobutane synthesized from the crystalline isomer. Fifteen such experiments were carried out. The combined mother liquors showed that, along with additional precipitating crystals, a thick noncrystallizing oil remained. We did not undertake a detailed investigation of this product.

3. Synthesis of hexachlorobutadiene. 20 g of octachlorobutane in 200 ml of alcohol was placed in the flask of an apparatus equipped with a mechanical stirrer. With vigorous stirring, an aqueous-alcoholic 1 N solution of NaOH was added until a stable pink coloration of the reaction mass appeared with phenolphthalein; at the same time a rise in temperature from 20 to 32–34° was observed. Stirring was continued at 30° for a further 1–1.5 hr, and the precipitated sodium chloride was filtered off. Alcohol was removed from the filtrate in vacuo, and after dilution with water the reaction product was separated, diluted slightly with ether, and dried over calcium chloride. After distillation in vacuo, 10.4 g (67%) of hexachlorobutadiene was obtained—an oily colorless liquid with a pleasant turpentine odor, having the following constants: b.p. 214°/755 mm, 57.5-58°/2 mm, 58-60°/2.5 mm; n_D^{20} 1.5540; 1.5542.

Found, %:	C 18.67; 18.79; Cl 81.38; 81.24
C_4Cl_6. Calculated, %:	C 18.42; Cl 81.58

Literature data: m.p. −21°, b.p. 215°/760 mm, n_D^{20} 1.5542, d_4^{20} 1.6820 (^{5,7}); 210°/760 mm, 64-65°/0.5 mm, n_D^{20} 1.5531 (^{6}).

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Note: Figure translations are in progress. See original paper for figures.