8,15-Dibenzyl-1,6-diaza-9,14-dioxacyclohexadecane-7,9,13,16-tetraone (XI). This compound was similarly obtained and was recrystallized from carbon tetrachloride.

9,16-Dibenzyl-1,7-diaza-4,10,15-trioxaheptadecane-8,10,14,17-tetraone (XII). This compound was similarly obtained from the chloride of acid IV and 3-hydroxy-1,5-diaminopentane. After removal of the solvent by distillation, the reaction product was isolated by column chromatography on silica gel [acetone—hexane (1:2)].

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NEW METHOD FOR THE SYNTHESIS OF TETRACHLOROTHIOPHENE*

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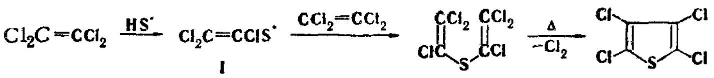
The reaction of tetrachloroethylene with hydrogen sulfide at 450-500°C leads to the formation of tetrachlorothiophene as the principal product, along with hexachlorobutadiene, the yield of which increases as the reaction temperature is raised.

The previously investigated [2] reaction of vinyl chloride with hydrogen sulfide takes place at 530-550°C and leads to the formation of thiophene. It seemed of interest to use a similar scheme involving tetrachloroethylene to obtain tetrachlorothiophene, which is usually obtained by the reaction of sulfur with hexachlorobutadiene at 160-300°C [3] or with tetrachloroethylene at 150-600°C at high pressure [4].

Tetrachloroethylene reacts with hydrogen sulfide in a flow system at a lower temperature (450-500°C) than vinyl chloride and at a slower rate; its conversion per pass is 10-15%, and the reaction was therefore investigated in a flow-recirculation system by the method in [5]. The principal reaction product is tetrachlorothiophene, which is obtained in 75% yield [6]. The possible intermediates, viz., tetrachlorovinylthiol and tetrachlorovinyl sulfide, were not detected in the products of the reaction of hydrogen sulfide with tetrachloroethylene, since, if they were formed, they would be continuously recirculated in the reaction zone, thereby undergoing conversion to the final product.

The temperatures of the formation of the thiylation products from vinyl chloride and tetrachloroethylene are inversely related to their nuclear quadrupole resonance (NQR) frequencies (33.411 and 38.684, respectively); as in the case of aromatic derivatives, this is associated with the strengths of the C—Cl bonds.

The lower reactivity of tetrachloroethylene as compared with vinyl chloride is evidently explained by the greater possibility of stabilization of the intermediate thiyl radical (I) responsible for the chain process [7] due to additional p—π conjugation of the chlorine atoms with the double bond:



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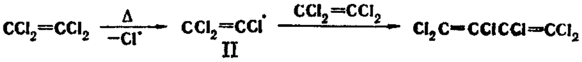
At temperatures above 450°C, in addition to tetrachlorothiophene, one observes the simultaneous formation of hexachlorobutadiene, which becomes the principal product [up to 80% in the condensate (46.2% yield)] at 600-650°C. The mechanism of its formation is associated with the possibility of cleavage of the C—Cl bond in tetrachloroethylene, which is weaker than the C—Cl bond in vinyl chloride:



$$CCl_2{=}CCl_2 \xrightarrow[-Cl^{\cdot}]{\Delta} \underset{II}{CCl_2{=}CCl^{\cdot}} \xrightarrow{CCl_2=CCl_2} Cl_2C{=}CClCCl{=}CCl_2$$

The II radical is capable of giving rise to a chain process that is parallel to the principal process.

EXPERIMENTAL

Analysis by gas-liquid chromatography (GLC) was carried out with an LKhM-8MD (2) chromatograph in a linear programming system; the column temperature ranged from 35 to 190°C, the stationary liquid phase was Lukopren NAW—HMDS, and the carrier gas was helium (the column was 2 m long).

1. In accordance with the method in [5], 85 g (0.51 mole) of tetrachloroethylene was recirculated in the course of 15.5 h in a stream of hydrogen sulfide (v = 2 liters/h) through a hollow quartz tube (30 × 400 mm) heated to 450°C. The reaction products that accumulated in the still of the system were subjected to fractionation with isolation of the fraction with bp 230°C (730 mm), which, according to GLC, was tetrachlorothiophene; the yield was 42.18 g (74% based on the converted tetrachloroethylene).

2. Similarly, 7.94 g (38.5%) of tetrachlorothiophene and 14.28 g (27.9%) of hexachlorobutadiene (according to GLC) were formed from 51 g (0.307 mole) of tetrachloroethylene at 550°C after 4 h.

3. Similarly, 51.1 g (46.2%) of hexachlorobutadiene and 22.3 g (30.5%) of tetrachlorothiophene (according to GLC) were obtained from 85 g (0.51 mole) of tetrachloroethylene at 600°C after 9 h.

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