REARRANGEMENT OF RADICALS IN THE COURSE OF

THE DIMERIZATION OF 3,3,3-TRICHLOROPROPENE

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When 3,3,3-trichloropropene is kept for a long time or is acted upon by initiators of free-radical processes, it polymerizes with formation of a solid polymer. When it is heated in presence of benzoyl peroxide in a solvent, not only polymeric products, but also a dimer is formed, which was isolated and characterized by Nesmeyanov, Freidlina, and Firstov [1, 2]. The structure of the dimer was not studied. Skinner and co-workers [3] studied the polymerization of 3,3,3-trichloropropene and its copolymerization with various unsaturated compounds; they noted that polymers of 3,3,3-trichloropropene, and also some of its copolymers, are fite-resistant (cf. [4]). In the present work we studied the structure of the dimer of 3,3,3-trichloropropene. We carried out dimerization by heating the trichloropropene in benzene solution with addition of 0.5-1 mole % of benzoyl peroxide. The dimer was purified by distillation through a column. According to gas-liquid chromatography, the dimer isolated was pure. As by-products small amounts of high-boiling substances, and also 1,1,3-trichloropropene, were obtained. In a special experiment it was shown that 1,1,3-trichloropropene undergoes no change under the conditions of the experiment. Carrying out the experiment without solvent, whether in presence of benzoyl peroxide or with ultraviolet irradiation of 3,3,3trichloropropene is probably a chain radical process in which the chain carrier is a chlorine atom, as is proposed in the case of the dimerization of, for example, 2-methylallyl chloride [5, 6]:



In our case, reaction proceeding by an analogous scheme should lead to a dimer of structure

$$\begin{array}{c} \text{ClCH}_2 - \text{CH} - \text{CH}_2\text{CH} = \text{CCl}_2.\\ |\\ \text{CCl}_3 \end{array}$$

However, when account is taken of the fact that the intermediately formed radical $ClCH_2CHCCl_3$ [see scheme (2)] readily rearranges with 1,2-migration of chlorine, as shown previously [7], it can be seen that the reaction may proceed by the following scheme:

This leads to the formation of a dimer of normal structure. Investigation showed that this is indeed the structure of the dimer obtained, i.e., it is 1,1,4,4,5,6-hexachloro-1-hexene.

The presence of a $-CH = CCl_2$ group in the product was shown by its hydrolysis with sulfuric acid to tetrachlorohexanoic acid. On treatment with zinc in acetic acid this acid gives a chlorohexenoic acid with the chlorine at the double bond, since its hydrolysis gives a keto acid, which was characterized as its 2,4-dinitrophenylhydrazone. Finally, hydrogenation of the chlorohexenoic acid over Pd/BaSO₄ gave hexanoic acid, which was identified as its amide:

The linear structure of the dimer may therefore be considered to be proved unequivocally. Also, the presence of the grouping $CH_2ClCHClCCl_2$ — in the dimer was shown by a study of the reaction of the dimer with zinc and by the transformations of the products. The reaction of the hexachlorohexene with zinc goes stagewise with simultaneous formation of 1,1,4,6-tetrachloro-1,4-hexadiene, 1,1,4-trichloro-1,4-hexadiene, and 1,1-dichlorohexadiene, i.e., it appears that in the first place two chlorine atoms are eliminated from neighboring carbon atoms with formation of a compound that can readily undergo replacement of only one chlorine atom under the action of diethylamine:

$$CCl_{2} = CHCH_{2}CCl_{2}CHClCH_{2}Cl \xrightarrow{Zn} CCl_{2} = CHCH_{2}CCl = CHCH_{2}Cl$$

$$\downarrow HN (C_{2}H_{s})_{2}$$

$$CCl_{2} = CHCH_{2}CCl = CHCH_{2}N (C_{2}H_{5})_{2}$$

There then occurs the reduction of the allyl chlorine atom with formation of $CCl_2 = CHCH_2CCl = CHCH_3$; the presence of the -CH = CCl grouping in this was shown by the hydrolysis of this trichlorohexadiene in the cold to the corresponding ketone, which was characterized as its 2,4-dinitrophenylhydrazone:

The formation of 1,1-dichloro-1,4-hexadiene shows that partial reduction occurs also of the vinyl chlorine atom:

$$CCl_2 = CHCH_2CCl = CHCH_3 \rightarrow CCl_2 = CHCH_2CH = CHCH_3$$

Hence, scheme (2), which includes the rearrangement of the radical ClCH₂CHCCl₃ into the radical ClCH₂CHClCCl₂ and the formation of a dimer of structure ClCH₂CHClCCl₂CH₂CH=CCl₂, appears to be the most probable scheme. If the mechanism of the polymerization of 3,3,3-trichloropropene is similar to that of its dimerization, then it may be supposed that as a result of rearrangement of the growing radical with 1,2-migration of chlorine, the polymer will consist of elementary units of structure $-CH_2CHClCCl_2-$.

EXPERIMENTAL

Dimerization of 3,3,3-Trichloropropene. A solution of 50 g of 3,3,3-trichloropropene in twice that amount of benzene was heated at 80-85° for eight hours. In the course of this time 0.5 g of benzoyl peroxide was added in hourly portions. A mixture of benzene and trichloropropene was distilled off at 100 mm; the residue amounted to

16 g. On distillation of the residue we isolated 13.5 g (27%) of the dimer of 3,3,3-trichloropropene (1,1,4,4,5,6-hexachloro-1-hexene); b.p. 107° (1 mm); n_D^{20} 1.5370; d_4^{20} 1.5541. According to Firstov [2]: b.p. 114° (1.5 mm); n_D^{20} 1.5370; d_4^{20} 1.5452. Found: C 24.98; 24.88; H 1.99; 2.04%; MR 58.45; C₆H₆Cl₆. Calculated: C 24.78; H 2.08%; MR 58.64.

The low-boiling distillate was washed with sodium carbonate solution and with water, dried over CaCl₂, and distilled through a column. We then isolated 27 g of 3,3,3-trichloropropene; b.p. 101-102°; n_D^{20} 1.4680; d_4^{20} 1.3286 (the literature [1] gives: b.p. 101-102°; n_D^{20} 1.4680; d_4^{20} 1.3292); also 3.5 g of 1,1,3-trichloropropene; b.p. 131-132°; n_D^{20} 1.4940; d_4^{20} 1.3944 (the literature [1] gives: b.p. 131-132°; n_D^{20} 1.4938; d_4^{20} 1.3940).

Hydrolysis of 1,1,4,4,5,6-Hexachloro-1-hexene. With stirring, 13 ml of 95% sulfuric acid was added to 5 g of the hexachlorohexene. The liberation of hydrogen chloride began at 60°. The reaction was accompanied by resinification. The reaction solution was poured onto ice and extracted with chloroform. Acid products were extracted with sodium carbonate solution. The alkaline extract was acidified, and the acid was extracted with chloroform. Distillation gave 2.7 g (62%) of 4,4,5,6-tetrachlorohexanoic acid; b.p. 160-161° (2 mm); m.p. 56° (from petroleum ether). Found: C 28.34; 28.53; H 3.20; 3.25; Cl 55.56; 55.87; C₆H₈Cl₄O₂. Calculated: C 28.27; H 3.17; Cl 55.63%.

Action of Zinc on 4,4,5,6-Tetrachlorohexanoic Acid. With stirring 5 g of the tetrachlorohexanoic acid in 5 ml of acetic acid was added dropwise to 8 g of zinc dust in 10 ml of acetic acid. Reaction went with the rise in temperature. After the addition of all the acid the reaction mixture was heated in a boiling water bath for three hours. The mixture was cooled, the precipitate was filtered off, and the filtrate was diluted with water and repeatedly extracted with ether. The ether extract was dried over calcium chloride, ether and acetic acid were distilled off, and the residue was vacuum-distilled. We obtained 1.5 g (52%) of 4-chloro-4-hexenoic acid; b.p. 100° (2 mm); n_D^{20} 1.4620; d_4^{20} 1.1190; found MR 35.68; calculated MR 35.84. By the hydrolysis of this acid with 95% sulfuric acid in the cold we obtained 4-oxohexanoic acid. The 2,4-dinitrophenylhydrazone had m.p. 183-184° (from acetic acid). Found: C 46.05; 46.27; H 4.68; 4.65; N 17.78%. C₁₂H₁₄N₄O₆. Calculated: C 46.45; H 4.56; N 18.06%.

<u>Hydrogenation of 4-Chloro-4-hexenoic Acid.</u> To 0.5 g of freshly reduced Pd/BaSO₄ we added 0.7 g of the chlorohexenoic acid in 1 ml of absolute ethanol and 3 ml of absolute ethanol saturated with ammonia. Hydrogenation was carried out at room temperature, and after 20 minutes the theoretical amount of hydrogen had been absorbed. The alcoholic solution was filtered from catalyst and ammonium chloride and evaporated. The residue was dissolved in water, and the solution was acidified with hydrochloric acid and extracted with ether. Ether was distilled off, and we then obtained 0.4 g (71%) of hexanoic acid, which, without being distilled, had the following constants: n_D^{20} 1.4180; d_4^{20} 0.9310; found MR 31.41; calculated MR 31.44. The literature [8] gives: n_D^{20} 1.4165; d_4^{20} 0.9280. Its amide had m.p. 101° (from water); the literature [9] gives m.p. 100-101°. A mixture with known hexanamide melted without depression.

Action of Zinc on 1,1,4,4,5,6-Hexachloro-1-hexene. With stirring, 10 g of the dimer in 10 ml of glacial acetic acid was added dropwise to 5 g of zinc dust in 10 ml of glacial acetic acid. The reaction was accompanied by the evolution of heat. To complete reaction the mixture was heated for 30 minutes at 90°. Water was added to the cooled solution, and the organic layer was separated and dried over CaCl₂. After two fractional distillations we isolated the following products: I: 1,1-dichlorohexadiene (0.9 g; 17.7%); b.p. 64-65° (30 mm); n_D²⁰ 1.4750; d₄²⁰ 1.0933. Found: C 47.60; 47.68; H 5.27; 5.32%; MR 38.88. C₆H₈Cl₂. Calculated: C 47.71; H 5.34%; MR 38.71. II: 1,1,4-trichloro-1,4-hexadiene (1.05 g; 16.4%); b.p. 71-72° (8 mm); n_D²⁰ 1.5020; d₄²⁰ 1.2488. Found: C 38.90; 38.67; H 3.86, 3.91%; MR 43.83. C₆H₇Cl₃. Calculated: C 38.85; H 3.80%; MR 43.57.

By the hydrolysis of this trichlorohexadiene with sulfuric acid at 40° we obtained 6,6-dichloro-5-hexen-3-one. 2,4-Dinitrophenylhydrazone, m.p. 104-105° (from alcohol). Found: C 41.67; H 3.61; Cl 20.18%. $C_{12}H_{12}Cl_{2}N_4O_4$. Calculated: C 41.51; H 3.48; Cl 20.43%. III: 1,1,4,6-tetrachloro-1,4-hexadiene (1.55 g; 24%); b.p. 100-101° (2 mm); n_D^{20} 1.5090; d_4^{20} 1.3556. Found: C 32.59; 32.63; H 2.64; 2.67%; MR 48.44. C₆H₆Cl₄. Calculated: C 32.76; H 2.75%; MR 48.44. The picrate of the diethylamine derivative had m.p. 134-135° (from alcohol). Found: C 39.77; 40.03; H 4.03; 4.03; N 11.45; 11.39%. C₁₆H₁₉Cl₈N₄O₇. Calculated: C 39.56; H 3.94; N 11.54%.

SUMMARY

1. The homolytic dimerization of 3,3,3-trichloropropene was studied. The dimer has a normal structure and is 1,1,4,4,5,6-hexachloro-1-hexene.

2. The formation of a dimer of normal structure in the dimerization of 3,3,3-trichloropropene is explained by the rearrangement of the intermediately formed radical with 1,2-migration of chlorine.

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