Nitrogen was used to flush the system before and after each experiment and a very small stream was fed through the tube during the experiment.

The pyrolyzate issuing from the hot portion was cooled to condense vapors; permanent gases were collected over acid-salt solution. The liquid product was distilled (after a small amount of hydroquinone was added to prevent polymerization) to determine the nature and amounts of the products.

Acrylamide-Acid Fractions.—Even when an efficient column was used to distill the dimethylacetoxypropionamide pyrolyzates, the yield of the acrylamide fraction was high (Table I), and titration of this fraction revealed an acid (approximately 15%, computed as acetic). A very careful redistillation of the acrylamide fraction from the pyrolyzate of experiment 8 through a 50-plate column did not isolate two fractions of the same acid content or refractive index, despite boiling point constancy. The acid contents in this distillation ranged from 70 to 2%; the average content was 21%. In a number of instances a *p*-bromophenacyl ester of the acid was obtained from the sodium salt and *p*-bromophenacyl bromide; it melted at 84–85° and when mixed with authentic *p*-bromophenacyl acetate the melting point of the mixture was the same. On the basis of the melting point of the bromophenacyl ester and the discrepancy between titratable acidity and acetic acid recovered from the pyrolyzates by distillation (Table I), it is believed that most or all of the acid associated with the acrylamide was acetic acid.

Several unsuccessful attempts were made to separate the acid and the acrylamide by azeotropic distillation. Excess heptane was added to one sample of the impure dimethylacrylamide to strip out acetic acid as the heptane–acetic acid azeotrope. The heptane distilled almost acid free. To another sample was added excess toluene for a similar purpose. Here some acid was removed, but a 300% excess of toluene removed less than half the acid. A third sample was distilled with a 500% excess of triethylamine to distil out the high-boiling acid–amine azeotrope,[24] but no appreciable purification resulted.

A synthetic mixture of dimethylacrylamide (prepared from acrylyl chloride and dimethylamine), glacial acetic acid and heptane was not effectively fractionated into pure components by a 37-plate still; the heptane fractions contained 5 to 6% acetic acid and the amide fractions 6 to 39% acid. No pure acid was obtained.

The most satisfactory method of purifying the dimethylacrylamide comprised treating the acidic amide fraction with either excess anhydrous sodium carbonate or the theoretical quantity of 50% aqueous sodium hydroxide, filtering and distilling the filtrate (in the presence of hydroquinone) under reduced pressure. The recovery of dimethylacrylamide (containing about 2% acid) after one such treatment was approximately 70%. Dimethylacrylamide obtained by the complete removal of acidic impurities (by further treatment with base) followed by redistillation had properties (b. p., 73.5–74° at 16.5 mm.; d^{20}_4 0.9651; n^{20}_D, 1.4732; M^{20}_D, 28.81; N found, 14.25; calcd., 14.13) similar to those of the amide prepared from acrylyl chloride and dimethylamine.

Summary

N,N-Dimethyl-α-acetoxypropionamide resembles methyl α-acetoxypropionate in that thermal decomposition yields acetic acid and the corresponding acrylic acid derivative. Pyrolysis affords a convenient method of converting lactic acid, through the acetyl derivative of N,N-dimethyllactamide, into N,N-dimethylacrylamide. The dimethylacrylamide polymerizes readily, yielding a hard, transparent, water-soluble polymer.

[24] H. S. Van Klooster and W. A. Douglas, *J. Phys. Chem.*, **49**, 67 (1945).

PHILADELPHIA 18, PA.

RECEIVED JANUARY 9, 1947

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO.]

Pentachlorophenyl Derivatives. I. The β-Chlorination of Ethylpentachlorobenzene and the Preparation of Pentachlorostyrene

BY SIDNEY D. ROSS, MOUSHY MARKARIAN AND MATTHEW NAZZEWSKI

It is reported in the patent literature[1] that direct chlorination of ethylpentachlorobenzene gives 1-pentachlorophenyl-1-chloroethane having m. p. 52.5° and b. p. 193–203° at 15 mm. and that, furthermore, treatment of this product with heat or alcoholic potassium hydroxide gives pentachlorostyrene, which boils at 311–312° and is not polymerized by heat, acid or sunlight. We have not found it possible to repeat these results and were consequently led to study the peroxide-catalyzed sulfuryl chloride chlorination as well as the direct chlorination of ethylpentachlorobenzene.

We find that when ethylpentachlorobenzene is heated to 200° and illuminated with a 200-watt unfrosted bulb it rapidly takes up chlorine to give, in addition to recovered starting material, three products, none of which have the properties of the reported 1-pentachlorophenyl-1-chloroethane. The major product is a solid, I, analyzing correctly for $C_8H_4Cl_6$ and melting at 89–90°. It can be recovered unchanged after refluxing for forty-eight hours in glacial acetic acid containing an equivalent of potassium acetate. The same product can be obtained in 55% yield by ring chlorination of 1-phenyl-2-chloroethane by the excellent method of Silberrad[2] which employs sulfuryl chloride as the chlorinating agent and aluminum chloride and sulfur monochloride as the catalysts. This would seem to indicate that I is 1-pentachlorophenyl-2-chloroethane, but since there is some danger of rearrangement in the Silberrad reaction we prepared 1-pentachlorophenyl-1-chloroethane, VI, by the unambiguous route indicated below. Pentachlorotoluene, II, was prepared as directed by Silberrad.[2] It was chlorinated to give pentachlorobenzal chloride, III, following the procedure of Lock.[3] In hydrolyzing III to pentachlorobenzaldehyde, IV, we have

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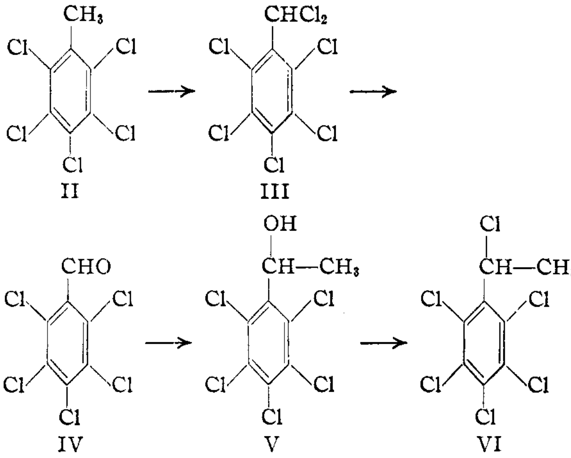
[1] Levine and Cass, "Chlorinated Aromatic Hydrocarbons," U. S. Patent 2,193,823, March 19, 1940.

[2] Silberrad, *J. Chem. Soc.*, **127**, 1267 (1925).

[3] Lock, *Ber.*, **66**, 1527 (1933).



II III

IV V VI

found the procedure of Newton[4] more convenient than that reported by Lock.[3] Treatment of IV with a methyl Grignard gave methyl pentachlorophenylcarbinol, V, which reacted readily with thionyl chloride to give the desired 1-pentachlorophenyl-1-chloroethane, VI, which is the only hitherto unreported compound in this series of reactions. The α-chloride, VI, proved to be a solid melting at 103.5–104.5° which, unlike the β-chloride, I, is unstable to distillation. Moreover, both chlorides, I and VI, on treatment with alcoholic potassium hydroxide give pentachlorostyrene, VII, which we find is a white crystalline solid which melts from 113–114.5°, polymerizes with benzoyl peroxide, and can be co-polymerized with other monomers.[5] The styrene, VII, was also obtained by dehydrating methyl pentachlorophenylcarbinol, V, over aluminum oxide. There is no doubt as to the structures of the two chlorides, I and VI, and the styrene, VII.

In addition to 1-pentachlorophenyl-2-chloroethane we isolated from the high-temperature chlorination lesser quantities of two solids. The first was present in the fractions of ethylpentachlorobenzene, from which it was readily separable by virtue of its relative insolubility in cold chloroform and trichloroethylene. After purification the solid melted at 227–229° and was shown to be hexachlorobenzene by a mixed melting point with an authentic sample, obtained from the Hooker Electrochemical Company.

The second solid was isolated from the final fraction obtained on distillation of the crude chlorination product. It has not as yet been completely characterized, but analysis indicates it has the empirical formula, $C_8H_2Cl_8$, and it is in all probability a trichloroethylpentachlorobenzene.

When the chlorination was carried out at 68–73° the product obtained differed in composition from that obtained at 200°. The initial stages of the distillation were accompanied by extensive evolution of hydrogen chloride. A crude distillation indicated the presence of hexachlorobenzene, 1-pentachlorophenyl-2-chloroethane, and a third product which came over at about the same temperature as ethylpentachlorobenzene. To facilitate isolation of this third product we added 10% more than the theoretical amount of chlorine to minimize the amount of unreacted ethylpentachlorobenzene. When this was done we found that the early distillation fractions were largely pentachlorostyrene. The only other product which we could isolate from the early fractions was hexachlorobenzene. The separation of the hexachlorobenzene from the styrene, VII, proved more difficult than its separation from ethylpentachlorobenzene, but the technique used was the same in both instances. Pentachlorostyrene is, of course, not a primary product of the chlorination reaction. It is our opinion that it is formed during the early stages of the distillation by loss of hydrogen chloride from 1-pentachlorophenyl-1-chloroethane. We have found that the pure α-chloride, VI, readily loses hydrogen chloride when subjected to the same conditions of temperature and pressure that prevail in the distillation of the chlorination product. However, our efforts to isolate undecomposed 1-pentachlorophenyl-1-chloroethane from the chlorination mixture have proved unsuccessful. The major product again proved to be 1-pentachlorophenyl-2-chloroethane.

This preponderance of β-chlorination was unexpected. The peroxide-catalyzed sulfuryl chloride chlorination of Kharasch[6] is reported to attack aromatic side chains in the α-position, and we were, therefore, interested in determining whether or not this mode of chlorination would give α-chlorination of ethylpentachlorobenzene. When the reaction was run with an excess of ethylpentachlorobenzene using benzoyl peroxide as catalyst hydrogen chloride was slowly evolved over a seventeen-hour period. After this period more than half of the ethylpentachlorobenzene could be recovered unchanged and the only products obtained were hexachlorobenzene and 1-pentachlorophenyl-2-chloroethane. Neither the α-chloride, VI, nor pentachlorostyrene could be isolated from the reaction. Even when the reaction was run using an excess of sulfuryl chloride and heating until exactly the theoretical quantity of hydrogen chloride was evolved, no product other than hexachlorobenzene and the β-chloride, I, could be isolated.

That the Kharasch chlorination does not reverse the direction of substitution is not surprising. Both in this reaction and in the direct chlorination the product determining step is reaction I in which a chlorine atom abstracts a hydrogen atom

$$C_6Cl_5CH_2CH_3 + Cl\cdot \longrightarrow C_6Cl_5CH_2CH_2\cdot + HCl \quad (I)$$

from ethylpentachlorobenzene to give a new free

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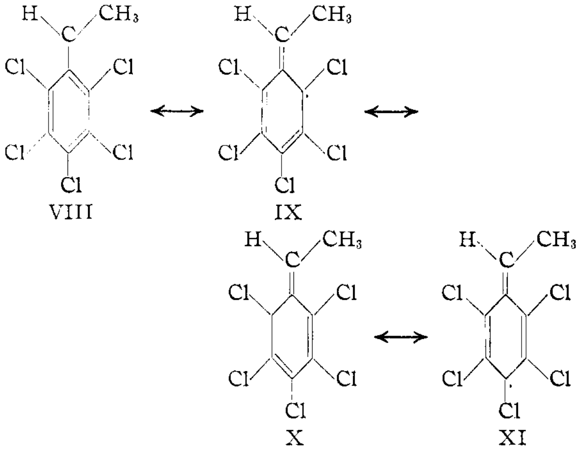
[4] Newton, "Manufacture and Production of Pentachlorobenzaldehyde and Dyestuffs Derived Therefrom," British Patent 29,143; December 14, 1911.

[5] Work on the polymerization characteristics of pentachlorostyrene is now in progress in these laboratories and will be reported on at some future date.

[6] Kharasch and co-workers, THIS JOURNAL, **61**, 2142, 3432 (1939); **62**, 925, 3435 (1940); **63**, 526 (1941).

radical. Since the two reactions can be run at the same temperature they differ only in the nature of the medium and the method of generating the chlorine atoms. It is, however, surprising that the hydrogen atom should be abstracted from the β-position for the free radical formed in this case cannot distribute its odd electron, whereas the free radical which would be formed by abstraction of a hydrogen atom from the α-position could be stabilized by the contributing structures VIII–XI. An explanation which immediately suggests itself is that interference between the *ortho* chlorine atoms and the methyl group in structures IX, X and XI prevents a planar configuration about the extracyclic double bond in these structures and thus reduces the mesomerism indicated by structures VIII–XI. The low dipole moment of nitrodurene as compared to nitrobenzene is attributed to such an effect.[7] However, this explanation is not completely satisfactory, for as will be shown in paper II of this series, on bromination ethylpentachlorobenzene gives 1-pentachlorophenyl-1-bromoethane as the major product, and it is difficult to see why an ortho effect[8] should operate in the chlorination but not in the bromination. An answer to this apparent anomaly will have to await a more intimate knowledge of the mechanisms of the reactions involved.


VIII IX X XI

Experimental[9]

Direct Chlorination of Ethylpentachlorobenzene.—Ethylpentachlorobenzene (772 g., 2.76 moles), obtained from the Dow Chemical Company, was placed in a one-liter, three-necked flask equipped with a chlorine inlet tube, reflux condenser and thermometer and heated to 200°. The liquid was then illuminated with a 200-watt unfrosted bulb set close to the reaction flask, and chlorine, dried by bubbling through concentrated sulfuric acid, was run in until the gain in weight was 80 g. (84% of the theoretical). The crude product was distilled at 0.9 mm. through a 10-inch Widmer column with heated jacket yielding the following fractions: (1) 80 g., b. p. 120–132°; (2) 200 g., b. p. 132–135°; (3) 93 g., b. p. 135–138°; (4) 74 g., b. p. 138–154°; (5) 319 g., b. p. 154–160°; (6) 48 g., b. p. 160–164°. In working up these fractions our primary interest was in isolating and identifying all of the products formed rather than in isolating the maximum possible yield of any particular product. Attempts to purify fractions 1–4 by crystallization from 95% ethanol were attended by extensive loss of material and in every case the crystallized product melted over a wide range. By treating these fractions with their own weight of cold trichloroethylene they could be separated into a soluble and insoluble portion. The insoluble portions proved identical in each case and they were combined and crystallized several times from boiling trichloroethylene yielding 15 g. of a solid melting at 227–229° which was shown to be hexachlorobenzene since it gave no depression on mix-melting with an authentic sample obtained from the Hooker Electrochemical Company. On removal of the solvent from the soluble portions of fractions 1–3 the same solid melting at 51–53° was obtained in each case. A mixed-melting point with ethylpentachlorobenzene showed no depression. When the soluble portion of fraction 4 was treated in the same manner a solid melting at 80–84° was obtained. Several crystallizations from 95% ethanol raised the melting point to 89–90°. This was later identified as 1-pentachlorophenyl-2-chloroethane, I.

Anal. Calcd. for $C_8H_4Cl_6$: C, 30.71; H, 1.29. Found: C, 30.70, 30.52; H, 1.40, 1.26.

Fraction 5 on crystallization from 95% ethanol also gave 1-pentachlorophenyl-2-chloroethane. However, almost half of the material was lost during the purification process. Fraction 6 on crystallization from 95% ethanol gave 24.5 g. of a solid melting from 90–93°. Recrystallization gave a solid melting sharply at 93–94°; mix melting points with I, VI and VII showed a strong depression. This compound has not been completely characterized but analysis indicates it is probably a trichloroethylpentachlorobenzene.

Anal. Calcd. for $C_8H_2Cl_8$: C, 25.12; H, 0.52. Found: C, 25.29, 25.44; H, 0.72, 0.56.

In the chlorination of 2 moles of ethylpentachlorobenzene (557 g.) at 68–73° addition of chlorine was continued until 10% more than the theoretical weight of chlorine had been added. When distillation of the crude product was attempted there was extensive evolution of hydrogen chloride. The crude product was warmed and evacuated with a water pump until this gas evolution stopped and was then distilled yielding the following fractions: (1) 140 g., b. p. 152–177° at 8.5 mm.; (2) 93 g., b. p. 175–181° at 8 mm.; (3) 325 g., b. p. 183–191° at 7 mm. Fractions 1 and 2 were separated into soluble and insoluble portions by treatment with an equal weight of chloroform. In both cases the insoluble portion proved to be hexachlorobenzene. The filtrates were evaporated to dryness and the solids obtained were crystallized from 95% ethanol. The solid obtained was pentachlorostyrene, VII, but it was still contaminated with hexachlorobenzene and several repetitions of the chloroform treatment and crystallization were necessary before a reasonably pure sample, m. p. 108–113°, could be obtained. More than 50% of the material was lost during this extensive purification process. The sample finally obtained showed no depression with pure pentachlorostyrene and polymerized to a resin when heated with a small amount of benzoyl peroxide. Fraction 3 after several crystallizations from 95% ethanol gave a better than 50% yield of 1-pentachlorophenyl-2-chloroethane, I, m. p. 89–90°. No other compounds could be isolated from the reaction mixture.

Peroxide-catalyzed Sulfuryl Chloride Chlorination of Ethylpentachlorobenzene.—In typical runs redistilled ethylpentachlorobenzene (348 g., 1.25 mole) and redistilled sulfuryl chloride (135 g., 1 mole) were refluxed with 0.75 g. of benzoyl peroxide. The rate of hydrogen chloride evolution was slow. To follow the progress of the reaction we collected the effluent gases in a known volume of potassium hydroxide solution after first letting them pass through a condenser packed with glass beads and a Dry Ice condenser to trap out entrained sulfuryl chloride.

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(7) Ingham and Hampson, *J. Chem. Soc.*, 981 (1939).

(8) For an excellent discussion of the ortho effect see Watson, "Modern Theories of Organic Chemistry," Oxford University Press, New York, N. Y., 1941, pp. 241–254.

(9) The microanalyses were performed by Dr. Carl Tiedcke.

Aliquots of the absorbing solution were analyzed for chloride ion by the Volhard method. In this way it was possible to show that the reaction had a long induction period which could be shortened by starting with redistilled materials or by adding fresh benzoyl peroxide. Also, the use of excess sulfuryl chloride gave a faster rate of hydrogen chloride evolution. In a run using the quantities indicated above, hydrogen chloride was slowly evolved over a seventeen-hour period. At the end of this period unreacted sulfuryl chloride was removed at the water pump and the crude product was distilled at 0.35 mm. through a heated 16-inch Vigreux column yielding the following fractions: (1) 141 g., b. p. 115–125°; (2) 85 g., b. p. 125–129°; (3) 102 g., b. p. 129–138°; (4) 26 g., b. p. 138–141°.

By treating fraction 1 with chloroform as before it was possible to separate 8 g. of hexachlorobenzene. Removal of the chloroform gave recovered ethylpentachlorobenzene. Fraction 2 was crystallized repeatedly from 95% ethanol. This raised the melting point slightly but did not narrow the range. By crystallizing from acetic acid we succeeded in isolating 6 g. of 1-pentachlorophenyl-2-chloroethane, I, m. p. 85–87°, mixed melting point with pure I, 87–89°. No other pure compound could be isolated from this fraction. Fractions 3 and 4 after several crystallizations from 95% ethanol gave pure I. In both cases the yields of pure product were about 40% and no other products could be isolated.

1-Pentachlorophenyl-2-chloroethane, I.—To a mixture of 1-phenyl-2-chloroethane (68.3 g., 0.5 mole) and aluminum chloride (2.5 g.) in a two-necked flask, fitted with an efficient reflux condenser and a dropping funnel was added dropwise a mixture of sulfuryl chloride (404 g.) and sulfur monochloride (4.1 g.). The addition required two hours and the reaction mixture was maintained between 70 and 85° during the addition. Heating was continued for an additional hour after which the evolution of hydrogen chloride ceased. The reaction mixture was taken up in benzene and washed with dilute hydrochloric acid and water. The benzene solution was dried and distilled yielding 87 g. (55%) of product of b. p. 185–197° at 11 mm. and melting point 77–81°. Two crystallizations from 95% ethanol raised the m. p. to 89–90°.

Pentachlorobenzaldehyde, IV.—Pentachlorotoluene, II, was prepared according to Silberrad[2] and converted to pentachlorobenzal chloride, III, as directed by Lock.[3] The hydrolysis of the pentachlorobenzal chloride is herein described because the procedure followed is in the less available patent literature.[4] Pentachlorobenzal chloride (531 g.) was treated with 2655 g. of 20% fuming sulfuric acid at 50–60° for two hours and 80° for one hour. After standing overnight at room temperature, the mixture was poured onto crushed ice. The white precipitate obtained was filtered with suction and washed with water. The crude product was crystallized from boiling benzene containing enough alcohol to decrease the solubility yielding 398 g. of the aldehyde melting at 196°. This was used without further purification.

Methylpentachlorophenylcarbinol, V, was prepared as directed by Lock,[3] the only change being that methylmagnesium bromide was used in place of methylmagnesium iodide.

1 - Pentachlorophenyl - 1 - chloroethane, VI.—Thionyl chloride (28.6 g., 0.24 mole) in 50 cc. of benzene was added dropwise to methylpentachlorophenylcarbinol (29.45 g., 0.1 mole) in 75 cc. of benzene and at the same time the mixture was heated slowly until refluxing began. Refluxing was continued until the evolution of hydrogen chloride had become negligible (about four hours). The excess thionyl chloride and benzene were then removed with the water pump. The crude product was crystallized from ethanol, decolorizing with Darco in the process, yielding 20.9 g. (66%) of 1-pentachlorophenyl-1-chloroethane m. p. 99–101.5°. Crystallization from acetone raised the melting point to 103.5–104.5°.

Anal. Calcd. for $C_8H_4Cl_6$: C, 30.71; H, 1.29. Found: C, 30.58, 30.80; H, 1.40, 1.24.

Pentachlorostyrene, VII, from V.—Molten methylpentachlorophenylcarbinol (30 g., 0.02 mole) was dropped into a glass tube, 18-inches long and 1-inch in diameter, fitted with standard taper joints at top and bottom, and filled to 15 inches of its length with Harshaw aluminum oxide pellets. The tube was wrapped with a heating element and maintained at 340° and was connected to a receiver which was chilled in a Dry Ice-bath. The receiver was kept evacuated to 42 mm. with a water pump during the addition of the molten carbinol which required twenty to twenty-five minutes. The product collected in the receiver was a slightly yellowish melt. This was extracted with 500 cc. of boiling methanol. On cooling crystals deposited. These were filtered off and the crude product was again extracted using the same 500 cc. of methanol. Four such extractions yielded in all 17 g. (61%) of the styrene, m. p. 109–112°. Crystallization from ethanol raised the melting point to 113–114.5°.

Anal. Calcd. for $C_8H_3Cl_5$: C, 34.72; H, 1.10; mol. wt., 276.5. Found: C, 34.45, 34.58; H, 1.13, 1.01; mol. wt. by Rast, 279.5, 275.6.

Pentachlorostyrene from I.—Crude 1-pentachlorophenyl-2-chloroethane melting at 84–85° (6.26 g., 0.02 mole) was refluxed for three hours with a solution of 1.5 g. of potassium hydroxide in 30 cc. of absolute ethanol. Ethanol (100 cc.) was added and the solution was filtered boiling hot. The filtrate was diluted to 300 cc. with water. On standing crystals separated. These were crystallized from methanol yielding 3.35 g. (60%) of the styrene, m. p. 106–108.5°. Crystallization from ethanol raised the melting point to 113–114.5° and a mix melting point with the styrene prepared by dehydration of the carbinol showed no depression.

Pentachlorostyrene from VI.—Treatment of 1-pentachlorophenyl-1-chloroethane, VI, as above gave a mixture of oil and crystals from which it was possible to isolate only a 3.6% yield of the pure styrene.

Summary

The major product isolated from the chlorination of ethylpentachlorobenzene is 1-pentachlorophenyl-2-chloroethane.

Methods of preparation and structural proofs for 1-pentachlorophenyl-2-chloroethane, 1-pentachlorophenyl-1-chloroethane and pentachlorostyrene are described.

NORTH ADAMS, MASSACHUSETTS

RECEIVED FEBRUARY 25, 1947