nm (ϵ 9660), 279 (960), 286 (745); nmr (DMSO-d_6) δ *ca.* 7.8 (m, 3, aromatic), 5.07 (s, 2, CH_2SO_2), 2.91 ppm (s, 3, SO_2CH_3).

Anal. Calcd for $C_9H_9ClO_4S$: C, 43.46; H, 3.65; Cl, 14.26; 14.26; S, 12.90. Found: C, 43.47; H, 3.65; Cl, 14.45; S, 12.76.

Registry No.—**3**, 7499-07-2; **4**, 7499-06-1; **5**, 31579-08-5; **6**, 31579-09-6; *p*-chlorobenzotrifluoride, 98-56-6; methylsulfinyl carbanion, 13810-16-7.

Acknowledgment.—We wish to thank Dr. Harold R. Almond for the spectroscopic data and his assistance in their interpretation.

An Investigation of the Formation of By-Products in the Nitration of Pentachlorobenzene

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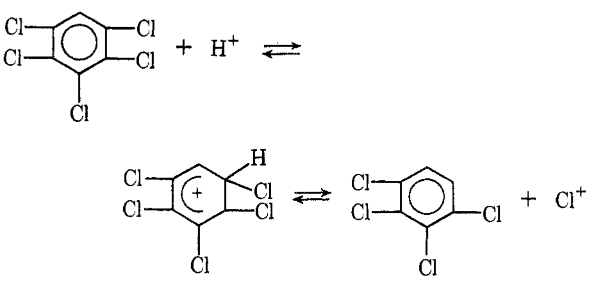
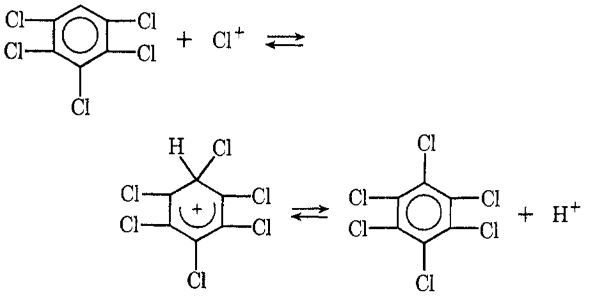
Pentachloronitrobenzene (PCNB) is an extensively used soil fungicide produced by both foreign and domestic manufacturers. A variety of methods have been used in the production of PCNB,[1-3] but it is commonly prepared by the direct nitration of pentachlorobenzene (PCB).

We have observed in our investigation of this process that the desired PCNB is produced in 83–89% yield based on the amount of PCB reacting, some unchanged PCB being recovered due to sublimation thus removing it from the nitrating mixture. Careful analysis of the reaction mixture by gas chromatography showed that a by-product, hexachlorobenzene (HCB), is formed during the course of reaction.

It was first suspected that the possible displacement of a chloronium ion from the PCB by a proton from the acids employed, with subsequent attack of this chloronium ion on PCB, would lead ultimately to formation of HCB. This mechanism may be represented by eq 1 and 2. This route was discarded as a likely mechanism when only two products, HCB and PCNB, were found in the reaction mixture; no detectable amount of tetrachlorobenzene was produced in the nitration of PCB. In addition, no hexachlorobenzene or tetrachlorobenzene could be detected when PCB was heated with fuming sulfuric acid, even for extended periods of time.


(1)


(2)

In subsequent studies of the nitration of PCB, the presence of molecular chlorine as a reaction product was established. It has then been postulated that the molecular chlorine arose *via* destructive oxidation of PCB since it is known that ring oxidation is sometimes a significant side reaction in the direct nitration of aromatic systems.[4] The destructive oxidation process of PCB would be expected to give, in addition to molecular chlorine, low-molecular-weight fragments. Infrared and nmr analysis of the off-gas from the nitration process established the presence of the products identified generally as low-molecular-weight carboxylic acids. No aromatic products were observed in the off-gas. Subsequent attack of the molecular chlorine on PCB would lead to the formation of the observed HCB. The process involves chlorination of the aromatic system in the absence of catalyst (ZnX_2, FeX_3, etc.) normally employed in halogenations. The reaction path followed is probably similar to that suggested in earlier halogenation studies by Keefer and Andrews.[5,6] The molecular chlorine reacts with the PCB to form an aromatic halogen π complex, which collapses into a σ complex as a result of attack on the halogen–halogen bond by a polar reagent. It has been suggested[5] that in the absence of a catalyst the halogen itself may fill the role of the polar reagent. However, under the conditions of the nitration of PCB, there are a number of species formed that are stronger electrophilic reagents than chlorine and are more likely to function as the polar reagent.

It has also been observed that HCB is formed in small amounts when PCB is heated with fuming nitric acid, the amount of HCB formed in a given time being increased by the introduction of anhydrous chlorine. Treatment of PCB with anhydrous chlorine in the presence of hydrochloric acid or anhydrous hydrogen chloride gave no detectable amount of HCB in reaction periods up to 1.5 hr. This lends support to the concept that chlorination of PCB to form HCB is promoted by some polar reagent formed during the nitration process or by nitric acid itself.

Experimental Section

Gas chromatographic analyses were performed on a Hewlett-Packard F & M Model 700 chromatograph. Columns used in this study were 10% OV-17 silicone on Chromosorb G, H. P., 80–100 mesh, 5% Carbowax 20M on Anakrom AS, 80–90 mesh, and 5% Aroclor 1232 on Chromosorb T, 40–60 mesh. Ir spectra

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[1] H. Furst, H. Dietz, P. Ehrentrant, and P. Rammelt, German (East) Patent 10,655 (Oct. 19, 1955); *Chem. Abstr.*, **52**, P-16288*e* (1956).

[2] E. A. Lojewski, U. S. Patent 30,26358 (March 20, 1962); *Chem. Abstr.*, **57**, 7170*f* (1962).

[3] M. Hedayatullah, C. Olle, and L. Dienville, *C. R. Acad. Sci., Ser. C*, **264**, 106 (1967); *Chem. Abstr.*, **66**, 104756*e* (1968).

[4] J. Hine, "Physical Organic Chemistry," McGraw-Hill, New York, N. Y., 1956, p 332.

[5] R. M. Keefer and L. J. Andrews, *J. Amer. Chem. Soc.*, **78**, 5626 (1956).

[6] L. J. Andrews and R. M. Keefer, *ibid.*, **79**, 5172 (1957).

were obtained with a Perkin-Elmer Model 337 spectrophotometer. Nmr spectra were obtained on a Varian A-60D spectrometer and in reference to benzene as an internal standard.

Nitration of Pentachlorobenzene (Runs 1, 2, and 3).—Pentachlorobenzene (25.0 g, 0.1 mol) was heated to 140°. The nitrating mixture, consisting of 9.0 ml of fuming nitric acid (Baker analyzed reagent) in 31.0 ml of fuming sulfuric acid (Baker analyzed reagent, 30–33%), was added to the liquid pentachlorobenzene, maintaining a temperature of 140–145° during the addition. After addition of the nitrating mixture was completed, the temperature was held at 150–155° for a period of 1.5 hr. The reaction mixture was cooled to room temperature and the solid product was collected by suction filtration, followed by thorough washing with cold water. The product was dried under reduced pressure.

Run 4.—The procedure was identical with that employed in runs 1–3, except 75.0 g of pentachlorobenzene was used. The nitrating mixture consisted of 27.0 ml of fuming nitric acid and 93.0 ml of fuming sulfuric acid. Gas chromatographic analysis of the reaction mixture on the OV-17 and on the more polar Carbowax columns showed only two products, pentachloronitrobenzene (PCNB) and hexachlorobenzene (HCB). Identification was based upon retention times on the two columns and the lack of evidence from either column of additional components when standard HCB was added to the mixture of products. Experimental results are summarized in Tables I and II.

TABLE I

Run	Unchanged PCB, g	Yield of PCNB, g	% yield, PCNB
1	3.4	22.2	89.5
2	4.7	21.5	83.7
3	4.0	20.6	83.0
4	18.5	55.5	85.9

TABLE II

GAS CHROMATOGRAPHIC ANALYSIS

Run	Reactant (PCB), %	Product mixture, % by wt	
		PCNB	HCB
1	100	99	1
2	100	98.5	1.5
3	100	98.1	1.9
4	100	98.4	1.6

Collection and Inspection of Off Gases.—The gases liberated during the nitration of pentachlorobenzene were collected as follows.

Fraction 1: off-gases passed into a 50-ml portion of benzene for a 30-min period.

Fraction 2: off-gases passed into a fresh 50-ml portion of chloroform for a 30-min period.

Fraction 3: off-gases passed into a 10% aqueous solution of silver nitrate for a 2-min period. A heavy precipitate, identified as silver chloride, formed.

Fraction 4: off-gases passed into a fresh 50-ml portion of chloroform for a 20-min period.

Ir, Nmr, and Gc Analysis (Fractions 1, 2, and 4).—Ir spectra of fractions 1, 2, and 4 exhibited an intense band at 5.74 μ and a broad, intense band at 3.3 μ indicative of $C=O$ stretching and OH stretching, respectively, in a carboxylic acid dimer. No absorption was observed in the aromatic region of the spectra of fractions 2 and 4.

The nmr spectrum of fraction 1 exhibited a singlet at δ 10.33, representing the carboxylic acid proton. Spectra of fractions 2 and 4 exhibited no acid proton signal, likely due to the use of chloroform as a solvent. Spectra of fractions 2 and 4 also exhibited no aromatic proton signal.

Samples taken from the off-gas stream in front of the solution phase collector were chromatographed on Arochlor 1232. The presence of chlorine in these samples was established by retention time and by increase in chlorine peak area, without evidence of resolution, on addition of chlorine to the off-gas mixture.

Treatment of Pentachlorobenzene with Fuming Sulfuric Acid.—A 5.0-g sample of pentachlorobenzene was added to 18.0 ml of fuming sulfuric acid and the mixture was heated at 150–160° for periods of 1–8 hr. The mixture was cooled to room temperature and poured over crushed ice. The product was collected by suction filtration, thoroughly washed with cold water, and dried. Solid material (5.0 g) was collected. The product was subjected to gas chromatographic analysis and was found to be pure pentachlorobenzene. No trace quantities of other materials were detected.

Treatment of Pentachlorobenzene with Fuming Nitric Acid.—The procedure was identical with that employed in using fuming sulfuric acid. The product was subjected to gas chromatographic analysis and hexachlorobenzene, pentachloronitrobenzene, and pentachlorobenzene were found to be present. The procedure was repeated and anhydrous chlorine was passed through the mixture. It was observed that the amount of hexachlorobenzene forming in a given time increased.

Treatment of Pentachlorobenzene with Hydrogen Chloride and Chlorine.—A 5.0-g sample of pentachlorobenzene was melted and anhydrous hydrogen chloride and chlorine were passed through the melt for 1.5 hr. The mixture was cooled to room temperature, thoroughly washed with water, and collected. The product was subjected to gas chromatographic analysis and was found to be unchanged pentachlorobenzene. No detectable quantities of other materials were detected. The process was repeated using 20.0 ml of concentrated hydrochloric acid rather than anhydrous hydrogen chloride. The result was the same as above.

Registry No.—PCB, 608-93-5; PCNB, 82-68-8; HCB, 118-74-1.

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A Novel Rearrangement of 2-Isocyanato-4-(alkylthio) Acid Chlorides

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α-Isocyanato acid chlorides have been prepared from amino acids, phosgene, and hydrogen chloride.[1] While studying a series of reactions of these materials with various amines, the need arose for 2-isocyanato-(4-methylthio)butyryl chloride. Utilizing the method of Iwakura, Uno, and Kang,[1] methionine was converted to the expected α-isocyanato acid chloride. This was evidenced by the infrared spectrum of the crude product which exhibited peaks at 4.5 (NCO) and 5.65 μ (COCl). However, upon attempted purification by vacuum distillation a vigorous evolution of hydrogen chloride was found to occur. After the evolution of the gas had ceased, the distillation proceeded without further incident.

The infrared spectrum of the reaction product finally obtained after distillation exhibited an intense peak at 4.5 μ characteristic of the isocyanate grouping but lacked the characteristic acid chloride absorbance at 5.65 μ. There was, however, an additional intense absorption at 6.05 μ attributable to a thiol ester grouping. The nuclear magnetic resonance spectrum of this unknown material consisted of a doublet at 1.91 (3 H), a singlet at 2.42 (3 H), and a quartet at 6.53 ppm (1 H) downfield from an internal tetramethylsilane standard in

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[1] Y. Iwakura, K. Uno, and S. Kang, *J. Org. Chem.*, **30**, 1158 (1965).