ane, then with ether, and the dried extracts (magnesium sulfate) were worked up separately.

Removal of the dichloromethane from the first extract by evaporation was accompanied by free bromine and gave 1.7 g. of a crude oily residue which showed carbonyl and nitrile absorption in the infrared. After decolorizing a benzene solution of the mixture, 0.92 g. (17%) of 3-bromo-3,3-dinitropropionamide, m.p. 105–107°, was obtained with the same infrared spectrum as the analytical sample prepared in 85% sulfuric acid described above.

The ether extract was decolorized with charcoal and the solvent was removed by evaporation leaving 2.74 g. of a semisolid residue. Trituration with 10 ml. of dichloromethane gave 0.57 g. of colorless needles as a residue, m.p. 199–201°. Recrystallization from 1,2-dichloroethane or toluene gave an analytical sample of unchanged melting behavior. The infrared spectrum in potassium bromide disks showed bands of nearly equal medium intensity at 3.10, 7.10, 10.02, and 11.72 and weak bands at 3.56–3.60, 6.06, and 6.17 μ. By comparison of this infrared spectrum with that of an authentic sample of dichloroglyoxime,[10] and the following analytical data, the sample was identified as dichloroglyoxime. It was obtained in 16% yield.

Anal. Calcd. for $C_2H_2Cl_2N_2O_2$: C, 15.30; H, 1.28; Cl, 45.18; N, 17.85. Found: C, 15.81; H, 1.56; Cl, 44.58; N, 17.86.

The dichloromethane solution from which the dichloroglyoxime had been filtered showed an infrared spectrum devoid of nitro content and was not further investigated.

Hydrolysis of 3-chloro-3,3-dinitropropionitrile, under similar conditions, gave 3-chloro-3,3-dinitropropionamide in 48% yield and some recovered nitrile.

Attempted Preparation of Methyl 3-Bromo-3,3-dinitropropionate.—A solution of 5 g. (0.022 mole) of 3-bromo-3,3-dinitropropionitrile in 25 ml. of methanol was saturated with dry hydrogen chloride at −10° and stirred at the slowly melting ice bath and then room temperature for a total of 24 hr. after which it was poured into 50 ml. of water and ice. The liquid phase, containing liberated bromine, was separated from a yellow crystalline solid by filtration and was then extracted with dichloromethane. Removal of the solvent from the dried dichloromethane solution gave a liquid residue (2.3–2.6 g.) containing 4–6% nitrogen (methyl 3-bromo-3,3-dinitropropionate requires 10.90% N). Infrared analyses indicated that the crude product was composed of at least two esters; these could not be separated by molecular distillation and they decomposed on attempted distillation through a column under reduced pressure.

The yellow crystalline solid which had been separated from the reaction mixture above, m.p. 172–176°, was obtained in 1.73–2.21-g. quantities. Crystallization from 70% ethanol, water, or benzene gave 80–95% recoveries of a bright yellow crystalline product, m.p. 185–187° with decomposition. It sublimed unchanged at 70–80° (0.02 mm.). Its ultraviolet absorption spectrum was characterized by a broad band, λ_{max} 360 mμ (log ϵ 3.06), and a narrower band, λ_{max} 235 mμ (log ϵ 4.10), in 95% ethanol. In the infrared, in a potassium bromide pressing, the following prominent bands were observed: strong bands at 6.02–6.06 (doublet), 6.61, 7.57, 12.01; medium intensity bands at 2.94, 3.08, 3.13, 6.44; and weak bands at 7.36, 8.62, 9.68, and 10.60 μ. In an acetone solution, n.m.r. examination showed the presence of a substantial amount of water even after the sample was sublimed.[11]

Anal. Calcd. for $C_3H_2ClN_3O_3 \cdot 0.5H_2O$: C, 20.88; H, 1.75; Cl, 20.55; N, 24.36. Found: C, 21.91; H, 1.75; Cl, 20.16; N, 24.44.

A pale yellow acetyl derivative, m.p. 121–122°, was obtained by heating a solution of the yellow solid with acetic anhydride for 2 hr. In the infrared it showed strong bands at 5.89, 6.11, 6.42, 6.75, 7.43, 8.10, and 11.98 μ; medium bands at 5.89, 7.75, and 9.00 μ; and weak absorption at 7.30, 6.62, 10.00, and 10.22 μ in a potassium bromide pressing.

Anal. Calcd. for $C_5H_4ClN_3O_4$: C, 29.21; H, 1.96; Cl, 17.25; N, 20.44. Found: C, 29.35; H, 2.04; Cl, 17.08; N, 19.50.

On the basis of these data and its mass spectral fragmentation pattern,[11] the yellow crystalline by-product is believed to be 3-chloro-4-nitroso-5-aminoisoxazole 2-oxide,[12] although other isomeric structures have not been completely excluded. The acetyl derivative is believed to be the corresponding 5-acetylaminoisoxazole oxide.

(10) G. Ponzio and F. Baldracco, *Gazz. chim. ital.*, **60**, 415 (1930).

(11) The n.m.r. and mass spectral analyses were made by E. M. Roberts and E. D. Loughran, respectively, of this laboratory.

(12) This structure requires a β-nitro group, in its *aci* form, or an oximino group to add to the nitrile group to give the 5-iminooxazole ring. Nitrosation on the α-carbon atom and replacement of a β-nitro group by chlorine, also required for this structure, have been observed in the hydrolysis of the bromodinitronitrile and in the methanolysis of the parent 3,3-dinitropropionitrile, respectively.

Phosphonitrilic Compounds. IV. Preparation and Polymerization of Allylaminophosphonitrile Compounds[1,2]

H. R. ALLCOCK, P. S. FORGIONE, AND K. J. VALAN

Chemical Department, Central Research Division, American Cyanamid Company, Stamford, Connecticut

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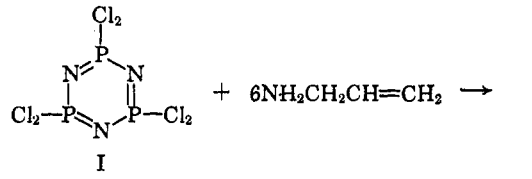
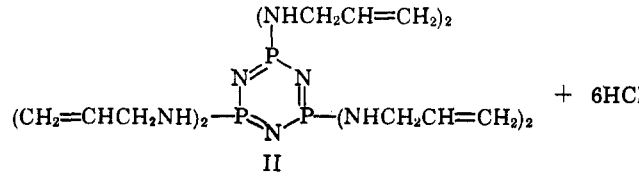
Although the reactions of halophosphonitriles with amines have been widely reported,[3] the reactions with allylamine have not been described in detail.[4] The preparation of allylaminophosphonitrile compounds was of particular interest, however, since the allyl groups would provide a valuable means for the incorporation of phosphonitrile units into polymeric systems. We now report the synthesis of three representative compounds in this series together with preliminary polymerization data.

Hexachlorocyclotriphosphonitrile (I) was treated with 6 equiv. of allylamine in benzene or tetrahydrofuran, to yield hexa(allylamino)cyclotriphosphonitrile (II). Excess allylamine or triethylamine were used as



I



II

hydrohalide acceptors. These reactions afforded II in yields of up to 30%. The remaining reaction product in each case was a resinous conglomerate which resisted purification and which appeared to contain

(1) Part III: H. R. Allcock and L. A. Siegel, *J. Am. Chem. Soc.*, **86**, 5140 (1964).

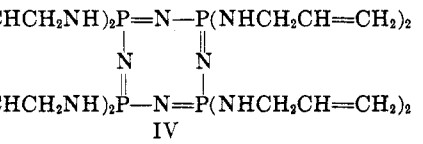
(2) Good reasons have been put forward (see ref. 3a) for adapting an alternative "phosphazene" nomenclature for compounds which contain the –P=N– unit. The *Chemical Abstracts* notation considers these compounds as "hydro azaphosphorine" derivatives. In the present paper, the more familiar "phosphonitrile" terminology is retained but the alternative names based on the *Chemical Abstracts* classification are also given in the Experimental.

(3) For reviews of this topic see (a) R. A. Shaw, B. W. Fitzsimmons, and B. C. Smith, *Chem. Rev.*, **62**, 247 (1962); (b) C. D. Schmulbach, *Progr. Inorg. Chem.*, **4**, 275 (1962).

(4) During the course of this work, E. T. McBee and S. E. French [*Dissertation Abstr.*, **24**, 4993 (1964)] reported the synthesis of the monohydrochloride of hexaallylaminophosphonitrile trimer.

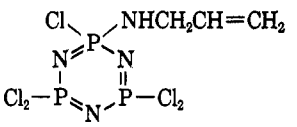
partially substituted chloroallylaminophosphonitrile compounds. Compound II, when pure, was a white crystalline solid, m.p. 90–91°, which was readily soluble in most organic solvents. The infrared spectrum provided evidence for the groups: allyl (912, 997, 1420, 1647, and 3090 cm.$^{-1}$), CN (1090 cm.$^{-1}$), -P=N (1177 cm.$^{-1}$), and NH (3220 cm.$^{-1}$). This compound was only moderately stable when stored at room temperature and underwent a slow polymerization and discoloration.

Octachlorocyclotetraphosphonitrile, $(NPCl_2)_4$ (III), was treated with an excess of allylamine to yield white, crystalline octa(allylamino)cyclotetraphosphonitrile (IV). The infrared spectrum of this material was consistent with the expected structure and included peaks which were assigned to the groups: allyl (915, 997, 1425, 1645, and 3090 cm.$^{-1}$), CN (1090 cm.$^{-1}$), —P=N (1220 cm.$^{-1}$), and NH (3220 cm.$^{-1}$). Compound IV closely resembled II with respect to stability.



IV

Allylamino pentachlorocyclotriphosphonitrile (V) was prepared by reaction of I with 1 equiv. each of allylamine and triethylamine. The mixture of products



V

which formed in this reaction also contained phosphonitrile compounds with a higher ratio of allylamino to chloro groups. The infrared spectrum of V provided evidence for the groups: allyl (930, 998, 1655, 2860, 2920, and 2990 cm.$^{-1}$), C–N (1090 cm.$^{-1}$), P=N (1215 cm.$^{-1}$), and NH [3260 and 3350 (sh) cm^{-1}]. Compound V, when freshly prepared, was a transparent oil. The compound was moderately stable in contact with the atmosphere, but the phosphorus–chlorine bonds were hydrolyzed in aqueous solutions.

The polymerization behavior of II was examined. In the absence of a catalyst, no appreciable polymerization of the molten monomer occurred after 48 hr. at 200°. When II was heated at temperatures below 100°, in bulk or in benzene solution, with free-radical initiators such as benzoyl peroxide, *t*-butylperoxypivalate, or azobisisobutyronitrile, oligomers were formed. Although these products were insoluble in common organic solvents, it was apparent from the low melting points (below 100°) and from the fact that infrared spectra showed only a minimal decrease in aliphatic unsaturation that negligible cross linking had occurred.

However, use of initiators such as *t*-butyl peroxide or 2,5-dimethyl-2,5-di-*t*-butylperoxy-*n*-hexane at 180 to 220° yielded hard, insoluble, cross-linked polymers. Infrared spectra of these polymers were similar to that of II except for a marked decrease in the heights of the aliphatic unsaturation peaks. The fact that the sensitive P=N stretching frequency at 1177 cm.$^{-1}$ underwent no shift indicated that polymerization had occurred through the allyl unsaturation and that the six-membered phosphonitrile ring had remained essentially intact. However, the polymerization was accompanied by a decrease in the carbon, hydrogen, and nitrogen content. This suggested the existence of a deamination process, probably involving the peroxide catalyst. Similar experimental conditions were required for the polymerization of the tetrameric analog IV, but in this case the tetrameric P=N infrared peak at 1220 cm.$^{-1}$ underwent a general broadening (1220–1160 cm.$^{-1}$) during polymerization. These polymers were stable to water.

Compound II was found to be of low reactivity in free radical copolymerization reactions with methyl methacrylate and acrylonitrile, a result which is consistent with the behavior of other allyl monomers.

Experimental

Materials.—Hexachlorocyclotriphosphonitrile and octachlorocyclotetraphosphonitrile (Hooker Chemical Corp.) were recrystallized from *n*-heptane before use. Triethylamine and allylamine (Eastman Organic Chemicals) were used as received. The solvents used were dry, reagent-grade materials.

Preparation of Hexa(allylamino)cyclotriphosphonitrile (II) [2,2,4,4,6,6-Hexakis(allylamino)-2,2,4,4,6,6-hexahydro-1,3,5,2,4,6-triazatriphosphorine]. A. Dehydrochlorination by Excess Allylamine.—A solution of hexachlorocyclotriphosphonitrile (34.8 g., 0.1 mole) in benzene (150 ml.) was added slowly to a stirred solution of allylamine (106 g., 1.8 moles) in benzene (100 ml.). During the 90-min. addition time the reaction mixture was cooled to 20°. The reaction was allowed to proceed at 25° for 4 hr. and the volatile compounds were then removed at reduced pressure. The solid residue was extracted continuously with diethyl ether and the extracts were cooled to −30° to give crystals of II. This product was recrystallized from hot cyclohexane to yield II, 11.5 g. (24%), m.p. 90–91°.

Anal. Calcd. for $C_{18}H_{36}N_9P_3$: C, 45.85; H, 7.64; N, 26.76; P, 19.74; mol. wt., 471.6. Found: C, 45.86; H, 7.48; N, 26.52; P, 19.62; mol. wt. (by vapor pressure lowering), 448.

B. Dehydrochlorination by Triethylamine.—A solution of triethylamine (404 g., 4.0 moles) and allylamine (620 g., 10.8 moles) in benzene (800 ml.) was added dropwise over 2 hr. to a stirred solution of hexachlorocyclotriphosphonitrile (348 g., 1.0 mole) and triethylamine (202 g., 2.0 moles) in benzene (2 l.) at a temperature of 10°. The reaction mixture was stirred at 25° for 24 hr. and then at reflux temperature for 24 hr. The upper benzene layer was decanted from the triethylamine hydrochloride and the oily bottom layer. The benzene solution was washed with water and dried over anhydrous magnesium sulfate. Filtration and evaporation of the filtrate at reduced pressure gave a waxy solid. This product was extracted with diethyl ether (200 ml.) and the extracts were cooled to −40° to yield white crystals. These were removed by filtration, washed at −30° with cooled diethyl ether (50 ml.), and dried to yield II, 103 g., m.p. 90–91°. The oily layer from the reaction mixture was extracted with boiling benzene (1 l.), and evaporation of this solution followed by recrystallization of the residue from cold ether, yielded a further 28 g. of II, m.p. 90–91°. The total yield of II, based on I, was 29.2%.

Preparation of Octa(allylamino)cyclotetraphosphonitrile (IV) [2,2,4,4,6,6,8,8-Octakis(allylamino)-2,2,4,4,6,6,8,8-octahydro-1,3,5,7,2,4,6,8-tetrazatetraphosphorine].—Allylamine (20 g., 0.35 moles) was added dropwise to a stirred solution of octachlorocyclotetraphosphonitrile (III, 4.6 g., 0.01 mole) in benzene (150 ml.) cooled to a temperature of 10°, and the reaction was allowed to proceed at 25° for 5 hr. The mixture was then washed with three 25-ml. portions of water, and the benzene layer was dried over anhydrous calcium sulfate. After filtration, benzene was removed from the filtrate by vacuum distillation. The white residue was then recrystallized from cyclohexane to yield IV, 3.6 g. (57.4%), m.p. 77–78°.

Anal. Calcd. for $C_{24}H_{48}N_{12}P_4$: C, 45.85; H, 7.64; N, 26.76; P, 19.74; mol. wt., 628. Found: C, 46.02; H, 7.93; N, 26.51; P, 19.35; mol. wt. (by vapor pressure lowering), 593.

Preparation of Allylaminopentachlorocyclotriphosphonitrile (V) [2-(Allylamino)-2,4,4,6,6-pentachloro-2,2,4,4,6,6-hexahydro-1,3,-

5,2,4,6-triazatriphosphorine].—A solution of allylamine (17.1 g., 0.3 mole) and triethylamine (30 g., 0.3 mole) in diethyl ether (200 ml.) was added dropwise over 3 hr. to a stirred solution of hexachlorocyclotriphosphonitrile (104 g., 0.3 mole) in diethyl ether (500 ml.). After completion of the addition, the mixture was stirred at 25° for 24 hr. The white precipitate of triethylamine hydrochloride (49.8 g.) was washed with ether and the combined filtrates were evaporated to leave a colorless oil. The oil was then vacuum distilled. Unchanged hexachlorocyclotriphosphonitrile (10.2 g.) sublimed initially and contaminated the distillate. A second distillation yielded impure fractions of V, 50 g., b.p. 115–130° (0.5 mm.), $n^{25}D$ 1.5480. Vapor phase chromatography on a silicone column at 175 and 225° indicated that these mixtures contained I (1–6%), V (~93%), two di(allylamino) tetrachlorocyclotriphosphonitrile isomers (1–4%), and a tri(allylamino)-trichlorocyclotriphosphonitrile trimer (0.3–1.8%). These latter three compounds were identified on the basis of retention times only. A pure sample of V was isolated by vapor phase chromatography.

Anal. Calcd. for $C_3H_6Cl_5N_4P_3$: C, 9.77; H, 1.63; Cl, 48.13; N, 15.21; P, 25.25; mol. wt., 368.3. Found: C, 9.95; H, 1.99; Cl, 48.33; N, 15.12; P, 24.59; mol. wt. (by vapor pressure lowering), 377.

Higher boiling fractions (43.5 g.), b.p. 120–150° (0.5 mm.), $n^{25}D$ 1.5480, were also isolated, in which the chlorine analysis was lower (43–46%). These fractions presumably contained mixtures of products with a higher number of allylamino groups. The total yield of V from this reaction was estimated to be more than 50% based on I.

Polymerization of II. A. Solution Reactions.—Mixtures of II (1 g.), benzene (2 ml.), and azobisisobutyronitrile, benzoyl peroxide, or *t*-butylperoxy pivalate (0.04 g.) were degassed and sealed in a nitrogen atmosphere in thick-walled glass tubes. The tubes were then heated at 60° for 4 days. No solid had precipitated after this time, and evaporation of the solvent yielded a semicrystalline mixture of II and low molecular weight oligomers.

B. Bulk Reactions.—Compound II was mixed with 2 wt. % 2,5-dimethyl-2,5-di-*t*-butylperoxy-*n*-hexane (Lupersol 101) and the mixture was degassed and sealed under nitrogen in glass tubes. After 48 hr. at 130°, or after 17 hr. at 158°, the product was a hard, insoluble glass which did not melt below 300°. Similarly, when 2 wt. % di-*t*-butyl peroxide was used as a catalyst, the material formed a cross-linked, amber-colored glass after 17 hr. at 128° and after 2 hr. at 170°.

Anal. Found: C, 40.40; H, 6.52; N, 25.77; P, 20.46.

Thermogravimetric analysis of a powdered polymer of II, using a 10°/min. temperature increase in air, showed no weight loss at 250°, 1% weight loss at 300°, 10% weight loss at 400°, 30% weight loss at 500°, and 34% weight loss at 600°. The total weight loss at 1000° varied from 65 to 85%.

Acknowledgment.—We thank Dr. W. M. Thomas for his interest and suggestions, Dr. R. Feinland for the gas chromatographic separations, and Mrs. R. Marcus for technical assistance.

Synthesis of ω-(Aminooxy)alkanethiols[1,2]

LUDWIG BAUER, K. S. SURESH, AND B. K. GHOSH

Department of Chemistry, College of Pharmacy, University of Illinois at the Medical Center, 833 South Wood Street, Chicago, Illinois 60612

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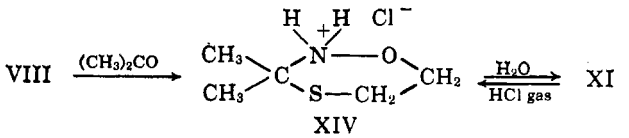
As part of our program on the synthesis of antiradiation drugs we set out to prepare two short-chain aminooxyalkanethiols, $H_2NO(CH_2)_nSH$ (n = 2 or 3). Previous attempts to prepare β-aminooxyethyl mercaptan by the alkaline hydrolysis of S-[β-(phthalimidooxy)-ethyl]isothiuronium bromide[3] or the acid hydrolysis of sodium S-[β-(phthalimidooxy)ethyl] thiosulfate[3] failed, phthalic acid being the only recognizable product. Thus we turned to S-[ω-(phthalimidooxy)alkyl] thiolacetates as precursors for the required compounds since acid hydrolysis would readily liberate the aminooxy[4] and thiol groups simultaneously and in the last step.

Two routes seemed feasible to prepare S-[ω-(phthalimidooxy)alkyl] thiolacetates. The reaction of β-(phthalimidooxy)ethyl bromide[3] with sodium thiolacetate furnished a number of unidentifiable products while the reaction of N-hydroxyphthalimide with ω-bromoalkyl thiolacetates afforded these essential intermediates. The reaction of 1,2-dibromoethane and 1,3-dibromopropane with sodium thiolacetate furnished the required ω-bromoalkyl thiolacetates. Reaction of β-bromoethyl thiolacetate with N-hydroxyphthalimide yielded a mixture of the required S-[β-(phthalimidooxy)-ethyl] thiolacetate (V) and N-acetoxyphthalimide,[5] which were separated by fractional crystallization. However, when N-hydroxyphthalimide was treated with γ-bromopropyl thiolacetate, the required product VI was isolated and no N-acetoxyphthalimide could be found in the reaction mixture.

Acid hydrolysis of V and VI (n = 2 and 3) produced the corresponding aminooxythiols which were isolated as their hydrochlorides (VIII and IX, respectively) and characterized by analysis and their n.m.r. spectra. Table I presents a summary of the n.m.r. spectra of the compounds described in this work.

Condensation of β-(aminooxy)ethyl mercaptan hydrochloride with acetone furnished a product assigned the cyclic structure XIV, also prepared when β-(isopropylideneaminooxy)ethyl mercaptan was treated with hydrogen chloride in dry ether. The salt was hydrolyzed in water to the oximinothiol XI, which was



XIV

synthesized independently from the corresponding bromide X, with sodium hydrosulfide. The infrared spectrum of XI showed a weak broad band for SH (2550 in liquid film, 2430 cm.$^{-1}$ in $CHCl_3$) as well as the

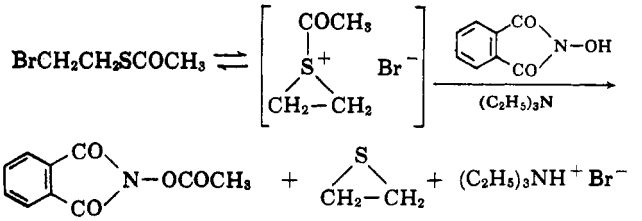
(1) Presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

(2) This project was sponsored by the office of the Surgeon General, U. S. Army Medical Research and Development Command (Contract DA-49-193-MD-2047), whose generous support is gratefully acknowledged.

(3) L. Bauer and K. S. Suresh, *J. Org. Chem.*, **28**, 1604 (1963).

(4) L. Bauer, A. Shoeb, and V. C. Agwada, *ibid.*, **27**, 3153 (1962).

(5) The formation of this product could easily be explained if S-acetylepisulfonium bromide is considered as a logical reactive intermediate in the reaction. Such an intermediate has been postulated in another reaction by H. Böhme and H. D. Stachel [*Ann.*, **606**, 75 (1957)]. Such a mechanism



would demand the formation of ethylene sulfide. When the aqueous mother liquors of our reaction were extracted exhaustively with toluene and the first 10% of that solution was distilled, it was shown that ethylene sulfide was present (infrared and n.m.r. spectra). It was further shown that under similar reaction conditions, N-hydroxyphthalimide was not acetylated by *n*-butyl thiolacetate nor by 1,2-bis(acetylmercapto)ethane.