plet resulting from coupling with the aluminum nucleus and this multiplet would be broadened by the quadrupole moment. An NH peak is often too broad to be seen for reasons similar to those given for the AlH peak. A PH proton resonance would probably be observed in the nmr spectrum because it is split by about 200–300 cps giving two peaks, and it is improbable that both peaks would be hidden. The solvolysis of a sample of this material does not produce hydrogen gas, indicating that there is no hydrogen bonded to aluminum. This leads us to postulate the presence of a hydrogen atom attached to nitrogen. If the hydrogen atom were attached to the nitrogen atom, the molecule would be a zwitterion because the nitrogen and the phosphorus would each be charged.

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Reactions of Phenyl Azide or Hydrogen Azide and Chlorophosphines[1]

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The phosphine imines $C_6H_5NPCl_3$, $C_6H_5NPCl_2C_6H_5$, and $C_6H_5NPCl(C_6H_5)_2$ have been prepared by the reaction of phenyl azide and the appropriate phosphine or phosphorus trichloride. Photolysis with ultraviolet light of hydrogen azide in phosphorus trichloride gives a viscous liquid with the stoichiometry $P_5N_8Cl_9$ instead of the anticipated trichlorophosphine imine. Evidence in support of a linear structure for the compound $P_5N_8Cl_9$ is given. Indirect evidence for the existence of a reactive trichlorophosphine imine intermediate in the photolysis reaction is discussed. Pyrolysis of the $P_5N_8Cl_9$ polymer gives a new, highly polymeric compound with the stoichiometry $P_3N_3Cl_5$ as well as trimeric and tetrameric cyclic chlorophosphonitriles and uncharacterized solids. Chlorodiphenylphosphine imine has been prepared from the photolytic reaction of hydrogen azide and chlorodiphenylphosphine in benzene. The strong tendency of this compound to dehydrochlorinate with the formation of phenyl-substituted phosphonitriles is described. A stable adduct, $HN_3 \cdot PCl(C_6H_5)_2$, has been isolated from the reaction that produced the chlorodiphenylphosphine imine.

Introduction

Trichlorophosphine imine, $HNPCl_3$, has been proposed as a reactive intermediate in the formation of chlorophosphonitrile polymers from the reaction of ammonium chloride and phosphorus pentachloride.[3,4] There is a considerable body of indirect evidence to support the existence of trichlorophosphine imine and the related phosphine imines, $HNPCl_2(C_6H_5)$ and $HNPCl(C_6H_5)_2$.[5] Whereas the reactions of primary amines (or their hydrochloride salts) with PCl_5 in an inert solvent results in the formation of N-substituted trichlorophosphine imines with the elimination of hydrogen chloride,[6] the reaction of ammonia and ammonium chloride with phosphorus pentachloride results always in chlorophosphonitrile polymers.[3,7] All evidence suggests that for those phosphine imines which contain an imino functional group and a chloride functional group, the stability of the compound is reduced or the chemical activity increased to such an extent that a rather facile dehydrochlorination occurs with the formation of polymeric linear or cyclic phosphonitriles.

The principal objective of this research was to prepare phosphine imines that contain the imino and chloro functional groups. A demonstration of the ease with which these phosphine imines would dehydrochlorinate and the conditions for this dehydrochlorination were sought.

The failure to isolate trichlorophosphine imine was thought to stem from the rather severe reaction conditions to which others had subjected the ammonium chloride–phosphorus pentachloride system. Reaction temperatures in excess of 150° were always employed. Since a reduction in reaction temperatures greatly enhances the probability of isolating a highly reactive species or one of low thermal stability, the reaction of phosphines and azides, which are known to give phosphine imines under mild conditions,[8–10] was considered a promising route for the synthesis of HN-containing chlorophosphine imines. (No phosphine imines containing both the imino and chloro functional groups have been reported.) Furthermore, photolysis of covalent azides produces a short-lived nitrene radical,

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[1] Abstracted in part from the Ph.D. thesis of Roger K. Bunting, The Pennsylvania State University, Sept. 1965.

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[3] N. L. Paddock and H. T. Searle, *Advan. Inorg. Chem. Radiochem.*, **1**, 347 (1959).

[4] M. Becke-Goehring and W. Lehr, *Z. Anorg. Allgem. Chem.*, **327**, 128 (1964).

[5] For a detailed summary see N. L. Paddock, *Quart Rev.* (London), **18**, 168 (1964).

[6] I. N. Zhmurova and A. V. Kirsanov, *Zh. Obshch. Khim.*, **30**, 3044 (1960); *Chem. Abstr.*, **55**, 17551 (1961).

[7] C. P. Haber, "Inorganic Polymers," Special Publication No. 15, The Chemical Society, London, 1961, pp 115–146.

[8] H. Staudinger and E. Hauser, *Helv. Chim. Acta*, **4**, 861 (1921).

[9] H. Staudinger and J. Meyer, *ibid.*, **2**, 635 (1919).

[10] L. Horner and A. Gross, *Ann.*, **591**, 117 (1955).

NH, which possesses electrophilic character[11] and which can be generated at very low temperatures. Therefore, the photolytic degradation of hydrogen azide in the presence of chlorophosphines was considered the most promising route to chlorophosphine imines. The oxidation of tertiary phosphines to phosphine imines with chloramine[12] and with hydroxylamine-O-sulfonic acid[13] has been reported. Oxidation with either of these reagents gives first the phosphonium salts which are treated in turn with a strong base, such as sodium amide, to produce the phosphine imine. The necessity of strong bases to effect deprotonation of the phosphonium ion greatly diminishes the usefulness of these methods for the synthesis of chlorophosphine imines because of the sensitivity of the phosphorus–chlorine bond to cleavage by nucleophilic reagents.

Results

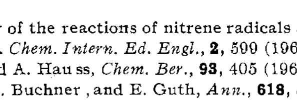
The reactions of phenyl azide and chlorophenylphosphines and of phenyl azide and phosphorus trichloride were first examined according to the conditions summarized in eq 1. Phosphorus trichloride and dichlorophenylphosphine previously were reported to react with benzoyl azide to a negligible extent.[9] The current study shows that the reactions of phosphorus trichloride, dichlorophenylphosphine, or chlorodiphenylphosphine and phenyl azide give the corresponding phosphine imines in good yields.

$$C_6H_5N_3 + PCl_{3-n}(C_6H_5)_n \xrightarrow[\text{reflux}]{C_6H_6} C_6H_5N{=}PCl_{3-n}(C_6H_5)_n + N_2 \qquad (1)$$

The photolytic reaction of hydrogen azide dissolved in phosphorus trichloride proceeded according to eq 2.

$$HN_3 + PCl_3 \xrightarrow[h\nu;\ 3\text{ hr}]{-78\text{ to }-67^\circ} (P_5N_8Cl_9)_4 + HCl + N_2 \qquad (2)$$

Very small quantities of ammonium chloride were also formed. The compound $(P_5N_8Cl_9)_4$ is a pale yellow viscous liquid. The infrared spectrum of a neat sample of this compound has a broad intense absorption centered at 1239 cm^{-1} with a shoulder at 1295 cm^{-1}. This lies in the region of the P=N stretching vibration of phosphonitrile polymers.[14] In addition there is a sharp band at 2157 cm^{-1} which is assigned to an azide asymmetric stretching vibration.[15] No other well-defined peaks are present. Values for the molecular weight of $(P_5N_8Cl_9)_4$, determined cryoscopically in benzene, were 2200 and 2010. On the basis of these results and other supporting evidence the most likely structure for this compound is



with a random attachment of azide groups to provide the necessary Cl:N$_3$ ratio of 9:1. Additional support for the proposed structure comes from the ^{31}P nmr spectrum. The spectrum contains two bands, a broad, strong resonance band in the region of +17 ppm (relative to 85% orthophosphoric acid) and a second weak signal at +8 ppm. This spectrum bears a striking similarity to that of a polymer reported to have the linear structure $H\text{—}(N{=}PCl_2\text{—})_nCl$.[16] The ^{31}P nmr spectrum of this compound showed two bands with the area ratio of $1:(n - 1)$ at +7.7 and +16.8 ppm, respectively. The strong resonance band at 17 ppm in the spectrum of $P_5N_8Cl_9$ is assigned to the phosphorus nuclei in the body of the linear polymer, while the weak signal is assigned to a phosphorus nucleus in the terminal position. The band area ratio of the strong to weak band is 15–20:1. The elements of hydrogen chloride are thought to serve as end-capping groups in the $P_5N_8Cl_9$ polymer.

The $P_5N_8Cl_9$ polymer decomposes vigorously when heated to 140° under vacuum. In addition to trimeric and tetrameric chlorophosphonitriles there was a quantity of semisolid material that was not characterized but was thought to be a mixture of high molecular weight cyclic chlorophosphonitrile polymers. A white, fibrous, intractable material was also recovered, which from elemental analysis was shown to have the stoichiometry $P_3N_3Cl_5$. This compound is insoluble in polar and nonpolar solvents. The origin of $P_3N_3Cl_5$, its lack of reactivity, and its stoichiometry suggest a highly cross-linked polymeric species.

The product of the photolytic reaction of hydrogen azide and dichlorophenylphosphine is a yellow viscous liquid. A neat sample of this compound gave an intense, broad band centered at 1250 cm^{-1} with a shoulder at 1287 cm^{-1}, which may be assigned to the P=N vibration. The presence of the azide group was indicated by a sharp absorption band at 2145 cm^{-1}. There were no bands which could be assigned to the N–H moiety. The compound is considered to be analogous to $P_5N_8Cl_9$. Since preparation of the phosphineimine was paramount, no further characterization of the compound was undertaken.

The photolytic reaction of hydrogen azide and chlorodiphenylphosphine was carried out at 5° in benzene. Dilution of the reactants in benzene was employed in an effort to reduce the chemical reactivity of the product species. Because the photodecomposition of HN_3 in benzene produces the insertion product aniline in <10% yield,[17] the use of this solvent as a diluent was considered preferable to saturated hydrocarbon solvents, which exhibit a strong tendency toward proton abstraction by the nitrene radical.[18]

A compound with the stoichiometry $HN_3 \cdot PCl(C_6H_5)_2$ was isolated. This compound is a white solid which melts at 126.0–126.5° with decomposition. The infrared spectrum of $HN_3 \cdot PCl(C_6H_5)_2$ showed a sharp

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[11] For a review of the reactions of nitrene radicals see L. Horner and A. Christmann, *Angew. Chem. Intern. Ed. Engl.*, **2**, 599 (1963).

[12] R. Appel and A. Hauss, *Chem. Ber.*, **93**, 405 (1960).

[13] R. Appel, W. Buchner, and E. Guth, *Ann.*, **618**, 53 (1958).

[14] See C. D. Schmulbach, *Progr. Inorg. Chem.*, **4**, 275 (1962).

[15] L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd ed, John Wiley and Sons, New York, N. Y., 1958, p 263.

[16] M. Becke-Goehring and G. Koch, *Chem. Ber.*, **92**, 1188 (1959).

[17] D. H. R. Barton and L. R. Morgan, *J. Chem. Soc.*, 622 (1962).

[18] R. N. Keller and P. A. S. Smith, *J. Am. Chem. Soc.*, **66**, 1122 (1944).

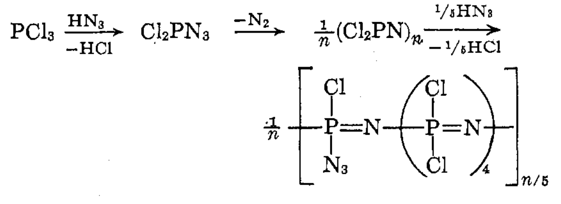
absorption band at 2157 cm^{-1}, which confirms the presence of the covalent azide. Pyrolysis of this compound at 130° resulted in the evolution of nitrogen and hydrogen chloride and small quantities of hydrogen azide. Octaphenylcyclotetraphosphonitrile, mp 319–320°, was identified as the major solid pyrolysis product. Unidentified intractable polymeric species were also obtained.

In addition to the azide–phosphine adduct, a compound with a stoichiometry that agrees favorably with chlorodiphenylphosphine imine was isolated. This compound begins to melt around 50° with decomposition and is completely melted at 100°. It evolves hydrogen chloride slowly at room temperature. Thermal decomposition at 250° gave a high yield of octaphenylcyclotetraphosphonitrile (54% of theoretical yield) along with intractable polymers and hydrogen chloride gas. The infrared spectrum of the chlorodiphenylphosphine imine contains no band in the region of the azide asymmetric stretching vibration. In addition, a broad absorption band was observed at 1239 cm^{-1} with a shoulder at 1295 cm^{-1}. This is assigned to the P═N stretching mode.

Discussion

The results of the photolysis reaction of hydrogen azide and phosphorus trichloride provide strong indirect evidence for a highly reactive trichlorophosphine imine intermediate. The isolation of the chlorophenyl-N-phenylphosphine imines and trichloro-N-phenylphosphine imine from the reaction of phenyl azide and the appropriate phosphines and the preparation of chlorodiphenylphosphine imine provide direct evidence that the products of azide–phosphine systems will give rise to phosphine imines provided the phosphine imines are sufficiently unreactive (chlorodiphenylphosphine imine) or are incapable of further condensation (N-phenylphosphine imines). The possibility that the trichlorophosphine imine, which is proposed as a reactive intermediate in the hydrogen azide–phosphorus trichloride reaction, polymerized upon warming is eliminated since extensive evolution of hydrogen chloride occurred at very low temperatures immediately upon the application of ultraviolet light.

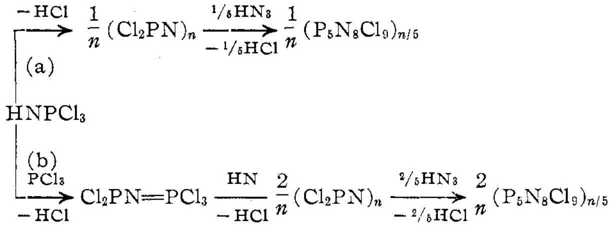
A reaction path involving a preliminary azide–chloride exchange between phosphorus trichloride and hydrogen azide may be formulated according to the scheme



$$PCl_3 \xrightarrow[-HCl]{HN_3} Cl_2PN_3 \xrightarrow{-N_2} \frac{1}{n}(Cl_2PN)_n \xrightarrow[-{}^1/_5HCl]{{}^1/_5HN_3} \frac{1}{n}\left[-\underset{N_3}{\overset{Cl}{P}}{=}N-\left(\underset{Cl}{\overset{Cl}{P}}{=}N\right)_4-\right]_{n/5} \quad (3)$$

More complicated mechanisms involving the condensation of Cl_2PN_3 with PCl_3 or polymeric species of the type $Cl_3P{=}N{-}(Cl_2PN)_n{-}PCl_2$ may be involved. Azidodiphenylphosphine decomposes at 13.6–13.8° to give the phenyl-substituted polymers.[19] The reaction of phosphorus(III) halides with sodium azide gives the corresponding halophosphonitriles, presumably by formation of X_2PN_3.[20] The absence of any but traces of hydrogen chloride in the gases purged from a solution of hydrogen azide in phosphorus trichloride at −78°, in the absence of ultraviolet light, suggests that a mechanism requiring extensive initial azide–chloride exchange contributes only to a very minor extent to the formation of the polymeric products.

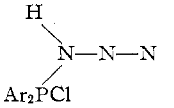
The application of ultraviolet light to the hydrogen azide–phosphorus trichloride mixture results in the immediate evolution of copious quantities of hydrogen chloride. This observation, coupled with the observation that chlorodiphenylphosphine imine is isolated from the photolytic reaction of hydrogen azide and chlorodiphenylphosphine, suggests a mechanism that includes trichlorophosphine imine as an intermediate. Trichlorophosphine imine is formed by the reaction of the nitrene radical and phosphorus trichloride and then reacts further *via* path (a) or path (b). Path (a) may involve either an intermolecular or intramolecular reaction of the $HNPCl_3$. The actual azide species which undergoes photolytic decomposition may be an adduct of the type $HN_3 \cdot PCl_3$. Such a possibility is given some support from the isolation of a 1:1 adduct of hydrogen azide and chlorodiphenylphosphine. A limited azide–chloride exchange occurs to give the necessary 1:9 azide to chloride ratio in the product.



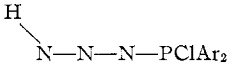
$$HNPCl_3 \xrightarrow[(a)]{-HCl} \frac{1}{n}(Cl_2PN)_n \xrightarrow[-{}^1/_5HCl]{{}^1/_5HN_3} \frac{1}{n}(P_5N_8Cl_9)_{n/5}$$

$$HNPCl_3 \xrightarrow[-HCl]{(b)\ PCl_3} Cl_2PN{=}PCl_3 \xrightarrow[-HCl]{HN} \frac{2}{n}(Cl_2PN)_n \xrightarrow[-{}^2/_5HCl]{{}^2/_5HN_3} \frac{2}{n}(P_5N_8Cl_9)_{n/5}$$

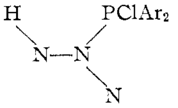
The isolation of $HN_3 \cdot PCl(C_6H_5)_2$ in numerous experiments of the photochemical reaction of hydrogen azide and chlorodiphenylphosphine establishes the fact that this compound is invariably a product of the reaction. The formation of a compound of this type is not surprising in view of the number of 1:1 addition compounds between azides and triphenylphosphine previously reported.[8,21–24] Of the adducts which have been reported only one, the triphenylsilyl azide adduct of triphenylphosphine, shows an azide asymmetric stretching vibration in its solid-state infrared spectrum.[24] Three structures are possible for the hydrogen azide–phosphine adduct. The presence or absence of the azide asymmetric stretching vibration in the infrared spectrum has been used as a criterion to differentiate between structures I and II.[24] Structure I



I



II



III

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[19] K. L. Paciorek and R. Kratzer, *Inorg. Chem.*, **3**, 594 (1964).

[20] D. L. Herring, *Chem. Ind.* (London), 717 (1960).

[21] H. Hock and W. Wiegrabe, *Angew. Chem.*, **75**, 790 (1963).

[22] J. E. Franz and C. Osuch, *Tetrahedron Letters*, 841 (1963).

[23] L. Horner and A. Christmann, *Chem. Ber.*, **96**, 388 (1963).

[24] J. S. Thayer and R. West, *Inorg. Chem.*, **3**, 406 (1964).

has been assigned to adducts whose infrared spectra contain the band and structure II to adducts which do not. Structure III would also not be expected to give the asymmetric stretching vibration. Since the infrared spectrum of $HN_3 \cdot PCl(C_6H_5)_2$ contains the azide stretching vibration at 2157 cm^{-1}, structure I is indicated. The additional possibility that the adduct is an ionic phosphonium salt can be discounted. The spectrum of the adduct is completely free of absorption in the 2300–2400 cm^{-1} region, which indicates absence of the P–H moiety.[25] Also, the absorption frequency at which the azide band occurs is comparable to that of other covalent azides, whereas the azide ion usually absorbs at frequencies about 100 cm^{-1} lower.[26]

The isolation of the tetramer of diphenylphosphonitrile from the pyrolysis of $HNPCl(C_6H_5)_2$ or $HN_3 \cdot PCl(C_6H_5)_2$ is a curious fact. Other members of the homologous series undoubtedly are formed but in yields too small to be conveniently isolated. The preference for eight-membered rings has been observed in the preparation of fully-phenylated phosphonitrile polymers by a conventional method.[27] The reaction of diphenyltrichlorophosphorane with ammonium chloride exhibits a similar though less pronounced tendency.[27]

Experimental Section

Reagents.—Fisher purified sodium azide and Baker and Adamson reagent grade phosphorus trichloride were used without further purification. Technical grade chlorodiphenylphosphine and dichlorophenylphosphine were generously supplied by the Victor Division of Stauffer Chemical Co. and were purified by vacuum distillation. The fractions boiling at 179–181° (16 mm) and 138–140° (55 mm), respectively, were retained. The reported boiling points are 179–180° (16 mm)[28] and 140–142° (57 mm), respectively.

Technical grade benzene was dried over sodium ribbon and distilled. The center, constant-boiling fraction was retained. Technical grade petroleum ether was dried with sodium ribbon and used without further purification.

Phenyl azide was synthesized according to the method of Lindsay and Allen.[29] The phenyl azide prepared in this manner has a boiling point of 48–50° (5 mm) [49–50° (5 mm) reported].

Elemental Analyses.—All elemental analyses were made by the Galbraith Laboratories, Inc., Knoxville, Tenn.

Spectroscopic Measurements.—Infrared spectral measurements were made on a Beckman IR-8 spectrophotometer. The frequencies were calibrated with the spectrum of polystyrene as the standard. Solid samples were examined as potassium bromide pellets or as mulls in Nujol or hexachlorobutadiene.

The nuclear magnetic resonance spectrum was measured with a Varian Model V-4311 spectrometer made available through the courtesy of the Inorganic Division of the Monsanto Company, St. Louis, Mo. The sample was examined as a benzene solution.

Melting Points.—Melting points were determined in open capillaries and are uncorrected.

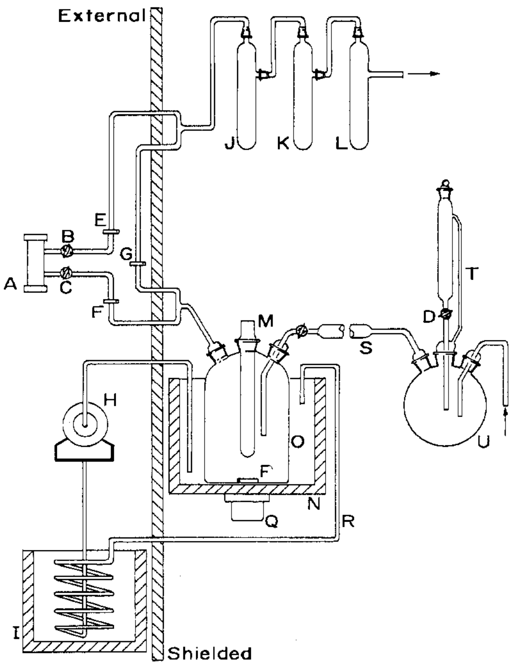

Figure 1.—Apparatus for photolytic reactions of hydrogen azide and chlorophosphines: A, gas infrared cell; B, C, D, stopcocks; E, F, G, pinchclamps; H, centrifugal circulating pump; I, constant-temperature bath (2-l. dewar flask); J, moisture trap (anhydrous calcium chloride); K, acid trap (aqueous potassium hydroxide, concentrated); L, azide detector (aqueous ferric nitrate, 1% solution); M, lamp jacket (quartz, 32 × 200 mm); N, coolant vessel (unsilvered dewar flask, 1.5-l. capacity); O, reaction flask (600-ml capacity); P, magnetic stirring bar; Q, magnetic stirring motor; R, circulatory system; S, drying column (anhydrous calcium chloride, 20 × 700 mm); T, dropping funnel; U, round-bottomed reaction flask (250-ml capacity).

Photolytic Reaction Apparatus.—The photolytic reactions of hydrogen azide and chlorophosphines were conducted in the apparatus diagrammed in Figure 1. Owing to the toxicity and the explosive hazards of hydrogen azide, all reactions involving this material were conducted with appropriate safety precautions. The shielded sections of the apparatus were contained in an exhaust hood, and the operator was completely protected with a removable section of 0.75-in. plywood. The shield contained an observation port that was covered by a laminated safety-glass shield. Stopcock manipulations could be effected by means of wooden shafts inserted through holes in the shield. Furthermore, reaction temperatures could be controlled by circulation of a coolant through a constant-temperature bath which was externally located. Samples of the effluent gases from the reactions could be taken conveniently for infrared spectra under protection of the shield. In addition to the details shown in Figure 1, the dewar flask, N, surrounding the reaction vessel was fitted with a toluene thermometer (−95 to +30°). The hydrogen azide drying column S was wrapped entirely with heating tape from the ground joint of the generator to the ground joint of the reaction vessel. The ultraviolet source, which was inserted in tube M, was a Hanovia Type 612C quartz, high-pressure mercury vapor lamp. This lamp has an arc length of 40 mm. The maximum radiation intensity of this lamp is 5461 A, with lower intensities at wavelengths extending to well below 2000 A. The lamp was supplied with a Hanovia Multi-watt Stabilizer ballast capable of producing lamp output wattages of 100–400 w depending upon the capacitance of the lamp circuit.

General Procedure for Photolytic Reactions.—In the photolysis reactions of hydrogen azide and chlorophosphines the flask U of the hydrogen azide generator was first charged with the desired quantity of solid sodium azide and the dropping funnel filled with a quantity of concentrated sulfuric acid in excess of the stoichiometric requirement for complete conversion of the sodium azide to hydrogen azide. Trap J was filled with calcium chlo-

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[25] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, p 297.

[26] Reference 25, pp 77, 176.

[27] C. P. Haber, D. L. Herring, and E. A. Lawton, *J. Am. Chem. Soc.*, **80**, 2116 (1958).

[28] J. Meisenheimer, J. Casper, M. Horing, W. Lauter, L. Lichtenstadt, and W. Wamuel, *Ann.*, **449**, 213 (1926).

[29] R. O. Lindsay and C. F. H. Allen, "Organic Syntheses," Coll. Vol. III, E. C. Horning, Ed., John Wiley and Sons, Inc., New York, N. Y., 1955, p 710.

ride to prevent back-diffusion of moisture, trap K was filled with concentrated aqueous potassium hydroxide to neutralize hydrogen azide that escaped condensation, and trap L was filled with an aqueous solution of ferric nitrate (1%) to indicate the presence of any hydrogen azide that might escape neutralization in the base trap. The drying column S was maintained at 40 to 50° to ensure that no hydrogen azide (bp 37°) would condense in the column.

With pinchclamps E and F closed and G open, and with a slow stream of nitrogen flowing through the apparatus, the quartz lamp jacket M was removed and the phosphine and solvent (if used) were quickly introduced into the reaction flask. The contents of the cell O were allowed to come to the temperature of the bath. Hydrogen azide generation was begun. Generation of the hydrogen azide required 0.5–1 hr. Small droplets of liquid hydrogen azide remained condensed on the cold interior of the delivery tube. An additional period of about 0.5 hr was allowed while those droplets evaporated and their vapor was swept into solution by the nitrogen stream.

At this stage the ultraviolet radiation source was activated and gas evolution from the photolysis commenced immediately. Photolysis was continued until the evolution of gas was no longer visible. During the photolysis interval the reaction solution was stirred rapidly in order to provide as nearly uniform temperature throughout the reaction solution as possible.

Pinchclamp G was kept open and clamps E and F were kept closed except when a sample of the effluent gas mixture was required for infrared analysis. On these occasions the stopcocks B and C were opened, E and F were opened, and G was closed. Effluent gases were allowed to pass through the infrared cell for at least 10 min.

After cessation of gas evolution, the ultraviolet radiation was stopped and the reaction mixture was allowed to warm gradually to room temperature over a period of about 2 hr. As the reaction solution warmed, the nitrogen stream was continued at an increased flow rate in order to rid the solution of the last traces of hydrogen azide. Insoluble materials were removed from the reaction mixture by vacuum filtration under nitrogen, and soluble products were recovered by evaporation of the reaction solution under reduced pressure at or below room temperature.

Reaction of Hydrogen Azide and Phosphorus Trichloride.—In a typical reaction the hydrogen azide generator was charged with 10 g (0.15 mole) of sodium azide, and 250 ml of phosphorus trichloride was introduced into the reaction vessel. The contents of the reaction vessel were cooled to −67° with a Dry Ice–acetone mixture in the cooling circulatory system. An experiment in which a *n*-heptane slush was used as the coolant to give a temperature of −78° around the reaction flask gave results that were essentially the same as those at the higher temperature. When the ultraviolet source was activated gas evolution was immediate. The sample was irradiated for about 3 hr. A thin coating of ammonium chloride formed slowly on the surface of the quartz lamp jacket M. Most of this solid adhered to the quartz surface and decreased the amount of effective radiation, particularly toward the end of the photolysis period.

Prior to ultraviolet irradiation, and at 1-hr intervals throughout the radiation period, infrared spectra were taken of the gases which were expelled from the reaction solution. A high concentration of hydrogen azide vapor was found to be present in all samples of a run, but the peak height diminished toward the end of the reaction. An extremely high concentration of hydrogen chloride was also observed with the commencement of radiation. The concentration of hydrogen chloride diminished greatly as the photolysis reached completion Only trace quantities of hydrogen chloride were observed in the spectra of samples taken before photolysis was begun.

After the ammonium chloride was removed by filtration, the excess phosphorus trichloride was evaporated at reduced pressure and 3–7 g of a slightly yellow, viscous liquid was recovered. This material was dissolved in benzene and then separated from the solvent by the addition of petroleum ether. This procedure was twice repeated to rid the material of any phosphorus trichloride. Finally, traces of benzene were removed under reduced pressure.

Elemental analysis of the viscous liquid agrees well with the stoichiometry $P_5N_8Cl_9$.

Anal. Calcd for $P_5N_8Cl_9$: P, 26.43; N, 19.12; Cl, 54.45. Found: P, 26.03; N, 18.82; Cl, 54.23.

The compound was further characterized by infrared analysis and by cryoscopic molecular weight measurements.

A 0.32-g sample of $P_5N_8Cl_9$ decomposed vigorously when heated to temperatures above 140° under vacuum to give 0.03 g of trimeric chlorophosphonitrile, 0.02 g of the chlorophosphonitrile tetramer, and 0.03 g of an uncharacterized semisolid which is thought to be a mixture of higher molecular weight chlorophosphonitrile polymers. In addition to the phosphonitriles 0.14 g of a white, fibrous, intractable material was recovered. Elemental analysis of this material gives a stoichiometry of $P_3N_3Cl_5$.

Anal. Calcd. for $P_3N_3Cl_5$: P, 29.76; N, 13.46; Cl, 56.78. Found: P, 29.67; N, 13.62; Cl, 56.78.

The vigor of the decomposition made quantitative recovery of the reaction products difficult. It is obvious, however, that the compound $P_3N_3Cl_5$ is a major product.

Reaction of Hydrogen Azide and Chlorodiphenylphosphine.—The procedure was essentially that described for the hydrogen azide–phosphorus trichloride reaction. In this case, however, 33 g (0.15 mole) of chlorodiphenylphosphine was introduced into the reaction flask containing 230 ml of benzene. The temperature of the reaction mixture was maintained below 5° by a water–ethylene glycol bath cooled externally by an ice–salt bath. A turbidity gradually developed during the photolysis, and after about 1 hr the evolution of gases decreased abruptly accompanied by the formation of a precipitate. The precipitate, a white solid, was filtered, washed with benzene, and dried under vacuum. It melts sharply at 126.0–126.5° with the evolution of gas. Elemental analysis of this solid is in agreement with that for the 1:1 adduct $HN_3 \cdot PCl(C_6H_5)_2$.

Anal. Calcd for $C_{12}H_{11}N_3ClP$: C, 54.66; H, 4.21; N, 15.94; Cl, 13.45; P, 11.75. Found: C, 54.78; H, 5.68; N, 14.91; Cl, 13.45; P, 11.10.

Pyrolysis of the adduct at 130° gave octaphenylcyclotetraphosphonitrile as a major constituent of the pyrolysis residue.

A 4.9-g quantity of a white flocculent solid was precipitated from the benzene filtrate by the slow addition of the benzene solution to rapidly stirred petroleum ether. The white solid was filtered, washed with petroleum, and dried under vacuum. The elemental analysis of this compound approximates that for chlorodiphenylphosphine imine.

Anal. Calcd for $C_{12}H_{11}NClP$; C, 61.16; H, 4.70; N, 5.94; Cl, 15.05; P, 13.14. Found: C, 64.23; H, 5.04; N, 6.04; Cl, 13.08; P, 13.63.

A drastic reduction of the chlorine content to 8.07% for the sample used in this analysis was observed after the sample had stood for 3 weeks at room temperature in a desiccator over phosphorus pentoxide. The spontaneous loss of hydrogen chloride was confirmed on numerous samples.

The pyrolysis of 0.31 g of chlorodiphenylphosphine imine at 250° gave 0.14 g of octaphenylcyclotetraphosphonitrile, mp 318–320° (319.5–321.0° reported).[27] The identity of this product was confirmed by comparison of its infrared spectrum with that of an authentic sample. The yield of the tetramer is 54% theoretical.

Hydrolysis of the chlorodiphenylphosphine imine in hot acetone–water solution gave the expected diphenylphosphinic acid, mp 190–192°.

Synthesis of Trichloro-N-phenylphosphine Imine.—A 6.12-g (0.0513 mole) sample of phenyl azide and 28.0 g (0.204 mole) of phosphorus trichloride dissolved in 50 ml of benzene were refluxed for a period of 3 days. A white crystalline solid separated from the solution; it was separated by filtration, washed with benzene, and dried. The product melts at 180–181°, compared to 180–182° reported for trichloro-N-phenylphosphine imine.[6] The yield of product was 6.56 g, 56% of the theoretical value.

Anal. Calcd for $C_6H_5NCl_3P$: C, 31.54; H, 2.21; N, 6.13. Found: C, 31.44; H, 2.32; N, 6.20.

Synthesis of Dichlorophenyl-N-phenylphosphine Imine.—The procedure is essentially that described for trichloro-N-phenylphosphine imine except that the reflux time was 24 hr. The yield was 73% of the theoretical quantity. The melting point of the product is 119–119.5° (119–120° reported).[30]

Anal. Calcd for $C_{12}H_{11}NCl_2P$: C, 53.36; H, 3.73; N, 5.19; Cl, 26.26; P, 11.47. Found: C, 55.48; H, 4.39; N, 5.49; Cl, 22.05; P, 12.09.

The low values for chlorine content and correspondingly high values for other elemental analyses are due to hydrolysis of this highly moisture-sensitive material.

Synthesis of Chlorodiphenyl-N-phenylphosphine Imine.—The procedure was essentially that described for trichloro-N-phenylphosphine imine except that the reflux time was only 2 hr. The yield of the chlorodiphenyl-N-phenylphosphine imine was 8.01 g, 69% of the theoretical value. The melting point is 89–92° (88–90° reported).[31]

Anal. Calcd for $C_{18}H_{15}NClP$: C, 69.36; H, 4.85; N, 4.49; Cl, 11.38; P, 9.94. Found: C, 68.79; H, 5.01; N, 4.52; Cl, 11.24; P, 9.87.

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CONTRIBUTION FROM THE U. S. NAVAL ORDNANCE LABORATORY
CORONA, CALIFORNIA

Beryllium Phosphonitrilates[1]

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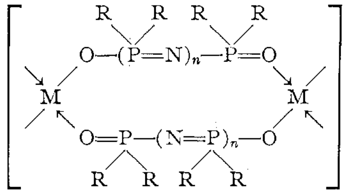
Interaction of beryllium acetylacetonate with the phosphonitrilic derivatives $(C_6H_5)_2P(O)NP(C_6H_5)_2OH$ and $(C_6H_5)_2P(O)[NP(C_6H_5)_2]_3OH$ yielded exclusively monomeric species. Both mono- and disubstituted products were prepared. Treatment of the monosubstituted materials $Be(C_5H_7O_2)(OP(C_6H_5)_2[NP(C_6H_5)_2]_{1,3}O)$ with diphenylphosphinic acid resulted mainly in disproportionation. Structural arrangements and reactions of these compounds are discussed.

Introduction

Block, *et al.*,[3] successfully synthesized thermally stable polymers by interaction of beryllium and other metal acetylacetonates with diphenylphosphinic acid. However, these materials proved to be insoluble in common organic solvents and did not lend themselves to usual fabrication techniques. In view of this finding, it appeared advantageous to consider a system embodying the ladder concept, but at the same time imparting greater flexibility by having longer chains between the metal atoms. Phosphonitriles as exemplified by cyclic diphenylphosphonitrilic tetramer possess high thermal and oxidative stability. Consequently a P–N chain might be incorporated in the general structure



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Two oxygen-terminated phosphonitrilic derivatives, $(C_6H_5)_2P(O)NP(C_6H_5)_2OH$ and $(C_6H_5)_2P(O)[NP(C_6H_5)_2]_3OH$, were chosen as candidate materials for this investigation; the latter was believed to be surely incapable of chelating to a central metal atom.

Experimental Section

Commercial $Be(C_5H_7O_2)_2$, mp 108–109°, was purified by crystallization from heptane, then dried *in vacuo* at 50°. Compounds $(C_6H_5)_2P(O)[NP(C_6H_5)_2]_3OH$, mp 171–172°, and $(C_6H_5)_2P(O)NP(C_6H_5)_2OH$, mp 269–270°, obtained by hydrolysis of $(C_6H_5)_2P(O)[NP(C_6H_5)_2]_3Cl$[4] and $[(C_6H_5)_2P(NH_2)NP(NH_2)(C_6H_5)_2]Cl$,[5] respectively, were dried *in vacuo* at 100° prior to use. Diphenylphosphinic acid, mp 196–197°, was prepared by hydrolysis of $(C_6H_5)_2POCl$ (in aqueous acetonitrile) followed by crystallization from water and drying *in vacuo* at 100°.

Reactions were carried out in evacuated sealed ampoules, each equipped with a small side-arm collection tube; the solid reagents were finely ground and thoroughly mixed.

All melting points were determined in sealed capillaries and are uncorrected. Molecular weights were determined in benzene employing a Mechrolab osmometer. The elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

The infrared absorptions of the starting materials and the products are compiled in Table I. Unfortunately, in this series of compounds, no useful correlations are apparent with the exception of the obvious features such as, for example, the presence of absorptions at about 1590 and 1525 cm^{-1} in the materials containing the acetylacetonate group. Thus, infrared spectral analyses were employed merely for identification of the various products obtained.

Preparation of $Be(C_5H_7O_2)[OP(C_6H_5)_2NP(C_6H_5)_2O]$ (II).—A mixture of $Be(C_5H_7O_2)_2$ (1.809 g, 8.73 mmoles) and $(C_6H_6)_2P(O)NP(C_6H_5)_2OH$ (2.149 g, 5.15 mmoles) was heated at 103° for

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[2] MHD Research, Inc., Newport Beach, Calif. 92663.

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