The Reactions of Nitrogen Trichloride with some Tertiary Phosphines

ROBERT M. KREN and HARRY H. SISLER*

Department of Chemistry, University of Florida, Gainesville, Fla. 32611, U.S.A.

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Abstract

Nitrogen trichloride reacts with trimethyl-, tri-ethyl-, tri-n-butyl-, and triphenylphosphine to yield dichlorophosphoranes of the general formula R_3PCl_2 plus dinitrogen. Nitrogen trichloride reacts with phosphorus trichloride to yield phosphorus pentachloride plus dinitrogen. Chloramine reacts with phosphorus trichloride to yield a mixture of dichlorophosphazene trimer and tetramer.

Introduction

Previous work from this laboratory [1] has clearly demonstrated that chloramine reacts with trialkyl- and triphenylphosphines acting as aminating agent to yield aminophosphonium chlorides in accordance with eqn. (1):

$$R_3P + H_2NCl \longrightarrow (R_3PNH_2)Cl \qquad (1)$$
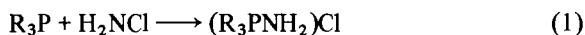
Sisler and co-workers have also shown that dimethyl-chloramine reacts with tris-dimethylaminophosphine to yield tris-dimethylaminodichlorophosphorane and (probably) tetramethylhydrazine [2] as shown by eqn. (2):

$$((CH_3)_2N)_3P + 2(CH_3)_2NCl \longrightarrow$$
$$((CH_3)_2N)_3PCl_2 + (CH_3)_2NN(CH_3)_2 \qquad (2)$$
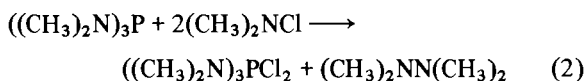
Chloramine has also been shown to engage in oxid-ative coupling reactions by removal of hydrogen from primary and secondary phosphines [3], primary and secondary arsines [4], mercaptans [5], and selenols [6]. Likewise the authors of this paper have shown that dichloroalkylamines react with triphenylphosphine to yield N-chloro-N-akylamino-triphenylphosphonium chloride [7] as shown by eqn. (3):

$$(C_6H_5)_3P + RNCl_2 \longrightarrow ((C_6H_5)_3PNRCl)Cl \qquad (3)$$
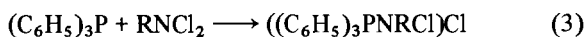
Nitrogen trichloride has been much less studied with respect to its reactions with nucleophilic bases, however, even though other aspects of its chemistry

are rather well known. Most of the reaction chemistry of nitrogen trichloride has been with organic systems because of the mutual solubility of this compound and many organic species in low-polarity solvents. Some reactions with 'inorganic' systems have been reported, however, including reactions with tri-phenylphosphine [8], phenyldichlorophosphine [9], phosphorus trichloride [10], thioethers [11], and copper(I) chloride [12]. Typically, the reported products of these reactions were ionic, and displayed P=N–P and S=N–S linkages, with some chlorinated alkyl species, but in only one case [9] was there a simple phosphorane among the products, and dinitro-gen was not usually found among the products.

It was, therefore, of interest to us to examine the reactions of nitrogen trichloride with some tertiary alkyl phosphines and with triphenylphosphine. In this study we have found that the reactions of nitro-gen trichloride with trimethyl-, triethyl-, and tri-n-butylphosphines yield the respective dichlorotrialkyl-phosphoranes, the reaction of nitrogen trichloride with triphenylphosphine yields dichlorotriphenyl-phosphorane, and the reaction of nitrogen trichloride with phosphorus trichloride yields phosphorus pentachloride. Dinitrogen is also a product of all these reactions.

We have also examined the reactions of chloramine with phosphorus trichloride, and have found that the product of this reaction is a mixture of dichloro-phosphazene trimer and tetramer.

Experimental

Materials

Trimethyl- and triethylphosphines were purchased from Strem Chemicals and were used as received. Tributylphosphine was obtained from Carlisle Chem-ical Works, and was distilled under vacuum before being used. Triphenylphosphine from Eastman Kodak Co. was checked for purity by taking its melting point (79 °C; lit. 79–81 °C [13]), and checking its infrared spectrum [14] for the presence of triphenylphosphine oxide. An approximately 2 M solution of nitrogen trichloride in chloroform was made by the method of Noyes [15].

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*Author to whom correspondence should be addressed.

Manipulations and Measurements

All manipulations of air- and moisture-sensitive substances were carried out in an atmosphere of purified nitrogen using a Vacuum Atmospheres Model HE-43 drybox fitted with a Model HE-93B Dri-Train, and/or using standard inert-atmosphere benchtop procedures [16, 17]. Melting points were measured in sealed capillary tubes, using a Thomas-Hoover melting point apparatus; all were uncorrected. Infrared spectra were recorded from Nujol mulls held between potassium bromide plates, on a Beckman IR-10 spectrophotometer. Nuclear magnetic resonance spectra were recorded in acetonitrile solutions, using either a Varian EM-360 spectrometer or a Varian XL-100 spectrometer. Gas evolution was monitored using a manometer attached to a volume-calibrated standard vacuum line. Solvents were purified by distillation from tetraphosphorus decaoxide, and were stored over Linde Molecular Sieve 4A. Halide analyses were carried out in this laboratory, using a modified Volhard procedure.

All the reactions were carried out at or slightly below room temperature, so decomposition of nitrogen trichloride to dinitrogen and chlorine may be ruled out. In a typical reaction, a weighed sample of one of the phosphines was dissolved in 10 mL of chloroform in a 2-neck T 14/20 round-bottom flask equipped with a magnetic stirbar. A vacuum-line adapter was placed in one of the flask's necks, and a pressure-equalizing addition funnel with a stopcock in the equalizing arm was placed in the other. An aliquot portion of a standardized nitrogen trichloride solution [15] was placed in the addition funnel, and the funnel was purged several times with dry nitrogen gas before the reaction assembly was attached to the vacuum line and chilled in liquid nitrogen. Two freeze-thaw cycles were carried out to degas the phosphine solution. The nitrogen trichloride solution was then added to the flask open to the vacuum line. After half an hour of stirring magnetically, a liquid nitrogen trap was placed around the flask and all condensibles trapped. The 'non-condensible gas' volume was corrected for the small amount of nitrogen introduced through the opening of the addition funnel. A small amount of the reaction liquor was checked for oxidizing capabilities toward an acidified aqueous solution of potassium iodide, so as to determine the amount (if any) of unreacted nitrogen trichloride. The reaction liquor was then stripped of solvent on a rotary evaporator, and the crude solid products further purified by recrystallization from hot acetonitrile.

The phosphine and nitrogen trichloride were mixed in a mol ratio of 1:1, except in the case of a few preliminary trials where 2:1 phosphine:nitrogen trichloride and 1:2 phosphine:nitrogen trichloride ratios were tried; a lower percent yield of phosphor-

ane was found in those trials where the nitrogen trichloride was in molar excess.

Results and Discussion

In all the experiments, after mixing of the nitrogen trichloride solution with the phosphine, a yellowing of the solution was observed, along with the evolution of a non-flammable gas that was not condensable at liquid nitrogen temperature, *viz.* dinitrogen gas. Only when trimethylphosphine was added to the nitrogen trichloride solution, rather than the nitrogen trichloride solution being added to the phosphine, was there evolved less dinitrogen than that indicated by the stoichiometry of eqn. (4):
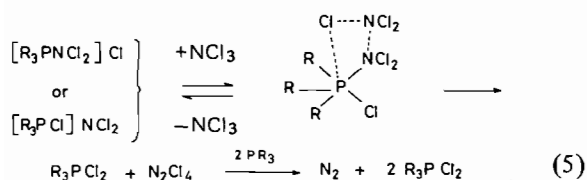
$$3PR_3 + 2NCl_3 \longrightarrow N_2 + 3PR_3Cl_2 \qquad (4)$$
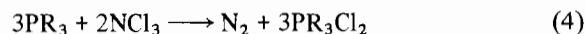
This suggests that the possibility of forming P–N compounds may be enhanced when nitrogen trichloride is kept in excess, as was found by Fluch and Reinisch [9]. Aside from this small evidence, however, our studies gave no indication that nitrogen trichloride reacts with these tertiary phosphines as an aminating agent analogous to the behavior of chloramine toward these nucleophiles. It is of interest to note that other workers in this area [8–11] detected no dinitrogen evolution, but their experiments were not designed to find dinitrogen.

The phosphorane derivatives obtained in these reactions were identified by infrared spectroscopy, melting point determination, nuclear magnetic resonance spectroscopy, and halide analysis.

The reactions of tertiary phosphines with phosphorus trichloride and halophosphines have been studied [18, 19], and have been shown to result either in the formation of adducts or in oxidative coupling. The arguments advanced [19] to explain the observed products typically involve bond dissociation energies or ionic crystal lattice enthalpies. The formation of phosphoranes in the present study must be recognized to involve not only the reducing strengths of the phosphines involved, but also the formation of dinitrogen, the extremely large bond energy of which must be considered an important driving force.

We may speculate on the means of formation of the phosphoranes found in the present study. Initial attack on the lone-pair of phosphorus may occur by the nitrogen atom to form $R_3PNCl_2^+Cl^-$, or by one of the chlorine atoms to form $R_3PCl^+NCl_2^-$. We have shown [7] that R_3PNCl^+ species do not react with phosphines, so $R_3PNCl_2^+$ may be assumed to be unreactive. Subsequent formation of trialkyl-(dichloroamino)chlorophosphorane, and attack by more nitrogen trichloride on that species can lead to the observed products, as shown by sequence (5):

$$[R_3PNCl_2]Cl \quad \left.\begin{array}{c} \\ or \\ \\ [R_3PCl]NCl_2 \end{array}\right\} \quad \begin{array}{c} +NCl_3 \\ \rightleftharpoons \\ -NCl_3 \end{array}$$

$$R_3PCl_2 + N_2Cl_4 \xrightarrow{\;2\,PR_3\;} N_2 + 2\,R_3PCl_2 \qquad (5)$$

Or possibly attack on the $R_3PNCl_2{}^+$ species, and subsequent reaction of N_2Cl_4 with R_3P may lead to the same result, as shown by eqn. (6):

$$\xrightarrow{\hspace{1.5cm}} N_2Cl_4 \ (reacts\ further) + R_3PCl_2 \qquad (6)$$
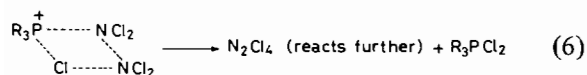
Dichlorodiimide species, chlorine atoms, or nitrogen–chlorine free radicals may also be postulated to participate in the formation of the observed products.

It is of general synthetic interest that chlorination of the organic moieties of the phosphines does not occur when nitrogen trichloride reacts with the phosphines, in contrast to the ability of elemental chlorine, in some instances, to chlorinate the side-chains of tertiary phosphines [20].

The reaction of ammonia-free chloramine with phosphorus trichloride in diethyl ether proceeds at $-78\ ^\circ$C to form a white solid, which decomposes upon warming to evolve hydrogen chloride gas. The residue from this decomposition, after the solvent is removed, has the infrared spectrum of a mixture of dichlorophosphazene trimer and tetramer. We suggest that this reaction proceeds through the elusive species [21] $[P(NH_2)Cl_3]Cl$, which decomposes at low temperatures to form the phosphazenes. The trapping of the gaseous product of this reaction, in a standard solution of sodium hydroxide, and the subsequent back-titration of the excess hydroxide with standardized hydrochloric acid, indicated a stoichiometry in accordance with eqn. (7):

$$PCl_3 + NH_2Cl \longrightarrow [P(NH_2)Cl_3]Cl \longrightarrow$$
$$\tfrac{1}{n}(PNCl_2)_n + 2HCl \qquad (7)$$
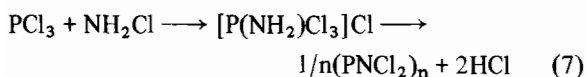
We are seeking to isolate $[P(NH_2)Cl_3]Cl$ and find its ^{31}P nuclear magnetic resonance chemical shift, to determine if this species may possibly be involved in the formation of phosphonitrilics by standard procedures.

References

1 H. H. Sisler, A. Sarkis, H. S. Ahuja, R. J. Drago and N. L. Smith, *J. Am. Chem. Soc., 81*, 2982 (1959).
2 S. R. Jain, L. K. Krannich, R. E. Highsmith and H. H. Sisler, *Inorg. Chem., 6*, 1058 (1967).
3 R. E. Highsmith and H. H. Sisler, *Inorg. Chem., 7*, 1740 (1968).
4 L. K. Krannich and H. H. Sisler, *Inorg. Chem., 8*, 1032 (1969).
5 H. H. Sisler *et al., J. Org. Chem., 35*, 1742 (1970).
6 H. H. Sisler and N. K. Kotia, *J. Org. Chem., 36*, 1700 (1971).
7 R. M. Kren and H. H. Sisler, *Inorg. Chem., 10*, 2630 (1971).
8 R. Appel and G. Buchler, *Z. Naturwiss., 17b*, 422 (1962).
9 E. Fluck and R. M. Reinisch, *Chem. Ber., 96*, 3085 (1963).
10 M. Becke-Goehring and E. Fluck, *Angew. Chem., Int. Ed. Engl., 280*, 1 (1962); see also H. Davy, *Phil. Trans. R. Soc. London, 103*, 242 (1813).
11 R. Appel and G. Buchler, *Justus Liebigs Ann. Chem., 684*, 112 (1965).
12 E. Nachbaur, *Monatsh. Chem., 97*, 361 (1966).
13 P. Walden and R. Z. Swinne, *Phys. Chem., 79*, 714 (1912).
14 D. W. Daasch and D. C. Smith, *Anal. Chem., 23*, 853 (1951).
15 W. A. Noyes, *Inorg. Synth., 1*, 65 (1939).
16 S. Herzog *et al.*, 'Technique of Inorganic Chemistry, Vol. VII', Interscience, New York, 1968, p. 119.
17 D. Shriver, 'The Manipulation of Air-Sensitive Compounds', McGraw-Hill, New York, 1969.
18 S. F. Spangenberg and H. H. Sisler, *Inorg. Chem., 8*, 1006 (1969).
19 J. C. Summers and H. H. Sisler, *Inorg. Chem., 9*, 862 (1970).
20 G. M. Kosolapoff and L. Maier, 'Organic Phosphorus Compounds, Vol. 3', Wiley, New York, 1972, p. 205.
21 I. Haiduc, 'The Chemistry of Inorganic Ring Systems, Part. 2', Wiley-Interscience, New Yorik, 1970, p. 627.