mixture, and 0.5 g. of material of similar infrared spectrum separated on chilling the hot filtrate. A suitable recrystallization solvent was not found. The major crop was insoluble in hot acetone, acetonitrile, and 1,2-dichloroethane. It was soluble in a hot mixture of acetonitrile and 1,2-dichloroethane but did not separate on cooling. The crude material was extracted for several hours with 1,2-dichloroethane in a Soxhlet extractor. No solid separated from the solvent on chilling. The material in the thimble was dried and analyzed.

Anal. Calcd. for $B_{10}H_{1.5}Br_{6.5}(C_5H_9NO)_2$: C, 14.6; H, 2.4; B, 13.1; Br, 62.7; N, 3.4. Found: C, 14.4, 14.8; H, 2.8, 2.7; B, 13.1; Br, 62.7; N, 2.8, 2.8, 3.2.

Notes

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
THE UNIVERSITY OF TEXAS, AUSTIN, TEXAS 78712

The Iodides of Phosphorus. II. The Reaction of Bromine with Diphosphorus Tetraiodide

BY A. H. COWLEY AND S. T. COHEN

Received February 17, 1965

Although a large number of mixed phosphorus trihalides are possible only a few have been prepared. Those that have been isolated include $PClF_2$,[1,2] PCl_2F,[1,2] $PBrF_2$,[3] and PBr_2F.[3] Others have been identified in the course of ebullioscopic,[4] Raman spectral,[4] and n.m.r.[5] studies. In each case their preparation or identification has involved either halogen exchange or reorganization reactions. We have investigated the reaction of bromine with P_2I_4 as a possible route to the new mixed trihalide $PBrI_2$, since reaction of stoichiometric quantities of halogen with other compounds involving one P–P bond, such as organo-substituted diphosphines, results in excellent yields of the corresponding monohalo compounds.[6]

Experimental

The compound P_2I_4 was prepared by the procedure of Germann and Traxler.[7] The bromine and CS_2 were both reagent grade chemicals. The CS_2 was dried over CaH_2 and carefully fractionated before use. All operations were carried out either *in vacuo* or under a dry nitrogen atmosphere.

In a typical run 5.709 g. (35.7 mmoles) of Br_2 in 100 ml. of CS_2 was added dropwise with stirring to 20.347 g. (35.7 mmoles) of P_2I_4 dissolved in 400 ml. of CS_2. The orange color of the P_2I_2 was gradually darkened during the addition. Removal of the CS_2 under reduced pressure left a deep red liquid, $d = 3.53$ g./ml. and f.p. 8–12°; yields were ~90% assuming the product to be $PBrI_2$.

Anal. Calcd. for $PBrI_2$: Br, 21.91; I, 69.60; P, 8.49. Found: Br, 21.74, 21.92; I, 69.50, 69.40; P, 8.48, 8.57.

The infrared spectra (in CS_2 or CH_2Cl_2 solution) were measured in a CsI solution cell on a Beckman IR 7 spectrophotometer equipped with CsI optics. The P^{31} n.m.r. spectra were recorded on a Varian V-4300B spectrometer operating at 24.3 Mc. For the percentage composition measurements the signal-to-noise ratio was improved by time averaging with a Nuclear Data, Inc., Model 800 digital memory oscilloscope. The mass spectra were measured on a CEC 21-102 instrument equipped with a heated inlet system.

Results and Discussion

The infrared spectrum of the reaction product showed peaks at 379 and 329 cm.$^{-1}$ with a shoulder at 306 cm.$^{-1}$. The 379 cm.$^{-1}$ peak is assigned to P–Br stretching and the 329 cm.$^{-1}$ absorption plus the 306 cm.$^{-1}$ shoulder is assigned to P–I stretching.

Although the analytical and infrared data are in agreement with the formulation $PBrI_2$, subsequent n.m.r. and mass spectral studies have indicated that the product is a mixture. The mass spectrum (room temperature) of the reaction product showed peaks, together with the appropriate isotopic intensity distributions, corresponding to PI_3^+, $PBrI_2^+$, PBr_2I^+, PI_2^+, I_2^+, $PBrI^+$, PBr_2^+, PI^+, I^+, PBr^+, and Br^+, suggesting that the liquid is a mixture of PI_3, PBr_3, and the two new mixed trihalides, $PBrI_2$ and PBr_2I. This result was confirmed by the P^{31} n.m.r. spectrum of the pure liquid (Figure 1), which showed peaks at -184, -208, -223, and -227 p.p.m. relative to 85% H_3PO_4. We assign the -184 and -227 p.p.m. peaks to PI_3 (-178 p.p.m.[8]) and PBr_3 (-227 p.p.m.[9]); hence it is reasonable to attribute the -208 and -223 p.p.m. peaks to $PBrI_2$ and PBr_2I, respectively, on the basis that there is evidence for these molecules in the mass spectrum. As estimated from the areas under the n.m.r. peaks the composition of the mixture is 8.2% PBr_3, 13.8% PBr_2I, 33.2% $PBrI_2$, and 44.8% PI_3. Because of the discrepancy between our value for the chemical shift of PI_3 in the reaction mixture (-184 p.p.m.) and that reported[8] for pure PI_3 (-178 p.p.m.), we decided to redetermine the chemical shift of PI_3 (in CS_2 solution). However, since our value (-179 p.p.m.) confirmed the earlier result, the PI_3 resonance is apparently shifted downfield by dissolution in the other halides.

The fact that good analyses are obtained for the composition $PBrI_2$ suggests that reaction proceeds to $PBrI_2$ initially. If this is the case two reactions that could give rise to the observed products are

$$2PBrI_2 \rightleftharpoons PBr_2I + PI_3$$

$$3PBr_2I \rightleftharpoons 2PBr_3 + PI_3$$

---

[1] H. S. Booth and A. R. Bozarth, *J. Am. Chem. Soc.*, **61**, 2927 (1939).

[2] R. R. Holmes and W. P. Gallagher, *Inorg. Chem.*, **2**, 433 (1963).

[3] H. S. Booth and S. G. Frary, *J. Am. Chem. Soc.*, **61**, 2934 (1939).

[4] D. S. Payne, *Quart. Rev.* (London), **15**, 177 (1961), and references therein.

[5] E. Fluck, J. R. Van Wazer, and L. C. D. Groenweghe, *J. Am. Chem. Soc.*, **81**, 6363 (1959).

[6] L. Maier, *Progr. Inorg. Chem.*, **5**, 73 (1963), and references therein.

[7] F. E. E. Germann and R. N. Traxler, *J. Am. Chem. Soc.*, **49**, 307 (1927).

[8] H. S. Gutowsky and D. W. McCall, *J. Chem. Phys.*, **22**, 162 (1954).

[9] N. Muller, P. C. Lauterbur, and J. Goldenson, *J. Am. Chem. Soc.*, **78**, 3557 (1956); J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *ibid.*, **78**, 5715 (1956).

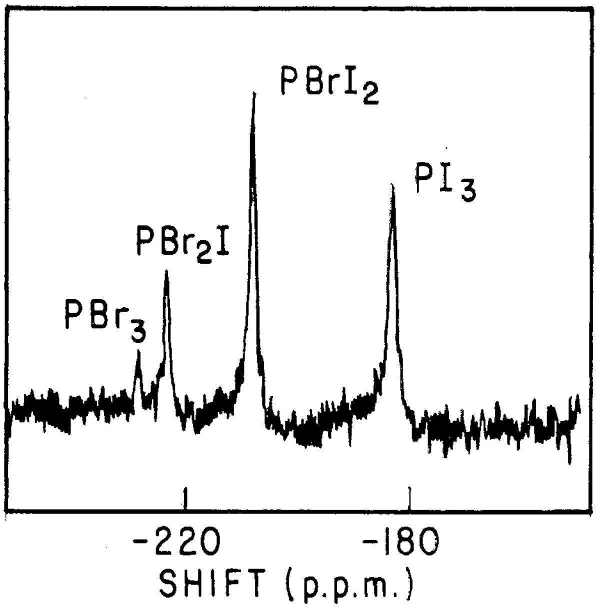


Figure 1.—P^{31} n.m.r. spectrum of a P_2I_4–bromine reaction mixture (pure liquid).

The bromo iodides can also be detected in PBr_3–PI_3 mixtures. A 2:1 mole ratio mixture of PI_3 and PBr_3 undergoes an endothermal reorganization reaction within a few minutes to yield a product with P^{31} n.m.r. and mass spectra that are very similar to those of the P_2I_4–bromine reaction product. The rate of reorganization seems to increase along the series F < Cl < Br < I. Thus, the PBr_3–PCl_3 system[10] requires 1.5 hr. for equilibration while the PBr_2F–PCl_3 system[10] requires 60 hr. Further evidence for the relative lability of the bromo–iodo system is our study of the mass spectra of the P_2I_4–bromine reaction product at various temperatures. Upon raising the temperature of the heated inlet system in steps of 30 to 40° one finds that the PI_3 and $PBrI_2$ peaks increase in intensity at the expense of the PBr_2I and PBr_3 peaks. The lability of the system, plus its lack of volatility, has precluded a separation of the reaction mixture into its components.

Acknowledgment.—The financial support of The Robert A. Welch Foundation is gratefully acknowledged.

[10] M. L. Delwaulle and M. Bridoux, *Compt. rend.*, **248**, 1342 (1959).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF FLORIDA, GAINESVILLE, FLORIDA

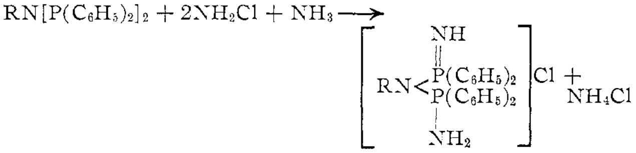
Further Studies in the Chloramination of Some Aminophosphines

BY DONALD F. CLEMENS AND HARRY H. SISLER

Received March 25, 1965

It has recently been shown that chloramine reacts with aminophosphines to form aminophosphonium salts.[1] All the previously reported chloraminations were, however, concerned with phenylphosphino derivatives and none of them contained alkyl–phosphorus bonds. Furthermore, with the exception of 1,1-bis(diphenylphosphino)-2,2-dimethylhydrazine,[2] none of the previously chloraminated nitrogen–phosphorus derivatives contained more than one phosphorus atom attached to a nitrogen atom.

The present work was undertaken to determine if, as in the case of the previously studied[1] aminophenylphosphines, chloramination of aminoalkylphosphines and of bis(diphenylphosphino)amines occurs on the phosphorus atom(s) rather than the nitrogen atom. The results have established that this is indeed the case and that the chloramination of the bis(diphenylphosphino)amines occurs in accordance with the equation



$$\mathrm{RN[P(C_6H_5)_2]_2 + 2NH_2Cl + NH_3} \longrightarrow \left[\mathrm{RN}<\begin{array}{c}\mathrm{NH}\\ \| \\ \mathrm{P(C_6H_5)_2}\\ \mathrm{P(C_6H_5)_2}\\ | \\ \mathrm{NH_2}\end{array}\right]\mathrm{Cl} + \mathrm{NH_4Cl}$$

This work has further shown that if the R group on the nitrogen atom in the bisphosphinoamines is a hydrogen atom the compound obtained on chloramination is $[(C_6H_5)_2P(NH_2)NP(NH_2)(C_6H_5)_2]Cl$, which has been synthesized by the ammonolysis of diphenyltrichlorophosphorane[3] and by the ammonolysis and chloramination of diphenylchlorophosphine.[4]

Experimental

Materials.—Solvents used were dried over calcium hydride. The anhydrous amines were obtained from The Matheson Company, Inc., and were used as received. Diphenylchlorophosphine was provided by the Victor Chemical Works. Tributylphosphine was obtained from Food Machinery and Chemical Corp. Dibutylchlorophosphine was prepared by the pyrolysis of tributyldichlorophosphorane.[5]

Analyses.—Elemental analyses were done by Galbraith Microanalytical Laboratories. Melting points were obtained in wax-sealed capillary tubes in a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Infrared Spectra.—The infrared spectra were recorded on a Perkin-Elmer Model 137 spectrometer using sodium chloride optics. The spectra of the solids were obtained from Nujol mulls. A summary of the data is found in Table I.

Nuclear Magnetic Resonance Spectra.—Nuclear magnetic resonance spectra were obtained on a Varian high-resolution spectrometer, Model V-4300-2, equipped with field homogeneity control, magnet insulation, and field stabilizer. A summary of the data is found in Table II.

Preparation of Aminophosphines.—Some of the aminophosphines used in this work have been reported previously.[6,7] Using similar methods two new aminophosphines have been prepared. These are ethylaminodibutylphosphine, $C_2H_5NHP(C_4H_9)_2$, and bis(diphenylphosphino)amine, $HN[P(C_6H_5)_2]_2$. Analytical and melting point data are listed in Table III.

Procedure for Chloramination Reactions.—The procedure out-

---

[1] W. A. Hart and H. H. Sisler, *Inorg. Chem.*, **3**, 617 (1964).
[2] R. P. Nielsen, J. F. Vincent, and H. H. Sisler, *ibid.*, **2**, 760 (1963).
[3] I. I. Bezman and J. H. Smalley, *Chem. Ind.* (London), 839 (1960).
[4] H. H. Sisler, H. S. Ahuja, and N. L. Smith, *Inorg. Chem.*, **1**, 84 (1962).
[5] S. E. Frazier, R. P. Nielsen, and H. H. Sisler, *ibid.*, **3**, 292 (1964).
[6] A. B. Burg and P. J. Slota, *J. Am. Chem. Soc.*, **80**, 1107 (1958).
[7] G. Ewart, A. P. Lane, J. McKechnie, and D. S. Payne, *J. Chem. Soc.* 1543 (1964).