TABLE IV

MASS SPECTRA OF IODOTHIOPHOSPHORYL
DIFLUORIDE AND SOME OF ITS DERIVATIVES

| Ion | Intensity[a] | | |
| | $X = I$[b] | $X = OCH_3$[c] | $X = SCH_3$[d] |
| --- | --- | --- | --- |
| $^{34}SPF_2X$ | 2.4 | 1.9 | 2.5 |
| $^{33}SPF_2X$ | 0.5 | 0.9 | 0.9 |
| $^{32}SPF_2X$ | 51.9[e] | 34.1[e] | 27.9[e] |
| $^{34}SPF_2$ | 1.4 | ... | ... |
| $^{32}SPF_2$ | 24.0 | 6.7 | 3.3 |
| $^{32}SPFX$ | ... | 0.9 | ... |
| $^{32}SPF$ | 1.4 | 1.1 | 0.9 |
| $PF_2$ | 8.9 | 15.6 | 11.7 |
| $PX$ | ... | ... | 1.1 |
| $PF$ | 1.4 | 1.1 | 1.3 |
| $^{32}SP$ | 1.4 | 0.9 | 1.3 |
| $^{32}S$ | 1.4 | 1.1 | 1.3 |
| $X$ | 3.8 | 3.9[f] | 7.5 |

[a] Intensities are expressed relative to the total ionization defined as $\Sigma_n$ (intensity) for all ions with mass greater than 30 whose intensity is greater than 2% of the base peak. [b] Also observed: $^{32}SI^+$ (2.1%). [c] Also observed: $^{34}SPF_2H^+$ (0.9%), $^{32}SPF_2H_2^+$ (2.8%),[e] $^{32}SPF_2H^+$ (12.2%), $PF_2OCH_2^+$ (4.7%), $OPF_2^+$ (0.9%), $PO^+$ (5.8%). [d] Also observed: $^{32}S_2PF_2^+$ (1.5%), $^{32}SPF_3^+$ (0.7%), $^{32}SPF^+$ (1.5%), $^{34}SCH_2^+$ (1.2%), $^{32}SCH_2^+$ (23.0%), $^{32}SCH^+$ (8.8)%, $^{32}SC^+$ (0.7%). [e] Identity confirmed by exact mass measurement. [f] Possibly also contains $P^+$.

features. All compounds show strong P—F absorptions in the 850–950-cm$^{-1}$ region. The P=S stretch appears to be best assigned to strong bands at 713 cm$^{-1}$ in SPF$_2$I and 733 cm$^{-1}$ in SPF$_2$SCH$_3$ and the weak band at 654 cm$^{-1}$ in SPF$_2$OCH$_3$. The last compound does not show a strong band in the 1200–1500-cm$^{-1}$ region; thus we can exclude the possibility of the methyl ester having the F$_2$P(O)SCH$_3$ isomeric structure.

**D. Some Further Properties of Iodothiophosphoryl Difluoride.**—The compound appears to possess appreciable thermal stability since less than 5% decomposition occurred after 4 days at 150°. Under ordinary illumination, samples appear to photolyze slightly liberating molecular iodine. The other product of the photolysis has not been identified but could possibly be

the diphosphorus compound F$_2$(S)P–P(S)F$_2$. Attempts to synthesize this compound or its isomers by means of coupling reactions of the iodofluoride with active metals such as mercury, copper, antimony, etc., have not yet been successful in spite of the many well-established syntheses of diphosphorus compounds from reactions of the iodophosphorus compound with metals such as mercury.[21] The lack of success in the synthesis of diphosphorus compounds by either the coupling reactions or the reaction with dimethylphosphine might suggest that the diphosphorus compounds involving pentavalent phosphorus are much less stable than trivalent diphosphines, especially when the phosphorus atom carries highly electronegative substituents such as fluorine.

Replacement of iodine by chlorine can be effected with mercuric chloride[22] but silver chloride, which has often been used for this purpose,[21b] did not react appreciably with SPF$_2$I, possibly because of surface effects.

Hydrolysis of iodothiophosphoryl difluoride appears to involve all of the halogens and also the P=S bond. The reaction involves equimolar proportions of iodofluoride and water and yields SiF$_4$ (presumably from attack of the liberated HF on the glass vessel), SPF$_2$H (presumably arising from the formation of HI followed by reduction according to eq 3), and H$_2$S. The involatile residue is probably phosphorous acid OPH(OH)$_2$ or the thio analog SPH(OH)$_2$. The iodothiophosphoryl difluoride was apparently consumed initially with formation of SPF$_2$H which is also hydrolyzed[2] but apparently at a reduced rate. The course and stoichiometry of the reaction have not yet been completely determined.

(21) See for example: (a) R. W. Rudolph, R. C. Taylor, and R. W. Parry, *J. Am. Chem. Soc.*, **88**, 3729 (1966); (b) F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, *J. Chem. Soc.*, 1565 (1953); (c) W. Mahler and A. B. Burg, *J. Am. Chem. Soc.*, **80**, 6161 (1958).

(22) A. B. Burg and J. F. Nixon, *ibid.*, **86**, 356 (1964); J. F. Nixon and R. G. Cavell, *J. Chem. Soc.*, 5983 (1964).

# Reactions of Triphenylphosphine with S$_4$N$_3$Cl

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It has been shown that S$_4$N$_3$Cl gives a complex series of reactions in which [(C$_6$H$_5$)$_3$P=NP(C$_6$H$_5$)$_3$]Cl (I), [(C$_6$H$_5$)$_3$PNH$_2$]Cl (II), and [{(C$_6$H$_5$)$_3$PN}$_3$S]Cl$_3$ (III) are produced. Compound III reacts with two molecules of triphenylphosphine giving [{(C$_6$H$_5$)$_3$PN}$_3$S]Cl$_3$·2P(C$_6$H$_5$)$_3$ (IV), which crystallizes out of acetone with 2 moles of acetone. N-Chlorotriphenylphosphinimine is suggested as a probable intermediate in these reactions.

## Introduction

We have been concerned with the chloramination of a variety of electron-donor species, more particularly amines, phosphines, and aminophosphines. We spec-

ulated that S$_4$N$_3$Cl, even though it has been shown to be principally ionic in character, might behave toward electron-donor molecules in a manner analogous to that of chloramine. The research reported below has

been carried out to check the validity of this hypothesis.

## Experimental Section

**Materials.**—Reagent grade solvents were distilled from over calcium hydride and stored in an inert atmosphere over calcium hydride. Reagent grade carbon tetrachloride and acetone were stored over anhydrous calcium sulfate and anhydrous magnesium sulfate, respectively. Commercial triphenylphosphine, obtained from the Metal and Thermit Corp., was recrystallized from ether to remove any triphenylphosphine oxide present. Sulfur monochloride was obtained from Eastman Organic Chemicals and used as obtained.

**Analyses.**—Elemenal analyses and determinations of molecular weight were carried out by Galbraith Microanalytical Laboratories. Molecular weights were determined in chloroform using a vapor pressure osmometer. Several nitrogen analyses were carried out in this laboratory using a Coleman Model 29 nitrogen analyzer. Chloride analyses were done in this laboratory by the Volhard method. Melting points were obtained in Pyrex capillary tubes in a Thomas-Hoover capillary melting point apparatus and are uncorrected.

**Infrared Spectra.**—The infrared spectra were determined on a Beckman IR-10 spectrophotometer or a Perkin-Elmer Model 137 spectrometer. The spectra of all of the solid materials were determined using KBr disks.

**Nuclear Magnetic Resonance Spectra.**—Nuclear magnetic resonance spectra (both $^1H$ and $^{31}P$) were determined with a Varian Model V-4300-2 high-resolution spectrometer equipped with a field-homogeneity control, magnet insulation, and a superstablizer. The spectra of solid products were determined on solutions in chloroform and deuterated chloroform.

**Preparation of $S_4N_3Cl$.**—$S_4N_3Cl$ was prepared as described by Jolly, Maguire, and Rabinovich.[1] The infrared spectrum of the $S_4N_3Cl$ prepared showed peaks at 8.55, 10.00, and 14.75 $\mu$ as described in the literature.[1]

*Anal.* Calcd for $S_4N_3Cl$: N, 20.38; Cl, 17.24. Found: N, 20.23; Cl, 17.36.

**Preparation of $[(C_6H_5)_3P=NP(C_6H_5)_3]Cl$.**—$S_4N_3Cl$ (12.1 mmol) and triphenylphosphine (53.4 mmol) were mixed in a 300-ml round-bottomed flask under dry nitrogen. A small Teflon-covered stirring bar was also inserted into the flask. The flask was then connected to the vacuum line and evacuated for 1 hr. The mixture was slowly heated and it started to turn orange-red. When the mixture had just started to melt, the stirrer was started. When the mixture had completely melted, an orange-yellow smoke was seen in the flask and the pressure in the vacuum line had increased. The stirring was continued for 4 hr after which time there was no gas evolution. The heating and stirring were discontinued and the contents of the flask were allowed to come to room temperature. The flask was detached from the vacuum line and filled with dry nitrogen.

The solid, brown hard cake remaining in the flask was powdered and washed with dry, cold hexane to remove unreacted triphenylphosphine. The residue was extracted with ether. The ether-soluble portion yielded a dirty white solid. Repeated recrystallization from ethanol yielded a white crystalline material which was identified as triphenylphosphine sulfide (20.0 mmol); mp 161°, lit.[2] mp 161°.

The infrared spectrum of the material shows a strong peak in the $> P=S$ region at 632 cm$^{-1}$ which is in agreement with the value 627 cm$^{-1}$ reported in literature[3] for the $> P=S$ stretching frequency in triphenylphosphine sulfide.

The white solid (I) left in the extraction thimble was recrystallized by dissolving it in the least possible amount of hot chloroform and reprecipitating with ether. This process was repeated three times; mp 266°. The melting point reported in the literature

for $[(C_6H_5)_3P=NP(C_6H_5)_3]Cl$ is 269-271°.[4] The yield was 8.44 mmol (69.8% of theory based upon $S_4N_3Cl$).

*Anal.* Calcd for $[(C_6H_5)_3P=NP(C_6H_5)_3]Cl$: C, 75.32; H, 5.23; N, 2.44; Cl, 6.19; P, 10.81. Found: C, 73.20; H, 5.32; N, 2.45; Cl, 5.92; P, 10.68.

An ethanolic solution of sodium tetraphenylborate was added gradually to an ethanolic solution of compound 1. A white solid precipitated immediately and was filtered and dried; mp 267-269°.

*Anal.* Calcd for $[(C_6H_5)_3P=NP(C_6H_5)_3][B(C_6H_5)_4]$: N, 1.63. Found: N, 1.72.

The hexafluorophosphate salt of I was prepared by a procedure similar to that above; mp 266°.

*Anal.* Calcd for $[(C_6H_5)_3P=NP(C_6H_5)_3]PF_6$: N, 2.04. Found: N, 2.00.

The infrared spectrum of I has a strong band at 1230–1300 cm$^{-1}$ characteristic of the $P=N-P$ stretch.[5] The infrared spectrum also contains an intense sharp peak at 1115 cm$^{-1}$ which is assigned to tetracoordinated phosphorus attached to a phenyl group.[6] The infrared spectrum of the hexafluorophosphate derivative of I has a very strong band characteristic of the $PF_6^-$ grouping at 835 cm$^{-1}$.

The $^1H$ nmr spectrum of I has only one peak (complex), which falls in the aromatic region showing the equivalence of all the phenyl groups in the compound. The chemical shift was 2.32–2.68 ppm with respect to tetramethylsilane as internal standard. The $^{31}P$ nmr spectrum shows only one peak, indicating that both of the phosphorus atoms are equivalent. The chemical shift was found to be $-20.1$ ppm from 85% phosphoric acid. The chemical shift reported in the literature[7] for $[(C_6H_5)_3P=NP(C_6H_5)_3]Br$ is $-21 \pm 1$ ppm. One of the gases evolved in this reaction was not condensable at liquid nitrogen temperature and probably is elementary nitrogen. Traces of tetrasulfur tetranitride were also observed as a by-product of the reaction.

**Preparation of Triphenylaminophosphonium Chloride.**—$S_4N_3Cl$ (6.32 mmol) was added to a 500-ml round-bottomed flask containing 23.8 mmol of triphenylphosphine dissolved in 200 ml of reagent grade benzene, to which 1 ml of water had been added. The reaction mixture was refluxed for 4 hr with continuous stirring. Throughout the reaction, sulfur dioxide gas was evolved. The light brown solid was filtered off, dried, and recrystallized by dissolving in chloroform and reprecipitating by adding ether. The white crystalline material (II) obtained melts at 240°. The melting point reported for triphenylaminophosphonium chloride in the literature[8] is 230-232°.

*Anal.* Calcd for triphenylaminophosphonium chloride $[(C_6H_5)_3PNH_2]Cl$: N, 4.46; Cl, 11.32. Found: N, 4.46; Cl, 11.24.

The infrared spectrum of this product was found to be identical with the infrared spectrum of triphenylaminophosphonium chloride made by the direct chloramination of triphenylphosphine.[8] The yield was 3.82 mmol (60.4% of theory based upon $S_4N_3Cl$).

After separating the triphenylaminophosphonium chloride, the benzene was evaporated from the solution. The solid residue was washed with hexane to remove any unreacted triphenylphosphine. The residue was recrystallized from ether, yielding white needles of triphenylphosphine sulfide (7.14 mmol). The residue insoluble in ether was recrystallized from ethanol which yielded white crystalline solid melting at 153-154°; yield, 1.62 mmol. The melting point of this solid, as well as the absence of chlorine and nitrogen in it, and its insolubility in ether indicated it to be triphenylphosphine oxide. Triphenylphosphine oxide melts at 156°.

**Preparation of $[\{(C_6H_5)_3PN\}_3S]Cl_3$.**—$S_4N_3Cl$ (7.2 mmol) was added to a solution of 37.10 mmol of triphenylphosphine in 150

(1) W. L. Jolly, K. D. Maguire, and D. Rabinovich, *Inorg. Chem.*, **2**, 1304 (1963).

(2) W. Strecker and C. Grossmann, *Chem. Ber.*, **49**, 63 (1916).

(3) R. A. Zingaro, *Inorg. Chem.*, **2**, 194 (1963).

(4) R. Appel and G. Büchler, *Z. Naturforsch.*, **17b**, 422 (1962).

(5) H. H. Sisler, H. S. Ahuja, and N. L. Smith, *Inorg. Chem.*, **1**, 84 (1962).

(6) W. A. Hart and H. H. Sisler, *ibid.*, **3**, 617 (1964).

(7) R. Appel and A. Haus, *Z. Anorg. Allgem. Chem.*, **311**, 290 (1961).

(8) H. H. Sisler, A. Sarkis, H. S. Ahuja, R. I. Drago, and N. L. Smith, *J. Am. Chem. Soc.*, **81**, 2982 (1959).

ml of extremely dry benzene. The reaction was carried out in an inert-atmosphere box. The contents were continuously stirred with a magnetic stirrer. After about 10 min, a bright red solid began to form and the solution turned dark red. As the bulk of red material increased in the flask, more dry benzene was added to the reaction mixture. After 72 hr, the bright red material was filtered off and thoroughly washed with dry benzene until the wash liquid became colorless. The bright red material was dissolved in the least possible amount of extremely dry chloroform and 10 ml of dry benzene was added to the resulting red solution. Dry ether was gradually added to this solution with constant stirring and a red crystalline powder reprecipitated. This solid was filtered off and washed with dry benzene until the wash liquid was colorless. This procedure was repeated two or three times and the resulting red crystalline material (III) was dried. The yield was 2.16 g (90% of theory based upon $S_4N_3Cl$); mp 101–104° dec.

*Anal.* Calcd for $[\{(C_6H_5)_3PN\}_3S]Cl_3$: C, 67.04; H, 4.66; N, 4.34; Cl, 11.02; S, 3.31; P, 9.62; mol wt, 966.5. Found: C, 66.90; H, 4.96; N, 4.24; Cl, 10.92; S, 3.52; P, 8.66; mol wt, 870 (chloroform).

The infrared spectrum of this product shows a tetracoordinated phosphorus peak at 1106 cm$^{-1}$.[6] The $^1$H nmr spectrum shows only one peak which falls in the aromatic region, indicating the equivalence of the three triphenylphosphine groups. The chemical shift is 2.21–2.82 ppm from tetramethylsilane as internal standard. The $^{31}$P nmr spectrum in chloroform shows a single peak, indicating the equivalence of the three phosphorus atoms. The chemical shift is −16.0 ppm from 85% phosphoric acid. This compound is soluble in acetone, chloroform, and polar solvents, such as dimethylformamide, dimethyl sulfoxide, and various alcohols. It is insoluble in less polar solvents, such as ether, benzene, toluene, and hexane.

After separating the bright red solid $[\{(C_6H_5)_3PN\}_3S]Cl_3$, benzene was evaporated from the filtrate. The residual solid (5.6 g) was washed with dry isopropyl ether to remove any triphenylphosphine. The residue was recrystallized from ether, yielding white needles of triphenylphosphine sulfide; yield, 4.12 g (14.0 mmol).

**Preparation of** $[\{(C_6H_5)_3PN\}_3S]Cl \cdot 2P(C_6H_5)_3$.—A 1.47-g sample of the crude red material, $[\{(C_6H_5)_3PN\}_3S]Cl_3$, was mixed with 3.73 g of triphenylphosphine in a 50-ml flask. A Teflon-covered stirring bar was inserted in the flask. The flask was connected to the vacuum line and evacuated for 0.5 hr. The flask was gradually heated until the mixture melted. The molten contents was stirred for 4 hr and the heating was stopped. No gas evolution was observed. The flask was filled with dry nitrogen. The hard, solid cake was powdered and extracted with 100 ml of benzene to remove unreacted triphenylphosphine and some triphenylphosphine sulfide obtained as one of the reaction products. The insoluble white solid residue was extracted with 100 ml of acetone. The acetone-insoluble residue was found to be $[(C_6H_5)_3P=NP(C_6H_5)_3]Cl$. To the acetone solution, ether was added. A white crystalline powder was precipitated and dried. This solid was dissolved in the least possible amount of hot acetone and reprecipitated by gradually adding ether. This process of recrystallization was repeated three times, and the white crystalline material (IV) was dried. As the analysis below indicates, the solid contains 2 mol of acetone; yield, 1.2 g; structure changes at 135° and melts with decomposition at 220–225° to give a dark red melt.

*Anal.* Calcd for $[\{(C_6H_5)_3PN\}_3S]Cl_3 \cdot 2P(C_6H_5)_3 \cdot 2(CH_3)_2$-$C=O$: C, 71.71; H, 5.42; N, 2.61; Cl, 6.63; P, 9.65. Found: C, 70.02; H, 5.53; N, 2.72; Cl, 6.58; P, 9.54.

The infrared spectrum of the above compound is similar to that of $[\{(C_6H_5)_3PN\}_3S]Cl_3$, except that it shows a broad band at 1255–1305 cm$^{-1}$ which may be attributed to the P=N—P stretch. A peak at 1703 cm$^{-1}$ is assigned to the >C=O group in acetone. Tetracoordinated P is found at 1110 cm$^{-1}$. The $^{31}$P nmr in chloroform shows three peaks, indicating three different kinds of P atoms. The chemical shifts are found at −25, −11, and −7.3 ppm, relative to 85% phosphoric acid. The $^1$H

nmr spectrum shows two peaks, one at a chemical shift of 7.81 ppm (CH$_3$) with respect to tetramethylsilane and the other at 2.32–2.84 ppm (C$_6$H$_5$). This compound is stable in the atmosphere, is soluble in acetone, chloroform, and alcohols, but is insoluble in ether, hexane, benzene, and toluene.

In one experiment, the acetone-free material was isolated. The molecular weight was determined to be 1423 in chloroform and the calculated molecular weight for $[\{(C_6H_5)_3PN\}_3S]Cl_3 \cdot 2P$-$(C_6H_5)_3$ is 1490. The infrared spectrum was similar to that of the acetone adduct of the compound, except for the >C=O peak. The analysis (except for carbon) of this product agrees with the formula for the acetone-free compound.

*Anal.* Calcd for $[\{(C_6H_5)_3PN\}_3S]Cl_3 \cdot 2P(C_6H_5)_3$: C, 72.48; H, 5.03; N, 2.82; Cl, 7.14; S, 2.15. Found: C, 66.67; H, 5.23; N, 3.11; Cl, 7.49; S, 2.13.

## Discussion and Conclusions

The results of these experiments show that $S_4N_3Cl$, instead of giving the simple 1:1 adduct $[S_4N_3 \cdot P(C_6H_5)_3]^+Cl^-$, gives a more complex series of reactions which involve the breaking of the S—N ring and the production of compounds $[(C_6H_5)_3P=NP(C_6H_5)_3]Cl$ (I), $[(C_6H_5)_3PNH_2]Cl$ (II), $[\{(C_6H_5)_3PN\}_3S]Cl_3$ (III), $(C_6H_5)_3PS$, $(C_6H_5)_3PO$, and $[\{(C_6H_5)_3PN\}_3S]Cl_3 \cdot 2P$-$(C_6H_5)_3$ (IV), depending on the reaction conditions. Smaller amounts of tetrasulfur tetranitride, nitrogen, and sulfur dioxide are also produced.

The reaction scheme below represented by steps 1–3 accounts for several of the products but must be regarded as tentative at the present. Step 1 of this scheme involves the formation of N-chlorotriphenylphosphinimine, either by an attack of triphenylphosphine on a nitrogen atom in $S_4N_3Cl$ or by the attack of

triphenylphosphine on two sulfur atoms in the immediate neighborhood of a nitrogen atom in $S_4N_3Cl$ to form triphenylphosphine sulfide, chloronitrene, and some sulfur–nitrogen compound. It is postulated that the chloronitrene then reacts with triphenylphosphine to give N-chlorotriphenylphosphinimine.

$$S_4N_3{}^+Cl^- \xrightarrow{(C_6H_5)_3P} [S_4N_3 \cdot P(C_6H_5)_3]^+Cl^-$$

$$\downarrow P(C_6H_5)_3 \qquad\qquad \downarrow \text{unstable}$$

$$(C_6H_5)_3PS + SN\ compd + {>}NCl$$

$$\quad\quad\quad\quad (C_6H_5)_3P{=}NCl + SN\ compd \quad (1)$$
$$\quad\quad\quad\quad (C_6H_5)_3P \uparrow$$

$$(C_6H_5)_3PNCl + (C_6H_5)_3P \longrightarrow [(C_6H_5)_3P{=}NP(C_6H_5)_3]^+Cl^- \quad (2)$$
$$\text{I}$$

$$(C_6H_5)_3PNCl + H_2O \longrightarrow (C_6H_5)_3PNHCl$$
$$\qquad\qquad\qquad\qquad\qquad\qquad \downarrow \text{OH}$$
$$NH_2Cl + (C_6H_5)_3P{=}O$$
$$\qquad\qquad \downarrow P(C_6H_5)_3$$
$$[(C_6H_5)_3PNH_2]^+Cl^- \quad (3)$$
$$\text{II}$$

Step 2 of this mechanism is a known reaction. It has been reported in the literature[4] and has been confirmed in our laboratory.

The $^{31}P$ and $^1H$ nmr spectra of I show the two phosphorus atoms to be equivalent and all of the phenyl groups to be equivalent. The structure of I may be rationalized as a resonance hybrid of such structures as $[(C_6H_5)_3P{=}N{-}P^+(C_6H_5)_3]Cl^-$, $[(C_6H_5)_3P^+{-}N{=}P-(C_6H_5)_3]Cl^-$, $[(C_6H_5)_3P{=}N^+{=}P(C_6H_5)_3]Cl^-$, and $[(C_6H_5)_3P{\cdots}N{\cdots}(C_6H_5)_3]^+Cl^-$, analogous to those postulated by Appel[7] for $[(C_6H_5)_3PNP(C_6H_5)_3]Br$.

We have verified step 3 of this mechanism by carrying out the reaction of N-chlorotriphenylphosphinimine with triphenylphosphine in ordinary benzene which has not been dried. This reaction yields triphenylaminophosphonium chloride and triphenylphosphine oxide. The hydrolysis scheme for N-chlorotriphenylphosphinimine to give chloramine and triphenylphosphine oxide is analogous to the known hydrolysis of phosphinimine to give ammonia and triphenylphosphine oxide. We had thought that compound III is produced by the reaction of N-chlorotriphenylphosphinimine with sulfur. However, we have not been able to make compound III by this process. The mechanism for the formation of compound III is not understood at the present time. Again, it should be

observed that the mechanism just described should be considered only as a reasonable postulate as yet not completely confirmed.

A tentative structure for compound III, in which the bonding state of sulfur may be analogous to that of sulfur in sulfur trioxide, is proposed. Various resonance forms could contribute to this structure.

$$\left[ \begin{array}{c} (C_6H_5)_3PN{\cdots}S{\cdots}NP(C_6H_5)_3 \\ \vdots \\ N \\ P \\ (C_6H_5)_3 \end{array} \right]^{3+} 3Cl^-$$

The identical environments of the three phosphorus atoms, a chemical shift of $-16.0$ ppm which falls in the range to be expected for tetracoordinate phosphorus, the equivalence of all the phenyl groups as evidenced by $^1H$ nmr, the presence of a tetracoordinate phosphorus atom attached to a phenyl group as indicated by the band in the infrared absorption at 1106 cm$^{-1}$,[6] and the absence of the $-P{=}N$-stretching frequency suggest, but do not prove, a structure of the above type. The structure in which three chlorine atoms are covalently bonded to a sulfur atom may be ruled out on the steric grounds that there is little likelihood of hexacoordinated sulfur with such bulky groups. Also, the S—Cl stretching frequency is not found in the infrared spectrum. A strong band is found at 1040 cm$^{-1}$ in the spectrum of this compound and its adduct with triphenylphosphine and could be assigned to S=N stretch, since this band does not occur in the infrared spectra of I and II. The corresponding S=O stretch in sulfur trioxide is found at 1069 cm$^{-1}$.[9]

The Lewis acid character of III is probably demonstrated in its reaction with triphenylphosphine to give IV according to

$$[\{(C_6H_5)_3PN\}_3S]Cl_3 + 2P(C_6H_5)_3 \longrightarrow$$
$$[\{(C_6H_5)_3PN\}_3S]Cl_3 \cdot 2P(C_6H_5)_3$$
$$\text{IV}$$

(9) K. Nakamoto, "The Infra-Red Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963.