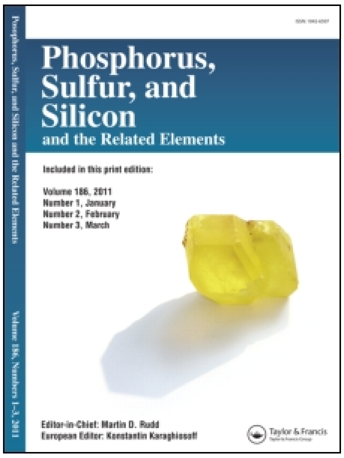

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REACTIONS OF SULFUR DIOXIDE WITH AMINOPHOSPHINES

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REACTIONS OF SULFUR DIOXIDE WITH AMINOPHOSPHINES

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The reactions of SO_2 with *tris*-dimethylaminophosphine, *bis*-dimethylaminofluorophosphine, *bis*-dimethylaminochlorophosphine, dimethylaminodifluorophosphine, dimethylaminodichlorophosphine, 1,3-dimethyl-2-fluoro-1,3,2-diazaphospholidine and 1,3-dimethyl-2-chloro-1,3,2-diazaphospholidine have been investigated. The complex reactions are dominated by facile oxidation of the respective phosphine to phosphoryl and thiophosphoryl derivatives. The new heterocyclic phosphines $CH_3\overline{NCH_2CH_2N(CH_3)P}(O)F$ and $CH_3\overline{NCH_2CH_2N(CH_3)P}(S)F$ have been isolated and characterized by NMR, infrared, and mass spectrometry.

INTRODUCTION

The reactions of small molecules, e.g., CO, CO_2, NO, O_2, CS_2, and SO_2 with coordinatively unsaturated transition metal complexes have recently drawn attention in the context of catalytic conversion of these molecules to useful products. In this area we have been exploring the interactions of several small molecules with aminophosphine stabilized coordinatively unsaturated coordination complexes. During the course of this study we have found it appropriate to explore the reactions of CO_2, COS, CS_2[1], and SO_2 with several uncoordinated aminophosphine ligands. An interesting chemical diversity has been systematized, and we report here on the SO_2 reactions with

$[(CH_3)_2N]_3P$, $[(CH_3)_2N]_2PCl$, $[(CH_3)_2N]_2PF$, $(CH_3)_2NPF_2$, $(CH_3)_2NPCl_2$, $CH_3\overline{NCH_2CH_2N(CH_3)P}F$, $CH_3\overline{NCH_2CH_2N(CH_3)P}Cl$.

Sulfur dioxide behaves both as an electrophilic and nucleophilic reagent.[2] For example, it acts as an electron acceptor toward alkylamines with the resultant formation of strong charge transfer complexes.[2–4] Organophosphines, on the other hand, are generally oxidized in the presence of SO_2;[5–8] trimethylphosphine is oxidized to $(CH_3)_3PO$ and elemental sulfur is released while triphenylphosphine is oxidized to ϕ_3PO and ϕ_3PS.[5–7] Multifunctional aminophosphine ligands[9] appear to provide several more potential reaction modes in combination with SO_2. These include coordination of SO_2 (S or O bound) with the phosphorus atom or nitrogen atom lone pairs, bidentate SO_2 coordination to the PN bond, phosphorus atom oxidation to phosphoryl or thiophosphoryl derivatives and SO_2 insertion into the PN bond. That several of these reaction modes may be found is suggested by conflicting reports in the literature. Fluck and Binder[6] as part of a survey of SO_2 reactions with a variety of phosphines reported that $[(CH_3)_2N]_3P$ and $[(CH_3)_2N]P(C_2H_5)_2$ are slowly oxidized by SO_2 at 50° to the respective phosphoryl and thiophosphoryl derivatives. In the only other report of aminophosphine-SO_2 interactions, Das and Zuckerman,[10] suggested that $CH_3\overline{NCH_2CH_2N(CH_3)P}C_6H_5$ in benzene interacts with SO_2 by insertion in the PN bond and oxidation products were not reported. These results suggested some reactivity differences between cyclic and acyclic aminophosphines toward SO_2

RESULTS AND DISCUSSION

The combination of excess SO_2 with $[(CH_3)_2N]_3P$ at 25°C resulted in a complex reaction which is summarized by the following equation.

$$\underset{\mathbf{1}}{P[N(CH_3)_2]_3} + \text{xs } SO_2 \longrightarrow \underset{\mathbf{2}}{OP[N(CH_3)_2]_3} + \underset{\mathbf{3}}{SP[N(CH_3)_2]_3} + \text{polymeric products} \quad (1)$$

Compound **2** (5% yield) and compound **3** (20% yield) were identified as $OP[N(CH_3)_2]_3$ and $SP[N(CH_3)_2]_3$ based upon their mass spectra and ^{31}P chemical shifts:[11], ^{31}P δ 23.0 ppm and δ 81.5 ppm. The predominant product was a mixture of polymeric building units:[12] two forms of $OP[N(CH_3)_2]_2(O—)$ (30%) δ ^{31}P -10.6 and -10.2 ppm; $OP[N(CH_3)_2]_2(O—)_2$ (20%) δ ^{31}P 12.3 ppm; $SP(S—)_3$ (10%) δ ^{31}P -61.0 ppm and a mixed oxide-sulfide unit (5%) δ ^{31}P -43.7 ppm. These results are in agreement with the partial analysis of the total reaction mixture first made by Fluck and Binder.[6]

The combinations of excess SO_2 with $[(CH_3)_2N]_2PF$ and $[(CH_3)_2N]_2PCl$ at 25°C resulted in reactions summarized by the following equations.

$$\underset{\mathbf{4}}{[(CH_3)_2N]_2PF} + xs\,SO_2 \longrightarrow \underset{\mathbf{5}}{OPF[N(CH_3)_2]_2} + \underset{\mathbf{6}}{SPF[N(CH_3)_2]_2} \quad (2)$$

$$\underset{\mathbf{7}}{[(CH_3)_2N]_2PCl} + xs\,SO_2 \longrightarrow \underset{\mathbf{8}}{OPCl[N(CH_3)_2]_2} + \underset{\mathbf{9}}{SPCl[N(CH_3)_2]_2} \quad (3)$$

Reactions **2** and **3** proceeded more rapidly to completion than reaction **1** and only traces of side products were identified: yields **5** ~ 60%, **6** ~ 40%, PF_3 trace, $OP[N(CH_3)_2]_2(O—)$ unit trace, **8** ~ 50%, **9** ~ 50%, PCl_3 trace. The product identification was accomplished with mass spectral data in which the parent ions were detected and from NMR data summarized in Table I. The phosphorus chemical shifts are in agreement with data in the literature for the same compounds prepared by oxidation of the aminophosphines by elemental oxygen and sulfur.[13,14]

The combinations of $(CH_3)_2NPF$ and $(CH_3)_2NPCl$ with excess SO_2 gave no discernible reactions after several days at 25°C. The mixture of

$CH_3\overline{NCH_2CH_2N(CH_3)P}Cl$

and SO_2 led to a very limited reaction: the products

$CH_3\overline{NCH_2CH_2N(CH_3)P}(O)Cl$

and $CH_3\overline{NCH_2CH_2N(CH_3)P}(S)Cl$,

were obtained with about 5% yields, and they were identified by observation of the corresponding mass spectral parent ions.

The reaction of $CH_3\overline{NCH_2CH_2N(CH_3)P}F$ **10** with excess SO_2 was facile, and it led to the formation of oxidation and ionic products as described by the following equation.

$$\begin{aligned} \mathbf{10} + xs\,SO_2 \longrightarrow\ & \underset{\mathbf{11}}{CH_3\overline{NCH_2CH_2N(CH_3)P}(O)F} \\ & + \underset{\mathbf{12}}{CH_3\overline{NCH_2CH_2N(CH_3)P}(S)F} \\ & + \underset{\mathbf{13}}{[CH_3\overline{NCH_2CH_2N(CH_3)P}(O)^+]} \\ & + \underset{\mathbf{14}}{[CH_3\overline{NCH_2CH_2N(CH_3)P}(S)^+]} + [PF_6^-] + [PO_2F_2^-] \end{aligned} \quad (4)$$

TABLE I

Comparison of NMR data

Compound	δ ^{31}P	δ ^{19}F	δ $^{13}C_{CH_3}$	δ $^{13}C_{CH_2}$	δ $^{1}H_{H_3C}$	δ $^{1}H_{H_2C}$	J_{PF}	J_{CH_3NP}	J_{CH_2NP}	J_{H_3CNP}
2	23.0									
3	81.5									
4	151.4	-98.8	38.7		2.5		1045	19 J_{CNPF} = 2.0	15	10
5	17.1	-82.9	37.6		2.5		941	4.1		10.4
6	87.0	-59.5	38.9		2.7		1014	3.8		13.9
7	160.0									12.0
8	29.3									
9	91.7									
10	138.0	-63.2	33.9	53.2	2.7	3.1	1047	24.2	9.8	13
11	23.5	-71.8	34.8	49.4	2.7	3.3	993	3.6	15	10
12	84.2	-28.9	35.8	51.4	2.8	3.3	1092	6.0	9.0	12
13	78.1		32.4	47.9				6.7	6.5	
14	16.8									

The previously unreported compounds **11** (~25% yield) and **12** (~20% yield) were easily identified from their mass and NMR spectra (Table I) by comparison with samples prepared by alternative routes.[15,16] The anions $[PF_6^-]$ (yields ~10%) and $[PO_2F_2^-]$ (yield ~5%) were identified by their characteristic ^{31}P NMR spectra.[14] The assignment of **13** and **14** as cationic pentavalent species is more speculative based upon NMR data and additional chemistry. The ^{31}P NMR spectra for **13** (~16.8 ppm) and **14** (~78.1 ppm) are singlets indicating that the large PF couplings present in **11** and **12** have been removed. Further, attempts were made to synthesize the ionic compounds by alternate halide abstraction reactions summarized by the following equations.

$$CH_3\overline{NCH_2CH_2N(CH_3)P}(S)F + PF_5 \longrightarrow \underset{\mathbf{15}}{[CH_3\overline{NCH_2CH_2N(CH_3)P}(S)^+][PF_6^-]} \quad (5)$$

$$CH_3\overline{NCH_2CH_2N(CH_3)P}(O)F + PF_5 \longrightarrow \text{undefined products} \quad (6)$$

The ^{31}P shift for **15** is identical to that of **14** and comparable to the shifts found in other thiophosphoryl cations.[17] The failure to prepare the phosphoryl derivative **13** by the alternate halide extraction reaction leave the identity of **13** open to further study.

The reactions of SO_2 with several aminohalophosphines under conditions employed here lead predominantly to the formation of phosphoryl and thiophosphoryl products. No evidence was found for PN bond insertion by SO_2 in contrast to the report of Zuckerman and Das.[10] The reactions are apparently not mechanistically simple as evidenced by the variety of products obtained in reactions (1) and (4). Attempts to identify reaction intermediates by low temperature ^{31}P NMR techniques were unsuccessful; the resonance for the free ligand disappeared as final product resonances appeared and transient species were not observed. Further studies of the interactions between SO_2 and aminophosphine ligands bound to transition metals will be presented in the near future.

EXPERIMENTAL

Standard high vacuum synthetic techniques were used for the manipulations of the volatile compounds. Mass spectra were recorded on a Dupont Model 21-491 spectrometer operating at 70 eV. Infrared spectra were recorded on a Perkin Elmer Model 621 infrared spectrometer using mull and thin film techniques. The NMR spectra were recorded on a Varian XL-100 instrument operating at 100.0 MHz (^1H), 25.2 MHz (^{13}C), 40.4 MHz (^{31}P), and 94.1 MHz (^{19}F). A Nicolet TT-100 data system was used to collect the data in the pulse mode. Samples were contained in sealed 5 mm tubes rigidly placed in a 12 mm tube containing a deuterated lock sample. Standards are $CFCl_3$ (^{19}F), TMS (^1H, ^{13}C) and H_3PO_4 (^{31}P).

$[(CH_3)_2N]_3P$[18] **1**, $[(CH_3)_2N]_2PF$[19] **4**, $[(CH_3)_2N]_2PCl$[18] **7**, $(CH_3)_2NPF_2$[19]

$CH_3\overline{NCH_2CH_2N(CH_3)P}F$[20] **10**, and

$CH_3\overline{NCH_2CH_2N(CH_3)P}Cl$[21]

were prepared by literature methods. SO_2 was purchased from Scientific Gas Products and it was subjected to trap to trap distillation prior to use.

Reactions of Aminophosphine Ligands and SO_2. Typically a 10 mmol sample of aminophosphine ligand was condensed into a flask attached to the vacuum system and a 2 to 5 fold excess of SO_2 was condensed onto the ligand. The flask was warmed to 0°C and held there for 1 hr. The flask was frozen to −196° and then slowly warmed to 25°C. After several hours the volatile products were vacuum distilled through traps maintained at 0°, −78°, and −196°. The products of interest remained as solids or oils in the reaction flask. The extracted products were moisture sensitive and they were handled in a nitrogen filled glove bag.

Low temperature NMR samples were prepared by condensing the ligand and SO_2 into a medium walled NMR tube at −196°C. The tube was warmed slowly to about −100°C and ^{31}P NMR spectra were than recorded at 10°–20°C intervals. In each case the free ligand resonance disappeared with the appearance of oxidized products. No evidence was found to indicate the presence of low temperature intermediate compounds.

Characterization Data

$[(CH_3)_2N]_3PO$ **2**. Mass spectrum [m/e, assignment, rel. inten.]: 179, $OPN_3\,C_6H_{18}^+$, 2; 135, $OPN_2C_4H_{12}^+$, 5; 119, $PN_2C_4H_{12}^+$, 27; 92, $OPNC_2H_7^+$, 96; 91, $OPNC_2H_6^+$, 2; 76, $PNC_2H_7^+$, 18; 75, $PNC_2H_6^+$, 1; 60, $PNCH_3^+$, 7; 47, PO^+, 1; 45, $NC_2H_7^+$, 26; 44, $NC_2H_6^+$, 100; 43, $NC_2H_5^+$, 22; 42, $NC_2H_4^+$, 51. NMR spectrum (neat) 25°C: ^{31}P, δ 23.0 ppm.

$[(CH_3)_2N]_3PS$ **3**. Mass spectrum: 195, $SPN_3C_6H_{18}^+$, 12; 152, $SPN_2C_4H_{13}^+$, 8; 151, $SPN_2C_4H_{12}^+$, 13; 136, $SPN_2C_3H_9^+$, 10; 119, $PN_2C_4H_{12}^+$, 27; 108, $SPNC_2H_7^+$, 4; 107, $SPNC_2H_6^+$, 2; 76, $PNC_2H_7^+$, 18; 75, $PNC_2H_6^+$, 1; 64, SO_2^+, 34; 63, PS^+, 3; 60, $PNCH_3^+$, 7; 48, SO^+, 22; 45, $NC_2H_7^+$, 26; 44, $NC_2H_6^+$, 100. NMR spectrum (neat) 25°C: ^{31}P δ 81.5 ppm.

$[(CH_3)_2N]_2P(O)F$ **5** and *$[(CH_3)_2N]_2P(S)F$* **6**. Mass spectrum of the product mixture: 170, $SPN_2C_4H_{12}F^+$, 6; 154, $OPN_2C_4H_{12}F^+$, 4; 153, $OPN_2C_4H_{11}F^+$, 1; 137, $PN_2C_4H_{11}^+$, 2; 126, $SPNC_2H_6F^+$, 3; 119, $PN_2C_4H_{12}^+$, 1; 110, $OPNC_2H_6F^+$, 11; 94, $FPNC_2H_6^+$, 24; 92, $FPNC_2H_4^+$, 10; 78, $FPNCH_2^+$, 1; 76, $PNC_2H_7^+$, 2; 64, SO_2^+, 1; 60, $PNCH_3^+$, 1; 52, $PNCH^+$, 2; 48, SO^+, 1; 45, $NC_2H_7^+$, 14; 44, $NC_2H_6^+$, 100; 43, $NC_2H_5^+$, 8; 42, $NC_2H_4^+$, 25; 41, $NC_2H_3^+$, 2. NMR spectra (neat) 25°C: ^{31}P, **5** δ 17.1 ppm; **6** δ 87.0 ppm.[11]

$[(CH_3)_2N]_2P(O)Cl$ **8** and $[(CH_3)_2N]_2P(S)Cl$ **9**. Mass spectrum of the product mixture: 186, $SPN_2C_4H_{12}Cl^+$, 4; 170, $OPN_2C_4H_{12}Cl^+$, 6; 151, $SPN_2C_4H_{12}^+$, 5; 135, $OPN_2C_4H_{12}^+$, 8; 126, $OPNC_2H_6Cl^+$, 7; 119, $PN_2C_4H_{12}^+$, 5; 110, $PNC_2H_6Cl^+$, 13; 92, $OPNC_2H_7^+$, 9; 76, $PNC_2H_7^+$, 2; 64, SO_2^+, 6; 63, PS^+, 2; 60, $PNCH_3^+$, 3; 58, $PNCH^+$, 2; 48, SO^+, 4; 47, PO^+, 2; 45, $NC_2H_7^+$, 12; 44, $NC_2H_6^+$, 100; 43, $NC_2H_5^+$, 5. NMR spectra ($CHCl_3$) 25°C: ^{31}P, **8** δ 29.3 ppm; **9** δ 91.7 ppm.[11]

$CH_3\overline{NCH_2CH_2N(CH_3)P}(O)F$ **11**. Mass spectrum: 152, $OPN_2C_4H_{10}F^+$, 42; 151, $OPN_2C_4H_9F^+$, 17; 137, $PN_2C_4H_{11}F^+$, 1; 136, $PN_2C_4H_{10}F^+$, 3; 135, $PN_2C_4H_9F^+$, 1; 133, $OPN_2C_4H_{10}^+$, 2; 122, $OPN_2C_2H_4F^+$, 2; 111, $OPNC_2H_7F^+$, 1; 110, $OPNC_2H_6F^+$, 18; 109, $OPNC_2H_5F^+$, 6; 97, $PN_2C_3H_2^+$, 1; 96, $PN_2C_3H^+$, 1; 94, $PNC_2H_6F^+$, 2; 93, $PNC_2H_5F^+$, 2; 86, $N_2C_4H_{10}^+$, 2; 85, $N_2C_4H_9^+$, 2; 69, $NC_4H_7^+$, 1; 67, $NC_4H_5^+$, 1; 58, $CHNP^+$, 2; 57, PNC^+, $NC_3H_7^+$, 21; 56, $NC_3H_6^+$, 3; 55, $NC_3H_5^+$, 2; 54, $NC_3H_4^+$, 1; 47, PO^+, 2; 45, PN^+, $NC_2H_7^+$, 7; 44, $NC_2H_6^+$, 100; 43, $NC_2H_5^+$, 60; 42, $NC_2H_4^+$, 45. Infrared spectrum (cm^{-1}) (nujol mull): 1568 (w), 1303 (s), 1256 (m), 1218 (w), 1167 (s), 1075 (vw), 1037 (m), 965 (w, br), 942 (m), 890 (vw), 843 (sh), 830 (s), 815 (sh), 750 (s), 723 (s), 676 (w), 630 (w). NMR spectra (neat) 25°C: ^{31}P, δ 23.5 ppm, $^1J_{PF} = 993$ Hz.[11]

$CH_3\overline{NCH_2CH_2N(CH_3)P}(S)F$ **12**. Mass spectrum:[22] 170–168, $SPN_2C_4H_{10}F^+$, total 11; 151–149, $SPN_2C_4H_{10}^+$, total 10; 136, $PN_2C_4H_{10}F^+$, 1; 135, $PN_2C_4H_9F^+$, 13; 126, $SPNC_2H_6F^+$ 1; 125, $SPN_2C_2H_5^+$, 6; 117, $PN_2C_4H_{10}^+$, 5; 94, $PNC_2H_6F^+$, 1; 93, $PNC_2H_5F^+$, 4; 92, $PNC_2H_4F^+$, 3; 88, PNC_2F^+, 1; 86, $N_2C_4H_{10}^+$, 1; 85, $N_2C_4H_9^+$, 3; 83, $N_2C_4H_7^+$, 1; 80, $N_2C_4H_4^+$, 1; 78, $PNCH_4F^+$, 4; 71, $N_2C_4H_7^+$, 2; 67, $NC_4H_5^+$, 1; 63, PS^+, 2; 60, $PNCH_3^+$, 1; 58, $PNCH^+$, 2; 43, $NC_2H_5^+$, 3; 44, $NC_2H_6^+$, 100; 43, $NC_2H_5^+$, 26; 42, $NC_2H_4^+$, 49; 41, $NC_2H_3^+$, 23. Infrared spectra (cm^{-1}) (nujol mull): 1568 (vw), 1356 (m), 1262 (sh), 1252 (m), 1214 (s), 1160 (s), 1089 (vw), 1036 (s), 947 (s), 895 (vw), 864 (w), 813 (sh), 804 (vs), 790 (s), 736 (m), 606 (vw), 593 (m), 460 (w), 432 (w). NMR spectra (neat) 25°C: ^{31}P, δ 84.2 ppm, $^1J_{PF} = 1092$ Hz.[11]

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