# Reactions of Group V Metal Compounds with Sulfur Trioxide

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Trialkylphosphines react with equimolar amounts of sulfur trioxide to form the 1:1 adducts $R_3P^{\oplus}$–$SO_3^{\ominus}$. Trialkylarsines and -stibines undergo sulfur trioxide insertion reactions across the metal-carbon bond to give the trisulfonates of the metal $M(OSO_2R)_3$ (M=As, Sb). The reactions of trialkyl phosphites, with sulfur trioxide yield trialkyl phosphates, trialkyl thiophosphates, dialkyl alkylphosphonates, dialkyl sulfates, and polymers which contain phosphorus atoms. The reactions of trialkoxyarsines and -stibines result in the insertion of sulfur trioxide across the metal-oxygen bond to form the alkoxymetal alkylsulfates $(RO)_{3-n}M(OSO_3R)_n$ (M=As, Sb; $n$=1, 2, 3) depending on the stoichiometric ratios of the reagents used. Pyrolysis of the metal sulfates gives dialkyl sulfates and undistillable residues containing the metals.

In a previous paper,[1] we reported that the reactions of trialkoxyarsines and -stibines with sulfur dioxide gave dialkyl sulfites and metal oxides, whereas trialkyl phosphites were oxidized to the phosphates and the thiophosphates. There are a few reports[2-4] concerning the reaction of sulfur trioxide with tervalent arsenic or antimony halides. Recently, Touzin and Mitacek[5] reported that arsenic(III) fluoride forms the mono-, di-, and tri-$SO_3$ insertion products $F_{3-n}As(OSO_2F)_n$ depending on the stoichiometric molar ratios. On the other hand, Schmidt and Bipp[6] reported that the 1:1 adducts of triphenyl-, diphenylchloro-, and phenyldichlorophosphines with sulfur trioxide were obtained by the reaction at −78 °C, but phosphine oxides and sulfur dioxide were formed by the reaction at room temperature. Becke-Gogehring and Thielemann[7] reported that triphenyl- and tricyclohexylphosphines, -arsines, and -stibines gave the sulfates $(C_6H_{11})_3AsSO_4$ and $(C_6H_5)_3SbSO_4$ in addition to the corresponding adducts $(C_6H_5)_3P^{\oplus}$–$SO_3^{\ominus}$, $(C_6H_{11})_3P^{\oplus}$–$SO_3^{\ominus}$, and $(C_6H_5)_3As^{\oplus}$–$SO_3^{\ominus}$. However, there has been no report about the insertion reaction of sulfur trioxide across the metal-carbon or metal-oxygen bond of the compounds containing the group V elements. We have investigated the reactions of trialkyl- and trialkoxyphosphines, -arsines, and -stibines with sulfur trioxide.

## Results and Discussion

*Trialkylphosphines.* Trialkylphosphines reacted readily with sulfur trioxide in dichloromethane at −78 °C to give 1:1 adducts of the type $R_3P^{\oplus}$–$SO_3^{\ominus}$ in good yields. The adduct of trialkylphosphine (**1a**)

$$R_3P + SO_3 \longrightarrow R_3P^{\oplus}\text{-}SO_3^{\ominus} \quad (1)$$

is a colorless crystal (mp 35—39 °C); it disproportionated to triethylphosphine oxide and a small amount of triethylphosphine sulfide with evolution of sulfur dioxide on distillation under reduced pressure. The adduct of triisopropylphosphine (**1b**) is a stable crystal and has a very high melting point compared with the others. $Ph_2Bu^nP^{\oplus}$–$SO_3^{\ominus}$ (**1c**) was obtained in 70% yield by the equimolar reaction of butyldiphenylphosphine with sulfur trioxide. The IR spectrum of the adduct (**1c**) shows the symmetric and asymmetric stretching vibrations of the $SO_3^{\ominus}$ group[8] at 1270, 1120, and 1038 $cm^{-1}$. Assignments of the $^{13}C$ NMR spectra of the adducts were done according to the literature.[9] Both the large P–C coupling constants observed for the all adducts and the upfield shift of ipso-carbon of the phenyl group of the adduct (**1c**) are characteristic of the phosphonium compounds.[10-12] The 1:1 adduct of triethylphosphine with $SO_3$ (**1a**) reacted at room temperature with 3 molar excess of triethylphosphine to give 3 mol of triethylphosphine oxide and 1 mol of triethylphosphine sulfide. The

$$\mathbf{1a} + 3Et_3P \longrightarrow 3Et_3PO + Et_3PS \quad (2)$$

phosphonium ion structures of the adducts were also confirmed by their reactions with methyllithium, hydrogen chloride, and acetic acid. The structures of

$$\mathbf{1a} + MeLi \longrightarrow Et_3MePSO_3Li \quad (3)$$

$$\mathbf{1a} + HCl \longrightarrow Et_3ClPSO_3H \quad (4)$$

$$\mathbf{1a} + CH_3COOH \longrightarrow Et_3P(OCOCH_3)SO_3H \quad (5)$$

these reaction products were confirmed by their spectroscopic data and also by elemental analyses.

*Trialkylarsines and -stibines.* Arsenic or antimony tris(alkanesulfonate) were formed on treatments of trialkylarsines or -stibines with a 3 molar excess of sulfur trioxide. The yields and some spectroscopic data of

$$R_3M + 3SO_3 \longrightarrow M(OSO_2R)_3 \quad (6)$$
$$M=As, Sb$$

these insertion products are shown in Table 1. The reactivity order among the trialkyl derivatives was found to be $R_3Sb > R_3As$. Trialkylarsines and -stibines behave quite differently from triphenylarsine and -stibine[7] and also trialkylphosphines during the reactions with sulfur trioxide. This difference in the chemical behavior might be attributable to the fact that the metal-carbon bond of trialkylarsines and -stibines is weaker than the metal-phenyl or the phosphorus-alkyl bond.[13]

*Trialkyl Phosphites.* When sulfur trioxide was added to an equimolar amount of trimethyl phosphite at −78 °C, a violent reaction took place to give trimethyl phosphate, trimethyl thiophosphate, dimethyl methylphosphonate, dimethyl sulfate, and polymeric compounds containing phosphorus atoms. The reaction does not obey a simple stoichiometry. Table 2

$$(RO)_3P + nSO_3 \longrightarrow (RO)_3PO + (RO)_3PS + (RO)_2P(O)R + (RO)_2SO_2 + \text{“P-polymers”} \quad (7)$$

shows the effects of the alkyl group of trialkyl phosphite, the molar ratio of the reactants, and the reaction temperature on the distribution of reaction products.

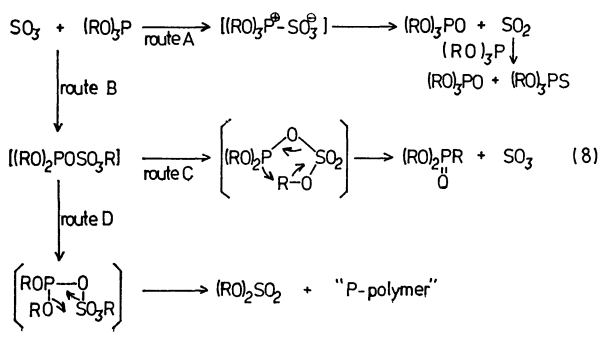
Table 1. Sulfonation product of trialkylarsine and -stibine; $M(SO_3R)_3$

| M | R | Yield % | IR $\nu(SO_2)/cm^{-1}$ | $^{13}$C-NMR($\delta$) $C_1$ | $C_2$ | $C_3$ | $C_4$ | $^1$H-NMR($\delta$) |
|---|---|---|---|---|---|---|---|---|
| As | *i*-Pr | 88 | 1185<br>1035 | 37.9 | 18.0 | | | 1.58(t, 3H)<br>3.68(m, 1H) |
| | *n*-Bu | 92 | 1190<br>1045 | 34.0 | 24.9 | 24.9 | 13.2 | 1.00(t, 3H)<br>1.17—2.25(m, 4H)<br>3.07(t, 2H) |
| Sb | *i*-Pr | 90 | 1195<br>1050 | 37.9 | 18.0 | | | 1.67(d, 6H)<br>3.56(m, 1H) |
| | *n*-Bu | 84 | 1185<br>1040 | 34.3 | 26.5 | 25.0 | 13.3 | 0.97(*t*, 3H)<br>1.13—2.16(m, 4H)<br>2.80(t, 2H) |

Table 2. Effect of alkyl group, molar ratio, and temperature on the reaction of trialkyl phosphite with $SO_3$

| $P(OR)_3$ | Molar ratio $P(OR)_3/SO_3$ | Temp °C | Products distribution/% $(RO)_3PO$ | $(RO)_3PS$ | $(RO)_2SO_2$ | $(RO)_2P(O)R$ |
|---|---|---|---|---|---|---|
| R=Me | 1/1 | −50 | 7 | 0 | 93 | 0 |
| Me | 1/1 | −78 | 22 | 4 | 55 | 19 |
| Me | 1/1 | −95 | 100 | 0 | 0 | 0 |
| Me | 3/1 | −50 | 56 | 0 | 18 | 26 |
| Me | 4/1 | −50 | 55 | 1 | 12 | 32 |
| Me | 4/1 | −78 | 48 | 16 | 3 | 9 |
| Me | 4/1 | −95 | 25 | 4 | 0 | 71 |
| Et | 1/1 | −50 | 55 | 0 | 17 | 28 |
| Et | 1/1 | −78 | 64 | 0 | 14 | 22 |
| Et | 4/1 | −50 | 64 | 21 | 3 | 11 |
| Et | 4/1 | −78 | 70 | 23 | 2 | 5 |
| Et | 1/2 | −78 | 30 | 0 | 65 | 5 |
| Et | 1/3 | −78 | 2 | 0 | 97 | 1 |
| *i*-Pr | 1/1 | −50 | 18 | 0 | 72 | 0 |
| *i*-Pr | 4/1 | −50 | 67 | 25 | 8 | 0 |
| *n*-Bu | 1/1 | −50 | 70 | 0 | 28 | 2 |
| *n*-Bu | 4/1 | −50 | 64 | 22 | 2 | 12 |

The relative amounts of the products varied depending on the molar ratio of the reactants and the temperature. The selective oxidation of phosphite was observed at low temperature with formation of sulfur dioxide. The formation of sulfates is favored at high temperature and by increasing the amounts of sulfur trioxide. The formation of thiophosphates occured mainly under the reaction conditions where the excess amount of trialkyl phosphite was used. From these results of product distributions, we wish to propose a tentative reaction mechanism as follows:




Trialkyl phosphite is an electron donor which forms a donor-acceptor complex with various electron acceptors. The sulfur atom of sulfur trioxide is the most electrophilic center in the molecule. Therefore, it is reasonable to assume that trialkyl phosphite reacts preferentially with the sulfur atom of sulfur trioxide to give alkoxyphosphonium intermediate (route A), which is not stable because of the electron-withdrawing alkoxyl group on the phosphorus atom. The phosphonium ion decomposed to trialkyl phosphate and sulfur dioxide, which, in turn, reacts with an additional trialkyl phosphite to give trialkyl phosphate and thiophosphate.[1] To explain the formation of dialkyl sulfate and dialkyl alkylphosphonate, we propose a mechanism involving the insertion of sulfur trioxide across the P–O bond of phosphite (route B). The formation of dialkyl alkylphosphonate can be explained by an intramolecular rearrangement of the insertion intermediate with elimination of sulfur trioxide (route C). An analogous mechanism has been reported by Lemper and Tieckman[14] for the rearrangement of diethyl 1-methylallyl phosphite to the phosphonate. Dialkyl sulfate and "P-polymers" might

be formed through the route D. Concerning the formation of dialkyl sulfate and "P-polymers," there might be another mechanism involving the reaction of trialkyl phosphate (formed through route A) with sulfur trioxide as reported by Du Plessis.[15] The reaction of trimethyl phosphate with sulfur trioxide gave dimethyl sulfate and methyl polyphosphates.[15] Trialkyl phosphates whose alkyl substituents were higher than the ethyl group, however, formed stable 1:1 adducts with sulfur trioxide and the corresponding dialkyl sulfates and "P-polymers" were not obtained from the adducts.[16] Therefore, the route D in the reaction mechanism proposed is much more probable than the latter route.

$$(MeO)_3PO + SO_3 \longrightarrow (MeO)_2SO_2 + \text{"P-polymers"} \quad (9)$$

*Trialkoxyarsines and -stibines.* When sulfur trioxide and trialkoxyarsines were allowed to react at −50 °C in 1:1, 1:2, and 1:3 molar ratios, the corresponding insertion products were obtained almost quantitatively. The insertion products are sensitive to moisture and oxygen, while they are stable at room temperature under an inert atmosphere. Attempts to distill the insertion products under reduced pressure (0.1 mmHg (1 mmHg≈133.322 Pa)) resulted in decomposition giving dialkyl sulfates and white or brown-black residues containing arsenic atoms.

$$As(OR)_3 + nSO_3 \longrightarrow (RO)_{3-n}As(OSO_3R)_n \quad (10)$$
$$n=1, 2, 3$$

Trialkoxystibines also gave the corresponding insertion products with cleavage of the Sb–O bond. The reactivity of trialkoxystibines toward sulfur trioxide is somewhat greater than that of trialkoxyarsines because of higher polarizability of the metal-oxygen bond of trialkoxystibines than that of trialkoxyarsines. The insertion products were viscous liquids and very sensitive to air and moisture. Attempts to purify these products by distillation or recrystallization were unsuccessful. Pyrolysis under reduced pressure gave dialkyl sulfates along with charred decomposition products containing antimony atoms. The IR, $^1H$ NMR, and $^{13}C$ NMR spectra of the arsenic or antimony mono-, bis-, and tris(alkyl sulfates) are given in Table 3 along with the parent metal alkoxide. The IR spectra exhibit symmetric and asymmetric stretching vibrations of $SO_2$ group at 1220 and 1390 $cm^{-1}$, respectively. In the $^{13}C$ NMR spectra, α-methylene carbons shift to low field by the shielding effect of $SO_2$ group.[17]

$$Sb(OR)_3 + nSO_3 \longrightarrow (RO)_{3-n}Sb(OSO_3R)_n \quad (11)$$
$$n=1, 2, 3$$

## Experimental

All reactions were carried out under an atmosphere of argon or nitrogen. Infrared spectra were recorded on a Shimadzu IR 430 spectrometer. $^1H$ NMR spectra were recorded on a JEOL C 60 HL spectrometer and $^{13}C$ NMR spectra on a JEOL JNM-FX 60 FT NMR instrument. Analytical GLC was carried out on a Shimadzu GC 60A apparatus using a 3 m grass column packed with PEG 6000 (10%) with helium as a carrier gas. Dichloromethane was dried over calcium chloride and distilled through a fractionating column.

*Reagent.* Sulfur trioxide (bp 46 °C) was distilled from sulfuric anhydride (Yotsuhata Chem. Co.) into an ice-cooled flask containing dichloromethane. The concentration of sulfur trioxide was determined by a titration with a standard

Table 3. Spectroscopic data of the alkoxyarsenic or alkoxyantimony alkyl sulfates; $(ROSO_3)_nM(OR)_{3-n}$

| M | R | n | $^1H$ NMR (δ) | | $^{13}C$ NMR (δ) | | IR |
|---|---|---|---|---|---|---|---|
| | | | $ROSO_3$ | RO | $ROSO_3$ | RO | $\nu(SO_3)/cm^{-1}$ |
| As | $CH_3$ | 0 | — | 3.60 (s) | — | 50.0 | — |
| | | 1 | 4.01 (s, 1H) | 3.90 (s, 2H) | 58.0 | 52.5 | 1400<br>1218 |
| | | 2 | 4.07 (s, 2H) | 3.98 (s, 1H) | 59.1 | 54.1 | 1390<br>1216 |
| | | 3 | 4.11 (s) | — | 59.4 | — | 1388<br>1218 |
| As | $C_2H_5$ | 0 | — | 1.27 (t, 3H)<br>3.94 (q, 2H) | — | 18.1<br>58.5 | — |
| | | 1 | 1.42 (t, 3H)<br>4.34 (q, 2H) | 1.33 (t, 6H)<br>4.17 (q, 4H) | 14.7<br>68.4 | 17.6<br>61.3 | 1400<br>1218 |
| | | 2 | 1.46 (t, 2H)<br>4.49 (q, 2H) | 1.38 (t, 1H)<br>— | 14.5<br>71.1 | 17.2<br>65.2 | 1390<br>1216 |
| | | 3 | 1.43 (t, 3H)<br>4.46 (q, 2H) | — | 14.5<br>71.3 | — | 1388<br>1215 |
| Sb | $C_2H_5$ | 0 | — | 1.37 (t, 3H)<br>4.01 (q, 2H) | — | 19.8<br>58.9 | — |
| | | 1 | 1.38 (t, 3H)<br>4.34 (t, 2H) | 1.40 (t, 6H)<br>4.29 (q, 4H) | 14.8<br>67.2 | 18.8<br>61.3 | 1392<br>1230 |
| | | 2 | 1.41 (t, 6H)<br>4.40 (q, 4H) | 1.45 (t, 3H)<br>4.36 (q, 2H) | 14.7<br>68.7 | 17.1<br>63.7 | 1388<br>1210 |
| | | 3 | 1.43 (t, 3H)<br>4.49 (q, 2H) | — | 14.6<br>67.7 | — | 1389<br>1216 |

solution of sodium hydroxide. Trimethyl phosphite, triethyl phosphite and tributyl phosphite were of commercial material and distilled before use. Tripropyl phosphite (bp 84—87 °C/14 mmHg) and triisopropyl phosphite (bp 63—66 °C/12 mmHg) were prepared by the method described in the literature.[18] Trialkoxyarsines and -stibines[19] were prepared by the reaction of arsenic or antimony trichloride with an appropriate alcohol in the presence of ammonia; $As(OMe)_3$; bp 95—96 °C/35 mmHg, $As(OEt)_3$; bp 59—60 °C/14 mmHg, $Sb(OEt)_3$; bp 49—52 °C/14 mmHg.

*Equimolar Reaction of Trialkylphosphine with Sulfur Trioxide.* Sulfur trioxide (19.7 mmol in 5 cm³ of dichloromethane) was added to a solution of triethylphosphine (2.31 g, 19.6 mmol) in 10 cm³ of dichloromethane at −78 °C. The mixture was kept for 2 h at −78 °C and then warmed up gradually to room temperature. After removal of the solvent, the product was recrystallized from petroleum ether/chloroform (5/1) to give $Et_3P^{\oplus}$–$SO_3^{\ominus}$ (3.27 g, 84%), mp 35—39 °C. $^1H$ NMR ($CDCl_3$): $\delta$=1.40 (dt, 3H, $^3J_{PH}$=19.2 Hz) and 2.49 (dq, 2H, $^2J_{PH}$=12.0 Hz). $^{13}C$ NMR ($CHCl_3$): $\delta$=5.2 (d, $^2J_{PC}$=4.9 Hz) and 18.2 (d, $^1J_{PC}$=64.7 Hz). $^{31}P$ NMR ($CHCl_3$): $\delta$=−79.5. IR ($CHCl_3$): $\nu(SO_3^-)$ 1276, 1160, and 1040 cm$^{-1}$. Found: C, 36.9; H, 7.74; P, 15.0%. Calcd for $C_6H_{15}O_3PS$: C, 36.36; H, 7.63; P, 15.62%. An attempted distillation resulted in a decomposition which gave triethylphosphine oxide (78%) and triethylphosphine sulfide (5%). In a similar way, reaction of triisopropylphosphine (2.05 g, 12.8 mmol) with an equimolar amount of sulfur trioxide gave white crystals, $i$-$Pr_3P^{\oplus}$–$SO_3^{\ominus}$ (2.27 g, 74%), mp 201—203 °C (dec). $^1H$ NMR ($CDCl_3$): $\delta$=1.59 (dd, 6H, $^3J_{PC}$=16.8 Hz) and 2.87 (m, 1H). $^{13}C$ NMR ($CHCl_3$): $\delta$=17.3 (d, $^2J_{PC}$=2.9 Hz) and 24.8 (d, $^1J_{PC}$=51.9 Hz). IR (KBr): $\nu(SO_3^-)$ 1238, 1168, and 1020 cm$^{-1}$. Found: C, 45.3; H, 8.73; P, 13.1%. Calcd for $C_9H_{21}O_3PS$: C, 44.98; H, 8.81; P, 12.89%. Reaction of butyldiphenylphosphine (1.03 g, 4.25 mmol) with an equimolar amount of sulfur trioxide gave $Ph_2BuP^{\oplus}$–$SO_3^{\ominus}$ (0.96 g, 70%); $^{13}C$ NMR ($CHCl_3$): $\delta$=28.2 ($^1J_{PC}$=70.8 Hz), 23.2 ($^2J_{PC}$=1.2 Hz), 23.9 ($^3J_{PC}$=12.2 Hz), 13.4 ($^4J_{PC}\approx$0 Hz), 129.8 (ipso, $J_{PC}$=100.1 Hz), 130.92 (ortho, $J_{PC}$=9.77 Hz), 129.06 (meta, $J_{PC}$=12.21 Hz), and 132.7 (para, $J_{PC}$=3.1 Hz). IR (neat): $\nu(SO_3^-)$ 1270, 1120, and 1038 cm$^{-1}$.

*Reactions of $Et_3P^{\oplus}$–$SO_3^{\ominus}$ with Various Reagent.* Triethylphosphine (1.94 g, 16.4 mmol) was added to $Et_3P^{\oplus}$–$SO_3^{\ominus}$ (1.09 g, 5.47 mmol) in 5 cm³ of dichloromethane at −78 °C. The mixture was warmed up to room temperature and an exothermic reaction took place to give triethylphosphine oxide (1.61 g, 55%) and triethylphosphine sulfide (0.53 g, 16%). The structures of both compounds were confirmed by comparison of the physical properties and spectroscopic data with those of authentic samples.[20] An equimolar reaction of $Et_3P^{\oplus}$–$SO_3^{\ominus}$ (1.01 g, 5.12 mmol) and methyllithium in ether gave the lithium sulfonate $Et_3PMeSO_3Li$ (0.93 g, 87%), a brown solid, mp>250 °C. $^{13}C$ NMR ($CHCl_3$): $\delta$=6.2 ($^2J_{PC}$=4.6 Hz, $CH_3CH_2$), 17.4 ($^1J_{PC}$=35.6 Hz, $CH_2$), and 19.3 ($J_{PC}$=66.7 Hz, $CH_3P$). Found: P, 14.1%. Calcd for $C_7H_{18}PSO_3Li$: P, 14.07%. Reaction of $Et_3P^{\oplus}$–$SO_3^{\ominus}$ (1.84 g, 9.29 mmol) with anhydrous hydrogen chloride in ether gave the sulfonic acid $Et_3P(Cl)SO_3H$ (2.09 g, 96%) as a viscous liquid. $^1H$ NMR ($CDCl_3$): $\delta$=1.28 (dt, 9H, $^1J_{PH}$=19.1 Hz), 2.23 (dq, 6H, $^2J_{PH}$=12.4 Hz), and 12.44 (s, 1H, $SO_3H$). $^{13}C$ NMR ($CHCl_3$): $\delta$=5.1 ($^2J_{PC}$=5.5 Hz) and 17.2 ($^1J_{PC}$=62.9 Hz); IR (neat): $\nu$(OH) 2240, $\nu(SO_2)$ 1198, 1050, and $\nu$(P–C) 560 cm$^{-1}$. Found: P, 13.5%. Calcd for $C_6H_{16}PSO_3Cl$; 13.20%. Reaction of $Et_3P^{\oplus}$–$SO_3^{\ominus}$ (0.58 g, 2.93 mmol) with acetic acid (0.20 g, 3.33 mmol) gave the corresponding acetate $Et_3P(OCOCH_3)$-$SO_3H$ (0.69 g, 92%) as a viscous liquid. $^1H$ NMR ($CDCl_3$): $\delta$=1.26 (dt, 9H, $^2J_{PH}$=19.4 Hz), 2.18 (dq, 6H, $^3J_{PH}$=12.6 Hz), 2.09 (s, 3H, $CH_3CO$), and 12.41 (s, 1H, $SO_3H$): $^{13}C$ NMR ($CHCl_3$): $\delta$=5.0 ($^2J_{PC}$=5.1 Hz), 16.6 ($^1J_{PC}$=16.6 Hz), 20.9 ($CH_3CO$), and 176.1 ($CH_3Co$). IR (neat): $\nu$(C=O) 1724 cm$^{-1}$. Found: P, 11.6%. Calcd for $C_8H_{19}$-$O_5PS$: P, 11.99%.

*Reaction of Trialkylarsines with Sulfur Trioxide.* Sulfur trioxide (20.5 mmol in 10 cm³ of dichloromethane) was added to triisopropylarsine (1.40 g, 6.83 mmol) in 10 cm³ of dichloromethane at −50 °C. After removal of the solvent, arsenic tris(2-propanesulfonate) (2.67 g, 88%) was obtained as a viscous liquid. Found: C, 24.3; H, 4.83%. Calcd for $C_9H_{21}AsO_9S_3$: C, 24.32; H, 4.74%. Reaction of tributylarsine (1.78 g, 7.28 mmol) with 3 molar excess of sulfur trioxide gave arsenic tris(1-butanesulfonate) (3.26 g, 92%). Found: C, 28.9; H, 5.52%. Calcd for $C_{12}H_{27}$-$AsO_9S_3$: C, 29.63; H, 5.60%.

*Reaction of Trialkylstibines with Sulfur Trioxide.* Triisopropylstibine (2.06 g, 8.20 mmol) and sulfur trioxide (24.6 mmol) were treated in 20 cm³ of dichloromethane at −50 °C. Antimony tris(2-propanesulfonate) (3.62 g, 90%) was obtained as a viscous liquid. Found: C, 22.4; H, 4.56%. Calcd for $C_9H_{21}O_9S_3Sb$: C, 21.96; H, 4.30%. Tributylstibine (2.08 g, 7.11 mmol) and 3 molar excess of sulfur trioxide gave antimony tris(1-butanesulfonate) (3.18 g, 84%), a viscous liquid. Found: C, 27.4; H, 5.12%. Calcd for $C_{12}H_{27}O_9S_3Sb$: C, 27.03; H, 5.10%.

*Reaction of Trialkyl Phosphite with Sulfur Trioxide.* A typical reaction is described. When a solution of sulfur trioxide (19.2 mmol in 5 cm³ of dichloromethane) was added to trimethyl phosphite (2.38 g, 19.2 mmol) in 10 cm³ of dichloromethane at −78 °C, a violent reaction took place. After removal of the solvent, the mixture was distilled under reduced pressure to give a fraction (2.57 g) of the bp range of 60—86 °C/12 mmHg. The following substances were isolated from this fraction (1.50 g) by column chromatography on silica gel (changing eluent from cyclohexane to benzene and then to chloroform): trimethyl phosphate (0.33 g), trimethyl thiophosphate (0.06 g), dimethyl methylphosphonate (0.30 g), and dimethyl sulfate (0.82 g). All these compounds were identified by comparing the physical and spectroscopic (IR, $^1H$, $^{13}C$, and $^{31}P$ NMR) data with those of the authentic samples.[21] In a similar manner, the reactions of other trialkyl phosphites with sulfur trioxide were performed and the distribution of the reaction products were analyzed by analytical GLC.

*Reaction of Triakoxyarsines with Sulfur Trioxide.* A solution of sulfur trioxide (17.3 mmol in 5 cm³ of dichloromethane) was added slowly to trimethoxyarsine (2.93 g, 17.4 mmol) in 10 cm³ of dichloromethane at −50 °C. After the solvent was evaporated, dimethoxyarsenic methyl sulfate (3.90 g, 90%) was obtained as a colorless liquid. A distillation of the crude product (2.65 g) under reduced pressure gave pure dimethoxyarsenic methyl sulfate (1.01 g, 39%), bp 96—97 °C/0.22 mmHg; Found: C, 14.3; H, 3.63%. Calcd for $C_3H_9O_6SAs$: C, 14.52; H, 3.66%, along with dimethyl sulfate (0.35 g, 27%) and a residue (1.18 g) containing arsenic atoms. Reaction of trimethoxyarsine (1.65 g, 9.82 mmol) and sulfur trioxide (19.7 mmol) was carried out under similar conditions. The white crystals which formed were washed with hexane. Methoxyarsenic bis(methyl sulfate) (3.03 g, 94%) was obtained, mp 59—63 °C. The distillation of the crude methoxyarsenic bis(methyl sulfate) (1.93 g) gave methoxyarsenic bis(methyl sulfate) (0.54 g, 28%), bp 98—103 °C/0.2 mmHg; Found: C, 10.7;

H, 2.89%. Calcd for $C_3H_9O_9S_2As$: C, 10.98; H, 2.76%, dimethyl sulfate (0.52 g, 38%) and a grayish residue (0.60 g). Reaction of trimethoxyarsine (1.97 g, 11.7 mmol) with sulfur trioxide (35.2 mmol) gave crude arsenic tris(methyl sulfate) (4.49 g, 94%). Distillation of this crude product gave arsenic tris(methyl sulfate) (19%), bp 82—85 °C/0.08 mmHg, Found: C, 8.76; H, 2.28%. Calcd for $C_3H_9O_{12}S_3As$: C, 8.83; H, 2.20%, and dimethyl sulfate (21%). Equimolar reaction of triethoxyarsine (1.65 g, 7.86 mmol) and sulfur trioxide gave diethoxyarsenic ethyl sulfate (2.02 g, 88%). The distillation gave diethoxyarsenic ethyl sulfate (44%), bp 107—110 °C/0.1 mmHg and diethyl sulfate (36%), bp 94—96 °C/18 mmHg; IR (neat): $\nu(SO_2)$ 1385, and 1158 $cm^{-1}$; $^1H$ NMR ($CCl_4$): $\delta=1.43$ (t, 3H), and 4.30 (q, 2H); $^{13}C$ NMR ($CHCl_3$): $\delta=14.6$, and 69.8. When reaction of triethoxyarsine with sulfur trioxide was carried out in 1:2 and 1:3 molar ratios of the reagents, the corresponding oily insertion products were obtained in 97 and 92% yields, respectively. Attempted distillation of the adducts caused a complete decomposition which afforded diethyl sulfate (54 and 40%, respectively).

*Reaction of Triethoxystibine with Sulfur Trioxide.* A solution of sulfur trioxide (20.0 mmol in 10 $cm^3$ of dichloromethane) was added to triethoxystibine (5.12 g, 19.9 mmol) in 10 $cm^3$ of dichloromethane at −50 °C. In a few minutes, white crystals were formed. The mixture was warmed to room temperature and the crystals were collected by filtration. Recrystallization from benzene/chloroform (9/1) gave diethoxyantimony ethyl sulfate (5.9 g, 88%), mp 76—80 °C. Found: C, 20.5; H, 4.54%. Calcd for $C_6H_{15}O_6SSb$: C, 21.38; H, 4.49%. An attempted distillation of the diethoxyantimony ethyl sulfate (1.23 g, 3.64 mmol) caused the decomposition which gave diethyl sulfate (0.40 g, 2.58 mmol) and a residue (0.82 g). A solution of sulfur trioxide (19.7 mmol in 5 $cm^3$ of dichloromethane) was added to triethoxystibine (2.55 g, 9.92 mmol) in 10 $cm^3$ of dichloromethane at −50 °C. After removal of the solvent, the residue was dried under reduced pressure (5 h, at 15—20 °C/0.07 mmHg), leaving a brown viscous liquid (3.96 g) which was used without further purification for $^1H$ and $^{13}C$ NMR and IR spectra measurements. These spectra proved the product to be ethoxyantimony bis(ethyl sulfate) (96%). Found: C, 17.8; H, 3.42%. Calcd for $C_6H_{15}O_9S_2Sb$: C, 17.28; H, 3.62%. In a similar way, the reaction of triethoxystibine (3.37 g, 13.1 mmol) and sulfur trioxide (39.4 mmol) in 20 $cm^3$ of dichloromethane gave antimony tris(ethyl sulfate) (6.03 g, 93%), orange oil. Found: C, 14.5; H, 3.00%. Calcd for $C_6H_{15}O_{12}S_3Sb$: C, 14.49; H, 3.04%. Pyrolysis of the tris (sulfate) (2.00 g, 4.02 mmol) under reduced pressure gave diethyl sulfate (0.53 g, 3.42 mmol) and a charred residue (1.37 g).

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