

## REACTIONS OF AMINOARSINE AND AMINOSTIBINE WITH HETEROCYCLIC COMPOUNDS

JUGO KOKETSU\*, SEIJI KOKJMA and YOSHIO ISHII

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Nagoya (Japan)

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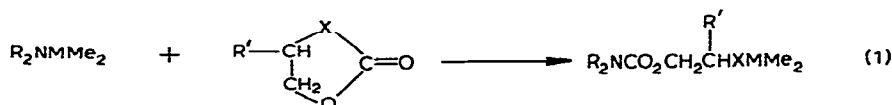
### SUMMARY

The reactions of (diethylamino)dimethylarsine and (dimethylamino)dimethylstibine with cyclic carbonates or thiocarbonate has been shown to take place through the addition of As-N or Sb-N bonds across oxygen-carbonyl or sulfur-carbonyl bonds of carbonates or thiocarbonates to give the insertion products. (Dimethylamino)dimethylstibine reacts with lactones and epoxides to give 2-substituted alkoxy metal derivatives. The structures of the 1/1 insertion products have been determined by spectroscopy or from degradation reactions.

### INTRODUCTION

In previous papers, the reactions of (dialkylamino)dimethylarsine with  $\beta$ -propiolactone and epoxides<sup>1</sup>, and the insertions of heterocumulene into the Sb-N bonds<sup>2,3</sup> were described. Recently, Manoussakis *et al.*<sup>4</sup> published a paper on the insertion of CO<sub>2</sub> and CS<sub>2</sub> into Sb-N bonds. In this paper we describe the reactions of heterocyclic compounds with Group V metal amides.

(Diethylamino)dimethylarsine, and (dimethylamino)dimethylstibine both reacted with cyclic carbonates or thiocarbonates to give 1/1 insertion products:



R = Me or Et  
M = As or Sb

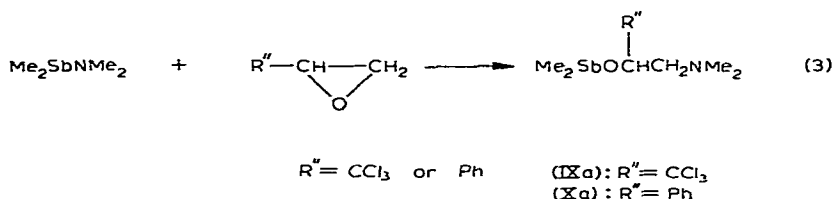
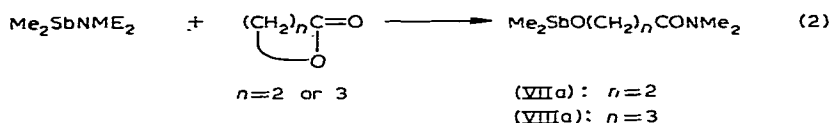
R' = H or Me  
X = O or S

(Ia): R = Et, R' = H, M = As, X = O  
(IIa): R = Et, R' = Me, M = As, X = O  
(IIIa): R = Et, R' = H, M = As, X = S  
(IVa): R = Me, R' = H, M = Sb, X = O  
(Va): R = Me, R' = Me, M = Sb, X = O  
(VIa): R = Me, R' = H, M = Sb, X = S

The structure of the adducts was confirmed not only by elementary analyses, IR, and NMR data, but also by the results of degradation of the products, (Ia)-(VIa).

\* Present address: Department of Industrial Chemistry, Chubu Institute of Technology, Kasugai (Japan).

The reaction of (dimethylamino)dimethylstibine with lactones ( $\beta$ -propiolactone and  $\gamma$ -butyrolactone), and epoxides (1,1,1-trichloro-2,3-epoxypropane, and styrene oxide) took place under moderate reaction conditions and gave the insertion products resulting from acyl-oxygen bond fission of lactones and normal bond fission of epoxides:



The modes of ring opening of lactones and epoxides are comparable with those which occur in the reactions of aminoarsine<sup>1</sup>.

## EXPERIMENTAL

### General remarks

All reactions except hydrolyses were carried out under dry nitrogen. IR spectra were run on a Nippon Bunko IR403G spectrometer. NMR spectra were measured on a Japan Electron Optics HL 60 spectrometer. The cyclic carbonate esters,  $\beta$ -propiolactone,  $\gamma$ -butyrolactone, and styrene oxide were distilled before use. 1,1,1-Trichloro-2,3-epoxypropane was synthesised by the method of ref. 1. Aminoarsine and aminostibine were prepared as previously described<sup>1,2</sup>.

### Reaction of aminoarsine with ethylene carbonate, and hydrolysis of the product (Ia)

An equimolar mixture of (diethylamino)dimethylarsine and ethylene carbonate was sealed in a tube under nitrogen and heated at 80° for 10 days. The viscous liquid product was distilled under reduced pressure. [2-(Diethylcarbamoyloxy)-ethoxy]dimethylarsine (Ia) (nc) was obtained in 78% yield, b.p. 75–78.5°/0.4 mm. (Found: C, 40.31; H, 7.54; N, 5.16.  $\text{C}_9\text{H}_{20}\text{AsNO}_3$  calcd.: C, 40.76; H, 7.56; N, 5.28%.) NMR ( $\text{CCl}_4$ ):  $\tau$  8.73 t ( $\text{AsMe}_2$ , 6H), 8.88 t and 6.70 q ( $\text{NEt}_2$ , 10H), 5.86 and 6.16  $\text{A}_2\text{B}_2$  type ( $\text{CH}_2\text{CH}_2$ , 4H). IR ( $\text{CHCl}_3$ ):  $\nu(\text{C=O})$  1680 s,  $\delta(\text{CH}_3)$  1375 s,  $\nu(\text{C-O})$  1048–1090 m,  $\nu(\text{AsC}_2)$  580  $\text{m cm}^{-1}$ . Hydrolysis of the product (Ia) was performed by allowing a mixture of (Ia) and water to stand at room temperature for 2 weeks. After extraction of the mixture with a large amount of ether and drying over calcium hydride, 2-(diethylcarbamoyloxy)ethanol was separated by column chromatography on silica gel in 50% yield based on (Ia), b.p. 74.5–75.5°/0.22 mm. (Found: C, 52.03; H, 9.38.  $\text{C}_7\text{H}_{15}\text{NO}_3$  calcd.: C, 52.16; H, 9.38%.) NMR ( $\text{CCl}_4$ ):  $\tau$  8.88 t and 6.80 q ( $\text{NEt}_2$ , 10H), 6.35 and 5.90  $\text{A}_2\text{B}_2$  type ( $\text{CH}_2\text{CH}_2$ , 4H), IR ( $\text{CHCl}_3$ ):  $\nu(\text{OH})$  3360 m,  $\nu(\text{C=O})$  1675 s,  $\delta(\text{CH}_3)$  1380 m,  $\nu(\text{C-O})$  1080  $\text{s cm}^{-1}$ .

*Reaction of aminoarsine with propylene carbonate, and hydrolysis of the product (IIa)*

When an equimolar mixture of (diethylamino)dimethylarsine and propylene carbonate in a sealed tube was heated at 100° for 2 months there was no change in the IR spectrum of the mixture, and both reagents were recovered completely. When  $\text{ZnCl}_2$  was used as a catalyst (1 wt.%), the reaction was complete within 3 days at 100°, but further heating was necessary when other strong Lewis acids were used, e.g. 2 weeks for  $\text{FeCl}_3$  and 1 month for  $\text{AlCl}_3$ . The product, [2-(diethylcarbamoyloxy)propoxy]dimethylarsine (IIa) (nc) was isolated by distillation under reduced pressure in 80–90% yield, b.p. 63.5–64.0°/0.05 mm. (Found: C, 43.51; H, 7.98; N, 4.84.  $\text{C}_{10}\text{H}_{22}\text{AsNO}_3$  calcd.: C, 43.02; H, 7.94; N, 5.02%) NMR ( $\text{CCl}_4$ ):  $\tau$  8.82 s ( $\text{AsMe}_2$ , 6H), 8.98 t and 6.82 q ( $\text{NEt}_2$ , 10H), 8.75 d ( $\text{CCH}_3$ , 3H), 6.35 m ( $\text{CH}_2$ , 2H), 5.38 m (CH, 1H). IR ( $\text{CHCl}_3$ ):  $\nu(\text{C}=\text{O})$  1682 s,  $\delta(\text{CH}_3)$  1382 m,  $\nu(\text{C}-\text{O})$  1090–1050 s,  $\nu(\text{AsC}_2)$  580  $\text{m cm}^{-1}$ . Hydrolysis of (IIa) with water, as described above, gave 2-(diethylcarbamoyloxy)propanol (IIb) in 92% yield based on (IIa), b.p. 66.5–68.0°/0.15 mm. (Found: C, 55.13; H, 9.70.  $\text{C}_8\text{H}_{17}\text{NO}_3$  calcd.: C, 54.84; H, 9.78%) NMR ( $\text{CCl}_4$ ):  $\tau$  8.90 t and 6.80 q ( $\text{NEt}_2$ , 10H), 8.80 d ( $\text{CCH}_3$ , 3H), 6.20 m ( $\text{CH}_2$ , 2H), 5.30 m (CH, 1H). IR ( $\text{CHCl}_3$ ),  $\nu(\text{OH})$  3350 m,  $\nu(\text{C}=\text{O})$  1680 s,  $\delta(\text{CH}_3)$  1380 m,  $\nu(\text{C}-\text{O})$  1080  $\text{s cm}^{-1}$ .

*Reaction of aminoarsine with ethylene thiocarbonate, and hydrolysis of the product (IIIa)*

The reaction of (diethylamino)dimethylarsine with ethylene thiocarbonate was performed by heating an equimolar mixture of the reagents at 80° for 10 days. The addition product, [2-(diethylcarbamoyloxy)ethylthio]dimethylarsine (IIIa) (nc), had b.p. 77.5–78.0°/0.01 mm, yield 82%. (Found: C, 38.17; H, 7.30; N, 5.22.  $\text{C}_9\text{H}_{20}\text{AsNO}_2\text{S}$  calcd.: C, 38.44; H, 7.17; N, 4.98%) NMR ( $\text{CCl}_4$ ):  $\tau$  8.69 s ( $\text{AsMe}_2$ , 6H), 8.80 t and 6.78 q ( $\text{NEt}_2$ , 10H), 7.24 t ( $\text{SCH}_2$ , 2H), 5.94 t ( $\text{OCH}_2$ , 2H). IR ( $\text{CHCl}_3$ ):  $\nu(\text{C}=\text{O})$  1685 s,  $\delta(\text{CH}_3)$  1380 m,  $\nu(\text{C}-\text{O})$  1070 m,  $\nu(\text{AsC}_2)$  570 w,  $\nu(\text{As}-\text{S})$  370  $\text{w cm}^{-1}$ . Hydrolysis of (IIIa) with water gave 2-(diethylcarbamoyloxy)ethanethiol (IIIb) in 52% yield based on (IIIa). (IIIb) was decomposed on the distillation, and so was purified by column chromatography. (Found: C, 47.02; H, 8.66; S, 18.56.  $\text{C}_7\text{H}_{15}\text{NO}_2\text{S}$  calcd.: C, 47.43; H, 8.53; S, 18.09%) NMR ( $\text{CCl}_4$ ):  $\tau$  8.90 t and 6.75 q ( $\text{NEt}_2$ , 10H), 6.85 t ( $\text{SCH}_2$ , 2H), 5.85 t ( $\text{OCH}_2$ , 2H). IR ( $\text{CHCl}_3$ ):  $\nu(\text{SH})$  2550 w,  $\nu(\text{C}=\text{O})$  1700 s,  $\delta(\text{CH}_3)$  1380 m,  $\nu(\text{C}-\text{O})$  1070  $\text{m cm}^{-1}$ . The  $\text{AgNO}_3$  test<sup>5</sup> for SH group of (IIIb) gave a positive result, and molecular weight of (IIIb) in benzene was found to be 176 (calcd. 177.3).

*Reaction of aminostibine with ethylene carbonate, and hydrolysis of the product (IVa)*

When ethylene carbonate was added to (dimethylamino)dimethylstibine, an exothermic reaction took place and the mixture became homogeneous. Distillation under reduced pressure then gave [2-(dimethylcarbamoyloxy)ethoxy]dimethylstibine (IVa) (nc) in 92% yield, b.p. 81.5–82.5°/0.15 mm. (Found: C, 29.63; H, 5.75; N, 5.10.  $\text{C}_9\text{H}_{20}\text{NO}_3\text{Sb}$  calcd.: C, 29.61; H, 5.68; N, 4.93%) NMR ( $\text{CCl}_4$ ):  $\tau$  8.93 s ( $\text{SbMe}_2$ , 6H), 7.05 s ( $\text{NMe}_2$ , 6H), 5.95 and 6.05  $\text{A}_2\text{B}_2$  type ( $\text{CH}_2\text{CH}_2$ , 4H). IR ( $\text{CHCl}_3$ ):  $\nu(\text{C}=\text{O})$  1685 s,  $\delta(\text{CH}_3)$  1390 m,  $\nu(\text{C}-\text{O})$  1050 m, 1090 m,  $\nu(\text{SbC}_2)$  517  $\text{m cm}^{-1}$ . When a stoichiometric amount of water was added to the adduct (IVa), a white precipitate slowly formed. The mixture was kept at room temperature for a week, and then a large amount of ether was added to the mixture. After removal of the precipitate and

the solvent, 2-(dimethylcarbamoyloxy)ethanol (IVb) was obtained in 85% yield by distillation at 70.5–71.5°/0.25 mm. (Found: C, 44.64; H, 8.29.  $C_5H_{11}NO_3$  calcd.: C, 45.10; H, 8.33%.) NMR ( $CCl_4$ ):  $\tau$  7.20 s ( $NMe_2$ , 6H), 6.30 and 6.00  $A_2B_2$  type ( $CH_2CH_2$ , 4H), 5.55 s (OH, 1H). IR ( $CHCl_3$ ):  $\nu(OH)$  3400 m,  $\nu(C=O)$  1685 s,  $\delta(CH_3)$  1400 m,  $\nu(C-O)$  1079 and 1050  $cm^{-1}$ .

*Reaction of aminostibine with propylene carbonate, and hydrolysis of the product (Va)*

The reaction of (dimethylamino)dimethylstibine with propylene carbonate was exothermic [2-(dimethylcarbamoyloxy)propoxy]dimethylstibine (Va) (nc) was isolated in 87% yield by distillation at 64.5–65.5°/0.01 mm. (Found: C, 32.11; H, 6.15; N, 4.50.  $C_{10}H_{22}NO_3Sb$  calcd.: C, 32.25; H, 6.09; N, 4.70%.) NMR ( $CCl_4$ ):  $\tau$  8.98 s ( $SbMe_2$ , 6H), 7.15 s ( $NMe_2$ , 6H), 8.85 d ( $CCH_3$ , 3H), 6.22 m ( $CH_2$ , 2H), 5.25 m ( $CH$ , 1H). IR ( $CHCl_3$ ):  $\nu(C=O)$  1680 s,  $\delta(CH_3)$  1380 m,  $\nu(C-O)$  1080 and 1050 m,  $\nu(SbC_2)$  516 w  $cm^{-1}$ . Hydrolysis of (Va) with water gave 2-(dimethylcarbamoyloxy)propanol (Vb) in 90% yield based on (Va), b.p. 95.5–96.5°/3.2 mm. (Found: C, 48.68; H, 8.89.  $C_6H_{13}NO_3$  calcd.: C, 48.97; H, 8.90%.) NMR ( $CCl_4$ ):  $\tau$  7.15 s ( $NMe_2$ , 6H), 8.85 d ( $CCH_3$ , 3H), 6.35 m ( $CH_2$ , 2H), 5.35 m ( $CH$ , 1H), 4.10 s (OH, 1H). IR ( $CHCl_3$ ):  $\nu(OH)$  3400 m,  $\nu(C=O)$  1695 s,  $\delta(CH_3)$  1380 m,  $\nu(C-O)$  1060  $cm^{-1}$ .

*Reaction of aminostibine with ethylene thiocarbonate, and hydrolysis of the product (VIa)*

[2-(Dimethylcarbamoyloxy)ethylthio]dimethylstibine (VIa) (nc) was obtained from the exothermic reaction of (dimethylamino)dimethylstibine with an equimolar amount of ethylene thiocarbonate in 88% yield, b.p. 96.5–97.0°/0.02 mm. (Found: C, 28.30; H, 5.86; N, 4.59.  $C_9H_{20}NO_2SSb$  calcd.: C, 28.30; H, 5.34; N, 4.67%.) NMR ( $CCl_4$ ):  $\tau$  8.90 s ( $SbMe_2$ , 6H), 7.15 s ( $NMe_2$ , 6H), 7.20 t ( $SCH_2$ , 2H), 6.00 t ( $OCH_2$ , 2H). IR ( $CHCl_3$ ):  $\nu(C=O)$  1690 s,  $\delta(CH_3)$  1400 m,  $\nu(C-O)$ , 1080 and 1040 m,  $\nu(SbC_2)$  514  $cm^{-1}$ . Hydrolysis of (VIa) with water gave product (VIb) which was purified by column chromatography because it decomposed on distillation. In the IR spectra of (VIb) neither OH nor SH absorptions were present, and the  $AgNO_3$  test<sup>5</sup> for SH group was negative. However, the molecular weight of (VIb) in benzene was found to be 298 (theor. 298.4 calcd. as disulfide). From these observations and the NMR and IR spectra shown below, (VIb) was identified as bis[2-(dimethylcarbamoyloxy)ethyl]disulfide, formed from the initial hydrolysis product, 2-(dimethylcarbamoyloxy)ethanethiol. (Found: C, 40.03; H, 7.28; S, 21.39.  $C_{10}H_{20}N_2O_4S_2$  calcd.: C, 40.25; H, 7.43; S, 21.49%.) NMR ( $CCl_4$ ):  $\tau$  7.20 s ( $NMe_2$ , 12H), 4.90 t ( $OCH_2$ , 4H). IR ( $CHCl_3$ ):  $\nu(C=O)$  1720 s,  $\delta(CH_3)$  1400 m,  $\nu(C-O)$  1063 m,  $\nu(S-S)$  535 w  $cm^{-1}$ .

*Determination of the type of carbamoyloxy alcohols derived from hydrolysis of (IIa) and (Va)*

In order to determine the structure of the adducts, (IIa) and (Va), the rates of esterification of carbamoyloxy alcohols, (IIb) and (Vb) with phenylacetic acid were determined. When primary, secondary and tertiary alcohols are treated with phenylacetic acid at 156° (in the vapour of refluxing bromobenzene) for 1 h, the rates of esterification (calculated as percentage of the consumed alcohols) were found to be less than 10%, 20–30%, and more than 50% for tertiary, secondary, and primary alcohols, respectively<sup>6</sup>. The rates for the carbamoyloxy alcohols (IIb) and (Vb) are

shown in Table 1, along with those for the primary alcohols, (Ib) and (IVb). From these results, (IIb) and (Vb) can be seen to be primary alcohols.

TABLE 1

RATES OF ESTERIFICATION OF (Ib), (IIb), (IVb), AND (Vb) WITH PHENYLACETIC ACID AT 156° (% of consumed alcohols)

| Alcohols | Rates of esterification (%) |
|----------|-----------------------------|
| (Ib)     | 69                          |
| (IIb)    | 63                          |
| (IVb)    | 58                          |
| (Vb)     | 69                          |

*Reaction of aminostibine with lactones, and hydrolysis of the products (VIIa and VIIa)*

To a solution of (dimethylamino)dimethylstibine in ether, an equimolar amount of  $\beta$ -propiolactone was added. The mixture was heated under reflux for 4 h. The solvent was then recovered and the product was obtained by distillation. [2-(dimethylcarbamoyl)ethoxy]dimethylstibine (VIIa) (nc) (43% yield) had b.p. 88–90°/0.35 mm. (Found: C, 31.46; H, 5.92; N, 5.16.  $C_7H_{16}NO_2Sb$  calcd.: C, 31.37; H, 6.02; N, 5.23%.) NMR ( $CCl_4$ ):  $\tau$  9.00 s ( $SbMe_2$ , 6H), 7.82 t ( $CH_2$ , 2H), 7.68 and 7.37 ( $CONMe_2$ , 6H), 5.98 t ( $OCH_2$ , 2H). IR ( $CHCl_3$ ):  $\nu(C=O)$  1634 s,  $\delta(CH_3)$  1400 m,  $\nu(SbC_2)$  520 w  $cm^{-1}$ . Hydrolysis of (VIIa) with water, as above, gave 3-hydroxy-*N,N*-dimethylpropionamide (VIIb) in 80% yield based on (VIIa), b.p. 78–79°/0.65 mm. (Found: C, 52.26; H, 9.67.  $C_5H_{11}NO_2$  calcd.: C, 51.26, H, 9.46%.) NMR ( $CCl_4$ ):  $\tau$  7.10 and 7.00 ( $CONMe_2$ , 6H), 7.53 t ( $CH_2$ , 2H), 6.25 t ( $OCH_2$ , 2H), 5.40 s (OH, 1H). IR ( $CHCl_3$ ):  $\nu(OH)$  3440 s,  $\nu(C=O)$  1622 s,  $\nu(C-O)$  1058 s. The reaction of (dimethylamino)dimethylstibine with  $\gamma$ -butyrolactone was performed similarly, except that the mixture in ether was kept at 40° for 4 days. [3-(dimethylcarbamoyl)propoxy]dimethylstibine (VIIIa) (nc) (56% yield) had b.p. 94.5–95.5°/0.08 mm. (Found: C, 34.39; H, 6.60; N, 5.61.  $C_8H_{18}NO_2Sb$  calcd.: C, 34.07; H, 6.43; N, 4.97%.) NMR ( $CCl_4$ ):  $\tau$  8.94 s ( $SbMe_2$ , 6H), 8.05 m ( $CCH_2C$ , 2H), 7.60 t ( $COCH_2$ , 2H), 7.08 and 6.98 ( $CONMe_2$ , 6H), 6.27 t ( $OCH_2$ , 2H). IR ( $CHCl_3$ ):  $\nu(C=O)$  1630 s,  $\nu(C-O)$  1048 m,  $\nu(SbC_2)$  515 w  $cm^{-1}$ . Hydrolysis of (VIIIa) gave 4-hydroxy-*N,N*-dimethylbutyramide (VIIIb) in 70% yield based on (VIIIa), b.p. 93–95°/0.38 mm. (Found: C, 54.94; H, 9.86.  $C_6H_{13}NO_2$  calcd.: C, 54.14; H, 9.99%.) NMR ( $CCl_4$ ):  $\tau$  8.05 m ( $CCH_2C$ , 2H), 7.50 t ( $COCH_2$ , 2H), 7.05 and 6.05 ( $CONMe_2$ , 6H), 6.35 t ( $OCH_2$ , 2H). IR ( $CHCl_3$ ):  $\nu(OH)$  3365 s,  $\nu(C=O)$  1623 s,  $\nu(C-O)$  1055 m.

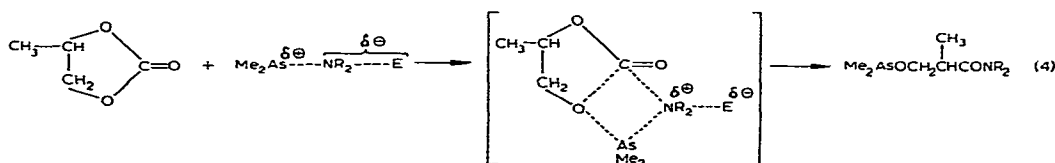
*Reaction of aminostibine with epoxides, and hydrolyses of the products, (IXa) and (Xa)*

When equimolar amounts of (dimethylamino)dimethylstibine and 1,1,1-trichloro-2,3-epoxypropane were heated at 55° for 2 h, the corresponding adduct, [2-(dimethylamino)-3,3,3-trichloropropoxy]dimethylstibine (IXa) (nc) was obtained in 45% yield by distillation at 62–63°/0.18 mm. (Found: C, 23.50; H, 4.06; N, 4.01.  $C_7H_{15}Cl_3NOSb$  calcd.: C, 23.20; H, 4.21; N, 3.92%.) NMR ( $CCl_4$ ):  $\tau$  8.96 s ( $SbMe_2$ , 6H), 7.67 s ( $NMe_2$ , 6H), 7.22 m ( $CH_2$ , 2H), 5.82 q (CH, 1H). IR ( $CHCl_3$ ):  $\nu(C-O)$

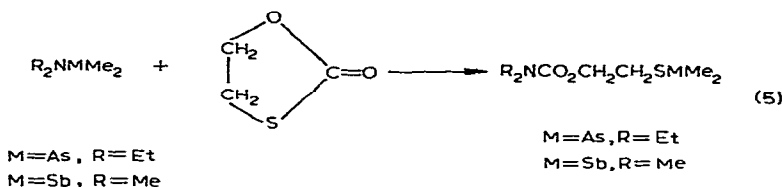
1045 m,  $\nu(\text{CCl}_3)$  750 s,  $\nu(\text{SbC}_2)$  518 w  $\text{cm}^{-1}$ . Hydrolysis of (IXa) gave white crystals which were shown to be 2-(dimethylamino)-3,3,3-trichloro-1-propanol by the comparison of the m.p. (118–119°) and NMR and IR spectra with those of an authentic sample<sup>7</sup>. By similar treatment of styrene oxide with (dimethylamino)dimethylstibine, except that the reaction mixture was kept at 50° for 10 h, the corresponding adduct, [2-(dimethylamino)-2-phenylethoxy]dimethylstibine (Xa) (nc) was obtained in 35% yield, b.p. 68–69°/0.015 mm. (Found: C, 46.28; H, 6.60.  $\text{C}_{12}\text{H}_{20}\text{NOSb}$  calcd.: C, 45.57; H, 6.38%.) NMR ( $\text{CCl}_4$ ):  $\tau$  9.10 s ( $\text{SbMe}_2$ , 6H), 7.72 s ( $\text{NMe}_2$ , 6H), 7.70 m ( $\text{CH}_2$ , 2H), 5.38 q (CH, 1H), 2.89 m (Ph, 5H). IR ( $\text{CHCl}_3$ ):  $\nu(\text{Ph})$  1603 w and 1495 s,  $\nu(\text{C-O})$  1042 s,  $\nu(\text{SbC}_2)$  515 m  $\text{cm}^{-1}$ . Hydrolysis of (Xa) gave 2-(dimethylamino)-2-phenylethanol in 50% yield based on (Xa), b.p. 72–73°/0.65 mm. (Found: C, 72.75; H, 9.15.  $\text{C}_{10}\text{H}_{15}\text{NO}$  calcd.: C, 72.68; H, 9.11%.) NMR ( $\text{CCl}_4$ ):  $\tau$  7.72 s ( $\text{NMe}_2$ , 6H), 7.74 m ( $\text{CH}_2$ , 2H), 5.46 q (CH, 1H), 6.30 s (OH, 1H). IR ( $\text{CHCl}_3$ ):  $\nu(\text{OH})$  3400 s,  $\nu(\text{Ph})$  1604 w, 1495 s,  $\nu(\text{C-O})$  1070 m  $\text{cm}^{-1}$ .

## RESULTS AND DISCUSSION

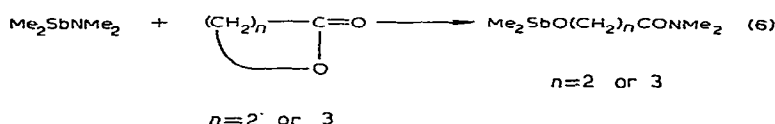
The insertion reaction of aminophosphine with cyclic carbonate was found to involve the P–N bond, in contrast with the deoxygenation reported by Corey *et al.*<sup>9</sup> for reaction with trialkyl phosphites. The reactions of aminoarsine and aminostibine with cyclic carbonates or thiocarbonates, took place under more moderate conditions than those of aminophosphines, except for the reaction with propylene carbonate. In the case of reaction of aminoarsine with propylene carbonate, the addition of a catalytic amount of Lewis acid was necessary, probably because of the steric hindrance between the methyl group of propylene carbonate and the entering aminoarsine, or of the poor solubility of aminoarsine in propylene carbonate. The catalytic activity of the Lewis acid used ( $\text{ZnCl}_2$ ,  $\text{FeCl}_3$ , and  $\text{AlCl}_3$ ) was in reverse order of their generally accepted Lewis acidities. This can be explained by assuming that a weak Lewis acid catalyst can activate the As–N bond by coordinating moderately to the nitrogen atom of aminoarsine, but that a stronger Lewis acid would coordinate too firmly to the nitrogen atom to enter into reaction with the carbonyl carbon atom of the carbonate. In general, the reactivity increased from aminophosphine to



aminostibine; this tendency can be ascribed to the increasing polarizability of the metal–nitrogen bonds. The adducts, (IIa) and (Va), were shown to be (1,2-disubstituted ethoxy)dimethylarsine and -stibine by comparing the rates of esterification of their hydrolysis products, (IIb) and (Vb), with those of (Ib) and (IVb), which clearly have primary hydroxyl groups. For the adducts (IIIa) and (VIa), (ethylthio)arsine and -stibine structures were confirmed by the fact that their hydrolysis products, (IIIb) and (VIb), were 2-substituted ethanethiol or bis(2-substituted ethyl) disulfide, as



indicated by their spectra, chemical behaviour, and molecular weights. Aminostibine reacted with  $\beta$ -propiolactone and  $\gamma$ -butyrolactone and gave 1/1 addition products



resulting from acyl-oxygen bond fission. In the case of phosphoramidite<sup>10</sup> and aminoarsines<sup>1</sup>, alkyl-oxygen bond fission was observed. This contrasting behaviour can be explained by Pearson's SHAB concept. Because the nitrogen atom of phosphoramidite and aminoarsine has hard-base character, the nitrogen atom will attack the hard-acid site of  $\beta$ -propiolactone, i.e., the  $sp^3$  carbon atom. When the substituent on the nitrogen atom is replaced by antimony, the hard character of the nitrogen atom will be substantially reduced because of the symbiotic effect of the antimony atom. Thus the nitrogen atom on aminostibine will prefer an  $sp^2$  rather than an  $sp^3$  carbon atom. In the reaction of  $\beta$ -propiolactone with phosphoramidite, alkyl-oxygen bond fission occurs<sup>10</sup>, but in this case the basic site of phosphoramidite is the phosphorus atom.

The reaction of epoxides with aminostibine proceeded through normal ring opening of epoxides, in keeping with the behaviour of aminoarsine<sup>1</sup>. This could be caused by steric hindrance between the substituents in the epoxides and the entering reagent.

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