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PREPARATION AND PROPERTIES OF DIETHYLAMINOORGANOANTIMONY(III) DERIVATIVES*

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Information on organoantimony(III) derivatives of the types R_2SbX and $RSbX_2$ is scarce and, so far, has remained largely limited to the organoantimony(III) halides (2).

In the present communication we wish to report some of our results on the preparation and properties of organoantimony(III)-nitrogen derivatives.

Mono-, bis- and trisdialkylaminoarsines have been prepared by the aminolysis of the corresponding haloarsines (3, 4). Attempts to prepare trisdimethylaminostibine by essentially the same method were unsuccessful. However, this compound can be easily obtained by reacting lithium dimethylamide with antimony trichloride (5). We have observed that whereas the reaction of diethylamine with halostibines does not result in the isolation of pure products, the lithium diethylamide route affords the title compounds in high yields and purity.

$$R_nSbX_{(3-n)} + (3-n)\,LiNEt_2 \longrightarrow R_nSb(NEt_2)_{3-n} + (3-n)\,LiX$$

$$(R = \text{alkyl, phenyl};\ X = Cl, Br;\ n = 1, 2)$$

The diethylaminoalkylstibines are colourless liquids. The phenyl analogues are slightly yellow oils. The diethylaminodialkylstibines are particularly sensitive towards oxidation by air oxygen. All aminostibines are sensitive towards hydrolysis by moist air.

The various compounds prepared, their yields as well as analytical and boiling point data are listed in Table 1.

Attempts directed towards the preparation of Me_2SbNEt_2 resulted in the isolation of this compound in only 10-20% yield (colourless liquid, b.p. 70°/10 mm). Its extreme air-sensitivity seriously hampered the analysis for antimony (Sb, found 51.82%; calcd. 54.37%). We can offer no explanation for the low yields obtained in the preparation of this compound.

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TABLE 1

Yields, Boiling points and Analytical data for Mono- and Bisdiethylaminostibines

Compound	B.p. °C (mm Hg)	Sb (%) Found	Sb (%) Calcd.	Yield (%)
Et_2SbNEt_2	77-80 (12)	47.20[a]	48.41	83.0
Pr_2SbNEt_2	53 (0.1)	43.16	43.48	96.4
Bu_2SbNEt_2	100-105 (1.4)	39.93	39.61	97.0
Ph_2SbNEt_2	130-133 (0.3)	34.51	35.06	67.8
$EtSb(NEt_2)_2$	70-72 (1.3)	41.36	41.27	74.0
$PrSb(NEt_2)_2$	58-60 (0.1)	38.77	39.39	57.2
$BuSb(NEt_2)_2$	67-70 (0.1)	38.10	37.68	84.0
$PhSb(NEt_2)_2$	94-95 (0.1)	35.99	35.48	70.7

a) Difficult to analyse due to extreme sensitivity towards oxidation.

The IR spectra of the aminostibines show absorption bands in the region 600-400 cm^{-1}, which are absent in the spectra of the corresponding halostibine and accordingly have been assigned to Sb—N stretching modes. Relevant stretching frequencies are given in Table 2.

TABLE 2

IR Stretching Frequencies of some Mono- and Bisdiethylaminostibines in the 600-400 cm^{-1} Region

Compound	Stretching Frequencies (cm^{-1}) Sb—N	Sb—C
Me_2SbNEt_2	561 w-m	507 vs
Et_2SbNEt_2	561 w-m	497 s
Ph_2SbNEt_2	561 w-m	a
$EtSb(NEt_2)_2$	560 s; 459 w	504 m
$BuSb(NEt_2)_2$	560 s; 458 w	505 w
$PhSb(NEt_2)_2$	565 s; b	a

a) Ph-absorptions at 450-460 cm^{-1}; b ν(Sb—N) sym. obscured by Ph-absorptio

PMR spectroscopy was used in order to establish the purity of the compounds discussed in this paper. The benzene solution spectrum of Me_2SbNEt_2 shows a singlet for the Me-(Sb) protons at δ 0.69 ppm. The spectra of both Et_2SbNEt_2 and $EtSb(NEt_2)_2$ show an unresolved signal at δ 1.0-1.4 for the Et-(S proton resonances, whereas all compounds discussed in this paper show a tri and a quartet for the diethylamino protons at δ 0.90-1.00 and 3.00-3.15 ppm, respectively.

Experimental

All reactions were carried out under an atmosphere of dry nitrogen. The halostibines R_2SbBr, $RSbBr_2$ (R = Et, Pr, Bu) (6), Me_2SbCl (6), Ph_2SbCl (7) and $PhSbCl_2$ (8) used as starting materials were prepared by methods essentially similar to those reported.

IR spectra were run as a liquid between KBr-disks on a Grubb-Parsons Spectromaster.

PMR spectra were measured on a Varian Associates HA-100 spectrometer.

Preparation of Mono- and Bisdiethylaminostibines

Diethylaminodiethylstibine. A solution of 7.3 g (100 mmoles) of diethylamine in 40 ml of diethyl ether was slowly added to a cooled solution (-80°) of 75 mmoles of n-butyllithium in 75 ml of hexane. The resulting suspension of lithium diethylamide was stirred for 30' and subsequently 19.5 g (75 mmoles) of bromodiethylstibine in 20 ml of diethyl ether was dropwise added (temp. -80°). The reaction mixture was allowed to warm up to room temperature and then refluxed for 1 h. After evaporation of the solvents, 100 ml of pentane was added. The insoluble lithium bromide was removed by filtration. The filtrate afforded upon distillation 15.7 g of diethylaminodiethylstibine, as a colourless air-sensitive liquid. B.p. 77-80° (12 mm), Yield 83.0%.

The other aminostibines listed in Table 1 were prepared by essentially the same method.

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References

1. H.A.MEINEMA and J.G.NOLTES, J.Organometal.Chem., in the press.
2. M.DUB, Organometallic Compounds, Vol. III, Springer-Verlag, New York, 1968, p. 682-707.
3. K. MöDRITZER, Chem.Ber., 92 (1959) 2637.
4. W.R.CULLEN and H.J.EMELEUS, J.Chem.Soc., (1959) 372.
5. K.MöDRITZER, Inorg.Chem., 3 (1964) 609.
6. G.T.MORGAN and G.R.DAVIES, Proc.Roy.Soc., A 110 (1926) 523.
7. A.E.GODDARD, J.N.ASHLEY and R.B.EVANS, J.Chem.Soc., 121 (1922) 978.
8. G.O.DOAK and H.H.JAFFE, J.Amer.Chem.Soc., 72 (1950) 3025.