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Addition Reactions of Heterocumulenes to the Sb-N Bond

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Even though much information on the reactions of Group Va metal amides with various unsaturated compounds is available, it has largely been limited to those of phosphorus and arsenic amide.[1-3] In this communication, some of our results on the reactions of organoantimony(III) amide with alkyl or aryl isocyanate or isothiocyanate are presented.

The reactions of *N,N*-dimethylaminodimethylstibine with equimolar alkyl or aryl isocyanate or isothiocyanate in ethyl ether took place exothermally at room temperature to give the simple insertion products as shown below.

$$Me_2SbNMe_2 + RNCX \longrightarrow Me_2Sb(R)NC(X)NMe_2$$

R=Me, Et, Bu^t, Ph; X=O or S

These addition products are very hygroscopic liquids and decomposed into white solids when exposed to air. The yield, physical properties, and the relevant spectral data are shown in experimental section and Tables 1 and 2.

The spectral data suggest that the 1:1 addition products are formed across the Sb–N bond.

Hydrolysis of all the addition products was performed with dilute hydrochloric acid, and the hydrolysis product were identified as trisubstituted urea and thiourea derivatives by their spectral data and by their failure to depress the melting points on admixture with authentic samples.

Experimental

Preparation of N,N-*Dimethylaminodimethylstibine.* To a solution of lithium amide, prepared from dimethylamine and *n*-buthyllithium in petroleum ether, an equimolar amount of dimethylchlorostibine, prepared according to the method of Davies,[4] was added slowly with ice cooling. The reaction mixture was heated for 1hr under reflux. Separation of lithium chloride by decantation and removal of the solvent gave crude *N,N*-dimethylaminodimethylstibine, which was purified by column distillation. Bp 62—65°C/75mmHg, yield 46%.

TABLE 1. PHYSICAL PROPERTIES AND ELEMENTAL ANALYSES OF $Me_2Sb(R)NC(X)NMe_2$

	Compound	Reaction	Bp (°C/mmHg) [Mp °C]	Yeild (%)	Found (%)			Calcd (%)		
					C	H	N	C	H	N
I	R=Et, X=O	Exothermic	72.5— 73.5/0.25	78	32.07	6.37	10.80	31.49	6.42	10.49
II	R=Bu^t, X=O	Exothermic	28.5— 29.0/0.15	72	36.91	7.35	9.23	36.64	7.17	9.49
III	R=Ph, X=O	Exothermic	98 — 99/0.07 [59.0— 60.0]	62	42.94	5.32	8.15	41.94	5.44	8.89
IV	R=Me, X=S	Exothermic	76 — 77/0.31	59	26.20	5.69		26.79	5.62	
V	R=Ph, X=S	Exothermic	117 —118/0.02	73	39.69	5.02	8.95	39.91	5.18	8.46

TABLE 2. RELEVANT IR FREQUENCIES AND NMR ABSORPTIONS OF $Me_2Sb(R)NC(X)NMe_2$

Compound	(IR cm^{-1})[a]				NMR (τ, ppm)[c]
	ν(N=C=X)[b]		ν(SbC_2)		
	asym.	sym.	asym.	sym.	
I	1638 (s)	1523 (s)	532 (w)	518 (w)	6.70 (q, 2H, NCH_2-), 8.92 (t, 3H, -CH_3) 7.15 (s, 6H, NMe_2), 9.05 (s, 6H, $SbMe_2$)
II	1640 (s)	1513 (s)	533 (w)	518 (w)	7.05 (s, 6H, NMe_2), 8.71 (s, 9H, NBu^t) 9.08 (s, 6H, $SbMe_2$)
III	1680 (w)	1560 (s)	519 (w)	509 (w)	3.20 (m, 5H, NPh), 7.43 (s, 6H, NMe_2) 9.45 (s, 6H, $SbMe_2$)
IV	1540 (s)	1345 (s)	522 (w)	518 (w)	6.65 (s, 3H, NMe), 7.00 (s, 6H, NMe_2) 9.06 (s, 6H, $SbMe_2$)[d]
V	1580 (s)	1360 (s)	515 (w)	510 (w)	3.29 (m, 5H, NPh), 7.00 (s, 6H, NMe_2) 9.22 (s, 6H, $SbMe_2$)

a) In $CHCl_3$, b) X=O or S, c) 10% solution in $CHCl_3$, d) 10% solution in C_6H_6

1) G. Oertel, H. Mals, and H. Haltschmidt, *Chem. Ber.*, **97**, 891 (1964).
2) H. J. Vetter and H. Nöth, *Angew. Chem.*, **75**, 417 (1963).
3) H. J. Vetter and H. Nöth, *Z. Naturforsch.* **19b**, 167 (1964).
4) G. T. Morgan and G. R. Davies, *Proc. Roy. Soc.*, **110**, 523 (1926).

Reaction of N,N-*Dimethylaminodimethylstibine with Isocyanates.* Typical experiment is described. Further details are shown in Tables 1 and 2. Methyl isocyanate (0.38 g, 6.67 mmol) in ethyl ether was added dropwise with constant stirring to *N,N*-dimethylaminodimethylstibine (1.30 g, 6.64 mmol) in the same solvent (5 m*l*). The reaction was exothermic. The white crystals formed. The crystals, *N,N,N'*-trimethylureidodimethylstibine (1.05g, 63%), were collected by filtration and washed several times with ethyl ether. Mp 75°C; ν(N=C=O), 1640(s), 1530(s); $\nu(SbC_2)$, 530, 518cm^{-1}; τ, 7.10 (s, 3H, NMe), 7.12 (s, 6H, NMe_2), 9.05 (s, 6H, $SbMe_2$).

Found: C, 27.91; H, 6.57; N, 11.38%. Calcd for $C_6H_{15}N_2OSb$: C, 28.49; H, 5.98; N, 11.08%.

A portion (0.1g) of this product was treated with dilute hydrochloric acid to give white crystals which were proved to be *N,N,N'*-trimethylurea (0.37g, 98%) by comparison of its mp and spectral data with those of an authentic sample.