[Jour. Indian Chem. Soc., Vol. 37, No. 6, 1960]

COMPLEX COMPOUNDS OF STANNOUS BROMIDE WITH AMINES AND HETEROCYCLIC BASES

BY SARJU PRASAD, K. S. R. KRISHNAIAH AND V. HARIHARAN

Compounds of stannous bromide with primary (mono and di) and secondary amines and heterocyclic bases have been prepared in ether medium, their properties studied and structures discussed.

Compounds of stannous halides with ammonia (Biltz and Fischer, *Z. anorg. allgem. Chem.*, 1923, **129**, 1; Sofianopoulis, *Compt. rend.*, 1911, **152**, 865) and methylamine (Everest, *J. Chem. Soc.*, 1952, 1670) have been previously described. Karanthsis (*Bull. Soc. Chim.*, 1926, *iv*, **39**, 43) prepared $SnI_3.NMe_4$ by dissolving molecular proportions of SnI_2 and Me_4NI in the presence of an excess of HCl. By a similar method he prepared the corresponding compounds: $SnI_3.NH_3Ph$ and $SnI_3.NHPh$. Dimitron (*Praktika*, 1929, **4**, 140) isolated the compounds $MeSnI_3.2\ C_5H_5N$, $SnCl_4.2C_9H_7N$ and $SnBr_4.2C_9H_7N$.

It is evident that practically no work has been done on the formation of compounds of $SnBr_2$ with amines and heterocyclic bases. The present investigation was therefore undertaken with a view to studying the preparation and properties of these compounds.

EXPERIMENTAL

The amines and heterocyclic bases used were of Merck's or B.D.H. 'extra pure' quality. Ether was distilled over metallic sodium. Anhydrous $SnBr_2$ was prepared by passing dry HBr gas on molten tin and extracted with ether.

A dilute ether solution of the amine or heterocyclic base was added to $SnBr_2$ solution in ether with constant stirring till complete precipitation. The precipitate was filtered and washed with anhydrous ether till the washings did not form any precipitate with $SnBr_2$ solution. It was dried at the room temperature, analysed, and its properties studied.

Bromine was estimated by Piria and Schiff's method and tin as SnO_2. Nitrogen was estimated by Kjeldahl's method in a few cases and for the rest it was obtained by difference. The results are recorded in Table I.

Almost all the compounds are semicrystalline powders, insoluble in ether but sparingly soluble in benzene. These are fairly stable in dry atmosphere, but when exposed to moist air these absorb moisture and decompose. These are readily soluble in moderately strong HCl, but decompose into the corresponding amine, sodium bromide and tin hydroxide when treated with dilute NaOH.

$$Sn(2\ Am)\ Br_2 + 2NaOH \rightarrow Sn(OH)_2 + 2\ NaBr + 2Am.$$

When heated, all the compounds decompose before melting excepting the compounds obtained with benzylamine and phenylhydrazine, which melt at 238° and 186° respectively.

TABLE I

Compounds of stannous bromide with amines and heterocyclic bases.

	Bases.	Compound formed.	% Tin Found.	% Tin Calc.	% Bromine. Found.	% Bromine. Calc.	% Nitrogen. Found.	% Nitrogen. Calc.
1.	Aniline	$Sn(C_6H_5NH_2)_2 Br_2$	25.42	25.58	34.33	34.41	6.042	6.029
2.	α-Naphthylamine	$Sn(C_{10}H_7NH_2)_2 Br_2$	20.88	21.03	28.18	28.31	4.912	4.961
3.	β-Naphthylamine	Do	21.12	21.03	28.38	28.31	4.953	4.961
4.	*o*-Toluidine	$Sn(CH_3.C_6H_4.NH_2)_2 Br_2$	24.21	24.11	32.22	32.44	5.634	5.685
5.	*m*-Toluidine	Do	23.98	24.11	32.26	32.44	5.646	5.685
6.	*p*-Toluidine	Do	24.18	24.11	32.18	32.44	5.672	5.685
7.	*o*-Anisidine	$Sn(CH_3O.C_6H_4.NH_2)_2 Br_2$	22.48	22.62	30.42	30.45	5.342	5.335
8.	*m*-Anisidine	Do	22.71	22.62	30.31	30.45	5.352	5.335
9.	*p*-Anisidine	Do	22.57	22.62	30.38	30.45	5.328	5.335
10.	*o*-Phenetidine	$Sn(C_2H_5O.C_6H_4.NH_2)_2 Br_2$	21.39	21.47	28.88	28.91	5.042	5.065
11.	*p*-Phenetidine	Do	21.51	21.47	28.97	28.91	5.102	5.065
12.	Benzylamine	$Sn(C_6H_5.CH_2NH_2)_2 Br_2$	24.02	24.11	32.38	32.44	5.691	5.685
13.	Benzidine	$Sn(NH_2C_6H_4\text{-}C_6H_4NH_2) Br_2$	25.72	25.67	34.42	34.56	6.098	6.056
14.	*o*-Tolidine	$Sn(CH_3.NH_2.C_6H_3\text{-}C_6H_3.NH_2.\text{-}CH_3) Br_2$	24.28	24.20	32.43	32.58	5.682	5.710
15.	*o*-Phenylenediamine	$Sn\{C_6H_4(NH_2)_2\}Br_2$	30.74	30.71	41.10	41.33	7.228	7.244
16.	*m*-Phenylenediamine	Do	30.82	30.71	41.23	41.33	7.316	7.244
17.	*p*-Phenylenediamine	Do	30.62	30.71	41.27	41.33	7.287	7.244
18.	*o*-Dianisidine	$Sn(CH_3O.NH_2.C_6H_3\text{-}C_6H_3.NH_2.\text{-}OCH_3) Br_2$	22.60	22.72	30.52	30.58	5.351	5.359
19.	Phenylhydrazine	$Sn(C_6H_5NH.NH_2) Br_2$	30.83	30.71	41.30	41.33	7.304	7.244
20.	Methylaniline	$Sn(C_6H_5.NHCH_3)_2 Br_2$	24.20	24.11	32.18	32.44	5.672	5.685
21.	Ethylaniline	$Sn(C_6H_5.NHC_2H_5)_2 Br_2$	22.74	22.81	30.60	30.70	5.368	5.380
22.	Pyridine	$Sn(C_5H_5N)_2 Br_2$	27.16	27.19	36.40	36.60	6.459	6.415
23.	Piperidine	$Sn(C_5H_{11}N)_2 Br_2$	26.53	26.46	35.48	35.62	6.223	6.243
24.	Piperazine	$Sn(C_4H_{10}N_2) Br_2$	32.60	32.57	43.56	43.83	7.762	7.683

DISCUSSION

In all the cases studied, two molecules of a monoamine or a heterocyclic base and one molecule of a diamine attach themselves to one molecule of $SnBr_2$ and only the covalency of four is attained. It appears that amines or heterocyclic bases attach themselves to the central atom, chelete compounds being formed in the case of diamines and can be represented as $Sn(2Am)Br_2$ (where A= monoamine or heterocyclic base) and $Sn(D)Br_2$ (where D=diamine). The E.A.N. does not assume the inert gas configuration and therefore the compounds are not very stable.

The authors' sincere thanks are due to the authorities of the Banaras Hindu University for providing the necessary facilities.

CHEMICAL LABORATORIES,
BANARAS HINDU UNIVERSITY,
VARANASI-5.

Received January 28, 1960.