308. *The Preparation and Properties of Triarylstibines.*

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The influence of nuclear substituents on the reaction of phenylmagnesium halides with antimony trichloride has been examined, and triphenylstibines containing methoxyl, ethoxyl, phenoxyl, chlorine, and bromine as substituents have been prepared. Attempts have also been made to prepare *tri-β-naphthylstibine* through the interaction of β-naphthylmagnesium iodide and antimony trichloride. A preliminary examination has been made of the thermal stability of the triphenylstibines.

The reaction between a substituted phenylmagnesium halide and antimony trichloride has not been studied extensively, and little information is available concerning the influence of nuclear substituents on the properties of triarylstibines. Under ordinary conditions in ethereal solution the reaction between 1 mol. of antimony trichloride and 3 mols. of arylmagnesium halide leads to the formation of the tertiary stibine, $SbAr_3$, and there appears to be no record of the formation of the diarylstibinous chloride, $SbAr_2Cl$, in reactions of this type. In the present investigation, however, it was found that *di-*o*-anisylstibinous chloride* and *tri-*o*-anisylstibine* were produced when the antimony halide and *o*-anisylmagnesium bromide reacted in ethereal solution at 40°. It is noteworthy that Makin and Waters (*J.*, 1938, 843) found that triarylstibine dichlorides, $SbAr_3Cl_2$, triarylstibines, and diarylstibinous chlorides were generally produced when diazonium chlorides reacted with antimony under acetone. From bases containing *o*-substituents, only traces of quinquevalent antimony compounds were formed, the main products being the triarylstibines accompanied by a smaller quantity of the diarylstibinous chloride, and it was suggested that the non-formation of quinquevalent antimony compounds may be due to steric hindrance. In the Grignard synthesis, however, there is no possibility of the formation of triarylstibine dichloride, and though the conversion of di-*o*-anisylstibinous chloride into the tertiary stibine may be affected to some extent by steric hindrance, it is evident that this is a subsidiary factor in view of the fact that *o*-phenetylmagnesium bromide reacts with antimony trichloride to give a relatively high yield of *tri-*o*-phenetylstibine*.

Previous workers have experienced some difficulty in preparing *m*-substituted triphenylstibines by the Grignard synthesis. Thus Challenger and Pritchard (*J.*, 1924, **125**, 869) were able to isolate only tri-*m*-tolylstibine hydroxychloride in an attempted preparation of tri-*m*-tolylstibine, and Goddard (*J.*, 1923, **123**, 2319) found that the Grignard method gave a low yield of tri-*m*-xylylstibine although the compound may be obtained in high yield by the action of sodium on 4-bromo-*m*-xylene and antimony trichloride. In the present work, it was found that *m*-anisylmagnesium iodide reacted smoothly with antimony trichloride to form *tri-*m*-anisylstibine* in good yield. The fact that *tri-*p*-phenoxyphenylstibine* was obtained in fair yield by the Grignard synthesis shows that a phenoxyl group does not interfere appreciably with the normal formation of a tertiary stibine.

A chlorine atom in the *p*-position was found to have little effect on the course of the reaction, and the yield of *tri-*p*-chlorophenylstibine* was good. O'Donnell (*Iowa State Coll. J. Sci.*, 1945, **20**, 34) has reported that tri-*p*-bromophenylstibine prepared by the Grignard method is obtained as an oil which can only be converted into crystals, m. p. 134—135°, by inoculation with a specimen of the stibine prepared by reduction of the stibine dichloride, m. p. 184—185°. In the present investigation tri-*p*-bromophenylstibine was obtained as an oil from which a small amount of the crystalline stibine, m. p. 108—109°, was isolated. This material in alcoholic solution gave on treatment with cupric chloride the stibine dichloride, m. p. 200—201°, which agrees with the value given by Makin and Waters (*loc. cit.*), who prepared the dichloride from the diazonium salt and metallic antimony.

The only information given in the literature concerning the thermal stability of triarylstibines is that triphenylstibine undergoes some decomposition when distilled under ordinary pressure (Michaelis and Reese, *Annalen*, 1886, **233**, 48) and that tri-*p*-diphenylylstibine decomposes at the boiling point with formation of antimony, diphenyl, and other products (Worrall, *J. Amer. Chem. Soc.*, 1930, **52**, 2048). A survey has therefore been made of the behaviour of triarylstibines at high temperature in nitrogen and in oxygen. When triphenylstibine is kept at 320° in nitrogen for 3 hours it decomposes into benzene, diphenyl (10%), free antimony (17%), and a non-crystallisable antimony compound. The formation of the hydrocarbons arises through the rupture of the Sb—C linkage and the subsequent hydrogenation and dimerisation of the free phenyl radicals to form benzene and diphenyl, respectively. The disproportionation of the radical $SbPh_2$, the dimeric form of which has been prepared by Blicke (*J. Amer. Chem. Soc.*, 1931, **53**, 1025), is doubtless responsible for the liberation of free antimony and the formation of the complex antimony compound. When triphenylstibine is heated in a sealed tube at 360° for 3 hours, only 9% of the antimony appears in the free state and the amount of diphenyl formed is small. The decomposition is thus facilitated by removal of the more volatile products from the reaction system.

An indication of the thermal stability of a triarylstibine may be obtained by observing the temperature at which the melt becomes turbid when heated in nitrogen. The different influence of *o*-methoxyl and *m*-methoxyl is reflected in the low and the high decomposition temperature, respectively, of tri-*o*- and tri-*m*-anisylstibine as compared with that of triphenylstibine. Tri-*o*-phenetylstibine also has a relatively low decomposition temperature. Nuclear chlorine or bromine does not greatly affect the decomposition temperature but the rate of decomposition is materially reduced. The decomposition temperatures of the triarylstibines in oxygen do not differ appreciably from those in nitrogen, but the rate of reaction is much higher. The behaviour towards oxygen, which is so markedly different from that of the trialkylstibines, shows that the tendency of the antimony atom to increase its 3-covalency is greatly reduced by the presence of aryl groups.

The triarylstibines form dihalides, $SbAr_3X_2$, in which the halogen atoms are probably attached to the antimony atom by resonance linkages of the type known to occur in the trialkylstibine dihalides (Wells, *Z. Krist.*, 1938, **99**, 367). All the dichlorides and dibromides, except the tri-*o*-phenetyl derivatives, melt without appreciable decomposition. The majority of the alkyloxy- and halogeno-substituted triphenylstibine di-iodides not only melt with decomposition but darken below the melting point.

*Tri-*o*-chlorophenylstibine*, tri-*p*-chlorophenylstibine, and tri-*p*-bromophenylstibine are similar to triphenylstibine inasmuch as they do not form a stable addition compound with mercuric chloride at ordinary temperature. It appears that such a compound is formed as an unstable intermediate which undergoes disproportionation into the arylmercuric chloride, HgArCl, and antimony trichloride. The inhibitory influence of alkyloxy- and methyl substituents upon this reaction is much greater than that of halogen substituents.

EXPERIMENTAL.

*Tri-*o*-anisylstibine.*—A filtered solution of *o*-anisylmagnesium bromide (1 mol.) was treated with an ethereal solution of antimony trichloride (0·25 mol.). After being boiled for an hour, the mixture was poured into ice-water, and the whole filtered. The residue was extracted first with warm ether (this extract being reserved for later treatment) and then with benzene. The *stibine* was deposited on concentrating the benzene solution; lustrous plates, m. p. 189°, from benzene–chloroform (Found : C, 56·2; H, 5·0; Sb, 27·5. $C_{21}H_{21}O_3Sb$ requires C, 56·9; H, 4·8; Sb, 27·5%).

*Di-*o*-anisylstibinous Chloride.*—The ethereal extract from the above preparation was concentrated, and the deposited *chloride*, after several crystallisations from benzene–alcohol, was obtained in plates, m. p. 116—117° (Found : Cl, 9·3; Sb, 32·4. $C_{14}H_{14}O_2ClSb$ requires Cl, 9·8; Sb, 32·8%).

*Tri-*m*-anisylstibine.*—*m*-Anisylmagnesium iodide was treated with antimony trichloride as described above. After treatment with ice-water, the ethereal solution was evaporated and the residual oil was subjected to steam-distillation to remove volatile material. From an alcoholic solution of the oil, the *stibine* separated in plates; yield 50%. The pure stibine had m. p. 88·5—89·0° (Found: C, 56·8; H, 5·0; Sb, 27·2. $C_{21}H_{21}O_3Sb$ requires C, 56·9; H, 4·8; Sb, 27·5%).

*Tri-*o*-phenetylstibine.*—Prepared from *o*-phenetylmagnesium bromide and antimony trichloride, the *stibine* was obtained in 56% yield; needles, m. p. 123·5—123·8°, from alcohol (Found : C, 59·7; H, 5·6; Sb, 25·2. $C_{24}H_{27}O_3Sb$ requires C, 59·4; H, 5·6; Sb, 25·1%).

*Tri-*p*-phenoxyphenylstibine.*—*p*-Phenoxyphenylmagnesium bromide was prepared by refluxing for 24 hours *p*-bromodiphenyl ether, ether, and magnesium powder which had been activated *in situ* by strong heating with iodine. To favour completion of the reaction, benzene was added in the latter stages. The filtered solution was treated with antimony trichloride as previously described. The *stibine* was obtained as a white solid, m. p. 157°, after repeated crystallisation from alcohol (Found : C, 69·1; H, 4·5; Sb, 19·4. $C_{36}H_{27}O_3Sb$ requires C, 68·7; H, 4·3; Sb, 19·4%).

*Tri-*o*-chlorophenylstibine.*—The *stibine* was prepared from *o*-chlorophenylmagnesium bromide and antimony trichloride, but the yield was very low. After repeated crystallisation from glacial acetic acid and then from alcohol–benzene, the compound was obtained in white feathery crystals, m. p. 136—137° (Found : Cl, 23·1; Sb, 26·4. $C_{18}H_{12}Cl_3Sb$ requires Cl, 23·3; Sb, 26·7%). The stibine did not reduce cupric chloride in alcoholic solution at room temperature, but it reacted with bromine and iodine. The stibine did not form a stable mercurichloride.

Tri-p-chlorophenylstibine.—No appreciable amount of dimagnesium derivative was produced in the reaction of *p*-chlorobromobenzene with magnesium (cf. Bodroux, *Compt. rend.*, 1903, **136**, 1138). Treatment of *p*-chlorophenylmagnesium bromide with antimony trichloride gave the *stibine*; feathery crystals, m. p. 99·5—100·5°, from alcohol–benzene (Found: C, 47·3; H, 2·5; Cl, 23·5; Sb, 26·9. $C_{18}H_{12}Cl_3Sb$ requires C, 47·4; H, 2·7; Cl, 23·3; Sb, 26·7%).

Tri-p-bromophenylstibine.—Interaction of *p*-bromophenylmagnesium bromide and antimony trichloride gave a low yield of the stibine; glistening crystals, m. p. 109·8—110·4°, from alcohol–benzene (Found: Br, 40·5; Sb, 20·4. Calc. for $C_{18}H_{12}Br_3Sb$: Br, 40·6; Sb, 20·6%). The pure stibine was very soluble in benzene, ether, and chloroform, but only slightly soluble in light petroleum. It reacted with mercuric chloride in alcoholic solution to form a white precipitate which could not be recrystallised from the usual solvents.

Tri-β-naphthylstibine.—*β*-Iodonaphthalene (Schmidlin and Huber, *Ber.*, 1910, **43**, 2829) was converted into the magnesium derivative, which was treated with antimony trichloride in accordance with the usual procedure. After the solution had been boiled for an hour and then treated with ice-water, the mixture was filtered. The solid was repeatedly extracted with hot benzene, and after removal of the solvent, the residual oil was triturated with ligroin until it solidified. Repeated crystallisation of the material from acetone gave the *stibine* as a yellow solid which partly melted at 195° (Found: C, 69·3; H, 4·9; Sb, 23·3. $C_{30}H_{21}Sb$ requires C, 71·6; H, 4·2; Sb, 24·2%). The yield was very low and the stibine could not be further purified owing to its slight solubility in the usual organic solvents. It did not form an addition compound with mercuric chloride and did not reduce cupric chloride, but it reacted with light petroleum solutions of bromine and iodine.

Addition Compounds.—The addition compounds listed in the table were prepared by treating the triarylstibine with solutions of cupric chloride, bromine, iodine, or mercuric chloride. Inasmuch as the majority of the di-iodides are susceptible to hydrolysis by traces of moisture, all reagents used in their preparation were thoroughly dried before use.

Stibine dichlorides, Ar_3SbCl_2.

Ar.	Cryst. form and solvent.*	M. p.	Found, %.		Formula.	Required, %.	
			Cl.	Sb.		Cl.	Sb.
o-Anisyl	White crystals; A	237—238°	14·2	23·4	$C_{21}H_{21}O_3Cl_2Sb$	13·8	23·7
m-Anisyl	As above	81·5—82·5	14·2	23·6	$C_{21}H_{21}O_3Cl_2Sb$	13·8	23·7
o-Phenetyl	Colourless crystals; B	231—232 †	13·0	22·1	$C_{24}H_{27}O_3Cl_2Sb$	12·8	21·9
p-Phenoxyphenyl	Needles; B	106—107	10·3	16·9	$C_{36}H_{27}O_3Cl_2Sb$	10·1	17·4
p-Chlorophenyl	Needles; C	193·0—193·5	13·5 ‡	23·1	$C_{18}H_{12}Cl_5Sb$	13·5 ‡	23·1
p-Bromophenyl	Needles; B	200—201	10·6	18·3	$C_{18}H_{12}Br_3Cl_2Sb$	10·7	18·4
Stibine dibromides, Ar_3SbBr_2.							
			Br.	Sb.		Br.	Sb.
o-Anisyl	Glistening crystals; A	225—226	26·8	20·5	$C_{21}H_{21}O_3Br_2Sb$	26·5	20·2
m-Anisyl	Pale yellow needles; B	74·5—75·5	26·9	20·0	$C_{21}H_{21}O_3Br_2Sb$	26·5	20·2
o-Phenetyl	As above	237—238 †	24·9	18·8	$C_{24}H_{27}O_3Br_2Sb$	24·8	18·9
p-Phenoxyphenyl	White needles; B	151—152	20·4	15·0	$C_{36}H_{27}O_3Br_2Sb$	20·3	15·4
p-Chlorophenyl	Lustrous plates; D	189·5—190·0	26·3	20·0	$C_{18}H_{12}Cl_3Br_2Sb$	25·9	19·8
p-Bromophenyl	Needles; B	182	21·5 ‡	16·4	$C_{18}H_{12}Br_5Sb$	21·3 ‡	16·3
Stibine di-iodides, Ar_3SbI_2.							
			I.	Sb.		I.	Sb.
o-Anisyl	Yellow solid; D	141—142 †	36·7	17·3	$C_{21}H_{21}O_3I_2Sb$	36·4	17·5
m-Anisyl	Pale yellow plates; B	99·5—100·0	36·2	17·6	$C_{21}H_{21}O_3I_2Sb$	36·4	17·5
o-Phenetyl	As above	143 †	34·6	16·6	$C_{24}H_{27}O_3I_2Sb$	34·3	16·5
p-Phenoxyphenyl	As above	140 †	28·5	14·1	$C_{36}H_{27}O_3I_2Sb$	28·7	13·8
p-Chlorophenyl	Yellow plates; E	137—138 †	36·2	17·2	$C_{18}H_{12}Cl_3I_2Sb$	35·7	17·2
p-Bromophenyl	Pale yellow needles; C	155—156 †	29·9	14·6	$C_{18}H_{12}Br_3I_2Sb$	30·1	14·4
Mercurichlorides, $Ar_3Sb,HgCl_2$.							
			Cl.	Sb.		Cl.	Sb.
o-Anisyl	White solid; B	160—161	10·4	28·5§	$C_{21}H_{21}O_3Sb,HgCl_2$	9·9	28·1§
m-Anisyl	As above	180 †	10·2	16·9	$C_{21}H_{21}O_3Sb,HgCl_2$	9·9	17·0
o-Phenetyl	As above	170·9	9·7	16·1	$C_{24}H_{27}O_3Sb,HgCl_2$	9·4	16·1
p-Phenoxyphenyl	White crystals; F	175—176 †	—	13·3	$C_{36}H_{27}O_3Sb,HgCl_2$	—	13·5

* A = $CHCl_3$–light petroleum; B = alcohol–chloroform; C = light petroleum; D = carbon tetrachloride–light petroleum; E = alcohol–light petroleum; F = benzene–alcohol.

† With decomposition. ‡ Values relate to hydrolysable halogen. § Hg, not Sb.

Thermal Stability of Triarylstibines.—The temperature of the stibine was raised at a rate of 3—4°/min. by heating the material in a stream of nitrogen or oxygen in a small vessel provided with a side-tube in communication with U-tubes for the condensation of volatile products. The temperature at which turbidity first appeared in the molten stibine was taken as the decomposition temperature; those in nitrogen and oxygen, respectively, were as follows: triphenylstibine, 250°, 265°; tri-*o*-anisylstibine, 200°, 200°; tri-*m*-anisylstibine, 258°, 260°; tri-*o*-phenetylstibine, 200°, 205°; tri-*o*-chlorophenylstibine, 260°, —; tri-*p*-chlorophenylstibine, 230°, 265°; tri-*p*-bromophenylstibine, 262°, 250°; tri-*p*-phenoxyphenylstibine, 265°, 260°. Although there was generally little difference between the decomposition temperatures in nitrogen and in oxygen, the rate of reaction was invariably higher in the latter.

Triphenylstibine (1 g.), maintained at 325° for 3 hours under nitrogen in the above apparatus, gave a small amount of benzene, and diphenyl (0·1 g.). The grey residue in the pyrolysis vessel consisted of a viscous oil and a finely-divided solid. After being washed with acetone, the solid (0·17 g.) was shown to be free antimony (Found : Sb, 99·4%). The acetone solution of the oil gave a positive test for antimony, but no solid product could be isolated.

Triphenylstibine (10 g.) was maintained at 360° in a sealed tube for 3 hours. On cooling, the tube was found to be free from excess pressure, and the pyrolysis product consisted of free antimony (0·3 g. Found : Sb, 99·3%) and a pale green viscous liquid. The latter on fractionation gave triphenylstibine (8·4 g.) and a residue which could not be crystallised. In a repetition of the experiment, the pyrolysis product was subjected to steam-distillation, but the amount of diphenyl isolated was small.

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