CCLIX.—Researches on Antimony. Part I. Tri-mxylylstibine and its Derivatives.

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ALTHOUGH arsenic and antimony show so many points of resemblance, our knowledge of the organo-metallic compounds of the latter is much the less extensive. The aim of the present research is to investigate comprehensively antimonials of the types R_3Sb , R_2SbX , R_2SbX_3 , $RSbX_2$, and $RSbX_4$, the derived acids, the sulphonation, nitration, reduction, and halogenation products, and the influence of antimony on the orientation of the various substituents. The work so far carried out is indicated by the following scheme:



The initial material, 4-bromo-*m*-xylene, was prepared by the bromination of commercial xylene at 0° , iron powder being used as a catalyst; from the mixture, 3-bromo-*o*-xylene, 4-bromo-*m*-xylene, and 2-bromo-*p*-xylene were separated by fractional distillation. This method gives better yields than that in which bromination is carried out in carbon disulphide solution; moreover, the objectionable by-products which arise from partial bromination of the solvent are avoided (Stilp, *Diss.*, Rostock, 1910).

Tri-*p*-xylylstibine, recently described by the author (this vol., p. 1170), and the corresponding meta-compound (I) have been obtained in much better yields by the Fittig than by the Grignard reaction, which was previously employed. The latter compound, like most stibines, gives rise to a *dichloride, dibromide,* and *mercurichloride*.

Tri-m-xylylstibine dissolved readily in fuming nitric acid, yielding apparently a mixture of tri-5-nitrotri-m-xylylstibine oxide (IV), hydroxy-nitrate, and dinitrate (V); the last, which formed the largest proportion of the product, was isolated in the pure state by fractional crystallisation from alcohol. When it was heated in a sealed tube for six hours with phosphorus pentabromide and chloroform, 4-bromo-6-nitro-m-xylene was obtained, the nitrogroup thus being proved to be in the meta-position to the antimony and in the para-position to a methyl group (compare Morgan and Micklethwait, T., 1911, **99**, 2286). Since the same three products were obtained when tri-m-xylylstibine was boiled with fuming nitric acid for thirty minutes, the hydrogen atom in the position ortho to both methyl groups is efficiently protected.

Reduction of the dinitrate with hydrogen sulphide in ammoniacal probably takes place in alcoholic solution two stages: \equiv Sb(NO₂), $\rightarrow \equiv$ SbS $\rightarrow \equiv$ Sb. In addition to these compounds, the final liquors contained amino-derivatives which were diazotisable. pointing to partial reduction of the nitro-groups. The chief product was tri-5-nitrotri-m-xylylstibine(V), the intermediate formation of the sulphide being assumed from the fact that when hydrogen sulphide is passed into an ammoniacal alcoholic solution of triphenylstibine dichloride or dibromide, triphenylstibine sulphide first results and then the free stibine (Kaufmann, D.R.-P. 223694; 240316).

The reduction of tri-5-nitrotri-m-xylylstibine dinitrate by zine dust in ammoniacal alcoholic solution containing ammonium chloride led to the production of tri-5-aminotri-m-xylylstibine (III). This was converted into its tribenzoyl derivative by benzoyl chloride, whereas Gunther (Diss., Rostock, 1904; Annalen, 1902, 381, 184) found that triaminotriphenylstibine lost its antimony on treatment with this reagent.

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Michaelis (Annalen, 1902, **321**, 185) failed to isolate any derivatives of triaminotriphenylarsine by means of the diazo-reaction. The present author encountered some difficulty in working with tri-5-aminotri-m-xylylstibine, but nevertheless succeeded in isolating tri-5-iodotri-m-xylylstibine (VIII), although the diazo-reaction in this case tended to give rise to viscous products. The base forms a sparingly soluble diazonium chloride which couples with alkaline β -naphthol, with resorcinol, and with H-acid to form azo-derivatives.

Tri-5-nitrotri-m-xylylstibine dinitrate is hydrolysed to the oxide (IV) by a large excess of phosphorous acid, whereas trinitrotritolylarsine oxide is reduced to the free arsine (Michaelis, *loc. cit.*, p. 212). The same oxide results when the dinitrate is treated with sodium hypophosphite. On dissolution in glacial acetic acid, it is converted into the *diacetate*, although in the case of the tritolylstibines only hydroxyacetates have been isolated (Michaelis and Genzken, Annalen, 1887, 242, 176).

Bromination of the oxide results in the formation of a tribromoderivative, a compound of considerable interest on account of the lability of the bromine atoms. It has been shown above that only one nitro-group can be introduced into each xylyl residue, the hydrogen atom in the second meta-position being unreactive, and it may be inferred that bromination cannot take place in this position. By treatment of the tribromo-derivative with zinc dust in alcoholic ammonia, the bromine atoms are eliminated and the nitro-groups reduced, tri-5-aminotri-m-xylylstibine, the orientation of which has already been determined, being produced. Further, it is known that in compounds containing a halogen atom in the ortho- or para-position to a nitro-group, one of the substituents is labile, reaction with hydrogen sulphide or sodium thiosulphate vielding a sulphide. In the present case, not only were the bromine atoms removed by boiling thiosulphate solution, but also the oxide was reduced to the known tri-5-nitrotri-m-xylylstibine. It is therefore to be inferred that the bromine substituents occupy position 6, ortho- both to the antimony and to the nitro-groups, and consequently the tribromo-derivative is tri-6-bromotri-5-nitrotri-m-xululstibine oxide (VI).

When the free nitrostibine is brominated, it may be supposed that the tribromo-derivative produced is *tri-6-bromotri-5-nitrotri-m-xylylstibine dibromide* (VII).

The condensation product of the base (III) and picryl chloride in alcoholic solution in the presence of sodium acetate is the orangecoloured tripicryltri-5-aminotri-m-xylylstibine (IX). This product is readily brominated, yielding tri-6-bromotripicryltri-5-aminotri-m-xylylstibine dibromide, a lemon-yellow powder (X). Although bromination products of arylstibines are not described in the literature, it is highly probable from these experiments that bromine can be directly introduced into such substances. This point is being more fully investigated.

EXPERIMENTAL.

Preparation of 4-Bromo-m-xylene.—To commercial xylene (1156 grams), cooled in a freezing mixture, about 1 gram of iron powder was added, and 800 grams of bromine were slowly run in during five hours. The mixture, after being kept for two days at room temperature, was treated with 1,500 c.c. of water, and the oil separated off and steam-distilled. The oil from the distillate was dried, and fractionated several times, about 200 grams of pure 4-bromo-m-xylene, b. p. 203.5°, being obtained. The quantity of the other isomerides produced varied with the sample of xylene used.

Tri-m-xylylstibine (I).—(a) By the Grignard reaction. To the solution prepared from 48 grams of bromoxylene and 7 grams of magnesium in 75 c.c. of ether, 18 grams of antimony trichloride in 25 c.c. of the same solvent were added and the mixture was boiled for six hours. After decomposition with water, the compound was extracted with benzene and worked up as below. Yield 7.2 grams (19 per cent.).

(b) By the Fittig reaction. Bromoxylene (56 grams) and 23 grams of antimony trichloride were dissolved in 150 c.c. of dry benzene, and 50 grams of metallic sodium (thrice the required amount) added in thin slices. After completion of the reaction, which usually had to be started by warming, the solution, having been kept over-night, was filtered, and the residue extracted three times with boiling benzene, these liquors being added to the main filtrate. The benzene was evaporated and the oily product poured into absolute alcohol, when long needles of the stibine separated in a few minutes. Yield 25 grams of crude product (57 per cent.) (Found: Sb = 27.56. C₂₄H₂₇Sb requires Sb = 27.61 per cent.).

Tri-m-xylylstibine crystallises from alcohol in masses of felted needles. These melt at 148° to a clear liquid which becomes cloudy at about 255° and, when cooled, solidifies to a transparent mass. The stibine is soluble in cold chloroform, acetone, light petroleum, or pyridine, moderately soluble in alcohol, and is more soluble than the para-compound in glacial acetic acid.

Tri-m-xylylstibine Dichloride.—A chloroform solution of the stibine was saturated in the cold with dry chlorine and allowed to evaporate spontaneously. Small, white, granular crystals separated, m. p. 189° (Found : Cl = 13.81. $C_{24}H_{27}Cl_2Sb$ requires Cl = 14.01 per cent.).

Tri-m-xylylstibine Dibromide.—To 2 grams of the stibine in 5 c.c. of chloroform, bromine was added until the solution was just coloured. On evaporation, a syrup was obtained which solidified on treatment with alcohol. The product was best crystallised from chloroform-alcohol, a crystalline powder being deposited, m. p. 195° (Found : Br = 27.16. $C_{24}H_{27}Br_2Sb$ requires Br = 26.85 per cent.). The compound is moderately soluble in light petroleum.

Tri-m-xylylstibine Mercurichloride.—The stibine (1.18 grams) in 50 c.c. of absolute alcohol was added in the cold to 0.67 gram of mercuric chloride in 100 c.c. of the same solvent. The product obtained by slow evaporation of the solution was recrystallised from ether, fine needles being isolated, m. p. 158° (Found : Cl = 9.80. $C_{24}H_{27}Cl_2HgSb$ requires Cl = 9.70 per cent.).

Tri-5-nitrotri-m-xylylstibine Dinitrate (II).-Twenty-one grams of tri-m-xylylstibine were added slowly to 100 c.c. of nitric acid (d 1.16), complete solution taking place, and the mixture, after being warmed for twenty minutes on the water-bath, was poured into 3 litres of water. The white, flocculent precipitate that separated was collected after fifteen minutes and dried (38.2 grams). This crude product (Found: N = 8.71 per cent.) appeared to consist of the hydroxynitrate and the dinitrate. After six crystallisations from alcohol, the dinitrate, a white, crystalline powder, was obtained; it sintered at 150° and melted at 175° with frothing Sb = 17.33.(Found: N = 10.06; $C_{24}H_{24}O_{12}N_5Sb$ requires N = 10.09; Sb = 17.31 per cent.). The dinitrate is soluble in warm chloroform or acetic acid, slightly soluble in alcohol, and soluble in light petroleum.

Orientation Experiments.—One gram of the above dinitrate, 10 c.c. of chloroform, and 6 grams of phosphorus pentabromide were heated in a sealed tube at 130° for five hours. The chloroform was then removed by distillation in steam, very little other organic matter distilling over. The residue was crystallised several times from alcohol, when 4-bromo-6-nitro-m-xylene, m. p. 57°, was obtained, the yield being about 65 per cent. of the calculated amount (Found : Br = 34.93. Calc., Br = 34.78 per cent.).

Tri-5-nitrotri-m-xylylstibine (V).--(a) Two grams of the dinitrate were dissolved in 200 c.c. of absolute alcohol, 20 c.c. of concentrated aqueous ammonia were added, and hydrogen sulphide was passed into the boiling solution for six hours. The precipitate formed on cooling was collected, and recrystallised from alcohol, small needles of the stibine being obtained, melting at 192–193° to a clear liquid.

(b) Tri-6-bromotri-5-nitrotri-m-xylylstibine oxide (1.8 grams) in 40 c.c. of hot absolute alcohol was added to the boiling solution of 1.4 grams of sodium thiosulphate in 25 c.c. of water, and the boiling continued for thirty minutes. A white solid containing neither sulphur nor halogen separated out, which melted at 192° after crystallisation from chloroform-petroleum solution (Found : N = 7.47, 7.34, 7.43; Sb = 21.59. $C_{24}H_{24}O_6N_3Sb$ requires N = 7.37; Sb = 21.57 per cent.).

Tri-5-aminotri-m-xylylstibine (III).—Five grams of the mixture of nitration products obtained by the action of fuming nitric acid on tri-m-xylylstibine were added to a boiling solution of 400 c.c. of absolute alcohol containing 3.5 grams of ammonium chloride, 20 c.c. of concentrated aqueous ammonia, and 22 grams of zinc dust. The boiling was continued for eight hours, a further five grams of zinc dust being added at the end of each hour. The solution was filtered while hot into 3 litres of ice-cold water, a pink precipitate separating out. This solid, after filtration, was warmed with 200 c.c. of 10 per cent. hydrochloric acid, any insoluble matter filtered off, and the filtrate treated with concentrated aqueous ammonia, when 3.5 grams of crude amine were obtained (yield 97 per cent.). This product was purified by several crystallisations from a mixture of chloroform and light petroleum, a brownish-pink powder resulting, which blackened at about 112° and melted rather indefinitely at 123-124° (Found : N = 8.76: Sb = 25.05. $C_{24}H_{30}N_3Sb$ requires N = 8.75; Sb = 25.02 per cent.).

Tri-5-benzoylaminotri-m-xylylstibine.—A mixture of the amine (1·2 grams), dissolved in 16 c.c. of pyridine, and 1·6 grams of benzoyl chloride was warmed on the water-bath and poured into water. The viscous product was freed from benzoic acid by repeated boiling with water, but it could not be crystallised. It contained antimony and melted at 99° (Found : N = 5.24. $C_{45}H_{42}O_3N_3Sb$ requires N = 5.19 per cent.).

Tri-5-iodotri-m-xylylstibine (VIII).—One gram of the amine, dissolved in 7 c.c. of concentrated hydrochloric acid and 200 c.c. of water, was diazotised with 0.66 gram of sodium nitrite. The diazonium chloride separated as a yellow precipitate, to which 1.5 grams of potassium iodide in 20 c.c. of water were added, the yellow colour changing to red, the precipitate resembling ferric hydroxide. After being warmed on the water-bath, and kept for three hours, the solid was filtered off (1.5 grams) and recrystallised five times from a mixture of chloroform and petroleum, a brownishred, crystalline powder being obtained, which melted at 153° to a clear red liquid (Found: I = 46.80; Sb = 14.63. $C_{24}H_{24}I_3Sb$ requires I = 46.83; Sb = 14.78 per cent.).

Tri-5-nitrotri-m-xylylstibine Oxide (IV).—Five grams of the corresponding dinitrate were boiled for five hours with 300 c.c. of

absolute alcohol containing 25 grams of phosphorous acid. The resulting solution was poured into 2 litres of water, a flocculent, cream-coloured precipitate separating (3.8 grams). After this had been dried, and precipitated from chloroform solution by light petroleum, a white, crystalline powder was obtained which sintered slightly at 210° and melted at 218° (Found : N = 6.91, 7.08; Sb = 20.26. C₂₄H₂₄O₇N₃Sb requires N = 7.17; Sb = 20.50 per cent.). The oxide is soluble in alcohol, and forms an orange-coloured solution in chloroform.

Tri-5-nitrotri-m-xylylstibine Diacetate.—The above oxide was dissolved in glacial acetic acid, and after partial evaporation, ether was added, a white precipitate of the diacetate being deposited which softened at 160° and melted at about 198° (Found : N = 5.92; Sb = 17.29. C₂₈H₃₀O₁₀N₃Sb requires N = 6.11; Sb = 17.46 per cent.).

Tri-6-bromotri-5-nitrotri-m-xylylstibine Oxide (VI).—Trinitrotrim-xylylstibine oxide (1.0 gram) was dissolved in chloroform and a solution of bromine in light petroleum added. The precipitate was purified by treatment with these two solvents, the product being a white, crystalline substance, melting at 162° to a yellow liquid, which decomposed with gas evolution at 168° (Found : N = 5.18; Br = 28.79. C₂₄H₂₁O₇N₃Br₃Sb requires N = 5.07; Br = 28.92 per cent.).

To the oxide (1.7 grams) in 150 c.c. of alcohol, 1.5 grams of ammonium chloride, 5 c.c. of concentrated aqueous ammonia, and 11 grams of zinc dust were added and the mixture was boiled for seven hours. The product was worked up as in the case of triaminotri-*m*-xylylstibine, and 0.85 gram of this substance was obtained, m. p. 123-124°.

Tri-6-bromotri-5-nitrotri-m-xylylstibine Dibromide (VII).— A chloroform solution of the corresponding stibine was treated with bromine until the colour of the latter persisted. The dibromide was precipitated by light petroleum and recrystallised from a mixture of the above two solvents, a white, crystalline powder being obtained (Found : Br = 41.49. $C_{24}H_{21}O_6N_3Br_5Sb$ requires Br = 41.32 per cent.).

Tripicryltri-5-aminotri-m-xylylstibine (IX).—Two grams of the amine, dissolved in the smallest possible quantity of 10 per cent. hydrochloric acid, were added to 75 c.c. of alcohol containing 3 grams of picryl chloride and 8 grams of sodium acetate. The mixture was warmed at 30° for fifteen minutes, an orange precipitate separating. This crude condensation product (3.9 grams) was boiled with 75 c.c. of water to remove sodium acetate, then dissolved in dry chloroform to remove sodium picrate, and the stibine was precipitated from the filtered solution by the addition of light petroleum. The compound thus isolated was a bronze, crystalline powder which sintered at 178° and then gradually blackened, but did not melt at 290° (Found: N = 14.60; Sb = 10.98. $C_{42}H_{33}O_{18}N_{12}Sb$ requires N = 15.10; Sb = 10.79 per cent.). The compound is soluble in alcoholic potash, giving a carmine solution, from which the potassium salt separates in scarlet, octahedral crystals on slow evaporation.

Tripicryltri-6-bromotri-5-aminotri-m-xylylstibine Dibromide (X). —The above stibine (0.5 gram) was dissolved in 3 c.c. of chloroform, and bromine in light petroleum added until the colour changed from orange to red. Addition of light petroleum precipitated a lemon-yellow, crystalline powder (0.5 gram) (Found : N = 11.19. $C_{42}H_{30}O_{18}N_{12}Br_5Sb$ requires N = 11.13 per cent.). The compound, which contained both bromine and antimony, blackened at 183° and melted at 188°. It behaved towards alcoholic potash in the same way as the preceding compound.

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