XCVIII.—*Researches on Antimony. Part II. Derivatives of Tri*-p-*tolylstibine.*

By ARCHIBALD EDWIN GODDARD and VICTOR EMMANUEL YARSLEY.

FOR the degradation of triarylstibines to diarylhalogenostibines the authors have devised an easier method than those hitherto available, which are either difficult in practice, or applicable only to special compounds (see Hasenbäumer, *Ber.*, 1898, **31**, 2914; Goddard, J., 1922, **123**, 484). The method, which is similar to that by which Morgan and Yarsley (*Proc. Roy. Soc.*, 1926, **110**, 534; see also Morgan and Davies, *Nature*, 1925, **116**, 499) obtained dimethylcyanostibine from trimethylstibine cyanobromide, consists in heating, *e.g.*, tritolylstibine dichloride, dibromide, or di-iodide under diminished pressure; a halogenotoluene distils off, leaving the ditolylhalogenostibine. This work is being continued with the object of degrading diarylchlorostibines to aryldichlorostibines.

Schmidt (*Annalen*, 1922, **429**, 140), by heating triphenylstibine in saturated methyl-alcoholic hydrogen chloride in an atmosphere of carbon dioxide, obtained a small quantity of diphenylstibinic acid and a good yield of diphenylhydroxystibine. The application of this method to tri-*p*-tolylstibine gave a small quantity of the acid, and a little plastic residue which could not be identified as the hydroxide.

A second method used by Schmidt was to treat a hot acetone solution of the triarylstibine with 5*N*-sodium hydroxide and 3% hydrogen peroxide solution, and here the authors agree with him in obtaining a diarylstibinic acid and a diarylstibine trichloride, namely, *ditolylstibinic acid* and *ditolylstibine trichloride.*

Schmidt's methods of degrading diarylhydroxystibines to monoarylstibinous oxides also gave poor results, and the authors used the diazo-reaction in the preparation of *p*-tolylstibinic acid, which was identical with the acid obtained by Hasenbäumer from *p*-tolylstibine tetrachloride by hydrolysis.

Tri-*p*-tolylstibine, on treatment with cold fuming nitric acid, gave *tri*-m-*nitrotri*-p-*tolylstibine dinitrate.* Since tri-*m*-xylylstibine on similar treatment gives tri-5-nitrotri-*m*-xylylstibine dinitrate (Goddard, J., 1923, **123**, 2315), these results together with that of Morgan and Micklethwait (J., 1911, **99**, 2286) seem to show that the nitro-group always enters the nucleus in the meta-position to the antimony.

Hydrolysis of the dinitrate by a large excess of phosphorous acid gave the corresponding *oxide*, whereas Michaelis (*Annalen*, 1902, **321**, 212) showed that trinitrotritolylarsine oxide in presence of phosphorous acid produces the free arsine.

Tri-m-*aminotri*-p-*tolylstibine* was prepared by reducing the nitro-compound with zinc dust and ammonia in alcoholic solution, and converted into *tri*-m-*iodotri*-p-*tolylstibine* by the Sandmeyer reaction.

EXPERIMENTAL.

Di-p-*tolylhalogenostibines.*—Tri-*p*-tolylstibine dichloride (2 g.), when heated under 5—7 mm. pressure, gave *p*-chlorotoluene (b. p. 160°) at 60—65° and *di*-p-*tolylchlorostibine* at 160—200°; after being washed with light petroleum and alcohol, the latter was a white solid (Found: Cl, 10·4. $C_{14}H_{14}ClSb$ requires Cl, 10·45%).

In a similar way, the dibromide (2 g.) gave *p*-bromotoluene (m. p. 23°) at 70—75° and *di*-p-*tolylbromostibine* (obtained, after repeated washing with alcohol, as a pale cream compound, melting above 290° and only slightly soluble in warm organic solvents. Found: Sb, 31·8. $C_{14}H_{14}BrSb$ requires Sb, 31·75%) at 170—210°; and the di-iodide (2 g.) gave *p*-iodotoluene (m. p. 35°) at 80° and *di*-p-*tolyliodostibine* at 180—200°, the latter, after being washed with alcohol and with ether, being a white solid, m. p. 233°, almost insoluble in cold, but soluble in warm, organic solvents (Found: Sb, 28·4. $C_{14}H_{14}ISb$ requires Sb, 28·3%). The yield of di-*p*-tolylhalogenostibine was in each case almost quantitative.

Di-p-*tolylstibinic Acid*, $(C_7H_7)_2SbO{\cdot}OH$.—(1) Tri-*p*-tolylstibine (9 g., suspended in 150 c.c. of methyl alcohol), when mixed with 30 c.c. of methyl alcohol (saturated with hydrogen chloride) and boiled on the water-bath in a current of carbon dioxide, dissolved after 15 minutes. The yellow solution was boiled for 1¼ hours, cooled, and made distinctly alkaline with dilute aqueous sodium hydroxide. The white precipitate produced was removed as a suspension in ether and added to the solid obtained from the aqueous layer by precipitation with acetic acid. Recrystallisation from alcohol gave a white, amorphous product, sintering at 230° and melting at 260°. The yield was very small (Found: Sb, 36·2. $C_{14}H_{15}O_2Sb$ requires Sb, 36·2%).

(2) A solution of 6 g. of tri-*p*-tolylstibine in acetone was gradually added to a boiling mixture of 113 c.c. of water, 37 c.c. of 5*N*-sodium hydroxide, and 22·5 c.c. of 6% hydrogen peroxide. The solution, filtered from a slight precipitate, was treated with dilute sulphuric acid, and the voluminous white precipitate obtained was partly dried, washed with warm alcohol, and recrystallised from benzene (Found: Sb, 35·95%). The acid is slightly soluble in hot or cold alcohol or cold benzene and readily soluble in hot benzene.

Di-p-*tolylstibine Trichloride*.—The precipitate obtained on addition of sulphuric acid as in method (2) was reprecipitated, first from 5*N*-hydrochloric acid as the pyridine double salt and then from dilute sodium hydroxide solution by dilute acetic acid. Thereafter it was dissolved in fairly concentrated, boiling hydrochloric acid, and the solution evaporated to small bulk; the colourless needles of *di*-p-*tolylstibine trichloride* obtained crystallised from benzene in colourless plates, sintering at 130° and melting at 141—142° (Found: Sb, 29·7. $C_{14}H_{14}Cl_3Sb$ requires Sb, 29·7%).

p-*Tolylstibinic Acid*, $C_7H_7{\cdot}SbO_3H_2$.—Two solutions, one of diazotised *p*-toluidine (26 g. of the base, 37 g. of concentrated sulphuric acid, 250 c.c. of water, and 18 g. of sodium nitrite) and the other of 56·6 g. of antimony trichloride in 15 g. of hydrochloric acid (*d* 1·16) and 41 c.c. of water to which 150 g. of sodium hydroxide in 750 c.c. of water had been added, were mixed at 0° and treated with copper bronze. The liquid was filtered after 2 days, nearly neutralised with dilute sulphuric acid, again filtered if necessary, and acidified with dilute hydrochloric acid. The mixture (50 g.) of *p*-tolylstibinic acid and antimony trioxide obtained was dissolved in 27 g. of hydrochloric acid (*d* 1·16) and 98 c.c. of water, and the boiling solution saturated with solid ammonium chloride. The mixture of *p*-tolylstibinic oxychloride and ammonium chloride that crystallised on cooling was filtered off and dissolved in sodium carbonate solution, and the stibinic acid was precipitated by acidification with dilute hydrochloric acid and crystallised from spirit and from ether. Yield, 8 g. (Found : Sb, 46·3. Calc. for $C_7H_9O_3Sb$: Sb, 46·3%).

Tri-m-*nitrotri*-p-*tolylstibine Dinitrate*, $(C_7H_6{\cdot}NO_2)_3Sb(NO_3)_2$.—Tri-*p*-tolylstibine (5 g.) was slowly added to the calculated quantity of well-cooled fuming nitric acid; and the solution poured into water (1 l.). The *dinitrate*, precipitated as a light cream-coloured powder, after several recrystallisations from alcohol, melted sharply at 182° with frothing. It was soluble in the usual organic media (Found : Sb, 18·9; N, 10·8. $C_{21}H_{18}O_{12}N_5Sb$ requires Sb, 18·6; N, 10·7%).

The position of the nitro-group was determined by heating the compound with bromine and phosphorus pentabromide in a sealed tube at 130° for 4 hours, 4-bromo-2-nitrotoluene, m. p. 45°, being obtained.

Tri-m-*nitrotri*-p-*tolylstibine Oxide*.—The dinitrate (2 g.) was heated for 8 hours with 10 g. of phosphorous acid in 100 c.c. of absolute alcohol, and the solution poured into water (1 l.). The *oxide*, which separated as a cream-coloured powder, was washed with hot water, dried, and crystallised from alcohol, being obtained as a white powder, m. p. 225° after softening at 220°; on further heating, it blackened and became pyrophoric (Found : Sb, 22·0; N, 7·6. $C_{21}H_{18}O_7N_3Sb$ requires Sb, 22·2; N, 7·7%).

Tri-m-*aminotri*-p-*tolylstibine*, $(C_7H_6{\cdot}NH_2)_3Sb$.—The dinitrate (7 g.) was boiled for 8 hours with a solution of 250 c.c. of 90% alcohol containing 5 g. of ammonium chloride, 15 c.c. of aqueous ammonia, and 15 g. of zinc dust, a further 3 g. of zinc dust being added each hour. The solution was filtered at room temperature into water (2 l.). The brown solid obtained was collected and dissolved in 250 c.c. of warm 15% hydrochloric acid, and the filtered solution was treated with concentrated aqueous ammonia until no further precipitate appeared. The crude *amine* was crystallised from chloroform–light petroleum, yielding a pinkish-grey powder, m. p. 92° (Found : Sb, 27·7. $C_{21}H_{24}N_3Sb$ requires Sb, 27·7%).

Tri-m-*iodotri*-p-*tolylstibine.*—The amine (3 g.), dissolved in 20 c.c. of concentrated hydrochloric acid and 200 c.c. of water, was diazotised with 2 g. of sodium nitrite, 5 g. of potassium iodide in 50 c.c. of water were added, and the mixture was gently warmed on the water-bath for 3 hours. The precipitate obtained, when crystallised from chloroform–light petroleum, gave a reddish-brown powder, which sintered at 136° and melted at 146° to a dark red liquid (Found : I, 24·4. $C_{21}H_{18}I_3Sb$ requires I, 24·4%).

EIDGENÖSSISCHE TECHNISCHE HOCHSCHULE,
ZÜRICH, SWITZERLAND.

[*Received, December 23rd,* 1927.]