[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF MICHIGAN]

Distibyls. II. Tetra-*p*-bromotetraphenyl- and Tetra-*p*-tolyldistibyl. Di-α-naphthyliodostibine[1]

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It has been shown that tetraphenyldistibyl[3] behaves similarly to tetraaryldiarsyls in that it reacts almost instantly with an amount of oxygen equivalent to that required for the formation of a peroxide. An analogous behavior characterizes the new distibyls which we have prepared—tetra-*p*-bromotetraphenyl- and tetra-*p*-tolyldistibyl.

No evidence could be obtained by molecular weight determinations in favor of the assumption that tetraphenyl- or tetra-*p*-tolyldistibyl dissociates into diarylstibyl radicals.[4]

In the case of di-α-naphthyliodostibine only a few grams of the pure iodide were isolated by a laborious process from five kilograms of α-naphthylamine, hence the corresponding distibyl was not prepared.

The diaryliodostibines, which yielded the distibyls when treated with sodium hypophosphite, were synthesized by means of the following series of reactions: the required aryl amine was diazotized and allowed to react with antimony trichloride, the arylstibinic acid produced was reduced to the aryldichlorostibine and the latter hydrolyzed to the corresponding oxide. The oxide, when heated, was converted into the tetraarylstibyl oxide and antimony trioxide.[5] Treatment with acetic acid converted the tetraarylstibyl oxide into the diarylstibyl acetate; this compound yielded the diaryliodostibine when mixed with hydriodic acid.

Experimental Part

***p*-Bromophenyldichlorostibine.**—*p*-Bromophenylstibinic acid[6] was obtained from *p*-bromoaniline according to the method used by Dunning and Reid[7] for the preparation of other arylstibinic acids. Two hundred grams of the air-dried acid was dissolved in 500 cc. of cold, concd. hydrochloric acid, the solution stirred and 550 cc. of water added. The flocculent material was removed by filtration and 25 g. of charcoal was added to the red filtrate, the mixture shaken frequently and filtered after twelve hours. The filtrate was cooled with ice and saturated with sulfur dioxide. The *p*-bromophenyldichlorostibine (40–60 g.) which precipitated was air dried and recrystallized from heptane; m. p. 90–92°. The dichloro compound is very soluble in benzene, less soluble in acetic acid.

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(1) This paper represents the third part of a dissertation to be submitted to the Graduate School by Mr. Oakdale in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

(2) Parke, Davis and Company Fellow.

(3) Blicke and Oakdale, THIS JOURNAL, **53**, 1025 (1931).

(4) Failure to obtain data indicative of dissociation by molecular weight determinations does not prove that distibyls do not dissociate in solution; the degree of dissociation may be of such a low magnitude that it cannot be detected by the ordinary molecular weight procedures.

(5) This series of reactions was developed for the preparation of organic antimony compounds by Schmidt, *Ann.*, **421**, 234 (1920).

(6) Fargher and Gray, *J. Pharmacol.*, **18**, 354 (1921).

(7) All stibinic acids were prepared according to the general method of Dunning and Reid, THIS JOURNAL, **49**, 2871 (1927).

Anal. Calcd. for $C_6H_4SbCl_2Br$: Sb, 34.93; Cl, 20.34; Br, 22.92. Found: Sb, 34.77; Cl, 20.22; Br, 23.10.

***p*-Bromophenyldiiodostibine.**—In order to obtain *p*-bromophenylstibine oxide, 35 g. of the dichloride was dissolved in 100 cc. of acetone and added slowly to a mixture prepared from 1000 cc. of water, 100 cc. of ammonia water and ice. The oxide which precipitated was filtered and air dried. To a solution of 12.5 g. of the oxide in 30 cc. of acetic acid, 14 cc. of hydriodic acid (sp. gr. 1.65) was added; *p*-bromophenyldiiodostibine precipitated as a yellow, crystalline solid. The material was washed thoroughly with water and dried in a desiccator; yield 22 g. The iodide was recrystallized from absolute alcohol which contained a small amount of hydriodic acid; m. p. 124–125°.

Anal. Calcd. for $C_6H_4SbBrI_2$: Br, 15.03; I, 47.76. Found: Br, 15.25; I, 47.69.

Di-*p*-bromodiphenyliodostibine.—Di-*p*-bromodiphenylstibyl acetate was obtained in the following manner: 20 g. of *p*-bromophenylstibine oxide was placed in an Erlenmeyer flask and heated in a bath (145°) in a stream of nitrogen for one hour. The pasty material was extracted with hot alcohol, the alcoholic solution filtered and the solvent removed. The oily tetra-*p*-bromotetraphenylstibyl oxide was treated with a small amount of acetic acid, whereupon it became crystalline through conversion of the stibyl oxide into the corresponding acetate; the yield of crude product was 17 g. In order to recrystallize the acetate, 10 g. of the material was dissolved in a mixture of 5 cc. of acetic acid, 10 cc. of benzene and 40 cc. of heptane. The acetate melts at 134–135°.

To 4.9 g. of the acetate, dissolved in 20 cc. of hot acetic acid, there was added 2 cc. of hydriodic acid (sp. gr. 1.65). The mixture was cooled with ice and the crystalline di-*p*-bromodiphenyliodostibine removed by filtration. The iodide was thoroughly dried and then extracted in a Soxhlet apparatus with 150 cc. of petroleum ether (30–60°). The petroleum ether solution was decanted from the oily impurity which adhered to the sides of the extraction flask. The iodide, which separated from the cold solution, was recrystallized from heptane; m. p. 73–74°. The material is quite soluble in alcohol and benzene.

Anal. Calcd. for $C_{12}H_8SbBr_2I$: Sb, 21.72; Br, 28.51; I, 22.64. Found: Sb, 21.60; Br, 28.76; I, 22.64.

Tetra-*p*-bromotetraphenyldistibyl.—A solution of 4 g. of di-*p*-bromodiphenyliodostibine in 50 cc. of absolute alcohol and 2.5 g. of sodium hypophosphite, dissolved in 4 cc. of water and 4 cc. of alcohol, was poured into a free-radical bulb and after twelve hours the liquid decanted from the tan colored, crystalline precipitate. The product was washed twice with a mixture of 25 cc. of alcohol and 2 cc. of water, twice with absolute alcohol, twice with 20 cc. of hot xylene and finally with petroleum ether (30–60°). The product was dried under diminished pressure in a bath at 60° and isolated in a carbon dioxide atmosphere. The light greenish-yellow distibyl melted with decomposition at 211–213° in a sealed tube filled with nitrogen.

Anal. Calcd. for $C_{24}H_{16}Sb_2Br_4$: Sb, 28.08; Br, 36.85. Found: Sb, 27.95; Br, 36.83.

Dissolved in bromobenzene 1.272 g. of the distibyl absorbed 34 cc. (N. T. P.) of oxygen in one minute; calcd. absorption, 33 cc.

Di-*p*-tolyliodostibine.—To 400 g. of crude *p*-tolylstibinic acid, dissolved in 800 cc. of warm concd. hydrochloric acid, 800 cc. of water was added and the cold mixture filtered. The filtrate was diluted further with water until it became turbid. Sulfur dioxide was passed into the solution for a few minutes and after the removal of the gum the filtrate was cooled with ice and saturated with sulfur dioxide; yield 150 g. of practically colorless, crystalline *p*-tolyldichlorostibine; m. p. 89–92°.[8]

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(8) Hasenbäumer, *Ber.*, **31**, 2914 (1898).

The dichlorostibine was dissolved in acetone and treated with ammonia water, whereupon *p*-tolylstibine oxide was obtained. The latter was washed with acetone and dried. *p*-Tolylstibine oxide was heated in a bath (100°) for two hours in order to convert it into tetra-*p*-tolylstibyl oxide. The crude oxide was extracted with hot alcohol. After recrystallization from alcohol the oxide melted at 101°.

Anal. Calcd. for $C_{28}H_{28}OSb_2$: Sb, 38.57. Found: Sb, 39.04.

In order to obtain di-*p*-tolylstibyl acetate, tetra-*p*-tolylstibyl oxide was dissolved in hot acetic acid. The acetate separated in crystalline form when the solution cooled; after recrystallization from heptane the acetate melted at 122–123°.

Anal. Calcd. for $C_{16}H_{17}O_2Sb$: Sb, 33.55. Found: Sb, 33.07.

To 10 g. of di-*p*-tolylstibyl acetate, dissolved in 50 cc. of acetic acid, 20 cc. of constant boiling hydriodic acid, diluted with 20 cc. of water, was added. The crude di-*p*-tolyliodostibine was washed free from hydriodic acid and extracted with petroleum ether; m. p. after recrystallization from absolute alcohol, 76–78°.[9]

Anal. Calcd. for $C_{14}H_{14}SbI$: Sb, 28.26; I, 29.46. Found: Sb, 28.23; I, 29.30.

Tetra-*p*-tolyldistibyl.—A solution, prepared from 3.5 g. of di-*p*-tolyliodostibine and 60 cc. of absolute alcohol, was poured into a free radical apparatus. There was added 2.5 g. of sodium hypophosphite, dissolved in 5 cc. of water and 20 cc. of alcohol. After twelve hours the supernatant liquid was decanted from the pale greenish-yellow crystals, the material washed several times with 90% alcohol and then with absolute alcohol. The product was isolated in a carbon dioxide atmosphere; m. p. 155–157° in a sealed tube filled with nitrogen.

Anal. Calcd. for $C_{28}H_{28}Sb_2$: Sb, 40.07. Found: Sb, 39.50.

Dissolved in bromobenzene 0.917 g. of the distibyl absorbed 40 cc. (N. T. P.) of oxygen in three minutes; calcd. absorption 34 cc.

TABLE I

MOLECULAR WEIGHT DETERMINATIONS

The determinations were made in benzene by the Menzies method. A current of dry nitrogen was passed over the top of the apparatus during the determinations

Concn., %	ΔT, °C.	Mol. wt. found	Mol. wt. calcd. for $R_2Sb-SbR_2$
1.48	0.0766	621	607
2.44	.1250	627	
3.29	.1744	607	
4.32	.2248	619	

Di-α-naphthyliodostibine.—Two hundred grams of crude, dry α-naphthylstibinic acid[10] was dissolved in 500 cc. of cold hydrochloric acid, 200 cc. of water added and the mixture stirred for some time. After the removal of a black by-product by filtration, the filtrate was shaken with 25 g. of charcoal for twelve hours, filtered and the filtrate centrifuged in order to separate a black oil. The clear filtrate was cooled with ice and saturated with sulfur dioxide; α-naphthyldichlorostibine separated in crystalline form. After recrystallization from heptane, the material melted at 105–106°. The chloride is very soluble in benzene and absolute alcohol.

Anal. Calcd. for $C_{12}H_7SbCl_2$: Sb, 38.08; Cl, 22.18. Found: Sb, 38.07; Cl, 21.95.

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(9) Goddard and Yarsley [*J. Chem. Soc.*, 719 (1928)] described a compound, m. p. 233°, as di-*p*-tolyliodostibine which they obtained from tri-*p*-tolylstibine di-iodide. The high melting point alone indicates that their substance must possess a different structure.

(10) Riddell and Basterfield, *Trans. Royal Soc. Canada*, Third Series, Vol. XXIII, Part 1, Section III, p. 48 (1929).

The dichlorostibine was hydrolyzed in the manner described above and 25 g. of the crude α-naphthylstibine oxide was heated (bath temperature 105–110°) in a stream of nitrogen for forty-five minutes. The tetra-α-naphthylstibyl oxide formed was extracted from the pasty reaction mixture with acetone and the acetone removed. The oxide was dissolved in 35 cc. of acetic acid and 8 cc. of constant boiling hydriodic acid was added. Yellow di-α-naphthyliodostibine separated as an oil which became crystalline when cooled and rubbed. The dry iodide was extracted with petroleum ether; m. p. 136–137°.

Anal. Calcd. for $C_{20}H_{14}SbI$: Sb, 24.22; I, 25.24. Found: Sb, 24.19; I, 25.22.

Procedure for the Determination of Antimony.—Compounds in which both antimony and halogen were to be determined were analyzed by the method of Thompson and Oakdale.[11] However, if antimony only is to be estimated, decomposition of the organic material can be effected in five minutes according to the following procedure. The sample and 20 cc. of concd. sulfuric acid are boiled in a 300-cc. Kjeldahl flask. If the sample contains iodine, the latter must be removed at this stage by the addition of several 2-cc. portions of hydrogen peroxide. Perchloric acid (70%) is added, dropwise, until the solution becomes colorless; 1 cc. is usually sufficient. The mixture is boiled for five minutes longer, cooled and diluted with four times its own volume of water. The pentavalent antimony is reduced to the trivalent state by treatment of the solution with sulfur dioxide for a short time. After the solution has been heated on a water-bath for one hour, it is boiled for fifteen minutes to remove sulfur dioxide completely, transferred to a 500-cc. Erlenmeyer flask and 10 cc. of concd. hydrochloric acid added. It is then titrated, at 60°, with 0.1 *N* potassium bromate solution with the use of methyl orange as indicator.

Summary

The following antimony compounds, hitherto unknown, have been prepared in a pure state: *p*-bromophenyldichlorostibine, *p*-bromophenyldiiodostibine, di-*p*-bromodiphenylstibyl acetate, di-*p*-bromodiphenyliodostibine, tetra-*p*-bromotetraphenyldistibyl, tetra-*p*-tolylstibyl oxide, di-*p*-tolylstibyl acetate, di-*p*-tolylstibyl iodide, tetra-*p*-tolyldistibyl, α-naphthyldichlorostibine and di-α-naphthyliodostibine.

The distibyls possess properties similar to those of diarsyls.

A procedure for the determination of antimony is described.

ANN ARBOR, MICHIGAN

RECEIVED SEPTEMBER 13, 1932
PUBLISHED MARCH 7, 1933

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(11) Thompson and Oakdale, THIS JOURNAL, **52**, 1199 (1930).