twelve hours the precipitated oxide was filtered; yield 16.5 g. or 94% of the calcd. amount.

The oxide is insoluble in all of the common organic solvents but dissolves in sodium hydroxide solution and precipitates upon the addition of acid. For analysis the crude oxide was washed with hot 10% sodium carbonate solution and then with water until free from sodium carbonate and halides; m. p. 247–248° with decomposition.

Anal. Calcd. for $C_7H_6O_4NAs$: As, 30.84. Found: As, 30.94.

Summary

The preparation of fifteen arsonic and arsinic acids, ten haloarsines and three arsine oxides has been described.

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

Diarsyls. VIII. Amino and Hydroxydiarsyls[1]

BY F. F. BLICKE AND G. L. WEBSTER[2]

It was to be expected that water-soluble tetraaryldiarsyls could be obtained by the preparation of salts of tetraaryldiarsyls which contained nuclear amino or hydroxyl groups. It has been found that 3,3′,3″,3‴-tetra-(aminophenyl)-diarsyl[3] forms a water-soluble hydrochloride and that the sodium salts of 4,4″-dihydroxytetraphenyldiarsyl[4] and 3,3′,3″,3‴-tetra-(hydroxyphenyl)-diarsyl[4] are soluble in water.

A study of 2,2″-diaminotetraphenyldiarsyl has shown that this substance, dissolved in benzene, separates from the solution when the latter is shaken with concentrated hydrochloric acid in the form of a crystalline, benzene-insoluble compound. When water is added to the mixture the crystalline product dissolves and the diarsyl is found to be present in the benzene layer. This behavior indicates that the hydrochloride of this diarsyl is hydrolyzed extensively by water.

2,2″-Diaminotetraphenyldiarsyl was prepared by two methods: (a) interaction of 2,2″-diaminotetraphenylarsyl oxide with diphenylarsine, a reaction which yields both 2,2″-diaminotetraphenyldiarsyl and tetraphenyldiarsyl: (b) reaction between 2,2″-diaminotetraphenylarsyl oxide and 2-aminodiphenylarsine.

When diphenylarsine was added to 2,2″-dihydroxytetraphenylarsyl oxide, dissolved in benzene, tetraphenyldiarsyl began to precipitate at once but we were not able to isolate the alkali-soluble 2,2″-dihydroxytetraphenyldiarsyl in crystalline form.

2-Methoxydiphenyliodoarsine, dissolved in benzene, reacted rapidly with molecular silver. Although the reaction product could be obtained only in the form of an oil, the halogen-free material seemed to be 2,2″-dihydroxytetraphenyldiarsyl since it decolorized iodine instantly to yield 2-methoxydiphenyliodoarsine.

3,3″-Dihydroxytetraphenyldiarsyl was formed when 3,3′-dihydroxydiphenylarsinic acid was reduced with hypophosphorous acid. The compound is soluble in alkali and reacts rapidly with oxygen when dissolved in an organic solvent.

When 3,3″-dihydroxytetraphenyldiarsyl was methylated with dimethyl sulfate the corresponding 3,3″-dimethoxydiarsyl was produced. This compound also reacts rapidly with oxygen.

A very limited chemical study of dimethyl-di-(3-amino-4-hydroxyphenyl)-diarsyl was made by Bertheim.[5] He treated methyl-3-amino-4-hydroxyphenylarsinic acid with hypophosphorous acid, whereupon the crystalline dihypophosphite of the diarsyl precipitated. He analyzed this compound and stated that it irritates the mucous membrane. Upon treatment of the dihypophosphite with hydrochloric acid a water-soluble dihydrochloride was produced. Bertheim concluded his study of this diarsyl with the analysis of this salt.

We prepared the dihypophosphite of dimethyl-di-(3-amino-4-hydroxyphenyl)-diarsyl in the manner described above, treated the material with sodium hydroxide solution until a clear solution was obtained, acidified the latter with acetic acid and isolated the precipitated diarsyl. The dihydrochloride was prepared from the free base. It was found that this salt, as well as an aqueous, alkaline solution of the diarsyl, absorbed oxygen.

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(1) This paper represents part of a dissertation submitted to the Horace H. Rackham School of Graduate Studies by G. L. Webster in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

(2) University Fellow in the Horace H. Rackham School of Graduate Studies.

(3) Blicke, Oakdale and Oneto, THIS JOURNAL, **56**, 141 (1934).

(4) Blicke and Oneto, *ibid.*, **56**, 685 (1934).

(5) Bertheim, *Ber.*, **48**, 359 (1915).

Experimental Part

The apparatus shown in the accompanying drawing was found to be very useful for the preparation of amino and hydroxy diarsyls. When an aminodiarsyl is precipitated from an acid solution or a hydroxydiarsyl from an alkaline solution the diarsyls tend to separate in a somewhat flocculent state, hence are difficult to wash by decantation. By the use of the modified free radical bulb the product can be filtered by means of the glass filter (Jena filter). A slight pressure from a tank of nitrogen is applied through the side arm attached to the bulb. After filtration the diarsyl is dissolved from the filter plate by a suitable solvent and the solution decanted into the usual type of radical bulb.

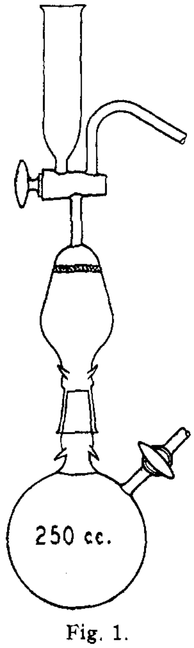

Fig. 1.

2,2″ - Diaminotetraphenyldiarsyl. (a) **From 2,2″-Diaminotetraphenylarsyl Oxide and Diphenylarsine.**—To 3.6 cc. (0.02 mole) of diphenylarsine, washed into a radical bulb filled with nitrogen with 10 cc. of absolute alcohol, there was added 5.0 g. (0.01 mole) of 2,2″-diaminotetraphenylarsyl oxide, dissolved in 10 cc. of alcohol. After twelve hours the alcoholic mother liquor was decanted from the precipitated diarsyls and discarded and the latter washed several times with small amounts of alcohol. The material was dried under diminished pressure, dissolved in 35 cc. of benzene, the solution transferred to a modified radical apparatus (see illustration) and shaken with 25 cc. of hydrochloric acid. The white, crystalline precipitate, the dihydrochloride of the diaminodiarsyl, was filtered, the crystals washed three times with 20 cc. of benzene and the benzene added to the original benzene filtrate which had been collected in a second radical bulb (this solution contained tetraphenyldiarsyl).

The white, crystalline material was shaken with a mixture of 50 cc. of water and 20 cc. of benzene, whereupon the product dissolved in the benzene layer. The aqueous layer was removed, the solvent distilled from the benzene layer under diminished pressure and the crystalline residue dissolved in 10 cc. of hot alcohol. 2,2″-Diaminotetraphenyldiarsyl separated from the cold solution and was then recrystallized from 20 cc. of alcohol; yield 2.3 g.

The diarsyl is very soluble in benzene, acetone and ether and the solutions rapidly turn dark red when exposed to air.

Dissolved in bromobenzene 0.860 g. of the diarsyl absorbed 30 cc. (N. T. P.) of oxygen in one minute.

In order to isolate the tetraphenyldiarsyl the solvent was removed from the benzene solution in the second radical bulb, the crystalline residue washed with alcohol and then recrystallized from 200 cc. of this solvent; yield 2.6 g.; m. p. 129–131° in a sealed tube filled with nitrogen.[6]

The rather peculiar behavior of the hydrochloride of the diaminodiarsyl was studied again after the diarsyl had been isolated. A sample of the diarsyl, dissolved in benzene, was shaken with hydrochloric acid, whereupon a white, crystalline precipitate appeared. After the addition of water the precipitate disappeared and the diarsyl was recovered from the benzene layer. Apparently the hydrochloride is hydrolyzed very extensively by water.

When 0.57 g. of the diaminodiarsyl was dissolved in 1 cc. of acetic anhydride, heated for thirty minutes, cooled and treated with water the gummy diacetyl derivative was obtained. This material was dissolved in 2 cc. of acetic acid and treated with 0.3 g. of iodine, dissolved in benzene. The iodine was decolorized instantly and after removal of the solvents 1 g. of crude 2-acetylaminodiphenyliodoarsine[7] was obtained; m. p. 147–148° after recrystallization from acetic acid.

(b) **From 2,2″-Diaminotetraphenylarsyl Oxide and 2-Aminodiphenylarsine.**—From a mixture of 2.3 g. of 2-aminodiphenylarsine, dissolved in 20 cc. of alcohol, and 2.5 g. of 2,2″-diaminotetraphenylarsyl oxide, dissolved in 30 cc. of the same solvent, there had precipitated, at the end of twenty-four hours, 2.1 g. of the diaminodiarsyl; m. p. 133–135° after recrystallization from 50 cc. of alcohol.

3,3″-Diaminotetraphenyldiarsyl.—Ammonia water was added to 4.5 g. of 3-aminodiphenylchloroarsine hydrochloride,[7] dissolved in water, the gummy precipitate extracted with ether, the ether solution poured into a radical bulb and the solvent removed. The colorless, oily 3,3″-diaminotetraphenylarsyl oxide was dissolved in 20 cc. of 50% hypophosphorous acid which contained four drops of hydriodic acid. The mixture was heated at 70° for three hours and after twelve hours made alkaline with 10% sodium hydroxide solution, the precipitate washed with water, dissolved in 100 cc. of alcohol and filtered into a second radical bulb. After distillation of about 75 cc. of alcohol the diarsyl separated in crystalline condition.

Dissolved in acetophenone 1.1550 g. of the diarsyl absorbed 47 cc. (N. T. P.) of oxygen in thirty seconds; calcd. amount 53 cc.

A mixture of 1.2 g. of the diarsyl, 15 cc. of acetone and 3 cc. of acetic anhydride was heated for one hour and the solvents removed. Since the residue would not crystallize the acetylated diarsyl was treated with 0.66 g. of iodine, dissolved in 10 cc. of alcohol. The iodine color disappeared instantly. The alcohol was removed and the residue rubbed under 3 cc. of acetic acid whereupon the product crystallized; this compound, 3-acetylaminodiphenyliodoarsine,[7] melted at 146–147° after recrystallization from acetic acid; mixed m. p. 146–147°.

3,3″-Dihydroxytetraphenyldiarsyl.—A mixture of 5.8 g. of 3-hydroxydiphenylarsinic acid, 10 cc. of alcohol, two drops of hydriodic acid and 20 cc. of 50% hypophosphorous acid in a modified radical bulb was heated in a bath at 70° for three hours. To the cold solution, 200 cc. of water was added slowly. The diarsyl precipitated as a liquid which soon became crystalline. The liquid was decanted, the diarsyl washed thoroughly with water, dried under reduced pressure, dissolved in hot benzene, the solution filtered, cooled, and the diarsyl precipitated by the addition of 150 cc. of petroleum ether (90–100°); yield 3.6 g.

The hydroxydiarsyl is soluble in alkali: 0.417 g. of the

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[6] Blicke, Weinkauff and Hargreaves [This Journal, **52**, 782 (1930)] reported 129–130°.

[7] Blicke and Webster, *ibid.*, **59**, 536 (1937).

material dissolved in a mixture of 0.14 g. of sodium hydroxide and 10 cc. of water. Upon the addition of hydrochloric acid the diarsyl was recovered unchanged. It is also soluble in benzene and very soluble in alcohol and acetone. Dissolved in acetophenone the diarsyl absorbed oxygen rapidly.

3,3″-Dimethoxytetraphenyldiarsyl.—The 3,3″-dihydroxytetraphenyldiarsyl, obtained from 5.8 g. of 3-hydroxydiphenylarsinic acid, was dissolved in a mixture of 10 cc. of 40% sodium hydroxide solution and 25 cc. of water and shaken with 3 cc. of dimethyl sulfate. The methylation process was repeated with 20 cc. of 40% sodium hydroxide solution and 6 cc. of dimethyl sulfate. The mixture, from which the methoxy derivative had settled as a gum, was heated for some time; when cooled, the product crystallized. It was washed with alkali and water, dissolved in 35 cc. of benzene and the solution filtered into a second radical bulb. The benzene was removed and the diarsyl recrystallized from 20 cc. of alcohol; yield 3.8 g.

A solution obtained from 1.28 g. of the diarsyl and 20 cc. of acetophenone absorbed 52 cc. (N. T. P.) of oxygen in thirty seconds; calcd. 55 cc.

Dimethyl-di-(3-amino-4-hydroxyphenyl)-diarsyl.—A solution prepared from 4.6 g. of methyl-3-amino-4-hydroxyphenylarsinic acid and 30 cc. of 50% hypophosphorous acid was introduced into the modified radical bulb and a mixture of 0.5 cc. of hydriodic acid and 20 cc. of hypophosphorous acid added. After about thirty minutes the precipitated diarsyl hypophosphite[5] (p. 358) was filtered and the material washed three times with 50-cc. portions of water. It was then dissolved in a hot alkaline solution, prepared from 15 g. of sodium hydroxide (70%) and 50 cc. of water, and the hot solution acidified to phenolphthalein with 25% acetic acid. The pure white mat of crystalline product was filtered, washed free from acid with water and then washed with 50 cc. of acetone. The product was washed from the filter plate into the bulb of the apparatus with the aid of a small amount of acetone, the acetone removed by distillation under reduced pressure and the crystalline diarsyl dried at 80–85° for four hours under reduced pressure.

In order to obtain the diarsyl dihydrochloride 2.5 g. of the diarsyl was dissolved in a mixture of 27 cc. of 0.5 *N* hydrochloric acid and 75 cc. of methyl alcohol and the solvents removed at 35° under reduced pressure. The residue was dried at 85–90° under reduced pressure for six hours and isolated in a carbon dioxide atmosphere; m. p. 168–170° in a sealed tube filled with nitrogen.

Anal. Calcd. for $C_{14}H_{20}O_2N_2Cl_2As$: As, 31.95; . Cl, 15.12. Found: As, 31.44; Cl, 14.81.

TABLE I

DIARSYLS

	M. p., °C.[a]	Formula	As, % Calcd.	As, % Found
2,2″-Diamino-tetraphenyl	133–134	$C_{24}H_{22}N_2As_2$	30.71	30.76
3,3″-Diamino-tetraphenyl	146–148	$C_{24}H_{22}N_2As_2$	30.71	30.39
3,3″-Dihydroxy-tetraphenyl	134–136	$C_{24}H_{20}O_2As_2$	30.59	30.24
3,3″-Dimethoxy-tetraphenyl	98– 99	$C_{26}H_{24}O_2As_2$	28.92	28.86
Dimethyl-di-(3-amino-4-hydroxyphenyl)	184–185	$C_{14}H_{18}O_2N_2As_2$	37.84	37.59

[a] Determined in a sealed tube filled with nitrogen.

2-Aminodiphenylarsine.—A solution of 46 g. of 2-aminodiphenylarsinic acid[8] in 280 cc. of hydrochloric acid was placed in a three-liter, three-necked flask the necks of which were fitted with a mercury trap, through which hydrogen could escape, a mechanical stirrer and a wide-stemmed funnel. The stem of the funnel was connected to the flask by means of a short piece of rubber tubing which could be opened and closed with the aid of a pinch clamp. The mixture was stirred and 90 g. of dry, amalgamated zinc dust was added during the course of two hours. A dark colored, sandy precipitate formed. After five hours 100 cc. of hydrochloric acid was added and the mixture stirred for twelve hours longer; 500 cc. of 40% sodium hydroxide solution and 400 cc. of ether, previously saturated with nitrogen, were then added. The ether layer was siphoned into a nitrogen-filled separatory funnel which contained soda-lime. The dry ether solution was allowed to flow, very slowly, into a small Claisen distillation flask heated on a steam-bath. After removal of the ether the arsine was distilled; b. p. 218–220[a] under 35 mm. pressure. The arsine absorbs oxygen extremely rapidly and becomes deep red-brown in color.

When 5.81 g. of the arsine, dissolved in benzene, was allowed to oxidize in air there were obtained 1.43 g. of 2-aminodiphenylarsinic acid and 4.53 g. of 2,2″-diaminotetraphenylarsyl oxide.

Summary

The preparation and properties of 2,2″-diamino-, 3,3″-diamino-, 3,3″-dihydroxy- and 3,3″-dimethoxytetraphenyldiarsyl as well as of dimethyl-di-(3-amino-4-hydroxyphenyl)-diarsyl and 2-aminodiphenylarsine have been described.

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[8] Kalb, *Ann.*, **423**, 60 (1921).