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

Diarsyls. IV. The Interaction of Diphenyldiiododiarsyl with Alkali, with Phenylarsine and with Diphenylarsine[1]

BY F. F. BLICKE AND L. D. POWERS

It seemed that diphenyldihydroxydiarsyl, a substance which has never been described, should be produced from the interaction of diphenyldiiododiarsyl[2] and alkali

$$C_6H_5(I)As—As(I)C_6H_5 + 2NaOH = C_6H_5(OH)As—As(OH)C_6H_5 + 2NaI$$

Diphenyldiiododiarsyl, suspended in ether, was shaken with excess sodium hydroxide solution in a free radical apparatus filled with nitrogen. The halogen was removed rapidly and quantitatively from the diarsyl and a crystalline, alkali-insoluble material remained partly dissolved and partly suspended in the ether layer. Upon separation and acidification of the alkaline solution a considerable amount of phenylarsine oxide was obtained. The alkali-insoluble product, after it had been recrystallized twice from benzene, possessed properties which in some respects resembled those of arsenobenzene; in certain other characteristics, however, the material was decidedly dissimilar to this substance as is shown by the following tabulation.

ALKALI-INSOLUBLE PRODUCT	ARSENOBENZENE
Separates from a benzene solution in the form of large, granular crystals	Separates from a benzene solution in the form of fine needles
M. p. 195–197°.[a] Mixed with arsenobenzene, m. p. 190–195°[b]	M. p. 210–212°
Mol. wt., 603[c]	Mol. wt. 867;[d] calcd. 304
% As, 47.12[e]	% As, 49.31
Absorbs oxygen rapidly[f]	Does not absorb oxygen
Dissolves rapidly in ether upon the addition of HCl or HBr; arsenobenzene precipitates quickly from the solution	Does not dissolve in ether upon the addition of a halogen acid
One hundred cubic centimeters of boiling benzene dissolve 7.9 g. of the material	One hundred cubic centimeters of boiling benzene dissolve 1.4 g. of this compound
Yields diphenyldiiododiarsyl when treated with iodine in ether	Yields diphenyldiiododiarsyl when treated with iodine in ether

[a,b] The melting point was determined in a sealed tube filled with nitrogen. [c] This result represents the average of six determinations on three different samples of material. The determinations were made in boiling benzene in a stream of nitrogen. [d] This value was obtained in boiling benzene in a stream of nitrogen; previously the molecular weight had been found to be 895 and 915, under the same experimental conditions [Blicke and Smith, THIS JOURNAL, **52**, 2950 (1930)]. [e] This figure represents the average value of six analyses made with three different samples of material. [f] 1.042 g. of the product absorbed 73 cc. (N. T. P.) of oxygen in five minutes.

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(1) This paper represents the second part of a dissertation submitted to the Graduate School by L. D. Powers in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

(2) Blicke and Smith, THIS JOURNAL, **52**, 2937 (1930).

Diphenyldibromodiarsyl, when hydrolyzed, yielded products identical with those obtained from diphenyldiiododiarsyl. Di-*p*-anisyldiiododiarsyl yielded *p*-anisylarsine oxide and an alkali-insoluble compound which, to some extent, resembled di-*p*-methoxyarsenobenzene, yet seemed to be different from this material.

It has been claimed by Steinkopf and Smie[3] that diphenyldiiododiarsyl, suspended in alcohol, reacts with diphenylarsine at 70° to form hexaphenyltetraarsine $(C_6H_5)_2As—As(C_6H_5)—As(C_6H_5)—As(C_6H_5)_2$. The only experimental fact offered in support of this structure was an arsenic analysis, which differed from the calculated amount of arsenic by 2.98%, and the behavior of the material with iodine; in the latter reaction phenyldiiodoarsine and diphenyliodiarsine were formed in approximately equivalent amounts. No melting point was recorded and the above mentioned investigators admitted that their product was impure.

We have found that the compounds under discussion react at ordinary temperature in an entirely different manner, namely, with the formation of tetraphenyldiarsyl and arsenobenzene. Such a mixture would, of course, contain the same amount of arsenic as hexaphenyltetraarsine and, upon treatment with iodine, would yield phenyldiiodoarsine and diphenyliodoarsine in equivalent amounts. It seems very probable that the tetraarsine of Steinkopf and Smie was, in reality, a mixture of tetraphenyldiarsyl and arsenobenzene.

$$C_6H_5(I)As—As(I)C_6H_5 + 2(C_6H_5)_2AsH = (C_6H_5)_2As—As(C_6H_5)_2 + C_6H_5As{=}AsC_6H_5 + 2HI$$

Diphenyldiiododiarsyl and phenylarsine react to form arsenobenzene.

$$2C_6H_5(I)As—As(I)C_6H_5 + 2C_6H_5AsH_2 = 3C_6H_5As{=}AsC_6H_5 + 4HI$$

Steinkopf and Smie[3] stated that these compounds yield cyclic triphenyltriarsine, $\underline{C_6H_5As—As(C_6H_5)—As}C_6H_5$, but since no melting point was reported for the triarsine and the calculated analytical data for this compound are the same as for arsenobenzene, the alleged formation of the triarsine in this reaction seems to have been based on an insufficient amount of experimental evidence.

Experimental Part

Hydrolysis of Diphenyldi-iododiarsyl.—The diiododiarsyl was prepared from 24.4 g. of phenyldiiodoarsine,[4] 50 cc. of absolute alcohol and 40 g. of crystalline phosphorous acid, dissolved in 200 cc. of alcohol. The diarsyl was then suspended in 100 cc. of ether, shaken for one hour with 100 cc. of 10% sodium hydroxide solution, the alkaline layer decanted and the ether layer extracted three times with 50-cc. portions of alkali. Upon neutralization of the alkaline extracts with sulfuric acid in a nitrogen atmosphere,

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(3) Steinkopf and Smie, *Ber.*, **59**, 1462 (1926).

(4) This material, after it has been preserved for some time in a glass-stoppered bottle, becomes very dark in color and often contains a considerable amount of a crystalline product. The iodide, however, seems to undergo little, if any, decomposition if it is kept under a layer of concd. hydriodic acid.

3.8 g. of phenylarsine oxide was obtained, mixed m. p. 145–147°,[5] after recrystallization from benzene–ether.

The ether layer, which contained suspended material, was concentrated to a volume of 15 cc. and the liquid decanted. The latter possessed a very strong odor similar to that of phenylarsine. The slightly yellow crystalline material was washed with alcohol, then with ether and dried under diminished pressure. After a second recrystallization from benzene the product, which was halogen free, weighed 3.2 g.

When 2.06 g. of the material, suspended in 50 cc. of ether, was shaken with 25 cc. of hydrobromic acid 1.13 g. of arsenobenzene, m. p. 210–212°, was obtained.

Anal. Calcd. for $C_{12}H_{10}As_2$: As, 49.31. Found: As, 49.26.

From 1.72 g. of the product, 50 cc. of ether and 1.4 g. of iodine there was produced 1.45 g. of diphenyldiiododiarsyl; m. p. 177–178°.

Hydrolysis of Di-*p*-anisyldiiododiarsyl.—When the diiododiarsyl,[6] obtained from 13.1 g. of *p*-anisyldiiodoarsine,[7] was hydrolyzed in the manner described above, there was obtained 2.5 g. of *p*-anisylarsine oxide, m. p. 136–138°, and 1.7 g. of a crystalline halogen-free, alkali-insoluble product, m. p. 220–230°: % As found, 40.02 and 40.20.

Dissolved in bromobenzene 1.082 g. of the alkali-insoluble product absorbed 61 cc. of oxygen in two minutes.

When the alkali-insoluble material was suspended in ether and treated with hydrochloric or hydrobromic acid di-*p*-methoxyarsenobenzene was obtained; mixed m. p. 233–235°.[8]

Phenylarsine and Diphenyldi-iododiarsyl.[9]—To 6.79 g. (0.012) mole of diphenyldiiododiarsyl, suspended in 75 cc. of absolute alcohol, there was added 2.4 g. (1.8 cc., 0.015 mole) of phenylarsine. After the mixture had been shaken for twelve hours the deep yellow color of the diiododiarsyl had disappeared and a pale yellow compound remained suspended in the solvent. The alcohol was decanted, the solid material washed with alcohol and ether and then dried for some time in the radical bulb under diminished pressure. This material melted from 140–212° and absorbed oxygen: 0.600 g. absorbed 11 cc. in two minutes. The smallest possible amount of boiling xylene necessary to dissolve the product was introduced into the radical bulb; after two days 2.8 g. of pure arsenobenzene had separated from the solution; mixed m. p. 209–210°; calcd. yield 5.5 g.[10]

Anal. Calcd. for $C_{12}H_{10}O_2$: As, 49.31. Found: As, 49.07.

When alcohol was replaced by absolute ether in the above experiment and the mixture shaken for three days, 87% of the diiododiarsyl was recovered unchanged.

Diphenylarsine and Diphenyldiiododiarsyl.—The diphenyldiiododiarsyl, obtained from 8.12 g. (0.02 mole) of phenyldiiodoarsine, 14 g. of crystalline phosphorous acid and 100 cc. of absolute alcohol—approximately 0.01 mole[11]—was suspended in 60

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(5) For further identification the oxide was converted into phenyldichloroarsine and the latter identified as phenylarsylene N-pentamethylenedithiocarbamate [Blicke and Oakdale, THIS JOURNAL, **54**, 2995 (1932). The melting point of this compound should be 183–184° instead of 173–174° as recorded previously.

(6) Blicke and Smith, *ibid.*, **52**, 2943 (1930).

(7) Blicke, Powers and Webster, *ibid.*, **54**, 2946 (1932).

(8) A sample of di-*p*-methoxyarsenobenzene, obtained by reduction of *p*-anisylarsine oxide in acetic acid with hypophosphorous acid, melted at 228–230° after recrystallization from bromobenzene.

(9) A description of the apparatus used in this and the following experiment was published previously [Blicke and Powers, *ibid.*, **54**, 3356 (1932)].

(10) The yield was, undoubtedly, lowered to a decided extent by recrystallization. In the recrystallization of pure arsenobenzene from xylene the yield of crystalline product which separated from the xylene was about 50%; only gummy material could be obtained from the mother liquor.

(11) The diiododiarsyl was not removed from the free radical bulb in which it had been prepared. In a number of instances in which the diarsyl, prepared by this method, had been isolated the yield of pure product was never less than 90% of the calcd. amount.

cc. of absolute alcohol and 4.60 g. (3.54 cc., 0.02 mole) of diphenylarsine added.[12] The mixture, initially yellow in color, was shaken vigorously for twelve hours; after thirty minutes it had become colorless. The alcohol was decanted from the solid material into a second radical bulb and the alcohol removed by distillation under reduced pressure. In order to separate the compounds formed, arsenobenzene and tetraphenyldiarsyl, advantage was taken of the fact that the latter substance is soluble in ether while arsenobenzene is practically insoluble in this solvent. One hundred cubic centimeters of ether was poured onto the mixture, whereupon most of the tetraphenyldiarsyl dissolved. The ether solution was then decanted through a Jena filter into the second bulb. The purpose of the filter was to retain finely divided arsenobenzene which remained suspended in the ether. The arsenobenzene was washed with ether until free from the diarsyl. The residue of arsenobenzene weighed 2.97 g.; m. p. 203–207°; calcd. yield 3.04. After recrystallization from bromobenzene it melted at 208–210°.

The ether solution in the second bulb was shaken with alkali to remove traces of unchanged iodides, washed free from alkali and then concentrated to a volume of 25 cc.; a copious precipitate of tetraphenyldiarsyl was obtained. After recrystallization from absolute alcohol, the material weighed 2.6 g., m. p. 128–130°.[13] Upon concentration of the mother liquor an additional 0.4 g. of product was obtained; calcd. yield 4.58 g.

Anal. Calcd. for $C_{24}H_{20}As_2$: As, 32.73. Found: As. 32.72, 32.69.

Summary

Several diaryldihalodiarsyls were treated with alkali whereupon an arylarsine oxide and an alkali-insoluble product were formed.

Phenylarsine and diphenyldiiododiarsyl react to form arsenobenzene; diphenylarsine and the diiododiarsyl yield arsenobenzene and tetraphenyldiarsyl. It has been claimed in the literature, on the basis of meager experimental data, that cyclic triphenyltriarsine is formed in the first instance and hexaphenyltetraarsine in the second.

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(12) No reaction seemed to take place when ether was used as a solvent.

(13) Blicke, Weinkauff and Hargreaves, THIS JOURNAL, **52**, 782 (1930).