of benzene and petroleum ether and then with the latter. The yield was 25 g. After one recrystallization it melted at 210° (corr.) alone or admixed with an authentic specimen.[9] The mother liquor yielded 25 g. of unchanged α-hydrindone when it was washed with dilute alkali, dried and distilled under reduced pressure.

This is the fifth communication submitted during the tenure by one of us of the Eli Lilly and Company Fellowship.[10] The authors desire to express their appreciation not only to the executive staff of this company for the privilege thus enjoyed, but also to the members of the technical staff for their generous coöperation.

Summary

1. A new synthesis of alkylaryl diketones which promises to be quite general is described.

2. The synthesis of a cyclic *o*-diketone was not accomplished.

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TETRA-ARYLDIARSYLS. I[1]

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In view of the fact that tetra-arylhydrazines[3] and hexa-arylethanes[4] dissociate spontaneously into diarylnitrogen radicals and triarylmethyls, respectively, it seemed possible that tetra-aryldiarsyls might behave in a similar manner

$$\begin{aligned} R_2As\text{—}AsR_2 &\rightleftarrows 2R_2As\text{—} \\ R_2N\text{—}NR_2 &\rightleftarrows 2R_2N\text{—} \\ R_3C\text{—}CR_3 &\rightleftarrows 2R_3C\text{—} \end{aligned}$$

Several investigators have studied tetraphenyldiarsyl with regard to its tendency to dissociate into diphenylarsyl. Schlenk[5] determined the molecular weight of the substance in boiling benzene but found no evidence of dissociation. According to Porter and Borgstrom,[6] as well as Borgstrom and Dewar,[7] molecular weight determinations in naphthalene by the cryo-

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[9] Gabriel and Stelzner, *Ber.*, **29**, 2604 (1896).

[10] Richard H. F. Manske.

[1] This paper represents the third part of a dissertation submitted to the Graduate School by Mr. Smith in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

[2] Parke, Davis and Company Fellow, 1927–1929.

[3] Wieland, "Die Hydrazine," Ferdinand Enke, Stuttgart, **1913**.

[4] References to the literature on hexa-arylethanes is to be found in "Organic Radicals," Gomberg, *Chemical Reviews*, **1**, 141 (1924); also in Walden, "Chemie der freien Radikale," S. Hirzel, Leipzig, **1924**.

[5] Schlenk, *Ann.*, **394**, 220 (1912).

[6] Porter and Borgstrom, This Journal, **41**, 2051 (1919).

[7] Borgstrom and Dewar, *ibid.*, **44**, 2919 (1922).

scopic method indicate that tetraphenyldiarsyl is associated rather than dissociated.

It seemed to us that more favorable results might be obtained in the case of tetra-*p*-anisyl-, tetra-α-naphthyl- and tetrabiphenyldiarsyl; at least it has been found that the anisyl, naphthyl and biphenyl nuclei further dissociation in the hexa-arylethane group.[8]

We decided to investigate these tetra-aryldiarsyls and had intended to prepare them by reduction[9] of the tetra-arylarsyl oxides, since satisfactory methods of preparation for these oxides have been developed.[10] However, a much simpler procedure was found. The tetra-arylarsyl oxides are converted readily by the action of hydrogen chloride into the diarylarsyl chlorides and the latter react with sodium iodide to form the corresponding iodides. Interaction of the latter with metals, at ordinary temperature, yields the tetra-aryldiarsyls. For example, the halogen is removed quantitatively if diphenylarsyl iodide, dissolved in bromobenzene,[11] is shaken vigorously with mercury for twenty minutes. Such a solution, in less than thirty seconds, absorbs almost exactly the quantity of oxygen[12] calculated for the formation of a peroxide, $(C_6H_5)_2As\text{-}O\text{-}O\text{-}As(C_6H_5)_2$ and decolorizes instantly a carbon tetrachloride solution of iodine.

In fact, the solution obtained after removal of the halogen from diphenylarsyl iodide is strikingly similar in behavior toward oxygen and iodine to that obtained when triphenylmethyl chloride, dissolved in bromobenzene, is treated with mercury; however, in the former case the solution is colorless, in the latter it is yellow.

In order to obtain tetraphenyldiarsyl in the solid state, diphenylarsyl iodide was dissolved either in benzene or absolute ether and, after removal of the halogen by mercury, the solution was filtered and the solvent removed under diminished pressure. During these operations precaution must be taken to prevent oxygen from coming in contact with the material. The crystalline diarsyl, when dissolved in bromobenzene, absorbs the amount of oxygen calculated for peroxide formation.

The behavior of tetraphenyldiarsyl and other tetra-aryldiarsyls described in this paper indicates that these compounds dissociate to some

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[8] In the tetra-arylhydrazine series, according to Wieland, tetra-*p*-anisylhydrazine dissociates to a greater extent than tetraphenylhydrazine but tetrabiphenylhydrazine undergoes less dissociation than the phenyl analog.

[9] Michaelis and Schulte, *Ber.*, **15**, 1952 (1882).

[10] Blicke and Smith, THIS JOURNAL, **51**, 1558 (1929).

[11] This solvent was chosen because of its comparatively low vapor pressure, an essential feature if the solution is to be used subsequently for an oxygen-absorption determination. As far as the removal of halogen and formation of the diarsyl is concerned, other solvents such as ether or benzene serve equally well.

[12] The apparatus devised by Gomberg and Schoepfle, THIS JOURNAL, **39**, 1661 (1917), for oxygen absorption was employed.

extent into diarylarsyls, that is, divalent arsenic radicals. Molecular weight determinations of the various diarsyls are now being carried out in the hope that the dissociation, in some cases at least, is of such a magnitude that it can be detected by this method.

The behavior of other diarylarsyl iodides with mercury is described in the experimental part of this paper.

A further study of tetra-aryldiarsyls is in progress in this Laboratory and the action of metals on diarylstibinyl halides and on diarylbismuthyl halides is being investigated.

Experimental Part

Diphenylarsyl iodide, dissolved in bromobenzene, ether or benzene, reacts very rapidly at ordinary temperature with mercury, slower with molecular silver and zinc powder and very slowly, if at all, with magnesium powder or magnesium ribbon. In one instance $^1/_{200}$ mole of diphenylarsyl iodide, 6 g. of mercury and 15 cc. of bromobenzene were placed in the absorption bottle and the mixture was shaken continuously by hand. The amount of oxygen which had reacted after twenty minutes was 56 cc.; after thirty minutes, 59 cc. No further amount of oxygen was absorbed after an hour. The calculated quantity of oxygen required for peroxide formation is 56 cc.

A mixture prepared from 6 g. of mercury, 0.6 g. of iodine and 15 cc. of bromobenzene was rotated for four hours in a sealed tube. The mixture did not absorb oxygen; neither did diphenylarsyl iodide dissolved in bromobenzene absorb the gas.

It was found by analysis[13] of the mercury halide formed that mercury removes the halogen rapidly from di-*p*-tolyl-, di-*p*-anisyl-, di-α-naphthyl- and dibiphenylarsyl iodide.

Bromobenzene solutions obtained by shaking diphenyl-, di-*p*-tolyl- and di-*p*-anisyl iodide, respectively, with mercury, after complete removal of the iodine, absorb at once the calculated quantity of oxygen with the evolution of a considerable amount of heat. If the solution which has absorbed oxygen is allowed to remain in contact with the gas for a long period of time, a further *slow* absorption takes place due, probably, to the decomposition of the peroxide into secondary products which react with oxygen. A similar behavior is characteristic of triarylmethyl peroxides. In the case of solutions obtained from di-α-naphthyl- and dibiphenylarsyl iodide there was an immediate absorption of oxygen in excess of that required for the formation of a peroxide, the absorption varying from 125–130% of the calculated amount. At present we are unable to account for this phenomenon.

Relation between the Quantity of Oxygen Absorbed and the Amount of Halogen Removed.—Two sets of sealed tubes were rotated for definite periods of time. Each tube of the one set contained $^1/_{200}$ mole of diphenylarsyl iodide, 15 cc. of bromobenzene and 3.0 g. of molecular silver (80–100 mesh). Each tube of the second set contained one-fifth of the above quantities of material. At intervals one tube from each set was removed from the rotating apparatus. The tube which contained the larger quantities was used for oxygen absorption; the contents of the other tube were poured on a filter, the residue of silver and silver iodide was washed several times with boiling xylene and then with acetone. The mixture was removed from the filter and the silver dissolved with hot, dilute nitric acid. The silver iodide was filtered and weighed.

A comparison of Line 4 with Line 3 shows that the percentage of oxygen absorbed is comparable, within the limit of experimental error, to the

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[13] The analytical procedure of Kohn, *Z. anorg. Chem.*, 59, 108 (1908), was used but the iodine was determined volumetrically by the Volhard method.

percentage of silver iodide formed. The actual amount of oxygen absorbed, Line 2, is practically the same as that calculated, Line 5, from the quantity of silver iodide.

TABLE I

EXPERIMENTAL DATA

Time shaken, hours	6	11	24	48
O_2 abs. after 1 min., cc., N.T.P.	14	26	41	53
Silver iodide, %	22	44	72	94
Oxygen absorbed, %	25	46	73	95
Abs. calcd. from AgI, cc.	12	25	40	52

It was found that diphenylarsyl iodide and triphenylmethyl bromide react instantly, when dissolved in bromobenzene, to form a deep red solution. The tendency for reaction is so great that when the two compounds are mixed in the solid state a red color develops at the points of contact. The solution absorbs oxygen rapidly. Undoubtedly the two compounds react in accordance with the following equation

$$(C_6H_5)_2AsI + (C_6H_5)_3CBr = (C_6H_5)_2AsBr + (C_6H_5)_3CI; \ (C_6H_5)_3CI \rightleftharpoons (C_6H_5)_3C- + I$$

However, the volume of oxygen absorbed (50 cc.) is greatly in excess of that calculated (28 cc.) for the amount of triphenylmethyl which could be produced. Other diarylarsyl iodides behave in an entirely analogous manner with triphenylmethyl bromide.

No color was developed when a mixture of diphenylarsyl bromide and triphenylmethyl bromide was dissolved in bromobenzene, and the solution did not absorb oxygen. No oxygen was absorbed by a mixture of diphenylarsyl bromide, iodine and bromobenzene.

A mixture of $^1/_{200}$ mole of diphenylarsyl iodide, 3 g. of silver and 15 cc. of bromobenzene was rotated for two days. The mixture absorbed 56 cc. of oxygen or 100% of the calculated amount. A similar mixture, except that $^1/_{200}$ mole of triphenylmethyl bromide was used in place of the arsyl iodide, absorbed under similar conditions 52 cc. of oxygen or 93% of the calculated amount. One four-hundredth mole of diphenylarsyl iodide, $^1/_{400}$ mole of triphenylmethyl bromide, 3 g. of silver and 15 cc. of bromobenzene were rotated for two days; the mixture absorbed 73 cc. of oxygen or 130% of the calculated amount.

Preparation and Properties of Tetraphenyldiarsyl.[14]—One-hundredth mole of diphenylarsyl iodide, 12 g. of mercury and 60 cc. of dry benzene[15] were put into a bottle which had been filled previously with dry, oxygen-free nitrogen. The bottle was stoppered tightly and then shaken by fastening it to the rim of a slowly revolving wheel. After the halogen had been removed the mixture was filtered into an apparatus similar to that used for the isolation of triarylmethyls.[16] The bulb of the apparatus was placed in a cone-shaped coil made from lead pipe, steam was passed through the latter

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[14] This procedure applies also to the preparation of tetra-*p*-tolyldiarsyl and tetra-*p*-anisyldiarsyl.

[15] The benzene had been saturated with dry, oxygen-free nitrogen and was preserved over sodium. Ether may be used in place of benzene as a solvent.

[16] Gomberg and Cone, *Ber.*, **37**, 2033 (1904).

and most of the solvent in the bulb was removed under diminished pressure.[17] The greater portion of the diarsyl separates as a colorless, crystalline precipitate. The contents of the bulb were treated with 20 cc. of dry, oxygen-free ether and the liquid poured out of the apparatus. The precipitate was dried by applying suction to the bulb and maintaining the latter at a temperature of 70–80° for three hours to insure complete removal of the solvent. The apparatus was then filled with nitrogen and the diarsyl transferred to a small test-tube in a stream of the gas.[18] The compound melted at 120–125°.[19]

In several instances oxygen absorptions were made with the tetraphenyldiarsyl isolated from ether. It was found that 0.5440 g. of the diarsyl, dissolved in bromobenzene, absorbed after one minute 26 cc. (calculated amount, 26.5 cc.). In a second experiment 0.5005 g. of the material was dissolved in ethylene bromide. The solution absorbed 25 cc. (calculated amount, 24 cc.).

Potassium permanganate dissolved in acetone was added to tetraphenyldiarsyl dissolved in the same solvent. The diarsyl decolorized instantly the amount of permanganate required theoretically to convert the substance into diphenylarsinic acid, although the latter was not isolated. Tetraphenylarsyl oxide and diphenylarsyl iodide also decolorized immediately an acetone solution of potassium permanganate.

Tetraphenyldiarsyl, tetraphenylarsyl oxide and diphenylarsyl iodide all decolorized instantly iodine dissolved in carbon tetrachloride. In the case of the tetraphenyldiarsyl the exact amount of iodine was added which was necessary for the formation of the diphenylarsyl iodide. A black, gummy precipitate formed which was, no doubt, a periodide. The solution was decanted from the precipitate and after removal of the solvent the black, viscous residue was covered with water and treated with sulfur dioxide. A yellow, crystalline substance was obtained which, after recrystallization from alcohol, melted at 42–43°. This material was diphenylarsyl iodide.

That a solution of tetraphenyldiarsyl is stable toward light, at least in the presence of mercury salts, is shown by the following experiment: 1.78 g. ($^1/_{200}$ mole) of diphenylarsyl iodide, 6 g. of mercury and 15 cc. of bromobenzene were rotated for eighteen hours. The tube which contained the material was then placed outdoors for nineteen days. The contents of the tube absorbed the calculated amount of oxygen, that is, 56 cc.

Summary

It has been shown that a number of tetra-aryldiarsyls can be prepared readily, from the interaction of a diarylarsyl iodide and mercury.

Because of the extremely great reactivity of these compounds toward oxygen, and other reagents, it seems that their behavior can be explained best by the assumption that the tetra-aryldiarsyls dissociate spontaneously into diarylarsyls, that is, divalent arsenic radicals.

ANN ARBOR, MICHIGAN

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[17] If all of the solvent was removed, the diarsyl obtained was somewhat gummy.

[18] The diarsyls are so extremely reactive toward oxygen that it was found advisable to remove the compound from the apparatus in a large, specially designed box which was filled with dry carbon dioxide. All operations which involved exposure of the diarylarsyl, such as the preparation of pellets for molecular weight determinations, were carried out in this box.

[19] Michaelis and Schulte, ref. 9, state that the compound melts at 135°; Borgstrom and Dewar, ref. 7, recorded the melting point as 130.5° (corr.).