

strong tendency to separate out from solution as an oil, but on standing in a cool place microscopic crystals were obtained softening above 160° and melting to a cloudy liquid at $192-193^{\circ}$. The analysis indicated the presence of alcohol of crystallization. This assumption is substantiated by the fact that on heating the substance in a test-tube, it melts with foaming and a combustible gas is evolved.

Anal. Calcd. for $C_{27}H_{23}PO \cdot C_2H_5OH$: P, 7.0. Found: P, 7.0.

The phosphine oxide may be obtained free from alcohol by drying the crystals in vacuo over sulfuric acid.

Tri-biphenyl benzylphosphonium bromide reacted differently with alcoholic potash. Toluene was set free, recognizable by its odor, while tri-biphenylphosphine oxide melting at $233-234^{\circ}$ crystallized out in a few minutes.

Tri-biphenyl Phosphobetaine.—Tri-biphenylphosphine oxide also formed when the phosphonium salt obtained by the action of ethyl chloro-acetate was warmed with alcoholic potash. If, however, the solutions were mixed at the temperature of melting ice and subsequently poured into ice water, the betaine formed. It was washed free from alkali before recrystallization from alcohol. A pale yellow precipitate of brilliant diamond-shaped plates was obtained, melting at $109-110^{\circ}$ with preliminary softening.

Anal. Calcd. for $C_{38}H_{29}PO_2$: P, 5.9. Found: P, 5.9.

It changes into tri-biphenylphosphine oxide on standing at room temperature.

Summary

Tri-biphenylphosphine has been obtained by the action of sodium in benzene on chlorodiphenyl and phosphorus trichloride and its chemical properties were investigated. Phosphonium salts were formed with methyl iodide, allyl bromide, benzyl bromide and ethyl chloro-acetate, which on warming in alkaline solution decomposed into phosphine oxides and hydrocarbons.

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

DIARSYLS. III. DIARYLDI-IODODIARSYLS¹

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Arsenobenzenes, in the form of salvarsan and its analogs, have been made the subject of intensive investigations. Especially important from a chemotherapeutic standpoint are the oxidation products of these compounds.

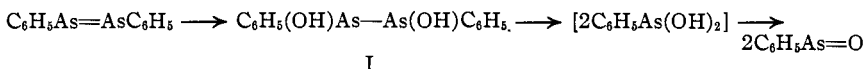
It has been shown by experiments *in vitro* that, in general, the parasiticidal action of arseno compounds is relatively low compared with that of compounds of the arsine oxide type. Furthermore, when an arseno compound is introduced into an infected animal, there is a fairly long latent period during which there is no evidence of any parasiticidal action.

¹ This investigation was made possible by the generous financial assistance of Parke, Davis and Company and we wish to express our sincere appreciation for the aid which has been given us.

Voegtlin² accounts for the therapeutic activity of salvarsan by the assumption that the latter compound, in the body, is oxidized slowly to the corresponding arsine oxide.

It seemed to us that another substance, a possible precursor of the arsine oxide, might play an important role in the transformation of an arseno compound in the animal body.

If a substance of the arseno type, arsenobenzene for example, undergoes progressive oxidation in the presence of moisture, the first oxidation product may be a compound of structure I—*sym.*-diphenyldihydroxydiarsyl. Upon further oxidation this substance would be converted into phenylarsine oxide.



It seemed to us desirable to prepare a series of dihydroxy compounds of the above type which we have called "arsenicols" because of their structural resemblance to pinacols.

One of the several methods which suggested themselves for the preparation of diphenylarsenicol was the hydrolysis of diphenyldi-iododiarsyl, $\text{C}_6\text{H}_5(\text{I})\text{As}-\text{As}(\text{I})\text{C}_6\text{H}_5$. We found that this latter substance can be prepared easily but that, when dissolved, it absorbs oxygen with great rapidity. In fact, a solution of this material is just as reactive toward oxygen as solutions of tetra-aryldiarsyls or triarylmethyls.

In view of this property and other unexpected reactions which diphenyldi-iododiarsyl undergoes it seemed not only desirable but necessary to study a series of diaryldi-iododiarsyls before we undertook the synthesis of the corresponding dihydroxyl derivatives.

We have obtained, in addition to the diphenyl compound, the di-*p*-tolyl-, di-*p*-anisyl-, di- α -naphthyl- and dibiphenyldi-iododiarsyl and found that these substances behave essentially in the same manner as the phenyl analog.

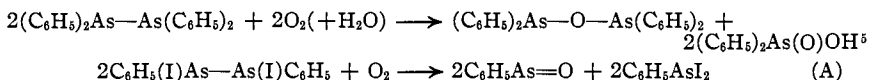
Diphenyldi-iododiarsyl was prepared by the action of crystalline phosphorous acid on phenyldi-iodo-arsine, dissolved in alcohol. The diarsyl had been obtained previously by Michaelis and Schulte³ by this method

² Voegtlin and Smith, *J. Pharmacol.*, **16**, 199 (1920); Voegtlin, *Physiol. Reviews*, **5**, 79 (1925).

³ Michaelis and Schulte, *Ber.*, **14**, 913 (1881); *ibid.*, **15**, 1953 (1882). These investigators also isolated the compound in an impure state from the interaction of phenylarsine oxide, phosphorous and hydriodic acids. Michaelis, *Ann.*, **320**, 333, 337 (1902), states that 2,2',4,4'-tetramethylarsenobenzene and 2,2',5,5'-tetramethylarsenobenzene react additively with iodine to form the corresponding diaryldi-iododiarsyls but no description of these compounds, other than the analyses and melting points, is given. Steinkopf, Schmidt and Smie, *Ber.*, **59**, 1469 (1926), obtained ethylphenyldi-iododiarsyl, $\text{C}_2\text{H}_5(\text{I})\text{As}-\text{As}(\text{I})\text{C}_6\text{H}_5$, from ethylphenyldiarsylene, $\text{C}_2\text{H}_5\text{As}=\text{AsC}_6\text{H}_5$, and iodine.

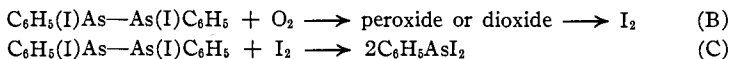
and was described as a very unstable substance which decomposes into phenyldi-iodo-arsine and phenylarsonic acid when exposed to the air.

Dissolved in bromobenzene, tetraphenyldiarsyl⁴ reacts with oxygen, instantly, in the ratio of one molecular equivalent of the diarsyl to *one* molecular equivalent of the gas; under the same conditions diphenyldi-iododiarsyl absorbs oxygen in the proportion of one molecular equivalent of the former to *one-half* of a molecular equivalent of the latter.



The aryarsine oxide and the aryldi-iodo-arsine were isolated, in the case of the phenyl and *p*-tolyl compounds, in good yields with respect to formulation A.

In addition to the difference in the amount of oxygen absorbed, another essential variation in the behavior of tetraphenyldiarsyl and diphenyldi-iododiarsyl is that during the oxidation of the former compound the group $(\text{C}_6\text{H}_5)_2\text{As}-$ remains intact while in the case of the latter substance iodine is eliminated from the radical $\text{C}_6\text{H}_5(\text{I})\text{As}-$. A red color develops during the oxidation of diphenyldi-iododiarsyl and its analogs but disappears very rapidly; if the solution of the diarsyl is shaken too slowly during the interaction with oxygen, the formation of this color may escape notice. The red color⁶ is due, undoubtedly, to the formation of free iodine. The evolution of iodine indicates that formulation A represents the summation of several reactions. Probably the first reaction is one which ensues from diphenyldi-iododiarsyl and oxygen with the formation of a peroxide or dioxide which decomposes spontaneously with the liberation of iodine. The latter reacts rapidly with diphenyldi-iododiarsyl to form phenyldi-iodo-arsine, as we have shown in a separate experiment.



As soon as phenylarsine oxide is formed (formulation A) this compound, too, reacts instantly with iodine, presumably, to form an unstable com-

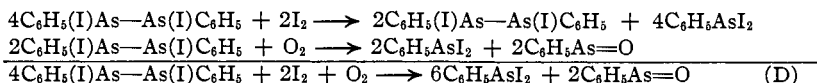
⁴ (a) Blicke and Smith, *THIS JOURNAL*, **51**, 2273 (1929); (b) Blicke, Weinkauff and Hargreaves, *ibid.*, **52**, 780 (1930).

⁵ The initial reaction product may be a peroxide. When the oxidized solution of the tetra-aryldiarsyl is exposed to the moisture in the atmosphere and the solvent then removed, tetraphenylarsyl oxide and diphenylarsinic acid are formed, but so far we have not been able to obtain them in the ratio indicated above.

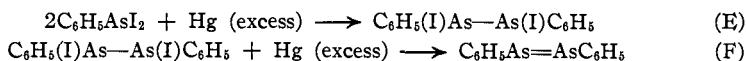
⁶ This phenomenon can be observed best if a saturated ether solution of diphenyldi-iododiarsyl is placed in a tall open cylinder over a small amount of solid diphenyldi-iododiarsyl. An intense red color soon develops in the upper part of the solution and disappears instantly when the mixture is shaken; in a short time the red color reappears. This process can be repeated as long as any unchanged diphenyldi-iododiarsyl is present. The iodine color finally becomes permanent.

pound of the type $C_6H_5(I_2)As=O$. Neither phenylarsine oxide nor phenyldi-iodo-arsine absorbs oxygen.

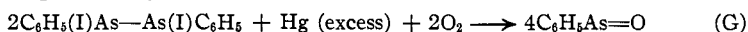
Since iodine interacts with diphenyldi-iododiarsyl to form phenyldi-iodo-arsine, diphenyldi-iododiarsyl should absorb less oxygen after the addition of iodine. Accordingly, it was found that after the addition of two molecular equivalents of iodine, four molecular equivalents of the diarsyl absorb only one molecular equivalent of the gas.



Mercury reacts almost instantly with phenyldi-iodo-arsine to form diphenyldi-iododiarsyl; the latter compound also reacts with mercury, but much more slowly, to form arsenobenzene.

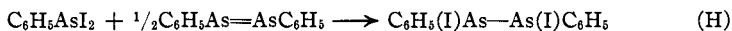


It was stated previously that diphenyldi-iododiarsyl absorbs one-half of a molecular equivalent of oxygen; however, if mercury is added to a solution of diphenyldi-iododiarsyl and the latter then allowed to react with oxygen immediately after addition of the metal, *one* molecular equivalent of the gas is absorbed for each molecular equivalent of the diarsyl. Phenylarsine oxide is the only reaction product formed and this substance was isolated in practically quantitative yield.



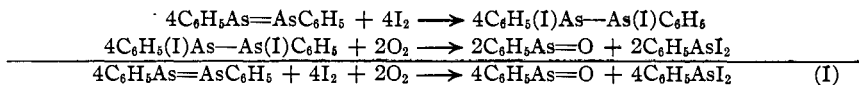
In this instance the diarsyl reacts first with oxygen according to formulation A and the phenyldi-iodo-arsine produced is then converted rapidly by mercury into diphenyldi-iododiarsyl (formulation E). Reactions A and E continue, alternately, until all of the diarsyl is oxidized to phenylarsine oxide. The mercury also reacts with the iodine, as fast as it is liberated, and thus prevents the formation of phenyldi-iodo-arsine from diphenyldi-iododiarsyl and iodine (formulations B and C).

Since it was found that phenyldi-iodo-arsine and arsenobenzene react almost instantly at ordinary temperature to form diphenyldi-iododiarsyl, phenyldi-iodo-arsine and arsenobenzene mixed in accordance with the ratio

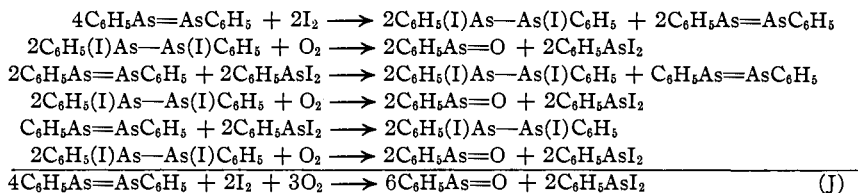


shown in formulation H should absorb rapidly one-half of a molecular equivalent of oxygen (formulation A). This was found to be the case.

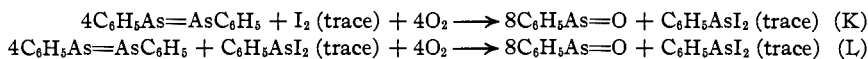
Arsenobenzene, suspended in bromobenzene, does not absorb oxygen. However, if iodine is added to the solution the latter absorbs the gas with great rapidity; furthermore, the amount of the gas which enters into the reaction depends upon the quantity of iodine added. For example, when four molecular equivalents of iodine were used the solution absorbed, very rapidly, two molecular equivalents of oxygen (formulation I) but



when only two molecular equivalent of the halogen were used the solution absorbed three molecular equivalents of the gas (formulation J). If only

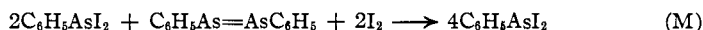


a trace of iodine or phenyldi-iodo-arsine is added to the solution of arsenobenzene, the latter in each case should react with four molecular equivalents of oxygen in accordance with formulations K and L. In these

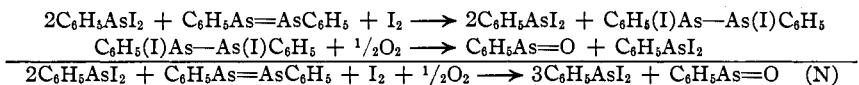


instances we found, however, that the amount of oxygen absorbed was in excess of four molecular equivalents—in the case of iodine the absorption was between five and six molecular equivalents and when phenyldi-iodo-arsine was used the solution absorbed between four and five equivalents of the gas. We have no explanation, at present, for this apparent anomalous behavior.

If phenyldi-iodo-arsine, arsenobenzene and iodine are mixed in the ratio expressed in formulation M, the mixture does not absorb oxygen because



of the quantitative formation of phenyldi-iodo-arsine; but if one-half of the amount of iodine, employed in reaction M, is used the mixture absorbs one-half of a molecular equivalent of oxygen for each two molecular equivalents of diphenyldi-iodo-arsine.



Diphenyldibromodiarsyl was prepared from phenyldibromo-arsine and arsenobenzene. This compound, after isolation, proved to be just as reactive toward oxygen as the corresponding iodo derivative. However, the amount of oxygen absorbed by diphenyldibromodiarsyl is greater than that absorbed by an equivalent quantity of diphenyldi-iododiarsyl and is less than that required for the oxidation of tetraphenyldiarsyl.

Several unsuccessful attempts were made to obtain diphenyldichlorodiarsyl from phenyldichloro-arsine and arsenobenzene.

A series of molecular weight determinations of various diaryldihalo-diarsyls proved that in the event that any of these compounds dissociated

into divalent arsenic radicals the degree of dissociation is too low to be established by the molecular weight method.

Experimental Part

Aryldi-iodo-arsines.—The arylarsine oxides were heated on a steam-bath for two hours with approximately ten times the calculated amount of hydriodic acid (sp. gr. 1.7). The iodides, which precipitated either as oils or solids, were separated, washed with water and dried in a vacuum desiccator over soda lime. Although aryl-di-iodo-arsines can be obtained from aryldichloro-arsines and sodium iodide in acetone⁷ solution, this method, in the case of phenyldi-iodo-arsine, yielded an oily iodide which rapidly turned deep red and gradually deposited a considerable amount of solid material. The phenyl,⁸ tolyl⁹ and anisyl¹⁰ derivatives are oils. The α -naphthyl and the biphenyl compounds, which had not been prepared hitherto, are yellow solids which crystallize readily from benzene.

TABLE I
ARYLDI-iodo-ARSINES

Compound	M. p., °C.	Formula	Iodine analyses ^a	
			Calcd.	Found
α -Naphthyl	106–108	C ₁₀ H ₇ AsI ₂	55.70	55.56
Biphenyl	104–106	C ₁₂ H ₉ AsI ₂	52.69	52.47

^a Thompson and Oakdale method, *THIS JOURNAL*, **52**, 1195 (1930).

Diaryldi-iododiarsyls.—These compounds can be prepared according to the following general methods illustrated in the case of phenyldi-iododiarsyl: (a) six g. of phenyldi-iodo-arsine, suspended in 25 cc. of absolute alcohol, and 10 g. of crystalline phosphorous acid, dissolved in 125 cc. of absolute alcohol, were introduced separately into a free radical apparatus¹¹ of 250 cc. capacity and the latter rotated for twelve hours on a shaking machine. The diarsyl separated in a finely divided, deep yellow, crystalline form. The supernatant alcoholic layer was removed through the side arm of the apparatus with the aid of suction and the product washed four times with anhydrous ether which had been saturated with nitrogen. In order to dry the compound the apparatus was allowed to remain attached to a suction pump for five hours; to avoid decomposition the material should not be heated during this process. The diarsyl was isolated in the manner described previously in the case of tetra-aryldiarsyls.^{4b}

(b) Phenylarsine oxide, suspended in 25 cc. of absolute alcohol, was put into a free radical apparatus. Ten cc. of hydriodic acid (sp. gr. 1.7) and 10 g. of phosphorous acid, dissolved in 125 cc. of absolute alcohol, were then added. The oxide dissolves immediately and after a short time the diarsyl begins to precipitate.

(c) Arsenobenzene, suspended in alcohol, was put into a radical apparatus and treated with phenyldi-iodo-arsine, suspended in the same solvent. The compounds were used in the ratio of one mole of the arseno compound to two and one-half moles of the di-iodide. The mixture was rotated for twelve hours.

(d) One and one-half grams of arsenobenzene, suspended in 25 cc. of benzene which had been saturated with nitrogen, was treated slowly in a radical apparatus with 1.3 g. of iodine dissolved in benzene. The mixture was rotated for three hours.

⁷ Steinkopf and Schwen, *Ber.*, **54**, 1463 (1921).

⁸ Michaelis and Schulte, *ibid.*, **14**, 913 (1881); Burrows and Turner, *J. Chem. Soc.*, **117**, 1376 (1920); Steinkopf and Schwen, *Ber.*, **54**, 1463 (1921).

⁹ LaCoste and Michaelis, *ibid.*, **11**, 1889 (1878); *Ann.*, **201**, 248 (1880).

¹⁰ Michaelis, *ibid.*, **320**, 301 (1902). Bertheim, *Ber.*, **47**, 276 (1914).

¹¹ Gomberg and Cone, *ibid.*, **37**, 2034 (1904). The lower stopcock was eliminated.

The benzene layer was decanted from the solid material which had separated and the latter was washed with ether.

(e) Six grams of phenyldi-iodo-arsine, dissolved in 100 cc. of oxygen-free bromobenzene, was shaken with 10 g. of mercury for fifteen minutes in a tightly stoppered bottle. The mixture was warmed in a bath, without exposure to air, in order to dissolve the diarsyl which had separated, and then filtered into a radical apparatus. The latter was immersed in a bath heated to 80° and about 75 cc. of the solvent was removed under diminished pressure. Ether was then added to precipitate the diarsyl, the solvent removed by decantation and the solid material washed with ether.

Diphenyldibromodiarsyl.—One and one-half grams (0.005 mole) of arsenobenzene and 5.0 g. (0.008 mole) of phenyldibromo-arsine were washed into a free radical apparatus of 100-cc. capacity with the aid of ether. The side arm of the apparatus was connected with a suction pump and after the ether had been removed under diminished pressure the bulb of the apparatus was heated in a glycerol-bath to 135° until a clear yellow liquid was obtained. The diarsyl, which separated in crystalline form when the mixture was cooled, was washed five times with oxygen-free ether in order to remove all excess phenyldibromo-arsine. In order to dry the material, the bulb of the apparatus was evacuated continuously, at ordinary temperature, for five hours. The compound was removed from the apparatus in the manner described previously. Diphenyldibromodiarsyl is a light yellow, crystalline substance which melts, in a tube filled with nitrogen, at 122–124°. Dissolved in bromobenzene, 1.099 g. of the material absorbed 38 cc. of oxygen, under standard conditions of temperature and pressure, in less than thirty seconds.

Anal. Calcd. for $C_{12}H_{10}As_2Br_2$: Br, 34.48. Found: Br, 35.05.

TABLE II

DIARYLDI-IODODIARSYLS

Diarsyl ^{a,b}	M. p., °C. ^c	Oxygen absorp., (N. T. P.)			Iodine analyses ^e		
		Cc.	Sample, g.	% Absorp. ^d	Formula	Calcd.	Found
Diphenyl	176–177 ^f	33	1.569	103	$C_{12}H_{10}As_2I_2$	45.58	45.52
Di- <i>p</i> -tolyl	149–150	31	1.567	105	$C_{14}H_{14}As_2I_2$	43.34	42.87
Di- <i>p</i> -anisyl	135–137	18	0.981	103	$C_{14}H_{14}O_2As_2I_2$	41.10	40.54
Di- α -naphthyl	176–178	18	1.068	105	$C_{20}H_{14}As_2I_2$	38.60	34.35 ^g
Dibiphenyl	244–246 ^h	38	2.304	105	$C_{24}H_{18}As_2I_2$	35.77	32.50 ^g

^a All of these compounds were prepared according to Method (a). In the case of the naphthyl and biphenyl diarsyls the di-iodide was dissolved in the least amount of warm benzene instead of alcohol. ^b The diarsyls listed above are all deep yellow, well-defined crystalline compounds and are insoluble in alcohol. The phenyl compound is slightly soluble in hot benzene and hot chloroform while the tolyl and naphthyl derivatives are quite soluble in these solvents. ^c All melting points were determined in sealed tubes filled with nitrogen. The compounds softened somewhat at temperatures below the melting points, gradually changed in color from yellow to red and melted with the formation of a deep red liquid. ^d Calculated on the basis of formulation A. ^e Thompson and Oakdale method, *THIS JOURNAL*, **52**, 1195 (1930). ^f Michaelis and Schulte [*Ber.*, **14**, 913 (1881); *ibid.*, **15**, 1954 (1882)] recorded no melting point for this substance. ^g A number of iodine analyses were made in the case of the naphthyl and biphenyl compounds but the results obtained were invariably low. Although the material had always been dried to constant weight before analysis, the latter may still have been contaminated by a small amount of solvent or, possibly, by a small quantity of the corresponding arseno compound. ^h Melts with decomposition.

Attempt to Prepare Diphenyldichlorodiarsyl.—There is no apparent reaction between phenyldichloro-arsine and arsenobenzene when the compounds are mixed at ordinary temperature. However, the mixture absorbs oxygen, as is shown by the following experiment.

Six hundred and eight thousandths of a gram (0.002 mole) of arsenobenzene, suspended in 25 cc. of oxygen-free bromobenzene, was put into an absorption bottle. Eight hundred and ninety thousandths of a gram (0.004 mole) of phenyldichloro-arsine was placed in a thin-walled test-tube and the latter introduced into the absorption bottle. When the test-tube was broken and the components were allowed to mix, oxygen was absorbed immediately. The suspended arsenobenzene gradually dissolved and, after the mixture had been agitated continuously for twenty minutes on a shaking machine, a clear, colorless solution was obtained. Seventy cc. (N. T. P.) or 0.003 mole of the gas was absorbed.

When arsenobenzene and excess phenyldichloro-arsine were heated, the former substance dissolved. A crystalline precipitate was obtained when the mixture was cooled but from the latter we were able to isolate only arsenobenzene.

Oxidation Products of Diphenyl- and Di-*p*-tolyl-di-iododiarsyl.—Ten grams of solid diphenyldi-iododiarsyl was exposed to the air for twelve hours. The semi-liquid mass was extracted with a mixture of equal parts of ether and petroleum ether (40–60°)

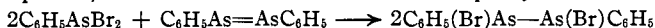
TABLE III
OXYGEN ABSORPTIONS^a

Phenyl-dihalo-arsine moles	Arsenobenzene, mole	Hg, cc.	Iodine, mole	Absorp. found, cc. (N. T. P.)	Absorp. calcd. according to equation, cc.
1 0.004 (I)	..	1 ^b	...	48	45 (E)
2 .004 (I)	..	1 ^c	...	0	0 (E-F)
3 .004 (I)	0.002	44	45 (H)
4005	.	0.0050	62	56 (I)
5005	.	0.0025	88	84 (J)
6002	.	Trace	62	45 (K)
7002	.	Trace	62	45 (K)
8 1 drop (I)	.002	58	45 (L)
9 0.004 (Br) ^d	.002	75	..
10 .004 (Cl)	.002	70	..
11 .004	.002	.	.004	0	0 (M)
12 .004	.002	.	.002	22	22 (N)

1.377 g. of diphenyldi-iododiarsyl and 1 cc. of Hg (F) absorbed 63 cc. after the mixture had been shaken for several minutes in the presence of oxygen; calcd. 56 cc.

^a In the first nine experiments listed, as well as in Expt. 12, the volume of oxygen recorded was absorbed in less than two minutes. In Expt. 10 the absorption was slower, hence the volume recorded in this experiment was that obtained after one-half hour's contact with the gas. ^b The mixture was shaken for ten minutes prior to absorption.

^c The mixture of phenyldi-iodo-arsine and mercury was shaken in a sealed tube for twenty-four hours prior to the absorption. ^d Four thousandths of a mole of phenyldi-bromo-arsine and two thousandths of a mole of arsenobenzene yield, according to the following equation, four thousandths of a mole of diphenyldibromodiarsyl. This



mixture absorbed 75 cc. (N. T. P.) of oxygen. It was found that 1.17 g. (0.0025 mole) of isolated diphenyldibromodiarsyl absorbed 48 cc. (N. T. P.) of oxygen. If exactly four thousandths of a mole of the diarsyl had been used, the absorption would have been 75 cc.

TABLE IV
 MOLECULAR WEIGHT DETERMINATIONS^{a, b}

R	R(X)As—As(X)R	X	Solvent	Δt , °C.	Mol. wt. found	Mol. wt. calcd.
1	Phenyl	I	Benzene	0.3129	527	558
2	Phenyl	I	Chloroform	.1155	559	558
3	Phenyl	I	Biphenyl	.538	528	558
4	<i>p</i> -Tolyl	I	Benzene	.1887	570	586
5	<i>p</i> -Tolyl (oxidized)	I	Benzene	.1023	290	293 ^c
6	α -Naphthyl	I	Benzene	.1056	610	658
7	Phenyl	Br	Benzene	.2739	430	464

^a A considerable number of molecular weight determinations have been made but in order to conserve space we have recorded only the values obtained with the highest concentrations, approximately 3%, of the diarsyl solutions. In several series of duplicate determinations with the same diarsyl, low molecular weight values would be obtained occasionally in one series of experiments. These low values were due, undoubtedly, to the presence of traces of oxygen in the molecular weight apparatus at the time the first pellet of the diarsyl was introduced. The decomposition by oxygen of a diaryldi-iododiarsyl into an arylarsine oxide and an aryldi-iodo-arsene would tend to lower the molecular weight value and after complete oxidation the molecular weight found should be approximately one-half that calculated for the diaryldi-iododiarsyl. In the case of di-*p*-tolyl-di-iododiarsyl a stream of oxygen was passed through a benzene solution of the material after the molecular weight had been determined. Prior to oxidation (Expt. 4) the molecular weight was found to be 570; after oxidation the value 290 (Expt. 5) was obtained. In Expt. 3 the cryoscopic method was used; all other determinations were made by the ebullioscopic procedure with the use of the Menzies apparatus. All solvents used had been saturated with dry, oxygen-free nitrogen and the molecular weight apparatus was filled with nitrogen prior to a determination. A stream of nitrogen passed through the top of the apparatus prevented the entrance of oxygen. Because of the insolubility of dibiphenyldi-iododiarsyl the molecular weight of this substance was not determined. ^b The purity of each diarsyl was established by analysis, oxygen absorption and melting point prior to the molecular weight determination. ^c Approximate value.

in order to remove phenyldi-iodo-arsine. There were obtained 2.45 g. of phenylarsine oxide, m. p. 138–140°, and 7.8 g. of phenyldi-iodo-arsine. The calculated amount (formulation A) of the former substance is 3.0 g. and that of the latter is 7.4 g. In order to identify phenyldi-iodo-arsine it was hydrolyzed with alkali to phenylarsine oxide.

From 1.5 g. of di-*p*-tolyl-di-iododiarsyl there was obtained 0.4 g. of tolylarsine oxide, m. p. 179–182°, and 1.1 g. of tolyldi-iodo-arsine. The latter substance was identified by conversion into the corresponding arsine oxide.

Action of Mercury on Phenyldi-iodo-arsine and Diphenyldi-iododiarsyl.—Six grams of phenyldi-iodo-arsine, dissolved in 125 cc. of oxygen-free benzene, was shaken for three days with 3 cc. of mercury in a tightly stoppered bottle. The reaction mixture was filtered and the residue washed thoroughly with benzene. From the benzene filtrate a very small quantity of triphenylarsine was isolated in the form of the mercuric chloride addition product.¹² The residue was moistened with alcohol and then treated with an aqueous solution of potassium iodide in order to remove mercury salts. Arsenobenzene was obtained and identified by a mixed melting point. The yield was 2.1 g. or 95% of the calculated amount.

¹² A much larger amount of the triphenylarsine mercuric chloride addition product was obtained when arsenobenzene was shaken with mercury and mercuric iodide.

When diphenyldi-iododiarsyl was treated in the manner described above, arsenobenzene was obtained as a reaction product.

Summary

Diphenyl-, di-*p*-tolyl-, di-*p*-anisyl-, di- α -naphthyl- and dibiphenyldi-iododiarsyl as well as diphenyldibromodiarsyl have been prepared. Each of the above-mentioned di-iododiarsyls, in solution, absorbs oxygen with great rapidity but the amount of gas absorbed is only one-half of that required for the oxidation of an equivalent amount of a tetra-aryldiarsyl. The molecular quantity of oxygen absorbed by diphenyldibromodiarsyl is intermediate between the amount required for the oxidation of a diaryldi-iododiarsyl and a tetra-aryldiarsyl.

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

THE PROPERTIES AND MOLECULAR STATE OF CERTAIN ORGANIC ARSENICALS

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During our investigations of diarsyls it became necessary to prepare a variety of simple aromatic arsenicals. Inasmuch as the properties of some of the compounds had not been determined very extensively, we studied a number of them more in detail. It was found that arsenobenzene and certain of its analogs, contrary to most of the statements in the literature, are *colorless, stable* compounds which undergo no decomposition when exposed to the atmosphere or to pure oxygen under ordinary conditions. Maschmann² claims that arsenobenzene reacts explosively with oxygen at ordinary temperature and Palmer and Scott,³ although they obtained arsenobenzene in a colorless state,⁴ took great precautions in the isolation of the material to prevent oxidation.

We found, however, that if traces of certain substances are added to a solution of arsenobenzene the latter begins, instantly, to absorb oxygen and in a comparatively short time has reacted with an amount of the gas which corresponds, in some instances at least, to the quantity of oxygen required for the formation of phenylarsine oxide. Substances discovered so far which induce the absorption of oxygen by arsenobenzene are hydrochloric, hydrobromic, hydriodic, sulfuric and nitric acids, iodine, diphenylbromo-arsine, diphenyliodo-arsine, phenyldichloro-arsine, phenyldibromo-arsine, phenyldi-iodo-arsine and triphenylbromomethane.

¹ Parke, Davis and Company Research Assistant, 1929-1930.

² Maschmann, *Ber.*, **59**, 1143 (1926).

³ Palmer and Scott, *THIS JOURNAL*, **50**, 537 (1928).

⁴ Steinkopf and Dudek [*Ber.*, **62**, 2494 (1929)] reported that arsenobenzene is colorless.