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

DIARSYLS. II. TETRA-ARYLDIARSYLS[1]

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Recently it was discovered[2] in this Laboratory that diarylarsyl iodides, dissolved in ether or benzene, react rapidly with mercury at ordinary temperature to form tetra-aryldiarsyls. Hitherto these compounds have been obtained by reduction of diarylarsinic acids or tetra-arylarsyl oxides with phosphorous acid in hot alcoholic[3] or acetic acid solution. Inasmuch as elevated temperatures, solvents and acids which may interact with the diarsyls are entirely eliminated, the first-mentioned method is especially adapted for the preparation of such extremely reactive compounds as the tetra-aryldiarsyls.

We prepared, previously, solutions of tetraphenyl-, tetra-*p*-tolyl-, tetra-*p*-anisyl-, tetranaphthyl and tetrabiphenyldiarsyl but only the phenyl compound was isolated in the solid state. With the exception of tetraphenyldiarsyl[4] none of the five compounds mentioned had ever been prepared.[5] We have isolated now, in the solid state, all of the diarsyls mentioned above with the exception of tetrabiphenyldiarsyl and, in addition, dibiphenylenediarsyl and 6.6-bisphenoxarsine.

The great interest in the tetra-aryldiarsyls lies in the question as to whether or not they undergo spontaneous dissociation in solution into diarylarsyls, that is, into divalent arsenic radicals, $R_2As—AsR_2 \rightleftharpoons 2R_2As—$. The extreme rapidity with which a solution of tetraphenyldiarsyl and other tetra-aryldiarsyls absorb an amount of oxygen which corresponds to the volume of this gas required for the formation of a peroxide and the great reactivity of the diarsyls toward other reagents indicates that solutions of these substances contain a very reactive arsenic compound,

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[1] This investigation was made possible by a grant from the Faculty Research Fund of the University of Michigan.

[2] Blicke and Smith, THIS JOURNAL, 51, 2272 (1929).

[3] Porter and Borgstrom [*ibid.*, 41, 2050 (1919)] showed that hot alcohol decomposes tetraphenyldiarsyl with the formation of diphenylarsine.

[4] LaCoste and Michaelis, *Ann.*, **201**, 222 (1880); Michaelis and Schulte, *Ber.*, **15**, 1952 (1882); Michaelis, *Ann.*, **321**, 148 (1902); Schlenk, *ibid.*, 394,216 (1912); Porter and Borgstrom, THIS JOURNAL, 41, 2048 (1919); Borgstrom and Dewar, *ibid.*, **44**, 2915 (1922).

[5] Other investigators claim to have obtained in solid form the following aromatic tetra-aryldiarsyls but no special precautions seem to have been taken to prevent oxidation of the diarsyl during the isolation of the latter: tetra-3-nitrophenyl- [Michaelis, *Ann.*, **321**, 149 (1902)], tetra-3-aminophenyl- [French Patent, 440,128; Michaelis, *ibid.*, **321**, 150 (1902)], tetra-3-acetylaminophenyl- [Michaelis, *ibid.*, **321**, 150 (1902)], tetra-3-amino-4-hydroxyphenyldiarsyl [Fargher, *J. Chem. Soc.*, 115, 987 (1919)] and 6,6-bisphenoxarsine [Lewis, Lowry and Bergeim, THIS JOURNAL, **43**, 894 (1921)]. None of these compounds have been studied in detail.

possibly one in which arsenic is in a divalent state. During this investigation we sought to obtain positive proof of a dissociation of tetra-aryldiarsyls through molecular weight determinations.

As a result of our investigation we can only say that in the event any of the five diarsyls tested undergo dissociation, under the conditions used in our experiments, the dissociation in no case exceeds 10%. Unfortunately, due to the magnitude of the errors inherent in our present methods for the determination of molecular weights, trustworthy evidence of dissociation cannot be obtained in the case of compounds which dissociate only to a comparatively slight extent.

A variety of other tetra-aryldiarsyls are being prepared in the hope that compounds may be found which will dissociate to such a degree that positive evidence of dissociation may be secured through molecular weight determinations.

Experimental Part

The preparation of diphenyl-, di-*p*-tolyl-, di-*p*-anisyl- and di-α-naphthylarsyl iodides has been described previously.[6]

Biphenylene-arsyl Iodide.—Biphenylene-arsyl chloride[7] was prepared in the following manner. Seventy-seven g. of diphenyl (0.5 mole). 135 g. of arsenic trichloride (0.75 mole) and 10 g. of aluminum chloride were placed in a flask fitted with a reflux condenser. The flask was heated in a metal-bath for about three and one-half hours. when the temperature of a thermometer which dipped into the mixture reached 165°. Ten g. more of aluminum chloride was added and the mixture heated for about an hour longer, when the temperature reached 185°. The reaction product was then boiled for about fifteen minutes with 250 cc. of benzene and a small quantity of hydrochloric acid. The benzene layer was separated. dried and after removal of most of the benzene the residue was distilled under diminished pressure. The material which boiled between 225–245° under 30-mm. pressure was collected. The yield of crude product was 27 g. After recrystallization from benzene the diphenylene-arsyl chloride melted at 161°. The chloride was dissolved in acetone and treated with one and one-half times the calculated amount of sodium iodide dissolved in the same solvent. After eight hours the mixture was decanted into an equal volume of water. whereupon the yellow iodide precipitated in crystalline form. The iodide was recrystallized from a mixture of benzene and petroleum ether: m. p. 166–167°.

Because of the great insolubility of the diarsyl we isolated only enough of this material for an oxygen absorption. a melting point determination and an analysis.

6-Iodophenoxarsine.—6-Chlorophenoxarsine was prepared by a method described by Pope.[8] The chloride was then converted into the iodide in the usual manner: the

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[6] Blicke and Smith. THIS JOURNAL. **51**, 1565 (1929).

[7] This compound has been obtained by Aeschlimann. Lees. McCleland and Nicklin [*J. Chem. Soc.*. **127**, 66 (1925)] by the reduction of biphenylene-arsinic acid in the presence of hydrochloric acid: the iodide was described also. These investigators made an unsuccessful attempt to prepare the diarsyl by the reduction of the arsinic acid with zinc and hydrochloric acid.

[8] This method is mentioned in an article by Lewis. Lowry and Bergeim. THIS JOURNAL. **43**, 892 (1921).

arsyl iodide melted at 145–146°. From *p*-bromodiphenyl ether,[9] arsenic trichloride and aluminum chloride we obtained a colorless, oily reaction product which, when treated with sodium iodide in acetone solution, yielded a yellow, crystalline product. The structure and properties of this substance will be discussed in a later paper.

Preparation and Isolation of the Diarsyls.—One hundredth mole of the diarylarsyl iodide was put into a three-ounce, narrow-necked bottle and enough dry benzene, which had been saturated previously with dry nitrogen, was added to almost fill the bottle. A stream of nitrogen was passed through the solution for a short time and after the addition of 12 g. of mercury the bottle was stoppered and shaken for ten hours. The solution was then filtered into a special apparatus.[10] The bulb of the apparatus was immersed in a water-bath, the temperature of which was about 70°, and the benzene was removed under diminished pressure.[11] The crystalline residue was washed three times with 10 cc. of oxygen-free, absolute ether and the ether removed through the upper outlet tube with the aid of suction. The solid material in the bulb of the apparatus was heated again in the water-bath (80–90°) under a pressure of 20 mm. for four hours.[12]

The diarsyls were obtained in the form of powders which did not adhere to the sides of the bulb. The apparatus was now put into a cylindrical can which was ten inches high and nine inches in diameter. In the bottom of the latter there had been placed several disks of solid carbon dioxide and a stream of the dry gas was passed into the can. The short tube at the bottom of the bulb was broken and the diarsyl transferred to a test-tube. The diarsyl was then pressed into pellets in a pill machine and each pellet, the average weight of which was about 0.2 g., was placed in a small weighed tube which was just large enough to contain it. All of the above operations were carried out in the can filled with carbon dioxide.

TABLE I

DATA ON COMPOUNDS

Diarsyl	M. p.,[a] °C.	% Absorp., N. T. P.	Formula	Arsenic, % Calcd.	Found
Tetraphenyl	129–130	107	....		
Tetra-*p*-tolyl	165–167	105	$C_{28}H_{28}As_2$	29.18	29.23
Tetra-*p*-anisyl[b]	172–175	107	$C_{28}H_{28}O_4As_2$	25.94	25.74
Tetra-α-naphthyl[c]	249–252	173[d]	$C_{40}H_{28}As_2$	22.79	22.91
6,6-Bisphenoxarsine[e]	176–177	104	$C_{24}H_{16}O_2As_2$	30.61	30.63
o,o'-Dibiphenylenediarsyl	269–273	108	$C_{24}H_{16}As_2$	33.04	33.20

[a] All melting-point determinations were made in sealed tubes filled with nitrogen.

[b] Because of the insolubility of this diarsyl there was used three times the amount of benzene necessary for the preparation of the phenyl analog.

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[9] Suter, THIS JOURNAL, 51, 2585 (1929).

[10] Gomberg and Schoepfle, *ibid.*, 39, 1659 (1917). We modified this apparatus to the extent that the lower stopcock was removed.

[11] At this point the contents of one or two more bottles were siphoned into the apparatus so that 4–5 g. of the diarsyl could be isolated. In one instance we attempted to isolate a much larger quantity of the diarsyl but it was found that the compound retained benzene so tenaciously that the last traces of the solvent could not be eliminated completely by heating the bulb of the apparatus in a water-bath.

[12] In one instance tetraphenyldiarsyl, after it had been washed with ether and dried for a short time with the aid of suction, was placed in a test-tube and dried in a vacuum drying apparatus at 80° under 20-mm. pressure for four hours; 5.1090 g. of the material lost 0.0183 g. in weight. The material was heated for an hour longer but the loss in weight was negligible. The diarsyl seems to be oxidized much more readily when it contains traces of benzene than when it is thoroughly dry.

[c] Prepared from 3.42 g. of di-α-naphthylarsyl iodide. 9 g. of mercury and 90 cc. of bromobenzene.

[d] An absorption considerably over 100% is characteristic for tetra-α-naphthyldiarsyl and for tetrabiphenyldiarsyl.[2] The oxidation of the diarsyls proceeds in two stages. The first stage is the extremely rapid addition of one molecular equivalent of oxygen with the formation of a substance which may be a peroxide. The second stage of oxidation takes place much more slowly and. if moisture is present. the final oxidation products are the tetra-arylarsyl oxide and the diarylarsinic acid. The high absorption obtained immediately upon exposure of tetranaphthyldiarsyl to oxygen might be accounted for. *a priori*. in one of two ways: tetranaphthyldiarsyl decomposes. spontaneously, to a considerable extent in solution into products which absorb more oxygen than the parent substance: such an assumption. however, is disproved by the fact that pure tetranaphthyldiarsyl is obtained in good yield from a solution of the diarsyl upon removal of the solvent. The second stage of oxidation in the case of this substance proceeds with a much greater velocity than is ordinarily the case: at present we are inclined to favor this latter assumption.

[e] Lewis. Lowry and Bergeim. Ref. 5. prepared this substance by reduction of 6-phenoxarsine oxide with phosphorous acid in hot alcoholic solution. It was described as a yellow compound which melted at 159° and oxidized in air to a mixture of phenoxarsinic acid and 6-phenoxarsine oxide.

Molecular Weight Determinations

Procedure.—The Menzies[13] apparatus was used for all boiling point determinations. The apparatus was filled with dry, oxygen-free nitrogen. A short inverted test-tube to which a side arm had been attached was placed over the top of the apparatus and held in position by means of a thin ring of cork. A continuous stream of nitrogen was then passed through the side arm of the test-tube and escaped through a slit in the cork.

For freezing-point determinations the Beckmann apparatus was used and the solutions were agitated by means of a platinum stirrer which was operated by an electromagnet. The solvents used were saturated with nitrogen prior to the molecular weight determinations and a continuous stream of the gas was led through the top of the apparatus.

Before each series of molecular weight determinations the purity and activity of the diarsyl was established by means of melting point and oxygen absorption.

In some instances we demonstrated that the diarsyl had lost little or no activity during the molecular weight determinations. After the completion of a series of determinations in diphenyl the solution was allowed to solidify. The Beckmann tube, which contained the material, was closed with a stopper through which a dropping funnel and an outlet tube had been inserted and was then attached to the absorption apparatus in place of the ordinary absorption bottle. The whole apparatus was

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[13] Menzies. This Journal, **43**, 2309 (1921): Menzies and Wright. *ibid.*, **43**, 2314 (1921).

filled with oxygen[14] and then 50 cc. of bromobenzene was introduced into the Beckmann tube through the dropping funnel. After the solid material had all dissolved and the absorption of oxygen had ceased, 50 cc.[15] was added to the amount of absorbed gas and the volume was calculated for normal temperature and pressure. Since a mixture of bromobenzene and diphenyl had served as a solvent for the diarsyl, a mixture of these two substances was used in the gas buret instead of pure bromobenzene.

Titration with iodine to determine the amount of diarsyl present in solution may give very unreliable results since one of the oxidation prod-

TABLE II

MOLECULAR WEIGHT DETERMINATIONS[a]

	Diarsyl	Concn., %	ΔT, °C.	Mol. wt., Found	Mol. wt., Calcd.
1	Tetraphenyl	0.91	0.0520	455	458
		1.63	.0933	456	
	M. p. 129–130°	2.51	.1452	452	
	Solvent 29.3 cc. A.[b] Eb.[c]	3.39	.1940	456	
Av. of 21 detns. on 4 different samples				455	
2	Tetraphenyl	0.98	.185	419	
	M. p. 129–130°	2.07	.379	434	
	Solvent 20.0 g. C[b], Cry.[c]	3.18	.591	430	
Av. of 7 detns. on 2 different samples				432	
3	Tetraphenyl. B.[b] Eb.			432[d]	458
4	Tetraphenyl. D.[b] Cry.			429	458
5	Tetra-*p*-tolyl. A. Eb.			515	514
6	Tetra-*p*-tolyl. C. Cry.			467	514
7	Tetra-*p*-anisyl. A. Eb.			583	582
8	Tetra-*p*-anisyl. C, Cry.			551	582
9	Tetra-α-naphthyl. A. Eb.			667	658
10	Tetra-α-naphthyl. C. Cry.			615	658
11	6.6-*Bis*-phenoxarsine. A. Eb.			506	490
12	6.6-*Bis*-phenoxarsine. C, Cry.			460	490

[a] In order to conserve space. complete experimental data has been given for only two series of determinations.

[b] A represents benzene. B ethyl acetate. C diphenyl and D naphthalene.

[c] Eb.—ebullioscopic method: Cry.—cryoscopic method.

[d] In this instance. as well as those which follow. the values recorded represent the average of 4 to 8 determinations on several different samples of material.

In those instances in which an oxygen absorption was carried out after the completion of the molecular weight determinations. the following results were obtained: Expt. 2. 102%: Expt. 6. 103%: Expt. 8. 103%: Expt. 10. 168%; Expt. 12. 109%.

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[14] A possible refinement to the procedure would be the addition of a small quantity of paraffin. which had been warmed just enough to allow it to flow through the dropping funnel. to the Beckmann tube. The paraffin would congeal and protect the solid surface of the diarsyl solution from oxidation while the apparatus was being filled with oxygen.

[15] Due to a possible contraction in volume when the solvents were mixed. the volume of the gas displaced by the bromobenzene may have been slightly less than 50 cc.

ucts of the diarsyl—the tetra-aryldiarsyl oxide—also decolorizes, **instantly**, iodine dissolved in organic solvents.

Discussion of Results

Schlenk[16] obtained the value of 462 for the molecular weight of tetraphenyldiarsyl in boiling benzene; the calculated value is 458. Porter and Borgstrom[4] found 755 and 765 in naphthalene by the cryoscopic method. Borgstrom and Dewar[4] obtained an initial value of 686 in naphthalene but noticed a gradual increase in molecular weight as the solution of the diarsyl aged. Thus, after four hours, the molecular weight was found to be 766.

Our results differ materially from those of the last mentioned investigators. In boiling benzene we found that the molecular weight value remained perfectly constant for a period of two hours and in naphthalene there was no appreciable increase during a three-hour period of observation. Furthermore, the molecular weight of tetraphenyldiarsyl, determined in naphthalene, never exceeded the value 458.

It can be seen from the table that the average molecular weight values obtained in boiling benzene correspond on the whole quite well with the calculated values. However, the average molecular weights found in diphenyl are uniformly low. While we cannot state that these low values represent dissociation, it seems that the differences between the calculated molecular weights for the diarsyls and the molecular weights found are somewhat too large to represent experimental errors. If the results obtained with biphenyl as a solvent are calculated in terms of dissociation, it will be found that the amount of possible dissociation is from 6–10%.

Our procedures were tested for accuracy by molecular weight determinations of pure tetraphenylarsyl oxide. The calculated molecular weight of this substance is 474. In boiling benzene the average value of seven determinations was 472; in diphenyl, by the freezing-point method, the average value of three determinations was 467. All of these molecular weight determinations were carried out in a stream of dry, oxygen-free nitrogen.

All of the diarsyls which we isolated are colorless substances and yield colorless solutions when dissolved with the exception of 6,6-*bis*-phenoxarsine, which was yellow. Most of the crude diarsyls were somewhat yellow and tetra-*p*-anisyldiarsyl was distinctly yellow but the color was found to be due to the presence of an impurity which was removed when the diarsyl was washed with ether.

When protected from air and light the solid diarsyls are stable, at least over a period of several days.

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[16] Schlenk, *Ann.*, **394**, 216 (1912).

Summary

A number of tetra-aryldiarsyls have been isolated in the solid state. Molecular weight determinations have shown that in the event any of the diarsyls used in our experiments undergo dissociation, the magnitude of the dissociation, at 80°, does not exceed 10%.

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THE EFFECT OF HEAT UPON *d*-ALPHA-PINENE[1]

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In the paper on Port Orford cedar wood oil by Thurber and Roll[2] the suggestion is made that since the pinene from the oil studied did not form a trace of the inactive nitroso chloride, it is probable that the product is a *d*-α-pinene isomeric with the ordinary form of *d*-α-pinene which is isolated from American turpentine oil. The purpose of this paper is to present some evidence in support of that suggestion.

Smith[3] determined the rate of racemization of *d*-α-pinene and calculated its heat of activation. He suggested that since α-pinene has two asymmetric carbon atoms "it would be expected that four isomeric modifications of the molecule, that is, two dextro and two levo forms, should exist." We would add that geometric isomers might also be expected because of the presence of the double bond. Many investigators have assumed that only two of these isomers, one dextro and one levo, are stable enough under ordinary conditions so that they may be isolated. However, a consideration of some of the common derivatives of α-pinene, such as the hydrochloride and the nitroso chloride, might lead one to a different conclusion. Thus we find that α-pinene nitroso chloride when prepared from highly optically active pinene is unstable in the air and is entirely different from the product prepared from inactive pinene. Also, pinene hydrochloride prepared from *d*-pinene is reported to be inactive, while that prepared from *l*-pinene is reported to have a negative rotation, the numerical value varying with the activity of the pinene used in the preparation. Likewise, the constants, such as melting points, reported in the literature for these compounds vary over a considerable range. It is clear that all of these differences which have been noted could be accounted for readily by assuming that the derivatives prepared, which show differences in properties, were made not from the same compound but from isomeric compounds. Rather than make such an assumption the differences noted are generally ascribed to differences in molecular aggregation or to degree of purity of the sample examined.

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[1] Revised paper: original received February 23, 1928.

[2] Thurber and Roll, *Ind. Eng. Chem.*, 19, 739 (1927).

[3] Smith, THIS JOURNAL, 49, 43 (1927).