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.

ANN ARBOR, MICHIGAN

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

THE PROPERTIES AND MOLECULAR STATE OF CERTAIN ORGANIC ARSENICALS

BY F. F. BLICKE AND F. D. SMITH[1]

RECEIVED MARCH 12, 1930 PUBLISHED JULY 3, 1930

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. Maschmann[2] 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.

The fact that other investigators have reported unsubstituted aromatic arseno compounds[5] to be unstable toward oxygen is due, undoubtedly, to the circumstance that the arseno compounds obtained by them were contaminated by traces of impurities. The statements that their arseno compounds were colored and the fact that they melted at temperatures much lower than those found by us also lead one to this conclusion. Impurities may have been introduced as the result of either insufficient or too complete reduction of the arylarsonic acid or the arylarsine oxide from which the arseno compounds were obtained. In the former case there may have been produced small amounts of a diaryldihydroxydiarsyl, R(OH)As-As(OH)R, a type of compound which will be discussed in a later paper; in the latter instance a small quantity of a diaryldiarsyl R(H)AsAs(H)R, or an arylarsine, $RAsH_2$, may have been formed. Furthermore, it is possible that the arseno compounds may have been contaminated with traces of such substances as have been listed above.

Phenylarsine oxide, phenylarsine sulfide, phenylarsine imide, arsenobenzene and a number of aromatic analogs of these compounds exist, when dissolved, in an associated state and the degree of association is dependent upon the solvent in which the compound is dissolved.[6]

Certain regularities have been observed as far as the substances which we have investigated are concerned. Thus compounds in which the arsenic atom is linked by a single bond to another atom except arsenic[7] are stable toward oxygen and yield normal molecular weight values; these compounds have been placed in Group I. Compounds which contain an arsenic atom attached to arsenic or some other atom by a double bond do not react with oxygen under ordinary conditions and exist, in solution, in an associated state; these have been placed in Group II. Finally, arsenicals in which an arsenic atom is attached directly to another arsenic atom by a single bond react instantly with oxygen under ordinary conditions. Based on molecular weight determinations and chemical behavior there is some indication that such compounds may dissociate into divalent arsenic radicals, although the experimental results obtained so far are not conclusive.[8] Substances of the latter type represent Group III.[9]

Group I—Normal molecular weight, stable toward oxygen.

Group II—Abnormal molecular weight (association), stable toward oxygen.

Group III—Molecular weights somewhat abnormal (dissociation ?), react with oxygen instantly.

---

[5] The behavior of substituted aromatic arseno compounds is being investigated.

[6] Undoubtedly temperature is another factor which affects the degree of association.

[7] It is possible that compounds which contain arsenic attached to phosphorus, nitrogen, antimony or bismuth would behave in a similar manner.

[8] Blicke, Weinkauff and Hargreaves, This Journal, **52**, 780 (1930).

[9] Whether or not all aromatic arsenicals can be grouped in accordance with the above scheme can only be determined by a more extensive investigation.

GROUP I

$(C_6H_5)_2AsI$
$C_6H_5AsCl_2$ $(C_6H_5)_3As$
$(C_6H_5)_2As{-}O{-}As(C_6H_5)_2$
$(p\text{-}CH_3C_6H_4)_2As{-}O{-}As(C_6H_5CH_3\text{-}p)_2$
$(\alpha\text{-}C_{10}H_7)_2As{-}O{-}As(C_{10}H_7{-}\alpha)_2$
$(C_6H_5)_2As{-}S{-}As(C_6H_5)_2$

GROUP II

$(C_6H_5As{=}O)_x$ $(p{-}CH_3C_6H_4As{=}O)_x$
$(p\text{-}CH_3OC_6H_4As{=}O)_x$
$(C_6H_5As{=}S)_x$ $(C_6H_5As{=}NH)_x$
$(C_6H_5As{=}AsC_6H_5)_x$
$(p\text{-}CH_3C_6H_4As{=}AsC_6H_4CH_3\text{-}p)_x$
$(p\text{-}CH_3OC_6H_4As{=}AsC_6H_4OCH_3\text{-}p)_x$

GROUP III

$R_2As{-}AsR_2$[a] $R(I)As{-}As(I)R$[b]

[a] The properties and molecular weights of a series of aromatic compounds of this type are discussed by Blicke and Smith, THIS JOURNAL, **51**, 2272 (1929), and by Blicke, Weinkauff and Hargreaves, *ibid.*, **52**, 780 (1930). Compounds of this type will be described in our next publication.

Experimental Part

Arylarsine Oxides.—All of the oxides with the exception of phenylarsine oxide were prepared as outlined previously.[10] In order to obtain phenylarsine oxide one part of phenylarsonic acid,[11] dissolved in two parts of concd. hydrochloric acid, was reduced to phenyldichloro-arsine with sulfur dioxide and a trace of potassium iodide. The dichloro compound was purified by distillation under diminished pressure. It was then added, drop by drop, with vigorous stirring to an excess of aqueous alkali. The alkaline solution of phenylarsine oxide was filtered and the oxide precipitated by the addition of ammonium chloride. The crude, dry oxide was dissolved in chloroform and precipitated by the addition of ether; m. p. 142–144°.

Phenylarsine Sulfide.—This substance was prepared from phenyldichloro-arsine and hydrogen sulfide in alcoholic solution.[12] The sulfide, which separated as an oil, was dissolved in hot benzene, filtered, cooled and precipitated with alcohol. After recrystallization from bromobenzene the compound melted at 174–176°. Schulte recorded the melting point at 152°.

Anal. Calcd. for C_6H_5AsS: S, 17.42. Found: S, 17.60.

For the analysis of sulfur compounds we used a modification of the procedure developed by Wolesensky[13] for the determination of sulfur in rubber.[14] The sample, 0.5–1.0 g., is treated, cautiously, with 10 cc. of concd. nitric acid (sp. gr. 1.42) in a 300-cc. Kjeldahl flask. After the initial reaction has subsided the mixture is boiled until the organic matter is charred completely. Twenty cc. of 70% perchloric acid is added and the mixture heated until a clear, colorless solution is obtained. The nitric acid is then removed completely by boiling the mixture; the latter should be heated until fumes of perchloric acid become pronounced. The solution is transferred to a 800-cc. beaker and diluted to 400 cc. After neutralization with sodium hydroxide and the addition of 5 cc. of concd. hydrochloric acid, $N/4$ barium chloride solution is added slowly to the hot solution until precipitation is complete. The mixture is heated for an hour on a hot-plate, filtered, the precipitate washed with hot water and ignited.

Arsenic and sulfur can be determined in the same sample, provided the latter does not contain bromine or iodine, in the following manner: after decomposition of the organic matter and the removal of the nitric acid as described above, 10 g. of hydrazine

---

[10] Blicke and Smith, THIS JOURNAL, **51**, 3480 (1929).

[11] Bart, *Ann.*, **429**, 76 (1929).

[12] Schulte, *Ber.*, **15**, 1953 (1882).

[13] Wolesensky, *Ind. Eng. Chem.*, **20**, 1234 (1928).

[14] We wish to express our indebtedness to Mr. J. J. Thompson and Mr. U. O Oakdale for their assistance in this part of the investigation.

hydrochloride, 110 cc. of concd. hydrochloric acid and 1 g. of potassium bromide are added. The arsenic trichloride is then distilled[15] and titrated with $N/10$ potassium bromate; methyl orange is used as indicator.

The residue is treated with nitric acid to destroy the excess hydrazine hydrochloride and boiled until fumes of perchloric acid appear. The subsequent procedure for the determination of sulfur is the same as described above.

If the sample contains only arsenic the following process can be used. After decomposition of the organic matter and removal of the nitric acid the perchloric acid solution is diluted to 100 cc. The solution is then treated with sulfur dioxide in order to reduce the arsenic to the trivalent state. Excess sulfur dioxide is expelled by heat. The mixture is cooled to 60°, 25 cc. of hydrochloric acid is added and the arsenite is titrated with $N/10$ potassium bromate with methyl orange as indicator.

Arseno Compounds.—The following method was found most convenient for the preparation of these substances. The aryldichloro-arsines were dissolved in hot acetone and treated with approximately five times the calculated amount of a 50% solution of hypophosphorous acid. The arseno compounds crystallized from the hot solution. They were filtered, washed with acetone and recrystallized from bromobenzene. No colored by-products were obtained.

TABLE I

ARSENO COMPOUNDS

R As=As R	M. p., °C.	Formula	Arsenic analyses[a] Calcd.	Found
Phenyl,[b] colorless	212–213	$C_{12}H_{10}As_2$	49.34	49.34
p-Tolyl,[c] colorless	218–219	$C_{14}H_{14}As_2$	45.18	45.11
p-Anisyl,[d] colorless	230–232	$C_{14}H_{14}As_2O_2$	41.20	41.15

[a] The method of Thompson and Oakdale described above was used in the determination of arsenic. [b] Other melting points which have been recorded are 195° [Palmer and Scott, THIS JOURNAL, **50**, 539 (1928)], 196° [Michaelis and Schulte, *Ber.*, **14**, 912 (1881)], 208° [Binz, Bauer and Hallstein, *ibid.*, **53**, 427 (1920)], and 212° [Michaelis and Schäfer, *ibid.*, **46**, 1742 (1913)]. [c] Michaelis [*Ann.*, **320**, 301 (1902)] stated the melting point to be 184°. [d] Michaelis [*ibid.*, **320**, 299 (1902)] described this substance as a yellow compound which decomposed at 200°.

TABLE II

ABSORPTION OF OXYGEN BY ARSENOBENZENE IN THE PRESENCE OF CERTAIN COMPOUNDS

Arsenobenzene dissolved in 20 cc. of bromobenzene,[a] g.	Substance added		Cc. of oxygen absorbed after given time (N. T. P.)	Cc. of oxygen required for phenylarsine oxide
0.608	HCl	5 Drops	50 (30 min.)	44.8
.608	HBr	5 Drops	44 (15 min.)	44.8
.608	HI	2 Drops	70 (15 min.)	44.8
.608	H_2SO_4	2 Drops	26 (30 min.)	44.8
.608	H_2SO_4	2 Drops	45 (60 min.)	44.8
.608	HNO_3	2 Drops	87 (5 min.)	44.8
.608	I	Trace	62 (5 min.)	44.8
.608	$C_6H_5AsI_2$	1 Drop	58 (5 min.)	44.8

[a] Bromobenzene was chosen as a solvent because of its low vapor pressure. The absorption apparatus used was that designed by Gomberg and Schoepfle, THIS JOURNAL, **39**, 1661 (1917).

---

[15] Scott, "Standard Methods of Chemical Analysis," D. Van Nostrand Company, **1927**, Vol. I, p. 39b.

Hitherto, aromatic arseno compounds have been obtained by reduction of an arylarsonic acid or an arylarsine oxide, in alcoholic solution, with phosphorous or hypophosphorous acid.

TABLE III

MOLECULAR WEIGHT DETERMINATIONS

Compound	Solvent[a,b]	Δt, °C.[c]	Mol. wt. found, A	Mol. wt. calcd., B	A/B
$(C_6H_5)_2AsI$	Camphor	11.3	354	356	0.99
$C_6H_5AsCl_2$	Benzene	0.1968	234	223	1.05
$(C_6H_5)_3As$	Camphor	22.5	313	306	1.02
$(C_6H_5)_4As_2O$	Benzene	0.1658	472	474	0.99
$(\alpha\text{-}C_{10}H_7)_4As_2O$	Naphthalene	.059	683	674	1.01
$(C_6H_5)_4As_2S$	Camphor	8.0	499	490	1.02
$C_6H_5As{=}O$	Biphenyl[d]	0.133	664	168	3.94
$C_6H_5As{=}O$	Carbon tetrachloride[e]	.0686	672	168	4.00
$C_6H_5As{=}O$	Benzene	.0955	663	168	3.94
$C_6H_5As{=}O$	Camphor	17.5	672	168	4.00
$p\text{-}CH_3C_6H_4As{=}O$	Benzene	0.0948	716	182	3.93
$p\text{-}CH_3C_6H_4As{=}O$	Chloroform	.120	554	182	3.04
$p\text{-}CH_3C_6H_4As{=}O$	Camphor	16.2	727	182	3.99
$p\text{-}CH_3OC_6H_4As{=}O$	Benzene	0.0869	768	198	3.88
$p\text{-}CH_3OC_6H_4As{=}O$	Chloroform	.1626	395	198	1.99
$p\text{-}CH_3OC_6H_4As{=}O$	Camphor	15.0	785	198	3.97
$C_6H_5As{=}S$	Biphenyl	0.240	738	184	4.01
$C_6H_5As{=}S$	Carbon tetrachloride	.0152	743	184	4.04
$C_6H_5As{=}S$	Camphor	20.0	740	184	4.02
$C_6H_5As{=}NH$[f]	Benzene	...	642	167	3.84
$C_6H_5As{=}AsC_6H_5$[g]	Benzene	0.0205	895	304	2.94
$C_6H_5As{=}AsC_6H_5$[g]	Benzene	.0216	915	304	3.01
$p\text{-}CH_3C_6H_4As{=}AsC_6H_4CH_3$	Chloroform	.0241	810	332	2.44
$p\text{-}CH_3C_6H_4As{=}AsC_6H_4CH_3$	Chloroform	.0444	832	332	2.54
$p\text{-}CH_3OC_6H_4As{=}C_6H_4OCH_3$	Chloroform	.0271	1080	364	2.97
$p\text{-}CH_3OC_6H_4As{=}C_6H_4OCH_3$	Chloroform	.0434	1270	364	3.49

[a] The constant for each solvent was determined by the use of benzophenone. [b] The Rast method, *Ber.*, **55**, 1051 (1922), was employed whenever camphor was used as a solvent. Molecular weights were determined in benzene, chloroform and carbon tetrachloride by the ebullioscopic procedure in the Menzies apparatus, THIS JOURNAL, **43**, 2309, 2314 (1921). The cryoscopic method was used in the case of naphthalene and biphenyl. [c] In many instances, because of the limited solubility of the compounds in the solvents employed, higher values for Δt than those recorded could not be obtained. [d] Purification of biphenyl, Chipman and Peltier, *Ind. Eng. Chem.*, **21**, 1106 (1929). [e] The constant for carbon tetrachloride is given by Menzies and Wright, THIS JOURNAL, **43**, 2320 (1921), as 32.4. By the use of benzophenone, we determined the constant to be 34. This latter value was used in our calculations. [f] The molecular weight of this compound has been determined very recently by Ipatiew, Rasuwajew and Stromski, *Ber.*, **62**, 604 (1929). The cryoscopic method was used with benzene as a solvent. The molecular weight value given in the above table is that obtained by these investigators. [g] Michaelis and Schulte, *ibid.*, **46**, 1742 (1913), determined the molecular weight of arsenobenzene in benzene by the ebullioscopic method. They obtained the value 399. Palmer and Scott, THIS JOURNAL, **50**, 539 (1928), with naphthalene as a solvent found the molecular weight to be 642; in benzene, by the ebullioscopic method, 402 and in carbon disulfide 334.

Summary

The properties and molecular weight determinations of a number of simple aromatic arsenic compounds have been recorded. Some of these compounds are stable in air, others absorb oxygen instantly; certain arseno compounds, indifferent toward oxygen, react instantly with the gas in the presence of traces of certain reagents. A number of aromatic arsenicals which contain an arsenic atom attached to arsenic or some other atom by a double bond are associated in the dissolved state.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE MAGNETIC PIGMENT CO., TRENTON, N. J.]

SUBSTITUTION OF ONE ATOM OF NITROGEN FOR THREE ATOMS OF CHLORINE IN ORGANIC COMPOUNDS. I. ACTION OF AMMONIUM CHLORIDE ON BENZO-TRICHLORIDE

BY PETER FIREMAN

RECEIVED MARCH 19, 1930 PUBLISHED JULY 3, 1930

The present paper describes some work in continuation of an investigation begun more than a quarter of a century ago and of which the first contribution was published[1] in 1904. The investigation was interrupted and has only lately been resumed.

While the first paper reported the results obtained from the study of the action of ammonium chloride on metallic chlorides, the present communication is concerned with the action of sal ammoniac on benzo-trichloride, is concerned with the beginning of a study of the substitution of one atom of nitrogen for three atoms of chlorine in organic compounds.

I. It was expected that benzo-trichloride and ammonium chloride when heated in a closed tube would react as follows

$$C_6H_5CCl_3 + NH_3HCl = C_6H_5CN + 4HCl$$

In accordance with the above equation monomolecular quantities of benzo-trichloride and ammonium chloride are required. I soon learned, however, that only with an excess of at least 60% of benzo-trichloride a smooth reaction takes place whereby all the ammonium chloride is used up in the formation of benzonitrile. The experiments here described were all carried out using such an excess of benzo-trichloride.

In the end the following procedure was adopted. The glass tubes contained each 2.14 g. (4 mols) of ammonium chloride and 12.52 g. (6.4 mols) of benzo-trichloride. The heating took place between 210 and 220°. Heating periods of four to six hours are convenient. As with the quantities of the reacting bodies indicated, nearly 6 g. of hydrogen chloride was set

---

[1] Fireman, THIS JOURNAL, 26, 741 (1904).