Solution is the reverse of gelation. Swelling is determined by osmotic forces and the Donnan equilibrium.

The influence of electrolytes, of varying hydrogen-ion concentration, and of the valence of the combining ion has been studied upon several of the characteristic properties of gelatin and found to be entirely in agreement and to give additional evidence in support of the theory presented.

Data on the mutarotation of gelatin were found to be in accord with the theory.

The occlusion theory of Loeb is reviewed and found not to be out of harmony with the present theory, but rather to explain the distribution of absorbed water and its variation with hydrogen-ion concentration mathematically in terms of the Donnan equilibrium.

PITTSBURGH, PENNSYLVANIA

THE REACTIONS OF THE ARSINES. II. CONDENSATION OF AROMATIC PRIMARY ARSINES WITH ALDEHYDES[1]

BY CHARLES SHATTUCK PALMER WITH ROGER ADAMS[2]

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The arsines, in spite of their close relationship in constitution to the amines, have been investigated only to a slight extent. The known reactions of the primary arsines are limited to: (1) the ready oxidation by air or inorganic oxidizing agents to arseno compounds, arsine oxides or arsonic acids;[3] (2) the replacement of hydrogen bound to arsenic by halogens or sulfur by treatment with halogens, sulfur, or compounds which readily give up these elements;[4] (3) the formation of quaternary arsonium halides by heating with alkyl halides;[5] (4) the condensation with compounds of the type $RAsO$, $RSbO$, $RAsCl_2$, $RSbCl_2$, $SbCl_3$, $BiBr_3$, etc., to yield compounds of the type $RAs=AsR$, $RAs=SbR$, $RAs=BiBr$, etc.[6] In addition might be mentioned the fact that the arsines

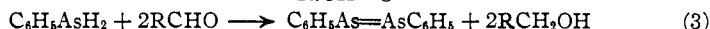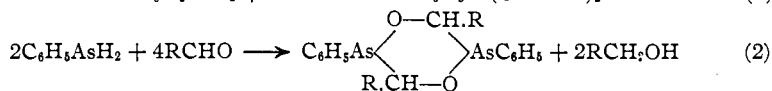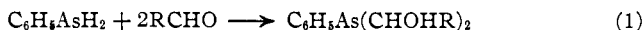[3] Ber., **34**, 3597, 3599 (1901); Am. Chem. J., **33**, 124, 144, 149 (1905); **40**, 105ff (1908).

[4] Am. Chem. J., **33**, 126, 150 (1905); **40**, 105 (1908).

[5] Ibid., **33**, 128, 145, 152 (1905); **40**, 112 (1908).

[6] Ibid., **40**, 108 (1908); Ber., **46**, 3564 (1913). Ger. pat. 254,187; 269,743; 269,744; 269,745; 270,259.

show practically no basicity. The lack of study of the more common reactions such as take place with primary amines has led to a further investigation of the arsines. This paper reports the results of the condensation between primary aromatic arsines and aldehydes.

In the literature may be found two instances in which attempts have been made to condense arsines with aldehydes. The first is a statement by Dehn[7] that formaldehyde and gaseous methylarsine do not react. It is also stated in a German patent[8] that 3-amino-4-hydroxyphenylarsine reacts with benzaldehyde-*m*-sulfonic acid, but in this instance only the amino group reacts with the aldehyde. In a reliminary article published a short time ago,[9] it was pointed out that phenylarsine reacts readily with aldehydes to give an addition compound composed of two molecules of aldehyde and one of arsine. Further investigation of this reaction has shown that the conditions are a very important factor in the nature of the products obtained. It is possible to cause the aromatic arsines to react with the aldehydes in three ways as illustrated by Equations 1, 2 and 3.

$$C_6H_5AsH_2 + 2RCHO \longrightarrow C_6H_5As(CHOHR)_2 \tag{1}$$

$$2C_6H_5AsH_2 + 4RCHO \longrightarrow C_6H_5As{\overset{O-CH.R}{\underset{R.CH-O}{\big<}}}AsC_6H_5 + 2RCH_2OH \tag{2}$$

$$C_6H_5AsH_2 + 2RCHO \longrightarrow C_6H_5As{=}AsC_6H_5 + 2RCH_2OH \tag{3}$$

The first reaction takes place readily to give yields of 60–95% when phenylarsine and an excess of aromatic or aliphatic aldehyde and a little conc. hydrochloric acid, with or without a solvent, are stirred together vigorously and the temperature kept down by means of ice water. For the condensation with aromatic aldehydes, the best results are obtained by the use of anhydrous hydrogen chloride but this method cannot be employed with the aliphatic aldehydes. These products, $C_6H_5As(CHOHR)_2$, are, in general, oils in the aliphatic series and solids in the aromatic series, and possess decided stability toward water, dil. alkalies, cold or hot, and cold dil. acids. This behavior forms a striking contrast to that of the isomeric esters[10] of phenylarsenious acid, $C_6H_5As(OCH_2R)_2$.

The substances derived from aliphatic aldehydes and from some of the aromatic aldehydes are oxidized slowly in air with the formation of an arsonic acid and aldehyde. The oxidation goes much more rapidly when the substances are dissolved in a solvent such as carbon tetrachloride, even causing the reaction mixture to heat up under these conditions.

$$2 RAs(CHOHR)_2 + 3O_2 \longrightarrow 2 RAsO_3H_2 + 4RCHO$$
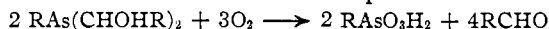
Oxidizing agents such as potassium permanganate and nitric acid cause

[7] Dehn, *Am. Chem. J.*, **40**, 108 (1908).

[8] Ger. pat. 272,035.

[9] THIS JOURNAL, **42**, 2375 (1920).

[10] *Ann.*, **320**, 286 (1902).

the decomposition of both the aliphatic and aromatic aldehyde deriva-
tives to take place in the same way as the oxidation with air. It is particu-
larly noticeable that these substances with oxidizing agents, halogens, phos-
phorus pentachloride, and phenylarsenious chloride, act exactly as though
they were mixtures of phenylarsine and aldehyde. These reactions are
described in more detail in the experimental part of this communication.

The aliphatic derivatives may be titrated quantitatively in ether so-
lution with iodine, under which conditions the following reaction immedi-
ately takes place.

$$RAs(CHOHR)_2 + 2I_2 \longrightarrow RAsI_2 + 2HI + 2RCHO.$$
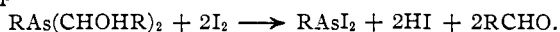
The aromatic aldehyde derivatives react slowly with iodine solution but
quantitative titration is impossible.

The compounds are decidedly stable toward reducing agents and also
toward dehydrating agents (with the exception of anhydrous hydro-
chloric acid, acid chlorides or acid anhydrides under certain conditions).

The aliphatic aldehyde compounds form unstable addition products
with halogen acids; no such addition products with other tertiary ar-
sines have been described. The substances also form characteristic
stable addition compounds with chloroplatinic acid.

It might be expected that the products would show reactivity with acid
chlorides or anhydrides or with other hydroxyl group reagents. They do
not, however, give the desired derivatives. Moreover, they do not react
with methyl or ethyl magnesium iodide to give methane or ethane. The
action of the acid chlorides and anhydrides is explained below but the
unexpected non-reactivity of the Grignard reagent is not yet clearly under-
stood. It seems probable that a soluble addition compound is immedi-
ately produced which prevents a reaction with the hydroxyl groups.
Water decomposes the Grignard mixture into the unchanged aldehyde-
arsine addition product and the normal decomposition products of the
Grignard reagent. In spite of the fact that no simple derivatives of these
aldehyde-arsine compounds could be obtained except the addition prod-
ucts with chloroplatinic acid, the formula which has already been suggested
is the only one which will account for the known reactions.

The cause for the non-formation of the normal derivatives of the hy-
droxyl groups can be accounted for by the fact that certain dehydrating
agents such as acetyl chloride, acetic anhydride or even anhydrous hydro-
gen chloride cause a secondary reaction to take place readily. Two
molecules of these *bis-α*-hydroxy tertiary arsines by this treatment lose
2 molecules of alcohol with the production of rings which may be desig-
nated as tetrahydro-1,4,2,5-dioxdiarsines.
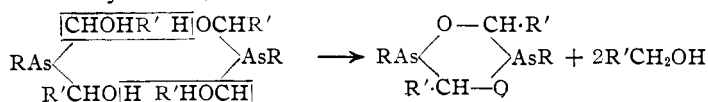
These compounds are thus derivatives of the basic ring 1,4,2,5,-dioxdiar-

$$\text{sine having the structure } \underset{(5)}{As} \underset{\underset{(6)\quad(1)}{CH-O}}{\overset{\overset{(4)\quad(3)}{O-CH}}{\diagdown}} As(2).$$
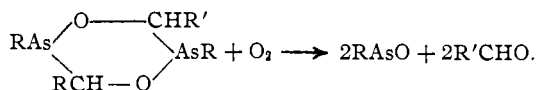
They represent the second

type of substance which can be obtained directly from primary aromatic arsines and aldehydes. They are formed by merely allowing a mixture of aromatic arsine and aldehyde to remain for a day or two in the presence of anhydrous hydrogen chloride at ordinary temperature. Under these conditions, the amount of the product which consists of *bis-α*-hydroxy tertiary arsine is small and the amount of the tetrahydro-dioxdiarsine large.

The formation of the tetrahydro-dioxdiarsines as just described undoubtedly takes place in two steps—the formation first of the *bis-α*-hydroxy tertiary arsines and then the further condensation of these latter products to tetrahydro-dioxdiarsines. This mechanism was proved by treating pure *bis-α*-hydroxy tertiary arsines with dry hydrogen chloride and obtaining from the reaction mixture, after standing several days, tetrahydro-dioxdiarsines. The presence of the water in the hydrochloric acid used to catalyze the formation of the *bis-(α*-hydroxyalkyl) arsines evidently prevents further condensation. No ring compounds have been isolated as yet when using aromatic aldehydes; as mentioned before, anhydrous hydrochloric acid causes aromatic aldehydes and arsines to condense to a very good yield of *bis-(α*-hydroxybenzyl) arsines and no secondary condensation apparently takes place.

A reaction of particular interest is that between paraformaldehyde and phenylarsine in the presence of aqueous hydrochloric acid. The condensation is carried out in the usual way but a product having the formula $C_6H_5As(CH_2OH)_2$ cannot be isolated. During the distillation decomposition occurs, and the final product is the corresponding tetrahydrodioxdiarsine.

These ring compounds are unaffected by long standing with water, dil. acids or alkalies, or even hot 10% alcoholic potassium hydroxide solution.

The tetrahydro-dioxdiarsines oxidize in the air and form arsine oxides and aldehyde according to the following equation.

$$RAs\underset{\underset{RCH-O}{\diagdown}}{\overset{\overset{O----CHR'}{\diagup}}{}}AsR + O_2 \longrightarrow 2RAsO + 2R'CHO.$$

The stability of the formaldehyde derivative is much less than that of the acetaldehyde compound or higher homologs. With oxidizing agents such as nitric acid, phenylarsonic acid and aldehyde, or phenylarsonic acid and aldehyde oxidation products are formed.

With iodine in ether solution, the substances decompose to aldehyde and arsine di-iodide; the compounds, however, cannot be titrated quantitatively with iodine solution.

The substances form double salts with chloroplatinic acid, and cupric chloride, both of which are stable to air although the latter have a tendency to turn green on standing. They do not form the unstable halogen acid addition products noticed with the *bis*-(α-hydroxyalkyl) arsines.

With phosphorus pentachloride there are formed aldehyde and phenyl dichloro-arsine.

The structure of the tetrahydro-dioxdiarsines can be determined definitely from the mode of formation. The alcohol, which is produced at the same time, may be isolated as such, or in the form of an acetal or, ester; moreover the molecular weight and analysis indicate the formula given. Two other possible structures which suggest themselves are

$$\text{C}_6\text{H}_5\text{As} \Big\langle \begin{matrix} \text{O—CH·R} \\ \\ \text{O—CH·R} \end{matrix} \Big\rangle \text{AsC}_6\text{H}_5 \quad \text{and} \quad \text{C}_6\text{H}_5\text{As} \Big\langle \begin{matrix} \text{R·CH} \\ \\ \underset{\text{O}}{\text{R·CH}} \end{matrix} \Big\rangle \text{AsC}_6\text{H}_5.$$

The first of these two cannot be correct since all arsenic compounds of the general formula $\text{RAs}(\text{OCH}_2\text{R})_2$, into which class this compound falls, are decidedly unstable to water and aqueous alkalies; the tetrahydro-dioxdiarsines are stable to water and alkali. The second structure will not explain the decomposition of the products into phenyl-di-iodo-arsine and aldehyde by the action of iodine; it is also inconsistent with the oxidation by air and with the physcial properties of the products.

The third equation given at the beginning of this communication illustrating the reducing power of the arsines, takes place when a higher temperature is used with or without a catalyst, or when the arsines and the aldehydes are allowed to stand for a long time at room temperature without a catalyst. Under any of these conditions the formation of the condensation products is completely prevented. Thus it has been found that a mole of benzaldehyde and a mole of phenylarsine, when boiled in the presence of acetic acid as a solvent, yield an almost quantitative amount of arsenobenzene and benzyl acetate. Other aromatic aldehydes give the same results. If, however, aldehydes and arsines are mixed in different proportions from those just mentioned, the reactions take place in a somewhat different way and more complex products are produced. A further study of the reduction products of aldehydes and ketones is now being made.

Chloral, when treated with phenylarsine, yields phenylarsenious chloride, illustrating the ease with which hydrogen in the arsines is replaced by halogen.

The formation of the aldehyde-arsine addition compounds from aldehydes and arsines makes it evident that the carbonyl group in aldehydes

and ketones will not react with the primary arsine group with the elimination of water, such as takes place when an aldehyde or ketone reacts with a primary amine. It seems probable, therefore, that the general reaction which has been studied by other investigators, whereby the primary arsines condense with compounds of the type RAsO and RSbO to give RAs=AsR and RAs=SbR, does not take place so simply as is ordinarily explained, namely, by the direct elimination of water. It seems much more likely that the arsine reduces the arsine or stibine oxides to corresponding arseno or stibino compounds and is itself oxidized to another arseno compound.

$$2R'AsO + 2RAsH_2 \longrightarrow R'As{=}AsR' + RAs{=}AsR + 2H_2O.$$

The rearrangement of two arseno compounds into the unsymmetrical derivative takes place very smoothly and practically quantitatively.[11]

$$R'As{=}AsR' + RAs{=}AsR \longrightarrow 2RAs{=}AsR'.$$
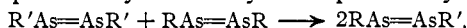
There are thus formed exactly the same products as obtained by the simpler mechanism. It is probable that the reactions between the primary arsines and the arsine halides, bismuth halides or stibine halides, take place in an analogous manner.

$$2R'SbCl_2 + 2RAsH_2 \longrightarrow R'Sb{=}SbR' + RAs{=}AsR + 4HCl$$
$$R'Sb{=}SbR' + RAs{=}AsR \longrightarrow 2RAs{=}SbR'.$$
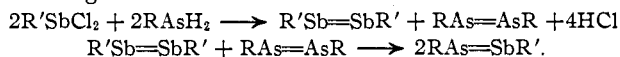
It is, of course, possible that in the reaction just mentioned reduction occurs in such a way that nascent radicals having the formulas RAs=, RSb=,R'As=are first formed and that these then combine directly to give the unsymmetrical arseno or the corresponding arsenic antimony compounds rather than to give symmetrical compounds as intermediates.

It is also possible that there is merely an addition product formed first from the oxide and arsine which subsequently decomposes with the elimination of water.

$$R'AsO + RAsH_2 \longrightarrow R'As(OH)AsHR \longrightarrow R'As = AsR + H_2O.$$
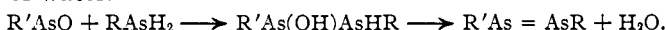
Experimental

Phenylarsine and Derivatives

Phenylarsonic Acid,[12] $C_6H_5AsO_3H_2$.—For the production of phenylarsonic acid on a large laboratory scale, a 25-liter cylindrical copper tank, provided with mechanical stirrer, is employed. In the tank are placed 4 liters of water, 2 kg. of anhydrous sodium carbonate, 1 kg. of technical arsenious oxide (about 20% excess), and 45 g. of crystallized copper sulfate. All of the solid material does not dissolve unless the solution is heated. The stirrer is started and the walls of the tank are cooled by several streams of water. As soon as the temperature of the arsenite solution falls to 15°, (part of the sodium ar-

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[11] Ger. pat. 251,104; Brit. pat. 17,482; *Ber.*, **49**, 1648 (1916).   Ger. pat. 253,226; 270,255.

[12] *Ber.*, **9**, 1568 (1876); **10**, 626 (1877); **15**, 1954 (1882); **27**, 265 (1894); **41**, 1855 (1908); **54**, 438 (1921).   *Ann.*, **201**, 203 (1880); **320**, 293 (1902). Ger. pat. 250,264; 254,092; 264,924. *J. Ind. Eng. Chem.*, **11**, 824 (1919). The method of Schmidt, *Ann.*, **421**, 168 (1920), is unsuitable for runs of any considerable size.

senite precipitates at this temperature), the addition of diazo solution is begun. It is found convenient to prepare the latter in four portions. A mixture of 186 g. of aniline, 400 cc. of conc. hydrochloric acid, 1 liter of water and sufficient ice to bring the total volume to 3 liters is made and placed in a 4-liter Florence flask. This mixture is diazotized in the usual manner with a concentrated solution of 140 g. of sodium nitrite. Three hours or more are required for running four of these diazo solutions into the arsenite, the temperature of the latter being maintained at 15°. During this addition, foaming can be controlled by regulating the speed of stirring and also by adding about 10 cc. of benzene whenever excessive foaming threatens to occur.

Stirring is continued for one hour after all the diazo solution has been added. The mixture is now filtered and the filtrate concentrated to a volume of approximately 5 liters; this is deep brown in color. Conc. hydrochloric acid is added in small portions and the tarry material which separates is filtered off. The acid is added until after filtering a clear, pale yellow solution results. The phenylarsonic acid is now precipitated by the addition of more hydrochloric acid. An excess must be avoided since it causes a certain amount of the phenylarsonic acid to go into solution. When this neutralized mixture has cooled, the product is filtered off and washed with a little distilled water. Small quantities of phenylarsonic acid remaining in the filtrate may be precipitated as the ferric salt by adding ferric chloride.[13] The average yield of white or cream colored product exceeds 800 g. (50% of that calculated) and in many cases runs well over 1000 g. This crude material is perfectly satisfactory for use in the preparation of phenylarsine. If, however, a pure product is desired, it may be crystallized from water which frees it from small amounts of sodium chloride. The product is then practically white and softens at 158°, passing into the infusible anhydride, $C_6H_5AsO_2$.

Phenylarsine,[14] $C_6H_5AsH_2$.—A 5-liter round-bottom flask is provided with a long bulb reflux condenser. A 2-hole stopper at the upper end of the condenser carries a 2-liter dropping funnel and an outlet tube connected to a mercury-filled U-tube. In the flask is placed an intimate mixture of 400 g. of crude phenylarsonic acid made in the way just described, and 800 g. of amalgamated zinc dust, a little water and 1 liter of ether. Two liters of conc. hydrochloric acid is added drop by drop; by proper regulation the apparatus can be allowed to run overnight without attention. When the reduction is complete, the condenser is removed and replaced by a 2-hole stopper carrying a 15cm. funnel and a delivery tube. By pouring water into the funnel, the ether layer is forced through the delivery tube into a 2-liter separatory funnel filled with carbon dioxide. Lumps of anhydrous calcium chloride are added. When dry, the solution is transferred in portions to a 500cc., Claisen distillation flask filled with carbon dioxide, with fractionating column side-arm fitted with a receiver of equal size. Most of the ether is removed by heating on the steam-bath, a constant current of carbon dioxide being passed through the apparatus. The distillation is continued under diminished pressure, the receiver being cooled in ice and water. By a little practice it is found possible to change receivers without oxidation of the phenylarsine, so that use of a Brühl apparatus suggested by a previous investigator is unnecessary. The product boiling at about 93° at 70 mm. is collected. A redistillation is advisable if a very pure product is desired, but the material obtained at this point was used directly for the condensations with aldehydes described in this communication. When the distillation is complete, carbon dioxide is admitted until atmospheric pressure is reached, and the product sealed in large test-tubes which have previously been constricted near the open end and filled with carbon dioxide. The best yield obtained was 83% of the calculated amount, obtained by using recrystallized phenylarsonic acid; the average yield, using crude arsonic acid, was between 50 and

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[13] Suggested by Mr. J. L. Hall.
[14] *Ber.*, **34**, 3598 (1901). *Am. Chem. J.*, **33**, 147 (1905). *Chem. Ztg.*, **1912**, 1099.

60% of the calculated amount, depending largely on the grade of crude arsonic acid used. Phenylarsine is a clear, colorless liquid of disagreeable odor. It causes painful blisters when it comes in contact with the skin and is highly irritating to the mucous membrane. Constants not given in the literature are: d_{25}^{25}, 1.349; n_D^{25}, 1.6082.

General Method for the Preparation of Aryl *Bis*-α-hydroxyalkyl Arsines.

—A 500cc. wide-mouth bottle is provided with a mechanical stirrer. Carbon dioxide is passed into the bottle and then 100 g. (1 mol.) of aryl arsine and a few cubic centimeters of conc. hydrochloric acid are added. The mixture is cooled well in an ice-bath, the stirrer started, and 2 moles of aliphatic aldehyde or polymeric aldehyde are added drop by drop. When using aldehydes of a volatile nature it is advisable to add a slight excess instead of exactly 2 moles. In small runs mechanical stirring is not necessary, merely occasional shaking by hand. ·The carbon dioxide is passed in continuously and stirring continued for a couple of hours after the addition of the aldehyde. The reaction mixture is then shaken with a little fused potassium carbonate to remove the hydrochloric acid, any arylarsonic acid which is formed, and moisture. The products are distilled under diminished pressure.

If desired, the ether solution formed in the preparation of the aryl arsine may be utilized directly in synthesizing the aldehyde addition compound. In this way a larger yield per gram of arylarsonic acid can be obtained.

The substances which are produced as described above are insoluble in water but readily soluble in organic solvents. They are perfectly stable toward dil. alkalies even on boiling. They are also stable toward dil. acid, but decompose gradually on standing with conc. hydrochloric acid at room temperature, and rather rapidly on heating.

The physical constants described under the individual compounds were taken in every instance on freshly prepared products. If allowed to stand without proper precautions to prevent oxidation, the indices of refraction soon become considerably lower, due undoubtedly to oxidation.

Certain of the substituted arsines were prepared and condensed with aldehydes before it was realized that precautions must be taken with the products to prevent gradual decomposition in the air. For this reason, a few of the substances when analyzed showed a variation from the theoretical percentage compositions.

Bis-(α-hydroxyethyl)phenylarsine, $C_6H_5As(CHOHCH_3)_2$.—From 100 g. of phenylarsine, 2 cc. of conc. hydrochloric acid and 75 g. of acetaldehyde or paraldehyde, 127 g. (81%) of redistilled product is obtained boiling at 175–176° at 22 mm. The product is a colorless oil; d_{25}^{25}, 1.252; n_D^{25}, 1.5619.

Analyses. Subs., 0.2637: CO_2, 0.4743; H_2O, 0.1420. Subs., 0.1356, 0.1274: 10.2 cc., 9.65 cc. iodine (1 cc. = 0.0041 g. As). Subs., 0.6072: benzene, 22.0: f. p. lowering, 0.564°. Calc. for $C_{10}H_{15}O_2As$: C, 49.59; H, 6.19; As, 30.99; mol. wt. 242. Found: C, 49.03; H, 6.02; As, 30.83, 31.05; mol. wt. 246.

Bis-(α-hydroxy-*n*-propyl)phenylarsine, $C_6H_5As(CHOHC_2H_5)_2$.—From 17 g. of propionic aldehyde and 23 g. of phenylarsine with 1 cc. of hydrochloric acid, 28 g. (70% yield) of product is obtained boiling at 196–197° at 24 mm. The product is a colorless oil; d_{25}^{25} 1.176; n_D^{25} 1.5425.

Analysis. Subs., 0.2043: 13.8 cc. iodine (1 cc. = 0.0041 g. As). Calc. for $C_{12}H_{19}O_2As$: As, 27.77. Found: 27.69.

Bis-(α-hydroxy-*n*-butyl)phenylarsine, $C_6H_5As(CHOHC_3H_7)_2$.—From 50 g. of phenylarsine, 50 g. of butyraldehyde and 1 cc. of conc. hydrochloric acid, 75 g. of pure product is obtained. The substance is a colorless oil boiling at 187° at 10 mm.; d_{25}^{26} 1.116; n_D^{25}, 1.5271. A mistake was made in the refractive index as reported in the preliminary paper.[15].

Analyses. Subs., 0.2296, 0.2210: 14.0 cc., 13.5 cc. iodine (1 cc. = 0.0041 g. As). Calc. for $C_{14}H_{23}O_2As$: As, 25.17. Found: 25.00, 25.05.

Bis-(α-hydroxy*iso*valeryl)phenylarsine, $C_6H_5As[CHOHC_4H_9(iso)]_2$.—From 16 g. of *iso*valeraldehyde, 15 g. of phenylarsine and 0.5 cc. of conc. hydrochloric acid, a colorless oil (59% yield) is obtained boiling at 170° at 6 mm.; d_{25}^{25}, 1.079; n_D^{25}, 1.5202. By cooling it well with ice and salt, the product solidifies. On recrystallization from ether, needles form which melt sharply at 62°.

Analysis. Subs., 0.1980: 11.1 cc. iodine (1 cc. = 0.0041 g. As). Calc. for $C_{16}H_{27}O_2As$: As, 22.87. Found: 22.98.

Bis-(α-hydroxy-*n*-heptyl)phenylarsine, $C_6H_5As(CHOHC_6H_{13})_2$.—From 15 g. of oenanthol and 8 g. of phenylarsine with 0.5 cc. of conc. hydrochloric acid, a good yield of substance is produced. It cannot be distilled even under diminished pressure without considerable decomposition. A small amount of distilled material was obtained, b. p. 263–264° at 2 mm.; d_{25}^{25}, 1.069; n_D^{25}, 1.4650. The substance solidifies, but does not crystallize, in a freezing mixture.

Analysis. Subs., 0.1798: 7.8 cc. iodine (1 cc. = 0.00446 g. As). Calc. for $C_{20}H_{35}O_2As$: As, 19.63. Found: 19.30.

General Method for the Preparation of *Bis*-(α-hydroxybenzyl)arylarsines.

—Although aryl arsines and aromatic aldehydes condense readily in the presence of conc. hydrochloric acid to give the expected condensation products, better yields are generally obtained provided anhydrous hydrogen chloride and any convenient solvent are used and the mixture mechanically stirred at the same time. A general procedure is as follows. Two moles of aldehyde are dissolved in 5 times the weight of dry ether and dry hydrogen chloride is passed in for a few minutes. The mixture is stirred, dry carbon dioxide is, of course, passed in continuously to prevent oxidation, and one mole of aryl arsine is added. Formation of the product starts almost immediately and in many cases it separates as a solid. In the case of acetone as a solvent, the products generally do not precipitate at all. The reaction mixture is stirred for 2 or 3 hours. The precipitate is filtered, or if no precipitate is present the solvent is evaporated until the product separates. By concentrating the mother liquors a further crop of product may be obtained. There is always formed along with the normal reaction product a small

[15] Ref. 9, p. 2376.

amount of arylarsonic acid which is difficult to remove. It is advisable, therefore, after crystallizing the product once, to allow it to stand with dil. alkali for some time in order to dissolve out the arylarsonic acid. The product is filtered, washed with water, then, if possible, with alcohol and ether, and finally dried. A purer product is obtained by not crystallizing again after the extraction with alkali. Apparently these compounds are slightly oxidized to arylarsonic acid and aldehyde when they are in hot solution and exposed to the air. The yields vary from 40% to practically quantitative, depending largely upon the ease of purification.

The benzaldehyde derivative forms with much greater ease than the substituted benzaldehydes, the former going very smoothly.

The aromatic aldehyde condensation product also forms in the presence of a solvent and conc. hydrochloric acid, but the yields are not as satisfactory as where anhydrous hydrochloric acid is used. The substituted phenylarsine condensation products with aromatic aldehydes were made in this way before it was discovered that anhydrous hydrogen chloride worked better.

Bis(-α-hydroxybenzyl)phenylarsine, $C_6H_5As(CHOHC_6H_5)_2$.—This substance has been described in the preliminary article[16] but was made by direct addition of phenylarsine and benzaldehyde. By the process described in the general procedure, it is possible to obtain from 58 g. of benzaldehyde, 40 g. of phenylarsine, anhydrous hydrogen chloride and 300 cc. of ether, practically a quantitative yield of white, silky needles which on recrystallization from chlorobenzene melt at 193°. The product is insoluble in water, slightly soluble in hot alcohol, ether, more readily soluble in hot benzene and chlorobenzene.

Analyses. Subs., 0.1522, 0.1876: CO_2, 0.3704, 0.4499; H_2O, 0.0695, 0.0843. Subs., 0.1740, 0.1505: 8.7, 8.5 cc. iodine (1 cc. = 0.0041 g. As). Subs., 1.3709; naphthalene, 26.73: f. p. lowering, 0.972°. Calc. for $C_{20}H_{19}O_2As$: C, 65.58; H, 5.18; As, 20.49; mol. wt,, 366. Found: C, 65.70, 65.41; H, 5.11, 5.01; As, 20.47, 20.43; mol. wt., 364.

Bis-(α-hydroxy-*p*-chlorobenzyl)phenylarsine, $C_6H_5As[CHOHC_6H_4Cl(p)]_2$.—This substance forms colorless needles from chlorobenzene melting at 164° and is more soluble in common organic solvents than the benzaldehyde compound. The yield is low (40%) since the product tends to become oily and is purified with difficulty.

Analyses. Subs., 0.1057: 4.3 cc. iodine (1 cc. = 0.0042 g. As). Subs., 0.1411: AgCl, 0.0905. Calc. for $C_{20}H_{17}O_2Cl_2As$: As, 17.24; Cl, 16.48. Found: As, 17.08; Cl, 16.65.

Bis-(α-hydroxy-*p*-methoxybenzyl)phenylarsine, $C_6H_5As[CHOHC_6H_4OCH_3(p)]_2$.— From 27 g. of anisaldehyde, 15 g. of phenylarsine, 200 cc. of dry ether and anhydrous hydrogen chloride, an oil is obtained after allowing the mixture to stand overnight in contact with air to oxidize any phenylarsine which has not reacted, and then evaporating the solvent at room temperature. To purify, the oil is dissolved in ether, shaken several times with aqueous sodium hydrogen sulfite and then with water, and the ethereal solution dried, filtered and evaporated. A yellowish oil results which proves by analysis to be the expected derivative. The product is insoluble in water but readily soluble in organic solvents, except petroleum ether.

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[16] Ref. 9, p. 2377.

Analyses. Subs., 0.1835, 0.2013: 7.65, 8.5 cc. iodine (1 cc. = 0.0041 g. As). Calc. for $C_{22}H_{23}O_4As$: As, 17.61. Found: 17.09, 17.31.

Bis-[*o*-(**carboxymethoxy**)-α-**hydroxybenzyl**]**phenylarsine**, $C_6H_5As[CHOHC_6H_4OC-H_2CO_2H(o)]_2$.—From 30 g. of *o*-aldehydophenoxy-acetic acid, 13 g. of phenylarsine, 100 cc. of acetone and 1 cc. of conc. hydrochloric acid a solution is obtained which upon spontaneous evaporation (since heating in presence of hydrochloric acid causes decomposition) of the solvent yields an oil soluble in sodium hydroxide. By the concentration of the alkaline solution, an orange-brown sodium salt is obtained. This is dissolved in water and fractionally precipitated with hydrochloric acid. The first small fractions are considerably colored and are discarded. The material forms a yellowish powder which weighs 42 g. and melts at 145–147° with loss of carbon dioxide. By solution in glacial acetic acid and precipitation with water, the product may be obtained colorless.

Analyses. Subs., 0.2794, 0.1945: 9.8, 7.1 cc. iodine (1 cc, = 0.00446 g. As). Subs., 0.1480: 5.0 cc. 0.1187 N NaOH. Calc. for $C_{24}H_{23}O_8As$: As, 16.18; neut. equiv., 241. Found: As, 16.28, 16.27; neut. equiv., 249.

Analyses of the sodium salt (dried *in vacuo* at 100°) were also made.

Analyses. Subs., 0.1574, 0.1941: 4.8, 5.8 cc. iodine (1 cc. = 0.00446 g. As). Calc. for $C_{24}H_{21}O_8AsNa_2$: As, 13.42. Found: As, 13.59, 13.26.

General Method for the Preparation of Tetrahydro-1,4,2,5-dioxdiarsines.

—A 150cc. Erlenmeyer flask is fitted with a 3-hole rubber stopper carrying a 50cc. separatory funnel, an inlet tube reaching nearly to the bottom of the flask and an outlet tube connected to a calcium chloride tube. The flask is filled with carbon dioxide and cooled with ice. A mole of phenylarsine is now added and a stream of dry hydrogen chloride is passed through it. At the same time that the hydrogen chloride is started, two moles of aliphatic aldehyde are added drop by drop and the stream of gas continued about half an hour after completion of the addition of the aldehyde. After standing for a day or two the reaction mixture is distilled, at first under ordinary pressure in order to remove hydrochloric acid, unchanged aldehyde and any alcohol or alcohol derivatives which have been produced in the reaction. The residual mixture is now distilled under diminished pressure and the first fraction consisting of the *bis-*(α-hydroxyalkyl)phenylarsine is obtained. The residue consists of the tetrahydro-dioxdiarsine in 50 to 90% yields. On account of the extremely high boiling point of the tetrahydro-dioxdiarsines it is difficult to obtain a large yield of purified product from the crude material. This is due to the fact that there is a partial decomposition during distillation even at pressures below 2 mm. The undistilled material, however, is practically pure as shown by analyses in several instances. These compounds from aliphatic aldehydes are practically colorless oils which are insoluble in water and soluble in the common organic solvents.

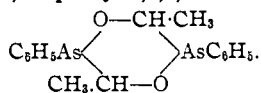**Tetrahydro-2,5-diphenyl-1,4,2,5-dioxdiarsine,** $C_6H_5As\!\!\begin{array}{c}O-CH_2\\ \diagdown\quad\diagup\\CH_2-O\end{array}\!\!AsC_6H_5.$—This substance is obtained by mixing paraformaldehyde, phenylarsine and conc. hydrochloric acid. After shaking the reaction mixture occasionally for some time and allowing it to

stand for a few hours, it is distilled. By this method one would expect to obtain *bis*·(hydroxymethyl)phenylarsine, but this product is apparently unstable as obvious from the gradual evolution of gas during the vacuum distillation and the fact that no constant boiling point is reached until the point at which the tetrahydro-dioxdiarsine distils.

The low·boiling distillate contains methyl alcohol, as shown by the preparation of the 3,5-dinitrobenzoate which melts at 106–107°. The product after distilling twice, boils constant at 215–216° at 9 mm.; d_{25}^{25}, 1.547; n_D^{25}, 1.6522. This compound is very readily oxidized in the air and consequently all operations must be performed in an atmosphere of carbon dioxide. The yield of pure product from 15 g. of phenylarsine is about 10 g.

Analyses. Subs., 0.2560: CO_2, 0.4320; H_2O, 0.0970. Subs., 0.3953, 0.1617: 39.4, 16.1 cc. iodine (1 cc. = 0.0042 g. As). Subs., 0.7900: 22.0 g. benzene; f. p. lowering, 0.506°. Calc. for $C_{14}H_{14}O_2As_2$: C, 46.15; H, 3.85; As, 41.21; mol. wt., 364. Found: C, 46.01; H, 4.08; As, 41.81; 41.82; mol. wt. 355.

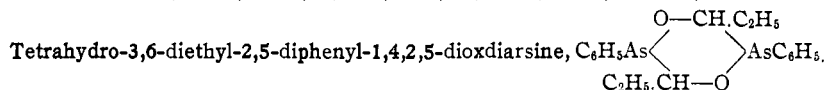**Tetrahydro-3,6-dimethyl-2,5-diphenyl-1,4,2,5-dioxdiarsine,**

$$\text{C}_6\text{H}_5\text{As}\underset{\text{CH}_3\cdot\text{CH}-\text{O}}{\overset{\text{O}-\text{CH}\cdot\text{CH}_3}{\diagdown\diagup}}\text{AsC}_6\text{H}_5.$$

—By using the general method, a colorless oil is obtained boiling at 257° at 10 mm. with slight decomposition; d_{25}^{25}, 1.369; n_D^{25}, 1.6332.

This substance may also be obtained by heating *bis*-(α-hydroxyethyl)phenylarsine with half its weight of acetic anhydride under a reflux condenser in an oil-bath at 140–150° for 7 hours. The reaction mixture is carefully distilled, first at atmospheric pressure, and a portion boiling at 75–90° collected. Ethyl acetate is present in this fraction. Diminished pressure is then used and the main portion of material collected from 250–265° at 10 mm. After purification by one or more redistillations, a product boiling at the above point and with the same constants is produced.

A third method of preparation consists merely in allowing *bis*-(α-hydroxyethyl) phenylarsine to stand a few days in the presence of anhydrous hydrogen chloride. By obtaining the tetrahydro-dioxdiarsine on distillation of this reaction mixture, it is shown that the *bis*-(α-hydroxyalkyl)phenylarsine is an intermediate in the production of tetrahydro-dioxdiarsine from aldehyde and primary arsine.
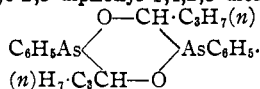
Analyses. Subs., 0.2158, 0.1478: CO_2, 0.3913, 0.2638; H_2O, 0.1000, 0.0668. Subs., 0.1786, 0.1577: 16.5, 14.6 cc. iodine (1 cc. = 0.0041 g. As). Subs., 0.5415: 22.0 g. benzene: f. p. lowering, 0.320°. Calc. for $C_{16}H_{18}O_2As_2$: C, 48.98; H, 4.59; As, 38.27; mol. wt., 392. Found: C, 48.98; 48.75; H, 5.19, 5.06; As, 37.88, 37.87; mol. wt., 384.

Tetrahydro-3,6-diethyl-2,5-diphenyl-1,4,2,5-dioxdiarsine, $\text{C}_6\text{H}_5\text{As}\underset{\text{C}_2\text{H}_5\cdot\text{CH}-\text{O}}{\overset{\text{O}-\text{CH}\cdot\text{C}_2\text{H}_5}{\diagdown\diagup}}\text{AsC}_6\text{H}_5.$

—This substance is readily obtained by the general method, using propionic aldehyde in slight excess and phenylarsine. The yield of crude material is practically quantitative. The substance boils at such a high point, however, that not more than 25% of pure material can be obtained by vacuum distillation, owing to the decomposition during that procedure. The distilled substance boils at 212° at 2 mm.; d_{25}^{25}, 1.336; n_D^{25}, 1.6217.

Analyses. Subs., 0.1173, 0.1030: 9.3, 8.2 cc. iodine (1 cc. = 0.0446 g. As). Calc. for $C_{18}H_{22}O_2As_2$: As, 35.71. Found: 35.45, 35.50.

Tetrahydro-3,6-di-*n*-propyl-2,5-diphenyl-1,4,2,5-dioxdiarsine,

$$\text{C}_6\text{H}_5\text{As}\underset{(n)\text{H}_7\cdot\text{C}_3\text{CH}-\text{O}}{\overset{\text{O}-\text{CH}\cdot\text{C}_3\text{H}_7(n)}{\diagdown\diagup}}\text{AsC}_6\text{H}_5.$$

—By the general method an excellent yield of light yellow oil is produced after all the low-boiling material has been removed. This substance gave good analyses for the tetra-hydro-dioxdiarsine. An attempt was made to distil the product but there was considerable decomposition during this procedure and only a small percentage could be obtained pure. The boiling point is 241–242° at 2 mm.; d_{25}^{25}, 1.297; n_D^{25}, 1.5856.

This same substance was also obtained by the action of acetic anhydride upon *bis*-(α-hydroxy-*n*-butyl)phenylarsine by 6 hours' refluxing. The lowest-boiling fraction is distilled under ordinary pressure and consists of a mixture of acetic anhydride and *n*-butyl acetate. Under diminished pressure a small fraction of *bis*-(α-hydroxy-*n*-butyl) phenylarsine comes over first. The residue after the temperature has reached 220° at 8 mm. is dissolved in acetone, the solution filtered and the filtrate evaporated *in vacuo*, thus giving a yellow oil. This consists of practically pure tetrahydro-dioxdiarsine.

Analyses. Subs., 0.1055, 0.1627: 8.7, 13.4 cc. iodine (1 cc. = 0.0041 g. As). Calc. for $C_{20}H_{26}O_2As$: As, 33.48. Found: 33.81, 33.77.

Tetrahydro-3,6-di*iso*butyl-2,5-diphenyl-1,4,2,5-dioxdiarsine,

$$O—CH \cdot C_4H_9(iso)$$
$$C_6H_5As \diagdown \diagup AsC_6H_5.—$$
$$(iso)C_4H_9 \cdot CH—O$$
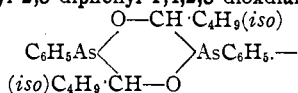
Eight g. of phenylarsine and 9 g. of *iso*valeraldehyde are condensed by the general method with the additional procedure of vigorous agitation of the reaction mixture during the addition of aldehyde. After standing for several days the reaction mixture is distilled under diminished pressure and the portion which boils below 240° at 16 mm. discarded. The remainder is dissolved in acetone and filtered through bone-black on a folded filter. On evaporation of the filtrate in a vacuum desiccator, there remains a nearly colorless oil, weighing 5.5 g. The product is comparatively stable in air; d_{25}^{25}, 1.296; n_D^{25}, 1.5869.

Analyses. Subs., 0.1066, 0.1166: 7.5, 8.2 cc. iodine (1 cc. = 0.00446 g. As). Calc. for $C_{22}H_{30}O_2As_2$: As, 31.51. Found: 31.38, 31.37.

Tetrahydro-3,6-difuryl-2,5-diphenyl-1,4,2,5-dioxdiarsine,

$$O—CH \cdot C_4H_3O$$
$$C_6H_5As \diagdown \diagup AsC_6H_5.$$
$$C_4H_3O \cdot CH—O$$
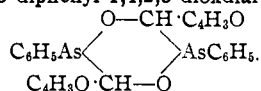
—This substance forms with extreme ease and in quantitative yield when freshly distilled furfural and phenylarsine are mixed and a small amount of aqueous or anhydrous hydrogen chloride is added. The reaction is so violent that it is necessary to keep the mixture cooled at all times with ice and salt. The product consists of a hard mass which when powdered resembles zinc dust. It burns without melting, leaving no residue. It is insoluble in all solvents and before analysis was boiled successively with dil. alkali, water, alcohol and benzene. The same substance is formed when furfural is added drop by drop to a benzene solution of phenylarsine at 20° in the presence of conc. hydrochloric acid.

Analyses. Subs., 0.2557: CO_2, 0.5214; H_2O, 0.0879. Subs., 0.1477, 0.1470: 7.05, 7.1 cc. iodine (1 cc. = 0.0064 g. As). Calc. for $C_{22}H_{18}O_4As_2$: C, 53.23; H, 3.62; As, 30.24. Found: C, 55.61; H, 3.85; As, 30.54, 30.90.

Para-chlorophenylarsine and Derivatives

The experimental work on the preparation of *p*-chlorophenylarsine and its derivatives was carried out by W. A. Carothers.

p-Chlorophenylarsonic acid, $ClC_6H_4AsO_3H_2$[17].—A solution of 126 g. of *p*-chloro-aniline in 600 cc. of water and 180 cc. of conc. hydrochloric acid is cooled to 0° and diazotized with 68 g. of sodium nitrite in 250 cc. of water, the temperature being kept constantly below 7°. A solution is made of 350 g. of technical arsenious oxide (1.8 moles) in 565 g. of sodium carbonate dissolved in 1.5 liters of water by heating on a water-bath for 2 hours with occasional shaking; if this solution is not clear, it is filtered. About 15 g. of powdered copper sulfate is now dissolved in the sodium arsenite solution and the mixture cooled to room temperature. The diazo solution is siphoned into it very slowly. During the addition, constant mechanical stirring is carried on. The speed of the addi·tion is limited by the tendency of the reaction mixture to foam. Addition of a few cubic centimeters of benzene from time to time tends to prevent this foaming. The reaction is allowed to continue for 3 to 4 hours after the addition is complete, the mixture allowed to stand for 12 hours without stirring and then is filtered from any tarry product that may have separated. The filtrate is acidified with glacial acetic acid, the addition being made carefully in order to prevent excessive foaming in the mixture. Arsenious oxide is thus precipitated, while the *p*-chlorophenylarsonic acid remains in solution. After filtration, the latter is precipitated by the addition of conc. hydrochloric acid. It is filtered, washed with cold water and dried. A yield of from 160 to 200 g. is readily obtained (60–85%). After crystallization from alcohol the substance decomposes at about 348°. For analysis it was crystallized once from glacial acetic acid and twice from ethyl alcohol and then dried at 90° *in vacuo*.

Analyses. Subs., 0.1612, 0.1782, 0.1966: 26.38, 28.77, 31.60 cc. iodine (1 cc. = 0.001975 g. As). Subs., 0.4190, 0.5190: 0.2539, 0.3176 g. AgCl. Calc. for $C_6H_6O_3ClAs$: As, 31.75; Cl, 15.01. Found: As, 31.58, 31.99, 31.74; Cl, 14.99, 15.14.

p-Chlorophenylarsine, $ClC_6H_4AsH_2$.—The preparation of this substance is not possible by the use of the directions which are given under phenylarsine. It is necessary to use methyl alcohol instead of water. This presumably acts as a solvent and hastens the reaction. In a 3-liter round-bottom flask are placed 70 g. of *p*-chlorophenylarsonic acid, 350 g. of well amalgamated zinc dust and 250 cc. of methyl alcohol. The flask is provided with a 2-hole rubber stopper; through one hole is inserted a reflux condenser, the upper end of which is provided with a mercury trap; in the other hole is placed a 500cc. separatory funnel. Conc. hydrochloric acid is placed in this funnel and allowed to drop into the reaction mixture regularly at the rate of about 3 or 4 drops a minute. About 1 liter of acid is thus added and the reaction is considered complete when prac-tically all the zinc has disappeared. This required, in various runs, from 3 days' to 1 weeks' time. The stopper is removed from the flask and quickly replaced by another holding 3 tubes, 2 of which extend to the bottom of the flask, 1 allowing for the entrance of steam, the second for carbon dioxide, and the third tube is attached to a condenser set for downward distillation. The receiver at the end of the condenser consists of a suction flask attached tightly by means of an adapter to the condenser. The whole apparatus is filled with carbon dioxide, and a slow stream of carbon dioxide is con-tinued while steam is blown into the reaction mixture. The *p*-chlorophenylarsine distils with the water and methyl alcohol, and occasionally solidifies in the condenser. When no more arsine distils, the stopper holding the adapter leading to the receiver is removed and replaced by one carrying a right-angle tube through which carbon dioxide is con-ducted. The *p*-chlorophenylarsine remains in the bottom of the receiver as a dark solid. By using care, a considerable portion of the water and dilute alcohol above the arsine can be poured from the side arm of the suction flask receiver, allowing the carbon dioxide to enter at the same time. The stopper holding the tube through which

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[17] This compound has been previously made by the diazotization of arsanilic acid and replacement of the diazo group by chlorine; *Ber.*, **41**, 1856 (1908).

the carbon dioxide enters is partially removed, and 200 cc. of ether added. The side-tube of this suction flask is now inserted in the mouth of a 500cc. separatory funnel filled with carbon dioxide and the ether layer containing the p-chlorophenylarsine forced into it by means of a stream of carbon dioxide. Washing the aqueous distillate with one or two portions of ether is advisable. Any water may be separated from the ether solution which is thus obtained, after which it is dried over solid potassium hydroxide. The ether solution is transferred to a vacuum distilling flask as follows. A funnel containing the ether solution is inserted through a 2-hole rubber stopper which closes the main neck of the Claisen flask. The usual capillary tube is extended through the other opening and a carbon dioxide cylinder is attached. The apparatus is evacuated several times and filled with carbon dioxide in order that all the air may be removed. Finally, it is evacuated and the stopcock of the separatory funnel opened to allow the ether solution to enter the Claisen flask. The ether is removed and the p-chlorophenylarsine distils. After one or sometimes two redistillations, it is absolutely pure and then boils at 116° at 33 mm., or 159° at 200 mm. It melts at 30.5–30.7°, forming thin, transparent leaves sometimes as large as 1.5 cm. square. The yield, after complete purification, varies from 16 to 26 g.; d_{25}^{25}, 1.507; n_D^{25}, 1.6143.

Analyses. Subs., 0.5147, 0.3622: 103.64, 72.20 cc. iodine (1 cc. = 0.001975 g. As). Subs., 0.4259, 0.4592, 0.2539: 0.3184, 0.3520, 0.1914 g. AgCl. Calc. for C_6H_6ClAs: Cl, 18.81; As, 39.79. Found: As, 39.75, 39.37; Cl, 18.50, 18.97, 18.65.

Bis-(α-hydroxybenzyl)p-chlorophenylarsine, $ClC_6H_4As(CHOHC_6H_5)_2$.—One mole of arsine and 2 moles of aldehyde are mixed and a small amount of conc. hydrochloric acid is added. Within a half hour, the whole mass sets to an amorphous solid. On standing for an hour, even in an atmosphere of carbon dioxide, it is found to have completely changed to a canary-yellow color. By extracting the reaction mixture with hot chlorobenzene, there crystallize from this solvent long, white, silky needles which can be purified from a mixture of chlorobenzene and alcohol and then melt at 218–218.5°. The yield is small. Moreover, analysis indicates the product at hand is not quite pure in spite of careful crystallization. The chlorobenzene-insoluble residue consists of a bright yellow, sticky mass containing benzaldehyde; after standing in the air, however, this becomes dry and on long standing lighter colored, and finally is found to consist chiefly of p-chlorophenylarsonic acid.

Analyses. Subs., 0.1082, 0.1144: 8.95, 9.21 cc. iodine (1 cc. = 0.001975 g. As). Subs., 0.1406, 0.1676: 0.0473, 0.0558 g. AgCl. Calc. for $C_{20}H_{18}O_2ClAs$: As, 18.72; Cl, 8.85. Found: Cl, 8.32, 8.23; As, 16.34, 15.90.

Bis-(α-hydroxyethyl)p-chlorophenylarsine, $ClC_6H_4As(CHOHCH_3)_2$.—This substance is obtained in the usual way and when pure is a colorless oil boiling at 183° at 23 mm.; d_{25}^{25}, 1.336; n_D^{25}, 1.5728.

Analyses. Subs., 0.3674, 0.3771: 50.01, 52.18 cc. iodine (1 cc. = 0.001975 g. As). Subs., 0.3215, 0.3601: 0.1620, 0.1820 g. AgCl. Calc. for $C_{10}H_{14}O_2ClAs$: Cl, 12.82; As, 27.12. Found: Cl, 12.47, 12.50; As, 26.88, 27.33.

Ortho-chlorophenylarsine and Derivatives

The experimental work on the preparation of o-chlorophenylarsine and its derivatives was carried out by E. E. Parks.

o-Chlorophenylarsonic acid, $ClC_6H_4AsO_3H_2$.—This acid is prepared according to the same general directions as used for p-chlorophenylarsonic acid. The crude material forms in yields varying from 60 to 75%. It is readily purified by crystallization from hot water or dilute alcohol and then melts at 186–187°. The acid is dried for 1 hour at 100° before analysis.

Analyses. Subs., 0.2595: 18.5 cc. of iodine (1 cc. = 0.00446 g. As). Calc. for $C_5H_6O_3ClAs$: As, 31.75. Found: 31.83.

o-**Chlorophenylarsine,** $ClC_6H_4AsH_2$.—This substance is prepared by the general directions used for phenylarsine except that no ether is used and after the reduction is complete the *o*-chlorophenylarsine is distilled with steam from the reaction mixture. In this preparation it is not necessary to use methyl alcohol as described under *p*-chlorophenylarsine. The product boils at 206° at atmospheric pressure and forms in yields of 45 to 60%; d_{25}^{25}, 1.519; n_D^{25}, 1.6250.

Analysis. Subs., 0.1206: 10.75 cc. iodine (1 cc. = 0.00446 g. As). Calc. for C_6H_6ClAs: As, 39.79. Found: 39.75.

*Bis-(α-*hydroxybenzyl)*o*-chlorophenylarsine, $ClC_6H_4As(CHOHC_6H_5)_2$.—This substance is readily produced in the usual way by the action of *o*-chlorophenylarsine upon benzaldehyde. It forms white crystals which are readily crystallized from either ether or alcohol. When pure it melts at 146–147°. The analyses on this product are low unless the product is heated to 110–120° for one-half to one hour. Under these conditions the product seems to fuse slightly and turn a trifle brown, but gives correct analyses for the product at hand and, on recrystallizing, it is found that no decomposition has taken place. It seems probable that this substance holds tenaciously the alcohol from which it is crystallized and only by heating to 120° is this removed.

Analyses. Subs., 0.2894, 0.3558: 6.63, 8.61 cc. $AgNO_3$ (1 cc. = 0.003722 g. Cl). Calc. for $C_{20}H_{18}O_2ClAs$: Cl, 8.85. Found: 8.53, 9.00.

Para-tolylarsine and Derivatives

The experimental work on *p*-tolylarsine and its derivatives was carried out by G. O. Burr.

p-**Tolylarsonic acid,**[18] $CH_3C_6H_4AsO_3H_2$.—A solution is made of 214 g. of *p*-toluidine in 2 liters of water and 5 moles of hydrochloric acid. The temperature is reduced to 0° and 2 moles of sodium nitrite in conc. aqueous solution is added drop by drop from a separatory funnel. During the addition, the solution should be mechanically stirred. One and two-tenths moles of arsenious oxide is dissolved in a solution of slightly more than 4 moles of sodium carbonate in a liter of water. The solution is heated for some time but does not become clear; 20 g. of crystallized copper sulfate is dissolved in this solution, which is then cooled to 17°. At this point the cold diazo solution is siphoned slowly into the arsenite (45 minutes) and the reaction mixture then stirred for 12 hours. Tar separates which is filtered, and the filtrate is acidified with hydrochloric acid. *p*-Tolylarsonic acid is precipitated as a white powder and may be purified by crystallization from water. The yield varies from 50 to 65%.

p-**Tolylarsine,** $CH_3C_6H_4AsH_2$.—The same procedure is used in the preparation of this substance as in the preparation of phenylarsine but the use of a slightly greater amount of zinc is desirable. The product is a colorless liquid boiling at 113.5° at 44 mm. It crystallizes in white, shiny plates which melt at 20°. The yields vary from 30 to 50%; d_{25}^{25}, 1.295; n^{25}, 1.5891.

Analyses. Subs., 0.1670; CO_2, 0.3045; H_2O, 0.0776. Calc. for C_7H_9As: C, 50.00; H, 5.36. Found: C, 49.74; H, 5.20.

*Bis-(α-*hydroxybenzyl)*p*-tolylarsine, $CH_3C_6H_4As(CHOHC_6H_5)_2$.—This is prepared in the same manner as is the phenyl derivative, but is not produced in so good yields.

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[18] This substance has been previously made by the hydrolysis of *p*-tolyl-phenyl-arsenious chloride; *Ann.*, **320**, 303 (1902); **201**, 256 (1880); also by the action of sodium toluene-*iso*diazotate on sodium arsenite; Ger. pat. 250,264.

It forms long, white needles which after crystallization from a mixture of benzene and alcohol melt at 208°.

Analyses. Subs., 0.2185: CO_2, 0.5280; H_2O, 0.0940. Calc. for $C_{23}H_{21}O_2As$: C, 66.14, H, 5.51. Found: C, 65.92; H, 4.83.

Subs., 0.2033, 0.2031: 18.37, 18.27 cc. iodine (1 cc. = 0.00206 g. As). Calc. for $C_{23}H_{21}O_2As$: As, 19.73. Found: 18.55, 18.53.

Bis-(α-**hydroxyethyl**)*p*-**tolylarsine,** $CH_3C_6H_4As(CHOHCH_3)_2$.—A mixture of paraldehyde and arsine with a few drops of hydrochloric acid is allowed to stand for 15 hours. After working up in the usual way, the product is distilled and then gives an 80% yield of a colorless oil boiling at 176–177° at 22 mm; d_{25}^{18}, 1.2331; n_D^{20}, 1.5570. On exposure to air it oxidizes readily.

Analyses. Subs., 0.1438: CO_2, 0.2682; H_2O, 0.0809. Subs., 0.1862: 25.47 cc. iodine (1 cc. = 0.00216 g. As). Calc. for $C_{11}H_{17}O_2As$; C, 51.56; H, 6.64; As, 29.30. Found: C, 50.88; H, 6.30; As, 29.54.

Ortho-tolylarsine and Derivatives

The experimental work on *o*-tolylarsine and its derivatives was carried out by J. S. Pierce.

o-**Tolylarsonic acid,**[19] $CH_3C_6H_4AsO_3H_2$.—The procedure used in the preparation of this substance is approximately the same as for the *p*-tolylarsonic acid. The yield, however, is considerably lower on account of the greater solubility and amounts in general to not over about 40%. The melting point is 159–160°, which agrees with that given in the literature.

o-**Tolylarsine,** $CH_3C_6H_4AsH_2$.—This product is made in the same way as phenylarsine. The product is a colorless oil boiling at 121° at 93 mm; d_{25}^{25}, 1.301; n_D^{25}, 1.5925.

Analyses. Subs., 0.1925, 0.2342: 24.13, 29.61 cc. iodine (1 cc. = 0.003515 g. As). Calc. for C_7H_9As: As, 44.60. Found: 44.06, 44.44.

On exposure to air the arsine oxidizes rapidly to the arseno compound which can be separated from traces of admixed arsonic acid by sodium hydroxide. By crystallization from benzene a pure sample was obtained melting at 205–208°.

Analysis. Subs., 0.1530: 20.18 cc. iodine (1 cc. = 0.003515 g. As). Calc. for $C_{14}H_{14}As_2$: As, 45.14. Found: 46.36.

Bis-(α-**hydroxybenzyl**)*o*-**tolylarsine,** $CH_3C_6H_4As(CHOHC_6H_5)_2$.—The product is purified by crystallization from ether, forming white, needle-like crystals which melt at 140°.

Analyses. Subs., 0.0596, 0.0488: 3.29, 2.68 cc. iodine (1 cc. = 0.003515 g. As). Calc. for $C_{21}H_{21}O_2As$: As, 19.71. Found: 19.40, 19.30.

Bis-(α-**hydroxyethyl**)*o*-**tolyl**sine, $CH_3C_6H_4As(CHOHCH_3)_2$.—This is a colorless oil boiling at 165° at 21 mm.; d_{25}^{25}, 1.244; n_D^{30}, 1.5573. This substance has a slightly greater tendency to oxidize than other analogous compounds, so it should be kept in an atmosphere of carbon dioxide. The ease of decomposition probably accounts for the low analysis.
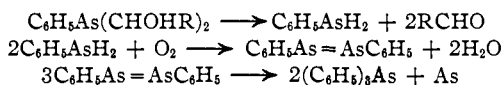
Analyses. Subs., 0.0974, 0.1527: 7.67, 12.04 cc. iodine (1 cc. = 0.003528 g. As). Calc. for $C_{11}H_{17}O_2As$: As, 29.25. Found: 27.78, 27.82.

Reactions of the Condensation Products, $C_6H_5As(CHOHR)_2$

Stability.—When heated strongly over a free flame, the substances

[19] The product has previously been made by the hydrolysis of *o*-tolylarsenious chloride; *Ann.*, **201**, 255 (1880).

are decomposed into aldehyde and phenylarsine. The latter is immediately oxidized to arsenobenzene in the presence of air. Arsenobenzene is changed completely into triphenylarsine, m. p. 58°, and free arsenic.[20] The following reactions are indicated for the heat decomposition.

$$C_6H_5As(CHOHR)_2 \longrightarrow C_6H_5AsH_2 + 2RCHO$$
$$2C_6H_5AsH_2 + O_2 \longrightarrow C_6H_5As = AsC_6H_5 + 2H_2O$$
$$3C_6H_5As = AsC_6H_5 \longrightarrow 2(C_6H_5)_3As + As$$

The products are perfectly stable in long continued contact with water, dil. sodium hydroxide and cold dil. hydrochloric acid.

When 5 g. of *bis*-(α-hydroxy-*n*-butyl)phenylarsine is mixed with 25 cc. of water and sealed in a bomb tube, the lower end of which is immersed in an oil-bath heated at 140° for 30 hours, it is unchanged. In a similar manner 1 g. of *bis*-(α-hydroxybenzyl) phenylarsine is recovered unchanged in weight and melting point after 65 hours' heating. *Bis*-(α-hydroxy-*n*-butyl)phenylarsine and *bis*-(α-hydroxybenzyl)phenylarsine are unaffected by 24 hours' heating with 10% sodium hydroxide solution. On the other hand, heating for only a short time with dil. hydrochloric acid is sufficient to cause decomposition. This reaction is discussed under the heading "Halogen Acids."

Oxidation.—When the *bis*-(α-hydroxyalkyl)arylarsines are allowed to stand for a few days in contact with the air a white solid is gradually deposited. The liquid portion is found to have lost arsenic and to give a strong fuchsin aldehyde test. The solid is identified as the respective aryl arsonic acid. This oxidation is more rapid in solution, particularly in carbon tetrachloride.

Thus 1 g. of *bis*-(α-hydroxyethyl)phenylarsine is completely decomposed by dissolving it in 10 cc. of carbon tetrachloride and passing a slow stream of air through the solution for 1 hour. Heat is evolved, the solution becomes turbid, and the odor of phosgene is very distinct. The mixture gives a strong aldehyde test and on evaporation phenylarsonic acid is the only substance obtained. No action is observed when a stream of carbon dioxide is substituted for air. *Bis*-(α-hydroxy-*n*-butyl)phenylarsine is oxidized in exactly the same way, but *bis*-(α-hydroxybenzyl)phenylarsine is perfectly stable in carbon tetrachloride solution.

In a 50cc. Claisen flask connected to a spiral condenser and receiver, both cooled by ice and water, is placed 5 g. of *bis*-(α-hydroxy-*n*-butyl)phenylarsine. Through a separatory funnel 18 cc. of 35% nitric acid is now added drop by drop. A vigorous reaction takes place. The distillate, weighing 2 g., is butyraldehyde. On evaporation of the liquid remaining in the Claisen flask 2.75 g. of phenylarsonic acid is recovered.

$$C_6H_5As(CHOHR)_2 + 6HNO_3 \longrightarrow C_6H_5AsO_3H_2 + 2RCHO + 3H_2O + 6NO_2$$

Alkaline potassium permanganate gives a similar result. The same reactions occur when *bis*-(α-hydroxyethyl)phenylarsine is treated with nitric acid or potassium permanganate.

Reduction.—A number of attempts have been made to reduce *bis*-(α-hydroxyethyl)phenylarsine $C_6H_5As(CHOHCH_3)_2$, to phenyldiethyl arsine, $C_6H_5As(CH_2CH_3)_2$. Zinc and hydrochloric acid, zinc and acetic acid, aluminum powder and sodium hydroxide and sodium and absolute alcohol do not reduce this compound, the original substance being recovered in

[20] *Ber.*, **14**, 913 (1881).

each case. In the first three instances the condensation product appears to coat the metal so that the latter reacts with great difficulty.

Dehydration.—When a solution of *bis*-(α-hydroxyethyl)phenylarsine in dry ether is allowed to stand with phosphorus pentoxide, slight charring occurs but most of the product is recovered unchanged. Fused zinc chloride dissolves in the same compound with formation of a thick sirup, probably an addition product.

Ten g. of *bis*-(α-hydroxyethyl)phenylarsine and 2 g. of metallic sodium are placed in a small beaker and allowed to stand in a desiccator over sulfuric acid for 2 weeks. During that time the sodium becomes discolored, but the unchanged condensation product can be recovered by dissolving in dry ether, filtering, and distilling the filtrate.

Halogens.—Two moles of solid iodine are placed in the apparatus which has been described in connection with oxidation by nitric acid. One mole of *bis*-(α-hydroxy-*n*-butyl)phenylarsine is added drop by drop. The liquid which distils over below 80° is butyraldehyde. A heavy, dark oil remaining in the Claisen flask cannot be distilled under 20 mm. pressure without decomposition. It gives free iodine and phenylarsonic acid when treated with conc. nitric acid. This behavior is characteristic of phenylarsenious iodide.[20] Other condensation products give similar results.

$$C_6H_5As(CHOHR)_2 + 2I_2 \longrightarrow C_6H_5AsI_2 + 2HI + 2RCHO$$
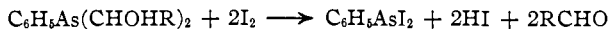
The aliphatic aldehyde compounds may be dissolved in ether and titrated quantitatively with standard iodine solution as represented in the above equation. The end-point is reached when the ether solution assumes a permanent yellow color. The results indicate the absorption of 4 atoms of iodine to 1 molecule of arsine. After neutralization of the ether solution at the end of titration, a strong fuchsin aldehyde test is obtained.

Bis-(α-hydroxy-*n*-propyl)phenylarsine: subs., 0.1208: 16.1 cc. of iodine (1 cc. = 0.0164 g. I). Calc. for $C_{12}H_{19}O_2As$: 16.05 cc.

Bis-(α-hydroxy-*n*-butyl)phenylarsine: subs., 0.1383: 16.3 cc. iodine (1 cc. = 0.0164 g. I). Calc. for $C_{14}H_{23}O_2As$: 16.46 cc.

Bromine reacts violently leaving a heavy reddish oil. Since the latter gives phenylarsonic acid and free bromine when treated with nitric acid, it is probably phenyl-dibromo-arsine. The reaction doubtless follows the same course as with iodine, although the formation of aldehyde has not been proved.

A stream of moist chlorine is passed into several grams of *bis*-(α-hydroxyethyl)phenylarsine. A violent reaction accompanied by considerable decomposition takes place. On cooling, needles form which have been identified after recrystallization from alcohol as phenylarsonic acid. It is concluded that the reaction followed a course similar to that given by iodine, phenyl-dichloro-arsine being formed. The production of phenyl-arsonic acid is explained as follows.[21]

[21] *Ber.*, **9**, 1568 (1876).

$$C_6H_5AsCl_2 \xrightarrow{Cl_2} C_6H_5AsCl_4 \xrightarrow{3H_2O} C_6H_5AsO_3H_2 + 4HCl$$
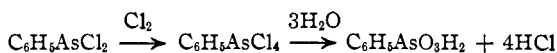
It is noteworthy that the *bis*-(α-hydroxyalkyl)arylarsines do not form addition products with chlorine as do the isomeric esters[22] of phenylarsenious acid.

Ethyl Iodide.—Three g. of *bis*-(α-hydroxyethyl)phenylarsine and 2 g. of ethyl iodide, when sealed in a test-tube and allowed to stand for 6 months, form gradually a dark sirupy mass which cannot be purified.

Six g. of *bis*-(α-hydroxy-*n*-butyl)phenylarsine and 4 g. of ethyl iodide are refluxed gently for 20 hours. The solution is transferred to a crystallizing dish and evaporated spontaneously. The residue consists of phenylarsenic oxide, m. p. 120–122°. The same product is obtained when *bis*-(α-hydroxybenzyl)phenylarsine is used in this reaction.

Phosphorus Pentachloride.—Thirty-five g. of phosphorus pentachloride is placed in a small Claisen flask connected to a glass worm condenser, which is cooled by a freezing mixture, and 20 g. of *bis*-(α-hydroxyethyl)phenylarsine is added slowly through a dropping funnel. The heat of the reaction is great but immersion of the Claisen flask in ice water holds back any material from the distillate which boils above 60°. Five g. of low-boiling product is collected; on decomposition with water (added drop by drop) practically all goes into solution and on neutralization of the latter a strong aldehyde test is obtained. The few immiscible drops are undoubtedly ethylidene chloride. The distillation is continued under diminished pressure. A fraction boiling below 60° at 80 mm., (31 g.) consists mainly of phosphorus trichloride. The fraction (16 g.), boiling at 153–155° at 18 mm., is phenylarsenious chloride.

Subs., 0.2127: 11.0 cc. iodine (1 cc. = 0.0064 g. As). Subs., 0.1663: AgCl, 0.2173. Calc. for $C_6H_5Cl_2As$: As, 33.63; Cl, 31.84. Found: As, 33.57; Cl, 32.29.

$$C_6H_5As(CHOHR)_2 + 2PCl_5 \longrightarrow C_6H_5AsCl_2 + 2HCl + 2PCl_3 + 2RCHO$$
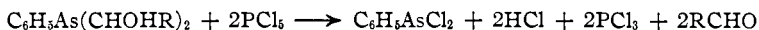
Phenylarsenious Chloride.—One g. of *bis*-(α-hydroxyethyl)phenylarsine is mixed with an equal weight of phenylarsenious chloride. Slight warming and turbidity are observed. After 1 week the mixture is practically solid. It is transferred to a filter and washed thoroughly with ether. The residue is arsenobenzene, identified by a mixed melting point at 196–199°. The washings give an aldehyde test.

$$C_6H_5As(CHOHR)_2 + C_6H_5AsCl_2 \longrightarrow C_6H_5As = AsC_6H_5 + 2HCl + 2RCHO$$
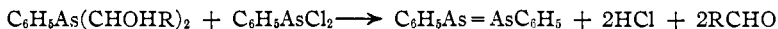
Acid Chlorides.—Many attempts to prepare esters from all of the simple condensation products by means of acetyl chloride, acetic anhydride, oxalyl bromide, oxalyl chloride, benzoyl chloride and *p*-nitrobenzoyl chloride have been made. In the cold without solvent (except in the case of oxalyl chloride which acts as a chlorinating agent in the manner of phosphorus pentachloride), in the Schotten-Baumann reaction and in

[22] *Ann.*, **320,** 287 (1902).

pyridine solution the compounds are unaffected. The result of heating certain of these substances with acid chlorides or anhydrides is discussed under the preparation of tetrahydro-dioxdiarsines.

Grignard Reagents.—The substances do not give any apparent reaction with methyl magnesium iodide in dry ether solution. Using the method of Zerewitinoff,[23] there is no evidence of reaction with methyl magnesium iodide in *n*-butyl ether either at room temperature or 150°.

Halogen Acids.—When constant-boiling hydriodic acid is added to *bis*-(α-hydroxyethyl)phenylarsine, heat is evolved, the acid is decolorized and a yellow solid is formed within a few minutes. The product, filtered off and washed with ether, is a yellow powder, m. p. 94–96°, insoluble in water, slightly soluble in organic solvents. It is stable to alkali, but soon melts in the air to a pasty mass. It is therefore advisable to analyze immediately without any attempt at purification. The results show the formation of an addition compound between 1 mole of arsine and 1 mole of hydriodic acid.

Subs., 0.3208: 15.0 cc. iodine (1 cc. = 0.0446 g. As). Calc. for $C_{10}H_{15}O_2As.HI$: As, 20.27. Found: 20.85.

Bis-(α-hydroxy-*n*-butyl)phenylarsine forms an addition product with hydriodic acid, m. p. 157–158°. If too much hydriodic acid is used decomposition may take place rather than addition.

Hydrobromic acid adds much more slowly than hydriodic acid and the products are somewhat more stable. *Bis*-(α-hydroxyethyl)phenylarsine hydrobromide, m. p. 117–118°; *bis*-(α-hydroxy-*n*-butyl)phenylarsine hydrobromide, m. p. 111–112°. All of the above melting points were obtained by inserting the capillary in the bath heated to about 5° below the melting point and raising the temperature very slowly.

Some solid is formed when *bis*-(α-hydroxyethyl)phenylarsine is allowed to stand for several weeks with constant-boiling hydrochloric acid, but the principal reaction is decomposition.

Bis-(α-hydroxybenzyl)phenylarsine does not form addition compounds with any of the halogen acids even on long standing.

Addition Compounds with Chloroplatinic Acid.—When treated in alcoholic solution with a slight excess of chloroplatinic acid, the *bis*-(α-hydroxyalkyl)arylarsines form addition compounds in 1:1 proportion. By addition of water, the product is thrown down as a flocculent precipitate. After several crystallizations from dil. alcohol, the substances are finally pure. In final form they are light yellow powders. The following have been prepared.

Bis-(α-hydroxyethyl)phenylarsine chloroplatinate, $C_6H_5As(CHOHCH_3)_2.H_2PtCl_6$.— M. p., 169–170°.

[23] Zerewitinoff, *Ber.*, **40**, 2023 (1907); **41**, 2233 (1908).

Analysis. Subs., 0.1372: Pt, 0.0408. Calc. for $C_{10}H_{15}O_2As.H_2PtCl_6$: Pt, 29.91. Found: 29.73.

Bis-(α-hydroxy-*n*-propyl)phenylarsine chloroplatinate,$C_6H_5As(CHOHC_2H_5)_2.H_2Pt$-$Cl_6$.—M. p., 148–149°.

Analysis. Subs., 0.2942: Pt, 0.0824. Calc. for $C_{12}H_{19}O_2As.H_2PtCl_6$: Pt, 28.66. Found: 28.01.

Bis-(α-hydroxy-*n*-butyl)phenylarsine chloroplatinate, $C_6H_5As(CHOHC_3H_7)_2.H_2Pt$-$Cl_6$.—M. p., 119–121°.

Analysis. Subs., 0.3024: Pt, 0.0822. Calc. for $C_{14}H_{23}O_2As.H_2PtCl_6$: Pt, 27.54. Found: 27.17.

Bis-(α-hydroxy*iso*valeryl)phenylarsine chloroplatinate, $C_6H_5As(CHOHC_4H_9)_2.H_2$-$PtCl_6$.—M. p., 84–85°.

Analysis. Subs., 0.4109: Pt, 0.1086. Calc. for $C_{16}H_{27}O_2As.H_2PtCl_6$: Pt, 26.53. Found: 26.43.

Reactions of the Tetrahydro-dioxdiarsines

Unless otherwise designated, the technique for the work described below is the same as that employed for the corresponding reactions of the compounds $C_6H_5As(CHOHR)_2$.

Stability.—The methyl compound is unaffected by long standing in the cold with water, dil. hydrochloric acid or dil. sodium hydroxide. Twenty g. of the same product is recovered unchanged after heating for 3 hours under a reflux condenser with a solution of 10 g. of potassium hydroxide in 50 cc. of absolute alcohol. This result is distinctly favorable to the symmetrical tetrahydro-dioxdiarsine structure which has been advanced. The compound,[24] $(C_6H_5)_2AsOC_6H_5$, is less easily hydrolyzed than the esters[10] of phenylarsenious acid. The tetrahydro-dioxdiarsine structure successfully explains the still greater stability which has been observed.

Oxidation.—The first member of the series, tetrahydro-2,5-diphenyl-1,4,2,5-dioxdiarsine, is oxidized very rapidly by air. A solution of 17 g. of the substance in 50 cc. of acetone warms on exposure to air and soon gives a strong fuchsin aldehyde test. After standing for some hours, the acetone is evaporated and the white, microcrystalline residue weighing 16 g. is recrystallized from alcohol. Although the resulting product gives a melting point about 10° below that of pure phenylarsine oxide, m. p. 119–120°, analysis provides a complete identification.

Subs., 0.2611, 0.1577: CO_2, 0.3980, 0.2410; H_2O, 0.0752, 0.0451. Subs., 0.1649: 16.6 cc. iodine (1 cc. =0.00446 g. As). Calc. for C_6H_5OAs: C,42.86; H, 2.98; As, 44.64. Found: C, 41.67, 41.63; H, 3.22, 3.19; As, 44.89.

The higher members of the series are oxidized much more slowly and in a number of cases the oxide obtained has a correct melting point.

When 1 g. of methyl compound is treated with conc. nitric acid, aldehyde

[24] *Ann.*, **321**, 143 (1902).

is evolved, and phenylarsonic acid is obtained by evaporation of the re-action mixture.

$$(C_6H_5AsOCHR)_2 + 8HNO_3 \longrightarrow 2C_6H_5AsO_3H_2 + 2RCHO + 8NO_2 + 2H_2O$$
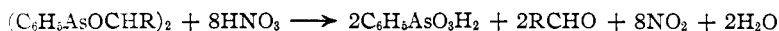
Iodine.—One g. of methyl compound is dissolved in a few cubic centi-meters of ether and iodine is added in small portions. The solution gives an aldehyde test. On evaporation there remains a heavy, dark oil, which is washed with ether by decantation and shown to be phenylarsine di-iodide by a method described above.

$$(C_6H_5AsOCHR)_2 + 2I_2 \longrightarrow 2C_6H_5AsI_2 + 2RCHO$$

The tetrahydro-dioxdiarsines cannot be titrated quantitatively with iodine solution.
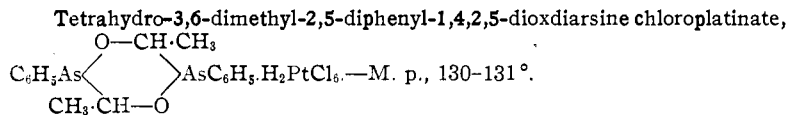
Halogen Acids.—Constant-boiling halogen acids do not form addition products. Slow decomposition takes place with production of aldehyde. No attempt has been made to identify other products of the reaction.

Ethyl Iodide.—Two g. of methyl compound and a considerable excess of ethyl iodide are refluxed for 4 hours. On evaporation of the ethyl iodide, the original tetrahydro-dioxdiarsine is recovered unchanged and practically quantitatively.
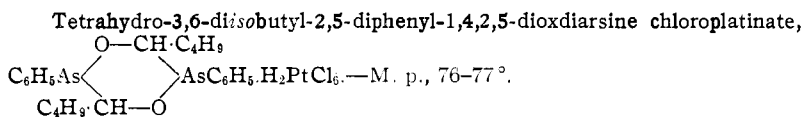
Phosphorus Pentachloride.—An excess of phosphorus pentachloride is mixed with 1 g. of the methyl derivative. A vigorous reaction with evo-lution of aldehyde takes place. The reaction mixture is treated cautiously with water and the precipitated oil removed by a capillary pipet. It yields phenylarsonic acid on treatment with chlorine and water and so is undoubtedly phenyl-dichloro-arsine.[21]

$$(C_6H_5AsOCHCH_3)_2 + 2PCl_5 \longrightarrow 2C_6H_5AsCl_2 + 2PCl_3 + 2RCHO$$
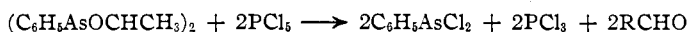
Addition Compounds with Chloroplatinic Acid.—These are prepared in the same manner as the similar substances from the di-α-hydroxy-alkyl arsines. The compounds crystallize in colorless flocks from dil. alcohol.

Tetrahydro-3,6-dimethyl-2,5-diphenyl-1,4,2,5-dioxdiarsine chloroplatinate,

$$C_6H_5As\underset{CH_3 \cdot CH-O}{\overset{O-CH \cdot CH_3}{\diagup \diagdown}}AsC_6H_5 . H_2PtCl_6.$$—M. p., 130–131°.

Analysis. Subs., 0.1069: Pt, 0.0258. Calc. for $C_{16}H_{18}O_2As_2 . H_2PtCl_6$: Pt, 24.31. Found: 24.14.

Tetrahydro-3,6-di*iso*butyl-2,5-diphenyl-1,4,2,5-dioxdiarsine chloroplatinate,

$$C_6H_5As\underset{C_4H_9 \cdot CH-O}{\overset{O-CH \cdot C_4H_9}{\diagup \diagdown}}AsC_6H_5 . H_2PtCl_6.$$—M. p., 76–77°.

Analysis. Subs., 0.1338: Pt, 0.0292. Calc. for $C_{22}H_{30}O_2As_2 . H_2PtCl_6$: Pt, 22.01. Found: 21.82.

Addition Compounds with Cupric Chloride.—In a similar manner to the above there are obtained addition products with cupric chloride.

These crystallize in colorless flocks from dil. alcohol. The cuprichlorides turn green on standing in air and decompose rather quickly at 110°.

Tetrahydro-3,6-dimethyl-2,5-diphenyl-1,4,2,5-dioxdiarsine cuprichloride,

$$C_6H_5As \underset{CH_3 \cdot CH-O}{\overset{O-CH \cdot CH_3}{\diagup \diagdown}} AsC_6H_5 . CuCl_2. \text{—M. p., 150-152°.}$$
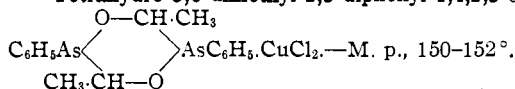
Analyses. Subs., 0.1970, 0.2010: 11.6, 11.8 cc. iodine (1 cc. = 0.00446 g. As). Calc. for $C_{16}H_{18}O_2As_2 . CuCl_2$: As, 26.59. Found: 26.25, 26.22.

Tetrahydro-3,6-di*iso*butyl-2,5-diphenyl-1,4,2,5-dioxdiarsine cuprichloride,

$$C_6H_5As \underset{C_4H_9 \cdot CH-O}{\overset{O-CH \cdot C_4H_9}{\diagup \diagdown}} AsC_6H_5 . CuCl_2. \text{—M. p., 78-79°.}$$
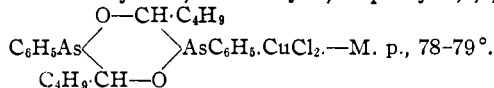
Analyses. Subs., 0.1415, 0.1730: 8.2, 9.5 cc. iodine (1 cc. = 0.00446 g. As). Calc. for $C_{22}H_{30}O_2As_2 . CuCl_2$: As, 24.57. Found: 24.71, 24.55.

Reduction Reactions

Benzaldehyde.—A mixture of 7.5 g. of phenylarsine, 5 g. of benzaldehyde and 25 cc. of glacial acetic acid is heated under a reflux condenser in a current of carbon dioxide for 2 hours. The precipitated solid is filtered off, washed with ether and identified as arsenobenzene (6.75 g.). This and many other samples of arsenobenzene which have been obtained contain a slight impurity of phenylarsonic acid. The very high melting anhydride of the latter, which is formed above 158°, causes the arsenobenzene to melt as much as 25° *high*. By extraction with aqueous alkali and one or more recrystallizations from benzene or chlorobenzene, a melting point[20] and mixed melting point of 196–197° can be obtained.

Subs., 0.2466: 28.6 cc. iodine (1 cc. = 0.0042 g. As). Calc. for $C_{12}H_{10}As_2$: As, 49.33. Found: 49.24.

The filtrate from the arsenobenzene has a very strong ester odor. On distillation, acetic acid is recovered at first. A fraction is collected which boils at 200–210° under atmospheric pressure. This is refluxed for several hours with conc. sodium hydroxide solution. The reaction mixture is distilled with steam, the non-aqueous portion of the distillate separated and identified as benzyl alcohol by preparation of the *p*-nitrobenzoate,[25] m. p. 84–88°. A portion of the residue which remains in the distilling flask is evaporated to dryness and the presence of acetic acid shown by the cacodyl test.

$$2C_6H_5CHO + 2C_6H_5AsH_2 + 2CH_3COOH \longrightarrow 2C_6H_5CH_2OOCCH_3 +$$
$$C_6H_5As = AsC_6H_5 + 2H_2O$$
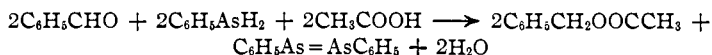
Phenylarsine is oxidized in a similar manner when heated at 100° with benzaldehyde in 1:1 proportion in a sealed tube filled with carbon dioxide. The reduction takes place even in the presence of conc. hydrochloric acid, the condensation reaction being entirely prevented at 100°.

[25] *Ber.*, **30,** 2288 (1897).

Anisic Aldehyde.—A mixture of 6.5 g. of anisic aldehyde, 7.5 g. of phenylarsine and 5 g. of fused sodium acetate is sealed in a bomb tube filled with carbon dioxide. After 6 hours' heating on the boiling water-bath, the tube is opened, the contents filtered and the residue washed with absolute alcohol. The filtrate and washings are set aside to evaporate, and the residue washed with water to remove sodium acetate. There remains undissolved only arsenobenzene (dry weight, 6 g.).

On evaporation of the alcohol washings, an oil is obtained. It is heated under a reflux condenser with conc. sodium hydroxide solution for 2 hours and then distilled with steam from the reaction mixture. In this way anisic alcohol,[26] m. p. 45°, is isolated.

$$2CH_3OC_6H_4CHO + 2C_6H_5AsH_2 \longrightarrow 2CH_3OC_6H_4CH_2OH + C_6H_5As = AsC_6H_5$$
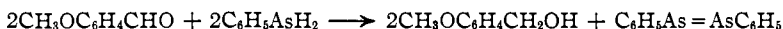
p-Chlorobenzaldehyde.—Nine g. of p-chlorobenzaldehyde and 10 g. of phenylarsine are dissolved in 75 cc. of benzene, 1 g. of fused zinc chloride is added, and the mixture allowed to stand for 5 days in a sealed flask filled with carbon dioxide. The flask is opened and the arsenobenzene (dry weight, 10 g.) filtered off. On concentration of the filtrate, long prisms crystallize, m. p. 70–71°, weight, 9 g. This is p-chlorobenzyl alcohol.[27]

Subs., 0.1216: AgCl, 0.1258.   Calc. for C_7H_7OCl: Cl, 24.84.   Found: 25.59.

m-Nitrobenzaldehyde.—When attempts are made to condense m-nitro benzaldehyde and phenylarsine by the general method, a thick sirup is formed. Crystals can be obtained from this product with considerable difficulty. These are invariably arsenobenzene. Apparently the action is reduction of the nitro group.

As a check upon this view, 2 g. of nitrobenzene is dissolved in ether, the calculated quantity of phenylarsine added and the solution sealed in a flask filled with carbon dioxide. After standing overnight, it is found that the nitrobenzene is reduced to hydrazobenzene, m. p. 128–132°.

$$4C_6H_5NO_2 + 10C_6H_5AsH_2 \longrightarrow 2C_6H_5NHNHC_6H_5 + 5C_6H_5As = AsC_6H_5 + 8H_2O$$

Cinnamic Aldehyde reacts vigorously when mixed with an equimolecular proportion of phenylarsine. Even in the presence of conc. hydrochloric acid, reduction takes place. The reaction mixture is extracted with ether, the arsenobenzene filtered off, the ethereal solution evaporated, and the residual oil identified as cinnamic alcohol by preparation of the phenylurethane[28] derivative, m. p. 90–92°.

Crotonic Aldehyde and **Salicylic Aldehyde** are reduced in a similar manner with the formation of arsenobenzene and other products which have not been identified.

[26] Ber., **19,** 2376 (1886).

[27] Am. Chem. J., **2,** 88 (1880).

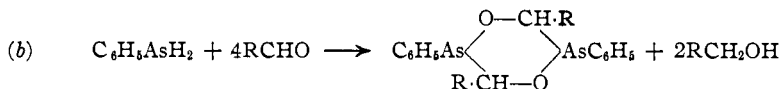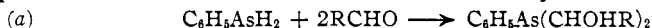[28] Rosenthaler, "Der Nachweis organischer Verbindungen," Ferdinand Enke, Stuttgart, **1914,** p. 87.

Chloral.—When chloral or chloral hydrate is allowed to react with phenylarsine according to the general method for the preparation of *bis*-(α-hydroxyalkyl)arylarsines, a violent reaction takes place. On distillation of the reaction mixture much excess of chloral is recovered. The fraction which boils at 180–182° at 70 mm. consists of phenylarsenious chloride.

In another experiment, 3.5 g. of chloral is placed in a Claisen flask filled with carbon dioxide connected to a glass worm surrounded by a freezing mixture. Five g. of phenylarsine is added drop by drop through a separatory funnel. A considerable quantity of gas is lost, but the few drops of distillate collected in a well-cooled receiver are identified as acetaldehyde by boiling point and aldehyde test. Some arsenobenzene is obtained despite rigid exclusion of air. Doubtless this is formed by interaction[29] of $C_6H_5AsCl_2$ and $C_6H_5AsH_2$.

$$3C_6H_5AsH_2 + 2CCl_3CHO \longrightarrow 3C_6H_5AsCl_2 + 2CH_3CHO$$
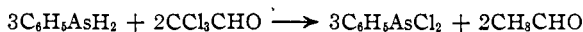
Summary

1. Primary aryl arsines and aldehydes react in three ways, depending upon the conditions of the reaction, as shown by the following equations.

(a) $$C_6H_5AsH_2 + 2RCHO \longrightarrow C_6H_5As(CHOHR)_2$$

(b) $$C_6H_5AsH_2 + 4RCHO \longrightarrow C_6H_5As\left\langle \begin{array}{c} O-CH\cdot R \\ R\cdot CH-O \end{array} \right\rangle AsC_6H_5 + 2RCH_2OH$$

(c) $$C_6H_5AsH_2 + 2RCHO \longrightarrow C_6H_5As{=}AsC_6H_5 + 2RCH_2OH$$

2. Aromatic primary arsines and aliphatic aldehydes condense in the presence of conc. hydrochloric acid at room temperature to give compounds of the formula $C_6H_5As(CHOHR)_2$.

3. Aromatic primary arsines condense with aromatic aldehydes, with or without a solvent, best in the presence of hydrogen chloride to give compounds of the general formula $C_6H_5As(CHOHR)_2$.

4. Primary aromatic arsines condense with aliphatic aldehydes in the presence of anhydrous hydrochloric acid to give tetrahydro-dioxdiarsines of the general formula given in (1b). These same substances may be formed by the action of acetyl chloride, acetic anhydride, or anhydrous hydrochloric acid upon compounds mentioned in (2).

5a. The substances $RAs(CHOHR)_2$, where the aldehyde used is aliphatic, oxidize readily in the air to form an arylarsonic acid and aldehyde. Other oxidizing agents, such as potassium permanganate or nitric acid, cause decomposition to take place in the same way. Air does not oxidize most of the compounds which are derived from aromatic aldehydes.

[29] Ger. pat., 254,187, *Ber.*, **46**, 3565 (1913).

5b. With halogens, phosphorus pentachloride and phenylarsenious chloride, products are obtained which would be expected, providing the original substances were mechanical mixtures of aldehyde and arsine. The compounds may be titrated quantitatively with a solution of iodine in ether.

5c. The compounds form unstable addition products with halogen acids, and stable addition compounds with chloroplatinic acid.

6a. The tetrahydro-dioxdiarsines formed according to Equation (1b), oxidize in the air to give aryl arsine oxides and aldehydes. This is particularly noticeable where the product is a derivative of formaldehyde.

6b. The compounds form double salts with chloroplatinic acid and cupric chloride.

6c. With iodine or phosphorus pentachloride, products are obtained which might be expected from a mixture of aryl arsine and aldehyde.

7. Aromatic primary arsines reduce aromatic aldehydes to alcohols with the formation of arsenobenzene, when a mixture is made at room temperature with no hydrochloric acid as a catalyst, or when a mixture is heated with or without hydrochloric acid.

8. A discussion of the structure of the various condensation products is given.

9. The probable mechanism for the condensation of aromatic primary arsines and aromatic arsine oxides, antimony tri-chloride, etc., is discussed.

URBANA, ILLINOIS

AN ELECTROCHEMICAL STUDY OF THE REVERSIBLE REDUCTION OF ORGANIC COMPOUNDS[1]

BY J. B. CONANT, H. M. KAHN, L. F. FIESER AND S. S. KURTZ, JR.

Introduction

Certain organic substances, such as anthraquinone, indigo and the vat dyes, have the rather unique property of being easily reduced in aqueous solutions by such reagents as sodium hydrosulfite and titanous chloride. The reaction is readily reversible, and the reduced material may be re-oxidized by almost any mild oxidizing agent, and even by oxygen itself. These reactions are very rapid, and take place at room temperature. They seem to involve a different kind of process from such irreversible reductions as the hydrogenation of ethylene derivatives, or the reduction of aldehydes, ketones, and nitriles. It is of interest to determine, if possible, the mecha-

[1] The theoretical portions of this paper and an account of some preliminary experiments were presented to the Northeastern Section of the American Chemical Society, April 8, 1921.