derivative and the aniline, while in the cold, stannous chloride in the presence of hydrochloric acid gave the aniline along with the unchanged hydrazobenzene.

The tables indicate the conditions of attempted rearrangement and the products isolated.

Summary

1. A study of the properties of *sym.*-hexabromohydrazobenzene has shown that it cannot be responsible for the formation of a pentabromoquinoneimine obtained by the oxidation of *sym.*-tribromoaniline in acid solution with chromic anhydride. It is, therefore, probable that N analogs of the type A and type B radicals postulated in the oxidation of *sym.*-halogenated phenols play the important role.

2. *Sym.*-hexabromohydrazobenzene and 2,4,2',4'-tetrabromohydrazobenzene do not undergo the benzidine type of rearrangement. Instead they oxidize and reduce to the corresponding azo and aniline derivatives in the presence of a mineral acid without a reducing agent; in the presence of a reducing agent they are split to the anilines.

3. A method for the preparation of azo compounds is described.

MINNEAPOLIS, MINNESOTA

THE INTERACTION OF PHENYLARSINES WITH PHENYLHALOARSINES[1]

BY F. F. BLICKE AND L. D. POWERS

Several years ago it was announced by Steinkopf and Smie[2] that phenyldichloroarsine and diphenylarsine react to form triphenylchlorodiarsyl.

$$C_6H_5AsCl_2 + (C_6H_5)_2AsH = C_6H_5(Cl)As—As(C_6H_5)_2 + HCl$$
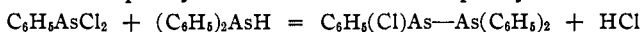
Since we wished to prepare triphenylhydroxydiarsyl,[2a] hydrolysis of the corresponding chloro compound suggested itself as a preparative procedure. Phenyldichloroarsine and diphenylarsine were allowed to react in the proportions used by the above-mentioned investigators but instead of triphenylchlorodiarsyl, arsenobenzene and diphenylchloroarsine were obtained in yields which correspond closely to those calculated from equation A.[3]

A $4C_6H_5AsCl_2 + 4(C_6H_5)_2AsH = 2C_6H_5As\!\!=\!\!AsC_6H_5 + 4(C_6H_5)_2AsCl + 4HCl$

The reaction between diphenylarsine, as well as phenylarsine, and each of the following compounds was then investigated: phenyldichloroarsine, phenyldi-iodoarsine, diphenylchloroarsine and diphenyliodoarsine.

It has been shown in separate experiments that two molecular equivalents of phenyldichloroarsine and four equivalents of diphenylarsine yield arsenobenzene and tetraphenyldiarsyl (B), that equivalent amounts

B $2C_6H_5AsCl_2 + 4(C_6H_5)_2AsH = C_6H_5As\!\!=\!\!AsC_6H_5 + 2(C_6H_5)_2As\!\!-\!\!As(C_6H_5)_2 + 4HCl$
C $2C_6H_5AsCl_2 + 2(C_6H_5)_2As\!\!-\!\!As(C_6H_5)_2 = 4(C_6H_5)_2AsCl + C_6H_5As\!\!=\!\!AsC_6H_5$
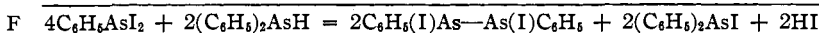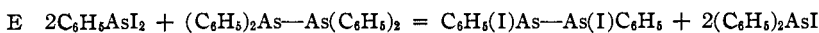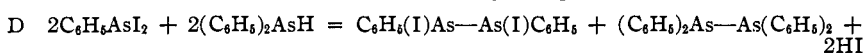
A $4C_6H_5AsCl_2 + 4(C_6H_5)_2AsH = 2C_6H_5As\!\!=\!\!AsC_6H_5 + 4(C_6H_5)_2AsCl + 4HCl$
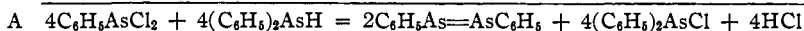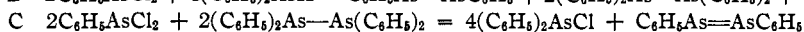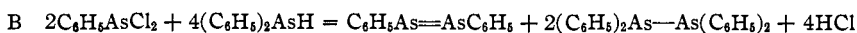
of phenyldichloroarsine and tetraphenyldiarsyl react to form diphenylchloroarsine and arsenobenzene (C) and that no reaction takes place at ordinary temperature between diphenylchloroarsine and arsenobenzene or between diphenylarsine and arsenobenzene.

When phenyldi-iodoarsine is allowed to react with diphenylarsine in the ratio shown in formulation F diphenyldi-iododiarsyl and diphenyl-iodoarsine are formed. The di-iododiarsyl is produced in this instance

D $2C_6H_5AsI_2 + 2(C_6H_5)_2AsH = C_6H_5(I)As\!\!-\!\!As(I)C_6H_5 + (C_6H_5)_2As\!\!-\!\!As(C_6H_5)_2 + 2HI$

E $2C_6H_5AsI_2 + (C_6H_5)_2As\!\!-\!\!As(C_6H_5)_2 = C_6H_5(I)As\!\!-\!\!As(I)C_6H_5 + 2(C_6H_5)_2AsI$

F $4C_6H_5AsI_2 + 2(C_6H_5)_2AsH = 2C_6H_5(I)As\!\!-\!\!As(I)C_6H_5 + 2(C_6H_5)_2AsI + 2HI$

due to the fact that phenyldi-iodoarsine, unlike phenyldichloroarsine, reacts at ordinary temperature with arsenobenzene.[4] The mechanism of this reaction may, possibly, be explained on the basis of reactions D and E since these reactions have been established by separate experiments.

Steinkopf and Smie[5] mixed phenyldi-iodoarsine and diphenylarsine in the ratio expressed in formulation D and stated that phenyliodoarsine, $C_6H_5As(I)H$, and diphenyliodoarsine were produced. The "phenyliodoarsine" described by them was, undoubtedly, diphenyldi-iododiarsyl. Furthermore, these investigators stated[6] that one molecular equivalent of phenyldi-iodoarsine and two equivalents of diphenylarsine react to form pentaphenyltriarsine, $(C_6H_5)_2As\!\!-\!\!As(C_6H_5)\!\!-\!\!As(C_6H_5)_2$; neither melting point nor any other property of this compound was recorded. The nature of the reaction product was merely deduced from the fact that treatment of the reaction product with iodine yielded phenyldi-iodoarsine and diphenyliodoarsine in a certain ratio. The experimental data yield of a chlorine analysis and on the fact that phenylarsonic acid and diphenylarsinic acid were obtained upon oxidation of the reaction product. Obviously, the same data would be obtained from a mixture which consisted of arsenobenzene and twice the molecular quantity of diphenylchloroarsine.

[4] Blicke and Smith, THIS JOURNAL, **52**, 2942 (1930).

[5] Ref. 2, p. 1460.

[6] Ref. 2, p. 1461.

little or no evidence in favor of the contention that pentaphenyltriarsine was formed in this reaction.

Diphenylchloroarsine and diphenylarsine, dissolved in ether, yielded tetraphenyldiarsyl and the interaction of these substances represents a satisfactory method for the preparation of the diarsyl.

$$\text{G} \quad (C_6H_5)_2AsCl + (C_6H_5)_2AsH = (C_6H_5)_2As\text{---}As(C_6H_5)_2 + HCl$$
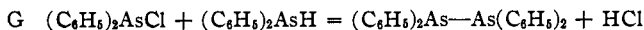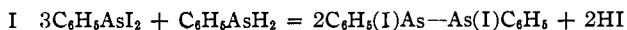
Diphenyliodoarsine and diphenylarsine, dissolved in alcohol, also react to form tetraphenyldiarsyl.

Phenyldichloroarsine reacts with phenylarsine to form arsenobenzene.

$$\text{H} \quad C_6H_5AsCl_2 + C_6H_5AsH_2 = C_6H_5As\text{==}AsC_6H_5 + 2HCl$$
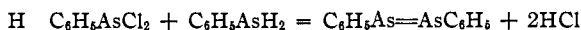
Phenyldi-iodoarsine and phenylarsine yield the same reaction product when they are mixed in equivalent amounts. However, if three molecular equivalents of the di-iodo compound react with one equivalent of phenylarsine diphenyldi-iododiarsyl is formed.

$$\text{I} \quad 3C_6H_5AsI_2 + C_6H_5AsH_2 = 2C_6H_5(I)As\text{---}As(I)C_6H_5 + 2HI$$

When diphenylchloroarsine and phenylarsine are allowed to react in the ratio expressed in the following equation arsenobenzene and tetra-

$$\text{J} \quad 4(C_6H_5)_2AsCl + 2C_6H_5AsH_2 = C_6H_5As\text{==}AsC_6H_5 + 2(C_6H_5)_2As\text{---}As(C_6H_5)_2 + 4HCl$$

phenyldiarsyl are produced. If the above-mentioned compounds are mixed in equimolecular quantities arsenobenzene and tetraphenyldiarsyl are again formed as reaction products. Steinkopf and Smie[7] stated that diphenylchloroarsine and phenylarsine react to form triphenyldiarsyl, $(C_6H_5)_2As\text{---}As(H)C_6H_5$. These investigators merely analyzed their reaction product, which was not characterized by a melting point, and considered the arsenic analysis and the fact that a mixture of phenylarsonic and diphenylarsinic acids was obtained upon oxidation of their product with nitric acid sufficient proof for the claim that triphenyldiarsyl had been formed. The data published by Steinkopf and Smie would be almost identical with that obtained from a mixture which consisted of one equivalent of arsenobenzene and two equivalents of tetraphenyldiarsyl.

Diphenyliodoarsine and phenylarsine, mixed in the proportion given below, yield arsenobenzene and tetraphenyldiarsyl.

$$\text{K} \quad 4(C_6H_5)_2AsI + 2C_6H_5AsH_2 = C_6H_5As\text{==}As_36H_5 + 2(C_6H_5)_2As\text{---}As(C_6H_5)_2 + 4HI$$
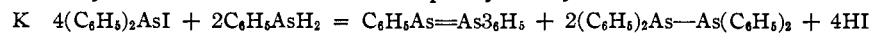
Experimental Part

Since phenylarsine, diphenylarsine and many of the reaction products absorb oxygen with great rapidity, it was necessary to carry out all experiments in an inert atmosphere. The apparatus used for this purpose is shown in the accompanying sketch. By manipulation of the stopcocks the free radical bulb, as well as the buret above it, was evacuated and filled with dry, oxygen-free nitrogen. This operation was repeated several times until all air had been removed from the system. The arsine was introduced

[7] Ref. 2, p. 1458.

into the buret from the reservoir[8] and allowed to flow into the evacuated radical bulb. The walls of the buret were then washed free from arsine by the introduction of ether, benzene or alcohol from the dropping funnel. After the radical bulb had been filled with nitrogen, it was disconnected and the substance added with which the arsine was to react.[9] In the event that pressure developed in the bulb the side arm of the latter was connected to the mercury trap shown in the lower left-hand corner of the diagram or photograph.

All solvents were saturated with nitrogen prior to use and only the absolute grades of alcohol and ether were employed. A dextrin–mannitol–glycerol stopcock lubricant[10] was found to be very satisfactory when ether or benzene was used as a solvent. The melting points of compounds which absorb oxygen were determined in a sealed tube filled with nitrogen. The reaction mixtures were shaken for at least twenty-four hours. Absorption experiments were carried out in bromobenzene solution.

Phenyldichloroarsine and Diphenylarsine (A, B).—Six and ninety-two hundredths grams (5.32 cc., 0.030 mole) of diphenylarsine[11] was added to 8.50 g. (0.038 mole) of phenyldichloroarsine, dissolved in 50 cc. of ether. After a short time a heavy, crystalline precipitate had formed. The ether was decanted into a second radical bulb and the precipitate, which proved to be arsenobenzene, washed with ether a number of times until it was entirely free from halogen compounds;[12] mixed m. p. 210–212°. The material was recrystallized from xylene for analysis.

Anal. Calcd. for $C_{12}H_{10}As_2$: As, 49.31. Found: As, 49.23, 49.38.

The yield was 3.96 g. or 87% of the calcd. amount.

Fig. 1.

[8] After each arsine had been prepared it was distilled directly into a reservoir of the type shown through the short side arm. In such containers the arsines can be protected from oxidation for a long time.

[9] In some instances the arsine was introduced after the other component of the reaction had been placed in the radical bulb.
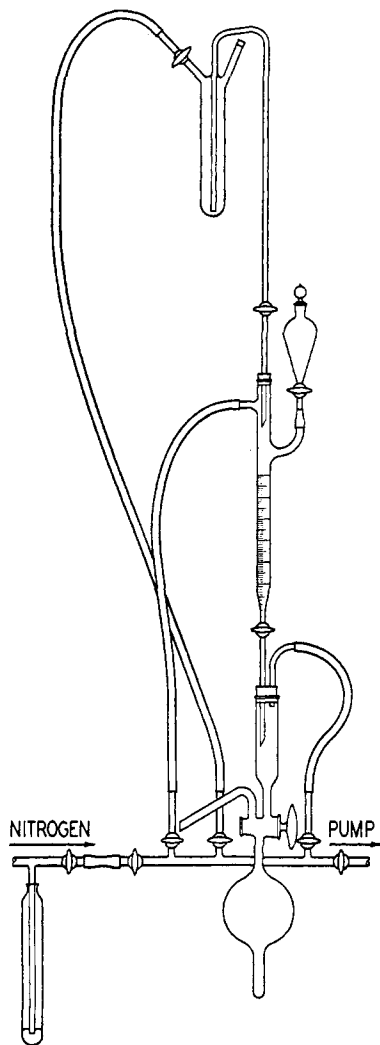
[10] The directions for the preparation of this lubricant were furnished us by C. C. Meloche and W. G. Fredrick.

[11] The following constants were determined for diphenylarsine: d_{25}^{25} 1.30; b. p. 158–160° under 16 mm. pressure.

[12] Arsenobenzene absorbs oxygen rapidly unless it is washed free from all traces of halogen compounds.

NITROGEN   PUMP

The ether layer from the reaction mixture, which contained diphenylchloroarsine and unchanged phenyldichloroarsine, was treated with alkali in order to convert the chlorides into oxides. Phenylarsine oxide dissolved in the aqueous layer while 6.78 g. or 95% of the calcd. amount of tetraphenylarsyl oxide was isolated from the ether layer. The latter oxide, after it had been washed with petroleum ether (30–60°), melted at 94–95°.

Mixed in the ratio shown in formulation B, 4.6 g. (3.5 cc., 0.02 mole) of diphenylarsine reacted with 2.2 g. (0.01 mole) of phenyldichloroarsine, dissolved in 25 cc. of ether, to form a bulky, crystalline precipitate. In order to expel the hydrogen chloride formed[13] the ether was removed by distillation, the residue treated with 25 cc. of ether and the solvent again expelled. After the product had been dried for two hours under 15 mm. pressure the mixture was extracted a number of times with ether in order to remove tetraphenyldiarsyl; about 500 cc. of ether was used for this purpose. The tetraphenyldiarsyl obtained melted at 125–129°;[14] 0.887 g. of the material absorbed 43 cc. (N. T. P.) of oxygen, which is the calculated amount. The arsenobenzene, which remained as a residue, weighed 1.3 g.; calcd. amount 1.5 g.; mixed m. p. 209–211°.

Phenyldichloroarsine and Tetraphenyldiarsyl (C).—Two and forty-five hundredths grams (0.005 mole) of tetraphenyldiarsyl was allowed to react with 1.2 g. (0.005 mole) of phenyldichloroarsine, dissolved in 100 cc. of ether. About three-fourths of the solvent was then removed by distillation and after some time a precipitate of arsenobenzene was obtained. The supernatant liquid was decanted and the arsenobenzene washed free from chlorine compounds with ether. There was isolated 0.22 g. of the arseno compound which melted at 196–206°. The ether washings were exposed to air and the residue obtained after evaporation of the solvent was treated with a mixture of ether and low-boiling petroleum ether; 0.92 g. of diphenylchloroarsine, m. p. 41–42°, was obtained.

Phenyldi-iodoarsine and Diphenylarsine (D, F).—Diphenyldi-iododiarsyl precipitated almost immediately when 4.06 g. (0.01 mole) of phenyldi-iodoarsine, dissolved in 100 cc. of ether, was mixed with 2.30 g. (0.01 mole) of diphenylarsine. After twenty-four hours the solvent was completely removed by distillation and the residue, a mixture of diphenyldi-iododiarsyl and tetraphenyldiarsyl, dried for two hours under diminished pressure in order to expel hydrogen iodide. The mixture was extracted four times with 50-cc. portions of ether and the ether layers, which contained tetraphenyldiarsyl, decanted into a second radical bulb. The residue of diphenyldi-iododiarsyl weighed 2.43 g.; calcd. amount 2.79 g.; m. p. 176–179°.[15]

The combined ether extracts were shaken with alkali to remove traces of iodine compounds and the solvent then removed. An oil was obtained which was treated with 25 cc. of alcohol; after the solvent had been partially removed by distillation tetraphenyldiarsyl separated in crystalline form. After recrystallization from absolute alcohol, 1.3 g. of material was obtained which melted at 128–130°.

Anal. Calcd. for $C_{24}H_{20}As_2$: As, 32.73. Found: As, 32.58, 32.28.

From the alcoholic mother liquor 0.4 g. more of the diarsyl was obtained. The calcd. yield is 2.29 g. Upon exposure to oxygen, 0.587 g. of the compound absorbed 30 cc. (N. T. P.) of the gas; calcd. amount 29 cc.

In accordance with formulation F 2.30 g. (0.01 mole) of diphenylarsine was added to 8.11 g. (0.02 mole) of phenyldi-iodoarsine, dissolved in 50 cc. of ether. A copious

[13] Removal of the hydrogen chloride seems to facilitate the quantitative isolation of arsenobenzene and also prevents oxidation of the latter.

[14] Blicke and Smith, THIS JOURNAL, **51**, 2275 (1929); Blicke, Weinkauff and Hargreaves, *ibid.*, **52**, 782 (1930).

[15] Blicke and Smith, THIS JOURNAL, **52**, 2943 (1930).

yellow precipitate of diphenyldi-iododiarsyl formed immediately. The ether layer was decanted, the precipitate washed a number of times with ether and then dried at 50° under 15 mm. pressure for two hours. The product melted at 177–178°; yield 5.32 g.; calcd. yield 5.57 g. From the ether mother liquor an oil was obtained which solidified in the form of a yellow crystalline mass when cooled; m. p. 39–41°. This material, diphenyliodoarsine, weighed 3.76 g. in the crude state; calcd. yield 3.55 g.

Phenyldi-iodoarsine and Tetraphenyldiarsyl (E).—Four and one-tenth grams of phenyldi-iodoarsine was added to about 2 g. of tetraphenyldiarsyl, dissolved in benzene. Diphenyldi-iododiarsyl soon precipitated from the mixture; after it had been washed with ether it melted at 175–177° and weighed 1.4 g. The benzene mother liquor and ether washings were combined and shaken with alkali in order to convert the halides to oxides. The diphenyliodoarsine was isolated, therefore, as tetraphenylarsyl oxide; yield 1.4 g. Eight-tenths of a gram of phenylarsine oxide was also obtained as the result of hydrolysis of the excess phenyldi-iodoarsine used.

Diphenylchloroarsine and Diphenylarsine (G).—To 3.4 g. (0.015 mole) of diphenyl-arsine there was added 4.4 g. (0.016 mole) of diphenylchloroarsine, dissolved in 50 cc. of ether. After two hours the solution was concentrated to a volume of about 10 cc., whereupon tetraphenyldiarsyl precipitated. The ether mother liquor was decanted, a small quantity of fresh ether added and the ether suspension shaken a number of times with water until all hydrochloric acid had been removed. The ether was then removed by distillation and the material dried under diminished pressure; m. p. 124–127°. The yield was 6.0 g.; calcd. yield, 6.8 g.

Diphenyliodoarsine and Diphenylarsine.—Tetraphenyldiarsyl precipitated instantly when 3.56 g. of diphenyliodoarsine, dissolved in 50 cc. of alcohol, was added to 2.30 g. of diphenylarsine. The diarsyl was purified in the manner described above; m. p. 129–130°. The yield was 3.4 g.; calcd. amount, 4.6 g.

Phenyldichloroarsine and Phenylarsine (H).—A mixture prepared from 3.34 g. (0.015 mole) of phenyldichloroarsine, 2.30 g. (0.015 mole) of phenylarsine and 65 cc. of ether was shaken for twenty-four hours. The ether layer was decanted from the crystalline material into a second radical bulb and the solid product washed with ether until it was completely free from hydrogen chloride. The material, which was arsenobenzene, weighed 1.94 g.; m. p. 209–211°. From the ether layer 2.20 g. more of arsenobenzene was obtained. The total yield was 4.14 g.; calcd. amount, 4.56 g.

Phenyldi-iodoarsine and Phenylarsine (I).—No apparent reaction took place after 2.30 g. (0.015 mole) of phenylarsine had been shaken with 1.68 g. (0.01 mole) of phenyl-arsine oxide, dissolved in benzene, for twenty-four hours.[16] There was then added 12.2 g. (0.03 mole) of phenyldi-iodoarsine, dissolved in benzene. Diphenyldi-iododiarsyl precipitated immediately; m. p. 178–180°. The yield was 14.3 g.; calcd. yield, based on 0.04 mole of phenyldi-iodoarsine, 14.8 g.

Diphenylchloroarsine and Phenylarsine (J).—When 12 g. (0.045 mole) of diphenyl-chloroarsine was added to 2.97 g. (0.019 mole) of phenylarsine, dissolved in 100 cc. of ether, there was no visible sign of reaction. Twenty-five cubic centimeters of alcohol was then added, whereupon a crystalline precipitate soon began to form. After twelve hours the solvents were removed by distillation and the residue dried for two hours under 15 mm. pressure in order to remove hydrogen chloride completely. One hundred cubic centimeters of ether was added to the residue, the mixture shaken for several hours and the ether solution of tetraphenyldiarsyl decanted into a second radical bulb. This

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[16] These compounds were mixed in order to determine whether or not they reacted under the given experimental conditions. The hydrogen iodide, formed subsequently as a result of the interaction of phenylarsine and phenyldi-iodoarsine, converted the phenylarsine oxide into phenyldi-iodoarsine.

process was repeated until a test portion of the ether extract left no residue upon evaporation of the solvent; about 500 cc. of ether was required. From the ether solutions there was obtained 9.08 g. of tetraphenyldiarsyl; m. p. 123–127°; calcd. yield 9.16 g. When 0.915 g. of the compound was exposed to oxygen, 47 cc. of the gas was absorbed; calcd. absorption, 45 cc. The residue after extraction of the reaction mixture with ether was pure arsenobenzene; m. p. 210–211°. The yield was 2.70 g.; calcd. yield, 3.04 g.

Anal. Calcd. for $C_{12}H_{10}As_2$: As, 49.31. Found: As, 49.57, 49.23.

In the following experiment the compounds were allowed to react in amounts which are practically equimolecular. To 5.29 g. (0.020 mole) of diphenylchloroarsine, dissolved in 100 cc. of alcohol, there was added 3.24 g. (0.021 mole) of phenylarsine; an oil precipitated which soon became crystalline. The alcohol layer was decanted into a second bulb and after complete removal of hydrogen chloride and unchanged arsine the tetraphenyldiarsyl was extracted with ether; m. p. 123–130°. The yield was 2.33 g.; calcd. yield, 4.58 g. One and fifty-four hundredths grams of arsenobenzene, m. p. 207–210°, was left as a residue; calcd. amount, 1.52 g.

The alcoholic solution which had been decanted contained the remainder of the diarsyl; the latter was allowed to oxidize in air. The alcohol was removed, the mixture of diphenylarsinic acid and tetraphenylarsyl oxide treated with sulfur dioxide and hydriodic acid in the presence of hydrochloric acid and the diphenylhaloarsines hydrolyzed to tetraphenylarsyl oxide; yield, 1.93 g.; m. p. 92–95°.

Any pentaphenyltriarsine or triphenyldiarsyl which might have been formed in this reaction would have been present in the decanted alcoholic solution and upon oxidation would have been converted into tetraphenylarsyl oxide and phenylarsine oxide; only a trace of the latter was found to be present in the oxidized solution.

Diphenyliodoarsine and Phenylarsine (K).—No apparent reaction took place when 8.50 g. (0.024 mole)[17] of diphenyliodoarsine was mixed with 1.08 g. (0.007 mole) of phenylarsine in 100 cc. of ether. Upon the addition of 25 cc. of alcohol a precipitate soon formed. After forty-eight hours the supernatant liquid was decanted into a second bulb and the precipitated arsenobenzene washed six times with 50-cc. portions of ether; m. p. 200–204°. The yield was 0.93 g.; calcd. yield, 1.07 g.

The ether–alcohol layer which had been decanted contained tetraphenyldiaryl and the excess diphenyliodoarsine. The solution was concentrated to about 15 cc., whereupon tetraphenyldiarsyl and some diphenyliodoarsine precipitated. The mother liquor was decanted and the product washed a number of times with petroleum ether (30–60°) in order to remove the iodoarsine. The yield of tetraphenyldiarsyl was 1.40 g.; m. p. 129–130°; calcd. amount, 3.21 g.

Each of the following compounds, dissolved in ether, was shaken with arsenobenzene for three days at ordinary temperature: phenyldichloroarsine, diphenylchloroarsine, diphenyliodoarsine, diphenylarsine and phenylarsine. In the case of each mixture at least 90% of each component was recovered unchanged. Furthermore, it was found that neither phenylarsine nor diphenylarsine reacts with tetraphenyldiarsyl at ordinary temperature.

Summary

The interaction of phenylarsine, as well as diphenylarsine, and each of the following compounds has been investigated: phenyldichloroarsine, phenyldi-iodoarsine, diphenylchloroarsine and diphenyliodoarsine. Substances such as tetraphenyldiarsyl, diphenyldi-iododiarsyl and arsenobenzene have been obtained as reaction products.

[17] This quantity represents an excess over that demanded by the formulation

It seems that compounds such as phenyliodoarsine, triphenyldiarsyl, triphenylchlorodiarsyl and pentaphenyltriarsine are not produced by interaction of the above-mentioned arsines although the formation of these substances has been reported by other investigators.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

RESEARCHES ON NITROGENOUS GLYCOSIDES. I. THE UTILIZATION OF GLYCOSE ISOCYANATES FOR GLYCOSIDE SYNTHESES

BY TREAT B. JOHNSON AND WERNER BERGMANN[1]

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So far as the writers are aware, only one sugar isocyanate derivative has been described in the chemical literature, namely, tetraacetyl-*d*-glycose-*l*-isocyanate, $C_{14}H_{19}O_9NCO$. This interesting compound was described by Emil Fischer in a paper entitled "Synthese neuer Glycoside," in 1914[2] but since this publication, apparently no attention has been paid to its chemistry. Fischer obtained this sugar derivative by the action of silver cyanate on tetraacetobromoglycose, but the chief product of this reaction was an amorphous substance having the same composition as the glycose isocyanate but whose constitution was not established by Fischer.[3]

We have now repeated Fischer's preliminary experiments in order to obtain his isocyanate derivative for new glycoside syntheses. We find that silver cyanate interacts with tetraacetylbromoglycose in xylene solution to give, besides resinous substances, three definite compounds which have been identified, namely, two modifications of the glycose isocyanate (A and B), melting at 120 and 92°, respectively, and the amorphous substance previously described by Fischer as a product of this reaction. We conclude that this amorphous material is without doubt impure *sym.*-octaacetyl-*d*-diglycose urea, which is formed by the interaction of tetraacetylglycose isocyanate with water. It can be purified easily to give a beautiful crystalline substance melting at 160–161°. That this is octaacetyl-glycose urea is not only established by the results of our analyses, but also by its characteristic behavior toward aqueous ammonia. By treatment with this reagent it is transformed by hydrolysis smoothly into *sym.*-*d*-diglycose urea. The

[1] Sterling Research Assistant in Organic Chemistry, 1931–1932.

[2] E. Fischer, *Ber.*, **47**, 1377 (1914).

[3] Fischer also examined the behavior of silver isothiocyanate toward tetraacetylbromoglycose and observed the smooth formation of the corresponding glycose-isothiocyanate derivative, $C_{14}H_{19}O_9NCS$. Here also practically no attention has been paid to the chemistry of this mustard oil since Fischer's work in 1914. The results of a new research dealing with specific reactions of this interesting compound will be discussed in a future paper from this Laboratory by Miss Katherine Haring.