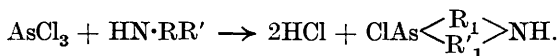


LIX.—10-Chloro-5 : 10-dihydrophenarsazine and its Derivatives. Part II. The Action of Primary Chloroarsines on Diphenylamine and its Homologues.

By HAROLD BURTON and CHARLES STANLEY GIBSON.

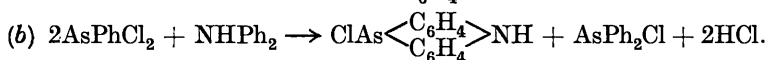
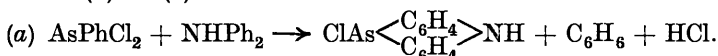
It has been shown (preceding paper) that the reaction between arsenious chloride and diphenylamine and its homologues goes very readily either when the two substances are heated alone, or more conveniently, in the presence of a suitable solvent, dihydrophenarsazine derivatives being formed. The reaction taking place may be generally expressed ($R_1 = R - H$; $R'_1 = R' - H$):



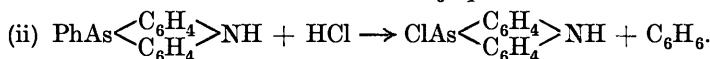
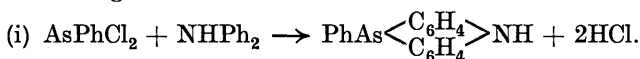
It seemed desirable to investigate the application of the reaction to the case of dichloroarsines with a view to obtain dihydrophenarsazine derivatives of the type $\text{XAs}\left\langle \begin{array}{c} R_1 \\ R'_1 \end{array} \right\rangle \text{NH}$ [$\text{X} =$ univalent hydrocarbon or substituted hydrocarbon radical]. The most

convenient dichloroarsine was phenyldichloroarsine, easily prepared by reducing phenylarsinic acid, which in turn is readily obtainable by the Bart reaction on aniline.

When the reaction between phenyldichloroarsine and diphenylamine was carried out under the conditions employed for preparing 10-chloro-5 : 10-dihydrophenarsazine, *viz.*, with equimolecular quantities heated in the presence of *o*-dichlorobenzene, the product was not 10-phenyl-5 : 10-dihydrophenarsazine, but 10-chloro-5 : 10-dihydrophenarsazine, the substance obtained by the condensation of arsenious chloride and diphenylamine. It appeared that the reaction to produce 10-chloro-5 : 10-dihydrophenarsazine might be either (a) or (b).



It was also recognised that reaction (a) might be the final result of the following two reactions.



In a preliminary experiment two molecules of the chloroarsine and one molecule of diphenylamine were heated together in *o*-dichlorobenzene solution. A theoretical yield of 10-chloro-5 : 10-dihydrophenarsazine calculated on the quantity of diphenylamine taken was obtained, and instead of the easily recognisable diphenylchloroarsine, only phenyldichloroarsine was obtained on examining the filtrate from the solid product. Experiments using molecular proportions of the reacting substances, heated for a longer time, also gave theoretical amounts of 10-chloro-5 : 10-dihydrophenarsazine, but it was not until the reaction was carried out in the absence of solvent that we were able to collect a volatile substance, which was identified as benzene.

In view of these results, the publication of a paper by Lewis and Stiegler (*J. Amer. Chem. Soc.*, 1925, **47**, 2551) containing experiments on the condensation of β -chlorovinyl-dichloroarsine with diphenylamine and phenyl- α -naphthylamine, and the description of the condensation products "6- β -chlorovinylphenarsazine," and "7- β -chlorovinyl-7 : 12-dihydro- γ -benzophenarsazine," seemed somewhat anomalous to us, especially as the melting points of the two compounds quoted (186—187° and 213°, respectively) were so near to those of 10-chloro-5 : 10-dihydrophenarsazine and 7-chloro-

7:12-dihydrobenzophenarsazine (191—192° and 219—220°, respectively), and therefore we decided to repeat our work; extend it to other diarylamines; and finally repeat Lewis and Stiegler's experiments.

We have done this and find that our initial observations are correct. The extension of the work consisted in studying the action of phenyldichloroarsine on phenyl-*p*-tolylamine, *pp'*-ditolylamine, and phenyl- α -naphthylamine. In each case, the reaction proceeded as with diphenylamine and instead of the *As*-phenyl derivatives we obtained the chlorodihydrophenarsazine derivative.

The compound isolated from phenyl-*p*-tolylamine, namely, 10-chloro-2-methyl-5:10-dihydrophenarsazine,* has been synthesised from the former substance and arsenious chloride. The *N*-acetyl derivative of this compound has been prepared, and also the corresponding *phenarsazinic acids*, using the method of Burton and Gibson (J., 1924, 125, 2276). The compound obtained from *pp'*-ditolylamine is referred to in the German Patent (D.R.-P. 281049, Friedländer, "Fortschritte," 1914, XII, 843), but so far as we can discover, this substance, 10-chloro-2:8-dimethyl-5:10-dihydrophenarsazine, has not yet been described in the literature. We have prepared it from *pp'*-ditolylamine and arsenious chloride, and also obtained its *N*-acetyl derivative.

A repetition of Lewis and Stiegler's work, adhering as far as possible to their quantities and conditions, showed that the reaction between diphenylamine and β -chlorovinyl-dichloroarsine proceeded in a similar manner to that using phenyldichloroarsine. In the presence of *o*-dichlorobenzene a quantitative yield of 10-chloro-5:10-dihydrophenarsazine was obtained, which after crystallisation from carbon tetrachloride melted at 186—187° and did not depress the melting point of a pure specimen. Further crystallisation from the same solvent gave a pure product, m. p. 190—191°, identical with an authentic specimen. From phenyl- α -naphthylamine in boiling *o*-dichlorobenzene solution we isolated 7-chloro-7:12-dihydrobenzophenarsazine, also in quantitative yield. In the absence of solvent, the yields were not so good, but the products obtained were identical with those from the experiments done in *o*-dichlorobenzene. It was found necessary to crystallise the crude 10-chloro-5:10-dihydrophenarsazine twice from carbon tetrachloride before it would melt at 190—191°, and although the product from phenyl- α -naphthylamine was crystallised from xylene, following Lewis and Stiegler's directions, it melted three degrees low, and had to be further crystallised from toluene before it was pure. We were able

* The nomenclature of these compounds is described in the preceding paper.

to prove the formation of vinyl chloride in these experiments by passing the hydrogen chloride and vinyl chloride evolved through a solution of bromine in carbon tetrachloride, when the colour of the bromine was discharged. That this decoloration was not due to acetylene produced by decomposition of the β -chlorovinyl-dichloroarsine was further demonstrated by washing the carbon tetrachloride solution with dilute sodium carbonate solution, and after subsequent drying and removal of the carbon tetrachloride, determining the boiling point of the residue. This was 160—162°, which is in good agreement with the b. p., 162.5—163°, recorded by Biltz (*Ber.*, 1902, **35**, 3526) for α -bromo- β -chlorobromoethane.* During these experiments we were unable to isolate any compound of the type $\text{XAs} \left\langle \begin{smallmatrix} \text{R}_1 \\ \text{R}'_1 \end{smallmatrix} \right\rangle \text{NH}$.

EXPERIMENTAL.

Freshly-made phenyldichloroarsine, b. p. 247—250°/752 mm., and β -chlorovinyl-dichloroarsine, b. p. 93—94°/24 mm., were used in the following experiments. The diphenylamine and *o*-dichlorobenzene also were freshly distilled.

Condensations of Phenyldichloroarsine with Diphenylamine and Related Compounds.—(a) *In the presence of solvent.* In the preliminary experiments a mixture of diphenylamine (8.45 g.), phenyldichloroarsine (22.3 g.), and *o*-dichlorobenzene (20 c.c.) was heated under reflux for 8 hours. Hydrogen chloride had then ceased to be evolved. The green solution was cooled, mixed with petrol (20 c.c.), and the solid filtered off. This, after being washed with petrol (30 c.c.) and dried to constant weight at 100°, crystallised from benzene in yellow needles, m. p. 189—190°, and was identical in all respects with an authentic sample of 10-chloro-5 : 10-dihydrophenarsazine prepared from diphenylamine and arsenious chloride. The yield was almost theoretical.

Similar experiments using (a) phenyl-*p*-tolylamine, (b) di-*p*-tolylamine, and (c) phenyl- α -naphthylamine gave (a) 10-chloro-2-methyl-5 : 10-dihydrophenarsazine, m. p. 199—200° (decomp.), (b) 10-chloro-2 : 8-dimethyl-5 : 10-dihydrophenarsazine, m. p. 261—262°, after

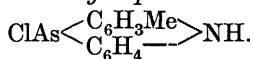
* Lewis and Stiegler, in calculating the value for the percentage of chlorine in the supposed 10- β -chlorovinyl-5 : 10-dihydrophenarsazine, arrived at too high a value, the actual figure being 11.69% instead of 12.00%. Their low analytical data for a sample of pure 10-chloro-5 : 10-dihydrophenarsazine together with its low melting point explain, in all probability, the reason they have assigned the wrong constitution to this compound. The obvious impurity of their 7-chloro-7 : 12-dihydrobenzophenarsazine, the m. p. of which was 6° below that of a pure specimen, is, no doubt, the cause of their low analytical data.

previous decomposition, and (c) 7-chloro-7:12-dihydrobenzophenarsazine, m. p. 218—219°.

In the second series of experiments, half the quantity of phenyldichloroarsine was used and the mixture was boiled for 16 hours. The product was treated in the same manner, and a yield of 93% of the theoretical quantity of 10-chloro-5:10-dihydrophenarsazine was obtained. (The yields of the other chlorodihydrophenarsazines varied from 90—95%.)

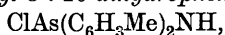
(b) *In the absence of solvent.* These experiments consisted in heating mixtures of diphenylamine and phenyldichloroarsine, in the molecular ratio of 1:1 and 1:2, in a metal-bath, the temperature of which was raised to 230° during 30 minutes and maintained for 45 minutes. The volatile product, after being washed with dilute sodium carbonate solution and dried, boiled at 80°; it was benzene. The residue in the flask, after crystallising from boiling *o*-dichlorobenzene, was 10-chloro-5:10-dihydrophenarsazine.

10-Chloro-2-methyl-5:10-dihydrophenarsazine,



—A mixture of phenyl-*p*-tolylamine (36.6 g.), arsenious chloride (40 g.), and *o*-dichlorobenzene (80 c.c.) was boiled under reflux for 4 hours. On cooling, the chloro-compound (51 g.) separated as a mass of green crystals. On crystallisation from benzene, the substance was obtained in yellow needles, m. p. 199—200° (decomp.) (Found: Cl, 12.3. $\text{C}_{13}\text{H}_{11}\text{NClAs}$ requires Cl, 12.2%).

10-Chloro-2:8-dimethyl-5:10-dihydrophenarsazine,



was prepared by heating together for 4 hours a mixture of di-*p*-tolylamine (32.7 g.), arsenious chloride (33.2 g.), and *o*-dichlorobenzene (133 c.c.). The crude chloro-compound (44.7 g.) crystallised from nitrobenzene in orange prisms, m. p. 261—262° with previous decomposition (compare D.R.-P., *loc. cit.*) (Found: As, 24.2. $\text{C}_{14}\text{H}_{13}\text{NClAs}$ requires As, 24.5%).

10-Chloro-5-acetyl-2-methyl-5:10-dihydrophenarsazine was prepared by boiling a mixture of the corresponding phenarsazine (30 g.) with acetic anhydride (60 c.c.) for 3½ hours. On cooling, the *acetyl* derivative (25 g.) separated in almost colourless crystals. It separated from benzene-light petroleum in clusters of almost colourless needles, m. p. 154—155° (Found: Cl, 10.7. $\text{C}_{15}\text{H}_{13}\text{ONClAs}$ requires Cl, 10.6%).

10-Chloro-5-acetyl-2:8-dimethyl-5:10-dihydrophenarsazine.—A suspension of the chloroarsine (10 g.) in acetic anhydride (50 c.c.) was boiled for 2 hours, when solution was complete and the colour of

the original compound had almost disappeared. After removal of half the acetic anhydride by distillation the crude acetyl compound separated in nearly colourless needles. It separated from benzene-light petroleum in colourless needles, m. p. 164—165° (Found : As, 21.4. $C_{16}H_{15}ONClAs$ requires As, 21.6%)

2-Methylphenarsazinic acid, $NH \left\langle \begin{array}{c} C_6H_3Me \\ C_6H_4 \end{array} \right\rangle AsO \cdot OH$, separated in good yield when a mixture of the chloroarsine and chloramine-T had stood for 12 hours. It crystallised from aqueous acetic acid in colourless, fine needles which did not melt when heated but decomposed above 300° (Found : As, 25.6. $C_{13}H_{12}O_2NAs$ requires As, 25.9%). The *sodium* salt crystallises from water in colourless, hair-like needles. The *hydrochloride* was obtained by treating a suspension of the acid in boiling alcohol with concentrated hydrochloric acid until crystalline matter began to separate. On cooling, the hydrochloride separated in colourless, small prisms, m. p. 209—211° (decomp.) (Found : Cl, 10.9. $C_{13}H_{12}O_2NAs, HCl$ requires Cl, 10.9%).

2 : 8-Dimethylphenarsazinic acid was prepared by boiling a suspension of the chloroarsine (10 g.) in acetone (200 c.c.) with a solution of chloramine-T (18.5 g. in 185 c.c. of water) for 30 minutes. The orange colour of the original substance disappeared and colourless, crystalline matter was produced. The *acid* (6.3 g.) separated from aqueous acetic acid in colourless, glistening plates, which decomposed without melting at a high temperature (Found : As, 24.5. $C_{14}H_{14}O_2NAs$ requires As, 24.7%). The *sodium* salt crystallises from water in colourless needles, and the *hydrochloride*, prepared as above, was obtained in colourless needles, m. p. 216° (decomp.) after previous softening (Found : As, 21.7. $C_{14}H_{14}O_2NAs, HCl$ requires As, 22.1%).

N-Acetyl-2 : 8-dimethylphenarsazinic acid, prepared in the usual manner, separated from dilute acetic acid in colourless prisms, m. p. 240° (decomp.) (Found : As, 21.65. $C_{16}H_{16}O_3NAs$ requires As, 21.7%).

Condensation of β -Chlorovinylchloroarsine with Diphenylamine and Phenyl- α -naphthylamine.—(a) *In the presence of solvent.* The mixture of diphenylamine (10.6 g.), β -chlorovinylchloroarsine (13.0 g.), and *o*-dichlorobenzene (25 c.c.) was boiled under reflux for 12 hours. Owing to the formation of a certain amount of tarry matter, the crude compound, isolated as in the phenyldichloroarsine experiments, was extracted in a Soxhlet with carbon tetrachloride. The 10-chloro-5 : 10-dihydrophenarsazine obtained melted at 187° without further crystallisation, and a sample of it did not depress

the melting point of an authentic specimen. The yield was quantitative. Further crystallisation from the same solvent gave pure 10-chloro-5 : 10-dihydrophenarsazine, m. p. 190—191°. A similar experiment using phenyl- α -naphthylamine gave 7-chloro-7 : 12-dihydrobenzophenarsazine, m. p. 218—219°.

(b) *In the absence of solvent.* The quantities and conditions used in these experiments were the same as those described by Lewis and Stiegler. The only difference in procedure after the initial reaction was that the crude mass from the diphenylamine was extracted with carbon tetrachloride in a Soxhlet apparatus and finally crystallised from carbon tetrachloride. In this way, we obtained a specimen of pure 10-chloro-5 : 10-dihydrophenarsazine, m. p. 190—191° (Found : Cl, 12.8; As, 26.8%). From the phenyl- α -naphthylamine experiment pure 7-chloro-7 : 12-dihydrobenzophenarsazine was obtained, m. p. 219—220° (compare Lewis and Hamilton, *J. Amer. Chem. Soc.*, 1921, **43**, 2218) after a further crystallisation from toluene (Found : Cl, 10.9%).

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