

Anal. Calcd. for $C_4H_7AsCl_2O$: Cl, 33.31. Found: Cl, 32.83.

Di- α -furylchloroarsine.—The compound is a colorless liquid and is relatively stable if stored cold and in the dark.

Anal. Calcd. for $C_8H_6AsClO_2$: Cl, 14.68. Found: Cl, 14.67.

Di- α -furylcianoarsine.—A solution of II (82 g.) in benzene (100 ml.) was added slowly with stirring to a suspension of silver cyanide (59 g.) in benzene (150 ml.). The reaction was protected from moisture during the addition and a subsequent reflux period of ten hours. After cooling, the precipitated silver chloride was removed by filtration and washed with benzene. The filtrate and washings were distilled to yield 55 g. (70%) of a viscous, halogen-free liquid boiling at 142–143° (2.3 mm.).

Anal. Calcd. for $C_8H_6AsNO_2$: As, 31.87. Found: As, 31.47.

Summary

1. Mercuric chloride has been found to catalyze the disproportionation of furan arsenicals, arsenic trichloride and tri- α -furylarsine being formed at the expense of α -furyldichloroarsine and di- α -furylchloroarsine.

2. An improved method of synthesis for these three furan arsenicals is given. Better yields and stability of products result if mercuric chloride is absent.

3. The preparation of di- α -furylcianoarsine is described.

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The Reaction Products of Phenylchloroarsine and Acetylene¹

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Hunt and Turner² and Das Gupta³ have reported on the reaction of phenylchloroarsine with acetylene. The products identified by the two investigators, and the properties assigned to them are markedly different. Since one of the compounds, phenyl-(β -chlorovinyl)-chloroarsine, was of possible interest as a toxic agent, the re-

considerably from both of the previous reports. Furthermore, it was demonstrated that the complete equilibrium involved not only the various possible acetylene addition products but also disproportionations involving the phenyl radical. Of all the possible products, only arsenic trichloride and diphenylchloroarsine were not identified. It is conceivable that they were present in quantities too minute for detection. Catalysts other than aluminum chloride were tried without success.

TABLE I

| Frac- tion | Wt., g. | Identity | Arsenic, ^a % | | B. p., °C. | | | Derivative | |
|---------------|------------|---|-------------------------|-------|-------------------|-----------------------------------|------------------|--------------------------|---|
| | | | Calcd. | Found | Exptl. (4 mm.) | Hunt and Turner (10 mm.) | Das Gupta Mm. | | |
| I | | (β -Chlorovinyl)-dichloroarsine | | | 30–35 | Present | | Arsenic acid, m. p. 130° | |
| II | | Di-(β -chlorovinyl)-chloroarsine | | | 35–107 | Present | | Arsenic acid, m. p. 120° | |
| III | | Tri-(β -chlorovinyl)-arsine | | | 107–108 | Present | | M. p. 23° | |
| IV | | Phenylchloroarsine | | | 127 | Present | | Arsenic acid, s. 160° | |
| V | 48 | Phenyl-(β -chlorovinyl)-chloroarsine | 30.08 | 29.91 | 165 | 140–145 | 135–140 | 4 | Arsenic acid, ^b m. p. 170–171° |
| VI | 50 | Phenyl-di-(β -chlorovinyl)-arsine | 27.24 | 27.20 | 175–177 | 150–170 | 170–178 | 5 | HgCl ₂ salt, m. p. 156–157° |
| VII | 49 | Diphenyl-(β -chlorovinyl)-arsine | 25.78 | 25.85 | 194–195 | | 190–195 | 5 | HgCl ₂ salt m. p. 247–249° |
| VIII | 8 | Triphenylarsine | 24.46 | 24.60 | 205 | | | | M. p. 58° |

^a Arsenic was determined by a modification of the method of Cislak and Hamilton, THIS JOURNAL, 52, 635 (1930).

^b Calcd.: As, 30.38. Found: As, 29.96.

action was again studied in an effort to determine the product produced.

Pure benzenearsonic acid was converted to phenylchloroarsine, treated with aluminum chloride and acetylene and the reaction products carefully separated. A comparison of the products found with those reported by Hunt and Turner and Das Gupta is made in Table I. In general, our results agreed with those of Das Gupta rather than Hunt and Turner. In the case of phenyl-(β -chlorovinyl)-chloroarsine, our product differed

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(1a) Official investigator.

(2) Hunt and Turner, *J. Chem. Soc.*, 127, 996 (1925).

(3) Das Gupta, *J. Indian Chem. Soc.*, 14, 349 (1937).

Experimental

Reaction of Phenylchloroarsine and Acetylene.—A dried 2-liter, 3-necked flask was equipped with a mercury-sealed stirrer, condenser and inlet tube. Anhydrous aluminum chloride (45 g.) and phenylchloroarsine (325 g.) were added to the flask with cooling. After the heat of solution and reaction had been dissipated, the flask was placed in an ice-bath and dry, acetone-free acetylene passed into the solution stirring for two hours while maintaining a temperature of 0–5°. Stirring was continued for two hours and the product poured over ice (1 kg.) and concentrated hydrochloric acid (1.2 liters). The insoluble oil was separated, dried over sodium sulfate and fractionally distilled from a modified Vigreux-Claissen flask at 4 mm. pressure. Ten fractions were taken: 30–35, 35–107, 107–110, 110–124, 124–126, 126–150, 150–170, 170–180, 180–195° and the residue. On re-distillation at 4 mm., eight fractions described in the table were separated.

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