over 2 kg. of ice. The crude product was dissolved in sodium carbonate solution, made neutral to litmus paper, charcoaled and reprecipitated with acid. It was then recrystallized from ethanol-water (20-80).

bis-(3-Nitrophenyl)-cyano- and Thiocyanoarsines.—Potassium cyanide (7.15 g.) or sodium thiocyanate (9 g.) was dissolved in dry methanol (115 ml.) in equipment protected from moisture. bis-(3-Nitrophenyl)-chloroarsine (35.4 g.) was added and the mixture refluxed with stirring for two hours. The precipitated salt was filtered off and the filtrate evaporated to dryness. The crude products were recrystallized from benzene-petroleum ether mixtures.

Summary

1. A number of nitroaryldichloroarsines were prepared by reduction of the corresponding arsonic acids in hydrochloric acid with sulfur dioxide and potassium iodide.

2. The Michaelis and Loesner product previously identified as 3-nitroarsenosobenzene was shown to be 3,3′-diarsonoazoxybenzene. 3-Nitroarsenosobenzene was prepared by an unequivocal method.

3. The diazonium complex of 2-aminophenyldichloroarsine was decomposed to 2-chlorophenyldichloroarsine.

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[Contribution from Avery Laboratory of Chemistry of the University of Nebraska]

Furan Arsenicals[1]

By Jack F. Morgan, E. J. Cragoe, Jr., Bill Elpern and Cliff S. Hamilton[2]

Lowe and Hamilton[3] found that three moles of arsenic trichloride reacted with four moles of α-chloromercurifuran to yield nearly the theoretical amount of mercuric chloride and a mixture of α-furyldichloroarsine (I), di-α-furylchloroarsine (II) and tri-α-furylarsine (III). However, after the required number of fractional distillations at reduced pressure, the combined yield of pure furan arsenicals amounted to only 5% of the calculated amount. Furthermore, these products were very unstable.

In repeating this work it was found that repeated distillation not only failed to effect purification but markedly changed the relative amounts of the three furan arsenicals present. Arsenic trichloride and III were being produced at the expense of I and II. The equilibrium reactions involved are listed below, where R represents the α-furyl radical.

$$1)\quad \underset{(I)}{2RAsCl_2} \rightleftarrows \underset{(II)}{R_2AsCl} + AsCl_3$$

$$2)\quad \underset{(II)}{2R_2AsCl} \rightleftarrows \underset{(III)}{R_3As} + \underset{(I)}{RAsCl_2}$$

$$3)\quad \underset{(I)}{RAsCl_2} + \underset{(II)}{R_2AsCl} \rightleftarrows \underset{(III)}{R_3As} + AsCl_3$$

Obviously, the rapid removal of the low boiling arsenic trichloride under distillation conditions magnifies the loss of $RAsCl_2$ and R_2AsCl.

Since mercuric chloride was found to be present in the distillates, the possible catalytic effect of mercuric chloride on this equilibrium system was investigated. It was discovered that a mixture of these three furan arsenicals, if free of mercury salts, could be distilled with greatly increased yields of I and II. Thus, it was demonstrated that small amounts of mercuric chloride greatly increased the reaction rates in the above listed equilibria resulting in a more mobile equilibrium system.

Removal of mercury salts from the reaction led to a superior method of preparing the three furan arsenicals. III was obtained in good yields by the interaction of one mole of arsenic trichloride with three moles of α-chloromercurifuran. It could be freed of mercury salts by steam distillation of the alkaline mixture. Pure III was then equilibrated with arsenic trichloride by refluxing several hours to yield a mixture of furan arsenicals which could be separated into relatively pure products by distillation.

Di-α-furylcyanoarsine was prepared for the first time by a metathetical reaction between di-α-furylchloroarsine and silver cyanide.

Experimental

Tri-α-furylarsine, III.—A mixture of α-chloromercurifuran (151 g.) and arsenic trichloride (30.1 g.) in benzene (200 ml.) was refluxed with stirring for twenty-four hours. After cooling, the precipitated mercuric chloride was removed by filtration and the benzene distilled under reduced pressure. An aqueous solution of sodium carbonate (10 g.) was added to the residue and the mixture steam distilled. The oil was separated from the distillate and the aqueous layer extracted twice with ether (600 ml.). The oil and ether solution were combined, dried with anhydrous sodium sulfate and the ether removed by distillation. The residue yielded, after two distillations, 29.6 g. (59%) of III; b. p. 153° (3 mm.), m. p. 33.5°. The compound darkened on prolonged exposure to sunlight.

Anal. Calcd. for $C_{12}H_9AsO_3$: As, 27.13. Found: As, 27.10.

α-Furyldichloroarsine, I, and Di-α-furylchloroarsine, II—III (74 g., 0.27 mole) and arsenic trichloride (98 g., 0.54 mole) were refluxed for six hours. After several fractionations, 12 g. (10.6%) of I, b. p. 80–93° (0.7 mm.), and 17 g. (17.3%) of II, b. p. 122–127° (1 mm.) were obtained. When the molar ratio of III to arsenic trichloride was changed to 2:1, the yield of the II was increased to 58 (crude) or 36% when purified.

α-Furyldichloroarsine.—This colorless liquid is sensitive to light but is relatively stable if stored cold and in the dark.

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[1] The work herein described was done under Contracts NDCrc-16 and OEMsr-85, recommended by the National Defense Research Committee between the Office of Scientific Research and Development and the Board of Regents of the University of Nebraska.

[2] Official investigator.

[3] Lowe and Hamilton, This Journal, **57**, 1081 (1935).

Anal. Calcd. for $C_4H_3AsCl_2O$: 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-furylcyanoarsine.—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 $C_9H_6AsNO_2$: 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-furylcyanoarsine is described.

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The Reaction Products of Phenyldichloroarsine and Acetylene[1]

BY C. K. BANKS, F. H. KAHLER AND CLIFF S. HAMILTON[1a]

Hunt and Turner[2] and Das Gupta[3] have reported on the reaction of phenyldichloroarsine 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 reaction was again studied in an effort to determine the product produced.

Pure benzenearsonic acid was converted to phenyldichloroarsine, 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 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

Fraction	Wt., g.	Identity	Arsenic,[a] % Calcd.	Arsenic,[a] % Found	B. p., °C. Exptl. (4 mm.)	B. p., °C. Hunt and Turner (10 mm.)	B. p., °C. Das Gupta	Mm.	Derivative
I		(β-Chlorovinyl)-dichloroarsine			30–35	Present	.....		Arsonic acid, m. p. 130°
II		Di-(β-chlorovinyl)-chloroarsine			35–107	Present	.....		Arsinic acid., m. p. 120°
III		Tri-(β-chlorovinyl)-arsine			107–108	Present	.....		M. p. 23°
IV		Phenyldichloroarsine			127	Present	.....		Arsonic acid, s. 160°
V	48	Phenyl-(β-chlorovinyl)-chloroarsine	30.08	29.91	165	140–145	135–140	4	Arsinic acid,[b] m. p. 170-171°
VI	50	Phenyldi-(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.

Experimental

Reaction of Phenyldichloroarsine 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 phenyldichloroarsine (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-Claisen 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 redistillation at 4 mm., eight fractions described in the table were separated.

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[1] The work herein described was done under Contracts NDCrc-16 and OEMsr-85, recommended by the National Defense Research Committee and between the Office of Scientific Research and Development and the Board of Regents of the University of Nebraska.

[1a] Official investigator.

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

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