column, 0.75 in. diam., packed with 0.25 in. Raschig rings. The reflux ratio was 15 to 1.

(4) **Cyanoarsines.**—Dry benzene (750 ml.) and silver cyanide (2 moles) reacted with the alkyldichloroarsine (1 mole) or dialkylchloroarsine (2 moles) by refluxing with stirring for forty-eight hours in equipment protected from moisture. The insoluble silver chloride was filtered off, the filtrate treated with charcoal, concentrated and the product precipitated with petroleum ether. Mixtures of benzene and petroleum ether were used for recrystallization.

(5) **Ethyldipropoxyarsine.**—Sodium (25 g.) was dissolved in dry propanol (500 ml.), ethyldichloroarsine (95 g.) was added over a period of two hours and the reaction stirred an additional two hours. After removing the salt formed, the excess propanol was distilled and the product purified by fractionation.

(6) ***n*-Propyldiacetoxyarsine.**—Silver acetate (0.75 mole), benzene (400 ml.) and propyldichloroarsine (0.3 mole) were stirred under reflux for six hours. The silver chloride formed was removed and the filtrate distilled to obtain the product.

(7) **As,N-Diethylarsenimide.**—The ethylamine (2.2 moles) was cooled to −15° and added with stirring to chloroform at −5°. Ethyldichloroarsine (0.7 mole) was added over a two-hour period with cooling and the mixture stirred overnight. After filtering, the chloroform was distilled off *in vacuo* and the viscous residue fractionated.

(8) **Dimethylcyanoarsine.**—Sodium cyanide (10.5 g.) in water (21 ml.) was stirred under nitrogen and dimethylchloroarsine (25 g.) added dropwise. After an hour, the solution was extracted with benzene and the benzene extracts washed with water, dried over calcium chloride and distilled.

(9) **γ-Chloromethoxypropyldichloroarsine.**—Di-(γ-dichloroarsinopropoxy)(γ-hydroxypropyl)-arsine, $(Cl_2AsCH_2CH_2CH_2O)_2AsCH_2CH_2CH_2OH$, (210 g.)[7] was added to 40% formaldehyde solution (174 g.) and saturated with hydrogen chloride. The insoluble oil formed was extracted with chloroform and the extract dried over calcium chloride and distilled.

(10) ***n*-Pentylarsine.**—Zinc amalgam prepared from zinc dust (275 g.) and mercuric chloride (55 g.) and *n*-pentylarsonic acid (120 g.) were placed in a 3-liter flask protected from oxygen, water (10 ml.) and ether (500 ml.) added. Concentrated hydrochloric acid (1 liter) was added over seven hours and the mixture allowed to stand twenty-four hours. The ether layer was removed, dried over calcium chloride and distilled in a stream of carbon dioxide. *n*-Pentylarsine was very sensitive to oxygen.

(11) **Ethyl-*n*-propylthiocyanoarsine.**—A solution of ethyl-*n*-propylchloroarsine (50 g.) in acetone (100 ml.) was added dropwise to potassium thiocyanate (50 g.) in acetone (100 ml.) with stirring. After stirring overnight at room temperature, the mixture was filtered, the filtrate concentrated *in vacuo* and the residue treated with benzene. The precipitated salt was removed, the filtrate concentrated, treated with more benzene and the process repeated until all solids were removed. The product was then distilled.

Summary

1. Alkyldichloroarsines and dialkylchloroarsines have been prepared by reducing the corresponding pentavalent compounds in concentrated hydrochloric acid with sulfur dioxide in the presence of potassium iodide as a catalyst. Sixteen alkyldichloroarsines and three dialkylchloroarsines were prepared in this manner.

2. Two alkyldibromoarsines were synthesized by an analogous reaction.

3. Δ-4-Pentenyl-, β-methoxyethyl-, β-ethoxyethyl-, 2-methylallyl-, β-phenoxyethylarsonic acids, bis-(β-arsono)-ethyl ether, bis-(β-arsono)-ethyl sulfone, bis-(β-phenylarsinico)-ethyl sulfide and bis-(β-phenylarsinico)-ethyl sulfone are reported for the first time.

4. Allyl-, Δ-4-pentenyl-, *n*-heptyl-, β-methoxyethyl-, β-ethoxyethyl- and γ-chloromethoxypropyldichloroarsine, bis-β-(β-dichloroarsinoethoxy)-ethyl ether and bis-(β-dichloroarsino)-ethyl sulfone have been prepared for the first time.

5. Cyano, thiocyano, propoxy and imide derivatives of alkyl- and dialkylarsines are described.

6. The Meyer reaction has been found to be generally applicable to the synthesis of primary alkylarsonic acids. Unsaturation β to the reactive halogen aids the reaction.

7. It has been shown that the stability of substituted alkyldichloroarsines is not affected by β-alkoxy groups or unsaturation more than three carbon atoms from arsenic; β-unsaturation and β-halogen caused instability.

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[7] Gough and King, *J. Chem. Soc.*, 2426 (1928).

[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

Nitroaryldichloroarsines and Related Compounds[1]

BY J. F. MORGAN, E. J. CRAGOE, JR., R. J. ANDRES, BILL ELPERN, R. F. COLES, JAMES LAWHEAD, R. L. CLARK, E. B. HATLELID, F. H. KAHLER, H. W. PAXTON, C. K. BANKS AND CLIFF S. HAMILTON[2]

Isacescu[3] has reported that 3-nitrophenyldichloroarsine has sternutatory properties. In order to investigate the toxicity of this and other nitroaryldichloroarsines, a series of nitrobenzenearsonic acids were reduced in concentrated hydrochloric acid with sulfur dioxide, using potassium iodide as a catalyst. A few of the resulting products have been reported previously but, for the most part, they were prepared by more cumbersome methods.

Most of the arsonic acids were available from previous studies but several new acids were prepared by standard procedures. bis-(3-Nitrophenyl)-arsinic acid was also converted to the chloroarsine and this compound in turn to the cyano and thiocyano derivatives. In the course of some experiments with the related 2-aminophenyldichloroarsine, the diazonium complex analogous to that reported for the corresponding

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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] Isacescu, *Bull. Soc. Chem. Roumania*, **18A**, 131 (1936).

TABLE I

Compound	M. p., °C.	Yield, %	Color	Recryst. from	Molecular formula	Arsenic,[a] % Calcd.	Arsenic,[a] % Found	Intermediate reference
2-Nitrophenyldichloroarsine[b]	49	88	Lt. yellow	CCl₄–Pet. ether	$C_6H_4AsCl_2NO_2$	27.96	27.95	b
3-Nitrophenyldichloroarsine[c]	55	90	Off white	CCl₄	$C_6H_4AsCl_2NO_2$	27.96	27.99	d
4-Nitrophenyldichloroarsine	54–55	75	Lt. yellow	Benzene	$C_6H_4AsCl_2NO_2$	27.96	28.10	e
2,4-Dinitrophenyldichloroarsine[f]	69–70.5	75	Lt. yellow	CCl₄–Pet. ether	$C_6H_3AsCl_2N_2O_4$	23.94	23.64	e
2-Nitro-1,4-phenylenetetrachlorodiarsine[g]	72.6–74.3	48	Yellow	CCl₄–Pet. ether	$C_6H_3As_2Cl_2NO_2$	36.30	36.33	h
3,5-Dinitro-4-methylphenyldichloroarsine	126–127.5	86	Off white	Benzene-Pet. ether	$C_7H_5AsCl_2N_2O_4$	22.91	22.88	i
3,5-Dinitro-4-ethoxyphenyldichloroarsine	81–82.3	74	Cream	CCl₄	$C_8H_7AsCl_2N_2O_5$	20.98	21.04	i
2-Chlorophenyldichloroarsine	44–45	86	White	Distillation	$C_6H_4AsCl_3$	29.11	29.24	j
4-β-Chloroethylmercaptophenyldichloroarsine	186–193 (0.25 mm.)	68	Yellow	....	$C_8H_8AsCl_3S$	23.59	23.52	k
3-ω-Chloroacetylphenyldichloroarsine	215–218 (15 mm.)	94	Colorless	....	$C_8H_6AsCl_3O$	25.02	25.46	l
bis-(3-Nitrophenyl)-chloroarsine[m]	112–113	91	White	Benzene-Pet. ether	$C_{12}H_8AsClN_2O_4$	21.13	21.04	n
bis-(3-Nitrophenyl)-cyanoarsine	151–152	93	White	Benzene-Pet. ether	$C_{13}H_8AsN_3O_4$	21.71	22.45	i
bis-(3-Nitrophenyl)-thiocyanoarsine	103–105	77	White	Benzene-Pet. ether	$C_{13}H_8AsN_3O_4S$	19.76	19.90	i
3,5-Dinitro-4-methylbenzenearsonic acid	.....	64	Yellow	Ethanol	$C_7H_7AsN_2O_7$	24.48	24.48	e
3,5-Dinitro-4-ethoxybenzenearsonic acid	.....	64	Yellow	Ethanol	$C_8H_9AsN_2O_8$	22.29	22.34	e
3-Nitroarsenosobenzene	184.5–187.5	72	White	[i]	$(C_6H_4AsNO_3)x$	35.17	34.96	d
3,3′-Diarsonoazoxybenzene	[p]	90	Yellow	[i]	$C_{12}H_{12}As_2N_2O_7$	33.59	33.71	d
3,3′-Tetrachlorodiarsinoazoxybenzene	119–120	81	Yellow	CCl₄–Pet. ether	$C_{12}H_{12}As_2Cl_4N_2O$	30.64	30.92	i

[a] Determined by a modification of the method of Cislak and Hamilton, THIS JOURNAL, **52**, 638 (1930). [b] Kalb, *Ann.*, **423**, 39 (1921). The product reported by Karrer, *Ber.*, **47**, 1783 (1914), contained no chlorine. [c] Ref. 3 and 5, also Blicke, Powers and Webster, THIS JOURNAL, **54**, 2945 (1932). [d] Hamilton and Sly, *ibid.*, **47**, 435 (1925). [e] Bart, *Ann.*, **429**, 96 (1922). [f] Mention by Karrer, *Ber.*, **47**, 2275 (1944) but no preparation given. [g] Berlin, *J. Gen. Chem.*, U. S. S. R., **9**, 1856 (1939). [h] Lieb and Wintersteiner, *Ber.*, **56**, 425 (1923) from 3-amino-4-nitrobenzenearsonic acid prepared by the method of Bertheim, *ibid.*, **44**, 3093 (1911). [i] Experimental. [j] Palmer and Adams, THIS JOURNAL, **44**, 1356 (1922). [k] Morgan and Hamilton, *ibid.*, **66**, 874 (1944). [l] Clark and Hamilton. *ibid.*, **65**, 635 (1943). [m] Michaelis, *Ann.*, **321**, 141 (1902). [n] Wieland and Rheinheimer, *ibid.*, **423**, 36 (1921). [p] Explodes on heating.

para isomer[4] was prepared. In contrast to the para isomer, the ortho compound decomposed in acetic acid and ether with the evolution of nitrogen. When cuprous ions were present, the decomposition gave nearly the theoretical yield of a product identified as 2-chlorophenyldichloroarsine. Since the compound has not been reported previously, the synthesis was confirmed by reduction of 2-chlorobenzenearsonic acid in the usual manner.

Michaelis and Loesner[5] have reported the conversion of 3-nitrophenyldichloroarsine by aqueous alkali to a product thought to be 3-nitroarsenosobenzene. On repeating their procedure, the product isolated proved to be 3,3′-diarsonoazoxybenzene, formed by the autooxidation-reduction of three moles of the trivalent compound according to equation 1.

$$3O_2NC_6H_4As(OH)_2 \xrightarrow{OH^-} H_2O_3C_6H_4N(O)NC_6H_4AsO_3H_2 + O_2NC_6H_4AsO_3H_2 \quad (1)$$

This was proved by catalytic reduction with hydrogen and identification of the resulting product as 3-aminobenzenearsonic acid. Further proof was furnished by the synthesis of 3,3′-diarsonoazoxybenzene from 3-nitrobenzenearsonic acid by reduction with alkaline arsenite.[6] Both the Michaelis and Loesner product and the arsenite reduction product gave the same tetrachlorodiarsine on reduction with sulfur dioxide in hydrochloric acid. 3-Nitroarsenosobenzene was prepared by the reduction of the arsonic acid in dilute sulfuric acid.

Experimental

Chloroarsines.—The arsonic acid (0.5 mole) was dissolved in warm to boiling concentrated hydrochloric acid (0.5–3 liters) and a trace (*ca.* 0.1 g.) of potassium iodide added. Sulfur dioxide was passed into the solution until no more reaction was apparent, keeping the solution warm to prevent crystallization of the arsonic acid. The products separated as oils which solidified on cooling. They were recrystallized from appropriate solvents. Two products which remained as oils were distilled.

3-Nitroarsenosobenzene.—3-Nitrobenzenearsonic acid (25 g.) was dissolved in boiling 4 *N* sulfuric acid (400 ml.) and the solution saturated with sulfur dioxide in the presence of potassium iodide (0.1 g.). After five hours, the reaction mixture was cooled, the supernatant decanted and the residual solid recrystallized from alcohol and then from acetone.

3,3′-Diarsonoazoxybenzene.—3-Nitrobenzenearsonic acid (50 g.) was dissolved in water (100 ml.) and sodium hydroxide (16.2 g.). A solution of arsenic trioxide (40 g.) in water (200 ml.) and sodium hydroxide (48.5 g.) was added and the resulting mixture boiled thirty minutes. The solution was made acid to Congo red paper, the crude product separated and purified by solution in cold sodium bicarbonate solution, filtration and reacidification.

3,5-Dinitro-4-methylbenzenearsonic Acid.—4-Methyl-3-nitrobenzenearsonic acid (237 g.) was added slowly (forty minutes) to well-stirred cold fuming sulfuric acid (480 ml., 20% oleum). Fuming nitric acid (200 ml., sp. g. 1.6) was added dropwise (ninety minutes) with cooling in an ice–salt-bath. After warming to room temperature, the mixture was heated on a steam-bath for seven hours, poured into a mixture of water (600 ml.), sodium hydroxide (560 g.) and ice (4.5 kg.). The product was filtered off and purified by solution in ammonia water, decolorization with charcoal and reprecipitation with acid. It was then recrystallized from ethanol.

3,5-Dinitro-4-ethoxybenzenearsonic Acid.—4-Ethoxybenzenearsonic acid (86 g.) was added slowly with cooling to concentrated sulfuric acid (250 ml.). Fuming nitric acid (62 ml., sp. g. 1.5) was added dropwise (two hours) with stirring, maintaining a temperature of 0–5°. Stirring was continued for two hours and the mixture then poured

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(4) Schmidt and Hoffmann, *Ber.*, **59**, 560 (1926).

(5) Michaelis and Loesner, *ibid.*, **27**, 269 (1894).

(6) Hamilton and Ludeman, THIS JOURNAL, **52**, 3284 (1930).

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).