sole is split completely to phenol by aluminum bromide in chlorobenzene after 18 hours at 60° (for the sulfur analog, see Table).

During this work several new aryl sulfides were prepared, which are described in the experimental part. It was found, however, that aluminum bromide caused hydrogen sulfide evolution from *p*-thiocresol, *β*-thionaphthol, and 4-phenylthiophenol, and hence kinetic runs could not be made on sulfides derived from these thiols. It was shown that aluminum bromide in chlorobenzene solution formed biphenyl from 4-phenylthiophenol.

$$p\text{-}C_6H_5C_6H_4SH \xrightarrow[C_6H_5Cl]{AlBr_3} C_6H_5C_6H_5$$

In benzene solution the products appeared to be biphenyl and diphenyl sulfide.

The carboxy sulfides in the table were found to be unaffected even by aluminum bromide–acetyl bromide, a combination which gives very rapid cleavage of benzyl phenyl sulfide.[2a]

Experimental[12]

The amount of cleavage was determined by the consumption of 0.02 *N* alcoholic iodine solution either directly as mercaptan or after hydrolysis of the thiol ester.[2b]

The sulfides below were prepared in the usual manner by adding alkyl halide to a solution of the thiophenol in alcoholic potassium hydroxide.

Sulfide	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
4-Biphenylyl benzyl sulfide[a]					
p-$C_6H_5C_6H_4SCH_2C_6H_5$	127.5-128.5	82.56	82.18	5.83	5.77
4-Biphenylyl ethyl sufide					
p-$C_6H_5C_6H_4SCH_2CH_3$	74-75	78.46	78.20	6.58	6.56
β-Naphthyl benzyl sulfide					
β-$C_{10}H_7SCH_2C_6H_5$	88.5-89	81.56	81.33	5.64	5.76

[a] The sulfoxide was prepared from the reaction of bromine water on a solution of the sulfide in *t*-butyl alcohol[2b]; m.p. 198–199°. Calcd. for $C_{19}H_{16}OS$: C, 78.05; H, 5.51. Found: C, 77.84; H, 5.40.

CLEAVAGE OF SULFIDES, C_6H_5SR

R	AlBr₃[a] Time, hr.	AlBr₃[a] Cleavage, %	HBr[b, c, d] Time, hr.	HBr[b, c, d] Temp., °C.	HBr[b, c, d] Cleavage, %
$C_6H_5CH_2$	5	85	6[b]	200	Decomp.
	73(0°)	42	24[c]	150	30
$C_6H_5CH_2CH_3$	18	0			
	2(79°)	10-20			
$(C_6H_5)_2CH$	0.2	86[e]	4[d]	Reflux	0
	0.2(0°)	64	0.2[c]	Reflux	10–20
$(C_6H_5)_3C$	18	≫50[e]	0.02[b]	Reflux	>5
	0.2(0°)	>50	1[h]	Reflux	>5
CH_3	24	0[h]			
	24(93°)	0			
$(CH_3)_2CH$	18	0[f]			
	6(72°)	5–10			
$(CH_3)_3C$	0.2	5–10			
CH_2COOH	4(50°)	0[g]			
	0.2(reflux)	0			
CH_2CH_2COOH	4(50°)	0			
	0.2(reflux)	0			

[a] Chlorobenzene as solvent; 28° unless otherwise stated. [b] 32% aqueous solution. [c] 32% solution in acetic acid. [d] 48% aqueous solution. [e] Diphenyl disulfide isolated from the reaction. [f] $AlBr_3$ without solvent gave 50–60% cleavage after 24 hours at 28°. [g] No cleavage when fused with $AlBr_3$ in absence of solvent. [h] Dilute aqueous hydrochloric acid.

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[12] Analyses by Mrs. G. Sauvage; melting points are corrected.

Arsenicals Containing Quinoline and Quinazoline Nuclei

BY YAO-HUA WU AND CLIFF S. HAMILTON

For a number of years various workers in this Laboratory have been employing the Bart reaction[1] to prepare different aromatic and heterocyclic arsonic acids as possible therapeutic agents. This reaction has now been utilized to synthesize 4-hydroxyquinoline- and 4-hydroxyquinazolinearsonic acids.

6-Amino-4-hydroxyquinoline, 6-amino-4-hydroxy-2-methyl-quinoline, 5-amino-4-hydroxyquinazoline, 6-amino-4-hydroxyquinazoline and 7-amino-4-hydroxyquinazoline were prepared by the reduction of the corresponding nitro compounds. The arsonic acids were obtained by diazotizing these amines and subsequent coupling with sodium arsenite. Some of these arsonic acids were reduced to their arsenoso derivatives by the action of sulfur dioxide and hydriodic acid.

The condensation of heterocyclic compounds containing an "active" halogen with aminoarylarsonic acids has been studied extensively by Banks and co-workers[2] and Hamilton and co-workers.[3] In most cases an aqueous suspension containing a trace of hydrochloric acid was used. Banks[2] pointed out that the trace of hydrochloric acid is necessary because the reaction rate in aqueous solution or suspension is increased by an increase in the hydrogen ion concentration. Because of the instability of the 4-haloquinolines and 4-haloquinazolines in aqueous acid solutions, the condensation with *p*-arsanilic acid was accomplished in N-dimethylformamide as a solvent.

Experimental

6-Amino-4-hydroxyquinolines.—6-Amino-4-hydroxyquinoline was prepared according to the direction of Albert, Brown and Duewell.[4] 6-Amino-4-hydroxy-2-methylquinoline was obtained by the method of Kermack and Weatherhead.[5]

Amino-4-hydroxyquinazolines.—The 4-hydroxynitroquinazoline (3.8 g.) was added gradually in portions to a warm solution of stannous chloride ($SnCl_2 \cdot 2H_2O$, 20.3 g.) in concd. hydrochloric acid (30 ml.). After all the solid had been added, the solution was heated gently under reflux for 1 hour. The hot solution was diluted with water and care-

TABLE I

Compound	Yield, %	M.p., °C. Liter.	M.p., °C. Found
5-Amino-4-hydroxyquinazoline	76.4	235–236[6]	236
6-Amino-4-hydroxyquinazoline	67.0	318[7]	316
7-Amino-4-hydroxyquinazoline[a]	53.7	......	315

[a] *Anal.* Calcd. for $C_8H_7ON_3$: C, 59.61; H, 4.38; N, 26.07. Found: C, 59,86; H, 4.25; N, 25.98.

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(1) H. Bart, German Patent 250,264 (1910) [*Chem. Zentr.*, **83**, IV, 882 (1912)].

(2) C. K. Banks, O. M. Gruhzit, E. W. Tillitson and J. Controulis, THIS JOURNAL, **66**, 1771 (1944); C. K. Banks and J. Controulis, *ibid.*, **68**, 944 (1946).

(3) E. J. Cragoe, Jr., and C. S. Hamilton, *ibid.*, **67**, 536 (1945); R. J. Andres and C. S. Hamilton, *ibid.*, **67**, 946 (1945); I. H. Witt and C. S. Hamilton, *ibid.*, **67**, 1078 (1945); B. Elpern and C. S. Hamilton, *ibid.*, **68**, 1436 (1946).

(4) A. Albert, D. J. Brown and H. Duewell, *J. Chem. Soc.*, 1284 (1948).

(5) W. O. Kermack and A. P. Weatherhead, *ibid.*, 563 (1939).

(6) M. T. Bogert and V. S. Chambers, THIS JOURNAL, **28**, 207 (1906).

(7) O. W. Magidson and E. S. Golovchinskaya, *J. Gen. Chem.* (*U. S. S. R.*), **8**, 1797 (1938).

TABLE II

Name	Color	M.p., °C.	Yield, %	Formula	As analyses, %[8] Calcd.	Found
4-Hydroxyquinoline-6-arsonic acid	White	>320	29.7	$C_9H_8O_4NAs$	27.84	27.97
4-Hydroxy-2-methylquinoline-6-arsonic acid	White	>320	31.6	$C_{10}H_{10}O_4NAs$	26.46	26.48
4-Hydroxyquinazoline-5-arsonic acid	White	>320	48.3	$C_8H_7O_4N_2As$	27.74	27.89
4-Hydroxyquinazoline-6-arsonic acid	White	>320	22.2	$C_8H_7O_4N_2As$	27.74	27.82
4-Hydroxyquinazoline-7-arsonic acid	White	>320	42.2	$C_8H_7O_4N_2As$	27.74	27.70
6-Arsenoso-4-hydroxyquinoline	White	317	53.2	$C_9H_6O_2NAs \cdot H_2O$	29.60	29.90
6-Arsenoso-4-hydroxy-2-methylquinoline	White	310	75.1	$C_{10}H_8O_2NAs \cdot H_2O$	27.97	27.80
7-Arsenoso-4-hydroxyquinazoline	White	295	69.1	$C_8H_5O_2N_2As \cdot H_2O$	29.49	29.41
4-(4′-Arsonoanilino)-8-nitroquinoline	Yellow	288	30.2	$C_{15}H_{12}O_5N_3As$	19.25	19.08
4-(4′-Arsonoanilino)-2-methylquinoline	Light gray	285	33.2	$C_{16}H_{14}O_3N_2As$	20.95	21.06
4-(4′-Arsonoanilino)-2-methyl-6-nitroquinoline	Yellow	288	50.1	$C_{16}H_{14}O_5N_3As$	18.58	18.39
4-(4′-Arsonoanilino)-quinazoline	Light gray	>320	58.0	$C_{14}H_{12}O_3N_3As$	21.71	21.66

fully neutralized with calcium carbonate. The mixture was then heated to boiling and filtered through a hot-water funnel. The undissolved portion was repeatedly extracted with boiling water. From the combined filtrate and washings the amino-4-hydroxyquinazoline crystallized in long white needles on cooling.

4-Hydroxyquinolinearsonic Acids and 4-Hydroxyquinazolinearsonic Acids.—A solution of 3.5 g. of the amine in 35 ml. of 2 *N* hydrochloric acid was cooled to a temperature below 5° and diazotized with sodium nitrite solution. The diazonium solution was poured with mechanical stirring into a water solution composed of sodium arsenite (5 g.), sodium hydroxide (3 g.) and a few crystals of copper sulfate. After being stirred for 2 hours and having stood overnight, the mixture was warmed at 80° for 10 minutes, and filtered to remove the dark tarry impurity. The filtrate was neutralized with hydrochloric acid, treated with charcoal, filtered and the filtrate was made acidic to congo red paper with hydrochloric acid. The crude arsonic acid separated as white needles and was purified by dissolving in 5% sodium bicarbonate solution and reprecipitating with the addition of 1 *N* hydrochloric acid until acid to congo red paper.

Arsenoso-4-hydroxyquinolines and Arsenoso-4-hydroxyquinazolines.—One gram of the pure arsonic acid was dissolved or suspended in 35 ml. of 1.5 *N* hydrochloric acid containing a trace of potassium iodide. The solution was cooled in an ice-bath and saturated with sulfur dioxide for two hours. After remaining in a refrigerator overnight, the solution was neutralized with concd. ammonium hydroxide. The white precipitate was filtered and dissolved in 1 *N* sodium hydroxide. The arsenoso derivative was isolated as white needles by passing carbon dioxide into the alkaline solution.

Condensation of 4-Chloroquinolines and 4-Chloroquinazolines with *p*-Arsanilic Acid.—The 4-chloroquinoline or the 4-chloroquinazoline (0.005 mole) and *p*-arsanilic acid (0.0045 mole) were dissolved in 5 ml. of dimethylformamide at 50°. The solution was heated at 80–90° for 3–4 hours. A solid product usually separated after 2–3 hours of heating. A less pure product could be recovered from the mother liquor by neutralizing with ammonium hydroxide. The crude product was purified by dissolving in hot 5% sodium bicarbonate solution and reprecipitating with the addition of 2 *N* hydrochloric acid. The condensation products are hygroscopic.

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[8] Cislak and Hamilton, THIS JOURNAL, 52, 638 (1930).

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Attempted Preparation of Thorium(III) Fluoride[1a,b]

BY JAMES C. WARF[2]

An attempt to prepare a lower fluoride of thorium was undertaken to aid in clarifying the role of thorium as an actinide element. While the presence of an f electron in thorium is not essential to the general actinide hypothesis,[3] a trifluoride, isostructural with uranium(III) fluoride, would be predicted on the basis of an electron in the 5 f orbital, paralleling the cerium(III) ion with a 4 f electron.

The method employed involved the reduction of thorium(IV) fluoride by thorium metal, following a technique successful in the analogous synthesis of uranium(III) fluoride.[4] The thorium tetrafluoride, prepared by hydrofluorination of the oxide, was analyzed by pyrohydrolysis.[5] Calcd. for ThF_4: Th, 75.33; F, 24.67. Found: Th, 75.37; F, 24.60. Its freezing point was 1068 ± 2°. The thorium metal, prepared by bomb reduction, contained approximately 0.1% ThO_2 and 0.2% zinc.

Two attempts to carry out the reaction

$$Th + 3ThF_4 = 4ThF_3$$

were made using platinum boats. Thorium (1 g.) was converted to its hydride by heating to 750° in hydrogen (purified over uranium at 700°), and ground intimately with the stoichiometric quantity of thorium tetrafluoride. The mixture in a platinum boat was heated in a quartz tube by means of a platinum-wound resistance furnace. An atmosphere of helium purified over uranium powder at 800° was maintained at all times. A temperature of 1175° was reached in the first run, and 1280° in the second. In both cases the platinum boats were attacked, being reduced to metallic globules of a thorium–platinum alloy in the second case. The gray residues were examined by X-ray diffraction, and all the lines in both cases could be accounted for by the presence of Th, ThF_4 and ThH_2.

Another run was made as above using a boat fashioned from 1-mm. rolled thorium sheet. A temperature of 1290° was maintained 30 minutes. Practically all of the thorium tetrafluoride had volatilized away, and the boat had been etched. An X-ray diffraction pattern of the dark residue could be interpreted on the basis of the Th, ThF_4 and ThO_2.

Finally, two bombs were fabricated from thorium metal; each was tapped, and sealed with a threaded thorium plug. The first was charged with 10 g. of intimately ground stoichiometric Th–ThF_4 mixture, and heated to 1600° in vacuum in an induction furnace. The bomb was sawed open lengthwise, which revealed that the thorium powder had settled to the bottom, and that the inside wall was attacked. X-Ray analysis showed Th and ThF_4 only. The second bomb was filled with thorium tetrafluoride alone,

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[1] (a) Based on work done in 1946–1947, Ames Laboratory of the Atomic Energy Commission, declassified as AECD-2654 on July 14, 1949. (b) Presented at the Chicago, Illinois, Meeting of the American Chemical Society, September, 1950.

[2] Department of Chemistry, University of Southern California, Los Angeles 7, California.

[3] See G. T. Seaborg, "The Transuranium Elements," "NNES," Div. IV, Vol. 14 B, McGraw-Hill Book Co., Inc., New York, N. Y., 1949, pp. 1492–1524.

[4] J. Warf, Plutonium Project Report CC-1525 (March 14, 1944) (AECD-2523); also J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," "NNES," Div. VIII, Vol. 5, McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p. 349 ff.

[5] J. Warf, "Analytical Chemistry of the Manhattan Project," "NNES," Div. VIII, Vol. 1, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 729 ff.