[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NEBRASKA AND WALLA WALLA COLLEGE]

The Reactivity of Nuclear Chlorine in the Isomeric 1,2- and 2,1-Chloronaphthalenearsonic Acids

BY GEORGE W. BOWERS AND CLIFF S. HAMILTON

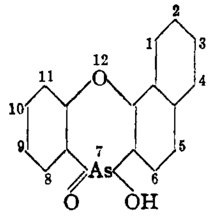
In the benzene nucleus the reactivity of chlorine ortho or para to the arsono group has been investigated[1,2,3] in this Laboratory. The object of this study was to extend the work to naphthalenearsonic acids.

In the preparation of the parent chloronaphthalenearsonic acids, the methods worked out previously[4] were found helpful. β-Naphthylamine was used in the production of both the isomers and 1-chloro-2-naphthalenearsonic acid was prepared readily. However, the synthesis of 2-chloro-1-naphthalenearsonic acid presented several difficulties and experimental methods finally developed must be followed carefully particularly in the arsonation reaction in order to obtain workable yields.

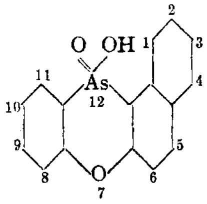
The most favorable conditions for the condensation reactions were determined by a series of experiments in which variations were made in the temperature, solvent, catalyst, time and proportion of reactants. Nitrobenzene proved the best solvent and the optimum temperature was approximately 140°. A small piece of bright copper foil was found the best catalyst and the reaction time was ten to twelve hours.

The reactivity of chlorine in these naphthalenearsonic acids is less than that found in the benzenearsonic acids, for neither the aliphatic nor the aromatic amines showed any evidence of reaction and, in general, the yields are smaller for the condensation product with phenols. Of the two chloroarsonic acids, the 1-chloro-2-naphthalenearsonic acid is apparently more reactive but due to the formation of tars the ethers were very difficult to isolate.

When the ethers resulting from the reactions of these chloronaphthalenearsonic acids and the phenols were boiled with glacial acetic acid they, without exception, lost the elements of water and two series of heterocyclic naphthalene arsenicals were produced. The following structures and names are proposed



α-Benzophenoxarsinic acid



γ-Benzophenoxarsinic acid

These structures are assigned for the following reasons: (1) the arsenic and oxygen atoms are in the same relative positions as in the parent ether compounds. (2) The arsenic analyses indicate the loss of water from the parent ethers. (3) These arsinic acids do not hydrolyze even by treatment with hot sodium hydroxide solution. They certainly would do so if the arsono group alone were involved in the dehydration. (4) The parent chloroarsonic acids are not dehydrated by the action of glacial acetic acid. This fact indicates again that the dehydration is not due to the arsono group alone. (5) It is assumed that ortho hydrogen of the phenolic group is involved because of the stability of six-membered rings. (6) The insolubility of the sodium salt of the similar phenoxyphenylarsinic acid in an excess of sodium carbonate has previously been observed.[5]

Experimental

1-Chloro-2-naphthalenearsonic Acid.—Twenty-one and two-tenths grams of 1-amino-2-naphthalenearsonic acid, prepared according to Saunders and Hamilton's[4] directions, was precipitated in a finely divided state by dissolving the pulverized compound in 2 *N* sodium hydroxide and acidifying to Congo red paper with 2 *N* hydrochloric acid. The mixture was diluted to 400 cc., 30 cc. of concentrated hydrochloric acid added, and diazotization carried out at −5° by adding dropwise 8 g. of sodium nitrite in 32 cc. of water over a period of one hour.

Meanwhile a cuprous chloride suspension was prepared in the usual way from 25 g. of crystallized copper sulfate and was dissolved in 72 cc. of concentrated hydrochloric acid. To this solution the diazotized amine was added in small portions. The resulting mixture was made alkaline by the addition of solid sodium carbonate and then filtered. Upon acidification of the filtrate to Congo red paper with hydrochloric acid, a light red precipitate of 1-chloro-2-naphthalenearsonic acid separated; purified by dissolving in sodium carbonate and reprecipitating by hydrochloric

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(1) Etzelmiller and Hamilton, THIS JOURNAL, **53**, 3085 (1931).

(2) Maclay and Hamilton, *ibid.*, **54**, 3310 (1932).

(3) Hall and Hamilton, *ibid.*, **56**, 1779 (1934).

(4) Saunders and Hamilton, *ibid.*, **54**, 636 (1932).

(5) Roberts and Turner, *J. Chem. Soc.*, 2004 (1925).

TABLE I

1-Arsono-2-( )-naphthalene	Yield, %	M. p., °C.	Formula	Arsenic analyses, % Calcd.	Found	
-(Phenoxy)	51	211–295[a]	$C_{16}H_{13}O_4As$	21.78	21.82	21.85
-(2′-Methylphenoxy)	48	295	$C_{17}H_{15}O_4As$	20.93	20.95	20.96
-(4′-Methylphenoxy)	30	225–273[b]	$C_{17}H_{15}O_4As$	20.93	20.95	20.99
-(2′-Chlorophenoxy)	42	230–231	$C_{16}H_{12}O_4ClAs$	19.80	19.76	19.82
-(4′-Chlorophenoxy)	24	217–219	$C_{16}H_{12}O_4ClAs$	19.80	19.80	19.82

[a] Substance partially melts at 211° then solidifies and finally melts at 295°. [b] Substance partially melts at 225° then solidifies and finally melts at 273°.

TABLE II

2-Arsono-1-( )-naphthalene	Yield, %	M. p., °C.	Formula	Arsenic analyses, % Calcd.	Found	
-(Phenoxy)	66.5	322	$C_{16}H_{13}O_4As$	21.78	21.80	21.78
-(2′-Methylphenoxy)	18	181	$C_{17}H_{15}O_4As$	20.93	20.88	20.90

acid, followed by recrystallization from 50% acetic acid; white needles; m. p. 317°; yield 82%; soluble in methyl and ethyl alcohols, but insoluble in water and benzene.

Anal. Calcd. for $C_{10}H_8O_3ClAs$: As, 26.16; Cl, 12.38. Found: As, 25.99, 26.10;[6] Cl, 12.21, 12.20.[7]

2-Chloro-1-nitronaphthalene.—From α-nitro-β-naphthylamine in 82% yields following the method of Hodgson and Walker,[8] for diazotization.

2-Chloro-1-aminonaphthalene.—Five grams of 2-chloro-1-nitronaphthalene was dissolved in 100 cc. of 95% alcohol, about 1 g. of Raney nickel added and the mixture exposed with shaking to molecular hydrogen under 40 lb. (2.66 atm.) pressure. Reduction was complete in twenty minutes. The catalyst was filtered from the mixture, the filtrate evaporated to 25 cc., 10 cc. of water was added and the solution placed in the refrigerator. The amine separated in long white needles; yield, quantitative; m. p. 56°.

2-Chloro-1-naphthalenearsonic Acid.—In a 600-cc. beaker was placed 17.7 g. of crude 2-chloro-1-aminonaphthalene and 196 cc. of 6 *N* hydrochloric acid. The mixture was cooled to 0° and 8 g. of sodium nitrite dissolved in 47 cc. of water was added dropwise over a period of two hours. Meanwhile in a 2-liter beaker an arsenite solution was made up by dissolving 50 g. of sodium metarsenite in 206 cc. of water in which was dissolved 2 g. of copper sulfate. This solution was cooled to 5°. The 2-liter beaker was fitted with a mechanical stirrer, and two funnel tubes extending to the bottom. A dropping funnel was adjusted at the top of each funnel tube. In one was placed 146 cc. of 6 *N* sodium hydroxide and in the other the filtered diazotized amine. With stirring the two solutions were dropped in rapidly at such a rate that the mixture in the beaker was always slightly basic. After the diazotized amine had all been added, stirring was continued for fifteen minutes longer and the mixture filtered through a carbon mat. Upon acidification to Congo red paper with hydrochloric acid the 2-chloro-1-naphthalenearsonic acid separated as an almost white precipitate. After dissolving in a sodium carbonate solution and reprecipitating with hydrochloric acid, the arsonic acid was used in this state of purity for subsequent condensations; purified by dissolving in 50% acetic acid and decolorizing with activated charcoal. Upon cooling colorless needles appeared, m. p. 296°; yield 56%; soluble in ethyl alcohol but insoluble in ether and benzene.

Anal. Calcd. for $C_{10}H_8O_3ClAs$: As, 26.16; Cl, 12.38. Found: As, 25.99, 26.10; Cl, 12.48, 12.38.

Phenyl Ether Derivatives

General Procedure.—A mixture of 5 g. of 2-chloro-1-naphthalenearsonic acid or 1-chloro-2-naphthalenearsonic acid, 10 g. of phenol or substituted phenol, 5 g. of anhydrous potassium carbonate, 25 cc. of nitrobenzene and a small piece of bright copper foil was placed in a 125-cc. Erlenmeyer flask fitted with ground-glass connections. The mixture was agitated by means of a stirrer extending through the length of the reflux condenser. The flask and its contents were heated in an oil-bath at 140° for ten to twelve hours. The resulting mixture was steam distilled to remove the nitrobenzene and excess phenol, and treated with activated charcoal. After filtering, the mixture was acidified to Congo red paper with hydrochloric acid, whereupon the phenyl ether derivatives of the arsonic acid precipitated. The crude products were charcoaled and crystallized from 50% acetic acid. The melting points are high, and more or less decomposition takes place as indicated by darkening.

Benzophenoxarsinic Acids and Derivatives

General Procedure.—The corresponding phenoxynaphthalenearsonic acids were boiled with glacial acetic acid and an equal volume of water was added. A portion of the arsinic acids precipitated and sufficient 50% acetic acid was added to bring them into solution at the boiling temperature. Upon cooling, the benzophenoxarsinic acids crystallized out in quantitative yields. No further puri-

TABLE III

	M. p., °C.	Formula	Arsenic analyses, % Calcd.	Found	
α-Benzophenoxarsinic acid[9]	319	$C_{16}H_{11}O_3As$	22.98	23.02	23.05
11-Methyl-α-benzophenoxarsinic acid	177	$C_{17}H_{13}O_3As$	22.04	22.00	22.02

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(6) The potentiometric method of Cislak and Hamilton [THIS JOURNAL, 52, 638 (1930)] was used for the quantitative determination of arsenic in all of the compounds prepared.

(7) The Carius method was used for the quantitative determination of chlorine in this arsonic acid and its isomer.

(8) Hodgson and Walker, *J. Chem. Soc.*, 1620 (1933).

(9) Aeschlimann, *J. Chem. Soc.*, 811 (1925).

TABLE IV

-Phenoxarsinic acid	M. p., °C.	Formula	Arsenic analyses, % Calcd.	Found	
γ-Benzo	278–280	$C_{16}H_{11}O_3As$	22.98	23.04	23.00
8-Methyl-γ-benzo	205–270[a]	$C_{17}H_{13}O_3As$	22.04	22.04	22.08
10-Methyl-γ-benzo	215–217	$C_{17}H_{13}O_3As$	22.04	22.04	22.06
8-Chloro-γ-benzo	216–218	$C_{16}H_{10}O_3ClAs$	20.79	20.90	20.92
10-Chloro-γ-benzo	214	$C_{16}H_{10}O_3ClAs$	20.79	20.78	20.76

[a] Substance partially melts at 205°, then solidifies and finally melts sharply at 270°.

fication was necessary if the corresponding phenoxynaphthalenearsonic acids used were pure. All were insoluble in sodium carbonate and cold sodium hydroxide solutions, but were soluble in hot sodium hydroxide solutions.

Summary

1. The isomeric 1,2- and 2,1-chloronaphthalenearsonic acids have been prepared for the first time. The synthesis of the latter involved the developing of methods for the quantity production of the intermediates 2-chloro-1-nitronaphthalene and 2-chloro-1-aminonaphthalene and the necessary modifications of the Bart reaction.

2. Two new series of naphthyl phenyl ether derivatives have been prepared by the condensation of the parent compounds with phenol and substituted phenols. 1-Chloro-2-naphthalenearsonic acid has been condensed with phenol and *o*-cresol. 2-Chloro-1-naphthalenearsonic acid has been condensed with phenol, *o*- and *p*-cresols, and *o*- and *p*-chlorophenols.

3. By the elimination of water, heterocyclic benzophenoxarsinic acids have been prepared from all the above naphthyl phenyl ethers. No benzophenoxarsinic acids have been reported previously.

4. No condensations were possible, under the conditions employed, with either aniline, the aliphatic amines or the aliphatic alcohols.

5. Chlorine in these naphthalenearsonic acids was found less reactive than chlorine in a similar position in the benzene nucleus.

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The Normal Potential of the Silver–Silver Bromide Electrode from 5 to 40°[1]

BY BENTON BROOKS OWEN AND LOUISE FOERING

Experimental difficulties inherent in the direct comparison of certain electrodes with the hydrogen standard have led to the extensive use of secondary standards such as the familiar calomel half-cells. Because of the thermodynamic objections to the estimation of liquid junction potential involved in the ordinary use of such standards, it is important to be able to perform the comparison in cells without liquid junctions. It has recently been shown[2] that cells containing dilute borax buffers can be very conveniently employed in this connection. Although the method is general in principle, the use of borax solutions, under certain prescribed conditions, has the peculiar advantage of eliminating the need for an extrapolation to infinite dilution. This labor-saving feature and the convenience of borax as a buffering agent make it desirable to test the accuracy and reliability of the method by investigating a system which can be readily checked by more orthodox procedures.

For this purpose we have measured the electromotive forces of cells of the type

$$H_2 \mid HBO_2(m),\ NaBO_2(m),\ KX(m) \mid AgX - Ag$$

in which X represents either bromide or chloride, and $m \approx 0.005$ molal. After a small correction[2] to the electromotive forces to make them correspond exactly to $m = 0.005$, the equation

$$E^0_{HBr} = E^0_{HCl} + E^{0.005}_{KBr} - E^{0.005}_{KCl} \qquad (1)$$

permits the calculation of E^0_{HBr} in terms of known values of E^0_{HCl} taken as standard. Comparison can then be made with values of E^0_{HBr} obtained by direct extrapolation of measurements on cells containing dilute hydrobromic acid. We have employed electrodes containing fused silver bromide because the corresponding normal potentials have

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(1) This communication embodies part of the experimental material to be presented by Louise Foering to the Graduate School of Yale University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) Owen, THIS JOURNAL, **57**, 1526 (1935). Full particulars regarding the calculations are given.