

and the reaction product washed on the funnel successively with 95% ethanol (400 cc.), hot ethanolamine (75°, two 500-cc. portions of a 3% solution in 95% ethanol to remove the chlorinated lignin), 95% ethanol (two 500-cc. portions), and cold water and then the woodmeal transferred to a fresh filter. This cycle of operations was repeated seven times until the residual product remained white after chlorination and washing with ethanolamine. The maple holocellulose was finally washed with ethanol and vacuum-dried; yield, 120 g.; Klason lignin, 0.0%.

Separation and Fractionation of Holocellulose Hydrogenation Products (see table).—The combined dioxane solutions of the maple holocellulose hydrogenation products (from 75 g. of maple holocellulose) were concentrated in a Claisen distilling flask, approximately one-fifth of the solvent being removed at atmospheric pressure (under carbon dioxide atmosphere) to avoid loss of low-boiling products (Fraction I), and the remaining dioxane removed under vacuum (20 mm. at 75°), leaving 12.4 g. of residual oils (Fraction II). The combined low-boiling distillates were then re-fractionated (450 mm. × 10 mm. vapor-jacketed Fenske column/760 mm.) in order to separate any higher-boiling material entrained in the first distillation, to isolate quantitatively the dioxane-water azeotrope (145 g. containing 24 g. of water^{2b}), and finally to remove the low-boiling alcohols (b. p. <80° (760 mm.)) prior to a quantitative determination of the methanol (1 g.) and ethanol (5 g.) content according to the method of Cooke.⁸ The small residual higher-boiling concentrate (11 cc.) (b. p. >101° (760 mm.) and containing a small amount of dioxane) thus obtained was added to the original liquid concentrate (Fraction II) and the mixture dissolved in 35 cc. of pentane. This solution was then extracted successively with 100, 50, 30, 25 and 20 cc. portions of water giving

(8) Cooke, McCarthy and Hibbert, *THIS JOURNAL*, **68**, 3052 (1941).

water-insoluble (Fraction III) and water-soluble (Fraction IV) fractions.

The latter product (IV) was now fractionated through the above-mentioned Fenske column, whereby an initial fraction of dioxane-water, a small amount of a water immiscible "oil" (probably entrained), and a residual oil (3.18 g.) were obtained. The last-named, oil fractionation through a Podbielniak column (900 × 3.8 mm.), distilled to the extent of approximately 85% at 40–125° (1 mm.), in the manner indicated in the table.

The water-insoluble oils (Fraction III, 6.71 g.) were fractionated similarly, b. p. 70–180° (20 to 1 mm.), the results being summarized in the table; approximately 83% was distillable.

Acknowledgment.—The authors wish to thank the Canada Paper Company and the Canadian Pulp and Paper Association for kind financial assistance. The authors wish also to express their indebtedness to Dr. L. M. Cooke for assistance in the preparation of the manuscript.

Summary

1. Maple wood holocellulose was hydrogenated under the same conditions as used for maple wood by Godard, McCarthy and Hibbert.¹

2. By comparison of the fractionation results thus found with those obtained for maple wood, it was possible to (a) eliminate the necessity of investigating many difficultly separable (maple wood) fractions shown to be of no interest as sources of lignin products, and (b) indicate a fraction of probable lignin origin.

MONTREAL, CANADA

RECEIVED AUGUST 25, 1941

[CONTRIBUTION FROM THE COLLEGE OF PHARMACY, UNIVERSITY OF CALIFORNIA]

Sulfophenylarsonic Acids and Certain of their Derivatives. V. *p*-(*p*-Sulfophenyl)- and *p*-(*p*-Sulfonamidophenyl)-phenylarsonic Acids¹

BY JOHN F. ONETO AND E. L. WAY

The following paper deals with the preparation of a number of sulfo- and sulfonamido derivatives of *p*-(phenyl)-phenylarsonic acid. This acid was obtained, (1), by application of the Scheller reaction² to *p*-aminobiphenyl and, (2), as a by-product from the preparation of phenylarsonic acid by the Bart reaction. The isolation and purification of the acid in the latter instance was essentially the method described by Schmidt.³

(1) Supported by grants from John Wyeth and Brother, and from the Research Board of the University of California.

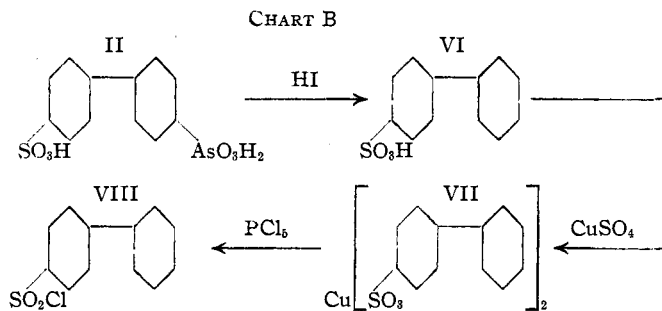
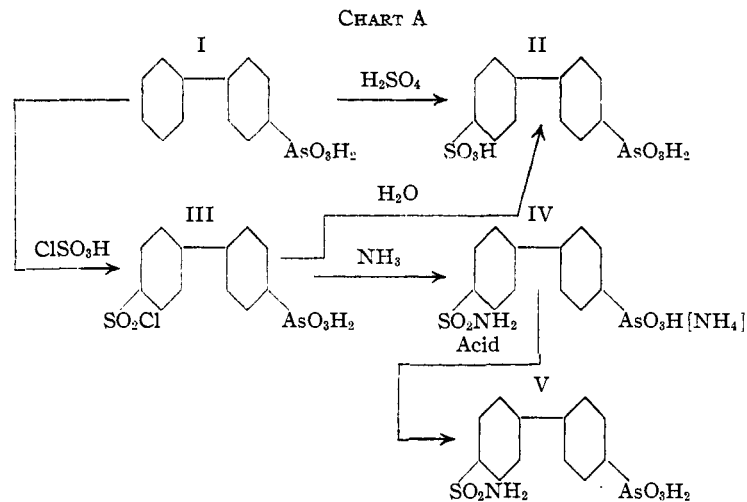
(2) Scheller, French Patent, 624,028, *Chem. Zentr.*, **98**, II, 229 (1927).

(3) Schmidt, *Ann.*, **421**, 169 (1920).

Chart A indicates the structures and preparation of the parent compounds, *p*-(*p*-sulfophenyl)-phenylarsonic acid, (II), and *p*-(*p*-sulfonamidophenyl)-phenylarsonic acid, (V).

Chart B illustrates the procedures carried out in determination of the relative positions of the substituent sulfo- and sulfonamido- groups in the para arsonated biphenyl nucleus. The resulting *p*-phenylbenzenesulfonyl chloride (VIII) proved to be of particular value in this instance because of its ease of purification, sharp melting point and stability toward hydrolysis.

We were unable to obtain (II) or (V) by appli-



cation of either the Bart or Scheller reactions to the corresponding substituted biphenylamines.

Experimental Part

p-(Phenyl)-phenylarsonic Acid (I).—Method (1)—prepared by the Scheller reaction as follows: fifteen grams of *p*-aminobiphenyl was dissolved in 400 cc. of absolute alcohol. The solution was then treated with 7 cc. of concentrated sulfuric acid, the resulting slurry cooled to 8°, and subsequently diazotized with the calculated amount of a saturated solution of sodium nitrite in water. After standing for two hours the mixture was treated with 28 g. of arsenic trichloride dissolved in 100 cc. of absolute alcohol. One-half hour after the addition of the arsenic trichloride, the mixture was treated with 2 g. of powdered cuprous bromide, heated gradually to 70° and maintained at that temperature until the evolution of nitrogen ceased. After steam distillation of the mixture, the insoluble granular material remaining in the steam distillation flask was removed by suction, air dried, and then washed thoroughly with acetone. The crude acid thus obtained was dissolved in dilute sodium hydroxide, treated with decolorizing carbon, filtered and finally precipitated from the colorless alkaline solution by the addition of hydrochloric acid. The final step of purification consisted in several crystallizations from 50% acetic acid, yield 9.5 g., m. p., unmelted up to 360°.^{4a,b} The melting point of the

corresponding diiodoarsine was 109–110°; mixed m. p., 109–110°.

Method (2)—the crude by-product obtained in the preparation of phenylarsonic acid by the Bart reaction was recrystallized several times from 50% acetic acid and then from water; unmelted up to 360°. The corresponding diiodoarsine melted at 109–110°. *Anal.* Calcd. for C₁₂H₁₁O₃As: As, 26.93. Found: As, 27.13.

p-(*p*-Sulfophenyl)-phenylarsonic Acid (II).—Ten grams of (I) was dissolved in 40 cc. of 96% sulfuric acid. The solution was then heated in an oil-bath at 110–120° for three hours, cooled to room temperature, and then poured into a mixture of 800 cc. of crushed ice and ice water. The dilute solution was treated with 85 g. of barium carbonate, heated on the steam-bath for eight hours and filtered with suction. The residue was extracted with several portions of hot water and the washings added to the original filtrate. The combined filtrate and washings mixture which was acid to congo red paper was evaporated to a small volume and allowed to stand for twenty-four hours. The resulting crystalline precipitate of (II) was removed by filtration and washed with several

portions of acetone; crude yield, 10 g.

Four grams of the crude material was dissolved in 50 cc. of hot, 95% alcohol, refluxed with decolorizing carbon and filtered. The hot filtrate, treated with 100 cc. of boiling 99% acetic acid, yielded 2.25 g. of colorless, crystalline acid after chilling in ice.

Anal. Calcd. for C₁₂H₁₁O₃SA₂: As, 20.91. Found: As, 20.92.

Three grams of crude (II) was dissolved in 25 cc. of boiling water, decolorized with carbon, and filtered. The hot filtrate, upon acidification with 10 cc. of 37% hydrochloric acid and chilling in ice yielded 2.4 g. of crystalline material. After standing in a vacuum desiccator for two days over calcium chloride, analysis for arsenic indicated the presence of one molecule of water in the compound.

Anal. Calcd. for C₁₂H₁₁O₃SA₂·H₂O: As, 19.91. Found: As, 20.22.

In a second procedure, (II) was prepared as follows. Five grams of (I) was added in portions to 20 cc. of technical grade chlorosulfonic acid. The temperature during the addition was maintained below 20°. The reaction mixture was then heated on the steam-bath for one hour, cooled, and then poured on crushed ice. The resulting precipitate of (III) was filtered off, washed with ice water and then hydrolyzed to (II) by boiling with 50 cc. of water until solution occurred. Concentration of the solution yielded 4.3 g. of (II). Two grams of this material was converted to (VIII); yield 0.5 g. after several crystallizations from glacial acetic acid; m. p. and mixed m. p. 114–115°.

(4a) Schmidt, *Ann.*, **421**, 169 (1920); unmelted up to 300°.

(4b) Lettermann, Dissertation, 1911, Rostock, page 20, gives the m. p. as 275°.

Barium Salt of *p*-(*p*-Sulfophenyl)-phenylarsonic Acid.—To a hot solution of 1 g. of purified (II) dissolved in 50 cc. of water was added 0.2 cc. of 37% hydrochloric acid and 1 cc. of a saturated solution of barium chloride. The crystalline barium salt started to precipitate immediately; yield 1 g. after washing with water then with acetone.

Anal. Calcd. for $C_{24}H_{20}O_{12}S_2As_2Ba$: As, 17.59. Found: As, 17.82.

Sodium Salt of *p*-(*p*-Sulfophenyl)-phenylarsonic Acid.—Two grams of purified (II) was dissolved in 20 cc. of boiling water. The hot solution was rendered alkaline to phenolphthalein with 10% sodium hydroxide solution and then immediately adjusted with 37% hydrochloric acid until strongly acid to congo red paper. The sodium salt which started crystallizing at once was removed by filtration after chilling the solution in ice; yield, 1.75 g.

Anal. Calcd. for $C_{12}H_{10}O_6SAsNa$: As, 19.70. Found: As, 19.85.

***p*-(*p*-Sulfophenyl)-phenyldiiodoarsine Sodium Salt.**—Two grams of *p*-(*p*-sulfophenyl)-phenylarsonic acid sodium salt was ground in a glass mortar with a mixture of 5 cc. of glacial acetic acid and 5 cc. of 50% hydriodic acid. The mixture was allowed to evaporate spontaneously to dryness which required several days. The residue was washed with several portions of glacial acetic acid and then recrystallized from 300 cc. of glacial acetic acid; yield, 2 g. The compound decomposed on heating.

Anal. Calcd. for $C_{12}H_8O_3SAsI_2Na$: As, 12.80. Found: As, 13.10.

***p*-(*p*-Sulfophenyl)-phenylarsine Oxide Sodium Salt.**—Two grams of the corresponding diiodoarsine was treated with 12 cc. of 10% ammonium hydroxide and the mixture allowed to stand overnight. The insoluble oxide was removed by filtration and crystallized several times from water; yield, 0.6 g.

Anal. Calcd. for $C_{12}H_8O_4SAsNa$: As, 21.64. Found: As, 21.92.

Direct Synthesis of *p*-(*p*-Sulfonamidophenyl)-phenylarsonic Acid.—Ten grams of dry (I) was converted to crude (III) using 50 cc. of technical grade chlorosulfonic acid. The total yield of crude (III) was dissolved in 100 cc. of 10% ammonium hydroxide, the solution heated to boiling and then concentrated on the steam-bath to approximately 85 cc. The mixture was then chilled in ice, the crystalline product removed by suction and purified by crystallization from water. The yield of purified crystalline ammonium salt (IV) thus obtained was 4 g.

Anal. Calcd. for $C_{12}H_{10}O_6N_2SAs$: As, 20.02. Found: As, 20.20.

Two grams of pure (IV) was dissolved in 75 cc. of boiling water. The resulting solution was rendered acid to congo red paper with 10% sulfuric acid. The free acid (V) precipitated almost at once in a crystalline state.; yield, 1.7 g.

Anal. Calcd. for $C_{12}H_{12}O_6NSAs$: As, 20.97. Found: As, 20.98.

***p*-(*p*-Sulfonamidophenyl)-phenyldiiodoarsine.**—A mixture consisting of 1 g. of (IV) and 10 cc. of 50% hydriodic acid was heated to 75–80°. One hundred and seventy cc. of glacial acetic acid was then added and the whole boiled until complete solution resulted. The diiodoarsine crystallized on cooling; yield, after crystallization from glacial acetic acid, 1 g. The compound does not melt below 200°.

Anal. Calcd. for $C_{12}H_{10}O_2NSAsI_2$: As, 13.35. Found: As, 13.80.

***p*-(*p*-Sulfonamidophenyl)-phenylarsine Oxide.**—A mixture consisting of 0.8 g. of *p*-(*p*-sulfonamidophenyl)-phenyldiiodoarsine and 20 cc. of 10% ammonium hydroxide was heated to boiling and then chilled in ice. The resulting oxide was purified by precipitation from alkaline solution with dilute hydrochloric acid; yield 0.3 g.

Anal. Calcd. for $C_{12}H_{10}O_3NSAs$: As, 23.18. Found: As, 23.32.

Determination of Configuration.—Four grams of (II) was treated with 30 cc. of 50% hydriodic acid after which the mixture was evaporated to dryness on the steam-bath. The residue was washed with small portions of ether to remove the excess iodine and then dissolved in 200 cc. of boiling water. The hot solution was treated with an excess of saturated solution of copper sulfate, filtered and allowed to stand overnight. The yield of crystalline (VII) was 1 g. One gram of dry (VII) was triturated with 3 g. of phosphorus pentachloride. The reaction mixture was allowed to stand for twenty minutes and then decomposed with water. The crude, insoluble (VIII) was purified by crystallizing several times from glacial acetic acid; yield 0.4 g.; m. p. 114–116°; mixed m. p. 114–116°.

The material for determining the mixed m. p. was prepared according to the procedure described by Kumler and Halverstadt.⁵

Summary

The preparation of *p*-(*p*-sulfophenyl)- and *p*-(*p*-sulfonamidophenyl)-phenylarsonic acids and a number of their derivatives have been described.

SAN FRANCISCO, CALIFORNIA

RECEIVED SEPTEMBER 4, 1941

(5) Kumler and Halverstadt, *THIS JOURNAL*, **63**, 2186 (1941).