thol was 88%. After recrystallizations from methanol-water (1:1), the compound melted at 83°.

From the aqueous solution which remained after the last ether extraction above, benzoic acid was recovered in 94% yield.

1-Bromo-2-naphthol.[6]—This compound was prepared in almost quantitative yield from equimolecular proportions of bromine and 2-naphthol dissolved in glacial acetic acid. The mixture was heated on a steam-bath for two hours and poured into water. The crude product was distilled at 10 mm. pressure and recrystallized twice from benzene-ligroin (1:3)[7]; m. p. 80–81°.[6] A mixture of this product and that of m. p. 83°, obtained by hydrolysis of the brominated ester, melted without depression.

1-Bromo-2-naphthyl Acetate.[8]—A sample (0.6 g.) of the bromonaphthol described above was refluxed gently for one hour in acetic anhydride (15 ml.) to which had been added anhydrous sodium acetate (1 g.). The reaction mixture was poured into 200 ml. of water and, after thirty hours, excess sodium carbonate was added. The ester was extracted with ether. The oil which was recovered was dissolved in warm ethanol and crystallization was effected by rapid cooling in a carbon dioxide–acetone mixture. After the first recrystallization from ethanol, a 70% yield resulted; the second recrystallization gave a product which melted at 55–56°.[10]

1-Bromo-2-naphthyl Benzoate.—From 0.7 g. of 1-bromo-2-naphthol, 1-bromo-2-naphthyl benzoate was obtained[5] in almost quantitative yield. Recrystallizations from methanol gave a product which melted at 98.5–99.5°. A mixture of this product and that of m. p. 98–99°, obtained by the bromination of 2-naphthyl benzoate, melted without depression.

(6) Smith, *J. Chem. Soc.*, **35**, 789 (1879) ("Beilsteins Handbuch der organischen Chemie," Verlag Julius Springer, Berlin, 4th ed., Vol. VI, 1923, p. 650).

(7) Boiling range of the ligroin, 30–60°.

(8) In order to be certain that the bromonaphthol which was obtained in this work was the 1-bromo compound, it was necessary to convert it to the corresponding acetate, for both 1-bromo-2-naphthol[9] and 3-bromo-2-naphthol[9] melt at almost the same temperatures, *viz.*, 83 or 84°; the m. p. of 1-bromo-2-naphthyl acetate is 56°[10] and that of the 3-bromo isomer is 94°.[9]

(9) Fries and Schimmelschmidt, *Ann.*, **484**, 268 (1930).

(10) Hewitt and Mitchell, *J. Chem. Soc.*, **89**, 1173 (1906).

Summary

The bromination of 2-naphthyl benzoate in glacial acetic acid results in the formation of 1-bromo-2-naphthyl benzoate.

PULLMAN, WASHINGTON RECEIVED MAY 27, 1940

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

Sulfophenylarsonic Acids and Certain of their Derivatives. III. *p*-Sulfo- and *p*-Sulfonamidodiphenylarsonic Acids

BY J. F. ONETO AND E. L. WAY

Doak's[1] recent publication called our attention to the alcoholic Bart reaction described by Scheller.[2] When this reaction was applied to sulfanilic acid and phenyldichloroarsine, unreacted sulfanilic acid (64%) and phenylarsonic acid (84%) were recovered from the reaction mixture. We have shown in a separate experiment that nitrous acid in alcoholic solution is capable of oxidizing the trivalent arsenic in phenyldichloroarsine to a pentavalent state. On subsequent steam distillation of the reaction mixture an 86% yield of phenylarsonic acid resulted. *p*-Sulfodiphenylarsonic acid was obtained, however, through the barium salt stage, by first diazotizing the sulfanilic acid in aqueous solution, adding alcohol and then carrying out the Scheller reaction in the usual way.

On application of the Bart reaction to sulfanilic acid and phenyldisodium-arsenite, 70–75% yields of phenylarsonic acid resulted when coupling was carried out in alkaline solution. We were unable to isolate *p*-sulfodiphenylarsonic acid from the reaction products.

p-Sulfonamidophenylarsonic acid was obtained in relatively low yields by application of the Bart reaction and Sakellarios'[3] modification of the Bart reaction to sulfanilamide and phenyldisodium arsenite. Coupling in both instances was carried out in acid solution, the yields of *p*-sulfonamidodiphenylarsonic acid being 11 and 23%, respectively. Sixty to 65% yields of phenylarsonic acid were obtained from the Bart reaction when the order of coupling was reversed. The Scheller reaction gave 29–32% yields of *p*-sulfonamidodiphenylarsonic acid when applied to sulfanilamide and phenyldichloroarsine.

p-(N-Chloro)-sulfonamidodiphenylarsonic acid was obtained on treating the corresponding acid in alkaline solution with sodium hypochlorite. The N-chloro compound precipitates on acidification with sulfuric acid.

(1) Doak, THIS JOURNAL, **62**, 167 (1940).

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

(3) Sakellarios, *Ber.*, **57**, 1514 (1924).

Experimental Part

p-Sulfodiphenylarsonic Acid.—A mixture consisting of 17.3 g. of sulfanilic acid and 40 cc. of water was heated to 80° and 40% sodium hydroxide added until solution occurred and the reaction was alkaline to litmus. The solution was diluted with 200 cc. of water, chilled to 0° by external cooling and diazotized with 7 g. of sodium nitrite and 9 g. of concentrated sulfuric acid. After standing for one hour, the diazotized mixture was diluted with 350 cc. of 95% alcohol. A solution of 22 g. of phenyldichloroarsine in 50 cc. of 95% alcohol was then added with good stirring. The mixture was subsequently treated with 1 g. of powdered cuprous bromide, heated at 80° until the evolution of nitrogen ceased and finally steam distilled. The *p*-sulfodiphenylarsonic acid was isolated from the residue via the barium salt stage and purified by recrystallizing from water. The acid is practically insoluble in acetone or glacial acetic acid; yield, 6 g.

Anal. Calcd. for $C_{12}H_{11}O_5SAs$: As, 21.90. Found: As, 21.85.

p-Sulfonamidodiphenylarsonic Acid.—A solution consisting of 17 g. of phenylarsine oxide, 16 g. of sodium hydroxide and 0.2 g. of copper sulfate dissolved in 1000 cc. of water was added at 0° to 17 g. of diazotized sulfanilamide in 500 cc. of water. After standing for twenty-four hours, the thick, foamy mixture was concentrated on the steam-bath to 350 cc., made acid to congo red paper with concentrated hydrochloric acid and allowed to stand for several days. The resulting precipitate of gum and crystals was filtered off, dried and the gum removed with acetone. The residue was purified by recrystallizing from either water or 10% acetic acid; yield 11%; m. p. 229–231°.

Anal. Calcd. for $C_{12}H_{12}O_4NSAs$: As, 21.96. Found: As, 21.75.

The yield of purified acid from the Sakellarios method was 23%, m. p. 229–231°; mixed m. p. of the bromoarsine, 100–101°.

The Scheller reaction, as described by Doak, gave 28–30% yields of *p*-sulfonamidodiphenylarsonic acid, m. p. 229–230°; mixed m. p. of the bromoarsine, 100–101°.

Oxidation of Phenyldichloroarsine with Nitrous Acid.—A solution consisting of 5 g. of concentrated sulfuric acid and 16 g. of phenyldichloroarsine in 200 cc. of absolute alcohol was treated at 0° with a saturated solution of sodium nitrite in water equivalent to 2.5 g. of sodium nitrite. After standing for twelve hours the mixture was steam distilled, the residue concentrated to a small volume and the crystalline precipitate of phenylarsonic acid removed by filtration; yield, 86%; m. p., softens at 156–158°.

***p*-Sulfonamidodiphenylchloroarsine.**—Six grams of *p*-sulfonamidodiphenylarsonic acid was dissolved in 45 cc. of 37% hydrochloric acid, a trace of hydriodic acid added and the mixture then saturated with sulfur dioxide. The resulting crystalline chloroarsine was removed by filtration, air dried and purified by recrystallizing from a chloroform–carbon tetrachloride mixture; yield 3.7 g.; m. p. 106–107°.

Anal. Calcd. for $C_{12}H_{11}O_2NSAsCl$: As, 21.86. Found: As, 21.70.

***p*-Sulfonamidodiphenylbromoarsine.**—Five grams of *p*-sulfonamidodiphenylarsonic acid was dissolved in 48 cc. of 48% hydrobromic acid containing a trace of hydriodic acid. The solution was then saturated with sulfur dioxide, chilled in ice and the crystalline precipitate purified by recrystallizing from a 10% chloroform–90% carbon tetrachloride mixture; yield 3.1 g.; m. p. 100–101°.

Anal. Calcd. for $C_{12}H_{11}O_2NSAsBr$: As, 19.31. Found: As, 19.27.

***p*-Sulfonamidodiphenyliodoarsine.**—Six grams of *p*-sulfonamidodiphenylarsonic acid suspended in 15 cc. of glacial acetic acid was treated with 20 cc. of hydriodic acid, sp. gr. 1.5. The resulting solution was heated just to the boiling point, then chilled in ice. The yield of iodoarsine after recrystallizing from a chloroform–carbon tetrachloride mixture was 6 g.; m. p. 121–122°.

Anal. Calcd. for $C_{12}H_{11}O_2NSAsI$: As, 17.22. Found: As, 17.64.

***p*-Sulfonamidotetraphenylarsyl Oxide.**—The crude bromoarsine from 10 g. of *p*-sulfonamidodiphenylarsonic acid was treated with 50 cc. of 10% ammonium hydroxide and then heated on the steam-bath for one-half hour. The insoluble gummy oxide was purified by dissolving in 10% sodium hydroxide solution and precipitating with 5% sulfuric acid; yield, 5 g.

Anal. Calcd. for $C_{24}H_{22}O_5N_2S_2As_2$: As, 23.70. Found: As, 23.45.

***p*-(N-Chloro)-sulfonamidodiphenylarsonic Acid.**—A solution consisting of 2 g. of purified *p*-sulfonamidodiphenylarsonic acid in 60 cc. of a 1% sodium hydroxide solution was treated with the calculated amount of an alkaline solution of sodium hypochlorite. After standing for one-half hour, the free chloramide was precipitated by rendering the solution acid to congo red paper with 5% sulfuric acid. The gummy precipitate which soon crystallized on standing, was washed several times with water and then dried at 100° for two hours; yield, 1.2 g.; m. p., effervesces at 160–161°.

Anal. Calcd. for $C_{12}H_{11}O_4NSAsCl$: As, 19.92; Cl, 9.41. Found: As, 19.92; Cl, 9.53.

Summary

The preparation of *p*-sulfo- and *p*-sulfonamidodiphenylarsonic acids as well as a number of derivatives of *p*-sulfonamidodiphenylarsonic acid have been described.

SAN FRANCISCO, CALIFORNIA RECEIVED JUNE 18, 1940