they were identified only qualitatively. The selenides were identified by conversion to their dibromides or dichlorides, the aryl bromides by nitration. In every case, the expected compounds were obtained.

When the mercury diaryls and selenium tetrabromide were allowed to stand together in carbon bisulfide without shaking or stirring, or when an excess of selenium tetrabromide was used, the precipitated aryl mercuric bromide was contaminated with mercuric bromide. The presence of the latter was shown by the formation of yellow mercuric oxide when sodium hydroxide solution was added to the precipitate. When one mole of selenium tetrabromide and three of phenylmercuric bromide were shaken together for six days, pure mercuric bromide was formed and identified by its reaction with mercury diphenyl in acetone solution to form phenylmercuric bromide. The other reaction products were diphenyl selenide and bromobenzene. Even when less than the theoretical amount of phenylmercuric bromide was shaken with selenium tetrabromide, these were the only products, and no trace of diphenyl selenium dibromide was found. Owing to the insolubility of the naphthyl- and biphenylmercuric bromides in carbon bisulfide, it was impossible to carry this reaction to completion with them in a reasonable time.

Summary

Diaryl mercury compounds react with selenium tetrabromide to give almost quantitative yields of aryl mercuric bromides, diaryl selenides and aryl bromides. The aryl mercuric bromides can react with more selenium tetrabromide to give mercuric bromide, diaryl selenides and aryl bromides. These reactions can be used for the synthesis of diaryl selenides, especially those of the type of dinaphthyl or dibiphenyl selenides.

COLUMBUS, OHIO RECEIVED JANUARY 5, 1938

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

Arsenicals Containing the Furan Nucleus. III. Some beta-Substituted Furan Arsenicals

BY WILLIAM W. BECK[1] AND CLIFF S. HAMILTON

Furan arsenicals, in which arsenic is linked to the furan nucleus in the alpha position, have been reported in previous communications.[2,3] The availability of certain beta-substituted furan mercurials suggested the possibility of synthesizing and studying furan arsenicals containing arsenic in a beta position.

When three equivalents of 3-chloromercurifuran was treated with one equivalent of arsenic trichloride in benzene solution, there was obtained tri-3-furylarsine. Arsenation proceeded less rapidly than in the case of 2-chloromercurifuran under similar conditions. When the arsine was treated with one equivalent of mercuric chloride in alcoholic solution, the complex addition product, tri-3-furylarsine mercurichloride, was obtained. Under similar conditions, the 2-isomer undergoes cleavage of the carbon–arsenic bond to form 2-chloromercurifuran. Thus, tri-3-furylarsine resembles triphenylarsine, which also forms an addition product with mercuric chloride,[4] more than it does its isomer, tri-2-furylarsine, as regards stability of the carbon–arsenic bond. If cleavage of the carbon–arsenic linkage in aromatic arsenicals by mercuric chloride be considered as one of the criteria of aromaticity, it may be concluded that the beta positions in furan are less aromatic in character than are the alpha positions.[5]

The mercurial was recovered unchanged when methyl 4-chloromercuri-5-bromo-2-furoate was refluxed with arsenic trichloride in xylene solution. When arsenic tribromide was substituted for arsenic trichloride, arsenation proceeded rapidly and completely, and 2-carbomethoxy-5-bromo-4-furyldibromoarsine was obtained. Scission of the carbon–arsenic linkage was not caused by mercuric chloride or iodine. Prolonged boiling with water cleaved the bond, and methyl 5-bromo-2-furoate was obtained.

Mercuration of ethyl 5-bromo-2-furoate gave the ethyl analog of the methyl mercurial, and arsenation of the ethyl mercurial gave a dibromoarsine.

Attempts were made to apply other standard methods of preparing aromatic arsenicals to the furan series. No furan arsenicals were obtained by direct arsonation of furoic esters with arsenic acid nor by the Rosenmund reaction[6] with halogen-substituted furans.

---

(1) Parke, Davis and Company Fellow.

(2) Lowe and Hamilton, THIS JOURNAL, **57**, 1081 (1935).

(3) Lowe and Hamilton, *ibid.*, **57**, 2413 (1935).

(4) LaCoste and Michaelis, *Ann.*, **201**, 241 (1880).

(5) Gilman and Towne, *Rec. trav. chim.*, **51**, 1056 (1932).

(6) Rosenmund, *Ber.*, **54**, 438 (1921).

Experimental

Tri-3-furylarsine.—Nine and one-tenth grams (0.03 mole) of 3-chloromercurifuran[7] and 1.8 g. (0.01 mole) of arsenic trichloride in 50 cc. of benzene were refluxed for three hours. The solution was cooled, filtered, the benzene removed by distillation, and the residue was steam distilled. A clear yellow oil was extracted from the distillate with ether, the ether extract dried, and the ether removed. The brown oil remaining was placed in a vacuum desiccator and the latter exhausted with a water pump for twenty-four hours; yield, 1.0 g., or 36%. From the mercuric chloride precipitate there was obtained, by fractional crystallization from ethanol, 1.5 g. of tri-3-furylarsine mercurichloride, corresponding to an additional 28% of tri-3-furylarsine.

Anal. Calcd. for $(C_4H_3O)_3As$: As, 27.14. Found: As, 26.95, 27.02.

Tri-3-furylarsine Mercurichloride.—Five-tenths gram of tri-3-furylarsine and 0.5 g. of mercuric chloride were refluxed for fifteen minutes with 25 cc. of 95% ethanol. On cooling, the mercurichloride crystallized out. It was recrystallized from ethanol, from which it separated in thick, elongated white prisms melting at 152–153°; yield, 0.7 g., or 70%.

Anal. Calcd. for $(C_4H_3O)_3As \cdot HgCl_2$: Hg, 36.64. Found: Hg, 36.68, 36.74.

Methyl 4-Chloromercuri-5-bromo-2-furoate.—The method employed was a modification of that of Vander Wal.[8] Ten and three-tenths grams (0.05 mole) of methyl 5-bromo-2-furoate was mixed intimately with 16 g. (0.05 mole) of mercuric acetate and, while stirring, the mixture was heated in an oil-bath at 155–160° for ten minutes. After cooling, the contents were refluxed with 100 cc. of acetone, filtered, and the residue reëxtracted with 50 cc. of acetone. The combined filtrates were chilled, and the acetoxymercuri compound separating was filtered, washed with a little cold acetone, and dried at 100°. From the mother liquors 4.1 g. of methyl 5-bromo-2-furoate was recovered; yield 7.0 g., or 50%, based on reacted ester. After two recrystallizations from xylene the mercurial was obtained as a white crystalline powder melting at 198–199°.

Anal. Calcd. for $C_8H_7O_5BrHg$: Hg, 43.28. Found: Hg, 43.59, 43.54.

Seven grams of the above mercurial melting at 195–196° was dissolved in 50 cc. of boiling acetone and 5 g. of calcium chloride in 25 cc. of 80% ethanol added. The solution was poured with stirring into 500 cc. of cold water. After several hours of standing the chloromercuri compound was filtered, washed with a little cold methanol, and dried at 100°; yield 5.8 g. or 43% based on methyl 5-bromo-2-furoate. After two recrystallizations from xylene the white crystalline powder melted at 238°.

2-Carbomethoxy-5-bromo-4-furyldibromoarsine.—Twelve grams (0.027 mole) of methyl 4-chloromercuri-5-bromo-2-furoate and 8.6 g. (0.027 mole) of arsenic tribromide were refluxed with 75 cc. of xylene for three hours. After standing overnight in the refrigerator, the solution was filtered from precipitated mercuric salts, the xylene distilled off under reduced pressure, and the residue dissolved in sufficient hot petroleum ether (b. p. 40–50°) to take it in solution. On cooling, the dibromoarsine separated out. It was redissolved in petroleum ether, treated with a little fuller's earth, and filtered. The dibromoarsine crystallized on cooling in clusters of white needle-like crystals; m. p. 95–96°; yield, 6.0 g., or 50%.

Anal. Calcd. for $C_6H_4O_3Br_3As$: As, 17.01; Br, 54.65; mol. wt., 439. Found: As, 16.99, 17.03; Br, 54.67, 54.47; mol. wt. (by boiling point rise of benzene), 416.

Ethyl 4-Chloromercuri-5-bromo-2-furoate.—The procedure was identical with that used for the methyl compound. From 15.4 g. (0.07 mole) of ethyl 5-bromo-2-furoate and 22.5 g. (0.07 mole) of mercuric acetate, 8.4 g. of the acetoxymercuri compound was obtained, and 3.3 g. of ester was recovered; yield 32%. After two recrystallizations from xylene, the mercurial melted at 188–189°.

Anal. Calcd. for $C_9H_9O_5BrHg$: Hg, 42.01. Found: Hg, 42.29, 42.27.

The acetoxymercuri compound was converted to the chloromercuri compound with calcium chloride in acetone–ethanol. From 8.4 g. of acetoxymercuri compound 6.1 g. or 28% of chloromercuri compound based on ethyl 5-bromo-2-furoate was obtained. After two recrystallizations from xylene the mercurial melted at 162°.

Anal. Calcd. for $C_7H_6O_3BrHgCl$: Hg, 44.18. Found: Hg, 44.27, 44.35.

2-Carbethoxy-5-bromo-4-furyldibromoarsine.—The procedure was identical with that used for the methyl compound. From 8.9 g. (0.02 mole) of ethyl 4-chloromercuri-5-bromo-2-furoate and 6.2 g. (0.02 mole) of arsenic tribromide in 50 cc. of xylene, a yield of 3.5 g. of the product, or 39% was obtained. The arsenical separated from petroleum ether in thick elongated white prisms melting at 52–53°.

Anal. Calcd. for $C_7H_6O_3Br_3As$: As, 16.55. Found: As, 16.38, 16.43.

Summary

Arsenic has been linked to the furan nucleus in the beta position for the first time. Tri-3-furylarsine, 2-carbomethoxy-5-bromo-4-furyldibromoarsine, and 2-carbethoxy-5-bromo-4-furyldibromoarsine were prepared from furan mercurials, and the chemistry of the arsenicals was studied. Attempts to prepare furan arsenicals from other starting materials than furan mercurials were unsuccessful.

LINCOLN, NEBRASKA RECEIVED JANUARY 20, 1938

---

[7] Gilman and Wright, THIS JOURNAL, **55**, 3302 (1933).

[8] Gilman and Vander Wal, unpublished results.