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Bromonitrothiophene

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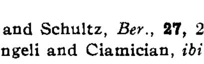
Although iodonitrothiophene has been prepared by the earliest workers in the thiophene series,[1] the corresponding bromine compound has scarcely been mentioned in the literature.[2] After describing the nitration of iodothiophene, Kreis[1] (pp. 2073–2075) stated that due to difficulties encountered in the preparation of bromothiophene its nitration was not attempted.

At the present time the preparation of bromothiophene does not present insurmountable difficulties. Although the yield of the costly product is under the most favorable conditions barely over one-half of that required by theory, a number of convenient methods are available for its preparation.[3] The bromothiophene used in this investigation was prepared from thiophene and acetbromamide, the method of Steinkopf and Otto[3b] (p. 69) being employed with certain modifications.

The Nitration of Bromothiophene.—The nitration of negatively substituted thiophene derivatives has been possible in a number of instances with the usually employed nitric–sulfuric acid mixture.[4] Contrary to expectation, the presence of the strongly negative bromine atom in bromothiophene does not inhibit undesirable side reactions when the compound is treated with this nitrating mixture. Töhl and Schultz[5] have shown that concentrated sulfuric acid reacts very readily with bromothiophene at the ordinary temperature, converting it into dibromothiophene, dithienyl derivatives, and two isomeric sulfonic acids. Moreover, observations made in this Laboratory support the conclusion that the nitric acid in the nitrating mixture oxidizes a part of the bromothiophene into open chain decomposition products. With pure nitric acid the reaction proceeds with almost explosive violence, yielding a dark oil in which sulfuric acid may be identified. It may also be added that by the action of fuming nitric acid Angeli and Ciamician[6] have almost completely converted the more stable tetrabromothiophene into dibromomaleic anhydride and sulfuric acid; and the study of other brominated compounds in the thiophene series has led the authors to the conclusion that these halogen derivatives oxidize into products in which the atomic grouping  $-\underset{\underset{O}{\|}}{C}-C=C-\underset{\underset{O}{\|}}{C}-$ may in general be recognized[6b] (p. 1347).

It is clear that while the presence of bromine tends to make the thiophene ring more resistant to oxidation, the formation of by-products in

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(1) (a) Kreis, *Ber.*, **17**, 2073 (1884); (b) Meyer, "Die Thiophengruppe," Braunschweig, 1888, p. 104.

(2) The experimental work outlined in this paper had almost been completed when a brief paragraph on bromonitrothiophene appeared in *Ann.*, **512**, 161 (1934). The conditions under which the compound was produced are not stated, and there is no reference to the yield of the product or its properties. Its melting point is given as 48–49°.

(3) (a) Töhl and Schultz, *Ber.*, **27**, 2835 (1894); (b) Steinkopf and Otto, *Ann.*, **424**, 69 (1921); (c) Steinkopf and co-workers, *ibid.*, **430**, 98 (1922); (d) Krause and Renwanz, *Ber.*, **62B**, 1710 (1929).

(4) (a) Kreis, *ibid.*, **17**, 2074 (1884); (b) Rosenberg, *ibid.*, **18**, 3028 (1885); (c) Rosenberg, *ibid.*, **19**, 652 (1886); (d) Babasinian, THIS JOURNAL, **50**, 2751 (1928).

(5) Töhl and Schultz, *Ber.*, **27**, 2835 (1894).

(6) (a) Angeli and Ciamician, *ibid.*, **24**, 75 (1891); (b) Ciamician and Angeli, *ibid.*, **24**, 1347 (1891).

large quantities can hardly be prevented if an attempt is made to nitrate bromothiophene with pure nitric acid or a mixture of nitric and sulfuric acids.

Nitration in Acetic Anhydride and Glacial Acetic Acid.—Side reactions are checked to a great extent when bromothiophene dissolved in acetic anhydride is nitrated with a solution of nitric acid in the same solvent. Under these conditions there is a decided increase in the yield of bromonitrothiophene if a reaction temperature of −5 to 0° is maintained during nitration.

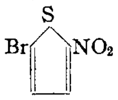
An acetic anhydride solution of bromothiophene may also be nitrated at 5° with a solution of nitric acid in glacial acetic acid. Moreover, nitration takes place at 50° when acetic acid alone is employed as a solvent. However, the yield of bromonitrothiophene is always poor when the anhydride is either diluted with glacial acetic acid or is entirely replaced by it. The use of pure acetic anhydride is therefore suggested for the nitration of bromothiophene.

Experimental

Twenty-five grams of bromothiophene (b. p. 149.5–150.5°) dissolved in 50 cc. of acetic anhydride was introduced into a half-liter round flask, provided with a stirrer and a cooling device. At −5° the liquid was treated, during rapid stirring, with a solution of 25 g. of nitric acid (sp. gr. 1.51) dissolved in 50 cc. of ice-cold acetic anhydride. The acid was added dropwise within a period of forty-five minutes and the temperature was not permitted to rise above 0°. In the earlier phases of the reaction a faint yellow color developed in the mixture. This was followed by the formation of a lemon-yellow precipitate weighing less than a gram. The color of the precipitate and its quantity remained practically unchanged during the nitration. At the end of the forty-five-minute period the stirring was continued for half an hour. The nitrating flask was then surrounded with ice and kept in a refrigerator for twenty-four hours. It was poured, with stirring, into finely crushed ice. The yellow-brown crystalline solid formed in this way was dried in a brown desiccator over sulfuric acid. It was dissolved in a large volume of hot ligroin, decolorized with darco and concentrated to crystallization at the room temperature. The first fraction of crystals consisted of long faint-yellow prisms. From the mother liquor three additional fractions were obtained, the last and smallest fraction being darker in color. The acid filtrate was found to contain a very small quantity of the product upon neutralization with sodium carbonate and distillation with steam. The total yield of the crude product was 21.3 g., or 66% of that required by theory. This was purified by distillation with steam; weight of the pure product 19.5 g., or 61% of the theoretical quantity.

Anal. Calcd. for $C_4H_2S(NO_2)Br$: S, 15.41; Br, 38.42. Found: S, 15.39; Br, 38.37.

Properties.—Bromonitrothiophene is a pale yellow solid, usually crystallizing in fine prisms. It melts at 45–46° and distils at 235–237° (750 mm.) with only slight decomposition. It has a sweetish taste, developing an extremely astringent after-taste. The compound is very volatile with steam. The steam distillate forms snow-white fine prisms. In a very short time the product assumes a yellow color. The same changes in color are noticed upon crystallization from solvents. It is very soluble in ether, methanol, chloroform, carbon tetrachloride, methyl formate, ethyl alcohol and benzene. It dissolves sparingly in petroleum ether. By slow crystallization it separates out from this solvent in beautiful transparent needles.

Bromonitrothiophene is assumed to be the 2,5-derivative of thiophene. Its provisional formula  remains to be established.

Summary

1. Bromothiophene may be nitrated into bromonitrothiophene in pure acetic anhydride. The yield of the product is over 60% when a reaction temperature of −5 to 0° is maintained.

2. The yield is not satisfactory when nitration is carried out in a mixture of acetic anhydride and glacial acetic acid at 5°, or in pure acetic acid at 50°.

3. The properties of bromonitrothiophene are described. The compound is assumed to be the 2,5-derivative of thiophene.

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