phenylmagnesium bromide prepared from 10.3 g. (0.066 mole) of bromobenzene and 1.64 g. (0.067 g. atom) of magnesium turnings. After working up the reaction mixture according to the method described previously there was obtained 1.9 g. (54.3%) of *o*-fluorophenyldiphenylcarbinol melting at 113–115°. An additional crystallization from petroleum ether (b.p. 60–70°) raised the melting point to 116–117°.

A mixed melting point of this compound with that obtained from the reaction of *o*-fluorophenyllithium and benzophenone showed no depression.

The melting point of *o*-fluorophenyldiphenylcarbinol prepared from methyl *o*-fluorobenzoate and phenylmagnesium bromide has been reported as 116°.[8]

Attempted Preparation of *o*-Fluorophenyllithium at −15°.—Thirty-seven milliliters of a 0.98 *N* *n*-butyllithium solution was added over a period of 6 minutes to a rapidly stirred solution of 6.0 g. (0.0342 mole) of *o*-fluorobromobenzene in 55 ml. of anhydrous ether. The temperature was not permitted to rise above −15° during the addition. Immediately on completion of the addition, Color Test I was positive while Color Test II[9] was negative. The reaction mixture was poured jetwise over a Dry Ice–ether slurry. The carbonated mixture was hydrolyzed with water and then the ethereal layer was separated. The organic layer was washed twice with two 50-ml. portions of 5% sodium hydroxide and the extracts were combined with the original aqueous layer. The residual ether was boiled from the aqueous solution and then the solution was acidified with hydrochloric acid. A milky solution resulted and after cooling a fine precipitate settled out. This precipitate was filtered and air-dried to yield 0.20 g. of light brown powder melting over the range 200–210° with decomposition. Attempts to recrystallize the unknown material have been unsuccessful.

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[8] E. Bergmann, *Rec. trav. chim.*, **58**, 863 (1939).

[9] H. Gilman and J. Swiss, THIS JOURNAL, **62**, 1847 (1940).

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The Nitration of Some 2- and 3-Amino Derivatives of Dibenzothiophene

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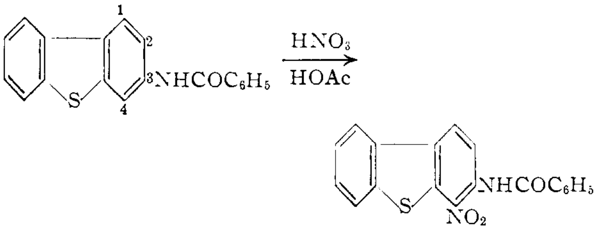
2-Carbethoxyaminodibenzothiophene[1] and 2-acetaminodibenzothiophene[2] have been shown to nitrate predominantly in the 1-position as opposed to the structurally similar 2-acetaminodibenzofuran, which nitrates in the 3-position.[3] 2-Benzenesulfonamidodibenzothiophene,[4] as well as 2-benzamidodibenzothiophene, however, nitrate almost exclusively in the 3-position, indicating that steric factors may play a significant role in the direction of electrophilic attack on the 2-substituted aminodibenzothiophene derivatives.

The nitration of 3-acetaminodibenzothiophene affords a 77% yield of 4-nitro-3-acetaminodibenzothiophene[1] as opposed to the nitration of 3-acetaminodibenzofuran which gives the 2-nitro-3-acetamino derivative in a 75% yield.[2]

In a similar fashion then, it was thought that nitration of 3-benzamidodibenzothiophene would yield mostly the 2-nitro product; however, a 79.5% crude yield of 4-nitro-3-benzamidodibenzothiophene was obtained, indicating that steric factors do not have so strong an effect in influencing entering groups in the 4-position.



Experimental[5]

2-Benzamidodibenzothiophene.—Seven grams (0.0352 mole) of 2-aminodibenzothiophene[6] was dissolved in 100 ml. of benzene to which had been added 3.0 ml. of pyridine. This solution was warmed slightly and treated with 5.0 ml. of benzoyl chloride giving rise to a precipitate. The mixture then was cooled and the precipitate filtered and washed with small portions of dil. hydrochloric acid. This crude material was crystallized from methyl Cellosolve to yield 6.0 g. (60.0%) of 2-benzamidodibenzothiophene melting at 199–200°.

Anal. Calcd. for $C_{19}H_{13}NOS$: S, 10.57. Found: S, 10.42.

3-Benzamidodibenzothiophene.—This material was prepared in a similar fashion as above from 3-aminodibenzothiophene[7] to yield 96.7% of 3-benzamidodibenzothiophene melting at 227–228°.

Anal. Calcd. for $C_{19}H_{13}NOS$: S, 10.57. Found: S, 10.51.

4-Nitro-3-benzamidodibenzothiophene.—Into a 250-ml. round-bottomed, three-necked flask equipped with a mechanical stirrer and reflux condenser were placed 3.5 g. (0.015 mole) of 3-benzamidodibenzothiophene and 100 ml. of glacial acetic acid. To the stirring mixture was added over a period of 15 min., 8.0 ml. of nitric acid (90%). A precipitate formed during the addition of the nitric acid and the reaction mixture was stirred for 15 min. The resulting precipitate was filtered and dried to yield 3.2 g. (79.5%) of crude, orange product, m.p. 225–233°. This material was crystallized from methyl Cellosolve to yield 2.1 g. (52.0%) of orange, fiber-like needles of 4-nitro-3-benzamidodibenzothiophene melting at 246–247°.

Anal. Calcd. for $C_{19}H_{12}N_2O_3S$: S, 9.21. Found: S, 8.91.

4-Nitro-3-aminodibenzothiophene.—Into a 125-ml. erlenmeyer flask equipped with a reflux condenser were placed 1.0 g. (0.00288 mole) of 4-nitro-3-benzamidodibenzothiophene, 5.0 g. of potassium hydroxide, 25 ml. of water and 25 ml. of ethanol. The reaction mixture was allowed to reflux for a period of two hours at which time 50 ml. of water was added to the system and the contents cooled. The reddish-orange material was filtered and dried to yield 0.57 g. (81.0%) of 4-nitro-3-aminodibenzothiophene melting at 244–245° and giving no depression in melting point when admixed with an authentic specimen of 4-nitro-3-aminodibenzothiophene.

3-Nitro-2-benzamidodibenzothiophene.—Into a 250-ml. round-bottomed, three-necked flask equipped with a mechanical stirrer and reflux condenser were placed 5.5 g. (0.0182 mole) of 2-benzamidodibenzothiophene, 50 ml. of glacial acetic acid and 7.0 ml. of nitric acid (90%). A precipitate formed almost immediately; however, stirring was continued for a period of 15 min. The resulting precipitate was filtered and crystallized from methyl Cellosolve to yield 4.2 g. (67.0%) of golden needles melting at 213–214°.

Anal. Calcd. for $C_{19}H_{12}N_2O_3S$: S, 9.21. Found: S, 9.30.

A small sample of this material was hydrolyzed in a manner described for the hydrolysis of the 3-benzamido product to yield a compound which corresponds to the nitro-amine obtained from the nitration of 2-benzenesulfonamidodibenzothiophene[4] followed by hydrolysis, which melted at 246–247°.

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[1] E. Sawicki, *J. Org. Chem.*, **18**, 1492 (1953).

[2] H. Gilman and G. R. Wilder, THIS JOURNAL, **76**, 2906 (1954).

[3] H. Gilman, G. E. Brown, W. G. Bywater and W. H. Kirkpatrick, *ibid.*, **56**, 2473 (1934).

[4] E. Sawicki, *J. Org. Chem.*, **19**, 608 (1954).

[5] All melting points are uncorrected.

[6] H. Gilman and J. F. Nobis, THIS JOURNAL, **71**, 274 (1949).

[7] H. Gilman and J. F. Nobis, *ibid.*, **67**, 1479 (1945).

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