[Contribution from the Chemical Laboratory of Iowa State College]

RELATIVE REACTIVITIES OF ORGANOMETALLIC COMPOUNDS. XVIII. SELECTIVE METALATIONS OF DIBENZOTHIOPHENE

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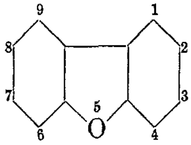
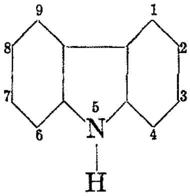
INTRODUCTION

Metalation of dibenzofuran (I) has invariably involved the 4 position, irrespective of the kind of metalating agent (metals, inorganic salts like mercuric acetate or organometallic compounds).[1]



I



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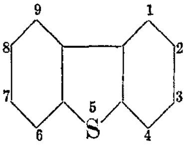

III

Metalation of carbazole (II) or 5-ethylcarbazole by means of organometallic compounds also involves the 4 position, but when mercuric acetate is used metalation takes place in the 2 position.[2]

When dibenzothiophene (III) is metalated by organoalkali compounds, metalation takes place in the 4 position[3] as might have been expected from the close similarity of dibenzothiophene and dibenzofuran. However, metalation of dibenzothiophene by phenylcalcium iodide involves the 3 position. This result was quite unexpected because organocalcium compounds are uncommonly like organoalkali compounds in chemical reac-

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[1] (*a*) Gilman and Young, *J. Am. Chem. Soc.*, **56**, 1415 (1934); **57**, 1121 (1935).

(*b*) Gilman and co-workers, *Rec. trav. chim.*, **55**, 79 (1936), for metalation of dibenzofuran by phenylcalcium iodide.

[2] (*a*) Gilman and Kirby, J. Org. Chem., **1**, 146 (1936).

(*b*) Miller and Bachman [*J. Am. Chem. Soc.*, **57**, 2447 (1935)] have shown that mercuration of fluorene in acetic acid takes place in the 4 position, and mercuration with no solvent involves both the 3 and the 4 positions.

[3] Gilman and Jacoby, J. Org. Chem., **3**, 108 (1938).

tivity.[4] It is significant that metalation of dibenzothiophene involves positions hitherto not accessible by direct nuclear substitutions.

Proof of structure of substituents in the 3 position.—Two indirect procedures were used to show that metalation by phenylcalcium iodide involved the 3 position. The first of these was by analogy with the established orientation of the related dibenzofuran. Prior to these studies, but one of the four possible dibenzothiophenecarboxylic acids was known: namely, that one having the carboxyl group in the 2 position. In the preceding paper it was shown that the acid obtained by carbonation of the dibenzothienyl alkali compound (prepared from dibenzothiophene by metalation with RLi or RK) has the carboxyl group in the 4 position. The acid obtained by phenylcalcium iodide metalation must have been either the 1 or the 3 derivative. The 1-acid was then prepared (by reactions strictly analogous with the preparation of the corresponding acid of dibenzofuran) and shown to be unlike the acid prepared *via* phenylcalcium iodide.

The second method for establishing the 3 position was by means of the related dioxide or sulfone of dibenzothiophene. Cullinane, Davies, and Davies[5] recently showed that nitration and bromination of dibenzothiophene-5-dioxide gave 3,7-dinitrodibenzothiophene-5-dioxide and 3,7-dibromodibenzothiophene-5-dioxide, respectively. No mononuclear substitution was reported. After several unsuccessful experiments, conditions were found for mononitration in satisfactory yields. The nitro compound must be the 3-nitrodibenzothiophene-5-dioxide, because further nitration gave the authentic and symmetrical 3,7-dinitrodibenzothiophene-5-dioxide. As illustrated in the following chart of transformations, the 3-nitrodibenzothiophene-5-dioxide was converted through the corresponding amine and diazonium compound to the 3-bromodibenzothiophene-5-dioxide. Unfortunately, this bromo-sulfone could not be reduced to the corresponding 3-bromodibenzothiophene because of the removal of nuclear bromine during reduction. If 3-bromodibenzothiophene had become available in this way, the 3-acid could readily have been prepared by means of the corresponding Grignard reagent.

The acid obtained from phenylcalcium iodide metalation must have the carboxyl group in either the 1 or the 3 position, and it was an easy matter to rule out the 1 position. This was done by showing that the authentic 3-bromodibenzothiophene-5-dioxide was unlike the bromodibenzothiophene-5-dioxide prepared by oxidation of the bromodibenzothiophene from which the supposed, but not previously established, 1-acid was prepared.

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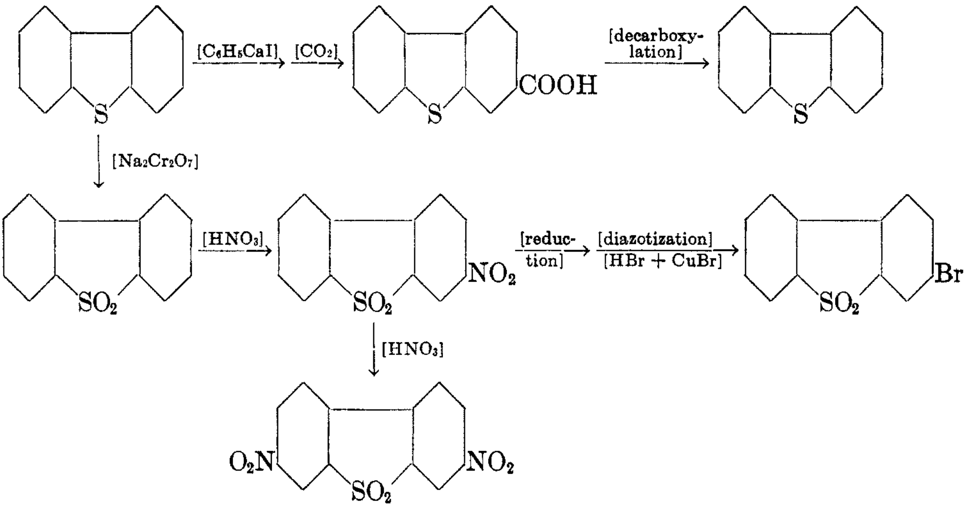
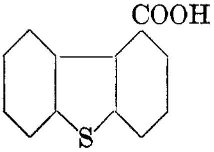
[4] GILMAN AND BAILIE, *ibid.*, **2**, 84 (1937).

[5] CULLINANE, DAVIES, AND DAVIES, *J. Chem. Soc.*, **1936**, 1437.



See preceding paper for syntheses of



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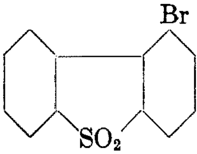

EXPERIMENTAL

Preparation of dibenzothiophene-3-carboxylic acid.—Phenylcalcium iodide was prepared in the customary manner,[1b] using 122.4 g. (0.6 mole) of iodobenzene, 48 g. (1.2 g. atom) of calcium turnings, and 300 cc. of ether. The mixture was allowed to settle overnight, and then the ether solution of phenylcalcium iodide was decanted into a 1-l. flask containing 27.6 g. (0.15 mole) of dibenzothiophene and 250 cc. of ether. The mixture was refluxed gently for 24 hours and then carbonated with solid carbon dioxide. The acid was isolated, by extracting first with dilute sodium hydroxide and then precipitating by hydrochloric acid, as a yellow heavy precipitate. Subsequent to digestion with boiling water, filtration gave 3 grams of brownish acid which when recrystallized from methanol yielded an almost colorless product. The dibenzothiophene-3-carboxylic acid appeared to decompose or decarboxylate at 300-305°, but had no sharp melting point.

Neutralization equivalent: calc'd, 228; found, 234. The low yields of acid obtained by carbonation subsequent to metalation are reminiscent of experiments on the metalation of related heterocycles by phenyl*calcium* iodide.[1b, 2a]

Decarboxylation. About 0.1-0.2 g. of the 3-acid was heated in 2-3 cc. of quinoline at 200° for one hour with an equal amount of copper powder. Evolution of gas was noticed as low as 120°. The mixture was then cooled and transferred to a small distilling flask where it was mixed with 50 cc. of water and 3 cc. of concentrated sulfuric acid. Distillation gave a yellowish, crystalline solid in the distillate. The solid, after sublimation, melted at 97–98° and was shown to be dibenzothiophene.

Methyl dibenzothiophene-3-carboxylate.—The methyl ester was prepared from the acid and diazomethane in ether solution. Recrystallization from a 1:2 mixture of methanol and ethanol gave colorless crystals melting at 129–130°.

Anal. Calc'd for $C_{14}H_{10}O_2S$: S, 13.2. Found: S, 13.1.

Preparation of dibenzothiophene-5-dioxide.[6]—To a cold mixture of 550 cc. of glacial acetic acid, 200 cc. of 50% sulfuric acid and 75 g. sodium dichromate was added 55.2 g. (0.3 mole) dibenzothiophene. The mixture was kept at 60° and shaken for one-half hour, after which the temperature started to drop. The reaction mixture was poured into cold water, and the yellowish heavy precipitate was filtered off. Crystallization from benzene gave a 90% yield of dioxide melting at 232°.

3-Nitrodibenzothiophene-5-dioxide.—To a mixture of 5.5 cc. of glacial acetic acid and 5.5 cc. of concentrated sulfuric acid in a 200-cc. three-necked flask equipped with stirrer, thermometer, and dropping funnel, was added 2.5 g. of dibenzothiophene-5-dioxide. A paste formed, and this was kept at a temperature of 4° while 8.85 g. of fuming nitric acid (sp. gr., 1.5) was added during a five-minute period. After stirring for one-half hour, the reaction mixture was poured into 100 cc. of cold water, and the precipitate filtered and washed with water. The melting point was 265–266° after two crystallizations from acetone and two from 1,4-dioxane. The yield was 82%.

Anal. Calc'd for $C_{12}H_7NO_4S$: N, 5.36. Found: N, 5.47.

3-Nitrodibenzothiophene-5-dioxide was nitrated at 80° by a mixture of equal parts of nitric acid (sp. gr., 1.5) and concentrated sulfuric acid to give 3,7-dinitrodibenzothiophene-5-dioxide which was shown to be identical with a specimen prepared in accordance with the directions of Cullinane and co-workers.[5]

3-Aminodibenzothiophene-5-dioxide.—A mixture of 18 g. of 3-nitrodibenzothiophene-5-dioxide, 45 g. of granulated tin, 225 cc. of concentrated hydrochloric acid, 600 cc. of water, and 200 cc. of ethanol was refluxed until the suspension became a clear solution. On cooling, white plate-like crystals of the hydrochloride separated. These were washed with hydrochloric acid, dried, and then treated with 10% sodium hydroxide to obtain the yellowish amine which after recrystallization from methanol melted at 259–260°. The yield was 33%.

Anal. Calc'd for $C_{12}H_9NO_2S$: N, 6.06. Found: N, 6.30.

3-Bromodibenzothiophene-5-dioxide. A solution of 7 g. of 3-aminodibenzothiophene-5-dioxide in 160 cc. of hot glacial acetic acid was cooled rapidly to room temperature and gradually stirred into a solution of nitrosyl sulfuric acid which had been prepared by adding with vigorous stirring 5 g. of finely powdered sodium nitrite to 35 cc. of concentrated sulfuric acid. The diazotization was conducted below 20°, and the diazo solution was poured gradually into a solution of 15 g. of cuprous bromide in 160 cc. of hydrobromic acid. The procedure was essentially that of Hodgson and Walker.[7]

The 3-bromo compound was isolated by customary procedures, and after recrystallization from ethanol melted at 224–225°. The yield was 95%.

Anal. Calc'd for $C_{12}H_7BrO_2S$: S, 10.8. Found: S, 10.7.

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[6] Private communication from Professor Ch. Courtot. See, also, STENHOUSE, *Ann.*, **156**, 332 (1870).

[7] HODGSON AND WALKER, *J. Chem. Soc.*, **1933**, 1620.

SUMMARY

Metalation of dibenzothiophene by organoalkali compounds takes place in the 4 position, as is the case with the related dibenzofuran. However, metalation by phenylcalcium iodide (which markedly resembles organoalkali compounds in other respects) occurs in the 3 position. Both positions are otherwise inaccessible by direct nuclear substitution reactions.