The solution was extracted twice with ether to remove unreacted oxime. Ammonium hydroxide was added until the solution was basic, and the solution was again extracted twice with ether. The ethereal extracts containing the free base were combined and dried over anhydrous sodium sulfate. Subsequent to filtration of the drying agent, the filtrate was saturated with dry hydrogen chloride. The precipitated amine hydrochloride was recrystallized twice from dilute hydrochloric acid to give 3.0 g. (69%), m.p. 223–223.5°.

Anal. Calcd. for $C_{15}H_{16}ClNO_2$: N, 5.06. Found: N, 5.12.

Acetylation of 3-Acetyl-4-hydroxydibenzofuran Oxime.—A suspension of 3.5 g. (0.0146 mole) of 3-acetyl-4-hydroxydibenzofuran oxime in acetic anhydride was refluxed until solution was effected. Upon cooling, there was obtained 3.6 g. (87%) of product, m.p. 165–171° dec. Recrystallization from acetic anhydride raised the melting point to 169–171.5° dec. The compound decomposed somewhat on exposure to light.

Anal. Calcd. for $C_{16}H_{13}NO_4$: N, 4.95. Found: N, 4.85.

3-Methylbenzofuro[3,2-g]-1,2-benzisoxazole.–The method employed for the preparation of this compound was essentially that used by Lindemann and Romanoff[13] for the preparation of 3-methylindoxazine.

Two and one-half grams (0.0089 mole) of 3-acetyl-4-hydroxydibenzofuran acetyloxime was heated at 200° for 15 minutes. Rapid decomposition of the compound took place, and vapors having the sharp odor of acetic acid were evolved. After the reaction mixture had cooled, concd. hydrochloric acid was added and the mixture was refluxed 1 hour. The mixture was filtered and the solid collected was dissolved in a minimum amount of hot ethanol. Decolorizing charcoal was added and the mixture filtered. Cooling yielded tan needles, recrystallization of which from petroleum ether (b.p. 60–68°) gave 0.62 g. (31%) of faintly pink needles, m.p. 172–174°.

Anal. Calcd. for $C_{14}H_9NO_2$: N, 6.28. Found: N, 6.38.

1-Bromo-2-acetoxydibenzofuran.[14]—Two drops of concd. sulfuric acid was added to a suspension of 9.2 g. (0.035 mole) of crude 1-bromo-2-hydroxydibenzofuran[1c] (m.p. 103–112°) in 15 ml. of acetic anhydride. The mixture was refluxed for 10 minutes, cooled to room temperature and diluted with water. The precipitated product, m.p. 133–135°, was recrystallized twice from ethanol to give 7.8 g. (73%) of ester, m.p. 135–136°.

Anal. Calcd. for $C_{14}H_9BrO_3$: Br, 26.3. Found: Br, 26.1, 26.2.

1-Methyl-2-methoxydibenzofuran.—To 4.7 g. (0.017 mole) of 1-bromo-2-methoxydibenzofuran[1c] in 75 ml. of dry benzene was added 0.0154 mole of *n*-butyllithium[15] in ether under an atmosphere of nitrogen. There was an immediate evolution of heat with the development of a slightly reddish color. After 15 minutes of vigorous stirring, 10 ml. of dimethyl sulfate was added dropwise as rapidly as the rate of reflux permitted. Following 2 hours stirring, the reaction mixture was allowed to stand overnight; then the white precipitate which had formed was filtered off. The filtrate was washed with 10% sodium hydroxide solution and then with water. After separation of the layers, the ether–benzene solution was dried over anhydrous sodium sulfate and then the solvents removed by distillation. The residual oil solidified on standing. Two recrystallizations from petroleum ether (b.p. 60–86°) gave 2.0 g. (56%) of product, m.p. 60–61°.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.2; H, 5.67. Found: C, 79.1; H, 5.73.

1-Methyl-2-hydroxydibenzofuran.—One and one-half grams (0.007 mole) of the above methyl ether was refluxed in a mixture of 10 ml. of 47% hydrobromic acid and 10 ml. of glacial acetic acid for 10 hours. The reaction mixture was diluted with water, and the product which initially came down as an oil, was filtered off upon solidification. Recrystallization from petroleum ether (b.p. 60–86°) gave 0.9 g. (65%) of needles, m.p. 135–136°.

Anal. Calcd. for $C_{13}H_{10}O_2$: C, 78.7; H, 5.05. Found: C, 78.5; H, 5.00.

1-Methyl-2-acetoxydibenzofuran.—Two drops of concd. sulfuric acid was added to a solution of 0.7 g. (0.0035 mole) of 1-methyl-2-hydroxydibenzofuran in 5 ml. of acetic anhydride. The solution was refluxed for 30 minutes and then was poured into a large volume of water. Two recrystallizations of the precipitate from petroleum ether (b.p. 60–86°) yielded 0.63 g. (75%) of crystals, m.p. 80–81°. In spite of the narrow melting point range this material was somewhat impure as indicated by the analysis.

Anal. Calcd. for $C_{15}H_{12}O_3$: C, 74.98; H, 5.03. Found: C, 75.6; H, 4.9.

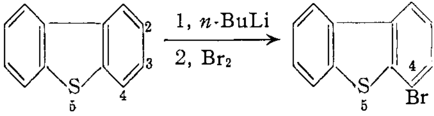
DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

Some Derivatives of Dibenzothiophene

BY HENRY GILMAN AND DONALD L. ESMAY

RECEIVED JULY 1, 1954

In connection with studies of some heterocycles, several derivatives of dibenzothiophene have been prepared and certain of their reactions studied. The preparation of 4-bromodibenzothiophene-5-dioxide was achieved readily by the oxidation of 4-bromodibenzothiophene with hydrogen peroxide in glacial acetic acid. 4-Bromodibenzothiophene[1] was prepared easily by treating 4-dibenzothienyllithium with bromine. Contrary to the bromination of the organolithium compound, no bromodibenzothiophene was isolated by a similar bromine treatment of the product obtained from the reaction of phenylcalcium iodide with dibenzothiophene. It has been established[1,6] that dibenzothiophene is metalated in the 3-position by phenylcalcium iodide and not in the 4-position as in the case of *n*-butyllithium.



Nitration of 2,8-dibromodibenzothiophene with warm, fuming nitric acid yielded a dinitro-2,8-dibromodibenzothiophene-5-oxide tentatively established as 2,8-dibromo-3,7-dinitrodibenzothiophene-5-oxide on the basis of general considerations of the nitration reactions of dibenzofuran, dibenzothiophene and their derivatives. Attempts to nitrate 2,8-dibromodibenzothiophene-5-dioxide by similar procedures were unsuccessful. The preparation of 2,8-dibromodibenzothiophene-5-dioxide was accomplished readily by the oxidation of 2,8-dibromodibenzothiophene with hydrogen peroxide in glacial acetic acid.

Experimental[2]

4-Bromodibenzothiophene.—To a stirred solution of 27.6 g. (0.15 mole) of dibenzothiophene in 250 ml. of ether was added 140 ml. of a 1.32 *M* ether solution of *n*-butyllithium[3]

---

(13) H. Lindemann and S. Romanoff, *J. prakt. Chem.*, **122**, 214 (1929).

(14) This experiment was carried out by F. A. Yeoman.

(15) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, THIS JOURNAL, **71**, 1499 (1949).

(1) This compound has been prepared in a different manner; H. Gilman and A. L. Jacoby, *J. Org. Chem.*, **3**, 108 (1938).

(2) All melting points are uncorrected.

(3) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, THIS JOURNAL, **71**, 1499 (1949). A similar procedure has been used successfully for the preparation of *n*-propyllithium in yields in excess of 80%. Some initial experiments on the metalation of dibenzothiophene have indicated that *n*-propyllithium reacts at a much faster rate than *n*-butyllithium and gives on carbona-

(0.184 mole). After stirring and refluxing for 20 hours Color Test II[4] was only weakly positive. The temperature of the solution was then maintained below 5° by means of an ice-bath while 24.0 g. (0.15 mole) of bromine was admitted by entrainment in a slow stream of nitrogen. Bromine vapor was plainly visible going into the reaction flask, but at no time was there evidence of bromine vapor above the reaction mixture. After addition of the bromine was completed (4.5 hours) the mixture was hydrolyzed by pouring into an equal volume of water. The ether and water layers were separated and the aqueous layer washed with ether. The combined ether layers were washed first with sodium bisulfite solution and then with water. Removal of the solvent from the dried ether layer left an oily residue which was crystallized from ethanol to yield 13.3 g. (33.6%) of crude 4-bromodibenzothiophene melting at 70–73°. Fractional crystallization from ethanol and diluted ethanol with simultaneous digestion with Norit-A gave 8.4 g. (21.3%) of pure product; m.p. 83–84°. The infrared spectrum showed absorption bands at 13.35 and 13.5 μ characteristic of 1,2,3- and 1,2-substitution of the benzene rings, respectively.

Anal. Calcd. for $C_{12}H_7BrS$: Br, 30.4. Found: Br, 29.9, 30.2.

3-Bromodibenzothiophene[5] (Attempted).—Phenylcalcium iodide was prepared in 74.4% yield by the reaction of calcium with iodobenzene in ether. In accordance with the previously published procedure[6] 0.373 mole of phenylcalcium iodide in 450 ml. of ether was run into a stirred solution of 27.6 g. (0.15 mole) of dibenzothiophene in 250 ml. of ether. The mixture was then refluxed for 17 hours, stirred at room temperature for 11 hours, and cooled in an ice-bath. Bromination and product work-up were carried out as described above. The only materials isolated were unreacted dibenzothiophene (56.5% recovery), a small amount of 2,8-dibromodibenzothiophene, and a liquid tentatively identified as either bromobenzene or iodobenzene.

2,8-Dibromodibenzothiophene-5-dioxide.—A stirred suspension of 27.4 g. (0.08 mole) of 2,8-dibromodibenzothiophene[1] in 350 ml. of glacial acetic acid was heated to just below reflux temperature without obtaining complete solution. To the hot suspension was added 40 ml. (0.32 mole) of 30% aqueous hydrogen peroxide. The mixture was then stirred and refluxed for 1.5 hours during which time the suspended material became very finely divided and much denser. An additional 20 ml. (0.16 mole) of peroxide was then added and stirring and refluxing were continued for 1.5 hours more. The mixture was cooled and the white product filtered off and dried. The slightly impure 2,8-dibromodibenzothiophene-5-dioxide[7] weighed 28.5 g. (95.3%) and melted at 357–360°. The product was digested one hour with boiling dioxane, then cooled slowly. Filtration yielded 26.5 g. (88.6%) of white, finely divided, pure dioxide, m.p. 360–361°. The infrared spectrum showed absorption bands at 8.59 and 12.5 μ characteristic of the sulfone group and 1,2,4-substitution of the benzene ring, respectively.

2,8-Dibromo-3,7-dinitrodibenzothiophene-5-oxide.—Eighty ml. of fuming nitric acid (90%) was added to 6.8 g (0.02 mole) of 2,8-dibromodibenzothiophene.[1] The resulting mixture was warmed slowly to 50° and heated at this temperature for one hour. After pouring upon crushed ice, filtration yielded 7.8 g. (86.7%) of product melting at 283–292°. Two recrystallizations from glacial acetic acid gave 5.0 g. (55.6%) of pure 2,8-dibromo-3,7-dinitrodibenzothiophene-5-oxide. The infrared spectrum showed absorptions at 9.7 and 11.5 μ, characteristic of the sulfoxide group and of a tetrasubstituted benzene ring, respectively. Bands indicating the presence of a sulfone group were absent.

Anal. Calcd. for $C_{12}H_4Br_2N_2O_5S$: Br, 35.7. Found: Br, 35.6, 35.6.

Nitration of 2,8-Dibromodibenzothiophene-5-dioxide (Attempted).—Essentially a quantitative recovery of starting material was obtained from an attempt to nitrate 2,8-dibromodibenzothiophene-5-dioxide with fuming nitric acid as in the above procedure. Use of a mixture of concentrated sulfuric acid and concentrated nitric acid as the nitrating agent yielded a very small amount of yellow material melting at 331–333° which gave a melting point depression when admixed with starting material. However, no pure compound was isolated or identified.

Acknowledgment.—The authors wish to express their thanks to Dr. V. A. Fassel and Mr. M. Margoshes, and the Ames Laboratory, for the infrared analyses.

DEPARTMENT OF CHEMISTRY
IOWA STATE COLLEGE
AMES, IOWA

---

tion higher yields of 4-dibenzothiophenecarboxylic acid. In addition, washing of the crude acid with water gives a much purer product from the *n*-propyllithium reaction due to the greater solubility of butyric acid over valeric acid.

(4) H. Gilman and J. Swiss, THIS JOURNAL, **62**, 1847 (1940).

(5) G. Illuminati, J. F. Nobis and H. Gilman, *ibid.*, **73**, 5887 (1951).

(6) H. Gilman, A. L. Jacoby and H. A. Pacevitz, *J. Org. Chem.*, **3**, 120 (1938). The reported preparation of 3-dibenzothiophenecarboxylic acid was satisfactorily checked prior to attempting the preparation of 3-bromodibenzothiophene.

(7) C. Courtot and C. Chaix, *Compt. rend.*, **192**, 1667 (1931).

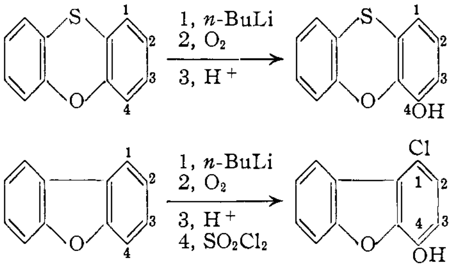
Hydroxy Derivatives of Dibenzofuran, Phenoxathiin and Thianthrene

BY HENRY GILMAN AND DONALD L. ESMAY

RECEIVED JULY 1, 1954

The excellent antiseptic properties of phenols[1] in general have long been known. In addition, halogenated phenols as a rule are more active as antiseptics than the unsubstituted phenols. Hexachlorophene, 2,2′-dihydroxy-3,5,6,3′,5′,6′-hexachlorodiphenylmethane, is an example of a halogenated phenol which has achieved considerable importance as a useful bactericide.[2]

As dibenzofuran, phenoxathiin and thianthrene have been shown to possess the power to kill various organisms,[3] it seemed of interest to prepare representative hydroxyl derivatives for bactericidal tests. This Note describes the preparation of 1-chloro- and 1,3-dichloro-4-hydroxydibenzofuran, 4-hydroxyphenoxathiin and 1-hydroxythianthrene. The results of tests for bactericidal activity will be reported elsewhere.



Experimental[4]

1-Chloro-4-hydroxydibenzofuran.—4-Hydroxydibenzofuran[5] was prepared in a 45% yield (57.5% based on unrecovered dibenzofuran) by metalation of dibenzofuran with *n*-butyllithium in diethyl ether followed by oxidation with molecular oxygen in the presence of *n*-butylmagnesium bromide. To a solution of 9.2 g. (0.05 mole) of 4-hydroxydibenzofuran and 0.1 g. of iodine in 200 ml. of chloroform

---

(1) For a comprehensive review of the relation between the structure and bactericidal action of phenols, see C. M. Suter, *Chem. Revs.*, **28**, 269 (1941).

(2) M. John, *J. Am. Pharm. Assoc. Pract. Pharm. Ed.*, **10**, 488 (1949).

(3) For example, see L. E. Smith and R. Melvin, *J. Econ. Entomol.*, **36**, 475 (1943), and J. P. Linduska, F. A. Morton and W. C. McDuffie, *ibid.*, **41**, 43 (1948).

(4) All melting points are uncorrected.

(5) H. Gilman, L. C. Cheney and H. B. Willis, THIS JOURNAL, **61**, 951 (1939).