for veratralrhodanine, in a yield of 98%. Yellow needles were obtained from a water–acetone mixture, m. p. 212–213°.

Anal. Calcd. for $C_8H_5ONS_3$: S, 42.31. Found: S, 42.27.

2-Phenyl-4-(3-thenal)-5-oxazolone (VIb).—This material was prepared, following the procedure described by Gillespie and Snyder[27] for the preparation of 2-phenyl-4-benzal-5-oxazolone, in a yield of 63.5%. Yellow needles were obtained on crystallization from benzene, m. p. 188–190°.

Anal. Calcd. for $C_{14}H_9O_2NS$: S, 12.56. Found: S, 12.62.

Acknowledgment.—The authors wish to thank Dr. George A. Harrington of the Socony Vacuum Oil Company for the generous gift of 3-methylthiophene used in this investigation.

Summary

A synthesis, based on the side-chain bromination of 3-methylthiophene with N-bromosuccinimide, has been described for a number of 3-substituted thiophenes.

New compounds which have been prepared in this investigation are 3-thenyl bromide, 3-thienylacetic acid, 3-acetothienone, *sym*-di-3-thienylethane, 3-thenalrhodanine, 2-phenyl-4-(3-thenal)-5-oxazolone, 3,3′-thenoin, and some esters of 3-thenoic acid.

Bloomington, Indiana Received August 21, 1947

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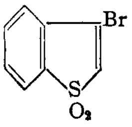
[27] Gillespie and Snyder, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 490.

[Contribution from the Chemical Laboratory of Northwestern University]

Studies in the Thianaphthene Series. I. Reactivity of the Bromine Atom in 3-Bromothianaphthene-1-dioxide

By F. G. Bordwell and C. J. Albisetti, Jr.[1]

Komppa[2] found that the bromine atom in 3-bromothianaphthene was inert to boiling alcoholic alkali and 30% aqueous alkali. In contrast, 3-bromothianaphthene-1-dioxide (I) liberates bromide ion rapidly when treated with hot alkaline solutions, and several reactions in which the bromine atom of I was replaced with other groups were found to occur readily. By oxidation of 3-bromothianaphthene[2] with 30% hydrogen peroxide in acetic acid–acetic anhydride solution I was obtained in good yields.



I

The reaction of I with piperidine in refluxing alcoholic solution was rapid, a 96% yield of 3-(1-piperidino)-thianaphthene-1-dioxide being obtained within thirty minutes. In a similar manner excellent yields of 3-butylaminothianaphthene-1-dioxide and 3-diethylaminothianaphthene-1-dioxide were obtained. When I was dissolved in liquid ammonia no reaction occurred at −38°, but heating the reaction mixture at 110° for one and one-half hours in a pressure vessel gave 3-aminothianaphthene-1-dioxide. Aqueous ammonia at 110° gave only highly colored non-crystalline material. Less basic amines including aniline, 2-aminopyridine and 2-aminopyrimidine did not react with I in refluxing alcoholic solution.[3] Refluxing I with 2-aminopyridine in phenol also failed to effect the desired replacement; instead a small quantity of 3-phenoxythianaphthene-1-dioxide was obtained.

The hydrolytic behavior of 3-diethylaminothianaphthene-1-dioxide was tested in a few experiments. In refluxing solution hydrolysis to 3-hydroxythianaphthene-1-dioxide occurred within ten minutes in the presence of 10% sulfuric acid. 3-Aminothianaphthene-1-dioxide was also hydrolyzed rapidly in acidic solutions. In neutral or basic solutions 3-diethylaminothianaphthene-1-dioxide was more stable to hydrolysis.

It seems probable that the bromine atom in I can be replaced by reaction with nucleophilic reagents other than aliphatic amines. Thus far, the reaction with only one other class of reagents has been investigated. By refluxing I in methanol solution in the presence of an equimolar quantity of potassium hydroxide an excellent yield of 3-methoxythianaphthene-1-dioxide was obtained. When phenol was included in the reaction mixture 3-phenoxythianaphthene-1-dioxide was isolated. Refluxing a methanol solution of I for thirty minutes with an equimolar portion of sodium cyanide also gave 3-methoxythianaphthene-1-dioxide.

To test quantitatively the activity of the bromine atom, I was refluxed in benzene solution with excess piperidine as described by Spitzer and Wheland[4] for the determination of the activity of the bromine atoms in *p*- and *o*-nitrobromobenzenes

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[1] Du Pont Fellow, 1946–1947. Present address: Du Pont Experimental Station, E. I. du Pont de Nemours and Company, Wilmington, Delaware. Abstracted from the Ph.D. dissertation of C. J. Albisetti, Jr.

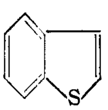
[2] Komppa, *J. prakt. Chem.*, **122**, 319 (1929).

[3] The bromine atom in I is less active than that in 3-bromoindone, since Schlossberg, *Ber.*, **33**, 2426 (1900), found that the latter reacts readily in alcoholic solution with aniline to give 3-anilinoindone.

[4] Spitzer and Wheland, This Journal, **62**, 2995 (1940).

and related compounds. The authors[4] report the reaction of *p*-nitrobromobenzene to be about 52% complete in eight hours, whereas with *o*-nitrobromobenzene the reaction was about 82% complete in one hour. With I, the reaction was found to be essentially complete under these conditions even when the reaction time was shortened to one-quarter hour.[5] It is impossible from these data to calculate a rate constant to compare with those given,[4] but the bromine atom in I must be at least four times as reactive as that in *o*-nitrobromobenzene. Since Todd and Shriner[6] found that an *o*-methylsulfonyl group is only about one-fifteenth as effective as an *o*-nitro group in activating an aryl halogen atom in a similar type of reaction, the bromine atom in I must be much more easily replaced than that in *o*-methylsulfonylbromobenzene.

For thianaphthene, resonance structures, II, III and IV, may be written, comparable to those for naphthalene. In view of the lower aromaticity of thianaphthene[7a] it is probable, however, that IV contributes less to the structure of the molecule than does II or III.[7b] For thianaphthene-1-dioxide no structure comparable to IV may be written, since the sulfur atom has no unshared electrons. Charge separation structures such as V and VI, may be written for thianaphthene and its 1-dioxide, but in structures for the latter the sulfur atom must again be given ten electrons. It seems likely, therefore, that the hetero ring in the dioxide has less aromatic character than that in thianaphthene. The chemical evidence indicates that the 2–3 bond in thianaphthene-1-dioxide is olefinic in type, since it will add bromine,[8a,b] ethyl alcohol[8b] and hydrogen[8b] under conditions similar to those used for α-β-unsaturated sulfones.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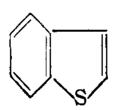
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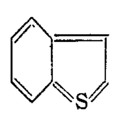
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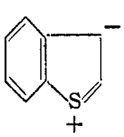
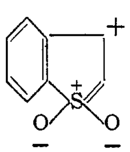
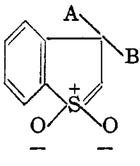
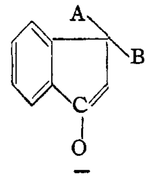

V


VI

The relative inertness of aryl halides in replacement reactions initiated by nucleophilic reagents has been ascribed[9] to the inability of the reagent to approach the carbon atom holding the halogen atom in such a way as to give a reasonable transition state, unless the Kekulé-type resonance is disrupted in the process. The activation of the halogen of aryl halides by substitution of *meta*-directing groups in *o*- and/or *p*-positions, is accounted for by increased resonance stabilization in the transition state. The fact that 2,4-dinitro-1-chloronaphthalene reacts about twenty times as rapidly with methoxide ion as does 2,4-dinitrochlorobenzene[10] is understandable since more structures can be written for the transition state in the naphthyl halide. The effective activation of the bromine atom in I and in 3-bromoindone has a similar explanation, since resonance structures of the type VII and VIII can be written for the transition state of a displacement reaction involving the attack of the anion, A⁻. The higher order of activity of the bromine atom in 3-bromoindone,[3] despite the greater electron attracting power of a sulfonyl group, can be accounted for by a smaller amount of resonance stabilization by structures such as VII due to the ten electrons around the sulfur atom.



VII



VIII

Acknowledgment.—The authors wish to thank Professor Ralph Pearson for helpful suggestions.

Experimental[11]

3-Bromothianaphthene-1-dioxide (I).—A mixture of 8.0 g. (0.037 mole) of 3-bromothianaphthene,[2,12] 50 ml. of acetic anhydride and 50 ml. each of acetic acid and hydrogen peroxide (30%) was brought carefully to reflux temperature. The initial ebullition was very vigorous. The mixture was refluxed for one hour, 200 ml. of water was added, and the solution thoroughly cooled. By filtration there was obtained 6.5 g. (70.6%) of 3-bromothianaphthene-1-dioxide, m. p. 180–182°. The compound crystallized as short white needles from alcohol; m. p. 183.5–184°.

Anal. Calcd. for $C_8H_5O_2SBr$: C, 39.20; H, 2.06. Found: C, 39.07; H, 1.85.

3-(1-Piperidino)-thianaphthene-1-dioxide.—A mixture of 1.2 g. (0.005 mole) of I, 25 ml. of 85% alcohol and 1.3 g. (0.015 mole) of piperidine was refluxed for thirty minutes and cooled. There separated 1.20 g. (96%) of a yellow crystalline solid, m. p. (dec.) 223–227°. After three crystallizations from alcohol the material decomposed at 246° with gas evolution.

Anal. Calcd. for $C_{13}H_{15}O_2NS$: C, 62.23; H, 6.07. Found: C, 62.04; H, 5.85.

A similar reaction of I with diethylamine gave a 67% yield of **3-diethylaminothianaphthene-1-dioxide**. Crystallization from alcohol and twice from ethyl acetate gave long yellow needles, m. p. 186.5–187°.

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(5) We wish to thank Mr. W. H. McKellin for carrying out this determination.

(6) Todd and Shriner, THIS JOURNAL, **56**, 1382 (1934).

(7) (a) Fieser and Kennelly, *ibid.*, **57**, 1611 (1935); (b) Schomaker and Pauling, *ibid.*, **61**, 1769 (1939), estimate that structures for thiophene in which the sulfur atom is given ten electrons are important, but less so than structures in which sulfur has eight electrons.

(8) (a) Lanfry, *Compt. rend.*, **154**, 519 (1912); (b) unpublished results of W. H. McKellin of this Laboratory.

(9) Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall, Inc., New York, 1941, p. 447.

(10) Talen, *Rec. trav. chim.*, **47**, 329 (1928).

(11) The microanalyses reported were by Mrs. Margaret Ledyard, Mrs. Nelda Mold and Miss Patricia Craig.

(12) We wish to thank the Texas Company, Beacon, New York, for a generous supply of thianaphthene.

Anal. Calcd. for $C_{12}H_{15}O_2NS$: C, 60.73; H, 6.37. Found: C, 60.58; H, 6.46.

The reaction of I with butylamine gave 83% of **3-butylaminothianaphthene-1-dioxide**, which was obtained as fine white needles, m. p. 145°, after crystallization from methanol–water and twice from ethyl acetate.

Anal. Calcd. for $C_{12}H_{15}O_2NS$: C, 60.73; H, 6.37. Found: C, 60.91; H, 6.47.

The kinetic experiments[5] were run essentially by the method described by Spitzer and Wheland,[4] except that silver bromide was determined gravimetrically. In one hour 99% of the bromine was liberated from I and in one-fourth hour 97% of the theoretical amount of silver bromide was obtained.

Attempted Preparation of 3-(2-Pyridylamino)-thianaphthene-1-dioxide.—After refluxing an alcoholic solution of I and 2-aminopyridine for eighteen hours I was recovered unchanged. No reaction occurred when an alcoholic solution of I and aniline was refluxed for thirty minutes or when an alcoholic solution of I and 2-aminopyrimidine was refluxed for eighteen hours.

Refluxing a solution of I and 2-aminopyridine in phenol for three hours gave a very small amount of 3-phenoxythianaphthene-1-dioxide (properties reported below).

3-Aminothianaphthene-1-dioxide.—A mixture of 3.7 g. (0.015 mole) of I and 25 ml. of liquid ammonia was heated at 110° for one and one-half hours in a glass liner in a pressure vessel. After evaporation of the ammonia the product was washed from the liner with absolute ethanol. There was obtained 1.5 g. (53%) of a yellow powder which melted at 200–205° with the evolution of gas. The gas evolved by heating a small amount of the material in a shallow tube turned litmus paper blue. Purified from absolute ethanol, the material melted at 211–213°.

Anal. Calcd. for $C_8H_7O_2NS$: C, 53.03; H, 3.90; N, 7.73. Found: C, 53.22: H, 4.13; N, 7.25.

Hydrolysis of 3-Diethylaminothianaphthene-1-dioxide.—A mixture of 0.1 g. of 3-diethylaminothianaphthene-1-dioxide and 10 ml. of 10% sulfuric acid was refluxed for ten minutes. On cooling there separated 0.05 g. of 3-hydroxythianaphthene-1-dioxide, m. p. 132–133°. The most recent reference to this compound[13] gives the melting point as 133.5–134°. From a similar experiment with 10% potassium hydroxide the starting material was recovered almost quantitatively.

3-Methoxythianaphthene-1-dioxide.—A solution of 2.45 g. (0.01 mole) of I and 0.56 g. (0.01) mole of potassium hydroxide in 30 ml. of dry methanol was refluxed one hour and cooled. By filtration there was obtained 1.5 g. (77%) of small white crystals, m. p. 208–210°. Several purifications from boiling ethanol gave large white flat blades, m. p. 220°.[14]

Anal. Calcd. for $C_9H_8O_3S$: C, 55.10; H, 4.11. Found: C, 55.11; H, 4.27.

An 84% yield of 3-methoxythianaphthene-1-dioxide was obtained in a somewhat less pure state by substituting sodium cyanide for potassium hydroxide in the above experiment.

3-Phenoxythianaphthene-1-dioxide.—A mixture of 2.45 g. (0.01 mole) of I, 1.0 g. (0.01 mole) of phenol and 0.56 g. (0.01 mole) of potassium hydroxide was dissolved in 20 ml. of absolute ethanol and the solution refluxed for one hour and cooled. The crude material melted at 110–124°. Several purifications from ethanol gave a small quantity of clear plates, m. p. 137°. The yield could undoubtedly be improved.

Anal. Calcd. for $C_{14}H_{10}O_3S$: C, 65.00; H, 3.87. Found: C, 64.80; H, 3.98.

Summary

1. Excellent yields of 3-alkylamino-, 3-amino- and 3-methoxythianaphthene-1-dioxides were readily obtained by the reaction of 3-bromothianaphthene-1-dioxide (I), respectively, with primary and secondary amines, anhydrous ammonia, and methanol in the presence of potassium hydroxide. Aryl amines did not react with I under comparable conditions.

2. The bromine atom in I was displaced at least four times as rapidly as that in *o*-nitrobromobenzene in the reaction with excess piperidine in benzene solution.

3. The reactivity of the bromine atom in I and related compounds is discussed on the basis of current theory.

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(13) Weston and Suter, THIS JOURNAL, **31**, 389 (1939).

(14) Arndt and Martius, *Ann.*, **499**, 282 (1932), report a m. p. of 215°.

EVANSTON, ILLINOIS RECEIVED OCTOBER 3, 1947

[CONTRIBUTION FROM THE VENABLE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

Preparation and Polymerization of *m*-Cyanostyrene

BY RICHARD H. WILEY AND NEWTON R. SMITH

Many substituted styrenes, including *p*-cyanostyrene[1,2] and *o*-cyanostyrene[2] have been described in a number of recent papers[3] but no mention has been made of *m*-cyanostyrene. We have prepared *m*-cyanostyrene by the decarboxylation of *m*-cyanocinnamic acid. Poly-*m*-cyanostyrene resembles poly-*p*-cyanostyrene in that both are insoluble in aromatic hydrocarbons and are soluble in nitromethane. The principle of vinylogy which by reference to polyacrylonitrile predicts the insolubility of poly-*p*-cyanostyrene does not apply to the meta isomer. The relative insolubility of each is undoubtedly caused by the polarity of the cyano group but it is not possible, with the meta isomer, to relate this effect vinylogously to the behavior of the polyacrylonitrile.

Experimental

***m*-Cyanobenzaldehyde.**—*m*-Tolunitrile (Eastman Kodak Co.) was converted to the aldehyde by the procedure used in "Organic Syntheses" for the preparation of *p*-

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(1) (a) Overberger and Allen, THIS JOURNAL, **68**, 722 (1947); (b) Marvel and Overberger, *ibid.*, **67**, 2250 (1945); (c) Mowry, Renoll and Huber, *ibid.*, **68**, 1105 (1946).

(2) Wingfoot Corp., British Patent 571,829; *C. A.*, **41**, 3323 (1947).

(3) (a) Marvel, *et al.*, THIS JOURNAL, **68**, 1088 (1947); (b) Emerson, *et al.*, *ibid.*, **69**, 1905 (1947); (c) Bachman, *et al.*, *ibid.*, **69**, 2022 (1947); (d) Strassburg, Gregg and Walling, *ibid.*, **69**, 2141 (1947); (e) Inskeep and Deanin, *ibid.*, **69**, 2237 (1947); (f) Frank, *et al.*, *ibid.*, **68**, 1365 (1946); (g) Renoll, *et al.*, *ibid.*, **68**, 1159 (1946).