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).

bromobenzaldehyde.[4] Eight to ten hours were required to complete the bromination of the nitrile. The dibromide was hydrolyzed with calcium carbonate. The aldehyde was separated by steam distillation and, after cooling, was collected on a filter. The yield of dried *m*-cyanobenzaldehyde was 45%, m. p. 76–77°.[5]

***m*-Cyanocinnamic Acid.**—The procedure of Walling and Wolfstirn[6] was followed. A solution of 48.0 g. (0.37 mole) of crude *m*-cyanobenzaldehyde and 42.5 g. (0.41 mole) of malonic acid (E.K. Co.) in 5 ml. of pyridine and 50 ml. of 95% alcohol was heated for ten hours on a steam-bath. The precipitate was collected and recrystallized from alcohol to give 45.3 g., 71.4% of the theoretical amount, of *m*-cyanocinnamic acid, m. p. 247° cor.

Anal. Calcd. for $C_{10}H_7NO_2$: eq. wt., 173.2; N, 8.08. Found: eq. wt., 174.5; N, 8.04, 8.09.

***m*-Cyanostyrene.**—*m*-Cyanocinnamic acid was decarboxylated by the method of Walling and Wolfstirn.[6] To 125 g. of boiling quinoline and 2 g. of copper powder in a 250-ml. Claisen flask was added 40 g. of *m*-cyanocinnamic acid in 10-g. portions. Twenty five ml. of distillate was collected after each addition. The distillate was taken up in ether, extracted with 3 *N* hydrochloric acid, and dried over anhydrous sodium sulfate. After removing ether from the dried solution, the residue was fractionated to give 16.2 g., 51% of the theorectical amount, of *m*-cyanostyrene, b. p. 81–5° (3.5 mm.). Refractionation of 22 g. of crude styrene gave 19.6 g. of purified *m*-cyanostyrene, b. p. 83° (3.5 mm.), n^{20}_D 1.5630.

Anal. Calcd. for C_9H_7N: N, 10.85. Found: N, 11.03, 11.05.

The dibromide was prepared by adding bromine to a solution of *m*-cyanostyrene in carbon tetrachloride. The crystals obtained on evaporation of the carbon tetrachloride were recrystallized from alcohol, m. p. 71–72°.

Anal. Calcd. for $C_9H_7NBr_2$: N, 4.96. Found: N, 5.01.

Polymerization of *m*-Cyanostyrene.—A solution of 0.002 g. (*ca.* 0.1% by weight) of benzoyl peroxide in 1.71 g. of purified monomer was prepared in a test-tube, stoppered, and heated with protection from the air for twenty-four hours at 80° to form a hard, brittle, transparent, slightly yellow solid. A control without benzoyl peroxide did not polymerize. The polymer softens at 100°, sticks at 135°, and turns into a thick gum at 190°. It is soluble in nitromethane and acetone and swells in hot toluene and benzene. Relative viscosity 1.270 for concentration of 0.400 g. in 100 ml. of nitromethane; 2.835 for 2.000 g. in 100 ml. of nitromethane.

Summary

m-Cyanostyrene has been prepared from *m*-cyanobenzaldehyde through *m*-cyanocinnamic acid and polymerized to a brittle, transparent polymer.

CHAPEL HILL, NORTH CAROLINA

RECEIVED DECEMBER 18, 1947

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[4] Coleman and Honeywell, "Organic Syntheses," John Wiley and Sons, Inc., New York, N. Y., Coll. Vol. II, 1943, p. 89.

[5] P. Reinglass, *Ber.*, **24**, 2421 (1891), gives m. p. 79–81°.

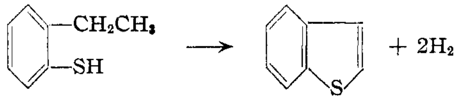
[6] C. Walling and K. B. Wolfstirn, THIS JOURNAL, **69**, 825 (1947).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, POMONA COLLEGE]

The Vapor Phase Catalytic Synthesis of Thianaphthenes

BY CORWIN HANSCH AND WILLIAM A. BLONDON

The synthesis of thianaphthenes from *o*-alkylbenzenethiols was undertaken in this Laboratory as a part of a general investigation of the vapor phase catalytic synthesis of hetrocyclic compounds. Preparation of thianaphthene itself was taken as the model reaction on which the catalysts and apparatus were developed. The following equation gives the over-all reaction.



The arylthiols used in this work were prepared from the corresponding hydrocarbons (ethylbenzene, *n*-propylbenzene, isopropylbenzene) by treating them with chlorosulfonic acid and reducing the resulting sulfonyl chloride with sulfuric acid and zinc dust. The pure sulfonylchlorides were not isolated, in fact the propylbenzenesulfonyl chlorides were found to be quite unstable to heat. Attempts to distill these compounds, even under reduced pressure, resulted in explosive decompositions.

The apparatus used in this work was similar to that described by Hoog, Verheus and Zuiderweg.[1]

Experimental

Catalyst Preparations. I. Chromium on Aluminum Oxide.—To a boiling solution of 36.4 g. of chromic anhydride in 400 ml. of distilled water, was added 200 g. of ALORCO alumina,[2] H-40 Grade R2200, 8–14 mesh. The solution was allowed to stand for two minutes and filtered, then the product was dried at 100°.

II. **Molybdenum Sulfide.**—One hundred grams of alumina was added to a boiling solution of 60 g. of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in 200 ml. of distilled water. The mixture was allowed to stand for a few minutes and then a rapid stream of hydrogen sulfide was passed into the catalyst for twenty minutes. The catalyst was filtered, washed repeatedly with water and dried at 100°.

III. **Platinum on Charcoal.**—To 75 ml. of distilled water was added 5 g. of chloroplatinic acid containing 40% platinum. The solution was heated to boiling and 12 g. of activated charcoal[3] was added. This mixture was boiled for five minutes and then the catalyst was filtered and dried at 100°.

Preparation of Ethylbenzenethiol.—To 2300 g. of chlorosulfonic acid, cooled to 0° in an efficient ice-bath, 652 g. of ethylbenzene was added, with stirring. The temperature of the mixture was held at 0° during the addition, after which the reaction mixture was stored in a refrigerator at 0° for eighteen hours. After this period of standing, the product was poured, with vigorous stirring, onto 6 liters of crushed ice. The lower oily layer was then separated and divided into three equal portions to facilitate reduction.

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[1] Hoog, Verheus and Zuiderweg, *Trans. Faraday Soc.*, **35**, 995 (1939).

[2] This type of alumina was used exclusively in this research.

[3] The activated charcoal used in this work was Type B15P, 6–8 mesh, obtained from the Pittsburgh Coke & Chemical Co.