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

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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°.

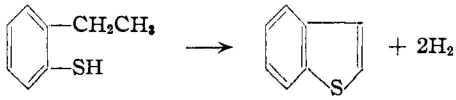
[6] C. Walling and K. B. Wolfstirn, THIS JOURNAL, **69**, 825 (1947).

[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.

Three 5-liter round-bottom flasks were fitted with efficient stirrers and surrounded with ice–salt mixtures. Into each flask was placed 4 liters of crushed ice and 1300 g. of concd. sulfuric acid. When the temperature of this mixture had reached 0°, the sulfonyl chloride was allowed to drop into the mixture, with rapid stirring. After the addition of the sulfonyl chloride, 650 g. of zinc dust was added to each flask in small portions so that the temperature never rose above 5°. When all of the zinc had been added, the flasks were fitted with reflux condensers and permitted to come to room temperature slowly. After the initial evolution of hydrogen had ceased, the reaction mixtures were boiled for six hours. The upper oily layer was then separated, washed and dried. Distillation gave 621 g. (68%) of *o*-ethylbenzenethiol, b. p. 207–209° (730 mm.).

***o*-Propylbenzenethiols.**—*o,n*-Propylbenzenethiol and *o*-isopropylbenzenethiol were synthesized by the above procedure, giving 76% yield of the former, b. p. 219–221° (730 mm.) and 70% yield of the latter, b. p. 225–227° (730 mm.).

	Calcd.		Found	
	C, %	H, %	C, %	H, %
Ethylbenzenethiol	69.50	7.25	69.50	7.59
n-Propylbenzenethiol	71.05	7.89	70.96	7.97
Isopropylbenzenethiol	71.05	7.89	71.03	7.89

α-(*o*-Carboxyphenylmercapto)-propionic Acid.—In 300 ml. of boiling water were dissolved 10 g. of anhydrous sodium carbonate and 20 g. of *o,o'*-dithiodibenzoic acid.[4] When all of the acid had dissolved, 30 g. of sodium hydrosulfite was added slowly, with stirring. The reactants were refluxed for fifteen minutes and then cooled to room temperature. To this cooled solution was added 49 g. of α-bromopropionic acid (previously neutralized with sodium bicarbonate) in 150 ml. of water. This mixture was boiled for fifteen minutes and then acidified to congo red paper while hot. On cooling, the α-(*o*-carboxyphenylmercapto)-propionic acid crystallized and was filtered and dried; yield 20 g. Recrystallization from 700 cc. of boiling water gave 15 g. of product, m. p. 192–194° (dec.).

2-Methylthianaphthene.—Ten grams of α-(*o*-carboxyphenylmercapto)-propionic acid, 5 g. of anhydrous sodium acetate and 25 ml. of acetic anhydride were placed in a round-bottom flask and slowly warmed to 75°, at which temperature the evolution of carbon dioxide began. After the gas evolution had subsided somewhat, the temperature was raised to 140° and held there for twenty minutes. Excess 50% sodium hydroxide was then added and the solution refluxed for one hour. It was then acidified with phosphoric acid and steam-distilled, giving a yellow oil: 2-methyl-3-thianaphthenol. Five grams of this oil was dissolved in 50 ml. of acetic acid, the resulting mixture being refluxed for two hours with 10 g. of zinc dust, then made basic with sodium hydroxide and steam-distilled. About 1 g. of a water-white oil distilled and solidified on cooling; m. p. 42–47°. Recrystallization from an alcohol–water mixture gave a product which melted at 51–52°.

Anal. Calcd. for C_9H_8S: C, 72.96; H, 5.41. Found: C, 72.73; H, 5.90.

2-Methylthianaphthene, formed by catalytic dehydrogenation of *o*-isopropylbenzenethiol, possessed the same melting point. A mixed melting point of the two substances showed no depression. Both preparations yielded picrates; m. p. 108–109°.

Anal. Calcd. for $C_{15}H_{11}N_3O_7S$: C, 47.75; H, 2.92. Found: C, 47.90; H, 3.28.

Catalytic Preparation of Thianaphthene.—The following is an example of a typical dehydrogenation run made in this research, using *o*-ethylbenzenethiol and chromium on alumina (I) catalyst. Ten milliliters of catalyst (I) was reduced *in situ* with a slow stream of hydrogen at a temperature of 400° for one hour, after which the catalytic tube was swept free of hydrogen with a stream of nitrogen. Then, 82 g. of *o*-ethylbenzenethiol was passed over the catalyst during a period of two hours. The temperature of the catalyst was held at 475 ± 3° during this reaction. The condensate (72 g.) was extracted with dilute sodium hydroxide, and by this means 4.5 g. of unchanged mercaptan was recovered. The alkali insoluble portion was distilled through a 1.5 ft. column using a variable take-off head with a reflux ratio of 5 to 1. Twenty-six grams boiled at 132–140° and was identified as mainly ethylbenzene. The 5 g. distilling at 140–210° was ethylbenzene with some thianaphthene. Twenty-two grams, which distilled between 210–230°, solidified on cooling; m. p. 22–24°. Crystallization from alcohol gave a product, m. p. 31–32°, the temperature at which thianaphthene melts.

Catalytic Preparation of 2-Methylthianaphthene.—2-Methylthianaphthene was prepared in the same manner, using 10 ml. of chromium oxide catalyst. Thirty grams of *o,n*-propylbenzenethiol was processed at 450° during a one-hour period, yielding 8 g. of oil insoluble in dilute sodium hydroxide. Fourteen grams of unchanged mercaptan was recovered. Distillation of the alkali insoluble fraction gave 3 g., b. p. 220–265°. This fraction was heated under reflux with 0.5 g. of sulfur for four hours to dehydrogenate any dihydromethylthianaphthene, then steam-distilled from an alkaline solution. The white solid collected was crystallized from alcohol; yield 1.6 g., m. p. 51–52°.

Attempted Catalytic Preparation of 3-Methylthianaphthene.—*o*-Isopropylbenzenethiol (65 g.), processed over 10 ml. of catalyst (I) at a temperature of 425° during a ninety-minute period, yielded 16 g. of isopropylbenzene and 7.5 g. of a substance which distilled at 235–250°. Fifteen grams of unchanged thiol was recovered. Considerable decomposition occurred on the catalyst. Attempts to purify the material boiling at 235–250°, by crystallization of its picrate, were unsuccessful. A sharp melting point could not be obtained with the picrate in spite of repeated crystallizations from various solvents. Attempts to crystallize the thianaphthene itself were also unsuccessful.

Discussion

It should be pointed out that although over fifty runs were made (mostly with *o*-ethylbenzenethiol) using various catalysts and conditions, the authors feel that by continued study the yield of thianaphthenes could be improved. It has been shown recently,[5] however, that thianaphthene may be made in good yield by the vapor phase catalytic reaction of styrene and hydrogen sulfide. Preliminary work in this Laboratory has shown that ethylbenzene and hydrogen sulfide may be catalytically converted into thianaphthene. At present, work is in progress to develop a general method of synthesis from alkylbenzenes and hydrogen sulfide.

The catalysts employed in this work which were at all effective were: chromium oxide on alumina (I), molybdenum sulfide on alumina (II), platinum on charcoal (III), and type J-2 dehydrogenation catalyst obtained from Universal Oil Products. Of the above catalysts, the platinum was the least effective because of rather rapid poisoning. The molybdenum sulfide, although effective in cyclization and resistant to poisoning, was not practical because of its great tendency to desulfurize the thiols to the corresponding hydro-

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[4] Allen and MacKay, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 580.

[5] Moore and Greensfelder, THIS JOURNAL, **69**, 2008 (1947).

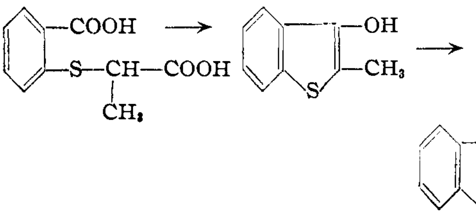
carbons. Apparently, hydrogen, formed during the dehydrogenation, reacted with the thiols to convert them to hydrocarbons and hydrogen sulfide. This side reaction occurred with all catalysts used but was most pronounced with molybdenum sulfide. The best catalyst found in this work was chromium oxide (I), although the J-2 catalyst from Universal Oil Products was almost as active.

Table I summarizes below the results of a series of comparable runs, and shows the effect of temperature and space velocity on the dehydrogenation of *o*-ethylbenzenethiol, using chromium on alumina catalyst (I).

TABLE I

Temp., °C.	Space vel., ml./ml. cat./hr.	% Conversion to thianaphthene
350	600	10
400	600	32
450	800	42
500	600	35
450	1500	28
450	900	40
450	800	42
450	200	42

In an attempt to extend the reaction to other alkylbenzene thiols, several runs were made using *o,n*-propylbenzenethiol. Conversions of 10–12% of 2-methylthianaphthene were obtained. Since its synthesis had not been reported previously, this compound was prepared by a known procedure[6] to check its identity.



The 2-methylthianaphthene prepared catalytically was identical with that made by the method illustrated.

The ultraviolet absorption spectrum determined for 2-methylthianaphthene followed closely that of thianaphthene (Fig. 1), with maxima at 288.5 and 297 mμ, and a minimum at 299 mμ. The absorption spectrum for thianaphthene was in close agreement with that previously reported,[7] with maxima at 288 and 297.5 mμ, and a minimum at 295 mμ. All of the absorption measurements were made with methanol solutions at dilutions of 1/100,000, by means of a Beckman quartz spectrophotometer.

An attempt to prepare 3-methylthianaphthene was not completely successful. A liquid was obtained which had the expected boiling point, but attempts to purify it by distillation or crystallization of the picrate were unsuccessful. It is interesting to note that this substance possessed an absorption spectrum (Fig. 1) closely resembling that of thianaphthene and 2-methylthianaphthene.

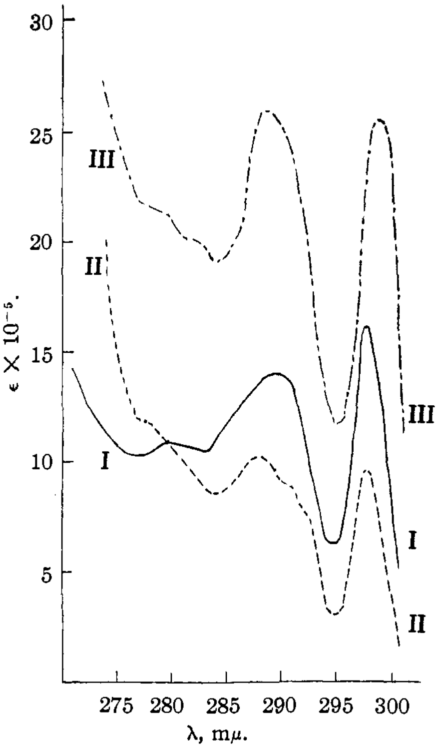
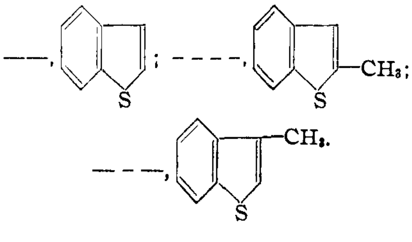


Fig. 1.—Ultraviolet absorption spectra of thianaphthene and 2-methylthianaphthene:



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Summary

1. The preparation of two new alkylbenzenethiols is described.

2. A study of the cyclodehydrogenation of the thiols to the corresponding thianaphthenes is discussed.

3. The ultraviolet absorption spectra are reported for the thianaphthenes.

4. A special synthesis for 2-methylthianaphthene is reported.

CLAREMONT, CALIF. RECEIVED NOVEMBER 12, 1947

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(6) Hansch and Lindwall, *J. Org. Chem.*, **10**, 381 (1945).

(7) Charlampowicz and Marchlewski, *C. A.*, **25**, 5097 (1931).