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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POMONA COLLEGE]

Catalytic Synthesis of Heterocycles. VIII.[1] Dehydrocyclization of *o*-Ethylbenzenethiols to Thianaphenes.[2]

CORWIN HANSCH, BENO SCHMIDHALTER, FRED REITER, AND WILLIAM SALTONSTALL

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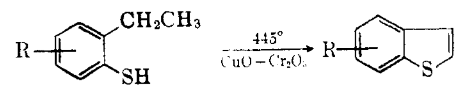
The synthesis and catalytic dehydrocyclization of the following compounds have been investigated: *o*-ethylbenzenethiol, 5-amino-2-ethylbenzenethiol, 3-amino-2-ethylbenzenethiol, 5-cyano-2-ethylbenzenethiol, and 5-carbomethoxy-2-ethylbenzenethiol.

The study of the dehydrogenation of a number of substituted *o*-ethylbenzenethiols according to the following equation was made to learn something of the scope of this reaction:

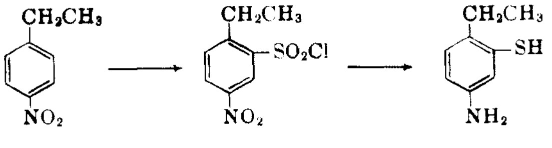


Of the substituent groups studied, —H, —NH_2, —$COOCH_3$, and —C≡N only compounds having the first two were converted to the corresponding thianaphthenes. Introduction of the —NH_2 group *para* to the ethyl group gave a substance which dehydrogenated more rapidly than 2-ethylbenzenethiol itself. Ethylbenzenethiol gave 68% thianaphthene while under the same conditions 5-amino-2-ethylbenzenethiol gave 80% 6-aminothianaphthene. This is a very convenient method for the preparation of 6-aminothianaphthene and the product from this procedure is easily obtained in pure form. It is interesting that when the amino group is shifted to a position *para* to the —SH group the yield of dehydrocyclization product drops. Dehydrocyclization of 4-amino-2-ethylbenzenethiol gave only 20% of 5-aminothianaphthene. The reason for the low yield is that hydrogenolysis of the —SH group was the primary reaction affording 50% conversion to hydrogen sulfide and *m*-ethylaniline. Only a few experiments were made in this dehydrogenation, and it is very likely that a thorough study of conditions would improve the yield. Thus the position of the amino group is very important in determining the course of the reaction.

Dehydrocyclization of 5-carbomethoxy-2-ethylbenzenethiol gave 39% thianaphthene together with 21% 5-carboxy-2-ethylbenzenethiol. It appears probable that in the formation of thianaphthene decarboxylation occurred prior to cyclization, since no 5-carboxythianaphthene was found among the products and 21% of the starting material remained undecarboxylated.

The dehydrogenation of 5-cyano-2-ethylbenzenethiol proceeded with the reduction of the cyano group to a methyl group giving a low yield of what appeared to be 6-methylthianaphthene and some thianaphthene.

Of the four molecules investigated only *o*-ethylbenzenethiol and 5-amino-2-ethylbenzenethiol dehydrocyclize smoothly enough to be interesting from the practical synthetic point of view. Actually dehydrogenation of the latter molecule offers an easy approach to 6-aminothianaphthene and therefore to almost any 6-substituted thianaphthene. The 5-amino-2-ethylbenzenethiol was prepared by the chlorosulfonation of *p*-nitroethylbenzene and then one-step reduction of the sulfonyl chloride to the aminothiophenol.



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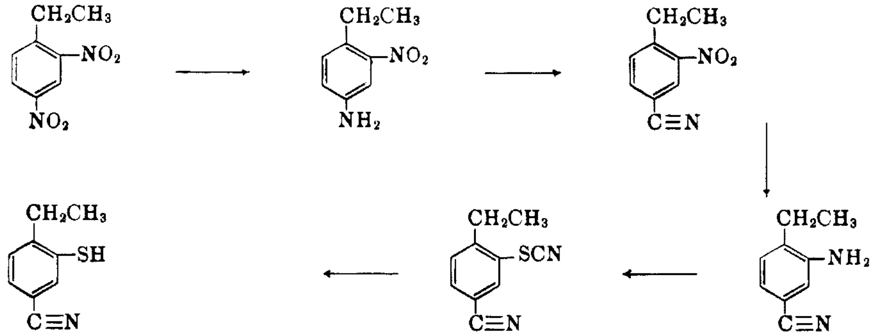
(1) For the previous paper in this series see *J. Am. Chem. Soc.*, **74**, 4554 (1952).

(2) This research was supported by the Office of Naval Research under contract N9onr 676(00).

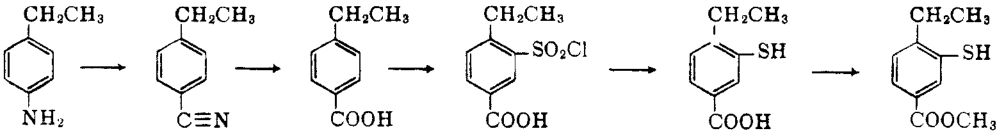
The preparation of 4-amino-2-ethylbenzenethiol is more difficult. This substance was prepared in 30% yield from 2-chloro-5-nitroethylbenzene[3] by refluxing it with sodium sulfide in water according to the procedure of Price and Stacey.[4] Attempts to improve this yield by treating 2-chloro-5-nitroethylbenzene with sodium disulfide to convert it to 4-nitro-2-ethylbenzenethiol and then to reduce this to the aminothiol did not give better results. Attempts to convert 2-amino-5-nitroethylbenzene to the thiol *via* the xanthate gave only traces of the desired product.

5-Cyano-2-ethylbenzenethiol was prepared from 2,4-dinitroethylbenzene. The dinitro compound was reduced with ammoniacal hydrogen sulfide to 4-amino-2-nitroethylbenzene which then was converted to 4-cyano-2-aminoethylbenzene. The amino group then was converted to the thiocyanate which in turn was hydrolyzed to 5-cyano-2-ethylbenzenethiol.



The yields in this group of reactions were good except for the last one. The conversion of the thiocyanate to the thiol offered considerable difficulty. Hydrolysis of the thiocyanate with alcoholic potassium hydroxide gave what appeared to be a good yield of crude 5-cyano-2-ethylbenzenethiol, however attempts to purify this product by vacuum distillation, even at pressures as low as 0.1 mm., caused much of it to resinify. Thus the yield of pure thiol obtained from 4-cyano-2-aminoethylbenzene was only 24%. Conversion of the amino group to the thiol by means of the xanthate intermediate was even less satisfactory.

5-Carbomethoxy-2-ethylbenzenethiol was prepared from *p*-ethylaniline by a convenient series of reactions all of which gave reasonable yields. *p*-Ethylaniline was converted to 5-carbomethoxy-2-ethylbenzenethiol as follows:



A number of efforts were made to prepare 2-ethyl-6-aminobenzenethiol from 2-amino-3-nitroethylbenzene, a by-product in the preparation of 2-amino-5-nitroethylbenzene. Efforts to convert the amino group *via* the xanthate or thiocyanate to the —SH group were unsuccessful. The latter compound could be obtained in good yield, but could not be hydrolyzed either with alcoholic KOH or sulfuric acid to the —SH compound. Steric hindrance apparently prevented hydrolysis. Attempts to break the C—S bond in the thiocyanate group by hydrogenolysis also met with failure. The product isolated appeared to be 2-amino-6-ethylbenzothiazole.

EXPERIMENTAL[5]

o-Ethylbenzenethiol. To a solution of 121 g. of *o*-ethylaniline in 194 g. of conc'd hydrochloric acid was added 200 g. of crushed ice. The resulting mixture was diazotized by adding 72 g. of sodium nitrite in 120 ml. of water. The temperature of the mixture was kept below 2° during this addition. A solution of 240 g. of potassium ethylxanthate in 300 ml. of water was heated to 40° and the diazonium solution was added dropwise to the xanthate with stirring. During this operation the temperature was maintained between 40 and 50°. After all of the diazonium salt was added the mixture was heated to 80° for a few minutes, cooled, and extracted with ether. The ether solution was washed with 10% sodium hydroxide and then with water. Evaporation of the ether gave an oil which was dissolved in 600 ml. of ethanol in which 200 g. of potassium hydroxide had been dissolved. After refluxing for 8 hrs. about half of the ethanol was evaporated and the residue was diluted with water and extracted with ether. The aqueous layer was acidified with dilute sulfuric acid and extracted with ether. The ether solution was dried over magnesium sulfate, evaporated, and the residue was distilled to give 76 g., b.p. 203–205°, (51.5%). This procedure gives a purer product than the previously reported method.[6]

5-Nitro-2-ethylbenzenesulfonyl chloride. Into a 3-necked flask equipped with a sealed stirrer, a thermometer, and a calcium chloride drying tube vented to a hood, was placed 100.6 g. of *p*-nitroethylbenzene[7] and 234 g. of chlorosulfonic acid. The mixture was gradually heated to 100° (at about

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(3) Hansch, *J. Org. Chem.*, **20**, 1026 (1955).

(4) Price and Stacey, *J. Am. Chem. Soc.*, **68**, 499 (1946).

(5) Microanalysis are by C. F. Geiger, Chaffey College, Ontario, Calif.

(6) Hansch and Blondon, *J. Am. Chem. Soc.*, **70**, 1561 (1948).

(7) Gift of the Monsanto Chemical Company.

80° hydrogen chloride commenced to be rapidly but smoothly evolved) and held there for four hours. The temperature then was raised to 130° for a few minutes and the reaction mixture was cooled to room temperature. This solution was poured with continuous stirring onto crushed ice (700 g.) in 700 ml. of water. The oil which separated soon solidified, after which it was filtered, pressed dry, and dried over P_2O_5 in a vacuum. The yield of crude product was 140 g. (84%). This material was not purified further, but was used in the next step.

5-Amino-2-ethylbenzenethiol. Into a 5-liter three-necked flask fitted with a stirrer and a reflux condenser was placed 240 g. of crude 5-nitro-2-ethylbenzenesulfonyl chloride and 2650 ml. of conc'd hydrochloric acid. Stirring was started and 760 g. of granulated tin was added in several portions. The reaction was allowed to run on its own heat for $^1/_2$ hr. and then the temperature was slowly raised to the boiling point and held there until all of the tin dissolved. This solution was cooled to room temperature, and the tin salts which separated were removed by filtration and dissolved in sodium hydroxide solution. Hydrogen sulfide was bubbled into this solution until tests showed precipitation of the tin to be complete. After removing the tin sulfide by filtration the filtrate was carefully acidified with acetic acid and extracted with ether several times. Evaporation of the ether and distillation of the residue gave 80 g. of material, b.p. 109–111°/2 mm., n^{25}_{D} 1.6180. This represented a yield of 44%; on smaller runs yields as high as 60% were obtained.

Anal. Calc'd for $C_8H_{11}NS$: C, 62.70; H, 7.24. Found: C, 62.63; H, 7.60.

5-Amino-2-ethylbenzenethiol bis-benzoate. 5-Amino-2-ethylbenzenethiol was converted to the bis-benzoate by the Schotten-Baumann procedure. After crystallization from ethanol the product melted at 137–138°.

Anal. Calc'd for $C_{22}H_{19}NO_2S$: C, 73.10; H, 5.18. Found: C, 73.49; H, 5.07.

2,4-Dinitroethylbenzene. To 530 g. of ethylbenzene at 60° was added with stirring a mixture of 850 ml. of fuming nitric acid and 1175 ml. of conc'd sulfuric acid. The temperature was held at 60° by regulating the rate of acid addition and by occasional cooling in a water-bath. The mixture then was heated on a water-bath at 60° for three hrs., after which it was poured onto ice and extracted with ether. After washing the ether solution with sodium bicarbonate and then with water it was dried over sodium sulfate and evaporated. The product then was distilled at 1 mm. through a 30″ spinning band column. The first fraction (b.p. 113–117°) was 90.4 g. which turned to a semi-solid mass. Crystallization from alcohol gave a product of m.p. 55–56° (2,6-dinitroethylbenzene). The second fraction contained 92.4 g., b.p. 117–124° which was mostly 2,4-dinitroethylbenzene. The third fraction contained 657 g., b.p. 124–127°, n^{25}_{D} 1.5655. Great care must be taken in distilling 2,4-dinitroethylbenzene. If it is too strongly heated it decomposes violently, therefore a good vacuum must be maintained or the mixture will become too hot. This procedure gave consistently better results than that previously reported.[8]

4-Amino-2-nitroethylbenzene. In a 2-liter three-necked flask fitted with a stirrer and a dropping-funnel was placed 235.2 g. of 2,4-dinitroethylbenzene and 700 ml. of ethanol. To this solution was added with stirring, the temperature being held at −10°, a solution of 136 g. of hydrogen sulfide in 700 ml. of conc'd ammonia. The addition required about three hours and a very efficient cooling bath was necessary as the reaction was exothermic. If the temperature was allowed to rise above 0° the yield was reduced considerably. After the addition the mixture was slowly allowed to come to room temperature and then let stand for 100 hours at room temperature. It was acidified with hydrochloric acid, heated on the steam-bath, filtered to remove the sulfur, cooled to room temperature, and 400 ml. of 12 *N* sulfuric acid was added. On cooling overnight in the ice box the amine sulfate separated. The sulfate was decomposed with potassium carbonate solution and the amine was extracted with ether. The ether was concentrated and diluted with ligroin and on cooling the pure amine separated, m.p. 42–43°. The yield was 80%. This procedure gave much better results than that reported by Schultz.[9]

4-Cyano-2-nitroethylbenzene. In a solution of 180 ml. of conc'd hydrochloric acid and 450 ml. of water was suspended 149 g. of 4-amino-2-nitroethylbenzene. The mixture was cooled in an ice-bath and diazotized with 101.2 g. of sodium nitrite in 300 ml. of water. The diazonium salt then was added to a solution of cuprous cyanide at 0° (prepared from 563 g. of $CuSO_4{\cdot}5H_2O$)[10] covered with 200 ml. of benzene to prevent frothing. After the addition the mixture was stirred for $^1/_2$ hr. at 0° and then was heated to 50° for 15 min. The product was extracted with ether, and the ether was washed with dilute sodium hydroxide, then with water, and finally was dried over sodium sulfate. The oil obtained from evaporation of the ether gave on distillation 84.7 g., b.p. 111–113°/0.25 mm., m.p. 57–58°.

Anal. Calc'd for $C_9H_8N_2O_2$: C, 61.36; H, 4.58. Found: C, 61.66; H, 4.19.

4-Cyano-2-aminoethylbenzene. In 750 ml. of ethanol 82.3 g. of 4-cyano-2-nitroethylbenzene was dissolved. To this was added 118 g. of granulated tin. Then with stirring and cooling so that the temperature did not rise above 30°, 500 ml. of conc'd hydrochloric acid was added dropwise. The temperature was raised to 50° and stirring was continued for one hour, after which the alcohol was removed by evaporation under reduced pressure and the remaining mixture was made strongly alkaline with potassium hydroxide. From this the amine was extracted with ether and on evaporation of the ether the solid amine was obtained. It could be crystallized from ether-ligroin. The yield was 57.4 g., m.p. 80–81°.

Anal. Calc'd for $C_9H_{10}N_2$: C, 73.94; H, 6.90. Found: C, 74.28; H, 7.02.

N-(1-Ethyl-4-cyano-2-phenyl)benzamide. The amine was treated with benzoyl chloride in pyridine and the resulting product was crystallized from ethanol to give material of m.p. 156–157°.

Anal. Calc'd for $C_{16}H_{14}N_2O$: C, 76.78; H, 5.64. Found: C, 77.06; H, 5.60.

5-Cyano-2-ethylbenzenethiol. In 175 ml. of 30% sulfuric acid 14.6 g. of 4-cyano-2-aminoethylbenzene was diazotized with 8.29 g. of sodium nitrite in 40 ml. of water. To this, a solution of 11.5 g. of KSCN in 40 ml. of water was added while the temperature was maintained at 0–5°. Then a paste of CuSCN made from 24.9 g. of $CuSO_4{\cdot}5H_2O$, 61.4 g. of $FeSO_4{\cdot}7H_2O$, and 11.5 g. of KSCN[11] was added and the mixture was stirred for one hour, then allowed to stand overnight, after which it was heated on a water bath for three hours with stirring. It then was cooled and filtered. The brown precipitate was extracted with ether. Extraction of the ether solution with sodium hydroxide solution and acidification of the alkaline extract gave 1.5 g. of 4-cyano-2-hydroxyethylbenzene. Evaporation of the ether gave 13.7 g. of red oil. The oil was placed in a solution of 8.6 g. of potassium hydroxide in 100 ml. of ethanol and 20 ml. of water. Sodium hydrosulfite (2 g.) was added, and the mixture was refluxed for 3 hours. The ethanol then was evaporated under reduced pressure and the residue was diluted with water and extracted with ether. Evaporation of the ether gave 3.5 g. of oil. The alkaline solution was acidified with acetic acid and extracted with ether, and the 10 g. of oil obtained from evaporation of the ether was distilled to give 3.9 g., b.p. 104–106°/0.5 mm., n^{25}_{D} 1.5895. The low yield was due to extensive resinification.

Anal. Calc'd for C_9H_9NS: C, 66.37; H, 5.56. Found: C, 66.10; H, 5.89.

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[8] Hansch and Helmkamp, *J. Am. Chem. Soc.*, **73**, 3080 (1951).

[9] Schultz, *Ber.*, **42**, 2633 (1909).

[10] Gilman and Blatt, *Org. Syntheses*, Coll. Vol. I, 2nd Ed., 46 (1941).

[11] Pfeiffer and Jager, *Ber.*, **75**, 1885 (1942).

Benzoate of 5-cyano-2-ethylbenzenethiol. The benzoate was prepared by the Schotten-Baumann procedure and the product was crystallized from ethanol (m.p. 78–79°).

Anal. Calc'd for $C_{16}H_{13}NOS$: C, 71.88; H, 4.90; N, 5.24. Found: C, 72.00; H, 5.06; N, 5.17.

5-Cyano-2-ethylphenol. This substance resulted as a by-product in the preparation of the corresponding mercaptan. It was a white solid, m.p. 95.5–96°, and could be crystallized from acetone-ligroin.

Anal. Calc'd for C_9H_9NO: C, 73.45; H, 6.16. Found: C, 73.88; H, 6.15.

2-Nitro-4-hydroxyethylbenzene. In a mixture of 150 ml. of conc'd sulfuric acid and 350 ml. of water 80.3 g. of 2-nitro-4-aminoethylbenzene was suspended and then was diazotized with 34.5 g. of sodium nitrite in 125 ml. of water. This diazonium salt solution then was added slowly to a boiling solution of 250 ml. of conc'd sulfuric acid and 250 ml. of water. After the addition was completed the mixture was boiled for 15 min., cooled, and then was extracted with ether. The ether solution was washed with water, and then was extracted with dilute sodium hydroxide solution which on acidification yielded the phenol. This was extracted with ether, and the ether solution was dried over sodium sulfate and distilled. The yield was 42.6 g., b.p. 123–125°/0.1 mm., n_D^{25} 1.5705.

Anal. Calc'd for $C_8H_9NO_3$: C, 57.47; H, 5.43. Found: C, 57.73; H, 5.53.

p-Nitrobenzoate of 2-nitro-4-hydroxyethylbenzene. The p-nitrobenzoate was prepared by the Schotten-Baumann procedure and after crystallization from ethanol melted at 124.5–125°.

Anal. Calc'd for $C_{15}H_{12}N_2O_6$: C, 56.96; H, 3.83. Found: C, 57.26; H, 4.08.

2-Amino-4-hydroxyethylbenzene. In 50 ml. of ethanol 37.6 g. of 2-nitro-4-hydroxyethylbenzene was dissolved. This was hydrogenated at room temperature and atmospheric pressure using palladium as the catalyst. Almost the theoretical amount of hydrogen was taken up in 3 hours, and the mixture then was filtered and distilled. The yield was 29.8 g., b.p. 132–135°/0.1 mm. The product crystallized on cooling and was recrystallized from ligroin giving a white solid, m.p. 130–131°.

Anal. Calc'd for $C_9H_{11}NO$: C, 70.04; H, 8.08. Found: C, 70.30; H, 8.21.

Bis-p-nitrobenzoate of 2-amino-4-hydroxyethylbenzene. This compound was prepared by refluxing equal parts of p-nitrobenzoyl chloride and 2-amino-4-hydroxyethylbenzene for one hour in pyridine. Crystallization from ethanol gave a product of m.p. 232–233°.

Anal. Calc'd for $C_{22}H_{17}N_3O_7$: C, 60.69; H, 3.94. Found: C, 60.91; H, 3.94.

4-Carboxy-2-ethylbenzenesulfonyl chloride. In 330 g. of chlorosulfonic acid 94.8 g. of 4-ethylbenzoic[12] acid was dissolved and the solution was heated to 100° for 30 min. The temperature then was momentarily raised to 135° after which it was cooled to room temperature and poured over crushed ice. The solid product was filtered and dried. The yield was 108.4 g., m.p. 178–181°. After recrystallization from benzene the substance melted at 184–184.5°.

Anal. Calc'd for $C_9H_9ClO_4S$: C, 43.47; H, 3.65. Found: C, 43.55; H, 3.69.

5-Carboxy-2-ethylbenzenethiol. The crude sulfonyl chloride from the above preparation (88.7 g.) was dissolved in 900 ml. of acetic acid and 715 ml. of water in a three-necked flask equipped with a stirrer and a condenser. After cooling the mixture to 0° stirring was started and 270 g. of zinc dust was added. During this operation the temperature was held at 0° by means of an efficient ice-bath. Next, 180 ml. of conc'd sulfuric acid was added in small portions at such a rate that the temperature did not rise above 0°. The mixture then was slowly heated to 100° and held there for 2 hours after which it was filtered while hot and the filter cake was washed with 500 ml. of 50% acetic acid. The filtrate was diluted with water and cooled overnight in the ice-box. The 36.7 g. of product which separated melted at 158–160°. Recrystallization from ethanol raised the melting point to 159–160°.

Anal. Calc'd for $C_9H_{10}O_2S$: C, 59.32; H, 5.53. Found: C, 59.78; H, 5.89.

5-Carbomethoxy-2-ethylbenzenethiol. In 290 ml. of methanol and 16 ml. of conc'd sulfuric acid 42 g. of 5-carboxy-2-ethylbenzenethiol was dissolved. The solution was refluxed for 6 hrs., and then most of the methanol was removed by heating on the steam-bath. The remaining solution was diluted with water, neutralized with bicarbonate, and extracted several times with ether. The combined ether extracts were dried over magnesium sulfate and then were distilled to give 41.6 g., b.p. 121–122°/0.5 mm., n_D^{25} 1.5688.

Anal. Calc'd for $C_{10}H_{12}O_2S$: C, 61.19; H, 6.17. Found: C, 61.31; H, 6.33.

3-Methylthio-4-ethylbenzoic acid. One gram of 5-carboxy-2-ethylbenzenethiol was dissolved in 10 ml. of 10% sodium hydroxide. To this was added 1 ml. of dimethyl sulfate. After a few minutes shaking the solution became clear and it was allowed to stand a few hours, then was extracted with ether. The aqueous layer was acidified and the precipitate was filtered and dried. After several crystallizations from ethanol-water the melting point of the product was 133–134°.

Anal. Calc'd for $C_{10}H_{12}O_2S$: C, 61.19; H, 6.17. Found: C, 61.31; H, 6.33.

4-Amino-2-ethylbenzenethiol. In a solution of 122 g. of $Na_2S \cdot 9H_2O$ in 260 ml. of water was placed 33 g. of 2-chloro-5-nitroethylbenzene.[3] The mixture was refluxed with stirring for 17 hours, then was cooled and extracted with ether. The aqueous phase then was carefully acidified with acetic acid and extracted with ether. This ether extract was evaporated and the residue was distilled giving 10 g. of product, b.p. 108–110°/0.5 mm., n_D^{25} 1.6180.

Anal. Calc'd for $C_8H_{11}NS$: C, 62.70; H, 7.24. Found: C, 63.09; H, 7.34.

Bis-benzoate of 4-amino-2-ethylbenzenethiol. Treatment of the aminothiophenol under Schotten-Baumann conditions yielded a white solid which after two crystallizations from ethanol melted at 156–157°.

Anal. Calc'd for $C_{22}H_{19}NO_2S$: C, 73.10; H, 5.30. Found: C, 73.18; H, 5.59.

Bis-4-amino-2-ethylphenyldisulfide. 4-Amino-2-ethylbenzenethiol on standing turned into a solid substance which after crystallization from benzene-ligroin melted at 78–79°. Analysis indicated that this substance was the disulfide.

Anal. Calc'd for $C_{16}H_{20}N_2S_2$: C, 63.13; H, 6.62. Found: C, 63.66; H, 6.65.

4-Nitro-2-ethylphenylthiocyanate. In 12 ml. of 30% sulfuric acid 2 g. of 4-nitro-2-aminoethylbenzene was diazotized with 0.9 g. of sodium nitrite. This solution was cooled to −5° and 1.6 g. of KSCN in 5 ml. of ice water was added whereupon the solution turned dark red, but the temperature did not rise above −5°. To the red solution was added CuSCN prepared from 3.5 g. of $CuSO_4 \cdot 5H_2O$.[11] Vigorous bubbling occurred with the separation of a dark tar. The reaction mixture was allowed to stand for 3 hours, then was heated to 70°, cooled, and extracted with ether. Evaporation of the ether gave 2.07 g. of a light red oil which solidified. Recrystallization from ethanol gave about 1 g. of material of m.p. 62–65°. Recrystallization from benzene-ligroin gave 0.5 g. product, m.p. 65.5–67°.

Anal. Calc'd for $C_9H_8N_2O_2S$: C, 51.91; H, 3.87. Found: C, 52.33; H, 3.90.

4-Nitro-2-ethylbenzenethiol. This substance could be obtained from the hydrolysis of 4-nitro-2-ethylphenylthiocyanate or better by treating 4-nitro-2-chloroethylbenzene with sodium disulfide. 4-Nitro-2-chloroethylbenzene (10 g.) was dissolved in 15 ml. of ethanol and the solution was heated to 80°. To this was added in several portions over a

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(12) Birch, Dean, Fidler, and Lowry, *J. Am. Chem. Soc.*, **71**, 1362 (1949).

period of one hour a solution of 9 g. of $Na_2S \cdot 9H_2O$ and 1.25 g. of sulfur in 7 ml. of water and 15 ml. of ethanol. This mixture was allowed to stand at 80° for $1^{1}/_{2}$ hours, and 2.9 g. of potassium hydroxide in 15 ml. of alcohol then was introduced. After heating an additional $^{1}/_{2}$ hour at 80° the mixture was poured into 250 ml. of water, acidified, and cooled in the ice box. The product was filtered, redissolved in dilute sodium hydroxide, filtered, and reprecipitated with acid. The yield was 3.5 g. After recrystallization from ligroin the m.p. was 46–47°. About an equal amount of additional product could be obtained by treating the alkali-insoluble material with more sodium disulfide and alkali. The product could be reduced with stannous chloride to the aminothiophenol.

Anal. Calc'd for $C_8H_9NO_2S$: C, 52.48; H, 4.95. Found: C, 52.48; H, 4.91.

Bis-4-nitro-2-ethylphenyldisulfide. On standing in air the 4-nitro-2-ethylbenzenethiol slowly oxidized to a substance which after crystallization from ethanol melted at 148–149°.

Anal. Calc'd for $C_{16}H_{16}N_2O_4S_2$: C, 52.73; H, 4.43. Found: C, 53.02; H, 4.29.

6-Nitro-2-ethylphenylthiocyanate. In a solution of 24 g. of sulfuric acid and 45 ml. of water 10 g. of 2-amino-3-nitroethylbenzene was suspended. After cooling, diazotization was accomplished with 4.3 g. of sodium nitrite in 15 ml. of water. To the cold solution (−5°) was added 7.6 g. of KSCN in 15 ml. of cold water. Then CuSCN made from 14.6 g. of $CuSO_4 \cdot 5H_2O$[11] was stirred into the solution. After standing overnight the mixture was heated to 60° for a few minutes, cooled and extracted with ether. Evaporation of the ether and distillation of the residue gave 7.5 g. of orange oil, b.p. 135–140°/0.25 mm. Attempts to hydrolyze or hydrogenolyze this to the corresponding thiophenol were unsuccessful.

Anal. Calc'd for $C_9H_8N_2O_2S$: C, 51.91; H, 3.87. Found: C, 52.14; H, 4.21.

2-Amino-6-ethylbenzothiazole. Tin (10 g.) was mixed with 2.25 g. of 6-nitro-2-ethylphenylthiocyanate and to this was added in portions 40 ml. of HCl with shaking. The mixture became very hot, but it was necessary to heat it on the water-bath to finally dissolve almost all of the tin. The solution then was decanted from the remaining bit of tin, cooled, and filtered to give 3 g. of tin salt. This product was decomposed with sodium bicarbonate solution and the aminobenzothiazole was taken up in ether. Evaporation of the ether gave 1.2 g. of product m.p. 174–175°. Recrystallization from benzene raised the melting point to 176–176.5°. Attempts to hydrolyze this substance to the thiophenol with concentrated KOH were unsuccessful.

Anal. Calc'd for $C_9H_{10}N_2S$: C, 60.64; H, 5.66. Found: C, 60.66; H, 5.77.

Dehydrocyclization technic. In each dehydrogenation 10 ml. of fresh catalyst[13] was used. All of the catalyst used in this work was prepared in one batch and the apparatus used was that previously described.[14] The gas evolved from the reaction was passed through two wash bottles of lead acetate, through a wet-test meter, and then was analyzed in a Fisher gas analyzer.

Dehydrocyclization of o-ethylbenzenethiol. The thiol (20 g.) was processed over the Cr_2O_3-CuO-charcoal catalyst at 445° at a uniform rate in the course of 42 minutes. During the reaction 4070 ml. of gas was evolved. Analysis showed it to be 96% hydrogen and 4% saturated hydrocarbons. The lead sulfide precipitate in the two wash bottles was filtered, dried, and weighed. This corresponded to 1.32 g. of sulfur. The liquid condensate from the reaction was dissolved in ether and washed with 10% KOH to remove unreacted benzenethiol. Acidification of the alkaline extract gave, upon extraction with ether, 0.72 g. (3.6%) *o*-ethylbenzenethiol. The ether solution from the alkaline extraction was evaporated and the residue was dissolved in 50 ml. of alcohol. One ml. of this solution was treated with 15 ml. of saturated ethanolic picric acid solution and on cooling 520 mg. of thianaphthene picrate separated. Diluting the filtrate with water caused 192 mg. more of picrate to separate. Both fractions melted sharply at 148–149° and corresponded to a 67.8% yield of thianaphthene. Assuming that the hydrogen sulfide was formed from the hydrogenolysis of ethylbenzenethiol to ethylbenzene this represents a yield of 26.7% ethylbenzene. Addition of the recovered thiol plus the thianaphthene plus the ethylbenzene gave a material balance of 98%. The yield of thianaphthene obtained above is better than that previously reported[6] because of the more precise method of yield determination. In the earlier work yield was determined by distillation and the loss by hold back in the column was considerable. Also the yield is better on small runs. The catalyst gradually loses activity with use.

Dehydrocyclization of 5-amino-2-ethylbenzenethiol. The aminothiol (29.6 g.) was processed over the catalyst during a period of 47.5 minutes at 445°. During the reaction 7630 ml. of gas was evolved and two gas analyses, one after 12 minutes and one after 42 minutes, each showed the composition of the gas to be 95% hydrogen and 5% saturated hydrocarbons. Lead sulfide (6.9 g.) equivalent to 15.2% ethylaniline was obtained. The semi-solid condensate was dissolved in ether and extracted with sodium hydroxide solution. Acidification of the alkaline solution and extraction with ether gave 0.42 g. of aminothiophenol (1.4%). Evaporation of the alkali extracted ether and crystallization of the product from ether-petroleum ether gave 22.5 g. (78%) of product, m.p. 114–115°. A similar run gave a yield of 81%.

Dehydrocyclization of 3-amino-2-ethylbenzenethiol. In this reaction 18.6 g. of the thiol was passed over the catalyst at a uniform rate in 40 min. at 445°. During the reaction 1595 ml. of gas was evolved which consisted of 95.5% hydrogen and 4.5% saturated hydrocarbons. The weight of lead sulfide was equivalent to 0.0655 mole of sulfur. The condensate was diluted with ether and washed with dilute sodium hydroxide. Evaporation of the ether gave 13.7 g. of a red oil. This oil was chromatographed over 400 g. of alumina. The column was eluted with 200-ml. portions of solvent starting with 30–60° petroleum ether. The first two fractions yielded, on evaporation of the solvent, 8.9 g. of liquid which appeared to be mostly *m*-ethylaniline. The next 10 fractions of petroleum ether gave 3.7 g. of semi-solid material which after recrystallization from ether-ligroin weighed 3.5 g. (19.4%) and melted at 71.2°. Conversion of this product to the acetate with acetic anhydride gave an acetyl derivative of m.p. 103°. The melting point of 5-aminothianaphthene has been reported as 72° and its acetyl derivative as 106°.[15]

N-(5-Thianaphthyl)-p-nitrobenzamide. A small amount of the amine was refluxed in pyridine with an equivalent amount of *p*-nitrobenzoyl chloride for one hour. Crystallization of the product from ethanol gave a substance m.p. 226–227°.

Anal. Calc'd for $C_{15}H_{10}N_2O_3S$: C, 60.39; H, 3.38. Found: C, 60.38; H, 3.48.

Dehydrocyclization of 5-cyano-2-ethylbenzenethiol. At a temperature of 445° 16.5 g. of pure 5-cyano-2-ethylbenzenethiol was processed over the catalyst during a period of 25 min. The condensate was distilled giving 5.38 g. of material b.p. 200–220°. This was dissolved in 50 ml. of a saturated alcoholic picric acid solution and on cooling 1.33 g. of picrate separated, m.p. 108–110°. The picrate was decomposed with KOH solution and the oil was extracted with ether. Evaporation of the ether and sublimation of the residue gave a white solid of m.p. 37–38° which appeared to be 6-methylthianaphthene. Tarbell and Fukushima[16] report this compound to melt at 42° and its picrate to melt at 114°.

Anal. Calc'd for C_9H_8S: C, 72.93; H, 5.44. Found: C, 72.90; H, 5.61.

Dehydrocyclization of 5-carbomethyoxy-2-ethylbenzenethiol.

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(13) Catalyst No. 2, in Hansch, Crosby, Sadoski, Leo, and Percival, *J. Am. Chem. Soc.*, **73**, 704 (1951).

(14) Hansch, *Chem. Revs.*, **53**, 391 (1953).

(15) Fries, Heering, Hemmecke, and Siebert, *Ann.*, **527**, 83 (1936).

(16) Tarbell and Fukushima, *J. Am. Chem. Soc.*, **68**, 1456 (1946).

The thiol (25 g.) was passed over the catalyst at 445° during a period of 45 minutes. During the reaction 4839 ml. of gas was evolved. Analysis showed that 23.3% of this was soluble in KOH solution and probably consisted of CO_2 and COS. Only 34.3% was hydrogen and 42.5% was hydrocarbon. Lead sulfide equivalent to 0.00134 mol. of sulfur was obtained. The condensate was dissolved in ether and washed with dilute sodium hydroxide. Evaporation of the ether gave 15.4 g. of a red oil. Acidification of the sodium hydroxide solution precipitated 4.9 g. of solid, m.p. 155–157° which proved to be 3-mercapto-4-ethylbenzoic acid. Chromatography of a small sample of the ether-soluble material indicated that it consisted of mostly thianaphthene and ethylbenzene. A sample then was analyzed with picric acid for the thianaphthene content which was found to be 39%. No trace could be found of 6-carboxythianaphthene or 6-carbomethoxythianaphthene.

CLAREMONT, CALIFORNIA.