

formamide, 18.4 g. (0.1 mole) of 1,2-dodecylene oxide,<sup>10</sup> 11.9 g. (0.1 mole) of phenyl isocyanate, and 0.2 g. of tetraethylammonium bromide. The reaction mixture was heated for 4 hr. at 160°. The solvent was removed by distillation at 10-mm. pressure, and the reaction products cooled. The product was recrystallized from 250 ml. of petroleum ether (b.p. 30–60°). The product (7.2 g., 25% yield) melted at 68.5–68.7°. A mixed melting point with authentic 3-phenyl-5-*n*-decyl-2-oxazolidone (preparation described below) showed no depression.

*3-Phenyl-5-n-decyl-2-oxazolidone (method of Homeyer<sup>9</sup>).* Aniline (56 g.) and 57 g. of 1,2-dodecylene oxide were heated for 2 hr. at 185° in a flask equipped as in the experiment described above. After removing the unreacted starting materials by distillation at 20-mm. pressure the alkanolamine was allowed to solidify (64 g.). Then, 30 g. of diethyl carbonate, 0.2 g. of sodium, and 100 ml. of xylene were added, and a

(10) Becco Chemicals Division (Food Machinery & Chemicals Corp.), Station B, Buffalo 7, N. Y.

column packed with 2 × 20 cm. of stainless steel protruded packing was attached to the reaction flask. The mixture was heated and distillation continued until 20 ml. of ethanol was collected. The solid that separated on cooling the flask contents was recrystallized from petroleum ether. This sample of 3-phenyl-5-*n*-decyl-2-oxazolidone melted 68.5–69.7°.

*Resin from Epon 828<sup>11</sup> and toluene diisocyanate.* To a 3-necked 300-ml. round-bottom flask equipped with a stirrer, nitrogen inlet tube, thermometer, condenser, and drying tube was added 20 g. of Epon 828, 17.4 g. of 2,4-toluene-diisocyanate, and 0.4 g. of tetramethylammonium iodide. The reaction mixture was heated for 4 hr. at 165°. A yellow resin (37 g.) was obtained which showed no tendency to melt up to 300°.

AUSTIN, TEXAS

(11) Shell Chemical Corp., 50 W. 50 St., New York 20, N. Y. [A polyepoxide from 2,2-bis(4-hydroxyphenyl)propane and epichlorohydrin.]

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POMONA COLLEGE]

## Catalytic Synthesis of Heterocycles.<sup>1</sup> X. Dehydrocyclization of 4-Ethyl-3-pyridinethiol to 6-Azathianaphthene

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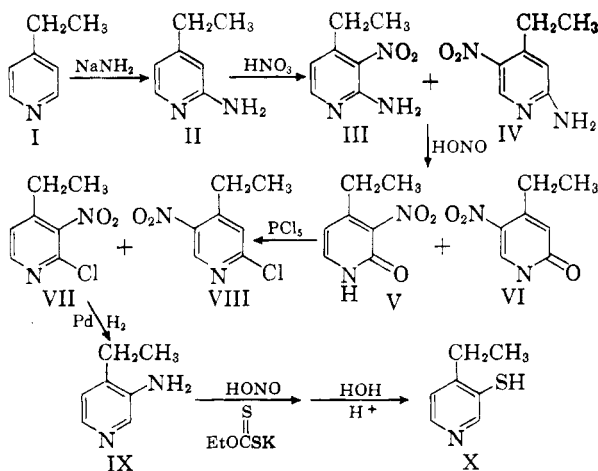
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A procedure for the synthesis of 4-ethyl-3-pyridinethiol from 4-ethylpyridine has been developed. The dehydrogenation of this *o*-ethylthiol to 6-azathianaphthene is discussed.

In the previous paper in this series<sup>2</sup> it was shown that the thiophene ring could be formed on the pyridine nucleus by the dehydrocyclization of 2-methyl-5-ethyl-4-pyridinethiol to 6-methyl-5-azathianaphthene. The conversion to azathianaphthene was not high, being of the order of 20–25%. The low yield was due principally to hydrogenolysis of the C—S bond. The low yield in the above reaction was not unexpected since it was recognized that the

4-pyridinethiol would be in equilibrium with the thione form which would be much more likely to undergo hydrogenolysis. For this reason it was decided to investigate the dehydrogenation of a 3-thiol in which the possibility of the thione form would be absent. The scheme shown for the synthesis of 4-ethyl-3-pyridinethiol was worked out.

4-Ethylpyridine (purchased from the Reilly Tar and Chemical Co.) was converted in 60% yield to 2-amino-4-ethylpyridine (II). This material was nitrated in concentrated sulfuric acid according to the procedure of Seide<sup>3</sup> to give 90% yield of a mixture of 3- and 5-nitro-2-amino-4-ethylpyridine. About three times as much 3 isomer formed as 5. It was not necessary to separate the isomers at this point and the crude mixture was simply converted with nitrous acid<sup>4</sup> to a mixture of the pyridones V and VI in 70 to 75% yield. The mixed pyridones, V and VI, were then converted to the mixed chloropyridines, VII and VIII, by means of phosphorus pentachloride according to Phillips.<sup>5</sup> The yield of the mixed chloropyridines was 75%. The mixed chlorides were then smoothly converted to the single substance, 3-amino-4-ethylpyridine, by catalytic hydrogenation using palladium-on-calcium carbonate.<sup>6</sup> Yields of



(1) This research was supported in part by the Office of Naval Research under contract N9onr 676(00) and in part by a grant from the National Science Foundation.

(2) C. Hansch and W. Carpenter, *J. Org. Chem.*, **22**, 936 (1957).

(3) O. Seide, *Ber.*, **57**, 791 (1924).

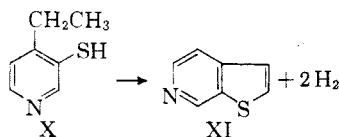
(4) W. T. Caldwell and E. C. Kornfield, *J. Am. Chem. Soc.*, **64**, 1696 (1942).

(5) M. A. Phillips, *J. Chem. Soc.*, 9 (1941).

(6) M. Busch and H. Stove, *Ber.*, **49**, 1065 (1916).

80–90% were obtained. The 3-amino-4-ethylpyridine (IX) was diazotized and the diazonium salt converted to the xanthate. Hydrolysis of this gave the thiol X in yields of only 25% of pure product. It was found that potassium thiocyanate could be used as well as potassium ethyl xanthate for the introduction of the SH group.

The dehydrogenation of the 4-ethyl-3-pyridinethiol to 6-azathianaphthene went much more smoothly with much less hydrogenolysis than did the dehydrogenation of 3-ethyl-4-pyridinethiol.<sup>2</sup> Very little charring occurred during the dehydrogenation and yields of about 50% were obtained according to the following equation:



6-Azathianaphthene prepared according to this method corresponded in its properties to that reported previously.<sup>7</sup>

#### EXPERIMENTAL<sup>8</sup>

*2-Amino-4-ethylpyridine* (II). 4-Ethylpyridine (454 g.) and 182 g. of sodamide were placed in 1000 ml. of mineral oil and heated at 145° for 8 hr. Good stirring with a heavy duty stirrer is necessary to obtain the maximum yield since the reaction mixture becomes very thick during the heating. After heating the mixture was cooled and extracted with dilute hydrochloric acid. The extract was made basic with basic with sodium hydroxide and the oil which separated was extracted with ether. After drying the ether solution over magnesium sulfate it was evaporated and the residue distilled. About 40 g. of 4-ethylpyridine was recovered. The product (308 g.) was distilled at 80–87°/0.6 mm. Crystallization from ligroin gave material of m.p. 65.5–66.5°.

*Anal.* Calcd. for C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>: C, 68.81; H, 8.25. Found: C, 69.10; H, 8.48.

In addition to the material which distilled at 80–87° there was obtained 75 g. which distilled at 160–165°/0.6 mm. On cooling it solidified and after recrystallization from methanol it melted at 115–116°. The use of an iron stirrer seemed to promote the formation of this substance. Analysis indicates that it might be a bis-2-amino-4-ethylpyridine.

*Anal.* Calcd. for C<sub>14</sub>H<sub>18</sub>N<sub>4</sub>: C, 69.39; H, 7.49. Found: C, 69.16; H, 7.62.

The residue from the above distillation was extracted with dilute hydrochloric acid and the extract made basic with sodium hydroxide. The crystals which separated were extracted with ether. Evaporation of the ether gave a few grams of tan crystals which after two recrystallizations from benzene-ligroin melted at 149–150°. Analysis indicates that this substance may be 2,6-diamino-4-ethylpyridine.

*Anal.* Calcd. for C<sub>7</sub>H<sub>11</sub>N<sub>3</sub>: C, 61.28; H, 8.08. Found: C, 60.72; H, 8.37.

*Nitration of 2-amino-4-ethylpyridine.* 2-Amino-4-ethylpyridine (150 g.) was dissolved in 700 ml. of concd. sulfuric acid with cooling so that the temperature did not rise above 30°. This mixture was cooled to 5° and held at this temperature while 90 ml. of concd. nitric acid dissolved in 200 ml. of concd. sulfuric was added dropwise with good stirring.

(7) W. Herz and L. Tsai, *J. Am. Chem. Soc.*, **75**, 5122 (1953).

(8) Microanalyses by C. F. Geiger, Chaffey College, Ontario, Calif.

After the addition of the nitric acid the mixture was allowed to stand at 5° for 1 hr. and then heated to 50–55° and held at this temperature for 3 hr. It was then poured onto crushed ice and neutralized with ammonium hydroxide, whereupon 189 g. of greenish crystals of mixed 2-amino-3-nitro- and 2-amino-5-nitro-4-ethylpyridines separated. This material could be used without further purification for the preparation of 3-amino-4-ethylpyridine.

Separation of the aminonitroethylpyridines III and IV was accomplished by steam distillation. Compound III steam distilled to give a product of melting point 103–110°. Sublimation of this material gave pure crystals of m.p. 110.5–111.5°.

*Anal.* Calcd. for C<sub>7</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub>: C, 50.29; H, 5.42. Found: C, 50.26; H, 5.67. The residue from the steam distillation was crystallized from methanol to give IV of m.p. 180–182° (dec.).

*Anal.* Calcd. for C<sub>7</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub>: C, 50.29; H, 5.41. Found: C, 50.26; H, 5.67. The residue from the steam distillation was crystallized from methanol to give IV of m.p. 180–182° (dec.).

*Anal.* Calcd. for C<sub>7</sub>H<sub>9</sub>N<sub>3</sub>O<sub>2</sub>: C, 50.29; H, 5.42. Found: C, 50.30; H, 5.43.

*Preparation of mixed pyridones V and VI.* Crude mixed aminonitroethylpyridines (155 g.) were dissolved in a solution of 100 ml. of concd. sulfuric acid and 1000 ml. of water. The solution was cooled to 0° and then 85 g. of sodium nitrite in 200 ml. of water was added with stirring. After the addition was complete the mixture was heated to 50° for a few minutes, cooled, and filtered. The yield was 114 g.

*4-Ethyl-5-nitro-2-pyridone* (VI). When the above procedure was used with pure 2-amino-4-ethyl-5-nitropyridine bright yellow crystals of compound VI were obtained which after crystallization from methanol melted at 147.5–149°.

*Anal.* Calcd. for C<sub>7</sub>H<sub>8</sub>N<sub>2</sub>O<sub>3</sub>: C, 50.00; H, 4.79. Found: C, 50.03; H, 5.02.

*Preparation of chloronitroethylpyridines (VII and VIII).* A mixture of 128 g. of the pyridones V and VI, 178 g. of phosphorus pentachloride, and 10.9 ml. of phosphorus oxychloride was heated at 110° for 5 hr. It was then vacuum evaporated as much as possible by means of an aspirator and steam bath. The resulting product was poured onto crushed ice, neutralized with sodium bicarbonate, and extracted with chloroform. After drying the solution over magnesium sulfate the chloroform was evaporated and the resulting oil distilled. Yield was 106 g. b.p. 90–104°/1 mm.

*2-Chloro-4-ethyl-5-nitropyridine* (VIII). Compound VI (10.3 g.) was mixed with 14.3 g. of phosphorus pentachloride and 1.1 ml. of phosphorus oxychloride and the mixture heated at 110° for 3 hr. The product was isolated as above. The yield was 9.2 g., b.p. 70°/0.2 mm., *n*<sub>D</sub><sup>20</sup> 1.5552.

*Anal.* Calcd. for C<sub>7</sub>H<sub>7</sub>ClN<sub>2</sub>O<sub>2</sub>: C, 45.05; H, 3.78. Found: C, 44.93; H, 3.97.

*3-Amino-4-ethylpyridine* (IX). Mixed nitro-2-chloro-4-ethylpyridines (32.5 g.) and 16 g. of 2% palladium-on-calcium carbonate were placed in 250 ml. of methanol and the mixture hydrogenated in a Parr apparatus. Hydrogen adsorption was complete in 2½ to 3 hr. after which the catalyst was removed and the solvent vacuum evaporated. Flash distillation of the residue gave 19.6 g. of yellow crystals b.p. 113–123°/1.5 mm. Crystallization from benzene-ligroin gave 18 g. of product with m.p. 80–83°. Sublimation raised the m.p. to 82–83°.

*Anal.* Calcd. for C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>: C, 68.81; H, 8.25. Found: C, 69.05; H, 8.49.

*Benzenesulfonyl derivatives of 3-amino-4-ethylpyridine.* When the above amine was treated with excess benzenesulfonyl chloride and dilute sodium hydroxide two derivatives were formed. One was the monoamide which was soluble in dilute sodium hydroxide. It was precipitated from the alkaline solution and crystallized from ethanol-water and then benzene to give a product of m.p. 153.5–155°.

*Anal.* Calcd. for C<sub>13</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub>S: C, 59.58; H, 5.38. Found: C, 59.75; H, 5.79.

The *disulfonamide* which was insoluble in dilute alkali was crystallized from ethanol-water. This product melted at 148–149.5°.

*Anal.* Calcd. for  $C_{19}H_{18}N_2O_4S_2$ : C, 56.70; H, 4.51; N, 6.96. Found: C, 56.79; H, 4.77; N, 7.36.

*4-Ethyl-3-pyridinethiol* (X). 3-Amino-4-ethylpyridine (54 g.) was dissolved in a mixture of 90 ml. of concd. hydrochloric acid and 90 g. of ice. The amine was then diazotized with a solution of 20.5 g. of sodium nitrite in 40 ml. of water. The temperature was held below 5° during this process. The solution of the diazonium salt was then added to a solution of 108 g. of potassium ethyl xanthate in 108 ml. of water at 50°. After the addition the mixture was heated to 80°, cooled, and extracted with ether. The ether layer was washed with water, sodium hydroxide, and again with water. Vacuum evaporation of the ether gave 56.2 g. of red oil. This was placed in a solution of 62 g. of potassium hydroxide in 450 ml. of ethanol. A small amount of sodium hydrosulfite was added and the mixture refluxed for 23 hr. The ethanol was then removed by vacuum evaporation and then the solid residue dissolved in water. The aqueous solution was extracted with chloroform to remove unhydrolyzed xanthate and then carefully acidified with acetic acid. The pyridine-thiol was then extracted with chloroform. Evaporation of

the chloroform gave 15.5 g. of a yellow solid, m.p. 123–128°, which was sublimed under vacuum. Resublimation gave 12 g. m.p. 122–125°.

*Anal.* Calcd. for  $C_7H_8NS$ : C, 60.39; H, 6.52. Found: C, 59.99; H, 6.64.

*6-Azathianaphthene* (XI). Ten grams of 4-ethyl-3-pyridine-thiol was dissolved in 60 ml. of hot pyridine and the solution was passed over 10 ml. of catalyst<sup>2</sup> at 425° during the course of 30 min. Most of the pyridine was removed from the condensate by distillation from an efficient column. The residue was dissolved in ether and washed with dilute sodium hydroxide and the water. After drying the ether solution over magnesium sulfate it was evaporated and the residue vacuum distilled. Yield was 4.5 g. b.p. 106°/5.5 mm. On cooling this material solidified and vacuum sublimation of a sample gave a product of m.p. 55–57°. Recrystallization from ligroin, then alcohol and resublimation gave a product of m.p. 58–59°. The picrate of this material melted at 211–212°.

Herz and Tsai<sup>7</sup> report a melting point of 54–55° and a picrate of m.p. 207.5–208.5°.

*Anal.* Calcd. for  $C_7H_8NS$ : C, 62.18; H, 3.72. Found: C, 62.05; H, 4.02.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NORTHWESTERN UNIVERSITY]

## Reaction of Quinoline and Iodine with Quinaldine, and with 2,6-Dimethylquinoline

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When quinaldine reacts with iodine and quinoline, the reaction product is diquino[1,2-*a*,1',2'-*c*]imidazolium iodide. In a similar manner 2,6-dimethylquinoline reacts with quinoline and iodine to give 10-methylidiquino[1,2-*a*,1',2'-*c*]imidazolium iodide. This represents a novel one-step synthesis for this type of compound.

In a recent paper from this laboratory<sup>2</sup> it was shown that quinaldine reacts with iodine and pyridine or certain pyridine-like bases to give quaternary salts of type I. Quaternary salts were prepared where  $N \llcorner \left\{ R \right.$  was pyridine, isoquinoline, 3-methylisoquinoline and 3-picoline. When this reaction was carried out using quinaldine, iodine, and quinoline, the expected 1-(2-quinolylmethyl)quinaldinium salt (IIa) was not obtained. Instead, a different product subsequently shown to be diquino[1,2-*a*,1',2'-*c*]imidazolium iodide (IIIa), was produced.

The assignment of the structure for IIIa is based on the following lines of evidence.

1. Compound IIIa was synthesized by an independent route, thus 1-(2-quinolylmethyl)quinaldinium bromide (IIb)<sup>3</sup> was prepared from  $\omega$ -bromoquinaldine<sup>4</sup> and quinoline. Compound

IIb on treatment with iodine and pyridine gave compound IIIa in near quantitative yield.

2. Diquino[1,2-*a*,1',2'-*c*]imidazolium bromide IIIb was synthesized by the method of Brown and Wild<sup>5</sup> and converted to the picrate (IIIc). This picrate was identical with the corresponding substance prepared from IIIa. Furthermore, the ultraviolet<sup>5</sup> and infrared spectra of IIIa and IIIb (Table 1) were similar.

3. On basic hydrolysis IIIa gave a compound which had the same properties as the *N*-(2-quinolylmethyl)carbostyryl (IV)<sup>6</sup> prepared by Brown and White<sup>7</sup> from diquino[1,2-*a*,1',2'-*c*]imidazolium bromide (IIIb).

In view of these observations we believe that the reaction of quinoline with iodine and quinaldine gives a cation identical with the diquino[1,2-*a*,1',2'-*c*]imidazolium cation described by Brown and White.<sup>7</sup> The reaction described herein

(1) From the Ph.D. Thesis of S. V. Abramo (1956). Present address, E. I. du Pont de Nemours & Co., Wilmington, Del.

(2) L. C. King and S. V. Abramo, *J. Org. Chem.*, **23**, 1609 (1958).

(3) D. L. Hammick, C. N. Lammiman, E. D. Morgan, and A. M. Roe, *J. Chem. Soc.*, 2440 (1955).

(4) D. I. Hammick, *J. Chem. Soc.*, 2882 (1923).

(5) B. R. Brown and E. H. Wild, *J. Chem. Soc.*, 1158 (1956).

(6) Brown and White, ref. 7, were unable to prepare this compound from  $\omega$ -bromoquinaldine and carbostyryl. We confirm this observation.

(7) B. R. Brown and D. White, *J. Chem. Soc.*, 1589 (1957).