(1.17 moles) dissolved in 700 ml. chloroform during 1 hr. at −50°. The solution was kept 1 hr. at −50° and warmed gradually over 2 hr. to −10°C. The liquid was washed with 300 ml. of 10% sodium sulfite, twice with water, and dried over anhydrous sodium sulfate. After evaporating chloroform, 151 g. (75%) of colorless 5,6-dichloro-1,3-dioxepane boiling at 56° at 1 mm. was obtained.

Anal. Calcd. for $C_5H_8Cl_2O_2$: C, 35.12; H, 4.68; Cl, 41.50. Found: C, 40.75; H, 5.00; Cl, 40.75.

2-Hexyl-1,3-dioxep-5-ene. A mixture of 114 g. *n*-heptaldehyde (1.0 mole), 88 g. 2-butenediol-1,4 (1.0 mole), and 0.2 g. *p*-toluenesulfonic acid was heated gradually to 150°. The distillate had two layers. The lower aqueous fraction was discarded, and the upper *n*-heptaldehyde fraction was returned to the still pot. After water evolution became slow the pressure was lowered gradually to 2 mm., keeping the oil bath temperature 150°, and the distillate was dried over sodium sulfate. Redistillation gave some low-boiling fractions and 98 g. (53%) of 2-hexyl-1,3-dioxep-5-ene, boiling at 93° at 2 mm.

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[COMMUNICATION NO. 1873 FROM THE KODAK RESEARCH LABORATORIES]

By-products of the Willgerodt Reaction Applied to α- and γ- Picoline

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An additional by-product of the Willgerodt reaction of aniline, γ-picoline, and sulfur has been identified as *N,N'*-diphenylisonicotinamidine and its structure confirmed by independent synthesis. The structure of 2-(4-pyridyl)benzothiazole also obtained in this reaction has been confirmed by an independent synthesis. The Willgerodt reaction of aniline, α-picoline, and sulfur produced 2-(2-pyridyl)benzothiazole, *N,N'*-diphenylpicolinamidine and the expected thiopicolinanilide.

In order to obtain 2-(4-pyridyl)benzothiazole (I) from readily available materials, the reaction of γ-picoline, aniline, and sulfur at elevated temperatures, as reported by Porter,[1] was carried out by a similar procedure but at 180–220°. The reaction product after distillation melted at 120–160° instead of 126–130° and, after recrystallization from alcohol, still melted in this same range. It was found that a separation into two materials, one melting at 133–135° (I) and the other melting at 194–196° (II) could be accomplished by extracting with ligroin, in which the low melting material was soluble.

The lower melting product was the desired 2-(4-pyridyl)benzothiazole, as reported and as synthesized by an independent method. Following the method as described in the literature[2] for the reaction of *o*-aminobenzenethiol with aldehydes and ketones, 2-(4-pyridyl)benzothiazoline (V) was prepared by the reaction of *o*-aminobenzenethiol (III) and 4-pyridinecarboxaldehyde (IV). Subsequent oxidation of (V) by ferric chloride produced the desired benzothiazole (I). The higher melting material (II) contained only carbon, nitrogen, and hydrogen; its molecular weight was found to be 281.

At the time of this investigation, we were unaware of the publication of Emmert and Holz[3] reporting the isolation of *N,N'*-diphenylisonicotinamidine from the reaction of γ-picoline, sulfur and either nitrobenzene or aniline under vigorous reflux. This reference was pointed out to us by H. D. Porter. The high melting material (II) was found to be the amidine derivative; its structure was confirmed by an independent synthesis following the procedure of Gerhardt,[4] for the preparation of *N,N'*-diphenylbenzamidine as outlined in Chart I.

When α-picoline, aniline, and sulfur were heated at 180–220° for 12 hr. instead of at 160° as reported,[1] the thiopicolinanilide (VIII) was obtained, but 2-(2-pyridyl)benzothiazole (X)[5] and *N,N'*-diphenylpicolinamidine (IX) were also isolated among the products of the reaction. The structures of these products were confirmed as outlined in Chart II.

EXPERIMENTAL

2-(4-Pyridyl)benzothiazole (I) *and N,N'-diphenylisonicotinamidine* (II). A suspension of 96.2 g. (3.0 g. atom) of sulfur, 93.1 g. (1.0 mole) of γ-picoline and 139.7 g. (1.5 moles) of aniline was heated under reflux for 24 hr., the inner temperature rising from 180 to 220°. The unreacted aniline and γ-picoline were removed by distillation under a vacuum at 7 mm. and, on continuing the distillation, the material boiling at 198–220° (7 mm.) was collected. On recrystallization from absolute alcohol, the distillate consisted of a yellow, crystalline material, m.p. 120–160°. An alternate method consisted in removing the unreacted aniline and γ-picoline by distillation under a vacuum and crystallizing the tarry residue out of absolute alcohol; the yellow crystalline material again melted at 120–160°; and distillation, b.p. 200–210° at 2 mm., as well as subsequent recrystallization from absolute alcohol, did not alter the melting point range. Extraction of this material for 16 hr. in a Soxhlet extractor with ligroin (b.p. 65–75°) produced a soluble frac-

(1) H. D. Porter, *J. Am. Chem. Soc.*, **76**, 127 (1954).

(2) A. W. Hofmann, *Ber.*, **13**, 1236 (1880); M. Claasz, *Ber.*, **45**, 1031 (1912); M. T. Bogert and A. Stull, *J. Am. Chem. Soc.*, **47**, 3078 (1925); H. P. Lankelma and P. X. Sharnoff, *J. Am. Chem. Soc.*, **53**, 2654 (1931).

(3) B. Emmert and A. Holz, *Chem. Ber.*, **87**, 676 (1954).

(4) C. Gerhardt, *Ann.*, **108**, 219 (1858).

(5) B. Emmert and M. Groll, *Chem. Ber.*, **86**, 208 (1953).

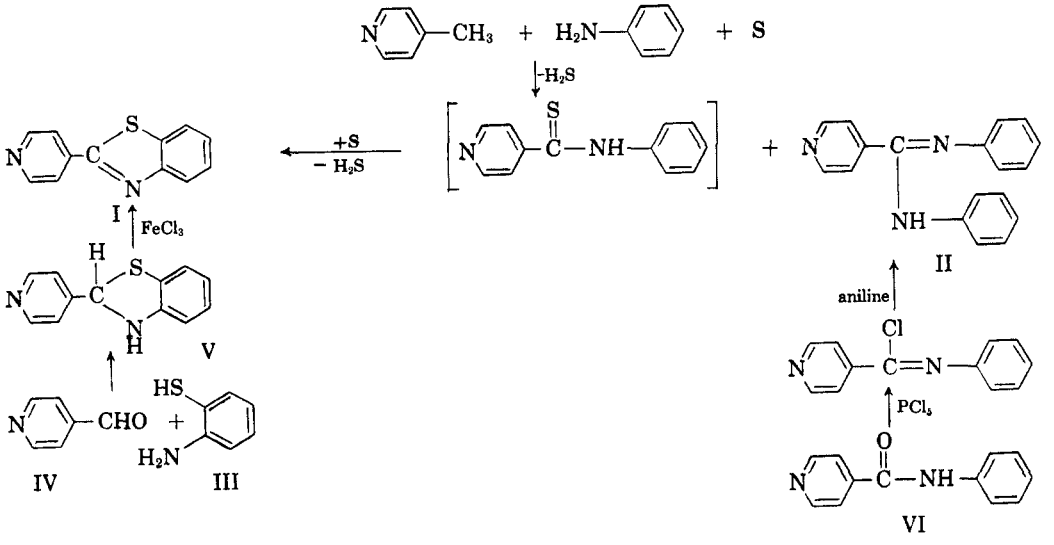

Chart I

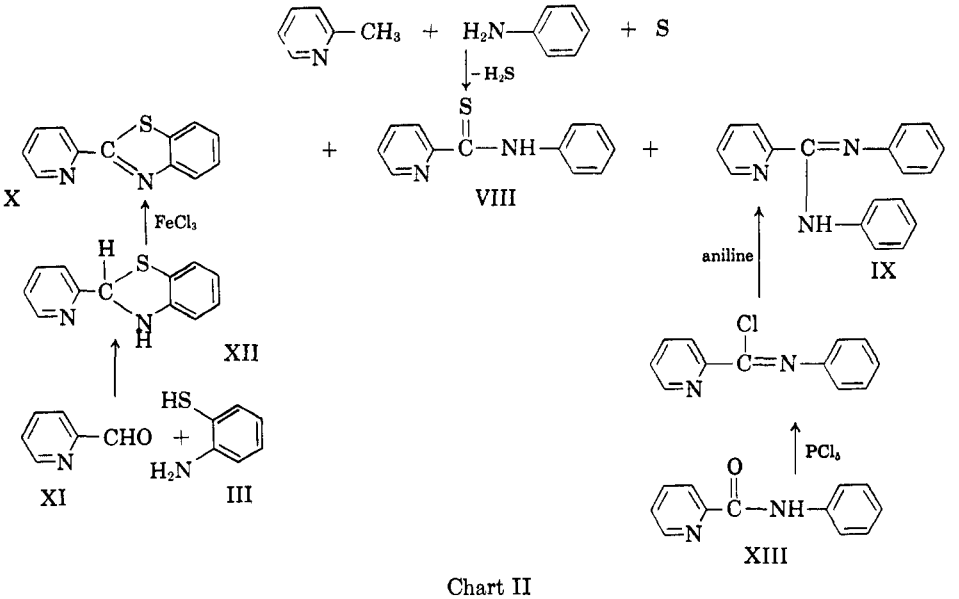

Chart II

tion from which the 2-(4-pyridyl)benzothiazole (I), m.p. 133–134°, was isolated from absolute alcohol (yield, 28–36 g.).

Anal. Calcd. for $C_{12}H_8N_2S$: C, 67.9; H, 3.8; N, 13.2; S, 15.1. Found: C, 68.0; H, 3.9; N, 13.1; S, 14.7.

The material II which was insoluble in ligroin was also crystallized from absolute alcohol, m.p. 194–196°, yield, 24–30 g.

Anal. Calcd. for $C_{13}H_{15}N_3$: C, 79.1; H, 5.5; N, 15.4; mol. wt. 273. Found: C, 79.3; H, 5.6; N, 15.1; mol. wt. 281 (ebullioscopic in absolute alcohol).

2-(4-Pyridyl)benzothiazoline hydrochloride (V). Into a solution of 2.5 g. (0.02 mole) of *o*-aminobenzenethiol in 30 ml. of absolute alcohol was passed an equimolar amount of hydrogen chloride gas (0.73 g.). A vigorous reaction ensued as 2.14 g. of 4-pyridinecarboxaldehyde (from the Aldrich Chemical Co.) was added to the warm solution. Bright-yellow crystals separated from the orange-brown solution on cooling. On recrystallization from alcohol, 4.2 g. of the benzothiazoline salt was obtained, m.p. 192°.

Anal. Calcd. for $C_{12}H_{11}ClN_2S$: C, 57.47; H, 4.42; N, 11.17. Found: C, 57.6; H, 4.0; N, 11.3.

2-(4-Pyridyl)benzothiazole (I). An aqueous solution of 1.0 g. (0.004 mole) of the benzothiazoline and 1.3 g. (0.008 mole) of anhydrous ferric chloride was heated about 15 min., cooled, and filtered. The precipitate was recrystallized from a small volume of alcohol, giving needles, m.p. 133–135°. (Lit. 131–132°.[1]) A mixed melting point with a sample from the Willgerodt reaction showed no depression.

Reaction of isonicotinic acid with thionyl chloride and aniline. Thirty-eight g. (0.33 mole) of thionyl chloride was added to 12.3 g. (0.1 mole) of isonicotinic acid in a 250-ml. round-bottomed flask, equipped with a Claisen head and a condenser. After the first vigorous reaction had subsided, the mixture was warmed on the steam bath for 30 min. The excess thionyl chloride was removed at 3 mm. pressure with gentle warming on the steam bath. The residue was cooled and 9.30 g. (0.1 mole) of aniline in 100 ml. of benzene was added. The reaction mixture was heated on the steam bath for 1 hr., cooled, and filtered. One half of the crude precipitate was dissolved in 100 ml. of cold water, filtered, and 5% sodium hydroxide was added until the *p*H reached 7.0. The white precipitate which formed was filtered and washed with water to give 5.7 g. (57.5%) of isonicotinanilide VI), m.p. 170–172°. Recrystallization from absolute alcohol did not change the melting point.

Anal. Calcd. for $C_{12}H_{10}N_2O$: C, 72.6; H, 5.5; N, 14.1. Found: C, 73.0; H, 5.2; N, 14.2.

Reaction of isonicotinanilide hydrochloride with phosphorus pentachloride and aniline. One half of the crude isonicotinanilide hydrochloride described in a preceding section (0.0288 mole) in 50 ml. of dry benzene was heated to 50° in a round-bottomed flask and 20 g. of phosphorus pentachloride was added slowly. The reaction mixture was then heated to 140° for 1 hr., all of the solvent distilling off. Aniline (0.1 mole) in 100 ml. of benzene was then added to the residue and the reaction mixture was heated on the steam bath for 45 min. and 10 ml. more of aniline was added. The mixture was cooled and filtered, the precipitate was taken up in 10% hydrochloric acid, treated with Norit, filtered, and taken to *p*H 4.0 with 5% sodium hydroxide. The precipitate which formed was recrystallized from ethyl alcohol to give 0.9 g. (10.4%) of *N,N'*-diphenylisonicotinamidine, melting at 192–193° (Fisher-Johns). A mixed melting point with the product from the Willgerodt reaction was not depressed.

Thiopicolinanilide (VIII); *2-(2-pyridyl)benzothiazole* (X); *and N,N'-diphenylpicolinamidine* IX. A suspension of 96.2 g. (3.0 g. atom) of sulfur, 93.1 g. (1.0 mole) of α-picoline, and 139.7 g. (1.5 moles) of aniline was heated under reflux for 16 hr., the inner temperature rising from 180–220°. The unreacted aniline and α-picoline were removed by distillation under a vacuum. Excess sulfur was removed by solution of the pot residue in 1500 ml. of alcohol, cooling, and filtering. The filtrate, after concentration to 600 ml. and chilling, deposited 15 g. of yellow crystals, m.p. 126–133°. One recrystallization out of alcohol gave a material, m.p. 133–135°; the mixed melting point with 2-(2-pyridyl)benzothiazole was not depressed.

After removal of the benzothiazole, the filtrate was concentrated and distilled under a vacuum at 1 mm. to give the following fractions:

(1) b.p. 140–170° (96 g.)
(2) b.p. 170–176° (54 g.)
(3) b.p. 176–185° (with slight decomposition) 8 g.

The first fraction, upon solution in warm alcohol (40°), yielded two crystalline solids: 2-(2-pyridyl)benzothiazole, m.p. 126–133°, 45 g., only slightly soluble in alcohol, and thiopicolinanilide, m.p. 51–53° (42 g.), which is more soluble and crystallized from the filtrate upon chilling.

The second fraction, upon solution in alcohol and chilling, yielded thiopicolinanilide, m.p. 51–53°.

The third fraction, upon solution in alcohol and chilling, yielded *N,N'*-diphenylpicolinamidine (IX), m.p. 93–95°, after recrystallization from absolute alcohol and ligroin.

Anal. Calcd. for $C_{18}H_{15}N_3$: C, 79.1; H, 5.5; N, 15.4; mol. wt., 273. Found: C, 79.4; H, 5.6; N, 15.1; mol. wt., 284.

2-(2-Pyridyl)benzothiazoline hydrochloride (XII). This isomer was prepared by the method just described for compound V from 2-pyridinecarboxaldehyde (Aldrich Chemical Co.). The bright yellow crystals melted, with decomposition, at 166–168°.

Anal. Calcd. for $C_{12}H_{11}ClN_2S$: C, 57.47; H, 4.42; N, 11.17. Found: C, 57.9; H, 4.4; N, 11.5.

2-(2-Pyridyl)benzothiazole (X). The oxidation of the benzothiazoline was accomplished by the procedure just described for compound I to give the benzothiazole, m.p. 133–135°. A mixed melting point with a sample from the Willgerodt reaction showed no depression.

Anal. Calcd. for $C_{12}H_8N_2S$: C, 67.90; H, 3.80; N, 13.20. Found: C, 67.9; H, 3.8; N, 13.2.

N,N'-Diphenylpicolinamidine (IX). Picolinanilide XIII, m.p. 72–74° was prepared by the method of Engler.[6] A suspension of 6.6 g. of picolinanilide in 25 ml. of dry benzene was treated with 10 g. of phosphorus pentachloride at 50°. The reaction mixture was then heated to 110° for 3 hr., all of the solvent distilling off. Aniline (10 ml.) in 60 ml. of dry benzene was then added to the residue and the reaction mixture was heated on the steam bath for 1 hr. The mixture was cooled, filtered, and the precipitate was dissolved in 100 ml. of 10% hydrochloric acid. This solution was treated with carbon, filtered, and taken to *p*H 6.0 with 10% sodium hydroxide solution. Upon cooling, a precipitate was formed which was recrystallized from alcohol, m.p. 93–95°. A mixed melting point with the product from the Willgerodt reaction was not depressed.

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(6) C. Engler, *Ber.*, **27**, 1786 (1894).

[CONTRIBUTION FROM THE DEPARTMENT OF ORGANIC CHEMISTRY, RADIUM INSTITUTE, UNIVERSITY OF PARIS]

Tritylation of Some Phenols and Naphthols

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The Baeyer-Villiger condensation reaction of triphenylcarbinol with some phenols, naphthols, and dihydroxynaphthalenes is investigated, and the constitution of several of the resulting substitution products is discussed.

The Baeyer-Villiger condensation of triphenylcarbinol with phenols, phenol ethers, and naphthols to give tritylated products was extensively investigated by Hardy,[1] who found that condensation occurred only in the position *para* to a phenol or an ether group. In the case of β-naphthol, however, Hardy assigned the structure of 1-trityl-2-naphthol (I) to the monotritylated product, without offering any proof of constitution. Recently, Schönberg, Mustafa, and Shalaby[2] reported an unequivocal synthesis of 1-trityl-2-naphthol by reacting phenylmagnesium bromide with *o*-naphthofuchsone; the reaction product, m.p. 155°, differed from Hardy's substance, which melted at 228°. This observation led us to investigate anew the tritylation reaction of phenolic compounds, to ascertain whether there would be true instances of *ortho* substitution.

Repetition of Hardy's experiments with β-naphthol gave a tritylnaphthol melting at 230°, which condensed readily with 2,3-dichloro-1,4-naphthoquinone in pyridine to give a furanoquinone. This reaction proved that the position 1 adjacent to the hydroxy group was free,[3] thus confirming Schön-

(1) Hardy, *J. Chem. Soc.*, 1000 (1929).

(2) Schönberg, Mustafa, and Shalaby, *J. Am. Chem. Soc.*, **77**, 5756 (1955).

(3) *Cf.* Buu-Hoï, *J. Chem. Soc.*, 489 (1952); Buu-Hoï and Demerseman, *J. Chem. Soc.*, 4699 (1952).