Anal. Calcd. for $C_{15}H_{10}ClNO$: Cl, 13.86. Found: Cl, 13.75.

The hydrochloride prepared from the purified base was recrystallized from isopropyl alcohol, m.p. 207.5–210° (cor.).

Anal. Calcd. for $C_{15}H_{10}ClNO \cdot HCl$: Cl, 24.27; N, 4.80. Found: Cl, 23.60[14]; N, 4.74.

The Effect of Acid and Base on the Reaction of 4,7-Dichloroquinoline with Phenol (Table II).—In each of seven test-tubes was placed 0.01 mole of 4,7-dichloroquinoline (or the hydrochloride, Run 21) and the phenol and other reagents were added as indicated in Table II. The stoppered tubes were heated simultaneously at 100° for one hour with initial shaking to insure thorough mixing. At the end of this time the test-tubes were cooled in an ice-bath and worked up separately.

The contents of each tube were treated with 20 ml. of 10% sodium hydroxide solution and ether and transferred to a separatory funnel. After shaking vigorously, the aqueous layer was removed and the ether washed twice with water (and then with a buffered solution[15] for Runs 18–20, to remove the N^1,N^1-diethyl-N^4,N^4-dimethyl-1,4-pentanedi-

(14) The compound apparently loses hydrogen chloride very easily.

(15) Prepared by treating dilute ammonium hydroxide with acetic acid until just acid to litmus.

amine). After drying and removing the ether by distillation an oil was obtained which was a mixture of 4,7-dichloroquinoline and 7-chloro-4-phenoxyquinoline. In Runs 18 and 21 the oil consisted mainly of the former and solidified on standing.

The amount of unchanged 4,7-dichloroquinoline present in the mixture was determined by its conversion to 7-chloro-4-hydroxyquinoline. In each case, the mixture was heated with 3 ml. of acetic acid and 1 ml. of triethylamine at 125° for seventy-five minutes. The reaction mixture was then treated with 80 ml. of 10% sodium hydroxide solution and ether, shaken thoroughly and the layers separated. The ether was washed twice with water and the washings combined with the alkaline solution. Acidification with acetic acid gave 7-chloro-4-hydroxyquinoline.

The 7-chloro-4-phenoxyquinoline was obtained from the ether layer after removal of the ether by distillation.

In order to check the accuracy of the above method of analysis, a mixture containing known amounts of 4,7-dichloroquinoline, 7-chloro-4-phenoxyquinoline and N^1,N^1-diethyl-N^4,N^4-dimethyl-1,4-pentanediamine was assayed. This work indicated that although the results tabulated in Table II are reasonably precise, the values for the phenoxy compound probably should be about 5% lower and that for the dichloroquinoline about 10–15% higher.


[CONTRIBUTION FROM DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN]

The Synthesis of Heterocyclic Compounds from Aryl Azides. II. Carbolines and Thienoindole[1]

BY P. A. S. SMITH AND J. H. BOYER

o-(α-Pyridyl) and *o*-(β-pyridyl)-phenyl azide have been prepared from the corresponding anilines by diazotization and coupling with sodium azide. The former is converted to *o*-(α-pyridyl)-aniline (XII) when heated in "inert" solvents, but the latter cyclizes to a mixture of α- and γ-carboline (VIII, IX) in good yield. *o*-(α-Thienyl)-aniline was prepared by coupling diazotized *o*-nitroaniline with thiophene followed by reduction. The product was then converted to the corresponding azide, which was cyclized in good yield to 4-thieno[3,2-b]indole (VI).

Since the thermal decomposition of *o*-azidobiphenyl (I) and certain substituted derivatives proved a convenient synthesis of carbazole (II) and corresponding derivatives,[1b] an investigation of the application of the reaction for the synthesis of compounds isosteric with carbazole was undertaken. The investigation of *o*-(α-thienyl)-phenyl azide and *o*-(α-pyridyl)-phenyl azide and its β-isomer are reported here.

I   II
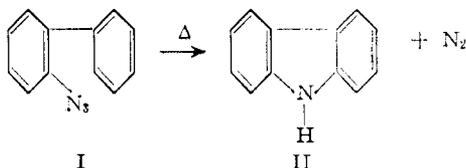
o-(α-Thienyl)-phenyl azide (V) was readily prepared by a three-step process from diazotized *o*-nitroaniline and thiophene. Several examples of the coupling of diazonium derivatives with thiophene to give arylthiophenes have been reported,[2,3] but only in the case of *m*-cyanophenyldiazonium acetate, which gave α-(*m*-cyanophenyl)-thiophene,[4] has the position taken by the entering aryl group

been clearly determined. The product formed in our experiment was shown to be α-(*o*-nitrophenyl)-thiophene (III) by reducing the nitro group and deaminating the resulting aminophenylthiophene to the known α-phenylthiophene (IV).

After reduction of the nitro group using sodium sulfide according to a general procedure developed by Hodgson,[5] the diazotized amine was treated with sodium azide and hydrochloric acid. *o*-(α-Thienyl)-phenyl azide (V) separated immediately. Thermal decomposition of this compound in one per cent. solutions in decalin (preferred), kerosene, or trichlorobenzene at 170–180° brought about the loss of nitrogen accompanied by ring closure to the carbazole analog, 4-thieno(3,2-b)indole (VI). The numbering system used here is that recommended by the Ring Index,[5a] in place of those previously reported.[6,7]

Whereas 4-thieno(3,2-b)indole itself has not before been reported, several derivatives of it have been prepared in different ways. Benary and Baravian[6] reported that 3-hydroxy-4-carbethoxy-5-methylthiophene undergoes the Fischer indole synthesis to form 3-carbethoxy-2-methyl-4-thieno-(3,2-b)indole, which was saponified and decarboxyl-

(1) (a) Presented at the National Meeting of the Am. Chem. Soc., Chicago, Ill., Sept., 1950; (b) Part I of this series: P. A. S. Smith and B. B. Brown, THIS JOURNAL, **73**, 2435 (1951).

(2) M. Gomberg and W. E. Bachmann, *ibid.*, **46**, 2339 (1924).

(3) E. Bamberger, *Ber.*, **30**, 3666 (1897).

(4) W. E. Bachmann and R. A. Hoffman, Chap. 6 in R. Adams, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York City, N. Y., 1944.

(5) H. H. Hodgson and S. Birtwell, *J. Chem. Soc.*, **75** (1944) (for leading references).

(5a) A. M. Patterson and L. T. Capell, "The Ring Index," Reinhold Publ. Corp., New York, N. Y., 1940, p. 198.

(6) E. Benary and A. Baravian, *Ber.*, **48**, 593 (1915).

(7) Ng. Ph. Buū-Hoï, Ng. Hoan, Ng. H. Khoi and Ng. D. Xuong, *J. Org. Chem.*, **14**, 802 (1949).

III

IV

VI
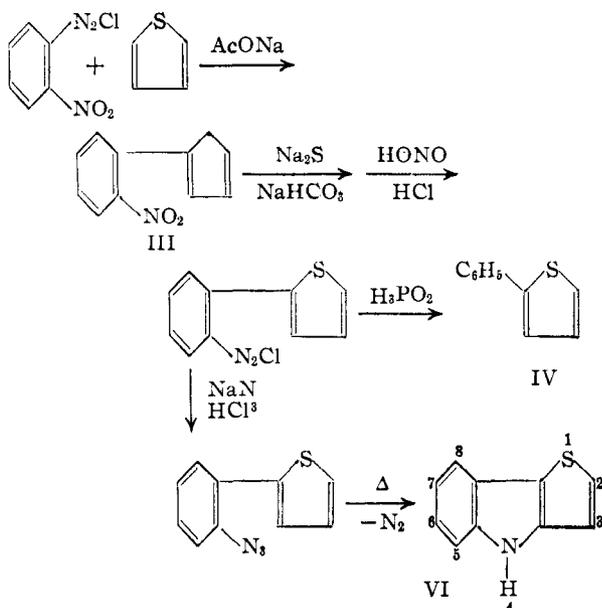
ated to give 2-methyl-4-thieno(3,2-b)indole. Buü-Hoi[7] has recently performed the same series of operations with substituted arylhydrazines and obtained yields from thirty to one hundred per cent. The deep halochromic coloration of our 4-thieno-(3,2-b)indole with sulfuric acid, its fluorescence, and its extremely dark red picrate are characteristic of the other known thienoindoles as well as the carbazoles.

Pyridine couples with diazohydroxides to give mixtures of α-, β- and γ-arylpyridines. In general, it is the α-isomer which predominates, but diazotized o-nitroaniline gives equal quantities of α- and β-isomers and only a trace of the γ-isomer.[8,9] Reduction of α- and β-(o-nitrophenyl)-pyridines[9] to the corresponding aminophenylpyridines was effected by stannous chloride.[8,10] α- and β-(o-azidophenyl)-pyridines (X, VII) were then prepared by the action of sodium azide on the diazotized amines.

VII   VIII

IX
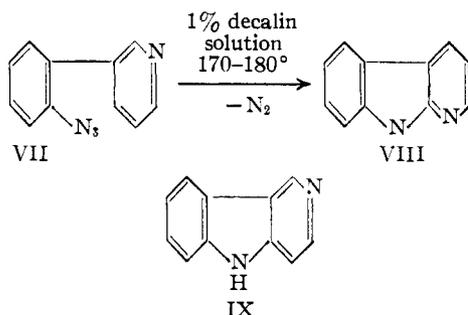
Only the β-isomer (VII) underwent ring closure upon thermal decomposition. Cyclization occurred at both the α- and γ-carbon atoms of the pyridine nucleus and produced the two isomers, α- and γ-carboline (VIII, IX).

α-(o-Azidophenyl)-pyridine (X) failed to undergo

ring closure into δ-carboline (XI). Instead, the thermal decomposition in either decalin or trichlorobenzene was accompanied by abstraction of two hydrogen atoms from either the solvent or similar molecules and brought about the formation of the corresponding primary aromatic amine, α-(o-aminophenyl)-pyridine (XII).

H   XI

X →

XII
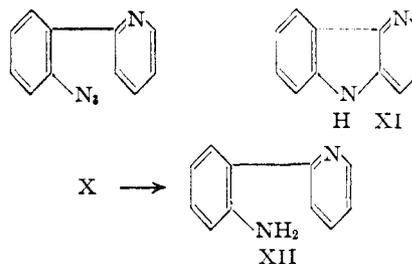
This reduction of an aromatic azide to the corresponding primary amine is reminiscent of the action of halogen acids on aromatic azides[11] which effects simultaneous reduction to the amine and liberation of halogen. It has already been shown that the thermal decomposition of o-azidobiphenyl in such hydrogen-providing solvents as benzyl mercaptan, diethyl malonate, aniline, and decalin results in cyclization in all cases without any reduction. Apparently reduction of the azido group occurs only in those cases in which ring closure is too difficult under the conditions employed. The formation of α-naphthylamine from α-naphthyl azide in decalin at 170–180° instead of ring closure supports this viewpoint. Further investigation of the conditions which lead to reduction is proposed.

Experimental[12]

α-(o-**Nitrophenyl**)-**thiophene** (III).—o-Nitrophenyldiazonium acetate was prepared and treated with thiophene according to the general procedure of Gomberg and Bachmann[2,4] for coupling aromatic diazonium acetates with aromatic nuclei.

A mixture of 28 g. (0.2 mole) of o-nitroaniline (m.p. 70–71°), 80 ml. of water and 45 ml. of concentrated hydrochloric acid was placed in a 500-ml. round-bottomed flask equipped with a stirrer and a dropping funnel and cooled in an ice–salt-bath to 0–5°.

The amine hydrochloride was then diazotized by adding dropwise a solution of 14.5 g. of a reagent grade of sodium nitrite in 50 ml. of water. Stirring was then continued for one hour at 0–5°. The diazonium solution was filtered from traces of insoluble impurities, and was returned to a one liter round-bottomed flask. To the diazonium solution was added 500 g. of thiophene and the mixture was again cooled to 0–5°. A solution of 80 g. of sodium acetate trihydrate in 200 ml. of water was added dropwise with stirring to the cold reaction mixture. Stirring was continued for three hours at 5–10°, after which time the mixture was allowed to warm to room temperature and stirring was continued for 48 hours. A small amount of carbonaceous material was removed by filtration and the layers were separated. The water layer was thoroughly extracted with ether, which was subsequently removed by distillation and the residue added to the organic layer. Distillation of the product at atmospheric pressure gave 475 g. of thiophene and a viscous, dark-colored residue. Distillation was then

(8) J. W. Haworth, I. M. Heilbron and D. H. Hey, *J. Chem. Soc.*, 349 (1940).

(9) α- and β-(o-nitrophenyl)-pyridines were kindly provided by Dr. B. B. Brown.

(10) J. A. Petrow, M. V. Stack and W. R. Wragg, *J. Chem. Soc.*, 316 (1943).

(11) P. A. S. Smith and B. B. Brown, THIS JOURNAL, **73**, 2438 (1951); E. Bamberger, *Ann.*, **424**, 233 (1921) (for leading references).

(12) Analyses by Micro-Tech Laboratories, Skokie, Illinois. All melting points are uncorrected.

continued at 0.3–0.5 mm. and yielded 25.6 g. of a red oil, b.p. 126–132°. Considerable decomposition accompanied this distillation and accounted for a large amount of very hard, resinous residue. Redistillation was not accompanied by decomposition, and the product was obtained as a light yellow oil, b.p. 128–132° (0.3 mm.), 152–154° (0.8 mm.). Upon a third redistillation the product solidified to an oily mass of golden prisms, m.p. 51–52°. Recrystallization from methanol removed the red, oily impurity, and α-(o-nitrophenyl)-thiophene separated as brilliant light yellow needles, m.p. 51–52°, wt. 21 g. (51%).

Anal. Calcd. for $C_{10}H_7NO_2S$: C, 58.52; H, 3.44; N, 6.83; S, 15.62. Found: C, 58.64; H, 3.61; N, 7.20; S, 15.35.

Other runs in which a smaller excess of thiophene was used resulted in markedly lower yields.

α-(o-Aminophenyl)-thiophene.—Reduction of the nitro compound to the corresponding amine was successfully accomplished by using sodium sulfide according to a general method developed by Hodgson.[6]

To a solution of 4.2 g. (0.020 mole) of α-(o-nitrophenyl)-thiophene in 50 ml. of boiling methanol in a 500-ml. round-bottomed flask equipped with a reflux condenser and a dropping funnel was added dropwise over a period of twenty minutes a preheated solution of 40 g. of crystalline sodium sulfide nonahydrate and 5 g. of sodium bicarbonate in 50 ml. of water. The reaction mixture was then allowed to reflux for 12 hours. An equal volume of water was then added and the mixture was filtered to remove traces of sulfur and undissolved inorganic salts. The dark red solution was thoroughly extracted with ether, the ether solution dried with anhydrous magnesium sulfate, and the ether removed by distillation. The product, a yellow oily residue, upon distillation at 0.2 mm. gave only one fraction, b.p. 123–126°. Cooling the product in a Dry Ice-bath induced crystallization to fine yellow needles, m.p. 35–36°, wt. 2.9 g. (82%).

Anal. Calcd. for $C_{10}H_9NS$: C, 68.54; H, 5.18; N, 7.99; S, 18.29. Found: C, 68.42; H, 5.20; N, 8.20; S, 18.20.

Addition of a 20% solution of hydrochloric acid caused immediate precipitation of the amine hydrochloride. Upon recrystallization from hydrochloric acid and from water the salt separated as light blue to colorless plates, m.p. 210–212°.

Anal. Calcd. for $C_{10}H_9NS \cdot HCl$: Cl, 16.75. Found: Cl, 16.96, 16.58.

An excess of a saturated ether solution of picrolonic acid and an ether solution of the amine were mixed and allowed to stand in the refrigerator for 48 hours. The picrolonate separated as straw-colored, needle-shaped crystals, m.p. 193–194° (dec.), constant after several recrystallizations from methanol.

Anal. Calcd. for $C_{20}H_{17}N_5O_5S$: C, 54.66; H, 3.90; N, 15.94; S, 7.30. Found: C, 54.47; H, 3.89; N, 16.20; S, 7.05.

The yield of the reduction is dependent upon the size of the run. Thus, from 1.0 g. of the nitro compound was obtained a 91% yield of the pure amine whereas from 13.5 g. of the nitro compound a 58% yield was obtained.

α-Phenylthiophene (IV).—A mixture of 0.45 g. of the amine and 10 ml. of 20% hydrochloric acid was cooled to 5–10° and diazotized in the usual manner. To the ice-cold diazonium solution was added 15 ml. of 50% hypophosphorous acid. Separation of the solid α-phenylthiophene, m.p. 40–41°,[13] commenced almost immediately; however, the reaction mixture was allowed to stand at room temperature for two hours. The product isolated on a Buchner funnel had a sharp melting point which did not change on recrystallization. A quantitative yield, 0.41 g., of this isomer was obtained and no trace of the β-isomer, m.p. 91.4–92°,[13] was found.

α-(o-Azidophenyl)-thiophene (V).—A mixture of 4.8 g. (0.027 mole) of α-(o-aminophenyl)-thiophene and 30 ml. of 20% hydrochloric acid was cooled in an ice-salt-bath. To the cold solution was added 2.1 g. of a reagent grade of sodium nitrite in 10 ml. of water. The cold reaction mixture was then allowed to stand with frequent stirring for 15

minutes or until no more solid amine hydrochloride was present. The cold, orange-colored diazonium solution was then treated with a solution of 2.0 g. of sodium azide in 10 ml. of water, added dropwise. Vigorous nitrogen evolution commenced immediately and was accompanied with excessive frothing. After all of the azide had been added, the solution was allowed to stand at room temperature for half an hour. The dark-red oil which formed was separated, and combined with ether-extracts of the water layer. Evaporation of the ether left 4.7 g. (87%). Purification was effected by evaporative distillation at 0.04 mm. on half-gram portions using a sublimation tube and a jacket temperature of 100–110°. After one such operation on 0.50 g. the product was a light yellow oil (0.46 g.) which rapidly darkened upon exposure to the atmosphere.

Anal. Calcd. for $C_{10}H_7N_3S$: C, 59.68; H, 3.51; N, 20.88. Found: C, 59.94; H, 3.72; N, 20.95.

4-Thieno[3,2-b]indole (VI).—A solution of 1.0 g. (0.005 mole) of α-(o-azidophenyl)-thiophene (not distilled) in 100 ml. of freshly distilled decalin was heated to 180°. At 135° nitrogen evolution started sluggishly and became quite vigorous at 170–180°. After ten minutes at this temperature there was no more visible gas evolution. The dark-colored, crystalline residue which was obtained by evaporation of the solvent in an air stream on a steam cone was taken up in an excess of aqueous ethanol and treated with charcoal, filtered, and the solution evaporated to the cloudy point. Upon cooling, colorless plates of 4-thieno[3,2-b]indole separated, m.p. 173–175°, wt. 0.80 g. (93%). Recrystallization from ethanol–water, benzene, and finally several times from ethanol–water produced colorless plates, m.p. 175°.

Anal. Calcd. for $C_{10}H_7NS$: C, 69.33; H, 4.07; N, 8.09; S, 18.51. Found: C, 69.61; H, 4.14; N, 8.13; S, 18.33.

The picrate was prepared in ether, from which it separated only after more than 24 hours as very dark purple needles, m.p. 172–174°. After three recrystallizations from ethanol, an analytical sample melted at 174–175°.

Anal. Calcd. for $C_{16}H_{10}N_4O_7S$: C, 47.76; H, 2.51; N, 13.93; S, 7.97. Found: C, 48.06; H, 2.66; N, 15.52; S, 7.67. (The figure for nitrogen is assumed to be in error.)

α-(o-Azidophenyl)-pyridine (X).—A solution of α-(o-aminophenyl)-pyridine (3.8 g.) in 8 ml. of concentrated hydrochloric acid and 12 ml. of water was cooled to 5–10° and treated with 2.4 g. of a reagent grade of sodium nitrite in 20 ml. of water according to the directions of Haworth[6] and of Petrow.[10] After a few minutes urea was added to destroy the excess nitrous acid. The chilled solution was then treated with 1.7 g. of sodium azide in 5 ml. of water, which brought about immediate evolution of nitrogen. The solution was allowed to stand one hour, treated with an excess of dilute sodium or ammonium hydroxide and extracted with ether. After removal of the ether by distillation, a light brown, oily residue remained which crystallized from aqueous methanol as light tan needles, m.p. 39–43°, wt. 2.8 g. (67%). After several more recrystallizations from aqueous methanol, the product separated as colorless needles, m.p. 46°.

Anal. Calcd. for $C_{11}H_8N_4$: C, 67.33; H, 4.11; N, 28.56. Found: C, 66.88, 63.66; H, 4.17, 4.11; N, 26.37.

Combustion analysis of azides has been found unsatisfactory in some cases in the past.[14] Concentrated sulfuric acid, however, has long been known to liberate quantitatively two-thirds of the azide nitrogen in aromatic azides. This reaction was therefore used to analyze for the azide nitrogen content in these two compounds. Ten to fifty milligram samples of the azide in a 2-ml. beaker of sulfuric acid were placed in a closed system in which a steady stream of carbon dioxide swept all gases into a graduated (8 cc.) Dumas tube filled with 50% potassium hydroxide from a levelling bulb. After all air was swept out of the system the sample and acid were mixed by tipping the beaker with a sharp shake. The reaction was almost instantaneous and after a very few minutes all of the nitrogen was collected.[15]

(14) M. O. Forster and H. E. Fierz, *J. Chem. Soc.*, **93**, 669 (1908).

(15) It has been reported (K. A. N. Rao and P. R. Venkataraman, *J. Indian Chem. Soc.*, **15**, 194 (1938)) that two aromatic azides, o- and m-azidobenzoic acids, liberate close to one-half of their azide nitrogen content together with carbon monoxide upon treatment with concentrated sulfuric acid. It has been our experience that o-azido-

(13) I. M. Heilbron, "Dictionary of Organic Compounds," Vol. 3, Oxford University Press, New York, N. Y., 1938, p. 461.

Anal. Calcd. for $C_{11}H_8N_4$: $^2/_3$ azide N, 14.3. Found: $^2/_3$ azide N, 14.2, 14.3.

β-(o-Azidophenyl)-pyridine (VII).—Addition of 1.4 g. of sodium azide in 5 ml. of water to the diazonium salt solution prepared from 3.0 g. (0.018 mole) of β-(o-aminophenyl)-pyridine in the foregoing manner followed by isolation of the product as before, gave 1.8 g. (51%) of β-(o-azidophenyl)-pyridine as a brown oil. This compound was purified by evaporative distillation at a pressure of 0.5 mm. and jacket temperature of 140–145°. The pure product obtained after two such operations was a light yellow-green, viscous oil which darkened upon exposure to the atmosphere. The yield was 1.7 g. (48%).

Anal. Calcd. for $C_{11}H_8N_4$: $^2/_3$ azide N, 14.3. Found: $^2/_3$ azide N, 14.3.

Thermal Decomposition of α-(o-Azidophenyl)-pyridine (X).—A solution of 0.10 g. (0.0005 mole) of the azide in 10 ml. of redistilled decalin was heated to 180°. Nitrogen evolution occurred smoothly at this temperature and subsided after ten to fifteen minutes. The solution was allowed to cool to room temperature and then was mixed with an excess of picric acid in ether. A copious precipitate (0.30 g., 95%) of the dipicrate of α-(o-aminophenyl)-pyridine (XII) was obtained, m.p. 210–213°. Several recrystallizations from aqueous ethanol gave stocky, orange needles, m.p. constant at 214–216° (dec.). A mixed melting point determination with an authentic sample showed no depression.

Anal. Calcd. for $C_{23}H_{16}N_8O_{14}$: C, 43.95; H, 2.57; N, 17.83. Found: C, 44.47; H, 2.53; N, 18.52.

α-Naphthyl azide was prepared according to the method of Forster and Fierz.[16] When a solution of 1.0 g. (0.06 mole) was heated in 100 ml. of redistilled decalin, nitrogen was given off slowly at 140° and vigorously at 180°. Evaporation in an air stream to approximately 50 ml. was followed by the addition of 1.5 g. (0.065 mole) of picric acid in 100 ml. of ether. The solution was allowed to stand overnight. The picrate of α-naphthylamine separated as a dark red solid, m.p. 175–180°. After several recrystallizations from aqueous ethanol it formed yellow-green needles, m.p. 182–183° after blackening at 170°.[17] The yield of pure picrate was 0.65 g. (29.4%). A mixed melting point determination with an authentic sample showed no depression.

Thermal Decomposition of β-(o-Azidophenyl)-pyridine (VII).—A solution of 0.45 g. (0.0023 mole) of the azide in 45 ml. of decalin was heated to 170–180°. Nitrogen evolution commenced at 160° and became vigorous at 180°. After ten to fifteen minutes there were no more signs of gas evolution and the solution was allowed to cool. Immediately a mixture of α- and γ-carbolines (VIII, IX), m.p. 175–190°, precipitated. The weight of the crude mixture after washing with petroleum ether and air drying was 0.35 g. (94%).

α-Carboline (VIII) was found to be relatively insoluble in hot 30% aqueous methanol and was separated by filtration. After several recrystallizations from methanol and from ben-

zene a small amount of material was obtained with m.p. constant at 212–213°.[18,19]

Evaporation of the mother liquor to the cloudy point produced a mixture of α- and γ-carbolines which was separated by filtration. Recrystallization from benzene–petroleum ether (b.p. 60–75°) separated the less soluble γ-isomer (IX). Several recrystallizations from benzene finally gave a small amount of colorless prismatic needles, m.p. 226–228°.[18,20] A mixed melting point with the product of m.p. 212–213° showed a marked depression.

Picrates of the two isomers were prepared by adding a saturated ether solution of picric acid to benzene solutions of the free bases. Immediate precipitation occurred in each case. Both picrates form fine, canary yellow needles. γ-Carboline picrate was recrystallized in aqueous ethanol to a constant m.p. of 262–264°.[19] α-Carboline picrate was recrystallized from ethanol and from benzene until the m.p. was constant at 266–270°.[17] A mixed melting point determination showed no depression.

Chromatographic adsorption on an 8-g. magnesol–celite column 20 cm. in length and 12 mm. in diameter provided a more quantitative separation of the two isomers. A solution of 0.17 g. of crude mixture of α- and γ-carbolines in 150 ml. of reagent benzene was applied to the column and followed by two 200-ml. portions of reagent benzene. Two fluorescent bands were soon detected. After all of the solution had been added, a brilliant light blue fluorescence in the top inch of the column, a light yellow-green fluorescence in the next four inches, and no fluorescence in the remainder of the column was easily detected by ultraviolet light. Evaporation of the first 150 ml. of percolate left no residue. The following 200 ml. of percolate then brought about complete removal of the lower band. Evaporation left a white crystalline residue which weighed 0.08 g. (47%), m.p. 212–214°, and was recrystallized without loss in weight from aqueous methanol from which it separated as long, white needles, m.p. 215–216°. This was then assumed to be α-carboline (see above). The next 200 cc. of percolate completely removed the blue fluorescent band. Evaporation of this case left a white, crystalline solid which weighed 0.04 g. (23%), m.p. 225–227°, and was recrystallized without loss in weight from benzene–petroleum ether from which it separated as long, white needles, m.p. 225–227°. This was assumed to be γ-carboline (see above). Based on the total recovery from the column (0.12 g.), which represents 70% of the starting material, it appears that ring closure involved predominantly (65–70%) the α-position of the pyridine ring. Again a mixed melting point determination of the two isomers showed large depression. Application of more eluent and increasing the polarity of eluent by adding increasing amounts of the ethanol in benzene brought down no more of either isomer. Absolute ethanol did bring down some of the adsorbent through the column, resulting in residue following evaporation.

Well-formed crystals of each of the two isomers were then submitted to Mr. Marion Denny of the Mineralogy Department, University of Michigan, for determination of the following indices of refraction (±0.002) at 25°, which are useful in characterizing these isomers: α-carboline, α < 1.54, β 1.556, γ 1.695; γ-carboline, α < 1.53, β 1.535, γ 1.664.

benzoic acid gives up exactly two-thirds of its azide nitrogen under these conditions. No carbon monoxide could be detected by allowing the evolved gas to bubble through a hydrochloric acid solution of cuprous chloride.

Anal. Calcd. for $C_7H_5N_3O_2$: $^2/_3$ azide N, 17.2. Found $^2/_3$ N, 16.9.

(16) M. O. Forster and H. E. Fierz, *J. Chem. Soc.*, **91**, 1942 (1907).

(17) L. Vignon and E. Evieux, *Bull. soc. chim. France*, [4] **3**, 1027 (1908).

(18) W. Lawson. W. H. Perkin, Jr., and R. Robinson, *J. Chem. Soc.*, **125**, 626 (1924).

(19) K. Elter, *Monatsh.*, **79**, 17 (1948).

(20) R. Robinson and S. Thornley, *J. Chem. Soc.*, **125**, 2169 (1924).