[CONTRIBUTION FROM AVERY LABORATORY, UNIVERSITY OF NEBRASKA]

Cinnolines. II. 4-Hydroxy-3-nitrocinnoline and Derivatives[1,2]

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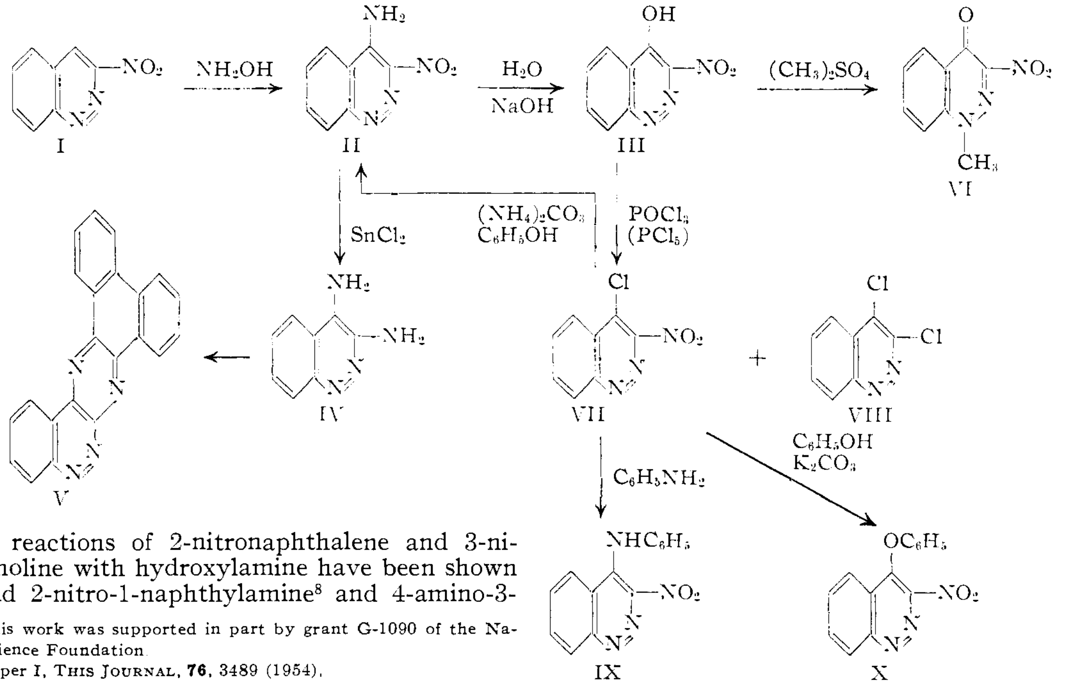
The reaction of 3-nitrocinnoline with hydroxylamine yielded 4-amino-3-nitrocinnoline and alkaline hydrolysis of the latter gave 4-hydroxy-3-nitrocinnoline, the properties of which were in substantial agreement with those of a nitro-4-hydroxycinnoline obtained by Schofield and Simpson[3] as one product in the nitration of 4-hydroxycinnoline. Several derivatives of 4-hydroxy-3-nitrocinnoline and of 4-amino-3-nitrocinnoline are described, including the previously inaccessible 3,4-diaminocinnoline.

Schofield and Simpson[3] have reported that the nitration of 4-hydroxycinnoline gave, depending upon the conditions, as many as three isomeric mononitro-4-hydroxycinnolines, two of which have been shown to be 6-nitro-4-hydroxycinnoline[3] and 8-nitro-4-hydroxycinnoline.[4] To the third isomer, obtained in largest yield when the nitration was carried out at 50° in the absence of sulfuric acid, tentatively has been assigned the structure 3-nitro-4-hydroxycinnoline (III) on the basis of the non-identity of the substance with authentic 5-, 6-, 7- or 8-nitro-4-hydroxycinnoline.[5,6] Inasmuch as the third isomer may play a role of some importance in any complete description of the nitration of heterocyclic systems,[5,7] we have undertaken and report here the unambiguous synthesis of III. In the first paper[2] of this series we described a synthesis of 3-nitrocinnolines from *o*-aminoaryl compounds, which, however, was not successful when applied to anthranilic acid, the substance which might have yielded III directly. The present preparation of III started from 3-nitrocinnoline (I), a substance readily prepared by the earlier synthesis.



The reactions of 2-nitronaphthalene and 3-nitroquinoline with hydroxylamine have been shown to yield 2-nitro-1-naphthylamine[8] and 4-amino-3-nitroquinoline,[9] respectively. Application of this reaction to I gave 4-amino-3-nitrocinnoline (II) in 50–62% yield. The identity of II was established by reduction with stannous chloride and hydrochloric acid to 3,4-diaminocinnoline (IV) in 76% yield and condensation of the latter with phenanthrenequinone to form 9,10,11,16-tetraazotribenzo[*a,c,h*]anthracene (V). The identification of V was based on analysis and the display of the halochromy in concentrated sulfuric acid said to be characteristic of many quinoxaline derivatives.[10]

The preparation of IV is of interest *per se*, for earlier attempts to prepare 3,4-diaminocinnolines by the ammonolysis of 3,4-dihalocinnolines were unsuccessful.[11]

Although we first contemplated the replacement of the amino group in II by hydroxyl through treatment of II with nitrous acid, attempts to bring about this exchange in dilute or concentrated hydrochloric or sulfuric acids, at low or high temperatures, gave unsatisfactory results, no significant amount of III being formed. However, warming II with dilute aqueous potassium hydroxide

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[1] This work was supported in part by grant G-1090 of the National Science Foundation

[2] Paper I, THIS JOURNAL, **76**, 3489 (1954).

[3] K. Schofield and J. C. E. Simpson, *J. Chem. Soc.*, 512 (1945).

[4] J. C. E. Simpson, *ibid.*, 237 (1947).

[5] K. Schofield and T. Swain, *ibid.*, 1367 (1949).

[6] K. Schofield and R. S. Theobald, *ibid.*, 204 (1949).

[7] K. Schofield, *Quart. Revs.*, **4**, 382 (1950).

[8] J. Meisenheimer and E. Patzig, *Ber.*, **39**, 2533 (1906).

[9] M. Colonna and F. Montanari, *Gazz. chim. ital.*, **81**, 744 (1951).

[10] J. C. E. Simpson, "Condensed Pyridazine and Pyrazine Rings," Interscience Publishers, Inc., New York, N. Y., 1953, p. 203.

[11] K. Schofield and T. Swain, *J. Chem. Soc.*, 392 (1950).

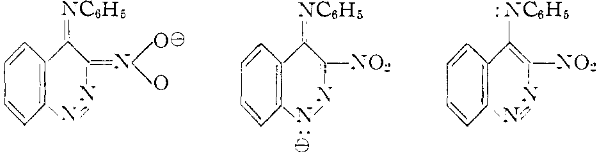
brought about the rapid hydrolysis of II to III in 75–83% yield. Comparison of the melting point and infrared spectrum of our III with the melting point and infrared spectrum of the original nitration product obtained by Schofield and Simpson[3] indicated that the two substances were identical.[12] Definite identification of III as a nitration product of 4-hydroxycinnoline lends support to the suggestion of Schofield and Swain[5] that the nitrations of 4-hydroxycinnoline and 4-hydroxyquinoline at higher temperatures in the absence of sulfuric acid may follow similar paths, yielding in part products nitrated in the hetero ring, although the reasons for such nitration remain obscure.[7]

The reaction of III with methyl sulfate in alkaline solution gave a substance to which has been assigned tentatively the structure 1-methyl-3-nitro-4-cinnolone (VI) based on the behavior of the other isomeric nitro-4-hydroxycinnolines.[3,6]

The course of the reaction of III with phosphorus oxychloride showed a considerable dependence on the reaction conditions. Thus, treatment of III with *aged* phosphorus oxychloride at 95° for 15 to 20 minutes gave 4-chloro-3-nitrocinnoline (VII) in 50–67% yields, whereas with *aged* phosphorus oxychloride and phosphorus pentachloride III reacted rapidly to give a mixture of at least two products, VII and 3,4-dichlorocinnoline (VIII) (identified by its melting point and by preparation from it of the known 3-chloro-4-phenoxycinnoline[13]).[14,15] Furthermore, when VII was heated with aged phosphorus oxychloride and phosphorus pentachloride at 110° for three hours, VIII was formed in 87% yield, indicating that replacement of the 3-nitro group may have (and probably did) occur after replacement of the hydroxyl group. This replacement of the 3-nitro group by chlorine in VII is reminiscent of the replacement of a 6-nitro group by chlorine in 7-chloro-6-nitro-4-hydroxycinnoline[15] and of the replacement of a 3-bromo group by chlorine in several compounds[12] under similar conditions.

The reaction of VII with phenol and ammonium carbonate gave II in essentially quantitative yield. This behavior is different from that of the other nitro-4-hydroxycinnolines studied previously,[6,17,18] which gave under similar conditions only the 4-phenoxy derivatives or, in a single instance,[16] a mixture of the 4-amino and the 4-phenoxy derivatives. 3-Nitro-4-phenoxycinnoline (X) could be prepared in rather poor yield by treatment of VII with phenol and potassium carbonate (or potassium hydroxide).

The reaction of VII with aniline gave 4-anilino-3-nitrocinnoline (IX) in 72% yield. Compound IX dissolved readily in cold 10% aqueous potassium hydroxide, forming a bright red solution from which IX could be recovered essentially unchanged on acidification. This interesting behavior suggests that IX forms a potassium salt, the anion of which might be represented by a hybrid of several structures, among which may be



Experimental[19]

4-Amino-3-nitrocinnoline (II).—To a stirred mixture of 5.0 g. (0.028 mole) of 3-nitrocinnoline,[2] 12.5 g. (0.18 mole) of hydroxylamine hydrochloride and 300 ml. of 95% ethanol in a flask placed in a water-bath at 27° was added dropwise over a period of 0.5 hour a filtered solution of 25 g. (*ca.* 0.38 mole) of potassium hydroxide in 100 ml. of methanol. Addition of the methanolic potassium hydroxide caused the temperature of the bath to rise to 30°. At this point the solution contained a voluminous precipitate and was bright orange-red in color. (Addition of this precipitate and solution to water yielded none of the desired product but gave an amorphous precipitate after standing 24 hours.) The solution was heated with stirring to 50° and held at that temperature for 0.5 hour. The bath was removed and stirring was continued for 0.5 hour. The mixture of red-brown solution and precipitate was poured into 1.5 l. of ice and water mixture. After standing one hour the cold mixture was filtered, and the crude, yellow product was dried *in vacuo*, giving 3.4 g. (64%) of crude 4-amino-3-nitrocinnoline, m.p. 302–304°. In three similar experiments the crude yields were 50, 56, 62%; in three experiments using three times the above quantities the yields were 50, 50, 55%. The crude material could be used satisfactorily for the preparation of 4-hydroxy-3-nitrocinnoline.

The product was not very soluble in the following organic solvents, which are listed in the order of decreasing solvent power: ethanol, ethyl acetate, methanol, acetone, benzene, chloroform. The product was best purified by dissolution in refluxing ethanol, in which it dissolved only very slowly and to the extent of about 0.15 g. per 100 ml. of hot solvent followed by *rapid* chilling of the solution in ice. The above preparation gave 2.7 g. (50%) of pure 4-amino-3-nitrocinnoline, m.p. 308–308.5°, as a yellow, cottony solid, which under the microscope appeared as tiny yellow needles. On the Kofler hot-stage the needles underwent a characteristic change of crystal form at 289–291° to large flat plates melting at 305–306°.

Anal. Calcd. for $C_8H_6N_4O_2$: C, 50.53; H, 3.18; N, 29.46. Found: C, 50.42; H, 3.00; N, 29.32.

3,4-Diaminocinnoline (IV).—To a mixture of 2.0 g. (0.011 mole) of 4-amino-3-nitrocinnoline in 40 ml. of concd. hydrochloric acid was added a solution of 10.0 g. (0.044 mole) of stannous chloride dihydrate in 25 ml. of concd. hydrochloric acid. The resultant suspension was heated gently on the steam-bath for two hours, poured onto crushed ice, made alkaline with 275 g. of cold 33% potassium hydroxide, chilled and filtered. The pale yellow prod-

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[12] We are deeply indebted to Dr. K. Schofield both for making a comparison of the two products in his own laboratory and for sending us a sample of the original nitration product.

[13] K. Schofield and T. Swain, *J. Chem. Soc.*, 384 (1950).

[14] After treatment of III with *fresh* phosphorus oxychloride at 120° for two hours, III could be recovered quantitatively unchanged. With *fresh* phosphorus oxychloride and phosphorus pentachloride VII could be obtained somewhat more slowly, in somewhat lower yield and at the expense of some decomposition. The variability in the activity of phosphorus oxychloride with age had been observed earlier by A. Albert and W. Gledhill, who found that hydroxyacridines reacted more readily with the aged than with the fresh reagent. They attributed the difference in activity to the presence of phosphoric acid in the aged reagent. Whether or not this explanation is entirely correct, in the present work the addition of a *small* amount of sirupy phosphoric acid to a mixture of III and fresh phosphorus oxychloride did enhance the reactivity of the latter, although the result was not quite as satisfactory as that obtained with naturally aged phosphorus oxychloride. In a limited series of experiments the similar addition of polyphosphoric acid to fresh phosphorus oxychloride appeared to have no beneficial effect.

[15] A. Albert and W. Gledhill, *J. Soc. Chem. Ind.*, **64**, 169 (1945).

[16] J. R. Keneford, J. S. Morley and J. C. E. Simpson, *J. Chem. Soc.*, 1702 (1948).

[17] J. R. Keneford, K. Schofield and J. C. E. Simpson, *ibid.*, 358 (1948).

[18] J. R. Keneford and J. C. E. Simpson, *ibid.*, 354 (1948).

[19] Microanalyses by Clark Microanalytical Laboratory, Urbana, Ill. Melting points, which are corrected, were taken using hard glass capillaries in an internally, electrically heated Hershberg apparatus with a rate of heating of 1–2° per minute unless otherwise specified.

uct was dried *in vacuo*. The crude product, 1.6 g. (94%), was recrystallized from 70 ml. of water (charcoal), giving 1.3 g. (76%) of 3,4-diaminocinnoline, m.p. 220–220.5° dec. For analysis a sample was recrystallized a second time from water and dried to constant weight, the melting point being unchanged.

Anal. Calcd. for $C_8H_8N_4$: C, 59.99; H, 5.04; N, 34.98. Found: C, 59.51; H, 4.83; N, 35.13.

A mixture of 20 mg. of the above product and 26 mg. of phenanthrenequinone in 1 ml. of glacial acetic acid was heated on the steam-bath for one hour, cooled and filtered. The orange solid was recrystallized from 3 ml. of pyridine, giving 30 mg. (72%) of 9,10,11,16-tetraazatribenz[*a,c,h*]-anthracene, m.p. 315–316°, identical with that described below.

A mixture of 0.50 g. (0.0026 mole) of 4-amino-3-nitrocinnoline and 2 g. (0.009 mole) of stannous chloride dihydrate in 8 ml. of 1 *N* hydrochloric acid was heated for five hours on the steam-bath. The mixture was diluted to 200 ml. with distilled water and the resultant solution was saturated with hydrogen sulfide. The filtered solution was evaporated to dryness at 40° under reduced pressure and the crude product was washed onto a filter with ether, giving 0.41 g. (80%) of crude bright yellow **3,4-diaminocinnoline monohydrochloride**, m.p. 316–317° dec. A 0.2-g. portion of the product was recrystallized from 15 ml. of absolute ethanol giving 0.09 g. of bright yellow crystals, m.p. 320–321.5° dec.

Anal. Calcd. for $C_8H_9N_4Cl$: C, 48.86; H, 4.61; N, 28.50. Found: C, 48.45; H, 4.23; N, 27.92.

9,10,11,16-Tetraazatribenz[*a,c,h*]anthracene (V).—A suspension of 0.20 g. (0.001 mole) of crude 3,4-diaminocinnoline hydrochloride, 0.6 g. of fused potassium acetate and 0.20 g. (0.001 mole) of phenanthrenequinone in 10 ml. of glacial acetic acid was heated on the steam-bath for one hour, during which time orange needles slowly separated from solution. The cooled solution was filtered and the orange solid was washed with water, giving 0.16 g. (50%) of bright orange needles, m.p. 312–315.5°. The product was twice recrystallized from 10 ml. of pyridine (charcoal), giving 0.08 g. of 9,10,11,16-tetraazatribenz[*a,c,h*]anthracene, m.p. 315.5–316°, as bright orange needles. The product was soluble in hot pyridine, slightly soluble in hot benzene, ethanol, dioxane and ethyl acetate and insoluble in hot acetone and petroleum ether. With concd. sulfuric acid the compound gave a red-violet color (changing to a fine red precipitate on standing) on the spot plate.

Anal. Calcd. for $C_{22}H_{12}N_4$: C, 79.50; H, 3.64; N, 16.86. Found: C, 80.03; H, 3.71; N, 16.64.

4-Hydroxy-3-nitrocinnoline (III).—A suspension of 5.0 g. (0.026 mole) of 4-amino-3-nitrocinnoline in a solution of 5 g. (0.13 mole) of sodium hydroxide in 75 ml. of water was heated on the steam-bath for one hour. The amino compound dissolved slowly in the hot alkaline solution, giving a deep red solution (acidification of this red solution gave a very impure and difficultly purified product) which slowly changed in color to yellow or yellow-orange. The hot solution was treated with charcoal, filtered and chilled. Acidification of the solution with acetic acid and collection and drying of the precipitate gave 4.6 g. (92%) of crude 4-hydroxy-3-nitrocinnoline, m.p. 274–278°, as a pale yellow solid. Similar experiments using the same proportions of reagents gave crude yields of 85–99%. Recrystallization of the crude product from 275 ml. of 95% ethanol (charcoal) gave 3.4 g. (69%) of pure 4-hydroxy-3-nitrocinnoline, m.p. 284.5–285.5°, as light yellow needles. By working up the ethanolic filtrate an additional 0.4 g. (8%) of product could be recovered.

Anal. Calcd. for $C_8H_5N_3O_3$: C, 50.46; H, 2.77; N, 21.71. Found: C, 50.27; H, 2.64; N, 21.98.

A sample of 4-hydroxy-3-nitrocinnoline obtained from the nitration of 4-hydroxycinnoline[3,12] was compared with the above product. The nitration product was in the form of pale brown needles (which, under the microscope, differed little in appearance from the yellow product obtained in this work) and melted in our apparatus at 278–279.5° dec.[20] A 1:1 mixture of the two products softened at 279° and melted at 283.5–284.5° dec.[21] The infrared spectra of the two compounds determined on Nujol mulls were identical, both compounds showing peaks at 655 (w), 720 (w), 740 (w), 765 (m), 812 (m), 859 (m), 892 (m), 920 (m), 1150 (m), 1170 (m), 1227 (m), 1245 (m), 1258 (m), 1271 (m), 1326 (s), 1346 (s), 1365 (s), 1436 (s), 1495 (s), 1538 (s), 1588 (s), 1606 (s), 1638 (m) and *ca.* 3160 cm.$^{-1}$. The ultraviolet spectrum of the product prepared in this work was determined on a 10^{-4} *M* solution of the product in 95% ethanol using a Cary recording spectrophotometer and displayed the following maxima (log ϵ), 210 mμ (4.30), 334 mμ (4.05); inflection points, 235 mμ (4.01), 263 mμ (3.46), 346 mμ (3.96) and minimum, 282 mμ (325).[22]

1-Methyl-3-nitro-4-cinnolone (VI).—To a solution of 1.20 g. (0.0063 mole) of 4-hydroxy-3-nitrocinnoline and 1.4 g. of potassium hydroxide (*ca.* 0.02 mole) in 150 ml. of water heated to 50° on the steam-bath was added 3 ml. of dimethyl sulfate in 1-ml. increments with vigorous stirring. The precipitated product was collected by filtration, washed with 5% potassium hydroxide and with water and recrystallized from 200 ml. of ethanol (charcoal), giving 0.77 g. (59%) of pale yellow needles, m.p. 232.5–233.5°. Another experiment using one-half the above quantities gave a crude yield of 0.45 g. (71%) and purified yield of 0.26 g. (41%) of 1-methyl-3-nitro-4-cinnolone. The product darkened rapidly on exposure to light.

Anal. Calcd. for $C_9H_7N_3O_3$: C, 52.68; H, 3.44; N, 20.48. Found: C, 52.70; H, 3.35; N, 20.58.

Reaction of III with Phosphorus Oxychloride.—The aged phosphorus oxychloride used in these experiments was taken from an imperfectly sealed bottle that had been stored for some time (as evidenced by corrosion of the label, paper wrapper and interior of the protective metal can). This material was a pale yellow in color. The fresh phosphorus oxychloride came from a bottle showing no evidence of leakage and was a colorless liquid.

In Table I are listed the quantities of reactants and the essential reaction variables for some typical experiments, all of which were conducted using the following procedure. The mixture of reactants was heated under reflux in the oil-bath for the specified time. In experiments using aged phosphorus oxychloride the solids dissolved giving a clear yellow solution in five minutes or less. In experiments using fresh phosphorus oxychloride and phosphorus pentachloride the solids dissolved in 15 to 30 minutes giving a tan to dark brown solution. After the heating period the solution was chilled and poured onto crushed ice. The mixture was stirred vigorously until the excess phosphorus oxychloride was decomposed, neutralized to congo red with solid sodium acetate and filtered. The dried solid[23] was recrystallized from Skellysolve C,[24] using 20 ml. of solvent for each 0.1 g. of 4-chloro-3-nitrocinnoline or for each 0.6 g. of 3,4-dichlorocinnoline. The two products could be separated fairly readily by fractional crystallization from this solvent.

An analytical sample of **4-chloro-3-nitrocinnoline (VII)** was prepared by recrystallizing one sample of product, m.p. 168–169°, twice from Skellysolve C, giving pale yellow needles, m.p. 169–170°. On the hot-stage the compound sublimed at *ca.* 140°, forming nearly perfect rhombic plates, m.p. 169–170°. Although the compound was stable toward storage for short periods, after five months the above sample melted at 153–163°.

Anal. Calcd. for $C_8H_4N_3O_2Cl$: C, 45.85; H, 1.92; N, 20.05. Found: C, 46.29; H, 2.35; N, 19.78.

A mixture of 0.75 g. (0.0036 mole) of crude 4-chloro-3-nitrocinnoline (m.p. 164–168°), 1.0 g. of phosphorus pentachloride and 5 ml. of aged phosphorus oxychloride was heated under reflux at 110° for three hours, cooled, poured on ice, neutralized and worked up as described above, giving 0.73 g. of crude product. Recrystallization of the latter

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(20) The melting points of both materials were depressed when determinations were made in carefully washed soft glass capillaries. The yellow crystals melted at 276–277° dec. and the brown crystals at 275–276° dec.

(21) Dr. Schofield reported to us the following uncorrected m.p.'s: yellow crystals, 272–274°; brown crystals, 274–275°; mixture, 272–274°.

(22) We are indebted to Miss E. M. Shelton for the determination of the infrared and ultraviolet spectra.

(23) Preferably dried in the vacuum desiccator. Although the solid could be dried in the oven, the hot solid evolved vapors that were quite irritating to the skin.

(24) A hydrocarbon solvent, b.p. 88–98°.

TABLE I

REACTION OF III WITH PHOSPHORUS OXYCHLORIDE

III, g.	PCl_5, g.	$POCl_3$, ml.[a]	Temp., °C.	Time, min.	Crude yield, g.	Purified yield, %	M.p. of prod., °C.[b]
0.75	..	8 (F)	120	120[c]	0.75	99	284-285[d]
.30	..	3 (A)	95	20	.29	67	167-169.5
.75	..	8 (A)	95	30	.73	60	167.5-169.5
.30	..	3 (A)	100	45	.30	55	164-168
.30	0.5	3 (A)	95	10	.29	49	168-169
1.00	2.5	10 (A)	120	30	1.04	27	135-160
						52	122-125
0.75	1.0	5 (A)	110	180	0.73	83	128-129
.90	1.0	10 (F)	120	90	..	56	169-170
.20	0.2	2 (F)	120	90	..	46	169-170
.30	..	2 (F)	95	20	0.32	46	164-168
		2 (A)					
.30	[e]	3 (F)	100	40	0.30	55	154-160
.30	[f]	3 (F)	100	30	..	43	160-164

[a] A = aged $POCl_3$; F = fresh $POCl_3$. [b] Mixed m.p. experiments showed that products with m.p. greater than 160° were largely (more than 80%) 4-chloro-3-nitrocinnoline; those with m.p. less than 140° were largely (more than 80%) 3,4-dichlorocinnoline. [c] Solid did not dissolve during heating. [d] Recovered III. [e] Heated 15 min., then five drops of phosphoric acid (85%) added dropwise at 5 min. intervals. [f] Five drops of phosphoric acid (85%) added at beginning and five drops after 15 min.

from 25 ml. of Skellysolve C (charcoal) gave 0.62 g. (87%) of 3,4-dichlorocinnoline as snow-white needles, m.p. 128–129° (lit.[13] m.p. 126–127°). For identification the latter was converted to the known 3-chloro-4-phenoxycinnoline. A mixture of 0.35 g. of potassium carbonate and 1.5 g. of phenol was heated to 120° (oil-bath) and 0.51 g. of 3,4-dichlorocinnoline was added. The mixture was heated at 120° for one hour, diluted with a solution of 1.5 g. of potassium hydroxide in 20 ml. of water and filtered. The dried solid product was twice recrystallized from 20 ml. of Skellysolve C, giving 0.16 g. of 3-chloro-4-phenoxycinnoline, m.p. 127–128° (lit.[13] m.p. 120–121°).

Anal. Calcd. for $C_{14}H_9N_2OCl$: C, 65.50; H, 3.61; N, 10.92. Found: C, 65.70; H, 3.82; N, 10.87.

Reaction of VII with Ammonium Carbonate and Phenol.—A mixture of 0.30 g. (0.0014 mole) of 3-chloro-4-nitrocinnoline, 1.0 g. of ammonium carbonate and 2.5 g. of phenol was warmed gently until reaction with evolution of gas started. After the initial reaction subsided, the mixture was heated at 90° for 0.5 hour, poured into a cold solution of 1.5 g. of sodium hydroxide in 30 ml. of water and filtered. The solid was washed well with water and dried at 90°, giving 0.27 g. (100%) of yellow powder, m.p. 298–300°. The product was insoluble in hot benzene or hot Skellysolve C. The product was recrystallized from absolute ethanol, giving 0.20 g. (74%) of 4-amino-3-nitrocinnoline, m.p. 305–306°, mixed m.p. with an authentic sample the same.

3-Nitro-4-phenoxycinnoline (X).—A mixture of 0.30 g. (0.0014 mole) of 4-chloro-3-nitrocinnoline, 0.22 g. (0.0016 mole) of potassium carbonate and 0.75 g. of phenol was heated at 100° for 0.5 hour, diluted with a cold solution of 2.0 g. of potassium hydroxide in 50 ml. of water and filtered. The filter cake was washed with 5% potassium hydroxide and dried *in vacuo*. The crude, greenish product, 0.12 g., was recrystallized twice from 20 ml. of Skellysolve C (charcoal), giving 0.081 g. (21%) of 3-nitro-4-phenoxycinnoline, m.p. 144.5–145°, as pale tan plates.

Anal. Calcd. for $C_{14}H_9N_3O$: C, 62.92; H, 3.40; N, 15.72. Found: C, 63.00; H, 3.48; N, 15.42.

In a similar experiment using 0.11 g. (0.0016 mole) of powdered potassium hydroxide instead of potassium carbonate, the crude yield was 0.12 g., the final yield, 0.050 g.

4-Anilino-3-nitrocinnoline (IX).—A mixture of 0.30 g. (0.0014 mole) of 4-chloro-3-nitrocinnoline and 3 ml. of aniline was heated under reflux on the steam-bath for 0.5 hour, chilled in ice and diluted with 9 ml. of dry ether. The yellow precipitate was collected, washed free of aniline hydrochloride with water and dried *in vacuo*, giving 0.30 g. (99%) of yellow crystals, m.p. 186–188°. The product was recrystallized from 20 ml. of ethanol, giving 0.22 g. (72%) of bright yellow needles, m.p. 187–188°.

The above procedure was repeated using 0.40 g. of 4-chloro-3-nitrocinnoline, 4 ml. of aniline and 12 ml. of ether, the crude yield being 0.37 g. (74%). The product was dissolved in 50 ml. of 10% potassium hydroxide at room temperature. (The product dissolved very slowly in more dilute base and decomposed in 33% potassium hydroxide.) The dark red solution was filtered, chilled and acidified with acetic acid. The yellow precipitate was collected, air-dried and recrystallized from 30 ml. of ethanol, giving 0.32 g. (63%) of 4-anilino-3-nitrocinnoline, m.p. 187–188°, as bright yellow needles.

Anal. Calcd. for $C_{14}H_{10}N_4O_2$: C, 63.15; H, 3.79; N, 21.04. Found: C, 63.24; H, 4.14; N, 20.48.

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