Cinnolines. X. The Oxidative-Rearrangement of 1-Aminooxindoles to 3-Cinnolinols (1,2)

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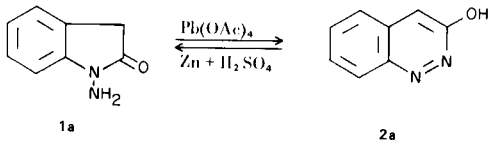
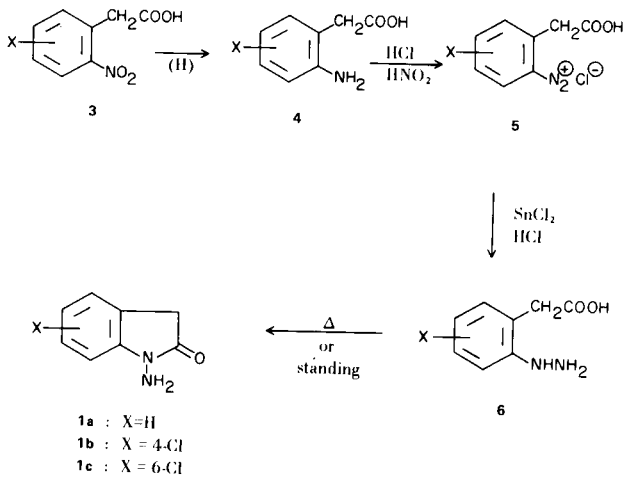
An improved route for the oxidative-rearrangement of 1-aminooxindoles, treatment with equimolar amounts of *t*-butyl hypochlorite, produces nearly quantitative yields of 3-cinnolinols of excellent purity. The syntheses of the previously inaccessible 4- and 6-chloro-1-aminooxindoles has shown that this method, first applied to 1-aminooxindole, may be reasonably general. The mechanism of this reaction is discussed in terms of nitrene and nitrenoid intermediates.

The preparation of 3-cinnolinol (3-cinnolinone) (**2a**) through the action of mercuric acetate (low yield) and lead tetraacetate (78% yield) on 1-aminooxindole (**1a**) and the reductive-rearrangement of **2a** back to **1a** with zinc and sulfuric acid was reported (3) as part of the reinvestigation of the structure of "Neber's lactam", (**1a**).



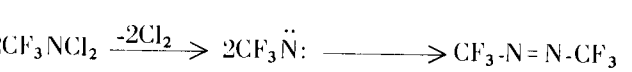
SCHEME I



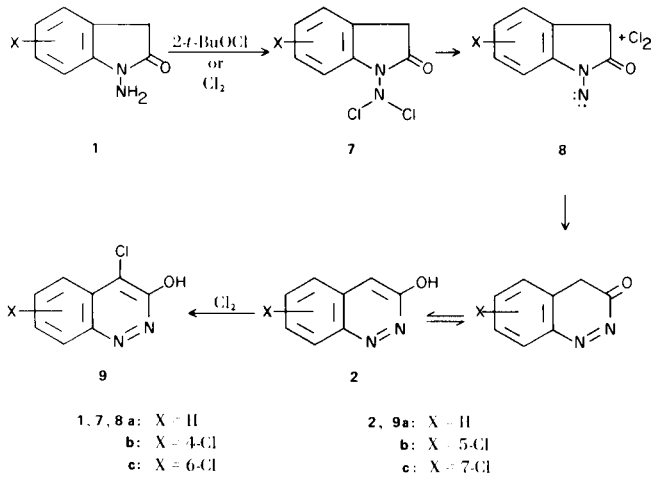
Since the oxidative-rearrangement represented a new synthetic route to the cinnoline nucleus of unknown generality, it was of interest to examine its application to other substituted 1-aminooxindoles and to study the mechanism of the rearrangement.

The parent member of this series, **1a**, is the only reported 1-aminooxindole. Although the general procedure used for the preparation of **1a** (**3** → **1**) (3) ultimately gave 4- and 6-chloro-1-aminooxindole, careful control of experimental conditions was necessary to obtain reproducible results (4). Overall yields of up to 59% of 4-chloro-1-aminooxindole (**1b**) and 55% of 6-chloro-1-aminooxindole (**1c**) (based on the chlorinated *o*-nitrophenylacetic acids) were obtained.

Although previously the oxidative-rearrangement of 1-aminooxindole had been carried out satisfactorily only through action of lead tetraacetate, it seemed possible that the presumed nitrene intermediate (3) could also be generated from a *N,N*-dichloro-1-aminooxindole (**7**), either spontaneously or by the action of a suitable dechlorinating agent as shown in the sequence **1** → **7** → **8** → **2** (See Scheme II). Thus, Chambers, Tullock, and Coffman (6) have reported that *N,N*-dichlorotrifluoromethylamine decomposes spontaneously to perfluoroazomethane, a reaction that can be formulated as proceeding through a nitrene.



SCHEME II



However, when 1a was treated at room temperature with two equivalents of *t*-butyl hypochlorite in benzene, the product was neither the desired dichloroamine, **7a**, nor **2a**. The structure of the bright yellow orange product was established as 4-chloro-3-cinnolinol (**9**) by its elemental analysis, its infrared spectrum, analogy of physical characteristics, and chemical reactions. The infrared spectrum of **9** was analogous to that of the known 3-cinnolinols (3,6) in the characteristic 3100-2700 cm^{-1} and 1695-1600 cm^{-1} regions. The color, high melting point, and solubility properties of **9** were characteristic of known 3-cinnolinols. Treatment of **9** with phosphorus pentachloride or a mixture of phosphorus pentachloride and phosphorus oxychloride gave a very low yield of 3,4-dichlorocinnoline (7). Reduction of **9** with zinc and sulfuric acid gave **1a** in 73% yield. The similar reductions of the 5- and 7-chloro-3-cinnolinols, **2b** and **2c**, yielded the corresponding chloro-1-aminooxindoles *without loss of halogen*. Unfortunately, difficulties encountered in preparing the intermediates necessary for the synthesis of the only unknown benzene-chloro cinnolinol, 8-chloro-3-cinnolinol, precluded the study of the lability of chlorine in the 8-position toward this reduction. However, it seems reasonable that a halogen in the 4-position of the 3-cinnolinol ring would be more susceptible than those in the 5, 6, 7, or 8-positions to reduction during the ring-opening and rearrangement sequence involved in this reaction (3).

The possibility that the chlorine substituent of **9** was bonded in some fashion other than covalently was also tested. Dissolution of **9** in aqueous sodium hydroxide could be followed by reprecipitation with acetic or hydrochloric acids. Similarly, **9** could be recovered quantitatively by neutralization with nitric acid. No silver chloride was obtained.

Finally, it was demonstrated that **2a** was converted to **9** in 70-76% yielded by the action of *t*-butyl hypochlorite. This result suggests that the probable reaction sequence was an oxidative-rearrangement of **1a** followed by attack of positive halogen on the 4-position of **2a**.

When benzene solutions of **1a**, **1b**, or **1c** were treated with equimolar amounts of *t*-butyl hypochlorite, virtually quantitative yields of the respective 3-cinnolinol (**1a**, **2b**, or **2c**) precipitated rapidly from solution after a brief induction period. Infrared spectral and melting point comparisons confirmed the identity of the known 3-cinnolinol (**1a**) and 7-chloro-3-cinnolinol (**2c**). Proof of structure of 5-chloro-3-cinnolinol (**2b**) was based on its infrared spectrum, analogy of physical properties, elemental analysis, method of synthesis, and its conversion back to 4-chloro-1-aminooxindole in 90% yield by zinc-sulfuric acid reduction.

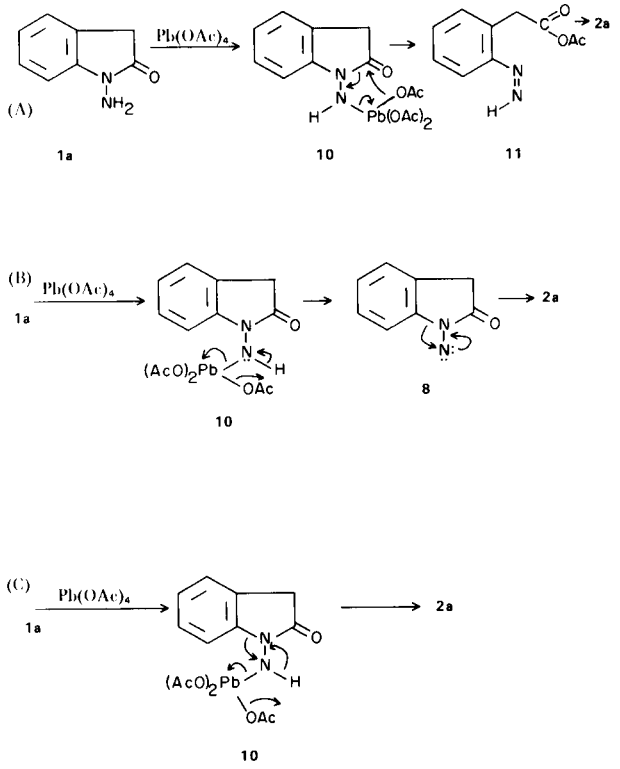
Although a number of other oxidizing agents (8) have been used successfully in the conversion of *N*-amino amides into tetrazene derivatives (8,9) or other products (9) that could arise from nitrene-like intermediates, attempted oxidations of **1a** with mercuric oxide (8), potassium bromate (8), bromine (8), or iodosobenzene diacetate (9) gave either very, very low or no yields of **2a**. Chlorine gas could be substituted for *t*-butyl hypochlorite but in small-scale experiments was less easily added in the required equimolar amount.

In our earlier report (3) two mechanisms for the oxidative rearrangement with lead tetraacetate were suggested. These are shown (sequences A and B, Scheme III) in a somewhat more detailed and modified form based on an extensive study (9) of the oxidative reactions of *N*-amino amides. Although reactions leading to aryl diimides such as **11** (sequence A) are now easily realized, thus far the acylation of such intermediates has not been observed. Instead, the diimide has either lost nitrogen to give the corresponding arene or undergone further oxidation to the diazonium ion (9). Apparently a similar sequence can be obtained with **1a** with certain oxidizing agents (*e.g.*, iodosobenzene diacetate), but the reaction is complex and requires further study.

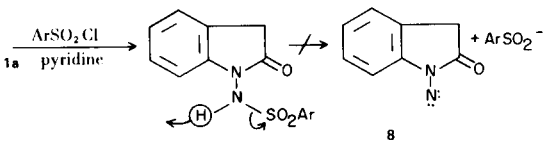
These observations apparently leave sequence B as the preferred mechanism, and this mechanism gains some support from the results of related oxidations (10-14), including recent nitrene trapping experiments (which, however, failed with **1a**). However, much still remains to be learned about intermediates such as **10**; thus, it is perhaps premature to conclude that nitrenes are necessary intermediates in the present (or perhaps other amide or *N*-amino amide) oxidations. It is becoming increasingly

apparent that -Pb(OAc)$_3$ is a good leaving group (15) and many lead tetraacetate reactions may depend on this property. Therefore, it is entirely possible that the rearrangement and loss of -Pb(OAc)$_3$ occur more or less simultaneously and that **10** is serving as a nitrenoid intermediate (sequence C).

SCHEME III



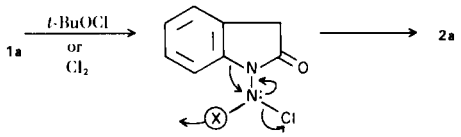
The possibility of a nitrene intermediate was tested by preparing two arene sulfonamides (**11**) of **1a** and subjecting them to base-catalyzed chemical or photochemical treatments of the type used to generate certain acyl nitrenes (16).



11a: Ar = *p*-$CH_3C_6H_4$-
11b: Ar = *p*-$NO_2C_6H_4$-

In none of approximately thirty-five experiments carried out under a variety of conditions was any **2a** formed nor could any nitrene trapping products be obtained by adding various olefins to the system. Somewhat related results have been obtained by Schlosser (17), who failed to generate benzyne in the base-catalyzed decomposition of 1-(*N*-tosylamido)benzotriazole despite the fact that the oxidation of 1-aminobenzotriazole gives excellent yields of benzyne-derived products in a reaction sequence thought to involve a nitrene (10,11). Finally, the elegant trapping experiments (12-14) reported to date, although strongly suggestive, do not completely resolve the question of whether nitrene or nitrenoid intermediates are involved in lead tetraacetate oxidations of some or all *N*-amino amides, for, in the absence of definitive experimental detail, the briefly reported results can be explained on the basis of either intermediate.

A similar ambiguity exists in the *t*-butyl hypochlorite and chlorine oxidations, which could proceed through the *N*,*N*-dichloroamine and a nitrene as shown above or through an *N*-chloroamine (**12a**) or *N*,*N*-dichloroamine (**12b**) acting as a nitrenoid intermediate.



12a: X = H
12b: X = Cl

EXPERIMENTAL (18)

1-Aminooxindole (**1a**).

(a) Reduction of 3-Cinnolinol.

Numerous experiments in this laboratory have shown that the procedure reported earlier (1) can give erratic results. The conditions must be optimized (particularly for the substituted 3-cinnolinols) so that they are sufficiently vigorous to bring about reduction and rearrangement but not so vigorous that the product, 1-aminooxindole, is further reduced to oxindole. The following procedure has been reasonably reliable.

To a solution of 5.9 g. (0.040 mole) of 3-cinnolinol in 240 ml. of absolute ethanol was added 7.0 g. (0.11 g. atom) of zinc dust. The mixture was heated and stirred at the reflux temperature while 113 ml. of 6*N* sulfuric acid was added over a 6-minute period. Heating and stirring were continued until the yellow-green color of the solution became nearly colorless (an additional 15 minutes). The reaction mixture was filtered, and the zinc residue was washed with small portions of hot ethanol. The combined ethanolic solutions were evarporated on a rotary evaporator, 100 ml. of water was added to the residue, and the mixture was made sufficiently basic with concentrated ammonium hydroxide to dissolve the zinc salts. Chilling gave 4.7 g. of a light gray crystalline material, m.p. 128-131° (lit. (3) m.p. 127.5-128°) mixture m.p. with authentic material 126-129°. Extraction of the filtrate with chloroform gave another 0.2 g. of product (total crude yield, 4.9 g. (85%)). This product was sufficiently pure for most purposes but could be recrystallized from benzene or sublimed.

(b) Reduction of 4-Chloro-3-cinnolinol.

A mixture of 1.00 g. (0.0055 mole) of 4-chloro-3-cinnolinol, 0.79 g. (0.012 g. atom) of zinc dust and 40 ml. of ethanol was stirred vigorously and heated to reflux, and 20 ml. of 6*N* sulfuric acid was added dropwise in 2 minutes. The yellow color of the mixture disappeared after about 10 minutes and the mixture was allowed to stir an additional 20 minutes. Filtration gave no zinc residue. The solution was diluted with 10 ml. of water and evaporated in the rotary evaporator at 50° to remove most of the ethanol. The remaining solution was chilled, and concentrated ammonium hydroxide was added to bring the *p*H to about 10. The yellow-orange product was collected by filtration and dried, 0.73 g. (89%). The product had an infrared spectrum identical with that of 1-aminooxindole. Sublimation of this crude material gave 0.60 g. (73%) of 1-aminooxindole, m.p. 126° (lit. (3) m.p. 127.5-128°).

3-Cinnolinol (**2a**).

(a) From *o*-Nitrobenzaldehyde.

3-Cinnolinol for use as a starting material was prepared by the procedure of Alford and Schofield (7).

(b) Oxidative-rearrangement of 1-Aminooxindole.

A solution of 0.50 g. (0.0034 mole) of 1-aminooxindole in 250 ml. of dry benzene was stirred while a solution of 0.36 g. (0.0034 mole) of *t*-butyl hypochlorite in 100 ml. of benzene was added dropwise but rapidly. During the addition a yellow-orange precipitate began to form. Stirring was continued for a total reaction time of 25 minutes. A quantitative yield of crude product was collected by filtration. The product was recrystallized from ethanol (60-72% recovery) or (with less ease) benzene. Its infrared spectrum corresponded to that of an authentic sample of 3-cinnolinol (3).

4-Chloro-1-aminooxindole (**1b**).

(a) From 6-Chloro-2-nitrophenylacetic Acid.

The precedure developed used the method of McKenzie and Stewart (19) for the reduction of the aromatic nitro group in the presence of halogen and a modification of the procedure used by Baumgarten, Creger, and Zey (3), for the remainder of the synthesis (4). To a mixture of 10 g. (0.046 mole) of 6-chloro-2-nitrophenylacetic acid (20) and 22 g. (0.070 mole) of barium hydroxide octahydrate was added, with stirring, 500 ml. of boiling water, followed by a solution of 84 g. (0.30 mole) of ferrous sulfate heptahydrate in 80 ml. of boiling water and a suspension of 108 g. (0.34 mole) of barium hydroxide octahydrate in 300 ml. of boiling water. The brown sludge was heated at the reflux temperature and stirred for 3 hours, then filtered with difficulty. The chocolate brown residue was extracted with two 200-ml. portions of boiling water, and the combined pale yellow solutions were saturated with carbon dioxide gas. The white barium carbonate precipitate was removed by filtration, and the filtrate was evaporated by boiling to a volume of about 300 ml. A solution of 3 g. (0.06 mole) of sodium carbonate dissolved in a minimum amount of water was added, and the barium carbonate precipitate was removed by filtration. The solution was evaporated to a final volume of about 150 ml.

To 75 ml. of concentrated hydrochloric acid chilled to -1° by an ice-salt bath was added slowly through an ice-salt cooled, jacketed addition funnel the cold (-1°) solution of sodium 6-chloro-2-aminophenylacetate and 4.06 g. (0.059 mole) of sodium nitrite with stirring and monitoring of the temperature of the reaction mixture (maintained below 3°). Stirring was continued for 35 minutes after the completion of the addition; then the solution was filtered through a prechilled (dry ice) apparatus to remove small amounts of decomposition product.

The solution of the diazonium chloride was added dropwise through the ice-salt cooled, jacketed addition funnel to a vigorously stirred, pre-chilled (0°) solution of 35 g. (0.16 mole) of stannous chloride dihydrate in 75 ml. concentrated hydrochloric acid. Cooling was maintained by an ice-salt bath while the mixture was stirred for an additional hour. The solution was allowed to stand at room temperature overnight. The yellow-white product which had precipitated was collected by filtration. When sublimed (in several small batches) the product yielded 4.97 g. (59% based on 6-chloro-2-nitrophenylacetic acid) of pale yellow solid m.p. 175-179°. Recrystallization for analysis of this product (which was suitable without purification for further reactions) could be carried out in benzene or ethanol (charcoal) to give white needles, m.p. 183°; ir (chloroform) cm^{-1}, 3340 (NH); 1719 (C=O); (potassium bromide), 3325 (NH), 3280 (NH) 1718 (C=O), 1625 (NH_2).

Anal. Calcd. for $C_8H_7ClN_2O$: C, 52.60; H, 3.87; N, 15.33. Found: C, 52.63; H, 3.98; N, 15.15.

(b) Reduction of 5-Chloro-3-cinnolinol.

4-Chloro-1-aminooxindole was prepared in 91% yield (crude, m.p. 176-178°) by the procedure described above for the reduction of 4-chloro-3-cinnolinol. Its spectrum was essentially identical with that of the analytical sample.

6-Chloro-1-aminooxindole (**1c**).

(a) From 4-Chloro-2-nitrophenylacetic Acid (21).

The procedure used was similar to that used for the preparation of 4-chloro-1-aminooxindole. The best yield obtained was 55% of sublimed product, m.p. 164-166°. When recrystallized from ethanol, then benzene (charcoal) for analysis, this product formed white needles, m.p. 168-169°; ir (potassium bromide) cm^{-1}, 3310 (NH), 3270(NH), 1710(C=O), 1630 (NH_2).

Anal. Calcd. for $C_8H_7ClN_2O$: C, 52.60; H, 3.87; N, 15.33; O, 8.76; Cl, 19.44. Found: C, 52.88; H, 3.97; N, 15.17; O, 8.99; Cl, 19.30.

(b) Reduction of 6-Chloro-3-cinnolinol.

6-Chloro-1-aminooxindole was prepared in 90% crude yield, m.p. 162-163°, (60% sublimed yield) by the procedure described above for the reduction of 4-chloro-3-cinnolinol. Its infrared spectrum was identical with that of an authentic sample.

5-Chloro-3-cinnolinol (**2b**).

(a) Oxidative-Rearrangement of 4-Chloro-1-aminooxindole.

The method described above for the oxidative-rearrangement of 1-aminooxindole gave a 95-98% yield of crude, bright yellow product, m.p. 263°. Recrystallization from absolute ethanol (charcoal) gave 60-72% yield of 5-chloro-3-cinnolinol, m.p. 268°; ir (potassium bromide) cm^{-1}, 2770 broad (NH), 1650 (C=O). The infrared spectra of the crude and recrystallized products were identical.

Anal. Calcd. for $C_8H_5ClN_2O$: C, 53.20; H, 2.79; N, 15.51; O, 8.86; Cl, 19.63. Found: C, 53.46; H, 3.04; N, 15.28; O, 9.01; Cl, 19.08.

(b) Treatment of 4-Chloro-1-aminooxindole with Chlorine.

A solution of 0.22 g. (0.0012 mole) of 4-chloro-1-aminooxindole in 55 ml. of benzene was stirred magnetically and treated

with chlorine gas. When a precipitate began to form, chlorine addition was stopped, and separation of product by filtration gave 0.18 g. (82%) of crude 5-chloro-3-cinnolinol. The product was recrystallized from absolute ethanol (70% recovery) to give a sample whose infrared spectrum was identical with that of an authentic sample of 5-chloro-3-cinnolinol.

7-Chloro-3-cinnolinol (**2c**).

(a) Oxidative-Rearrangement of 6-Chloro-1-aminooxindole.

The method described above for the oxidative-rearrangement of 1-aminooxindole gave a 94-98% yield of crude bright yellow product, m.p. 253°. Recrystallization from absolute ethanol (charcoal) gave 61-71% yield of 7-chloro-2-cinnolinol, m.p. 255° dec. (lit. (22) m.p. 256°). An infrared spectrum of the product was essentially identical with that of an authentic sample (6).

(b) Treatment of 6-Chloro-1-aminooxindole with Chlorine.

A solution of 0.078 g. (0.00043 mole) of 6-chloro-1-aminooxindole in 10 ml. of benzene was stirred magnetically and treated with chlorine gas. When a precipitate began to form, chlorine addition was stopped. Separation of the precipitate by filtration gave 0.053 g. (68%) of crude product. Recrystallization from ethanol gave bright yellow needles (72% recovery) whose infrared spectrum (Nujol) corresponded to that of an authentic sample of 7-chloro-3-cinnolinol.

4-Chloro-3-cinnolinol (**9**).

(a) Treatment of 1-Aminooxindole with *t*-Butyl Hypochlorite.

To a stirred solution of 1.0 g. (0.0066 mole) of 1-aminooxindole in 100 ml. of benzene was added (in *ca.* 1 minute) a solution of 1.43 g. (0.0132 mole) of *t*-butyl hypochlorite in 50 ml. of benzene. Stirring was continued over 0.5 hour and the solution was allowed to stand overnight. The bright yellow product was collected by filtration, 1.1 g. (93%), m.p. 205-210°. Four recrystallizations of a portion of this material from large quantities of benzene (or smaller quantities of ethanol) produced yellow needles, m.p. 220°, whose infrared spectrum was virtually identical with that of the crude product: (chloroform) cm^{-1} 3360 (NH), 2850 broad (NH), 1660 (C=O); (potassium bromide) cm^{-1} 2830 broad (NH), 1642 (C=O).

Anal. Calcd. for $C_8H_5ClN_2O$: C, 53.20; H, 2.79; N, 15.51. O, 8.86; Cl, 19.63. Found: C, 53.31; H, 2.79; N, 15.51; O, 8.59; Cl, 19.61.

(b) Chlorination of 3-Cinnolinol.

To a solution of 30 g. (0.021 mole) of 3-cinnolinol in 1700 ml. of benzene was added dropwise with stirring a solution of 2.5 g. (0.023 mole) of *t*-butyl hypochlorite in 200 ml. of benzene and the mixture was stirred for 3 hours at room temperature. Filtration gave 2.6 g. (70%) of 4-chloro-3-cinnolinol, m.p. 210-212°, infrared spectrum (potassium bromide) identical with that of the analytical sample.

3,4-Dichlorocinnoline.

(a) From 4-Chloro-3-cinnolinol.

A mixture of 0.50 g. (0.0028 mole) of 4-chloro-3-cinnolinol and 5.0 g. (0.024 mole) of phosphorus pentachloride was stirred, heated in an oil bath (bath temperature 155°) for 8 hours, chilled, and pured over ice. The solution was brought to *p*H 11 (with external cooling) by addition of 50% sodium hydroxide solution. The solution was extracted with three 200-ml. portions of ethyl ether, and the ether solution was dried (magnesium sulfate) and evaporated on a steam bath. White needles formed on the side of vessel, although most of the residue was a black tar. These white crystals of 3,4-dichlorocinnoline, m.p. 126.5° (lit. (22) m.p. 128-129°), had an infrared spectrum identical with that of an authentic sample prepared according to the reported (23) procedure. Acidification of the alkaline extract gave a 95% recovery of 4-chloro-3-cinnolinol.

N-(*p*-Toluenesulfonyl)-1-aminooxindole (**11a**).

To a mixture of 6.0 g. (0.041 mole) of 1-aminooxindole and 12.2 g. (0.0637 mole) of recrystallized *p*-toluenesulfonyl chloride was added with stirring 30 ml. of pyridine. The solids soon dissolved, and a precipitate gradually formed, until a solid yellowish mass was present. It was necessary to stir this mass vigorously with water (50 ml.) before it became red (a few minutes). The dull orange solid was collected by filtration, washed thoroughly with water, and recrystallized from ethanol (charcoal), yielding 7.42 g. (60%) of fluffy, electrostatically active, snow white solid, m.p. 266°; ir (potassium bromide) cm^{-1}, 3215 (NH), 3150 (NH), 1720 (C=O). Other experiments gave yields in the 60-78% range.

Anal. Calcd. for $C_{15}H_{14}N_2O_3S$: C, 59.59; H, 4.67; N, 9.27. Found: C, 59.99; H, 4.80; N, 9.72.

N-(*p*-Nitrophenylsulfonyl)-1-aminooxindole (**11b**).

A solution of 1.5 g. (0.010 mole) of 1-aminooxindole and 2.7 g. (0.012 mole) of *p*-nitrobenzenesulfonylchloride in 20 ml. of dry pyridine was stirred vigorously at room temperature for a few minutes until a precipitate began to form. Stirring was continued for 5 minutes, 100 ml. of water was added, and the pale yellow crystals were collected by filtration and extracted with ethanol. The ethanol-soluble portion was recovered by evaporation and twice recrystallized from chloroform to yield 0.33 g. (10%) of fluffy white crystals, m.p. 225-226°; ir (potassium bromide) cm^{-1} 3200 (NH), 3150 (NH), 1737 (C=O).

Anal. Calcd. for $C_{14}H_{11}N_3O_5S$: C, 50.40; H, 3.32; N, 12.62; S, 9.61. Found: C, 50.37; H, 3.41; N, 12.45; S, 9.57.

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