collected and crystallized from acetic acid to give 16 g. of **10**, m.p. 240°.

Anal. *Calcd.* for $C_{19}H_{10}O_5$: C, 71.6; H, 3.1. Found: C, 71.4; H, 3.3.

Bindone (12).—A suspension of 2.0 g. of **13** and 2 g. of sodium acetate in 20 ml. of methanol was stirred until the reactants were in solution (about 10 min.), 20 ml. of water was added, and the resulting deep red solution was filtered. The filtrate was refluxed for 1 hr., and the dark precipitate was collected and crystallized from 1,2,4-trichlorobenzene to give 0.9 g. of **12** as dark red crystals, m.p. 310°.

3-(2-Bromo-1,3-dioxoindan-2-yl)-2-hydroxy-1,4-naphthoquinone (13).—A suspension of 10 g. of **10** in 75 ml. of acetic acid containing 2 ml. of bromine was heated to 80°. The mixture solidified after about 5 min. Heating was continued at 90–100° for 1 hr., and the product was collected by filtration and crystallized from a large volume of acetic acid to give 11 g. of **13**,[3] m.p. 240°.

2,2′-Dibromobindone (14).—A suspension of 2 g. of **13** in 15 ml. of 10% methanolic potassium hydroxide was heated under reflux for 0.5 hr., 15 ml. of water was added, and heating was continued for a further 10 min. Acidification of the reaction mixture gave crude bindone, which was brominated in acetic acid solution at 60° to give **14**,[5] m.p. 278°.

3-(1,3-Dioxoindan-2-ylidene)-2-hydroxy-3-methoxy-2,3-dihydro-1,4-naphthoquinone (16).—A suspension of 6 g. of **13** in 600 ml. of methanol was refluxed on the steam bath for 5 hr. and filtered hot to remove a small amount of starting material. The filtrate was cooled to give 3.8 g. of **16**: m.p. 228° (from a mixture of chloroform and methanol); ultraviolet spectrum in acetonitrile, λ_{max}, mμ (ϵ), 231 (76,800), ~250 (26,700), ~290 (2500).

Anal. Calcd. for $C_{20}H_{12}O_6$: C, 69.0; H, 3.5. Found: C, 68.7; H, 3.2.

Acknowledgment.—We gratefully acknowledge the assistance of T. H. Regan and R. L. Young, of these laboratories, for the determination and interpretation of the n.m.r. spectra which were determined by using a Varian A-60 spectrometer at the ambient probe temperature, 35°. The polarographic data were supplied by D. G. Bush, also of these laboratories, to whom we are also indebted.

Nitration of Indoles. IV. The Nitration of 2-Phenylindole[1]

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Nitration of 2-phenylindole (**1**) follows the orientation rules previously established for 2-methylindole, except that trinitration has not been observed. Thus, nitration of **1** in concentrated sulfuric acid gives 5-nitro-2-phenylindole (**8**), while nitration of **1** in concentrated nitric acid gives 3,6-dinitro-2-phenylindole (**4**) and further nitration of **8** in concentrated nitric acid gives 3,5-dinitro-2-phenylindole (**9**). Catalytic hydrogenation of **8** gives 5-amino-2-phenylindole (**12**). The nitration product of 2-phenylisatogen (**13**) and nitric acid has been shown to be 5-nitro-2-phenylisatogen (**14**), an observation of interest because of the structural resemblance of **13** to the conjugate acid (**15**) of **1**.

In 1900 Angeli and Angelico[3] reported the preparation of a dinitro-2-phenylindole (**4**) by nitrosation of 2-phenylindole (**1**) to 2-phenyl-3H-indol-3-one oxime (**2**), followed by *in situ* nitration (accompanied by oxidation) with nitric acid in acetic acid. Alternatively (see Chart I), **4** could be obtained from 3-nitro-2-phenylindole (**3**), isolated from a prior oxidation of **2**, by warming **3** with nitric acid in acetic acid. These reactions establish that one of the nitro groups in **4** is in the 3-position of the indole nucleus. In 1938 Womack, Campbell, and Dodds[4] showed that **4** could best be obtained by direct nitration of **1** with concentrated nitric acid. Attempted further nitration of **4** to a trinitro derivative of **1** was unsuccessful, giving either unchanged **4** or, under the more vigorous conditions of boiling concentrated nitric acid, oxidation to acidic compounds, from which a small amount of N-benzoyl-5-nitroanthranilic acid (**10**) was reported[4] to have been isolated. Furthermore, oxidative degradation of **4** with potassium permanganate in acetic acid gave a product (m.p. 257–258°) which was said[4] to be "identical" with a sample (m.p. 257–260°) of N-benzoyl-5-nitroanthranilic acid (**10**) prepared from authentic 5-nitroanthranilic acid.[5] Consequently, Womack, Campbell, and Dodds[4] assigned to their dinitro derivative the structure (incorrect, see below) 3,5-dinitro-2-phenylindole, and drew the further inference (now disproved[1]) that the dinitro derivative of 2-methylindole,[6] formed under similar conditions, was 3,5-dinitro-2-methylindole.

Since the orientation claimed (3,5)[4] for nitration of **1** was at variance with that which we have observed (3,6)[1] for nitration of 2-methylindole under similar conditions (concentrated nitric acid), and since the melting point observed[4] for the oxidation product of **4** is also similar to that reported (m.p. 251° dec.,[7] 252°[8]) for N-benzoyl-4-nitroanthranilic acid (**5**), the expected oxidation product of 3,6-dinitro-2-phenylindole, we repeated the oxidative degradation of **4**. Our sample of the oxidation product (m.p. 248.5–251°) of **4** was identical, as shown by infrared and mixture melting point comparison, with a sample of N-benzoyl-4-nitroanthranilic acid (**5**) prepared[7] by oxidation of 5′-nitro-*o*-benzotoluidide (**7**), but depressed (233–247°) the melting point of N-benzoyl-5-nitroanthranilic acid (**10**). Furthermore, our sample of **5** from oxidation of **4** was decarboxylated to the known 3′-nitrobenzanilide (**6**), prepared[9] by benzoylation of *m*-nitroaniline. Thus, the

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(1) Paper III: W. E. Noland, L. R. Smith, and K. R. Rush, *J. Org. Chem.*, **30**, 3457 (1965).

(2) Taken in part from (a) K. R. Rush, Ph.D. Thesis, University of Minnesota, Sept. 1963; *Dissertation Abstr.*, **25**, 2241 (1964); National Science Foundation Graduate Fellow, 1961–1963; and (b) L. R. Smith, 1960, research not included in his Ph.D. Thesis; Dow Chemical Co. Fellow, 1959–1960.

(3) (a) A. Angeli and F. Angelico, *Gazz. chim. ital.*, **30**, II, 268 (1900); (b) A. Angeli, *Samml. Chem. Chem.-Tech. Vortr.*, **17**, 311 (1912).

(4) E. B. Womack, N. Campbell, and G. B. Dodds, *J. Chem. Soc.*, 1402 (1938).

(5) M. T. Bogert and G. Scatchard, *J. Am. Chem. Soc.*, **41**, 2066 (1919).

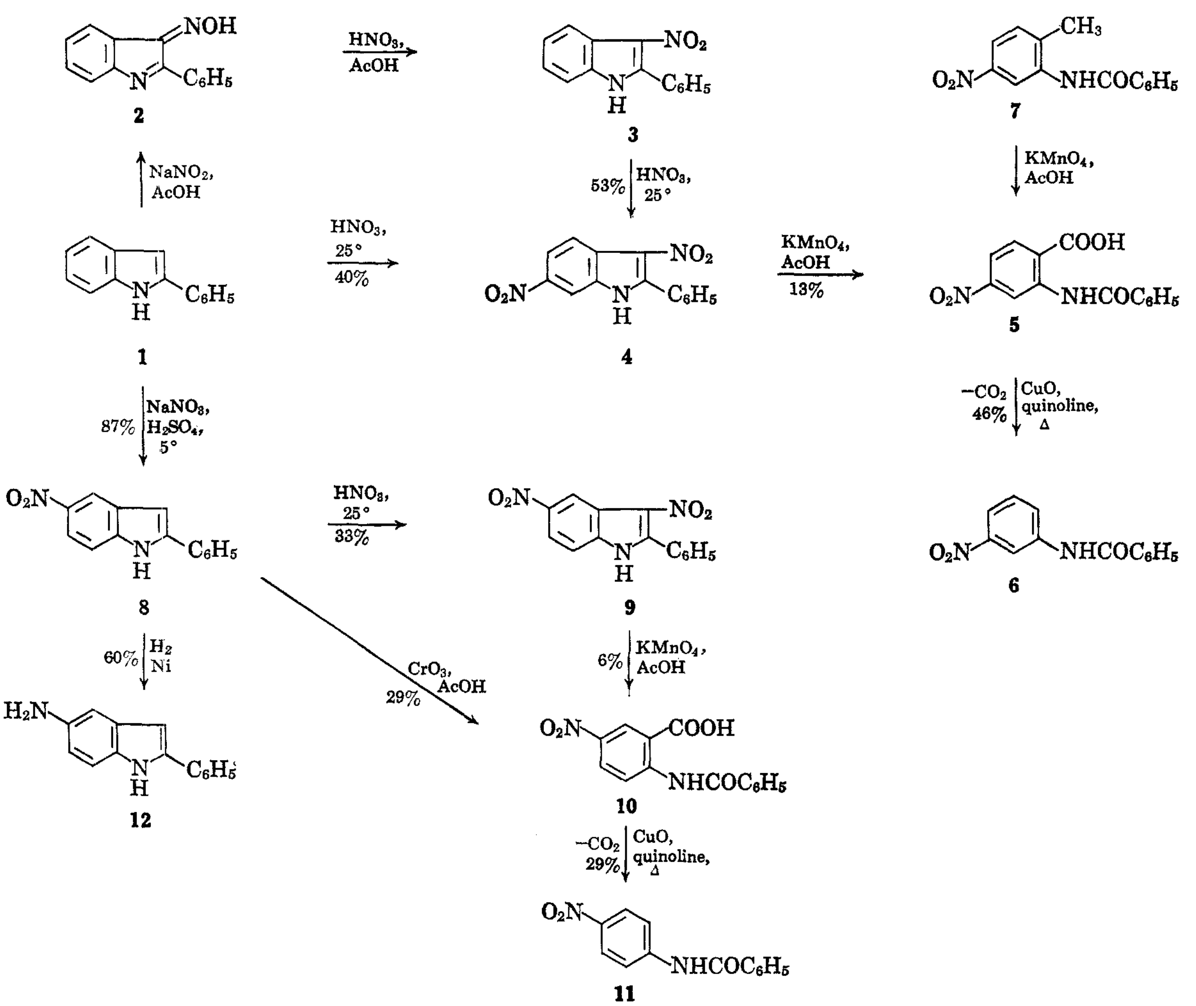
(6) R. von Walther and J. Clemen, *J. prakt. Chem.*, [2] **61**, 249 (1900).

(7) P. Ruggli, A. Zimmerman, and O. Schmid, *Helv. Chim. Acta*, **16**, 1249 (1933).

(8) P. Ruggli and W. Leonhardt, *ibid.*, **7**, 898 (1924).

(9) (a) C. A. Bell, *Chem. Ber.*, **7**, 497 (1874); (b) F. Sachs and M. Goldman, *ibid.*, **35**, 3342 (1902).

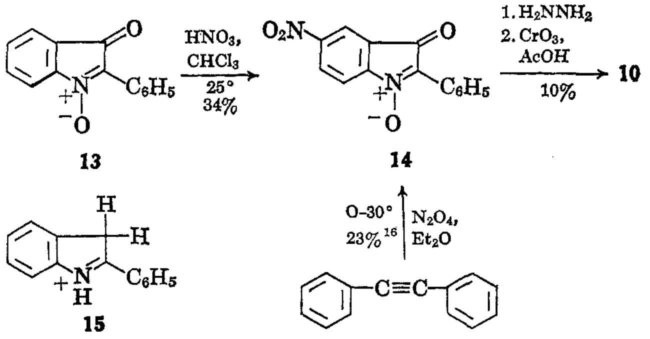
CHART I



structure of **4** is now shown to be 3,6-dinitro-2-phenylindole.[10] The fact that 2-phenylindole (**1**) nitrates at room temperature in concentrated nitric acid, while 2-methylindole and 1,2-dimethylindole must be warmed to initiate the reaction promptly,[1] is attributed to the lower basicity of **1** relative to the 2-methylindoles,[11] which would leave a larger proportion of **1** unprotonated and available for nitration.

Nitration of 2-phenylindole in concentrated sulfuric acid[12] gave 5-nitro-2-phenylindole (**8**). The structure of **8** was established by oxidation to N-benzoyl-5-nitroanthranilic acid[4] (**10**) and subsequent decarboxylation of **10** to the known 4'-nitrobenzanilide (**11**), prepared[13] by benzoylation of *p*-nitroaniline. Hydrogenation of **8** gave the known 5-amino-2-phenylindole[14] (**12**). Nitration of **8** in concentrated nitric acid gave 3,5-dinitro-2-phenylindole (**9**). The structure of **9** was established by oxidation to **10**, identical with the sample from oxidation of **8**.

Nitration of 2-phenylisatogen (**13**) in chloroform solution with a second phase of concentrated nitric acid containing a few drops of sulfuric acid is reported[15] to produce a yellow-gold mononitro derivative of m.p. 220°. Subsequently, Campbell, Shavel, and Campbell,[16] evidently unaware of the earlier work of Bakunin and Vitale,[15] isolated from the reaction of diphenylacetylene with dinitrogen tetroxide a deep orange-red compound (m.p. 238–239°), which they proved to be 5-nitro-2-phenylisatogen (**14**) by reduction with hydrazine and oxidation with chromic anhydride



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(10) The "ethyl ether" of **4**, m.p. 221°,[3] is, therefore, now assumed to be 1-ethyl-3,6-dinitro-2-phenylindole. Since **4** is the only dinitro-2-phenylindole which had been described up to that time, it is assumed that the "2-phenyl-3,5-dinitroindole" referred to (without indication of source) in the reference cited below is really **4** and should be reformulated as 3,6-dinitro-2-phenylindole: J. F. Gaddum, K. A. Hameed, D. E. Hathway, and F. F. Stephens, *Quart. J. Exptl. Physiol.*, **40**, 49 (1955).

(11) The pK_a of the conjugate acid of 2-phenylindole in perchloric acid based on the H_I acidity function is -1.76 ± 0.04 (S. P. Hiremath, M. M. Kreevoy, and W. E. Noland, University of Minnesota, 1965). This compares with pK_a values of -0.28 ± 0.01 for 2-methylindole and $+0.30 \pm 0.01$ for 1,2-dimethylindole [R. L. Hinman and J. Lang, *J. Am. Chem. Soc.*, **86**, 3796 (1964)].

(12) Paper II: W. E. Noland, L. R. Smith, and D. C. Johnson, *J. Org. Chem.*, **28**, 2262 (1963).

(13) A. Kaufmann, *Chem. Ber.*, **42**, 3480 (1909).

(14) R. Adams and W. P. Samuels, Jr., *J. Am. Chem. Soc.*, **77**, 5375 (1955).

(15) M. Bakunin and T. Vitale, *Rend. Accad. Sci. Fis. Mat.* (Soc. Naz. Sci. Napoli), [3] **33**, 270 (1927); *Chem. Abstr.*, **23**, 2969 (1929).

(16) K. N. Campbell, J. Shavel, Jr., and B. K. Campbell, *J. Am. Chem. Soc.*, **75**, 2400 (1953).

and acetic acid to **10**. We have also obtained **10** by application of this degradation procedure to our sample (orange, m.p. 240–243°) of the nitration product[15] of 2-phenylisatogen, thus establishing that the nitration has occurred in the 5-position. This orientation of nitration (in a medium consisting largely of nitric acid) is of interest, because of the structural resemblance of 2-phenylisatogen (**13**) to the conjugate acid **15** of 2-phenylindole, which is assumed by analogy with 2-methylindole[1,12] to be the form in which 2-phenylindole undergoes 5-nitration in concentrated sulfuric acid. Kamlet and Dacons[17] have presented convincing ultraviolet evidence that 2-phenylindoles are fully protonated at the 3-position in 85% phosphoric acid, concentrated sulfuric acid, and in concentrated hydrochloric acid. In addition, and of great significance to the orientation of nitration of 2-phenylindoles, they have shown that in substituted 2-phenylindoles, with protonation at the 3-position, the 5-position becomes the conjugated position, whereas in neutral media the 2-phenylindoles substituted at the 4- (or 6-) positions absorbed at the longer wave lengths.[17]

The nitration of 2-phenylindole (**1**) follows the orientation rules previously established for 2-methylindole,[1,12] except that trinitration has not been observed. Our results also agree with the results and conclusions recently reported[18] for the nitration of other phenyl-substituted indoles. Thus, where nitration is assumed to involve the unprotonated indole,[1,12,18] nitration occurs with concentrated nitric acid at the 3- and 6-positions in 2-phenylindole (**1**) and at the 3-position in 5-nitro-2-phenylindole (**8**), and with nitric acid [or copper(II) nitrate[18]] in acetic acid with 2,3-diphenylindole[18,19] or 1-acyl-2,3-diphenylindoles.[20] In concentrated sulfuric acid, where nitration involves the 3-protonated indole,[1,12,18] nitration occurs at the 5-position in 2-phenylindole (**1**) and in 3-methyl-2-phenylindole,[18] and first at the *para* position of the 3-phenyl substituent and then at the 5-position of 2,3-diphenylindole[18] and 2-methyl-3-phenylindole.[18] In agreement with the findings of Da Settimo and Saettone,[18] we have not observed any nitration of the 2-phenyl substituent in either concentrated nitric or sulfuric acids.

An improved procedure for the polyphosphoric acid catalyzed preparation of 2-phenylindole is described in the Experimental Section.

Experimental Section

Melting points were determined on calibrated hot stages. Where not specified, the drying agent used for organic solutions was anhydrous magnesium sulfate. Except where otherwise specified, the petroleum ether used was the fraction, b.p. 60–68° (Skellysolve B).

2-Phenylindole (1) (With Michael Jarcho, 1965).—The polyphosphoric acid catalyzed cyclization[21] is better than the older zinc chloride method.[22] When applied on a scale as large as 1 mole, however, the polyphosphoric acid method produced a violent and uncontrollable eruption. Consequently, the procedure has been modified[23] to allow for a gradual addition of acetophenone phenylhydrazone to maintain the reaction temperature at 160 ± 5°.

Acetophenone (120 g., 1.00 mole) and phenylhydrazine (110 g., 1.02 moles) were warmed in a 250-ml. beaker on a steam bath. After 15 min., about 40 ml. of the resulting partially molten acetophenone phenylhydrazone was then added, with stirring, to polyphosphoric acid (470 g.) in a 1-l., three-necked, round-bottomed flask equipped with a thermometer and mechanical stirrer. Stirring was continued, and the resulting mixture was warmed in a hot-water bath for about 5 min. until the temperature reached 110–120°. At this point the exothermic reaction became vigorous, and the temperature rose at the rate of about 1°/sec. The hot-water bath was removed, and, when the temperature reached 155°, an ice bath was applied. After the flask had been cooled with the ice bath for about 15 sec., the temperature stabilized at 160° and the ice bath was removed. Whenever the temperature dropped below 160°, additional portions (about 5–10 ml. each) of the partially molten phenylhydrazone were added, with continuous stirring, at a rate such that the reaction temperature was maintained at 160 ± 5°.

After addition of the phenylhydrazone was complete (about 30 min. after the onset of the reaction), stirring was continued and the flask was heated at 160° with a heating mantle for 1 hr. The hot solution was then poured into a dry 3- or 4-l. beaker, and allowed to cool to at least 30–40°. A mixture of ice and water (total 2 l.) was added, with stirring. The mixture was then warmed on a steam bath and stirred to break up the solid mass. After being allowed to cool to room temperature, the mixture was filtered and the solid was washed on the filter until the washings were only mildly acidic (pH 5–6, as measured by pH paper). To remove the black tarry substance dispersed in the greenish white solid product, the product was dissolved in a minimum amount of ether (more than 1 l. is required); the tar congealed and was removed with a stirring rod. Water (1 l.) was then added to the ether solution, and the ether was evaporated by warming the mixture gently on a steam bath. The solid dispersed in the water was filtered off and dried under reduced pressure at 65–70° overnight, giving 2-phenylindole as a greenish white solid (189 g., 98%), m.p. 190–192° (uncor.).

A similar run, carried out on one-half the scale, gave an 89% yield, m.p. 184–186° (uncor.).

Purification of 2-Phenylindole (1).[2a]—For purification, nonpolar solvents, such as benzene, alkanes, or carbon tetrachloride[24] are advantageous. The following illustrates the procedure. 2-Phenylindole (7.45 g.) was dissolved in boiling benzene (125 ml.) and the solution was treated with charcoal (2–3 g.) and filtered. Boiling petroleum ether (400 ml.) was added, and the solution was then cooled in an ice bath. Filtration removed a light yellow powder, which was redissolved in boiling benzene (60 ml.), and the solution was treated with charcoal (1 g.) and filtered. Boiling petroleum ether (350 ml.) was added, and the solution was then cooled in an ice bath. Filtration gave white crystals (2.02 g., 27%), m.p. 188–189°. The combined filtrates from the two crystallizations were concentrated by distillation until crystals formed. Cooling completed separation of the light yellow powder, which was redissolved in boiling benzene (50 ml.), and the solution was treated with charcoal (1 g.) and filtered. Boiling petroleum ether (300 ml.) was added, and the solution was then cooled in an ice bath. Filtration gave additional white crystals (1.77 g., 24%), m.p. 188–189°, lit.[22] m.p. 188–189°. The total yield of purified 2-phenylindole was 3.79 g. (51%).

2-Phenyl-3H-indol-3-one oxime (2)[2b,25] was observed to be orange with m.p. 276–278° dec.; it has been reported to be yellow,

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(17) M. J. Kamlet and J. C. Dacons, *J. Org. Chem.*, **26**, 220 (1961).

(18) A. Da Settimo and M. F. Saettone, *Tetrahedron*, **21**, 823 (1965).

(19) D. A. Kinsley and S. G. P. Plant, *J. Chem. Soc.*, 1 (1958).

(20) (a) R. C. G. Fennel and S. G. P. Plant, *ibid.*, 2872 (1932); (b) K. Schofield and R. S. Theobald, *ibid.*, 1505 (1950).

(21) H. M. Kissman, D. W. Farnsworth, and B. Witkop, *J. Am. Chem. Soc.*, **74**, 3948 (1952).

(22) R. L. Shriner, W. C. Ashley, and E. Welch, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 725; *Org. Syn.*, **22**, 98 (1942). Among the 18 students who have carried out this zinc chloride procedure in the Advanced Organic Laboratory course at the University of Minnesota, the median yields were acetophenone phenylhydrazone, 76 ± 13% (average deviation), and 2-phenylindole, 43 ± 28%, or 33 ± 27% from acetophenone and phenylhydrazine.

(23) The modified procedure was first employed by E. H. Jancis in this laboratory in 1964.

(24) Charles F. Hammer, Ph.D. Thesis, University of Minnesota, May 1959; *Dissertation Abstr.*, **21**, 1060 (1960).

(25) (a) R. Möhlau, *Chem. Ber.*, **15**, 2480 (1882); **18**, 163 (1885); (b) E. Fischer, *Ann. Chem.*, **236**, 126 (1886); (c) E. Fischer and T. Schmitt, *Chem. Ber.*, **21**, 1071 (1888); (d) M. Spica and F. Angelico, *Gazz. chim. ital.*, **29**, II, 49 (1899); (e) V. Castellana and A. D'Angelo, *Atti Reale Accad. Lincei Rend. Classe Sci. Fis. Mat. Nat.*, [5] **14**, II, 145 (1905); *Chem. Zentr.*, II, 899 (1905); (f) L. Kalb and J. Bayer, *Chem. Ber.*, **45**, 2150 (1912); (g) N. Campbell and R. Cooper, *J. Chem. Soc.*, 1208 (1935).

m.p. 244°,[25a] 250°,[25d] 258° dec.,[25c] or orange, m.p. 280° dec.[25g] The spectrum showed $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$, mμ (log ε), 264 (4.69), 334 (3.64), 389 (3.60); ν^{Nujol} 2620–2480 (OH) (mw) (broad) cm.$^{-1}$; lit.[25g] $\lambda_{\max}^{\mathrm{abs\ EtOH}}$, mμ (log ε), ~268 (4.2), ~338 (3.6), ~397 (3.5).

3-Nitro-2-phenylindole (3)[2b,3a,4,26] had $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$, mμ (log ε), 229 (infl.) (4.21), 261 (4.32), 359 (3.93); ν^{Nujol} 3230 (m) (OH or NH), no NO_2 at ~1525, but at 1365 (s) (partly Nujol) or 1335 (ms) cm.$^{-1}$.

3,6-Dinitro-2-phenylindole (4).[2b] **A. From 2-Phenylindole.**—The procedure is similar to that of Womack, Campbell, and Dodds,[4] who erroneously believed their product, obtained in unstated yield, to be 3,5-dinitro-2-phenylindole. 2-Phenylindole (1.30 g., 0.00673 mole) was added in small portions, with shaking, to concentrated nitric acid (*d* 1.42, 50 ml.) at room temperature (26°). Ice–water was then added, and the mixture was filtered. The filtered solid was dissolved in aqueous 20% potassium hydroxide solution and reprecipitated by addition of concentrated hydrochloric acid. Recrystallization from ethanol–water (or better from acetone) yielded yellow crystals (0.76 g., 40%): m.p. 318–320° (reported as yellow plates, m.p. >280°,[3a] 312° dec.[4]); $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$, mμ (log ε), 225 (4.28), 302 (4.32), 338 (4.24), 414 (infl.) (3.40); ν^{Nujol} 3170 (m) (NH), 1520 (m), 1346 (s) (NO_2) [or 1375 (m), 1328 (ms), or 1310 (m)] cm.$^{-1}$.

B. From 3-Nitro-2-phenylindole.—This reaction has been carried out previously in unstated yield by action of excess concentrated nitric acid in acetic acid solution on a steam bath.[3a] 3-Nitro-2-phenylindole (0.30 g., 0.00126 mole) was added to concentrated nitric acid (*d* 1.42, 40 ml.) and the mixture was kept at room temperature (26°) for 0.5 hr. Ice–water (200 ml.) was added, and the mixture was filtered. The tan solid was recrystallized from ethanol–water, yielding yellow crystals (0.19 g., 53%), m.p. 318–320°. There was no depression in mixture melting point with the sample prepared from 2-phenylindole, and the infrared spectra in Nujol were identical.

Oxidative Degradation of 3,6-Dinitro-2-phenylindole (4).[2a]—The procedure is essentially that of Womack, Campbell, and Dodds,[4] who erroneously believed that they were oxidizing 3,5-dinitro-2-phenylindole to N-benzoyl-5-nitroanthranilic acid, obtained in unstated yield. Potassium permanganate (6.00 g., 0.0380 mole) was added to a solution of 3,6-dinitro-2-phenylindole (2.00 g., 0.00706 mole) in acetic acid (130 ml.). The mixture was refluxed for 4 hr., and then poured into water, decolorized with sodium sulfite, and extracted with ether. The ether extracts were extracted with aqueous saturated sodium bicarbonate solution until carbon dioxide was no longer evolved. Evaporation of the ether left unchanged 3,6-dinitro-2-phenylindole (0.32 g., 16% recovery). The sodium bicarbonate extracts were acidified to pH 2 with concentrated hydrochloric acid and extracted with ether, and the ether extracts were dried and evaporated. Recrystallization of the residue from benzene–petroleum ether (b.p. 90–100°) yielded **N-benzoyl-4-nitroanthranilic acid (5)** as whitish crystals (0.23 g., 13% based on unrecovered starting material): m.p. 248.5–251° [reported as light yellow leaflets, m.p. 251° dec. (rapid heating),[7] m.p. 252°,[8] 257–258°[27]]; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$, mμ (log ε), 272 (4.44), 344 (3.50); ν broad and diffuse NH, 3430 (m) (broad), 2610 (w) (OH) in KBr, 2550 (w) (OH) in Nujol, 1710 (ms), 1650 (ms) (C=O in KBr, 1698 (ms), 1644 (ms) (C=O) in Nujol, 1534 (s), 1350 (s) (NO_2) in KBr, 1528 (s), 1347 (ms) (NO_2) cm.$^{-1}$ in Nujol; an anomalous spectrum, apparently that of a dimorph, was also obtained in KBr—ν broad and diffuse NH, 3430 (m) (broad), 2600 (w) (OH), 1680 (ms), 1644 (w) (C=O), 1516 (s), 1349 (ms) (NO_2) cm.$^{-1}$. There was no depression in mixture melting point, 249–251°, with a sample of m.p. 251–252° prepared[7] by oxidation of 5′-nitro-*o*-benzotoluidide, and the infrared spectra in Nujol and ultraviolet spectra in 95% ethanol were identical.

The mixture melting point with N-benzoyl-5-nitroanthranilic acid of m.p. 257–259° was depressed, 233–247°.

5′-Nitro-*o*-benzotoluidide (7).[2a]—Preparation of this compound has been reported previously,[7] but the ratios of reactants, melting point, elemental analyses, and spectral data were not given. Benzoyl chloride (5.00 g., 0.0356 mole) was added dropwise to a boiling solution of 5-nitro-*o*-toluidine (5.00 g., 0.0328 mole) and pyridine (2 ml.) in benzene (50 ml.). The solution was boiled for 0.5 hr. and then decanted from the pyridine hydrochloride layer and the solution was cooled. The precipitate which formed was filtered and recrystallized from acetone, yielding white needles (6.15 g., 73%): m.p. 186–187° (an "almost quantitative" yield was reported[7]); $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$, mμ (log ε), 236–248 (plateau) (4.23); ν^{Nujol} 3230 (ms) (NH), 1641 (s) (C=O), 1525 (s), 1348 (s) (NO_2) cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{12}N_2O_3$ (256.25): C, 65.62; H, 4.72; N, 10.93. Found: C, 65.75; H, 4.58; N, 11.09.

Decarboxylation of N-Benzoyl-4-nitroanthranilic Acid (5).[2a]—A mixture of N-benzoyl-4-nitroanthranilic acid (0.13 g., 0.00045 mole, derived from oxidative degradation of 3,6-dinitro-2-phenylindole) and copper(II) oxide (0.08 g., 0.0010 mole) in quinoline (15 ml.) was refluxed for 3 hr. The mixture was cooled and poured onto a mixture of concentrated hydrochloric acid (50 ml.) and crushed ice. The mixture was then filtered and the filtrate was extracted with ether. The ether was evaporated and the white crystalline residue was recrystallized from methanol, giving red-orange flakes, the color of which was not diminished by repeated recrystallization from methanol. Sublimation conditions at 100° (1 mm.) for 0.5 hr. left a residue in which the color of the flakes had changed from red-orange to yellow. Recrystallization of the yellow flakes from methanol yielded **3′-nitrobenzanilide (6)** as white flakes (0.05 g., 46%): m.p. 155–156°; lit.[9a] m.p. 152°; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$, mμ (log ε), 262 (4.40), 324 (infl.) (3.28); ν^{Nujol} 3310 (m) (NH), 1659 (s) (C=O), 1520 (s), 1353 (s) (NO_2) cm.$^{-1}$. There was no depression in mixture melting point, 155–156°, with a sample of m.p. 155–156°, prepared by benzoylation[9] of *m*-nitroaniline in benzene solution containing pyridine and purified by extraction with hydrochloric acid and aqueous sodium bicarbonate solutions, followed by recrystallization from methylene chloride–petroleum ether. The infrared spectra of the two samples in Nujol were identical.

5-Nitro-2-phenylindole (8).[2a]—Purified 2-phenylindole is necessary for this preparation. A solution of purified 2-phenylindole (3.00 g., 0.0155 mole) in concentrated sulfuric acid (100 ml.) was cooled to 5° in an ice bath. A solution of sodium nitrate (1.40 g., 0.0165 mole) in concentrated sulfuric acid (50 ml.), also cooled to 5°, was added, with swirling. The resulting solution was kept for 5 min. and then poured onto crushed ice. The flocculent yellow precipitate was filtered and dried. Crystallization from methylene chloride–petroleum ether yielded microscopic yellow needles (3.20 g., 87%): m.p. 201–203°; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$, mμ (log ε), 223 (infl.) (4.15), 297 (4.60), 341 (infl.) (4.01); ν^{Nujol} 3360 (ms) (NH), 1510 (m), 1331 (s) (NO_2) cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_{10}N_2O_2$ (238.24): C, 70.58; H, 4.23; N, 11.76. Found: C, 70.33; H, 4.20; N, 11.52.

Oxidative Degradation of 5-Nitro-2-phenylindole (8).[2a]—A solution of chromium(VI) oxide (10.0 g., 0.100 mole) in water (10 ml.) was added to a solution of 5-nitro-2-phenylindole (2.00 g., 0.00838 mole) in acetic acid (100 ml.). The solution was refluxed for 6 hr. and then poured into water. The resulting precipitate was filtered off and the filtrate was extracted with ether. The ether was evaporated, water was added to the residual acetic acid solution, and the resulting precipitate was filtered off. The two precipitates were dried and crystallized from benzene, yielding **N-benzoyl-5-nitroanthranilic acid (10)** as white crystals (0.70 g., 29%): m.p. 258–259°; lit. (light yellow crystals) m.p. 255–256°,[16] 257–260°[4]; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$, mμ (log ε) (does not obey Beer's law), at 4.30×10^{-5} *M* 219 (infl.) (4.36), 241 (infl.) (4.23), 328 (4.40), and at 2.58×10^{-5} *M* 219 (infl.) (4.34), 241 (4.24), 330 (4.37); ν broad and diffuse NH and OH, 2590 (m) (OH) in KBr, 1702 (ms), 1664 (ms) (C=O) in KBr, 1700 (ms), 1668 (ms) (C=O) in Nujol, 1519 (s), 1504 (ms), 1349 (s), 1333 (ms) (NO_2) in KBr, 1515 (ms) (infl.), 1350 (s), 1330 (ms) (NO_2) cm.$^{-1}$ in Nujol.

The mixture melting point with N-benzoyl-4-nitroanthranilic acid of m.p. 254–258° was depressed, 233–247°.

Decarboxylation of N-Benzoyl-5-nitroanthranilic Acid (10).[2a]—A mixture of N-benzoyl-5-nitroanthranilic acid (0.28 g., 0.00098 mole, derived from oxidative degradation of 5-nitro-2-phenylindole) and copper(II) oxide (0.13 g., 0.0016 mole) in quinoline (25 ml.) was refluxed for 2 hr. and then worked up as described for the decarboxylation of N-benzoyl-4-nitroanthranilic acid. The residue from evaporation of the ether was crystallized from methanol, yielding **4′-nitrobenzanilide (11)** as white needles (0.07 g., 29%): m.p. 199.5–200.5°; lit.[13] m.p. 197°; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$, mμ (log ε), 231 (4.15), 320 (4.28); ν^{Nujol} 3340 (m) (NH), 1652 (s) (C=O), 1500 (s), 1341 (s) (NO_2) cm.$^{-1}$. There was no depression in mixture melting point, 199.5–200.5°, with a sample

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(26) T. Ajello, *Gazz. chim. ital.*, **69**, 646 (1939).

(27) Erroneously claimed[4] to be the melting point of N-benzoyl-5-nitroanthranilic acid.

of m.p. 199.5–200.5° prepared by benzoylation of *p*-nitroaniline according to the procedure of Kaufmann[13] (except that benzoyl chloride was substituted for benzoic anhydride), and the infrared spectra in Nujol were identical.

5-Amino-2-phenylindole (12).[2a]—A solution of 5-nitro-2-phenylindole (0.42 g., 0.00176 mole) in absolute ethanol (100 ml.) was shaken with Raney nickel (0.2 g.) under hydrogen at 2 atm. for 1 hr. The catalyst was filtered off and the solution was evaporated under reduced pressure. The white crystalline residue was recrystallized from methylene chloride–petroleum ether, with charcoal, yielding white crystals (0.22 g., 60%), m.p. 234–235°, which gave no depression in mixture melting point, 234–235°, with an authentic sample[14,28]: lit.[14] m.p. 231.5–233°; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$, m$\mu$ (log ϵ), 230 (4.42), 319 (4.39); ν^{Nujol} 3370 (mw), 3290 (w), 3170 (vvw) (NH) cm.$^{-1}$. The ultraviolet spectrum is in satisfactory agreement with that reported.[14]

Acetyl Derivative of 12. 5-Acetamido-2-phenylindole.—Acetylation of 5-amino-2-phenylindole with acetic anhydride gave the compound in 90% yield as reported,[14] after crystallization with charcoal from methylene chloride–petroleum ether, in the form of white crystals: m.p. 213–214°; lit. m.p. 214.5–215.5°,[14] 217°[29]; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$, m$\mu$ (log ϵ), 249 (4.45), 259 (infl.) (4.41), 319 (4.42); ν^{Nujol} 3250 (ms) (NH), 1629 (s) (C=O) cm.$^{-1}$.

3,5-Dinitro-2-phenylindole (9).[2a]—5-Nitro-2-phenylindole (0.46 g., 0.00193 mole) was dissolved in concentrated nitric acid (*d* 1.42, 50 ml.) and the solution was kept at room temperature for 15 min. The resulting greenish crystalline precipitate was filtered off and recrystallized from ethanol, with charcoal, yielding bright yellow-green needles (0.18 g., 33%): m.p. 309–310° dec.; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$, m$\mu$ (log ϵ), 263 (4.49), 333 (4.10); ν^{Nujol} 3180 (m) (NH), 1545 (m), 1532 (mw), 1343 (s) (NO_2) cm.$^{-1}$.

Anal. Calcd. for $C_{14}H_9N_3O_4$ (283.24): C, 59.36; H, 3.20; N, 14.84. Found: C, 59.64; H, 3.28; N, 15.10.

Oxidative Degradation of 3,5-Dinitro-2-phenylindole (9).[2a]—Potassium permanganate (1.58 g., 0.0100 mole) was added to a solution of 3,5-dinitro-2-phenylindole (0.50 g., 0.00177 mole) in acetic acid (50 ml.). The mixture was refluxed for 4 hr. and then water was added and the mixture was decolorized with sodium sulfite. The decolorized solution was extracted with ether, and the ether was evaporated. Water was added to the residual acetic acid solution and the resulting white crystalline precipitate was filtered off and dried. Recrystallization from methylene chloride–petroleum ether yielded **N-benzoyl-5-nitroanthranilic acid** (10) as white crystals (0.03 g., 6%), m.p. 255–258°. There was no depression in mixture melting point, 254–257°, with the sample prepared from 5-nitro-2-phenylindole, and the infrared spectra in KBr showed the compounds to be the same.

Anal. Calcd. for $C_{14}H_{10}N_2O_5$ (286.24): C, 58.74; H, 3.52; N, 9.79. Found: C, 58.68; H, 3.65; N, 9.75.

5-Nitro-2-phenylisatogen (14).[2a]—Essentially by the method of Bakunin and Vitale,[15] concentrated nitric acid (*d* 1.42, 6 ml.) and concentrated sulfuric acid (10 drops) were added to a solution of 2-phenylisatogen[30] (0.83 g., 0.00372 mole) in chloroform (25 ml.), and the two-phase mixture was shaken for 5 min. The resulting precipitate was filtered, washed with water, dried. and recrystallized from acetone, yielding orange flakes (0.34 g., 34%): m.p. 240–243°; lit. (golden yellow platelets) m.p. 220°,[15] (orange-red crystals) m.p. 238–239°[16]; $\lambda_{\max}^{95\%\ \mathrm{EtOH}}$, m$\mu$ (log ϵ), 244 (infl.) (4.12), 287 (4.20), 346 (3.91); ν^{Nujol} 1713 (s) (C=O), 1550 (s), 1353 (s) (NO_2) cm.$^{-1}$. The ultraviolet spectrum is in fair agreement with that reported.[16]

Anal. Calcd. for $C_{14}H_8N_2O_4$ (268.22): C, 62.69; H, 3.01; N, 10.45. Found: C, 62.63; H, 3.16; N, 10.59.

Nitration of 2-phenylisatogen (0.95 g., 0.0043 mole) in a solution of concentrated nitric acid (*d* 1.42, 10 ml.) and concentrated sulfuric acid (1.0 ml.) at room temperature for a few minutes gave *p*-nitrobenzoic acid (0.14 g., 20%), m.p. 238–239°, identical as shown by mixture melting point and infrared comparison with an authentic sample.

Reductive and Oxidative Degradation of 5-Nitro-2-phenylisatogen (14).[2a]—Essentially, according to the procedure described by Campbell, Shavel, and Campbell,[16] hydrazine hydrate (95%, 0.75 ml., 0.022 mole) was added to a slurry of 5-nitro-2-phenylisatogen (0.45 g., 0.00168 mole) in ethanol (10 ml.). After the vigorous reaction had subsided, the resulting solution was refluxed gently for 0.5 hr. and then evaporated to dryness. The black residue was dissolved in hot acetic acid (8 ml.) and chromium(VI) oxide (0.50 g., 0.0050 mole) was added. After the vigorous reaction ceased, the solution was diluted with water and the resulting precipitate was filtered and dissolved in ether. The black ether solution was washed with water and extracted with aqueous sodium bicarbonate solution until carbon dioxide was no longer evolved. The sodium bicarbonate extracts were acidified with hydrochloric acid and extracted with ether, and the ether extracts were dried and evaporated. The residue (0.07 g.) was sublimed at 220° (1 mm.), yielding **N-benzoyl-5-nitroanthranilic acid** (10) as white crystals (0.05 g., 10%), m.p. 254–257°. There was no depression in mixture melting point, 254–257°, with the sample prepared from 5-nitro-2-phenylindole, and the infrared spectra in Nujol were identical.

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[28] We wish to thank Professor Roger Adams for sending us (Oct. 29, 1962) a sample of his 5-amino-2-phenylindole for comparison.

[29] P. Ruggli, and R. Grand, *Helv. Chim. Acta*, **20**, 373 (1937).

[30] (a) F. Kröhnke and M. Meyer-Delius, *Chem. Ber.*, **84**, 932 (1951); (b) F. Kröhnke and I. Vogt, *ibid.*, **85**, 376 (1952).