

These studies of spectra of indanthrone and related compounds in the ultraviolet, visible and infrared regions of the spectrum have led to the conclusion that indanthrone in the solid state and in inert solvents exists primarily in a keto form. The evidence is summarized: (1) An N-H stretching band is present in the infrared spectrum of indanthrone and N-methylindanthrone at  $3.16 \mu$ . (2) Indanthrone, N-methylindanthrone and N,N'-dimethylindanthrone all have approximately the same integrated absorbancy index for the carbonyl

stretching absorption band at about  $6.0 \mu$ . (3) Nearly identical spectra are observed for indanthrone and its N-methyl substituted derivatives in both the ultraviolet and visible regions of the spectrum.

**Acknowledgments.**—The authors are indebted to Dr. A. L. Bluhm for some valuable discussions, and to Mr. J. A. Sousa who prepared some of the compounds, and to Mr. C. DiPietro for the analyses.

NATICK, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF IOWA STATE COLLEGE]

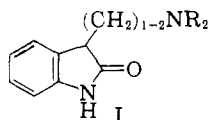
### 3-Hydroxymethyleneoxindole and its Derivatives

BY ERNEST WENKERT, JOHN H. UDELHOFEN AND NABA K. BHATTACHARYYA<sup>1</sup>

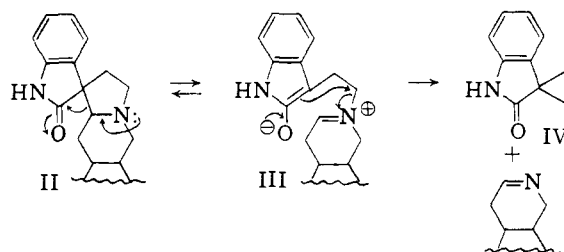
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Various aminations of 3-hydroxymethyleneoxindole and its N-methyl derivative are described. Alkylations and reductions of the resulting products are discussed. Various chemical operations on the carbonyl group of 2-methoxy-3-formylindole, a formerly described O-methylation product of 3-hydroxymethyleneoxindole, and its N-methyl derivative are portrayed.

In a continuing study of the chemistry of oxindole we have investigated the chemical behavior of compounds of structure I in view of their structural similarity to many naturally occurring indolic compounds and because of their potential value as synthetic precursors of oxindole alkaloids.



Since the initial suggestion<sup>2</sup> and proof<sup>3</sup> of the structure of the common degradation product IV of various oxindole alkaloids, the structures of several of these natural products have become known. Rhyncophylline (dihydrocorynoxine<sup>5</sup>)<sup>4a,5,6</sup> and corynoxine<sup>5</sup> have been shown to be oxindole analogs of the corynantheine-type system, while uncarine-A,<sup>6</sup> formosanine<sup>7</sup> (uncarine-B<sup>6</sup>) and mitraphylline<sup>4b,6</sup> have been portrayed as the oxindole counterparts of the ajmalicine-type alkaloids. The one-step degradation of these compounds to IV is readily explicable on the basis of their now commonly accepted part structure II, if it be assumed that the latter is convertible first to the *retro*-Mannich product III, or its diradical equivalent (IV, etc.). The equilibrium between II and III, the latter most likely complexed as an acetate, is undoubtedly responsible for the acetic anhydride-induced interconversions of uncarine-A and formosanine as well as rhyncophylline and isorhyncophylline.<sup>6</sup>

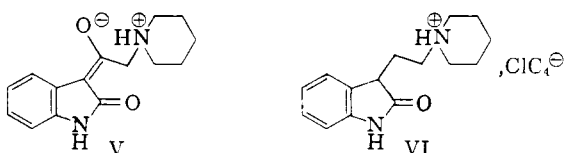


Since II is both a 3-aminomethyloxindole and 3-( $\beta$ -aminoethyl-)oxindole, both systems (I) came under scrutiny. Condensation of oxindole with ethyl 1-piperidinoacetate yielded 3-[ $\alpha$ -hydroxy- $\beta$ -(1-piperidino-)ethylidene-]oxindole. Its lone  $6.23 \mu$  (Nujol) peak in the C=O and C=C infrared region, in contrast to a  $6.02 \mu$  absorption for most 3-acyloxindole enols,<sup>8</sup> but in consonance with a  $6.17 \mu$  absorption of its sodio salt, indicated the zwitterion nature (V) (possibly intra- or intermolecularly hydrogen-bonded) of the product. Its perchlorate exhibited a  $6.02 \mu$  infrared absorption peak. Compound V resisted hydrogenation with palladium-charcoal in ethanol and led to an inseparable amorphous mixture on hydrogenation with platinum in acetic acid. Hydrogenation of the perchlorate of V with palladium-charcoal in ethanol yielded 3-[ $\beta$ -(1-piperidino)-ethyl]oxindole perchlorate (VI). Attempted liberation of the base from VI led only to amorphous, unworkable products whose solutions decomposed fairly rapidly on standing in air. Preliminary oxidative cyclization experiments on VI or its free base were equally unsuccessful. The instability of similarly constituted oxindolyl bases as well as the difficulties inherent in their formation from 3-acyloxindoles has been encountered previously.<sup>9</sup>

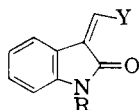
- (1) Upjohn Co. postdoctorate fellow, 1954-1955.
- (2) E. Wenkert and T. L. Reid, *Chemistry & Industry*, 1390 (1953).
- (3) E. Wenkert, N. K. Bhattacharyya, T. L. Reid and T. E. Stevens, *THIS JOURNAL*, **78**, 797 (1956).
- (4) (a) J. C. Seaton and L. Marion, *Can. J. Chem.*, **35**, 1102 (1957); (b) J. C. Seaton, R. Tondeur and L. Marion, *ibid.*, **36**, 1301 (1958).
- (5) N. An Cu, R. Goutarel and M.-M. Janot, *Bull. soc. chim. France*, 1292 (1957).
- (6) T. Nozoye, *Pharm. Bull. (Japan)*, **6**, 300, 306, 309 (1958).
- (7) Raymond-Hamet, *Compt. rend.*, **245**, 1458 (1957).

(8) E. Wenkert, B. S. Bernstein and J. H. Udelhofen, *THIS JOURNAL*, **80**, 4899 (1958).

(9) P. L. Julian, A. Magnani, J. Pikel and W. J. Karpel, *ibid.*, **70**, 174 (1948). While reduction of a compound analogous to V, reported herein, produced uncrystallizable substances, hydrogenation of its



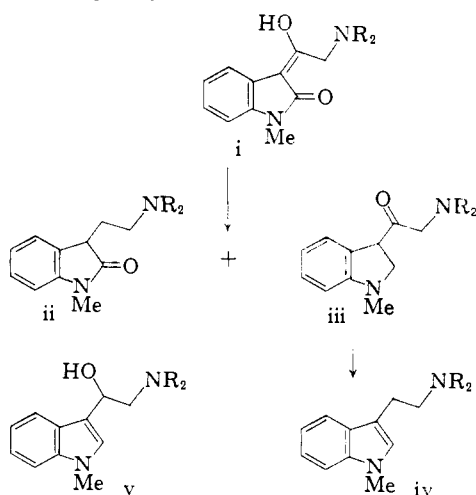
**3-Hydroxymethyleneoxindole.**—With the approach toward a 3-( $\beta$ -aminoethyl)-oxindole at least temporarily blocked, the synthesis of 3-amino-methyloxindole (I) derivatives acquired importance. One apparent method of their preparation was the reduction of amino derivatives of 3-hydroxymethyleneoxindoles (VIIa and b).<sup>3</sup>



- VIIa, R = H, Y = OH  
 b, R = Me, Y = OH  
 c, R = H, Y = NH<sub>2</sub>  
 d, R = Me, Y = NH<sub>2</sub>  
 e, R = H, Y = Cl  
 f, R = H, Y = N(Ac)OAc  
 g, R = Y = H  
 h, R = H, Y = NHAc  
 i, R = H, Y = NHMe  
 j, R = H, Y = NMe<sub>2</sub>  
 k, R = H, Y = N(Me)Ac  
 l, R = H, Y = OMe  
 m, R = H, Y = COCH<sub>2</sub>Cl  
 n, R = H, Y = NHCH<sub>2</sub>CO<sub>2</sub>Et

Standard oximation of VIIa and b<sup>10</sup> led to products whose spectra showed them to be the unconjugated oxindoles VIIa and b, respectively, but whose melting points were much higher than those previously reported.<sup>11</sup> Hydrogenation of ethanol solutions of the oximes over palladium-charcoal yielded 3-methyloxindole (IXa) and 1,3-dimethyl-

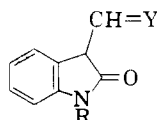
N-methyl derivative (i) led to the desired 3-alkyloxindole (ii) as well as an isomer, to which structure iii was assigned. The unprecedented reduction of the amide linkage, side by side with survival of the ketonic carbonyl group, under catalytic hydrogenation conditions puts the latter structure in grave doubt. Furthermore, its conversion by sodium and alcohol to the indole iv, a transformation with no apparent mechanistic basis, makes structure iii even more dubious. In the absence of any other data no rigorous assignment can be made, although v may serve temporarily as a tentative alternative to iii.



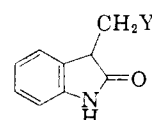
(10) Mr. Bruce S. Bernstein performed the oximation of the N-methyl compound VIIb and acetylation of the resulting oxime.

(11) P. Friedländer and S. Kielbasinski, *Ber.*, **44**, 3098 (1911).

oxindole, respectively. This result is in sharp contrast to the consequences of catalytic hydrogenation of other 3-acyloxindole oximes<sup>8</sup> and reminiscent of the fate of a 3-methoxymethyleneoxindole on hydrogenation.<sup>12</sup> It implies, that, in the absence of any alkyl substituent on the methylene group on C-3, the intermediate 3-hydroxylaminomethyloxindoles suffer  $\beta$ -elimination of hydroxylamine, followed by reduction of the resulting 3-methylene compounds, faster than dehydration to imines and tautomerization to the stable enamines. Acetylation of the oximes VIIa and b gave their O-acetates, whose structures VIIc and d, respectively, were verified by their ultraviolet and infrared spectra. The latter also revealed the low-wave length carbonyl absorption ( $5.70 \mu$ ) of the ester, characteristic of O- or N-negatively substituted esters or amides.<sup>13</sup> Hydrogenation of the oxime acetates afforded 3-aminomethyleneoxindole (VIIc) and its N<sub>a</sub>-methyl derivative VIId. It is noteworthy that the presence of the acetate leaving group in the starting materials of these reductions shifts the competitive reaction paths, cited above, in favor of imine (and thence enamine) formation. 3-Aminomethyleneoxindole (VIIc) could be prepared also by the reaction of 3-chloromethyleneoxindole (VIIe)<sup>14</sup> and ammonia.



- VIIIa, R = H, Y = NOH  
 b, R = Me, Y = NOH  
 c, R = H, Y = NOAc  
 d, R = Me, Y = NOAc



- IXa, Y = H  
 b, Y = NHAc  
 c, Y = N(Ac)OAc  
 d, Y = N(Me)Ac  
 e, Y = NH<sub>2</sub>

After discovery of the recently reported conversion of 3-acyloxindole oximes to indoles<sup>3</sup> the oximation of 3-hydroxymethyleneoxindole (VIIa) was re-examined. Firstly, it could be shown that indole, a now not unexpected side-product, was formed along with the oxime VIIIa, m.p. 221–222°. Secondly, a short reaction time led to an isomer of the oxime, m.p. 160°. The latter underwent a ready thermal conversion to VIIIa. Its ultraviolet spectrum and infrared carbonyl absorption were analogous to those of 3-aminoalkyldeneoxindoles,<sup>8</sup> while the absence of any infrared absorption at  $2.8 \mu$  suggested that the hydroxyl group was internally hydrogen-bonded.<sup>16</sup> On this basis structure X could be assigned to the oxime isomer. This formulation was in agreement with the chemical behavior of the compound toward hydrogenation and acetylation. In contrast to the results from its stable isomer VIIIa it yielded 3-aminomethyleneoxindole

(12) E. Wenkert, A. K. Bose and T. L. Reid, *THIS JOURNAL*, **75**, 5514 (1953).

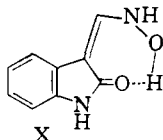
(13) This infrared effect was studied on variously acylated hydroxylamines and hydrazines by Mr. R. M. Epstein in this Laboratory. For further data see his M. S. Thesis, Iowa State College, 1955, and for a recent report cf. J. P. Freeman, *ibid.*, **80**, 5954 (1958).

(14) H. Behringer and H. Weissauer, *Chem. Ber.*, **85**, 743, 774 (1952).

(15) Most probably this compound is identical with the Friedländer product,<sup>11</sup> m.p. ca. 150°. It also is of interest that the latter was reported to give off a skatole-like odor on refluxing in dilute acid.

(16) A most helpful discussion with Professor George S. Hammond on these points is gratefully acknowledged.

(VIIc) on reduction and the diacetate VIIf on acylation. It was worthy of note that the reduction proceeded exclusively by hydrogenolysis of the N-O linkage. However, hydrogenation of the diacetate VIIf, which afforded a mixture of 3-methyloxindole (IXa) and 3-acetamidomethyloxindole (IXb), must have followed both a hydrogenative (*i.e.*, VIIf  $\rightarrow$  IXc  $\rightarrow$  IXa) and hydrogenolytic [*i.e.*, VIIf  $\rightarrow$  VIIg  $\rightarrow$  IXb (*vide infra*)] path.



The reduction of 3-aminomethyleneoxindole (VIIc), 3-methylaminomethyleneoxindole (VIIi), 3-dimethylaminomethyleneoxindole (VIIj)<sup>14</sup> as well as their acetyl derivatives VIIh and k was also studied. The enamines VIIc and j<sup>14</sup> were on hand, while VIIi could be prepared by the reaction of ammonia and 3-chloromethyleneoxindole (VIIe)<sup>14</sup> or 3-methoxymethyleneoxindole (VIIl).<sup>3</sup> The acyl compounds VIIh and k were synthesized by acylation of VIIc and i, respectively. Whereas VIIc had been shown to be resistant to hydrogenation over palladium-charcoal, both VIIi and j were reduced exclusively to 3-methyloxindole (IXa). Hydrogenation of the amides VIIh and k gave the 3-alkyloxindoles IXb and d, respectively. Thus it appears that the last two substances are the only 3-aminomethyleneoxindole derivatives readily available by reduction of 3-( $\alpha$ -aminoalkylidene)-oxindoles. This fact bodes ill for attempts to prepare oxindole analogs of such naturally occurring substances as gramine. An experiment to produce 3-aminomethyloxindole (IXe) by alkaline hydrolysis of 3-acetamidomethyloxindole (IXb) merely led to poly-3-methyloxindole, the end product of a previously attempted oxygramine synthesis.<sup>17</sup>

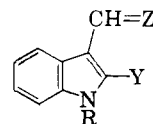
Preliminary trials of synthesis of models of the spirooxindole structure II from various of the above substances have been singularly unsuccessful. 3-Aminomethyleneoxindole (VIIc) as well as its acetyl derivative VIIh proved inert to alkylation by ethylene dibromide under various reaction conditions. The chloroacetamide VIIm, obtained by an interaction of VIIc with chloroacetyl chloride, did not react with potassium carbonate in acetone, reverted to VIIc under the influence of sodium ethoxide and lost its chlorine with the production of 3-acetamidomethyloxindole (IXb) on catalytic hydrogenation. Finally, condensation of 3-hydroxymethyleneoxindole (VIIa) with ethyl glycinate yielded VIIn, which, however, reverted to VIIa on attempted basic ester hydrolysis.

**2-Methoxy-3-formylindole.**—The discovery of 2-methoxy-3-formylindole (XIa),<sup>3</sup> the second recorded 2-alkoxyindole,<sup>18</sup> stimulated a study of its chemical properties and a comparison of them with those of 3-formylindole (XIb).

Alkylation of both XIa and b with methyl iodide and potassium *t*-butoxide converted them to their

(17) Footnotes 7-9 in ref. 12.

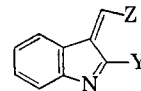
(18) For the one previous case cf. R. J. S. Beer, H. F. Davenport and A. Robertson, *J. Chem. Soc.*, 1262 (1953).



- XIa, R = H, Y = OMe, Z = O  
 b, R = Y = H, Z = O  
 c, R = Me, Y = OMe, Z = O  
 d, R = Me, Y = H, Z = O  
 e, R = Ac, Y = OMe, Z = O  
 f, R = Y = H, Z = H<sub>2</sub>

- g, R = Ac, Y = OMe, Z =  $\begin{matrix} \text{CO}_2\text{H} \\ | \\ \text{CNHCOC}_6\text{H}_5 \end{matrix}$   
 h, R = H, Y = OMe, Z = NOH  
 i, R = Y = H, Z = NOH  
 j, R = H, Y = OMe, Z = NOAc  
 k, R = Y = H, Z = NHMe

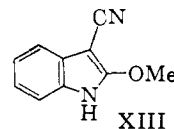
N-methyl derivatives XIc<sup>3</sup> and d,<sup>19</sup> respectively. Treatment of XIa with acetic anhydride and sodium acetate yielded an acetyl derivative whose spectra fitted best structure XIe, although XIIa could not be excluded rigorously.



- XIIa, Y = OMe, Z = OAc  
 b, Y = OMe, Z = NHMe  
 c, Y = H, Z = NMe<sub>2</sub>

While catalytic hydrogenation of 2-methoxy-3-formylindole (XIa) yielded no definable products, lithium aluminum hydride reduction afforded skatole (XIh), the reduction product also of 3-formylindole (XIb).<sup>20</sup> The chemical reduction thus causes the previously observed hydrogenolysis of the formyl oxygen atom<sup>20</sup> as well as that of the 2-methoxy group. The course of the reaction is readily explained by a variation of a former suggestion.<sup>20</sup>

Condensation of 2-methoxy-3-formylindole (XIa) with hippuric acid, acetic anhydride and sodium acetate under conditions, which with 3-formylindole (XIb) had yielded an azlactone,<sup>21</sup> gave an acetylated partly hydrolyzed product, whose acetyl group was associated most likely with the indole nitrogen atom (XIg). Oximation of XIa and b gave normal oximes, XIh and i, respectively. While attempted dehydration of XIh with acetic anhydride led merely to an acetate, probably the O-acetate XIj, pyrolysis afforded the nitrile XIII.



While thus far the reactions of the two 3-formylindoles had complemented one another, the condensation of XIa and b with methylamine led to strikingly different results. Whereas XIb yielded the imine XIk in crystalline form, it having been obtained previously in an amorphous state,<sup>22</sup> XIa formed an indolenine compound (XIIb), the tautomer of the expected imine. Structure XIIb was

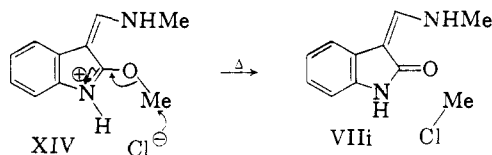
(19) H. Wieland, W. Konz and H. Mittasch, *Ann.*, **513**, 1 (1934).

(20) E. Leete and L. Marion, *Can. J. Chem.*, **31**, 775 (1953).

(21) A. Ellinger and C. Flamand, *Ber.*, **40**, 3029 (1907).

(22) G. F. Smith, *J. Chem. Soc.*, 3842 (1954).

unmistakable in view of the extraordinary similarity of its ultraviolet absorption curve with those of 3-methylaminomethyleneoxindole (VIIi) and 3-dimethylaminomethyleneindolenine (XIIc).<sup>22</sup> Furthermore, the hydrochloride XIV of the new indolenine was transformed into VIIi at its melting point



It would seem that subtle electronic and steric factors may suffice in making 3-acylindoles and their derivatives more stable in their tautomeric 3-alkylideneindolenine forms.<sup>23</sup>

**Acknowledgment.**—The authors express their sincere thanks to the Upjohn Co. for financial support and to the Institute for Atomic Research for the use of a Baird infrared spectrophotometer.

### Experimental

**3-[ $\alpha$ -Hydroxy- $\beta$ -(N-piperidino)-ethylidene]-oxindole (V).**—A slurry of 4 g. of oxindole and 6 g. of ethyl N-piperidinoacetate was added to a warm sodium ethoxide solution, prepared from 1 g. of sodium and 5 ml. of absolute ethanol. After two hours of refluxing of the mixture, the precipitated sodium salt was filtered and dissolved in water. Neutralization of the aqueous solution led to a white solid, m.p. 255–260°, which on several crystallizations from ethanol gave white crystals of V, m.p. 260°; spectra: ultraviolet (95% ethanol),  $\lambda_{\max}$  268  $\mu$  (log  $\epsilon$  4.22) and 317  $\mu$  (log  $\epsilon$  4.13); infrared (Nujol), NH 3.16(s), C=O and C=C 6.22(m) and 6.51(s)  $\mu$ .

*Anal.* Calcd. for  $C_{15}H_{18}O_2N_2$ : C, 69.80; H, 6.98; N, 10.85. Found: C, 69.99; H, 7.30; N, 10.9.

Dissolution of V in acetic acid and addition of saturated potassium perchlorate solution precipitated a perchlorate, which could be crystallized from ethanol, m.p. 245°; spectra: ultraviolet (95% ethanol),  $\lambda_{\max}$  256  $\mu$  (log  $\epsilon$  4.22) and 318  $\mu$  (log  $\epsilon$  4.08); infrared (Nujol), OH and NH 3.03(m), 3.30(m), C=O and C=C 6.02(s), 6.13(m), 6.25(m)  $\mu$ .

*Anal.* Calcd. for  $C_{15}H_{18}O_2N_2 \cdot HClO_4$ : C, 50.25; H, 5.31; N, 7.81. Found: C, 49.84; H, 5.25; N, 7.81.

The precipitated sodio salt above was washed with ether and dried; infrared spectrum (Nujol): NH 3.00(w), C=O and C=C 6.18(s), 6.35(w)  $\mu$ .

Condensation of N-methylloxindole with ethyl N-piperidinoacetate by the above procedure gave a 74% crude yield of a solid which on crystallization from ether-chloroform yielded 1-methyl-3-[ $\alpha$ -hydroxy- $\beta$ -(N-piperidino)-ethylidene]-oxindole, m.p. 170°.

*Anal.* Calcd. for  $C_{16}H_{20}O_2N_2$ : C, 70.60; H, 7.36; N, 10.30. Found: C, 70.32; H, 7.20; N, 10.15.

**3-[ $\beta$ -(N-Piperidino)-ethyl]-oxindole (VI).**—A mixture of 900 mg. of 3-[ $\alpha$ -hydroxy- $\beta$ -(N-piperidino)-ethylidene]-oxindole perchlorate and 90 mg. of palladium-charcoal in 50 ml. of ethanol was reduced under hydrogen at atmospheric pressure. When hydrogen uptake had ceased, the catalyst was filtered and the solvent evaporated under vacuum. The remaining oil slowly solidified on standing. Crystallization from acetone yielded 400 mg. (47%) of perchlorate, m.p. 170°; ultraviolet spectrum (95% ethanol):  $\lambda_{\max}$  252  $\mu$  (log  $\epsilon$  4.07) and 296  $\mu$  (log  $\epsilon$  3.68).

**Formation of Oximes.**—The recently reported oxime preparation<sup>8</sup> was used for the following compounds.

(23) Since the completion of this phase of the work<sup>1</sup> a few examples of stable indolenines of type XII have been reported; cf. M. F. Bartlett, D. F. Dickel and W. I. Taylor, *THIS JOURNAL*, **80**, 126 (1958); F. G. Mann and T. J. Willcox, *J. Chem. Soc.*, 1525 (1958); F. Millich and E. I. Becker, *J. Org. Chem.*, **23**, 1096 (1958).

3-Hydroxymethyleneoxindole (VIIa) (4.0 g.) was converted to 2.5 g. of its oxime VIIi as an amorphous solid, m.p. 221–222°; spectra: ultraviolet (95% ethanol),  $\lambda_{\text{shoulder}}$  240–260  $\mu$  (log  $\epsilon$  3.75–3.65); infrared (KBr), OH and NH 2.84(s), 2.99(s) and 3.15(s), C=O 5.83(s), C=C 6.21(s)  $\mu$ . Concentration of the benzene extract of the aqueous mother liquor from the oxime preparation, followed by alumina chromatography of the concentrate and elution with petroleum ether, yielded 140 mg. of indole, m.p. 54°; no depression of mixed m.p. and identity of infrared spectrum with those of an authentic specimen.

When the reaction time in the synthesis of VIIi was cut to five minutes, a new pale green product was obtained. Crystallization from tetrahydrofuran gave 3-hydroxylaminomethyleneoxindole (X), m.p. 160°, solidified at 165° and m.p. 220° (identical with VIIi); spectra: ultraviolet (95% ethanol),  $\lambda_{\max}$  250  $\mu$  (log  $\epsilon$  4.10) and 276  $\mu$  (log  $\epsilon$  4.10); infrared (KBr), NH 3.01(m) and 3.10–3.20(m) (shoulder), C=O and C=C 6.09(s), 6.21(s) (shoulder) and 6.32(s)  $\mu$ .

1-Methyl-3-hydroxymethyleneoxindole (VIIb) (773 mg.) was transformed into 561 mg. (67%) of its amorphous oxime. Several crystallizations from methanol gave VIIb, m.p. 221° dec. after darkening from 195° upward; infrared spectrum (Nujol), NH 3.02(m), 3.15(m), C=O 5.83(s), C=C 6.21(s)  $\mu$ .

*Anal.* Calcd. for  $C_{10}H_{10}O_2N_2$ : C, 63.11; H, 5.30; N, 14.73. Found: C, 62.85; H, 5.03; N, 14.8.

3-Formylindole oxime (XIi), m.p. 202–203°; ultraviolet spectrum (95% ethanol),  $\lambda_{\max}$  222  $\mu$  (log  $\epsilon$  4.56) and 268  $\mu$  (log  $\epsilon$  4.12),  $\lambda_{\text{shoulder}}$  300  $\mu$  (log  $\epsilon$  3.98),  $\lambda_{\min}$  245  $\mu$  (log  $\epsilon$  3.82).

The crude yield of 2-methoxy-3-formylindole oxime (XIh) from 500 mg. of XIa was 530 mg. Several crystallizations from ethanol gave colorless rosettes, m.p. 181–182°; ultraviolet spectrum (95% ethanol),  $\lambda_{\max}$  228  $\mu$  (log  $\epsilon$  4.33), 271  $\mu$  (log  $\epsilon$  4.28) and 294  $\mu$  (log  $\epsilon$  4.19),  $\lambda_{\min}$  250  $\mu$  (log  $\epsilon$  3.95) and 284  $\mu$  (log  $\epsilon$  4.16).

**Oxime Acetates.**—A solution of 1 g. of oxime in 10 ml. of acetic anhydride was heated on a steam-bath for 2–20 min. After cooling, either the solution was concentrated, water added to the residue and the resulting solid filtered, or the reaction mixture was treated with saturated sodium bicarbonate solution, extracted with chloroform, the organic solution dried over sodium sulfate and the solvent evaporated.

3-Formylloxindole oxime (VIIIa) gave an O-acetate (VIIIc), m.p. 168–170°; spectra: ultraviolet (95% ethanol),  $\lambda_{\text{shoulder}}$  235–245  $\mu$  (log  $\epsilon$  3.75–3.70),  $\lambda_{\max}$  290  $\mu$  (log  $\epsilon$  3.10); infrared ( $CHCl_3$ ), NH 2.94(m), 3.10(m), C=O 5.70(s), 5.83(s), C=C 6.20(s)  $\mu$ .

3-Hydroxylaminomethyleneoxindole (X) gave a yellow diacetate VIIf which on crystallization from methanol had m.p. 220°; spectra: ultraviolet (95% ethanol),  $\lambda_{\max}$  280  $\mu$  (log  $\epsilon$  4.19); infrared (Nujol), NH 3.17(w), C=O 5.71(s), 5.80(s), 6.01(s), C=C 6.15(s) (shoulder), 6.31(s)  $\mu$ .

*Anal.* Calcd. for  $C_{13}H_{12}O_4N_2$ : N, 10.78. Found: N, 10.9.

1-Methyl-3-formylloxindole oxime (VIIIb) (3.0 g.) gave 2.3 g. of an O-acetate VIIId, m.p. 180°, after two crystallizations from benzene; spectra: ultraviolet (95% ethanol),  $\lambda_{\text{shoulder}}$  235–245  $\mu$  (log  $\epsilon$  3.85–3.80) and 290  $\mu$  (log  $\epsilon$  3.20); infrared ( $CHCl_3$ ), C=O 5.69(s), 5.84(s), C=C 6.21(s)  $\mu$ .

*Anal.* Calcd. for  $C_{12}H_{12}O_3N_2$ : C, 62.08; H, 5.21; N, 12.07. Found: C, 62.35; H, 5.07; N, 11.9.

2-Methoxy-3-formylindole oxime (XIh) gave a quantitative yield of an acetate XIj. Several crystallizations from dilute alcohol yielded white needles, m.p. 138–139°; spectra: ultraviolet (95% ethanol),  $\lambda_{\max}$  249  $\mu$  (log  $\epsilon$  4.05), 273  $\mu$  (log  $\epsilon$  4.17) and 307  $\mu$  (log  $\epsilon$  4.27),  $\lambda_{\min}$  239  $\mu$  (log  $\epsilon$  3.97), 257  $\mu$  (log  $\epsilon$  3.98) and 283  $\mu$  (log  $\epsilon$  4.08); infrared ( $CHCl_3$ ), NH 2.91(m), 3.10(m), C=O 5.75(s), C=C 6.17(s), 6.27(s) and 6.32(s)  $\mu$ .

*Anal.* Calcd. for  $C_{12}H_{12}O_3N_2$ : C, 62.1; H, 5.17; N, 12.1. Found: C, 62.3; H, 5.30; N, 12.5.

**3-Aminomethyleneoxindole and Derivatives.**—A solution of 1.00 g. of 3-chloromethyleneoxindole (VIIe)<sup>14</sup> in 100 ml. of ethanol, which had been saturated with ammonia gas at ice temperature, was left standing for three hours, whereupon it was concentrated under vacuum and water added.

The resulting 800 mg. (89%) of solid was crystallized from ethyl acetate leading to crystalline 3-aminomethyleneoxindole (VIIc), m.p. 220°, solidified at 240° without remelting below 300°; spectra: ultraviolet (95% ethanol),  $\lambda_{\max}$  268  $\mu$  (log  $\epsilon$  4.30), 272  $\mu$  (log  $\epsilon$  4.30) and 315  $\mu$  (log  $\epsilon$  4.10); infrared (CHCl<sub>3</sub>), NH 2.91(w), 3.08(w), C=O 5.98(s), C=C 6.17(s)  $\mu$ .

*Anal.* Calcd. for C<sub>9</sub>H<sub>9</sub>O<sub>2</sub>N<sub>2</sub>: C, 67.5; H, 5.00; N, 17.5. Found: C, 67.35; H, 5.10; N, 17.25.

A solution of 1.00 g. of 3-aminoethyleneoxindole (VIIc), 30 ml. of acetic anhydride and 5 ml. of pyridine was heated gently on the steam-bath for two minutes. On cooling of the mixture, 1.00 g. (80%) of a pale green solid deposited. Several crystallizations from ethanol yielded needles of 3-acetamidomethyleneoxindole (VIIh), m.p. 251°; spectra: ultraviolet (95% ethanol),  $\lambda_{\max}$  273  $\mu$  (log  $\epsilon$  4.36) and 320  $\mu$  (log  $\epsilon$  4.23); infrared (Nujol), NH 3.12(w), C=O 5.91(s), C=C 6.22(s)  $\mu$ .

*Anal.* Calcd. for C<sub>11</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub>: C, 65.40; H, 4.95; N, 13.85. Found: C, 66.02; H, 4.90; N, 13.70.

A mixture of 500 mg. of 3-aminomethyleneoxindole (VIIc), 400 mg. of chloroacetyl chloride and 1 g. of anhydrous potassium carbonate in 50 ml. of dry acetone was refluxed for 10 minutes. The red mixture was filtered, and the filtrate concentrated under vacuum. Several crystallizations of the red residue led to 450 mg. (65%) of yellow crystals of 3-chloroacetamidomethyleneoxindole (VIIIm), m.p. 265–267°; infrared spectrum (Nujol), NH 3.18(w), C=O 5.93(s), C=C 6.25(s)  $\mu$ .

*Anal.* Calcd. for C<sub>11</sub>H<sub>9</sub>O<sub>2</sub>N<sub>2</sub>Cl: C, 56.00; H, 3.81; N, 11.85. Found: C, 55.70; H, 3.91; N, 11.95.

A solution of 100 mg. of VIIIm and sodium ethoxide, prepared by dissolution of 10 mg. of sodium in 15 ml. of absolute ethanol, was refluxed for 3 hr. It then was neutralized with dilute hydrochloric acid and extracted with chloroform. The organic extract was washed with sodium bicarbonate and water, dried over sodium sulfate, and concentrated to dryness. The remaining solid (50 mg., 73%), m.p. 220°, proved identical with 3-aminomethyleneoxindole (VIIc).

A mixture of 200 mg. of 3-methoxymethyleneoxindole (VII<sup>3</sup>) in 6 ml. of a 25% aqueous methylamine solution was warmed for 15 minutes and stirred for 3 hr. Thereupon the precipitate was filtered, washed with water and dried, 175 mg. (88%), m.p. 233–234°. Crystallization from dilute alcohol yielded pale yellow needles of 3-methylaminomethyleneoxindole (VIIi), m.p. 235°; spectra: ultraviolet (95% ethanol),  $\lambda_{\max}$  275  $\mu$  (log  $\epsilon$  4.26) and 342  $\mu$  (log  $\epsilon$  4.12),  $\lambda_{\text{shoulder}}$  318  $\mu$  (log  $\epsilon$  4.06); infrared (CHCl<sub>3</sub>), NH 2.94(w), 3.11(w), C=O 5.98(s), C=C 6.22(s)  $\mu$ .

*Anal.* Calcd. for C<sub>10</sub>H<sub>10</sub>O<sub>2</sub>N<sub>2</sub>: C, 69.0; H, 5.75; N, 16.1. Found: C, 69.4; H, 5.73; N, 16.4.

A mixture of 1.00 g. of 3-chloromethyleneoxindole (VIIe)<sup>14</sup> and 40 ml. of a 25% aqueous methylamine solution was allowed to stir for 18 hr. Vacuum concentration of the mixture and addition of water gave 900 mg. (92%) of a tan solid which on crystallization from dilute ethanol proved to be VIIi, m.p. 235°.

The above procedure for the acetylation of VIIc was used on 1.00 g. of 3-methylaminomethyleneoxindole (VIIi) leading to 900 mg. (73%) of solid. Crystallization from ethanol gave yellow-green crystals of 3-(N-methylacetamidomethylene)-oxindole (VIIk), m.p. 185°; infrared spectrum (CHCl<sub>3</sub>), NH 2.94(w), 3.14(w), C=O 5.91(s), C=C 6.21(s)  $\mu$ .

*Anal.* Calcd. for C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub>: C, 66.75; H, 5.61; N, 12.95. Found: C, 66.21; H, 5.56; N, 12.65.

A solution of 3.5 g. of 3-hydroxymethyleneoxindole (VIIa)<sup>3</sup> and 2.8 g. of ethyl glycinate hydrochloride in 20 ml. of pyridine was stirred for 16 hr. at room temperature. After vacuum distillation of the solvent and trituration of the oily residue with 95% ethanol, a solid, m.p. 175–180°, precipitated. Several crystallizations from ethanol gave white crystalline 3-carbomethoxymethylaminomethyleneoxindole (VIIIn), m.p. 197°; spectra: ultraviolet (95% ethanol),  $\lambda_{\max}$  274  $\mu$  (log  $\epsilon$  4.32) and 318  $\mu$  (log  $\epsilon$  4.12).

*Anal.* Calcd. for C<sub>13</sub>H<sub>14</sub>O<sub>2</sub>N<sub>2</sub>: C, 63.40; H, 5.69; N, 11.38. Found: C, 63.55; H, 5.28; N, 11.40.

A solution of 500 mg. of 2-methoxy-3-formylindole (XIa)<sup>3</sup> in 12 ml. of a 25% aqueous methylamine was left standing for 5 hr. at room temperature. The reaction mixture was extracted with benzene, the extract washed with water and

dried over sodium sulfate. Evaporation of the solvent left a viscous oil which solidified to 400 mg. (78%) of granular crystals, m.p. 172–174°, on trituration with ether. Several crystallizations from benzene-petroleum ether yielded long fine pale green needles of 2-methoxy-3-methylaminomethyleneoxindole (XIIf), m.p. 177–178°; spectra: ultraviolet (95% ethanol),  $\lambda_{\max}$  273  $\mu$  (log  $\epsilon$  4.22), 278  $\mu$  (log  $\epsilon$  4.25) and 334  $\mu$  (log  $\epsilon$  4.36),  $\lambda_{\min}$  247  $\mu$  (log  $\epsilon$  3.68) and 290  $\mu$  (log  $\epsilon$  3.51); infrared (CHCl<sub>3</sub>), NH 2.95(m), C=N 6.07(s), C=C 6.30(m)  $\mu$ .

*Anal.* Calcd. for C<sub>11</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub>: C, 70.3; H, 6.4; N, 14.9. Found: C, 70.5; H, 6.22; N, 14.9.

A solution of ether, saturated with dry hydrogen chloride, was added to an ether-chloroform solution of XIIf, causing an immediate precipitation of a solid, m.p. 146–147°. Several dissolutions of the latter and reprecipitations with ether yielded the hydrochloride of XIIf, m.p. 147–148°, liberation of gas and resolidification, second m.p. 230–231°. Drying of the hydrochloride in a drying pistol under vacuum at 100° resulted in its conversion to the new substance, m.p. 230–233°. Finally, the hydrochloride, m.p. 147–148°, was heated in a test-tube at 160–170° until all gas evolution had ceased and a solid had deposited on the walls of the tube. The pyrolysis mixture was taken up in chloroform-ethanol, filtered, and the filtrate concentrated. The fine needles, m.p. 232–233°, were shown by m.p., m.m.p. and infrared spectrum to be 3-methylaminomethyleneoxindole (VIIj).

3-Dimethylaminomethyleneoxindole (VIIj),<sup>14</sup> m.p. 185°; spectra: ultraviolet (95% ethanol),  $\lambda_{\max}$  275  $\mu$  (log  $\epsilon$  4.24) and 345  $\mu$  (log  $\epsilon$  4.14),  $\lambda_{\text{shoulder}}$  320  $\mu$  (log  $\epsilon$  4.10); infrared (CHCl<sub>3</sub>), NH 2.95(w), 3.19(w), C=O 5.99(s), C=C 6.26(s)  $\mu$ .

**Hydrogenation of the Oximes, 3-Aminomethyleneoxindoles and Their Derivatives.**—All the following oxindole derivatives were hydrogenated in an ethanol solution, 1.00 g. in 50 ml., over palladium-charcoal, 10% of the weight of starting oxindole, at atmospheric pressure. Upon cessation of hydrogen uptake, the catalyst was filtered and the filtrate evaporated to dryness at low temperatures. The remaining residue then was crystallized or chromatographed on alumina.

3-Aminomethyleneoxindole (VIIc), 100 mg., resisted hydrogenation and was recovered unchanged.

Reduction of 200 mg. of 3-methylaminomethyleneoxindole (VIIi) led to 150 mg. (89%) of 3-methyloxindole (IXa), m.p. 124° (lit.<sup>24</sup> m.p. 124°), on sublimation.

Hydrogenation of 40 mg. of 3-dimethylaminomethyleneoxindole (VIIj) afforded 25 mg. (80%) of 3-methyloxindole (IXa),<sup>24</sup> m.p. 124°, after sublimation.

Reduction of 760 mg. of 3-acetamidomethyleneoxindole (VIIh) yielded 700 mg. (92%) of a solid, m.p. 215–219°, which on crystallization from ethanol led to fluffy white crystals of 3-acetamidomethyloxindole (IXb), m.p. 220°; spectra: ultraviolet (95% ethanol),  $\lambda_{\max}$  250  $\mu$  (log  $\epsilon$  3.90),  $\lambda_{\text{shoulder}}$  272–285  $\mu$  (log  $\epsilon$  3.15–3.10); infrared (Nujol), NH 3.08(m), 3.19(m), C=O 5.97(s), 6.15(s), C=C 6.22(m)  $\mu$ .

*Anal.* Calcd. for C<sub>11</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub>: C, 64.75; H, 5.88; N, 13.72. Found: C, 64.38; H, 5.96; N, 13.60.

While 3-chloroacetamidomethyleneoxindole (VIIIm) resisted reduction in ethyl acetate solution in the presence of palladium-charcoal, it (100 mg.) was hydrogenated successfully in 30 ml. of glacial acetic acid over 30 mg. of platinum oxide. Filtration of the catalyst and removal of the solvent under vacuum led to 60 mg. of a white solid, m.p. 200°, which after crystallization from ethanol (m.p. 218–220°) proved identical with the above 3-acetamidomethyleneoxindole (IXb).

Hydrogenation of 400 mg. 3-(N-methylacetamidomethylene)-oxindole (VIIk) produced a clear oil which solidified on trituration with alcohol. Crystallization from dilute ethanol gave 320 mg. (80%) of 3-(N-methylacetamidomethyl)-oxindole (IXd), m.p. 135°; spectra: ultraviolet (95% ethanol),  $\lambda_{\max}$  252  $\mu$  (log  $\epsilon$  3.92); infrared (CHCl<sub>3</sub>), NH 2.95(m), 3.17(m), C=O 5.83(s), 6.15(s)  $\mu$ .

Reduction of 180 mg. of 3-formyloxindole oxime (VIIIn) gave 150 mg. (84%) of 3-methyloxindole (IXa),<sup>24</sup> m.p. 122°, after sublimation.

Hydrogenation of 350 mg. of 1-methyl-3-formyloxindole oxime (VIIIf) yielded 200 mg. (66%) of 1,3-dimethyloxindole,<sup>3</sup> m.p. 54°, on sublimation.

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Hydrogenation of 3-hydroxylaminomethylene oxindole (X) (1.00 g.) afforded 850 mg. (95%) of 3-aminomethylene-oxindole (VIIc), m.p. 220°, on crystallization from ethyl acetate.

Reduction of 200 mg. of 3-formyloxindole oxime acetate (VIIIc) led to 150 mg. of an oil, which on sublimation and crystallization from ethyl acetate gave 100 mg. of 3-aminomethyleneoxindole (VIIc), m.p. 220°.

Hydrogenation of 500 mg. of 1-methyl-3-formyloxindole oxime acetate (VIII d) produced 300 mg. (80%) of 1-methyl-3-aminomethyleneoxindole (VII d) which crystallized from ether-chloroform, m.p. 145–146°; ultraviolet spectrum (95% ethanol):  $\lambda_{\max}$  272 m $\mu$  (log  $\epsilon$  4.30), 276 m $\mu$  (log  $\epsilon$  4.31) and 315 m $\mu$  (log  $\epsilon$  4.10).

*Anal.* Calcd. for C<sub>10</sub>H<sub>10</sub>ON<sub>2</sub>: C, 69.00; H, 5.75; N, 16.10. Found: C, 69.20; H, 5.89; N, 15.95.

Reduction of 500 mg. of 3-hydroxylaminomethyleneoxindole diacetate (VII f) gave an oil, which on chromatography resolved into 150 mg. (53%) of an ether eluate of 3-methyl-oxindole (IXa),<sup>24</sup> m.p. 124°, and 125 mg. (32%) of a chloroform eluate of 3-acetamidomethyl-oxindole (IXb), m.p. 220°.

**Attempted Hydrolysis of 3-Acetamidomethyl-oxindole (IXb).**—A solution of 100 mg. of 3-acetamidomethyl-oxindole (IXb) in 30 ml. of 5% aqueous sodium hydroxide was refluxed for 1 hour. The solution was neutralized with dilute hydrochloric acid and extracted with chloroform. After drying of the organic extract over sodium sulfate, the solvent was removed, leaving an amorphous solid residue. Despite several crystallizations from ethanol the solid showed no distinct m.p. It exhibited the characteristic oxindole ultraviolet absorption at 250 m $\mu$  and infrared absorptions at 2.96 and 3.15  $\mu$  for NH and 5.82  $\mu$  for C=O.

**Alkylations and Acylations of the 3-Formylindoles (XIa and b).**—3-Formylindole (XIb) (1.45 g.) was added to a stirred potassium *t*-butoxide solution, prepared from 420 mg. of potassium in 50 ml. of *t*-butyl alcohol, under nitrogen. The orange red solution was stirred at room temperature for 1 hr., whereupon 2 ml. of methyl iodide was added dropwise and the stirring continued. The color soon discharged and a white precipitate appeared. The solution now was refluxed for 5 hr., then water added and the mixture extracted with ether. The extract was washed with water, dried over sodium sulfate and the solvent evaporated under vacuum. The oily residue crystallized on trituration with ether and yielded 1.35 g. of 1-methyl-3-formylindole (XI d), m.p. 68–69° (lit.<sup>19</sup> m.p. 65°).

A similar run with 230 mg. of 2-methoxy-3-formylindole (XIa), 1 ml. of methyl iodide and 25 ml. of a *t*-butoxide solution, from 60 mg. of potassium, led to 175 mg. of 1-methyl-2-methoxy-3-formylindole (XIc), m.p. 138–139°, no depression on admixture with an authentic sample.<sup>8</sup>

A mixture of 100 mg. of 2-methoxy-3-formylindole (XIa), 100 mg. of dry sodium acetate and 1.5 ml. of acetic anhydride was heated at 170° for 10 minutes, whereupon 1 ml. of dilute hydrochloric acid was added to the solidified mass and the mixture extracted with ether. The extract was dried over anhydrous sodium sulfate, the solvent evaporated and the residue triturated with ethanol. The resulting precipitate was washed with ethanol and crystallized from chloroform, containing a trace of ethanol, leading to long colorless needles of 1-acetyl-2-methoxy-3-formylindole (XIe), m.p. 161–163°; spectra: ultraviolet (95% ethanol),  $\lambda_{\max}$  222 m $\mu$  (log  $\epsilon$  4.42), 252 m $\mu$  (log  $\epsilon$  4.12) and 303 m $\mu$  (log  $\epsilon$  3.94),  $\lambda_{\min}$  240 m $\mu$  (log  $\epsilon$  4.02) and 277 m $\mu$  (log  $\epsilon$  3.77); infrared (CHCl<sub>3</sub>), C=O 5.83(s), 6.06(s), 6.40(s), C=C 6.34(m)  $\mu$ .

*Anal.* Calcd. for C<sub>12</sub>H<sub>11</sub>O<sub>3</sub>N: C, 66.5; H, 5.07. Found: C, 66.4; H, 5.14.

**Reduction of 2-Methoxy-3-formylindole (XIa).**—A mixture of 125 mg. of 2-methoxy-3-formylindole (XIa) and 100 mg. of lithium aluminum hydride in 70 ml. of anhydrous ether was stirred at room temperature for 16 hr. Sufficient water was added dropwise to decompose all remaining unreacted hydride, followed by an addition of 7 ml. of 10% sodium hydroxide solution, filtration of the resulting precipitate and extraction of the aqueous filtrate with ether. The combined ether fractions were dried over sodium sulfate, and the solvent evaporated. The residue was sublimed at 100–120° and 20 mm. to yield 75 mg. of a pale yellow, foul-smelling solid, m.p. 92–93°, whose m.p., mixed m.p. and m.p. of its brick-red picrate, m.p. 173–174°, proved it to be skatole (XI f) by comparison with authentic samples.

**Condensations of the 3-Formylindoles (XIa and b).**—A mixture of 3 g. of 3-formylindole (XIb) and 30 ml. of 25% methylamine solution was warmed for 10 minutes and then left standing for 5 hr. The precipitated solid was filtered, washed five times with 5-ml. portions of water, and dried for 12 hr. The solid, 2.98 g., m.p. 124–125°, could be crystallized from benzene-petroleum ether yielding pale orange needles, m.p. 123–124°, and sublimed at the toluene reflux temperature and 2 mm. to colorless XIk, m.p. 123–124°, strong absorption peaks at 260 and 293 m $\mu$ .

*Anal.* Calcd. for C<sub>10</sub>H<sub>10</sub>N<sub>2</sub>: C, 76.0; H, 6.34; N, 17.7. Found: C, 75.7; H, 6.24; N, 18.0.

The addition of an ethereal HCl solution to an ether solution of XIk caused immediate precipitation of a solid. Filtration thereof gave a salt, m.p. 249–250°, which on crystallization from absolute ethanol produced a pale yellow crystalline hydrochloride of XIk, m.p. 251–252° (lit.<sup>22</sup> m.p. 240–242°).

*Anal.* Calcd. for C<sub>10</sub>H<sub>11</sub>NCl: C, 61.7; H, 5.66; N, 14.4. Found: C, 62.1; H, 5.64; N, 14.3.

A mixture of 120 mg. of 2-methoxy-3-formylindole (XIa), 180 mg. of hippuric acid and 70 mg. of sodium acetate in 1 ml. of acetic anhydride was warmed on a steam-bath for 10 min. On cooling, the red solution solidified. Water was added and the mixture stirred to break up the solid mass. The remaining solid was filtered, m.p. 255–258°. Several crystallizations from large volumes of chloroform yielded colorless glistening flakes of XIg, m.p. 271–272°; ultraviolet spectrum (95% ethanol):  $\lambda_{\max}$  231 m $\mu$  (log  $\epsilon$  4.21) and 284 m $\mu$  (log  $\epsilon$  4.02),  $\lambda_{\text{shoulder}}$  275–280 m $\mu$  (log  $\epsilon$  3.98–4.00),  $\lambda_{\min}$  261 m $\mu$  (log  $\epsilon$  3.83).

*Anal.* Calcd. for C<sub>21</sub>H<sub>18</sub>O<sub>3</sub>N<sub>2</sub>: C, 67.7; H, 4.76; N, 7.4. Found: C, 67.4; H, 4.22; N, 7.55.

**2-Methoxy-3-cyanoindole (XIII).**—2-Methoxy-3-formylindole oxime (XIh) (65 mg.) was heated at 165–180° at atmospheric pressure until all solid had changed to a red liquid and bubbling had ceased. The liquid then was sublimed at 160–170° and 2 mm., yielding 30 mg. of solid sublimate. Several crystallizations from benzene yielded a pale brown granular nitrile (XIII), m.p. 197–198°; spectra: ultraviolet (95% ethanol),  $\lambda_{\max}$  245 m $\mu$  (log  $\epsilon$  3.99) and 281 m $\mu$  (log  $\epsilon$  3.78); infrared (Nujol), NH 3.17(m), C≡N 4.52(m), C=C 6.17(w), 6.30(w) and 6.38(m)  $\mu$ .

*Anal.* Calcd. for C<sub>10</sub>H<sub>9</sub>O<sub>2</sub>N<sub>2</sub>: C, 69.76; H, 4.65; N, 16.28. Found: C, 69.56; H, 5.22; N, 16.2.

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