

# The Reaction of Some Indoles and Indolines with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone

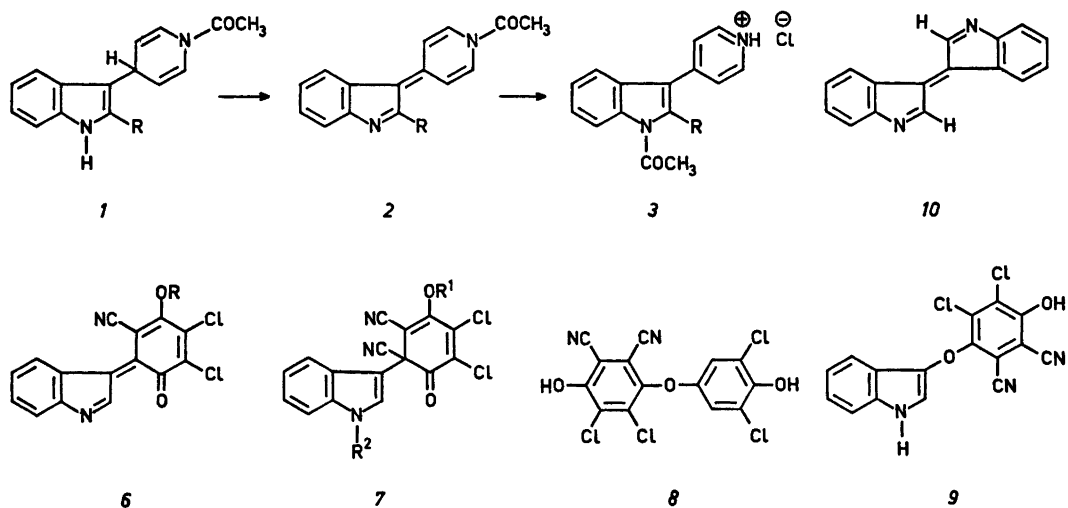
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Indole and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) form a 1:1 donor-acceptor complex, which was found to be stable in the crystalline state in dichloromethane. In solvents such as dioxane the complex gave rise to a substitution product (4), which on heating eliminated HCN affording the quinone (5). 3-Alkyl indoles and DDQ gave 3-alkylidene-3*H*-indoles (which could be isolated as, *e.g.*, sulfates). DDQ dehydrogenated 3-(*N*-acetyl-1,4-dihydro-4-pyridyl) indoles yielding a transacetylated salt (19). The dehydrogenation of indolines by DDQ was complicated as the desired indoles could participate in consecutive substitution reactions. Dehydrogenation of *N*-acylated indolines in dioxane at 75 °C followed by hydrolysis was found to be a convenient method for the preparation of indoles.

In the transformation of 3-(*N*-acetyl-1,4-dihydro-4-pyridyl) indole (1, R=H) to 4-(*N*-acetyl-3-indolyl)pyridinium chloride (3, R=H) by the action of *N*-acetylpyridinium chloride, the 3-alkylidene-3*H*-indole (2, R=H) was suggested<sup>1</sup> to be a key intermediate. In order to substantiate this mechanism it appeared desirable to prepare the intermediate 2 by dehydrogenation of 1 under neutral conditions as 2 should be sensitive to basic<sup>2,3</sup> as well as acidic conditions. In this paper the results of the reaction of 1 as well as several model compounds with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) are reported.



Scheme 1. 6 a, R=H; b, R=CH<sub>3</sub>; c, R=COCH<sub>3</sub>. 7 a, R<sup>1</sup>=COCH<sub>3</sub>, R<sup>2</sup>=H; b, R<sup>1</sup>=CH<sub>3</sub>, R<sup>2</sup>=H; c, R<sup>1</sup>=R<sup>2</sup>=CH<sub>3</sub>; d, R<sup>1</sup>=COCH<sub>3</sub>, R<sup>2</sup>=CH<sub>3</sub>.

## RESULTS

*A. Reaction of 2- and 3-unsubstituted indoles with DDQ.* DDQ rapidly reacts (within 3 min) with indole in dichloromethane at 25 °C to give dark-blue crystals (98 % yield) of a stable 1:1 charge-transfer complex. The complex may be recrystallized from hot tetrachloroethylene and was found to be stable for several months. The infrared spectrum of the complex was composed of the spectra of the components, indicating a nonionic, diamagnetic complex. The visible spectrum showed a charge-transfer band at 592 nm. An analogous, stable 1:1 complex from carbazole and DDQ has recently been reported by several groups.<sup>4-6</sup>

The DDQ-indole complex also formed quickly in dry dioxane, but in this solvent the complex is transformed to an orange-red, acidic (soluble in aqueous NaHCO<sub>3</sub> and forming stable pyridine salts) compound in nearly quantitative yield within 2 h. Addition of a small amount of water or methanol reduced the time of conversion to a few seconds. Elemental analysis and spectral data (MS, <sup>1</sup>H NMR, IR) are in agreement with structure *4a*. In refluxing aqueous ethanol or heating above its melting point (*ca.* 130 °C) *4a* eliminated HCN yielding the dark-blue quinone *5a*, which was readily reduced to give the corresponding hydroquinone. Addition of suitable bases (*e.g.* pyridine) facilitated the elimination. The reactions are summarized in Scheme 2.

The reaction of indole with benzoquinone probably proceeds similarly, however, in this case only the final product, 3-indolylbenzoquinone, has been isolated.<sup>7,8</sup> Interestingly the reaction of indole and tetracyanoethylene<sup>9-12</sup> also seems to involve a similar sequence as the reaction of indole with DDQ, including elimination of HCN (facilitated by base) to give the

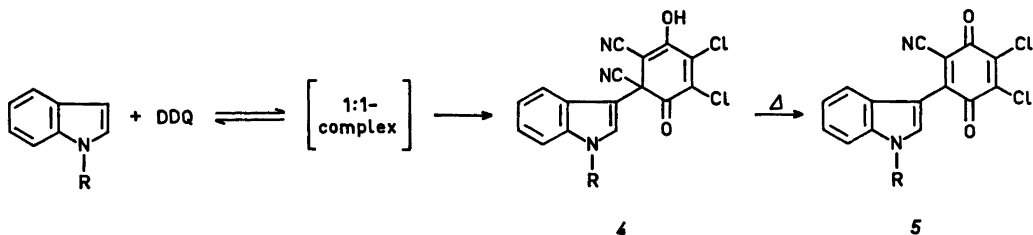
final product, 3-tricyanovinylindole.

Since the UV spectra of *5b* (prepared *via* *N*-methylindole and DDQ) and *5a* are somewhat different, a significant contribution from the tautomer *6a* cannot be excluded. Attempts to prepare *6b* and *6c* by elimination of HCN from *7a* and *7b* resulted in hydrolysis to *5a* (when heated in aqueous ethanol) or in the formation of high-molecular tarry products when thermolysed. The reluctance of *7a* and *7b* to eliminate HCN as compared with *4a* is also evident from their mass spectra. While the spectra of *7a* and *7b* showed strong parent ion peaks, that of *4a* was lacking such a peak.

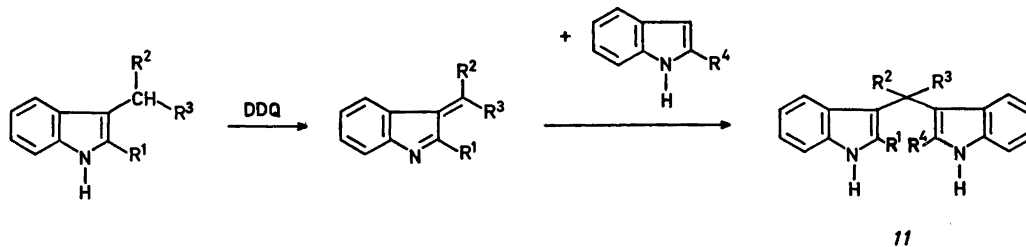
In an extensive study<sup>13-17</sup> of the reactions of phenols with DDQ Becker has isolated products of several types, notably the adduct *8*. The corresponding indole DDQ adduct *9* (isomeric with *4a*) could not be detected along with *4a*, which probably reflects the higher reactivity of indole for electrophilic substitution. No adducts corresponding to *4* have been found in the phenol series.

In methanol solution the formation of *4a* from indole and DDQ is completed within 1 min (as compared to 2 h in dioxane). The reaction is, however, less clean and 3,3-biindolyl and the known<sup>18</sup> compound *10* were formed as minor products. Analogous to the oxidative coupling of phenols,<sup>13</sup> DDQ readily dehydrogenated 3,3-biindolyl to give *10*.

*B. Reaction of 2- and/or 3-alkyl indoles with DDQ.* Several reagents are known<sup>3</sup> to dehydrogenate 3-alkylindoles to the corresponding 3-alkylidene-3*H*-indoles. Accordingly, DDQ was found to effect this transformation under mild conditions. The 3-alkylidene-3*H*-indole formed can, in certain cases, be isolated as a salt. Thus, addition of sulfuric acid to the reaction mixture obtained from 2-methyl-3-isopropyl-



Scheme 2. *4* and *5 a*, R = H; *b*, R = CH<sub>3</sub>.



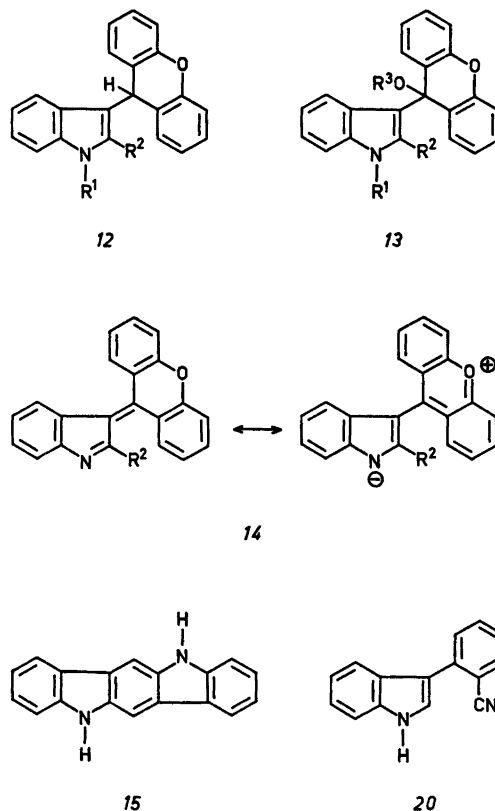
Scheme 3.

indole and DDQ in tetrahydrofuran-ether gave the known <sup>19</sup> hydrogen sulfate of 2-methyl-3-isopropylidene-3*H*-indole. The 3-alkylidene-3*H*-indole formed can also be trapped by addition of a 3-unsubstituted indole. Unsymmetrical diindolylmethanes (e.g. 11, R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> = H, R<sup>4</sup> = CH<sub>3</sub>) may be prepared by this route. By-products (unidentified) are, however, formed and for preparative purposes the conventional technique <sup>20,21</sup> (heating of a gramine with the appropriate indole) is preferred. Mild hydrolysis of the 3-alkylidene-3*H*-indoles formed gave an indole and a carbonyl compound. Thus, treatment of the reaction mixture from 3-(diphenylmethyl)-2-methylindole and DDQ with dilute sodium hydroxide in water/ethanol gave benzophenone and 2-methylindole. Attempts to isolate the free 3-alkylidene-3*H*-indole failed (cf. Ref. 2). However, they were readily isolated as salts. Not even the resonance-stabilized 3-alkylidene-3*H*-indole (14) could be isolated as a free base. The violet-blue salts of 14 prepared by dehydrogenation of 12 with DDQ slowly absorbed water giving, probably *via* 13*a*, xanthone and more complex products (not isolated). Addition of sodium ethylate in ethanol to 12*c* and 12*d* gave the known <sup>22</sup> compounds 13*b* and 13*c*, respectively. Hydrolysis of the salts of 14 with sodium hydroxide in water gave as expected xanthone and the appropriate indole.

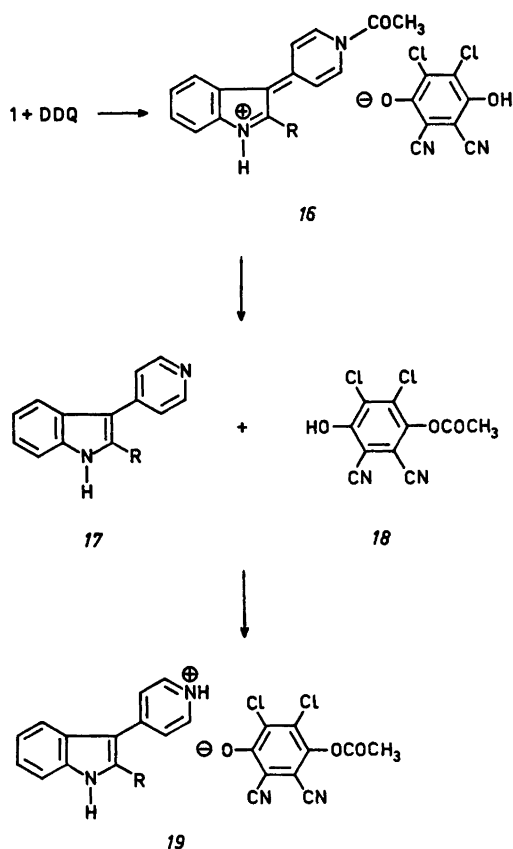
The reactions of 3-unsubstituted 2-alkylindoles with DDQ in methanol were found to be very complex. For example, from the reaction of 2-methylindole with DDQ only the highly insoluble indolo[3,2*b*]carbazole <sup>23</sup> (15) was isolated. Interestingly, Becker <sup>18-17</sup> has described related DDQ-induced C-C couplings in the phenol series.

C. Reaction of 3-(*N*-acetyl-1,4-dihydro-4-pyridyl)indoles with DDQ. 3-(*N*-Acetyl-1,4-

dihydro-4-pyridyl)indoles (1) rapidly reacted with DDQ in ethyl acetate forming a brown unstable solid (16), which was gradually (0.5–2 h) converted to a light-yellow (often crystalline) salt (19) in high yield. The structure of the salt (19) is evident from an independent preparation from the base (17) and the acid (18), thus



Scheme 4. 12 *a*, R<sup>1</sup> = R<sup>2</sup> = H; *b*, R<sup>1</sup> = H, R<sup>2</sup> = CH<sub>3</sub>; *c*, R<sup>1</sup> = R<sup>2</sup> = CH<sub>3</sub>; *d*, R<sup>1</sup> = H, R<sup>2</sup> = C<sub>6</sub>H<sub>5</sub>. 13 *a*, R<sup>1</sup> = R<sup>3</sup> = H, R<sup>2</sup> = CH<sub>3</sub>; *b*, R<sup>1</sup> = R<sup>2</sup> = CH<sub>3</sub>, R<sup>3</sup> = C<sub>2</sub>H<sub>5</sub>; *c*, R<sup>1</sup> = H, R<sup>2</sup> = C<sub>6</sub>H<sub>5</sub>, R<sup>3</sup> = C<sub>2</sub>H<sub>5</sub>.



Scheme 5.

mimicking the last step in the reaction pathway suggested in Scheme 5.

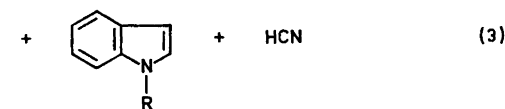
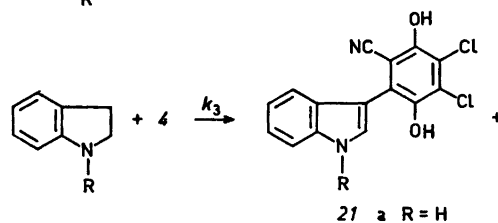
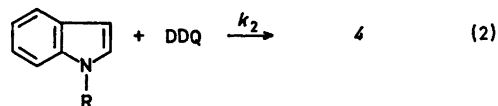
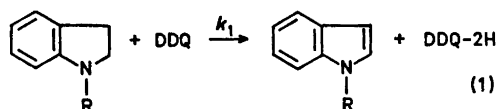
The brown unstable solid (16) was found to be a powerful acetylating agent. Thus, phenyl acetate and *N*-acetylindole, were rapidly formed on treatment of 16 with phenol and indole, respectively. The formation of a small amount of 2,3-dichloro-5,6-dicyanohydroquinone diacetate along with 19 is thus not surprising.

By treatment with sodium hydroxide in aqueous ethanol 19 was readily converted into the corresponding free base, (cf. Ref. 25). The fact that 16 is an acylation agent supports the earlier formulated transformation ( $I \rightarrow 3$ ). In consonance it was found that 3-(4-pyridyl)indole was converted to *N*-acetyl-3-(4-pyridyl)indole by a reagent formed from, e.g., 3-(*N*-acetyl-1,4-dihydro-4-pyridyl)-5-bromoindole and DDQ.

The reaction of 3-(*N*-acetyl-1,4-dihydro-3-cyano-4-pyridyl)indole with DDQ was rather slow and required 1 h at reflux temperature (ethyl acetate). The product formed is readily soluble in this solvent and obviously is not a salt but is probably best described as a complex between 18 and 3-(3-cyano-4-pyridyl)indole (20).<sup>\*</sup> The components could readily be separated by column chromatography or by extraction of 18 with sodium acetate (aq., 5.0 %).

*D. Some implications of the results.* The reaction between indole and DDQ is rapidly performed under mild conditions (25 °C) giving 4a which seems to be in contradiction to the reported dehydrogenations<sup>27-32</sup> of 3-unsubstituted indolines, e.g. 1-(5'-*O*-trityl-2',3'-di-*O*-acetyl- $\beta$ -D-ribofuranosyl)indoline to 3-unsubstituted indoles at rather high temperatures (~130 °C, refluxing xylene). For this reason we investigated the reaction between one equiv-

<sup>\*</sup> Compound 20 should be a considerably weaker base than 3-(4-pyridyl)indole. The protonated forms of 3-cyanopyridine and pyridine have the  $pK_a$  values<sup>26</sup> 1.5 and 5.2, respectively.



Scheme 6.

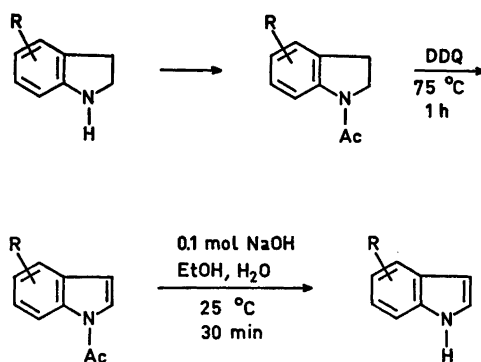
alent indoline with one equivalent DDQ in dioxane at 25 °C.\* The main products were indole and 2,3-dichloro-5,6-dicyano-1,4-hydroquinone (DDQ-2H) with 21a as a minor product, showing that *under these conditions* the dehydrogenation (eqn. 1) is faster than the substitution (*i.e.*  $k_1 > k_2$ ). When two equivalents of DDQ were used, 4a and DDQ-2H were the only products.

Eqn. 3 accounts for the formation of the minor product (21). In separate experiments it was found that pure 4a smoothly dehydrogenated indolines in good yields. DDQ-2H could not be detected in these experiments, indicating that 4a or 5a and not DDQ formed by dissociation of 4a is the active dehydrogenative agent in this reaction. In a complementary competitive (DDQ vs 4a) dehydrogenation of indoline it was shown that  $k_1 \gg k_3$ .

The choice of solvent is important for the outcome of the reaction of DDQ with indoline. Thus, when one equivalent of indoline was reacted with one equivalent of DDQ in methanol the predominant products were 21a, DDQ-2H, and indole indicating that in this solvent the substitution (eqn. 2) is faster than the dehydrogenation (eqn. 1) (*i.e.*  $k_2 > k_1$ ). Reaction 3 is slower than reaction 1 in this solvent too, as evidenced from an analogous competitive experiment (*i.e.*  $k_1 > k_3$ ). DDQ has been used extensively<sup>27-31</sup> for dehydrogenation of indolines containing sugar-residues in position 1. From our results with simple indolines we consider it likely that compounds similar to 4 and 21 may be formed, especially if protic solvents are used, along with the desired dehydrogenated products. In this connection it is interesting to note that Preobrazhenskaya *et al.*<sup>27</sup> obtained fractions containing unidentified indoles from the dehydrogenation of 1-(5'-*O*-trityl-2',3'-di-*O*-acetyl- $\beta$ -D-ribofuranosyl)indoline with DDQ.

In order to dehydrogenate indolines more cleanly we have developed the following procedure.

The dehydrogenation step is smoothly effected in high yield at 75 °C in dioxane. In contrast tetrachloro-1,4-quinone could not effect dehydrogenation of *N*-acetylated indolines even



Scheme 7.

in refluxing dioxane. In separate experiments it was found that *N*-acetylindoles do not react with DDQ under these conditions. The *N*-acetylindole, which may be isolated, is readily hydrolyzed under mild conditions. By this procedure, *e.g.* 5-iodoindole and 5-acetaminoindole can be conveniently prepared.

DDQ has been suggested<sup>34</sup> as a non-destructive reagent for detection of indoles by taking advantage of the formation of the highly coloured charge-transfer complex. However, in view of the transformation to secondary products now demonstrated, we consider that other reagents suggested such as polynitrofluorenones are more suitable.<sup>35,36</sup> Actually, we could recover indole after treatment with DDQ only if non-polar solvents ( $\text{CH}_2\text{Cl}_2$ , benzene) were used. As materials such as silica gel and cellulose were found to strongly catalyze the conversion of the complex into the adduct (4), any work up by chromatography prohibits the use of DDQ as non-destructive reagent.

## EXPERIMENTAL

Melting points were determined on a micro hot stage melting point apparatus and are uncorrected. Elemental analyses were carried out by A. Bernhardt, Elbach über Engelskirchen, West Germany, or Centrala Analys-laboratoriet, Uppsala, Sweden. IR spectra were recorded with a Perkin Elmer 421 infrared spectrophotometer, the spectra of solids being determined as KBr discs and oils as liquid films.  $^1\text{H}$  NMR spectra were recorded with a Varian-A60 instrument or a JEOL JNM-MH-100 instrument. The spectra were obtained on  $\text{CDCl}_3$  solutions or  $\text{DMSO}-d_6$  solutions. Mass

\* Interestingly, Baxter *et al.* recently<sup>33</sup> have used diethyl ether as solvent for dehydrogenations of indoline derivatives with DDQ.

spectra were recorded with a LKB 9000 instrument. Unless otherwise stated column chromatography was performed with silica gel (Merck 0.05–0.2 mm) using dichloromethane with 5% methanol as eluent. UVIS spectra were recorded with a Beckmann DK2-instrument.

**Indole-DDQ-(1:1)-complex.** A solution of indole (1.17 g, 0.01 mol) in dry dichloromethane (10 ml) was added to a stirred solution of DDQ (2.27 g, 0.01 mol) in dry dichloromethane (100 ml). The dark blue crystals formed were collected after 5–10 min and dried in a desiccator. Yield 3.38 g (98%). On heating, the complex decomposed without melting. The complex may, however, be recrystallized from hot tetrachloroethylene or dichloromethane; IR: 3390 (NH), 2232 (w, CN), 1663 (CO), 1553, 1450, 1347, 1243, 1171, 1094, 887, 789, 776, 750, 711, and 666  $\text{cm}^{-1}$ . VIS [ $\text{CH}_2\text{Cl}_2$  (log  $\epsilon$ )] 592 (2.03) nm. Anal.  $\text{C}_{16}\text{H}_7\text{Cl}_2\text{N}_3\text{O}_2$ : C, H, N.

**Reaction of indole with DDQ in dioxane.**  
**Synthesis of 4a.** A solution of indole (11.7 g, 0.1 mol) in dioxane (50 ml) was added dropwise to DDQ (22.7 g, 0.1 mol) in dioxane (150 ml) at 20 °C without cooling. During the addition the temperature increased to ~30 °C, and the molecular complex precipitated. After 0.5–1.5 h. the dark blue complex had been transformed into an orange-red crystalline product (containing crystal-dioxane), which was collected on a filter and dried *in vacuo*. Yield 28.6 g (86%); m.p. 130–135 °C. By addition of light petroleum to the filtrate an additional crop (4.5 g) was obtained. The analytical sample was recrystallized from ether-light petroleum and carefully dried. IR: 3400 (NH), 3115 (broad, OH), 2215 (w, CN), 1684 (CO), 1527, 1448, 1415, 1350, 1228, 1114, 1080, 890, 867, 827, 765, and 740  $\text{cm}^{-1}$ . UV, VIS [ethanol(log  $\epsilon$ )] 215(4.48), 262(4.31), and 359(3.81) nm. The mass spectrum is identical with that of compound 5a, due to the ready elimination of HCN. Anal.  $\text{C}_{18}\text{H}_{11}\text{Cl}_2\text{N}_3\text{O}_2$ : C, H, N.

**Methylation of 4a with one equivalent of diazomethane.** **Synthesis of 7b.** Compound 4a (0.172 g, 0.5 mmol) in ether (5 ml) was methylated with a solution of diazomethane (0.5 mmol) in ether at 0 °C. The mixture obtained was cooled to –30 °C and the precipitate collected and washed repeatedly with cool ether. Yield 66 mg (37%); m.p. 222–224 °C. The analytical sample was recrystallized from ethanol; m.p. 231–233 °C. IR: 3365 (NH), 2206 (CN), 1702 (CO), 1603, 1559, 1458, 1420, 1348, 1328, 1244, 1235, 1057, 782, 761, and 693  $\text{cm}^{-1}$ . UV,VIS [ethanol(log  $\epsilon$ )] 214 (4.49), 342 (4.56) and 445 (2.91) nm. MS *m/e* [(% rel.int.)]: 359 (55), 357 (86), 344 (45), 342 (65), 327 (61), 325 (100), 316 (64), 314 (96), 294 (60), 279 (58), 262 (28), 251 (54), 189 (34), 165 (41), and 87 (51). Only peaks stronger than 25% of the base peak are listed. Anal.  $\text{C}_{17}\text{H}_9\text{Cl}_2\text{N}_3\text{O}_2$ : C, H, N.

**Acetylation of 4a.** **Synthesis of 7a.** A solution of 4a (344 mg) in acetic acid (5 ml) and acetic anhydride (1 ml) was stirred at 25 °C for 2 h and

left overnight. Water (5 ml) was added and after ca. 5 min a precipitate separated which was collected, washed with 50% acetic acid and dried in an exsiccator over KOH. Yield 170 mg (44%), m.p. 170–173 °C. IR: 3425 (NH), 2210 (w, CN), 1790 (CO), 1701 (CO), 1535, 1465, 1422, 1342 1311, 1248, 1234, 1144, 1025, 910, 774, and 748  $\text{cm}^{-1}$ . UV,VIS [ethanol(log  $\epsilon$ )] 217 (4.58), 264 (4.06), 282 (4.11) and 462 (2.99) nm. Anal.  $\text{C}_{18}\text{H}_9\text{Cl}_2\text{N}_3\text{O}_3$ : C, H, N.

**Acetylation of 4b.** **Synthesis of 7d.** The same procedure as described for the acetylation of 4a was used. Yield 65%; m.p. 172–176 °C (after crystallization from ethanol). IR: 2212 (w, CN), 1797 (s, CO), 1709 (s, CO), 1535, 1310, 1258, 1240, 1168, 1143, 1040, 1017, 909, 781 and 758  $\text{cm}^{-1}$ . UV,VIS [ethanol(log  $\epsilon$ )] 217 (4.58), 264 (4.06), 282 (4.07) and 462 (2.99) nm. MS [*m/e*(% rel.int.)]: 401 (32), 399 (45), 359 (66), 358 (42), 357 (100), 356 (34), 334 (39), 332 (76), 330 (42), 322 (32), 315 (42), 313 (61) 294 (76), 165 (47), 131 (30), and 87 (30). Only peaks stronger than 30% of the base peak and above *m/e* 50 are listed. Anal.  $\text{C}_{19}\text{H}_{11}\text{Cl}_2\text{N}_3\text{O}_3$ : C, H, N.

**5,6-Dichloro-3-cyano-2-(3-indolyl)-1,4-benzoquinone (5a).** **Method A.** Compound 4a (344 mg, 1 mmol) was heated (140 °C) until the evolution of HCN had ceased. The cooled dark blue reaction mixture was extracted with ether. The extract was concentrated, light petroleum was added and the resulting solution cooled to –30 °C. The dark blue precipitate obtained was collected. Yield 290 mg (92%); m.p. 225–232 °C. The analytical sample was recrystallized from ethanol; m.p. 232–234 °C. IR: 3400 (NH), 2210 (w, CN), 1695 (CO), 1542, 1353, 1208, 1113, 867, 768, 741 and 681  $\text{cm}^{-1}$ . UV,VIS[ethanol(log  $\epsilon$ )] 213 (4.57), 277 (4.08), 302 (4.11) and 600 (3.67) nm. MS [*m/e*(% rel.int.)]: 320 (23), 319 (17), 318 (83), 317 (23), 316 (100), 290 (13), 288 (17), 253 (17), 225 (14), 190 (13), 166 (28), 139 (19), 87 (20), and 37 (10). Only peaks stronger than 10% of the base peak are recorded. Anal.  $\text{C}_{18}\text{H}_6\text{Cl}_2\text{N}_3\text{O}_2$ : C, H, N.

**Method B.** A mixture of 4a (344 mg, 1 mmol), ethanol (2.5 ml) and water (2.5 ml) was heated at reflux for 1.5 h. After cooling the dark blue solid obtained was collected, dried and recrystallized from ethanol. Yield 240 mg (76%); m.p. 232–234 °C.

**5,6-Dichloro-3-cyano-2-(3-N-methyl-indolyl)-1,4-benzoquinone (5b).** **Method B** (see above) was used. Yield 71%; m.p. 228–230 °C. UV,VIS [ethanol(log  $\epsilon$ )] 216 (4.23), 302 (3.77), 381 (2.66), and 602 (3.45) nm. Anal. calc. for  $\text{C}_{18}\text{H}_8\text{Cl}_2\text{N}_3\text{O}_2$ : C 58.0; H 2.14; N 8.5. Found: C 57.5; H 2.5; Cl 20.9; N 8.4.

**Reaction of 1-methylindole with DDQ.** **Synthesis of 4b.** Compound 4b was prepared analogously to 4a, except that water (200 ml) was added before the collection of the precipitate. The crude product was recrystallized from tetrahydrofuran-light petroleum and dried. Yield 88%; m.p. 130–135 °C, dec. IR: 3390 (NH), 2975, 2880, 2218 (CN), 1705, 1535, 1468,

1362, 1340, 1290, 1257, 1236, 1042, 880, 780, 750 and 690  $\text{cm}^{-1}$ . UV, VIS [ethanol(log  $\epsilon$ )] 219 (4.65), 263 (4.38), and 380 (3.36) nm. The mass spectrum is identical with that of compound 5b. Anal.  $\text{C}_{17}\text{H}_9\text{Cl}_2\text{N}_3\text{O}_2$ : C, H, N.

**Methylation of 4b. Synthesis of 7c.** The same procedure as described for 7b was used. Yield 22%; m.p. 183–186 °C (after crystallization from ethanol). IR: 2203 (CN), 1698 (CO), 1603, 1534, 1465, 1320, 1256, 1240, 1048, 1022, 782 and 748  $\text{cm}^{-1}$ . UV[ethanol(log  $\epsilon$ )] 217 (4.62) and 283 (4.10) nm. MS[m/e(% rel.int.)]: 373 (58), 371 (88), 357 (65), 355 (100), 341 (38), 339 (59), 330 (66), 328 (100), 310 (28), 308 (68), 293 (58), 276 (25), 265 (41), 189 (26), 168 (32), 165 (35), and 87 (32). Only peaks stronger than 25% of the base peak are listed. Anal. calc. for  $\text{C}_{18}\text{H}_{11}\text{Cl}_2\text{N}_3\text{O}_2$ : C, H, N.

**Indolo[3,2-b]carbazole (15).** DDQ (1.36 g, 6 mmol) was added to a stirred solution of 2-methylindole (262 mg, 2 mmol) in methanol (25 ml). After 3 h at 25 °C the solvent was evaporated and the residue extracted with sodium carbonate (2 × 20 ml, aq. 5%). The insoluble material was washed with water and extracted with acetic acid. The extract residue after washing with water and recrystallization from pyridine gave indolo[3,2-b]carbazole. Yield 28 mg (11%); m.p. >400 °C. The IR and MS spectra were identical with those of an authentic<sup>23</sup> sample.

**3-(Diphenylmethyl)-2-methylindole.** 2-Methylindole (6.55 g, 0.05 mol), diphenyl carbinol (9.2 g, 0.05 mol) and acetic acid (35 ml) were refluxed for 2 h. The crystals formed on cooling were collected and washed with cold methanol. Yield 11.6 g (78%); m.p. 159–161 °C. Anal.  $\text{C}_{22}\text{H}_{19}\text{N}$ : C, H, N.

**3-(Diphenylmethyl)indole** was prepared as described earlier;<sup>37</sup> m.p. 126–127 °C (lit.<sup>37</sup> 126–127 °C).

**3-(9-Xanthyl)indole (12a).** Xanthidrol (3.96 g, 0.02 mol), indole (2.34 g, 0.02 mol) and acetic acid were mixed and stirred at 30 °C for 0.5 h. After cooling (+10 °C) the solid formed was collected and washed with methanol. Yield 4.1 g (69%); m.p. 142–146 °C. The analytical sample was recrystallized from methanol; m.p. 146–147 °C. Anal.  $\text{C}_{21}\text{H}_{15}\text{NO}$ : C, H, N.

The following compounds were similarly prepared.

**2-Methyl-3-(9-xanthyl)indole (12b).** Yield 76%; m.p. 194–195 °C. Anal.  $\text{C}_{22}\text{H}_{17}\text{NO}$ : C, H, N.

**1,2-Dimethyl-3-(9-xanthyl)indole (12c).** Yield 80%; m.p. 185–168 °C. Anal.  $\text{C}_{23}\text{H}_{19}\text{NO}$ : C, H, N.

**2-Phenyl-3-(9-xanthyl)indole (12d).** The reaction conditions were changed from 30 °C (0.5 h) to 50 °C (1 h). Yield 92%; m.p. 219–221 °C. Anal.  $\text{C}_{22}\text{H}_{19}\text{NO}$ : C, H, N.

**Dehydrogenation of 2-phenyl-3-(9-xanthyl)indole, preparation of 2-phenyl-3-(9-xanthylidene)3H-indolium 2,3-dichloro-5,6-dicyano-1,4-hydroquinolate.** A solution of DDQ (227 mg,

1 mmol) in ethyl acetate (3 ml) was added to a solution of 2-phenyl-3-(9-xanthyl)indole (373 mg, 1 mmol) in ethyl acetate (5 ml). After 1 h at 25 °C the dark blue crystals formed were collected and dried. Yield 530 mg (88%); m.p. 228–231 °C. IR: 2222 (CN), 1620, 1600, 1572, 1480, 1425, 1377, 1218, 1138, 1115, 1055, 885, 787, 780, 755, 745, 732, 710, and 701  $\text{cm}^{-1}$ . Anal.  $\text{C}_{25}\text{H}_{15}\text{Cl}_2\text{N}_3\text{O}_2$ : C, H, N.

**2-Phenyl-3-(9-ethoxy-9-xanthyl)indole (13c).** To a mixture (prepared as described above) of 2-phenyl-3-(9-xanthylidene)-3H-indolium 2,3-dichloro-4,5-dicyano-1,4-hydroquinolate (600 mg, 1 mmol) and ethyl acetate was added sodium ethoxide (prepared from 117 mg, 5 mmol of sodium) in ethanol (8 ml). After 10 min at 25 °C the solvents were evaporated *in vacuo*. The residue extracted with ether gave after recrystallization from ethanol 2-phenyl-3-(9-ethoxy-9-xanthyl)indole. Yield 206 mg (49%); m.p. 165–167 °C (lit.<sup>22</sup> 166–168 °C). A sample<sup>22</sup> kindly provided by Dr. N. E. Evans was identical with our product.

**1,2-Dimethyl-3-(9-ethoxy-9-xanthyl)indole (13b).** The method described above was used starting from 1,2-dimethyl-3-(9-xanthyl)indole (12c), without isolation of the intermediate xanthylidene salt. Yield 54%; m.p. 173–175 °C (lit.<sup>22</sup> 174–176 °C). A sample<sup>22</sup> kindly provided by Dr. N. E. Evans was identical with our product.

**Hydrolysis of 2-phenyl-3-(9-xanthylidene)-3H-indolium 2,3-dichloro-5,6-dicyano-1,4-hydroquinolate.** A mixture of 2-phenyl-3-(9-xanthylidene)-3H-indolium 2,3-dichloro-5,6-dicyano-1,4-dihydroquinolate (300 mg, 0.5 mmol), sodium hydroxide (50 ml, aq., 5%) and ether (80 ml) was stirred for 3 h. The ether phase was dried and evaporated. The residue treated with methanol gave xanthone. Yield 30 mg (31%); m.p. 174–175 °C. The methanol mother liquor contained 2-phenylindole and several unidentified products as evidenced by TLC ( $\text{SiO}_2$ ,  $\text{CH}_2\text{Cl}_2$ ).

**Dehydrogenation of 3-(diphenylmethyl)-2-methylindole, preparation of 2-methyl-3-(diphenylmethylene)-3H-indolium chloride.** A solution of 3-(diphenylmethyl)-2-methylindole (297 mg, 1 mmol) in dioxane (5 ml). After 2 h at 25 °C the crystals of DDQ-2H formed were filtered off and the clear brown solution treated with HCl(g). The brown crystals formed were collected after 2 h and dried; m.p. 205–206 °C (lit.<sup>38</sup> 205–206 °C).

**2-Methyl-3-isopropylidene-3H-indolium hydrogen sulfate. Method A.** Sulfuric acid (6 ml) was slowly added to a well-stirred solution of 2-methylindole (6.05 g, 0.05 mol) in dry ether (60 ml) and dry acetone (20 ml) at 5 °C. The yellow salt obtained was collected immediately and dried in an exsiccator. Yield 12.4 g (96%); m.p. 160–165 °C, dec. (lit.<sup>19</sup> 165 °C, dec.)

**Method B.** DDQ (227 mg, 1 mmol) in THF (5 ml) was added to a stirred solution of 2-methyl-3-isopropylindole (173 mg, 1 mmol) in

ether (5 ml) followed, 5 min later, by sulfuric acid (98.1 mg, 1 mmol). The precipitated salt is identical with that obtained according to method A.

**2-Methyl-3-isopropylindole.** 2-Methyl-3-isopropylindole-3*H*-indolium hydrogen sulfate (5.38 g, 0.02 mol) was added in portions to a refluxing mixture of lithium aluminium hydride (2.0 g) in ether (250 ml). After completed addition the reflux was continued for 6 h, whereupon water was carefully added. The ether phase was collected, dried and evaporated. Distillation (110 °C/3 mmHg) of the residue gave 2-methyl-3-isopropylindole. Yield 2.95 g (88 %); m.p. 34–36 °C. <sup>1</sup>H NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 1.35 (6, CH<sub>3</sub>, d), 2.02 (3, CH<sub>3</sub>, s), 3.16 (1, CH, sept.), 6.7–8.0 (4, arom.). Anal. C<sub>12</sub>H<sub>15</sub>N: C, H, N:

**3-Indolyl-(2-methyl-3-indolyl)methane** (11 R<sup>1</sup>=R<sup>2</sup>=R<sup>3</sup>=H, R<sup>4</sup>=CH<sub>3</sub>). DDQ (227 mg, 1 mmol) in dioxane (4 ml) was added to 2,3-dimethylindole (145 mg, 1 mmol) in dioxane (3 ml). After 2 min indole (117 mg, 1 mmol) in dioxane (2 ml) was added. The DDQ-2*H* formed was filtered off after 2 h and the solvent evaporated. The residue was separated by preparative TLC on silica gel using CH<sub>2</sub>Cl<sub>2</sub> as eluent. Yield 174 mg (67 %); m.p. 140–141 °C (lit.<sup>20</sup> 137–138 °C).

**Di(2-methyl-3-indolyl)methane.** Following the description given above, 192 mg (70 %) of the title compound was obtained; m.p. 233–235 °C (lit.<sup>29</sup> 235–238 °C).

**Dehydrogenation of 3,3-biindolyl.**<sup>37</sup> Preparation of 10. 3,3-Biindolyl (232 mg, 1 mmol) in hot ethyl acetate (25 ml) was treated with DDQ (227 mg, 1 mmol) in ethyl acetate (5 ml). The mixture was refluxed for 5 min, cooled and filtered through a short column of alumina. The purified (removal of DDQ-2*H*) solution was concentrated and allowed to crystallize. Yield 154 mg (67 %). The absorption spectrum (EtOAc) was in agreement with that reported.<sup>18</sup>

**5-Iodoindole.** DDQ (2.27 g, 10 mmol) in dioxane was added to a solution of 5-iodo-*N*-acetylindole<sup>40</sup> (2.87 g, 10 mmol) in dioxane (80 ml) at 75 °C. After 2 h at this temperature the mixture was cooled, DDQ-2*H* removed, and the residue evaporated under reduced pressure. The residue was dissolved in methanol (20 ml) and water (25 ml) containing sodium hydroxide (1.5 g). After 30 min at 25 °C the solvents were removed under reduced pressure. The residue extracted with ether gave, after evaporation and recrystallization from hexane, 5-iodoindole. Yield 2.2 g (90 %); m.p. 100–102 °C (lit.<sup>41</sup> m.p. 99–102 °C).

5-Bromoindole [yield 82 %; m.p. 88–89 °C (lit.<sup>42</sup> m.p. 89–89.5 °C)] and indole (yield 77 %) were similarly prepared.

**5-Bromo-*N*-acetylindole.** Method A. 5-Bromo-*N*-acetylindole (10 mmol) was treated as described above except that the sodiumhydroxide treatment was omitted. Yield (2.19 g, 92 %). After recrystallization from light petroleum

(with final cooling to –25 °C); m.p. 101–102 °C. <sup>1</sup>H NMR (100 MHz, CDCl<sub>3</sub>): δ 2.49 (3, CH<sub>3</sub>, s), 6.43 (1, 3-*H*, d), 7.0–8.2 (4, arom.) MS [*m/e* (% rel.int.): 239 (25), 237 (25), 198 (8), 197 (95), 196 (11), 195 (100), 179 (34), 117 (6), 116 (64), 115 (20), 114 (7), 89 (20), 88 (12), 63 (9), and 62 (9)]. Only peaks stronger than 5 % of the base peak are listed. Anal. calc. for C<sub>10</sub>H<sub>8</sub>BrNO: C 50.4; H 3.4; Br 33.6; N 5.9. Found: C 50.6; H 3.5; Br 33.1; N 5.7.

**Method B.** 5-Bromoindole (1.96 g, 10 mmol) and *N*-acetyl imidazole (1.21 g, 11 mmol) in dimethyl sulfoxide (20 ml) were heated at 120 °C for 2 h. To the cooled solution water (80 ml) was added and the product extracted with ether and then treated as in method A. Yield 2.10 g (88 %), m.p. 101–102 °C.

***N*-(Chloroacetyl)indole.** Method A. As described for 5-bromo-*N*-acetylindole starting with *N*-(chloroacetyl)indoline.<sup>43</sup> Yield 79 %; m.p. 116–117 °C. NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 5.18 (2, CH<sub>2</sub>, s), 6.75 (1, 3-*H*, d), 7.84 (1, 2-*H*, d), *J*<sub>23</sub> 4.1 Hz. MS [*m/e* (% rel.int.): 195 (9), 194 (3), 193 (27), 130 (4), 118 (9), 117 (100), 116 (17), 90 (12), 89 (22), 88 (3), 77 (5), 69 (3), 68 (14), 67 (5), 51 (4), 50 (3), 49 (6), and 39 (6)]. Only peaks stronger than 3 % of the base peak are listed. Anal. C<sub>10</sub>H<sub>8</sub>ClNO: C, H, N.

**Method B.** Indole (11.7 g, 0.1 mol) and chloroacetic anhydride (17.1 g, 0.1 mol) in dioxane (90 ml) were refluxed for 3 h. Thereafter cooled water was added and the semisolid mass obtained was crystallized from methanol with final cooling to –20 °C. Yield 14.4 g (75 %); m.p. 116–117 °C.

**5-Acetaminoindole.** 5-Acetamino-*N*-acetylindole<sup>44,45</sup> (2.18 g, 0.01 mol) and DDQ (2.27 g, 0.01 mol) in ethyl acetate (100 ml) were refluxed for 3 h. The solvent was removed using reduced pressure and the residue extracted with ether and sodium carbonate (5 %, aq.). The evaporated ether extract recrystallized from acetonitrile gave the title compound. Yield 1.07 g (62 %); m.p. 117–118 °C (lit.<sup>46</sup> m.p. 117–118 °C).

**3-(*N*-Acetyl-1,4-dihydro-4-pyridyl)-2-methylindole.** Pyridine (8.1 ml) was added at 20–25 °C to acetyl chloride (3.5 ml) in dry dioxane (60 ml). 2-Methylindole (6.05 g, 0.05 mol) in dioxane (10 ml) was added. After 2 h at 30 °C the mixture was poured into water (300 ml). The light-brown oil obtained was separated, washed with water and triturated with methanol. The crystals formed were recrystallized from methanol. Yield 6.5 g (52 %); m.p. 154–156 °C. <sup>1</sup>H NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 2.21 (3, CH<sub>3</sub>, s), 2.34 (3, CH<sub>3</sub>, s), 5.48 (1, CH, s), 5.99 (2, CH, t), 7.6–8.8 (arom + CH, 6), 10.72 (1, NH, s). Anal. C<sub>15</sub>H<sub>15</sub>N<sub>2</sub>O: C, H, N.

**3-(*N*-Acetyl-1,4-dihydro-3-cyano-4-pyridyl)-indole.** The same procedure as for 3-(*N*-acetyl-1,4-dihydro-4-pyridyl)-2-methylindole was used except that the reaction temperature was kept at 50 °C. Yield 64 %; m.p. 191–192 °C. <sup>1</sup>H NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ 2.30 (3, CH<sub>3</sub>, s), 4.60



(1, CH, s), 5.14 (1, CH, quart.), 6.3–9.0 (7, arom), 10.98 (1, NH, s). Anal.  $C_{18}H_{13}N_3O$ : C, H, N.

**3-(*N*-Acetyl-1,4-dihydro-4-pyridyl)-5-bromoindole.** The same procedure as for 3-(*N*-acetyl-1,4-dihydro-4-pyridyl)-2-methylindole was used except that the temperature was kept at 45 °C. Yield 71 %; m.p. 188–190 °C.  $^1H$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  2.21 (3, CH<sub>3</sub>, s), 4.40 (1, CH, s), 6.6–8.1 (6, arom), 9.94 (1, NH, s). Anal.  $C_{15}H_{13}BrN_2O$ : C, H, N.

**4-(2-Methyl-3-indolyl)pyridinium 4-acetoxy-2,3-dichloro-5,6-dicyanophenolate.** DDQ (227 mg, 1 mmol) in ethyl acetate (5 ml) was added to a supersaturated solution (25 °C) of 3-(*N*-acetyl-1,4-dihydro-4-pyridyl)-2-methylindole (252 mg, 1 mmol) in ethyl acetate (20 ml). The mixture obtained was stirred at 40 °C for 1 h. The crystals formed were collected and washed with ethyl acetate and recrystallized from methanol (with final cooling to –25 °C). Yield 442 mg (72 %); m.p. 185–188 °C. Anal.  $C_{24}H_{16}Cl_2N_4O_2$ : C, H, N. Preparative TLC (silica gel, CH<sub>2</sub>Cl<sub>2</sub>) of the concentrated ethyl acetate mother liquor gave 2,3-dichloro-4,5-dicyano-1,4-hydroquinone diacetate (2 mg, 0.8 %); m.p. 180–181 °C (lit.<sup>47</sup> 181–182 °C).

**5-Bromo-3-(4-pyridyl)indole. Method A.** Pyridine (8.1 ml) was added at 20–25 °C to acetyl chloride (7.0 ml) in dioxane (80 ml). 5-Bromoindole (9.8 g, 0.05 mol) was then added and the temperature was kept at 50 °C for 3 h. The mixture was filtered and the crude 4-(*N*-acetyl-5-bromo-3-indolyl)pyridinium chloride was collected and hydrolysed by refluxing (1 h) in 2 M sodium hydroxide (75 ml) and ethanol (75 ml). Water slowly added to the cooled solution gave crystals of 5-bromo-3-(4-pyridyl)indole. Yield 5.9 g (43 %); m.p. 218–220 °C. MS [*m/e* (% rel. int.)]: 275 (15), 274 (97), 273 (18), 272 (100), 194 (5), 193 (16), 192 (12), 182.5 (8), 182 (9), 167 (21), 166 (8), 165 (7), 140 (6), 139 (10), 138 (5), 96.5 (10), and 69.5 (5). Only peaks stronger than 5 % of the base peak are listed. Anal.  $C_{13}H_9BrN_2$ : C, H, N.

**Method B.** 4-(5-Bromo-3-indolyl)pyridinium 4-acetoxy-2,3-dichloro-5,6-dicyanophenolate was dissolved in a solution of sodium hydroxide in ethanol and water. The solution obtained was slowly diluted with water and the crystals obtained were collected.

**2-Methyl-3-(4-pyridyl)indole.** DDQ (2.27 g, 10 mmol) in ethyl acetate (40 ml) was added to a supersaturated solution (25 °C) of 3-(*N*-acetyl-1,4-dihydro-4-pyridyl)-2-methylindole (2.52 g, 10 mmol) in ethyl acetate (150 ml). The mixture obtained was stirred at 40 °C for 1 h. The salt formed was collected and dissolved in a solution of sodium hydroxide (5.0 g) in ethanol (35 ml) and water (10 ml). The solution obtained was slowly diluted with water and the crystals obtained were collected and recrystallized from acetonitrile. Yield 1.25 g (60 %); m.p. 192–193 °C (lit.<sup>25</sup> 186–187 °C).

**3-(3-Cyano-4-pyridyl)indole and 2,3-dichloro-5,6-dicyano-1,4-dihydroquinone monoacetate.**

DDQ (2.27 g, 10 mmol) in ethyl acetate (25 ml) was added to a hot solution of 3-(*N*-acetyl-1,4-dihydro-3-cyano-4-pyridyl)indole (2.63 g, 10 mmol) in ethyl acetate (50 ml). After 2 h at reflux the solvent was evaporated and the residue extracted with sodium acetate (2 × 25 ml, aq., 8 %). The residue from the extraction was dissolved in hot ethanol (25 ml) containing water (3 ml) and sodium hydroxide (1.0 g). The solution was cooled to 25 °C and water was slowly added giving crystals of 3-(3-cyano-4-pyridyl)indole. Yield 1.36 g (62 %); m.p. 200–202 °C. Anal.  $C_{14}H_9N_3$ : C, H, N. IR 3330 (NH), 2195 (CN), 1578, 1515, 1470, 1449, 1408, 1387, 1316, 1248, 1177, 820, and 727  $cm^{-1}$ . MS [*m/e* (% rel. int.)]: 220 (18), 219 (100), 218 (17), 217 (5), 192 (6), 191 (8), 165 (7), 164 (13), 138 (5), 82.5 (5), and 63 (5). Only peaks stronger than 5 % of the base peak are listed. The pH of the cooled sodium acetate extract was adjusted to ca. 0.5 by addition of conc. HCl. The crystals obtained recrystallized from acetonitrile gave 2,3-dichloro-5,6-dicyano-1,4-dihydroquinone monoacetate; m.p. 185–186 °C (lit.<sup>47</sup> 184–185 °C). IR 3400, 2190 (CN), 1770, 1625, 1553, 1510, 1440, 1340, 1264, 1201, 1166, 1070, and 1008  $cm^{-1}$ . MS [*m/e* (% rel. int.)]: 270 (18), 268 (27), 230 (43), 229 (17), 228 (70), 200 (20), 110 (16), 109 (25), 101 (18), 100 (17), 89 (30), 87 (100), and 86 (22). Only peaks stronger than 15 % of the base peak and above *m/e* 80 are listed.

**2,3-Dichloro-5,6-dicyano-1,4-dihydroquinone diacetate.** The reaction just described was repeated starting with 1 mmol of the reactants. The reaction mixture was separated by preparative TLC (silica gel) using CH<sub>2</sub>Cl<sub>2</sub>–CH<sub>3</sub>OH (95:5) as eluent. Yield 11 mg (4 %); m.p. 180–181 °C (lit.<sup>47</sup> 181–182 °C).

**Reduction of 5a. Synthesis of 21a. Method A.** 5a (344 mg, 1 mmol) in ethanol (5 ml) and sodium sulfite (aq., 5 %, 5 ml) was heated (60 °C) for 30 min. After cooling and acidification with conc. HCl the mixture was evaporated and the dry residue extracted with methyl acetate. The extract obtained was concentrated and toluene was added. The cooled (finally to –25 °C) solution deposited crystals of 21a. Yield 191 mg (59 %); m.p. 248 °C, dec. MS [*m/e* (% rel. int.)]: 320 (5), 319 (2), 318 (7), 88 (5), 73 (5), 70 (9), 61 (16), 45 (16), 44 (4), 43 (100), 42 (5), 31 (3), 29 (15), 28 (3), 27 (7), 18 (4), and 15 (6). Only peaks stronger than 2 % of the base peak are listed. UV, VIS [ethanol (log  $\epsilon$ )] 219 (4.81), 278 (3.95) and 354 (3.98) nm. IR: 3495, 3380, 3225, 2250 (CN), 1587, 1538, 1440, 1419, 1351, 1290, 1230, 1209, 1175, 1135, 895, 880, and 741  $cm^{-1}$ . Anal.  $C_{16}H_8Cl_2N_2O_2$ : C, H, N.

**Method B.** To 5a (344 mg, 1 mmol) in dioxane (4 ml) was added 1-methylindoline (131 mg, 1 mmol) in dioxane (1 ml). After 30 min at 35 °C the mixture was evaporated *in vacuo*. The residue was extracted first with hexane

and then with methyl acetate. After concentration and cooling the methyl acetate solution gave crystals of 10a. Yield 75 %. The hexane extract was filtered through a short column containing silica gel. Evaporation of the purified extract gave 1-methylindole (104 mg, 79 %).

*Method C. 5a* (317 mg, 1 mmol) in ethyl acetate (25 ml) was hydrogenated (H<sub>2</sub>, Pd/C) until the theoretical amount of hydrogen had been consumed (ca 5 min, also indicated by a colour-change; dark blue to light yellow). The catalyst was filtered off and the solution worked up as described above. Yield 97 %.

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