Registry No.—Cl_3CCO_2H, 76-03-9; Cl_3CCOCl, 76-02-8; $Cl_2C{=}C{=}O$, 4591-28-0; $POCl_3$, 10025-87-3.

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Electrochemical Acetoxylation of *N*-Acetylindolines and *N*-Acetylindoles. A New Synthesis of Indigos

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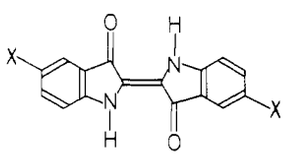
Electrochemical acetoxylation of *N*-acetylindolines **3** in AcOH–Et_3N at potentials 1.1–1.7 V vs. SCE, 4 faradays/mol of electricity, using platinum electrodes afforded the corresponding 2,3-diacetoxyindolines **5** in 70–77% yields. Likewise, *N*-acetylindoles **4** gave **5** in 76–82% yields. The acetate **5** could also be prepared from indoline (**2**) without isolating the intermediates **3** and **4**. Thermal decomposition of **5** at 140–145 °C gave *N*-acetylindoxyl acetates **7** in 81–87% yields and subsequent hydrolysis with 1 M aqueous sodium hydroxide provided indigos in 86–96% yields. Electrochemical bromination of **3a** (X = H) using various alkali bromides led to the corresponding bromide **3b** (X = Br) in 95–99% yields, which can be used as a precursor of bromoindigo synthesis.

Recent revival in the use of indigo dyes has stimulated new synthetic interest. Instead of the well-known preparative methods involving alkali fusion of phenylglycine[1] or phenylglycine-*o*-carboxylic acid,[2] we have examined the possibility of using an electrochemical reaction as a nonpolluting procedure for preparing indigos.[3]

We described herein electrochemical acetoxylation of *N*-acetylindolines **3** and *N*-acetylindoles **4** leading to the corresponding 2,3-diacetoxyindolines **5** as well as two-step conversion of the diacetates **5** into indigos **1** via *N*-acetylindoxyl



1a X=H
b X=Br

acetates **7** and also the electrochemical bromination of **3a** (X = H) leading to **3b** (X = Br) as a precursor of bromoindigo synthesis. Actually, we have succeeded in obtaining **5** directly from **2** without isolating **3** and **4** in a one-batch procedure.

A reverse synthetic pathway from indigos **1** to indoline (**2**) via the key intermediate **5** is outlined in Scheme I. Here, it can be seen that our novel indigo synthesis consists of three steps starting from either **2, 3,** or **4** via the intermediates **5** and **7.** Electrolysis of **3a** (X = H) in AcOH–Et_3N at potentials 1.1–1.7 V vs. SCE, applied voltages 2.0–2.9 V, current densities 3.3 mA/cm^2, using platinum foil electrodes consumed ca. 4 faradays/mol of electricity (over 80% of current efficiency) for 3 h (Table I, entry 1). All three products, 1-acetyl-2,3-diacetoxyindoline (**5a,** X = H, 77%), **4a** (X = H, 3%), and 1-acetylindoxyl acetate (**7a,** X = H, 2%) were separable and were

Scheme I

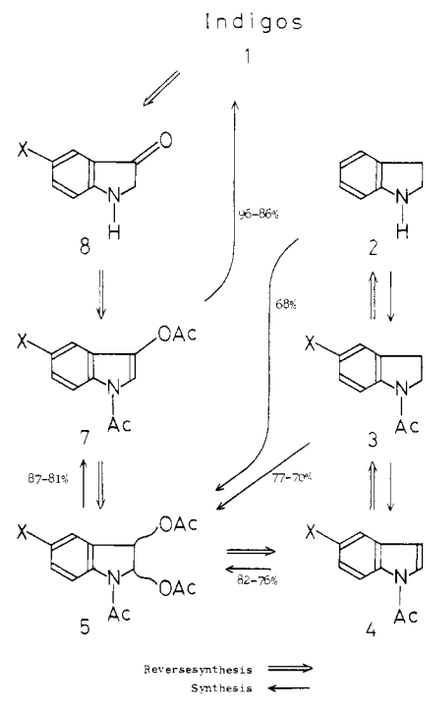


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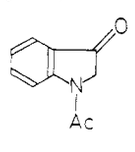
Table I. Conditions[a] and Results of Electrochemical Acetoxylation of *N*-Acetylindolines (3) and *N*-Acetylindoles (4)

Entry	Substrate (0.62 mmol)	Registry no.	Solvent AcOH, mL	Supporting electrolyte (mL)	Current density, mA/cm²	Quantity of electricity, faradays /mol	Product yields,[b] % 4	5	6	7	Recovered 3
1	**3a**	16078-30-1	9	Et_3N (1)	3.3	4.0	3	77		2	
2	**3a**		9	Et_3N (1)	1.8–0.1[c]	0.9	22				64
3	**4a**	576-15-8	9	Et_3N (1)	1.7	2.0	3	82		2	
4	**3a**		9.5	DBU (0.5)	6.7	4.5	3	77		2	
5	**3a**		9	Pyridine (1)	6.7	5.0	1	70		2	
6	**3a**		9	Et_2NH (1)	6.7	5.0	2	61		1	5
7	**3a**		9	Piperidine (1)	6.7	5.0	2	53		1	6
8	**3a**		9	Cyclohexylamine (1)	6.7	5.0	3	49		2	3
9	**3a**		10	$AcONH_4$ (250)[d]	1.7	3.0	6	48		5	10
10	**3a**		10/0.2[e]	Et_4NClO_4 (100)[d]	1.7	3.0					74
11	**3a**		8	Et_4NOTs (100)[d]	1.7–1.0	2.0					90
12	**3a**		10/0.5[e]	AcONa–Et_4NClO_4(100/100)[d]	3.3	3.0	1	2	20		26
13	**3a**		8/1[e]	Et_3N (1)	3.3	4.0	4	8	48		10
14	**3b**	22190-38-1	9	Et_3N (1)	3.3	4.0	7	70			
15	**4b**	61995-52-6	9	Et_3N (1)	3.3	2.0	4	76			
16	**3b**		8/1[e]	Et_3N (1)	5.0	4.5	10	5	51		

[a] The electrolyses were carried out at 22–28 °C, Pt, 3 cm². [b] Isolated yields. [c] Under controlled potential at 1.4 V vs. SCE. [d] The quantity is shown in mg scale. [e] Milliliter of water mixed in the solvent.

characterized. One-batch electrosynthesis of **5a** from **2** could be achieved on treatment with acetic anhydride–acetic acid upon heating for 2 h before the electrolysis.

The voltammetric results (Figure 1) from the electrolysis of **3a** reveal that the electrolytic oxidation of **3a** at 1.1–1.4 V vs. SCE would provide **4a** preferably, however, the competitive electrolysis of **4a** would proceed at 1.4–1.7 V vs. SCE, giving **5a.** Actually, the controlled potential electrolysis of **3a** at 1.4 V vs. SCE at the current from 1.8 to 0.13 mA/cm², 0.9 faraday/mol of electricity, for 9.5 h afforded **4a** (22%, current efficiency 49%) as well as the recovered **3a** (64%) (entry 2). In the same electrolytic conditions as given in entry 1, conversion of **4a** into **5a** could be carried out smoothly in 82% yield along with the formation of **7a** (2%) after passing 2 faradays/mol of electricity (entry 3). The minor product **7a** is expected to arise from the elimination of acetic acid from **5a.** The complete conversion of **5a** to **7a** was accomplished in 87% yield by heating **5a** at 140–145 °C for 5 h. However, 1-acetylindoxyl (**9**) was obtained in 71% yield, when a benzene solution of **5a**



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was refluxed for 10 h in the presence of potassium hydrogen sulfate.

The electrolytic acetoxylation of **3a** using various tertiary amines as a supporting electrolyte shows that triethylamine, 1,8-diazabicyclo[5.4.0]-7-undecene (DBU), and pyridine are a surprisingly effective supporting electrolyte in acetic acid, giving 77–70% yields of **5a** (entries 1, 4, and 5). Secondary and primary amines, including diethylamine, piperidine, and cyclohexylamine, and ammonium acetate were less effective and furnished **5a** in 61–48% yields (entries 6, 7, 8, and 9). In contrast, tetraethylammonium perchlorate and/or tosylate was completely ineffective as a supporting electrolyte in the medium (entires 10 and 11), since no detectable amount of **5a** was found in the electrolysis products. The results demonstrate apparent discrepancy in comparison with the Eberson's investigation, indicating that the side-chain acetoxylation does not require the presence of acetate ion, whereas nuclear acetoxylation cannot be achieved in the absence of acetate ion.[4] Since the side-chain acetoxylation products have been obtained in the media such as AcOH–$NaClO_4$ and/or AcOH–Et_4NOTs, it will be also noted that in the electrolysis of **3a** in the presence of acetate ion (entries 1, 2, 4–9) absence of nuclear acetoxylation products distinguishes the reported assumption. However, complex products including nuclear methoxylation derivatives were obtained, when **3a** was electrolyzed in MeOH–Et_4NClO_4. On the other hand, electrolysis of **2** in MeOH–Et_4NClO_4 afforded the dimeric product **10**[5] in 40–50% yield as a major product. The electrolysis of **2** without protecting the secondary amino group in AcOH–Et_3N did not yield **5a** but provided a film on the anode.[6]

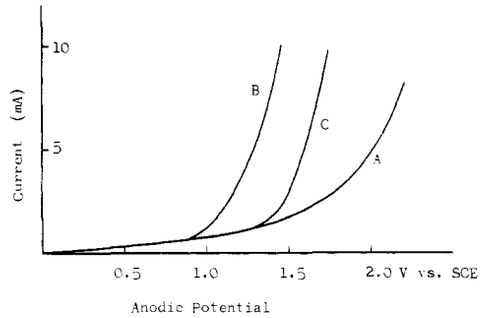
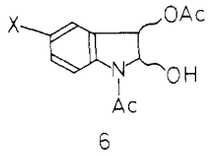


Figure 1. Current–potential curves: (A) Et_3N–AcOH (1:9) solution; (B) in the presence of 0.06 M of *N*-acetylindoline (**3a**); (C) in the presence of 0.06 M of *N*-acetylindole (**4a**), Pt electrodes, at 20 °C.

Use of acetic acid containing a small amount of water with triethylamine or AcONa–Et_4NClO_4 as an electrolyte led to the formation of **6a** (X = H, 20–48%) as a major product along with minor products **4a** (1–4%) and **5a** (2–8%) (entries 12 and



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13). Treatment of the monoacetate **6a** with acetic anhydride–pyridine at 40 °C for 2 h afforded **5a** smoothly.

In view of both the comparison of ^1H NMR spectra of **6a**

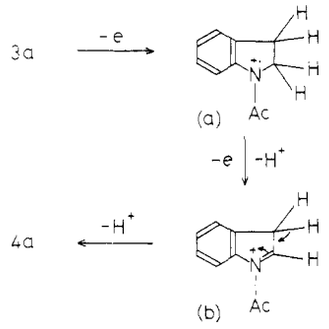
Table II. Electrochemical Bromination of *N*-Acetylindoline (3a) with Various Bromides in Aqueous 93% AcOH[a]

Entry	Supporting electrolyte (mg)	Current density mA/cm^2	Quantity of electricity, faradays/mol	Product yield, %[b] of **3b**
17	NH_4Br (100)	5.0–2.7	2.2	96
18	LiBr (81)	3.8–2.0	2.0	98
19	NaBr (100)	2.7–1.7	2.2	95
20	KBr (120)	3.8–2.7	2.7	99
21	$MgBr_2 \cdot 6H_2O$ (234)	2.0–1.5	2.0	99

[a] A solution of **3a** (100 mg) in aqueous 93% AcOH (10 mL) was electrolyzed at 22–25 °C at 3 V (applied voltage), Pt, 3 cm^2. [b] Isolated yields.

with **5a** and thermal dehydration of **6a**, affording **7a**, there must be present a hydroxy group at the C(2) position of **6a**. This assumption is confirmed by a chemical shift of the C(2) proton at δ 5.60 in the ^{1}H NMR spectrum of **6a** and one at δ 6.64 in the spectrum of **5a**. In this connection, the ^{1}H NMR spectra of **5a** and **6a** have signals as a singlet at δ 5.88 and 5.87 due to every C(3) proton

A reasonable explanation for the electrochemical acetoxylation of **3a** leading to **5a** involves the formation of *N*-acetylindole (**4a**). The formation of **4a** from **3a** can be explained in terms of the mechanism suggested by Mann and his coworkers[7] for the anodic oxidation of aliphatic amines at platinum electrodes in acetonitrile. This mechanism leads to a cation radical intermediate (a), after **3a** undergoes one-



electron discharge on the anode, which suffers from further one-electron oxidation followed with deprotonation to produce the cation intermediate (b) as a precursor of **4a**. It will be noted that highly basic amines, i.e., triethylamine, DBU, and pyridine, all of which have a tertiary nitrogen atom, would assist the elimination of hydrogen atom at the C(3) carbon of **3a**. The electrochemical conversion of **4a** to **5a** would proceed in a similar fashion to the electrolytic acetoxylation of 3-alkylindene, giving the corresponding 1,2-diacetoxyindane.[8]

Efficient electrobromination of **3a** with various bromides was carried out under several conditions and the yields of **3b** are shown in Table II. Otherwise, the chemical bromination of **3a** with bromine in acetic acid has been shown to give **3b** in 85% yield.[9] Electrolysis of **3a** with ammonium bromide in aqueous 93% acetic acid at the potential between 0.8 and 0.9 V vs. SCE, an applied voltage 3 V, current densities 3–5 mA/cm^2, consumed ca. 2.2 faradays/mol of electricity (87% of current efficiency), giving **3b** (96%) (entry 17). Change of bromides did not affect the excellent yield of the formation of **3b** (entries 18–21).

In considering the formation of **3b** from **3a** at 0.8–0.9 V vs. SCE, a cationic species of **3a** on the aromatic ring is unlikely due to the lower oxidation potential of ammonium bromide (Figure 2) in comparison with that of **3a** (anodic limit ca. 1.0 V). The treatment of **3a** with a bromine solution, prepared

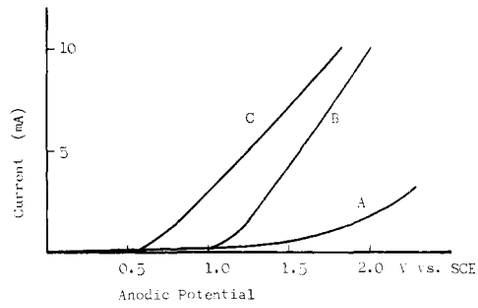


Figure 2. Current–potential curves: (A) 0.13 M $LiClO_4$ aqueous 93% AcOH; (B) in the presence of 0.06 M *N* acetylindoline (**3a**); (C) 0.1 M NH_4Br aqueous 93% AcOH (Pt electrodes, at 20 °C).

previously by electrolysis of AcOH–NH_4Br with 2 faradays/mol of electricity (based on **3a**), afforded **3b** in 25% yield. The inferior result from the chemical bromination in the same medium may be accounted for by considering lack of some contribution from the electrode process. A mechanistic explanation for this reaction would be provided by the assumption based on the aromatic–bromine charge transfer complex[10] and/or the absorption of bromine atoms at the surface of the platinum electrodes.[11]

Subsequent electrolytic acetoxylation of **3b** was performed under a constant current of 3.3 mA/cm^2, applied voltages of 2.1–3.1 V, ca. 4 faradays/mol, at 22–23 °C, giving **5b** in 70% yield as well as **4b** (7%) (Table I entry 14). Likewise, electrolysis of **4b** prepared by dehydrogenation[12] of **3b** afforded **5b** in 76% yield (entry 15). In wet AcOH–Et_3N, electrolysis of **3b** afforded **6b** (X = Br, 51%) as well as **4b** (10%) and **5b** (5%) (entry 16). This diacetate **5b**, when heated to 135–145 °C for 5 h under diminished pressure, decomposed to give **7b**[13] (81%).

Indigo and 5,5′-dibromoindigo (**1a** and **1b**[14]) were obtained in 86–96% yields, respectively, after the indoxyl acetates **7a** and **7b** were hydrolyzed by aqueous 1 M sodium hydroxide at 60–65 °C under exposure to atmosphere. Similarly, base-catalyzed hydrolysis of **9** also gave **1a** in excellent yield.[15a] The direct transformation of **7** into **1** would be considered to undergo oxidative coupling[15] of **8** and/or **9** by the aid of oxygen after the alkaline hydrolysis.

Experimental Section

All melting and boiling points were uncorrected. IR spectra were recorded on a JASCO model IRA-1 spectrometer. ^{1}H NMR spectra were obtained with a Hitachi R-24 spectrometer. Mass spectral analyses were carried out on a JEOL JMS D-100 spectrometer at 75 eV. Current–potential measurements were performed by using Kowa Electronics models PGS-1550 potentio-galvanostat and FG-102A function generator. Column chromatography was carried out using Wako gel C-200 (silica gel) with benzene–AcOEt as an eluent.

Materials. Commercially available indoline (**2**), AcOH, and Et_3N were distilled under reduced pressure before use. *N*-Acetylindoline (**3a**) was obtained on treatment of **2** with Ac_2O in the presence of pyridine.[16] *N*-Acetylindole (**4a**) was prepared from **3a** according to the reported procedure.[12]

Electrolysis Apparatus. An undivided cell was equipped with two platinum foil electrodes (3 cm^2, 5 mm apart), a gas lead pipe, and a thermometer. The vessel was immersed in a water bath at 22–25 °C.

1-Acetyl-2,3-diacetoxyindoline (5a) from 3a. A mixture of **3a** (100 mg, 0.62 mmol) and Et_3N (1 mL) in AcOH (9 mL) was electrolyzed under a constant current (3.3 mA/cm^2) at applied voltages of 2.0–2.9 V, 1.1–1.7 V vs. SCE at 23–25 °C. After 4 faradays/mol of electricity were passed, the solvent was evaporated. The solution concentrated was taken up in benzene–AcOEt (10:1) and washed with aqueous $NaHCO_3$ and brine and dried (Na_2SO_4). After removal of most of the solvent, the residue was chromatographed (SiO_2, benzene–AcOEt 20:1) to give three fractions: The first eluent contained 3 mg of **4a** (3%): bp 115–118 °C (5 mm) (lit.[17] bp 152–153 °C (14 mm)); IR (neat) 1705 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ 2.54 (s, 3, AcN), 6.57

(d, 1, $J \simeq 4$ Hz, HC=CN), 7.05–7.60 (m, 4, ArH, C=CHN), 8.25–8.55 (m, 1, ArH). The second fraction consisted of 3 mg of **7a** (2%): mp 81 °C (lit.[13] mp 82 °C); IR (Nujol) 1745 (C=O), 1700 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.33 (s, 3, AcO), 2.55 (s, 3, AcN), 7.18–7.62 (m, 3, ArH), 7.63 (s, 1, C=CHN), 8.30–8.47 (m, 1, ArH). The third run involved 132 mg of **5a** (77%, trans/cis 9:1 evaluated by ^1H NMR integration). The trans isomer of **5a** was isolated by careful column chromatography (SiO_2, benzene–AcOEt 30:1) as first coming fraction, white crystals, mp 126 °C (cyclohexane): IR (Nujol) 1735 (C=O), 1682 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.08 (s, 3, AcO), 2.11 (s, 3, AcO), 2.30 (s, 3, AcN), 5.94 (s, 1, HCCN), 6.71 (s, 1, HCN), 6.95–7.65 (m, 3, ArH), 7.95–8.20 (m, 1, ArH); mass spectrum *m/e* (rel intensity) 277 (M^+, 23), 235 (10), 176 (17), 175 (32), 133 (100), 123 (23), 117 (17), 93 (12), 77 (13). Anal. Calcd for $C_{14}H_{15}O_5N$: C, 60.63; H, 5.45. Found: C, 60.78; H, 5.39.

In a similar manner, the electrolysis of **3b** (3.3 mA/cm^2, 2.1–3.1 V, 4.0 faradays/mol, 22–23 °C) gave **1-acetyl-5-bromo-2,3-diacetoxyindoline (5b,** 70%) together with 1-acetyl-5-bromoindole (**4b,** 7%). The diacetate **5b:** mp 112 °C (cyclohexane); IR (Nujol) 1745 (C=O), 1690 cm^{-2} (C=O); ^1H NMR ($CDCl_3$) δ 2.11 (s, 3, AcO), 2.14 (s, 3, AcO), 2.30 (s, 3, AcN), 5.90 (s, 1, HCCN), 6.70 (s, 1, CHN), 7.30–7.70 (m, 2, ArH), 8.05 (d, 1, $J \simeq 9$ Hz, ArH); mass spectrum *m/e* (rel intensity) 357 ($M^+ + 2$, 5), 355 (M^+, 5), 315 (5), 255 (22), 253 (21), 213 (46), 211 (48), 43 (100). Anal. Calcd for $C_{14}H_{14}BrNO_5$: C, 47.21; H, 3.96. Found: C, 47.17; H, 4.14.

The 5-bromoindole **4b:** mp 109 °C (hexane-benzene 5:1); IR (Nujol) 1700 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.58 (s, 3, Ac), 6.54 (d, 1, J = 4 Hz, HC=CN), 7.25–7.55 (m, 2, C=CHN, ArH), 7.65 (d, 1, J = 2 Hz, ArH), 8.30 (d, 1, J = 8 Hz, ArH). Anal. Calcd for $C_{10}H_8BrNO$: C, 50.44; H, 3.36. Found: C, 50.44; H, 3.53.

One-Batch Synthesis of 5a from 2 To a mixture of Ac_2O (210 mg, 2.06 mmol), AcOH (18 mL), and Et_3N (2 mL) was added indoline (**2**) (238 mg, 2.00 mmol). After being stirred at 35–40 °C for 2 h, the solution was allowed to cool to 20 °C and electrolyzed under the same conditions as described above and worked up. The residue was chromatographed (SiO_2, benzene–AcOEt 20:1) to give **5a** (68%) as well as minor products **4a** (5%) and **7a** (8%).

Electrolytic Acetoxylation of 4a. A mixture of **4a** (100 mg, 0.63 mmol), AcOH (9 mL), and Et_3N (1 mL) was electrolyzed under a constant current (1.7 mA/cm^2), at applied voltages of 1.9–3.0 V, 1.4–1.7 V vs. SCE at 26–27 °C. After passing 2 faradays/mol of electricity (7 h), the mixture was concentrated. The residue was worked up in the usual manner and chromatographed (SiO_2, benzene–AcOEt 20:1) to give **5a** (82%) along with **4a** (3%) and **7a**[13] (2%).

Similarly, the electrolysis of **4b** (2 faradays/mol, 3.3 mA/cm^2, 2.3–3.4 V, 22–23 °C) gave **5b** (76%) and **4b** (4%).

1-Acetylindoxyl Acetate (7a). The trans isomer of **5a** (100 mg, 0.36 mmol) was heated to 140–145 °C under reduced pressure (20–25 mm) for 5 h and then the mixture was chromatographed (SiO_2, benzene) to give **7a** (67 mg, 87%): mp 81 °C (lit.[13] mp 82 °C); IR (Nujol) 1740 (C=O), 1695 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.35 (s, 3, AcO), 2.56 (s, 3, AcN), 7.15–7.65 (m, 3, ArH), 7.71 (s, 1, C=CHN), 8.30–8.60 (m, 1, ArH).

In a similar manner, the thermal deacetoxylation of **5b** gave **1-acetyl-5-bromoindoxyl acetate (7b)** in 81% yield: mp 122–123 ° C (hexane–benzene 5:1) (lit.[13] mp 124 °C); IR (Nujol) 1760 (C=O), 1710 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.37 (s, 3, AcO), 2.58 (s, 3, AcN), 7.30–7.75 (m, 3, ArH, C=CHN), 8.30 (d, J = 9 Hz, ArH).

3-Acetoxy-1-acetyl-2-hydroxyindoline (6a). A mixture of **3a** (100 mg, 0.62 mmol), AcOH (8 mL), Et_3N (1 mL), and H_2O (1 mL) was electrolyzed under a constant current (3.3 mA/cm^2) at 24–26 °C. After 4 faradays/mol of electricity were passed, the solution was worked up in the usual manner to give **6a** (48%) as well as four minor products **3a** (10%), **4a** (4%), and the cis and trans isomers **5a** (8%). The hydroxyindoline **6a,** white crystals: mp 142 °C (benzene); IR (Nujol) 3200 (OH), 1740 (C=O), 1625 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.06 (s, 3, AcO), 2.35 (s, 3, AcN), 4.70 (b, 1, OH), 5.60 (b, 1, HCN), 5.87 (s, 1, HCAr), 6.85–7.60 (m, 3, ArH), 7.80–8.25 (m, 1, ArH); mass spectrum *m/e* (rel intensity) 235 (M^+, 35), 193 (19), 175 (24), 162 (8), 150 (23), 133 (100), 122 (99), 105 (19), 104 (21), 94 (20), 93 (19), 78 (13), 77 (27), 51 (12), 43 (96). Anal. Calcd for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57. Found: C, 61.43; H, 5.70.

3-Acetoxy-1-acetyl-5-bromo-2-hydroxyindoline (6b). The electrolysis of **3b** in AcOH–Et_3N–H_2O (8:1:1) (5.0 mA/cm^2, 2.2–2.3 V, 4.5 faradays/mol, 24–25 °C) gave **6b** in 51% yield togehter with **4b** (10%) and **5b** (5%). The acetate **6b,** white crystals: mp 136 °C (benzene); IR (Nujol) 3160 (OH), 1730 (C=O), 1640 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.10 (s, 3, AcO), 2.36 (s, 3, AcN), 4.75 (b, 1, OH), 5.65 (b, 1, HCN), 5.87 (s, 1, HCAr), 7.30–7.60 (m, 2, ArH), 7.75–8.15 (m, 1, ArH); mass spectrum *m/e* (rel intensity) 315 ($M^+ + 2$, 19), 313 (M^+, 17), 273 (18), 271 (15), 255 (6), 242 (7), 213 (31), 211 (32), 202 (23), 200 (28), 133 (20), 45 (21), 43 (100), 41 (23). Anal. Calcd for $C_{12}H_{12}BrNO_4$: C, 45.88; H, 3.85. Found: C, 45.77; H, 3.93.

Acetylation of 6a. A solution of **6a** (30 mg, 0.13 mmol) in Ac_2O (1 mL) and pyridine (1 mL) was stirred for 2 h at 40 °C. After removal of most of the solvents, the residue was diluted with water and extracted with benzene–AcOEt (10:1). Usual work-up followed by chromatography (SiO_2, benzene–AcOEt 20:1) gave **5a** (93%).

1-Acetylindoxyl (9). A mixture of **5a** (80 mg, 0.29 mmol) and $KHSO_4$ (400 mg) in benzene (5 mL) was refluxed for 10 h. Removal of the solvent followed by column chromatography (SiO_2, benzene–AcOEt 10:1) gave **9** (39 mg, 71%): mp 133–134 °C (EtOH–H_2O 3:1) (lit.[13] mp 138 °C); IR (Nujol) 1720 (C=O), 1675 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.33 (s, 3, Ac), 4.30 (s, 2, CH_2N), 7.00–7.75 (m, 3, ArH), 8.30–8.60 (b, 1, ArH).

Electrolytic Bromination of 3a. A solution of **3a** (100 mg, 0.62 mmol) and NH_4Br (100 mg, 1.02 mmol) in aqueous 93% AcOH (10 mL) was electrolyzed under a constant applied voltage of 3 V, 0.8–0.9 V vs. SCE, 5–3 mA/cm^2, at 23–24 °C. After 2.2 faradays/mol of electricity was passed, the solvent was evaporated under reduced pressure. The residue was taken up in benzene, washed with aqueous $NaHCO_3$ and brine, dried (Na_2SO_4), and concentrated. The residue was chromatographed (SiO_2, benzene–AcOEt 10:1) to give 1-acetyl-5-bromoindoline (**3b**) (146 mg, 96%) as white crystals: mp 118 °C (MeOH) (lit.[9] mp 118–119 °C); IR (Nujol) 1653 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ 2.16 (s, 3, Ac), 3.07 (t, 2, J = 9 Hz, CH_2Ar), 3.99 (t, 2, J = 9 Hz, CH_2N), 7.00–7.40 (m, 2, ArH), 8.05 (d, 1, J = 9 Hz, ArH). The yields of **3b** using various bromides are shown in Table II.

Indigo (1a) was obtained on treatment of **7a** (120 mg, 0.55 mmol) with aqueous 1 M NaOH (10 mL) at 60–65 °C for 5 h. The indigo-blue solution was acidified to pH 6 with aqueous 5% HCl and the blue solid material was filtered off and washed with water. After drying, there was obtained 67 mg (96%) of **1a,** whose spectral data were identical with those of authentic sample.

Similarly, 5,5′-dibromoindigo (**1b**) was obtained from **7b** in 86% yield.

Registry No.—**1a,** 482-89-3; **1b,** 84-40-2; *cis*-**5a,** 66358-39-2; *trans*-**5a,** 66358-40-5; **5b,** 66358-41-6; **6a,** 66358-42-7; **6b,** 66358-43-8; **7a,** 16800-67-2; **7b,** 33588-54-4; **9,** 16800-68-3; **10,** 66358-44-9.

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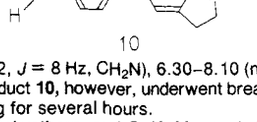

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