Color and Constitution. Part 8 [1]. Some Novel Dyestuffs Containing Indoxyl Residues

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Novel dyes containing *C*-likned indoxyl residues are prepared by two routes: (a) by the reaction of *C*-electrophiles with *N*-acetylindoxyl and (b) by the reaction of active methylene compounds with 2-chloroindole-3-one. The visible absorption spectra are recorded and discussed.

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Indigo **1** is one of the most important of all dyestuffs, with a deep blue color of excellent stability [2]. The importance of the indoleninone nucleus has been recognized since the classical researches into indigo chemistry, and extensive studies have widely extended the indigo class of dyes [3]. We formulated the concept of the "merostabilization" in 1964 [4], and prepared several merostabilized radicals [5,6] which accord with early theoretical suggestions of Dewar [7]. More recently, the intense color of indigo and its derivatives has been attributed to merostabilization in the excited state and the six atom fragment **2** is the chromophore of indigo [8,9]. Recent theoretical calculations suggest significant merostabilization in polar media [10]. The theory of merostabilization of the excited state led us to synthesize isomers of indigo and of azaanalogues containing nitrogen at a ring fusion position [1c]; we also used this concept to guide our search for new class of dyestuffs including bisalkylidine-piperazinediones [1e] and derivatives of maleimide and naphthoquinone [1f,1g]. The present paper is similarly concerned with derivatives of indoxyl, which because of their structural similarity to the chromophore of indigo **2** represent a continuation on our efforts to prepare deeply colored heterocyclic compounds which might be useful dyestuffs and which could allow further exploration of the principle of merostabilization.

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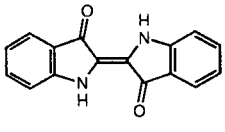

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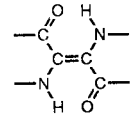

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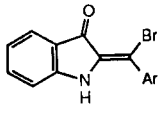

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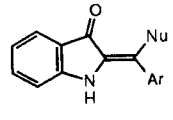

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Our first aims were to synthesize 2-arylideneindolin-3-ones as intermediates for the preparation of 2-(α-bromoarylidene)indolin-3-ones **3** and to attempt reaction of these bromo-derivatives with various nucleophiles to give addition-elimination adducts **4**. A series of 2-arylideneindolin-3-ones **5** was readily synthesized by the reactions of *N*-acetylindoxyl or 3-indolyl acetate with aromatic aldehydes. *N*-Acetylindoxyl was prepared from anthranilic acid in three steps as previously described [11,12]. The 2-arylideneindolin-3-ones **5** were produced by heating *N*-acetylindoxyl and appropriate aldehyde under a nitrogen atmosphere in 50% aqueous ethanol containing 1.5 *N* sodium hydroxide (method A) [13] or by stirring in dimethylformamide and triethylamine as base at room temperature (method B). Alternatively the reaction was carried out with 3-indolyl acetate in aqueous basic ethanol solution under nitrogen (method C).

Reaction of *N*-acetylindoxyl with terephthaldicarboxaldehyde afforded a red crystalline solid, the structure of which was assigned as *p*-phenylenebis(2-ylidineindolin-3-one) **5k**. However, the condensation of acetylindoxyl with ketones or α-diketones (*e.g.* benzil) failed under various conditions. The preparations of various 2-arylideneindoline-3-one derivatives **5a-5k** are summarized in Table I. Assigned structures are consistent with their spectra and analyses (Tables I, II). In the infrared spectra the three expected characteristic bands were found for ν NH, ν C = O and ν C=C. In the ^{1}H nmr spectra, the NH appeared as a broad downfield signal while the methine was characteristic at 6.45-6.90 ppm. The most significant ^{13}C bands are also shown in Table II. The color of these 2-arylideneindoline-3-ones **5** ranges from orange to deep red and they showed spectral maxima at 470-520 nm which underwent a slight bathochromic shift in 1*M* hydrochloric acid.

Attempts to convert the 2-arylindeneindoline-3-ones **5** into the corresponding bromo derivatives **3** by bromination with bromine failed in various conditions, all the attempts gave what appeared to be mixtures of di-, tri- or tetra-bromoderivatives.

Table I

Preparation of Indoxyl Derivatives **5**

Compound	Method	Yield (%)	Crystal form	mp (°C)	lit [13] mp	Calcd. C	Calcd. H	Calcd. N	Formula	Found C	Found H	Found N
5a	A	70	orange	176-178	176-178	81.14	5.01	6.33	$C_{15}H_{11}NO$	81.46	5.04	6.21
5b	A	52	red	154-156	157-158	75.68	4.50	12.61	$C_{14}H_{10}N_2O$	75.85	4.43	12.46
5c	A	45	red	203-205	205-206	75.68	4.50	12.61	$C_{14}H_{10}N_2O$	75.30	4.44	12.39
5d	B	73	orange	178-180	180-181	76.49	5.18	5.58	$C_{16}H_{15}N_2O$	76.10	5.28	5.31
5e	B	88	red	232-234	236-238	-	-	-		-	-	-
5f	B	45	red	271-273	273-274	67.67	3.76	10.53	$C_{15}H_{10}N_2O_3$	67.80	3.66	10.36
5g	B	36	red	193-195	-	67.67	3.76	10.53	$C_{15}H_{10}N_3O_3$	67.42	3.65	10.40
5h	B	47	orange	233-235	-	67.67	3.76	10.53	$C_{15}H_{10}N_2O_3$	67.31	3.70	10.36
5i	C	53	green	208-210	-	74.29	4.76	13.33	$C_{13}H_{10}N_2O$	73.95	4.58	13.56
5j	C	56	orange	219-221	-	75.00	5.36	12.50	$C_{14}H_{12}N_2O$	74.91	5.28	12.52
5k	B	56	red	195-197	-	79.12	4.40	7.69	$C_{24}H_{16}N_2O_2$	78.88	4.65	7.50

Table II

Spectral Data of Indoxyl Derivatives **5**

Compound	UV/Vis (ε) (ethanol)	UV/Vis (ε) (1*M* HCl)	IR (bromoform) cm^{-1} ν NH	ν C=O	ν C=C	^{1}H NMR (dimethyl sulfoxide-d_6) δ NH (br)	CH= (s)	Ar-H (m)	^{13}C NMR (δ) C=O	C=	=CH
5a	472 (9860)	488	3425	1685	1620	10.10	6.76	6.95-7.90	186.1	103.0	134.8
5b	480 (10200)	496	3220	2690	1600	10.20	6.65	6.80-7.80 [a]	190.7	104.4	135.9
5c	471 (10600)	504	3220	1700	1590	9.90	6.60	6.90-7.90 [b]	186.1	104.8	136.1
5d	476 (7600)	484	3665	1695	1630	9.25	6.78	6.80-7.80	179.2	106.5	135.2
5e	520 (13400)	545	3320	1660	1620	9.50	6.60	6.60-7.50	178.5	100.2	134.2
5f	488 (12300)	495	3380	1680	1699	10.20	6.80	6.90-8.50	183.3	101.9	132.4
5g	474 (7700)	485	3420	1690	1595	9.70	6.90	6.91-8.70	201.4	102.5	133.1
5h	470 (12100)	490	3350	1685	1625	10.00	6.70	6.85-8.52	186.4	106.3	135.1
5i	497 (20800)	520	3280	1720	1590	9.15	6.50	6.60-7.80	184.8	102.9	135.2
5j	502 (19500)	535	3300	1650	1600	9.50	6.45	6.85-7.80	184.8	100.0	135.1
5k	487 (21000)	521	3380	1680	1620	10.15	6.80	7.00-8.30	185.5	105.2	136.4

[a] Also 8.80 (1H, d). [b] Also 8.75 (2H, d).

Table III

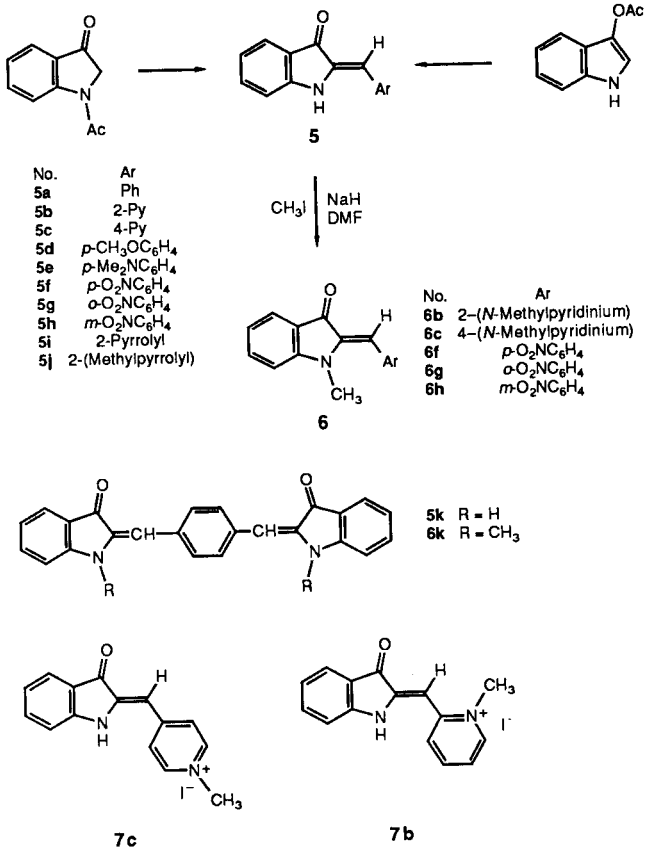
Preparation of Methylated 2-Arylideneindolin-3-ones **6**

Compound	Yield (%)	Crystals	mp (°C)	Calcd. C	Calcd. H	Calcd. N	Formula	Found C	Found H	Found N
6b	68	red	236-238	50.81	3.97	7.41	$C_{16}H_{15}N_2IO$	50.52	3.85	7.14
6c	73	black	295-297	50.81	3.97	7.41	$C_{16}H_{15}N_2IO$	50.49	3.82	7.16
6f	71	red	220-222 [a]	68.57	4.29	10.00	$C_{16}H_{12}N_2O_3$	68.56	4.12	9.76
6g	43	orange	120-122	68.57	4.29	10.00	$C_{16}H_{12}N_2O_3$	68.17	4.09	9.75
6h	57	red	131-133	68.57	4.29	10.00	$C_{16}H_{12}N_2O_3$	68.45	3.97	9.94
6k	48	red	244-246	76.10	5.37	6.80	$C_{26}H_{22}N_2O_3$	75.83	5.08	6.45
7b	69	red	251-253	49.46	3.57	7.69	$C_{15}H_{13}N_2IO$	49.64	3.28	7.39
7c	70	red	286-288	49.46	3.57	7.69	$C_{15}H_{13}N_2IO$	49.80	3.64	7.52

[a] Lit [13] mp 217-218°.

Methylation of the 2-arylideneindoline-3-ones **5** with methyl iodide in dimethylformamide (sodium hydride as base) afforded the corresponding 1-methyl-2-arylideneindolin-3-one **6** in good yield (Scheme 1). Reaction of *p*-phenylenebis(2-ylidineindolin-3-one) **5k** with excess methyl iodide yielded dimethylated product **6k** in 38% yield. In the cases of 2-(2- or 4-pyridylidene)indolin-3-one, two different methylation products were produced by varying reaction conditions: by reacting 2-pyridylideneindolin-3-one with excess methyl iodide in the presence of sodium hydride, dimethylated derivatives **6b** and **6c** were formed. 2-(*N*-Methylpyridinium)methylideneindolin-3-one iodides **7b** and **7c** were obtained in the absence of sodium hydride. All the methyl derivatives were fully character-

Scheme 1



ized by their ^1H and ^{13}C nmr spectra and by elemental analyses (Tables III and IV). Both in the ^1H and ^{13}C nmr spectra the chemical shifts of CH_3 attached to a positively charged pyridinium ring nitrogen were seen considerably downfield to those attached to the neutral indole *N*-atom.

As shown in Tables II and IV, comparisons of the visible spectra of the 2-arylideneindolin-3-ones with those of the corresponding 1-methylated derivatives demonstrated a bathochromic shift with very little change in extinction coefficient after methylation at the NH group. For example, a 35 nm red shift was achieved in going from 2-(4-nitrophenylidene)indolin-3-one **5f** to its methylated derivative **6f**, and 62 nm from 2-(4-pyridylidene)indolin-3-one **5c** to its dimethyl derivative **6c**.

Recently, 3,4-dichloro-*N*-phenylmaleimide and 2,3-dichloro-1,4-naphthoquinone have been condensed with various mono- and bis-nucleophiles to yield a range of novel chromophoric systems [1f,1g]. We have now shown that 3,4-dichloro-*N*-phenylmaleimide and 3,4-dichloro-1,4-naphthoquinone react respectively with one and two moles of *N*-acetylindoxyl in the presence of triethylamine to produce derivatives in which *N*-acetylindoxyl has acted as a carbon nucleophile, in the first of these transformations the second chlorine atom is hydrolyzed. 3-(3-Oxo-2-indolylidene)-4-oxo-*N*-phenylmaleimide **8** and 2,3-bis(3-oxo-2-indolylidene)-1,4-naphthoquinone **9** thus obtained (Scheme 2) had their structural assignments supported by ^1H nmr and ir spectra and by microanalysis. Compound **8**

Table IV

Spectral Data of Methylated 2-Arylideneindolin-3-ones **6** and **7**

Compound	UV/Vis (ε) (ethanol)	IR (bromoform) cm^{-1} ν C=O	ν C=C	^1H NMR (dimethyl sulfoxide-d$_6$) δ CH= (s)	Ar-H (m)	PyN$^+$CH$_3$	N-CH$_3$	^{13}C NMR δ C=O	PyN$^+$CH$_3$	N-CH$_3$
6b	508 (11100)	1700	1610	6.60	6.90-9.10	4.45	3.50	185.2	41.2	29.4
6c	538 (13700)	1640	1580	6.65	7.00-8.90	4.35	3.45	185.1	46.8	29.30
6f	523 (13500)	1640	1570	6.70	6.90-8.20	-	3.35	-	-	-
6g	486 (9630)	1680	1620	6.90	7.00-9.15	-	3.60	185.5	-	28.8
6h	504 (10100)	1680	1610	6.60	7.00-8.20	-	3.35	184.1	-	28.7
6k	509 (14200)	1685	1610	6.80	7.10-8.10	-	3.35	190.0	-	28.7
7b	490 (10100)	1610	1580	6.75	7.15-9.35	4.45	-	186.1	45.9	-
7c	488 (11300)	1690	1590	6.60	7.30-9.10	4.40	-	186.5	46.9	-

Table V

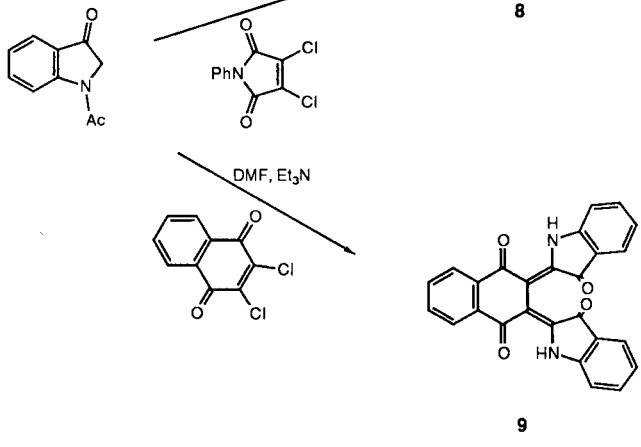
Preparation of Indoxylidene Derivatives **11-15**

Compound	Yield (%)	Crystals	mp (°C)	Calcd. C	H	N	Formula	Found C	H	N
11	60	violet	233-235	81.72	4.02	4.33	$C_{22}H_{13}NO_2$	81.37	4.33	3.99
12	62	red	276-278	74.18	3.27	5.04	$C_{17}H_{19}NO_3$	73.85	3.08	4.75
13	64	violet	>280	73.53	3.92	6.86	$C_{25}H_{16}N_2O_4$ [a]	73.52	3.92	6.83
14	47	brown	205-207	74.15	4.49	7.86	$C_{22}H_{16}N_2O_3$ [a]	74.00	4.32	7.55
15	39	brown	165-167	72.45	4.15	5.28	$C_{16}H_{13}NO_3$ [a]	72.67	4.26	5.65

[a] Monohydrate.

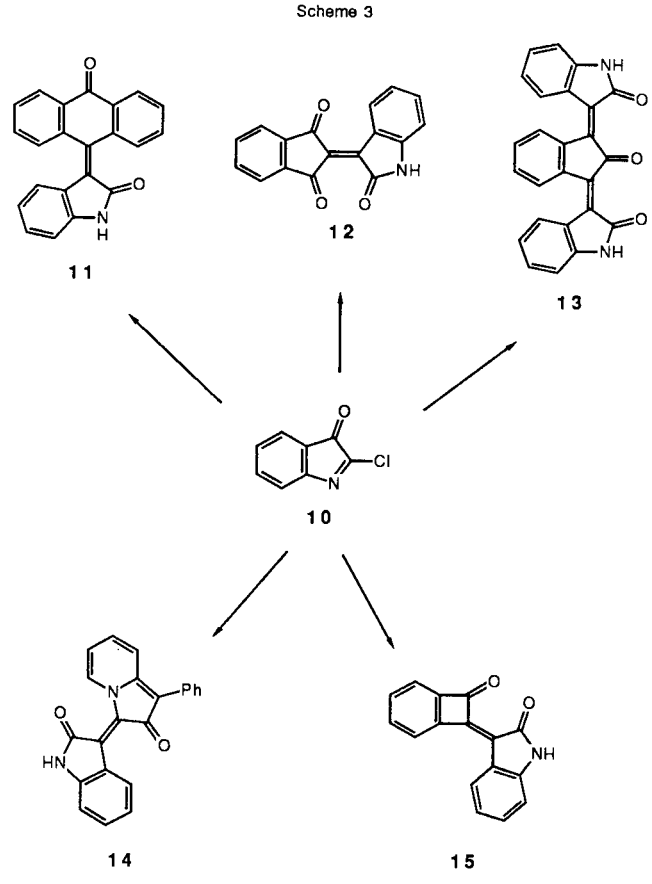
is black in the solid state but reddish violet in solution (see experimental).

Scheme 2



We have also prepared novel colored indoxyl derivatives by the reaction of 2-chloroindol-3-one **10** with compounds containing active methylene groups. 2-Chloroindol-3-one was readily available by treatment of isatin with phosphorus pentachloride in benzene, and has previously been used to synthesize dyestuffs by reactions with amines or diamines [14,15], phenols or naphthols [16], and hydantoins [17]. Recently, a variety of novel dioxopiperazine derivatives were prepared by the reactions of di- and mono-acetylpiperazine-2,5-diones with 2-chloroindol-3-one [1e]. However, these compounds are 2-oxo-3-indolylidene derivatives, and not the expected 3-oxo-2-indolylidene isomers (indigo analogue) as shown by comparing their properties with that of authentic specimen [1e] and by the X-ray results [18]. Presumably, these 2-oxo-3-indolylidenes are formed when 2-chloroindol-3-one **10** is reacted in dimethylformamide because this chloroisatin derivative is readily hydrolysed [19] in the presence of trace of water (detailed structural and mechanistic studies of reactions of **10** will be published separately [18]).

Scheme 3



Anthrone reacted with 2-chloroindol-3-one in dimethylformamide with triethylamine as a base at room temperature to give the violet red derivative 10-(2-oxo-3-indolylidene)anthrone **11** in 60% yield (Scheme 3). In similar manner, the reaction of 2-chloroindol-3-one **10** with 1,3-indandione gave a red solid (62%) the structure of which was assigned as 2-(2-oxo-3-indolylidene)-1,3-indandione **12**. 1,3-Bis(2-indolylidene)-2-indanone monohydrate **13** was obtained as purple microcrystals by reacting two equivalents of 2-chloroindol-3-one **10** with 2-indanone in dimethylformamide and two equivalents of triethylamine at 20° (Scheme 3). With 1-phenyl-2,3-dihydroindolizin-2-one as the starting material, the brown dyestuff 3-(2-oxo-3-

Table VI

Spectral Data of Indoxylidene Derivatives **11-15**

Compound	UV/Vis (ε) (ethanol)	MS (M⁺)	IR (bromoform) cm⁻¹ ν NH	ν C=O	ν C=O	ν C=C	¹H NMR (dimethyl sulfoxide) δ
11	548 (11000)	323	3350	1695	1660	1610	7.1-8.9 (m)
12	506 (11000)	275	3250	1730	1700 [a]	1610	7.3-8.5 (m)
13	558 (29000)	-	3350	1720	1660	1620	7.0-8.3 (m)
14	440 (9700)	338	3200	1700	1665	1620	-
15	439 (7100)	-	3250	1760	1720	1640	7.3-8.7 (m)

[a] Also 1660 cm⁻¹.

indolylidene)-1-phenylindolizin-2-one **14** was afforded which analysed correctly without further purification. The hydrolysis of 1,1-dichlorobenzocyclobutene (prepared from benzyne produced by heating benzenediazonium-2-carboxylate) gave benzocyclobutenone [20,21] which reacted with 2-chloroindol-3-one in dimethylformamide and triethylamine to afford the brown (2-oxo-3-indolylidene)benzocyclobutenone **15** in 39% yield. The preparations and elemental analyses of the new derivatives **11-15** are summarized in Table V.

The characterization of these novel indoxyl derivatives **11-15** was achieved by ^{1}H nmr and ir spectra, by mass spectra and by microanalysis (see Table VI). In the ir spectra, the NH absorbances of secondary amides were seen at from 3350 to 3250 cm^{-1}, and the bands for ν C=O and ν C=C groups were easily assigned in the range of 1700 to 1600 cm^{-1}. Their ^{1}H nmr supported the assigned structures although they are not very characteristic because all the protons are aromatic and thus the signals are multiplets. However, the two possible structures (2-oxo-3-indolylidene and 3-oxo-2-indolylidene) should show different H-1 one proton signal for the NH group. For 2-oxo-3-indolylidenes the signal should appear at low field (8.5-9.5 ppm), characteristic of a secondary amide, whereas 3-oxo-2-indolylidenes should absorb at higher field (4-5 ppm), characteristic of a secondary amine [22]. Indeed, no such high field signals were observed for the indoxyl derivatives **11-15**, all resonances appear at low field (around 9 ppm), which agrees with the 2-oxo-3-indolylidene (amide) structures. The very low solubility of these compounds in nmr solvents precluded obtaining ^{13}C nmr spectra. Mass spectral molecular ions provide further evidence for the structures (for details see Table VI).

EXPERIMENTAL

Melting points were determined using a Thomas-Hoover capillary melting point apparatus without correction. Spectra were recorded on the following instruments: ^{1}H nmr with a Varian Model EM 360L with TMS as internal standard. ^{13}C nmr with a JEOL Model JNM-FX 100 (25.05 MHz); ir with a Perkin-Elmer Model 283B grating spectrophotometer; uv/vis spectra with a Perkin-Elmer 330 spectrophotometer and mass spectra with an AEI MS 30. The following compounds were prepared by the literature method quoted: *N*-acetylindoxyl, mp 133-135° (lit [12] 136°); 2-chloroindol-3-one **10**, mp 176-178° (lit [23] 180°); 1-phenyl-2,3-dihydroindolizin-2-one, mp 136-138° (lit [1c] 135-138°); benzocyclobutenone, bp 68-70°/2 torr (lit [21] 60-62°/1 torr).

2-Arylideneindolin-3-one, General Procedure.

Method A.

N-Acetylindoxyl (0.01 mole) was heated under reflux for 1 hour in an atmosphere of nitrogen with 50% aqueous ethanol (50 ml) containing 1.5 *N* sodium hydroxide (55 ml). The appropriate aldehyde (0.01 mole) in ethanol was then added and heating was continued for a further 2 hours. After cooling, the indolinone was collected by filtration and recrystallized by methanol or ethanol (see Table I).

Method B.

N-Acetylindoxyl (0.01 mole), the appropriate aromatic aldehyde (0.01 mole) and triethylamine (0.01 mole) were stirred in dimethylformamide at 20° overnight. The reaction mixture was poured into water, the resulting precipitate was filtered off and washed with water and ethanol. Recrystallization from methanol or ethanol gave the desired products (see Table I).

Method C.

3-Indoxyl acetate (0.01 mole) and the aldehyde are refluxed for 1 hour under a nitrogen atmosphere in ethanol (45 ml) and 1.5 *N* sodium hydroxide (55 ml). The product which separated on cooling was collected, washed with diethyl ether and crystallized from ethanol (see Table I).

Methylation of Arylideneindolin-3-one. General Procedure.

The reaction mixture of arylideneindolin-3-one (5 mmoles) and sodium hydride (6 mmoles) was stirred in dimethylformamide (20 ml) at 20° for 20 minutes. Methyl iodide (6 mmoles, in the case of **5b** and **5c**, 12 mmoles) was added and stirring was continued for 20 hours. The reaction mixture was diluted with water. The precipitate formed was collected by filtration and recrystallized from acetone to give the pure product **6** (see Table III).

1-Methyl-2-(*N*-methyl-2-or-4-pyridinlene)indolin-3-one **7b** and **7c**.

Compound **5b** or **5c** was heated with methyl iodide in dimethylformamide at 100° for 5 hours. After cooling, the resulting deep red precipitate was filtered off and washed with water. Recrystallization from methanol gave **7b** or **7c** (See Table III).

3-(3-Oxo-2-indolylidene)-4-oxo-*N*-phenylmaleimide **8**.

A mixture of 1.41 g (5 mmoles) of 3,4-dichloro-*N*-phenylmaleimide, 1.75 g (10 mmoles) of *N*-acetylindoxyl and 1.01 g (10 mmoles) of triethylamine in 30 ml dimethylformamide was stirred at 120° for 48 hours. The whole was cooled and poured into water, filtered and washed with water and ethanol. Recrystallization from methanol gave 0.65 g (41%) of **8** as a black microcrystals, mp 251-253°; ^{1}H nmr (dimethyl sulfoxide-d_6): 10.05 (br, 1H, NH), 7.1-8.0 (m, 9H, Ar-H); ir (bromoform): ν max 3250 (NH), 1710 (C=O), 1660 (C=O), 1600 (C=C), 1580, 1500 and 1370 cm^{-1}; uv/vis (ethanol): λ max 562 nm (6300).

Anal. Calcd. for $C_{18}H_{10}N_2O_4$: C, 67.92; H, 3.15; N, 8.81. Found: C, 67.76, H, 3.25, N, 9.11.

2,3-Bis(3-oxo-2-indolylidene)-1,4-naphthoquinone **9**.

Preparation as above, isolated as monohydrate, greenish red powder, yield 64%, mp >300°; ^{1}H nmr (dimethyl sulfoxide-d_6): 7.15-7.90 (m); ir (bromoform): ν max 3300 (NH), 1710 (C=O), 1660 (C=O), 1600 (C=C), 1570, 1450, 1300 cm^{-1}; uv/vis (ethanol): λ max 436 (7400).

Anal. Calcd. for $C_{26}H_{14}N_2O_4.H_2O$: C, 71.55; H, 3.66; N, 6.46. Found: C, 71.69; H, 3.72; N, 6.17.

Reaction with 2-Chloroindol-3-one, Preparation of Compounds **11** to **15**.

2-Chloroindol-3-one (10 mmoles, 20 mmoles for 2-indanone) was stirred with the appropriate compounds containing methylene group (10 mmoles) in dimethylformamide with triethylamine (11 mmoles, in the case of 2-indanone, 22 mmoles) as a base at room temperature overnight. The reaction mixture was diluted with water, and the solid was collected by filtration and washed with water and ethanol. Recrystallization from ethanol gave the pure products.

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REFERENCES AND NOTES

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