TABLE II
SPECIFIC AND MOLECULAR ROTATIONS OF LYCORENINE, HOMOLYCORINE, AND ANALOGOUS ALKALOIDS

Compd	No.	Registry no.	Structure R	R1	R2	R3	R4	C7	[α]D (solvent), deg	Δα[D], deg	MD, deg	Δ[M]D, deg
Deoxylycorenine	3	13255-14-6						CH_2	+95 (EtOH)	57	+288	282
Lycorenine[a]	3	477-19-0						CHOH	+152 (EtOH)	67	+570	202
Homolycorine	3	477-20-3						C=O	+85 (EtOH)		+368	
Deoxykrigenamine	4	32247-13-5	CH_3O	O_2CH_2		H	H	CH_2	+123 (EtOH)	87	+385	315
Krigenamine	4	1165-00-0	CH_3O	O_2CH_2		H	H	CHOH	+210 ($CHCl_3$)	103	+695	325
Oxokrigenamine	4	1165-01-0	CH_3O	O_2CH_2		H	H	C=O	+117 ($CHCl_3$)		+370	
Oduline	4	477-18-9	H	O_2CH_2		H	H	CHOH	+239 ($CHCl_3$)	99	+720	300
Masonine	4	568-40-1	H	O_2CH_2		H	H	C=O	+140 ($CHCl_3$)		+420	
Krigeine	4	905-37-3	CH_3O	O_2CH_2		H	OH	CHOH	+234 ($CHCl_3$)	72	+813	254
Neronine	4	1167-58-4	CH_3O	O_2CH_2		H	OH	C=O	+162 ($CHCl_3$)		+559	
Nerinine	4	481-44-7	H	OCH_3	OCH_3	OCH_3	H	CHOH	+155 ($CHCl_3$)	83	+538	293
Albomaculine	4	668-63-3	H	OCH_3	OCH_3	OCH_3	H	C=O	+72 ($CHCl_3$)		+225	
Unsevine	4	4838-99-7	H	O_2CH_2		H	OCH_3	CHOH	+170 ($CHCl_3$)	69	+564	231
Nivaline	4	568-40-1	H	O_2CH_2		H	OCH_3	C=O	+101 ($CHCl_3$)		+333	

[a] Registry number for methiodide, 32367-48-9.

comparisons (see Table II) it is most probable that the C_7 hydroxyl groups of oduline, nerinine, krigeine, unsevine, and krigenamine have α configurations as well.

A Synthesis of 4-Azaoxindole

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The condensation product of ethyl cyanoacetate and 2-chloro-3-nitropyridine (**1**) was converted by reduction, cyclization, and acid hydrolysis into 4-azaoxindole (**4**). A study of the dibenzyl-4-azaoxindole derivatives **5**, **9**, and **13** was made to evaluate the type and extent of the tautomerism possible with this system. Rapid autoxidation of the 3-benzyl-4-azaoxindole (**11**) to the dioxindole **14** was observed. The presence of virtual coupling in the nmr spectrum of **4** was noted.

Azaindoles have attracted considerable interest in view of their potential relationship to pharmacologically important indoles, *e.g.*, serotonin, and a review of azaindoles has recently appeared.[1]

Azaoxindoles, on the other hand, are virtually unknown, with only the preparation of 7-azaoxindole[2,3] and 3,3-dimethyl-7-azaoxindole[4] and unsuccessful attempts at 5-azaoxindole[5] and 4-azaoxindole[6] preparation being described.

Our earlier interest in azaindole chemistry[7] and our current interest in arylations with 2-chloro-3-nitropyridine motivated us to make a contribution to this area. We describe now the synthesis of the previously undescribed 4-azaoxindole and some of its chemistry.

The arylation of ethyl cyanoacetate by 2-chloro-3-nitropyridine was described by Willette.[6] The resulting product, for which we favor the tautomeric structure **1** on the basis of infrared evidence (a very strong CN stretching and the ester C=O at 1628 cm^{-1}), could be reduced in our hands in excellent yield by hydrogenation in ethanol over 10% palladium on carbon at 50 psi and room temperature. Reflux of the product **2** in xylene effected ring closure to the 3-cyano-4-azaoxindole **3**. Some of the interesting chemistry of this new system was evident with this first member, for it is amphoteric. In fact, **3** is best purified by precipitation, from a solution of aqueous sodium hydroxide, with a stream of carbon dioxide. Reflux of **3** in concentrated hydrochloric acid converted it to the unsubstituted 4-azaoxindole **4** (Scheme I), which is shown in the principle tautomeric form **4a** based on the nmr evidence (2-proton singlet at δ 3.6). This is a very easily enolizable compound and uv evidence suggests the presence of the tautomer **4b** in protic solvents [λ max 359 mμ (ε 2070)]. In order to explore this interesting tautomerism we decided to prepare and obtain the physical data on alkyl derivatives of assignable structure, where the alkylation had blocked or restricted the tautomeric possibilities. Benzyl was chosen as the alkyl group for the study and as **4** has three acidic protons, we attempted the synthesis of as many dibenzyl compounds as possible. Reaction of **4** (see Scheme I) with 2 equiv of sodium hydride and benzyl chloride in dimethylformamide yielded a dibenzyl compound **5**. From the nmr spectrum of **5** (4-proton singlet at δ 3.30, a low-field exchangeable proton) it seemed that both benzyl groups were bound to carbon. Thus the only tautomerism available to **5** is normal amide enolization. There was no spectral evidence of this and therefore the spectral data for **5** can be taken as being representative of the pure oxindole tautomer **4a**. Benzylation of the 3-cyano-4-azaoxindole **3** yielded a monobenzyl compound **6**, whose nmr spectrum showed that the benzyl group was attached to a heteroatom, not to carbon (2-proton singlet at δ 5.72). Reaction of **6** under benzylating conditions yielded a dibenzyl-3-cyano-4-azaoxindole **7**, which no longer had an exchangeable proton in its nmr spectrum and where both benzyl groups were attached to heteroatoms (2-proton singlets at δ 5.72 and 5.09).

(1) R. E. Willette, *Advan. Heterocycl. Chem.*, **9**, 27 (1968).
(2) H. Kagi, *Helv. Chim. Acta*, **24**, 141E (1941).
(3) S. Okuda and M. M. Robison, *J. Amer. Chem. Soc.*, **81**, 740 (1959).
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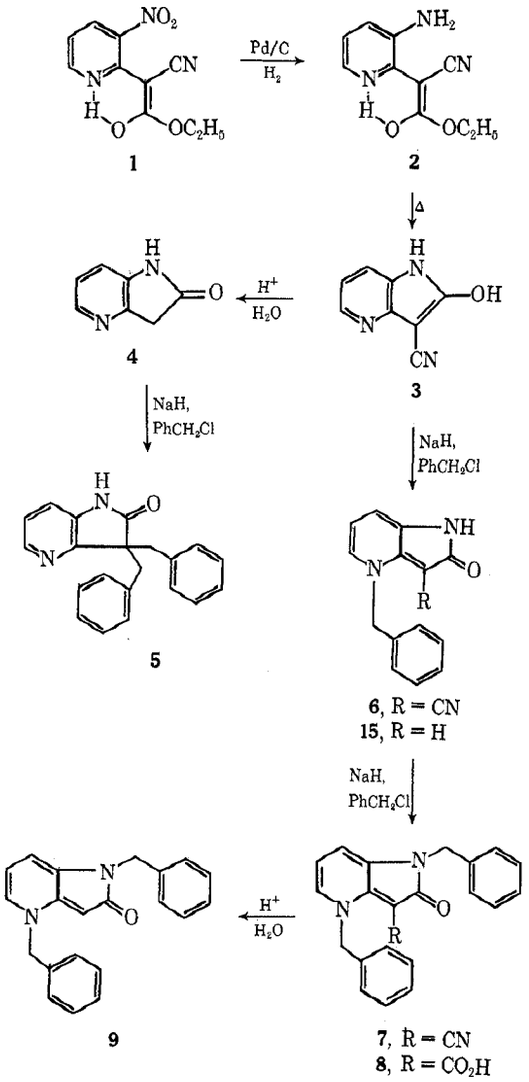
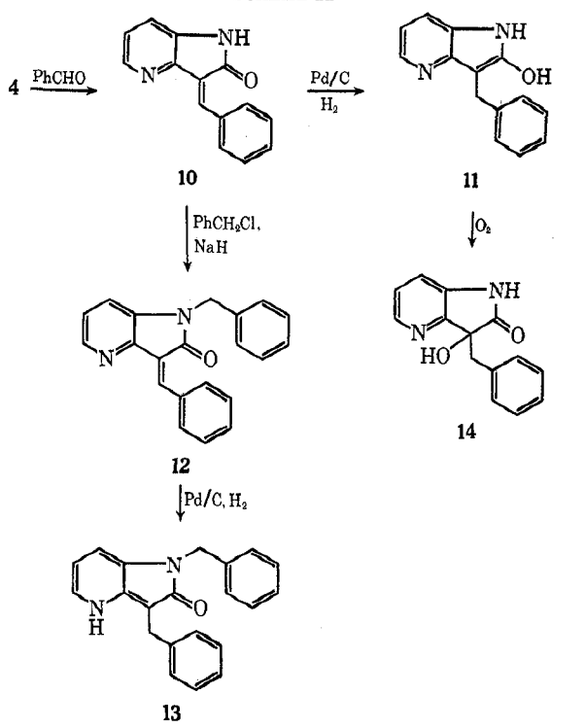
(5) S. Okuda and M. M. Robison, *J. Org. Chem.*, **24**, 1008 (1959).
(6) R. E. Willette, *J. Chem. Soc.*, 5874 (1965).
(7) M. M. Robison and B. L. Robison, *J. Amer. Chem. Soc.*, **77**, 457 (1955).

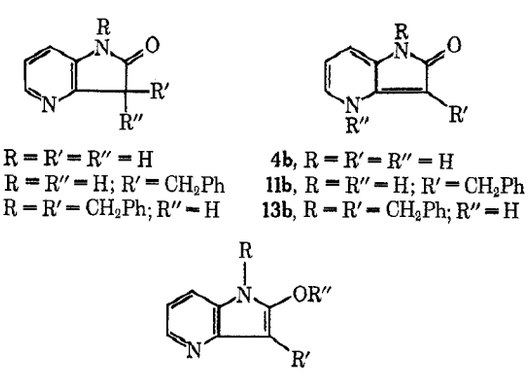
SCHEME I



SCHEME II



parent substance, *i.e.*, **4a**, **4b**, and **4c**. This situation, alas, did not appertain in solution.



4a, R = R′ = R″ = H
11a, R = R″ = H; R′ = CH_2Ph
13a, R = R′ = CH_2Ph; R″ = H

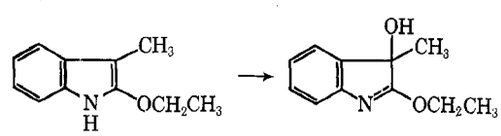
4b, R = R′ = R″ = H
11b, R = R″ = H; R′ = CH_2Ph
13b, R = R′ = CH_2Ph; R″ = H

4c, R = R′ = R″ = H
11c, R = R″ = H; R′ = CH_2Ph
13c, R = R′ = CH_2Ph; R″ = H

Reflux of **7** in acid proceeded *via* the acid **8** to the dibenzyl-4-azaoxindole **9**. As both the benzyl groups were retained during the acid reflux, we may assume that they are attached to nitrogen. This particular dibenzyl compound **9** cannot tautomerize and therefore its spectral data can be taken as being representative of the **4b** tautomer of 4-azaoxindole. A third dibenzyl compound **13** was prepared as outlined in Scheme II. Reaction of 4-azaoxindole with benzaldehyde gave the benzylidene derivative **10**. This is blocked to enolization, except of the amide type, and as the infrared spectrum showed a strong carbonyl absorption, this type of tautomerism could be discounted. Benzylation of **10** gave a monobenzyl derivative **12**. The benzyl group of **12** was attached to the oxindole nitrogen, rather than oxygen, as the carbonyl band in the infrared spectrum of **10** was still present in that of **12**. Catalytic reduction of **12** yielded the dibenzyl-4-azaoxindole **13**, which lacked major absorption in the infrared above 1600 cm^{-1}. This is in contrast to the dibenzyl azaoxindole **9**, which has a strong band at 1620 cm^{-1}. Thus in the solid state **13** prefers the 2-hydroxy-4-azaindole form **13c**, which means that each of the dibenzyl-4-azaoxindoles prepared, **5**, **9**, and **13**, was representative of one of the three most reasonable tautomers possible for the

The nmr spectrum in dimethyl sulfoxide of **13** showed that three tautomers were present in the approximate ratio of 4:1:1 (three different NCH_2Ph and three different CCH_2Ph signals). In view of the similarity of the uv spectrum of **13** in methanol with that of **9**, it is assumed that the principal form in solution is **13b**, with minor contributions from **13a** and **13c**. Hydrogenation of the benzylidene derivative **10** before benzylation yielded a monobenzyl-4-azaoxindole **11**. This compound **11** also lacked a carbonyl group in the infrared spectrum suggesting the solid form was **11c**. Analogously to **13**, the nmr spectrum of **11** in dimethyl sulfoxide showed it to be a mixture of tautomers, although in this case only two were evident, in the approximate ratio of 4:1, based on the CCH_2Ph signal. As the spectrum of the principal tautomer of **11** resembled that of the principal tautomer of **13**, it was assigned structure **11b**; the minor isomer could be assigned structure **11a** based on the multiplicity of the benzyl signal.

The uv spectrum of **11** in methanol was in general agreement, although quantitatively it would seem that more of isomers **11a** and/or **11c** were present in this protic solvent. Support for this view came when **11** was recrystallized from ethanol; the unsolvated material obtained by drying in high vacuum showed a carbonyl band in its infrared spectrum (1720 cm^{-1}). Interestingly, though, the ethanol solvate obtained by simple air drying lacked a carbonyl band entirely. The presence of this tautomer **11c** could be inferred, in some aprotic solvents, by a rapid autoxidation of **11**. For example, on attempted recrystallization from acetonitrile, **11** was converted into the 4-azadioxindole **14**. The carbonyl band present in the infrared spectrum of **14**, 1742 cm^{-1}, is somewhat higher than that of the analogous benzo compound (1730 cm^{-1}),[8] but generally dioxindoles do absorb at higher frequency than the corresponding oxindoles. The ultraviolet spectrum also supports the structural assignment of **14** and there are several analogies for this transformation. The most pertinent is perhaps the extremely rapid autoxidation of **16** to **17**, on its liberation from the fluoroborate salt.[9]



16 **17**

The mechanism of this process has recently been discussed in detail.[10]

One interesting physical property of 4-azaoxindole **4**, unrelated to our study, is the presence of virtual coupling[11] in the nmr spectrum, in which the C_6 and C_7 protons are fortuitously chemically equivalent. This explains the simplicity of the aromatic pattern of **4**, *i.e.*, a 2-proton doublet at δ 7.16 ($J_{5,6} + J_{5,7} = 6$ Hz) and a 1-proton triplet at δ 8.10 ($J = 3$ Hz).[12] That this in fact was the case was supported by the observation that running the nmr spectrum in D_2O–DCl one obtains an ABX type of multiplicity for the pyridine protons.

In conclusion, it is evident from our preliminary study that free-energy differences between the principal tautomers of 4-azaoxindoles are small and that relatively minor changes of substitution or solvent can have major effects on the position of equilibrium. It is, therefore, unwise to make predictions with regard to the outcome for alkylations with other reagents or even benzylation under other experimental conditions. Nevertheless, with the spectral data and assignments made in this study, it should be possible to readily determine what in fact does occur in a specific case during further studies.

Experimental Section[13]

Ethyl α-Cyano-3-nitro-2-pyridine Acetate (1).—To a stirred solution of 172.2 g (1.6 mol) of potassium *tert*-butoxide in 2 l. of *tert*-butyl alcohol was added 181.2 g (1.6 mol) of ethyl cyanoacetate. To the resultant suspension was added a hot solution of 126.1 g (0.8 mol) of 2-chloro-3-nitropyridine in 2 l. of *tert*-butyl alcohol. The mixture was refluxed for 6 hr. Evaporation of the *tert*-butyl alcohol yielded a red residue which was treated with 800 ml of 1 *N* hydrochloric acid. The insoluble solid was collected, washed with water, and recrystallized from methanol to yield 148 g (79%) of product. One recrystallization from methanol gave an analytical sample: mp 139–141° (lit.[6] 136–137°); ν_{max}^{Nujol} 2850, 2190, 1625, 1560, 1250 cm^{-1}; nmr ($CDCl_3$) δ 1.20 (t, 3, $J = 7$ Hz), 4.25 (q, 2, $J = 7$ Hz), 6.7 (m, 2), 8.4 (m, 2); mass spectrum (70 eV) *m/e* 235 (parent peak).

Anal. Calcd for $C_{10}H_9N_3O_4$: C, 51.06; H, 3.86; N, 17.87. Found: C, 50.91; H, 4.06; N, 17.59.

Ethyl 3-Amino-α-cyano-2-pyridine Acetate (2).—A solution of 146 g (0.62 mol) of ethyl α-cyano-3-nitro-2-pyridine acetate (**1**) in 3 l. of 95% ethanol was hydrogenated at 50 psi in the presence of 14.6 g of 10% palladium on carbon. After the catalyst had been removed by filtration, the ethanol was evaporated to yield 123 g of product **2** (100%). An analytical sample was prepared by recrystallization from methanol: mp 115–117°; $\lambda_{max}^{methanol}$ 222 mμ (ε 18,070), 292 (9810), 387 (15,580); ν_{max}^{Nujol} 3480, 3350, 2170, 1640, 1450, 1280 cm^{-1}; nmr ($CDCl_3$) δ 1.32 (t, 3, $J = 7$ Hz), 4.23 (q, 2, $J = 7$ Hz), 4.95 (m, 2), 6.78 (m, 2), 7.25 (m, 1).

Anal. Calcd for $C_{10}H_{11}N_3O_2$: C, 58.53; H, 5.40; N, 20.45. Found: C, 58.79; H, 5.80; N, 20.27.

3-Cyano-4-azaoxindole (3).—A stirred solution of 110 g (0.530 mol) of ethyl 3-amino-α-cyano-2-pyridine acetate (**2**) in 7 l. of xylene was refluxed for 20 hr. The reaction mixture was cooled to 0° and the resulting tan solid was collected by filtration. The product was purified by dissolving it in 2 l. of 3% sodium hydroxide solution, filtering the solution through activated charcoal, and reprecipitating the product by bubbling carbon dioxide into the solution. This procedure yielded 42.6 g of purified product **3** (50%): mp >325°; $\lambda_{max}^{methanol}$ 215 mμ (ε 28,290), 252 (10,510), 353 (12,120); ν_{max}^{Nujol} 3080, 2200, 1660, 1620, 1340 cm^{-1}; nmr (DMSO-d_6) δ 7.08 (t, 1, $J = 8$ Hz), 7.41 (d, 1, $J = 8$ Hz), 7.83 (d, 1, $J = 8$ Hz), 10.16 (m, 1); mass spectrum (70 eV) *m/e* 159 (parent peak).

Anal. Calcd for $C_8H_5N_3O$: C, 60.37; H, 3.17; N, 26.41. Found: C, 60.10; H, 3.41; N, 26.05.

Hydrolysis of 3 to 4-Azaoxindole (4).—A stirred solution of 50 g (0.314 mol) of 3-cyano-4-azaoxindole (**3**) in 5 l. of concentrated hydrochloric acid was refluxed for 22 hr. After cooling, the hydrochloric acid solution was evaporated to dryness. The residue was dissolved in a minimal amount of water. The aqueous solution was made basic with solid sodium bicarbonate and evaporated to dryness. The dry residue was extracted six times with 300-ml portions of boiling chloroform. Evaporation of the chloroform extracts yielded 24 g of product **4** (56%). An analytical sample was prepared by recrystallization from toluene: mp 205–207°; $\lambda_{max}^{methanol}$ 220 mμ (ε 5150), 246 (11,720), 289 (3420), 359 (2070); ν_{max}^{Nujol} 3200, 1700, 1610, 1430 cm^{-1}; nmr (DMSO-d_6) δ 3.62 (s, 2), 7.17 (d, 2), 8.10 (t, 1), 10.4 (s, 1, exchanges); mass spectrum (70 eV) *m/e* 134 (parent peak).

Anal. Calcd for $C_7H_6N_2O$: C, 62.68; H, 4.51; N, 20.89. Found: C, 62.72; H, 4.60; N, 20.77.

Benzylation of 4 to 3,3-Dibenzyl-4-azaoxindole (5).—To a stirred solution of 0.5 g (3.73 mmol) of 4-azaoxindole (**4**) in 50 ml of dry dimethylformamide was added 0.314 g (7.44 mmol) of sodium hydride (57% in oil) under a nitrogen atmosphere. After 20 min, 0.94 g (7.44 mmol) of benzyl chloride was added all at once. The solution was heated to 50° and stirred for 18 hr. The dimethylformamide was taken off under reduced pressure. To the residue was added 50 ml of 1 *N* hydrochloric acid. This solution was washed with petroleum ether and then made basic with solid potassium carbonate. The basic solution was extracted three times with methylene chloride. The methylene chloride was dried and evaporated. The residue was recrystallized from acetonitrile to yield 0.5 g (38%) of product **5**: mp 281–283°; $\lambda_{max}^{methanol}$ 252 mμ (ε 8310), 291 (3602); ν_{max}^{Nujol} 1710, 1610, 1580 cm^{-1}; nmr (DMSO-d_6) δ 3.3 (s, 4), 6.82 (m, 2), 7.0 (m, 10), 8.28 (d, 1, $J = 6$ Hz), 10.02 (s, 1).

Anal. Calcd for $C_{21}H_{18}N_2O$: C, 80.23; H, 5.77; N, 8.91. Found: C, 80.01; H, 5.91; N, 9.10.

Benzylation of 3 to 4-Benzyl-3-cyano-4-azaoxindole (6).—A 0.54-g (0.0132 mol) sample of 57% sodium hydride–mineral oil was added to a stirred solution of 2.0 g (0.0126 mol) of 3-cyano-4-azaoxindole (**3**) in 30 ml of DMF under a nitrogen atmosphere. After 0.5 hr 1.58 g (0.0126 mol) of benzyl chloride was added all at once. The mixture was heated to 50° and allowed to stir for

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(11) J. I. Musher and E. J. Corey, *Tetrahedron*, **18**, 791 (1962).

(12) We are indebted to Professor Peter Yates for this explanation.

(13) Melting points were obtained in a Thomas-Hoover melting point apparatus and are uncorrected. Nmr spectra were obtained on a Varian A-60 instrument. Mass spectra were obtained on a MS-9 instrument.

16 hr. The DMF was removed under reduced pressure. The residue was washed with 50 ml of 1 *N* hydrochloric acid and then recrystallized from ethanol–dimethylformamide to yield 1.7 g of product **6** (54%): mp 308–310°; nmr (DMSO-d_6) δ 5.72 (s, 2), 6.88 (t, 1, J = 8 Hz), 7.15 (d, 1, J = 8 Hz), 7.38 (s, 5), 7.78 (d, 1, J = 8 Hz), 11.30 (m, 1); $\lambda_{max}^{methanol}$ 210 mμ (ϵ 29,260), 258 (9660), 362 (12,910); ν_{max}^{Nujol} 2200, 1630, 1580, 1450, 1370 cm^{-1}.

Anal. Calcd for $C_{15}H_{11}N_3O$: C, 72.27; H, 4.45; N, 16.86. Found: C, 72.41; H, 4.77; N, 16.57.

Benzylation of 6 to 1,4-Dibenzyl-3-cyano-4-azaoxindole (7).—To a stirred solution of 5.0 g (20.1 mmol) of 4-benzyl-3-cyano-4-azaoxindole (**6**) in 150 ml of dimethylformamide was added 0.93 g of sodium hydride (57% in oil) under a nitrogen atmosphere. After 20 min 2.8 g (22 mmol) of benzyl chloride was added all at once. The solution was heated to 60° and allowed to stir for 18 hr. The dimethylformamide was removed under reduced pressure. The residue was washed with 20 ml of petroleum ether and then 50 ml of water. The washed residue was recrystallized from methyl alcohol to yield 5.3 g (76%) of product **7**: mp 198–200°; $\lambda_{max}^{methanol}$ 210 mμ (50,280), 263 (14,360), 363 (17,640); γ_{max}^{Nujol} 2205, 1670, 1645, 1600 cm^{-1}; nmr (DMSO-d_6) δ 5.09 (s, 2), 5.76 (s, 2), 6.94 (t, 1), 7.34 (m, 11), 7.9 (d, 1).

Anal. Calcd for $C_{22}H_{17}N_3O$: C, 77.85; H, 5.05; N, 12.38. Found: C, 77.46; H, 5.30; N, 12.44.

Hydrolysis of 7 to 1,4-Dibenzyl-4-azaoxindole (9).—A solution of 1.0 g (2.97 mmol) of 1,4-dibenzyl-3-cyano-4-azaoxindole (**7**) in 100 ml of concentrated hydrochloric acid was refluxed for 72 hr. The hydrochloric acid was evaporated. A minimal amount of water was added to the residue. The solution was then made basic with solid sodium bicarbonate and extracted three times with 75-ml portions of methylene chloride. The methylene chloride was dried and evaporated. Recrystallization of the residue from acetonitrile yielded 0.5 g (56%) of product **9**: mp 175–177°; $\lambda_{max}^{methanol}$ 233 mμ (ϵ 12,580), 262 (6610), 286 (1710), 362 (6240); ν_{max}^{Nujol} 1638, 1570, 1590, 1370 cm^{-1}; nmr (DMSO-d_6) δ 5.02 (s, 2), 5.26 (s, 2), 5.17 (s, 1), 6.4 (t, 1, J = 8 Hz), 6.81 (d, 1, J = 8 Hz), 7.32 (m, 10), 7.56 (d, 1, J = 8 Hz).

Anal. Calcd for $C_{21}H_{18}N_2O$: C, 80.23; H, 5.77; N, 8.91. Found: C, 80.55; H, 5.97; N, 9.10.

Hydrolysis of 6 to 4-Benzyl-4-azaoxindole (15).—A stirred solution of 1.2 g (4.82 mmol) of 4-benzyl-3-cyano-4-azaoxindole (**6**) in 150 ml of concentrated hydrochloric acid was refluxed for 65 hr. The hydrochloric acid solution was evaporated to dryness. The residue was dissolved in a minimal amount of water. The solution was saturated with solid sodium bicarbonate and then extracted six times with 50-ml portions of methylene chloride. The methylene chloride was dried over anhydrous sodium sulfate and evaporated. Two recrystallizations of the residue from ethanol–acetonitrile 4:1 yielded 0.6 g (55%) of pure product: mp 257–258°; $\lambda_{max}^{methanol}$ 216 mμ (ϵ 25,350), 256 (12,360), 276 (3770), 360 (12,110); ν_{max}^{Nujol} 2850, 1620, 1580, 1450 cm^{-1}; nmr (DMSO-d_6) δ 4.9 (s, 1), 5.13 (s, 2), 6.30 (t, 1, J = 8 Hz), 6.63 (d, 1, J = 7 Hz), 7.25 (s, 5), 7.41 (d, 1, J = 7 Hz), 10.13 (m, 1).

Anal. Calcd for $C_{14}H_{12}N_2O$: C, 74.99; H, 5.38; N, 12.35. Found: C, 74.65; H, 5.48; N, 12.35.

Benzylidene Derivative of 4-Azaoxindole (10).—A solution of 3.02 g (0.022 mol) of 4-azaoxindole (**4**), 2.39 g (0.022 mol) of benzaldehyde, and 1 ml of piperidine in 700 ml of toluene was refluxed for 4 hr. After the toluene was evaporated, the residue was recrystallized from ethanol–benzene to yield 3.75 g of product **10** (75%): mp 206–208°; $\lambda_{max}^{methanol}$ 253 mμ (ϵ 9270), 290 (12,860), 316 (17,140), 391 (6,110); ν_{max}^{Nujol} 3130, 1700, 1600, 1370, 1200 cm^{-1}; nmr (DMSO-d_6) δ 7.20 (d, 2, J = 4 Hz), 7.45 (m, 3), 7.65 (s, 1), 8.23 (t, 1, J = 4 Hz), 8.75 (m, 2), 10.07 (m, 1).

Anal. Calcd for $C_{14}H_{10}N_2O$: C, 75.65; H, 4.54; N, 12.61. Found: C, 75.65; H, 4.77; N, 12.38.

Benzylation of 10 to 12.—To a stirred solution of 1.0 g (5.0 mmol) of 3-benzylidene-4-azaoxindole (**10**) in 50 ml of dry dimethylformamide was added 0.24 g (5.5 mmol) of sodium hydride (57% in oil) under a nitrogen atmosphere. After 20 min 0.699 ml (5.0 mmol) of benzyl chloride was added all at once. The solution was heated to 50° and allowed to stir for 18 hr. The dimethylformamide was removed under reduced pressure. The residue was washed with 20 ml of petroleum ether and then 40 ml of 1 *N* hydrochloric acid was added. The solution was then made basic with solid potassium carbonate at 0° and extracted with methylene chloride. The methylene chloride was dried and evaporated. The residue was recrystallized from benzene–hexane to yield 0.7 g (47%) of product **12**: mp 122–125°; $\lambda_{max}^{methanol}$ 232 mμ (ϵ 10,140), 320 (22,340), 394 (4830); ν_{max}^{Nujol} 1713, 1630, 1600 cm^{-1}; nmr ($CDCl_3$) δ 4.98 (s, 1), 6.99 (m, 2), 7.29 (m, 5), 7.50 (m, 3), 8.02 (s, 1), 8.29 (q, 1), 8.79 (m, 2).

Anal. Calcd for $C_{21}H_{16}N_2O$: C, 80.75; H, 5.16; N, 8.97. Found: C, 81.25; H, 5.31; N, 9.03.

1,3-Dibenzyl-4-azaoxindole (13).—A solution of 0.5 g (1.6 mmol) of 1-benzyl-3-benzylidene-4-azaoxindole (**12**) in 50 ml of 95% ethanol was hydrogenated at 1 atm in the presence of 50 mg of 10% palladium on carbon. After the catalyst had been removed by filtration, the ethanol was evaporated. The residue was recrystallized from methanol to yield 0.3 g (66%) of product **13**: mp 158–160°; uv $\lambda_{max}^{methanol}$ 260 mμ (ϵ 10,280), 288 (3720), 364 (3910); ν_{max}^{Nujol} 1610 (w) 1560 cm^{-1}; nmr (DMSO-d_6) δ 3.86 (s, 2), 5.07 (s, 2), 6.27 (t, 1, J = 8 Hz), 6.75 (d, 1, J = 7 Hz), 7.0 (m, 10), 8.25 (d, 1, J = 6 Hz).

Anal. Calcd for $C_{21}H_{18}N_2O$: C, 80.23; H, 5.77; N, 8.91. Found: C, 80.22; H, 5.97; N, 9.02.

Hydrogenation of 10 to 3-Benzyl-4-azaoxindole (11).—A solution of 2.5 g (0.011 mol) of 4-azaoxindole benzal **10** in 150 ml of ethanol was hydrogenated at 1 atm in the presence of 0.25 g of 10% palladium on carbon. The catalyst was removed by filtration through filter cell and the ethanol evaporated. The yellow solid which remained was recrystallized from ethanol to yield 2.3 g of product **11** (92%): mp 188–190°; $\lambda_{max}^{methanol}$ 257 mμ (ϵ 12,280), 284 (4040), 372 (5580); ν_{max}^{Nujol} 1602, 1590, 1575 cm^{-1}; nmr (DMSO-d_6) δ 1.06 (t, 3), 3.70 (s, <2), 7.18 (m, 7); mass spectrum (70 eV) m/e 224 (parent peak) <5% of 240.

Anal. Calcd for $C_{14}H_{12}N_2O \cdot C_2H_5OH$: C, 71.20; H, 6.65; N, 10.30. Found: C, 70.92; H, 6.84; N, 9.91.

A portion of the solvate was recrystallized from ethanol with rapid cooling and scratching. The crystals were collected and dried for 18 hr in high vacuum at 100°: ν_{max}^{Nujol} 1720, 1586, 1570 cm^{-1}; nmr (DMSO-d_6) δ 3.24 (m, ~0.4 H), 3.70 (s, ~1.6 H), 7.18 (m, 7).

Anal. Calcd for $C_{14}H_{12}N_2O$: C, 74.99; H, 5.38; N, 12.49. Found: C, 74.82; H, 4.92; N, 12.90.

3-Benzyl-4-azadioxindole (14). A.—Three recrystallizations of 3-benzyl-4-azaoxindole (**11**) from acetonitrile yielded **14** in 50% yield: mp 278–280°; $\lambda_{max}^{methanol}$ 245 mμ (10,060), 292 (2670); ν_{max}^{Nujol} 3196, 1745, 1626, 1604 cm^{-1}; nmr (DMSO-d_6) δ 3.20 (s, 2), 6.90 (m, 8); mass spectrum m/e 240 (M^+).

Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 70.00; H, 5.00; N, 11.68. Found: C, 70.32; H, 5.14; N, 11.90.

B.—**11** (0.3 g, 1.25 mmol) was dissolved in acetic acid (30 ml). Hydrogen peroxide (0.155 g, 1.37 mmol) was added with stirring. The solution was heated (70°) for 2 hr. The acetic acid was removed under reduced pressure. The residue (0.30 g, 98% yield) was crystalline, mp 276–278°, and was identical (mmp and ir) with the material from A.

Registry No.—**1**, 32501-02-3; **2**, 32501-03-4; **3**, 32501-04-5; **4a**, 32501-05-6; **4b**, 32501-06-7; **4c**, 32501-07-8; **5**, 32501-08-9; **6**, 32544-48-2; **7**, 32501-09-0; **9**, 32605-76-8; **10**, 32500-77-9; **11a**, 32500-78-0; **11b**, 32500-79-1; **11c**, 32500-80-4; **12**, 32500-81-5; **13a**, 32500-82-6; **13b**, 32500-83-7; **13c**, 32500-84-8; **14**, 32500-85-9.

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