procedure given by Kresze;[13] it was a pale yellow oil, bp 73° (0.5 mm) [lit.[21] 184° (100 mm)].

**Reactions of 2-Methyl-N-sulfinylaniline (5).**—The heating of this compound on its own, or in solution, at temperatures between 100 and 200°, failed to yield any 2,1-benzisothiazole. If, however, thionyl chloride was added to a solution of 5 in xylene, or other inert solvent with a boiling point of between about 140 and 170°, and the mixture was heated to reflux, then 2,1-benzisothiazole could be detected in the reaction mixture by vpc within a few minutes. Formation of 2,1-benzisothiazole paralleled the disappearance of thionyl chloride; it ceased when the latter was exhausted, and could be reestablished by further addition of thionyl chloride. In this way, using 3 or more equiv of thionyl chloride, yields of up to 80% (by vpc) of 2,1-benzisothiazole could be produced. However, the increasing viscosity and darkening of the reaction mixture led to difficulties in isolation of the product. 2-Amino-5-chlorotoluene (as its N-sulfinyl derivative) and 5-chloro-2,1-benzisothiazole were also formed in this reaction in yields of a few percent. Doubtless the chlorine came from the thermal decomposition of the thionyl chloride.

(21) A. Michaelis, *Ann.*, **274**, 226 (1893).

**Reaction of 2-Amino-3-methylpyridine with Thionyl Chloride.**—A mixture of 5.4 g (50 mmol) of 2-amino-3-methylpyridine was treated with thionyl chloride and xylene as in general procedure A. Neutralization of the final dilute hydrochloric acid solution with ammonia solution afforded a yellow oil which crystallized slowly. On recrystallization from hot water, it afforded colorless leaflets (0.8 g, 11%) of 2-amino-5-chloro-3-methylpyridine, mp 66°.

*Anal.* Calcd for $C_6H_7ClN_2$: C, 50.5; H, 4.9; Cl, 24.9; N, 19.6. Found: C, 50.4; H, 4.8; Cl, 24.9; N, 19.6.

# 2-Alkylidene-2H-indole Intermediates. The Thermolysis of 2-Hydroxydiphenylmethylindole[1,2]

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The solution thermolysis of 2-hydroxydiphenylmethylindole (1) has been studied and, unlike 1-hydroxytetrahydrocarbazole, does not yield a simple "head-to-tail" dimer but affords a mixture of 2 monomers and 3 dimers: 2-diphenylmethylindole (5), 11-phenyl-10-H-indolo[1,2-a]indole (7), 11,11',10,10'-biindolo[1,2-a]indole (9), 11-phenyl-10-[3-(2-diphenylmethyl)indolyl]indolo[1,2-a]indole (8), and 11,11'-diphenyl-10,10'-biindolo[1,2-a]indolylidene (10). Monomer 7 appears to have formed from the 2-alkylidene-2H-indole 3. The composition of the product mixture is concentration dependent. The structures of the monomers were determined by their uv and nmr spectra, and those of the dimers were determined by their uv and mass spectra and chemical transformations. Compound 5 was synthesized by the zinc–acetic acid reduction of carbinol 1 and by the lithium aluminum hydride hydrogenolysis of 2-methoxydiphenylmethylindole (4). Dimer 10 was obtained when 7 was treated with N-bromosuccinimide followed by exposure to base.

A number of transformations of substituted indoles can be rationalized by 2-alkylidene-2H-indole intermediates or their conjugate acids. The hydrogenolysis of 2-indolecarbinols by lithium aluminum hydride has been suggested to proceed *via* a 2-alkylidene-2H-indole intermediate[4] and the dimerization of 1-hydroxytetrahydrocarbazole undoubtedly involves such a species or its conjugate acid.[5] Moreover, these intermediates are obviously implicated in the biosynthesis and synthesis of the dimeric *Vocanga* and *Vinca* alkaloids.[5,6]

It was the purpose of the present study to examine the stability and transformations of such species. An attractive compound for such a study appeared to be 2-hydroxydiphenylindole (1) since the stability of the derived triarylcarbonium ion (2) could be examined directly and the corresponding 2-alkylidene-2H-indole intermediate (3) would be expected to be exceptionally stable.
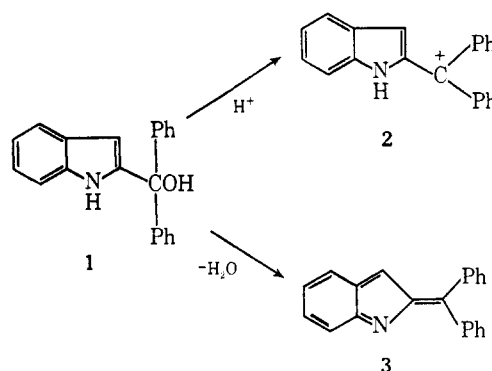
Carbinol 1 was obtained in 78% yield from the reaction of 2-carbethoxyindole with phenylmagnesium bromide. The carbinol affords a highly stable carbonium ion (2) ($pK_R^+$ [7] = −1.50) in aqueous sulfuric acid solution.[8] The solvolysis of 1 in acidic methanol gave 2-methoxydiphenylmethylindole (4) in high yield.
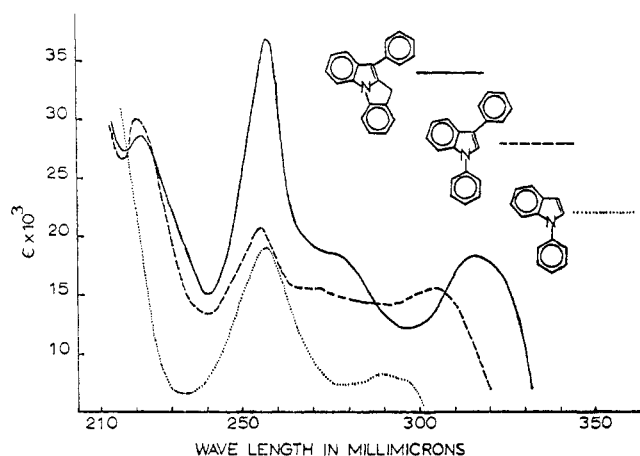
Figure 1.—The uv spectra of 11-phenyl-10H-indolo[1,2-a]indole (7), 1-phenylindole, and 1,3-diphenylindole.

Ether 4 underwent hydrogenolysis when stirred for 40 min at room temperature with lithium aluminum hydride giving a quantitative yield of 2-diphenylmethylindole (5). This reaction probably takes place by an elimination–addition sequence involving intermediate 3. Carbinol 1 does not undergo any apparent hydrogenolysis under the same conditions or in refluxing ether.

Indole 5, which was also obtained by the zinc–acetic reduction[9] of 1, suffers air oxidation quite easily and was characterized as the trinitrobenzene complex. Indole 5 shows $\lambda_{max}^{EtOH}$ 291 m$\mu$ ($\epsilon$ 7100) and its nmr spectrum shows the indole 3 proton at 5.92 and the methine proton at 5.23 ppm. This compound proved to be of importance in resolving the complex reaction mixture obtained in the thermolysis of 1.

It was originally thought that the thermolysis of 2-hydroxydiphenylmethylindole (1) would lead to a "head-to-tail" dimer (6a) as in the case of 1-hydroxytetrahydrocarbazole or other simple dimers. No such dimers were obtained in the reaction which instead gave a complex mixture of products.



6a
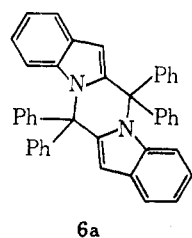
Thermolysis of 2-hydroxydiphenylmethylindole (1) in refluxing bromobenzene at various concentrations afforded five compounds: 5, 11-phenyl-10H-indolo-[1,2-a]indole (7), 11-phenyl-10-[3-(2-diphenylmethyl)indolyl]indolo[1,2-a]indole (8), 11,11'-diphenyl-10,10'-biindolo[1,2-a]indole (9), and 11,11'-diphenyl-10,10'-biindolo[1,2-a]indolidene (10). The per cent yields are from a 0.01 M reaction (Chart I).

The initial decompositions were carried out in tetralin solution giving a deep blue mixture which showed nine compounds by thin layer chromatography (tlc). However, the reaction mixture was less complex using bromobenzene as solvent.

The indoloindole 7 was first isolated from the early

(9) H. Kauffmann and P. Panwitz, *Ber.*, **45**, 766 (1912).

CHART I



5, 27%          7, 12%



8, trace          9, 42%



10, trace

SCHEME I



11          12

          14          13
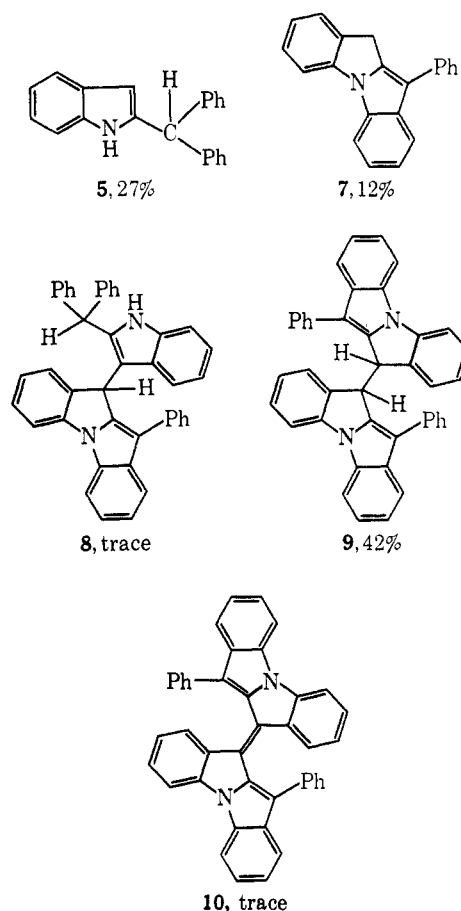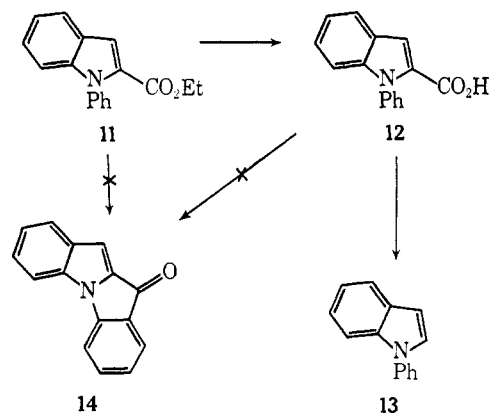
chromatographic fractions of a 0.40 M tetralin run and proved to be a key in determining the structures of the dimers. The proposed structure is supported by its ultraviolet (uv) spectrum (Figure 1); its infrared spectrum showing no N–H absorption; and its nmr spectrum which shows a multiplet at $\delta$ 6.8–7.9 (13 H) and a singlet at 3.87 (2 H). The nature of the uv chromophore was determined from comparisons with 1-phenylindole and 1,3-diphenylindole.

It is hoped that compound 7 could be synthesized independently *via* the ketoindoloindole 14. However, we were unable to obtain 14 by cyclization of 11 or 12 with polyphosphoric acid[10] (Scheme I).

(10) D. Shirley and P. Roussel, *J. Amer. Chem. Soc.*, **75**, 376 (1963). These authors claim to have isolated 14 in low yield from the reaction of n-butyllithium with 1-phenylindole followed by treatment with carbon dioxide. Attempts to synthesize 14 from 12 and its acid chloride failed.

SCHEME II



15



16      17
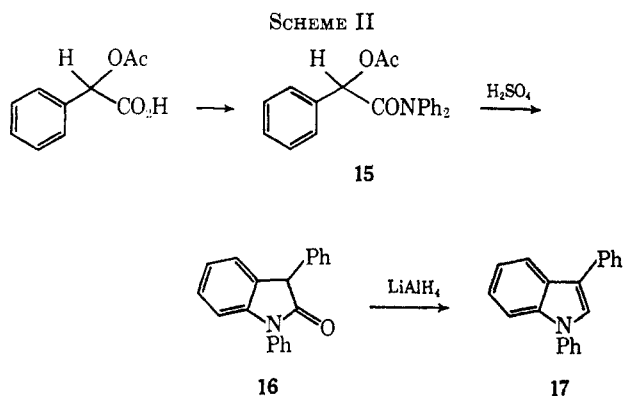
The synthesis of 1,3-diphenylindole was accomplished in a more straightforward manner than found in the literature.[11] Our sequence is outlined in Scheme II. We were unable to detect compound **18**, the double-bond isomer of **7**, in the reaction mixture although the structures of the dimers suggest that **18** is formed.



18
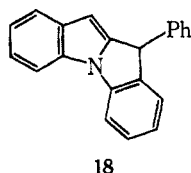
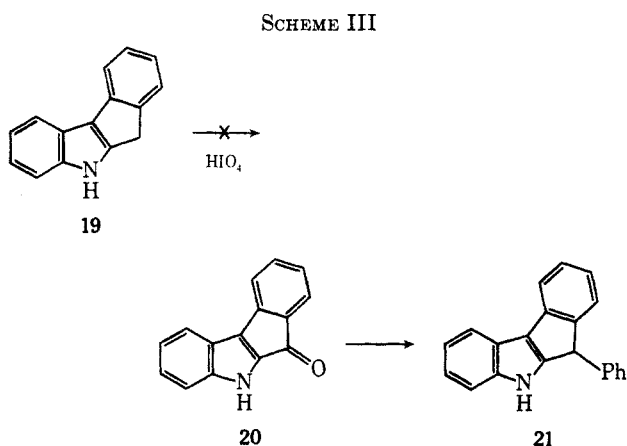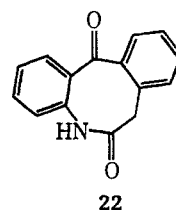The isolation of compound **7** also suggested that compound **21** might be formed by an alternative cyclization. Hence we attempted to synthesize compound **21** to aid in examining the products from the thermolysis reaction. The attempted sequence is outlined in Scheme III.

SCHEME III



19



20      21

A synthetic sequeuce involving the periodic acid oxidation[12] of the indenoindole **19** to the keto compound **20** followed by reaction with phenylmagnesium bromide and hydrogenolysis by lithium aluminum hydride was thwarted at the initial step. Oxidation of **19** by either periodic acid or sodium metaperiodate gave the dibenzoazocinedione **22** exclusively.

(11) E. E. Baroni and K. A. Kovyrzina, *Zh. Obshch. Khim.*, **29**, 3815 (1959); *Chem. Abstr.*, **54**, 19643*h* (1960).
(12) L. J. Dolby and D. L. Booth, *J. Amer. Chem. Soc.*, **88**, 1049 (1966).



22

Although **21** was not isolated from the thermolysis reaction, the nmr spectrum of **19** showed that the methylene protons appear at $\delta$ 3.70 which was further corroboration for the assignment of the methylene protons of **7**.

Dimer **8** was obtained when the residue from a thermolysis reaction was dissolved in benzene followed by dilution with pentane to give crude crystalline **8** in 42% yield.

The uv of pure **8** is strikingly similar to that obtained from a 1:1 mixture of **5** and **7** (see Figure 2).
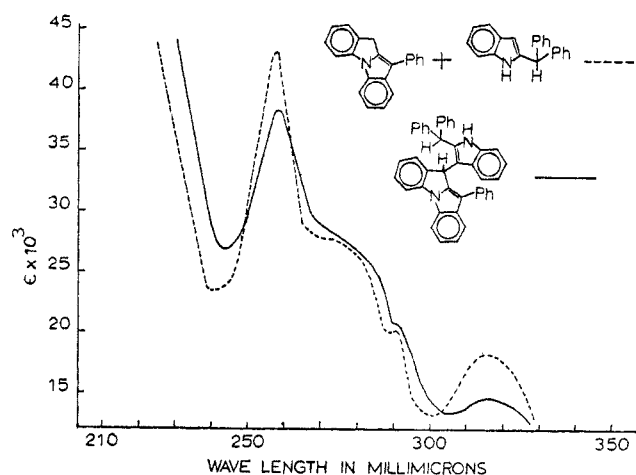


Figure 2.—The uv spectra of 11-phenyl-10-[3-(2-diphenylmethyl)indolyl]indolo[1,2-*a*]indole (**8**) and an equimolar solution of 2-diphenylmethylindole (**5**) and 11-phenyl-10H-indolo-[1,2,*a*]indole (**7**).

The infrared (ir) spectrum of **8** displayed an N–H peak at 2.95 $\mu$ and the mass spectrum had peaks at $m/e$ 562, 395, and 280.



8
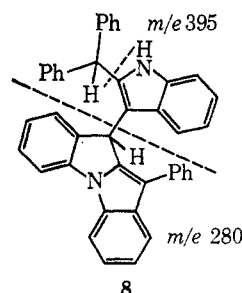
Additional proof of the structure of **8** was obtained when it underwent reductive cleavage by the action of zinc dust in refluxing glacial acetic acid to give a 1:1 mixture of **5** and **7**.[13] Several derivatives of isoindigo have been subjected to similar conditions for brief periods of time to give only the leuco products.[14] However, the reductive cleavage of **8** can be rationalized without difficulty.

(13) For reduction of indole by zinc and phosphoric acid, see L. J. Dolby and G. H. Gribble, *J. Heterocycl. Chem.*, **3**, 124 (1966).
(14) H. de Diesbach and E. Heppner, *Helv. Chim. Acta*, **32**, 687 (1949).

Upon closer examination of the reaction mixtures in subsequent runs of the thermolysis in concentrated solution (0.5–0.1 *M*), **5** could be observed in the later chromatographic fractions by the nmr peaks of the methine and 3-indole protons and the characteristic indole absorption in the uv.

Thermolysis of **1** in dilute solution gave a reaction mixture which displayed three spots upon tlc corresponding to **5**, **7**, and **9** and showing only a trace of **8**. The highly insoluble **9** crystallized when an attempt was made to dissolve the reaction mixture.

Dimer **9** was obtained as a high melting white powder whose uv spectrum resembled that of **7** quite markedly. The combustion analysis fit well for $C_{42}H_{28}N_2$ but the highest mass peak in the mass spectrum occurred at *m/e* 558 which is two atomic mass units lower than expected. A very intense base peak at *m/e* 280 appeared to rise from either symmetrical cleavage of the unobserved molecular ion *m/e* 560 or ionization of radicals obtained if **9** undergoes symmetrical thermolytic cleavage.

The possibility that **9** undergoes dehydrogenation and other changes upon being heated under high vacuum was confirmed when attempted sublimation of **9** at 200° and $2.3 \times 10^{-5}$ mm afforded two other compounds, one of which was blue. The importance of this observation became clear when it was found that treatment of **9** with chloranil in refluxing toluene produced the deep blue crystalline dimer **10** whose mass spectrum exhibited a base peak at *m/e* 558. Dimer **10** was also synthesized when **7** was treated with N-bromosuccinimide and the crude product obtained was stirred with base.[15]

Conclusive proof for the structural assignments of **9** and **10** came from their reactions with zinc and acetic acid. Dimer **9** underwent reductive–cleavage to give **7** only. When **10** was subjected to the same conditions until the blue color was discharged, dimer **9** was obtained and prolonged reaction gave **7**.

Although **10** was never isolated from the thermolysis reaction mixtures, it was the only blue compound obtained in this study. Dimer **10** obtained from **7** and **9** had an identical tlc $R_f$ value with that of the blue compound observed in the reaction mixtures of the thermolysis of **1**.

After isolating and characterizing all of the products of the thermolysis reaction, it became of interest to determine yields of the products as a function of concentration. This was readily accomplished in the case of the reaction in dilute solution where chromatography over Florisil gave a fairly good separation of the products. The product mixture from the thermolysis in concentrated solution was much more difficult to analyze and attempted analysis by preparative tlc and uv spectroscopy gave erratic results. However, one point does emerge, as the concentration is increased the yield of dimer **8** increases at the expense of the symmetrical dimer **9**. Whereas dimer **8** was formed only in trace amounts in 0.01 *M* solution, it was obtained in 22–48% yields from more concentrated (0.1 and 0.5 *M*) reactions. The yield of the symmetrical dimer from more concentrated solutions appeared to fluctuate but was

consistently below the yield of 40% observed in the dilute reaction mixture.

A reasonable reaction scheme can be put forward to account for all of the products from the reaction. A particularly interesting feature of the reaction is that intermediate **3** of its conjugate acid can enter into three transformations. One of these species must cyclize to eventually yield compound **7**. It appears that compound **18** must be formed as well although we were unable to isolate it from the reaction mixture or obtain it by isomerization of **7**. However, electrophilic substitution on **18** by intermediate **3** or its conjugate acid would yield dimer **8**. Dimer **9** may be formed by two pathways both involving hydride abstraction by intermediates **2** or **3** which accounts for the large amount of 2-diphenylmethylindole (**5**) formed in the reaction. One pathway to dimer **9** involves hydride abstraction from either compound **7** or **18** followed by electrophilic substitution on **18**. Another likely pathway involves hydride abstraction from dimer **8** followed by internal cyclization to yield **9**. The trace amounts of the blue dimer **10** likely arise by oxidation of dimer **9** either by atmospheric oxygen or one of the several potential hydride abstractors in the reaction mixture.

The complexity of the reaction makes it a difficult one to study. None of the available information demands that 2-alkylidene-2H-indole intermediate **3** be invoked to rationalize the products, although it is attractive to propose this intermediate for several reasons. A major fraction of the products from the thermolysis reaction are derived by internal cyclization of intermediate **3** or its conjugate acid **2**, the triarylcarbonium ion. However, it appears that the triarylcarbonium ion **2** cyclizes only very slowly since quenching its solutions in strong acid affords the starting triarylcarbinol. Thus it seems reasonable to suggest that the internal cyclization proceeds *via* intermediate **3**. The fact that intermediate **3** has been observed directly lends further support to this proposal. However, there is no basis for deciding between intermediate **3** and its conjugate acid as the reactive species in the hydride abstraction reaction or the electrophilic substitution processes.

## Experimental Section[16]

(15) The latter reaction is analogous to the conversion of 9-bromofluorene of 9-bromofluorene to 9,9'-bifluoreneylidene when treated with base: J. Thiele and A. Wanscheidt, *Ann.*, **376**, 278 (1910).

(indole 3-H, d, 1), and 2.95 (O-H, s, 1); ir λ 2.80 μ (O-H) and 2.90 (N-H).

*Anal.* Calcd for $C_{21}H_{17}NO$: C, 84.25; H, 5.73; N, 4.68. Found: D, 84.43, 83.73; H, 6.47, 5.75; N, 4.73, 4.73.

**Measure of the $pK_R^+$ of 2-Hydroxydiphenylmethylindole (1).**— The $pK_R^+$ of carbinol 1 was obtained from the absorbance of the ion in the visible region when 5 was dissolved in aqueous sulfuric acid solutions of known composition (per cent by weight). The $H_R$ ($C_0$) acidity functions were calculated from published data[7] and the $pK_R^+$ was calculated from the following equation.

$$pK_R^+ = H_R + \log \frac{c_R^+}{c_{ROH}}$$

The carbinol was assumed to be entirely dissociated in concentrated sulfuric acid solution. The ion 6 displays $\lambda_{max}$ 476 mμ (ε 53600) which shifts gradually to 472 mμ until 58.2% acid solution is used and then remains constant.

The average value obtained for the $pK_R^+$ was found to be −1.50 ± 0.03 ($T° = 26.8 ± 0.5$). The carbinol could be recovered in 90% yields from 80% acid by dilution with water.

**2-Methoxydiphenylmethylindole (4).**—A solution of 1 (300 mg, 0.97 mmol), 2 drops of glacial acetic acid, and 10 ml of methanol was refluxed on a steam bath for 30 min. The solution was left to cool at room temperature overnight. Slightly tan, well-formed crystals were obtained and a second crop was combined to give 229 mg (95.2%) with mp 136–140°. A second recrystallization gave material with mp 138–140°; ir 2.88 μ (N-H); nmr (CCl₄) δ 6.45 (indole 3-H, d, 1), 3.10 (OCH₃, s, 3), and 7.85 (N-H, broad s, 1).

*Anal.* Calcd for $C_{22}H_{19}NO$: C, 84.31; H, 6.11; N, 4.47. Found: C, 84.21; H, 6.20; N, 4.36.

**2-Diphenylmethylindole (5).**—To 500 mg (13.2 mmol) of lithium aluminum hydride in 25 ml of ether was added, with cooling, 1.40 g (4.48 mmol) of 4 in 20 ml of ether. The reaction mixture was stirred at room temperature for 10 min at which point tlc showed only one spot with violet circumference and yellow center. The excess hydride was cautiously destroyed with absolute ethanol and water and the gelatinous mixture was poured into 50 ml of water and 10 ml of concentrated hydrochloric acid. Extraction with ether, followed by washing of the ether layer with 10% hydrochloric acid and saturated salt solution, drying, and evaporation, afforded a quantitative yield of 5 as a pale yellow gum. Attempted distillation at 0.10 mm led to decomposition. The trinitrobenzene complex was obtained as orange needles, mp 167–169°, by heating a 1:1 mixture of 2-diphenylmethylindole and trinitrobenzene in ethanol solution.

*Anal.* Calcd for $C_{27}H_{20}N_4O_6$: C, 65.32; H, 4.06; N, 11.29. Found: C, 65.15; H, 4.03; N, 11.35.

Pure indole 5 could be obtained by filtration of a solution of the complex over alumina. The compound thus obtained showed $\lambda_{max}^{EtOH}$ 291 mμ (ε 7100); nmr (CCl₄) δ 5.92 (indole 3-H, d, 1) and 5.23 (methine H, s, 1).

Identical results were obtained when 1 was stirred with zinc dust in refluxing acetic acid for 1 hr.

**Isolation of 11-Phenyl-10H-indolo[1,2-a]indole (7).**—A solution of crude 1 (5.86 g, 0.020 mol) in 50 ml of tetralin was refluxed under nitrogen for 3 hr. Thin layer chromatography showed nine spots, of which only four were large and intense.

The dark green mixture was chromatographed over 300 g of Alcoa alumina packed in petroleum ether (bp 30–60°). The column was eluted with petroleum ether until all of the tetralin was recovered. Elution was continued with benzene–petroleum ether (3:7). Fractions were collected until the intense blue band began to elute. All fractions except one showed the presence of at least two compounds (tlc). Crystallization of the fraction showing one compound from ethyl acetate yielded 135 mg (2.3%) of slightly blue crystalline 7: mp 139–140° (two further recrystallizations removed the blue color but did not change the melting point); uv $\lambda_{max}^{EtOH}$ 315 mμ (ε 18,300), 275 sh (18,500), 257 (36,800), and 222 (28,600); nmr δ 6.8 to 8.0 (aromatic H, m, 13) and 3.87 (CH₂, s, 2).

*Anal.* Calcd for $C_{21}H_{15}N$: C, 89.65; H, 5.37 N, 4.98. Found: C, 89.46; H, 5.48; N, 4.89.

**N,N-Diphenylacetylmandelamide (15).**—A solution of acetylmandelic acid (21.88 g, 0.113 mol) in 35 ml of thionyl chloride was refluxed for 4 hr. The excess thionyl chloride was removed under reduced pressure and the crude acid chloride was added portionwise to a chilled solution of diphenylamine (19.30 g, 0.114 mol) and pyridine (10.30 g, 0.130 mol) in 140 ml of dichloromethane. The reaction mixture was then refluxed for 1 hr.

The cooled reaction mixture was poured into water and the dichloromethane layer was washed with 10% phosphoric acid and water, dried, and evaporated to dryness. The powder obtained was recrystallized from boiling ether to give 24.62 g (63.2%) of amide as well-formed prisms: mp 125–130° (two more recrystallizations raised this to mp 130–133°; ir $\lambda_{max}$ 5.80 and 6.00 μ (C=O); nmr (CCl₄) δ 6.01 (benzylic H, s, 1) and 2.10 (CH₃C=O, s, 3).

*Anal.* Calcd for $C_{22}H_{19}NO_3$: C, 76.50; H, 5.55; N, 4.06. Found: C, 76.47; H, 5.44; N, 3.91.

**1,3-Diphenyloxindole (16).**—To 50 ml of cold, stirring concentrated sulfuric acid was added 5.00 g (14.5 mmol) of 15, portionwise over a period of 20 min. The mixture was stirred at 0° for 2 hr and then poured onto ice. The product was extracted with dichloromethane, washed with saturated salt solution, dried, and evaporated to give a white powder. Recrystallization from ether–petroleum ether (bp 30–60°) gave 2.85 g (68.0%) of crystals, mp 93–96°. Two more recrystallizations raised the melting point to 109–111° (lit.[17] mp 114°).

**1,3-Diphenylindole (17).**—To a mixture of 250 mg (6.60 mmol) of lithium aluminum hydride in 15 ml of ether was added 679 mg (2.38 mmol) of 16 in 5 ml of ether. The reaction mixture was stirred at room temperature for 4 hr. The excess hydride was cautiously destroyed with ethanol and water. The reaction mixture was worked up in the usual manner and the residue was recrystallized from methanol to give 395 mg (62%) of 17 as fine needles: mp 102–103° (lit.[11] mp 103–104°); uv $\lambda_{max}^{EtOH}$ 305 mμ (ε 15,500), 255 (20,700), and 221 (15,400). A slight shoulder was observed at 272 mμ (ε 15,400).

**1-Phenyl-2-carbethoxyindole (11).**—A solution containing 2.32 g (0.020 mol) of ethyl pyruvate, 3.68 g (0.020 mol) of N,N-diphenylhydrazine, and 2 drops of acetic acid in 10 ml of absolute ethanol was heated on a steam bath for 5 min. The mixture was then added to 100 ml of absolute ethanol saturated with hydrogen chloride gas and the ensuing deep red mixture was refluxed on a steam bath for 30 min.

The solvent was evaporated, the milky residue was swirled with water and dichloromethane, and the dichloromethane layer was washed with water and evaporated to a brown oil. Recrystallization from petroleum ether (bp 30–60°) afforded tan plates (4.00 g, 75.5%), mp 59–62°. Sublimation at 100° (0.35 mm) followed by recrystallization from benzene–petroleum ether gave white crystals: mp 63.5–65.0°; uv $\lambda_{max}^{EtOH}$ 293 mμ (ε 19,700) and 217 (25,800); ir $\lambda_{max}$ 5.85 (C=O).

*Anal.* Calcd for $C_{17}H_{15}NO_2$: C, 76.96; H, 5.70; N, 5.28. Found: C, 76.91; H, 5.77; N, 5.16.

**1-Phenylindole-2-carboxylic acid (12).**—A mixture of 2.65 g (0.010 mol) of 11 in 35 ml of ethanol and 30 ml of 1.00 N sodium hydroxide solution was heated on a steam bath for 35 min. The reaction mixture was acidified with concentrated hydrochloric acid, poured into 30 ml of salt solution, and extracted with dichloromethane. The dichloromethane solution was washed with salt solution, dried, and evaporated, leaving 2.27 g (95.8%) of pale tan powder. Recrystallization from ethanol–water gave small tan needles, mp 173–175° (lit.[18] mp 176°).

**1-Phenylindole (16).**—Under an atmosphere of nitrogen, 478 mg (2.0 mmol) of 12 was heated at 210° for 3 hr. The brown oil obtained (365 mg, 93.5%) could be distilled at 114–117° (0.35 mm): $n^{25}$D 1.6564; [(lit.[19] bp 179–180° (11 mm); $n^{25}$D 1.6555)]; uv $\lambda_{max}^{EtOH}$ 290 mμ (ε 8170) and 257 (19,000).

**6H-Indeno[2,1-b]indole (19).**—To a solution of 4.22 g (31.9 mmol) of 2-indanone and 0.5 ml of acetic acid in 25 ml of absolute ethanol was added 5.00 g (46.2 mmol) of freshly distilled phenylhydrazine. The mixture was stirred for 30 min after which 50 ml of alcohol was added and hydrogen chloride gas was bubbled in for 20 min. The reaction mixture was poured into water and extraction with dichloromethane, followed by washing with 10% sodium carbonate solution and water, drying, and evaporation gave a green solid. Chromatography of the residue over 400 g of alumina with benzene–cyclohexane (3:2) gave 2.29 g (35.0%) of tan solid. Recrystallization from ethanol gave crystals: mp 199° dec (lit.[20] mp 200° dec); uv $\lambda_{max}^{EtOH}$ 292 mμ sh (ε 17,700), 278 (22,900), 240 (26,600), 235 sh (24,000), and 226 (24,600); nmr (CDCl₃) δ 3.70 (CH₂, s, 2).

(17) J. C. Sheehan and J. W. Frankenfeld, *J. Amer. Chem. Soc.*, **83**, 4792 (1961).

(18) E. Fischer and O. Hess, *Ber.*, **17**, 559 (1884).

(19) A. F. Pozharskii, B. K. Martsohka, and A. M. Simonov, *Zh. Oshch. Khim.*, **33**, 1005 (1963); *Chem. Abstr.*, **59**, 7515f (1963).

(20) J. W. Armit and R. Robinson, *J. Chem. Soc.*, **121**, 838 (1922).

**5,6,7,12-Tetrahydrodibenzo[b,e]azocine-6,12-dione (22). A. By Oxidation of 19 with Sodium Metaperiodate.**—A solution of 19 (597 mg, 2.97 mmol) in 6 ml of methanol and 2.5 ml of tetrahydrofuran was added to a stirring solution of sodium metaperiodate (1.38 g, 6.46 mmol) in 11 ml of water. The reaction mixture became turbid and was stirred at room temperature for 5 hr. The mixture was diluted with water and extracted with dichloromethane which, after washing with saturated salt solution, drying, and evaporating, gave a white powder (496 mg, 70.5%). Recrystallization from benzene gave fine white needles: mp 210–212°; uv $\lambda_{max}^{EtOH}$ 243 m$\mu$; ir $\lambda_{max}$ 2.95 $\mu$ (N—H) and 5.99–6.06 (C=O); nmr (CDCl₃) δ 8.30 (N—H, broad s, 1) and 3.76 (CH₂, broad s, 2).

*Anal.* Calcd for C₁₅H₁₁NO₂: C, 75.93; H, 4.67; N, 5.90. Found: C, 75.83; H, 4.51; N, 5.94.

**B. By Oxidation of 19 with Periodic Acid.**—A solution of 19 518 mg, 2.53 mmol) in 10 ml of methanol and 1 ml of tetrahydrofuran was added dropwise to a solution of periodic acid (1.42 g, 6.23 mmol) in 8 ml of water over a period of 5 min. The reaction mixture became a deep red during the addition of 22.1 g. Thin layer chromatography showed two spots, the largest corresponding to compound 25 previously obtained.

Dilution of the reaction mixture with water was followed by extraction with ether, washing with 10% sodium thiosulfate solution, water, drying, and evaporation. When *ca.* 1 ml of dichloromethane was added to the residue, a white precipitate was obtained which, upon recrystallization from benzene, gave 295 mg (49%) of 22.

**Isolation of Dimer 8.**—To refluxing bromobenzene (65 ml) with nitrogen bubbling through it was added 6.00 g (0.020 mol) of carbinol 1 and the mixture was refluxed for 2 days. The solvent was removed at 100° under reduced pressure and the blue residue was dissolved in ethyl acetate and refrigerated for 5 days.

A gray, crystalline compound (100 mg, 1.8%) was obtained which, upon two more recrystallizations, had mp 224–229° dec; uv $\lambda_{max}^{EtOH}$ 317 m$\mu$ (ε 13,300). 293 (13,300), and 264 (27,400); and mol wt 562 (mass spectrum). The compound gave erratic combustion analyses. This compound, an isomer of 8, was only found when the thermolysis of 1 was carried out for prolonged periods of time. It showed the same tlc color and $R_f$ value as 8, and it was later found that when 8 was heated for 2 days in bromobenzene it underwent isomerization to this material.

The residue from the ethyl acetate mother liquor was then eluted over Florisil in a constant-elution chromatography column. Fractions were eluted with cyclohexane, carbon tetrachloride, and carbon tetrachloride–benzene (9:1).

The last fraction contained dimer 8 upon recrystallization of the residue from chloroform–pentane (1.03 g, 18.3%). Two more recrystallizations gave crystals: mp 197–205°; uv $\lambda_{max}^{EtOH}$ 317 m$\mu$ (ε 15,700), 292 (20,400), 285 sh (25,300), 257 (38,400), and 223 (66,300); ir (C₆H₆) $\lambda_{max}$ 2.88 $\mu$ (N—H); mol wt 562 (mass spectrum).

*Anal.* Calcd for C₄₂H₃₀N₂: C, 89.65; H, 5.37; N, 4.98. Found: C, 89.65, H, 5.46; N, 4.88.

Dimer 8 was obtained in higher yield (2.75 g, 41.9%) when 7.00 g (0.023 mol) of 8 was stirred in 500 ml of refluxing bromobenzene under nitrogen for 2 hr. When the residue from the reaction mixture was dissolved in benzene and diluted with pentane until turbid, dimer 8 was obtained as gray crystals. Two further recrystallizations gave material identical with that previously obtained.

**Reductive-Cleavage of Dimer 8.**—A mixture of 102 mg (0.179 mmol) of 8 and 1.50 g (0.0229 g-atom) of zinc dust was stirred vigorously in 10 ml of refluxing glacial acetic acid under nitrogen for 24 hr. The reaction mixture was filtered and evaporated. The residue was extracted with boiling benzene and evaporated. The residue showed 5 and 7 to be present in a 1:1 ratio (tlc, nmr, and uv).

The residue was dissolved in hot methanol and refrigerated for 5 hr. The crystals obtained (40 mg, 80%), upon a further recrystallization, were identical with 7 in all respects.

The methanol mother liquor was evaporated and then heated with 40 mg (0.19 mmol) of 1,3,5-trinitrobenzene in 5 ml of ethanol and afforded orange crystals which, after two recrystallizations, were identical with the TNB–complex of 5.

**Thermolysis of 1 in Dilute Solution (0.0124 M).**—To 900 ml of refluxing bromobenzene with a stream of nitrogen bubbling through it was added 3.46 g (0.0116 mol) of 1 in 30 ml of bromobenzene. After 6 hr all of the starting material had reacted and tlc of the reaction mixture showed four spots: the first and fastest moving corresponding to 7; the second was similar in color to the first; the third corresponded to 5; and the fourth and faintest occurred at the base of the third spot and corresponded to dimer 8.

Removal of the solvent followed by swirling the green, gummy residue with hot dichloromethane gave dimer 9 as a fine, white powder (1.28 g, 39.4%).

Dimer 9, which corresponded to the second tlc spot, was highly insoluble in most solvents but could be recrystallized from boiling toluene to give a white powder: mp 303° dec (sealed tube); uv $\lambda_{max}^{EtOH}$ 322 m$\mu$ (ε 20,000), 258 (46,600), and 222 (41,900). The mass spectrum showed an apparent molecular weight of 558 and a base peak at $m/e$ 280. Attempted sublimation at 200° and 2.3 × 10⁻⁵ mm gave two different compounds as indicated by tlc of the sublimate; one of these was blue.

*Anal.* Calcd for C₄₂H₂₆N₂: C, 89.97; H, 5.03; N, 5.00. Found: C, 90.04; H, 5.19; N, 5.02.

The dichloromethane filtrate was evaporated and the residue was dissolved in carbon tetrachloride and eluted over 250 g of Florisil. The products were collected in 13 100-ml fractions: fractions 1–9 were eluted with carbon tetrachloride; 10 and 11 were eluted with carbon tetrachloride–benzene 1:1; and the remainder was eluted with benzene.

Fractions 1–3 afforded 0.405 g (12.4%) of 7. Fractions 4–11 were swirled with boiling methanol and filtered to give an additional 0.091 g of dimer 9 (total yield 42%). Evaporation of the filtrates and combination with fraction 12 gave 0.869 g (26.7%) of crude 5. The remaining fraction contained a small amount of 5 and 8 but the compounds could not be separated. One reaction at an initial concentration of 0.5 M afforded dimer 9 in 34% yield whereas a similar reaction at 0.1 M gave 9 in 21% yield.

**Chloranil Dehydrogenation of Dimer 9.**—A mixture of 9 (442 mg, 0.790 mmol) and chloranil (214 mg, 0.872 mmol) in 30 ml of toluene was refluxed under nitrogen for 24 hr. The solvent was evaporated and the residue dissolved in dichloromethane, washed with water, 10% sodium carbonate solution, and water, dried, and evaporated. Filtration through alumina with benzene afforded 266 mg (60.3%) of dimer 10. Recrystallization from boiling acetone gave deep blue needles, mp 283–287°. The analytical sample was recrystallized twice from benzene–pentane. The uv showed $\lambda_{max}^{EtOH}$ 624 m$\mu$ (ε 26,800), 480 (7680), 414 (5790), 319 (27,600), 301 (30,700), 285 sh (34,700), 271 (39,000), and 251 (45,900); and the molecular weight was 558 (mass spectrum).

*Anal.* Calcd for C₄₂H₂₆N₂: C, 90.29; H, 4.69; N, 5.02. Found: C, 90.07; H, 4.66; N, 5.23.

**Dimer 10 from Indoloindole 7.**—A solution of 7 (66.5 mg, 0.236 mmol), N-bromosuccinimide (43.0 mg, 0.244 mmol), and benzoylperoxide (0.4 mg, 0.002 mmol) in 5 ml of carbon tetrachloride was refluxed under nitrogen for 30 min. The hot solution was filtered and evaporated. Thin layer chromatography showed essentially one product with only a trace of 10 being formed. The residue was stirred with 5 ml of dimethyl sulfoxide and 1.0 ml of 1.00 N sodium hydroxide solution at room temperature for 4 hr. The reaction mixture was poured into 10 ml of saturated salt solution and extracted with methylene chloride and the methylene chloride solution was washed with saturated salt solution, dried, and evaporated. Filtration through alumina with benzene gave 35.0 mg (53.2%) of deep blue solid which was identical in all respects with dimer 10 previously obtained.

**Reductive Cleavage of the Symmetrical Dimer 9.**—A mixture of 20 mg (0.036 mmol) of 9 and 500 mg (0.0076 g-atom) of zinc dust was vigorously stirred in 3 ml of refluxing glacial acetic acid for 24 hr under nitrogen. The reaction mixture was worked up as previously described and afforded a quantitative yield of indoloindole 7.

**Reduction of Dimer 10 to Dimer 9.**—A mixture of dimer 10 (35 mg, 0.063 mmol) and zinc dust (500 mg, 0.0076 g-atom) in 5 ml of glacial acetic acid was refluxed with vigorous stirring until the blue color was completely discharged (2.5 hr). The reaction mixture was worked up in the usual manner and afforded dimer 9 in 93% yield.