

DIINDOLYLS

I. SYNTHESIS OF 3,5'- and 5,5'-DIINDOLYLS

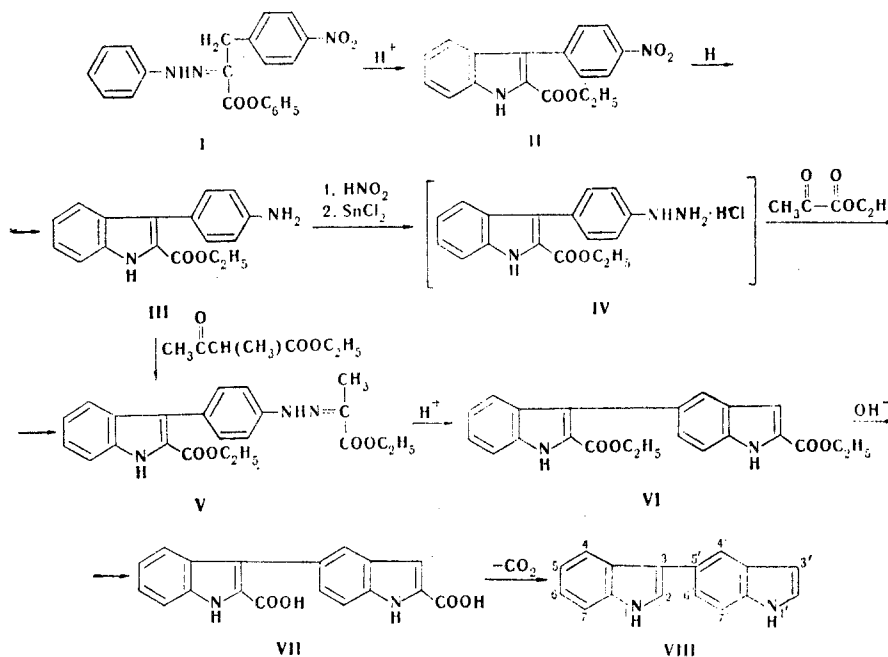
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3,5'- and 5,5'-Diindolyls were obtained from ethyl pyruvate 4-(2-carbethoxy-3-indolyl)phenylhydrazone and ethyl pyruvate 4,4'-biphenyldihydrazone by Fischer cyclization and subsequent saponification and decarboxylation. The formation of 5-phenyl-2-carbethoxyindole, from which 5-phenylindole was obtained, was observed in the indolization of ethyl pyruvate 4,4'-biphenyldihydrazone.

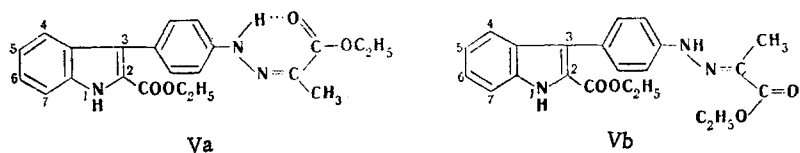
The synthesis of diindolyls in which the bond between the indole molecules is realized through the carbon atoms of the pyrrole ring was reported in [1-4]. Compounds of this type are not of interest because of their low reactivities. Diindolyls in which the rings are joined through the carbon atoms of the benzene ring are more important, but little study has been devoted to this class of compounds. There are two papers [5, 6] in which the synthesis of 3,6'-diindolyl and 2,2'-dimethyl-5,5'-diindolyl derivatives are described, but data on the synthesis and properties of the corresponding unsubstituted heterocycles are unavailable.

In the present research we were able to use the Fischer reaction for the synthesis of unsubstituted 3,5'- and 5,5'-diindolyls.



In the method for the preparation of II described in [7] the cyclization was carried out in acetic acid in the presence of boron trifluoride etherate. According to our observations, it is more convenient to use a 15% solution of HCl in absolute ethanol for the cyclization of large amounts; this makes it possible to obtain a rather pure compound. Hydrazone V is produced in the form of a mixture of two geometrical isomers, which could be separated into the syn and anti forms (Va,b) by preparative column chromatography.

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Absorption bands were observed at λ_{\max} ($\log \epsilon$) 210 (4.3), 241 (4.4), 303 (4.2), and 366 nm (4.4) in the UV spectrum (in ethanol) of isomer Va, whereas absorption maxima were observed at 210 (4.4), 241 (4.4), 301 (4.3), and 354 nm (4.4) in the UV spectrum of isomer Vb. Since a bathochromic shift (12 nm) of the long-wave absorption band is observed for isomer Va, the syn-isomer structure should be assigned to it, and the anti-isomer structure should be assigned to Vb [8].

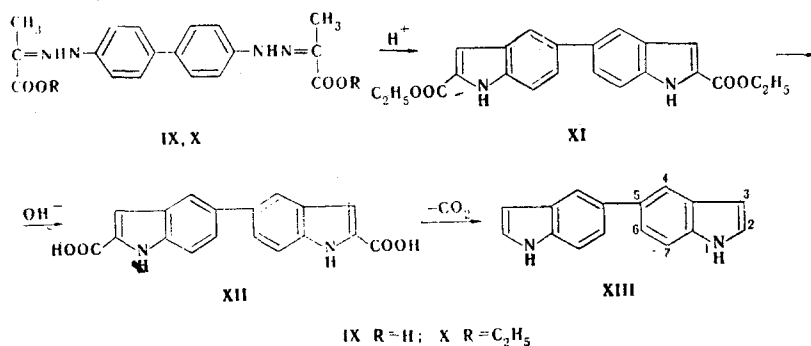
A difference in the position of the absorption bands of the NH group is observed in the IR spectra of hydrazones Va and Vb (in mineral oil). A band at 3335 cm^{-1} is observed for isomer Va, whereas a band at 3290 cm^{-1} is observed for Vb. The spectra of chloroform solutions of both isomers contain an absorption band at 3475 cm^{-1} ; this is characteristic for stereoisomeric hydrazones [9]. The frequencies of the absorption of the carbonyl groups for the pair of isomers remain virtually constant (1680 for Va and 1685 cm^{-1} for Vb). However, splitting of the band of the carbonyl group is observed for isomer Vb (in mineral oil), and a less intense band appears at 1710 cm^{-1} .

A comparison of the PMR spectra of hydrazones Va and Vb shows a shift in the signal of the NH proton of the hydrazone group of isomer Va to weaker field (12.2 ppm) relative to the signal of the corresponding proton of hydrazone Vb (7.9 ppm) (Table 1). This shift is evidently explained by participation of the NH proton in strong intramolecular hydrogen bonding, possibly in the case of syn orientation of the substituent. The IR and PMR spectroscopic data confirms the conclusions drawn on the basis of the UV spectra.

In the preparation of hydrazone V through hydrazine IV the syn:anti ratio is 2:3, as compared with 7:3 when the hydrazone is prepared via the Japp-Klingemann reaction. However, according to our observations, the different isomer ratios do not affect the yield of the diindolyl in the cyclization process; this is evidently explained by the ability of these forms to undergo isomerization.

We were able to effect the cyclization of hydrazones V and X by means of polyphosphoric acid ester. The indolization of hydrazone V also takes place when dry HCl is bubbled into an alcohol solution of the hydrazone. The yield of VI ranges from 30 to 40% and depends on the degree of purity of the starting hydrazone. The cyclization of hydrazones V, IX, and X under the influence of concentrated sulfuric acid in ethanol gives the products in no higher than 7-8% yields.

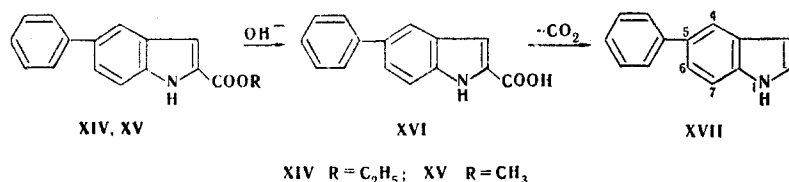
To obtain 5,5'-diindolyl we used Fischer cyclization of pyruvic acid 4,4'-biphenyldihydrazone (IX) and ethyl pyruvate 4,4'-biphenyldihydrazone (X):



During the cyclization of dihydrazones IX and X we observed the formation of 5-phenyl-2-carbethoxyindole (XIV).

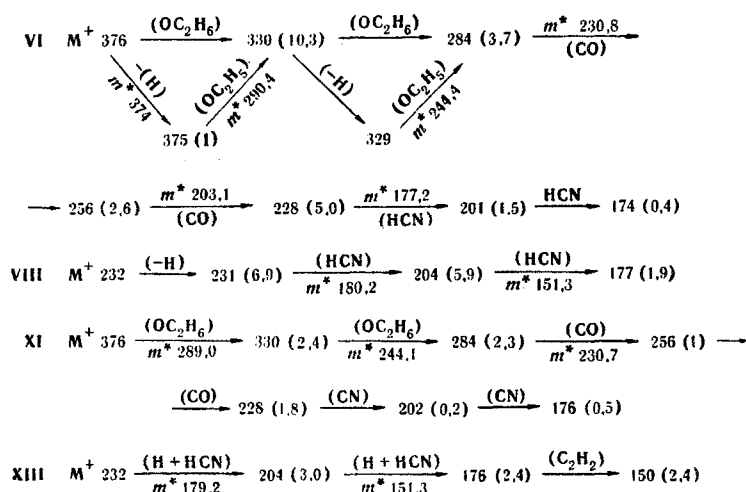
It may be assumed that one of the hydrazone groups is split out because of decomposition of the azo form of the hydrazone at high temperatures; this does not contradict the data in

[11, 12]. A similar phenomenon has been observed in the case of acetone 4,4-biphenyldi-hydrazone [6].



Saponification of esters VI, XI, and XIV leads to the corresponding unstable dicarboxylic VII and XII or to 5-phenyl-2-carboxyindole (XVI). Unsubstituted diindolyls VIII and XIII and 5-phenylindole (XVII) were obtained by decarboxylation of these acids.

The PMR spectra are in agreement with the proposed structures of VI, VIII, XI, and XIII-XVII (Table 1). The molecular weights of VI, VIII, XI, and XIII, determined by mass spectroscopy, are in good agreement with the calculated values, and the character of the subsequent fragmentation, confirmed by the metastable transitions, does not contradict the proposed structures.†



The fragmentation of the molecular ions of the indicated compounds under the influence of electron impact does not differ fundamentally from the scheme of the fragmentation of indole itself [10].

Bands at 217, 231, and 254 nm are observed in the UV spectrum of diindolyl VIII (in alcohol). A long-wave band of low intensity at 291.6 nm is observed when the concentration of VIII in heptane is increased. The band at 231 nm is absent in the spectrum of diindolyl XIII (in alcohol), and the band at 249 nm is somewhat more intense than the corresponding band in the spectrum of diindolyl VIII (Fig. 1).

A comparison with the spectrum indole (curve 1) shows that the position of the short-wave maximum of the three compounds coincide (see curves 3-5), while the long-wave portion of the spectrum differs substantially, since the characteristic indole absorption at 280 nm is absent in the spectra of both diindolyls. As expected, the spectrum of diindolyl XIII reminds one somewhat more of the spectrum of biphenyl than of the spectrum of diindolyl VIII. An increase in the polarity of the solvent leads to a small (11 nm) bathochromic shift of the long-wave absorption band of diindolyls.

Two bands corresponding to the absorption of free (3490 cm⁻¹) and associated (in self-associates) (3430-3440 cm⁻¹) NH groups are observed in the IR spectrum of VIII in chloroform. The position of the band of the free NH group coincides with the corresponding band in the

†The m/e values are presented, and the relative intensities with respect to the total ion current are given in parentheses.

TABLE 1. PMR Spectra

Compound	R	1-H	4-H	5-H	6-H	7-H	C ₆ H ₅ , Ph	NH	CH ₂ (C ₂ H ₅)	CH ₃ (C ₂ H ₅)	CH ₃				
Va		9,35 br s		7,1-7,8				12,2 br s	4,32 q 4,35 q 4,33 q 4,36 q	1,24 t 1,36 t 1,26 t 1,40 t	2,20 s 2,15 s				
Vb		9,19 br s		7,1-7,8				7,9 br s							
		1'-H	2'-H	3'-H	4'-H	6'-H	7'-H	1-H	2-H	4-H	5-H	6-H	7-H	CH ₂ (C ₂ H ₅)	CH ₃ (C ₂ H ₅)
VI	COOC ₂ H ₅	12,0 br s*	—	7,36 s	7,94 s	7,65	12,1 br s							4,30 q 4,46 q	1,15 t 1,36 t
VII	H	11,15 br s*	7,46 t	6,80 t	7,99 s	~7,60	11,3 br s	7,68 s	7,68 s	8,06 m	~7,25	~7,65 m			
		1-H	2-H	3-H	4-H	6-H	7-H		CH ₂ (C ₂ H ₅)					CH ₃ (C ₂ H ₅)	
XI	COOC ₂ H ₅	11,85 br s		7,20 s	7,92 s	7,55s				4,36 q				1,32t	
XII	H	~11,90 br s	7,23 t	6,40 t	7,68 s	7,35									
		1-H	2-H	3-H	4-H	6-H	7-H	Ph						CH ₃	
XIV	COOCH ₃	11,85 br s		7,12 d	7,81 s		7,3-7,6							3,90	
XV	COOH	~11,65 br s		7,14 d	7,88 s		7,3-7,6								
XVI	H	11,1 br s	7,35 t	6,48 t	7,80 s		7,2-7,6								

*Abbreviations: s is singlet, d is doublet, t is triplet, q is quartet, m is multiplet, and br s is broad singlet.

TABLE 2. Absorption Band of the NH Group of Indole and Diindolyl VIII in the Presence of Some Acceptors

	Indole, ν , cm^{-1}	3,5'-Diindolyl, ν , cm^{-1}
Chloroform	3410, 3495	3430—3440, 3490
Mineral oil	3420	3420
THF	3315	3320
Ether	3320	3330
Dioxane	3330	3360
Acetonitrile	3385	3415
Pyridine	3240	3220
Acetone	3410	3420

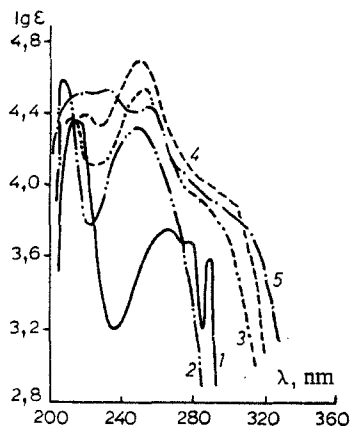


Fig. 1. UV absorption spectra: 1) indole; 2) biphenyl; 3) 5-phenylindole; 4) 5,5'-diindolyl; 5) 3,5'-diindolyl.

spectrum of indole (3495 cm^{-1}), whereas the band of the associated NH group is located in the region of somewhat higher frequencies (3410 cm^{-1} in the case of indole).

Analysis of the data in Table 2, in which the frequencies of the absorption of the NH group for associates of diindolyl VIII with some acceptors are presented, shows that in most cases the shift of the absorption band of the associated NH group of the diindolyl is somewhat smaller than in the case of indole. Consequently, diindolyl VIII has somewhat less pronounced donor properties than indole in the formation of complexes by means of hydrogen bonds.

The fluorescence spectrum of diindolyl VIII is much more structured than the spectrum of indole and is shifted considerably to the long-wave region (360, 363, 372, 387, 402, as compared with 320 nm for indole), and the intensity of the spectrum of diindolyl VIII is considerably lower than in the case of indole.

EXPERIMENTAL

Monitoring of the reactions and the purity of the compounds and the determination of the R_f values were accomplished by thin-layer chromatography (TLC) on Silufol UV-254. Neutral Al_2O_3 (activity II on the Brockmann scale) and silica gel (particle size 100–250 nm) were used as sorbents for preparative column chromatography. The IR spectra were recorded with a UR-20 spectrometer. The UV spectra of ethanol solutions of the compounds were recorded with a Specord spectrophotometer. The PMR spectra were recorded with a JNM-MH-100 spectrometer with hexamethyldisiloxane as the internal standard. The mass spectra were recorded with an MKh-1303 spectrometer with a modified system for the introduction of the samples (direct introduction of the samples into the ion source) at an ionizing-electron energy of 50 eV. The luminescence spectra were obtained at 77°K with an SDL-1 luminescence spectro-

photometer with monochromatic excitation (λ 254 nm) and with a photoelectric apparatus with a spark phosphoroscope (with W-Fe electrodes).

2-Carbethoxy-3-(p-nitrophenyl)indole (II). This compound, with mp 218-219°C, was obtained by the method in [7].

2-Carbethoxy-3-(p-aminophenyl)indole (III). A 2-4-g sample of Raney nickel was added to a suspension of 31 g (100 mmole) of ester II in 0.9 liter of isopropyl alcohol, the mixture was heated to the boiling point, and 62 ml of hydrazine hydrate was added dropwise in the course of 3 h. The mixture was refluxed with stirring for 1 h, after which the hot solution was filtered, and the filtrate was cooled. The precipitated crystals were removed by filtration and dried to give 24.5 g (85%) of a product with mp 163.5-164.5°C (from alcohol). IR spectrum (in mineral oil): 3200 (broad band); 3340 and 3405 (NH); 1695 cm^{-1} (C=O). UV spectrum, λ_{max} (log ϵ): 204 (4.07), 243 (4.10), and 308 nm (3.82). Found: C 72.3; H 5.8; N 9.9%. $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2$. Calculated: C 72.8; H 5.7; N 10.0%.

Ethyl Pyruvate 4-(2-Carbethoxy-3-indolyl)phenylhydrazone (V). A) solution of 1.45 g (20 mmole) of NaNO_2 in 7 ml of water was added dropwise in the course of 15 min at 0-2°C to a mixture of 6.3 g (20 mmole) of the hydrochloride of III, 200 ml of water, and 6 ml of concentrated HCl, and the mixture was maintained at this temperature for 30 min. A solution of 13 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 35 ml of concentrated HCl was then added in the course of 45 min at such a rate that the temperature did not exceed 0°C. The mixture was maintained at this temperature for 2 h, after which the temperature was gradually raised to room temperature. The precipitate was removed by filtration and washed with a cold saturated aqueous solution of NaCl until the wash solution was neutral. The damp precipitate was squeezed thoroughly and dried in the funnel for 1 h. The crystals were placed in a three-necked flask, 15 ml of ethanol was added, and the stirred mixture was heated at 60°C and treated dropwise with 2.4 g (20 mmole) of ethyl pyruvate. Hydrazine IV dissolved, and after a few minutes a yellow precipitate formed. The reaction mixture was heated at the same temperature for 20 min, after which it was cooled and poured into water. The resulting precipitate was removed by filtration, washed with hot water, and dried to give 5.8 g (74%) of product. To separate the stereoisomers, 0.4 g of hydrazone V was dissolved in 15 ml of chloroform, and the solution was passed through a column filled with silica gel [elution with CCl_4 -ether (1:1)]. The first fraction contained syn isomer Va. Removal of the solvent gave 0.13 g (39%) of isomer Va with mp 142-143°C. IR spectrum (in mineral oil): 3335 (NH) and 1680 cm^{-1} (C=O). UV spectrum, λ_{max} (log ϵ): 210 (4.31), 241 (4.42), 303 (4.22), and 366 nm (4.37). Found: C 67.6; H 6.2; N 10.2%. $\text{C}_{22}\text{H}_{23}\text{N}_3\text{O}_4$. Calculated: C 67.2; H 5.8; N 10.7%. The second fraction contained anti isomer Vb. Removal of the solvent by distillation gave 0.2 g (61%) of isomer Vb with mp 176-176.5°C. IR spectrum (in mineral oil): 3290 (NH); 1710 and 1685 cm^{-1} (C=O). UV spectrum λ_{max} (log ϵ): 210 (4.38), 241 (4.45), 301 (4.35), and 354 (4.41). Found N 10.2%. Calculated N 10.7%.

B) Preparation by the Japp-Klingemann Reaction. A solution of 1.45 g (20 mmole) of NaNO_2 in 7 ml of water was added with stirring to a cooled (to 0-2°C) mixture of 6.3 g (20 mmole) of the hydrochloride of III in 200 ml of water and 6 ml of concentrated HCl, during which the temperature was maintained at 0-2°C. At the end of the diazotization, a solution of 3.1 g of sodium acetate trihydrate was added to the mixture; a solution of 2.9 g (20 mmole) of methyl acetoacetate in 10 ml of methanol, to which a solution of 1.45 g (20 mmole) of KOH in 50 ml of methanol was added with stirring and cooling prior to coupling, was then added rapidly to the cooled (to 2°C) mixture. The pH must be maintained strictly at five. The mixture was stirred at 2°C for 3 h, after which it was extracted with chloroform. The solvent was removed from the extract by distillation to give hydrazone V in quantitative yield. The separation of the hydrazone into its isomers is described in method A. Separation of 0.5 g of the mixture of isomers gave 0.29 g (69%) of syn isomer Va and 0.13 g (31%) of anti isomer Vb.

2,2'-Dicarbethoxy-3,5'-diindolyl (VI). A) A suspension of 3.7 g (9.2 mmole) of hydrazone V in 20 ml of absolute ethanol was saturated with dry hydrogen chloride in the course of 3 h at 20°C, after which the mixture was allowed to stand at room temperature for 12 h. It was then poured into water, and the precipitate was removed by filtration, washed to neutrality with water, dried, and dissolved in 15 ml of chloroform. The chloroform solution was passed through a column filled with silica gel [elution with CCl_4 -ether (1:1)]. The solvent was removed from the eluate by evaporation to give 1.24 g (35%) of VI with mp 203-204°C (from alcohol). IR spectrum (in mineral oil): 3310 and 3360 (NH); 1685 and 1695 cm^{-1} (C=O). UV spectrum, λ_{max} (log ϵ): 210 (4.38), 232 (4.57), and 300 nm (4.45). Found: C 70.1; H 5.5; N 7.3%. $\text{C}_{22}\text{H}_{20}\text{N}_2\text{O}_4$. Calculated: C 70.2; H 5.3; N 7.5%.

B) A 1-g (2.5 mmole) sample of hydrazone V was added to 10 g of polyphosphoric acid ester, and the mixture was heated at 70°C for 15 min with constant stirring. It was then cooled and poured into cold water, and the precipitate was separated, washed with water, dried, and dissolved in 10 ml of chloroform. Workup as indicated above gave 0.31 g (36%) of diindolyl VI.

2,2'-Dicarboxy-3,5'-diindolyl (VII). A suspension of 0.38 g (1.2 mmole) of VI in 150 ml of 10% aqueous KOH solution was refluxed with stirring for 5 h, after which it was cooled and filtered, and the filtrate was acidified with 10% HCl solution. The precipitate was extracted with ethyl acetate, and the extract was dried over MgSO₄ and filtered. The solvent was removed from the filtrate by distillation to give 0.3 g (95%) of a product with mp 218-220°C (dec.). IR spectrum (in mineral oil): 3460, 3360 (NH); 1700, 1680 cm⁻¹ (C=O). UV spectrum, λ_{max} (log ε): 208 (4.49), 233 (4.47), and 296 nm (4.25). Found: C 67.7; H 4.5; N 8.1%. C₁₈H₁₂N₂O₄. Calculated C 67.5; H 3.7; N 8.7%.

3,5'-Diindolyl (VIII). A 0.8-g (3.4 mmole) sample of VII was heated rapidly to 250-260°C in a stream of argon for 5 min, after which it was cooled and dissolved in chloroform. The chloroform solution was passed through a column filled with Al₂O₃ (elution with ether) to give 0.25 g (43%) of diindolyl VIII with mp 178-179°C (from ether-pentane). IR spectrum (in mineral oil): 3410 cm⁻¹ (NH). UV spectrum, λ_{max} (log ε): 217 (4.75), 231 (4.76), and 254 nm (4.68). Found: C 82.7; H 5.5; N 12.2%. C₁₆H₁₂N₂. Calculated: C 82.8; H 5.2; N 12.1%.

Pyruvic Acid 4,4'-Biphenyldihydrazone (IX). This compound, with mp 196-197°C (dec.) (mp 197-198°C [6]), was obtained by the method in [6] from 4,4'-biphenyldihydrazine dihydrochloride.

Ethyl Pyruvate 4,4'-Biphenyldihydrazone (X). A hot solution of 2.87 g (10 mmole) of 4,4'-biphenyldihydrazine dihydrochloride in 200 ml of water was added in a fine stream with stirring to a solution of 3.48 g (30 mmole) of freshly distilled ethyl pyruvate in 20 ml of ethanol, and the mixture was stirred for 2 h. The yellow-green precipitate was removed by filtration, washed repeatedly with hot water, and dried in a vacuum desiccator over P₂O₅ to give 2.54 g (62%) of product with mp 203-204°C (dec., from alcohol). IR spectrum (in mineral oil): 3300, 3330 (NH); 1720, 1680 cm⁻¹ (C=O). UV spectrum, λ_{max}: 206 and 360 nm. Found: C 64.8; H 6.0; N 13.2%. C₂₂H₂₆N₄O₄. Calculated: C 64.4; H 6.3; N 13.6%.

2,2'-Dicarbethoxy-5,5'-diindolyl (XI). A total of 70 ml of a solution of H₂SO₄ in ethanol (volume ratio 1:3) was added to 6.15 g (15 mmole) of dihydrazone X in a three-necked flask equipped with a stirrer and a reflux condenser, and the suspension was heated with stirring to 75-80°C. The yellow suspension was converted to a light-brown suspension, which turned dark brown as 75°C was reached, after which a solution formed. The mixture was stirred at this temperature for another 30 min, after which it was poured into 0.7 liter of water. The precipitate was removed by filtration, washed to neutrality with water, and dried in a vacuum desiccator over concentrated H₂SO₄. The same compound can be obtained under similar conditions for dihydrazone IX. Compound XI was purified with a column filled with Al₂O₃ (elution with ether). A product with mp 233°C (from ethanol) and R_f 0.66 [acetone-benzene (1:5)] was obtained in 5-6% yield. IR spectrum (in chloroform): 3475 (NH) and 1710 cm⁻¹ (C=O). UV spectrum, λ_{max} (log ε): 225 (4.45) shoulder, 265 (4.7), and 305 nm (4.6). Found: C 70.0; H 5.6; N 7.4%. C₂₂H₂₀N₂O₄. Calculated: C 70.2; H 5.3; N 7.4%.

2,2'-Dicarboxy-5,5'-diindolyl (XII). A 0.5-g (1.4 mmole) sample of XI was suspended in 500 ml of 10% aqueous KOH solution, and the suspension was refluxed with stirring for 3 h. The resulting solution was cooled and filtered, and the filtrate was acidified with 10% HCl. The precipitate was removed by filtration, washed with water, and dried in a vacuum desiccator over concentrated H₂SO₄ to give 0.35 g (82%) of a product with mp 276-278°C (dec.). IR spectrum (in mineral oil): 3370 (NH) and 1715 cm⁻¹ (C=O). Found: C 66.9; H 4.4; N 8.4%. C₁₈H₁₂N₂O₄. Calculated: C 67.5; H 3.8; N 8.7%.

5,5'-Diindolyl (XIII). A 0.5-g (1.7 mmole) sample of XII was heated to 280-290°C in a stream of argon until CO₂ evolution ceased, after which the material was cooled and purified with a column filled with Al₂O₃ [elution with hexane-ether (1:2)] to give 0.11 g (30%) of a product with mp 200-202°C (from hexane) and R_f 0.23 (benzene). IR spectrum (in chloroform): 3490 cm⁻¹ (NH). UV spectrum, λ_{max} (log ε): 215 (4.41), 249 (4.72), and 301 nm (3.92) shoulder. Found: C 82.4; H 5.4; N 11.7%. C₁₆H₁₂N₂. Calculated: C 82.8; H 5.2; N 12.1%.

5-Phenyl-2-carbomethoxyindole (XIV). A side product in the synthesis of 2,2'-dicarbomethoxy-5,5'-diindolyl (XI) was XIV, which was isolated with a column filled with Al_2O_3 [elution with hexane-ether (1:1)] in 5-6% yield and had R_f 0.8 [acetone-benzene (1:5)] and mp 174.5-175°C. IR spectrum (in chloroform): 3475 (NH) and 1715 cm^{-1} (C=O). UV spectrum, λ_{max} (log ϵ): 205 (4.38), 261 (4.59), and 301 nm (4.17). Found: C 77.2; H 5.7; N 5.4%. $\text{C}_{17}\text{H}_{15}\text{NO}_2$. Calculated: C 77.0; H 5.7; N 5.3%.

5-Phenyl-2-carbomethoxyindole (XV). When a solution of H_2SO_4 in methanol was used as the cyclizing agent, XV was obtained along with the products of cyclization and transesterification of dihydrazone X. The reaction conditions were the same as in the case of XIV. Compound XV was purified with a column filled with Al_2O_3 [elution with hexane-ether (1:1)] to give the product, with R_f 0.8 [acetone-benzene (1:5)] and mp 156-157°C (from petroleum ether), in 4-5% yield. IR spectrum (in chloroform): 3470 (NH) and 1715 cm^{-1} (C=O). UV spectrum, λ_{max} (log ϵ): 206 (4.42), 261 (4.63), and 301 nm (4.22) shoulder. Found: C 77.2; H 5.6; N 5.6%. $\text{C}_{16}\text{H}_{13}\text{NO}_2$. Calculated: C 76.5; H 5.2; N 5.6%.

5-Phenyl-2-carboxyindole (XVI). A suspension of 0.8 g (3 mmole) of XIV in 200 ml of 10% aqueous KOH solution was refluxed with stirring for 3 h, and the resulting solution was then cooled and filtered. The filtrate was acidified with 10% HCl, and the precipitate was removed by filtration, washed with water, and dried in a vacuum desiccator over concentrated H_2SO_4 to give 0.58 g (80%) of a product with mp 245-246°C (dec.). IR spectrum (in mineral oil): 3330, 3380 (NH); 1715 and shoulder at 1675 cm^{-1} (C=O). UV spectrum, λ_{max} (log ϵ): 206 (4.40), 261 (4.61), and 300 nm (4.06) shoulder. Found: N 5.8%. $\text{C}_{15}\text{H}_{11}\text{NO}_2$. Calculated: N 5.9%.

5-Phenylindole (XVII). A 0.5-g (2 mmole) sample of XVI was decarboxylated at 250-255°C by the method described above to give 0.2 g (50%) of product. The product was purified with a column filled with silica gel (elution with benzene) and had mp 69-70°C (from hexane) and R_f 0.63 (benzene). IR spectrum (in chloroform): 3490 cm^{-1} (NH). UV spectrum, λ_{max} (log ϵ): 207 (4.39), 252 (4.56), and 2.83 nm (3.97) shoulder. Found: M^+ 193 (by mass spectrometry). Calculated: M^+ 193. Found: C 87.4; H 5.8; N 7.2%. $\text{C}_{14}\text{H}_{11}\text{N}$. Calculated: C 87.1; H 5.7; N 7.3%.

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