

Regioselective Proton-Catalyzed Diarylmethylation of Indoles with 9*H*-Xanthyrol, Dibenzosuberanol, and Bis[4-dimethylaminophenyl]methanol

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Received February 1, 1988

3-Isopropylindole (**4**) is xanthenylated both at N-1 (stereocontrolled major reaction), C-2, and on the phenyl nucleus of the indole skeleton by xanthyrol (**1**). Other carbinols such as dibenzosuberanol (**2**) and bis[4-dimethylaminophenyl]methanol (**3**) with lower electrophilic S_N1 activities than **1** do not react with **4** but do react very selectively with simple methylindoles to form diarylmethylated derivatives.

J. Heterocyclic Chem., **25**, 1199 (1988).

Introduction.

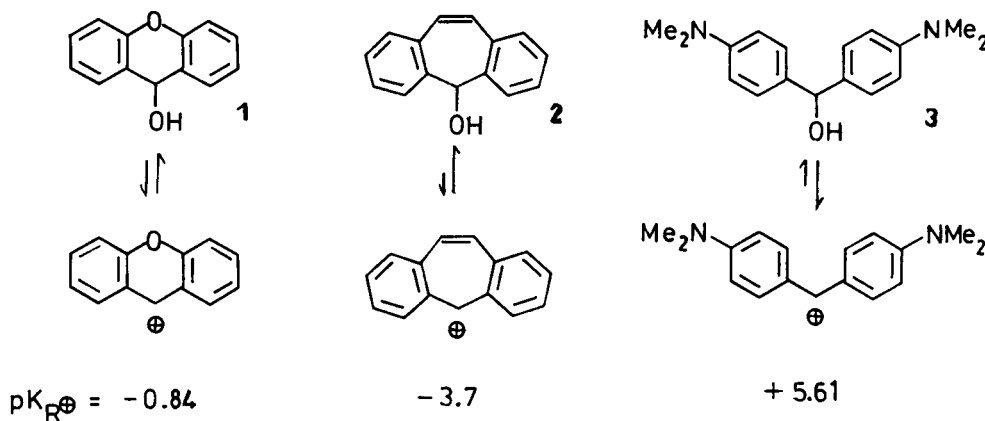
We have previously reported on the first xanthenylations of some selected methylindoles [1] and physiologically active derivatives [2]. By means of specific control of the reaction conditions and under proton catalysis, novel xanthenylindoles were obtained using 9-hydroxy-9*H*-xanthene (xanthyrol, **1**) and, on the basis of the synthetic results, it was possible to determine order of the nucleophilicities of the individual indole atoms [1]. In continuation of these investigations, we now report on the first xanthenylation reactions of 3-isopropylindole (**4**) in order to ascertain, for example, the influence of steric effects on the product distribution. In addition, we describe the first diarylmethylations of methylindoles by the carbinols 5-hydroxy-5*H*-dibenzo[*a,d*]cycloheptene (dibenzosuberanol, **2**) and bis[4-dimethylaminophenyl]methanol (Michler's hydrol, **3**) which are electronically related to 9-hydroxy-9*H*-xanthene (**1**).

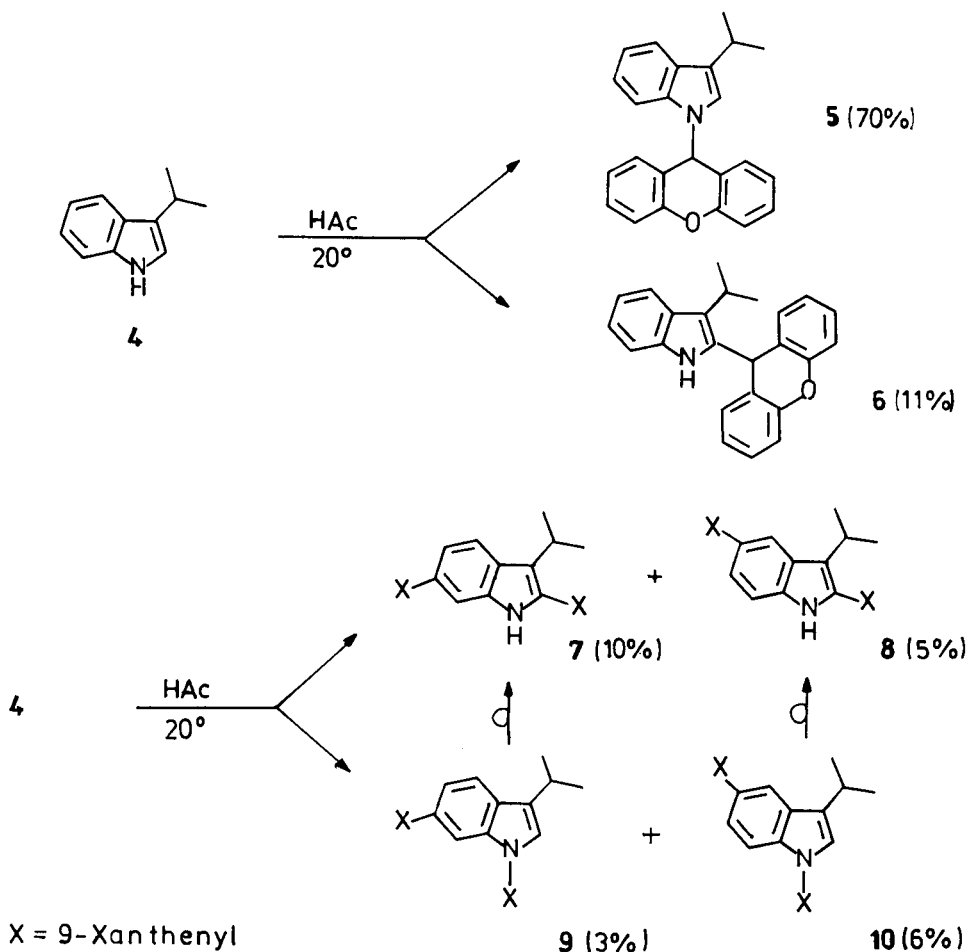
In the presence of Lewis or proton acids, these S_N1 active alcohols **1-3** form thermodynamically stable, highly resonance-stabilized cations of the diarylcarbenium ion type. On the basis of the experimentally determined pK_{R^+} values [3-5], the thermodynamic stability of the cations formed from the carbinols **1-3** increases in the (carbinol) order **2** < **1** < **3**. As illustrated by the following re-

actions, the cations generated *in situ* from **1-3** by a proton acid still possess a sufficiently high electrophilic potential towards the tested indoles [1]. However, the unfavorable equilibrium position of the heterolysis of **2** and the extremely high thermodynamic stability of the diarylcarbenium ion derived from **3** are assumed to be responsible for fact that the S_N1 reactivities of **2** and **3** are somewhat less than that of 9-hydroxy-9*H*-xanthene (**1**).

Results and Discussion.

3-Isopropylindole (**4**) reacts with **1** in completely anhydrous glacial acetic acid to give substitution products analogous to those previously isolated for the first time by us from the reaction of 3-methylindole (**13**) with **1** [1]. The novel xanthenylindoles **5** and **6** were obtained from the 1:1 molar reaction of **4** with **1**. In contrast to the reaction of 3-methylindole, the *N*-substitution product **5** (70% yield) is the major product as a result of steric effects (in the xanthenylation of 3-methylindole, the *N*-substitution product is formed in only 10% yield) [6]. In a 1:2 molar reaction of **4** with **1**, four products **7-10** are formed (400 MHz ¹H-nmr spectroscopic analysis of the crude product mixture). Of these reaction products, only the sufficiently stable compounds **7**, **8**, and **10** could be isolated in the pure state.



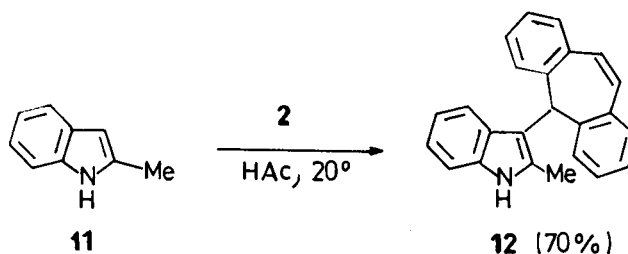


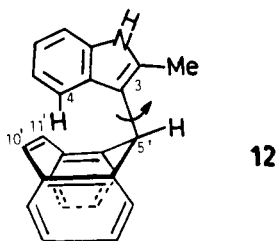
Products **9** and **10** undergo rapid intermolecular rearrangement on contact with acid or silica gel (cross-coupling experiment, see also ref [1]) to furnish the thermodynamically more stable *C*-xanthenylindoles **7** and **8**.

In an analogous manner, compound **5**, for example, can be induced to rearrange practically quantitatively to **6** in methanolic hydrochloric acid.

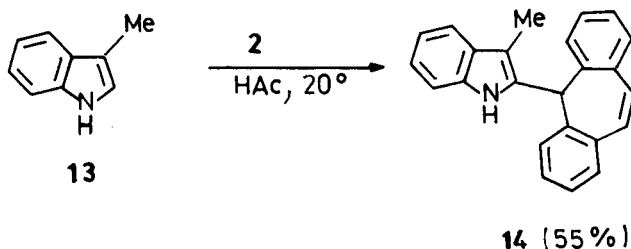
On reaction with the diarylcarbinols **2** and **3**, 3-isopropylindole (**4**) did not produce any stable and characterizable diarylmethylated indoles. Thus, we concentrated our attention on the more successful reactions with 2-methylindole (**11**), 3-methylindole (**13**), and 2,3-dimethylindole (**15**). Monitoring of the time course of the reactions of the carbinols **2** and **3** with 2-methylindole (**11**) (quantitative tlc remission measurements on silica gel plates) showed a markedly lower electrophilic reactivity in comparison to the reaction with 9-hydroxy-9*H*-xanthene (**1**). It is assumed that, in the case of **2**, the equilibrium concentration of the cation in the glacial acetic acid reaction mixture is too low and, in the case of **3**, that the high thermodynamic stability of the cation generated from **3** (ground state effect) are responsible for these observations.

2-Methylindole (**11**) reacts with **2** both in a 1:1 and a 1:2 molar ratio to give exclusively the 3-diarylmethylated indole **12**. It is apparent from the 400 MHz ¹H-nmr spectroscopic analysis that the indole hydrogen atom H-4 in **12** has an unusually large diamagnetic shift ($\delta = 6.34$ ppm in (deuteriochloroform, broad signal). Observations of molecular models indicate that a, with respect to the nmr time scale, slowed down rotation about the C-3/C-5' σ -bond is responsible for this. As a result of the sterically preferred pseudo-boat conformation of the seven-membered carbocyclic ring, both the indole H-4 and the indole 2-methyl group are localized on time averaging in the deshielding region of the C-10'/C-11' double bond of the central seven-membered ring.



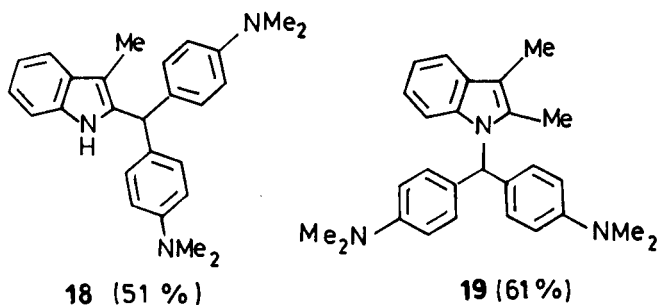
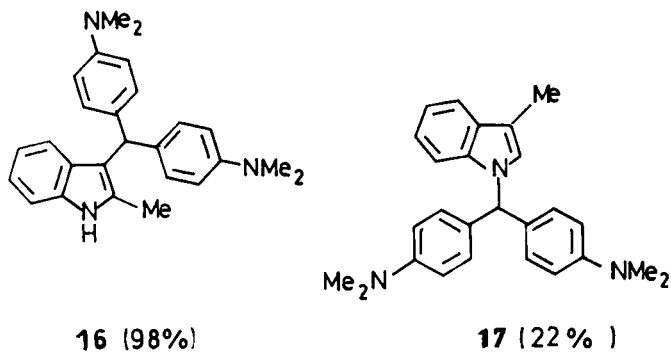


3-Methylindole (**13**) also reacts with **2** to form exclusively a stable 2-dibenzocycloheptenylindole **14**. No *N*-dibenzocycloheptenylindoles were detected in the above-mentioned reactions of **11** and **13**. The acidity of the reaction medium is apparently sufficient to convert any possibly formed *N*-substitution products back into the starting materials.



Since compound **2**, in general, exhibits a lower electrophilicity than **1** and since potential *N*-substitution products with dibenzocycloheptenyl moieties possess insufficient life-times, it is understandable that the reaction of 2,3-dimethylindole (**15**) with **2** does not produce any diarylmethylated products (tlc monitoring).

The electrophilic substitution with bis[4-dimethylaminophenyl]methanol (**3**) was tested using compounds **11**, **13** and 2,3-dimethylindole (**15**) as examples. Since compound **3** also has a lower electrophilicity in comparison to 9-hydroxy-9*H*-xanthene (**1**), diarylmethylation reactions can only take place at the reactive enamine subunits of the indoles. In anhydrous glacial acetic acid at 20°, both 1:1 and 1:2 molar reactions of **11** produce the diarylindolylmethane **16** regiospecifically, reaction of 3-methylindole (**13**) gives the regioisomeric "leuco bases" **17** and **18**, and 2,3-dimethylindole (**15**) reacts to furnish the *N*-substitution product **19** regiospecifically.



The constitutions of all of the new indole derivatives described above were confirmed by 400 MHz ¹H-nmr spectroscopy (selective decoupling, ¹H{¹H}-nOe difference measurements) and, in some cases, also by ¹³C-nmr spectroscopy. The *N*-diarylmethylated indoles gave very low intensity (<5%) molecular ion peaks in the electron impact mass spectra at 70 eV, thus demonstrating, together with the fragmentation patterns, the lability of the $\text{N-CH}(\text{AR})_2$ σ -bond.

EXPERIMENTAL

The ¹H- and ¹³C-nuclear magnetic resonance (nmr) spectra were recorded on a Bruker WL 400 spectrometer at 400 and 100.6 MHz, respectively (δ scale in ppm). The mass spectra (ms) were obtained using an LKB Producter LKB 2091 spectrometer at 70 eV. Elemental analyses (C,H,N) were performed on a Carlo Erba Strumentazione Model 1106 apparatus, melting points were determined using a Reichert Kofler hot stage microscope and are not corrected. Silica gel 60 (Merck, particle size 0.063-0.200 mm) was used for column chromatography.

General Procedure for the Preparation of the Monoxanthenylindoles **5** and **6**.

3-Isopropylindole (**4**) (10 mmoles) and 9-hydroxy-9*H*-xanthene (**1**) (2.0 g, 10 mmoles) were separately dissolved in small amounts of completely anhydrous glacial acetic acid. The two solutions were combined and the resultant mixture stirred at 20° for 2 hours.

3-Isopropyl-1-(9*H*-xanthen-9-yl)indole (**5**).

The crystals that separated after a reaction time of 2 hours were separated, yield 2.40 g (70%), colorless crystals, mp 151° (methanol); ¹H-nmr (deuteriochloroform): δ = 1.29 (d, 6H, isopropyl-CH₃, ³J = 6.9 Hz), 3.16 (dsept, 1H, isopropyl-CH, ³J = 6.9 Hz, ⁴J = 0.6 Hz), 6.71 (s, 1H, xanthenyl-CH), indole H, 6.79 (d, 1H, C2-H, ⁴J = 0.6 Hz), 7.05-7.13 (m, 2H, C5-H, C6-H), 7.19-7.25 (m, 1H, C7-H), 7.61-7.68 (m, 1H, C4-H), xanthenyl Ar-H, 6.91 (mt, 2H, H2', H7', ³J = 6.7 Hz, ³J = 7.8 Hz, ⁴J = 1.2 Hz), 6.95 (dd, 2H, H1', H8', ³J = 7.8 Hz, ⁴J = 2.0 Hz), 7.16 (dd, 2H, H4', H5', ³J = 8.1 Hz, ⁴J = 1.2 Hz), 7.28 (mt, 2H, H3', H6', ³J = 6.7 Hz, ³J = 8.1 Hz, ⁴J = 2.0 Hz, ⁴J = 0.5 Hz); ¹³C-nmr (deuteriochloroform): δ = 23.3 (isopropyl-CH₃), 25.5 (isopropyl-CH), 51.0 (xanthenyl-CH), indole C, 109.7, 118.9, 119.7, 121.6, 122.5, 124.1 (q), 127.7 (q), 136.9 (q) [(q) = quaternary indolic sp² carbon atom], xanthenyl Ar-C, 116.7 (C4', C5'), 120.5 (C1a', C8a'), 123.6 (C2', C7'), 128.4 (C1', C8' or C3', C6'), 129.3 (C3', C6' or C1', C8'), 150.8 (C4a', C5a'); ms: (70 eV, electron impact) m/e 339 (M⁺, 3%), 181 (100%).

Anal. Calcd. for C₂₂H₂₁NO (339.44): C, 84.92; H, 6.24; N, 4.13. Found: C, 85.02; H, 6.17; N, 4.05.

3-Isopropyl-2-(9*H*-xanthen-9-yl)indole (**6**).

The acetic acid reaction solution remaining after separation of **5** was poured into ice/water and carefully made alkaline by addition of 10% aqueous ammonia solution. The mixture was extracted with dichloro-

methane, the organic phase was separated, dried, concentrated, and the residue subjected to column chromatographic purification over silica gel 60 using petroleum ether (bp 40-60°/toluene (2:1) as eluent, yield 376 mg (11%), colorless crystals, mp 208-211° dec (diisopropyl ether/*n*-hexane); ¹H-nmr (deuteriochloroform): δ = 1.57 (d, 6H, isopropyl-CH₃, ³J = 7.1 Hz), 3.43 (sept, 1H, isopropyl-CH, ³J = 7.1 Hz), 5.65 (s, 1H, xanthenyl-CH), 7.37 (s, 1H, NH), indole H, 7.00-7.07 (m, 3H, C5-H, C6-H, C7-H), 7.75-7.81 (m, 1H, C4-H), xanthenyl Ar-H, 6.90 (mt, 2H, H2', H7', ³J = 6.7 Hz, ³J = 7.7 Hz, ⁴J = 1.2 Hz), 6.94 (dd, 2H, H1', H8', ³J = 7.7 Hz, ⁴J = 2.2 Hz), 7.10 (dd, 2H, H4', H5', ³J = 7.9 Hz, ⁴J = 1.2 Hz), 7.17 (mt, 2H, H3', H6', ³J = 6.7 Hz, ³J = 7.9 Hz, ⁴J = 2.2 Hz, ⁴J = 0.6 Hz); ¹³C-nmr (deuteriochloroform): δ = 23.6 (isopropyl-CH₃), 26.2 (isopropyl-CH), 35.0 (xanthenyl-CH), indole C, 111.0, 118.9, 120.4, 120.5 (q), 121.6, 126.5 (q), 134.7 (q), 136.6 (q) [(q) = quaternary indolic sp² carbon atom], xanthenyl Ar-C, 116.6 (C4', C5'), 122.3 (Cl', C8a'), 123.5 (2', C7'), 128.5 (Cl', C8' or C3', C6'), 129.5 (C3', C6' or Cl', C8'), 151.3 (C4a', C5a'); ms: (70 eV, electron impact) m/e 339 (M⁺, 52%), 324 (100%).

Anal. Calcd. for C₂₄H₂₁NO (339.44): C, 84.92; H, 6.24; N, 4.13. Found: C, 85.18; H, 6.34; N, 4.02.

Regiospecific Preparation of **6**.

A mixture of 0.9 g (5.65 mmoles) of **4** and 1.12 g (5.65 mmoles) of **1** in methanolic hydrochloric acid (45 ml of methanol and 13 ml of 36% hydrochloric acid) was stirred at 20° for 50 minutes. The resultant precipitate was separated, washed with water, dried and recrystallized, yield 1.82 g (95%).

General Procedure for the Preparation of Dixanthenylindoles **7**, **8** and **10**.

3-Isopropylindole (**4**) (3.8 mmoles) and 9-hydroxy-9H-xanthen (**1**) (1.5 g, 7.6 mmoles) were separately dissolved in small amounts of completely anhydrous glacial acetic acid. The two solutions were combined and the resultant mixture stirred at 20° for 3 hours. The precipitate formed (compound **5**) was filtered off, the filtrate was poured into ice/water and the mixture carefully made alkaline by addition of 10% aqueous ammonia solution. The resultant solution was extracted with diethyl ether, the organic phase was washed until free of alkali, dried with sodium sulfate, concentrated on a rotary evaporator and the residue was purified by column chromatography on silica gel 60 using petroleum ether (bp 40-60°/toluene (2:1) as eluent.

3-Isopropyl-2,6-bis[9H-xanthen-9-yl]indole (**7**).

This compound was obtained as colorless crystals, yield 206 mg (10%), mp 340° (chloroform/methanol); ¹H-nmr (deuteriochloroform): δ = 1.54 (d, 6H, isopropyl-CH₃, ³J = 7.1 Hz), 3.43 (sept, 1H, isopropyl-CH, ³J = 7.1 Hz), 5.26 (s, 1H, xanthenyl-CH at C6), 5.63 (s, 1H, xanthenyl-CH at C2), 6.83 (d, 1H indole C7-H, ⁴J = 1.5 Hz), 6.91-6.99 (m, 6H, xanthenyl Ar-H), 7.01 (dd, 1H, indole C5-H, ³J = 8.5 Hz, ⁴J = 1.5 Hz), 7.06-7.23 (m, 10H, xanthenyl Ar-H), 7.31 (s, 1H, NH), 7.65 (d, 1H, indole C4-H, ³J = 8.5 Hz); ms: (70 eV, electron impact) m/e 519 (M⁺, 45%), 181 (100%).

Anal. Calcd. for C₃₇H₂₉NO₂ (519.64): C, 85.52; H, 5.62; N, 2.70. Found: C, 85.47; H, 5.64; N, 2.63.

3-Isopropyl-2,5-bis[9H-xanthen-9-yl]indole (**8**).

This compound was obtained as colorless crystals, yield 92 mg (5%), mp 330° (chloroform/methanol); ¹H-nmr (deuteriochloroform): δ = 1.57 (d, 6H, isopropyl-CH₃, ³J = 7.0 Hz), 3.46 (sept, 1H, isopropyl-CH, ³J = 7.0 Hz), 5.33 (s, 1H, xanthenyl-CH at C5), 5.67 (s, 1H, xanthenyl-CH at C2), 6.81 (dd, 1H indole C6-H, ³J = 8.4 Hz, ⁴J = 1.6 Hz), 6.93-7.01 (m, 6H, xanthenyl Ar-H), 7.07 (d, 1H, indole C7-H, ³J = 8.4 Hz), 7.10-7.25 (m, 10H, xanthenyl Ar-H), 7.35 (s, 1H, NH), 7.67 (d, 1H, indole C4-H, ⁴J = 1.6 Hz); ms: (70 eV, electron impact) m/e 519 (M⁺, 39%), 181 (100%).

Anal. Calcd. for C₃₇H₂₉NO₂ (519.64): C, 85.52; H, 5.62; N, 2.70. Found: C, 85.41; H, 5.66; N, 2.52.

3-Isopropyl-1,5-bis[9H-xanthenyl]indole (**10**).

This compound was obtained in 6% yield (100 mg), mp 220° dec (petroleum ether (bp 40-60°/toluene); ms: (70 eV, electron impact) m/e

519 (M⁺, 2%), 181 (100%).

Anal. Calcd. for C₃₇H₂₉NO₂ (519.64): C, 85.52; H, 5.62; N, 2.70. Found: C, 85.23; H, 5.45; N, 2.52.

2-Methyl-3-(5H-dibenzo[a,d]cyclohepten-5-yl) indole (**12**).

2-Methylindole (**11**) (1.0 g, 7.62 mmoles) and dibenzosuberone (**2**) (1.6 g, 7.68 mmoles) in 30 ml of glacial acetic acid were stirred at 20° for 2 hours. The precipitate formed was filtered off, washed with a small amount of glacial acetic acid, and recrystallized from methanol, yield 1.72 g (70%), colorless crystals, mp 194° (methanol); ¹H-nmr (deuteriochloroform): δ = 1.55 (s, broadened, 3H, CH₃), 5.44 (s, 1H, methine-H), 7.40 (s, 1H, NH), indole H, 6.34 (d, broadened, 1H, C4-H), 6.74 (dt, broadened, 1H, C5-H, ³J = 7.5 Hz, ⁴J = 1.1 Hz), 6.95 (dt, 1H, C6-H, ³J = 7.5 Hz, ⁴J = 1.1 Hz), 7.07 (md, 1H, C7-H, ³J = 8.1 Hz, ⁴J = 1.1 Hz, ⁴J = 0.8 Hz), arylmethyl Ar-H, 6.79 (s, 2H, H10', H11'), 7.24 (dt, 2H, H2', H8' or H3', H7', ³J = 7.6 Hz, ⁴J = 1.2 Hz), 7.28 (dd, 2H, H1' or H4', H6', ³J = 7.9 Hz, ⁴J = 1.8 Hz), 7.32 (dt, 2H, H3', H7' or H2', H8', ³J = 7.6 Hz, ⁴J = 1.8 Hz), 7.59 (dd, 2H, H4', H6' or H1', ³J = 8.0 Hz, ⁴J = 1.2 Hz) [As a result of an intermolecular dynamic process, signal broadening occurs (indole-CH₃, indole C4-H, indole C5-H)]; ms: (70 eV, electron impact) m/e 321 (M⁺, 100%), 306 (44%), 304 (23%), 160.5 (M⁺, 13%).

Anal. Calcd. for C₂₄H₁₉N (321.42): C, 89.68; H, 5.96; N, 4.36. Found: C, 89.75; H, 5.88; N, 4.18.

3-Methyl-2-(5H-dibenzo[a,d]cyclohepten-5-yl)indole (**14**).

Prepared as described above for product **12** but with a reaction time of 4 hours at 20°, yield 1.35 g (55%), colorless crystals, mp 198-199° (methanol); ¹H-nmr (deuteriochloroform): δ = 1.67 (s, 3H, CH₃), 5.56 (s, 1H, methine-H), 6.77 (s, 2H, dibenzocycloheptenyl H10', H11'), 6.94-7.05 (m, 3H, 3 indole Ar-H), 7.21 (s, 1H, NH), 7.25-7.39 (m, 7H, 6 dibenzocycloheptenyl Ar-H + 1 indole Ar-H), 7.47 (dd, 2H, dibenzocycloheptenyl H1', H9' or H4', H6', ³J = 7.6 Hz, ⁴J = 1.0 Hz); ms: (70 eV, electron impact) m/e 321 (M⁺, 98%), 178 (100%), 160.5 (M⁺, 15%).

Anal. Calcd. for C₂₄H₁₉N (321.42): C, 89.68; H, 5.96; N, 4.36. Found: C, 89.88; H, 6.03; N, 4.10.

General Procedure for the Preparation of the Diarylindolylmethanes **16**, **17**, **18** and **19**.

The indole **11**, **13**, or **15** (7.4 mmoles) and bis[4-dimethylaminophenyl]methanol (Michler's hydrol, **3**) (2.0 g, 7.4 mmoles) were dissolved in 50 ml of glacial acetic acid and the mixture stirred at 20° for 0.5 hour for **11**, or about 24-30 hours for **13** and **15**. The resultant mixtures were then poured into ice/water, carefully made alkaline by addition of 10% aqueous ammonia solution, and extracted with dichloromethane. The organic phases were washed with water until free of alkali, dried with sodium sulfate, concentrated, and the residues purified by recrystallization or column chromatography.

Bis[4-dimethylaminophenyl][2-methylindol-3-yl]methane (**16**).

This compound was obtained in 98% yield (2.78 g) as crystals having a violet coloration on their surfaces (air oxidation), mp 210° (*n*-hexane, dichloromethane); ¹H-nmr (deuteriochloroform): δ = 2.09 (s, 3H, CH₃), 2.87 (s, 12H, NCH₃), 5.55 (s, 1H, methine-H), 7.64 (s, 1H, NH), indole H, 6.86 (mt, 1H, C5-H, or C6-H, ³J = 8.0 Hz, ³J = 7.0 Hz, ⁴J = 1.0 Hz), 7.00 (mt, 1H, C6-H or C5-H, ³J = 8.0 Hz, ³J = 7.0 Hz, ⁴J = 1.0 Hz), 7.14 (d, 1H, C7-H, ³J = 8.0 Hz), 7.23 (d, 1H, C4-H, ³J = 8.0 Hz), aralkyl Ar-H, 6.62-6.67 (m, 4H, H3', H5', H3'', H5'', J = 8.8 Hz), 7.04-7.09 (m, 4H, H2', H6', H2'', H6'', J = 8.8 Hz); ms: (70 eV, electron impact) m/e 383 (M⁺, 100%), 382 (42%), 261 (58%), 191.5 (M⁺, 9%).

Anal. Calcd. for C₂₆H₂₉N₃ (383.53): C, 81.42; H, 7.62; N, 10.96. Found: C, 81.37; H, 7.60; N, 10.87.

Bis[4-dimethylaminophenyl][3-methylindol-1-yl]methane (**17**).

This compound was purified by column chromatography using diisopropyl ether/petroleum ether (bp 40-60°) (1:1) as eluent, yield 625 mg (22%), colorless crystals, mp 184° [diisopropyl ether/petroleum ether (bp 40-60°)]; ¹H-nmr (deuteriochloroform): δ = 2.26 (d, 3H, CH₃, ³J = 1.0 Hz), 2.91 (s, 12H, NCH₃), 6.61-6.67 (m, 6H, methine-H, indole C2-H,

aralkyl H3', H5', H3'', H5''), 6.93-6.98 (m, 4H, aralkyl H2', H6', H2'', H6'', J = 8.6 Hz), 7.04-7.11 (m, 2H, indole C5-H, C6-H), 7.19-7.24 (m, 1H, indole C7-H), 7.52-7.57 (m, 1H, indole C4-H); ms: (70 eV, electron impact) m/e 383 (M⁺, 1%), 253 (100%).

Anal. Calcd. for C₂₆H₂₉N₃ (383.53): C, 81.42; H, 7.62; N, 10.96. Found: C, 81.41; H, 7.55; N, 10.87.

Bis[4-dimethylaminophenyl][3-methylindol-2-yl]methane (18).

This compound was purified by column chromatography using diisopropyl ether/petroleum ether (bp 40-60°) (1:1) as eluent, yield 1.45 g (51%), pale blue colored needles, mp 189-190° (*n*-hexane, dichloromethane); ¹H-nmr (deuteriochloroform): δ = 2.16 (s, 3H, CH₃), 2.91 (s, 12H, NCH₃), 5.59 (s, 1H, methine-H), 6.63-6.68 (m, 4H, aralkyl H3', H5', H3'', H5'', J = 8.7 Hz), 6.98-7.03 (m, 4H, aralkyl H2', H6', H2'', H6'', J = 8.7 Hz), 7.04-7.10 (m, 2H, indole C5-H, C6-H), 7.13-7.18 (m, 1H, indole C7-H), 7.46-7.53 (m, 2H, indole C4-H, NH); ms: (70 eV, electron impact) m/e 383 (M⁺, 100%), 263 (45%), 247 (56%), 191.5 (M²⁺, 11%).

Anal. Calcd. for C₂₆H₂₉N₃ (383.53): C, 81.42; H, 7.62; N, 10.96. Found: C, 81.28; H, 7.68; N, 10.85.

Bis[4-dimethylaminophenyl][2,3-dimethylindol-1-yl]methane (19).

This compound was obtained in 61% yield (1.8 g) as crystals having a pale green-blue coloration on their surfaces, mp 200-203° (*n*-hexane,

dichloromethane); ¹H-nmr (deuteriochloroform): δ = 2.22 (s, 3H, C2-CH₃), 2.24 (s, 3H, C3-CH₃), 2.87 (s, 12H, NCH₃), 6.58-6.63 (m, 4H, aralkyl H3', H5', H3'', H5'', J = 8.8 Hz), 6.74 (s, 1H, methine-H), 6.78 (d, 1H, indole C7-H, ³J = 8.0 Hz), 6.85 (mt, 1H, indole C5-H or C6-H, ³J = 8.0 Hz, ³J = 6.9 Hz), 6.95-7.01 (m, 5H, aralkyl H2', H6', H2'', H6'', indole C6-H or C5-H), 7.45 (d, 1H, indole C4-H, ³J = 8.0 Hz); ¹³C-nmr (deuteriochloroform): δ = 8.9 (C3-CH₃), 11.4 (C2-CH₃), 40.4 (NCH₃), 61.5 (methine-C), indole C, 107.0 (q), 111.6, 117.5, 118.1, 120.1, (129.0 (q; only recognizable in off-resonance spectrum), 133.3 (q), 136.4 (q), aralkyl Ar-C, 112.2, 128.1 (q), 129.0, 149.6 (q), [(q) = quaternary sp² carbon atom]; ms: (70 eV, electron impact) m/e 397 (M⁺, 1%), 253 (100%).

Anal. Calcd. for C₂₇H₃₁N₃ (397.56): C, 81.57; H, 7.86; N, 10.57. Found: C, 81.75; H, 7.94; N, 10.66.

REFERENCES AND NOTES

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