Registry No. **1a**, 584-70-3; **1b**, 61495-08-7; **1c**, 61495-07-6; **1d**, 78987-16-3; **1e**, 61495-04-3; **1f**, 61495-05-4; **1g**, 54898-71-4; **8a**, 948-65-2; **8b**, 5883-96-5; **8c**, 23746-76-1; **8d**, 13228-36-9; **9a**, 22978-49-0; **9b**, 78987-17-4; **11**, 78987-18-5; **14**, 78987-19-6; **15a**, 1805-65-8; **15b**, 61495-03-2; **15c**, 26845-72-7; **16a**, 120-66-1; **16b**, 40748-53-6; **18a**, 78987-20-9; **18b**, 41951-12-6; **19**, 78987-21-0; **20**, 78987-22-1; **22**, 78987-23-2; **23**, 33555-17-8; **24**, 78987-24-3; **25**, 23612-46-6; **26**, 10586-52-4; **27**, 78987-25-4; **28**, 79005-34-8; *o*-toluidine, 95-53-4; 2-methyl-*p*-anisidine, 102-50-1; 4-chloro-*o*-toluidine, 95-69-2; *o*-ethylaniline, 578-54-1; 2-amino-3-picoline, 1603-40-3; 2-mehtyl-1-naphthylamine, 2246-44-8; 5,6,7,8-tetrahydro-1-naphthylamine, 2217-41-6; benzoyl chloride, 98-88-4; pivaloyl chloride, 3282-30-2; 1-methylcyclohexanecarbonyl chloride, 2890-61-1; 1-adamantanecarbonyl chloride, 2094-72-6; *o*-toluoyl chloride, 933-88-0; α-phenyl-*o*-toluoyl chloride, 55810-66-7; acetyl chloride, 75-36-5; phenylacetyl chloride, 103-80-0; cinnamoyl chloride, 102-92-1.

Novel Cycloaddition Products Formed by the Modified Madelung Indole Synthesis

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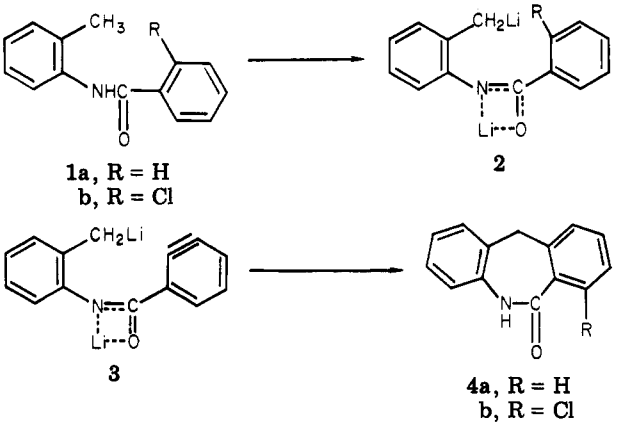
Several *N*-aryl-2,6- or -2,4-dichlorobenzamides when treated with *n*-butyllithium in THF under modified Madelung indole synthesis conditions underwent [4_π + 2_π] cycloaddition reaction to form 6,8a-ethenobenz[*cd*]isoindol-2(1*H*)-ones. *N*-(1-Naphthyl)-2,6-dichlorobenzamide under similar conditions gave rise to the [4_π + 2_π] adduct 3-chloro-6,10b-ethenonaphth[1,2,3-*cd*]isoindol-2(1*H*)-one.

In the preceding paper[1] from this laboratory it was proposed that the dilithio species **2**, formed by treating amide **1** with *n*-BuLi in THF, was an intermediate in the formation of indoles by the Madelung synthesis.[2] In the case where R is a Cl atom (**1b**) we speculated that it might be possible to form the aryne **3** and initiate an internal attack to form the dibenzazepinone **4a** (Scheme I). The present work reports our attempt to form **4** and an unexpected [4_π + 2_π] cycloaddition reaction.

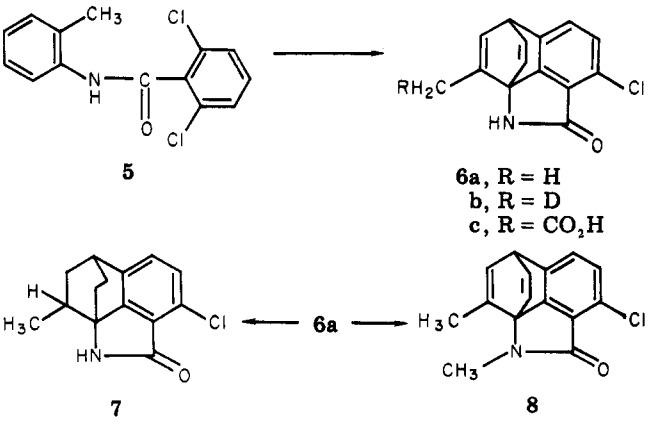
Treatment of **5** with 3 equiv of *n*-BuLi in THF at −60 °C resulted in the formation of a $C_{14}H_{10}ClNO$ compound, A, in 25% yield that gave spectral data inconsistent with the expected **4b**. The mass spectrum of A gave strong M^+ - 26 and M^+ - 40 fragments corresponding to loss of HC≡CH and HC≡CCH$_3$, respectively. The ^{1}H NMR spectrum showed a CH$_3$ doublet at δ 1.95 with a small splitting of 2 Hz, one H at δ 5.00 that was a doublet of triplets, one H at δ 6.50 as a doublet, and four H in the δ 6.82–7.38 region. These data, together with the IR and ^{13}C spectra, are best satisfied by assigning A as the novel tetracyclic 6,8a-ethenobenz[*cd*]isoindol-2(1*H*)-one **6a** (Scheme II). Additional support for this structure was obtained when **6a** absorbed 2 equiv of H_2 on catalytic reduction to form one of the two isomers of **7**. The ^{1}H NMR spectrum of **7** gave a CH$_3$ doublet (J = 6 Hz) at δ 0.4, seven aliphatic protons between δ 0.8–2.50, and a benzyl H at δ 3.20 as an unresolved multiplet. Seven signals in the ^{13}C spectrum between δ 17.8 and 58.3 were consistent with the tetrahedral C atoms found in structure **7**. Methylation of the sodium salt of **6a** afforded a *N*-methyl compound **8** that gave spectral data consistent with the assigned structure.

The formation of **6a** can best be explained by a [4_π + 2_π] cycloaddition of intermediate **9a** or **9b** to form **10a** or **10b** and then hydrolysis to **6a** (Scheme III). In order to distinguish between these possibilities, the reaction of **5** with 3 equiv of *n*-BuLi was quenched separately with D_2O or solid CO_2. In both cases only **6a** was isolated in ca. 25% yield and the deuterated or carboxylated derivatives **6b**

Scheme I



Scheme II

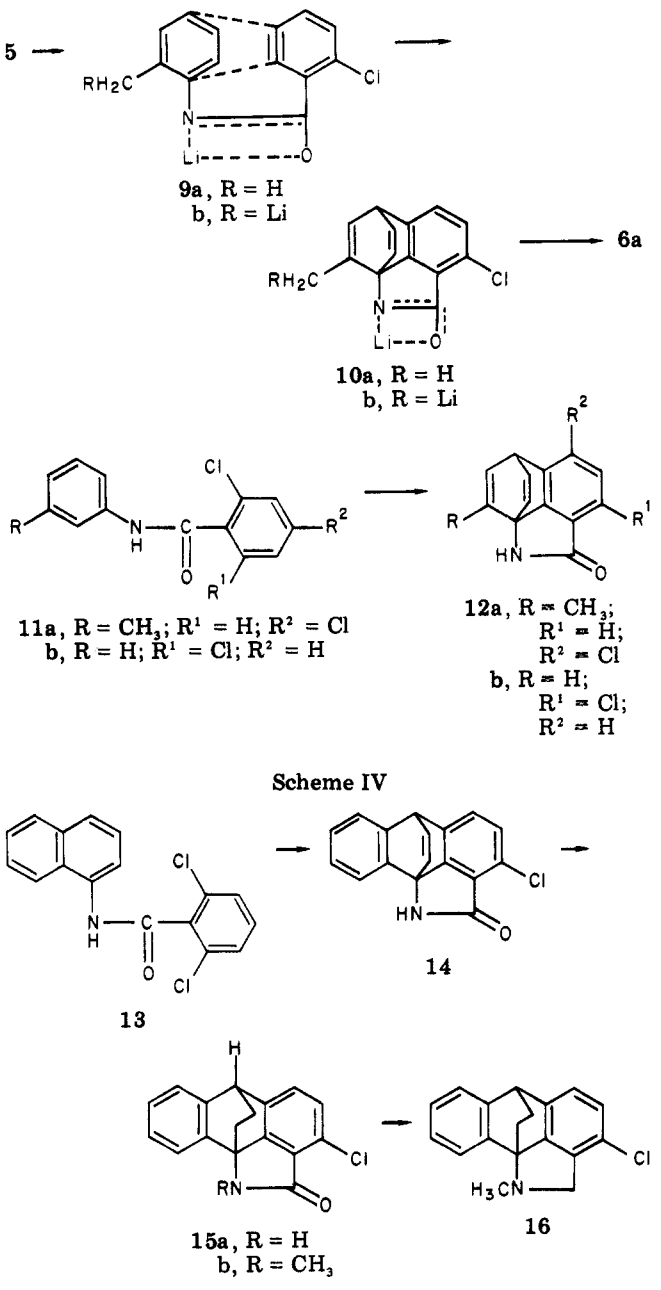


(1) W. J. Houlihan, V. A. Parrino, and Y. Uike, *J. Org. Chem.*, preceding paper in this issue.

(2) For a comprehensive review of the Madelung synthesis see R. K. Brown in "Indoles", W. J. Houlihan, Ed., Wiley, New York, 1972, Part I, pp 385–396.

0022-3263/81/1946-4515$01.25/0

Scheme III



Scheme IV

or **6c**, respectively, were not detected by ^{1}H NMR and mass spectral analysis. These data suggest that aryne formation to **9a** followed by cyclization to **10a** proceeds faster than the lithiation of the methyl group on **5**.

Cyclization of the dichlorobenzamides **11a** and **11b** gave the tetracyclic amides **12a** and **12b** in 8.6% and 4.4% yields, respectively, indicating that the reaction is very sensitive to changes on either phenyl group.

Extension of the cyclization procedure to *N*-naphthylbenzamide **13** resulted in the formation of the novel 6,10-ethenonaphth[1,2,3-*cd*]isoindole[3] derivative **14** in 41% yield. The structure of **14** was confirmed by the ^{1}H NMR spectrum where a one-hydrogen doublet of doublets (J = 6 Hz, J' = 2 Hz) could be assigned to the bridgehead proton at C-6, and the mass spectrum gave an intense loss of an M^+ - 26 fragment that can be due to loss of HC≡CH from the 6,10-etheno group. Hydrogenation of **14** resulted in the uptake of 1 equiv of H_2 to give a compound that gave ^{1}H NMR and mass spectra in agreement with structure **15a**. N-Methylation of **15a** to **15b** followed by $LiAlH_4$ reduction in THF afforded the amine **16** in good yield.

(3) W. J. Houlihan, U.S. Patent 4 036 978 (1977).

Experimental Section[4]

^{13}C NMR spectra were obtained at 25.2 MHz on a Varian XL-100-12 spectrometer system, equipped with a 620/L 16K computer, in the Fourier transform mode with sample concentrations of ca. 0.5 M when possible. Chemical shifts are relative to Me_4Si as an internal standard (coupling constants are in hertz), and those assignments marked with an asterisk may be interchanged. The mass spectra were obtained on a LKB 900 mass spectrometer. The solvent used to develop TLC plates was $CHCl_3$–CH_3OH (95:5).

Preparation of Amides. A mixture of 0.10 mol of amine, 0.10 mol of acid chloride, and 0.10 mol of triethylamine in 150 mL of anhydrous toluene was stirred and refluxed for 3 h and then allowed to stand for ca. 16 h at room temperature. The resulting solids were filtered off and stirred at room temperature for ca. 1.5 h with 150 mL of H_2O. The remaining solid was filtered off and recrystallized to give the following. **5**: 91%; mp 178–180 °C (toluene–pentane); R_f 0.5; IR ($CHCl_3$) 2.92 (NH), 5.93 μm (CO). Anal. Calcd for $C_{14}H_{11}Cl_2NO$; C, 60.2; H, 3.9; Cl, 25.4; N, 5.0. Found: C, 59.9; H, 3.7; Cl, 25.6; N, 4.9. **11a**: 87%; mp 167–168 °C (toluene); R_f 0.45; IR ($CHCl_3$) 2.92 (NH), 5.98 μm (CO). Anal. Calcd for $C_{14}H_{11}Cl_2NO$: C, 60.2; H, 3.9; Cl, 25.4; N, 5.0. Found: C, 60.3; H, 3.8; Cl, 25.2; N, 4.8. **11b**: 86%; mp 174–175 °C (toluene); R_f 0.40; IR ($CHCl_3$) 2.92, 3.03 (NH), 5.96 μm (CO). Anal. Calcd for $C_{13}H_9Cl_2NO$: C, 58.6; H, 3.4; Cl, 26.7; N, 5.3. Found: C, 58.5; H, 3.3; Cl, 26.7; N, 5.2. **13**: 87%; mp 202–203 °C (toluene–pentane); R_f 0.8; IR (KBr) 2.85, 2.93 (NH), 5.93 μm (CO). Anal. Calcd for $C_{17}H_{11}Cl_2NO$: C, 64.6; H, 3.8; Cl, 22.4; N, 4.4. Found: C, 64.6; H, 3.6; Cl, 22.6; N, 4.5.

3-Chloro-8-methyl-6*H*-6,8a-ethenobenz[*cd*]isoindol-2-(*H*)-one (6a). A stirred solution (N_2 atmosphere) of 43.2 mL (0.06 mol of *n*-BuLi) of 1.4 M *n*-BuLi in hexane and 25 mL of the THF was cooled to an internal temperature of –60 °C and then treated dropwise with a solution of 5.60 g (0.02 mol) of **5** in 40 mL of THF. After an additional 3 h at –55 ± 5 °C, cooling was removed from the orange suspension and a clear red solution resulted at ca. –20 °C. The solution was maintained at –20 ± 5 °C and treated dropwise with 25 mL of cold 2 N HCl. The organic layer was separated, dried with anhydroous $MgSO_4$, filtered, and concentrated in vacuo to give 5.49 g of a hard amber oil. Treatment of the oil with Et_2O gave 1.23 g (25%) of **6a**: mp 178–179 °C; R_f 0.38; IR ($CHCl_3$) 2.90, 3.12 (NH), 5.88 (C=O) μm; ^{1}H NMR ($CDCl_3$) δ 1.95 (3 H, d, J = 2, CH_3), 5.00 (1 H, dt, J = 6, J' = 2, >CH), 6.50 (1 H, split d, J = 6, HC=CMe), 6.82–7.38 (4 H, m, HC=CH, C_6H_2); ^{13}C NMR ($CDCl_3$) 15.1 (CH_3), 46.3 (C-6), 70.7 (C-8a), 121.0 (*C-8b), 125.4 (*C-5a), 125.6 (*C-4), 126.4 (*C-5), 132.8 (C-7), 137.3 (C-10), 140.6 (C-9), 141.5 (C-3), 146.8 (C-8), 159.8 (C-2a), 172.3 ppm (C=O); mass spectrum, m/e 243 (M^+), 217 (M^+ - HC≡CH), 203 (M^+ - HC≡CCH$_3$), 182 (M^+ - HC≡CH,Cl). Anal. Calcd for $C_{14}H_{10}ClNO$: C, 69.2; H, 4.1; Cl, 14.5; N, 5.7. Found: C, 69.2; H, 4.3; Cl, 14.3; N, 5.7.

3-Chloro-8-methyl-7,8-dihydro-6*H*-6,8a-ethanobenz[*cd*]-isoindol-2(1*H*)-one (7). A mixture of 3.64 g (0.015 mol) of **6a**, 0.1 g of platinum oxide, and 200 mL of acetic acid was hydrogenated on a Parr hydrogenation apparatus at 50 psi of H_2 and room temperature. After the uptake ceased (2.1 equiv of H_2) the mixture was filtered through Celite and the filtrate concentrated in vacuo to give 3.65 g of oil with R_f 0.40 and 0.47 (**6a**). Crystallization from ether–CCl_4 gave 1.64 g (44%) of **7**: mp 161–163 °C; R_f 0.40; IR ($CHCl_3$) 2.90, 3.10 (NH), 5.88 (CO) μm; ^{1}H NMR (Me_2SO-d_6) δ 0.4 (3 H, d, J = 6, CH_3), 0.80–2.50 (7 H, m, CH_2CHMe, CH_2CH_2), 3.20 (1 H, unresolved m, >CH), 7.38 (2 H, s, HC=CH), 8.60 (1 H, s, NH); ^{13}C NMR (Me_2SO-d_6) 17.8 (CH_3), 28.3, 30.4, 31.5, 32.2 (C-7 to C-10), 38.4 (C-6), 58.3 (C-8a), 124.3 (C-8b), 126.2 (C-5a), 127.0 (C-4), 129.2 (C-5), 137.5 (C-3), 151.5 (C-2a), 168.6 (C=O); mass spectrum, m/e 247 (M^+). Anal. Calcd for $C_{14}H_{14}ClNO$: C, 67.9; H, 5.7; Cl, 14.3; N, 5.7. Found: C, 67.7; H, 5.7; Cl, 14.1; N, 5.7.

3-Chloro-1,8-dimethyl-6*H*-6,8a-ethenobenz[*cd*]isoindol-2-

(4) See the preceding paper for a more detailed description of the experimental procedures.

(1*H*)-one (8). A solution of 3.64 g (0.015 mol) of **6a** in 10 mL of DMF was added dropwise to a stirred slurry of 0.8 g (0.018 mol) of 55% NaH in mineral oil in 20 mL of DMF under a N_2 atmosphere. The mixture was heated at 65 °C for 2 h, cooled to 20 °C, treated dropwise with 2.56 g (0.015 mol) of methyl iodide in 10 mL) of DMF, and then allowed to stand overnight at room temperature. The solvent was removed in vacuo, and the residue (4.96 g) was dissolved in toluene and chromatographed on silica gel with toluene–acetone (95:5) as eluant to give 3.52 g (94%) of **8**: mp 108–109 °C (Et_2O–CH_3OH); R_f 0.55; ^1H NMR ($CDCl_3$) δ 1.83 (3 H, d, J = 2.0, CH_3), 3.42 (3 H, s, NCH_3), 4.90 (1 H, dt, J = 6, J' = 2, >CH), 6.42 (1 H, split d, J = 6, HC=CMe), 6.60–7.25 (4 H, series of m, CH=CH and C_6H_2); ^{13}C NMR (Me_2SO-d_6) 15.1 (CCH_3), 28.4 (NCH_3), 45.9 (c-6), 61.5 (C-8a), 120.6 (*C-8b), 123.6 (*C-5a), 125.8 (*C-4), 126.2 (*C-5), 134.0 (*C-7), 134.6 (*C-10), 141.5 (C-9), 141.9 (C-3), 146.1 (C-8), 157.9 (C-2a), 167.5 ppm (C=O); mass spectrum, m/e 257 (M^+), 242 ($M^+ - CH_3$), 231 ($M^+ - HC{\equiv}CH$), 228 ($M^+ - NCH_3$), 217 ($M^+ - CH_3C{\equiv}CH$), 214 ($M^+ - CO, CH_3$), 200 ($M^+ - CO, NCH_3$) 188, 182, 161, 152, 139, 126. Anal. Calcd for $C_{15}H_{12}ClNO$: C, 69.9; H, 4.7; Cl, 13.8; N, 5.4. Found: C, 69.7; H, 4.7; Cl, 13.5; N, 5.3.

5-Chloro-8-methyl-6*H*-6,8a-etheno[*cd*]isoindol-2(1*H*)-one (12a). A stirred solution (N_2 atmosphere) of 28.8 mL (0.04 mol of *n*-BuLi) of 1.4 M *n*-BuLi in 15 mL of THF was treated with 5.62 g (0.02 mol) of **11a** in 40 mL of THF under the same conditions used to prepare **6a**. The resultant semisolid (6.1 g) was treated with Et_2O, and the insoluble material was filtered off to give 4.27 g of starting **11a** (mp 166–167 °C). The filtrate was chromatographed on silica gel with toluene–acetone (95:5) as eluant to give **12a**: 0.38 g (8.6%, 29% based on recovered **11a**); mp 216–217 °C; R_f 0.40; ^1H NMR ($CDCl_3$) δ 1.92 (3 H, d, J = 2, CH_3), 5.18 (1 H, dt, J = 6, J' = 2), 6.42 (1 H, qd, J = 6, J' = 2), 6.80–7.38 (4 H, m, HC=CH, C_6H_2), 8.65 (1 H, s, NH); ^{13}C NMR ($CDCl_3$) 15.5 (CH_3), 44.7 (C-6), 71.4 (C-8a), 120.6 (C-3, C-8b), 126.9 (C-4, C-5a), 130.8 (C-5), 132.2 (C-7), 137.9 (C-10), 140.3 (C-9), 147.5 (C-8), 159.0 (C-2a), 172.0 ppm (C=O). Anal. Calcd for $C_{14}H_{10}ClNO$: C, 69.2; H, 4.1; Cl, 14.5; N, 5.7. Found: C, 69.0; H, 4.0; Cl, 14.6; N, 5.5.

3-Chloro-6*H*-6,8a-ethenobenz[*cd*]isoindol-2(1*H*)-one (12b). A stirred solution (N_2 atmosphere) of 43.2 mL (0.06 mol of *n*-BuLi) of 1.4 M *n*-BuLi in 25 mL of THF was treated with 5.33 g (0.02 mol) of **11b** in 40 mL of THF under the same conditions used to prepare **6a**. Treatment of the resulant thick oil with Et_2O–petroleum ether gave **12b**: 0.20 g (4.4%); mp 230–231 °C; R_f 0.35; IR ($CHCl_3$) 2.95 (NH) 5.87 (C=O) μm; ^1H NMR ($CDCl_3$–Me_2SO-d_6) 5.0 (1 H, m, >CH), 6.40–7.30 (6 H, m, 2HC=CH, C_6H_2). Anal. Calcd for $C_{13}H_8ClNO$: C, 67.5; H, 5.6; Cl, 15.3; N, 6.1. Found: C, 67.3; H, 5.4; Cl, 15.2; N, 6.0.

3-Chloro-6,10b-ethenonaphth[1,2,3-*cd*]isoindol-2(1*H*)-one (14). A stirred suspension (N_2 atmosphere) of 28.5 g (0.09 mol) of **13** in 150 mL of THF was cooled to an internal temperature of −50 °C and treated dropwise with 130 mL (0.18 mol of *n*-BuLi) of 1.4 M *n*-BuLi in hexane at such a rate that the temperature did not exceed −40 °C. The resultant amber solution was held at −30 °C for ca. 0.5 h and then treated dropwise with 100 mL of 2 N HCl. The solid material was filtered off and washed with THF to give **14**: 10.47 g (41%); mp 280 °C; R_f 0.5; IR (KBr) 2.92, 2.98, 3.12 (NH), 5.88 (CO) μm; ^1H NMR (Me_2SO-d_6) 5.30 (1 H, dd, J = 6, J' = 2, ArCHAr'), 6.60–7.42 (8 H, series of m, HC=HC, C_6H_4, C_6H_2) 9.60 (1 H, s, NH); ^{13}C NMR (Me_2SO-d_6) 47.9(C-6), 66.7 (C-10b), 119.9, 121.8, 123.6, 125.0, 125.3, 127.4, 137.5, 140.6, 141.2, 143.4, 145.5, 158.1 (C-2a), 169.4 ppm (C=O); mass spectrum, m/e 279 (M^+), 253 ($M^+ - HC{\equiv}CH$), 244 ($M^+ - Cl$), 216 ($M^+ - HC{\equiv}CH, Cl$). Anal. Calcd for $C_{17}H_{10}ClNO$: C, 73.0; H, 3.6; Cl, 12.7; N, 5.0. Found: C, 72.9; H, 3.8, Cl, 12.6; N, 5.0.

3-Chloro-6,10b-ethanodibenz[*cd*,*g*]indol-2(1*H*)-one (15a). A mixture of **14** (5.00 g, 0.018 mol), 0.1 g of platinum oxide, and 250 mL of acetic acid was hydrogenated and processed as described in the preparation of **7**. There was obtained **15a**: 4.37 g (86.5%); mp 232–234 °C (HOAc); R_f 0.5; IR (KBr) 3.12 (NH, br), 6.00 (C=O) μm; ^1H NMR (Me_2SO-d_6) δ 1.22–2.20 (4 H, m, CH_2CH_2), 4.60 (1 H, s, >CH), 7.00–7.62 (6 H, m, C_6H_4, C_6H_2), 9.75 (1 H, s, NH); mass spectrum, m/e 281 (M^+, very weak), 253 ($M^+ - CH_2{=}CH_2$), 224 ($M^+ - CH_2{=}CH_2$, CO), 190 ($M^+ - CH_2{=}CH_2$, CO, Cl). Anal. Calcd for $C_{17}H_{12}ClNO$: C, 72.5; H, 4.3; Cl, 12.6; N, 5.0. Found: C, 72.3; H, 4.3; Cl, 12.9; N, 5.0.

3-Chloro-1-methyl-6,10b-ethanodibenz[*cd*,*g*]indol-2-(1*H*)-one (15b). A solution of 5.75 g (0.0204 mol) of **15a** in 55 mL of DMF was added dropwise to a stirred slurry of 3.4 g (0.08 mol) of 55% NaH in 30 mL of DMF under a N_2 atmosphere. The resultant pasty mixture was heated to 90 °C for 2 h, cooled to 20 °C, and treated dropwise with 11.4 g (5 mL, 0.08 mol) of methyl iodide in 60 mL of DMF, and allowed to stand overnight at room temperature. The solvent was removed in vacuo, and the residue was treated with 100 mL of CH_2Cl_2, dried with $MgSO_4$, filtered, and concentrated in vacuo to give 7.44 g of oil, R_f 0.5 and 0.65. Chromatography on a silica gel column gave fraction 1 (3.98 g; acetone–toluene, 0.5:95.5; R_f 0.65) and fraction 2 (1.58 g of **15a**, acetone–toluene, 2:98; R_f 0.5). Fraction 1 was crystallized from acetic acid to give 3.68 g (62%) of **15b**: mp 160–161 °C; ^1H NMR ($CDCl_3$) δ 1.21 (1 H, m, H_A), 1.78–2.42 (3 H, m, $CH_AH_BCH_CH_D$), 3.47 (3 H, s, CH_3), 4.50 (1 H, unresolved q, $J \simeq 2$, >CH), 6.95–7.45 (6 H, m, C_6H_4, C_6H_2); mass spectrum, m/e 295 (M^+, very weak), 267 ($M^+ - CH_2CH_2$), 253 ($M^+ - CH_3$, CH_2CH_2), 240 ($M^+ - CO$, CH_2CH_2), 204 ($M^+ - Cl$, CO, CH_2CH_2). Anal. Calcd for $C_{18}H_{14}ClNO$: C, 73.0; H, 4.7; Cl, 12.0; N, 4.7. Found: C, 73.2; H, 4.8; Cl, 12.1; N, 4.8.

3-Chloro-1-methyl-1,2-dihydro-6,10b-ethanodibenz[*cd*,*q*]indole (16). A solution of 4.64 g (0.0158 mol) of **15b** in 60 mL of dry THF was added dropwise to a stirred mixture of 1.0 g (0.026 mol) of $LiAlH_4$ in 50 mL of THF (N_2 atmosphere) and then refluxed for 4 h. The mixture was cooled in an ice bath, treated dropwise with 2 mL of 2 N NaOH, 3 mL of H_2O, and anhydrous Na_2SO_4, and after being stirred for ca. 1 h, filtered through Celite. The filtrate was concentrated in vacuo to give 4.31 g (93%) of **16** as an oil: R_f 0.8; IR ($CHCl_3$) no C=O; ^1H NMR ($CDCl_3$) δ 1.38–1.98 (4 H, series of m, CH_2CH_2), 2.92 (3 H, s, CH_3), 4.10 and 4.73 (AB q, J = 14, NCH_AH_B), 4.23 (1 H, m, ArCHAr'), 6.90–7.63 (6 H, m, C_6H_2, C_6H_4). The oil was dissolved in ca. 100 mL of Et_2O and saturated with anhydrous HCl to give 4.24 g of **16**·HCl, mp >250 °C. Anal. Calcd for $C_{18}H_{17}Cl_2N$: C, 67.9; H, 5.4; Cl, 22.3; N, 4.4. Found: C, 67.8; H, 5.3; Cl, 22.4; N, 4.1.

Acknowledgment. We thank S. DiCataldo, A. Kahle, and B. Owens for determination of spectra, B. Bonkowski and his associates for microanalyses, and Dr. Michael Shapiro for his assistance in the interpretation of the ^{13}C NMR spectra.

Registry No. **5**, 74933-42-9; **6a**, 78986-87-5; **7**, 78986-88-6; **8**, 78986-89-7; **11a**, 78986-90-0; **11b**, 3797-94-2; **12a**, 78986-91-1; **12b**, 78986-92-2; **13**, 64215-42-5; **14**, 64215-43-6; **15a**, 64215-44-7; **15b**, 64215-45-8; **16**, 78986-93-3; **16**·HCl, 78986-94-4; *o*-methylaniline, 95-53-4; *m*-methylaniline, 108-44-1; aniline, 62-53-3; 1-aminonaphthalene, 134-32-7; 2,6-dichlorobenzoyl chloride, 4659-45-4; 2,4-dichlorobenzoyl chloride, 89-75-8.