degassed three times and sealed at a pressure of 10^{-5} torr. The sealed cell was then placed in the thermostated compartment of a Cary 219 spectrophotometer. The absorbance at 525 nm was recorded at a constant chart speed until a stable infinity reading was reached. Concentrations of DPPH were calculated from the absorbance readings based on an extinction coefficient of 12670. For each absorbance reading $-\ln((2[\text{dimer}]_0 - [\text{DPPH}]_0 + [\text{DPPH}]_t)/2[\text{dimer}]_0)$ was plotted vs. time. Rate constants were obtained from least-squares slopes of these plots. The errors reported are the standard deviations in the slopes. The activation energy and A factor were obtained from the least-squares slopes and intercepts of the Arrhenius plot, and the errors are the standard deviations from the least-squares analysis. The enthalpy and entropy of activation were calculated as described earlier.[15] The error in the free energy of activation was obtained through a propagation of error technique for the errors associated with enthalpy of activation and the entropy of activation.

Kinetic Measurements of the Unimolecular Bond Homolysis of 5 and 6. In a typical experiment, 1.50 mL of a 6.30×10^{-3} M solution of *N*-methylisatin in spectral quality chloroform was added to 1.50 mL of a 3×10^{-3} M solution of radical dimer or mixture of radical dimers in chloroform in a Pyrex cuvette. The solution was degassed, sealed, and placed in the thermostated compartment of a Cary 219 spectrophotometer. The absorbance at 420 nm was recorded at a constant chart speed until a stable infinity reading was reached. For each absorbance reading $-\ln(A_t - A_\infty)$ was plotted vs. time where A_∞ is the infinity absorbance reading. Rate constants were obtained from least-squares slopes of these plots. At this point calculations were carried out exactly as described for the kinetics with DPPH as a trapping agent.

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Registry No. 1, 57765-64-7; 3, 86527-90-4; (*R**,*R**)-4, 86527-91-5; (*R**,*S**)-4, 86527-92-6; (*R**,*R**)-5, 86527-93-7; (*R**,*S**)-5, 86527-94-8; 6, 86527-95-9; 7, 86527-96-0; 8, 86527-97-1; 9, 86527-98-2; 10, 86527-99-3; 11, 86528-01-0; 13, 86528-02-1; 14, 86528-03-2; 15, 86528-00-9; 17, 53153-46-1.

Intramolecular [3 + 2] Cycloaddition Routes to Carbon-Bridged Dibenzocycloheptanes and Dibenzazepines†

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Utilization of several intramolecular [3 + 2] cycloaddition reactions for the synthesis of functionalized carbon-bridged dibenzocycloheptanes and dibenzazepines is described. Reaction of the aldehydes **4**, **7**, and **10** with *N*-methylhydroxylamine led to the formation of the bridged polycyclic isoxazolidines **14**, **15**, and **17**, respectively. Dissolving metal reduction of these compounds afforded representatives of the title compounds **1** and **2** (X = OH, Y = $NHCH_3$). Alternatively, reaction of **7** with the acylhydrazine **18** yielded directly the diaza cycloadduct **20**, a precursor to **1** and **2** (X = NHR, Y = NHR). A novel [3 + 2] cycloaddition was observed when **7** was reacted with sarcosine ethyl ester (**21**), leading to the polycyclic proline derivative **23**, presumably via the zwitterionic intermediate **22**.

The synthesis of bridged polycyclic molecules has long been of importance to organic chemists, primarily because of a theoretical interest in the physical properties of such systems.[1] More recently, reports of significant biological activities in certain of these classes have appeared, thus sparking a renewed interest in their synthesis.[2] We describe a novel preparation of carbon-bridged dibenzocycloheptanes[1a] and dibenzazepines of general structures **1** and **2**, respectively, relying on key intramolecular [3 + 2] cycloadditions for their construction. The use of this reaction mode has increased in recent years and has proven valuable for the preparation of complex ring systems[3] as well as several natural products.[4] A further advantage of

1 X = OR, NHR; Y = NHR; Z = $(CH_2)_n$, n = 0,1 **2**

† Contribution 3183.

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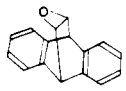
our approach to the title compounds is the production of useful functionality (X and Y in 1 and 2) for subsequent manipulation.

We required the olefinic aldehydes 4, 7, and 10 as substrates for the cycloaddition reactions. An acid-catalyzed rearrangement of the epoxide 3, obtained by peroxidation of the Diels–Alder adduct of anthracene and acetylene,[5] readily afforded the carboxaldehyde 4 in high yield. The homologous aldehyde 7 was prepared from the acid 5[6] by reduction with LAH to the alcohol 6 followed by oxidation with PCC. Lastly, azastilbene (8) was alkylated with bromoacetaldehyde diethyl acetal to yield the acetal 9, which was hydrolyzed to the acetaldehyde derivative 10.[7]



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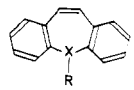
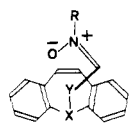
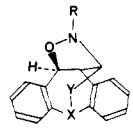


4 R = CHO, X = CH
5 R = CH_2CO_2H, X = CH
6 R = $(CH_2)_2OH$, X=CH
7 R = CH_2CHO, X = CH
8 R = H, X = N
9 R = $CH_2CH(OET)_2$, X = N
10 R = CH_2CHO, X=N

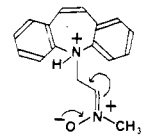
Each of these substrates differed in its behavior toward N-substituted hydroxylamines, requiring precise conditions for both nitrone formation and the subsequent cyclization to allow formation of the desired bridged isoxazolidines 12 by [3 + 2] cycloaddition chemistry of the reactive intermediates 11. Our findings in this series may have some



11 X = CH,N
Y = $(CH_2)_n$, n = 0,1



12

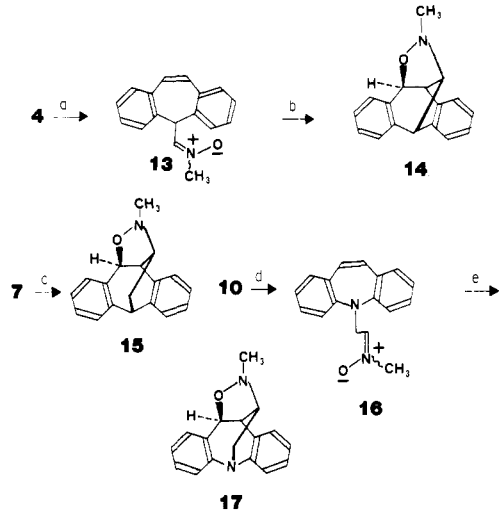


12A

generality for the preparation of other isoxazolidines that do not form under standard conditions. Thus, treatment of the aldehyde 4 with *N*-methylhydroxylamine hydrochloride in an alcoholic solvent with sodium acetate lead to the stable nitrone olefins 13 as a mixture of syn–anti isomers (Scheme I). After isolation, this mixture underwent an intramolecular [3 + 2] nitrone–olefin cycloaddition in refluxing toluene to yield the desired tetracyclic isoxazolidine 14 in quantitative yield. This two-step preparation of 14 was found to be superior to any one-pot procedure leading directly to the cycloadduct.

The ease of the corresponding [3 + 2] cycloaddition of the nitrone derived from the homologous aldehyde 7 was evidenced by the spontaneous formation of its cycloadduct 15 at room temperature. Finally, the azastilbene-derived aldehyde 10, an isostere of 7, did not undergo cycloaddition directly but yielded the nitrones 16, which were then cyclized in refluxing toluene to the desired product 17. All

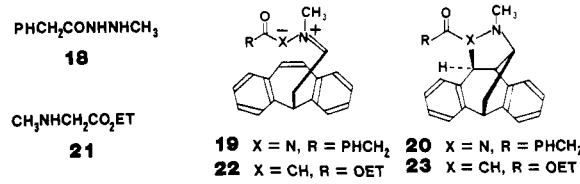
Scheme I[a]



[a] (a) $CH_3NHOH\cdot HCl$, NaOAc, EtOH, 1 h, 25 °C (100%), (b) $PhCH_3$, 3.5 h, Δ (90%), (c) $CH_3NHOH\cdot HCl$, Et_3N, CH_2Cl_2, 72 h, 25 °C (70%), (d) $CH_3NHOH\cdot HCl$, $NaHCO_3$, CH_3OH, 2 h, 25 °C (90%), (e) $PhCH_3$, 0.5 h, Δ (87%).

other conditions designed to generate 17 resulted in a facile decomposition of the intermediate 16 to azastilbene 8 and the *N*-methylnitrone of acetaldehyde via the mechanism shown in 12a. The isoxazolidines 14, 15, and 17 were smoothly reduced by a dissolving zinc reduction to yield the title compounds 1 and 2 (X = OH, Y = NHR).

The ability of the aldehyde 7 to function as a substrate for other [3 + 2] cycloadditions is illustrated by its reaction with *N*-(phenylacetyl)-*N'*-methylhydrazine (18).[8] This



18

21

19 X = N, R = $PHCH_2$ **20** X = N, R = $PHCH_2$
22 X = CH, R = OET **23** X = CH, R = OET

yielded directly the pentacyclic product 20, a precursor to 1 and 2 (X = NHR, Y = NHR), presumably via the *C*-alkenylazomethine imine 19.[9] The formation of the zwitterionic 19 is facilitated by the acylated nitrogen atom (X = N in 19) attached to the azomethine moiety. We wondered whether substitution of a less electronegative atom such as carbon at that position (X = C in 22) would still allow for a [3 + 2] cycloaddition. To this end, 7 was reacted with sarcosine ethyl ester hydrochloride (21) in refluxing toluene in the presence of sodium bicarbonate and yielded directly the novel adduct 23, presumably via the analogous reactive zwitterion 22.[10] *This latter reaction mode simultaneously makes two carbon-carbon bonds, forms complex ring systems with a high degree of stereocontrol, and incorporates a proline moiety into a molecule.* These characteristics are expected to endow this reaction with significant importance in view of the broad applicability that nitrone–olefin cycloaddition methodology has realized. We have therefore begun an extensive investigation into the scope and limitations of this stabilized

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imminium ylide cycloaddition chemistry. Applications to the total synthesis of natural products are presently underway as well. These and other results concerning the further chemistry of the isoxazolidines **14**, **15**, and **17** will be reported in due course.

Experimental Section

General Methods. Melting points were determined with a Fisher-Johns hotplate instrument or a Hoover capillary melting point apparatus and are uncorrected. Infrared spectra were recorded on a Nicolet 7199 FT-IR spectrophotometer. Frequencies are reported in reciprocal centimeters (cm^{-1}) and were calibrated with use of polystyrene's 1601.8-cm^{-1} reference peak. ^1H NMR spectra were obtained with Varian EM360 and EM390 instruments in the solvent indicated. Chemical shifts are reported in parts per million (δ) downfield from tetramethylsilane ($\delta = 0.00$). Coupling constants (J) are given in cycles per second (Hz). Mass spectra were recorded at 70 eV on a VG Micromass 70-70H double-focusing high-resolution spectrometer. Column chromatography was carried out with 230–400-mesh silica gel and with a Waters Prep-500 instrument using the solvent system indicated.

5*H*-Dibenzo[*a*,*d*]cycloheptene-5-carboxaldehyde (4). To a solution of 80.0 g (392 mmol) of 9,10-dihydro-9,10-ethenoanthracene[5] in 1.0 L of methylene chloride and 42 g (500 mmol) of sodium dicarbonate was added a total of 96 g (470 mmol) 85% *m*-chloroperoxybenzoic acid. The slurry was mechanically stirred for 20 h. After partitioning between 1 *N* sodium hydroxide and CH_2Cl_2 (3 × 500 mL), the organic layer was dried (Na_2SO_4) and evaporated to give 88.8 g of the epoxide **3** as a yellow solid. This crude material was dissolved in 1.0 L of benzene, treated with 20.0 g (105 mmol) of *p*-toluenesulfonic acid monohydrate, and refluxed for 0.5 h. After cooling, the solution was partitioned between 10% $NaHCO_3$ and CH_2Cl_2 (3 × 1000 mL). The organic layer was dried (Na_2SO_4) and evaporated to give a brown oil, which was dissolved in CH_2Cl_2 and diluted with hexanes. A total of 5.71 g (64%) of the aldehyde **4** separated and was collected. Recrystallization from EtOAc/hexanes gave pure **4** as colorless needles: mp 105–106 °C; IR (KBr) 3020, 2790, 1720, 1490, 810 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 9.52 (s, 1 H), 7.2 (m, 8 H), 6.88 (s, 2 H), 4.54 (s, 1 H); mass spectrum, m/e 220.0887 (calcd for $C_{16}H_{12}O$, 220.0888).

(5*H*-Dibenzo[*a*,*d*]cyclohepten-5-yl)acetic Acid (5). A solution of 40.0 g (192 mmol) of 5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol and 22.0 g (210 mmol) of malonic acid in 150 mL of acetic acid was heated to 70 °C for 18 h with mechanical stirring. After the solution cooled in an ice bath for 1 h, the product separated, and colorless flakes were filtered and dried in vacuo, yielding 44.6 g (79%) of crude material. The product, (5*H*-dibenzo[*a*,*d*]cyclohepten-5-yl)malonic acid, was dissolved in 115 mL of pyridine and gently refluxed for 3.5 h. The pyridine was removed in vacuo, and the dark oil was partitioned between 4 *N* HCl/ether (3 × 1000 mL). The ether layer was dried ($MgSO_4$) and evaporated, leaving 27.8 g of a solid. Recrystallization from EtOAc/hexanes produced 26.0 g (73% overall) of the acid **5** as colorless flakes: mp 162–163 °C; IR (KBr) 3420, 3010, 2910, 1700 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 9.12 (br, 1 H), 7.26 (m, 8 H), 6.91 (s, 2 H), 4.48 (t, 1 H, J = 7.5 Hz), 2.72 (d, 2 H, J = 7.5 Hz); mass spectrum, m/e 250.0990 (calcd for $C_{17}H_{14}O$, 250.0994).

1-(5*H*-Dibenzo[*a*,*d*]cyclohepten-5-yl)ethanol (6). To a solution of 26.0 g (104 mmol) of the acid **5** in 500 mL of dry THF at 0 °C under N_2 was slowly added 7.9 g (208 mmol) of LAH. The slurry was then refluxed for 2 h, cooled, and treated with 50 g of $Na_2SO_4 \cdot 10H_2O$. The mixture was mechanically stirred until a white granular solid was obtained (4 h). Suction filtration followed by evaporation of the solvent in vacuo afforded 23.6 g (96%) of the alcohol **6** as a light yellow solid. A small sample was recrystallized from EtOAc/hexanes to give colorless clusters of crystals: mp 71–75 °C; IR (KBr) 3400, 3060, 3010, 2950, 1490, 1030, 800, 760 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 8.27 (m, 8 H), 6.87 (s, 2 H), 4.18 (t, 1 H, J = 8.0 Hz), 3.28 (t, 2 H, J = 6.5 Hz), 1.95 (m, 2 H), 1.29 (br, 1 H); mass spectrum, m/e 236.1196 (calcd for $C_{17}H_{16}O$, 236.1201).

2-(5*H*-Dibenzo[*a*,*d*]cyclohepten-5-yl)acetaldehyde (7). To a mechanically stirred mixture of 20.0 g (93 mmol) of pyridinium chlorochromate and 11.6 g (140 mmol) of sodium acetate in 300 mL of CH_2Cl_2 was added a solution of 11.0 g (46.6 mmol) of the alcohol **6** in 100 mL of CH_2Cl_2. After 2 h, the black mixture was diluted with 1500 mL of ether and decanted. The dark liquid was passed through a column of Florisil followed by 200 mL of ether. Evaporation gave an oil, which was partitioned between 1 N HCl and CH_2Cl_2. The organic layer was dried (Na_2SO_4), evaporated, and column chromatographed on silica gel (petroleum ether/Et_2O, 4/1) to give 7.86 g (72%) of aldehyde **7** as a light yellow solid. Crystallization from Et_2O/petroleum ether gave colorless clusters of needles: mp 60–61.5 °C; IR (KBr) 3050, 3005, 2810, 1720, 1590, 800, 760 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 9.47 (br, 1H), 7.31 (m, 8 H), 6.95 (s, 2 H), 4.63 (t, 1 H, J = 7.0 Hz), 2.85 (m, 2 H); mass spectrum, m/e 234.1042 (calcd for $C_{17}H_{14}O$, 234.1044).

2-(5*H*-Dibenz[*b*,*f*]azepin-5-yl)acetaldehyde (10). To a solution of 10.0 g (51.8 mmol) of **8** in 200 mL of dry dioxane under nitrogen was added 3.7 g (77 mmol) of sodium hydride (50% dispersion in oil). The slurry was refluxed for 1 h and treated with 12.0 mL (79.8 mmol) of bromoacetaldehyde diethyl acetal. The mixture was refluxed 20 h, cooled, and slowly treated with methanol until bubbling ceased. The red solution was partitioned between ether (3 × 200 mL) and water. The organic layer was dried with $MgSO_4$ and evaporated to give an oil. TLC and NMR showed essentially pure product **9**. A solution of this material in 220 mL of acetone/water (10/1) containing 1.2 g of *p*-toluenesulfonic acid was refluxed for 2.0 h. The mixture was partitioned between 10% $NaHCO_3$ and CH_2Cl_2 (3 × 200 mL), and the organic layer was washed with brine. After drying with Na_2SO_4 and evaporating, a green oil was obtained. Column chromatography on silica gel (CH_2Cl_2/hexanes, 1/1) gave a yellow oil, which was recrystallized from EtOAc/hexanes to give a total of 8.27 g (68% from **8**) of **10** as yellow cubic crystals: mp 68–70 °C; IR (KBr) 3020, 2830, 1735, 1590, 1485, 1460, 790, 765 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 9.49 (m, 1 H), 6.7–7.3 (m, 10 H), 4.36 (br, 2 H); mass spectrum,, m/e 235.0996 (calcd for $C_{16}H_{13}NO$, 235.0997).

***N*-[(5*H*-Dibenzo[*a*,*d*]cyclohepten-5-yl)methylene]methanamine *N*-Oxide (13).** To a slurry of 49.7 g (226 mmol) of aldehyde **4** and 24.8 g (298 mmol) of sodium acetate in 900 mL of ethanol was added 20.8 g (248 mmol) *N*-methylhydroxylamine hydrochloride. The slurry was stirred at ambient temperature for 1 h. The mixture was partitioned between 10% $NaHCO_3$ and CH_2Cl_2 (3 × 1000 mL). Drying (Na_2SO_4) followed by evaporation afforded 56.8 g (100%) of pure nitrone **13**: mp 195–198 °C (single crystal from CH_2Cl_2); IR (KBr) 3080, 3020, 2950, 1590, 1490, 1170 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 7.1–7.6 (m, 8 H), 6.99 (m, 3 H), 5.53 (d, 1 H, J = 7.0 Hz), 3.50 (s, 3 H); mass spectrum, m/e 249.1132 (calcd for $C_{17}H_{15}NO$, 249.1154). Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.07; N, 5.61. Found: C, 81.99; H, 6.06; N, 5.60.

3,3a,8,8a-Tetrahydro-1-methyl-3,8[1′,2′]-benzeno-1*H*-indeno[2,1-*c*]isoxazole (14). A slurry of powdered nitrone **13** (10.0 g, 40 mmol) in 830 mL of toluene was heated to reflux for 3.5 h. Dissolution occurred just below the boiling point. The toluene was evaporated at 1 mmHg and the remaining oil was chromatographed on silica gel (EtOAc/hexanes, 1/1, then pure EtOAc) to give 9.0 g (90%) of isoxazolidine **14** as a solid. Recrystallization from EtOAc/hexanes provided colorless cubes: mp 143–144 °C; IR (KBr) 3040, 2960, 1450, 990, 750, 735 cm^{-1}; NMR ($CDCl_3$), 90 MHz) δ 6.9–7.4 (m, 8 H), 5.08 (d, 1 H, J = 4.5 Hz), 4.0–4.4 (m, 3 H), 2.87 (s, 3 H); mass spectrum, m/e 249.1155 (calcd for $C_{17}H_{15}NO$, 249.1152). Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.07; N, 5.61. Found: C, 81.67; H, 6.07; N, 5.58.

2,3,3a,12b-Tetrahydro-2-methyl-3,8-methano-8*H*-dibenzo[*a*,*d*]isoxazolo[4,5-*f*]cycloheptane (15). To a solution of 15.7 g (67.0 mmol) of the aldehyde **7** in 350 mL of CH_2Cl_2 was added 6.04 g (72 mmol) of *N*-methylhydroxylamine hydrochloride followed by 9.0 mL of triethylamine. The mixture was stirred at ambient temperature for 72 h. After partitioning between 10% $NaHCO_3$ and CH_2Cl_2 (3 × 300 mL), the organic layer was dried (Na_2SO_4) and evaporated, leaving 18.2 g of a white solid. Column chromatography on silica gel (CH_2Cl_2, then EtOAc) gave 12.4 g (70%) of **15** as a white solid. Recrystallization from EtOAc/hexanes provided colorless cubes: mp 142–143 °C; IR (KBr) 3020, 2955, 2930, 2115, 1485, 1445, 770, 755, 745 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 7.1–7.4 (m, 8 H), 5.30 (d, 1 H, J = 7.0 Hz), 4.24 (t, 1 H, J = 7.0 Hz), 3.98 (m, 1 H), 3.48 (m, 1 H), 2.87 (s, 3 H), 2.33

(m, 2 H). Anal. Calcd for $C_{18}H_{17}NO$: C, 82.09; H, 6.51; N, 5.32. Found: C, 81.73; H, 6.43; N, 5.16.

***N*-[2-(5*H*-dibenzo[*b*,*f*]azepin-5-yl)ethylidene]methanamine *N*-Oxide (16).** To a solution of 2.51 g (10.6 mmol) of aldehyde **10** in 70 mL of methanol was added 15 mL of 10% $NaHCO_3$ followed by 1.1 g (13 mmol) *N*-methylhydroxylamine hydrochloride. This slurry was stirred at ambient temperture for 16 h. After partitioning between 10% $NaHCO_3/CH_2Cl_2$ (3 × 100 mL) and drying (Na_2SO_4), the solvent was evaporated to give 2.49 g (89%) of nitrone **16** as a yellow solid. Crystallization from EtOAc/hexanes provided yellow flakes of **16**: mp 138–139 °C; IR (KBr) 3100, 3060, 1610, 1545, 1485, 1200, 760 cm^{-1}; NMR ($CDCl_3$, 60 MHz) δ 7.1 (m, 8 H), 6.72 (s, 2 H), 6.57 (t, 1 H, *J* = 5.0 Hz), 4.73 (dd, 2 H, *J* = 5.0, 1.0 Hz), 3.48 (br, 3 H); mass spectrum, *m/e* 264.1262 (calcd for $C_{17}H_{16}N_2O$, 264.1262).

2,3,3a,12b-Tetrahydro-2-methyl-3,8-methano-8*H*-dibenzo[*b*,*f*]isoxazolo[4,5-*d*]azepine (17). A mixture of 2.49 g (9.4 mmol) of nitrone **16** and 40 mL of toluene was refluxed for 0.5 h (dissolution occurred upon heating). The toluene was removed at 1 mmHg and the remaining yellow oil was chromatographed on 30 g of silica gel (hexanes/EtOAc, 1/1) to give 2.17 g (87%) of isoxazolidine **17** as a colorless solid. Crystallization from EtOAc/hexanes gave colorless plates of **17**: mp 127–129 °C; IR (KBr) 2955, 2920, 1595, 1480, 770 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 7.1–7.4 (m, 8 H), 5.32 (d, 1 H, *J* = 7.0 Hz), 4.20 (t, 1 H), *J* = 7.0 Hz), 3.61 (m, 3 H), 2.85 (s, 3 H); mass spectrum, *m/e* 264.1245 (calcd for $C_{17}H_{16}N_2O$, 264.1262). Anal. Calcd for $C_{17}H_{16}N_2O$: C, 77.24; H, 6.10; N, 10.60. Found: C, 77.59; H, 6.31; N, 10.83.

1,2,3,3a,12b-Pentahydro-2-methyl-1-(1-oxo-2-phenylethyl)-3,8-methano-8*H*-dibenzo[*a*,*d*]cyclohepta[4,5-*f*]pyrazole (20). A solution of 0.442 g (1.89 mmol) of aldehyde **4** and 0.33 g (2.0 mmol) of *N*-(phenylacetyl)-*N'*-methylhydrazine in 20 mL of toluene was refluxed under N_2 into a Dean-Stark trap continuing 4-Å molecular sieves for 24 h. The toluene was evaporated, and the oil was chromatographed on silica gel (hexanes/EtOAc, 2/1), yielding 370 mg (52%) of an amorphous solid. Recrystallization from hexanes/EtOAc gave pyrazolidine **20** as colorless needles: mp 145–147 °C; IR (KBr) 3020, 2955, 2925, 1640, 1490, 1410, 755 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 7.58 (m, 1 H), 6.8–7.3 (m, 12 H), 5.48 (d, 1 H, *J* = 7.5 Hz), 3.3–4.3 (m, 5 H), 2.72 (s, 3 H), 2.33 (m, 1 H), 1.68 (m, 1 H); mass spectrum, *m/e* 380.1908 (calcd for $C_{26}H_{24}N_2O$, 380.1889).

Ethyl 1,2,3,3a,12b-Pentahydro-2-methyl-3,8-methano-8*H*-dibenzo[*a*,*d*]cyclohepta[4,5-*f*]pyrrole-3-carboxylate (23). A mixture of 2.15 g (9.19 mmol) of the aldehyde **7**, 1.70 g (11.0 mmol) of sarcosine ethyl ester hydrochloride (**21**), and 1.08 g (12.9 mmol) of sodium bicarbonate in 90 mL of toluene was refluxed for 48 h. The toluene was removed in vacuo, and the remaining oil chromatographed on silica gel (hexanes/EtOAc, 9/1) to give 1.75 g (57%) of pyrrolidine **23** as a clear oil: IR (KBr) 3060, 3015, 2925, 1727, 1590, 1485, 1445, 1180, 760 cm^{-1}; NMR ($CDCl_3$, 90 MHz) δ 6.9–7.3 (m, 8 H), 4.27 (q, 2 H, *J* = 7.5 Hz), 3.3–4.0 (m, 5 H), 2.50 (s, 3 H), 1.7–2.5 (m, 2 H), 1.35 (t, 3 H, *J* = 7.5 Hz); mass spectrum, *m/e* 331.1731 (calcd for $C_{22}H_{23}NO_2$, 333.1729).

***N*-(10,11-Dihydro-11-*syn*-hydroxy-5,10-enthano-5*H*-dibenzo[*b*,*f*]azepin-12-yl)methylamine (2; X = OH, Y = NHMe, *n* = 1).** A slurry of 30.0 g (113 mmol) of the isoxazolidine **17** and 90 g of zinc dust (Fisher) in 800 mL of acetic acid/water (1/2) was heated to 70 °C for 3 h with mechanical stirring. The mixture was made basic (pH 11) by adding 30% ammonium hydroxide while the temperature was kept below 50 °C with ice. The product was extracted with CH_2Cl_2 (3 × 1.0 L), and the organic layer was dried (Na_2SO_4) and evaporated to give 29.5 g (98%) of a light yellow solid. An analytical sample was obtained by recrystallization from EtOAc/hexanes, giving pure **2** (X = OH, Y = NHMe, *n* = 1): mp 145–146 °C; IR (KBr) 3310, 3070, 2920, 2860, 2800, 1480, 1025; NMR ($CDCl_3$, 90 MHz) δ 7.0–7.6 (m, 8 H), 4.92 (d, 1 H, *J* = 4.0 Hz), 3.1–4.05 (m, 5 H), 2.53 (s, 3 H); mass spectrum, *m/e* 266.1433 (calcd for $C_{17}H_{18}N_2O$, 266.1419). Anal. Calcd for $C_{17}H_{18}N_2O$: C, 76.66; H, 6.81; N, 10.52. Found: C, 76.27; H, 6.77; N, 10.41.

***N*-(10,11-Dihydro-11-*syn*-hydroxy-5,10-ethano-5*H*-dibenzo[*a*,*d*]cycloheptan-12-yl)methylamine (1; X = OH, Y = NHMe, *n* = 1).** A slurry of 12.2 g (46.3 mmol) of the isoxazolidine **15** and 13.6 g of zinc dust in 500 mL of acetic acid/water (1/2) was heated to 70 °C for 2 h with mechanical stirring. With use of the same workup as with amino alcohol **2**, 12.4 g (100%) of a colorless, amorphous solid was obtained. Crystallization from EtOAc/hexanes provided colorless crystals of **1** (X = OH, Y = NHMe, *n* = 1): mp 128–129 °C; IR (KBr) 3320, 3050, 3010, 2915, 2895, 2850, 1470, 1025, 740 cm^{-1}; NMR ($CDCl_3$ 80 MHz) δ 7.53 (m, 1 H), 7.2 (m, 7 H), 5.05 (dd, 1 H, *J* = 4.5, 1.0 Hz), 3.85 (m, 2 H), 2.7–3.4 (m, 2 H), 2.57 (s, 3 H), 2.03 (ddd, 1 H, *J* = 14, 6.5, 1.0 Hz); mass spectrum, *m/e* 265.1442 (calcd for $C_{18}H_{19}NO$, 265.1467). Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.10; H, 7.07; N, 5.18.

***N*-(10,11-Dihydro-11-*syn*-hydroxy-5,10-methano-5*H*-dibenzo[*a*,*d*]cycloheptan-12-yl)methylamine (1; X = OH, Y = NHMe, n = 0).** A slurry of 20.0 g (80.3 mmol) of the isoxazolidine **14** and 22.4 g of zinc dust in 900 mL of acetic acid/water (1/2) was heated to 70 °C for 2 h as in the previous examples. Workup as before afforded 20.2 g (100%) of **1** (1; X = OH, Y = NHMe, *n* = 0) as a white, amorphous solid. Crystallization from hexanes/EtOAc gave colorless crystals: mp 210–212 °C; IR (KBr) 3325, 2920, 2880, 1480, 1470, 1040, 765 cm^{-1}; NMR ($CDCl_3$, 80 MHz) δ 7.0–7.4 (m, 8 H), 4.54 (m, 1 H), 3.6–4.0 (m, 3 H), 2.70 (br, 2 H), 3.01 (s, 3 H); mass spectrum, *m/e* 251.1294 (calcd for $C_{17}H_{17}NO$, 251.1310). Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.83; N, 5.46. Found: C, 81.09; H, 6.82; N, 5.57.

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Registry No. 1 (X = OH; Y = NHMe; *n* = 0), 86569-05-3; 1 (X = OH; Y = NHMe; *n* = 1), 86569-06-4; 2 (X = OH; Y = NHMe; *n* = 1), 86584-10-3; **3**, 6372-67-4; **4**, 1605-13-6; **5**, 1643-43-2; **6**, 24330-12-9; **7**, 86569-07-5; **8**, 256-96-2; **9**, 80224-75-5; **10**, 80224-76-6; *syn*-**3**, 86569-08-6; *anti*-**13**, 86569-15-5; **14**, 86569-09-7; **15**, 86569-10-0; **16**, 86569-11-1; **17**, 86569-12-2; **18**, 1199-86-6; **20**, 86569-13-3; **21**·HCl, 52605-49-9; **23**, 86569-14-4; 9,10-dihydro-9,10-ethenoanthracene, 30521-30-3; 5*H*-dibenzo[*a*,*d*]cyclohepten-5-ol, 10354-00-4; malonic acid, 141-82-2; (5*H*-dibenzo[*a*,*d*]cycloheptene-5-yl)malonic acid, 1796-78-7; bromoacetaldehyde diethyl acetal, 2032-35-1.