NH_4Cl (200 μL), stirred an additional 0.5 h, filtered, and dried over anhydrous $MgSO_4$. The solvent was removed and the oil was purified by preparative GLC to yield 13 mg (0.08 mmol) of a colorless oil (73%): $[\alpha]_D$ −2.48° (c 0.013, $CHCl_3$); IR (neat) 3320, 1470, 1390, 1370, 1030, 915, and 745 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.80–0.93 (12 H, $-CH_3$), 1.00–1.85 (8 H, m), and 3.48 (2 H, m).

$LiAlH_4$ Reduction of the 2*R*,3*S* Ester 6a. The ester (30 mg, 0.16 mmol) was reduced as above to yield a clear oil (94%): IR (neat) 3340, 1465, 1380, 1360, 1250, 1020, and 790 cm^{-1}; ^1H NMR ($CDCl_3$, 90 MHz) δ 0.80–0.93 (12 H, $-CH_3$), 1.00–1.85 (8 H, m), and 3.47 (2 H, m).

Epimerization of Lactone A (11). The lactone (20 μL), 2 mL of MeOH, and 3 mL of 10% NaOH were refluxed for 1 h. The mixture was acidified with dilute HCl and extracted with Et_2O (3 × 5 mL), and the combined organic layers were dried over anhydrous $MgSO_4$. Concentration in vacuo followed by GLC analysis revealed two components with retention times of 24.1 and 27.3 min (38 ft Tween-80) corresponding to lactones A and B, respectively.

Epimerization of Lactone Mixture B/B′ (12 and 14). The same procedure as above was followed. The GLC coinjection studies and GC/MS data were consistent with the formation of lactones A (24.1 min) and C (32.6 min).

Epimerization of Lactone C (13). The same epimerization procedure was followed, and the GLC coinjection studies and GC/MS data verified the observation that lactone B′ (27.9 min) was produced.

$LiAlH_4$ Reduction of Lehi Lactone B (12). The lactone (90 mg, 0.54 mmol) was dissolved in anhydrous Et_2O and added dropwise to a stirred solution of $LiAlH_4$ (15 mg, 0.39 mmol) in Et_2O. After 1 h the reaction was quenched with excess $Na_2SO_4 \cdot 10H_2O$ and allowed to stir an additional 0.5 h. The solution was filtered and concentrated to yield 112 mg of an oil.

Hydrogenolysis of the Crude Diol. To a solution of the previous product (112 mg) in 30 mL of MeOH and 1 mL of 10% $HClO_4$ was added 60 mg of Pd/C (5%), and the mixture shaken for 24 h under 10 psi H_2. The mixture was filtered, taken up in pentane, and concentrated to yield 59 mg of an oil. Preparative GLC purification yielded 9.6 mg (0.06 mmol) of the desired alcohol **9** (11% from **12**). The alcohol was 85% pure by analytical GLC: $[\alpha]_D$ +25.9° (c 0.096, $CHCl_3$); ^1H NMR ($CDCl_3$, 90 MHz) δ 0.80–1.08 (12 H, $-CH_3$), 1.15–1.85 (7 H, m), 2.13 (1 H, s), 3.50 (2 H, m).

Epimerization of Lactone B (12). The same general epimerization procedure was followed as for lactone A. The appearance of lactone A (24.1 min) was supported by GLC coinjection studies and GC/MS data.

^1H NMR Nonequivalence Studies. Price lactone A (**11**; 24 mg, 0.145 mmol), (*S*)(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol (120 mg, 0.435 mmol), and 0.73 mL of CCl_4 were placed in a 5-mm NMR tube and the spectrum was recorded. Lehi lactone A (**11**; 14 mg, 0.084 mmol), (*S*)(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol (70 mg, 0.254 mmol), and 0.42 mL of CCl_4 were placed in a 5 mm NMR tube and the spectrum was recorded after the shift reagent was completely dissolved.

Acknowledgment. We express appreciation to the National Institutes of Health (GM 20196) for financial support of this research.

Registry No. 7a, 70898-15-6; **7b**, 70898-16-7; (2*S*,3*R*)-**8**, 70954-03-9; (2*R*,3*R*)-**8**, 66428-33-9; **9a**, 66321-21-9; **9b**, 66321-17-3; **11**, 70898-17-8; **12**, 70898-18-9; **13**, 70898-19-0; **14**, 70898-20-3.

Transannular Reactions of Dibenzo[*a*,*d*]cycloalkenes. 1.[1a] Synthesis of Dibenzo[*a*,*d*]cycloocten-6,12-imines and Dibenzo[*a*,*d*]cyclohepten-5,10-imines

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A strategy for the synthesis of dibenzo[*a*,*d*]cycloocten-6,12-imines based on the initial construction of a hydrocarbon framework containing the appropriate functionality for transannular nitrogen ring closure was developed. The key to this approach was the synthesis of the symmetrical diketone, 5,6,7,12-tetrahydrodibenzo[*a*,*d*]cyclooctene-6,12-dione (**15**). Reductive amination of **15** occurred regioselectively at the 6 position giving rise directly to the dibenzocycloocten-6,12-imine ring system by transannular carbinolamine formation. The diketone **15** was converted through the oxime **26** to the hydroxylamine **28**. Thermal cyclization of **28** to **29** established a second transannular route to the dibenzo[*a*,*d*]cycloocten-6,12-imines. This latter method also was used successfully for the synthesis of 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5,10-imines. The proximity of functional groups at the 6 and 12 positions of dibenzo[*a*,*d*]cyclooctanes which favored nitrogen bridging reactions also promoted other transannular reactions such as the facile conversion of **26** to **27**.

A number of heterocyclic molecules of medicinal interest contain a tricyclic hydrocarbon framework with a nitrogen-bridged central ring flanked by two aromatic rings to form at least one benzhydryl bridgehead carbon (Figure 1).[1a-e] The simplest construction of this type and the only one with two such carbons is 9,10-dihydroanthracen-9,10-imine. Recently, we described a broad analysis of the cycloaddition approach to this heterocycle.[1b] The next higher homologue, 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5,10-imine,[1c-d] has received limited attention in the literature and the larger 5,6,7,12-tetrahydrodibenzo[*a*,*d*]cycloocten-6,12-imines have not been reported. Described here are efficient syntheses of both of these ring systems. In each case the strategy was to construct the required hydrocarbon framework containing the appropriate functionality for subsequent transannular nitrogen ring closure. The methods set forth below were developed

(1) (a) Part 2: B. E. Evans, P. S. Anderson, M. E. Christy, C. D. Colton, D. C. Remy, K. E. Rittle, and E. L. Engelhardt, *J. Org. Chem.*, following paper in this issue; (b) P. S. Anderson, M. E. Christy, C. D. Colton, W. Halczenko, G. S. Ponticello, and K. L. Shepard, *ibid.*, **44**, 1519 (1979); (c) Roussel Uclaf, U.S. Patent 3 892 756 (1975); (d) J. H. Dygos, *J. Heterocycl. Chem.*, **13**, 1355 (1976); (e) D. C. Remy, P. S. Anderson, M. E. Christy, and B. E. Evans, *J. Org. Chem.*, **43**, 4311 (1978).

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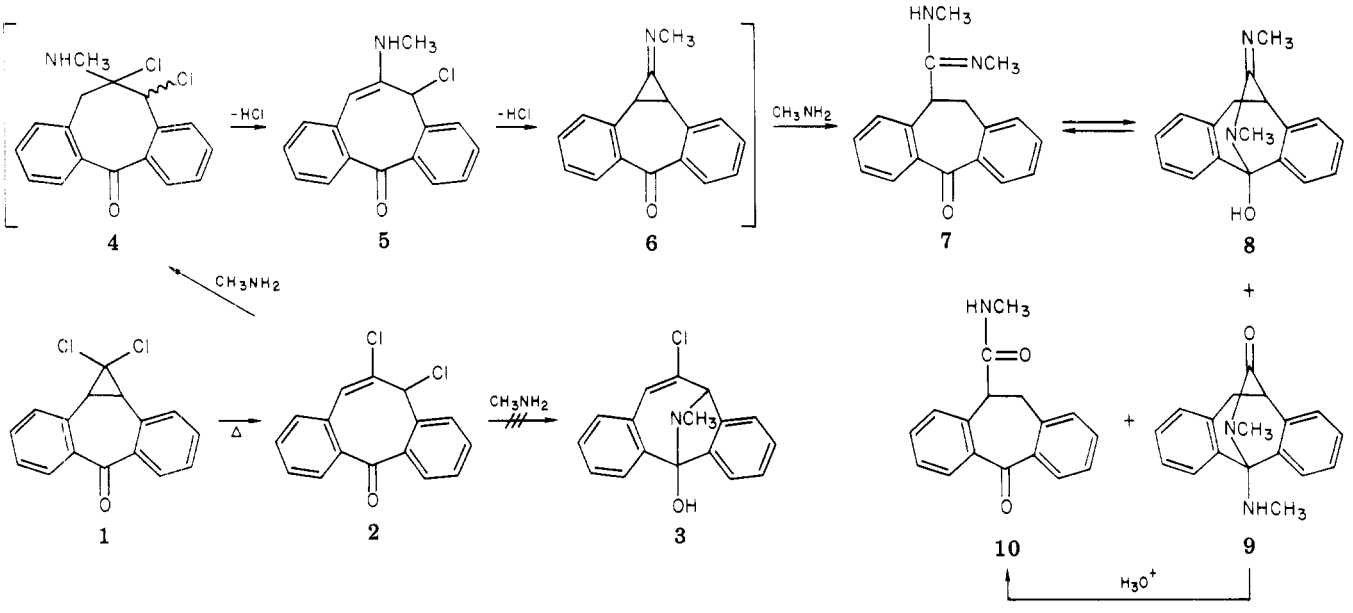
Scheme I



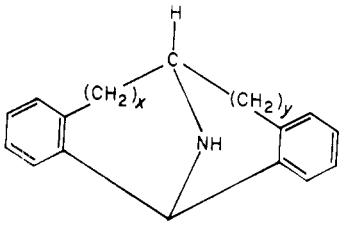


Figure 1. (a) 9,10-Dihydroanthracen-9,10-imine ($x = y = 0$); (b) 10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5,10-imine ($x = 0, y = 1$); (c) 5,6,7,12-tetrahydrodibenzo[*a*,*d*]cycloocten-6,12-imine ($x = y = 1$).

to avoid stereochemical complications and to ensure regioselectivity where appropriate.

Reactions of 2 with Methylamine (Scheme I). Recently, we described some thermal rearrangement reactions of 8,8-dichloro-2,3:5,6-dibenzobicyclo[5.1.0]octane derivatives.[1e] The thermolysis of **1** was an excellent source of **2**, a compound which contains the carbon skeleton needed for the dibenzo[*a*,*d*]cyclooctenimines. However, attempts to directly elaborate **2** to a nitrogen-bridged structure of this type were unsuccessful. The benzylic chloride in **2** was surprisingly unreactive and did not undergo displacement with methylamine to yield **3**. Although the double bond in **2** proved to be a Michael acceptor for primary amines, the end result of this process was a collapse of the central ring in **2** from eight to seven members. This led to mixtures of **7–10** with the composition being dependent on the reaction conditions.

Treatment of **2** with aqueous methylamine in THF at room temperature gave mainly **8** (50%) accompanied by a small amount of **10**. Liquid methylamine in a pressurized container at 80 °C converted **2** to a mixture in which **9** was the major component and **8** was a minor product. Recognizing that **8–10** might exist as either ring or chain tautomers or as an equilibrating mixture, we interpreted the following spectral data as supportive of the indicated structural assignments. Comparison of the carbonyl region of the IR spectra of **8** and **9** showed the amidine absorption at 1610 cm^{-1} in **8** and the amide carbonyl peak at 1650 cm^{-1} in **9**. The mass spectral fragmentation of **8** supported the contention that oxygen was attached to the hydrocarbon framework (*m*/*e* 208 and 207) and that both nitrogen atoms were in the bridging group (*m*/*e* 71). In contrast, the fragments of **9** suggested that nitrogen was attached to the hydrocarbon framework (*m*/*e* 221 and 220) and that the bridge contained nitrogen and oxygen (*m*/*e* 58 and 57). The ^1H NMR spectra of both **8** and **9** showed the expected pattern for the ethylene bridge protons of a dibenzo[*a*,*d*]cycloheptene system. In addition, the ^1H NMR spectral data for **9** were comparable to the published spectra of *N*-methyl-10,11-dihydro-5,10-iminomethano-5*H*-dibenzo[*a*,*d*]cyclohepten-12-one.[2a]

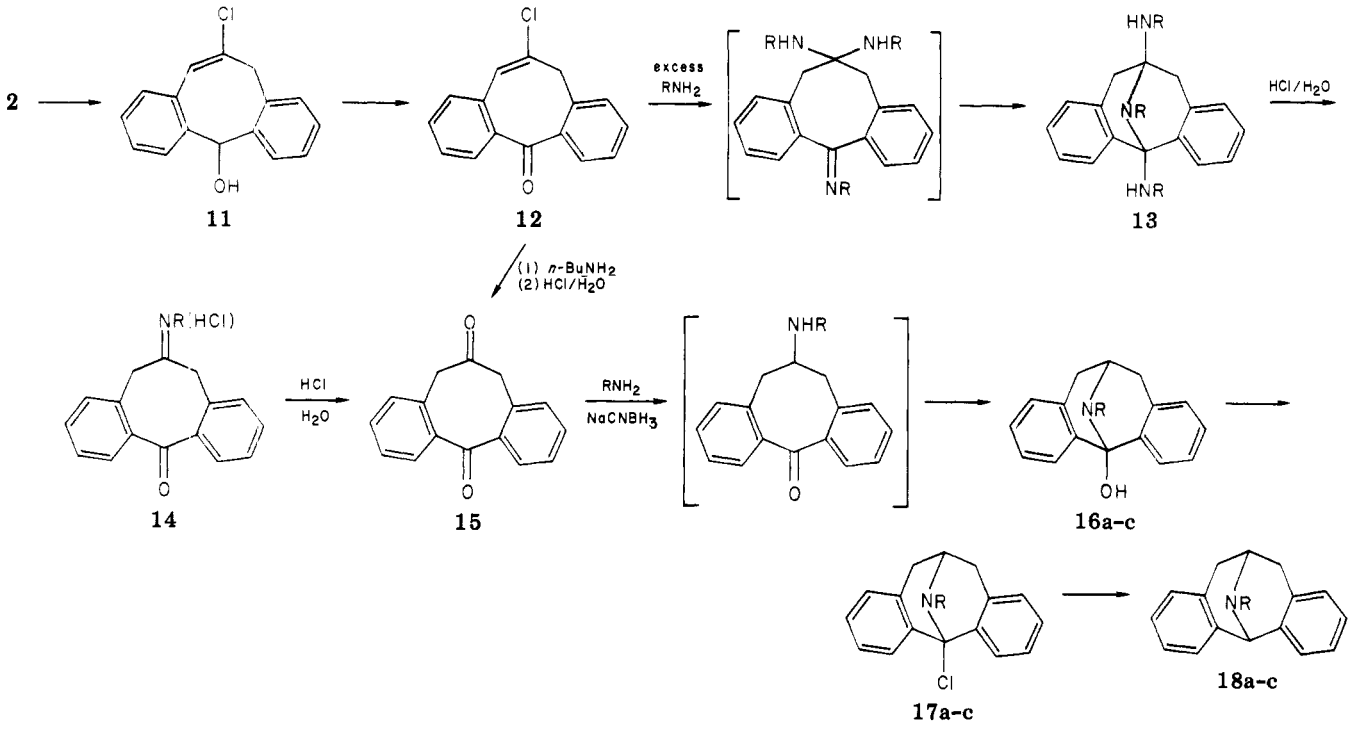
Finally, it was the ^{13}C NMR spectra that provided convincing evidence that these structural assignments were correct. In addition, these spectral data answered the ring–chain tautomer question. Thus, the ^{13}C NMR spectrum of **9** contained 18 lines, including ones at 78 (C-5) and 174 ppm (C=O), indicating the assigned ring tautomer structure. In contrast, the ^{13}C NMR spectrum of **8** contained 36 lines, suggesting a tautomeric equilibrium between **7** and **8** in solution (D_2O/DCl). This equilibrium was shifted toward **7** by added acid, allowing the resonances associated with **7** to be distinguished from those of **8**. The key peaks for **8** appeared at 86.1 (C-5) and 165 ppm (C=N) while those for **7** were at 197.5 (C-5) and 166.7 ppm (C=N). These and the remaining ^{13}C NMR spectral assignments which are listed in the Experimental Section indicated that **8** has the ring tautomer structure and **7** is the chain tautomer. It should be noted that a comparison of the resonances for C-5 in **9** (78 ppm) and **8** (86.1 ppm) supports the concept that the former structure has two nitrogens attached to this center while the latter has one nitrogen and one oxygen.

While the IR, ^1H NMR, and mass spectral data for **10** were consistent with this known structure,[2b] it was again the ^{13}C NMR spectrum which confirmed that **10** was a chain tautomer. As indicated in the Experimental Section, this spectrum contained 17 lines including a resonance at 193.8 ppm showing that C-5 was a carbonyl carbon. The above structural assignments are consistent with the observation that **9** is more readily hydrolyzed to **10** by acid than is the case with **7** ⇌ **8**.

The foregoing results suggested a common pathway for the reaction of **2** with methylamine under both sets of conditions. This can be rationalized (Scheme I) on the basis of an initial addition of methylamine to the polarized

(2) (a) G. N. Walker, D. Alkalay, A. R. Engle, and R. J. Kempton, *J. Org. Chem.*, 36, 466 (1971); (b) G. N. Walker, U.S. Patent 3812119 (1974).

Scheme II



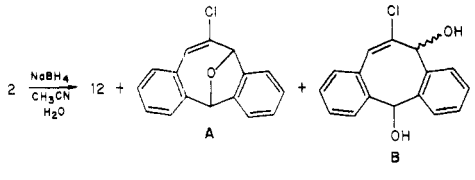
a, R = CH_3
b, R = $CH_2C_6H_5$
c, R = H

olefinic linkage of **2** to provide **4** which then undergoes two dehydrohalogenations. The second of these (**5** → **6**) is a Favorski-type reaction which has been reported in similar systems.[3] The mixture **7** ⇄ **8** and **10** observed with aqueous methylamine results from addition of methylamine or water, respectively, to **6**. Partial conversion of the benzophenone carbonyl in **6** to a Schiff base by liquid methylamine under pressure would generate water which could account for the product mixture (**7** ⇄ **8** and **9**) observed under these conditions.

Synthesis of Dibenzo[*a*,*d*]cycloocten-6,12-imines (Scheme II). The above reactions and the apparent high reactivity of the 6,7 double bond in **2** suggested that if the benzylic halide were removed, the resulting structure **12** would be ideally functionalized for elaboration of the dibenzo[*a*,*d*]cycloocten-6,12-imines. Lithium aluminum hydride reduction of **2** gave the carbinol **11** which was oxidized with Jones' reagent to the monochloro ketone **12**.[4] The enone **12** failed to react with aqueous methylamine at room temperature; however, heating with anhydrous methylamine under pressure gave the labile bridged imine **13** as demonstrated by ^{1}H NMR analysis (3 NCH_3 groups at δ 1.97, 2.27, and 2.43). Cold acid hydrolysis of **13** gave the ketimine **14** which on further hydrolysis afforded the 6,12-diketone **15**. As in the case of the dichloro ketone **2**, this sequence appears to stem from an initial addition of methylamine to the 5,6 olefinic bond of **12**. In this situation, Schiff base or enamine formation by dehydrohalogenation followed by addition of methylamine to this intermediate would establish the pathway for transannular ring closure to **13**. Apparently, the benzophenone carbonyl must be converted to a Schiff base under the reaction conditions prior to ring closure. Since the amine moieties are lost during the hydrolysis step, a more convenient synthesis of **15** was realized by using refluxing butylamine for the first step followed by acid hydrolysis without isolation of the intermediates. The difference in reactivity of the two carbonyl groups in the diketone **15** made it an ideal precursor for the symmetrical dibenzo[*a*,*d*]cyclooctenimine ring system. Reductive amination of **15** with methylamine under modified Borch conditions[5] regioselectively replaced the 6-keto group with a methylamine functionality. This intermediate spontaneously cyclized to the 6,12-imino-bridged carbinol **16a**. This result had been anticipated from entropy considerations based on inspection of molecular models.[6] The spectral data for **16a** supported the assigned structure. Thus, the ^{1}H NMR spectrum contained the lines for the expected three-spin system comprised by the bridgehead proton and the nonequivalent methylene protons at C-5 and C-7 (H_{5x} and H_{7x} are identical as are H_{5n} and H_{7n}). In the mass spectrum, the M^+ appeared at m/e 251 and the IR spectrum exhibited OH at 3420 cm^{-1} and no carbonyl absorptions. Removal of the bridgehead hydroxyl group was accomplished in two steps via conversion to the chloride **17a** with thionyl chloride followed by lithium aluminum hydride reduction to yield the unsubstituted 6,12-imine **18a**. The three N substituents (R = CH_3, CH_2Ph, H) examined in this sequence indicate its general

(3) E. Jongejan, H. Steinberg, and Th. J. deBoer, *Tetrahedron Lett.*, 397 (1976), and other references cited therein.

(4) Reduction of **2** to **12** could also be accomplished by using sodium borohydride under strictly anhydrous conditions.



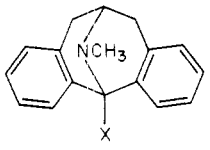
In the presence of water, sodium borohydride reduction of **2** led to the contamination of **12** with the byproducts A and B.

(5) R. F. Borch, M. D. Bernstein, and H. D. Durst, *J. Am. Chem. Soc.*, 93, 2897 (1971).

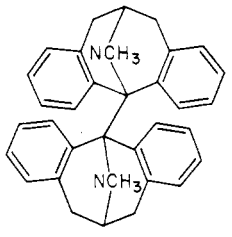
(6) J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, 738 (1976).

scope with overall yields of the imines 18 ranging from 35 to 65%.

Preparation of 12-Alkyldibenzo[a,d]cycloocten-6,12-imines. A. From Bridgehead Halides. Since nitrogen-bridged structures having a quaternary bridgehead center are difficult to synthesize, the question of whether or not 17 could serve as an intermediate to this end was investigated. Attempted coupling of **17a** with either methyl Grignard or methyllithium gave no detectable alkylation. A reduction product, the unsubstituted imine **18a**, was the only material isolated. The bromide **19** was prepared from **16a** with phosphorus tribromide.



19, X = Br
20, X = n-C_4H_9
22, X = C_2H_5
23, X = OCH_3



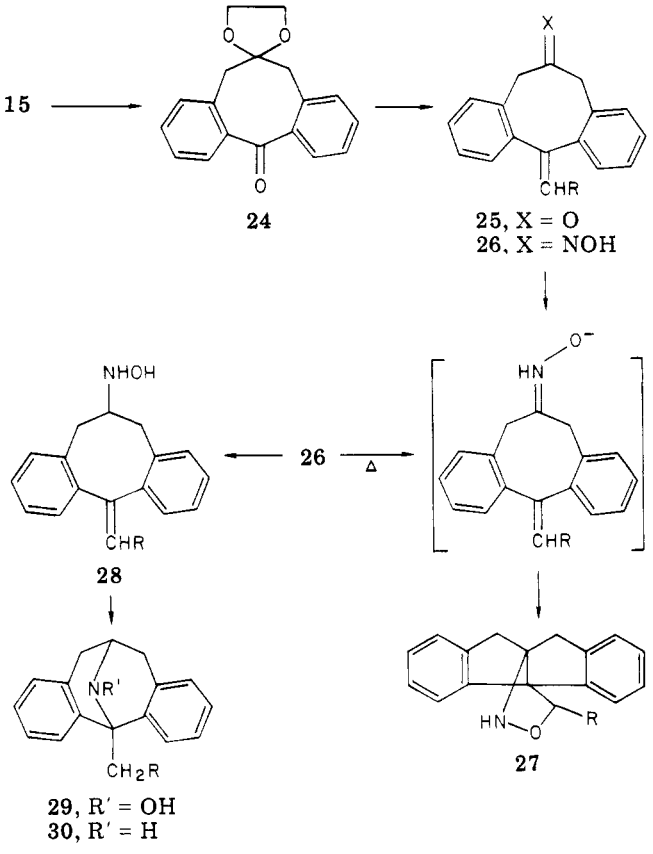
21

Treatment of **19** with methyllithium also yielded **18a**, but with n-butyllithium, the production of the bridgehead butyl derivative **20** was demonstrated clearly by the spectral data (see Experimental Section). The major product of this reaction, however, was the dimer **21**. When **19** was treated with ethyllithium, a low yield of the bridgehead ethyl derivative **22** was realized, accompanied by the dimer **21**. These data suggest a radical mechanism for the reactions of the bridgehead halide derivatives with alkyllithiums.

A substitution reaction of **19** that proceeded cleanly was that with sodium methoxide in refluxing methanol, producing the bridgehead methoxy derivative **23** in excellent yield. This result is consistent with the reported facile solvolysis of the bridgehead chloride in the analogous imino-bridged cyclooctane derivative 1-chloro-9-methyl-9-azabicyclo[3.3.1]nonane.[7]

B. Via Cyclization of Unsaturated Hydroxylamines (Scheme III). The recently reported[8] cyclization of certain unsaturated hydroxylamines suggested an attractive alternative approach to the 12-alkyldibenzo-[a,d]cycloocten-6,12-imines. As expected, the diketone **15** was converted selectively to the keto ketal **24** on treatment with ethylene glycol in the usual way. Addition of methyllithium to the remaining carbonyl group followed by warming with aqueous acid, which served both to dehydrate the newly formed tertiary alcohol and to remove the carbonyl protecting group, gave the keto olefin **25a** in high yield. The attempted conversion of **25a** to an oxime under conventional conditions (hydroxylamine hydrochloride, pyridine, refluxing ethanol) gave instead a product which was identified as the pentacyclic isoxazolidine **27a**. While elemental and mass spectral analysis showed that **27a** and **26a** had the same composition, the ^1H NMR spectrum of **27a** was definitive for this structure. Thus, the methylene group between O and C was a singlet (δ 4.20) and the benzylic methylene groups were identical, with the geminal protons nonequivalent (doublets at δ 3.23 and 3.33 with J = 18 Hz). The formation of this compound with an indeno[1,2-a]indene backbone was subsequently shown to be a base-catalyzed thermal reaction of the oxime **26a** which was prepared from **25a** under milder conditions

Scheme III



a, R = H
b, R = CH_3

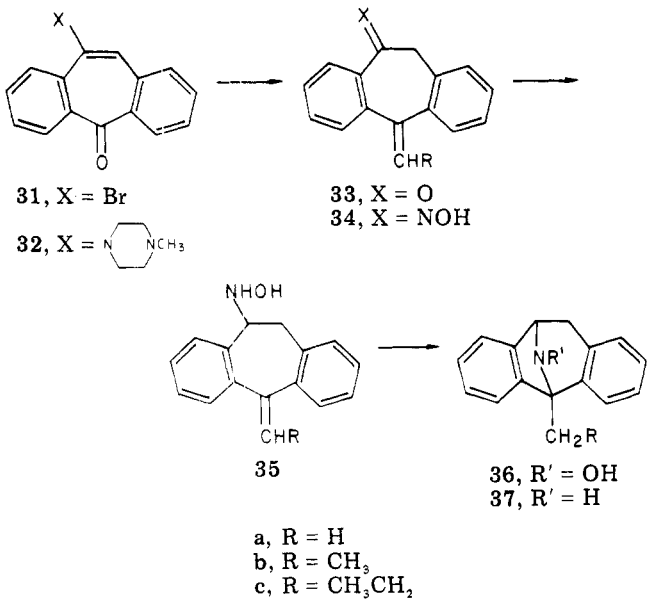
(hydroxylamine hydrochloride, sodium acetate, moist ether at room temperature). The oxime **26a** was converted easily to **27a** on warming to 75 °C in toluene for 3 h or more readily, and at lower temperature, on addition of a few drops of pyridine. These results are best understood in terms of an intramolecular 1,3-dipolar cycloaddition of an intermediate nitrone to the methylene group. Although intramolecular nitrone–olefin cycloadditions are well documented,[9] we believe this to be the first reported example of an oxime following this pathway.[10] Inspection of molecular models revealed that such a process would be entropically favored by the proximity of the reaction centers.[6]

Preparation of **26a** under the milder conditions surmounted these difficulties and allowed the synthesis (Scheme III) of the 12-methyldibenzo[a,d]cycloocten-6,12-imine **30a** to proceed uneventfully through reduction of the oxime **26a** to the hydroxylamine **28a**, subsequent thermal cyclization of this intermediate, and finally reductive removal of the NOH group from **29a**.[8] The rapid, highly efficient ring closure observed with **28a** was favored by a conformation of this molecule which placed the hydroxylamine and olefin functionalities in close proximity. Similar results were obtained when this series of reactions was repeated with the ethylidene ketone **25b**.

Synthesis of 5-Alkyldibenzo[a,d]cyclohepten-5,10-imines (Scheme IV). Two transannular ring closure

(7) H. O. Krabbenhoft, J. R. Wiseman, and C. B. Quinn, *J. Am. Chem. Soc.*, **96**, 258 (1974).
(8) H. O. House and L. F. Lee, *J. Org. Chem.*, **41**, 863 (1976).
(9) For a recent review see W. Oppolzer, *Angew. Chem., Int. Ed. Engl.*, 16, 10 (1977).
(10) The intermolecular addition of formaldoxime and the oximes of benzophenone, acetone, and cyclohexanone to Michael acceptors by a 1,3-dipolar mechanism involving the nitronic tautomer of the oxime has been reported: M. Ochiai, M. Obayashi, and K. Morita, *Tetrahedron*, **23**, 2641 (1967); A. LaBlache-Combier and M. L. Villaume, *ibid.*, **24**, 6951 (1968); E. Winterfeldt and W. Krohn, *Angew. Chem., Int. Ed. Engl.*, **6**, 709 (1967).

Scheme IV



routes to dibenzo[a,d]cyclohepten-5,10-imines have been described.[1c,d] Due to the solvolytic lability of benzhydrylamines[11] and the propensity of tertiary benzhydryl halides and tosylates toward elimination reactions, the applicability of either of these methods to the synthesis of 5-alkyldibenzo[a,d]cyclohepten-5,10-imines (**37**) is severely limited. Since the regioselective transannular addition of an amine to an exocyclic olefin described above avoided these problems, its usefulness in the synthesis of this ring system was explored.

The required olefinic ketone **33a** was prepared from commercial 10-bromo-5*H*-dibenzo[a,d]cyclohepten-5-one (**31**) by initial conversion to the enamino ketone **32** followed by addition of methyllithium to the carbonyl. Subsequent acid hydrolysis served to effect both the dehydration of the tertiary alcohol and the generation of the 10-ketone functionality. The remaining steps (conversion to the oxime **34a**, reduction to the hydroxylamine **35a**, thermal cyclization to **36a**, and reductive removal of the NOH to yield **37a**) all occurred smoothly as described in the Experimental Section. It should be pointed out that the choice of the enamino ketone **32** for this synthesis was important. Other enamino ketones on addition of methyllithium gave tertiary carbinols which on exposure to acid were converted to bridged ring ethers, species much more resistant to acid hydrolysis to the desired olefinic ketones **33**. Furthermore, for the synthesis of higher homologues (ethylidene and propylidiene) of **33**, the Wittig procedure was used to avoid the competing carbonyl reduction reaction which was observed with the ethyl and propyl Grignard and lithium reagents.[12] Lastly, in this case, intramolecular cyclization reactions of the oximes **34** were not observed. Inspection of molecular models showed that the oxime and exocyclic olefin groups are not in close proximity in **34**. It is only after reduction to the hydroxylamine **35** that the reactive centers approach each other. Again it is this proximity which accounts for the highly efficient, regioselective transannular ring closure of **35**.

(11) J. Nally, J. Nazareno, J. Polesuk, and H. V. Maulding, *J. Pharm. Sci.*, **64**, 437 (1975).

(12) Although the desired olefinic ketones could be prepared by this method, the yield was less than 20% and the product was a mixture of geometric isomers. The Wittig reaction occurred in excellent yield and was highly regioselective for one of the isomers. ^{1}H NMR spectral studies with shift reagents did not conclusively establish the structure of this isomer.

Summary

Synthetic approaches to dibenzo[a,d]cycloocten-6,12-imines with and without a functionalized benzhydryl bridgehead position have been described. The synthesis of 5-alkyldibenzo[a,d]cyclohepten-5,10-imines has been outlined. Routes to the intermediates necessary in the accomplishment of these goals have been set forth. The intermediates were selected to establish a unifying strategy of regioselective transannular nitrogen ring closure as the key step in these constructions. An unusual intramolecular oxime–olefin cycloaddition resulting in the collapse of a 6,12-disubstituted dibenzo[a,d]cyclooctene into an indeno[1,2-a]indene has been recognized.

Experimental Section

Melting points (Thomas-Hoover melting point apparatus) and boiling points are uncorrected. Spectra were obtained as follows: IR spectra on a Perkin-Elmer 237 spectrophotometer; mass spectra on an AEI MS 902 spectrometer by direct insertion; ^{1}H NMR spectra on a Varian T-60 or EM 390 spectrometer, using $(CH_3)_4Si$ as an internal standard; and ^{13}C NMR spectra on a Varian CFT-20 spectrometer. Analytical TLC was carried out on 250 μm, 5 × 20 cm, silica gel GF plates (Analtech, Inc.), using ultraviolet light and Dragendorff spray for visualization.

Reaction of 2 with Aqueous Methylamine. A solution of **2** (2.88 g, 0.01 mol) and 40% aqueous methylamine (10 mL) in THF (100 mL) was stirred at 27 °C for 24 h. The solvent was removed under reduced pressure. The residue was slurried in 0.6 N aqueous hydrochloric acid (200 mL) and extracted with ether (2 × 100 mL). The pH of the aqueous solution was adjusted to 10 with 20% aqueous NaOH, and the resulting mixture was extracted with chloroform (3 × 100 mL). The combined chloroform extracts were dried over Na_2SO_4 and filtered, and the filtrate was evaporated to dryness. The crystalline residue was recrystallized from acetonitrile to yield 1.4 g (50%) of **8**: mp 217–218 °C; ^{1}H NMR (Me_2SO-d_6 + DCl) δ 2.90 (br d, 1 H, benzylic, J = 19 Hz), 3.13 (s, 3 H, NCH_3), 3.27 (s, 3 H, NCH_3), 3.57 (dd, 1 H, benzylic, J = 19 Hz, J = 3 Hz), 5.0 (m, 1 H, bridgehead), 5.60 (br s, 1 H, OH), 7–7.9 (m, 8 H, aromatic); MS *m/e* (%) 278 (11, M^+), 249 (9), 248 (17), 208 (18), 207 (15), 179 (8), 178 (23), 72 (42), 71 (100); IR (KBr) 3425 (OH), 1610 (C=NCH_3) cm^{-1}; ^{13}C NMR (D_2O + DCl) δ 28.0 (C-11 in **8**), 28.2 (C-11 in **7**), 29.9 (C-10 in **7**), 30.3 (C-10 in **8**), 32.3 (NCH_3 in **8**), 34.1 (NCH_3 in **7**), 37.6 (NCH_3 in **8**), 44.6 (NCH_3 in **7**), 86.1 (C-5 in **8**), 121.1, 122.6, 126.1, 128.0, 128.7, 128.9, 129.1, 129.6, 130.1, 130.9, 131.3, 131.4, 133.1, 134.3, 135.6, 137.5, 139.2, 141.3, 165.0, 166.7 (aromatic, **7** and **8**), 197.5 (C-5 in **7**).

Anal. Calcd for $C_{18}H_{18}N_2O$: C, 77.68; H, 6.51; N, 10.06. Found: C, 77.39; H, 6.71; N, 9.96.

The above ether extract on evaporation gave 0.8 g of **10**: mp 212–213 °C (lit.[2b] mp 212–213 °C); MS *m/e* (%) 265 (92, M^+), 208 (49), 207 (100), 193 (14), 179 (17), 178 (41), 58 (12); IR (KBr) 3450 (NH), 1675, 1660 (C=O), 1645 (C=O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.36 (d, 3 H, NCH_3, J = 3 Hz), 3.82 (m, 2 H, benzylic), 4.00 (m, 1 H, H-10), 5.10 (br s, 1 H, NH), 7.1–8.15 (m, 8 H, aromatic); ^{13}C NMR (Me_2SO-d_6) δ 25.6 (C-11), 37.7 (C-10), 49.7 (NCH_3), 126.5, 127.0, 128.7, 129.2, 130, 130.3, 132, 132.3, 137.5, 138.5, 139.2, 139.9 (aromatic), 171.2 (amide C=O), 193.8 (C-5).

Reaction of 2 with Anhydrous Methylamine. The ketone **2** (25.0 g, 0.0865 mol) and methylamine (180 mL) were heated in a glass-lined bomb at 80 °C for 12 h. After the bomb was cooled and vented, the remaining methylamine was removed under reduced pressure. The residual solid was triturated with ether and filtered, and the filtrate was discarded. The precipitate was triturated with chloroform and filtered. Evaporation of the filtrate left 23.3 g of light brown solid, mp 167–172 °C, that was recrystallized twice from toluene, filtering from insoluble material, to yield 9.0 g (37%) of **9**: mp 197–200 °C. Recrystallization from benzene gave a purified sample: mp 203–205 °C; IR (KBr) 3380 (NH), 1650 (C=O) cm^{-1}; MS *m/e* (%) 278 (9, M^+), 222 (12), 221 (70), 220 (100), 206 (20), 178 (16), 57 (10), 58 (6); ^{1}H NMR ($CDCl_3$) δ 2.43 (s, 3 H, NCH_3), 2.87 (s, 3 H, NCH_3), 2.90 (dd, 1 H, $J_{11n,10}$ = 3 Hz, $J_{11n,11x}$ = 18 Hz, H-11n), 3.43 (dd, 1 H, $J_{11x,10}$ = 3 Hz, $J_{11x,11n}$ = 18 Hz, H-11x), 3.87 (t, 1 H, J = 3 Hz, H-10), 7.30 (m, 8 H,

aromatic); ^{13}C NMR ($CDCl_3$) δ 26.5 (C-11), 29.5 (C-10), 35.5 (NCH_3), 47.5 (NCH_3), 78.0 (C-5), 122.5, 124.2, 125.6, 125.7, 127.0, 128.1, 128.3, 132.2, 134.3, 135.3, 138.7, 139.3 (aromatic), 174.0 (C=O).

Anal. Calcd for $C_{18}H_{18}N_2O$: C, 77.67; H, 6.52; N, 10.06. Found: C, 77.81; H, 6.70; N, 9.89.

The toluene-insoluble material (4.0 g) separated from the above product was dissolved in water. The solution was made basic with aqueous NaOH, and the resulting mixture was extracted with chloroform (3 × 300 mL). The combined chloroform extracts were dried over Na_2SO_4 and filtered, and the filtrate was evaporated to dryness. The crystalline residue was recrystallized from acetonitrile to yield 2.6 g (11%) of **8**: mp 217–219 °C. This material was identical (TLC, mixture melting point, NMR) with that produced from the reaction of **2** with aqueous methylamine.

Hydrolysis of **9** was effected by heating a sample (0.2 g) in 3 N HCl (5 mL) for 16 h on a steam bath. The precipitate (0.17 g) was recrystallized from acetonitrile: mp 212–213 °C. Comparison (mixture melting point, IR, NMR) with an authentic sample of **10** showed identity.

6-Chlorodibenzo[*a*,*d*]cycloocten-12(7*H*)-one (12). A solution of the ketone **2** (40 g, 0.138 mol) in THF (100 mL)–ether (250 mL) was added dropwise to a stirred slurry of lithium aluminum hydride (10.5 g) in ether (1 L). When the addition was complete, the mixture was refluxed for 2 h. The remaining lithium aluminum hydride was destroyed by the dropwise addition of ethyl acetate (25 mL). Water then was added until a clear ether layer was obtained. The ether phase was decanted and the residue of inorganic salts was extracted with several portions of ether. The combined ether phases were dried over $MgSO_4$, filtered, and concentrated to give 34 g (96%) of the alcohol **11** as a viscous oil: ^1H NMR ($CDCl_3$) δ 2.40 (s, 1 H, OH, exchanged with D_2O), 3.51 (s, 2 H, allylic), 6.06 (s, 1 H, methine), 7.01 (s, 1 H, vinyl), 7.1–7.9 (m, 8 H, aromatic).

A solution of 1.4 M chromium trioxide in 4.4 N H_2SO_4 was added dropwise to an ice-cooled solution of the alcohol **11** (34 g, 0.133 mol) in acetone (1.2 L) until the yellow color persisted (ca. 120 mL). After 1 h at room temperature, the excess oxidant was destroyed with 2-propanol and the bulk of the acetone was evaporated. Water was added and the mixture was extracted with ether. The ether phase was washed, dried, and concentrated. The solid **12** obtained was recrystallized from methanol: 31 g (92%); mp 109–110 °C; ^1H NMR ($CDCl_3$) δ 3.53 (s, 2 H, allylic), 6.77 (s, 1 H, vinyl), 7.1–7.5 (m, 6 H, aromatic), 8.1 (m, 2 H, aromatic).

Anal. Calcd for $C_{16}H_{11}ClO$: C, 75.45; H, 4.35; Cl, 13.92. Found: C, 75.49; H, 4.24; Cl, 14.08.

Reaction of 12 with Methylamine. The ketone **12** (7.8 g, 0.03 mol) and methylamine (40 mL) were heated in a glass-lined bomb at 80 °C for 12 h. After the bomb was cooled and vented, the contents were triturated with chloroform and filtered. The filtrate was evaporated to yield 8.5 g (96%) of **13** as a viscous oil: ^1H NMR ($CDCl_3$) δ 1.97 (s, 3 H, NCH_3), 2.27 (s, 3 H, NCH_3), 2.43 (s, 3 H, NCH_3), 2.80 (s, 2 H, benzylic), 3.0 (s, 2 H, benzylic), 7.0 (m, 6 H, aromatic), 7.6 (m, 2 H, aromatic).

A solution of **13** (8.25 g, 0.028 mol) in benzene (200 mL) was shaken with ice-cold 0.1 N HCl (100 mL). The separated benzene phase, upon standing at room temperature, deposited 5.8 g (73%) of **14**: mp 135–140 °C dec; ^1H NMR (Me_2SO-d_6) δ 2.53 (s, 3 H, NCH_3), 3.16 (s, 2 H, benzylic), 3.23 (s, 2 H, benzylic), 7.3 (m, 6 H, aromatic), 8.1 (m, 2 H, aromatic); IR (Nujol) 1630 (C=O at 12) cm^{-1}.

A slurry of **14** (4.2 g, 0.0147 mol) in water (125 mL) was heated for 2 h on a steam bath, cooled to 5 °C, and filtered. The crystalline product was washed with water and dried to yield 3.25 g (94%) of **15**: mp 160–162 °C. Comparison (mixture melting point, TLC, NMR) with an authentic sample of **15** proved identity (vide infra).

5,6,7,12-Tetrahydrodibenzo[*a*,*d*]cyclooctene-6,12-dione (15). A solution of **12** (40 g, 0.157 mol) in *n*-butylamine (200 mL) was heated under reflux for 18 h. The solvent was removed under reduced pressure and the residue was stirred with 0.5 N HCl (800 mL) for 4 h at 0–5 °C. After filtration, the filtrate was heated for 3 h on a steam bath, cooled to 5 °C, and filtered. The crystalline residue was washed with water and dried to yield 35.2 g (93%) of **15**: mp 159–161 °C; IR ($HCCl_3$) 1720 (C=O at 6), 1640 (C=O at 12) cm^{-1}; *m/e* (%) 236 (46, M^+), 207 (100, M – 29), 194 (26), 178 (46); ^1H NMR ($CDCl_3$) δ 3.76 (br s, 4 H, CH_2), 7.4 (m, 6 H, aromatic), 8.2 (m, 2 H, aromatic); ^{13}C NMR ($CDCl_3$) δ 46.69 (s, benzylic), 193.6 (s, C-12), 204.8 (s, C-6).

Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.33; H, 5.12. Found: C, 81.44; H, 5.22.

13-Methyl-6,12-imino-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cycloocten-12-ol (16a). The diketone **15** (5.78 g, 0.0245 mol) dissolved in 304 g of a solution of THF containing methylamine (3.8 g, 0.1225 mol) was stirred with 3A molecular sieves for 3 h at room temperature and then cooled to 10 °C. Glacial acetic acid (4.41 g, 0.0735 mol) was added and after 15 min, sodium cyanoborohydride (4.62 g, 0.0735 mol) was added in portions. The resulting mixture was stirred for 18 h at room temperature. After filtration, the solvent was removed and the residue was partitioned between benzene–ether (1:1) and water. The separated organic phase was extracted with 0.5 N HCl. The cooled acid extract was made basic with 40% NaOH, and the precipitated solid was extracted into chloroform. The chloroform extract was washed, dried, and concentrated. The crystalline residue was recrystallized from benzene to yield 5.0 g (81%) of **16a**: mp 237–239 °C; IR (KBr) 3420 (OH) cm^{-1}; *m/e* (%) 251 (32, M^+), 250 (18, M – H), 160 (100, M – 91); ^1H NMR ($CDCl_3$) δ 1.73 (s, 3 H, CH_3), 2.43 (d, 2 H, J = 16 Hz, H-5n and H-7n), 3.36 and 3.53 (overlapping dd and t, 3 H, J = 16, 6, and 6 Hz, H-5x, H-7x, and H-6), 5.63 (br s, 1 H, OH, exchanged with D_2O), 7.0 (m, 6 H, aromatic), 7.63 (m, 2 H, aromatic).

Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.23; H, 6.78; N, 5.32.

13-Benzyl-6,12-imino-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cycloocten-12-ol (16b) was prepared from the diketone **15** and benzylamine by a procedure analogous to that for **16a**. Treatment of the organic extract of the reaction product with aqueous HCl gave a precipitate that was collected, washed with ether, and dried to yield 77% of **16b**·HCl: mp 254–256 °C. Recrystallization from water gave a purified sample: mp 258–260 °C; IR (KBr) 3440 (OH) cm^{-1}; ^1H NMR ($CDCl_3$ + NaOD) δ 2.48 (d, 2 H, H_{5n} and H_{7n}, J = 16 Hz), 2.48 (br s, 1 H, OH, exchanged by D_2O), 3.1–3.9 (overlapping dd, s and t, 5 H, H_{5x} and H_{7x}, benzylic and H_6), 7.23–7.77 (m, 13 H, aromatic).

Anal. Calcd for $C_{23}H_{21}NO$·HCl: C, 75.91; H, 6.10; N, 3.85; Cl, 9.74. Found: C, 76.23; H, 6.47; N, 3.72; Cl, 9.49.

6,12-Imino-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cycloocten-12-ol (16c) was obtained from **15** and ammonia in the same way as **16a** in 67% yield: mp 228–231 °C. A sample of this base in acetone was converted to the hydrochloride salt with ethanolic HCl. Recrystallization from methanol–ether gave **16c**·HCl·$^1/_2CH_3OH$: mp 166–170 °C.

Anal. Calcd for $C_{16}H_{15}NO$·HCl·1/2CH_3OH: C, 68.38; H, 6.26; N, 4.83 Cl, 12.24. Found: C, 68.45; H, 6.32; N, 4.79; Cl, 12.19.

12-Chloro-13-methyl-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cycloocten-6,12-imine (17a). A solution of **16a** (5 g, 0.02 mol) in thionyl chloride (100 mL) was heated under reflux for 2 h. The solvent was evaporated under reduced pressure and the last traces were removed by repeated coevaporation with benzene. The residual crystalline hydrochloride salt was treated with aqueous NaOH and the base was extracted into benzene–ether (1:1). Evaporation of the washed and dried organic phase yielded 4.77 g (88%) of **17a**: mp 150–153 °C. Recrystallization from cyclohexane gave a purified sample: mp 153–154.5 °C; *m/e* (%) 269 (27, M^+), 268 (19, M – H), 234 (100, M – Cl), 232 (46, M – 47), 178 (78, M – 91); ^1H NMR ($CDCl_3$) δ 2.4 (s, 3 H, CH_3), 2.4 (d, 2 H, $J_{5n,5x} = J_{7n,7x}$ = 16 Hz, H-5n and H-7n), 3.33 (dd, 2 H, $J_{5x,6} = J_{7x,6}$ = 7.5 Hz, $J_{5x,5n} = J_{7x,7n}$ = 16 Hz, H-5x and H-7x), 3.66 (t, 1 H, $J_{6,5x} = J_{6,7x}$ = 7.5 Hz, H-6), 7.06 (m, 6 H, aromatic), 7.77 (m, 2 H, aromatic H-1 and H-11).

Anal. Calcd for $C_{17}H_{16}ClN$: C, 75.68; H, 5.98; N, 5.19. Found: C, 76.06; H, 5.94; N, 5.36.

13-Benzyl-12-chloro-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cycloocten-6,12-imine (17b) was obtained in the same way as **17a** from **16b** and thionyl chloride in 78% yield. A recrystallized (benzene–hexane) sample melted at 149–151 °C: *m/e* (%) 345 (15, M^+), 310 (33, M – Cl), 294 (14, M – 51), 254 (37, M – 91), 218 (42, M – 127), 91 (100, C_7H_7); ^1H NMR ($CDCl_3$) δ 2.38 (d, 2 H, J = 16 Hz, H-5n and H-7n), 3.30 (dd, 2 H, J = 16 and 7 Hz, H-5x and H-7x), 3.75 (overlapping s and t. 3 H, CH_2 and H-6), 7.25 (m, 13 H, aromatic).

Anal. Calcd for $C_{23}H_{20}NCl$: C, 79.86; H, 5.82; N, 4.05; Cl, 10.25. Found: C, 80.02; H, 6.07; N, 4.09; Cl, 10.11.

12-Chloro-5,6,7,12-tetrahydrodibenzo[a,d]cycloocten-6,12-imine (17c). Conversion of **16c** to **17c** with thionyl chloride required 16 h of heating under reflux. Workup in the manner described for **17a** gave crude **17c**, mp 140–145 °C, in 88% yield. A sample purified by chromatography (silica gel, chloroform saturated with 28% NH_3 as eluant) and recrystallization (cyclohexane) melted at 150–151 °C: *m/e* (%) 255 (30, M^+), 254 (11, M – H), 220 (85, M – Cl), 218 (100, M – 37), 164 (51, M – 91); ^1H NMR ($CDCl_3$) δ 2.53 and 2.70 (overlapping d and s, 3 H, H-5n, H-7n, and NH), 3.40 (dd, 2 H, *J* = 16 and 6 Hz, H-5x and H-7x), 4.0 (t, 1 H, *J* = 6 Hz, H-6), 7.07 (m, 6 H, aromatic), 7.70 (m, 2 H, aromatic).

Anal. Calcd for $C_{16}H_{14}ClN$: C, 75.14; H, 5.52; N, 5.48. Found: C, 75.51; H, 5.71; N, 5.37.

13-Methyl-5,6,7,12-tetrahydrodibenzo[a,d]cycloocten-6,12-imine (18a). To a solution of **17a** (2.7 g, 0.01 mol) in THF (40 mL) and ether (20 mL) was added 0.95 g of lithium aluminum hydride (51.6% in mineral oil). The mixture was stirred for 30 min at room temperature and 1 h at reflux. Water was added until a clear organic layer was obtained and the organic phase was decanted. The residue of inorganic salts was extracted several times with ether, and the combined organic phases were concentrated. The residual oily base was dissolved in benzene and treated with a solution of oxalic acid (1 g) in acetone (10 mL). Dilution with ether precipitated a solid that was collected, washed with benzene, and recrystallized from methanol to yield 2.0 g (61%) of the hydrogen oxalate salt of **18a**: mp 177–179 °C; *m/e* (%) 235 (26, M^+), 234 (34, M – H), 144 (100, M – 91); ^1H NMR (CH_3OH-d_4) δ 2.87 (s, 3 H, CH_3), 3.0 (d, 2 H, *J* = 18 Hz, H-5n and H-7n), 3.70 (dd, 2 H, *J* = 7 and 18 Hz, H-5x and H-7x), 4.30 (t, 1 H, *J* = 7 Hz, H-6), 5.53 (s, 1 H, H-12), 7.30 (m, 8 H, aromatic).

Anal. Calcd for $C_{17}H_{17}N{\cdot}C_2H_2O_4$: C, 70.14; H, 5.88; N, 4.30. Found: C, 69.82; H, 6.11; N, 4.06.

13-Benzyl-5,6,7,12-tetrahydrodibenzo[a,d]cycloocten-6,12-imine (18b) was obtained by lithium aluminum hydride reduction of **17b** by the above procedure. A benzene solution of the oily product was stirred with aqueous HCl. The solid obtained was recrystallized twice from methanol–ether to give **18b**·HCl: mp >270 °C; 75% yield; ^1H NMR (CH_3OH-d_4) δ 3.13 (d, 2 H, *J* = 18 Hz, H-5n and H-7n), 3.80 (dd, 2 H, *J* = 18 and 7 Hz, H-5x and H-7x), 4.40 (overlapping s and t, 3 H, *J* = 7 Hz, CH_2 and H-6), 5.44 (s, 1 H, H-12), 7.42 (m, 13 H, aromatic).

Anal. Calcd for $C_{23}H_{21}N{\cdot}HCl$: C, 79.40; H, 6.37; N, 4.02; Cl, 10.19. Found: C, 79.13; H, 6.35; N, 4.17; Cl, 10.14.

5,6,7,12-Tetrahydrodibenzo[a,d]cycloocten-6,12-imine (18c) was prepared by lithium aluminum hydride reduction of **17c** by a procedure analogous to that for **18a**. The crude product was chromatographed on silica gel, using chloroform–methanol (99:1) as the eluant. The TLC-homogeneous solid obtained, mp 96–102 °C, was dissolved in acetone and treated with ethanolic HCl, and the precipitate of **18c**·HCl was recrystallized from methanol: yield 46%; mp >270 °C; *m/e* (%) 221 (47, M^+), 220 (54, M – H), 179 (12, M – 42), 130 (100, M – 91); ^1H NMR (base in $CDCl_3$) δ 2.08 (s, 1 H, NH), 2.50 (d, 2 H, *J* = 17 Hz, H-5n and H-7n), 3.23 (dd, 2 H, *J* = 7 and 17 Hz, H-5x and H-7x), 3.76 (t, 1 H, *J* = 7 Hz, H-6), 4.83 (s, 1 H, H-12), 7.03 (m, 8 H, aromatic).

Anal. Calcd for $C_{16}H_{15}N{\cdot}HCl$: C, 74.55; H, 6.26; N, 5.43. Found: C, 74.74; H, 6.46; N, 5.36.

12-Bromo-13-methyl-5,6,7,12-tetrahydrodibenzo[a,d]cycloocten-6,12-imine (19). A mixture of the carbinol **16a** (8.0 g, 0.032 mol), phosphorus tribromide (9.5 g, 0.035 mol), and toluene (150 mL) was stirred at reflux for 24 h. After removal of the solvent under reduced pressure, the residual solid was cooled in an ice bath and stirred with ice–water (750 mL), benzene (600 mL), ether (300 mL), and 10% sodium hydroxide (40 mL) for 3 h. The clear organic phase was separated and the remaining mixture was stirred with fresh benzene (350 mL) and ether (150 mL) for 2 h in the cold. The separated organic phases were combined, dried, and concentrated. The solid obtained was triturated with benzene (20 mL) and filtered immediately, and the undissolved solid was triturated again with benzene (10 mL). The insoluble material was collected and dried to obtain 0.77 g, mp 220–233 °C, identified as recovered **16a** by ^1H NMR comparison with an authentic sample. The benzene filtrate was concentrated to afford 7.3 g (73%) of **19**: mp 140–145 °C. Recrystallization from cyclohexane gave a purified sample: mp 147–149 °C; *m/e* 313 (M^+), 312 (M – H), 234 (M – Br); ^1H NMR ($CDCl_3$) δ 2.42 and 2.50 (overlapping d and s, 5 H, H-5n, H-7n, and CH_3), 3.37 and 3.72 (overlapping dd and t, 3 H, H-5x, H-7x, and H-6), 7.07 (m, 6 H, aromatic), 7.77 (m, 2 H, aromatic).

Anal. Calcd. for $C_{17}H_{16}BrN$: C, 64.98; H, 5.13; N, 4.46; Br, 25.43. Found: C, 64.98; H, 5.01; N, 4.50; Br, 25.26.

13-Methyl-5,6,7,12-tetrahydrodibenzo[a,d]cycloocten-6,12-imine Dimer (21). To a slurry of **19** (0.94 g, 0.003 mol) in ether (70 mL) cooled in an ice bath was added dropwise with stirring a solution (1.9 mL, 1.9 M) of *n*-butyllithium in hexane. After 1 h, the mixture was hydrolyzed in ice–water. The organic phase was separated, dried over Na_2SO_4, and filtered, and the filtrate was concentrated. The residual oil was triturated with warm acetone (15 mL). The solid **21** obtained (0.38 g, 27%) was recrystallized from hexane: mp 216–217 °C; *m/e* 468 (5, M^+), 453 (0.4, M – 15), 377 (1, M – 91), 363 (2, M – 105), 234 (100, M – 234); ^1H NMR ($CDCl_3$) δ 2.33 (s, 3 H, NCH_3), 2.10, 2.64, 3.23 and 3.60 (m, 4 H, benzylic), 3.74 (m, 1 H, NCH), 6.18, 6.36, 6.51, 6.76, 6.83, 6.88, 7.03, 9.36 (m, 8 H, aromatic).

Anal. Calcd for $C_{34}H_{32}N_2$: C, 87.13; H, 6.88; N, 5.98. Found: C, 87.53; H, 6.89; N, 5.98.

The acetone mother liquor from **21** was concentrated and the residual oil was triturated with hexane (3 mL). The mixture was centrifuged and the clear supernatant solution was separated and evaporated. The residual oil (0.27 g), although not TLC homogeneous, contained **12-butyl-13-methyl-5,6,7,12-tetrahydrodibenzo[a,d]cycloocten-6,12-imine (20)**: *m/e* (%) 291 (25, M^+), 290 (13, M – H), 248 (14, M – 43), 234 (100, M – 57), 218 (46, M – 73), 205 (33, M – 86), 200 (88, M – 91); ^1H NMR ($CDCl_3$) δ 1.1 (m, *n*-Bu), 2.37 (s, NCH_3), 2.0–4.0 (overlapping signals), 7.0 (m, aromatic).

12-Ethyl-13-methyl-5,6,7,12-tetrahydrodibenzo[a,d]-cycloocten-6,12-imine (22). To a solution (25 mL, 0.95 M) of ethyllithium in benzene cooled in an ice bath was added dropwise with stirring a solution of **19** (4.6 g, 0.0146 mol) in ether (270 mL)–benzene (30 mL). After 1.5 h, the reaction mixture was quenched in ice–water. The organic phase was separated, dried over Na_2SO_4, and filtered, and the filtrate was evaporated. The residual oil was triturated with warm hexane (25 mL). The solid obtained (1.4 g, mp 207–210 °C) was identified as the dimer **21** by ^1H NMR comparison with an authentic sample. The hexane filtrate was evaporated and the residual oil (2.35 g) was chromatographed on silica gel, eluting with 95% ethanol–toluene (10:90). Fractions of the eluate containing the TLC-homogeneous major component of the mixture were combined and evaporated. The oily **22** obtained was dissolved in methanol and treated with ethanolic HCl. Dilution with ether yielded 0.8 g (18%) of **22**·HCl: mp 267–268 °C dec. Recrystallization from methanol–acetone gave a purified sample: mp 273–274 °C dec; *m/e* 263 (M^+), 248 (M – 15), 234 (M – 29), 207 (M – 56), 172 (M – 91); ^1H NMR (D_2O) δ 1.10 (t, 3 H, *J* = 7 Hz, CH_3), 2.87 (s, 3 H, NCH_3), 2.80–4.63 (overlapping signals, 7 H), 7.50 (m, 8 H, aromatic).

Anal. Calcd for $C_{19}H_{21}N{\cdot}HCl$: C, 76.11; H, 7.40; N, 4.67; Cl, 11.83. Found: C, 75.81; H, 7.42; N, 4.56; Cl, 11.96.

12-Methoxy-13-methyl-5,6,7,12-tetrahydrodibenzo[a,d]-cycloocten-6,12-imine (23). A solution of **19** (1.6 g, 0.005 mol) and sodium methoxide (0.3 g, 0.0055 mol) in methanol (30 mL) was heated under reflux for 6 h. The solvent was evaporated and the residue was partitioned between ether and water. The ether phase was washed, dried, and concentrated. The solid **23** obtained (1.28 g, 96%, mp 89–93 °C) was dissolved in methanol and treated with ethanolic HCl, and the precipitate of **23**·HCl was recrystallized from methanol: mp 269–271 °C dec; *m/e* 265 (M^+), 250 (M – 15), 234 (M – 31), 232 (M – 33), 174 (M – 91); ^1H NMR (Me_2SO-d_6 + D_2O) δ 2.69 (s, 3 H, NCH_3), 3.02 (d, 2 H, *J* = 18 Hz, H-5n and H-7n), 3.59 (s, 3 H, OCH_3), 3.70–3.97 (overlapping signals, 3 H, H-5x, H-7x, and H_2O), 4.47 (t, 1 H, *J* = 5 Hz, H-6), 7.33 (m, 6 H, aromatic), 7.60 (m, 2 H, aromatic).

Anal. Calcd for $C_{18}H_{19}NO{\cdot}HCl$: C, 71.63; H, 6.68; N, 4.64; Cl, 11.75. Found: C, 71.89; H, 6.39; N, 4.60; Cl, 11.67.

6,6-Ethylenedioxy-7,12-dihydrodibenzo[a,d]cyclooctan-12(5*H*)-one (24). A soluton of **15** (35 g, 0.15 mol) in benzene (500 mL) containing *p*-TosOH (200 mg) was slurried with ethylene glycol (30 mL) and heated under reflux with H_2O

separation (Dean–Stark trap) for 24 h. The reaction mixture was washed with H_2O (200 mL), dried over Na_2SO_4, and filtered, and the filtrate was evaporated under reduced pressure. The crystalline residue was washed with hexane and recrystallized from methanol to yield 40.8 g (97%) of **24**: mp 197–199 °C; IR (KBr) 1630 (C=O) cm^{-1}; *m/e* (%) 280 (56, M^+), 279 (95, M – H), 207 (42, M – 73), 179 (34, M – 101), 86 (100, M – 194); ^1H NMR ($CDCl_3$) δ 2.9 (s, 4 H, CH_2), 4.1 (s, 4 H, OCH_2CH_2O), 7.4 (m, 6 H, aromatic), 8.2 (m, 2 H, aromatic).

Anal. Calcd for $C_{18}H_{16}O_3$: C, 77.12; H, 5.75. Found: C, 77.29; H, 5.76.

12-Methylene-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cyclooctene-6-one (25a). To a solution of **24** (44.3 g, 0.157 mol) in ether (1000 mL) was added dropwise with stirring a solution (125 mL, 2.0 M) of methyllithium in ether. After 18 h, the reaction mixture was hydrolyzed in ice–water. The organic solution was separated, dried over Na_2SO_4, and filtered, and the filtrate was evaporated. The crystalline residue of **6,6-ethylenedioxy-12-methyl-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cycloocten-12-ol**, mp 138–140 °C, was stirred and heated under reflux in a mixture of $HCCl_3$ (400 mL) and 4 N aqueous HCl (200 mL) for 18 h. The $HCCl_3$ layer was separated, washed with H_2O (50 mL), dried over Na_2SO_4, and filtered, and the filtrate was evaporated. Recrystallization of the crystalline residue from hexane gave 34.5 g (94%) of **25a**: mp 68–70 °C; IR (KBr) 1710 (C=O) cm^{-1}; *m/e* (%) 234 (36, M^+), 205 (31, M – 29), 192 (100, M – 42); ^1H NMR ($CDCl_3$) δ 3.63 (s, 4 H, CH_2), 5.37 (s, 2 H, $=CH_2$), 7.3 (m, 8 H, aromatic).

Anal. Calcd for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 86.91; H, 6.16.

12-Methylene-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cyclooctene-6-one Oxime (26a). A mixture of **25a** (23.4 g, 0.1 mol), hydroxylamine hydrochloride (10 g, 0.14 mol), sodium acetate trihydrate (19.6 g, 0.14 mol), and wet ether (500 mL) was stirred at room temperature for 20 h. The ether solution was decanted from the wet solid and this residue was washed thoroughly with ether. The combined ether phases were washed (H_2O), dried (Na_2SO_4), and concentrated. The crystalline residue was washed with hexane to yield 22.3 g (90%) of **26a**: mp 122–124 °C. A purified sample was obtained by recrystallization from cold toluene–hexane: mp 125–127 °C; IR (KBr) 3250 (OH) cm^{-1}; *m/e* (%) 249 (37, M^+), 230 (28.5, M – 19), 219 (100, M – 30), 204 (70, M – 45); ^1H NMR ($CDCl_3$) δ 3.5 (s, 2 H, CH_2), 3.8 (s, 2 H, CH_2), 5.3 (d with fine splitting, *J* = 12 Hz, 2 H, $=CH_2$), 7.2 (m, 8 H, aromatic), 8.9 (s, 1 H, OH, exchanged with D_2O).

Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.42; N, 5.62. Found: C, 81.85; H, 6.10; N, 5.65.

1,3,3a,8,8a,9-Hexahydroindeno[1′,2′:1,2]indeno[1,2-*d*]isoxazole (27a). A mixture of **25a** (1.65 g, 0.007 mol), hydroxylamine hydrochloride (1.0 g, 0.015 mol), ethanol (15 mL), and pyridine (2 mL) was heated under reflux for 2.5 h. The solvent was evaporated and the residue was partitioned between chloroform and water. The chloroform phase was separated, dried ($MgSO_4$), and concentrated. The solid **27a** obtained (1.6 g, 92%) was recrystallized from hexane: mp 104–105 °C; IR (KBr) 3170 (NH) cm^{-1}; *m/e* 249 (M^+), 233 (M – 16), 218 (M – 31), 204 (M – 45); ^1H NMR ($CDCl_3$) δ 3.23 (d, 2 H, *J* = 18 Hz, CH_2), 3.33 (d, 2 H, *J* = 18 Hz, CH_2), 4.20 (s, 2 H, OCH_2), 5.06 (s, 1 H, NH, exchanged with D_2O), 7.30 (m, 8 H, aromatic).

Anal. Calcd for $C_{17}H_{15}NO$: C, 81.90; H, 6.07; N, 5.62. Found: C, 81.98; H, 6.24; N, 5.50.

Conversion of the oxime **26a** to **27a** was accomplished by heating a sample (50 mg) in toluene (4 mL) at 75 °C for 3 h. Evaporation of the solvent left a crystalline, TLC-homogeneous residue that was recrystallized from hexane: mp 104–106 °C. The product was compared with an authentic sample of the isoxazolidine **27a** and shown to be identical (TLC, mixture melting point).

***N*-(12-Methylene-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cyclooctene-6-yl)hydroxylamine (28a).** Sodium cyanoborohydride (6.3 g, 0.1 mol) was added in portions over 30 min to a stirred solution of the oxime **26a** (22.3 g, 0.09 mol) in methanol (650 mL) and 7 N ethanolic HCl (15 mL). After 30 min, another 5 mL of 7 N ethanolic HCl was added and stirring was continued for 1.5 h. The solvent was evaporated and the residue was partitioned between chloroform and 10% aqueous NaOH. The chloroform extract was washed, dried, filtered, and concentrated to yield 22.6 g (100%) of **28a** as a colorless glass. A sample of this product in ethanol was treated with 7 N ethanolic HCl. Dilution with ether precipitated the salt that was recrystallized from acetonitrile to obtain **28a**·HCl: mp 155–160 °C dec; IR (base, KBr) 3410 (OH) cm^{-1}; *m/e* 251 (M^+), 234 (M^+ – OH), 218 (M^+ – NHOH), 203, 193, 178; ^1H NMR (D_2O) δ 2.66 (d, 4 H, *J* = 6 Hz, CH_2), 3.40 (m, 1 H, *J* = 6 Hz, H-6), 5.00 (s, 2 H, $=CH_2$), 6.97 (m, 8 H, aromatic).

Anal. Calcd for $C_{17}H_{17}NO$·HCl: C, 70.95; H, 6.30; N, 4.87. Found: C, 71.13; H, 6.34; N, 4.84.

12-Methyl-13-hydroxy-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cycloocten-6,12-imine (29a). A solution of **28a** (5.0 g, 0.02 mol) in xylene (200 mL) was added dropwise to refluxing xylene (200 mL). The solvent was removed under reduced pressure and the residue recrystallized from 95% ethanol to yield 4.0 g (80%) of **29a**: mp 192–194 °C; ^1H NMR ($CDCl_3$) δ 2.1 (s, 3 H, CCH_3), 2.2–3.8 (m, 4 H, CH_2), 4.1 (m, 1 H, bridgehead), 7–7.6 (m, 8 H, aromatic), 8.2 (br s, 1 H, OH, exchanged by D_2O); mass spectrum *m/e* 251 (M^+), 234 (M^+ – OH), 219, 193, 144.

Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.82; N, 5.57. Found: C, 81.60; H, 6.79; N, 5.34.

12-Methyl-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cycloocten-6,12-imine Hydrochloride (30a). To a solution of **29a** (5.0 g, 0.02 mol) in glacial acetic acid (20 mL) was added portionwise zinc dust (5.6 g). The mixture was stirred and heated at 55–60 °C for 2.5 h. The cooled reaction mixture was diluted with ether (300 mL) and filtered. The ether filtrate was washed with 10% aqueous NaOH, dried over Na_2SO_4, and filtered, and the filtrate was evaporated to dryness. The white crystalline residue (3.7 g, mp 99–102 °C; *m/e* 235 (M^+), 220 (M^+ – CH_3)) was dissolved in ethanolic hydrogen chloride, and the solution was evaporated to dryness. The residue was recrystallized from ethanol to yield **30a**·HCl: mp >300 °C; ^1H NMR ($CDCl_3$) δ 2.3 (s, 3 H, CCH_3), 2.8 (d, 2 H, methylene, *J* = 17 Hz), 3.7 (dd, 2 H, methylene, *J* = 17 Hz, *J* = 7 Hz), 4.5 (t, 1 H, bridgehead, *J* = 7 Hz), 7.2–7.8 (m, 8 H, aromatic).

Anal. Calcd for $C_{17}H_{17}N$·HCl: C, 75.12; H, 6.67; N, 5.15. Found: C, 75.12; H, 6.84; N, 4.93.

12-Ethylene-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cyclooctene-6-one (25b). To a slurry of ethyltriphenylphosphonium bromide (41.7 g, 0.112 mol) in ether (400 mL) and under nitrogen was added dropwise a solution (53 mL, 2.08 M) of *n*-butyllithium in hexane. To the resulting red solution of the Wittig reagent was added a solution of **24** (21.0 g, 0.075 mol) in THF (300 mL). The mixture was stirred and heated to refluxing for 12 h. Water (25 mL) was added and the supernatant solution was decanted. The residue was triturated with boiling hexane, combined with the ether solution, and concentrated. The solid obtained was chromatographed on silica gel, eluting with chloroform. Evaporation of the eluate yielded 21.05 g (95%) of **6,6-ethylenedioxy-12-ethylidene-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cyclooctene**; mp 82–87 °C. Recrystallization from petroleum ether gave a purified sample: mp 84–86 °C; ^1H NMR ($CDCl_3$) δ 1.40 (d, 3 H, *J* = 7 Hz, CH_3), 2.65 (s, 2 H, benzylic), 3.05 (s, 2 H, benzylic), 4.00 (s, 4 H, OCH_2CH_2O), 6.05 (q, 1 H, *J* = 7 Hz, =CH), 7.20 (m, 8 H, aromatic).

The ketal (21 g, 0.072 mol) was stirred and heated under reflux in a mixture of $HCCl_3$ (500 mL) and 4 N aqueous HCl (250 mL) for 3 h. The $HCCl_3$ layer was separated, washed with water, dried over Na_2SO_4, and filtered, and the filtrate was evaporated to obtain 17.7 g (99%) of **25b**: mp 142.5–145.5 °C. Recrystallization from cyclohexane gave a purified sample: mp 145–147 °C; IR (KBr) 1705 (C=O) cm^{-1}; *m/e* 248 (M^+), 233 (M – CH_3), 230 (M – H_2O), 205 (M – 43), 192 (M – 56); ^1H NMR ($CDCl_3$) δ 1.50 (d, 3 H, *J* = 7 Hz, CH_3), 3.50 (s, 2 H, CH_2), 3.60 (s, 2 H, CH_2), 5.77 (q, 1 H, *J* = 7 Hz, =CH), 7.25 (m, 8 H, aromatic).

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.49. Found: C, 87.16; H, 6.51.

12-Ethylidene-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cyclooctene-6-one Oxime (26b). A mixture of **25b** (12.7 g, 0.051 mol), hydroxylamine hydrochloride (5.0 g, 0.072 mol), sodium acetate trihydrate (9.75 g, 0.072 mol), and wet ether (300 mL) was stirred at room temperature for 40 h. The ether solution was decanted from the wet solid and this residue was washed thoroughly with ether. The combined ether phases were washed with water, dried over Na_2SO_4, and filtered, and the filtrate was concentrated. The crystalline residue was washed with hexane to yield 11.5 g (86%)

of **26b**: mp 127–130 °C; *m/e* 263 (M^+), 246 (M – OH), 231 (M – 32), 218 (M – 45), 204 (M – 59); ^1H NMR ($CDCl_3$) δ 1.45 (d, 3 H, *J* = 6 Hz, CH_3), 3.45 (d, 2 H, *J* = 18 Hz, CH_2), 3.62 (d, 2 H, *J* = 14 Hz, CH_2), 5.73 (overlapping qq, 1 H, *J* = 6 Hz, =CH), 7.13 (m, 8 H, aromatic), 9.20 (s, 1 H, OH).

***N*-(12-Ethylidene-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cyclooocten-6-yl)hydroxylamine (28b)** was obtained by sodium cyanoborohydride reduction of the oxime **26b** in a manner analogous to that described for **28a** in 100% yield as a colorless glass: ^1H NMR ($CDCl_3$) δ 1.43 (d, 3 H, *J* = 6 Hz, CH_3), 2.60–3.60 (overlapping signals, 6 H), 5.96 (q, 1 H, *J* = 6 Hz, =CH), 7.23 (m, 8 H, aromatic).

12-Ethyl-13-hydroxy-5,6,7,12-tetrahydrodibenzo[*a*,*d*]-cycloocten-6,12-imine (29b). The hydroxylamine **28b** (5.0 g, 0.0189 mol) was added in portions to degassed *n*-decane (250 mL) heated in an oil bath at 160 °C. When the addition was complete, the bath temperature was raised to 180 °C and heating was continued for 5 h. The bulk of the solvent then was distilled (60–70 °C (0.5 mm)). The solid residue was washed with petroleum ether to obtain 4.4 g (88%) of **29b**. A sample recrystallized from cyclohexane gave the following: mp 142–143 °C; IR ($CHCl_3$) 3575 (OH) cm^{-1}; *m/e* 265 (M^+), 248 (M – OH), 218, 178, 174, 158; ^1H NMR ($CDCl_3$) δ 0.87 (t, 3 H, *J* = 6 Hz, CH_3), 2.10–4.20 (overlapping signals, 7 H), 5.23 (br s, 1 H, OH, exchanged with D_2O), 7.0 (m, 7 H, aromatic), 7.4 (m, 1 H, aromatic).

Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.23; N, 5.28. Found: C, 81.88; H, 7.25; N, 5.31.

12-Ethyl-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cyclooocten-6,12-imine (30b) was obtained in 53% yield from the reduction of **29b** by a procedure similar to that described for **29a** (mp 119–121 °C). **30b**·HCl (EtOH): mp >270 °C; *m/e* 249 (M^+), 220 (M – C_2H_5), 158; ^1H NMR (CH_3OH-d_4) δ 1.07 (t, 3 H, *J* = 6 Hz, CH_3), 2.73 (q, 2 H, *J* = 6 Hz, CH_2), 2.84 (d, 2 H, *J* = 15 Hz, H-5x and H-7x), 3.63 (dd, 2 H, *J* = 6 and 15 Hz, H-5n and H-7n), 4.33 (t, 1 H, *J* = 6 Hz, H-6), 7.10–7.55 (m, 8 H, aromatic).

Anal. Calcd for $C_{18}H_{19}N$·HCl: C, 75.64; H, 7.05; N, 4.90; Cl, 12.41. Found: C, 75.57; H, 7.34; N, 4.66; Cl, 12.25.

5-Methylene-10-oxo-10,11-dihydro-5*H*-dibenzo[*a*,*d*]-cycloheptene (33a). To a solution of 10-bromo-5*H*-dibenzo-[*a*,*d*]cyclohepten-5-one (**31**) (100 g, 0.35 mol) and *N*-methylpiperazine (70 g, 0.7 mol) in *tert*-butyl alcohol (1000 mL) was added potassium *tert*-butoxide (50 g, 0.44 mol). The reaction mixture was stirred and heated under reflux for 4 h. The solvent was evaporated under reduced pressure, and the residue was slurried with H_2O (800 mL) and extracted with chloroform (3 × 350 mL). The combined extracts were evaporated to dryness, and the residue was recrystallized from acetonitrile to yield 84 g (80%) of 10-(4′-methylpiperazin-1-yl)-5*H*-dibenzo[*a*,*d*]cyclohepten-5-one (**32**): mp 133–135 °C. To a solution of **32** (65.6 g, 0.22 mol) in THF (350 mL) was added with stirring methyllithium in ether (1.4 M, 200 mL) while the temperature was maintained at 0–5 °C. After 4 h, TLC (silica gel eluted with 1:9 CH_3OH–$HCCl_3$) showed the disappearance of **32** (R_f 0.5) and the presence of product (R_f 0.4). The solvent was evaporated, the residue was slurried with ice-water (300 mL), and the solid was collected by suction filtration. The solid was dissolved in ethanol (200 mL), and ethanolic HCl (100 mL, 11 N) and hydrochloric acid (75 mL, 6 N) were added. After this solution was heated under reflux for 1 h, the solvent was concentrated under reduced pressure, and the concentrate was diluted with H_2O (300 mL) and extracted with ether (3 × 200 mL). The combined extracts were dried over $MgSO_4$ and filtered, and the filtrate was evaporated. Recrystallization of the residue from hexane gave 38.8 g (80%) of **33a**: mp 84–86 °C; ^1H NMR ($CDCl_3$) δ 4.07 (s, 2 H, benzylic), 5.43 (d, 1 H, =CH_2, *J* = 1 Hz), 5.8 (d, 1 H, =CH_2, *J* = 1 Hz), 7.4 (m, 7 H, aromatic), 8.13 (m, 1 H, aromatic); *m/e* (%) 220.0879 ($C_{10}H_{12}O$, 16, M^+), 192 (100, M^+ – CO); IR (Nujol) 1680 (C=O), 1595, 1285, 920, 785, 775, 765, 760, 750, 710 cm^{-1}.

Anal. Calcd for $C_{10}H_{12}O$: C, 87.24; H, 5.49. Found: C, 87.54; H, 5.54.

5-Methylene-10-hydroximino-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene (34a). A solution of **33a** (16.5 g, 0.0743 mol), hydroxylamine hydrochloride (6.6 g, 0.095 mol), and CH_3CO_2Na (8.2 g, 0.1 mol) in methanol (200 mL) was heated under reflux for 5 h. TLC (silica gel eluted with chloroform) indicated complete conversion of **33a** (R_f 0.64) to **34a** (R_f 0.28). The solvent was removed under reduced pressure, the residue was slurried in H_2O (200 mL), the pH was adjusted to 8 with concentrated aqueous NH_3, and the slurry was extracted with ether (3 × 150 mL). The combined extracts were dried over Na_2SO_4 and filtered, and the filtrate was evaporated. The crystalline residue was recrystallized from hexane to yield 16.6 g (94%) of **34a**: mp 155–161 °C; ^1H NMR ($CDCl_3$) δ 4.03 (s, 2 H, benzylic), 5.30 (d, 1 H, vinyl, *J* = 2 Hz), 5.67 (d, 1 H, vinyl, *J* = 2 Hz), 7.8–8 (m, 8 H, aromatic), 10.6 (br s, 1 H, OH, exchanged by D_2O); *m/e* (%) 235.1002 ($C_{16}H_{13}NO$, 64, M^+), 219 (20), 218 (42), 217 (100), 216 (37), 202 (14), 203 (17), 192 (14), 191 (43), 190 (24), 189 (23); IR (Nujol) 3240, 3280, 1340, 1060, 960, 950, 945, 930, 780, 750, 710 cm^{-1}.

Anal. Calcd for $C_{16}H_{13}NO$: C, 81.68; H, 5.57; N, 5.95. Found: C, 81.99; H, 5.62; N, 5.79.

5-Methylene-10-hydroxamino-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene (35a). To a solution of **34a** (15.3 g, 0.065 mol) in methanol (500 mL) was added $NaCNBH_3$ (12 g) in one portion followed by 12 N hydrochloric acid in methanol (1:1 (v/v)) added dropwise to maintain the pH at 3–3.4. After 5 h, TLC (alumina developed with 5% ethanol in toluene) indicated disappearance of **34a**. The solvent was removed under reduced pressure and the residue was slurried with 1 N aqueous hydrochloric acid (200 mL). The pH was adjusted to 8 with concentrated aqueous NH_3, and the mixture was extracted with ether (3 × 175 mL). The combined extracts were dried over Na_2SO_4 and filtered, and the filtrate was evaporated to dryness. The crystalline residue was washed with cold methanol to yield 12.8 g (83%) of **35a**: mp 117–118 °C; ^1H NMR ($CDCl_3$) δ 3.3 (d, 2 H, benzylic, *J* = 5 Hz), 4.4 (t, 1 H, NCH, *J* = 5 Hz), 5.3 (d, 1 H, vinyl, *J* = 2 Hz), 5.5 (d, 1 H, vinyl, *J* = 2 Hz), 6.0 (s, 2 H, NH + OH, exchanged by D_2O), 7–7.4 (m, 8 H, aromatic); *m/e* (%) 237.1136 ($C_{16}H_{15}NO$, 3, M^+), 220 (28), 206 (23), 205 (100), 204 (45), 203 (44), 202 (18), 178 (22); IR (Nujol) 3240, 1030, 970, 920, 890, 870, 800, 780, 750 cm^{-1}.

Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37; N, 5.90. Found: C, 81.21; H, 6.47; N, 5.91.

12-Hydroxy-5-methyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*]-cyclohepten-5,10-imine (36a). A solution of **35a** (8.8 g, 0.037 mol) in warm xylene (200 mL) was added dropwise to refluxing xylene (80 mL) over 40 min. TLC (alumina eluted with 5% ethanol in toluene) showed disappearance of **35a** (R_f 0.65) after 1 h. The solvent was removed under reduced pressure and the residue was recrystallized from cyclohexane to yield 8.5 g (96%) of **36a**: mp 145–147 °C; ^1H NMR ($CDCl_3$) δ 2.0 (s, 3 H, CCH_3), 2.6 (m, 1 H, benzylic), 3.6 (m, 1 H, benzylic), 4.6 (m, 1 H, bridgehead), 7.1 (m, 8 H, aromatic); *m/e* (%) 237.1160 ($C_{16}H_{15}NO$, 24, M^+), 221 (35), 220 (100), 206 (15), 205 (46), 204 (24), 191 (15), 179 (44), 178 (29), 160 (21); IR (KBr) 3240 (OH), 960, 740 cm^{-1}.

Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.36; N, 5.90. Found: C, 81.29; H, 6.35; N, 5.71.

5-Methyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5,10-imine (37a). To a solution of **36a** (2.37 g, 0.01 mol) in acetic acid (15 mL) was added portionwise zinc dust (2.2 g). The mixture was stirred and heated at 60–70 °C for 3.5 h. The mixture was filtered and the filter cake was washed with ether (200 mL). The filtrate was concentrated under reduced pressure and the concentrate was slurried with 5% aqueous NaOH and extracted with ether (3 × 100 mL). The combined extracts were dried over Na_2SO_4 and filtered, and the filtrate was concentrated under reduced pressure to yield 2.1 g (90%) of **37a**: ^1H NMR ($CDCl_3$) δ 1.78 (s, 3 H, CCH_3), 2.4 (s, 1 H, NH, exchanged by D_2O), 2.6 (d, 1 H, benzylic, $J_{11x,11n}$ = 17 Hz), 3.4 (dd, 1 H, benzylic, $J_{11x,11n}$ = 17 Hz, $J_{10,11x}$ = 6 Hz), 4.6 (d, 1 H, bridgehead, $J_{10,11x}$ = 6 Hz), 6.8–7.3 (m, 8 H, aromatic); *m/e* (%) 221 (100, M^+), 220 (71), 206 (12), 180 (20), 179 (53), 178 (31), 144 (27).

A solution of **37a** (1.5 g) in acetone (20 mL) was mixed with a solution of oxalic acid (0.6 g) in acetone (20 mL). The resulting crystalline solid was collected by suction filtration and recrystallized from methanol–acetone to yield 1.8 g of **37a** hydrogen oxalate: mp 216–218 °C.

Anal. Calcd for $C_{18}H_{17}NO_4$: C, 69.44; H, 5.50; N, 4.49. Found: C, 69.68; H, 5.40; N, 4.31.

5-Ethylidene-10-oxo-10,11-dihydro-5*H*-dibenzo[*a*,*d*]-cycloheptene (33b). To a stirred slurry of ethyltriphenylphosphonium bromide (21 g, 0.057 mol) in ether (400 mL) was

added dropwise butyllithium in hexane (48 mL, 1.3M). To the resulting solution was added a solution of **32** (13.5 g, 0.044 mol) in THF (100 mL). The resulting mixture was stirred and heated under reflux for 3.5 h, cooled, and poured into ice–water (300 mL). The organic phase was separated and the aqueous phase extracted with ether (2 × 150 mL). The combined organic solutions were concentrated under reduced pressure. The concentrate was stirred with a mixture of 1 N aqueous hydrochloric acid (300 mL) and ether (300 mL). The ether phase was separated, the aqueous phase was extracted with ether, and combined ether solutions were dried over Na_2SO_4 and filtered, and the filtrate was concentrated to 100 mL. Triphenylphosphine oxide was removed by filtration and the filtrate was chromatographed on silica gel which was eluted with chloroform to yield 10.1 g (98%) of **33b**: mp 93–95 °C; ^1H NMR ($CDCl_3$) δ 1.95 (d, 3 H, CCH_3, J = 7 Hz), 3.7 (d, 1 H, benzylic, J = 12 Hz), 4.4 (d, 1 H, benzylic, J = 12 Hz), 5.9 (q, 1 H, vinyl, J = 7 Hz), 7.1–7.5 (m, 7 H, aromatic), 8.2 (m, 1 H, aromatic); m/e (%) 234 (65, M^+), 219 (30, M – CH_3), 206 (100, M – CO), 205 (70), 204 (11), 203 (18), 202 (22), 191 (83), 189 (27), 178 (21); IR (Nujol) 1675 (C=O), 1590, 1280, 1150, 1020, 780, 765, 755 cm^{-1}.

Anal. Calcd for $C_{17}H_{14}O$: C, 87.14; H, 6.02. Found: C, 87.39; H, 5.96.

5-Ethylidene-10-hydroximino-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene (34b). A solution of **33b** (12.2 g, 0.052 mol), hydroxylamine hydrochloride (4.6 g, 0.065 mol), and sodium acetate (5.33 g, 0.065 mol) in methanol (250 mL) was heated under reflux for 3 h. The solvent was evaporated, and the residue was slurried with 0.5 N aqueous NH_3 (150 mL) and extracted with ether (3 × 150 mL). The combined extracts were dried over Na_2SO_4 and filtered, and the filtrate was evaporated to dryness. The residue was recrystallized from cyclohexane to yield 11.2 g (86%) of **34b**: mp 128–131 °C; ^1H NMR ($CDCl_3$) δ 1.9 (d, 3 H, CCH_3, J = 7 Hz), 4.2 (s, 2 H, benzylic), 5.9 (q, 1 H, vinyl, J = 7 Hz), 7.3 (m, 7 H, aromatic), 7.8 (m, 1 H, aromatic), 10.6 (br s, 1 H, OH, exchanged by D_2O); m/e (%) 249 (100, M^+), 233 (23), 232 (42), 231 (39), 230 (77), 218 (11), 217 (35), 216 (32), 215 (20), 206 (14), 205 (37), 204 (29), 203 (29), 202 (20); IR (Nujol) 3220, 3260, 950, 925, 775, 765, 750 cm^{-1}; TLC (silica gel, toluene) R_f 0.24.

Anal. Calcd for $C_{17}H_{15}NO$: C, 81.89; H, 6.02; N, 5.61. Found: C, 81.71; H, 5.88; N, 5.53.

5-Ethylidene-10-hydroxamino-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene (35b). To a solution of **34b** (10.3 g, 0.041 mol) and $NaCNBH_3$ (8 g) in methanol (300 mL) was added dropwise with stirring a solution of 12 N aqueous hydrochloric acid in methanol (1:1 (v/v)) to maintain the pH at 3–3.4. After 3 h, TLC (alumina eluted with 5% ethanol in toluene) showed disappearance of **34b** (R_f 0.82) and formation of **35b** (R_f 0.74). The solvent was removed under reduced pressure, the residue was slurried with 1 N aqueous hydrochloric acid (200 mL), the pH was adjusted to 8.5 with concentrated aqueous NH_3, and the mixture was extracted with ether (3 × 150 mL). The combined extracts were dried over Na_2SO_4 and filtered, and the filtrate was evaporated. The residue was recrystallized from cyclohexane to yield 9.1 g (89%) of **35b**: mp 121–124 °C; ^1H NMR ($CDCl_3$) δ 1.8 (d, 3 H, CCH_3, J = 7 Hz), 3.3 (m, 2 H, benzylic), 4.5 (br t, 1 H, CHN), 5.8 (s, 2 H, NH + OH, exchanged by D_2O), 5.9 (q, 1 H, vinyl, J = 7 Hz), 7.1 (m, 8 H, aromatic); m/e (%) 251 (10, M^+), 236 (20), 235 (20), 234 (28), 219 (100), 218 (41), 217 (33), 204 (36), 203 (32), 202 (26), 178 (24); IR (Nujol) 3240, 1035, 775, 755, 745 cm^{-1}.

Anal. Calcd for $C_{17}H_{17}NO$: C, 81.22; H, 6.82; N, 5.57. Found: C, 80.92; H, 7.13; N, 5.58.

5-Ethyl-12-hydroxy-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5,10-imine (36b). A mixture of **35b** (12.5 g, 0.05 mol) and *n*-decane (450 mL) was heated at 185 °C for 3 h. The *n*-decane was removed under reduced pressure (2 torr). The residue was stirred with 0.5 M aqueous hydrochloric acid (350 mL) and ether (150 mL). The aqueous layer was separated, washed with ether (100 mL), made basic (pH 8.5) with concentrated aqueous NH_3, and extracted with ether (3 × 150 mL). These combined extracts were dried over Na_2SO_4 and filtered, and the filtrate was evaporated. The residue (5.6 g) was chromatographed on a silica gel column which was eluted with 2% methanol in chloroform to obtain 3.3 g of **36b**. Recrystallization from hexane gave 2.6 g (21%) of **36b**: mp 112–116 °C; ^1H NMR ($CDCl_3$) δ 1.2 (m, 3 H, CCH_3), 2.2–3.0 (m, 3 H, CH_2CH_3 + benzylic), 3.4–3.9 (m, 1 H, benzylic), 4.6–4.9 (m, 1 H, bridgehead), 6.8–7.4 (m, 9 H, aromatic + OH); m/e (%) 251 (48, M^+), 236 (16, M^+ – CH_3), 235 (25, M^+ – O), 234 (100, M^+ – OH), 222 (7), 206 (20), 205 (54), 204 (25), 179 (59), 178 (25), 174 (33); IR (Nujol) 3200, 970, 890, 780, 745 cm^{-1}.

Anal. Calcd for $C_{17}H_{17}NO$: C, 81.22; H, 6.82; N, 5.57. Found: C, 81.37; H, 6.92; N, 5.45.

5-Ethyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5,10-imine (37b). To a soluton of **36b** (2.5 g, 0.01 mol) in acetic acid (30 mL) was added portionwise with stirring zinc dust (1.6 g). The mixture was stirred and heated at 65 °C for 3.5 h, cooled, and filtered, and the filter cake was washed with ether (200 mL). The filtrate was concentrated under reduced pressure, and the residue was slurried with 1 N aqueous NH_3 and extracted with ether (3 × 150 mL). The combined extracts were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The concentrate was chromatographed on alumina which was eluted with 0.5% methanol in ether to obtain 2.1 g (90%) of **37b**: ^1H NMR ($CDCl_3$) δ 1.1 (t, 3 H, CCH_3, J = 6.5 Hz), 2.4 (q, 2 H, CH_2CH_3, J = 6.5 Hz), 2.4 (s, 1 H, NH, exchanged by D_2O), 2.65 (d, 1 H, benzylic, $J_{11x,11n}$ = 17 Hz), 3.45 (dd, 1 H, benzylic, $J_{11x,11n}$ = 17 Hz, $J_{10,11x}$ = 6 Hz), 4.65 (d, 1 H, bridgehead, $J_{10,11x}$ = 6 Hz), 7.0 (m, 8 H, aromatic); m/e (%) 235 (70, M^+), 234 (28), 221 (17), 220 (100), 206 (20), 180 (22), 179 (22), 178 (20).

To a solution of **37b** (1.42 g) in acetone (25 mL) was added oxalic acid (0.54 g) in acetone (25 mL). The resulting crystalline solid was collected by suction filtration and recrystallized from methanol–acetone to yield 1.7 g of **37b** hydrogen oxalate: mp 240–241 °C.

Anal. Calcd for $C_{19}H_{19}NO_4$: C, 70.14; H, 5.89; N, 4.30. Found: C, 69.95; H, 5.86; N, 4.15.

5-Propylidene-10-oxo-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene (33c). A solution of **32** (7 g, 0.023 mol) in THF (52 mL) was added to the Wittig reagent prepared from *n*-propyltriphenylphosphonium bromide (11.5 g, 0.03 mol) and *n*-butyllithium in hexane (16.8 mL, 2.1 M) in ether (180 mL). Proceeding as described for **33b**, there was isolated 4.8 g (84%) of **33c**: mp 89.5–91.5 °C (ethanol); ^1H NMR ($CDCl_3$) δ 1.02 (t, 3 H, CCH_3, J = 7 Hz), 2.28 (m, 2 H, =CCH_2), 3.5–4.75 (m, 2 H, benzylic), 5.75 (t, 1 H, =CH, J = 7 Hz), 6.8–7.8 (m, 8 H, aromatic); IR (Nujol) 1670 (C=O) cm^{-1}; m/e (%) 248 (66, M^+), 233 (47, M – CH_3), 219 (100, M – C_2H_5).

Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 87.42; H, 6.68.

5-Propylidene-10-hydroximino-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene (34c). The oxime **34c** was prepared as described for **34a** from **33c** (26 g, 0.1 mol), hydroxylamine hydrochloride (9.17 g, 0.132 mol), and sodium acetate (10.83 g, 0.132 mol) in methanol (500 mL). Recrystallization from ethanol gave 26.6 g (95%) of **34c**: mp 118.5–120.5 °C; ^1H NMR ($CDCl_3$) δ 1.03 (t, 3 H, CCH_3, J = 7 Hz), 2.28 (m, 2 H, CH_2CH_3), 4.16 (s, 2 H, benzylic), 5.70 (t, 1 H, vinyl, J = 7 Hz), 6.8–7.9 (m, 8 H, aromatic), 9.56 (s, 1 H, OH); m/e 263 (M^+), 247 (M – O), 246 (M – OH).

Anal. Calcd for $C_{18}H_{17}NO$: C, 82.10; H, 6.51; N, 5.32. Found: C, 82.37; H, 6.80; N, 5.42.

5-Propylidene-10-hydroxamino-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cycloheptene (35c). The hydroxylamine **35c** was prepared by reduction of **34c** (26.3 g, 0.10 mol) with $NaCNBH_3$ (17 g, 0.27 mol) in methanolic hydrogen chloride (700 mL) as described for **35a**. Trituration of the crude product with hexane gave 24.0 g (91%) of **35c**: mp 107–111 °C; ^1H NMR ($CDCl_3$) δ 1.02 (t, 3 H, CCH_3, J = 7 Hz), 2.17 (m, 2 H, CH_2CH_3), 3.33 (br, 2 H, benzylic), 4.52 (br, 1 H, NCH), 5.70 (t, 1 H, vinyl, J = 7 Hz), 5.75 (br, 2 H, NH + OH, exchanged by D_2O), 6.8–7.8 (m, 8 H, aromatic); m/e (%) 265 (12, M^+), 263 (13, M – 2 H), 233 (98, M – NHOH), 217 (100).

Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.58; H, 7.34; N, 5.50.

5-Propyl-12-hydroxy-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5,10-imine (36c). Compound **36c** was prepared by heating a solution of **35c** (7.0 g, 0.026 mol) in *n*-decane (120 mL) under reflux for 30 min. Proceeding as described for **36a**, the crude product was isolated and recrystallized from cyclohexane to yield 3.8 g (54%) of **36c**: mp 178.5–180 °C; ^1H NMR ($CDCl_3$) δ 1.09

(m, 3 H, CH_3), 1.2–1.9 (m, 2 H, CH_2CH_3), 1.97–3.0 (m, 3 H, $CH_2CH_2CH_3$ + 1 benzylic), 3.03–3.84 (m, 1 H, 1 benzylic), 4.47–4.81 (m, 1 H, bridgehead), 5.75–7.75 (m, 9 H, aromatic + OH); *m/e* (%) 265 (M^+, 38), 250 (M – CH_3, 9), 249 (60), 248 (82), 220 (91), 206 (62), 205 (64), 179 (100).

Anal. Calcd for $C_{18}H_{19}NO$: C, 81.47; H, 7.22; N, 5.28. Found: C, 81.76; H, 7.26; N, 5.29.

5-Propyl-10,11-dihydro-5*H*-dibenzo[*a*,*d*]cyclohepten-5,10-imine Hydrochloride (37c). Reduction of an acetic acid (50 mL) solution of **36c** (3.2 g, 0.012 mol) with Zn dust (3 g, 0.046 mol) for 1 h at 65 °C followed by column chromatography on neutral activity I aluminum oxide (eluted with 0.5% methanol in ether) gave 1.9 g (63%) of **37c** as the base: ^1H NMR ($CDCl_3$) δ 0.8–1.07 (m, 3 H, CH_3), 1.1–2.9 (m, 6 H, $CH_2CH_2CH_3$ + 1 benzylic + NH), 3.4 (dd, 1 H, benzylic, *J* = 16 Hz and 5 Hz), 4.63 (d, 1 H, bridgehead, *J* = 5 Hz), 6.7–7.6 (m, 8 H, aromatic). Treatment of this product with ethanolic hydrogen chloride gave **37c**: mp 298–299.5 °C (ethanol); ^1H NMR (CF_3CO_2D) δ 1.2 (t, 3 H, CH_3, *J* = 7 Hz), 1.4–2.1 (m, 2 H, CH_2CH_3), 2.5–2.95 (m, 2 H, $CH_2CH_2CH_3$), 3.13 (d, 1 H, benzylic, *J* = 18 Hz), 3.93 (dd, 1 H, benzylic, *J* = 18 Hz and 5 Hz), 5.55 (t, 1 H, bridgehead, *J* = 5 Hz), 7.0–7.6 (m, 8 H, aromatic), 7.6–8.5 (br, 2 H, NH_2^+); *m/e* (%) 249 (M^+, 49), 220 (M – C_2H_5, 100); IR (Nujol) 3360, 2780–2400, 768, 758, 720, 710 cm^{-1}.

Anal. Calcd for $C_{18}H_{19}N$·HCl: C, 75.64; H, 7.05; N, 4.90; Cl, 12.41. Found: C, 76.13; H, 7.16; N, 4.93; Cl, 12.54.

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Registry No. 2, 67464-60-2; **8**, 70912-55-9; **9**, 70912-56-0; **10**, 26899-84-3; **11**, 70912-57-1; **12**, 70313-34-7; **13a**, 70912-58-2; **14a**, 70912-59-3; **15**, 70313-35-8; **16a**, 70313-36-9; **16b**·HCl, 70912-60-6; **16c**, 70912-61-7; **16c**·HCl, 70912-62-8; **17a**, 70313-42-7; **17b**, 70912-63-9; **17c**, 70912-64-0; **18a** hydrogen oxalate, 70313-44-9; **18b**·HCl, 70912-65-1; **18c**, 70912-66-2; **18c**·HCl, 70912-67-3; **19**, 70313-39-2; **20**, 70912-68-4; **21**, 70912-69-5; **22**, 70912-70-8; **22**·HCl, 70313-40-5; **23**, 70313-41-6; **23**·HCl, 70912-71-9; **24**, 70313-45-0; **25a**, 70313-46-1; **25b**, 70313-52-9; **26a**, 70313-53-0; **26b**, 70912-72-0; **27a**, 70912-73-1; **28a**, 70313-54-1; **28a**·HCl, 70912-74-2; **28b**, 70912-75-3; **29a**, 70313-55-2; **29b**, 70912-76-4; **30a**, 70313-56-3; **30a**·HCl, 70912-77-5; **30b**, 70912-78-6; **30b**·HCl, 70912-79-7; **31**, 17044-50-7; **32**, 16171-52-1; **33a**, 70449-91-1; **33b**, 70449-96-6; **33c**, 70912-80-0; **34a**, 70449-92-2; **34b**, 70449-97-7; **34c**, 70912-81-1; **35a**, 70449-85-3; **35b**, 70449-98-8; **35c**, 70912-82-2; **36a**, 70449-93-3; **36b**, 70469-63-5; **36c**, 70912-83-3; **37a**, 70449-94-4; **37a** hydrogen oxalate, 70449-95-5; **37b**, 70449-99-9; **37b** hydrogen oxalate, 70450-00-9; **37c**, 70912-84-4; **37c**·HCl, 70912-85-5; methylamine, 74-89-5; 6,6-ethylenedioxy-12-methyl-5,6,7,12-tetrahydrodibenzo[a,d]cyclooctene-12-ol, 70912-86-6; 6,6-ethylenedioxy-12-ethylidene-5,6,7,12-tetrahydrodibenzo[a,d]cyclooctene, 70313-51-8; benzylamine, 100-46-9; *N*-methylpiperazine, 109-01-3.

Transannular Reactions of Dibenzo[*a*,*d*]cycloalkenes.[1] 2.[2] Synthesis of Bridgehead Substituted Dibenzo[*a*,*d*]cycloalkenimines by a Regiospecific Transannular Amine to Olefin Addition

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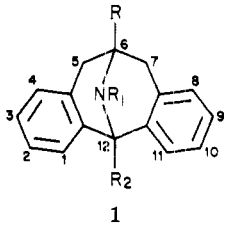
New synthetic approaches to dibenzo[a,d]cycloheptene-5,10-imines (**2**) and to dibenzo[a,d]cyclooctene-5,12- and -6,12-imines (**3** and **1**, respectively) have been devised. These routes have been designed specifically to allow for incorporation of alkyl substituents at the bridgeheads. They make use of an unusual, regiospecific, intramolecular amine to olefin addition to establish both the nitrogen bridge and the bridgehead alkyl group in a single step. Thus, **5** is converted rapidly (<30 min) and regiospecifically to **6** upon treatment with a small amount of *n*-butyllithium in tetrahydrofuran at room temperature. Entropic bias provided by the carbon skeleton and a radical mechanism mediated by the benzhydryl olefin are postulated to facilitate and direct this transformation.

In the course of studies[2,3] on the synthesis of dibenzo[a,d]cycloalkenimines (**1**–**3**), the problem of constructing such molecules with alkyl substituents at both bridgehead positions arose. Derivatives of **1** and **2** substituted at the benzhydryl bridgehead were synthesized by the hydroxylamine to olefin transannular addition described in the previous work.[2] However, this method was unsuitable for placing alkyl substituents at both bridgeheads due to the inaccessibility of the required hydroxylamine intermediate. Furthermore, its use in the synthesis of **3** was precluded entirely by the facile cyclization of the requisite diketone to an indeno[1,2-a]indene (see Scheme V). Thus, the goal of the present work was



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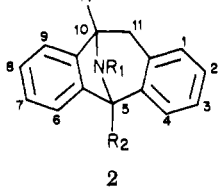

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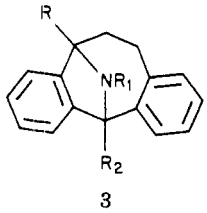

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(1) Presented in part at the 176th National Meeting of the Americal Chemical Society, Miami Beach, Fla., Septemper 11–15, 1978; Abstract ORGN53.

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