(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.

Acknowledgment. The authors thank the following people for assistance in recording and interpreting spectral and analytical data: Dr. David Cochran and Mrs. Joan Murphy for NMR spectra; Mr. Robert Rhodes for mass spectra; and Mr. K. B. Streeter and Mrs. Jan Stranick for microanalyses. We also are indebted to Professors Robert Stevens, Samuel Danishefsky, and Cal Meyers for many valuable discussions.

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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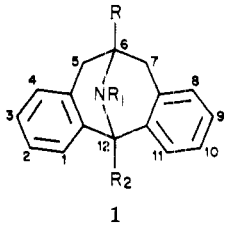
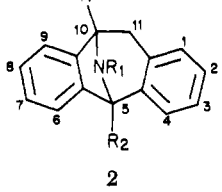
New synthetic approaches to dibenzo[a,d]cycloheptene-5,10-imines (**2**) and to dibenzo[a,d]cyclooctene-5,12- and -6,12-imines (**3** and **1**, respectively) have been devised. These routes have been designed specifically to allow for incorporation of alkyl substituents at the bridgeheads. They make 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.

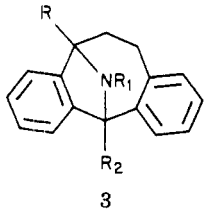
In the course of studies[2,3] on the synthesis of dibenzo[a,d]cycloalkenimines (**1**–**3**), the problem of constructing such molecules with alkyl substituents at both bridgehead positions arose. Derivatives of **1** and **2** substituted at the benzhydryl bridgehead were synthesized by the hydroxylamine 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



1



2



3

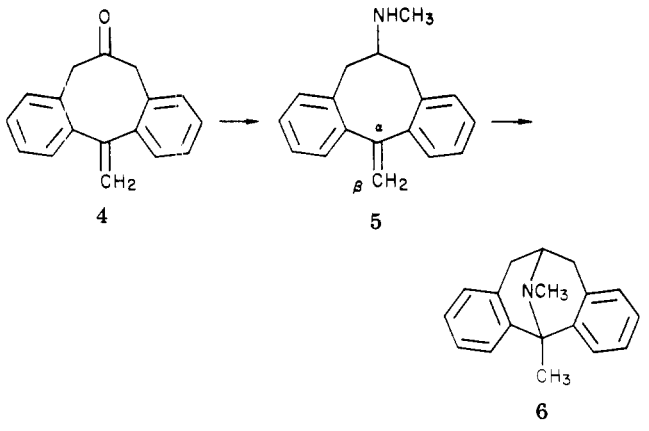
(1) Presented in part at the 176th National Meeting of the Americal Chemical Society, Miami Beach, Fla., Septemper 11–15, 1978; Abstract ORGN53.

(2) M. E. Christy, P. S. Anderson, S. F. Britcher, C. D. Colton, B. E. Evans, D. C. Remy, and E. L. Engelhardt, *J. Org. Chem.*, preceding paper in this issue.

(3) D. C. Remy, P. S. Anderson, M. E. Christy, and B. E. Evans, *J. Org. Chem.*, **43**, 4311 (1978).

0022-3263/79/1944-3127$01.00/0

Scheme I



4 5 6

to establish a useful alternative to the hydroxylamine ring closure and to apply it to the synthesis of these ring systems (**1–3**).

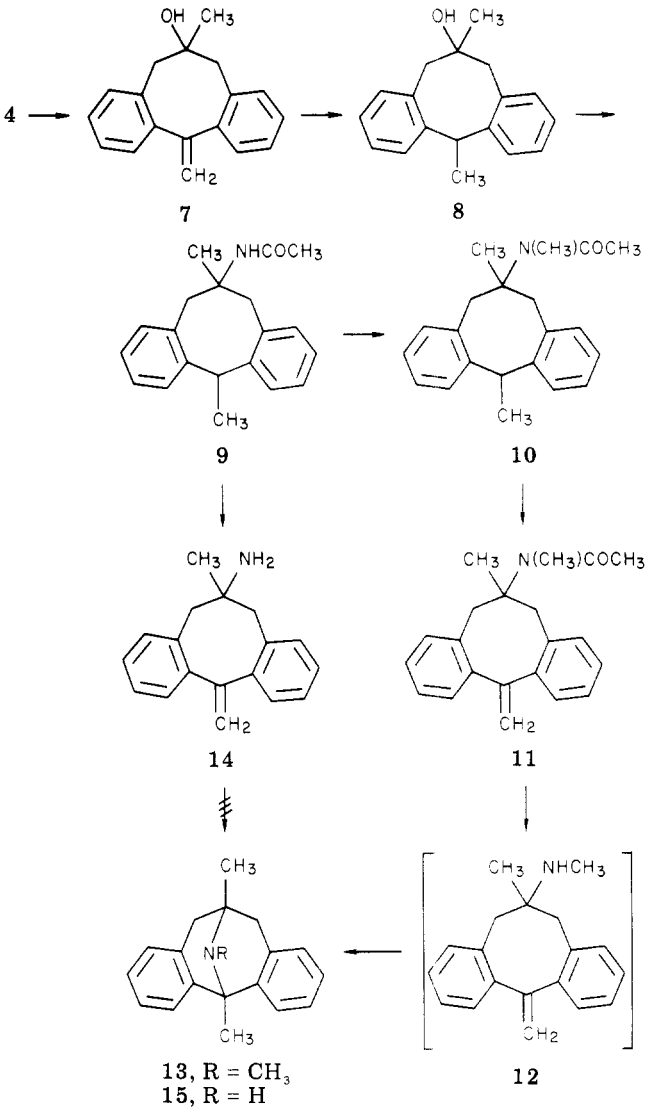
In the development of such a method, it was desirable to retain the regioselectivity and freedom from stereochemically complex intermediates characteristic of the hydroxylamine route,[2] while avoiding the known liability of benzhydrylamines[4] and tertiary halides[5] toward elimination reactions. Reported herein is a new synthetic approach to **1–3** which satisfied all of these criteria. The key to this strategy is an unusual intramolecular amine to olefin addition, the utility of which is described in the following examples.

Dibenzo[*a,d*]cycloocten-6,12-imines. A. 12 Substituted (Scheme I). Reductive amination by a modified Borch procedure[6] of the readily available keto olefin **4**[2] gave the amine **5** which served as the model substrate for testing cyclization methods. Inspection of a Dreiding model of **5** revealed a conformation which placed the amine and olefin functionalities in close proximity which might entropically favor ring closure.

Initial attempts to effect this closure by heating **5** or its hydrochloride to nearly 200 °C in an inert solvent (undecane, bp 196 °C) were unsuccessful. In a polar protic solvent, however, the desired conversion was observed. Thus, heating **5** in refluxing ethylene glycol (bp 198 °C) resulted in slow ($t_{1/2}$ ca. 5 h) but completely regiospecific cyclization to **6**. The hydrochloride of **5** was inert under these conditions but cyclized as before when excess KOH was added. Together with the few existing reports of intermolecular additions of amines to unactivated olefins in the presence of strong base,[7a-d] these results prompted an examination of the effects of added strong base on the cyclization of **5**.

When a solution of **5** in tetrahydrofuran (THF) was treated with lithium diisopropylamide (LDA) at room temperature, no cyclization was observed. With as little as 0.1 equiv of butyllithium, however, a rapid ($t_{1/2}$ ca. 10 min) and efficient conversion of **5** to **6** was seen under the same conditions. For preparative purposes, **5** was purified

Scheme II



as the hydrochloride and treated directly with 1.1 equiv of butyllithium to induce cyclization of **6** as described above.

B. 6,12 Disubstituted (Scheme II). Having established the conditions for the above ring closure, we pursued its application in the more difficult synthesis of **13** with quaternary centers at both bridgehead positions. For this synthesis, the required acyclic amine or amine derivative must be attached to a tertiary carbon center. Among the relatively few routes to such functional groups, the Ritter reaction[8] was particularly attractive and in fact served to accomplish this goal. The keto olefin **4** again served as the starting material. Treatment with methylmagnesium bromide[9] gave the carbinol **7** containing the methyl group which would ultimately become the 6 substituent in **13**. It was necessary to protect the exocyclic olefin in **7** by hydrogenation to **8**[11] in order to carry out successfully the subsequent Ritter reaction with acetonitrile and sulfuric acid.[10] With **8** as substrate, Ritter conditions efficiently introduced the required secondary amide functionality at

(4) J. Nally, J. Nazareno, J. Polesuk, and H. V. Maulding, *J. Pharm. Sci.*, **64**, 437 (1965).

(5) The activating effect of α-phenyl substituents in elimination reactions is well-known. For example, see J. March, "Advanced Organic Chemistry, Reactions, Mechanisms, and Structure", 2nd ed, McGraw-Hill, New York, N.Y., 1977, pp 914–5.

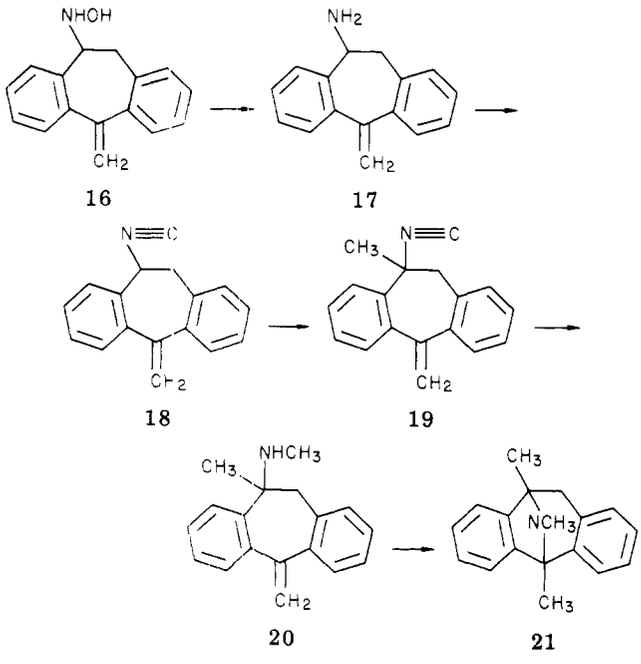
(6) R. F. Borch, M. D. Bernstein, and H. D. Durst, *J. Am. Chem. Soc.*, **93**, 2897 (1971).

(7) (a) R. J. Schlott, J. C. Falk, and K. W. Narducy, *J. Org. Chem.*, **37**, 4243 (1972); (b) T. Fujita, K. Suga, and S. Watanabe, *Chem. Ind. (London)*, 231 (1973); (c) R. Wegler and G. Pieper, *Chem. Ber.*, **83**, 1 (1950); (d) J. Wollensak and R. D. Closson, "Organic Syntheses", Collect. Vol. 5, Wiley, New York, N.Y., 1973, pp 575–7, and references cited therein.

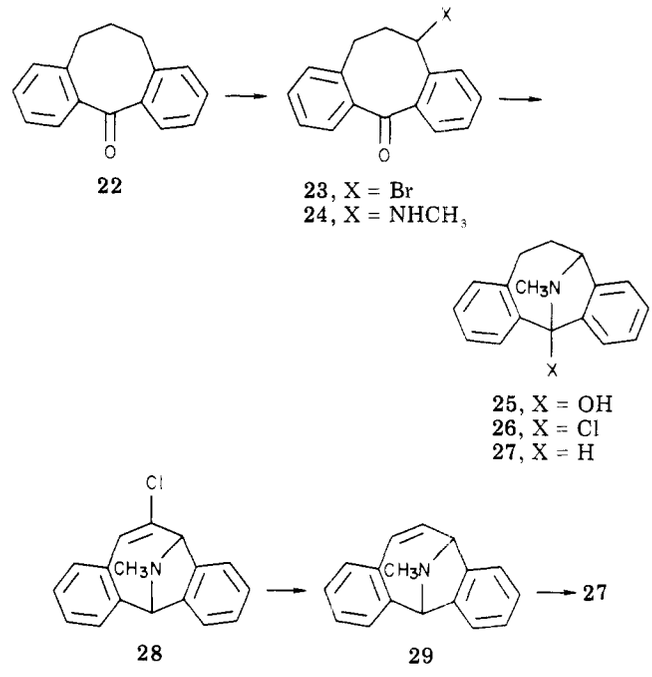
(8) For a review of the Ritter reaction, see L. I. Krimen and D. J. Cota, *Org. React.*, **17**, 213 (1969).

(9) With methyllithium, **4** underwent addition to both the ketone and olefin to give 12-ethyl-6-methyl-5,6,7,12-tetrahydrodibenzo[*a,d*]cyclooctene-6-ol as a mixture of geometrical isomers: MS *m/e* (%) 266 (37, M^+), 235 (60, $M^+ - C_2H_5$), 234 (24), 205 (22), 192 (42), 72 (34), 71 (32).

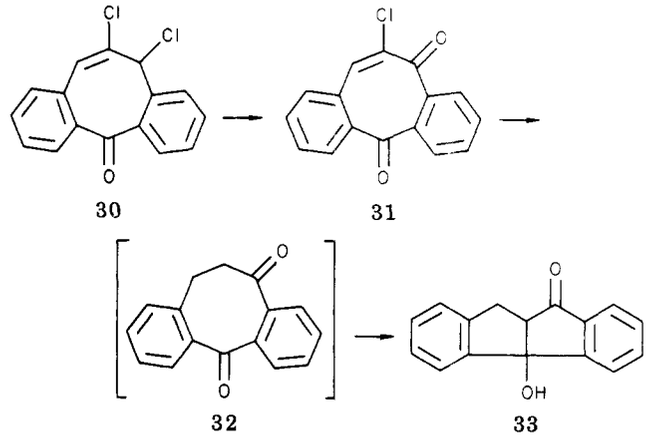
Scheme III



Scheme IV



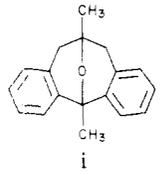
Scheme V



the 6 position to give **9**[12] which was converted to the tertiary amide **10** on N alkylation with lithium diisopropylamide (LDA) and iodomethane. Following attempts with a number of oxidizing agents, DDQ was found to be the reagent of choice for regenerating the exocyclic olefin (**10** to **11**).[13] When **11** was heated under reflux in ethylene glycol containing potassium hydroxide to remove the *N*-acetyl group, conversion to the target cyclic amine **13** was achieved. As with **5**, the ring closure presumably proceeded via the amine **12** which cyclized spontaneously under these conditions. Interestingly, under the same conditions, the primary amine **14** was totally inert toward cyclization. The methyl group on nitrogen rather than that on the α carbon appears to dictate the ease of cyclization in this series of amines. Since the *N*-methyl group facilitates rather than retards the reaction, the effect is probably not steric and perhaps reflects the influence of the substituent on an intermediate radical or radical anion. In addition to this effect, the proper orientation and close proximity of the reacting groups must also contribute to the facility of the amine to olefin addition under these conditions.

Dibenzo[*a,d*]cyclohepten-5,10-imines (Scheme III). Synthetic approaches to **21** are restricted even more than the routes to **13** by the availability of the necessary intermediates. Since the amine precursor **20** is a *tert*-carbinyl, benzylic, and β-phenethyl type amine, it must be generated and cyclized under conditions which will preclude the possibility of an elimination reaction at this labile center. In view of these considerations, the sequence of reactions outlined in Scheme III was derived. The strategy was to convert the hydroxylamine **16**[2] to the isocyanide **18** thus activating this benzylic position for the alkylation reaction which would introduce the required methyl group. Zinc and acetic acid reduction of **16** gave **17**, which despite the presence of the olefinic linkage, reacted with dichlorocarbene to give a high yield of the isocyanide **18**. Methylation of **18** at C-10 occurred smoothly with LDA and iodomethane to yield **19** which was reduced to the amine **20** with lithium aluminum hydride. Treatment of

(10) An attempt to effect the Ritter reaction on the olefinic carbinol **7** led to transannular carbinol to olefin addition which gave ether **i**: ^{1}H NMR ($CDCl_3$) δ 1.55 (s, 3 H, CCH_3), 1.98 (s, 3 H, CCH_3), 2.64 (d, 2 H, benzylic, J = 17 Hz), 3.10 (d, 2 H, benzylic, J = 17 Hz), 6.9–7.7 (m, 8 H, aromatic); MS *m/e* (%) 250 (32, M^+), 235 (22, $M^+ - CH_3$).



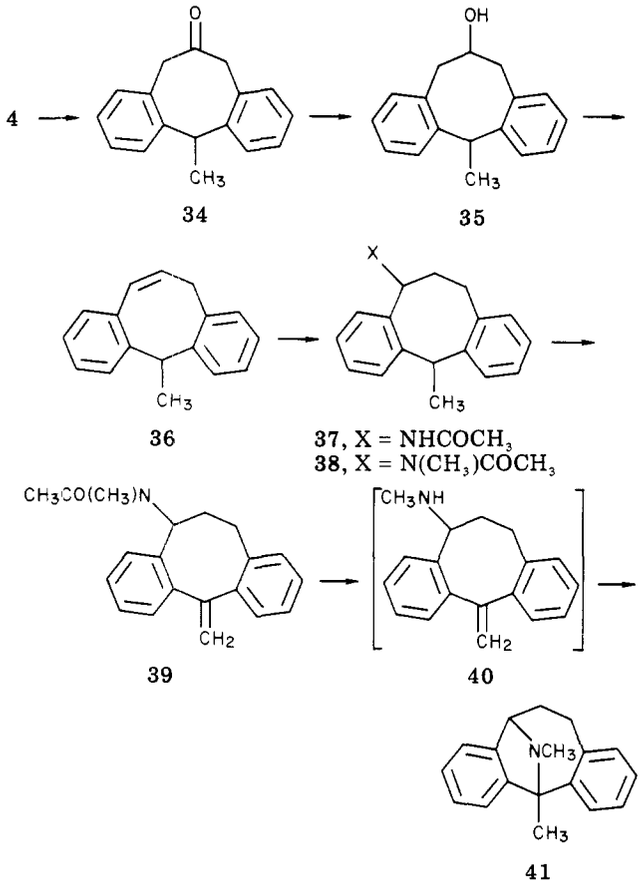
i

(11) As a result of this hydrogenation, two chiral centers are created simultaneously (positions 6 and 12), and **8** is in fact obtained as a mixture of two diasteromers. The isomer *trans*-**8** in which the 6- and 12-methyl substituents are trans predominates slightly over *cis*-**8** by ca. 1.4:1. The Grignard addition/hydrogenation of **4** can also be carried out in the reverse order. The stereochemical results are quite different, however. Thus, hydrogenation of **4** gave the ketone **34** (see Scheme VI) which, upon addition of methylmagnesium bromide, provided *trans*-**8** stereospecifically and in excellent yield.

(12) Amide **9** is obtained as a mixture of two diastereomers, *cis*-**9** with the 6- and 12-methyl substituents in a cis configuration, and *trans*-**9** with the opposite configuration. The ratio of *cis*-**9** to *trans*-**9** is dependent on the isomer composition of the starting carbinol **8**. Thus, pure *trans*-**8** gave a roughly equimolar mixture of *cis*-**9** and *trans*-**9** (cis/trans = 1.5/1), while pure *cis*-**8** gave a preponderance of *cis*-**9** (*cis*-**9**/*trans*-**9** = 10/1). These results indicate a slight preference for attack on position 6 at the face trans to the 12-methyl substituent. With this 12 substituent as an equatorial-preferring conformational anchor, models indicate greater accessibility to this face. The observed stereochemical result, however, may be due to a combination of steric hinderance and participation by an intermediate phenonium ion.

(13) The stereochemical complexity described in ref 11 and 12 vanished with simultaneous destruction of both chiral centers in this step (position 6 reverts to its original prochiral status).

Scheme VI



20 with butyllithium in THF at room temperature effected an efficient conversion to the desired cyclic amine 21. Thus, this type of transannular nitrogen ring closure can be applied with equal success in seven-membered rings.

Dibenzo[*a*,*d*]cycloocten-5,12-imines (Scheme IV–VI). The final application of the amine to olefin cyclization was in the synthesis of 12,13-dimethyl-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cycloocten-5,12-imine (41) (Scheme VI). Since this is a new heterocyclic ring system, initial exploratory studies directed toward the synthesis of the parent compound (27) were investigated. The synthesis of 27 was achieved in very low overall yield by the route outlined in Scheme IV. This involved bromination of the ketone 22[14] ($Br_2/h\nu$) followed by treatment of the benzyl bromide 23 with methylamine. This bromination method as well as others[15] gave a complex mixture from which 23 was obtained in poor yield. As expected,[2] the isolated product of the methylamine reaction was the carbinolamine 25 rather than the amine 24. Treatment of 25 with thionyl chloride gave 26. Reduction with lithium aluminum hydride gave the desired amine 27. An alternate synthesis of 27 that proceeded in much better yield was the two-step reduction of 28[3] to 29 (LAH) and 29 to 27 (hydrogenation). Neither of these routes, however, was potentially useful for the synthesis of the bridgehead substituted amine 41.[16]

An attempt to adapt the hydroxylamine cyclization method[2] for the preparation of 41 (Scheme V) was precluded by the instability of the required intermediate diketone 32. Although the ketone 30[3] was easily oxidized with silver tetrafluoroborate in dimethyl sulfoxide to the diketone 31, hydrogenation of this diketone even under mild conditions gave only 33 rather than 32. Undoubtedly, 32 was formed initially but underwent an intramolecular aldol condensation. These results discouraged further work along the hydroxylamine to olefin cyclization pathway and led to the successful synthesis of 41 using the alternate amine to olefin cyclization procedure as outlined in Scheme IV.

Again, the versatile keto olefin 4 served as the starting material and the Ritter reaction introduced the required nitrogen functionality. Catalytic hydrogenation of 4 gave the ketone 34 with the exocyclic methylene group protected as a methyl substituent. Sodium borohydride reduction gave the alcohol 35[17] which was dehydrated to the olefin 36 with phosphorus oxychloride in pyridine. Directed now by the adjacent aromatic ring, the Ritter reaction with acetonitrile provided regioselectively the benzylic amide 37. Subsequent N methylation with LDA and iodomethane to yield 38 followed by DDQ oxidation to regenerate the exocyclic olefin in 39 set the stage for the final cyclization reaction. As with 11, heating a solution of 39 in ethylene glycol containing KOH effected cleavage of the amide and concomitant cyclization of 40 to amine 41.[18]

Stereochemistry

The intermediates 8–10, 35, 37, and 38 described in this work all contain two chiral carbon atoms and hence can exist in two diasteromeric forms. While this distinction disappeared on regeneration of the 12-methylene group during the synthesis of the target dibenzo[*a*,*d*]cyclooctenimines, certain results relevant to medium-ring stereochemistry were obtained and merit brief discussion here.

The parent hydrocarbon, 5,6,7,12-tetrahydrodibenzo[*a*,*d*]cyclooctene, has been subjected to conformational analysis.[19] This ring system is reported to prefer a rigid chair conformation (98%) with a relatively high barrier to inversion. The NMR spectra of 8–10 and 35 showed a remarkable consistency in the chemical shifts for the 12-methyl (1.75–1.83 ppm) and hydrogen (4.53–4.83 ppm) substituents irrespective of the relative stereochemistry of substituents at the 6 position. This observation is interpreted as evidence that these molecules retain the same rigid chair conformation. In other possible conformations of this ring system, the chemical shift for a 12 substituent would be expected to differ as a function of substituent stereochemistry at the 6 position due to the presence or absence of proximate diaxial interactions.

Placing the dibenzo[*a*,*d*]cyclooctane ring in a rigid chair conformation with the 12-methyl group in the less hindered pseudoequatorial position established a reference point for describing the relative substituent stereochemistry at the 6 position. Relative to a pseudoequatorial 12-methyl group, the 6 substituent can be cis (pseudoaxial) or trans (pseudoequatorial). Inspection of a Dreiding model of the

(14) S. O. Winthrop, M. A. Davis, F. Herr, J. Stewart, and R. Gaudry, *J. Med. Chem.*, 6, 130 (1963).

(15) Bromine and ultraviolet light with HgO gave nearly the same results.

(16) The difficulty in using an organometallic reagent to displace a bridgehead chloride or bromide was discussed in ref 2.

(17) As with 8, simultaneous creation of two chiral centers implies the possibility of diastereomers of 35. In fact, however, no evidence for more than one isomer was obtained by either NMR or TLC. On the basis of the unusually high field absorption of the OH proton at δ 0.78, the single product obtained was assigned the configuration wherein the 6-hydroxy and 12-methyl groups are cis. This is the stereochemistry seen in the preferred trans isomer of 8 (δ(OH) 0.92). Repetition of the reduction with aluminum isopropoxide under Meerwein–Ponndorf–Verley conditions gave identical results.

(18) Since it was possible to methylate 34 at C-5, it is clear that Scheme VI, modified in this way, also could be used for the synthesis of 5,-12,13-trimethyl-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cycloocten-5,12-imine.

(19) F. E. Elhadi, W. D. Ollis, and J. F. Stoddart, *Angew, Chem., Int. Ed. Engl.*, 15, 224 (1976).

dibenzo[a,d]cyclooctane ring in the rigid chair conformation revealed that a pseudoaxial 6 substituent would be shielded by an aromatic ring. The NMR resonance for this group should appear at higher field than that for the corresponding pseudoequatorial group.[20] The observation of these resonances was the experimental basis used to make stereochemical assignments to the isolated cis and trans isomers of **8** and **9**.[11,12] Thus, in cis isomers the 6-methyl resonance appears at approximately 0.80 ppm, and in trans isomers it is near 1.5 ppm. The stereochemical assignments for **10** and **35** follow from this argument. Thus, **10** has a shielded 6-methyl group (0.68 ppm) and **35** has a shielded 6-OH (0.78 ppm) similar to that observed in *trans*-**8** (0.92 ppm).

A similar argument could be made to assign cis stereochemistry to **37** and **38**. However, only a single isomer was isolated in each case, and the respective NMR spectra do not conclusively establish these stereochemical assignments.

Conclusion

In all of the syntheses cited above, the key step is the amine to olefin ring closure. This reaction is remarkable both for its ease, particularly in the case of the butyllithium-mediated process, and for its regiospecificity.

Previous reports indicated that the direct intermolecular addition of amines to unactivated olefins in a strongly basic medium generally required strenuous conditions with respect to time and temperature.[7a-d] Furthermore, the preferred mode of addition to styrenes[7a-c] and 1,1-diphenylethylene[7a] was that which generated a β-phenethylamine.

By contrast, the butyllithium cyclizations of **5** to **6** and **20** to **21** took place rapidly at room temperature, and both these and the ring closures in ethylene glycol gave the α-phenethylamine regiospecifically. These results are most likely due to the close proximity[21] of the reacting groups established in these cases by the carbon framework. Inspection of Dreiding models showed that the amine nitrogen in the acyclic precursors (**5**, **12**, **20**, **40**) can be held in close (1.3–3.3 Å) proximity to both olefinic carbon atoms, with the amine lying in or very near the plane orthogonal to the plane of the olefinic bond.

However, the angle of approach[22] to the benzhydryl carbon differs significantly from that to the exocyclic terminus of the methylene group. The angle of approach to the exocyclic center ("endo" cyclization, β-phenethylamine product) is between 50 and 80° while the approach angle to the benzhydryl carbon ("exo" cyclization, α-phenethylamine product) is approximately 100° in every case. It is estimated that the optimum approach angle for addition to an olefinic double bond is ca. 110°.[24] Clearly the observed mode of cyclization to an α-phenethylamine is favored by this criterion.[25]

However, this argument appears insufficient to explain adequately the remarkable facility of butyllithium to induce cyclizations. As noted above, strong base alone (lithium diisopropylamide) proved ineffective for cyclizing **5** to **6**: butyllithium was required specificially. Furthermore, the ring closure was inhibited by seemingly minor changes in N substituent and by such radical scavengers as oxygen and *p*-dinitrobenzene in amounts stoichiometrically less than the butyllithium. These observations suggest a radical chain process[27] initiated by electron transfer from butyllithium, with the 1,1-diphenylethylene system as a likely acceptor. In this view, the presence of a suitable electron acceptor permits electron transfer to occur, and the proximity and orientation effects described above ensure the efficient regioselective trapping of the resulting benzhydryl radical to give the observed cyclic product.

While the detailed mechanism is as yet uncertain, it seems clear that these ring closures represent examples of the effect of entropy on selective organic transformations.

In summary, this paper has described a new synthetic approach to dibenzo[a,d]cycloalkenimines which allows placement of alkyl substituents at both bridgehead positions. The key to this approach is an unusual intramolecular amine to olefin addition which proceeds with complete regioselectivity.

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 by direct insertion; ^{1}H NMR spectra on a Varian T-60 or EM 390 spectrometer, using $(CH_3)_4Si$ as an internal standard. 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.

6-(Methylamino)-12-methylene-5,6,7,12-tetrahydrodibenzo[a,d]cyclooctene Hydrochloride (5). To a solution of **4** (2.0 g, 0.0085 mol) in THF (200 mL) containing methylamine (6.5 g) was added $NaCNBH_3$ (2.0 g) followed by acetic acid (3 g). After 24 h of stirring, the mixture was evaporated. Water (150 mL) was added and the pH was adjusted to 1 (concentrated HCl). After 1 h of stirring, the aqueous solution was made basic (NH_4OH) and extracted with ether (3 × 100 mL). The combined extracts were dried over Na_2SO_4 and filtered, and the filtrate was evaporated. The residue was dissolved in methanolic hydrogen chloride (11 mL, 1.0 N), and the solution was evaporated to dryness. Recrystallization of the residue from acetonitrile gave 1.9 g (79%) of the hydrochloride of **5**: mp 241–243 °C; ^{1}H NMR (Me_2SO-d_6) δ 2.53 (t, J = 4 Hz, 3 H, NCH_3, collapses to s with D_2O added), 2.93 (d, J = 5 Hz, 4 H, benzylic), 3.40 (m, 1 H, HCN), 5.47 (s, 2 H, $=CH_2$), 7.2–7.6 (m, 8 H, aromatic), 9.2 (br s, 2 H, NH_2); MS m/e (%) 249 (51), 234 (15), 218 (36), 217 (30), 203 (18), 158 (26), 44 (100).

Anal. Calcd for $C_{18}H_{20}NCl$: C, 75.64; H, 7.05; N, 4.90. Found: C, 75.44; H, 6.79; N, 4.92.

Thermolysis of 5 in Ethylene Glycol. A solution of **5** (0.1 g, 4 mmol) in dry ethylene glycol (4 mL) was heated at reflux under nitrogen for 23 h. After being quenched in ice water (50 mL), the reaction mixture was extracted with chloroform (3 × 50 mL). The combined extracts were washed with water (3 × 25 mL), dried over K_2CO_3, and filtered, and the filtrate was evaporated to yield 0.08 g (80%) of **6**. The NMR and mass spectra and TLC R_f (silica gel, $HCCl_3$ elution) were identical with the data described for **6** below.

12,13-Dimethyl-5,6,7,12-tetrahydrodibenzo[a,d]cyclooctene-6,12-imine Hydrogen Oxalate (6). To a stirred slurry of the hydrochloride of **5** (2.1 g, 0.0074 mol) in dry THF (25 mL)

(20) This assignment is consistent with those made for a number of heterocyclic analogues of this ring system: R. P. Gellatly, W. D. Ollis, and I. O. Sutherland, *J. Chem. Soc., Perkin Trans. 1*, 913 (1976).

(21) A. C. Cope, R. J. Cotter, and G. G. Roller, *J. Am. Chem. Soc.*, **77**, 3590 (1955). These authors recognized and defined proximity effects in medium-sized rings. They noted that unusual reactions may be facilitated when reacting groups on opposite sides of these rings are "...brought into close proximity by the geometric conformations of the rings".

(22) The definition of the approach angle follows that of Baldwin.[23]

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

(24) The optimum angle for amine approach to the olefin is assumed to be essentially the same as that for approach to a carbonyl group.[23]

(25) In these cyclizations, a regiochemical distinction between 6-exo vs. 7-endo trig in **1** and 5-exo vs. 6-endo trig in **2** and **3** is evident. The question of whether or not these cyclizations should be discussed in terms of Baldwin's Rules[26] is less clear.

(26) J. E. Baldwin, *J. Chem. Soc., Chem. Commun.*, 734 (1976).

(27) For a brief summary of some of the basic properties of free radical reactions, their detection, and their inhibition, see E. S. Gould, "Mechanism and Structure in Organic Chemistry", Holt, Rinehart and Winston, New York, N.Y., 1959, pp 672–95.

under N_2 was added dropwise butyllithium in hexane (5.4 mL, 1.5 M). The mixture was stirred for 2 h, treated with ice water (2 mL), and concentrated under reduced pressure. The residue was diluted with water (50 mL) and extracted with ether (3 × 25 mL). The combined extracts were washed with water, dried over K_2CO_3, filtered, and evaporated to dryness to give **6**: ^1H NMR ($CDCl_3$) δ 2.0 (s, 3 H, CCH_3), 2.3 (s, 3 H, NCH_3), 2.53–2.8 (m, 1 H, CHN), 3.1–3.8 (m, 4 H, benzylic), 6.85–7.50 (m, 8 H, aromatic); MS *m/e* (%) 249 (58, M^+), 234 (31, $M^+ - CH_3$), 158 (100). A solution of **6** (1.4 g) in acetone (2 mL) was treated with oxalic acid (0.96 g) in acetone (10mL) to give, on cooling, **6** hydrogen oxalate (2.4 g, 96%). Recrystallization from methanol gave 1.2 g (48%) of **6** hydrogen oxalate: mp 181.5–183.5 °C; ^1H NMR (Me_2SO-d_6) δ 2.17 (s, 3 H, CCH_3), 2.63 (s, 3 H, NCH_3), 2.81 (d, J = 17 Hz, 2 H, H_{5n} and H_{7n}), 3.63 (dd, $J_{5x,6} = J_{7x,6}$ = 7.5 Hz, $J_{5x,5n} = J_{7x,7n}$ = 17 Hz, 2 H, H_{5x} and H_{7x}), 4.17 (t, J = 7.5 Hz, 1 H, H_6), 7.0–7.8 (m, 8 H, aromatic).

Anal. Calcd for $C_{20}H_{21}NO_4$: C, 70.78; H, 6.24; N, 4.13. Found: C, 70.62; H, 6.47; N, 3.96.

6-Methyl-12-methylene-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cycloocten-6-ol (7). A solution of **4**[2] (0.5 g, 0.0021 mol) in ether (3 mL) was added dropwise to a stirred ethereal solution of methylmagnesium bromide (1.4 mL, 2.9 M) under a nitrogen atmosphere. After 1 h of stirring at room temperature, ice–water (1 mL) was added, the resulting slurry was filtered, and the inorganic salts were washed with ether. The ether solution was separated, washed with water, dried over Na_2SO_4, filtered, and evaporated. The resulting oil (0.55 g) crystallized from petroleum ether to give 0.45 g (82%) of **7**: mp 71–72.5 °C; ^1H NMR ($CDCl_3$) δ 1.22 (s, 3 H, CH_3), 1.63 (s, 1 H, OH), 2.63 (s, 4 H, benzylic), 5.46 (s, 2 H, $=CH_2$), 6.8–7.7 (m, 8 H, aromatic); MS *m/e* (%) 250 (19, M^+), 235 (32, $M^+ - CH_3$), 232 (14, $M^+ - H_2O$), 217 (70), 207 (43), 193 (100), 192 (41); IR (Nujol) 3522, 3400, 1110, 1050, 900, 773, 765, and 750 cm^{-1}.

Anal. Calcd for $C_{18}H_{18}O$: C, 86.36; H, 7.24. Found: C, 86.71; H, 7.23.

6,12-Dimethyl-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cycloocten-6-ol (8). A solution of **7** (1.1 g, 0.0044 mol) in 95% ethanol (20 mL) was hydrogenated (3 atm, 25 °C, 100 mg of 10% Pd/C) for 18 h on a Parr apparatus. Removal of the catalyst by filtration, evaporation under reduced pressure of the filtrate, trituration of the residue with petroleum ether, and recrystallization of the resulting solid from ethanol gave 0.64 g (58%) of **8** as a 1.4:1 mixture of diastereomers:[11] mp 164–166 °C; ^1H NMR ($CDCl_3$) δ 0.75 and 1.56 (s, C(OH)C**H**$_3$), 1.10 (s, OH), 1.71 and 1.77 (d, J = 7 Hz, CHC**H**$_3$), 2.73 and 2.82 (d, J_{gem} = 14 Hz, benzylic), 3.63 and 3.50 (d, J_{gem} = 14 Hz, benzylic), 4.62 (q, J = 7 Hz, C**H**CH$_3$), 6.8–7.45 (m, 8 H, aromatic); MS *m/e* (%) 252 (100, M^+), 237 (14), 234 (17), 219 (38), 209 (45), 195 (68), 193 (45), 179 (25), 178 (40), 117 (88).

Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.37; H, 8.06.

Evaporation of the petroleum ether from the above trituration and recrystallization of the residue from 95% ethanol gave the diastereomer *trans*-**8** in which the methyl groups are trans (0.089 g, 8%): mp 123.5–126 °C; ^1H NMR ($CDCl_3$) δ 0.92 (s, 1 H, OH, exchanged by D_2O), 1.55 (s, 3 H, C(OH)C**H**$_3$), 1.77 (d, J = 7 Hz, 3 H, CHC**H**$_3$), 2.82 (d, J_{gem} = 14 Hz, 2 H, benzylic), 3.50 (d, J_{gem} = 14 Hz, 2 H, benzylic), 4.63 (q, J = 7 Hz, 1 H, C**H**CH$_3$), 6.8–7.5 (m, 8 H, aromatic); MS *m/e* (%) 253 (16, $M^+ + 1$), 252 (100, M^+), 237 (14), 219 (26), 209 (45), 195 (65), 193 (36), 178 (32), 117 (87).

Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.99; H, 8.06.

Chromatography of **8** (0.31 g) on silica gel (45 g; 10% (v/v) acetone in toluene elution) separated *trans*-**8** (0.16 g) from *cis*-**8** (0.11 g): mp 166.5–167.5 °C; ^1H NMR ($CDCl_3$) δ 0.81 (s, 3 H, C(OH)C**H**$_3$), 1.76 (d, J = 7 Hz, CHC**H**$_3$), 2.03 (s, 1 H, OH, exchange by D_2O), 2.83 (d, J_{gem} = 13.5 Hz, 2 H, benzylic), 3.71 (d, J_{gem} = 13.5 Hz, 2 H, benzylic), 4.67 (q, J = 7 Hz, 1 H, C**H**CH$_3$), 6.8–7.5 (m, 8 H, aromatic); MS *m/e* (%) 253 (18, $M^+ + 1$), 252 (100, M^+), 237 (17), 234 (16), 219 (35), 209 (40), 195 (71), 193 (39), 179 (23), 178 (35), 117 (73).

Anal. Calcd for $C_{18}H_{20}O$: C, 85.67; H, 7.99. Found: C, 85.66; H, 8.15.

6-(Acetylamino)-6,12-dimethyl-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cyclooctene (9). To stirred 95% sulfuric acid (67 mL) cooled by an ice bath was added dropwise at a rate to maintain the temperature below 20 °C a solution of crude **8** (16.2 g, 0.064 mol) in acetonitrile (160 mL). Upon completion of the addition, the mixture was stirred 3 h at room temperature and quenched in ice–water (1 L). The resulting suspension was stirred 1 h and extracted with chloroform (3 × 200 mL). The chloroform solution was washed with 1 M NaOH (3 × 20 mL) and water (2 × 20 mL), dried over K_2CO_3, and filtered, and the filtrate was evaporated under reduced pressure to give crude **9** (17.7 g, 94%) as a tan solid. Recrystallization from 95% ethanol gave the diastereomer *cis*-**9** in which the methyl groups are cis (8.8 g, 48%): mp 232–233.5 °C; ^1H NMR ($CDCl_3$) δ 0.79 (s, 3 H, C(N)CH_3), 1.75 (d, J = 7 Hz, 3 H, CHC**H**$_3$), 2.03 (s, 3 H, C**H**$_3$CO), 2.92 (d, J_{gem} = 14 Hz, 2 H, benzylic), 4.26 (d, J_{gem} = 14 Hz, 2 H, benzylic), 4.72 (q, J = 7 Hz, 1 H, C**H**CH$_3$), 5.72 (s, 1 H, NH), 6.85–7.50 (m, 8 H, aromatic); MS *m/e* (%) 293 (16, M^+), 235 (19, $M^+ - CH_3CONH$), 234 (100, $M^+ - CH_3CONH - H$), 219 (56), 192 (33); IR (Nujol) 3300, 2980–2820, 1645, 1540 cm^{-1}.

Anal. Calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.78. Found: C, 81.79; H, 7.91; N, 4.66.

The other diastereomer, *trans*-**9**, was obtained from crude **9** (2.5 g) by high-pressure liquid chromatography (Waters Associates, Prep PAK-500/silica, 5.7 × 30 cm, 5% (v/v) acetone in toluene, 250 mL/min). The solid (0.57 g) was recrystallized from 95% ethanol: mp 154–156 °C; ^1H NMR ($CDCl_3$) δ 1.50 (s, 3 H, C(N)CH_3), 1.80 (d, J = 7 Hz, 3 H, CHC**H**$_3$), 1.85 (s, 3 H, C**H**$_3$CO), 3.25 (d, J_{gem} = 14 Hz, 2 H, benzylic), 3.45 (d, J_{gem} = 14 Hz, 2 H, benzylic), 4.72 (q, J = 7 Hz, 1 H, C**H**CH$_3$), 4.78 (s, 1 H, NH, exchanged by D_2O), 7.0–7.6 (m, 8 H, aromatic); MS *m/e* (%) 293 (10, M^+), 235 (18, $M^+ - CH_3CONH$), 234 (100, $M^+ - CH_3CONH - H$), 219 (54), 192 (24); IR ($CHCl_3$) 3360, 2980–2880, 1660, 1480, 1440 cm^{-1}.

Anal. Calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.78. Found: C, 81.78; H, 8.02; N, 4.73.

6-(Acetylamino)-*N*,6,12-trimethyl-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cyclooctene (10). A solution of lithium diisopropylamide prepared from diisopropylamine (15.2 g, 0.15 mol) and ethereal methyllithium (85 mL, 1.8 M) in THF (150 mL) was added dropwise to a solution of crude **9** (25.4 g, 0.087 mol) and triphenylmethane (0.1 g) in THF (150 mL) with stirring at 0 °C under a nitrogen atmosphere. When the red-orange color of lithium triphenylmethide persisted, iodomethane (78 g, 0.55 mol) in THF (20 mL) was added dropwise at a rate to keep the internal temperature below 10 °C. After 2 h of stirring, the mixture was allowed to warm to room temperature and quenched in ice–water. The reaction was extracted with chloroform (3 × 300 mL). The combined extracts were washed with 1 N HCl (2 × 300 mL) and water (2 × 300 mL), dried over K_2CO_3, and filtered, and the filtrate was evaporated. Trituration with petroleum ether gave 20.7 g of crude **10** which was chromatographed on silica gel (chloroform elution) to yield 13.8 g (52%) of *cis*-**10** after recrystallization from acetone–hexane (1:1): mp 150–151.5 °C; ^1H NMR ($CDCl_3$) δ 0.68 (s, 3 H, C(N)CH_3), 1.73 (d, J = 7 Hz, 3 H, CHC**H**$_3$), 2.17 (s, 3 H, CH_3CO), 2.60 (d, J_{gem} = 15 Hz, 2 H, benzylic), 3.00 (s, 3 H, NCH_3), 4.95 (d, J_{gem} = 15 Hz, 2 H, benzylic), 4.83 (q, J = 7 Hz, 1 H, C**H**CH$_3$), 6.8–7.6 (m, 8 H, aromatic); MS *m/e* (%) 307 (15, M^+), 234 (62), 219 (40), 192 (32), 58 (36), 56 (100); IR (Nujol) 1640, 1630 cm^{-1}.

Anal. Calcd for $C_{21}H_{25}NO$: C, 79.70; H, 8.28; N, 4.43. Found: C, 79.92; H, 7.94; N, 4.40.

The diastereomer *trans*-**10** was evident in the NMR spectrum of crude **10** ([cis]/[trans] $\approx$ 2/1) but was not separately isolated and characterized.

6,12,13-Trimethyl-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cyclooctene-6,12-imine Hydrochloride (13). A mixture of **10** (8.8 g, 0.029 mol) and DDQ (7.3 g, 0.032 mol) in benzene (850 mL) was heated under reflux in a nitrogen atmosphere for 40 h. DDQ (1 g) was added and heating was continued for 18 h. The mixture was cooled, washed with 1 M NaOH (3 × 150 mL) and water (2 × 150 mL), dried over K_2CO_3, and filtered, and the filtrate was evaporated to yield **11** (7 g, 80%) as a brown oil. Chromatography on silica gel (chloroform elution) gave purified **11**: ^1H NMR ($CDCl_3$) δ 1.47 (s, 3 H, C(N)CH_3), 2.07 (s, 3 H, CH_3CO), 2.44 (d, J = 12.5 Hz, 2 H, benzylic), 2.56 (s, 3 H, NCH_3), 3.60 (d, J = 12.5 Hz, 2 H, benzylic), 5.46 (s, 2 H, $=CH_2$), 6.8–7.8 (m, 8 H, aromatic). This material was dissolved in ethylene glycol (70 mL) containing

KOH (2.3 g, 0.042 mol), and the solution was heated under reflux in a nitrogen atmosphere for 24 h. The cooled solution was quenched in water (1 L) and extracted with chloroform (3 × 100 mL). The combined extracts were washed with water (2 × 100 mL), dried over K_2CO_3, and filtered, and the filtrate was evaporated to give **13** as a yellow oil: MS *m/e* (%) 263 (82, M^+), 248 (42, $M^+ - CH_3$), 193 (94), 192 (100). A solution of **13** in ethanolic hydrogen chloride was evaporated and the residue was recrystallized from ethanol to yield 4.2 g (49% from **10**) of **13**-HCl: mp 282–283 °C; ^1H NMR ($CDCl_3$ + NaOD) δ 1.50 (s, 3 H, C-6 CH_3), 2.00 (s, 3 H C-12 CH_3), 2.19 (s, 3 H, NCH_3), 2.57 (d, J_{gem} = 17 Hz, 2 H, benzylic), 3.07 (d, J_{gem} = 17 Hz, 2 H, benzylic), 6.9–7.6 (m, 8 H, aromatic).

Anal. Calcd for $C_{19}H_{22}ClN$: C, 76.11; H, 7.40; N, 4.67; Cl, 11.82. Found: C, 76.49; H, 7.59; N, 4.50; Cl, 11.69.

6-Amino-6-methyl-12-methylene-5,6,7,12-tetrahydrodibenzo[a,d]cyclooctene (14). A mixture of **9** (5.3 g, 0.018 mol) and DDQ (5.3 g, 0.023 mol) in benzene (500 mL) was heated under reflux in a nitrogen atmosphere for 8 h. The cooled mixture was washed with 1 N NaOH solution (3 × 200 mL) and water (3 × 150 mL). The washed benzene layer was dried over K_2CO_3 and filtered, and the filtrate was evaporated. Trituration of the residue with ether–hexane (1:1) gave 5.2 g (98%) of 6-(acetylamino)-6-methyl-12-methylene-5,6,7,12-tetrahydrodibenzo[a,d]cyclooctene: ^1H NMR ($CDCl_3$) δ 1.48 (s, 3 H, CCH_3), 1.87 (s, 3 H, $COCH_3$), 2.57 (d, J_{gem} = 13 Hz, 2 H, benzylic), 3.00 (d, J = 13 Hz, 2 H, benzylic), 5.13 (s, 1 H, NH), 5.47 (s, 2 H, $=CH_2$), 6.8–7.8 (m, 8 H, aromatic). A solution of this material (2 g, 0.007 mol) and KOH (1.1 g, 0.0196 mol) in ethylene glycol (35 mL) was heated under reflux in a nitrogen atmosphere for 24 h. The cooled reaction mixture was quenched in ice–water (250 mL). The aqueous mixture was extracted with ether (3 × 50 mL). The combined extracts were dried over K_2CO_3 and filtered, and the filtrate was evaporated. The residue was dissolved in ethanolic HCl and the solution was evaporated to dryness. The solid residue was recrystallized from acetone and then ethanol to yield 1.3 g (66%) of **14**-HCl: mp 312–313.5 °C; ^1H NMR (Me_2SO-d_6) δ 1.25 (s, 3 H, CCH_3), 2.25–3.25 (m, 4 H, benzylic), 5.39 (s, 2 H, $=CH_2$), 7.0–7.75 (m, 8 H, aromatic), 8.1 (br s, 3 H, NH_3^+); MS *m/e* (%) 249 (40, M^+), 234 (20, $M^+ - CH_3$), 232 (13, $M^+ - NH_3$), 217 (36), 192 (13), 44 (100, $CH_3CH{=}NH_2^+$).

Anal. Calcd for $C_{18}H_{20}NCl$: C, 75.64; H, 7.05; N, 4.90; Cl, 12.41. Found: C, 75.60; H, 7.24; N, 4.94; Cl, 12.29.

10-Amino-5-methylene-10,11-dihydro-5*H*-dibenzo[a,d]cycloheptene (17). Solid 16[2] (10 g, 0.042 mol) was added portionwise to a stirred slurry of zinc dust (9.0 g) in glacial acetic acid (100 mL) maintained at 65 °C. After 2 h at this temperature, the reaction mixture was filtered, the filtrate was diluted with water (500 mL), the pH was adjusted to 10 with aqueous ammonia, and the mixture was extracted with ether (3 × 100 mL). The combined ether layers were washed with water (3 × 50 mL), dried over Na_2SO_4, and filtered, and the filtrate was evaporated to dryness. The residue was recrystallized from hexane to give 7.8 g (84%) of **17**: mp 85–87 °C; ^1H NMR ($CDCl_3$) δ 1.68 (s, 2 H, NH_2, exchanged by D_2O), 2.97 (dd, J_{gem} = 14.7 Hz, $J_{H_{10},H_{11b}}$ = 8 Hz, 1 H, benzylic), 3.47 (dd, J_{gem} = 14.7 Hz, $J_{H_{10},H_{11e}}$ = 3 Hz, 1 H, benzylic), 4.33 (dd, $J_{H_{10},H_{11b}}$ = 8 Hz, $J_{H_{10},H_{11e}}$ = 3 Hz, 1 H, CHN), 5.38 (d, J = 1.5 Hz, 1 H, $=CH_2$), 5.49 (d, J = 1.5 Hz, 1 H, $=CH_2$), 7.05–7.6 (m, 8 H, aromatic); MS *m/e* (%) 221 (83, M^+), 220 (54, $M^+ - 1$), 206 (18), 205 (25), 204 (100, $M^+ - NH_3$), 203 (91), 202 (28), 179 (20), 178 (78).

Anal. Calcd for $C_{16}H_{15}N$: C, 86.84; H, 6.83; N, 6.33. Found: C, 86.85; H, 6.67; N, 6.53.

10-Isocyano-5-methylene-10,11-dihydro-5*H*-dibenzo[a,d]cycloheptene (18). To a solution of **17** (8.1 g, 0.037 mol) in chloroform (180 mL) were added NaOH (4.42 g, 0.11 mol), benzyltriethylammonium chloride (0.42 g), and water (0.5 mL). The mixture was stirred in a nitrogen atmosphere until the NaOH dissolved. The reaction mixture was dried over K_2CO_3 and filtered, and the filtrate was evaporated. The residue was dissolved in chloroform (180 mL), NaOH (1.5 g) and benzyltriethylammonium chloride (0.2 g) were added, and the mixture was stirred in a nitrogen atmosphere for 18 h. The reaction mixture was dried over K_2CO_3 and filtered, and the filtrate was evaporated. The residue was chromatographed on a silica gel column (chloroform elution) and the resulting solid was recrystallized from ether to give 4 g (47%) of **18**: mp 96–98 °C; ^1H NMR ($CDCl_3$) δ 3.32 (dd, J_{gem} = 15 Hz, $J_{H_{10},H_{11a}}$ = 9 Hz, 1 H, benzylic), 3.58 (dd, J_{gem} = 15 Hz, $J_{H_{10},H_{11b}}$ = 4 Hz, 1 H, benzylic), 5.32 (dd, $J_{H_{10},H_{11a}}$ = 9 Hz, $J_{H_{10},H_{11b}}$ = 4 Hz, 1 H, CHN≡C), 5.50 (s, 2 H, $=CH_2$), 7.1–7.7 (m, 8 H, aromatic); MS *m/e* (%) 231 (57, M^+), 230 (20), 216 (32), 205 (22), 204 (100), 203 (72), 202 (62), 191 (30), 101 (37); IR (KBr) 2106 (N≡C), 980, 960, 930, 750–800, 680 cm^{-1}.

Anal. Calcd for $C_{17}H_{13}N$: C, 88.28; H, 5.66; N, 6.06. Found: C, 88.06; H, 5.67; N, 5.99.

10-Isocyano-10-methyl-5-methylene-10,11-dihydro-5*H*-dibenzo[a,d]cycloheptene (19). A solution of **18** (2.4 g, 0.01 mol) in THF (25 mL) was added dropwise with stirring over 45 min to a solution of lithium diisopropylamide (1.1 g, 0.011 mol of diisopropylamine and 5.0 mL of 2.2 M *n*-butyllithium in hexane) in THF (25 mL) maintained at −78 °C in a nitrogen atmosphere. After 15 min, iodomethane (4.6 g, 0.032 mol) was added to this deep red solution and stirring was continued for 2 h. The solvent was evaporated and the residue was chromatographed on a silica gel column (methylene chloride elution) to yield **19** which was recrystallized from ether to give 1.46 g (57%) of **19**: mp 146–148 °C; ^1H NMR ($CDCl_3$) δ 1.7 (t, J_{HCCN} = 2 Hz, 3 H, CH_3), 3.3 (dt, J_{gem} = 14 Hz, J_{HCCN} = 2 Hz, 1 H, benzylic), 3.75 (d, J_{gem} = 14 Hz, 1 H, benzylic), 5.33 (d, J = 1.5 Hz, 1 H, $=CH_2$), 5.65 (d, J = 1.5 Hz, 1 H, $=CH_2$), 7.05–7.90 (m, 8 H, aromatic); MS *m/e* (%) 245 (11, M^+), 230 (19, $M^+ - CH_3$), 219 (19), 218 (100), 217 (38), 216 (11), 215 (22), 205 (22), 203 (51), 202 (49), 191 (22), 189 (12), 101 (19); IR (KBr) 3440, 3080, 3000, 2990, 2950, 2920, 2850, 2105 (N≡C), 1488, 1455, 1440, 1385, 1250, 1145, 1077, 912 cm^{-1}.

Anal. Calcd for $C_{18}H_{15}N$: C, 88.13; H, 6.16; N, 5.71. Found: C, 88.19; H, 6.14; N, 5.94.

10-Methyl-10-(methylamino)-5-methylene-10,11-dihydro-5*H*-dibenzo[a,d]cycloheptene Hydrochloride (20). To a stirred slurry of LAH (0.53 g, 0.014 mol) in ether (40 mL) maintained in a nitrogen atmosphere was added dropwise a solution of **19** (1.8 g, 0.007 mol) in ether (10 mL). After 1 h of heating under reflux, water (1.5 mL) was cautiously added and the inorganic material was separated by filtration with ether washing. The filtrate was evaporated and the residue was treated with ethanolic hydrogen chloride. The solvent was evaporated and the residue was recrystallized from ethanol to yield 1.7 g (81%) of **20**-HCl: mp 238–240 °C; ^1H NMR ($CDCl_3$) δ 1.93 (s, 3 H, CCH_3), 2.33 (t, J = 5 Hz, 3 H, NCH_3), 3.41 (d, J_{gem} = 14 Hz, 1 H, benzylic), 3.96 (d, J_{gem} = 14 Hz, 1 H, benzylic), 5.37 (d, J = 1.5 Hz, 1 H, $=CH_2$), 5.70 (d, J = 1.5 Hz, 1 H, $=CH_2$), 7.2–7.7 (m, 7 H, aromatic), 8.16 (d, 1 H, aromatic), 9.8–10.8 (br, 2 H, NH_2); MS *m/e* (%) 249 (100, M^+) 248 (46), 235 (17), 234 (74), 220 (11), 219 (24), 218 (22), 217 (24), 205 (18), 204 (18), 203 (39), 202 (31), 191 (11), 189 (11), 178 (17), 144 (13).

Anal. Calcd for $C_{18}H_{20}NCl$: C, 75.64; H, 7.05; N, 4.90; Cl, 12.41. Found: C, 75.65; H, 7.14; N, 4.87; Cl, 12.18.

5,10,12-Trimethyl-10,11-dihydro-5*H*-dibenzo[a,d]cyclohepten-5,10-imine Hydrochloride (21). To a solution of **20** (1.6 g, 0.0064 mol) in THF (40 mL) maintained in a nitrogen atmosphere was added dropwise with stirring over 5 min a solution of *n*-butyllithium in hexane (3.0 mL, 2.2 M). The reaction mixture was stirred for 10 min and then quenched with ice–water (3 mL). The organic solvent was removed under reduced pressure and the residue was extracted with ether (100 mL). The ether solution was washed with water (2 × 50 mL), dried over Na_2SO_4, and filtered, and the filtrate was evaporated to dryness. The residue was chromatographed on a silica gel column (methylene chloride + increasing (1–5%) amounts of methanol elution) to yield **21**. A solution of **21** in ethanol (50 mL) was treated with 8 N ethanolic hydrogen chloride and evaporated under reduced pressure. The residue was recrystallized from ethanol to yield 2.3 g (53%) of **21**-HCl: mp 295–297 °C; ^1H NMR (Me_2SO-d_6) δ 1.88 (s, 3 H, C-10 CH_3), 2.15 (s, 3 H, C-5 CH_3), 2.61 (s, 3 H, NCH_3), 2.93 (d, J_{gem} = 19 Hz, 1 H, benzylic), 3.42 (d, J_{gem} = 19 Hz, 1 H, benzylic), 6.9–7.5 (m, 8 H, aromatic); MS *m/e* (%) 250 (22), 249 (100, M^+), 248 (24).

Anal. Calcd for $C_{18}H_{20}NCl$: C, 75.64; H, 7.05; N, 4.90; Cl, 12.41. Found: C, 75.75; H, 7.14; N, 4.64; Cl, 12.27.

12-Hydroxy-13-methyl-5,6,7,12-tetrahydrodibenzo[a,d]cycloocten-5,12-imine (25). A solution of **22** (5 g, 0.022 mol), bromine (3.8 g, 0.023 mol), and dibenzoyl peroxide (0.05 g) in carbon tetrachloride (100 mL) was heated under reflux and ir-

radiated with a 275-W GE sunlamp for 64 h. The cooled solution was washed with 10% aqueous $NaHSO_3$ solution (50 mL) and water (50 mL), dried over Na_2SO_4, and filtered, and the filtrate was evaporated. The residual crude bromo ketone **23** and anhydrous methylamine (8 g, 0.26 mol) were heated in a stainless steel bomb at 50 °C for 1 h. The vented bomb was flushed with chloroform (50 mL). The chloroform solution was washed with water (3 × 30 mL) and extracted with 0.5 M aqueous citric acid (5 × 15 mL). The combined extracts were made basic with 1 M NaOH and extracted with ether (3 × 25 mL). The combined ether extracts were dried over Na_2SO_4, filtered, and evaporated to yield 1.4 g of **24**; mp 153–163 °C. Recrystallization from 95% ethanol gave 0.6 g (11%) of **25**: mp 170–172 °C; ^1H NMR ($CDCl_3$) δ 1.2–2.7 (m, 4 H, CH_2CH_2), 2.2 (s, 3 H, NCH_3), 4.40 (m, 1 H, bridgehead H), 6.9–8.0 (m, 8 H, aromatic); MS *m/e* (%) 251 (18, M^+), 222 (31, $M^+ - NCH_3$), 192 (30), 160 (100, $M^+ - C_7H_7$); IR (Nujol) 3300–3000, 1056, 991, 938, 778, 770, 754 cm^{-1}.

Anal. Calcd for $C_{17}H_{17}NO$: C, 81.24; H, 6.81; N, 5.57. Found: C, 81.06; H, 7.06; N, 5.57.

13-Methyl-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cycloocten-5,12-imine (27). Method A. A mixture of **25** (1.2 g, 0.0048 mol) and thionyl chloride (20 mL) was stirred and heated under reflux for 1 h. The resulting solution was evaporated to dryness to yield crude **26**: MS *m/e* (%) 271 (9, M^+), 269 (27, M^+), 234 (100, M^+ - Cl). This material was dissolved in THF (20 mL) and the solution was added dropwise to a stirred slurry of LAH (1.0 g, 0.026 mol) in THF (20 mL). The slurry was stirred and heated under reflux for 1.5 h, cooled, and treated dropwise with ice–water (2 mL). The inorganic material was separated by filtration and washed with ether. On evaporation to dryness the filtrate gave 0.6 g (54%) of **27** as an oil: ^1H NMR ($CDCl_3$) δ 1.4–2.8 (m, 4 H, CH_2CH_2), 2.2 (s, 3 H, NCH_3), 4.33 (m, 1 H, bridgehead), 4.85 (s, 1 H, benzhydryl bridgehead), 6.8–7.9 (m, 8 H, aromatic); MS *m/e* (%) 235 (100, M^+), 234 (29), 183 (28), 158 (29), 144 (62). This material was chromatographed on silica gel (chloroform elution), and the resulting oil (0.45 g) was dissolved in acetone (4 mL) containing oxalic acid (0.173 g). The cooled solution gave 0.27 g (17%) of **27** hydrogen oxalate: mp 186.5–188 °C; MS *m/e* (%) 236 (19, $M^+ + 1$), 235 (100, M^+), 234 (23), 220 (53), 178 (21), 149 (24), 144 (64).

Method B. A solution of **29**-HCl (9.0 g, 0.03 mol) and potassium acetate (10 g, 0.1 mol) in 95% ethanol (200 mL) was hydrogenated (3 atm, 25 °C, 1 g of 10% Pd/C) for 1 h. The catalyst was removed by filtration and the filtrate was evaporated. The residue was dissolved in water (300 mL), the pH was adjusted to 12 with 1 N NaOH, and the mixture was extracted with ether (3 × 100 mL). The combined extracts were washed with water (100 mL), dried over Na_2SO_4, and filtered, and the filtrate was evaporated to yield as a colorless oil 6.6 g (94%) of **27**. The NMR spectrum of this material was identical with that reported for **27** above. The oil was dissolved in ethanolic HCl and the solution was evaporated to dryness. The residue was recrystallized from acetonitrile to give 3.6 g (45%) of **27**-HCl: mp 246–248 °C.

Anal. Calcd for $C_{17}H_{18}NCl$: C, 75.12; H, 6.68; N, 5.15; Cl, 13.05. Found: C, 75.26; H, 6.94; N, 5.18; Cl, 13.08.

13-Methyl-5,12-dihydrodibenzo[*a*,*d*]cycloocten-5,12-imine Hydrochloride (29). To a slurry of LAH (0.65 g, 0.017 mol) in THF (30 mL) was added $TiCl_4$ (1.38 g, 0.007 mol) dissolved in THF (20 mL). The mixture was stirred for 15 min in a nitrogen atmosphere. To this stirred slurry was added portionwise **28**-HCl[3] (2 g, 0.007 mol). After 5 h of heating under reflux, ice–water (3 mL) was added to the cooled mixture and the organic solvent was removed under reduced pressure. The residue was suspended in water (10 mL) and extracted with ether (5 × 50 mL). The combined ether extracts were washed with water (100 mL), dried over Na_2SO_4, and filtered, and the filtrate was evaporated. The residue was dissolved in methanolic HCl and the solution was evaporated to dryness. Recrystallization of the residue from aqueous acetone (1% water) gave 0.7 g (39%) of **29**-HCl: mp 244–253 °C; ^1H NMR ($CDCl_3$ + NaOD) δ 2.30 (s, 3 H, NCH_3), 4.63 (d, J = 5 Hz, 1 H, bridgehead), 5.13 (s, 1 H, benzhydryl bridgehead), 6.03 (dd, J = 11 Hz, J = 5 Hz, 1 H, CH=CHCH), 6.34 (d, J = 11 Hz, 1 H, CH=CHCH), 7.02–7.80 (m, 8 H, aromatic); MS *m/e* (%) 233 (100, M^+), 232 (66), 218 (26), 217 (26), 216 (16), 203 (13), 202 (14), 192 (24), 191 (57).

Anal. Calcd for $C_{17}H_{16}NCl \cdot 0.25H_2O$: C, 74.44; H, 6.06; N, 5.11; Cl, 12.93. Found: C, 74.47; H, 6.44; N, 5.19; Cl, 12.94.

6-Chloro-5,12-dihydrodibenzo[*a*,*d*]cyclooctene-5,12-dione (31). Solid **30**[3] (15 g, 0.052 mol) was added portionwise over 2 min to a solution of $AgBF_4$ (19.3 g, 0.1 mol) in dry Me_2SO (60 mL). After 24 h of stirring, triethylamine (6 mL) was added with stirring (15 min) and the reaction mixture was quenched in ice–water (400 mL). The mixture was extracted with ether (4 × 100 mL). The combined extracts were washed with water (4 × 100 mL), dried over $MgSO_4$, and filtered, and the filtrate was evaporated to dryness. The residue was recrystallized from acetone–hexane (1:1) to give 10.5 g (40%) of **31**: mp 118–121 °C; ^1H NMR ($CDCl_3$) δ 6.94 (s, 1 H, vinyl), 6.85–7.20 (m, 1 H, aromatic), 7.20–7.50 (m, 3 H, aromatic), 7.50–8.0 (m, 4 H, aromatic); MS *m/e* (%) 270 (37, M^+), 269 (22), 268 (100, M^+), 267 (18), 239 (24), 234 (22), 233 (12), 214 (11), 212 (30), 206 (11), 205 (57), 189 (11), 177 (33), 176 (56), 175 (11); IR (Nujol) 1781 (C=O), 1776 (C=O), 1590, 933, 894, 764, 724 cm^{-1}.

Anal. Calcd for $C_{16}H_9ClO_2$: C, 71.52; H, 3.38; Cl, 13.20. Found: C, 71.26; H, 3.36; Cl, 13.38.

4b-Hydroxy-4b,9,9a,10-tetrahydroindeno[1,2-*a*]inden-10-one (33). A solution of **31** (2.0 g, 0.0074 mol) and potassium acetate (6.5 g, 0.066 mol) in 95% ethanol (80 mL) was hydrogenated (3 atm, 25 °C, 10% Pd/C) until hydrogen uptake stopped (45 min). The catalyst was removed by filtration and the filtrate was evaporated to dryness under reduced pressure. The residue was slurried with water and extracted with ether (3 × 50 mL). The combined extracts were washed with water (2 × 50 mL), dried over Na_2SO_4, and filtered, and the filtrate was evaporated. Recrystallization of the residue from ether gave 0.48 g (27%) of **33**: mp 109–111 °C; ^1H NMR ($CDCl_3$) δ 2.80–3.90 (m, 4 H, CH_2, CH, and OH), 6.90–8.00 (m, 8 H, aromatic); MS *m/e* (%) 237 (15, $M^+ + 1$), 236 (100, M^+), 219 (24), 218 (87), 208 (18), 207 (16), 190 (16), 189 (32), 105 (44); IR (Nujol) 3445 (OH), 1700 (C=O), 1598, 1045, 925, 784, 773, 752, 738 cm^{-1}.

Anal. Calcd for $C_{16}H_{12}O_2$: C, 81.33; H, 5.12. Found: C, 81.20; H, 5.01.

12-Methyl-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cycloocten-6-one (34). A solution of **4**[2] (5.7 g, 0.024 mol) in 95% ethanol (50 mL) was hydrogenated (3 atm, 25 °C, 0.1 g of 10% Pd/C) for 1 h. Hydrogen uptake stopped after 22 min. The solution was filtered and the filtrate was evaporated under reduced pressure. The white, solid residue was recrystallized from ethanol to give 5.2 g (90%) of **34**: mp 156–158 °C; ^1H NMR ($CDCl_3$) δ 1.72 (d, J = 7 Hz, 3 H, CH_3), 3.50 (d, J_{gem} = 13 Hz, 2 H, benzylic), 4.19 (d, J_{gem} = 13 Hz, 2 H, benzylic), 4.41 (q, J = 7 Hz, 1 H, $CHCH_3$), 6.75–7.75 (m, 8 H aromatic); MS *m/e* (%) 236 (15, M^+), 221 (12, $M^+ - 15$), 115 (28), 89 (23); IR (Nujol) 1695 (C=O), 785, 794, 740 cm^{-1}.

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.67; H, 7.10.

12-Methyl-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cycloocten-6-ol (35). Solid $NaBH_4$ (1.1 g, 0.03 mol) was added portionwise to a stirred solution of **34** (7 g, 0.03 mol) in 2-propanol (112 mL). The solution was heated at 90 °C for 0.5 h and cooled, and the solvent was removed under reduced pressure. The residue was slurried with water (200 mL) and extracted with ether (3 × 100 mL). The combined extracts were washed with water (2 × 100 mL), dried over Na_2SO_4, and filtered, and the filtrate was evaporated. The solid residue **35** (6.8 g, 96%) was recrystallized from ethanol to give one diastereomer of **35**: mp 148–150 °C; ^1H NMR ($CDCl_3$) δ 0.78 (d, J = 11 Hz, 1 H, OH, exchanged by D_2O), 1.75 (d, J = 7 Hz, 3 H, CH_3), 3.05 (dd, J_{gem} = 14 Hz, J_{H_5,H_6} = 7 Hz, 2 H, benzylic), 3.42 (d, J_{gem} = 14 Hz, 2 H, benzylic), 4.3 (m, 1 H, HCO), 4.53 (q, J = 7 Hz, 1 H, $CHCH_3$), 6.75–7.5 (m, 8 H, aromatic); MS *m/e* (%) 239 (12, $M^+ + 1$), 238 (84, M^+), 223 (20), 221 (15), 220 (49), 207 (22), 205 (50), 195 (32), 193 (39), 192 (20), 179 (24), 178 (46), 131 (24), 119 (100), 117 (33), 91 (44); IR (Nujol) 3530 (OH), 1060, 1045, 1040, 750, 720 cm^{-1}.

Anal. Calcd. for $C_{17}H_{18}O$: C, 85.67; H, 7.61. Found: C, 85.80; H, 7.67.

5-(Acetylamino)-12-methyl-5,6,7,12-tetrahydrodibenzo-[*a*,*d*]cyclooctene (37). To a stirred solution of **35** (30 g, 0.126 mol) in pyridine (250 mL) was added dropwise $POCl_3$ (151 g, 1.0 mol). The resulting mixture was heated under reflux for 3 h, cooled, and carefully quenched in ice–water (2 L). The suspension

was extracted with ether (3 × 200 mL). The combined extracts were washed with 2 N aqueous hydrochloric acid (3 × 100 mL) and water (2 × 100 mL), dried over Na_2SO_4, and filtered, and the filtrate was evaporated to give 25.3 g (91%) of liquid **36**: ^1H NMR ($CDCl_3$) δ 1.62 (d, J = 7.5 Hz, 3 H, CH_3), 3.10 (dd, J_{gem} = 17 Hz, J_{H_6,H_7} = 8 Hz, 1 H, benzylic), 3.65 (ddd, J_{gem} = 17 Hz, J_{H_6,H_7} = 5 Hz, J_{H_5,H_7} = 1.5 Hz, 1 H, benzylic), 4.75 (q, J = 7.5 Hz, 1 H, C**H**CH_3), 5.9 (ddd, J_{H_5,H_6} = 12 Hz, J_{H_6,H_7} = 8 Hz, J_{H_6,H_7} = 5 Hz, 1 H, CH=C**H**CH_2), 6.68 (dd, J_{H_5,H_6} = 12 Hz, J_{H_5,H_7} = 1.5 Hz, 1 H, C**H**=$CHCH_2$), 6.9–7.6 (m, 8 H, aromatic); MS m/e 220.1242 (m/e (calcd) for $C_{17}H_{16}$ 220.1252). A solution of **36** (10 g, 0.045 mol) in acetonitrile (140 mL) was added dropwise with stirring to 85% sulfuric acid (100 mL) with external cooling to maintain the temperature below 25 °C. The reaction mixture was stirred at room temperature until TLC (silica gel, 10% methanol in chloroform) indicated completion of the reaction (6 h). The reaction mixture was carefully quenched in ice–water (2 L) and extracted with chloroform (3 × 150 mL). The combined extracts were washed with 5% aqueous $NaHCO_3$ (2 × 150 mL) and water (2 × 150 mL), dried over K_2CO_3, and filtered, and the filtrate was evaporated under reduced pressure to give 11 g (79%) of **37**: mp 168–169 °C (EtOH); ^1H NMR ($CDCl_3$) δ 1.83 (d, J = 7 Hz, 3 H, C**H**$_3$CH), 2.07 (s, 3 H, CH_3CO), 1.4–3.9 (m, 4 H, benzylic), 4.60 (q, J = 7 Hz, 1 H, C**H**CH_3), 5.27 (m, 1 H, C**H**NH), 6.07 (s, 1 H, NH), 7.0–7.7 (m, 8 H, aromatic); MS m/e (%) 279 (36, M^+), 221 (12), 220 (59), 219 (26), 206 (18), 205 (100), 193 (22), 192 (64), 191 (25); IR (Nujol) 3230, 3180, 1665, 1635, 1483, 1295, 755 cm^{-1}.

Anal. Calcd for $C_{19}H_{21}NO$: C, 81.68; H, 7.58; N, 5.01. Found: C, 81.48; H, 7.47; N, 4.82.

5-(Acetylamino)-*N*,12-dimethyl-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cyclooctene (38). A solution of **37** (3 g, 0.012 mol) in THF (36 mL) was added dropwise with stirring to a cooled (−78 °C) solution of lithium diisopropylamide (diisopropylamine (1.3 g, 0.013 mol) and methyllithium (7.9 mL, 1.6 M) in ether) in THF (18 mL) maintained in a nitrogen atmosphere. After 1 h, iodomethane (14 g, 0.1 mol) was added and stirring was continued for 0.5 h at −78 °C and for 18 h at room temperature. The solvent was removed under reduced pressure, the residue was slurried with water (150 mL), and the mixture was extracted with ether (3 × 50 mL). The combined extracts were washed with 1 N aqueous hydrochloric acid (2 × 50 mL) and water (50 mL), dried over Na_2SO_4, and filtered, and the filtrate was evaporated. The residue in ether (25 mL) was refrigerated and then filtered to give 1.1 g of recovered **37**.

The filtrate was evaporated and the residue was chromatographed on 75 g of silica gel eluted with methylene chloride followed by 0.75% (v/v) ethanolic methylene chloride. Evaporation provided **38** as a colorless glass (2 g, 63%): ^1H NMR ($CDCl_3$) δ 1.8 (d, J = 7 Hz, 3 H, CHC**H**$_3$), 2.0 (s, 3 H, CH_3CO), 2.0–3.0 (m, 4 H, CH_2CH_2), 3.0 (s, 3 H, NCH_3), 4.7 (q, J = 7 Hz, 1 H, C**H**CH_3), 4.9–5.5 (br s, 1 H, CHN), 6.85–7.5 (m, 8 H, aromatic); MS m/e (%) 293 (15, M^+) 250 (11, $M^+ - CH_3CO$), 221 (20), 220 (100, $M^+ - CH_3CONHCH_3$), 219 (30), 206 (19), 205 (99), 204 (16), 203 (11), 202 (13), 193 (16), 192 (76), 191 (19), 178 (14), 91 (18), 74 (14), 56 (13), 43 (21); IR ($CHCl_3$) 3000–2900, 1630, 1485, 1445, 1400, 1380, 1200, 1060 cm^{-1}.

Anal. Calcd for $C_{20}H_{23}NO$: C, 81.87; H, 7.90; N, 4.77. Found: C, 81.35; H, 8.00; N, 4.97.

12,13-Dimethyl-5,6,7,12-tetrahydrodibenzo[*a*,*d*]cyclooctene-5,12-imine Hydrochloride (41). A mixture of **38** (10.5 g, 0.034 mol) and DDQ (9.5 g, 0.041 mol) in benzene (750 mL) was stirred and heated under reflux in a nitrogen atmosphere for 3.5 h. The mixture was cooled, washed with 1 N aqueous NaOH (4 × 100 mL) and water (2 × 50 mL), dried over K_2CO_3, and filtered, and the filtrate was evaporated under reduced pressure to yield 9.5 g (90%) of **39**: ^1H NMR ($CDCl_3$) δ 2.07 (s, 3 H, CH_3CO), 3.1 (s, 3 H, NCH_3), 1.8–3.8 (m, 5 H, CH_2CH_2CHN), 5.4 (d, J = 14 Hz, 2 H, $=CH_2$), 6.8–8.0 (m, 8 H, aromatic); MS m/e (M^+) 291.1630 (m/e (calcd) for $C_{20}H_{21}NO$ 291.1623). This material (9.5 g, 0.033 mol) was heated under reflux in ethylene glycol (166 mL) containing KOH (7.6 g, 0.136 mol) for 24 h in a nitrogen atmosphere. After being diluted with ice–water (2 L), the mixture was extracted with chloroform (3 × 100 mL). The combined extracts were washed with water (2 × 100 mL), dried over K_2CO_3, and filtered, and the filtrate was evaporated. The residue was stirred with acetic anhydride (18 mL) for 20 min, and the mixture was made basic with 1 N aqueous NaOH and extracted with chloroform (3 × 100 mL). The combined chloroform extracts were washed with water (2 × 50 mL) and extracted with 0.5 M citric acid (3 × 50 mL). The combined acidic extracts were washed with chloroform (25 mL), made basic with 1 N aqueous NaOH, and extracted with chloroform (3 × 50 mL). The combined extracts were washed with water (2 × 50 mL), dried over K_2CO_3, and filtered, and the filtrate was evaporated under reduced pressure to yield 2.6 g (29% from **38**) of **41**: ^1H NMR ($CDCl_3$) δ 1.3–3.1 (m, 4 H, CH_2CH_2), 1.82 (s, 3 H, CCH_3), 2.05 (s, 3 H, NCH_3), 4.55 (t, 1 H, CHN), 6.8–7.6 (m, 8 H, aromatic). This material was dissolved in ethanolic HCl and the solution was evaporated to dryness under reduced pressure. The residue was recrystallized from acetone to give 1.2 g of **41**·HCl: mp 239–242 °C; ^1H NMR ($CDCl_3$) δ 2.40 (s, 3 H, CCH_3), 2.45 (d, 3 H, NCH_3), 1.9–2.6 (m, 4 H, CH_2CH_2), 5.3 (m, 1 H, CHN), 7.1–7.6 (m, 8 H, aromatic); MS m/e (%) 249 (16, M^+), 159 (11), 158 (100).

Anal. Calcd for $C_{18}H_{20}NCl$: C, 75.64; H, 7.05; N, 4.90; Cl, 12.41. Found: C, 75.50; H, 7.04; N, 4.89; Cl, 12.40.

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Registry No. **4**, 70313-46-1; **5**, 70865-03-1; **5**·HCl, 70313-47-2; **6**, 70313-49-4; **6** hydrogen oxalate, 70313-50-7; **7**, 70313-58-5; *cis*-**8**, 70314-56-6; *trans*-**8**, 70313-59-6; *cis*-**9**, 70314-57-7; *trans*-**9**, 70313-60-9; *cis*-**10**, 70314-58-8; *trans*-**10**, 70313-61-0; **11**, 70313-62-1; **12**, 70865-04-2; **13**, 70865-05-3; **13**·HCl, 70313-63-2; **14**, 70865-06-4; **14**·HCl, 70865-07-5; **16**, 70449-85-3; **17**, 70450-32-7; **18**, 70449-87-5; **19**, 70450-33-8; **20**·HCl, 70450-34-9; **21**·HCl, 70450-35-0; **22**, 1022-14-6; **23**, 70865-08-6; **25**, 70313-70-1; **26**, 70865-09-7; **27**, 70313-71-2; **27** hydrogen oxalate, 70313-72-3; **27**·HCl, 70313-69-8; **28**·HCl, 67464-70-4; **29**·HCl, 70313-80-3; **30**, 67464-60-2; **31**, 70865-10-0; **33**, 70865-11-1; **34**, 70313-73-4; **35**, 70865-12-2; **36**, 70313-75-6; **37**, 70313-76-7; **38**, 70313-77-8; **39**, 70313-78-9; **41**, 70865-13-3; **41**·HCl, 70313-79-0.