Aryl Radical Cyclizations onto Enamine Double Bonds

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Aryl radicals from *N*-alkyl-*N*-(2-bromobenzyl)-1-cyclohexenylamine **2** and *N*-alkyl-*N*-(2-bromobenzyl)-cyclopentenylamine **11** cyclize readily onto the enamine double bond by 6-endo and 5-exo closure. In the case of **2**, 6-endo cyclization is the major pathway; however, the 6-endo to 5-exo ratio is dependent upon the *N*-alkyl substituent. In both cases, the dominant isomer from 6-endo cyclization is the cis isomer. For **2a** in toluene, values of $k_{6\text{-endo}}$ and $k_{5\text{-exo}}$ at 80 °C were 4.6×10^8 s^{-1} and 1.5×10^8 s^{-1}, respectively.

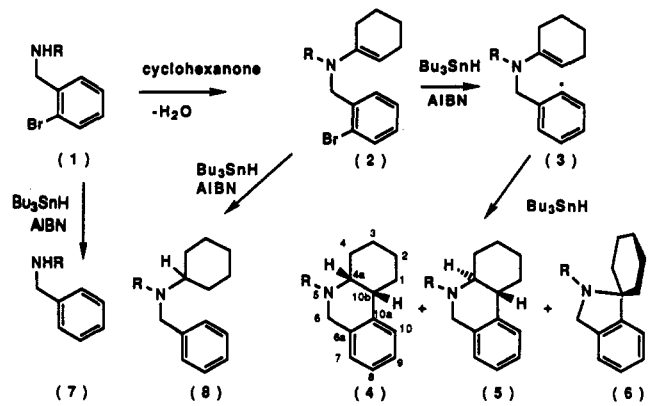
Introduction

Radical cyclizations onto unsaturated systems have become widely used in synthetic chemistry, and the scope and limitations of such reactions have been the subject of recent reviews.[1] They proceed usually with high regiospecificity and often with good stereoselectivity. In particular, the cyclizations onto olefins are well understood, and ring closure in 5-hexenyl radicals and their hetero analogues proceeds in good conversions and yields the corresponding cyclopentylmethyl radicals as a rule.

Recently, Warkentin and Tomaszewski have studied the analogous cyclizations onto imine double bonds.[2] The results are strikingly different in that aryl radical cyclization to form five- and six-membered rings occurs at the imine carbon in preference to the nitrogen, and it is this rule which determines the regioselectivity of such cyclizations in spite of the fact that an aminoalkyl radical is resonance stabilized and the alternative aminyl radical is not. This cyclization may be under molecular orbital control in that the atom with largest coefficient in the LUMO is carbon.[3]

Enamines are another interesting class of substrates in which cyclization onto the α- and β-carbons will yield product radicals of quite disparate stabilities, and we were interested in whether radical stabilization would favor β-attack or, alternatively, whether conventional stereoelectronic effects controlling cyclizations onto simple olefins would prevail. To our knowledge, a limited number of radical cyclizations onto enamine double bonds have been reported previously but these were components of synthetic sequences and involved conjugated enamines.[4] No cyclizations onto simple enamines have been carried out to date. Russell has reported intermolecular radical additions to enamines.[5] Accordingly, we have synthesized **2** and have investigated the selectivity of the aryl radicals (**3**) with use of the well-known reductive tin hydride reaction system (Scheme I).

Scheme I



(a) R = *n*-butyl; (b) R = ethyl; (c) R = methyl

Results and Discussion

Enamines **2a-c** were formed from cyclohexanone and the corresponding *N*-alkyl-2-bromobenzylamines **1a-c** by refluxing in toluene with a small amount of *p*-toluenesulfonic acid as catalyst. Water was collected in the conventional way but in no case could the reaction be driven to completion, and cyclizations were carried out on mixtures of cyclizeable enamine (**2**) and amine (**1**). A 3:1 mixture of *N*-butylenamine **2a** was achieved after ca. 4 days under reflux whereas the *N*-methylamine **1c** gave the same result in half the time. Furthermore, the enamines were exceptionally moisture sensitive. We attribute these facts to the considerable bulkiness of the *o*-bromobenzyl substituent at nitrogen, which must contribute to a large, negative reaction entropy, and to mild endothermicity.

Progress of enamine formation was monitored by ^{1}H NMR spectroscopy of the neat reaction mixture using presaturation of the toluene methyl resonance. For the reaction of **1a** with cyclohexanone, the presence of enamine was evidenced by a 0.44 ppm downfield shift of the benzylic

(1) Neumann, W. P. *Synthesis* **1987**, 665. Curran, D. P. *Synthesis* **1988**, 417 and 489. Giese, B. *Radicals in Organic Synthesis: Formation of Carbon-Carbon Bonds*; Pergamon Press: Oxford, 1986.

(2) Warkentin, J.; Tomaszewski, M. J. *Tetrahedron Lett.* **1992**, *33*, 2123.

(3) Since the π^* as well as the π orbital are lower in energy than corresponding olefinic orbitals, it is expected that the SOMO-LUMO interaction will be important.

(4) Takano, S.; Suzuki, M.; Kijima, A.; Ogasawara, K. *Tetrahedron Lett.* **1990**, *31*, 2315. Takano, S.; Suzuki, M.; Ogasawara, K. *Heterocycles* **1990**, *31*, 1151. Cladingboel, D. E.; Parsons, P. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1543. Ziegler, F. E.; Jeroncic, L. O. *J. Org. Chem.* **1991**, *56*, 3479. Beckwith, A. L. J.; Westwood, S. W. *Tetrahedron* **1989**, *45*, 5269.

(5) Russell, G. A.; Wang, K. *J. Org. Chem.* **1991**, *56*, 3475.

0022-3263/93/1958-2115$04.00/0

Table I. Isolated Yields (%) and Ratios of Products from Reaction of 2a–c and 11 with Bu_3SnH (1.45 equiv) in Toluene at 80 °C

	R	reduced	cis-endo	trans-endo	*exo*-spirane	endo:exo[a] (4 + 5):6	cis:trans[a] 4:5
2a	butyl	(8a) 19.0	(4a) 30.0	(5a) 11.0	(6a) 9.20	3.10	2.33
2b	ethyl	(8b) 12.4	(4b) 31.0	(5b) 13.0	(6b) 28.0	2.90	2.91
2c	methyl	(8c) 37.0	(4c) 12.0		(6c) 28.0	0.54	>10
11	ethyl	(14) 29.0 (15) 16.0	(12) 17.0		(13) 18.0	0.82	>10

[a] Approximate ratios based on ^1H NMR spectra of the initial reaction mixtures prior to separation.

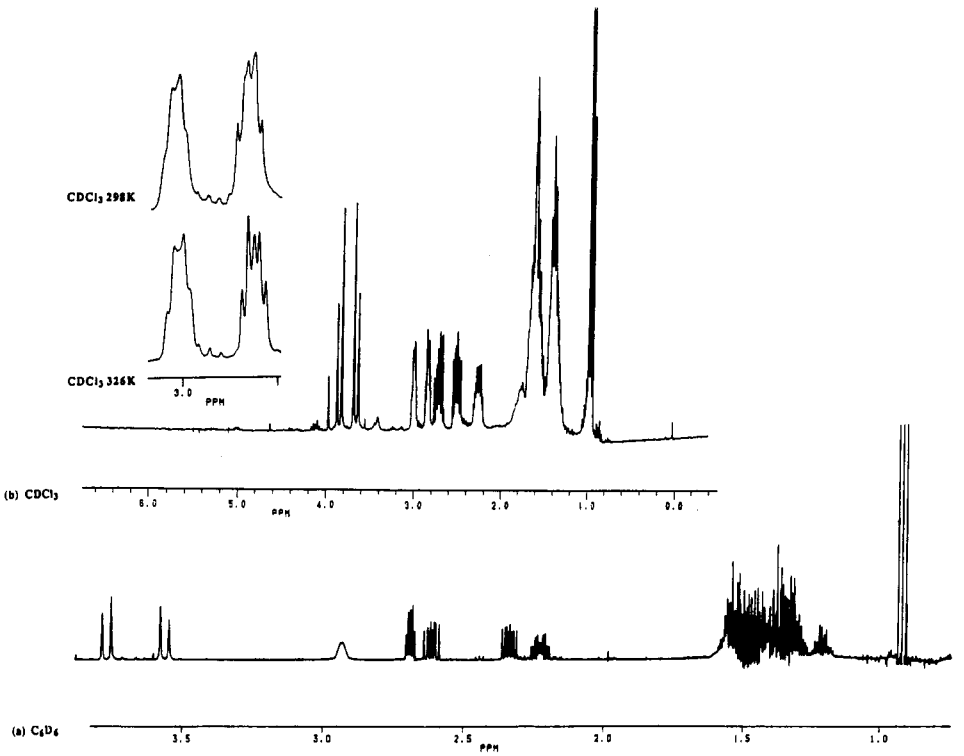


Figure 1. (a) Aliphatic region of the 500-MHz ^1H NMR spectrum of **4a** in C_6D_6 at 298 K; (b) aliphatic region of the 300-MHz ^1H NMR spectrum of **4a** in $CDCl_3$ at 326 K and C_{10b}-H (δ 3.0) and C_{4a}-H (δ 2.84) signals at 326 and 298 K.

methylenic protons as well as observation of a triplet for the vinylic proton a further 0.25 ppm downfield. The enamine solutions were used directly as attempts at isolating the enamines resulted in re-formation of the amines. Thus, an appropriate quantity of tri-*n*-butyltin hydride (1.45 equiv based on 1 and 2) and AIBN initiator were added to the toluene reaction mixture which was suspended at 80 °C until NMR spectroscopy in toluene indicated complete consumption of the enamine. The product amines were isolated together by an acid–base workup of the toluene mixture and separated out by chromatography. In all cases the complex mixtures contained both reduction and cyclization products derived from the enamine starting materials together with *N*-alkylbenzylamines **7** from reduction of the starting 2-bromobenzylamines.

Enamine **2a** gave a 50% conversion to three cyclic products identified as *cis*- and *trans*-octahydrophenanthridines (**4a** and **5a**) as well as the azaspirane (**6a**) (Scheme I, Table I). The stereochemistry in **4a** and **5a** was assigned by 500-MHz spectroscopy, NOE difference spectroscopy, COSY, TOCSY, and CH-correlated 2D experiments. The bridgehead methine protons in **4a** resonate at δ 2.69 and 2.92 in deuteriobenzene (Figure 1a). An NOE was observed for the downfield proton (δ 2.92) and the lowest field aromatic doublet (δ 7.21), and these two frequencies were assigned to C_{10b}-H and C_{10}-H, respectively, enabling complete assignment of all ^1H and ^{13}C NMR resonances. At room temperature in deuteriobenzene the other bridgehead proton adjacent to nitrogen (C_{4a}-H) displayed coupling constants of 3.6, 3.6, and 7.3 Hz. A similar splitting pattern was evident in deuteriochloroform at 326 K (Figure 1b). However, at room temperature in deuteriochloroform this proton was a broadened quartet with three small couplings of ca. 3.6 Hz. This is consistent with a cis-fused ring junction and the chair conformation illustrated in Figure 2a which is predicted by AM1 calculations to be 0.6 kcal mol^{-1} lower in energy than the conformation in Figure 2b. At elevated temperatures or in deuteriobenzene, there is a rapid equilibration of the two chair conformations, and the bridgehead proton experiences both a trans-diaxial (ca. 10 Hz) and an axial–equatorial coupling (3.6 Hz) with the neighboring axial proton on C_4. Similarly, the axial proton at C_1 (δ 2.2) (Figure 2a) (J_{vic} = 7.9 and 7.8 Hz) experiences the mean of two trans-diaxial and two axial–equatorial couplings. This proton resonates well downfield due to its average orientation near the plane of the benzene ring. The C_{10b} proton was significantly broadened due to coupling to C_8-H and C_{10}-H as well as conformational changes.

The bridge protons at C_{4a} and C_{10b} in **5a** were clearly defined triplets (two trans-diaxial couplings) of doublets (one axial–equatorial coupling) and must accord with the trans ring junction. Consequently, the C_1 equatorial

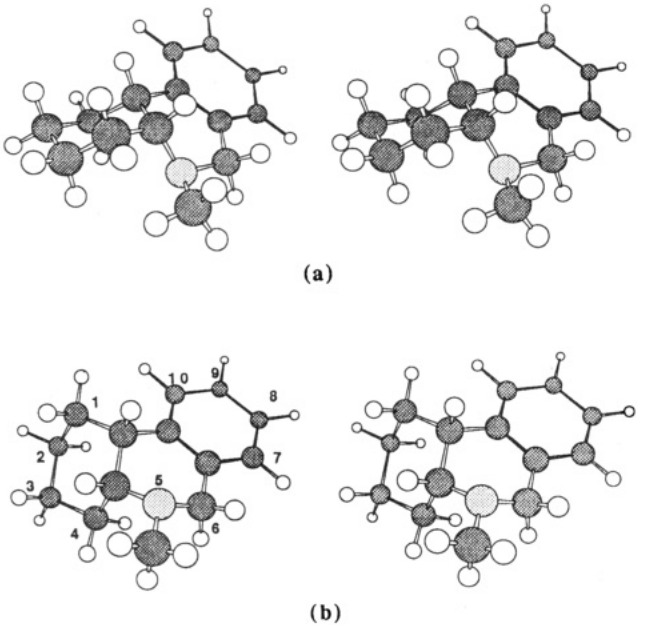


Figure 2. Stereoviews of lowest energy conformations of **4c** determined by AM1 calculations.

proton (δ 2.4) lies near the plane of the benzene ring and is shifted significantly downfield relative to the C_1 axial proton (δ 1.2).

Another interesting feature in the NMR spectra of **4a** and **5a** is the diastereotopic nature of both the methylenic protons α to nitrogen as well as the pair β to it. A cross section of the TOCSY spectrum of **4a** showed a considerable difference in the chemical shifts of both sets of protons. The azaspirane **6a** on the other hand was characterized by the achiral quaternary carbon at the ring junction as well as the non diastereotopic nature of the α and β protons on the butyl side chain.

The *N*-ethyl-1-cyclohexenylamine **2b** gave cyclic products similar to those from **2a** although significantly more of the exo product was formed. The *N*-methyl analogue **2c** afforded the azaspirane as the major product while only the cis-endo cyclization product could be detected (Table I). All three cyclizations afforded *N*-cyclohexylbenzylamines **8** which are derived from the bromoenamines **2**. ^{1}H NMR studies indicated that the enamines **2a** and **2b** are relatively stable in toluene in the presence of tri-*n*-butyltin hydride, and reduction of the double bond must occur under radical chain conditions. ^{1}H NMR spectra in toluene after cyclization but prior to acid–base workup indicated the absence of significant amounts of debrominated enamine. A qualitative estimate of the relative rates of enamine and bromide reduction was made by treating *N*-cyclohexyl-*N*-ethyl-2-bromobenzylamine (**9b**) and *N*-benzyl-*N*-ethyl-1-cyclohexenylamine (**10**) with tin hydride and AIBN in toluene at 80 °C. After 75 min the benzylic singlet in **9b** at δ 3.65 was completely replaced by one at δ 3.45 corresponding to the benzylic protons of **8b**. The corresponding singlet in **10** remained unchanged over the same period. Hence, with **2b** at least, reduction of the enamine double bond must occur after the competition between reduction and cyclization reactions of the intermediate free radicals (**3b**).

Neither **2a** nor **2b** gave *N*-cyclohexyl-2-bromobenzylamines (**9a** and **9b**) but some *N*-methyl-*N*-cyclohexyl-2-bromobenzylamine (**9c**) was detected in the reaction mixture from **2c**. Tin hydride reduction of the enamine

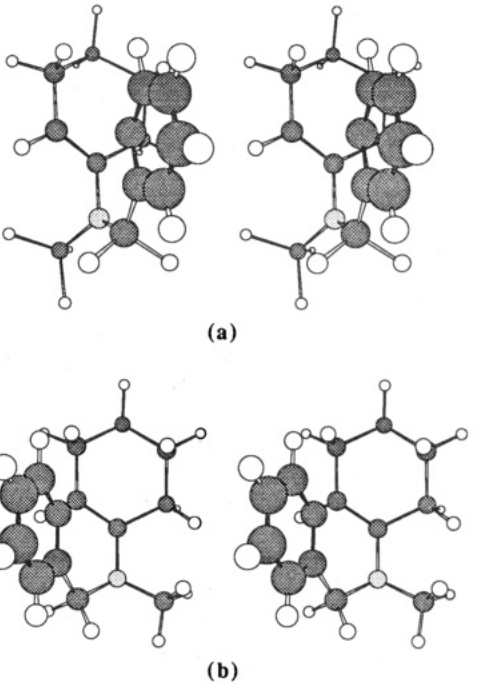
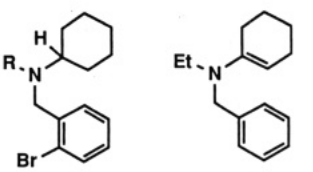


Figure 3. Stereo representations of (a) exo and (b) endo transition states for cyclization of **3c**.

double bond appears to be competitive with bromide reduction in this case. This reaction also gave a much larger proportion of reduction product **8c**.



(9) (10)

(a) R=butyl
(b) R=ethyl
(c) R=methyl

Analysis of the relative amounts of endo- and exo-cyclized products indicates a significant dependence upon the nature of the *N*-alkyl substituent. Such a variation in endo/exo ratio is indicative that there is little difference between the activation parameters for both cyclization modes. Clearly, exo cyclization is preferable with the smaller substituents at nitrogen. The geometric requirements for intramolecular radical cyclization to the C_5 in 5-hexenyl systems are understood to induce less strain in the transition state relative to attack at the terminal carbon, and under normal circumstances, exo cyclization is kinetically more favorable than the endo mode of attack.[6] Analysis of Dreiding models, however, indicates that in these enamine reactions exo-cyclization would require both loss of conjugation within the enamine system together with eclipsing of the *N*-alkyl substituent and the α-benzylic protons (Figure 3a). Endo-cyclization could, on the other hand, proceed without such destabilization (Figure 3b). In this finely balanced competition, it would appear that the size of the N-substituent is important. With the larger *N*-butyl group, the combination of loss of conjugation and eclipsing with the benzylic protons results in more of the

(6) Beckwith, A. L. J. *Tetrahedron* **1981**, *37*, 3073. Beckwith, A. L. J.; Schiesser, C. H. *Tetrahedron Lett.* **1985**, *26*, 373. *Tetrahedron* **1985**, *41*, 3925.

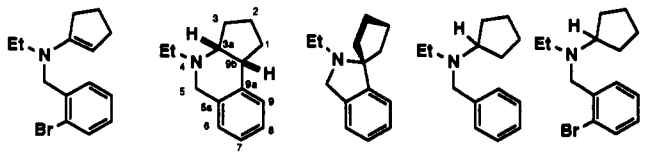
Table II. Product Ratios and Rate Constants for Cyclization of 2a at 80 °C

[SnH]/M	[endo]/[red]	[exo]/[red]	(k_{exo}/k_T)M	(k_{endo}/k_T)/M
0.278	4.49	1.49	0.41	1.25
0.373	3.60	1.26	0.47	1.34
0.671	1.61	0.60	0.40	1.08
0.934	1.39	0.48	0.45	1.30
1.345	0.80	0.30	0.41	1.08

normally less favorable endo attack while, with an *N*-methyl group, the exo mode of attack is again more competitive.

The *N*-alkyl substituent also has an influence upon the cis/trans ratio (Table I). Transfer of hydrogen from the bulky tin hydride in the chain-transfer step is likely to occur from the least hindered face of the radical intermediate. If this radical has conformations similar to those predicted by AM1 for the cis-endo form (Figure 2a and b), then transfer to the β-face would be sterically less demanding. With the bulkier *N*-butyl substituent and to a lesser extent with the *N*-ethyl group, however, at least some transfer to the α-face is evident.

The cyclization of **2a** was performed at 80 °C with several different concentrations of tin hydride. The ratio of cyclized products was unchanged indicating that neither cyclization is reversible under the reaction conditions. The ratios exo/reduced and endo/reduced, determined from ^{1}H NMR spectroscopy, are given in Table II together with estimated ratios of rate constants, k_{exo}/k_T and k_{endo}/k_T at 80 °C, where k_T is the rate of hydrogen transfer from tri-*n*-butyltin hydride to an aryl radical.[7] Plots of [endo]/[reduced] and [exo]/[reduced] against 1/[Bu_3SnH] gave $k_{endo} = 1.32k_T = 4.6 \times 10^8$ s^{-1}, and $k_{exo} = 0.43k_T = 1.5 \times 10^8$ s^{-1} and endo-cyclization appears to be measurably faster than the corresponding exo-cyclization onto the olefinic side-chain of the 2-(3-butenyl)phenyl radical ($k_c = 0.9\ k_T$ at 80°).[8]



(11) (12) (13) (14) (15)

Cyclization of **11** derived from *N*-ethyl-2-bromobenzylamine (**1b**) and cyclopentanone afforded products similar to those from **2** (Table I). The only endo-cyclized material detected was the cis-fused tricyclic **12**. Substrate **11** gave a significant yield of partially reduced material (**15**) and, like the *N*-methyl-1-cyclohexenylamine **2c**, a significantly higher proportion of fully reduced amine **14**. Clearly, the enamine reduction competes favorably with bromine atom abstraction in this case. The preponderance of the cis-endo cyclized product when compared to the cyclohexenylamine **2b** is undoubtedly due to the puckered shape of the radical intermediate. Whether the radical center adjacent to nitrogen is sp^2-hybridized or tetrahedral, models indicate that hydrogen atom transfer by tri-*n*-butyltin hydride to the α-face of the molecule would be relatively hindered, accounting for the preponderance of the cis-endo configuration.

Experimental Section

Mass spectra and accurate masses were recorded on a VG Analytical ZAB-E mass spectrometer, and high-resolution spectra were obtained at a resolution of 5000.

^{1}H and ^{13}C NMR spectra were recorded on Bruker AM500 (500 MHz), AC300P (300 MHz), and AC200 (200 MHz) spectrometers as well as on a Varian EM 390 spectrometer using TMS or $CHCl_3$ as internal standards.

Centrifugal chromatography was carried out on a Harrison Research Chromatotron Model 7924T.

AM1 calculations were executed on a Gould NP1 computer using MOPAC.[9] The conformations for **4c** were determined by complete optimization of all geometrical parameters. Starting geometries were based on Dreiding molecular models.

2-Bromobenzyl bromide and tri-*n*-butyltin hydride were obtained from Aldrich Chemical Co.

Synthesis of *N*-Alkyl-2-bromobenzylamines (1). *N*-Butyl-2-bromobenzylamine (1a). 2-Bromobenzyl bromide (1.00 g, 4 mmol) was added to *n*-butylamine (2.92 g, 40 mmol) in benzene (25 mL) and the mixture refluxed overnight. The reaction mixture was washed successively with excess 10% aqueous Na_2CO_3 and with water. It was dried over sodium sulfate. Concentration afforded pure **1a** (0.89 g, 3.7 mmol, 92%) as a pale yellow oil, bp 55 °C, 0.01 mm: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (t, CH_3), 1.30 (septet, CH_2CH_3), 1.50 (pentet, NCH_2CH_2), 2.60 (t, NCH_2), 3.82 (s, CH_2Ar), 7.05 (t, C_4-H), 7.22 (t, C_5-H), 7.34 (d, C_6-H), 7.51 (d, C_3-H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 13.75 (q, CH_3), 20.19 (t, CH_2CH_3), 31.98 (t, NCH_2CH_2), 48.69 (t, NCH_2), 53.56 (t, CH_2Ar), 123.63 (s, C_2), 127.03 (d, C_5), 128.1 (d, C_4), 129.87 (d, C_6), 132.38 (d, C_3), 139.19 (s, C_1); mass spectrum (EI) *m/z* (relative intensity) 242 and 244 ($M^{\cdot+}$ + 1, 100), 198 and 200 (38), 169 and 171 (50).

***N*-Ethyl-2-bromobenzylamine (1b).** 2-Bromobenzyl bromide (5.00 g, 20 mmol) in ethanol (15 mL) was added very slowly over 3 h to a mixture of aqueous ethylamine (12.80 g, 70%) and ethanol (20 mL). The reaction mixture was concentrated to remove ethanol, diluted with water (100 mL), and extracted with chloroform (3 × 25 mL). The extracts were dried over sodium sulfate and concentrated to afford pure **1b** as a pale yellow oil: ^{1}H NMR (200 MHz, $CDCl_3$)[10] δ 1.14 (t, CH_3) 1.52 (s, NH), 2.67 (q, NCH_2), 3.86 (s, CH_2Ar), 7.09 (t, C_4-H), 7.27 (t, C_5-H), 7.36 (d, C_6-H), 7.55 (d, C_3-H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 15.11 (q, CH_3), 43.23 (t, NCH_2), 53.47 (t, CH_2Ar), 123.75 (s, C_2), 127.19 (d, C_5), 128.31 (d, C_4), 130.05 (d, C_6), 132.55 (d, C_3), 139.13 (s, C_1).

***N*-Methyl-2-bromobenzylamine (1c).** 2-Bromobenzyl bromide (5.00 g, 20 mmol) in ethanol (15 mL) was added very slowly to a solution of methylamine prepared from methylamine hydrochloride (13 g, 200 mmol) and sodium hydroxide (8.0 g, 200 mmol) in 40 mL of ethanol–water (50:50). The reaction mixture was concentrated to remove ethanol, diluted with water (100 mL), and extracted with dichloromethane (3 × 25 mL). The extracts were dried over sodium sulfate and concentrated to afford a mixture of mainly *N*-methyl-2-bromobenzylamine and some *N,N*-bis(2-bromobenzyl)methylamine (4.30 g). **1c** distilled as a clear oil, bp 45–50 °C, 0.05 mm: ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.67 (s, NH), 2.41 (s, CH_3), 3.78 (s, CH_2Ar), 7.08 (t, C_4-H), 7.23 (t, C_5-H), 7.34 (d, C_6-H) and 7.50 (d, C_3-H); mass spectrum (CI) *m/z* 200, 202 ($M^{\cdot+}$ + 1), (EI) *m/z* 200, 202 ($M^{\cdot+}$ + 1), 169, 171 (25), 120 ($M^{\cdot+}$ − Br, 76), 91 (32).

***N*-Cyclohexyl-*N*-ethyl-2-bromobenzylamine (9b).** 2-Bromobenzyl bromide (1.00 g, 4 mmol) in benzene (20 mL) was added to excess ethylcyclohexylamine (1.10 g, 8 mmol) in benzene (25 mL). The mixture was refluxed overnight and poured onto water (100 mL). The benzene layer was separated, dried, and concentrated to an oil (1.10 g) which distilled as pure **9b**, bp 70 °C,

(7) Beckwith, A. L. J. Private communication. Approximate rate constants for hydrogen atom abstraction by ortho-substituted aryl radicals have recently been determined and log $k_T = 9.6–1.7/\theta$ where $\theta = 2.3RT$ kcal mol^{-1}; at 80 °C, $k_T = 3.52 \times 10^8$ M^{-1} s^{-1}.

(8) Beckwith, A. L. J. Private communication. log $k_c = 10.8 - 3.7/\theta$ where $\theta = 2.3RT$ kcal mol^{-1}.

(9) Dewar, M. J. S.; Zoebisch, E. G.; Healy, E. F.; Stewart, J. J. P. *J. Am. Chem. Soc.* **1985**, *107*, 3902.

(10) Krohn, K.; Carboo, D.; Puttfarcken, U. *Liebigs Ann. Chem.* **1978**, 608.

0.01 mm: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.00 (t, CH_3), 1.10–2.00 (m, cyclohexyl CH_2), 2.55 (overlapping q and quintet, NCH_2CH_3 and NCH) 4.37 (s, CH_2Ar), 7.05 (t, C_4-H), 7.26 (t, C_5-H), 7.50 (d, C_6-H), 7.64 (d, C_3-H); ^{13}C NMR (50 MHz, $CDCl_3$) 14.24 (q, CH_3), 26.20, 26.42 and 29.22 (t, ring CH_2), 44.75 (t, NCH_2CH_3), 53.74 (t, CH_2Ar), 59.86 (d, CH), 123.53 (s, C_2), 126.98 (d, C_5), 127.55 (d, C_4), 130.17 (d, C_6), 132.11 (d, C_3), 140.99 (s, C_1); mass spectrum (EI) m/z (relative intensity) 295 and 297 ($M^{\cdot+}$, 25), 280 and 282 ($M^{\cdot+}$ – CH_3, 21), 252 and 254 (100), 216 ($M^{\cdot+}$ – Br, 40), 169 and 171 (70), 91 (30); mass spectrum (high res.) 295.0947, calcd for $C_{15}H_{22}BrN$ 295.0934.

General Procedure for Enamine Formation. *N*-Alkyl-2-bromobenzylamine (10 mmol) and cyclic ketone (10 mmol) in toluene (75 mL) were refluxed together with anhydrous *p*-toluenesulfonic acid (0.1 g) in a two-necked round-bottomed flask fitted with a Dean–Stark water trap and a reflux condenser. The progress of the reaction was monitored by 200-MHz ^{1}H NMR spectroscopy in neat toluene by presaturating the toluene methyl resonance. Enamine formation was indicated by a downfield shift of the benzylic protons together with observation of a vinylic triplet. Tin hydride reductions were generally performed with enamine, amine mixtures (typically ca. 4:1).

Formation and Cyclization of *N*-Butyl-*N*-(2-bromobenzyl)-1-cyclohexenylamine (2a). *N*-Butyl-2-bromobenzylamine (2.26 g, 9.34 mmol), cyclohexanone (0.92 g, 9.6 mmol), and *p*-toluenesulfonic acid (0.07 g) were refluxed in toluene for 5 days. ^{1}H NMR analysis in toluene indicated an enamine/amine ratio of 3.7:1. Removal of toluene from an aliquot followed by vacuum distillation (60 °C, 0.1 mm) resulted in an enriched (6:1) mixture of the enamine and amine which was analysed by NMR: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.86 (t, CH_3), 1.10–1.80 (m), and 2.00–2.20 (m), 3.00 (t, NCH_2CH_2), 4.15 (s, CH_2Ar), 4.25 (t, NC=CH), 7.00–7.60 (m, 4 ArH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.01 (q, CH_3), 20.40 (t, CH_2CH_3), 22.79, 23.51, 24.63, 26.78 (t, ring CH_2), 29.66 (t, NCH_2CH_2), 49.89 (t, NCH_2CH_2), 53.47 (t, CH_2Ar), 95.94 (d, NC=CH), 122.56 (s, CBr), 127.11, 127.73, 128.61, 132.34 (d, ArCH), 139.09 (s, CCH_2), 142.24 (s, NC=CH).

Tributyltin hydride (3.54 g, 12.2 mmol) and AIBN (0.1 g) were added to 9/10 of the toluene reaction mixture which was then suspended at 80 °C for 2.5 h when ^{1}H NMR spectroscopy in toluene indicated complete consumption of enamine. The bases were extracted into cold dilute hydrochloric acid (3 × 30 mL, 0.5 M) which was washed with toluene (2 × 25 mL) and basified with cold dilute sodium hydroxide (0.2 M). Products were extracted into chloroform (3 × 25 mL) which was dried (Na_2SO_4) and concentrated to an oil (1.6 g). Centrifugal chromatography on silica gel with hexane/ethyl acetate gave five components as light oils which were as follows: (increasing R_f):

***N*-Cyclohexyl-*N*-butylbenzylamine (8a)** (0.30 g, 19%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.93 (t, CH_3), 1.00–1.90 (m, 14 H), 2.50 (overlapping t and m, *N*-CH_2 and *N*-CH), 3.62 (s, CH_2Ph), 7.20–7.50 (m, 5 ArH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.06 (q, CH_3), 20.47 (t, CH_2CH_3), 26.24, 26.50 and 28.86 (t, ring CH_2), 30.93 (t, NCH_2CH_2), 49.83 (t, CH_2N), 54.35 (t, CH_2Ph), 59.07 (d, NCH), 126.25 (d, *p*-C), 127.95 and 128.27 (d, *o*- and *m*-C) 142.9 (s, *i*-C); mass spectrum (CI) m/z (relative intensity) 246 ($M^{\cdot+}$ + 1), (EI) m/z 245 ($M^{\cdot+}$, 15), 202 (100), 91 (benzyl, 40).

***N*-Butylbenzo[*c*]-1-azaspiro[4.5]decane (6a)** (0.15 g, 9.2%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.95 (t, CH_3), 1.10–2.00 (m, 14 H), 2.68 (t, NCH_2), 4.00 (s, CH_2Ph), 7.10–7.30 (m, 3ArH), 7.60 (m, 1 ArH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.09 (q, CH_3), 20.62 (t, CH_2CH_3), 22.81, 25.67 and 31.85 (t, ring CH_2), 31.42 (t, NCH_2CH_2), 47.67 (t, NCH_2), 55.42 (t, CH_2Ar), 67.32 (s, *N*-C), 122.46, 123.42, 125.91 and 126.25 (d, ArC), 139.03 (s, C_{ipso}-CH_2), 149.07 (s, C_{ipso}-C); mass spectrum (CI) m/z (relative intensity) 244 ($M^{\cdot+}$ + 1), (EI) m/z 243 ($M^{\cdot+}$, 35), 200 ($M^{\cdot+}$ – Pr, 100), 185 (18), 172 (15), 145 (22).

***cis*-*N*-Butyl-1,2,3,4,4a,5,6,10b-octahydrophenanthridine (4a)** (0.47 g, 30%): ^{1}H NMR (500 MHz, C_6D_6) δ 0.94 (t, CH_3), 1.17–1.23 (m, 1 H), 1.25–1.58 (m, 11 H), 2.22 (dtd, J_{gem} = 13.6, J_{vic} = 7.91 and 7.85, J_{ae} = 3.6 Hz, C_1-H_{axial}), 2.33 (ddd, J_{gem} = 12.2, J_{vic} = 5.3 and 8.5 Hz, C_1′-H), 2.6 (ddd, J_{gem} = 12.2, J_{vic} = 8.5 and 6.3 Hz, C_1′-H′), 2.69 (tdd, $J_{10b,4a}$ = 3.6, $J_{4,4a}$ = 7.3 and 3.7 Hz, C_{4a}-H), 2.92 (broad m, C_{10b}-H), 3.57 (d, J_{gem} = 15.5 Hz, C_6-H), 3.8 (d, J_{gem} = 15.5 Hz, C_6-H′), 7.06 (d, C_7-H), 7.09 (t, C_8-H), 7.14 (t, C_9-H), 7.21 (d, C_{10}-H); ^{13}C NMR (125 MHz, $CDCl_3$) 14.12 (q, CH_3), 20.75 (t, CH_2CH_3), 22.90, 23.25 and 23.40 (t, ring CH_2), 29.07 (t, NCH_2CH_2), 29.86 (t, C_1), 39.49 (d, C_{10b}), 52.65 (t, C_6), 53.39 (t, NCH_2CH_2), 57.92 (d, C_{4a}), 125.25, 126.04, 126.28 and 126.67 (d, Ar-C), 135.06 (s, C_{10a}), 138.18 (s, C_{6a}); mass spectrum (CI) m/z (relative intensity) 244 ($M^{\cdot+}$ + 1), (EI) m/z 243 ($M^{\cdot+}$, 28), 242 (22), 200 ($M^{\cdot+}$ – Pr, 100), 186 (28), 144 (126), 130 (32), 115 (30), 91 (27), 77 (12); mass spectrum (high res.) 243.1992, calcd for $C_{17}H_{25}N$ 243.1989.

***trans*-*N*-Butyl-1,2,3,4,4a,5,6,10b-octahydrophenanthridine (5a)** (0.18 g, 11%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.94 (t, CH_3), 1.22 (qd, C_1-H_{ax}), 1.30 (sextet, CH_2CH_3), 1.28, 1.40, 1.42 (m, C_3-H_{ax}, C_4-H_{ax}, C_2-H_{ax}), 1.50 (m, NCH_2CH_2), 1.85 (d of m, C_2-H_{eq}), 1.88 (d of m, C_3-H_{eq}), 2.7 (d of m, C_4-H_{eq}), 2.30 (td, $J_{10b,4a}$, $J_{4ax,4a}$ = 10.5, $J_{4eq,4a}$ = 3.3 Hz, C_{4a}-H), 2.4 (d of m, C_1-H_{eq}), 2.49 (ddd, J_{gem} = 12.6, J_{vic} = 6.5 and 9.5 Hz, C_1′-H), 2.57 (br td, $J_{4a,10b}$, $J_{1ax,10b}$ = 10.5, $J_{1eq,10b}$ = 3.3 Hz, C_{10b}-H), 2.65 (ddd, J_{gem} = 12.6, J_{vic} = 8.5 and 6.9 Hz, C_1′-H′), 3.78 (d, J_{gem} = 15.5 Hz, C_6-H), 3.93 (d, J_{gem} = 15.5 Hz, C_6-H′), 7.03 (d, C_7-H), 7.10 (t, C_8-H), 7.16 (t, C_9-H), 7.24 (d, C_{10}-H); ^{13}C NMR (50 MHz, $CDCl_3$) 14.06 (q, CH_3), 20.81 (t, CH_2CH_3), 25.72 (t, C_3), 26.22 (t, C_2), 29.05 (t, NCH_2CH_2), 30.38 (t, C_1), 30.85 (t, C_4), 40.93 (d, C_{10b}), 50.07 (t, NCH_2CH_2), 54.80 (t, C_6), 64.15 (d, C_{4a}), 125.24, 125.59, 126.12 and 126.54 (d, Ar-C), 134.57 (s, C_{10a}), 138.52 (s, C_{6a}); mass spectrum (CI) m/z (relative intensity) 244 ($M^{\cdot+}$ + 1), (EI) 243 ($M^{\cdot+}$, 20), 242 (20), 200 ($M^{\cdot+}$ – Pr, 100), 186 (8), 129 (12); mass spectrum (high res.) 243.1985, calcd for $C_{17}H_{25}N$ 243.1989.

***N*-Butylbenzylamine (7a)** (0.24 g, 73% based on **1a** in starting material) which was identical to an authentic sample: ^{1}H NMR (90 MHz, $CDCl_3$) δ 0.90 (t, CH_3), 1.20–1.70 (overlapping sextet and pentet, CH_2CH_2), 2.75 (t, NCH_2), 3.89 (s, CH_2Ar), 7.35 (s, 5ArH); mass spectrum (EI) m/z (relative intensity) 164 ($M^{\cdot+}$, 100), 120 (40), 91 (54).

Determination of Relative Rates of Cyclization of *N*-Butyl-*N*-(2-bromobenzyl)-1-cyclohexenylamine (2a). Enamine mixture (0.93 mmol reducible bromide) was treated with tributyltin hydride (2.72 g, 9.34 mmol) and AIBN (0.1 g) and made up to 10 mL with anhydrous toluene. The reaction was suspended at 80 °C for 2.5 h. Acid–base workup gave a mixture (0.23 g) which was analyzed by 500-MHz ^{1}H NMR in $CDCl_3$. Average areas for the benzylic methylenic protons were determined from four integrations from which the average ratios of products were as follows: endo/reduced = 1.39, exo/reduced = 0.48, endo/exo = 2.94, and $endo_{cis}/endo_{trans}$ = 2.28. Identical ratios of products were obtained from a control experiment in which the reaction mixture was degassed by several freeze–thaw cycles prior to heating. The reaction was repeated with different concentrations of tributyltin hydride and with a [tributyltin hydride]:[**2a**] ratio of at least 10:1. The product ratios were determined in each case by ^{1}H NMR spectroscopy and are given in Table II.

Formation and Cyclization of *N*-Ethyl-*N*-(2-bromobenzyl)-1-cyclohexenylamine (2b). *N*-Ethyl-2-bromobenzylamine (2.00 g, 9.34 mmol), cyclohexanone (0.92 g, 9.6 mmol), and *p*-toluenesulfonic acid (0.06 g) were refluxed in toluene (75 mL) for 3 days. ^{1}H NMR analysis in toluene indicated an enamine/amine ratio of 3.2:1. Tributyltin hydride (3.93 g, 13.5 mmol) and AIBN (0.11 g) were added to the reaction mixture which was then suspended at 80 °C for 2.5 h when ^{1}H NMR in toluene indicated complete consumption of enamine. Acid–base workup yielded an oil (2.18 g) of which a portion (0.60 g) was separated on a Chromatotron apparatus (silica gel, 2-mm plate, with hexane/ethyl acetate) into five components as light oils which were as follows (increasing R_f):

***N*-Benzyl-*N*-cyclohexylethylamine (8b)** (0.05 g, 12.4%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.97 (t, CH_3), 1.00–1.90 (m, 14 H), 2.52 (overlapping q and m, NCH_2 and NCH), 3.60 (s, CH_2Ph), 7.20–7.40 (m ArH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.02 (q, CH_3), 26.23, 26.51 and 29.09 (t, ring CH_2), 44.08 (t, CH_2N), 53.87 (t, CH_2Ph), 59.08 (d, NCH), 126.30 (d, *p*-C), 127.99 and 128.31 (d, *o*- and *m*-C) 143 (s, *i*-C); mass spectrum (EI) m/z (relative intensity) 217 ($M^{\cdot+}$, 32), 202 (12), 174 (100), 91 (92, benzyl); mass spectrum (high res.) 217.1841, calcd for $C_{15}H_{23}N$ 217.1830.

***N*-Ethylbenzo[*c*]-1-azaspiro[4.5]decane (6b)** (0.36 g, 28%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.18 (t, CH_3), 1.60–1.90 (m, 10H), 2.72 (q, NCH_2), 3.97 (s, CH_2Ph), 7.10–7.30 (m, 3 ArH), 7.56 (m, 1 ArH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.82 (q, CH_3), 22.83, 25.70 and 31.80 (t, ring CH_2), 41.79 (t, NCH_2), 54.95 (t, CH_2Ar),

67.30 (s, *N*-C), 122.50, 123.44, 125.95 and 126.25 (d, ArC), 138.95 (s, C_{ipso}-CH_2), 149.10 (s, C_{ipso}-C); mass spectrum (CI) *m/z* (relative intensity) 215 ($M^{\cdot+}$, 25), 186 (18), 172 (100), 159 (27); mass spectrum (high res.) 215.1678, calcd for $C_{15}H_{21}N$ 215.1674.

***cis*-*N*-Ethyl-1,2,3,4,4a,5,6,10b-octahydrophenanthridine (4b)** (0.13 g, 31%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.15 (t, CH_3), 1.30–1.42 (m, 3 H), 1.57–1.66 (m, 4 H), 2.22 (m, C_1-H_{axial}), 2.60 (qd, J_{gem} = 12.5, J_{vic} = 7.1 Hz, C_1'-H), 2.76 (qd, J_{gem} = 12.5, J_{vic} = 7.1 Hz, C_1'-H'), 2.86 (tdd, $J_{10b,4a}$ = 4.2, $J_{4,4a}$ = 6.8 and 4.2 Hz, C_{4a}-H), 2.98 (broad m, C_{10b}-H), 3.69 (d, J_{gem} = 15.6 Hz, C_6-H), 3.78 (d, J_{gem} = 15.6 Hz, C_6-H'), 7.00 (d, C_7-H), 7.09 (t, C_8-H), 7.13 (t, C_9-H), 7.20 (d, C_{10}-H); ^{13}C NMR (50 MHz, $CDCl_3$) 11.87 (q, CH_3), 23.6 (3 × t, ring CH_2), 29.92 (t, C_1), 39.49 (d, C_{10b}), 47.17 (t, NCH_2CH_3), 52.15 (t, C_6), 57.35 (d, C_{4a}), 125.27, 126.06, 126.31 and 126.69 (d, Ar-C), 134.92 (s, C_{10a}), 138.50 (s, C_{6a}); mass spectrum (EI) *m/z* (relative intensity) 215 ($M^{\cdot+}$, 58), 214 (48), 200 ($M^{\cdot+}$ – Me, 8), 172 (100), 186 (28), 158 (20); mass spectrum (high res.) 215.1685, calcd for $C_{15}H_{21}N$ 215.1674.

***trans*-*N*-Ethyl-1,2,3,4,4a,5,6,10b-octahydrophenanthridine (5b)** (0.05 g, 13%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.10 (t, CH_3), 1.22 (qd, J_{gem}, $J_{10b,1a}$, $J_{2ax,1ax}$ = 12.4, $J_{2eq,1ax}$ = 3.3 Hz, C_1-H_{ax}), 1.28–1.45 (m, C_3-H_{ax}, C_4-H_{ax}, C_2-H_{ax}), 1.86 (d of m, C_2-H_{eq}), 1.88 (d of m, C_3-H_{eq}), 2.07 (d of m, C_4-H_{eq}), 2.28 (td, $J_{10b,4a}$, $J_{4ax,4a}$ = 10.5, $J_{4eq,4a}$ = 3.2 Hz, C_{4a}-H), 2.42 (d of m, C_1-H_{eq}), 2.57 (br td, $J_{4a,10b}$, $J_{1ax,10b}$ = 10.5, $J_{1eq,10b}$ = 3.2 Hz, C_{10b}-H), 2.60 (qd, J_{gem} = 12.8, J_{vic} = 7.2 Hz, C_1'-H), 2.78 (qd, J_{gem} = 12.8, J_{vic} = 7.2 Hz, C_1-H'), 3.75 (d, J_{gem} = 15.24 Hz, C_6-H), 3.94 (d, J_{gem} = 15.2 Hz, C_6-H'), 7.02 (d, C_7-H), 7.11 (t, C_8-H), 7.16 (t, C_9-H), 7.26 (d, C_{10}-H); ^{13}C NMR (50 MHz, $CDCl_3$) 11.54 (q, CH_3), 25.63 (t, C_3), 26.13 (t, C_2), 30.30 (t, C_1), 30.60 (t, C_4), 41.46 (d, C_{10b}), 44.2 (NCH_2CH_3), 53.95 (t, C_6), 63.87 (d, C_{4a}), 125.18, 125.56, 126.11 and 126.45 (d, Ar-C), 134.39 (s, C_{10a}), 138.33 (s, C_{6a}); mass spectrum (EI) *m/z* (relative intensity) 215 ($M^{\cdot+}$, 50), 214 (50), 200 (15, $M^{\cdot+}$ – CH_3), 172 (100), 158 (20), 146 (10); mass spectrum (high res.) 215.1685, calcd for $C_{15}H_{21}N$ 215.1674.

Formation and Cyclization of *N*-Methyl-*N*-(2-bromobenzyl)-1-cyclohexenylamine (2c). *N*-Methyl-2-bromobenzylamine (1.10 g, 5.5 mmol), cyclohexanone (0.54 g, 5.5 mmol), and *p*-toluenesulfonic acid (0.10 g) were refluxed in toluene (50 mL) for 3 days. ^{1}H NMR analysis in toluene indicated an enamine/amine ratio of 7:1. Tributyltin hydride (2.09 g, 7.18 mmol) and AIBN (0.1 g) were added to 9/10 of the reaction mixture. Immediate NMR analysis in toluene indicated an enamine/amine ratio of 50:50. The reduction mixture was suspended at 80 °C for 3 h when ^{1}H NMR spectroscopy in toluene indicated complete consumption of enamine. Acid–base workup yielded an oil (0.76 g) which was separated on a Chromatotron apparatus (silica gel with hexane/ethyl acetate) into four components, each as a light oil. The fraction with the lowest R_f (0.13 g) was a mixture of *N*-cyclohexyl-*N*-methyl-2-bromobenzylamine (**9c**) and *N*-benzyl-*N*-cyclohexylmethylamine (**8c**) in an approximate ratio of 1:1. Subsequent fractions were as follows, in increasing R_f:

***N*-Benzyl-*N*-cyclohexylmethylamine (8c)** (88 mg, 37% [with estimate from first fraction]): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.00–1.90 (m, 10 H), 2.20 (s, NCH_3), 2.40 (m, *N*-CH), 3.52 (s, CH_2Ph), 7.20–7.40 (m, ArH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 25.94, 26.36, and 28.61 (t, ring CH_2), 37.57 (q, CH_3N), 57.74 (t, CH_2Ph), 62.43 (d, NCH), 126.52 (d, *p*-C), 128.03 and 128.65 (d, *o*- and *m*-C) 140.33 (s, *i*-C); mass spectrum (EI) *m/z* (relative intensity) 203 ($M^{\cdot+}$, 30), 160 (100), 146 (14), 91 (benzyl, 40); mass spectrum (high res.) 203.1682, calcd for $C_{14}H_{21}N$ 203.1674.

***cis*-*N*-Methyl-1,2,3,4,4a,5,6,10b-octahydrophenanthridine (4c)** (59 mg, 12%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.39–1.68 (m, 6 H), 1.96 (m, 2 H), 2.38 (s, NCH_3), 2.54 (tdd, $J_{4,4a}$ = 5.3 and 3.3, $J_{10b,4a}$ = 3.3 Hz, C_{4a}-H), 2.77 (broad m, C_{10b}-H), 3.47 (d, J_{gem} = 15.3 Hz, C_6-H), 3.89 (d, J_{gem} = 15.3 Hz, C_6-H'), 6.99 (d, C_7-H), 7.07–7.13 (m, C_8, C_9, C_{10}-H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 21.08, 25.39, 26.52, 31.48 (4 × t, ring CH_2), 40.86 (d, C_{10b}), 41.73 (t, NCH_3), 58.14 (t, C_6), 59.57 (d, C_{4a}), 125.37, 125.88, 125.99 and 127.40 (d, Ar-C), 134.27 (s, C_{10a}), 139.76 (s, C_{6a}); mass spectrum (EI) *m/z* (relative intensity) 201 ($M^{\cdot+}$, 45), 200 (42), 158 (100), 144 (36), 91 (15); mass spectrum (high res.) 201.1519, calcd for $C_{14}H_{19}N$ 201.1517.

***N*-Methylbenzo[*c*]-1-azaspiro[4.5]decane (6c)** (0.14 g, 28%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.50–1.90 (m, 10 H), 2.47 (s, NCH_3), 3.97 (s, CH_2Ph), 7.10–7.30 (m, 3 H, ArH), 7.53 (m, 1 ArH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 22.72, 25.65 and 31.70 (t, ring CH_2), 34.76 (q, CH_3), 58.22 (t, CH_2Ar), 66.78 (s, *N*-C), 122.33, 123.25, 125.98 and 126.28 (d, ArC), 139.14 (s, *i*-C-CH_2), 148.99 (s, *i*-C-C); mass spectrum (EI) *m/z* (relative intensity) 201 ($M^{\cdot+}$, 18), 158 (100), 144 (25), 84 (30); mass spectrum (high res.) 201.1523, calcd for $C_{14}H_{19}N$ 201.1517.

Formation and Cyclization of *N*-Ethyl-*N*-(2-bromobenzyl)-1-cyclopentenylamine (11). *N*-Ethyl-2-bromobenzylamine (3.00 g, 14.7 mmol), cyclopentanone (1.26 g, 14.7 mmol), and *p*-toluenesulfonic acid (0.10 g) were refluxed in toluene (70 mL) for 2 days. ^{1}H NMR analysis in toluene indicated an enamine/amine ratio of 16:1. Tributyltin hydride (3.39 g, 1.62 mmol) and AIBN (0.1 g) were added to 0.56 of the total reaction mixture after which the enamine/amine ratio was 3:1. After the mixture was heated at 80 °C for 4 h, ^{1}H NMR spectroscopy in toluene indicated complete consumption of enamine and acid–base workup yielded an oil (1.46 g) which was separated on a Chromatotron apparatus (silica gel with hexane/ethyl acetate) into five components as light oils which were as follows (increasing R_f):

***N*-Cyclopentyl-*N*-ethyl-2-bromobenzylamine (15)** (0.27 g, 16%): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.97 (t, CH_3), 1.40–1.70 (m, 8 H), 2.60 (q, *N*-CH_2), 3.13 (quintet, *N*-CH), 3.67 (s, CH_2Ph), 7.04 (t, C_4-H), 7.25 (t, C_5-H), 7.45 (d, C_6-H), 7.65 (d, C_3-H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 11.76 (q, CH_3), 24.16 and 29.58 (t, ring CH_2), 46.12 (t, CH_2N), 54.78 (t, CH_2Ph), 63.50 (d, NCH), 123.51 (s, C_2), 127.03 (d, C_5), 127.68 (d, C_4), 130.50 (d, C_6), 132.20 (d, C_3), 140.53 (s, C_1); mass spectrum (EI) *m/z* (relative intensity) 281 and 283 ($M^{\cdot+}$, 22), 266 and 268 ($M^{\cdot+}$ – CH_3, 42), 202 ($M^{\cdot+}$ – Br, 35), 169 and 171 (*o*-Br benzyl, 100), 112 (34), 84 (65); mass spectrum (high res.) 281.0785 calcd for $C_{14}H_{20}BrN$ 281.0779.

***N*-Benzyl-*N*-cyclopentylethylamine (14)** (0.35 g, 29%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.98 (t, CH_3), 1.40–1.60 (m, 4 H), 1.60–1.73 (m, 2 H), 1.75–1.85 (m, 2 H), 2.57 (q, *N*-CH_2), 3.07 (quintet, *N*-CH), 3.62 (s, CH_2Ph), 7.20 (t, *p*-H), 7.28 (t, *m*-H), 7.34 (d, *o*-H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 10.94 (q, CH_3), 24.22 and 29.77 (t, ring CH_2), 44.72 (t, CH_2N), 55.06 (t, CH_2Ph), 62.88 (d, NCH), 126.53 (d, *p*-C), 128.05 and 128.75 (d, *o*- and *m*-C) 140.65 (s, *i*-C); mass spectrum (EI) *m/z* (relative intensity) 203 ($M^{\cdot+}$, 20), 188 ($M^{\cdot+}$ – CH_3, 28), 174 (50), 146 (10), 112 (10), 91 (benzyl, 100); mass spectrum (high res.) 203.1693, calcd for $C_{14}H_{21}N$ 203.1674.

***N*-Ethylbenzo[*c*]-1-azaspiro[4.4]nonane (13)** (0.22 g, 18%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.21 (t, CH_3), 1.70 (m, 2 H), 1.78 (m, 4 H), 2.03 (m, 2 H), 2.72 (q, NCH_2), 3.90 (s, CH_2Ph), 7.10–7.30 (m, 4 ArH); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.54 (q, CH_3), 25.72 and 34.35 (t, ring CH_2), 41.65 (t, NCH_2), 55.64 (t, CH_2Ar), 76.19 (s, *N*-C), 120.70, 121.89, 126.02 and 126.83 (d, ArC), 137.75 (s, *i*-C-CH_2), 151.43 (s, *i*-C-C); mass spectrum (EI) *m/z* (relative intensity) 201 ($M^{\cdot+}$, 25), 186 (7), 172 (100), 160 (29), 158 (37), 144 (13), 91 (12); mass spectrum (high res.) 201.1530, calcd for $C_{14}H_{19}N$ 201.1517.

***cis*-*N*-Ethyl-4-aza-2,3,3a,4,5,9b-hexahydrobenz[*e*]indene (12)** (0.21 g, 17%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.13 (t, CH_3), 1.53 (m, C_2-H), 1.64 (m, C2-H'), 1.64–1.75 (m, C_1-H, C_3-H), 1.85 (m, C_3-H'), 2.17 (m, C_1-H'), 2.42 (qd, J_{gem} = 12.6, J_{vic} = 7.2 Hz, C_1'-H), 2.77 (qd, J_{gem} = 12.6, J_{vic} = 7.1 Hz, C_1'-H'), 3.14 (ddd, $J_{9b,3a}$ = 6.8, $J_{1,9b}$ = 7 and 7 Hz, C_{9b}-H), 3.17 (ddd, $J_{3a,9b}$ = 6.8, $J_{3,3a}$ = 6.8 and 6.8 Hz, C_{3a}-H), 3.41 (d, J_{gem} = 14.7 Hz, C_5-H), 3.76 (d, J_{gem} = 14.7 Hz, C_5-H'), 7.03 (d, ArH), 7.07 (t, ArH), 7.15 (m, 2 × ArH); ^{13}C NMR (50 MHz, $CDCl_3$) 11.79 (q, CH_3), 23.75, 28.33, 33.72 (3 × t, ring CH_2), 41.38 (d, C_{9b}), 48.37 (t, NCH_2CH_3), 51.67 (t, C_6), 62.44 (d, C_{3a}), 125.04, 126.08, 126.49 and 127.95 (d, Ar-C), 134.42 (s, C_{9a}), 138.50 (s, C_{5a}); mass spectrum (EI) *m/z* (relative intensity) 201 ($M^{\cdot+}$, 68), 200 (66), 186 (28), 172 ($M^{\cdot+}$ – Et, 100), 158 (72); mass spectrum (high res.) 201.1530, calcd for $C_{14}H_{19}N$ 201.1517.

Reduction of *N*-Benzyl-*N*-ethyl-1-cyclohexenylamine (10) and *N*-Cyclohexyl-*N*-ethyl-2-bromobenzylamine (9b). *N*-Ethylbenzylamine (1.68 g, 13.9 mmol), cyclohexanone (1.36 g, 13.9 mmol), and *p*-toluenesulfonic acid (0.10 g) were refluxed in toluene (15 mL) for 5 days. ^{1}H NMR analysis in toluene indicated an enamine/amine ratio of 5.6:1. A portion of this enamine mixture (1.5 mL, 1.4 mmol) was added to a solution of *N*-cyclohexyl-*N*-ethyl-2-bromobenzylamine (0.44 g, 1.48 mmol), tri-

butyltin hydride (0.43 g, 1.48 mmol), and AIBN (0.03 g), in dry toluene (2 mL). The mixture (under nitrogen) was heated at 80 °C for 2 h and analyzed at various intervals by ^{1}H NMR spectroscopy in toluene employing presaturation of the toluene methyl resonance. After 75 min the resonance at δ 3.65 due to the benzylic protons of **9b** were replaced by those of the *N*-cyclohexyl-*N*-ethylbenzylamine (**8b**) at δ 3.45. The enamine resonance at δ 3.8 remained unaltered during this time.

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Supplementary Material Available: ^{1}H NMR spectra for compounds **1a**, **1c**, **9b**, **2a**, **8a**, **6a**, **5a**, **7a**, **8b**, **6b**, **4b**, **5b**, **8c**, **4c**, **6c**, **15**, **14**, **13**, and **12**, ^{13}C NMR spectra for compounds **1a**, **2a**, **6a**, **6b**, **8c**, **6c**, and **15**, COSY spectra for **4a** and **5a**, and TOCSY spectrum for **4a** (23 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.