more obvious consequence in terms of conformation is that the tri-, tetra-, and pentapeptides exclusively populate the single, double, and triple β-bend structures, respectively. This conclusion is supported by the excellent correlation with all the solid-state structures of homo oligo(α-aminoisobutyric acids) so far solved by X-ray diffraction (this work and ref 16 and 40), which unequivocally demonstrate that the type-III (or type-III') 4 → 1 intramolecular hydrogen-bonded conformations are those exclusively adopted whenever possible (i.e., in the N-protected tripeptides and their higher homologues). However, it is evident that the present conformational analysis in deuteriochloroform at high dilution cannot exclude categorically the occurrence of either the 3 → 1[43,44] or the 5 → 1 intramolecular hydrogen-bonded conformations (the latter at the level of the tetra- and pentapeptides). These conformations can exist either as the only species in solution or as components of the equilibrium mixtures, which could also involve the 4 → 1 intramolecular hydrogen-bonded forms.

At 5×10^{-2} M concentration the IR absorption spectral patterns in the N-H stretching region change only marginally for the C-protected peptides. The C-deblocked compounds were not examined owing to their low solubility under these experimental conditions. Interestingly, the A_H/A_F ratio of all the three C-protected peptides increases, with the 100-times increases in concentration (the bands due to the intra- and intermolecular hydrogen-bonded N-H groups overlap[50]). This result strongly supports the view that at 5×10^{-2} M concentration the N—H···O=C intermolecular hydrogen-bonded species exist in all three compounds, the extend of which is higher for the pentapeptide and lower for the tripeptide.[50] in this context, it should be recalled that the urethane N-H is the one responsible for the aggregation of the incipient 3_{10} helices of Z-(Aib)$_3$-O-*t*-Bu, Z-(Aib)$_4$-OH, and Z-(Aib)$_5$-O-*t*-Bu in the solid state.

Conclusions

The solid-state conformational anslysis, carried out by X-ray diffraction and IR absorption, of the N-benzyloxycarbonyl homotri-, and tetra-, and pentapeptides from the Aib residue has indicated the onset of incipient 3_{10} helices, formed by one, two, and three type-III (or type-III') β turns (4 → 1 intramolecular hydrogen-bonded structures), respectively. α-Helical structures, although having pairs of ϕ,ψ torsional angles close to those of the 3_{10} helices, are not compatible with the observed N—H··O=C hydrogen-bonding schemes of the tetra- and pentapeptides, being characterized by 5 → 1 intramolecular hydrogen-bonded peptide forms. The signs of the ϕ,ψ torsional angles of the last Aib residue in the sequences of the homo oligo(α-aminoisobutyric acids) are opposite to those of the preceding residues. The existence of a correlation between the conformational space of the Aib residue and its geometry at the C^α carbon atom has been discussed. The effect of the presence of a free -COOH group at the C-terminal end of the peptide chain on the type of folding was found to be negligible; however, it acts as donor in the intermolecular hydrogen-bonding scheme.

In solvents of low polarity (e.g., deuteriochloroform) the IR absorption data are in favor of the occurrence of the same intramolecular hydrogen-bonded folded forms as found in the solid state. Aggregation of these structures takes place at high concentrations.

Clearly, since segments containing up to four α, α-alkylated, α-amino acid residues in a row have been found in the peptide antibiotics of the alamethicin family, the 3_{10}-helical structure must be taken into consideration in suggesting a model of folding of these parts of their sequences containing a high proportion of Aib and Iva residues.

Acknowledgment. This work was supported in part by a research grant from the C.N.R. of Italy (Grant No. 79/1348).

Registry No. (*Z*)-Aib$_3$-O-*t*-Bu, 4512-37-2; (*Z*)-Aib$_4$-O-*t*-Bu, 4512-38-3; (*Z*)-Aib$_5$-O-*t*-Bu, 4512-39-4.

Supplementary Material Available: Tables of positional and thermal parameters, anistropic thermal parameters, and structure factor amplitudes for Z-(Aib)$_3$-O-*t*-Bu, Z-(Aib)$_4$-OH, and Z-(Aib)$_5$-O-*t*-Bu (52 pages). Ordering information is given on any current masthead page.

(53) R. Nagaraj and P. Balaram, *Biochemistry*, **20**, 2828 (1981).

Palladium-Catalyzed Cyclization of ω-Olefinic Tosamides. Synthesis of Nonaromatic Nitrogen Heterocycles

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Abstract: The cyclization of aliphatic amino olefins to nonaromatic nitrogen heterocycles has been accomplished by conversion of the amine to the corresponding *p*-toluenesulfonamide, followed by Pd(II)-catalyzed intramolecular amination of the olefin. The resulting tosylated enamines could be reduced and photolytically deprotected to give the saturated nitrogen heterocycle. The same product was obtained by reduction of the tosylated enamines with sodium bis(2-methoxyethoxy)aluminum hydride (Red-al).

Introduction

Transition metal organometallic reagents have been used extensively in the synthesis of heterocyclic compounds.[1] In our laboratories, the palladium(II)-catalyzed intramolecular amination[2] and carboxylation[3] of olefins, converting *o*-allylanilines to indoles and *o*-allylbenzoic acids to isocoumarins, have been developed. In this paper we describe the synthesis of nonaromatic nitrogen heterocycles using this approach.

Results and Discussion

Although *o*-allylanilines cyclized smoothly to indoles when treated with a catalytic amount of palladium(II) chloride under

(1) For reviews of recent activity in this area, see: L. S. Hegedus, *J. Organomet. Chem.*, **207**, 299 (1981); **180**, 419 (1979); **163**, 287 (1978).
(2) L. S. Hegedus, G. F. Allen, J. J. Bozell, and E. L. Waterman, *J. Am. Chem. Soc.* **100**, 5800 (1978).
(3) D. E. Korte, L. S. Hegedus, and R. K. Wirth, *J. Org. Chem.*, **42**, 1329 (1977).

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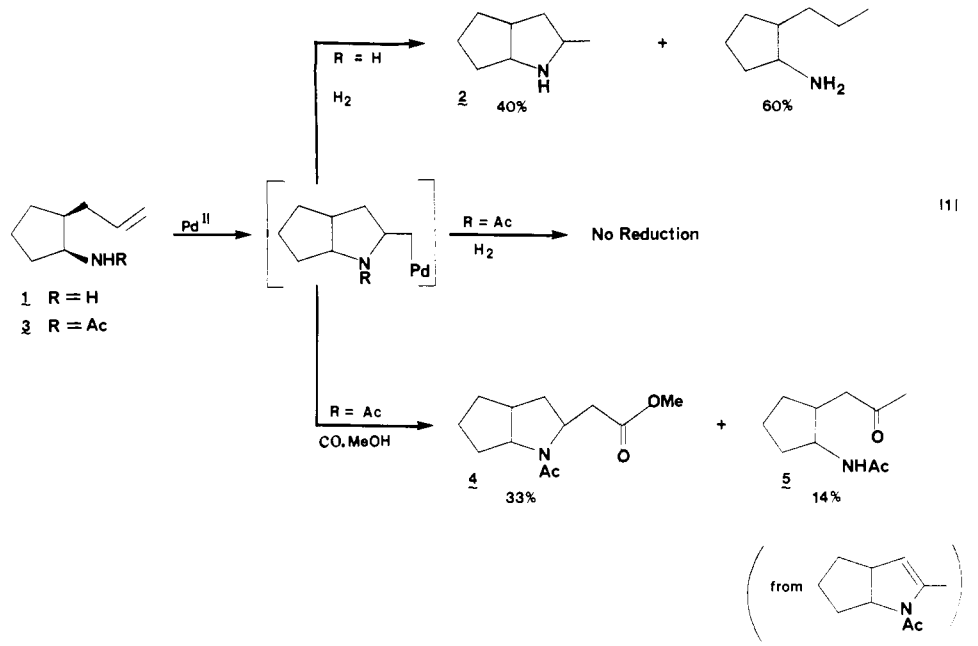
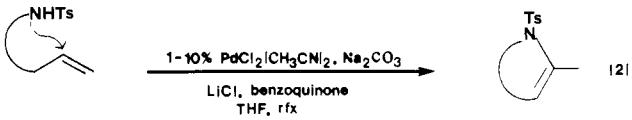


(1)

oxidizing conditions, attempts to cyclize nonaromatic amino olefins under similar conditions were unsuccessful. Reaction of 2-(1-propenyl)cyclopentylamine (**1**) with stoichiometric amounts of palladium chloride, in both the presence and absence of added triethylamine produced intractable organopalladium complexes, which produced only small amounts of cyclized product **2** along with larger amounts of 2-(*n*-propyl)cyclopentylamine and palladium metal upon reduction.[4] Exposure of this same substrate to standard catalytic cyclization conditions (10% $PdCl_2(MeCN)_2$, benzoquinone, THF at reflux) resulted in the amination of the quinone by the substrate rather than in cyclization. Both of these problems appeared to be due to the increased basicity ($\sim 10^6$) and nucleophilicity of the aliphatic amine group relative to the corresponding aromatic amine group. To ameliorate this problem, the free NH_2 group was acetylated and the resulting acetamide (**3**) was subjected to a variety of cyclization conditions. Under catalytic cyclization conditions, no reaction was observed. Under stoichiometric conditions, stable organopalladium complexes which resisted reduction (H_2, 90 psi) were formed. However, exposure of this solution to carbon monoxide and methanol produced cyclized, carbonylated product **4**, as well as unreacted starting material, and *N*-acetyl-2-(acetonyl)cyclopentylamine (**5**), which must have arisen from hydrolysis of the desired enamide during isolation (eq 1). These results suggested that the acetamide still complexed too strongly to palladium to permit a catalytic cyclization and that the enamides produced were rather unstable. Thus, the olefinic tosamides were synthesized and their cyclization reactions examined.

p-Toluenesulfonamides were attractive substrates for a number of reasons. They are easily prepared from primary amines, as well as from olefins via $TsNBr_2$.[5] They are stable crystalline solids, easy to purify and to handle. Finally, the anticipated product from cyclization, a tosylated enamine, was expected to be sufficiently stable to permit isolation and purification, yet sufficiently reactive to be a useful synthetic intermediate.

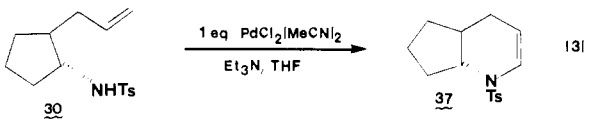
Thus, a number of olefinic tosamides were synthesized and catalytically cyclized under the conditions shown in eq 2. The results are summarized in Table I.



(2)

This reaction is generally useful for the formation of cis-fused 5,5 ring systems. The nature of the sulfonamide group is not critical, since *p*-tolyl-, methane-, and benzylsulfonamides cyclize in roughly the same yields. Both allyl and vinyl side chains cyclize readily, giving high yields of bicyclic tosylated enamines. With the substrate having a vinyl side chain (**14**) the stability of a five-membered ring (vs. four) overrides the normal regiochemistry of the cyclization. Cis-fused 6,5 ring systems (**17**) also form, but are rather unstable toward hydrolysis, and substantial amounts of ketone (from hydrolysis during isolation) are obtained. With the corresponding trans substrate **18**, ketone **19** is the sole product of the reaction, indicating that cyclization had occurred, but that the product was unstable and hydrolyzed despite a careful isolation. Benz-fused six-membered rings (**21**) (dihydroisoquinolines) and spiro-6,5 ring systems (**22**) also form in high yield. Acyclic olefinic tosamides (**24–28**) also cyclize to form five-membered rings readily. The simplest member of this series (**24**) again was somewhat unstable and partially hydrolyzed during isolation. As substitution on this chain increased, the stability and yield of cyclic product increased.

Remarkably, a number of closely related olefinic tosamides failed to react at all under the standard catalytic cyclization conditions, instead giving good recoveries of unreacted starting materials. The substrate which would form a trans-5,5 ring system (**30**) was inert to these conditions, undoubtedly because of the ring strain associated with this trans-fused ring system, as well as the high energy of activation to close to form a six-membered ring (less favored regiochemistry for Pd(II)-assisted ring closure). This same substrate closed to the trans-fused 5,6 ring system when treated with a stoichiometric amount of palladium(II) (eq 3).



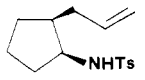
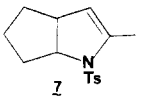
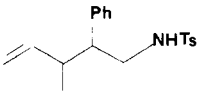
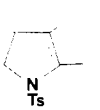
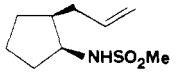
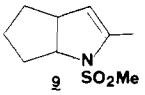
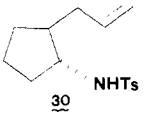
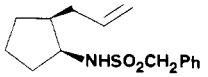
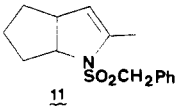
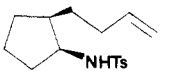
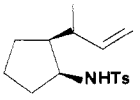
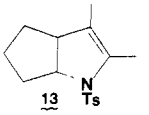
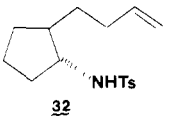
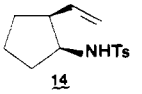
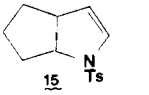
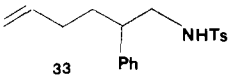
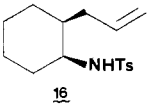
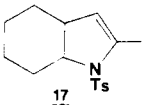
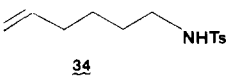
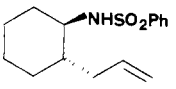
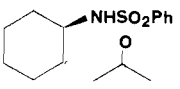
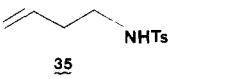
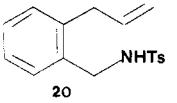
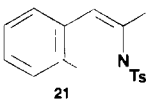
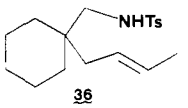
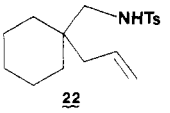
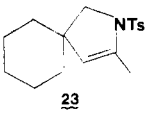
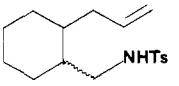
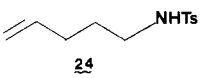
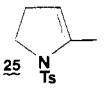
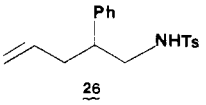
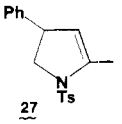
(3)

(4) In a recent paper (L. M. Venanzi and B. Pugin, *J. Organomet. Chem.*, **214**, 125 (1981)) Venanzi and Pugin showed that simple aminoalkenes such as $CH_2{=}CH(CH_2)_3NH_2$ formed stable complexes with Pd(II) in which both the amine and olefin groups were coordinated to the metal, making amination of the olefin impossible. By forming the trifluoromethansulfonate salt of the aminoalkenes followed by treatment with Pd(II) to form the olefin complex, followed by low-temperature treatment with diethylamine, stoichiometric amination of the olefin was achieved. Reduction of the resulting σ-alkylpalladium complex produced reasonable yields of the saturated nitrogen heterocycles. We thank Professor Venanzi for making these available to us prior to publication.

(5) M. S. Kharash and H. M. Priestley, *J. Am. Chem. Soc.*, **61**, 3425 (1939).

(6) J. A. Pincock and A. Jurgens, *Tetrahedron Lett.*, 6029 (1979).

Table I

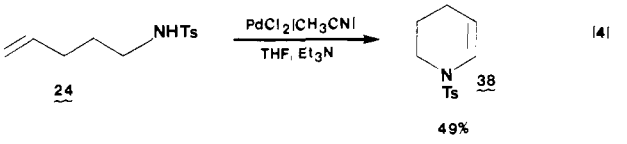
substrate	product	yield,[a] %	substrate	product	yield,[a] %
 6	 7	85	 28	 29	92
 8	 9	63	 30	c	-
 10	 11	76	 31	c	-
 12	 13	82	 32	c	-
 14	 15	57	 33	c	-
 16	 17	48[b]			
			 34	c	-
 18	 19	~100			
			 35	c	-
 20	 21	84			
			 36	c	-
 22	 23	78			
			 37	c	-
 24	 25	42[b]			
 26	 27	60			

[a] Yields reported are for isolated, purified products. [b] Substantial amounts of the noncyclized ketone were obtained, indicating that the cyclization had proceded in good yield but that product was lost by hydrolysis during isolation. [c] Unreacted starting material was recovered in high yield.

In general, six-membered rings formed with difficulty under catalytic cyclization conditions. Substrates which would give trans- (**31**) or cis- (**32**) fused 5,6 ring systems, and acyclic substrates which would give six-membered rings (**33**,**34**) failed to react under catalytic conditions. Similarly the shorter chain 4-tosamido-1-butene (**35**) failed to cyclize, since formation of the most stable five-membered ring would entail attack at the less favored (terminal) carbon of the olefin.

Two other substrates failed to cyclize under catalytic conditions. The precursor to the spiro compound having a 2-butenyl side chain (**36**) was inert under catalytic conditions. This closure would require amination of a disubstituted olefin, which complexes less strongly to palladium(II) than do terminal olefins. Although *o*-allylanilines having di- and even trisubstituted allyl side chains cyclized easily to indoles or quinolines,[2,3] apparently the tosamide nitrogen is significantly less reactive, and closure does not occur. Finally, the saturated analogue of the isoquinoline precursor (**37**) failed to cyclize under standard catalytic conditions. This is perplexing, since both the reactivity of the olefin and tosamide groups and their spatial relationship relative to each other are virtually the same as in the isoquinoline precursor which closed readily.

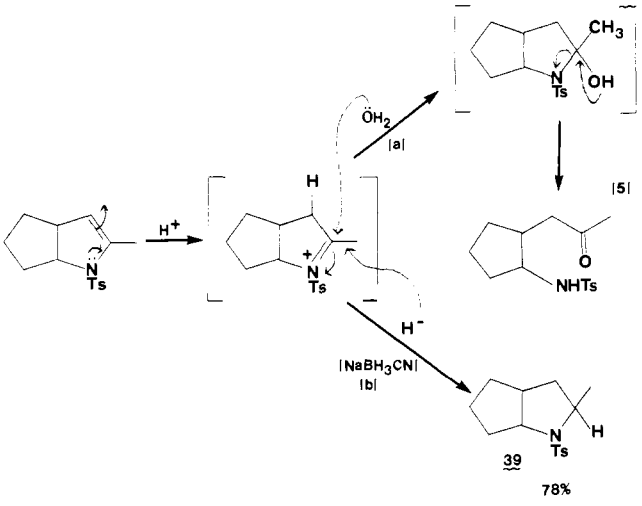
Although these substrates fail to cyclize under the standard catalytic conditions, it is clear that these and other substrates should cyclize provided appropriate conditions are used. This is suggested by the results in eq 3, and work continues along these lines. That this cyclization is sensitive to reaction conditions is further evidenced by the cyclization of 5-tosamido-1-pentene (**24**) under stoichiometric conditions (eq 4), a reaction which produces



24 38 49% (4)

a six-membered ring product exclusively. In contrast, cyclization of this same substrate under catalytic conditions produced the five-membered ring exclusively.

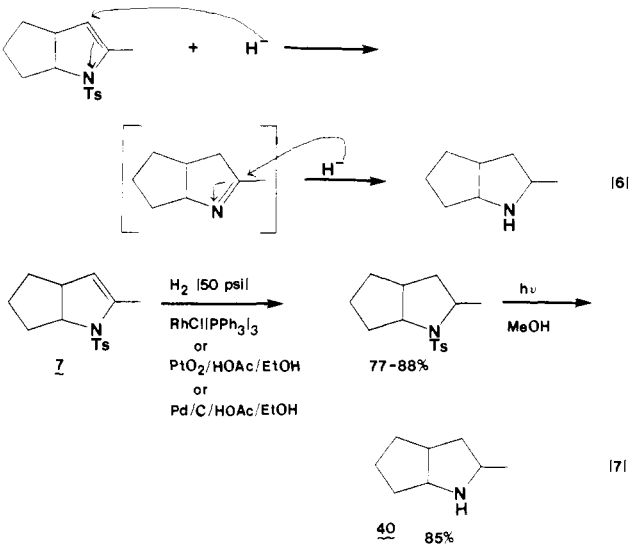
The products from these cyclization, *N*-vinylsulfonamides, are not readily available by standard synthetic methods and their chemistry is relatively unexplored. They are remarkably easy to hydrolyze, converting to the corresponding keto tosamide upon exposure to mild acid or even dry silica gel (eq 5a). They are



39 78%

inert to both sodium borohydride and sodium cyanoborohydride. However, treatment with 1 equiv of trifluoroacetic acid followed by sodium cyanoborohydride results in clean reduction to the saturated tosamide in high yield (eq 5b). Both of these processes are thought to occur by protonation at the 3 position followed by nucleophilic attack at the 2 position. This suggests a general route to the introduction of nucleophilic substituents at the 2 position of these nitrogen heterocycles. This is currently being explored.

Red-al reduces these substrates all the way to the saturated amine in a process thought to involve initial S_N2' displacement of the tosyl group followed by rapid reduction of the thus-formed imine (eq 6). If this is indeed the case, this class of compounds should be generally reactive toward nucleophiles, permitting the introduction of functionality at both the 2 and 3 ring positions. The *N*-vinyltosamide is also reduced under catalytic hydrogenation conditions to produce the saturated tosamide which deprotects under photolytic conditions to give the free amine (eq 7).



40 85%

The chemistry reported above permits the facile synthesis of a number of nonaromatic nitrogen heterocycles from amino olefins. The tosylated enamine intermediates are not readily available by standard synthetic methods and are potentially of use for further functionalization of the heterocyclic system. Applications of this methodology to synthesis are currently being developed.

Experimental Section

Materials. All solvents were freshly distilled and stored under either a nitrogen or an argon atmosphere. Dimethylformamide (DMF) (Baker Analyzed Reagent) was distilled from CaH_2 at 15–20 mmHg. Tetrahydrofuran (THF) (Baker Analyzed Reagent) and diethyl ether (Baker Analyzed Reagent) were distilled from sodium/benzophenone ketyl at atmospheric pressure. Benzene (MCB ACS Reagent thiophene-free) was used without further purification. Dimethyl sulfoxide (Me_2SO) (Baker Analyzed Reagent) was used without further purification. Pyridine (Baker Analyzed Reagent) was distilled from CaH_2 and stored under an argon atmosphere. Allyl bromide, 2-bromotoluene, cyclohexanecarboxaldehyde, lithium acetylide–ethylenediamine complex, diethyl azodicarboxylate, crotyl alcohol, phthalimide, and triphenylphosphine were purchased from Aldrich and used without further purification. Cyclohexene oxide and cyclopentene oxide were purchased from Arapahoe and used without further purification. The olefinic bromides used in the preparation of the acyclic olefinic amines were purchased from PCR Inc. and used without further purification.

General. All melting points are uncorrected. ^1H NMR spectra (60 MHz) were measured using either a Varian Model T-60 or EM-360 spectrometer. Tetramethylsilane was used as the internal standard and all spectra are reported in δ units. Infrared spectra were recorded on a Beckman Acculab 3 spectrophotometer and are reported in cm^{-1}. Medium-pressure liquid chromatography (MPLC) was performed at 10–60 psi (damped system) using Ace Michler columns packed with Woelm Type 260 silica gel unless otherwise noted. Samples of 0.05–1.00 g were run on a 2.2 × 30 cm column and 1.00–4.50 g on a 3.7 × 35 cm column. The products were detected by an ISCO-UA5 detector at 254 nm. Analyses were peformed by Midwest Microanalytical Labs, Indianapolis, Ind.

Preparation of Olefinic Tosamides in Table I. Two general procedures were used to prepare the required olefinic tosamide substrates. **Method A**: The ring opening of an oxirane by a Grignard reagent gave substituted alcohols.[7] These alcohols were then converted with inversion to amines using triphenylphosphine, diethyl azodicarboxylate, and phthalimide in THF.[8] Sulfonamides were then prepared from the amines using the appropriate sulfonyl chloride in pyridine.[9] **Method B**: The reaction of an olefin with *N,N*-dibromo-*p*-toluenesulfonamide gave a 2-bromo-1-sulfonamide.[5] These substrates, when treated with base, gave a *p*-toluenesulfonylazirdine,[5] which could then be treated with an appropriate Grignard reagent to give the desired substrate.[10]

(7) V. Spezialē, M. Armat, and A. Lattes, *J. Heterocycl. Chem.*, **13**, 349 (1976).
(8) O. Mitsunobu, M. Wada, and T. Sano, *J. Am. Chem. Soc.*, **94**, 679 (1972).
(9) K. Onodera, S. Kitaoka, and H. Ochiai, *Bull. Chem. Soc. Jpn.* **27** 156 (1962).

Procedure A. Characterization of Alcohols. ***trans*-2-(2-Propenyl)cyclopentanol**: ^{1}H NMR ($CDCl_3$) δ 1.0–2.4 (m, 9, CH_2), 3.0–3.3 (br, 1, OH), 3.7–4.1 (m, 1, CH–O), 4.8–5.3 (m, 2, $=CH_2$), 5.5–6.2 (m, 1, CH=); IR (neat) 3550–3250 (s, OH), 3100 (s), 3020–2840 (vs), 1650 (m), 1000 (m), 920 (s). From 33.60 g (0.40 mol) of cyclopentene oxide, 47.89 g (0.38 mol, 95% yield) of the product (bp 56 °C) (0.7 mmHg) was obtained as a clear oil.

***trans*-2-(1-Methyl-2-propenyl)cyclopentanol**: ^{1}H NMR ($CDCl_3$) δ 1.0(d, J = 7 Hz, 3, CH_3), 1.5–2.7 (m, 8, CH_2), 3.3–3.8 and 4.3–4.5 (br s, 1, OH), 4.0 (m, 1, CH–O), 4.8–5.3 (m, 2, $C=CH_2$), 5.4–6.2 (m, 1, CH=C); IR (neat) 3550–3100 (s, OH), 3060 (m, CH=), 2960–2840 (s, CH), 1650 (m, C=C), 990 (m, C=C), 900 (m, C=C). From 7.19 g (85.5 mmol) of cyclopentene oxide, 9.46 g (67.4 mmol, 79% yield) of the product (bp 90–100 °C (17 mmHg), a mixture of diastereoisomers, was obtained.

***trans*-2-(2-Propenyl)cyclohexanol**:[7] ^{1}H NMR ($CDCl_3$) δ 0.8–2.1 (m, 10, CH_2), 2.3–2.7 (m, 1, CH), 2.9–3.4 (m, 1, CH–O), 3.5 (s, 1, OH), 4.8–5.3 (m, 2, $=CH_2$), 5.4–6.2 (m, 1, CH=); IR (neat) 3550–3250 (s, OH), 3100 (m, HC=), 2940 (s, CH), 2880 (s, CH), 1650 (m, C=C), 1000 (m, C=C), 910 (s, C=C). From 18.52 g (189 mmol) of cyclohexene oxide, 25.84 g (184 mmol, 98% yield) of the product (bp 86–88 °C/(23 mmHg)), a colorless liquid, was obtained.

***trans*-2-(3-Butenyl)cyclopentanol**: ^{1}H NMR ($CDCl_3$) δ 1.2–2.6 (m, 11, ring CH_2, $CHCH_2CH_2C=$), 3.2–4.4 (m, 2, CHOH), 4.8–5.2 (m, 2, $=CH_2$), 5.5–6.2 (m, 1, HC=); IR (neat) 3600–3200 (s, OH), 3090 (m, HC=), 3000–2840 (s, CH), 1640 (m, C=C), 910 (m, C=C). From 7.16 g (85 mmol) of cyclopentene oxide, 5.97 g (43 mmol, 51% yield) of product (bp 85–95 °C/(0.7 mmHg)) was obtained as a colorless liquid.

1-(1-(2-Propenyl)cyclohexyl)methanol:[11] ^{1}H NMR ($CDCl_3$) δ 1.4 (br s, 10, ring CH_2), 2.10 (d, J = 7.4 Hz, 2, $CH_2C=$), 3.3 (s, 1, OH), 3.3–3.7 (m, 2, CH_2O), 4.8–5.2 (m, 2, $=CH_2$), 5.4–6.2 (m, 1, CH=); IR (neat) 3550–3220 (s, OH), 3080 (m, HC=), 3000–2860 (s, CH), 1640 (m, C=C), 1450 (s, CH), 910 (s, C=C). From 4.32 g (28.4 mmol) of the aldehyde precursor, 2.40 g (16 mmol, 55% yield) of the product (bp 60–120 °C/(1.0 mmHg) was obtained as a colorless liquid.

***trans*-2-Ethynylcyclopentanol** was prepared according to the method of Norton et al.:[12] ^{1}H NMR ($CDCl_3$) δ 1.4–2.3 (m, 6, ring CH_2), 2.1 (d, J = 2.6 Hz, 1, $\equiv$CH), 2.4–2.8 (m, 1, CHC$\equiv$), 3.1 (s, 1, OH), 4.0–4.4 (m, 1, CH–O); IR (neat) 3500–3200 (s, OH), 3000–2880 (s, C–H), 2120 (m, C$\equiv$C). From 15.0 g (178 mmol) of cyclopentene oxide, 14.49 g (132 mmol, 74% yield) of the product (bp 75–83 °C/(7 mmHg)) was obtained as a colorless liquid.

***trans*-2-Ethynylcyclopentanol** (6.98 g, 63.5 mmol) in pyridine (10 mL) was reduced at atmospheric pressure and room temperature with hydrogen gas over a 5% Pd-on-$BaSO_4$ catalyst, over the course of 6 days. Routine isolation gave a colorless liquid, 6.92 g (97% yield): ^{1}H NMR ($CDCl_3$) δ 1.32–2.52 (m, 7, CH_2, CHC=), 3.22 (s, 1, OH), 3.70–4.07 (m, 1, CH–O), 4.80–5.20 (m, 2, $=CH_2$), 5.41–6.05 (m, 1, CH=); IR (neat) 3600–3200 (s, OH), 3050 (m, CH=), 3000–2880 (s, CH), 1640 (m, C=).

Conversion of Trans Alcohols to Cis Amines. The general procedure of Mitsunobu was used to convert the above alcohols to their corresponding amines.[8] An explicit procedure is given below.

Preparation of *cis*-2-(2-Propenyl)cyclopentylamine. Phthalimide (5.89 g, 40 mmol) and triphenylphosphine (10.5 g, 40 mmol) were placed into a 500-mL, 24–40 three-necked round-bottomed flask which was fitted with two rubber serum caps and a 24–40 stopcock. The flask was evacuated and filled with argon several times, and then tetrahydrofuran (200 mL) was added via syringe. The reaction was stirred, and the substrate (5.04 g, 40 mmol) and diethyl azodicarboxylate (6.97 g, 40 mmol) were then added dropwise, simultaneously, to the reaction mixture. As the addition progressed, heat was evolved. Stirring was continued at 25 °C for 3 days, and then the solvent was removed under reduced pressure. The resulting semisolid was dissolved in methanol (200 mL), and hydrazine (95%, 2.4 mL, 80 mmol) was cautiously added. After this addition, the reaction mixture was heated at reflux for 10 h, then cooled to 25 °C. Concentrated HCl (6 mL) was carefully added, and the solution was heated at reflux overnight, and cooled to 25 °C; the solvent was removed under reduced pressure to give a light yellow solid. This was washed with a dilute acid solution (200 mL of water, 7 mL of concentrated HCl) in portions of 50 mL. The combined aqueous layers were suction filtered, and then washed with chloroform (7 × 30 mL) and diethyl ether (3 × 30 mL). The aqueous layer was cooled to 0 °C (ice/water bath) and then made very basic (pH ~13) using a saturated NaOH solution. The resulting two layers were then extracted with diethyl ether (5 × 40 mL). The combined organic solution was then washed with a saturated NaCl solution (4 × 50 mL) and dried ($MgSO_4$). This solution was gravity filtered and the solvent was removed under reduced pressure to yield a dark oil. This oil was Kugelrohr distilled (bp 90–120 °C (1 mmHg)) to give a clear oil, 3.80 g, 76% yield.

***cis*-2-(2-Propenyl)cyclopentylamine**: ^{1}H NMR ($CDCl_3$) δ 0.8 (s, 2, NH_2), 1.3–2.4 (m, 9, CH_2, CH), 3.1–3.4 (m, 1, HC–N), 4.8–5.2 (m, 2, $=CH_2$), 5.4–6.1 (m, 1, HC=); IR (neat) 3440–3260 (m, NH_2), 3010–2880 (vs, CH), 1650 (s, C=C), 920 (vs, C=C).

***cis*-2-(1-Methyl-2-propenyl)cyclopentylamine**: ^{1}H NMR ($CDCl_3$) δ 1.1 (2d, J = 6 Hz, 3, CH_3), 1.4–2.6 (m, 10, NH_2, CH_2, CH), 3.3 (m, 1, CH–N), 4.7–5.2 (m, 2, $=CH_2$), 5.4–6.1 (m, 1, CH=); IR (neat) 3500–3200 (s, NH), 3100 (s, =CH), 3000–2860 (vs, CH), 1690–1550 (m, NH), 1650 (s, C=C), 1000 (s, C=C), 910 (s, C=C). From 3.36 g (24 mmol) of the alcohol, 0.62 g (7.0 mmol, 29% yield) of the product was obtained as a colorless liquid.

***cis*-2-Ethenylcyclopentylamine**: ^{1}H NMR ($CDCl_3$) 1.45–1.95 (m, 8, CH_2, NH_2), 2.25–2.70 (m, 1, CHC=), 3.10–3.45 (m, 1, CH–N), 4.80–5.25 (m, 2, $=CH_2$), 5.50–6.13 (m, 1, CH=); IR (neat) 3400–3250 (m, NH), 3100 (m, CH=), 3000–2880 (s, CH), 1650 (m, C=C), 1650–1570 (m, NH_2), 1000 (m, C=C), 915 (s, C=C). From 4.49 g (40 mmol) of the alcohol, 1.96 g (18 mmol, 44% yield) of the product was obtained as a colorless liquid.

***cis*-2-(2-Propenyl)cyclohexylamine**: ^{1}H NMR ($CDCl_3$) δ 1.0–1.8 (m, 13, CH_2 CH, NH_2), 1.8–2.2 (m, 2, $CH_2C=$), 3.0 (s, 1, CH–N), 4.8–5.2 (m, 2, $C=CH_2$), 5.3–6.1 (m, 1, CH=C); IR (neat) 3420–3200 (w, NH_2), 3100 (m, CH=), 3000–2860 (s, CH), 1650–1560 (m, NH_2), 1640 (m, C=C), 1000 (m, C=C), 910 (s, C=C). From 5.61 g (40 mmol) of the alcohol, 2.81 g (20 mmol, 50% yield) of the product was obtained as a colorless liquid.

1-(1-(2-Propenyl)cyclohexyl)methylamine. The starting alcohol was obtained by sodium borohydride reduction of the corresponding aldehyde:[11] ^{1}H NMR ($CDCl_3$) δ 1.4 (m, 12, CH_2, NH_2), 2.16 (d, J = 7 Hz, 2, $CH_2C=$), 2.5 (s, 2, CH_2–N), 4.8–5.2 (m, 2, $=CH_2$), 5.4–6.1 (m, 1, CH=C); IR (neat) 3600–3400 (w, NH_2), 3100 (m, CH=), 3000–2860 (s, CH), 1650–1560 (m, NH), 1640 (m, C=C), 1000 (m, C=), 910 (s, C=C). From 2.40 g (15.6 mmol) of the alcohol, 1.26 g, (18.2 mmol, 52% yield) of the product was obtained as a colorless liquid.

***cis*-2-(3-Butenyl)cyclopentylamine**: ^{1}H NMR ($CDCl_3$) δ 1.0–2.0 (m, 11, CH_2, $CHCH_2$, NH), 2.0–2.4 (m, 2, $CH_2C=$), 3.4 (m, 1, CHN), 4.8–5.3 (m, 2, =CH), 5.6–6.3 (m, 1, CH=); IR (neat) 3420–3280 (m, NH_2), 3100 (m, CH=), 3020–2840 (s, CH), 1660–1570 (m, NH), 1650 (m, C=C), 1000 (m, C=C), 910 (s, C=C). From 5.97 g (43 mmol) of the alcohol, 2.23 g (16 mmol, 37% yield) of the product was obtained as a colorless liquid.

2-(2-Propenyl)benzylamine: ^{1}H NMR ($CDCl_3$) δ 1.60 (br s, 2, NH_2), 3.41 (d of t, J_1 = 6 Hz, J_2 = 1.9 Hz, 2, $CH_2C=$), 3.81 (s, 2, CH_2N), 4.72–5.13 (m, 2, $CH_2=$), 5.60–6.27 (m, 1, CH=), 7.03–7.23 (m, 4, ArH); IR (neat) 3400–3260 (m, NH_2), 3080 (m, CH=), 3020 (m, CH=), 3000–2840 (m, CH), 1640 (m, C=C), 1640–1580 (m, NH), 995 (m, C=C), 910 (s, C=C), 750 (s, Ar). From 0.83 g (4.43 mmol) of 2-bromobenzylamine, 0.35 g (2.35 mmol, 53% yield) of the product, a colorless liquid, was obtained by the procedure of Hegedus et al.[13]

Preparation of Sulfonamides. The sulfonamides of the above amines were prepared by the reaction of the amine with the appropriate sulfonyl chloride in pyridine.[9]

Characterization of Tosamides. ***cis*-1-*N*-Tosyl-2-(2-propenyl)cyclopentylamine (6)**: ^{1}H NMR ($CDCl_3$) δ 1.0–2.3 (m, 9, CH_2, CH_2), 2.41 (s, 3, CH_3), 3.4–3.8 (m, 1, CHN), 4.7–5.1 (m, 3, $=CH_2$, NH), 5.2–6.1 (m, 1, CH=), 7.25 (d, J = 8 Hz, 2, ArH), 7.8 (d, J = 8 Hz, 2, ArH); IR (CCl_4) 3320–3200 (vs, NH), 3080–3050 (m, ArH, =CH), 2960–2860 (s, CH), 1655–1560 (m, NH), 1645 (m, C=C), 1010 (s, C=C), 910 (s, C=C). From 4.00 g (32 mmol) of the amine, 6.16 g (22 mmol, 69% yield) of the product (white solid, mp 110–110.5 °C) was obtained.

***cis*-1-*N*-Tosyl-2-(1-methyl-2-propenyl)cyclopentylamine (12)**: ^{1}H NMR ($CDCl_3$) δ 1.0 (d, J = 6 Hz, 3, CH_3), 1.2–1.9 (m, 7, CH_2, CH), 1.9–2.5 (m, 1, CH), 2.5 (s, 3, $ArCH_3$), 3.5–3.9 (m, 1, CHN), 4.6–5.2 (m, 3, $=CH_2$, NH), 5.3–6.0 (m, 1, CH=), 7.3 (d, J = 8 Hz, 2, ArH), 7.8 (d, 2, ArH); IR (KBr) 3260 (s, NH), 3080 (w, ArH), 2980–2850 (s, CH), 1650 (w, C=C), 1600 (m, Ar), 1500 (m, Ar), 1330 (s, SO_2), 1150 (s, SO_2), 800. From 0.89 g (6.4 mmol) of the amine, 0.63 g (2.13 mmol, 33% yield) of the product, a white solid (mixture of diastereoisomers), was obtained.

(10) A. P. Kozikowski, H. Ishida, and K. Isobe, *J. Org. Chem.*, **44**, 2788 (1979).

(11) This material was obtained by modified $NaBH_4$ reduction in EtOH: "Sodium Borohydride" booklet, Thiokol Ventrol Division, p 6. The parent aldehyde was synthesized by the method of P. Groenewegen, H. Kallenberg, and A. van de Gen, *Tetrahedron Lett.*, 491 (1978).

(12) T. F. Murray, V. Varma, and J. R. Norton, *J. Chem. Soc., Chem. Commun.*, 907 (1976).

(13) L. S. Hegedus, G. F. Allen, J. J. Bozell, and E. Waterman, *J. Am. Chem. Soc.*, **100**, 5800 (1978).

***cis*-1-*N*-Tosyl-2-ethenylcyclopentylamine (14)**: ^{1}H NMR ($CDCl_3$) δ 1.5–1.9 (m, 6, CH_2), 2.3–2.5 (m, 1, CHC=), 2.4 (s, 3, $ArCH_3$), 3.5–3.7 (m, 1, CHN), 4.5–5.3 (m, 3, $=CH_2$, NH), 5.4–6.0 (m, 1, CH=), 7.4 (d, J = 8 Hz, 2, ArH), 7.8 (d, J = 8 Hz, 2, ArH); IR (KBr) 3280 (s, NH), 3120–3060 (w, CH=), 3000–2900 (m, CH), 1650 (w, C=C), 1610 (m, Ar), 1500 (m, Ar), 1330 (s, SO_2), 1160 (s, SO_2), 820 (m). From 4.0 g (36.0 mmol) of the amine, 7.26 g (27.4 mmol, 76% yield) of the product, a white solid (mp 96–97 °C) was obtained.

***cis*-1-*N*-Tosyl-2-(2-propenyl)cyclohexylamine (16)**: ^{1}H NMR ($CDCl_3$) δ 1.0–1.7 (m, 9, CH_2, CH), 1.8–2.2 (m, 2, CH_2), 2.4 (s, 3, $ArCH_3$), 3.3–3.7 (m, 1, CHN), 4.7–5.1 (m, 2, $=CH_2$), 5.3–6.0 (m, 2, NHCH=), 7.3 (d, J = 8 Hz, 2, ArH), 7.9 (d, J = 8 Hz, 2, ArH); IR (KBr) 3300 (s, NH), 3090 (w, HC=), 3000–2880 (s, CH), 1650 (w, C=C), 1610 (m, Ar), 1500 (w, Ar), 1340 (s, SO_2), 1170 (s, SO_2), 1000 (s), 910 (s, C=C), 820 (s). From 0.28 g (2.0 mmol) of the amine, 0.46 g (1.6 mmol, 80% yield) of the product (white solid, mp 141–142 °C) was obtained.

***N*-Tosyl-(1-(2-propenyl)cyclohexyl)methylamine (22)**: ^{1}H NMR ($CDCl_3$) 1.4 (s, 10, CH_2), 2.1 (d, J = 7 Hz, 2, CH_2C=), 2.4 (s, 3, $ArCH_3$), 2.8 (d, J = 6.4 Hz, 2, CH_2N), 4.58 (t, J = 6.4 Hz, 1, NH), 4.8–5.2 (m, 2, $=CH_2$), 5.4–6.1 (m, 1, CH=), 7.3 (d, J = 8 Hz, 2, ArH), 7.7 (d, J = 8 Hz, 2, ArH); IR (KBr) 3280 (s, NH), 3080 (w, HC=), 3000–2860 (s, CH), 1640 (w, C=C), 1600 (w, Ar), 1500 (w, Ar), 1330 (s, SO_2), 1160 (s, SO_2), 1010 (w, C=C), 910 (m, C=C). From 1.26 g (8.20 mmol) of the amine, 1.21 g (3.90 mmol, 48% yield) of the product (white solid, mp 69–70 °C) was obtained.

***cis*-1-*N*-Methanesulfonyl-2-(2-propenyl)cyclopentylamine (8)**: ^{1}H NMR ($CDCl_3$) δ 1.5–2.5 (m, 9, CH_2, CH), 2.9 (s, 3, SO_2CH_3), 3.6–4.0 (m, 1, CHN), 4.7–5.2 (m, 3, $=CH_2$, NH), 5.4–6.1 (m, 1, CH=); IR (KBr) 3270 (s, NH), 3080 (w, CH=), 3020 (w, ArH), 3000–2880 (s, CH), 1640 (m, C=C), 1300 (vs, SO_2), 1150 (s, SO_2), 910 (s, C=C), 760 (s). From 0.50 g (4.00 mmol) of the amine, 0.23 g (1.13 mmol, 29% yield) of the product (white solid, mp 69–70 °C) was obtained.

***cis*-1-*N*-Benzylsulfonyl-2-(2-propenyl)cyclopentylamine (10)**: ^{1}H NMR ($CDCl_3$) δ 1.3–2.4 (m, 9, CH_2, CH), 3.5–3.9 (m, 1, CHN), 4.1–4.3 (br, 1, NH), 4.2 (s, 2, CH_2SO_2), 4.8–5.2 (m, 3, C=CH_2, NH), 5.4–6.2 (m, 1, CH=), 7.4 (s, 5, ArH); IR (KBr) 3320 (s, NH), 3110–3060 (w, CH=), 3000–2800 (m, CH), 1650 (w, C=C), 1310 (s, SO_2), 1120 (s, SO_2), 1010 (w, C=C), 880 (m, C=C), 700 (s). From 1.00 g (8.00 mmol) of the amine, 0.73 g (2.60 mmol, 32% yield) of the product (white plates, mp 132–132.5 °C) was obtained.

***cis*-1-*N*-Tosyl-2-(3-butenyl)cyclopentylamine (31)**: ^{1}H NMR ($CDCl_3$) δ 1.2–2.4 (m, 11, CH_2, $CHCH_2CH_2$), 2.5 (s, 3, $ArCH_3$), 3.5–3.8 (m, 1, CHN), 4.7–5.3 (m, 3, $=CH_2$, NH), 5.4–6.2 (m, 1, CH=), 7.2 (d, J = 8 Hz, 2, ArH), 7.7 (d, J = 8 Hz, 2, ArH); IR (KBr) 3280 (s, NH), 3080 (w, HC=), 1640 (w, C=C), 1160 (s, SO_2). From 1.00 g (7.20 mmol) of the amine, 0.85 g (2.90 mmol, 40% yield) of the product (white solid, mp 142–143 °C) was obtained. Anal: ($C_{16}H_{23}NO_2S$) C, H, N.

Procedure B. General Procedure for the Formation of Olefinic Tosamides from *N*-Tosylaziridine. The reaction of an olefin with *N*,*N*-dibromo-*p*-toluenesulfonamide gave a 2-bromo-1-sulfonamide.[9] These substrates, when treated with base, gave a *p*-toluenensulfonylaziridine,[9] which could then be treated with an appropriate Grignard reagent to give the desired substrate.[10]

Characterization of 2-Bromo-1-tosamides. 1-*N*-Tosylamino-1-phenyl-2-bromoethane: ^{1}H NMR ($CDCl_3$) δ 2.4 (s, 3, CH_3), 3.6 (d, J = 6 Hz, 2, CH_2Br), 4.6 (q, J = 6 Hz, 1, CH), 5.2–5.4 (m, 1, NH), 7.2 (m, 7, ArH), 7.6 (d, J = 8 Hz, 2, ArH); IR (KBr) 3280 (vs, NH), 3060 (m, =CH), 1610 (m, Ar), 1170 (s, SO), 660 (s). From 11.5 g (67 mmol) of the tosamide, 12.75 g (36 mmol, 54% yield) of the product (white solid, mp 168–170 °C; lit.[9] 167 °C) was obtained.

***trans*-1-*N*-Benzenesulfonylamino-2-bromocyclohexane.** This material was prepared according to the procedure of Ueno et al.[14] and used without further purification to make the *N*-benzenesulfonylaziridine.

***trans*-1-*N*-Tosylamino-2-bromocyclopentane**: ^{1}H NMR ($CDCl_3$) δ 1.2–2.4 (m, 6, CH_2), 2.4 (s, 3, $ArCH_3$), 3.6–3.9 (m, 1, CHN), 4.0–4.3 (m, 1, CHBr), 5.7 (d, J = 6 Hz, 1, NH), 7.3 (d, J = 8 Hz, 2, ArH), 7.8 (d, J = 8 Hz, 2, ArH); IR (neat) 3360–3240 (s, NH), 3080 (w, CH=), 3000–2880 (s, CH), 1600 (m, Ar), 1500 (m, Ar), 1160 (s, SO_2). This material was used without further purification to make the *N*-tosylaziridine.

Characterization of *N*-Tosylaziridines. *N*-Benzenesulfonyl-7-azabicyclo[4.1.0]heptane: ^{1}H NMR ($CDCl_3$) δ 1.10–1.47 (m, 4, CH_2), 1.47–1.95 (br s, 4, CH_2CHN), 3.0 (br s, 2, CHN), 7.4–7.6 (m, 3, ArH), 7.78–8.0 (m, 2, ArH); IR (neat) 3080 (w, ArH), 3020 (w, ArH), 2980–2870 (s, CH), 1320 (vs, SO_2), 1170 (vs, SO_2). From 3.62 g (11.4 mmol) of *trans*-*N*-benzenesulfonyl-2-bromocyclohexane, 1.91 g (8.1 mmol, 75% yield) of the product, a clear liquid, was obtained.

***N*-Tosyl-2-phenylaziridine**: ^{1}H NMR ($CDCl_3$) δ 2.3 (d, J = 8 Hz, 1, CH cis to Ph), 2.4 (s, 3, CH_3), 2.9 (d, J = 8 Hz, 1, CH trans to Ph), 3.8 (d of d, J = 7.6 Hz, J = 8 Hz, 1, CHAr), 7.2 (s, 5, ArH), 7.3 (d, 2, ArH), 7.9 (d, J = 8 Hz, 2, ArH; IR ($CHCl_3$) 1495 (m, Ar), 1320 (s, SO_2), 1160 (s, SO_2), 900 (s). From 6.10 g (17 mmol) of the 1-*N*-tosyl-1-phenyl-2-bromomethane, 4.36 g (16 mmol, 96% yield) of the product (white solid, mp 90–91 °C) was obtained.

***N*-Tosyl-6-azabicyclo[3.1.0]hexane**: ^{1}H NMR ($CDCl_3$) 1.4–2.4 (m, 6, CH_2), 2.4 (s, 3, $ArCH_3$), 3.4 (s, 2, CHNCH), 7.3 (d, J = 8 Hz, 2, ArH), 7.7 (d, J = 8 Hz, 2, ArH); IR (neat) 3080–2860 (s, C–H), 1600 (s, Ar), 1500 (s, Ar). From 13.79 g (43 mmol) of *trans*-1-*N*-tosyl-2-bromocyclopentane, 7.12 g (30 mmol, 70% yield) of the product (light yellow oil) was prepared.

Reaction of *N*-Tosylaziridines with Grignard Reagents. *trans*-1-*N*-Benzenesulfonyl-2-(2-propenyl)cyclohexylamine (18): ^{1}H NMR ($CDCl_3$) δ 0.95–2.05 (m, 10, CH_2), 2.20–3.20 (m, 2, CHN, CH), 4.65–5.95 (m, 4, CH=, CH_2=, NH), 7.35–7.55 (m, 3, ArH), 7.75–7.97 (m, 2, ArH); IR (KBr) 3280 (s, NH), 3090 (w, HC=), 2960–2860 (s, CH), 1640 (w, C=C), 1450 (s), 1320 (s, SO_2), 1170 (s, SO_2). From 5.59 g (23.0 mmol) of the aziridine, 4.37 g (15.6 mmol, 70% yield) of the product (white solid, mp 104–105.5 °C) was obtained. Anal: ($C_{15}H_{21}NO_2S$) C, H, N.

N-Tosyl-2-phenyl-4-pentenylamine (26): ^{1}H NMR ($CDCl_3$) δ 2.2–3.5 (m, 5, CH_2, CH), 2.4 (s, 3, CH_3), 4.7–5.1 (m, 3, C=CH_2, NH), 5.2–6.0 (m, 1, HC=), 6.8–7.3 (m, 7, ArH), 7.6 (d, J = 7.6 Hz, 2, ArH); IR (KBr) 3300 (s, NH), 3100–2900 (w, CH), 1640 (w, C=C), 1320 (s, SO_2), 1150 (s, SO_2), 910 (m, C=C). From 4.00 g (14.6 mmol) of the aziridine, 4.27 g (13.5 mmol, 93% yield) of the product (white solid, mp 62–64 °C) was obtained.

***N*-Tosyl-2-phenyl-3-methyl-4-pentenylamine (28)**: ^{1}H NMR ($CDCl_3$) δ 0.6 (d, J = 6 Hz, 3, allyl CH_3), 0.8 (d, J = 6 Hz, 3, allyl CH_3), 2.3 (s, 6, $ArCH_3$ from both diastereomers), 2.3–3.6 (m, 8, $CHCH_2N$, CHC=, both diastereomers), 4.2–5.9 (m, 8, CH=CH_2, NH, both diastereomers), 6.6–7.3 (m, 4, ArH ortho to CH_3, both diastereomers), 7.5–7.7 (d's, J = 8 Hz, 4, ArH ortho to SO_2, both diastereomers); IR ($CHCl_3$) 3400–3240 (s, NH), 3100–2800 (s, CH), 1650 (m, C=C), 1610 (s, Ar), 1510 (s, Ar), 1340 (vs, SO_2), 1170 (vs, SO_2), 920 (s, C=C). From 1.75 g (6.40 mmol) of the aziridine, 2.11 g (6.40 mmol, ~100% yield) of the product, a mixture of diastereomers (~60:40), was obtained.

***trans*-1-*N*-Tosyl-2-(2-propenyl)cyclopentylamine (30)**: ^{1}H NMR ($CDCl_3$) δ 1.1–2.4 (m, 9, CH_2, $CHCH_2C$=), 2.4 (s, 3, $ArCH_3$), 3.25 (t, J = 7 Hz, 1, CHN), 4.8–5.3 (m, 3, H_2C=, NH), 5.3–6.1 (m, 1, CH=), 7.3 (d, J = 8 Hz, 2, ArH), 7.8 (d, J = 8 Hz, 2, ArH); IR (neat) 3320–3220 (s, NH), 3080 (m, HC=), 3000–2880 (s, CH), 1650 (m, C=C), 1600 (m, Ar), 1500 (m, Ar), 1160 (s, SO_2), 810 (s). From 2.55 g (10.7 mmol) of the aziridine, 2.11 g (7.55 mmol, 70% yield) of the product (light yellow solid, mp 62–63 °C) was obtained. Anal: ($C_{15}H_{21}NO_2S$) C, H, N.

***trans*-2-*N*-Tosyl-2-(3-butenyl)cyclopentylamine (32)**: ^{1}H NMR ($CDCl_3$) 0.8–2.0 (m, 11, CH_2, $CHCH_2CH_2C$=), 2.45 (s, 3, $ArCH_3$), 3.0–3.4 (m, 1, CHN), 4.7–5.3 (m, 3, $=CH_2$, NH), 5.4–6.0 (m, 1, CH=), 7.3 (d, J = 8 Hz, 2, ArH), 7.8 (d, J = 8 Hz, 2, ArH); IR (neat) 3340–3220 (s, NH), 3080 (w, HC=), 3000–2860 (s, CH), 1640 (m, C=C), 1600 (m, Ar), 1500 (m, Ar), 1160 (s, SO_2), 910 (s, C=C). From 0.43 g (1.83 mmol) of the aziridine, 0.14 g (0.47 mmol, 26% yield) of the product (white solid, MP 62–63 °C was formed. Anal.: ($C_{16}H_{23}NO_2S$) C, H, N.

***N*-Tosyl-2-phenyl-5-hexenylamine (33)**: ^{1}H NMR ($CDCl_3$) 1.5–1.9 (m, 4, CH_2CH_2C=), 2.4–3.5 (m, 3, CH_2N, ArCH), 4.4 (m, 1, NH), 4.6–5.1 (m, 2, $=CH_2$), 5.3–6.0 (m, 1, CH=), 6.9–7.4 (m, 7, ArH), 7.7 (d, J = 8 Hz, 2, ArH); IR (neat) 3380–3200 (s, NH), 1640 (m, C=C), 1600 (s, Ar), 1500 (s, Ar), 1160 (s, SO_2), 910 (s, C=C). A mixture of two products (0.279 g, 0.85 mmol) was obtained from 0.50 g (1.83 mmol) of the aziridine. This material was used without further purification.

1-*N*-Tosyl-4-pentenylamine (24): ^{1}H NMR ($CDCl_3$) δ 1.6 (m, 2, CH_2CN), 2.0 (m, 2, CH_2C=), 2.4 (s, 3, $ArCH_3$), 2.9 (q, J = 6.2 Hz, 2, CH_2N), 4.7–6.0 (m, 4, CH=CH_2, NH), 7.3 (d, J = 8 Hz, 2, ArH), 7.8 (d, J = 8 Hz, 2, ArH); IR ($CHCl_3$) 3360–3240 (s, NH), 3080 (w, CH=), 3000–2880 (m, CH), 1650 (m, C=C), 1600 (m, Ar), 1500 (m, Ar), 1330 (s, SO_2), 920 (m, C=C). From 1.00 g (8.80 mmol) of the amine, 2.02 g (8.40 mmol, 96% yield) of the product (colorless oil) was obtained.

1-*N*-Tosyl-5-hexenylamine (34): ^{1}H NMR ($CDCl_3$) δ 1.3–1.7 (m, 4, CH_2CH_2CC=), 1.8–2.2 (m, 2, CH_2C=), 2.5 (s, 3, $ArCH_3$), 3.00 (q, J = 6 Hz, 2, CH_2N), 4.7–5.2 (m, 2, $=CH_2$), 5.2–6.1 (m, 2, CH=, NH), 7.3 (d, J = 8 Hz, 2, ArH), 7.8 (d, J = 8 Hz, 2, ArH); IR (neat) 3380–3220 (s, NH), 3080 (m, CH=), 3000–2860 (s, CH), 1650 (m, C=C), 1610 (m, Ar), 1500 (m, Ar), 1170 (s, SO_2), 910 (s, C=C), 820

(14) Y. Ueno, S. Takemura, Y. Ando, and H. Terauchi, *Chem. Pharm. Bull.*, **15**, 1193 (1967).

(15) J. B. Hendrickson and R. Bergeron, *Tetrahedron Lett.*, 345 (1970).

(s). From 0.60 g (3.7 mmol) of 1-bromo-5-hexene, 0.50 g (2.00 mmol, 54% yield) of the product (yellow oil) was obtained. Anal: ($C_{13}H_{19}NO_2S$) C, H, N.

1-*N*-Tosyl-4-butenylamine (35): ^{1}H NMR ($CDCl_3$) δ 2.20 (q, J = 7 Hz, 2, CH_2C=), 2.40 (s, 3, $ArCH_3$), 2.98 (q, J = 6.4 Hz, 2, CH_2N), 4.75–5.98 (m, 4, CH=, CH_2=, NH), 7.20 (d, J = 8 Hz, 2, ArH), 7.75 (d, J = 8 Hz, 2, ArH); IR (neat) 3400–3200 (s, NH), 3080 (m, CH=), 3000–2880 (s, CH), 1650 (m, C=C), 1600 (m, Ar), 1500 (m, Ar), 1370–1300 (s, SO_2), 1170–1140 (s, SO_2). From 0.50 g (3.70 mmol) of 1-bromo-3-butene, 0.26 g (1.14 mmol, 31% yield) of the product (yellow oil) was obtained. Anal. ($C_{11}H_{15}NO_2S$) C, H, N.

***N*-Tosyl-2-(2-propenyl)benzylamine (20).** This was prepared from *o*-allylbenzylamine[13] under standard tosylation conditions: ^{1}H NMR ($CDCl_3$) δ 2.5 (s, 3, $ArCH_3$), 3.3 (d of t, J_1 = 6 Hz, J_2 = 2 Hz, CH_2C=), 4.1 (d, J = 5 Hz, 2, CH_2N), 4.6–5.2 (m, 3, =CH_2, NH), 5.5–6.2 (m, 1, CH=), 7.18 (s, 4, ArH), 7.3 (d, J = 8 Hz, 2, ArH), 7.7 (d, J = 8 Hz, 2, ArH); IR ($CHCl_3$) 3270 (m, NH), 3000–2840 (s, CH–ArH), 1640 (w, C=C), 1600 (w, Ar), 1330 (m, SO_2), 1160 (s, SO_2), 900 (m, C=C). From 0.70 g (4.75 mmol) of the amine, 0.94 g (3.13 mmol, 66% yield of the product (white solid, mp 70–71.5 °C) was obtained.

***cis*- and *trans*-1-*N*-Tosyl-(2-propenyl)cyclohexylmethylamine[16] (37)**: ^{1}H NMR ($CDCl_3$) δ 1.3–2.2 (m, 13, CH_2, $CHCH_2C$=), 2.4 (s, 3, $ArCH_3$), 2.85 (t, J = 6 Hz, 2, CH_2N), 4.7–6.0 (m, 4, CH=CH_2, NH), 7.3 (d, J = 8 Hz, 2, ArH), 7.7 (d, J = 8 Hz, 2, ArH); IR (neat) 3340–3200 (s, NH), 3080 (m, HC=), 2980–2850 (s, CH), 1650 (m, C=C), 1610 (m, Ar), 1500 (m, Ar), 1180 (s, SO_2), 1100 (m), 810 (m). This material was used without further purification. From 1.45 g (9.50 mmol) of the amine, 1.09 g (3.52 mmol, 37% yield) of the product (light yellow oil) was obtained.

***N*-Tosyl-(1-(3-methyl-2-propenyl)cyclohexyl)methylamine (36)**: ^{1}H NMR ($CDCl_3$) δ 1.40 (br s, 10, CH_2), 1.55–1.75 (m, 3, CH_3C=), 1.85–2.18 (m, 2, CH_2C=), 2.52 (s, 3, $ArCH_3$), 2.83 (d, J = 6.4 Hz, 2, CH_2N), 4.52–4.85 (m, 1, NH), 5.25–5.58 (m, 2, CH=), 7.3 (d, J = 8 Hz, 2, ArH), 7.78 (d, J= 8 Hz, 2, ArH); IR (KBr) 3300 (s, NH), 3050 (w, CH=), 3000–2880 (s, CH), 1650 (w, C=C), 1600 (m, Ar), 1330 (s, SO_2), 1160 (s, SO_2). From 0.81 g (4.80 mmol) of the amine, 0.84 g (2.61 mmol, 54% yield) of the product (white solid, mp 94–95.5 °C) was obtained. Anal: ($C_{18}H_{27}NO_2S$) C, H, N.

General Procedure for the Small-Scale Catalytic Cyclization of Olefinic Sulfonamides Using Benzoquinone as the Reoxidant. A 50-mL, one-necked with side arm, 14–20 round-bottomed flask was fitted with a reflux condenser and a rubber serum cap. The substrate (150 to 300 mg, 0.50 to 1.00 mmol), $PdCl_2$·$2CH_3CN$ (13 to 26 mg, 10 mol %), lithium chloride (2 equiv), benzoquinone (1 equiv, 54–108 mg), and sodium carbonate (2 equiv, 53–106 mg) were placed into the flask, and tetrahydrofuran (20 mL/mmol of substrate) was added. The reaction was then heated at reflux for 24 to 48 h while being monitored by thin layer chromatography (4:1:1 hexane/chloroform/ethyl acetate). Upon disappearance of starting material, the reaction was cooled to 25 °C, and ethyl acetate (15–25 mL) was added. The resulting solution was washed with 1:1 1% sodium hydroxide/saturated sodium chloride (until the aqueous layer was clear). It was then washed with saturated sodium chloride solution (2 × 20 mL) and dried over $MgSO_4$. Removal of solvent under vacuum followed by injection onto a solvent-saturated 1C column and elution gave pure material.

Large-Scale Catalytic Cyclization of 1-*N*-Tosyl-2-(2-propenyl)cyclopentylamine (6). The same procedure used in the small-scale cyclization reaction was applied to the larger scale reactions, with the following modifications. The substrate (**6**), 1.00 g (3.58 mmol) to 4.50 g (16.0 mmol), $PdCl_2$·$2CH_3CN$ (10 mol%), benzoquinone (1.0 equiv), sodium carbonate (2.0 equiv), and lithium chloride (5.0 equiv) were placed into a suitable round-bottomed flask (generally a 250-mL, 24–40 one-necked flask), and tetrahydrofuran (100–125 mL) was added. The mixture was then heated to reflux. The reaction was complete in 4–6 h. Purification (Silica gel, 4:1 hexane/ethyl acetate) gave a white, crystalline product in 84–86% yield.

***cis*-*N*-Tosyl-3-methyl-2-azabicyclo[3.3.0]oct-3-ene (7)**: ^{1}H NMR ($CDCl_3$) δ 1.40–2.00 (m, 6, CH_2), 2.10 (m, 3, CH_3C=), 2.40 (s, 3, $ArCH_3$), 2.80–3.20 (m, 1, CHC=), 4.20–4.50 (m, 1, CHN), 4.70 (m, 1, CH=), 7.30 (d, J = 8 Hz, 2, ArH), 7.70 (d, J = 8 Hz, 2, ArH); IR (KBr) 3000–2900 (s, ArH, CH), 1600 (m, C=C), 1595 (m, Ar), 1490 (m, Ar), 1350 (vs, SO_2), 1160 (vs, SO_2), 960 (s), 710 (vs). From 2.00 g (7.16 mmol) of substrate, 1.72 g (6.20 mmol, 86% yield) of the product (white solid, mp 92–93 °C) was obtained. Anal: ($C_{15}H_{19}NO_2S$) C, H, N, S.

***cis*-*N*-Methanesulfonyl-3-methyl-2-azabicyclo[3.3.0]oct-3-ene (9)**: ^{1}H NMR ($CDCl_3$) δ 1.50–1.90(m, 6, CH_2), 2.00 (m, 3, CH_3), 2.90 (s, 3, SO_2CH_3), 3.25–3.55 (m, 1, CHC=), 4.33–4.65(m, 1, CHN), 4.83 (m, 1, CH=); IR (KBr) 3000–2920 (m, CH), 2880 (w, CH), 1670 (w, C=C), 1340 (s, SO_2), 1160 (s, SO_2), 770 (m). From 0.11 g (0.50 mmol) of substrate, 0.60 g (0.32 mmol, 63% yield) of the product (white solid, mp 39–41 °C) was obtained. Anal: ($C_9H_{15}NO_2S$) C, H, N.

***cis*-*N*-Benzylsulfonyl-3-methyl-2-azabicyclo[3.3.0]oct-3-ene (11)**: ^{1}H NMR ($CDCl_3$) δ 1.40–2.00 (m, 6, CH_2), 1.80 (m, 3, CH_3C=), 3.0–3.3 (m, 1, CHC=), 3.90–4.20 (m, 1, CHN), 4.20 (s, 2, SO_2CH_2), 4.60 (br s, 1, HC=), 7.30 (s, 5, ArH); IR (KBr) 3090 (w, CH=), 3000–2940 (m, CH), 2880 (m, CH), 1675 (m, C=C), 1350 (s, SO_2), 1160 (s, SO_2), 790 (m), 700 (s). From 0.14 g (0.50 mmol) of substrate, 0.11 g (0.38 mmol, 76% yield) of the product (white solid, mp 81–82 °C) was obtained. Anal: ($C_{15}H_{19}NO_2S$) C, H, N.

***cis*-*N*-Tosyl-3,4-dimethyl-2-azabicyclo[3.3.0]oct-3-ene (13)**: ^{1}H NMR ($CDCl_3$) δ 1.3–1.7 (m, 9, CH_2, CH_3), 2.0 (s, 3, CH_3–C–N), 2.5 (s, 3, $ArCH_3$), 2.6–3.1 (m, 1, CHC=), 4.1–4.5 (m, 1, CHN), 7.3 (d, J = 8 Hz, 2, ArH), 7.7 (d, J = 8 Hz, 2, ArH); IR ($CDCl_3$) 3000–2880 (s, CH, ArH), 1610 (m, Ar), 1500 (m, Ar), 1350 (s, SO_2), 1120 (s, SO_2), 915 (s), 810 (s). From 0.16 g (0.55 mmol) of the substrate, 0.13 g (0.45 mmol, 82% yield) of the product (white solid, mp 76–77 °C) was obtained. Anal: ($C_{16}H_{21}NO_2S$) C, H, N.

***cis*-*N*-Tosyl-2-azabicyclo[3.3.0]oct-3-ene (15)**: ^{1}H NMR ($CDCl_3$) δ 1.42–2.32 (m, 6, CH_2), 2.40 (s, 3, $ArCH_3$), 3.00–3.30 (br, 1, CHC=), 3.82–4.18 (m, 1, CHN), 4.85 (d of d, J_1 = 4 Hz, J_2 = 4 Hz, 1, CHC=), 6.21 (d of d, J_1 = 4 Hz, J_2 = 4 Hz, 1, NCH=), 7.20 (d, J = 8 Hz, 2, ArH), 7.60 (d, J = 8 Hz, 2, ArH); IR (KBr) 3000–2880 (m, CH), 1640 (w, C=C), 1600 (w, Ar), 1500 (w, Ar), 1340 (s, SO_2), 1170 (s, SO_2). From 0.16 g (0.60 mmol) of the substrate, 0.09 g (0.34 mmol, 57% yield) of the product (white solid, mp 109–110.5 °C) was obtained. Anal: ($C_{14}H_{17}NO_2S$) C, H, N.

***cis*-*N*-Tosyl-3-methyl-2-azabicyclo[4.3.0]non-3-ene (17)**: ^{1}H NMR ($CDCl_3$) δ 1.21–2.00 (m, 8, CH_2), 2.11 (m, 3, CH_3), 2.35–2.62 (br, 1, CHC=), 2.45 (s, 3, $ArCH_3$), 3.80–4.20 (m, 1, CHN), 4.35 (m, 1, CH=), 7.22 (d, J = 8 Hz, 2, ArH), 7.70 (d, J = 8 Hz, 2, ArH); IR (KBr) 2990–2900 (s), 2860 (m), 1650 (m, C=C), 1600 (m, Ar), 1500 (m, Ar), 1340 (s, SO_2), 1160 (s, SO_2), 660(s). From 0.20 g (0.68 mmol) of the substrate, 0.10 g (0.34 mmol, 48% yield) of the product was obtained. Anal: ($C_{16}H_{21}NO_2S$) C, H, N.

***N*-Tosyl-2-methyl-Δ^2-pyrroline (25)**: ^{1}H NMR ($CDCl_3$) δ 2.0 (m, 3, =CCH_3), 2.0–2.5 (br m, 2, CH_2C=), 2.5 (s, 3, $ArCH_3$), 3.6–4.0 (m, 2, CH_2N), 4.9 (m, 1, CH=), 7.3 (d, J = 8 Hz, 2, ArH), 7.7 (d, J = 8 Hz, 2, ArH); IR ($CDCl_3$) 3000–2940 (m, CH, ArH), 1660 (m, C=C), 1600 (m, Ar), 1500 (m, Ar), 1360 (s, SO_2), 1170 (s, SO_2), 820 (m). From 0.09 g (0.38 mmol) of the substrate, 0.04 g (0.15 mmol, 41% yield) of the product (clear oil) was obtained. Anal: ($C_{12}H_{15}NO_2S$) C, H, N.

***N*-Tosyl-2-methyl-4-phenyl-Δ^2-pyrroline (27)**: ^{1}H NMR ($CDCl_3$) δ 2.2 (s, 3, =C-CH_3), 2.5 (s, 3, $ArCH_3$), 3.5–4.6 (m, 3, CHAr, CH_2N), 5.0 (m, 1, CH=), 6.8–7.4 (m, 7, ArH, ArH), 7.7 (d, J = 8 Hz, 2, ArH); IR (neat) 3100–2840 (m, CH, ArH), 1660 (m, C=C), 1600 (m, Ar), 1500 (m, Ar), 1350 (s, SO_2), 1170 (s, SO_2), 760 (s). From 0.15 g (0.48 mmol) of the substrate, 0.09 g (0.29 mmol, 60% yield) of the product (white solid, mp 85–86 °C) was obtained. Anal: ($C_{18}H_{19}NO_2S$) C, H, N.

***N*-Tosyl-2,3-dimethyl-4-phenyl-Δ^2-pyrroline (29)**: ^{1}H NMR ($CDCl_3$) δ 1.4(m, 3, =CCH_3), 2.7 (s, 3, $NCCH_3$), 2.5 (s, 3, $ArCH_3$), 3.4–4.4 (m, 3, CH, CHAr), 6.8–7.4 (m, 7, ArH), 7.7 (d, J = 8 Hz, 2, ArH); IR (KBr) 3080 (m, ArH), 3040 (ArH), 3000–2980 (m, CH), 1700 (m, C=C), 1610 (m, ArH), 1500 (s, Ar), 1350 (s, SO_2), 1170 (s, SO_2), 1090 (s), 810 (s). From 0.33 g (1.00 mmol) of the substrate, 0.30 g (0.92 mmol, 92% yield) of the product (white solid, mp 97–98 °C) was obtained. Anal: ($C_{19}H_{21}NO_2S$) C, H, N.

***N*-Tosyl-3-methyl-2-azaspiro[5.6]undec-3-ene (23)**: ^{1}H NMR ($CDCl_3$) 1.00–1.40 (br m, 10, CH_2), 2.10 (s, 3, =CCH_3), 2.50 (s, 3, $ArCH_3$), 3.60 (s, 2, CH_2N), 4.80 (m, 1, CH=), 7.30 (d, J = 8 Hz, 2, ArH), 7.70 (d, J = 8 Hz, 2, ArH); IR (neat) 3060 (w, =CH), 3020 (w, ArH), 3000–2840 (s, CH), 1650 (m, C=C), 1500 (m, Ar), 1350 (s, SO_2), 1170 (s, SO_2), 800 (m), 700 (s). From 0.21 g (0.68 mmol) of the substrate, 0.16 g (0.53 mmol, 78% yield) of the product (white solid, mp 48–49 °C) was obtained. Anal: ($C_{17}H_{23}NO_2S$) C, H, N.

***N*-Tosyl-3-methyl-1,2-dihydroisoquinoline (21)**: ^{1}H NMR ($CDCl_3$) δ 2.20 (s, 3, $ArCH_3$), 2.23 (d, J = 2 Hz, 3, CH_3C=), 4.70 (s, 2, CH_2N), 6.00 (br s, 1, CH=), 6.40–7.00 (m, 6, ArH), 7.30 (d, J = 9 Hz, 2, ArH); IR ($CHCl_3$) 3100–3040 (m, ArH, CH=), 1645 (m, C=C), 1350 (s, SO_2), 1170 (s, SO_2), 1100 (s, C=C), 910 (s, C=C). From 0.30 g (1.00 mmol) of the substrate, 0.25 g (0.84 mmol, 84% yield) of the product

(16) This substrated was prepared in the following manner: the *trans*-2-(2-propenyl)cyclohexanol was converted to the *p*-toluenesulfonate and then reacted with sodium cyanide to form a mixture of the *cis*- and *trans*-2-(2-propenyl)cyclopentylnitrile [B. A. Pauson, H. C. Chenug, S. Gurbani, and G. Saucey, *J. Am. Chem. Soc.*, **92**, 336 (1970)]. This nitrile was then reduced to the amine using lithium aluminum hydride [R. F. Nystrom and W. G. Brown, *J. Am. Chem. Soc.* **70**, 3738 (1948)].

(white solid, mp 81.5–82.5 °C) was obtained. Anal: ($C_{17}H_{17}NO_2S$) C, H, N. Mass spectrum: parent ion *m/e* 299.

General Procedure for the Stoichiometric Palladium-Assisted Cyclization of Olefinic Sulfonamides (Eq 3 and 4). $PdCl_2 \cdot 2CH_3CN$ (1 equiv) was placed into a 50-mL one-necked, with side arm, 14–20 round-bottomed flask fitted with a 14–20 stopcock and a rubber serum cap. The flask was evaculated and filled with argon several times, and then tetrahydrofuran (30 mL) was added via syringe. The substrate (generally 0.34–0.72 mmol) was dissolved in tetrahydrofuran (5 mL), and then this solution was added to the palladium salt via syringe. The reaction was stirred for 45 min, and then 1 equiv of triethylamine was added via syringe. At 1-h intervals, the next 2 equiv of triethylamine was added to the reaction, and the resulting mixture was stirred for 8–10 h at room temperature. Isolation and purification in the usual manner gave the pure material.

***trans*-*N*-Tosyl-2-azabicyclo[4.3.0]non-3-ene (37)**: ^1H NMR ($CDCl_3$) δ 1.45–2.47 (m, 10, CH_2, CHC=, CHN), 2.40 (s, 3, $ArCH_3$), 4.78–5.03 (m, 1, NCH=), 6.48–6.70 (m, 1, CH=), 7.10 (d, *J* = 8 Hz, 2, ArH), 7.53 (d, *J* = 8 Hz, 2, ArH); IR (KBr) 3100 (w, CH=), 3070 (w, CH=), 3000–2920 (s, CH), 2900–2860 (m, CH), 1650 (w, C=C), 1600 (w, Ar), 1500 (w, Ar), 1350 (s, SO_2), 1170 (s, SO_2), 810 (m), 710 (m), 690 (m). From 0.12 (0.42 mmol) of the substrate, 0.04 g (0.42 mmol, 36% yield) of the product (white solid, mp 129–130 °C) was obtained. Anal: ($C_{15}H_{19}NO_2S$) C, H, N.

***N*-Tosyl-Δ²-piperidine (38)**: ^1H NMR ($CDCl_3$) δ 1.52–2.20 (m, CH_2), 2.41 (s, $ArCH_3$), 4.80–5.10 (m, NCH=), 6.48–6.70 (m, HC=C), 7.25 (d, *J* = 8 Hz, ArH), 7.65 (d, *J* = 8 Hz, ArH); IR (neat) 3000–2840 (s, CH), 1650 (m, C=C), 1600 (m, Ar), 1500 (m, Ar), 1340 (s, SO_2), 1160 (s, SO_2), 910 (s), 730 (s). This material was obtained in an impure state only, and decomposed upon attempted purification.

Reduction of 7 Using Wilkinson's Catalyst. The substrate (0.893 g, 3.2 mmol) and $RhCl(PPh_3)_3$ (0.119 g, 0.32 mmol) were placed in a small Fischer–Porter pressure reactor along with a magnetic stir bar. The reactor was then evacuated and filled with argon several times. THF (30 mL) was added via syringe, and hydrogen (1 atm) was introduced. The reaction mixture was allowed to stir overnight. Ethyl acetate (30 mL) was then added, and the reaction mixture was filtered through a 2 in. layer of silica gel in a fritted funnel. The filtrate was concentrated under reduced pressure to give a red solid. Purification was accomplished using MPLC (3:1 hexane/EtOAc) giving 0.789 g (88% yield) of product: ^1H NMR ($CDCl_3$) δ 1.10–2.18 (m, 8, CH_2), 1.35 (d, *J* = 6 Hz, 3, CH_3), 2.39 (s, 3, $ArCH_3$), 3.13–3.50 (m, 1, $CHCH_3$), 3.67–4.00 (m, 1, $CHCH_2$), 7.18 (d, *J* = 8 Hz, 2, ArH), 7.60 (d, *J* = 8 Hz, 2, ArH); IR (neat) 3050 (m, ArH), 3000–2980 (m, CH), 2900 (m, CH), 1610 (m, Ar), 1500 (m, Ar), 1350 (m, SO_2), 1160 (m, SO_2). From 0.89 g (3.20 mmol) of substrate, 0.79 g (2.82 mmol, 88% yield) of the product (white solid, mp 80–81.5 °C) was obtained. Anal: ($C_{15}H_{21}NO_2S$) C, H, N.

Reduction of 7 Using Platinum Oxide under Acidic Conditions. The substrate (7) (0.278 g, 1.00 mmol) and Adam's catalyst (PtO_2) (11.4 mg, 0.05 mmol) were placed into a Fischer–Porter pressure bottle fitted with a pressure head. The bottle was evacuated and filled with argon several times, and then a degassed solution of absolute ethanol (20 mL) and acetic acid (1 mL) was added to the bottle via syringe. Reduction for 10 h at 50 psi gave the reduced material (0.24 g, 0.80 mmol, 80% yield) identical in all respects with that obtained from Wilkinson's catalyst.

Reduction of 7 Using Palladium on Carbon under Acidic Conditions. The procedure used here was identical with that used in the immediately proceeding reduction, with the following exceptions. This reaction was run in a larger amount of solvent (39 mL of absolute ethanol) and was done using a higher pressure of hydrogen (59 psi). After 38 h, isolation of the product gave 212 mg (0.76 mmol) of material which was identical in all respects with that obtained by the reduction of 7 using Wilkinson's catalyst, yield 76%.

Deprotection of *cis*-*N*-Tosyl-3-methyl-2-azabicyclo[3.3.0]octane. The saturated sulfonamide (0.587 g, 2.10 mmol), prepared from the reduction of 7 using Wilkinson's catalyst, was placed into a large ultraviolet light reactor vessel and 2-propanol (300 mL) was added. The solution was irradiated using a 200-W mercury vapor lamp for 4.5 h. Concentrated HCl (2 mL) was added, and the solvent was removed under reduced pressure to give a brown oil. This was taken up in saturated NaOH solution and extracted with diethyl ether (3 × 30 mL). The combined organic layer was washed using saturated NaCl solution (2 × 20 mL) and then dried over $MgSO_4$. Gravity filtration, followed by solvent removal under reduced pressure, gave a brown oil, which, when Kugelrohr distilled gave a light yellow oil (223 mg, 85% yield). This material was identical with that obtained from the $Hg(OAc)_2$-assisted ring closure of 2-(2-propenyl)cyclopentylamine:[17] ^1H NMR ($CDCl_3$) δ 1.19(d, 3, *J* = 6 Hz, CH_3), 1.20–3.29(m, 9, CH_2, CH), 2.59 (s, 1, NH), 3.50–3.80 (m, 2, CHN); IR (neat) 3500–3100 (m, NH), 3000–2860 (s, CH), 1655 (m, NH), 1450 (m, CH_2), 1380 (m), 750 (m).

Deprotection of 7 Using Bis(2-methoxyethoxy)aluminum Hydride (Red-Al^R). The procedure of Gold and Babad,[18] using toluene as the solvent, gave a product which was identical with that obtained above; 0.062 g (0.50 mmol) (46% yield) was obtained from 0.296 g (1.07 mmol) of the substrate.

Reduction of *cis*-*N*-Tosyl-3-methyl-2-azabicyclo[3.3.0]oct-3-ene Using Trifluoroacetic Acid and Sodium Cyanoborohydride. The substrate (100 mg, 0.36 mmol) was placed into a 25-mL one-necked, with side arm, 14–20 round-bottomed flask fitted with a 14–20 stopcock and a rubber serum cap. The flask was evacuated and filled with argon several times, and then tetrahydrofuran (5 mL) was added via syringe. Trifluoroacetic acid (28 μL, 0.36 mmol) was then added via syringe and the reaction was stirred for 2 h. Sodium cyanoborohydride (23 mg, 0.36 mmol) was dissolved in tetrahydrofuran (5 mL), and then this was added to the reaction via syringe. This reaction was then stirred overnight. The reaction was washed with a 1:1 solution of water and saturated sodium chloride (2 × 15 mL) and then the organic layer was washed with saturated sodium chloride (2 × 15 mL). It was then dried over $MgSO_4$ and filtered. The filtrate was concentrated on a rotary evaporator to give 130 mg of a yellow oil. This oil was purified using medium-pressure column chromatography (hexane:ethyl acetate 4:1 as eluent) to give 78 mg (0.28 mmol, 78%) of a white solid. This solid was a mixture of diastereomers (~84:16): ^1H NMR ($CDCl_3$) δ 1.20 (d, *J* = 6 Hz, 0.47, CH_3), 1.43 (d, *J* = 6 Hz, 2.53, CH_3), 1.43–2.27 (m, 9, CH_2), 2.47 (s, 3, $ArCH_3$), 3.20–3.70 (m, 1, CHNMe), 3.70–4.17 (m, 1 $CHNCH_2$), 7.27 (d, *J* = 8 Hz, 2, ArH), 7.70 (d, *J* = 8 Hz, 2, ArH); IR (KBr) 3000–2940 (m, CH), 2890 (m, CH), 1605 (w, Ar), 1500 (w, Ar), 1345 (s, SO_2), 1160 (s, SO_2), 1100 (m), 810 (m), 710 (m), 690 (m).

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Registry No. 1, 81097-02-1; **2**, 74195-75-8; **3**, 81097-03-2; **4**, 81097-04-3; **5**, 81097-05-4; **6**, 81097-06-5; **7**, 81097-07-6; **8**, 81097-08-7; **9**, 81097-09-8; **10**, 81097-10-1; **11**, 81097-11-2; **12**, isomer 1, 81097-12-3; **12**, isomer 2, 81132-14-1; **13**, 81097-13-4; **14**, 81097-14-5; **15**, 81097-15-6; **16**, 81097-16-7; **17**, 81097-17-8; **18**, 81097-18-9; **19**, 81097-19-0; **20**, 81097-20-3; **21**, 81097-21-4; **22**, 81097-22-5; **23**, 81097-23-6; **24**, 81097-24-7; **25**, 81120-68-5; **26**, 70197-11-4; **27**, 81120-69-6; **28**, isomer 1, 81097-25-8; **28**, isomer 2, 81097-26-9; **29**, 81097-27-0; **30**, 81097-28-1; **31**, 81097-29-2; **32**, 81097-30-5; **33**, 81097-31-6; **34**, 81097-32-7; **35**, 10285-80-0; **36**, 81097-33-8; *cis*-**37**, 81097-34-9; *trans*-**37**, 81097-35-0; **38**, 81097-36-1; **39**, isomer 1, 81097-37-2; *trans*-2-(2-propenyl)cyclopentanol, 74743-89-8; *trans*-2-(1-methyl-2-propenyl)cyclopentanol, isomer, 81097-38-3; *trans*-2-(1-methyl-2-propenyl)cyclopentanol, isomer 2, 81132-15-2; *trans*-2-(2-propenyl)cyclohexanol, 24844-28-8; *trans*-2-(3-butenyl)cyclopentanol, 81097-39-4; 1-(1-(2-propenyl)cyclohexyl)-methanol, 67838-03-3; *trans*-2-ethynylcyclopentanol, 61967-50-8; *trans*-2-ethenylcyclopentanol, 6401-11-2; 2-(1-methyl-2-propenyl)cyclopentylamine, 81097-40-7; *cis*-2-ethenylcyclopentylamine, 81097-41-8; *cis*-2-(2-propenyl)cyclohexylamine, 81097-42-9; 1-(1-(2-propenyl)cyclohexyl)methylamine, 81097-43-0; *cis*-2-(3-butenyl)cyclopentylamine, 81097-44-1; 2-(2-propenyl)benzylamine, 59816-88-5; 1-*N*-tosylamino-1-phenyl-2-bromoethane, 5485-71-2; *trans*-1-*N*-benzenesulfonylamino-2-bromocyclohexane, 81097-45-2; *trans*-1-*N*-tosylamino-2-bromocyclopentane, 81097-46-3; *N*-benzenesulfonyl-7-azabicyclo[4.1.0]heptane, 81097-47-4; *N*-tosyl-2-phenylaziridine, 24395-14-0; *N*-tosyl-6-azabicyclo[3.1.0]hexane, 81097-48-5; **39** isomer 2, 81176-45-6; *cis*-2-propyl-1-aminocyclopentane, 81097-49-6; $PdCl_2$, 7647-10-1.

(17) J. J. Perie, J. P. Laval, J. Roussel, and A. Lattes, *Tetrahedron*, **28**, 675 (1972).

(18) E. H. Gold and E. Babad, *J. Org. Chem.*, 37, 2208 (1972).