experimental value is 1.835 kcal/mol while the value from MM2 is 1.841 kcal/mol. For the *Z* isomer **2b**, the experimental value is 0.375 kcal/mol and the value from MM2 is 0.892 kcal/mol, which, while somewhat high, does reflect the increased ease of rotation in the *Z* isomer **2b**.

Conclusion

The MM2 force field has been extended to include the oxime functional group and a set of parameters has been developed which reproduces, with reasonable accuracy, the experimentally available data. It is now possible to extend these parameters to more complicated systems and to attempt to predict their geometries. This work is underway.

Acknowledgment. Fruitful discussions with Professor N. L. Allinger and Dr. Y. H., Yuh are gratefully acknowledged.

Registry No. Formaldoxime, 75-17-2; (*E*)-acetaldoxime, 5780-37-0; (*Z*)-acetaldoxime, 5775-72-4; acetone oxime, 127-06-0.

Supplementary Material Available: Tables comparing the experimental data for **1**, **2a**,**b**, and **3** with other published computational [ab initio (STO-3G, 4-31G, SCF-DZ), semiempirical (CNDO/2, INDO), and force field (CFF)] results (10 pages). Ordering information is given on any current masthead page.

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(21) Böhlig, H.; Näther, M.; Fruwert, J.; Geiseler, G. *Z. Phys. Chem. (Leipzig)* **1976**, *257*, 634.

(22) Ohashi, O.; Hara, H.; Nohi, K.; Sakaizumi, T.; Onda, M.; Yamaguchi, I. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 834.

(23) Basu, S.; Cumper, S. W. N. *J. Chem. Soc., Perkin Trans. 2* **1974**, 235.

(24) Le Fevre, R. J. W.; Perrins, R. K.; Steel, K. D. *Aust. J. Chem.* **1986**, *19*, 1796.

Carbon-to-Nitrogen Rearrangement in *N*-(Arylsulfonoxy)amines as a Route to Azacyclic Compounds

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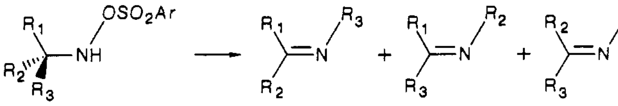
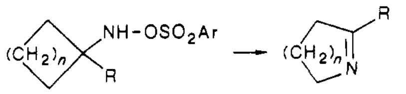
A series of cyclic amines **1–10** was converted to the *N*-((*p*-nitrophenyl)sulfonoxy)amine derivatives with (*p*-nitrophenyl)sulfonyl peroxide. These compounds rearranged to ring-expanded cyclic imines in fair to good yields. Conversion of the amine to its hydroxylamine analogue and treatment with *p*-nitrobenzenesulfonyl chloride/triethylamine also gave the ring-expanded cyclic imines; however, yields were superior due to the basicity of the reaction mixture.

It was earlier demonstrated that, in the absence of base, *N*-(arylsulfonoxy)amines undergo facile carbon-to-nitrogen rearrangements to give imine products (eq 1).[1] A number of studies suggest that concerted, cationic rearrangement of the migrating group accompanies ionization of the arylsulfonoxy group from nitrogen;[2] thus discrete cationic nitrenium ions are not involved in these rearrangements.[3]

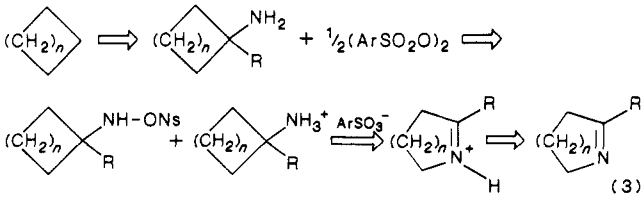


(1)

When dissimilar migrating groups are attached to C-1 of the *N*-(arylsulfonoxy)amine precursor, a mixture of products can result. The relative proportions of products were found to depend on three factors: (a) the inherent migratory aptitudes of these groups, (b) electronic effects at the migration origin, and (c) stereoelectronic effects that require an antiperiplanar relationship between the departing arenesulfonate leaving group and the migrating group.[1] The interplay of these factors is not a priori predictable; however, it was observed that in cyclic amine substrates with tertiary carbon at the migration origin, only ring expansion was observed (eq 2).[1,3] It was concluded that in such systems, stereoelectronic effects were the principal factor in determining the products of rearrangement.[1] The synthetic consequence of such behavior is that attachment of an amine functionality to a cyclic system, followed by conversion to the an *N*-arylsulfonoxy derivative and cationic rearrangement, could provide a convenient method for the insertion of nitrogen into rings to give ring-expanded iminium/imine products (eq 3).



(2)



(3)

Other reactions that accomplish this type of change (ring expansion and insertion of nitrogen) include the Beckman rearrangement[4] and the Schmidt reaction[5] of cyclic ke-

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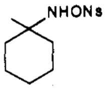
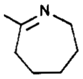
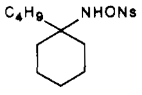
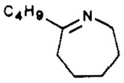
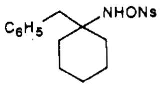
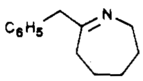
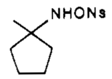
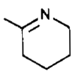
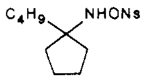
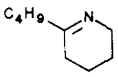
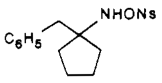
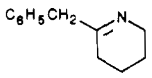
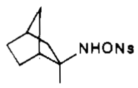
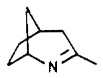
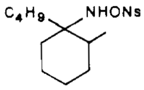
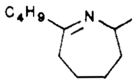
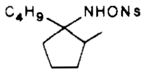
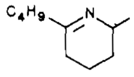
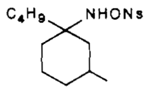
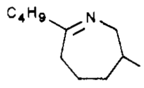
[1] Hoffman, R. V.; Kumar, A. *J. Org. Chem.* **1975**, *50*, 1859.

[2] (a) Hoffman, R. V.; Cadena, R.; Poelker, D. J. *Tetrahedron Lett.* **1978**, 203. (b) Hoffman, R. V.; Poelker, D. J. *J. Org. Chem.* **1979**, *44*, 2364. (c) Gassman, P. G.; Hartman, G. D. *J. Amer. Chem. Soc.* **1973**, *95*, 449. (d) Heesing, A.; Herdering, W. *Chem. Ber.* **1983**, *116*, 1081. (e) Biehler, J.-M.; Fleury, J.-P. *Tetrahedron* **1971**, *27*, 3171.

[3] Hoffman, R. V.; Kumar, A.; Buntain, G. A. *J. Am. Chem. Soc.* **1985**, *107*, 4731 and references therein.

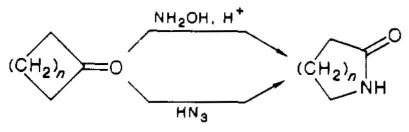
[4] (a) McCarty, G. C. In *The Chemistry of the Carbon–Nitrogen Double Bond*; Patai, S., Ed.; Wiley-Interscience: New York, 1970; pp 408–439. (b) See Maruoka et al. (Maruoka, K.; Miyazaki, T.; Ando, M.; Matsumura, Y.; Sakane, S.; Hattori, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1983**, *105*, 2831) for recent applications.

Table I. Rearrangements of *N*-(Arylsulfonoxy)amines by Reaction with *p*-NBSP in Ethyl Acetate at 25 °C[f]

entry	starting amine	product[a]	yield, % −78 °C[b]	yield, % −30 °C	*m*-TFBSP[d]
1	 **1a**	 **11**	82		60
2	 **2a**	 **12**	67	38	
3	 **3a**	 **13**	42		
4	 **4a**	 **14**	43	65	
5	 **5a**	 **15**	79	60	54
6	 **6a**	 **16**	63		
7	 **7a**	 **17a** +  **17b**	51[e]	50	
8	 **8a**	 **18**	0		
9	 **9a**	 **19**	0		
10	 **10a**	 **20**	0		

[a] After neutralization of the iminium product with base. [b] The *N*-(arylsulfonoxy)amine was prepared at −78 °C. [c] The *N*-(arylsulfonoxy)amine was prepared at −30 °C. [d] (*m*-(Trifluoromethyl)phenyl)sulfonyl peroxide was used to prepare the *N*-(arylsulfonoxy)amine at −78 °C. [e] A mixture of **17a** and **17b** (1:4) was obtained. [f] Yields were determined by GC analysis of the crude product (see Experimental Section).

tones, which are converted to ring-expanded cyclic amides through the agency of hydroxylamine and hydrazoic acid, respectively (eq 4). Treatment of tertiary, cyclic alcohols



(4)

with hydrazoic acid can also yield ring-expanded iminiums,[6] however, carbon-to-nitrogen rearrangement is not highly selective. A preparation of β-lactams was reported by a related ring expansion of chloramines.[7]

We have investigated the rearrangements of a variety of cyclic *N*-(arylsulfonoxy)amine substrates and have found that they provide a useful method for the incorporation of nitrogen into rings. We wish to report on the scope and limitations of these rearrangements.

Results and Discussion

Cyclic amines **1–10** were converted to their coresponding *N*-((*p*-nitrophenyl)sulfonoxy) (N-ONs) derivatives **1a–10a** by reaction with (*p*-nitrophenyl)sulfonyl peroxide (*p*-NBSP) in ethyl acetate at −78 °C.[8] After purification of the reaction mixture by filtration through silica gel at −78 °C, the yellow solution containing **1a–10a** was stirred at

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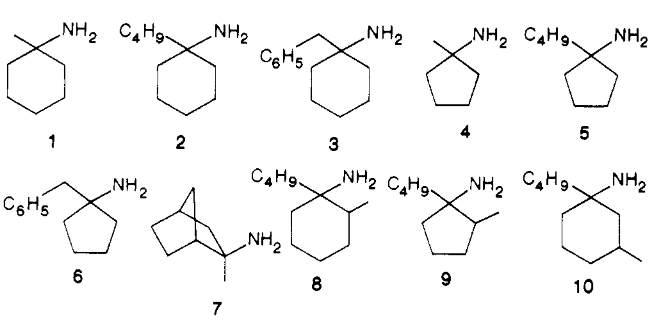
[5] (a) Koldobski, G. I. *Russ. Chem. Rev.* **1971**, *40*, 835. (b) Krow, G. R. *Tetrahedron* **1981**, *37*, 1283. (c) Fikes, L. A.; Shechter, H. *J. Org. Chem.* **1979**, *44*, 741. (d) Krow, G. R. *Tetrahedron* **1987**, *43*, 1987.

[6] (a) Boyer, J. H.; Canter, F. C. *J. Am. Chem. Soc.* **1955**, *77*, 3287. (b) Koldobski, G. I. *Russ. Chem. Rev.* (*Engl. Transl.*) **1978**, *47*, 1084. (c) Saski, T.; Eguchi, S.; Okano, T. *J. Org. Chem.* **1984**, *49*, 444.

[7] Wasserman, H. H.; de Ochoa, E.; Adickes, H. W. *J. Am. Chem. Soc.* **1971**, *93*, 5586.

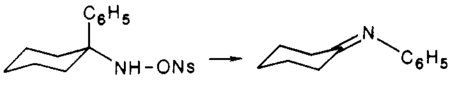
[8] Hoffman, R. V.; Belfoure, E. L. *Synthesis* **1983**, 34.



1 2 3 4 5 6 7 8 9 10

room temperature for 24 h. Basic aqueous workup gave ring-expanded imine products **11–20** in the yields indicated in Table I.[9] Products were identified by the comparison of their spectral properties with literature data or by structural proof described in the Experimental Section. Compound **7** gave a 1:4 mixture of **17a** and **17b**, resulting from competitive migration of the 1,2 and 2,3 bonds, respectively. Fair to good yields were obtained for **1a–7a**, which had unsubstituted alicyclic rings undergoing ring expansion (entries 1–7).

Substrates **8a–10a**, which had a methyl group attached to the alicyclic ring, failed to give any rearrangement products under these conditions (entry 8). 1-Phenylcyclohexylamine **21** did not give ring enlargement as the primary rearrangement process. The vastly greater migratory aptitude of the phenyl ring overcame the more modest stereoelectronic effect so that phenyl migration (34%) was the primary event (eq 5).



21 (5)

Several factors were identified that affected the yield of the reaction as well as the purity of the crude product. It is crucial to keep the peroxide oxidant in solution during the formation of the N-ONs adduct. This was best achieved by the slow addition of a cold solution of the peroxide to the amine at −78 °C. If the addition was too fast and the peroxide crystallized out of solution or if the peroxide was added as a solid, then incomplete conversion of the amine to its N-ONs derivative was observed. This resulted in reduced yields and caused the product imine to be contaminated with unreacted starting amine. If the reaction temperature was raised to −30 °C to increase the solubility of *p*-NBSP in the reaction mixture, somewhat lower yields resulted from the instability of the N-ONs adduct at this temperature during its formation (Table I). The use of (*m*-(trifluoromethyl)phenyl)sulfonyl peroxide (*m*-TFBSP),[1] in spite of its greater solubility, gave lower yields of rearrangement (Table I) because the byproduct ammonium salts were not completely removed during low-temperature silica gel treatment (vide infra).

A second requirement for satisfactory yields and high purity of the crude product is that the ammonium salt produced as a byproduct in the formation of the N-ONs adduct (eq 3) must be removed at low temperature before rearrangement occurs. This was normally accomplished by filtering the reaction mixture through a short column of silica gel cooled to −78 °C, which served to remove the precipitated salt as well as that fraction of the salt that was soluble in the reaction mixture. In those cases where the byproduct salts were soluble in the reaction mixture, they were not completely removed by the silica gel. Low yields and dark product mixtures resulted. Amines **8–10**, which had a methyl group attached to the ring, all gave highly soluble *p*-nitrobenzenesulfonate salts that were not removed from the N-ONs derivative by silica gel. All failed to produce ring-expanded iminium products upon warming, and the starting amine was a major component in the dark product mixture. Likewise the use of *m*-TFBSP gave ammonium *m*-(trifluoromethyl)benzenesulfonate salts that were not completely removed by silica gel, and the yields of rearrangement suffered as a result.

The role played by ammonium salts in lowering the yield of rearranged products is not clear. It is known that the N-ONs adducts are sensitive to acid.[3] One possibility is that ammonium salts can act as acids toward the N-ONs, thus promoting other modes of decomposition. This hypothesis seems unlikely since the iminium ion product formed in the reaction mixture should be more acidic ($pK_a \sim 6.5$)[10] than the ammonium salt ($pK_a \sim 11$). Thus a much stronger acid than the ammonium salt is always present, even in reactions that give high yields of rearrangement.

A more likely rationale is that the equilibrium concentration of free amine in the reaction mixture results in nucleophilic addition to the cyclic iminium product, ring opening, and ultimately oligomerization. No direct proof is available to support this hypothesis, but reactions run in the presence of ammonium salts do appear to contain large amounts of high molecular weight byproducts.

Our results confirmed that under the proper circumstances, rearrangements of *N*-(arylsulfonoxy)amines offer a smooth and selective route to azacyclic compounds. It also became apparent, however, that the generation of N-ONs adducts from amines and *p*-NBSP has several disadvantages, all related to the fact that 1 equiv of *p*-nitrobenzenesulfonic acid is produced in the reaction. Two equivalents of starting amine is required, the byproduct salt is sometimes difficult to remove, and the reaction environment is fundamentally acidic.

Many of these problems might be circumvented if the N-ONs derivative could be produced under basic conditions. There are several reports in the literature of the O-sulfonylation of hydroxylamines.[2c–e,11] Hydroxylamines **22–24** were prepared by reduction of the corresponding nitro compounds.[12] These were sulfonylated either by conversion to the potassium salt by potassium hydride and reaction with *p*-nitrobenzenesulfonyl chloride at −78 °C or by treatment with triethylamine and the sulfonyl chloride at −30 °C. In either method the formation of the N-ONs derivative was indicated by the development of a bright yellow color and active oxygen in the solution by iodometric titration. The reaction was stirred at room temperature until the rearrangement was complete as evidenced by iodimetry. High yields of rearranged azacyclic products were obtained that required minimal purification (eq 6). Sulfonylation appears to occur only on

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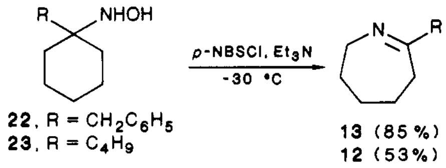
(9) Yields are based on the theoretical amount of N-ONS derivative that would be produced from 1 equiv of peroxide reacting with 2 equiv of amine according to the stoichiometry of eq 3.

(10) Smith, J. W. In *The Chemistry of the Carbon of the Carbon–Nitrogen Double Bond*; Patai, S., Ed.; Interscience: London, 1970; pp 236–238.

(11) (a) Gassman, P. G.; Granrud, J. E. *J. Am. Chem. Soc.* **1984**, *106*, 1498. (b) *Ibid.* **1984**, *106*, 2448. (c) Boche, G.; Bosold, F.; Niessner, M. *Tetrahedron Lett.* **1982**, *23*. (d) Bernheim, M.; Boche, G. *Angew, Chem., Int. Ed. Engl.* **1980**, *19*, 1010. (e) Barton, D. H. R.; Bould, L.; Clive, D. L. J.; Magnus, P. D.; Hase, T. *J. Chem. Soc.* C **1971**, 2204. (f) Boche, G.; Bernheim, M.; Niessner, M. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 53. (g) Abraham, T.; Curran, D. *Tetrahedron* **1982**, *38*, 1019. (h) Boche, G.; Mayer, N.; Bernheim, M.; Wagner, K. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 687. (i) Berlin, A. Y.; Shchukina, M. N.; Sayonova, E. D. *Zh. Obshch. Khim.* **1944**, *14*, 249.

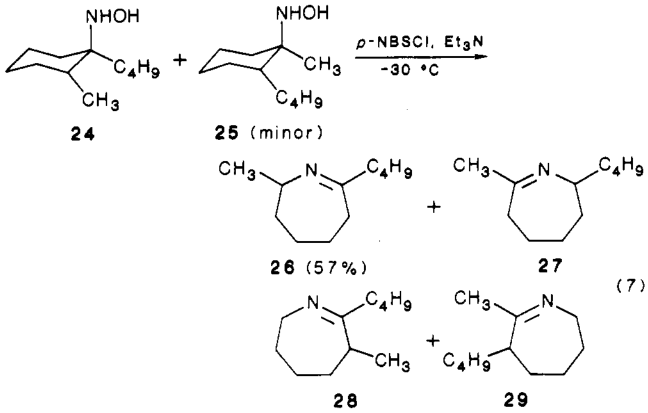
(12) Ashburn, S. P.; Coates, R. M. *J. Org. Chem.* **1984**, *49*, 3127.



(6)

the oxygen of the hydroxylamine, presumably due to steric shielding of the nitrogen by the tertiary alkyl group. The high yields indicate that both the reactants and products are stable to basic, nonnucleophilic conditions.

Of further note is that rearrangement of what was thought to be pure **24** gave 2-*n*-butyl-7-methyl-1-azacycloheptene (26; 57%) as the major product and three other minor components that had ^{1}H NMR splitting patterns very similar to those of **26**, and gave identical parent ions by GC/MS. These are probably the structural isomers **27–29**. These results suggest that hydroxylamine **24** was contaminated (~10%) with the 1-methyl-2-*n*-butyl isomer, **25**, which could not be detected in the rather featureless ^{1}H NMR spectrum of **24** or by VPC. Since **24** was prepared from **8**, a hyride shift in 1-*n*-butyl-2-methylcyclohexyl cation, formed in the Ritter reaction in the synthesis of **8**, caused **24** to be comtaminated with its regioisomer **25**. The minor products **27-29** presumably result from migration of the more highly substituted ring bond in **25**, and migration of the less highly substituted ring bonds in **24** and **25** (eq 7). The product of distribution indicates that the more substituted ring bond migrates with some selectivity (>3:1). The total yield of rearranged products was 78%, in sharp contrast to the failure seen when amine **8** is reacted with *p*-NBSP to generate **8a**. The product mixture could be reduced with sodium borohydride to give 2-butyl-7-methyl-1-azacycloheptane (63% from **24** and **25**) from the reduction of **26** and **27**.



(7)

Conclusions

Cationic rearrangements of *N*-(arylsulfonoxy)amines have good potential as a synthetic method for the construction of azacyclic compounds. While the N-ONs precursors can be obtained from amines and *p*-NBSP, a better route involves the O-sulfonylation of N-substituted hydroxylamines. To bring this strategy to full flower, more convenient and general syntheses of the hydroxylamine precursors are required. This aspect is currently under investigation.

Experimental Section

Melting points are uncorrected. Proton NMR spectra were recorded on either Jeol PS-100 or Varian XL-200 instruments; chemical shifts are reported for chloroform -*d* solutions in ppm relative to Me$_4$Si. Infrared spectra were recorded on a Perkin-Elmer 283B spectrometer as potassium bromide disks for solids or as thin films for neat liquids. Mass spectra were obtained on a Hitachi RMU-6E or a Hewlett-Packard 5995 spectrometer. Analytical VPC was carried out on a HP-5890 gas chromatograph with bonded silica columns (Alltech): A, 0.53 mm × 10 dm Superox (polyethylene glycol); B, 0.53 mm × 10 m RSL-300 (phenylmethylsilicone); C, 0.53 mm × 10 m RSL-150 (methylsilicone). GC yields were determined by evaporation of the reaction mixture, weighing the crude product to obtain the crude yield, injection (neat) on the appropriate column, and correcting the crude yield for other volatile products (solvent etc.) observed in the crude product. Purification of the product could normally be accomplished by bulb-to-bulb distillation or sometimes, for analytical samples, by preparative VPC, which was carried out on a Varian Aerograph 920 gas chromatograph using packed columns: D, 6 mm × 3 m 10% Carbowax–2% KOH; E, 6 mm × 2 m 10% QF-1. Elemental analyses were performed by MicAnal Analytical of Tuscon, and exact mass measurements were performed by the Midwest Center for Mass Spectrometry at the University of Nebraska.

Starting amines **1–10** were prepared by Grignard addition to a cyclic ketone to give a cyclic, tertiary alcohol,[13] which was converted to the corresponding primary amine by the Ritter reaction.[14] All amines were stored (often as the HCl salt) and handled under nitrogen to minimize reaction with atmospheric carbon dioxide. Amines **1**,[15] **2**,[16] **3**,[17] **4**,[18] **5**,[19] **6**,[17] and **7**[20] were known compounds. Sulfonyl peroxides *p*-NBSP[21] and *m*-TFBSP[22] were prepared by literature procedures.

1-Butyl-2-methylcyclohexylamine (8) was prepared by the addition of *n*-butylmagnesium bromide to 2-methylcyclohexanone and treatment of the resulting alcohol with sodium cyanide and sulfuric acid, followed by hydrolysis in concentrated HCl.[14] The amine was purified by conversion to its hydrochloride salt by HCl in ether, separation, and neutralization with aqueous NaOH, and Kugelrohr distillation. Amine **8** is a viscous oil that gave the following spectra data: ^{1}H NMR δ 0.7–1.8, broad multiplet that had a distinct doublet at 0.95 (J = 5 Hz) for the methyl group at C-2; IR (cm^{-1}) 3360 and 3300 (NH$_2$), 2700–2980 (C–H), 1450 (CH$_3$). Elemental analysis was obtained on the hydrochloride salt. Calcd for $C_{11}H_{24}NCl$: C, 64.23; H, 11.68; N, 6.81. Found: C, 63.96; H, 11.96; N, 6.86. From results reported for **24** below, which was prepared from **8**, it is evident that **8** contains a small amount (~10%) of its regioisomer (2-*n*-butyl-1-methylcyclohexylamine, presumably formed by hydride rearrangement during the Ritter reaction used in its preparation. The relatively featureless ^{1}H NMR spectrum did not allow us to detect this isomer, nor did it permit any assignment of stereochemistry in either isomer.

1-Butyl-2-methylcyclopentylamine (9) was prepared and purified by a similar sequence from *n*-butylmagnesium bromide and 2-methylcyclopentanone. Amine **9** was a viscous oil that had the following properties: ^{1}H NMR δ 0.78–2.0, broad multiplet that had a distinct doublet at δ 0.9 (J = 6 Hz) for the methyl group at C-2; IR (cm^{-1}) 3360 and 3300 (NH$_2$), 2740–2980 (C–H), 1450 (CH$_3$). Elemental analysis was obtained on the hydrochloride salt. Calcd for $C_{10}H_{22}NCl$: C, 62.66; H, 11.49; N, 7.31. Found: C, 62.39; H, 11.75; N, 7.35. While **9** may contain some of its 2-butyl-1-methylcyclopentylamine regioisomer as seen for **8**, the featureless ^{1}H NMR spectrum did not permit its detection, nor any stereochemical assignments in **9**. Furthermore, since **9** did not give rearrangement products (method A), chemical evidence of an isomeric mixture was not obtained.

1-Butyl-3-methylcyclohexylamine (10) was prepared and purified by a similar sequence from *n*-butylmagnesium bromide and 3-methylcyclohexanone. Amine **10** was a viscous oil that had

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the following properties: ^{1}H NMR δ 0.6–1.8, broad multiplet that had a distinct doublet at δ 0.82 (J = 6 Hz) for the methyl group at C-3; IR (cm^{-1}) 3360 and 3300 (NH_2), 2720–2980 (C–H), 1450 (CH_3). Elemental analysis was obtained on the hydrochloride salt. Calcd for $C_{11}H_{24}NCl$: C, 64.23; H, 11.68; N, 6.81. Found: C, 64.33; H, 12.15, N, 7.09. Due to the relatively featureless ^{1}H NMR spectrum, no stereochemical assignment of **10** was possible.

***N*-(1-Benzylcyclohexyl)hydroxylamine (22)** was prepared by the reduction of 1-benzyl-1-nitrocyclohexane[23] with zinc–ammonium chloride[12] to give **22** (96%): mp 112–113; ^{1}H NMR δ 1.51 (m, 10 H, ring H), 2.81 (s, 2 H, benzylic H), 5.3 (br, s, 2 H, N–H, O–H), 7.27 (m, 5 H, aromatic H). Upon standing at room temperature, both **22** and its HCl salt discolored (blue), and correct elemental analysis could not be obtained. The identity was founded on the method of preparation from 1-benzyl-1-nitrocyclohexane, the NMR spectrum, and the products of rearrangement.

***N*-(1-Butylcyclohexyl)hydroxylamine (23)** was prepared from amine **2** by oxidation to the nitro compound with *m*-CPBA (96%)[24] followed by zinc–ammonium chloride reduction[12] and purification by Kugelrohr distillation (65 °C, 0.05 Torr) to give **23** (80%) as a clear oil: ^{1}H NMR δ 0.92 (t, 3 H, J = 6 Hz, CH_3), 1.05–1.90 (m, 16 H); IR (cm^{-1}) 3520–3015 (br), 2910, 1450. Upon standing at room temperature, both **23** and its HCl salt discolored (blue), and correct elemental analysis could not be obtained. The identity was founded on the method of preparation from **2**, the NMR spectrum, and the products of rearrangement.

***N*-(1-Butyl-2-methylcyclohexyl)hydroxylamine (24)** was prepared from amine **8** by oxidation to the nitro compound with *m*-CPBA (83%)[24] followed by zinc–ammonium chloride reduction[12] and purification by flash chromatography (ether–ethyl acetate, 2:1) to give **24** (79%) as a clear oil ^{1}H NMR δ 0.91 (m, 6 H, methyl H), 1.0–1.88 (m, 14 H, methylene H), 1.90–2.04 (m, 1 H, methine H), 4.60–6.50 (br s, 2 H, N–H, O–H); IR (cm^{-1}) 3650–3040 (br), 2920, 2855, 1455, 1413, 1372. Upon standing at room temperature, both **24** and its HCl salt discolored (blue), and correct elemental analysis could not be obtained. The identitiy was founded on the method of preparation from **8**, the NMR spectrum, and the products of rearrangement. It was evident from the products of rearrangement that **24** is contaminated with a small amount of its regioisomer **25** (~10%), but this could not be distinguished in the spectral data of **24**.

Conversion of 1-Methylcyclohexylamine (1) to the *N*-(Arylsulfonoxy)amine and Subsequent Rearrangement. Method A. 1-Methylcyclohexylamine (**1**) (810 mg, 7 mmol) in ethyl acetate (40 mL) was cooled to −78 °C under nitrogen, and a solution of *p*-NBSP (1.44 g, 3.5 mmol) in ethyl acetate (60 mL) was added dropwise (30 min). A bright yellow color developed immediately and a cream-colored solid formed. After the addition was complete, the reaction mixture was stirred at −78 °C for 7 h and then filtered through a 2-in. glass fritted funnel filled with silica gel and cooled to −78 °C. A small portion of cold ethyl acetate (10 mL) was used to wash the funnel. The solid retained in the funnel was identified as the ammonium *p*-nitrobenzenesulfonate salt of **1**. The yellow, homogeneous filtrate, which tested positive for active oxygen (starch iodine test), was stirred at room temperature for 24 h (or until no active oxygen was detected). The solvent was removed by rotary evaporation, and the pale brown residue was taken up in dichloromethane (50 mL) and washed with 15% sodium hydroxide (3 × 20 mL). The basic washes were extracted with dichloromethane (20 mL), and the combined organic layers were dried (K_2CO_3) and evaporated to yield 2-methyl-1-azacycloheptene (**11**) as a clear oil[25] (330 mg, 82%): ^{1}H NMR δ 1.16–1.94 (m, 6 H, ring H), 2.01 (s, 3 H, CH_3), 2.52 (m, 2 H, allylic H), 3.50 (m, 2 H, $=NCH_2$); IR (cm^{-1}) 2929, 2858, 1662.

Method B. In this variation the solution of *p*-NBSP was added to the amine solution, which was cooled to −30 °C under a nitrogen atmosphere and stirred at −30 °C for 1 h. After this reaction period, the reaction mixture was cooled to −78 °C, and chromatography and rearrangement were carried out as in method A.

Method C. A solution of **1** (810 mg, 7 mmol) in dichloromethane (40 mL) was cooled to −78 °C under nitrogen, and a solution of *m*-TFBSP (1.58 g, 3.5 mmol) in dichloromethane (40 mL) was added dropwise with stirring. A bright yellow color developed. After the addition was complete, the mixture was stirred for 5 h and then filtered through a 2-in. glass fritted funnel filled with silica gel and cooled to −78 °C. The yellow homogeneous filtrate was stirred at room temperature until the active oxygen was gone (usually overnight). Workup as in method A gave **11** (60%) as determined by VPC (column D). Also present was starting amine **1** (32%), which had passed through the silica gel filter as the ammonium salt.

1-Butylcyclohexylamine (2). Method A was used to convert **2** to 2-butyl-1-azacycloheptene (**12**)[26] in 68% yield by VPC (column A). The crude product showed only traces of **2** and could be readily purified by Kugelrohr distillation. Method B gave **12** in 38% yield, and the product was contaminated with higher molecular weight products.

1-Benzylcyclohexylamine (3). Method A was used to convert **3** to 2-benzyl-1-azacycloheptene (**13**) in 42% yield by VPC (column B). Due to the flocculent nature of the *p*-nitrobenzenesulfonate salt of **3**, the reaction was filtered through a cooled (−78 °C) frit before filtering through silica gel. ^{1}H NMR δ 1.22 (m, 2 H, ring H), 1.65 (m, 2 H, ring H), 1.70 (m, 2 H, ring H), 2.28 (m, 2 H, allylic H), 3.56 (s, 2 H, benzylic H), 3.62 (m, 2 H, $CH_2N=$), 7.27 (m, 5 H, aromatic H); IR (cm^{-1}) 3120–3600, 3080, 3058, 3020, 2920, 2840, 1710, 1655; MS *m/e* 188 (P + 1), 187 (P). As seen from the IR spectrum, the imine was accompanied by a small amount of ring-opened keto amine form. Thus **13** was reduced with sodium borohydride[27] to 2-benzylazacycloheptane (82%), which was treated with *p*-nitrobenzoyl chloride in pyridine to give the *p*-nitrobenzamide (90%). Recrystallization from ethanol–water gave an analytical sample, mp 139–140 °C. Calcd for $C_{20}H_{22}N_2O_3$: C, 70.98; H, 6.55; N, 8.28. Found: C, 70.80; H, 6.51; N, 8.26.

1-Methylcyclopentylamine (4). Method A was used to convert **4** to 2-methyl-1-azacyclohexene (**14**)[25] in 42% yield by VPC (column A). The crude product was easily purified by Kugelrohr distillation to a clear oil: ^{1}H NMR δ 1.44–1.80 (m, 4 H, ring H), 1.90 (s, 3 H, CH_3), 2.10 (m, 2 H, allylic H), 3.49 (m, 2 H, $CH_2N=$); IR (cm^{-1}) 2913, 2830, 1663, 1530, 1440, 1368. Use of Method B gave **14** in 65% yield.

1-Butylcyclopentylamine (5). Method A was used to convert **5** to 2-butyl-1-azacyclohexene (**15**)[25] in 79% yield by VPC (column D). The crude product was easily purified by Kugelrohr distillation to give a clear oil: ^{1}H NMR δ 0.88 (t, 3 H, CH_3), 1.2–1.9 (m, 8 H, methylene H), 2.16 (m, 2 H, allylic H), 3.53 (m, 2 H, $CH_2N=$); IR (cm^{-1}) 2922, 2860, 1662, 1535, 1460. Use of method B gave **15** in 60% yield. Method C gave **15** in 54% yield, but the product was contaminated with starting amine **5** (65%), whose salt was not retained on the silica gel during filtration.

1-Benzylcyclopentylamine (6). Method A was used to convert **6** to 2-benzyl-1-azacyclohexene (**16**) in 63% by VPc (column B). Due to the flocculent nature of the *p*-nitrobenzenesulfonate salt of **6**, the reaction mixture was filtered through a cold fritted glass funnel before filtering through silica gel. Product **16**: ^{1}H NMR δ 1.40–1.86 (m, 4 H, ring H), 2.0 (m, 2 H, allylic H), 3.46 (s, 2 H, benzylic H), 3.98 (m, 2 H, $CH_2N=$); IR (cm^{-1}) (3080, 3055, 3020, 2932, 2860, 1657, 1562, 1450. Preparative VPC (Column D) gave an analytical sample. Calcd for $C_{12}H_{15}N$: C, 83.17; H, 8.72; N, 8.08. Found: C, 82.80; H, 8.49; N, 8.00.

***exo*-2-Amino-2-methylnorbornane (7).** Method A was used to convert **7** to a mixture of **17a** and **17b** in 51% by VPC (column D). Since these isomers could not be resolved by VPC, the mixture was reduced with $NaBH_4$[27] to a mixture of 3-methyl-2-azabicyclo[3.2.1]octane and 2-methyl-3-azabicyclo[3.2.1]octane (1:4). A sample of the latter isomer was collected by preparative VPC (column D): ^{1}H NMR δ 0.92 (d, 3 H), 1.36–1.82 (m, 6 H), 1.86 (br s, 1 H), 2.08 (br m, 1 H), 5.24–5.80 (m, 3 H); IR (cm^{-1}) 3600–3040, 2930, 2860, 2800, 1455, 1370; exact mass calcd for $C_8H_{15}N$: 125.1205. Found: 125.1201. Methyl migration in **7a** was ruled out by hydrolysis of the crude product with 2.5 M HCl

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and steam distillation. No norcamphor was detected in organic extracts of the steam distillate. Method B gave a yield of 50% of **17** in the same ratio.

1-Butyl-2-methylcyclohexylamine (8). When **8** was subjected to the reaction conditions of method A, the solution remained homogeneous due to the greatly increased solubility of the *p*-nitrobenzenesulfonate salt, and the salt was not retained on the silica gel in the filtration step. The only identifiable product was the starting amine **8** (1.48 equiv out of 2 equiv). Method B gave the same result.

1-Butyl-2-methylcyclopentylamine (9). Use of method A failed to yield any product except the starting amine **9**. As seen for **8**, the reaction remained homogeneous, and the salt was not retained of the silica gel filter.

1-Butyl-3-methylcyclohexylamine (10). Use of method A failed to yield any product except starting amine **10**. As seen for **8**, the reaction remained homogeneous, and the salt was not retained on the silica gel filter.

Rearrangement of *N*-(1-Benzylcyclohexyl)hydroxylamine (22). A solution of **22** (500 mg, 2.44 mmol) and triethylamine (530 mg, 5.24 mmo) in dry THF (15 mL) was cooled to −30 °C, and a solution of *p*-nitrobenzenesulfonyl chloride (540 mg, 2.44 mmol) in dry THF (10 mL) was added dropwise over 10 min. The solution was stirred at −30 °C for 1 h and allowed to warm to room temperature. After 4 h at room temperature, during which time a heavy precipitate formed, the mixture was filtered, and the filtrate was stirred with 10% sodium hydroxide for 30 min. The layers were separated, the basic layer was extracted with dichloromethane (3 × 30 mL), and the combined organic fraction was dried ($MgSO_4$) and evaporated. The resulting pale yellow oil was dried in vacuo to give **13** (390 mg, 85%).

Rearrangement of *N*-(1-Butylcyclohexyl)hydroxylamine (23). By the procedure described above, **23** (340 mg, 1.96 mmol) was reacted with *p*-nitrobenzenesulfonyl chloride (430 mg, 1.96 mmol) and triethylamine (450 mg, 4.4 mmol) to give 12 (170 mg, 53%). Also present was **2** (10%). The same conversion could be accomplished in 44% by first making the potassium salt of **23** with KH in THF at −78 °C and then adding the sulfonyl chloride solution. After reaction for 3 h, the solution was warmed to room temperature and the above procedure continued.

Rearrangement of *N*-(1-Butyl-2-methylcyclohexyl)hydroxylamine (24). By the procedure described above, **24** (350 mg, 1.9 mmol) was reacted with *p*-nitrobenzenesulfonyl chloride (420 mg, 1.9 mmol) and triethylamine (400 mg, 4 mmol) to give a mixture of ring-expanded imines **26**–**29** (78%), of which the major component was **26** (57%). Imine **26** was isolated by preparative VPC (column D) as a clear oil: ^1H NMR δ 0.90 (t, 3 H, butyl CH_3), 1.03–1.83 (m, 10 H, methylene H), 2.05 (d, 3 H, CH_3), 2.26 (m, 2 H, allylic H), 2.46 (m, 2 H, allylic H), 3.22 (m, 1 H, CHN=); IR (cm^{-1}) 2920, 2850, 1710 (weak), 1658, 1442; MS *m/e* 167 (P), 152 (P − 15), 138, 124, 110 (P − 57), 95. As seen in the IR, a small amount of ring opening was observed in the imine. Therefore the imine was reduced with $NaBH_4$[27] to 2-butyl-7-methyl-1-azacycloheptane; exact mass calculated for $C_{11}H_{23}N$, 169.1832; found, 169.1832.

The other imine components could not be collected in sufficient amounts and purity for full characterization; however, GC–MS showed them to have parent ions of 167, indicating them to be isomeric with **26**. Reduction of the crude imine product gave 63% of 2-butyl-7-methyl-1-azacycloheptane, which is in the reduction product of both **26** and **27**. Two other minor components were shown by GC–MS to have parent ions of 169; thus they are likely the reduction products of **28** and **29**. They were not further studied. Use of KH as described above gave a mixture of the imine products in 54% yield.

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Registry No. 1, 6526-78-9; **1a**, 96913-39-2; **2**, 2626-61-1; **2a**, 114635-54-0; **3**, 19165-94-7; **3a**, 114635-55-1; **4**, 40571-45-7; **4a**, 114635-56-2; **5**, 68288-41-5; **5a**, 114635-57-3; **6**, 19165-95-8; **6a**, 114635-58-4; **7**, 51655-31-3; **7a**, 114635-59-5; **8**, 114635-60-8; **8**·HCl, 114635-61-9; **8a**, 114635-62-0; **9**, 114635-63-1; **9**·HCl, 114635-64-2; **9a**, 114635-65-3; **10**, 114635-66-4; **10**·HCl, 114635-67-5; **10a**, 114635-68-6; **11**, 3338-03-2; **12**, 3338-06-5; **13**, 3338-08-7; **14**, 1462-92-6; **15**, 1462-94-8; **16**, 95018-41-0; **17a**, 114635-69-7; **17b**, 114635-70-0; **21**, 114635-71-1; **22**, 114635-72-2; **23**, 114635-73-3; **23**·K, 114635-74-4; **24**, 114635-75-5; **25**, 114635-76-6; **26**, 114635-77-7; **27**, 114635-78-8; **28**, 114635-79-9; **29**, 114635-80-2; *p*-NBSP, 6209-72-9; *m*-TFBSP, 35673-10-0; *N*-phenylcyclohexylimine, 1132-38-3; *n*-butylmagnesium bromide, 693-03-8; 2-methylcyclohexanone, 583-60-8; 2-(*n*-butyl)-1-methylcyclohexylamine, 114635-81-3; 2-methylcyclopentanone, 1120-72-5; 3-methylcyclohexanone, 591-24-2; 1-benzyl-1-nitrocyclohexane, 70367-75-8; 1-butyl-1-nitrocyclohexane, 92540-95-9; 1-butyl-2-methyl-1-nitrocyclohexane, 114635-82-4; 2-benzylazocycloheptane, 68840-81-3; *p*-nitrobenzoyl chloride, 122-04-3; 1-(*p*-nitrobenzoyl)-2-benzylazacycloheptane, 114635-83-5; *p*-nitrobenzenesulfonyl chloride, 98-74-8; 2-butyl-7-methyl-1-azocycloheptane, 114635-84-6.

Oxiranes from Methylenation of the Ester Carbonyl Group by Diazomethane

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Esters suitably substituted by electronegative groups were found to react with diazomethane with the anchimeric assistance of a π-system or a trifluoromethyl group close to the ester oxygen to yield 2-alkoxy-2-substituted-oxiranes in good to excellent yields without catalysts.

The addition of methylene to the carbonyl π-bond (1) of aldehydes and ketones with diazomethane to yield homologated carbonyl compounds and/or oxiranes is well established.[1] On the other hand, there are only two recorded instances of the latter reaction with the ester carbonyl, one in which diazoethane reacted with a complex lactone, i.e., a pyrazoline derivative of 3-nitrocoumarin (unreported yield),[2] and the other upon irradiation of a diazomethane solution containing methyl formate or acetate.[3]

The initial step is assumed to be the nucleophilic attack of the diazoalkane on the carbonyl to yield the zwitterion

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