From 100 mg (0.54 mmol) of **27b** and 70 mg (0.50 mmol) of dimethyl acetylenedicarboxylate in 10 ml of ether (48 hr, 25°), there was obtained 130 mg (76.4%) of **38**: mp 116–117° (from ether); ν_{max}^{KBr} 1755, 1718, 1310, 1160, and 1138 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.40–6.70 (m, 2, vinyl), 4.00–4.45 (m, 2, bridgehead), 3.60–3.85 (m, 1, >CHN<), 3.75 (s, 6, carboxylate methyls), 3.00–3.25 (m, 2, $-CH_2N<$), 2.81 (s, 3, CH_3SO_2-), and 2.50–2.90 (m, 1, methine).

Anal. Calcd for $C_{14}H_{17}NO_6S$: C, 51.37; H, 5.23. Found: C, 51.57; H, 5.40.

O-Methylation of 36a.—A mixture of 6.49 g (24 mmol) of **36a** and 3.5 g (2.8 mmol) of trimethyloxonium fluoroborate in 60 ml of dry methylene chloride was stirred at 0° for 10 hr. Aqueous sodium carbonate solution was carefully added until the solution became neutral. The organic layer was separated, washed with water, dried, and evaporated to give a viscous oil. This oil was dissolved in 50 ml of anhydrous ether and ethanolic perchloric acid (1:1) was added dropwise with cooling until the supernatant liquid showed no cloudiness. Filtration of the crystals, followed by thorough rinsing with ether and drying, afforded 7.86 g (86%) of **37** perchlorate, mp 162–164.5° (from methanol). Liberation of the free base from the purified perchlorate furnished **37** as a colorless crystalline solid: mp 85–87° (from ether–pentane); $\nu_{max}^{CCl_4}$ 1745, 1725, 1635, 1623, and 1603 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.54–6.73 (m, 2, vinyl), 3.99 (s, 9, $-OCH_3$), 3.90–4.25 (m, 2, bridgehead), 1.61 and 1.49 (s, 3 and 3, methyls).

Anal. Calcd for $C_{16}H_{19}NO_5$: C, 62.95; H, 6.27; N, 4.59. Found: C, 63.22; H, 6.27; N, 4.52.

Registry No.—**4**, 27070-39-9; **8**, 24321-92-4; **10**, 27062-83-5; **16**, 27062-84-6; **17**, 27062-85-7; **19**, 27062-86-8; **20**, 27062-87-9; **24**, 27062-88-0; **25a**, 27062-89-1; **25b**, 27062-90-4; **26a**, 27062-91-5; **26b**, 27062-92-6; **27a**, 27062-93-7; **27a** *N*-phenylmaleimide adduct, 27062-94-8; **27b**, 27062-95-9; **27b** *N*-phenylmaleimide adduct, 27062-96-0; **36a**, 27111-68-8; **36b**, 27062-43-7; **37**, 27062-44-8; **37** perchlorate, 27062-45-9; **38**, 27062-46-0.

Acknowledgment.—The authors are grateful to the National Institutes of Health and the Lilly Research Laboratories for grants which contributed to the financial support of this research.

Neighboring-Group Participation by Sulfonamide Nitrogen. The 7-Azabicyclo[4.2.0]oct-3-ene to 6-Azabicyclo[3.2.1]oct-2-ene Rearrangement[1]

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The addition of bromine to *N*-sulfonyl derivatives of 1,6-dimethyl-7-azabicyclo[4.2.0]oct-3-ene (**3**) resulted in skeletal rearrangement and formation of *N*-sulfonyl-1,2-dimethyl-4-bromo-6-azabicyclo[3.2.1]oct-2-enes (30–37%). The structures (including exo stereochemistry for the bromo substituent) were assigned on the basis of their 100-MHz nmr spectra, their ready dehydrohalogenation to conjugated dienes, and the chemical behavior of these dienes. The rearrangements probably proceed by way of intramolecular SN2 displacement of trans-disposed bromine by neighboring sulfonamide nitrogen. Furthermore, a significant portion of **3** undergoes rupture of the azetidine ring with ultimate formation of dibromide **5** and the derived sulfonamide. A possible mechanism is presented.

Despite the extensive amount of research which has been accorded to skeletal rearrangements of carbobicyclic structures, similar transformations of related nitrogen heterocycles are notably few in number at the present time. The first reported example appears to be the racemization of L-(+)-2-α-tropanol,[2] which proceeds with participation of an amino nitrogen. At a later date, the isoquinuclidine system was shown to be particularly prone to conversion into derivatives of azabicyclo[3.2.1]octane, even when neighboring-group participation by amide nitrogen is required.[3] More recently, skeletal rearrangement of bicylic nitrenium ions has been demonstrated to be a general reaction type.[4] In the course of work directed at the synthesis of polyolefinic medium-ring nitrogen compounds,[1] we observed an unprecedented and unusual example of sulfonamide nitrogen migration with skeletal reorganization. In this paper we describe the details of several such transformations together with a number of affiliated chemical changes.

Results

cis-1,6-Dimethyl-7-azabicyclo[4.2.0]oct-3-ene (**2**) was prepared by treating previously described β-lactam **1**[5] with lithium aluminum hydride. Reaction of **2** with *p*-toluenesulfonyl, benzenesulfonyl, and methanesulfonyl chlorides readily afforded **3a**, **3b**, and **3c**, respectively. After addition of bromine to **3a** at 0°, the product was refluxed in hexane for 30 min. Direct crystallization of the reaction mixture led to the isolation of **4b** in 37% yield; chromatographic purification of the residual material on silica gel afforded 4,5-dibromo-4,5-dimethyl-1-cyclohexene (**5**, 17%), *p*-toluenesulfonamide (**6**, 29%), and a dibromosulfonamide identified as **7** (12%). *N*-Sulfonylazetidines **3b** and **3c** have similarly been found to undergo ready conversion to **4b** and **4c**. The structures of **4a–4c** follow from analyses, infrared and ultraviolet, and particularly nmr spectra. Spin-decoupling studies of **4b** at 100 MHz, for example, showed that vinyl proton H_c is coupled vicinally to H_d (J = 4.4 Hz), allylically to the low field methyl absorp-

(1) Unsaturated Heterocyclic Systems. LXXVIII. For the previous paper in this series, see L. A. Paquette, T. Kakihana, and J. F. Kelly, *J. Org. Chem.*, **36**, 435 (1971).

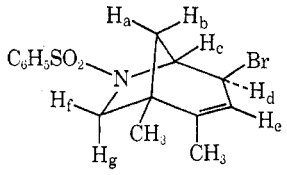
(2) S. Archer, T. R. Lewis, M. R. Bell, and J. W. Schulenberg, *J. Amer. Chem. Soc.*, **83**, 2386 (1961).

(3) (a) G. Büchi, D. L. Coffen, K. Kocsis, P. E. Sonnet, and F. E. Ziegler, *ibid.*, **88**, 3099 (1966); (b) J. W. Huffman, T. Tamiya, and C. B. S. Rao, *J. Org. Chem.*, **32**, 700 (1967), and pertinent references cited in these papers; (c) J. D. Hobson and W. D. Riddell, *Chem. Commun.*, 1178 (1968).

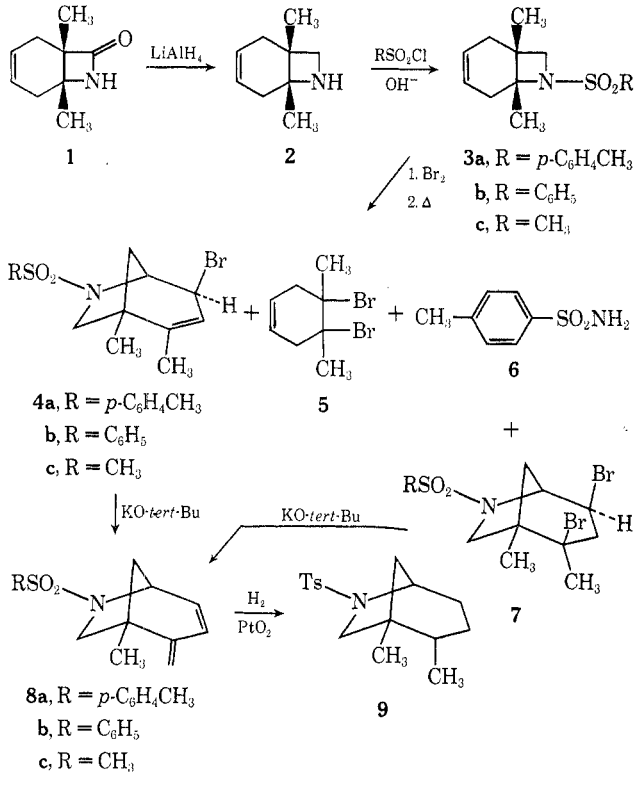
(4) P. G. Gassman, *Accounts Chem. Res.*, **3**, 26 (1970).

(5) L. A. Paquette, T. Kakihana, J. F. Hansen, and J. C. Philips, *J. Amer. Chem. Soc.*, **93**, 152 (1971); L. A. Paquette and T. Kakihana, *ibid.*, **90**, 3897 (1968).

tion (J = 1.3 Hz), and long range to H_e (J = 1.5 Hz) because of their W-plan arrangement. The expected

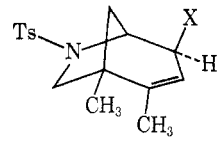


magnetic nonequivalence of the two sets of methylene protons was clearly in evidence, there being the predictable $J_{a,b}$ = 11.3 Hz and $J_{f,g}$ = 8.4 Hz. Furthermore, the differing long-range interactions of the individual methylene bridge protons ($J_{b,g}$ = 1.5 Hz, $J_{a,d} \approx$ 0.5 Hz) clearly attests to the determinative influence exerted by the rigid molecular skeleton in enforcing two



somewhat unequivalent W-plan atomic arrangements. In a result that stems from differing dihedral angle relationships,[6] H_c is strongly coupled to H_a ($J_{a,c}$ = 5.5 Hz), but very weakly spin related to H_b ($J_{b,c} < 0.5$ Hz). The stereochemistry at C_4, the halogen-bearing center, was established as exo on the basis of the previously mentioned long-range spin interaction of H_d with H_a and the magnitude of its coupling constants with H_e (4.4 Hz) and H_c (1.5 Hz).[7]

The most direct proof of structure for **4a–4c** is based on their dehydrohalogenation in the presence of potassium *tert*-butoxide which proceeds smoothly to give the conjugated dienes **8a–c**, respectively. Ultraviolet absorption bands of these sulfonamides at 235–239 nm (ϵ 10,000–12,000) indicate the introduction of extended conjugation,[8] whereas the presence of two singlets in the δ 4.9 region are diagnostic for the presence of a terminal methylene group.[7a] Catalytic reduction of **8a** over Adams' catalyst proceeded rapidly with the uptake of 2 mol of hydrogen to give **9**. The conjugated nature of the diene moiety in **8a** was additionally evident in its capability to react with various reagents by way of 1,4 addition. For example, dissolution of **8a** in aqueous hydrobromic acid at room temperature regenerated **4a**, whereas exposure to aqueous hydrochloric acid and methanol afforded **10a** and **10b**, respectively. The

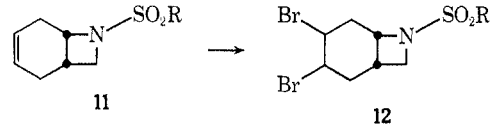


10a, X = Cl
b, X = OCH_3

exo stereochemistry of the functional groups newly introduced in these reactions follows from the nmr spectra of the products, the previously established configuration of **4**, and the recognized preference of bicyclo[3.2.1]oct-2-enes to give rise to products of exo attack at the allylic site.[9]

Discussion

The rearrangement of **3** to **4** represents a unique situation involving a 1,4 shift of sulfonamide nitrogen. The fact that this rearrangement does not occur in the related structures (**11** → **12**) lacking the two methyl substituents (which brominate normally and are thermally stable[1]) indicates that considerable cationic character develops at the carbon center to which the nitrogen substituent is originally attached; *i.e.*, the developing tertiary carbonium ion in **3** renders the process energetically feasible.



11 **12**

With this in mind, it is now possible to view the rearrangement as involving ionization of the C–N bond to place a negative charge on nitrogen, thereby endowing it with significant nucleophilic character. At this stage, two possibilities exist: the sulfonamide functionality could intramolecularly displace a trans-disposed bromine at C_4 (*cf.* **13**) to give **15**; or, the SN2 displacement could occur at C_3 in **16** to give **4**. However, no products corresponding to **15** are observed. Although this may signify that **3** is brominated exclusively to afford trans dibromide **16**, this conclusion is not totally unequivocal since a significant portion of **3** is diverted to an alterna-

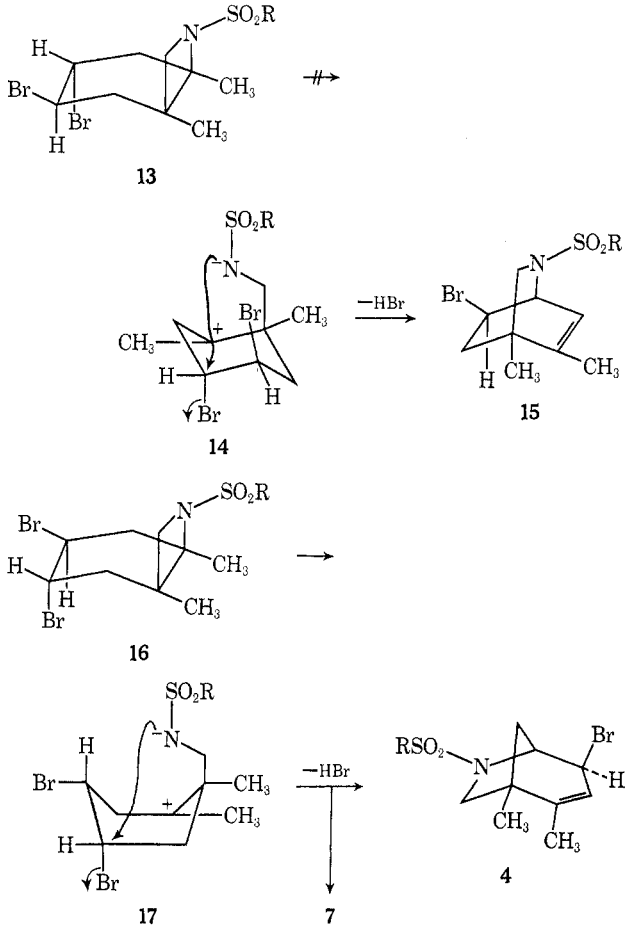
(6) M. Karplus, *J. Amer. Chem. Soc.*, **85**, 2870 (1963); *J. Chem. Phys.*, **30**, 11 (1959).

(7) We wish to draw attention to the striking parallel between the vicinal, allylic, and long-range couplings experienced by **4a–4c** and related interactions in the bicyclo[3.2.1]oct-2-ene system: C. W. Jefford, J. Gunsher, and K. C. Ramey, *J. Amer. Chem. Soc.*, **87**, 4384 (1965), and earlier references cited therein.

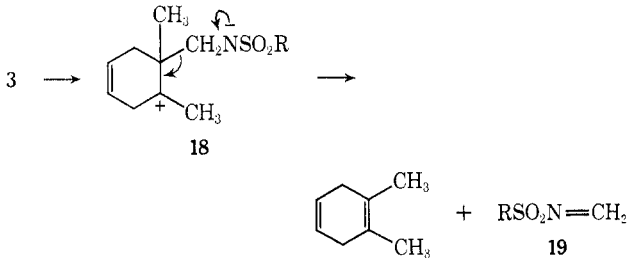
(8) Compare the ultraviolet spectrum of 3-bromo-4-methylenebicyclo[3.2.1]oct-2-ene: $\lambda_{max}^{cyclohexane}$ 242 nm (ϵ 20,000) [ref 7a and C. W. Jefford and W. Wojnarowski, *Tetrahedron Lett.*, 199 (1968)].

(9) C. W. Jefford and E. H. Yen, *ibid.*, 4477 (1966).

tive fragmentation pathway leading to the formation of dibromide **5** and *p*-toluenesulfonamide (**6**).



The genesis of **5** and **6** would appear to be founded also in the lability of the more highly substituted C–N bond in **3** under the conditions of bromination. This concomitant reaction could involve initial heterolytic fragmentation of **3** to give **18**, followed by ejection of **19** and production of 1,2-dimethyl-1,4-cyclohexadiene.



Hydrolysis of **19** during the work-up would rationalize the isolation of **6** and related sulfonamides, whereas selective bromination of the diene (also established independently) would give **5**. The remarkable observation that rupture of the C–N bond in **3** is facilitated in the presence of molecular bromine merits further consideration.

Experimental Section[10]

1,6-Dimethyl-7-azabicyclo[4.2.0]oct-3-ene (2).—To a stirred suspension of 12.0 g (0.32 mol) of lithium aluminum hydride in 300 ml of anhydrous tetrahydrofuran was added dropwise a solution of 50 g (0.32 mol) of **1**[5] in 150 ml of the same solvent. The resulting mixture was stirred at reflux for 30 hr, cooled in ice, and treated sequentially with 12 ml of water, 12 ml of 30% sodium hydroxide solution, 25 ml of water, and finally 10 g of anhydrous magnesium sulfate. The solids were separated by filtration, the filtrate was evaporated, and the residue was distilled to give 28 g (62%) of **2**: bp 57° (2 mm); ν_{max}^{neat} 3205 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 6.10–6.25 (m, 2, vinyl), 3.20 (s, 2, $-CH_2-N<$), 1.85–2.10 (m, 4, allyl), 1.45–1.75 (m, 1, >NH), 1.29 and 1.20 (s, 3 each, methyls).

Anal. Calcd for $C_9H_{15}N$: C, 78.77; H, 11.02. Found: C, 78.78; H, 11.26.

From the residue of the distillation, 5.5 g (11%) of β-lactam **1** was recovered.

***N*-*p*-Toluenesulfonyl-1,6-dimethyl-7-azabicyclo[4.2.0]oct-3-ene (3a).**—To a vigorously stirred mixture of 13.7 g (0.10 mol) of **2** and 100 ml of 30% aqueous sodium hydroxide solution cooled in an ice bath was added 23 g (0.12 mol) of tosyl chloride in small portions during 10 min. The mixture was stirred for 30 min at room temperature and extracted with ether (four 50-ml portions). The combined ether extracts were dried, filtered, and evaporated to give 29 g (100%) of **3a**: mp 69–70°; ν_{max}^{KBr} 1340, 1330, and 1160 cm^{-1}.

Anal. Calcd for $C_{16}H_{21}NO_2S$: C, 65.94; H, 7.26; N, 4.82. Found: C, 65.92; H, 7.29; N, 4.82.

***N*-Benzenesulfonyl-1,6-dimethyl-7-azabicyclo[4.2.0]oct-3-ene (3b)** was obtained analogously in quantitative yield, mp 86–87°.

Anal. Calcd for $C_{15}H_{19}NO_2S$: C, 64.96; H, 6.91; N, 5.05. Found: C, 64.83; H, 6.99; N, 5.07.

***N*-Methanesulfonyl-1,6-dimethyl-7-azabicyclo[4.2.0]oct-3-ene (3c).**—From 3.0 g (0.022 mol) of **2** and 4.0 g (0.026 mol) of methanesulfonyl chloride, there was obtained 4.1 g (82%) of **3c**, mp 60–61°.

Anal. Calcd for $C_{10}H_{17}NO_2S$: C, 55.78; H, 7.96; N, 6.51. Found: C, 55.78; H, 7.95; N, 6.41.

Reaction of 3a with Bromine.—To an ice-cold stirred solution of 2.91 g (0.01 mol) of **3a** in 15 ml of methylene chloride was added dropwise 1.6 g (0.01 mol) of bromine. The solvent was evaporated and the residue was refluxed with 50 ml of hexane for 30 min. The residue was then extracted with additional boiling hexane (five 20-ml portions), and the combined hydrocarbon extracts were permitted to stand at −20° for 3 days. The precipitated solid was removed by filtration and recrystallized from hexane to give 1.25 g (36.8%) of **4a**: mp 152–154°; ν_{max}^{KBr} 1335 and 1155 cm^{-1}; $\lambda_{max}^{isooctane}$ 230 nm (ε 11,800);[11] $\delta_{TMS}^{CDCl_3}$ 7.25–7.85 (AB pattern, 4, aryl), 5.40–5.60 (m, 1, vinyl), 4.65–4.90 (m, 1, >CH-Br), 4.15–4.40 (m, 1, $>CH-N<$), 3.05 (AB pattern, J_{AB} = 9 Hz, $\Delta\nu_{AB}$ = 27 Hz, B portion exhibits fine splitting, J = 1.5 Hz, $-CH_2N<$), 2.45 (s, 3, aryl methyl), 2.08 (dd, J = 1.3 and 12 Hz, 1, bridge methylene proton), 1.73 (t, J = 1.2 Hz, 3, allylic methyl), 1.31 (dd, J = 6 and 12 Hz, 1, other bridge proton), and 1.11 (s, 3, saturated methyl).

Anal. Calcd for $C_{16}H_{20}BrNO_2S$: C, 51.89; H, 5.44; N, 3.78. Found: C, 51.92; H, 5.50; N, 3.69.

The filtrate from above was concentrated and chromatographed on silica gel. Elution with hexane gave 0.30 g (17%) of 4,5-dibromo-4,5-dimethylcyclohex-1-ene (**5**), mp 140–141°, which was identical in all respects with the monobromination product of 1,2-dimethyl-1,4-cyclohexadiene:[12] $\delta_{TMS}^{CDCl_3}$ 5.72 (m, 2, vinyl), 2.80–2.97 (m, 4, allyl), and 2.00 (s, 6, methyls).

Elution with hexane–ether (4:1) afforded 550 mg (12.2%) of **7**: mp 149–150°; ν_{max}^{KBr} 1335 and 1150 cm^{-1} (SO_2); $\delta_{TMS}^{CDCl_3}$ 7.20–7.85 (AB pattern, 4, aryl), 4.00–4.50 (m, 2, >CHBr and >CHN<), 3.48 (d, J = 11 Hz, 1), 2.90 (d, J = 11 Hz, 2), 2.59 (d, J = 4 Hz, 2), 2.41, 1.71, and 1.14 (singlets, 3 each, methyls), and 1.0–1.30 (m, 1).

Anal. Calcd for $C_{16}H_{21}Br_2NO_2S$: C, 42.59; H, 4.80; N, 3.17. Found: C, 42.74; H, 4.76; N, 3.02.

Elution with ether–hexane (3:2) led to the isolation of 0.50 g (29.2%) of *p*-toluenesulfonamide (**6**), mp 137°, identical with an authentic sample prepared from tosyl chloride and ammonia.

Reaction of 3b with Bromine.—Treatment of 20.0 g (0.072 mol) of **3b** with 11.6 g (0.072 mol) of bromine in the predescribed manner afforded 7.95 g (31%) of **4b**: mp 149–151°; ν_{max}^{KBr}

(10) Melting points were taken in open capillaries and are corrected, while boiling points are uncorrected.

(11) For the ultraviolet spectrum of *p*-toluenesulfonamide hydrate in ethanol, consult L. Lang, Ed., "Absorption Spectra in the Ultraviolet and Visible Region," Vol. 2, Academic Press, New York, N. Y., 1961, Spectrum No. 117.

(12) L. A. Paquette and J. H. Barrett, *Org. Syn.*, **49**, 62 (1969).

1375, 1190, and 1180 cm^{-1}; $\lambda_{max}^{isooctane}$ 223 nm (ϵ 11,400), $\delta_{TMS}^{CDCl_3}$ 7.40–8.00 (m, 5, aryl), 5.40–5.55 (m, 1, vinyl), 4.65–4.85 (m, 1, >CHBr), 4.15–4.40 (m, 1, H_c), 3.04 (AB pattern, J_{AB} = 8.4 Hz, $\Delta\nu_{AB}$ = 27 Hz, B portion exhibits fine splitting, J = 1.5 Hz, 2, -CH_2N<), 2.08 (dd, J = 11.3 and 1.5 Hz, H_b), 1.73 (t, J = 1.3 Hz, 3, allylic methyl), 1.28 (dd with fine splitting, J = 11.3 and 5.5 Hz, H_a), and 1.11 (s, 3, methyl).

Anal. Calcd for $C_{15}H_{18}BrNO_2S$: C, 50.57; H, 5.09; N, 3.93; Br, 22.43. Found: C, 50.44; H, 5.15; N, 3.92; Br, 22.82.

Chromatography of the residue afforded products analogous to those obtained with **3a**.

Reaction of 3c with Bromine.—Treatment of 1.15 g (5.0 mmol) of **3c** with 0.8 g (5.0 mmol) of bromine as described above gave 0.50 g (32.5%) of **4c**: mp 130–132°; ν_{max}^{KBr} 1320, 1170, 1150, and 1143 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 5.45–5.65 (m, 1, vinyl), 4.65–4.85 (m, 1, >CHBr), 4.20–4.45 (m, 1, >CHN<), 2.90–3.30 (m, 2, -CH_2-N<), 2.90 (s, 3, -SO_2CH_3), 2.15–2.50 (m, 1, bridge methylene proton), 1.20–1.70 (m, 1, other bridge proton), 2.80 (t, J = 1.3 Hz, 3, allylic methyl), and 1.29 (s, 3, methyl).

Anal. Calcd for $C_{10}H_{16}BrNO_2S$: C, 40.82; H, 5.48; N, 4.76. Found: C, 40.77; H, 5.44; N, 4.60.

Chromatography of the residue afforded products analogous to those obtained with **3a**.

Dehydrohalogenation of 4a.—To an ice-cold stirred solution of 1.1 g (2.7 mmol) of **4a** in 15 ml of dry tetrahydrofuran was added a suspension of 560 mg (5.0 mmol) of potassium *tert*-butoxide in 15 ml of the same solvent. The mixture was stirred at 0° for 15 min and the solvent was evaporated *in vacuo*. The residue was extracted with boiling ether (two 25-ml portions) and the combined extracts were filtered and evaporated. Recrystallization of the residue from hexane gave 650 mg (92.2%) of **8a**: mp 109–111°; ν_{max}^{KBr} 1335 and 1165 cm^{-1}; $\lambda_{max}^{ethanol}$ 235 nm (ϵ 12,000); $\delta_{TMS}^{CDCl_3}$ 7.20–7.90 (AB pattern, 4, aryl), 6.00–6.20 (m, 2, ring vinyls), 4.82 and 4.92 (s, 1 each, exo methylenes), 4.30–4.65 (m, 1, bridgehead), 3.22 (s, 2, -CH_2N<), 2.45 (s, 3, aryl methyl), 1.45–1.85 (m, 2, bridge methylenes), and 1.30 (s, 2, methyl).

Anal. Calcd for $C_{16}H_{19}NO_2S$: C, 66.40; H, 6.59; N, 4.84. Found: C, 65.96; H, 6.62; N, 4.75.

Dehydrohalogenation of 4b.—From 1.75 g (4.0 mmol) of **4b**, there was obtained 1.05 g (94.4%) of **8b**: mp 83–84°; ν_{max}^{KBr} 1335 and 1165 cm^{-1}; $\lambda_{max}^{isooctane}$ 233 nm (ϵ 12,800); $\delta_{TMS}^{CDCl_3}$ 7.40–8.00 (m, 5, aryl), 5.95–6.15 (m, 2, ring vinyls), 4.82 and 4.92 (s, 1 each, exo methylenes), 4.30–4.55 (m, 1, bridgehead), 3.22 (s, 2, -CH_2N<), 1.45–1.85 (m, 2, bridge methylenes), and 1.28 (s, 3, methyl).

Anal. Calcd for $C_{15}H_{17}NO_2S$: C, 65.43; H, 6.22; N, 5.08. Found: C, 65.30; H, 6.29; N, 5.06.

Dehydrohalogenation of 4c.—From 930 mg (3.3 mmol) of **4c**, there was obtained 110 mg (16%) of crude **8c**, mp 53–57°. This compound could not be purified because of decomposition and apparent polymerization: ν_{max}^{KBr} 1330 and 1152 cm^{-1}; $\lambda_{max}^{isooctane}$ 239 nm (ϵ 9780); $\delta_{TMS}^{CDCl_3}$ 6.18 (m, 2, ring vinyls), 4.90 and 4.97 (s, 1 each, exo methylenes), 4.15–4.55 (m, 1, bridgehead), 3.21 (AB pattern, J_{AB} = 11 Hz, $\Delta\nu_{AB}$ = 9 Hz, 2, -CH_2N<), 2.77 (s, 3, -SO_2CH_3), 1.65–2.10 (m, 2, bridge methylenes), and 1.38 (s, 3, methyl).

***N*-*p*-Toluenesulfonyl-1,2-dimethyl-6-azabicyclo[3.2.1]octane (9).**—A solution of 0.50 g of **8a** in 50 ml of ethanol was hydrogenated over 10% palladium on charcoal at 50 psig in a Parr apparatus. The usual processing gave 0.48 g (96%) of **9**: mp 115–116°; ν_{max}^{KBr} 1340, 1172, and 1163 cm^{-1}.

Anal. Calcd for $C_{16}H_{23}NO_2S$: C, 65.51; H, 7.90; N, 4.78. Found: C, 65.50; H, 7.90; N, 4.78.

Hydrobromination of 8a.—A mixture of 580 mg (2.0 mmol) of **8a** and 20 ml of 4 *N* hydrobromic acid was stirred at room temperature for 1 hr and then extracted with ether (three 25-ml portions). The combined extracts were dried, filtered, and evaporated to give 546 mg (74%) of **4a**, mp 152–154°, after recrystallization from hexane.

Hydrochlorination of 8a.—A mixture of 580 mg (2.0 mmol) of **8a** and 20 ml of 4 *N* hydrochloric acid was stirred at room temperature for 1 hr and then worked up as above to give 450 mg (71%) of **10a**: mp 118–119°; ν_{max}^{KBr} 1350, 1332, 1175, 1160, and 1150 cm^{-1}; $\delta_{TMS}^{CDCl_3}$ 7.25–7.85 (AB pattern, 4, aryl), 5.30–5.50 (m, 1, vinyl), 4.40–4.70 (m, 1, >CHCl), 4.05–4.30 (m, 1, >CHN<), 3.00 (AB pattern, J_{AB} = 8.5 Hz, $\Delta\nu_{AB}$ = 27 Hz, -CH_2N<), 2.42 (s, 3, aryl methyl), 2.04 (d with fine structure, J = 11 Hz, 1, bridge methylene proton), 1.74 (t, $J \approx$ 1 Hz, 3, allylic methyl), 1.20 (m, 1, other bridge proton), and 1.11 (s, 3, methyl).

Anal. Calcd for $C_{16}H_{20}ClNO_2S$: C, 58.97; H, 6.19; N, 4.30. Found: C, 58.77; H, 6.28; N, 4.24.

4-Methoxy-1,2-dimethyl-6-tosyl-6-azabicyclo[3.2.1]oct-2-ene (10b).—A solution of 290 mg (1.0 mmol) of **8a** in 15 ml of methanol was refluxed for 1 hr.[13] The solvent was evaporated and the residue was recrystallized from hexane to afford 240 mg (74.6%) of **10b**: mp 153–154°; ν_{max}^{KBr} 1337, 1178, and 1163 cm^{-1}; $\delta_{max}^{CDCl_3}$ 7.25–7.90 (AB pattern, 4, aryl), 5.30–5.65 (m, 1, vinyl), 4.00–4.35 (m, 1, >CHN<), 3.65–3.85 (m, 1, >CHO–), 3.44 (s, 3, -OCH_3), 2.97 (AB pattern, J_{AB} = 7.5 Hz, $\Delta\nu_{AB}$ = 29 Hz, with B coupled to anti bridge proton, J = 1 Hz, 2, -CH_2N<), 2.45 (s, 3, aryl methyl), 1.75 (t, J = 1.5 Hz, allylic methyl), *ca.* 1.83 (m partially masked by methyl absorption, 1, bridge methylene), 1.10 (s, 3, methyl), and *ca.* 1.05 (m, 1, other bridge methylene).

Anal. Calcd for $C_{17}H_{23}NO_3S$: C, 63.52; H, 7.21; N, 4.36. Found: C, 63.17; H, 7.22; N, 4.19.

Dehydrohalogenation of 7.—To a solution of 65 mg (0.14 mmol) of **7** in 5 ml of anhydrous tetrahydrofuran was added 47 mg (0.42 mmol) of powdered potassium *tert*-butoxide. After stirring at room temperature for 10 min, the solvent was evaporated and the residue was extracted with ether. The ether extract was filtered and evaporated, and the residue was recrystallized once from hexane to give 42 mg (78.5%) of **8a**, mp 108–110°.

Registry No.—**2**, 27070-26-4; **3a**, 27070-27-5; **3b**, 27070-28-6; **3c**, 27070-29-7; **4a**, 27111-67-7; **4b**, 27070-30-0; **4c**, 27070-31-1; **7**, 27070-32-2; **8a**, 27070-33-3; **8b**, 27070-34-4; **8c**, 27070-35-5; **9**, 27070-36-6; **10a**, 27070-37-7; **10b**, 27070-38-8.

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(13) This reaction is presumably catalyzed by traces of acid present in this solution.