Rearrangement of 2-Benzocycloammonium *N*-Methylides

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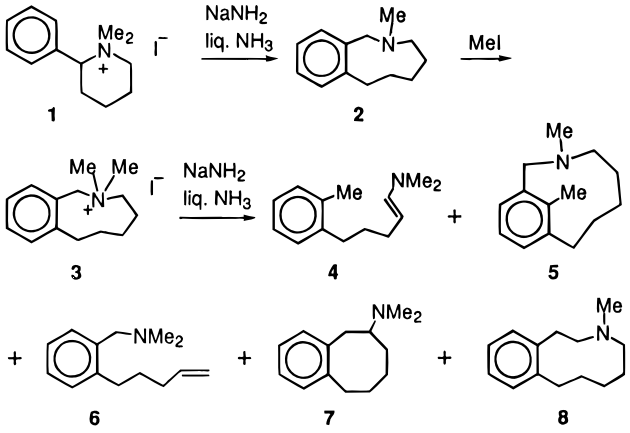
2-Methyl-2-[(trimethylsilyl)methyl]-2,3,4,5,6,7-hexahydro-1*H*-2-benzazoninium iodide (**9**), 2-methyl-2-[(trimethylsilyl)methyl]-1,2,3,4,5,6-hexahydro-2-benzazocinium iodide (**15**), and 2-methyl-2-[(trimethylsilyl)methyl]-2,3,4,5-tetrahydro-1*H*-2-benzazepinium iodide (**23**) exist as mixtures of two stable conformational isomers (types A and B) in an aprotic solvent at room temperature. The corresponding conformational isomers of *N*-methylides **10A**,**B**, **16A**,**B**, and **24A**,**B** were generated by fluoride ion-induced desilylation, and their rearrangement was investigated. Type A ylides gave [2,3] sigmatropic rearrangement products (isotoluenes) **11**, **17**, **18**, and **27**, while type B ylides gave Stevens rearrangement products **8**, **20**, and **29** via radical-cleavage and -recombination pathways.

Introduction

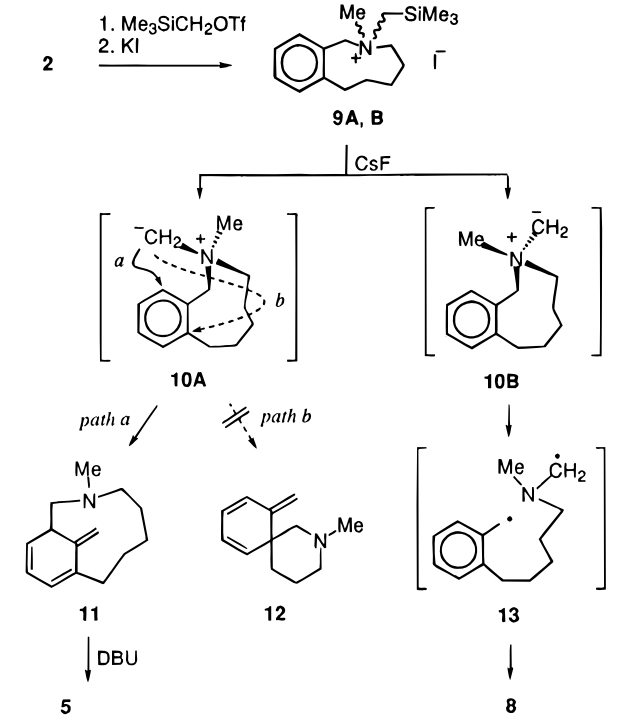
Sommelet−Hauser rearrangement of α-phenylcycloammonium *N*-methylides is useful for three-carbon ring enlargement of cyclic amines.[1,2] For example, 2-methyl-2,3,4,5,6,7-hexahydro-1*H*-2-benzazonine (**2**) was obtained in high yield by the reaction of 1,1-dimethyl-2-phenylpiperidinium iodide (**1**) with sodium amide in liquid ammonia.[2a] Hasiak and co-workers[3] reported that similar treatment of 2,2-dimethyl-2,3,4,5,6,7-hexahydro-1*H*-2-benzazoninium iodide (**3**) prepared from **2** gave a mixture of five amines (**4**−**8**), as shown in Scheme 1. All of these are isomerization products of three kinds of ylides which were generated by α-deprotonation of **3**.

Fluoride ion-induced desilylation of *N*-[1-(trimethylsilyl)alkyl]ammonium salts in an aprotic solvent is suitable for the selective formation of *N*-alkylides.[4,5] Under these reaction conditions, [2,3] sigmatropic rearrangement products (isotoluenes) of the benzylammonium ylides can be isolated at room temperature, especially in the case of benzocycloammonium *N*-methylides.[6] Treatment of 2-methyl-2-[(trimethylsilyl)methyl]-2,3,4,5,6,7-hexahydro-1*H*-2-benzazoninium iodide (**9**) with cesium fluoride will selectively form ylide **10**, which is a precursor of **5** and **8** (Scheme 2). We report here the reaction of **9** and the related eight- and seven-membered cycloammonium compounds **15** and **23** with cesium fluoride.

Scheme 1



Scheme 2



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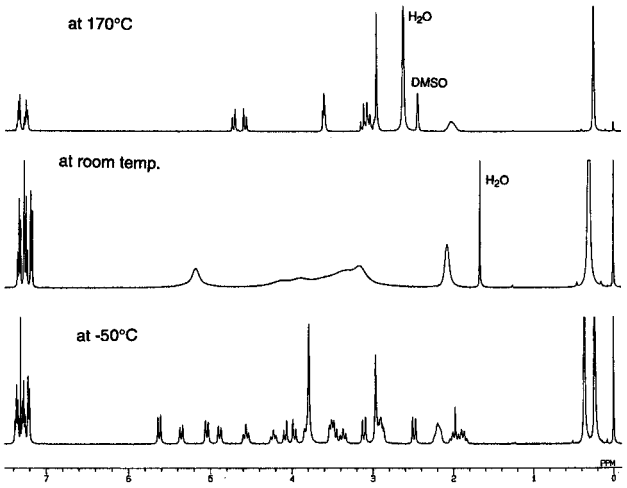

Figure 1. ^{1}H NMR spectra (400 MHz) of **23** at 170 °C in $(CD_3)_2SO$ (top), at room temperature in $CDCl_3$ (middle), and at −50 °C in $CDCl_3$ (bottom).

Results and Discussion

2-Methyl-2-[(trimethylsilyl)methyl]-2,3,4,5,6,7-hexahydro-1*H*-2-benzazoninium iodide (**9**), 2-methyl-2-[(trimethylsilyl)methyl]-1,2,3,4,5,6-hexahydro-2-benzazocinium iodide (**15**), and 2-methyl-2-[(trimethylsilyl)methyl]-2,3,4,5-tetrahydro-1*H*-2-benzazepinium iodide (**23**) were prepared by quaternization of the corresponding cyclic amines **2**, **14**, and **22** with (trimethylsilyl)methyl triflate or iodomethane (Schemes 2−4). These all have sharp melting points and gave good results in microcombustion analyses (<±0.3%). Nevertheless, the signals in the ^{1}H NMR spectra ($CDCl_3$, at 400 or 500 MHz) of **9** and **15** were observed as doubled patterns of the expected proton signals, except for the aromatic protons, from −50 to 170 °C. Although the signal of **23** was also doubled at −50 °C, similar to those of **9** and **15**, it was much broader at room temperature and became simpler at 170 °C, which supports the structure of **23** (Figure 1).

These results suggest that **9** and **15** exist in solution as mixtures of two stable conformational isomers, and the isomers of **23** convert into each other slowly at room temperature and quickly at 170 °C. We calculated the optimized geometries of these compounds by MOPAC[7] and found that two conformational isomers, type A and type B, can exist as stable forms (Figure 2). The chemical shifts of the (trimethylsilyl)methyl groups of type A will be at a higher field than those of type B due to the diamagnetic anisotropy effect of the benzene rings, and the relations of their *N*-methyl groups are reversed (Table 1).

Reaction of **9** with cesium fluoride in DMF for 0.5 h at room temperature gave a mixture of **8** and a new product, **11** (Table 2, entry 1). Although chromatographic isolation of **11** failed, the structure was considered to be 3-methyl-13-methylene-3-azabicyclo[7.3.1]trideca-9,11-diene (isotoluene) based on a comparison of the ^{1}H NMR, ^{13}C NMR, and UV spectra of the mixture with those of an authentic sample of **8**. The product ratio did not change after 24 h (entry 2). However, when the reaction was repeated in the presence of DBU (2.5 mol equiv),[8] **5** was formed with decreasing yield of **11** (entry 3).

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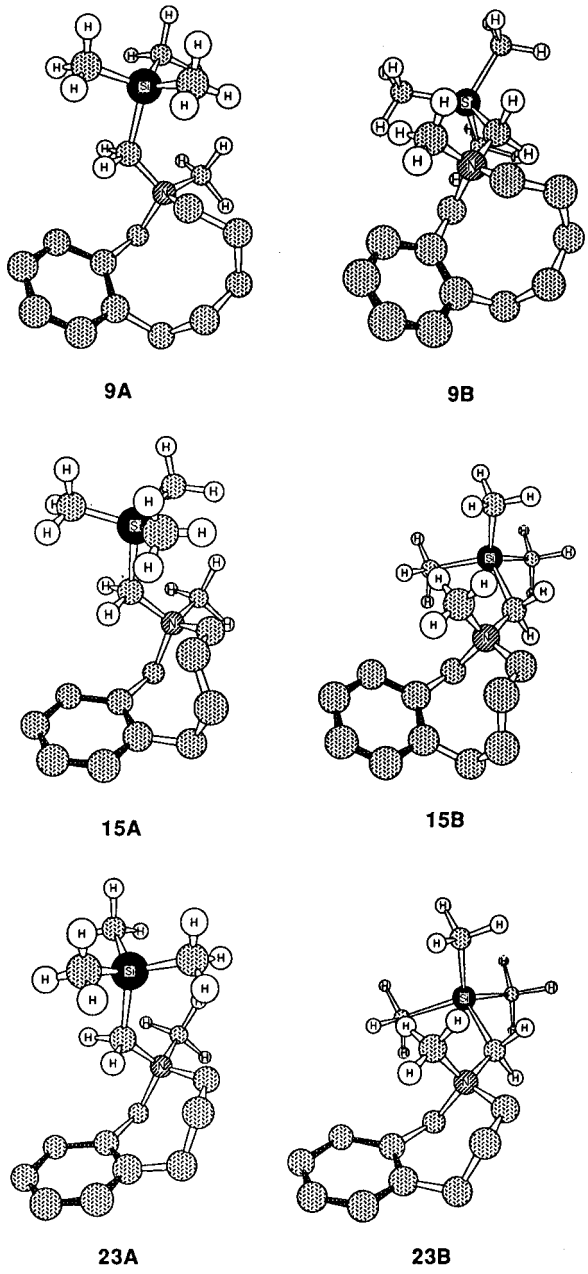


Figure 2. Optimized structures of conformational isomers **9A**,**B**, **14A**,**B**, and **23A**,**B** (selected hydrogens are shown).

Table 1. ^{1}H NMR Chemical Shifts of 9A,B, 15A,B, and 23A,B at Room Temperature

		^{1}H NMR ($CDCl_3$) δ		
salt	ratio[a]	Me_3Si	N−Me	N−CH_2−Si
9A	31	0.27	3.34	2.64, 3.39
9B	69	0.33	3.09	3.27, 3.40
15A	40	0.27	3.75	not assigned
15B	60	0.34	3.26	not assigned
23A[b]	55	0.23	3.79	2.48, 3.13
23B[b]	45	0.37	2.96	3.97, 4.07

[a] Determined from the proton ratio in the ^{1}H NMR spectrum. [b] Measured at −50 °C.

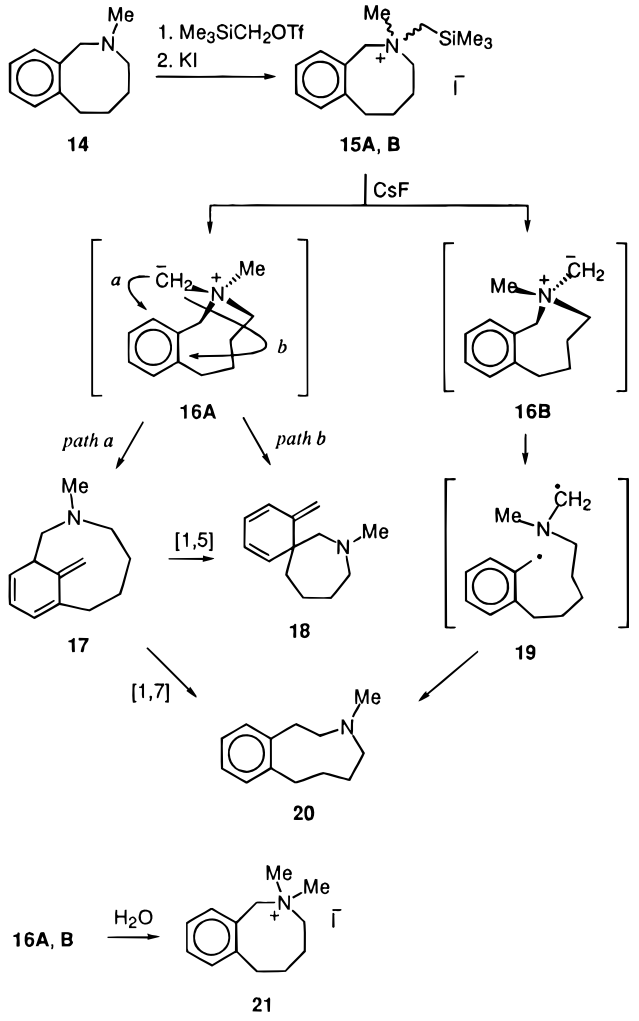
Isotoluene **11** is a [2,3] sigmatropic rearrangement product of ylide **10** and a precursor of **5**. It is unlikely that **8** was formed from **11** by a [1,3] shift because **11** is stable at room temperature and the amount of **8** was not affected by the addition of DBU.[8] The ratio of **8** to **11** (71−73:29−27) is close to the ratio of **9B** to **9A** (69:31). Isotoluene **11** may be formed exclusively from ylide **10A**,

Table 2. Reaction of 9, 15, and 23 with CsF in DMF at Room Temperature

entry	salt	reaction time, h	additive	total amine yield, %	amines (ratio)[a]					ammonium salt yield, %
					Sommelet−Hauser	Stevens	isotoluene	spiro compd	other	
1	**9**	0.5		86		**8** (71)	**11** (29)	**12** (0)		
2	**9**	24		82		**8** (73)	**11** (27)	**12** (0)		
3	**9**	24	DBU	79	**5** (14)	**8** (70)	**11** (16)	**12** (0)		
4	**15**	24		46		**20** (48)	**17** (38)	**18** (14)		**21** (32)
5	**15**	24	DBU	40		**20** (47)	**17** (40)	**18** (13)		**21** (30)
6	**23**	24		23		**29** (9)	**26** (0)	**27** (84)	**25** (7)	**30** (54)

[a] Determined from the proton ratios in the ^{1}H NMR spectra.

Scheme 3



which is generated from **9A**, and its ylide anion is located near the benzene ring. Stevens product **8** may be formed from ylide **10B**, which is generated from **9B**, via a diradical intermediate (**13**) because the ylide anion is located far from the benzene ring.

In the reaction of **15** with cesium fluoride, a mixture of 3-methyl-12-methylene-3-azabicyclo[6.3.1]dodeca-8,10-diene (**17**, isotoluene), 8-methyl-5-methylene-8-azaspiro-[5.6]dodeca-1,3-diene (**18**, spiro compound), and 3-methyl-2,3,4,5,6,7-hexahydro-1*H*-3-benzazonine (**20**, Stevens rearrangement product) was obtained from the ethereal extract of the reaction mixture, and 2,2-dimethyl-1,2,3,4,5,6-hexahydro-2-benzazocinium iodide (**21**) was isolated from the aqueous layer after ether extraction (Scheme 3, Table 2, entry 4). Although isolation of pure **18** was difficult because of poor separation from **20** on an HPLC column, structural assignment of the products was achieved by comparison of the ^{1}H NMR and UV spectra. The strained structure of **17** was supported by a hypsochromic shift of the UV spectrum compared with the absorption maximum of the conjugated triene chromophore[6] (**17**, λ_{max}(ether) 285 nm; **18**, λ_{max}(ether) 303 nm).

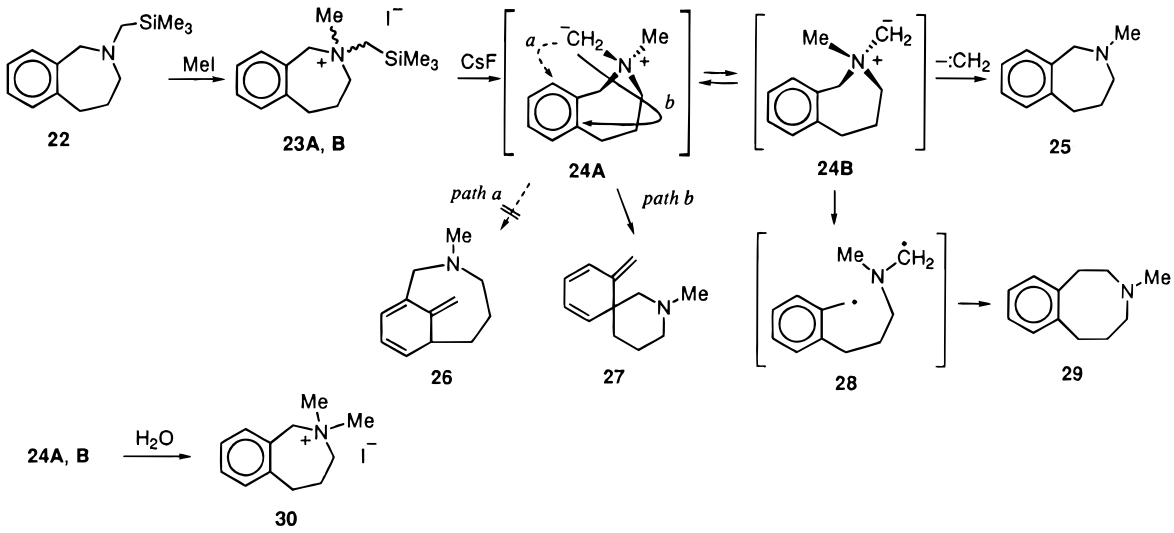
Compounds **17** and **18** may be formed competitively from ylide **16A**, which is generated from **15A**, via either of two sigmatropic rearrangement pathways a and b. Compound **20** is a Stevens rearrangement product from ylide **16B** in which the ylide anion is located far from the benzene ring. Some **18** and **20** would also be formed from **17** via a [1,5] or [1,7] sigmatropic shift, respectively, because the ratio of **17**:**18**:**20** (38:14:48) changed to 11:29:60 when the ^{1}H NMR spectrum was measured again after 3 days. Ammonium salt **21** may be formed by protonation of **16** during the reaction. Thus, the ratio of both **17** and **18** (52) to **20** (48) does not agree with the ratio of **15A** to **15B** (40:60). Aromatization of **17** to a Sommelet−Hauser rearrangement product did not occur when the reaction was carried out in the presence of DBU (entry 5).

In the reaction of **23** with cesium fluoride, 3-methyl-11-methylene-3-azaspiro[5.5]undeca-7,9-diene (**27**) was obtained as the main product along with small amounts of 2-methyl-2,3,4,5-tetrahydro-1*H*-2-benzazepine (**25**) and 3-methyl-1,2,3,4,5,6-hexahydro-1*H*-3-benzazocine (**29**) from the ethereal extract of the reaction mixture (Scheme 4). The total amine yield was low, and the expected isotoluene compound **26** was absent, whereas 2,2-dimethyl-2,3,4,5-tetrahydro-1*H*-2-benzazepinium iodide (**30**) was isolated in a yield of 54% from the aqueous layer after ether extraction (Table 2, entry 6). Spiro compound **27** may be formed from ylide **24A**, and Stevens product **29** and demethylene product **25** are generated from ylide **24B**.

Sigmatropic rearrangement in the seven-membered ring (from **24A** to **27**) requires a higher ring tension in the transition state than that in the eight-membered ring (from **16A** to **17** or **18**) or the nine-membered ring (from **10A** to **11**). Conversion between **24A** and **24B** may also be possible, similar to the equilibrium between **23A** and **23B**. This would delay the rearrangement and result in a lower yield of the amines and a higher yield of **30** by protonation.

Thus, [2,3] sigmatropic rearrangement of benzocycloammonium *N*-methylides **10**, **16**, and **24** occurs exclusively on type A ylides, and their ring sizes affect the reaction points on the benzene rings (paths a and b). Thus, on nine-membered ylide **10A**, rearrangement occurs selectively at the 11-position (path a) to give isotoluene compound **11**; on eight-membered ylide **16A**, paths a and b compete at the 6a- and 10-positions to give isotoluene **17** and spiro compound **18**; on seven-membered ylide **24A**, only one route (path b) is allowed at the 5a-position to give spiro compound **27**.

Scheme 4



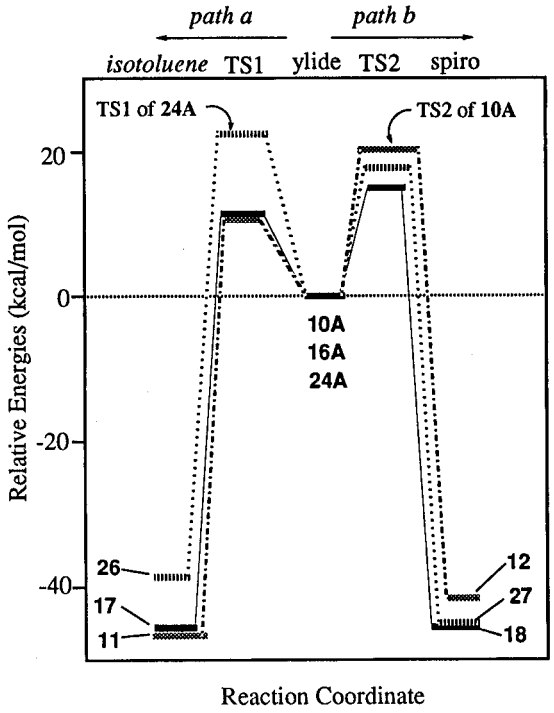


Figure 3. Reaction coordinate of the [2,3] sigmatropic rearrangement of ylides **10A**, **16A**, and **24A** calculated by the AM1 method.

We calculated the reaction coordinate of the [2,3] sigmatropic rearrangement of **10A**, **16A**, and **24A** by the AM1 method. The energies of the respective transition structures TS1 and TS2 in paths a and b are shown in Figure 3. While path a to **11** is more favorable than path b to **12** in the reaction of **10A**, paths a and b might be comparable in the reaction of **16A** to **17** and **18**. Although path b to **27** is more favorable than path a to **26** in the reaction of **24A**, both activation energies are high, compared with the reactions of **10A** and **16A**. This may cause a low yield of **27**.

Experimental Section

Dichloromethane was distilled from CaH_2. DMF was dried by distillation under reduced pressure from BaO. CsF was dried over P_2O_5 at 180 °C under reduced pressure. ^1H NMR spectra were recorded at 270, 400, or 500 MHz. Mass spectra were obtained using EI ionization (70 eV). Aluminum oxide (Merck; aluminum oxide F_{254} (type E), 0.25 mm, 20 × 20 cm) was used for preparative TLC. All melting points and boiling points are uncorrected.

2-Methyl-2-[(trimethylsilyl)methyl]-2,3,4,5,6,7-hexahydro-1*H*-2-benzazoninium Iodide (9). A solution of 2-methyl-2,3,4,5,6,7-hexahydro-1*H*-2-benzazonine[2a] (**2**) (7.1 g, 38 mmol) and (trimethylsilyl)methyl triflate (15.0 g, 64 mmol) in CH_2Cl_2 (40 mL) was heated at reflux for 5 days. The solvent was evaporated under reduced pressure, and the residue was added to a mixture of $CHCl_3$ (30 mL) and saturated aqueous KI (30 mL). The precipitated yellow solid was separated and recrystallized from MeOH−Et_2O to give **9** (14.0 g, 92%): mp 202−204 °C; IR (Nujol) 1487, 1256, 1032, 850 cm^{-1}; two conformational isomers (**9A**,**B**) were observed in the ^1H NMR spectrum (**9A**:**9B**, 31:69); ^1H NMR ($CDCl_3$) δ for **9A** 0.27 (s, 9 H), 2.64 (d, 1 H, J = 14.6 Hz), 3.34 (s, 3 H), 3.39 (d, 1 H, J = 14.6 Hz), 4.47 (1 H, J = 13.4 Hz), 5.02 (d, 1 H, J = 13.4 Hz), 7.50 (d, 1 H, J = 7.9 Hz), for **9B** 0.33 (s, 9 H), 3.09 (s, 3 H), 3.27 (d, 1 H, J = 15.3 Hz), 3.40 (d, 1 H, J = 15.3 Hz), 4.41 (1 H, J = 14.0 Hz), 4.97 (d, 1 H, J = 14.0 Hz), 7.45 (d, 1 H, J = 7.9 Hz), other signals overlapped 1.41−1.50 (1 H), 1.51−1.63 (1 H), 1.76−1.94 (2 H), 2.13−2.34 (2 H), 2.60−2.78 (2 H), 2.84−2.92 (1 H), 3.19−3.23 (1 H), 7.22−7.25 (2 H), 7.32−7.41 (1 H). Anal. Calcd for $C_{17}H_{30}NISi$: C, 50.62; H, 7.49; N, 3.47. Found: C, 50.41; H, 7.44; N, 3.66.

Reaction of 9 with CsF. A. Ammonium salt **9** (813 mg, 2 mmol) and 4A molecular sieves (2.0 g) were placed in a 30-mL flask equipped with a magnetic stirrer and a septum, and a test tube was connected to the flask by a short piece of bent glass tubing. CsF (760 mg, 5 mmol) was placed in the test tube. The apparatus was dried under reduced pressure and flushed with N_2. DMF (20 mL) was added to the flask with a syringe. After stirring for 30 min, CsF was added to the mixture from the test tube. The mixture was stirred for 0.5 or 24 h at room temperature, poured into 1% $NaHCO_3$ (200 mL), and extracted with ether (3 × 100 mL). The ethereal extract was washed with water (3 × 100 mL) and saturated aqueous NaCl (100 mL), dried ($MgSO_4$), and concentrated under reduced pressure to give a mixture (348 or 331 mg) of 3-methyl-1,2,3,4,5,6,7,8-octahydro-3-benzazecine[3c] (**8**) and 3-methyl-13-methylene-3-azabicyclo[7.3.1]trideca-9,11-diene (**11**). Isolation of pure samples by chromatography was difficult due to insufficient separation. The ratio was determined on the basis of the proton ratios in the ^1H NMR spectra of the ethereal extracts. The results are summarized in Table 2.

Mixture of **8** and **11**: UV λ_{max}(ether) 320 nm; ^1H NMR ($CDCl_3$) δ for **11** 2.17 (s, 3 H), 4.92 (s, 1 H), 5.20 (s, 1 H), 5.66 (d, 1 H, J = 5.1 Hz), 5.77 (dd, 1 H, J = 5.5, 5.1 Hz), 5.94 (dd, 1 H, J = 9.5, 5.5 Hz), for **8** 2.04 (s, 3 H), other signals

overlapped; ^{13}C NMR ($CDCl_3$) δ for **11** 20.5 (CH_2), 22.2 (CH_2), 27.0 (CH_2), 29.7 (CH_2), 30.3 (CH), 33.3 (CH_2), 45.8 (CH_3), 56.6 (CH_2), 113.3 (CH_2), 123.6 (CH), 124.1 (CH), 130.5 (CH), 137.3 (C), 147.4 (C). Anal. Calcd for $C_{14}H_{21}N$: C, 82.70; H, 10.41; N, 6.89. Found: C, 82.29; H, 10.56; N, 6.93.

B. In a manner similar to that described above, **9** (813 mg, 2 mmol), 4A molecular sieves (2.0 g), and CsF (760 mg, 5 mmol) were placed in an apparatus and dried. DMF (20 mL) and DBU (760 mg, 5 mmol) were added to the flask with syringes. After the mixture stirred for 30 min, CsF was added to the solution from the test tube. The mixture was stirred for 24 h at room temperature and worked up to give a mixture (322 mg) of 3,13-dimethyl-3-azabicyclo[7.3.1]trideca-1,9,11-triene (5,2-aza(7)metacyclophane[3c]) (**5**), **8**, and **11**. Compound **5** was separated by preparative aluminum oxide TLC with hexane. The ratio of **5**, **8**, and **11** was determined based on the proton ratios in the ^{1}H NMR spectrum of the mixture.

2-Methyl-2-[(trimethylsilyl)methyl]-1,2,3,4,5,6-hexahydro-2-benzazocinium Iodide (15). A solution of 2-methyl-1,2,3,4,5,6-hexahydro-2-benzazocine[2] (**14**) (2.6 g, 15 mmol) and (trimethylsilyl)methyl triflate (5.1 g, 20 mmol) in CH_2Cl_2 (25 mL) was heated at reflux for 4 days. The solvent was evaporated under reduced pressure, and the residue was added to a mixture of $CHCl_3$ (15 mL) and saturated aqueous KI (15 mL). The mixture was stirred at room temperature for 1 h. The organic layer was separated, and the aqueous layer was extracted with $CHCl_3$ (3 × 5 mL). The combined extract was dried ($MgSO_4$) and concentrated. The residue was recrystallized from MeOH−Et_2O to give **15** (4.7 g, 81%): mp 224−225 °C; IR (Nujol) 1425, 1256, 1032, 858, 770, 708 cm^{-1}; two conformational isomers were observed in the ^{1}H NMR spectrum (**15A**:**15B**, 40:60); ^{1}H NMR ($CDCl_3$) δ for **15A** 0.27 (s, 9 H), 3.75 (s, 3 H), 7.65 (d, 1 H, J = 7.3 Hz), for **15B** 0.34 (s, 9 H), 3.26 (s, 3 H), 7.61 (d, 1 H, J = 7.3 Hz), other signals could not be assigned because the peaks were broad. Anal. Calcd for $C_{16}H_{28}NISi$: C, 49.35; H, 7.25; N, 3.60. Found: C, 49.16; H, 7.32; N, 3.33.

Reaction of 15 with CsF. A. In a manner similar to that described for **9**, **15** (390 mg, 1 mmol), 4A molecular sieves (1.0 g), and CsF (380 mg, 2.5 mmol) in DMF (10 mL) were treated to give a mixture (87 mg) of 3-methyl-12-methylene-3-azabicyclo-[6.3.1]dodeca-8,10-diene (**17**), 8-methyl-5-methylene-8-azaspiro-[5.6]dodeca-1,3-diene (**18**), and 3-methyl-2,3,4,5,6,7-hexahydro-1*H*-3-benzazonine (**20**). The mixture was chromatographed on an HPLC column (Nakarai Cosmosil 5NH_2, 10 × 250 mm). The mobile phase was initially a mixture of 0.5% Et_2O in hexane at a flow rate of 5 mL/min and was increased linearly to 3% in 9 min and then to 10% in 2 min. Fractions of **17** (6−7 min), a mixture of **18** and **20** (9−10 min), and **20** (10−11 min) were collected. The product ratio was determined based on the proton ratios in the ^{1}H NMR spectrum of the mixture.

17: ^{1}H NMR ($CDCl_3$) δ 1.35 (m, 1 H), 1.44−1.60 (m, 2 H), 1.86−2.00 (m, 2 H), 2.20 (m, 2 H), 2.26 (s, 3 H), 2.42 (dt, 1 H, J = 12.5, 4.0 Hz), 2.58 (dd, 1 H, J = 13.4, 8.1 Hz), 2.73 (m, 2 H), 4.94 (s, 1 H), 5.06 (s, 1 H), 5.66 (d, 1 H, J = 2.6 Hz), 5.93 (m, 2 H); MS m/z 189 (98, M$^+$), 149 (68), 105 (92), 84 (100); UV λ_{max}(ether) 285 nm; exact mass calcd for $C_{13}H_{19}N$ 189.1519, found 189.1514.

18: ^{1}H NMR ($CDCl_3$) δ 1.66 (m, 4 H), 1.77 (m, 2 H), 2.31 (s, 3 H), 2.46 and 2.50 (AB-q, 2 H, J = 14.1 Hz), 2.50−2.62 (m, 2 H), 5.02 (s, 1 H), 5.21 (s, 1 H), 5.77 (dd, 1 H, J = 9.0, 5.8 Hz), 5.90 (dd, 1 H, J = 9.6, 5.8 Hz), 6.05 (d, 1 H, J = 9.6 Hz), 6.07 (d, 1 H, J = 9.6 Hz); UV λ_{max}(ether) 303 nm.

20: ^{1}H NMR ($CDCl_3$) δ 1.14 (m, 2 H), 1.77 (m, 2 H), 2.35 (s, 3 H), 2.44 (t, 2 H, J = 5.8 Hz), 2.54 (m, 2 H), 2.78 (m, 2 H), 3.06 (t, 2 H, J = 6.2 Hz), 7.00−7.10 (m, 4 H); MS m/z 189 (95, M$^+$), 174 (15), 146 (30), 105 (41), 84 (100), 71 (43); exact mass calcd for $C_{13}H_{19}N$ 189.1519, found 189.1522.

The aqueous layer after ether extraction was evaporated under reduced pressure, and the residue was extracted with $CHCl_3$. Evaporation of the solvent gave 2,2-dimethyl-1,2,3,4,5,6-hexahydro-2-benzazocinium iodide[9] (**21**) (100 mg, 32%).

B. In a manner similar to that described above, **15** (390 mg, 1 mmol), 4A molecular sieves (1.0 g), and CsF (380 mg, 2.5 mmol) were placed in a flask. DMF (10 mL), DBU (380 mg, 2.5 mmol), and CsF (380 mg, 2.5 mmol) were successively added, and the mixture was treated as described above. The results are shown in Table 2 (entry 5).

2-Methyl-2-[(trimethylsilyl)methyl]-2,3,4,5-tetrahydro-1*H*-2-benzazepinium Iodide (23). A mixture of 2,3,4,5-tetrahydro-1*H*-2-benzazepine[10] (4.0 g, 27 mmol), (chloromethyl)-trimethylsilane (8.0 g, 66 mmol), and K_2CO_3 (4.0 g, 29 mmol) in acetonitrile (100 mL) was heated at reflux for 24 h. The mixture was poured into water (300 mL) and extracted with ether (3 × 100 mL). The extract was washed with water, dried ($MgSO_4$), and concentrated under reduced pressure. The residue was chromatographed on aluminum oxide (hexane−Et_2O) to give 2-[(trimethylsilyl)methyl]-2,3,4,5-tetrahydro-1*H*-2-benzazepine (**22**) (5.5 g, 87%): IR (film) 2928, 1453, 1248, 855, 754 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.06 (s, 9 H), 1.69−1.74 (m, 2 H), 1.91 (s, 2 H), 2.87−2.90 (br t, 2 H, J = 5.6 Hz), 3.10−3.13 (br t, 2 H, J = 5.2 Hz), 3.90 (s, 2 H), 7.09−7.18 (m, 4 H). Anal. Calcd for $C_{14}H_{23}NSi$: C, 72.04; H, 9.93; N, 6.00. Found: C, 71.89; H, 10.03; N, 5.84.

A solution of **22** (1.9 g, 8.2 mmol) and iodomethane (10.1 g, 71 mmol) in acetonitrile (30 mL) was stirred at room temperature for 2 h. The solvent was evaporated under reduced pressure, and the residue was recrystallized from acetone to give **23** (2.8 g, 92%): mp 180−182 °C; IR (Nujol) 1256, 984, 914, 764 cm^{-1}; two conformational isomers were observed in the ^{1}H NMR spectrum at −50 °C (**23A**:**23B**, 55:45); ^{1}H NMR ($CDCl_3$, at −50 °C) δ for **23A** 0.23 (s, 9 H), 2.48 (d, 1 H, J = 15.4 Hz), 3.13 (d, 1 H, J = 15.4 Hz), 3.79 (s, 3 H), 4.54−4.60 (m, 1 H), 5.03 (d, 1 H, J = 12.8 Hz), 5.36 (d, 1 H, J = 12.8 Hz), 7.76 (d, 1 H, J = 7.3 Hz), for **23B** 0.37 (s, 9 H), 2.96 (s, 3 H), 3.97 and 4.07 (AB-q, 2 H, J = 14.5 Hz), 4.20−4.26 (m, 1 H), 4.88 (d, 1 H, J = 13.7 Hz), 5.36 (d, 1 H, J = 13.7 Hz), 7.69 (d, 1 H, J = 7.0 Hz), other signals overlapped 1.83−2.01 (1 H), 2.19−2.24 (1 H), 2.85−2.96 (1 H), 3.34−3.54 (1 H, 2 H), 3.79−3.85 (1 H), 7.20−7.38 (m, 3 H); ^{1}H NMR (DMSO-d_6, at 170 °C) δ 0.25 (s, 9 H), 2.03 (br s, 2 H), 2.92−3.03 (m, 2 H), 2.95 (s, 3 H), 3.06 and 3.11 (AB-q, 2 H, J = 15.0 Hz), 3.60 (t, 2 H, J = 5.7 Hz), 4.58 and 4.71 (AB-q, 2 H, J = 13.6 Hz), 7.26 (t, 2 H, J = 7.7 Hz), 7.35 (m, 2 H). Anal. Calcd for $C_{15}H_{26}NISi$: C, 47.80; H, 6.98; N, 3.73. Found: C, 47.58; H, 6.85; N, 3.90.

Reaction of 23 with CsF. In a manner similar to that described for **9**, a mixture of **23** (375 mg, 1 mmol), 4A molecular sieves (1.0 g), and CsF (380 mg, 2.5 mmol) in DMF (10 mL) was treated to give a mixture (40 mg) of 3-methyl-11-methylene-3-azaspiro[5.5]undeca-7,9-diene (**27**), 3-methyl-1,2,3,4,5,6-hexahydro-1*H*-3-benzazocine (**29**), and 2-methyl-2,3,4,5-tetrahydro-1*H*-2-benzazepine (**25**). Samples were isolated by preparative TLC (aluminum oxide, Et_2O−hexane, 1:3). The ratio was determined based on the proton ratios in the ^{1}H NMR spectrum of the mixture.

27: ^{1}H NMR ($CDCl_3$) δ 1.25−1.33 (m, 1 H), 1.55−1.60 (m, 1 H), 1.75−1.78 (m, 1 H), 1.85 (d, 1 H, J = 11.0 Hz), 1.90−2.00 (m, 2 H), 2.20 (s, 3 H), 2.75 (d, 1 H, J = 11.0 Hz), 2.84−2.85 (m, 1 H), 5.07 (s, 1 H), 5.13 (s, 1 H), 5.80 (ddt, 1 H, J = 9.2, 5.5, 1.2 Hz), 5.96 (ddd, 1 H, J = 9.8, 5.5, 1.2 Hz), 6.11 (d, 1 H, J = 9.2 Hz), 6.36 (d, 1 H, J = 9.8 Hz); MS m/z 175 (78, M$^+$), 132 (42), 117 (99), 70 (100), 57 (23); exact mass calcd for $C_{12}H_{17}N$ 175.1362, found 175.1396.

29: ^{1}H NMR ($CDCl_3$) δ 1.67−1.72 (m, 2 H), 2.29 (t, 2 H, J = 5.5 Hz), 2.38 (s, 3 H), 2.73 (dd, 2 H, J = 6.1, 4.9 Hz), 2.80 (dd, 2 H, J = 6.7, 6.1 Hz), 2.84 (dd, 2 H, J = 6.1, 4.9 Hz), 7.09−7.16 (m, 4 H); MS m/z 175 (100, M$^+$), 132 (39), 117 (80), 70 (99), 57 (21); exact mass calcd for $C_{12}H_{17}N$ 175.1362, found 175.1388.

25: ^{1}H NMR ($CDCl_3$) δ 1.74−1.78 (m, 2 H), 2.31 (s, 3 H), 2.88 (t, 2 H, J = 5.5 Hz), 3.01 (dd, 2 H, J = 5.5, 4.9 Hz), 3.79 (s, 2 H) 7.10−7.15 (m, 4 H). MS m/z 161 (100, M$^+$), 160 (96), 146 (36), 132 (35), 117 (72); exact mass calcd for $C_{11}H_{15}N$ 161.1206, found 161.1200.

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The aqueous layer after ether extraction was concentrated under reduced pressure and extracted with $CHCl_3$. Evaporation of the solvent gave 2,2-dimethyl-2,3,4,5-tetrahydro-1*H*-2-benzazepinium iodide (**30**; 175 mg, 58%): ^{1}H NMR ($CDCl_3$) δ 7.19 (d, 1 H, J = 7.3 Hz), 7.25 (ddd, 1 H, J = 7.9, 6.7, 1.2 Hz), 7.33 (ddd, 1 H, J = 7.9, 6.7, 1.2 Hz), 7.72 (d, 1 H, J = 6.7 Hz), other signals were broad. Anal. Calcd for $C_{12}H_{18}NI$: C, 47.54; H, 5.98; N, 4.62. Found: C, 47.33; H, 6.18; N, 4.54.

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Supporting Information Available: Coordinates and energies for structures in Figures 2 and 3 optimized at the AM1 level (42 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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