Small Charged Rings. XIII.[1] Abnormal Ring Expansion of Polycyclic Aziridinium Salts[2]

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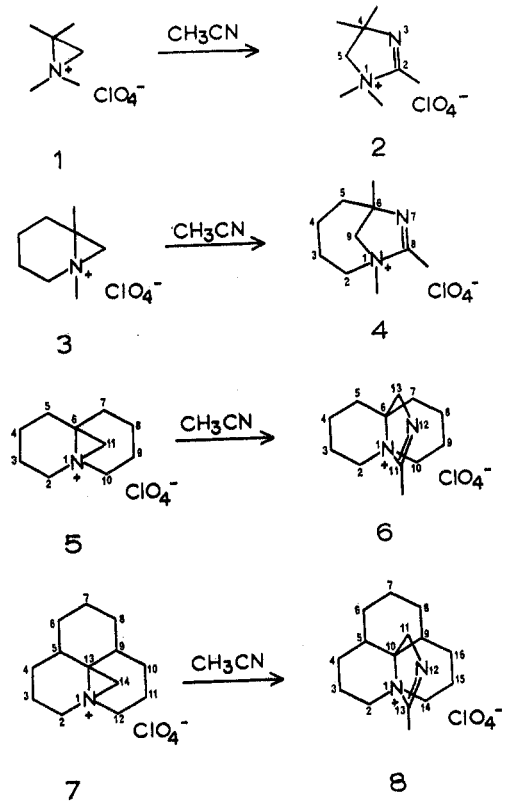
Abnormal ring expansion products are formed when the tri- and tetracyclic aziridinium salts, 1-azoniatricyclo-[4.4.1.$0^{1,6}$]undecane perchlorate (**5**) and 1-azoniatetracyclo[7.3.2.$0^{1,13}$.$0^{5,13}$]tetradecane perchlorate (**7**), are caused to react with acetonitrile to give 11-methyl-12-aza-1-azoniatricyclo[4.4.3.$0^{1,6}$]tridec-11-ene perchlorate (**6**) and 13-methyl-12-aza-1-azoniatetracyclo[7.4.3.$0^{1,10}$.$0^{5,10}$]hexadec-12-ene perchlorate (**8**), respectively, and when **5** is caused to react with the nitrone, 5,5-dimethyl-Δ^1-pyrroline 1-oxide, to give 5,5-dimethyl-7-oxa-6-aza-1-azoniatetracyclo[7.4.4.$0^{1,9}$.$0^{2,6}$]heptadecane perchlorate (**16**). By contrast, the mono- and bicyclic aziridinium salts 1,1,2,2-tetramethylaziridinium perchlorate (**1**) and 1,6-dimethyl-1-azoniabicyclo[4.1.0]heptane perchlorate (**3**) react with acetonitrile to give normal ring expansion products, 1,1,2,4,4-pentamethylimidazolinium perchlorate (**2**) and 1,6,8-trimethyl-7-aza-1-azoniabicyclo[4.2.1]non-7-ene perchlorate (**4**), respectively, and with the nitrone to give the normal products, 3,3,5,5,9,9-hexamethyl-2-oxa-1-aza-5-azoniabicyclo[4.3.0]nonane perchlorate (**14**) and 1,5,5,8-tetramethyl-7-oxa-6-aza-1-azoniatricylo[6.4.1.$0^{2,6}$]tridecane perchlorate (**15**), The acetonitrile ring expansion products of the normal and abnormal reactions are substituted imidazolinium salts, and the nitrone adducts contain the oxadiazinium ring system. Normal ring expansion reaction involves the 1,2 bond breaking of a 1,1,2,2-tetrasubstituted aziridinium salt while abnormal ring expansion involves 1,3 bond breaking. Compounds **1** and **3** react with benzaldehyde and acetone to give normal ring expansion products but **5** would not react with either reagent. The structures of the products of aziridinium ring expansion were established by spectroscopic methods and by spectroscopic and chemical identification of their degradation products. Some of the compounds (*e.g.*, **6**, **8**, **16**) fall into the structural category of "propellanes."

Previous papers in this series[3] have described the ring expansion reactions of aziridinium salts. Aldehydes[4] and ketones[5] react to form substituted oxazolidinium salts, nitriles[6] to form substituted imidazolinium salts, and stable nitrones[7] to give 1:1 ring-expanded adducts with formation of an oxadiazinium ring. These ring expansions appear to proceed by reaction of the polar or dipolar species with the more substituted of the two possible β-aminocarbonium ion intermediates developable from the aziridinium salt. Thus, in the normal ring expansion of aziridinium salts, the heteroatom of the polar (aldehyde, ketone, nitrile) or dipolar (nitrone) species reacts at the more substituted carbon of the aziridinium ring. We have now observed cases of *abnormal* ring expansion in which the nitrogen atom of a nitrile and the oxygen atom of a nitrone react at the less substituted aziridinium carbon. We recognize that the designation abnormal does not represent abnormality of the chemical process as much as it represents a lack of adherence to predictability on the basis of our past experience. Nevertheless, we find this categorization more arresting than the designation 1,3 bond breaking. The aziridinium salts that underwent abnormal ring expansion were those that also had been found to give abnormal solvolysis products with carboxylic acids, *i.e.*, compounds in which the acyloxy group becomes attached to the former aziridinium carbon that was less substituted. The conditions and steric requirements for abnormal solvolysis have been described in the preceding article.[1]

A series of sterically graduated aziridinium salts was selected for the ring expansion reaction in order to compare normal and possible abnormal products and to determine the structural requirements for any abnormal ring expansion. The following compounds satisfied these criteria: 1,1,2,2-tetramethylaziridinium perchlorate (**1**),[5] 1,6-dimethyl-1-azoniabicyclo[4.1.0]heptane perchlorate (**3**),[1] 1-azoniatricyclo[4.4.1.$0^{1,6}$]undecane perchlorate (**5**),[8] and 1-azoniatetracyclo[7.3.2.-$0^{1,13}$.$0^{5,13}$]tetradecane perchlorate (**7**).[8] Acetonitrile



(1) For preceding article in this series, see N. J. Leonard and D. B. Dixon *J. Org. Chem.*, **35**, 3483 (1970).

(2) We are pleased to acknowledge the support of the National Science Foundation by Research Grant GP-8407X.

(3) For reference and a summary of work in this field, see (a) N. J. Leonard, *Rec. Chem. Progr.*, **26**, 211 (1965); (b) D. R. Crist and N. J. Leonard, *Angew. Chem.*, **81**, 953 (1969); (c) D. R. Crist and N. J. Leonard, *Angew. Chem., Int. Ed. Engl.*, **8**, 962 (1969).

(4) N. J. Leonard, E. F. Kiefer, and L. E. Brady, *J. Org. Chem.*, **28**, 2850 (1963).

(5) N. J. Leonard, J. V. Paukstelis, and L. E. Brady, *ibid.*, **29**, 3383 (1964).

(6) N. J. Leonard and L. E. Brady, *ibid.*, **30**, 817 (1965).

(7) N. J. Leonard, D. A. Durand, and F. Uchimaru, *ibid.*, **32**, 3607 (1967).

(8) N. J. Leonard, K. Jann, J. V. Paukstelis, and C. K. Steinhardt, *J. Org. Chem.*, **28**, 1499 (1963).

and the nitrone, 5,5-dimethyl-Δ^1-pyrroline 1-oxide, were caused to react with this set of aziridinium salts.

When heated in acetonitrile at reflux for 3 hr, aziridinium salts **1** and **3** were found to give the normal ring expanded products, 1,1,2,4,4-pentamethylimidazolinium perchlorate (**2**) and 1,6,8-trimethyl-7-aza-1-azoniabicyclo[4.2.1]non-7-ene perchlorate (**4**), respectively. However, aziridinium salts **5** and **7** were found to react with acetonitrile at reflux during 68 and 38 hr, respectively, to give abnormal ring expansion products as the isolable products, namely, 11-methyl-12-aza-1-azoniatricyclo[4.4.3.$0^{1,6}$]tridec-11-ene perchlorate (**6**) and 13-methyl-12-aza-1-azoniatetracyclo-[7.4.3.0.$^{1,15}0^{5,10}$]hexadec-12-ene perchlorate (**8**). The yields were unfortunately variable throughout the series. Evidence of imidazolinium ring formation in all four products consisted of satisfactory microanalyses, the presence of infrared absorption maxima between 1690 and 1710 cm^{-1} arising from the C=N function, and the appearance of a three-proton resonance between τ 7.28 and 7.59 in the nmr spectrum of each compound.

The nmr spectra of products **2**, **4**, **6**, and **8** permitted the assignments of the products to the normal or abnormal category. The resonances of the former aziridinium methylene protons in the spectrum of product **2** appeared as a singlet at τ 6.02 while the resonance of the corresponding methylene protons in product **4** appeared as an AB system of doublets centered at τ 6.09. The resonance of the other methylene protons adjacent to charged nitrogen in **4** appeared at τ 6.22. The chemical shifts of these former aziridinium methylene protons appear where expected for methylene protons adjacent to charged nitrogen.[8] The chemical shifts and their proximity to the chemical shift of the α-methylene protons not in the imidazolinium ring of product **4** confirm the assignment of structures **2** and **4** as normal ring expansion products.

The resonances of the former aziridinium methylene protons in the nmr spectra of products **6** and **8** appeared as quartet signals at τ 5.72 and 5.62, respectively. The resonances of the two methylene groups adjacent to charged nitrogen but not in the imidazolinium ring appeared at τ 6.35 and 6.20, respectively. The chemical shift of 0.4 ppm to lower field for the imidazolinium methylene protons in products **6** and **8** from those in **2** and **4** suggests[6,8] that the methylene group in **6** and **8** is α to the sp^2 nitrogen and β to the quaternary nitrogen, indicating that these two compounds are abnormal ring expansion products possessing the assigned structures.

Important details in the nmr spectrum of **6** include the quartet at τ 5.72, J = 1.9 Hz, assigned to the imidazolinium methylene protons, and a triplet at τ 7.28, J = 1.9 Hz, assigned to the methyl protons. Similar features are found in the spectrum of **8** at τ 5.62, J = 2.0 Hz, and 7.33, J = 2.0 Hz. It was suspected that this multiplicity arose from long-range coupling between the imidazolinium methylene and the methyl protons through five bonds.[9] Spin-spin decoupling at 100 MHz confirmed the existence of long-range coupling in compound **6**. Irradiation at τ 5.72 converted the signal at τ 7.28 to a sharp singlet with $W_{1/2}$ = 2.0 Hz compared to $W_{1/2}$ = 4.5 Hz before irradiation. In like manner, irradiation at τ 7.28 converted the signal at τ 5.72 to a sharp singlet with $W_{1/2}$ = 2.5 Hz compared with $W_{1/2}$ = 6.0 Hz before irradiation. The tricyclic ring system in **6** and tetracyclic ring system in **8** hold the imidazolinium ring in the rigid conformation required for long-range coupling through the C=N portion of the ring. Coupling through five bonds of a homoallylic system has been found to be of magnitude 1.2 to 2.8 Hz in acyclic systems and 1.9 to 3.0 Hz in cyclic systems.[9] Homoallylic systems in which nitrogen has replaced one of the sp^2 carbons have exhibited long range coupling constants of 1.0 to 5.5 Hz.[10-13] Thus, the values of 1.9 and 2.0 Hz for the coupling constants observed in the spectra of **6** and **8** are in the range of those found in similar systems.

Further verification of the structures of the normal and abnormal ring expansion products was considered desirable, and chemical degradations of **2** and **6** were carried out as representatives of each series. One approach was to attempt to hydrogenate 1,1,2,4,4-pentamethylimidazolinium perchlorate (**2**) with Adams catalyst in glacial acetic acid. The result was somewhat unexpected since the major product was 2-acetamido-N^1,N^1-dimethyl-2-methylpropylamine (**11**) perchlorate and the overall result was the replacement of the $\geq$C—CH_3 fragment with an acetyl group attached to the nitrogen which originated from the nitrile. Because this reaction formally represented the addition of 1 mol of water to **2**, the necessity of hydrogen and catalyst was suspect; indeed, a control experiment showed that the same conversion could be accomplished efficiently with acetic acid alone. The base, N-(1,1-dimethylamino-2-methylprop-2-yl)acetamide, was identified by microanalysis, infrared spectrum, and nmr spectrum, which showed a signal at τ 8.13 characteristic of acetyl methyl protons. Lithium aluminium hydride reduction of **2** in tetrahydrofuran resulted in reductive opening of the imidazolinium ring to N^1,N^1-dimethyl-N^2-ethyl-2-methyl-1,2-diaminopropane (**9**), characterized as the dipicrate. This hydride reduction method of structure determination was considered less satisfactory because of low conversions and problems in the derivatization of diamine products. We therefore returned to amino amide products for identification. N-(2-Dimethylamino-2-methylprop-1-yl)acetamide (**10**), the isomer of **11**, was prepared (30% yield) *via* a direct displacement on the less hindered, methylene carbon of the aziridinium ring of **1** by acetamide anion, prepared by treatment of acetamide with sodium hydride. This constitutes a new SN2-type ring opening of aziridinium salts. The compound exhibited an nmr signal characteristic of the acetyl methyl group. There is a distinct difference in the chemical shift and coupling of the methylene protons in the two isomers, **10** and **11**, with the former showing a doublet, J = 5.0 Hz, at τ 6.89, and the latter a singlet at τ 7.58. Both spectra were obtained for methylene chloride solutions. The characteristic chemical shift of methylene adjacent

(9) (a) For a review of long-range coupling, see S. Sternhell, *Rev. Pure Appl. Chem.*, **14**, 15 (1964); (b) also M. Barfield and B. Chakrabarti, *Chem. Rev.*, **69**, 757 (1969).

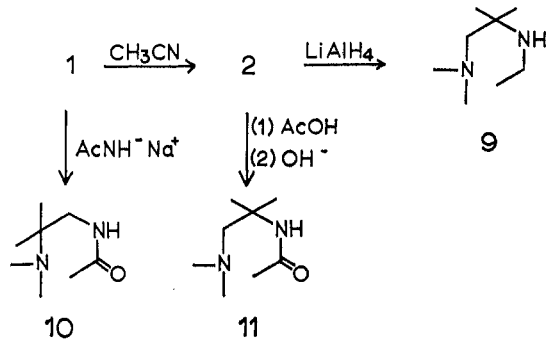
(10) M. A. Weinberger and R. Greenhalgh, *Can. J. Chem.*, **41**, 1038 (1963).

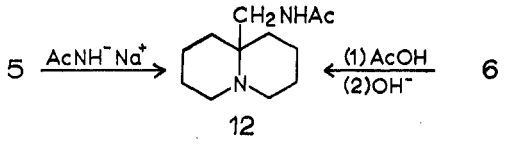
(11) M. D. Mehter, D. Muller, and E. F. Mooney, *J. Chem. Soc.*, 6695 (1965).

(12) G. O. Dudek, *J. Amer. Chem. Soc.*, **85**, 694 (1963).

(13) N. J. Leonard and J. V. Paukstelis, *J. Org. Chem.*, **28**, 3021 (1963).

to amide nitrogen[14] and the spin–spin coupling by the amide proton produces a definitive signal for that grouping in **10**. These amino amides firmly established the structure of the imidazolinium perchlorate **2** and provided models for the degradation products of **6**.



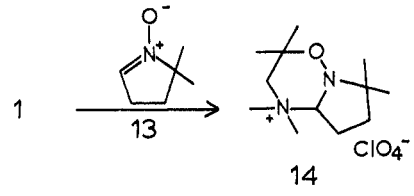


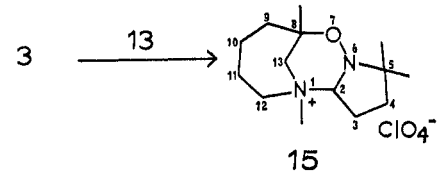
The structure of compound **6** was verified in the following way. A derivative of compound **5** was prepared for comparison by utilizing the direct displacement by acetamide anion upon the aziridinium ring methylene. Compound **12**, 6-acetamidomethyl-1-azabicyclo[4.4.0]decane, was produced in 30% yield and was found to give a satisfactory microanalysis and an infrared spectrum very similar to that of **10**. The nmr spectrum of **12** was distinguished by the signals for the acetyl protons at τ 8.06 and the methylene protons at τ 6.57, a doublet, J = 5.5 Hz, as expected. Compound **6** was then hydrolyzed in acetic acid as was done with **2**. The nmr spectrum of the product after conversion to the free base was identical with that of **12**, along with the infrared spectrum, mass spectrum, melting point, and mixture melting point.

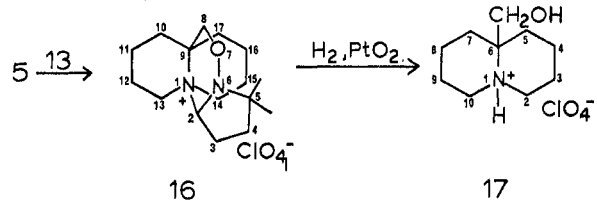
An investigation of the nitrone ring expansion reaction utilizing the above aziridinium salts gave normal and abnormal type adducts parallel to those in the acetonitrile ring expansion reaction. It has been previously reported that aziridinium salt **1** underwent normal ring expansion when treated with 5,5-dimethyl-Δ^1-pyrroline 1-oxide (**13**) to give 3,3,5,5,9,9-hexamethyl-2-oxa-1-aza-5-azoniabicyclo[4.3.0]nonane perchlorate (**14**).[7] Aziridinium salt **3** likewise gave the normal product 1,5,5,8-tetramethyl-7-oxa-6-aza-1-azoniatricyclo[6.4.1.$0^{2,6}$]tridecane perchlorate (**15**). The structure of adduct **14** has been established previously by means of chemical degradation.[7] A comparison of the nmr spectra of **14** and **15** in dimethyl sulfoxide-d_6 and in methylene chloride served to prove that **15** is a normal ring expansion product. The resonance of the methine proton adjacent to both nitrogens appeared at τ 5.64 in **14** and 5.52 in **15**. The resonance of the former aziridinium methylene appeared as an AB system in both compounds centered at τ 6.58 in **14** and at 6.45 in **15** (CH_2Cl_2). The signals for the N-methyl protons appeared at τ 6.81 and 6.98 in **14** and 6.82 (3 H) in **15**.

(14) L. M. Jackman, "Applications of Nuclear Magnetic Spectroscopy in Organic Chemistry," Pergamon Press, London, 1959, p 56.

The resonances of the *gem* dimethyl groups of the pyrrolidine ring appeared at τ 8.81 and 8.95 in **14** and 8.68 and 8.87 in **15**. The similar resonances of these groups confirm that compound **15** contains a 1,2,4-oxadiazinium ring and is a normal ring expansion product.





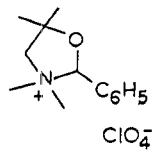


By contrast, when the tricyclic aziridinium salt, 1-azoniatricyclo[4.4.1.$0^{1,6}$]undecane perchlorate (**5**) was treated with 5,5-dimethyl-Δ^1-pyrroline 1-oxide (**13**), the product of abnormal ring expansion, 5,5-dimethyl-7-oxa-6-aza-1-azoniatetracyclo[7.4.4.$0^{1,9}$.$0^{2,6}$]heptadecane perchlorate (**16**) was isolated. The nmr spectrum of **16** was compared with that of adduct **15**. Evidence for the existence of a 1,2,4-oxadiazinium ring in **16** was obtained from comparison of the signals of the *gem* dimethyl protons of the pyrrolidine ring of **16** at τ 8.69 and 8.80 with those of **15** at τ 8.68 and 8.87. In addition, the methine proton adjacent to both nitrogens gave a signal at τ 4.66 in **16** compared with 5.52 in **15**. Apparently the conformation of an abnormal tetracyclic product acts to deshield the methine proton with respect to the conformation of the normal tricyclic product **15**. Verification that **16** was an abnormal ring expansion product was obtained by examination of the resonance of the former aziridinium methylene protons. This signal in **16** appeared as an AB system of doublets centered at τ 5.83 while in **15** the AB system was centered at 6.45. This chemical shift for **15** is reasonable for methylene protons adjacent to oxygen but not for methylene protons adjacent to charged nitrogen. Chemical evidence for the abnormal product **16** was obtained by catalytic hydrogenolysis. When **16** dissolved in 1:1 methanol–acetic acid was treated with Adams' catalyst under hydrogen there was obtained 6-hydroxymethyl-1-azabicyclo[4.4.0]decane perchlorate (**17**), identified by analysis, infrared spectrum, and nmr spectrum. The former aziridinium methylene signal in the nmr spectrum appears at τ 5.80 in **17**. Upon conversion to the free amine, the methylene signal moved upfield to τ 6.50.[8] In comparison, the resonance of the former aziridinium methylene of the isomeric 6-hydroxy-1-azabicyclo[4.4.1]undecane perchlorate appeared at τ 6.41 and shifted to τ 6.90 upon liberation of the free amine.[8] Also, compound **17** has a melting

point of 191–193°, whereas the [4.4.1] isomer had a melting point of 98–99°.

Attempts at formation of a nitrone adduct by reaction of aziridinium salt **7** with 5,5-dimethyl-Δ^1-pyrroline 1-oxide (**13**) were not successful. A heat of mixing or reaction was observed but no crystalline material could be isolated.

Expansion of the aziridinium ring by reaction of compounds **1**, **3**, and **5** with benzaldehyde was also examined. Compounds **1** and **3** gave the normal ring expansion products,[4] 2-phenyl-3,3,5,5-tetramethyloxazolidinium perchlorate (**18**) and 1,6-dimethyl-8-phenyl-7-oxa-1-azoniabicyclo[4.2.1]nonane perchlorate (**19**), respectively. Attempts at the preparation of the



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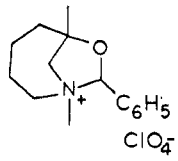

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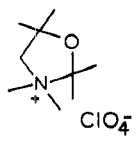

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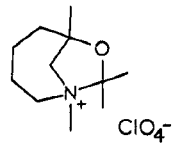

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benzaldehyde adduct of aziridinium salt **5** did not result in the isolation of a product, and the presence of a ring-expanded product could not be detected in the nmr spectra of the crude reaction mixtures. The structure of the normal ring expanded product **19** was determined by chemical degradation. Lithium aluminum hydride reduction[4] of **19** in tetrahydrofuran resulted in the formation of 3-benzyloxy-1,3-dimethyl-1-azacycloheptane perchlorate, the same product being obtained by solvolysis of the aziridinium salt **3** in benzyl alcohol at 80°.

Compounds **1** and **3** also formed normal ring expansion products with acetone[5] to give 2,2,3,3,5,5-hexamethyloxazolidinium perchlorate (**20**) and 1,6,8,8-tetramethyl-7-oxa-1-azoniabicyclo[4.2.1]nonane perchlorate (**21**), respectively, whereas the formation of an acetone adduct of compound **5** could not be detected by nmr spectroscopy, even after attempted reaction in sealed tubes at elevated temperatures.

It has been observed that mono- and bicycloaziridinium salts react to form normal ring expanded products while the tri- and tetracyclic aziridinium salts selected react to form abnormal ring expanded products. These statements obtain for the compounds which can actually be isolated, and they are not meant to be exclusive. They also hold at the level of nmr detectability in the crude reaction mixtures obtained for most of the combinations. The formation of abnormal products can be explained if one visualizes the β-amino-*t*-carbonium ion that could be an intermediate in the normal ring expansion reaction. Acetonitrile and nitrone **13** are considerably different in regard to their bulk and their degree of nucleophilicity toward aziridinium salts. Consequently, the ring expansion reaction should be considered separately for each reactant.

In the transition state for 1,2 bond breaking the process may be well advanced toward β-amino-*t*-carbonium ion formation, especially for mono- and bicyclic aziridinium salts **1** and **3**. This concept of the transition state for the aziridinium ring opening should be applicable to product formation by either a one-step cycloaddition process or a two-step addition, ring-closure process, the difference between the two processes being the orientation of the solvent–reactant molecules in the intermediate and the degree of covalent bonding by the solvent–reactant to carbon and to nitrogen. In the case of the tricyclic aziridinium salt **5**, as we have seen from preceding papers,[1,8] initial aziridinium ring opening can lead to the bicyclo[4.4.1]undecane system under kinetic control. *endo* addition of acetonitrile with respect to the methylene bridge appears subject to steric constraint at the tertiary carbon, and the CH_3—$C^+{\equiv\!\equiv}N$— group may be lost before ring closure to the even more strained tricyclic[4.4.2.$1^{1,6}$] system (isomeric with **6**) can result. *exo* addition of acetonitrile with respect to the methylene bridge would result in a species which is prevented sterically from ring closure to nitrogen. In the case of the tetracyclic aziridinium salt **7** there is not only greater steric resistance to formation of the β-amino-*t*-carbonium ion but greater steric hindrance to its capture by acetonitrile. The transition state for 1,3 bond breaking may be pictured as containing appreciable covalent bonding to the solvent–reactant as the N^+–CH_2 bond is cleaved. Covalent bond formation with acetonitrile followed by ring closure or possibly cycloaddition across the 1,3 bond provides the abnormal ring expansion product.

The nitrone ring expansion reactions occur more readily than those with acetonitrile. Heat is evolved on mixing **1**, **3**, or **5** with **13**, the reaction proceeds at ambient temperature, it does not require more than 100% excess of nitrone as solvent–reactant, and high yields are obtained. Where steric hindrance is minimal, as with **1** and **3**, nucleophilic displacement occurs at the more reactive position (as with water, methanol, and acetic acid) and the new ring is formed. When steric hindrance becomes significant, as in **5**, displacement occurs at the less reactive, but more accessible, methylene carbon. There may be a reversible addition to the substituted aziridinium carbon of **5** from the *exo* direction, but the intermediate would be sterically prevented from formation of a new 1,2,4-oxadiazinium ring, as in the nitrile case. Applying the same steric considerations, the normal and abnormal ring expansion reactions may also proceed by concerted cycloaddition.

Experimental Section[15]

1,1,2,4,4-Pentamethylimidazolinium Perchlorate (2).—A solution of 2.22 g (11.1 mmol) of 1,1,2,2-tetramethylaziridinium perchlorate (**1**)[5] in 10 ml of acetonitrile was heated at reflux for 3 hr under a slow stream of nitrogen. The solvent was removed *in vacuo* and the resulting oil crystallized upon cooling. After trituration with ether and recrystallization from ethanol the feather-like colorless crystals had mp 168.5–169.5°; yield 0.93 g (35%); ν_{max}^{Nujol} 1710 cm^{-1} (C=N); pmr (CF_3COOH) τ 6.02 (s,

(15) Melting points are corrected. Nuclear magnetic resonance spectra were obtained on a Varian Associates A-60, A-60A, A-56/60, or HA-100 spectrometer using tetramethylsilane as an internal reference. We thank Mr. Robert L. Thrift for his assistance with the nmr spectra. Infrared spectra were obtained on a Perkin-Elmer Model 337 grating spectrophotometer. Microanalyses were performed by Mr. Josef Nemeth and his staff. In nuclear magnetic resonance data, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, v = very, and br = broad.

2, CH_2N^+), 6.41 [s, 6, $(CH_3)_2N^+$] 7.38 (s, 3, $CH_3C{=}N$), and 8.36 [s, 6, $(CH_3)_2C$].

Anal. Calcd for $C_8H_{17}ClN_2O_4$: C, 39.83; H, 7.05; N, 11.62. Found: C, 40.24; H, 7.09; N, 11.50.

1,6-Dimethyl-1-azoniabicyclo[4.1.0]heptane Perchlorate (3).[1]—An excess of ethereal diazomethane was added in portions to a solution of 0.50 g (2.36 mmol) of 1,2-dimethyl-3,4,5,6-tetrahydropyridinium perchlorate[16] in 40 ml of stirred methylene chloride cooled at 0°. The solution was stirred 30 min, the excess diazomethane was evaporated with warm water, and the remaining solvent was evaporated *in vacuo*. The colorless solid was taken up in methylene chloride, ether was added to the cloud point, and the solution was allowed to stand at −20° until crystals formed. The cold solvent was removed under a blanket of nitrogen with a fritted glass filterstick and the colorless needles obtained were dried *in vacuo*: mp 151.5–153°; yield 0.45 g (84%); no OH, N^+H, or $C{=}N^+$ absorptions in the infrared spectrum; pmr (CH_2Cl_2) τ 6.42 (br t, 2, J = 6.0 Hz, CH_2N^+), 6.78 and 7.04 (AB system of doublets, 2, J_{AB} = 5.0 Hz, aziridinium methylene), 6.85 (s, 3, CH_3N^+), 7.86 (br t, 2, J = 6.0 Hz, CH_2C), and 8.27 (br s, 7, CH_3C and 4 ring protons).

Anal. Calcd for $C_8H_{16}ClNO_4$: C, 42.48; H, 7.08; N, 6.19. Found: C, 42.33; H, 7.01; N, 6.33.

1,2,6-Trimethyl-1-azoniabicyclo[4.1.0]heptane Perchlorate.—A slight excess of ethereal diazomethane was added to a stirred solution of 0.50 g (2.21 mmol) of 1,2,6-trimethyl-3,4,5,6-tetrahydropyridinium perchlorate[16] in 40 ml of CH_2Cl_2 cooled in an ice bath. The solution was stirred for 30 min and the solvent was evaporated *in vacuo* to yield 0.53 g (100%) of light yellow powder. The product was dissolved in CH_2Cl_2 and ether added to the cloud point of the solution. The solution was allowed to stand 2 days at −20°, and the product was collected by filterstick removal of the cold solvent under a nitrogen atmosphere, small colorless prisms: mp 161–162°; pmr (CH_2Cl_2) τ 6.15–6.55 (m, 1, CH), 6.72 and 7.23 (AB system of doublets, J_{AB} = 5 Hz, assigned to aziridinium methylene protons in one of the two diastereomeric racemates), 6.87 and 7.02 (2 s, 3, N^+CH_3 of each racemate), 7.02 (center of overlapping AB system assigned to aziridinium methylene protons in the second racemate), 7.88 (br m, 2, CCH_2), 8.22 and 8.27 (2 s, 3, CCH_3 of each racemate), 8.22 (br m, 4, CH_2CH_2-CH_2), 8.53 and 8.59 (2 d, 3, J = 7.0 Hz, for $CHCH_3$ of each racemate).

Anal. Calcd for $C_9H_{18}ClNO_4$: C, 45.00; H, 7.50; N, 5.83. Found: C, 45.30; H, 7.56; N, 6.02.

1,6,8-Trimethyl-7-aza-1-azoniabicyclo[4.2.1]non-7-ene Perchlorate (4).—A slight excess of ethereal diazomethane was added to a solution of 0.50 g (2.36 mmol) of 1,2-dimethyl-3,4,5,6-tetrahydropyridinium perchlorate[16] in 40 ml of stirred methylene chloride cooled to 0°. The solution was stirred 30 min, the solvent was removed *in vacuo*, and the colorless solid was taken up in 10 ml of redistilled acetonitrile. The acetonitrile solution was heated at reflux under a slow stream of nitrogen for 3 hr. The acetonitrile was evaporated *in vacuo*, and the product was recrystallized from ethanol to yield 0.31 g (49%) of colorless prisms. Three recrystallizations from ethanol furnished analytically pure material: mp 118.5–120°; ν_{max}^{Nujol} 1700 cm^{-1} (C=N band); pmr (CH_2Cl_2) τ 5.60 and 6.57 (AB system of doublets, 2, J_{AB} = 13 Hz, N^+CH_2C), 6.22 (br m, 2, $CH_2CH_2N^+$), 6.47 (s, 3, N^+CH_3), 7.59 (s, 3, $CH_3C{=}N$), 8.17 (br s, 6, $CH_2CH_2CH_2$), and 8.52 (s, 3, CH_3C).

Anal. Calcd for $C_{10}H_{19}ClN_2O_4$: C, 44.94; H, 7.12; N, 10.49. Found: C, 45.25; H, 7.14; N, 10.63.

1,2,6,8-Tetramethyl-7-aza-1-azoniabicyclo[4.2.1]non-7-ene Perchlorate.—A slight excess of ethereal diazomethane was added to a stirred solution of 0.50 g (2.21 mmol) of 1,2,6-trimethyl-3,4,5,6-tetrahydropyridinium perchlorate[16] in 30 ml of methylene chloride cooled by an ice bath. The solution was stirred 30 min, and the solvent was removed *in vacuo*. The colorless solid was dissolved in 10 ml of redistilled acetonitrile, and the solution was heated at reflux for 20 hr. Upon cooling, a slight turbidity was removed by filtration, and the product was precipitated by addition to a large volume of stirred ether. The oily product was taken up in methylene chloride, reprecipitated, and washed with ether. The product was then dissolved in hot ethanol. The cooled solution deposited colorless prisms in two crops: first crop 0.163 g, mp 116–119°; second crop 0.165 g, mp 115–122°; total yield 0.328 g (53%); ν_{max}^{Nujol} 1690 cm^{-1} (C=N); pmr (CH_2Cl_2) τ 5.67 and 6.61 (AB system of doublets, J_{AB} = 12 Hz, imidazolinium methylene protons of one racemate), 5.83 and 6.94 (AB system of doublets, J_{AB} = 13 Hz, imidazolinium methylene protons of other racemate), 6.05 (br m, $CHCH_3$), 6.57 and 6.72 (2 s, 3, N^+CH_3 of racemate), 7.63 (s, 3, $CH_3C{=}N$), 8.24 (br s, 6, $CH_2CH_2CH_2$), 8.47 (d, 3, J = 7.0 Hz, $CHCH_3$), 8.56 (s, 3, CH_3C).

Anal. Calcd for $C_{11}H_{21}ClN_2O_4$: C, 46.98; H, 7.49; N, 9.96. Found: C, 47.13; H, 7.52; N, 10.16.

11-Methyl-12-aza-1-azoniatricyclo[4.4.3.0^{1,6}]tridec-11-ene Perchlorate (6).—A solution of 0.75 g (2.98 mmol) of 1-azoniatricyclo[4.4.1.0^{1,6}]undecane perchlorate (5)[8] in 20 ml of acetonitrile under a slow stream of nitrogen was heated at reflux for 68 hr. The solvent was removed *in vacuo*, and the reddish oil obtained was dissolved in approximately 75 ml of hot ethanol. Upon cooling, some noncrystalline material precipitated and was removed by filtration. The ethanol solution was then concentrated *in vacuo* to about 20 ml, heated, and allowed to stand. Reddish yellow prisms were collected in 250-mg yield. The combined product was then recrystallized from methanol to give two crops of yellow prisms: mp (both crops) 221–237° with charring; yield 159 and 32 mg, respectively (total, 22%). Further recrystallization from methanol yielded analytically pure light yellow prisms: mp 241–244° dec; ν_{max}^{Nujol} 1690 cm^{-1} (C=N); pmr (CF_3COOH) τ 5.72 (q, 2, J = 1.9 Hz, $CCH_2N{=}$), 6.00–6.70 (m, 4, $CH_2N^+CH_2$), 7.28 (t, 3, J = 1.9 Hz, CH_3), and 7.98 (v br s, 12, remaining ring methylenes).

Anal. Calcd for $C_{12}H_{21}ClN_2O_4$: C, 49.15; H, 7.17; N, 9.56. Found: C, 49.28; H, 7.30; N, 9.38.

13-Methyl-12-aza-1-azoniatetracyclo[7,4.3.0^{1,10}.0^{5,10}]hexadec-12-ene Perchlorate (8).—A solution of 0.70 g (2.4 mmol) of 1-azoniatetracyclo[7.3.2.0^{1,13}.0^{5,13}]tetradecane perchlorate (7)[8] in 10 ml of anhydrous acetonitrile was heated at reflux for 36 hr. The reddish solution obtained was poured into a large volume of stirred ether and the precipitate was triturated with ether to give a dark red semisolid. Attempted crystallization from ethanol was unsuccessful. The ethanol was evaporated *in vacuo*, the oil obtained was treated with aqueous potassium carbonate, and the mixture was extracted several times with ether. The mixture was then extracted with methylene chloride, and the extracts were dried over anhydrous potassium carbonate. The solvent was evaporated *in vacuo* and the residual yellow oil was recrystallized twice from ethanol–ether, yield 75 mg (9%) of light yellow needles of analytically pure product: mp 213–214.5°; ν_{max}^{Nujol} 1710 cm^{-1}; pmr (CF_3CO_2H) τ 5.62 (q, 2, J = 2.0 Hz, CCH_2N), 6.20 (br m, 4, $CH_2N^+CH_2$), 7.33 (t, 3, J = 2.0 Hz, CH_3), and 8.05 (br m, 16, remaining ring methylenes).

Anal. Calcd for $C_{15}H_{25}ClN_2O_4$: C, 54.05; H, 7.51; N, 8.41. Found: C, 54.18; H, 7.76; N, 8.33.

Lithium Aluminum Hydride Reduction of 1,1,2,4,4-Pentamethylimidazolinium Perchlorate (2). N^1,N^1-Dimethyl-N^2-ethyl-2-methyl-1,2-diaminopropane (9) Dipicrate.—To a cooled, stirred mixture of 1.00 g (26 mmol) of lithium aluminum hydride in 50 ml of tetrahydrofuran was added in one portion 1.00 g (4.15 mmol) of 1,1,2,4,4-pentamethylimidazolinium perchlorate (2). The mixture was allowed to warm to ambient temperature and then heated at reflux for 16 hr. The heating bath was removed, and 1.0 ml of water was added dropwise, followed by 1.0 ml of 15% sodium hydroxide and then 3.0 ml of water. The mixture was then heated at reflux for 2 hr. Upon cooling, the precipitate was removed by filtration and washed with ether. The combined solutions were dried over anhydrous potassium carbonate followed by evaporation of the solvents *in vacuo*. The product was dissolved in a small amount of ethanol, an adequate amount of a saturated ethanolic solution of picric acid was added, and the solution was heated (steam bath) for a short time. Yellow prisms were obtained upon cooling which were recrystallized from ethanol containing a slight excess of picric acid: mp 207–210°; yield 0.152 g (6%); pmr (CH_2Cl_2) τ 6.28 (s, 2, CCH_2N^+), 6.83 (q, 2, J = 7.5 Hz, CH_2CH_3), 6.87 [s, 6, $(CH_3)_2N^+$], 8.37 [s, 6, $(CH_3)_2C$], and 8.64 (t, 3, J = 7.5 Hz, CH_3CH_2).

Anal. Calcd for $C_{20}H_{26}N_8O_{14}$: C, 39.87; H, 4.32; N, 18.60. Found: C, 40.04; H, 4.43; N, 18.52.

N-1-(2-Dimethylamino-2-methylpropyl)acetamide (10).—A solution of 0.59 g (10 mmol) of acetamide in 5 ml of dry dimethylformamide was added dropwise to a stirred mixture of 0.40 g (10 mmol) of a 60% mineral oil dispersion of sodium hydride in 10 ml of dry dimethylformamide, and the mixture was stirred for 1.5 hr under nitrogen. A solution of 2.12 g (10.6 mmol) of 1,1,2,2-tetramethylaziridinium perchlorate (1)[4] in 5 ml of dry dimethyl-

(16) N. J. Leonard and F. P. Hauck, Jr., *J. Amer. Chem. Soc.*, **79**, 5279 (1957).

formamide was then added dropwise to the mixture, and the suspended material disappeared during addition. The solution was stirred an additional 3 hr before the solvent was removed *in vacuo*. The viscous oil was dissolved in water, and the solution was saturated with potassium carbonate. The solution was extracted with chloroform, and the combined extracts were dried over anhydrous potassium carbonate before being evaporated *in vacuo*. The product was distilled *in vacuo*: bp 71° (0.20 mm); yield 0.47 g (30%); ν_{max}^{film} 3290, 3070, 1655, and 1545 cm^{-1}; pmr (CH_2Cl_2) τ ~3.50 (v br m, 1, NH), 6.89 (d, 2, J = 5.0 Hz, $CH_2NHC{=}O$), 7.82 [s, 6, $(CH_3)_2N$], 8.07 (s, 3, $CH_3C{=}O$), and 9.02 [s, 6, $(CH_3)_2C$].

Anal. Calcd for $C_8H_{18}N_2O$: C, 60.76; H, 11.39; N, 17.72. Found: C, 60.49; H, 10.98; N, 17.81.

Reaction of 1,1,2,4,4-Pentamethylimidazolinium Perchlorate (2) with Acetic Acid. N-(1,1-Dimethylamino-2-methylprop-2-yl)acetamide (11).—The reaction was first run as an attempted reduction of 1,1,2,4,4-pentamethylimidazolinium perchlorate (2) in commercial glacial acetic acid with platinum and hydrogen, but it was later found that the identical product was obtained when the platinum and hydrogen were omitted. A 0.10-g (0.4 mmol) sample of 1,1,2,4,4-pentamethylimidazolinium perchlorate (2) was stirred with 7.5 ml of glacial acetic acid at ambient temperature for 3 hr. The solvent was removed by evaporation in vacuo at 50°. The residue was dissolved in 6 ml of absolute ethanol and the solvent was removed, leaving 98 mg (91%) of 2-acetamido-N^1,N^1-dimethyl-2-methylpropylamine (11) perchlorate as a white powder. The perchlorate salt was recrystallized from ethanol as colorless prisms of **2-acetamido-N^1,N^1-dimethyl-2-methylpropylamine perchlorate**: mp 120–121°; ν_{max}^{Nujol} 3350, 3060, 1665, and 1550 cm^{-1}; pmr (CF_3COOH) τ 2.43 (br s, 1, $NHC{=}O$), 6.38 (d, 2, J = 4 Hz, N^+CH_2), 6.84 [d, 6, J = 5 Hz, $(CH_3)_2N^+$], 7.67 (s, 3, $CH_3C{=}O$), 8.36 [s, 6, $(CH_3)_2C$].

Anal. Calcd for $C_8H_{19}ClN_2O_5$: C, 37.07; H, 7.34; N, 10.81. Found: C, 37.13; H, 7.39; N, 10.83.

The reaction appeared to proceed slightly faster in 2:1 acetic acid–water and the purity of the product was not affected.

A portion of the salt was dissolved in water, and the solution was saturated with sodium bicarbonate. The solution was extracted with methylene chloride, and the extracts were dried over anhydrous potassium carbonate. The solvent was evaporated *in vacuo* to yield the free base, **N-(1,1-dimethylamino-2-methylprop-2-yl)acetamide (11)**, possessing the following pmr (CH_2Cl_2): τ ~3.55 (v br m, 1, $NHC{=}O$), 7.58 (s, 2, CH_2), 7.70 [s, 6, $(CH_3)_2N$], 8.13 (s, 3, $CH_3C{=}O$), and 8.71 [s, 6, $(CH_3)_2C$].

6-Acetamidomethyl-1-azabicyclo[4.4.0]decane (or 10-Acetamidomethylquinolizidine) (12).—A solution of 0.234 g (3.97 mmol) of acetamide in 5 ml of dry dimethylformamide was added dropwise to a stirred suspension of 0.159 g (3.97 mmol) of a 60% mineral oil dispersion of sodium hydride in 10 ml of dry dimethylformamide. The suspension was stirred overnight under nitrogen, and a solution of 1.00 g (3.97 mmol) of 1-azoniatricyclo[4.4.-$1.0^{1,6}$]undecane perchlorate (**5**)[8] in 5 ml of dry dimethylformamide was added dropwise with the suspended material disappearing during addition. The mixture was stirred for an additional 2 hr. The solvent was evaporated *in vacuo*, and the oily product was dissolved in a small portion of water. The aqueous solution was saturated with sodium bicarbonate and extracted with four portions of chloroform. The combined extracts were dried over anhydrous potassium carbonate, and the chloroform was evaporated under a stream of nitrogen. The product was sublimed at 80° (0.25 mm) to give 0.25 g (30%) of a wet looking solid. The product was washed with two small portions of ether and resublimed at 60° (0.20 mm): prisms; mp 120–122.5°; ν_{max}^{Nujol} 3250, 3070, 1635, and 1565 cm^{-1}; pmr (CH_2Cl_2) τ 3.64 (v br m, 1, $NHC{=}O$), 6.57 (d, 2, J = 5.5 Hz, CH_2NH), ~7.37 (br m, 4, CH_2NCH_2), 8.06 (s, 3, $CH_3C{=}O$), and ~8.53 (br m, 12, remaining ring methylenes).

Anal. Calcd for $C_{12}H_{22}N_2O$: C, 68.57; H, 10.48; N, 13.33. Found: C, 68.35; H, 10.43; N, 13.32.

Attempted Catalytic Reduction of 11-Methyl-12-aza-1-azoniatricyclo[4.4.3.$0^{1,6}$]tridec-11-ene Perchlorate (6).—A solution of 140 mg of compound 6 in 75 ml of glacial acetic acid with 50 mg of platinum oxide was shaken under 3 atm hydrogen at ambient temperature for 15 hr. The catalyst was removed by filtration, and the solvent evaporated *in vacuo*. The tacky product was dissolved in hot ethanol which yielded upon cooling 31 mg of starting material. Ether was added to the filtrate to produce a small amount of flocculent material which was removed by filtration. The ethanol was removed *in vacuo*, and the remaining oil was dissolved in water. The aqueous solution was saturated with potassium carbonate and extracted with methylene chloride. The combined extracts were dried over anhydrous potassium carbonate followed by evaporation of the solvent *in vacuo*. The solid product was sublimed, washed with two small portions of ether, and sublimed again. The product obtained was identical with 6-acetamidomethyl-1-azabicyclo[4.4.0]decane (12) (see above) judged by infrared and nmr spectra and identical melting point (121–123.5°) and mixture melting point (120.5–123.5°).

Anal. Calcd for $C_{12}H_{22}N_2O$: C, 68.57; H, 10.48; N, 13.33. Found: C, 68.75; H, 10.44; N, 13.33.

To show that acetic acid alone was sufficient to effect the reaction a 5.2 mg (0.02 mmol) sample of 6 was treated with 1.0 ml of acetic acid and the mixture was allowed to stand at 38–42° for 4 days. The solvent was then removed by evaporation and the residue was treated with 1 ml of ethanol–xylene (1:1). The ir spectrum of the residue after evaporation had $\nu_{max}^{CH_3OH}$ 1670 cm^{-1}. The product was then dissolved in 10 ml of methanol and treated with 1 ml of basic ion-exchange resin (Dowex 1X-2, 100-200 mesh, OH^- form, which had been washed with methanol prior to use), and the mixture was allowed to stand at ambient temperature for 1.5 hr. The resin was removed by filtration, and the residue after evaporation, 3.0 mg (81%), was identical with 12 as judged by superimposable infrared spectra, mass spectra which had the same fragmentation patterns, and melting point (120.5–123.5°).

5,5-Dimethyl-Δ^1-pyrroline 1-oxide (13) was prepared by reductive cyclization of the corresponding γ-nitroaldehyde according to the method of Bonnett, Brown, Clark, Sutherland, and Todd.[17] The nitrone was stored at −20° under nitrogen.

Reaction of 1,6-Dimethyl-1-azoniabicyclo[4.1.0]heptane Perchlorate (3) with 5,5-Dimethyl-Δ^1-pyrroline 1-Oxide (13).—To 1.00 g (8.85 mmol) of 5,5-Dimethyl-Δ^1-pyrroline 1-oxide (13) was added in portions 1.00 g (4.42 mmol) of 1,6-dimethyl-1-azoniabicyclo[4.1.0]heptane perchlorate (3) with the evolution of heat. The reactants were mixed thoroughly during the addition, and the mixture was allowed to stand at ambient temperature for 5 days. The semisolid mixture was triturated with ethyl acetate to give a colorless solid. Recrystallization from acetonitrile–ether afforded 1.02 g (68%) of colorless prisms of **1,5,5,8-tetramethyl-7-oxa-6-aza-1-azoniatricyclo[6.4.1.$0^{2,6}$]tridecane perchlorate (15)**. A further recrystallization afforded an analytical sample: mp 157–158°; no infrared maxima corresponding to O–H or N^+–H; pmr (CH_2Cl_2) τ 5.52 (t, 1, N^+CHN), 5.9–6.2 (br, m, 1 $CHHN^+$), 5.98 and 6.92 (AB system of doublets, 2, J_{AB} = 14 Hz, N^+CH_2C), 6.4–6.8 (br, m, 1, $CHHN^+$), 6.82 (s, 3, CH_3N^+), 7.5–8.4 (complex multiplet, 10, remaining ring methylenes), 8.68 (s, 3, CH_3C), and 8.68 and 8.87 (2 s, 6 $(CH_3)_2C$].

Anal. Calcd for $C_{14}H_{27}ClN_2O_5$: C, 49.56; H, 7.96; N, 8.26. Found: C, 49.79; H, 7.95; N, 8.16.

Reaction of 1-Azoniatricyclo[4.4.1.$0^{1,6}$]undecane Perchlorate (5) with 5,5-Dimethyl-Δ^1-pyrroline 1-Oxide (13).—To 1.12 g (9.9 mmol) of 5,5-dimethyl-Δ^1-pyrroline 1-oxide (13) was added 1.24 g (4.9 mmol) of 1-azoniatricyclo[4.4.1.$0^{1,6}$]undecane perchlorate (5) in portions with the evolution of heat. The reactants were thoroughly mixed until the viscous mixture solidified within 15 min. After allowing it to stand at ambient temperature for 20 hr, the mixture was triturated with ethyl acetate to yield a solid product. Two recrystallizations from acetonitrile–ether gave 1.04 g (58%) of thick colorless prisms of analytically pure **5,5-dimethyl-7-oxa-6-aza-1-azoniatetracyclo[7.4.4.0.^{1,9}0^{2,6}]heptadecane perchlorate (16)**: mp 122.5–124.5°; no infrared maxima corresponding to O–H or N^+–H; pmr (CD_3CN) τ 4.66 (br t, 1, J = 3.5 Hz, N^+CHN), 5.21 and 6.44 (AB system of doublets, 2, J_{AB} = 6.5 Hz, CCH_2O), 5.48 (complex t, 1, J = 13 Hz, $CHHN^+$), 5.95 (complex t, 1, J = 13 Hz, $CHHN^+$), 6.97 (complex t, 2, J = 13 Hz, N^+CH_2), 7.2–8.6 (complex multiplet, 16, remaining ring methylenes), and 8.69 and 8.80 [2 s, 6, $(CH_3)_2C$].

Anal. Calcd for $C_{16}H_{29}ClN_2O_5$: C, 52.60; H, 7.95; N, 7.67. Found: C, 52.77; H, 8.04; N, 7.63.

Reduction of the Nitrone Adduct of 1-Azoniatricyclo[4.4.1.$0^{1,6}$]undecane Perchlorate (5).—A solution of 250 mg (0.68 mmol) of 5,5-dimethyl-7-oxa-6-aza-1-azoniatetracyclo[7.4.4.$0^{1,9}$.$0^{2,6}$]heptadecane perchlorate (16) in 50 ml of 1:1 methanol–acetic acid was shaken at ambient temperature under 3 atm of hydrogen for 30 hr in the presence of 50 mg of Adams catalyst. The

(17) R. Bonnett, R. F. C. Brown, V. M. Clark, I. O. Sutherland, and Sir A. Todd, *J. Chem. Soc.*, 2094 (1959).

catalyst was removed by filtration and washed with fresh solvent. Evaporation of the solvent *in vacuo* yielded an oil which was recrystallized to give 70 mg (37%) of colorless prisms from 2-propanol–ether, **6-hydroxymethyl-1-azabicyclo[4.4.0]decane perchlorate (17)**: mp 191–193°; ν_{max}^{Nujol} 3510 and 3105 cm^{-1}; pmr (CF_3CO_2H) τ 5.80 (s, 2, CH_2O), 6.46 (br m, 4, $CH_2N^+CH_2$), and 8.03 (br s, 12, remaining ring methylenes).

Anal. Calcd for $C_{10}H_{20}ClNO_5$: C, 44.44; H, 7.41; N, 5.19. Found: C, 44.65; H, 7.40; N, 5.25.

A portion of the product was treated with aqueous potassium carbonate, and the free amine was extracted with methylene chloride. The solution was dried over anhydrous potassium carbonate and concentrated *in vacuo* to obtain an nmr spectrum of **6-hydroxymethyl-1-azabicyclo[4.4.0]decane**: pmr (CH_2Cl_2) τ 6.50 (s, 2, CH_2O), 7.26 (complex multiplet, 4, CH_2NCH_2), and 8.52 (br s, 12, remaining ring methylenes).

5,5-Dimethyl-1-ethoxy-Δ^1-pyrrolinium Fluoroborate.—This compound was made as an nmr model for the occurrence of single C–O bond formation with **13** rather than cycloaddition. A solution of 3.36 g (30 mmol) of 5,5-dimethyl-Δ^1-pyrroline 1-oxide (**13**) in 10 ml of dry methylene chloride was added to a cooled solution of 5.65 g (30 mmol) of triethyloxonium fluoroborate in 30 ml of dry methylene chloride. After 10 min the solvent was evaporated *in vacuo*. The oil initially obtained solidified to give 6.5 g (94%) of crude material. The product was recrystallized from ethanol–ether at −20°. The solvent was removed under a blanket of nitrogen with a filter stick: waxy needles; mp 52–52.5°; pmr (CF_3COOH) τ 1.73 (br t, 1, J = 2.0 Hz, CH=N$^+$), 5.47 (q, 2, J = 7.0 Hz, CH_2CH_3), 6.74 (t of d, 2, $J_{3,4}$ = 7.5 Hz, $J_{2,3}$ = 2.0 Hz, CH_2C=), 7.59 (t, 2, J = 7.5 Hz, CH_2C), 8.33 [s, 6, $(CH_3)_2C$], and 8.46 (t, 3, J = 7.0 Hz, CH_2CH_3).

Anal. Calcd for $C_8H_{16}BF_4NO$: C, 41.92; H, 6.99; N, 6.11. Found: C, 42.22; H, 7.22; N, 6.16.

2-Phenyl-3,3,5,5-tetramethyloxazolidinium Perchlorate (18).—A solution of 0.95 g (4.75 mmol) of 1,1,2,2-tetramethylaziridinium perchlorate (**1**) in 5 ml of benzaldehyde was heated at 60° under a nitrogen atmosphere for 24 hr. Upon cooling, the solution was poured into 200 ml of rapidly stirred ether, the ether was decanted, and the sticky product was triturated with ether. The product was dissolved in a small amount of methylene chloride, and the precipitation process was repeated. Recrystallization from ethanol yielded 0.76 g (57%) of colorless prisms: mp 130.5–131.5°; nmr (CH_2Cl_2) τ 2.47 (s, 5, C_6H_5), 4.00 (s, 1, ArCH), 6.21 (apparent d, 2, J = 2.5 Hz, CH_2N^+), 6.78 and 7.27 [singlets, 6, $(CH_3)_2N^+$) and 8.38 [s, 6, $(CH_3)_2C$].

Anal. Calcd for $C_{13}H_{20}ClNO_5$: C, 50.98; H, 6.54; N, 4.58. Found: C, 50.85; H, 6.64; N, 4.83.

1,6-Dimethyl-8-phenyl-7-oxa-1-azoniabicyclo[4.2.1]nonane Perchlorate (19).—A slight excess of ethereal diazomethane was added to a solution of 0.50 g (2.36 mmol) of 1,2-dimethyl-3,4,5,6-tetrahydropyridinium perchlorate[8] in 40 ml of stirred methylene chloride cooled to 0°. The solution was stirred 30 min, the solvent was evaporated *in vacuo*, and the colorless solid was taken up in 5 ml of benzaldehyde. The benzaldehyde solution was heated at 60° under a nitrogen atmosphere for 20 hr. After cooling, the solution was slowly poured into 200 ml of rapidly stirred ether with precipitation of a colorless solid. The solid was washed with ether and recrystallized from ethanol: colorless prisms; mp 172–173°; yield 0.46 g (59%); pmr (dimethyl sulfoxide-d_6) τ 2.37 (s, 5, C_6H_5), 3.88 (s, 1, ArCH), 5.64 and 6.32 (AB system of doublets, 2, J_{AB} = 12.5 Hz, N^+CH_2C), 6.68 and 6.82 (singlets, 3, N^+CH_3), 7.05 (m, 2, $CH_2CH_2N^+$), 8.15 (br s, 6, $CH_2CH_2CH_2$), and 8.47 (s, 3, CH_3C).

Anal. Calcd for $C_{15}H_{22}ClNO_5$: C, 54.22; H, 6.63; N, 4.22. Found: C, 54.24; H, 6.63; N, 4.29.

3-Benzyloxy-1,3-dimethyl-1-azacycloheptane Perchlorate.—A solution of 0.50 g (2.2 mmol) of 1,6-dimethyl-1-azoniabicyclo[4.1.0]heptane perchlorate (**3**) in 5 ml of benzyl alcohol was heated at 80° for 22 hr.[4] After cooling, the solution was poured into 150 ml of stirred ether containing 4 drops of ethanolic perchloric acid (1:1). The colorless solid obtained was washed several times with ether before being recrystallized twice from 2-propanol: colorless prisms; mp 106–107°; yield 0.53 g (72%); ν_{max}^{Nujol} 3110 cm^{-1} (N^+H); pmr (CH_2Cl_2) τ 2.63 (m, 5, Ar), 5.48 (s, 2, $ArCH_2$), 6.30–6.85 (m, 4, $CH_2N^+CH_2$), 7.08 (s, 3, N^+CH_3), 7.70–8.50 (m, 6, $CH_2CH_2CH_2$), 8.73 (s, 3, CH_3C).

Anal. Calcd for $C_{15}H_{24}ClNO_5$: C, 53.89; H, 7.18; N, 4.19. Found: C, 54.13; H, 7.29; N, 4.28.

Reduction of 1,6-Dimethyl-8-phenyl-7-oxa-1-azoniabicyclo[4.2.1]nonane Perchlorate (19).—A mixture of 0.120 g (3.16 mmol) of lithium aluminum hydride in 50 ml of tetrahydrofuran was cooled in an ice bath with stirring, and to the mixture was added in one portion 1.00 g (3.0 mmol) of 1,6-dimethyl-8-phenyl-7-oxa-1-azoniabicyclo[4.2.1]nonane perchlorate (**19**). The mixture was allowed to warm to ambient temperature and then was heated at reflux for 3 hr. The mixture was allowed to cool, and 0.12 ml of water, then 0.12 ml of 15% sodium hydroxide, and then 0.36 ml of water were carefully added. The resulting white suspension was heated at reflux for 1 hr, cooled, and removed by filtration. The white residue was washed with ether, and the combined solutions were dried with anhydrous magnesium sulfate. The dried solution was titrated with ethanolic perchloric acid (1:1) to the congo red end point, and the precipitate was washed with ether. The product was recrystallized twice from 2-propanol to give colorless prisms: mp 106.5–107.5°; mmp (with identical solvolysis product) 106–107°; yield 0.67 g (67%); ν_{max}^{Nujol} 3110 cm^{-1} (N^+H); pmr (CH_2Cl_2) identical with that of the product of the solvolysis reaction.

Anal. Calcd for $C_{15}H_{24}ClNO_5$: C, 53.89; H, 7.18; N, 4.19. Found: C, 53.95; H, 7.33; N, 4.31.

1,6,8,8-Tetramethyl-7-oxa-1-azoniabicyclo[4.2.1]nonane Perchlorate (21).—A solution of 0.50 g (2.2 mmol) of 1,6-dimethyl-1-azoniabicyclo[4.1.0]heptane perchlorate (**3**) in 10 ml of anhydrous acetone was heated at reflux for 21 hr under a nitrogen atmosphere. The solution was then poured into a large volume of stirred ether and the precipitate was triturated with ether. An nmr spectrum of the crude product indicated incomplete reaction. The mixture was dissolved in ethanol and heated at reflux for 30 min to open the ring of the aziridinium salt remaining. The ethanol was evaporated *in vacuo* and the oil was treated with aqueous potassium carbonate. The aqueous suspension was first extracted with ether followed by extraction with methylene chloride. The methylene chloride extracts were dried over anhydrous potassium carbonate, and the solvent was evaporated *in vacuo*. The oily product was recrystallized twice from ethanol–ether to give an analytically pure sample: mp 178–179°; yield 73 mg (12%); no OH or N^+H maxima in the infrared spectrum; pmr (CH_2Cl_2) τ 5.87 and 6.18 (AB system of doublets, 2, J_{AB} = 13 Hz, N^+CH_2C), 6.2–6.6 (br m, 2, $CH_2CH_2N^+$), 6.82 (s, 3, CH_3N^+), 7.8–8.4 (br m, 6, remaining ring methylenes), 8.27 [s, 6, $(CH_3)_2C$], and 8.49 (s, 3, CCH_3).

Anal. Calcd for $C_{11}H_{22}ClNO_5$: C, 46.48; H, 7.75; N, 4.93. Found: C, 46.44; H, 7.77; N, 4.76.

Registry No.—**2**, 25516-25-0; **3**, 25516-26-1; **4**, 25516-27-2; **6**, 25568-60-9; **8**, 25568-61-0; **9** dipicrate, 25516-28-3; **10**, 25516-29-4; **11**, 25516-30-7; **12**, 25641-44-5; **15**, 25568-62-1; **16**, 25568-63-2; **17**, 25516-31-8; **17** free amine, 25516-32-9; **18**, 25516-33-0; **19**, 25516-34-1; **21**, 25516-35-2; 1,2,6-trimethyl-1-azoniabicyclo[4.1.0]heptane perchlorate, 25568-64-3; 1,2,6,8-tetramethyl-7-aza-1-azoniabicyclo[4.2.1]non-7-ene perchlorate, 25516-38-5; 2-acetamido-N^1,N^1-dimethyl-2-methylpropylamine perchlorate, 25516-36-3; 5,5-dimethyl-1-ethoxy-Δ^1-pyrrolinium fluoroborate, 25529-24-2; 3-benzyloxy-1,3-dimethyl-1-azacycloheptane perchlorate, 25516-37-4.