Registry No.—Table I—1, 14970-97-9; 2, 14970-98-0; 3, 14971-00-7; 4, 24515-92-0; 5, 24515-93-3; 6, 18795-65-8; 7, 18795-63-6; 8, 18795-64-7; 9, 24515-97-7; 10, 18795-66-9; 11, 18795-62-5; 12, 24516-00-5; 13, 18174-52-2; 14, 18174-53-3; 15, 24516-03-8; 16, 24516-04-9; 17, 18174-54-4; 18, 19323-42-3; 19, 24514-62-3; 20, 18174-55-5; Table II—1, 23592-26-9; 2, 23592-27-0; 3, 23592-28-1; 4, 23592-30-5; 5, 23592-38-3; 6, 23592-31-6; 7, 23592-32-7; 8, 24514-71-4; 9, 23592-33-8; 10, 23592-34-9; 11, 23592-35-0; 12, 24514-75-8; 13, 23592-40-7; 14, 23592-36-1; 15, 23592-37-2; 16, 24514-79-2; **1**, 7555-16-0; **2**, 7445-61-6; ethyl 3,3,3-trifluoro-2-{4-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-dithietane-2-ylidene}propionate, 24515-27-3; 2,4-bis[2,2,2-trifluoro-1-(ethoxycarbonyl)ethylidene]-1,3-dithietane, 24515-15-9; **3**, 7445-60-5; **4**, 7555-17-1; **5**, 7592-88-3; 3,3-bis(chlorodifluoromethyl)-3H-diazirine, 24515-31-9; **6**, 24515-32-0; **7**, 24553-67-1; 2-(*p*-dimethylaminophenyl)-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-dithietane, 15008-38-5; 2-(*p*-diethylaminophenyl)-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-dithietane, 14970-99-1; 2-(*p*-dimethylaminostyryl)-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-dithietane, 24515-35-3; **14**, 24515-36-4; 2-[3,3,3-trifluoro-2-(trifluoromethyl)propenyl]indan, 24515-37-5; 2-(*p*-methoxyphenyl)-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]thietane 1,1,-dioxide, 23592-41-8; quadricyclene adduct with bis(trifluoromethyl)-thioketene, 19438-57-4; 7-chloroquadricyclene adduct with bis(trifluoromethyl)thioketene, 24515-17-1; 7-acetoxyquadricyclene adduct with bis(trifluoromethyl)thioketene, 24515-18-2; 3-*p*-tolyl-2-(*p*-tolylimino)-4-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-thiazetidine, 24515-56-8; dicyclohexylcarbodiimide adduct with bis(trifluoromethyl)thioketene, 24515-57-9; diisopropylcarbodiimide adduct with bis(trifluoromethyl)thioketene, 24515-58-0; 3-benzylideneamino-2-phenyl-4-[2,2,2-trifluoro-1-(trifluoromethyl)-ethylidene]-1,3-thiazetidine, 24515-59-1; 3-cyclohexylideneamino-2-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-thiaazaspiro[3.5]nonane, 24515-60-4; **15**, 7527-44-8; **16a**, 20877-47-8; **16a** dioxide, 20877-48-9; **16b**, 19441-45-3; **16c**, 20877-50-3; **17**, 24515-71-7; **18**, 24515-72-8; **19**, 24515-73-9; **20**, 24515-74-0; **22**, 24515-76-2; 3-phenyl-5-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,4,2-oxathiazole, 24515-77-3; 2-methyl-3-phenyl-5-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,4,2-oxathiazolidine, 24515-78-4; 3-phenyl-5-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,4,2-oxathiazolidine, 24515-80-8; 3-*p*-chlorophenyl-5-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,4,2-oxathiazolidine, 24515-81-9.

Acknowledgment.—The author is indebted to Drs. J. E. Carnahan, C. G. Krespan, B. C. McKusick, and W. A. Sheppard for helpful discussions; to Drs. H. Foster and G. S. Reddy, Mr. C. B. Matthews, and Mrs. Jean L. Read for nmr consultations; and to Misses Carol J. Hermann, Naomi E. Schlichter, and Ellen Wallace for ir and uv spectra interpretations.

Small Charged Rings. XII.[1] Aziridinium Ring Opening by Carboxylic Acids[2]

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Polycyclic aziridinium salts have been found to react with carboxylic acids at elevated temperatures to give compounds possessing amine salt and ester functionality. The monocyclic aziridinium salt 5-azoniadispiro[4.0.5.1]dodecane perchlorate (**1**) was found to rearrange thermally before carboxylic acid addition occurred. The bicyclic aziridinium salt, 1,6-dimethyl-1-azoniabicyclo[4.1.0]heptane perchlorate (**4**), reacted with carboxylic acids, probably *via* a β-amino tertiary carbonium ion intermediate, to form an ammonium ester (**5**). The tri- and tetracyclic aziridinium salts, 1-azoniatricyclo[4.4.1.$0^{1,6}$]undecane perchlorate (**6**) and 1-azoniatetracyclo[7.3.2.$0^{1,13}$.$O^{5,13}$]tetradecane perchlorate (**8**), reacted "abnormally" at the aziridinium methylene to give ammonium esters of primary alcohols, *e.g.*, 6-acetoxymethyl-1-azabicyclo[4.4.0]decane perchlorate (**7a**) and 13-acetoxymethyl-1-azatricyclo[7.3.1.$0^{5,13}$]tridecane perchlorate (**9a**), respectively. The position of carboxylic acid reaction with the aziridinium ring was determined by following the nmr chemical shift of the methylene protons from the original aziridinium ring to the ammonium ester product, and then to the corresponding free amine ester.

Discovery of the reaction of diazomethane with ternary iminium perchlorates and fluoroborates to form aziridinium salts has made a variety of substituted aziridinium salts readily available and has permitted investigation of their chemistry.[3] Previous papers in the series have described the reaction of 1,1,2,2-tetra-substituted aziridinium salts. The aziridinium salts have been found to undergo ring opening by solvolysis-type reaction at the more substituted ring carbon;[3b] nucleophilic displacement at the less hindered, less substituted ring carbon;[3b] thermal rearrangement;[3b] and ring opening and expansion *via* cycloaddition of aldehydes,[4] ketones,[5] nitriles,[6] and nitrones.[7] The solvolytic ring opening, ring expansion, and thermal

(1) For the preceding article in this series, see N. J. Leonard and D. A. Durand, *J. Org. Chem.*, **33**, 1322 (1968).

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

(3) For pertinent references and general summaries of work in this field, see (a) N. J. Leonard, *Rec. Chem. Progr.*, **26**, 211 (1965), and (b) D. R. Crist and N. J. Leonard, *Angew. Chem.*, **81**, 953 (1969); *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).

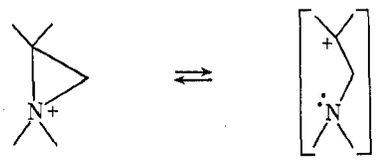
(5) N. J. Leonard, J. V. Paukstelis, and L. E. Brady, *ibid.*, **29**, 3383 (1964).

(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).

rearrangement reactions appear to proceed *via* β-amino tertiary carbonium ion intermediates where sterically possible (Scheme I). We have now found that the

SCHEME I



aziridinium ring is opened with carboxylic acids, *e.g.*, acetic acid and benzoic acid, and we have tested the course of the reaction by means of a series of sterically graduated aziridinium salts.

The series of aziridinium salts selected included 5-azoniadispiro[4.0.5.1]dodecane perchlorate (**1**),[8] 1,6-dimethyl-1-azoniabicyclo[4.1.0]heptane perchlorate (**4**),[9] 1-azoniatricyclo[4.4.1.0^{1,6}]undecane perchlorate (**6**),[8] and 1-azoniatetracyclo[7.3.2.0^{1,13}.0^{5,13}]tetradecane perchlorate (**8**).[8] Attempts at bringing about reaction of compound **1** with the representative carboxylic acids were conducted at 70° for 14 hr in glacial acetic acid and in a 2-nitropropane solution of benzoic acid. Even under these moderated conditions only thermal rearrangement products **2** and **3**[10] were obtained.[3b] When solutions of compounds **4**, **6**, and **8** in glacial acetic acid were heated at reflux, ammonium ester products **5a**, **7a**, and **9a**, respectively, were produced. Mixtures of compounds **6** and **8** with benzoic acid, when heated for 10 min at 135° and 20 min at 145°, respectively, gave the corresponding products, **7b** and **9b**. Evidence of reaction of **4** with benzoic acid was obtained from nmr spectra, but a pure product, **5b**, analogous to that obtained with acetic acid, was not isolated.

In general, the products produced by carboxylic acid addition were characterized by microanalysis and by their infrared and proton magnetic resonance spectra. For the ammonium ester products, the position of attachment of the carboxylate group was determined by examining the change in the pmr chemical shift of the methylene protons from the original aziridinium ring to the ammonium ester product, and then to the corresponding tertiary amine ester liberated from this salt. These data are presented in Table I. The methylene protons originally in the aziridinium ring of **4**, when traced to **5a**, exhibited a doublet at τ 6.42 in the nmr spectrum. This changed to an AB system centered at 7.23 when **5a** was converted to the free amine. The shift of 0.81 ppm is of the order expected[8] for an α_{N^+}-CH_2 to α_N-CH_2 conversion and compares favorably with the 1.02 ppm upfield shift of the other α-methylene group during the same conversion. By contrast, the resonances of the former aziridinium methylene protons, when traced to **7a**, **7b**, **9a**, and **9b**, fell between τ 5.03 and 5.45. Conversion to free amine in each of these cases caused the chemical shifts of the methylene groups to move upfield by only 0.14–0.17 ppm. The lower field signals of the methylene groups in this family of salts is evidence for their attachment to oxygen, and the relatively small change in chemical shift upon liberation of the free amines confirms the assigned structures.

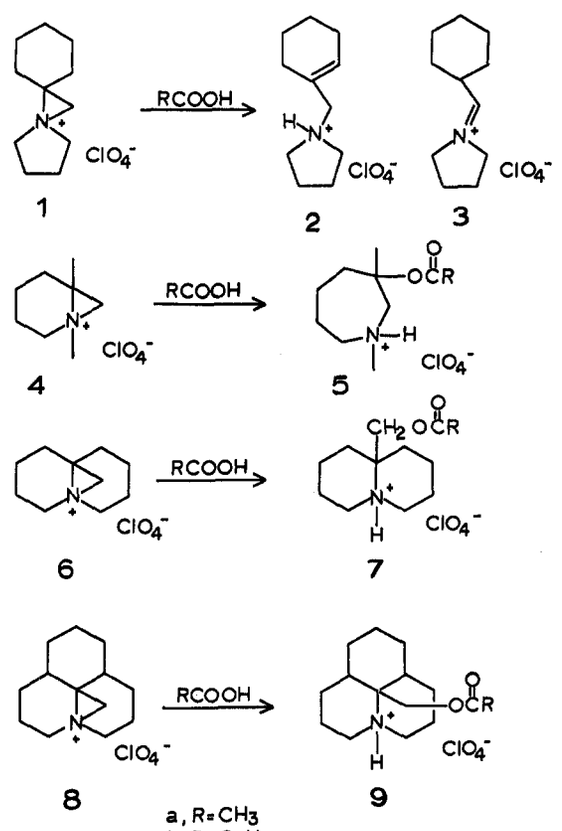
TABLE I

PRODUCTS OF CARBOXYLIC ACID REACTION WITH AZIRIDINIUM SALTS

Compd	Yield, %	Pmr of α-CH$_2$[a,b] Salt	Pmr of α-CH$_2$[a,b] Free amine
5a	53	6.42(d)[c]	7.08, 7.38[d]
7a	64	5.45[e]	5.62
7b	72	5.17[e]	5.33
9a	55	5.28	5.44
9b	69	5.03	5.17

[a] Former aziridinium methylene group. [b] Chemical shifts, τ (methylene chloride, TMS). [c] J = 4.5 Hz. [d] AB system, J_{AB} = 14 Hz. [e] In CF_3COOH.

The diversity of products resulting from the heating of the selected aziridinium salts with carboxylic acids seems inconsistent at first inspection. Thus, compound **1** does not yield an ammonium ester but instead gives thermal rearrangement products **2** and **3**. Compound **4** gives the product of reaction of acetic acid at the more substituted aziridinium carbon atom, which corresponds to the normal position for solvolytic ring opening. Compounds **6** and **8** give products of reaction of acetic and benzoic acids at the less substituted aziridinium carbon. This variety of products may be explained by considering β-aminocarbonium ion intermediates in equilibrium with the aziridinium salt.



The solvolysis of 5-azoniadispiro[4.0.5.1]dodecane perchlorate (**1**) in methanol (65°) and ethanol (78°) to yield the corresponding N-[1-methoxy(ethoxy)cyclo-

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

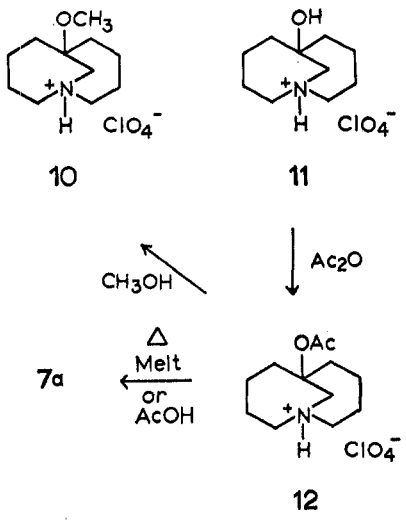
(9) The preparation from the iminium salt was similar to that for 6-ethyl-1-methyl-1-azoniabicyclo[4.1.0]heptane perchlorate in ref 8. For the preparation of the iminium salt precursor, 1,2-dimethyl-3,4,5,6-tetrahydropyridinium perchlorate, see N. J. Leonard and F. P. Hauck, Jr., *J. Amer. Chem. Soc.*, **79**, 5279 (1957).

(10) P. C. Kelley, Ph.D. Thesis, University of Illinois, 1965.

hexylmethyl]pyrrolidine perchlorates[11] and the thermolysis of 1 in the melt (145°) to give a mixture of ene–ammonium (2) and iminium (3) salts[10] are best explained as proceeding through the β-amino tertiary carbonium ion derived from opening of the strained aziridinium ring. In acetic acid and benzoic acid, even when the temperature was maintained as low as possible (70°) to give appreciable reaction, the products isolated were not the corresponding N-[1-(acetoxy- or benzoyloxy)cyclohexylmethyl]pyrrolidine perchlorates but rather the products, 2 and 3, of hydrogen migration in the proposed β-amino tertiary carbonium ion intermediate. The experiments do not preclude formation of the acetoxy and benzoyloxy compounds during the reaction, since any reversal by an E1 elimination would proceed through the same carbonium ion.

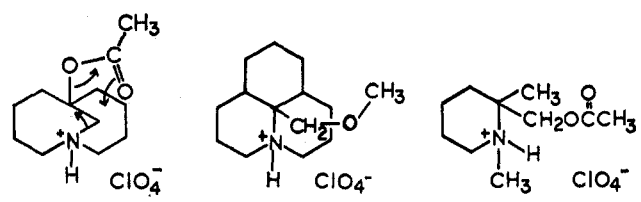
The bicyclic aziridinium salt 4 did not undergo thermal rearrangement as readily as 1. The major product obtained from 4 and glacial acetic acid at reflux was 3-acetoxy-1,3-dimethyl-1-azacycloheptane perchlorate (5a), the structure of which was determined spectroscopically as described above. This may be regarded as the *normal* solvolysis product; methanolysis of the homolog, 6-ethyl-1-methyl-1-azoniabicyclo[4.1.0]heptane perchlorate, had produced an analogous product, 3-ethyl-3-methoxy-1-methyl-1-azacycloheptane perchlorate.[8]

With respect to the methanolysis product of 6, namely, 6-methoxy-1-azabicyclo[4.4.1]undecane perchlorate (10),[8] the acetolysis product of 6, 6-acetoxymethyl-1-azabicyclo[4.4.0]decane perchlorate (7a) is *abnormal*, that is, the acetoxyl group ends up attached to the former aziridinium carbon that was less substituted. For comparison, 6-acetoxy-1-azabicyclo[4.4.1]undecane perchlorate (12) was synthesized by



treatment of 6-hydroxy-1-azabicyclo[4.4.1]undecane perchlorate (11)[8] with acetic anhydride.[12] This isomer was converted to 7a by heating in the melt (170°) for 1–2 min; moreover, 12 was also converted, approximately 64% in 30 min., to 7a in refluxing glacial acetic acid. This suggests that the initial aziridinium ring opening of 6 in methanol or acetic acid leads to the bicyclo[4.4.1]undecane system under kinetic control. When the methanol product 10 is obtained, the methoxyl group is not readily displaced under the reaction conditions. If the acetoxy product 12 is formed, however, the acetoxyl group can be displaced by partial dissociation of the salt, ionization, and participation of the neighboring amino nitrogen.[13] As shown by the conversion of 12 to 7a, at least under the stated reaction conditions, 7a is the thermodynamically more stable acetoxy isomer. As further indication of the ionization of the [4.4.1]acetate (12) and the intermediacy of 6, the reaction of 12 in refluxing methanol was observed to give 6-methoxy-1-azabicyclo[4.4.1]undecane perchlorate (10) (nmr determination), as in the direct methanolysis of 6. By contrast, 6-methoxy-1-azabicyclo[4.4.1]undecane perchlorate remained unchanged when refluxed in glacial acetic acid for 30 min.

Logical mechanistic sequences can be developed for these interconversions based on the equilibration of the aziridinium ion in 6 with the related, solvated β-amino-carbonium ions. In the transition state leading to rapid ring opening at the more substituted carbon, cleavage of the N^+–C bond may be well advanced toward β-amino tertiary carbonium ion formation. In the transition state leading to ring opening at the less substituted carbon, appreciable covalent bonding to the solvent-reactant may be taking place with cleavage of the N^+–C bond, possibly assisted by proton transfer from carboxylic acid to nitrogen. Full development of the new C–O bond completes the solvolysis process.[14,15] The driving force for the observed conversion of 12 to 7a appears to be relief of strain energy in going from the bridged dual seven-membered ring system to the fused six-membered rings of the azadecalin system. Ionization of acetate 12 permits the conversion, whereas this pathway would not occur as readily with the methoxy compound 10. A logical mechanism has been described above for the conversion of 12 to 7a through 6. Another distinct possibility lies in the participation of acetoxyl as a neighboring group[16] (*e.g.*, through 13).



(11) N. J. Leonard and K. Jann, *J. Amer. Chem. Soc.*, **84**, 4806 (1962).

(12) R. A. Johnson, M. E. Herr, H. C. Murray, and G. S. Fonken, *J. Org. Chem.*, **33**, 3187 (1968).

(13) (a) C. F. Hammer and S. R. Heller, *Chem. Commun.*, 919 (1966); (b) R. C. Fuson and C. L. Zirkle, *J. Amer. Chem. Soc.*, **70**, 2760 (1948).

(14) The aziridinium and β-amino carbonium ion solvates may be cognate to ion-pair intermediates [see R. A. Sneen and J. W. Larsen, *J. Amer. Chem. Soc.*, **91**, 362 (1969), and references therein], but the forces of interaction here are between cations or developing carbonium ions and, for example, alcohols or carboxylic acids.

(15) The overall situation is somewhat complicated by the fact that in the solvated β-amino-*t*-carbonium ion first formed by ring opening of 6 the unshared electron pair on nitrogen may be *endo*. Scale molecular models indicate that this form is more strained than the N-inverted form in which the unshared pair is *exo* with respect to the methylene bridge. Strained ring systems having sp^2 hybridization at the bridgehead, including S = 9, [4.4.1] types [(a) F. S. Fawcett, *Chem. Rev.*, **47**, 219 (1950)], have been previously described [see (b) T. L. Westman and R. D. Stevens, *Chem. Commun.*, 459 (1965), and references therein; (c) A. C. Cope, R. J. Cotter, and G. G. Roller, *J. Amer. Chem. Soc.*, **77**, 3590 (1955); (d) K. Biemann, G. Büchi, and B. H. Walker, *ibid.*, **79**, 5558 (1957); (e) W. J. McMurray, Ph.D. Thesis, University of Illinois, 1963]. Although an equilibrium may disfavor the electron-pair–*endo* form, it is apparent from the experiments that this does not prevent interconversion from one bicyclic system to the other.

(16) (a) S. Winstein, E. Grunwald, R. E. Buckles, and C. Hanson, *J. Amer. Chem Soc.*, **70**, 816 (1948); (b) S. Winstein, E. Grunwald, and L. L. Ingraham, *ibid.*, **70**, 821 (1948).

The ring system in **8** provides an extreme case where methanolysis and acetolysis both follow the abnormal course. Thus, 1-azoniatetracyclo[7.3.2.0^{1,13}.0^{5,13}]tetradecane perchlorate (**8**) yielded 13-methoxymethyl-1-azatricyclo[7.3.1.0^{5,13}]tridecane perchlorate (**14**) in refluxing methanol,[8] 13-acetoxymethyl-1-azatricyclo[7.3.1.0^{5,13}]tridecane perchlorate (**9a**) in refluxing glacial acetic acid, and 13-benzoyloxymethyl-1-azatricyclo[7.3.1.0^{5,13}]tridecane perchlorate (**9b**) when heated with benzoic acid at 145°. In this case there is not only steric resistance to formation of the β-amino-*t*-carbonium ion but probably steric hindrance to its capture by the methanol or carboxylic acid. With these restrictions imposed, the methoxy or acyloxy group becomes attached to the methylene aziridinium carbon, probably through a transition state in which there is appreciable covalent bonding to the solvent-reactant. The possibility of direct displacement by acetate[17] or benzoate on the less hindered methylene carbon depends upon the availability of the carboxylate anion arising from self-ionization. The self-ionization product of glacial acetic acid, as determined by conductivity measurements, has been found to be 2.1×10^{-13} at 105.7°[18] and 2.5×10^{-13} at 25°.[19] Potentiometric measurements gave the value 3.5×10^{-15} at 25°.[20] Thus, the very low acetate ion concentration available probably means that acetate does not play a significant role in the reaction **8** → **9a**. Moreover, no products of methylene attack were observed for **1** and **4** with acetic acid alone. In the case of 1,6-dimethyl-1-azoniabicyclo[4.1.0]heptane perchlorate (**4**) it was possible to obtain some of the isomeric 2-acetoxymethyl-1,2-dimethylpiperidine salt (**15**) of **5a** when **4** was treated with glacial acetic acid containing anhydrous sodium acetate. The added acetate was a requirement for the observation of this type of product (nmr determination) from **4**, whereas it was not in the cases of the tricyclic (**6**) and tetracyclic (**8**) aziridinium salts. Consequently, the only obligatory reagent for the abnormal aziridinium ring opening in these special systems (**6** and **8**) to give products such as **7** and **9** appears to be the carboxylic acid.

Experimental Section[21]

5-Azoniadispiro[4.0.5.1]dodecane perchlorate (1), 1-azoniatricyclo[4.4.1.0^{1,6}]undecane perchlorate (6), and 1-azoniatetracyclo[7.3.2.0^{1,13}.0^{5,13}]tetradecane perchlorate (8) were prepared as described previously[8] by the addition of ethereal diazomethane to the corresponding iminium perchlorate in methylene chloride at 0°. The aziridinium salts were stored in a vacuum desiccator at room temperature. 1,6-Dimethyl-1-azoniabicyclo[4.1.0]heptane perchlorate (**4**) was prepared in a similar manner from 1,2-dimethyl-3,4,5,6-tetrahydropyridinium perchlorate:[9] mp 151.5–153°; yield 84%; no O—H, $^+$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.

Thermal Rearrangement Products from 5-Azoniadispiro[4.0.5.1]dodecane Perchlorate (1) in the Presence of Acetic Acid and Benzoic Acid.—Solutions of 1.00 g (3.76 mmol) of 5-azoniadispiro[4.0.5.1]dodecane perchlorate (**1**)[11] in 5 ml of glacial acetic acid and the same quantity of aziridinium salt plus 3.0 g of benzoic acid in 10 ml of 2-nitropropane were heated at 70° for 14 hr. Both solutions were then poured into a large volume of stirred ether and the resulting precipitates were triturated with additional ether. Both semisolid products were dissolved in small volumes of methylene chloride, reprecipitated in stirred ether, and triturated with ether. The characteristic odor of aldehyde could be detected in both crude products.[10] Cyclohexanecarboxaldehyde would arise from the hydrolysis of the iminium salt **3**, produced by thermal rearrangement of the aziridinium salt. The nmr spectra (CH_2Cl_2) of the crude products showed no proton resonances attributable to benzoyl or acetyl groups. However, evidence for the presence of the ene–ammonium salt **2**, the other thermal rearrangement product,[10] was indicated by the broad resonances at about τ 2.3 for N$^+$–H and at τ 3.98 for the olefinic protons in both spectra.[22]

General Procedure of the Aziridinium Salt–Carboxylic Acid Reaction. Preparation of 6-Benzoyloxymethyl-1-azabicyclo[4.4.0]decane Perchlorate (7b).—A mixture of 0.50 g (2.0 mmol) of 1-azoniatricyclo[4.4.1.0^{1,6}]undecane perchlorate (**6**) and 1.00 g (8.1 mmol) of benzoic acid was heated at 135° for 10 min with attendant darkening of the melt. After cooling, the solid was triturated several times with ether before dissolution in methylene chloride and precipitation by addition to ether with stirring. The solid was recrystallized from acetonitrile–ether to give 0.52 g (72%) of tan prisms. Two further recrystallizations gave colorless prisms: mp 218–220° ν_{max}^{Nujol} 3090 and 1710 cm^{-1}; pmr (CF_3CO_2H), τ 1.90 and 2.48 (2 m, 5, Ar hydrogens), 5.17 (s, 2, CH_2O), 6.42 (br s, 4, $CH_2N^+CH_2$), and 8.00 (br s, 12, ring methylenes).

Anal. Calcd for $C_{17}H_{24}ClNO_6$: C, 54.54; H, 6.42; N, 3.74. Found: C, 54.69; H, 6.31; N, 3.86.

A portion of the perchlorate salt was converted to the free amine by treatment with aqueous potassium carbonate and extraction with methylene chloride. The combined extracts were dried, filtered, and concentrated *in vacuo*. The nmr spectrum was definitive for **6-benzoyloxymethyl-1-azabicyclo[4.4.0]decane**: pmr (CH_2Cl_2) τ 2.03, 2.52 (2 m, 5, Ar hydrogens) 5.33 (s, 2 CH_2O), 7.00–7.70 (v br m, 4 CH_2NCH_2), and 8.00–8.80 (v br m, 12 ring methylenes).

In a similar manner the products given below were obtained.

From a solution of 0.66 g (2.9 mmol) of 1,6-dimethyl-1-azoniabicyclo[4.1.0]heptane perchlorate (**4**) in 10 ml of glacial acetic acid heated at reflux for 3 hr there was obtained from ethanol-ether 440 mg (53%) of **3-acetoxy-1-3-dimethyl-1-azacycloheptane perchlorate (5a)**. A colorless, analytically pure sample, prisms, had mp 113.5–115°; ν_{max}^{Nujol} 3120 amd 1710 cm^{-1}; pmr (CH_2Cl_2), τ 6.42 (br d, 4, J = 4.5 Hz, $CH_2N^+CH_2$), 6.96 (d, 3, J = 5.0 Hz, N^+CH_3), 7.60–8.35 (v br m, 6, ring methylenes), 7.86 (s, 3, CH_3CO_2), and 8.50 (s, 3, CCH_3). When the reaction was run in acetic acid with anhydrous sodium acetate present some of the 2-acetoxymethyl-1,2-dimethylpiperidine salt was formed in addition to **5a**.

Anal. Calcd for $C_{10}H_{20}ClNO_6$: C, 41.96; H, 6.99; N, 4.90. Found: C, 42.12; H, 6.98; N, 4.92.

The free amine obtained gave an nmr spectrum confirming the structure as **3-acetoxy-1,3-dimethyl-1-azacycloheptane**: pmr (CH_2Cl_2) τ 7.08 and 7.38 (AB system of doublets, 2, J_{AB} = 14 Hz, NCH_2C), 7.30–7.60 (br m, 2, CH_2N), 7.65 (s, 3, NCH_3), 8.06 (s, 3, CH_3CO_2), 8.0–8.5 (br m, 6, ring methylenes), and 8.55 (s, 3, CH_3C).

From a solution of 0.50 g (2.0 mmol) of 1-azoniatricyclo[4.4.1.0^{1,6}]undecane perchlorate (**6**) in 2.0 ml of glacial acetic acid heated at reflux for 30 min there was obtained in two crops from ethanol 390 mg (64%) of light tan needles of **6-acetoxymethyl-1-azabicyclo[4.4.0]decane perchlorate (7a)**. Two further recrystallizations gave an analytically pure sample: mp 183–184.5°; ν_{max}^{Nujol} 3135 and 1760 cm^{-1}; pmr (CF_3CO_2H), τ 3.35 (v br m, 1, N$^+$H), 5.45 (s, 2, CH_2O), 6.45 (br m, 4, $CH_2N^+CH_2$), 7.63 (s, 3, CH_3), and 8.03 (br m, 12 ring methylenes).

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(21) All melting points are corrected. Infrared spectra were obtained with a Perkin-Elmer Model 337 grating spectrophotometer. Microanalyses were performed by Mr. Josef Nemeth and his staff. Nuclear magnetic resonance spectra were obtained on a Varian Associates Model A-60, A-60A or 56-60A spectrometer using tetramethylsilane as an internal standard. In the nuclear magnetic resonance data, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, v = very, and br = broad.
(22) Further discussion is reserved for a complete paper on thermal rearrangements.

Anal. Calcd for $C_{12}H_{22}ClNO_6$): C, 46.15; H, 7.05; N, 4.49. Found: C, 46.29; H, 6.93; N, 4.46.

The free amine obtained gave an nmr spectrum definitive for **6-acetoxymethyl-1-azabicyclo[4.4.0]decane**: pmr (CH_2Cl_2), τ 5.62 (s, 2, CH_2O), 7.00–7.75 (v br m, 4, CH_2NCH_2), 7.98 (s, 3, CH_3), 8.17–8.80 (br m, 12, ring methylenes).

A solution of 1.00 g (3.4 mmol) of 1-azoniatetracyclo[7.3.2.$0^{1,13}$.$0^{5,13}$]tetradecane perchlorate (**8**) in 5 ml of glacial acetic acid heated at reflux for 30 min yielded 660 mg (55%) of tan needles of **13-acetoxymethyl-1-azatricyclo[7.3.1.$0^{5,13}$]tridecane perchlorate** (**9a**) from ethanol–ether. Three further recrystallizations gave an analytically pure sample: mp 206–208°; ν_{max}^{Nujol} 3160 and 1760 cm^{-1}; pmr (CH_2Cl_2) τ 5.28 (s, 2, CH_2O), 6.67 (br m, 4, $CH_2N^+CH_2$), 7.70–8.80 (v br m, 16, ring methylenes), and 7.85 (s, 3, CH_3CO_2).

Anal. Calcd for $C_{15}H_{25}ClNO_6$: C, 51.28; H, 7.12; N, 3.99. Found: C, 51.53; H, 7.42; N, 4.00.

An nmr spectrum of the free amine confirmed the structure of **13-acetoxymethyl-1-azatricyclo[7.3.1.$0^{5,13}$]tridecane**: pmr (CH_2Cl_2) τ 5.44 (s, 2, CH_2O), 7.20–7.70 (br m, 4, CH_2NCH_2), 7.90–8.90 (v br m, 16, ring methylenes), and 7.97 (s, 3, CH_3CO_2).

A mixture of 0.50 g (1.7 mmol) of 1-azoniatetracyclo[7.3.2.$0^{1,13}0^{5,13}$]tetradecane perchlorate (**8**) and 1.0 g of benzoic acid heated at 145° for 20 min yielded 490 mg (69%) of tan needles of **13-benzoyloxymethyl-1-azatricyclo[7.3.1.$0^{5,13}$]tridecane perchlorate** (**9b**). A second recrystallization afforded an analytically pure sample of light tan needles: mp 198.5–200.5°; ν_{max}^{Nujol} 3050 and 1710 cm^{-1}; pmr (CH_2Cl_2) τ 1.98 and 2.47 (2 m, 5, Ar), 5.03 (s, 2, CH_2O), 6.60 (br m, 4, $CH_2N^+CH_2$) and 7.50–8.70 (v br m, 16, ring methylenes).

Anal. Calcd for $C_{20}H_{28}ClNO_6$: C, 57.97; H, 6.76; N, 3.38. Found: C, 57.97; H, 6.62; N, 3.57.

The nmr spectrum of the free amine confirmed the structure of **13-benzoyloxymethyl-1-azatricyclo[7.3.1.$0^{5,13}$]tridecane**: pmr (CH_2Cl_2), τ 1.94 and 2.52 (2 m, 5, Ar), 5.17 (s, 2, CH_2O), 6.95–7.67 (v br m, 4, CH_2NCH_2), and 7.82–8.90 (v br m, 16, ring methylenes).

6-Acetoxy-1-azabicyclo[4.4.1]undecane Perchlorate (12).—A solution of 0.50 g (1.85 mmol) of 6-hydroxy-1-azabicyclo[4.4.1]-undecane perchlorate (**11**)[8] in 10 ml of acetic anhydride was heated on a steam bath for 1 hr. The solvent was evaporated *in vacuo* to give light yellow crystals. The product was triturated with ether before recrystallization from ethanol to give light tan platelets: mp 163–164° (dec); yield 0.35 g (61%); ν_{max}^{Nujol} 3110 and 1690 cm^{-1}; pmr (CF_3COOH) τ 5.78 and 6.15 (2 d, 2, J = 3.0 Hz, CCH_2N^+ of *cis* and *trans* isomers respectively), 6.43 (br m, 4, $CH_2N^+CH_2$), 7.76 and 7.82 (2 s, 3, $CH_3C{=}O$ of *trans* and *cis* isomers respectively),[14b] and 7.94 (br s, 12, remaining ring methylenes).

Anal. Calcd for $C_{12}H_{22}ClNO_6$: C, 46.15; H, 7.05; N, 4.49. Found: C, 46.31; H, 7.04; N, 4.50.

Conversion of 6-Acetoxy-1-azabicyclo[4.4.1]undecane Perchlorate (12) to 6-Acetoxymethyl-1-azabicyclo[4.4.0]decane Perchlorate (7a).—A solution of 150 mg of 6-acetoxy-1-azabicyclo-[4.4.1]undecane perchlorate (**12**) in 5 ml of glacial acetic acid was heated at reflux for 30 min. The solvent was evaporated *in vacuo* and the solid was triturated with ether. The product was dissolved in methanol and slowly added to a large volume of stirred ether. The product was then triturated with ether and dried *in vacuo*. The nmr spectrum (CF_3COOH) exhibited signals corresponding to 64% conversion of **12** to **7a**. The conversion was also carried out in the molten state. A sample of 100 mg of **12**, mp 163–164°, was heated at 170° for 1–2 min with a darkening of the melt. The nmr spectrum of the melt showed signals corresponding to essentially complete conversion of **12** to **7a**.

Reaction of 6-Acetoxy-1-azabicyclo[4.4.1]undecane Perchlorate (12) with Methanol.—A solution of 200 mg of 6-acetoxy-1-azabicyclo[4.4.1]undecane perchlorate (**12**) in 20 ml of methanol was heated at reflux for 2 hr. The solvent was evaporated *in vacuo* and an nmr spectrum (CF_3CO_2H) of the colorless solid was obtained. The spectrum was marked by the appearance of a sharp singlet at τ 6.60 (OCH_3), a decrease in the intensity of the signal arising from the acetyl group, and the appearance of a doublet at τ 6.18. Integration of the spectrum indicated approximately 47% conversion to 6-methoxy-1-azabicyclo[4.4.1]undecane perchlorate (**10**) under the stated conditions. 6-Methoxy-1-azabicyclo[4.4.1]undecane perchlorate was unchanged, as judged by nmr, when heated for 30 min at reflux in glacial acetic acid.

Registry No.—**4**, 25516-26-1; **5a**, 25568-58-5; **5a** free amine, 25516-17-0; **7a**, 25516-18-1; **7a** free amine, 25516-19-2; **7b**, 25516-20-5; **7b** free amine, 25516-21-6; **9a**, 25516-22-7; **9a** free amine, 25516-23-8; **9b**, 25516-24-9; **9b** free amine, 25568-59-6; **12**, 25529-23-1.