neutralization of the acid with sodium methoxide solutions.

2,6-Di-*tert*-butylpyrylium perchlorate (**1a**),[4] 2,6-di-*tert*-butyl-4-methylpyrylium fluoroborate (**2a**),[16] 2,4,6-tri-*tert*-butylpyrylium perchlorate (**3a**),[4] and 2,6-di-*tert*-butyl-4-(1,1-diethylpropyl)-pyrylium perchlorate (**4a**)[17] were available from our previous work.

^{1}H NMR Measurements. Spectra were recorded on a Bruker WP 80 SY spectrometer. Low-temperature (−40 °C) and room-temperature (25 °C) ^{1}H NMR measurements for the reaction of the cation **2a** with CD_3ONa in CD_3OD, were carried out according to the procedure previously described.[4]

The ^{1}H NMR shifts relative to TMS for **2a–d** in methanol solution are as follows.

2a: δ 1.53 (s, 18 H, *t*-Bu), 2.80 (s, 3 H, Me), 8.01 (s, 2 H, H-3).

2b:[18] δ 1.18 (s, 18 H, *t*-Bu), 1.31 (s, 3 H, Me), 4.56 (s, 2 H, H-3).

2c:[18] δ 0.93 (s, 9 H, 2-*t*-Bu), 1.15 (s, 9 H, 6-*t*-Bu), 1.83 (d, 3 H, $J_{H\text{-}3,Me}$ = 1.41 Hz, Me), 4.88 (m, 1 H, $J_{H\text{-}3,H\text{-}5}$ = 1.32 Hz, $J_{H\text{-}3,Me}$ = 1.41 Hz, H-3), 4.92 (d, 1 H, $J_{H\text{-}3,H\text{-}5}$ = 1.32 Hz, H-5).

2d: δ 1.14 (s, 18 H, *t*-Bu), 4.07 (s, 2 H, CH_2), 5.51 (s, 2 H, H-3).

Rate Measurements. Kinetic experiments were carried out on a Durrum 110 stopped-flow spectrophotometer or on a Cary 219 spectrophotometer, at 25.0 °C, under pseudo-first-order conditions, with MeONa or Et_3N/Et_3NH^+ buffers in methanol. The methoxide ion concentrations of each buffer was calculated from the pK_a value of Et_3N (10.88)[15] and from the methanol autoprotolysis constant (pK_{MeOH} = 16.92).[19] Substrate concentrations were in the range (1–4) × 10^{-5} M. Ionic strength was 5 × 10^{-3} M in the case of the cation **1a** and lower than 1 × 10^{-3} M with the other cations. The reaction solutions were freshly prepared and handled under argon.

In the case of the cations **1a**, **3a**, and **4a** two widely separated first-order process were monitored. In the case of the cation **2a** only the first process, relative to the 4*H* adduct formation, was investigated. The reactions were monitored at the following wavelengths: **1a**, 293 (τ_1), 275 nm (τ_2); **2a**, 287 nm (τ_1); **3a**, 290 nm (τ_1 and τ_2); **4a**, 290 (τ_1), 280 nm (τ_2).

At the wavelengths where τ_2 was monitored the 4*H* adduct does not absorb; therefore these were the wavelengths of choice for the evaluation of the k_4/k_2 ratio for the cations **3a** and **4a**, according to eq 6.

Equilibrium Measurements. The equilibrium constants K_4 for the cations **1a** and **2a** were determined at 25.0 °C on a Durrum 110 stopped-flow. The reactions were carried out at MeO^- concentrations low enough to leave a detectable amount of the substrate in equilibrium with the 4*H* adduct at the end of the first process. The buffers used were $ClCH_2CO_2H/ClCH_2CO_2^-$ (pK_a = 7.7)[20] for the cation **1a**, and Et_3N/Et_3NH^+ for the cation **2a**. Measurements of the absorbance of the substrate at zero time (OD_0) and at the end of the first process ($OD_{\infty 1}$) afforded the equilibrium constant K_4 by eq 12.

$$K_4 = \frac{(OD_0 - OD_{\infty 1})}{OD_{\infty 1}[MeO^-]} \quad (12)$$

The equilibrium constants K_2 for the cations **1a**, **3a**, and **4a** were determined at 25.0 °C on a Cary 219 spectrophotometer, by measuring the residual absorbance of the substrate ($OD_{\infty 2}$) after equilibration with $ClCH_2CO_2H/ClCH_2CO_2^-$ buffers. The addition of an excess of methanolic $HClO_4$ to these mixtures shifts the equilibrium completely toward the substrate, thus permitting the measurement of OD_0, after correction of the observed OD value for dilution. The $OD_{\infty 2}$ values are contaminated by a small absorbance contribution due to the 2*H* adducts and must be corrected by eq 13, where ϵ_s and ϵ_{2H} are the molar absorbances of

$$OD_{\infty 2}{}^c = \frac{OD_{\infty 2}\epsilon_s - OD_0\epsilon_{2H}}{\epsilon_s - \epsilon_{2H}} \quad (13)$$

the substrate and of the 2*H* adduct, respectively. The K_2 constants were obtained by eq 14. The concentration of the substrates was

$$K_2 = \frac{(OD_0 - OD_{\infty 2}{}^c)}{OD_{\infty 2}{}^c[MeO^-]} \quad (14)$$

in the range (1–5) × 10^{-5} M. Ionic strength was always lower than 3 × 10^{-3} M. The absorbance measurements were carried out with Teflon-stoppered 4-cm quartz cells for the cation **1a** and 1-cm quartz cells for the cations **3a** and **4a**.

Acknowledgment. Partial Financial Support by the Ministero della Pubblica Istruzione, Roma, is greatly acknowledged.

Registry No. **1a**, 50478-27-8; **1b**, 104086-47-7; **2a**, 46426-69-1; **2b**, 112321-29-6; **2d**, 112321-31-0; **3a**, 46914-07-2; **3b**, 104086-42-2; **3c**, 104086-26-2; **4a**, 104086-48-8; **4b**, 112321-30-9; **4c**, 104086-27-3; **5a**, 75882-53-0; **5b**, 104086-44-4; **5c**, 81128-16-7; MeO^-, 3315-60-4.

(16) Doddi, G.; Ercolani, G. *Synth. Commun.* **1987**, *17*, 817.

(17) Doddi, G.; Ercolani, G. *Abstracts*, XV Convegno Nazionale di Chimica Organica, Società Chimica Italiana, Sirmione, September 1985.

(18) In view of the use of deuteriated methanol, the chemical shift values of the 4- and 2-OMe group in the 4*H*-pyran **2b** and in the 2*H*-pyran **2c**, respectively, are not quoted.

(19) Koskikallio, J. *Suom. Kemistil. B* **1957**, *30*, 111.

(20) Clare, B. W.; Cook, D.; Ko, E. C. F.; Mac, Y. C.; Parker, A. J. *J. Am. Chem. Soc.* **1966**, *88*, 1911.

Ring-Opening Reactions. 5.[1] Elimination vs Substitution in the Cleavage of 1,1,2,2,3,3-Hexamethylaziridinium Ion

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Received May 21, 1987

The syntheses of the highly strained 1,2,2,3,3-pentamethylaziridine and 1,1,2,2,3,3-hexamethylaziridinium triflate, iodide, and perchlorate are reported. Reaction of hexamethylaziridinium triflate with $NaOCD_3$ in CD_3OD at 50 °C yields two ring-opened products in a ratio of 2:1 that result from competing substitution and elimination reactions. The changes in relative reactivity of progressively more methylated aziridinium ions with sodium methoxide in methanol are attributed to a significant reduction of nonbonded interactions in the transition state of the S_N2 opening of a small ring combined with a presumably loose transition state.

In studies of the effects of strain and stereochemical factors on the ring-opening reactions of cyclic ammonium ions,[1] we have reported that *cis*-1,1,2,3-tetramethylaziridinium ion (**1**) is cleaved by sodium methoxide in

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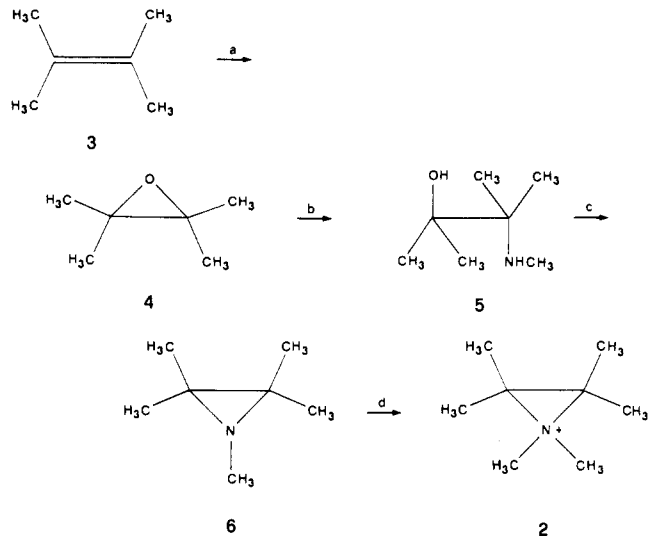
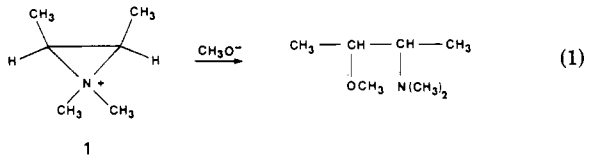
Scheme I[a]

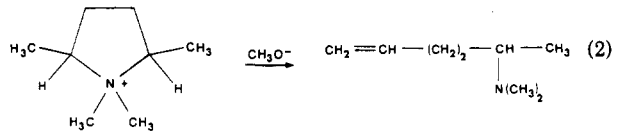


[a] (a) 3-Chloroperbenzoic acid, 0 °C; (b) aqueous CH_3NH_2, 120 °C; (c) Ph_3P–Br_2, 0 °C; (d) methyl trifluoromethanesulfonate, −78 °C.

methanol exclusively by an S_N2 reaction (eq 1). Conversely, the four-, five-, and six-membered homologues of the same series, i.e., the 1,1,2,ω-tetramethyl cyclic ammonium ions, undergo exocyclic eliminative cleavage as the main or exclusive process (e.g., eq 2).[2]

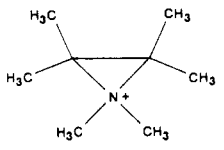


(1)



(2)

Because of the crucial role of the three-membered ring in understanding the effect of strain on reactivity,[3] we wished to study the cleavage of 1,1,2,2,3,3-hexamethylaziridinium ion (**2**), which we expected to undergo ring opening with elimination rather than with an S_N2 substitution. Surprisingly, neither ion **2** salts nor their precursor, 1,2,2,3,3-pentamethylaziridine were reported in the literature.



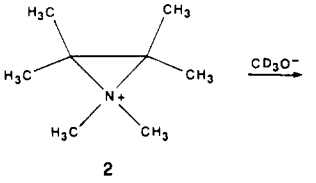
In this paper we report on the synthesis of pentamethylaziridine and its conversion into hexamethylaziridinium triflate and on the kinetics of the reaction of the latter with tetradeuteriomethanol in the presence and absence of sodium trideuteriomethoxide at 50 °C.

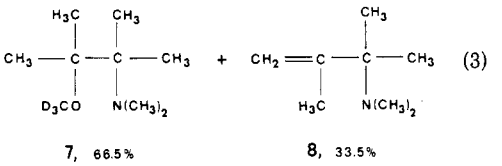
(1) Part 4: Di Vona, M. L.; Illuminati, G.; Lillocci, C. *J. Chem. Soc., Perkin Trans. 2* **1985**, 1943.
(2) Cospito, G.; Illuminati, G.; Lillocci, C.; Petride H. *J. Org. Chem.* **1981**, *46*, 2944.
(3) Stirling, C. J. M. *Tetrahedron* **1985**, *41*, 1613.

Results and Discussion

Synthesis of Substrates. Pentamethylaziridine and hexamethylaziridinium ion were prepared by the sequence of Scheme I. Amino alcohol **5** was obtained by known procedures. It was cyclized to pentamethylaziridine (**6**) with Ph_3PBr_2, by using a modification of the literature procedure[6] because of the volatility of **6**. An attempt to obtain **6** by N-methylation of 2,2,3,3-tetramethylaziridine[4] according to the Eschweiler–Clarke procedure[5] was unsuccessful.

Reaction of 2 Triflate with $NaOCD_3$ in CD_3OD. The reaction at 50 °C yielded a substitution product, 2,3-dimethyl-2-(dimethylamino)-3-(trideuteriomethoxy)butane (**7**) and an elimination product, 2,3-dimethyl-3-(dimethylamino)-1-butene (**8**) in the ratio 66.5:33.5 (eq 3). The overall yield was 97%.



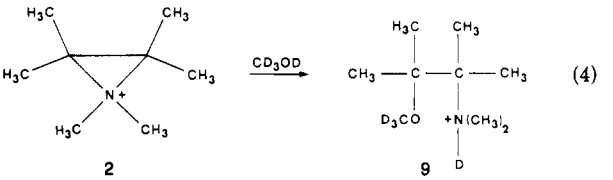


(3)

The kinetics of the reaction were followed by ^1H NMR, using 0.084 N $NaOCD_3$ and 0.047 N aziridinium salt. The overall second-order rate constant was 3.44×10^{-2} M^{-1} s^{-1}, and the constants of the individual bimolecular reactions were 2.27×10^{-2} M^{-1} s^{-1} for the S_N2 reaction and 1.17×10^{-2} M^{-1} s^{-1} for the E2 reaction.

In another kinetic run with a higher concentration of $NaOCD_3$ (0.156 N), the overall second-order rate constant was practically unchanged (3.39×10^{-2} M^{-1} s^{-1}), as was the composition of the reaction mixture.

Solvolysis of 2 Triflate in CD_3OD. Reaction of **2** triflate with CD_3OD at 50 °C in the absence of base yielded quantitatively only the substitution product **9**, the conjugate acid of amino ether **7** (eq 4). The observed rate



(4)

constant of this reaction, obtained by ^1H NMR measurements, was 4.7×10^{-5} s^{-1}.

Ring-Opening Reactivity. The kinetics of the reaction of **2** triflate with $NaOCD_3$ in CD_3OD at two different base concentrations indicate the bimolecular nature of the reactions. Moreover, the low rate constant of the reaction of this aziridinium ion with the solvent alone rules out any effect of the latter reaction on the measured reactivities.

The *elimination reaction* of eq 3 represents the first example, to our knowledge, of the eliminative cleavage of

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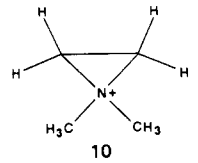
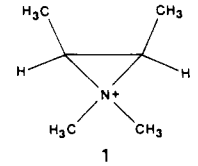
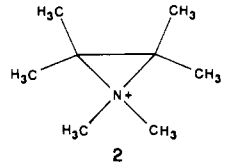
Table I. Second-Order Rate Constants for the S_N2 Ring-Opening Reaction of Some Aziridinium Ions with Sodium Methoxide in Methanol at 50 °C

compd	k_2, M^{-1} s^{-1}	k_{rel}
 10	12.9[a]	568
 1	0.541[a]	24
 2	2.27×10^{-2} [b]	1

[a] Value obtained by the activation parameters reported in ref 1. [b] Reaction carried out with $Na^+OCD_3^-$ in CD_3OD.

an aziridinium ion.[7] The acquisition of reactivity data on the elimination reaction of the three-membered ring calls for extension of the research to the larger homologues of ion **2** in order to obtain a homogeneous set of data on the ring-opening elimination reaction.

The interest in the opening of small rings by elimination is related also to the anomaly found for these compounds in ring opening by an S_N2 mechanism.[8] In the latter reaction the reactivity differences have been found much larger than expected on the basis of ring-strain differences, and we wish to demonstrate that this anomaly does not occur in the elimination opening of small rings, which has different stereochemical requirements.

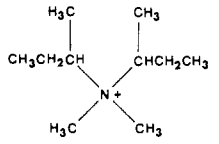
The *substitution reaction* affords an unambiguous determination of the S_N2 reactivity of a tertiary carbon atom and allows a comparison of the rates of attack at primary, secondary, and tertiary carbon atoms in this system. In Table I are shown the second-order rate constants at 50 °C for the S_N2 ring-opening reactions of some aziridinium ions promoted by sodium methoxide in methanol.

As expected, the data of Table I indicate decreasing reactivity with increasing steric hindrance at the reaction center. However, the observed decrease is rather small compared with the literature values[9] on the S_N2 reaction of alkyl substrates. Indeed, increasing methyl substitution on both carbon atoms of the cyclic system should have depressed the reactivity much more than shown by our results, since it is well established that S_N2 reactions are strongly inhibited by both α and β branching. On this ground the reactivity ratios in Table I relative to ion **2** appear small.

We believe that the relative reactivities shown in Table I are related to the anomaly shown by small rings in S_N2 ring-opening[8] and ring-closure[10] reactions, which has been tentatively explained in terms of a significant reduction in nonbonded interactions in the transition states in a small ring. Such an effect should give a nucleophile much easier access to the reaction center in a small ring than in an open-chain analogue or a large ring. Moreover, More O'Ferrall's diagrams suggest that in the transition state the C–O⁻ bond is much less formed and the C–N⁺ bond much more broken in the S_N2 opening of the aziridinium ion **2** than in the corresponding reaction of an open-chain analogue. Thus a significant reduction of the steric hindrance on the reaction center and a presumably loose transition state combine to make the carbon atom reaction center only "formally" tertiary (or neopentylic) in ion **2** and cause the low reactivity ratios shown in Table I.

That small rings feel steric effects in an anomalous way had been well realized by Kirby[11] who stated "but it is clear that steric effects in intramolecular reactions, especially the formation of small rings, are much smaller than in the corresponding bimolecular processes". Although this statement referred to ring-closure reactions, we have shown that it is equally valid for ring-opening reactions.

The anomalous behavior of small rings in the S_N2 reaction is well illustrated by comparing the reactions of ions **1** and **11** with sodium methoxide in methanol. The



11

aziridinium ion **1** yields 100% substitution product (eq 1), while the open-chain ion **11** affords 97% elimination product[2] plus 3% demethylation, despite the fact that the steric situation around the reaction center is formally the same in the two ions. The dramatically different behavior is clearly due to the small ring structure of ion **1**, which strongly favors the substitution pathway.

Experimental Section

^1H NMR were taken on a Bruker 80 SY spectrometer. Gas chromatography (GC) was performed on a Hewlett-Packard 5830A instrument using a 6 ft × 2 mm i.d. glass column packed with 10% Carbowax 20M–2% KOH on 80/100 Chromosorb W (Supelco); the same type of column was used for GC/MS experiments. Mass spectra were determined at 70 eV on a Carlo Erba Fractovap 4000 gas chromatograph/Kratos MS 80 mass spectrometer. Preparative GC was carried out on a Carlo Erba Fractovap ATC/F instrument using a 15 ft × 6 mm o.d. column packed with 20% Carbowax 20M–2% KOH on 40/60 Chromosorb W (C. Erba). Elemental analyses were performed by Alfred Bernhardt Mikroanalytisches Laboratorium. All melting points are uncorrected.

Tetramethyloxirane (4) was prepared in 70% yield from 2,3-dimethyl-2-butene (**3**) and 3-chloroperbenzoic acid in diglyme at 0 °C.[12]

2,3-Dimethyl-3-(methylamino)-2-butanol (5) was prepared in 65% yield from the oxirane **4** and aqueous methylamine in a steel bomb at 120 °C.[13]

1,2,2,3,3-Pentamethylaziridine (6) was prepared from the amino alcohol **5** by using triphenylphosphine dibromide.[5] To a 0 °C cooled solution of 5.2 g (0.02 mol) of triphenylphosphine in 50 mL of dry acetonitrile was added dropwise a solution of 3.2 g (0.02 mol) of bromine in 20 mL of acetonitrile with stirring. The addition finished, a solution of 2.6 g (0.02 mol) of 2,3-dimethyl-3-(methylamino)-2-butanol (**5**) in 10 mL of acetonitrile was added dropwise with stirring and ice cooling. To the mixture so obtained was added dropwise a solution of 4.0 g (0.04 mol) of triethylamine in 10 mL of acetonitrile with ice cooling. The

(7) Stirling, C. J. M. *Chem. Rev.* **1978**, *78*, 530; Deyrup, J. A. *In Small Ring Heterocycles*; Hassner, A., Ed.; Wiley-Interscience: New York, 1983; Vol 42, Part 1, p 172.
(8) Di Vona, M. L.; Illuminati, G.; Lillocci, C. *J. Chem. Soc., Chem. Commun.* **1985**, 380.
(9) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985; p 299 and references therein.
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(11) Kirby, A. J. *Adv. Phys. Org. Chem.* **1980**, *17*, 183.
(12) Pasto, D. J.; Cumbo, C. C. *J. Org. Chem.* **1965**, *30*, 1271.
(13) Bottini, A. T.; VanEtten, R. L. *J. Org. Chem.* **1965**, *30*, 2994.

solution was stirred at 0 °C for 2 h and left overnight at room temperature. The reaction mixture was cooled to −20 °C and the precipitated triethylamine hydrobromide filtered off quickly. The solution was distilled at atmospheric pressure until the temperature reached 82 °C; the distillate was neutralized with 6 N HCl. The solvent was then removed by a rotatory evaporator and the solid residue dissolved in a few milliliters of water; the solution was made alkaline with some pellets of NaOH. The amine products were extracted with 2 mL of ether; the ethereal solution, dried over anhydrous potassium carbonate, was found by GC analysis to contain two products in comparable amount, one of which was triethylamine. The aziridine **6** was separated by preparative GC and was 99.5% pure by GC: yield, 0.6 g (27%); ^{1}H NMR ($CDCl_3$) δ 2.07 (s, 3 H, NCH_3), 0.99 (s, 6 H, 2 CCH_3), 0.92 (s, 6 H, 2 CCH_3); MS, m/z 113 (M^+), 86 (base).

Anal. Calcd for $C_7H_{15}N$: C, 74.27; H, 13.35; N, 12.37. Found: C, 74.14; H, 13.44; N, 12.24.

1,1,2,2,3,3-Hexamethylaziridinium (2) Triflate. This salt was prepared from aziridine **6** according to the procedure described by us for the synthesis of 1,1-dimethylaziridinium salts starting from 1-methylaziridines.[1] The crude white precipitate formed was isolated by filtration under anhydrous atmosphere and recrystallized from acetone: yield, 0.3 g (49%); mp 176 °C dec; ^{1}H NMR (CD_3OD) δ 2.94 (s, 6 H, $^+N(CH_3)_2$), 1.61 (s, 12 H, 2 $C(CH_3)_2$).

Anal. Calcd for $C_9H_{18}F_3NO_3S$: C, 38.98; H, 6.54; N, 5.05. Found: C, 38.95; H, 6.59; N, 4.97.

1,1,2,2,3,3-Hexamethylaziridinium (2) Iodide. To a stirred solution of 0.1 g (0.9 mmol) of 1,2,2,3,3-pentamethylaziridine (**6**) in 2 mL of chloroform was added dropwise at 0 °C a solution of 0.2 mL (3 mmol) of methyl iodide in 2 mL chloroform. The solution was stirred for 1 h at room temperature, during which time a white precipitate separated. The solvent was removed by a rotatory evaporator, giving the product: yield, 0.1 g (44%); mp 181 °C dec; ^{1}H NMR (CD_3CN) δ 2.79 (s, 6 H), 1.46 (s, 12 H).

1,1,2,2,3,3-Hexamethylaziridinium (2) Perchlorate. To a stirred solution of 76 mg (0.3 mmol) of 1,1,2,2,3,3-hexamethylaziridinium iodide in 5 mL of a 1:1 mixture of acetonitrile/methanol was added dropwise a solution of 67 mg (0.3 mmol) of silver perchlorate monohydrate in 5 mL of the same solvent. The precipitated silver iodide was removed by filtration. The solution was evaporated to dryness by a rotatory evaporator, giving a white residue: yield, 65 mg (96%); mp 194 °C dec; ^{1}H NMR (CD_3OD) δ 2.94 (s, 6 H), 1.52 (s, 12 H).

Product Analysis. The product composition was determined under kinetic conditions. The reaction products were identified by ^{1}H NMR, directly on the samples used for the kinetic measurements, and by GC/MS, after extraction of the amine product from the reaction mixture according to a previously described procedure.[14]

Yields were checked by ^{1}H NMR by adding known amounts of benzene to the reaction mixtures.

Product ratios were determined by GC and found to be consistent with the NMR measurements.

The analytical data of the products of the reactions were as follows.

Reaction with $Na^+OCD_3^-$. 2,3-Dimethyl-2-(dimethylamino)-3-(trideuteriomethoxy)butane (**7**): ^{1}H NMR (CD_3OD) δ 2.35 (s, 6 H, $N(CH_3)_2$), 1.16 (s, 6 H, $NC(CH_3)_2$), 1.05 (s, 6 H, $OC(CH_3)_2$); MS, m/z (relative intensity) 162 (M^+, <1), 147 (4), 128 (14), 86 (base).

2,3-Dimethyl-3-(dimethylamino)-1-butene (**8**): ^{1}H NMR (CD_3OD) δ 4.8–4.9 (m, 2 H, CH_2=), 2.16 (s, 6 H, $N(CH_3)_2$), 1.75 (m, 3 H, CH_3C=), 1.15 (s, 6 H, 2 $NCCH_3$); MS, m/z (relative intensity) 127 (M^+, 38), 112 (83), 86 (base).

Solvolysis in CD_3OD. *N*-Deuterio-*N*,*N*-dimethyl-*N*-[2,3-dimethyl-3-(trideuteriomethoxy)-2-butyl]ammonium (**9**) triflate: ^{1}H NMR (CD_3OD) δ 2.90 (s, 6 H, $^+N(CH_3)_2$), 1.40 (s, 6 H, $^+NC(CH_3)_2$), 1.33 (s, 6 H, $OC(CH_3)_2$). The mass spectrum was determined on the etheral solution obtained after extraction of the amine product from the reaction mixture;[14] the spectrum was identical with that of the amino ether **7**.

Rate Measurements. The reactions were carried out in tetradeuteriomethanol (C. Erba 99.5%) and followed to complete conversion by ^{1}H NMR, keeping the probe at 50 °C and recording the spectra at fixed time intervals. The progress of the reaction was followed by measuring the decrease of the signal of $^+N(CH_3)_2$ at 2.94 ppm with time, by using benzene as the internal standard.

Reaction with $Na^+OCD_3^-$. The reaction mixture was obtained directly in the NMR tube by adding with a syringe 40 μL of a 1.13 N solution of $Na^+OCD_3^-$ in CD_3OD to 0.5 mL of a 0.0505 N solution of **2** triflate in CD_3OD. The final concentrations were 0.084 N in the base and 0.047 N in the aziridinium salt. The second-order rate constant was calculated from the formula $k_2 = [1/t(a-b)] \ln [b(a-x)/a(b-x)]$, where t is the time in seconds, a and b are the initial concentrations of base and aziridinium salt, and x is the concentration of aziridinium salt destroyed in time t. The total second-order rate constant was divided into its components, $k(S_N2)$ and $k(E2)$, on the basis of GC measurements of the proportions of products formed.

Reaction with CD_3OD. The rate constant was calculated from the integrated first-order rate equation.

Acknowledgment. We are grateful to Professor L. Mandolini for valuable discussions and to Mr. G. Frachey for skillful assistance with the NMR measurements. We thank the Ministero della Pubblica Istruzione for financial support.

Registry No. **2**·$CF_3SO_3^-$, 113181-25-2; **2**·I^-, 113181-30-9; **2**·ClO_4^-, 113181-31-0; **3**, 563-79-1; **4**, 5076-20-0; **5**, 113181-26-3; **6**, 108065-02-7; **7**, 113181-27-4; **8**, 113181-28-5; **9**, 113181-29-6.

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