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RING-OPENING REACTIONS. 6.* ELIMINATIVE RING FISSION OF AZIRIDINIUM AND AZETIDINIUM IONS

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The reactivity ratio between the three- and four-membered cyclic ammonium ions in ring-opening elimination reactions was measured. The comparison with the analogous ratio obtained in a previous study on ring-opening substitution reactions suggests a substantial difference in the effect of the stereochemical factors governing the two ring-opening reactions and confirms the anomalous behaviour of small rings in the ring-opening substitution reaction.

INTRODUCTION

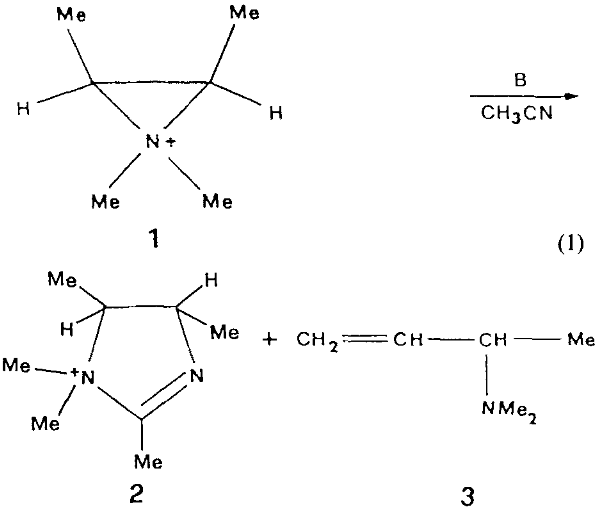
The relative reactivity of three- and four-membered rings has often been considered, with attention to the controversial role of strain on their behaviour, e.g. in the field of synthesis,[2] ring-closure[3,4] and ring-opening[5–8] reactivity and theoretical calculations.[9,10] That knowledge of this subject is far from complete has been well defined in Page *et al.*'s statement:[5] 'In fact, it appears to be an unexplained general phenomenon that four-membered rings are opened and closed slowly whereas the similarly strained three-membered rings open and close readily.' Although the generality of the phenomenon is a matter of discussion (a reasonable explanation has been offered for the reactivity of the small rings in S_N2 ring-closure[3] and ring-opening[11] reactions), we consider that Page *et al.*'s statement expresses a widespread opinion on this matter.

The aim of this work was to compare the three- and four-membered rings in ring-opening *elimination* reactions. The substrates chosen for this study were cyclic ammonium ions. This choice originates from the possibility of comparing our results with the considerable body of data obtained in previous studies on the ring-opening elimination and substitution reactions of a wide range of cyclic ammonium ions.[1,11–15] Here we discuss the reactions of the *cis*-1,1,2,3-tetramethylaziridinium (**1**) and *cis*-1,1,2,4-tetramethylazetidinium (**4**) ions with *N*-ethyldiisopropylamine (Hünig's base) in anhydrous acetonitrile at 130 °C. The reactions of **1** and **4** with the solvent acetonitrile at 130 °C was also investigated. For the above-mentioned reactions, product analyses and measurements of rate constants were carried out.

RESULTS

Reaction of 1 triflate with Hünig's base (B) in acetonitrile

The reaction at 130 °C yielded a ring-expansion product, 4,5-dihydro-1,1,2,4,5-pentamethylimidazolium (**2**) triflate and an elimination product, *N*,*N*-dimethyl-3-aminobut-1-ene (**3**) in the ratio 83 : 17 [equation (1)]. The overall yield was virtually quantitative.



1 (1)

2 **3**

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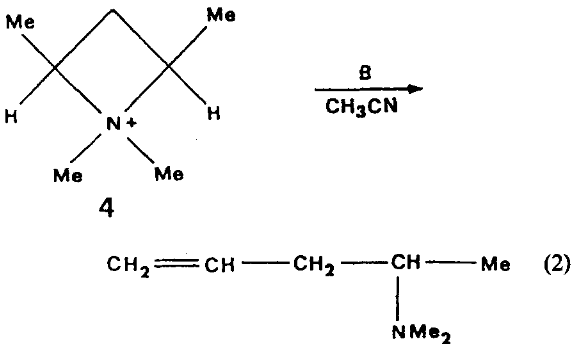
Products of equation 1 resulted from the aziridinium ion **1** through two competitive reactions, i.e. a reaction with the solvent to yield **2** and a reaction with the base to yield **3**, as shown in the Discussion [equations (3) and (4)].

The kinetics of the reaction were followed by ^1H NMR using 1 M Hünig's base and 0·1 M aziridinium salt in CD_3CN. The overall first-order rate constant was $1{\cdot}13 \times 10^{-3} s^{-1}$ and the constants of the individual reactions were $9{\cdot}8 \times 10^{-4} s^{-1}$ and $1{\cdot}5 \times 10^{-4} l\,mol^{-1} s^{-1}$, respectively.

Reaction of 4 perchlorate with Hünig's base (B) in acetonitrile

The reaction at 130 °C yielded quantitatively only the elimination product, *N,N*-dimethyl-4-aminopent-1-ene (**5**) [equation (2)]. The rate constant of this reaction was $1{\cdot}6 \times 10^{-5} l\,mol^{-1} s^{-1}$.



4

$CH_2{=}CH{-}CH_2{-}CH(NMe_2){-}Me$ (2)

5

Reaction of 1 triflate with acetonitrile

Reaction of **1** triflate with CD_3CN at 130 °C in the absence of base yielded quantitatively only the ring-expansion product **2**. The observed rate constant of this reaction, obtained by ^1H NMR measurements, was $4{\cdot}7 \times 10^{-4} s^{-1}$.

Reaction of 4 perchlorate with acetonitrile

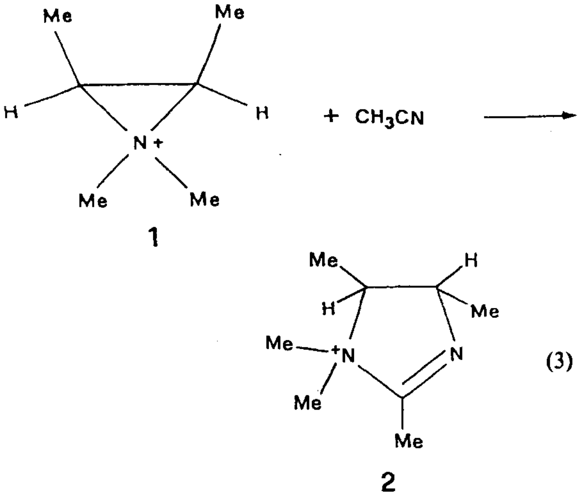
Compound **4** was found to be virtually unreactive in CD_3CN at 130 °C.

DISCUSSION

In a previous paper[15] we pointed out the opportunity of obtaining reactivity data on the elimination reactions of small rings and stressed the significance of a comparison between the three- and four-membered rings in the S_N2 and *E*2 ring-opening reactions. We also reported on our failure to obtain elimination products from the reaction of **1** with sodium methoxide in methanol; this result was unexpected since the four-, five- and six-membered analogues of this ion yielded the elimination product as the main or exclusive result of the same reaction.[14]

After that experience, we searched for conditions under which, despite the disappointing previous results, the elimination should have some chance of taking place in the reaction of the aziridinium system with bases. In this study we tried a hindered non-nucleophilic base to depress substitution. This attempt was successful and the eliminative cleavage could be detected along with an unexpected ring-expansion reaction, as shown in equation (1).

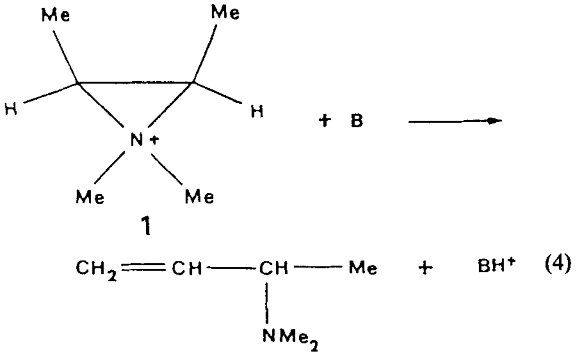
A comparison of the products obtained from the reactions of **1** carried out both in the presence and absence of the base allowed us to evaluate the reaction mixture of equation (1) as due to two competing reactions, i.e. a reaction with the solvent to yield the imidazolium salt **2** [equation (3)] and an elimination reaction promoted by the base to yield the aminoalkene **3** [equation (4)].



1

2

(3)



1

$CH_2{=}CH{-}CH(NMe_2){-}Me + BH^+$ (4)

3

The agreement between the rate constants of the reaction of **1** with the solvent as obtained either in the direct determination ($k = 4\cdot 7 \times 10^{-4}$ s^{-1}) or from the reaction in the presence of the base ($k = 9\cdot 8 \times 10^{-4}$ s^{-1}) can be considered good if the considerable change in the medium due to the base is taken into account.

The reactivity picture emerging from this study can be discussed in terms of the reactivity ratio between the three- and four-membered rings in the elimination reaction and the reactivity of aziridinium and azetidinium ions towards acetonitrile.

Reactivity ratio between the three- and four-membered rings in the elimination reaction

The title reactivity ratio obtained from the rate constants of this study is 9. This reactivity ratio is small if compared with the ratio of 4×10^3 at 50 °C reported previously[11] for the substitution ring-opening reaction. In that case the comparison was between the 1,1-dimethylaziridinium and 1,1-dimethylazetidinium ions in the reaction with sodium methoxide in methanol. The large difference found in the reactivity ratios suggests that the influence of ring-size effects, and of strain in particular, is different in the two ring-opening reactions. Unfortunately, the strain energies of cyclic ammonium ions are not known. However, on the basis of the strain energy values available in the literature[16] for pairs of three- and four-membered rings, such as cyclopropane and cyclobutane, oxirane and oxetane, and aziridine and azetidine, the strain difference in our case should not exceed 2 kcal mol^{-1} (1 kcal = 4·184 kJ), a value which corresponds to a reactivity ratio of the same order of magnitude as that obtained for the elimination reaction in this study. Therefore, the present results suggest that the eliminative cleavage of small rings is controlled by the strain relief caused by the opening of the ring and strengthen our finding about the anomalous behaviour of small rings in the S_N2 reaction.[11]

An inspection of other values of this reactivity ratio available in the literature for ring-opening reactions discloses a clear difference between substitution and elimination reactions. Indeed, the ratios reported for the former reaction range over a narrow interval (regardless of the actual substrate chosen), and our value of 4×10^3 obtained from the reaction of cyclic ammonium ions with sodium methoxide at 50 °C matches well the values of $1\cdot 1 \times 10^3$ found for the reaction of cyclic ethers with OH^- at 25 °C,[17] $1\cdot 9 \times 10^3$ for the reaction of cyclic ethers with $S_2O_3^{2-}$ at 50 °C[18] and 10^4–10^5 for the reactions of 2-methylaziridine and 2-methylazetidine with aliphatic amines at 120 °C.[19]

In contrast, literature values[8] for the elimination reaction range from 10^3 to 10^{10}, at variance with our own result of 10. We cannot explain this wide variety of results, which probably arises from the possibility of the elimination reaction occurring according to several mechanisms.

In our case, the consistency of the reactivity comparison between the two ring-opening reactions is assured by the fact that both reactions were studied on the same type of substrates, i.e. cyclic ammonium ions.

The comparison of the reactivity ratios in the two ring-opening reactions allows us to explain why aziridinium ions undergo elimination reactions with extreme difficulty: these compounds are so reactive towards the substitution reactions that also very weak nucleophiles (such as acetonitrile in this study) prevent the elimination reaction from prevailing. The reversal of this reactivity picture is that aziridinium ions show substitution reactions that are unknown for larger rings or open-chain analogues.[1,20]

In the similarly strained four-membered ring the S_N2 reaction is less favoured that in the three-membered ring, hence the structural changes carried out to make the elimination reaction easier are effective, and the latter reaction prevails.

Reactivity of aziridinium and azetidinium ions towards acetonitrile

The reaction of the aziridinium ion **1** with the solvent to yield the imidazolium derivative **2** partially nullified the advantage of using the hindered base to favour the elimination reaction. Nevertheless, the occurrence of that unexpected reaction turned out to be useful for providing a further measurement of the reactivity ratio in an S_N2 ring-opening reaction.

The transformation of aziridinium ions into imidazolium derivatives such as **2** promoted by acetonitrile has been reported by Leonard and Brady.[21] We are now investigating the mechanism of this reaction with particular interest in its stereochemistry. Preliminary results[22] strongly support an S_N2 ring opening of the aziridinium ion promoted by acetonitrile as the nucleophile in the first step of the reaction, which is rate determining. The S_N2 character of this ring opening accounts for the different reactivities of **1** and **4** towards acetonitrile: the azetidinium derivative **4** was found to be unreactive when subjected to the actual reaction conditions under which the aziridinium ion **1** yielded **2**, since its reactivity is presumably three or four orders of magnitude lower than that of **1**.

The validity of the above statement can be confirmed as follow. An upper limit for the rate of the reaction of **4** with acetonitrile can be evaluated as lower than 1% of the elimination rate constant obtained from the reaction with Hünig's base. The limiting rate constant so obtained can be estimated to be no higher than $1\cdot 6 \times 10^{-7}$ s^{-1}. Consequently, the reactivity ratio for the reaction with acetonitrile should not be lower than 10^3, i.e. a limiting value consistent with the values found for other S_N2 reactions.

CONCLUSIONS

The results of this study allow us to compare the different sensitivities of the substitution and elimination ring-opening reactions of cyclic ammonium ions with the ring-size effects: a three-membered ring is more reactive than a four-membered ring by a factor of *ca* 10^3 in the substitution reaction and of *ca* 10 in the elimination reaction. These reactivity ratios explain the extreme reluctance of aziridinium ions to undergo an elimination reaction, which, nevertheless, was observed by making use of a hindered non-nucleophilic base.

EXPERIMENTAL

General methods. ^{1}H and ^{13}C NMR spectra were taken on Bruker 80 SY and Varian XL300 spectrometers and chemical shifts are reported in parts per million (δ) from tetramethylsilane. Fast atom bombardment (FAB) mass spectrometry (MS) was carried out on glycerol solutions with a Kratos MS80 mass spectrometer, operating with a xenon beam of 6 keV energy and a current of *ca* 30 μA. Infrared spectra were recorded on a Nicolet FT 510 instrument in the solvent subtraction mode, using 0·1 mm CaF_2 cells, and are reported in cm^{-1}. Elemental analyses were performed by H. Melissa and G. Reuter Analytische Laboratorien. Boiling and melting points are uncorrected. Coupling constants (J) are given in Hz.

Gas chromatography (*GC*). Quantitative GC was carried out on a Hewlett-Packard 5830A instrument using a 2 m × 2 mm i.d. glass column packed with 10% Carbowax 20M–2% KOH on Chromosorb W (80–100 mesh) (Supelco). Preparative GC was carried out on a Carlo Erba Fractovap ATC/F instrument using a 5 m × 6 mm o.d. column packed with 20% Carbowax 20M–2% KOH on Chromosorb W (40–80 mesh) (Carlo Erba). GC–MS experiments were performed on a Hewlett-Packard 5970 mass-selective detector equipped with a Hewlett-Packard 5890 gas chromatograph using a 15 m capillary column coated with fluid methylsilicone.

Materials. *N*-Ethyldiisopropylamine (Hünig's base) (Fluka) was purified by refluxing with tosyl chloride and distillation, followed by refluxing with sodium and distillation. Anhydrous acetonitrile was obtained by refluxing with P_2O_5 and distillation, and subsequent refluxing with anhydrous potassium carbonate and distillation. Deuterated acetonitrile [Fluka (99·8% D) and Merck (99·95% D)] was dried on 0·5 nm molecular sieves (Merck), activated by heating in a high vacuum at 250 °C.

cis-1,1,2,3-Tetramethylaziridinium triflate (**1**) was obtained in 15% overall yield starting from *cis*-but-2-ene (Matheson) as described previously.[15]

cis-1,1,2,4-Tetramethylazetidinium perchlorate (**4**) was prepared in very low yield starting from 3,5-dimethylisoxazole (Aldrich) as described previously.[14] **Caution**: the use of this perchlorate may result in explosions by heat or shock, although we did not experience such an effect. Small amounts ($\leqslant$0·5 g) of the dry substance were handled in each experiment.

The following preparations were intended to be independent syntheses of authentic specimens for use in product analysis.

4,5-Dihydro-1,1,2,4,5-pentamethylimidazolium triflate (**2**) was obtained from the reaction of *cis*-1,1,2,3-tetramethylaziridinium triflate (**1**) with anhydrous acetonitrile at 130 °C [equation (3)]. A 20 ml volume of a 0·1 M solution of **1** in CH_3CN was heated in sealed ampoules at 130 °C for 3 h. The content of the ampoules was collected in a flask and the solvent removed in a high vacuum at room temperature: a white solid residue (0·56 g, 97% yield) was obtained. An analytical sample of the new compound **2** was obtained by recrystallization with benzene–acetone:
m.p. 135 °C; IR (CH_2Cl_2), 1716 cm^{-1} (C=N); ^{1}H NMR (300 MHz, CD_3CN), δ 4·02–3·90 (1 H, dqq, $J = 10·1$, 6·7, 2·3), 3·48–3·35 (1 H, dq, $J = 10·1$, 6·7), 3·17 (3 H, s), 2·90 (3H, s), 2·31 (3H, d, $J = 2·3$), 1·46 (3 H, d, $J = 6·7$), 1·33 (3 H, d, $J = 6·7$); ^{13}C NMR (75 MHz, CD_3CN), δ 157·62, 121·05, 75·07, 66·67, 47·68, 42·17, 16·09, 11·65, 8·83; MS, *m*/*z* 141, corresponding to the cation (FAB). Analysis: calculated for $C_9H_{17}F_3N_2O_3S$, C 37·23, H 5·90, N 9·65; found, C 37·26, H 5·72, N 9·60%.

N,*N*-Dimethyl-3-aminobut-1-ene (**3**) was obtained in very low yield from crotyl chloride (Fluka) according to a literature procedure.[15] An analytical sample was obtained from the crude product by preparative GC; ^{1}H NMR (80 MHz, $CDCl_3$), 5·4–5·8 (m, 1 H, CH=C), 4·8–5·1 (m, 2 H, CH_2=C), 2·6–2·9 (m, 1 H, CH), 2·1 (s, 6 H NCH_3), 1·0 (d, 3 H, CCH_3); MS, *m*/*z* 99 (M^+), 72 [base peak, $CH^+(CH_3)N(CH_3)_2$].

N-Ethyldiisopropylammonium triflate, i.e. the triflate of the conjugate acid (BH^+) of the Hünig's base (B) [see equation (4)], was obtained in quantitative yield from *N*-ethyldiisopropylamine (Fluka) and trifluoromethanesulphonic acid (Fluka) in anhydrous acetonitrile at 0 °C. Recrystallization from benzene–acetone yielded white leaflets with m.p. 106–107 °C; ^{1}H NMR (80 MHz, CD_3CN), δ 3·9–3·4 (2 H, m), 3·3–3·0 (2 H, q), 1·4–1·1 (15 H, m); MS, *m*/*z* 144, corresponding to the cation (FAB).

Product analysis. The product analysis was carried out under kinetic conditions.

Identification. The identification of the reaction products was carried out according to the following procedure. The flask containing the reaction mixture was connected to a vacuum line and kept at room temperature in a high vacuum. A volatile fraction was recovered in a trap cooled with liquid nitrogen and a solid residue was obtained in the reaction flask. The volatile fraction and solid residue were analysed separately according to their contents of amines and ammonium salts, respectively.

The volatile fraction was acidified with 2 M HCl, the solvent was removed under reduced pressure and the amines were released from their hydrochlorides by treat-ment with concentrated NaOH solution. The mixtures of amines were analysed by GC–MS and NMR.

The solid residue initially obtained from the separation of the volatile fraction was analysed by NMR.

Hünig's base was used in tenfold excess with respect to the ammonium salts **1** and **4** (see rate measurements), so it was found to be present in the volatile fraction as such and, as its conjugate acid, in the solid residue. We do not mention it further for the sake of brevity.

The product analysis resulted as follows.

Reaction of **1** *with Hünig's base* [equation (1)]. The reaction product present in the volatile fraction was identified as *N*,*N*-dimethyl-3-aminobut-1-ene (**3**) by comparison (NMR, GC–MS and GC) with an authentic sample of this compound (see relevant section). The solid residue was identified as a mixture of 4,5-dihydro-1,1,2,4,5-pentamethylimidazolium triflate (**2**) and *N*-ethyldiisopropylammonium triflate (BH^+), on the basis of NMR comparison with authentic samples of the two compounds (see relevant sections).

Reaction of **4** *with Hünig's base* [equation (2)]. The only reaction product present in the volatile fraction was identified as *N*,*N*-dimethyl-4-aminopent-1-ene (**5**): ^{1}H NMR (80 MHz, CD_3CN), δ 5·4–6·1 (m, 1 H, $CH{=}C$), 4·9–5·2 (m, 2 H, $CH_2{=}C$), the Hünig's base peaks covering the rest of the spectrums; MS, *m*/*z* 113 (M^+), 72 [base peak, $CH^+(CH_3)N(CH_3)_2$].

Product composition and yields. The amounts of the reaction products were determined by the use of internal standards, which enabled us to evaluate the relative percentage yields of the reaction products, where necessary, and the absolute yields of the reactions themselves.

Reaction of **1** *with Hünig's base.* The amount of compound **2** was determined by NMR, by adding a suitable amount of benzene to the reaction mixture. The comparison between the peak of the standard (δ 7·15) with those of the methyl groups (δ 3·2 and 2·9) on the N^+ of the imidazolium derivative **2** enabled us to quantify the latter as 83% of the aziridinium ion **1**. The procedure for the determination of **3** was analogous to that used for its identification, apart from the addition to the reaction mixture, at the end of the reaction, of a suitable amount of *N*,*N*-dimethyl-5-aminopent-1-ene,[23] used as the internal standard. A GC comparison between the signal of the standard and that of **3** enabled us to quantify the latter as 17% of the aziridinium ion **1**. These results show that the overall yield was virtually quantitative.

Reaction of **4** *with Hünig's base.* The yield of the aminoalkene **5** was found to be virtually quantitative by NMR comparison of the benzene signal with those of the vinyl group (δ 4·9–6·1) of **5**.

Rate measurements. The reactions were carried out in trideuteroacetonitrile (99·8% D) (Fluka) and followed to complete coversion by ^{1}H NMR.

Reactions with Hünig's base. The reactions of **1** and **4** with Hünig's base were carried out under pseudo-first-order conditions by using a tenfold excess of Hünig's base. The reaction mixture was obtained directly in the NMR tube by adding with a syringe the base to a solution of ammonium salt in CD_3CN. The final concentrations were 1·0 M in the base and 0·1 M in the ammonium salt. The tube was sealed and kept in a thermostated bath at 130 °C for suitable time intervals, with spectra recorded accordingly. The progress of the reaction was followed by measuring the increase in the signals of the vinyl group with time, using benzene as the internal standard. The rate constants were calculated from the integrated first-order rate equation and were reproducible to within ± 5%. In the case of **1**, the rate constants of the two competitive reactions were calculated from the overall rate constant and the composition data. The second-order rate constants for the elimination reactions were numerically equal to the first-order rate constants, because the Hünig's base concentration was 1·0 M. Although the appropriate experiment could not be done without substantially changing the reaction medium, the reaction order for the elimination reaction may be assumed to be second-order since in an experiment performed at a higher base concentration (*ca* 2 M) the numerical value for the rate constant was comparable to that obtained at lower base concentrations.

Reactions with CD_3CN. The reactions were carried out as described above, but without Hünig's base. The progress of the reaction of **1** was followed by recording the increase in the signals of the methyl groups on the N^+ (δ 3·2 and 2·9) with time, using benzene as the internal standard.

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