Evidence for Extensive Recombination of the Ring-opened to the Original Cyclic Molecular Ions of 2-Substituted Piperidines and Pyrrolidines after Electron Impact

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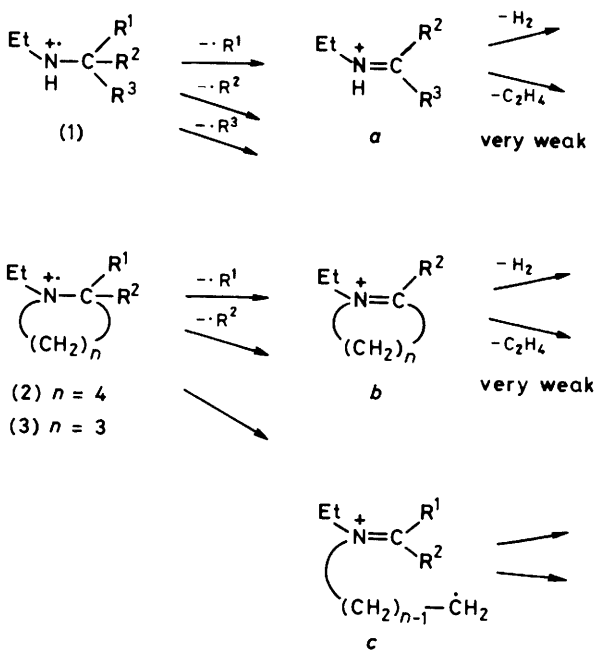
The unusually preferred formation of $(M - \text{alkyl})^+$ ions by α-fission of 2,2-dialkyl-substituted *N*-ethyl-piperidines (2) and -pyrrolidines (3) and the virtual absence of ring degradation products is caused by facile recombination of the ring-opened to the original cyclic molecular ions. Suppression of ring opening of the initially formed molecular ions or conversion of the ring-opened into other isomeric molecular ions as explanations of the mass spectrometric behaviour of (2) and (3) are excluded.

Electron impact (EI) mass spectra of cyclic amines are dominated by fragmentations involving bond fission at the carbons adjacent to the nitrogen (α-fission).[1,2] Normal (70 eV) mass spectra of α-carbon-substituted piperidines and pyrrolidines are characterized by a very intense fragment ion peak from loss of the substituent by α-fission. α-Fission to form ring-opened molecular ions is considered the primary key reaction of these typical fragmentation modes which do not have a counterpart in their open-chain analogues. Thus, the importance of α-fission of molecular ions and of successive fragmentations to explain the fragmentation behaviour of cyclic amines is qualitatively well established, In α-disubstituted cyclic amines α-fission at the branched carbon atom should be so much favoured that α-fission at the unbranched carbon atom and other fission reactions play virtually no role in the production of ions. Thus, the ion products of the former reactions may be studied undisturbed by isomeric products of the latter.

Mass spectrometric investigations on tertiary alkylamines (1) [3] showed that these compounds give only minute molecular ion peaks at all electron energies upon electron impact and decompose nearly exclusively by competitive α-fission and loss of the side chain as an alkyl radical (Scheme 1). The resulting immonium ions *a* are formed in ratios which are the reciprocal of their masses [3] and internal degrees of freedom,[4] respectively (ion mass effect), and they do not decompose further to an appreciable extent up to relatively high electron energies (*ca.* 25 eV).

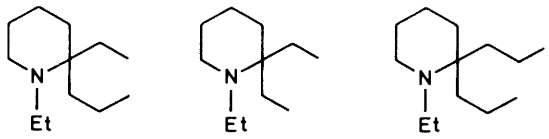
This quantitative relationship and the favourable circumstance that ions *a* decompose only very slowly provide a suitable tool to compare thoroughly the actual mass spectrometric behaviour of α-disubstituted cyclic amines (2) and (3) with expectations from analogous amines (1).

For such a comparison some basic assumptions must be made. First, strictly speaking, structures of gaseous ions of organic compounds are not known. However, from the low ionization energies of aliphatic amines compared with those of the corresponding hydrocarbons it can be reasonably inferred that the predominant ionization process is loss of an electron from the lone electron pair of the nitrogen leading to the initial molecular ion. The predominant α-fission of (especially α-branched) amines is easily explained as starting from these $M^{+\cdot}$ ions leading to ' immonium ' fragment ions. Secondly, the cyclic amines behave like their open-chain analogues, *i.e.* the initial $M^{+\cdot}$ ions are analogous to the $M^{+\cdot}$ ions of the open-chain amines, and the predominant primary fragmentation is α-fission leading to analogous immonium ions, as shown by qualitative comparison of open-chain and cyclic amines.



Scheme 1.

On this basis no energy difference for bond breaking is expected between α-fission to lose an alkyl radical and to open the ring, respectively, when there is no ring strain. The principal difference between (1) and (2) [or (3)] lies in the fact that in the case of (2) the radical and ionic parts of one of the α-fission products (ring-opened $M^{+\cdot}$ ion) cannot drift apart, *i.e.* that the entropy changes for formation of *b* + R· and for formation of *c* are different. This, however, should have no major influence on the initial α-cleavage reaction, because the radical and ionic parts of *c* do not know at this stage that they cannot escape from each other. The consequence of this difference should be mainly reflected in the different fates of *b* and *c*. Therefore, as for (1), the mass spectra of (2) [and (3)] (Scheme 1) should exhibit initial, cyclic $M^{+\cdot}$ ions of negligible relative intensities, while the ring-opened $M^{+\cdot}$ ions *c* and both ion species *b* should be the main primary fragment ions. Since ions *b* (like *a*) are expected not to decompose appreciably up to 25 eV and ions from other primary reactions are expected to be negligible, the fate of *c* should be easily followed from the mass spectra ($\leqslant$25 eV).



(2a) (2b) (2c)

For this purpose the mass spectra of selected cyclic amines (2) and (3) have been investigated.

Results and Discussion

Although it cannot be expected that the ion intensity relationship found for α-fission product ions of open-chain amines and related compounds is also quantitatively valid for analogous cyclic amines, one may expect from the introductory considerations that the two ions *b* and ion *c* are initially formed from (2) and (3) in a ratio of *ca.* 1 : 1 : 1, *i.e.* that the sum of the relative abundances of *c* and its fragment ions should be about as large as the relative abundance of one of the ions *b*.

The mass spectrometric behaviour of the first cyclic amines investigated (2a—c) was completely different from these expectations. The 20 eV spectra nearly exclusively consisted of fragment peaks arising from loss of either of the alkyl groups (R) by α-fission (Scheme 1). Except for small molecular ion peaks (0.3—1% relative intensity) and small peaks from fragmentations of *b* other peaks were virtually absent. This is in sharp contrast to what was expected, for in the case of a low $M^{+\cdot}$ ion peak (from *c*) fragment ions of *c* of considerable abundance should be formed.

As an illustration the 20 eV mass spectra of (2a) and the corresponding open-chain (1a) are shown in Figure 1. While $(M -$ ethyl$)^+$ (b_1) and $(M -$ propyl$)^+$ (b_2) are formed by α-fission in the expected ratio (corresponding to the ratio of a_1 and a_2), the ion intensity of *c* is much smaller than that of the corresponding ion a_3. Except for small peaks at *m/z* 112, 126, 138, and 152 no other appreciable peaks emerge. These peaks originate from b_1 and b_2, respectively, by loss of hydrogen and ethene, respectively, as shown by the corresponding small peaks in the spectrum of (1a) [typical for (1)] and by appropriate metastable ion transitions. In the spectra of (2b and c), respectively, $(M -$ propyl$)^+$ from (2b) and $(M -$ ethyl$)^+$ from (2c) have only 0.5% relative intensity beside the α-fission products $(M -$ ethyl$)^+$ from (2b) and $(M -$ propyl$)^+$ from (2c) of 100% relative intensity. This rules out the possibility that a considerable proportion of fragments not arising from loss of R· contributes to the main fragment peaks in the spectra of (2a—c). Therefore, no appreciable fragments expected from ring degradation of the ring-opened $M^{+\cdot}$ ions [1] can be detected. Loss of an alkyl substituent R directly from *c* without interaction of the radical [5] and the ionic centre can be excluded, because the immonium moiety has no tendency to decompose in this fashion [6] and, according to the analogous moiety in *a*, is unreactive with respect to decomposition.

What is the cause for the unexpected mass spectrometric behaviour of (2a—c)? First, the original, cyclic $M^{+\cdot}$ ions do not (appreciably) open the ring to generate ions *c*. This means that the general premises derived from open-chain amines are not valid for the cyclic compounds. Secondly, ions *c* are generated as expected but have no favourable direct decomposition pathways and, instead, form isomeric $M^{+\cdot}$ ions by reaction of the radical with the ionic centre from which loss of R· can easily take place. This means that the premises are valid but an unexpected reaction blurs the results. In this second case two alternatives may be distinguished, namely

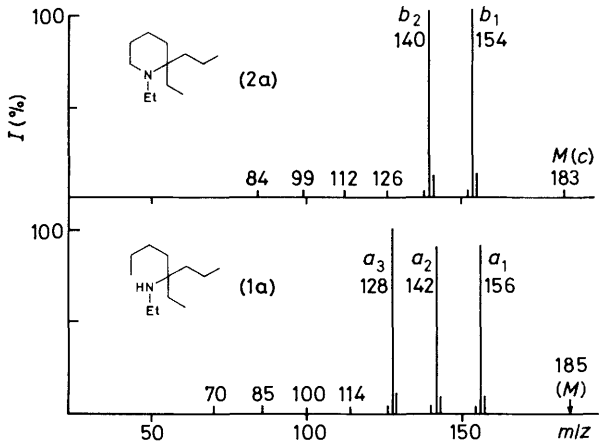


Figure 1. EI Mass spectra of (1a) and (2a) at 20 eV

recombination to the original $M^{+\cdot}$ ions and reaction of the radical with the ionic centre in another fashion to form other isomeric $M^{+\cdot}$ ions, respectively.

None of the possibilities can be ruled out *a priori*. The enhanced formation of ions from loss of the alkyl substituent in α-substituted cyclic amines is usually assumed (though without proof) to be caused by reduction of ring opening.* On the other hand the reverse reaction of ring opening (recombination to the original $M^{+\cdot}$ ion) can be assumed to occur,[7] because the reverse activation energy of simple fission reactions is generally accepted to be close to zero. But it is astonishing that hitherto it has not been explicitly taken into consideration to explain the fragmentation behaviour of cyclic compounds. Finally, conversion of cyclic $M^{+\cdot}$ ions *via* ring-opened $M^{+\cdot}$ ions to isomeric cyclic $M^{+\cdot}$ ions has been observed for related cyclic compounds.[8] Because of its general importance for mass spectrometry this point needs closer inspection.

Ring Opening.—Conclusions were drawn from three independent experiments: (a) change of the energy requirement for ring opening relative to α-fission to lose alkyl; (b) comparison of the metastable ion transitions of (1) and (2); (c) dependence of the relative $M^{+\cdot}$ ion intensities on thermal energy.

(a) The heats of formation of *b* plus R· [$\Delta H_f°(b + R·)$] and of *c* [$\Delta H_f°(c)$] must be nearly the same, because *c* will only be neglibibly stabilized or destabilized by through-bond interaction of the radical and ionic centres at this bond distance. Relief of conformational strain by ring opening might possibly result in a rather lower $\Delta H_f°(c)$. Thus, if an energy barrier is denied or assumed to be equal, bond fission energies should be equal or slightly lower for ring opening than for loss of R·, and one might expect an equal chance for all α-fissions at the branched carbon atom or a slight preference for formation of *c* (ring opening) from the $M^{+\cdot}$ ions of (2). If an unnoticed effect would raise $\Delta H_f°(c)$ over $\Delta H_f°(b + R·)$ by a small amount, it still appears to be improbable that this would cause such a drastic reduction of ring opening at electron energies far above the threshold as might be inferred from the mass spectra of (2a—c).

Nevertheless, an intentional change of $\Delta H_f°(c)$ relative to $\Delta H_f°(b + R·)$ by selection of a suitable model compound may help to gain more clarity. Replacing the ethyl groups at the carbon atom of (2b) by methyl groups should lead to the desired relative change of $\Delta H_f°$.

Experimentally it is known from essentially all α-fissions of

* See *e.g.* refs. 1*a* and *b*.

aliphatic compounds that loss of methyl is much disfavoured *versus* loss of larger alkyl groups. For α-branched aliphatic amines it can be inferred that α-fission to lose a larger alkyl group is energetically favoured over loss of methyl by *ca.* 3 kcal mol^{-1}. This can be deduced from the ΔH_f° values of alkyl radicals [9] and of immonium ions.[10] $\Delta H_f^\circ(\cdot CH_3) - \Delta H_f^\circ(\cdot C_2H_5)$ is *ca.* +8 kcal mol^{-1}. Since introduction of an inert CH_2 unit (no stabilization effect) into an aliphatic skeleton leads to a lowering of ΔH_f° of 5 kcal mol^{-1},* the ethyl radical is stabilized over methyl by 3 kcal mol^{-1}. On the other hand, $\Delta H_f^\circ(\overset{+}{H_2}N{=}CHCH_3) - \Delta H_f^\circ(\overset{+}{H_2}N{=}CHCH_2CH_3)$ is +5 kcal mol^{-1}. Thus, already for these low homologous immonium ions, insertion of a CH_2 unit does not exert further stabilization. This will be the case for *b* and *c*, as well, regardless of whether R in (2) is methyl or ethyl. From this it follows that $\Delta H_f^\circ(b + R\cdot) - \Delta H_f^\circ(c)$ for (2) with R = methyl is raised by 3 kcal mol^{-1} over $\Delta H_f^\circ(b + R\cdot) - \Delta H_f^\circ(c)$ for (2b) (R = ethyl). Additional lowering of $\Delta H_f^\circ(c)$ relative to $\Delta H_f^\circ(b + R\cdot)$ might be effected by introduction of a methyl group at the 3-position of the ring, leading to a (more stabilized) secondary radical site in *c* and thereby stabilizing *c*. A similar effect on *b* can be denied from the above energy considerations (insertion of an inert CH_2 unit in *b*).

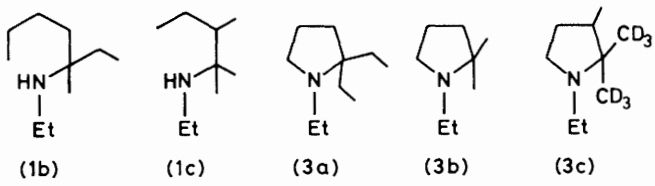
Thus, both from experimental experience on aliphatic compounds and from energy considerations it can be expected that these structural changes will effect changes in α-fissions of (2) in favour of ring opening.

To study the effects of these structural changes on the intensity ratios of the α-fission products the open-chain amines (1b and c) and the cyclic amines (3a—c) were investigated and compared with (2b). CD_3 groups were introduced in the 2-position of (3c) to be able to distinguish between the different positions of the methyl groups.

General inspection of the 20 eV mass spectra of (3a—c) showed that the fragmentation pattern of (3a) is very similar to that of (2b), indicating that α-dialkyl-substituted pyrrolidines behave like the corresponding piperidines. For (3b and c) fragments not arising from decomposition of *b* are somewhat enhanced compared to (3a) but are still low. Loss of the methyl group from the 3-position in (3c) leads to a fragment of only 2% relative intensity. Loss of methyl by α-fission at the *N*-ethyl group is negligible as deduced from the spectra of (1)—(3) with no methyl group at the branched carbon atom.

For the open-chain amines (1b and c) the effect of the replacement of a larger alkyl group by methyl is pronounced and in accord with the above energy considerations. At 20 eV the intensity ratio of $(M -$ butyl$)^+$ *versus* $(M -$ methyl$)^+$ was found to be 11 : 1 for (1b) and *ca.* 40 : 1 (per methyl group) for (1c) [ratio $(M -$ ethyl$)^+$ *versus* $(M -$ methyl$)^+$ for (1b) *ca.* 10 : 1]. At 11 eV these ratios rise to 200 : 1 and 600 : 1, respectively, indicating increased appearance energies for loss of methyl *versus* loss of larger alkyl.

The effect of the structural changes on the mass spectra of the cyclic amines depends on the cause of the unexpected fragmentation behaviour. This is briefly discussed. (i) There is a reduction of ring opening, caused by a larger bond fission energy in (2b) and (3a) for α-fission to open the ring than for α-fission to lose R. For (3b and c) the difference between the bond fission energies would be lowered by ⩾ 3 kcal mol^{-1}, regardless of whether an unknown energy barrier for ring opening is assumed or not [this barrier would not change from (3a) to (3b and c)]. By this effect the bond fission energies in (3b and c) for ring opening may still be larger [but lowered compared with (2b) and (3a)] than for loss of R or may be lower. In the first case it is expected that the intensity ratios of *c* ($M^{+\cdot}$) *versus b* should rise from (2b) and (3a) to (3b and c) at the same electron energies but decrease for (2b) and (3a—c) when the electron energy is lowered, because loss of R would remain the lower energy process. In the second case the ratios should rise from (2b) and (3a) to (3b and c) and additionally be >1 (referred to one methyl group) for (3b and c) but decrease for (2b) and (3a) and increase for (3b and c) at lowered electron energies, because for (3b and c) ring opening would be the lower energy process. (ii) No reduction of ring opening, but isomerization of *c* to another $M^{+\cdot}$ ion from which formation of *b* occurs. In this case bond fission energies for ring opening would be about the same as for loss of R in (2b) and (3a) and lower than for loss of R by ⩾3 kcal mol^{-1} in (3b and c), and the intermediate isomeric $M^{+\cdot}$ ions would decompose to *b* to an increasing degree with increasing electron energies. This would lead to an increase of the ratios of $M^{+\cdot}$ *versus b* from (2b) and (3a) to (3b and c) at the same electron energies and to an increase for (2b) and (3a—c) at lowered electron energies, but the ratios will be substantially lower than the corresponding ratios for (1b and c), because $M^{+\cdot}$ decomposes to *b* to a high degree.



(1b) (1c) (3a) (3b) (3c)

The intensity ratios of $M^{+\cdot}$ *versus b* (relative abundance of $M^{+\cdot}$) at 20 eV were found: 0.003 for (2b), 0.01 for (3a), 0.11 for (3b), and 0.09 for (3c) [only the peaks of the fully deuteriated corresponding ions of (3c) used]. At 11 eV the corresponding ratios were 0.02, 0.06, 0.44, and 0.35 for (2b), (3a), (3b), and (3c), respectively [for (3c) see above]. Thus, the ratios rise from (2b) and (3a) to (3b and c) at the same electron energies and from 20 to 11 eV for all compounds, but remain low compared with the corresponding ratios from (1b and c). This is in accord with isomerization of *c* and successive formation of *b* but in disagreement with the reduction of ring opening.

(b) Comparison of the metastable ion transitions $M^{+\cdot} \longrightarrow (M - R)^+$ reveals that (1) and (2) behave totally differently with respect to this process. For the open-chain amines (1) no corresponding metastable ion peaks from these transitions could be detected in their mass spectra. In contrast, abundant corresponding metastable ion peaks are found for all compounds (2) [and (3)]. The initially formed cyclic $M^{+\cdot}$ ions of (2) are analogous to those of (1) and must be as short-lived and, especially, must lose R· by α-fission in the same reaction process. Therefore, they cannot be responsible for the abundant metastable ions found. As a consequence these metastable ions must arise from some other process. Regardless of what the reacting ion species is from which the metastable ion transition occurs, the only reasonable initial step of this process is ring opening to *c*. The prolonged lifetime of the reacting species is most plausibly explained by reverse reaction of *c* to the original cyclic $M^{+\cdot}$ ion or reaction to an isomeric $M^{+\cdot}$ ion (from which loss of R may easily occur) and a relative inertness of *c* towards other fragmentations (ring degradation). The latter assumption is supported by the general fragmentation behaviour of (2).

(c) Finally, evidence for isomerization of *c* and successive fragmentation to *b* (or isomer thereof) and against suppression of ring opening arises from the dependence of the relative $M^{+\cdot}$ ion intensities of (2) and (3) on the source temperature of the mass spectrometer.

* Compare the data in ref. 9.

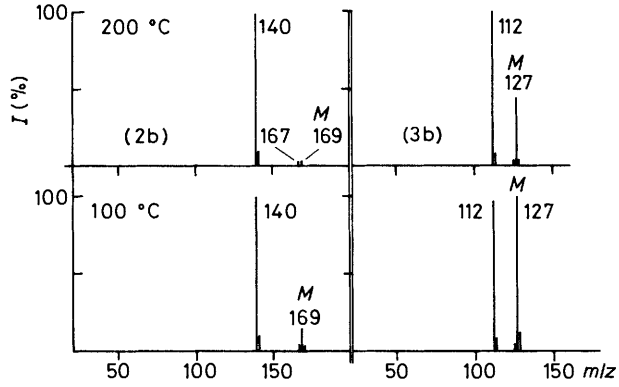


Figure 2. 11 eV Mass spectra of (2b) and (3b) at 100 and 200 °C source temperatures

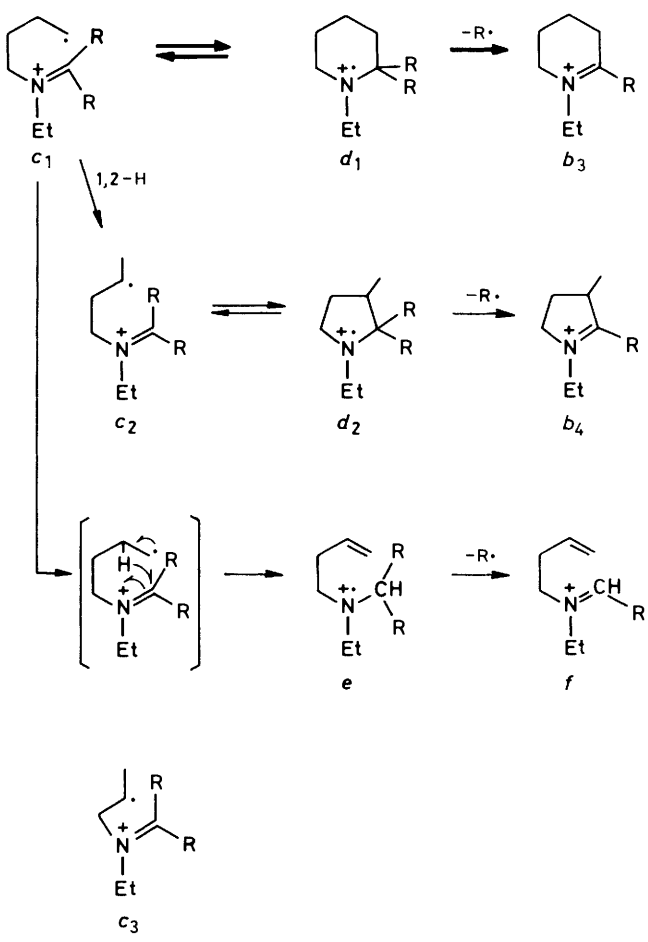
For the open-chain amines (1a—c) no such dependence on source temperature is observed, and the relative $M^{+\cdot}$ ion intensities are below 0.1%Σ_{20}. From this it is excluded that the observed changes for (2) and (3) originate from a change of the relative intensities of the initially formed, intact cyclic molecular ions.

At the usually applied source temperature of *ca.* 200 °C the relative $M^{+\cdot}$ ion intensities at 11 eV were 1.5 for (2b), 5.0 for (3a), 31 for (3b), and 25% Σ_{20} for (3c). At 100 °C these values rise to 12 for (2b), 18 for (3a), 51 for (3b), and 50%Σ_{20} for (3c) [calculated for (3c) from the peak height of the fully deuteriated $M^{+\cdot}$ ion; including all differently labelled $M^{+\cdot}$ ions the values for (3c) rise to 29.5 at 200 °C and 54%Σ_{20} at 100 °C], accompanied by an appropriate rise of the metastable ion abundances from the transition $M^{+\cdot} \longrightarrow b$.

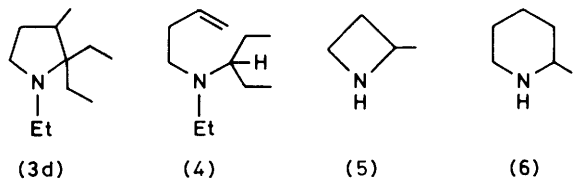
The complete mass spectra of (2) and (3) consist only of peaks from $M^{+\cdot}$, *b*, a small peak from $(M - H)^{+\cdot}$, and a small peak from the metastable ion (see above). Therefore, taking together the 11 eV mass spectra and the increase of the relative molecular ion intensities of (2) and (3) at lowered thermal energies, as well as the corresponding results from (1a—c), this shows unequivocally that a large proportion of ions *c* formed survives intact or after isomerization to reach the detector as $M^{+\cdot}$ ions at lower temperatures and after isomerization * decomposes to *b* (or isomer) at elevated temperatures. In contrast, these results are not in accord with the suppression of ring opening. As an illustration, the 11 eV spectra of (2b) and (3b) at 100 and 200 °C are given in Figure 2.

Intermediate for Loss of R· *from Ion* c.—As ring opening is not suppressed this only leaves the alternative that *c* in some way reacts to lose R. Loss of R directly from *c* in a reaction triggerred by the immonium moiety without interaction of the radical site must be discounted. Reaction of *c* to lose R by interaction of the radical centre should only occur *via* some intermediate which can easily lose R. This last condition excludes bond formation between the radical site and the nitrogen as an alternative,[8b] and reasonable possible intermediates are presented in Scheme 2.

To study the mass spectrometric behaviour of the possible intermediates in the reactions of c_1 to b_3, b_4, and *f*, respectively, the mass spectra of (2b), (3d), and (4) were compared, the initial molecular ions of which are d_1, d_2, and *e* (Scheme 2). Ions d_2 and *e* must be considered as serious alternatives to d_1, since their formation can be imagined to occur in low-energy



Scheme 2.

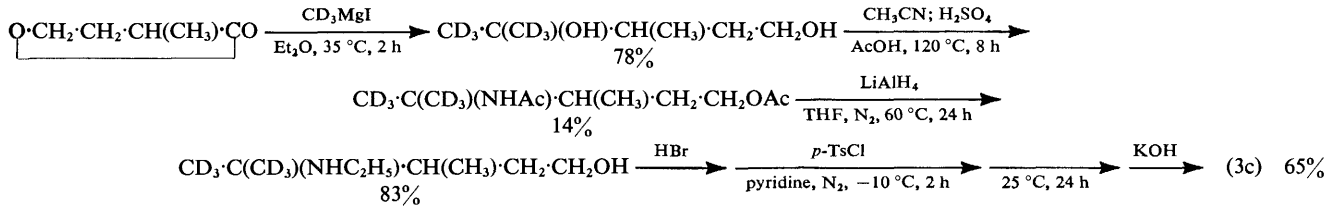


pathways and c_2 is thermodynamically more stable than c_1 (secondary radical site in c_2).

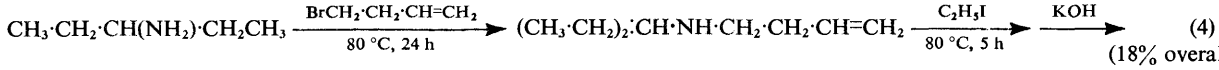
(a) There are two experimental arguments against ring contraction of a ring-opened $M^{+\cdot}$ ion of (2) or (3) (*e.g.* $c_1 \longrightarrow d_2$). First, ring contraction should have a better chance compared to recombination, when the driving force is formation of a secondary radical site in the isomeric ion (*e.g.* c_2) from a ring-opened $M^{+\cdot}$ ion with a primary radical site (*e.g.* c_1). For pyrrolidines such as (3a) this would lead to c_3, which is expected to form a four-membered cyclic $M^{+\cdot}$ ion not as readily but to exhibit ring degradation to a higher extent. This is followed from a comparison of the mass spectra of (5) [11] and (6) at 12 eV. While fragmentation of (5) is dominated by ring degradation, no corresponding product ions are formed from (6), but the sole fragmentation product is $(M - CH_3)^+$ from α-fission (base peak, 75%Σ_{20}). Therefore, the fragmentation behaviour of *e.g.* (3a) would be expected to differ considerably from (2*b*), if c_3 and c_2 were formed to a considerable degree. The fragmentation behaviour of (3a) is closely analogous to that of (2b), however.

Secondly, more convincing evidence arises from the com-

* For an argument that *c* cannot decompose to *b* directly see earlier.



Scheme 3.



Scheme 4.

parison of the mass spectra of (2b) and (3d). Although their mass spectra are very similar at first glance and the $(M - R)^+$ ions decompose only to a very low degree in both cases, the metastable decompositions of the $(M - R)^+$ ions from (2b) and (3d) are distinctly different. As is general for the open-chain amines (1) and analogous to (2a), (2c), and (3a) $(M - R)^+$ from (2b) shows metastable loss of C_2H_4 (*m* 89.7) but no other metastable losses except of H_2. Most of the $(M - R)^+$ ions from (2b) consist of b_3 through direct α-cleavage of the initially formed $M^{+\cdot}$ ion (d_1); a smaller fraction (*ca.* $\frac{1}{3}$) might have structure b_4, if reaction of c_1 *via* d_2 occurred. Ion b_4 is predominantly formed by direct α-cleavage of the initial $M^{+\cdot}$ ion (d_2) of (3d). In contrast to (2b), $(M - R)^+$ from (3d) shows major metastable loss of C_2H_5 (*m* 88.1) and additional of CH_3 (*m* 111.6) but only minor loss of C_2H_4. Therefore, if from (2b) part of the $(M - R)^+$ ions had structure b_4, this should be detectable by the major metastable transition $b_4 \longrightarrow (b_4 - C_2H_5)$. Within the experimental detection limit this is not the case, and a contribution of b_4 of >5% can be safely excluded. Thus, reaction of c_1 *via* c_2 and d_2 to b_4, at most, can only be minor.

(b) A corresponding comparison of the mass spectra of (2b) and (4) revealed that formation of *e* from c_1 is no real alternative to recombination to d_1. As might be anticipated, α-fission of *e* [$M^{+\cdot}$ ion of (4)] to lose the resonance-stabilized allyl radical from the unbranched α-carbon competes successfully with loss of R· from the branched α-carbon. In fact, loss of $\cdot C_3H_5$ seems to be energetically more favoured than loss of $\cdot C_2H_5$ as deduced from the intensity ratios of the ions formed. At 20 eV the ratio of $(M - C_3H_5)^+$ to $(M - C_2H_5)^+$ is 9.5 : 1 and rises with lower electron energies (22 : 1 at 11 eV). The $(M - C_3H_5)^+$ ion decomposes further by loss of C_5H_{10}, the ion thus formed (*m*/*z* 58) giving rise to the base peak in the 20 eV spectrum of (4). There is no hint for formation of a $(M - C_3H_3)^+$ ion from (2b) at any electron energy. Therefore, formation of *e* from (2b) *via* c_1 can be ruled out, even if one takes into account different internal energies of *e* on starting from (2b) and (4), respectively.

Thus, the actual mass spectrometric behaviour of (2a—c) is described by the bold arrows in Scheme 2, and the pyrrolidines (3a—d) behave analogously.

The extensive recombination of the ring-opened to the original cyclic molecular ions and the suppression of ring degradation of the ring-opened molecular ions in favour of this recombination have not been demonstrated before. Observations on simpler cyclic amines [*e.g.* (6)] and 2,2-dialkyl-substituted tetrahydropyrans (unpublished results) suggest that recombination is of more general importance for the mass spectrometric behaviour of such cyclic compounds. In view of the general importance of this aspect of the reactions of such ring-opened species it is astonishing that it has not received attention before.

Experimental

Mass spectra were obtained using a Varian MAT CH 5 mass spectrometer and a Siemens Kompensograph pen recorder. The accelerating voltage was 3 kV, and the electron energies given in the text are nominal. Introduction of the samples was performed *via* a batch inlet (EMI) at 120 °C. If not otherwise stated, the source temperature was kept at *ca.* 200 °C.

Compound (6) was a commercial sample, additionally purified by preparative g.c. (SE-30). Other compounds were prepared by conventional methods, purified by distillation in a modified sublimation apparatus (60—120 °C at 15—60 Torr) and preparative g.c. (SE-30; 90—140 °C), and were checked for purity. Amines (1) were prepared as described before.[3] Amines (2) and (3) were prepared by cyclization of the corresponding 1-tosyl- or 1-bromo-*N*-ethylalkylamines.[4] More conveniently (2b), (2c), (3a), (3b), and (3d) can be obtained by the Grignard reaction of the appropriate lactones with alkyl bromides and methyl iodide, respectively, to yield (1), *n*-diols, and further conversion according to the reaction sequence shown for (3c). The deuteriated amine (3c) was prepared as shown in Scheme 3. After neutralization of the 1-hydroxy-amine with HBr the salt was dried, dissolved in dry pyridine under nitrogen, and a small excess of *p*-tosyl chloride was added at −10 °C. After stirring for 2 h at −10 °C the resulting tosylate was cyclized to (3c) *in situ* by allowing it to stand at room temperature for 24 h and then by treatment with dilute KOH. Ether extraction, washing with water, and cautious removal of the ether from the dried solution resulted in a pale brown liquid containing *ca.* 25% pyridine and *ca.* 75% (3c). Preparative g.c. (SE-30; 100 °C) resulted in (3c) of *ca.* 99% purity, $\delta_H(CDCl_3)$ 0.88 (3 H, d,) 1.08 (3 H, t), 1.30 (1 H, m), 1.90 (2 H, m), 2.20 (2 H, m), 2.65 (1 H, m), and 3.10 (1 H, m). The deuterium content was 89 ± 2% (starting material CD_3I 99% D). Partial loss of label occurred in the second step.

Amine (4) was prepared by the reaction sequence in Scheme 4. After removal of starting materials the distilled (100—120 °C at 60 Torr) aminobutene containing *ca.* 20% of tertiary amine was treated with ethyl iodide in a closed vessel. The two phases which resulted both contained (4) and were treated with dilute KOH. The residue of the dried ether extract was distilled at 120—130 °C and 20 Torr yielding an amine mixture of *ca.* 60% (4) besides starting material and the tertiary amine from the first step. Separation by preparative g.c. (SE-30; 140 °C) resulted in (4) of >99% purity, $\delta_H(CDCl_3)$ 0.88 (6 H, t), 1.00 (3 H, t), 1.30 (4 H, 11 lines), 2.15br (2 H, q), 2.25 (1 H, quintet), 2.45 (4 H, q.), 5.0br (2 H, t,), and 5.80 (1 H, m).

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