Unimolecular Reactions of Isolated Organic Ions: Reactions of the Immonium Ions $CH_2=N^+(CH_3)CH(CH_3)_2$, $CH_2=N^+(CH_3)CH_2CH_2CH_3$ and $CH_2=N^+(CH_2CH_2CH_3)_2$

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The reactions of metastable $CH_2=N^+(CH_3)C_3H_7$ immonium ions have been investigated by means of ^2H-labelling experiments and kinetic energy release measurements. Loss of C_3H_6, with specific β-H transfer, is the sole channel for dissociation of $CH_2=N^+(CH_3)CH(CH_3)_2$. This process gives rise to a Gaussian metastable peak. The isomeric ion, $CH_2=N^+(CH_3)CH_2CH_2CH_3$, also expels C_3H_6; however, both α-H and γ-H as well as β-H transfer occurs in this case, and the reaction proceeds with an increased kinetic energy release. The role of ion-neutral complexes in C_3H_6 loss from $CH_2=N^+(CH_3)C_3H_7$ ions is discussed. In addition, $CH_2=N^+(CH_3)CH_2CH_2CH_3$ eliminates C_2H_4. This fragmentation yields a broad dish-topped metastable peak, corresponding to a very large kinetic energy release ($T_{\frac{1}{2}} \sim 73$ kJ mol^{-1}), and it involves specific and unidirectional γ-H transfer. A potential energy profile summarising the reactions of $CH_2=N^+(CH_3)CH_2CH_2CH_3$ and $CH_2=N^+$-$(CH_3)CH(CH_3)_2$ is constructed. The mechanisms by which immonium ions of this general class eliminate C_3H_6 and C_2H_4 have been further probed by studying the behaviour of the higher homologue, $CH_2=N^+(CH_2CH_2CH_3)_2$. The mechanistic conclusions derived from this work are found to be in excellent qualitative agreement with those of previous studies.

The chemistry of $C_nH_{2n+2}N^+$ immonium ions contains several interesting features.[1] Two ubiquitous reactions are observed in the fragmentation of metastable immonium ions in which there is at least one intact alkyl group, R, comprising three or more carbon atoms directly attached to nitrogen. The first process, which is sometimes known as the 'onium' reaction, involves expulsion of an alkene (C_nH_{2n}, if R = C_nH_{2n+1}) derived by formal hydride anion abstraction from the carbonium ion, R^+, produced by cleavage of the C–N bond in $R^1R^2C=N^+R^3R$ (R^1, R^2, R^3 = H or alkyl group smaller than R). The second fragmentation proceeds by elimination of an alkene containing fewer carbon atoms than the principal alkyl group. Typically, but not always, $C_{n-1}H_{2n-2}$, comprising one less carbon atom than R^+ is lost. The second dissociation channel can be formulated as a symmetry-allowed,[2] six-electron pericyclic process, in which γ-hydrogen transfer accompanies fission of the C_α–C_β bond in R. This route for alkene loss bears some resemblance to the well-known McLafferty rearrangement[3-7] of ionised carbonyl compounds.

Many aspects of these reactions have been delineated quite clearly.[1,8-10] It is commonly, though not universally, accepted that expulsion of C_nH_{2n} involves species in which there is an elongated N---R^+ bond. Such Ion-Neutral Complexes[11-15] (INCs) offer a means of interpreting a large number of otherwise inexplicable reactions. The alternative process, elimination of $C_{n-1}H_{2n-2}$, apparently proceeds via a two-step mechanism: a γ-H is wholly or partly transferred from R to the carbon atom of the C=N entity, before the C_α–C_β bond in R begins to break.[8,9] Similar mechanistic conclusions have been reached for the McLafferty rearrangement, in which γ-hydrogen transfer occurs before C–C cleavage, at least at low-internal energies.[4,5,7]

Early work[8] on metastable $CH_2=NH^+CD_2CH_2CH_3$ ions revealed that propene elimination involves a significant probability of α-D transfer. Moreover, the ratio of $C_3H_4D_2$ loss (β-H or γ-H transfer) to C_3H_5D expulsion (α-D transfer) was 71:29. This ratio is close to that (67:33) which would be expected if the n-propyl group isomerised to an isopropyl structure (here CHD_2CHCH_3) via a unidirectional, 1,2-H shift before specific β-hydrogen transfer occurred from either methyl

group. Parallel behaviour was subsequently reported for the homologous $CH_3CH=NH^+CD_2CH_2CH_3$ species.[16] Furthermore, the finding[17] that $CH_2=N^+(CH_3)CH_2CH_2CD_3$ expels $C_3H_3D_3$ (α-H or β-H transfer) and $C_3H_4D_2$ (γ-D transfer) in the ratio of ~60:40 is also broadly explicable given that the incipient $^+CH_2CH_2CD_3$ cation rearranges to $CH_3CH^+CD_3$, from which H- and D-transfer should occur at approximately equal rates.

In order to delineate the mechanism of propene elimination from immonium ions containing an n-propyl substituent, a more detailed investigation of ^2H-labelled analogues of $CH_2=N^+(CH_3)C_3H_7$ species was undertaken. However, before a preliminary account of this work was published,[18] a definitive paper[19] describing the behaviour of numerous ^2H-labelled analogues of $CH_2=N^+(CH_2CH_2CH_3)_2$, $CH_2=N^+[CH(CH_3)_2]_2$ and $CH_2=N^+(CH_3)CH_2CH_2CH_3$ appeared. The present paper seeks to compare the results and mechanistic conclusions of the two independent studies. In addition, special attention is given to the energetics of alkene elimination from $CH_2=N^+$-$(CH_3)C_3H_7$ ions and to the significance of isotope effects on the kinetic energy releases that accompany ethylene expulsion from $CH_2=N^+(CH_3)CH_2CH_2CH_3$ and $CH_2=N^+(CH_2CH_2CH_3)_2$ and their ^2H-labelled analogues. Neither of these two issues was addressed in detail in the other study.

Results and Discussion
The reactions of metastable $C_5H_{12}N^+$ ions generated as $CH_2=N^+(CH_3)CH(CH_3)_2$, 1, and $CH_2=N^+(CH_3)CH_2CH_2$-CH_3, 2, are given in Table 1. Data for propene and ethylene losses from several ^2H-labelled analogues of 1 and 2 are shown in Tables 2 and 3, respectively. When available, results from the independent study[19] are included in the Tables for purposes of comparison.

These results establish that 1 and 2 have distinct chemistries: only 2 eliminates C_2H_4. This divergence in the behaviour of isomeric immonium ions that differ solely in the structure of the N-propyl groups is apparently quite general.[1] In contrast, the corresponding oxonium ions often show quite similar or even

Table 1 Reactions of metastable $C_5H_{12}N^+$ ions

| | Neutral species lost | | | |
| | C_2H_4 | | C_3H_6 | |
Ion structure	RA^a	$T_{\frac{1}{2}}^b$	RA^a	$T_{\frac{1}{2}}^b$
$CH_2=N^+(CH_3)CH(CH_3)_2$			100	2.2^c
$CH_2=N^+(CH_3)CH_2CH_2CH_3$	76	73^d	24	3.0^c

^{a} RA = Relative abundance, measured from product ion counts (corresponding to metastable peak areas) formed by dissociation of metastable ions in the second field-free region (between the magnetic and electric sectors) of a research mass spectrometer of unusually large dimensions. Data were normalised to a total metastable ion current of 100 units. ^{b} $T_{\frac{1}{2}}$ = kinetic energy release (in kJ mol^{-1}) estimated from the width at half-height of the associated metastable peak. ^{c} Gaussian metastable peak. ^{d} Dish-topped metastable peak.

essentially identical chemistries [e.g. $CH_2=O^+CH(CH_3)_2$ and $CH_2=O^+CH_2CH_2CH_3$ expel CH_2O and H_2O in almost exactly the same ratio [20] and with kinetic energy (KE) releases that are identical within experimental error [21-24]]. The contrast between the divergent behaviour of 1 and 2 and the closely similar reactions shown by $CH_2=O^+CH(CH_3)_2$ and $CH_2=O^+$-$CH_2CH_2CH_3$ probably reflects two important differences in the energetics of the corresponding pairs of INCs [$C_3H_7^+$ $Z=CH_2$] and [C_3H_6 $^+HZ=CH_2$] {Z = CH_3N or O}. In the oxonium ion series, the first INC is likely to be more substantially stabilised, relative to the energy of the separated components, because the neutral component, CH_2O, has a larger electric dipole moment than $CH_2=NCH_3$. This factor favours interconversion of these $CH_2=O^+C_3H_7$ species with one another or with common structures accessible to both these $C_4H_9O^+$ oxonium ions. A more important influence is the differences in proton affinity (PA) of the $CH_2=Z$ and C_3H_6 molecules in the INCs. Those for CH_2O and C_3H_6 (718 and 751 kJ mol^{-1}, respectively [25]) are sufficiently similar to permit at least limited interconversion of [$C_3H_7^+$ $O=CH_2$] and [C_3H_6 $^+HO=CH_2$] via reversible hydrogen exchange to compete with dissociation. However, the PA of $CH_2=NCH_3$ (880 kJ mol^{-1}) [26] is so much greater than that of C_3H_6 that unidirectional hydrogen transfer {[$C_3H_7^+$ $CH_2=NCH_3$]→[C_3H_6 $CH_2=NH^+CH_3$]} and subsequent separation to products occurs, thus pre-empting interconversion of 1 and 2.

Reactions of $CH_2=N^+(CH_3)CH(CH_3)_2$.—Propene loss from 1 gives rise to a Gaussian metastable peak. The corresponding KE release is fairly small ($T_{\frac{1}{2}}$ = 2.2 kJ mol^{-1}). Specific β-H transfer from the isopropyl group to nitrogen occurs, as is most clearly shown by the expulsion of solely C_3HD_5 from $CH_2=N^+$-$(CH_3)CH(CD_3)_2$.

All these data are consistent with a mechanism in which INCs play a significant role, Scheme 1. There are two INCs (1a and 4) in this mechanism. In early work on alkene loss from immonium ions homologous to 1 and 2, both the species corresponding to 1a and 2a, in which the C–N bond has been stretched, were considered to be INCs. [8,9] However, more recent terminology restricts the expression INC to species in which mutual rotation of the partners can occur. This facility for rotation opens up new routes for dissociation of INCs which would be impossible if the two components remained conventionally bound together. In the case of 2a, rotation is probably pre-empted by a 1,2-hydride shift. True INCs are represented in this paper by the separate partners enclosed in a common square bracket; the transient species such as 2a are not enclosed in brackets, but the elongated bond is depicted by a dashed line.

The sequence of steps visualised in Scheme 1 corresponds to a 1,2-elimination of C_3H_6 from 1 occurring with a very low
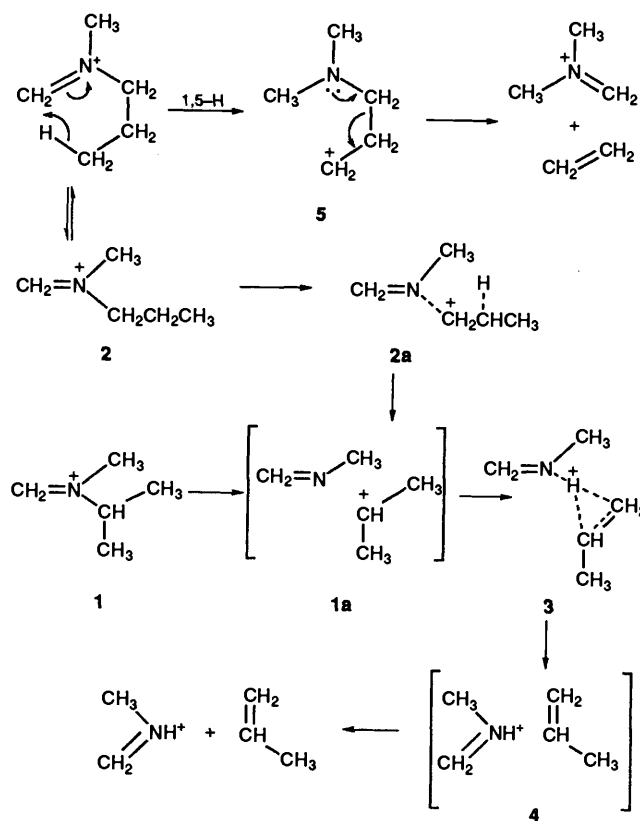
Scheme 1

degree of concert. The proton-bridged complex (PBC), 3, in which $CH_3N=CH_2$ and $CH_3CH=CH_2$ are attached to a common proton, is also shown in Scheme 1. However, since the PAs of the components of this PBC are very different, 3 is probably only an approximation to the transition state for the reorganisation of 1a to 4.

Specific β-H transfer often takes place in alkene losses that may be formulated via mechanisms involving INCs in which the initial carbocation is stable with respect to isomerisations by 1,2-H or 1,2-alkyl shifts. [11-13] In the present case, 1a contains a stable isopropyl cation. Furthermore, the H-transfer step is thermodynamically very favourable since, as noted above, $CH_2=NCH_3$ has a much greater proton affinity (880) than C_3H_6 (751 kJ mol^{-1}). [25,26] In these circumstances, H-transfer is unidirectional, [27] and a moderate KE release is observed. [28]

Reversible H-transfers are normal when the two neutral species in the pair of INCs corresponding to 1a and 4 have similar PAs. Interconversion of the INCs is then revealed by H-exchange and by the observation of an extremely small KE release accompanying the final dissociation step. [28] Such a situation is realised for the oxonium ions $CH_2=O^+CH(CH_3)_2$ and $CH_2=O^+CH_2CH_2CH_3$, both of which expel CH_2O with an extremely small KE release ($T_{\frac{1}{2}}$ ~ 0.2 kJ mol^{-1}). [21,24] This finding is consistent with interconversion of these oxonium ions via $CH_2=O\text{-}\text{-}\text{-}^+CH_2CH_2CH_3$ and [$CH_2=O$ $^+CH(CH_3)_2$]. ^{2}H-Labelling cannot reveal whether [$CH_2=O$ $^+CH(CH_3)_2$] also interconverts with [$CH_2=OH^+$ C_3H_6] prior to CH_2O loss because the initial $CH_2=O$ unit is always expelled and any exchange of protium and deuterium atoms within the propyl group remains undetected. However, the site selectivity shown in water elimination from metastable $CH_2=O^+C_3H_{7-n}D_n$ species is consistent with at least limited interconversion of $CH_2=O\text{-}\text{-}\text{-}^+CH_2CH_2CH_3$, [$CH_2=O$ $^+CH(CH_3)$] and [$CH_2=OH^+$ C_3H_6] prior to this reaction. [24] In particular, $CH_2=O$ $^+CH(CH_3)CD_3$ and $CH_2=O^+CH_2CH_2CD_3$ expel H_2O, HOD and D_2O in ratios (23:67:10) that are the same

Table 2 Propene losses from metastable $C_5H_nD_{12-n}N^+$ ions

Ion structure	C₃H₆		C₃H₅D		C₃H₄D₂		C₃H₃D₃		C₃H₂D₄		C₃HD₅		C₃D₆		Σ(C₃HₙD₆₋ₙ)[e]
	RA[a]	T‡[b]	RA[a]	T‡[b]	RA[a]	T‡[b]	RA[a]	T‡[b]	RA[a]	T‡[b]	RA[a]	T‡[b]	RA[a]	T‡[b]	RA[a]
$CH_2=N^+(CH_3)CH(CD_3)_2$											100	2.2[c]			100
$CH_2=N^+(CH_3)CH(CH_3)CD_3$					42	2.3[c]	58	2.3[c]							100
$CH_2=N^+(CH_3)CHDCH_2CH_3$	4.0	3.6[c]	21.3	3.3[c]											25.3
$CD_2=N^+(CH_3)CH_2CH_2CH_3$	25 (25)	3.1[c]	<0.5 (0)												25
$CH_2=N^+(CH_3)CD_2CH_2CH_3$			8.2 (5.8)	2.7[c]	15.3 (17.3)	3.0[c]									23.5
$CH_2=N^+(CH_3)CH_2CD_2CH_3$			4.0 (2.9)	4.2[c]	17.2 (18.3)	3.6[c]									21.2
$CH_2=N^+(CH_3)CH_2CH_2CD_3$			<0.5		12.2 (10.5)	3.1[c]	17.9 (19.5)	3.3[c]							30

[a–d] See footnotes to Table 1. Data in parentheses in the 'RA' column are taken from ref. 19 and normalised to the same Σ(C₃HₙD₆₋ₙ); information on the KE release accompanying dissociation is not available from these linked-scan experiments. [e] Total RA of all propene losses.

Table 3 Ethylene loses from metastable $C_5H_nD_{12-n}N^+$ ions

Ion structure	C₂H₄		C₂H₃D		C₂H₂D₂		C₂HD₃		ΣC₂HₙD₄₋ₙ[f]
	RA[a]	T‡[b]	RA[a]	T‡[b]	RA[a]	T‡[b]	RA[a]	T‡[b]	RA[a]
$CH_2=N^+(CH_3)CHDCH_2CH_3$	75	73[d]							75
$CD_2=N^+(CH_3)CH_2CH_2CH_3$	75	74[d]							75
$CH_2=N^+(CH_3)CD_2CH_2CH_3$	76	73[d]							76.5
$CH_2=N^+(CH_3)CH_2CD_2CH_3$					79	74[d]			79
$CH_2=N^+(CH_3)CH_2CH_2CD_3$					70	72			70

[a,b,d] See footnotes to Table 1. [f] Total RA of all ethylene losses.

within experimental error. This behaviour is intelligible given that both ions rearrange to a common INC {[CH₂=O +CH-(CH₃)CD₃]}, which undergoes extensive hydrogen exchange via further rearrangement to [CH₂=OH⁺ CH₂=CHCD₃], [CH₂=OD⁺ CD₂=CHCH₃], CH₂=O---⁺CH₂CH₂CD₃, CH₂=O---⁺CD₂CHDCH₃ and related species. Access to ²H-labelled analogues of CH₂=O---⁺CH₂CH₂CH₃ is necessary in order to explain the extensive exchange of protium and deuterium atoms within the original propyl groups of CH₂=O⁺-C₃H₇₋ₙDₙ species. In the case of **1**, any reversion of **4** and/or **3** to **1a** or **1** would not result in H/D exchange within the propyl group of CH₂=N⁺(CH₃)CH(CD₃)₂. Such exchange would be most easily envisaged as occurring via isomerisation of **1a** to **2a**, but this possibility is not realised for metastable immonium ions, as is shown by the disparate behaviour of **1** and **2**. Consequently, although interconversion of **1a** and **4** cannot be excluded on the basis of ²H-labelling experiments, the KE release for propene loss from **1** is sufficiently large to permit the conclusion to be drawn that the sequence of steps **1→3→4** is essentially ireversible. The unidirectional nature of the hydrogen transfer step in propene loss in the immonium ion series simplifies the task of interpreting the ²H-labelling data.
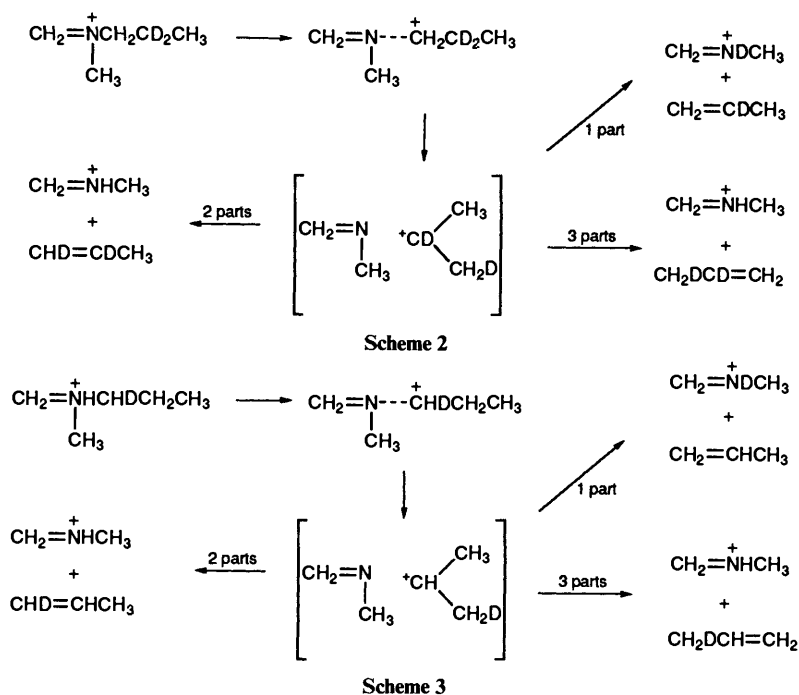
The fragmentation of CH₂=N⁺(CH₃)CH(CH₃)CD₃ is interesting. This ion eliminates C₃H₃D₃ (β-H transfer from the CH₃ group of the N-isopropyl substituent) and C₃H₄D₂ (β-D transfer from the corresponding CD₃ group) in the ratio 1.38 : 1. This appreciable, but not especially large, overall isotope effect on the hydrogen transfer step is good evidence that the rate-limiting step for propene loss from **1** involves fission of a C–H bond in a methyl group of the isopropyl substituent. This overall isotope effect arises from a combination of a primary

isotope effect (cleavage of a C–D instead of a C–H bond) and a secondary isotope effect (a CD₂ substituent rather than a CH₂ sp²-methylene group is being formed as the C–D or C–H bond is broken). These effects should reinforce one another.

Similar moderate overall isotope effects operate in propene loss from CH₃CH=N⁺(CH₃)CH(CH₃)CD₃ (C₃H₃D₃ and C₃H₄D₂ elimination in the ratio ~1.2:1)[29] and CH₂=N⁺-[CH(CH₃)₂]CH(CH₃)CD₃ (C₃H₃D₃ and C₃H₄D₂ expulsion in the ratio 1.57:1).[19] All these data point to a mechanism for propene loss in which the N–C bond is at least partially broken before rate-limiting C–H fission occurs. The conclusions derived from investigating ²H-labelled analogues of CH₂=N⁺-[CH(CH₃)₂]₂ are especially compelling. In this definitive work,[19] a full set of immonium ions with ²H-labels at some or all sites in one isopropyl substituent were studied. A mathematical treatment of the results allowed the influence of deuteriation at each site within an isopropyl group to be isolated and evaluated. In particular, the finding[19] that propene loss is not significantly suppressed by deuteriation at the methine position suggests that elongation of the C–N bond is not rate-limiting in this fragmentation.

No discernible isotope effect is found on the KE release for propene elimination from **1** and its ²H-labelled analogues. All the $T_{\ddagger}$ values lie in the range 2.2–2.3 kJ mol⁻¹, with an estimated uncertainty of ±0.1 kJ mol⁻¹. Since the rate-limiting step in this reaction involves cleavage of a C–H bond, an isotope effect on the KE release might have been expected, but any such effect must be of negligible importance.

Reactions of CH₂=N⁺(CH₃)CH₂CH₂CH₃.—*Propene loss.* This reaction is accompanied by a somewhat greater KE release

$$CH_2=\overset{+}{N}CH_2CD_2CH_3 \longrightarrow CH_2=\overset{+}{N}\text{---}CH_2CD_2CH_3$$
$$\underset{CH_3}{|} \qquad\qquad \underset{CH_3}{|}$$

$$CH_2=\overset{+}{N}DCH_3$$
$$+$$
$$CH_2=CDCH_3$$
1 part

$$CH_2=\overset{+}{N}HCH_3$$
$$+ \qquad \xleftarrow{\text{2 parts}} \qquad \left[CH_2=\overset{|}{\underset{CH_3}{N}} \quad ^+CD \diagup^{CH_3}_{\diagdown CH_2D} \right] \xrightarrow{\text{3 parts}}$$
$$CHD=CDCH_3$$

$$CH_2=\overset{+}{N}HCH_3$$
$$+$$
$$CH_2DCD=CH_2$$

Scheme 2

$$CH_2=\overset{+}{N}HCHDCH_2CH_3 \longrightarrow CH_2=\overset{+}{N}\text{---}CHDCH_2CH_3$$
$$\underset{CH_3}{|} \qquad\qquad \underset{CH_3}{|}$$

$$CH_2=\overset{+}{N}DCH_3$$
$$+$$
$$CH_2=CHCH_3$$
1 part

$$CH_2=\overset{+}{N}HCH_3$$
$$+ \qquad \xleftarrow{\text{2 parts}} \qquad \left[CH_2=\overset{|}{\underset{CH_3}{N}} \quad ^+CH \diagup^{CH_3}_{\diagdown CH_2D} \right] \xrightarrow{\text{3 parts}}$$
$$CHD=CHCH_3$$

$$CH_2=\overset{+}{N}HCH_3$$
$$+$$
$$CH_2DCH=CH_2$$

Scheme 3

($T_{\frac{1}{2}} = 3.0$ kJ mol^{-1}) than that associated with C_3H_6 loss from 1; however, both metastable peaks are Gaussian in shape. The increased KE release accompanying C_3H_6 expulsion from 2 suggests that this ion rearranges unidirectionally to 1 (or structures accessible to 1) before this dissociation takes place.[30,31]

The selectivity of hydrogen transfer (apparent α-, β- and γ-D transfer is observed in appropriately ^{2}H-labelled analogues of 2) contrasts sharply with the specific β-D transfer found for $CH_2=N^+(CH_3)CH(CD_3)_2$. The data reported in Table 2 are in good agreement with those of the independent study[19] in every case in which comparison is possible. Thus, C_3H_6 expulsion from 2 cannot be explained in terms of a 1,2-elimination. This finding, which appears to be general for immonium ions containing n-alkyl groups attached to nitrogen,[1] persists even for relatively fast reactions.[32]

A logical explanation for the distinct selectivities in hydrogen transfer accompanying C_3H_6 elimination from 1 and 2 is that unidirectional isomerisation of the N-n-propyl group to an N-isopropyl group takes place (2a→1a), Scheme 1. This unified mechanism allows hydrogens in both the α- and γ-positions to become part of a methyl group in the N-(isopropyl) substituent. Consequently, they are properly located to participate in the steps (1a→3→4→products) that result in hydrogen transfer to nitrogen.

The ratios of C_3H_5D and $C_3H_4D_2$ losses which occur from $CH_2=N^+(CH_3)CD_2CH_2CH_3$ and $CH_2=N^+(CH_3)CH_2CD_2$-CH_3 are 35:65 and 19:81, respectively. Similarly, $CH_2=N^+$-$(CH_3)CH_2CH_2CD_3$ expels $C_3H_4D_2$ and $C_3H_3D_3$ in the ratio 59:41. The ratios expected on the basis of the mechanistic model of Scheme 1 are 33:67, 17:83 and 50:50, respectively, assuming that there are no isotope effects on the H/D-transfer steps. The experimental ratios (25:75, 14:86 and 35:65, respectively) found in the independent study[19] of propene loss from ^{2}H-labelled analogues of 2 are in good agreement with those reported here.

The overall agreement between the observed and expected ratios is clear evidence in favour of the essence of the explanation suggested in Scheme 1. The fragmentation of $CH_2=N^+(CH_3)CH_2CD_2CH_3$ is especially revealing. This ion, which would eliminate only C_3H_5D if propene loss took place via a 1,2-elimination, actually expels predominantly $C_3H_4D_2$. Preferential loss of C_3H_5D is, however, sensibly interpreted

given that the $^+CH_2CD_2CH_3$ ion isomerises to CH_2DCD^+-CH_3, from which β-H-transfer to nitrogen should occur at approximately five times the rate of β-D-transfer. The behaviour of $CH_2=N^+(CH_3)CHDCH_2CH_3$, which was not studied in the independent work, supports this interpretation. Elimination of C_3H_5D (H-transfer) and C_3H_6(D-transfer) is found in the ratio 84:16; Scheme 1 predicts a ratio of 83:17. The similar ratios of H- and D-transfer that occur in propene expulsion from $CH_2=N^+(CH_3)CH_2CD_2CH_3$ and $CH_2=N^+(CH_3)$-$CHDCH_2CH_3$ reflect the consequences of the 1,2-H/D shift that accompanies isomerisation of the incipient ^{2}H-labelled n-propyl cations. The original N-n-propyl groups in each of these ions should rearrange to an N-isopropyl structure (CH_2-DCD^+CH_3 and $CH_2DCH^+CH_3$, respectively) containing a total of five protium and one deuterium atoms in the two methyl groups. Therefore, the ratio of protium transfer to deuterium transfer should be ~83:17 in both cases, Schemes 2 and 3.

The deviation of the experimental ratios from those expected from the simple mechanistic model has been interpreted[19] in terms of a small preference factor favouring transfer of a hydrogen atom originating from the α- or β-positions. In other words, the rate of hydrogen transfer from the methyl group that is created by the 1,2-shift slightly exceeds that for transfer from the existing methyl group containing the γ-carbon atom. This small preference factor (~1.13[19]) arises because of geometrical restraints on the transition state for hydrogen transfer. Figuratively speaking, the two methyl groups in the newly-formed isopropyl cation in the INC 2 are not equivalent. The one derived from the α-methylene group and a β-hydrogen atom in the developing n-propyl cation is initially nearer to the nitrogen atom. Therefore, the probability of hydrogen transfer to nitrogen from this methyl group is slightly enhanced relative to that for transfer from the more distant γ-methyl substituent. This situation corresponds to an 'entropic bottleneck'.[11,12] It may be considered to arise because rotation of the components within the INC is not sufficiently rapid to permit the orientation of the cation and neutral to reach a random distribution before hydrogen transfer takes place.

Such effects might be expected to decrease in importance as ions of longer lifetimes and lower average internal energies are sampled. Thus, the deviations from the expected ratios are
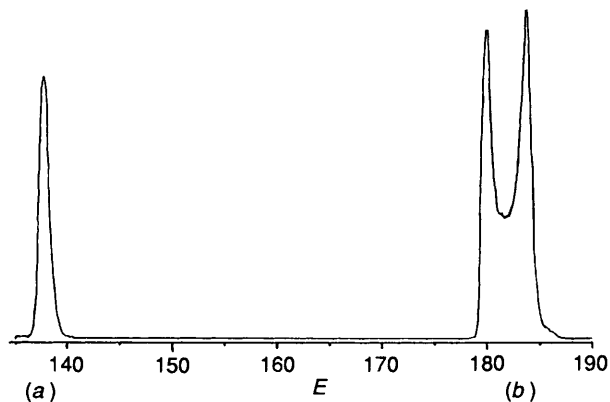
Fig. 1 Metastable peaks for loss of (a) C_3H_6; and (b) C_2H_4 from $CH_2=N^+(CH_3)CH_2CH_2CH_3$. The ordinate corresponds to the signal intensity (in arbitrary units), the abscissa corresponds to the voltage difference (E) between the plates of the electric sector; the voltage difference (E_0) required to transmit the parent ion was 270 V.

smaller in this work than in the research reported independently.[19] The metastable ions studied in this work were exceptionally long-lived on account of the extremely large dimensions of the 'MMM' instrument[33] with which the mass-analysed ion kinetic energy (MIKE) spectra[31] were recorded. In contrast, the independent study[19] mainly utilised linked scan (constant B/E[34]) techniques, which allow metastable ions of shorter lifetimes that dissociate in the first field-free region to be investigated. Alternatively, the slightly different deviations found in the two studies may arise from other causes, including random and systematic errors.

In view of the detailed interpretation of the nature and significance of isotope effects on propene elimination from ^2H-labelled analogues of 2 that has been presented elsewhere,[19] only a brief discussion of certain salient points is given here. First, isotope effects on the final hydrogen transfer step are small, especially when compared to the moderate isotope effect on the corresponding step in ^2H-labelled analogues of 1.[19] This trend is in accord with the mechanistic model. Starting from 1, cleavage of a β-C–H/D bond occurs in the rate-limiting step. In contrast, isomerisation of the species containing an incipient n-propyl cation to an INC comprising $CH_3N=CH_2$ and an isopropyl cation is rate determining in propene loss from ^2H-labelled analogues of 2. Consequently, any isotope effect on the subsequent H/D-transfer should be diminished, as is observed in both studies of propene loss. However, the 1,2-H/D shift converting the species containing a developing n-propyl cation into an INC which contains an isopropyl cation may be subject to an isotope effect. A marginal trend in this direction is discernible in the total amounts of propene and ethylene that are lost from labelled analogues of 2. Deuteriation at the β-position slightly suppresses the total relative abundance of propene elimination $[\Sigma RA(C_3H_{6-n}D_n)]$ compared to the sum of ethylene loss $[\Sigma RA(C_2H_{4-n}D_n)]$.

A small isotope effect may also be manifest on the KE releases for propene expulsion from analogues of 2. Significantly larger $T_{\frac{1}{2}}$ values are found for C_3H_5D and $C_3H_4D_2$ loss from $CH_2=N^+$-$(CH_3)CH_2CD_2CH_3$. This effect is particularly noticeable for C_3H_5D elimination, which requires both a 1,2-D shift and subsequent D-transfer. Loss of C_3H_5D from $CH_2=N^+(CH_2$-$CH_2CH_3)CH_2CD_2CH_3$ also proceeds with an enhanced KE release. A possible explanation is that the necessity for a 1,2-D shift in the rate-limiting step sufficiently elevates this transition state energy to increase the excess energy in the isomerised $[CH_2=NR\ CH_2DCD^+CH_3]$ species, thus raising the associated $T_{\frac{1}{2}}$ value.

Ethylene loss. In contrast to C_3H_6 elimination, C_2H_4 loss involves specific γ-hydrogen transfer. Thus, $CH_2=N^+(CH_3)$-

$CH_2CH_2CD_3$ loses only $C_2H_2D_2$ in ethylene elimination. Similarly, butene loss from ^2H-labelled analogues of $CH_2=N^+$-$(CH_3)CH_2CH_2CH_2CH_2CH_3$ proceeds with γ-hydrogen transfer, as is best emphasised by the elimination of solely C_4H_7D from $CH_2=N^+(CH_3)CH_2CH_2CD_2CH_2CH_3$.[29] This process is formally isoelectronic with the retro 'ene' reaction.[35] Another obvious difference between C_3H_6 and C_2H_4 eliminations is the very large KE release $(T_{\frac{1}{2}} \sim 73\ kJ\ mol^{-1})$ for C_2H_4 loss. The metastable peak for C_2H_4 expulsion is dish-topped and extremely broad. This contrast between the shape and the widths of the peaks for C_2H_4 and C_3H_6 losses, which is illustrated in Fig. 1, points to fundamental differences in the mechanisms for the two classes of alkene eliminations.

The large KE release for C_2H_4 loss is intelligible if transfer of the γ-hydrogen atom and cleavage of the C_α–C_β bond are not synchronously concerted. Dissociation of a high-energy transition state, resembling the open-chain carbonium ion, 5, provides a rationalisation for the origin of the KE release.[1,8] Moreover, the variation of the $T_{\frac{1}{2}}$ values with the level of substitution on the γ-carbon atom in higher homologues of 2 is also explained.[8,9] Studies on the homologous series of metastable immonium ions $CH_2=N^+(CH_3)R$ (R = n-C_nH_{2n+1}; $n = 3, 4, 5, 6, 8, 10, 14$ and 18)[36] reveal that the specificity of γ-H transfer in this reaction is general. In addition to the reduction in the $T_{\frac{1}{2}}$ value induced by homologation on the γ-carbon atom, a gradual diminution in the KE release accompanying alkene elimination via this channel was found. These data were interpreted in terms of a two-step mechanism; the decline in the $T_{\frac{1}{2}}$ values for larger immonium ions was attributed to a degrees-of-freedom effect.[36]

A small, but significant, isotope effect is discernible on the ratio of $\Sigma RA(C_2H_{4-n}D_n)$ to $\Sigma RA(C_3H_{6-n}D_n)$ elimination from ^2H-labelled variants of 2. There is a slight reduction in $\Sigma RA(C_2H_{4-n}D_n):\Sigma RA(C_3H_{6-n}D_n)$ from 3.2:1 for 2 to 2.3:1 for $CH_2=N^+(CH_3)CH_2CH_2CD_3$, for which ethylene elimination requires rupture of a C–D bond. The ratios for analogues of 2 labelled in other positions lie in the range 3.0 to 3.7:1. This trend in $\Sigma RA(C_2H_{4-n}D_n):\Sigma RA(C_3H_{6-n}D_n)$ is further evidence that cleavage of a C–H bond of the γ-methyl group occurs in the rate-limiting step for ethylene loss. However, the trend is not sufficiently pronounced to permit a distinction to be made between a mechanism in which complete C–H fission precedes rupture of the C–C bond and one involving partial cleavage of both bonds in the transition state.

The $T_{\frac{1}{2}}$ values for $C_2H_nD_{4-n}$ elimination from ^2H-labelled analogues of 2 are not significantly different from that for C_2H_4 loss from 2. All the data lie in the range 72–74 kJ mol^{-1}, with an estimated uncertainty of $\pm 2\ kJ\ mol^{-1}$. The absence of a sizeable isotope effect on the $T_{\frac{1}{2}}$ values for ethylene expulsion fits naturally into a mechanistic interpretation in which the C–H/D bond is predominantly or completely broken before C–C cleavage begins. If the transition state for ethylene loss involved fission of the C–H and C–C bonds in concert, an isotope effect on the $T_{\frac{1}{2}}$ values (and perhaps even the shape of the associated metastable peak) for $C_2H_2D_2$ elimination from $CH_2=N^+$-$(CH_3)CH_2CH_2CD_3$ might have been expected. This argument, which is based on the absence of sizeable isotope effects, is hardly compelling, however.

In the case of butene loss from ^2H-labelled variants of the higher homologue, $CH_2=N^+(CH_3)CH_2CH_2CH_2CH_2CH_3$,[29] a small isotope effect on the KE release may be apparent. Most of the $T_{\frac{1}{2}}$ values lie in the range 29–31 kJ mol^{-1}, but that (35 kJ mol^{-1}) for C_4H_7D expulsion from $CH_2=N^+(CH_3)CH_2CH_2$-$CD_2CH_2CH_3$ via specific γ-D transfer is possibly significantly greater. This increase (5 $\pm$ 1 kJ mol^{-1}) is barely more than the estimated uncertainty (± 3 kJ mol^{-1}) of the data. Consequently, it is best to conclude that the effect of isotopic substitution on the $T_{\frac{1}{2}}$ values does not permit a confident decision to be made on the

Table 4 Reactions of a metastable $C_7H_{16}N^+$ ion

| | Neutral species lost | | | |
| | C_2H_4 | | C_3H_6 | |
Ion structure	RA[a]	$T_\frac{1}{2}{}^b$	RA[a]	$T_\frac{1}{2}{}^b$
$CH_2=N^+(CH_2CH_2CH_3)_2$ $\left\{\begin{array}{l} \\ \\ \end{array}\right.$	74[g] 69[h]	71[d,g] 70[d,h]	26[g] 31[h]	3.3[c,g] 4.0[c,h]

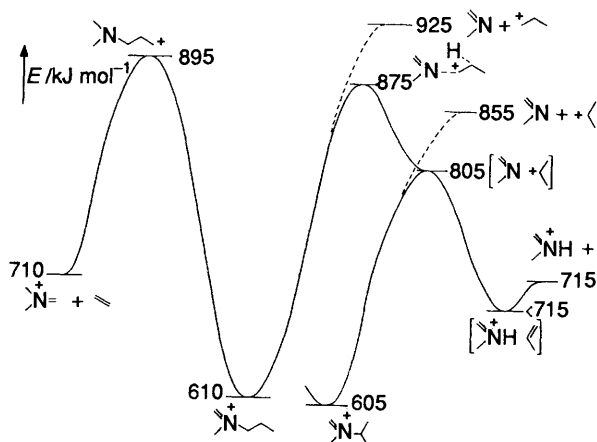[a-d] See footnotes to Table 1. [g] This work. [h] Data from ref. 9.

Fig. 2 Potential energy profile for isomerisation and fragmentation of $CH_2:N^+(CH_3)_2$ and $CH_2=N^+(CH_3)CH_2CH_2CH_3$

nature of the transition state for alkene loss via this general route.

Finally, the chemistry of **1** and **2** is summarised by the potential energy profile[37] (PEP) of Fig. 2. This PEP is constructed from known[25,26,38-42] or estimated[43-47] thermochemical data.

Reactions of $CH_2=N^+(CH_2CH_2CH_3)_2$.—The reactions of $CH_2=N^+(CH_2CH_2CH_3)_2$, **6**, are summarised in Table 4. The new data obtained in this work for dissociation of **6** are in remarkably good agreement with those obtained previously[9] with another mass spectrometer of very different dimensions and geometry. Relevant ^2H-labelling results are shown in Table 5.

As expected, **6** resembles **2** in that it loses both C_2H_4 [dish-topped metastable peak, large KE release ($T_\frac{1}{2} \sim 71$ kJ mol^{-1})] and C_3H_6 [Gaussian peak, moderate KE release ($T_\frac{1}{2} = 3.3$ kJ mol^{-1})]. These processes are explicable by means of mechanisms analogous to those depicted in Scheme 1 for dissociation of **2**. The following additional points deserve mention.

Propene loss. In view of the extensive ^2H-labelling data on this fragmentation that have already been reported and discussed,[19] only the most salient points need be emphasised. The results found in this work are in excellent agreement with those previously reported.[19] Elimination of propene can occur from either propyl group; thus, C_3H_6 loss from the unlabelled n-propyl substituent competes with $C_3H_nD_{6-n}$ expulsion from the labelled side chain. The ratio of the abundances of propenes eliminated from the two propyl group is significant. For example, expulsion of C_3H_6 from the C_3H_7 group and $C_3H_4D_2$ plus $C_3H_3D_3$ from the $C_3H_4D_3$ group of $CH_2=N^+(CH_2-CH_2CH_3)CH_2CH_2CD_3$ take place in a ratio (1.07 from the MIKES data or 1.09 from the independent study[19]) close to unity. This result suggests that isotope effects on the final H/D-transfer step exert at most only a very minor influence on the gross abundance of propenes lost from unlabelled and labelled propyl substituents. This very small overall isotope effect [1.02–1.03 (*i.e.* $\sqrt[3]{1.07} - \sqrt[3]{1.09}$) per γ-deuterium atom] is below the

upper limit that might be anticipated from secondary effects on stretching or cleavage of the C–N bond in ^2H-labelled analogues of **6**. Thus, α-cleavage of $CH_3CH_2CH_2CH_2CH_2-N(CH_3)CH_2CH_2CH_2CD_2CH_3{}^{\cdot+}$ is subject to a secondary isotope effect of 1.03_7 for dissociations taking place in the second field-free region of the MMM instrument.[17] Although α-cleavage of ionised tertiary amines is not completely analogous to the process leading from **6** to $CH_2=N(CH_2CH_2CH_3)--- {}^+CH_2CH_2CH_3$ (a C–C bond, as opposed to a C–N bond is being broken), the deuterium labels are located on a carbon atom that is separated by two CH_2 residues from the site of bond fission. Consequently, the observed isotope effect is consistent with a mechanism for propene loss in which the C–N bond is at least partially broken in the transition state.

A greater overall isotope effect (1.46:1 from the MIKES data or 1.43:1 from the independent study[19]) favouring elimination of C_3H_6 over loss of $C_3H_5D/C_3H_4D_2$ is found for dissociation of $CH_2=N^+(CH_2CH_2CH_3)CH_2CD_2CH_3$. The magnitude of this effect would be 1.20 ± 0.01 (*i.e.* $\sqrt{1.43} - \sqrt{1.46}$) per deuterium atom, if it arose solely from a secondary isotope effect on the C–N cleavage step. This value seems implausibly large: the corresponding secondary isotope effects on α-cleavage of $CH_3CH_2CH_2N(CH_3)CH_2CH_2CD_3{}^{\cdot+}$ and similar ionised ^2H-labelled tertiary amines are typically 1.09 to 1.14 per deuterium atom. Therefore, it is likely that the overall isotope effect contains a contribution from isotope effects on the 1,2-D shift which converts the developing $^+CH_2CD_2CH_3$ into $CH_2D-CD^+CH_3$. This effect will consist of at least two components (a primary effect discriminating against fission of the C–D bond and a secondary effect arising because the carbon atom of the C–D bond that remains at the migration origin changes its formal hybridisation from sp^3 to sp^2).

Only a very small overall isotope effect (1.05:1, *i.e.* 1.02 per deuterium atom) has been reported[19] for propene loss from $CH_2N^+(CH_2CH_2CH_3)CD_2CH_2CH_3$. Secondary isotope effects for alkyl radical elimination from ionised tertiary amines labelled at the β-position are typically 1.30–1.32 per deuterium atom.[17] These data suggest that the discrimination against expelling propene from a propyl group deuteriated in the α-position is much less than the maximum that could be envisaged if the C–N bond were completely broken in the transition state.

A logical interpretation of these overall isotope effects is that the transition state for propene loss involves partial fission of the C–N bond and one C–H bond in the β-methylene residue of that propyl substituent. The latter effect is probably more pronounced. This view was reached in the independent study,[19] which concluded that the distribution-determining step is subject to primary and secondary isotope effects of 2.28 and 0.86, respectively, with a preference factor of 1.34 favouring hydrogen transfer from the methyl group in [$CH_2=NCH_2CH_2CH_3$ $CH_3CH^+CH_3$] that is derived from the α-methylene group of **6**. The corresponding isotope effects in the case of **2** were found to be smaller (1.50–1.59 and 1.00, respectively), with a reduced preference factor (1.13) favouring hydrogen transfer from the methyl group of

Table 5 Reactions of metastable $C_7H_nD_{16-n}N^+$ ions

	Neutral species lost															
	C_2H_4		C_2H_3D		$C_2H_2D_2$		$\Sigma(C_2H_nD_{4-n})^f$	C_3H_6		C_3H_5D		$C_3H_4D_2$		$C_3H_3D_3$		$\Sigma(C_3H_nD_{4-n})^e$
Ion Structure	RA^a	$T_{\frac{1}{2}}^b$	RA^a	$T_{\frac{1}{2}}^b$	RA^a	$T_{\frac{1}{2}}^b$	RA^a	RA^a	$T_{\frac{1}{2}}^b$	RA^a	$T_{\frac{1}{2}}^b$	RA^a	$T_{\frac{1}{2}}^b$	RA^a	$T_{\frac{1}{2}}^b$	RA^a
$CH_2=N^+(CH_2CH_2CH_3)CD_2CH_2CH_3$	41^i	$74^{d,j}$	k		36^i	$73^{d,j}$	77	(12.8)		(3.6)		(8.6)				(25)
$CH_2=N^+(CH_2CH_2CH_3)CH_2CD_2CH_3$								13.9	3.4^c	1.7	3.8^c	7.8	3.4^c			23
								(13.5)		(1.2)		(8.2)				
$CH_2=N^+(CH_2CH_2CH_3)CH_2CH_2CD_3$	41^i	$73^{d,j}$	k		29^i	$69^{d,j}$	70	15.6	3.3^c	< 0.1		5.4	3.3^c	9.3	3.3^c	30
								(15.6)				(4.5)		(9.8)		

$^{a-d}$ See footnotes to Tables 1 and 2. ^{e,f} See footnotes to Tables 2 and 3. ^{i} Overlapping peaks. ^{j} $T_{\frac{1}{2}}$ estimated from half-width at half-height of non-overlapping parts of overlapping peaks. ^{k} Not detected; but this peak could theoretically have been obscured by the more intense signals for C_2H_4 and $C_2H_2D_2$ losses.

[CH$_2$=NCH$_3$CH$_3$CH$^+$CH$_3$] formed from the α-methylene residue. These variations were explained[19] in terms of differences in the vibrational excitation per degree of freedom of the immonium ions. As R in CH$_2$=N$^+$(R)CH$_2$CH$_2$CH$_3$ increases in size, the excitation per degree of freedom decreases, so enhancing the influence of isotope effects. Similarly, a larger R group results in greater steric effects which interfere with free rotation of the CH$_2$=NR and CH$_2$CH$^+$CH$_3$ components of the INC in which hydrogen transfer occurs, thus enlarging the preference factor.

The deviation of the MIKES data for propene loss from ^{2}H-labelled analogues of **6** (and **2**) from the behaviour expected on the basis of Scheme 1 are less than those found in the definitive study.[19] However, the same trend (greater deviation for R = C$_3$H$_7$ than R = CH$_3$) is found in both investigations of CH$_2$=N$^+$(R)CH$_2$CH$_2$CD$_3$. These data suggest strongly that the preference factor diminishes at longer lifetimes and lower average internal energies. It is probable that the isotope effects become more pronounced at the longer lifetimes appropriate to the MIKES data, but this cannot be deduced with certainty.

The conclusion[19] that the distribution-determining step in propene expulsion from CH$_2$=N$^+$(R)CH$_2$CH$_2$CH$_3$ (R =CH$_3$CH$_2$ or CH$_3$CH$_2$CH$_2$) is subject to an inverse secondary isotope effect is potentially very important. If such effects could be shown to occur in similar reactions that are INC-mediated, this correlation would provide a most useful means of establishing the intermediacy of INCs in ionic fragmentations. The only drawback would be the practical difficulty entailed in obtaining the complete range of ^{2}H-labelling data which is needed to permit the mathematical deconvolution procedure[19] to be performed.

Ethylene loss. Expulsion of ethylene from each of the propyl substituents can be distinguished by examining suitably ^{2}H-labelled analogues of **6**. As was found for ^{2}H-labelled analogues of **2**, this fragmentation involves specific γ-hydrogen trans-fer.[17,19] Thus, CH$_2$=N$^+$(CH$_2$CH$_2$CH$_3$)CH$_2$CH$_2$CD$_3$ loses C$_2$H$_4$ (from the C$_3$H$_7$ group) and C$_2$H$_2$D$_2$ (from the C$_3$H$_4$D$_3$ group) in the ratio 58:42. This isotope effect (1.41:1) is rather too large to be attributed solely to secondary effects arising from elongation of the C$_α$–C$_β$ bond. Even when the corresponding bond is fully broken in α-cleavage of CH$_3$CH$_2$CH$_2$N-(CH$_3$)CH$_2$CH$_2$CD$_3$$^{•+}$, the secondary isotope effect is only 1.10$_6$ per deuterium atom (*i.e.* 1.35:1 overall). Consequently, at least part of the overall effect must arise from discrimination against fission of a C–D bond in the terminal methyl group of the labelled propyl substituent. This discrimination probably consists of a combination of primary and secondary isotope effects: the former arises because a C–D, rather than a C–H bond is being broken; the latter reflects the changes in the bonding at CD$_2$ sp^2 methylene group that is forming as the C–D bond breaks.

The appreciably smaller isotope effect (overall 1.14:1 or 1.07 per deuterium atom) favouring C$_2$H$_4$ over C$_2$H$_2$D$_2$ elimination from CH$_2$=N$^+$(CH$_2$CH$_2$CH$_3$)CH$_2$CD$_2$CH$_3$ suggests that fission of the CH$_2$–CD$_2$ bond is far from complete in the transition state for C$_2$H$_2$D$_2$ loss. Secondary isotope effects induced by deuteriation at the β-position on α-cleavage of ionised tertiary amines are typically 1.30–1.32 per deuterium atom[17] (*i.e.* 1.69–1.72:1 overall). It is conceivable that the isotope effect arises from limited extension of the C$_α$–C$_β$ bond. Alternatively the marginal deviation of the isotope effect from unity could be attributed to different hyperconjugative inter-actions of the C$_β$-H and C$_β$-D bonds with the cationic site that develops on the adjacent γ-carbon atom. In either event, the isotope effects are consistent with an interpretation of ethylene elimination in which the C$_γ$-H/D bond is extensively or completely broken before C$_α$–C$_β$ bond cleavage becomes pronounced.

As is the case with **2**, isotope effects have no appreciable influence on the $T_{\frac{1}{2}}$ value for ethylene expulsion. There is a slight diminution in the total relative abundance of ethylene (C$_2$H$_4$ and C$_2$H$_2$D$_2$) lost from CH$_2$=N$^+$(CH$_2$CH$_2$CH$_3$)CH$_2$CH$_2$CD$_3$ compared to the quantity of C$_2$H$_4$ eliminated from **6**. This is further evidence that a significant, but not especially large, isotope effect discriminates against cleavage of the C$_γ$-H/D bond in ethylene loss.

Comparison of the Mechanisms Describing Propene and Ethylene Losses from N-(*n-Propyl*) *Groups.*—It is clear from the KE release and ^{2}H-labelling data that expulsion of propene and ethylene from an n-propyl substituent proceed *via* contrasting mechanisms. The differences between propene and ethylene losses probably reflect changes in the timing of the H-transfer and C–N or C–C bond cleavage steps.

Propene elimination involves H-transfer to nitrogen in a species in which the C-N bond has been sufficiently stretched to allow the developing cation to isomerise. The transition state corresponds to a species in which the C–N bond is partly broken and a rate-limiting 1,2-H shift in the incipient cation is beginning. The final H-transfer to nitrogen is delayed until after the cation has rearranged, thus creating a situation in which the transferred hydrogen atom appears to originate from the α- and γ-, as well as the expected β-positions of the initial n-propyl substituent. This dissociation takes places with a relatively small KE release.

On the other hand, ethylene expulsion requires specific γ-H transfer through an almost unstrained six-membered ring. This step leads to a transition state in which C–H fission is essentially complete before C$_α$–C$_β$ cleavage is well advanced. There is little or no opportunity for subsequent isomerisation processes to erode the specificity introduced by the original γ-H transfer. A large KE release accompanies this fragmentation.
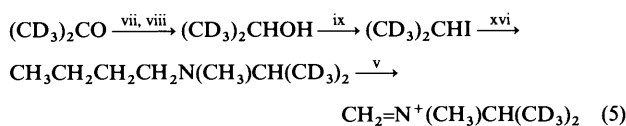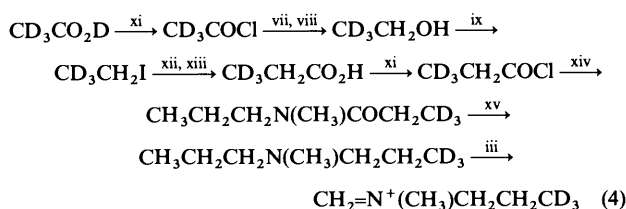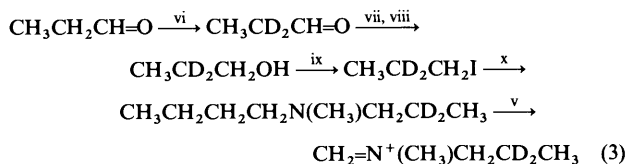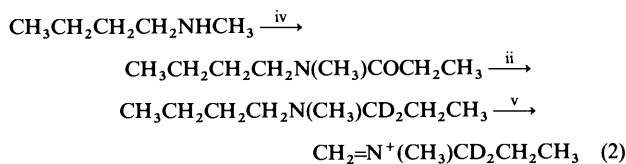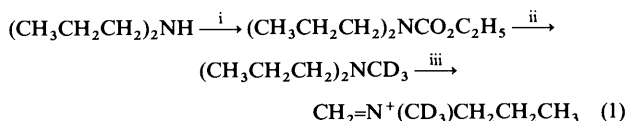
Conclusion

The ^{2}H-labelling results presented in this paper are strong evidence that C$_3$H$_6$ loss from NC$_3$H$_7$ substituents involves INCs. The rate-limiting step in propene elimination from CH$_2$=N$^+$(R)CH$_2$CH$_2$CH$_3$ ions is formation of a species, CH$_2$N(R)---$^+$CH$_2$CH$_2$CH$_3$, containing an elongated N–C bond and in which a 1,2-H shift in the developing n-propyl cation has begun to occur. Subsequent hydrogen transfer to nitrogen takes place relatively rapidly from either methyl group of the CH$_3$CH$^+$CH$_3$ cation in [CH$_2$=NR CH$_3$CH$^+$CH$_3$]. The overall result is that the hydrogen transferred to nitrogen appears to originate from the α-, β- and γ-carbon atoms of the n-propyl substituent in the ratio 33:17:50 to a first approxim-ation. In contrast, propene loss from CH$_2$=N$^+$ (CH$_3$)CH(CH$_3$)$_3$ ions involves specific β-hydrogen transfer in which an isotope effects favours H- over D-transfer. This contrast arises because no rate-limiting isomerisation of the incipient C$_3$H$_7$$^+$ cation precedes hydrogen transfer. Both the experimental results and the interpretation of these data are in excellent agree-ment with those reported in an independent[19] study and with earlier research[8-10,17] on related immonium ions.

Ethylene expulsion from CH$_2$=N$^+$(R)CH$_2$CH$_2$CH$_3$ ions is best interpreted by an altogether different mechanism, in which specific γ-hydrogen transfer to form CH$_3$N(R)CH$_2$CH$_2$CH$_2$$^+$ is essentially complete before C–C cleavage occurs to give CH$_3$N$^+$(R)=CH$_2$ and CH$_2$=CH$_2$. This view is also in accord with earlier work.[8-10,17]

Experimental

The immonium ions of interest were generated by dissociative ionisation of the appropriate tertiary amines. Synthesis of these

amines was achieved by conventional methods; illustrative examples are shown in Scheme 4, and further particulars are

$$(CH_3CH_2CH_2)_2NH \xrightarrow{i} (CH_3CH_2CH_2)_2NCO_2C_2H_5 \xrightarrow{ii}$$

$$(CH_3CH_2CH_2)_2NCD_3 \xrightarrow{iii}$$

$$CH_2=N^+(CD_3)CH_2CH_2CH_3 \quad (1)$$

$$CH_3CH_2CH_2CH_2NHCH_3 \xrightarrow{iv}$$

$$CH_3CH_2CH_2CH_2N(CH_3)COCH_2CH_3 \xrightarrow{ii}$$

$$CH_3CH_2CH_2CH_2N(CH_3)CD_2CH_2CH_3 \xrightarrow{v}$$

$$CH_2=N^+(CH_3)CD_2CH_2CH_3 \quad (2)$$

$$CH_3CH_2CH=O \xrightarrow{vi} CH_3CD_2CH=O \xrightarrow{vii, viii}$$

$$CH_3CD_2CH_2OH \xrightarrow{ix} CH_3CD_2CH_2I \xrightarrow{x}$$

$$CH_3CH_2CH_2CH_2N(CH_3)CH_2CD_2CH_3 \xrightarrow{v}$$

$$CH_2=N^+(CH_3)CH_2CD_2CH_3 \quad (3)$$

$$CD_3CO_2D \xrightarrow{xi} CD_3COCl \xrightarrow{vii, viii} CD_3CH_2OH \xrightarrow{ix}$$

$$CD_3CH_2I \xrightarrow{xii, xiii} CD_3CH_2CO_2H \xrightarrow{xi} CD_3CH_2COCl \xrightarrow{xiv}$$

$$CH_3CH_2CH_2N(CH_3)COCH_2CD_3 \xrightarrow{xv}$$

$$CH_3CH_2CH_2N(CH_3)CH_2CH_2CD_3 \xrightarrow{iii}$$

$$CH_2=N^+(CH_3)CH_2CH_2CD_3 \quad (4)$$

$$(CD_3)_2CO \xrightarrow{vii, viii} (CD_3)_2CHOH \xrightarrow{ix} (CD_3)_2CHI \xrightarrow{xvi}$$

$$CH_3CH_2CH_2CH_2N(CH_3)CH(CD_3)_2 \xrightarrow{v}$$

$$CH_2=N^+(CH_3)CH(CD_3)_2 \quad (5)$$

Scheme 4 *Reagents and conditions:* (i), CH_3CH_2OCOCl (0.9 mol), pyridine, CH_2Cl_2, $-30\,°C$; (ii), $LiAlD_4$, triglyme [triethylene glycol dimethyl ether, $CH_3O(CH_2CH_2O)_3CH_3$], $60\,°C$; (iii), $-e$, $-C_2H_5$; (iv), CH_3CH_2COCl (0.9 mol), pyridine, CH_2Cl_2, $-30\,°C$; (v), $-e$, $-C_3H_7$; (vi), D_2O, pyridine, reflux 48 h; repeat twice; (vii), $LiAlH_4$, triglyme, 20–40 °C; (viii), tetraethylene glycol [$HO(CH_2CH_2O)_4H$]; (ix), red P, I_2; (x), $CH_3CH_2CH_2CH_2NHCH_3$, (8 mol), 7 days; (xi), $(PhCO)_2O$, distil.; (xii), Mg, $(C_2H_5)_2O$; (xiii), solid CO_2; (xiv), $CH_3CH_2CH_2NHCH_3$ (1.5 mol), pyridine, CH_2Cl_2, $-30\,°C$; (xv) $LiAlH_4$, triglyme, $60\,°C$; (xvi), $CH_3CH_2CH_2CH_2NHCH_3$ (5 mol), 8 weeks

available on request. The level of deuterium incorporation in the ^2H-labelled species generally exceeded 97%, which was amply sufficient given that the ions of interest were specifically selected by transmission through the magnetic sector before their dissociations in the second field-free region were examined.

The mass spectra were recorded on a double-focussing research mass spectrometer of unusually large dimensions ('MMM'),[33] equipped with a post acceleration detector operating at 20 kV. Typical conditions were: source pressure, $1–2 \times 10^{-6}$ Torr;* ionising electron energy, 70 eV; accelerating voltage 8065–8068 V. Product ions formed from dissociation of metastable ions in the second field-free region were transmitted and detected by the MIKES[31] technique. MIKES spectra were measured by repetitive microcomputer-controlled scanning of the electric sector voltage over the range of voltage required to transmit the product ions. The data reported in Tables 1–5 correspond to integrated spectra obtained from 100–300 individual scans. Kinetic energy release data were estimated

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* 1 Torr $\approx$ 133 Pa.

from the width at half height of the requisite metastable peak, by means of a one-line formula,[31,48] after applying the usual correction for the width at half height of the main beam.[49] The electric sector voltage required to transmit the main beam of parent ions was 270 V.

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