Unimolecular Reactions of Isolated Organic Ions: Olefin Elimination from Immonium Ions $R^1R^2\overset{+}{N}{=}CH_2$

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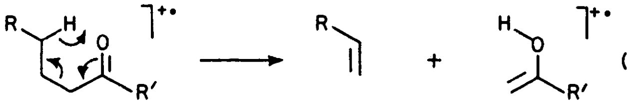
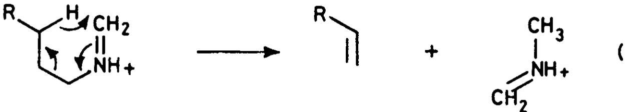
The slow unimolecular reactions of numerous tertiary immonium ions of general formula $R^1R^2\overset{+}{N}{=}CH_2$ are reported and discussed. Two distinct processes involving olefin loss are observed; the first reaction results in elimination of an olefin having the same number of carbon atoms as R^1 (or R^2), whilst the second proceeds with expulsion of a smaller olefin, having one less carbon atom than R^1 (or R^2). Evidence is presented to show that the latter reaction proceeds *via* transfer of a γ-hydrogen atom from R^1 or R^2 to the isolated CH_2 group, followed by σ-cleavage in the resulting open-chain carbonium ion. Whenever this process involves a secondary or tertiary cation, it dominates over the alternative route, for energetic reasons. However, when γ-hydrogen transfer produces a primary cation, both classes of olefin elimination occur in comparable abundance. Loss of olefins from R^1 and/or R^2, in competition, is likewise controlled by the nature of the intermediate cation.

REACTIONS involving six-membered ring transition states are of great importance in mechanistic organic chemistry. Such processes are involved in the unimolecular reactions of isolated organic ions; for example, the ubiquitous McLafferty rearrangement is a common decomposition route for ionised carbonyl compounds possessing a γ-hydrogen atom [equation (1)].[1] An interesting question arises concerning the degree of concert of the hydrogen transfer and olefin elimination in these processes. It is now well established that the hydrogen transfer occurs as a distinct step,[2,3] followed by alkene expulsion, at least at low internal energies. In some cases, the hydrogen transfer is reversible, as revealed by labelling studies.[3,4]



(1)

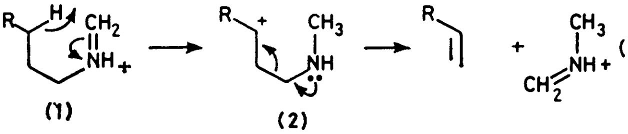
An analogous dissociation route has been reported for several $C_4H_{10}N^+$ and $C_5H_{12}N^+$ ions [equation (2)].[5]



(2)

(1)

Evidence was presented which shows that this reaction also proceeds with a low degree of concert at low internal energies. Instead, an interpretation of olefin loss by a two-step mechanism, *via* an open-chain carbonium ion (2) is more accurate [equation (3)]. This paper describes further work on $C_nH_{2n+2}N^+$ immonium ions, designed to investigate this reaction in more detail.



(3)

(1) (2)

RESULTS AND DISCUSSION

Although alkene loss from $C_nH_{2n+2}N^+$ immonium ions is an extremely common process, it has received relatively little attention. The Table shows the slow unimolecular reactions of several ions of general formula $R^1R^2\overset{+}{N}{=}CH_2$ (R^1 or R^2 = alkyl).

In addition to the dissociation *via* equation (3), a second major pathway for olefin elimination is observed (Scheme 1). Stretching of the appropriate C–N σ-bond gives rise to a complex (3a), in which an incipient carbonium ion is co-ordinated to an imine. A slight rearrangement in (3a) leads to (4), which comprises an imine and an olefin bound to a common proton. Dissociation of (4) takes place, with the neutral component having the greater proton affinity retaining the proton; in this case, imines have generally higher proton affinities than olefins; consequently, a smaller immonium ion ($R^1\overset{+}{N}H{=}CH_2$) is formed, with expulsion of the olefin.

Of the ions studied, three eliminate alkenes *via* this mechanism: (5) loses C_3H_6, (6) loses C_3H_6, and (8) loses C_4H_8. This reaction involves the loss of an entire alkyl side chain, with asociated hydrogen transfer to nitrogen; it is characterised by a relatively narrow metastable peak, corresponding to a relatively small kinetic energy release ($T_{\frac{1}{2}}$ 3—6 kJ mol^{-1}). The inability of this process to compete with the alternative decomposition route [equation (3)] for the other ions is significant and is discussed subsequently.

Expulsion of an olefin *via* equation (3) takes place from every ion investigated; this process is evidenced by a much broader metastable peak than is observed for the reaction shown in Scheme 1. The kinetic energy released lies within one of three ranges: C_4H_8 loss from (9), (11), and (12) releases 22—25 kJ mol^{-1} of kinetic energy; C_3H_6 loss from (7) and (10) releases 46—48 kJ mol^{-1}; and C_2H_4 loss from (5), (6), and (8), and C_3H_6 loss from (8) releases 66—75 kJ mol^{-1}. Furthermore, the metastable peaks for these reactions are clearly flat-topped or dish-topped in cases in the last two categories and very broad in the first. This is evidence that these reactions are qualitatively different from

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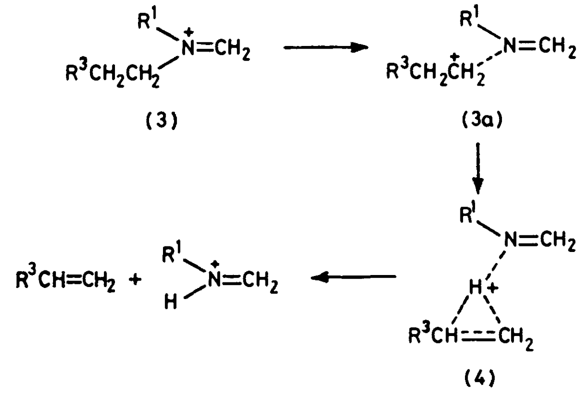
those in which the kinetic energy release is much smaller and narrow metastable peaks are observed. Representative peaks are depicted in the Figure.

Slow unimolecular reactions of isolated $R^1R^2\overset{+}{N}=CH_2$ ions

Ion	Reaction	Relative abundance [a]	Kinetic energy release [b]
$\begin{matrix}CH_3CH_2CH_2\\CH_3CH_2\end{matrix}>\overset{+}{N}=CH_2$ (5)	C_2H_4 loss C_3H_6 loss	49 ± 1 51 ± 1	74.5 ± 2.5 5.3 ± 0.3
$(CH_3CH_2CH_2)_2\overset{+}{N}=CH_2$ (6)	C_2H_4 loss C_3H_6 loss	69 ± 4 31 ± 2	70 ± 2 4.0 ± 0.5
$\begin{matrix}CH_3CH_2CH_2CH_2\\CH_3CH_2CH_2\end{matrix}>\overset{+}{N}=CH_2$ (7)	C_3H_6 loss	100	48 ± 1.5
$\begin{matrix}(CH_3)_2CHCH_2\\CH_3CH_2CH_2\end{matrix}>\overset{+}{N}=CH_2$ (8)	C_2H_4 loss C_3H_6 loss C_4H_8 loss	13 ± 1 29 ± 1 58 ± 2	71.5 ± 2 66.5 ± 2.5 3.4 ± 0.2
$\begin{matrix}(CH_3)_2CHCH_2CH_2\\CH_3CH_2CH_2\end{matrix}>\overset{+}{N}=CH_2$ (9)	C_4H_8 loss	100	23 ± 1.5
$(CH_3CH_2CH_2CH_2)_2\overset{+}{N}=CH_2$ (10)	C_3H_6 loss	100	46 ± 1.5
$\begin{matrix}(CH_3)_2CHCH_2CH_2\\CH_3CH_2CH_2CH_2\end{matrix}>\overset{+}{N}=CH_2$ (11)	C_4H_8 loss	100	22 ± 1
$[(CH_3)_2CHCH_2CH_2]_2\overset{+}{N}=CH_2$ (12)	C_4H_8 loss	100	24.5 ± 1.5

[a] Values measured by metastable peak areas for ions decomposing in the second field-free region and normalised to a total metastable ion current of 100 units. [b] All values in kJ mol^{-1}; these data represent the kinetic energy release measured from the width at half-height of the corresponding second field-free region metastable peak.

Where elimination of the olefin is fully concerted with transfer of the γ-hydrogen atom [equation (2)], no great differences in kinetic energy release would be expected on passing from smaller to larger homologous ions [for example, from (6) to (10) to (12)]. Neither would the position of an added methyl group be expected to have much influence on the kinetic energy release [for instance, (7) and (8) would be expected to expel C_3H_6 with similar kinetic energy releases]. However, it is clear from the data in the Table that both the size and nature of the side chain involved in the reaction have a profound influence on the kinetic energy release. These effects can be interpreted if an open-chain carbonium ion is involved in the mechanism (Schemes 2 and 3). Thus, in progressing from (6) to (10) to (12), a primary, secondary, and tertiary carbonium ion, respectively, is involved in alkene loss. Hence, the reverse activation energy is reduced, probably by *ca.* 70—75 kJ mol^{-1} in each step; therefore, the kinetic energy release also decreases in passing from (6) to (10) to (12). Although quantitative conclusions are not possible, owing to uncertainties in the heats of formation of the immonium ions, it would appear that about one-third of the reverse activation energy is partitioned as translation. This fraction is deduced from the reduction in the observed kinetic energy release (*ca.* 20—25 kJ mol^{-1}) caused by altering the open-chain carbonium ion from primary to secondary, or secondary to tertiary, in isomeric systems. Similar conclusions have been reached in homologous and analogous systems.[5-7] Secondly, the difference in behaviour of (7) and (8) can be understood (Scheme 3). Loss of C_3H_6 from (7) involves a secondary carbonium ion (16), whilst elimination of C_3H_6 from (8) proceeds *via* a primary carbonium ion (17). Consequently, a greater amount of kinetic energy is released when (8) expels C_3H_6 than is the case when (7) loses C_3H_6. Moreover, the fact that (8) also loses C_2H_4, from the C_3H_7 side chain, with a large kinetic energy release, is also interpretable in a natural fashion; this process also must proceed *via* a primary cation. Both C_2H_4 and C_3H_6 losses occur from (8) in similar abundance (13 and 29%, respectively) because both proceed *via* isomeric primary carbonium ions of similar heat of formation.



SCHEME 1

Ions (7), (9), and (11) furnish further evidence that olefin loss in not fully concerted with γ-hydrogen transfer. These ions eliminate C_3H_6 (but not C_2H_4), C_4H_8 (but not C_2H_4), and C_4H_8 (but not C_3H_6), respectively. The alternative processes, shown in parentheses, would also be expected on the basis of a concerted mechanism. However, the behaviour of (7), (9), and (11) can easily be understood, given the formation of

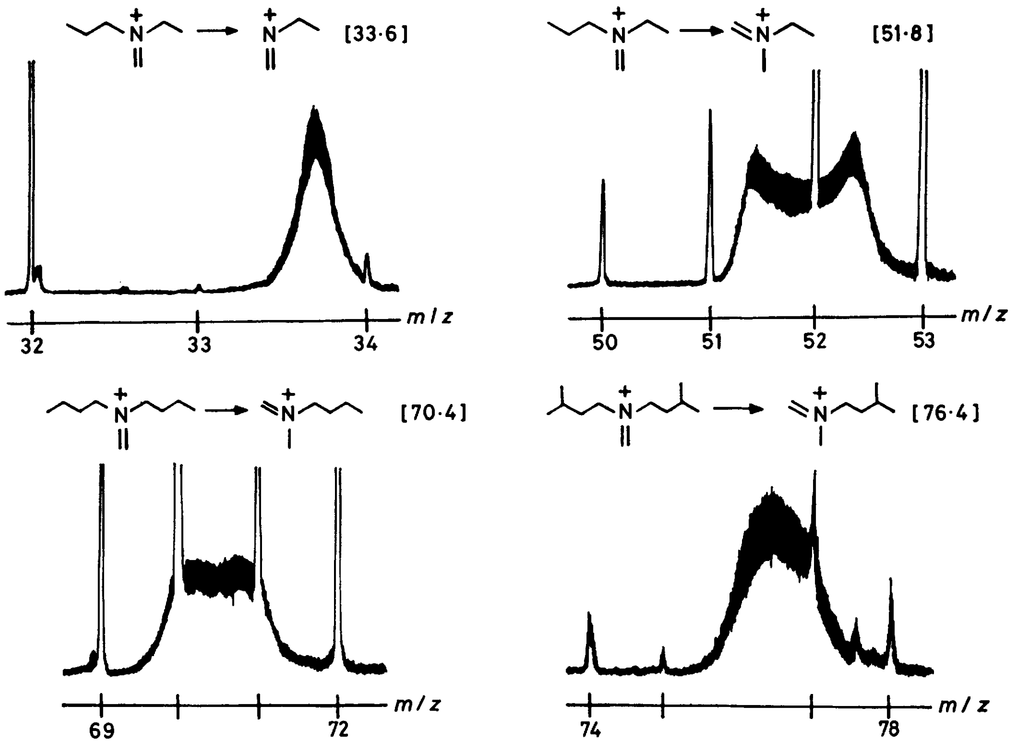
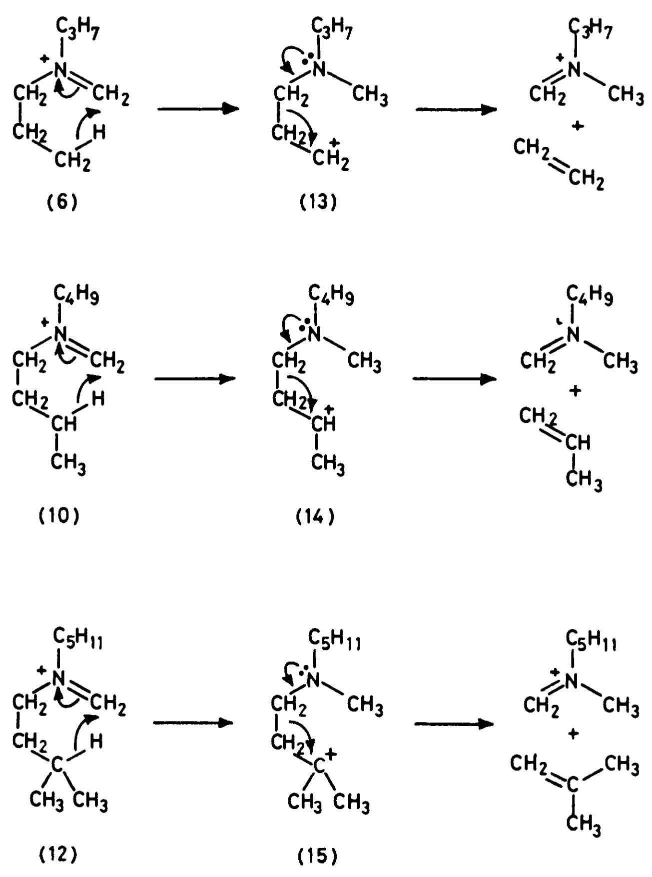


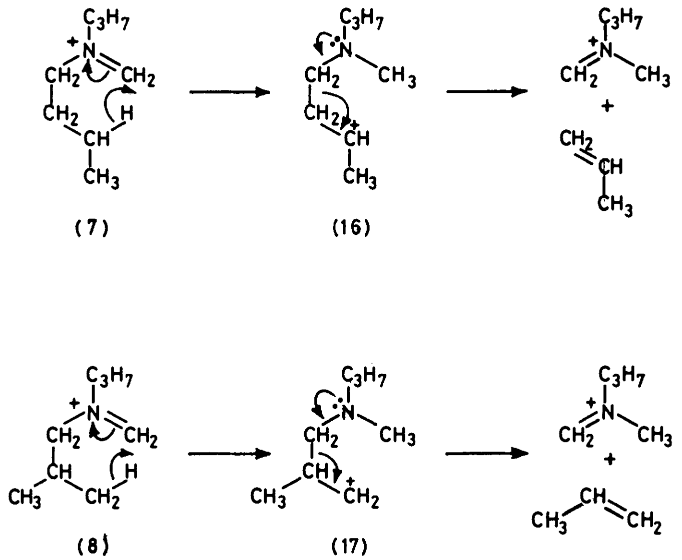
Figure Representative metastable transitions



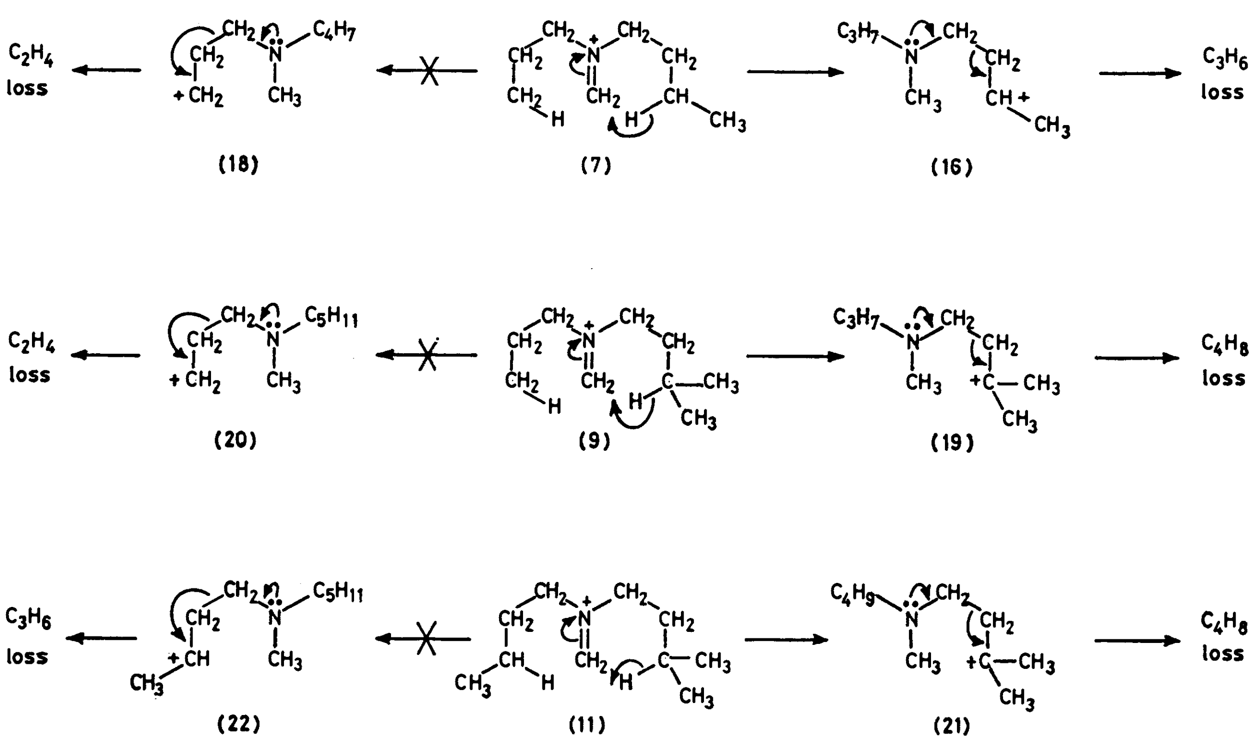
Scheme 2

only the more stable open-chain carbonium ion [(16) rather than (18), (19) rather than (20), and (21) rather than (22), respectively, Scheme 4].

Consideration of the data in the Table reveals that the alternative reaction shown in Scheme 1 is only able to compete in those cases in which γ-hydrogen transfer gives rise to a primary cation. When γ-hydrogen transfer produces a secondary or tertiary carbonium ion, it is favoured energetically and dominates at low



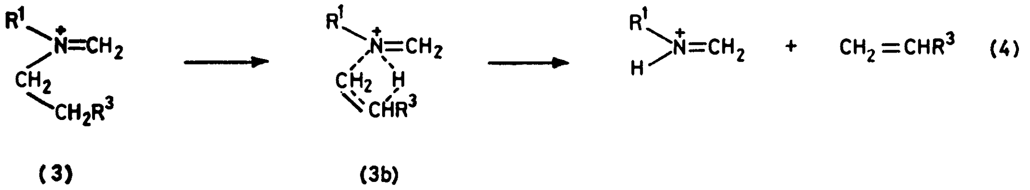
Scheme 3



SCHEME 4

internal energies (metastable ions). This correlation constitutes further evidence that γ-hydrogen transfer occurs essentially to completion before olefin expulsion takes place.

The consistency of this explanation also excludes the possibility of hydrogen transfer *via* a four-membered ring transition state [equation (4)]. Regardless of whether or not such hydrogen transfer were concerted with olefin expulsion, it is clear that this mechanism could not explain the variation in behaviour of $R^1R^2\overset{+}{N}{=}CH_2$ ions. This follows since the γ-hydrogen atom in (3) is not directly involved in elimination of the olefin; consequently, equation (4) cannot explain the changes in behaviour occasioned by substitution at the γ-carbon atom in (3).



Conclusions.—The elimination of olefins from ions of general formula $R^1R^2\overset{+}{N}{=}CH_2$, *via* γ-hydrogen transfer, is not consistent with the occurrence of a synchronous and concerted six-electron pericyclic process. Instead, the results establish that the build up of positive charge on the γ-carbon atom is considerable. These experimental data are indicative of a two-step process: first, a 1,5-hydride shift leads to the formation of an open-chain carbonium ion; secondly, σ-cleavage occurs, with resultant olefin expulsion.

EXPERIMENTAL

All mass spectra were recorded using an AEI KRATOS MS 902 double focusing mass spectrometer operating at a source pressure of *ca.* 10^{-6} Torr and with a nominal electron beam energy of 70 eV. Samples were introduced through the all-glass heated inlet system (AGHIS) and normal mass spectra were obtained using an accelerating voltage of 8 kV.

Ions decomposing in the first field-free region were detected and recorded by increasing the accelerating voltage, from an original value of 2 or 4 kV, at constant electric and magnetic field strengths.[8] When minor reactions were being investigated, the electric field strength was reduced, at constant accelerating voltage (8 kV) and magnetic field strength, in order to achieve maximum sensitivity.[9]

The kinetic energy release data were computed from the widths of the appropriate metastable peaks; no correction was applied for the width of the main beam; the results are the means of at least five measurements.

All compounds were available commercially or else synthesised *via* unexceptional procedures.

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