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ELECTRON IMPACT AND MOLECULAR DISSOCIATION—XVIII

THE LOW ENERGY SPECTRA OF β-KETO-ESTERS

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Abstract—It is argued that the variation in the relative abundance of a fragment ion with the energy of the incident electrons depends upon whether or not the particular species is obtained in a one-step or in a sequential, multi-step, process. This effect is used to investigate the origin of particular ions present in the mass-spectra of some β-keto-esters.

IT WOULD seem that some of the fragment ions present in a cracking pattern can be produced by both single- and multi-step processes and to investigate this possibility, the mass-spectra of the 26 β-keto-esters previously discussed (Part XVI)† have also been studied at electron energies of 30, 20, 15 and 11 V.

It is considered that upon impact a 70 V electron imparts enough energy to the molecule both to ionize it and also, by breaking one or more bonds, to produce fragment ions. Further, many of the ions so formed will dissociate in turn to yield further fragment ions, and the totality of these gives rise to the cracking-pattern which is a characteristic of the compound. This consideration is well-established and need not be elaborated further.

It is now argued that if a given parent molecular ion $\overset{+\cdot}{\mathrm{P}}$ fragments to yield a fragment ion $\overset{+}{\mathrm{N}}$, and further that if this fragmentation should proceed directly by a one-step process: $\overset{+\cdot}{\mathrm{P}} \rightarrow \overset{+}{\mathrm{N}} + \text{residue}$, as well as by a multi-step process:

$$\overset{+\cdot}{\mathrm{P}} \rightarrow \overset{+}{\mathrm{A}} + \mathrm{a}\cdot;\ \overset{+}{\mathrm{A}} \rightarrow \overset{+}{\mathrm{B}} + \mathrm{b}\cdot;\ \text{etc. to}\ \overset{+}{\mathrm{M}} \rightarrow \overset{+}{\mathrm{N}} + \mathrm{n}\cdot;$$

then provided the final ion $\overset{+}{\mathrm{N}}$ is of the same structure in both cases, the energy required for the sequential formation of this ion cannot be less and may often be greater than that required for the one-step process. The minimum energy for the production of the ion $\overset{+}{\mathrm{N}}$ from $\overset{+\cdot}{\mathrm{P}}$ in a one-step process is

$$\varepsilon^0 = \Delta H_f(\overset{+}{\mathrm{N}}) + \Delta H_f(\text{res.}\ddagger) - \Delta H_f(\overset{+\cdot}{\mathrm{P}})$$

but, in order that this ion should be observed in the spectrum additional energy is necessary (K_{PN}), the so-called kinetic shift,[1] so that the total energy to give a particular

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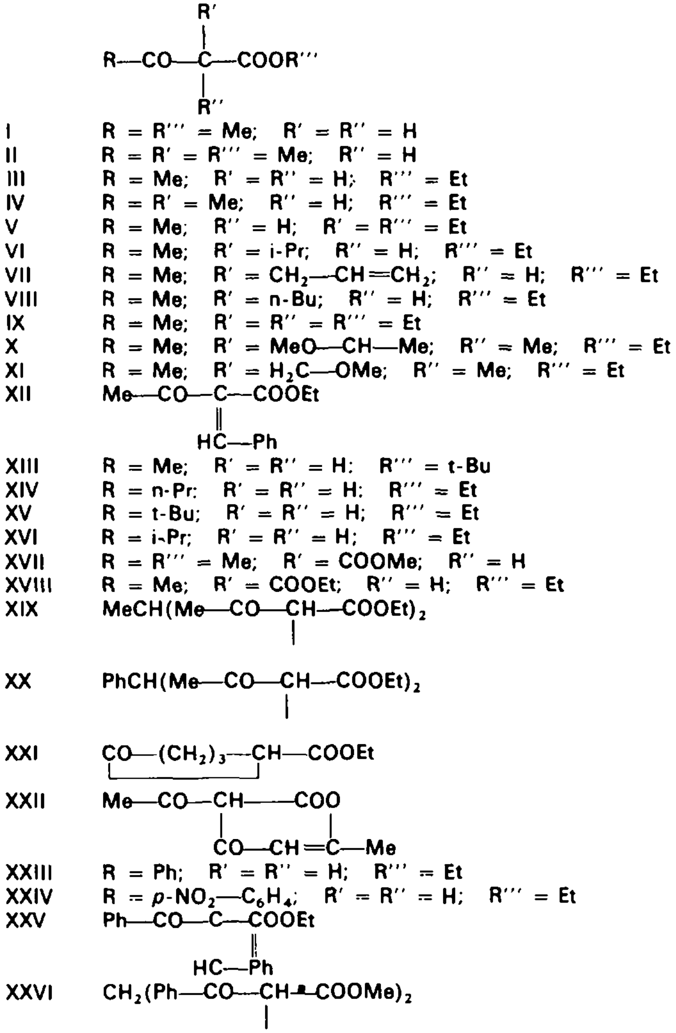
† Part XVI, *Tetrahedron* **23**, 2807 (1967).

‡ res = residue.

[1] L. Friedman, F. A. Long and M. Wolfsberg, *J. Chem. Phys.* **26**, 714 (1957).



$$\mathrm{R{-}CO{-}\overset{\displaystyle R'}{\underset{\displaystyle R''}{C}}{-}COOR'''}$$

I R = R''' = Me; R' = R'' = H
II R = R' = R''' = Me; R'' = H
III R = Me; R' = R'' = H; R''' = Et
IV R = R' = Me; R'' = H; R''' = Et
V R = Me; R'' = H; R' = R''' = Et
VI R = Me; R' = i-Pr; R'' = H; R''' = Et
VII R = Me; R' = CH_2—CH=CH_2; R'' = H; R''' = Et
VIII R = Me; R' = n-Bu; R'' = H; R''' = Et
IX R = Me; R' = R'' = R''' = Et
X R = Me; R' = MeO—CH—Me; R'' = Me; R''' = Et
XI R = Me; R' = H_2C—OMe; R'' = Me; R''' = Et
XII $\mathrm{Me{-}CO{-}\underset{\displaystyle \| \atop HC{-}Ph}{C}{-}COOEt}$
XIII R = Me; R' = R'' = H; R''' = t-Bu
XIV R = n-Pr; R' = R'' = H; R''' = Et
XV R = t-Bu; R' = R'' = H; R''' = Et
XVI R = i-Pr; R' = R'' = H; R''' = Et
XVII R = R''' = Me; R' = COOMe; R'' = H
XVIII R = Me; R' = COOEt; R'' = H; R''' = Et
XIX $\mathrm{MeCH(Me{-}CO{-}\underset{|}{C}H{-}COOEt)_2}$
XX $\mathrm{PhCH(Me{-}CO{-}\underset{|}{C}H{-}COOEt)_2}$
XXI $\mathrm{\underline{CO{-}(CH_2)_3{-}C}H{-}COOEt}$
XXII $\mathrm{Me{-}CO{-}\underset{\displaystyle | \atop CO{-}}{CH}{-}\underset{\displaystyle | \atop CH{=}C{-}Me}{COO}}$
XXIII R = Ph; R' = R'' = H; R''' = Et
XXIV R = p-NO_2—C_6H_4; R' = R'' = H; R''' = Et
XXV $\mathrm{Ph{-}CO{-}\underset{\displaystyle \| \atop HC{-}Ph}{C}{-}COOEt}$
XXVI $\mathrm{CH_2(Ph{-}CO{-}\underset{|}{C}H{-}COOMe)_2}$

FIG. 1.

abundance of the ion $\overset{+}{\mathrm{N}}$, say E_{PN} is given by

$$E_{PN} = \varepsilon^0 + K_{PN} = \Delta H_f(\overset{+}{\mathrm{N}}) + \Delta H_f(\mathrm{res}) - \Delta H_f(\overset{+\bullet}{\mathrm{P}}) + K_{PN} \qquad \ldots(\mathrm{i})$$

By analogous reasoning, the energy needed to produce an equal abundance of the ion $\overset{+}{\mathrm{N}}$ (i.e. E_s) in the same state, but by a multi-step process is

$$E_s = \sum_{\mathrm{A}}^{\mathrm{N}} \varepsilon_i^0 + \sum_{\mathrm{A}}^{\mathrm{N}} K_i = \Delta H_f(\overset{+}{\mathrm{N}}) + \sum_{a}^{n} \Delta H_f(\mathrm{i}\cdot) - \Delta H_f(\overset{+\bullet}{\mathrm{P}}) + \sum_{\mathrm{A}}^{\mathrm{N}} K_i \qquad \ldots(\mathrm{ii})$$

Subtracting (ii) from (i)

$$E_{PN} - E_s = \Delta H_f(\text{res}) = \sum_{a}^{n} \Delta H_f(\text{i}\cdot) + K_{PN} - \sum_{A}^{N} K_I < 0$$

Two conditions may be distinguished:

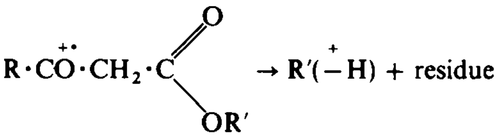
(i) $\Delta H_f(\text{res}) = \sum_{a}^{n} \Delta H_f(\text{i}\cdot)$. This somewhat unlikely condition would imply that the fragment (res) had decomposed into the separate individual species ·a, ·b, etc. The magnitude and sign of the left-hand side will now depend upon $K_{PN} - \sum_{A}^{N} K_I$. All the kinetic shifts are necessarily positive and this being so it is unreasonable to suppose that $K_{PN} > \sum_{A}^{N} K_I$, as sufficient energy has to be imparted at each step to make possible the succeeding one. Therefore, it is probable that $K_N - \sum_{A}^{N} K_I < 0$ and consequently $E_{PN} - E_s < 0$ also.

(ii) If the residue (res) contains, e.g., two of the fragments in a combined form, say, arbitrarily "*jk*". Then $\Delta H_f(\text{res}) < \sum_{a}^{n} \Delta H_f(\text{i}\cdot)$ by the amount of the bond-dissociation energy $D(j - k)$ and the probability that $E_{PN} - E_s < 0$ will be greater.

For our purpose here, however, it is only necessary to argue that if there is a difference in the energy requirements it will be in the sense that the one-step process required less.

We now consider a system in which the given ion $\overset{+}{N}$ is produced by the two routes such that each makes an equal contribution to the total abundance of this ion; and then reduce the incident electron energy. There will come a level at which insufficient energy is available to sustain the two processes and unless the energy initially imparted is always suitably partitioned in the ion-processes it is reasonable to suppose that the multi-step process (having a greater energy requirement) will be most affected. Accordingly if there is a more rapid diminution in the ion abundance in one process than in the other as the electron beam energy is lowered, the multi-step process will decrease more rapidly. Therefore, continuing to lower the electron energy one comes to the stage where, except for the parent molecular ion, the only ions observed of any abundance are obtained by a one-step process; a few formed by a two-step process could also remain, but ions formed by a multi-step process will have become vanishingly small. In general, therefore, one would expect that with the continued decrease in the energy of the bombarding electrons there will be an increase in the relative abundance of ions obtained by a one-step process and a relative decrease in the abundance of all the others, the parent molecular ion excepted.

In the β-keto-esters in which it may be plausibly argued that the charge is located upon one or other of the oxygen atoms present, the substitution of an alkyl group at the α- position ($\overset{\gamma}{R} \cdot \overset{\beta}{C}O \cdot \overset{\alpha}{C}H_2 \cdot CO_2Et$) increases the stability of the parent molecular ion somewhat; but will greatly increase that of the radicals obtained in certain of the fragmentation processes. However, in the γ-position an electron-releasing group, e.g. benzyl, will increase the stability of the parent molecular ion, but will be without effect upon the stability of the radicals or neutral particles formed, at least in the processes here discussed:



$$\mathrm{R\cdot C\overset{+\bullet}{O}\cdot CH_2\cdot C(=O)OR'} \rightarrow \mathrm{R'(\overset{+}{-}H)} + \text{residue}$$

Thus, with a decrease in the energy of the bombarding electrons the parent molecular ion should become, relatively even more abundant for compounds possessing an aryl substituent on the γ-position in comparison with materials having an alkyl-group on the α-carbon.*

Table 1

Abundance of the parent molecular ion (Compound)	Electron volts 70	30	20	15	11
$\mathrm{Me{-}CO{-}CH_2{-}CO_2Et}$	2·3	3·0	3·7	3·6	5·5
$\mathrm{Me{-}CO{-}CHMe_2{-}CO_2Et}$	0·6	0·7	0·8	0·9	1·4
$\mathrm{Me{-}CO{-}CH(CH_2{\cdot}CH{:}CH_2){-}CO_2Et}$	0·4	0·5	0·8	1·3	3·7
$\mathrm{Me{-}(CH_2)_2{-}CO{-}CH_2{-}CO_2Et}$	2·6	3·4	4·2	9·2	37·0[a]
$\mathrm{Me_2CH{-}CO{-}CH_2{-}CO_2Et}$	4·0	4·4	6·1	16·4[b]	47·0[a]
$\mathrm{Me_3C{-}CO{-}CH_2{-}CO_2Et}$	0·5	0·7	1·2	3·5	16·1[b]

[a] Base peak of the spectrum.

[b] Second most prominent peak in the spectrum.

Ions such as $[\mathrm{M\text{-}CH_3}]^+$ are not usually thermochemically very stable and consequently they are not very prominent, but even these ions increase in relative abundance at low electron energies. If ions considered to be obtained by a single-step process are rather abundant under usual impact conditions, then at low electron energies they tend to be amongst the most prominent of the ions in the mass-spectrum; frequently becoming the base-peaks. Thus the ion $[\mathrm{M\text{-}42}]^{+\bullet}$ which appears in the mass-spectra of compounds containing an acetyl group; which are thought to arise

Table 2

Abundance of $[\mathrm{M\text{-}Me}]^+$	Electron volts 70	30	20	15	11
Compound I	2·2	2·6	3·2	3·5	3·6
II	0·9	1·1	1·3	1·4	1·7
VI	0·1	0·1	0·2	0·5	0·7
XII	4·5	5·6	6·9	7·1	8·0
XX	0·4	0·3	0·4	0·7	1·2

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* Henceforward the abundance of the ion is given as a percentage of the total ion current ingoring, however, the ions below $m/e = 28$, as well as $m/e = 32, 40$ and 44.

through a McLafferty type rearrangement,[2] and which are abundant in the 70 eV spectra, become very prominent ions at low voltages. As discussed previously (Part XVI) there is a decomposition sequence of the form:

TABLE 3

Abundance of $[M\text{-}42]^{+\cdot}$	Electron volts 70	30	20	15	11
Compound I	3·9	4·7	6·4[b]	7·6[b]	9·7[b]
VII	5·8	3·0[c]	9·8[c]	13·0[b]	21·0[b]
VIII	4·6	6·4	8·5	14·8[c]	18·5[b]
IX	12·4[b]	13·8[a]	26·5[a]	36·2[a]	57·0[a]

[a] Base peak of the spectrum.
[b] Second most prominent peak in the spectrum.
[c] Third most prominent peak in the spectrum.

$$M^{+\cdot} \rightarrow C_6H_5\overset{+}{C}O \rightarrow \overset{+}{C_6}H_5 \rightarrow \overset{+}{C_4}H_3;$$
$$m/e = 105 \quad m/e = 77 \quad m/e = 51$$

where $M^{+\cdot}$ is the molecular ion of compounds XXIII, XXV, and XXVI and there is in addition evidence from metastable transitions to indicate that direct decomposition of the form $M^{+\cdot} \rightarrow 77$, and $M^{+\cdot} \rightarrow 51$ also occur to a small extent. These latter ions quickly diminish in abundance as the electron energy is lowered.

TABLE 4

Abundance of ions	Electron volts 70	30	20	15	11
Compound XXV:					
$M^{+\cdot}$	10·9[c]	15·6[b]	19·1[b]	31·4[b]	55·6[a]
105^+	32·6[a]	32·1[a]	33·9[a]	23·1[b]	7·8
77^+	16·2[b]	11·9[c]	5·4	0·6	—
51^+	3·2	0·45	—	—	—
Compound XXVI:					
$M^{+\cdot}$	—	—	0·08	0·06	2·0
105^+	61·0[a]	67·0[a]	70·0[a]	59·0[a]	32·0[a]
77^+	19·5[b]	14·6[b]	4·0	0·3	0·1
51^+	4·9[c]	1·5	0·4	0·1	0·04

[a] Base peak of the spectrum.
[b] Second most prominent peak in the spectrum.
[c] Third most prominent peak in the spectrum.

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[2] F. W. McLafferty, *Mass Spectrometry of Organic Ions* p. 309. Academic Press, New York (1963).

Acetyl, as supported by the appropriate metastables, is obtained by several different multi-step processes as well as by a single fission in the parent molecular ion,

$$\begin{tikzcd} \mathrm{MeC\overset{+\cdot}{O}CHR''CO_2Et} \arrow[r] \arrow[d, "b"] & \mathrm{MeC\overset{+}{O}} + \text{residue}^* \\ \mathrm{MeC\overset{+}{O}CHR''} + \text{residue}^* \arrow[d, "c"] & \\ \mathrm{MeC\overset{+}{O}} + \text{residue} & \end{tikzcd}$$

where, for R = ethyl; $a = 17{\cdot}03$ (17·026 calc.), $b = 45{\cdot}73$ (45·728 calc.), and $c = 21{\cdot}75$ (21·753 calc.). In the particular example of methyl acetoacetate (I) where formation of the acetyl ion by multi-step processes would appear to be impossible and the species must be obtained mainly, if not entirely, through a single-step fragmentation, this ion should increase or at least not decrease in relative abundance with a lowering in the energy of the bombarding electrons. For more complicated molecules, on the other hand, multi-step processes should be more important as is supported by the observations upon compounds VII, IX and XVIII.

Table 5

Abundance of ion 43	Electron volts 70	30	20	15	11
Compound I	50[a]	50[a]	51[a]	50[a]	45·2[a]
VII	25·2[a]	20·4[a]	14·7[b]	12·3	6·45
IX	17·0[a]	12·0	8·3	7·3	3·6
XVIII	21·6[a]	20·6[a]	17·5[a]	10·6[b]	2·3

[a] Base peak of the spectrum.

[b] Second most prominent peak in the spectrum.

As mentioned above, the assumptions made may be somewhat oversimplified and further, complicating factors may be important. Firstly, at low electron energies the competition, for the energy available, between the different fragmentations involving a one-step process may become very important particularly if there are selection rules; and the parent molecular ion is exceedingly abundant compared with all the other ions present. Secondly, the location of the positive charge on either of the separating fragments

$$P^{+\cdot} \rightarrow \overset{+}{A} + B\cdot, \text{or } A\cdot + \overset{+}{B},$$

may be different at different electron energies.

Some other peculiarities of particular compounds have been observed. The relative

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* The residue so marked are understood to possess an odd electron somewhere in the system.

abundance of the ion $[M\text{-}H_2O]^{+\cdot}$ increases in the compounds XVIII and XIX as the electron energy is reduced although at 70 eV it may be considered insignificant.

TABLE 6

Abundance of $[M\text{-}H_2O]^{+\cdot}$	Electron volts 70	30	20	15	11
Compound XVIII	0·3	0·3	0·3	0·7	2·3
XIX	0·2	0·4	1·5	2·1	15·6[a]
XX	1·8	3·5	4·2	7·2	11·1[b]

[a] Second most prominent peak in the spectrum.
[b] Third most prominent peak in the spectrum.

Processes leading to the elimination of an alcohol also become more pronounced at low electron energies.

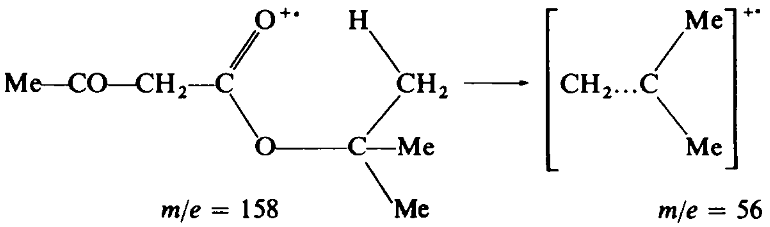
TABLE 7

Abundance of $[M\text{-}EtOH]^{+\cdot}$	Electron volts 70	30	20	15	11
Compound XVI	2·1	2·4	3·4	7·3	8·9[c]
XV	—	—	—	0·6	8·5
XVIII	2·2	3·6	4·8	9·7[c]	21·1[a]
XXI	1·8	9·7	12·2[b]	17·2[b]	12·1[c]

[a] Base peak of the spectrum.
[b] Second most prominent peak in the spectrum.
[c] Third most prominent peak in the spectrum.

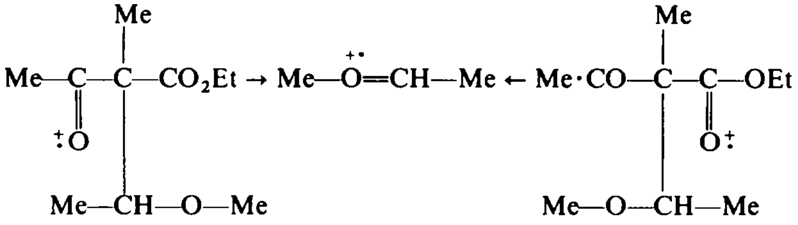
Within the seeming order produced by this classification, peculiar anomalies arise which may be mentioned, but not analysed at this time. Thus, the abundance of the ion m/e = 29 behaves inconsistently in compound XVI; from being the second most abundant ion in the spectrum obtained at 70 eV it decreases rapidly, as might be expected, and then suddenly increases to become second in abundance again at 11 eV.

Compound XIII shows marked evidence of a McLafferty rearrangement

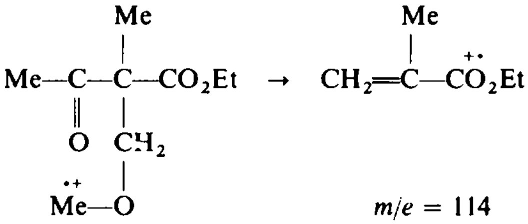


and the resulting ion *m/e* = 56 becomes more and more abundant until at 11 eV it is 91% of the "most abundant ion". Surprisingly, however, there seems to be no comparable McLafferty rearrangement in any of the other compounds examined.

There is a further distinction between the electron–impact–induced–dissociations of compounds X and XI which persists at all energies of the bombarding electrons. In the spectrum of X the most abundant ion, at all energies, is $m/e = 59$:



and is accompanied by a much less abundant ion $m/e = [\text{M-74}]^{+\cdot}$. In XI, on the other hand, $m/e = [\text{M-74}]^{+\cdot}$ is by far the more prominent ion although its formula $C_6H_{10}^{+\cdot}O_2$ would seem to require the simultaneous loss of acetyl and methoxyl groups:



This ion rapidly increases in relative abundance with decreasing electron energy which would indicate, on the present argument, that if the two fissions were not simultaneous they must at least be almost so.

TABLE 8

Abundance of ions		Electron volts				
		70	30	20	15	11
Compound XII:						
$[\text{M}]^{+\cdot}$	218	17·0[a]	17·0[a]	22·5[a]	36·6[a]	56·0[a]
$[\text{M-1}]^{+}$	217	11·1[b]	13·3[b]	14·0[b]	22·3[b]	23·2[b]
	216[d]	0·45	0·6	0·75	1·3	1·6
$[\text{M-15}]^{+}$	203	4·45	5·6	6·9	7·1[c]	8·0[b]
	189	2·1	2·5	3·1	2·7	---
$[\text{M-OEt}]^{+}$	173	4·45	5·15	5·7	5·0	3·0
$[\text{M-EtOH}]^{+\cdot}$	172	0·4	0·5	0·7	0·9	1·0
	135	2·5	2·9	3·9	2·7	1·2
	131	8·6[c]	9·8[c]	8·7[c]	5·3	2·0

[a] Base peak of the spectrum

[b] Second most prominent peak in the spectrum.

[c] Third most prominent peak in the spectrum.

[d] $m/e = 216$ is a metastable corresponding to the transition $218^+ \rightarrow 217^+ + 1$.

In compound XII, a comparison between the behaviour of single- and multi-step processes is possible and, although the parent molecular ion increases in relative abundance with decreasing electron energy, the ions which are considered to be formed mainly by a simple cleavage also increase at the expense of those formed in multi-step processes. The ions $m/e = 131$, 135 and 189 which are presumably obtained in two-step processes, firstly increase somewhat in abundance and then diminish—a behaviour not quite in accord with the simple picture here developed. However, in spite of this and other difficulties already alluded to it is thought that the low-energy spectra do provide further insight into the acceptable modes of fragmentation of the parent molecular ion.

EXPERIMENTAL

The mass-spectra were obtained upon an A.E.I. Ltd., M.S.9 double-focusing mass-spectrometer with the source operating at 150° and the sample admission system at 40°.

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