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ELECTRON IMPACT AND MOLECULAR DISSOCIATION—XVI

β-KETO ESTERS

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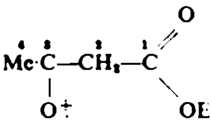
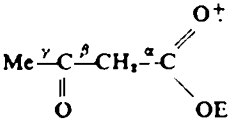
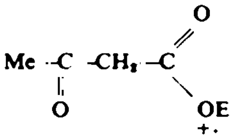
Abstract—The hitherto unreported mass-spectra of some eighteen β-keto esters have been examined. Some special characteristics are discussed. No evidence has been obtained for tautomeric changes in the parent molecular ion.

ALTHOUGH β-keto esters give rise to well-defined and rather characteristic mass-spectra,[1] there are, however, certain peculiarities in the spectra of some of these compounds which are here discussed; the compounds and the more abundant ions in the respective mass-spectra investigated being included in the following figure and the accompanying Table.

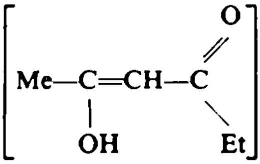
Practically all the fragment ions may be accounted for by assuming that the positive charge resides upon one or other of the oxygen atoms.[2,3] Several descriptions of the parent molecular ion of a β-keto ester are possible, including


$\overset{4}{\mathrm{Me}}\cdot\underset{\mathrm{O}^{+\cdot}}{\overset{3}{\mathrm{C}}}-\overset{2}{\mathrm{CH_2}}-\overset{1}{\mathrm{C}}(=\mathrm{O})\mathrm{OEt}$,


$\mathrm{Me}\overset{\gamma}{-}\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}\overset{\beta}{-}\mathrm{CH_2}\overset{\alpha}{-}\mathrm{C}(=\mathrm{O})\mathrm{OEt}^{+\cdot}$, and


$\mathrm{Me}-\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-\mathrm{CH_2}-\mathrm{C}(=\mathrm{O})\underset{+\cdot}{\mathrm{OEt}}$

Amongst other possibilities would be the enolic form of the ion


$\left[\mathrm{Me}-\underset{\mathrm{OH}}{\underset{|}{\mathrm{C}}}=\mathrm{CH}-\mathrm{C}(=\mathrm{O})\mathrm{Et}\right]^{+\cdot}$

which might arise in two ways: (i) by ionization of the enolic form of the parent molecule, or (ii) by the transfer of an appropriate hydrogen in the ketonic species first formed. As in general the equilibrium concentration of the enol form in the neutral species is small[4] and ionization is a rapid process compared with tautomeric change;[5] it is to be expected that for the compounds here discussed the formation of the enolic form of the parent molecular ion would arise largely by the second of the above alternatives. This is supported by observation. Arguments against the presence of the enolic ion are two-fold: (i) the facile elimination of an acetyl or a

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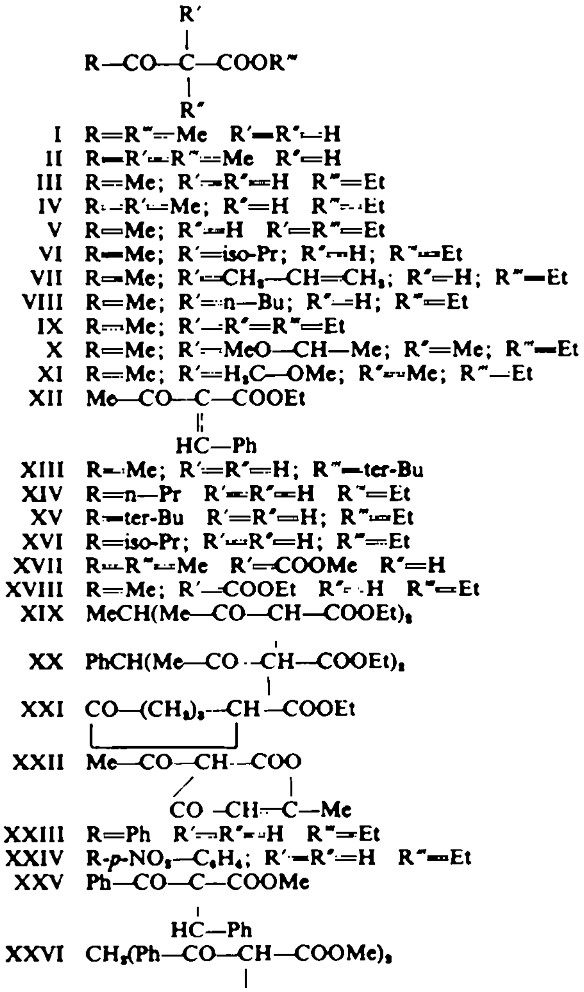
[1] J. H. Bowie, S-O. Lawesson, G. Schroll and D. H. Williams, *J. Am. Chem. Soc.* **87**, 5742 (1965).

[2] C. S. Cummings and W. Bleakney, *Phys. Rev.* **58**, 781 (1949).

[3] H. Budzikiewicz, C. Djerassi and D. H. Williams, *Interpretation of Mass Spectra of Organic Compounds*. Holden-Day, San Francisco (1964).

[4] C. K. Ingold, *Structure and Mechanisms in Organic Chemistry* p. 556. Bell, London (1953).

[5] H. M. Rosenstock and M. Krauss in *Mass Spectrometry of Organic Ions* (Edited by F. W. McLafferty), p. 2. Academic Press, New York (1963).



$R{-}CO{-}C(R')(R''){-}COOR'''$

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 $R=Me$; $R'=iso\text{-}Pr$; $R''=H$; $R'''=Et$

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 $Me{-}CO{-}C({=}HC{-}Ph){-}COOEt$

XIII $R=Me$; $R'=R''=H$; $R'''=ter\text{-}Bu$

XIV $R=n{-}Pr$ $R'=R''=H$ $R'''=Et$

XV $R=ter\text{-}Bu$ $R'=R''=H$; $R'''=Et$

XVI $R=iso\text{-}Pr$; $R'=R''=H$; $R'''=Et$

XVII $R=R'''=Me$ $R'=COOMe$ $R''=H$

XVIII $R=Me$; $R'=COOEt$ $R''=H$ $R'''=Et$

XIX $MeCH(Me{-}CO{-}CH{-}COOEt)_2$

XX $PhCH(Me{-}CO{-}CH{-}COOEt)_2$

XXI $CO{-}(CH_2)_3{-}CH{-}COOEt$

XXII $Me{-}CO{-}CH{-}COO$ / $CO{-}CH{=}C{-}Me$

XXIII $R=Ph$ $R'=R''=H$ $R'''=Et$

XXIV $R=p\text{-}NO_2{-}C_6H_4$; $R'=R''=H$ $R'''=Et$

XXV $Ph{-}CO{-}C{-}COOMe$ / $HC{-}Ph$

XXVI $CH_2(Ph{-}CO{-}CH{-}COOMe)_2$

FIG. 1

benzoyl group *per se* from the parent molecular ion and (ii) the small extent of the elimination of a OH group or a water molecule. The loss of a OH is not marked being for XVII (1·5%), XVIII (1·8%) and XXIV (1·0%); and for water as in VII (0·8%), XVII (1·5%) and XVIII (1·1%). In certain compounds the complementary ion $(M{-}H_2O)^{+\cdot}$ is present, notably XIX (2·1%) and XX (7·6%) and these ions may become still more abundant at lower electron energies (see part XVIII).

Amongst the eighteen compounds examined which possessed Ac groups the ion $m/e = 43$ $(C_2H_3\overset{+}{O})$ was the base peak in twelve cases and the second most abundant in two others. In a further two examples it is somewhat lower being 70% of the base peak for XIX and only 24% for XX. It is significant that in these two examples, but particularly in the latter, the equilibrium concentration of the enolic form of the neutral compound is much higher than the general level for β-keto esters.[4,6] These two compounds apart, there is no other evidence for the preponderance

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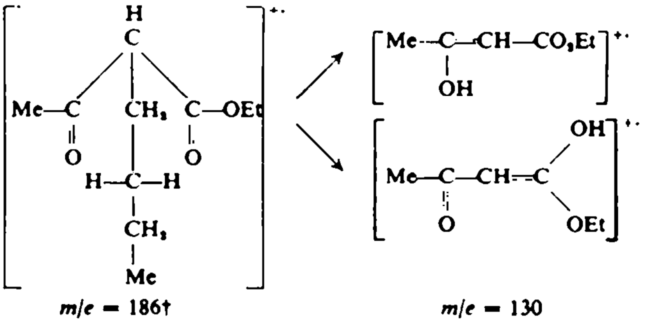
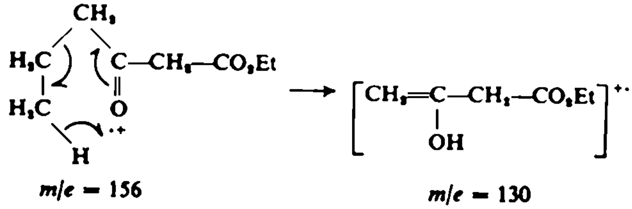
[6] C. K. Ingold, Ref. 4, p. 561.

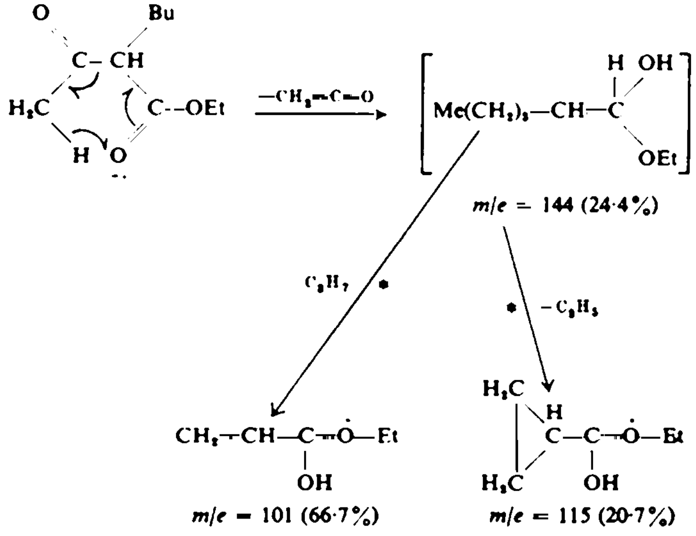
of the enolic form and, equally, there is no fragmentation process occurring which demands the migration of a hydrogen atom attached to carbon (2); the entirety of the fragmentation process observed may be adequately described in terms of a compound which is possessed of two functions, a keto and an ester group. However, although the existence of the enolic form of the parent molecular ion is unimportant in the decomposition sequence it can be argued that the terminal form of any given fragment ion may possess such a structure, e.g.



and



Such ions may further decompose giving rise to others which are prominent in the spectrum:



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† Exact mass-measurements have been carried out to determine the composition of all ions discussed in detail in the text when ambiguities of composition could exist.

* This symbol indicated that a metastable exists to confirm the loss of the particular fragment as a one-step process.

TABLE 1. IONIZING VOLTAGE 70 eV

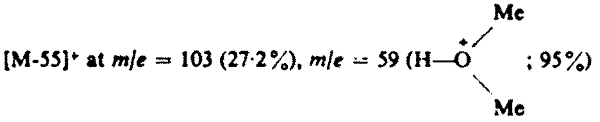
Compound.																											
I	m/e	116	101	88	85	84	74	69	59	57	43	42	41	31	29												
	%*	6·8	4·3	4·2	10·5	4·6	7·9	6·3	10·4	2·0	100	13·2	2·0	5·3	11·9												
II	m/e	130	99	98	88	87	83	70	59	57	56	45	43	42	41	31	29										
	%	4·2	9·0	2·5	36·0	6·6	2·4	2·4	10·2	22·9	6·0	2·4	100	3·0	4·8	3·0	9·6										
III	m/e	130	115	102	88	87	85	84	69	61	60	58	46	45	43	42	31	29									
	%	5·9	2·3	3·6	22·7	3·2	16·2	4·1	5·2	4·3	9·8	5·2	2·3	8·9	100	12·0	12·5	21·4									
IV	m/e	144	129	116	102	99	98	88	85	74	73	70	57	56	55	45	43	42	41	39	31	29					
	%	1·9	0·5	12·2	43·0	13·9	2·5	12·0	3·0	32·9	11·4	4·8	6·7	11·4	4·0	4·4	100	3·7	3·7	2·5	3·8	20·3					
V	m/e	158	143	130	116	115	113	101	88	87	85	84	73	71	70	69	59	55	45	43	42	41	39	31	29		
	%	1·2	1·1	8·0	30·6	3·0	18·7	34·7	16·5	6·6	6·6	5·8	41·0	11·3	8·8	8·8	9·1	17·1	6·6	100	6·9	11·0	10·2	8·5	28·1		
VI	m/e	172	157	144	130	127	115	102	101	87	85	84	83	69	55	45	43	41	39	31	29						
	%	0·5	0·6	1·3	50·5	24·3	80·3	8·1	6·8	54·1	17·6	13·5	10·8	29·7	8·1	7·8	100	17·6	13·0	7·6	27·0						
VII	m/e	170	152	128	127	125	124	109	101	100	99	97	83	82	81	73	58	57	56	55	54	53	45	43	41	39	29
	%	1·6	0·9	23·0	44·3	4·0	4·4	4·2	3·5	19·3	19·8	13·3	14·1	12·3	19·4	3·6	4·0	3·6	5·8	16·7	12·3	10·5	4·6	100	10·7	11·5	23·8
VIII	m/e	186	158	144	143	141	130	115	101	99	97	87	85	84	73	71	70	69	57	55	45	43	42	41	39	31	29
	%	1·0	2·2	24·4	7·4	13·3	29·6	20·7	66·7	10·4	13·3	8·9	7·4	9·6	44·4	17·8	7·4	14·8	11·1	25·9	6·3	100	10·4	18·5	11·1	4·1	37·0
IX	m/e	186	158	144	141	130	129	116	115	113	101	98	97	87	83	73	69	59	57	55	53	45	43	42	41	39	29
	%	0·7	2·0	73·0	13·7	5·5	73·0	21·6	13·2	14·8	80·0	12·0	6·7	13·7	21·9	11·5	13·2	2·8	5·6	17·4	4·2	11·2	100	3·4	21·7	11·5	35·0
X	m/e	202	159	145	144	129	128	115	113	100	99	83	82	59	55	45	43	41	39	31	29						
	%	—	7·1	8·0	7·4	6·4	26·4	16·7	25·1	38·3	29·6	18·6	12·5	100	19·0	4·5	52·1	9·5	6·5	9·5	26·1						
XI	m/e	188	146	145	143	118	115	114	102	100	99	90	87	86	85	75	74	73	70	69	68	61	59	57	56	55	
	%	—	6·8	19·5	3·8	5·4	11·1	27·8	4·9	6·7	28·1	4·9	8·1	27·6	5·4	8·1	6·8	3·0	6·2	69·0	4·9	4·6	4·6	3·5	4·9	4·1	
XI	m/e	45	43	42	41	39	31	29																			
contd.	%	60·0	100	4·1	29·7	7·3	5·7	35·1																			
XII	m/e	218	217	216	203	189	175	173	172	171	159	147	145	144	135	131	129	116	115	107	104	103	102	91	78		
	%	100	80·0	3·2	32·0	15·1	14·2	32·0	3·0	4·7	2·8	14·2	8·9	14·5	17·8	61·8	24·3	5·3	8·9	18·6	9·0	32·0	23·4	11·2	3·3		
XII	m/e	77	76	75	74	69	63	51	50	45	43	39	29														
contd.	%	20·7	8·9	6·2	4·4	3·3	5·0	11·0	5·0	1·0	60·7	3·8	21·9														
XIII	m/e	158	103	102	101	85	84	59	57	56	55	43	42	41	39	31	29										
	%	1·5	27·5	5·4	3·0	40·7	4·8	96·4	89·2	37·1	13·8	77·8	7·2	100	32·3	30·0	31·7										

XIV	*m/e*	158	143	130	115	113	112	88	87	84	73	71	70	69	60	57	55	45	43	42	41	39	31	29			
	%	12·4	1·9	5·7	23·8	6·7	2·9	11·4	19·0	8·6	2·4	76·0	14·3	19·0	9·5	9·5	6·7	7·6	100	23·8	28·6	14·3	14·3	62·0			
XV	*m/e*	172	144	127	117	115	111	88	87	85	70	69	61	60	59	57	56	55	45	43	42	41	39	31	29		
	%	2·4	13·3	3·0	3·6	23·6	3·3	30·3	24·2	18·2	13·9	17·0	12·7	14·5	10·3	100	16·4	9·1	15·1	26·7	12·1	46·7	17·0	12·7	43·0		
XVI	*m/e*	158	115	113	112	88	87	72	71	70	69	60	45	43	42	41	39	31	29								
	%*	17·8	30·7	9·2	9·2	9·2	23·3	3·1	42·9	16·6	16·6	15·3	12·3	100	21·5	29·4	12·3	12·3	55·2								
XVII	*m/e*	174	143	142	128	125	116	115	114	111	101	85	74	71	69	59	57	55	45	43	42	41	39	31	29		
	%	2·0	24·0	25·0	2·0	3·5	10·0	5·0	15·0	4·0	100	22·5	20·0	6·0	26·0	65·0	26·5	26·0	10·0	77·5	40·0	15·0	10·0	21·0	40·0		
XVIII	*m/e*	202	157	156	130	128	116	115	101	88	87	85	84	73	69	60	59	55	46	45	43	42	41	39	31	29	
	%*	0·9	12·6	10·0	5·4	5·4	4·5	36·0	9·0	15·5	13·6	10·0	6·8	9·0	18·2	12·7	7·7	6·8	5·0	20·0	100	26·0	9·0	4·5	37·0	82·0	
XIX	*m/e*	286	271	268	241	225	223	212	195	179	172	166	157	155	154	151	149	135	130	127	126	123	122	115	111	109	
	%*	0·35	2·8	2·1	2·0	11·0	10·3	14·2	63·8	9·9	21·3	17·7	20·9	10·6	27·3	13·8	37·9	13·5	21·3	24·8	35·4	53·2	14·2	28·3	14·8	19·5	
XIX	*m/e*	98	97	95	87	85	84	82	79	77	69	67	55	53	46	45	43	42	41	39	31	29					
contd.	%	49·6	14·2	27·7	22·3	14·9	11·3	17·7	17·0	14·9	100	14·9	13·5	17·0	14·9	35·5	69·2	10·6	28·8	29·1	71·0	78·0					
XX	*m/e*	348	330	302	284	274	257	228	211	185	177	155	131	130	115	104	103	102	91	46	45	43	41	39	31	29	
	%*	0·85	7·6	4·1	12·4	2·4	36·2	6·9	100	31·0	20·7	6·9	48·3	10·3	13·8	8·6	16·6	15·5	6·9	3·4	10·0	24·1	2·1	2·4	17·6	17·2	
XXI	*m/e*	156	128	111	110	101	100	99	83	82	73	69	68	55	54	53	43	42	41	39	31	29					
	%*	17·5	46·0	44·0	48·0	25·0	10·0	13·0	19·0	23·0	65·0	7·5	15·0	100	17·5	15·0	12·5	20·5	19·5	20·5	20·0	58·5					
XXII	*m/e*	168	153	140	129	126	125	111	102	101	99	98	88	85	84	74	73	69	67	60	55	53	43	42	41	39	29
	%*	100	63·5	4·3	3·5	3·5	33·0	15·0	3·5	2·6	10·0	19·1	5·7	80·0	17·4	3·5	2·6	29·6	4·3	2·6	9·6	6·1	93·0	10·0	3·5	9·6	13·8
XXIII	*m/e*	192	122	120	116	115	105	103	102	99	88	85	84	78	77	76	75	74	73	69	56	51	50	45	39	31	29
	%*	1·0	5·7	21·3	3·9	3·9	100	6·3	17·4	6·1	8·9	5·9	2·9	3·4	56·4	4·9	3·4	17·4	5·6	3·4	4·9	18·6	8·8	6·9	5·1	11·2	21·6
XXIV	*m/e*	237	192	191	165	150	120	104	103	92	89	87	76	75	69	64	63	51	50	46	45	43	42	31	29		
	%	11·0	6·5	6·5	2·9	100	5·8	18·4	3·5	6·5	3·2	2·2	11·9	5·8	5·8	2·3	2·9	2·6	6·4	4·5	12·3	4·8	2·9	22·6	16·8		
XXV	*m/e*	266	265	251	239	235	234	207	206	205	193	189	178	121	105	102	77	76	51	43	39	31					
	%	33·3	20·0	1·3	2·2	2·7	2·7	7·1	9·3	3·6	6·2	2·7	10·2	30·2	100	4·9	50	4·4	9·8	2·4	2·2	2·1					
XXVI	*m/e*	368	336	304	263	231	191	190	178	175	159	158	147	146	130	105	91	77	76	69	59	55	51	50	39	31	29
	%*	0·006	0·4	0·4	2·3	0·4	0·5	1·8	2·6	0·4	0·9	0·6	0·6	1·0	0·6	100	0·9	32·0	1·5	2·0	1·3	0·7	8·0	2·2	1·2	0·6	0·8

* Expressed as % of the base peak.

The ions $[M—OR'']^+$, $\overset{+}{RCO}$, $[M—R''OH]^{+\cdot}$, R^+, $[M—C_2H_4]^{+\cdot}$ in ethyl esters, and $[M—C_2H_2O]^+$ in esters possessed of an acetyl group, are very common in the remaining compounds.

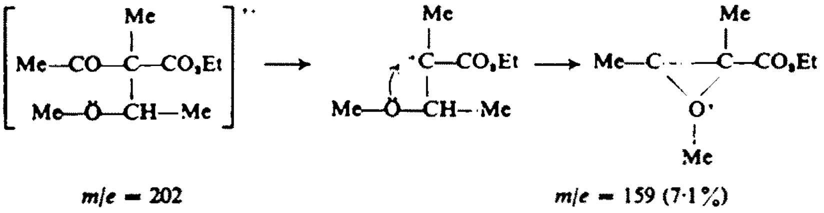
The features peculiar to the mass-spectra of certain substances may now be discussed. Most of the abundant ions in the mass-spectrum of XIII arise because of the presence of a t-Bu group, i.e.

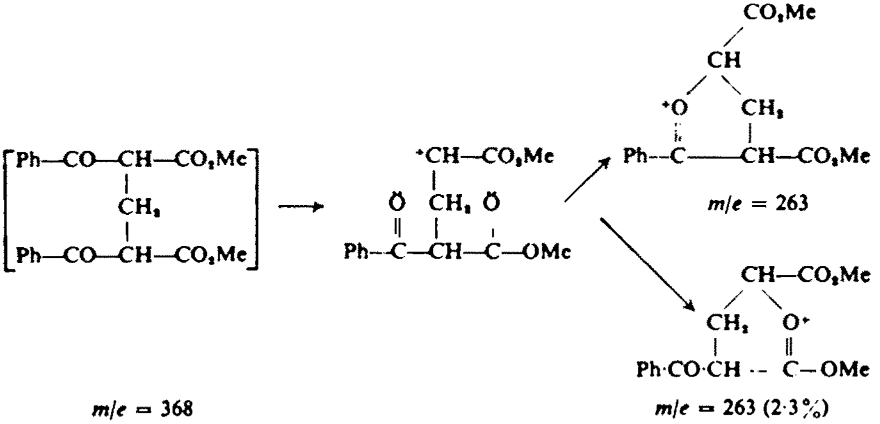


$$[M\text{-}55]^+ \text{ at } m/e = 103\ (27{\cdot}2\%),\ m/e = 59\ (H—\overset{+}{O}(Me)_2;\ 95\%)$$

$m/e = 57$ ($\overset{+}{C_4H_9}$; 88%), and $m/e = 56$ ($C_4H_8^{+}$; 36·6%). In compounds XIV and XVI, on the other hand, the ion $[M—R]^+$ is more prominent being 23·8% and 30·7% of the base peaks respectively, a fact which is attributed to the considerable thermodynamic stability of the radical R· (·C_3H_7) obtained in the same process.

In general, the fission of a bond α- or β- to the ester group with the charge remaining upon the 2-carbon can occur when certain stabilizing groups are present. Otherwise ions such as $\overset{+}{C_3H_5O}$ or $\overset{+\cdot}{C_4H_7O_2}$ are not normally observed.





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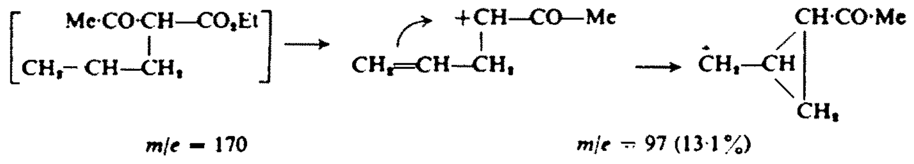
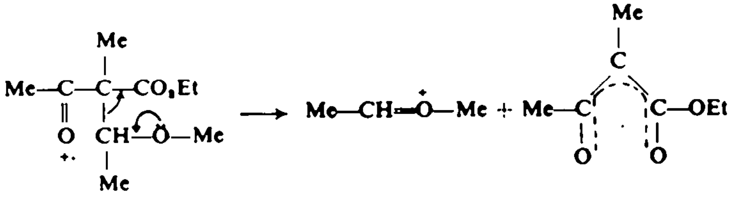


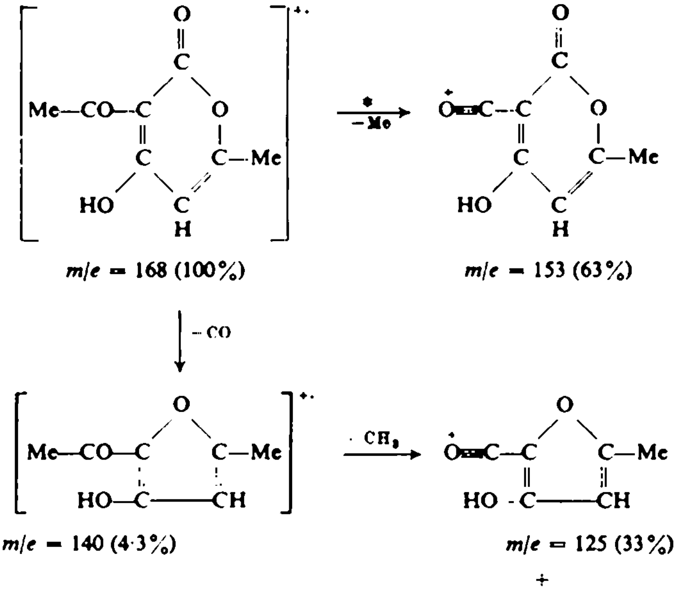
If an additional heteroatom is available in the molecule, then fragmentation patterns of a different type can arise e.g.



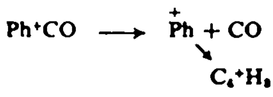
m/*e* = 59 (100%)

A similar process occurs in compound XI giving rise to *m*/*e* = 45 ($H_2C{:}\overset{+}{O}\cdot CH_3$; 59·2%), an ion that is prominent nowhere else.

The mass-spectrum of dehydroacetic acid (XXII) is consistent with the enolic form of the parent molecular ion which is the base peak in the spectrum being thermodynamically very stable, a consequence of the extended conjugation possessed by this ion. The ion $[M—CH_3]^+$ is also very stable and certain other fragmentations seem consistent with the suggested structures of the molecular ion.

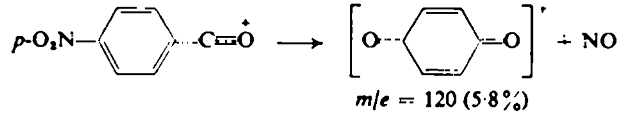


In compounds possessing aryl groups, *m*/*e* = 105 ($C_6H_5\overset{+}{C}O$) in XXIII, XXV, and XXVI, and *m*/*e* = 150 (*p* $NO_2\cdot C_6{}^+H_4\cdot CO$) in XXIV are not only the base peaks but also they are very much more abundant than any of the other ions present. At the same time the parent molecular ions are less abundant than those of the corresponding aliphatic compounds. The aroyl ion is thermodynamically much more stable than the acetyl and it is thought that this stability is the controlling force. However, the benzoyl ion tends further to decompose



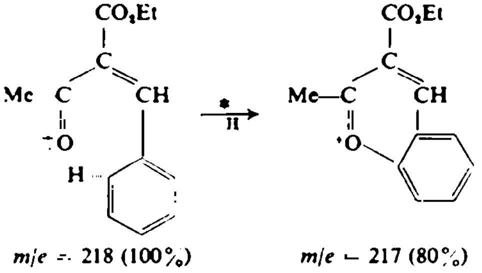
$$\begin{array}{lll} Ph^+CO & \longrightarrow & \overset{+}{Ph} + CO \\ & & \searrow \\ & & \quad C_4{}^+H_3 + C_2H_2; \end{array}$$

but the ion in compound XXIV ($m/e = 150$) decomposes by a different route

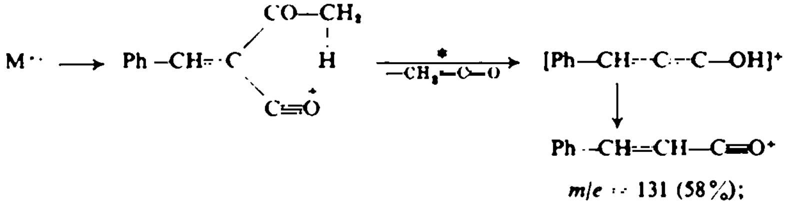


Such a cleavage is well established in the fragmentation processes associated with aromatic nitro-compounds.[7]

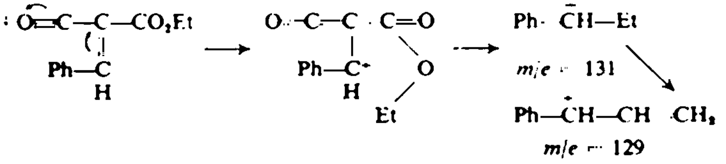
A further peculiarity is observed in the mass-spectrum of compound XII in which the parent molecular ion is the base peak, and in which the second most abundant ion occurs at $[P-1]^+$ (80%):



The ion $m/e = 131$ (61·8%) consists mainly of a species of formula $C_9{}^+H_7O$, the probable structure of which is



but there is also an ion $m/e = 131$ (3·8%, of formula $C_{10}{}^+H_{11}$) the production of which would require the migration of an ethyl group. The migration of methyl groups has previously been reported.[8] To confirm the present observation further studies are being made. The ion $m/e = 129$ (2·4%) is a doublet the major component having the formula $C_9H_5{}^+O$ and the minor, $C_{10}{}^+H_9$:



There are other ions which could only be obtained by an extensive rearrangement e.g. $m/e = 104$ ($\overset{+}{C_8H_8}$; 9%) and $m/e = 103$ ($\overset{+}{C_8H_7}$; 3·2%) although the latter is derived, at least partly, from the ion $m/e = 131$ already discussed. Surprisingly,

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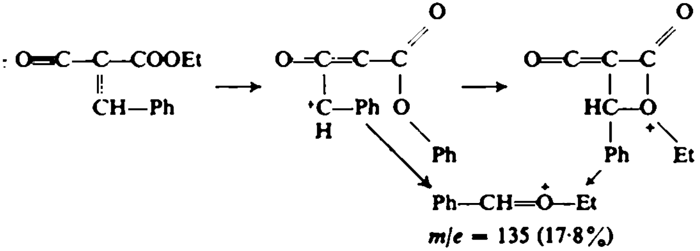
[7] J. H. Beynon, R. Saunders and A. E. Williams, *Ind. Chim. Belge* **29**, 311 (1964).

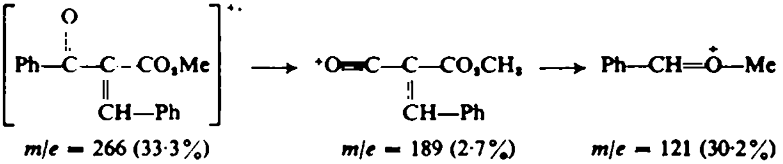
[8] J. H. Bowie, R. Grigg and D. H. Williams, and S.-O. Lawesson and G. Schroll, *Chem. Comm.* 403 (1965).

the ion $m/e = 135$ has the formula $C_9H_{11}O$; a formula which would seem to require the migration of an ethoxyl radical.

There is present also a metastable $m/e = 89{\cdot}80$ ($89{\cdot}78$ calc.) which supports the following degradation:



The same process may well occur in compound XXV where an analogous ion $m/e = 121$ ($C_8\overset{+}{H}_9O$) is obtained:



EXPERIMENTAL

The mass-spectra here reported were obtained upon an A.E.I. Ltd., M.S.9. double focusing mass-spectrometer operating with a source temperature of 150°, a sample inlet at 40° and an ionizing voltage of 70 eV.

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