

## Studies in Mass Spectroscopy

### Part XI.\* Mass Spectra of 1,4-Dicarbonyl Compounds

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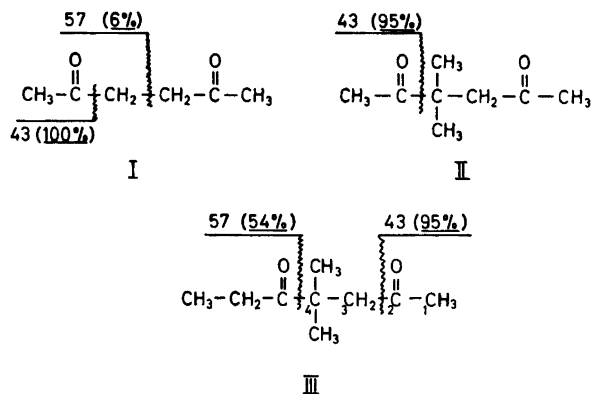
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The mass spectra of a series of  $\gamma$ -diketones and  $\gamma$ -ketoesters have been determined and interpreted with the aid of high resolution measurements. The spectra all contain molecular ions and are virtually free of skeletal rearrangement fragments. The fragmentation patterns are greatly dependent on the nature and location of substituents and hence mass spectrometry can be a great aid to structure determination in this class of synthetically important compounds.

1,4-Dicarbonyl compounds are substances of considerable synthetic importance, especially as precursors in the synthesis of furans, thiophenes, pyrroles, and  $\gamma$ -lactones. In the light of this synthetic importance, we have undertaken a study of the mass spectra of some  $\gamma$ -diketones and  $\gamma$ -ketoesters in the hope that mass spectrometry will serve as a useful method to characterise such compounds. Some details of the spectra (see Tables 1 and 2 and Figs. 1-6) of representative  $\gamma$ -diketones (I-IV), and  $\gamma$ -ketoesters (V-XIII) are discussed in this paper.

Generally speaking, all the compounds studied give molecular ions which are easily recognised. Moreover, exact mass measurements on a number of ions in many of the spectra have uncovered only a single composition which requires a skeletal rearrangement upon electron impact. Hence, the spectra of these diketones and ketoesters can be interpreted by reference to the more abundant ions, without the complications introduced by the skeletal rearrangements recently observed to occur in some compounds.<sup>1-6</sup>

\* Part X: Bowie, J. H., Grigg, R., Lawesson, S.-O., Madsen, P., Schroll, G. and Williams, D. H. *J. Am. Chem. Soc.* **88** (1966) 1699.



Details of the mass spectra on the  $\gamma$ -diketones I–III are summarised in Table 1 and in the formulae (I–III); in those cases where the composition of the ion has been established by exact mass measurements, the relative abundances are underlined.

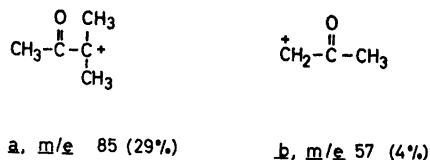
It should be pointed out that the base peak  $m/e$  43 ions from II and III are doublets, the complements to  $\text{CH}_3\text{C}\equiv\text{O}^+$  being associated with  $\text{C}_3\text{H}_7^+$  ions (5 % in both cases); this observation is understandable since II and III (in contrast to I) contain intact C-3 units carrying sufficient hydrogen atoms to afford a  $\text{C}_3\text{H}_7^+$  species by two bond cleavages and a hydrogen rearrangement. Similarly,  $m/e$  57 from III has a small hydrocarbon ( $\text{C}_4\text{H}_9^+$ ) contribution (which brings the total abundance of this ion to 62 %) that can arise in a similar manner.

In these compounds (I–III) cleavage of the centre carbon-carbon bond between the carbonyl groups does not seem to be a favourable process unless a substituted carbonium ion can be formed by such a cleavage. Thus, I gives only a low abundance ion ( $m/e$  57) due to rupture of the centre C–C bond; this behaviour is probably associated with the unfavourable nature<sup>7</sup> of a primary carbonium ion adjacent to a carbonyl group (as in the  $^+\text{CH}_2\text{COR}$

Table 1. Details of the mass spectra of some  $\gamma$ -diketones (I–III)

Compound	Relative abundances (%) of ions*							
	$\text{M}^+$	$\text{M}-\text{CH}_3$	$\text{M}-\text{H}_2\text{O}$	$\text{M}-\text{C}_2\text{H}_6$	$\text{M}-\text{CH}_2\text{CO}$	$\text{M}-\text{CH}_3\text{CO}$	$\text{M}-\text{C}_3\text{H}_4\text{O}$	$\text{M}-\text{C}_3\text{H}_5\text{O}$
I	6	22	—	—	—	12	—	6
II	5	2	1	—	11	6	—	29
III	6	2	2	14	—	—	6	13

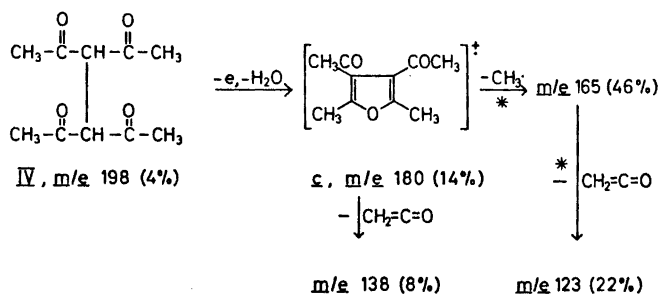
\* Related to the base peak arbitrarily taken as 100 %.



fragment). Moreover, II furnishes a prominent ion due to *a* ( $M - C_3H_5O$ , see Table 1) but a low abundance ion associated with *b*. Hence the major portion of the  $m/e$  57 ion ( $C_3H_5O^+$ ) from III can fairly confidently be ascribed to the cleavage indicated in III, rather than to rupture of the 3,4-bond.

The influence of a tertiary centre on the breakdown pattern is also evident from the finding that whereas II gives prominent  $M - CH_2CO$  and  $M - CH_3CO$  ions, III undergoes no such losses but gives only ions associated with the expulsion of an additional  $CH_2$ -group. Hence the  $M - CH_2CO$  and  $M - CH_3CO$  ions from II can be associated with the loss of the  $CH_3CO$ -group attached to the tertiary centre (with and without hydrogen rearrangement, respectively).

The majority of the fragmentation in the high mass region of the spectrum of 3,4-diacetylhexan-2,5-dione (IV) occurs from an  $M - H_2O$  ion ( $m/e$  180) as established by appropriate metastable peaks. The importance of the  $M - H_2O$  ion in determining the fragmentation pattern suggests, but does not prove, that this ion may have an especially favoured structure. A plausible structure for the  $m/e$  180 ion is the furan molecular ion *c*.<sup>\*</sup> Regardless of the structure assigned to  $m/e$  180, it decomposes by loss of the fragments indicated, as established by appropriate metastable peaks [indicated by an asterisk (\*)]; the  $m/e$  values indicated in the scheme account for all ions of abundance greater than 6% (relative to the  $m/e$  43 base peak) above  $m/e$  115.



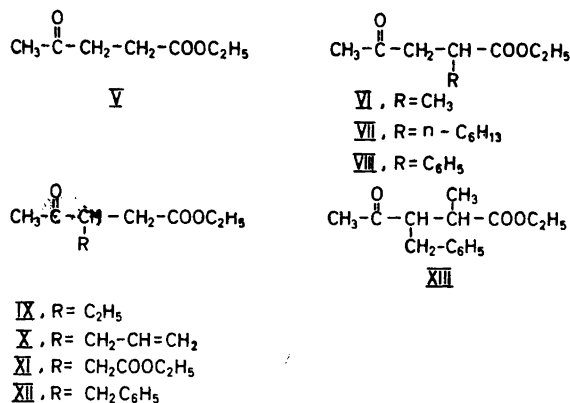
We now turn to a discussion of the spectra of ethyl laevulinate (V) and related compounds containing substituents  $\alpha$  to the ester group (VI–VIII) or  $\beta$  to the ester group (IX–XII); one  $\alpha, \beta$ -disubstituted ethyl laevulinate (XIII) has been studied. The composition of ions in Figs. 1–6 which have

\* Molecular ions of furans do not necessarily have the structures of the furans in the ground state.<sup>8</sup> Some of the structures used in this paper are nominal only, but serve the important purpose of relating the fragmentation pattern to the structure of the intact molecule.

Table 2. Compositions of some ions in the spectra of V, VI, VIII, IX, XII, and XIII (Figs. 1–6), established by exact mass measurements.

Compound

V	<i>m/e</i>	55	56	71	73	74	
	Comp.	C <sub>3</sub> H <sub>3</sub> O (90 %) C <sub>4</sub> H <sub>7</sub> (10 %)	C <sub>3</sub> H <sub>4</sub> O	C <sub>4</sub> H <sub>7</sub> O	C <sub>3</sub> H <sub>5</sub> O <sub>2</sub>	C <sub>3</sub> H <sub>6</sub> O <sub>2</sub>	
VI	<i>m/e</i>	69	71	73	87	88	101
	Comp.	C <sub>4</sub> H <sub>5</sub> O	C <sub>4</sub> H <sub>7</sub> O	C <sub>3</sub> H <sub>5</sub> O <sub>2</sub> (80 %) C <sub>4</sub> H <sub>9</sub> O (20 %)	C <sub>4</sub> H <sub>7</sub> O <sub>2</sub>	C <sub>4</sub> H <sub>9</sub> O <sub>2</sub>	C <sub>5</sub> H <sub>9</sub> O <sub>2</sub>
VII	<i>m/e</i>	171	183				
	Comp.	C <sub>10</sub> H <sub>19</sub> O <sub>2</sub>	C <sub>11</sub> H <sub>19</sub> O <sub>2</sub>				
IX	<i>m/e</i>	43	55	56	73	83	85
	Comp.	C <sub>2</sub> H <sub>3</sub> O	C <sub>4</sub> H <sub>7</sub> (80 %) C <sub>3</sub> H <sub>3</sub> O (20 %)	C <sub>4</sub> H <sub>8</sub>	C <sub>3</sub> H <sub>5</sub> O <sub>2</sub> (85 %) C <sub>4</sub> H <sub>9</sub> O (15 %)	C <sub>5</sub> H <sub>7</sub> O	C <sub>5</sub> H <sub>9</sub> O
XII	<i>m/e</i>	101	115	126	127	130	144
	Comp.	C <sub>5</sub> H <sub>2</sub> O <sub>2</sub>	C <sub>6</sub> H <sub>11</sub> O <sub>2</sub>	C <sub>7</sub> H <sub>10</sub> O <sub>2</sub>	C <sub>7</sub> H <sub>11</sub> O <sub>2</sub>	C <sub>7</sub> H <sub>14</sub> O <sub>2</sub>	C <sub>7</sub> H <sub>12</sub> O <sub>3</sub>
XIII	<i>m/e</i>	117	145	146	147	188	189
	Comp.	C <sub>5</sub> H <sub>9</sub>	C <sub>10</sub> H <sub>9</sub> O	C <sub>10</sub> H <sub>10</sub> O	C <sub>10</sub> H <sub>11</sub> O	C <sub>12</sub> H <sub>12</sub> O <sub>2</sub>	C <sub>12</sub> H <sub>13</sub> O <sub>2</sub>
XIII	<i>m/e</i>	43	131	147	148	159	173
	Comp.	C <sub>2</sub> H <sub>3</sub> O (85 %) C <sub>3</sub> H <sub>7</sub> (15 %)	C <sub>5</sub> H <sub>7</sub> O (35 %) C <sub>10</sub> H <sub>11</sub> (65 %)	C <sub>10</sub> H <sub>11</sub> O	C <sub>10</sub> H <sub>12</sub> O	C <sub>11</sub> H <sub>11</sub> O	C <sub>12</sub> H <sub>13</sub> O (60 %) C <sub>11</sub> H <sub>9</sub> O <sub>2</sub> (40 %)
XIII	<i>m/e</i>	174	177	178	202	203	
	Comp.	C <sub>12</sub> H <sub>14</sub> O (60 %) C <sub>11</sub> H <sub>10</sub> O <sub>2</sub> (40 %)	C <sub>12</sub> H <sub>17</sub> O	C <sub>12</sub> H <sub>16</sub> O	C <sub>13</sub> H <sub>14</sub> O <sub>2</sub>	C <sub>13</sub> H <sub>15</sub> O <sub>2</sub>	



been substantiated by exact mass measurements are summarised in Table 2. Only the formation of  $\text{C}_4\text{H}_9\text{O}^+$  ( $m/e$  73), a minor fragment from (VI) and (IX), requires a skeletal rearrangement for its formation.

Some of the important fragmentations suffered by ethyl laevulinate (V) upon electron impact are summarised in Fig. 1. The elimination of ketene from the molecular ion gives rise to an ion at  $m/e$  102 (Fig. 1) and it is of

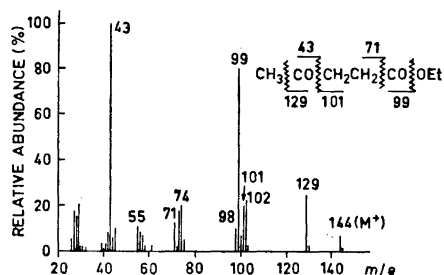
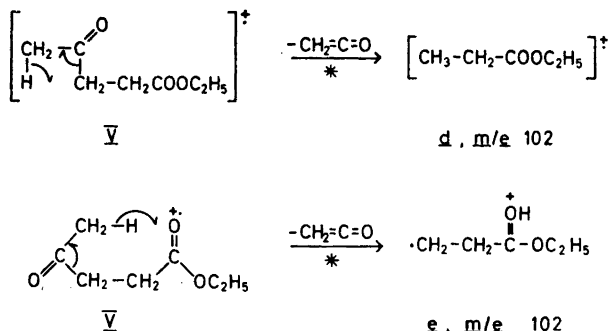


Fig. 1.

interest to try to determine whether the migrating hydrogen becomes bonded to carbon ( $\dot{\text{V}} \rightarrow d$ ) or to oxygen ( $\dot{\text{V}} \rightarrow e$ ) \* when such fragmentations occur in  $\gamma$ -dicarbonyl compounds.

If the hydrogen migration occurred to carbon with the formation of the ethyl propionate molecular ion ( $d$ ), then  $m/e$  102 might be expected to decompose as does ethyl propionate in its mass spectrum<sup>9</sup> [*i.e.*, by loss of an ethoxyl radical to give  $m/e$  57 (100%, base peak) from the molecular ion ( $m/e$  102, 16%]. Far from being an abundant ion,  $m/e$  57 is a very minor fragment in Fig. 1. Hydrogen rearrangement to oxygen ( $\dot{\text{V}} \rightarrow e$ ) is therefore a plausible alternative. This latter mode has been shown to operate in the loss of ketene from derivatives of ethyl acetoacetate,<sup>10</sup> but it should be noted that in such

\* A similar migration to the oxygen of the ethoxyl group is also feasible.



cases, the elimination can occur in a concerted manner *via* a six-membered cyclic transition state.

There is some evidence to support partial operation of the type of mechanism exemplified by  $\text{V} \rightarrow \text{e}$  in the spectrum (Fig. 2a) of the ethyl derivative IX (all the major ions in this spectrum have been analyzed by exact mass measurements as indicated in Table 2). In this spectrum (Fig. 2a), the  $\text{M} - \text{CH}_2\text{CO}$  ion ( $m/e$  130) decomposes by loss of an ethyl group (metastable peak at 78.5) to give  $m/e$  101. This behaviour is understandable if the ketene elimination is accompanied by a 1,2-hydrogen shift to generate the ionised enol  $f$  ( $m/e$  130), which can then lose an ethyl group by allylic cleavage to give  $g$  ( $m/e$  101). It is emphasised that the molecular ion of ethyl pentanoate (which would be generated by hydrogen migration to carbon) decomposes to some extent by loss of an ethyl radical, but mainly eliminates propylene (to give  $m/e$  88) and an ethoxyl radical (to give  $m/e$  85) as indicated in Fig. 2b;  $m/e$  85 and  $m/e$  88 are of relatively low abundance in Fig. 2a. McLafferty rearrangements<sup>11</sup> involving the ketone and ester carbonyl groups of IX (and a hydrogen atom from the methyl and methylene groups, respectively, of the ethyl substituent) may lead to the ions at  $m/e$  144 ( $\text{M} - \text{C}_2\text{H}_4$ ) and  $m/e$  88 ( $\text{M} - \text{CH}_3\text{CO} - \text{CH}=\text{CH}-\text{CH}_3$ ), but these processes do not dominate the fragmentation.

The important effect<sup>9</sup> of substituents on the prevalence of cleavage of the central C—C bond between the two carbonyl groups may be seen from a comparison of Figs. 3—6. The ion at  $m/e$  101 in Fig. 3, which corresponds to

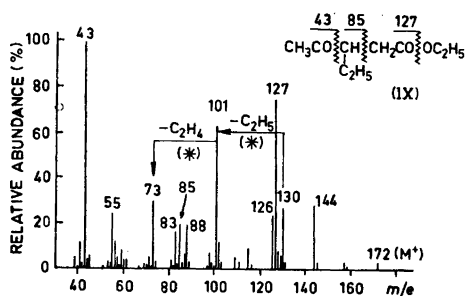


Fig. 2a.

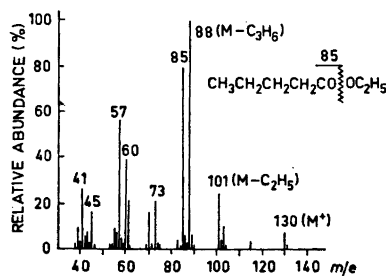
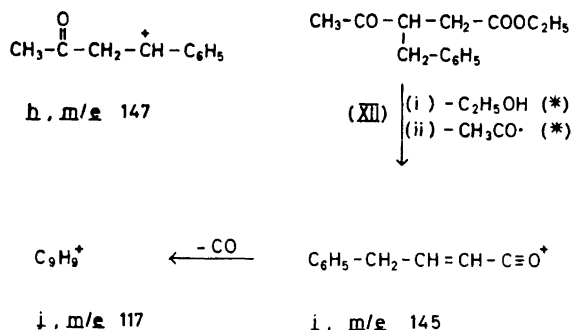


Fig. 2b.





IX to give  $m/e$  85 (see Fig. 2a) is not very pronounced, as it must be remembered that in the case of a benzyl group there is not only the possibility of group size causing secondary carbonium ion stabilisation, but also one of a 1,2-hydrogen shift accompanying the C—C bond fragmentation, so that  $m/e$  147 may be stabilised as the benzylic cation *h* (or as a related tropylium ion).

The formation of the very abundant ion at  $m/e$  145 in the spectrum (Fig. 5)

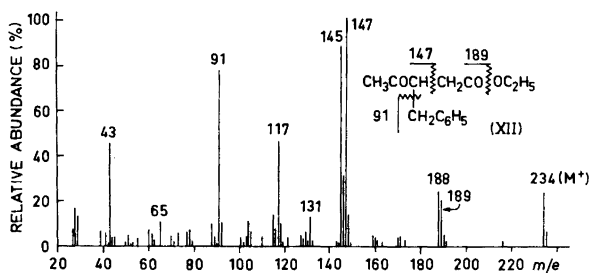


Fig. 5.

of XII is of some interest. Although exact measurements establish that loss of two hydrogen atoms from  $m/e$  147 would give a fragment of the required composition, the shift of this ion to  $m/e$  159 in the spectrum (Fig. 6) of XIII

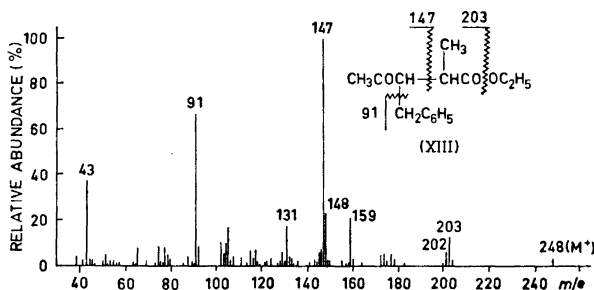
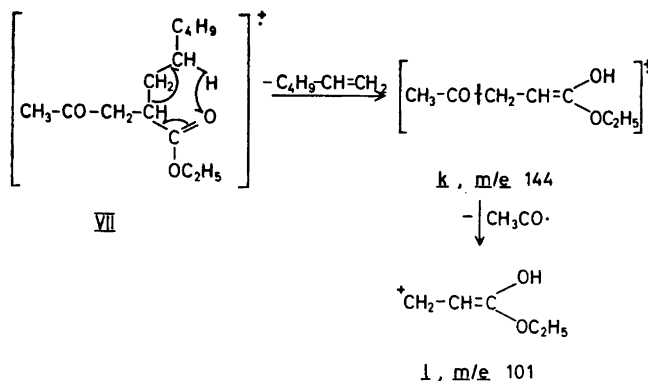


Fig. 6.





necessitates the retention of the carbon atom adjacent to the ester function in this fragment. Metastable peaks at  $m/e$  151.0 and  $m/e$  111.8 establish that it arises, at least in part, by the sequential loss of ethanol and an acetyl radical from the molecular ion. Hence, it may correspond to  $i$ ,  $\text{C}_{10}\text{H}_9\text{O}^+$ , (high resolution), which can decompose by loss of carbon monoxide to  $j$  ( $m/e$  117,  $\text{C}_9\text{H}_9^+$ , high resolution).

In the compounds studied, the McLafferty rearrangement<sup>11</sup> only gives rise to a diagnostically obvious decomposition path when the alkyl group is large (in VII, see Fig. 4). Elimination of a neutral olefin affords  $m/e$  144 ( $k$ ), whose enolic structure is suggested by the appearance of an ion at  $m/e$  101 (see Fig. 4), corresponding to  $l$  which can be formed by allylic cleavage in  $k$ .

The spectra of the allyl and carboethoxymethyl derivatives (X and XI) are largely unexceptional and do not merit separate discussion in this context, although the decomposition of the phenyl derivative VIII occurs quite specifically by loss of ethanol to  $m/e$  174. The phenyl substituent must make this process particularly favourable in VIII, although  $\text{M} - \text{C}_2\text{H}_5\text{OH}$  ions are a consistent feature in the spectra of this series of compounds (see, for example,  $m/e$  98 in Fig. 1,  $m/e$  126 in Fig. 2a,  $m/e$  112 in Fig. 3,  $m/e$  188 in Fig. 5, and  $m/e$  202 in Fig. 6).

The spectra of several  $\gamma$ -ketoacids of this series have been determined, but the spectra of the esters are more amenable to interpretation for structural purposes.  $\beta$ -Benzoylpropionic acid behaves somewhat exceptionally, affording a skeletal rearrangement ion at  $m/e$  122 (3 % of the abundance of the benzoyl cation base peak) corresponding in composition to ionised benzoic acid (high resolution).

In summary, the  $\gamma$ -diketones and  $\gamma$ -ketoesters studied give relatively simple spectra containing moderately abundant molecular ions. The fragmentation patterns are greatly dependent on the nature and location of substituents, while skeletal rearrangement processes are of negligible importance. Mass spectrometry should therefore prove to be a valuable analytical tool for the analysis of this important class of synthetic compounds.

#### EXPERIMENTAL

Mass spectra were determined in an A.E.I. MS 9 double focussing mass spectrometer at 70 eV and a source pressure in the range  $(0.1-2.0) \times 10^{-6}$  mm Hg. Samples were

introduced through a heated inlet system at a temperature of approximately 150°. High resolution measurements were carried out with a resolving power of approximately 12 000 (10 % valley definition).

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