Mass Spectra of Some Cyclic β-Diketones

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The mass spectral behaviour of a number of 1,3-cyclohexanedione (R=H) and dimedone (R=CH₃) derivatives have been investigated. The compounds are found to break down in a well-defined manner. The spectra show pronounced peaks at m/e 55 (R=H) and m/e 83 (R=CH₃). The relative intensity of these fragments is highly dependent on the substituents in the 2- and 5-positions. Noteworthy is the fragmentation process starting with elimination of CO and C_2H_4 (R=H) or C_4H_8 (R=CH₃) which reflects the ability of the 2-substituent to stabilize a double bond between the 2-carbon and the one next to it. Compounds with two enolizable β-dicarbonyl rings show characteristic breakdown patterns due to the ease with which enolizable protons take part in rearrangements.
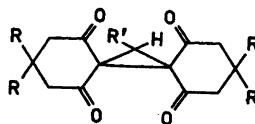
The mass spectra of cyclic β-diketones have recently been investigated by several groups.[1-5] During our studies on oxidative coupling of β-dicarbonyl compounds with iron(III) hexacyanoferrate(III) [6-9] we obtained a number of 1,3-cyclohexanedione and dimedone derivatives (Fig. 1). They all showed well-defined spectra on electron impact from which the fragmentation patterns could be established and used for the structural elucidation of new compounds of this type.

Methylene-bis-1,3-cyclohexanedione *(10)* on treatment with a solution containing iron(III) hexacyanoferrate(III) undergoes intramolecular oxidative carbon-oxygen and carbon-carbon coupling giving a mixture of the enol ether *21* and the isomeric dispiro cyclopropane derivative *18*.[7] From analogous experiments with dimedone derivatives of lower aldehydes *(11—14)*, four other coupling products *19, 20, 22,* and *23* have been isolated.[8,9]
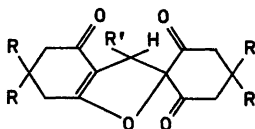
In order to investigate how a lengthening of the carbon chain between the cyclohexanedione rings would influence the course of the oxidative coupling reaction, the derivatives *15, 16,* and *17* have been prepared.[8,10] On reaction with iron(III) hexacyanoferrate(III), compound *16* affords several products, two of which (*24* and *25*) have been isolated. Compound *24* is obviously formed *via* carbon-oxygen coupling, while the γ-lactone *25* probably results from oxidative elimination of one dimedone ring in *16* with the formation of a carboxylic acid intermediate, undergoing oxidative cyclisation to *25*. Similar
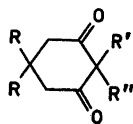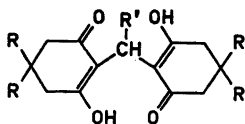
1. R=R′=R″=H
2. R=CH₃, R′=R″=H
3. R=R′=H, R″=CH₃
4. R=R′=CH₃, R″=H
5. R=R′=R″=CH₃
6. R=R′=H, R″=C₆H₅CH₂
7. R=CH₃, R′=H, R″=C₆H₅CH₂
8. R=H, R′=R″=C₆H₅CH₂
9. R=CH₃, R′=R″=C₆H₅CH₂

10. R=R′=H
11. R=CH₃, R′=H
12. R=R′=CH₃
13. R=CH₃, R′=C₂H₅
14. R=CH₃, R′=CH₃CO
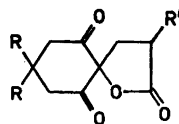
15. R=R′=H
16. R=CH₃, R′=H
17. R=CH₃, R′=C₂H₅

18. R=R′=H
19. R=CH₃, R′=C₂H₅
20. R=CH₃, R′=CH₃CO

21. R=R′=H
22. R=CH₃, R′=H
23. R=CH₃, R′=CH₃CO

24. R=CH₃

25. R=CH₃, R′=H
26. R=CH₃, R′=C₂H₅
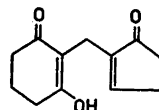
27.

Fig. 1.

reactions have been observed with some aromatic compounds.[11] The homologue *26* was obtained from *17* under the same conditions.

The compounds studied here (*1—27*, Fig. 1) which include some simple model compounds (*1—9*) give well-defined molecular peaks.

As detailed labelling experiments have not been performed, the various structures attributed to the fragment ions (Schemes 1—8) cannot be considered

as unambiguously established and are thus employed in an illustrative manner as an aid to generalisations suitable for use in structural elucidation. The use of numbers and Greek letters referring to various carbon atoms in compounds *1—27* is defined in Fig. 1, compounds *15—17*.

Fragmentation patterns for the enolizable derivatives, which closely resemble those from related 2,2-disubstituted derivatives, have generally been attributed to their keto forms. As indicated in Refs. 2 and 3 the only degradation which should preferentially be assigned to the enol form is the loss of $C_2H_4(R=H)$ or $C_4H_8(R=CH_3)$ from the molecular ion as outlined in Scheme 4.2, alternatively formulated as a retro Diels-Alder process.

The characteristic fragmentation patterns found for this group of compounds often arise from the initial α-cleavage at the keto-group, although specific substituents may alter this situation. The α-cleavage of cyclic β-diketones can occur in two ways with formation of ion radical a or b (Scheme 1).

Scheme 1.
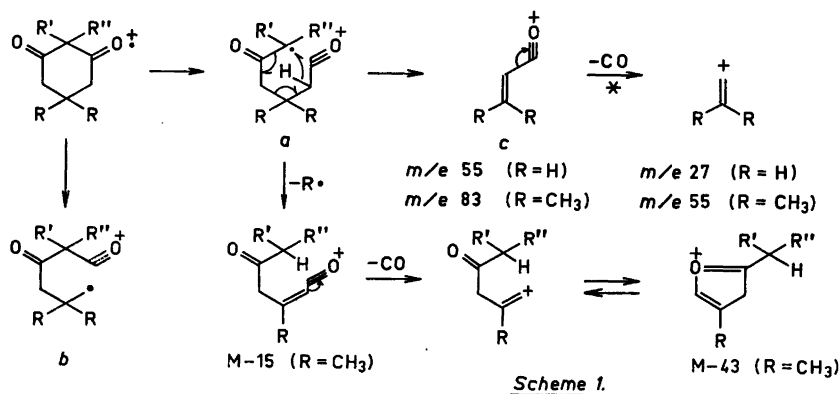
The cleavage of the 1—6 bond would give primary alkyl radical b. The alternative 1—2 bond rupture gives rise to radical a which is either primary, secondary, or tertiary depending upon the nature of R' and R''. The ion radical a is furthermore stabilized by resonance. Russell and Lokensgard [12] have, however, recently emphasized the relative unimportance of such a resonance interaction. From the evidence above it might be predicted that the formation of ion radical a would be favoured although with decreasing preference in the usual order tertiary>secondary>primary.

The most characteristic fragmentation of this group of compounds,[1-5] outlined in Scheme 1 is the formation of ion a followed by a subsequent hydrogen radical transfer and homolytic bond rupture to yield ketene, a radical and an ion c, m/e 55 (R=H) or m/e 83 (R=CH_3). Ion c often accounts for the base peak. Further decomposition of ion c with loss of CO gives rise to low intensity peaks at m/e 27 (R=H) and m/e 55 (R=CH_3), respectively.

The relative abundance of ion c seems to be highly dependent on the nature of the substituents R' and R'' in the 2-position as well as on the substituent R in the 5-position. As already observed by Vandewalle et al.,[2] the two methyl groups in the 5-position of dimedone derivatives greatly enhance

the stability of the fragment m/e 83 compared with the unsubstituted fragment m/e 55.

The influence of the substituents in the 2-position is illustrated by the spectra of dimedone (2), 2-methyldimedone (4), and 2,2-dimethyldimedone (5) where the relative importance of the fragment m/e 83 is lowest for 2 and highest for 5 (see Refs. 2 and 4). In the mass spectra of the spiro compounds 24, 25, and 26 in which one of the substituents in the 2-position is an oxy-function, the fragment m/e 83 is the base peak and the only fragment with an intensity of more than 25 % of that peak is the molecular ion. The same principal pattern is also found in the spectrum of 2-chloro-2-methyldimedone (Ref. 2) where the second most abundant fragment m/e 90 accounts for only 21 % relative intensity of the base peak, m/e 83. These results, at least for the dimedone derivatives, indicate that the α-cleavage of the 1,2-bond yielding ion a and its further breakdown to ion c (m/e 83) is favoured by substituents in the 2-position which are able to stabilize a free radical of type a. The stabilization is most important when the functional substituent is electron supplying, e.g. alkoxy.[13,14] Obviously the fragmentation process yielding ion c has diagnostic potential for structural elucidation.

The preference for cleavage of ion a to give ion c compared to the alternative mode outlined in Scheme 1 with loss of the radical R· is clearly apparent, although the latter is significant for dimedone derivatives which furnish the species M—15 and M—43, accounting for peaks up to 13 % relative intensity. No or only small peaks at M—1 can be observed in the spectra of 1,3-cyclohexanedione derivatives (R=H).

Another important pathway of disintegration starts with the elimination of CO from the molecular ion. Brown and Djerassi [15] have reviewed the subject

Fig. 2

Fig. 3

Fig. 4
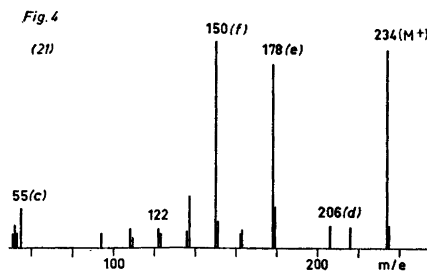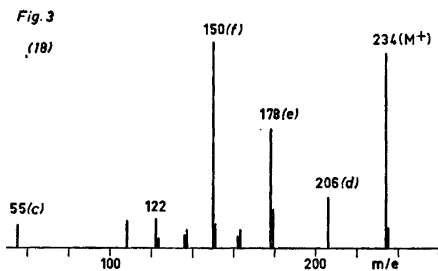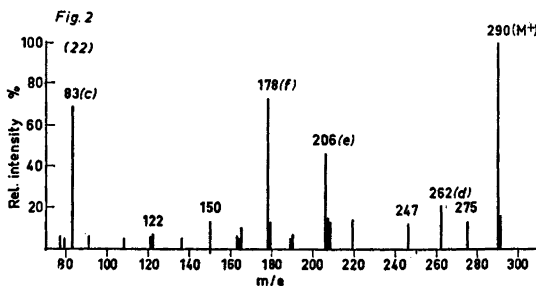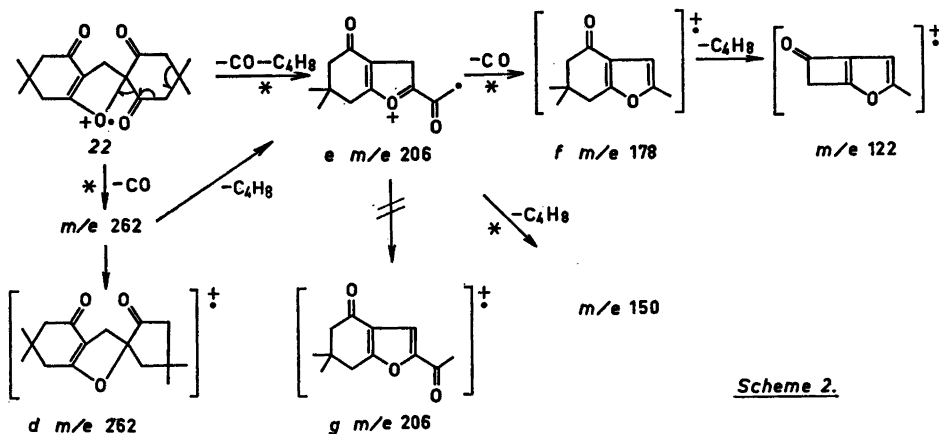
Scheme 2.

of CO elimination from ring compounds but have not discussed the decarbonylation process in cyclic β-diketones with the exception of some 1,3-cyclobutanedione derivatives. Goto et al.[1] have shown that dimedone and 2-ethyldimedone loose CO on electron impact. Vandewalle et al.[2] who also studied a number of other simple β-diketo derivatives, claim that such a process leads to low-abundant ions. For several substances studied by us, however, the elimination of CO and subsequent decomposition yields high intensity peaks, which is demonstrated by the mass spectra of the closely related derivatives 18, 21, and 22. (Figs. 2, 3, 4, and Scheme 2). Also in the spectra of 2-benzyl-1,3-cyclohexanedione (6), 2-benzyldimedone (7) and the cyclopentenone deriva-

tive *27* the intensity of the peaks due to initial CO elimination is greatly enhanced (Figs. 5, 6, 7, and Scheme 4).
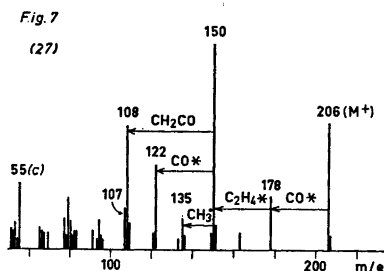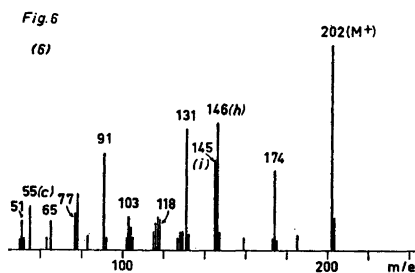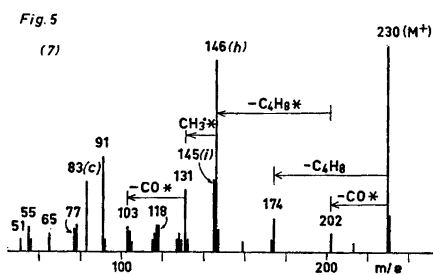
In the spectrum of *22* (Fig. 2) two main disintegration pathways are demonstrated. In the first the molecular ion decomposes according to the pathways outlined in Scheme 1 and gives rise to the peaks m/e 83 (69 %), m/e 55 (16 %), $m/e$ 275 (M—15, 13 %), and m/e 247 (M—43, 12 %, $C_{15}H_{19}O_3^+$).* Peaks corresponding to the last two are not present in the spectra of the 1,3-cyclohexanedione derivates *18* and *21*.

The second major breakdown yields three prominent fragments, m/e 262 (21 %, $C_{16}H_{22}O_3^+$), m/e 206 (46 %, $C_{12}H_{14}O_3^+$), and m/e 178 (73 %, $C_{11}H_{14}O_2^+$). The fragmentation process, outlined in Scheme 2, starts with the elimination of CO to yield m/e 262, which might recyclise to the cyclopentanone ion radical d (see below). Alternatively it undergoes subsequent elimination of 2-methylpropene (C_4H_8) to form ion radical e. The presence of a metastable peak at m/e $206^2/290 = 146.3$ constitutes certain but not conclusive evidence that ion e is derived directly from the molecular ion by simultaneous loss of CO and C_4H_8.[16] Ion e then eliminates a second molecule of CO to form m/e 178. Evidently the formation of the fragment M—2CO—C_4H_8 (m/e 178) is strongly favoured. An explanation to account for such behaviour is the formulation of this fragment as an ion radical f of a furan derivative. Ion radical f is very likely formed *via* a cyclopropanone ion radical intermediate which eliminates CO and undergoes subsequent allylic rearrangement. Cyclopropanone ion intermediates have earlier been suggested in the electron induced breakdown of, *e.g.*, 1,3-cyclobutanedione derivatives.[17] Both ion radicals e and f can also undergo successive loss of C_4H_8 from the cyclohexenone ring to yield m/e 150 and m/e 122, respectively.[5]

The alternative mode of degradation of ion radical e involving a hydrogen transfer to yield ion radical g can be regarded as less important solely from mechanistic considerations since the configuration of the five-membered heterocyclic ring makes a hydrogen atom transfer unfavourable. The absence of strong peaks at M—CO—C_4H_8—CH_3 and m/e 43 (CH_3CO^+) is in agreement with this conclusion.[18]

When run on an instrument with a heated inlet system at high temperatures, ($\sim$150°C), compounds *18* and *21* give similar mass spectra (Figs. 3 and 4) with strong peaks at M—28, M—56, and M—84, apparently derived *via* the pathways outlined in Scheme 2. A plausible explanation for the close similarity in fragmentation patterns of the isomers *18* and *21*, is the assumption that *18* rearranges to the thermally more stable spiro enol ether *21*. This assumption is supported by the observation that the spectrum of *18* changes significantly when run at low temperature and using a direct inlet system. Under such circumstances the intensity of the peak at m/e 192 not present in the spectrum of *21* increases from 3 % to 46 %. This fragment is presumably formed by the loss of ketene from the molecular ion, a process which is also important in the breakdown of the compounds *20* and *23* (see below).

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* The compositions of the fragments, for which formulae are given in the text, have been verified by high resolution measurements.
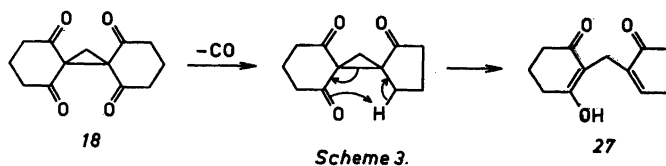
Scheme 3.

The tetraketone *18* as mentioned above decarbonylates not only on electron impact but also on heating.[7] Cautious, short-path distillation at 140°C, 1.5×10^{-4} mm yields the cyclopentenone derivative *27*, probably formed as indicated in Scheme 3. This thermally induced process seems to have few reported analogies among the β-diketones.[25] The reaction gives certain support for a cyclopentanone structure for the M—CO fragments (Scheme 2) formed by many cyclic β-diketones on electron impact.

2-Benzyldimedone (Fig. 5) referred to above breaks down by three main routes (Scheme 4). The most characteristic pathway, as has already been pointed out, starts with elimination of CO to yield m/e 202 which in turn looses C_4H_8 and gives rise to m/e 146 (86 %, $C_{10}H_{10}O^+$) formulated as the


Scheme 4.
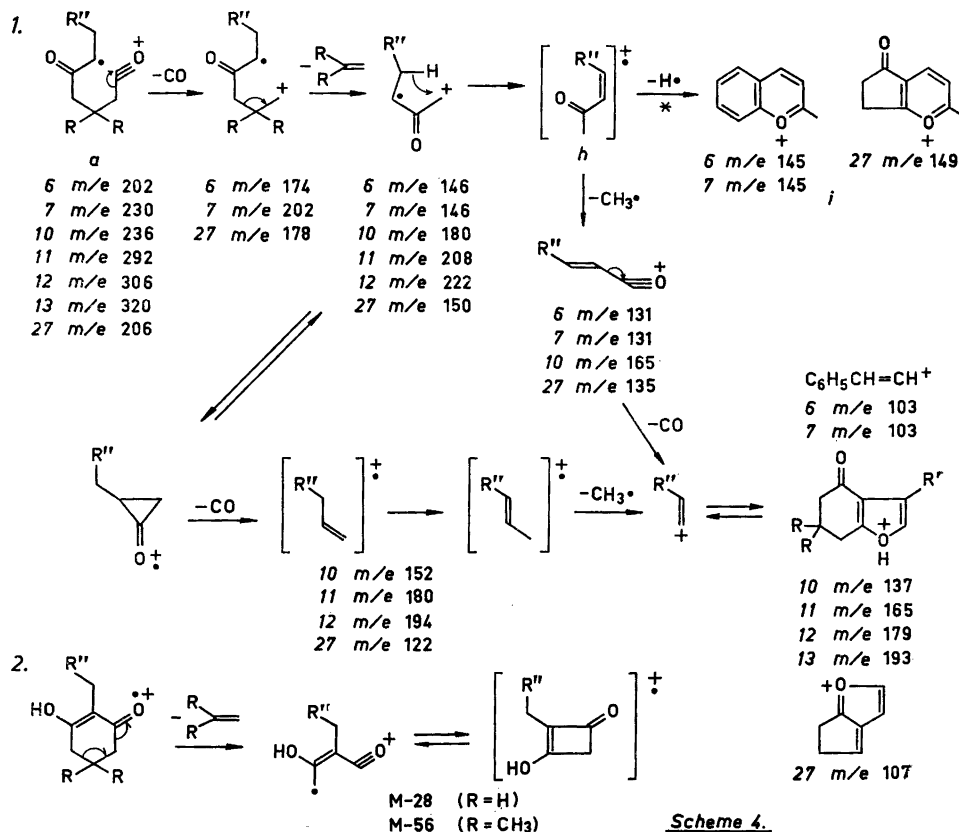
resonance stabilized ion radical h. The structure of the fragment ion h is supported by its further breakdown to m/e 131, m/e 103, m/e 77, and m/e 51, which is closely related to the behaviour of acetophenone and the methyl ester of cinnamic acid on electron impact.[19]

The origin of the fragment m/e 118 ($C_8H_6O^+$) is questionable due to the absence of well-defined metastable peaks resulting in the formation of this fragment. A breakdown involving loss of CO from m/e 146 analogous to the fragmentation outlined in Scheme 2 seems to be ruled out by the composition of the fragment ion.

2-Benzyldimedone also exhibits the typical degradation [2,3] attributed to the enol form with loss of C_4H_8 from the molecular ion to yield m/e 174 (15 %). High resolution measurements have shown that 60 % of the peak has the composition $C_{11}H_{10}O_2^+$. Other strong fragments are found at m/e 91 and m/e 65, typical for benzylic substitution.[20] The pronounced fragment at m/e 145 ($C_{10}H_9O^+$) is presumably formed through loss of a hydrogen atom from the aromatic ring in ion h (metastable peak at m/e 144.0) yielding a favourable oxonium ion i.[19]

The origin of the m/e 145 fragment in the spectra of the 2,2-dibenzyl derivatives 8 and 9 (Table 1) is undoubtedly different. Besides the base peak at m/e 91 (benzylic substitution) these derivatives give spectra which show largely one main degradative pathway (Scheme 5) initiated by loss of a benzyl

Scheme 5.
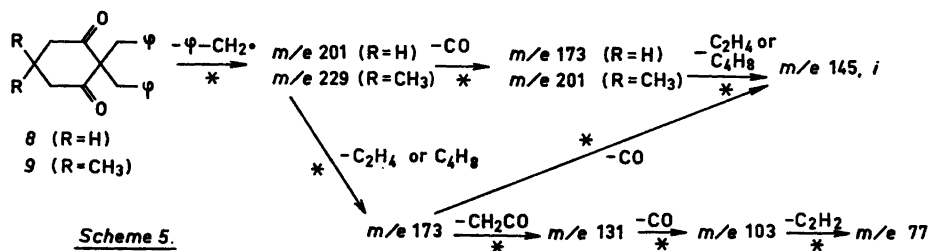
radical with charge retention on the diketo fragment, giving rise to m/e 201 (R=H) and m/e 229 (R=CH$_3$), respectively. The subsequent degradation may follow two paths. The first path starts with the loss of C_2H_4 (R=H) or C_4H_8(R=CH$_3$) leading to m/e 173 which in turn can loose either CO to give m/e 145 or ketene to yield m/e 131. The second path also leads to m/e 145, but starts with the loss of CO followed by elimination of C_2H_4 or C_4H_8.

The fragmentation process of 2-benzyl-1,3-cyclohexanedione (Fig. 6) is analogous to that of 2-benzyldimedone. The cyclopentenone derivative 27 also exhibits the fragmentation pattern outlined in Scheme 4.1 (Fig. 7). The fragment m/e 108, presumably formed through loss of ketene from m/e 150 is, however, surprisingly abundant although the corresponding fragment is present to a small extent in the spectra of, for example, compounds 18, 21, and 22.

From the results presented above it may be concluded that the relative abundance of the fragment ions M—CO, M—CO—C_2H_4 (R=H) or M—CO—C_4H_8 (R=CH$_3$) and fragments produced on subsequent degradation

Table 1. Principal mass spectral peaks of compounds *8, 9, 14, 17, 19, 20, 24, 25,* and *26.* All ions having a relative intensity of 5 % of the base peak or more are given in the table. The peaks are not corrected for isotopic distribution.
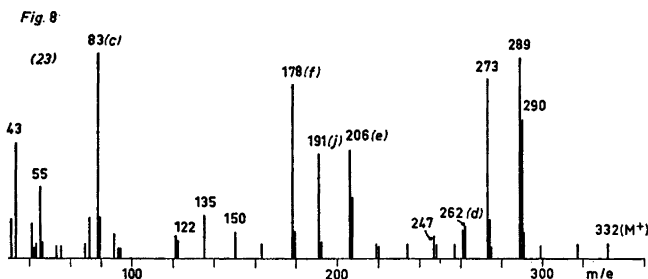
8. 41(6); 42(9); 55(12); 65(14); 77(7); 91(100); 92(10); 103(7); 115(13); 117(5); 131(7); 141(6); 145(22); 173(32); 174(5); 201(55); 202(9); 221(5); 292(16).

9. 41(12); 44(5); 55(18); 56(7); 65(14); 77(8); 83(58); 91(100); 92(10); 103(10); 115(14); 116(5); 117(7); 131(8); 145(26); 173(18); 201(17); 229(84); 230(15); 320(20).

14. 41(23); 42(10); 43(51); 53(16); 55(17); 56(23); 69(9); 70(10); 82(8); 83(100); 84(15); 95(6); 97(15); 98(8); 109(11); 110(15); 111(6); 112(14); 123(25); 124(12); 125(7); 137(8); 140(16); 151(8); 152(12); 154(5); 162(9); 179(10); 193(8); 194(20); 218(5); 273(22); 274(6); 291(29); 292(15); 301(11); 316(18); 334(2).

17. 41(7); 43(7); 55(8); 69(7); 83(12); 107(8); 108(21); 125(5); 141(8); 154(100); 155(10); 165(6); 167(9); 181(26); 182(29); 195(15); 263(5); 287(5); 334(32); 335(5).

19. 41(11); 43(7); 55(15); 56(5); 79(8); 83(100); 84(7); 191(13); 193(5); 206(7); 207(10); 217(11); 234(11); 247(6); 259(12); 261(11); 289(23); 290(10); 300(7); 318(10).

20. 41(28); 42(5); 43(62); 51(6); 53(9); 55(32); 56(11); 69(9); 77(5); 79(6); 83(100); 84(7); 91(6); 122(5); 150(5); 165(5); 178(10); 191(24); 206(6); 207(10); 220(5); 233(5); 247(36); 248(9); 249(10); 289(20); 290(5); 332(5).

24. 41(17); 43(8); 52(5); 53(6); 54(6); 55(24); 56(8); 66(7); 67(5); 68(7); 69(7); 83(100); 84(9); 109(5); 122(5); 137(6); 152(8); 165(11); 178(6); 206(6); 221(5); 222(12); 304(38).

25. 41(17); 42(8); 43(5); 53(5); 55(20); 56(25); 70(7); 83(100); 84(10); 210(7).

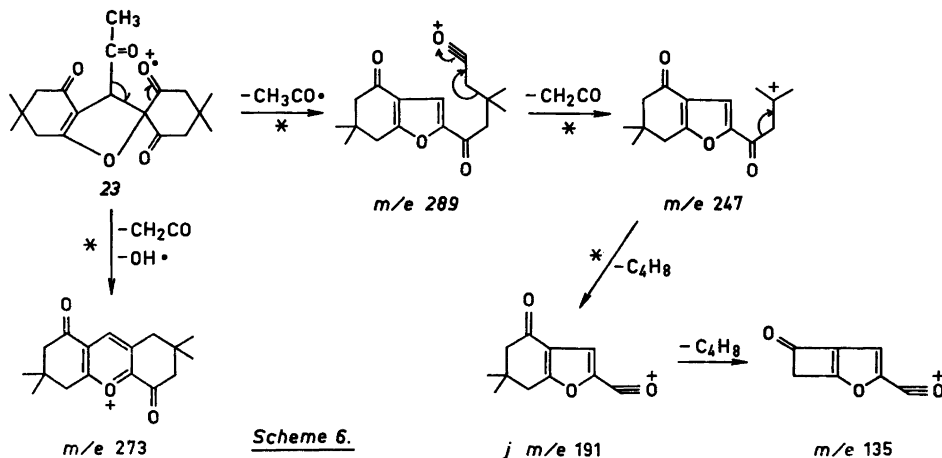*26.* 41(8); 44(5); 55(10); 56(9); 83(100); 84(7); 238(29).

is highly dependent on the nature of the substituents in the 2-position of the 1,3-cyclohexanedione ring. A substituent able to stabilize a double bond between the 2-carbon and the α-carbon strongly favours this type of degradation. In agreement with this observation, compound *24,* closely related to *22,* and the spirolactones *25* and *26* show no or very little sign of the fragmentation patterns outlined in Schemes 2 and 4.

Introduction of a substituent R' on the methylene group between the two six-membered rings in the spiro derivatives of type *18* and *21* changes the fragmentation pattern significantly.

The carbon-carbon and the carbon-oxygen coupling products *20* and *23,* respectively, derived from *14* [9] show essentially the same type of breakdown although there are variations in the intensity of the peaks (Fig. 8; Table 1).

The fragmentation illustrated by the spectrum of *23* (Fig. 8), outlined in Scheme 6, starts with loss of an acetyl radical to give ion *m/e* 289. This fragment apparently would not favour a breakdown according to Scheme 2. Instead the further decomposition with elimination of ketene (*m/e* 247) and

Fig. 8

CH₃
C=O

−CH₃CO·

*

−CH₂CO

*

23

m/e 289

m/e 247

−CH₂CO
−OH·

*

*−C₄H₈

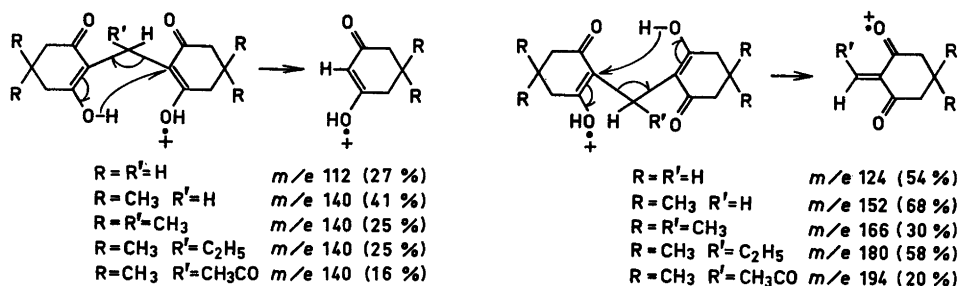−C₄H₈

m/e 273

Scheme 6.

j m/e 191

m/e 135

successive loss of 2-methylpropene (C_4H_8) yields a highly stabilized ion *j*, m/e 191.

A second important degradative pathway starts with loss of ketene to yield ion radical m/e 290, which shows a subsequent decomposition similar to that of the molecular ion of compound *22* (Scheme 2), yielding abundant fragments at m/e 262, m/e 206, and m/e 178.

The strong peak at m/e 273 formed from the molecular ion presumably *via* simultaneous loss of ketene and a hydroxyl radical, seems to be specific for the carbon-oxygen coupling product. An explanation to account for the abundance of this fragment in *23* is its formulation as a stabilized aromatic pyrylium ion. The fragment m/e 273 is almost negligible in the spectrum of the carbon-carbon coupling product *20* (Table 1) although an increase in sampling temperature leads to a spectrum with a closer resemblance to that of *23* including a considerable peak at m/e 273. This supports the observation that the carbon-carbon coupling products rearrange to the thermally more stable carbon-oxygen coupling isomers (*cf.* *18* and *21*).

If R′ is an ethyl group, as in *19*, the degradation paths are slightly changed. The initial loss of R′· yielding m/e 289 and subsequent decomposition to m/e 247 and m/e 191 is of primary importance (Table 1). No breakdown initiated by the loss of R′ as ethene can be found. However, the fragmentation process starting with the loss of CO to yield m/e 290 followed by elimination of C_4H_8 to give m/e 234 according to Scheme 2 or loss of an ethyl radical to give m/e 261 is observed.

Compounds with two enolizable *β*-diketo ring systems often exhibit highly characteristic fragmentation patterns, which appears to be due to the ease with which the enolizable hydrogen atom takes part in rearrangements. The mechanism recently suggested for the McLafferty rearrangement [21] clearly indicates that the nature of the radical species produced at the carbon from which hydrogen is transferred will strongly influence the feasibility of this mode of fragmentation, *i.e.* the more a radical in that position can be

| R = R′= H | m/e 112 (27 %) | | R = R′= H | m/e 124 (54 %) |
R = CH₃ R′= H	m/e 140 (41 %)		R = CH₃ R′= H	m/e 152 (68 %)
R = R′= CH₃	m/e 140 (25 %)		R = R′= CH₃	m/e 166 (30 %)
R = CH₃ R′= C₂H₅	m/e 140 (25 %)		R = CH₃ R′= C₂H₅	m/e 180 (58 %)
R = CH₃ R′= CH₃CO	m/e 140 (16 %)		R = CH₃ R′= CH₃CO	m/e 194 (20 %)

Scheme 7.

stabilized the more abundant will be the fragment resulting from such a process.

The 1,3-cyclohexanedione and dimedone derivatives of aldehydes constitute an important group of compounds of this type, and the mass spectra of some of these derivatives (*10—14*) have been investigated. Their general fragmentation pattern, summarized in Scheme 7, is demonstrated in the spectrum of methylene-bis-1,3-cyclohexanedione (*10*) (Fig. 9). In one sequence the molecular ion breaks down to m/e 112 ($C_6H_8O_2^+$) through a McLafferty rearrangement. Deuterium labelling of the enolizable protons leads to a shift of the peak by two mass units and provides support for the assumed mechanism. The fragment m/e 112 is formulated as a 1,3-cyclohexanedione ion radical, which is consistent with the appearance of the lower part of the spectrum (*cf.* Fig. 9 and Ref. 2, Fig. 2).

The second major fragmentation also involves a McLafferty rearrangement yielding an ion radical m/e 124 ($C_7H_8O_2^+$) which undergoes subsequent degradation to, *e.g.*, m/e 96 and m/e 68. Deuterium labelling of the enolizable protons of *10* does not produce a change in the peak at m/e 124.

Finally, methylene-bis-1,3-cyclohexanedione fulfills the requirements to give a breakdown according to Scheme 4.1, resulting in peaks, *e.g.* at m/e 137 and m/e 152 ($C_9H_{12}O_2^+$). The breakdown of the other aldehyde derivatives is analogous to that of methylene-bis-1,3-cyclohexanedione although the intensity of the peaks is variable (*cf.* Fig. 10, Table 1). The derivatives *13* and *14* also show an additional breakdown with loss of the radical R′· from the molecular ion as already indicated in Ref. 5.
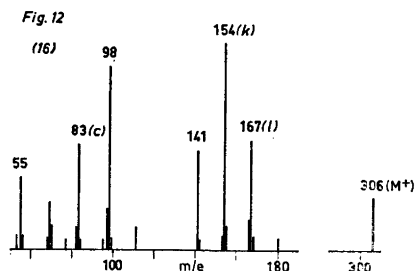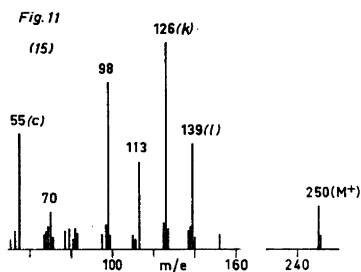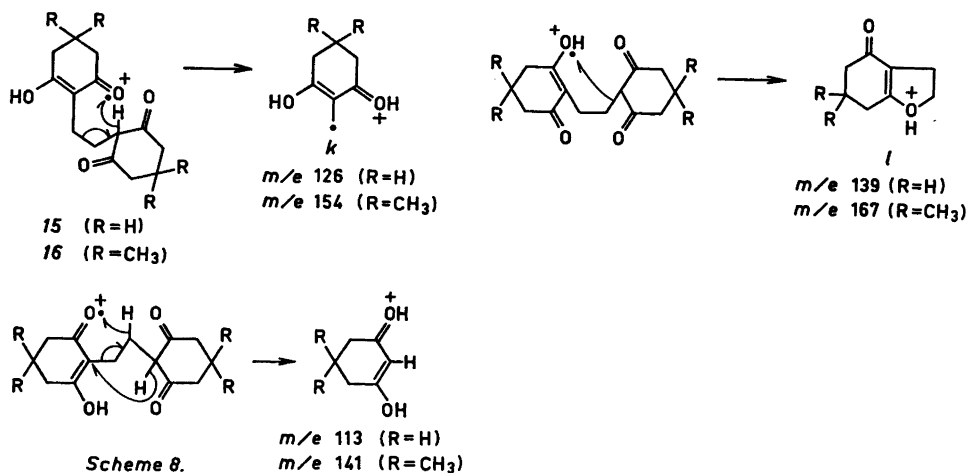
Fig. 9

Fig. 10
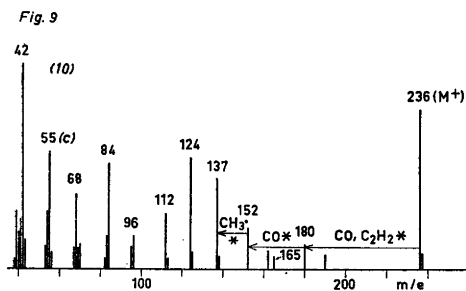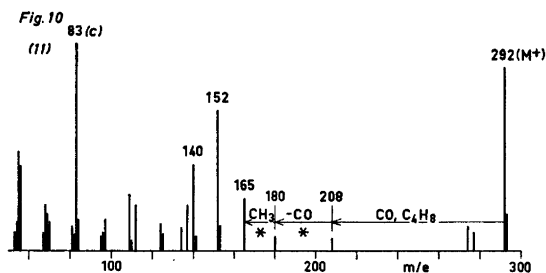
Contrary to the "methylene-bis-derivatives" compounds *15, 16,* and *17,* containing a two carbon chain between the rings, do not fragmentize in the manner indicated in Scheme 7. Some of the fragments observed here also appear in the spectrum of 2-butyl-1,3-cyclohexanedione studied by Vandewalle, Schamp and De Wilde.[3]

The base peak in the spectrum of *15, 16,* and *17* (m/e 126, R=H; m/e 154, R=CH$_3$) (Figs. 11, 12; Table 1) is probably formed through an initial transfer of the enolizable hydrogen atom in a seven-membered transition state, followed by homolytic bond breakage leading to ion *k* (Scheme 8). An alternative mechanism suggested in Ref. 2 with transfer of the enolizable hydrogen atom to the α-carbon through a four-membered intermediate yielding a 2-methyl-1,3-cyclohexanedione ion radical seems to be improbable as it involves an elimination reaction without participation of the electron deficient center.[22]

Other typical fragments are m/e 139 *(15),* m/e 167 *(16)* and m/e 195 *(17)* presumably formed by $\beta,2'$-bond cleavage to yield a five-membered ring ion *l.* Reactions initiated by cleavage of the α,β-bond are less important. Compounds *15* and *16* also give rise to abundant peaks at m/e 113 (R=H) and m/e 141 (R=CH$_3$), evidently formed (Ref. 3) by a double rearrangement resulting in a protonated cyclohexanedione, and a neutral fragment with considerable stability. The process is analogous to the double rearrangement occurring in *N*-alkyl-succinimides.[23] Deuteration with CH$_3$OD of *16* supports the mechanisms suggested for the breakdown to m/e 154, and m/e 141 which are shifted by two mass units and m/e 167 which is shifted by one mass unit. Compound *17* also gives significant peaks at m/e 181 (26 %) and m/e 182 (29 %). The fragmentation pathway to m/e 182 is analogous to the formation of ion *k* (Scheme 8).

Fig. 11

Fig. 12

m/e 126 (R=H)
m/e 154 (R=CH₃)

15 (R=H)
16 (R=CH₃)

k

l

m/e 139 (R=H)
m/e 167 (R=CH₃)

Scheme 8.

m/e 113 (R=H)
m/e 141 (R=CH₃)

EXPERIMENTAL

The mass spectra were recorded on a 180° instrument with an all glass heated inlet system at temperatures around 150°C or on an LKB 9000 instrument using a direct inlet system at temperatures varying from 20°C to 150°C. The ionization energy was 70 eV. Exact mass measurements were performed with the LKB 9000 instrument with a resolution of 1200 to 1500.[24]

Compounds 1—15 were prepared according to methods described in literature. Compounds 18, 21, 22, and 27 were synthesised as described in Ref. 7. The remaining compounds, not previously described in literature, were prepared in this laboratory.[8,9] The structures have been verified by IR-, UV-, and NMR-measurements.

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