# Studies in Mass Spectrometry. IX.[1] Mass Spectra of β-Diketones

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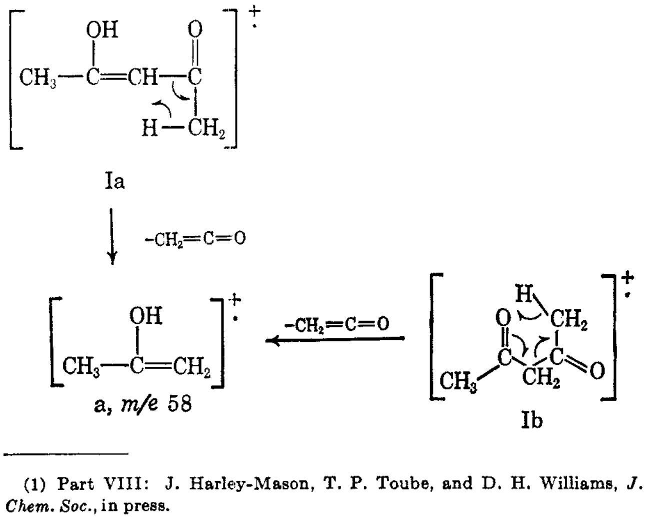
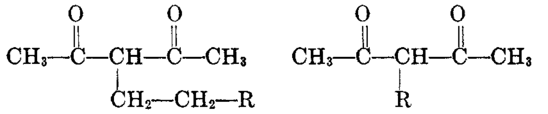
β-Diketones break down in a well-defined manner upon electron impact. The spectra have uncovered examples of methyl and phenyl migrations, but are most noteworthy for the elimination of ketene from the acetyl group of a β-diketone with the formation of a charged enolate, the further composition of which is dependent upon the nature of any alkyl substituents in the molecule.

The only mass spectra of β-diketones which appear to have been discussed are those of dimedone and ethyl dimedone.[2] In view of the importance of β-diketones as synthetic intermediates, we have undertaken, in addition to our examination of β-keto esters[3] and diethyl malonates,[4] a study of the mass spectra of representative members (I–XV) of this class of compounds; the results are summarized in Table I and Figures 1–5.

The mass spectrum (Figure 1) of the parent compound, acetylacetone (I), is noteworthy for the presence of an *m/e* 72 ion, which arises from the loss of carbon monoxide from the molecular ion [as established by high-resolution measurements and the spectrum (see Table I) of 3,3-$d_2$-pentane-2,4-dione (Ic)]. This process necessitates a methyl migration, substantiated examples of which are very few in mass spectrometry.[5] Other fragmentations are summarized in Figure 1. It will be seen subsequently that fragments formed by elimination of ketene from the molecular ion of β-diketones are best represented as the enol (a, *m/e* 58, in the present instance). Such an enol may be formed either by hydrogen rearrangement to carbon in the enol form (Ia → a) or hydrogen rearrangement to oxygen in the diketo form (Ib → a). By analogy to the McLafferty rearrangement,[6] the latter representation seems more plausible and is employed throughout the following discussion.



All the simple C-alkylacetylacetones examined (II–VI) afford low abundance M − $CH_3$, M − $H_2O$, and M − $CH_3$ − $H_2O$ ions in the high mass regions of their spectra and abundant acetyl ions at *m/e* 43. In those cases where the alkyl substituent is a saturated hydrocarbon chain of two or more carbon atoms (II–IV), the two main decomposition sequences summarized in Scheme I and Scheme II provide a self-consistent rationale for the formation of most of the abundant ions in the spectra.

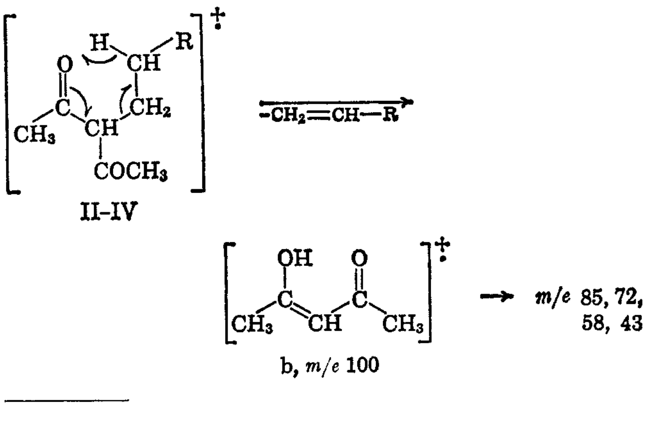


II, R = H
III, R = $CH_2CH_3$
IV, R = $CH(CH_3)_2$

V, R = $CH_2$-CH=$CH_2$
VI, R = $CH_2$-$C_6H_5$
VIa, R = $CD_2$-$C_6H_5$

The behavior summarized in Schemes I and II may be illustrated by reference to the spectrum (Figure 2) of 3-*n*-butylpentane-2,4-dione (III). Elimination of the *n*-butyl substituent, most plausibly as but-1-ene, through the McLafferty rearrangement,[6] can afford b (*m/e* 100); b is the enol form of the acetylacetone molecular ion and may accordingly decompose to *m/e* 85 (25% $C_4H_5O_2^+$), *m/e* 72, *m/e* 58, and *m/e* 43 (90% $CH_3C{\equiv}O^+$) as indicated in Figure 1. Alternatively, loss of ketene from the molecular ion gives an M − 42 species formulated as c [R = $C_2H_5$, *m/e* 114, 90% $C_7H_{14}O^+$ by high resolution (HR)]. Cleavage of the

SCHEME I



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[1] Part VIII: J. Harley-Mason, T. P. Toube, and D. H. Williams, *J. Chem. Soc.*, in press.

[2] T. Goto, A. Tatematsu, Y. Nakajima, and H. Tsuyama, *Tetrahedron Letters*, 757 (1965).

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

[4] J. H. Bowie, S.-O. Lawesson, G. Schroll, and D. H. Williams, *J. Org. Chem.*, in press.

[5] A. S. Newton and P. O. Strom, *J. Phys. Chem.*, **62**, 24 (1958); F. Komitsky, Jr., J. E. Gurst, and C. Djerassi, *J. Am. Chem. Soc.*, **87**, 1399 (1965); for related rearrangements, see also J. H. Bowie, R. Grigg, S.-O. Lawesson, G. Schroll, and D. H. Williams, *Chem. Commun.* (London), 403 (1965); D. R. Black, W. H. McFadden, and J. W. Corse, *J. Phys. Chem.*, **68**, 1237 (1964); W. H. McFadden, K. L. Stevens, S. Meyerson, G. J. Karabatsos, and C. E. Orzech, *J. Phys. Chem.*, **69**, 1742 (1965).

[6] F. W. McLafferty, "Determination of Organic Structures by Physical Methods," Vol. 2, Academic Press Inc., New York, N. Y., 1962, pp 129–149; S. Meyerson and J. D. McCollum, *Advan. Anal. Chem. Instr.*, **2**, 179 (1963).

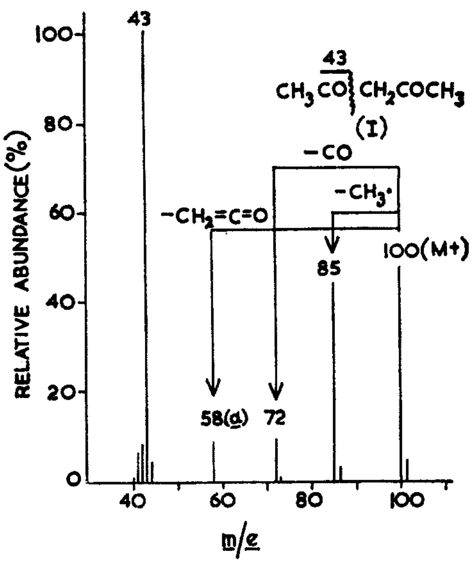


Figure 1.

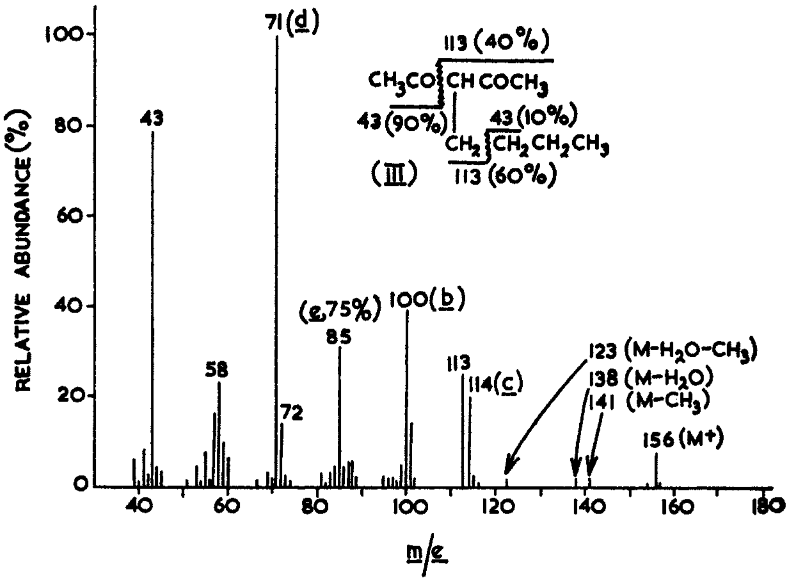
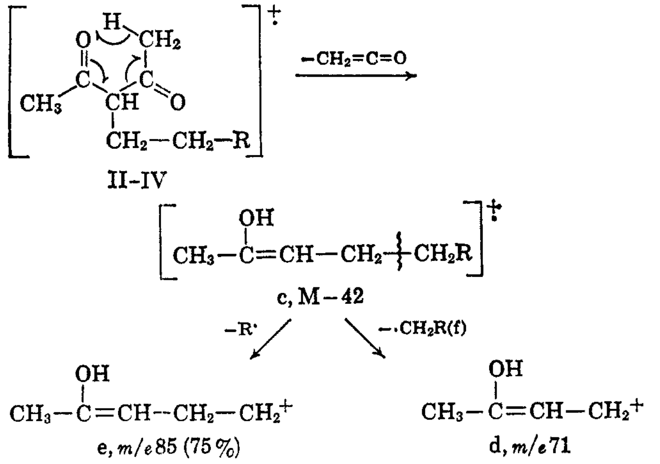


Figure 2.

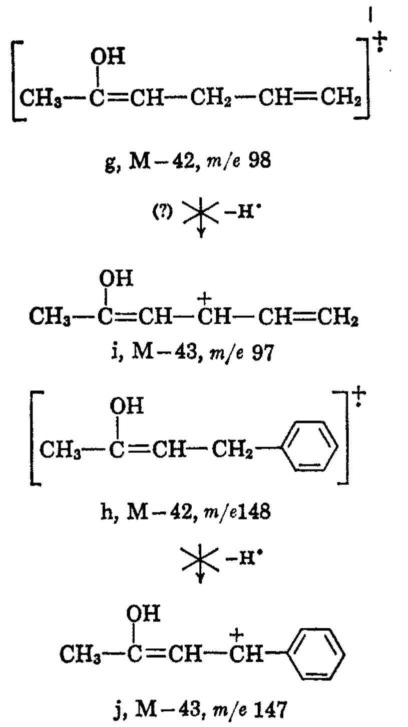
Scheme II



allylic bond in the enol c can then lead to the ion d (*m/e* 71, $C_4H_7O^+$ by HR) *via* elimination of the radical f (R = $C_2H_5$), although some homoallylic cleavage to give *m/e* 85, e, also occurs.

If the substituent is one which precludes the decomposition path indicated in Scheme I, as in the allyl derivative V and the benzyl derivative VI,[7] then the elimination of ketene to give an analog of c (Scheme II) is an important primary process. However, the M − 42 ions g and h (from V and VI, respectively) do not decompose by elimination of a vinyl radical, since either of these processes would necessitate the unfavorable cleavage of a vinylic bond. In principle, g and h (Scheme III) could each decompose by elision of a hydrogen radical to give stable M − 43 carbonium ions i and j (or its tropylium equivalent), respectively. However, the spectrum of the $d_2$-benzyl derivative VIa establishes that the abundant M − 43 ion in the spectrum of VI arises completely by simple loss of an intact acetyl group and not by the sequence $M^+ \rightarrow h \rightarrow j$. Evidently, the relatively large amount of energy required to eliminate a hydrogen radical is not completely offset by the favorable nature of the hypothetical carbonium ion j. By analogy, the M − 43 ion from the allyl derivative V is probably also derived by direct loss of an acetyl radical and not *via* the sequence V → g → i. Both the M − 43 ions from V and VI decompose further by elimination of water to *m/e* 79 and *m/e* 129, respectively, as evidenced by appropriate metastable peaks.

Scheme III



The spectra of the benzoyloxyacetylacetones examined (VII-IX) (Scheme IV) all contain pronounced M − $CH_2{=}C{=}O$ ions (k, M − 42).[8] The formulation of k as an enol is consistent with, but not proved by,

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[7] The inhibition of γ-hydrogen rearrangement in the spectrum of the allyl derivative V is consistent with the observation of a similar effect in the spectrum of 4-methylhept-6-en-3-one [L. Ahlquist, R. Ryhage, E. Stenhagen, and E. von Sydow, *Arkiv Kemi*, **14**, 211 (1959)]. The effect has been discussed by S. Meyerson and L. C. Leitch in a paper presented at the A.S.T.M. Committee E-14 Annual Conference on Mass Spectrometry, St. Louis, Mo., May, 1965.

[8] Processes supported by the presence of an appropriate metastable peak are indicated by an asterisk (*).

TABLE I

MASS SPECTRA OF SOME β-DIKETONES[a]

| | Compd | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| m/e | Ic[b] | II | IV | V | VI | VIa | VII | VIII | IX | X | Xa[c] | XI | XII | XVa[d] |
| 39 | 12 | 6 | 8 | 5 | | 3 | | | | 11 | 6 | | | 5 |
| 40 | 9 | 8 | | | | 4 | | | | 4 | | | | |
| 41 | 8 | 6 | 14 | 6 | 3 | 3 | | | 2 | 5 | 4 | | | 7 |
| 42 | 21 | 100 | 4 | | | | | | | 10 | | | | |
| 43 | 100 | 16 | 100 | 100 | 56 | 100 | 13 | 13 | 9 | 57 | 23 | 22 | 12 | 7 |
| 44 | 37 | | | 2 | | 7 | | | | 5 | 11 | | | 15 |
| 45 | 5 | | | | | | | | | | | | | |
| 50 | | | | | | 4 | 3 | 3 | | 19 | 6 | 4 | 3 | 6 |
| 51 | | | | | | 7 | 8 | 8 | 3 | 48 | 19 | 14 | 8 | 17 |
| 52 | | | | | | 6 | | | | 6 | 4 | | | 5 |
| 53 | | 4 | 4 | 3 | | 4 | | | | | | | | |
| 55 | 4 | 5 | 10 | 4 | 3 | | | | | 5 | | 6 | | 5 |
| 56 | 4 | | 3 | | | | | | | | | 4 | | 4 |
| 57 | 4 | 4 | 3 | | | 4 | | | | | | | | 6 |
| 58 | 9 | 8 | 13 | | | | | | | | | | | |
| 59 | 14 | | 3 | | | | | | | | | | | |
| 60 | 6 | | | | | | | | | | | | | |
| 62 | | | | | 3 | | | | | 7 | | | | |
| 63 | | | | | | 5 | | | | 9 | | | | |
| 64 | | | | | | 4 | | | | 4 | | | | |
| 65 | | | | | 4 | 4 | | | | 11 | | | | |
| 66 | | | | | | 5 | | | | 4 | | | | |
| 67 | | 6 | | | | 7 | | | | 4 | | | | |
| 68 | | | 3 | | | | | | | | | | | |
| 69 | 3 | 5 | 15 | | | | | | | 75 | 18 | | | 18 |
| 70 | 3 | | 14 | | | | | | | 4 | 27 | | | 18 |
| 71 | | 69 | 60 | 2 | | | | | | | | | | |
| 72 | 7 | 6 | 6 | | | | | | | | | | | |
| 73 | 15 | | | | | | | | | | | | | |
| 74 | 7 | | | | | | | | | 8 | 6 | | | |
| 75 | | | | | | | | | | 8 | 6 | | | |
| 76 | | | | | | | | | | 8 | 6 | 4 | | 5 |
| 77 | | | | 2 | | 6 | 22 | 22 | 20 | 83 | 47 | 50 | 28 | 48 |
| 78 | | | | | 6 | 10 | 3 | 3 | 3 | 19 | 13 | 8 | 3 | 11 |
| 79 | | | | 3 | | 6 | | | | 5 | 5 | | | 5 |
| 80 | | | | | | 5 | | | | | | | | |
| 81 | | | 3 | | | 5 | | | | | | | 3 | |
| 83 | | | | 9 | | | | | | | | | | |
| 85 | 39 | 8 | 22 | | | | | | | 21 | 4 | | | |
| 86 | 74 | 42 | 4 | | | | | | | | 6 | | | |
| 87 | 38 | 3 | 3 | | | | | | | | 6 | | | |
| 88 | 3 | | 3 | | | | | | | | | | | |
| 89 | | | | | | | | | | 6 | | | | |
| 90 | | | | | | | | | | 4 | | | | |
| 91 | | | | | 28 | 5 | | | | 14 | 3 | | 4 | 5 |
| 92 | | | | | 3 | 9 | | | | | 5 | | | 4 |
| 93 | | | | | | 24 | | | | | 4 | | | 3 |
| 94 | | | | | | 5 | | | | | | | | |
| 95 | | 5 | 13 | | | 4 | | | | | | | | |
| 97 | | | | 20 | 4 | | | | | | | | 4 | |
| 98 | | | 3 | 10 | | 5 | | | | | | | | |
| 99 | | | 3 | | | 5 | | | | | | | | |
| 100 | 28 | 11 | 31 | | | | | | | | | | | |
| 101 | 58 | | 15 | | | | | | | | | | | |
| 102 | 32 | | | | | | | | | 5 | | | | |
| 103 | 3 | | | | 5 | | | | | 5 | | | | |
| 104 | | | | | 3 | 5 | | | | | | | | |
| 105 | | | | | | 8 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| 106 | | | | | | 6 | 9 | 11 | 9 | 9 | 11 | 17 | 9 | 12 |
| 107 | | | | 2 | | 22 | | | | | | | | |
| 108 | | | | | | 5 | | | | | | | | |
| 109 | | | | | | 4 | | | | | | | | |
| 110 | | | 26 | | | 8 | | | | | | | | |
| 111 | | 3 | 4 | | | | | | | | | | | |
| 113 | | 12 | 16 | | | | | | | | | | | |
| 115 | | | | | 3 | | | | | 5 | | 3 | | |
| 120 | | | | | | | | | | 7 | 5 | | | |
| 121 | | | | | | | | | | | 6 | | | 4 |

Table I (*Continued*)

| | Compd | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| m/e | Ic[b] | II | IV | V | VI | VIa | VII | VIII | IX | X | Xa[c] | XI | XII | XVa[d] |
| 122 | | | | | | | 3 | 3 | | | 7 | | | 4 |
| 125 | | | | 2 | | | | | | | | | | |
| 128 | | 13(M) | 11 | | 3 | 3 | | | | | | | | |
| 129 | | | | | 13 | 5 | | | | | | | | |
| 130 | | | | | 3 | 10 | | | | | | | | |
| 131 | | | | | 3 | 11 | | | | | | | | |
| 132 | | | | | 5 | | | | | | | | | |
| 133 | | | | | | 4 | | | | | | 26 | | |
| 134 | | | | | | | | | | | | 24 | | |
| 135 | | | | | | 8 | | | | | | | | |
| 136 | | | | | | | 3 | | | | | | | |
| 138 | | | | 2 | | | | | | | | | | |
| 140 | | | | 3(M) | | | | | | | | | | |
| 144 | | | | | | | | | | | | 6 | | |
| 145 | | | | | | | | | | | | 5 | | |
| 146 | | | | | 3 | | | | | | | | | |
| 147 | | | | | 100 | | | | | 65 | 11 | | | 19 |
| 148 | | | | | 13 | 3 | 3 | | | 8 | 28 | | | 33 |
| 149 | | | | | | 83 | | | | | 23 | 7 | | 17 |
| 150 | | | | | | 17 | | | | | 5 | 3 | | |
| 151 | | | | | | 3 | | | | | | | | |
| 154 | | | | | | | | | 3 | | | | | |
| 155 | | | 3 | | | | | | | | | | | |
| 159 | | | | | | | | | | | | | 16 | |
| 160 | | | | | | | | | | | | | 7 | |
| 161 | | | | | | | | | | 34 | 7 | 3 | | |
| 162 | | | | | | | | | | 74(M) | 22 | | | |
| 163 | | | | | | | | 5 | | 9 | 41 | | | |
| 164 | | | | | | | | | | | 34 | | | |
| 165 | | | | | | | | | | | 13 | | | |
| 166 | | | | | | | | | | | 4 | | | |
| 170 | | | 5(M) | | | | | | | | | | | |
| 172 | | | | | 3 | 2 | | | | | | | | |
| 173 | | | | | | 3 | | | | | | | | |
| 175 | | | | | 4 | | | | | | | 5 | | |
| 176 | | | | | | | | | | | | 8(M) | | |
| 177 | | | | | | 3 | | | | | | | | |
| 178 | | | | | | | 13 | | 2 | | | | | |
| 190 | | | | | 7(M) | | | | | | | | | |
| 191 | | | | | | | | | 2 | | | | | |
| 192 | | | | | | 6(M) | | | | | | | | |
| 201 | | | | | | | | | | | | | 3 | |
| 202 | | | | | | | | | | | | | 10(M) | |
| 206 | | | | | | | | 27 | | | | | | |
| 207 | | | | | | | | 3 | | | | | | 3 |
| 208 | | | | | | | | | | | | | | 3 |
| 209 | | | | | | | | | | | | | | 3 |
| 220 | | | | | | | 3(M) | | | | | | | |
| 223 | | | | | | | | | | | | | | 27 |
| 224 | | | | | | | | | | | | | | 76 |
| 225 | | | | | | | | | | | | | | 75 |
| 226 | | | | | | | | | | | | | | 33 |
| 227 | | | | | | | | | | | | | | 6 |
| 234 | | | | | | | | | 18 | | | | | |
| 235 | | | | | | | | | 2 | | | | | |
| 248 | | | | | | | | 2(M) | | | | | | |
| 276 | | | | | | | | | 2(M) | | | | | |

[a] All ions having an abundance of 2% or greater relative to the base peak (100%) are recorded in the table. [b] $d_0$ = 25; $d_1$ = 50; $d_2$ = 25%. [c] $d_0$ = 17; $d_1$ = 45; $d_2$ = 35; $d_3$ = 3%. [d] $d_0$ = 28; $d_1$ = 47; $d_2$ = 25%.

the facile cleavage of the allylic C–O bond in k to give *m/e* 105 (l, base peak for VII–IX) as evidenced by appropriate metastable peaks in the spectra of VIII and IX. Fragmentation sequences arising from the McLafferty rearrangement involving the alkyl chains of VIII and IX are not observed.

The spectra of benzoylacetone (X) and its alkyl derivatives XI–XIV, and of dibenzoylmethane (XV) (Figure 3), show several interesting features. First, those compounds (X, XV) which do not contain an alkyl substituent, or those (XI,XII) containing an alkyl substituent which cannot promote any facile

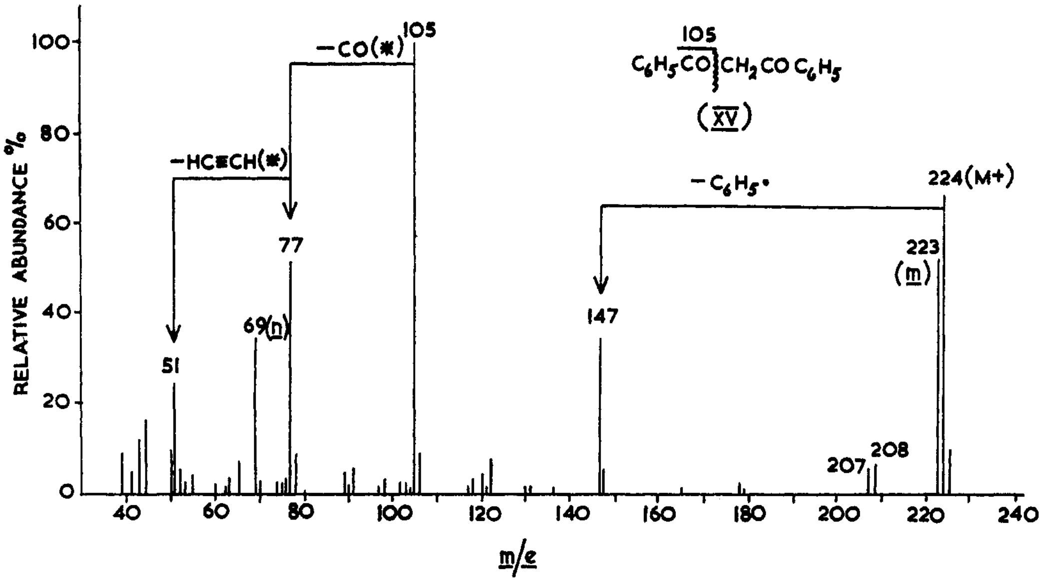


Figure 3.

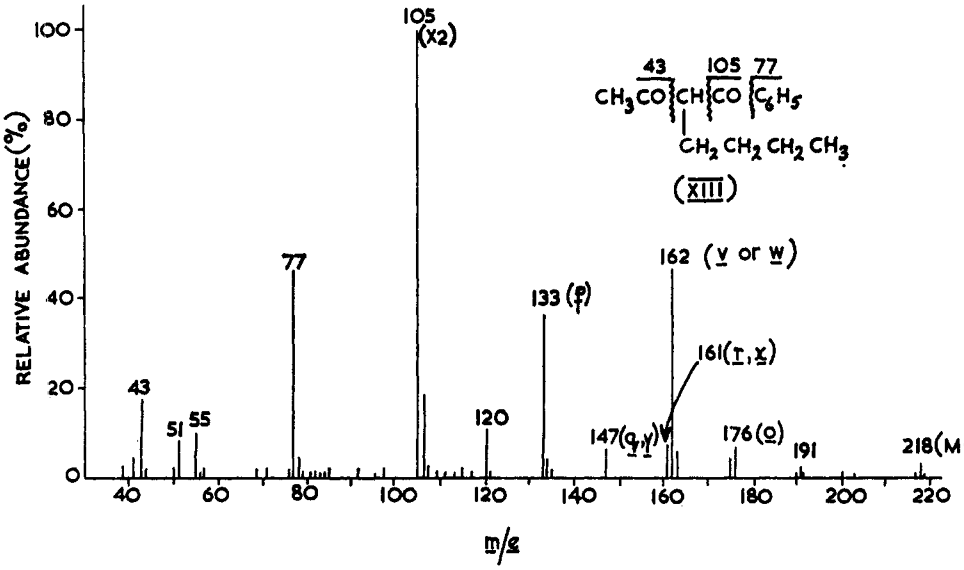
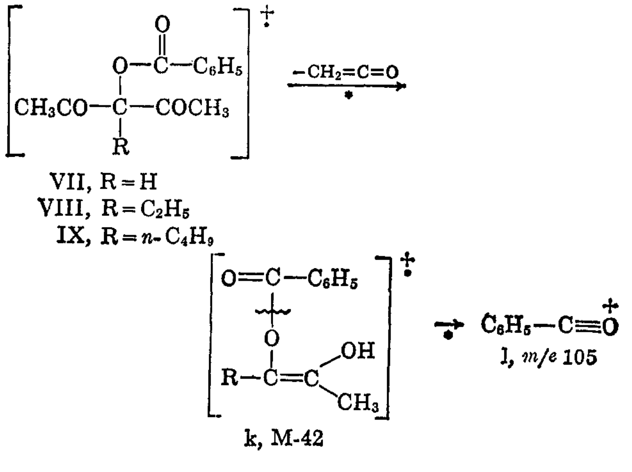


Figure 4.

Scheme IV



cleavage processes, all afford mass spectra exhibiting pronounced M − 1 ions (see Figure 3). Corresponding abundant M − 1 ions are not observed in the spectra of acetylacetone and its derivatives; therefore, this phenomenon has been investigated with the aid of the spectra of $d_2$-benzoylacetone (Xa) and $d_2$-dibenzoylmethane (XVa). The spectrum of XVa establishes that the M − 1 peak is formed by loss of a hydrogen atom from one of the aromatic rings, whereas that of Xa establishes that the M − 1 peak does not involve loss of a hydrogen atom from the active methylene group. These observations are compatible with the correspondence of the M − 1 ion to a favorable oxonium species which may be formed by aromatic substitution (*e.g.*, m from XV). The remaining fragmentations of dibenzoylmethane (XV), summarized in Figure 3, are unexceptional apart from the formation of M − O (*m/e* 208) and M − OH (*m/e* 207) ions and a $C_3HO_2^+$ species (n, *m/e* 69).[9]

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[9] The presence of M − O and M − OH ions in the spectrum (Figure 3) of XV is somewhat surprising. However, identical ions are quite abundant in the spectrum of the derived piperidine enamine [Ph–C($NC_5H_{10}$)=C–CO–Ph] (which is obviously structurally related to the enol form of XV) and also in the spectra of other enamines derived from β-diketones (H. J. Jakobsen, S.-O. Lawesson, J. T. B. Marshall, G. Schroll, and D. H. Williams, *J. Chem. Soc.*, submitted for publication).

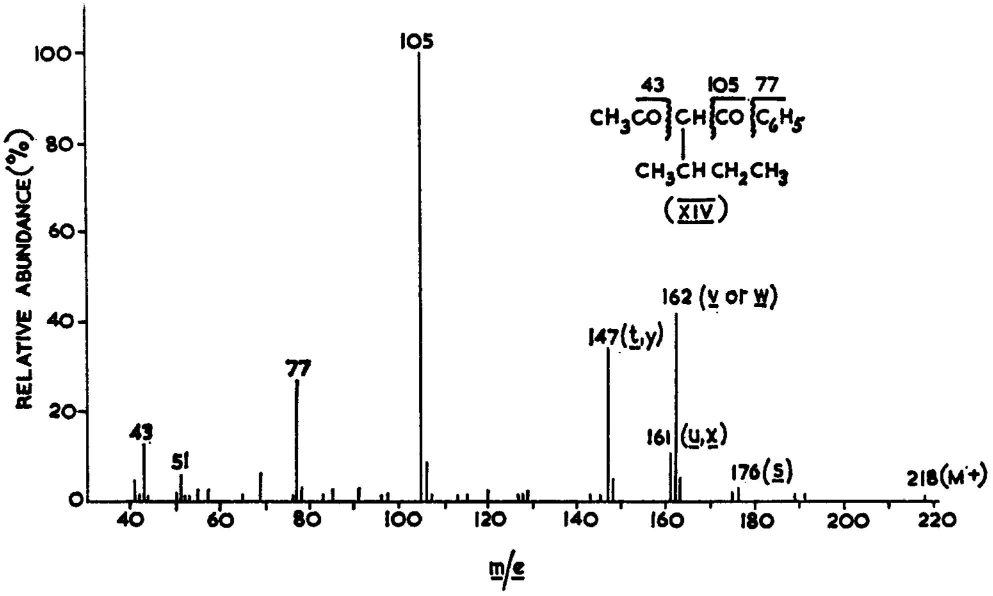


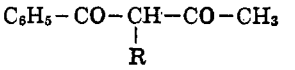
Figure 5.

The spectrum of benzoylacetone (X), in contrast with that of acetylacetone (I) (Figure 1) does not contain an M − CO ion which would establish the occurrence of a methyl or a phenyl migration. However, the presence of an *m/e* 91 ion (shifted to *m/e* 93 in the spectrum of Xa and due to the tropylium ion) in the spectrum of X proves that some phenyl migration to the active methylene group is taking place upon electron impact (see Scheme V).

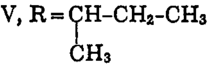
Scheme V

$C_6H_5{-}CO{-}CH_2{-}CO{-}CH_3$

X


$C_6H_5{-}CO{-}\underset{R}{\underset{|}{C}H}{-}CO{-}CH_3$

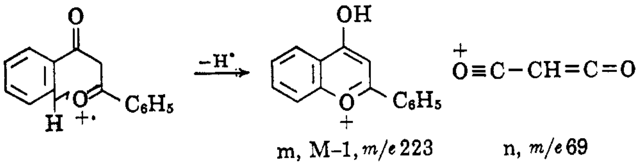
XI, $R = CH_3$
XII, $R = CH_2\text{-}CH{=}CH_2$
XIII, $R = CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$

XIV, 
$R = \underset{CH_3}{\underset{|}{C}H}\text{-}CH_2\text{-}CH_3$

$C_6H_5{-}CO{-}CH_2{-}CO{-}C_6H_5$
XV

$C_6H_5{-}CO{-}CD_2{-}CO{-}CH_3$
Xa

$C_6H_5{-}CO{-}CD_2{-}CO{-}C_6H_5$
XVa



m, M-1, *m/e* 223 n, *m/e* 69

Generally speaking, the spectra of benzoylacetone X and its substituted derivatives XI–XIV contain the benzoyl ion 1 (*m/e* 105) as base peak and M − $CH_2{=}C{=}O$ (M − 42) peaks of variable intensity in the high-mass region. The pronounced fragmentation, by allylic cleavage, of the enolic M − 42 ions derived from alkylated β-diketones requires that the breakdown pattern should be dependent on the nature of α branching in the alkyl substituent. This can readily be seen to be the case on comparison of the spectra of the isomeric *n*-butyl and *sec*-butyl derivatives XIII (Figure 4) and XIV (Figure 5). The enolate ion o (*m/e* 176), which is produced by elimination of ketene from XIII, decomposes almost completely by loss of a propyl radical to p (*m/e* 133) and only to a very small extent by loss of an ethyl radical to q (25% of *m/e* 147) or by loss of a methyl radical to r (5% of *m/e* 161) as indicated in Scheme VI. In sharp contrast, *m/e* 133 is completely absent in the spectrum (Figure 5) of XIV, since the enolate ion s (*m/e* 176) can only eliminate an ethyl radical to give t (65% of *m/e* 147) or a methyl radical to furnish u (15% of *m/e* 161); the elimination of the larger alkyl group is of course greatly preponderant[10] (Scheme VII). The loss of the alkyl substituent from either XIII or XIV as a neutral olefin may occur with hydrogen rearrangement to the carbonyl group of the acetyl moiety or the benzoyl moiety. The resulting enolates v and w (*m/e* 162) can lose a hydrogen radical and a methyl radical (most plausibly, respectively) to account for the doublet nature of *m/e* 161 and *m/e* 147 in both spectra (see Scheme VIII). The compositions of all the ions discussed above have been established by high-resolution measurements.

## Experimental Section

All mass spectra were determined using an AEI MS 9 mass spectrometer operating at 70 ev. Samples were introduced through a heated inlet system at a temperature of *ca.* 150°. The spectra of $d_2$-benzoylacetone (Xa) and $d_2$-dibenzoylmethane (XVa) were obtained by introducing the parent diketones into the inlet system of the spectrometer with deuterium oxide.[11] $d_2$-Benzyl alcohol, which was required as an intermediate in the preparation of $d_2$-benzylacetylacetone (VIa), was prepared by

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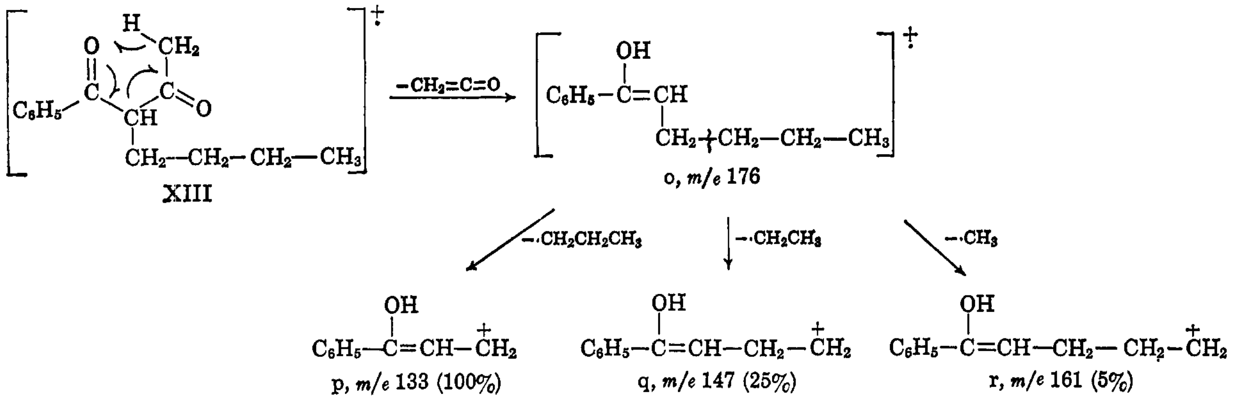
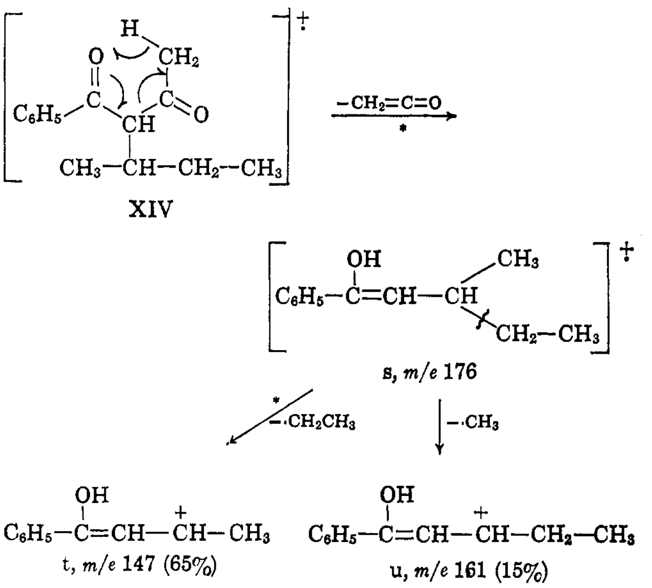
[10] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, p 29.

[11] J. S. Shannon, *Australian J. Chem.*, **15**, 265 (1962).

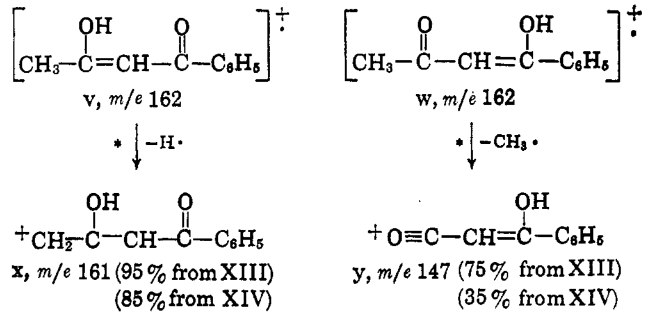
SCHEME VI



SCHEME VII



SCHEME VIII



reduction of ethyl benzoate with lithium aluminium deuteride.[12]

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# Intramolecular Reactions of Olefinic Diazo Ketones[1]

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The copper-catalyzed decomposition of a series of unsaturated diazo ketones has been studied to assess the usefulness of the method for the synthesis of compounds containing a bicyclo[x.1.0]moiety. On the basis of the results it appears that the proximity of the olefinic center and the diazoalkyl center is an important factor in determining the success of the reaction, while the nature or degree of substitution at the olefinic center has relatively little effect.

A number of years ago an investigation was initiated in this laboratory which was directed to the intramolecular reaction of olefinic diazo ketones. During the course of this work, several reports of similar and in some cases identical reactions have appeared.[2–8] The present commnnication records several examples which, with one exception, have escaped the published attention of others and which, it is hoped, will serve to round out some aspects of the scope and limitations of this synthesis.

To study the effect of the distance between the diazoalkyl group and the olefinic group and to study the effect of changing the steric and electronic environment around the olefinic group, a series of olefinic diazo ketones of structure I was synthesized (Scheme I). The yields of bicyclic ketones, II obtained upon copper-

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[2] G. Stork and J. Ficini, *J. Am. Chem. Soc.*, **83**, 4678 (1961).

[3] (a) W. von E. Doering, *Zh. Vses. Khim. Obshchestva im. D. I. Mendeleeva*, **7**, 308 (1962); (b) W. von E. Doering, E. T. Fossel, and R. L. Kaye, *Tetrahedron*, **21**, 25 (1965).

[4] S. Masamune, *J. Am. Chem. Soc.*, **86**, 735 (1964).

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[6] W. von E. Doering and M. Pomerantz, *Tetrahedron Letters*, **No. 17**, 961 (1964).

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