ELECTRON IMPACT STUDIES

VI.* MASS SPECTRA OF ESTERS AND THIOESTERS. SKELETAL REARRANGEMENT ON ELECTRON IMPACT

By J. H. Bowie,† R. G. Cooks,‡ P. Jakobsen,§ S.-O. Lawesson,§ and G. Schroll§

[*Manuscript received October* 20, 1966]

Summary

The mass spectra of representative series of simple alkyl acetoacetates, alkyl acetothioacetates, and some unsaturated esters derived from unsaturated alcohols or phenols are reported and discussed. The fragmentation schemes have been established by high resolution measurements, appropriate metastable ions, and by deuterium and ^{18}O labelling. Many of the spectra show significant skeletal rearrangement fragments arising from either loss of carbon monoxide or carbon dioxide.

The occurrence of skeletal rearrangement fragments has been observed in the mass spectra of β-diketones,[1,2] cyanoacetates,[3] α,β-unsaturated esters,[4] ethyl acetoacetates,[5] and in other groups of compounds containing carbonyl functions.[6–10] The presence of such fragments in the mass spectra of simple compounds is not only of importance in the understanding of fragmentation modes, but is also of obvious relevance to the element mapping technique.[11]

---

* Part V, *Chem. Commun.*, 1966, 539.

† Department of Organic Chemistry, University of Adelaide.

‡ University Chemical Laboratory, Lensfield Road, Cambridge, England.

§ Department of Organic Chemistry, Aarhus University, Aarhus C, Denmark.

[1] Bowie, J. H., Grigg, R., Williams, D. H., Lawesson, S.-O., and Schroll, G., *Chem. Commun.*, 1965, 403.

[2] Bowie, J. H., Lawesson, S.-O., Schroll, G., and Williams, D. H., *J. org. Chem.*, 1966, **31**, 1384.

[3] Bowie, J. H., Grigg, R., Lawesson, S.-O., Madsen, P., Schroll, G., and Williams, D. H., *J. Am. chem. Soc.*, 1966, **88**, 1699.

[4] Bowie, J. H., Williams, D. H., Madsen, P., Schroll, G., and Lawesson, S.-O., *Tetrahedron*, 1967, **23**, 305.

[5] Bowie, J. H., Lawesson, S.-O., Schroll, G., and Williams, D. H., *J. Am. chem. Soc.*, 1965, **87**, 5742.

[6] Fischer, M., and Djerassi, C., *Chem. Ber.*, 1966, **99**, 750.

[7] McFadden, W. H., Stevens, K. L., Meyerson, S., Karabatsos, A. J., and Orzech, C. E., *J. phys. Chem.*, 1965, **69**, 1742.

[8] Natalis, P., and Franklin, J. L., *J. phys. Chem.*, 1965, **69**, 2935.

[9] Brown, P., and Djerassi, C., *J. Am. chem. Soc.*, 1966, **88**, 2469; Thomson, J. B., Brown, P., and Djerassi, C., *J. Am. chem. Soc.*, 1966, **88**, 4049.

[10] Teeter, R. M., Tenth Annual Conference on Mass Spectrometry, A.S.T.M. Committee E-14, New Orleans, La., 1962, p. 51.

[11] Biemann, K., *Pure appl. Chem.*, 1964, **9**, 95; Biemann, K., Bommer, P., and Desiderio, D. M., *Tetrahedron Lett.*, 1964, 1725.

Aust. J. Chem., 1967, **20**, 689–97

TABLE 1

MASS SPECTRA OF ESTERS AND THIOESTERS

All ions greater than 2% of the base peak (arbitrarily taken as 100%) are recorded

(I)	m/e	27	28	29	39	41	42	43	44	58	59	60	61	69	84	85	102	103	
	I (%)	14	10	8	6	11	15	100	16	10	13	23	17	15	25	32	12	20	
	m/e	115	144(M$^+$)																
	I (%)	3	3																
(II)	m/e	28	39	41	42	43	44	57	58	59	69	84	85	87	102	103	116		
	I (%)	6	8	14	11	100	19	10	10	15	15	23	27	5	16	13	2		
	m/e	144(M$^+$)																	
	I (%)	3																	
(III)	m/e	27	28	29	39	41	42	43	44	55	56	57	58	60	69	84	85	103	
	I (%)	18	10	21	7	38	20	100	16	7	76	25	10	10	20	25	35	30	
	m/e	116	143	158(M$^+$)															
	I (%)	3	2	4															
(IV)	m/e	27	28	29	39	41	42	43	44	56	57	58	85	103					
	I (%)	25	18	13	12	34	25	100	43	14	10	13	14	5					
(V)	m/e	27	28	29	39	41	42	43	44	55	56	57	58	59	60	69	73	85	87
	I (%)	20	16	25	14	26	15	38	24	14	14	31	15	25	10	25	18	100	25
	m/e	102	103	129	158(M$^+$)														
	I (%)	15	37	3	2														
(VI)	m/e	27	28	29	39	41	43	44	56	57	58	59	60	69	84	85	103		
	I (%)	8	9	10	6	30	56	20	10	35	8	100	4	26	34	22	14		
	m/e	158(M$^+$)																	
	I (%)	2																	
(VIII)	m/e	27	28	29	39	41	43	44	55	56	57	58	67	69	71	81	82	85	99
	I (%)	18	4	14	19	24	100	23	12	8	65	14	19	6	6	9	38	7	18
	m/e	103																	
	I (%)	7																	
(XII)	m/e	27	28	39	41	42	43	69	76	84	85	86	118	160(M$^+$)					
	I (%)	8	15	5	12	11	97	8	11	10	100	5	12	24					
(XIV)	m/e	27	28	29	39	41	43	55	56	57	61	69	84	85	86	90	118		
	I (%)	8	9	8	4	13	65	5	20	8	4	7	10	100	5	10	2		
	m/e	174(M$^+$)																	
	I (%)	13																	
(XV)	m/e	27	28	29	39	41	43	56	57	58	61	69	84	85	86	89	90	118	
	I (%)	6	9	11	4	13	66	8	20	7	10	7	9	100	5	5	10	8	
	m/e	119	146	174(M$^+$)															
	I (%)	5	4	18															
(XVI)	m/e	27	28	29	39	41	42	43	55	56	57	58	69	84	85	90	91	118	
	I (%)	12	13	19	12	38	6	32	8	11	100	12	4	5	56	17	7	43	
	m/e	119	174(M$^+$)	175															
	I (%)	14	25	3															

TABLE 1 (*Continued*)

(XVII)	*m/e*	26	27	28	29	37	38	39	40	41	42	43	45	46	54	56	58	59	69
	I (%)	28	39	11	10	20	30	80	15	64	20	100	56	4	9	9	9	11	26
	m/e	73	74	85	125	168(M^+)													
	I (%)	13	7	14	3	2													
(XVIII)	*m/e*	39	41	42	43	56	57	71	72	100(M^+)									
	I (%)	9	10	4	100	10	15	2	2	2									
(XIX)	*m/e*	39	43	44	55	56	70	98(M^+)											
	I (%)	18	100	3	5	4	4	2											
(XXI)	*m/e*	39	41	51	77	91	105	106	117	122	123	162(M^+)							
	I (%)	6	6	8	20	2	100	9	6	3	2	12							
(XXII)	*m/e*	39	40	41	51	52	53	77	78	79	80	81	91	97	105	106	157	158	
	I (%)	19	10	23	24	7	18	54	4	52	24	40	4	15	100	9	3	2	
	m/e	202(M^+)																	
	I (%)	9																	
(XXIII)	*m/e*	39	50	51	63	65	76	77	93	94	105	106	198(M^+)						
	I (%)	19	9	26	5	13	4	45	3	3	100	13	12						

TABLE 2

EXACT MASS MEASUREMENTS IN THE MASS SPECTRA OF COMPOUNDS (I)–(XXII)

Compound	*m/e*	Composition	Compound	*m/e*	Composition
(I)	43	C_2H_3O(80%), C_3H_7(20%)	(VII)	69	C_3HO_2(50%), C_5H_9(50%)
	102	$C_5H_{10}O_2$(65%), $C_4H_6O_3$(35%)		43	C_2H_3O(70%), C_3H_7(30%)
	103	$C_4H_7O_3$	(IX)	114	$C_6H_{10}O_2$
(II)	43	C_2H_3O(80%), C_3H_7(20%)	(X)	164	$C_{10}H_{12}O_2$
	102	$C_4H_6O_3$(60%), $C_5H_{10}O_2$(40%)		58	C_3H_6O
	103	$C_4H_7O_3$	(XI)	118	$C_5H_{10}OS$(85%), $C_4H_6O_2S$(15%)
(III)	43	C_2H_3O(70%), C_3H_7(30%)	(XII)	43	C_2H_3O(60%), C_3H_7(40%)
	56	C_4H_8		118	$C_4H_6O_2S$
	69	C_3HO_2	(XIII)	43	C_2H_3O(55%), C_3H_7(45%)
	85	$C_4H_5O_2$		118	$C_4H_6O_2S$
	103	$C_4H_7O_3$		132	$C_6H_{12}SO$
	116	$C_6H_{12}O_2$	(XV)	43	C_2H_3O
(IV)	43	C_2H_3O(95%), C_3H_7(5%)		146	$C_7H_{14}OS$
(V)	43	C_2H_3O(95%), C_3H_7(5%)	(XVIII)	72	$C_4H_{10}O$
(VI)	43	C_2H_3O	(XIX)	70	C_4H_8O
	59	C_3H_7O	(XXI)	117	C_9H_9
	69	C_3HO_2		122	$C_7H_6O_2$
	84	$C_4H_4O_2$	(XXII)	80	C_6H_8
(VII)	142	$C_7H_{10}O_3$		81	C_6H_9
	128	$C_8H_{16}O$		91	C_7H_7
	110	C_8H_{14}		97	C_6H_9O
	99	$C_6H_{11}O$		105	C_7H_5O
	85	C_5H_9O(70%), $C_4H_5O_2$(30%)		157	$C_{12}H_{13}$
	81	C_6H_9		158	$C_{12}H_{14}$

Because of our interest in the skeletal rearrangement ions observed in the mass spectra of ethyl acetoacetates[5] we have investigated the relative abundance of such ions in the spectra of the alkyl acetoacetates (I)–(X) and have extended this study to include the alkyl acetothioacetates (XI)–(XVII) and the unsaturated esters (XVIII)–(XXIII). Some of this work has been reported in a previous communication;[12] we wish here to report the work in full.

$CH_3COCH_2CO_2R$

R	R
(I) $\mathrm{Pr^n}$	(VI) $\mathrm{Bu^t}$
(II) $\mathrm{Pr^i}$	(VII) 1-ethylcyclohexyl
(III) $\mathrm{Bu^n}$	(VIII) 1-isopropylcyclohexyl
(IV) $\mathrm{Bu^i}$	(IX) allyl
(V) $\mathrm{Bu^s}$	(X) CH_2Ph

$CH_3COCH_2C(=O)SR$

R	R
(XI) Et	(XVI) $\mathrm{Bu^t}$
(XII) $\mathrm{Pr^n}$	(XVII) allyl
(XIII) $\mathrm{Pr^i}$	
(XIV) $\mathrm{Bu^n}$	
(XV) $\mathrm{Bu^s}$	

Throughout this paper, an asterisk (*) denotes the presence of a metastable ion for the process indicated. The compositions of many fragment ions have been established by exact mass measurements and these are summarized in Table 2. The spectra of compounds (VII), (IX), (X), (XI), and (XIII) are recorded in Figures 1–5 (pp. 694–6) while the spectra of all other compounds are recorded in Table 1.

TABLE 3

RELATIVE ABUNDANCES (%) OF FRAGMENT IONS IN THE SPECTRA OF THE ALKYL ACETOACETATES (I)–(VI)

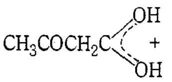
Compound	M^+	M—CO	$M-CH_2CO$	M—(R—2H·)	M—RO·	$C_3HO_2^+$ *m/e* 69	R^+	R—H·	$C_3H_7O^+$ *m/e* 59	CH_3CO^+ *m/e* 43
(I)	2	1	8	20	32	15	20	15	12	80
(II)	3	2	12	13	27	15	20	11	14	80
(III)	4	—	2	30	35	20	25	76	—	100
(IV)	—	—	—	5	15	2	10	15	—	100
(V)	—	—	—	37	100	25	31	26	15	35
(VI)	—	—	—	15	22	25	35	10	100	55

The mass spectra of methyl and ethyl acetoacetate have been discussed previously.[5] In the spectra of (I)–(X), the loss of ketene from the molecular ion to form enolic fragment ions (a significant process in the spectrum of ethyl acetoacetate), is either very small or absent, e.g. in the spectrum of the propyl derivative (I), the $M-CH_2CO$ ion constitutes 65% of *m/e* 102 (12% of the base peak); in the n-butyl derivative (III) only 2% of the base peak, while no loss of ketene is observed in the spectra of the other butyl derivatives (IV)–(VI). When R is a larger alkyl group than ethyl, the acetyl cation (*m/e* 43) is always pronounced, and processes occur which involve loss (from the molecular ion) of (1) the alkyl residue with double hydrogen rearrangement to give an ion corresponding to *a*,[13] together with (2) loss of an alkoxyl radical to yield *b* (*m/e* 85). The presence of the M^+-ROH ion (*m/e* 84) is

[12] Bowie, J. H., Cooks, R. G., Jakobsen, P., Lawesson, S.-O,. and Schroll, G., *Chem. Commun.*, 1966, 539.

[13] Bowie, J. H., Lawesson, S.-O., Schroll, G., and Williams, D. H., *J. org. Chem.*, 1966, **31**, 1792.

noted in the spectra of (I)–(III) and (VI), but not in those of (IV) and (V). No explanation can be offered for this anomalous observation. The general features of the spectra of (I)–(VI) are summarized in Tables 1 and 3. The relative abundance of skeletal rearrangement ions in the spectra of (I)–(VI) correspondingly decreases


$CH_3COCH_2C(OH)_2^+$

a

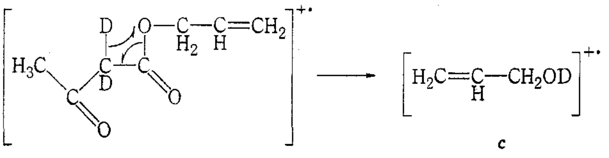
$CH_3COCH_2C{\equiv}O^+$

b

with increasing size of the alkoxyl group. Although small rearrangement ions are noted (Table 3) for the propyl derivatives (I) and (II), no skeletal rearrangements are observed in the spectra of the butyl derivatives (III)–(VI). When the alkoxyl group contains a saturated ring system as in (VII) and (VIII), the mass spectra are not characteristic of β-keto esters, apart from exhibiting ions corresponding to the acetyl cation (70% of *m/e* 43) and to *b* [30% of *m/e* 85 (Table 2)]. Instead fragment ions are present which arise primarily from the alkoxyl group, which after initial cleavage, has retained the charge. This is illustrated by the spectrum (Fig. 1) of (VII), while the compositions of the various fragment ions in this spectrum are summarized in Table 2.

Significant differences are observed in the spectra of β-keto esters containing unsaturation in the alkoxyl group. Skeletal rearrangement ions due to loss of carbon monoxide from the molecular ions are again observed, especially in the case of (X) ($R = PhCH_2$) where this ion constitutes 13% of the base peak. ^{18}O labelling[5,14] indicates that the carbon monoxide expelled originates from the ketone moiety (Fig. 3).

The benzyloxy cation (*m/e* 107) in this spectrum (Fig. 3) must at least partly arise by loss of $MeCH_2CO\cdot$ from the skeletal rearrangement ion (*m/e* 164) as this decomposition is evidenced by an appropriate metastable ion at *m/e* 70·1. Fragment ions due to the presence of the benzyl alcohol and allyl alcohol radical ions (*m/e* 108 and 58) are prominent in the spectra (Figs. 2 and 3) of (IX) and (X). As the genesis of such ions requires H rearrangement, (IXa) was synthesized (by direct D_2O exchange with (IX)) and its mass spectrum compared with that of (IX). The peak at *m/e* 58 in Figure 2 moves to *m/e* 59 while that at *m/e* 57 is not affected. This is consistent with deuterium transfer via a four-membered transition state, viz. (IXa) → *c*:


(IXa)

c

The mass spectra (Figs. 4 and 5, Table 1) of the thioesters (XI)–(XVI) bear some resemblance to the analogous β-keto esters. Because of the thermal decomposition that these compounds undergo at elevated temperatures, all spectra were determined by the direct insertion procedure using a source temperature of 50°. The spectra

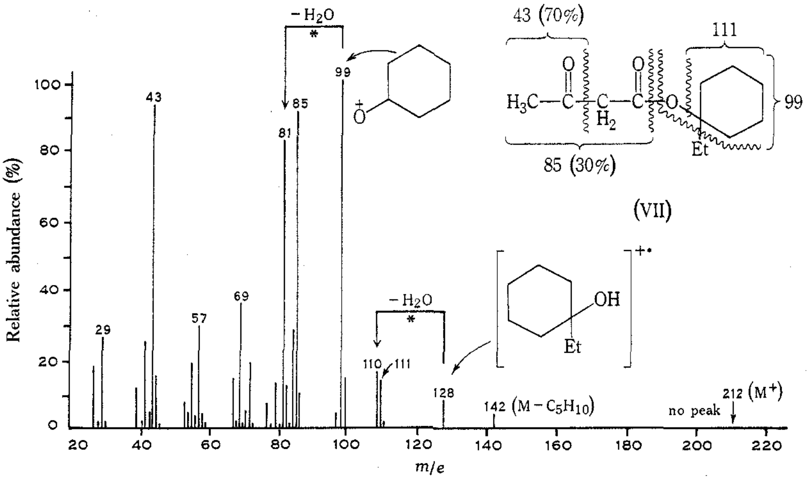
---

[14] Richter, W. J., Senn, M., and Burlingame, A. R., *Tetrahedron Lett.*, 1965, 1235.

are generally simple and readily interpretable. The mass spectra of (XI) and (XIII) are illustrated in Figures 4 and 5, while the major fragmentations of (XI)–(XVII) are summarized in Table 3.

The elision of ketene from the molecular ion to form enolic fragment ions, which is a preponderant process for ethyl acetoacetates, is neither observed in the spectrum of ethyl acetothioacetate (XI) nor in those of (XII)–(XVI). Instead, ready loss of the alkylthio radical by α-cleavage to C=O to furnish *b* (*m/e* 85) is the preponderant process in these spectra. The formation of the thiol radical ion ($RSH^{+\cdot}$) by hydrogen rearrangement is an observed process in all spectra. Comparison of the mass spectra of (XII) and of the labelled compound $CH_3COD_2C(=O)SPr^n$ (XIIa) (prepared analogously to (IXa)) shows a shift of *m/e* 76 to *m/e* 77. This indicates that $Pr^nSH^{+\cdot}$ (*m/e* 76) is formed by hydrogen transfer via a four-membered transition state. The analogous alcohol radical ion does not generally occur in the mass spectra of simple alkyl acetoacetates, but can be seen in cases where charge stabilization of the alcohol radical ion may occur, e.g. (IX) and (X). Here, as in the case of β-keto esters, skeletal rearrangement fragments are observed, their relative abundances decreasing as the size of the alkylthio group increases (Table 4). Strangely, no skeletal rearrangement ions are observed in the spectrum (Table 1) of the allyl derivative (XVII). Further fragmentations are summarized in Table 4 and Figures 4 and 5.

Fig. 1



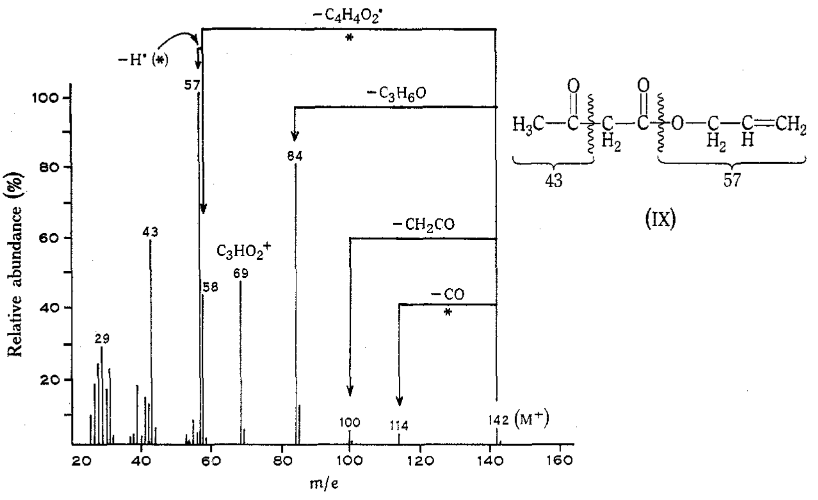
RCOOR′

	R	R′
(XVIII)	Me	allyl
(XIX)	Me	propargyl
(XX)	Ph	Me
(XXI)	Ph	allyl
(XXII)	Ph	cyclohex-2-enyl
(XXIII)	Ph	Ph

Finally, because of the skeletal rearrangement ions which are observed in the spectra of α,β-unsaturated esters,[4] the spectra of the unsaturated esters (XVIII)–

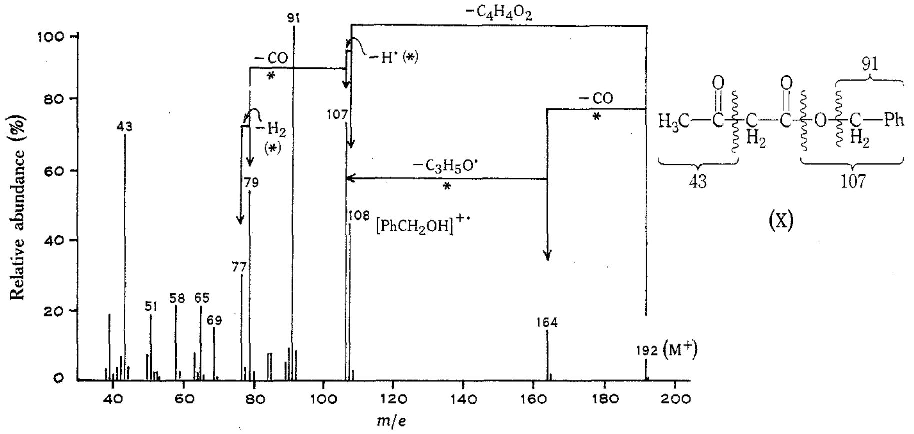
(XXIII) were determined. The general fragmentations (Table 1) of these compounds on electron impact are unexceptional and follow the normal ester decomposition modes.[15] The skeletal rearrangement ions are summarized in Table 4, p. 697. Neither

Fig. 2



(IX)

Fig. 3



(X)

methyl[16] nor phenyl benzoate (XX and XXIII) show any rearrangement ions in their spectra. The mass spectra of compounds containing R = Me and R′ = allyl or propargyl (XVIII and XIX) exhibit M−CO ions whereas (XXI) and (XXII) (R = Ph, R′ = allyl and cyclohex-2-enyl) exhibit $M-CO_2$ and $M-CO_2H$ rearrangement ions. The spectrum (Table 1) of (XXII) is also noteworthy for the occurrence

---

[15] Budzikiewicz, H., Djerassi, C., and Williams, D. H., "Interpretation of Mass Spectra of Organic Compounds." pp. 10–17. (Holden-Day: San Francisco 1964.)

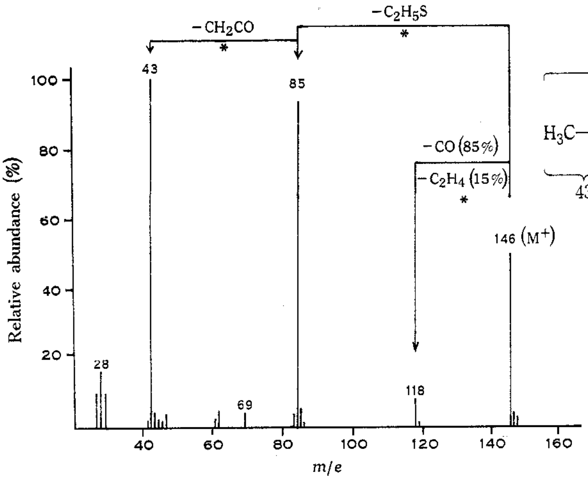
[16] "Catalog of Mass Spectral Data." Spectrum No. 1752. American Petroleum Institute Research Project 44. (Carnegie Institute of Technology: Pittsburg, Pa.)

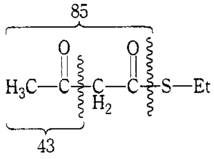
of a further skeletal rearrangement ion at *m/e* 91, $C_7H_7^+$ by high resolution (5% of the base peak), whose representation as the tropylium cation is substantiated by the decomposition

$$m/e\ 91 \xrightarrow[*]{-HC\equiv CH} m/e\ 65\ (C_5H_5^+\ \text{H.R.})$$

The compositions of all skeletal rearrangement ions indicated in Table 5 have been established by exact mass measurement.

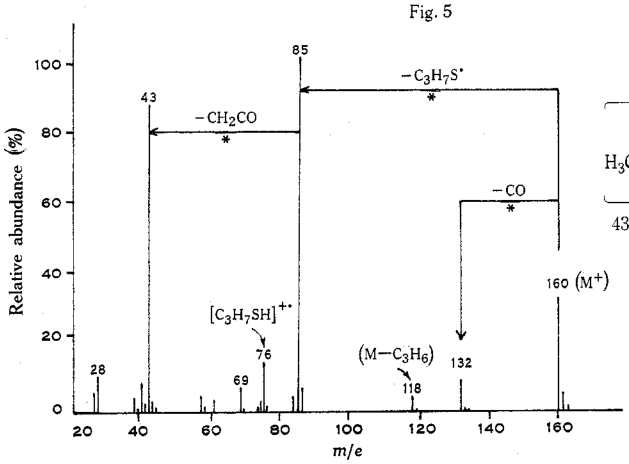
Fig. 4

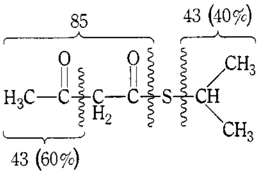




(XI)

Fig. 5





(XIII)

It has been suggested[4] that skeletal rearrangements which involve loss of CO or CO_2 apparently occur because removal of the π-electrons from double bonds (C=C or C=O) generates electron deficient centres which may then be utilized to promote C–C or C–O bond formation in reactions of the type $[ABC]^+ \rightarrow [AC]^+$.

EXPERIMENTAL

The spectra of the β-keto esters and the unsaturated esters were determined on a Hitachi Perkin–Elmer RMU-6D mass spectrometer, with samples being introduced into the source through a heated inlet system at a temperature of approximately 150°. The thio compounds were measured by the direct insertion procedure on an AEI MS9 mass spectrometer using a source temperature not in excess of 55°. Exact mass measurements were carried out with the MS9, at a resolution of 14,000 (10% valley definition), using heptacosafluorotributylamine to provide reference masses.

TABLE 4

RELATIVE ABUNDANCES (%) OF FRAGMENT IONS IN THE SPECTRA OF THE THIOESTERS (XI)–(XVI)

Compound	M^+	$M-CO$	$M-(R-H\cdot)$	RSH	$M-RS\cdot$	R^+	$MeCO^+$
(XI)	35	4	2	7	93	12	100
(XII)	24	—	12	11	100	49	58
(XIII)	23	11	2	12	100	45	49
(XIV)	13	—	3	10	100	8	65
(XV)	17	4	8	10	100	18	66
(XVI)	25	—	43	17	56	100	22

TABLE 5

RELATIVE ABUNDANCES (%) OF SKELETAL REARRANGEMENT IONS IN THE SPECTRA OF COMPOUNDS (XVIII)–(XXIII)

Rearranged Ion	(XVIII)	(XIX)	(XX)	(XXI)	(XXII)	(XXIII)
$M-CO$	2	4	—	—	—	—
$M-CO_2$	—	—	—	1	1	—
$M-HCO_2$	—	—	—	6	3	—

All liquid samples were distilled twice, if necessary further purified by gas chromatography. Purity was routinely checked by gas chromatography, and n.m.r. and mass spectrometry.

Compounds (XX) and (XXIII) were purified commercial samples; (I)–(VI), (IX), and (X) were prepared from diketene and the appropriate alcohol.[17,18] The following compounds were prepared by reported procedures: (VII) and (VIII),[19] (XVIII),[20] (XIX),[21] (XXI),[22] and (XXII).[23] Compounds (XI)–(XVII) were prepared from diketene and the corresponding thiols (experimental details will be published elsewhere).

ACKNOWLEDGMENTS

One of us (R.G.C.) is grateful for the award of an Elsie Ballot Fellowship. A grant from Statens Almindelige Videnskabsfond (to S.-O.L.) is gratefully acknowledged. The mass spectrometer was purchased with the aid of a grant from the Australian Research Grants Committee.

---

[17] Boese, A. B., U.S. Pat. 1939, 2, 167, 168.

[18] Lawesson, S.-O., Grönwall, S., and Sandberg, R., *Org. Synth.*, 1962, **42**, 28.

[19] Frisell, C., and Lawesson, S.-O., *Ark. Kemi.*, 1961, **17**, 401.

[20] Jeffery, G. H., and Vogel, A. I., *J. chem. Soc.*, 1948, 663.

[21] Henry, L., *Ber. dt. chem. Ges.*, 1873, **6**, 729.

[22] Robertson, P. W., Clare, N. T., McNaught, K. J., and Paul, G. W., *J. chem. Soc.*, 1937, 335.

[23] Kharasch, M. S., Sosnovosky, G., and Yand, N. C., *J. Am. chem. Soc.*, 1959, **81**, 5819.