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Mass Spectra of Halogenated Esters

7. Methyl Esters of 2-Chloro C_2–C_{20} *n*-Alkanoic Acids†

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The mass spectral fragmentation of a homologous series of methyl esters of 2-chloro *n*-alkanoic acids ranging from acetic (C_2) to eicosanoic (C_{20}) acid on electron impact has been investigated. The fragmentation pathways were elucidated with the aid of the first field-free region metastable ions, the results being presented with one compound, i.e. with ionized methyl 2-chloro-octanoate. Owing to the Cl/H exchanges and to the formation of the non-chlorinated parent esters prior to the fragmentations the spectra show the peak pairs with and without the chlorine atom. The effects become more evident with increasing chain length; shown most visually by the abundance ratios of the McLafferty rearrangement ions at *m/z* 108/110 and 74, and fragments at *m/z* 121/123 and 87.

INTRODUCTION

The studies of Ryhage and Stenhagen and their co-workers in the late 1950s and early 1960s seem to be the first clear demonstrations of the mass spectra of carboxylic acid esters.[1–6] The high-resolution mass spectra of lower aliphatic esters were obtained about the same time.[7] In order to study the fragmentation pathways under electron impact (EI) deuterium labelling with long-chain esters has been used.[5,6,8–11]

As a continuation of the studies of the mass spectral fragmentation of halogenated carboxylic acid derivatives,[12–22] the present paper gives the results of the methyl esters of chloroformic acid and 2-chloro *n*-alkanoic acids ranging from acetic (C_2) to eicosanoic (C_{20}) acid. The fragmentation pathways are elucidated with the aid of the first field-free region (1st FFR) metastable ions, the most prominent ones being given in the case of ionized methyl 2-chloro-octanoate. The results are compared with those reported earlier for the parent methyl esters of *n*-alkanoic acids.

EXPERIMENTAL

Materials

Methyl 2-chloro esters (**3**–**20**) were prepared from the corresponding 2-chloro acid chlorides[23] and methanol, except methyl chloroformate (**1**) and chloroacetate (**2**), which were obtained from commercial acids (Fluka, Buchs, Switzerland) by the usual sulphuric acid-catalysed esterification.

Before mass spectral analysis all esters were purified by preparative gas–liquid chromatography (GLC) under conditions reported previously,[24] the structures of compounds being verified by nuclear magnetic resonance (NMR) spectroscopy.[25]

Mass spectrometry

Mass spectra were recorded on a Varian MAT-212 mass spectrometer under the following operating conditions: ion accelerating voltage, 3 kV; trap current, 100 μA; ionizing energy, 70 eV; ion source temperature, 250 °C; scan time, 2.3 s per mass decade; resolution, 500. The lower esters were introduced using a direct inlet system (inlet temperature, 120–220 °C) and the higher isomers from quartz capillaries on the end of the unheated or heated direct insertion probe. The different inlet systems used seem to give identical mass spectra for the isomers studied, judging from the results obtained with the mid-chain isomers. The 1st FFR metastable ions were obtained by linked scans using a Varian Metascan unit. All mass spectral data were acquired and processed on a Spectro System MAT-188.

RESULTS AND DISCUSSION

The EI mass spectra of the following esters were investigated: methyl chloroformate (**1**) (not 2-chloro ester, but taken for comparison), chloroacetate (**2**), 2-chloropropanoate (**3**), 2-chlorobutanoate (**4**), 2-chloropentanoate (**5**), 2-chlorohexanoate (**6**), 2-chloroheptanoate (**7**), 2-chloro-octanoate (**8**), 2-chlorononanoate (**9**), 2-chlorodecanoate (**10**), 2-chloro-undecanoate (**11**), 2-chlorododecanoate (**12**), 2-chlorotridecanoate (**13**), 2-chlorotetradecanoate (**14**), 2-chloropentadecanoate (**15**), 2-chlorohexadecanoate (**16**), 2-chloroheptadecanoate (**17**), 2-chloro-octadecanoate (**18**), 2-chlorononadecanoate (**19**) and 2-chloroeicosanoate (**20**). The spectra of **4**, **8**, **12**, **16** and **20** are illustrated in Figs 1–5, respectively, whereas Table 1 gives the most prominent primary and secondary fragmenta-

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Table 1. Most characteristic primary and secondary fragmentations of the ionized methyl 2-chloro-octanoate based on the 1st FFR metastable ions

Mother ion *m/z*	Mother ion Fragment	Group lost	Daughter ion *m/z*	Daughter ion Fragment	Relative abundance (% of the sum)
192	$[C_9H_{17}ClO_2]^{+\cdot}$ = $M^{+\cdot}$	$CH_3^{\cdot}$	177	$[C_8H_{14}ClO_2]^+$	1.6
		C_2H_4	164	$[C_7H_{13}ClO_2]^{+\cdot}$	2.9
		$C_2H_5^{\cdot}$	163	$[C_7H_{12}ClO_2]^+$	52.4
		$Cl^{\cdot}$	157	$[C_9H_{17}O_2]^+$	2.9
		HCl	156	$[C_9H_{16}O_2]^{+\cdot}$	5.1
		C_4H_8	136	$[C_5H_9ClO_2]^{+\cdot}$	5.1
		$C_4H_9^{\cdot}$	135	$[C_5H_8ClO_2]^+$	1.6
		$C_2H_4Cl^{\cdot}$	129	$[C_7H_{13}O_2]^+$	9.9
		$C_3H_4Cl^{\cdot}$	117	$[C_6H_{13}O_2]^+$	1.2
		$C_3H_6Cl^{\cdot}$	115	$[C_6H_{11}O_2]^+$	16.0
		C_4H_7Cl	102	$[C_5H_{10}O_2]^{+\cdot}$	1.3
177	$[C_8H_{14}ClO_2]^+$ = $[M - CH_3]^+$	$Cl^{\cdot}$	142	$[C_8H_{14}O_2]^{+\cdot}$	9.9
		HCl	141	$[C_8H_{13}O_2]^+$	90.1
163	$[C_7H_{12}ClO_2]^+$ = $[M - C_2H_5]^+$	C_2H_4 / CO	135	$[C_5H_8ClO_2]^+$ / $[C_6H_{12}ClO]^+$	4.7
		$C_2H_5^{\cdot}$ / $CHO^{\cdot}$	134	$[C_5H_7ClO_2]^{+\cdot}$ / $[C_6H_{11}ClO]^{+\cdot}$	0.7
		$CH_3O^{\cdot}$	132	$[C_6H_9ClO]^{+\cdot}$	0.9
		CH_3OH	131	$[C_6H_8ClO]^+$	5.9
		$Cl^{\cdot}$	128	$[C_7H_{12}O_2]^{+\cdot}$	7.5
		HCl	127	$[C_7H_{11}O_2]^+$	70.9
		C_3H_6	121	$[C_4H_6ClO_2]^+$	0.6
		$C_4H_7^{\cdot}$	108	$[C_3H_5ClO_2]^{+\cdot}$	0.6
		C_4H_8	107	$[C_3H_4ClO_2]^+$	2.0
		$C_2H_4O_2$	103	$[C_5H_8Cl]^+$	1.0
		C_5H_8 / C_4H_4O	95	$[C_2H_4ClO_2]^+$ / $[C_3H_8ClO]^+$	3.0
		C_2H_3ClO	85	$[C_5H_9O]^+$	2.2
157	$[C_9H_{17}O_2]^+$ = $[M - Cl]^+$	$CH_3^{\cdot}$	142	$[C_8H_{14}O_2]^{+\cdot}$	1.1
		O	141	$[C_9H_{17}O]^+$	6.0
		CH_3OH	125	$[C_8H_{13}O]^+$	43.4
		C_3H_6 / CH_2CO	115	$[C_6H_{11}O_2]^+$ / $[C_7H_{15}O]^+$	1.9
		CO_2	113	$[C_8H_{17}]^+$	2.2
		C_4H_8 / C_3H_4O	101	$[C_5H_9O_2]^+$ / $[C_6H_{13}O]^+$	1.9
		$C_3H_7O^{\cdot}$ / $CH_3COO^{\cdot}$	98	$[C_6H_{10}O]^{+\cdot}$ / $[C_7H_{14}]^{+\cdot}$	6.4
		$C_2H_6O_2$	95	$[C_7H_{11}]^+$	0.9
		C_5H_8 / C_4H_4O	89	$[C_4H_9O_2]^+$ / $[C_5H_{13}O]^+$	1.1
		$C_5H_9^{\cdot}$ / $C_4H_5O^{\cdot}$	88	$[C_4H_8O_2]^{+\cdot}$ / $[C_5H_{12}O]^{+\cdot}$	0.9
		C_5H_{10} / C_4H_6O	87	$[C_4H_7O_2]^+$ / $[C_5H_{11}O]^+$	32.5
		$C_3H_6O_2$	83	$[C_6H_{11}]^+$	1.7
129	$[C_7H_{13}O_2]^+$ = $[M - C_2H_4Cl]^+$	C_2H_4 / CO	101	$[C_5H_9O_2]^+$ / $[C_6H_{13}O]^+$	20.7
	$[C_8H_{17}O]^+$ = $[M - COCl]^+$	CH_3OH	97	$[C_6H_9O]^+$ / $[C_7H_{13}]^+$	27.4
		C_3H_6	87	$[C_4H_7O_2]^+$ / $[C_5H_{11}O]^+$	12.3
		C_4H_8	73	$[C_3H_5O_2]^+$ / $[C_4H_9O]^+$	24.6
		C_6H_{12}	45	$[C_2H_5O]^+$	15.0
127	$[C_7H_{11}O_2]^+$ = $[M - C_2H_5 - HCl]^+$ = $[M - CH_3 - Cl - CH_3]^+$	C_2H_4 / CO	99	$[C_5H_7O_2]^+$ / $[C_6H_{11}O]^+$	2.4
		$CH_3O^{\cdot}$	96	$[C_6H_8O]^{+\cdot}$	5.2
		CH_3OH	95	$[C_6H_7O]^+$	78.1
		C_3H_6 / CH_2CO	85	$[C_4H_5O_2]^+$ / $[C_5H_9O]^+$	4.3
		C_4H_8 / C_3H_4O	71	$[C_3H_3O_2]^+$ / $[C_4H_7O]^+$	8.5
		C_3H_6O / $C_2H_2O_2$	69	$[C_4H_5O]^+$ / $[C_5H_9]^+$	1.5

Table 1. (*cont.*)

m/z	Mother ion Fragment	Group lost	m/z	Daughter ion Fragment	Relative abundance (% of the sum)
121	$[C_4H_6ClO_2]^+$ = $[M - C_2H_5 - C_3H_6]^+$	C_2H_2	95	$[C_2H_4ClO_2]^+$	20.0
		C_2H_4 / CO	93	$[C_2H_2ClO_2]^+$ / $[C_3H_6ClO]^+$	22.5
		CH_3OH	89	$[C_3H_2ClO]^+$	57.5
115	$[C_6H_{11}O_2]^+$ = $[M - Cl - C_3H_6]^+$	C_2H_4 / CO	87	$[C_4H_7O_2]^+$ / $[C_5H_{11}O]^+$	28.6
	$[C_7H_{15}O]^+$ = $[M - Cl - CH_2CO]^+$	CH_3OH	83	$[C_5H_7O]^+$ / $[C_6H_{11}]^+$	71.4
108	$[C_3H_5ClO_2]^{+\cdot}$ = McLafferty rearrangement	CHO·	79	$[C_2H_4ClO]^+$	1.7
		CH_3OH	76	$[C_2HClO]^{+\cdot}$	75.0
		HCl	72	$[C_3H_4O_2]^{+\cdot}$	17.4
		CO_2	64	$[C_2H_5Cl]^{+\cdot}$	5.9
97	$[C_7H_{13}]^+$ = $[M - C_2H_4ClO_2]^+$ $[C_6H_9O]^+$ = $[M - C_3H_8ClO]^+$	C_2H_4 / CO	69	$[C_5H_9]^+$ / $[C_4H_5O]^+$	100.0
95	$[C_7H_{11}]^+$ = $[M - C_2H_6ClO_2]^+$ $[C_6H_7O]^+$ = $[M - C_3H_{10}ClO]^+$	C_2H_4 / CO	67	$[C_5H_7]^+$ / $[C_4H_3O]^+$	100.0
87	$[C_4H_7O_2]^+$ = $[M - C_5H_{10}Cl]^+$ $[C_5H_{11}O]^+$ = $[M - C_4H_6ClO]^+$	CH_3OH	55	$[C_3H_3O]^+$ / $[C_4H_7]^+$	100.0
83	$[C_6H_{11}]^+$ = $[M - C_3H_6ClO_2]^+$ $[C_5H_7O]^+$ = $[M - C_4H_{10}ClO]^+$	C_2H_4 / CO	55	$[C_4H_7]^+$ / $[C_3H_3O]^+$	100.0

tions of the ionized methyl 2-chloro-octanoate $8^{+\cdot}$ based on the 1st FFR metastable ions.

As reported previously,[1] the relative abundance of the molecular ion peak of the parent methyl esters goes through a minimum for methyl *n*-pentanoate (1%) and then rises with increasing relative molecular mass of the ester, being with methyl *n*-hexacosanoate (C_{26}) about 50% of the base peak. Figures 1–5 show that with 2-chloro esters (**3**–**20**), however, the abundance of $M^{+\cdot}$ is low (2–4%) and increases only slightly with

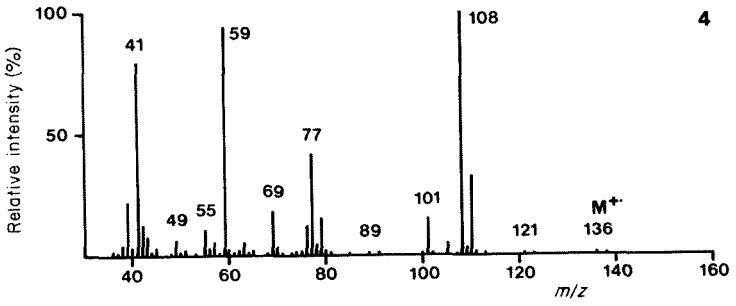


Figure 1. 70 eV mass spectrum of methyl 2-chlorobutanoate (**4**).

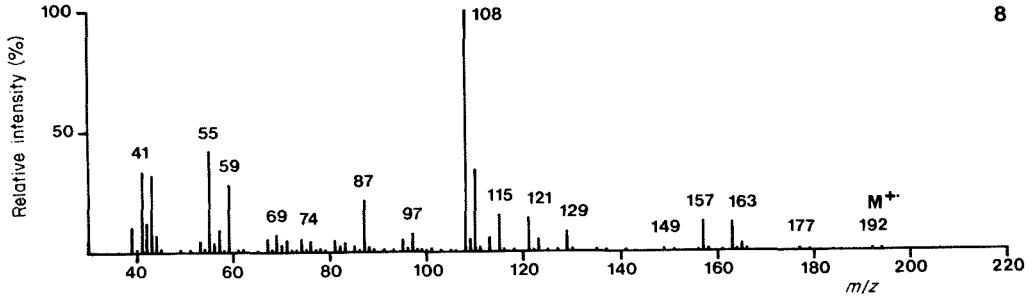


Figure 2. 70 eV mass spectrum of methyl 2-chloro-octanoate (**8**).

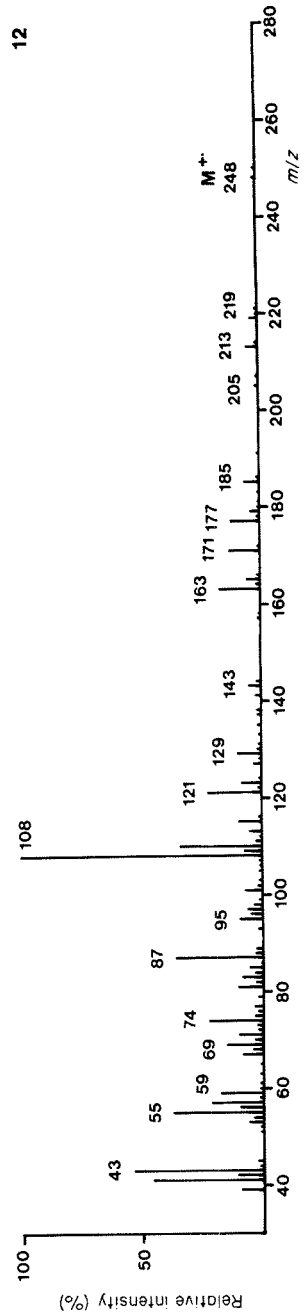


Figure 3. 70 eV mass spectrum of methyl 2-chlorododecanoate (**12**).

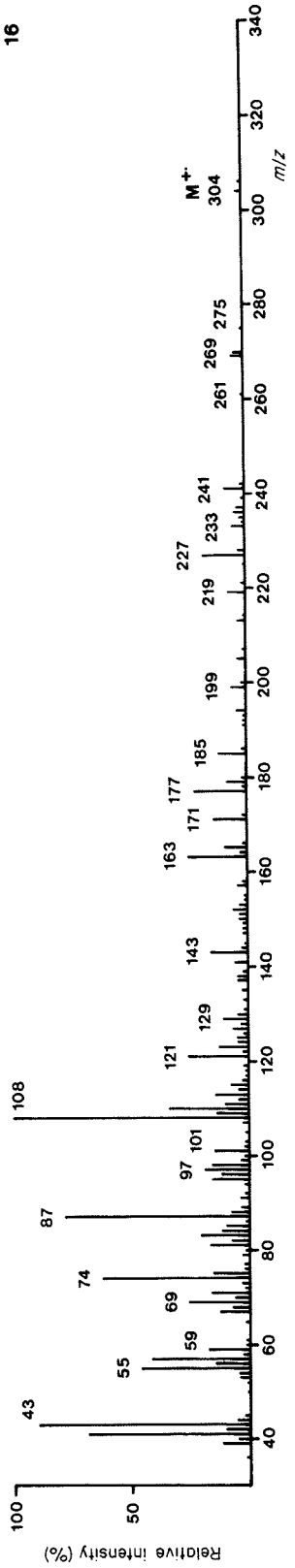


Figure 4. 70 eV mass spectrum of methyl 2-chlorohexadecanoate (**16**).

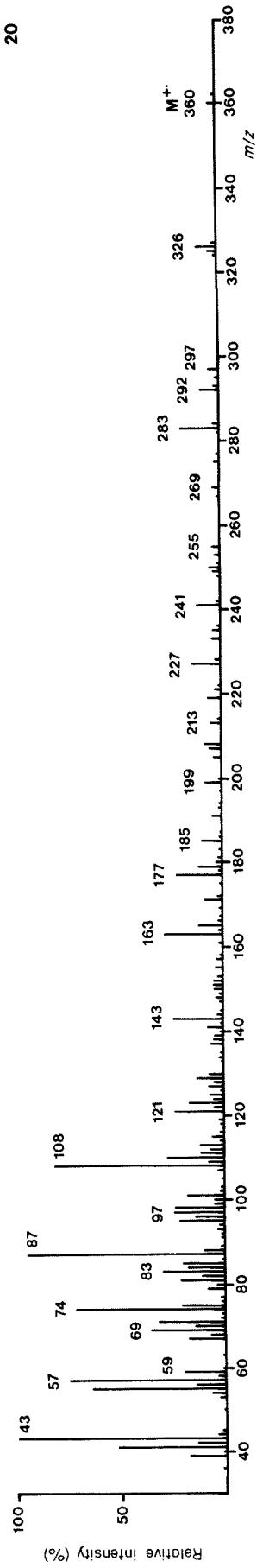


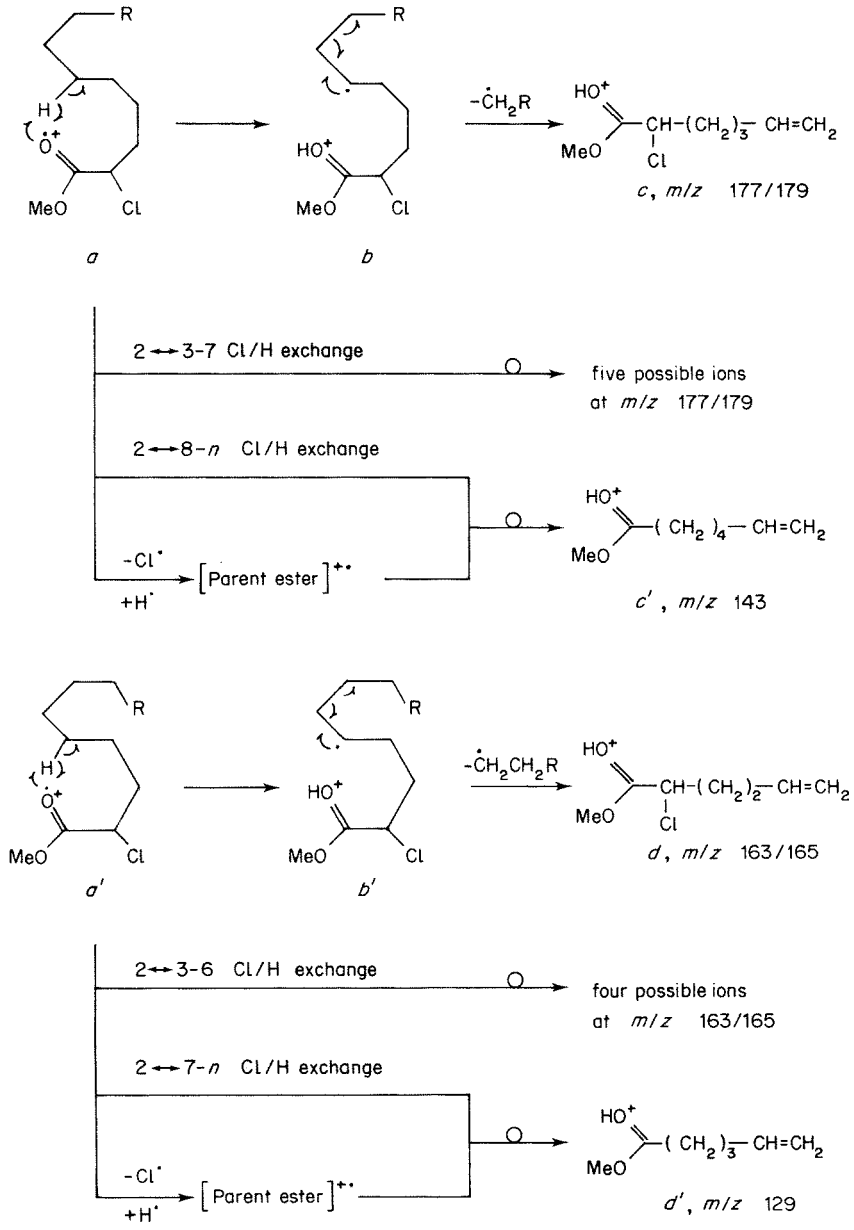
Figure 5. 70 eV mass spectrum of methyl 2-chloroeicosanoate (**20**).

increasing chain length. The α-cleavage fragment ions $[M - OCH_3]^+$ and $[M - COOCH_3]^+$ are shown of appreciable abundance only with the lower isomers (**1–5**).

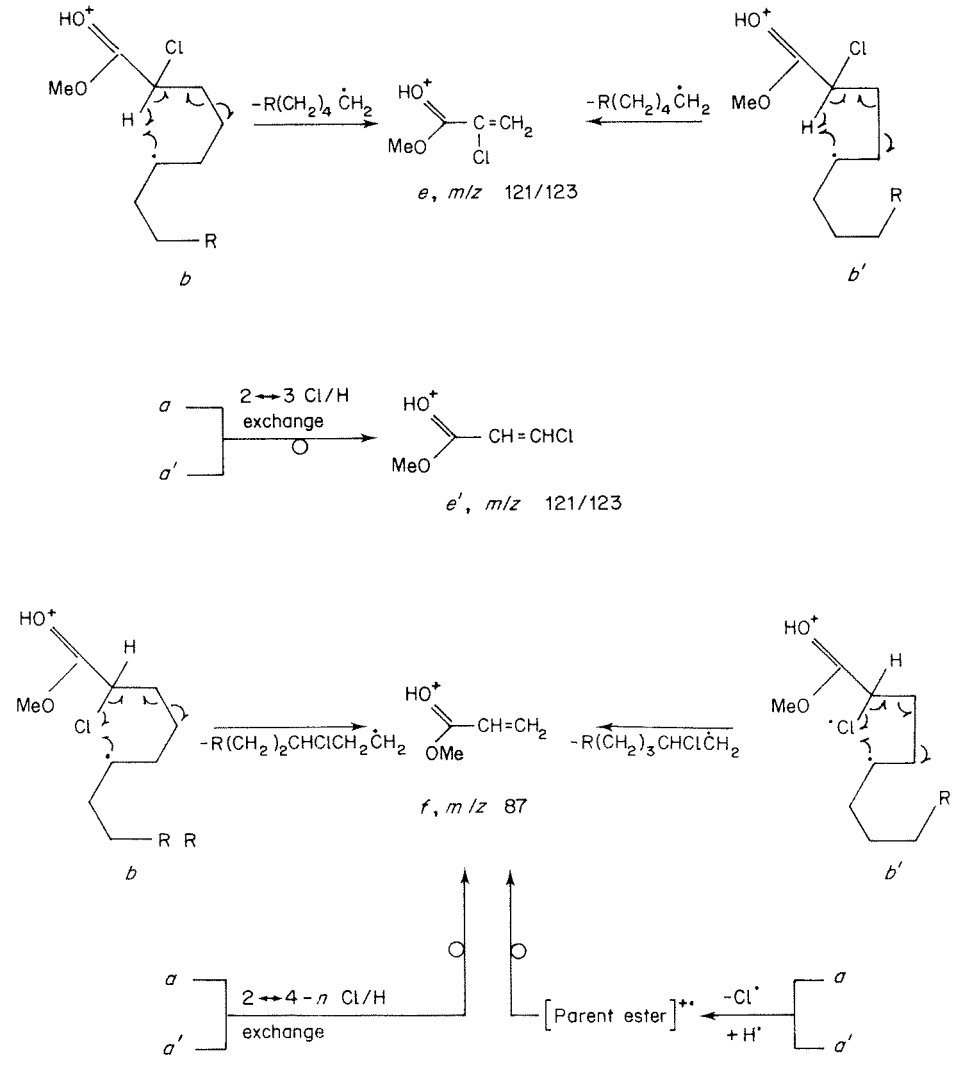
The McLafferty rearrangement gives for all C_4–C_{20} 2-chloro isomers (**4–20**) a very characteristic fragment ion at *m/z* 108/110, constituting the base peak in **4–16** (Figs 1–4). However, obviously owing to (i) the exchange of chlorine and hydrogen atoms and (ii) the formation of the non-chlorinated parent esters from the 2-chloro isomers (shown from the $[M - Cl + H]^{+\cdot}$ peaks particularly with the higher isomers (**17–20**), where its relative abundance overthrows even that of the $[M - Cl]^+$ peak) prior to the fragmentations, the appearance of the corresponding ion at *m/z* 74 typical for the parent[1] and the other chloro isomers,[12] is evident. The relative abundance of that peak increases gradually with increasing chain length, viz., from 2% for **4** to 85% for **19**, being with **19** and **20** even as high as the corresponding chlorine-containing fragment ion (Figs 1–5). It has been shown[6] previously with the partially deuteriated methyl esters that the exchange of deuterium and hydrogen atoms takes place between carbon atoms 2 and 5 and mainly 6. Owing to the lack of the deuteriated chloro compounds the positions of the exchanges between chlorine and hydrogen atoms could not be stated with the chloro isomers studied, but it seems evident that 2 ↔ 6 Cl/H exchange would be the most favoured one among the different possible exchanges.

Owing to the facts (i) and (ii) mentioned above the spectra of compounds studied also contain other peak pairs without and with the chlorine atom, i.e. the ion series at *m/z* 87, 101, 115, 129, 143, ..., and 121/123, 135/137, 149/151, 163/165, 177/179, ..., the probable formation of the most important ions being presented in Schemes 1 and 2.[26]

The relative abundance of ion *d* at *m/z* 163/165 is, with all compounds, higher than that of ion *c* at *m/z* 177/179 (Scheme 1), these fragments being very charac-



Scheme 1



Scheme 2

teristic for all higher 2-chloro esters occurring in the negligible manner with the $(3-\omega)$-chloro isomers, however.[27] The possible 2↔3–7 and 2↔3–6 Cl/H exchanges would produce different chlorine-containing ions at *m/z* 177/179 and 163/165, respectively, whereas the 2↔8 − *n* and 2↔7 − *n* Cl/H exchanges, as well as the parent esters formed, would lead to the formation of ions *c'* and *d'* at *m/z* 143 and 129, respectively (Scheme 1). It should be noted that with all methyl esters ion *c'* is more abundant than ion *d'*,[1] as is also the case with the spectra illustrated in Figs 1–5. The loss of HCl from ions *c* and *d* is the most favoured secondary fragmentation process, as shown in Table 1.

The abundance of ion *f* at *m/z* 87 increases with increasing chain length, whereas that of the chlorine-containing ion *e* (*e'*) remains quite constant with the different isomers. This might be due to the enhanced 2 → 6 Cl-transference in spite of the corresponding H-transference or to the increased tendency for facts (i) and (ii) mentioned (Scheme 2). On the other hand, the metastable ion analysis shows that the fragment ion at *m/z* 87 can also have been formed by several other routes, as is evident in Table 1. The elimination of CH_3OH is the most prominent secondary fragmentation from ions *e*, *e'* and *f*.

The primary loss of Cl· is shown by all the compounds, the intensity of the $[M-Cl]^+$ peak decreasing with increasing chain length, as would be expected. The secondary fragmentations of CH_3OH and C_5H_{10}/C_4H_6O are the most prominent ones, that of C_3H_6/CH_2CO occurring to a negligible extent (Table 1). However, the results show that the $[M-77]^+$ ion is formed preferentially direct from $M^{+\cdot}$ by the elimination of $C_3H_6Cl^{\cdot}$, the intensity of this peak being even greater than that of the $[M-Cl]^+$ peak (Figs 1–5). Correspondingly, the $[M-63]^+$ ion is formed by the loss of $C_2H_4Cl^{\cdot}$ from the molecular ion. The peaks formed through the primary losses of $C_3H_7^{\cdot}$ and $C_2H_5^{\cdot}$ (the main loss in **8**$^{+\cdot}$ based on the 1st FFR metastable ions) are not so significant, although shown, whereas the $[C_3H_7]^+$ ion at *m/z* 43 constitutes an intense peak, particularly with the higher isomers (base peak in **17–20**). These fragmentations obtained are in good accordance with those reported earlier for the parent methyl esters,[6] viz., by using the partially deuteriated esters it has been shown that the $[M-29]^+$ and $[M-43]^+$ ions are mainly formed through the elimination of $-C^2H_2-C^3H_2- +H^6$ and $-C^2H_2-C^3H_2-C^4H_2- +H^6$, respectively, and only to a small extent through the loss of the terminal ethyl

or propyl group. The hydrogen lost together with the methene groups is shown to come from the carbon atom at position 6.

The main fragmentation route for $\mathbf{8}^{+\cdot}$ based on the relative abundances of the 1st FFR metastable ions is shown to be $M - C_2H_5 - HCl - CH_3OH - CO$, i.e. with m/z values $192/194 \rightarrow 163/165 \rightarrow 127 \rightarrow 95 \rightarrow 67$, the routes of m/z $192/194 \rightarrow 115 \rightarrow 83 \rightarrow 55$ and $192/194 \rightarrow 129 \rightarrow 97 \rightarrow 69 \rightarrow 41$ being the next favoured ones, respectively. The possibility of the various fragmentations increases strongly with increasing chain length of the compounds studied, as shown in this work. Thus, the presentation of the generally accepted fragmentation routes for all isomers in the homologous series based on the data presented in Table 1 may not be sensible.

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REFERENCES

1. R. Ryhage and E. Stenhagen, *Arkiv Kemi* **13**, 523 (1959), and references therein.
2. R. Ryhage and E. Stenhagen, *Arkiv Kemi* **14**, 483 (1959).
3. R. Ryhage and E. Stenhagen, *Arkiv Kemi* **15**, 291 (1960).
4. R. Ryhage and E. Stenhagen, *Arkiv Kemi* **15**, 333 (1960).
5. Ng. Dinh-Nguyen, R. Ryhage and S. Ställberg-Stenhagen, *Arkiv Kemi* **15**, 433 (1960).
6. Ng. Dinh-Nguyen, R. Ryhage, S. Ställberg-Stenhagen and E. Stenhagen, *Arkiv Kemi* **18**, 393 (1961).
7. J. H. Beynon, R. A. Saunders and A. E. Williams, *Anal. Chem.* **33**, 221 (1961), and references therein.
8. Ng. Dinh-Nguyen, *Arkiv Kemi* **22**, 151 (1964).
9. Ng. Dinh-Nguyen, A. Raal and E. Stenhagen, *Chem. Scr.* **1**, 117 (1971).
10. Ng. Dinh-Nguyen, A. Raal and E. Stenhagen, *Chem. Scr.* **2**, 171 (1972).
11. Ng. Dinh-Nguyen and A. Raal, *Chem. Scr.* **10**, 173 (1976).
12. I. O. O. Korhonen and J. N. J. Korvola, *Acta Chem. Scand. (B)* **35**, 139 (1981).
13. I. O. O. Korhonen, *Acta Chem. Scand. (B)* **36**, 397 (1982).
14. I. O. O. Korhonen, *Acta Chem. Scand. (B)* **36**, 467 (1982).
15. I. O. O. Korhonen, M. Pitkänen and J. N. J. Korvola, *Tetrahedron* **38**, 2837 (1982).
16. I. O. O. Korhonen, *Org. Mass Spectrom.* **17**, 461 (1982).
17. I. O. O. Korhonen, *Org. Mass Spectrom.* **17**, 553 (1982).
18. I. O. O. Korhonen, *Acta Chem. Scand. (B)* **37**, 39 (1983).
19. I. O. O. Korhonen and J. Knuutinen, *J. Chromatogr.* **256**, 135 (1983).
20. I. O. O. Korhonen, *Org. Mass Spectrom.* **18**, 295 (1983).
21. I. O. O. Korhonen, *Org. Mass Spectrom.* **19**, 34 (1984).
22. I. O. O. Korhonen, *Org. Mass Spectrom.* **19**, 92 (1984).
23. D. N. Harpp, L. Q. Bao, C. J. Black, R. A. Smith and J. G. Gleason, *Tetrahedron Lett.* 3235 (1974).
24. I. O. O. Korhonen, *J. Chromatogr.* **209**, 96 (1981).
25. M. T. Pitkänen, I. O. O. Korhonen and J. N. J. Korvola, *Tetrahedron* **37**, 529 (1981).
26. G. Spiteller, M. Spiteller-Friedmann and R. Houriet, *Monatshefte* **97**, 121 (1966).
27. I. O. O. Korhonen, unpublished results.