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Chlorination of Carboxylic Acid Derivatives. IX. Liquid Phase Chlorination of Aliphatic C_2-C_8 Alkyl Acetates. EI Mass Spectra of Monochlorinated Esters

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A series of aliphatic alkyl acetates from ethyl to octyl acetate was chlorinated in the liquid phase in order to obtain monochlorinated products. The chlorination of esters was carried out with chlorine in the liquid phase in the absence and in the presence of benzene and with sulfuryl chloride in the presence of Bz_2O_2. The products were determined by gas-liquid chromatography and gas-liquid chromatography-mass spectrometry. Chlorination is appreciably deactivated at the 1-position, particularly with SO_2Cl_2, the deactivation at the 2-position being strongest with Cl_2 in the presence of benzene. The amounts of 1-chloro and ω-chloro isomers constituted the greatest disparity between the chlorination methods. The most characteristic mass spectral fragment ions of the 35 chlorinated alkyl acetates are given.

Numerous papers have been published on the free-radical substitution in aliphatic carboxylic acids and their derivatives induced by chlorinating reagents,[1-5] but very little has been reported on the reactivity of the alcohol chain in aliphatic esters. Bruylants and his co-workers have studied the chlorination of short-chain alkyl acetates,[6-10] Brown and Ash the chlorination of propyl acetate with chlorine and sulfuryl chloride,[11] Waddle and co-workers the chlorination of propyl and butyl trichloroacetates[12,13] and Singh and Tedder the halogenation of esters of 1-butanol.[14]

Recently, the chlorination of straight-chain methyl esters from propanoic to octadecanoic acid has been reported to produce monochloro isomers and, as side products, chloromethyl esters.[1-3] The amounts of the latter were only a few per cent due to the short-chain alcohol, and quantities decreased with an increase in acid chain length, as expected.

The present work was carried out in an attempt to study the chlorination of aliphatic C_2-C_8 alkyl acetates and to compare the results with those of our previous chlorination of methyl esters of aliphatic C_3-C_9 carboxylic acids.[1,2]

EXPERIMENTAL

Samples. Ethyl, propyl, butyl and pentyl acetates were commercial products from Fluka, AG. Hexyl, heptyl and octyl acetates were obtained from commercial (Fluka) alcohols and acetyl chloride as described earlier,[15] and C_2-C_8 alkyl chloroacetates from alcohols and chloroacetyl chloride (Fluka) by the same method.[15]

Chlorinations. Alkyl acetates were chlorinated with chlorine in the liquid phase at room temperature without solvent and in 10% benzene solution as described earlier.[1] The peroxide-catalyzed reaction with SO_2Cl_2 was carried out as described by Danechrad.[16] After removal of excess chlorination reagent and the liberated hydrogen chloride, the crude reaction mixtures were analyzed by gas-liquid chromatography (GLC) and gas-liquid chromatography-mass spectrometry (GLC-MS). Owing to a deficit of chlorinating agent variable amounts of unreacted substrates were observed, the amounts of higher chlorinated products being a few per cent.

Gas-liquid chromatography. GLC analyses were run on a Varian Model 2400 gas-liquid chromatograph, adapted for glass capillary work under the following conditions: Injector temperature, 220 °C; flame ionization detector, 240 °C; nitrogen carrier gas flow-rate, 1 ml/min; splitting ratio, 1:25; chart speed 10 mm/min; 5% Carbowax

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Table 1. The relative quantities[a] of monochloro isomers formed in the chlorinations of aliphatic C_2-C_8 alkyl acetates.

Chain length	Method[b]	Isomeric monochloro esters 1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl
C_2	A	1.7	1.0						
	B	1.8	1.0						
	C	0.7	1.0						
C_3	A	0.5	1.2	1.0					
	B	0.4	1.8	1.0					
	C	0.4	1.8	1.0					
C_4	A	0.3	0.9	1.8	1.0				
	B	0.1	1.3	4.6	1.0				
	C	–	1.5	2.6	1.0				
C_5	A	0.3	0.7	1.6	1.8	1.0			
	B	0.1	1.0	5.6	7.1	1.0			
	C	–	1.3	2.8	2.6	1.0			
C_6	A	0.2	0.6	1.3	1.7	1.8	1.0		
	B	0.1	0.8	3.7	6.5	5.8	1.0		
	C	–	1.1	2.4	2.9	2.6	1.0		
C_7	A	0.2	0.6	1.3	1.5	1.7	1.8	1.0	
	B	0.1	0.8	3.9	6.9	8.4	6.7	1.0	
	C	–	1.2	2.4	2.9	3.1	2.8	1.0	
C_8	A	0.2	0.7	1.3	1.5	1.7	1.8	1.8	1.0
	B	0.1	0.9	3.8	7.5	10.0	10.8	7.6	1.0
	C	–	1.2	2.4	2.9	3.1	3.2	2.9	1.0

[a] Relative to the ω-chloro isomers (= 1.0). The trace amounts of alkyl chloroacetates are not taken into consideration.
[b] Chlorination methods: (A) Cl_2, neat, 20 °C, UV-light; (B) Cl_2, benzene, 20 °C, UV-light; (C) SO_2Cl_2, neat, 60 °C, Bz_2O_2, dark.

Table 2. The relative quantities[a] of monochloro isomers formed in the Cl_2-chlorinations of aliphatic C_2-C_8 alkyl acetates and methyl esters of aliphatic C_3-C_9 carboxylic acids.

Chain length	Ester	Isomeric monochloro esters							
	(A) Alkyl acetate:	1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl
	(M) Methyl ester:	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl	9-Cl
C_2	A	1.7	1.0						
C_3	M	0.5	1.0						
C_3	A	0.5	1.2	1.0					
C_4	M	0.2	1.2	1.0					
C_4	A	0.3	0.9	1.8	1.0				
C_5	M	0.1	1.0	1.8	1.0				
C_5	A	0.3	0.7	1.6	1.8	1.0			
C_6	M	0.2	0.9	1.6	1.8	1.0			
C_6	A	0.2	0.6	1.3	1.7	1.8	1.0		
C_7	M	0.1	0.8	1.4	1.8	1.8	1.0		
C_7	A	0.2	0.6	1.3	1.5	1.7	1.8	1.0	
C_8	M	0.1	0.6	1.1	1.4	1.5	1.6	1.0	
C_8	A	0.2	0.7	1.3	1.5	1.7	1.8	1.8	1.0
C_9	M	0.1	0.7	1.0	1.3	1.4	1.5	1.5	1.0

[a] Relative quantities for the ω-chloro isomers taken as 1.0; the values for methyl esters are taken from our previous papers,[1,2] the proportions of chloromethyl esters not being taken into consideration.

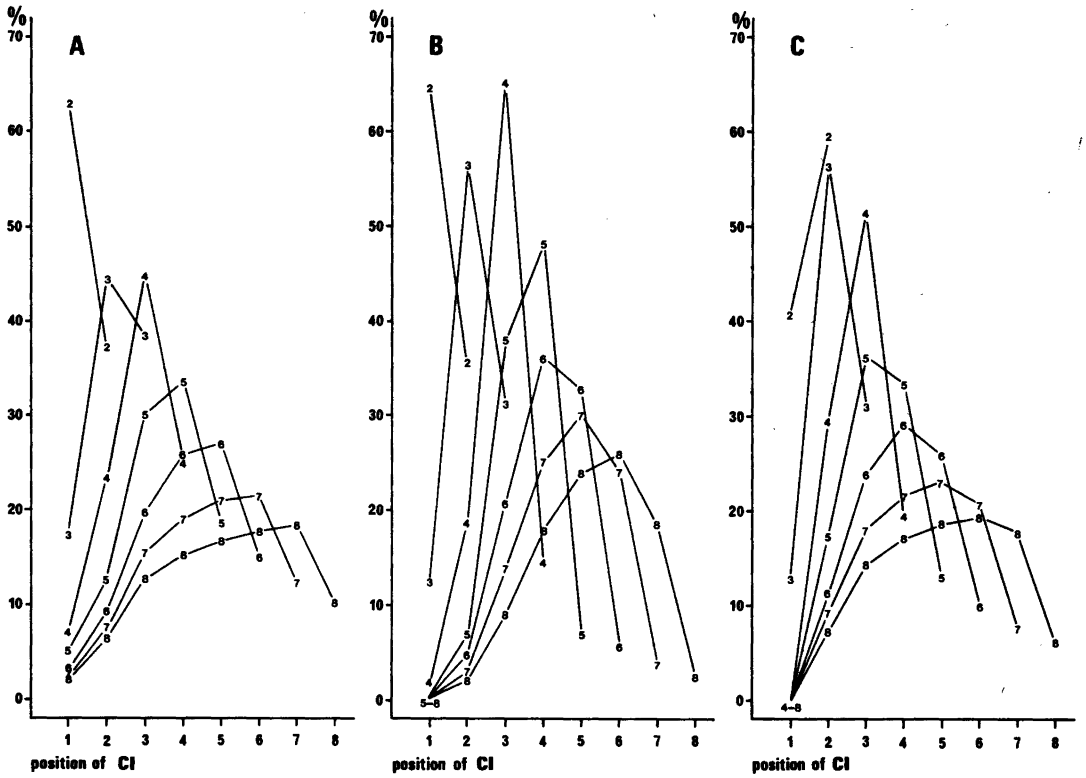

Fig. 1. Isomer distribution of monochlorinated C_2-C_8 alkyl acetates based on GLC analyses. Chlorination methods: (A) Cl_2, neat, 20 °C, UV-light; (B) Cl_2, benzene, 20 °C, UV-light; (C) SO_2Cl_2, neat, 60 °C, Bz_2O_2, dark. The number denotes the alcohol chain length.

Table 3. The relative quantities[a] of monochloro isomers in the SO_2Cl_2-chlorinations of aliphatic C_2-C_8 alkyl acetates and methyl esters of aliphatic C_3-C_9 carboxylic acids.

Chain length	Ester	Isomeric monochloro esters							
	(A) Alkyl acetate:	1-Cl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl
	(M) Methyl ester:	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl	9-Cl
C_2	A	0.7	1.0						
C_3	M	0.9	1.0						
C_3	A	0.4	1.8	1.0					
C_4	M	0.4	2.1	1.0					
C_4	A	–	1.5	2.6	1.0				
C_5	M	0.3	1.9	2.9	1.0				
C_5	A	–	1.3	2.8	2.6	1.0			
C_6	M	0.3	2.0	3.5	3.1	1.0			
C_6	A	–	1.1	2.4	2.9	2.6	1.0		
C_7	M	0.3	1.6	2.8	3.3	2.9	1.0		
C_7	A	–	1.2	2.4	2.9	3.1	2.8	1.0	
C_8	M	0.3	1.4	2.5	3.1	3.5	2.6	1.0	
C_8	A	–	1.2	2.4	2.9	3.1	3.2	2.9	1.0
C_9	M	0.3	1.1	2.5	2.9	3.1	3.1	2.7	1.0

[a] Relative quantities for the ω-chloro isomers taken as 1.0; the values for methyl esters are taken from our previous papers,[1,2] the proportions of chloromethyl esters not being taken into consideration.

Table 4. 70 eV EI-MS data (rel. int. ⩾5%) for monochlorinated alkyl acetates. Notation of compounds: the (*e.g.* 36 denotes 3-chlorohexyl acetate).

Ion	*m/z* >38	Compound 12	22	13	23	33	14	24	34	44	15	25	35	45	55	16
$C_8H_{14}^{\cdot+}$	110															
$C_5H_9Cl^{\cdot+}$	104												6			
$C_7H_{13}^{+}$	97															
$C_7H_{12}^{\cdot+}$	96															
$C_7H_{11}^{+}$	95															
$C_4H_7Cl^{\cdot+}$	90							7	11							
$C_5H_{10}O^{\cdot+}$	86										7			5		
$C_5H_9O^{+}$	85										6		5			
$C_6H_{11}^{+}$	83															
$C_6H_{10}^{\cdot+}$	82															
$C_6H_9^{+}$	81															
$C_3H_5Cl^{\cdot+}$	76											5				
$MeCO_2CH_2^{+}$	73		12		14	6		32	6	6		19		8	9	
$C_4H_8O^{\cdot+}$	72								5							
$C_5H_{10}^{\cdot+}$	70															
$C_5H_9^{+}$	69										5	5	14	15	8	
$C_5H_8^{\cdot+}$	68												10	27	17	
$C_5H_7^{+}$	67													7	7	
$MeCHCl^{+}$	63													5		
$C_2H_3Cl^{\cdot+}$	62		10													
$[MeCO_2+2H]^{+}$	61					19			8	9			10	11	16	
$C_4H_{10}^{\cdot+}$	58										5			5		5
$C_4H_9^{+}$	57			9												
$C_4H_8^{\cdot+}$	56												12			7
$C_4H_7^{+}$	55						6	11	22	15			5	6	13	5
$C_4H_6^{\cdot+}$	54									16						
$C_4H_5^{+}$	53															
$ClCH_2^{+}$	49															
$C_3H_7^{+}$, $MeCO^{+}$	43	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
$C_3H_6^{\cdot+}$	42	5	5						9		5	5	7	7	9	
$C_3H_5^{+}$	41			5	8	12				6	9	9	21	17	12	8
$C_3H_3^{+}$	39									5			6	5		

20 M glass capillary column (22 m × 0.3 mm I. D.), prepared in our laboratory;[17] column temperature program from 50 °C at 6 °C/min until the elution of peaks ceased. The chromatographic data were analyzed with a Hewlett-Packard Model 3390A Reporting Integrator using standard programs.

Mass spectra. GLC-MS data were recorded on a Varian MAT-212 mass spectrometer connected with a Varian Model 3700 gas-liquid chromatograph. It was equipped with a 25 m × 0.22 mm (I.D.) vitreous silica SF-30 WCOT column, supplied by Scientific Glass (North Melbourne, Australia), with a helium flow-rate of 1 ml/min. The column temperature was programmed from 50 °C at 6 °C/min. Electron ionizing energy was 70 eV and ion source temperature 220 °C. Data were acquired and processed on a Spectro System MAT-188.

RESULTS AND DISCUSSION

Fig. 1 illustrates the isomer distributions of monochlorinated products formed in three different chlorination processes. The relative quantities of products are presented in Table 1, tabulated relative to the ω-chloro isomers. Values are averages of two independent experiments and agree to within ±4%.

The isomeric monochlorinated alkyl acetates have been reported[14] to elute on GLC in direct order from 1-chloro to ω-chloro compound, as do the corresponding methyl derivatives.[18] Fig. 2 illustrates the GLC patterns of monochlorinated octyl acetates formed in three different chlorination processes. As can be seen, the isomers can be completely separated on Carbowax 20 M. On a non-

first number indicates the position of the Cl-substituent, the second number the alcohol chain length

26	36	46	56	66	17	27	37	47	57	67	77	18	28	38	48	58	68	78	88
																	6		
								5			10								12
							7	7	9										
							5	11	12	12									
																6	7	5	
	11	6					13							5					
		5						8											
8		8	14	5							6				7		5	6	5
	8	22	21	10										5	10	12	21	15	8
						6	18	25	35	34	14		6	14	17	21	31	14	5
5								6							5				
23		5	7	7		16		5	6	6	8		14		5		6	5	7
	5				5						9		6		7	9	6	5	
				8			6	8	6	10	12	7	6	14	20	16	22	18	20
							5	7	9	16	12		8	17	25	23	29	31	16
	16	21	33	17			10	11	16	11	13	8		13	19	22	24	24	14
	12	10	9	14			13	10	10	10	23			11	8	9	10	13	24
					5					5									
						7	7					7		6				6	
		5		8		7	11	10	16	10	10	8		11	8	7	8	6	12
5	23	23	23	18	5	11	31	32	36	29	30	8	10	22	20	29	27	28	28
				7			18	15	22	26	8			16	13	17	22	12	6
															5				
	5		5				8												
100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
5	11	10	10	8	8		10	8	7	7	12	5	9	8	9	11	10	11	11
10	16	17	13	17	9	13	23	16	21	20	16	11	15	25	27	23	28	28	24
	7	5	5	6			7	6	8	6	5		5	8	7	7	8	7	7

polar SE-30 column, however, the isomers are eluted closer together, leading to a poor separation of 6-chloro- and 7-chloro-octyl acetates. The polarity of the isomeric monochlorinated alkyl acetates increases with the increase in distance between the ether oxygen and the chlorine substituent, which leads to the better separations of the isomers on polar than on non-polar columns.

The results of the neat chlorinations of C_3-C_5 alkyl acetates given in this work are comparable agreement with those reported in the paper by Soumillion and Bruylants,[7] the main products being always the (ω-1)-chloro isomers. Fig. 1B and Table 1 show that benzene strongly affects the selectivity of the reagent as with the chlorinations of chloromethyl esters.[19] The main products were the (ω-1)-chloro isomers for C_2-C_5 esters and the (ω-2)-chloro isomers for the longer chain esters. The amounts of the ω-chloro products were 1.1 to 4.2 times as great in the absence as in the presence of benzene. Smaller amounts of 1- and 2-chloro isomers formed in the reactions with the solvent were also observed.

It has been previously reported that the sulfuryl chloride chlorination of propyl acetate yields quite similar isomer distribution than the photochemical chlorination under similar conditions.[11] As can be seen from Fig. 1 and Table 1, a quite different isomer distribution under reaction conditions used in this work is observed. The chlorinations with sulfuryl

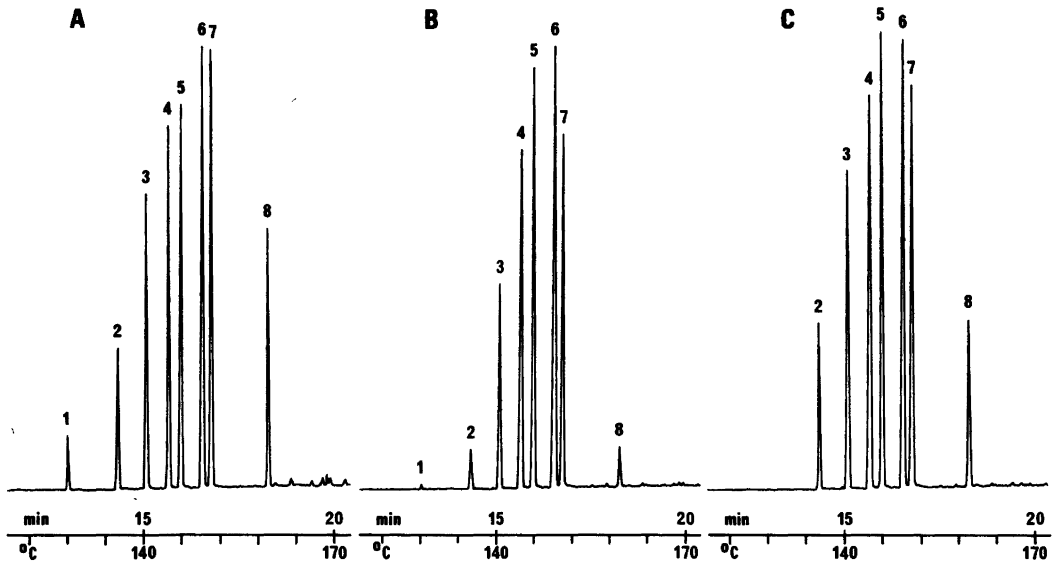

Fig. 2. GLC-patterns of monochlorinated octyl acetates formed by three different chlorination methods (A, B, C); see Table 1. Products were analyzed on Carbowax 20 M glass capillary column. The peak number indicates the position of the Cl-substituent.

chloride are appreciably deactivated at the 1-position and slightly at the 2-position. The trace amounts (or absences) of 1-chloro isomers formed at higher reaction temperature (60 °C) could be caused by the instability of products.[11] Nevertheless, greater amounts of 1-chloropropyl[11] and 1-chlorobutyl acetates[14] have been reported to be formed at higher reaction temperatures, wherefore the effect of the instability could also be negligible. Owing to the strong deactivation, the amount of ω-chloroethyl acetate was greater than that of 1-chloro isomer in the reaction with SO_2Cl_2, the other chlorination methods yielding the reverse proportion. The main products were the (ω-1)-chloro isomers for propyl and butyl acetates and the (ω-2)-chloro isomers for the other esters. The amounts of the ω-chloro isomers of C_3-C_8 alkyl acetates were 1.2 to 1.7 times as great with chlorine as with SO_2Cl_2, the ratio linearly increasing with an increase in the chain length.

Negligible amounts (<2%) of alkyl chloroacetates were found among the monochlorinated products of short-chain C_2-C_4 esters, the compounds being determined by comparison with model samples. The chlorine substitution seems to be much easier on the alcohol chain than on the acid chain, which can be seen from the relatively great amount of chloromethyl ester formed in the chlorination of methyl propanoate.[1] The chlorination of methyl acetate, for example, yielded *ca.* ten times as much chloromethyl acetate as methyl chloroacetate.[20] The process was very slow, moreover, and the total amount of chlorinated products was only 5% under the same reaction conditions as used in this work.

To compare the effects of different types of substituent, the relative quantities of monochlorinated isomers formed in the chlorinations of C_2-C_8 alkyl acetates and methyl esters of C_3-C_9 carboxylic acids are given in Tables 2 and 3. The values for methyl esters are taken from our previous papers,[1,2] the proportions of chloromethyl isomers not being taken into consideration. The results show that nearly the same isomer distributions of the corresponding esters are observed (acid chain length = alcohol chain length). Table 2, however, shows that in the reactions with Cl_2 the deactivation at the α-position seems to be stronger in methyl esters than in alkyl acetates, whereas with SO_2Cl_2 it is just the opposite (Table 3).

Mass spectra. The mass spectra of a large number of aliphatic alkyl acetates are reported in the literature,[21-27] but mass spectra for their chlorinated derivatives are few in number.[28]

EI-MS data for monochlorinated C_2-C_8 alkyl acetates are given in Table 4, all peaks greater or equal to 5% of the base peak (100%) being tabulated. Ions containing ^{37}Cl are not shown.

The molecular ion peaks of unchlorinated alkyl acetates are weak and can be seen only at lower molecular weight,[21] and $M^{\cdot+}$ is not shown by any of the chloro esters. α-Cleavage at the carbonyl group, $MeCO^+$, and to a small extent the $C_3H_7^+$ fragment ion, produce together the base peak at *m/z* 43 in all spectra. The loss of $C_3H_7^{\cdot}$ from $M^{\cdot+}$ clearly occurs most easily in the case of (ω-3)-chloro isomers (*14*, *25*, *36*, *47* and *58*), the remaining chlorine-containing fragment ion not being shown in the spectra, however.

The mass spectra of the short-chain monochlorinated alkyl acetates contain only a few additional peaks and the intensities are low. An additional α-cleavage reaction initiated by the saturated oxygen atom given $MeCO_2CH_2^+$ ions at *m/z* 73, the most intense peak in the spectra of 2-chloro isomers. The corresponding chlorine-containing fragment ion at *m/z* 107 is characteristic of 1-chloro isomers, but the intensity of the peak is very low (~1%).

The loss of acetic acid from the molecular ion *via* rearrangement of one hydrogen atom results in the formation of the $C_nH_{2n-1}Cl^{\cdot+}$ ion series at *m/z* 62, 76, 90, 104, ... This chlorine-containing fragment ion is the most abundant ion in the spectra of 2- and 3-chloro isomers of short-chain esters, but does not appear in those of long-chain esters. The subsequent loss of $Cl^{\cdot}$ or HCl gives $C_nH_{2n-1}^+$ and $C_nH_{2n-2}^{\cdot+}$ ion series. The peak at *m/z* 60, due to $MeCO_2H^{\cdot+}$, however, is not shown by any of the chlorinated acetates.

The rearrangement of two hydrogen atoms[24] is characteristic for alkyl acetates, giving the fragment ion, $[MeCO_2+2H]^+$, at *m/z* 61. This peak is the most intense peak in the spectra of the ω-chloro isomers. The chlorine substituent at 1- or 2-position, however, seems to make these hydrogen rearrangements difficult, giving rise to the smaller (<5%) peaks. Subsequent or simultaneous loss of $Cl^{\cdot}$ or HCl gives $C_nH_{2n-2}^{\cdot+}$ and $C_nH_{2n-3}^+$ ion series. These fragment ions are weak in all 1- and 2-chloro isomers.

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