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Chlorination of Carboxylic Acid Derivatives. VIII. Liquid Phase Chlorination of the Aliphatic C_5-Carboxylic Acids and Their Chlorides, Methyl Esters and Chloromethyl Esters with Chlorine

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The chlorinations of pentanoic, 3-methylbutanoic, 2-methylbutanoic and 2,2-dimethylpropanoic acids and their derivatives with chlorine in the liquid phase have been investigated. The monochloro products formed were determined by gas-liquid chromatography (GLC) and gas-liquid chromatography–mass spectrometry (GLC–MS) as their esters through comparison with authentic samples. The deactivation of position 2 decreases in the order $COCl > CO_2H > CO_2CH_2Cl > CO_2CH_3$, the effect of the COCl-group in pentanoic acid derivatives being 4.3 times stronger than that of the CO_2CH_3-group. The deactivation is smallest in 2-methylbutanoic acid derivatives owing to the electron-donating methyl group. The EI mass spectra of the methyl and chloromethyl esters have been studied in detail.

In earlier studies we have reported the chlorination of methyl esters of aliphatic C_3-C_{18} n-carboxylic acids,[1-3] propanoyl chloride,[4] butanoyl chloride[5] and its monochloro derivatives,[6] and chloromethyl esters of aliphatic C_3-C_{12} n-carboxylic acids.[7]

Some papers have appeared on the chlorination of pentanoic,[8-14] 3-methylbutanoic[15-18] and 2,2-dimethylpropanoic[18-23] acids and their derivatives, but none on the chlorination of 2-methylbutanoic acid or its derivatives.

This work has been undertaken to study the effect of the COR-group on the isomer distributions of monochloro products formed in the chlorination of aliphatic C_5-carboxylic acids and their derivatives. The EI mass spectra of chlorinated methyl and chloromethyl esters were studied in detail, with deuterium labelling and metastable ion analysis used to elucidate the mechanism of fragmentations.

RESULTS AND DISCUSSION

The structures and notation of compounds studied are given in connection with Table 1. The chlorinations of carboxylic acids and their derivatives were carried out at room temperature by passing dry chlorine through a sample of the neat compound. To minimize the formation of higher chlorinated products, less than an equimolar quantity of chlorine was used. For gas-liquid chromatographic analysis the mixtures of monochloro acids and acid chlorides were converted to methyl esters.

Identification. Products were identified by GLC and GLC-MS, through comparison with separately prepared reference esters, and estimated by GLC without weight response factors.[2] Monochloro chloromethyl esters were identified by GLC as described earlier:[7] acid chlorides were chlorinated, whereafter one part of the monochloro products was esterified with methanol and the other part was converted to chloromethyl esters.[24] The combined mixtures of the esters were analyzed by GLC, the separation of compounds indicating similar isomer distributions. A chromatogram of the mixture of methyl and chloromethyl 2-methylbutanoates is illustrated in Fig. 1.

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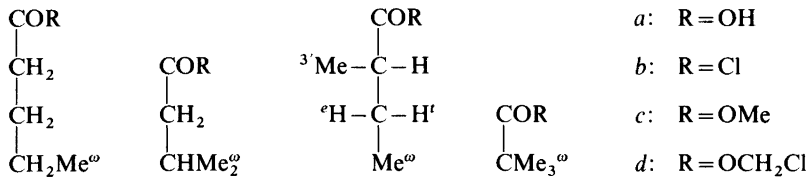
Table 1. Relative reactivity (r_x) of each hydrogen atom ($r_\omega = 100$) in the chlorination of the title compounds.



Cpd.	x	a	b	c	d
1	R	–	–	9	–
	2	14	4.3	21	18
	3	151	101	162	175
	4	282	278	279	304
2	R	–	–	13	–
	2	20	7	29	23
	3	339	357	387	341
3	R	–	–	16	–
	2	76	57	132	110
	3e	200	239	249	275
	3t	183	204	229	235
	3'	29	15	42	29
4	R	–	–	36	–

3-Chloro-2-methylbutanoic acid and its derivatives exist as pairs of diastereomers, the *erythro* and the *threo* forms. The addition of hydrogen chloride to methyl tiglate (methyl *trans*-2-methyl-2-butenoate) leads almost quantitatively to the *erythro* form. GLC analysis of the reaction mixture established the amount of the *threo* isomer to be only 1%. The free-radical substitution in the saturated compound, however, gives nearly equivalent amounts of the isomers (*3c3e* and *3c3t*), which were identified by comparing their behaviours with those of methyl *erythro*- and *threo*-2,3-dichlorobutanoates.[2,5] The following similarities are observed: the *erythro* form has a shorter retention time (GLC) than the *threo* isomer (Fig. 1); most chemical shifts (^{1}H NMR) for the *threo* form are slightly downfield as compared with the *erythro* isomer (see the Experimental section); the *threo* form gives a more abundant peak (MS) at *m/z* 115, M – Cl$^+$, than the *erythro* form, the mass spectra of the compounds being otherwise nearly identical (Table 3).

Isomer distribution. The results of the quantitative analyses of monochloro products formed in the chlorinations are presented in Table 1. The relative reactivity (r_x) of each hydrogen atom of the compounds is given, relative to ω-chloro isomers ($r_\omega = 100$). Values are the averages of two experiments, agreeing within $\pm 3\%$. It can be seen that the deactivating effect of the carbonyl group at the adjacent 2-position decreases in the order $COCl > CO_2H > CO_2CH_2Cl > CO_2CH_3$. The respective amounts of 2-chloro isomer formed in the pentanoic acid series were in the ratios 1.0:3.4:4.2:5.0. In the 2-methylbutanoic acid series, however, the electron-donating 2-methyl substituent strongly decreases this deactivation as well as the disparities between the four compounds, the ratios being 1.0:1.3:2.0:2.3. An opposite influence of the electronegative chlorine substituent at the 2-position has been reported earlier.[4-6] As can be seen from Table 1, the effect of the methyl substituent further away (3-methylbutanoic acid derivatives) is smaller.

Earlier studies have always reported [1,2] the (ω-1)-chloro isomers to be the main chlorination products of methyl esters of aliphatic short- and medium-chain n-acids such as the 4-chloro isomers of

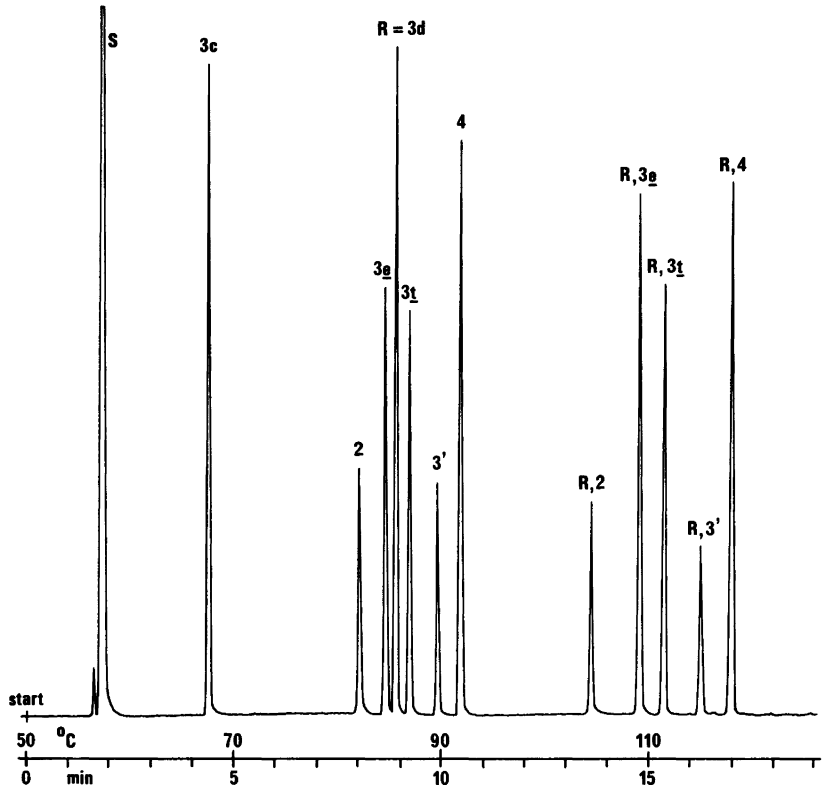


Fig. 1. Mixture of *3c* and its chloro derivatives analyzed by GLC on SE-30. S = solvent; the peak numbers indicate the chlorinated positions.

pentanoic acid derivatives in this work. However, in the case of 3-methylbutanoic acid derivatives, which contain six ω-hydrogen and only one (ω-1)-hydrogen, the main products were the ω-chloro isomers. It has been reported[18] that the chlorinations of 3-methylbutanoic acid and its derivatives give the following ratios of 2-, 3- and 4-chloro isomers: acid 26:69:5, acid chloride 32:60:8 and methyl ester 49:49:2. Although the chlorinations of acid chloride and methyl ester were carried out in the gas phase, the isomer distributions reported must be incorrect, since chlorination temperature has a relatively small effect on the product proportions.[1]

Table 1 shows the chlorinations of 2-methylbutanoic acid (*3a*) and its derivatives (*3b* – *3d*) favour the 3-position, the total amount of stereoisomers being between 44 and 52%. By contrast, substitution at a second 3-position giving 2-chloromethylbutanoic acid derivatives seems to be difficult and in most cases even more difficult than substitution at the 2-position.

The chlorinations of methyl esters lead to a reaction in the methoxyl group, the substitution decreasing with increase in chain length.[1,2] With the branched-chain esters studied in this work the greatest amount of chloromethyl ester was obtained for methyl 2,2-dimethylpropanoate (11%), the quantity being smaller than earlier reported[1] for methyl propanoate (18%).

Mass spectra. The mass spectra of methyl esters and their monochloro derivatives are given in Tables 2 and 3, all peaks greater or equal to 5% of the base peak (100%) being tabulated. Ions containing ^{37}Cl are not shown. Deuterium labelling (trideuteriomethyl esters) and metastable ion analysis were used to elucidate the mechanism of fragmentations.

The molecular ion peaks of chlorinated methyl esters are small and can be seen only at lower

Table 2. 70 eV EI-MS data for Cl-free methyl esters.

Ion	*m/z* >38	Rel. int. ≧5			
		1c	*2c*	*3c*	*4c*
M − Me·	101		8	15	
$M-C_2H_4$	88			74	
M − Et·	87	24		5	
M − MeO·	85	27	18	23	9
$M-C_3H_6$	74	100	79		
M − Me· − CO	73				10
$C_5H_9^+$, $C_4H_5O^+$	69		9	9	
$MeOCO^+$	59	28	34	25	8
$C_4H_9^+$	57	44	25	100	100
$C_4H_8^{\cdot+}$, $C_3H_4O^{\cdot+}$	56	8	6	22	25
$C_4H_7^+$	55	26		16	
$C_2H_5O^+$	45	7		7	
$C_3H_7^+$	43	74	100		15
$C_3H_6^{\cdot+}$, $CH_2CO^{\cdot+}$	42	19	17		
$C_3H_5^+$	41	52	43	78	73
$C_3H_3^+$	39	19	20	24	31

molecular weights.[1] The loss of a methyl radical from the molecular ion is more important in the parent esters than in chloro esters. Judging from the mass spectra of trideuteriomethyl esters, the loss of a methyl radical occurs from the acyl group and never from the methoxyl group. This fragmentation is the most prominent in *3c*; in chloro esters it occurs only in 3-chloro isomers (*1c3*, *2c3*, *3c3* and *4c3*) the peaks being small (< 5 %).

α-Cleavages give in the case of parent esters M − MeO· and M − MeOCO· ions at *m/z* 85 and 57, respectively, the latter peak always being more intense (base peak in *3c* and *4c*). In chloro esters the corresponding fragment ions appear at *m/z* 119 and 91. In all monochloro isomers of methyl 2-methylbutanoate (*3c*) and in methyl 3-chloro-2,2-dimethylpropanoate (*4c3*), and always in 2-chloro esters,[1] the M − MeOCO· ions are more abundant than the M − MeO· ions. In *1c3*, *1c4*, *2c3* and *2c4*, however, the opposite relation is observed.

The McLafferty rearrangement gives, in general, intense peaks (base peak in *1c*, *1c4*, *2c2*, *2c4* and *3c4*) at *m/z* 74 or 88 in the spectra of parent esters and at *m/z* 74, 88, 108 or 122 in those of chloro esters. The isomers substituted at the 2- or 3'-positions can easily by identified and distinguished from the other isomers on the basis of this fragment ion. In the case of 3- and 5-chloro esters, however, the β-cleavage with hydrogen rearrangement gives only small peaks.[26]

The β-cleavage produces $C^{\cdot}\ R^1R^2-CO_2CH_3$ ions in appreciable abundance only in the case of 3-chloro isomers, the fragmentation in *1c3* and *2c3* (base peak in *2c3* at *m/z* 73) being even more important than the McLafferty rearrangement.

γ-Cleavage in the parent esters gives the peak at *m/z* 87 or 101. In chloro esters, except *1c5* (34 %), it is weak and in 2- and 3-chloro isomers the corresponding chlorine-containing fragment ion is missing.

The loss of a chlorine atom from the molecular ion is appreciable only in the 3- and 5-chloro isomers, being intense in stereoisomers (*3c3e* and *3c3t*), 51 and 66 %, respectively. The intensity of the M − Cl· peak shows the greatest variation in the spectra of these different forms. On the basis of metastable ion analysis, there would seem to be losses of small neutral fragments such as CO, CH_2CO and CO_2 from the M − Cl· ion after migration of the methoxyl or methyl group, giving peaks at *m/z* 87, 73 and 71, respectively. Proton transfer from the adjacent carbon atom to the ether oxygen allows elimination of CH_3OH from the M − Cl· ion,[27] giving a peak at *m/z* 83.

The loss of hydrogen chloride from the molecular ion produces the unsaturated methyl ester, the fragmentation in *2c3* being even more important than the loss of Cl·. The loss of CH_3OH after HCl-elimination gives a peak at *m/z* 82, which in *1c3* and *2c3* is more intense than the M − Cl· − CH_3OH

Table 3. 70 eV EI-MS data (rel. int. ≧5) for methyl esters chlorinated at position *x*.

Ion	*m/z* >38	*1c*, *x* =					*2c*, *x* =				*3c*, *x* =						*4c*, *x* =	
		R (=*1d*)	2	3	4	5	R (=*2d*)	2	3	4	R (=*3d*)	2	3′	3*e*	3*t*	4	R (=*4d*)	3
$M-C_2H_4$	122										10	22	22					
$M-C_2H_5^{\cdot}$	121												12					
$M-MeO^{\cdot}$	119			9	13	14			25	12			9	8	11	10		6
$M-Cl^{\cdot}$	115		9	23		18			12				11	51	66			35
$M-HCl$	114			12		8			20					9				5
$M-C_3H_6$	108	12	79	5			11	100										
$M-HCl-Me^{\cdot}$	99													14	14			
$C_4H_8Cl^+$	91		9	6		19		8	18	6		42	18	20	25	14		33
$C_4H_7Cl^{\cdot+}$	90											20						14
$M-C_2H_3Cl$	88													9	15	100		
$M-C_2H_4Cl^{\cdot}$	87					34												
$M-Cl^{\cdot}-CO$	87												67	6				
$C_4H_6O_2^{\cdot+}$	86										15							
$M-ClCH_2O^{\cdot}$	85	55					30				43						15	
$C_4H_7CO^+$	83		11	32	22	22		9	28			7		16	9			10
$C_4H_6CO^{\cdot+}$	82			38	10	20			43	8				9	6			7
$ClCHCO^{\cdot+}$	76		10					20			9							
$M-C_3H_5Cl$	74		6	13	100	19			15	100								
$C_3H_5O_2^+$	73	6		18	10	16			100									16
$C_3H_4O_2^{\cdot+}$	72	13		16		8	14	7										
$C_5H_9^+, C_4H_5O^+$	69						7	8	5		6		6					
$MeCHCl^+$	63		7	6	8			6	5			8	8	9	15			8
$MeOCO^+$	59		57	51	29	51		34	37	34		39	38	75	78	37		25
$C_4H_9^+$	57	34	8		6	13	28				98			26	21	23	100	
$C_4H_8^{\cdot+}, C_3H_4O^{\cdot+}$	56	15	8		11		7		9		24		26	34	39	25	10	53
$C_4H_7^+$	55	27	100	100	72	100	5	39	60	31	15	100	100	100	100	69	5	100
$C_4H_6^{\cdot+}$	54			16	7	11			6				6	7	6			
$C_4H_5^+$	53		11	15	8	10		10	7		5	9	8	14	14	9		10
CH_2Cl^+	49	8	5	6	5	6	8			8	10		5			5	7	7
$C_2H_5O^+$	45	6		8	6								8	6	7	6		
$C_3H_7^+$	43	50	63	28	41	64	56	56	26	42	21	67		25	23	9	7	46
$C_3H_6^{\cdot+}, CH_2CO^{\cdot+}$	42	32	26	13	15	32	27	24	7	26	14		6	7	6	21	33	
$C_3H_5^+$	41	100	45	38	20	51	100	44	68	36	100	24	24	32	35	39	66	34
$C_3H_3^+$	39	29	37	34	22	43	33	52	34	20	37	27	25	42	36	33	32	59

Table 4. 70 eV EI-MS data (rel. int. ≧5) for chloromethyl esters chlorinated at position *x*.

Ion	*m/z* >38	*1d*, *x* =				*2d*, *x* =			*3d*, *x* =					*4d*
		2	3	4	5	2	3	4	2	3′	3*e*	3*t*	4	*x* = 3
$M-C_2H_4$	156								7					
$M-Cl^{\cdot}$	149										25	19		5
$M-C_3H_6$	142	38				72								
$M-C_2H_3Cl$	122										5		54	
$M-CO-Cl^{\cdot}$	121									16				
$M-ClCH_2O^{\cdot}$	119	17	39	41	30	22	66	52	6	16	46	46	44	15
$M-ClCH_2OH$	118		18		15		23	8			12	9		
$M-C_3H_5Cl$	108			70	5		5	100						
$M-C_3H_6Cl^{\cdot}$	107					6	21							
$C_3H_3ClO_2^{\cdot+}$	106	41	9			100								
$M-HCl-ClCH_2^{\cdot}$	99		12									6		
$C_4H_8Cl^+$	91	25	10		26	38	32	18	98	17	46	47	31	85
$C_4H_7Cl^{\cdot+}$	90		17	5	11		41	13	20		13	12		10
$C_4H_6O_2^{\cdot+}$	86										13	14	48	
$C_4H_7CO^+$	83	22	42	35	19	15	32	6	12	11	40	45		21
$C_4H_6CO^{\cdot+}$	82		17		7		15				12	13		7
Me_2CCl^+	77			6			33	8						9
$ClCHCO^{\cdot+}$	76	21				64								
$C_3H_4O_2^{\cdot+}$	72		6	38	8		6	59						
$C_5H_9^+$	69		6			17	8	13	7	7				5
$MeCHCl^+$	63	9	9	19	6	9	6	8	15	8	25	33	7	15
$C_2H_3Cl^{\cdot+}$	62	8	15						5					
$C_4H_9^+$	57		11	7	12		6				6	9		
$C_4H_8^{\cdot+}$	56	11	18	19	10	7	21		7	11	55	78	45	17
$C_4H_7^+$	55	100	100	100	100	63	68	70	100	100	100	100	100	100
$C_4H_6^{\cdot+}$	54		13	6	11		6			6				
$C_4H_5^+$	53	7	9	12	10	9	12	10	10	8	11	14	7	11
CH_2Cl^+	49	33	36	32	32	34	42	45	28	37	29	34	32	34
$C_3H_7^+$	43	38	39	35	33	70	57	36	20	17	67	34		13
$C_3H_6^{\cdot+}$, $CH_2CO^{\cdot+}$	42	9	15	41	30	13	21	58		5	6	13		12
$C_3H_5^+$	41	21	38	59	34	56	100	58	30	30	22	56	62	32
$C_3H_3^+$	39	18	34	30	41	43	53	35	30	28	25	39	19	36

peak at *m/z* 83.

The mass spectra of the chloromethyl esters differ somewhat from the spectra of methyl esters. EI–MS data for parent chloromethyl esters and their chlorinated derivatives are given in Tables 3 and 4. One α-cleavage gives the $M-ClCH_2O^{\cdot}$ ion, which in *1d* (=*1cR*) and *2d* (=*2cR*) at *m/z* 85 is more abundant than the other α-cleavage ion $M-ClCH_2OCO^{\cdot}$ at *m/z* 57. In chlorinated chloromethyl esters, in general, the former is more abundant, whereas in *3d* (=*3cR*) and *4d* (=*4cR*) the latter α-cleavage gives the more intense peak, as in the corresponding methyl esters and in all 2-chloro isomers (very intense, 98%, in *3d2*).

The β-cleavage with hydrogen rearrangement gives peaks of lower intensity in chloromethyl esters than in the corresponding methyl esters (base peak only in *2d4*). The McLafferty rearrangement and subsequent loss of HCl give a very characteristic peak of chloromethyl esters at *m/z* 72, $C_3H_4O_2^{\cdot+}$, or 86, $C_4H_6O_2^{\cdot+}$, the latter in *3d* derivatives. The corresponding chlorine-containing fragment at *m/z* 106 or 120 appears in the spectra of 2-chloro isomers (base peak in *2d2*), but in all 3-chloro esters it is weak owing to the small peak of the McLafferty rearrangement.

The elimination of CH_2ClOH from the $M-Cl^{\cdot}$ ion produces in the spectra of chlorinated chloromethyl esters a peak at *m/z* 83, and the loss of CO from this fragment gives in many cases the base peak at *m/z* 55. The α-cleavage and subsequent (or simultaneous) loss of HCl may also give the fragment ions at *m/z* 55 and 83.

EXPERIMENTAL

Materials and methods. Pentanoic (*1a*) and 3-methylbutanoic acid (*2a*) were commercial products from Fluka, AG. 2-Methylbutanoic (*3a*)[28] and 2,2-dimethylpropanoic acid (*4a*)[29] were obtained by a general method involving the carboxylation of the corresponding Grignard reagent; pentanoyl (*1b*), 3-methylbutanoyl (*2b*), 2-methylbutanoyl (*3b*) and 2,2-dimethylpropanoyl chloride (*4b*) by the reaction of benzoyl chloride with the corresponding acid;[30] methyl pentanoate (*1c*), 3-methylbutanoate (*2c*), 2-methylbutanoate (*3c*) and 2,2-dimethylpropanoate (*4c*) from the corresponding acid chlorides with methanol; chloromethyl pentanoate (*1d*), 3-methylbutanoate (*2d*), 2-methylbutanoate (*3d*) and 2,2-dimethylpropanoate (*4d*) from the corresponding acid chlorides and paraformaldehyde in the presence of a trace amount of zinc chloride.[24]

Authentic methyl monochloro esters were obtained as follows: 2-chloropentanoate (*1c2*), 2-chloro-3-methylbutanoate (*2c2*) and 2-chloro-2-methylbutanoate (*3c2*) from the corresponding 2-chloro acid chlorides[31] with methanol; 3-chloropentanoate (*1c3*), 3-chloro-3-methylbutanoate (*2c3*) and *erythro*-3-chloro-2-methylbutanoate (*3c3e*) from α,β-unsaturated methyl esters[32] (methyl *trans*-2-methyl-2-butenoate and methyl 3-methyl-2-butenoate were prepared from Merck commercial acids) with hydrogen chloride;[33] *threo*-3-chloro-2-methylbutanoate (*3c3t*), 2-chloromethylbutanoate (*3c3'*), 3-chloro-2,2-dimethylpropanoate (*4c3*), 4-chloropentanoate (*1c4*), 4-chloro-3-methylbutanoate (*2c4*) and 4-chloro-2-methylbutanoate (*3c4*) by isolation from the reaction mixtures of monochloro esters obtained by chlorinating the parent esters with chlorine; 5-chloropentanoate (*1c5*) from commercial acid (Merck) by esterification.

The mixtures of monochloro acid chlorides obtained by chlorination of the parent acid chlorides with chlorine were converted to trideuteriomethyl esters with CD_3OD and to authentic chloromethyl monochloro esters with paraformaldehyde.[24] The products were identified by GLC-MS.

The purity of separately prepared esters were checked by GLC and when required the products were purified by preparative GLC and structures confirmed by ^1H NMR and MS.

The chlorinations were carried out at room temperature as described earlier.[1] Monochloro acids were converted *via* thionyl chloride and methanol treatment and acid chlorides with methanol to the corresponding methyl esters. The conversion of isomeric monochloro derivatives was supposed to be nearly similar. Esters were analyzed by GLC, along with the chlorination products of methyl and chloromethyl esters. The amounts of higher chlorinated products were at greatest about 5%.

GLC analyses were run with a Perkin-Elmer Model Sigma 3 gas-liquid chromatograph with a flame ionization detector. A 25 m × 0.22 mm (I.D.) vitreous silica SE-30 WCOT column was used with a nitrogen flow-rate of 1 ml/min. The column temperature was programmed from 50 °C at 4 °C/min, the splitting ratio was 1:20 and the temperatures of injector and detector were 230 and 250 °C, respectively. The chromatographic data were analyzed with a Hewlett-Packard Model 3390A Reporting Integrator using standard programs.

The products were purified by a Perkin-Elmer Model 800 instrument, adapted for preparative work, on a 6 m × 9.5 mm (O.D.) aluminium tube packed with 10% Carbowax 20 M on Chromosorb W (60–80 mesh). Appropriate temperatures were

used, with a nitrogen flow-rate of 120 ml/min.

^1H NMR spectra were obtained on a Perkin-Elmer Model R 12 B 60 MHz spectrometer in carbon tetrachloride solutions using TMS as an internal standard. The spectra will be published later (only the chemical shifts for *3c3e* and *3c3t* are given: s = singlet; d = doublet; c = complex absorption).

Methyl erythro-*3-chloro-2-methylbutanoate (3c3e).* ^{1}H NMR (60 MHz, CCl_4): δ 1.27 (3 H, d), 1.48 (3 H, d), 2.56 (1 H, c), 3.63 (3 H, s), 4.22 (1 H, c).

Methyl threo-*3-chloro-2-methylbutanoate (3c3t).* ^{1}H NMR (60 MHz, CCl_4): δ 1.22 (3 H, d), 1.48 (3 H, d), 2.75 (1 H, c), 3.66 (3 H, s), 4.27 (1 H, c).

Mass spectra. MS and GLC-MS data were recorded with a Varian MAT-212 mass spectrometer connected with a Varian Model 3700 gas-liquid chromatograph. It was equipped with a 25 m × 0.30 mm (I.D.) 5 % SE-54 glass capillary column with a helium flow-rate of 1 ml/min. Electron ionizing energy was 70 eV and ion source temperature 250 °C. Data were acquired and processed on a Spectro System MAT-188. All peaks ($m/z > 38$) greater or equal to 5 % of the base peak (100 %) are tabulated. Metastable transitions were obtained by linked scans using a Varian Metascan unit.

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