

## Chlorination of Esters. II. Chlorination of Methyl Esters of Heptanoic, Octanoic, Nonanoic and Decanoic Acids. The Isomer Distribution of Monochloro Esters Formed

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The chlorination of straight-chain carboxylic acid methyl esters from heptanoic to decanoic acid with chlorine in the liquid and vapour phase and with sulfuryl chloride in the liquid phase has been studied. The monochloro esters formed were analyzed by GLC, the isomer distributions indicating chlorination with chlorine to favour the ( $\omega$ -1)-position and with sulfuryl chloride the ( $\omega$ -2)-position. Both methods gave nearly the same results with exception of the  $\omega$ -position, the substitution of an  $\omega$ -hydrogen occurring with  $\text{SO}_2\text{Cl}_2$  only to half of that with chlorine. A gas chromatogram of a combined mixture of chlorination products is given.

Recently, the chlorination of straight-chain methyl esters from propanoic to hexanoic acid has been reported to produce monochloro esters, the isomer distribution of products being influenced by the choice of chlorination method and the reaction temperature.<sup>1</sup> This work has been undertaken to study the effect of these factors on the chlorination of methyl esters from heptanoic to decanoic acid with chlorine in the liquid and vapour phase and with sulfuryl chloride in the liquid phase.

We have found only a few papers dealing with the chlorination of methyl esters of medium-chain carboxylic acids. The paper of Minisci<sup>2</sup> presents a selective ( $\omega$ -1)-chlorination of methyl heptanoate and decanoate with *N*-chloroamines under strongly acidic conditions. The same method has been used by Konen *et al.*<sup>3</sup> in the chlorination of methyl octanoate, nonanoate and decanoate.

Some papers also report the chlorination of free acids and acid chlorides. Danehrad<sup>4</sup> has studied

the benzoyl peroxide ( $\text{Bz}_2\text{O}_2$ ) catalyzed chlorination of octanoic acid with sulfuryl chloride and Deno and his group<sup>5–8</sup> the chlorination of octanoic acid with chlorine. Singh and Tedder<sup>9</sup> as well as Smit and den Hertog<sup>10,11</sup> have investigated the effects the solvent used has on the chlorinations of heptanoyl and octanoyl chlorides with chlorine.

As a summary from the references mentioned, it can be said that all possible monochloro isomers of carboxylic acid are obtainable by any of these methods. It has been reported, it is true, that the chlorination of octanoic acid with  $\text{SO}_2\text{Cl}_2$  gives only 2-, 3-, 4- and 5-chloro acids.<sup>4</sup> Due to the diverging results, we repeated this reaction and based on a GLC analysis of esterified product mixture, the chlorination produces all seven monochloro-octanoic acids. The inadequacy of the earlier gas chromatographic results may be a consequence of defective methods.

### RESULTS AND DISCUSSION

The results from the quantitative analyses of monochloro isomers formed in three different experiments are presented in Table 1. The qualitative analyses are based on both previously published data<sup>5,9</sup> and our experience from earlier GLC work<sup>1</sup> that the isomeric monochloro esters are eluted in direct sequence from 2-chloro to  $\omega$ -chloro compound.

Chloromethyl esters, which are also formed in the processes, were identified by GLC as compared with separately prepared reference compounds.

The quantitative isomer distributions are

Table 1. The isomer distribution for the chlorination products of C<sub>7</sub>–C<sub>10</sub> methyl esters. Values are the averages of two experiments analyzed by GLC.

Substrate	Method <sup>a</sup>	Monochloro esters formed (%)									
		Chloro-methyl	2-Cl	3-Cl	4-Cl	5-Cl	6-Cl	7-Cl	8-Cl	9-Cl	10-Cl
Methyl heptanoate	1	0.8	3.4	12.8	18.8	22.0	25.0	17.2			
	2	1.0	2.1	11.6	20.0	25.3	25.8	14.2			
	3	0.9	2.5	13.5	23.3	27.4	24.0	8.4			
Methyl octanoate	1	0.6	2.9	9.5	13.7	18.1	19.1	20.6	15.5		
	2	0.8	1.7	8.5	15.0	19.3	20.3	21.0	13.4		
	3	0.8	1.8	9.4	17.1	21.6	24.2	18.2	6.9		
Methyl nonanoate	1	0.4	2.3	8.6	11.1	13.5	15.7	17.4	17.9	13.1	
	2	0.6	1.3	7.7	12.1	14.9	16.3	17.4	18.0	11.7	
	3	0.7	1.5	6.8	14.8	17.3	18.4	18.5	16.0	6.0	
Methyl decanoate	1	0.3	2.1	7.6	9.6	11.2	13.4	14.2	15.0	15.2	11.4
	2	0.5	1.2	6.8	10.5	12.6	14.1	14.8	15.3	15.4	8.8
	3	0.5	1.1	5.4	10.9	13.8	15.1	16.2	16.8	15.9	4.3

<sup>a</sup>Chlorination at (1) b.p. of ester, Cl<sub>2</sub>, UV; (2) 20 °C, Cl<sub>2</sub>, UV; (3) 60 °C, SO<sub>2</sub>Cl<sub>2</sub>, Bz<sub>2</sub>O<sub>2</sub>, dark.

estimated on GLC without weight response factors, the determination of which would have required laborious syntheses of model compounds. However, on the basis of gas chromatographic studies of chlorinated methyl propanoates<sup>12</sup> and butanoates,<sup>13</sup> the differences between weight response factors of monochloro esters are supposed to be negligible.

In the chlorinations with chlorine the isomer distribution seems to be nearly independent of the reaction temperature (Table 1). On the total yield of monochloro esters, however, the temperature has a remarkable influence. At the higher temperatures hydrogen chloride is eliminated, particularly, from 4-chloro to ( $\omega$ -1)-chloro isomers, giving rise to the formation of unsaturated compounds, which in turn further react to unidentified products. To avoid this, long-chain esters should be chlorinated at low temperatures.

A stronger director is the ester group, which effectively prevents the substitution at 2-position. However, the influence on the positions farther away decreases evenly, the main product being always the ( $\omega$ -1)-chloro isomer.

There are some differences between the results from chlorination with chlorine and sulfuryl chloride. The most striking difference is the small amount of  $\omega$ -chloro isomer formed with SO<sub>2</sub>Cl<sub>2</sub>

compared with twice as great an amount when chlorine is used. At least partly this difference may be caused by the excessive use of SO<sub>2</sub>Cl<sub>2</sub>. The assumption is supported by the results from the chlorination of octanoyl chloride with chlorine,<sup>10,11</sup> the amount of  $\omega$ -chloro isomer being smaller when the reaction mixture contains benzene, a good solvent for chlorine.

As a consequence, the proportions of isomers from 4-chloro to ( $\omega$ -2)-chloro are higher in the SO<sub>2</sub>Cl<sub>2</sub>-chlorination, the ( $\omega$ -2)-isomer being always the main product.

GLC analyses were performed by using a glass capillary column and programmed temperature permitting a short analysis time and narrow peaks. A gas chromatogram of the combined mixture of chlorination products from methyl heptanoate to decanoate is illustrated in Fig. 1. Several columns, as well as various operating conditions, were tested before all the 34 products were resolvable. On polar phases, like FFAP and Carbowaxes, the separation of the monochloro isomers is excellent because the polarities increase with increasing distance between the chlorine and the ester group.

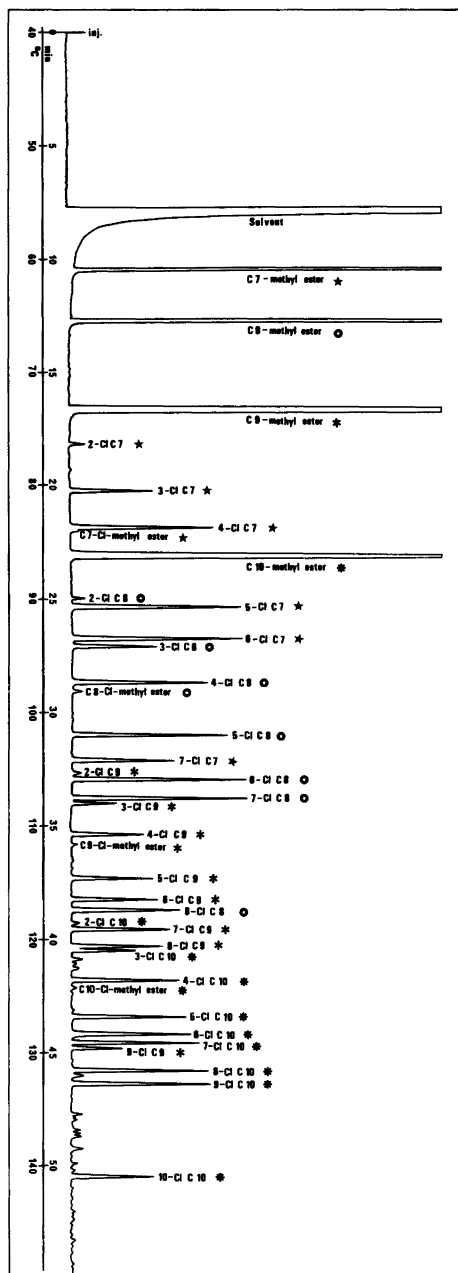


Fig. 1. Gas chromatogram of the combined mixture of chlorination products from methyl heptanoate to decanoate. For operating and other details see the experimental section.

## EXPERIMENTAL

**Materials and methods.** The preparation of methyl and chloromethyl esters as well as the chlorinations were carried out as described earlier.<sup>1</sup>

GLC analyses were performed on a Varian Model 2400 GC equipped with a flame ionization detector. A 60 m × 0.3 mm (I.D.) 4% Carbowax 20M glass capillary column was used with a flow rate of nitrogen of 1 ml/min. The column temperature was programmed from 40 to 150 °C at 2 °C/min, the split ratio being 1:20 and the chart speed 10 mm/min. The chromatographic data were obtained with a Perkin-Elmer Model M-2 Calculating Integrator.

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