Chlorination of Esters. III. Chlorination of Methyl Esters of Aliphatic C_{11}...C_{18} n-Carboxylic Acids. The Isomer Distribution of Monochloro Esters Formed

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The chlorinations of some long-chain n-acids,[1-3] acid chlorides[4] and methyl esters[5-7] have been reported. Recently, the results of the chlorinations of short-[8] and medium-chain[9] methyl esters have been given by the authors. This paper deals with the quantitative results from chlorinations of methyl esters from undecanoic to octadecanoic acid with chlorine and sulfuryl chloride in the liquid phase.

The isomer distributions of monochloro products (Figs. 1 and 2) were determined by GLC. The Carbowax 20M glass capillary column used separated all monochloro isomers of C_{11}- and C_{12}-acid esters only. The mid-chain isomers from 6-chloro to (ω-5)-chloro compounds of C_{13}...C_{18} esters, *e.g.* methyl 6-, 7-, 8- and 9-chlorotetradecanoate, were not separated.[10] The amounts of these unseparated isomers of different acid esters are given in figures as total amounts.

Our previous work[9] showed the chlorinations with chlorine to favour (ω-1)-position and with sulfuryl chloride (ω-2)-position. In these cases of longer chain esters, however, the main products seem to be (ω-2)-chloro isomers with chlorine and

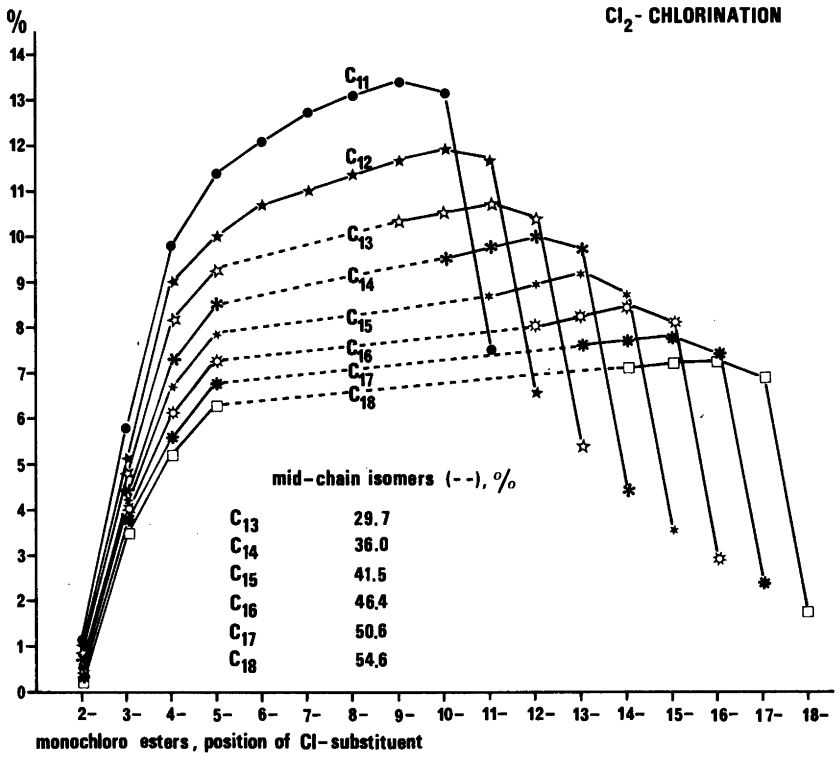

Fig. 1. The isomer distribution for methyl monochloro esters from undecanoic to octadecanoic acid based on GLC analyses. Chlorinations carried out with chlorine in the liquid phase at room temperature (at m.p. of solid ester) in the light.

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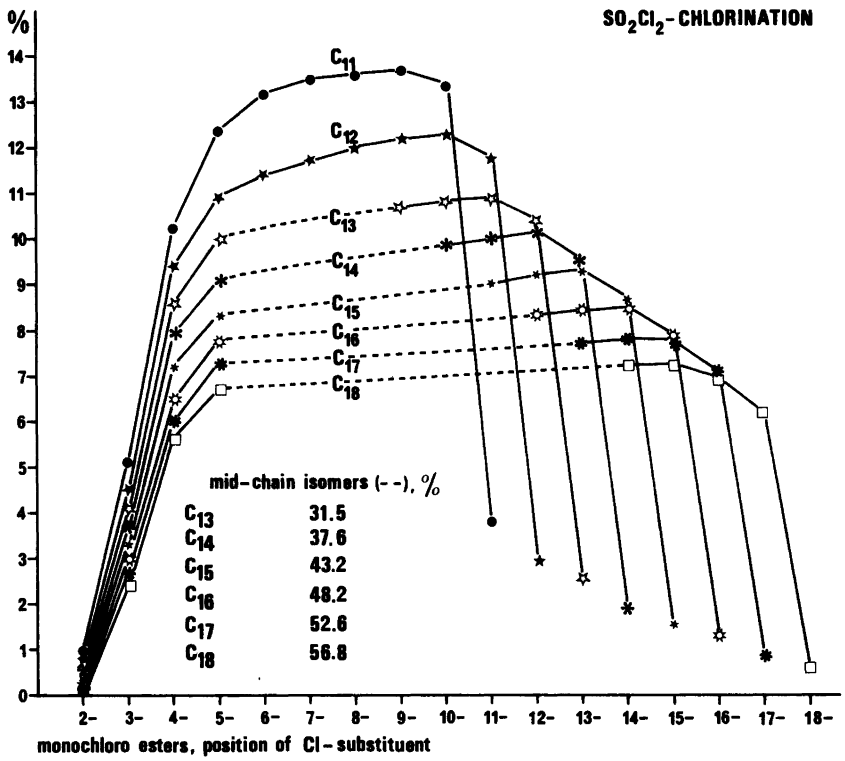

Fig. 2. The isomer distribution for methyl monochloro esters from undecanoic to octadecanoic acid based on GLC analyses. Chlorination carried out with sulfuryl chloride in the liquid phase at 60 °C in the dark.

(ω-2)- and (ω-3)-chloro isomers with sulfuryl chloride. Negligible amounts of chloromethyl esters were also formed in the processes, the amounts being greatest in the chlorinations of methyl undecanoate and dodecanoate.

Experimental. The preparations of methyl and chloromethyl esters as well as the chlorinations and GLC analyses were carried out as described earlier.[9] The column temperature was programmed from 50 to 200 °C at 2 °C/min. One example of the gas chromatograms is illustrated in Fig. 3. The chlorinations of methyl hexa-, hepta- and octadecanoate were performed with chlorine at temperatures of their melting points.

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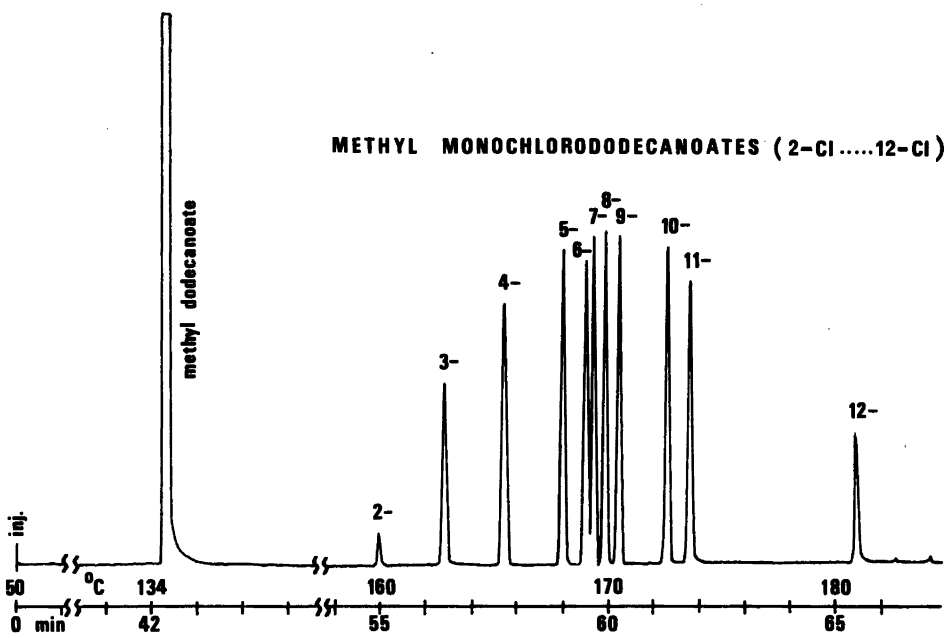

Fig. 3. Gas chromatogram of the chlorination products of methyl dodecanoate. For operating and other details see the experimental section.

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