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

ILPO O. O. KORHONEN and
JORMA N. J. KORVOLA

Department of Chemistry, University of Jyväskylä,
SF-40100 Jyväskylä 10, Finland

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 (\(\omega\)-5)-chloro compounds of C_{13}...C_{18}
esters, e.g. methyl 6-, 7-, 8- and 9-chlorotetradeca-
decanoate, 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 (\(\omega\)-1)-position and with
sulfuryl chloride (\(\omega\)-2)-position. In these cases of
longer chain esters, however, the main products
seem to be (\(\omega\)-2)-chloro isomers with chlorine and

![Diagram](image)

**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.

0302-4369/81/090673-03$02.50
© Acta Chemica Scandinavica
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. 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.

Acknowledgements. One of the authors, I. Korhonen, wishes to express his gratitude to the Emil Aaltonen Foundation, the Orion Corporation Research Foundation and the Academy of Finland for grants.

3. Lawlor, F. E. U.S. 2,571,901 (1951); Chem. Abstr. 46 (1952) 6143g.

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


Received September 25, 1981.