

CHROM. 16,021

## Note

### Gas chromatography of homologous esters

#### XXIII\*. Capillary column studies of chlorinated methyl propenoates

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(Received June 1st, 1983)

The temperature-programmed gas chromatographic (GC) separation of the chlorinated methyl propenoates has recently been reported on a low-polarity SE-30 and a polar OV-351 quartz capillary column with a study of the elution behaviour observed<sup>1</sup>.

Several of the chlorinated methyl propenoates have found minor use as monomers in the preparation of specialty polymers<sup>2,3</sup> although the simple propenoate esters are extensively used and have been the subject of systematic GC studies<sup>4,5</sup>.

The effect on retention of increasing chlorine substitution, of the positions of substitution and isomerism has not been shown and the present work shows the incremental effect in terms of retention indices on a low-polarity (SE-30) and a polar (OV-351) capillary column and the results are compared with those of studies on simple propenoate esters.

#### EXPERIMENTAL

##### *Esters*

The chlorinated methyl propenoates were prepared in the following manner: methyl 2-chloropropenoate by dehydrochlorination<sup>6</sup> of methyl 2,3-dichloropropenoate<sup>7</sup>, methyl *cis*- and *trans*-3-chloropropenoate from methyl propynoate (Fluka, Buchs, Switzerland) and hydrogen chloride<sup>8</sup>, methyl *cis*- and *trans*-2,3-dichloropropenoate by chlorination of methyl propynoate<sup>9</sup>, methyl 3,3-dichloropropenoate<sup>10</sup> and methyl 2,3,3-trichloropropenoate<sup>11</sup> by esterification of the appropriate acids.

##### *Gas chromatography*

GC was carried out using a Perkin-Elmer Sigma 3 instrument with flame ionization detection. The columns used were a vitreous silica SE-30 wall-coated open-

\* Part XXII: J. K. Haken, H. N. T. Hartley and D. Srisukh, *Chromatographia*, (1983) in press.

TABLE I  
RETENTION INDICES (*I*) OF CHLORINATED METHYL PROPENOATES ON SE-30

Methyl ester of	<i>I</i>		<i>b.p.</i> (°C/mm Hg)
	80°C	100°C	
2-Chloropropenoic acid	748	831	57-59/55 (ref. 15)
<i>cis</i> -3-Chloropropenoic acid	802	851	79-83/78 (ref. 9)
<i>trans</i> -3-Chloropropenoic acid	748	831	74-75/131 (ref. 9)
<i>cis</i> -2,3-Dichloropropenoic acid	930	941	72-74/13 (ref. 9)
<i>trans</i> -2,3-Dichloropropenoic acid	917	919	Unknown*
3,3-Dichloropropenoic acid	906	916	34-36/4**
2,3,3-Trichloropropenoic acid	1022	1023	178.5-180/760 (ref. 16)

\* Compound purified by preparative GC.

\*\* *b.p.* determined by the authors.

tubular column (WCOT) (25 m × 0.22 mm I.D.) supplied by SGE (North Melbourne, Australia) and a fused-silica (OV-351) WCOT column (25 m × 0.32 mm I.D.) supplied by Orion Analytica (Espoo, Finland). The columns were operated isothermally at 80, 100 and 120°C.

Retention times were measured from the time of sample injection and the retention indices were determined off-line using a Vector MZ microprocessor system, the dead volume being first determined by regression analysis from a series of appropriate *n*-alkanes using the procedure of Grobler and Balizs<sup>12</sup>.

## RESULTS AND DISCUSSION

Retention indices determined on both columns at several temperatures are shown in Tables I and II, while the boiling points of the esters are shown in Table I.

TABLE II  
RETENTION INDICES OF CHLORINATED METHYL PROPENOATES ON OV-351

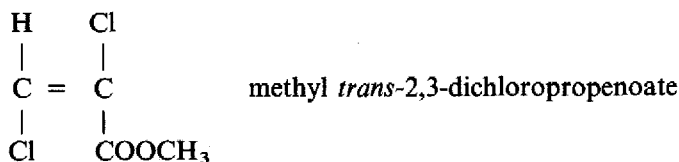
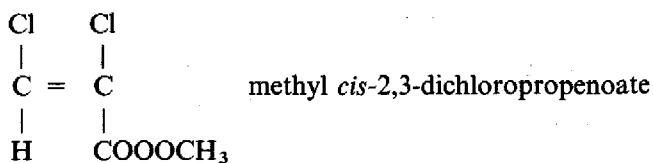
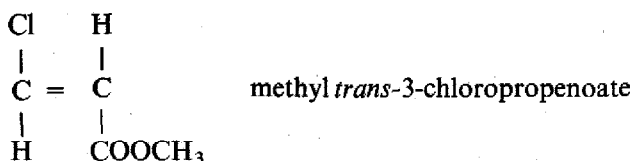
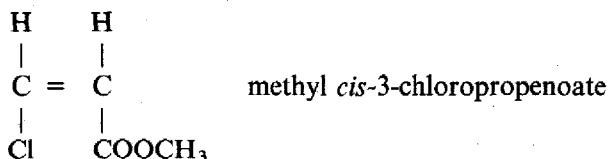
Methyl ester of	<i>I</i>		<i>I</i> <sub>OV-351</sub> - <i>I</i> <sub>SE-30</sub>
	80°C	100°C	
2-Chloropropenoic acid	1226	1226	478
<i>cis</i> -3-Chloropropenoic acid	1374	1382	572
<i>trans</i> -3-Chloropropenoic acid	1189	1191	441
<i>cis</i> -2,3-Dichloropropenoic acid	1438	1458	508
<i>trans</i> -2,3-Dichloropropenoic acid	1464	1473	547
3,3-Dichloropropenoic acid	1365	1382	459
2,3,3-Trichloropropenoic acid	1484	1500	462

The time of elution on SE-30, as expected, increases with the number of chlorine substituents and follows the boiling point sequence. In both situations where isomers occur the *trans* homologue is of lower retention on SE-30. With the OV-351 column generally enhanced retention is evident and the elution order is somewhat altered. While the *trans*-3-chloro isomer remains with lower retention than the *cis* isomer, the *trans*-2,3-dichloropropenoate is of significantly greater retention than the *cis* isomer.

The enhanced retention of the various isomers is shown effectively by subtraction of the non-polar contributions *i.e.*,  $I_{OV-351} - I_{SE-30}$ , in Table II for data obtained at 80°C. It is apparent that the increments fall into two general groups, the lower increments 441, 459, 462 and 478 for methyl *trans*-3-chloropropenoate, 3,3-dichloropropenoate, 2,3,3-trichloropropenoate and 2-chloropropenoate, respectively. The higher increments 508, 547 and 572 for methyl *cis*-2,3-dichloropropenoate, *trans*-2,3-dichloropropenoate and *cis*-3-chloropropenoate.

The elution order as observed with the earlier programmed-temperature study is unaltered<sup>1</sup> and the separations are not greatly different from those achieved isothermally.

With the polar column the elution order is greatly influenced by the compound structures<sup>1,13,14</sup> which are shown below.



The enhanced retention of the *cis*-3-isomer is due to the interaction between the chlorine atom and the alkoxy group. The similar effect with the *cis*-2,3-isomer is evident due to the proximity of the two chlorine atoms, while the *trans* isomer also

shows considerable enhancement it combining in part the feature of the *cis*-3-chloropropenoate with the effect of the additional chlorine at the 2-position.

The elution pattern of the other compounds similarly follows that of polychlorinated propanoate and butanoate esters.

(1) The retention of an ester with a single chlorine substituent increases as the distance from the carbonyl increases and retention is maximized with substitution in the terminal ( $\omega$ ) position *i.e.*  $< I_2 - < I_3 -$ ;

(2)  $\omega, \omega$ -disubstitution produces lower retention than  $\omega, (\omega - 2)$ - and  $\omega, (\omega - 1)$ -disubstitution.

The retention behaviour with the propenyl and butenyl esters<sup>4,5</sup> with a methyl substituent at the positions 2 and 3 on the chain have been extensively reported and the influence of the boiling point and the molecular shape have been considered and it is apparent that where comparisons are possible, similar results and trends are evident as in the present work.

#### ACKNOWLEDGEMENTS

I. O. O. K. gratefully acknowledges the aid of the Foundation for Research on Natural Resources in Finland and the Leo and Regina Wainstein Foundation.

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