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## Note

### Gas chromatographic retention behaviour of *Z/E*-isomeric chloroallyl and chlorovinyl compounds

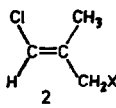
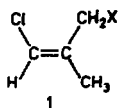
IRENE PRIBOTH\*, W. ENGEWALD, K. SCHULZE and BÄRBEL SCHULZE

Department of Chemistry, Karl-Marx-Universität, Liebigstrasse 18, DDR-7010 Leipzig (G.D.R.)

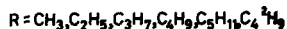
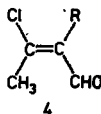
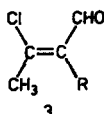
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In connection with the preparation of new pesticides, gas chromatographic (GC) investigations of the *Z/E*-isomeric olefins shown in Scheme 1, were necessary.

#### $\gamma$ -chloroallyl compounds



#### $\beta$ -chlorovinylaldehydes



Scheme 1.

These compounds should be useful as model compounds for investigations on the influence of intramolecular interactions on GC retention behaviour<sup>1,2</sup>. It was of special interest to establish whether GC retention could be used to indicate possible interactions between polar substituents. The structures and stereochemistry of these compounds were established from NMR data (chemical shifts, vicinal coupling constants, LIS and NOE effects)<sup>3-5</sup>.

#### EXPERIMENTAL

The retention indices of  $\gamma$ -chloroallyl and  $\beta$ -chlorovinyl compounds were determined on glass capillaries with different polarities: (i) OV-1 33 m  $\times$  0.30 mm I.D., pre-treated by high-temperature silylation with hexamethyldisilazane (HMDS); (ii)

Carbowax 20M, 50 m  $\times$  0.23 mm I.D., pre-treated by leaching with hydrochloric acid.

## RESULTS AND DISCUSSION

Table I gives the retention indices and the retention index differences on the two columns ( $\Delta I = I^C - I^{OV}$ ,  $\delta I_{Z-E} = I_Z - I_E$ ).

It is clear that there are different retention orders and also retention differences due to the substituent X and these are discussed below.

### $\gamma$ -Chloroallyl compounds

If the substituent X is Cl, OH, N(CH<sub>3</sub>)<sub>2</sub>, OCOCH<sub>3</sub> or SC<sub>3</sub>H<sub>7</sub> the lower boiling isomer which has the *Z*-configuration is eluted first. With mercapto and amino compounds the retention order is inverted with increasing carbon number in R. This retention behaviour could be explained by conformational effects, especially for the *Z*-isomers, as shown in Fig. 1.

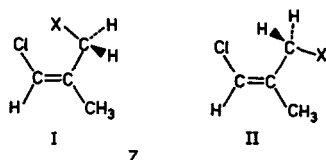


Fig. 1. Conformations I and II of the *Z*-isomer of  $\gamma$ -chloroallyl compounds.

Given that by mutual attraction of Cl and X the conformation I is preferred, the ability of Cl and X to undergo intermolecular interactions with the stationary phase should be diminished so that the *Z*-isomer is eluted before the *E*-isomer. With a bulky substituent X or repulsion between Cl and X, conformation II should be predominant and interactions with the stationary phase should be favoured. Therefore, the *E*-isomer is eluted first. This is apparent from the alterations in the elution order of amino and mercapto compounds depending on the carbon number of R.

### $\beta$ -Chlorovinylaldehydes

Table II gives the retention indices and retention index differences of *Z/E*-isomeric  $\beta$ -chlorovinyl compounds. It was found that the *E*-isomer is eluted before the *Z*-form with the exception of 3a/4a, where the *Z*-form is eluted first. This retention order is not affected by the polarity of the stationary phase. Obviously, this is due to a different steric arrangement for the dimethyl compound, leading to a reversed elution order. Mertens *et al.*<sup>6</sup>, who studied the retention behaviour of chlorovinylketones on the polar phase Carbowax 20M also observed that the *E*-isomers are eluted before the *Z*-isomers. This retention order is generally observed for unbranched substituted olefins<sup>7</sup>. The phenomenon of the *E*-isomer being eluted first was described by Reith<sup>8</sup>.

TABLE I

RETENTION INDICES ( $i^{OV}$ ,  $f^C$ ) OF Z/E-ISOMERIC  $\gamma$ -CHLOROALLYL COMPOUNDS AND THE RETENTION INDEX DIFFERENCES $\Delta I = f^C - i^{OV}$ ;  $\delta f^C_{Z-E} = f^C_Z - f^C_E$ ;  $\delta i^{OV}_{Z-E} = i^{OV}_Z - i^{OV}_E$ ;  $\Delta I_Z - \Delta I_E = \Delta I_Z - \Delta I_E$ ;  $\Delta I$  determined at 60°C on OV-1;  $f^C$  determined at 100°C on Carbowax 20M.

No.	X	$i^{OV}$	$f^C$	$\Delta I$	No.	$i^{OV}$	$f^C$	$\Delta I$	$\delta i^{OV}$	$\delta f^C$	$\Delta \delta I$
1a	Cl	818.1	1234.4	416.3	2a	832.8	1248.9	416.1	-12.0	-84.0	-72.0
1b	OH	758.7	1566.7	808	2b	770.7	1650.7	880	-14.7	-14.5	0.2
1c	N(CH <sub>3</sub> ) <sub>2</sub>	866.6	1048.2	181.6	2c	871.3	1050.7	179.4	-4.7	-2.5	2.2
1d	N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	1022.2	1154.1	131.9	2d	1028.5	1155.7	127.2	-6.3	-1.6	4.7
1e	N(CH <sub>3</sub> ,C <sub>2</sub> H <sub>5</sub> )	868.8	1051.8	183	2e	874.9	1052.5	177.6	-6.1	-0.7	5.4
1f	NHC <sub>2</sub> H <sub>5</sub>	954.7	1262.9	308.2	2f	934.5	1226.6	292.1	20.2	36.3	16.1
1g	N(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub>	1364.2	1487.4	123.2	2g	1362.8	1487.4	124.6	+1.4	0	-1.4
1h	N(C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub>	1525.2	1651.3	126.1	2h	1503.4	1628.6	125.2	+21.8	22.7	0.9
1i	SC <sub>3</sub> H <sub>7</sub>	818.8*	1166.2***	347.4	2i	832.2*	1245.0***	412.8	-13.4	-78.8	-65.4
1j	SC <sub>4</sub> H <sub>9</sub>	1240.4*	1610.3***	369.9	2j	1227.6*	1587.8***	360.2	12.8	22.5	9.7
1k	SC <sub>5</sub> H <sub>11</sub>	1340.3*	1697.2***	356.9	2k	1331.2*	1679.4***	348.2	9.1	17.8	8.7
1l	SCH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	1619.7**	2636.8 <sup>§</sup>	1017.1	2l	1619.7**	2616.2 <sup>§</sup>	996.5	0	20.6	20.6
1m	OCH <sub>3</sub>	812.0	1022.9	210.9	2m	798.8	989.5	190.7	13.2	33.4	20.2
1n	OC <sub>2</sub> H <sub>5</sub>	883.2	1150.9	267.7	2n	866.7	1113.8	247.1	16.5	37.1	20.6
1o	OC <sub>6</sub> H <sub>5</sub>	1377.7**	1897.3 <sup>§</sup>	519.6	2o	1356.5**	1828.5 <sup>§</sup>	472.0	21.2	68.8	47.6
1p	OCOCH <sub>3</sub>	971.7*	1382.4	410.7	2p	976.8*	1392.6	415.8	-5.1	-10.2	-5.1
1q	SCOCH <sub>3</sub>	1130.8*	1567.4***	436.6	2q	1146.1*	1623.6***	477.5	-15.3	-56.2	-40.9

\* Determined at 100°C.

\*\* Determined at 180°C.

\*\*\* Determined at 130°C.

§ Determined at 200°C.



## CONCLUSIONS

The results show that the elution order of *Z/E*-isomeric olefins is independent of the polarity of the stationary phase. Both electronic and conformational effects of the substituents influence the retention behaviour, leading to an alteration in the elution order of amino and mercapto compounds depending on the carbon number of the alkyl residue. With substituted ethers the *E*-isomer is eluted first, without any influence of the substituent.

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