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Note

Gas chromatographic behaviour of several glycidic esters

Influence of column temperature

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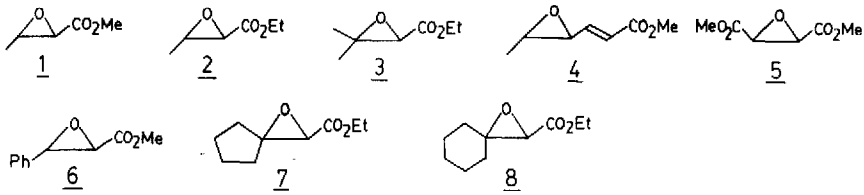
Although studies of the gas chromatographic (GC) retention of many different kinds of esters have been reported in the literature [see, for instance, the papers by Haken and co-workers[1,2] and Korhonen[3,4], among others (*e.g.* refs. 5–7)], we have not found references to the chromatographic behaviour of glycidic esters. For this reason we have selected and synthesized several glycidic esters (see Scheme 1) with the following aims: (i) determination of their Kováts retention indices (*I*) in a packed column coated with UCON 50 (LB 550X); (ii) study of the relationships between *I* and column temperature (*t*) for all glycidic esters studied; and (iii) study of the influence of the different structures of the glycidic esters selected according to their chromatographic behaviour.

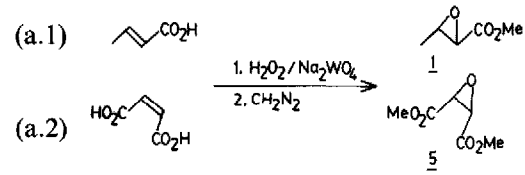


Scheme 1.

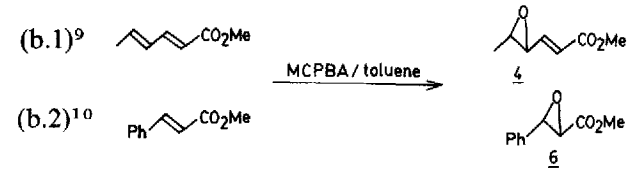
EXPERIMENTAL

The glycidic esters 1 and 3–8 were synthesized and purified by one of the three following procedures:

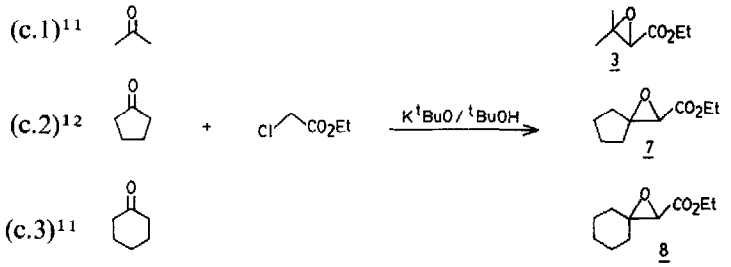
(a) H_2O_2/Na_2WO_4[8]:



(b) MCPBA (*m*-chloroperbenzoic acid)–toluene (reflux):



(c) Darzens condensation:



Compound 2 was supplied by Aldrich. The products were characterized by (IR and ^{1}H NMR spectroscopy).

Retention indices (I) of glycidic esters 1–8 were determined with a Perkin-Elmer Sigma 2B chromatograph equipped with a Hewlett-Packard Model 3390A integrator and a flame ionization detector. A stainless-steel column (2 m × 1/4 in. I.D.) packed with 10% UCON 50 (LB 550X) (Supelco) on Chromosorb P AW DMCS (60–80 mesh) was used. Nitrogen was used as the carrier gas at a flow-rate of 30 ml/min. The determinations were carried out in the range 140–240°C with the

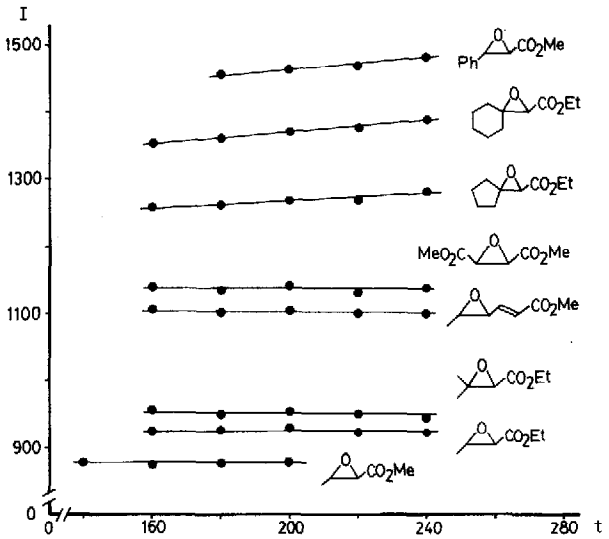
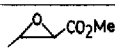
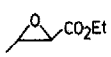
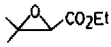
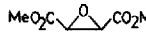
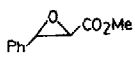
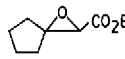
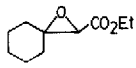


Fig. 1. Plots of I *vs.* column temperature (t) for the glycidic esters studied.

TABLE I

RETENTION INDICES (I) OF GLYCIDIC ESTERS AT DIFFERENT COLUMN TEMPERATURES

Compound No.	*Structure*	*Column temperature (°C)*					
		140	*160*	*180*	*200*	*220*	*240*
1		878	873	875	877	–	–
2		–	924	926	930	919	920
3		–	956	948	955	948	942
4		–	1111	1103	1105	1100	1128
5		–	1142	1132	1141	1128	1142
6		–	–	1453	1462	1467	1483
7		–	1257	1260	1267	1268	1283
8		–	1352	1360	1370	1375	1390

injector and flame ionization detector operating at 250°C. The esters were injected (0.4 μl) as solutions in diethyl ether (5–10%, w/w).

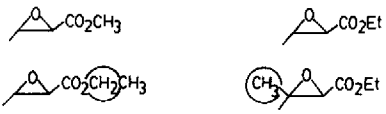
Retention times were measured from times of sample injection and the dead volume was determined by regression analysis from a series of n-alkanes using the procedure of Gröbler and Bálizs[13]. For all determinations, a homologous series of n-alkanes (C_8–C_{16}) was used.

RESULTS AND DISCUSSION

Linear dependences between I and the column temperature (t) are shown in Fig. 1 for all the glycidic esters studied. Values of I are given in Table I. These compounds show typical chromatographic behaviour[1–7,14–16] of linearity of I *vs.* t.

As can be seen in Table I, the values of ΔI/°C are almost neglibible except for spiroglycidic esters 7 and 8 with values of ΔI/°C of 0.5 (see entry 8), but these values are lower than those for other spiro compounds (Table II)[17].

The increment for the methylene group $\Delta I(CH_2)$, is higher in the ester chain (about 55 i.u.) than in the epoxy-acid chain (about 25 i.u.):

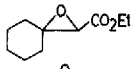
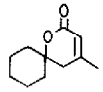


$\Delta I(CH_2) = 55$ $\Delta I(CH_2) = 25$

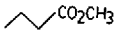
TABLE II

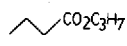
AI/°C FOR DIFFERENT SPIRO COMPOUNDS

Retention indices for compounds 9 and 10: 9, 1547 (220°C), 1557 (230°C), 1569 (240°C); 10, 1635 (220°C), 1649 (230°C), 1661 (240°C). Carrier gas (N_2) flow-rate, 37 ml/min; other conditions as described under Experimental.

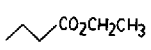
Compound No.	*Structure*	*AI*/°C
8		0.5
9		1.1
10		1.3

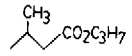
but these values are very similar to the corresponding conventional esters. For example, previous results for several esters on Carbowax 1540 and squalane[18] are in agreement with these assignements:





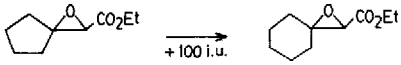
$AI(CH_2) = 50$





$AI(CH_2) = 28$

For spiroglycidic esters there is an increment of 100 i.u. from 7 to 8 in the temperature range studied:



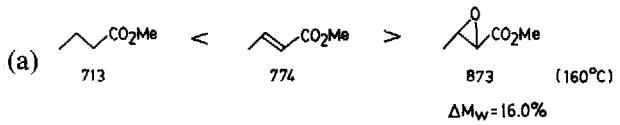
In order to obtain a qualitative evaluation of the relative position of a glycidic ester and the corresponding hypothetical unsaturated ester, which could be considered as the starting product, several unsaturated esters were injected under the same experimental conditions. Values of these retention indices are shown below.

Although the number of data is so small that no definitive conclusions can be drawn, the increment in the retention indices for the glycidic esters in comparison with the unsaturated esters could be interpreted as a sum of two factors:

(1) a positive factor which is the increment of molecular weight (ΔM_W = 16/molecular weight of the alkene):

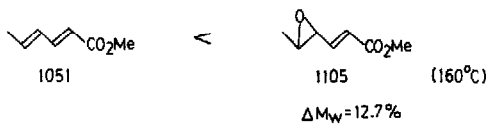
(2) a negative factor which is the decrease or disappearance of the molecular conjugation:

Several examples confirm these features:



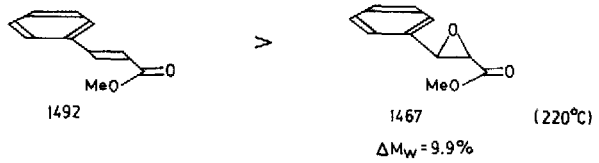
Although the conjugation dissapears, the experimental result indicates that ΔM_W is the main cause affecting to the retention index.

(b) This result can also be seen in the case of the vinylogous glycidic ester:



but as ΔM_W is lower, the difference between them would be smaller.

(c) On the other hand, when loss of CH=CH reduces the extent of the conjugation between phenyl and methoxy carbonyl groups, the decrease in the molecular conjugation is the main factor that determines the retention. Hence a change in the relative positions of the chromatographic peaks is observed.



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