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### Gas chromatography–mass spectrometry of C<sub>1</sub>–C<sub>10</sub> alkyl benzyl maleates

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In recent years, gas chromatography (GC)<sup>1</sup> and electron-impact mass spectrometry (EI-MS)<sup>2</sup> as well as their combination (GC–EI-MS)<sup>3,4</sup> have been increasingly used for the separation and identification of the benzyl esters of aliphatic and aromatic acids. Our investigations concern the GC–EI-MS behaviour of some benzyl esters of the dicarboxylic acids. We previously reported<sup>5</sup> the application of GC–EI-MS to the separation and identification of *n*-alkyl benzyl phthalates. This method has also been applied by us with good results to the investigation of some unsymmetrical esters of maleic acid.

In this paper we report the GC separation of ten *n*-alkyl (C<sub>1</sub>–C<sub>10</sub>) benzyl maleates (ABMs) and their electron-impact mass spectrometric behaviour.

#### EXPERIMENTAL

##### *Preparation of esters*

The C<sub>1</sub>–C<sub>10</sub> ABMs were obtained (similarly to alkyl benzyl phthalates by the reaction of maleic anhydride (BDH, Poole, U.K.) with benzyl chloride (P.P.H. POCh, Gliwice, Poland) and the appropriate alcohols (C<sub>1</sub>–C<sub>5</sub> aliphatic alcohols from P.P.H. POCh; C<sub>6</sub>–C<sub>10</sub> aliphatic alcohols from Fluka, Buchs, Switzerland) in the presence of triethylamine (Loba-Chemie, Vienna, Austria) as a catalyst<sup>6</sup>.

##### *Gas chromatography*

The GC separation of a mixture of ten ABMs, dissolved in acetone, was carried out with a Perkin-Elmer Model 900 gas chromatograph. The chromatographic conditions were as follows: column, 0.8 m × 3 mm I.D. stainless steel; packing, 3% OV-101 (Applied Science Labs., State College, PA, U.S.A.) on Gas Chrom Q (80–100 mesh); carrier gas (nitrogen or helium) flow-rate, 20 ml/min; injector temperature, 350°C; column temperature, programmed in the range 150–300°C at 12°C/min.

##### *Gas chromatography–electron-impact mass spectrometry*

The electron-impact (EI) mass spectra of all ABMs were recorded on an LKB 2091 instrument (GC–EI-MS system). The same column as above was used. The EI mass spectra were obtained under the following conditions: electron beam energy, 70

eV; accelerating voltage, 3.5 kV; trap current, 50  $\mu$ A; temperature of ion source, 250°C; temperature of Becker-Ryhage separator, 280°C. Mass numbers from  $m/z$  15 to 350 were recorded at a scan speed of 3 s per decade with a resolution of 1000.

## RESULTS AND DISCUSSION

The obtained chromatographic separation of the mixture of ten ABMs is illustrated in Fig. 1, and the retention indices,  $I_p$ , for the individual ABMs are given in Table I.

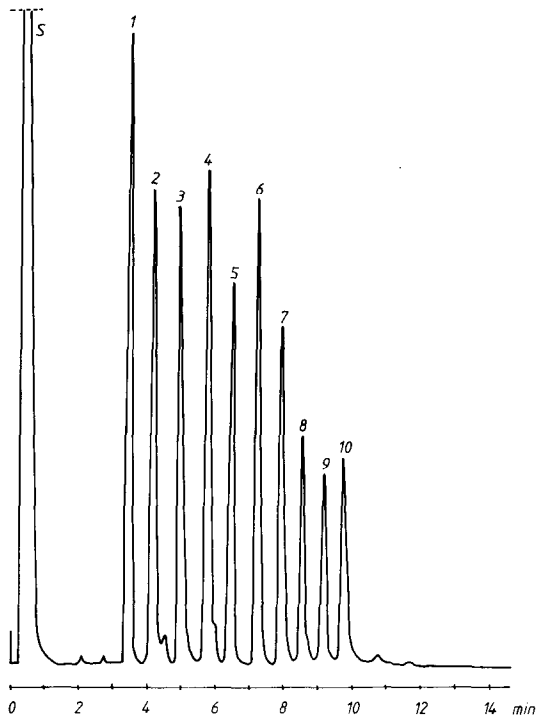


Fig. 1. Chromatogram of ten  $C_1$ - $C_{10}$  *n*-alkyl benzyl malcates (peaks 1-10); s = solvent (acetone). Stationary phase: 3% OV-101 on Gas Chrom Q. Column temperature programmed in the range 150-300°C at 12°C/min.

Fig. 2 shows the normalized mass spectra (the ion intensities are expressed as a percentage of the peak with the greatest intensity, *i.e.*, the base peak) of all the compounds investigated. Thanks to the presence of the benzyl substituent in one of the two ester groups all the ABMs, in contrast to dialkyl malcates greater than two carbon atoms in the alkyl group, give stable molecular ions  $M^{++}$  with 0.5-2.5% of the relative intensity.

Basing on our mass spectral data as well as the results of some deuterium labelling studies of ABMs<sup>7</sup> and information on the mass fragmentation of similar compounds<sup>8</sup>, it was possible to characterize the mass spectrometric behaviour of the

TABLE I

RETENTION INDICES,  $I_p^*$  OF *n*-ALKYL BENZYL MALEATES

Peak numbers refer to Fig. 1.

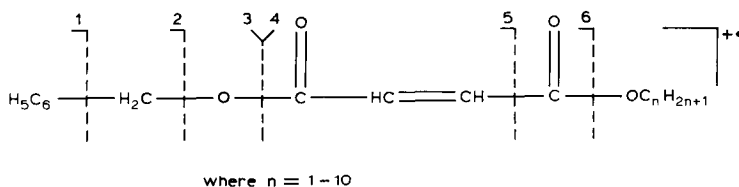
Peak No.	Compound	$I_p$
1	Methyl benzyl maleate	1645
2	Ethyl benzyl maleate	1749
3	<i>n</i> -Propyl benzyl maleate	1847
4	<i>n</i> -Butyl benzyl maleate	1948
5	<i>n</i> -Pentyl benzyl maleate	2050
6	<i>n</i> -Hexyl benzyl maleate	2153
7	<i>n</i> -Heptyl benzyl maleate	2255
8	<i>n</i> -Octyl benzyl maleate	2354
9	<i>n</i> -Nonyl benzyl maleate	2455
10	<i>n</i> -Decyl benzyl maleate	2556

\* The  $I_p$  values were calculated using the equation defined by Van den Dool and Kratz<sup>10</sup>

$$I_p = 100 \cdot \frac{T_i - T_z}{T_{z+1} - T_z} + 100z$$

where  $T_z < T_i < T_{z+1}$  and  $T_i$ ,  $T_z$ ,  $T_{z+1}$  are the retention times of component  $i$  and of the bracketing  $n$ -alkanes with  $z$  and  $z + 1$  carbon atoms, respectively.

series of ABMs. The mass fragmentation of all the ABMs, under EI-conditions has many common features. Similarly to the typical carboxylic acids esters, simple bond cleavages of the molecular ions  $M^{+\bullet}$  proceeds as shown:



Among the ions obtained in this way, the tropylium ion at  $m/z$  91 (2) is the most prominent. As seen in Fig. 2, this ion gives the base peak for methyl and ethyl benzyl maleates, but in the case of other maleates it has relatively lower abundance. In addition, the characteristic fragment ions produced as a result of cleavages as shown above appeared in all ABM mass spectra:  $[C_6H_5]^+$  at  $m/z$  77 (1);  $[OCH_2C_6H_5]^+$  at  $m/z$  107 (3);  $[M - OCH_2C_6H_5]^+$  at  $m/z$  113, 127, 141, ..... 239, respectively (4);  $[M - COOC_nH_{2n+1}]^+$  at  $m/z$  161 (5);  $[M - OC_nH_{2n+1}]^+$  at  $m/z$  189 (6). Another common feature of this fragmentation process also observed for all ABMs is the transfer of an hydrogen atom from a methylene group of the benzyl substituent and/or hydrogen atoms (especially from the  $\beta$  and  $\gamma$  positions) of the alkyl chain to their adjacent carbonyl oxygens followed by cleavage(s) of the ester

group bonds. As a consequence, some characteristic ions are formed. One of them is  $[\text{OHCCH}=\text{CHCOOH}]^{+\cdot}$ , at  $m/z$  100, as the base peak in the mass spectra of ABM with more than two carbon atoms in the alkyl chain. Similarly, the ion  $[\text{OHCCH}=\text{CHCOOC}_n\text{H}_{2n+1}]^+$  is formed for all ABMs. At low ionizing energy (12 eV) it becomes the base peak. The formation of this ion is shown in Fig. 3. The mass spectra of all ABMs investigated also show ions at  $m/z$  188, no doubt formed by the elimination of alcohol molecules (ROH, where R = alkyl group) from appropriate molecular ions  $M^{+\cdot}$ , leading to  $[\text{M}-\text{ROH}]^{+\cdot}$ . In this process the hydrogen atoms from the methylene group of the benzyl substituents also take part in elimination of

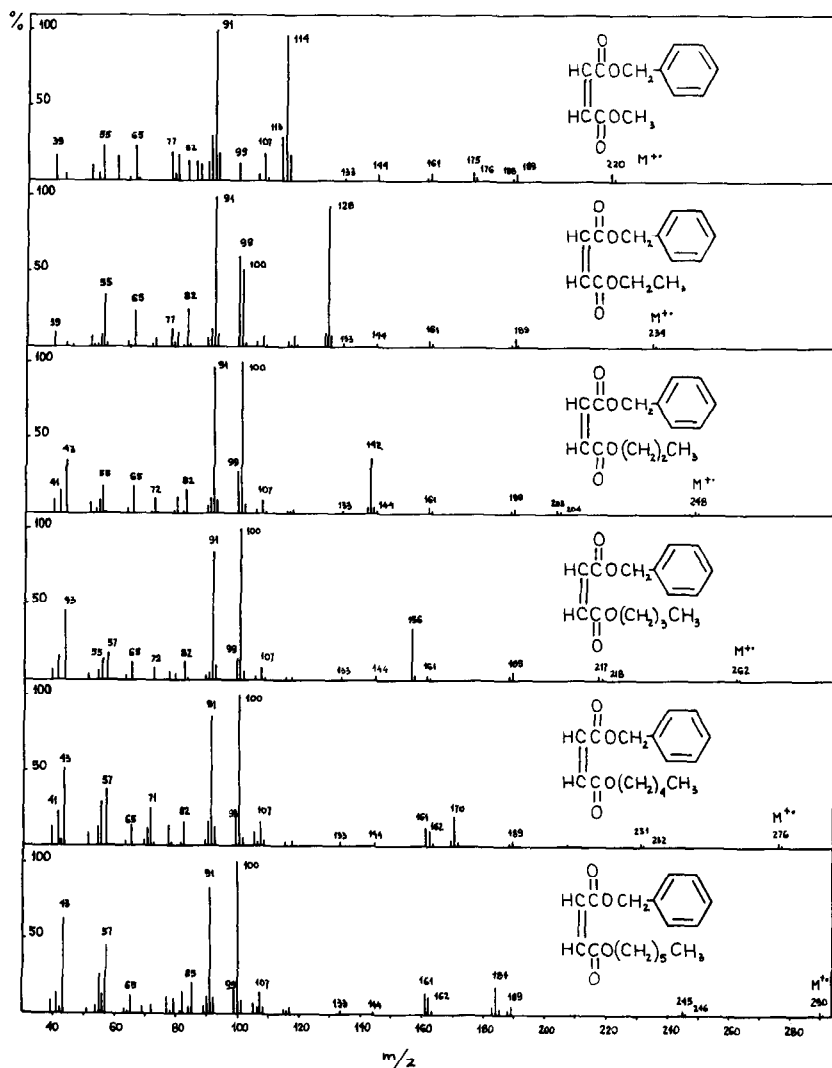


Fig. 2.

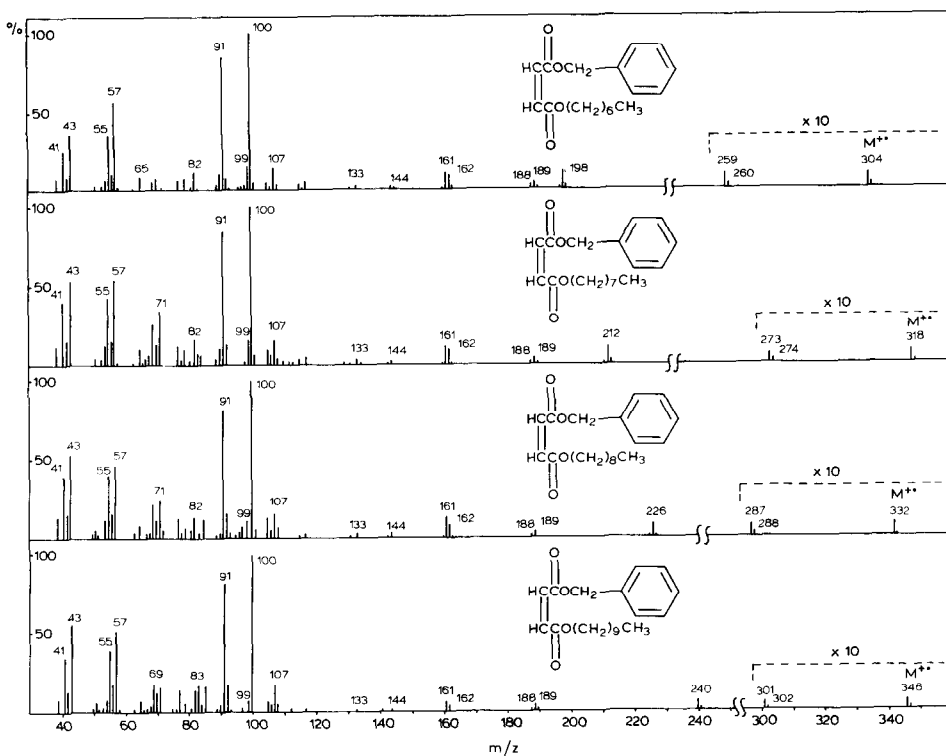


Fig. 2. Mass spectra of  $C_1$ - $C_{10}$  *n*-alkyl benzyl maleates.

ROH. The molecular ions  $M^{++}$  of all ABMs give rise to  $[M-44]^{++}$  and  $[M-45]^+$ . The formation of these ions is associated with the expulsion of  $CO_2$  via a six membered transition state, followed by the loss of the hydrogen radical, as in a similar fragmentation process reported previously by Weiss *et al*<sup>9</sup>. for benzyl esters of some allyl carboxylic acids. A series of peaks corresponding to ions derived from the fragmentation of alkyl substituents, *e.g.*, at  $m/z$  41, 43, 55, 57, 69, 71, etc., and the aromatic ring, *e.g.*, at  $m/z$  39, 51, 65 and 77, are also present. The relative intensities of the most characteristic ions change with increasing alkyl chain length. The amount

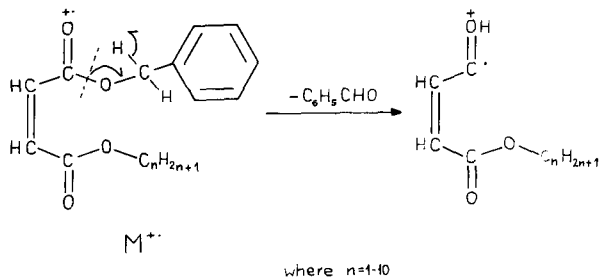


Fig. 3. Possible route of fragmentation of  $M^{++}$  of the *n*-alkyl benzyl maleates, leading to ions  $[\text{OHCCH}=\text{CHCOOC}_n\text{H}_{2n+1}]^+$ .

of ions with the general formula  $[C_nH_{2n+1}]^+$  increases, but the amount of the ions formed with participation of hydrogen atoms derived from the methylene group of the benzyl substituent decreases.

The mass spectrometric behaviour of the ABMs under electron impact has many features which are characteristic for fragmentation reactions of both benzyl and alkyl esters of the monocarboxylic acids. The results presented here can be used for the identification not only of ABMs but also of alkyl monoesters of maleic acid (after benzylation, as in the case of the alkyl benzyl phthalates) by GC, MS or GC-MS.

#### REFERENCES

- 1 D. L. Corina, K. E. Ballard and K. Isaac, *J. Chromatogr.*, 210 (1981) 146, and refs. therein.
- 2 D. L. Corina, J. N. Wright and K. E. Ballard, *Org. Mass Spectrom.*, 18 (1983) 60, and refs. therein.
- 3 U. Hintze, H. Röper and G. Gercken, *J. Chromatogr.*, 87 (1973) 481.
- 4 J. Oehlenschläger, U. Hintze and G. Gercken, *J. Chromatogr.*, 110 (1975) 53.
- 5 E. Dziwiński, J. Hetper and R. Kolodenny, *J. Chromatogr.*, 288 (1984) 221.
- 6 J. Novrocik and M. Novosadova, *Collect. Czech. Chem. Commun.*, 44 (1979) 2202, and refs. therein.
- 7 E. Dziwiński, *Mass Spectrom. J.*, submitted for publication.
- 8 J. H. Bowie, D. H. Williams, P. Madsen, G. Schroll and S. O. Lawesson, *Tetrahedron*, 23 (1967) 305.
- 9 F. Weiss, A. Isard and G. Bonnard, *Bull. Soc. Chim. Fr.*, (1965) 2332.
- 10 H. Van den Dool and P. Kratz, *J. Chromatogr.*, 11 (1963) 463.