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## Note

### Gas chromatography of homologous esters

#### XVII\*. Organophosphorus esters

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and

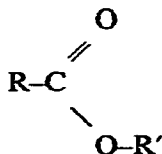
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Previously, the retention behaviour of various types of homologous esters including *n*-alkyl<sup>1,2</sup> and *n*-alkenyl<sup>3,4</sup> aliphatic esters and their corresponding branched-chain derivatives<sup>5</sup>, keto esters<sup>6</sup>, mono<sup>7</sup> and higher substituted chlorinated aliphatic<sup>8</sup> esters, aromatic<sup>9</sup> and cycloalkyl esters<sup>10</sup> has been considered.

The studies have examined the influence of the stationary phase polarity on retention, the effect of the position of a substituent group, either an alkyl group, unsaturation or a chlorine atom on retention<sup>7,8</sup>, the increasing contribution with increasing phase polarity of the carbonyl and phenyl group in esters on retention<sup>2,9</sup> and the relative influence of a substituent when in the alkyl or alcohol chain (R') or the acid or acyl chain of an ester according to the following representation



It has been shown that with all cases considered, *i.e.*, a methylene group, unsaturation, a ring or a chlorine atom, that addition of the substituent to the alcohol chain has a greater effect on retention than a corresponding addition to the acid chain. These all follow a logical boiling point sequence with inductive displacement along the C—O—R' towards the carbonyl with transmission of the polar effects of the appropriate function group through the oxygen atom.

Recent data of simple alkyl phosphorus esters, *i.e.*, phosphonate esters<sup>11</sup>, has

\* For Part XVI, see ref. 7.

allowed this effect to be further examined with compounds of related structure. It is evident that the relative contributions of methylene groups is reversed as compared with the series previously examined and this result is briefly discussed.

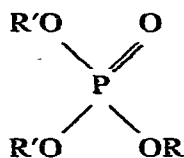
Other studies of the retention behaviour of these esters are not known to us although organophosphorus stationary phases have been studied by Novikov and co-workers<sup>12,13</sup> who indicated the phosphoryl group possessed a strong inclination towards hydrogen bond formation which was explained by the proton acceptor properties of the phosphoryl oxygen<sup>14,15</sup>.

## EXPERIMENTAL

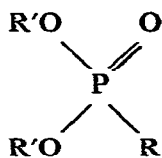
Gas chromatography was carried out using a Perkin-Elmer Model 3920B instrument with flame ionisation detection. Retention indices were obtained at 160°C using a 6 ft. × 2 mm I.D. column packed with 20% OV-17 on Gas-Chrom Q (80-100 mesh)

## RESULTS AND DISCUSSION

The retention indices of the alkyl phosphate and phosphonate esters are shown in Table I and Fig. 1, the substituent group following the representation:



Phosphates



Phosphonates

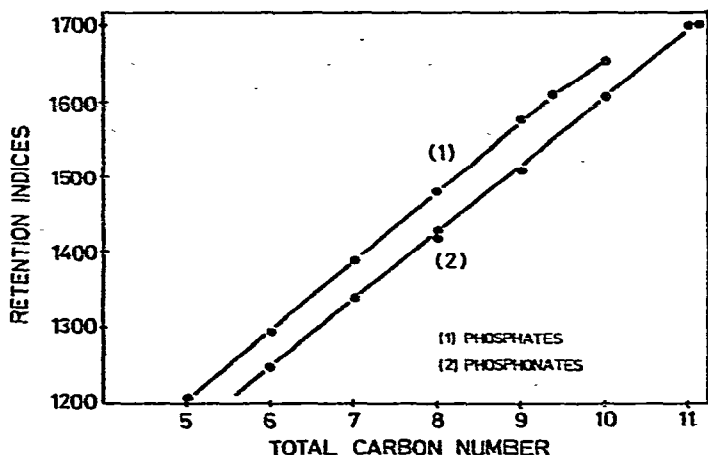
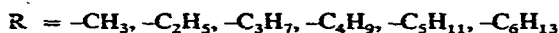


Fig. 1. Retention plot of phosphate and phosphonate esters on OV-17 at 160°C.

TABLE I

RETENTION INDICES (*I*) FOR HOMOLOGOUS SERIES OF PHOSPHATES AND PHOSPHONATES

Compound	R'	R	<i>I</i>	$\Delta\text{CH}_2\text{R}$
Diethyl alkyl phosphates	-C <sub>2</sub> H <sub>5</sub>	-CH <sub>3</sub>	1205	-
	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	1296	91
	-C <sub>2</sub> H <sub>5</sub>	-C <sub>3</sub> H <sub>7</sub>	1390	94
	-C <sub>2</sub> H <sub>5</sub>	-C <sub>4</sub> H <sub>9</sub>	1482	92
	-C <sub>2</sub> H <sub>5</sub>	-C <sub>5</sub> H <sub>11</sub>	1579	97
	-C <sub>2</sub> H <sub>5</sub>	-C <sub>6</sub> H <sub>13</sub>	1674	95
Diethyl alkylphosphonates	-C <sub>2</sub> H <sub>5</sub>	-C <sub>2</sub> H <sub>5</sub>	1246	-
	-C <sub>2</sub> H <sub>5</sub>	-C <sub>3</sub> H <sub>7</sub>	1340	94
	-C <sub>2</sub> H <sub>5</sub>	-C <sub>4</sub> H <sub>9</sub>	1430	90
	-C <sub>2</sub> H <sub>5</sub>	-C <sub>5</sub> H <sub>11</sub>	1525	95
Di- <i>n</i> -propyl alkylphosphonates	-C <sub>3</sub> H <sub>7</sub>	-C <sub>2</sub> H <sub>5</sub>	1420	-
	-C <sub>3</sub> H <sub>7</sub>	-C <sub>3</sub> H <sub>7</sub>	1510	90
	-C <sub>3</sub> H <sub>7</sub>	-C <sub>4</sub> H <sub>9</sub>	1604	94
	-C <sub>3</sub> H <sub>7</sub>	-C <sub>5</sub> H <sub>11</sub>	1700	96

Fig. 1 shows that plots of the two series of compounds are nearly parallel and that the phosphonates being of lower molecular weight are of lower retention. The contribution to the retention of the extra oxygen atom of the phosphates being nearly constant at about 50 index units.

With the phosphate esters the position of the three substituents is equivalent and from Table I it is evident that an increase of approximately 94 index units occurs with addition of a methylene unit, *i.e.*,  $\Delta\text{CH}_2\text{R} = \Delta\text{CH}_2\text{R}' = 94$ .

Consideration of the diethyl and di-*n*-propyl phosphonates shows that the addition of a methylene unit in the chain (R) adjacent to the -P=O group produces an essentially identical increase in retention to that observed with the trialkyl phosphates. Table II shows the effect of addition of a methylene unit in the R' chain of the phosphonates where a significantly reduced increase, *i.e.*,  $\Delta\text{CH}_2\text{R}' = 87$ , is observed as compared with corresponding addition in the R chain. The difference in contributions of  $\Delta\text{CH}_2\text{R}'$ , *i.e.*,  $\Delta\text{CH}_2\text{R} - \Delta\text{CH}_2\text{R}'$ , is about 7 units and is comparable in magnitude but not sign with the *n*-alkyl esters, where the difference  $\Delta\text{CH}_2\text{R}' - \Delta\text{CH}_2\text{R}$  was approximately 5 index units on a low-polarity phase, *i.e.*, SE-30, and

TABLE II

EFFECT OF ADDITION OF METHYLENE GROUP IN PHOSPHATE GROUP R' OF PHOSPHONATES (C<sub>3</sub>H<sub>7</sub>-C<sub>2</sub>H<sub>5</sub>)

R	Difference in index per methylene group
C <sub>2</sub> H <sub>5</sub>	174/2 = 87
C <sub>3</sub> H <sub>7</sub>	170/2 = 85
C <sub>4</sub> H <sub>9</sub>	174/2 = 87
C <sub>5</sub> H <sub>11</sub>	175/2 = 87.5

approximately 7.5 and 11 units on DC-710 (equivalent to OV-17) and on SILAR 5CP. (ref. 16).

The effect with the phosphonate esters might be explained on the basis that there are two  $-OR'$  chains and hence the inductive effect of the  $P=O$  group is split between the two and is thus reduced in magnitude. The effect with carbonyl esters on a similar phase was evident as a difference of about 7 index units and the variation indicated may be sufficient to explain the values observed. In addition the polarity of the phosphoryl group is less than that of the carbonyl group due to the effects of the d electrons in phosphorus which tend to neutralise the electron withdrawing effect of the  $=O$  atom. A study of the retention behaviour of borate and boronate esters would provide an interesting extension to this work.

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