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## Note

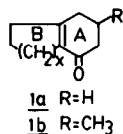
### Gas chromatography of bicyclo[n.4.0]alken-2-ones

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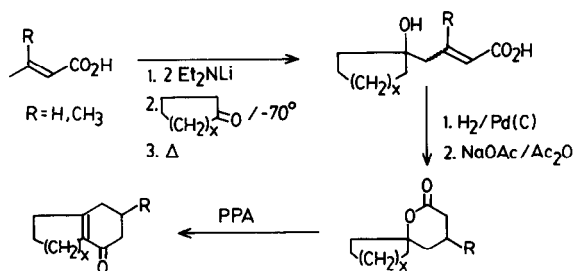
Bicyclo[n.4.0]alken-2-ones are interesting intermediates for the synthesis of medium-size and macrocyclic ketones by means of Eschenmoser fragmentation<sup>1</sup>. Although studies of the chromatographic behaviour of bicyclo[n.m.0]alkanes have been carried out<sup>2,3</sup>, few examples of bicyclo[n.4.0] systems have been reported<sup>2,3</sup> and there appear to have been no studies on the chromatographic retention of bicyclo[n.4.0]alken-2-ones.



The purposes of this work were as follows: (i) determination of the Kováts retention indices (*I*) of several bicyclo[n.4.0]alken-2-ones (1a and 1b) on a packed column coated with UCC at different temperatures and (ii) establishment of a valid general equation correlating accurately the Kováts retention indices with the number of carbon atoms (*n*), column temperature (*t*) and a structural parameter that selectively represents the two different kinds of bicycloalkenones studied.

### EXPERIMENTAL

The bicyclo[n.4.0]alken-2-ones were synthesized and purified by a general method described in an earlier paper<sup>4</sup>. The general procedure of the synthesis is shown below.



Retention indices of 1a and 1b were determined with a Hewlett-Packard Model 5830A chromatograph equipped with a Model 18850A integrator and a flame-ionization detector. A stainless-steel column (2 m  $\times$  1/4 in. I.D.) packed with 10% UCC (Supelco) on Chromosorb P AW DMCS (60–80 mesh) was used. Nitrogen was used as the carrier gas at a flow-rate of 37 ml/min. The determinations were carried out at 220, 230 and 240°C with the injector and flame-ionization detector operating at 250°C. The bicyclic compounds were injected (0.3  $\mu$ g) as solutions in diethyl ether (3%, w/w).

Retention times were measured from the 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<sup>5</sup>. For all determinations, a homologous series of *n*-alkanes (C<sub>10</sub>–C<sub>24</sub>) was used.

## RESULTS AND DISCUSSION

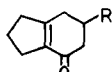
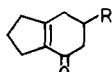
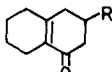
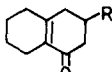
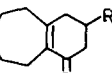
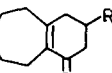
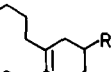
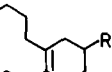
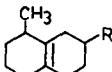
The retention indices of 1a and 1b are given in Table I.

A linear dependence between *I* and the number of carbon atoms (*n*), the column temperature (*t*) and the boiling point (*t<sub>b</sub>*) can be observed in Fig. 1 for compounds 1a. Similar results were obtained for compounds 1b.

On the other hand, a comparison of compounds of the two series with the

TABLE I

RETENTION INDICES (*I*), INCREMENT OF METHYL GROUP [ $\Delta(\text{Me})$ ],  $\Delta I/^\circ\text{C}$  AND BOILING TEMPERATURE (*t<sub>b</sub>*)\* OF BICYCLO[*n*.4.0]ALKEN-2-ONES ON UCC AT 220–240°C

No.	Compound		<i>I</i> (220°C)	$\Delta(\text{Me})$	<i>I</i> (230°C)	$\Delta(\text{Me})$	<i>I</i> (240°C)	$\Delta(\text{Me})$	$\Delta I/^\circ\text{C}$	<i>t<sub>b</sub></i> (°C)
1		R = H	1338		1346		1354		0.80	90
2		R = CH <sub>3</sub>	1380	42	1388	42	1396	42	0.80	90–92
3		R = H	1451		1461		1470		0.95	98–100
4		R = CH <sub>3</sub>	1489	38	1498	37	1507	37	0.90	98–100
5		R = H	1536		1545		1553		0.85	110
6		R = CH <sub>3</sub>	1570	34	1579	34	1588	34	0.90	115
7		R = H	2069		2077		2085		0.80	160
8		R = CH <sub>3</sub>	2105	36	2105	38	2124	39	0.95	180
9		R = H	1545		1554		1563		0.90	–

\* Kugelrohr oven at 0.8 mmHg.

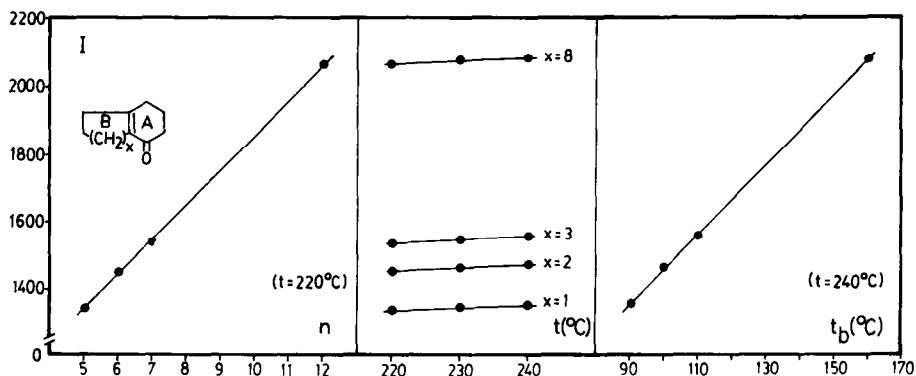
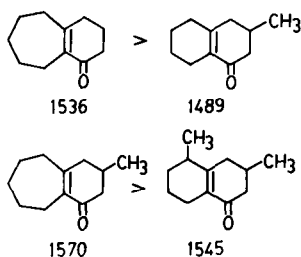


Fig. 1. Plots of  $I$  vs. total number of carbon atoms in ring B ( $n$ ),  $I$  vs. column temperature ( $t$ ) and  $I$  vs. boiling temperature ( $t_b$ ) of bicyclo[ $n.4.0$ ]alken-2-ones (1a).

same number of carbon atoms shows that an additional ring methylene group is responsible for a larger  $I$  increment than a methyl substituent.



All of the compounds studied have a very close values of  $\Delta I/^\circ\text{C}$ . The increment of a methyl group [ $\Delta(\text{Me})$ ] is very similar for all the compounds studied (see Table I). Hence, the behaviours of these two homologous series are almost identical and it is possible to obtain a general equation that represents the chromatographic behaviour of these compounds in the temperature range (220–240°C) studied:

$$I = 627.83 + 103.93n + 0.868t + P \quad (1)$$

$N = 24$ ;  $r = 1.000$ ;  $s = 8.60$ ;  $F = 25423.0$ ;  $E = 0.41\%$

where  $n$  = total number of carbon atoms in ring B,  $t$  = column temperature ( $^\circ\text{C}$ ),  $P$  = structural parameter [0 for  $\text{R} = \text{H}$  (1a) and 37.8 for  $\text{R} = \text{CH}_3$  (1b)],  $N$  = total number of experimental points,  $r$  = correlation coefficient,  $s$  = standard deviation,  $F$  = experimental value of the Snedecor test and  $E$  = average relative error.

In summary, the gas chromatographic behaviour of these two homologous series of bicycloketones can be described by a single equation.

#### ACKNOWLEDGEMENT

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