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CORRELATION OF THE BOILING POINTS OF NON-BRANCHED C_9 AND C_{10} OLEFINS WITH THE GAS CHROMATOGRAPHIC RETENTION INDICES

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SUMMARY

A correlation was made between the boiling points of fourteen non-branched nonenes and decenes and the retention indices, and also a comparison of the results obtained by known methods of calculation with the available tabulated data.

The gas chromatographic measurements were carried out on a 200-m long capillary column (stainless steel) coated with squalane at 86, 100 and 115° and permitted boiling points to be determined with a reproducibility of ± 0.1°. Substantial deviations were found from the KOVÁTS rule $\delta I \approx k_p\ \delta T_b$ for the behaviour of isomeric hydrocarbons on a non-polar stationary phase. In the case of the olefins studied, the proportionality constant, for which a value of approximately 5 is stated in the literature, fell within the range 1.8–13.9 on squalane. The correction factor f_c used for the calculation of I_B by MATUKUMA is constant only in the case of *trans*-alkenes, whereas for *cis*-alkenes and 1-alkenes it is dependent on the number of carbon atoms in the olefin molecule.

INTRODUCTION

One of the properties that substantially affects the position of a substance in a chromatogram is the vapour pressure of the substance, which is related to the boiling point. Correlations are made with the aid of linear relationships between the logarithm of the absolute or relative retention parameters and the boiling points of the substances[1,2]. While the relations between the boiling points of polar substances and the retention characteristics of polar and non-polar stationary phases are a complex function of the structural properties of the molecules, the interactions of hydrocarbons on hydrocarbon stationary phases afford substantial simplifications. Thus, by applying the theorem of corresponding states to his retention-index system, KOVÁTS[3] has suggested the relation $\delta I \approx 5\ \delta T_b$ for two isomers separated on a hydrocarbon liquid phase, where δI is the difference between the retention indices of the two isomers and δT_b is the difference between their boiling points.

ALTENBURG[4] used, for the calculation of boiling points, the description of the molecular structure and defined the relation between the retention index and the boiling point by means of properties such as the molecular diameter and the distance between the centres of atoms.

MATUKUMA[5] has introduced the concept of the boiling point index, I_B, which is calculated by the equation:

$$I_B = 10^{(0.00134024\ T_b+2.558916)} - 440.5 \qquad (1)$$

The value of I_B is calculated from the retention index of the substance, I_R ($I_R = I$), and from the known boiling points and retention indices of substances with the same structure but with one carbon atom less, and employing the paraffinic concept $\Delta I_{R-B}{}^{(p)}$. Thus, for C_8 alkenes:

$$I_B(C_8) = I_R(C_8) - \Delta I_{R-B}{}^{(p)}\ (C_8) + f_c \qquad (2)$$

where $\Delta I_{R-B}{}^{(p)}$ (C_8) is the difference between the retention index and the boiling point index of *n*-octane, having the same skeleton as the *n*-alkene, and f_c is the correction factor for calculating the boiling point T_b from the retention index I_R:

$$f_c = \Delta I_{R-B}{}^{(p)}\ (C_7) - \Delta I_{R-B}\ (C_7) \qquad (3)$$

BAUMANN *et al.*[6] determined the boiling points of the secondary straight-chain C_{11}–C_{15} alkylbenzene isomers from the correlation between the retention times and the known boiling points of some isomers. They ascertained interactions between the non-polar stationary phase (Apiezon, SF-96) and the alkylbenzenes being separated and as a result the calculated boiling points had to be corrected by 0.7–4.1°. The correction was a linear function of the difference between the boiling points of the original and derived isomers and increased when the phenyl group was shifted towards the centre of the side chain.

WILLIS[7] used the temperature programming of capillary columns for the determination of the boiling points of the positional isomers of linear C_{11}–C_{16} alkylbenzenes. The boiling points were read directly from the linear dependence of the retention time *versus* the boiling points of C_9–C_{15} 1-phenylalkanes.

The precision of the boiling points calculated by eqns. 1–3 is limited owing to the neglect of the dependence of the vapour pressure and activity coefficients on the column temperature, which is closely dependent on the linearity of the function of the logarithm of retention parameters and the boiling points ($\log t_r' = a + bT_b$). After correcting the values of I_B by the correction factor f_c in eqns. 2 and 3 for calculating the boiling points of the non-branched C_7 alkenes, the deviation of the calculated from the tabulated values, ΔT_b, did not exceed 0.8° (ref. 5).

In a previous paper[8], we have indicated certain relationships between the retention indices and boiling points of the non-branched C_6–C_8 alkenes. In the present paper, the above relationships are investigated for the non-branched C_6–C_{11} alkenes in order to calculate the boiling points of non-branched nonenes and decenes. Except for 1-alkenes, the above quantities are not precisely known[9,10] for nonenes and decenes, although they are important data for their isolation from the dehydrogenation products of *n*-alkanes.

EXPERIMENTAL

A Chrom 3 gas chromatograph with a flame-ionization detector was used. The capillary column was of stainless steel, 200 m long and 0.2 mm I.D., and was coated with squalane by the dynamic method. The working temperatures of the column were 86, 100 and 115°, the column inlet pressure of the carrier gas (nitrogen) was 4 kp/cm^2, the flow rate was 1.2 ml/min at 86°, and the sample size was 0.3–1 μl, the split ratio being 1:300.

For the identification and boiling point calculation, dehydrogenation products of the individual C_6–C_{11} alkanes were used which contained all the theoretically possible non-branched alkenes[8,9]. The retention indices were measured from the retention time of methane. The capillary column used was able to separate isomeric alkenes (with the same $\delta I/\delta T$) differing from each other in their boiling points by as little as 0.1°. The reproducibility of measuring the retention indices was ± 0.2 of a retention index unit (from four measurements). The calculation of the retention indices (I) and the boiling point indices (I_B) was carried out with the aid of an IBM 360/30 computer.

RESULTS AND DISCUSSION

Calculation of the boiling points of n-alkanes

The boiling points of non-branched alkenes were calculated preliminarily from the difference between the retention indices of the *n*-alkenes and *n*-alkanes and from the known boiling points of the *n*-alkanes between which the *n*-alkene in question was eluted, applying the rule of similar triangles:

$$T_{b_x} = T_{b_1} + \frac{\delta I(T_{b_2} - T_{b_1})}{100} \tag{4}$$

where T_{bx} is the boiling point of the alkene, T_{b2} and T_{b1} are the boiling points of the *n*-alkanes differing by one carbon atom, and δI is the difference between the retention indices of the alkene and *n*-alkane with boiling point T_{b1}.

The applicability of the relation was checked in advance for all the non-branched C_6–C_8 alkenes with known boiling points. The boiling points calculated by eqn. 4 for the non-branched C_6–C_8 alkenes are given in Table I. It can be seen on comparing the calculated boiling points with the tabulated data that the calculated boiling points display deviations (ΔT_b) of up to 1.4°, with certain regularities. The calculated boiling points of *cis*-alkenes are mostly higher and those of *trans*- and 1-alkenes are lower than the tabulated values. The deviations (ΔT_b) decrease with increasing number of carbon atoms in the molecule eventually to negative values, which is evident in the series *cis*-2-, *trans*-3- and 1-alkenes. The deviations for *trans*-2- and *cis*-2- isomers differ substantially from the other *trans*- or *cis*- isomers. On shifting the position of the double bond to the centre of the molecule, ΔT_b decreases for *cis*-alkenes, while for *trans*-alkenes the opposite occurs.

Similar dependences may be inferred from the boiling points published by MATUKUMA[5] (provided $I_B = I^S_{40}$) for non-branched C_6 alkenes, also quoted in Table I. All the boiling points of the C_7 alkenes published by MATUKUMA are higher than the tabulated values since the respective retention indices are also higher compared with those published by other authors$^{10-13}$. This may be the explanation of the deviations (ΔT_b) for the C$_8$ alkenes (except 4-octenes), since correction factors f_c (eqn. 2) calculated from imprecise retention indices for the C$_7$ alkenes were used in calculating these values.

Assuming $I_B \equiv I^{S}_{86}$, we calculated the boiling points of the C$_6$–C$_8$ alkenes (by eqn. 1). The deviations (ΔT_b) obtained agree to within 0.1–0.2° with the deviations calculated by eqn. 4. Hence calculations made by eqns. 1 and 4 give almost the same results since both methods are based on calculating the boiling points by means of *n*-alkanes. The deviations of the boiling points calculated for *cis*-, *trans*- and 1-non-branched C$_6$–C$_8$ alkenes by eqn. 4 can be related to the measured changes of the retention indices for non-branched alkenes with the column temperature, which decrease approximately in the sequence: *cis*- > 1- > *trans*-alkenes. Hence, eqns. 1 and 4 do not express precisely the differences in the activity coefficients and vapour pressures, or their different temperature dependences for *n*-alkanes and alkenes.

TABLE I

COMPARISON OF THE CALCULATED AND TABULATED BOILING POINTS OF NON-BRANCHED C$_6$–C$_8$ HYDROCARBONS

Alkene	*Boiling point (°C)*						
	Ref. 15	*Eqn. 4*	ΔT_b	*Ref. 5*	ΔT_b	*Eqn. 1*	ΔT_b
1-Hexene	63.49	63.24	−0.25	63.44	−0.05	63.49	0.00
cis-3-Hexene	66.44	66.46	0.02	66.59	0.15	66.58	0.14
trans-3-Hexene	67.08	65.93	−1.15	66.28	−0.80	66.07	−1.01
trans-2-Hexene	67.87	67.65	−0.22	67.84	−0.03	67.76	−0.11
cis-2-Hexene	68.84	70.25	1.41	69.71	0.87	70.27	1.43
1-Heptene	93.64	93.33	−0.31	94.19	0.55	93.58	−0.06
trans-3-Heptene	95.67	94.73	−0.94	95.97	0.30	94.93	−0.74
cis-3-Heptene	95.75	95.97	0.22	96.68	0.93	96.15	0.40
trans-2-Heptene	97.95	98.06	0.11	99.02	1.07	98.15	0.20
cis-2-Heptene	98.5	99.72	1.22	100.32	1.82	99.77	1.27
1-Octene	121.28	120.89	−0.39	120.66	−0.62	121.10	−0.18
trans-4-Octene	122.25	121.36	−0.89	121.69	−0.56	121.59	−0.66
cis-4-Octene	122.54	122.35	−0.19	122.11	−0.43	122.56	0.02
cis-3-Octene	122.9	122.82	−0.08	123.09	0.19	122.98	0.08
trans-3-Octene	123.3	122.51	−0.79	123.30	0.00	122.69	−0.61
trans-2-Octene	125.0	125.05	0.05	125.00	0.00	125.13	0.13
cis-2-Octene	125.64	126.45	0.81	124.88	−0.76	126.47	0.83

Calculation of corrected boiling points indices, I_B

We used for calculating boiling points eqns. 2 and 3, which are based on the I_B corrected by means of the correction factors f_c referred to the structure of the corresponding *n*-alkane and the double-bond conformation.

As the f_c values calculated for the C$_7$–C$_9$ alkenes displayed certain regularities, we arranged them for the individual series of the non-branched alkenes, according to the number of carbon atoms in the molecule, in Table II. Table II has been supplemented by the values of f_c calculated earlier for the C$_{10}$–C$_{11}$ alkenes. The increase in the f_c values with increase in the number of carbon atoms is evident for all the *cis*- and

TABLE II

DEPENDENCE OF THE CORRECTION FACTORS f_c ON THE NUMBER OF CARBON ATOMS FOR THE INDIVIDUAL SERIES OF NON-BRANCHED HYDROCARBONS

Number of carbon atoms	*Alkenes*								
	trans-2-	*trans*-3-	*trans*-4-	*trans*-5-	1-	*cis*-2-	*cis*-3-	*cis*-4-	*cis*-5-
7	0.6	3.3			0.1	−4.2	−0.3		
8	−0.3	2.9	2.9[a]		0.6	−4.2	−1.0	−1.0[a]	
9	−0.1	2.6	2.8		1.0	−2.9	0.0	0.2	
10	0.1	2.7	3.0	3.0[a]	1.6	−1.5	1.4	1.6	1.6[a]
11	0.2	3.1	3.6	3.6	1.9	−0.7	2.7	2.8	3.1

[a] Estimated values of f_c.

1-alkenes. For the individual series of *trans*-alkenes (considering $f_c = 0.4 \sim 0.1°$), f_c can be considered to be constant.

In calculating I_B, the correction factors f_c are used as calculated from the alkenes of the same structure, but having one carbon less in the molecule. Therefore, eqns. 2 and 3 are accurate only for calculations for *trans*-alkenes. The calculated boiling points of *cis*- and 1-alkenes will be lower than the actual ones since the respective f_c values increase with increase in the number of carbon atoms.

Calculation of the proportionality constant, k_p

We attempted to find more precise boiling points by correlating the structure of alkenes and their retention indices. By substituting into the KOVÁTS relation[3], we calculated, from the known boiling points of the non-branched C_6–C_8 alkenes, $\delta I_{calc.}$ ($\delta I_{calc.} = 5\ \delta T_b$). The differences between $\delta I_{calc.}$ and the measured $\delta I_{meas.}$ for various pairs of alkenes and different numbers of carbon atoms in the molecule are given in Table III. A relatively good applicability of the KOVÁTS relation has been proved only for comparison of geometric isomers, *trans–trans* and *cis–cis*. It can be seen that the deviations obtained are dependent on the number of carbon atoms, and decrease with increasing number of carbon atoms in the molecules of the non-branched alkenes being compared.

From a consideration of the above results, we modified the KOVÁTS relation to:

$$\delta I = k_p\ \delta T_b \qquad (5)$$

where k_p is a proportionality constant characterizing the difference between the reten-

TABLE III

DIFFERENCES $\delta I_{calc.} - \delta I_{meas.}$ FOR PAIRS OF NON-BRANCHED C_6–C_8 ALKENES

Alkenes	C_6	C_7	C_8
trans-/1-	8.4–9.7	5.5–5.7	3.0–4.0
cis-/1-	4.9–5.2	1.7–2.8	0.2–1.3
cis-/*trans*-	3.2–4.8	2.7–4.0	1.6–3.8
trans-/*trans*-	1.3	0.2	0.3–1.1
cis-/*cis*-	0.3	1.2	0.4–1.1

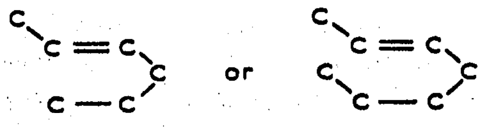
TABLE IV

DEPENDENCE OF THE PROPORTIONALITY CONSTANT k_p ON THE NUMBER OF CARBON ATOMS FOR PAIRS OF ALKENES COMPARED AT TEMPERATURES OF 86, 100 AND 115°

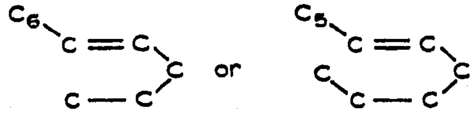
Number of carbon atoms	*trans-2-/1-alkene*			*trans-3-/1-alkene*			*cis-2-/1-alkene*		
	86°	*100°*	*115°*	*86°*	*100°*	*115°*	*86°*	*100°*	*115°*
6	3.1	2.9	2.9	2.3	2.0	1.8	4.0	3.9	4.0
7	3.7	3.6	3.5	2.3	2.1	1.9	4.5	4.5	4.5
8	4.1	4.0	3.9	3.0	2.8	2.6	4.7	4.7	4.8
9	4.7	4.6	4.4	3.4	3.1	2.9	5.0	5.0	5.1
10	5.2	5.1	5.0	3.7	3.3	3.1	5.3	5.3	5.4
11	5.8	5.7	5.5	4.0	3.6	3.4	5.6	5.6	5.6
	cis-3-/1-alkene			*trans-2-/trans-4-*			*cis-2-/cis-4-*		
6	3.3	3.2	3.3	–	–	–	–	–	–
7	4.2	4.2	4.2	–	–	–	–	–	–
8	4.4	4.4	4.5	4.9	4.9	4.8	4.8	4.8	4.8
9	4.2	4.3	4.5	5.6	5.6	5.5	5.2	5.2	5.2
10	3.9	4.2	4.5	6.3	6.3	6.3	5.6	5.5	5.6
11	3.6	4.1	4.6	7.1	7.0	7.1	6.1	5.9	5.9
	trans-2-/trans-3-			*cis-2-/cis-3-*			*cis-2-/trans-2-*		
6	6.7	6.8	7.3	4.8	4.8	4.9	8.1	8.7	9.3
7	4.9	5.0	5.0	4.7	4.8	4.8	12.2	13.0	13.9
8	5.5	5.5	5.5	4.8	4.9	4.9	8.0	8.9	9.8
9	5.8	5.9	5.8	5.3	5.3	5.3	7.0	7.7	8.5
10	6.2	6.3	6.2	5.7	5.6	5.6	6.0	6.6	7.2
11	6.6	6.6	6.6	6.1	6.0	6.0	5.0	5.5	6.0

tion indices of two alkenes when the difference between their boiling points is 1°. The values of k_p for the pairs of hexenes, heptenes, octenes and undecenes have been calculated from the measured retention indices[8,9] and tabulated boiling points[14-16]. The values of k_p for nonenes and decenes have been calculated by graphical interpolation from the dependence of k_p on the number of carbon atoms in the molecules of pairs of alkenes being compared. The calculated and interpolated values of k_p (for temperatures 86, 100 and 115°) for the pairs of non-branched alkenes compared are given in Table IV.

It can be seen from Table IV that the proportionality constant k_p in eqn. 5 differs from the value of 5 suggested by KOVÁTS. For the isomers of alkenes studied k_p is generally in the range 1.8–9.8, depending on the pair of isomers being compared and the number of carbon atoms in the alkenes or, eventually, the column temperature. Extraordinarily high values, 12.2–13.9, were found for the pair *cis*-2-/*trans*-2-C_7-alkenes. This deviation is not fortuitous but probably influenced by a special conformation of the carbon chain having a length just sufficient to allow the formation of the cyclic configuration:



It is significant in this context that anomalous chromatographic behaviour was observed also with *trans*-4-undecene and *trans*-5-undecene[9], which are the only isomers of all the straight-chain undecenes that can adopt a spatial arrangement similar to those above:



It is also interesting to note the deviations of the retention indices of those members of the homologous series of tetrahydrofuran acetals[17] which can adopt an annular configuration, even when a silicone elastomer rather than squalane has been used as stationary phase.

In most cases, the k_p values rise with increase in the number of carbon atoms. Certain deviations in the regularities of the above dependences may be expected from the dependences of the structural increments, H^S, on the number of carbon atoms of the non-branched C_6–C_{11} alkenes (*cf.* refs. 8 and 9). A decrease in k_p with the number of carbon atoms was found for pairs of *cis*-2-/*trans*-2- and *cis*-2-/*trans*-3-alkenes.

The boiling points of the nonenes and decenes were calculated by eqn. 5 rearranged to:

$$T_{b_x} = T_b + \frac{\delta I}{k_p} \tag{6}$$

where T_b is the boiling point of the reference alkene. The boiling points of *trans*-2-, *cis*-2-, *trans*-3- and *cis*-3-nonenes and-decenes were calculated from the known boiling points of 1-nonene and 1-decene and the proportionality constants k_p in Table IV. With respect to the small differences between the retention indices of 1- and 4-alkenes, the boiling points of *trans*-4- and *cis*-4-nonenes and -decenes were calculated by comparing the *trans*-2-/*trans*-4- and *cis*-2-/*cis*-4-alkenes from the already calculated boiling points of *trans*-2- and *cis*-2-nonenes and- decenes. The boiling points of *trans*-5- and *cis*-5-decenes were calculated from the values of their retention indices by interpolation from the boiling points and retention indices of *trans*-3 -and *trans*-4 and of *cis*-3- and *cis*-4-decenes since the variations of retention indices with temperature are very similar for the configurations *trans*-3-, -4-, -5- or *cis*-3-, -4-, -5- for alkenes[8,9].

The boiling points of the nonenes and decenes calculated by eqns. 3, 4 and 6 are given in Table V. Boiling points are given which are specified as approximate in the literature[14,15]. The boiling points calculated by eqn. 6 differ from the published (approximate) ones by as much as 3.7°. Since the boiling points of the C_6, C_7, C_8 and C_{11} alkenes calculated by eqn. 6 are identical with the tabulated values, we have used in Table V the values of the boiling points of the C_9 and C_{10} alkenes calculated by eqn. 6 as the basis for comparing the methods employed. It is apparent that the deviations, ΔT_b, for the nonenes and decenes calculated from eqns. 4 and 6 agree with the deviations for the C_6–C_8 alkenes. The values of ΔT_b for the C_9–C_{11} alkenes in the individual series of the *trans*-2-, -3-, -4-alkenes are nearly constant while for the *cis*-2-, -3-, -4-alkenes and 1-alkenes the ΔT_b values decrease regularly with the number of carbon atoms (a decrease by 0.3 or 0.1° for each carbon atom). The deviations, ΔT_b, calculated by eqns. 3 and 6 are nearly constant for the groups of *trans*-, *cis*- and 1-alkenes. For the *cis*-isomers and 1-alkenes, average deviations in both methods amount to -0.3 and $-0.1°$, respectively. These values correspond to the ascertained dependence

TABLE V

COMPARISON OF THE CALCULATED AND TABULATED BOILING POINTS OF NON-BRANCHED C_9–C_{10} ALKENES

Alkene	*Boiling point (°C)*					
	Ref. 14	*Eqn. 6*[a]	*Eqn. 4*	ΔT_b	*Eqn. 1*	ΔT_b
trans-4-Nonene	(144)	147.7	146.8	−0.9	147.7	0.0
cis-4-Nonene	(144)	147.5	147.0	−0.5	147.2	−0.3
1-Nonene	146.87	146.9	146.4	−0.5	146.8	−0.1
cis-3-Nonene	(147.9)	148.0	147.6	−0.4	147.7	−0.3
trans-3-Nonene	(147.9)	148.2	147.4	−0.8	148.2	0.0
trans-2-Nonene	—	150.0	150.0	0.0	150.0	0.0
cis-2-Nonene	148.5	150.7	151.2	0.5	150.5	−0.2
trans-4-Decene	(170.5)	170.9	170.0	−0.9	170.8	−0.1
cis-4-Decene	(170.5)	170.8	170.0	−0.8	170.4	−0.4
1-Decene	170.57	170.6	170.0	−0.6	170.5	−0.6
trans-2-Decene	170.6[b]	173.4	173.4	0.0	173.4	0.0
cis-2-Decene	170.6[b]	174.2	174.4	0.2	174.0	−0.2
cis-5-Decene	(170.7)	170.6	169.7	−0.9	170.2	−0.4
trans-5-Decene	(171.3)	171.3	170.4	−0.9	171.2	−0.1
cis-3-Decene	(173.3)	171.4	170.7	−0.7	171.1	−0.3
trans-3-Decene	(173.3)	171.5	170.7	−0.8	171.4	−0.1

[a] Our measurement.
[b] Ref. 15.

of f_c on the number of carbon atoms in the alkene molecule. For the *cis*-alkenes, f_c rises by about 1.3 for each carbon atom (Table III), which results in a boiling point lower by 0.3° when using eqn. 3 for calculations. Similarly, for 1-alkenes, the value of f_c increases by about 0.4 per carbon atom, which corresponds to boiling point 0.1° lower compared with the boiling point calculated by eqn. 6. The majority of the *trans*-alkenes show a perfect agreement of the boiling points calculated by both eqns. 3 and 6, which is again in agreement with f_c being independent of the number of carbon atoms, as has been found experimentally for the C_6–C_{11} *trans*-alkenes.

TABLE VI

BOILING POINTS OF THE 3-NONENES AND DECENES CALCULATED BY EQN. 6 FROM DIFFERENT REFERENCE ALKENES

Alkene	*Pairs compared*	k_p	*Calculated boiling point (°C)*
trans-3-Nonene	*trans*-3-nonene/1-nonene	3.4	148.2
	trans-2-nonene/*trans*-3-nonene	5.8	148.2
	cis-2-nonene/*trans*-3-nonene	6.1	148.3
cis-3-Nonene	*cis*-3-nonene/1-nonene	4.2	148.0
	trans-2-nonene/*cis*-3-nonene	4.8	148.0
	cis-2-nonene/*cis*-3-nonene	5.3	148.0
trans-3-Decene	*trans*-3-decene/1-decene	3.7	171.4
	cis-2-decene/*trans*-3-decene	6.0	171.6
	trans-2-decene/*trans*-3-decene	6.2	171.5
cis-3-Decene	*cis*-3-decene/1-decene	3.9	171.4
	trans-2-decene/*cis*-3-decene	5.7	171.4
	cis-2-decene/*cis*-3-decene	5.7	171.4

The reproducibility of the boiling points of the nonenes and decenes calculated by eqn. 6 was tested in calculating the boiling points of the 3-nonenes and 3-decenes. Different reference substances, *i.e.*, pairs with different k_p, were used in the calculation. The boiling points so calculated are given in Table VI. It is apparent that the choice of the reference alkene is not decisive, since the deviations in the boiling points calculated were less than ±0.1°. The values quoted were calculated from the chromatographic data obtained at a column temperature of 86°. The use of k_p determined for temperatures of 100° and 115° allows the calculation of the boiling points of the nonenes and decenes with almost the same result.

CONCLUSIONS

Relations based on data for *n*-alkanes, MATUKUMA's concept I_B, and a method based on the proportionality constant k_p ($k_p = \delta I/\delta T_b$) were tested in calculating the boiling points of 14 non-branched nonenes and decenes. The boiling points of the non-branched alkenes calculated from the difference in the retention indices of *n*-alkenes and *n*-alkanes and the known boiling points of the *n*-alkanes between which the alkene is eluted, $T_{b_x} = T_{b1} + \delta I(T_{b2} - T_{b1})/100$, agreed with those calculated after MATUKUMA, $I_B \equiv I_R$, to within 0.1–0.2°. For the C_6–C_8 alkenes (at a temperature of 86°), the above values differed from the tabulated ones by a maximum of 1.4°.

Boiling points calculated by the use of I_B corrected by the correction factor f_c displayed maximum deviations of 0.4°. It was ascertained that the correction factor f_c for *trans*-alkenes is independent of, but for *cis*-alkenes and 1-alkenes is dependent on, the number of carbon atoms in the molecule. Since the correction factors f_c calculated from alkenes of the same structure but having one carbon atom less in the molecule are used in calculating I_B, the relation holds precisely only for *trans*-alkenes (for which f_c does not vary with the number of carbon atoms).

More precise boiling points of the nonenes and decenes were found by correlating the structures of the alkenes with their boiling points. It was ascertained that the constant of the KOVÁTS relation $\delta I \approx 5\,\delta T_b$ does not have the value of 5 for hydrocarbons on a hydrocarbon stationary phase, but varies within the range 1.8–13.9, depending on the pair of isomers being compared and on the number of carbon atoms in the molecule, or on the column temperature. The values of k_p for the corresponding pairs of nonenes and decenes were interpolated from the graphical dependence of k_p on the number of carbon atoms. The above k_p values, known boiling points and the measured retention indices of 1-nonene and 1-decene were used in the calculation of the boiling points of the other nonenes and decenes from their respective retention indices. The boiling points so obtained differed from the literature (approximate) values by a maximum of 3.7°. The reproducibility of the calculated boiling points was ±0.1°.

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