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IDENTIFICATION OF STRAIGHT-CHAIN UNDECENES BY  
CAPILLARY GAS CHROMATOGRAPHY ON SQUALANE

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## SUMMARY

Separation of all nine straight-chain undecenes has been effected by means of capillary gas chromatography (stainless-steel column; length, 200 m; I.D., 0.2 mm) on squalane at 86°. Their identification was carried out by purely chromatographic means using the dependence of the structural increment,  $H^s$ , on the number of carbon atoms in the molecule of the homologous straight-chain alkenes and by using characteristic changes with the temperature in the retention indices of the corresponding geometrical *cis* and *trans* isomers.

The relative amounts of the individual positional undecenes from the dehydrogenation of *n*-undecane on an oxide catalyst at 400–500° were found to be approximately 1:4:4:3:3 for the 1-, 2-, 3-, 4- and 5- isomers at a ratio of about 2:1 for the *trans* and *cis* isomers.

## INTRODUCTION

Higher straight-chain alkenes serve as raw materials for the production of biologically degradable detergents, alcohols and several types of polymers and copolymers. The alkenes are formed during the catalytic dehydrogenation of *n*-alkanes on oxide dehydrogenation catalysts<sup>1</sup>. The main products are alkenes having one double bond with small amounts of alkyl aromatics. In the dehydrogenation products, all the theoretically possible straight-chain alkenes, the characteristic alkyl aromatics and the unreacted *n*-alkanes have been found<sup>2</sup>. The presence of greater amounts of hydrocarbons of other types, *e.g.*, cycloalkanes, was not determined. By means of an efficient capillary column coated with squalane and at temperatures in the range 86–115°, the dehydrogenation products of  $C_6$ – $C_{10}$  *n*-alkanes containing ap-

proximately 60 constituents were separated. Only the pair 1-decene + *trans*-4-decene remained unresolved<sup>2</sup>.

Within the systematic investigation of dehydrogenation of individual *n*-alkanes, this work deals with the separation and identification of straight-chain undecenes. Our own results<sup>2</sup> as well as investigations by several other authors<sup>3-6</sup> were consulted during the identification. Because of the narrow boiling range of the nine theoretically possible C<sub>11</sub> straight-chain alkenes (3-8°) and the very near or practically identical boiling points of isomers having the double bond on the 1-, 3-, 4- and 5- carbon atom, the use of an efficient capillary column was a necessity for a successful separation.

## EXPERIMENTAL

A Chrom-3 gas chromatograph (Laboratory Equipment, H.E., Prague, Czechoslovakia) with a flame-ionization detector was used. A stainless-steel capillary column of length 200 m and I.D. 0.2 mm was coated with squalane by the dynamic method. Column temperatures of 86, 100, 115 and 130° were used. The inlet pressure of the nitrogen carrier gas was 4 kp/cm<sup>2</sup>. The determinations were carried out with 0.5-1.0  $\mu$ l samples and a split of 1/300. For this column at the capacity ratio  $k' = 6.6$  and a temperature of 115°, the theoretical efficiency was  $n = 250,000$  theoretical plates and an effective efficiency of  $N = 190,000$  plates was found.

The dehydrogenation of *n*-undecane (purity 99.9%) was carried out in an isothermal reactor at 400-500° using various oxide catalysts. The reaction products were cooled to 0° and the non-condensable hydrogen, containing about 1% of light cracking gases, was separated from the liquid condensate. This liquid condensate, which represents about 99% of the total amount of hydrocarbons formed, was purified on a silica gel column, and the alkene fraction was investigated by gas chromatography.

The retention times were determined from the methane peak. For the representation of the retention data, the retention indices proposed by Kováts<sup>7</sup> were used. Reproducibilities of retention indices based on at least three determinations were  $\pm 0.2$  index unit.

The identification of the straight-chain C<sub>11</sub> alkenes was carried out by using the dependence of the structural increment,  $H^s$ , on the number of carbon atoms in the molecules of straight-chain C<sub>6</sub>-C<sub>10</sub> alkenes and by the characteristic changes in the retention indices with temperature for the corresponding geometrical *cis*- and *trans*-alkenes<sup>2</sup>.

## RESULTS AND DISCUSSION

In Fig. 1, a chromatogram is shown of the dehydrogenation products separated on a 200-m squalane capillary column at 115° (the identification of aromatics is described elsewhere<sup>8</sup>) and in Fig. 2 a chromatogram is presented of the straight-chain undecene fraction on the same column at 86°. The identification of the constituents, particularly of undecenes, in chromatograms is difficult because of the restricted application of mass spectrometry in the identification of *cis* and *trans* isomers, and this problem was solved in the following ways.

The dependence of the structural increment,  $H^s$ , of the straight-chain C<sub>6</sub>-C<sub>10</sub>

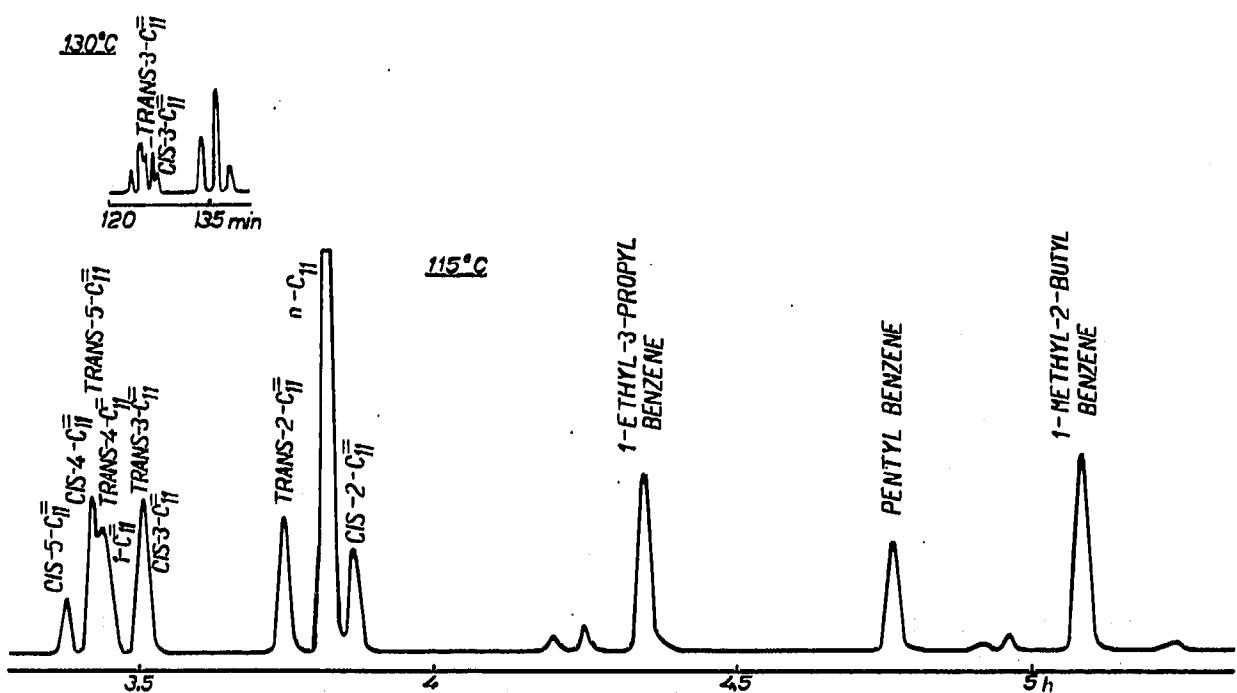


Fig. 1. Chromatogram of dehydrogenation products of *n*-undecane on a squalane column at 115° and separation of *cis*-3- and *trans*-3-undecene at 130°.

alkenes on the numbers of carbon atoms in the molecules<sup>2</sup> was used for the identification of the straight-chain undecenes. The retention data for the individual  $C_{11}$  alkenes were extrapolated from the decrease of  $H^s$  with the increase in the number of carbon atoms (at a column temperature of 115°). These extrapolated data were compared with the experimentally determined values. The results of the final identification are given in Table I. Undecane and straight-chain undecenes are listed in Table I in the order of their boiling points. The values of the retention indices determined at 86, 100,

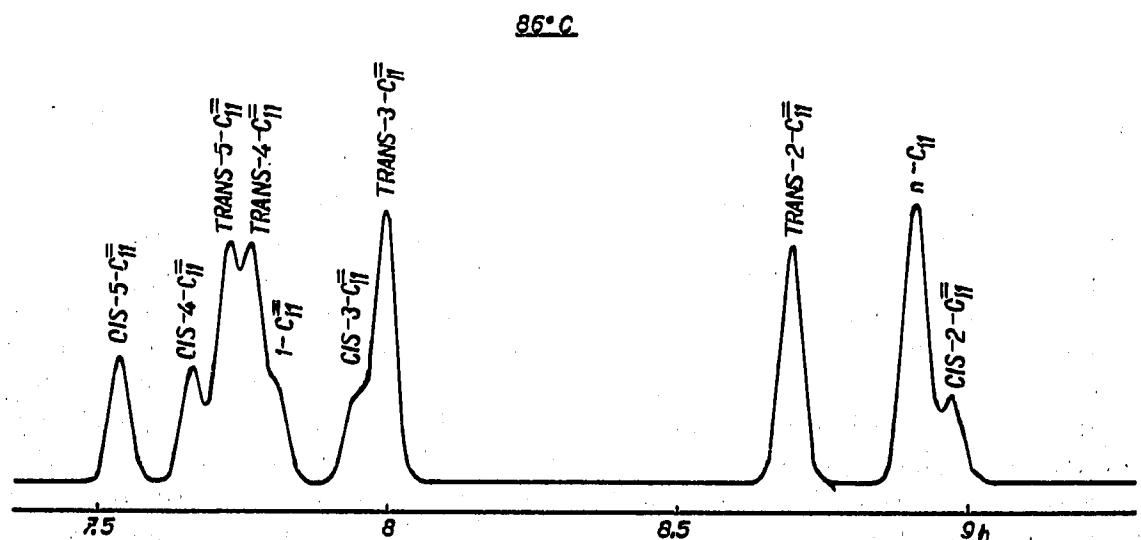


Fig. 2. Separation of all straight-chain undecenes on a squalane column at 86°.

TABLE I

RETENTION INDICES OF *n*-UNDECANE AND STRAIGHT-CHAIN UNDECENES ON SQUALANE AT 86, 100, 115 AND 130°

Component	Boiling point (°C)	$I^s_{86}$	$I^s_{100}$	$I^s_{115}$	$I^s_{130}$	$10 \left( \frac{\delta I^s}{\delta T} \right)$
<i>n</i> -Undecane	195.89	1100.0	1100.0	1100.0	1100.0	0.00
<i>cis</i> -5-Undecene	192.3	1077.6	1078.2	1078.9	1080.5	0.45
<i>cis</i> -4-Undecene	192.6	1079.9	1080.5	1081.1	1082.5	0.41
1-Undecene	192.7	1082.2	1082.4	1082.6	1083.5	0.14
<i>trans</i> -5-Undecene	193.0	1081.0	1081.1	1081.2	1082.5	0.07
<i>trans</i> -4-Undecene	193.0	1081.6	1081.8	1082.0	1083.5	0.14
<i>cis</i> -3-Undecene	193.4	1084.7	1085.3	1085.8	1086.6	0.38
<i>trans</i> -3-Undecene	193.5	1085.5	1085.4	1085.3	1085.5	-0.07
<i>trans</i> -2-Undecene	195.2	1096.6	1096.6	1096.5	1096.7	-0.03
<i>cis</i> -2-Undecene	196.1	1101.1	1101.5	1101.9	1102.7	0.28

115 and 130° and the calculated changes of the retention indices with temperature of column  $10(\partial I/\partial T)$  for the range 86–115° are also presented.

It must be mentioned that the retention indices of alkenes were calculated from the chromatogram for some constituents that were only partially separated. Retention indices of certain undecenes on squalane at 70° have been published by SCHOMBURG<sup>4</sup>. The comparison of these published data with our values, which were calculated for the temperature 70° by means of the temperature increments, showed differences from zero for 1-undecene to six index units for *cis*-5-undecene. All our retention indices for *trans* and *cis* isomers have lower values and greater differences for *cis* (from 2 to 6 index units) than for *trans* isomers (from 1 to 2 index units), regardless of whether the component was eluted alone or was only partially separated. The greatest deviation was found for *cis*-5-undecene which was well separated from the other components. Consequently, the differences in the retention indices of undecenes cannot be explained only by the shift of the peak maximum. An explanation may be that we have used a more efficient column and the retention indices were determined more precisely.

#### *The trans-cis configuration and the temperature increment of the retention indices*

The influence of column temperature on the retention indices is complex. A linear relationship between retention index and temperature (in the range 22–100°) for hydrocarbons on squalane as liquid phase was found by ETTRE AND BILLEB<sup>9</sup>. HIVELY AND HINTON<sup>10</sup> demonstrated that the temperature increment of the retention index on squalane increases with the increase of the cross-sectional area of the molecule. MATUKUMA<sup>5</sup> stated that the values of  $10(\partial I/\partial T)$  for alkenes are rather lower than those of alkanes with the same skeletal structure. LOEWENGUTH AND TOURRES<sup>6</sup> observed the specific temperature increments for olefins and diolefins, cycloolefins and cyclodiolefins (for monoolefins,  $10(\partial I/\partial T) < 0.5$ ). In our previous work<sup>2</sup>, we changed the separation selectivity of *cis* and *trans* straight-chain alkenes (with the double bond in positions 2- to 5-) by changing the squalane column temperature. The temperature increment of the C<sub>6</sub>–C<sub>10</sub> *cis*-alkenes ( $10(\partial I/\partial T) = 0.2$ –0.4) was always higher than the increment of the corresponding *trans*-alkenes (–0.3 to 0.2).

From the calculated values of the temperature increments for the straight-chain undecenes (Table I), it can be seen that for all *cis*-undecenes the values of  $10(\partial I/\partial T) = 0.28-0.45$  are again higher than for the corresponding *trans* isomers ( $-0.70$  to  $0.14$ ). This confirms the general validity of the above conclusion. A certain increase in the temperature increment with the shift of the double bond from the 2- to the 5-position, in the opposite direction to their boiling points<sup>11</sup>, distinct for *cis* isomers can be noticed. The temperature increment for 1-alkene ( $0.14$ ) is approximately within the limits of the increments for *trans* and *cis* isomers. Linear changes in retention indices with temperature were determined in the temperature range  $86-115^\circ$ . For a temperature of  $130^\circ$ , higher retention indices were found (maximum about 1 index unit) than would be expected from a linear dependence.

The determined changes in the retention indices with temperature on a squalane column for the straight-chain undecenes are rather small ( $10(\partial I/\partial T) < 0.5$ ) and therefore their application for identification and separation requires exact determination of the retention indices and the use of a very efficient open tubular column. Considering that under the given experimental conditions 0.5 index unit is sufficient for the partial resolution of two constituents, from the determined temperature increments we calculated the required temperature ( $86^\circ$ ) for the separation of all nine isomers of undecene. The effect of temperature on the separation selectivity of *cis* and *trans* isomers is clearly demonstrated by the separation of *cis*- and *trans*-undecenes. *cis*-3-Undecene is eluted first at  $86^\circ$  while at  $130^\circ$  (Fig. 1) the order is reversed.

#### *The position of the double bond and retention*

From Table I it can be seen that the *cis*-undecenes are eluted in accordance with the shifting of the position of the double bond nearer to the end of the chain (from the 5- to the 2- position) in agreement with the increase in their boiling points. The same sequence occurs for the *trans*-undecenes. The order for *trans*-4- and *trans*-5-undecenes is questionable, however, and seems to be influenced by the configuration of *trans*-4-alkenes which have a tendency to form a ring structure<sup>11</sup>. According to ASINGER *et al.*<sup>3</sup>, these isomers have the same boiling points. However, their separation on a squalane column shows a difference in retention which corresponds to a difference in boiling points of approximately  $0.1^\circ$ . In the case of the straight-chain *trans*-4- and *trans*-5-decene pair, the dehydrogenation mechanism indicated that *trans*-4-decene would be eluted before *trans*-5-decene, whereas on the basis of the dependence of the logarithm of the relative retention of the corresponding *trans* and *cis* isomers *versus* the position of the double bond, the reverse order seemed the more likely\*.

The retention of 1-undecene compared with the other undecenes is interesting, and comparison with the lower alkenes, for example at a temperature of  $86^\circ$ , shows that 1-nonene is eluted first from the squalane column followed by the other nonenes. Of the decenes, 1-decene is eluted after *cis*-5-decene together with *cis*-4- and *trans*-4-decene. Of the undecenes, 1-undecene is eluted immediately after the 5- and 4- isomers. For the products studied at present from *n*-dodecane dehydrogenation, an additional shift of the 1-dodecene retention to the 3-dodecenes was found. This is in contradiction to SCHOMBURG's statement<sup>4</sup>, which attributes to the 1-alkenes the smallest retention indices in comparison with the other straight-chain alkene isomers.

\* From our new results on elution behaviour of pairs *trans*-4- and *trans*-5-dodecenes and tri-decenes it follows that *trans*-4-undecene is eluted before *trans*-5-undecene.

The qualitative and quantitative evaluation of the chromatograms has confirmed the assumed dehydrogenation mechanism for *n*-undecane. The relative amounts of the individual 1-, 2-, 3-, 4- and 5- C<sub>11</sub> alkenes were found to be approximately 1:4:4:3:3 at a ratio about 2:1 for the *trans* and *cis* isomers. These results confirmed that the formation of the individual alkenes proceeds in accordance with the thermodynamic equilibria, from the viewpoint of both the double bond position and the formation of *trans-cis* geometrical isomers.

## REFERENCES

- 1 J. F. ROTH, J. B. ABELL AND A. R. SCHAEFER, *Ind. Eng. Chem. Product Res. Dev.*, 7 (1968) 254.
- 2 L. SOJÁK AND A. BUCÍNSKÁ, *J. Chromatogr.*, 51 (1970) 75.
- 3 F. ASINGER, B. FELL AND G. STEFFAN, *Chem. Ber.*, 97 (1964) 1555.
- 4 G. SCHOMBURG, *J. Chromatogr.*, 23 (1966) 1.
- 5 A. MATUKUMA, in C. L. A. HARBOURN AND R. STOCK (Editors), *Gas Chromatography 1968*, Institute of Petroleum, London, 1969, p. 55.
- 6 J. C. LOEWENGUTH AND D. A. TOURRES, *Z. Anal. Chem.*, 236 (1968) 170.
- 7 A. WEHRLI AND E. KOVÁTS, *Helv. Chim. Acta*, 42 (1959) 2709.
- 8 L. SOJÁK, P. MAJER, J. KRUPČÍK AND J. JANÁK, *J. Chromatogr.*, 65 (1972) 143.
- 9 L. S. ETTRÉ AND K. BILLEB, *J. Chromatogr.*, 30 (1967) 1.
- 10 R. A. HIVELY AND R. E. HINTON, *J. Gas Chromatogr.*, 6 (1968) 203.
- 11 L. SOJÁK, J. KRUPČÍK, K. TESAŘÍK AND J. JANÁK, *J. Chromatogr.*, 65 (1972) 93.

*J. Chromatogr.*, 65 (1972) 137-142