

It should be evident from Table 2 that the  $R_s$ -values are not constant. Underlined values for column 1 were determined about a month later than the others, for column 2 (3) — two weeks later, and for column 4 — a week later.  $R_s$ -values determined on newly prepared packings are fully satisfactory for the separation of *cis-trans*-isomer pairs of  $C_9$ — $C_{12}$  *n*-alkenes. At working temperatures of 75—110°, the separation ability decreases continuously, obviously because of the insufficient thermal stability of hexandiol-1,6. Column 1 proved to be more stable than the others. Wider peaks were an additional drawback of column 4.

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ИЗВЕСТИЯ АКАДЕМИИ НАУК ЭСТОНСКОЙ ССР. ТОМ 19  
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## SEPARATION AND PREPARATIVE PURIFICATION OF GEOMETRIC ISOMERS OF $C_9$ — $C_{12}$ *n*-ALKENES BY GAS CHROMATOGRAPHY, USING $AgNO_3$ AND HEXANDIOL-1,6 AS A STATIONARY PHASE

### II. PREPARATIVE SEPARATIONS

HELJU RAUDE, O. EISEN.  $C_9$ — $C_{12}$  *n*-ALKEENIDE GEOMEETRILISTE ISOMEERIDE LAHUTAMINE JA PUHASTAMINE GAASIKROMATOGRAAFILISEL MEETODIL, KASUTADES STATIONAARSE FAASINA  $AgNO_3$  JA HEKSAANDIOOLI-1,6.

### II. PREPARATIIVNE ERALDAMINE

ХЕЛЮ РАУДЕ, О. ЭЙЗЕН. РАЗДЕЛЕНИЕ И ПРЕПАРАТИВНАЯ ОЧИСТКА ГЕОМЕТРИЧЕСКИХ ИЗОМЕРОВ  $C_9$ — $C_{12}$  *n*-АЛКЕНОВ МЕТОДОМ ГАЗОВОЙ ХРОМАТОГРАФИИ С ИСПОЛЬЗОВАНИЕМ  $AgNO_3$  И ГЕКСАНДИОЛА-1,6 В КАЧЕСТВЕ СТАЦИОНАРНОЙ ФАЗЫ.

### II. ПРЕПАРАТИВНОЕ РАЗДЕЛЕНИЕ

This communication presents some results of purification of *cis-trans*-isomers of  $C_9$ — $C_{12}$  *n*-alkenes by preparative gas chromatography. Experiments were carried out on apparatus PGK-1, described in [1]. 3 columns were employed: 1) inner diameter 10 mm, solid support — Chromosorb P 20—30 mesh, 2) inner diameter 16 mm, solid support — Chromosorb A 45—60 mesh, 3) inner diameter 10 mm, solid support — Chromosorb W 45—60



Isomerization of some *cis*-isomers of  $C_{10}$ — $C_{12}$  *n*-alkenes

Compound	Column No.	Column temperature, °C	Content of <i>trans</i> -isomer in the primary sample, %	Content of <i>trans</i> -isomer in the recovered sample, %
<i>n</i> -Decene-2 ( <i>cis</i> )	I	80	3.8	0.3—0.7
	II	80	4.9	1.6—1.8
	III	80	4.9	not in detectable amounts
<i>n</i> -Undecene-4 ( <i>cis</i> )	I	100	0.8	1.5—3.1
	I	100	2.1	3.0—3.8
	II	100	1.9	7.1
	II	100	2.1	3.5—9.9
	II	100	2.1	7.4
	III	100	2.1	2.5—2.6
<i>n</i> -Undecene-5 ( <i>cis</i> )	I	100	2.2—2.8	3.8—5.7
	II	100	1.8	7.8—11.6
	II	100	1.8	3.2—9.5
	III	100	2.2—2.8	0.5—1.9
<i>n</i> -Dodecene-6 ( <i>cis</i> )	I	100	2.1	4.2—4.7
	II	100	2.1	12.1—13.1
	II	110	2.1	24.4
	III	100	2.1	1.5
	III	100	0.8	3.3
	III	110	0.8	6.4—7.6

mesh. All columns were of stainless steel, 2 meters in length. The contents of  $AgNO_3$  and hexandiol-1,6 in packings were the same as in corresponding analytical columns [2]. The carrier gas was nitrogen.

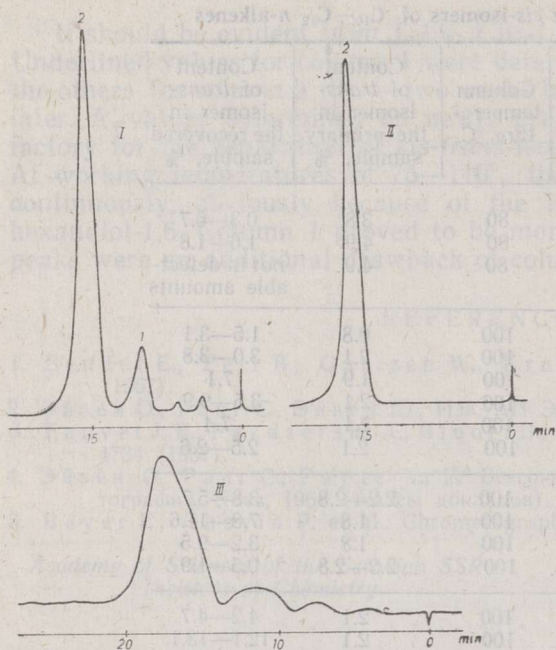
Analyses on  $AgNO_3$  and hexandiol-1,6 containing packings showed that almost all *cis*-isomers of  $C_9$ — $C_{12}$  *n*-olefins contained to some degree *trans*-isomers and other impurities. At the same time, *trans*-isomers were found to be mostly pure. This is the reason for experimenting mostly with *cis*-isomers in preparative separations. It became evident that one of the basic difficulties in preparative purification of geometric isomers of *n*-alkenes  $C_{10}$ — $C_{12}$  was isomerization of samples in chromatographic process.

Table gives results of some experiments with  $C_{10}$ — $C_{12}$  *n*-alkenes. Sample sizes per injection were within the range of 200—300  $\mu$ l. No isomerization took place at 80°C. However, maintaining preparative columns at 100° caused isomerization of *cis*-isomers into *trans*-isomers in considerable amounts. Results obtained at 110° showed a direct dependence of the extent of isomerization on the column temperature. Isomerization took place to the least extent in column 3. Evidently, the nature of support is one of the factors influencing *cis*-*trans*-isomerization. The most inferior support for our purpose seemed to be Chromosorb A. The preparative columns tested were more or less suitable for receiving purified *cis*- or *trans*-isomers of *n*-alkenes with up to 10 C atoms. Separation of geometric isomers of  $C_{11}$  *n*-alkenes needs column temperature not lower than 90°. At temperatures 90° and higher, columns begin bleeding, leading to contamination of recovered samples and impairing column separation abilities. Utilization of more stable stationary phases cannot offer a complete solution of the problem because of the isomerization of *n*-alkenes at 100° and higher temperatures, restricting the upper temperature limits of columns.

## Examples of some separations

1. *n*-decene-4 (*cis*)

The original sample of *n*-decene-4 (*cis*) consists of *cis*-isomer (87.1%), *trans*-isomer (10.8%) and other impurities (2.1%). Purification by preparative gas chromatography using column 3



I and II — apparatus GCHF-18.2; column 2 m  $\times$  0.6 cm; Chromosorb W coated with 35.6%  $\text{AgNO}_3$  and hexandiyl-1,6; temperature 100°C; He — 60 ml/min; sample size 7–8  $\mu\text{l}$ . 1 — *n*-decene-2 (*trans*), 2 — *n*-decene-2 (*cis*).

III — apparatus PGK-1; column 2 m  $\times$  1.0 cm; packing — as described above; temperature 75°C; sample size 100  $\mu\text{l}$ .

at 75°C gave pure *cis*-isomer. Sample size per injection did not exceed 150  $\mu\text{l}$ . For collecting we used the traps proposed by A. B. Carel [3] for smaller samples. Figure shows the chromatograms of this separation.

2. *n*-undecene-3 (*cis*)

The original sample consists of *cis*-isomer (67.2%), *trans*-isomer (1.1%) and other impurities (31.7%). Column 3 at 90°C gave purified sample consisting of *cis*-isomer in 99.5 and *trans*-isomer in 0.5%.

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