

LÜHIUURIMUSI * КРАТКИЕ СООБЩЕНИЯ

O. EISEN, HELJU RAUDE

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

I. PRELIMINARY EXPERIMENTS

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

О. ЭЙЗЕН, ХЕЛЮ РАУДЕ. 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. I. ПРЕДВАРИТЕЛЬНЫЕ ОПЫТЫ

Gas chromatographic separation and purification of geometric isomers of long-chain ($C \geq 8$) *n*-alkenes is a rather complicated problem. Bendel, Fell et al. [1] reported the successful separation of all of the geometric isomers of *n*-octenes, using solution of $AgBF_4$ in β , β' -oxydipropionitrile as a stationary phase. Both Eisen et al. [2] and Fauvet et al. [3] at first separated *trans*-isomers from *cis*-isomers by gas chromatography, using solution of $AgNO_3$ as a stationary phase. Collected *trans*- and *cis*-isomers were analyzed with the use of capillary columns. In such a way, geometric isomers of C_9 — C_{10} *n*-alkenes could be analyzed.

The purpose of present investigation was not in fact a separation of all geometric isomers of C_9 — C_{12} *n*-alkenes, but pairs of *cis-trans*-isomers of positional isomers of these *n*-alkenes. This paper presents the results of experimental work done with the purpose of finding suitable conditions for a purification of geometric isomers of C_9 — C_{12} *n*-alkenes by preparative chromatography.

We succeeded in separating and purifying geometric isomers of C_5 — C_9 *n*-alkenes, using solution of $AgNO_3$ and triethylene glycol as a stationary phase [4]. In the present investigation, an attempt was made to use higher boiling glycols as constituent parts of stationary phases. The glycols under investigation were: butandiol-1,4, hexandiol-1,6 and decandiol-1,10. Preliminary experiments revealed the good separation ability of hexandiol-1,6, comparable to butandiol-1,4 concerning geometric isomer pairs of C_9 — C_{12} *n*-alkenes. Packings containing decandiol-1,10 were much inferior in this respect. Considering the better thermal stability of hexandiol-1,6 in comparison with butandiol-1,4, the first-mentioned glycol was chosen for preparing column packings. $AgNO_3$ and hexandiol-1,6 were dissolved in methanol or ethanol (35—40°C). In coating the support, the solvent was removed in vacuum. The gas chromatograph was a GCHF-18.2 with an

thermal conductivity detector. All measurements were made with a detector current of 170 mA. The column dimensions were 200×0.6 cm. Helium was employed as the carrier gas, with a flow rate of 60 ml/min, measured at room temperature and atmospheric pressure.

We had at our disposal all geometric isomers of C_9-C_{12} *n*-alkenes with the exception of *n*-dodecene-3(*trans*). The estimation of the suitability of the columns (Table 1) was made mainly on the basis of relative retentions (*r*) and resolution (R_s) values. Reference substance for *n*-nonenes was *n*-nonane, for *n*-decenes — *n*-decane, etc. Relative retentions of *trans*-olefins and *cis*-olefins of certain homolog do not differ considerably. The difference decreases with shifting the double bond from the end of the chain towards the centre (4-, 5- and 6-isomers). R_s -values of geometric isomers of C_9-C_{12} *n*-alkenes in Table 2 illustrate the separation ability of the columns tested. As a rule, R_s -values for *n*-nonenes were measured at column temperature 75° , for *n*-decenes — at 85° , for *n*-undecenes — at 100° and for *n*-dodecenes — at 110° . Exceptions are marked in parentheses. R_s -values of a pair of geometric isomers were calculated according to [5]. The content of *cis*- and *trans*-isomers in synthetic blends was approximately equal. Sample size per injection was 4–6 μ l.

Table 1

Description of columns studied

No.	Solid support	Support mesh size	Stationary phase (AgNO ₃ +hexandiol-1,6), %	AgNO ₃ , %
1.	Chromosorb P	35–60	26.1	11.3
2.	Chromosorb W	45–60	35.6	15.4
3.	" "	45–60	35.6	15.4
4.	Chromosorb A	45–60	26.1	11.3

Table 2

 R_s -values of *cis-trans*-isomer pairs of C_9-C_{12} *n*-alkenes

<i>cis-trans</i> -isomer pairs	Resolution (R_s)			
	Column I	Column II	Column III	Column IV
<i>n</i> -Nonene-2	<u>1.89</u>	<u>2.57</u> <u>1.13</u>	—	—
<i>n</i> -Nonene-3	<u>2.64</u> <u>1.82</u>	<u>2.26</u> <u>1.00</u>	—	—
<i>n</i> -Nonene-4	<u>1.56</u>	2.26 (85°)	—	—
<i>n</i> -Decene-2	<u>2.81 (75°)</u> <u>1.72</u>	2.96	—	—
<i>n</i> -Decene-3	<u>1.61</u>	<u>2.56</u> <u>1.06</u>	—	<u>0.94 (110°)</u>
<i>n</i> -Decene-4	<u>2.25 (100°)</u> <u>1.41</u>	<u>2.49</u> <u>0.86</u>	—	<u>1.32 (100°)</u> <u>0.78 (100°)</u>
<i>n</i> -Decene-5	<u>2.23 (75°)</u> <u>1.41</u>	—	—	—
<i>n</i> -Undecene-2	<u>1.48</u>	3.06	—	1.73 <u>1.80 (110°)</u>
<i>n</i> -Undecene-3	<u>2.44</u> <u>1.61</u>	<u>0.81</u>	0.65	1.68
<i>n</i> -Undecene-4	<u>2.12</u> <u>1.05</u>	<u>2.47</u> <u>0.60</u>	—	2.02
<i>n</i> -Undecene-5	<u>1.13</u>	<u>2.40</u> <u>0.69</u>	—	1.48
<i>n</i> -Dodecene-2	<u>2.72 (100°)</u> <u>1.19</u>	1.78	—	—
<i>n</i> -Dodecene-4	<u>2.04 (100°)</u> <u>0.87</u>	1.09	1.45	—
<i>n</i> -Dodecene-5	<u>0.85</u>	1.39	<u>1.66</u> <u>0.62</u>	—
<i>n</i> -Dodecene-6	1.09	1.44	<u>1.72</u> <u>0.64</u>	—

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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Academy of Sciences of the Estonian SSR,
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HELJU RAUDE, O. EISEN

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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