

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 1.80 (110°)
<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.

REFERENCES

1. Bendel E., Fell B., Garitzen W., Kruse G., J. Chromatogr. **31**, 531—534 (1967).
2. Эйзен О., Ранг С., Эйзен Ю., Изв. АН ЭССР, Хим. Геол. **16**, 77—79 (1967).
3. Fauvet J. E., Pazdzerski A., Blugni B., Bull. Soc. Chim. France, No. 12, 4732—4734 (1967).
4. Эйзен О., Ранг С., Рауде Х., IV Всесоюзная конференция по газовой хроматографии, Киев, 1966 (тезисы докладов).
5. Bayer E., Chovin P. et al., Chromatographia, **1**, 153—159 (1968).

Academy of Sciences of the Estonian SSR,
Institute of Chemistry

Received
June 9, 1969

EESTI NSV TEADUSTE AKADEEMIA TOIMETISED. 19. KÕIDE
KEEMIA * GEOLOOGIA. 1970, Nr. 2

ИЗВЕСТИЯ АКАДЕМИИ НАУК ЭСТОНСКОЙ ССР. ТОМ 19
ХИМИЯ * ГЕОЛОГИЯ. 1970, № 2

HELJU RAUDE, O. EISEN

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