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## Abstract

## Full Text

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## CHEMISTRY

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# SEPARATION OF STEREOISOMERIC HEXENES BY PREPARATIVE GAS-LIQUID CHROMATOGRAPHY

*(Presented by Academician B. A. Kazanskii, 2 III 1962)*

The preparation of individual stereoisomers of olefins with an unbranched hydrocarbon chain presents very considerable difficulties, since the distillation of their mixtures cannot be carried out on ordinary rectification columns with an efficiency of 100 theoretical plates, owing to the closeness of their boiling points, and methods of stereospecific synthesis do not always lead to the preparation of sufficiently pure products (^1). To solve this problem we applied the method of preparative gas-liquid chromatography (^2). As the liquid phase we used a saturated solution of silver nitrate in ethylene glycol, whose high efficiency in the analysis of olefin stereoisomers has been shown in several studies (^3).

**Fig. 1.** Diagram of the preparative chromatograph: *1* –cylinder with nitrogen; *2* –valve; *3* –manometer; *4* –flowmeter at the inlet to the preparative chromatograph; *5* –dryer; *6* –check valve; *7* –evaporator; *8* –column jacket; *9* – two column sections; *10* –connecting tube; *11* –tee; *12* – "comb" ; *13* –traps; *14* –capillary; *15* –flowmeter at the outlet from the preparative chromatograph; *16* –inlet valve of the analytical chromatograph; *17* –flowmeter; *18* –detector (by thermal conductivity); *19* –flowmeter at the outlet from the detector working channel; *20* –shutoff valve of the analytical chromatograph; *21* –glass-wool plugs.

The apparatus used for the separation of olefins was assembled according to the scheme shown in Fig. 1. Nitrogen from the cylinder (*1*) passes through the dryer (a column with silica gel, *5*) and the check valve (*6*) into the evaporator (*7*)–a glass tube 20 cm long and 20 mm in diameter, filled with small steel balls

Figure 2 and Figure 3 chromatograms

Figure 2: Figure 2 and Figure 3 chromatograms

and equipped with electric heating, into which the mixture to be separated is fed from a burette. The vapors of the substance, mixed with nitrogen, po-

enter a glass column (9), consisting of two sections each 125 cm long and 20 mm in diameter, connected by means of ground joints with a glass tube (10) 10 cm long and 5 mm in diameter. Both sections of the column are filled with refractory brick (INZ-600 support), impregnated with 40% (by weight) of a saturated solution of silver nitrate in glycol. Each section of the column is mounted in a glass tube 125 cm long and 50 mm in diameter, provided with electric heating and insulated with asbestos. Regu-

**Fig. 2.** Chromatogram of hexenes-3 on the preparative chromatograph:
1 —peak of trans-hexene-3; 2 —peak of cis-hexene-3

**Fig. 3.** Analytical chromatograms of the obtained hexene isomers. Column 2.5 m × 5.5 mm with 40% solution of silver nitrate in glycol (9.5 g of silver nitrate in 10 ml of glycol) on INZ-600 support; temperature 40.00°C; carrier-gas flow rate (helium) 35 ml/min; sample size 0.76 $\mu$l.
a —trans-hexene-2; b —trans-hexene-3; v —cis-hexene-3; g —cis-hexene-3

lation of the temperature is carried out by means of an EPV-01 potentiometer; the circuit makes it possible to maintain the temperature within the range 40–100° with an accuracy of \$±\$1-1.5°. The gas mixture from the column enters a tee (11), from which the greater part of it (~95%) passes into the trapping system, maintained under a slight excess pressure (~5 mm Hg) by means of a capillary (14), while the remainder goes into the working channel of the detector (catharometer 18) of the analytical chromatograph (in the present work a chromatograph designed by the Special Design Bureau of the Institute of Organic Chemistry, Academy of Sciences of the USSR, was used). Nitrogen is supplied to the comparison channel of the detector through the inlet gas line of the chromatograph from the same cylinder. Regulation of the gas flow through the working channel of the detector is carried out by means of valve (20), which serves to shut off the gas circuit of the chromatograph, and regulation of the gas flow through the comparison channel by valve (16), which serves to regulate the gas feed to the column when the chromatograph is operated in the analytical mode. During operation the temperature of the detector was maintained 5–10° above the boiling temperature of the products being separated, and the temperature of the evaporator 50–70° higher.

The trapping system consists of a glass "comb" (12) with stopcocks and traps (13). The trap is a glass tube 15 cm long and 16 mm in diameter, wound with a coil sealed into its lower part, provided with a stopcock for draining the condensate and sealed into a beaker for the cooling mixture. To improve the trapping of the products being separated, central part of the trap is filled with copper packing for rectification columns.

In the apparatus described, separation was carried out of mixtures of cis- and trans-hexenes-2 and -3, obtained by "nuclear synthesis" according to Bord ($^4$). The separation was performed at a column temperature of 40° and a nitrogen flow rate of 400 ml/min. Under these conditions the emergence time of the cis isomer for hexene-2 is 13 min., and for hexene-3 it is 15 min. greater than the emergence time of the corresponding trans isomers, which makes it possible to separate 5–7 ml of mixture in one run. When the traps are cooled with a mixture of alcohol and liquid nitrogen (~ −100°), the losses of substance in the separation of 5 ml of mixture amount to approximately 10% of the quantity sent to trapping; with an increase in the load to 9-10 ml the losses decrease to 5-6%. The course of separation of each portion of the initial mixture was recorded by a chart recorder in the form of a chromatogram (Fig. 2). Toward the end of the recording of each peak, the tap of the corresponding trap was shut off on the "comb" (which is automatically recorded by the chart recorder as a vertical line), and until the beginning of the next peak the gas was vented to the air. A fresh portion of mixture was fed into the column with the traps shut off. The duration of one separation cycle was 35–40 min.

**Table 1**

| | b.p., °C at 760 mm Hg | $n_d^{20}$ | $d_4^{20}$ |
|---|---|---|---|
| Trans-hexene-2 | 67.9 | 1.3935 | 0.6783 |
| | 67.87 | 1.3935 | 0.6784 |
| Cis-hexene-2 | 68.8 | 1.3977 | 0.6863 |
| | 68.84 | 1.3977 | 0.6869 |
| Trans-hexene-3 | 67.1 | 1.3943 | 0.6772 |
| | 67.08 | 1.3943 | 0.6772 |
| Cis-hexene-3 | 66.4 | 1.3948 | 0.6796 |
| | 66.44 | 1.3947 | 0.6796 |

The hydrocarbons obtained after separation on the preparative chromatograph had constants very close to the most reliable literature data ($^5$), which are given for comparison in the second lines of Table 1.

Both the reaction mixtures and the fractions obtained by distilling these mixtures on a column of efficiency 100 theoretical plates were subjected to separation; the purity of the isomers obtained, determined by analytical gas-liquid chromatography (the analysis was carried out on a column with the same liquid phase, see Fig. 3), was the same in both cases. In the chromatograms of the isomers obtained, no impurities of either trans-hexene are detected (Figs. 3a, b). The chromatogram of cis-hexene-2 (Fig. 3c) shows the presence in it of about 0.5% impurity, and the chromatogram of cis-hexene-3 (Fig. 3d) about 1% impurity. These impurities, judging by their retention times, are not trans isomers.

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