PYRAN DERIVATIVES AS NEW PERFUMES

III.* STEREOCHEMISTRY OF 2-ALKYL-4-HYDROXYTETRAHYDROPYRANS AND THEIR ACETATES

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The stereoisomeric composition of 2-alkyl-4-hydroxytetrahydropyrans and their acetates was established. 2-Heptyl-4-hydroxytetrahydropyran isomers were isolated, and their acetates were obtained. The structures of the isomers were confirmed by IR and NMR spectroscopy.

The synthesis of 2-alkyl-4-hydroxytetrahydropyrans and their acetates has been reported [1]. Two incompletely separated peaks with predominance of the peak of the substance with the higher retention time (more than 90%) are visible in the gas-liquid chromatograms of these compounds. As the chain length of the alkyl substituent increases, these peaks merge into one unsymmetrical peak. In analogy with 3-alkyl-4-hydroxy(acetoxy)tetrahydropyrans [2], we assumed that the compounds that we synthesized are a mixture of cis and trans isomers that differ with respect to the conformation of the hydroxy or acetoxy group. These isomers could be separated by chromatography with a column filled with activity V aluminum oxide in the case of 2-heptyl-4-hydroxytetrahydropyran. It should be noted that the order of emergence of the isomers is similar to the order of emergence of isomers of cyclohexanol [3]: the trans isomer with an axial hydroxyl group is eluted first by both column and gas-liquid chromatography.

The IR spectral data that we obtained make it possible to state that the spectral rules that pertain to the stereoisomers of substituted cyclohexanols [4, 5] are applicable also to the stereoisomers of 4-hydroxytetrahydropyran derivatives. Thus the cis isomer of 2-heptyl-4-hydroxytetrahydropyran with an equatorial hydroxyl group absorbs at higher frequency in the region of the stretching vibrations of the C−O bonds than the trans isomer (1033 and 1018 cm^{-1}, respectively). The opposite effect is observed in the region of the stretching vibrations of the OH bonds: the low-frequency absorption band should be assigned to the equatorial hydroxyl group, while the high-frequency band should be assigned to the axial hydroxyl group (3610 and 3634 cm^{-1}). The acetates of the isomers of 2-heptyl-4-hydroxytetrahydropyran retain the configuration of the starting alcohols, as confirmed by the NMR spectra.

Thus the above confirms our assumption that 2-alkyl-4-hydroxytetrahydropyrans and their acetates are a mixture of stereoisomers with a considerable (more than 90%) predominance of the cis isomer with diequatorial substitutents.

EXPERIMENTAL

The gas-liquid chromatography was performed with a Willy Giede F-12 (German Democratic Republic) chromatograph with helium as the carrier gas and detection by thermal conductivity. The stationary phase was 20% octahydroxypropylsucrose on Chromosorb W with a 3-m long column with a diameter of 0.4 cm at 160° with a helium flow rate of 130 ml/min.

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*See [2] for communication II.

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The NMR spectra were recorded with a Varian HA-100 D spectrometer with an operating frequency of 100 MHz.* The shifts were measured relative to tetramethylsilane as the internal standard. The IR spectra were recorded with a UR-10 spectrograph in an NaCl cuvette.

Separation of the Isomers of 2-Heptyl-4-hydroxytetrahydropyran. The chromatography was carried out with a substance:adsorbent ratio of 1:50 with elution by petroleum ether (bp 40-60°) with the gradual addition of ether (up to 50%) to give 56 g of a substance with bp 135-140° (1-2 mm) and n_D^{20} 1.4620, which, according to the results of gas-liquid chromatography (GLC), contained 10% of low-boiling impurities. The isomers obtained were 99-100% pure (GLC).

Trans Isomer. This isomer (0.3 g) had bp 115-117° (0.5 mm), d_4^{20} 0.9413, and n_D^{20} 1.4629. MRD: found 58.60, calc., 58.59, IR spectrum,† cm^{-1} (d 0.02 mm): 712 m, 725 s, 775 m, 798 m, 840 m, 875 s, 904 m, 972 s, 995 s; 10% solution in CCl_4 (d 0.04 mm): 1018 w, 1072 s, 1105 m, 1130 w, 1140 w, 1190 w, 1208 w, 1242 w, 1268 w, 1336 w, 1362 w, 1382 w, 1412 w, 1435 w, 1465 m, 3608 w, and 3634 m. R_f 0.26 [activity V Al_2O_3, ethyl acetate–heptane (1:4)].

Cis Isomer. This isomer (25.5 g) had bp 122-122.5° (0.5 mm), d_4^{20} 0.9414, and n_D^{20} 1.4624. Found: C 72.1; H 12.1%; MR_D 58.54. $C_{12}H_{24}O_2$. Calculated: C 71.95; H 12.1%; MR_D 58.59. IR spectrum, cm^{-1} (d, 0.02 mm): 724 m, 740 w, 786 w, 808 m, 870 m, 918 w, 965 m, 990 m; 10% solution in CCl_4 (d 0.04 mm): 1033 m, 1050 m, 1087 s, 1105 m, 1125 w, 1140 m, 1150 m, 1169 w, 1255 w, 1305 w, 1347 w, 1370 m, 1380 m, 1455 w, 1468 w, 3610 s, and 3638 w. R_f 0.16.

cis- and trans-2-Heptyl-4-acetoxytetrahydropyrans. These isomers were obtained by the acetylation of the isomeric alcohols with acetic anhydride in the presence of perchloric acid [1]. The trans isomer was obtained by the acetylation of 0.1 g of alcohol in CCl_4 (to record the NMR spectrum) and was not isolated in pure form. NMR spectrum: H attached to $C_{(4)}$: δ H_e 5.02 ppm (quintet), J $H_{(4e)}$ 4.5 Hz; δ OAc_a 2.0 ppm (singlet). R_f 0.71 [acetone–heptane (1:3)].

Cis Isomer. This isomer had bp 121° (0.5 mm), d_4^{20} 0.9553, and n_D^{20} 1.4624. Found: C 69.4; H 10.9%; MR_D 68.04. $C_{14}H_{26}O_3$. Calculated: C 69.4; H 10.8%; MR_D 67.95. IR spectrum, cm^{-1} (d 0.02 mm): 725 w, 776 w, 811 w, 878 w, 902 w, 920 (shoulder) w, 970 s; 2% solution in CCl_4 (d 0.165 mm): 1035 s, 1090 s, 1164 m, 1170 (shoulder) m, 1244 vs, 1366 m, 1380 w, and 1744 s. R_f 0.59. NMR spectrum: H attached to $C_{(4)}$: δ H_a 4.69 ppm (multiplet consisting of nine lines), J $H_4H_{(3a)}$ 9 Hz, J $H_{(4)}H_{(3e)}$ 4.5 Hz; J $H_{(4)}H_{(5a)}$ 9 Hz, J $H_{(4)}H_{(5e)}$ 4.5 Hz, δ OAc_e 1.93 ppm (singlet). An alcohol whose properties, IR spectrum, and gas-liquid chromatogram were identical to those of the cis isomer of 2-heptyl-4-hydroxytetrahydropyan was obtained by the saponification of this acetate with alcoholic potassium hydroxide.

LITERATURE CITED

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*The NMR spectra were recorded and interpreted in the physical chemistry laboratory of the V. A. Korenevskii Institute.

†The following symbols were used: w corresponds to 20-40% absorption, m corresponds to 40-60% absorption, s corresponds to 60-90% absorption, and vs corresponds to greater than 90% absorption.