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SYNTHESIS OF DEUTERATED (-)-LIMONENE

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Studying the isomerization transformations of limonene, we have synthesized for the first time [3,3-$^2H_1$]- and [3-$^2H_1$]limonenes (ratio 3 : 1) by the dehydration of a mixture of deuterated stereoisomeric dihydrocarveols obtained by the reduction of deuterated dihydrocarbone.

According to our results (GLC and ^{13}C NMR spectrum), (−)-dihydrocarvone obtained from carvone [1] contains the cis and trans isomers in a ratio of 1 : 5.

The deuteration of the dihydrocarvone was performed by the method of Reich et al. [2]. A reaction product was obtained with a yield of 81% containing, according to GLC, the cis and trans isomers in a ratio of 1 : 5, bp 70-72°C (2 mm), $[\alpha]_D^{20}-16°$, $\alpha_4^{20}0.9427$, n_D^{20} 1.4708. IR spectrum (ν, in a thin layer), cm^{-1}: 895, 1640 ($CH_2=CH$), 1715 (C=O), 2140, 2235, 2375 (C−D). Mass spectrum: M^+ 155, 154, 152; isotopic composition: 81% of [1,3,3-$^2H_3$]dihydrocarvone (I), 15% of [3,3-$^2H_2$]dihydrocarvone, and 4% of undeuterated dihydrocarvone. ^{13}C NMR spectrum of the trans isomer (I) ($CDCl_3$, 0 − TMS; δ, isotope shift, ppm) 44.2, −0.5 (C^1); 46.2, −0.7 (C^3).

A mixture of 38 g of the deuterated dihydrocarvone, 10 g of sodium tetrahydroborate, and 300 ml of dioxane was stirred at room temperature for 10 h. After the usual working up and vacuum distillation, 32 g (85%) of a product was obtained which, according to GLC, contained the four stereoisomeric dihydrocarveols in a ratio of 1 : 4 : 10 : 15, bp 83-85°C (3-5 mm), $[\alpha]_D^{20}$ + 3°, d_4^{20} 0.9415, n_D^{20} 1.4781. IR spectrum (ν, in a thin layer, cm^{-1}): 890, 1640 ($CH_2=CH$), 2120, 2200 (C−D), 3360 (O−H).

At 110°C, 32 g of dihydrocarveol was added to a solution of 150 g of p-toluenesulfonyl chloride in 740 ml of pyridine, and the mixture was stirred for 5 h. After the usual working up of the reaction mixture and vacuum distillation, 9.0 g (32%) of a hydrocarbon fraction (bp 51-52°C/5-6 mm, $[\alpha]_D^{20}-106°$, $d_4^{20}0.8546$, $n_D^{20}1.4716$) was isolated, which, according to GLC, contained 96% of limonene, 3.4% of trans-isolimonene, and 0.6% of an unknown hydrocarbon, probably cis-isolimonene. IR spectrum (ν, in a thin layer), cm^{-1}: 870, 1640 ($CH_2=CH$), 2059, 2155 (C−D). Mass spectrum: M^+ 138, 137, 136; isotopic composition: 70% of [3,3-$^2H_2$] limonene (II), 21.5% of [3-$^2H_1$]limonene, and 8.5% of undeuterated limonene. ^{13}C spectrum of the limonene (II) (C_6D_6, 0 − TMS; δ, isotopic shift, ppm): 33.39, 0.110 (C^1), 122.11−0.126 (C^2), 31.98 −0.280 (C^3), 41.40, −1.180 (C^4) 28.34 −0.039 (C^5), 30.98, 0.004 (C^6), 23.57, 0.006 (C^7), 149.67, −0.006 (C^8), 108.90, 0.019 (C^9), 20.85, 0.008 (C^{10}).

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