cis – trans ISOMERISM IN THE OCTAHYDROBENZOFURAN SERIES

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The transformations of cis-2-methyl- and 2,2-dimethyloctahydrobenzofurans on acid catalysts – Al_2O_3 and $ZnCl_2/Al_2O_3$ – were studied. cis-2-Methyloctahydrobenzofuran undergoes cis–trans isomerization and is dehydrogenated to 2-methyl-2,3,4,5,6,8-hexahydrobenzofuran.

Continuing our study of the dehydrogenation and isomerization reactions of 2,3-dihydrobenzofurans and octahydrobenzofurans in contact with aprotic catalysts [1, 2], we have studied the transformations of cis-2-methyl- and 2,2-dimethyloctahydrobenzofurans in contact with Al_2O_3 and $ZnCl_2/Al_2O_3$; the acidity of the latter varied as a function of the percentage of zinc chloride in it.

When cis-2-methyloctahydrobenzofuran is in contact with Al_2O_3 at 200°C, it undergoes cis–trans isomerization, which was previously unknown for oxygen-containing condensed compounds. This sort of isomerization is described, for example, for the hydrindan system under the influence of aluminum halides [3, 4]. In addition to cis–trans isomerization, 2-methyl-2,3,4,5,6,8-hexahydrobenzofuran and a certain amount of cyclic hydrocarbons are formed. Raising both the temperature and acidity of the catalyst increases only the formation of the latter (Table 1).

The facts of the dehydrogenation and isomerization of 2,3-dihydrobenzofurans to chromans under the influence of aprotic acids, which we previously observed in [1, 2], were explained by the ionic character of the processes due to the hydride mobility of the hydrogen in the 2 position of the 2,3-dihydrobenzofuran molecule [5]. The previously obtained data make it possible to suppose that the transformations of cis-2-methyloctahydrobenzofuran also occur via an ionic scheme including detachment of a hydride ion from the 9 position under the influence of the aprotic centers of the catalyst. The presence of 2-methyl-2,3,4,5,6,8-hexahydrobenzofuran, the formation of which can be explained by deprotonation of cation I, in the reaction products is also evidence in favor of the above mechanism.

TABLE 1. Results of Experiments on the Transformation of cis-2-Methyloctahydrobenzofuran in a Flow System with a Space Velocity of 0.2 h^{-1}

Catalyst	Catalyst activity, meq/g	Exptl. temp., °C	Yield of liquid reaction products, based on the starting material, %			
			trans-2-methyloctahydrobenzofuran	2-methyl-2,3,4,5,6,8-hexahydrobenzofuran	2-methyl-2,3-dihydrobenzofuran	cyclic hydrocarbons
Al_2O_3	0,3	200	23	6	1	4
		225	24	6	2	13
		250	4	4	1	36
5% $ZnCl_2/Al_2O_3$	0,6	200	15	2	1	8
		225	14	2	—	22
		250	1	—	—	50
10% $ZnCl_2/Al_2O_3$	1,1	200	11	2	1	11
		225	5	1	—	29
		250	—	—	—	45

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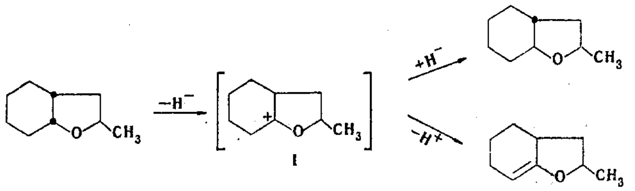

The introduction of two methyl groups into the 2 position of the octahydrobenzofuran system disrupts the stability of the system, and cyclic hydrocarbons were the only products of the transformations of cis-2,2-dimethyloctahydrobenzofuran under the described conditions.

EXPERIMENTAL

The IR spectra were recorded with an IKS-22 spectrometer. The PMR spectra were recorded in CCl_4 with a Varian T-60 spectrometer.

cis-2-Methyl- and 2,2-dimethyloctahydrobenzofurans were obtained by hydrogenation of the corresponding 2,3-dihydrobenzofurans according to the method in [6]. The physical constants and IR spectra were in agreement with the literature data [6].

The experiments were carried out in a flow system in a stream of nitrogen at atmospheric pressure. The liquid reaction products were analyzed with an LKhM-7A chromatograph with a thermal conductivity detector. The liquid phase was polyethylene glycol (mol. wt. 20,000), the solid support was Chromosorb W (60-80 mesh), the column was 5 m long, the temperature was 120°, and the helium flow rate was 35 ml/min.

trans-2-Methyloctahydrobenzofuran and 2-methyl-2,3,4,5,6,8-hexahydrobenzofuran were isolated from the catalysts by means of preparative GLC and were characterized by their IR and PMR spectra. trans-2-Methyloctahydrobenzofuran had bp 49° (9 mm) and n_D^{20} 1.4571 (bp 62° (18 mm) and n_D^{23} 1.4557 [6]). The structure of trans-2-methyloctahydrobenzofuran was confirmed by the IR spectrum, which contains absorption bands at 1070, 1085, and 1130 cm^{-1}; these bands coincide with the characteristic frequencies of a known preparation [7].

The structure of 2-methyl-2,3,4,5,6,8-hexahydrobenzofuran was confirmed by PMR spectroscopy. The PMR spectrum contains a doublet (3H) at 1.15 ppm due to the methyl protons, a "methylene elevation" (8H) centered at 1.95 ppm, a multiplet (1H) at 3.05 ppm due to the methylidyne proton in the 8 position, a multiplet (1H) at 4.10 ppm due to the proton in the 2 position, and a multiplet (1H) at 5.45 ppm due to an olefin proton. The starting 2-methyloctahydrobenzofuran was obtained by hydrogenation of 2-methyl-2,3,4,5,6,8-hexahydrobenzofuran.

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