EFFECT OF CONFORMATIONAL FACTORS ON THE DEGREE OF THE DEM'YANOV REARRANGEMENT DURING THE DESAMINATION OF cis- AND trans-4-tert-BUTYLCYCLOHEXYLCARBINYLAMINES

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In the present paper we studied the composition of the mixed products that are obtained in the desamination of the conformationally homogeneous cis- and trans-4-tert-butylcyclohexylcarbinylamines in order to ascertain the relationship between the conformation of the starting amine and the character of the products that are formed in the Dem'yanov rearrangement.

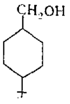
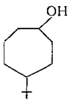
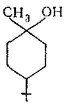
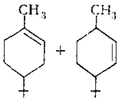
We were the first to obtain the starting amines by the reduction of the amides of cis- and trans-4-tert-butylcyclohexanecarboxylic acids with lithium aluminum hydride. The stereochemical purity of the acids was confirmed by the IR spectra. The desamination products were analyzed by GLC. The components of the mixture were identified by adding authentic samples to the analyzed mixture, which samples were synthesized by us. The analysis results are given in Table 1.

The degree of rearrangement, accompanied by expansion of the ring, was nearly 3 times greater for the cis-isomer than for the trans-isomer (the corresponding values are 27.9 and 10%).

Only rearranged alcohols and olefins are formed during the desamination of the cis-amine, while in the case of the desamination of the trans-amine the reaction products are found to contain a substantial amount of a primary (rearranged) alcohol. The obtained results can be explained if we take into account the stereochemical differences in the carbonium ions that are formed in the desamination of the cis- and trans-isomers. Steric strain exists in the molecule of the starting cis-4-tert-butylcyclohexylcarbinylamine and the corresponding diazonium ion, which is caused by the interaction of the axially situated carbinylamino group and the γ-axial hydrogen atoms (Scheme 1).

The rearrangements, caused by the migration of the hydride ion and the C–C bond, which lead to carbonium ions (IIa) and (IIb), facilitate a removal of the strain in the starting structure. The "backside" attack of the carbonium center by the molecule of the outer nucleophile is made difficult due to steric hindrance, which is created by the γ-axial hydrogen atoms. A primary alcohol with an unchanged structrue is not formed in the desamination of the cis-isomer.

TABLE 1. Composition of the Mixed Products Obtained in the Desamination of cis- and trans-4-tert-Butylcyclohexylcarbinylamines

Isomer	Composition of mixture				
					
cis	—	13,7	18	14,2	54
trans	39	5,1	25,3	4,9	25,7

In trans-4-tert-butylcyclohexylcarbinylamine, where the CH_2NH_2 group occupies an equatorial position and the carbonium center is readily accessible to attack by the outer nucleophile, one of the main desamination products is trans-4-tert-butylcyclohexylcarbinol (Scheme 2). A second principal product, namely, 1-methyl-4-tert-butylcyclohexanol, as well as olefins

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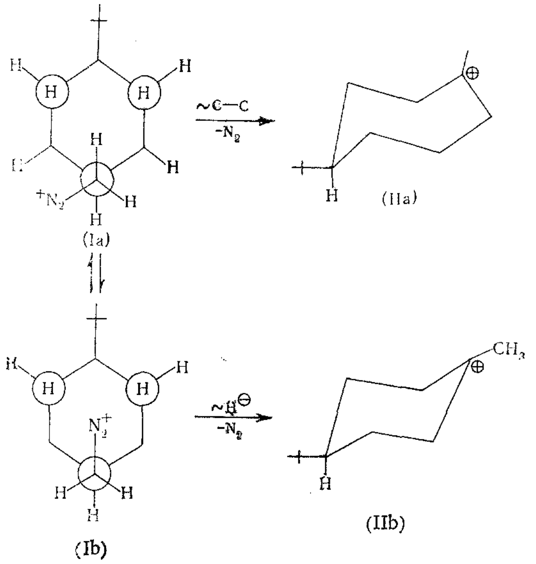
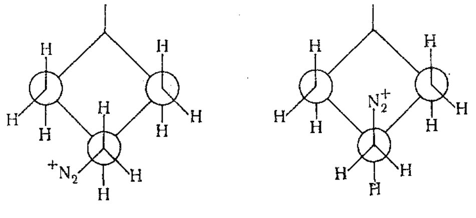


Scheme 1



(IIIa) (IIIb)

Scheme 2

of analogous structure, both indicate the substantial contribution made by the concurrent process of hydride-ion migration, which leads to the intermediate formation of the tertiary carbonium ion.

EXPERIMENTAL

cis- and trans-4-tert-Butylcyclohexanecarboxylic Acids. An aqueous solution of the Na salt of 4-tert-butylbenzoic acid was hydrogenated under pressure in an autoclave over Raney Ni catalyst. At the end of hydrogenation the precipitate represented the difficultly soluble salt of the trans-acid, from which the pure acid was isolated, followed by recrystallization from hexane; mp 174-175°. From [1]: mp 174-175.5°, [2]: 181-181.5°, [3]: 176-177°. The cis-acid was obtained from the mother liquor that remained after removal of the Na salt of the trans-acid, and it was purified through the ammonium salt. Recrystallization from hexane gave a product with mp 116-117°. From [1]: mp 117-118°; [2]: 119.5-120.5°. The IR spectra contained absorption bands for the cis-isomer at 1035 and 1155 cm^{-1}, and at 1050 and 1188 cm^{-1} for the trans-acid. From [3]: 1035, 1155 and 1045, 1187 cm^{-1}, respectively.

cis- and trans-4-tert-Butylcyclohexanecarboxamides. The 4-tert-butylcyclohexanecarboxylic acids were treated with a 1.5-fold excess of thionyl chloride. The crude acid chloride was added to conc. NH_3 solution that had been cooled to 0°C. The trans-amide was recrystallized from cyclohexane, mp 133.3-134.5°. From [2]: mp 134.5-135°, [4]: 134.2-135.8°. The cis-amide was recrystallized from alcohol, mp 159-160°. From [2]: mp 161°, [4]: 162.7-163°.

cis- and trans-4-tert-Butylcyclohexylcarbinylamines. The amines were obtained by the reduction of the corresponding amides with a 2-fold excess of $LiAlH_4$ in absolute ether. The cis-amine distilled at 92-94° (7 mm); n_D^{22} 1.4682; yield 70%. Found: C 77.90; H 13.60; N 7.64%. $C_{11}H_{23}N$. Calculated: C 78.02; H 13.71; N 8.26%. The trans-amine distilled at 91-91.5° (7 mm); n_D^{23} 1.4640; yield 75%. Found: C 77.95; H 13.63; N 7.48%. $C_{11}H_{23}N$. Calculated: C 78.02; H 13.71; N 8.26%.

cis- and trans-4-tert-Butylcyclohexylcarbinols. The carbinols were obtained by the reduction of the cis- and trans-4-tert-butyl-cyclohexanecarboxylic acids with $LiAlH_4$. The cis-4-tert-butylcyclohexylcarbinol was obtained in 65% yield; bp 110-111° (6 mm). From [5]: bp 133-136° (27 mm). The trans-4-tert-butylcyclohexylcarbinol was obtained in 60% yield; bp 109-110° (6 mm); n_D^{19} 1.4668. From [5]: bp 140-140.5° (28 mm); n_D^{20} 1.4683.

4-tert-Butylcyclohexanone. The oxidation of 4-tert-butylcyclohexanol with sodium dichromate gave a product with mp 49-49.5°. From [6]: mp 51.8-52°.

1-Methyl-4-tert-butylcyclohexanol. The reaction of 4-tert-butylcyclohexanone with methylmagnesium iodide [6] gave 1-methyl-4-tert-butylcyclohexanol; yield 80%; mp 57-58°. From [6]: mp 57-58°.

4-tert-Butylcycloheptanone. The compound was obtained in 44% yield by the method described for the synthesis of cycloheptanone [7]; bp 100-102° (7 mm); n_D^{17} 1.4585. From [8]: bp 95-100° (7 mm); n_D^{12} 1.4710.

4-tert-Butylcycloheptanol. The compound was obtained in 70% yield by the reduction of 4-tert-butylcycloheptanone with $LiAlH_4$ in absolute ether; bp 107-110° (10 mm); n_D^{22} 1.4740.

1-Methyl-4-tert-butyl-1-cyclohexene. Obtained by the dehydration of 1-methyl-4-tert-butylcyclohexanol by heating the latter with conc. H_2SO_4; bp 87-90° (20 mm). From [9]: bp 74-75° (11 mm); n_D^{16} 1.4626. Chromatographic analysis disclosed the presence of isomeric olefins (5%).

tert-Butylcycloheptenes. The compounds were obtained as a mixture of isomers by the dehydration of 4-tert-butylcycloheptanol using the above described method.

The desamination was run as described in [10], in aqueous medium in the presence of $HClO_4$.

The chromatographic analysis of the desamination products and of the standard alcohols and olefins was run on a Khrom-2 chromatograph, using a copper column (length 2 m, diameter 4 mm) filled with graphitized soot, a temperature of 216°, and a carrier-gas velocity of 8 ml/min. A flame-ionization detector was used.

CONCLUSIONS

1. The cis- and trans-4-tert-butylcyclohexylcarbinylamines were synthesized and their desamination was studied.

2. The role of conformational factors during the isomeric transformations, accompanying the desamination of stereoisomeric amines, was shown.

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