<u>2-Methyl-2,3-dihydro-4H-1,3-benzoxazin-4-one (X)</u>. A mixture of 6 g of hydrazide (IV) and 2.6 g of $CD(OAc)_2$ in 80 ml of dioxane was charged into an autoclave, acetylene was added, and the mixture was kept for 1.5 h at 180-190°. The obtained liquid was passed through a column. We isolated 1% of (X) with mp 145-147° (water) (cf. [5]). The mixed melting point with an authentic sample was not depressed.

CONCLUSIONS

The reactions of acetylene with salicylamide, salicylaldoxime, and salicylhydrazide gave the vinyl ethers of salicylamide and its bromo derivative. Depending on the catalyst, the vinylation of salicylhydrazide gives either the vinyl ether of salicylamide or 2-methyl-2,3-dihydro-4H-1,3-benzoxazin-4-one.

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ALKALI-CATALYZED HYDRATION OF

STEREOISOMERIC 3,4-EPOXYCARANES

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Comparative data are given in the literature on the direction of the acid- and base-catalyzed hydration of the stereoisomeric norcarene epoxides [1]. The results of studying the hydration of the trans- (I) and cisepoxides (II) of 3-carene in the presence of a base are reported in the present paper.

trans-Diols (III) and (IV) were isolated in an 85:15 ratio when trans-epoxide (I) was treated with aqueous alkali solution.



Glycols (III), (IV), and (V) are formed in a 1:2:1 ratio when cis-epoxide (II) is treated in a similar manner. The previously described [2, 3] products were identified by direct comparison with authentic samples.

As a result, the base-catalyzed hydration of the cyclic oxide occurs at both of the C-O bonds. Here, if in the trans-epoxide (I) the reaction proceeds predominantly at the secondary center, then in the cis-isomer (II) the products of opening at both of the C-O bonds are represented to equal degree. The fact that, together with

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expected (III) and (IV), the rearranged diol (V) is also formed when cis-epoxide (II) is opened testifies to a rebuilding of the carane structure to the bicyclo[3.1.0]hexane structure by the action of both acids [4] and bases.

EXPERIMENTAL

The melting points were determined on a Kofler block.

<u>Hydration of Oxide (I)</u>. A mixture of 2.3 g of (I), 50 ml of H_2O , and 2.5 g of KOH was heated in an autoclave for 17 h at 150°C, and then it was neutralized with HCl and extracted with ethyl acetate. The residue (1.9 g) from removal of the solvent was chromatographed on 50 g of SiO₂. Elution with a 3:2 petroleum etherether mixture gave 0.98 g of (III), mp 30° [2], 0.25 g of (IV), mp 89° [2], and 0.5 g of unreacted (I).

<u>Hydration of Oxide (II)</u>. Similarly, from 3 g of (II) we obtained 2.8 g of mixed diols, from which we isolated 0.4 g of (III), 0.9 g of (IV), 0.5 g of (V), mp 137° [3], and 0.47 g of unreacted (II).

CONCLUSIONS

The alkali-catalyzed hydration of the stereoisomeric 3,4-epoxycaranes gives a mixture of the expected glycols, together with the skeletal rearrangement product in the case of the cis-epoxide.

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HYDRATION OF 3-METHYL-2-NORCARENE EPOXIDES

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It is known that the acid-catalyzed hydration of a 2,3-epoxycarane with a trans arrangement of the epoxide and cyclopropane rings proceeds with a cleavage of the inner bonds of the three-membered rings and the formation of monocyclic unsaturated products [1, 2]. With a cis arrangement of these fragments as, for example, in cis-thiopsene, the cis-opening product of the oxide ring was isolated [3]. In the present paper we studied the behavior of the stereoisomeric 3-methyl-2-norcarene epoxides (I) and (II) in this reaction, whose hydration was run in either acetic acid or sulfuric acid of variable concentration.

cis-2,3-Epoxy-3-methylnorcarane (I) gives under the studied conditions the known diol (III) [4] in ~ 70% yield. The hydration of the isomeric oxide in 4% H_2SO_4 solution leads in ~ 75% yield to a mixture of the previously described [4, 5] glycols (V) and (VII) in an ~ 5:1 ratio, together with a new diol, whose yield reaches 50%. On the basis of the elemental and spectral (IR, PMR, MS) analysis data this product was assigned the structure of $2\beta-3\alpha$ -dihydroxy-3-methylnorcarane (VIII)

Scheme 1



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