TRANSFORMATIONS OF MONOTERPENE EPOXIDES IN SUPERCRITICAL SOLVENTS

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INTRODUCTION

Monoterpenes and their epoxides are valuable renewable starting materials for pharmaceutical and cosmetic industries, production of flavorings, pesticides, etc [1]. However, the transformations of these compounds, especially epoxides, in acid media may give due to isomerization and polymerization reactions not only the target products, but also a number of undesirable compounds [2]. Moreover, serious environmental problems are caused by large amount of toxic acid-containing waste. Reactions based on the transformations of monoterpene epoxides in supercritical solvents can be considered as an alternative to the conventional methods.

EXPERIMENTAL

In the present work, we have studied the transformations of some monoterpene epoxides (α-pinene, verbenone and verbenol epoxides (Fig. 1)) in various supercritical solvents for the first time.

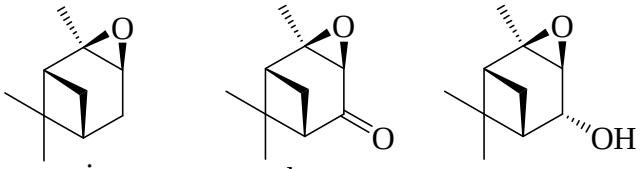

Figure 1. The epoxides structures

The transformations of epoxides in composite supercritical solvents that contain CO_2, lower alcohols (ethanol, isopropanol) with or without water were studied in the temperature range of 387-575 K at pressure 135-215 MPa. The addition of water to supercritical solvent will impart acidic properties to the system and thus make expectable the formation of products of acid-catalyzed transformations of the epoxide.

RESULTS

Campholenic aldehyde and carveol were shown to be the main products of α-pinene epoxide reactions in supercritical solvents containing water (Fig. 2). Both these compounds are valuable feedstock for fragrance industry.

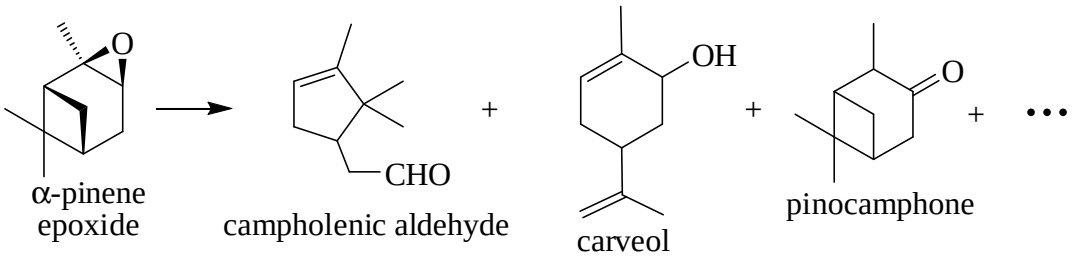

Figure 2. The α-pinene epoxide transformations

In the absence of water, thermolysis of α-pinene epoxide in supercritical solvent yields campholenic aldehyde and pinocamphone, with their total amount in the reaction mixture attaining 80%. In this case, judging from the composition of products being formed, the occurrence of two parallel processes can be assumed: thermal isomerization of α-pinene epoxide and its acid-catalyzed isomerization.

The transformations of verbenone and verbenol epoxides led to another types of the products. For example, the main identified products of verbenone epoxide isomerization in composite supercritical solvent containing CO_2, isopropanol with or without water were α-ketoalcohols **1** and **2** with camphane and *p*-menthane skeletons accordingly (Fig. 3).

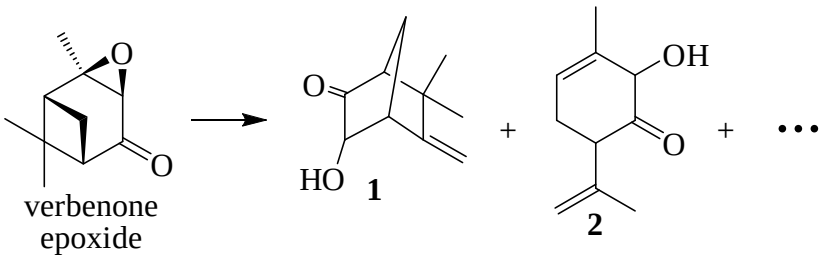

Figure 3. The verbenone epoxide transformations

The epoxide conversion and products distribution were dependent on the reactions conditions to a great extent.

CONCLUSION

The transformations of monoterpene epoxides in supercritical solvents of different compositions can be considered as new methods of obtaining the target isomerization products at short (up to 4 min) residence time in a continuous mode in ecologically friendly conditions.

REFERENCES

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[2] Il'ina, I.V.; Volcho, K.P.; Salakhutdinov, N.F. *Russ. J. Org. Chem*. Vol. 44, **2008,** p.1.