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Effect of the Nature of Exchange Cations in Montmorillonite Clay on the Direction of Verbenol Epoxide Transformations

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Abstract

Transformations of (–)-*cis*-verbenol epoxide **1** in the presence of montmorillonite clay containing different exchange cations were studied for the first time. It was demonstrated that the nature of a cation exerts a substantial effect both on the contribution from undesirable resinification and on the distribution of low-molecular products. The use of Co²⁺-containing montmorillonite clay allowed us to obtain a substantial (1.5 times) increase in the content of the target compound 3-methyl-6-(1-methylethenyl)cyclohex-3-ene-1,2-diol **2** in reaction mixture comparing to acidic montmorillonite clay species used earlier.

Key words: montmorillonite clay, verbenol epoxide, terpenoids, rearrangements

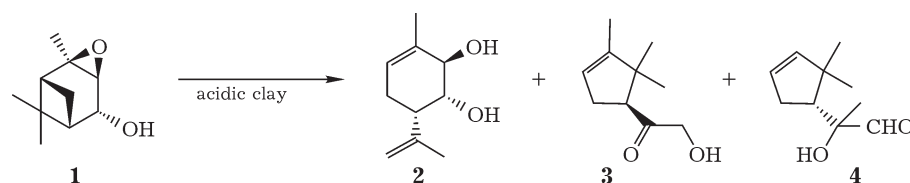
INTRODUCTION

Using clay species as catalysts for the transformation of terpenoids allows one not only to improve the characteristics of processes known earlier, but also frequently to direct reactions to other pathways, than it is in the presence of traditional acid catalysts. Owing to this, new potentialities for application of renewable plant raw materials in fine organic chemistry [1–3] were opened up. For example, earlier we demonstrated [4, 5] that verbenol epoxide **1** in presence of montmorillonite clay (natural acidic ascanite-bentonite clay or synthetic K-10 clay) can be converted into a mix of three compounds such as diol **2**, ketol **3** and α -hydroxyaldehyde **4** (Scheme 1). Of the greatest interest among the products obtained is compound **2**, exhibited a high anticonvulsant activity [6]. Its yield was varied depending on the loading value and catalyst used not exceeding 50 % [4, 5].

It should be noted that the use of other acidic catalysts instead of montmorillonite clay does not result in obtaining compounds **2** with the selectivity required. For example, in the presence of ZnBr₂ only compound **3** was isolated, no formation of diol **2** was observed [7]. The use of 0.7 % aqueous H₂SO₄ an acid catalyst, as demonstrated in the present work, results in the formation of a complex mixture of products (more than 10 substances, the total yield being of 62 %), the fraction of compound **2** wherein, according to GLC-MS data does not exceed 20 %.

ACIDIC CLAY

An important feature of montmorillonite clay consists in their ability exchange by cations located within interlayer space. In the case of acidic clay these cations are mainly presented by protons. It is known that varying the inter-



Scheme 1.

layer cations allows one to considerably change clay catalytic properties. This technique was successfully used both for performing the reactions monoterpenes [1]. For example, in the isomerisation of α -pinene the greatest activity is exhibited by montmorillonite clay containing cation Fe^{3+} [8, 9], whereas in the reaction of limonene with styrene the best results were obtained for clay species containing Cr^{3+} and Zn^{2+} cations [10].

The purpose of the present work consisted in studying the influence of the nature of exchange cations in montmorillonite clays upon the ratio of verbenol epoxide **1** isomerisation products.

EXPERIMENTAL

In the work we used acidic montmorillonite clay K-10 (Fluka) and naturally occurring acidic montmorillonite clay ascanite-bentonite (H^+ -AB), obtained *via* acidic activation of bentonite clay species from the Askan group of deposits (Georgia) meeting the requirements of the Standard OST 113-12-86-82.

The preparation of novel catalysts was performed *via* the substitution of a counter-ion in the mentioned clays using a technique described earlier [11].

Preparing the ion-exchange modifications of montmorillonite clay

Al^{3+} -K-10 and Al^{3+} -AB. To 5.0 g of acidic clay K-10 (Fluka) or acidic clay ascanite-bentonite was added 25 mL of a aqueous solution 0.1 N $\text{Al}(\text{NO}_3)_3$, stirred during 2 h, held at a room temperature for 22 h, then the water layer was decanted. To a deposit, was again added 25 mL of 0.1 N $\text{Al}(\text{NO}_3)_3$ solution, stirred during 2 h, held at a room temperature for 22 h, the water layer was decanted; then the procedure aforementioned was repeated for three times. A deposit was filtered, washed with distilled water (3×50 mL), dried during 3 h at 105 °C.

Fe^{3+} -AB. The catalyst is prepared according to the technique similar to that described above, with using 5.0 g of acidic clay ascanite-bentonite and 0.1 N $\text{Fe}_2(\text{SO}_4)_3$ aqueous solution.

Cr^{3+} -AB was prepared *via* the technique similar to that of obtaining Al^{3+} -K-10 and Al^{3+} -AB using 5.0 g of acidic clay ascanite-bentonite and 0.1 N $\text{Cr}(\text{NO}_3)_3$ aqueous solution.

Zn^{2+} -K-10 was prepared *via* the technique similar to that of obtaining Al^{3+} -K-10 and Al^{3+} -AB, using 5.0 g of acidic clay K-10 and 0.1 N $\text{Zn}(\text{NO}_3)_2$ aqueous solution.

Co^{2+} -K-10 and Co^{2+} -AB was prepared *via* the technique similar to that of obtaining Al^{3+} -K-10 and Al^{3+} -AB, using 5.0 g of acidic clay K-10 or acidic clay ascanite-bentonite and 0.1 N $\text{Co}(\text{NO}_3)_2$ aqueous solution.

Isomerisation of (-)-cis-verbenol epoxide 1 in the presence of ion-exchange clay

To a suspension of 0.100 g clay, preliminarily dried during 3 h at 100 °C suspended in 1 mL of CH_2Cl_2 was added at 20 °C a solution of 0.050 g (-)-cis-verbenol epoxide **1** in 1 mL CH_2Cl_2 and then all this was stirred at this temperature during 40 min; 3 mL of diethyl ether was added, with stirring for 10 min, the catalyst was filtered, the solvent was removed. To the residue was added 2.0 mL of ethyl acetate and 0.5 mL of 40 % dicyclopentadiene solution in ethyl acetate (internal standard).

The reaction mixture was analyzed using a chromatography-mass spectrometry technique. The qualitative analysis of reaction products was performed comparing the retention indices (Kovach indices) for components and their complete mass spectra with the corresponding data for pure compounds. The changing in the content of products in the reaction mixture was judged from changing the ratio between the areas of chromatographic peaks corresponding to these compounds, and the area of the internal standard peak. The results obtained are presented in Table 1.

Isomerisation of (-)-cis-verbenol epoxide 1 in the presence of 0.7 % H_2SO_4

To a suspension of 0.150 g (-)-cis-verbenol epoxide **1** in 1 mL of water was added 20 °C 2 mL 0.7 % H_2SO_4 solution in water, the mixture was held for 0.5 h at the same temperature, then was added Na_2CO_3 to obtain neutral pH, products were extracted by diethyl ether (3×5 mL). As a result, 0.093 g of a mixture was obtained (62 % of loaded amount), containing according to GLC-MS, 19.3 % of compound **2**.

TABLE 1

Ratio between the products of transformations (–)-*cis*-verbenol epoxide **1** transformation according to GLC-MS (ratio values are presented between chromatographic peak areas in reaction mixtures and the peak areas of the internal standard)

Exp. No.	Catalysts	Content of mixture components comparing to internal standard			Selectivity 2/(3 + 4)	Σ*
		2	3	4		
1	H ⁺ -K-10	3.8	1.9	0.8	1.4	6.5
2	Al ³⁺ -K-10	4.0	1.4	0.9	1.8	6.3
3	Al ³⁺ -AB	3.4	0.8	1.1	1.8	5.3
4	Fe ³⁺ -AB	3.4	1.7	0.8	1.4	5.9
5	Cr ³⁺ -AB	2.3	0.8	0.6	1.6	3.7
6	Zn ²⁺ -K-10	4.6	2.0	0.7	1.7	7.3
7	Co ²⁺ -K-10	5.6	2.2	0.8	1.9	8.6
8	Co ²⁺ -AB	5.1	2.1	1.0	1.7	8.2

Notes. 1. **2** is 3-methyl-6-(1-methylethenyl)cyclohex-3-ene-1,2-diol; **3** is 2-hydroxy-1-(2,2,3-trimethylcyclopent-3-enyl)ethanol; **4** is 2-(2,2-dimethylcyclopent-3-enyl)-2-hydroxypropanal. 2. The conversion of initial verbenol epoxide **1** in all cases was quantitative. 3. As the internal standard it was used dicyclopentadiene.

* The sum of peak areas for compounds **2-4** is presented according to chromatographic data.

RESULTS AND DISCUSSION

The studies performed have demonstrated that the use of clay K-10 for obtaining compound **2** is a little more efficient than that of ascanite-bentonite clay (see Table 1, Nos. 2 and 3, 7 and 8).

The further comparison was made with respect to acidic clay H⁺-K-10.

The application of clay containing Al³⁺ as a counter-ion resulted in changing the ratio between the products with para-menthane skeleton (compound **2**) and cyclopentane skeleton (compounds **3** and **4**) in favour of the former. At the same time, the use of the clay containing Fe³⁺, did not exert any considerable effect on the selectivity.

In the presence of clay Cr³⁺-AB, judging by a low value of the sum of peak areas in the chromatographic profile, a considerable resinification of the initial substance and/or isomerisation products occurred, which caused the lowest content of compound **2** among all the heterogeneous catalysts tested. On the contrary, in the case of using Zn²⁺-K-10 a considerable decrease in resinification contribution was observed, which, taking into account a relatively high selectivity resulted in

an 1.2-fold increase in the content of diol **2** in the reaction mixture comparing to acidic clay.

The best results were obtained with performing the isomerisation of (–)-*cis*-verbenol epoxide **1** in the presence of montmorillonite clay, containing as counterion Co²⁺ (see Table 1, Nos. 7 and 8). With using clay Co²⁺-K-10 as a catalyst the content of compound **2** in the reaction mixture almost 1.5 times increased comparing to clay H⁺-K-10. As it is in the case of zinc-containing clay, the increase in the content of diol **2** is connected with a decrease of the contribution of side resinification processes, and with an increase in selectivity.

It should be noted that though earlier cobalt-containing montmorillonites were successfully used for carrying out oxidative conversion processes [12–15], we did not revealed any examples for using such clay as acidic catalysts available in the literature.

The results obtained indicate that performing the isomerisation of (–)-*cis*-verbenol epoxide **1** for the purpose of synthesizing 3-methyl-6-(1-methylethenyl)cyclohex-3-ene-1,2-diol **2** in the presence of montmorillonite clay Co²⁺-K-10 provides an 1.47-fold increase in the content of

compound **2** in the reaction mixture comparing to catalyst H⁺-K-10 used earlier.

CONCLUSION

The transformations of (-)-*cis*-verbenol epoxide **1** in the presence of montmorillonite clay, containing various exchange cations were for the first time studied. It was revealed that the nature of a cation exerts a considerable effect both on the contribution of undesirable resinification processes, as well as on the distribution low-molecular products. The use of Co²⁺-containing montmorillonite clay allowed us increasing to a considerable extent (up to 1.5 times) the content of target compound – 3-methyl-6-(1-methylethenyl)-cyclohex-3-ene-1,2-diol **2** – in the reaction mixture comparing to acidic montmorillonite clays used earlier.

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