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Reaction of Sabinene with Aldehydes in the Presence of Montmorillonite K10 Clay

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Abstract—Transformations of sabinene catalyzed by montmorillonite K10 clay were studied. The main reaction paths were found to be oligomerization and isomerization. The reaction of sabinene with crotonaldehyde gave rise to several polyfunctional heterocyclic compounds.

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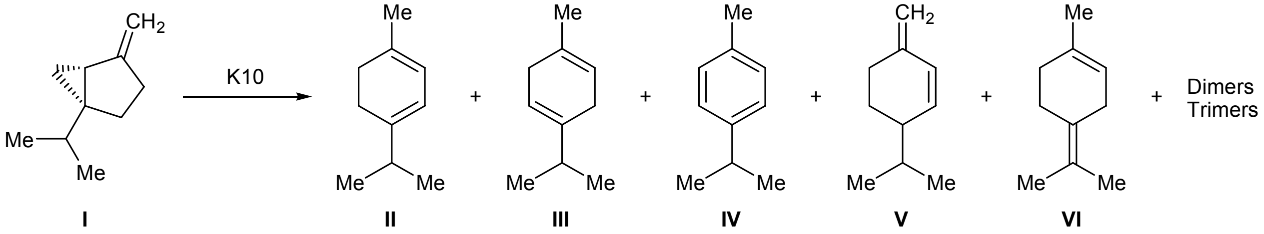
The use of natural montmorillonite askanite–bentonite clay and its commercially available analog K10 as catalysts in the transformations of monoterpenoids of the pinane, carane, and *para*-menthane series makes it possible to obtain new optically active polyfunctional heterocyclic compounds [1, 2]. These catalysts not only ensure milder reaction conditions and higher yield of products but also enhance regio- and stereoselectivity of the process due to definite spatial orientation of the reacting molecules, especially of those possessing several reaction centers. In the present work we examined for the first time the reactivity of sabinene (**I**) (monoterpene of the thujane series) in the presence of montmorillonite K10 clay.

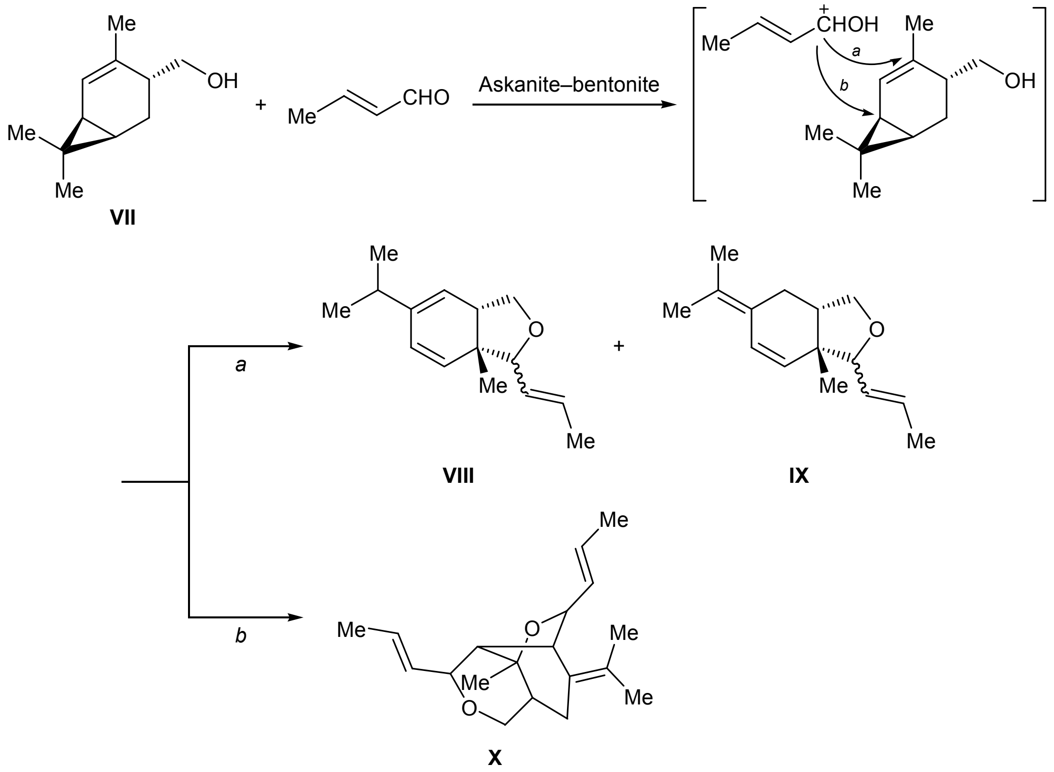
Sabinene (**I**) is a natural monoterpene having a bicyclo[3.1.0]hexane skeleton; it is a component of juniper essential oils [3]. Chemical transformations of sabinene (**I**) were reported in a few publications, whereas its behavior under conditions of heterogeneous catalysis is almost unknown. Compound **I** in the presence of acids generally undergoes isomerization into compounds having a *para*-menthane skeleton: α- and γ-terpinenes **II** and **III**, terpineol, and *p*-cymene (**IV**) [4]. When a solution of sabinene (**I**) in methylene chloride was kept for 30 min in the presence of K10, a complex mixture of products was formed. According to the GC–MS data, this mixture contained dimerization (~53%, more than 20 compounds) and trimerization products (~24%, more than 10 compounds), α- and γ-terpinenes **II** and **III** (2 and 5%, respectively), *p*-cymene (**IV**, 2%), β-phellandrene (**V**, 1%), and terpinolene (**VI**, 1%) (Scheme 1).

We previously [2] obtained a series of heterocyclic compounds **VIII**–**X** by reaction of crotonaldehyde with 4-hydroxymethylcar-2-ene (**VII**) which, like sabinene (**I**), possesses a double bond conjugated with cyclopropane ring. The formation of compounds **VIII**–**X** was rationalized by a mechanism involving protonated aldehyde as electrophilic species. Addition of the protonated aldehyde at the double bond of terpenoid **VII** gave compounds **VIII** and **IX** with an 8-oxabicyclo[4.3.0]nonane skeleton, while the addition at the cyclopropane ring led to the formation of tricyclic derivative **X** (Scheme 2).

Scheme 1.



Scheme 2.

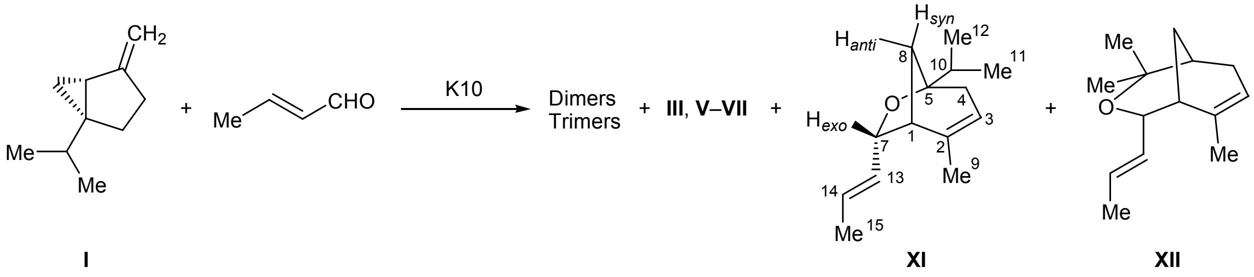


In the present work we made an attempt to perform reactions of monoterpene **I** with aldehydes in the presence of K10 clay. Sabinene (**I**) failed to react with salicylaldehyde, vanillin, and 4-methoxy- and 4-fluorobenzaldehydes over K10. In these cases, only isomerization and oligomerization of the initial compound occurred. We were the first to obtain bicyclic compounds **XI** (1.8%) and **XII** (1.3%) by reaction of sabinene (**I**) with crotonaldehyde in the presence of K10. However, the main reaction path (as before) involved dimerization and trimerization of the initial olefin (Scheme 3).

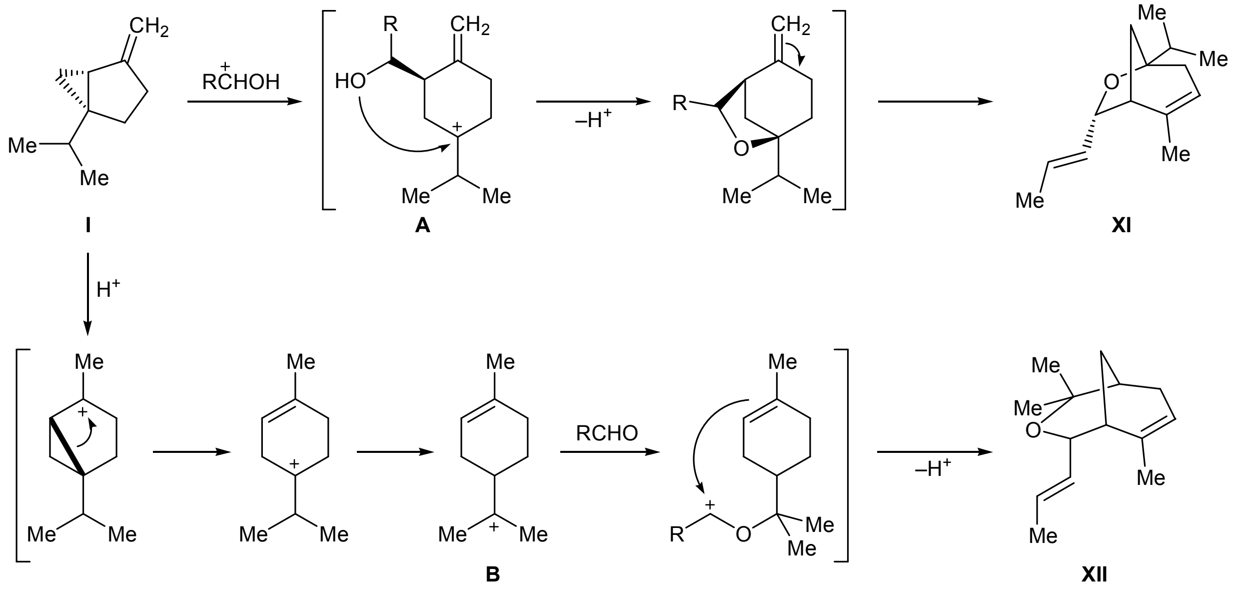
Scheme 4 illustrates possible mechanisms for the formation of compounds **XI** and **XII**. Attack by the protonated aldehyde on the cyclopropane ring in molecule **I** at the less sterically hindered side yields cation **A** whose subsequent intramolecular heterocyclization and isomerization lead to product **XI**. An alternative pathway is likely to involve carbocation **B** as electrophilic species, whereas crotonaldehyde acts as nucleophile. Cation **B** is generated by protonation and subsequent isomerization of olefin **I**. Analysis of the proposed mechanisms shows that the formation of compound **XII** should be accompanied by racemization. The facts that compound **XI** is optically active and that product **XII** is a racemate count in favor of the mechanisms shown in Scheme 4.

Despite the presence of similar structural fragments, the direction of the intermolecular transformation of sabinene (**I**) with crotonaldehyde over K10 clay considerably differs from analogous transformation of 4-hydroxymethylcar-2-ene (**VII**) [2].

Scheme 3.



Scheme 4.



R = (*E*)-MeCH=CH.

Compound **XI** was not reported previously, and its structure was determined on the basis of the ^{1}H and ^{13}C NMR spectra and high-resolution mass spectra. Derivatives having the same skeleton as in molecule **XI** but lacking substituent on C^{7} were obtained previously while studying transformations of alcohols of the carane series in superacidic medium (HSO_3F–SO_2FCl, –100°C) [5] and in the presence of natural montmorillonite clay (askanite–bentonite) [6]. Compound **XII** was synthesized by us previously via reaction of crotonaldehyde with limonene [7].

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer at 500.13 and 125.76 MHz, respectively, using $CDCl_3$–CCl_4 (~1 : 1 by volume) as solvent. The chemical shifts were measured relative to the residual proton and carbon signals of the solvent ($CHCl_3$, δ 7.24 ppm; $CDCl_3$, δ_C 76.90 ppm). Signals were assigned using ^{1}H–^{1}H double resonance, *J*-modulation (JMOD) with off-resonance decoupling from protons, and ^{13}C–^{1}H two-dimensional heteronuclear correlation (direct ^{13}C–^{1}H coupling constants, COSY, $^{1}J_{CH}$ = 135 Hz). The high-resolution mass spectra were obtained on a DFS Thermo Scientific instrument (direct sample admission into the ion source, electron impact, 70 eV, a.m.u range 0–500). The optical rotations $[\alpha]_D$ were determined on a polAAr 3005 polarimeter from solutions in $CHCl_3$.

The purity of the initial compounds and reaction products was checked, and the reaction mixtures were analyzed, by GLC on a Varian Model 3700 chromatograph equipped with a flame ionization detector and a VC-30 quartz capillary column, 15000 × 0.22 mm; carrier gas helium, inlet pressure 1 atm. Gas chromatographic–mass spectrometric analysis was performed on a Hewlett–Packard HP 5890 Series II chromatograph coupled with a n HP 5971 quadrupole mass-selective detector (HP-5MS quartz capillary column, 30000 × 0.25 mm; carrier gas helium).

Montmorillonite K10 clay (Merck) was calcined for 3 h at 110°C just before use. Methylene chloride was purified by passing through a column charged with calcined aluminum oxide. The products were separated by column chromatography on silicagel (60–200 μm, Macherey–Nagel). Sabinene (**I**) with an $[\alpha]_D^{20}$ value of +43° (*c* = 1.9, $CHCl_3$) was used.

Reaction of sabinene (I) with crotonaldehyde in the presence of montmotrillonite K10. A solution of 1 g (14 mmol) of crotonaldehyde was added to a suspension of 4 g of K10 clay in 15 ml of methylene chloride, a solution of 1 g (7 mmol) of sabinene (**I**) in 10 ml of methylene chloride was then added dropwise, and the mixture was stirred for 1 h at room temperature. The mixture was diluted with 10 ml of diethyl ether, the catalyst was filtered off, the filtrate was evaporated, and the residue was subjected to chromatography in a column charged with 10 g of silica gel using hexan–diethyl ether as eluent (gradient elution, 0 to 10% of diethyl ether). We isolated 0.028 g (1.8%) of compound **XI**, 0.019 g (1.3%) of compound **XII**, and 0.180 g of a mixture containing (according to the GC–MS data) ~48% of dimeric products (more than 20 compounds), ~21% of trimeric products (more than 10 compounds), 2% of α-terpinene (**II**), 5% of γ-terpinene (**III**), 2% of *p*-cymene (**IV**), 1% of β-phellandrene (**V**), and 1% of terpinolene (**VI**).

(1*R*,5*R*,7*S*)-5-Isopropyl-2-methyl-7-[(*E*)-prop-1-en-1-yl]-6-oxabicyclo[3.2.1]oct-2-ene (XI). $[\alpha]_D^{19} = -45°$ ($c = 0.6$, $CHCl_3$). ^1H NMR spectrum, δ, ppm: 0.90 d ($C^{11}H_3$, $J_{11,10} = 7.0$ Hz), 0.93 d ($C^{12}H_3$, $J_{12,10} = 7.0$ Hz), 1.64 d.d.d (C^9H_3, $J_{9,exo\text{-}4} = 2.0$, $J_{9,endo\text{-}4} = 2.0$, $J_{9,3} = 1.7$ Hz), 1.66 d.d ($C^{15}H_3$, $J_{15,14} = 6.5$, $J_{15,13} = 1.6$ Hz), 1.67 d.d (*syn*-8-H, $^2J = 10.4$, $J_{8,1} = 0.5$ Hz), 1.79 d.d.d (*anti*-8-H, $^2J = 10.4$, $J_{8,1} = 4.0$, $J_{8,endo\text{-}4} = 1.0$ Hz), 1.81 sept (10-H, $J = 7.0$ Hz), 1.96 d.m (*endo*-4-H, $^2J = 17.4$ Hz), 2.19 d.m (*exo*-4-H, $^2J = 17.4$ Hz), 2.25 d.d (1-H, $J_{1,anti\text{-}8} = 4.0$, $J_{1,exo\text{-}7} = 3.5$ Hz), 4.33 d.d (*exo*-7-H, $J_{7,13} = 8.4$, $J_{7,1} = 3.5$ Hz), 5.27 m (3-H), 5.39 d.d.q (13-H, $J_{13,14} = 15.2$, $J_{13,exo\text{-}7} = 8.4$, $J_{13,15} = 1.6$ Hz), 5.67 d.q.d (14-H, $J_{14,13} = 15.2$, $J_{14,15} = 6.5$, $J_{14,exo\text{-}7} = 0.7$ Hz). ^{13}C NMR spectrum, δ_C, ppm: 46.50 d (C^1), 136.49 s (C^2), 119.72 d (C^3), 36.54 t (C^4), 84.76 s (C^5), 87.23 d (C^7), 37.79 t (C^8), 23.77 q (C^9), 35.74 d (C^{10}), 17.79 q (C^{11}), 17.73 q (C^{12}), 130.53 d (C^{13}), 128.44 d (C^{14}), 17.77 q (C^{15}). The *exo* orientation of 7-H followed from the coupling constant between 7-H and 1-H ($J_{7,1} = 3.5$ Hz); the coupling constant between *endo*-7-H and 1-H should not exceed 1 Hz [8]. The lack of *W*-coupling between *syn*-8-H and 7-H also indicates *exo* orientation of the latter. Found: *m*/*z* 206.1656 $[M]^+$. $C_{14}H_{22}O$. Calculated: *M* 206.1665.

2,2,6-Trimethyl-4-[(*E*)-prop-1-en-1-yl]-3-oxabicyclo[3.3.1]non-6-ene (XII). $[\alpha]_D^{20} = 0$ ($c = 0.8$, $CHCl_3$). The spectral parameters of compound **XII** coincided with those reported in [7].

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