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Reactions of Epoxides Prepared from Some Monoterpenes with Acetic Anhydride on Aluminosilicate Catalysts

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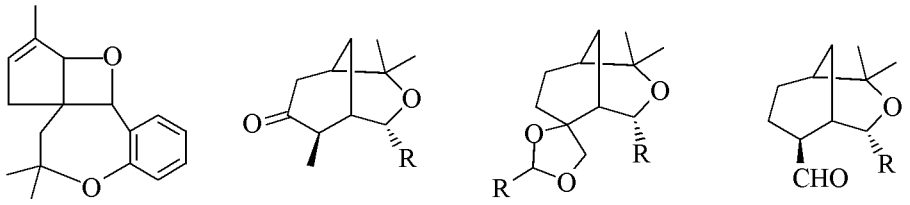
Abstract—Reactions of epoxides prepared from α-, β-pinenes and camphene with acetic anhydride on aluminosilicate catalysts (clay K-10, zeolite β) were investigated affording various products of skeleton rearrangements: mono- and diacetates with five- and six-membered rings, and also with norbornane and pinane cores.

We have formerly investigated reactions of some monoterpenes with acylating agents in the presence of crystalline aluminosilicate catalysts (zeolites and clays) [1]. The application of heterogeneous catalysts in these reactions improved the ecological characteristics of the processes and resulted in formation of previously unknown compounds. We also obtained good results in the study of reactions between monoterpenes epoxides and oxygen-containing compounds (aldehydes, ketones, and alcohols) catalyzed by zeolites and clays [2–4]. Bringing into reaction with aldehydes and ketones terpene epoxides in the presence of clay furnished versatile products: acetals with fuzed skeleton, keto-and aldoethers, acetals with a spirocyclic skeleton, and polycyclic diethers. The reactions of the α- and β-pinene epoxides with aldehydes on aluminosilicate catalysts took uncommon paths [3] and under environmentally tolerable conditions from simple initial compounds were obtained complex polyheterocyclic compounds, in particular, also with a previously unknown core:



The results obtained in the study of reaction between monoterpenes with acetic anhydride and of monoterpenes epoxides with oxygen-containing compounds prompted us to combine both these fields of research and to carry out an investigation on the reactions of some monoterpenes epoxides with acetic anhydride under catalysis with crystalline aluminosilicates. We chose as substrates epoxides of α- and β-pinenes and camphene since these terpenoids were prone to deep rearrangements in acid media and as showed our previous experience [1, 3] under conditions of heterogeneous catalysis might provide uncommon structures.

The reaction of α-pinene *trans*-epoxide (**I**) with acetic anhydride in dichloromethane in the presence of montmorillonite clay K10 (1.5 h, 20°C) gave rise to α-campholene aldehyde (**II**) (19%) and its acylal, 1-acetoxy-2-(2,2,3-trimethylcyclopent-3-enyl)ethyl acetate (**III**) (3%), and also compounds with a *p*-menthane skeleton: *trans*-sobrerol diacetate (**IV**) (22%) and in lesser amounts *trans*-carvyl acetate (**V**). When the reaction time was prolonged to 8 h the overall yield was reduced, and also diminished the relative content of products with the α-campholene skeleton; therewith besides compounds **II**–**V** the product mixture contained small amounts of *cis*-carvyl acetate (**VI**), 5,5-dimethyl-6-methylenebicyclo-[2.2.1]hept-2-yl *endo*-acetate (**VII**), *trans*-pinocarvyl acetate (**VIII**), and 1-acetoxy-2-(2,2,4-trimethylcyclopent-3-enyl)ethyl acetate (**IX**). The sharp decrease in

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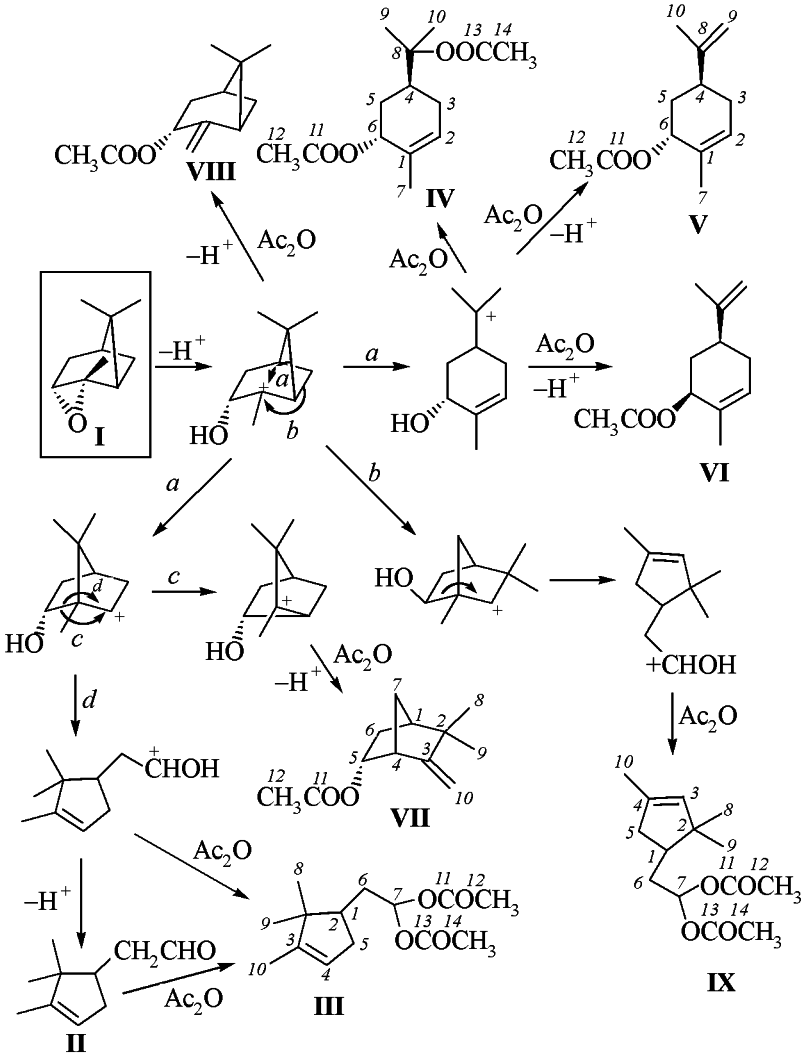
Scheme 1.



content of α-campholene aldehyde (**II**) in the reaction mixture at prolonged reaction time was caused both by its tarring and partial conversion into acylal **III**.

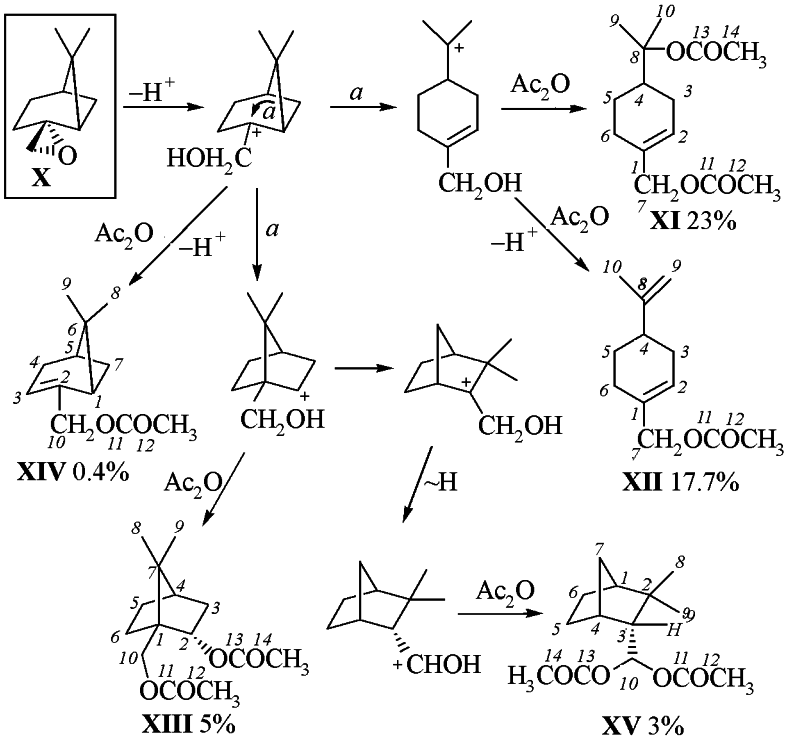
Probable mechanisms of compounds **II**–**IX** formation are given in Scheme 1.

Whereas in the reaction of α- and β-pinenes with the acetic anhydride on clay we obtained the same reaction products [1] due to identity of cations arising on protonation of these terpenes, the reactions with acetic anhydride on clay of epoxides prepared from these terpenes provided different reaction mixtures as should be expected. Actually, although the cationic center arising on protonation of epoxides is located on the same carbon atom both for α- and β-pinene epoxides, the hydroxy group is attached to different carbons thus resulting in different products.

The reaction of β-pinene *trans*-epoxide (2,10-epoxy-*cis*-pinane) (**X**) with Ac_2O in CH_2Cl_2 on the clay K-10 (1.5 h, 20°C) gave rise to a reaction mixture from which by column chromatography on Si_2 were isolated the following products:4-(1-acetoxy-1-methylethyl)cyclohex-1-enylmethyl acetate (**XI**), 4-isopropenylcyclohex-1-enylmethyl acetate (**XII**), (2-*endo*-acetoxy-7,7-dimethylbicyclo[2.2.1]hept-1-yl)methyl acetate (**XIII**), myrtenyl acetate (**XIV**), and acetoxy-(3,3-dimethylbicyclo[2.2.1]hept-2-yl)-*endo*-methyl acetate (**XV**) (Scheme 2). Although the main reaction path provides compounds with the *p*-methane skeleton, in the reaction mixture are present in sufficient amount also substances with the bicyclic skeletons.

Compounds we isolated in the study of reaction between α and β-pinene and acetic anhydride on clay were optically active.

Scheme 2.



At the use of β-zeolite instead of K-10 clay as catalyst of reactions between α- and β-pinenes and acetic anhydride the rate of the process significantly diminished (for instance, a notable conversion of the α-pinene epoxide in reaction with acetic anhydride on β-zeolite was attained only at 40°C). The reaction mixture was also more complicated.

The α- and β-pinenes were previously reacted with benzoic anhydride in polar solvents containing Cu^{2+} [5], and β-pinene epoxide was brought into reaction with acetic acid in the presence of sodium acetate and ion-exchange resin [6]. On hydrolysis of the intermediately formed benzoates and acetates the main products obtained were *trans*-carveol and perillic alcohol respectively; the structures of minor products arising in these reactions were not determined. We carried out a control experiment consisting in keeping β-pinene epoxide in acetic acid. The GC-MS method revealed that under these conditions the reaction mixture contained up to 10 compounds in comparable amounts, and the main part thereof was different from the substances forming at treating β-pinene epoxide with acetic anhydride on clay.

Compound **XV**, a minor component of products of reaction between β-pinene epoxide and acetic anhydride, was also obtained in reaction with acetic anhydride of a mixture of camphene epoxides **XVI** and **XVII** (~2.3 : 1) in the presence of β-zeolite in the H^+-form (1 h, 20°C); from the latter reaction mixture was also isolated 3,3-dimethybicyclo[2.2.1]heptane-*endo*-carbaldehyde (**XVIII**) (Scheme 3).

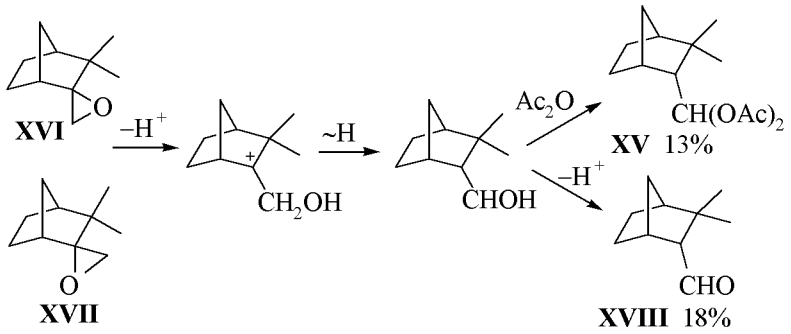
Aldehyde **XVIII** is unstable in air and is rapidly oxidized into the corresponding acid; therefore diacetate **XV** can be regarded as a precursor of aldehyde **XVIII** convenient for storage and use.

Although the initial mixture of epoxides **XVI** and **XVII** is optically active, compounds **XV** and **XVIII** obtained are racemic; thus the racemization of the arising carbocation occurs faster than the formation of neutral products.

A number of compounds **III, IX, XIII, XV** were not previously described; compounds **IV, V, VII, VIII, XI, XII, XIV** were obtained formerly by other methods, mainly by oxidation of α- or β-pinene with $Hg(OAc)_2$ [7] or $Pb(OAc)_4$ [8], and also by electrochemical procedure [9]; as a rule, complete ^1H and ^{13}C NMR spectra were not presented.

Thus we investigated reactions of α- and β-pinene and camphene epoxides with acetic anhydride in the presence of crystalline aluminosilicates; the structure of the reaction products, also that of the minor components, was reliably established. Taking into account the wide range of crystalline aluminosilicates

Scheme 3.



and the possibility of varying reaction conditions it is possible further if necessary to adjust the preparation conditions for obtaining from the epoxides we studied the desired compounds chosen among we isolated from the reaction mixture.

The structure of all compounds obtained was proved by ^{1}H and ^{13}C NMR spectra. In compounds **IV** and **V** as show the vicinal coupling constants of protons H^4 and H^6 the former is located axially, the latter pseudoequatorially, and thus they are placed *trans* to each other. The *exo*-position of H^5 in compound **VII** is confirmed by the value of coupling constant $^3J_{5k,4}$ equal to 4.5 Hz (at the *endo*-position the value $^3J_{5n,4}$ should be less than 1 Hz), and by the lack of W-interaction with the proton H^{7c}. The *exo*-position of the proton H^3 in the diacetate **XV** is confirmed by the observed W-coupling constant of the proton in the ^{1}H NMR spectrum with H^{5k} ($^4J_{3k,5k}$ 1.2 Hz), no such coupling with the proton H^{7an}, and also by the value of the vicinal coupling constant with the proton H^4 ($^3J_{3k,4}$ 3.5 Hz).

Note that for compounds **III** and **IX** the data for the cyclopentene parts of molecules are close to the corresponding data published in [10] and corresponding to aldehyde **II** and isocampholene aldehyde. The chemical shifts of signals in the ^{1}H NMR spectrum of compound **XIV** are similar to the corresponding proton signals of α-pinene except the resonances of H^1 and H^3 that deviate by 0.16 and 0.34 ppm because of replaced substituent at the C^2 atom [11].

The proton H^4 in compound **XII** is located axially as suggest its vicinal coupling constants with the protons H^{3a} and H^{5a}.

NMR spectra of compound **XVIII** are described in [4].

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were registered on spectrometer Bruker AM 400 at operating frequencies 400.13 and 100.61 MHz respectively from solutions of compounds in a mixture $CDCl_3$–CCl_4 (~1 : 1). The chloroform signals served as internal references (δ_H 7.24 ppm, δ_C 76.90 ppm). The structure of compounds was derived from the NMR spectra using the values of coupling constants obtained from the double resonance ^{1}H–^{1}H spectra, and basing on the analysis of the ^{13}C NMR spectra. The signals in the latter were assigned with the use of selective and off-resonance decoupling from protons, of LRJMD spectra with experimental conditions optimized for remote constants of $J_{C,H}$ 10 Hz, and also using two-dimensional spectra ^{13}C–^{1}H of heteronuclear correlation (COSY, using the value $^1J_{C,H}$ 135 Hz). High-resolution mass spectra were measured on Finnigan MAT 8200 instrument, GC-MS analyses were carried out on HP G 1800A setup. The optical rotation was recorded on spectrometer Polamat from solutions in $CHCl_3$, concentration expressed in gram per 100 ml of solution.

The checking of the purity of the initial compounds and analysis of the reaction products was carried out by GLC on chromatograph Biochrom-1 equipped with a flame-ionization detector, a quartz capillary column 15000 × 0.22 mm, stationary phase SE-54, carrier gas helium, excessive pressure 0.65 at.

The initial epoxides **XVI** and **XVII** were obtained as in [12]. $[\alpha]_{580}^{20}$ +5.2 (*c* 17.5). As catalysts were used β-zeolite in the H^+-form, [Si]/[Al] = 40, pore size 0.75–0.8 nm, containing the following oxides (wt%): 0.04% Na_2O, 5.14% Al_2O_3, 81.57% SiO_2, and montmorillonite clay K-10 (Fluka). Just before use the zeolite was calcined for 2 h at 500°C, and the clay was kept in a microwave oven for 20 min at a power of 450W. The solvent was passed through a column packed with calcined aluminum oxide. The reaction products were separated by column chromatography on silica gel (40–100μ).

Epoxides of α- and β-pinenes. To a suspension of 3.2 g of β-pinene and 10 g of Na_2CO_3 in 10 ml of

$CHCl_3$ cooled to 5°C was slowly added 0.053 mol of peracetic acid in 48 ml of $CHCl_3$. The mixture was stirred for 2.5 h at 20°C, then poured into 30 ml of water, the reaction product was extracted into chloroform, the extract was washed with saturated solution of Na_2CO_3, with water, dried with $MgSO_4$. After removing the solvent we obtained 3.15 g of β-pinene epoxide (**X**), $[\alpha]_{580}^{20}$ +5 (*c* 34). In a similar way from 3.1 g of α-pinene was obtained 2 g of α-pinene epoxide (**I**), $[\alpha]_{580}^{20}$ +24.6 (*c* 35).

Reaction of α-pinene trans-epoxide (I) with acetic anhydride. To a suspension of 1 g of clay in 9 ml of CH_2Cl_2 was added 3 ml of Ac_2O, 2 min later was added at stirring a solution of 0.60 g of epoxide **I** in 2 ml of CH_2Cl_2. The mixture was stirred for 8 h at 20°C, treated with a saturated solution of Na_2CO_3, the reaction products were extracted into ethyl ether, dried with magnesium sulfate. We obtained 0.64 g of compounds mixture. By column chromatography on SiO_2 (gradient elution with hexane–ethyl ether mixture with content of the latter 0.5–80%) we isolated: (1) 0.028 g of a mixture containing according to GC-MS data 42.4% of aldehyde **II**, 11.2% of acetate (**VIII**), 23.8% of acetates **V** and **VI** mixture; (2) 0.038 g of a mixture containing according to GC-MS data 11.6% of aldehyde **II**, 54.6% of acetate **V**; after the repeated chromatographing on SiO_2 (eluent 1% of ethyl ether in hexane) was isolated 0.017 g (2.2%) of acetate **V**; (3) 0.073 g (7.3%) of diacetate **III**; (4) 0.024 g (2.4%) of diacetate **III** and **IX** mixture (~1.7 : 1); (5) 0.165 g (16.5%) of diacetate **IV**; (6) 0.018 g (2.4%) of acetate **VII**.

Compound III, mp 68.5–70°C, $[\alpha]_{580}^{20}$ +2 (*c* 8). Found: *M* 152.11984. $C_{10}H_{16}O$ [*M*–$(CH_3CO)_2O$]. Calculated: *M* 152.12011. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.75 s, 0.96 s (C^8H_3, C^9H_3), 1.58 d.d.d ($C^{10}H_3$, $J_{10,5}$ 2.5, $J_{10,5'}$ 1.5, $J_{10,4}$ 1.5), 1.68 d.d.d (H^6, $J_{6,6'}$ 13, $J_{6,1}$ 11, $J_{6,7}$ 4.5), 1.77 d.d.d.d ($H^1$1, *J* 11, $J_{1,5}$ 9, $J_{1,5'}$ 7, $J_{1,6'}$ 2.5), 1.84 d.d.d ($H^{6'}$, *J* 13, $J_{6',7}$ 7, *J* 2.5), 1.92 d.d.q.d (H^5, $J_{5,5'}$ 15, *J* 9, 2.5, $J_{5,4}$ 1.5), 2.04 s, 2.05 s ($C^{12}H_3$, $C^{14}H_3$), 2.29 d.d.d.q (H^5, *J* 15, 7, $J_{5',4}$ 3, *J* 1.5), 5.17 d.d.q (H^4, *J* 3, 1.5, 1.5), 6.73 d.d (H^7, *J* 7, 4.5). ^{13}C NMR spectrum,* δ, ppm: 45.04 d (C^1), 46.90 s (C^2), 147.73 s (C^3), 121.95 d (C^4), 35.51 t (C^5), 33.79 t (C^6), 90.43 d (C^7), 25.47[a] q (C^8), 19.72[a] q (C^9), 12.63 q (C^{10}), 168.28[b] s (C^{11}), 20.79[c] q (C^{12}), 168.23[b] s (C^{13}), 20.70[c] q (C^{14}). Mass spectrum, *m/z* (I_{rel}, %): 152 (6.6), 109 (35), 108 (100), 93 (26.5), 43 (66).

* Here and hereinafter the chemical shifts values marked with the same letters (a–c) should probably be exchanged.

Compound (IV), $[\alpha]_{580}^{20}$ +10.9 (*c* 24.6). Found: *M* 152.11969. $C_{10}H_{16}O$ [*M*–$(CH_3CO)_2O$]. Calculated: *M* 152.12011. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.32 s, 1.35 s (C^9H_3, $C^{10}H_3$), 1.37 d.d.d (H^{5a} , $J_{5a,5e}$ 14, $J_{5a,4a}$ 13, $J_{5a,6e'}$ 4), 1.60 d.d.d (C^7H_3, $J_{7,3a'}$ 2.5), $J_{7,2}$ 1.5, $J_{7,3e'}$ 1.5), 1.75 m ($H^{3a'}$, $J_{3a',3e'}$ 17, $J_{3a',4a}$ 11.5, $J_{3a',7}$ 2.5, $J_{3a',2}$ 2, $J_{3a',6}$ 1.5), 1.86 d.d.d.d (H^{5e}, *J* 14, $J_{5e,5a}$ 2.5, $J_{5e,6e'}$ 2, $J_{5e,3e'}$ 2), 1.87 s, 1.97 s ($C^{12}H_3$, $C^{14}H_3$), 2.02 d.m ($H^{3e'}$, *J* 17, $J_{3e',2}$ 5.5, $J_{3e',4a}$ 5, *J* 2, 1.5), 2.16 d.d.d.d (H^{4a}, *J* 13, 11.5, 5, 2.5), 5.09 m ($H^{6e'}$, *J* 4, 2), 5.59 d.d.q (H^2, *J* 5.5, 2, 1.5). ^{13}C NMR spectrum,* δ, ppm: 131.04 s (C^1), 127.22 d (C^2), 26.49 t (C^3), 37.31 d (C^4), 29.57 t (C^5), 70.37 d (C^6), 20.47 q (C^7), 83.36 s (C^8), 23.40[a] q (C^9), 23.11[a] q (C^{10}), 170.13 s (C^{11}), 20.96[b] q (C^{12}), 169.40 s (C^{13}), 22.02[b] q (C^{14}). Mass spectrum, *m/z* (I_{rel}, %): 152 (15.5), 134 (42), 119 (100), 109 (34), 93 (28.6), 43 (84.6).

Compound (V), $[\alpha]_{580}^{20}$ +20 (*c* 2.3). Found: *M* 194.12976. $C_{12}H_{18}O_2$. Calculated: *M* 194.13067. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.59 d.d.d (H^{5a}, $J_{5a,5e}$ 14, $J_{5a,4a}$ 13, $J_{5a,6e'}$ 4), 1.65 d.d.d (C^7H_3, $J_{7,3a'}$ 2.5, $J_{7,3e'}$ 1.5, $J_{7,2}$ 1.5), 1.70 br.s ($C^{10}H_3$), 1.82 m ($H^{3a'}$, $J_{3a',3e'}$ 17, $J_{3a',4a}$ 11, *J* 2.5, $J_{3a',2}$ 2, $J_{3a',6e'}$ 1.5), 1.88 d.d. d.d (H^{5e}, *J* 14, $J_{5e,4a}$ 2.5, $J_{5e,3e'}$ 1.5, $J_{5e,6e'}$ 1.5), 2.02 s ($C^{12}H_3$), 2.16 m ($H^{3e'}$, *J* 17, $J_{3e',2}$ 5.5, $J_{3e',4a}$ 5, *J* 1.5, 1.5), 2.25 d.d.m (H^{4a}, *J* 13, 11, 5, 2.5, $J_{4a,9}$ 0.5), 4.66 m (H^9, $J_{9,9'}$ 1.5, $J_{9,10}$ 1, *J*0.5), 4.69 m ($H^{9'}$, *J* 1.5, $J_{9',10}$ 1.5), 5.19 m ($H^{6e'}$, *J* 4, 1.5, 1.5), 5.65 d.m (H^2, *J* 5.5, 2, 1.5). ^{13}C NMR spectrum, δ, ppm: 131.12 s (C^1), 127.51 d (C^2), 30.88 t (C^3), 35.80 d (C^4), 33.70 t (C^5), 70.20 d (C^6), 20.67 q (C^7), 148.21 s (C^8), 109.52 t (C^9), 20.88 q (C^{10}), 169.95 s (C^{11}), 21.15 q (C^{12}). Mass spectrum, *m/z* (I_{rel}, %): 194 (2) $[M]^+$, 152 (60), 134 (28.6), 119 (72), 109 (80), 93 (38), 91 (50.6), 84 (63), 43 (100).

Compound (VII), $[\alpha]_{580}^{20}$ –17.1 (*c* 1.75). Found: *M* 194.13053. $C_{12}H_{18}O_2$. Calculated: *M* 194.13067. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.06 s (C^8H_3), 1.08 s (C^9H_3), 1.33 d.d.d (H^{7an}, $J_{7an,7c}$ 10, $J_{7an,1}$ 1.5, $J_{7an,4}$ 1.5), 1.58 d.d.d (H^{6n}, $J_{6n,6k}$ 13.5, $J_{6n,7c}$ 4, $J_{6n,5k}$ 2.5), 1.76 d.d. d.d (H^{7c}, *J* 10, 4, $J_{7c,1}$ 1.5, $J_{7c,4}$ 1.5), 1.82 d.d.d (H^{6k}, *J* 13.5, $J_{6k,5k}$ 10, $J_{6k,1}$ 3.5), 1.85 br.d (H^1, *J* 3.5), 1.93 s ($C^{12}H_3$), 3.02 d.d.d.d (H^4, $J_{4,5k}$ 4.5, *J* 1.5, 1.5, $J_{4,1}$ 1.5), 4.67 s, 4.71 s ($2H^{10}$), 4.84 d.d.d (H^{5k}, *J* 10, 4.5, 2.5). ^{13}C NMR spectrum, δ, ppm: 47.53 d (C^1), 41.85 s (C^2), 158.03 s (C^3), 50.66 d (C^4), 74.16 d (C^5), 31.10 t

(C^6), 36.43 t (C^7), 29.97 q (C^8), 24.90 q (C^9), 104.49 t (C^{10}), 170.16 s (C^{11}), 21.07 q (C^{12}).

Compound (IX). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.77 s, 0.99 s (C^8H_3, C^9H_3), 1.63 br.s ($C^{10}H_3$), 1.65 m (H^6), 1.77–1.88 m (H^1, $H^{6'}$), 2.05 m (H^5), 2.05 s, 2.06 s ($C^{12}H_3$, $C^{14}H_3$), 2.27 d.d.m ($H^{5'}$, $J_{5',5}$ 16, $J_{5',1}$ 7.5, $J_{5',3}$ 1.2), 5.08 (H^3, $J_{3,5}$ 2.5, *J* 1.2, $J_{3,10}$ 1), 6.71 d.d (H^7, $J_{7,6}$ 7, $J_{7,6'}$ 4.5). ^{13}C NMR spectrum,* δ, ppm: 44.43 d (C^1), 46.18 s (C^2), 135.85 d (C^3), 136.60 s (C^4), 41.93 t (C^5), 33.64 t (C^6), 90.45 d (C^7), 27.85[a] q (C^8), 22.15[a] q (C^9), 16.69 q (C^{10}), 168.46[b] s (C^{11}), 20.77[c] q (C^{12}), 168.38[b] s (C^{13}), 20.69[c] q (C^{14}).

A suspension of 0.25 g of clay, 0.5 ml of Ac_2O, 0.1 g of epoxide **I** in 3.5 ml of CH_2Cl_2 was stirred for 1.5 h at 20°C. After the workup the product mixture was separated on a column packed with SiO_2 (gradient elution with ethyl ether–hexane mixture containing from 0.25 to 80% of the latter). We isolated 0.019 g (19%) of aldehyde **II**; 0.02 g of mixture containing according to GC-MS data 15.5% of aldehyde **II**, 25.5% of acetate **V**, and 3% of acetate **VIII**; 0.005 g (3%) of diacetate **III**, and 0.037 g (22%) of diacetate **IV**.

Reaction of β-pinene *trans*-epoxide (X) with acetic anhydride. A suspension of 1.5 g of clay, 5 ml of Ac_2O, 1 g of epoxide **X** in 12 ml of anhydrous CH_2Cl_2 was stirred for 1.5 h at 20°C. After the workup we obtained 1.28 g of the product mixture which was separated on a column packed with SiO_2 (gradient elution with ethyl ether–hexane mixture containing from 0.5 to 50% of the latter). We isolated 0.05 g (3%) of diacetate **XV**, 0.390 g (23%) of diacetate **XI**, 0.086 g (5%) of diacetate **XIII**, 0.225 g (17.7%) of acetate **XII**, and 0.038 g of a mixture containing according to GC-MS analysis 20% of acetate **XIV**. The latter mixture was subjected to repeated chromatography on SiO_2 to isolate 0.005 g of individual acetate **XIV** fit for recording NMR spectra.

Compound (XI), $[\alpha]_{580}^{20}$ –28.4 (*c* 16.6). Found: *M* 211.13499. $C_{12}H_{19}O_3$ (*M*–CH_3CO). Calculated: *M* 211.13341. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.12 m (H^{5a}), 1.22 s, 1.25 s (C^9H_3, $C^{10}H_3$), 1.66 d.m (H^{5e}, $J_{5e,5a}$ 12), 1.74 s ($C^{14}H_3$), 1.83 s ($C^{12}H_3$), 1.68–1.94 m ($2H^3$, H^4, $2H^6$), 4.18 br.d and 4.21 br.d ($2H^7$, *J* 12, $J_{7,3a}$ 1.5, $J_{7,3}44_e$ 1.5) system *AB*, 5.50 m (H^2). ^{13}C NMR spectrum,* δ, ppm: 132.64 s (C^1), 124.85 d (C^2), 25.76 t (C^3), 42.01 d (C^4), 22.97 t (C^5), 26.38 t (C^6), 67.38 t (C^7), 83.38 s (C^8), 22.90[a] q (C^9), 22.72[a] q (C^{10}), 168.93 s (C^{11}), 20.24 q (C^{12}), 168.55 s (C^{13}), 21.72 q (C^{14}). Mass spectrum, *m/z* (I_{rel}, %): 211 (2.9), 134 (48.4), 119 (30.3), 93 (30.3), 92 (100), 43 (71.4).

Compound (XII). ^{13}C NMR spectrum, δ, ppm: 132.71 s (C^1), 125.59 d (C^2), 30.41 t (C^3), 40.82 d (C^4), 27.29 t (C^5), 26.41 t (C^6), 68.10 t (C^7), 148.85 s (C^8), 109.22 t (C^9), 20.79 q (C^{10}), 169.73 s (C^{11}), 20.75 q (C^{12}).

Compound (XIII), $[\alpha]_{580}^{20}$ –27 (*c* 2.8). Found: *M* 254.15175. $C_{14}H_{22}O_4$. Calculated: *M* 254.15180. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.93 s, 0.99 s (C^8H_3, C^9H_3), 0.97 d.d (H^{3n}, $J_{3n}$$)_{,3k}$ 13.5, $J_{3n,2k}$ 3.5), 1.27 d.d.d (H^{5n}, $J_{5n,5k}$ 12.5, $J_{5n,6n}$ 9, $J_{5n,6k}$ 4.5), 1.41 d.d.d.d (H^{6k}, $J_{6k,6n}$ 12.5, $J_{6k,5k}$ 12, *J* 4.5, $J_{6k,2k}$ 2.2), 1.63 d.d (H^4, $J_{4,3k}$ 4.5, $J_{4,5k}$ 4.5), 1.77 m (H^{5k}, *J* 12.5, 12, 4.5, $J_{5k,6n}$ 4.5, $J_5k_{,3k}$ 3), 1.92 d.d.d (H^{6n}, *J* 12.5, 9, 4.5), 1.97 s ($C^{14}H_3$), 2.00 s ($C^{12}H_3$), 2.37 d.d.d.d (H^{3k}, *J* 13.5, $J_{3k,2k}$ 10, *J* 4.5, 3), 3.97 d and 4.00 d ($2H^{10}$, *J* 12) system *Ac*, 5.14 d.d.d (H^{2k}, *J* 10, 3.5, 2.2). ^{13}C NMR spectrum, δ, ppm: 51.23 s (C^1), 75.08 d (C^2), 36.56 t (C^3), 45.92 d (C^4), 27.70 t (C^5), 23.32 t (C^6), 48.06 s (C^7), 20.24[a] q (C^8), 19.90[a] q (C^9), 62.94 t (C^{10}), 170.16 s (C^{11}), 21.05 q (C^{12}), 170.08 s (C^{13}), 20.67 q (C^{14}). Mass spectrum, *m/z* (I_{rel}, %): 254 (2.6), 152 (25.9), 134 (68), 119 (33.2), 108 (58), 93 (35.2), 92 (52.7), 43 (100).

Compound (XV), $[\alpha]_{580}^{20}$ –18.6 (*c* 2.8). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.87 s (C^9H_3), 1.00 s (C^8H_3), 1.19 d.d.d (H^{7an}, $J_{7an,7c}$ 10, $J_{7an,1}$ 1.5, $J_{7an,4}$ 1.5), 1.28 m (H^{5k}, H^{6k}), 1.55 m (H^{5n}), 1.62 d.m (H^{7c}, *J* 10), 1.67 m (H^{6n}), 1.78 d.d.d (H^{3k}, $J_{3k,10}$ 10, $J_{3k,4}$ 3.5, $J_{3k,5kyy}$ 1.2), 1.78 br.s (H^1), 2.01 s, 2.05 s ($C^{12}H_3$, $C^{14}H_3$), 2.09 m (H^4), 6.87 d (H^{10}, *J* 10). ^{13}C NMR spectrum,* δ, ppm: 49.59 d (C^1), 36.96 s (C^2), 53.61 d (C^3), 40.02 d (C^4), 21.12 t (C^5), 24.66 t (C^6), 37.31 t (C^7), 32.52 q (C^8), 21.54 q (C^9), 90.24 d (C^{10}), 168.34[a] s (C^{11}), 20.89[b] q (C^{12}), 167.50[a] s (C^{13}), 20.75[b] q (C^{14}).

Reaction of camphene *cis*- and *trans*-epoxides (XVI, XVII) with acetic anhydride. A solution of 0.12 g of epoxides **XVI** and **XVII** mixture in 3 ml of anhydrous Ac_2O was added to a suspension of 0.12 g of β zeolite in 5 ml of Ac_2O, and the mixture was stirred for 1 h at 20°C. By column chromatography on silica gel (eluent pentane) was isolated 0.21 g (18%) of aldehyde **XVIII** and 0.185 g of a mixture that after repeated chromatography on SiO_2 with gradient elution by mixture pentane–ethyl ether (2–15%) provided 0.025 g (13%) of diacetate **XV**.

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REFERENCES

1. Volcho, K.P., Tatarova, L.E., Suslov, E.V., Korchagina, D.V., Salakhutdinov, N.F., and Barkhash, V.A., *Zh. Org. Khim.*, 2001, vol. 37, p. 1488.
2. Volcho, K.P., Tatarova, L.E., Korchagina, D.V., Salakhutdinov, N.F., and Barkhash, V.A., *Zh. Org. Khim.*, 2000, vol. 36, p. 41.
3. Il'ina, I.V., Korchagina, D.V., Salakhutdinov, N.F., and Barkhash, V.A., *Zh. Org. Khim.*, 2000, vol. 36, p. 1483.
4. Yarovaya, O.I., Korchagina, D.V., Gatilov, Yu.V., and Barkhash, V.A., *Zh. Org. Khim.*, 2002, vol. 38, p. 852.
5. Indian Patent IN137738, 1975. *Chem. Abstr.*, 1980, vol. 92, no. 181428.
6. US Patent US5994598, 1999; *Chem. Abstr.*, 1999, vol. 132, no. 3478.
7. Teresa, J. and Iglesias, M., *Real. Soc. Espan. Fis. Quim., Ser. B*, 1982, vol. 62, nos. 9–10, p. 989.
8. Yokoi, K. and Matsubara, Y., *Nippon Kagaku Kaishi*, 1979, no. 5, p. 641.
9 Gora, J., Smigielski, K., and Kula, J., *Synthesis*, 1989, no. 10, p. 759.
10. Polovinka, M.P., Korchagina, D.V., Gatilov, Yu.V., Vyglazov, O.G., and Barkhash, V.A., *Zh. Org. Khim.*, 1999, vol. 35, p. 1324.
11. Badjah-Hadj-Ahmed, A.Y., Merlati, B.Y., Waton, H., and Pham, Q.T.. *Magn. Res. Chem.*, 1992, vol. 30, no. 9, p. 807.
12. Yarovaya, O.I., Korchagina, D.V., Gatilov, Yu.V., and Barkhash, V.A., *Zh. Org. Khim.*, 2002, vol. 38, p. 852.