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Reactions of Caryophyllene 4β,5α-Epoxide with Carbonyl Compounds on Clay

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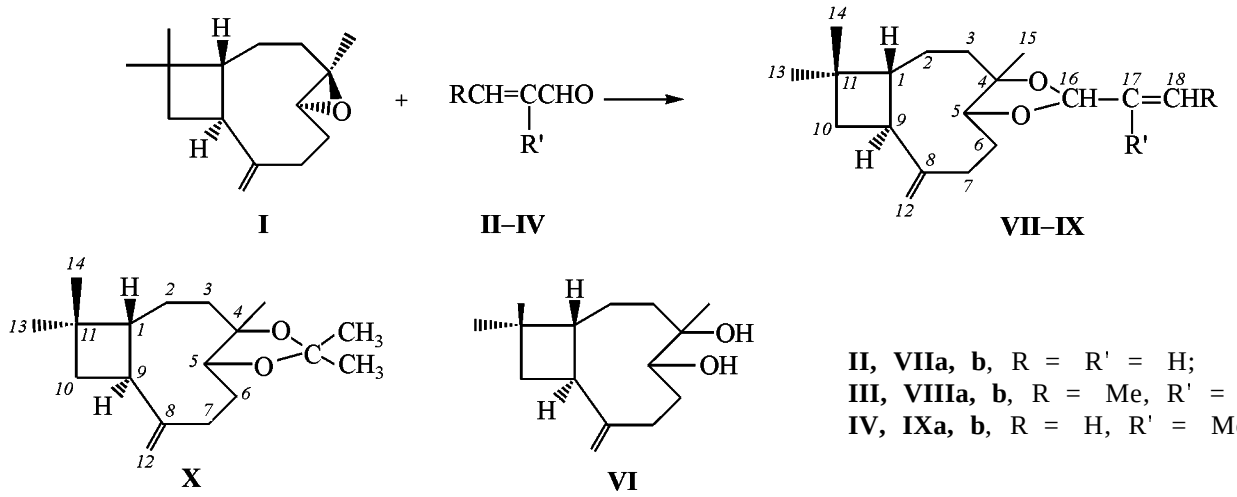
Abstract—Products of reaction between caryophyllene 4β,5α-epoxide and carbonyl compounds (acrolein, crotonaldehyde, α-methacrolein, and acetone) were synthesized on clay. Two diastereomers in reaction with each aldehyde and a single isomer with acetone were obtained. In reaction of the epoxide with acetone an isomerization product was isolated, 4,4,9-trimethyltricyclo[6.2.2.$0^{1,5}$]dodec-9-en-2β-ol that was unknown before.

We showed formerly that olefins of terpene series on aluminosilicate catalysts entered into various reactions with aldehydes providing heterocyclic compounds [1]. However for various reasons some terpenoids do not undergo this kind of transformations. We revealed [2] that epoxidation of olefins removedthese obstacles. For instance, *cis*- and *trans*-epoxides of (+)-3-carene and limonene with aldehydes in the presence of askanite–bentonite clay afford acetals. Therewith the sterical factors are decisive in determining the extent of intra- and intermolecular processes [2].

In extension of the studies on the poorly known reaction of epoxides with carbonyl compounds we investigated the reaction between caryophyllene 4β,5α-epoxide (**I**) and some carbonyl compounds. Note that quite a number of publications concerns the isomerization of epoxide **I** effected by proton or Lewis acids under homogeneous conditions (see, e.g., [3, 4]), but the data of intermolecular reactions of this compound are scarce [3, 4], especially under heterogeneous conditions [1].

We studied reactions of epoxide **I** with acrolein (**II**), crotonaldehyde (**III**), α-methacrolein (**IV**), and acetone (**V**) in the presence of askanite–bentonite clay at 20°C. In all reactions were isolated 1,3-dioxolanes, products of reaction between epoxide **I** and carbonyl compounds **II**–**V**. It were respectively compounds **VIIa, b** (two diastereomers), **VIIIa, b** (two diastereomers), **IXa, b** (two diastereomers), and **X**

Scheme 1.



II, VIIa, b, R = R' = H;
III, VIIIa, b, R = Me, R' = H;
IV, IXa, b, R = H, R' = Me.

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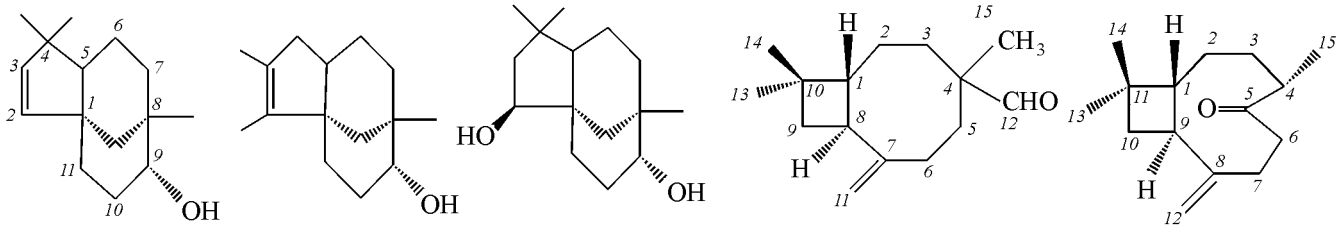
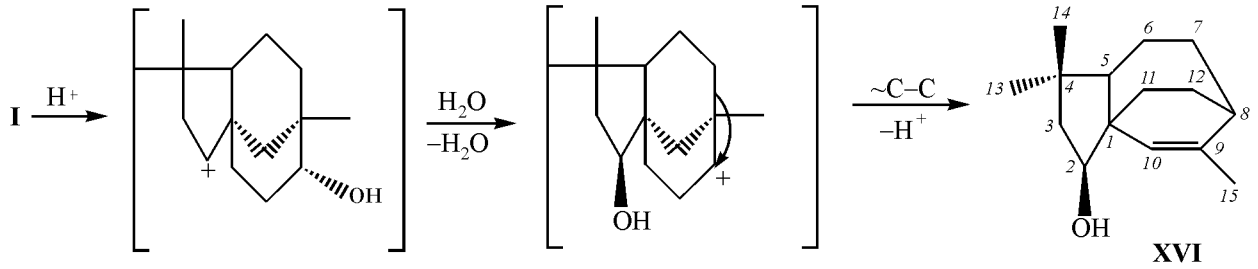
Scheme 2.



XI **XII** **XIII** **XIV** **XV**

Scheme 3.



XVI

(one diastereomer) (Scheme 1). The compounds fail to react in the absence of clay.

Alongside 1,3-dioxolans from the reaction mixtures were isolated products of intramolecular rearrangement of epoxide **I**, previously described alcohols: 9α-hydroxyclovene (**XI**), 2,3,8-trimethyl-12α-methylenetricyclo[6.3.1.$0^{1,5}$]dodec-2-ene-9α-ol (**XII**) and 2β,9α-dihydroxyclovane (**XIII**) [5], and also 4,10,10-trimethyl-7-methylenebicyclo[6.2.0]-decene4-carboxaldehyde (**XIV**) and 4α,11,11-trimethyl-8-methylenebicyclo[7.2.0]undecan-5-one (**XV**) [3] (Scheme 2). These substances arise also at keeping epoxide **I** on the clay without carbonyl compounds.

The reaction of epoxide **I** with ketone **V** gave rise alongside aldehyde **XIV**, ketone **XV**, acetal **X**, and diol **XIII** also a previously unknown compound 4,4,9-trimethyltricyclo[6.2.2.$0^{1,5}$]dodec-9-en-2β-ol (**XVI**) whose formation is presented in Scheme 3.

The structure of compounds obtained was established from ^{1}H and ^{13}C NMR spectra. In the ^{1}H NMR spectra of compounds **XIV** and **XV** only the signals of methyl groups and olefin protons were formerly reported, and in the spectrum of compound **XIV** also a signal of the aldehyde group proton [4, 6]. In the present paper we give more complete ^{1}H NMR spectra of these compounds, and also their ^{13}C NMR spectra. We assigned the α-configuration to the methyl group at C^4 carbon in compound **XV** in agreement with the published data [4].

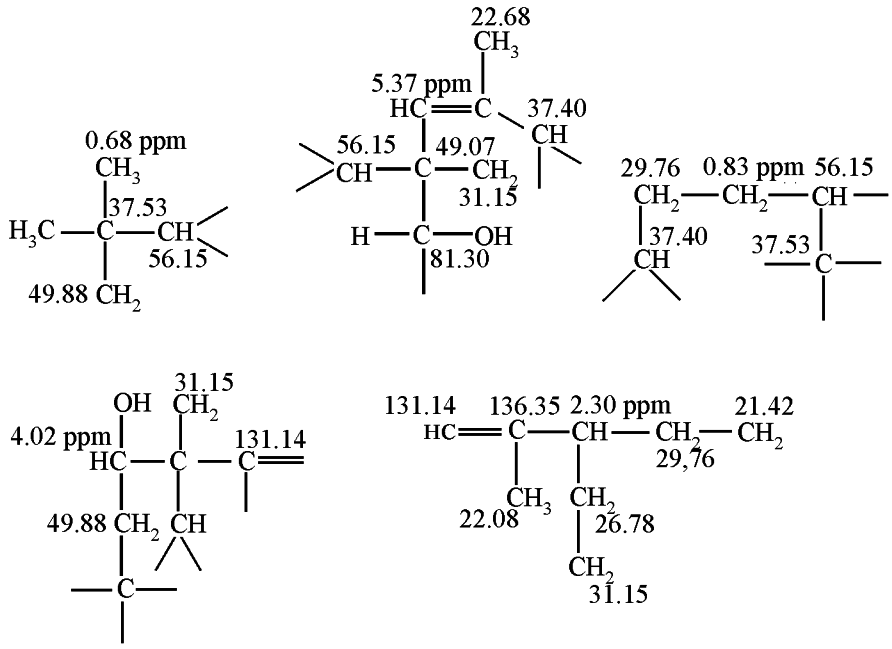
The ^{1}H and ^{13}C NMR spectra of compounds **XI, XII**, and of diol **XIII** are consistent with those published in [5].

It should be noted that because of insignificant difference in the ^{1}H and ^{13}C NMR spectra of acetal pairs **VIIa, b, VIIIa, b**, and **IXa, b** we did not succeed in establishing the cause of the isomerism: whether it was due to the α- or β-configuration of the methyl group at the C^4 atom or to different position of the alkenyl substituent attached to C^{16}. The formation of a single ketal **X** in the reaction of epoxide **I** and ketone **V**, and also the fact that in the ^{1}H NMR spectra of the above acetals the greatest difference in the chemical shifts is observed for the peaks from H^{16} suggest the second assumption to be more probable.

Note that for all the acetals obtained in this study the signals from C^1, C^2, C^3, C^6, and C^7 in the ^{13}C NMR spectra are considerably broadened. With rising temperature the signals get narrower. These reversible temperature changes are apparently due to the conformational lability of the nine-membered ring in the acetal molecules.

Let us consider the estimation of the structure of the previously unknown alcohol **XVI**. To the analysis of ^{1}H NMR spectra were applied the data obtained by double resonance ^{1}H–^{1}H and those of ^{13}C NMR spectra (also of the spectra with off-resonance and selective decoupling from protons and of two-di-

mensional spectra of $^{13}C-^{1}H$ correlation COSY). As a result we established the coupling between the corresponding protons, the number of methyl, methylene, methine groups and quaternary carbons in the molecule, and correlation between the carbon and hydrogen signals. To complete the determination of the carbon chain we turned to differential spectra modulated with remote spin-spin coupling (LRJMD, one-dimensional mode of $^{13}C-^{1}H$ correlation on remote constants). Basing on the results obtained by successive pulse irradiation of protons of methyl group with a signal at 0.68 ppm, of olefin proton with a signal at 5.37 ppm, and of protons resonating at 4.02, 2.30, and 0.83 ppm and taking into account the above mentioned data we were able to separate the structural fragments of the compound in question. All these fragments could be connected in only one way, namely, in the structure **XVI**.



EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were registered on spectrometer Bruker AM-400 at operating frequencies 400.13 and 100.61 ppm respectively from solutions of compounds in $CDCl_3$ or $CDCl_3$–CCl_4, 1:1 by volume. As internal reference served the signals of chloroform (δ 7.24, δ_C 76.90 ppm). The analysis of ^{1}H NMR spectra was performed with the use of double resonance spectra $^{1}H-^{1}H$. The assignment of signals in the ^{13}C NMR spectra was carried out by selective and off-resonance decoupling from protons. In some cases was performed registering of spectra modulated with remote coupling $^{13}C-^{1}H$ (LRJMD, experimental conditions optimized for remote coupling constants J_{CH} 10 Hz). For compounds **X, XIV– XVI** were additionally recorded two-dimensional heteronuclear correlation spectra $^{13}C-^{1}H$ (COSY, with the use of direct coupling constant $^{1}J_{CH}$ 134 Hz). The ^{13}C NMR spectra are listed in the table.

Elemental composition of the newly synthesized compounds was estimated from the high resolution mass spectra obtained on Finnigan MAT 8200 instrument

The purity of the initial compounds was checked and the reaction products were analyzed by GLC on Biokhrom-1 chromatograph equipped with flame-ionization detector, capillary quartz column 15000 × 0.22 mm, stationary phase SE-54, carrier gas helium. The optical rotation was measured on Polamat A instrument in $CHCl_3$.

The askanite–bentonite clay was obtained by acid activation of bentonite clays from Askanian deposits and corresponded to the Standard 113-12-86-82. The catalyst was calcined at 120°C for 3 h just before use.

Caryophyllene (**XVII**) was isolated from by-product of oil of cloves by column chromatography on Al_2O_3 activated for 5 h at 450°C, eluent hexane. Epoxide **I** was prepared from olefin **XVII** along procedure described in [7].

^{13}C NMR spectra of compounds **VIIa, VIIb, VIIIa, VIIIb, IXa, IXb, X, XIV, XV, XVI**[a] in $CDCl_3$–CCl_4 (1 : 1), δ, ppm

Atom	VIIa	VIIb	VIIIa	VIIIb	IXa	IXb	X	XIV[b]	XV	XVI
C^1	58.15 d	58.88 d	58.81 d	58.15 d	58.43 d	59.04 d	58.66 d	52.22 d	53.66 d	49.07 s
C^2	22.84 t	23.75 t	23.70 t	22.84 t	22.88 t	24.06 t	22.94 t	22.53 t	25.80 t	81.30 d
C^3	39.42 t	40.40 t	40.40 t	39.42 t	39.49 t	40.98 t	40.18 t	31.16 t	30.22 t	49.88 t
C^4	82.70 s	82.04 s	81.78 s	82.64 s	82.76 s	81.84 s	82.14 s	48.98 s	47.34 d	37.53 s
C^5	77.75 d	80.37 d	80.19 d	77.92 d	78.56 d	80.40 d	77.60 d	29.80 t	215.80 s	56.15 d
C^6	27.80 t	26.92 t	26.81 t	27.97 t	28.07 t	26.57 t	27.36 t	29.66 t	41.73 t	21.42 t
C^7	34.53 t	34.84 t	34.73 t	34.54 t	34.70 t	34.93 t	34.62 t	152.63 C	34.57 t	29.76 t
C^8	151.24 s	151.30 s	151.30 s	151.36 s	151.49 s	151.21 s	151.59 s	40.02 d	153.78 s	37.40 d
C^9	42.19 d	42.55 d	42.47 d	42.25 d	42.33 d	42.58 d	41.96 d	37.51 t	43.25 d	136.35 s
C^{10}	36.57 t	36.70 t	36.56 t	36.55 t	36.63 t	36.61 t	36.52 t	34.21 s	40.04 t	131.14 d
C^{11}	34.24 s	34.42 s	34.29 s	34.25 s	34.32 s	34.35 s	34.22 s	107.39 t	33.54 s	31.15 t
C^{12}	111.52 t	111.63 t	111.40 t	111.45 t	111.44 t	111.54 t	111.36 t	205.42 d	111.42 t	26.78 t
C^{13}	22.14 q	22.10 q	21.95 q	22.12 q	22.20 q	21.99 q	22.16 q	22.40 q	21.90 q	23.63 q
C^{14}	29.95 q	29.96 q	29.80 q	29.94 q	29.98 q	29.82 q	29.96 q	30.03 q	29.84 q	28.88 q
C^{15}	18.76 q	21.26 q	21.19 q	18.48 q	18.47 q	21.02 q	21.11 q	22.19 q	17.06 q	22.08 q
C^{16}	100.70 d	101.47 d	101.55 d	101.05 d	102.53 d	103.10 d	105.64 s			
C^{17}	136.63 d	136.14 d	129.25 d	129.84 d	143.78 s	142.09 s	26.95 q			
C^{18}	117.74 t	119.48 t	132.12 d	130.60 d	114.15 t	115.77 t	28.51 q			
C^{19}			17.48 q	17.49 q	16.05 q	15.74 q				

[a] Numeration of atoms corresponds to that of caryophyllene skeleton. [b] In $CDCl_3$.

Numeration of atoms in the NMR spectra corresponds to that of caryophyllene skeleton.

Reaction of caryophyllene 4β,5α-epoxide (I) with acrolein (II). To a suspension of 1 g of clay in 8 ml of anhydrous dichloromethane was added at 20°C a solution of 0.7 g of acrolein (**II**) in 2 ml of anhydrous dichloromethane*; the mixture was stirred for 5 min at 20°C, then was added a solution of 0.35 g of epoxide **I** in 2 ml of anhydrous dichloromethane. The stirring at 20°C continued for 2.5 h, then the reaction mixture was filtered, the solvent was removed, and 0.42 g of products mixture was obtained. The mixture was subjected to column chromatography on SiO_2 (100–160μ), gradient elution with hexane–ethyl ether (content of the latter from 0.25 to 100%). The following substances were isolated: (1) Compound **XIV**, 9 mg (3%).**

^{1}H NMR spectrum (δ, ppm, *J*, Hz): 0.97 s ($C^{14}H_3$), 0.98 s ($C^{13}H_3$), 0.99 s ($C^{15}H_3$), 1.34 m (H^2), 1.46 m ($H^{2'}$), 1.51 d.d.d (H^5, $J_{5,5'}$ 15.5, $J_{5,6}$ 7, $J_{5,5'}$ 3.5), 1.61 d.d.d (H^1, $J_{1,2}$ 11, $J_{1,8}$ 10, $J_{1,2'}$ 4), 1.62 d.d (H^9, $J_{9,9'}$ 10, $J_{9,8}$ 10), 1.64 d.d.d (H^3, $J_{3,3'}$ 15, $J_{3,2'}$ 10, $J_{3,2}$ 2.5) and 1.73 d.d.d ($H^{3'}$, *J* 15, $J_{3',2}$ 8, $J_{3',2'}$ 2.5) system *AB*, 1.77 d.d ($H^{9'}$, *J* 10, $J_{9',8}$ 8), 1.80 d.d.d ($H^{5'}$, *J* 15.5, $J_{5',6}$ 11, $J_{5',6'}$ 4), 2.12 br.d (H^6, $J_{6,6'}$ 16) and 2.18 br.d ($H^{6'}$, *J* 16) system *AB*, 2.62 d.d.d.d.d (H^8, *J* 10, 10, 8, $J_{8,11}$ 2, $J_{8,11'}$ 2), 4.45 d.d.d.d (H^{11}, *J* 2, $J_{11,11'}$ 2, $J_{11,6}$ 1, $J_{11,6'}$ 1), 4.65 d.d.d.d ($H^{11'}$, *J* 2, 2, $J_{11,6}$ 1.5, $J_{11',6'}$ 1.5), 9.38 c (H^{12}). 2) Ketone **XV**, 22 mg (7%), $[\alpha]_{580}^{19}$ −14.1° (*c* 5.4, $CHCl_3$). ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 0.91 s ($C^{13}H_3$), 0.95 s ($C^{14}H_3$), 1.00 d ($C^{15}H_3$, $J_{15,4}$ 7), 1.26–1.39 m ($2H^2$), 1.43 m (H^3), 1.51 d.d.d (H^1, $J_{1,2}$ 11, $J_{1,9}$ 10, $J_{1,2'}$ 3), 1.51 d.d (H^{10}, $J_{10,10'}$ 10, $J_{10,9}$ 10), 1.67 d.d ($H^{10'}$, *J* 10, $J_{10',9}$ 8), 1.72 d.d.d.d (H , $J_{3',3}$ 15.5, $J_{3',4}$ 10, $J_{3',2}$ 8, $J_{3',2'}$ 4), 2.17 d.d.d (H^9, *J* 10, 10, 8), 2.30– 2.52 m ($2H^6$, $2H^7$), 2.55 d.q.d (H^4, *J* 10, 7, $J_{4,3}$ 4), 4.90 br.d (H^{12}, $J_{12,12'}$ 2), 4.93 br.d (H^{12}, *J* 2), 3) 13α (or 13β-vinyl-1,5,5-trimethyl-8-methylene-4β,7–12,14-dioxatricyclo[9.3.0.0^{4,7}]tetradecane (**VIIa**), 52 mg (13%), $[\alpha]_{580}^{*19}$ −29.4° (*C* 6.12, $CHCl_3$). ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 0.96 s ($C^{13}H_3$), 0.98 s ($C^{14}H_3$), 1.11 s ($C^{15}H_3$), 1.24 m (H^2), 1.57 d.d (H^{10}, $J_{10,10'}$ 10, $J_{10,9}$ 8), 1.50–1.66 m (H^1, $H^{2'}$, H^3), 1.66–1.74 m ($2H^6$), 1.73 d.d ($H^{10'}$, *J* 10, $J_{10',9}$ 10), 1.93 br.d.d ($H^{3'}$, $J_{3',3}$ 14, $J_{3',2'}$ 10), 2.00 br.d.t (H^7, $J_{7,7'}$ 14, $J_{7,6}$ 5.5), 2.34 d.d.d (H^9, $J_{9,1}$ 10, J_{10}, 8), 2.38 d.d.d ($H^{7'}$, *J* 14, $J_{7',6}$ 8, $J_{7',6'}$ 6),

* The carbonyl compounds are added first in order to decrease the isomerization of epoxide **I**.

** Very unstable, suffers tarring both in pure state and in solution.

3.57 t (H^5, $J_{5,6}$ 5), 4.92 br.s (H^{12}), 4.96 br.s ($H^{12'}$), 5.19 d.d.d (H^{18cis}, $J_{18cis,17cis}$ 10, $J_{18cis,18trans}$ 1.5, $J_{18cis,16}$ 1), 5.29 d.d.d (H^{16}, $J_{16,17}$ 6, J 1, $J_{16,18trans}$ 1), 5.32 d.d.d ($H^{18trans}$, $J_{18trans,17cis}$ 17, J 1.5, 1), 5.74 d.d.d (H^{17}, J 17, 10, 6). Found: M 276.2095. $C_{18}H_{28}O_2$. Calculated: M 276.2099. 4) 13β (or 13α)-vinyl-1,5,5-trimethyl-8-methylene-4β,7–12,14-dioxatricyclo[9.3.0.$0^{4,7}$]tetradecane (**VIIb**), 12 mg (3%), $[\alpha]_{580}^{20}$ –20.8° (*C* 0.96, $CHCl_3$). ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 0.97 s ($C^{13}H_3$), 1.00 s ($C^{14}H_3$), 1.10 s ($C^{15}H_3$), 1.22 m (H^2), 1.49–1.68 m (H^1, $H^{2'}$, H^3), 1.59 d.d (H^{10}, $J_{10,10'}$ 10, $J_{10,9}$ 8), 1.76 d.d ($H^{10'}$, J 10, $J_{10',9}$ 10), 1.73–1.78 m ($2H^6$), 1.93 d.d.d ($H^{3'}$, $J_{3',3}$ 14, $J_{3',2'}$ 10, $J_{3',2}$ 1.2), 2.07 br.d.t (H^7, $J_{7,7'}$ 14, $J_{7,6}$ 5), 2.36 d.d.d (H^9, $J_{9,1}$ 10, J 10, 8), 2.41 d.t ($H^{7'}$, J 14, $J_{7'}$, 6 8), 3.58 t (H^5, $J_{5,6}$ 5), 4.95 d.d.d (H^{12}, $J_{12,7}$ 1.5, $J_{12,9}$ 1.5, $J_{12,7'}$ 1), 4.99 br.s ($H^{12'}$), 5.11 br.d (H^{16}, $J_{16,17}$ 6.5), 5.28 d.d.d (H^{18cis}, $J_{18cis,17cis}$ 10, $J_{18cis,18trans}$ 1.5, $J_{18cis,16}$ 1), 5.40 d.d.d ($H^{18trans}$, $J_{18trans,17cis}$ 17, J 1.5, $J_{18trans,16}$ 1), 5.77 d.d.d (H^{17}, J 17, 10, 6.5). 5) Alcohol **XI**, 6 mg (2%); alcohol **XII**, 4 mg (1%); diol **XIII**, 47 mg (16%); and 35 mg (12%) of a mixture of alcohols of unknown structure.

Reaction of epoxide I with crotonaldehyde (III). A suspension of 1.1 g of the clay askanite–bentonite, 0.35 g of epoxide **I**, and 0.7 g of aldehyde **III** in 12 ml of dichloromethane was stirred for 90 min at 20°C. By column chromatography on SiO_2 (100–160μ) at gradient elution with hexane–ethyl ether (content of the latter from 1 to 100%) were isolated 0.028 g (8%) of aldehyde **XIV**, 0.035 g (10%) of ketone **XV**, 0.032 g (7%) of acetal **VIIIa**, isolated: (1) Compound **XIV**, 9 mg (3%).** 0.02 g (4%) of acetal **VIIIb**, 0.008 g (2%) of alcohol **XII**, 0.115 g (32%) of diol **XIII** and 0.121 g of a mixture of alcohols of unknown structure. **1,5,5-Trimethyl-8-methylene-13α (or 13β)-[(*E*)-1-propenyl-4β,7α-12,14-dioxatricyclo-[9.3.0.$0^{4,7}$]tetradecane (VIIIa),** $[\alpha]_{580}^{20}$ –26.1° (*C* 5.1, $CHC1_3$). ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 0.95 s ($C^{13}H_3$), 0.98 s ($C^{14}H_3$), 1.09 s ($C^{15}H_3$), 1.23 m (H^2), 1.48–1.66 m (H^1, $H^{2'}$, H^3), 1.58 d.d (H^{10}, $J_{10,10'}$ 10, $J_{10,9}$ 8), 1.70 d.d ($C^{19}H_3$, $J_{19,18}$ 7, $J_{10,17}$ 1.5), 1.71–1.76 m ($2H^6$), 1.74 d.d (H^{10}, J 10, $J_{10',9}$-10), 1.91 br.d.d ($H^{3'}$, $J_{3',3}$ 14, $J_{3',2'}$ 10), 2.05 br.d.t (H^7, $J_{7,7'}$ 14, $J_{7,6}$ 5), 2.34 br.d.d.d (H^9, $J_{9,1}$ 10, J 10, 8), 2.39 br.d.t ($H^{7'}$, J 14, $J_{7',6}$ 8), 3.56 t (H^5, $J_{5,6}$ 5), 4.93 br.s (H^{12}), 4.98 br.s ($H^{12'}$), 5.09 d (H^{16}, $J_{16,17}$ 7), 5.43 d.d.q (H^{17}, $J_{17,18}$ 15, J 7, 1.5), 5.85 d.q (H^{18}, J 15, 7). Found: M 290.2253. $C_{19}H_{30}O_2$. Calculated: M 290.2246. **1,5,5-Trimethyl-8-methylene-13α (or 13β)[(*E*)-1-propenyl-4β,7α-12,14-dioxatricyclo[9.3.0.$0^{4,7}$]tetradecane (VIIIa),** $[\alpha]_{580}^{21}$ –41.4° (*c* 1.4, $CHC1_3$). ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 0.97 s ($C^{13}H_3$), 0.99 s ($C^{14}H_3$), 1.12 s ($C^{15}H_3$), 1.26 m (H^2), 1.52–1.66 m (H^1 $H^{2'}$, H^3), 1.58 d.d (H^{10}, $J_{10,10'}$ 10, $J_{10,9}$ 8), 1.71 d.d ($C^{19}H_3$, $J_{19,18}$ 7, $J_{19,17}$ 1.5), 1.74 d.d ($H^{10'}$, J 10, $J_{10',9}$ 10)-, 1.66–1.76 m ($2H^6$), 1.94 d.d.d ($H^{3'}$, $J_{3',3}$ 14, $J_{3',2'}$ 10, $J_{3',2}$ 1.2), 2.01 br.d.t (H^7, $J_{7,7'}$ 14, $J_{7,6}$ 5), 2.35 br.d.d.d (H^9, $J_{9,1}$ 10, J 10, 8), 2.40 br.d.t ($H^{7'}$, J 14, $J_{7',6}$ 8), 3.60 t (H^5, $J_{5,6}$ 5), 4.94 br.s (H^{12}), 4.98 br.s ($H^{12'}$), 5.29 d (H^{16}, $J_{16,17}$ 7), 5.43 d.d.q (H^{17}, $J_{17,18}$ 15, J 7, 1.5), 5.79 d.q (H^{18}, J 15, 7).

Reaction of epoxide I with α-methacrolein. A suspension of 2 g of clay K-10, 0.6 g of epoxide **I**, and 1.2 g of aldehyde **IV** in 18 ml of dichloromethane was stirred for 70 min at 20°C. By column chromatography on SiO_2 (100–160μ) with gradient elution with hexane–ethyl ether (content of the latter from 1 to 100%) was isolated 0.14 g of a mixture of ketone **XV** and acetals **IXa, b** in the ratio 1.3 : 2.6 : 1 respectively, and also 0.24 g of alcohols mixture. The first mixture was repeatedly subjected to chromatography on column charged with SiO_2 (100–160 μ, from Russia), gradient elution with hexane–ethyl ether (from 0.5 to 1%). We isolated 0.007 g of acetal **IXa**, $[\alpha]_{580}^{21}$ –17.3 (c 1.05, CHCl3), and 0.04 g of acetal IXb, $[\alpha]_{580}^{20}$ –26.6° (*c* 7.0, $CHCl_3$).

13α(or 13β)-Isopropenyl-1,5,5-trimethyl8-methylene-4β,7α-12,14-dioxatricyclo[9.3.0.$0^{4,7}$]-tetradecane (IXa). ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 0.97 s ($C^{13}H_3$), 0.99 s (C^{14}H3), 1.14 s (C^{15}H3), 1.26 m (H^2), 1.50–1.67 m (H^1, $H^{2'}$, H^3), 1.59 d.d (H^{10}, $J_{10,10'}$ 10, $J_{10,9}$ 8), 1.69 d.d ($C^{19}H_3$, $J_{19,18}$ 1.5, $J_{19,18'}$ 1), 1.67– 1.77 m ($2H^6$), 1.75 d.d ($H^{10'}$, J 10, $J_{10',9}$ 10), 1.95 d.d.d ($H^{3'}$, $J44_{3',3}$ 14, $J_{3',2'}$ 10, $J_{3',2}$ 1.2), 2.02 br.d.t (H^7, $J_{7,7'}$ 14, $J_{7,6}$ 5), 2.34 br.d.d.d (H^9, $J_{9,}$ 10, J 10, 8), 2.40 br.d.d.d ($H^{7'}$, J 14, $J_{7',6}$ 8, $J_{7',6'}$ 6), 3.62 t (H^5, $J_{5,6}$ 5), 4.91 d.q (H^{18}, $J_{18,18'}$ 2, J 1.5), 4.93 br.s (H^{12}), 4.97 br.s ($H^{12'}$), 5.07 d.q ($H^{18'}$, J 2, 1), 5.27 c (H^{16}). Found: M 290.2250. $C_{19}H_{30}O_2$. Calculated: M 290.2246.

13β(or 13α)-Isopropenyl-1,5,5-trimethyl8-methylene-4β,7α-12,14-dioxatricyclo[9.3.0.$0^{4,7}$]-tetradecane (IXb). ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 0.96 s ($C^{13}H_3$), 0.99 s ($C^{14}H_3$), 1.10 s ($C^{15}H_3$), 1.22 m (H^2), 1.48–1.69 m (H^1, $H^{2'}$, H^3), 1.59 d.d

(H^{10}, $J_{10,10'}$ 10, $J_{10,9}$ 8), 1.72 d.d ($C^{19}H_3$, $J_{19,18}$ 1.5, $J_{19,18'}$ 1.5), 1.72–1.78 m ($2H^6$), 1.76 d.d ($H^{10'}$, J 10, $J_{10',9}$ 10), 1.93 d.d.d ($H^{3'}$, $J_{3',3}$ 14, $J_{3',2'}$ 9, $J_{3',2}$ 1.2), 2.07 br.d.t (H^7, $J_{7,7'}$ 14, $J_{7,6}$ 5), 2.36 br.d.d.d (H^9, $J_{9,1}$ 10, J 10, 8), 2.41 br.d.t ($H^{7'}$, J 14, $J_{7',6}$ 8), 3.59 t (H^5, $J_{5,6}$ 5), 4.95 d.d.d (H^{12}, $J_{12,12'}$ 1.5, $J_{12,7}$ 1.5, $J_{12,7'}$ 0.5), 4.98 d.q (H^{18}, $J_{18,18'}$ 2, J 1.5), 5.00 br.s ($H^{12'}$), 5.07 C (H^{16}), 5.12 d.q ($H^{18'}$, J 2, 1.5).

Reaction of epoxide I with acetone. A suspension of 1.2 g clay, 0.4 g of epoxide **I**, and 0.8 g of acetone in 12 ml of dichloromethane was stirred for 2 h at 20°C. By column chromatography on SiO_2 (100–160μ, from Russia) at gradient elution with hexane–ethyl ether (from 1 to 100%) was isolated 0.04 g (10%) of aldehyde **XIV**, 0.06 g (15%) of ketone **XV**, 0.07 g (13%) of acetal **X**, 0.02 g (5%) of alcohol **XVI**, 0.07 g (16%) of diol **XIII**, 0.13 g (32%) of alcohols mixture.

4,4,9-Trimethyltricyclo[6.2.2.0^{1,5}]dodec-9-en-2β-ol (XVI), $[\alpha]_{580}^{24}$ –19.7°(*c* 1.22, $CHCl_3$). ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 0.68 s ($C^{13}H_3$), 0.83 d.d.d.d (H^6, $J_{6,6'}$ 13, $J_{6,5}$ 13, $J_{6,7}$ 13, $J_{6,7'}$ 6), 0.93 c ($C^{14}H_3$), 1.05 d.d.d.d (H^7, J 13, $J_{7,7'}$ 13, $J_{7,6'}$ 5, $J_{7,8}$ 1), 1.20 d.d (H^5, J 13, $J_{5,6'}$ 3.5), 1.25 d.d.d.d ($H^{6'}$, $J_{13,5}$ 3.5, $J_{6',7'}$ 2), 1.41 d.d (H^3, $J_{3,3'}$ 12, $J_{3,2}$ 10), 1.39 m (H^{11}), 1.45 m (H^{12}), 1.47 m ($H^{11'}$), 1.70 d (C^{15}H3, $J_{15,10}$ 2), 1.73 m ($H^{7'}$), 1.75 m ($H^{12'}$), 1.82 d.d ($H^{3'}$, J 12, $J_{3',2}$ 6.5), 2.30 d.d.d.d.d (H^8, $J_{8,7'}$ 7, $J_{8,12'}$ 7, $J_{8,10}$ 1.5, $J_{8,7}$ 1, $J_{8,12}$ 1), 4.02 d.d (H^2, J 10, 6.5), 5.37 q.d (H^{10}, J 2, 1.5). Found: *m* 220.18267. $C_{15}H_{24}O$. Calculated: *m* 220.18270.

1,5,5,13,13-Pentamethyl-8-methylene-4β,7α-12,14-dioxatricyclo[9.3.0.^{4,7}]tetradecane (X), $[\alpha]_{580}^{19}$ –40.5° (*c* 8.9, $CHCl_3$). ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 0.93 s ($C^{13}H_3$), 0.96 s ($C^{14}H_3$), 1.04 s ($C^{15}H_3$), 1.22 m (H^2), 1.23 s and 1.33 s ($C^{17}H_3$, $C^{18}H_3$), 1.43–1.63 m (H^1, $H^{2'}$, H^3), 1.55 d.d (H^{10}, $J_{10,10'}$ 10, $J_{10,9}$ 8), 1.63–1.71 m ($2H^6$), 1.72 d.d ($H^{10'}$, J 10, $J_{10',9}$ 10), 1.85 br.d.d ($H^{3'}$, $J_{3',3}$ 14, $J_{3',2'}$ 10), 1.99 br.d.t (H^7, $J_{7,7'}$ 14, $J_{7,6}$ 6), 2.33 br.d.d.d (H^9, $J_{9,1}$ 10, J 10, 8), 2.36 br.d.d.d ($H^{7'}$, J 14, $J_{7',6}$ 8.5, $J_{7',6'}$ 6), 3.68 t (H^5, $J_{5,6}$ 5), 4.91 br.s (H^{12}), 4.95 br.s ($H^{12'}$). Found: *M* 278.2249. $C_{18}H_{30}O_2$. Calculated: *M* 278.2246.

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