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Rearrangements of Epoxides of Linalool and Nerolidyl Acetate in Acid Media

T. M. Khomenko, L. E. Tatarova, D. V. Korchagina, and V. A. Barkhash

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

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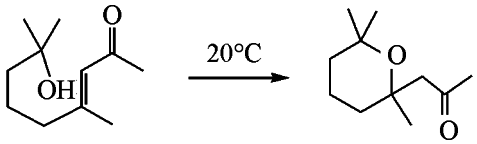
Abstract—The behavior of epoxides of linalool and *cis*-nerolidyl acetate was comparatively investigated in acids of various strength with the goal of establishing the effect of the structure of the initial compound and the medium character on the main direction of cationoid rearrangement. Linalool epoxides undergo cyclization of solid acid catalysts affording oxygen-containing heterocyclic compounds whereas the nerolidyl acetate epoxides yield the ketones originating from the opening of the epoxy ring followed by 1,2-hydride shift. 10,11-Epoxy derivative of *cis*-nerolidyl acetate affords 7-oxanorbornane as a minor product.

We investigated formerly the behavior of geraniol and nerol epoxides in liquid and on solid superacids. By an example of 2,3-epoxygeraniol we observed the changing place of the cationic center formation depending on the nature of the superacid; this fact resulted in alteration of the main direction of cationoid rearrangement [1]. Here we report on reactions with acids of 1,2- (**I**) and 6,7-epoxylinalool (**II**). Epoxides **Ia, b** (a mixture of diastereomers in ~1 : 0.2 ratio by ^{1}H NMR data) on β-zeolite at 20°C isomerized into a mixture of 2-*endo*- (**III**) and 2-*exo*- (**IV**) hydroxy-1-isopropyl-4-methyl-7-oxanorbornanes (56 and 28% respectively; here and hereinafter the content from GLC analysis of the reaction mixture). The alcohols **III** and **IV** are presumably formed along the following scheme (Scheme 1).

The heterocyclization of compounds **Ia, b** is apparently similar to the previously described heterocyclization reaction of hydroxyketone **V** [2] (Scheme 2).

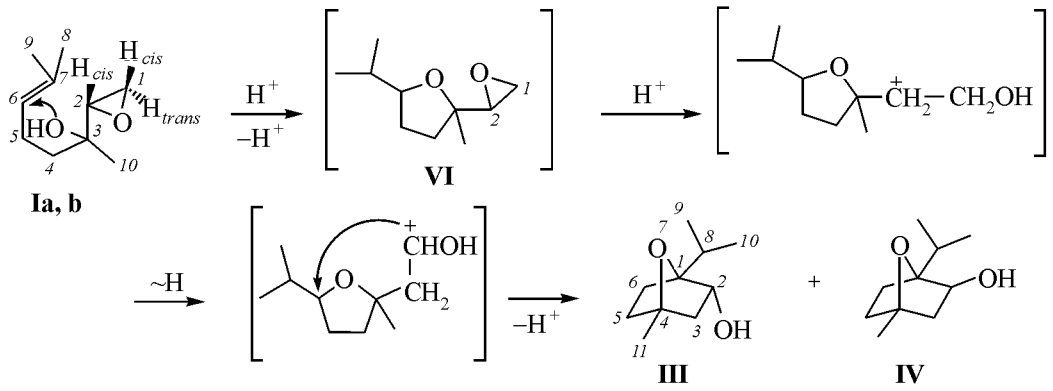
Scheme 2.



V

The opening of the epoxy ring should occur at the C^2–O bond of the intermediate compound **VI** for this ring commonly opens from the side of the carbon atom whose positive charge would be more delocalized after the rupture of C–O bond [3]. Likewise the process proceeds on zeolites [4]. The cleavage of the C^1–O bond would provide very unstable primary carbocation.

Scheme 1.



Ia, b **VI** **III** **IV**

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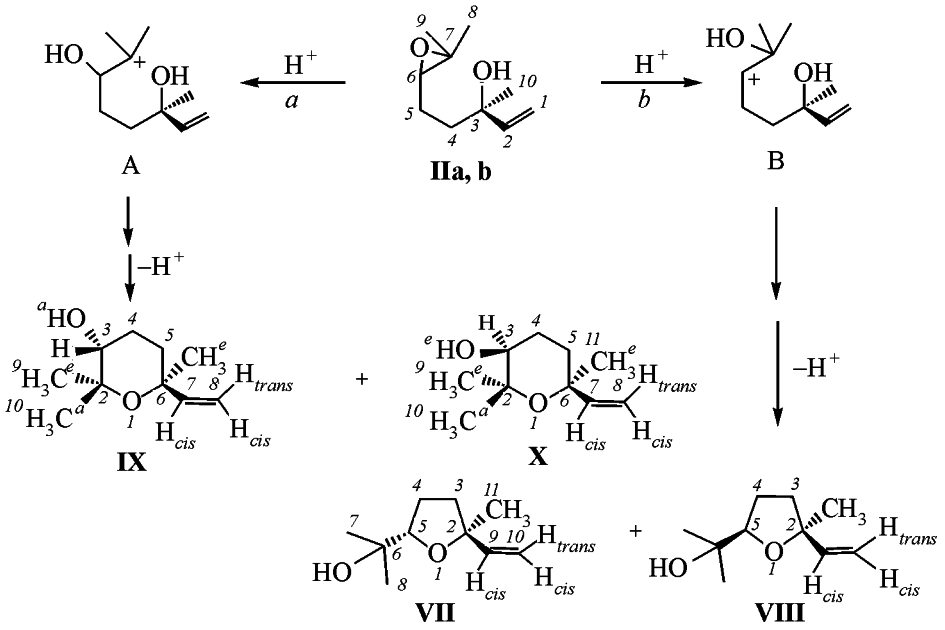
Scheme 3.



Epoxides **IIa, b** (a mixture of diastereomers in ~2.4 : 1 ratio by ^{1}H NMR data) reacted with the system HSO_3F–SO_2FCl at –100°C; after quenching with a mixture MeOH–Et_2O 2β-vinyl-5α-hydroxyisopropyl-2-methyltetrahydrofuran (**VII**) and 2β-vinyl-5β-hydroxyisopropyl-2-methyltetrahydrofuran (**VIII**) contained in the reaction mixture in 25 and 15% respectively were obtained. When the isomerization of epoxides **IIa, b** was performed in the presence of ZrO_2/SO_4^{2-} the resulting oxides mixture is more complicated. It contained compound **VII** (46% by GLC), **VIII** (26%), 6-vinyl-3α-hydroxy-2,2,6α-trimethyltetrahydropyran (**IX**) (19%), and 6-vinyl-3β-hydroxy-2,2,6α-trimethyltetrahydropyran (**X**) (9%) (Scheme 3).

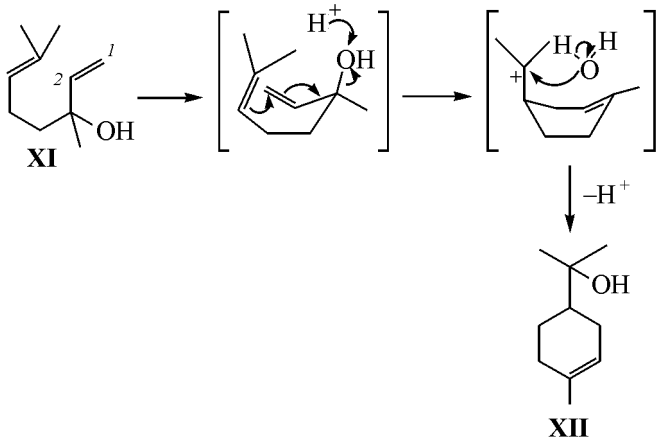
A specific feature of reactions occurring with compounds **IIa, b** on solid superacids is the opening of the epoxy ring along *a* and *b* pathways providing tertiary (A) and secondary (B) carbocations with prevalence of the second pathway (~7 : 3); therewith in the heterocyclization is used the hydroxy group of the initial alcohol **IIa, b**.

Thus the key moment in the rearrangement of 1,2- and 6,7-epoxy derivatives of linalool on solid catalysts (in contrast to isomerization of 2,3-epoxygeraniol [1]) is the heterocyclization stage at the expense of the oxygen atom of the hydroxy group. Therefore various oxygen-containing heterocycles were obtained, among them new alcohols **III, IV**.

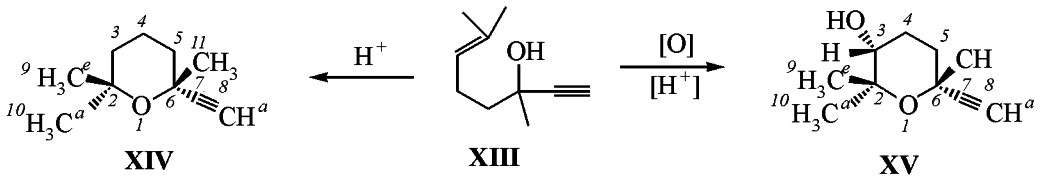
We previously pointed out by an example of epoxygeraniol rearrangements the importance of the reaction type leading to generation of the cationic center (protonation of the olefin or opening of the epoxy ring effected by the protic acid) for the direction of the rearrangement [1]. It turned out that the behavior of linalool (**XI**) on the solid superacid significantly differs from the rearrangements of its epoxides. Thus, alcohol **XI** on ZrO_2/SO_4^{2-} at room temperature afforded α-terpineol (**XII**) in agreement with the data on isomerization of compound **XI** in the aqueous citric acid [5].

Note that dehydrolinalool (**XIII**) under the same conditions furnishes a heterocyclization product,

Scheme 4.



Scheme 5.



XIV **XIII** **XV**

2,2,6β-trimethyl-6-ethynyltetrahydropyran (**XIV**). Thus is revealed the difference in behavior in the presence of solid superacid of compounds **XI** and **XIII** that differ in the structure by the multiplicity of the 1,2 bond. At the attempt to prepare 6,7-epoxide from dehydrolinalool by treating it with m-chloroperbenzoic acid a rearrangement occurs affording 3α-hydroxy-2,2,6β-trimethyl-6-ethynyltetrahydropyran (**XV**) (Scheme 5). Apparently the intermediately arising epoxide is unstable in acid medium.

The isomerization of 10,11 epoxy derivative of *cis*-nerolidyl acetate (**XVI**) analogous in structure to epoxides **IIa, b** gives quite unlike results: on TiO_2/SO_4^{2-} a mixture of 3-acetoxy-3,7.11-trimethyldodeca-1,6-dien-10-one (**XVII**) and 2-(3-acetoxy-3-methylpent-4-en-1-yl)-1,3,3-trimethyl-7-oxa-norbornanes (**XVIII**) forms in ~3 : 1 ratio (GLC). Thus after opening of the epoxy ring occur two processes: 1,2-hydride shift and heterocyclization; in the latter process unlike the case of epoxides **IIa, b** takes part the oxygen of the epoxide. Under the same conditions the 6,7-epoxide of *cis*-nerolidyl acetate **XIX** on TiO_2/SO_4^{2-} affords only the product of 1,2-hydride shift, 3-acetoxy-3,7,11-trimethyldodeca-1,10-dien-6-one (**XX**) (Scheme 6).

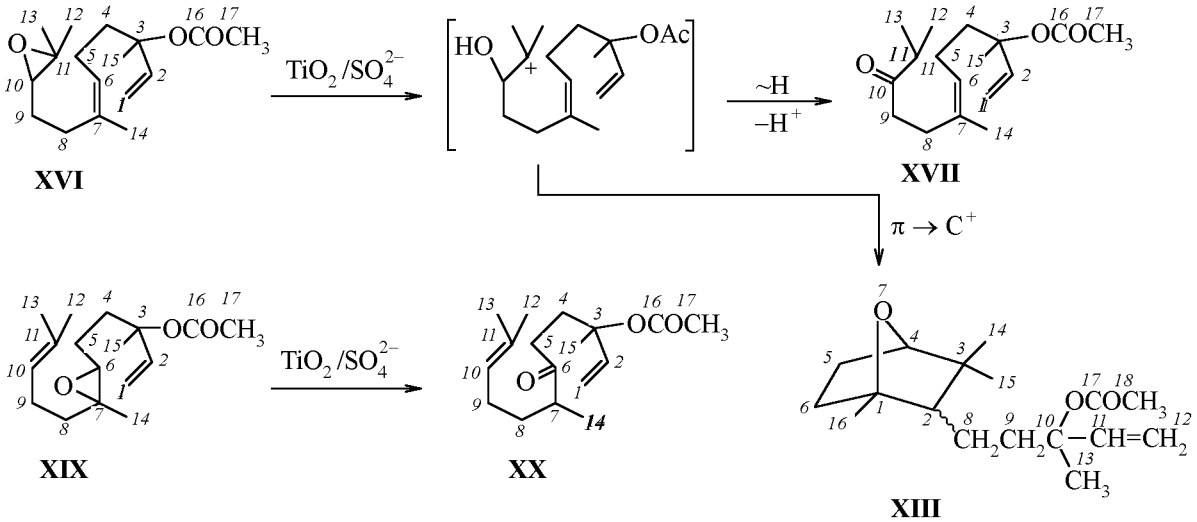
We earlier demonstrated [6] that cis-nerolidol (**XXI**) quite differently undergoes isomerization both in the system $HSO_3F–SO_2FCl$ at –110°C and in formic acid (Scheme 7).

Initial epoxides **IIa, b** (a mixture of diastereomers in ~2.4 : 1 ratio by ^{1}H NMR data) were prepared from linalool (**XI**) by reaction with monoperphthalic acid in a water solution of $NaHCO_3$. 1,2-Epoxylinalool (**Ia, b**, a mixture of diastereomers in ~1 : 0.2 ratio by ^{1}H NMR data) was obtained by reaction of alcohol **XI** with *t*-BuOOH + $VO(acac)_2$ [7] (Scheme 8).

Epoxides **XVI** and **XIX** were obtained by oxidizing *cis*-nerolidyl acetate (**XXII**) with *m*-chloroperbenzoic acid (Scheme 9).

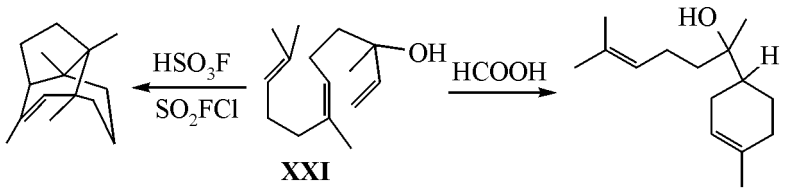
The structure of all newly prepared substances was established from ^{1}H and ^{13}C NMR spectra. Note some specific features in determining the structure of a number of compounds obtained. In the ^{1}H NMR spectrum of compound **III** the existence of remote *W* coupling constant between protons H^{6k} and H^2 ($^4J_{6k,2}$ 2 Hz) evidences the exo-position of the latter. In the ^{1}H spectrum of compound **IV** only two coupling constants for proton H^2 are observed: the coupling with protons H^{3k} and H^{3n} (*J* 7 and 2 Hz respectively),

Scheme 6.



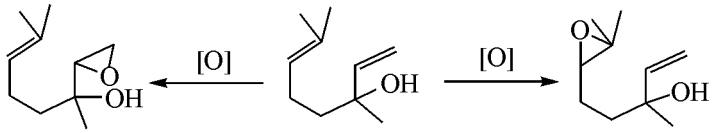
XVI **XVII** **XIX** **XX** **XIII**

Scheme 7.



XXI

Scheme 8



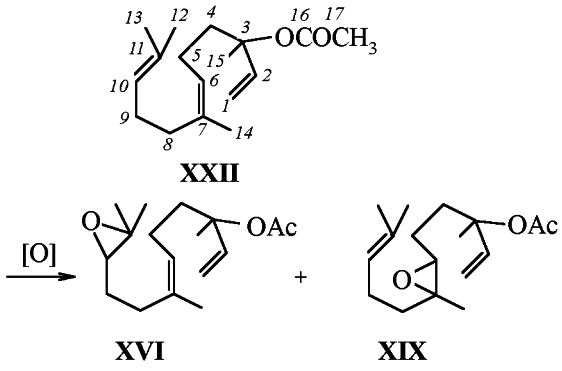
Ia, b **XI** **IIa, b**

therefore we attributed *endo*-position to H^2 proton. It is known [8] that in the spectra of norbornane and related structures the values of vicinal coupling constants are as a rule greater for *cis,diexo*-located protons (8.8–10 Hz) than for *cis,diendo*-located ones (J 6–9 Hz). The comparison of coupling constants between *cis*-located protons H^3 and H^2 in compound **III** ($J_{3k,2}$ 10 Hz) and **IV** ($J_{3n,2}$ 7 Hz) indicates the *exo*-position of H^2 proton in the former compound and its *endo*-position in the latter.

The comparison of ^{13}C NMR spectra of compounds **IX** and **X** with the corresponding spectra published in [9] shows that the hydroxy and vinyl groups are in trans-configuration in compound **IX** and in *cis*-configuration in compound **X**. We give the NMR spectral data for these compounds since there is no assignment of the signals in the published spectra.

The assignment of methyl group peaks in the ^1H and ^{13}C NMR spectra of compound **XV** and establishment of configuration for all substituents was done as follows. The decoupling from proton H^3 at 3.32 ppm

Scheme 9.



XXII

XVI **XIX**

results in appearance in the LRJMD spectrum alongside triplets at 26.48 and 38.96 ppm belonging to carbon atoms C^4 and C^5 and a singlet at 77.13 ppm corresponding to C^2 atom also of quartets at 29.74 and 19.27 ppm that may be assigned to *gem*-dimethyl groups C^9H_3 and $C^{10}H_3$. From the ^{13}C-^1H correlation spectrum on direct constants it was found that the signal at 19.27 ppm in the ^{13}C NMR spectrum corresponded to the methyl group peak at 1.40 ppm in the ^1H NMR spectrum; likewise the signal at 29.74 ppm in the former spectrum corresponded to that at 1.19 ppm in the latter. In the double resonance ^1H–^1H spectrum the decoupling from proton H^3 at 3.32 ppm caused narrowing of somewhat broadened signal of methyl group at 1.40 ppm evidencing the remote coupling between the axially located proton H^3 and the methyl group $C^{10}H_3$. The axial position of H^3 proton follows also from the values of vicinal coupling constants with two protons H^4 ($J_{3a,4a}$ 11.5 and $J_{3a,4e}$ 4.5 Hz). The downfield shift of proton signals in ^1H NMR spectrum from two methyl groups by ~0.2–0.3 ppm as compared with the peak of the third methyl group may be ascribed to the influence of the triple bond C^7–C^8. As seen from Dreiding models, the anisotropic effect for the $C^{10}H_3$ group may arise only if the ethynyl group take the axial position in the pyran ring. It may be concluded from the above reasoning that in compound **XV** the methyl group $C^{10}H_3$ and ethynyl group are in axial positions whereas the methyl groups C^9H_3 and $C^{11}H_3$ and also the OH group take the equatorial positions, and therefore the groups C–H and OH are cis with respect to each other.

Analogously to compound **XV** was performed the assignment of signals and determined the configuration of substituents in compound **XIV**: we took into account the similarity of chemical shifts of methyl

Table 1. ^{13}C NMR spectra of compounds **Ia, b, IIa, b, III, IV, IX, X, XIV, XV**, $CDCl_3$–CCl_4 (1 : 1), δ_C, ppm

Carbon no.	**Ia**	**Ib**	**IIa**	**IIb**	**III**
1	42.90 d	43.91 t	111.94 t	111.81 t	89.83 s
2	57.46 d	57.64 d	144.73 d	144.75 d	77.54 d
3	69.00 s	68.76 s	72.47 s	72.47 s	42.06 t
4	41.24 t	38.67 t	38.60 t	38.53 t	84.54 s
5	22.16 t	21.91 t	23.44 t	23.45 t	33.33 t
6	124.24 d	124.39 d	64.28 d	64.18 d	29.28 t
7	131.42 s	131.42 s	58.81 s	58.44 s	–
8	17.61 q	17.61 q	18.65 q	18.62 q	33.15 d
9	25.66 q	26.09 q	24.75 q	24.77 q	18.00 q
10	22.76 q	22.76 q	28.11 q	27.88 q	17.65 q
11					19.20 q

Carbon no.	**IV**	**IX**	**X**	**XIV**	**XV**, $^1J_{C,H}$, Hz
1	88.40 s	–	–	–	–
2	76.72 d	75.07 s	75.89 s	73.42 s	77.13 s
3	45.37 t	70.96 d	74.84 d	36.48 t	74.82 d, 140
4	85.46 s	24.34 t	25.90 t	17.56 t	26.48 t, 129
5	32.56 t	27.70 t	32.67 t	38.30 t	38.96 t, 130
6	32.85 t	73.27 s	73.27 s	67.04 s	66.69 s
7	–	147.16 d	146.61 d	89.08 s	88.45 s
8	32.56 d	110.17 t	110.44 t	71.31 d	72.03 d, 248
9	18.16 q	27.33 q	29.64 q	33.11 q	29.74 q, 129
10	18.16 q	26.37 q	20.77 q	25.25 q	19.27 q, 126
11	16.37 q	30.90 q	31.83 q	32.66 q	32.13 q, 129

Table 2. ^{13}C NMR spectra of compounds **XVI, XVII, XVIIIa,b, XIX, XX, XXII**, $CDCl_3$, δ_C, ppm

Carbon no.	**XVI**	**XVII**	**XVIIIa**	**XVIIIb**	**XIX**	**XX**	**XXII**
1	113.04 t	113.00 t	87.92 s	87.92 s	113.44 t	113.51 t	112.91 t
2	141.64 d	141.63 d	56.98 d	56.94 d	141.18 d	141.03 d	141.67 d
3	82.65 s	82.63 s	41.66 s	41.66 s	82.42 s	82.21 s	82.68 s
4	39.77 t	39.66 t	86.07 d	86.07 d	36.53 t	33.51 t	39.92 t
5	22.00 t	21.94 t	26.59 t	26.59 t	23.02 t	35.41 t	21.97 t
6	125.03 d	125.22 d	28.57 t	28.57 t	64.46 d	213.64 s	124.38 d
7	134.44 s	134.18 s	–	–	60.88 s	45.81 d	135.35 s
8	28.30 t	25.79 t	20.78 t	20.78 t	32.73 t	32.88 t	31.74 t
9	27.25 t	38.53 t	39.61 t	39.63 t	23.98 t	25.58 t	26.39 t
10	63.91 d	214.14 s	82.84 s	82.84 s	123.60 d	123.65 d	124.15 d
11	58.17 s	40.73 d	141.52 d	141.58 d	131.90 s	132.13 s	131.36 s
12	18.57 q	18.08 q	113.21 t	113.17 t	17.51 q	17.57 q	17.44 q
13	24.77 q	18.08 q	21.31 q	21.31 q	25.57 q	25.58 q	25.54 q
14	23.17 q	23.02 q	32.40 q	32.40 q	22.14 q	16.33 q	23.20 q
15	23.50 q	23.53 q	19.71 q	19.71 q	23.55 q	23.63 q	23.39 q
16	169.79 s	169.79 s	23.36 q	23.36 q	169.79 s	169.71 s	169.72 s
17	22.00 q	21.94 q	169.74 s	169.74 s	22.03 q	22.03 q	21.97 q
18			22.04 q	22.04 q			

groups resonances in the ^1H NMR spectrum and the narrowing of the methyl group signal at 1.43 ppm in the double resonance ^1H–^1H spectrum at decoupling from proton H^{3a} giving signal at 1.30 ppm.

^{13}C NMR spectra of compounds **VII** and **VIII** are consistent with published data [10]. According to ^1H and ^{13}C NMR spectra acetate **XVIII** is a mixture of compounds **XVIIIa, b** and **XVIIIc, d** in ~4:1 ratio. These compounds presumably are *exo*- and *endo*-isomers at carbon C^2, and each of them is a mixture of two diastereomers.

Compounds **XI, XIII**, and **XXII** were identified by comparing their NMR spectra with the published data [11].

EXPERIMENTAL

^1H 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. As internal reference served the signals of chloroform (δ 7.24, δ_C 76.90 ppm). The structure of compounds was established from NMR spectra basing on the coupling constants analysis with the use of double resonance spectra ^1H–^1H, and from the ^{13}C NMR spectra. 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 differential spectra modulated with remote coupling ^{13}C–^1H (LRJMD, experimental conditions optimized for remote coupling constants J_{CH} 10 Hz). For compounds **IX**, **XIV**, **XV** were additionally recorded two-dimensional heteronuclear correlation spectra ^{13}C–^1H (COSY, with the use of direct coupling constant $^1J_{CH}$ 135 Hz). The ^{13}C NMR spectra are presented in Tables 1 and 2.

The purity of the initial compounds was checked and the reaction products were analyzed by GLC on Biokhrom-1 chromatograph equipped with flameionization detector and two columns: (a) glass capillary column 530000 × 0.26 mm, stationary phase XE-60; (b) capillary quartz column 13000 × 0.22 mm, stationary phase SE-54, carrier gas helium, oven temperature 80–180°C. Elemental composition of the newly synthesized compounds was estimated from the high resolution mass spectra obtained on Finnigan MAT 8200 instrument. The GC/MS analysis was carried out on Hewlett Packard 618100A instrument. The optical rotation was measured on spectrometer Polomat A in $CHCl_3$.

Preparation methods for sulfated zirconium and titanium oxides are described in [12] and [13] respectively. The solvent was purified by passing through a column packed with calcined alumina.

Rearrangements of diastereomers of 1,2-epoxylinalool (Ia, b). Initial alcohol **XI** was purified by successive chromatography first on Al_2O_3 (II activity grade, gradient elution with hexane containing from 0 to 50% of ethyl ether), then on SiO_2 (100–160μ, the same eluent); $[\alpha]_{580}^{17}$ +15.45° (*c* 2.20, $CHCl_3$). To a solution of 0.82 g of alcohol **XI** in 7 ml of benzene was added 0.02 g of $VO(acac)_2$. At room temperature while stirring was added 1 ml of *t*-BuOOH (70%), then the mixture was boiled at stirring for 14 h. The reaction mixture was treated with water solution of $NaHCO_3$, washed with water, and dried with Na_2SO_4. On evaporating the solvent 0.65 g of residue was obtained containing 31% of compound **XI**, and 37% of compounds **Ia, b** (GLC). Chromatography of the residue on SiO_2 (100–160μ, eluent hexane containing from 10 to 50% of ethyl ether) afforded 0.23 g of initial alcohol **XI** and 0.163 g of epoxides **Ia, b** in ~1:0.2 ratio according to ^1H NMR data. $[\alpha]_{580}^{18}$ +6.09° (*c* 2.30, $CHCl_3$). Spectrum ^1H NMR of compound **Ia**, δ, ppm (*J*, Hz): 1.11 s ($C^{10}H_3$), 1.55 m ($2H^4$), 1.57 br.d (C^8H_3, $J_{8,6}$ 1.5), 1.63 d.t (C^9H_3, $J_{9,6}$ 1.5, $J_{9,5}$ 1), 1.86 br.s (OH), 2.05 m ($2H^5$), 2.59 d.d (H^{1cis}, $J_{1cis,1trans}$ 5.5, $J_{1cis,2cis}$ 4) and 2.67 d.d (H^{1trans}, *J* 5.5, $J_{1trans,2cis}$ 3) system *AB*, 2.85 d.d (H^{2cis}, *J* 4, 3), 5.04 t.q.q (H^6, $J_{6,5}$ 7, *J* 1.5, 1.5). For minor isomer **Ib** some signals both in ^1H and ^{13}C NMR spectra coincide with the corresponding signals of the main isomer **Ia**; in the ^1H NMR spectrum were individually observed only the following signals, δ, ppm (*J*, Hz): 1.10 s ($C^{10}H_3$), 1.47 m ($2H^4$), 1.76 br.s (OH), 2.63 d.d (H^{1cis}, $J_{1cis,1trans}$ 5.5, $J_{1cis,2cis}$ 4), 2.76 d.d (H^{1trans}, *J* 5.5, $J_{1trans,2cis}$ 3), 2.80 d.d (H^{2cis}, *J* 4, 3), 5.03 t.q.q (H^6, $J_{6,5}$ 7, $J_{6,8}$ 1.5, $J_{6,9}$ 1.5).

A solution of 0.075 g of epoxides **Ia, b** in 10 ml of CH_2Cl_2 and 0.145 g of β-zeolite (preliminary calcined for 2 h at 500°C) was stirred for 1 h at 20°C. After workup we obtained 0.07 g of products mixture that was applied to a column packed with Al_2O_3 of IV activity grade (eluent ethyl ether). The residue after evaporation of the solvent (0.035 g, 56% of **III**, 28% of **IV** by GLC data) was subjected to column chromatography on SiO_2 (40–100μ), eluent hexane containing from 0 to 50% of ethyl ether. We isolated 0.008 g of alcohol **III** and 0.004 g of alcohol **IV**. Alcohol **III**, $[\alpha]_{580}^{22}$ +6.48° (*c* 1.06, $CHCl_3$). Found

M^+ 170.13050. $C_{10}H_{18}O_2$. Calculated: *M* 170.13067. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.891 d and 0.893 d (C^9H_3, $C^{10}H_3$, *J* 7), 1.24 d.d (H^{3n}, $J_{3n,3k}$ 13, $J_{3n,2k}$ 4), 1.34 d.d.d.d (H^{6k}, $J_{6k,6n}$ 12, $J_{6k,5k}$ 12, $J_{6k,5n}$ 5.5, $J_{6k,2q}$ 2), 1.35 s ($C^{11}H_3$), 1.59 d.d.d.d (H^{5k}, $J_{5k,5n}$ 12, *J* 12, $J_{5k,6n}$ 5.5, $J_{5k,3k}$ 3), 1.63 m (H^{5n}), 1.81 br.s (OH), 1.91 septet (H^8, *J* 7), 2.00 d.d.d.d (H^{3k}, *J* 13, $J_{3k,2k}$ 10, *J* 3, 1), 2.27 d.d.d (H^{6n}, *J* 12, $J_{6n,5n}$ 8, *J* 5.5), 3.86 d.d.d (H^{2k}, *J* 10, 4, 2). Alcohol **IV**, $[\alpha]_{580}^{22}$ −2.47° (*c* 0.46, $CHCl_3$). Found M^+ 170.13067. $C_{10}H_{18}O_2$. Calculated *M* 170.13067. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.93 d, 0.95 d (C^9H_3, $C^{10}H_3$, *J* 7), 1.32 d.d.d (H^{3k}, $J_{3k,3n}$ 13, $J_{3k,5k}$ 3, $J_{3k,2n}$ 2), 1.38 s ($C^{11}H_3$), 1.36–1.59 m ($2H^5$, $2H^6$), 2.02 d.d (H^{3n}, *J* 13, $J_{3n,2n}$ 7), 2.03 septet (H^8, *J* 7), 3.66 d.d (H^{2n}, *J* 7, 2).

Rearrangements of diastereomers of 6,7-epoxylinalool (IIa, b). To a mixture of 1.04 g of alcohol **XI** and 195 ml of 0.25 M water solution of $NaHCO_3$ was added 66 ml of 0.15 M water solution of monoperphthalic acid. The mixture was stirred for 2 h at 0°C. After common workup 0.56 g of products mixture was obtained (69% of epoxides **IIa, b** by GLC data). The mixture was subjected to column chromatography on SiO_2 (Czechia, 40–100μ), eluent hexane containing from 0 to 50% of ethyl ether. We isolated 0.22 g of epoxides **IIa, b** (2.4 : 1, ^{1}H NMR data). ^{1}H NMR spectrum of epoxide **IIa**, δ, ppm (*J*, Hz): 1.20 s ($C^{10}H_3$), 1.22 s, 1.23 s (C^8H_3, C^9H_3), 1.41–1.72 m ($2H^4$, $2H^5$), 2.16 br.s (OH), 2.63 m (H^6), 4.98 d.d (H^{1cis}, $J_{1cis,2cis}$ 10.5, $J_{1cis,1trans}$ 1.5), 5.15 d.d (H^{1trans}, $J_{1trans,2cis}$ 17.5, *J* 1.5), 5.79 d.d (H^2, *J* 17.5, 10.5). ^{1}H NMR spectrum of epoxide **IIb**, δ, ppm (*J*, Hz): 1.20 s ($C^{10}H_3$), 1.22 s, 1.23 s (C^8H_3, C^9H_3), 1.41–1.72 m ($2H^4$, $2H^5$), 1.94 br.s (OH), 2.63 m (H^6), 4.97 d.d (H^{1cis}, $J_{1cis,2cis}$ 10.5, $J_{1cis,1trans}$ 1.5), 5.14 d.d (H^{1trans}, $J_{1trans,2cis}$ 17.5, *J* 1.5), 5.82 d.d (H^2, *J* 17.5, 10.5).

To a suspension of 0.32 g of ZrO_2/SO_4^{2-} (preliminary calcined for 2 h at 500°C) in 10 ml of CH_2Cl_2 was added a solution of 0.18 g of epoxides **IIa, b** in 2 ml of CH_2Cl_2. The stirring at 0°C continued for 0.5 h. After workup of the reaction mixture and passing of the residue through a column packed with Al_2O_3 (of IV activity grade, elution with hexane–ethyl ether, 1 : 1) we obtained 0.148 f of mixture containing by GLC data: compound **VII**, 46%; compound **VIII**, 26%; compound **IX**, 19%, and compound **X**, 9%. The mixture was subjected to column chromatography on SiO_2 (40–100μ), eluent hexane containing from 0 to 30% of ethyl ether. We isolated 0.022 g of oxide **VII**, 0.003 g of oxide **VIII**, 0.025 g of oxide **IX**, 0.009 g of oxide **X**, and 0.026 g of a mixture of compounds **VII** and **VIII**.

Compound **VII**, $[\alpha]_{580}^{20}$ −1.55° (*c* 1.93, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.07 s and 1.18 s (C^7H_3, C^8H_3), 1.28 s ($C^{11}H_3$), 1.68 m (H^3), 1.72–1.85 m ($2H^4$), 1.85 m ($H^{3'}$), 1.89 br.s (OH), 3.71 t (H^5, $J_{5,4}$ 7), 4.93 d.d (H^{10cis}, $J_{10cis,9cis}$ 10.5, $J_{10cis,10trans}$ 1.5), 5.13 d.d ($H^{10trans}$, $J_{10trans,9cis}$ 17.5, *J* 1.5), 5.80 d.d (H^{9cis}, *J* 17.5, 10.5).

Compound **VIII**, $[\alpha]_{580}^{24}$ +2.63° (*c* 1.33, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.09 s, 1.20 s (C^7H_3, C^8H_3), 1.29 s ($C^{11}H_3$), 1.76 m (H^3), 1.80–1.89 m ($2H^4$), 1.90 m ($H^{3'}$), 3.80 t (H^5, $J_{5,4}$ 7), 4.97 d.d (H^{10cis}, $J_{10cis,9cis}$ 11, $J_{10cis,10trans}$ 1.5), 5.15 d.d ($H^{10trans}$, $J_{10trans,9cis}$ 17.5, *J* 1.5), 5.93 d.d (H^9, *J* 17.5, 11).

Compound IX, $[\alpha]_{580}^{23}$ −8.60° (*c* 2.21, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.13 s, 1.17 s (C^9H_3, $C^{10}H_3$), 1.15 s (C^{11}H3), 1.63 m (H^4), 1.67–1.73 m ($2H^5$), 1.81 br.s (OH), 1.88 m ($H^{4'}$), 3.30 m (H^3), 4.88 d.d (H^{8cis}, $J_{8cis,7cis}$ 11, $J_{8cis,8trans}$ 1.2), 4.95 d.d (H^{8trans}, $J_{8trans,7cis}$ 18, *J* 1.2), 5.85 d.d (H^{7cis}, *J* 18, 11).

Compound X, $[\alpha]_{580}^{25}$ −3.70° (*c* 1.08, $CHCl_3$). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.11 s ($C^{11}H_3$), 1.12 s ($C^{10}H_3$), 1.18 s(C^9H3), 1.53 m (H^5), 1.59–1.69 m ($2H^4$), 2.08 m ($H^{5'}$), 3.35 m (H^3), 4.93 d.d (H^{8trans}, $J_{8trans,7cis}$ 18, $J_{8trans,8cis}$ 1), 4.94 d.d (H^{8cis}, $J_{8cis,7cis}$ 11, *J* 1), 5.92 d.d. (H^{7cis}, *J* 18, 11).

A solution of 0.077 g of epoxides **IIa, b** in 0.3 ml of SO_2FCl was added at −100°C to a solution of 0.87 g of HSO_3F in 1.7 ml of SO_2FCl. The reaction mixture was treated with a mixture of 10 ml of methanol and 4 ml of ethyl ether, neutralized with 17% water solution of Na_2CO_3, the reaction products were extracted with ethyl ether, the extract was dried on $MgSO_4$, and the solvent was evaporated. The residue was passed through a column packed with Al_2O_3 (of IV activity grade, eluent ethyl ether). We obtained 0.055 g of products mixture containing 27% of compound **VII** and 16% of compound **VIII** according to GC/MS data.

Linalool (XI) rearrangements. To a suspension of 0.3 g of ZrO_2/SO_4^{2-} (preliminary calcined for 2 h at 500°C) in 5 ml of CH_2Cl_2 was added a solution of 0.15 g of linalool (**XI**) in 1 ml of CH_2Cl_2, and the

mixture was stirred for 1 h at 20°C. After a workup and chromatography on a column packed with Al_2O_3 (of IV activity grade, eluent ethyl ether) we obtained 0.108 g of products mixture containing 55% of compound **XII** (GLC). The latter was subjected to chromatography on SiO_2 (40–100μ), eluent hexane containing from 0 to 50% of ethyl ether. We isolated 0.017 g of compound **XII**, $[\alpha]_{580}^{25}$ −2.38° (*c* 1.68, $CHCl_3$).

Dehydrolinalool (XIII) rearrangements. To a suspension of 0.34 g of ZrO_2/SO_4^{2-} (preliminary calcined for 2 h at 500°C) in 10 ml of CH_2Cl_2 was added a solution of 0.17 g of dehydrolinalool (**XIII**) in 2 ml of CH_2Cl_2, and the mixture was stirred for 0.5 h at 20°C. After a workup and chromatography on a column packed with Al_2O_3 (of IV activity grade, eluent ethyl ether) we obtained 0.155 g of products mixture containing 57% of compound **XIV** (GLC). The latter was subjected to chromatography on SiO_2 (40–100μ), eluent hexane containing from 0 to 50% of ethyl ether. We isolated 0.032 g of oxide **XIV**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.15 s (C^9H_3), 1.30 d.d.d.q (H^{3a}, $J_{3a,3e}$ 13, $J_{3a,4a}$ 13, $J_{3a,4e}$ 3.5, $J_{3a,10}$ 1), 1.35 d.d.d (H^{5a}, $J_{5a,5e}$ 13, $J_{5a,4a}$ 13, $J_{5a,4e}$ 3.5), 1.42 s ($C^{11}H_3$), 1.43 br.s ($C^{10}H_3$), 1.52 d.d.d.d (H^{3e}, *J* 13, 3.5, $J_{3e,4e}$ 3.5, $J_{3e,5e}$ 1.5), 1.59 d.d.d.d.d (H^{4e}, *J* 13, 3.5, 3.5, 3.5, $J_{4e,5e}$ 3.5), 1.81 d.d.d.d.d (H^{5e}, *J* 13, 3.5, 1.5, $J_{5e,4a}$ 3.5), 1.98 d.d.d.d.d (H^{4a}, *J* 13, 13, 13, 3.5, 3.5), 2.28 s (H^8).

To 0.092 g of dehydrolinalool (**XIII**), 4 ml of CH_2Cl_2, and 2 ml of saturated water solution of $NaHCO_3$ at 0°C was added 0.14 g of 80% *m*-$ClC_6H_4CO_3H$ [14], and the mixture was stirred at 0°C for 1 h. After workup we obtained 0.078 g of compounds **XIII** and **XV** in ~1:1 ratio (GLC). By column chromatography on silica gel (40–100μ, eluent hexane containing from 0 to 30% of ethyl ether) was isolated 0.13 g of initial alcohol **XIII** and 0.014 g of tetrahydropyran derivative **XV**. Compound **XV**. Found M^+ 168.11486. $C_{10}H_{16}O_2$. Calculated: *M* 168.11502. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.19 s (C^9H_3), 1.40 br.s ($C^{10}H_3$), 1.41 s ($C^{11}H_3$), 1.58 d.d.d (H^{5a}, $J_{5a,5e}$ 13, $J_{5a,4a}$ 13, $J_{5a,4e}$ 3.5), 1.72 d.m (H^{4e}, $J_{4e,4a}$ 13, $J_{4e,3a}$ 4.5, $J_{4e,5a}$ 3.5, $J_{4e,5e}$ 3.5), 1.93 d.d.d.d (H^{4a}, *J* 13, 13, $J_{4a,3a}$ 11.5, $J_{4a,5e}$ 3.5), 1.97 m (H^{5e}), 2.28 s (H^8), 3.32 d.d (H^{3a}, *J* 11.5, 4.5).

Rearrangements of *cis*-nerolidyl acetate (XXII) epoxides. Original acetate **XXI** was prepared from *cis*-nerolidol (**XXI**) by procedure from [15] in 97% yield. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.51 s ($C^{15}H_3$), 1.58 br.s ($C^{12}H_3$), 1.65 m and 1.66 br.s ($C^{13}H_3$, $C^{14}H_3$), 1.73 m and 1.79 m ($2H^4$), 1.90–2.06 m ($2H^5$, $2H^8$, $2H^9$), 1.97 s ($C^{17}H_3$), 5.06 t.m (H^6, $J_{6,5}$ 7), 5.08 t.m (H^{10}, $J_{10,9}$ 7), 5.08 d.d (H^{1cis}, $J_{1cis,2cis}$ 11, $J_{1cis,1trans}$ 1.2), 5.11 d.d (H^{1trans}, $J_{1trans,2cis}$ 17.5, *J* 1.2), 5.93 d.d (H^2, *J* 17.5, 11).

To 2 g of acetate **XXII**, 15 ml of CH_2Cl_2, and 40 ml of 7% water solution of $NaHCO_3$ at room temperature while stirring was added 2.15 g of 80% *m*-$ClC_6H_4CO_3H$. The stirring was continued for 1.5 h, and the reaction mixture was poured into a water–ether mixture. After a common workup we obtained 1.92 g of a mixture containing the original acetate, 10,11-epoxide **XVI**, 6,7-epoxide **XIX**, and a mixture of diepoxides in a ratio 1:3.2:2.1:1.6 (GLC). By column chromatography on silica gel (40–100μ, eluent pentane containing from 1 to 5% of ethyl ether) was afforded 1.03 g (49%) of a mixture of epoxides **XVI** and **XIX** in 2.2:1 ratio (GLC), 0.4 g (17.6%) of diepoxides mixture, and 0.24 g (12%) of original acetate (**XXII**). The repeated chromatography of the monoepoxides mixture on SiO_2 under the same conditions we isolated compounds **XVI** and **XIX** in the individual state. ^{1}H NMR spectrum of epoxide **XVI**, δ, ppm (*J*, Hz): 1.24 s, 1.28 s ($C^{12}H_3$, $C^{13}H_3$), 1.51 s ($C^{15}H_3$), 1.53–1.65 m ($2H^9$), 1.66 d.t ($C^{14}H_3$, $J_{14,6}$ 1.5, $J_{14,5}$ 1.5), 1.73 m and 1.84 m ($2H^4$), 1.96 m ($2H^5$), 1.97 s ($C^{17}H_3$), 2.05–2.19 m ($2H^8$), 2.67 t (H^{10}, $J_{10,9}$ 6.5), 5.09 d.d (H^{1cis}, $J_{1cis,2cis}$ 11, $J_{1cis,1trans}$ 1), 5.11 br.t (H^6, $J_{6,5}$ 7), 5.12 d.d (H^{1trans}, $J_{1trans,2cis}$ 17.5, *J* 1), 5.93 d.d (H^2, *J* 17.5, 11). ^{1}H NMR spectrum of epoxide **XIX**, δ, ppm (*J*, Hz): 1.27 s ($C^{14}H_3$), 1.44 d.d.d (H^8, $J_{8,8'}$ 13.5, $J_{8,9}$ 9, $J_{8,9'}$ 7), 1.51 m ($2H^5$), 1.54 s ($C^{15}H_3$), 1.60 br.s ($C^{12}H_3$), 1.67 br.s ($C^{13}H_3$), 1.89 m and 1.97 m ($2H^4$), 1.98 s ($C^{17}H_3$), 2.08 mm($2H^9$), 2.66 t (H^6, $J_{6,5}$ 6.5), 5.09 t.q.q (H^{10}, $J_{10,9}$ 7, $J_{10,12}$ 1.5, $J_{10,13}$ 1.5), 5.11 d.d (H^{1cis}, $J_{1cis,2cis}$ 11, $J_{1cis,1trans}$ 1), 5.14 d.d (H^{1trans}, $J_{1trans,2cis}$ 17.5, *J* 1), 5.91 d.d (H^2, *J* 17.5, 11).

A mixture of 0.038 g of epoxide **XIX**, 0.07 g of TiO_2/SO_4^{2-}, and 5 ml of CH_2Cl_2 was stirred for 15 min at 20°C. After common workup we obtained 0.019 g of a mixture containing ketone **XX** and original compound **XIX** in 8:1 ratio (GLC). By column chromatography on silica gel (40–100μ, eluent pentane containing from 3 to 4% of ethyl ether) was isolated 0.012 g of ketone **XX**. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 1.04 d ($C^{14}H_3$, $J_{14,7}$ 7), 1.32 d.m (H^8, $J_{8,8'}$ 13.5), 1.56 br.s ($C^{12}H_3$), 1.66 br.s

($C^{13}H_3$), 1.67 d.m ($H^{8'}$, J 13.5), 1.92 m ($2H^9$), 1.96 m and 2.11 m ($2H^4$), 1.99 s ($C^{17}H_3$), 2.33–2.48 m ($2H^5$), 2.50 d.d.q (H^7, $J_{7,8}$ 7, $J_{7,8'}$ 7, J 7), 5.04 t.q.q (H^{10}, $J_{10,9}$ 7, $J_{10,12}$ 1.5, $J_{10,13}$ 1.5), 5.11 d.d (H^{1cis}, $J_{1cis,2cis}$ 11, $J_{1cis,1trans}$ 1), 5.12 br.d (H^{1trans}, $J_{1trans,2cis}$ 17.5), 5.89 d.d (H^2, J 17.5, 11).

To a suspension of 0.1 g of TiO_2/SO_4^{2-} (preliminary calcined for 3 h at 400°C) in 3.5 ml of CH_2Cl_2 was added 0.06 g of epoxides **XVI** and **XIX** mixture (2.6 : 1, GLC), and stirring was carried on for 15 min at 20°C. The catalyst was filtered off, the solvent was distilled off, an 0.056 g of raw product was obtained. The product was passed through a column packed with SiO_2 (40–100μ, eluent pentane containing from 10% of ethyl ether) to afford 0.04 g of a mixture containing acetates **XVIII**, ketone **XVII**, and ketone **XX** in 1 : 3.1 : 1.8 ratio (GLC). The mixture was subjected to repeated chromatography on SiO_2 (40–100μ, eluent pentane containing from 5 to 7% of ethyl ether) to yield individual compounds **XVII** and **XX** and a mixture of acetates **XVIII**. ^{1}H NMR spectrum of ketone **XVII**, δ, ppm (J, Hz): 1.06 d ($C^{12}H_3$, $C^{13}H_3$, J 7), 1.49 s ($C^{15}H_3$), 1.62 d.t ($C^{14}H_3$, $J_{14,6}$ 1.5, $J_{14,5}$ 1.2), 1.72 m and 1.82 m ($2H^4$), 1.93 s ($2H^5$), 1.96 s ($C^{17}H_3$), 2.21 m ($2H^8$), 2.45 s ($2H^9$), 2.57 septet (H^{11}, J 7), 5.07 d.d (H^{1cis}, $J_{1cis,2cis}$ 11, $J_{1cis,1trans}$ 1), 5.08 br.t (H^6, $J_{6,5}$ 7), 5.11 d.d (H^{1trans}, $J_{1trans,2cis}$ 17.5, J 1), 5.92 d.d (H^2, J 17.5, 11). ^{1}H NMR spectrum of acetates **XVIIIa, b**, δ, ppm (J, Hz): 0.844 s and 0.841 s ($C^{15}H_3$), 1.033 s ($C^{14}H_3$), 1.348 s and 1.345 s ($C^{13}H_3$), 1.512 s ($C^{16}H_3$), 1.985 s ($C^{18}H_3$), 3.75 d (H^4, $J_{4,5q}$ 5), 5.107 d.d and 5.103 d.d (H^{12cis}, $J_{12cis,11cis}$ 11, $J_{12cis,12trans}$ 1), 5.123 d.d and 5.125 d.d ($H^{12trans}$, $J_{12trans,11cis}$ 17.5, J 1), 5.926 d.d and 5.929 d.d (H^{11}, J 17.5, 11), 1.07–1.20 m and 1.43–2.05 s (other protons). ^{1}H NMR spectrum of acetates **XVIIIc, d**, δ, ppm (J, Hz): 0.869 s, 0.876 s, 1.014 s ($C^{14}H_3$, $C^{15}H_3$), 1.282 s ($C^{13}H_3$), 1.503 s ($C^{16}H_3$), 1.975 s ($C^{18}H_3$), 3.68 d (H^4, $J_{4,5}$ 5), 5.092 d.d (H^{12cis}, $J_{12cis,11cis}$ 11, $J_{12cis,12trans}$ 1), 5.117 d.d ($H^{12trans}$, $J_{12trans,11cis}$ 17.5, J 1), 5.930 d.d and 5.934 d.d (H^{11}, J 17.5, 11). In the ^{13}C NMR spectrum of isomers **XVIIIc, d** we failed to separate and attribute all signals, δ_C, ppm: 18.75 q, 21.37 t, 21.48 q, 23.17 q, 23.29, 25.61 t, 26.00 q, 38.81 t, 39.75, 55.94 d (C^2), 83.00 s (C^{10}), 85.98 d (C^4), 86.59 s (C^1), 112.98 t and 113.10 t (C^{12}), 141.61 d and 141.64 d (C^{11}). ^{13}C NMR spectra of isomers **XVIIIa, b** are given in Table 2.

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