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Transformations of Diepoxy Derivatives of Limonene in Homogeneous Acidic Media

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Abstract—Transformations of diepoxy derivatives of limonene under conditions of homogeneous acid catalysis were studied, and their results were compared with those obtained over heterogeneous catalysts. A number of previously unknown compounds were isolated. The most possible transformation pathways were analyzed by computer simulation using molecular-mechanics and quantum-chemical methods.

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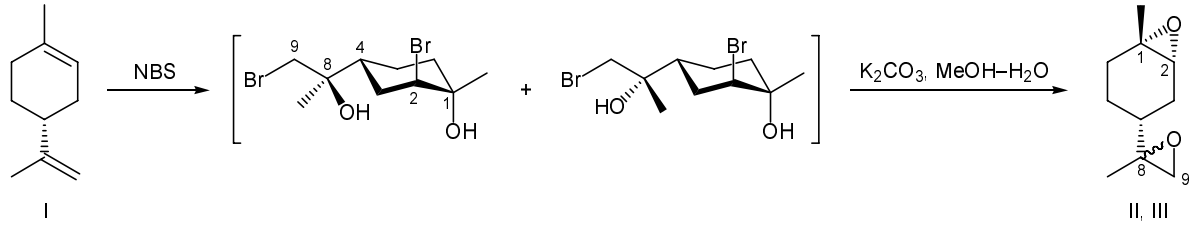
Being the major component of lemon oil (90%), (*R*)-(+)-limonene (**I**) is the most widespread cyclic monoterpene. According to published data, limonene in acid medium undergoes skeletal transformations leading to bicyclic compounds only under severe conditions (phosphoric acid, 200°C; silicophosphoric acid, 210–220°C), while under mild conditions migration of the double bonds occurs to give compounds of the *p*-menthane series [1, 2]. Transformations of limonene monoepoxides in acid medium lead to the corresponding diols as a result of opening of the oxirane ring, as well as to compounds containing an allyl alcohol moiety or a carbonyl group [3–6]. Despite abundance and accessibility of initial limonene, the behavior of diepoxy derivatives of this monoterpene in acid medium was not studied. The oxidation of limonene with 2 equiv of a peroxy acid (*m*-chloroperoxybenzoic or peroxyacetic) gives a mixture of four diastereoisomers. Treatment of limonene with *N*-bromsuccinimide, followed by decomposition of dihydroxy dibromide thus formed, leads to the formation of two diastereoisomeric limonene diepoxides **II** and **III** differing in the configuration of the 8,9-epoxy ring at a ratio of 3:2 [7] (Scheme 1) .

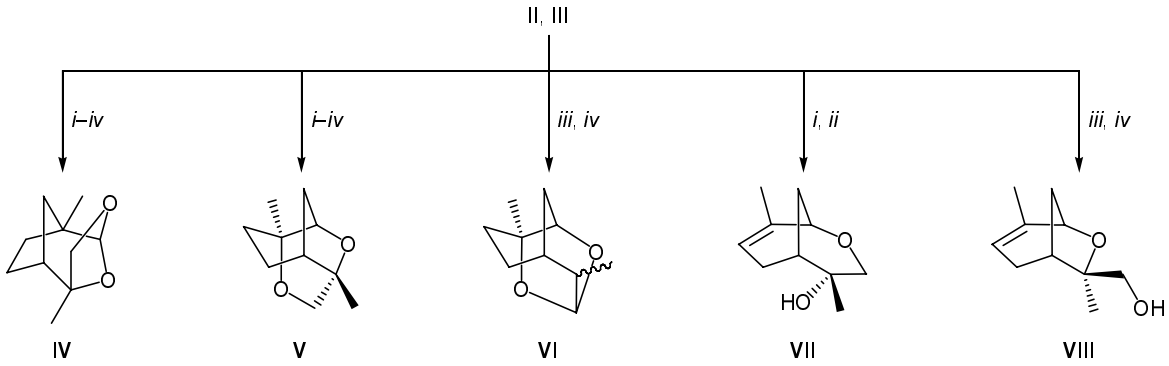
We previously studied the transformations of diastereoisomeric diepoxides **II** and **III** over solid acid catalysts and found that their isomerizations in the presence of β-zeolite, askanite–bentonite clay, K10 synhtetic clay, and TiO_2/SO_4 solid superacid give rise to bi- and tricyclic products **IV**–**VIII** [8] (Scheme 2). In these cases, the product composition (both qualitative and quantitative) depended on the catalyst nature.

In the present work we examined acid-catalyzed transformations of diepoxy derivatives **II** and **III** in homogeneous medium. Insofar as the molecule of limonene diepoxide contains two oxirane rings which are highly reactive under acidic conditions, the results of these transformations depended on mutual spatial arrangement of the epoxy groups. We performed quantum-chemical calculations of the most stable conformations of limonene diepoxides **II** and **III** (see table). It is seen that diepoxides **II** and **III** are characterized by almost similar stabilities. The most stable conformations for both compounds are *half-chair* with

Scheme 1.



Scheme 2.



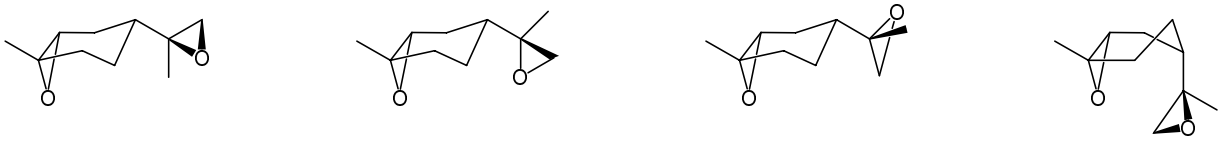
i: β-Zeolite; *ii*: TiO_2/SO_4; *iii*: K10 clay; *iv*: askanite–bentonite clay.

the equatorial epoxyisopropyl group (**IIa**–**IIc** and **IIIa**–**IIIc**). Axial orientation of that group (conformers **IId** and **IIId**) is considerably less favorable. The calculations were performed in terms of the density functional theory (DFT) for the gas phase using GAMESS program [9] (B3LYP/6-31G*) and PRIRODA software (BPE/cc-pVTZ) [10]. Possible conformations were sought for using Dreiding models and molecular-mechanics method.

Diepoxides **II** and **III** in formic acid or in the system formic acid–dioxane were converted into esters **IXa** and **IXb** at a ratio of 0.45:1 (Scheme 3). In the system trifluoroacetic acid–dioxane, compounds **Xa** and **Xb** were formed at a ratio of 0.8:1. Dissolution of **II** and **III** in a mixture of allyl alcohol and sulfuric acid gave a 1:1 mixture of compounds **XIa** and **XIb**. The same products were formed in the reaction of allyl alcohol with diepoxides **II** and **III** over β-zeolite, while the isomerization of **II** and **III** was shown [8] to give compounds **IV**, **V**, and **VII** at a ratio of 2:5:2 (GLC data). Isomers **IXa**/**IXb**–**XIa**/**XIb** differ by the configuration of substituents on C^3.

Scheme 4 illustrates a possible mechanism for formation of compounds **IXa**/**IXb**–**XIa**/**XIb**. According to the results of our calculations, proton addition to the oxygen atom of the 8,9-epoxy ring in **II** and **III** promotes spontaneous opening of that ring (there is no energy barrier between these two steps). The subsequent transformations of ions formed by opening of the oxirane rings are shown in Scheme 4; the corresponding relative energies ΔE (kcal/mol) are also given. The most favorable pathway includes (1) protonation and opening of the 8,9-epoxy ring in **II** and **III** with formation of the same cation **A**; (2) conformational transition *half-chair* → *twist*, the cationic center in the isopropenyl group of the *twist* conformer being spa-

Calculated energies (kcal/mol) of stable conformations of diepoxy derivatives **II** and **III**

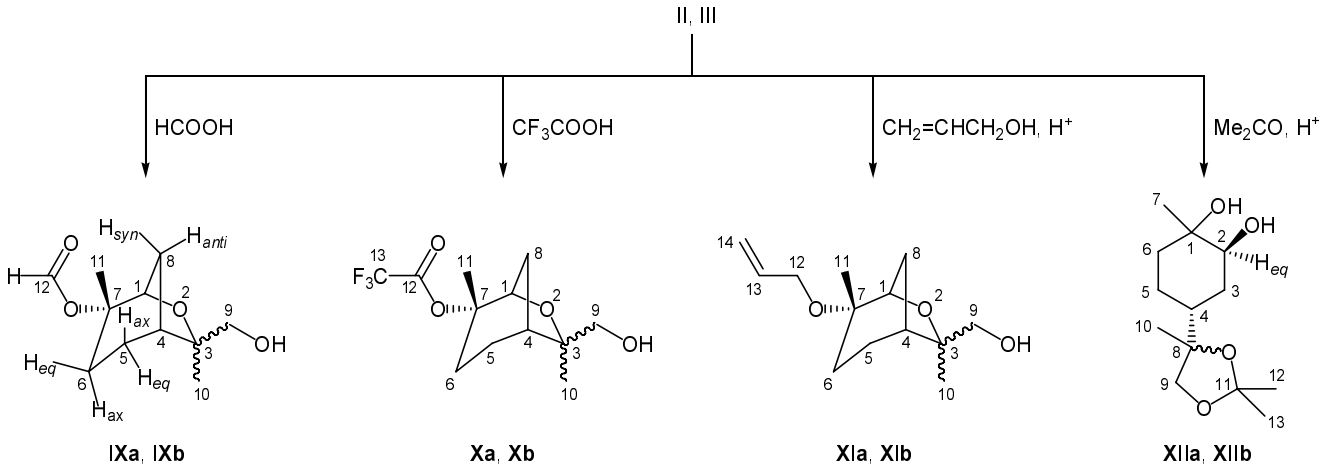


IIa IIb IIc IId

Parameter	IIa	IIb	IIc	IId	IIIa	IIIb	IIIc	IIId
B3LYP/6-31G*, ΔE[a]	0.0	1.6	0.6	–	0.1	0.0	1.2	–
$C^3C^4C^5C^6$,[b] deg	–64	–62	–64	59	–64	–63	–63	53
$C^3C^4C^7C^9$,[b] deg	–69	68	155	179	–68	64	171	44
PBE/cc-pVTZ, ΔE[c]	0.0	1.6	0.8	3.2	0.0	0.5	1.4	4.5
$C^3C^4C^5C^6$,[b] deg	–64	–62	–64	59	–64	–65	–64	55
$C^3C^4C^7C^9$,[b] deg	–68	73	156	177	–66	60	168	39

[a] E = –540.744578 H.
[b] Torsion angle.
[c] E = –540.606606 H.

Scheme 3.



tially close to the second epoxide ring; and (3) intramolecular attack on the cationic center by the oxygen atom of the 1,2-epoxy group to give oxonium ions **B** and **C**. Ring opening of the latter gives tertiary carbocations **D** and **E** (as most stable) with an 6-oxabicyclo[3.2.1]octane skeleton. Trapping of ions **D** and **E** by a nucleophile molecule [ROH, where R = HC(O), $CF_3C(O)$, CH_2=$CHCH_2$] yields final compounds **IXa**/**IXb**–**XIa**/**XIb**. Probably, ROH molecule reacts already with ions **B** and **C**, and the final products are formed following a synchronous mechanism.

Initial opening of the 1,2-epoxide ring in starting compounds **II** and **III** is less favorable from the thermodynamic viewpoint, and it does not occur, as follows from the absence of the corresponding products in the reaction mixture. An additional support for the initial opening of the 8,9-epoxy ring is provided by the fact that the ratio of the transformation products of limonene diepoxides in formic acid–dioxane does not depend on the ratio of the initial diepoxides. Compounds **IXa** and **IXb** are formed at a ratio of 0.45:1 from isomers **II** and **III** taken at ratios of both 1:0.95 and 1:0.6.

The formation of oxonium ions as intermediate species is indicated by published data. Long-lived oxonium ion **F** was generated from α-bisabolol (**XIII**) in the HSO_3F–SO_2FCl system at –80°C [11]; furthermore, oxonium ion **G** was postulated as intermediate product in the isomerization of 2,3-epoxygeraniol (**XIV**) in HSO_3F–SO_2FCl at –100°C [12] (Scheme 5).

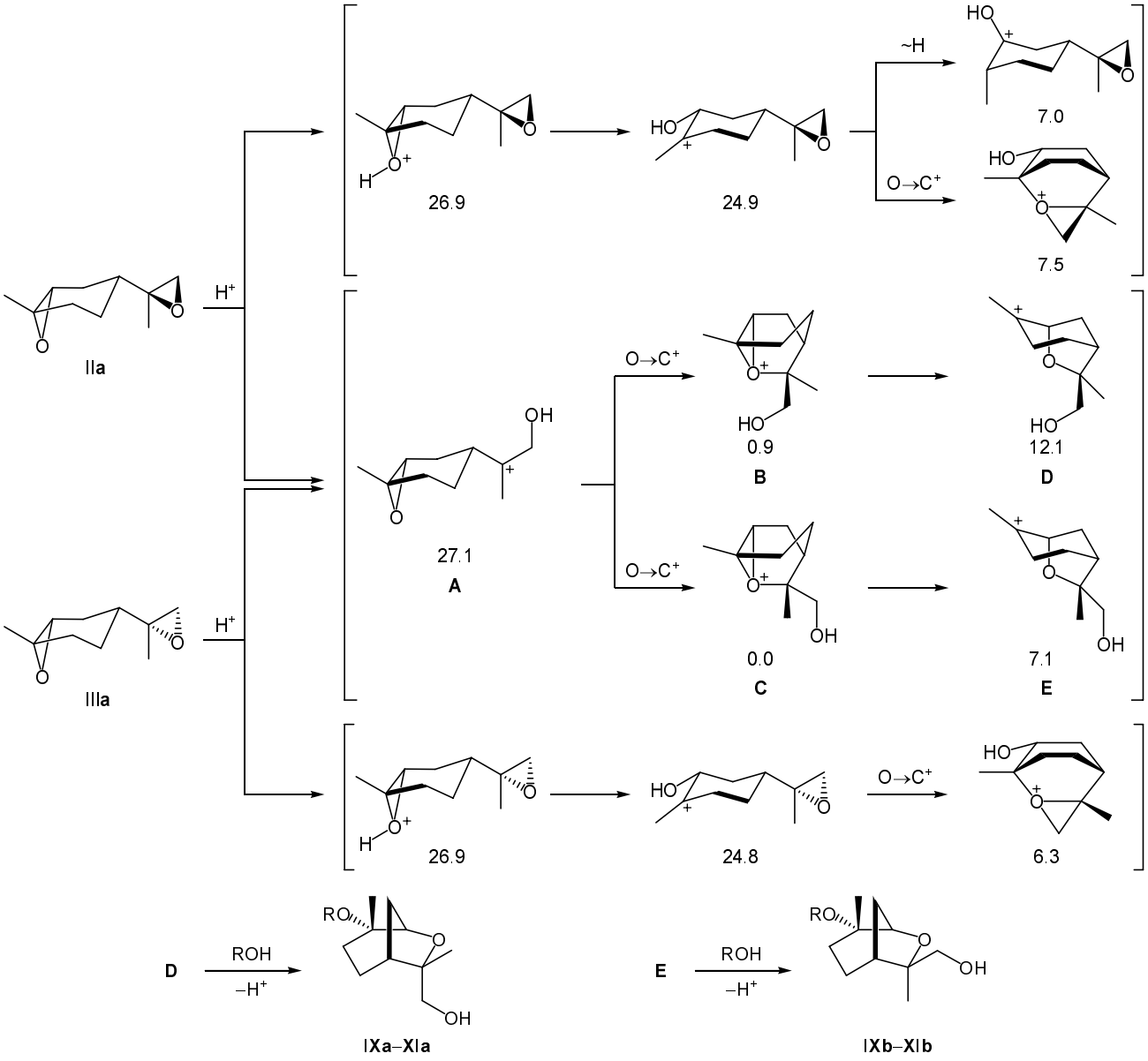
As an example, we calculated the energies of formation of isomers **IXa** and **IXb** and found that the former is less stable than the latter by 1.2 kcal/mol, in keeping with the experimental data.

A 1:0.8 mixture of epoxides **II** and **III** in the system acetone–water–sulfuric acid was converted into compounds **XIIa** and **XIIb** having a 1,3-dioxolane ring (Scheme 3). Isomers **XIIa** and **XIIb** differ by the orientation of substituents on C^8. A probable mechanism of formation of compounds **XIIa** and **XIIb** includes reaction of acetone molecule at the 8,9-epoxy group and opening of the 1,2-epoxy ring to give the corresponding diol. It should be noted that, like compounds **IXa**/**IXb** and **Xa**/**Xb**, the ratio of isomers **XIIa**/**XIIb** does not depend on the ratio of initial diepoxides **II** and **III**. Thus the transformation of limonene diepoxides in a weakly acidic medium (acetone–water–sulfuric acid) gives no compounds having a 6-oxabicyclo[3.2.1]octane skeleton.

Comparison of the results of transformations of diepoxy derivatives **II** and **III** over solid acid catalysts [8] and in homogeneous acidic media shows that an "organized" medium favors formation of bi- and tricyclic oxygen-containing products, while homogeneous nucleophilic media provide the possibility for chemical stabilization of carbocations formed as intermediates in intramolecular rearrangements. It should be noted that these rearrangements occur under fairly mild conditions.

Let us consider some details of structure determination of the obtained compounds. Axial orientation of the 4-H proton in isomer **II** follows from the vicinal coupling constants ($^3J_{HH}$) between that proton and protons in the neighboring methylene groups (see Experimental). The 2-H protons in both isomers **II** and **III** displayed only one vicinal coupling with 3-H_{eq}. According to the Dreiding models, the dihedral angle between 2-H_{eq} and 3-H_{ax} is about 90°; therefore, the $^3J_{2\text{-}eq,3\text{-}ax}$ value is close to zero (cf. [6]). The similar

Scheme 4.



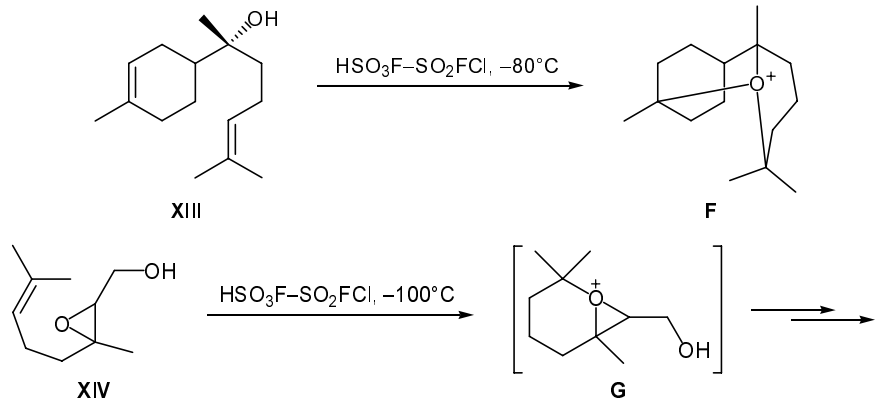
IX, R = HC(O); **X**, R = CF_3CO; **XI**, R = CH_2=$CHCH_2$.

chemical shifts of 2-H and protons of the C^7H_3 group in the ^{1}H NMR spectrum and equal vicinal coupling constants of 2-H and 3-H_{eq} indicate similar orientations of the methyl group on C^1 and 1,2-epoxy ring in both diepoxides. This means that isomeric diepoxy derivatives **II** and **III** differ by orientation of the 8,9-epoxy ring. This assumption is supported by the fact that the C^4 and C^8–C^{10} atoms are characterized by the maximal differences in chemical shifts in the ^{13}C NMR spectrum [7].

The maximal differences in chemical shifts of isomeric compounds **IXa** and **IXb** are observed in the ^{1}H NMR spectrum for protons of the methyl and hydroxymethyl groups on C^3, and in the ^{13}C NMR spectrum, for C^4, C^9, and C^{10}. Therefore, these isomers differ by orientation of the substituents on C^3. In keeping with published data for bicyclic structures [13], the signal from the *exo*-CH_3 group appears in a weaker field than that from the *endo*-CH_3 group. Correspondingly, the $C^{10}H_3$ group in isomer **IXa** was assumed to occupy *exo* position, and in isomer **IXb**, *endo* position.

Comparison of the chemical shifts of protons of the methyl and hydroxymethyl groups on C^3 in the ^{1}H NMR spectra and of the C^4, C^9, and C^{10} atoms in the

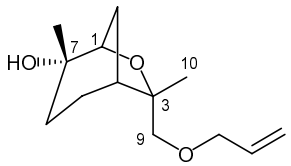
Scheme 5.



^{13}C NMR spectra of isomers **IXa** and **IXb** with the corresponding parameters of **Xa** and **Xb** led us to assign *exo* orientation to the $C^{10}H_3$ group in **Xa** and *endo* orientation of the same group in isomer **Xb**.

The isomerism of compounds **XIa** and **XIb** also originates from different orientations (*exo* or *endo*) of the substituents on C^3. The maximal differences in chemical shifts are observed in the ^{1}H NMR spectrum for protons in the methyl group on C^3 ($\Delta\delta$ = 0.35 and 0.45 ppm) and 8-H_{anti} ($\Delta\delta$ = 0.12 ppm), the latter being sensitive to the *exo*-substituent on C^3. Likewise, the chemical shifts of C^4, C^9, and C^{10} in the ^{13}C NMR spectra of isomers **XIa** and **XIb** differ most strongly ($\Delta\delta$ = 2, 3, and 6.5 ppm, respectively).

Alternative structure **XIII** was ruled out on the basis of the ^{13}C NMR spectra recorded in the presence of heavy water. Replacement of the OH group by OD leads to upfield shift (isotope effect) of the triplet signal from C^9H_2 at δ_C 69.22 ppm ($\Delta\delta_C$ = 0.15 ppm) for isomer **XIa** and δ_C 66.22 ppm ($\Delta\delta_C$ = 0.17 ppm) for **XIb**, while the singlets at δ_C 76.38 and 76.13 ppm (C^7) do not change their position.



XIII

Signals from methyl groups in the ^{1}H NMR spectrum were assigned using LRJMD technique. Simultaneous suppression of the methyl proton resonances at δ 1.11 and 1.09 ppm gave rise to the following signals in the LRJMD spectrum: doublets at δ_C 81.84 and 81.55 ppm (C^1 in both isomers), singlets at δ_C 76.38 and 76.13 ppm (C^7), and triplets at δ_C 29.02 and 28.89 ppm (C^6). The observed set of carbon signals suggests that the corresponding carbon nuclei are coupled with protons of the methyl group on C^7; therefore, the signals at δ 1.11 and 1.09 ppm belong to the $C^{11}H_3$ protons, and those at δ 1.30 and 1.20 ppm, to $C^{10}H_3$.

Signals from the C^1 and C^8 atoms in **XIIa** were also assigned on the basis of the LRJMD spectrum. Upon successive irradiation of the methyl protons (δ 1.18 and 1.23 ppm), in the LRJMD spectra we observed signals at δ_C 38.45 (d), 73.06 (t), and 83.09 ppm (s) in the first case and at δ_C 33.38 (t), 70.95 (s), and 73.71 ppm (d) in the second. These data allowed us to assign the signal at δ_C 70.95 ppm to C^1, and that at δ_C 83.09 ppm, to C^8. The ^{13}C NMR spectrum of **XIIa** recorded in $CDCl_3$ in the presence of D_2O showed that the hydroxy groups are attached to C^1 and C^2 rather than to C^8 and C^9. Replacement of the OH groups by OD resulted in upfield shift (isotope effect) of the singlet at δ_C 70.95 ppm ($\Delta\delta$ = 0.16 ppm) and of the doublet signal at δ_C 73.71 ppm ($\Delta\delta$ = 0.12 ppm), which belong to C^1 and C^2, respectively.

The maximal differences between chemical shifts in the ^{1}H and ^{13}C NMR spectra of an equimolar mixture of isomers **XIIa** and **XIIb** are observed for protons in the methyl group on C^8 and for the C^3, C^5, C^9, and C^{10} carbon nuclei. Therefore, isomers **XIIa** and **XIIb** are characterized by different orientations of the substituents on the C^8 atom.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-400 spectrometer at 400.13 MHz for ^{1}H and 100.61 MHz for ^{13}C; a 1:1 CCl_4–$CDCl_3$ mixture was used as solvent; and the chemical shifts were measured relative to the solvent signals ($CHCl_3$,

δ 7.24; $CDCl_3$, δ_C 76.90 ppm). Signals were assigned on the basis of spin–spin coupling constants in the ^1H–^1H double resonance spectra, ^{13}C NMR spectra recorded with selective decoupling from protons, off-resonance ^{13}C NMR spectra spectra, two-dimensional ^{13}C–^1H correlation spectra using direct ^{13}C–^1H couplings (COSY, $^1J_{CH}$ = 135 Hz), and one-dimensional ^{13}C–^1H correlation spectra using long-range ^{13}C–^1H couplings (LRJMD, J_{CH} = 10 Hz).

The initial compounds and reaction products were analyzed by GLC on a Biokhrom-1 chromatograph equipped with a flame ionization detector [SE-54 quartz capillary column, 13000 × 0.22 mm, or VS-30 (an analog of SE-30) quartz capillary column, 20000 × 0.27 mm; carrier gas helium]. The reaction mixtures were separated by column chromatography on silica gel (100–160 μm, Czechia). The specific optical rotations were measured on a Polamat A polarimeter. The elemental compositions were determined from the high-resolution mass spectra recorded on a Finnigan MAT-8200 spectrometer.

Commercial (*R*)-(+)-limonene (from Aldrich) with a purity of 97% (ee 98%) was used. Diepoxy derivatives **II** and **III** were prepared by the procedure reported in [7]; yield 32%, ratio ~3:2, $[\alpha]_{580}^{20}$ = +35.5° (*c* = 3.5, $CHCl_3$). The transformations described in the present article were performed using a mixture of isomers **II** and **III** at a ratio of ~3:2.

Transformations of diepoxy derivatives II and III in formic acid–dioxane. A mixture of isomeric diepoxides **II** and **III**, 0.20 g, was dissolved in a mixture of 1 ml of formic acid and 1 ml of 1,4-dioxane. After 30 min, the mixture was treated with a saturated solution of sodium carbonate and extracted with diethyl ether (3 × 30 ml), and the extract was dried over $MgSO_4$. According to the ^1H NMR data, the products were compounds **IXa** and **IXb** at a ratio of ~0.45:1 (0.18 g). By column chromatography on silica gel using hexane–diethyl ether (0 to 25% of the latter; gradient elution) we isolated 0.10 g (40%) of isomer mixture **IXa**/**IXb**, $[\alpha]_{580}^{20}$ = –57° (*c* = 4.55, $CHCl_3$). Found: *m*/*z* 214.12045 $[M]^+$. $C_{11}H_{18}O_4$. Calculated: *M* 214.12050. The NMR spectra were recorded from isomer mixture **IXa**/**IXb** at a ratio of ~1:0.7.

(1*R*,4*S*,5*R*,7*S*)-7-Hydroxymethyl-4,7-dimethyl-6-oxabicyclo[3.2.1]oct-4-yl formate (IXa). ^1H NMR spectrum, δ, ppm: 1.22 s ($C^{10}H_3$), 1.43 s ($C^{11}H_3$), 1.53–1.68 m (2H, 5-H), 1.69–1.84 m (6-H), 1.90 d (8-H_{syn}, $J_{8\text{-}syn,8\text{-}anti}$ = 12 Hz), 1.91–2.06 m (4-H, 6'-H), 2.16 m (8-H_{anti}, *J* = 12, $J_{8\text{-}anti,1}$ = 6.5, $J_{8\text{-}anti,4}$ = 4.5, $J_{8\text{-}anti,5\text{-}eq}$ = 2.2 Hz), 2.32 br.s (OH), 3.57 d (9-H, $J_{9,9'}$ = 11 Hz) and 3.74 d (9'-H, *J* = 11 Hz) (*AB* system), 4.42 br.d (1-H, $J_{1,8\text{-}anti}$ = 6.5 Hz), 7.89 s (12-H). ^{13}C NMR spectrum, δ_C, ppm: 79.36 d (C^1), 85.03 s (C^3), 39.22 d (C^4), 24.07 t (C^5), 30.91 t (C^6), 83.67 s (C^7), 31.71 t (C^8), 65.89 t (C^9), 24.68 q (C^{10}), 23.50 q (C^{11}), 159.66 d (C^{12}).

(1*R*,4*S*,5*R*,7*R*)-7-Hydroxymethyl-4,7-dimethyl-6-oxabicyclo[3.2.1]oct-4-yl formate (IXb). ^1H NMR spectrum, δ, ppm: 1.31 s ($C^{10}H_3$), 1.45 s ($C^{11}H_3$), 1.53–1.68 m (2H, 5-H), 1.69–1.84 m (6-H), 1.87 d (8-H_{syn}, $J_{8\text{-}syn,8\text{-}anti}$ = 12 Hz), 1.91–2.06 m (4-H, 6'-H), 2.06 m (8-H_{anti}, *J* = 12, $J_{8\text{-}anti,1}$ = 6.5, $J_{8\text{-}anti,4}$ = 4.5, $J_{8\text{-}anti,5\text{-}eq}$ = 1.5 Hz), 2.32 br.s (OH), 3.22 d (9-H, $J_{9,9'}$ = 11 Hz) and 3.31 d (9'-H, *J* = 11 Hz) (*AB* system), 4.38 br.d (1-H, $J_{1,8\text{-}anti}$ = 6.5 Hz), 7.89 s (12-H). ^{13}C NMR spectrum, δ_C, ppm: 79.59 d (C^1), 84.70 s (C^3), 37.27 d (C^4), 23.37 t (C^5), 30.97 t (C^6), 83.92 s (C^7), 31.65 t (C^8), 69.13 t (C^9), 17.94 q (C^{10}), 23.42 q (C^{11}), 159.63 d (C^{12}).

Transformations of diepoxy derivatives II and III in trifluoroacetic acid–dioxane. A mixture of isomeric diepoxides **II** and **III**, 0.15 g, was dissolved in a mixture of 1 ml of trifluoroacetic acid and 1 ml of 1,4-dioxane. After 1 h, the mixture was treated with a saturated solution of sodium carbonate and extracted with diethyl ether (3 × 30 ml), and the extract was dried over $MgSO_4$. According to the ^1H NMR data, the products were compounds **Xa** and **Xb** at a ratio of 0.8:1 (0.16 g). By column chromatography on silica gel using hexane–diethyl ether (0 to 30% of the latter; gradient elution) we isolated 0.05 g (20%) of isomer mixture **Xa**/**Xb**. The NMR spectra were recorded from isomer mixture **IXa**/**IXb** at a ratio of 0.8:1.

(1*R*,4*S*,5*R*,7*S*)-7-Hydroxymethyl-4,7-dimethyl-6-oxabicyclo[3.2.1]oct-4-yl trifluoroacetate (Xa). ^1H NMR spectrum, δ, ppm: 1.25 s ($C^{10}H_3$), 1.52 s ($C^{11}H_3$), 1.56–1.76 m (2H, 5-H), 1.84 m (6-H_{ax}), 1.86 d (8-H_{syn}, $J_{8\text{-}syn,8\text{-}anti}$ = 12 Hz), 2.02 m (4-H), 2.10 br.d.d (6-H_{eq}, $J_{6\text{-}eq,6\text{-}ax}$ = 15.5, $J_{6\text{-}eq,5\text{-}ax}$ = 7 Hz), 2.24 m (8-H_{anti}, *J* = 12, $J_{8\text{-}anti,1}$ = 6.5, $J_{8\text{-}anti,4}$ = 4.5, $J_{8\text{-}anti,5\text{-}eq}$ = 2.2 Hz), 3.60 d (9-H, $J_{9,9'}$ = 11 Hz) and 3.76 d (9'-H, *J* = 11 Hz) (*AB* system), 4.43 br.d (1-H, *J* = 6.5 Hz). ^{13}C NMR spectrum, δ, ppm: 78.72 d (C^1), 85.30 s (C^3), 39.10 d (C^4), 23.32 t (C^5), 30.20 t (C^6), 88.14 s (C^7), 31.86 t (C^8), 65.98 t (C^9), 24.77 q (C^{10}), 22.91 q (C^{11}), 155.74 q (C^{12}, J_{CF} = 42 Hz), 114.35 q (C^{13}, J_{CF} = 287 Hz).

(1*R*,4*S*,5*R*,7*R*)-7-Hydroxymethyl-4,7-dimethyl-6-oxabicyclo[3.2.1]oct-4-yl trifluoroacetate (Xb).

^{1}H NMR spectrum, δ, ppm: 1.34 s ($C^{10}H_3$), 1.53 s ($C^{11}H_3$), 1.62–1.76 m (2H, 5-H), 1.83 d (8-H_{syn}, $J_{8\text{-}syn,8\text{-}anti}$ = 12.5 Hz), 1.88 m (6-H_{ax}), 1.09 d.t (4-H, $J_{4,8\text{-}anti}$ = 4.5, $J_{4,5}$ = 3 Hz), 2.09 br.d.d (6-H_{eq}, $J_{6\text{-}eq,6\text{-}ax}$ = 15.5, $J_{6\text{-}eq,5\text{-}ax}$ = 6.5 Hz), 2.13 m (8-H_{anti}, J = 12.5, $J_{8\text{-}anti,1}$ = 6.5, $J_{8\text{-}anti,4}$ = 4.5, $J_{8\text{-}anti,5\text{-}eq}$ = 2.2 Hz), 3.25 d (9-H, $J_{9,9'}$ = 11 Hz) and 3.34 d (9'-H, J = 11 Hz) (*AB* system), 4.38 br.d (1-H, J = 6.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 78.94 d (C^1), 85.05 s (C^3), 37.18 d (C^4), 24.03 t (C^5), 30.28 t (C^6), 88.28 s (C^7), 31.78 t (C^8), 69.07 t (C^9), 18.02 q (C^{10}), 22.81 q (C^{11}), 155.74 q (C^{12}, J_{CF} = 42 Hz), 112.93 q (C^{13}, J_{CF} = 315 Hz).

Transformations of diepoxy derivatives II and III in allyl alcohol–sulfuric acid. A mixture of diepoxy derivatives **II** and **III**, 0.3 g, was added under stirring to a mixture of 0.3 ml of anhydrous allyl alcohol (purified by distillation) and 0.06 ml of sulfuric acid. After 5 min, the mixture was neutralized with a saturated solution of Na_2CO_3 and extracted with diethyl ether (3×30 ml), and the extract was dried over $MgSO_4$ and evaporated. The residue, 0.28 g, was subjected to column chromatography on silica gel (gradient elution with hexane–diethyl ether, 0.5 to 30% of the latter) to isolate 0.2 g of a mixture of isomers **XIa** and **XIb** at a ratio of 1:1. By repeated chromatography on silica gel containing 10% of $AgNO_3$ we isolated 0.08 g of isomer mixture **XIa**/**XIb** at a ratio of ~1:0.8, $[\alpha]_{580}^{20}$ = +22.9° (*c* = 3.5, $CHCl_3$). Found: *m*/*z* 226.15672 $[M]^+$. $C_{13}H_{22}O_3$. Calculated: *M* 226.15688.

(1*R*,4*S*,5*R*,7*S*)-(4-Allyloxy-4,7-dimethyl-6-oxabicyclo[3.2.1]oct-7-yl)methanol (XIa). ^{1}H NMR spectrum, δ, ppm: 1.11 s ($C^{11}H_3$), 1.30 s ($C^{10}H_3$), 1.44–1.67 m (4H, 5-H, 6-H), 1.84 d.t (4-H, $J_{4,8\text{-}anti}$ = 4.5, $J_{4,5}$ = 2.5 Hz), 1.92 d.d.d.d (8-H_{anti}, $J_{8\text{-}anti,8\text{-}syn}$ = 12, $J_{8\text{-}anti,1}$ = 6, $J_{8\text{-}anti,4}$ = 4.5, $J_{8\text{-}anti,5\text{-}eq}$ = 2.2 Hz), 2.17 d (8-H_{syn}, J = 12 Hz), 2.49 br.s (OH), 3.19 d (9-H, $J_{9,9'}$ = 10.5 Hz) and 3.29 d (9'-H, J = 10.5 Hz) (*AB* system), 3.75 d.d.d.d (12-H, $J_{12,12'}$ = 13, $J_{12,13}$ = 5, $J_{12,14\text{-}cis}$ = 1.5, $J_{12,14\text{-}trans}$ = 1.5 Hz), 3.80 d (1-H, $J_{1,8\text{-}anti}$ = 6 Hz), 3.83 d.m (12'-H, J = 13, $J_{12',13}$ = 5, $J_{12',14\text{-}cis}$ = 1.5, $J_{12',14\text{-}trans}$ = 1.5 Hz), 5.02 d.d.d.d (14-H_{cis}, $J_{14\text{-}cis,13}$ = 10.5, $J_{14\text{-}cis,14\text{-}trans}$ = 2, J = 1.5, 1.5 Hz), 5.17 d.d.d.d (14-H_{trans}, $J_{14\text{-}trans,13}$ = 17, J = 2, 1.5, 1.5 Hz), 5.80 d.d.d.d (13-H, J = 17, 10.5, 5, 5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 81.84 d (C^1), 84.27 s (C^3), 37.44 d (C^4), 24.21 t (C^5), 28.89 t (C^6), 76.38 s (C^7), 31.45 t (C^8), 69.22 t (C^9), 18.26 q (C^{10}), 22.64 q (C^{11}), 62.58 t (C^{12}), 135.80 d (C^{13}), 115.11 t (C^{14}).

(1*R*,4*S*,5*R*,7*R*)-(4-Allyloxy-4,7-dimethyl-6-oxabicyclo[3.2.1]oct-7-yl)methanol (XIb). ^{1}H NMR spectrum, δ, ppm: 1.09 s ($C^{11}H_3$), 1.20 s ($C^{10}H_3$), 1.44–1.67 m (4H, 5-H, 6-H), 1.89 d.t (4-H, $J_{4,8\text{-}anti}$ = 4.5, $J_{4,5}$ = 2.5 Hz), 2.05 m (8-H_{anti}, $J_{8\text{-}anti,8\text{-}syn}$ = 12, $J_{8\text{-}anti,1}$ = 6, $J_{8\text{-}anti,4}$ = 4.5, $J_{8\text{-}anti,5\text{-}eq}$ = 2.2 Hz), 2.19 d (8-H_{syn}, J = 12 Hz), 2.49 br.s (OH), 3.54 d (9-H, $J_{9,9'}$ = 10.5 Hz) and 3.74 d (9'-H, J = 10.5 Hz) (*AB* system), 3.75 d.d.d.d (12-H, $J_{12,12'}$ = 13, $J_{12,13}$ = 5, $J_{12,14\text{-}cis}$ = 1.5, $J_{12,14\text{-}trans}$ = 1.5 Hz), 3.83 d.m (12'-H, J = 13, $J_{12',13}$ = 5, $J_{12',14\text{-}cis}$ = 1.5, $J_{12',14\text{-}trans}$ = 1.5 Hz), 3.88 d (1-H, $J_{1,8\text{-}anti}$ = 6 Hz), 5.02 d.d.d.d (14-H_{cis}, $J_{14\text{-}cis,13}$ = 10.5, $J_{14\text{-}cis,14\text{-}trans}$ = 2, J = 1.5, 1.5 Hz), 5.17 d.d.d.d (14-H_{trans}, $J_{14\text{-}trans,13}$ = 17, J = 2, 1.5, 1.5 Hz), 5.78 d.d.d.d (13-H, J = 17, 10.5, 5, 5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 81.55 d (C^1), 84.64 s (C^3), 39.43 d (C^4), 23.53 t (C^5), 29.02 t (C^6), 76.13 s (C^7), 31.45 t (C^8), 66.22 t (C^9), 24.73 q (C^{10}), 22.66 q (C^{11}), 62.58 t (C^{12}), 135.80 d (C^{13}), 115.11 t (C^{14}).

Transformations of diepoxy derivatives II and III in acetone–water–sulfuric acid. A mixture of diepoxy derivatives **II** and **III**, 0.35 g, was dissolved in a mixture of 25 ml of acetone, 3 ml of water, and 0.5 ml of sulfuric acid. After 30 min, the mixture was treated with a saturated solution of Na_2CO_3 and extracted with diethyl ether (3×50), and the extract was dried over $MgSO_4$ and evaporated. According to the ^{1}H NMR data, the residue (0.19 g) contained compounds **XIIa** and **XIIb** at a ratio of 1:0.8. By column chromatography on silica gel (gradient elution with hexane–diethyl ether, 0 to 90%) we isolated 0.05 g (10%) of isomer mixture **XIIa**/**XIIb**.

(2*S*,4*R*)-1-Methyl-4-(2,2,4-trimethyl-1,3-dioxolan-4-yl)cyclohexane-1,2-diols (XIIa/XIIb). Diastereoisomer ratio 2:1; $[\alpha]_{580}^{20}$ = +36.4 (*c* = 0.55, $CHCl_3$). Found: *m*/*z* 169.12338 $[M]^+$. $C_{10}H_{17}O_2$. Calculated: *M* 169.12285. ^{1}H NMR spectrum of **XIIa** (from isomer mixture **XIIa**/**XIIb** at a ratio of ~1:0.25), δ, ppm: 1.18 s ($C^{10}H_3$), 1.23 s (C^7H_3), 1.33 s and 1.37 s ($C^{12}H_3$, $C^{13}H_3$), 1.36 m (2H, 5-H), 1.47 d.t.d (6-H_{eq}, $J_{6\text{-}eq,6\text{-}ax}$ = 14, $J_{6\text{-}eq,5}$ = 3.5, $J_{6\text{-}eq,2\text{-}eq}$ = 1.5 Hz), 1.70 m (6-H_{ax}), 1.75 m (2H, 3-H), 1.80 m (4-H_{ax}), 3.59 m (2-H_{eq}, $J_{2\text{-}eq,3}$ = 2.5, $J_{2\text{-}eq,6\text{-}eq}$ = 1.5 Hz), 3.62 d and 3.81 d (2H, 9-H, J = 8 Hz, *AB* system). ^{13}C NMR spectrum, δ_C, ppm: 70.95 s (C^1), 72.71 d (C^2), 30.00 t (C^3), 38.45 d (C^4), 22.91 t (C^5), 33.38 t (C^6), 27.65 q (C^7), 83.09 s (C^8), 73.06 t (C^9), 21.67 q (C^{10}), 109.01 s (C^{11}), 27.50 q and 26.94 q (C^{12}, C^{13}). ^{1}H NMR spectrum of isomer **XIIb** (from isomer mixture **XIIa**/**XIIb** at a ratio of ~1:0.75), δ, ppm: 1.16 s ($C^{10}H_3$), 1.17 s (C^7H_3), 1.29 s and 1.33 s ($C^{12}H_3$, $C^{13}H_3$), 3.49 m

(2-H_{eq}), 3.54 d and 3.76 d (2H, 9-H, J = 8 Hz, *AB* system); the other signals are obscured by those of the major diastereoisomer. ^{13}C NMR spectrum, δ_C, ppm: 70.85 s (C^1), 73.44 d (C^2), 30.80 t (C^3), 38.34 d (C^4), 21.99 t (C^5), 33.41 t (C^6), 27.53 q (C^7), 83.19 s (C^8), 72.31 t (C^9), 22.29 q (C^{10}), 108.87 s (C^{11}), 27.77 q and 26.97 q (C^{12}, C^{13}).

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