Russian Journal of Organic Chemistry, Vol. 37, No. 6, 2001, pp. 793–801. Translated from Zhurnal Organicheskoi Khimii, Vol. 37, No. 6, 2001, pp. 841–848.

Rearrangements of Epoxides of Some Acyclic Terpenoids in Acidic Media

T. M. Khomenko, D. V. Korchagina, and V. A. Barkhash

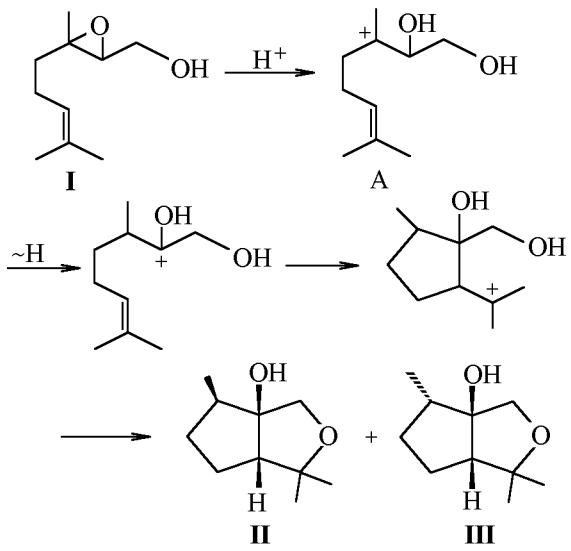
Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia

Received October 27, 2000

Abstract—2,3-Epoxygeraniol undergoes dissimilar rearrangements in contact with liquid superacids at low temperature or on solid superacids at room temperature due to different location of the arising cationic center depending on the superacid character. 2,3-Epoxynerol, 6,7-epoxycitronellol, and 6,7-geranyl acetate on $ZrO_2SO_4^{2-}$ afford the corresponding ketones via epoxy ring opening followed by 1,2-hydride shift. With 6,7-geranyl acetate 7-oxanobornane formed as a minor product. The mode of generation of the cationic center (either the olefin protonation or the epoxy ring opening) affects the rearrangement direction at similar conditions.

We showed formerly that the solvolysis of esters in acidic media and protonation of olefins with the same skeleton and the same location of the generated cationic center gave rise to different carbocations [1]. In terpene chemistry the comparison of behavior of olefins and epoxides prepared therefrom in the same acidic medium is more important. The epoxide cleavage effected by acids is interesting both for the physical organic chemistry since in this solvolysis reaction the "leaving group" remains in the molecule and for terpene chemistry because the epoxide opening may initiate biomimetic processes.

Scheme 1.



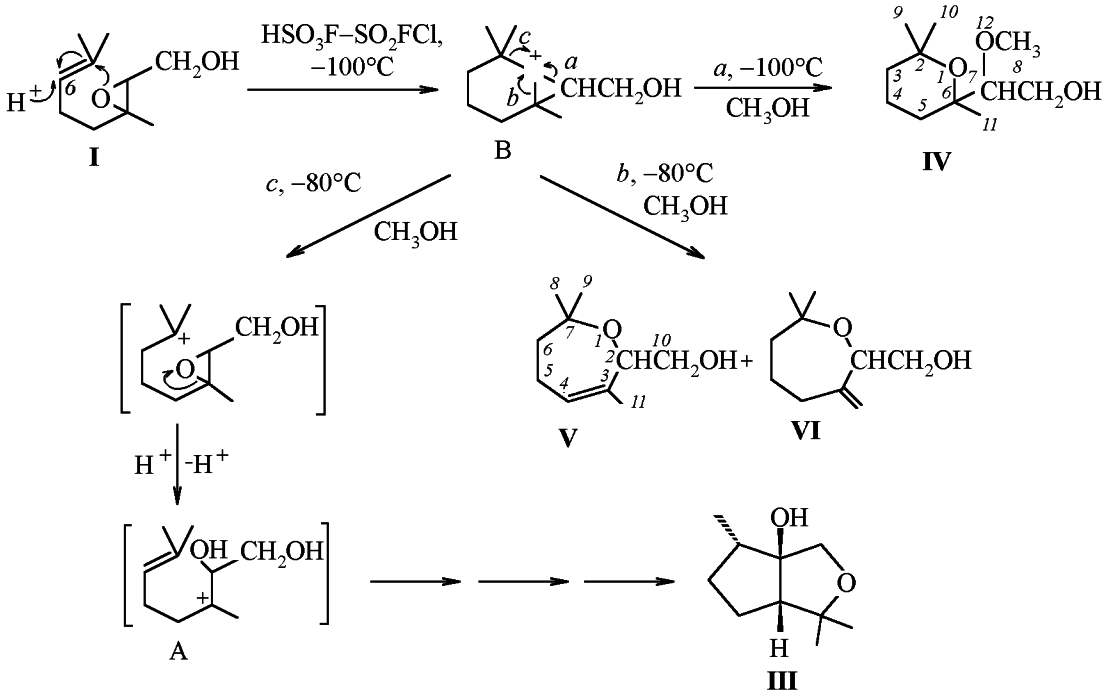
In the present study we investigated the behaviors of epoxides prepared from widely occurring acyclic monoterpenoids (geraniol, nerol, citronellol, and geranyl acetate) in a number of acidic media, under the action of liquid and solid superacids, in order to establish the role of the initial structure of compounds and the character of the medium on the main direction of the cationoid rearrangement.

2,3-Epoxygeraniol (**I**) was shown previously to yield in the system HSO_3F–SO_2 at –70°C epimer hydroxyoxides (**II**, main reaction product) and compound **III** [2] (Scheme 1).

In extension of the study on the behavior of epoxides from acyclic terpenoids in acidic media we decided to carry out the reaction of epoxide **I** at lower temperature than in [2] in order to reveal whether compounds **II** and **III** were the primary reaction products. It turned out that the "quenching" of the acid solution of epoxide **I** in HSO_3F–SO_2FCl (SO_2FCl–HSO_3F, 4:1 by volume, –100°C) with a mixture CH_3OH–$(C_2H_5)_2O$ provided as the main reaction product (67%, here and hereinafter content determined by GLC) 2,2,6-trimethyl-6-(2-hydroxy-1-methoxyethyl)tetrahydropyran (**IV**). If the acid solution was warmed before "quenching" to –80°C the reaction products mixture contained 2-hydroxymethyl-3,7,7-trimethyl-1-oxacyclohept-3-ene (**V**), 2-hydroxymethyl-7,7-dimethyl-3-methylen-1-oxacycloheptane (**VI**), and 5β-4,4,8α-trimethyl-3-oxabicyclo[3.3.0]octan-1β-ol (**III**) (**V** + **III** ~30%, **VI** ~36%, GLC). Compounds **III, V**, and **VI** were

1070-4280/01/3706-0793$25.00

Scheme 2.



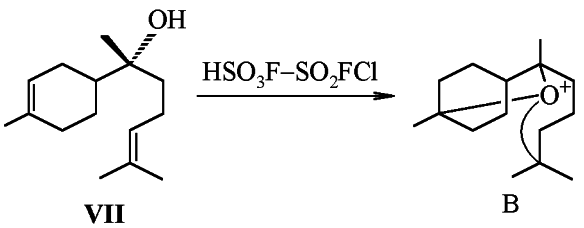
isolated as individual substances by column chromatography. The formation of these compounds is rationalized by Scheme 2.

The uncommon character of the process under consideration consists in the following. It was shown formerly by the example of 6,7- and 2,3-epoxides of humulene [3] that the cationic center in the unsaturated epoxides originated from the opening of the epoxy ring. To understand the results of the study in question it should be presumed that the cationic center appeared at C^7 atom due to a proton addition to C^6 atom, and then $(C^7)^+$ added to the epoxide oxygen to afford ion B of trialkyloxonium type. A similar stable ion C was generated from α-bisabolol (**VII**) in the system HSO_3F–SO_2FCl at –80°C [4] (Scheme 3).

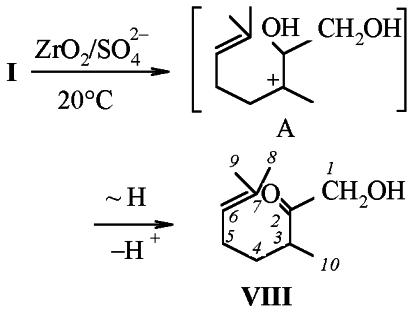
The "quenching" of the acidic solution of ion B salt at –100°C occurs with the cleavage of the C–O bond along the *a* path with a fairly unexpected formation of a secondary carbocation that is captured by methanol yielding compound **IV**. At heating the acidic solution to –80°C the C–O bonds in ion B suffer rupture along the *b* and *c* paths, and the "quenching" in this case affords compounds **V** + **VI** and **III**. Our data show that compound **III** isolated formerly in [2] under our conditions is a secondary product. Therewith the principal difference between Schemes 1 and 2 lies in the place of cationic center generation. In the former case initially occurs the cleavage of the epoxy ring followed by cyclization with the participation of the double bond; in the latter process first the double bond undergoes protonation, and then proceeds the attack on the epoxide oxygen.

We compared the behavior of epoxide **I** in the presence of a liquid (HSO_3F–SO_2FCl) and solid (ZrO_2/SO_4^{2-}) superacids. In the latter case the main reaction product (58%, GLC) is 1-hydroxy-3.7-dimethyloct-en-2-one (**VIII**) (Scheme 4).

Scheme 3.



Scheme 4.



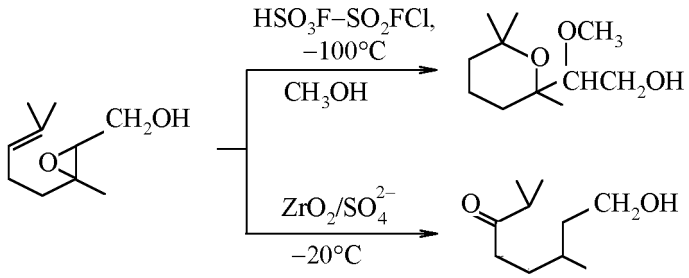
We indicated previously unlike behavior of 6,7- and 2,3-epoxides of α-humulene in the system HSO_3F–SO_2FCl and on solid catalysts although the cationic center was generated at the same point [3]. This difference was ascribed to the conformational control favored in the first case by low temperature. In the second case by the fixation of the substance on the surface of the solid catalyst. With epoxide **I** the conformational control apparently determines the different places of the cation center generation and therefore the dissimilar routes of the subsequent rearrangement. Moreover, the same ion A in the liquid acid suffers deeper rearrangement than on the solid superacid (cf. Schemes 1 and 4).

By the example of diastereomers of 6,7-epoxy citronellol (**IXa, b**) obtained from citronellol (**XXIII**) treated with monoperphthalic acid in the aqueous $NaHCO_3$ we showed that for conformationally nonrigid acyclic compounds with a single precursor of a carbocationic center the behavior in both systems HSO_3F–SO_2FCl and ZrO_2/SO_4^{2-} was similar (Scheme 5): in both cases arose 1-hydroxy-3,7- dimethyloctan-6-one (**X**) (yield 87 and 72% respectively, GLC).

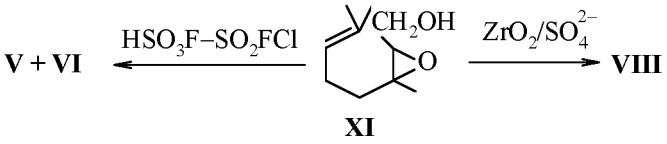
The substituents configuration in the 2,3-epoxy ring notably affects the reaction course in the liquid superacid. For instance, 2,3-epoxynerol (**XI**) in the system HSO_3F–SO_2FCl (–100°C) gives rise to a complex mixture of compounds. From this mixture were isolated oxides **V** and **VI** (Scheme 6). Yet on ZrO_2/SO_4^{2-} formed mainly ketone **VIII** (63%, GLC). Thus the isomeric epoxides **I** and **XI** react on the solid superacid in the same way.

After we had studied the behavior of the 2,3-epoxide of 2,6-diene **I** in various acid media we wished to investigate the rearrangements of the 6,7-epoxide of the same compound under similar conditions in order to reveal the effect of the place of the epoxy ring on the rearrangement mode. However it turned out that the 6,7-epoxide afforded complex mixtures both on liquid and solid superacids. Yet it was formerly demonstrated that geraniol **XII** and its acetate **XIII** in HSO_3F–SO_2FCl at –90 and –120°C respectively underwent initially the similar rearrangements: protonation occurred at C^6–C^7 double bond in *6* position, then proceeded carbocyclization by π–$(C^7)^+$ type. The further reaction pathways are different, and they result in formation via intermediate dehydration of a monocyclic allyl cation **XIV** [5] and of bicyclic carboxynium ion **XV** through heterocyclization [6] from alcohol **XII** and acetate **XIII** respectively (Scheme 7).

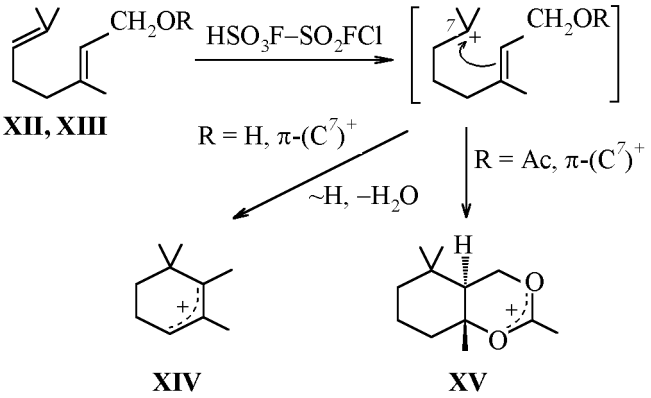
Scheme 5.



Scheme 6.



Scheme 7.

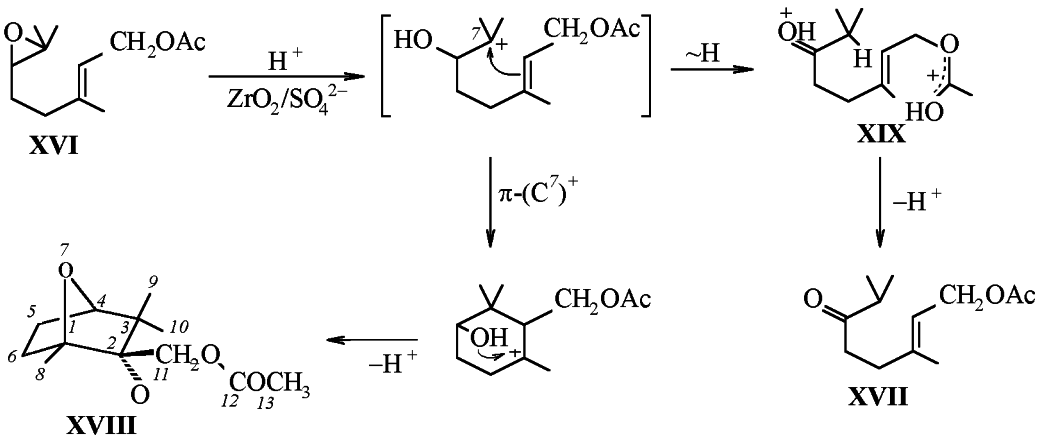


R = H (**XII**), Ac (**XIII**).

Here we report on the study of rearrangements of 6,7-epoxygeranyl acetate (**XVI**) on solid superacids. Compound **XVI** on ZrO_2/SO_4^{2-} at room temperature gave rise to a mixture of ketone **XVII** and 2-acetoxymethyl-1,3,3-trimethyl-7-oxabornane (**XVIII**) [7] (~3 : 1, GLC) (Scheme 8).

The main pathway of the reaction consists in 1,2-hydride shift to the carbocation center C^7 that has been formed by opening of the epoxy ring, and it is similar to the rearrangement pathway of epoxide **XVI** in HSO_3F–SO_2FCl at –120°C where a stable 1,7-dication **XIX** has been detected [6]. The other reaction route resulting in a bicyclic ether **XVIII** occurs through a series of carbo- and heterocyclizations unlike those observed with diene **XVII**. Note that in this case the carbocyclization occurs with

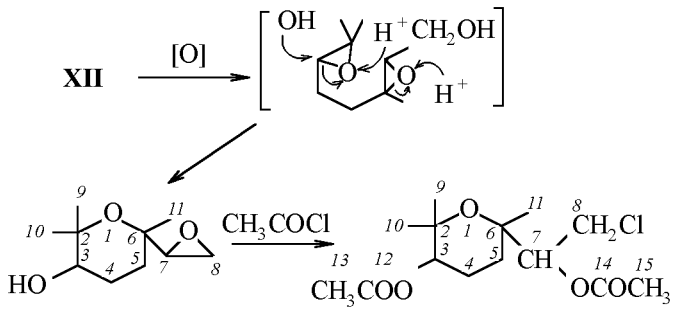
Scheme 8.



participation of the oxygen atom attached to C^6 in contrast to the rearrangement of acetate **XIII** in HSO_3F–SO_2FCl where the oxygen of the carbonyl group takes part in the cyclization.

The original epoxides **I** and **XI** were prepared by treating with monoperphthalic acid in aqueous NaOH of alcohol **XII** and nerol **XX** respectively. The oxidation of alcohol **XII** gave rise alongside epoxide **I** also to a side product 3-hydroxy-2,2,6-trimethyl-oxiranyltetrhydropyran (**XXIa, b**, two diastereomers, ~1:0.8 by the data of ^1H NMR). The oxidation presumably proceeds according to Scheme 9.

Scheme 9.



The reaction of diastereomers **XXIa, b** with acetyl chloride results in the cleavage of the epoxy ring to furnish diasteromers of 3-acetoxy-6-(1-acetoxy-2-chloroethyl)-2,2,6-trimethyltetrahydropyran (**XXIIa, b**, ~1 : 0.8 by the data of ^1H NMR).

The structure of all the newly prepared compounds was established from ^1H and ^{13}C NMR spectra. Note that in compound **IV** the coupling constant between the protons of the group $C^{11}H_3$ (J 0.5 Hz) and H^5 may evidence the axial orientation of the methyl group. The bonding of the OCH_3 group to the C^7 atom and of the hydroxy group to the C^8 atom and not vice versa was proved with the use of LRJMD spectrum: at decoupling from the signal of the OCH_3 group at 3.17 ppm in the LRJMD spectrum alongside the signals of the atoms C^7 and C^8 appears also the signal of C^6 atom at 79.61 ppm; if the OCH_3 group were attached to C^8 the latter signal would not be observed. The lack of the long-range W-coupling constant between the protons H^{6k} and H^2 may be due to the *endo*-position of the latter.

The data on ^1H and ^{13}C NMR spectra of epoxide **XI** were published in [8] without complete assignment of the signals. The chemical shifts in the spectra we registered are close to those reported in [8].

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded on the spectrometer Bruker AM-400 at 400.13 and 100.61 MHz respectively from solutions in $CDCl_3$ or in the mixture $CDCl_3$–CCl_4 (~1 : 1). The chloroform signal served as internal reference (δ 7.24 ppm, δ_C 76.90 ppm). The structure of compounds was determined from the NMR data basing on the analysis of coupling constants in the double resonance ^1H–^1H spectra and on ^{13}C NMR spectra. The assignment of signals in the latter was carried out with the use of spectra recorded with selective and off-resonance irradiation, and of differential spectra modulated with long-range spin-spin coupling ^{13}C–^1H (LRJMD,

^{13}C NMR spectra of compounds **IV**–**VI, VIII, IXa, b**–**XI, XVIII, XXIa, b,** δ_C, ppm

Carbon atom no.	**IV**[a]	**V**[a]	**VI**[a]	**VIII**[a]	**IXa**[a]	**IXb**[a]
1	–	–	–	66.86 t	60.51 t	60.51 t
2	75.01 s	72.88 d	75.77 d	213.35 s	39.33 t	39.58 t
3	40.36 t	135.28 s	151.17 s	41.91 d	29.01 d	29.21 d
4	18.82 t	128.18 d	32.58 t	32.78 t	33.46 t	33.46 t
5	40.65 t	23.54 t	24.11 t	25.39 t	25.96 t	26.18 t
6	79.61 s	39.41 t	39.44 t	123.13 d	64.47 d	64.51 d
7	74.57 d	75.55 s	76.18 s	132.51 s	58.30 s	58.18 s
8	62.58 t	26.13 q	24.33 q	17.49 q	18.46 q	18.41 q
9	28.33 q	27.84 q	30.06 q	25.47 q	24.66 q	24.66 q
10	27.12 q	63.63 t	66.03 t	16.22 q	19.40 q	19.24 q
11	16.14 q	19.88 q	109.20 t			
12	48.73 q					

Carbon atom no.	**X**[b]	**XI**[b]	**XVIII**[b]	**XXIa**[a] ($^1J_{C,H}$, Hz)	**XXIb**[a] ($^1J_{C,H}$, Hz)
1	60.65 t	61.01 t	85.62 s	–	–
2	39.52 t	64.09 d	54.17 d	70.39 s	71.22 s
3	29.03 d	61.18 s	44.80 s	86.49 d (136)	85.17 d (136)
4	30.19 t	33.14 t	85.80 d	25.97 t (128)	26.29 t (128)
5	37.74 t	24.20 t	25.83 t	32.44 t (131)	32.17 t (131)
6	214.79 s	123.51 d	38.37 t	81.00 s	81.86 s
7	40.78 d	132.13 s	–	56.78 d (174)	56.14 d (174)
8	18.24 q	17.65 q	18.18 q	43.48 t (175)	44.33 t (175)
9	18.24 q	25.71 q	23.10 q	23.94 q (126)	24.17 q (126)
10	19.53 q	22.20 q	25.78 q	27.01 q (126)	26.77 q (126)
11			63.25 t	23.90 q (126)	22.18 q (126)
12			170.48 s		
13			20.91 q		

[a] In $CDCl_3$. [b] In $CDCl_3$–CCl_4 (1 : 1).

experimental conditions optimized for long-range coupling constants $J_{C,H}$ 10 Hz). With diastereomers mixture **XXIa, b** was registered monoresonance spectrum. The ^{13}C NMR spectra are presented in the table.

The purity of the initial compounds was checked and the reaction products were analyzed by GLC on the chromatograph Biokhrom-1 equipped with a set of columns: (a) a glass capillary column 53000 × 0.26 mm, stationary phase XE-60; (b) quartz capillary column 13000 × 0.22 mm, stationary phase SE-54. Flame-ionization detector, carrier gas helium, columns at 80–180°C. The elemental composition of the compounds obtained was determined from the

high resolution mass spectra measured on Finnigan MAT 8200 instrument. The GC-MS analysis of the reaction products was performed on Hewlett Packard 618100A instrument.

Solutions of ion salts were prepared in twice distilled HSO_3F (bp 158–161°C). For dilution was used SO_2FCl purified by passing through sulfuric acid. The preparation of the ion salts solution and the "quenching" procedure were described in [9]. The nucleophilic agent used for "quenching" was a mixture methanol–ethyl ether (5 : 2 by volume). The preparation of the sulfated zirconium oxide was described in [3]; the catalyst was calcined just before the reaction for 2 h at 500°C. The solvent was passed through a column packed with calcined alumina. Compounds were separated by column chromatography on SiO_2 (Czechia, 40–100 μ).

Geraniol (**XII**) and citronellol (**XXIII**) were isolated as individual compounds from a mixture of alcohols **XII** and **XXIII** (~2 : 1) by chromatography on a column packed with SiO_2 + $AgNO_3$ (20%), eluent hexane ethyl ether containing ethyl ether from 0 to 50%. Geraniol and citronellol were identified by comparison of their NMR spectra with the published spectra [10].

2,3-Epoxygeraniol (I). (a) In keeping with procedure [11] to a mixture of 0.616 g of alcohol **XII** and 112 ml of 0.25 M water solution of NaOH was added 40 ml of 0.25 M water solution of monoperphthalic acid [12]. The reaction mixture was stirred for 6 h at 25°C, after workup 0.415 g of crude product was obtained that was subjected to chromatography on a column packed with SiO_2, gradient elution with a hexane–ethyl ether mixture containing 0–100% of ether. Epoxide **I** was obtained in 0.35 g amount. Its NMR spectra were in agreement with the data of [2].

(b) To a mixture of 0.6 g of alcohol **XII** and 100 ml of 0.25 M water solution of NaOH was added 0.25 M water solution of monoperphthalic acid (34 ml) [4]. The reaction mixture was stirred for 16 h and maintained for 80 h at 20°C. After workup 0.46 g of products mixture was obtained that was subjected to chromatography on a column packed with SiO_2, gradient elution with a hexane–ethyl ether mixture containing 0–50% of ether. We isolated 0.24 g of epoxide **I** and 0.12 g of a mixture of compounds **XXIa, b** (~1 : 0.8). Mass spectrum: *m/z* (I_{rel}, %): 143 (M^+ – $OCHCH_2$, 27), 85 (46), 84 (100), 70 (39), 59 (91), 43 (82), 41 (36). Found, %: M^+ 143.10740. $C_8H_{15}O_2$. Calculated, %: M^+ 143.10720. ^{1}H NMR spectrum of compound **XXIa** (δ, ppm, *J*, Hz): 1.03 s (C^9H_3), 1.11 s ($C^{10}H_3$), 1.17 s ($C^{11}H_3$), 1.48–1.57 m (1H^4, 1H^5), 1.68–1.78 (1H^5, 1H^4), 2.20 br.s (OH), 2.48 d.d (H^8, $J_{8,8'}$ 5, $J_{8,7}$ 3), 2.64 d.d (H$^{8'}$, *J* 5, $J_{8',7}$ 4), 2.93 d.d (H^7, *J* 4, 3), 3.68 s (H^3). ^{1}H NMR spectrum of compound **XXIb** (δ, ppm, *J*, Hz): 1.04 s (C^9H_3), 1.12 s ($C^{10}H_3$), 1.14 s ($C^{11}H_3$), 1.42 d.t (H^5, $J_{5,5'}$ 12, $J_{5,4}$ 7), 1.66–1.83 m (2H^4, H$^{5'}$), 2.33 br.s (OH), 2.51 d.d (H^8, $J_{8,8'}$ 5, $J_{8,7}$ 3), 2.67 d.d (H$^{8'}$, *J* 5, $J_{8',7}$ 4), 2.99 d.d (H^7, *J* 4, 3), 3.74 t (H^3, $J_{3,4}$ 7).

A solution of 0.025 g of the mixture of diastereomers **XXIa, b** (~1 : 0.8) in 1 ml of CH_3COCl was boiled for 1 h and left at 20°C overnight. The excess acetyl chloride was distilled off, the residue was dissolved in ethyl ether, the solution was washed with 10% water solution of $NaHCO_3$, and dried on $MgSO_4$. On removing the solvent we obtained 0.24 g of acetates **XIIa, b** (~1 : 0.8). ^{1}H NMR spectrum of acetate (**XXIIa**) (δ, ppm, *J*, Hz): 1.16 s ($C^{11}H_3$), 1.39 s and 1.41 s (C^9H_3, $C^{10}H_3$), 1.52–1,67 m and 1.77– 1.98 m (2H^4, 2H^5), 1.93 s and 2.10 s ($C^{13}H_3$, $C^{15}H_3$), 3.52 d.d (H^8, $J_{8,8'}$ 12, $J_{8,7}$ 9.5), 3.79 d.d (H$^{8'}$, *J* 12, $J_{8',7}$ 2.5), 4.01 d.d (H^3, $J_{3,4}$ 9, $J_{3,4'}$ 6), 5.08 d.d (H^7, *J* 9.5, 2.5). ^{1}H NMR spectrum of compound **XXIIb** (δ, ppm, *J*, Hz): 1.18 s ($C^{11}H_3$), 1.38 s and 1.49 s (C^9H_3, $C^{10}H_3$), 1.52–1.67 m and 1.77–1.98 m (2H^4, 2H^5), 2.04 s and 2.09 s ($C^{13}H_3$, $C^{15}H_3$), 3.53 d.d (H^8, $J_{8,8'}$ 12, $J_{8,7}$ 10), 3.86 d.d (H^3, $J_{3,4}$ 9, $J_{3,4'}$ 6.5), 3.87 d.d (H$^{8'}$, *J* 12, $J_{8',7}$ 2.2), 5.20 d.d (H^7, *J* 10, 2.2). ^{13}C NMR spectrum of isomers mixture **XXIIa, b** (δ_C, ppm): 82.14 s and 81.41 s (C^2, here and hereinafter the first signal corresponds to isomer **XXIIa**, and then follows that of isomer **XXIIb**), 85.18 d and 86.31 d (C^3), 26.09 t and 25.55 t (C^4), 36.46 t and 36.14 t (C^5), 83.60 s and 83.54 s (C^6), 75.69 d and 76.74 d (C^7), 43.42 t and 43.58 t (C^8), 22.07 q and 169.77 s (C^{11} and C^{14} of isomer XXIIa), 169.7 s, 169.97 s, 170.15 s (C^{12} of both isomers, C^{14} of isomer **XXIIb**), 22.68, 22.42, 22.32, 22.26, 21.58, 21.28, 20.76 all q (CH_3 groups of both isomers).

Isomerization of 2,3-epoxygeraniol (I). (a) A solution of 0.102 of epoxide **I** in 0.36 ml of SO_2FCl was added to a solution of 1.20 g of HSO_3F in 2.4 ml of SO_2FCl (–100°C), the reaction mixture was treated with a mixture of methanol (10 ml) and ethyl ether (4 ml), the resulting mixture was neutralized with 17% water solution of Na_2CO_3, the reaction products were extracted into ethyl ether, and the extract was dried on $MgSO_4$. After distilling off the solvent and percolation with ethyl ether through a column packed with Al_2O_3 (IV grade of activity) the

residue (0.79 g) was subjected to chromatography on a column packed with SiO_2, gradient elution with a hexane–ethyl ether mixture containing 0–50% of ether. We isolated 0.03 g of methyl ether **IV**. Mass spectrum, *m/z* (I_{rel}, %): 202 (M^+, 1), 140 (93), 125 (35), 85 (100), 72 (38), 43 (31), 41 (29). ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 1.11 s ($C^{9}H_3$), 1.15 d ($C^{11}H_3$, $J_{11,5a}$ 0.5), 1.17 s ($C^{10}H_3$), 1.31–1.42 m (H^{4a}, H^{5a}), 1.51 m (H^{3e}), 1.54 m (H^{4e}), 1.63 d.d.d (H^{3a}, $J_{3a,3e}$ 14.5, $J_{3a,4a}$ 8, $J_{3a,4e}$ 1.5), 1.90 d.d.d (H^{5e}, $J_{5e,5a}$ 11, $J_{5e,4a}$ 5.5, $J_{5e,4e}$ 1), 2.60 br.s (OH), 3.17 s (OCH_3), 3.38 d.d (H^8, $J_{8,8'}$ 11, $J_{8,7}$ 7), 3.52 d.d (H^7, *J* 7, $J_{7,8'}$ 6), 3.72 d.d ($H^{8'}$, *J* 11, 6).

(b) A solution of 0.153 g of epoxide **I** in 0.4 ml of SO_2FCl was added at –100°C to a solution of 1.8 g of HSO_3F in 3.8 ml of SO_2FCl, the mixture was warmed to –80°C. After "quenching" with a mixture CH_3OH–$(C_2H_5)_2O$, neutralization with 17% water solution of Na_2CO_3 and usual workup the residue was passed through a column with Al_2O_3 (of IV grade activity) (eluent ethyl ether). We obtained 0.085 g of product mixture that was subjected to chromatography on column packed with SiO_2 and then on that with SiO_2 + $AgNO_3$ (20%). As a result compounds **III, V**, and **VI** were isolated as individual substances. Mass spectra of compounds **V** and **VI**: M^+ 170 (0.92%) and M^+ 170(0.08%). In the mass spectra of isomers **V** and **VI** was observed an ion 139 (M^+ – CH_2OH). ^{1}H NMR spectrum of compound **V** (δ, ppm, *J*, Hz): 1.24 s, 1.26 s ($C^{8}H_3$, $C^{9}H_3$), 1.57 m ($C^{11}H_3$, *J* 1.5–2.5), 1.60 d.d.d (H^6, $J_{6,6'}$ 14, $J_{6,5}$ 6.5, $J_{6,5'}$ 2), 1.89 d.d.d.q ($H^{6'}$, *J* 14, $J_{6',5'}$ 12.5, $J_{6',5}$ 1.5, J_{6',CH_3} 1), 1.94 d.d.d.d.d (H^5, $J_{5,5'}$ 16, $J_{5,4}$ 8, *J* 6.5, 1.5, $J_{5,2}$ 1), 2.26 br.d.d (H^{12}, $J_{12,10'}$ 10, $J_{12,10}$ 2.5), 2.41 d.d.d.q.d.d ($H^{5'}$, *J* 16, 12.5, $J_{5',4}$ 2.5, $J_{5',11}$ 2.5, $J_{5',6}$ 2, $J_{5',2}$ 1.5), 3.50 d.d.d (H^{10}, $J_{10,10'}$ 11, $J_{10,2}$ 9, $J_{10,12}$ 2.5), 3.71 d.d.d ($H^{10'}$, *J* 11, 10, $J_{10',2}$ 3.5), 4.33 br.d.d (H^2, *J* 9, 3.5), 5.50 d.d.d.q H^4, *J* 8, 2.5, $J_{4,2}$ 2.5, $J_{4,11}$ 1.5). ^{1}H NMR spectrum of compound **VI** (δ, ppm, *J*, Hz): 1.20 s, 1.21 s ($C^{8}H_3$, $C^{9}H_3$), 1.41–1.52 m (H^5, H^6), 1.67 m ($H^{6'}$), 1.77 m ($H^{5'}$), 2.14 br.s (OH), 2.15 d.d.d (H^4, $J_{4,4'}$ 13, $J_{4,5}$ 5, $J_{4,5'}$ 5), 2.31 d.d.d.d.d ($H^{4'}$, *J* 13, $J_{4',5}$ 10, $J_{4',5'}$ 5, $J_{4',11'}$ 1.5, $J_{4',2}$ 1), 3.44 br.d.d (H^{10}, $J_{10,10'}$ 11, $J_{10,2}$ 5) and 3.47 br.d.d ($H^{10'}$, *J* 11, $J_{10',2}$ 8), *AB* system, 4.22 d.d.d.d (H^2, *J* 8, 5, $J_{2,11}$ 1.5, $J_{2,4'}$ 1), 4.71 d.d (H^{11}, *J* 1.5, $J_{11,11'}$ 1), 4.85 m ($H^{11'}$, *J* 1–1.5).

(c) To a dispersion of 0.135 g of ZrO_2/SO_4^{2-} in 10 ml of CH_2Cl_2 was added a solution of 0.152 g of epoxide **I** in 2 ml of CH_2Cl_2, and the mixture was stirred for 1 h at 25°C. After the usual workup we obtained 0.137 g of crude product that was percolated with ethyl ether through a column packed with Al_2O_3 (of IV grade activity). As a result 0.077 g of the reaction products mixture was separated and subjected to column chromatography on SiO_2 (gradient elution with a hexane–ethyl ether mixture containing 0–50% of ether). We isolated 0.025 g of ketone **VIII**. Mass spectrum: *m/z* (I_{rel}, %): 170 (M^+, 10), 88 (27), 82 (97), 69 (100), 67 (28), 55 (23), 41 (51). Found: M^+ 170.13030. $C_{10}H_{18}O_2$. Calculated: *M* 170.13067. ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 1.08 d ($C^{10}H_3$, $J_{10,3}$ 7), 1.39 d.d.d.d (H^4, $J_{4,4'}$ 13.5, $J_{4,5}$ 8, $J_{4,5'}$ 7, $J_{4,3}$ 7), 1.54 br.s ($C^{8}H_3$), 1.64 d.t ($C^{9}H_3$, $J_{9,6}$ 1.5, $J_{9,5}$ 1), 1.70 d.d.d.d ($H^{4'}$, *J* 13.5, $J_{4',5'}$ 8.5, $J_{4',5}$ 7, $J_{4',3}$ 7), 1.92 m ($2H^5$), 2.50 d.d.q (H^3, *J* 7, 7, 7), 3.16 br.s (OH), 4.20 d and 4.25 d ($2H^1$, *J* 19), *AB* system, 4.99 t.q.q (H^6, $J_{6,5}$ 7, $J_{6,8}$ 1.5, *J* 1.5).

Rearrangements of diastereomeric epoxides IXa, b. To a mixture of 0.108 g of citronellol (**XXIII**) and 19 ml of 0.25 M water solution of $NaHCO_3$ was added at 0°C 13 ml of 0.15 M water solution of monoperphthalic acid, and the mixture was stirred for 2 h at the same temperature. The workup furnished 0.101 g of the reaction products mixture that was subjected to column chromatography on SiO_2 (gradient elution with hexane–ethyl ether mixture containing 0–30% of ether). We separated 0.061 g of the mixture of epoxides **IXa, b**. ^{1}H NMR spectrum of compound **IXa** (δ, ppm, *J*, Hz): 0.91 d ($C^{10}H_3$), $J_{10,3}$ 6.5), 1.24 s, 1.28 s ($C^{8}H_3$, $C^{9}H_3$), 1.32–1.62 m ($2H^2$, $2H^4$, $2H^5$), 1.64 m (H^3), 2.18 br.s (OH), 2.68 d.d (H^6, $J_{6,5}$ 7, $J_{6,5'}$ 6), 3.65 d.t (H^1, $J_{1,1'}$ 10, $J_{1,2}$ 6.5) and 3.70 d.d.d ($H^{1'}$, *J* 10, $J_{1',2}$ 7, $J_{1',2'}$ 6), *AB* system. The chemical shifts of the signals from **IXb** isomer in the ^{1}H NMR spectrum of the **IXa, b** mixture are very close to that of the other isomer. In the ^{13}C NMR spectra of the isomers **IXa, b** some signals of the carbon atoms have slightly different chemical shifts (see table). To a dispersion of 0.1 g of ZrO_2/SO_4^{2-} in 5 ml of CH_2Cl_2 was added a solution of 0.051 g of epoxides **IXa** and **IXb** in 1 ml of CH_2Cl_2, and the mixture was stirred for 1 h at 20°C. After the usual workup we obtained a crude product that was percolated with ethyl ether through a column packed with Al_2O_3 (of **IV** grade activity). As a result 0.035 g of the reaction products mixture was separated (containing ~72% of ketone **X**, GLC) and subjected to column chromatography on SiO_2 (gradient elution with a hexane–ethyl ether mixture

containing 0–50% of ether). We isolated 0.017 g of ketone **X**. Found: M^+ 172.14653. $C_{10}H_{20}O_2$. Calculated: *M* 172.14632. ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 0.88 d ($C^{10}H_3$, $J_{10,3}$ 6.5), 1.06 d (C^8H_3, C^9H_3, *J* 7), 1.32 d.t.d (H^4, $J_{4,4'}$ 14, $J_{4,5}$ 7, $J_{4,3}$ 6.5), 1.39 m (H^2), 1.52 m ($H^{2'}$, H^3), 1.65 d.t.d ($H^{4'}$, *J* 14, $J_{4',5}$ 7, $J_{4',3}$ 4.5), 1.67 br.s (OH), 2.44 m ($2H^5$), 2.57 q.q (H^7, $J_{7,8}$ 7, $J_{7,9}$ 7), 3.63 d.t (H^1, $J_{1,1'}$ 10.5, $J_{1,2}$ 6.5) and 3.70 d.t ($H^{1'}$, *J* 10.5, $J_{1',2}$ 6.5), *AB* system.

Rearrangements of 2,3-epoxynerol (XI). To a solution of 1.7 g of citral in 32 ml of anhydrous ethyl ether was added dropwise at 0°C a mixture of 0.34 g of $LiAlH_4$ and 6 ml of ethyl ether. The stirring was carried out at 0°C for 30 min and then the reaction mixture was heated to 20°C within 30 min. Excess water was added and 2 ml of AcOH, and the products were extracted with ethyl ether. The extract was washed with 2% water solution of $NaHCO_3$, then with water, and dried on Na_2SO_4. On removing the solvent we obtained 1.7 g of a mixture of alcohols **XII** and **XX** (~3 : 2, GLC). The mixture was subjected to column chromatography on SiO_2 + $AgNO_3$ (20%) (gradient elution with a hexane–ethyl ether mixture containing 0–50% of ether) to afford the alcohol **XX** as an individual substance (^{1}H NMR spectrum). To a mixture of 0.32 g of alcohol **XX** and 56 ml of 0.25 M water solution of NaOH was added 20 ml of 0.25 M water solution of monoperphthalic acid, and the mixture was stirred for 5 h at 20°C. The workup yielded 0.316 g of substance that was subjected to column chromatography on SiO_2 (gradient elution with a mixture hexane–ethyl ether containing from 0 to 30% of ether). We isolated 0.047 g of alcohol **XX** and 0.221 g of epoxide **XI**. ^{1}H NMR spectrum epoxide **XI** (δ, ppm, *J*, Hz): 1.29 s ($C^{10}H_3$), 1.44 d.d.d (H^4, $J_{4,4'}$ 14, $J_{4,5'}$ 14, $J_{4,5}$ 9, $J_{4,5}$ 7), 1.58 br.d (C^8H_3, $J_{8,6}$ 1.5), 1.60 d.d.d ($H^{4'}$, *J* 14, $J_{4',5}$ 9, $J_{4',5'}$ 6), 1.65 d.t (C^9H_3, $J_{9,6}$ 1.5, $J_{9,5}$ 1), 2.02 br.d.d.d.d (H^5, $J_{5,5'}$ 15, *J* 9, 7, $J_{5,6}$ 7) and 2.09 d.d.d.d ($H^{5'}$, *J* 15, 9, 6, $J_{5',6}$ 7) – system *AB*, 5.04 d.d.q.q (H^6, *J* 7, 7, 1.5, 1.5).

A solution of 0.05 g of epoxide **XI** in 1 ml of CH_2Cl_2 was added to a dispersion of 0.1 g of in 5 ml of CH_2Cl_2, and the mixture was stirred for 2 h at 20°C. After the workup and passing of the residue through a column with Al_2O_3 (of IV activity grade), eluent ethyl ether, we obtained 0.03 g of a mixture (~63% of ketone **VIII**, GLC) that was subjected to chromatography on a column packed with SiO_2 (gradient elution with a mixture hexane–ethyl ether containing from 0 to 30% of ether). We isolated 0.012 g of ketone **VIII** (^{1}H NMR, GLC).

A solution of 0.136 g of epoxide **XI** in 0.4 ml of SO_2FCl was added to a solution of 1.56 g of HSO_3F in 2.4 ml of SO_2FCl (–100°C), "quenching" with a mixture of CH_3OH (20 ml) and $(C_2H_5)_2O$ (8 ml). The mixture was neutralized with 17% water solution of $NaCO_3$, the reaction products were extracted into ethyl ether, and the extract was dried on $MgSO_4$. The residue after evaporation of the solvent (0.119 g) was passed through a column with Al_2O_3 (of IV activity grade), eluent ethyl ether. The obtained 0.053 g of the products mixture was subjected to chromatography on a column packed with SiO_2 (gradient elution with a mixture hexane–ethyl ether containing from 0 to 100% of ether) to isolate compounds **V** and **VI** as individual substances (^{1}H and ^{13}C NMR).

Rearrangements of 6,7-epoxygeranyl acetate. To a dispersion of 0.4 g of ZrO_2/SO_4^{2-} in 18 ml of CH_2Cl_2 was added a solution of 0.2 g of epoxide **XVI** in 2 ml of CH_2Cl_2, and the mixture was stirred for 0.5 h at 20°C. After the usual workup the substance was passed through a column packed with Al_2O_3 (of **IV** grade activity), eluent ethyl ether, to afford 0.195 g of products mixture containing ~31% of ketone **XVII**, ~11% of ether **XVIII** (GLC). The latter mixture was subjected to chromatography on a column packed with SiO_2 (gradient elution with a mixture hexane–ethyl ether containing from 0 to 30% of ether). As a result we isolated 0.05 g of ketone **XVII** and 0.2 g of a mixture of compounds **XVII** and **XVIII** (~0.4 : 1, ^{1}H NMR). The compounds were identified with the use of ^{1}H and ^{13}C NMR spectra [6, 7]. Below are given for compound **XVIII** more complete data on ^{1}H NMR spectrum and refined assignments of methyl groups signals in the ^{13}C NMR spectrum. ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 1.01 s (C^9H_3), 1.05 s ($C^{10}H_3$), 1.32 s (C^8H_3), 1.42 d.d.d (H^6_{exo}, $J_{6exo,6endo}$ 12.5, $J_{6exo,5exo}$ 12, $J_{6exo,5endo}$ 4.5), 1.54 t (H^2_{endo}, $J_{2endo,11}$ 7.5), 1.54 d.d.d (H^6_{endo}, *J* 12.5, $J_{6endo,5endo}$ 9, $J_{6endo,5exo}$ 5), 1.68 d.d.d.d (H^{5e}xo, $J_{5exo,5endo}$12.5, *J* 12, 5, $J_{5exo,4}$ 5), 1.90 d.d.d (H^5_{endo}, *J* 12.5, 9, 4.5), 1.99 s ($C^{13}H_3$), 3.73 d (H^4, *J* 5), 3.94 d.d (H^{11}, $J_{11,11'}$ 11, *J* 7.5) and 4.08 d.d ($H^{11'}$, *J* 11, 7.5) – *AV* system.

REFERENCES

1. Barkhash, V.A. and Polovinka, M.P., *Usp. Khim.*, 1999, vol. 68, no. 5, pp. 430–453.
2. Baig, M.A., Banthorpe, D.V., Carr, G., and Whittaker, D., *J. Chem. Soc., Perkin Trans. II*, 1989, pp. 1981–1986.

3. Khomenko, T.M., Zenkovets, G.A., and Barkhash, V.A., *Zh. Org. Khim.*, 1997, vol. 33, no. 5, pp. 655–659.
4. Polovinka, M.P., Korchagina, D.V., Lyutina, L.G., Sal'nikov, G.E., Mamatyuk, V.I., and Barkhash, V.A., *Zh. Org. Khim.*, 1991, vol. 27, no. 10, pp. 2107–2115.
5. Gavrilyuk, O.A., Korchagina, D.V., Bagryanskaya, I.Yu., Gatilov, Yu.V., and Barkhash, V.A., *Zh. Org. Khim.*, 1992, vol. 28, no. 8, pp. 1602–1614.
6. Korchagina, D.V., Gavrilyuk, O.A., Barkhash, V.A., Vlad, P.F., Ungur, N.D., and Popa, N.D., *Zh. Org. Khim.*, 1993, vol. 29, no. 2, pp. 323–325.
7. Barrero, A.F., Alvarez-Manzaneda, E.J., and Palomino, P.L., *Tetrahedron*, 1994, vol. 50, no. 46, pp. 13239–13250.
8. Taber, D.F. and Houze, J.B., *J. Org. Chem.*, 1994, vol. 59, no. 14, pp. 4004–4006.
9. Osadchii, S.A., Polovinka, M.P., Korchagina, D.V., Pankrushina, N.A., Dubovenko, Zh.V., Barkhash, V.A., and Koptyug, V.A., *Zh. Org. Khim.*, 1981, vol. 17, no. 6, pp. 1211–1223.
10. Standart NMR Spectra. Sadtler Research Laboratories; Sadtler Standart Spectra: C-13 Nuclear Magnetic Resonance Spectra.
11. Fringuelli, F., Pizzo, F., and Germany, R., *Synlett.*, 1991, pp. 475–476.
12. Fiser, L. and Fiser, M., *Reagenty dlya organicheskogo sinteza* (Reagents for Organic Synthesis), Moscow: Mir, 1970, vol. 2, pp. 312–313.