Russian Journal of Organic Chemistry, Vol. 38, No. 6, 2002, pp. 810–822. Translated from Zhurnal Organicheskoi Khimii, Vol. 38, No. 6, 2002, pp. 852–864.

Acid-catalyzed Reactions of Camphene and α-Fenchene Epoxides

O. I. Yarovaya, D. V. Korchagina, Yu. V. Gatilov, and V. A. Barkhash

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

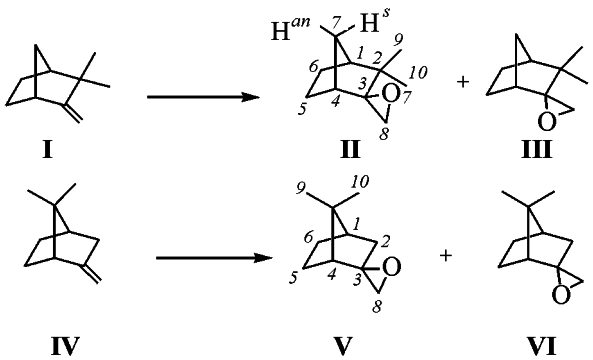
Received June 18, 2001

Abstract—Isomerization of camphene and α-fenchene epoxides under homogeneous and heterogeneous conditions in media of various acidity was studied. The intermolecular reactions of these epoxy compounds with unsaturated aldehydes, allyl alcohol and methanol on askanite-bentonite clay yielded spiroacetals, and open-chain hydroxyethers and acetals. The results obtained are compared to those for reactions with the initial monoterpenes.

Acid-catalyzed reactions of epoxy derivatives of natural substances are of great importance for the chemistry of terpenes. In the present study we investigated intra- and intermolecular reactions of camphene epoxides **II, III** and α-fenchene epoxides **V, VI** under homogeneous and heterogeneous conditions. Although the epoxides under investigation were prepared previously [1, 2], their acid-catalyzed intra- and intermolecular reactions are poorly understood. Besides we compared these reactions with analogous transformations of the initial bicyclic monoterpenes in order to establish the effect of the way of cationic center formation on the result of a cationoid rearrangement.

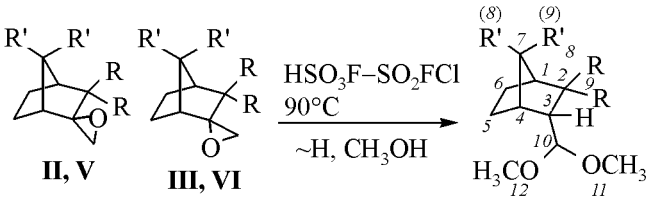
Epoxides **II, III** and **V, VI** obtained by treating with peracetic acid camphene (**I**) and α-fenchene (**IV**) formed in 2.3 : 1 and 1 : 1 ratio respectively (Scheme 1). Initial α-fenchene (**IV**) was prepared by acetolysis of α-fenchol tosylate as described in [3]. The epoxides used further in reactions contained the isomers in the above indicated ratio.

Scheme 1.



We studied acid-catalyzed reaction of a mixture of optically active epoxides **II** and **III**, and of a mixture of epoxides **V** and **VI** in a system HSO_3F–SO_2FCl at –90°C. The acid solutions were quenched with CH_3OH–$(C_2H_5)_2O$ mixture. From epoxy compounds **II** and **III** a racemic 2,2-dimethyl-3-*endo*-dimethoxymethylbicyclo[2.2.1]heptane (**VIIa**) was obtained (Scheme 2), and epoxy compounds **V** and **VI** yielded racemic 7,7-dimethyl-3-*endo*-dimethoxymethylbicyclo[2.2.1]heptane (**VIIb**). The products **VIIa, b** are racemic, thus before the ion takes up a methanol molecule it undergoes rearrangements resulting in racemization.

Scheme 2.

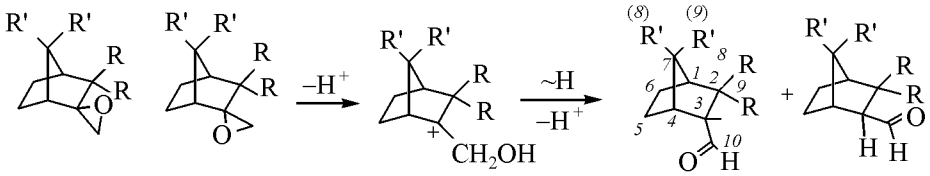


II, R = CH_3, R' = H; **III**, R = CH_3, R' = H; **V**, R = H, R' = CH_3; **VI**, R = H, R' = CH_3; **VIIa**, R = CH_3, R' = H; **VIIb**, R = H, R' = CH_3.

The variation of the acid medium provides a possibility to change the character of the arising products and to manage their ratio. The isomerization of epoxy compounds **II** and **III** on a solid superacid TiO_2/SO_4^{2-} or askanite-bentonite clay furnished a mixture of 2,2-dimethyl-3-*endo*- (**VIIIa**) and 2,2-dimethyl-3-*exo*-formylnorbornanes (**IXa**) with aldehyde **VIIIa**

1070-4280/01/3806-810$27.00 © 2002 MAIK "Nauka/Interperiodica"

Scheme 3.



II, V **III, VI** A **VIIIa, b** **I a, b**

II, R = CH_3, R' = H; **III**, R = CH_3, R' = H; **V**, R = H, R' = CH_3; **VI**, R = H, R' = CH_3; **VIIIa**, R = CH_3, R' = H; **IXa**, R = CH_3, R' = H; **VIIIb**, R = H, R' = CH_3; **IXb**, R = H, R' = CH_3.

prevailing, whereas the isomerization of the same epoxides **II** and **III** mixture in the formic acid provided mainly aldehyde **IXa** (Scheme 3).

Isomerization of epoxides **V** and **VI** on heterogeneous catalysts also resulted in formation of aldehydes with considerable prevalence of 7,7-dimethyl-3-endo-formylnorbornane (**VIIIb**), and in formic acid epoxides **V** and **VI** were converted into isomers **VIIIb** and **IXa** in 1 : 1 ratio. The aldehydes **VIIIa, b, IXa**) in contrast to compounds **VIIa, b** are optically active; thus the ratio of rates of 1,2-hydride shift in ion A arising at the opening of the epoxy ring in compounds **II, III, V, VI**, and the rates of the other rearrangements leading to racemization depends on the nature of the medium:

	VIIIa : IXa	**VIIIb : IXb**
Askanite-bentonite clay, 20°C	9 : 1	7 : 1
TiO_2/SO_4^{2-}, 20°C	9 : 1	5 : 1
HCOOH, 100°C	1 : 6	1 : 1

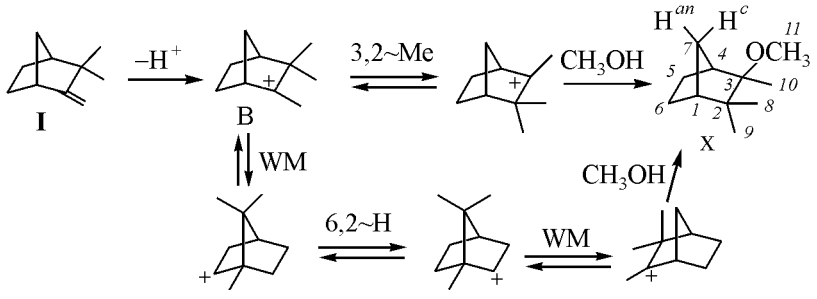
The isomerization of the initial bicyclic monoterpenes was investigated earlier. It is known [4] that isomerization of an optically active camphene (**I**) in acid medium results in racemization. In a superacid [5] a stable camphene-hydrocation B was generated from camphene. We showed that at quenching by a mixture CH_3OH–$(C_2H_5)_2O$ of a solution of compound **I** in acid system HSO_3F–SO_2FCl a racemic product was isolated, 2,2,3-trimethyl-3-*exo*-methoxynorbornane (**X**) originating from capture of cation B with a methanol molecule (Scheme 4).

The isomerization of the other initial olefin **IV** in superacid media at various temperature led to rearrangement of the fenchane skeleton and its opening into a monocyclic allyl cation [6].

We studied intermolecular reactions of epoxides **II, III, V, VI** with oxygen-containing compounds in the presence of heterogeneous catalysts, and we compared these processes with similar reactions of camphene (**I**). As was shown [7], camphene (**I**) with unsaturated aldehydes and ketones on wideporous zeolite β provided either compound **XI**, a product of [3+2]-carbocyclization with methacrolein, or compounds **XII** that could be formally regarded as products of ω-substitution of a hydrogen atom in the molecule of the initial compound (Scheme 5).

In both cases the positively charged β-olefin carbon of the carbonyl compound attacks the double bond of camphene with conservation of the carbonyl group. Reactions of epoxides **II, III** with aldehydes (acrolein, methacrolein, crotonic aldehyde), and epoxides **V, VI**

Scheme 4.[*]



[*] Here and hereinafter we use the following notation of protons: H^{7an} is *7anti*-H, H^{7c} is *syn*-H; *x* is *exo*, *n* is *endo*.

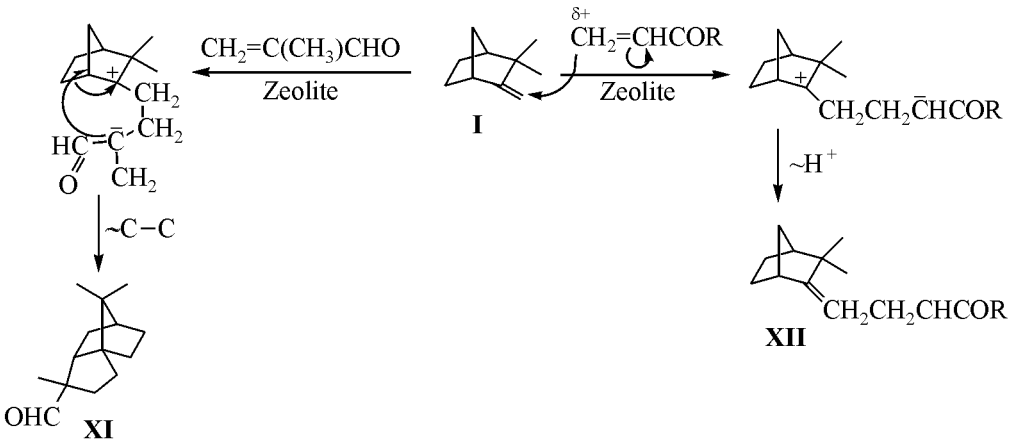
with acrolein on askanite-bentonite clay follow another route. The reaction products are spiroacetals **XIII** containing a 1,3-dioxolane ring (Scheme 6). The structure of 3,3-dimethylbicyclo[2.2.1]heptane-2(*S*)-spiro-5'-(2'-allyl-1',3'-dioxolane) (**XIIIa**), 3,3-dimethylbicyclo[2.2.1]heptane-2(*S*)-spiro-5'-(2'-propenyl-1',3'-dioxolane) (**XIIIb**), 3,3-dimethylbicyclo-[2.2.1]heptane-2(*S*)-spiro-5'-(2'-isopropenyl-1',3'-dioxolane) (**XIIIc**), 7,7-dimethylbicyclo[2.2.1]heptane-2(*S*)-spiro-5'-(2'-allyl-1',3'-dioxolane) (**XIIId**) was established from NMR spectra.

The side reaction, isomerization of the initial epoxides, affords the corresponding aldehydes. The ratio of the sum of isomerization products **VIIIa + IXa** to the products of the intermolecular reaction **XIIIa, b, c** in reactions of epoxides **II, III** with aldehydes amounted to ~1 : 1 and did not depend on the temperature; in reaction of epoxides **V, VI** with acrolein this ratio was (**VIIIb + IXb**) : (**XIIId**) = ~1 : 0.6.

Let us consider the probable mechanism of spiroacetals **XIIIa–d** formation in more detail. In order to reveal the most stable and thermodynamically feasible reaction products we performed on models calculations, semiempirical (AM1) for cations and by molecular mechanics (MMX) for neutral compounds. According to the calculations the protonation of epoxides **II** and **III** with no barrier provides the same cation A (Scheme 7, values ΔH_f^0, $\Delta G^{\neq}$, kcal mol^{-1}). Further reaction may take different routes: either the carbocation reacts with the oxygen of the aldehyde yielding an intermediate compound D, or the 1,2-hydride shift results in cation C. Cation C may either eliminate a proton to form aldehyde **VIIIa** or react with aldehyde to afford 1,3-dioxetane **XV**; however the latter compound was not observed. As show the calculations, compound **XV** is less stable than spiroacetal **XIV**. Therefore, since the acetal formation is reversible, the more stable 1,3-dioxolanes **XIV** should form as we actually observe.

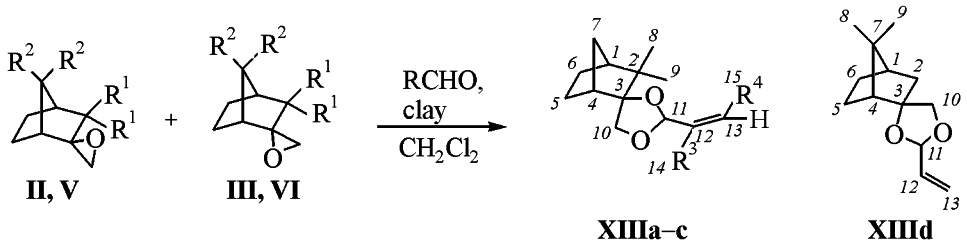
The choice between the alternative structures **XIVa** and **XIVb** in reactions of epoxides **II, III** with aldehydes and of epoxides **V, VI** with acrolein was made as follows. The calculations by MMX procedure show, that compounds **XIVa** and **XIVb** are

Scheme 5.



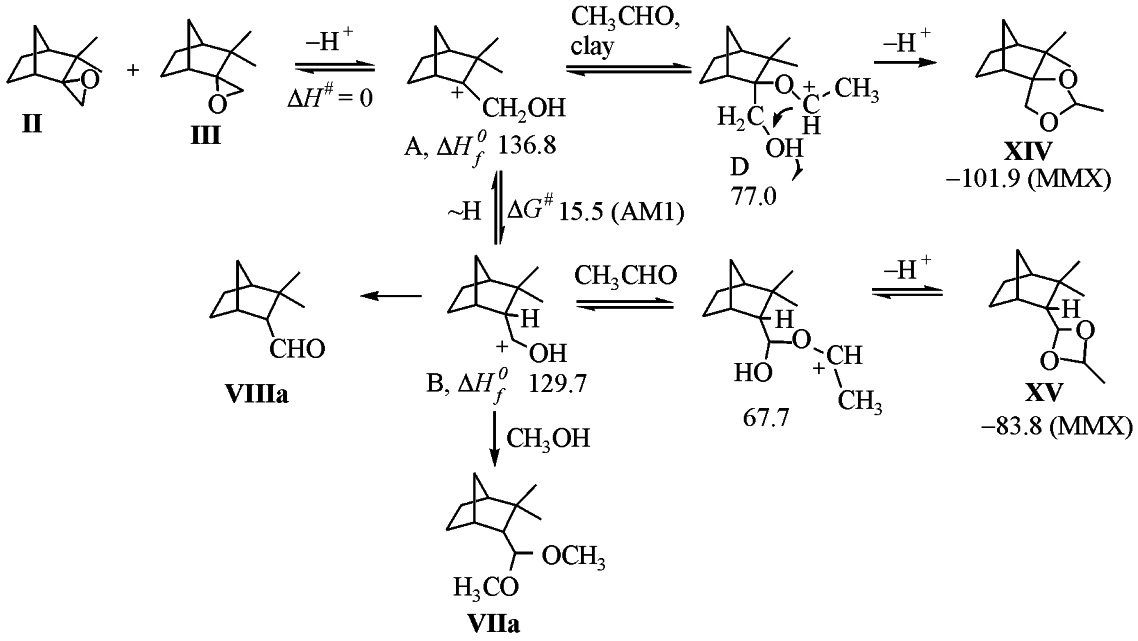
R = H, CH_3.

Scheme 6.

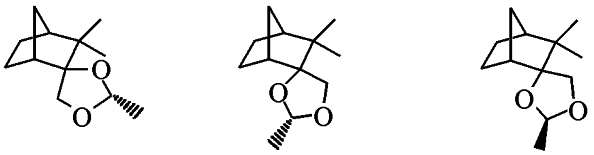


II, R^1 = CH_3, R^2 = H; **III**, R^1 = CH_3, R^2 = H; **V**, R^1 = H, R^2 = CH_3; **VI**, R^1 = H, R^2 = CH_3; **XIIIa**, R^3 = H, R^4 = H; **XIIIb**, R^3 = CH_3, R^4 = H; **XIIIc**, R^3 = H, R^4 = CH_3.

Scheme 7.



equally stable; also the configuration of CH_3 group in the heteroring does not notably affect the stability of compounds **XIVb** and **XIVc**.

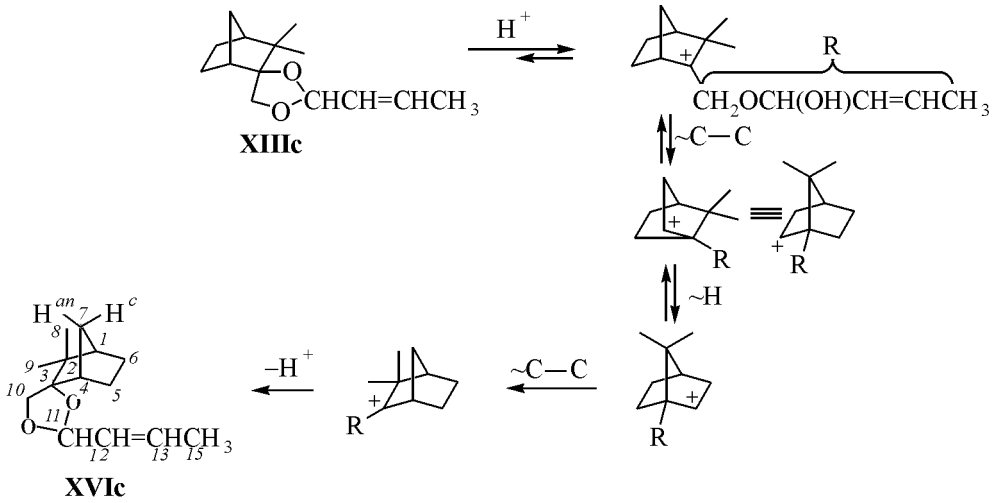


XIVa	**XIVb**	**XIVc**
ΔH_f^0 –101.9	–101.4	–101.0

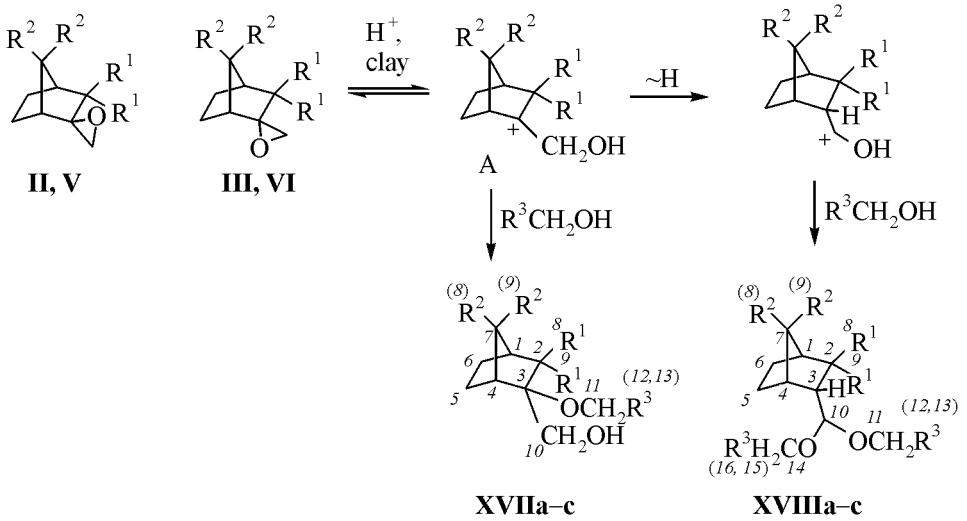
Yet it is known that nucleophiles attack the 3,3-substituted 2-norbornyl cations predominantly from the *exo*-side both in the liquid acids [8] and on aluminosilicate catalysts [9], whereas the 7,7-substituted 2-norbornyl cations are subjected to attack from the endo-side. Therefore we ascribed to the oxygen atom of the heteroring in the forming spiroacetals *exo*-orientation in compounds **XIIIa–c** and *endo*-orientation in compound **XIIId**.

In reaction of epoxides **II, III** with crotonic aldehyde the arising spiroacetal **XIIIc** at standing

Scheme 8.



Scheme 9.



II, V **III, VI** A **XVIIa–c** **XVIIIa–c**

	XVII	XVIII
(a) R^1 = CH_3, R^2 = H, R^3 = $CH{=}CH_2$	1	4.8
(b) R^1 = CH_3, R^2 = H, R^3 = H	1	1.5
(c) R^1 = H, R^2 = CH_3, R^3 = $CH{=}CH_2$	1	6

XVIIIb≡VIIa

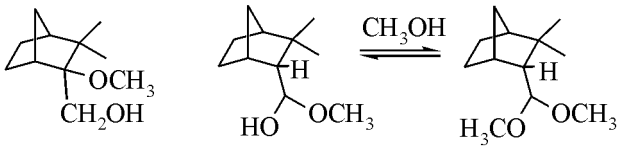
isomerizes into acetal **XVIc** with the *endo*-position of the oxygen in the heteroring (Scheme 8). At room temperature the isomer ratio of **XIIIc** and **XVIc** attains the value of 1:1.

Compound **XIIIc**, as also compounds **XIIIa, b, d**, is optically active, but acetal **XVIc** is racemic. This is an evidence of primary formation of acetal **XIIIc** that further isomerizes into compound **XVIc**. The racemization does not occur at the stage of ion A formation,for ion A is rapidly trapped by aldehydes. The racemization of acetal **XVIc** may be rationalized by Scheme 8.

It should be noted that reactions of epoxides with aldehydes were known [10], and Lewis acids were used as catalyst; however the processes occurring here were poorly investigated, and no spiroacetals were reported as products.

The reactions of epoxides **II, III** with allyl alcohol and methanol and epoxides **V, VI** with allyl alcohol carried out on askanite-bentonite clay provide hydroxyethers **XVII** and acetals **XVIII** (Scheme 9); alongside this process occurs isomerization of epoxides into the corresponding aldehydes.

The main products in reactions of epoxides with alcohols are usually hydroxyethers. The opening of the epoxy ring is an important method for preparation of *trans*-1,2-bifunctional molecules [11], but these processes also are poorly understood. In our case main products are acetals **XVIII**. We calculated stability of the final products **XVIIb** and **XVIIIb** in reactions between epoxides **II, III** and methanol. The stability of hydroxyether **XVIIb** should be compared not directly with acetal **XVIIIb**, but with its isomer, semiacetal **XIX** that is a precursor of acetal **XVIIIb**. Here also, as in reaction with aldehydes, the direction of the process is determined by the stability of the product, and compound **XIX** is by ~10 kcal mol^{-1} more stable than compound **XVIIb**.

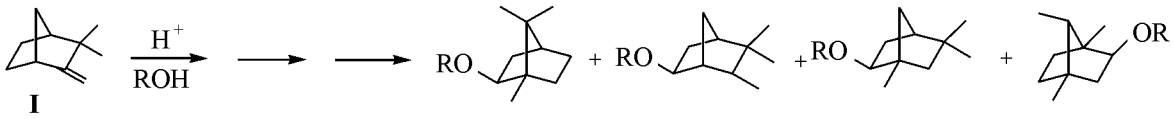


XVIIb **XIX** **XVIIIb**

ΔH_f^0 −100.5 (MMX) ΔH_f^0 −109.7 (MMX)

Thus whereas in reactions of epoxy compounds **II, III, V, VI** with aldehydes on clay arise spirocyclic acetals **XIIIa–d**, and therewith the epoxides are precursors of 1,2-diols, in reactions of the same epoxides **II, III, V, VI** with alcohols they provide the aldehyde fragment of open-chain acetals. In the latter

Scheme 10.



R = $CH_2CH{=}CH_2$.

reactions the skeleton of the initial bicyclic terpene remains intact.

Yet in the reaction we previously studied between olefin **I** and allyl alcohol on zeolite β [12] the process took another route: Deep rearrangements occurred in the skeleton of the initial terpene affording finally a mixture of alkoxylation products (Scheme 10).

All the intramolecular reactions studied occur only in the presence of the heterogeneous catalyst and are not realized in acetic acid medium. The use in these reactions of environmentally friendly solid catalysts (clay, zeolites, solid superacids) extends the opportunities of synthetic application for the easily available natural compound camphene and its isomer, α-fenchene.

The structure of all compounds obtained was established from ^1H and ^{13}C NMR spectra; elemental composition was confirmed by high-resolution mass spectra. Let us consider some problems in deriving structure of the new compounds obtained from the NMR spectra.

The *exo*-orientation of H^3 in compounds **VIIa, VIIIa,** and **XVIIIa** is confirmed by the presence in the ^1H NMR spectra of *W*-coupling constant with atoms H^{5x} ($^4J_{3x,5x}$ 1–2 Hz) and the lack of *W*-coupling constants with H^{7an} atoms. The value of coupling constant of H^3 protons with H^4 protons equal to 4 Hz also testifies to their *exo*-position in the above compounds (in case of *endo*-orientation the value $^3J_{3,4}$ should be less than 1 Hz).

For compounds **VIIb, VIIIb** and **XVIIIc** the *exo*-orientation of H^3 protons is proved by coupling with H^{5x} protons ($^4J_{3,5x}$ ~2 Hz) and by value of $^3J_{3x,4}$ 4 Hz. In compound **IXa** the coupling of H^3 proton with H^{7an} ($^4J_{3,7an}$ 2 Hz) and lack of coupling with H^4 and H^{5x} protons is an evidence of the *endo*-position of H^3 proton.

In compound **XVIIb** the addition of a methoxy group to the C^3 carbon and of an oxy group to C^{10} carbon and not vice versa was proved by the following data. In the ^1H NMR spectrum the protons of $C^{10}H_2$ group appear as doublets of *AB*-system with chemical shifts characteristic for CH_2OH substituent (3.60 and 3.65 ppm) [13], and the signal at 3.65 ppm is a broadened doublet that sharply narrows in the double resonance spectrum at decoupling from the proton of the hydroxy group at 2.00 ppm indicating that the latter is a neighboring group, In the ^{13}C NMR spectrum the chemical shift of C^{10} carbon atom also proves the presence of CH_2OH and not CH_2OCH_3 group [14]. In both ^1H and ^{13}C NMR spectra of compound **XVIIa** the chemical shifts of $C^{10}H_2$ are similar to those in the spectra of compound **XVIIb** thus suggesting that a hydroxymethyl group is attached to C^3 atom.

The presence of a hydroxymethyl group in compound **XVIIc** was demonstrated by LRJMD spectra: on decoupling from both protons of the $C^{10}H_2$ group with a signal at 3.45 ppm a signal from carbon atom C^{11} is lacking in the LRJMD spectrum; the signal should have appeared for the $C^{10}H_2OC^{11}H_2CH{=}CH_2$ group attaked to the C^3 atom. On decoupling from protons of the $C^{11}H_2$ group giving a signal at 3.81 ppm in the LRJMD spectrum is absent the signal from C^{10} atom, but appears the signal from the C^3 atom at 86.74 ppm confirming the bonding of the OR group to the latter and not to the C^{10} carbon atom.

The assignment of methyl group signals in the ^1H NMR spectra of compounds **VIIa, VIIIa, XIa**, and **XVIIIa** was carried out by analogy with the published data for the related structures [15], and the signals in the ^{13}C NMR spectra were attributed from the data of two-dimensional ^{13}C–^1H spectra.

Analysis of ^1H NMR spectra of compounds **VIIb, VIIIb, IXb, XIIId, XVIIc** and **XVIIIc** demonstrated that the chemical shifts of one among the methyl groups are in all cases of close values(0.92–0.97 ppm), and those of the second methyl group are different (0.71–1.20 ppm). Since the substituents in the molecules are different only at the C^3 atom, they should more affect the C^9H_3 group, and consequently the changing chemical shifts belong to this methyl group. It was concluded from the above reasoning that the methyl groups C^8H_3 have a signal at 0.92–

Table 1. ^{13}C NMR spectra of compounds synthesized (δ, ppm)

Carbon atom number	**II**	**III**	**V, VI**		**VIIa**	**VIIb**	**VIIIa**
1	48.28 d	48.81 d	44.95 d	44.89 d	49.48 d	43.84 d	49.14 d
2	38.81 s	37.32 s	36.98 t	38.41 t	37.05 ©	33.09 t	39.08 ©
3	71.92 s	71.32 s	66.56 s	66.85 s	50.89 d	39.93 d	63.39 d
4	45.00 d	43.65 d	49.52 d	50.30 d	40.26 d	45.59 d	39.95 d
5	23.69 t	23.23 t	22.78 t	24.59 t	21.64 t	22.42 t	21.99 t
6	24.92 t	24.10 t	28.28 t	27.74 t	24.73 t	29.50 t	24.43 t
7	35.67 t	35.01 t	47.02 s	46.88 s	37.15 t	47.26 s	37.22 t
8	47.97 t	51.51 t	55.89 t	48.63 t	32.57 q	21.25 q	32.52 q
9	23.60 q	27.42 q	21.43 q	21.22 q	20.99 q	20.89 q	23.01 q
10	24.06 q	21.08 q	21.64 q	21.43 q	103.52 d	106.51 d	204.21 d
11					49.85[a] q	52.65[a] q	
12					53.26[a] q	51.32[a] q	

[a] Here and hereinafter: the chemical shift values marked with the same letters should probably be interchanged within the same column.

Table 2. ^{13}C NMR spectra of compounds synthesized (δ, ppm)

Carbon atom number	**IXa**	**VIIIb**	**IXb**	**X**	**XIIIa** ($^1J_{C-n}$, Hz)	**XIIIb**	**XIIIc**
1	48.16 d	44.35 d	43.71 d	49.80 d	49.06 d (141)	49.00 d	48.94 d
2	42.42 s	28.55 t	31.16 t	44.68 s	42.74 s	42.40 s	42.68 s
3	65.27 d	53.20 d	56.43 d	83.92 s	90.64 s	90.82 s	90.29 s
4	39.12 d	45.66 d	45.90 d	44.52 d	46.44 d (141)	45.56 d	46.40 d
5	27.97 t	23.78 t	29.70[b] t	23.46 t	22.58 t (131)	22.38 t	22.35 t
6	24.21 t	28.98 t	28.70[b] t	24.24 t	24.15 t (131)	24.14 t	23.99 t
7	37.14 t	47.81 s	46.12 s	34.23 t	35.26 t (133)	35.10 t	35.16 t
8	25.54 q	20.69 q	21.27 q	25.37[b] q	26.04[b] q (126)	25.47[b] q	25.95[b] q
9	28.30 q	20.90 q	22.12 q	24.12[b] q	24.09[b] q (126)	24.32[b] q	23.99[b] q
10	203.00 d	203.89 d	203.07 d	15.28 q	67.67 t (146)	67.05 t	67.74 t
11				49.60 q	102.86 d (166)	104.14 d	103.11 d
12					135.20 d (158)	142.49 s	128.43 d
13					119.06 t (157)	114.76 t	131.49 d
14						16.30 q	
15							17.57 q

0.97 ppm, and C^9H_3 groups at 0.71–1.20 ppm. The assignment of these groups signals in the ^{13}C NMR spectra was performed with the use of a two-dimensional correlation ^{13}C–^1H procedure COSY.

The presence in compound **XIIIa** of a 1,3-dioxolane ring was confirmed by the values of direct coupling constants $^1J_{C-H}$ between C^{10} and C^{11} carbons obtained from the monoresonance spectra (see EXPERIMENTAL, cf. [16]).

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded on spectrometer Bruker AM-400 at operating frequencies 400.13 and 100.61 MHz respectively, as solvent was used a mixture $CDCl_3$–CCl_4, 1:1, as internal reference served the chloroform signals (δ_H 7.24 ppm, δ_C 76.90 ppm). The structure of compounds was established with the use of NMR spectra analysis: from the coupling constants estimated by the double

Table 3. ^{13}C NMR spectra of compounds synthesized (δ, ppm)

Carbon atom number	XVIc	XIIId	XVIIa	XVIIIa	XVIIb	XVIIc	XVIIIc
1	49.11 d	45.26 d	50.15 d	49.40 d	50.00 d	44.32 d	43.95 d
2	42.98 s	47.60 t	44.75 s	36.95 s	44.32 s	40.68 t	33.32 t
3	90.78 s	87.94 s	86.12 s	51.66 d	85.57 s	86.74 s	40.59 d
4	47.97 d	51.65 d	42.56 d	40.27 d	41.60 d	49.01 d	45.73 d
5	23.39 t	22.77 t	21.99 t	21.42 t	21.77 t	22.52 t	22.42 t
6	23.93 t	27.22 t	24.07 t	24.62 t	24.01 t	27.42 t	29.57 t
7	35.00 t	48.32 s	34.75 t	36.99 t	34.49 t	47.89 s	47.36 s
8	25.32[b] q	21.90 q	26.00[b] q	32.44 q	25.82[b] q	22.77 q	21.38 q
9	23.91[b] q	22.77 q	22.81[b] q	20.99 q	22.72[b] q	22.77 q	21.01 q
10	66.84 t	75.02 t	59.92 t	101.81 d	59.14 t	63.48 t	104.19 d
11	104.62 d	103.92 d	62.24 t	63.89[b] t	49.23 q	62.44 t	64.89[b] t
12	129.62 d	136.18 d	135.32 d	135.05[c] d		135.08 d	135.15[c] d
13	130.78 d	118.54 t	115.12 t	115.80[d] t		115.95 t	115.94 t
14				66.82[b] t			65.77[b] t
15	17.51 q			134.65[c] d			135.08[c] d
16				115.90[d] t			115.94 t

resonance $^1H-^1H$ spectra, from ^{13}C NMR monoresonance spectra, spectra obtained with selective and off-resonance proton decoupling, and from two-dimensional $^{13}C-^1H$ correlation spectra on direct coupling constants (COSY, the applied value $^1J_{C-H}$ 135 Hz) and unidimensional $^{13}C-^1H$ correlation spectra on remote constants (LRJMD, experimental conditions optimized for remote constants J_{C-H} 10 Hz). The data of ^{13}C NMR spectra are presented in Tables 1–3.

The purity of the initial compounds was checked and the reaction products were analyzed by GLC on Biokhrom-1 chromatograph equipped with flame-ionization detector and two columns: glass capillary column 53000×0.26 mm, stationary phase XE-60, and capillary quartz column 13000×0.22 mm, stationary phase BS-30 (analog of SE-30), carrier gas helium. The products were separated by column chromatography on silica gel (Czechia, 40–100 μ), 20%$AgNO_3$ on SiO_2, on alumina and alkaline alumina (II Brockmann activity). Elemental composition of compounds obtained was derived from high-resolution mass spectra measured on Finnigan MAT 8200 instrument. The optical rotation was measured on Polamat A polarimeter. The ion salts were prepared in a double distilled HSO_3F (bp 158–161°C). For dilution was used SO_2FCl purified by passing through sulfuric acid. As a nucleophilic quenching solution was applied a methanol–ethyl ether mixture (5:2 by volume). In reactions carried out in the presence of askanite-bentonite clay the catalyst used was calcined just before the experiment in a microwave oven for 10 min at a power 450 W or for 3 h in a thermostat cabinet at 110°C. The askanite–bentonite clay was obtained by acid activation of bentonite clays from Askanian deposits and corresponded to the standard 113-12-86-82. The sulfate of titanium oxide (TiO_2/SO_4^{2-}) was calcined for 2 h at 400°C, and wide-porous β zeolite HB-2 (SiO_2/Al_2O_3 40) with pore diameter 0.75–0.80 nm, and with oxides content Na_2O 0.04%, Al_2O_3 5.14%, SiO_2 81.57% was calcined before the reaction for 2 h at 500°C. The zeolite was produced at Research Center Zeosit (Novosibirsk). In the study was used α-fenchol Fluka, $[\alpha]_{580}^{20}$ 10.1, 98% purity, and camphene containing 17% of tricyclene, $[\alpha]_{580}^{20}$ 10.6 ($CHCl_3$, *c* 11.7).

Epoxidation of camphene (I) with peracetic acid. A mixture of 0.8 g of olefin **I** (5.8 mmol), 13 ml (6.8 mmol) of a solution of CH_3COOOH in CH_2Cl_2 (extracted from a mixture of 200 ml of CH_3COOH, 200 ml of 30% H_2O_2, and 10 ml of concn. H_2SO_4 and titrated with sodium thiosufate), and 0.9 g of anhydrous Na_2CO_3 was kept for 3 h. The reaction mixture was treated with saturated solution of Na_2CO_3, with water till neutral washings, and dried with $Na2SO4. The weight of crude product 0.89 g. Epoxides **II, III** were separated from unreacted compound **I** by column chromatography on Al_2O_3, eluent hexane. We isolated 0.18 g of tricyclene with camphene impurity and 0.51 g of a mixture of

epoxides **II** and **III** in 2.3 : 1 ratio, $[\alpha]_{580}^{20}$ of mixture 5.15 ($CHCl_3$, *c* 17.45). Further in the experiments was used the mixture containing epoxides **II** and **III** in this ratio. Mass spectra of the isomers were identical. Found: *M* 152.12034. $C_{10}H_{16}O$. Calculated: *M* 152.12011. ^{1}H NMR spectrum of compound **II** (δ, ppm, *J*, Hz): 0.75 s and 0.78 s (C^9H_3, $C^{10}H_3$), 1.12 d.d.d (H^{7an}, $J_{7an,7c}$ 10, $J_{7an,1}$ 1.5, $J_{7an,4}$ 1.5), 1.20–1.33 m (H^{5n}, H^{6q}), 1.50 m (H^{5x}), 1.55–1.63 m (H^1, H^{6n}), 1.83 m (H^4), 1.86 d.d.d.d.d (H^{7s}, *J* 10, $J_{7s,6n}$ 2.5, $J_{7s,1}$ = $J_{7s,4}$ = $J_{7s,5n}$ 1.5), 2.45 d and 2.47 d ($2H^8$, *J* 4.5) *AB* system. ^{1}H NMR spectrum of compound **III** (δ, ppm, *J*, Hz): 0.72 s and 0.89 s (C^9H_3, $C^{10}H_3$), 1.21 d.d.d (H^{7an}, $J_{7an,7s}$ 10, $J_{7an,1}$ 1.5, $J_{7an,4}$ 1.5), 1.28–1.78 m (5n), 1.82 d.d.d.d.d (H^{7s}, *J* 10, $J_{7c,6n}$ 2.5, $J_{7s,1}$ = $J_{7s,4}$ = $J_{7s,5n}$ = 1.5), 2.60 d and 2.63 d ($2H^8$, *J* 5) *AB* system.

Isomerization of epoxides II, III in HSO_3F–SO_2FCl at –90°C. To a solution of 2.9 g (1.7 ml) of HSO_3F in 6.8 ml of SO_2FCl was added at –90°C a solution of 0.36 g of the mixture of epoxides **II** and **III** in 1.8 ml of CH_2Cl_2, and solution was vigorously stirred for 5 min at the same temperature. The mixture was poured into 25 ml of a mixture MeOH–Et_2O. Yield of the crude product 0.314 g. From 0.1 g of products mixture by chromatography on SiO_2 was isolated 0.04 g of compound **VIIa**. Mass spectrum: fragment ion *M*–OCH_3; Found: *m/z* 167.14305. $C_{11}H_{19}O$. Calculated: 167.14358. ^{1}H NMR spectrum of compound **VIIa** (δ, ppm, *J*, Hz): 0.89 s (C^9H_3), 0.95 s (C^8H_3), 1.12 d.d.d (H^{7an}, $J_{7an,7s}$ 9.5, $J_{7an,1}$ 1.5, $J_{7an,4}$ 1.5), 1.26 m (H^{6x}), 1.31 m ($2H^5$), 1.60 d.d.d (H^{3x}, $J_{3x,10}$ 9.5, $J_{3x,4}$ 4, $J_{3q,5q}$ 1), 1.56–1.66 m (H^{7s}, H^{6n}), 1.71 m (H^1), 2.16 m (H^4, *J* 4, $J_{4,5x}$ 3, *J* 1.5, $J_{4,7s}$ 1.5), 3.21 s and 3.26 s ($2OCH_3$), 4.31 d (H^{10}, *J* 9.5).

Isomerization of camphene I in HSO_3F–SO_2FCl at –90°C. To a solution of 1.3 g (0.7 ml) of HSO_3F in 2.8 ml of SO_2FCl was added at –90°C a solution of 0.1 g of compound **I** in 0.8 ml of CH_2Cl_2, and solution was vigorously stirred for 5 min at the same temperature. Then it was poured into 15 ml of a mixture MeOH–Et_2O. Yield of the crude product 0.08 g. By chromatography on SiO_2 was isolated 0.055 g of compound **X**. Found: *M* 168.15142. $C_{11}H_{20}O$. Calculated: *M* 168.15141.

^{1}H NMR spectrum of compound **X** (δ, ppm, *J*, Hz): 0.86 s and 0.92 s (C^8H_3, C^9H_3), 0.93 d.d.d (H^{7an}, $J_{7an,7s}$ 10, $J_{7an,1}$ 1.5, $J_{7an,4}$ 1.5), 1.06 s ($C^{10}H_3$), 1.16–1.30 s (H^{5n}, H^{6x}), 1.40 d.d.d.d (H^{5x}, $J_{5x,5n}$ 13, $J_{5x,6q}$ 13, $J_{5x,4}$ 5, $J_{5x,6n}$ 3.5), 1.53 d.d.d.d (H^{6n}, $J_{6n,6x}$ 12.5, $J_{6x,5n}$ 9, *J* 3.5, $J_{6n,7s}$ 2.5), 1.65 d.m (H^1, $J_{1,6q}$ 4), 1.93 d.d.d.d.d (H^{7s}, *J* 10, 2.5, $J_{7c,5n}$ 2, $J_{7s,1}$ 1.5, $J_{7s,4}$ 1.5), 2.24 d.d.d.d (H^4, *J* 5, 1.5, 1.5, $J_{4,1}$ 1.5), 3.10 s (OCH_3).

Isomerization of epoxides II, III in formic acid. To 4 ml of HCOOH was added 0.15 g of the mixture of epoxides **II, III**. The reaction mixture was boiled for 1 h on an oil bath, cooled, the reaction products were extracted into hexane, the extract was washed with a water solution of Na_2CO_3, and dried with Na_2SO_4. The crude product weighed 0.128 g. According to GLC data the ratio of aldehydes **VIIIa** and **IXa** in the mixture was 1:6. By chromatography on silica gel was isolated 0.84 g of aldehyde **IXa** with 15% of compound **VIIIa** impurity, $[\alpha]_{580}^{20}$ –3.24 ($CHCl_3$, *c* 9.25). Found: *M* 152.11998. $C_{10}H_{16}O$. Calculated: *M* 152.12011.

^{1}H NMR spectrum of compound **IXa** (δ, ppm, *J*, Hz): 0.98 s (C^8H_3), 1.13 d.d.d.d (H^{5n}, $J_{5n,5x}$ 13, $J_{5n,6n}$ 9, $J_{5n,6x}$ 5, $J_{5n,7s}$ 2.5), 1.14 s (C^9H_3), 1.24 d.d.d.d (H^{7an}, $J_{7an,7s}$ 10, $J_{7an,3n}$ 2, $J_{7an,1}$ 1.5, $J_{7an,4}$ 1.5), 1.35 d.d.d.d (H^{6x}, $J_{6x,6}$ 13, $J_{6x,5x}$ 12, *J* 5, $J_{6x,1}$ 4), 1.57 d.d.d.d (H^{5x}, $J_{5x,5n}$ 13, *J* 12, $J_{5x,4}$ 5, $J_{5x,6n}$ 4), 1.69 d.d.d.d (H^{6n}, *J* 13, 9, 4, $J_{6n,7s}$ 2.5), 1.74 br.d (H^1, *J* 4), 1.78 d.d (H^{3n}, $J_{3n,10}$ 3.5, $J_{3n,7an}$ 2), 1.83 d.d.d.d.d (H^{7c}, *J* 10, 2.5, 2.5, $J_{7s,1}$ 1.5, $J_{7s,4}$ 1.5), 2.42 br.d (H^4, *J* 5), 9.54 d (H^{10}, *J* 3.5).

Reaction of epoxides II, III with acrolein on askanite-bentonite clay. To 0.45 g of askanite-bentonite clay calcined for 10 min in a microwave oven at the power of 450 W and dispersed in 5 ml of CH_2Cl_2 was added at stirring in succession 0.4 g (7 mmol) of acrolein, and a solution of 0.3 g (2 mmol) of the epoxides **II** and **III** mixture in 1 ml of CH_2Cl_2. In 3 min the reaction mixture was filtered, the clay was washed with ether, the solvents were distilled off to afford 0.46 g of the crude product. The product was subjected to chromatography in succession on SiO_2 and $SiO_2/AgNO_3$ (gradient elution with hexane containing from 0.5 to 2% of ethyl ether). We isolated 0.19 g of a mixture of aldehydes **VIIIa** and **IXa** in 7 : 1 ratio, and 0.06 g of acetal **XIIIa**. The specific rotation of the latter was $[\alpha]_{580}^{20}$ –3.6 ($CHCl_3$, *c* 5.06). Found: *M* 208.14625. $C_{13}H_{20}O_2$. Calculated: *M* 208.14632. The reaction was also carried out at –40 and 0°C, and the ratio of the isomerization products to the adduct was the same. ^{1}H NMR spectrum of compound **XIIIa** (δ, ppm, *J*, Hz): 0.93 s and 0.97 s (C^8H_3, C^9H_3), 1.10 m (H^{5n}, $J_{5n,5x}$ 13, $J_{5n,6n}$ 9, $J_{5n,6x}$ 5, $J_{5n,7s}$ 2), 1.14 d.d.d (H^{7an}, $J_{7an,7s}$ 10, $J_{7an,1}$ 1.5,

$J_{7an,4}$ 1.5), 1.27 m (H^{6x}), 1.50 d.d.d.d (H^{5x}, $J_{5x,5n}$ 13, $J_{5x,6x}$ 12, $J_{5x,4}$ 5, $J_{5x,6n}$ 3.5), 1.56 d.d.d.d (H^{6n}, $J_{6n,6x}$ 12.5, J 9, 3.5, $J_{6n,7s}$ 2.5), 1.77 d.m (H^{1}, $J_{1,6x}$ 4), 1.98 d.d.d.d.d (H^{7s}, J 10, 2.5, 2, $J_{7s,1}$ 1.5, $J_{7s,4}$ 1.5), 2.16 d.d.d.d (H^{4}, J 5, 1.5, 1.5, $J_{4,1}$ 1.5), 3.70 d and 3.87 d ($2H^{10}$, J 9), 5.10 d.d.d (H^{11}, $J_{11,12}$ 6, $J_{11,13trans}$ 1, $J_{11,13cis}$ 1), 5.26 d.d.d (H^{13ci}d^{s}, $J_{13cis,12}$ 10, $J_{13cis,13trans}$ 1.5, J 1), 5.40 d.d.d ($H^{13trans}$, $J_{13trans,12}$ 17, J 1.5, 1), 5.78 d.d.d (H^{12}, J 17, 10, 6).

Reaction of epoxides II, III with methacrolein on askanite-bentonite clay. To 0.45 g of askanite-bentonite clay calcined for 10 min in a microwave oven at the power of 450 W was added at stirring in succession a solution of 0.4 g (5.7 mmol) of methacrolein in 5 ml of CH_2Cl_2, and a solution of 0.3 g (2 mmol) of the epoxides **II** and **III** mixture in 1 ml of CH_2Cl_2. After workup the crude product (0.4 g) was subjected to chromatography in succession on SiO_2 and $SiO_2/AgNO_3$ (gradient elution with hexane containing from 0.5 to 2.5% of ethyl ether). We isolated 0.14 g of a mixture of aldehydes **VIIIa** and IXa, and 0.05 g of acetal **XIIIb**. The specific rotation of the latter was $[\alpha]_{580}^{20}$ +4.0° ($CHCl_3$, *c* 3.5). Found: *M* 222.15984. $C_{14}H_{22}O_2$. Calculated: *M* 222.16197. ^{1}H NMR spectrum of compound **XIIIb** (δ, ppm, *J*, Hz): 0.89 s and 0.99 s ($C^{8}H_3$, $C^{9}H_3$), 1.13 d.d.d (H^{7an}, $J_{7an,7s}$ 10, $J_{7an,1}$ 1.5, $J_{7an,4}$ 1.5), 1.14 m (H^{5n}), 1.26 d.d.d.d (H^{6x}, $J_{6x,6n}$ 12.5, $J_{6x,5x}$ 12, $J_{6x,5n}$ 5, $J_{6x,1}$ 4), 1.50 m (H^{5x}, $J_{5x,5n}$ 13, J 12, $J_{5x,4}$ 5, $J_{5x,6n}$ 3.5), 1.53 d.d.d.d (H^{6n}, J 12.5, $J_{6n,5n}$ 9, J 3.5, $J_{6n,7s}$ 2.5), 1.70 d.d ($C^{14}H_3$, $J_{14,13}$ 1.5, $J_{14,13'}$ 1.2), 1.76 d.m (H^{1}, J 4), 1.96 d.d.d.d.d (H^{7s}, J 10, 2.5, $J_{7s,5n}$ 2, $J_{7s,1}$ 1.5, $J_{7s,4}$ 1.5), 2.18 d.d.d.d (H^{4}, J 5, 1.5, 1.5, $J_{4,1}$ 1.5), 3.74 d and 3.79 d ($2H^{10}$, J 8.5) *AB* system, 4.94 d.q (H^{13}, $J_{13,13'}$ 2, J 1.5), 5.04 s (H^{11}), 5.09 m ($H^{13'}$, J 2, 1.2, $J_{13',11}$ 1).

Reaction of epoxides II, III with crotonic aldehyde on K-10 clay. To 0.8 g of K-10 clay calcined for 10 min in a microwave oven at the power of 450 W was added at stirring in succession a solution of 0.7 g (0.01 mol) of crotonic aldehyde in 8 ml of CH_2Cl_2, and a solution of 0.5 g (0.033 mol) of the epoxides **II** and **III** mixture in 2 ml of CH_2Cl_2. After workup the crude product (1.18 g) was subjected to chromatography in succession on SiO_2 and $SiO_2/AgNO_3$ (gradient elution with hexane containing from 0.5 to 2.5% of ethyl ether). We isolated 0.14 g of aldehydes **VIIIa** and **IXa** in 7:1 ratio, 0.127 g of a mixture of isomers **XIIIc** and **XIVc** in 1:1 ratio, and 0.08 g of individual acetal **XIIIc**, $[\alpha]_{580}^{20}$ −3.9° ($CHCl_3$, *c* 8.7). Found: *M* 222.15994. $C_{14}H_{22}O_2$. Calculated: *M* 222.16197. Compound **XIIIc** is unstable and at storage transforms into an equilibrium mixture with its geometrical isomer **XVIb** in the ratio 1:1. ^{1}H NMR spectrum of compound **XIIIc** (δ, ppm, *J*, Hz): 0.91 s and 0.96 s ($C^{8}H_3$, $C^{9}H_3$), 1.07 m (H^{5n}), 1.12 d.d.d (H^{7an}, $J_{7an,7s}$ 10, $J_{7an,1}$ 1.5, $J_{7an,4}$ 1.5), 1.25 d.d.d.d (H^{6x}, $J_{6x,6n}$ 12.5, $J_{6x,5x}$ 12, $J_{6x,5n}$ 5, $J_{6x,1}$ 4), 1.48 d.d.d.d (H^{5x}, $J_{5x,5n}$ 13, J 12, $J_{5x,4}$ 5, $J_{5x,6n}$ 3.5), 1.53 d.d.d.d (H^{6n}, J 12.5, $J_{6n,5n}$ 9, J 3.5, $J_{6n,7s}$ 2.5), 1.73 d.d ($C^{15}H_3$, $J_{15,13}$ 6.5, $J_{15,12}$ 1.5), 1.75 br.d (H^{1}, J 4), 1.95 d.d.d.d.d (H^{7c}, J 10, 2.5, $J_{7s,5n}$ 2, $J_{7s,1}$ 1.5, $J_{7c,4}$ 1.5), 2.13 d.d.d.d (H^{4}, J 5, 1.5, 1.5, $J_{4,1}$ 1.5), 3.66 d and 3.88 d ($2H^{10}$, J 8.5), 5.06 d (H^{11}, $J_{11,12}$ 7), 5.43 d.d.q (H^{12}, $J_{12,13}$ 15.5, J 7, 1.5), 5.85 d.q (H^{13}, J 15.5, 6.5). The isomer mixture of **XIIIc** and **XVIc** (0.2 g) was subjected to chromatography on SiO_2 with gradient elution by hexane containing from 0,5 to 2% of ethyl ether,. Thus was separated 0.06 g of racemic compound **XVIc**. Found: *M* 222.15995. $C_{14}H_{22}O_2$. Calculated: *M* 222.16197. ^{1}H spectrum of compound **XVIc** (δ, ppm, *J*, Hz): 0.91 s and 0.98 s ($C^{8}H_3$, $C^{9}H_3$), 1.09 m (H^{5n}), 1.11 d.d.d (H^{7an}, $J_{7an,7s}$ 10, $J_{7an,1}$ 1.5, $J_{7an,4}$ 1.5), 1.23 d.d.d.d (H^{6x}, $J_{6x,6n}$ 12.5, $J_{6x,5x}$ 12, $J_{6x,5n}$ 5, $J_{6x,1}$ 4), 1.48 m (H^{5x}), 1.51 d.d.d.d (H^{6n}, J 12.5, $J_{6n,5n}$ 9, $J_{6n,5x}$ 3.5, $J_{6n,7s}$ 2.5), 1.71 d.d ($C^{15}H_3$, $J_{15,13}$ 6.5, $J_{15,12}$ 1.5), 1.74 d.m (H^{1}, J 4), 1.96 d.d.d.d.d (H^{7s}, J 10, 2.5, $J_{7s,5n}$ 2, $J_{7s,1}$ 1.5, $J_{7s,4}$ 1.5), 2.10 d.d.d.d (H^{4}, $J_{4,5x}$ 5, $J_{4,1}$ 1.5, J 1.5, 1.5), 3.75 d and 3.80 d ($2H^{10}$, J 9) *AB* system, 5.13 d (H^{11}, $J_{11,12}$ 7), 5.41 d.d.q (H^{12}, $J_{12,13}$ 15.5, J 7, 1.5), 5.80 d.q.d (n^{13}, J 15.5, 6.5, $J_{13,11}$ 0.5).

Reaction of epoxides II, III with allyl alcohol on askanite-bentonite clay. To 1.5 g of clay in 3 ml of CH_2Cl_2 was added at stirring 1 g of allyl alcohol (preliminary dried by boiling with K_2CO_3 and distilled through a Vigreux column, bp 96°C) and after that 0.84 g of epoxides **II, III** mixture. The stirring was continued for 2–3 min, the reaction mixture was diluted with ether and filtered. The weight of the reaction mixture was 1.46 g. By chromatography on SiO_2 were separated in succession 0.29 g of acetal **XVIIIa**, 0.066 g of hydroxyether **XVIIa**, and 0.437 g of isomerization products of epoxides **II** and **III** (aldehydes **VIIIa, IXa**) containing compounds **XVIIIa, XVIIa** as impurities. Compound **XVIIa**. Found: *M* 210.1617. $C_{13}H_{22}O_2$. Calculated: *M* 210.16197. $[\alpha]_{580}^{20}$ −5.8° ($CHCl_3$, *c* 6.9). ^{1}H NMR spectrum of compound **XVIIa** (δ, ppm, *J*,

Hz): 1.03 s and 1.05 s ($C^{8}H_3$, $C^{9}H_3$), 1.03 d.d.d (H^{7an}, $J_{7an,7s}$ 10, $J_{7an,1}$ 1.5, $J_{7an,4}$ 1.5), 1.14 d.d.d.d (H^{5n}, $J_{5n,5x}$ 13, $J_{5n,6n}$ 9, $J_{5n,6x}$ 5, $J_{5n,7s}$ 2), 1.24 d.d.d.d (H^{6x}, $J_{6x,6n}$ 12.5, $J_{6x,5x}$ 12, J 5, $J_{6x,1}$ 4), 1.40 d.d.d.d (H^{5x}, J 13, 12, $J_{5x,4}$ 5, $J_{5x,6n}$ 3.5), 1.59 d.d.d.d (H^{6n}, J 12.5, 9, 3.5, $J_{6n,7s}$ 2.5), 1.69 br.d (H^{1}, J 4), 1.98 d.d.d.d.d (H^{7s}, J 10, 2.5, 2, $J_{7s,1}$ 1.5, $J_{7s,4}$ 1.5), 2.30 d.d.d.d (H^{4}, J 5, 1.5, 1.5, $J_{4,1}$ 1.5), 3.65 d and 3.74 d ($2H^{10}$, J 12) *AB* system, 3.79 d.d.d.d (H^{11}, $J_{11,11'}$ 13, $J_{11,12}$ 5, $J_{11,13cis}$ 1.5, $J_{11,13trans}$ 1.5), 3.94 d.d.d.d ($H^{11'}$, J 13, $J_{11',12}$ 5, $J_{11',13cis}$ 1.5, $J_{11',13trans}$ 1.5), 5.08 d.d.t (H^{13cis}, $J_{13cis,12}$ 10, $J_{13cis,13trans}$ 1.5, $J_{13cis,11}$ 1.5), 5.28 d.d.t ($H^{13trans}$, $J_{13trans,12}$ 17, J 1.5, $J_{13trans,11}$, 1.5), 5.87 d.d.d.d (H^{12}, J 17, 10, 5, 5). Compound **XVIIIa**. Found (fragment ion M–$OCH_2CH{=}CH_2$): *m/z* 193.15845. $C_{13}H_{21}O$. Calculated: 193.15923. $[\alpha]_{580}^{20}$ 1.6 ($CHCl_3$, *c* 47.0). ^{1}H NMR spectrum of compound **XVIIIa** (δ, ppm, *J*, Hz): 0.89 s ($C^{9}H_3$), 0.95 s ($C^{8}H_3$), 1.10 d.d.d (H^{7an}, $J_{7an,7s}$ 9.5, $J_{7an,1}$ 1.5, $J_{7an,4}$ 1.5), 1.23 m (H^{6x}, $J_{6x,6n}$ 12.5, $J_{6x,5x}$ 12, $J_{6x,5n}$ 6, $J_{6x,1}$ 4), 1.25–1.36 m ($2H^{5}$), 1.58 d.m (H^{7s}, J 9.5), 1.61 m (H^{6n}), 1.67 d.d.d (H^{3x}, $J_{3x,10}$ 9.5, $J_{3x,4}$ 4, $J_{3x,5x}$ 1.2), 1.70 br.s (H^{1}), 2.19 m (H^{4}), 3.89 d.d.d.d and 4.11 d.d.d.d ($2H^{11}$ or $2H^{14}$, J 13, 5, 1.5, 1.5), 3.96 d.d.d.d and 4.00 d.d.d.d ($2H^{14}$ or $2H^{11}$, J 13, 5, 1.5, 1.5), 4.56 d (H^{10}, J 9.5), 5.06 d.d.t and 5.07 d.d.t (H^{13cis} and H^{16cis}, J 10, 1.5, 1.5), 5.21 d.d.t and 5.23 d.d.t ($H^{13trans}$ and $H^{16trans}$, J 17, 1.5, 1.5), 5.84 d.d.t and 5.86 d.d.t (H^{12} and H^{15}, J 17, 10, 5).

Reaction of epoxides II, III with methanol on askanite-bentonite clay. To 1.5 g of clay in 2.5 ml of CH_2Cl_2 was added at stirring 0.8 g of methanol (preliminary dried by passing through a calcined alumina) and after that 0.65 g of epoxides **II, III** mixture. The stirring was continued for 2–3 min, the reaction mixture was diluted with ether and filtered. The weight of the reaction mixture was 0.735 g. By chromatography on SiO_2 were separated in succession 0.23 g of acetal **XVIIIb**, $[\alpha]_{580}^{20}$ +1.9° ($CHCl_3$, *c* 11.3) that was identical to compound VIIa, 0.17 g of hydroxyether **XVIIb**, and 0.17 g of isomerization products of epoxides **II** and **III** (aldehydes **VIIIa, IXa**) containing compounds **XVIIIb, XVIIb** as impurities. Compound **XVIIb**. Found: *M* 184.14634. $C_{11}H_{20}O_2$. Calculated: *M* 184.14632. $[\alpha]_{580}^{20}$ –2.7° ($CHCl_3$, *c* 15.7). ^{1}H NMR spectrum of compound **XVIIb** (δ, ppm, *J*, Hz): 0.90 s and 0.98 s ($C^{8}H_3$, $C^{9}H_3$), 0.96 d.d.d (H^{7an}, $J_{7an,7s}$ 10, $J_{7an,1}$ 1.5, $J_{7an,4}$ 1.5), 1.07 d.d.d.d (H^{5n}, $J_{5n,5x}$ 13, $J_{5n,6n}$ 9, $J_{5n,6x}$ 5, $J_{5n,7s}$ 2), 1.18 d.d.d.d (H^{6x}, $J_{6x,6n}$ 12.5, $J_{6x,5x}$ 12, J 5, $J_{6q,1}$ 4), 1.34 d.d.d.d (H^{5x}, J 13, 12, $J_{5x,4}$ 5, $J_{5x,6n}$ 3.5), 1.53 d.d.d.d (H^{6n}, J 12.5, 9, 3.5, $J_{6n,7s}$ 2.5), 1.60 d.m (H^{1}, $J_{1,6x}$ 4), 1.86 d.d.d.d.d (H^{7s}, J 10, 2.5, 2, $J_{7s,1}$ 1.5, $J_{7s,4}$ 1.5), 2.00 br.s (OH), 2.26 d.d.d.d (H^{4}, J 5, 1.5, 1.5, $J_{4,1}$ 1.5), 3.11 s (OCH_3), 3.60 d and 3.65 br.d ($2H^{10}$, J 12) *AB* system.

α-Fenchene (IV). To 24.5 g of α-fenchol in 70 ml of dry pyridine was added 36.5 g of toluenesulfonyl chloride in 70 ml of dry pyridine. The mixture was left standing in a refrigerator for 48 h, then was diluted with 450 ml of water, the precipitate was filtered off, washed with a mixture water–hydrochloric acid (1 : 1), with water, Na_2CO_3 solution, and dried on $MgSO_4$. We obtained 37 g of α-fenchol tosylate (mp 103.°C, publ. 99°C [3]). A mixture of 37 g of tosylate and 24.9 g of anhydrous sodium acetate in 440 ml of dry acetic acid was heated for 48 h to 90°C. The reaction mixture was washed with Na_2CO_3 solution, the reaction products were extracted into pentane, and the extract was dried on $MgSO_4$. We isolated 12 g of substance containing 95% of compound **IV** (GLC). After separation from impurities by column chromatography on SiO_2 we obtained 7.5 g of α-fenchene (**IV**), $[\alpha]_{580}^{20}$ +26.4° ($CHCl_3$, *c* 8.7).

Epoxidation of α-fenchene (IV) with peracetic acid. A mixture of 3.04 g of olefin **IV** (20 mmol), 25 ml (25 mmol) of a solution of CH_3COOOH in CH_2Cl_2 (extracted from a mixture of 200 ml of CH_3COOH, 200 ml of 30% H_2O_2, and 10 ml of concn. H_2SO_4 and titrated with sodium thiosufate), and 7 g of anhydrous Na_2CO_3 was vigorously stirred for 2 h. The reaction mixture was treated with saturated solution of Na_2CO_3, with water till neutral washings, and dried with Na_2SO_4. We isolated 3.51 g of epoxides **V, VI** mixture at a ratio 1 : 0.75. In further experiments was used the mixture with this isomers ratio. optical rotation measured for the mixture was $[\alpha]_{580}^{20}$ +18.6° ($CHCl_3$, *c* 10.1). Mass spectra of the isomers were identical. Found: *M* 152.12028. $C_{10}H_{16}O$. Calculated: *M* 152.12011. NMR spectra were recorded for the isomers mixture with the ratio close to 1 : 0.75. ^{1}H NMR spectrum of prevailing isomer (δ, ppm, *J*, Hz): 0.95 s ($C^{9}H_3$), 1.09 s ($C^{10}H_3$), 1.19 d (H^{4}, $J_{4,5x}$ 4), 1.21 d (H^{2n}, $J_{2n,2x}$ 13.5), 1.36 d.d.d (H^{6n}, $J_{6n,6x}$ 12, $J_{6n,5n}$ 8.5, $J_{6n,5x}$ 3), 1.64 d.d (H^{1}, $J_{1,2x}$ 4, $J_{1,6x}$ 4), 1.71–1.86 m

($2H^5$, H^{6x}), 2.10 d.d.d (H^{2x}, J 13.5, 4, $J_{2x,6x}$ 3), 2.63 d and 2.80 d ($2H^8$, J 5). ^{1}H NMR spectrum of minor isomer (δ, ppm, J, Hz): 0.93 s (C^9H_3), 1.15 s ($C^{10}n_3$), 1.14 m (H^4), 1.11–1.33 m and 1.71–1.86 m ($2H^5$, $2H^6$), 1.43 d (H^{2n}, $J_{2n,2x}$ 13.5), 1.69 d.d (H^1, $J_{1,2x}$ 4, $J_{1,6x}$ 4), 1.95 m (H^{2x}, J 13.5, 4, $J_{2x,6x}$ 3), 2.54 d and 2.59 d ($2H^8$, J 5) *AB* system.

Isomerization of epoxides V, VI mixture on askanite-bentonite clay. To 0.15 g of clay in 1 ml of dry CH_2Cl_2 was added a solution of 0.15 g of epoxides **V, VI** mixture in CH_2Cl_2. In 2 min the reaction mixture was separated from clay by passing through a layer of Al_2O_3. Weight of the crude reaction product was 0.11 g. According to ^{1}H NMR spectrum, the ratio of aldehydes **VIIIb** to **IXb** was 7 : 1. Aldehyde **VIIIb** was isolated by column chromatography on SiO_2, gradient elution with hexane containing from 0.5 to 3% of ethyl ether. We obtained 0.8 g of compound **VIIIb**, $[\alpha]_{580}^{20}$ +22.0° ($CHCl_3$, © 8.7). Found: M 152.12028. $C_{10}H_{16}O$. Calculated: M 152.12011. ^{1}H NMR spectrum of compound **VIIIb** (δ, ppm, J, Hz): 0.96 s (C^8H_3), 1.01 s (C^9H_3), 1.15 m (H^{6n}), 1.17 m (H^{5n}), 1.55 d.d (H^1, $J_{1,2x}$ 4, $J_{1,6x}$ 4), 1.58–1.77 m ($2H^2$, H^{5x}, H^{6x}), 1.98 d.d.d (H^4, $J_{4,3x}$ 4, $J_{4,5x}$ 4, $J_{4,1}$ 1), 2.88 m (H^{3x}), 9.68 br.s (H^{10}).

Isomerization of epoxides V, VI mixture in HSO_3F–SO_2FCl at –90°C. To a solution of 1.3 g (0.7 ml) of HSO_3F in 2.8 ml of SO_2FCl was added at –90°C a solution of 0.1 g of epoxides **V, VI** mixture in 0.3 ml of CH_2Cl_2, and solution was vigorously stirred for 5 min at the same temperature. Then it was poured into 15 ml of a mixture MeOH–Et_2O. Yield of the crude product 0.088 g. By chromatography on SiO_2 was isolated 0.05 g of compound **VIIb**. Mass spectrum of the fragment ion M–OCH_3. Found: M 167.14305. $C_{11}H_{19}O$. Calculated: M 167.14358. ^{1}H NMR spectrum of compound **VIIb** (δ, ppm, J, Hz): 0.85 d.d (H^{2n}, $J_{2n,2x}$ 13, $J_{2n,3x}$ 5), 0.96 s (C^8H_3), 1.01 s (C^9H_3), 1.07 d.d.d (H^{6n}, $J_{6n,6x}$ 12, $J_{6n,5n}$ 9.5, $J_{6n,5x}$ 4.5), 1.44 d.d.d (H^{5n}, $J_{5n,5x}$ 13, J 9.5, $J_{5n,6x}$ 4), 1.47 d.d (H^1, $J_{1,2x}$ 4, $J_{1,6x}$ 4), 1.51 d.d (H^4, $J_{4,3x}$ 4, $J_{4,5q}$ 4), 1.63 d.d.d.d.d (H^{5q}, J 13, $J_{5x,6x}$ 12, J 4.5, 4, $J_{5x,3x}$ 2), 1.75 d.d.d.d.d (H^{6x}, J 12, 12, 4, 4, $J_{6x,2x}$ 3.5), 1.89 d.d.d.d (H^{2x}, J 13, $J_{2x,3x}$ 11.5, J 4, 3.5), 2.36 d.d.d.d.d (H^{3x}, J 11.5, $J_{3x,10}$ 9, J 5, 4, 2), 3.23 x and 3.25 x ($2OCH_3$), 4.21 d (H^{10}, J 9).

Isomerization of epoxides V, VI in formic acid. To 2 ml of HCOOH was added 0.15 g of the mixture of epoxides **V, VI.** The reaction mixture was boiled for 1 h on an oil bath, cooled, the reaction products were extracted into hexane, the extract was washed with a water solution of Na_2CO_3, and dried with Na_2SO_4. The crude product weighed 0.8 g. According to ^{1}H NMR data the ratio of aldehydes **VIIIb** and **IXb** in the mixture was 1 : 1. We failed to isolate aldehyde **IXb** as an individual compound, therefore the NMR spectra were registered from the mixture of aldehydes **VIIIb** and **IXb** in nearly equimolar ratio. ^{1}H NMR spectrum of compound **IXb** (δ, ppm, J, Hz): 0.71 s (C^9H_3), 0.92 s (C^8H_3), 1.11–1.24 m and 1.63– 1.89 m ($2H^5$, $2H^6$), 1.61 d.d (H^1, $J_{1,2x}$ 4, $J_{1,6x}$ 4), 2.08 d (H^4, $J_{4,5x}$ 4), 1.41 m (H^{2n}) and 2.08–2.15 m (H^{2x}, H^{3n}) *ABCE* system, 9.64 s (H^{10}).

Reaction of epoxides V, VI with acrolein on askanite-bentonite clay. To 0.45 g of askanite-bentonite clay calcined for 3 h at 110°C and dispersed in 5 ml of CH_2Cl_2 was added at stirring in succession 0.4 g (7 mmol) of acrolein, and a solution of 0.3 g (2 mmol) of the epoxides **V** and **VI** mixture in 1 ml of CH_2Cl_2. In 5 min the reaction mixture was filtered, the clay was washed with ether, the solvents were distilled off to afford 0.404 g of the crude product. According to GLC data the ratio of sum of isomerization products **VIIIb** and **IXb** to the acrolein adduct **XIIId** was 1.6 : 1. The chromatography in succession on SiO_2 and SiO_2/$AgNO_3$ (gradient elution with hexane containing from 0.5 to 2% of ethyl ether) provided 0.21 g of aldehydes **VIIIb** and **IXb** mixture, and 0.056 g of spiroacetal **XIIId**. For compound **XIIId** $[\alpha]_{580}^{20}$ –13.2° ($CHCl_3$, c 6.8). Found: M 208.14605. $C_{13}H_{20}O_2$. Calculated: M 208.14632. ^{1}H NMR spectrum of compound **XIIId** (δ, ppm, J, Hz): 0.95 s (C^8H_3), 1.02 m (H^{6n}), 1.10 m (H^{5x}), 1.20 s (C^9H_3), 1.42 d (H^{2n}, $J_{2n,2x}$ 13), 1.62 m (H^1, H^4), 1.65–1.77 m (H^{5x}, H^{6x}), 2.13 d.d.d (H^{2x}, J 13, $J_{2x,1}$ 5, $J_{2x,6x}$ 2.5), 3.76 s ($2H^{10}$), 5.08 d (H^{11}, $J_{11,12}$ 6), 5.21 d.d.d (H^{13cis}, $J_{13cis,12}$ 10, $J_{13cis,13trans}$ 1.5, $J_{13cis,11}$ 0.5), 5.35 d.d.d ($n^{13trans}$, $J_{13trans,12}$ 17, J 1.5, $J_{13trans,11}$ 0.5), 5.74 d.d.d (H^{12}, J 17, 10, 6). This reaction was also carried out at –40 and 0°C, and the ratio of isomerization products to spiroacetal remained the same.

Reaction of epoxides V, VI with allyl alcohol on askanite-bentonite clay. To 0.55 g of clay in 2 ml of CH_2Cl_2 was added at stirring 0.35 g of allyl alcohol (preliminary dried by boiling with K_2CO_3 and distilled through a Vigreux column, bp 96°C) and after that 0.25 g of epoxides **V, VI** mixture. The stirring was continued for 5 min, the reaction mixture was diluted

with ether and filtered. The weight of the reaction mixture was 0.29 g. By chromatography on SiO_2 were separated in succession 0.44 g of acetal **XVIIIc**, 0.018 g of hydroxyether **XVIIc**, and 0.1 g of products of epoxides isomerization **VIIIb** and **IXb**. Compound **XVIIc**. Found: *M* 210.1617. $C_{13}H_{22}O_2$. Calculated: *M* 210.16197. $[\alpha]_{580}^{20}$ +25.0° ($CHCl_3$, *c* 2.3). ^{1}H NMR spectrum of compound **XVIIc** (δ, ppm, *J*, Hz): 0.96 s (C^8H_3), 0.99 m (H^{6n}), 1.04 d (H^{2n}, $J_{2n,2x}$ 13), 1.20 s (C^9H_3), 1.29 m (H^{5n}), 1.63 d.d.d (H^1, $J_{1,2x}$ 4.5, $J_{1,6x}$ 4, $J_{1,4}$ 1.2), 1.67 m (H^{5x}), 1.73 m (H^{6x}), 1.81 d.d (H^4, $J_{4,5x}$ 4.5, *J* 1.2), 2.03 d.d.d.d (H^{2x}, *J* 13, 4.5, $J_{2x,6x}$ 2.5, $J_{2x,10}$ 0.5), 3.45 d.d (H^{10}, *J* 12, 0.5) and 3.52 d ($H^{10'}$, $J_{10',10}$ 12) *AB* system, 3.81 d.d.d ($2H^{11}$, $J_{11,12}$ 5, $J_{11,13cis}$ 1.5, $J_{11,13trans}$ 1.5), 5.06 d.d.t (H^{13cis}, $J_{13cis,12}$ 10.5, $J_{13cis,13trans}$ 2, *J* 1.5), 5.22 d.d.t ($H^{13trans}$, $J_{13trans,12}$ 17, *J* 2, 1.5), 5.83 d.d.t (H^{12}, *J* 17, 10.5, 5). Compound **XVIIIc**. Found: (fragment ion *M*–$OCH_2CH{=}CH_2$), *m/z* 193.15845. $C_{13}H_{21}O$. Calculated: 193.15923. $[\alpha]_{580}^{20}$ –2.7° ($CHCl_3$, *c* 2.9). ^{1}H NMR spectrum of compound **XVIIIc** (δ, ppm, *J*, Hz): 0.89 d.d (H^{2n}, $J_{2n,2x}$ 13, $J_{2n,3x}$ 5), 0.97 s (C^8H_3), 1.02 s (C^9H_3), 1.08 d.d.d (H^{6n}, $J_{6n,6x}$ 12, $J_{6n,5n}$ 9, $J_{6n,5x}$ 4.5), 1.47 d.d (H^1, $J_{1,2x}$ 4.5, $J_{1,6x}$ 4), 1.47 d.d.d (H^{5n}, $J_{5n,5x}$ 13, *J* 9, $J_{5n,6x}$ 4), 1.54 d.d (H^4, $J_{4,3x}$ 4, $J_{4,5x}$ 4), 1.63 d.d.d.d.d (H^{5x}, *J* 13, 4.5, 4, $J_{5x,6x}$ 12, $J_{5x,3x}$ 2), 1.74 d.d.d.d.d (H^{6x}, *J* 12, 12, 4, 4, $J_{6x,2x}$ 3.5), 1.89 d.d.d.d (H^{2x}, *J* 13, 4.5, 3.5, $J_{2x,3x}$ 11), 2.40 d.d.d.d.d (H^{3x}, *J* 11, $J_{3x,10}$ 9, *J* 5, 4, 2), 3.90–4.03 m ($2H^{11}$, $2H^{14}$), 4.43 d (H^{10}, *J* 9), 5.06 d.d.d.d (H^{13cis}, H^{16cis}, *J* 10.5, 2, 1.5, 1.5), 5.20 d.d.t and 5.21 d.d.t ($H^{13trans}$ and $H^{16trans}$, *J* 17, 2, 1.5), 5.82 d.d.t (H^{12}, H^{15}, *J* 17, 10.5, 5).

REFERENCES

1. Sethi, S.C. and Natu, A.D., *Indian J. Chem.*, 1988, vol. 27B, pp. 974–980.
2. Huckel, W., Rothenwoehrer, W., and Vogt, O., *Suom. Remistilehti.*, 1964, vol. 42, no. 4, pp. 213–216.
3. Huckel, W. and Scheel, J., *Lieb. Ann.*, 1963, vol. 664, p. 61.
4. Lipp, P. and Stutsinger, G., *Ber.*, 1932, vol. 65, p. 241.
5. Haseltine, R., Huang, E., Ranganayakulu, K., and Sorensen, T.S., *Canad. J. Chem.*, 1975, vol. 53, no. 7, pp. 1056–1066.
6. Huang, E., Ranganayakulu, K., and Sorensen, T., *J. Am. Chem. Soc.*, 1972, vol. 94, pp. 1779–1780.
7. Tatarova, L.E., Volcho, K.P., Yarovaya, O.I., Korchagina, D.V., Salakhutdinov, N.F., and Barkhash, V.A., *Zh. Org. Khim.*, 1995, vol. 31, no. 7, pp. 982–995.
8. Barkhash, V.A., *Neklassicheskie karbokationy* (Non-Classic Carbocations), Novosibirsk: Nauka, 1984, p. 50.
9. Kheifits, L.A., Doctoral Sci. (Chem.) Dissertation, Moscow, 1986, p. 11.
10. Yandovskii, V.N., Karavan, V.S., ahd Temnikova, T.I., *Usp. Khim.*, 1970, no. 4, pp. 571–604.
11. *Solid Supports and Catalists in Organic Synthesis*, Smith, K., Ed., Prentece Hall, 1992, p. 83.
12. Fomenko, V.V., Korchagina, D.V., Yarovaya, O.I., Gatilov, Yu.V., Salakhutdinov, N.F., Ione, K.G., and Barkhash, V.A., *Zh. Org. Khim.*, 1999, vol. 35, no. 7, pp. 1031–1041.
13. Ionin, B.I., Ershov, B.A., and Kol'tsov, A.I., *YaMR-spektroskopiya v organicheskoi khimii* (NMR Spectroscopy in Organic Chemistry), Lenungrad: Khimiya, 1983, p. 139.
14. Kalinowski, H.O., Berger, S., and Braun, S., *^{13}CNMR Spektroskopie*, Stuttgart: Georg Thieme Verlag, 1984, pp. 156–165.
15. Buchbauer, G., Haslinger, E., Robien, W., and Vitek, R., *Monatsh. Chem.*, 1983, vol. 114, pp. 113–122; Lysenkov, V.I., *Zh. Org. Khim.*. 1988, vol. 24, no. 8, pp. 1677–1684.
16. Stothers, J.B., *Carbon-13 NMR Spectroscopy*, London: Academic Press, Inc., 1972, p. 324.