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Reactions of Some Terpenes and Their Derivatives with Acylating Agents in the Presence of Aluminosilicate Catalysts

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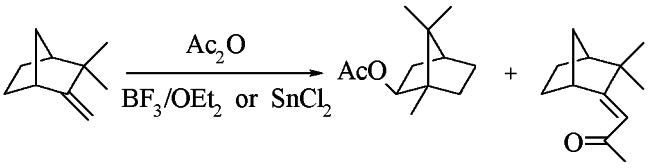
Abstract—Reactions of camphene, α-fenchene, limonene, caryophyllene, α- and β-pinenes, verbenol, walterol, and verbenone with acylating agents in the presence of clay K-10 and wide-porous β-zeolite were studied. Presumable schemes and rules of the occurring processes were considered.

Acylation is extensively used to functionalize organic compounds. Therefore it is no wonder that aluminosilicate catalysts (zeolites and clays), obviously more convenient than traditional Lewis acids, are well studied in these reactions. It was demonstrated that reaction of aromatic compounds [1, 2], aliphatic and cyclic olefins [3] with acetic anhydride in the presence of zeolites afforded the standard acylation products.

We showed formerly that the use of aluminosilicate catalysts in reactions of polyfunctional and conformationally flexible terpenoids often directed the reaction to a new path resulting in unexpected products [4]. The above data led us to study reactions of a terpenoid series with acylating agents in the presence of a synthetic clay K-10 and wide-porous β-zeolite.

It should be pointed out before discussing the experimental results that in reaction of terpenoids with acetic anhydride in the presence of aluminosilicate catalysts two types of intermolecular processes are presumable. The first is due to the attack of the formed acylium cation on the neutral terpenoid molecule followed by transformations of the arising intermediate to yield the corresponding ketone, acylation product. The second path should apparently start by protonation of the terpenoid molecule, then occur intramolecular rearrangements in the cation formed followed by trapping of the resulting cation with a molecule of acetic anhydride. In this case the final product results from acetoxylation. The relative probability of these paths apparently depends on the relative stability of the acylium cation and the cations formed from terpenoids in the presence of the aluminosilicate catalysts. Besides probably occur intramolecular rearrangements of substrate catalyzed by acetic anhydride in the presence of aluminosilicate catalyst and impossible in the absence of Ac_2O. Let us first consider the reaction of camphene (**I**) with acetic anhydride. This reaction was previously carried out in the presence of Lewis acids to obtain isobornyl acetate (**II**) and ω-acetylcamphene (**III**) [5] (Scheme 1).

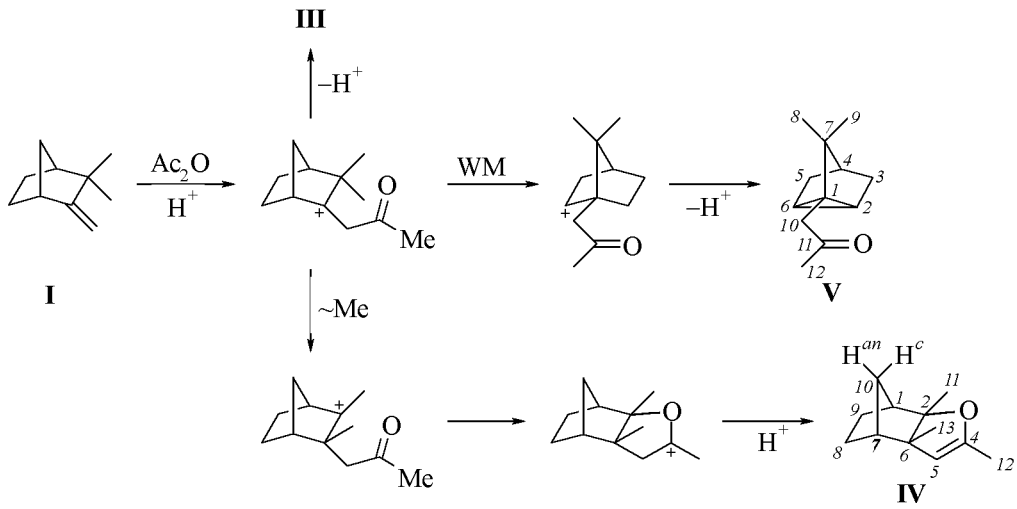
Scheme 1.



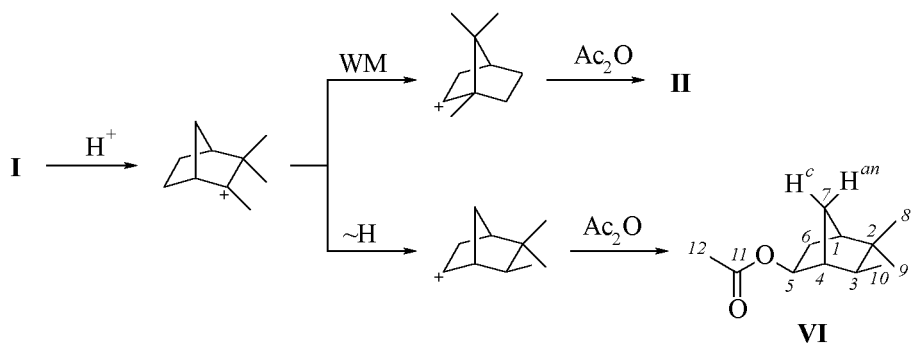
In reaction of terpene (**I**) with Ac_2O on β-zeolite alongside the expected compounds **II** and **III** the reaction mixture contained also 2,4,6-trimethyl-3-oxatricyclo[5.2.1.0^{2,6}]dec-4-ene (IV)*, 1-(7,7-dimethyltricyclo[2.2.1.0^{2,6}]hept-1-yl)propan-2-one (**V**), and 5-*exo*-acetoxy-2,2,3-*exo*-trimethylbicyclo[2.2.1]heptane (**VI**), and compounds **III** and **IV** prevailed. The presumable transformation mechanisms are presented in Schemes 2 and 3.

* The numeration of atoms given in the Schemes for this and the following compounds is also used in description of the corresponding NMR spectra.

Scheme 2.



Scheme 3.



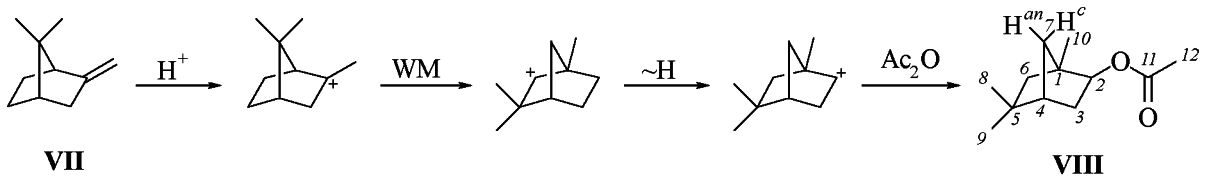
The reaction apparently takes two paths distinguished by the mode of primary carbocation generation. Along the first path acylium cation is presumed to attack the double bond of camphene followed by either deprotonation of the formed intermediate affording compound **III** or by further transformations (1,2- shift of a methyl group or Wagner–Meerwein [WM] rearrangement) with subsequent stabilization by intramolecular heterocyclization to compound **IV** or carbocyclization yielding compound **V** (Scheme 2).

The second path consists in primary protonation of camphene with further skeleton rearrangement of the arising cation or with a hydride shift therein. The reaction is completed by the interaction between the intermediates formed and the acetoxy group resulting in compounds **II** and **VI** (Scheme 3).

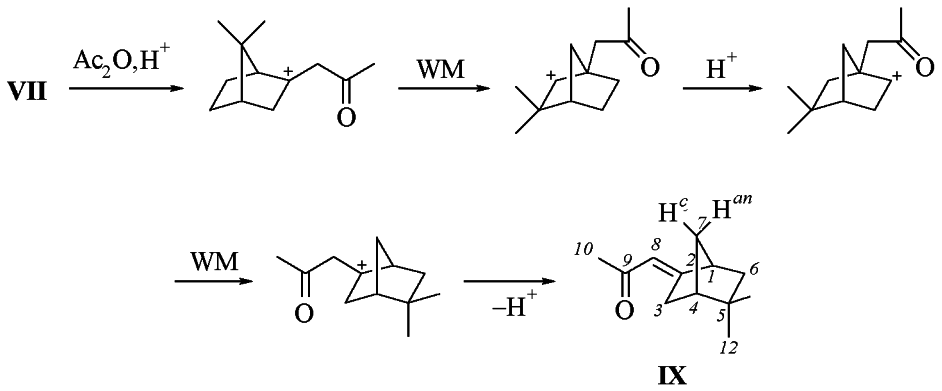
The reaction on β-zeolite gives rise to substances with the ratio of acylation and acetylation products equal to ~3 : 1, whereas the use as catalyst of Lewis acids either provides only acetate **II** or just a little (2%) of acylation product [5]. Yet the use of acetyl chloride as acylating product gives in the presence of β-zeolite results similar to those of [5]: the reaction mixture contains compounds **II** and **III** with acetoxylation product **II** notably prevailing. The overall yield of camphene reaction products on β-zeolite with acetyl chloride is significantly lower than with acetic anhydride (13 and 57% respectively). (Under homogeneous conditions the yield varied from 21 to 46% depending on the catalyst [5]). The montmorillonite K-10 turned out to be significantly worse catalyst of the above transformations.

The reaction of α-fenchene (**VII**) with acetic anhydride in the presence of β-zeolite gives rise to 2-*exo*-acetoxy-1,5,5-trimethylbicyclo[2.2.1]heptane (**VIII**) as the main product and to smaller amounts of 1-(5,5-dimethylbicyclo[2.2.1]-hept-2-ylidene)propan-2-one (**IX**), the acylation product. The presumable paths of compounds **VIII** and **IX** formation are presented on Figs. 4 and 5. Compound **VIII** would arise after primary protonation of terpene **VII** (Scheme 4) followed by Wagner–Meerwein rearrangement, 1,3-hydride shift, and reaction of the resulting carbocation with a molecule of acetic anhydride.

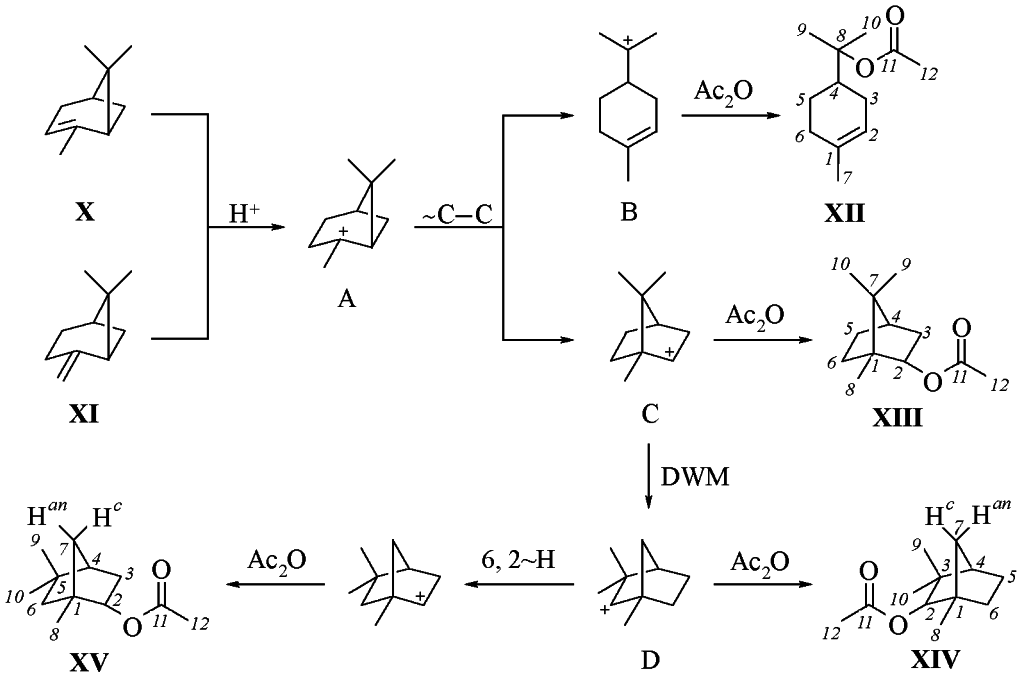
Scheme 4.



Scheme 5.



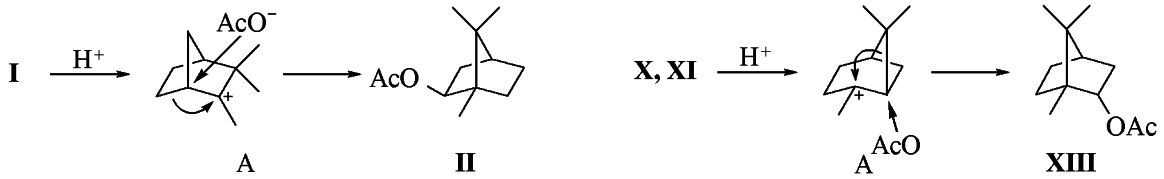
Scheme 6.



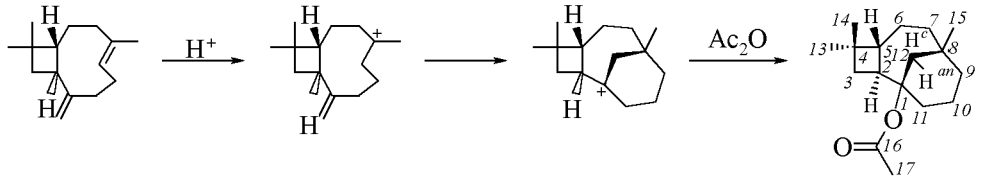
With compound **IX** the reaction apparently starts by an attack of an acylium cation on the double bond of compound **VII** (Scheme 5) with subsequent Wagner–Meerwein rearrangement, 1,3-hydride shift, and once more Wagner–Meerwein rearrangement. The deprotonation of the arising cation affords compound **IX**. As seen from Schemes 2 and 5 monoterpenes **I** and **VII** in the presence of heterogeneous catalyst, β-zeolite, undergo relatively deep multistep transformations affording unexpected compounds unavailable under homogeneous conditions. We did not find published data on compounds **IV, V**, and **IX**.

Although with compounds **I** and **VII** the K-10 clay was a catalyst of low efficiency, with α-(**X**) and β-pinenes (**XI**) the reaction of acetic anhydride on this catalyst was as successful as on β-zeolite. The

Scheme 7.



Scheme 8.



specific feature of isomeric pinenes **X** and **XI** reaction with acetic anhydride consisted in the composition of the reaction products that contained only acetoxylation products.

The initial protonation of isomeric pinenes yields the same cation A (Scheme 6) that suggests the identity of both reaction mixtures composition at treating of the substrates with acetic anhydride.

Let us consider the possible reaction mechanisms of the substrates in question with Ac_2O on K-10 clay. The initial intermediate A transforms along several paths. A rearrangement giving a *p*-menthyl cation B affords in its reaction with acetic anhydride 4-(1-acetoxy-1-methylethyl)-1-methylcyclohexene (**XII**). An intermediate cation C with a molecule of acetic anhydride yields 2-*endo*-acetoxy-1,7,7-trimethylbicyclo[2.2.1]heptane (**XIII**). A double Wagner–Meerwein (DWM) rearrangement of cation C providing cation D followed by reaction of the latter with Ac_2O results in 2-*endo*-acetoxy-1,3,3-trimethylbicyclo[2.2.1]heptane (**XIV**). The ratio of compounds **XII, XIII**, and **XIV** in reaction mixture yielded by compounds **X** and **XI** was respectively 5 : 3 : 1 and 4 : 2 : 1. At the use instead of K-10 clay of the wide-porous β-zeolite alongside the acetates **XII–XIV** was obtained in considerable amount also 2-*endo*-acetoxy-1,5,5-trimethylbicyclo[2.2.1]heptane (**XV**) that apparently arose from 6,2-hydride shift in cation D followed by the reaction of the resulting intermediate with Ac_2O.

Both at the use as catalyst of clay and zeolite in the reaction mixture appear the products of cation B transformation: *p*-cymene and dipentene. Besides some conclusions are due after analysis of terpene **X** reaction with Ac_2O. Firstly, as mentioned by Ehrman [6], the homogeneous catalysis by H_2SO_4 of reaction between terpene **X** and Ac_2O resulted mainly in olefins formation although the reaction conditions suggested acetates formation. We showed that with K-10 clay the latter arise in significant amount. Secondly, terpenes **I** and **X** give rise to epimeric acetates **II** and **XII** respectively. The latter fact is apparently caused by partial retention of the geometry of the preceding species by the intermediate carbocations. Therewith if the acetoxy group attacks from the side opposite to the motion of the cleaving C–C bond then at the rearrangement of cation E should expectedly form the *exo*-addition product and at the rearrangement of cation A should arise the *endo*-addition product as is actually observed (Scheme 7).

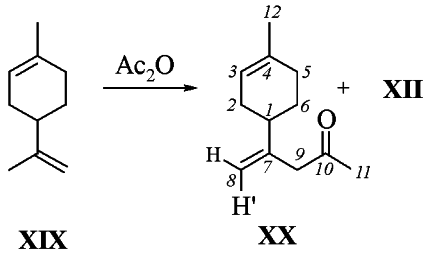
The α-pinene reaction with acetyl chloride on the clay under conditions similar to those in the process with acetic anhydride gave rise mainly to chlorine-containing terpenoids as showed the GC-MS data.

In reaction of a natural diene caryophyllene (**XVI**) with acetic anhydride in the presence of zeolite similarly to the process with the pinene isomers formed only acetoxylation product, caryolanol acetate (**XVII**) (Scheme 8). It should be noted that the transformation of diene **XVI** catalyzed by acids results in a complex mixture of substances [7] whereas under our conditions a single acetoxylation product has been obtained.

At the same time another diene, limonene (XIX), in reaction with acetic acid on the β-zeolite afforded mainly acylation product, 4-(4-methylcyclohex-3-enyl)pent-4-en-2-one (**XX**) alongside a small amount of compound **XII** (Scheme 9).

Now we shall regard the reaction of oxygen-containing terpenoids from the pinane series,

Scheme 9.

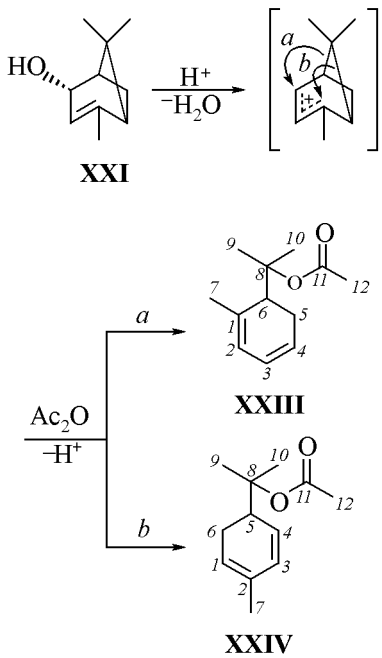


verbenol (**XXI**) and verbenone (**XXII**), with acetic anhydride in the presence of K-10 clay. The reaction with alcohol **XXI** yielded a mixture of 6-(1-acetoxy-1-methylethyl)-1-methylcyclohexa-1,3-diene (**XXIII**) and 5-(1-acetoxy-1-methylethyl)-2-methylcyclohexa-1,3-diene (**XXIV**) in 1 : 3.4 ratio (Scheme 10).

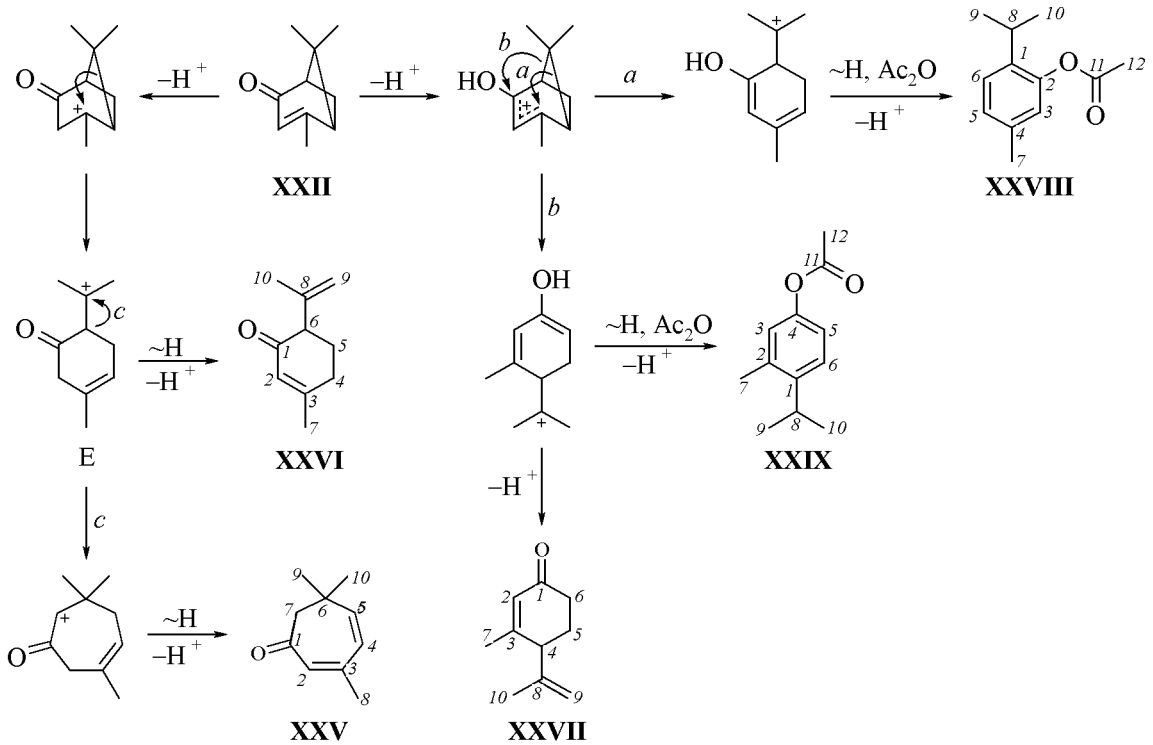
On keeping a mixture of alcohol **XXI** and acetic anhydride with β-zeolite a single product was obtained, *p*-cymene. We showed in [8] that ketone **XXII** did not react with aldehydes in the presence of clay indicating the difficult protonation of the ketone. The reaction of ketone **XXII** with Ac_2O on K-10 clay is quite different (Scheme 11).

As seen from the scheme, ketone **XXII** in the presence of Ac_2O on K-10 clay is involved both in intra- and intermolecular reactions. Along the first type arise 3,6,6-trimethylcyclohepta-2,4-dienone (**XXV**), 6-isopropenyl-3-methylcyclohex-2-enone (**XXVI**), and 4-isopropenyl-3-methylcyclohex-2-enone (**XXVII**). The structure of the former two compounds suggests that protonation of the substrate double bond takes place. The other reaction products originate from primary protonation of the carbonyl

Scheme 10.



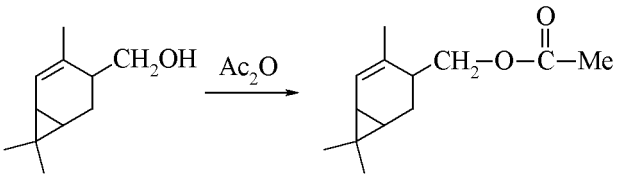
Scheme 11.



group in ketone **XXII**. Note the intramolecular cycle expansion in transition from ion F to compound **XXV**. Intramolecular transformations are prevailing in this reaction: the content of ketones **XXV–XXVII** in the reaction mixture amounts to ~44%. In lesser amounts in reaction of compound **XXII** and Ac_2O were obtained aromatic acetoxylation products: 2-acetoxy-1-isopropyl-4-methylbenzene (**XXVIII**) (9%) and 4-acetoxy-1-isopropyl-2-methylbenzene (**XXXIX**) (11%). It should be noted that keeping of the original ketone **XXII** on K-10 clay under the same conditions in the absence of acetic anhydride resulted in tarring, and no ketones **XXV–XXVII** were detected in the reaction mixture.

In conclusion we consider the reaction between walterol (**XXX**), an alcohol of carane series, with Ac_2O on β-zeolite (Scheme 12).

Scheme 12.



XXX **XXXI**

Unlike secondary alcohol **XXI** that suffers various rearrangements under the reaction conditions, primary alcohol **XXX** gives under these conditions a stable acetate of walterol (**XXXI**) in 80% yield.

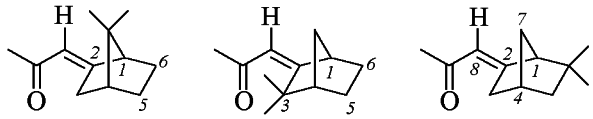
The structure of all compounds mentioned was proved by ^1H and ^{13}C NMR spectra. The ^{13}C NMR spectra of compounds **XII–XIV** are consistent with those published [9, 10]. The ^1H NMR spectra of ketone **XXVI** was published in [11], but we present more complete data; note that the chemical shifts in the spectrum we registered are close to those published. The parameters of the ^1H NMR spectrum of compound **XXXI** are identical to those described in literature [12].

Configurations of methyls attached to C^2 and C^6 carbons in compound **IV** can be derived from the following data: firstly, in 2-norbornyl cations 3,2-*exo*-methyl shift occurs very fast, and 3,2-*endo*-methyl shift is virtually nonexistent [13]; i.e. the methyl group at C^6 carbon in compound **IV** is in *exo*-position; secondly, the Dreiding models show, that in compounds of **IV** type the methyls at C^2 and C^6 can be present only in *cis*-configuration; besides it is known that at *cis*-junction of two five-membered or of a five- and a six-membered cycles the strain is significantly less than at trans-fusion [14]. Thus the methyl groups at C^2 and C^6 atoms in compound **IV** are in the *cis*-di-*exo*-configuration.

The presence of a cyclopropane ring in compound **V** is confirmed by the chemical shifts of C^1, C^2 and C^6 carbon atoms and also by the value of direct coupling constant $^1J_{CH}$ of 172 Hz for the two latter carbons.

The position of substituents at C^3 and C^5 atoms in compound **VI** was derived from the ^1H NMR spectra basing on analysis of the coupling constants for H^3 and H^5 protons. The *W*-constants of 1.5 Hz between protons H^3, H^{7c} and H^5, H^{7an} and no coupling between proper protons H^3 and H^5 evidences their *endo*-position. The *endo*-position of H^2 proton in compound **VIII** is confirmed by its coupling with the proton H^{7an}, $^4J_{2,7an}$ amounting to 1.5 Hz.

For compound **IX** the analysis of ^1H–^1H coupling constants permits to exclude the alternative isomeric structures **XXXII–XXXIV**.



XXXII **XXXIII** **XXXIV**

For instance, in the ^1H NMR spectra of compounds **XXXII** and **XXXIII** should have appeared for every proton signal from methylene groups $2H^5$ and $2H^6$ two coupling constants of 7–13 Hz. This actually is not observed, consequently, these structures are absent. In the ^1H NMR spectrum of compound **XXXIV** the signal from H^1 should have looked as a broadened singlet since the expected coupling constants with protons $2H^7$, H^4, and H^8 should be no greater than 2 Hz. For the signal of H^4 should be expected two vicinal coupling constants with the value of 3–5 Hz. In the spectrum under considerations both signals from protons H^1 and H^4 appear as broadened doublets with *J* 4.5 and 4 Hz indicating that these protons are neighbors of *exo*-protons; thus the structure **XXXIV** is not consistent with the observed spectrum. The comparison of the chemical shift of C^1 carbon (49.17 ppm) that is sensitive to the *cis, trans*-position of substituents at C^8 atom with the corresponding chemical shifts in the similar compounds having the other substituents [15] suggests that the acetyl group in compound **IX** is located *trans* to C^1 atom (in compounds with the *cis*- and *trans*-position of substituents the chemical shift of C^1 atom is respectively ~41 and ~48 ppm).

The presence in the ^{1}H spectrum of compound **XIV** of *W* coupling constant for the proton H^2 with the proton H^{6k} and no coupling with H^{7an} proton confirms the *exo*-position of the proton attached to C^2.

The positions of substituents in molecule **XV** were assigned by analysis of the geminal and vicinal coupling constants in the double resonance ^{1}H–^{1}H spectra.

It should be noted that as expected the parameters of the ^{13}C NMR spectrum of compound **XVII** are close to those of caryolanol spectrum save the position of the signal from C^1 atom [16].

Since in cyclohexane compounds the most bulky substituent is known to be located as a rule in equatorial position we assigned to H^1 proton in compound **XX** an axial configuration. This location is confirmed by the value of vicinal coupling constant of the proton with H^{6a} (*J* 12 Hz; the other *J* for H^1 proton to our regret were not detected due to overlapping of its signal in the ^{1}H NMR spectrum with the other resonances).

The alternative structures of compound **XXV** with the C^8H_3 group attached to C^2, C^4 or C^5 carbons are excluded basing on the data of LRJMD spectra at decoupling from protons of geminal methyl groups and C^8H_3: the first experiment provides unambiguous assignment of the C^5, signal, in the second LRJMD spectrum appear the doublet signals at 126.52 (C^4) and 130.01 ppm (C^2) and a singlet at 146.07 ppm (C^3) in agreement with **XXV** structure.

To proton H^6 in ketone **XXVI** was ascribed the axial position basing on the coupling constants with two H^5 protons.

The substituents positions in **XXVIII** and **XXIX** structures were derived from LRJMD spectra at decoupling from signals of C^7H_3 group and H^8 protons. The assignment was confirmed by calculation of the chemical shifts of aromatic carbon atoms with accounting for additive effect of substituents at the aromatic ring (the shift parameters from [17] were used in the calculations).

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were registered on spectrometer Bruker AM-400 at operating frequencies 400.13 MHz (^{1}H) and 100.61 MHz (^{13}C) from solutions in $CDCl_3$ or CCl_4–$CDCl_3$ (1 : 1 by volume). The signal of chloroform was used as internal reference (δ 7.24, δ_C 76.90 ppm). The structure of compounds obtained was established by analysis of coupling constants of protons in the double resonance ^{1}H–^{1}H spectra and from ^{13}C NMR spectra measured also with selective off-resonance irradiation of protons. We also recorded two-dimensional correlation spectra ^{13}C–^{1}H on direct constants (COSY, $^1J_{C,H}$ 134 Hz) and one-dimensional correlation ^{13}C–^{1}H spectra on long-range constants (LRJMD, $J_{C,H}$ 10 Hz). ^{13}C NMR spectra are listed in table. High-resolution mass spectra were measured on Finnigan MAT 8200 instrument, GC-MS spectra were obtained with HP G 1800A device. The specific rotation was determined with the use of spectrometer Polomat A from solutions in $CHCl_3$.

The checking of purity of the initial reagents and the analysis of reaction products was carried out by GLC on chromatographs equipped with flame-ionization detectors, oven temperature 60–150°C, carrier gas helium (at a pressure of 0.65 gage atmosphere). The instruments used were as follows: (1) Biokhrom-1, glass capillary column 53000×0.26 mm, stationary phase XE-60; 2) Biokhrom-1, quartz capillary column 13000×0.3 mm, stationary phase CE-54; 3) chromatograph 3700, glass capillary column 17000×0.25 mm, stationary phase VC-30.

The following compounds and catalysts were used in the study: camphene, 73% of the main substance, the main impurity tricyclene (14%), $[\alpha]^{20}_{580}$ +10.4 (*c* 5, $CHCl_3$); α-fenchene, 98% of the main substance, $[\alpha]^{20}_{580}$ +32 (*c* 1, $CHCl_3$); α-pinene, 82% of the main substance, the principal impurities camphene (5.2%) and 3-carene (4.3%), $[\alpha]^{20}_{580}$ +24.9 (*c* 7.8, $CHCl_3$); caryophyllene, 98% of the main substance, $[\alpha]^{20}_{580}$ –10.7 (*c* 41.3, $CHCl_3$); limonene, Fluka, $[\alpha]^{20}_{580}$ +123; verbenol. 96% of the main substance, $[\alpha]^{20}_{580}$ +63.1 (*c* 22.2, $CHCl_3$); verbenone, 72% of the main substance, the main impurity myrtenal (11%), $[\alpha]^{20}_{580}$ +101.4 (*c* 18.9, $CHCl_3$); walterol, 98% of the main substance, $[\alpha]^{20}_{580}$ +135.7 (*c* 16.8, $CHCl_3$); β-zeolite in the H^+-form, [Si]/[Al] = 40, pore size 0.75–0.8 nm, weight content of oxides: 0.04% Na_2O, 5.14% Al_2O_3, 81.57% SiO_2; montmorillonite K-10, Fluka. The clay was heated just before use for 3 h at 120°C, and zeolite was calcined at 500°C for 2 h. The solvent was passed through a column packed with calcined alumina.

The reaction products were separated by column chromatography on silica gel (40–100 μ).

Reaction of camphene (I) with acetic anhydride. To 0.45 g of zeolite in 20 ml of acetic anhydride was added 0.26 g of camphene, and the mixture was heated to 90°C for 2 h. After extraction with ethyl

^{13}C NMR spectra of compounds **IV–VI, VIII, IX, XV, XVII, XX, XXIII–XXIX**, δ_C, ppm

Atom no.	V	IV ($^1J_{CH}$, Hz)	VI	VIII	IX	XV	XVII
1	48.59 d	27.68 s	48.21 d	48.55 s	49.17 d	48.36 s	82.98 s
2	94.17 s	18.72 d (172)	38.68 s	78.25 d	170.68 s	78.07 d	42.67 d
3	–	31.26 t (133)	43.13 d	36.20 t	36.24 t	36.00 t	38.78 t
4	151.46 s	41.89 d (144)	51.08 d	47.16 d	47.42 d	46.99 d	34.13 s
5	103.13 d	31.26 t (133)	77.29 d	37.28 s	36.24 s	37.07 s	46.44 d
6	55.73 s	18.72 d (172)	34.22 t	50.12 t	45.64 t	49.93 t	23.66 t
7	47.53 d	43.87 s	32.44 t	40.91 t	38.78 t	40.70 t	39.02 t
8	22.16 t[a]	20.96 q (124)	24.33 q	30.90 q	117.13 d	16.46 q	34.58 s
9	26.38 t[a]	20.96 q (124)	27.06 q	26.54 q	196.91 s	30.69 q	36.37 t
10	35.78 t	40.59 t (125)	15.58 q	16.69 q	30.96 q	26.30 q	20.61 t
11	21.65 q	207.38 s	170.68 s	170.01 s	31.30 q	169.86 s	35.81 t
12	13.72 q	30.22 q (126)	21.29 q	21.03 q	26.95 q	20.80 q	45.72 t
13	22.54 q						20.58 q[b]

Atom no.	XX	XXIII	XXIV	XXV	XXVI	XXVII	XXVIII	XXIX
1	39.75 d	133.89 s	119.89 d	197.96 s	197.87 s	197.58 s	136.84 s	143.75 s
2	31.12 t	123.22 d	130.80 s	130.01 d	127.02 d	127.97 d	147.92 s	135.82 s
3	120.75 d	124.30 d	128.94 d	146.07 s	160.09 s	160.87 s	122.83 d	122.79 d
4	133.42 s	123.42 d	126.12 d	126.52 d	30.32 t	47.38 d	136.22 s	148.19 s
5	30.67 t	24.89 t	41.96 d	149.51 d	27.66 t	26.40 t	127.02 d	118.92 d
6	28.06 t	43.18 d	23.82 t	32.78 s	53.65 d	33.39 t	126.32 d	125.33 d
7	147.79 s	24.73 q	20.79 q	53.81 t	24.10 q	22.74 q	20.87 q[a]	19.18 q
8	112.53 t	86.30 s	84.53 s	27.20 q	143.04 s	142.59 s	27.14 d	28.82 d
9	50.70 t	24.46 q[a]	23.38 q[a]	27.09 q	113.48 t	113.23 t	23.14 q	23.22 q
10	203.96 s	24.36 q[a]	23.31 q[a]	27.09 q	20.79 q	26.40 q	23.14 q	23.22 q
11	28.70 q	169.56 s	170.23 s				168.85 s	168.49 s
12	23.68 q	22.74 q	22.29 q				20.85 q[a]	20.84 q

[a] These chemical shifts values may presumably be reversed within the same column.
[b] δ C^{14} 30.41 q, δ C^{15} 34.09 q, δ C^{16} 169.20 s, δ C^{17} 21.96 q.

ether and preliminary separation on a column packed with silica gel (eluent hexane) we separated 0.288 g of reaction products. The mixture was separated on the column with silica gel by gradient elution with hexane–ethyl ether (0.5–10%). We obtained 0.021 g (6%) of compound **II**, $[\alpha]^{20}_{580}$ –3 (*c* 1.5); 0.053 g (16%) of compound **III**, $[\alpha]^{20}_{580}$ 0; 0.06 g (18%) of compound **IV**, $[\alpha]^{20}_{580}$ –2 (*c* 1.8); 0.027 g (8%) of compound **V**, $[\alpha]^{20}_{580}$ 0, and 0.032 g (9%) of compound **VI**, $[\alpha]^{20}_{580}$ –2 (*c* 2.3).

Compound (IV). Found: *M* 178.13561. $C_{12}H_{18}O$. Calculated: *M* 178.13576. ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 0.97 s ($C^{13}H_3$), 1.18 s ($C^{11}H_3$), 1.20–1.28 m and 1.45–1.59 m (2H^8, 2H^9, 2H^{10}), 1.74 d ($C^{12}H_3$, $J_{12,5}$ 1.2), 1.85 m (H^7, *J* 1–2), 2.06 m (H^1, *J* 1–2), 4.14 br.s (H^5).

Compound (V). Found: *M* 178.13579. $C_{12}H_{18}O$. Calculated: *M* 178.13576. ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 0.79 s (C^8H_3, C^9H_3), 1.06 br.d (H^{3n}, H^{5n}, *J* 11), 1.07 d (H^2, H^6, *J* 1.2), 1.38 t.t (H^4, *J* 2, 1.5), 1.67 d.d.d (H^{3k}, H^{5k}, *J* 11, 2, 1.2), 2.09 s ($C^{12}H_3$), 2.46 s (2H^{10}).

Compound (VI). Found: *M* 196.14630. $C_{12}H_{20}O_2$. Calculated: M 196.14632. ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 0.847 d ($C^{10}H_3$, *J* 7), 0.852 s (C^8H_3), 0.88 s (C^9H_3), 1.09 q.d (H^{3n}, $J_{3n,10}$ 7, $J_{3n,7c}$ 1.5), 1.21 d.d.d.d (H^{6k}, $J_{6k,6n}$ 13.5, $J_{6k,1}$ 4, $J_{6k,5n}$ 3, $J_{6k,4}$ 1),

1.34 d.d.d.d (H^{7c}, $J_{7c,7an}$ 10.5, $J_{7c,1}$ = $J_{7c,4}$ = $J_{7c,3n}$ 1.5), 1.67 d.d.d.d.d (H^{7an}, J 10.5, $J_{7an,6n}$ 3, $J_{7an,1}$ = $J_{7an,4}$ = $J_{7an,5n}$ 1.5), 1.69 br.d (H^{1}, J 4), 1.81 br.s (H^{4}), 1.97 s ($C^{12}H_3$), 2.20 d.d.d (H^{6n}, J 13.5, 3, $J_{6n,5n}$ 7), 4.60 d.d.d.d (H^{5n}, J 7, 3, 1.5, $J_{5n,4}$ 0.5).

Reaction of camphene (I) with acetyl chloride. To 0.4 g of zeolite in 15 ml of CH_2Cl_2 was added 0.5 g of AcCl and 0.27 g of camphene in 12 ml of CH_2Cl_2. The reaction mixture was stirred for 21 h at room temperature. After extraction with ethyl ether the reaction products were separated on a column packed with silica gel, eluent hexane–ethyl ether, 0–10%. We obtained 0.1 g of unreacted compound **I**, 0.023 g (10%) of compound **II**, $[\alpha]^{20}_{580}$ –6.6 (*c* 1.2), and 0.006 g (3%) of compound **III**, $[\alpha]^{20}_{580}$ 0.

Reaction of α-fenchene (VII) with acetic anhydride. To 0.2 g of zeolite in 15 ml of acetic anhydride was added 0.19 g of α-fenchene, and the reaction mixture was heated to 70°C for 2 h. After extraction with ethyl ether the reaction products were separated on a column packed with silica gel, eluent hexane–ethyl ether, 0–10%. We obtained 0.19 g (69%) of compound **VIII** and 0.019 g (8%) of compound **IX**.

Compound VIII. $[\alpha]^{20}_{580}$ +39.2 (*c* 3.6). Fragment ion *M*–CH_3. Found: *M* 181.12274. $C_{11}H_{17}O_2$. Calculated: *M* 181.12285. ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 0.90 s ($C^{9}H_3$), 0.92 d.d (H^{6n}, $J_{6n,6k}$ 13, $J_{6n,7c}$ 2.5), 0.95 s ($C^{8}H_3$), 0.96 s ($C^{10}H_3$), 1.16 d (H^{6k}, J 13), 1.20 d.d.d (H^{3k}, $J_{3k,3n}$ 14, $J_{3k,4}$ 4, $J_{3k,2n}$ 3.5), system *AB* 1.34 d.d.d (H^{7c}, $J_{7c,7an}$ *10*, J 2.5, $J_{7c,4}$ 1.5) and 1.45 d.d.d.d (H^{7an}, J 10, $J_{7an,3n}$ 3, $J_{7an,2n}$ 1.5, $J_{7an,4}$ 1.5), 1.63 br.d (H^{4}, J 4), 1.96 s ($C^{12}H_3$), 2.27 d.d.d (H^{3n}, J 14, $J_{3n,2n}$ 7, $J_{3n,7an}$ 3), 4.45 d.d.d (H^{2n}, J 7, 3.5, 1.5).

Compound IX. $[\alpha]^{20}_{580}$ –100.8 (*c* 0.6). Found: *M* 178.13596. $C_{12}H_{18}O$. Calculated: *M* 178.13576. ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 0.93 c ($C^{12}H_3$), 1.02 s ($C^{11}H_3$), 1.04 d.d (H^{6n}, $J_{6n,6k}$ 12, $J_{6n,7c}$ 2.5), 1.34 d.d.d.d (H^{7c}, $J_{7c,7an}$ 10, J 2.5, $J_{7c,1}$ = $J_{7c,4}$ 1.5), 1.56 d.d.d (H^{6k}, J 12, $J_{6k,1}$ 4.5, $J_{6k,3k}$ 0.7), 1.75 d.d.d.d (H^{7an}, J 10, $J_{7an,3n}$ 4, $J_{7an,1}$ = $J_{7an,4}$ 1.5), 1.95 br.d (H^{4}, $J_{4,3k}$ 4), 2.12 s ($C^{10}H_3$), 2.24 d.d.d.d (H^{3k}, $J_{3k,3n}$ 19, J 4, $J_{3k,8}$ 3, J 0.7), 2.67 br.d (H^{1}, J 4.5), 2.96 d.d.d (H^{3n}, J 19, 4, $J_{3n,8}$ 2.5), 6.11 d.d (H^{8}, J 3, 2.5).

Reaction of α-pinene (X) with acetic anhydride on K-10 clay. To a dispersion of 1.5 g of clay in 12 ml of CH_2Cl_2 was added 10 ml of Ac_2O, and within 5 min was added dropwise a solution of 0.6 g of α-pinene in 2 ml of CH_2Cl_2. The mixture was left standing at room temperature for 19 h, then treated with 20 ml of saturated $NaHCO_3$ solution, the reaction products were extracted into 20 ml of ethyl ether, and the extract was dried with $MgSO_4$. By column chromatography on silica gel (eluent 0–20% of ethyl ether in hexane) we separated 0.238 g of a mixture containing according to GC-MS data dipentene (31%), α-pinene (16%), terpinolene (16%), camphene (10%), p-cymene (6%), and 3-carene (5%), and also 0.201 g of a mixture of compounds **XII, XIII**, and **XIV** in overall yield of 29% in the ratio 2.4 : 2.9 : 1 according to GC-MS data. The latter mixture was separated into individual compounds by column chromatography on silica gel using for elution 1–2% of ethyl ether in hexane. We obtained 0.05 g of compound **XII**, 0.031 g of compound **XIII**, and 0.003 g of compound **XIV**.

Compound XII. $[\alpha]^{20}_{580}$ +30.4 (*c* 8.3). Fragment ion *M*–CH_3COOH. Found: *M* 136.12467. $C_{10}H_{16}$. Calculated: *M* 136.12519. ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 1.21 d.d.d.d (H^{5a}, $J_{5a,5e}$ 12, $J_{5a,6a'}$ 12, $J_{5a,4a}$ 12, $J_{5a,6e'}$ 5.5), 1.33 s and 1.36 s ($C^{9}H_3$, $C^{10}H_3$), 1.56 br.s ($C^{7}H_3$), 1.71 d.d.d.d.d (H^{5e}, J 12, $J_{5e,6a'}$ 5.5, $J_{5e,4a}$ = = $J_{5e,6e'}$ = $J_{5e,3e'}$ 2), 1.72–2.02 m (2H^{3}, H^{4a}, 2H^{6}), 1.88 s ($C^{12}H_3$), 5.26 br.m (H^{2}).

Compound XIII. $[\alpha]^{20}_{580}$ +20.7 (*c* 5.2). Found: *M* 196.14649. $C_{12}H_{20}O_2$. Calculated: *M* 196.14632. ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 0.79 s ($C^{8}H_3$), 0.83 s ($C^{10}H_3$), 0.87 s ($C^{9}H_3$), 0.91 d.d (H^{3n}, $J_{3n,3k}$ 13.5, $J_{3n,2k}$ 3.5), 1.19 d.d.d (H^{5n}, $J_{5n,5k}$ 13, $J_{5n,6n}$ 9, $J_{5n,6k}$ 4.5), 1.24 d.d.d.d (H^{6k}, $J_{6k,6n}$ 13, $J_{6k,5k}$ 13, J 4.5, $J_{6k,2k}$ 2), 1.62 d.d (H^{4}, $J_{4,3k}$ 4.5, $J_{4,5k}$ 4), 1.70 m (H^{5k}), 1.88 m (H^{6n}), 2.00 s ($C^{12}H_3$), 2.30 d.d.d.d (H^{3k}, $J_{3k,3n}$ 13.5, $J_{3k,2n}$ 10, J 4.5, $J_{3k,5k}$ 3), 4.81 d.d.d (H^{2k}, J 10, 3.5, 2).

Compound XIV. ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 0.75 s ($C^{10}H_3$), 1.02 s ($C^{8}H_3$), 1.05 d.d.d.d (H^{6k}, $J_{6k,6n}$ 12, $J_{6k,5k}$ 12, $J_{6k,5n}$ 3, $J_{6k,2k}$ 2), 1.08 s ($C^{9}H_3$), 1.15 d.d (H^{7an}, $J_{7an,7c}$ 10, $J_{7an,4}$ 1.5), 1.43 d.d.d.d (H^{5k}, $J_{5k,5n}$ 12, J 12, $J_{5k,6n}$ 6, $J_{5k,4}$ 4), 1.56 d.d.d.d (H^{7c}, J 10, $J_{7c,5n}$ 3, $J_{7c,6n}$ 2, $J_{7c,4}$ 2), 1.67 d.d.d.d (H^{5n}, J 12, $J_{5n,6n}$ 9, J 3, 3), 1.69 m (H^{4}), 1.72 m (H^{6n}), 2.04 s ($C^{12}H_3$), 4.32 d (H^{2k}, J 2).

Reaction of α-pinene (X) with acetic anhydride on zeolite. To a dispersion of 1.75 g of zeolite in 10 ml of CH_2Cl_2 was added 10 ml of Ac_2O and a solution of 1.3 g of –pinene in 4 ml of CH_2Cl_2. The mixture was stirred at room temperature for 2 h 40 min and worked up as in the preceding experiment. With the column chromatography on silica gel using for elution 1–2% of ethyl ether in hexane we separated 0.784 g of a mixture containing the following main components as shown by GC-MS method: dipentene (24%), camphene (18%), α-terpinene (16%), terpinolene (11%), γ-terpinene (8%), *p*-cymene (4%), and 3-carene (3%). Also was separated 0.438 g (overall yield 29%) of a mixture of compounds **XII**, **XIII**, **XIV**, and **XV** in the ratio 4.7 : 6 : 1 : 8.5 according to GC-MS data. The latter mixture was separated by column chromatography on silica gel using for elution 0.25–0.5% of ethyl ether in hexane. We obtained 0.103 g of a mixture of compounds **XV** and **XIII** in 1.1 : 1 ratio.

Compound (XV). ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 0.84 s ($C^{10}H_3$), 0.85 d.d (H^{6n}, $J_{6n,6k}$ 13, $J_{6n,7c}$ 2.5), 0.89 s (C^9H_3), 0.90 s (C^8H_3), 1.11 d (H^{6k}, *J* 13), 1.15 d.d.d (H^{3k}, $J_{3k,3n}$ 13.5, $J_{3k,4}$ 4.5, $J_{3k,2n}$ 3.5), system *AB* 1.29 d.d.d (H^{7c}, $J_{7c,7an}$ 10, *J* 2.5, $J_{7c,4}$ 1.5) and 1.39 d.d.d.d (H^{7an}, *J* 10, $J_{7an,3n}$ 3, $J_{7an,4}$ 1.5, $J_{7an,2n}$ 1.5), 1.57 br.d (H^4, *J* 4.5), 1.89 s ($C^{12}H_3$), 2.21 d.d.d (H^{3n}, *J* 13.5, $J_{3n,2n}$ 7, *J* 3), 4.40 d.d.d (H^{2n}, *J* 7, 3.5, 1.5).

Reaction of β-pinene (XI) with acetic anhydride on K-10 clay. The reaction was carried out in a similar way as with α-pinene. From 0.15 g of β-pinene was obtained 0.015 g of isomerization products and 0.33 g of a mixture of compounds **XII, XIII**, and **XIV** in 3.7 : 1.8 : 1 ratio according to GC-MS data.

Reaction of caryophyllene (XVI) with acetic anhydride on zeolite. To 0.36 g of zeolite in 8 ml of acetic anhydride was added 0.29 g of caryophyllene in 7 ml of acetic anhydride. The reaction mixture was stirred for 6 h at 115°C. After workup similar to that in the preceding run we separated by column chromatography on silica gel (eluent 1–10% of ethyl ether in hexane) 0.067 g of a mixture of isomerization products of caryophyllene (according to GC-MS data) and 0.094 g (25%) of compound **XVII**, $[\alpha]^{20}_{580}$ +2.2 (*c* 3). Found: *M* 264.20930. $C_{17}H_{28}O_2$. Calculated: *M* 264.20892. ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 0.88 s ($C^{15}H_3$), 0.95 s ($C^{13}H_3$, $C^{14}H_3$), 1.07 m (H^{9a}), 1.15 m (H^7), 1.26 d.d (H^3, $J_{3,3'}$ 10, $J_{3,2}$ 10), 1.28 m (H^6), 1.29 d (H^{12an}, $J_{12an,12c}$ 13), 1.39 d.t.d (H^{9e}, $J_{9e,9a}$ 13, $J_{9e,10}$ 5, $J_{9e,12c}$ 1.5), 1.41–1.53 m (H^{11a}, $H^{6'}$, $H^{7'}$), 1.60–1.73 m ($2H^{10}$), 1.68 d.d ($H^{3'}$, *J* 10, $J_{3',2}$ 8), 1.80 d.d.d (H^5, $J_{5,2}$ 12, $J_{5,6}$ 9, $J_{5,6'}$ 5), 1.92 s ($C^{17}H_3$), 1.93 d.d.d (H^{12c}, *J* 13, $J_{12c,11e}$ 2.5, *J* 1.5), 2.30 d.d.d (H^2, *J* 12, 10, 8), 2.43 d.t.d (H^{11e}, $J_{11e,11a}$ 13, $J_{11e,10}$ 5, *J* 2.5).

Reaction of limonene (XIX) with acetic anhydride. To 0.3 g of zeolite in 10 ml of acetic anhydride was added 0.25 g of limonene in 2 ml of acetic anhydride, and the mixture was heated to 95°C for 4 h. The reaction products were separated on a column packed with silica gel (eluent hexane). We obtained 0.11 g of a mixture containing according to GC-MS data 14% of α-terpinene, 12% of p-cymene, 32% of limonene, 13% of γ-terpinene, 23% of terpinolene, and 5% of compound **XII**, and also 0.13 g (40%) of compound **XX**, $[\alpha]^{20}_{580}$ +10.3 (*c* 3.9). Found: *M* 178.13579. $C_{12}H_{18}O$. Calculated: *M* 178.13578. ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 1.42 d.d.d.d (H^{6a}, $J_{6a,6e}$ 12, $J_{6a,5a'}$ 12, $J_{6a,1a}$ 12, $J_{6a,5e'}$ 5.5), 1.62 br.s ($C^{12}H_3$), 1.80 d.d.d.d.d (H^{6e}, *J* 12, $J_{6e,5a'}$ 5.5, $J_{6e,1a}$ = $J_{6e,5e'}$ = $J_{6e,2e'}$ 2), 1.81– 2.14 m ($2H^2$, $2H^5$, H^1), 2.07 s ($C^{11}H_3$), 3.06 br.s ($2H^9$), 4.82 d.t (H^8, $J_{8,8'}$ 1.2, $J_{8,9}$ 1.2), 4.93 d.d ($H^{8'}$, *J* 1.2, $J_{8',1a}$ 1.2), 5.32 br.m (H^3).

Reaction of verbenol (XXI) with acetic anhydride. To a dispersion in 3 ml of acetic anhydride and 8 ml of CH_2Cl_2 of 0.8 g of clay preliminary heated in a microwave oven at 450 W for 20 min was added at cooling with ice water a solution of 0.2 g of verbenol in 2 ml of CH_2Cl_2. The mixture was stirred at cooling with ice water for 1 h. After neutralization and separation on a column packed with silica gel (eluent 1–60% of diethyl ether in hexane) we obtained 0.66 g (38%) of p-cymene, 0.04 g of a mixture containing according to GC-MS data 13% of verbenone and 74% of isomerized alcohols (overall yield of alcohols 20%), and 0.074 g of a mixture containing compounds **XXIII** and **XXIV** in 1 : 3.4 ratio. The repeated chromatography of the latter mixture on a column packed with silica gel (eluent 0.5% of ethyl ether in hexane) afforded 0.008 g of individual compound **XXIV**, $[\alpha]^{20}_{580}$ –15.7 (*c* 0.5). Fragment ion *M*–CH_3COOH. Found: *M* 134.10988. $C_{10}H_{14}$. Calculated: *M* 134.10954. ^{1}H NMR spectrum (δ, ppm, *J*, Hz): 1.40 s and 1.41 s (C^9H_3, $C^{10}H_3$), 1.68 d.d.d (C^7H_3, $J_{7,6a'}$ 2, $J_{7,6e'}$ 1.5, $J_{7,1}$ 1.5), 1.95 s ($C^{12}H_3$), system *AB* 2.04 d.d.d.q ($H^{6a'}$, $J_{6a',6e'}$ 17, $J_{6a',5a'}$ 14, $J_{6a',1}$ 3.5, *J* 2) and 2.13 d.d.d.q ($H^{6e'}$, *J* 17, $J_{6e',5a'}$ 9, $J_{6e',1}$ 5, *J* 1.5), 2.91 d.d.d.d.d ($H^{5a'}$, *J* 14, 9, $J_{5a',4}$ 3, $J_{5a',3}$ 2.5, $J_{5a',1}$ 0.5), 5.41 br.m (H^1),

5.64 d.d (H^4, $J_{4,3}$ 10, J 3), 5.80 d.d.d (H^3, J 10, 2.5, $J_{3,1}$ 1.5).

Compound (XXIII). ^{1}H NMR spectrum (δ, ppm, J, Hz): 1.43 s and 1.46 s (C^9H_3, $C^{10}H_3$), 1.86 br.s (C^7H_3), 1.93 s ($C^{12}H_3$), *AB* system 2.30 d.d.d ($H^{5e'}$, $J_{5e',5a'}$ 18, $J_{5e',4}$ 6, $J_{5e',6}$ 2) and 2.41 br.d.d.d.d ($H^{5a'}$, J 18, $J_{5a',6a'}$ 10, $J_{5a',4}$ 3, $J_{5a',3}$ 3), 2.79 d.d ($H^{6a'}$, J 10, 2), 5.51 d.d.d.d.q (H^4, $J_{4,3}$ 10, J 6, 3, $J_{4,2}$ 1, $J_{4,7}$ 0.5), 5.71 d.d.d (H^3, J 10, $J_{3,2}$ 5, J 3), 5.77 m (H^2).

Reaction of verbenone (XXII) with acetic anhydride. To a dispersion in 6 ml of acetic anhydride and 8 ml of toluene of 1.15 g of clay preliminary heated in a microwave oven for 10 min was added dropwise 0.64 g of verbenone in 2 ml of toluene, and the mixture was stirred for 6 h at 60°C. On evaporating the solvent the reaction mixture was passed through a short column packed with silica gel (eluent 0.2–2% of ethyl ether in hexane). We separated 0.35 g of a mixture of the original verbenone and compounds **XXVI** and **XXVII** in 1 : 1.3 : 1.3 ratio, and also 0.16 g of a mixture containing compounds **XXV, XXVIII**, and **XXIX**. Both mixtures were repeatedly subjected to column chromatography on silica gel (eluent 0.5–5% of ethyl ether in hexane) resulting in isolation of 0.15 g (3%) of compound **XXV**, 0.066 g (12%) of compound **XXVIII**, 0.078 g (14%) of compound **XXIX**, 0.011 g (2%) of compound **XXVI**, and 0.051 g of a mixture of the original verbenone and compound **XXVII** in 0.7 : 1 ratio.

Compound XXV. $[\alpha]^{20}_{580}$ +17.6 (c 2.3). Found: M 150.10460. $C_{10}H_{14}O$. Calculated: M 150.10446. ^{1}H NMR spectrum (δ, ppm, J, Hz): 1.08 s (C^9H_3, $C^{10}H_3$), 1.98 d (C^8H_3, $J_{8,2}$ 1.2), 2.52 s ($2H^7$), 5.68 d.d (H^4, $J_{4,5}$ 12, $J_{4,2}$ 1.2), 5.95 br.s (H^2), 6.00 br.d (H^5, J 12).

Compound XXVI. $[\alpha]^{20}_{580}$ –24.2 (c 1.6). ^{1}H NMR spectrum (δ, ppm, J, Hz): 1.70 br.s ($C^{10}H_3$), 1.92 br.s (C^7H_3), *AB* system 1.98 d.d.t (H^{5e}, $J_{5e,5a}$ 13, $J_{5e,6a'}$ 5, $J_{5e,4}$ 5) and 2.07 d.d.d.d (H^{5a}, J 13, $J_{5a,6a'}$ 11, $J_{5a,4}$ 8, $J_{5a,4'}$ 5), 2.22– 2.32 m ($2H^4$), 2.86 d.d.d ($H^{6a'}$, J 11, 5, $J_{6a',9}$ 1), 4.68 br.s (H^9), 4.87 d.q ($H^{9'}$, $J_{9',9}$ 1.5, $J_{9',10}$ 1.5), 5.81 t.q (H^2, $J_{2,4}$ 1.5, $J_{2,7}$ 1.5).

Compound XXVII. ^{1}H NMR spectrum (δ, ppm, J, Hz): 1.70 br.s ($C^{10}H_3$), 1.78 br.s (C^7H_3), 1.83–2.02 m ($2H^5$), *AB* system 2.10 d.d.d (H^{6e}, $J_{6e,6a}$ 17, $J_{6e,5a}$ 6, $J_{6e,5e}$ 4.5) and 2.24 d.d.d (H^{6a}, J 17, $J_{6a,5a}$ 11, $J_{6a,5e}$ 5), 2.77 m (H^4), 4.61 br.s (H^9), 4.84 m ($H^{9'}$, J 1.5–2), 5.79 m (H^2, J 1–1.5).

Compound XXVIII. $[\alpha]^{20}_{580}$ +25.5 (c 1.6). Found: M 192.11526. $C_{12}H_{16}O_2$. Calculated: M 192.11502. ^{1}H NMR spectrum (δ, ppm, J, Hz): 1.18 d (C^9H_3, $C^{10}H_3$, J 7), 2.29 s ($C^{12}H_3$), 2.31 br.s (C^7H_3), 2.94 septet (H^8, J 7), 6.75 d.d (H^3, $J_{3,5}$ 2, $J_{3,7}$ 0.5), 6.97 d.d.q (H^5, $J_{5,6}$ 8, J 2, $J_{5,7}$ 0.5), 7.14 d (H^6, J 8).

Compound XXIX. $[\alpha]^{20}_{580}$ –10.3 (c 1.8). Found: M 192.11488. $C_{12}H_{16}O_2$. Calculated: M 192.11502. ^{1}H NMR spectrum (δ, ppm, J, Hz): 1.24 d (C^9H_3, $C^{10}H_3$, J 7), 2.25 s ($C^{12}H_3$), 2.34 br.s (C^7H_3), 3.12 septet (H^8, J 7), 6.81 d (H^3, $J_{3,5}$ 2.5), 6.85 d.d (H^5, $J_{5,6}$ 8, J 2.5), 7.19 d (H^6, J 8).

Reaction of walterol (XXX) with acetic anhydride. To a dispersion of 0.4 g of zeolite in 0.6 ml of acetic anhydride and 6 ml of CH_2Cl_2 was added dropwise 0.2 g of walterol in 1 ml of CH_2Cl_2, the mixture was stirred for 40 min, treated with a saturated solution of $NaHCO_3$, the catalyst was filtered off, the reaction products were extracted into ethyl ether. On removing the solvents the reaction mixture was subjected to column chromatography on silica gel (eluent 0.5% of ethyl ether in hexane). We obtained 0.2 g (80%) of compound **XXXI**, $[\alpha]^{20}_{580}$ +125.5 (c 18.9).

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