Reactions of Allyl Alcohols of the Pinane Series and of Their Epoxides in the Presence of Montmorillonite Clay

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The reactivity of allyl alcohols of the pinane series and of their epoxides in the presence of montmorillonite clay in intra- and intermolecular reactions was studied. Mutual transformations of (+)-*trans*-pinocarveol ((+)-**2**) and (−)-myrtenol ((−)-**3a**) were major reactions of these compounds on askanite–bentonite clay (*Schemes 1* and *2*). However, the two reactions gave different isomerization products, indicating that the reactivity of the starting alcohol (+)-**2** or (−)-**3a** was different from that of the same compound (+)-**2** or (−)-**3** formed in the course of the reactions. (−)-*cis*- and (+)-*trans*-Verbenol ((−)-**16** and (+)-**12**, resp.), as well as (−)-*cis*-verbenol epoxide ((−)-**20**) reacted with both aliphatic and aromatic aldehydes on askanite–bentonite clay giving various heterocyclic compounds (*Schemes 4*, *5* and *7*); the reaction path depended on the structure of both the terpenoid and the aldehyde.

Introduction. – Interest in the chemistry of pinane terpenes and their O-containing derivatives is largely dictated by the accessibility of these substances, which are more widespread in nature than any other monoterpenes or their derivatives [1]. Due to their chemical reactivity and high optical purity, pinanes may be employed as substrates to obtain compounds potentially useful as synthons in asymmetric synthesis [2]. In acid media, however, pinenes and their derivatives generally undergo numerous transformations, giving complex mixtures of products, which is one of the obstacles to a wide application of these compounds in fine organic chemistry [1]. For example, acid-catalyzed isomerization of α-pinene oxide may yield up to two hundred products [3]. Therefore, reactions of pinane terpenoids in the presence of crystalline acidic aluminosilicate catalysts (clays, zeolites) are of considerable interest because of the possibility to bring about processes with drastically increased selectivity or an even unknown reaction pathway [3][4] (clay microreactors are known to occasionally display enzyme-like characteristics [4][5]).

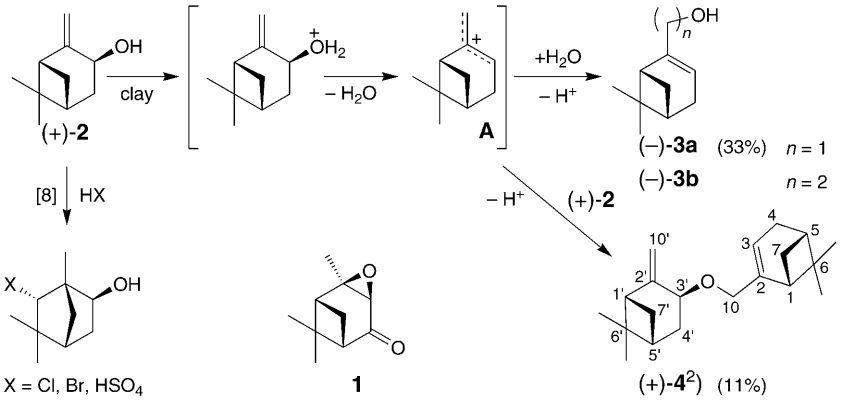
The interesting and unexpected data obtained in our previous study of the behavior of (−)-verbenone epoxide (**1**) in the presence of montmorillonite clay [6][1]) prompted us to investigate transformations of other compounds of the pinane series under the same

[1]) A series of new polyfunctional optically active heterocyclic compounds (α-hydroxy ketones, α-diketones, ketoaldehyde) was obtained. Important biological activity has recently been found in bicyclic ethers of this kind: compounds with a 3-oxabicyclo[3.3.1]nonane framework showed activity as estrogen receptor α and β agonists [7].

conditions. For the object of this investigation, we took a number of accessible optically active alcohols: (+)-*trans*-pinocarveol ((+)-**2**), (−)-myrtenol ((−)-**3a**), and verbenols (+)-**12** and (−)-**16**. The choice of these terpenoids is dictated by several reasons: *1*) these are widespread reactive pinenes possessing high optical purity; *2*) their behavior in the presence of aluminosilicate catalysts has not yet been studied; *3*) these terpenoids are allyl alcohols that differ only in the position of the double bond and hydroxy group, which allows an easy comparison of the results; *4*) their epoxides are readily accessible and thus can substantially expand the synthetic potential of the transformations being studied.

Results and Discussion. – (+)-trans-*Pinocarveol* ((+)-**2**) *and Myrtenol* ((−)-**3a**). As is known from the literature, in the presence of mineral acids, (+)-*trans*-pinocarveol ((+)-**2**) is mostly converted into fenchyl derivatives [8] (*Scheme 1*), while (−)-myrtenol ((−)-**3a**) forms either hydrocarbons when boiled with 10% sulfuric acid [9] or myrtenol acetate with AcOH [9]. When we exposed (+)-**2** for 3 h at room temperature to askanite–bentonite clay (its synthetic analog is the commercially available clay *K10*), the products isolated from the reaction mixture were unchanged alcohol (+)-**2** (conversion 75%), (−)-myrtenol ((−)-**3a**; 33%), and the condensation product (+)-**4** (11%); the given yields refer to converted alcohol (+)-**2** (*Scheme 1*)[2]). Compound **4** is probably formed by reaction of carbocation **A** with (+)-**2**. Interestingly, despite the presence of two alcohols in comparable proportion in the reaction mixture and their potential to add at two positions of cation **A**, only compound (+)-**4** was formed in appreciable amounts besides (−)-**3a**.

Scheme 1. *Transformations of (+)-*trans-*Pinocarveol* ((+)-**2**) *on Askanite-Bentonite Clay*

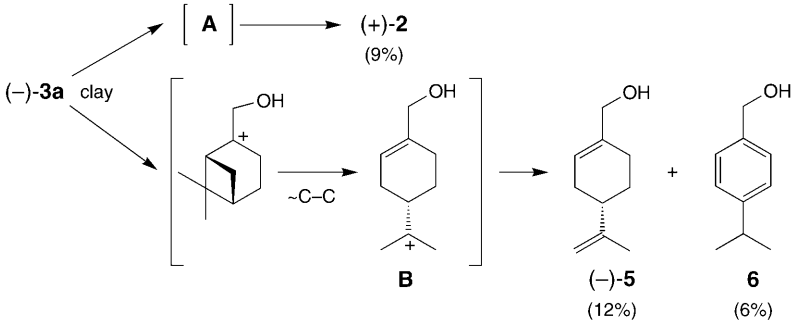


When (−)-myrtenol ((−)-**3a**) was kept on askanite–bentonite clay for 1 h at room temperature, the products were (+)-*trans*-pinocarveol ((+)-**2**; 9%), perillyl alcohol ((−)-**5**; 12%), and *para*-cymene derivative **6** (6%) (yields relative to converted (−)-**3a**, conversion 44%; *Scheme 2*). Since the reaction mixture contains products with a

[2]) Trivial or arbitrary atom numbering; for systematic names, see *Exper. Part.*

para-menthane framework, it follows that isomerization of (−)-**3a** occurs not only *via* formation of carbocation **A** from the protonated enol but also, obviously, *via* double-bond protonation with subsequent skeletal rearrangement of the resulting carbocation into cation **B**. Despite the high optical purity of the starting (−)-myrtenol ((−)-**3a**), the products of its isomerization had lower optical-activity characteristics than those reported in the literature. This is indicative of a racemization process occurring during the reaction. Thus, the specific rotation $[\alpha]_{580}$ was +9.1 ($c=3$, $CHCl_3$) for (+)-*trans*-pinocarveol ((+)-**2**) obtained from (−)-myrtenol ((−)-**3a**) ([10]: $[\alpha]_D=+52$ ($CHCl_3$) for pure (+)-**2**) and −17 ($c=3$, $CHCl_3$) for perillyl alcohol (**5**) ([11]: $[\alpha]_D=-121$ (neat)). At the same time, (−)-myrtenol ((−)-**3a**) formed from (+)-**2** (see *Scheme 1*) has a rather high optical purity ($[\alpha]_{580}^{20}=-40$ ($c=25$, $CHCl_3$); [12]: $[\alpha]_{580}^{20}=-50.6$ ($CHCl_3$)).

Scheme 2. *Transformations of (−)-Myrtenol* ((−)-**3a**) *on Askanite–Bentonite Clay*

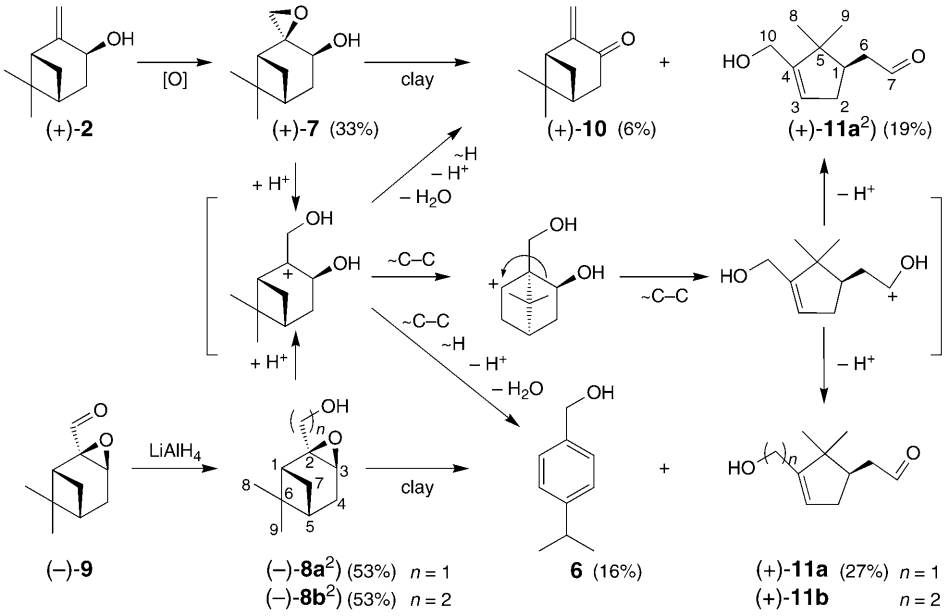


Thus mutual transformations are the main reaction paths of (+)-*trans*-pinocarveol ((+)-**2**) and (−)-myrtenol ((−)-**3a**) in the presence of askanite–bentonite clay. In both cases, the reaction mixture contained (+)-**2** and (−)-**3a**. However, 'nonoverlapping' isomerization products unexpectedly formed in each case, which actually means that clay is able to 'distinguish' between two states of the same compound (the state of the starting compound applied to clay and the state of the reaction product). Note that the behavior of (+)-*trans*-pinocarveol ((+)-**2**) and (−)-myrtenol ((−)-**3a**) on clay differs substantially from their reactivity in the presence of mineral acids [8][9].

(−)-Myrtenol Epoxide ((−)-**8**) *and (+)*-trans-*Pinocarveol Epoxide* ((+)-**7**). (+)-*trans*-Pinocarveol epoxide ((+)-**7**) was prepared by oxidation of (+)-*trans*-pinocarveol ((+)-**2**) with monoperphthalic acid in 33% yield according to [13]. (−)-Myrtenol epoxide ((−)-**8a**) was synthesized in 32% yield by oxidation of (−)-myrtenol ((−)-**3a**) with peracetic acid according to [14] or by reduction of (−)-myrtenal epoxide ((−)-**9**) with $LiAlH_4$ according to [15] (53%) (*Scheme 3*).

As in the case of the starting alcohols, storage of the epoxides (+)-**7** and (−)-**8** on clay gave unexpected results. Although the reactions were expected to yield identical cations due to cleavage of the protonated oxirane rings, isomerization products partly formed from only one particular starting compound. Thus, storage of (+)-pinocarveol epoxide ((+)-**7**) on askanite–bentonite clay for 1 h at room temperature gave a complex product mixture from which we isolated (+)-pinocarvone ((+)-**10**; 6%) and cam-

Scheme 3. *Transformations of (+)-Pinocarveol Epoxide* ((+)-**7**) *and (−)-Myrtenol Epoxide* ((−)-**8a**) *on Clay*



pholenic aldehyde analog (+)-**11a**; 19%)[3]) (*Scheme 3*). Transformations of (−)-myrtenol epoxide ((−)-**8a**) on clay under the same conditions yielded an aromatic alcohol **6** (16%) with a *para*-menthane framework and compound (+)-**11a** (27%) (*Scheme 3*). It should be emphasized that **6** was not formed from epoxide (+)-**7**, and ((+)-**10**) did not result from epoxide ((−)-**8a**). This may be explained, for example, by differences of adsorption of the epoxides (+)-**7** and (−)-**8a** on clay[4]).

The behavior of (−)-myrtenol epoxide ((−)-**8a**) in the presence of askanite–bentonite clay is similar to the previously studied transformations of its homologue (−)-nopol epoxide ((−)-**8b**) on montmorillonite clays [17][5]). We have not found any publications on the behavior of pinocarveol epoxide and myrtenol epoxide in acid media.

Pinocarveol (+)-**2**, myrtenol (−)-**3a**, and their epoxides (+)-**7** and (−)-**8a**, as well as (−)-nopol ((−)**3b**) and its epoxide (−)-**8b**, did not react with the aldehydes prop-2-enal, (2*E*)-but-2-enal, 2-hydroxybenzalaldehyde, or 4-methoxybenzaldehyde in the presence of askanite–bentonite clay.

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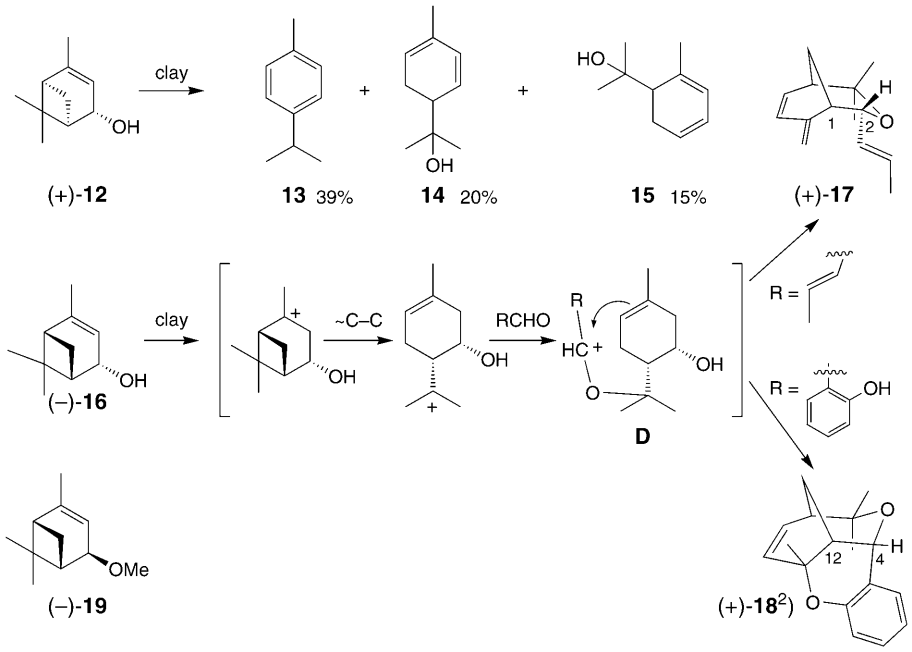
[3]) Racemic compound **11a** has been synthesized earlier by reaction of 6-*exo*-hydroxy-2,10-epoxycamphane with $HClO_4$ [16].

[4]) Intramolecular assistance of the primary-alcohol function in the oxirane-ring opening of (−)-**8a** may eventually afford a stereoisomer of hydroxy epoxide (+)-**7** as an intermediate.

[5]) The transformations of the latter compound also gave a campholenic aldehyde analog and three compounds with a *para*-menthane framework as the major products obtained on cooling. The reactivity of (−)-nopol epoxide ((−)-**8b**) on clay differed substantially from that in the presence of $ZnBr_2$, when aldehyde (+)-**11b** was obtained as a sole product [18].

Verbenols. As mentioned above, verbenol which can be accessible in the form of *cis*- and *trans*-isomers, was another alcohol from the pinane series which we chose for our investigation. According to GC/MS data, storage of (+)-*trans*-verbenol ((+)-**12**) on askanite–bentonite clay for 40 min at room temperature afforded *para*-cymene (**13**; 39%), 2-(4-methylcyclohexa-2,4-dienyl)propan-2-ol (**14**; 20%) and 2-(2-methylcyclohexa-2,4-dienyl)propan-2-ol (**15**; 15%) as the major products (*Scheme 4*). These results are in good agreement with the literature data on the behavior of verbenol in various acids (storage in the presence of sulfuric acid [19], treatment with acetic anhydride in the presence of clay *K-10* [20])[6]).

Scheme 4. *Transformations of Verbenols on Askanite–Bentonite Clay*



We investigated the behavior of the *cis*-stereoisomer (–)-*cis*-verbenol ((–)-**16**) on askanite–bentonite clay in the presence of (2*E*)-but-2-enal or 2-hydroxybenzaldehyde and found compounds (+)-**17** or (+)-**18**, optical antipodes of the corresponding heterocyclic compounds obtained from (+)-*trans*-verbenol ((+)-**12**)[6]) (*Scheme 4*). Thus the relative arrangement of the OH group in the starting verbenol did not affect the occurrence and direction of intermolecular reactions. Moreover, replacement of the OH group by a MeO group in passing from (+)-*trans*-verbenol ((+)-**12**) to (–)-*trans*-verbe-

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[6]) Previously, we showed that on askanite–bentonite clay, (+)-*trans*-verbenol ((+)-**12**) undergoes unusual reactions with aliphatic and aromatic aldehydes, resulting in heterocyclic compounds [21]. These transformations were accompanied by a skeletal rearrangement of the starting alcohol (+)-**12**, presumably forming a carbocation with a *para*-menthane framework which reacted with aldehydes. This was followed by intramolecular carbocyclization, leading to cyclic ethers.

nol methyl ether ((−)-**19**) did not change the reaction route either (*Scheme 4*). The presence of an OH group (or its ether) at C(4), however, is of critical importance in these reactions because verbenone (having an oxo substituent at C(4)), (−)-myrtenol ((−)-**3a**; OH group at C(10)), and α-pinene (no O-containing substituents) do not react with aldehydes on askanite–bentonite clay. It is noteworthy that the bicyclic ether (+)-**17** formed from (−)-*cis*-verbenol ((+)-**16**) has a much smaller optical rotation than the same compound obtained from (+)-*trans*-verbenol (+)-**12** or (−)-*trans*-verbenol methyl ether ((−)-**19**). Obviously, during the reaction of alcohol (−)-**16** with (2*E*)-but-2-enal, carbocyclization in cation **D** occurs less stereoselectively than in the case of the reactions of (+)-**12** or (−)-**19** with (2*E*)-but-2-enal. This may be explained, for example, by differences in adsorption of the starting compounds on clay.

(−)-cis-*Verbenol Epoxide* ((−)**20**). (−)-*cis*-Verbenol epoxide ((−)-**20**) could not be synthesized by epoxidation of (−)-*cis*-verbenol ((−)-**16**) with conventional oxidants (peracetic, monoperphthalic, or *meta*-chloroperbenzoic acid) because of the high lability of alcohol (−)-**16** and its epoxide in acid media. Instead of the desired epoxide, we obtained a complex mixture of isomerization products. Therefore, epoxy alcohol (−)-**20** was prepared by an alternative procedure, namely, by reduction of (−)-verbenone epoxide (**1**) with $LiAlH_4$ according to [15], which gave the *cis*-isomer (−)-**20** as the sole product; therefore, *trans*-verbenol epoxide was not prepared, and its reactivity with clay was not investigated. Storage of epoxide (−)-**20** on askanite–bentonite clay for 40 min at room temperature produced *trans*-diol (−)-**21** with a *para*-menthane framework as a major product (47%) and hydroxy ketone (−)-**22** as a minor product (5%) (*Scheme 5*). Previously, compound (−)-**22** has been synthesized as a major product in a study of the behavior of (−)-*cis*-verbenol epoxide ((−)-**20**) in the presence of $ZnBr_2$ [22]. In our case, however, this compound formed only as a minor product. *trans*-Diol (−)-**21** was not found in the literature and may be regarded as a precursor of a promising chiral ligand for an asymmetric metal-complex catalyst[7]). As in the case of compounds (+)-**2**, (−)-**3a**, and (−)-**8b**, epoxy alcohol (−)-**20** showed pronounced differences in reactivity in the presence of clay on one hand and of conventional acid catalysts on the other hand.

We found that in the presence of montmorillonite clay (−)-*cis*-verbenol epoxide ((−)-**20**) underwent intermolecular reactions with both aromatic and aliphatic aldehydes. In the reaction of (−)-**20** with 4-methoxybenzaldehyde in the presence of clay for 40 min at room temperature, in addition to the isomerization products (−)-**21** (33%) and (−)-**22** (7%), we also isolated compound (−)-**23** (13%). The hypothetical mechanism leading to (−)-**23** includes protonation and cleavage of the oxirane ring, skeletal rearrangement into a cation with a *para*-menthane framework, and its subsequent interaction with aldehyde (*Scheme 5*). Interestingly, at the last stage of this mechanism, heterocyclization in the resulting cation **E** is preferable to carbocyclization, as previously observed in reactions of other O-containing terpenoids of the pinane series [6][21]. When performed on synthetic montmorillonite clay *K-10*, this reaction gave the same products (GC/MS data) as in the case of the reaction carried out on an askanite–bentonite clay, but the product ratio changed, the content of the intermolecular-

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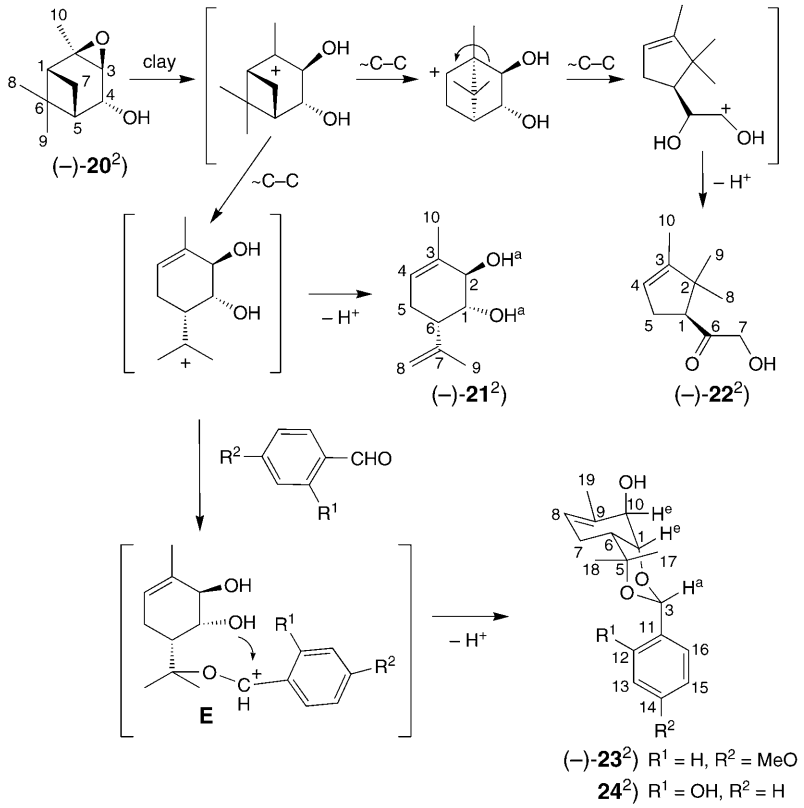
[7]) A *cis*-isomer of compound (−)-**21** has previously been obtained as one of the minor products during oxidation of 3-carene with thallium acetate [22].

Scheme 5. *Isomerization of (−)*-cis-Verbenol Epoxide ((−)-**20**) *on Askanite–Bentonite Clay*



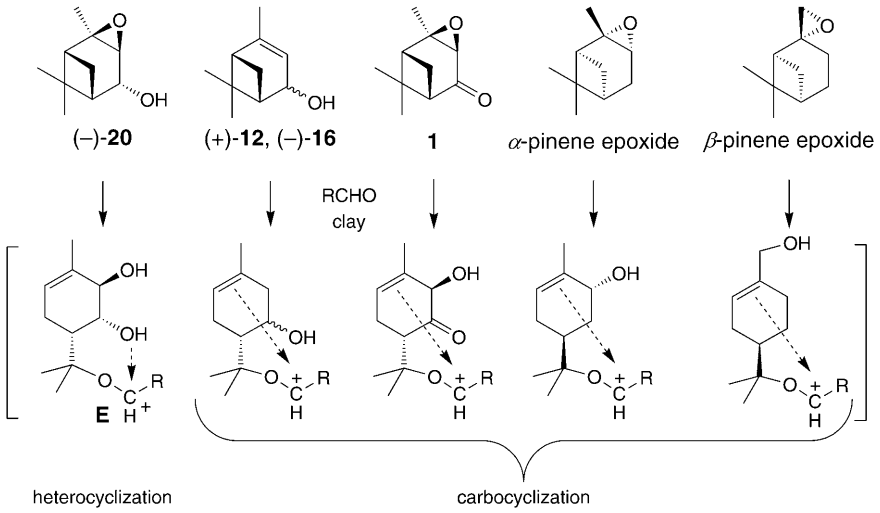
reaction product (−)-**23** increasing substantially and hydroxy ketone (−)-**22** being prevalent among isomerization products. When montmorillonite clays were replaced by zeolite Hβ, compound (−)-**23** vanished from the reaction mixture almost completely (GC/MS data).

It can be seen from *Scheme 6* that the structure of the cations possibly formed from *trans*- and *cis*-verbenols (+)-**12** and (−)-**16**, respectively, verbenone epoxide (**1**), and pinene epoxides during the interaction of these compounds with aldehydes on clay is very similar to the structure of cation **E**, believed to be formed from *cis*-verbenol epoxide ((−)-**20**). While in five cases, we obtained exclusively the products of carbocyclization that took place at the last stage of the reaction, verbenol epoxide (−)-**20** gave only the product of heterocyclization. Thus, with montmorillonite clay used as a catalyst, even relatively minor changes in the structure of a terpenoid can change the reaction path drastically.

Interaction of epoxide (−)-**20** with 2-hydroxybenzaldehyde on clay occurred in much the same way as in the case of 4-methoxybenzaldehyde, yielding *trans*-diol (−)-**21** (51%) and compound **24** in minor amounts (4%) (*Scheme 5*).

A new reaction path appeared on passing from aromatic aldehydes to the aliphatic (2*E*)-but-2-enal. Interaction of epoxide (−)-**20** with (2*E*)-but-2-enal for 1 h at room

Scheme 6



temperature yielded not only compound (–)-**25** (16%), an analog of compounds (–)-**23** and **24**, and as the isomerization products (–)-**21** (13%) and (–)-**22** (5%), but also a mixture of two diastereoisomers **26a**,**b** (9% and 5%, resp.), whose isomerism is due to the different orientation of the substituents at C(5) (*Scheme 7*). Moreover, we also isolated a small amount of triol **27** from the reaction mixture. *Scheme 7* shows a possible mechanism for the formation of **26a**,**b**; one can see that diol (–)-**21** can act as an intermediate neutral species in this reaction. To verify this assumption, we carried out a control experiment in which diol (–)-**21** was stored in the presence of (2*E*)-but-2-enal on clay for 2 h. A mixture of diastereoisomers **26a**,**b** (**26a**/**26b** 1:0.14) was formed in a total yield of 35% based on converted diol (–)-**21** (conversion 52%). This result confirmed that diol (–)-**21** can be an intermediate in the synthesis of compounds **26a**,**b** from epoxide (–)-**20**.

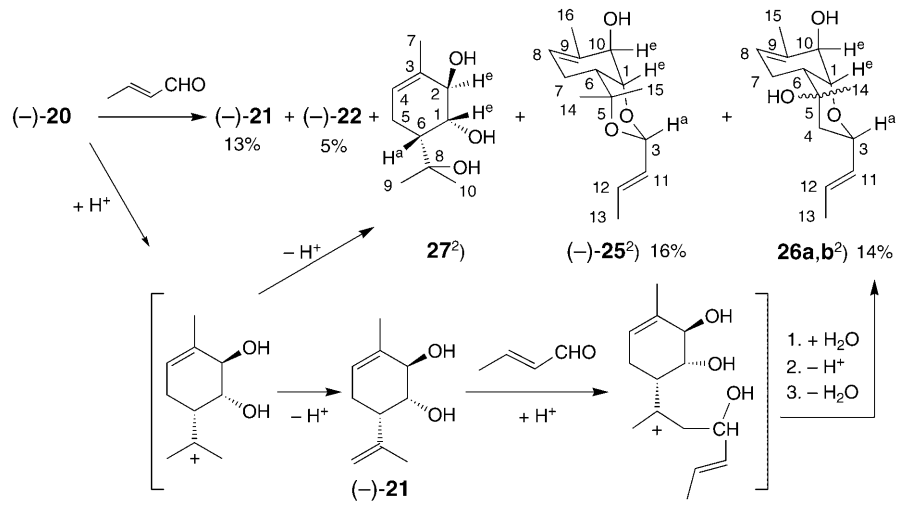
All products containing stereogenic centers obtained were optically active.

Structure Elucidation of Reaction Products. Compounds (+)-**4**, (–)-**21**, (–)-**23**, **24**, (–)-**25**, **26a**, **26b**, and **27** are not described in the literature. They were identified from ^{1}H- and ^{13}C-NMR data taking into account the configurations of the starting terpenoids.

In the ^{1}H-NMR spectrum of compound (+)-**17**, the coupling constant ^3J(1,2) is 2.5 Hz [21], analogous to ^3J(4,12) = 3 Hz in the spectrum of (+)-**18** [21], indicating that H–C(2) of (+)-**17** and H–C(4) of (+)-**18** are in the *exo*-position. The absence of W-coupling between these protons and the protons of the CH_2 bridge confirms that the former have an *exo*-position in both compounds. Quantum-mechanical calculations suggest that the six-membered heterocycle adopts a chair conformation in (+)-**17** and a boat-like conformation in (+)-**18** (*Scheme 4*).

In the ^{13}C-NMR spectrum of (–)-**21**, the signals of C(1) and C(2) and the signals of the Me groups were assigned by means of the long-range ^{13}C,^{1}H *J* modulated differential (LRJMD) spectrum. When the olefinic H–C(4) signal at δ(H) 5.56 was suppressed, the LRJMD spectrum showed a *d* at δ(C) 71.82 and a *q* at δ(C) 20.72, assigned to C(2) and C(10), respectively, as well as the expected *d* at δ(C) 39.82 (C(6))

Scheme 7. *Interaction of (−)-*cis*-Verbenol Epoxide* ((−)-**20**) *with (2*E*)-But-2-enal on Askanite–Bentonite Clay*



and *t* at δ(C) 24.65 (C(5)). In the ^{1}H-NMR spectrum, the low value of ^3J(1,2) (=3 Hz) points to the equatorial position of H–C(1) and H–C(3). The coupling constants between H_a–C(5) and H–C(6) are much higher (J(5a,6) = 11 Hz), indicating that the latter has an axial orientation. From the foregoing, one can conclude that the substituents at C(1) and C(6) are in *cis*-configuration relative to each other and in *trans*-configuration relative to the substituent at C(2).

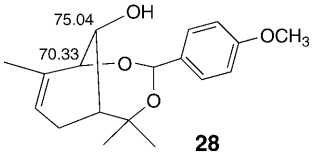
In the ^{1}H-NMR spectra of compounds (−)-**23**–**26a**,**b**, the corresponding vicinal constants ^3J(1,6), ^3J(1,10), and ^3J(6,7) are virtually identical. Therefore, ring fusion may be assumed to be the same in all these compounds. Since ^3J(1,6) = 2 Hz, which points to coupling of protons in the e,e or e,a conformation, *cis*-fusion of the six-membered rings is suggested in these cases. For compound (−)-**23**, ^3J(1,6) = 2 Hz indicates that an isomer with *cis* ring fusion is formed because in the case of the *trans*-isomer, the angular protons would occupy the axial positions and hence the coupling constant would be much larger. By analogy with *cis*-decalin, one can assume with certain allowances that both six-membered rings have a chair conformation. The high coupling constants ^3J(6,7) ≈ 11 and 6–7 Hz suggest that H–C(6) is axial in the cyclohexene ring in all cases, and hence H–C(1) has an equatorial conformation. In this situation, the low value of ^3J(1,10) (< 3 Hz) reflects e,e coupling between H–C(1) and H–C(10).

For compounds **26a** and **26b**, the ^3J(3,4) suggest that H–C(3) is axial in both cases. For compounds (−)-**23**, **24**, and (−)-**25**, therefore, H–C(3) may also be assumed to have axial conformations, and the bulkier substituents at C(3) are assumed to occupy equatorial positions.

From the foregoing it follows that in all compounds (−)-**23**–**26a**,**b**, H–C(1) and H–C(10) are equatorial, while H–C(3) and H–C(6) are axial. Isomers **26a** and **26b** arise from the different arrangements of substituents at C(5); the Me group is axial in **26a**, as indicated by the presence of the long-range ^4J(Me,4a) of 0.8 Hz, but equatorial in **26b**. In the latter case, as would be expected, the axial OH group causes a paramagnetic shift $\Delta\delta$ = 0.42 and 0.34 of the H–C(1) and H–C(3) signal, respectively, due to the 1,3-diaxial interaction.

In the ^{13}C-NMR spectrum of (−)-**23**, the signals of C(1) and C(10), as well as of C(9) and C(11), were assigned based on LRJMD spectral data. In the former case, after suppression of the signal of the olefinic H–C(8) at δ(H) 5.60, the LRJMD spectrum contained *d*s at δ(C) 70.33 and 33.98, a *t* at δ(C) 23.04, and a *q* at δ(C) 20.6, assigned to C(10), C(6), C(7), and C(20), respectively. In the latter case, when the H–C(1) signal at δ(H) 4.3 was suppressed, among the low-field *s* of interest was a *s* at δ(C) 130.89 assigned to C(9) in the LRJMD spectrum. Structure **28**, as an alternative for (−)-**23**, was rejected based on the ^{13}C-NMR spectrum of a CCl_4/$CDCl_3$ solution after D_2O addition. Due to the isotope effect in this solution, replace-

ment of OH by OD led to an upfield shift of the *d* at δ(C) 70.33 ($\Delta\delta = 0.12$) assigned to C(10) in the structure (−)-**23**. In the case of **28**, the isotope effect would be exhibited for a *d* appearing at δ(C) 75.0. Signal assignments in the ^{13}C-NMR spectra of compounds **24**–**26a**,**b** and structure elucidation were performed by analogy with those of (−)-**23**. For compound **27** the presence of OH groups was established by the ^{13}C-NMR spectrum of a $CDCl_3$ solution after D_2O addition. Due to the isotope effect in this solution, replacement of OH by OD led to upfield shifts of the *d* at δ(C) 71.04 and 72.16 and the *s* at δ(C) 73.25 ($\Delta\delta$ 0.12, 0.18, and 0.16 resp.).



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Conclusions. – The above results and our previous investigations [6][21] represent a systematic study of the reactivity of pinane alcohols ((+)-*trans*-pinocarveol ((+)-**2**), (−)-myrtenol ((−)-**3a**), (−)-*cis*-verbenol ((−)-**16**), (+)-*trans*-verbenol ((+)-**12**), and (−)-nopol ((−)-**3b**)] and of their epoxides (except for *trans*-verbenol epoxide) in the presence of acidic montmorillonite clay.

It was shown that on askanite–bentonite clay, these compounds undergo various transformations, mostly accompanied by skeletal rearrangements of the pinane framework and generally leading to a different set of products as compared to the products obtained in the presence of conventional homogeneous acids.

Mutual transformations of (+)-*trans*-pinocarveol ((+)-**2**) and (−)-myrtenol ((−)-**3a**) are the major reactions of these compounds on askanite–bentonite clay. In each case, however, the reactions gave different isomerization products, indicating that the reactivity of the starting alcohols was different from that of the same compounds formed in the course of reactions. The clay also proved very sensitive to minor changes in the structure of the terpenoids during the transformations of (+)-pinocarveol epoxide ((+)-**7**) and (−)-myrtenol epoxide ((−)-**8a**) in the presence of clay. Although fully identical cations were expected to be formed during cleavage of the protonated oxirane rings of these compounds, some isomerization products formed from only one particular starting compound.

Storage of (−)-*cis*-verbenol epoxide ((−)-**20**) in the presence of clay afforded 1,2-*trans*-diol ((−)-**21**) with a *para*-menthane framework as the major product. *cis*- and *trans*-Verbenols, as well as *cis*-verbenol epoxide, reacted with both aliphatic and aromatic aldehydes on askanite–bentonite clay, giving various heterocyclic compounds; the reaction path depended on the structure of both the terpenoid and the aldehyde.

Thus, in the presence of clay, the reactivity of O-containing terpenoids of the pinane series depends considerably on even minor changes of their structure.

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Experimental Part

1. *General.* As catalyst, we used askanite–bentonite clay obtained (according to Specs TU-113-12-86-82) by acidic activation of bentonite clays from the Askan group of deposits; a synthetic analog of this clay is *K10*. The clay was calcinated at 110° for 3 h immediately before use. GLC (purity control and product analyses); *3700* instrument; quartz capillary column (15 m × 0.22 mm), *VC-30* phase, flame-ionization detector, He (1 atm) as carrier gas. Column chromatography (CC): silica gel (70–230 mesh; *Merck*); 1–95% gradient Et_2O/hexane. Optical rotation: *Polamat-A* spectrometer; $CHCl_3$ soln. ^{1}H- and ^{13}C-NMR Spectra: *Bruker AM-400* apparatus at 400.13 MHz (^{1}H) and 100.61 MHz (^{13}C); in CCl_4/$CDCl_3$ 1:1 (*v*/*v*); chemical shifts δ in ppm rel. to residual $CHCl_3$ (δ(H) 7.24, δ(C) 76.90), *J* in Hz; assignments by *J*s and ^{1}H,^{1}H double-resonance spectra, and by considering the ^{13}C-NMR spectra under proton off-resonance saturation, including ^{13}C,^{1}H-type 2D-COSY (^1J(C,H) = 135 Hz), and ^{13}C,^{1}H-type 1D-LRJMD (*J*(C,H) = 10 Hz) spectra. HR-MS: *Finnigan MAT-8200* instrument; in *m*/*z*.

2. *Transformations of (+)-*trans*-Pinocarveol (=(1R,3S,5R)-6,6-Dimethyl-2-methylenebicyclo[3.1.1]-heptan-3-ol*; (+)-**2**) *on Askanite–Bentonite Clay.* To a suspension of askanite–bentonite clay (0.3 g) in CH_2Cl_2 (10 ml) was added a soln. of (+)-*trans*-pinocarveol (**2**; 0.300 g; $[\alpha]_{580}^{20} = +53$ (*c* = 23); obtained in 82% yield by oxidation of β-pinene (*Fluka*) with *t*-BuOOH in the presence of SeO_2 according to [24]) in CH_2Cl_2 (10 ml). The mixture was stirred for 3 h at 20°. Then Et_2O (5 ml) was added. The catalyst was filtered off and the solvent evaporated. The resulting mixture was separated by CC (silica gel (10 g)): (+)-**2** (0.075 g, 25%), (+)-**4** (0.046 g, 11%), and (−)-**3a** (0.075 g, 33%; $[\alpha]_{580}^{20} = -40$ (*c* = 25)); yields given based on converted (+)-**2**.

Data of (1R,5S)-2-{[(1R,3S,5R)-6,6-Dimethyl-2-methylenebicyclo[3.1.1]hept-3-yloxy]methyl}-6,6-dimethylbicyclo[3.1.1]hept-2-ene ((+)-**4**): $[\alpha]_{580}^{20} = +20$ (*c* = 20). ^{1}H-NMR[2]): 0.63 (*s*, Me(9′)); 0.83 (*s*, Me(9)); 1.18 (*d*, *J*(7*anti*,7*syn*) = 8.5, H_{anti}–C(7)); 1.26 (*s*, Me(8′)); 1.27 (*s*, Me(8)); 1.78 (*d*, *J*(7′*anti*, 7′*syn*) = 10, H_{anti}–C(7′)); 1.84–1.97 (*m*, H–C(5′), H–C(4′)); 2.04–2.17 (*m*, H–C(1), H–C(5), H–C(4′)); 2.22–2.29 (*m*, 2 H–C(4)); 2.26 (*m*, H_{syn}–C(7′)); 2.37 (*ddd*, *J* = 8.5, *J*(7*syn*,1) = 5.5, *J*(7*syn*, 5) = 5.5, H_{syn}–C(7)); 2.43 (*dd*, *J*(1′,7′) = 5.5, *J*(1′,5′) = 5.5, H–C(1′)); 3.73 (*ddt*, *J*(10a,10b) = 12.5, *J*(10a, 3) = 1.5, *J*(10a,4) = 1.5, H_a–C(10)); 3.88 (*ddt*, *J* = 12.5, *J*(10b,3) = 1.5, *J*(10b,4) = 1.5, H_b–C(10)); 3.89 (br. *d*, *J*(3′,4′) = 7.5, H–C(3′)); 4.80 (br. *s*, 2H–C(10′)); 5.40–5.46 (*m*, H–C(3)). ^{13}C-NMR[2]): 21.19 (*q*, C(9)); 22.01 (*q*, C(9′)); 26.25 (*q*, C(8′)); 26.39 (*q*, C(8)); 26.93 (*t*, C(7′)); 31.31 (*t*, C(4)); 31.60 (*t*, C(7)); 32.89 (*t*, C(4′)); 38.04 (*s*, C(6)); 39.75 (*d*, C(5′)); 41.00 (*d*, C(5)); 41.42 (*s*, C(6′)); 43.56 (*d*, C(1)); 50.74 (*d*, C(1′)); 70.08 (*t*, C(10)); 72.81 (*d*, C(3′)); 112.55 (*t*, C(10′)); 119.05 (*d*, C(3)); 145.93 (*s*, C(2)); 150.20 (*s*, C(2′)). HR-MS: 286.22968 (M^+, $C_{20}H_{30}O^+$; calc. 286.22965).

3. *Transformations of (−)-Myrtenol (=(1R,5S)-6,6-Dimethylbicyclo[3.1.1]hept-2-ene-2-methanol*; (−)-**3a**) *on Askanite–Bentonite Clay.* As described in *Exper. 2*, with (−)-myrtenol ((−)-**3a**; 0.500 g; $[\alpha]_{580}^{20} = -54$ (*c* = 12.5); obtained in 89% yield by reduction of (−)-myrtenal (*Aldrich*, 'purity 98%', $[\alpha]_{580}^{20} = -11.4$ (*c* = 17)) with $NaBH_4$ according to [25]) in CH_2Cl_2 (5 ml) and askanite–bentonite clay (0.5 g) in CH_2Cl_2 (15 ml) for 1 h at 20°. Workup with Et_2O (5 ml) followed by CC (silica gel (15 g)): (−)-**3a** (0.282 g, conversion 44%; $[\alpha]_{580}^{20} = -43$ (*c* = 10)), (+)-*trans*-pinocarveol ((+)-**2**; 21 mg, 9%; $[\alpha]_{580}^{20} = 9.1$ (*c* = 3)), perillyl alcohol ((−)-**5**; 12%; $[\alpha]_{580}^{20} = -17$ (*c* = 3)), and 4-isopropylbenzenemethanol (**6**; 6%); yields given based on converted (−)-**3a**). Compounds (−)-**5** and **6**: ^{13}C-NMR identical with reported data [26].

4. *Transformations of (+)-*trans*-Pinocarveol Epoxide (=(1R,2R,3S)-6,6-Dimethylspiro[bicyclo[3.1.1]heptane-2,2′-oxiran]-3-ol*; (+)-**7**) *on Askanite–Bentonite Clay.* (+)-*trans*-Pinocarveol epoxide ((+)-**7**; $[\alpha]_{580}^{20} = +34$ (*c* = 15)) was synthesized in 58% yield by oxidation of (+)-*trans*-pinocarveol ((+)-**2**) with monoperphthalic acid according to [13]. Data of **7**: corresponding to those reported in [27].

Then as described in *Exper. 2*, with (+)-**7** (0.300 g) in CH_2Cl_2 (5 ml) and askanite–bentonite clay (0.3 g) in CH_2Cl_2 (10 ml) for 1 h at 20°. Workup with Et_2O (5 ml) followed by CC (silica gel (15 g)): (+)-pinocarvone ((+)-**10**; 0.015 g, 6%; $[\alpha]_{580}^{20} = +10$ (*c* = 10)) and **11a** (0.056 g, 19%).

Data of (1R)-3-(Hydroxymethyl)-2,2-dimethylcyclopent-3-ene-1-acetaldehyde ((+)-**11a**): $[\alpha]_{580}^{20} = +20$ (*c* = 20). ^{1}H-NMR[2]): 0.85 (*s*, Me(9)); 1.04 (*s*, Me(8)); 1.91 (*ddtd*, *J*(5,5′) = 16, *J*(5,1) = 8.5, *J*(5,10) = 2.5, *J*(5, 4) = 2, H–C(5)); 2.25–2.34 (*m*, H–C(1)); 2.36 (*ddd*, *J*(6,6′) = 12, *J*(6,1) = 10, *J*(6,7) = 2, H–C(6)); 2.46 (*ddddd*, *J* = 16, *J*(5′,1) = 7.5, *J*(5′,4) = 3, *J*(5′,10) = 1.5, *J*(5′,10′) = 2, H′–C(5)); 2.46–2.51 (*m*, H′–C(6));

4.08 (*dddd*, *J*(10,10′) = 14, *J*(10,5) = 2.5, *J*(10,5′) = 1.5, *J*(10,4) = 1.5, H–C(10)); 4.13 (*dddd*, *J* = 14, *J*(10′, 5) = 2.5, *J*(10′,5′) = 2, *J*(10′,4) = 1.5, H′–C(10)); 5.52 (*ddt*, *J*(4,5′) = 3, *J*(4,5) = 2, *J*(4,10) = 1.5, H–C(4)); 9.75 (*t*, *J*(7,6) = 2, H–C(7)). ^{13}C-NMR[2]): 35.52 (*t*, C(2)); 44.49 (*t*, C(6)); 44.72 (*d*, C(1)); 46.28 (*s*, C(5)); 123.00 (*d*, C(3)); 151.65 (*s*, C(4)); 201.54 (*d*, C(7)); 25.80 (*q*, C(8)); 20.96 (*q*, C(9)); 59.57 (*t*, C(10)). HR-MS: 167.107723 ([*M* − 1]$^+$, $C_{10}H_{15}O_2^+$; calc. 167.10720).

5. *Transformations of (−)-Myrtenol Epoxide* (= *(1*R*,2*S*,4*S*,6*R*)-7,7-Dimethyl-3-oxabicyclo[4.1.1.0^{2,4}]-octane-2-methanol*; (−)-**8a**) *on Askanite–Bentonite Clay.* (−)-Myrtenol epoxide ((−)-**8a**) was prepared in two ways. In the first procedure, epoxide (−)-**8a** was obtained by oxidation of (−)-myrtenol ((−)-**3a**) with peracetic acid according to [14]. After purification by CC, the yield of (−)-**8a** was 32%. In the second procedure, oxidation of (−)-myrtenal (*Acros*) with 35% aq. H_2O soln. in the presence of 6N NaOH according to [28] gave (−)-myrtenal epoxide ((−)-**9**) in 74% yield. Subsequent reduction with $LiAlH_4$ according to the procedure of [15] gave (−)-**8a** (53%). $[\alpha]_{580}^{20} = -88$ (*c* = 8). ^{1}H-NMR[2]): 0.90 (*s*, Me(9)); 1.27 (*s*, Me(8)); 1.64 (*d*, *J*(7,7′) = 10, H–C(7)); 1.70–1.76 (*m*, H–C(5)); 1.87 (*dddd*, *J*(4′,4) = 15, *J*(4′, 3) = 4, *J*(4′,5) = 3, *J*(4′,7′) = 2, H′–C(4)); 1.93 (*dd*, *J*(1,5) = 5.5, *J*(1,7′) = 5.5, H–C(1)); 2.01 (*dd*, *J* = 15, *J*(4,5) = 3, H–C(4)); 1.97–2.05 (*m*, H′–C(7)); 3.30 (*dd*, *J*(3,4′) = 4, *J*(3,5) = 1, H–C(3)); 3.50 (*d*, *J*(10, 10′) = 13, H–C(10)); 3.67 (*d*, *J* = 13, H′–C(10)). ^{13}C-NMR[2]): 40.72 (*d*, C(1)); 63.67 (*s*, C(2)); 52.88 (*d*, C(3)); 27.21 (*t*, C(4)); 40.31 (*d*, C(5)); 40.57 (*s*, C(6)); 25.63 (*t*, C(7)); 26.65 (*q*, C(8)); 20.18 (*q*, C(9)); 62.69 (*t*, C(10)). HR-MS: 153.09107 ([*M* − 15]$^+$, $C_9H_{13}O_2^+$; calc. 153.09155).

Then as described in *Exper. 2*, with (−)-**8a** (0.188 g) in CH_2Cl_2 (5 ml) and askanite–bentonite clay (0.3 g) in CH_2Cl_2 (10 ml) for 40 min at r.t. Workup with Et_2O (5 ml) followed by CC (silica gel (10 g)): **6** (0.027 g, 16%) and (+)-**11a** (0.050 g, 27%; $[\alpha]_{580}^{22} = +20.7$ (*c* = 8)).

6. *(−)-*cis*-Verbenol* (= *(1*S*,2*S*,5*S*)-4,6,6-Trimethylbicyclo[3.1.1]hept-3-en-2-ol*; (−)-**16**) *and (−)-*trans*-Verbenol Methyl Ether* (= *(1*S*,4*R*,5*S*)-4-Methoxy-2,6,6-trimethylbicyclo[3.1.1]hept-2-ene*; (−)-**19**). (−)-*cis*-Verbenol ((−)-**16**; $[\alpha]_{580}^{20} = -10$ (*c* = 5)) was prepared by reduction of (−)-verbenone (*Acros*; purity 94%; $[\alpha]_{580}^{20} = -176$ (*c* = 20)) with $NaBH_4$ in MeOH according to [25]. ^{1}H- and ^{13}C-NMR: identical with those reported in [28] and [29], resp. This reaction gave (−)-*trans*-verbenol methyl ether ((−)-**19** (22%; $[\alpha]_{580}^{20} = -55$ (*c* = 0 = 6)) as a by-product. ^{1}H- and ^{13}C-NMR: identical with those reported in [30].

7. *Interaction of (−)-*cis*-Verbenol* ((−)-**16**) *with (2*E*)-But-2-enal on Askanite–Bentonite Clay.* A soln. of (2*E*)-but-2-enal (0.12 g) in CH_2Cl_2 (3 ml) was added to a suspension of askanite–bentonite clay (0.3 g) in CH_2Cl_2 (3 ml). Then a soln. of (−)-**16** (0.120 g) in CH_2Cl_2 (3 ml) was added dropwise. The mixture was stirred for 60 min at r.t. Then Et_2O (5 ml) was added. The catalyst was filtered off and the solvent evaporated. The resulting mixture was separated by CC (silica gel (5 g)): *(1*S*,2*R*,5*R*)-4,4-dimethyl-8-methylene-2-(prop-1-enyl)-3-oxabicyclo[3.3.1]non-6-ene* ((+)-**17**; 0.033 g, 21%; [21]: 26%). $[\alpha]_{580}^{19} = +18$ (*c* = 9) ([21]: $[\alpha]_D = -85$ for enantiomer). ^{1}H- and ^{13}C-NMR: identical with those reported in [21].

8. *Interaction of (−)-*cis*-Verbenol* ((−)-**16**) *with 2-Hydroxybenzaldehyde on Askanite–Bentonite Clay.* As described in *Exper. 7*, with 2-hydroxybenzaldehyde (0.12 g) in CH_2Cl_2 (3 ml), askanite–bentonite clay (0.3 g) in CH_2Cl_2 (3 ml), and (−)-**16** (0.100 g) in CH_2Cl_2 (3 ml) for 40 min at r.t. Workup with Et_2O (3 ml) followed by CC (silica gel (5 g)): *(4*S*,8*R*)-2,2,8-trimethyl-3,7-dioxa-5,6-benzotricyclo[6.2.2.0^{4,12}]dodec-9-ene* (= *(2*R*,5*R*,8*S*,13*R*)-5,6-Dihydro-2,6,6-trimethyl-5,2,8-ethanylylidene-2*H*,8*H*-1,7-benzodioxecin*; (+)-**18**; 0.059 g, 35%; [21]: 12%). $[\alpha]_{580}^{19} = +9$ (*c* = 19) ([21]: $[\alpha]_D = -26.7$ for enantiomer). ^{1}H- and ^{13}C-NMR: identical with those reported in [21].

9. *Interaction of (−)-*trans*-Verbenol Methyl Ether* ((−)-**19**) *with (2*E*)-But-2-enal on Askanite–Bentonite Clay.* As described in *Exper. 7*, with (2*E*)-but-2-enal (0.30 g) in CH_2Cl_2 (5 ml), askanite–bentonite clay (1.5 g) in CH_2Cl_2 (10 ml), and (−)-**19** (0.300 g) in CH_2Cl_2 (5 ml) for 40 min at r.t. Workup with Et_2O (5 ml) followed by CC (silica gel (10 g)): (+)-**17** (0.090 g, 24%; $[\alpha]_{580}^{19} = +83.5$ (*c* = 5)). Spectral data: identical with those reported in [21].

10. *Interaction of (−)-*trans*-Verbenol Methyl Ether* ((+)-**19**) *with 2-Hydroxybenzaldehyde on Askanite–Bentonite Clay.* As described in *Exper. 7*, with 2-hydroxybenzaldehyde (0.12 g) in CH_2Cl_2 (3 ml), askanite–bentonite clay (0.3 g) in CH_2Cl_2 (3 ml), and (−)-**19** (0.100 g) in CH_2Cl_2 (3 ml) for 40 min at r.t. Workup with Et_2O (3 ml) followed by CC (silica gel (5 g)): (+)-**18** (0.143 g, 30%). $[\alpha]_{580}^{19} = +10$ (*c* = 13)). Spectral data; identical with those reported in [21].

11. *(−)*-cis-*Verbenol Epoxide* (=*(1*R,*2*R,*4*S,*5*R,*6*S*)*-2,7,7-Trimethyl-3-oxatricyclo[4.1.1.0*^{2,4}*]octan-5-ol*; (−)-**20**). (−)-Verbenone epoxide (**1**; 1.0 g); ([6]: $[\alpha]_{580}^{20} = -137$ ($c = 3.5$)) was added to a suspension of $LiAlH_4$ (0.24 g) in Et_2O (5 ml) at 0°. The mixture was stirred for 4.5 h at 0°. Then H_2O (5 ml) was added, the mixture stirred for 5 min and extracted with Et_2O, the extract dried (K_2CO_3), and the solvent evaporated: (−)-**20** (0.84 g, 83%). $[\alpha]_{580}^{20} = -44$ ($c = 12$). ^{1}H-NMR[2]): 1.05 (*s*, Me(8)); 1.25 (*s*, Me(9)); 1.32 (*s*, Me(10)); 1.34 (*d*, *J*(7*anti*,7*syn*) = 9.5, H_{anti}–C(7)); 1.83–1.91 (*m*, H–C(1), H–C(5)); 1.91–1.99 (*dm*, *J*(7*syn*,7*anti*) = 9.5, H_{anti}–C(7)); 2.70 (br. *s*, OH); 2.96 (*d*, *J* = 2, H–C(3)); 4.03 (*d*, *J*(4,5) = 3, H–C(4)). ^{13}C-NMR[2]): 45.30 (*d*, C(1)); 60.55 (*s*, C(2)); 60.30 (*d*, C(3)); 69.95 (*d*, C(4)); 46.70 (*d*, C(5)); 40.62 (*s*, C(6)); 22.07 (*t*, C(7)); 27.17 (*q*, C(8)); 22.07 (*q*, C(9)); 21.97 (*q*, C(10)). HR-MS: 168.11486 (M^+, $C_{10}H_{16}O_2^+$; calc. 168.11502).

12. *Transformation of (−)*-cis-*Verbenol Epoxide* ((−)-**20**) *on Askanite–Bentonite Clay.* As described in *Exper. 2*, with (−)-(**20**) (0.200 g) in CH_2Cl_2 (7 ml) and askanite–bentonite clay (0.5 g) in CH_2Cl_2 (8 ml) for 40 min at 20°. Workup with Et_2O (5 ml) followed by CC (silica gel (10 g)): (−)-**21** (0.094 g, 47%) and (−)-**22** (0.009 g, 5%).

*Data of (1*R,*2*R,*6*S*)-3-Methyl-6-(1-methylethenyl)cyclohex-3-ene-1,2-diol* ((−)-**21**): $[\alpha]_{580}^{20} = -46$ ($c = 18$). ^{1}H-NMR[2]): 1.75 (*dddd*, *J*(10,5a) = 2.5, *J*(10,4) = 1.5, *J*(10,5e) = 1.5, *J*(10,2) = 1, Me(10)); 1.78 (br. *s*, Me(9)); 1.93 (*dddq*, *J*(5e,5a) = 17.5, *J*(5e,4) = 5, *J*(5e,6a) = 5, *J*(5e,10) = 1.5, H_e–C(5)); 2.16 (*dddqd*, *J* = 17.5, *J*(5a,6a) = 11, *J*(5a,4) = 2.5, *J*(5a,10) = 2.5, *J*(5a,2) = 1, H_a–C(5)); 2.35 (br. *dd*, *J*(6a, 5a) = 11, *J*(6a,5e) = 5, H_a–C(6)); 2.44 (br. *s*, 2 OH); 3.77 (br. *d*, *J*(2,1) = 3, H–C(2)); 3.82 (*dd*, *J*(1, 2) = 3, *J*(1,6) = 2, H–C(1)); 4.79 and 4.88–4.92 (br. *s* and *m*, 2 H–C(8)); 5.56 (*ddq*, *J*(4,5e) = 5, *J*(4, 5a) = 2.5, *J*(4,10) = 1.5, H–C(4)). ^{13}C-NMR[2]): 71.39 (*d*, C(1)); 71.82 (*d*, C(2)); 131.76 (*s*, C(3)); 124.89 (*d*, C(4)); 24.65 (*t*, C(5)); 39.82 (*d*, C(6)); 145.67 (*s*, C(7)); 111.46 (*t*, C(8)); 22.55 (*q*, C(9)); 20.72 (*q*, C(10)). HR-MS: 168.11503 (M^+, $C_{10}H_{16}O_2^+$; calc. 168.11502).

*Data of (1*S*)-2-Hydroxy-1-(2,2,3-trimethylcyclopent-3-enyl)ethanone* ((−)-**22**): $[\alpha]_{580}^{20} = -20.7$ ($c = 8.2$). ^{1}H-NMR[2]): 0.81 (*s*, Me(9)); 1.20 (*s*, Me(8)); 1.58 (*ddd*, *J*(10,4) = 2.5, *J*(10,5′) = 2.5, *J*(10, 5) = 1.5, Me(10)); 2.26 (*dddq*, *J*(5,5′) = 16, *J*(5,1) = 8, *J*(5,4) = 3, *J*(5,10) = 1.5, H–C(5)); 2.68 (*ddqd*, *J* = 16, *J*(5′,1) = 9, *J*(5′,10) = 2.5, *J*(5′,4) = 2, H′–C(5)); 2.87 (*dd*, *J*(1,5′) = 9, *J*(1,5) = 8, H–C(1)); 3.20 (br. *s*, OH); 4.16 (br. *d*, *J*(7,7′) = 19, H–C(7)); 4.23 (br. *d*, *J* = 19, H′–C(7)); 5.22 (*dqd*, *J*(4,5) = 3, *J*(4, 10) = 2.5, *J*(4,5′) = 2, H–C(4)); broadening of the H–C(7) signals because of the interactions with the OH proton, but sharp narrowing of these signals in the ^{1}H,^{1}H double-resonance spectrum due to signal suppression at δ 3.20. ^{13}C-NMR[2]): 58.41 (*d*, C(1)); 49.15 (*s*, C(2)); 145.80 (*s*, C(3)); 121.08 (*d*, C(4)); 31.06 (*t*, C(5)); 210.20 (*s*, C(6)); 69.12 (*t*, C(7)); 27.34 (*q*, C(8)); 21.17 (*q*, C(9)); 12.20 (*q*, C(10)). HR-MS: 168.11520 (M^+, $C_{10}H_{16}O_2^+$; calc. 168.11502).

13. *Interaction of (−)*-cis-*Verbenol Eepoxide* ((−)-**20**) *with 4-Methoxybenzaldehyde on Askanite–Bentonite Clay.* As described in *Exper. 7*, with 4-methoxybenzaldehyde (0.3 g) in CH_2Cl_2 (4 ml), askanite–bentonite clay (0.8 g) in CH_2Cl_2 (7 ml), and (−)-**20** (0.3 g) in CH_2Cl_2 (4 ml) for 40 min at 20°. Workup with Et_2O (5 ml) followed by CC (silica gel (10 g)): (−)-**21** (0.099 g, 33%), (−)-**22** (0.021 g, 7%), and (−)-**23** (0.071 g, 13%).

*Data of (2*S,*4a*R,*8*R,*8a*R*)-4a,5,8,8a-Tetrahydro-2-(4-methoxyphenyl)-4,4,7-trimethyl-4*H*-1,3-benzodioxin-8-ol* ((−)-**23**). $[\alpha]_{580}^{20} = -43$ ($c = 20$). ^{1}H-NMR[2]): 1.23 (*s*, Me(18)); 1.49 (*s*, Me(17)); 1.47 (*ddd*, *J*(6a,7a) = 11, *J*(6a,7e) = 6, *J*(6a,1e) = 2, H–C(6a)); 1.78 (*ddd*, *J*(20,7a) = 2.5, *J*(20,7e) = 1.5, *J*(20, 8) = 1.5, Me(19)); 2.03 (*dddq*, *J*(7e,7a) = 17.5, *J*(7e,6) = 6, *J*(7e,8) = 6, *J*(7e,20) = 1.5, H_e–C(7)); 2.43 (*dddqd*, *J* = 17.5, *J*(7a,6) = 11, *J*(7a,8) = 2.5, *J*(7a,20) = 2.5, *J*(7a,10) = 1.5, H_a–C(7)); 3.75 (*s*, MeO); 3.77–3.80 (*m*, H–C(10)); 4.25 (*dd*, *J*(1e,10) = 2.5, *J*(1e,6) = 2, H_e–C(1)); 5.60 (*ddq*, *J*(8,7e) = 6, *J*(8, 7a) = 2.5, *J*(8,20) = 1.5, H–C(8)); 5.69 (*s*, H–C(3)); 6.81 (*d*, *J* = 8 , H–C(13), H–C(15)); 7.33 (*d*, *J* = 8, H–C(12), H–C(16)). ^{13}C-NMR[2]): 20.63 (*q*, C(19)); 22.75 (*q*, C(17)); 23.04 (*t*, C(7)); 27.29 (*q*, C(18)); 33.98 (*d*, C(6)); 54.98 (*q*, MeO); 70.33 (*d*, C(10)); 74.35 (*s*, C(5)); 75.04 (*d*, C(1)); 95.70 (*d*, C(3)); 113.41 (*d*, C(13), C(15)); 125.14 (*d*, C(8)); 127.61 (*d*, C(12), C(16)); 130.89 (*s*, C(9)); 131.51 (*s*, C(11)); 159.83 (*s*, C(14)). HR-MS: 304.16725 (M^+, $C_{18}H_{24}O_4^+$; calc. 304.16745).

14. *Interaction of (−)*-cis-*Verbenol Epoxide* ((−)-**20**) *with 2-Hydroxybenzaldehyde on Askanite–Bentonite Clay.* As described in *Exper. 7*, with 2-hydroxybenzaldehyde (0.35 g) in CH_2Cl_2 (5 ml), askanite–

bentonite clay (1.0 g) in CH_2Cl_2 (10 ml), and (−)-**20** (0.330 g) in CH_2Cl_2 (5 ml) for 60 min at 20°. Workup with Et_2O (5 ml) followed by CC (silica gel (10 g)): 0.187 g of a 10:1 mixture (by ^{1}H-NMR) of (−)-**21** (51%) and **24** (4%).

Data of (2S,4aR,8R,8aR)-4a,5,8,8a-Tetrahydro-2-(2-hydroxyphenyl)-4,4,7-trimethyl-4H-1,3-benzodioxin-8-ol (**24**): ^{1}H-NMR[2]): 1.25 (*s*, Me(18)); 1.17 (*s*, Me(18)); 1.55 (*ddd*, *J*(6a,7) = 11, *J*(6a,7′) = 6, *J*(6a,1) = 2, H−C(6)); 1.74–1.77 (*m*, Me(19)); 2.07 (*dddq*, *J*(7′,7) = 18, *J*(7′,6) = 6, *J*(7′,8) = 5, *J*(7′, 19) = 1.5, H′−C(7)); 2.29–2.41 (*m*, H−C(7)); 3.81 (br. *s*, H−C(10)); 4.29 (*dd*, *J*(1,10) = 2.5, *J*(1,6a) = 2, H−C(1)); 5.58–5.62 (*m*, H−C(8)); 5.87 (*s*, H−C(3)); 6.74–6.80 (*m*, H−C(13), H−C(15)); 7.06 (*dd*, *J*(16,15) = 8, *J*(16,14) = 1.8, H−C(16)); 7.13 (*td*, *J*(14,13(15)) = 8, *J*(14,16) = 1.8, H−C(14)); 7.87 (*s*, OH−C(12)). ^{13}C-NMR[2]): 20.60 (*q*, C(19)); 22.45 (*q*, C(17)); 22.97 (*t*, C(7)); 26.99 (*q*, C(18)); 33.74 (*d*, C(6)); 69.77 (*d*, C(10)); 75.25 (*d*, C(1)); 75.54 (*s*, C(5)); 97.26 (*d*, C(3)); 117.08 (*d*, C(13)); 119.38 (*d*, C(15)); 122.09 (*s*, C(11)); 124.63 (*d*, C(8)); 128.04 (*d*, C(16)); 130.06 (*d*, C(14)); 130.97 (*s*, C(9)); 155.41 (*s*, C(12)).

15. *Interaction of (−)-*cis*-Verbenol Epoxide* ((−)-**20**) *with (2*E*)-But-2-enal on Askanite–Bentonite Clay.* As described in *Exper. 7*, with (2*E*)-but-2-enal (0.4 g) in CH_2Cl_2 (5 ml), askanite–bentonite clay (1.5 g) in CH_2Cl_2 (15 ml), and (−)-(**20**) (0.400 g) in CH_2Cl_2 (5 ml) for 60 min at r.t. Workup with Et_2O (5 ml) followed by CC (silica gel (10 g)): (−)-**21** (0.052 g, 13%), (−)-**22** (0.019 g, 5%), (−)-**25** (0.088 g, 16%), **26a**/**26b** 1:0.4 (by ^{1}H-NMR; 0.043 g) and **26a**/**26b**/**27** 1:0.7:0.4 (by ^{1}H-NMR; 0.036 g), *i.e.*, yield 8.5% for **26a**, 4.6% for **26b**, and 1% for **27**.

*Data of (2S,4aR,8R,8aR)-4a,5,8,8a-Tetrahydro-4,4,7-trimethyl-2-[(1*E*)-prop-1-enyl]-4H-1,3-benzodioxin-8-ol* ((−)-**25**): $[\alpha]_{580}^{20} = -66$ (*c* = 10). ^{1}H-NMR: 1.15 (*s*, Me(14)); 1.38 (*s*, Me(15)); 1.66 (*dd*, *J*(13, 12) = 6.5, *J*(13,11) = 2, Me(13)); 1.75 (br. *s*, Me(16)); 1.37 (*ddd*, *J*(6a,7) = 11, *J*(6a,7′) = 6, *J*(6a,1) = 2, H_a−C(6)); 1.93 (*dddq*, *J*(7′,7) = 17.5, *J*(7′,6) = 6, *J*(7′,8) = 5, *J*(7′,16) = 1.5, H′−C(7)); 2.28 (*dddqd*, *J*(7, 7′) = 17.5, *J*(7,6a) = 11, *J*(7,8) = 2.5, *J*(7,16) = 2.5, *J*(7,10) = 2, H−C(7)); 2.68 (br. *s*, OH); 3.72–3.75 (*m*, H−C(10)); 4.09 (*dd*, *J*(1,10) = 2.5, *J*(1,6a) = 2, H−C(1)); 5.13 (*d*, *J*(3,11) = 6, H−C(3)); 5.44 (*ddq*, *J*(11, 12) = 15.5, *J*(11,3) = 6, *J*(11,13) = 2, H−C(11)); 5.55 (*ddq*, *J*(8,7′) = 5, *J*(8,7) = 2.5, *J*(8,16) = 1.5, H−C(8)); 5.80 (*dqd*, *J*(12,11) = 15.5, *J*(12,13) = 6.5, *J*(12,3) = 0.5, H−C(12)). ^{13}C-NMR: 17.523 (*q*, C(13)); 20.62 (*q*, C(16)); 22.68 (*q*, C(15)); 22.87 (*t*, C(7)); 27.17 (*q*, C(14)); 33.83 (*d*, C(6)); 70.23 (*d*, C(10)); 73.85 (*s*, C(5)); 74.51 (*d*, C(1)); 95.46 (*d*, C(3)); 125.24 (*d*, C(8)); 128.87 (*d*, C(11)); 130.15 (*d*, C(12)); 130.72 (*s*, C(9)). HR-MS: 238.15711 (M^+, $C_{14}H_{22}O_3^+$; calc. 238.15688).

*Data of (2S,4R,4aS,8R,8aR)-3,4,4a,5,8,8a-Hexahydro-4,7-dimethyl-2-[(1*E*)-prop-1-enyl]-2H-1-benzopyran-4,8-diol* (**26a**; main isomer): ^{1}H-NMR (from mixture **26a**/**26b**)[2]): 1.42 (*d*, *J*(14,4a) = 0.8, Me(14)); 1.47 (*ddd*, *J*(4e,4a) = 13, *J*(4e,3a) = 3, *J*(4e,6a) = 1, H_e−C(4)); 1.65 (*dd*, *J*(13,12) = 6.5, *J*(13, 11) = 2, Me(13)); 1.69 (br. *dd*, *J*(4a,4e) = 13, *J*(4a,3a) = 11.5, H_a−C(4)); 1.73 (*dddd*, *J*(6a,7) = 10.5, *J*(6a, 7′) = 7, *J*(6a,1) = 2, *J*(6a,4e) = 1, H_a−C(6)); 1.77–1.80 (*m*, Me(15)); 2.00–2.17 (*m*, 2 H−C(7)); 3.65 (*dd*, *J*(1,10) = 2.5, *J*(1, 6a) = 2, H−C(1)); 3.83 (*ddddq*, *J*(3a,4a) = 11.5, *J*(3a,11) = 7, *J*(3a,4e) = 3, *J*(3a,12) = 1, *J*(3a,13) = 0.5, H_a−C(3)); 3.86 (br. *s*, H−C(10)); 5.45 (*ddq*, *J*(11,12) = 15,5, *J*(11,3) = 7, *J*(11,13) = 2, H−C(11)); 5.58–5.62 (*m*, H−C(8)); 5.68 (*dqd*, *J*(12,11) = 15.5, *J*(12,13) = 6.5, *J*(12,3) = 1, H−C(12)). ^{13}C-NMR: 17.63 (*q*, C(13)); 20.67 (*q*, C(15)); 22.58 (*t*, C(7)); 27.09 (*q*, C(14)); 38.34 (*d*, C(6)); 41.28 (*t*, C(4)); 70.57 (*d*, C(10)); 70.80 (*s*, C(5)); 76.43 (*d*, C(3)); 77.22 (*d*, C(1)); 124.79 (*d*, C(8)); 128.00 (*d*, C(11)); 131.25 (*d*, C(12)); 131.32 (*s*, C(9)).

*Data of (2S,4S,4aS,8R,8aR)-3,4,4a,5,8,8a-Hexahydro-4,7-dimethyl-2-[(1*E*)-prop-1-enyl]-2H-4-benzopyran-4,8-diol* (**26b**; minor isomer): ^{1}H-NMR (from mixture **26a**/**26b**)[2]): 1.19 (*s*, Me(14)); 1.41 (*ddd*, *J*(4e,4a) = 14, *J*(4e,3a) = 3, *J*(4e,6a) = 1.2, H_e−C(4)); 1.57 (*dd*, *J*(4a,4e) = 14, *J*(4a,3a) = 11.5, H_a−C(4)); 1.59 (*m*, H−C(6)); 1.64 (*dd*, *J*(13,12) = 6.5, *J*(13,11) = 2, Me(13)); 1.77–1.80 (*m*, Me(15)); 1.80–1.93 (*m*, H−C(7)); 1.92–2.01 (*m*, H′−C(7)); 3.88 (br. *s*, H−C(10)); 4.07 (*dd*, *J*(1,10) = 2.5, *J*(1,6) = 2, H−C(1)); 4.17 (*ddddq*, *J*(3a,4a) = 11.5, *J*(3a,11) = 7, *J*(3a,4e) = 3, *J*(3a,12) = 1, *J*(3a,13) = 0.5, H_a−C(3)); 5.43 (*ddq*, *J*(11,12) = 15.5, *J*(11,3) = 7, *J*(11,13) = 2, H−C(11)); 5.52–5.56 (*m*, H−C(8)); 5.68 (*dqd*, *J*(12, 11) = 15.5, *J*(12,13) = 6.5, *J*(12,3) = 1, H−C(12)); δ of H−C(6) was determined by 2D ^{13}C,^{1}H correlated spectroscopy on direct constants; after suppression of the H−C(8) signal at δ 5.54 in the ^{1}H,^{1}H double-resonance spectrum, *J*(7,7′) = 17 Hz for the H−C(7) signal and *J*(7′,7) = 17 Hz, *J*(7′,6) = 7 Hz, and

$J(7',6) = 2$ Hz for the H′–C(7) signal. ^{13}C-NMR[2]): 17.66 (*q*, C(13)); 20.77 (*q*, C(15)); 24.47 (*t*, C(7)); 28.37 (*q*, C(14)); 38.08 (*d*, C(6)); 40.13 (*t*, C(4)); 70.50 (*s*, C(5)); 70.57 (*d*, C(10)); 74.68 (*d*, C(1)); 74.72 (*d*, C(3)); 124.17 (*d*, C(8)); 127.71 (*d*, C(11)); 131.64 (*d*, C(12)); 131.81 (*s*, C(9)).

*Data of (1*R*,2*R*,6*R*)-6-(1-Hydroxy-1-methylethyl)-3-methylcyclohex-3-ene-1,2-diol* (**27**): ^{1}H-NMR (from mixture **26a**/**26b**/**27**)[2]): 1.23 (*s*, Me(9)); 1.38 (*s*, Me(10)); 1.60–1.65 (*m*, H–C(6)); 1.77–1.81 (*m*, Me(7)); 2.07–2.16 (*m*, H_e–C(5)); 2.23–2.35 (*ddm*, J(5a,5e) = 18, J(5a,6a) = 11, H_a–C(5)); 3.77 (br. *d*, J(2,1) = 3, H_e–C(2)); 4.29 (br. *dd*, J(1,2) = 3, J(1,6) = 1.5, H_e–C(1)); 5.58–5.62 (*m*, H–C(4)). ^{13}C-NMR[2]): 20.72 (*q*, C(10)); 20.89 (*q*, C(7)); 21.31 (*t*, C(5)); 28.54 (*q*, C(9)); 39.82 (*d*, C(6)); 71.04 (*d*, C(1)); 72.16 (*d*, C(2)); 73.25 (*s*, C(8)); 125.72 (*d*, C(4)); 131.09 (*s*, C(3)).

16. *Interaction of Diol* (–)-**21** *with (2*E*)-But-2-enal on Askanite–Bentonite Clay.* A soln. of (2*E*)-But-2-enal (0.05 g) and (–)-**21** (0.05 g) in CH_2Cl_2 (1 ml) was added to a suspension of askanite–bentonite clay (0.2 g) in CH_2Cl_2 (2 ml). The reaction mixture was stirred for 2 h at r.t. Workup and CC as described in *Exper. 7* gave (–)-**21** (0.024 g) and **26a**/**26b** (0.014 g, 35% based on converted (–)-**21**).

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