Unusual Reactions of (+)-Car-2-ene and (+)-Car-3-ene with Aldehydes on *K10* Clay

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The reactions of (+)-car-2-ene (**1**) and (+)-car-3-ene (**2**) with aldehydes in the presence of montmorillonite clay were studied for the first time (*Schemes 3* and *5*). The major products of these reactions are optically active, substituted hexahydroisobenzofurans, probably formed as a result of an attack of the protonated aldehyde at the cyclopropane ring. Quite unexpectedly, the products are *cis*-configured at the ring-fusion site; the fact was established by means of quantum-chemical calculations and NMR data. It appeared that the behavior of the 2 : 3 mixture **1/2** in reactions with aldehydes in the presence of *K10* clay differed substantially from the reactivities of the corresponding individual monoterpenes.

Introduction. – Monoterpenes are widespread natural compounds, which serve as recyclable and relatively inexpensive raw materials for pharmaceutical and cosmetic industries and the production of flavor additives, pesticides, *etc.* [1]. Examples of important optically active monoterpenes include (+)-car-2-ene (**1**) and (+)-car-3-ene (**2**). Due to the presence of a bicyclic framework, a reactive double bond, and a dimethylcyclopropane fragment, creating considerable steric hindrances on one side of the molecules, these compounds are very promising substrates for asymmetric synthesis.
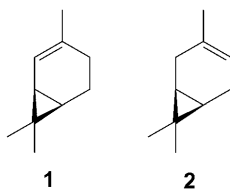
In particular, carenes were effectively used for the syntheses of chiral ligands for metallocomplex catalysis [2–4] and biologically active compounds (*e.g.*, chrysanthemic acid, which is useful in syntheses of pyrethroid insecticides) [5–8]. The numerous reactions of car-2-ene and car-3-ene and some of their derivatives, occurring with preservation or cleavage of the cyclopropane ring, were recently considered in a review [9].

Earlier, we have found unusual transformations, which occurred in reactions of *trans*-car-2-ene-4-methanol (**3**) with aldehydes in the presence of montmorillonite clays leading to various chiral polycyclic compounds, *i.e.*, **4 – 7** (*Scheme 1*), whose structures were largely determined by the structures of the starting aldehydes [10][11].

Scheme 1. *Interaction of* trans-*Car-2-ene-4-methanol* (**3**) *with Aldehydes on Askanite-Bentonite Clay*
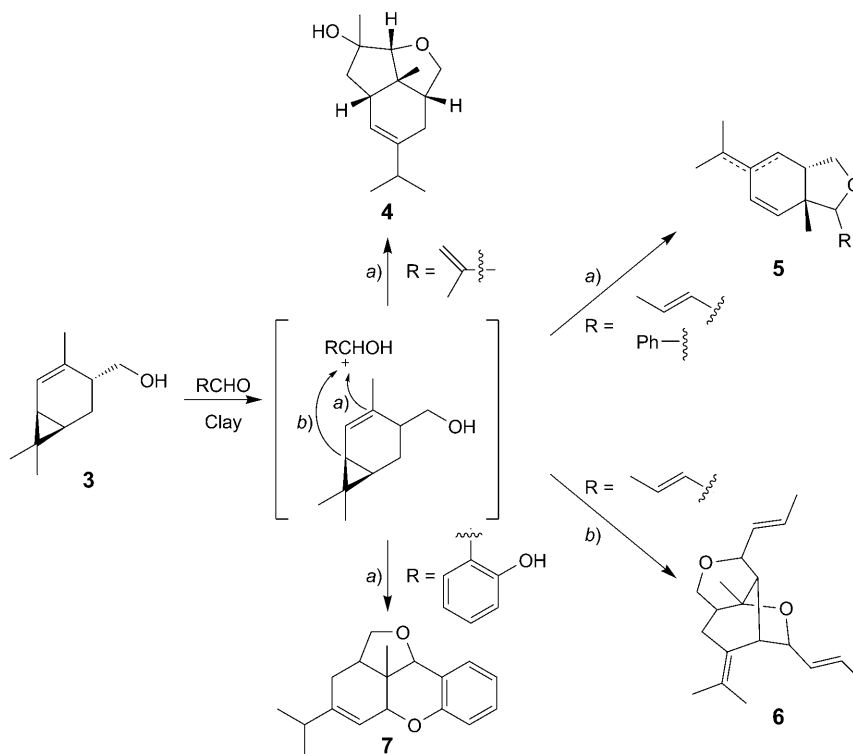
To explain the formation of **4 – 7**, mechanisms with protonated aldehyde acting as an electrophile were suggested. The reactions evidently started with the addition of protonated aldehyde to the C=C bond of the terpenoid, leading to the formation of a relatively stable cyclopropylmethyl ion (route *a*). The direction of further transformations depended on the structure of the aldehyde. At the same time, for crotonaldehyde ($=(2E)$-but-2-enal), product **6** was also obtained, whose formation can be explained [10] by the very rare attack of protonated crotonaldehyde at the cyclopropane ring at the first stage (route *b*).

Note that using montmorillonite clays as catalysts of the transformations of pinene, *para*-menthene, and carene monoterpenoids allows the synthesis of a wide range of new optically active compounds of various structural types, inaccessible by other synthetic procedures [12 – 14]. This can be explained by the fact that for labile polyfunctional substances (monoterpenoids included) used as substrates, preferable fixation of a certain conformation of the substrate or intermediate on the clay surface, setting the

mutual orientation of reagent molecules, and other factors are of great importance. As a result, transformations of terpenoids on clays often follow other routes than in the presence of traditional acid catalysts, leading to the synthesis of new interesting products from recyclable plant raw materials under ecologically safe conditions [11].

Despite of the interesting results of the reaction of compound **3** with aldehydes, the reactions of the unsubstituted (+)-car-2-ene (**1**) and (+)-car-3-ene (**2**) with aldehydes in the presence of montmorillonite clays were not studied. The aim of this work is to study these reactions.

Results and Discussion. – *Transformations of Carenes on* K10 *Clay.* Preliminary storage of (+)-car-2-ene (**1**) on montmorillonite *K10* clay at room temperature in CH_2Cl_2 for 30 min led to the formation of a complex mixture consisting (according to GC/MS measurements) of car-2-ene and car-3-ene (35% and 15%), α-terpinene (**8**; 11%), *para*-cymol (**9**; 4%), limonene (**10**; 2%), terpinolene (**11**; 2%), and γ-terpinene (**12**; 1%) (*Scheme 2*), as well as dimerization products (*ca.* 21%, over 30 compounds). The (+)-car-3-ene (**2**) remained almost unchanged under the same conditions, except for the formation of a small amount of car-2-ene (**1**; 1–2%) and dimerization products.

Scheme 2. *Transformations of (+)-Car-2-ene* (**1**) *on* K10 *Clay*
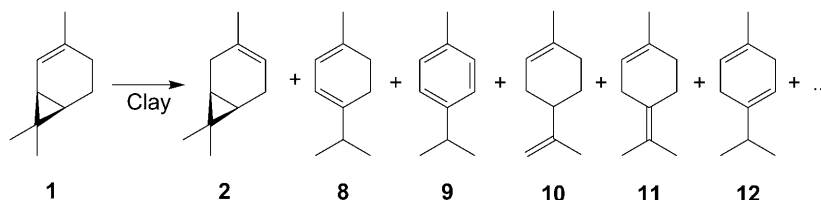
Interaction of Carenes **1** *and* **2** *with (2E)-But-2-enal on* K10 *Clay.* The reaction of (+)-car-2-ene (**1**) with (2*E*)-but-2-enal in the presence of *K10* clay for 3 days at room temperature led to products of intermolecular interaction, namely, compounds **13a**,**b**[1]) with a isobenzofuran framework in a ratio of 1.14:1 (*Scheme 3*). Products **13a**,**b** represent two diastereoisomers, which probably differ in the configuration of the newly formed asymmetric centers C(1) or C(7a). Structure elucidation of the products, especially with respect to the mutual spatial arrangement of substituents at C(1), C(3a), and C(7a), is discussed in detail below. Conversion of **1** amounted to 81%, and the total yield of isomers **13a**,**b** was 23%, based on starting **1**. The reaction was accompanied by oligomerization of the starting materials.

The hypothetical mechanism responsible for the formation of **13a**,**b** includes an attack of the protonated aldehyde at the cyclopropane ring of **1** followed by intramolecular cyclization. Note that in contrast to the previously studied reaction of car-2-ene-4-methanol (**3**; *Scheme 1*), the reaction of terpene **1** with (2*E*)-but-2-enal forms only products corresponding to the attack of the protonated aldehyde at the cyclopropane ring but not at the C=C bond.

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[1]) For convenience, an arbitrary atom numbering is used for the products **13**, **16**, **17**, **19**, and **20**; for systematic names, see *Exper. Part.*

Scheme 3. *Interaction of (+)-Car-2-ene* (**1**) *with (2E)-But-2-enal on* K10 *Clay*

1

R =

13a,b[1]) (23 %)
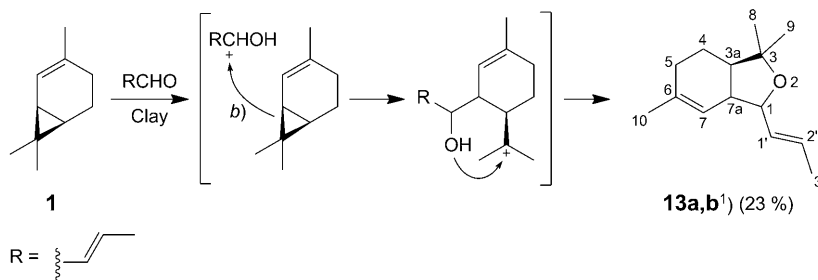
Compound **14** (*Scheme 4*), which is structurally related to **13a,b**, was previously obtained as a by-product of cyclizations of compound **15**, and it is also found in trace amounts in cabreuva oil [15].

Scheme 4. *Cyclization of Compound* **15** [15]

15   **14**
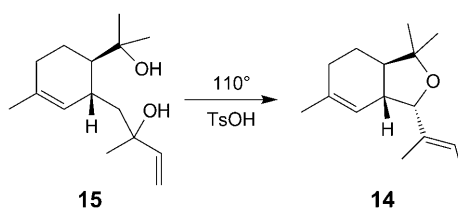
Note that in contrast to **1**, (+)-car-3-ene (**2**) did not react with (2E)-but-2-enal in the presence of clay.

Interaction of Carenes **1** *and* **2** *with Aromatic Aldehydes on* K10 *Clay.* Carenes **1** and **2** did not react with benzaldehyde, 2-hydroxybenzaldehyde, and 4-fluoro- and 4-bromobenzaldehydes. However, the reaction of **1** with 4-methoxybenzaldehyde on *K10* clay gave compounds **16a,b**[1]) (total yield 31%; isomer ratio 7:1), which are analogs of **13a,b**, and a smaller amount of compound **17** with a 3-oxabicyclo[3.3.1]nonane framework (yield 5%) (*Scheme 5*). The conversion of **1** amounted to 78%.

On the reaction path to **17**, carbocation **18**, which is formed by the protonation of **1** at the cyclopropane ring accompanied by isomerization to the *para*-menthane framework (*Scheme 5*), is probably the electrophile, and the aldehyde is the nucleophile, in contrast to the mechanisms described in *Schemes 1* and *3*. Racemic compound **17** was earlier obtained in the reaction of optically inactive limonene (**10**) with 4-methoxybenzaldehyde in the presence of natural montmorillonite clay askanite-bentonite [16]. It is not improbable that in our case, the bicyclic ether **17** is also formed from **1** *via* limonene (**10**) as intermediate, which gave cation **18** by protonation.

The reaction of **2** with 4-methoxybenzaldehyde in CH$_2$Cl$_2$ in the presence of *K10* clay, gave the same products as from **1**, namely, compounds **16a,b** and **17**, but in much lower yields (3% each). The isomer ratio of **16a/16b** was 20:1. The conversion of **2** amounted to 81%. Without solvent, the reaction of **2** with 4-methoxybenzaldehyde for

Scheme 5. *Interaction of (+)-Car-2-ene* (**1**) *with Aromatic Aldehydes on* K10 *Clay*
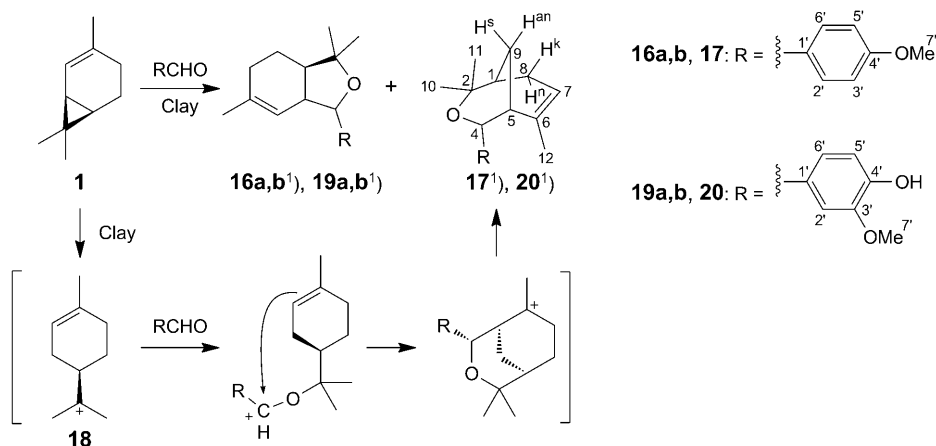
3 days led to insignificantly increased yields of **16a,b** and **17** (4% at 60% conversion of **2**).

Compounds **16a,b** cannot form from **2** without C=C bond migration (see the mechanism in *Scheme 3*). Since C=C bond migration in the product is improbable, it seems that **2** is initially rearranged on clay into **1**, which then reacts with 4-methoxybenzaldehyde. The possibility of this route is confirmed by the observed partial isomerization of **2** into **1** in the presence of clay. At the same time, it was logical to expect that the ratio of the diastereoisomeric products **16a** and **16b** would be the same, as in the case of **1**, but in fact it was not so (**16a/16b** 7:1 from **1** and 20:1 from **2**). Previously, we have already observed a considerable difference in the reactivity of monoterpenoids in the presence of clay, which depended on whether they were used as substrates or formed in the course of the reaction [17].

An analysis of the possible routes of formation of compound **17** from **2** (*Scheme 6*) shows that the reaction gives the same product but different enantiomers, depending on whether the reaction of the aldehyde occurs directly with **2** or *via* **1** as intermediate. As a result, we can expect that compound **17**, obtained in the reaction of **2** with 4-methoxybenzaldehyde on clay, will be partially racemized. Indeed, according to GC/MS analyses with a chiral column, the enantiomer excess (*ee*) was at least 99.5% for (+)-**17** obtained from (+)-car-2-ene (**1**) and 39% with a predominance of (−)-**17** obtained from (+)-car-3-ene (**2**). Therefore, we can conclude that from (+)-car-3-ene (**2**), compound **17** is predominantly formed *via* its direct reaction with the aldehyde, and smaller amounts are obtained *via* the intermediate rearrangement to (+)-car-2-ene (**1**).

Although (+)-car-2-ene (**1**) is widespread in nature, its content in essential oils is generally very low, and its isolation is a complex problem. Generally, (+)-car-2-ene (**1**) is obtained by isomerization of accessible and relatively inexpensive (+)-car-3-ene (**2**). As is known, isomerization of compound **2** in the presence of strong bases at high temperatures forms an equilibrium mixture of car-2-ene and car-3-ene in a ratio of 2:3

Scheme 6. *Formation of Compounds (−)- and (+)-**17** from (+)-Car-2-ene (**1**) and Car-3-ene (**2**)*
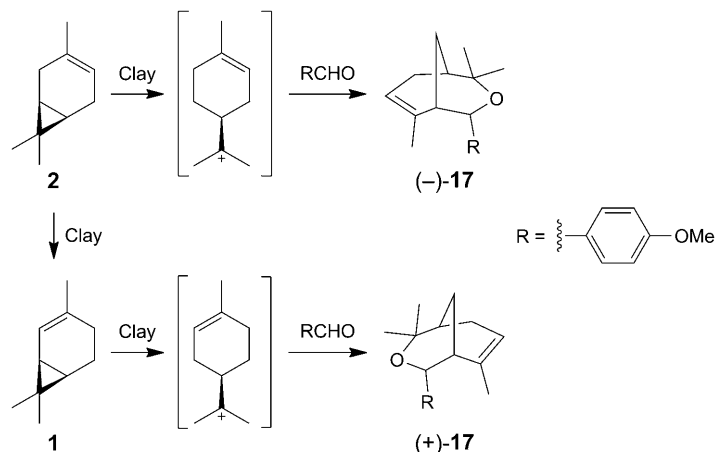
[18][19]. Thereafter, pure car-2-ene (**1**) is obtained by column fractionation of the mixture.

Since the reactions of both carenes **1** and **2** with 4-methoxybenzaldehyde on *K10* clay form the same products, we used a mixture **1/2** in a ratio of 2:3 in the reaction with 4-methoxybenzaldehyde in the presence of *K10* clay, giving **16a,b** and **17** with yields of 35% and 2%, respectively (here and below, the given yields are based on the sum of the starting terpenes). The ratio of **16a/16b** was 8:1. The reaction was performed in CH_2Cl_2 for 2 h at room temperature. The conversion was 100% for **1** and 65% for **2**. It is interesting that based on the yields of individual **1** and **2** and their initial ratio in this reaction, the total yield of **16a,b** was expected to be not higher than 14%.

Thus, using a mixture of **1** and **2** allowed us not only to avoid complex separation of the starting monoterpenes, but also to obtain unexpectedly high yields of compounds **16a,b** based on (+)-car-2-ene (**1**) (if we take into account the content of (+)-car-2-ene (**1**) in the starting mixture, but neglect the possibility of the substances formed from (+)-car-3-ene (**2**), the yield of **16a,b** is 88%). One of possible explanations is provided by the assumption that the side reactions of isomerization and oligomerization of (+)-car-2-ene (**1**) are largely suppressed in the presence of (+)-car-3-ene (**2**), for example, by partial catalyst poisoning.

The results of the optical-purity analysis of the minor compound **17** were also unexpected. In view of the comparable yields of this product based on the individual carenes **1** and **2**, the high optical purity of **17** when formed from **1**, and its low purity when formed from **2**, it was plausible to expect that the (+)-isomer (+)-**17** would be dominant in the reaction mixture. However, the major product was the (−)-isomer (−)-**17** with an enantiomer excess of 27%. This means that **17** predominantly formed directly from (+)-car-3-ene (**2**) (*Scheme 6*).

The reactions of (+)-car-2-ene (**1**) and (+)-car-3-ene (**2**) and their mixture with 4-hydroxy-3-methoxybenzaldehyde (vanillin) in the presence of *K10* clay proceeded in a similar way. We obtained compounds **19a,b**[1]) and **20**[1]) (*Scheme 5*), whose yields are

listed in *Table 1*. As in the case of 4-methoxybenzaldehyde, the yield of compounds **19a,b** increased considerably (from *ca.* 14% according to expectations to 52%) when we used a mixture of the carenes depending on the content of (+)-car-2-ene (**1**) in the mixture. Unfortunately, the enantiomer excess of compound **20** could not be determined because the enantiomers could not be separated by GC/MS on a *Cyclosil-B* capillary column. However, data on the specific rotation of compound **20** (see *Table 1*) obtained in different reactions confirm that the reactions of **1** and **2** with 4-hydroxy-3-methoxybenzaldehyde are similar to those with 4-methoxybenzaldehyde. Note that although the optical activities of compound **17** obtained in different experiments generally agree with GC/MS data on the optical purity, there are pronounced quantitative differences probably because of the presence of small optically active impurities in the substances. Therefore, the optical activity of compound **20** cannot be used for quantitative calculations of the enantiomer excess.

Table 1. *Results of the Reactions of (+)-Car-2-ene (**1**) and (+)-Car-3-ene (**2**) with Aromatic Aldehydes on K10 Clay*

	4-Methoxybenzaldehyde				4-Hydroxy-3-methoxybenzaldehyde			
	Conversion [%]	**16a,b**	**17**		Conversion [%]	**19a,b**	**20**	
		Yield [%]	Yield [%]	$[\alpha]_D^{20}$ (*ee* [%])		Yield [%]	Yield [%]	$[\alpha]_D^{20}$
1	78	31	5	+74 (99.5)	75	33	4	+122
2	81	3	3	−45 (39)	77	3	4	−78
1/2 2:3	100[a]), 65[b])	35 (88)[c])	2	−10 (27)	100[a]), 80[b])	21 (52)[c])	4	+7

[a]) Conversion of **1**. [b]) Conversion of **2**. [c]) The values in parentheses are the product yields based on the content of **1** in the starting mixture.

Configuration of Compounds **13a,b**, **16a,b**, *and* **19a,b**. The analysis of the configuration of compounds **13a,b**, **16a,b**, and **19a,b** is a complex problem. Since two new asymmetric centers are formed in the course of the reaction, four diastereoisomers can be formed (*Scheme 7*), of which we observed only two.

Scheme 7. *Possible Stereoisomers Formed in the Reaction of (+)-Car-2-ene (**1**) with Protonated Aldehydes*
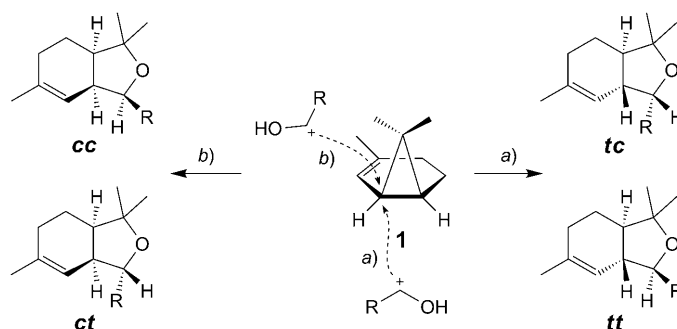
It should be stated that products **13a**,**b**, **16a**,**b**, and **19a**,**b** with *cis*-fusion of the two rings can be formed in principle. As is known, the addition of reagents at the C=C bond of (+)-car-2-ene (**1**) occurs selectively on the less hindered side, namely, in the *trans*-position relative to the cyclopropane ring [20][21]. At the same time, as shown by our (DFT/PBE/L1) quantum-chemical calculations, in the reaction with the cyclopropane ring, the C(1) atom of **1** can be attacked by protonated aldehyde from the bottom (*Path a*) or from the side (*Path b*; *Scheme 7*), and the reaction leads to compounds **13**, **16**, and **19** with *trans*- and *cis*-fusion of the two rings, respectively. For acetaldehyde as model aldehyde (R = Me), for which calculations were performed, the energy barriers of the attack in the gas phase were close, and the transition state of the bottom attack was 2.4 kcal/mol lower, which suggests that the formation of compounds with *trans*-fusion of the rings is preferred.

To determine the type of ring fusion and the spatial position of the R substituent in compounds **13**, **16**, and **19**, we performed DFT/PBE/L22 quantum-chemical calculations of the ^{1}H- and ^{13}C-NMR chemical shifts of the stereoisomers of these compounds. The ^{13}C-NMR spectra, the signal position of which is best reproduced in calculations, could not be chosen because the experimental and calculated spectra proved very similar (the standard deviation was *ca.* 4 ppm in all cases). The ^{1}H-NMR spectra were slightly more informative. Using the standard deviation of the two sets of chemical shifts as a criterion, we could find several stereoisomers, whose calculated spectra showed the greatest similarity to one of the experimental spectra (see *Table 2*). The agreement was in all cases slightly better for stereoisomers with *cis*-fusion of the two rings.

Table 2. *Calculated Relative Energies* [kcal/mol] *and Standard Deviations of the Chemical Shifts from the Experimental Values of the Epimers of Compounds* **13**, **16**, *and* **19** *with* cis- *and* trans-*Fusion of the Rings*

		cc[a])	*ct*[a])	*tc*[a])	*tt*[a])
13	ΔE[b])	1.7	0	3.7	2.0
	s_a[c])	0.32	**0.15**	0.24	0.17
	s_b[c])	**0.13**	0.20	0.20	0.34
16	ΔE[b])	2.2	0	4.3	2.1
	s_a[c])	0.35	**0.13**	0.32	0.20
	s_b[c])	**0.19**	0.30	0.30	0.44
19	ΔE[b])	2.2	0	4.4	2.1
	s_a[c])	0.34	**0.17**	0.34	0.22
	s_b[c])	**0.17**	0.31	0.28	0.41

[a]) In the column headings, the first letter *c* or *t* corresponds to the *cis*- or *trans*-fusion of the rings, and the second one to the *cis*- or *trans*-arrangement of H−C(1) and H−C(7a)[1]); for conformers, if any, data are given for the most stable representatives. [b]) ΔE are the relative energies obtained in the L22 basis for structures optimized in the L1 basis. [c]) s_a and s_b are the standard deviations of the calculated chemical shifts from the experimental values for **13a**, **16a**, and **19a**, and **13b**, **16b**, and **19b**, respectively. The minimum standard deviations are in bold.

The lack of difference between the spectra of isomers allowed no unambiguous conclusions about the configuration of compounds **13a**,**b**, **16a**,**b**, and **19a**,**b** and especially about the relative position of substituents at C(1), based on calculations.

For a more reliable determination of the 3D structure, we analyzed the vicinal spin-spin coupling constants $^3J(H,H)$ and the nuclear *Overhauser* effect (NOE) of the compounds. Thus, for compound **16a**, complete assignment of the ^{1}H- and ^{13}C-NMR signals was preliminarily performed based on 2D ^{1}H,^{1}H (COSY), ^{1}H,^{13}C one-bond (HSQC) and long-range (HMBC) correlation spectra, and also inverse-detected ^{13}C,^{13}C correlation (1,1-ADEQUATE). The calculated (DFT/PBE/L1) geometry of each of the four possible epimers of **16a** was used to evaluate the $^3J(H,H)$ by the *Karplus* equation [22]. The characteristic calculated and corresponding experimental $^3J(H,H)$ are listed in *Table 3*. A comparison of $^3J(H_a-C(3a),H_a-C(4))$ and $^3J(H_a-C(3a),H_e-C(4))$ allowed us to reliably differentiate the signals of the $H_a-C(4)$ and $H_e-C(4)$ protons. A comparison of the calculated and experimental values for other $^3J(H,H)$ provided evidence for the *ct* epimer as the most reliable one, while *tc* and *tt* did not agree with the experimental data at all.

Table 3. *Calculated $^1H,^1H$-Coupling Constants ($^3J(H,H)$ [Hz]) of the Possible Epimers of* **16a**[1]*) and the Corresponding Experimental Values*

	cc[a])	*ct*[a])	*tc*[a])	*tt*[a])	Exper. $^3J(H,H)$
$^3J(H-C(7), H-C(7a))$	4.2	5.7	2.0	2.1	4.6
$^3J(H_a-C(3a), H-C(7a))$	9.0	7.2	13.0	13.0	6.9
$^3J(H_a-C(3a), H_a-C(4))$	12.9	13.0	12.9	12.9	13.1
$^3J(H_a-C(3a), H_e-C(4))$	4.6	4.0	3.1	3.1	4.3
$^3J(H_e-C(4), H-C(7))$	3.5, 5.2	3.3, 5.5	2.3, 7.4	2.3, 7.3	3.0, 4.3

^{a}) In the column headings, the first letter *c* or *t* corresponds to the *cis-* or *trans*-fusion of the rings, and the second one to the *cis-* or *trans*-arrangement of $H-C(1)$ and $H-C(7a)$.

Moreover, using 2D selective *J*-resolved spectroscopy, we measured several long-range coupling constants $J(C,H)$ for **16a**. The vicinal $^3J(C,H)$ were evaluated by the *Karplus* equation for $^3J(C,H)$ [23] for each of the four epimers of **16a** and compared with the experimental values. The characteristic $^3J(C,H)$ are listed in *Table 4*. Thus, we

Table 4. *Calculated $^{13}C,^1H$-Coupling Constants $^3J(C,H)$ [Hz] of the Possible Epimers of* **16a**[1]*) and the Corresponding Experimental Values*

	cc[a])	*ct*[a])	*tc*[a])	*tt*[a])	Exper. $^3J(C,H)$
$^3J(C(3), H_a-C(4))$	3.0	2.6	1.8	1.8	3.1
$^3J(C(3), H_e-C(4))$	1.4	1.7	1.7	2.4	*ca.* 0
$^3J(C(3a), H-C(1))$	2.7	0.7	6.3	0.8	*ca.* 0
$^3J(C(6), H-C(7a))$	2.8	4.2	0.7	0.9	4.8
$^3J(C(7a), H_a-C(4))$	1.6	1.8	2.2	2.2	3.1
$^3J(C(7a), H_e-C(4))$	8.9	8.9	8.9	8.9	6.4
$^3J(C(8), H_a-C(3a))$	4.6	5.8	4.0	4.7	4.1
$^3J(C(9), H_a-C(3a))$	0.7	1.2	8.6	8.2	*ca.* 0
$^3J(C(1'), H-C(7a))$	3.5	3.7	7.3	3.3	4.0

^{a}) In the column headings, the first letter *c* or *t* corresponds to the *cis-* or *trans*-fusion of the rings, and the second one to the *cis-* or *trans*-arrangement of $H-C(1)$ and $H-C(7a)$.

can obtain evidence in favor of the correctness of the assignment of the $H_a-C(4)$ and $H_e-C(4)$ signals and have an opportunity to unambiguously identify the signal for C(8) and C(9) and the signals of corresponding Me H-atoms in the HSQC spectrum. A comparison of the values of other $^3J(C,H)$ and especially $^3J(C(6),H-C(7a))$ provides further evidence in favor of the ***ct*** epimer.

For final elucidation of the configuration of **16a** and reliable differentiation of its ***ct*** and ***cc*** epimers, we acquired the 2D-NOESY plot based on the $^1H,^1H$ nuclear *Overhauser* effect (NOE). A comparison of the calculated $^1H,^1H$ interatomic distances and the qualitative fact of the presence or absence of the corresponding cross-peak in the NOE spectrum (see *Table 5*), especially between $H-C(1)$ and $H_a-C(4)$, made it possible to unambiguously establish the *cis* ring fusion of **16a** and the *trans* relationship of $H-C(1)$ and $H-C(7a)$, corresponding to the ***ct*** epimer.

Table 5. *Calculated Interatomic Distances* r [Å] *between the ^1H Atoms of Possible Epimers of* **16a**[1]) *and the Presence of NOE between Them*

Involved H-atoms	r [Å]				Exper. NOE[a])
	cc[b])	***ct***[b])	***tc***[b])	***tt***[b])	
$H-C(1)$, $H_a-C(4)$	4.2	2.4	4.6	4.7	+
$H-C(1)$, $H_a-C(3a)$	3.8	3.9	3.7	2.4	–
$H-C(7a)$, Me(8)	> 2.3	> 2.4	> 4.6	> 4.5	+
$H-C(7a)$, $H-C(2',6')$	> 3.6	> 3.0	> 3.9	> 2.9	+
Me(8), $H-C(2',6')$	> 4.7	> 3.0	> 2.4	> 4.7	+

[a]) The '+' symbol denotes the presence of the corresponding NOE in the NOESY experiment for **16a**; '–' denotes the absence of this effect. [b]) In the column headings, the first letter ***c*** or ***t*** corresponds to the *cis*- or *trans*-fusion of the rings, and the second one to the *cis*- or *trans*-arrangement of the $H-C(1)$ and $H-C(7a)$.

The NMR spectra of the sample containing a mixture of **19a** and **19b** in a ratio of *ca.* 5:2 were analyzed in a similar way. The ^1H- and ^{13}C-NMR signals of these compounds were assigned according to the 2D-COSY, HSQC, and HMBC data. The spectra of **19a** resemble very strongly the spectra of **16a** discussed above; both the $\delta(H)$ and $\delta(C)$ and the shape of the ^1H-NMR *m*s (except for the signals of the aromatic ring) coincide very closely. The same shape of *m*s in the ^1H-NMR spectra is also characteristic of **19b**, but its chemical shifts differ significantly. This suggests that the configuration of **19a** coincides with that of **16a** (***ct*** epimer), and **19b** probably has the same ring fusion but differs in the orientation of the substituent (***cc*** epimer); this substantially changes the chemical shifts because of the difference in the chemical-shift anisotropy induced by the aromatic ring but does not change markedly the vicinal coupling constants. To strictly establish the 3D structure of **19a,b**, we also evaluated the vicinal $^3J(H,H)$ by the *Karplus* equation [22] (see *Table 6*) and calculated the interatomic distances (see *Table 7*). A comparison of the results with the experimental $^3J(H,H)$ and the presence or absence of cross-peaks in the NOE spectrum (see *Tables 6* and *7*) unambiguously established that the configuration of **19a** corresponds to the ***ct*** epimer and that of **19b** to the ***cc*** epimer.

Table 6. *Calculated $^1H,^1H$-Coupling Constants $^3J(H,H)$ [Hz] of the Possible Epimers of* **19a,b** *and the Corresponding Experimental Values*

	cc[a])	ct[a])	tc[a])	tt[a])	Exper. $^3J(H,H)$	
					19a	**19b**
$^3J(H_a-C(4), H_a-C(3a))$	12.9	13.0	12.9	12.9	13.1	*ca.* 13
$^3J(H_e-C(4), H_a-C(3a))$	4.6	4.0	3.1	3.1	*ca.* 4	*ca.* 4
$^3J(H-C(7a), H-C(7))$	4.1	5.6	2.0	2.1	4.7	4.0
$^3J(H-C(7a), H_a-C(3a))$	9.2	7.2	13.0	13.0	*ca.* 7	7.2

[a]) In the column headings, the first letter *c* or *t* corresponds to the *cis*- or *trans*-fusion of the rings, and the second one to the *cis*- or *trans*-arrangement of H−C(1) and H−C(7a).

Table 7. *Calculated Interatomic Distances* r [Å] *between the ^1H Atoms of Possible Epimers of* **19a,b**[1]) *and the Presence of NOE between Them*

Involved H-atoms	r [Å]				Exper. NOE[a])	
	cc[b])	ct[b])	tc[b])	tt[b])	**19a**	**19b**
H−C(1), H_a−C(4)	4.3	2.4	4.6	4.7	+	−
H−C(1), H_a−C(3a)	3.8	3.9	3.7	2.5	−	−
H−C(1), Me(8)	> 2.4	> 4.4	> 4.6	> 3.3	−	+
H−C(7a), Me(8)	> 2.3	> 2.4	> 4.6	> 4.5	+	+
H−C(7a), H−C(2′,6′)	> 3.6	> 3.0	> 3.9	> 2.9	+	−
Me(8), H−C(2′,6′)	> 4.7	> 2.9	> 2.4	> 4.6	+	−
Me(9), H−C(2′,6′)	> 3.3	> 4.6	> 4.8	> 2.9	−	+

[a]) '+' denotes the presence of NOE for **19a** and **19b** in the NOESY experiment; '−' denotes the absence of this effect. [b]) In the column headings, the first letter *c* or *t* corresponds to the *cis*- or *trans*-fusion of the rings, and the second one to the *cis*- or *trans*-arrangement of H−C(1) and H−C(7a).

A comparison of the chemical shifts of C(1) to C(9) (especially C(1), C(5), C(6), C(7a), and C(8)) in the ^{13}C-NMR spectra of **13a**, **16a**, and **19a** with those for **13b**, **16b**, and **19b** strongly suggests that isomer **13a** has the same 3D structure as **16a** and **19a** (*i.e.*, corresponds to the *ct* epimer), while isomers **13b** and **16b** have a 3D structure similar to that of **19b** (*i.e.*, correspond to the *cc* epimer). The $\delta(H)$ in the ^1H-NMR spectra of **13a** and **13b** differ from those of **16a**, **19a**, and **16b**, **19b**, respectively, because of the different effects of the R substituents, but the form of the *m*s and the $^3J(H,H)$ of the corresponding H-atoms change insignificantly, which confirms the above conclusions about the structures of **13a,b** and **16b**.

Synthesis of products with *cis*-fusion alone proved quite unexpected. To explain this, we can assume that the formation of an intermolecular product in the reaction of car-2-ene and aldehyde demands adsorption of these compounds on close-lying catalytic centers, for example, in the interlayer space of clay, which makes the bottom attack impossible. The same can partially account for the observed high sensitivity of the reaction to the structure of the aldehyde.

Conclusions. – To summarize, we have studied for the first time the reactions of (+)-car-2-ene (**1**) and (+)-car-3-ene (**2**) with aldehydes in the presence of montmorillonite

K10 clay. It was shown that the major products of these reactions were substituted chiral hexahydro-isobenzofuranes, probably formed as a result of an attack of protonated aldehyde at the cyclopropane ring. Quite unexpectedly, the products had *cis*-fusion of the rings. Though clay-catalyzed transformations of terpenoids generally give moderate yields, this disadvantage is compensated by the accessibility and relatively low cost of the starting terpenoids and reagents. It appeared that the behavior of the 2:3 mixture of **1** and **2** in reactions with aldehydes in the presence of *K10* clay differed substantially from the reactivities of the corresponding individual monoterpenes. For example, using a mixture **1/2** in reactions with aromatic aldehydes led to considerably increased yields of the products formed from (+)-car-2-ene (**1**). The optical purity of the minor products with a 3-oxabicyclo[3.3.1]nonane framework also changed as a nonlinear function.

Experimental Part

1. *General.* As catalyst, we used *K10* clay (*Merck*). The clay was calcinated at 110° for 3 h immediately before use. CH_2Cl_2 was passed through calcined Al_2O_3. Column chromatography (CC): silica gel (SiO_2; 60–200 μ, *Macherey–Nagel*). GC (purity control and products analyses): *3700* instrument; quartz capillary column (15 m × 0.22 mm), *VC-30* phase; flame-ionization detector; He (1 atm) as carrier gas. Optical rotation: *polAAr-3005* spectrometer; $CHCl_3$ soln. ¹H- and ¹³C-NMR Spectra: *Bruker-DRX-500* apparatus at 500.13 (¹H) and 125.76 MHz (¹³C), $CCl_4/CDCl_3$ 1:1 (*v/v*) solns.; *Bruker-Avance-III-600* apparatus at 600.30 (¹H) and 150.95 MHz (¹³C); $CDCl_3$ solns.; chemical shifts δ in ppm rel. to residual $CHCl_3$ (δ(H) 7.24, δ(C) 76.90), *J* in Hz; structure determinations by ¹H-NMR (including ¹H,¹H 2D), *J*-modulated ¹³C-NMR (JMOD), ¹³C-NMR with H-atom off-resonance saturation, and ¹³C,¹H 2D-COSY (*J*(C,H) = 135 Hz); 3D structure determination of **16a**, **19a**, and **19b** confirmed by ¹H,¹H COSY and NOESY, inverse ¹³C,¹H correlations on one-bond (HSQC) and long-range (HMBC) ³*J* and inverse-detected ¹³C,¹³C correlation (1,1-ADEQUATE); long-range *J*(C,H)s from 2D selective *J*-resolved spectra. GC/MS: *Hewlett-Packard-5890/II* gas chromatograph with a quadrupole mass spectrometer (*HP MSD 5971*) as detector; *HP-5MS* quartz column 30000 × 0.25 mm; He as carrier gas. Enantiospecific GC/MS: *6890N* gas chromatograph (*Agilent Tech.*, USA) and *5973-INERT* mass-selective detector (*Agilent Tech.*, USA); *Cyclosil-B* capillary column (30 m × 0.32 mm i.d., 0.25 μm; *Agilent Tech.*, USA); column temp. (thermostat): 50° for 2 min, then gradient of 2°/min up to 220°, then 220° for 5 min; evaporator and interface temp. 250°; He as carrier gas (flow rate 2 ml/min, flow division 99:1); sweep from *m/z* 29 to 500; 1 μl sample. HR-MS: *DFS-Thermo-Scientific* spectrometer in a full scan mode (0–500 *m/z*, 70 eV electron-impact ionization, direct sample introduction).

2. *Quantum-Chemical Calculations.* DFT Method (PBE functional [24], Priroda program [25][26]) neglecting the solvent effect; structure optimization was performed in the L1 basis (Λ01 [27], analog of the cc-pVDZ basis) ({6s2p}/[2s1p] for H; {10s7p3d}/[3s2p1d] for C, O). To calculate the chemical shifts by the GIAO technique, we used the L22 basis (Λ22 [27], analog of the cc-pCVTZ basis) ({8s4p2d}/[3s2p1d] for H; {12s8p5d2f}/[6s5p3d1f] for C, O). In calculations of δ (ppm), for the σ standard we took the values δ(H) 31.278 for H and δ(C) 172.94 for C.

3. *Transformation of Terpenes on* K10 *Clay.* A soln. of (+)-car-2-ene (**1**; *Fluka*, $[\alpha]_D^{20} = +88.6$ ($c = 1$, EtOH)) or (+)-car-3-ene (**2**; $[\alpha]_{580}^{22} = +10.14$ ($c = 2.5$); 0.050 g) in CH_2Cl_2 (1 ml) was added to a suspension of *K10* clay (0.5 g) in CH_2Cl_2 (3 ml). The mixture was stirred for 1 h at r.t. Then, Et_2O (5 ml) was added. The catalyst was filtered off, and the solvent evaporated. The resulting mixture was analyzed by GC/MS.

4. *Interaction of (+)-Car-2-ene* (**1**) *with (2E)-But-2-enal on* K10 *Clay.* (2*E*)-But-2-enal (0.400 g, 5.71 mmol) and **1** (0.400 g, 2.94 mmol) were added to *K10* clay (2.0 g). The mixture was left at r.t. for 3 d.

Then, AcOEt (10 ml) was added. The catalyst was filtered off, and the solvent evaporated. The resulting mixture was separated by CC (SiO$_2$ (10 g), hexane/AcOEt 100:0 → 95:5): **1** (0.077 g, conversion 81%) and **13a/13b** *ca.* 1.14:1 (by ^{1}H-NMR; 0.137 g, 23% (yield based on converted **1**)).

*(3*R*,3a*S*,7a*R*)-1,3,3a,6,7,7a-Hexahydro-1,1,5-trimethyl-3-[(1*E*)-prop-1-en-1-yl]isobenzofuran* (**13a**): ^{1}H-NMR (500 MHz)[1]: 1.17 (*s*, Me(9)); 1.22 (*s*, Me(8)); 1.44 (*dddd*, $J(4_a,4_e) = 13.3$, $J(4_a,3a_a) = 13.3$, $J(4_a,5_a) = 11.0$, $J(4_a,5_e) = 6.2$, H$_a$−C(4)); 1.61 – 1.67 (*m*, H$_e$−C(4)); 1.65 (br. *s*, Me(10)); 1.68 (*ddd*, $J(3',2') = 6.5$, $J(3',1') = 1.6$, $J(3',1) = 0.4$, Me(3')); 1.81 (*ddd*, $J(3a_a,4_a) = 13.3$, $J(3a_a,7a) = 6.8$, $J(3a_a,4_e) = 4.2$, H$_a$−C(3a)); 1.85 – 1.98 (*m*, CH$_2$(5)); 2.44 – 2.51 (*m*, H−C(7a)); 3.88 (*dd*, $J(1,7a) = 9.7$, $J(1,1') = 7.8$, H−C(1)); 5.19 – 5.23 (*m*, H−C(7)); 5.41 (*ddq*, $J(1',2') = 15.1$, $J(1',1) = 7.8$, $J(1',3') = 1.6$, H−C(1')); 5.59 (*dqd*, $J(2',1') = 15.1$, $J(2',3') = 6.5$, $J(2',1) = 0.7$, H−C(2')). ^{13}C-NMR (125 MHz)[1]: 17.69 (*q*, C(3')); 22.01 (*t*, C(4)); 23.55 (*q*, C(10)); 24.04 (*q*, C(9)); 30.07 (*t*, C(5)); 31.00 (*q*, C(8)); 45.73 (*d*, C(7a)); 46.02 (*d*, C(3a)); 81.97 (*s*, C(3)); 84.41 (*d*, C(1)); 119.31 (*d*, C(7)); 127.77 (*d*, C(2')); 132.59 (*d*, C(1')); 135.45 (*s*, C(6)). HR-MS: 206.1691 (M^+, C$_{14}$H$_{22}$O$^+$; calc. 206.1665).

*(3*S*,3a*S*,7a*R*)-1,3,3a,6,7,7a-Hexahydro-1,1,5-trimethyl-3-[(1*E*)-prop-1-en-1-yl]isobenzofuran* (**13b**): ^{1}H-NMR (500 MHz)[1]: 1.20 (*s*, Me(8)); 1.22 (*s*, Me(9)); 1.31 (*dddd*, $J(4_a,3a_a) = 12.8$, $J(4_a,4_e) = 12.5$, $J(4_a,5_a) = 11.0$, $J(4_a,5_e) = 6.0$, H$_a$−C(4)); 1.66 (*dd*, $J(3',2') = 6.5$, $J(3',1') = 1.6$, Me(3')); 1.68 (br. *s*, Me(10)); 1.63 – 1.72 (*m*, H$_e$−C(4)); 1.77 (*ddd*, $J(3a_a,4_a) = 12.8$, $J(3a_a,7a) = 7.3$, $J(3a_a,4_e) = 4.1$, H$_a$−C(3a)); 1.84 – 1.91 (*m*, CH$_2$(5)); 3.03 – 3.09 (*m*, H−C(7a)); 4.38 (*dd*, $J(1,7a) = 9.0$, $J(1,1') = 8.6$, H−C(1)); 5.09 – 5.13 (*m*, H−C(7)); 5.29 (*ddq*, $J(1',2') = 15.1$, $J(1',1) = 8.6$, $J(1',3') = 1.6$, H−C(1')); 5.54 (*dqd*, $J(2',1') = 15.1$, $J(2',3') = 6.5$, $J(2',1) = 0.7$, H−C(2')). ^{13}C-NMR (125 MHz)[1]: 17.73 (*q*, C(3')); 22.65 (*t*, C(4)); 23.74 (*q*, C(10)); 23.85 (*q*, C(9)); 27.27 (*q*, C(8)); 29.31 (*t*, C(5)); 42.07 (*d*, C(7a)); 45.27 (*d*, C(3a)); 80.26 (*d*, C(1)); 81.34 (*s*, C(3)); 119.69 (*d*, C(7)); 127.38 (*d*, C(2')); 132.43 (*d*, C(1')); 134.38 (*s*, C(6)). HR-MS: 206.1691 (M^+, C$_{14}$H$_{22}$O$^+$; calc. 206.1665).

5. *Interaction of* (+)*-Car-2-ene* (**1**) *with 4-Methoxybenzaldehyde on K10 Clay.* To a suspension of *K10* clay (2.5 g) in CH$_2$Cl$_2$ (8 ml) 4-methoxybenzaldehyde (0.50 g, 3.68 mmol) was added. Then, a soln. of **1** (0.500 g, 3.68 mmol) in CH$_2$Cl$_2$ (7 ml) was added dropwise. The mixture was stirred for 1.5 h at r.t. Then, Et$_2$O (5 ml) was added. The catalyst was filtered off, and the solvent evaporated. The resulting mixture was separated by CC (SiO$_2$ (10 g), hexane/AcOEt 100:0 → 85:15): **1** (0.112 g, conversion 78%), **17** (0.049 g, 5%), and **16a/16b** *ca.* 7:1 (by ^{1}H-NMR; 0.313 g, 31%); yields are based on converted **1**.

Note that aromatic aldehydes are stable on *K10* clay because they were isolated in unchanged form from reaction mixtures in all of their transformations with carenes. Since the large amounts of aldehydes hindered product separation, they were taken in a smaller ratio than for reactions with (2*E*)-but-2-enal.

4-(4-Methoxyphenyl)-2,2,6-trimethyl-3-oxabicyclo[3.3.1]non-6-ene (**17**): $[\alpha]_D^{19} = +74$ ($c = 0.9$). ^{1}H- and ^{13}C-NMR: identical with those reported in [15].

*(3*S*,3a*S*,7a*R*)-1,3,3a,6,7,7a-Hexahydro-3-(4-methoxyphenyl)-1,1,15-trimethylisobenzofuran* (**16a**): ^{1}H-NMR (600 MHz)[1]: 1.30 (*s*, Me(9)); 1.41 (*s*, Me(8)); 1.62 (*dddd*, $J(4_a,3a_a) = 13.1$, $J(4_a,4_e) = 12.8$, $J(4_a,5_a) = 9.5$, $J(4_a,5_e) = 7.0$, H$_a$−C(4)); 1.67 (br. *s*, Me(10)); 1.74 (*ddddd*, $J(4_e,4_a) = 12.8$, $J(4_e,3a_a) = 4.3$, $J(4_e,5_a) = 4.3$, $J(4_e,5_e) = 3.0$, $J(4_e,7a) = 0.5$, H$_e$−C(4)); 1.96 (*ddd*, $J(3a_a,4_a) = 13.1$, $J(3a_a,7a) = 6.9$, $J(3a_a,4_e) = 4.3$, H$_a$−C(3a)); 1.97 – 2.01 (*m*, CH$_2$(5)); 2.62 – 2.68 (*m*, H−C(7a)); 3.78 (*s*, MeO); 4.54 (*d*, $J(1,7a) = 10.1$, H−C(1)); 5.17 (br. *d*, $J(7,7a) = 4.6$, H−C(7)); 6.86 (*d*, $J = 8.6$, H−C(3'), H−C(5')); 7.27 (*d*, $J = 8.6$, H−C(2'), H−C(6')). ^{13}C-NMR (151 MHz)[1]: 21.91 (*t*, C(4)); 23.45 (*q*, C(10)); 24.06 (*q*, C(9)); 30.06 (*t*, C(5)); 31.03 (*q*, C(8)); 46.42 (*d*, C(3a)); 48.46 (*d*, C(7a)); 55.08 (*q*, C(7')); 82.24 (*s*, C(3)); 85.01 (*d*, C(1)); 113.55 (*d*, C(3'), C(5')); 118.66 (*d*, C(7)); 127.18 (*d*, C(2'), C(6')); 134.31 (*s*, C(1')); 136.16 (*s*, C(6)); 158.83 (*s*, C(4')). HR-MS: 272.1770 (M^+, C$_{18}$H$_{24}$O$_2^+$; calc. 272.1771).

*(3*R*,3a*S*,7a*R*)-1,3,3a,6,7,7a-Hexahydro-3-(4-methoxyphenyl)-1,1,5-trimethylisobenzofuran* (**16b**): For the minor product **16b**, we revealed only the following signals in the ^{1}H-NMR spectrum: ^{1}H-NMR (500 MHz)[1]: 1.32 (*s*, Me(8)); 1.35 (*s*, Me(9)); 1.47 (*m*, Me(10)); 1.79 – 1.84 (*m*, CH$_2$(5)); 1.91 – 1.97 (*m*, H−C(3a)); 3.14 – 3.20 (*m*, H−C(7a)); 3.76 (*s*, MeO); 4.75 – 4.78 (*m*, H−C(7)); 5.08 (*d*, $J(1,7a) = 9.2$, H−C(1)); 6.76 (*d*, $J = 8.6$, H−C(3'), H−C(5')); 7.10 (*d*, $J = 8.6$, H−C(2'), H−C(6')). ^{13}C-NMR (125 MHz)[1]: 22.60 (*t*, C(4)); 23.60 (*q*, C(10)); 23.87 (*q*, C(9)); 27.02 (*q*, C(8)); 28.66 (*t*, C(5)); 43.24 (*d*, C(7a)); 45.08 (*d*, C(3a)); 54.83 (*q*, C(7')); 80.85 (*d*, C(1)); 81.35 (*s*, C(3)); 112.96 (*d*, C(3'), C(5')); 120.46 (*d*, C(7)); 128.04 (*d*, C(2'), C(6')); 133.14 (*s*, C(1')); 133.68 (*s*, C(6)); 158.30 (*s*, C(4')). HR-MS: 272.1770 (M^+, C$_{18}$H$_{24}$O$_2^+$; calc. 272.1771).

6. *Interaction of (+)-Car-3-ene* (**2**) *with 4-Methoxybenzaldehyde on* K10 *Clay*. A soln. of 4-methoxybenzaldehyde (0.300 g, 2.21 mmol) in CH_2Cl_2 (2 ml) was added to a suspension of *K10* clay (1.2 g) in CH_2Cl_2 (10 ml). Then a soln. of **2** (0.300 g, 2.21 mmol) in CH_2Cl_2 (2 ml) was added dropwise. The mixture was stirred for 2 h 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 (SiO_2 (10 g), hexane/AcOEt 100:0 → 95:5): **2** (0.058 g, conversion 81%), **17** (0.018 g, 3%; $[\alpha]_D^{19} = -45$ ($c = 0.6$)), and **16a/16b** *ca.* 20:1 (by ^{1}H-NMR; 0.018 g, 3%); yields are based on converted **2**.

7. *Interaction of a (+)-Car-2-ene* (**1**) *and (+)-Car-3-ene* (**2**) *Mixture with 4-Methoxybenzaldehyde on* K10 *Clay*. A soln. of 4-methoxybenzaldehyde (0.50 g, 3.68 mmol) in CH_2Cl_2 (2 ml) was added to a suspension of *K10* clay (2.5 g) in CH_2Cl_2 (10 ml). Then, a soln. of **1** (0.200 g, 1.47 mmol) and **2** (0.300 g, 2.21 mmol) in CH_2Cl_2 (2 ml) was added dropwise. The mixture was stirred for 2 h 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 (SiO_2 (10 g), hexane/AcOEt 100:0 → 90:10): **2** (0.105 g, conversion of **1**, 100%; conversion of **2**, 65%), **17** (0.018 g, 2%; $[\alpha]_D^{19} = -10$ ($c = 0.6$)), and **16a/16b** *ca.* 8:1 (by ^{1}H-NMR; 0.351 g, 35%); yields are based on the sum of the starting terpenes.

8. *Interaction of (+)-Car-2-ene* (**1**) *with 4-Hydroxy-3-methoxybenzaldehyde on* K10 *Clay*. A soln. of 4-hydroxy-3-methoxybenzaldehyde (0.40 g, 2.36 mmol) in CH_2Cl_2 (3 ml) was added to a suspension of *K10* clay (2.0 g) in CH_2Cl_2 (8 ml). Then, a soln. of **1** (0.400 g, 2.94 mmol) in CH_2Cl_2 (3 ml) was added. The solvent was evaporated, and the mixture maintained at r.t. for 24 h. Then Et_2O (10 ml) and acetone (10 ml) were added. The catalyst was filtered off, and the solvent evaporated. The resulting mixture was separated by CC (SiO_2 (10 g), hexane/Et_2O 100:0 → 50:50): **1** (0.100 g, conversion 75%), **20** (0.031 g, 4%), and **19a/19b** *ca.* 1:1 (by ^{1}H-NMR; 0.275 g, 33%); yields are based on converted **1**.

2-Methoxy-4-(4,4,8-trimethyl-3-oxabicyclo[3.3.1]non-7-en-2-yl)phenol (**20**): $[\alpha]_D^{19} = +122$ ($c = 0.6$). ^{1}H-NMR (500 MHz)[1]: 0.92 (*ddd*, $J(12,7) = 2.4$, $J(12,8k) = 2.4$, $J(12,8n) = 1.8$, Me(12); diamagnetic shift of the signal due to the anisotropic effect of the phenol ring, which can manifest itself only in the case of the *endo*-position of the aryl residue); 1.31 (*s*, Me(10)); 1.37 (*s*, Me(11)); 1.53 (*dddd*, $J(1,8k) = 6.5$, $J(1,9s) = J(1,9an) = 3.0$, $J(1,8n) \approx 1$, H−C(1)); 1.70 (*ddd*, $J(9an,9s) = 12.3$, $J(9an,1) = J(9an,5) = 3.0$, H$_{an}$−C(9)); 2.06 (*dddq*, $J(8k,8n) = 18.5$, $J(8k,1) = 6.5$, $J(8k,7) = 3.0$, $J(8k,12) = 2.4$, H$_k$−C(8)); 2.11 (*ddd*, $J(5,9s) = J(5,9an) = 3.0$, $J(5,4) = 2.3$, H−C(5)); 2.31 (*dddd*, $J(9s,9an) = 12.3$, $J(9s,1) = J(9s,5) = 3.0$, $J(9s,8n) = 1.2$, H$_s$−C(9)); 2.37 (br. *d*, $J(8n,8k) = 18.5$, H$_n$−C(8)); 3.86 (*s*, MeO); 4.76 (*d*, $J(4,5) = 2.3$, H−C(4)); 5.38 (br. *s*, OH); 5.37–5.41 (*m*, H−C(7)); 6.74 (*dd*, $J(6',5') = 8.1$, $J(6',2') = 1.8$, H−C(6')); 6.77 (*d*, $J(5',6') = 8.1$, H−C(5')); 6.82 (*d*, $J(2',6') = 1.8$, H−C(2')). ^{13}C-NMR (125 MHz)[1]: 24.03 (*q*, C(11)); 24.29 (*q*, C(12)); 27.73 (*t*, C(8)); 28.31 (*t*, C(9)); 28.76 (*q*, C(10)); 34.06 (*d*, C(1)); 41.76 (*d*, C(5)); 55.83 (*q*, C(7')); 74.02 (*d*, C(4)); 75.24 (*s*, C(2)); 108.55 (*d*, C(2')); 113.71 (*d*, C(5')); 118.61 (*d*, C(6')); 123.02 (*d*, C(7)); 133.31 (*s*, C(6)); 134.86 (*s*, C(1')); 144.35 (*s*, C(4')); 146.10 (*s*, C(3')). HR-MS: 288.1725 (M^+, $C_{18}H_{24}O_3^+$; calc. 288.1770).

The NMR spectra of isomers **19a** and **19b** were recorded for their mixtures with one dominant isomer.

4-[(1S,3aR,7aS)-1,3,3a,4,5,7a-Hexahydro-3,3,6-trimethylisobenzofuran-1-yl]-2-methoxyphenol (**19a**): ^{1}H-NMR (600 MHz)[1]: 1.30 (*s*, Me(9)); 1.41 (*s*, Me(8)); 1.60 (*dddd*, $J(4_a,3a_a) = 13.1$, $J(4_a,4_e) = 12.7$, $J(4_a,5_a) = 9.8$, $J(4_a,5_e) = 7.1$, H$_a$−C(4)); 1.67 (br. *s*, Me(10)); 1.73 (br. *d*, $J(4_e,4_a) = 12.7$, H$_e$−C(4)); 1.93–1.99 (*m*, H$_a$−C(3a)); 1.97–2.01 (*m*, CH$_2$(5)); 2.61–2.68 (*m*, H−C(7a)); 3.87 (*s*, MeO); 4.51 (*d*, $J(1,7a) = 10.1$, H−C(1)); 5.18 (br. *d*, $J(7,7a) = 4.7$, H−C(7)); 5.58 (*s*, OH); 6.82 (*dd*, $J(6',5') = 8.1$, $J(6',2') = 1.8$, H−C(6')); 6.85 (*d*, $J(5',6') = 8.1$, H−C(5')); 6.90 (*d*, $J(2',6') = 1.8$, H−C(2')). ^{13}C-NMR (151 MHz)[1]: 21.92 (*t*, C(4)); 23.49 (*q*, C(10)); 24.06 (*q*, C(9)); 30.06 (*t*, C(5)); 30.99 (*q*, C(8)); 46.43 (*d*, C(3a)); 48.38 (*d*, C(7a)); 55.71 (*q*, C(7')); 82.28 (*s*, C(3)); 85.26 (*d*, C(1)); 108.55 (*d*, C(2')); 113.96 (*d*, C(5')); 119.01 (*d*, C(6')); 118.69 (*d*, C(7)); 134.22 (*s*, C(1')); 136.23 (*s*, C(6)); 144.79 (*s*, C(4')); 146.38 (*s*, C(3')). HR-MS: 288.1726 (M^+, $C_{18}H_{24}O_3^+$; calc. 288.1770).

4-[(1R,3aR,7aS)-1,3,3a,4,5,7a-Hexahydro-3,3,6-trimethylisobenzofuran-1-yl]-2-methoxyphenol (**19b**): ^{1}H-NMR (600 MHz)[1]: 1.32 (*s*, Me(8)); 1.35 (*s*, Me(9)); 1.37–1.45 (*m*, H$_a$−C(4)); 1.47–1.49 (*m*, Me(10)); 1.75 (br. *d*, $J(4_e,4_a) = 12.8$, H$_e$−C(4)); 1.80–1.84 (*m*, CH$_2$(5)); 1.92–1.97 (*m*, H$_a$−C(3a)); 3.14–3.19 (*m*, H−C(7a)); 3.82 (*s*, MeO); 4.79 (br. *d*, $J(7,7a) = 4.0$, H−C(7)); 5.06 (*d*, $J(1,7a) = 9.2$, H−C(1)); 5.52 (*s*, OH); 6.71 (*dd*, $J(6',5') = 8.0$, $J(6',2') = 2.0$, H−C(6')); 6.76 (*d*, $J(2',6') = 2.0$, H−C(2')); 6.79 (*d*,

$J(5',6') = 8.0$, H$-$C(5'). ^{13}C-NMR (151 MHz)[1]): 22.57 (t, C(4)); 23.49 (q, C(10)); 23.76 (q, C(9)); 26.96 (q, C(8)); 28.54 (t, C(5)); 43.15 (d, C(7a)); 44.90 (d, C(3a)); 55.74 (q, C(7')); 81.05 (d, C(1)); 81.51 (s, C(3)); 110.00 (d, C(2')); 113.48 (d, C(5')); 120.17 (d, C(6')); 120.27 (d, C(7)); 132.95 (s, C(1')); 133.76 (s, C(6)); 144.23 (s, C(4')); 145.91 (s, C(3')). HR-MS: 288.1726 (M^+, $C_{18}H_{24}O_3^+$; calc. 288.1770).

9. *Interaction of (+)-Car-3-ene* (**2**) *with 4-Hydroxy-3-methoxybenzaldehyde on* K10 *Clay.* A soln. of 4-hydroxy-3-methoxybenzaldehyde (0.600 g, 3.95 mmol) in CH_2Cl_2 (4 ml) was added to a suspension of *K10* clay (2.5 g) in CH_2Cl_2 (8 ml). Then, a soln. of **2** (0.600 g, 4.41 mmol) in CH_2Cl_2 (3 ml) was added. The solvent was evaporated. The mixture was maintained at r.t. for 4 days. Then AcOEt (10 ml) and acetone (10 ml) were added. The catalyst was filtered off, and the solvent evaporated. The resulting mixture was separated by CC (SiO_2 (10 g), hexane/Et_2O 100:0 → 0:100): **2** (0.137 g, conversion 77%), **20** (0.047 g, 4%; $[\alpha]_D^{19} = -78$ ($c = 0.9$)), and **19a/19b** *ca.* 2:1 (by ^{1}H-NMR; 0.040 g, 3%); yields are based on converted **2**.

10. *Interaction of a (+)-Car-2-ene* (**1**) *and (+)-Car-3-ene* (**2**) *Mixture with 4-Hydroxy-3-methoxybenzaldehyde on* K10 *Clay.* To a suspension of *K10* clay (3.0 g) in CH_2Cl_2 (7 ml), 4-hydroxy-3-methoxybenzaldehyde (0.70 g, 4.61 mmol) was added. Then a soln. of **1** (0.270 g, 1.99 mmol) and **2** (0.400 g, 2.94 mmol) in CH_2Cl_2 (10 ml) was added dropwise. The solvent was evaporated. The mixture was maintained at r.t. for 4 d. Then AcOEt (15 ml) was added. The catalyst was filtered off, and the solvent evaporated. The resulting mixture was separated by CC (SiO_2 (10 g), hexane/Et_2O 100:0 → 0:100): **2** (0.081 g, conversion of **1**, 100%; conversion of **2**, 80%), **20** (0.061 g, 4%; $[\alpha]_D^{19} = +7$ ($c = 1.2$)), and **19a/19b** *ca.* 3:1 (by ^{1}H-NMR; 0.299 g, 21%); yields are based on the sum of the starting terpenes.

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