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Thermal Isomerization of (+)-*cis*- and (−)-*trans*-Pinane Leading to (−)-β-Citronellene and (+)-Isocitronellene**

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Abstract: Catalyzed and uncatalyzed rearrangement reactions of terpenoids play a major role in laboratory and industrial-scale synthesis of fine chemicals. Herein, we present our results on the thermally induced isomerization of pinane (**1**). Investigation of the thermal behavior of (+)-*cis*- (**1a**) and (−)-*trans*-pinane (**1b**) in a flow-type reactor reveals significant differences in both reactivity and selectivity concerning the formation of (−)-β-citronellene (**2**) and (+)-isocitronellene (**3**) as main products. Possible explanations for these results are discussed on the basis of reaction mechanism and ground-state geometries for **1a** and **1b**. To identify side reactions caused from ene cyclizations of **2** and **3**, additional pyrolysis experiments were conducted that enabled the identification of almost all compounds in the network of $C_{10}H_{18}$-hydrocarbon products formed from **1**.

Keywords: ene reaction · NMR spectroscopy · pericyclic reaction · rearrangement · terpenoids

Introduction

Monoterpenes from renewables (e.g. limonene, β-citronellene (**2**), α-pinene, β-pinene) and terpenoids, such as 2-pinanol or citral, play an important role in the industrial synthesis of flavors and fragrances.[1–3] They are valuable chiral building blocks for the synthesis of ligands and natural products, and they are important chiral auxiliaries. The thermal isomerization of bicyclic terpenes with the pinane skeleton (**1**; Scheme 1) yields acyclic isomers and *p*-menthane-type monocyclic terpenes.[4–7] The rearrangement of α-pinene leads to the formation of limonene and alloocimene.[4,8] Linalool, an important building block in the synthesis of vitamin E and flavor compounds, is formed by thermal isomerization of 2-pinanol.[9] All of these isomerization reactions of bicyclic pinane-type compounds yield at least one acyclic

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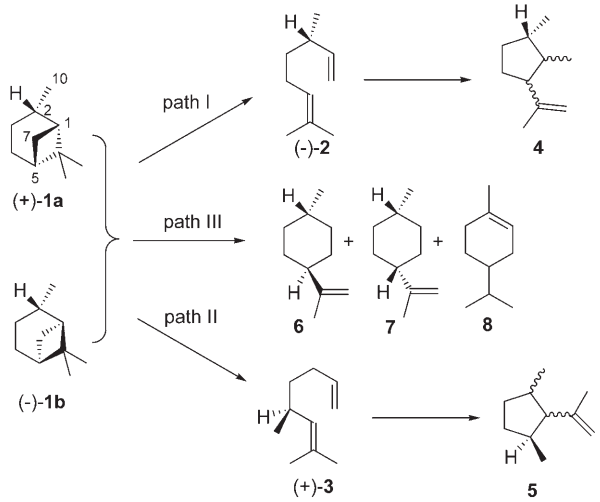


Scheme 1. Reaction network for the thermally induced rearrangement of (+)-*cis*- (**1a**) and (−)-*trans*-pinane (**1b**) including the main reaction pathways.

isomer. If the rearrangement includes biradical intermediates wherein at least one radical is resonance stabilized (e.g. α-pinene), the formation of *p*-menthane-type compounds is observed (e.g. limonene from α- or β-pinene).[4,5,8–11] The use of compounds without π-bonds in the reactive part of the bicyclic molecule (carbon atoms C^1, C^2 of **1**; Scheme 1)[12] leads to the formation of acyclic products only (e.g. **2** from **1** or linalool from 2-pinanol) by opening of the cyclobutane ring.[5,9] In most cases, the acyclic products undergo consecutive reactions leading to substituted cyclopentanes if 1,6-dienes are initially formed (e.g. **4**, **5** in Scheme 1).[4,5,9,13–15]

The products from the reaction network for the thermal rearrangement based on **1** are shown in Scheme 1. According to their general structure, they can be classified into three groups assigned by three reaction pathways. Two major reaction pathways (I and II) lead to the formation of β-citronellene (**2**)[4,5,13,16–20] and isocitronellene (**3**)[5,20] as the main products. Whereas the formation of **2** from **1** (path I) is thoroughly investigated, the formation of **3** (path III) is mentioned in only two references.[5,9] Evidently, most studies covering the pyrolysis of **1** were conducted by using the *cis*-isomer **1a** only as the starting material. The pyrolysis of **1a** leads to the formation of **2** and **3** with selectivities of 90 and 10%, respectively. *trans*-Pinane (**1b**) yields **2** and **3** also, but with a lower selectivity for **2** (60%) relative to **1a**.[5] Based on this knowledge, there seems to be an apparent oversight in not finding **3** in the product mixtures of most undertaken studies, despite its low but significant concentration. Additionally, as shown in Scheme 1, there is also a minor reaction pathway (path III) that yields monocyclic terpenes of the *p*-menthane-type (**6**–**8**).[4,19] Furthermore, consecutive reactions of **2** and **3** lead to the formation of substituted cyclopentanes **4** and **5**, respectively. To the best of our knowledge, the consecutive reaction after formation of **3** leading to **5** has not been investigated yet. Finally, a holistic approach of studying the reaction sketched in Scheme 1 in its entirety is much needed in light of the fact that differences in experimental setups, residence times, and analytical methods are most likely responsible for the oftentimes, contradicting yields, and compositions of the products reported in the literature.[4,5,13,19–21]

Herein, results concerning the thermal behavior of (+)-**1a** and (−)-**1b** and of their acyclic main products (−)-**2** and (+)-**3** in the gas-phase within a temperature range of 400–600 °C are presented. By using a combination of GC and NMR spectroscopic analytical techniques, the formation of side products and their structural elucidation is reported. The study of the thermal behavior of the title compounds (**1**–**3**) allows for the detailed description of their reaction behavior. Specifically, the stereochemical influence of the relative configuration of the methyl-group at C^2 on the reaction behavior of **1a** and **1b** in Scheme 1 is thoroughly investigated. Based on the composition of the liquid mixture of products from pyrolyses, conclusions on a number of details concerning the reaction mechanism are drawn.

Results and Discussion

Identification of the thermal isomerization products: To identify the products of pinane pyrolysis, comparative pyrolysis experiments of (+)-*cis*- (**1a**), (−)-*trans*-pinane (**1b**), (−)-β-citronellene (**2**), and (+)-isocitronellene (**3**) were conducted and the chromatograms are shown in Figure 1. Experiments were carried out in an electrically heated quartz reactor described previously by using oxygen-free nitrogen as the carrier gas.[10] Chromatograms depicted in Figure 1 resulted from experiments with the pure compounds listed on the right-hand side. Figure 1 reveals that **1a** and **1b** differ from each other with respect to the selectivity of the products formed. As described later, almost all compounds (**4**–**8**) were identified. Multiple assignments in the case of **4** and **5** refer to different diastereomers formed during the reaction and will be discussed later in this section. In each chromatogram of **1a** and **1b** there is one peak (marked as X) that has not been identified. These unidentified products occurred at temperatures (*T*) above 570 °C in amounts smaller than 3% and are, therefore, not relevant for the description of the thermal behavior of the investigated compounds that react at temperatures starting at 425 °C.

As can be seen from the chromatograms in Figure 1, the comparative pyrolysis experiments of **1a** and **1b** indicate that both pinane isomers yield **2** and **3** as the main products,

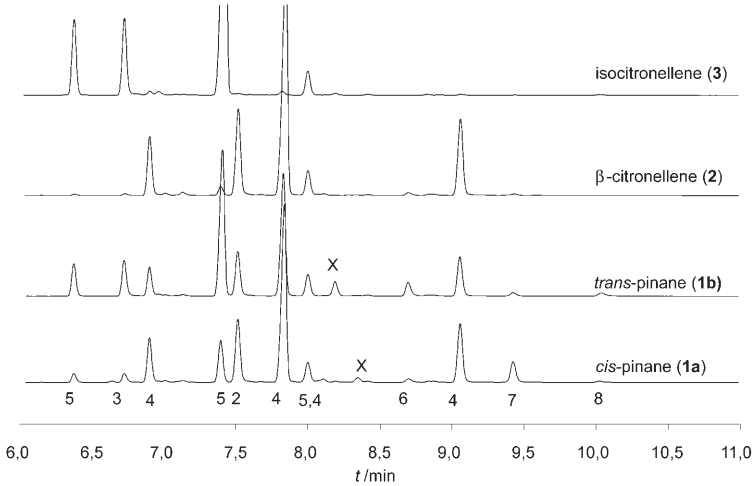
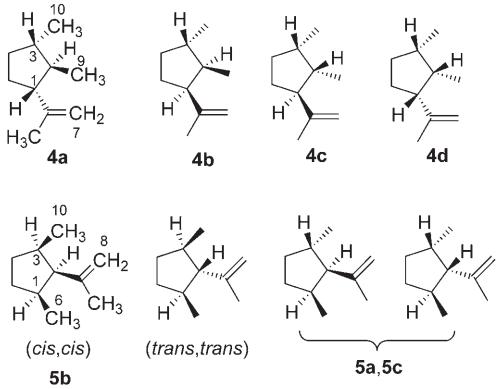


Figure 1. Chromatograms of the mixtures of pyrolysis products of the thermal isomerization of (+)-*cis*-pinane (**1a**), (−)-*trans*-pinane (**1b**), (−)-β-citronellene (**2**), and (+)-isocitronellene (**3**; *T*: 600 °C, 15 μL starting material, carrier gas: N_2, flow rate: 1.0 L min^{-1}, τ: 0.49 s; GC-FID; assigned compounds **4**–**8** are described in the text; X: unidentified compounds).

and the thermal treatment of these leads to the formation of further consecutive products (**4**, **5**; Scheme 1), arising from rearrangement reactions of the acyclic main products by ene-type cyclizations.[5,13,14,18,22] The chromatogram of the mixture of pyrolysis products obtained from **2** in Figure 1 shows that product **4** was formed exclusively from **2**, whereas **5** resulted from the thermal rearrangement of **3**. In addition, monocyclic products (*trans*-Δ8-*p*-menthene, **6**; *cis*-Δ8-*p*-menthene, **7**, and carvomenthene, **8**; Scheme 1) were found in the mixture of pyrolysis products of both pinane isomers. Structures were confirmed by using GCMS analysis upon comparison of their residence time and mass spectra with those from reference compounds. Compounds **6**–**8** were not present in either of the experiments carried out with **2** or **3** as the substrate, which indicated that they were produced directly from the rearrangement of **1a** and **1b**.

As shown in Figure 1, the thermal isomerization of **2** yields four different products of **4** which turned out to be diastereomers. According to their retention time (t) listed in Table 1 the diastereomers are named **4a**–**d**, starting with **4a** eluting at 6.9 min. Besides **4c**, all products were isolated by preparative GC. The determination of their structures and relative configurations was performed by a combination of different NMR spectroscopic techniques (^{1}H and ^{13}C NMR, HMBC, HSQC). Table 1 lists the most important data enabling structural elucidation of the four isomers (Scheme 2). Due to their nature as unsaturated cyclic hydrocarbons, determination of their structure is difficult because of overlapping chemical shifts (δ) in their proton NMR spectra. The signal sets for the substituents of the cyclopentane skeleton are suitable for structural interpretations, whereas the signals corresponding to the protons of cyclic CH or CH_2 majorities are not. The most conspicuous differences are found for the signal sets representing the $=C^7H_2$ protons, listed in Table 1. Depending on the relative orientation of the substituents at C^1 and C^2 (Scheme 2) either one or two signals occur. As found for **4b** and **4d** and indicated in Table 1, when both groups are placed on the same side of the ring (*cis* configuration) the proton spectrum shows two singlets, each singlet representing one proton.[22–26] Otherwise (*trans* configuration) the ^{1}H NMR spectrum shows only one signal representing both $=C^7H_2$ protons (**4a**, **4c**). Determination of the complete configuration by comparing δ and the coupling constants (J) for the CH protons of the cyclopentane skeleton was not possible due to severe signal overlapping. Nevertheless, considerations of the signal sets for the protons of the methyl substituents enable for complete elucidation. Data compiled in Table 1 (column 4) offers no significant change in δ and ^3J for the protons at C^9, but the differences in the chemical shifts of the protons at C^{10} are significant (column 5). The differences in δ for **4a** and **4b** (δ=0.16 ppm) is lower than for the differences towards **4d** (δ=0.38 and 0.22 ppm compared to **4a** and **4b**, respectively). Obviously, **4a** and **4d** differ extremely with regard to their stereochemistry, leading to the conclusion that **4a** has to have a *trans*,*trans*-configuration, whereas **4d** has to be *cis*,*cis*-configured (Table 1).[13,22] Determination in the case of **4b** an **4c** was possible upon consideration that only a total of four combinations of *cis* or *trans* are possible. Thus with **4b** containing a *cis*,*trans*-configuration, this leaves **4c** with the exact opposite configuration. Absolute configurations were assigned by comparing the enantiomeric excess (*ee*) of the products of **4** with the *ee* of **2** used herein, assuming that their formations are enantiospecific.[13,22,26]



Scheme 2. Configuration of the rearrangement products (**4a**–**d**, **5a**–**c**) obtained from the thermal isomerization of (−)-β-citronellene (**2**; Table 1) and (+)-isocitronellene (**3**), respectively.

Isomerization of **3** leads to the formation of three different products: **5a**, **5b**, and **5c** with residence times of 6.4, 7.4, and 8.0 min, respectively (Figure 1), which were separated by using preparative GC. Because of their low concentrations it was not possible to identify the structures for **5a** and **5c**, whereas the configuration of **5b** was elucidated based on ^{13}C and ^{1}H NMR spectroscopic data. The ^{13}C NMR spectrum reveals seven resonances, allowing for the conclusion that the molecule has a highly symmetrical structure (all-*cis*- or all-*trans*-**5**; Scheme 2). The carbon atoms C^1/C^3, C^4/C^5, and C^6/C^{10} showed identical δ values, which was proven by

Table 1. NMR spectroscopic data for structural elucidation of the rearrangement products **4a**–**d** (Scheme 2).

		^{1}H NMR spectroscopic signal for protons at C^iH_x [ppm][b]				
Product	t [min][a]	$=C^7H_2$	C^9H_3	$C^{10}H_3$	Relative orientations[c]	Absolute configuration[d]
4a	6.9	4.62 (s, 2H)	0.90 (d, ^3J=5.0 Hz)	0.81 (d, ^3J=4.8 Hz)	*trans*,*trans*	1*R*,2*R*,3*S*
4b	7.8	4.70 (s, 1H), 4.57 (s, 1H)	0.92 (d, ^3J=5.0 Hz)	0.65 (d, ^3J=5.2 Hz)	*cis*,*trans*	1*S*,2*R*,3*S*
4c	8.0	–[e]	–[e]	–[e]	*trans*,*cis*	1*S*,2*S*,3*S*
4d	9.1	4.74 (s, 1H), 4.58 (s, 1H)	0.87 (d, ^3J=5.1 Hz)	0.43 (d, ^3J=5.3 Hz)	*cis*,*cis*	1*R*,2*S*,3*S*

[a] Retention time from Figure 1. [b] c.f. Scheme 2. [c] Relative orientations of the isopropenyl group at C^1 (1st designation) and the methyl-group at C^3 (2nd designation) towards the methyl group at C^2 (Scheme 2). [d] Based on the assumption that the formation occurs enantiospecifically from (−)-(3*S*)-β-citronellene (**2**; cf. following section). [e] Not enough material for NMR spectroscopic measurement.

the ^{1}H NMR spectroscopic data, which showed identical δ and ^3J for the protons at C^6 and C^{10}. In analogy to **4b** and **4d** (Table 1) the proton NMR spectrum showed two singlets for the $=CH_2$ group in **5**, which enabled the conclusion that the isopropenyl group is located *cis* to either the methyl group at C^1 or C^2. Combination of these results leads to the conclusion that the all-*cis* configuration is the correct one for **5b**. The ^{13}C NMR spectra of **5a** and **5c** showed ten signals and both compounds have a similar fragmentation pattern (EIMS). Therefore, their configuration had to be either *cis*,*trans* or *trans*,*cis*, whereby an assignment was not possible.

Thermal behavior of *cis*- and *trans*-pinane: Studies of the thermal behavior of **1a** and **1b** in pyrolysis experiments were carried out within a temperature range of 400–600 °C for the pure compounds and for an equal mixture of **1a** and **1b**. In Figure 2, the dependency of pinane conversion (X) versus the reaction temperature (T) is depicted, revealing that **1a** is more reactive than **1b**. The T for equal conversions of **1a** and **1b** is shifted about 40° to higher values in the case of **1b** relative to the *cis* isomer.[5] The thermal treatment of the equal mixture of **1a** and **1b** also shown in Figure 2 confirms this trend because the curve of conversion corresponds with the behavior of the pure compounds. The conversion of the mixture is mainly affected by **1a** at lower temperature, whereas in experiments above 525 °C, the influence of **1b** on the curve is significantly higher. At reaction temperatures lower than 400 °C, neither for **1a** nor **1b** are detectable conversions observed, whereas at temperatures higher than 600 °C, the conversions for both are complete, and besides isomerization further decomposition of the $C_{10}H_{18}$ hydrocarbons to lower weight compounds takes place.

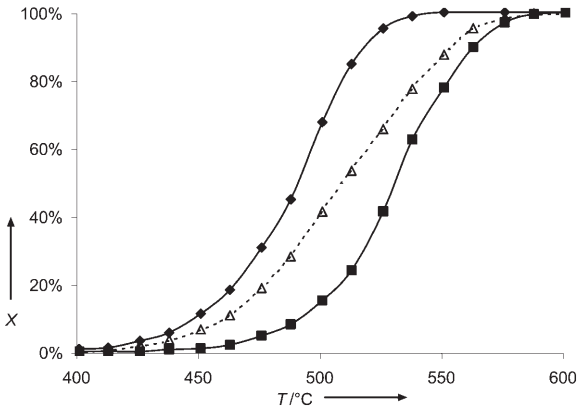


Figure 2. Conversion (X) of (+)-*cis*-pinane (**1a**; ◆), (−)-*trans*-pinane (**1b**; ■), and a mixture of **1a** and **1b** (**1a**/**1b** = 0.94; △) depending on the reaction temperature (15 μL starting material, carrier gas: N_2, flow rate: 1.0 L min^{-1}, τ: 0.47–0.61 s).

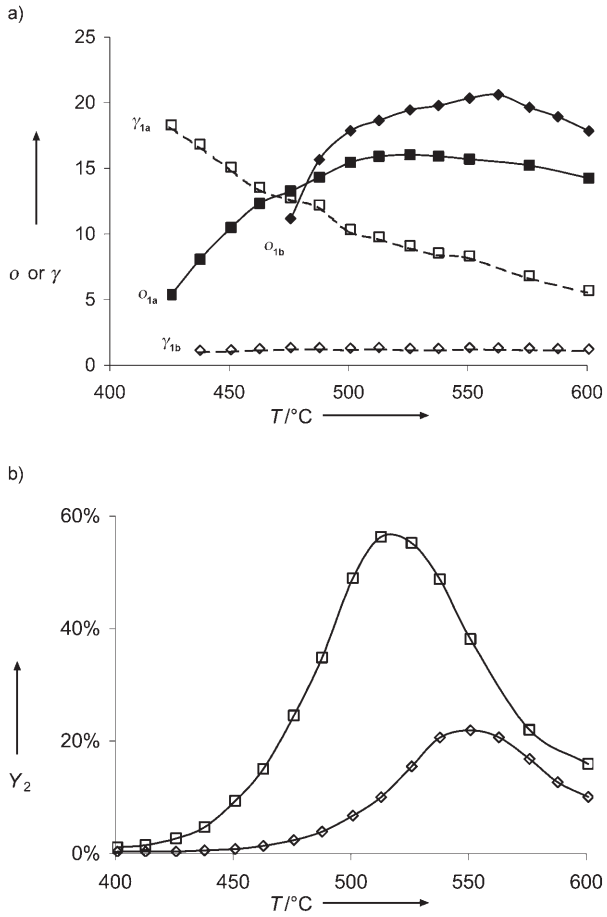


Figure 3. a) Ratio of the formation of acyclic to monocyclic products (o; [Eq. (1)]) and ratio of (−)-β-citronellene (**2**) to (+)-isocitronellene (**3**; γ; [Eq. (2)]) depending on reaction temperature (T) for the pyrolysis of (+)-*cis*- (**1a**, ■) and (−)-*trans*-pinane (**1b**, ◆; 15 μL starting material, carrier gas: N_2, flow rate: 1.0 L min^{-1}, τ: 0.47–0.61 s). b) Yield of (−)-β-citronellene (**2**; Y_2) depending on reaction temperature (T) for the pyrolysis of (+)-*cis*- (**1a**, □) and (−)-*trans*-pinane (**1b**, ■; 15 μL starting material, carrier gas: N_2, flow rate: 1.0 L min^{-1}, τ: 0.47–0.61 s).

Besides their behavior concerning the overall conversion, **1a** and **1b** differ in selectivity (S). Figure 3a and b illustrate the dependence of overall yielded products on pyrolysis temperature T, classified according to the reaction pathways depicted in Scheme 1. Three different classes of major products are formed from **1a** and **1b**: (−)-β-citronellene (**2**; path I), (+)-isocitronellene (**3**; path II), and monocyclic products (**6**–**8**; path III). The ratio, o, of paths I plus II (acyclic products) and path III (**6**–**8**) is expressed by Equation (1), whereby o considers only the initial reactions from **1**. Due to this fact, side products (**4**, **5**) have to be considered also. Despite the fact that **6**–**8** are formed in low amounts only (overall $<6\%$), o is higher than 1.0 for both **1a** and **1b** increasing with rising temperatures from 5.2 up to 14.1 (425–600 °C) and from 11 to 17.7 (475–600 °C), respectively (Figure 3a). After reaching a maximum at 512 °C (15.9) and at 550 °C (20.5), o drops slightly in favor of the formation of **6**–**8**. The maxima correspond to the maximal overall yields of the acyclic isomers (Figure 3b). Exemplary for **2**, Figure 3b expresses that the yields of **2** pass through maxima at 512 and 550 °C for isomerization of **1a** and **1b**, respectively. With in-

creasing temperature, the amount of rearranged products formed from the acyclic primary products increases.

$$\sigma = \frac{\text{path I} + \text{path II}}{\text{path III}} = \frac{[2] + [3] + [4] + [5]}{[6] + [7] + [8]} \quad (1)$$

$$\gamma = \frac{\text{path I}}{\text{path II}} = \frac{[2] + [4]}{[3] + [5]} \quad (2)$$

Additionally, data recorded in Figure 3a illustrate the ratio of reaction pathways I and II (γ) expressed by Equation (2), again including side reactions leading to **4** and **5**. The differences in γ between **1a** and **1b** are significant. It is evident from Figure 3a that $\gamma_{\mathbf{1a}}$ decreases linearly from 18.2 at 425 to 5.5 at 600 °C, whereas $\gamma_{\mathbf{1b}}$ remains flat between 1.0–1.2 over the investigated temperature range, which is a clear indicator for the similarities of the transition states leading to **2** or **3** (c.f. following section). Pyrolyses of the *trans*-isomer **1b** leads to lower selectivities of **2** in favor of **3**.

The formation of **2** and **3** from **1** proceeds as a highly enantioselective reaction. Table 2 lists the enantiomeric excess (*ee*) expressed by Equation (3) for the product mixtures from pyrolysis of both **1a** and **1b** at different temperatures. The *ee* remains constant for both starting materials within the temperature range investigated (conversion range, respectively). In contrast to α-pinene, no racemization occurred.[5,8] The configuration of the optically active acyclic reaction products (−)-**2** and (+)-**3** is determined by the absolute configuration of the starting material (Table 2).[5] Both almost optically pure diastereomers (+)-**1a** and (−)-**1b** used herein were *S*-configured at C^2 and the same configurations are found for the chiral centers of the formed products ((−)-**2**, (+)-**3**) with nearly identical *ee* (Table 2, Scheme 2).[5,17]

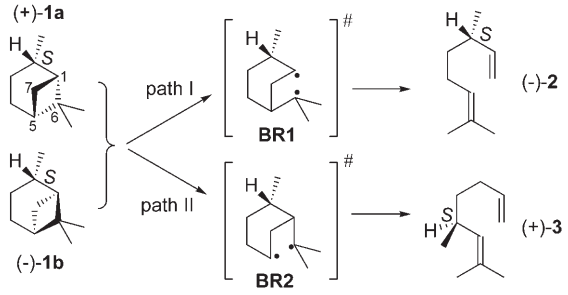
Table 2. Enantiomeric excess (*ee*; [Eq. (3)]) for (+)-*cis*- (**1a**) and (−)-*trans*-pinane (**1b**) and of the acyclic products ((−)-**2**, (+)-**3**) formed by thermal rearrangement of **1**.[a]

Entry	Substrate[b]	T [°C]	X [%][c]	$ee_{\text{substrate}}$ [%]	$ee_{(-)\text{-}\mathbf{2}}$ [%]	$ee_{(+)\text{-}\mathbf{3}}$ [%]
1	(+)-**1a**	475	31	94	93	98
2	(+)-**1a**	500	68	92	93	95
3	(+)-**1a**	525	95	100[d]	94	95
4	(−)-**1b**	475	5	93	96	97
5	(−)-**1b**	500	15	94	94	93
6	(−)-**1b**	525	41	92	94	94

[a] *ee* values were determined by enantioselective GC analysis by using a Supelco Beta-DEX™ 120 column from pyrolysis experiments with the substrates listed. [b] Initial *ee* values of (+)-**1a** and (−)-**1b** are 94 and 93%, respectively. [c] Conversion of substrate. [d] Due to high conversion, the signal for (−)-**1a** was below the detection limit.

$$ee_{(-)} = \frac{(-)-(+)}{(-)+(+)} \quad (3)$$

Reaction mechanisms for the primary pyrolysis reactions: Due to their different structures, the acyclic (**2**, **3**) and monocyclic products (**6**–**8**) formed from **1** seem to arise from different reaction pathways. Whereas **2** and **3** seem to arise from a fragmentation of the cyclobutane ring in **1** (path I and II; Scheme 3), the formation of *p*-menthenes **6**–**8** can be explained by using a biradical pathway combined with H-shift reactions[1,5] according to the formation of limonene from α- or β-pinene (path III; Scheme 5).[4,5,8–11]

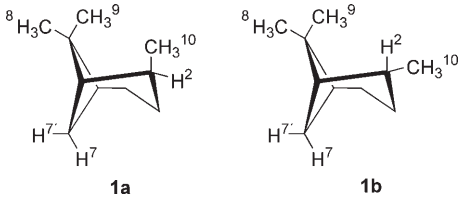


Scheme 3. Formation of (−)-β-citronellene (**2**; path I) and of (+)-isocitronellene (**3**; path II) from (+)-*cis*- (**1a**) and (−)-*trans*-pinane (**1b**).

Two possible mechanisms for the fragmentations of four-membered rings (cyclobutane, oxetane) are discussed in the literature.[27,28] A concerted mechanism of cyclobutane fragmentation has to proceed by a 4-π-electron-containing antiaromatic transition state. According to the Woodward–Hoffmann rules, those (retro)-[2+2]-cycloadditions are thermally forbidden reactions.[29] Nevertheless, some reports in the literature show some examples of rigid cyclobutanes, the thermal induced fragmentations of which seem to proceed as a thermally forbidden retro-[2+2]-cycloaddition.[28] The second and more plausible explanation for the formation of **2** and **3** from **1** involves a stepwise mechanism via biradical intermediates. Scission of C^1–C^6 or C^5–C^6 carbon–carbon bonds in either **1a** or **1b** yielded biradicals **BR1** and **BR2**, respectively (Scheme 3). Consecutive ring opening in these reaction intermediates leads to the formation of **2** and **3**. Nevertheless, there is one argument counting against a biradical route: the absence of a double bond at C^2 in **1** does not allow for stabilization of a formed 1,4-biradical. Without the presence of functional groups that can stabilize a free radical by conjugation (e.g. C=C in α- or β-pinene[4,8,10] or C=O in nopinone,[4,30]) the lifetime of the formed biradical is very short and the barrier of activation is high. Therefore, a decision as to which of the two routes (concerted or stepwise) leads to the detected acyclic main products requires further investigations focused on both kinetic experiments[31] and ab initio calculations[32] of the presumptive transition states.

Results reveal that **1a** and **1b** differ in both reactivity (Figure 2) and selectivity concerning the formation of **2** and **3** (Figure 3). A previous study suggests that the interaction of the C^2 methyl group with one of the two methyl groups at C^6 results in a weakening of the C^1–C^6 bond for the *cis*-isomer (**1a**), which leads to a higher reactivity in the active part of the molecule.[5] This behavior would allow for the ex-

planation of the higher reactivity of **1a** and the higher selectivity for the formation of **2** relative to γ_{1b} (Figure 3a). Apparently, the activation energies for the two possible transition states (Scheme 3) are influenced by the relative configuration of the C^2 methyl group. NMR NOE spectroscopic experiments were conducted to answer this question by detecting magnetic dipole interactions between protons through space if the distance between the protons is lower than approximately 5 Å. Scheme 4 illustrates the ground-

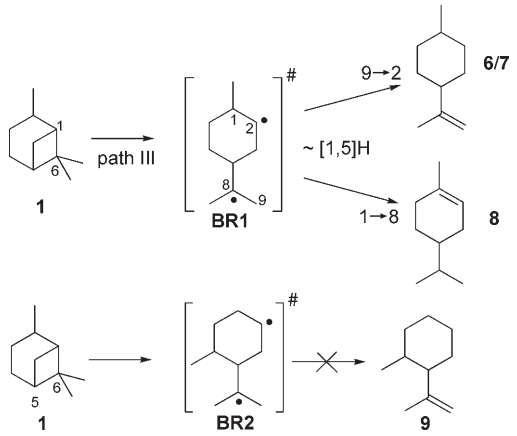


Scheme 4. (+)-*cis*- (**1a**) and (−)-*trans*-pinane (**1b**; superscript numbers refer to the numbering of nH^{1-10} listed in the ^1H NMR spectroscopic data (see the Experimental Section).

state conformation of both pinane isomers. If the conjectures would be correct, a NOE effect is to be expected between H−C^{10} and H−C^9 or H−C^2 and H−C^9 for **1a** and **1b**, respectively.

1D NOE experiments with pure **1a** showed no interaction between the protons at C^{10} and C^9 (Scheme 4), but a NOE contact between the proton H−C^7 and H−C^2 was observed. This contact was not detected in the case of **1b**, whereby an interaction of H−C^7 and H−$C^{7'}$ with H−C^{10} was observed. Therefore, the conjectures concerning an interaction between H^{10} and H^9 in case of **1a** could not be confirmed. Nevertheless, the results allow for the conclusion that the *trans* geometry is advantageous for stabilization of the molecule due to attractive interactions with other protons (H−C^7, H−$C^{7'}$, H−C^{10}), similar to the diaxial attraction in *cis*-1,3-disubstituted cyclohexanes. Therefore, **1b** is thermally the more stable molecule.

As shown in Figures 1 and 3b, monocyclic products **6–8** were found in the reaction mixtures of both pinanes in low amounts besides the acyclic main products (**2**, **3**). There are reports in the literature on the formation of similar *p*-menthane-type products in which α- or β-pinene is pyrolyzed. Both yield limonene and ψ-limonene, the latter as an additional monocyclic reaction product from the thermal isomerization of β-pinene.[4,8,10,33] According to the formation of **2** from **1a** and **1b**, the initial formation of a 1,4-carbon-centered biradical (**BR1**; cf. Scheme 3) by bond breakage between C^1 and C^6 is necessary for the side-reaction pathway leading to **6–8**. *p*-Menthenes **6–8** are formed by [1,5]H-shifts, in which the hydrogen migration from C^9 to C^2 yields those isomers with the exocyclic double bond. The reaction route by a hydrogen shift from C^1 to C^8 leading to **8** is suppressed in favor of the formation of **6** and **7** due to the higher selectivity (cf. Figure 1). Compound **1a** yields preferably the *cis*-isomer (**7**), whereas **1b** leads to the formation



Scheme 5. Formation of *cis*-/*trans*-Δ8-*p*-menthene (**7**/**6**) and Δ1(2)-*p*-menthene (**8**) from pinane (**1**; path III).

of **6** (Scheme 5, Figure 1). Because of the fact that the biradical formed from **1** did not have any influence on the configuration at C^4, the stereochemistry of the products is controlled by the configuration of the starting material, which was almost enantiomerically pure (+)-**1a** (*ee*: 94%) and (−)-**1b** (*ee*: 93%).

It has to be pointed out that **6–8** are formed with an accumulated overall selectivity of 6% only. Therefore, the additional reaction channel leading to **6–8** from **BR1** is a minor reaction pathway. Similar products from the *o*-menthene type (e.g. **9**) that might yield from a respective reaction channel of **BR2** (Scheme 5) have not been identified. With respect to these findings, pyrolysis of **1a** and **1b** initially passes through two different biradicals, in which subsequent fragmentation leads to **2** and **3**. The formation of monocyclic primarily formed products **6–8** is due to a minor reaction channel based on one of the two biradicals.

Thermal behavior of β-citronellene and isocitronellene: After passing through a maximum, the overall yields of the acyclic products drop with increasing temperature and the formation of consecutive products is observed (**4**, **5**; Figures 1, 3a, and 3b). To study the formation of these products, pyrolysis experiments with **2** and **3** were carried out in a temperature range from 400–600 °C. The comparison of the conversions of **2** (X_2; pointed line and empty symbols) is shown in Figure 4, that is, resulting from pyrolysis of the pure compound with those resulting from the thermal isomerization of **1a** and **1b**, while changing the reaction temperature *T*. The high accordance for X_2 of pure **2** and those from the reaction mixtures reveals the similarities between the three independent pyrolysis experiments of **1** (Figure 4). Additionally, Figure 4 illustrates the dependency of selectivity for the rearranged products (S_4) and *T*, revealing **4b** (*cis*, *trans*-**4**, Table 1, Scheme 2) as the main product from rearrangement of **2**. It is shown that the selectivities for the formation of **4b** and for **4d** drop in favor of the formation of the two other minor isomers (**4a**, **4c**). Whereas the decrease in the case of **4b** is linear, the selectivity profile for the *cis*,*cis*-isomer (**4d**) passes through a maximum.

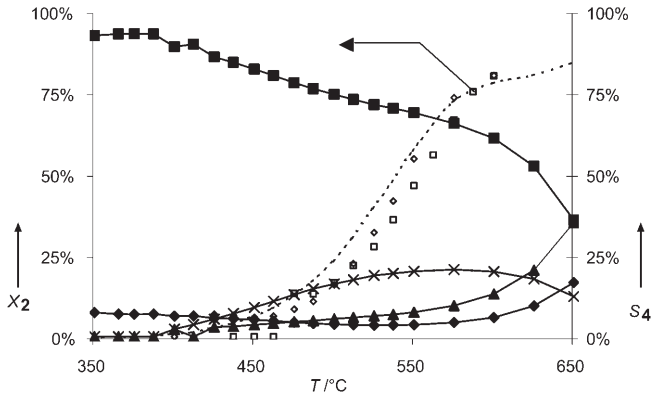


Figure 4. Conversion of (−)-β-citronellene (**2**; X_2) after pyrolysis of **1a**, **1b**, and direct conversion of **2** as a function of temperature. Selectivities (S_4) of rearranged products (**4a–c**) are shown on the right *y* axis. (15 μL starting material, carrier gas: N_2, flow rate: 1.0 L min^{-1}, τ: 0.47–0.66 s). -----: *X*; ◇: *X* from **1a**; □: *X* from **1b**; ▲: S_{4a}; ■: S_{4b}; ◆: S_{4c}; ×: S_{4d}.

Many examples of 1,6-dienes forming cyclization products as observed for **2** and **3** are reported in the literature.[5,13–16,34,35] For instance, the thermal treatment of linalool yields 1,2-dimethyl-3-isopropenylcyclopentanol,[9,14,24] and consecutive reactions of the acyclic main product from the pyrolysis of nopinone lead to the formation of 2-methyl-3-isopropenylcyclopentanone.[4,30] Generally, 1,6-dienes with hydrogen in the α position of any of the two double bonds are able to form substituted cyclopentanes. The cyclization of 1,7-dienes with α hydrogen lead to the formation of substituted cyclohexenes, whereas the ring formation of systems with fused rings failed.[34,35] The cyclization proceeds by a concerted ene-type reaction (Scheme 6).[36] It is obvious, that the configuration of the chiral center in **2** remains unchanged during the reaction. Therefore, the *ee* of the desired products is the same as for the initial **2**. Almost enantiomerically pure (−)-**2** used herein yielded cyclization products **4a–d** with a 3*S* configuration (Table 1, Scheme 2). The configurations of C^1 and C^2 in **4** (and, therefore, also their relative configurations) are attributed to the different presumptive transition states (Scheme 6). Due to the absence of repulsive 1,3-diaxial interactions of methyl substituents, intermediates leading to **4b** and **4d** are the most stable ones and **4b** and **4d** are, therefore, the major products obtained from the isomerization of **2** (Figure 4).[13,37]

In Figure 5, the dependency of the conversion of **3** (X_3) with the pyrolysis temperature, *T*, for the pure compound and for **3** from pyrolysis of **1a** and **1b** is illustrated. With increased temperatures, the increased X_3 raises the yields of the rearranged products (**5a–c**). The accordance between pyrolysis of pure **3** and **3** obtained after pyrolysis of the two pinane isomers (**1a**, **1b**) is not as high as for **2** shown in Figure 4. In contrast to the formation of rearrangement products yielded from **2**, data shown in Figure 5 suggest that one major rearrangement product (**5b**) is formed from **3** the selectivity of which remains constant when increasing the temperature. At reaction temperatures above 550 °C, the selectivity drops slightly in favor of the other rearrangement products. The rate of **5a**/**5b** and of **5c**/**5b** is about 0.08 and 0.085, respectively. According to other 1,6-dienes (**2**, myrcene, linalool) the formation of **5** also proceeds by ene-type cyclization (Scheme 7).[4,5,9,13,15,34,35] The presumptive transition state leading to the formation of **5b** reveals no repulsive diaxial interactions of methyl groups, explaining the high selectivity.

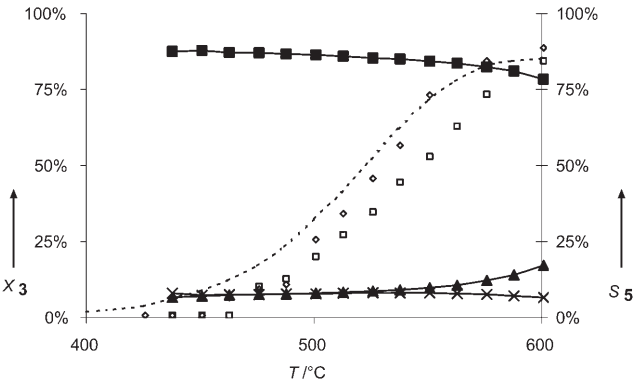
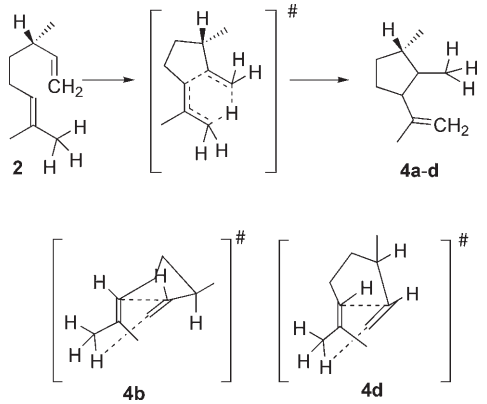
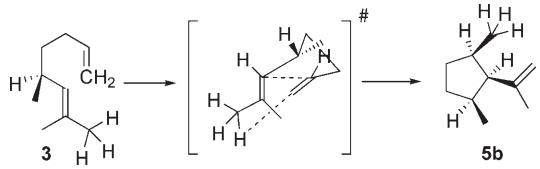


Figure 5. Conversion of (+)-isocitronellene (**3**, X_3) after pyrolysis of **1a**, **1b**, and direct conversion of **3** as a function of temperature. Selectivities (S_5) of rearranged products (**5a–c**) are shown on the right *y* axis (15 μL starting material, carrier gas: N_2, flow rate: 1.0 L min^{-1}, τ: 0.47–0.61 s). -----: *X*; ◇: *X* from **1a**; □: *X* from **1b**; ▲: S_{5a}; ■: S_{5b}; ×: S_{5c}.



Scheme 6. Formation of rearrangement products (**4**) obtained from the thermal isomerization of (−)-β-citronellene (**2**) and presumptive intermediates for the formation of **4b** and **4d**.



Scheme 7. Formation of the main rearrangement product **5b** obtained from the thermal isomerization of (+)-isocitronellene (**3**) by ene cyclization.

Conclusion

Gas-phase pyrolysis experiments of (+)-*cis*- (**1a**), (−)-*trans*-pinane (**1b**), (−)-β-citronellene (**2**), and (+)-isocitronellene (**3**) in an electrically heated flow-type reactor were carried out to study the thermal rearrangement of the title compounds (Scheme 1). It was shown that **1a** and **1b** differ tremendously in both reactivity and product selectivity, revealing **1a** as the more reactive compound. Whereas the *cis*-isomer of **1** yields **2** as the main component (selectivity: 90%), thermal isomerization of **1b** leads to the formation of **2** and **3** with a ratio of 55:45. It was shown that the acyclic main products are presumably formed by a highly enantioselective fragmentation of the cyclobutane ring in **1**. The absolute configuration of the products is determined by the configuration on C^2 of the starting material. In addition to **2** and **3**, monocyclic *p*-menthene-type products (**6–8**) are formed from both **1a** and **1b** with an overall selectivity of 6%. Apparently, the reactions responsible for the formation of products **6–8** pass through the same biradical transition states that are also responsible for the formation of **2**.

Stand-alone pyrolysis experiments of **2** led to the identification of consecutive reaction products (**4a–d**, Schemes 1 and 2), the relative configurations of which were determined by using NMR spectroscopic and GCMS techniques. Ene cyclization leads to the formation of **4**, whereas the desired transition states control the isomer distribution, yielding **4b** (*cis*,*trans*-isomer) as the main product. For the first time, the thermal isomerization of **3** was investigated, revealing that according to the formation of **4** from **2** products **5a–c** are formed by ene cyclization.

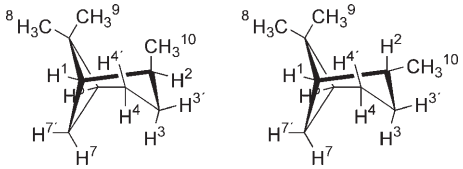
Experimental Section

General remarks: (1*R*,2*S*,5*R*)-*cis*-pinane ((+)-**1a**; purity: 99%, *ee*: 94%), (1*S*,2*S*,5*S*)-*trans*-pinane ((−)-**1b**; purity: 99%, *ee*: 93%), (3*S*)-β-citronellene ((−)-**2**; purity 95%, *ee*: 95%), and (5*S*)-isocitronellene ((+)-**3**; purity: 99%, *ee*: 98%) were purchased from Fluka and were used without further purification. Purity was determined by capillary gas chromatography. Ethyl acetate was used for the dilution of liquid pyrolysis products. All reported yields, selectivities, conversions, or any other parameter (*ee*, *o*, γ) and point data in the figures are based on mean values of at least two independent experiments.

Analyses were carried out in a 6890 Series GC and 5890 Series II/5972 Series MSD GC from Agilent Technologies. Products were identified by comparing either retention time and/or mass spectra of pure reference compounds. GC-FID: (HP 5, 30 m × 0.32 mm × 0.25 μm, H_2–5 psi, program): 35 °C (hold: 1 min), 4 K min^{-1} up to 80 °C, 4.5 K min^{-1} up to 90 °C, 35 K min^{-1} up to 280 °C (hold: 3 min), injector temperature: 250 °C, detector temperature: 280 °C. GC-MSD: (HP 5, 30 m × 0.32 mm × 0.25 μm, He −7 psi, program): 55 °C (hold 1 min), 5 K min^{-1} up to 150 °C, 20 K min^{-1} up to 280 °C (hold: 5 min), injector temperature: 280 °C, EI. NMR spectra were recorded by using a Bruker AV-400 spectrometer.

Enantiomeric excess values were determined with a permethylated β-cyclodextrine column (Supelco Beta-Dex 120, 30 m × 0.25 mm × 0.25 μm). Analyses were carried out with a HP 6890: H_2–12 psi, program: 68 °C (hold: 13.12 min), 25 K min^{-1} up to 240 °C (hold: 10 min), split ratio: 3.4, injector temperature: 240 °C, detector temperature: 280 °C.

Structural elucidation of *cis*- (1a) and *trans*-pinane (1b): NMR spectra of **1a** and **1b** in $CDCl_3$ were recorded on a Bruker DRX-600 system (^{13}C: 150.9, ^{1}H: 600.1 MHz) equipped with a 5 mm TBI probe head in 5 mm tubes at 27 °C. The referring numbering of the protons in both **1a** and **1b** is described in Scheme 8, wherein the superscript numbers refer to the superscript numbers of nH$^{1-10}$ listed below. The assignments of the chemical shifts to the desired protons were accomplished by using HSQC and



Scheme 8. (+)-*cis*- (**1a**) and (−)-*trans*-pinane (**1b**; superscript numbers refer to the numbering of nH$^{1-10}$ listed in the ^{1}H NMR spectroscopic data (see the Experimental Section).

HMBC techniques (reference ^{13}C: [D]$CHCl_3$ = 77.0 ppm; ^{1}H: TMS intern = δ = 0 ppm). 1D NOESY experiments (double gradient spin echo with selective pulse) were carried out by using the following parameters: mixing time: 800 ms, repetition time: 3.7 s, selective 180° pulse ("sinc"-profile), duration: 180 ms, excitation band width: ca. 20 Hz.

(1*R*,2*S*,5*R*)-2,6,6-Trimethylbicyclo[3.1.1]heptane ((+)-*cis*-pinane; (+)-1a): *ee* = 94%; ^{1}H NMR (600.1 MHz, [D]$CHCl_3$, 27 °C, TMS): δ = 2.31 (m, 1H^7), 2.13 (m, 1H^2), 1.95 (m, 1H^3), 1.93 (m, 1H^4), 1.87 (m, 1H^5), 1.82 (m, 1H$^{4'}$), 1.76 (td, 1H^1, $^3J_{1\to7}$ = 6.8, ^3J = 2.2 Hz), 1.42 (m, 1H$^{3'}$), 1.18 (s, 3H^8), 1.02 (s, 3H^9), 1.00 (d, 3H^{10}, $^3J_{10\to2}$ = 7.3 Hz), 0.86 ppm (d, 1H$^{7'}$, $^2J_{7'\to7}$ = 9.4 Hz); NOE-contacts: H−C^7→H−C^2, H−C^2→H−C^1, no contact H−C^7→H−C^{10} and H−C^7→H−C^9; ^{13}C NMR (150.9 MHz, [D]$CHCl_3$, 27 °C, TMS): δ = 48.1 (CH), 41.4 (CH), 38.8 (C), 35.9 (CH), 33.9 (CH_2), 28.3 (CH_3), 26.5 (CH_2), 23.8 (CH_2), 23.3 (CH_3), 22.8 ppm (CH_3); MS (70 eV): *m*/*z* (%): 138 (2) $[M]^+$, 123 (32) $[C_9H_{15}]^+$, 96 (33) $[C_7H_{12}]^+$, 95 (100) $[C_7H_{11}]^+$, 83 (46 $[C_6H_{11}]^+$, 82 (61) $[C_6H_{10}]^+$, 81 (57) $[C_6H_9]^+$, 67 (59) $[C_5H_7]^+$, 55 (58) $[C_4H_7]^+$.

(1*S*,2*S*,5*S*)-2,6,6-Trimethylbicyclo[3.1.1]heptane ((−)-*trans*-pinane; (−)-1b): *ee* = 93%; ^{1}H NMR (600.1 MHz, [D]$CHCl_3$, 27 °C, TMS): δ = 2.06 (m, 1H^2, ^3J = 7.4 Hz), 2.00 (dt, 1H^7, $^2J_{7\to7'}$ = 9.9, $^3J_{7\to1}$ = 5.9 Hz), 1.84 (m, 1H^5), 1.75 (m, 1H^4), 1.72 (m, 1H^4), 1.65 (m, 1H^3), 1.61 (t, 1H^1, ^3J = 6.0 Hz), 1.33 (d, 3H$^{7'}$, $^2J_{7'\to7}$ = 10.0 Hz), 1.21 (m, 1H$^{3'}$), 1.19 (s, 3H^8), 0.85 (d, 1H^{10}, $^3J_{10\to2}$ = 6.7 Hz), 0.82 ppm (s, 3H^9); NOE contacts: H−C$^{7'}$→H−C^{10}, H−C^7→H−C^{10}, no contact H−C^7→H−C^2; ^{13}C NMR (150.9 MHz, [D]$CHCl_3$, 27 °C, TMS): δ = 47.6 (CH), 40.9 (CH), 39.5 (C), 29.3 (CH), 26.8 (CH_3), 24.6 (CH_2), 23.9 (CH_2), 23.0 (CH_2), 21.6 (CH_3), 20.9 ppm (CH_3); MS (70 eV): *m*/*z* (%): 138 (2) $[M]^+$, 123 (35) $[C_9H_{15}]^+$, 96 (50) $[C_7H_{12}]^+$, 95 (100) $[C_7H_{11}]^+$, 83 (73) $[C_6H_{11}]^+$, 82 (62) $[C_6H_{10}]^+$, 81 (67) $[C_6H_9]^+$, 67 (62) $[C_5H_7]^+$, 55 (67) $[C_4H_7]^+$.

Pyrolysis experiments: The investigated terpenes were pyrolyzed at a temperature range of 400 to 600 °C. Dilution gas pyrolysis experiments were carried out in an electrically heated quartz tube of 50 cm length and with a pyrolysis zone of approximately 20 cm, by using apparatus reported previously.[10] In all experiments, oxygen-free nitrogen with a purity of 99.999% was used as the carrier gas. The starting material (15 μL) was introduced into a quartz ladle at the top part of the pyrolysis apparatus by using a glass syringe (50 μL). The starting material was carried along with the nitrogen stream into the reactor. Vaporization of the starting material was supported by heating the ladle to 250 °C with a hot blast. Pyrolysis products were collected in a cold trap (liquid nitrogen) and were dissolved in 1.5 mL of ethyl acetate. The liquid products obtained were analyzed by GC-FID and GCMS.

Structural elucidation of pyrolysis products: For structural elucidation of the reaction products from pyrolysis of β-citronellene (**2**) and isocitronellene (**3**), 1.5 mL of the desired substrates (30 × 50 μL) were pyrolyzed at a temperature of 550 °C with a flow rate of 0.8 L min^{-1} (τ = 0.62 s). The collected products were dissolved in 3 mL of ethyl acetate. These product mixtures were separated by using preparative GC (packed column,

10 m × 14 mm, coverage: 20% SE-54, support: Vol. A4 60–80 mesh, inlet temperature: 280 °C, detector temperature: 280 °C, carrier gas: N_2, flow rate: 618 mL min^{-1}, injection volume: 50–57 μL, number of cycles: 20) and the isolated fractions were analyzed and identified by using ^{1}H and ^{13}C NMR spectroscopy.

(*S*)-3,7-Dimethyl-1,6-octadiene ((−)-β-citronellene; (−)-2): *ee* = 94%; ^{1}H NMR (400 MHz, [D]$CHCl_3$, 25 °C, TMS): δ = 5.61 (m, 1H), 5.03 (t, 1H, ^3J = 1.4 Hz), 4.86 (m, 2H), 2.06 (m, 1H), 1,89 (m, 2H), 1.61 (s, 3H), 1,52 (s, 3H), 1.23 (m, 2H), 0.92 ppm (d, 3H, ^3J = 6.7 Hz); ^{13}C NMR (100 MHz, [D]$CHCl_3$, 25 °C, TMS): δ = 143.8 (=CH), 130.3 (=C), 123.6 (=CH), 111.4 (=CH_2), 36.3 (CH), 35.7 (CH_2), 24.7 (=C−*E*-CH_3, =C−CH_2); 19.1 (CH_3), 16.7 (=C−*Z*-CH_3); MS (70 eV): *m*/*z* (%): 138 (20) $[M]^+$, 123 (24) $[C_9H_{15}]^+$, 95 (83) $[C_7H_{11}]^+$, 82 (91) $[C_6H_{10}]^+$, 81 (52) $[C_6H_9]^+$, 69 (84) $[C_5H_9]^+$, 67 (100) $[C_5H_7]^+$.

(*S*)-5,7-Dimethyl-1,6-octadiene ((+)-isocitronellene; (+)-3): *ee* = 95%; ^{1}H NMR (400 MHz, [D]$CHCl_3$, 25 °C, TMS): δ = 5.79 (m, 1H, ^3J = 10.0, ^3J = 16.8, ^3J = 6.8 Hz), 4.97 (dd, 1H, ^3J = 17.2, ^2J = 1.6 Hz), 4.91 (d, 1H, ^3J = 10.0 Hz), 4.86 (d, 1H, ^3J = 9.6 Hz), 2.33 (m, 1H), 2.00 (m, 2H), 1.67 (s, 3H), 1.59 (s, 3H), 1.28 (m, 2H), 0.90 ppm (d, 3H, ^3J = 6.6 Hz); ^{13}C NMR (100 MHz, [D]$CHCl_3$, 25 °C, TMS): δ = 139.0 (=CH), 131.2 (=C), 130.0 (=CH), 114.7 (=CH_2), 37.0 (CH_2), 32.0 (CH), 31.8 (CH_2), 25.8 (=C−*E*-CH_3), 21.2 (CH_3), 18.0 ppm (=C−*Z*-CH_3); MS (70 eV): *m*/*z* (%): 139 (1) $[M+H]^+$, 138 (6) $[M]^+$, 123 (13) $[C_9H_{15}]^+$, 96 (25) $[C_7H_{12}]^+$, 95 (19) $[C_7H_{11}]^+$, 83 (44) $[C_6H_{11}]^+$, 82 (31) $[C_6H_{10}]^+$, 81 (100) $[C_6H_9]^+$, 67 (39) $[C_5H_7]^+$, 55 (16) $[C_4H_7]^+$.

(1*R*,2*R*,3*S*)-1-Isopropenyl-2,3-dimethylcyclopentane (2,3-*trans*,*trans*-4; 4a): ^{1}H NMR (400 MHz, [D]$CHCl_3$, 25 °C, TMS): δ = 4.62 (s, 2H), 1.98 (q, 1H, ^3J = 10.2 Hz), 1.70 (m, 2H), 1.52 (s, 3H), 1.46 (s, 1H), 1.12 (m, 3H), 0.90 (d, 3H, ^3J = 4.9 Hz), 0.81 ppm (d, 3H, ^3J = 4.8 Hz); ^{13}C NMR (100 MHz, [D]$CHCl_3$, 25 °C, TMS): δ = 146.1 (=C), 108.7 (=CH_2), 55.0 (cycl. CH), 44.6 (cycl. CH), 41.1 (cycl. CH), 31.9 (cycl. CH_2), 28.2 (cycl. CH_2), 18.1 (=C−CH_3), 17.9 (CH_3), 15.5 ppm (CH_3); MS (70 eV): *m*/*z* (%): 138 (10) $[M]^+$, 123 (15) $[C_9H_{15}]^+$, 96 (87) $[C_7H_{12}]^+$, 95 (60) $[C_7H_{11}]^+$, 81 (100) $[C_6H_9]^+$, 69 (53) $[C_5H_9]^+$, 67 (58) $[C_5H_7]^+$.

(1*S*,2*R*,3*S*)-1-Isopropenyl-2,3-dimethylcyclopentane (2,3-*cis*,*trans*-4; 4b): ^{1}H NMR (400 MHz, [D]$CHCl_3$, 25 °C, TMS): δ = 4.70 (s, 1H), 4.57 (s, 1H), 2.46 (q, 1H, ^3J = 8.5, ^3J = 7.8 Hz), 1.85 (m, 2H), 1.64 (s, 3H), 1.57 (m, 4H), 0.92 (d, 3H, ^3J = 5.0 Hz), 0.65 ppm (d, 3H, ^3J = 5.2 Hz); ^{13}C NMR (100 MHz, [D]$CHCl_3$, 25 °C, TMS): δ = 146.2 (=C), 108.6 (=CH_2), 52.2 (cycl. CH), 48.3 (cycl. CH), 42.0 (cycl. CH), 32.1 (cycl. CH_2), 27.0 (cycl. CH_2), 22.3 (=C-CH_3), 20.4 (CH_3), 14.6 ppm (CH_3); MS (70 eV): *m*/*z* (%): 138 (5) $[M]^+$, 123 (45) $[C_9H_{15}]^+$, 96 (43) $[C_7H_{12}]^+$, 95 (100) $[C_7H_{11}]^+$, 81 (90) $[C_6H_9]^+$, 69 (39) $[C_5H_9]^+$, 68 (56) $[C_5H_8]^+$, 67 (69) $[C_5H_7]^+$.

(1*S*,2*S*,3*S*)-1-Isopropenyl-2,3-dimethylcyclopentane (2,3-*trans*,*cis*-4; 4c): Apparently, the concentration of the isolated product was too low to perform NMR spectroscopic studies. It was still possible to determine the correct structure by comparing the data of the other isomers (cf. text). MS (70 eV): *m*/*z* (%): 138 (6) $[M]^+$, 123 (49) $[C_9H_{15}]^+$, 96 (37) $[C_7H_{12}]^+$, 95 (100) $[C_7H_{11}]^+$, 81 (79) $[C_6H_9]^+$, 69 (57) $[C_5H_9]^+$, 68 (82) $[C_5H_8]^+$, 67 (73) $[C_5H_7]^+$.

(1*R*,2*S*,3*S*)-1-Isopropenyl-2,3-dimethylcyclopentane (2,3-*cis*,*cis*-4; 4d): ^{1}H NMR (400 MHz, [D]$CHCl_3$, 25 °C, TMS): δ = 4.74 (s, 1H), 4.58 (s, 1H), 2.37 (m, 1H), 1.90 (m, 2H), 1.67 (s, 3H), 1.57 (m, 4H), 0.87 (d, 3H, ^3J = 5.1 Hz), 0.43 ppm (d, 3H, ^3J = 5.3 Hz); ^{13}C NMR (100 MHz, [D]$CHCl_3$, 25 °C, TMS): δ = 145.6 (=C), 108.3 (=CH_2), 50.5 (cycl. CH), 38.4 (cycl. CH), 37.1 (cycl. CH), 28.7 (cycl. CH_2), 23.7 (cycl. CH_2), 22.5 (=C−CH_3), 15.4 (CH_3), 6.7 ppm (CH_3); MS (70 eV): *m*/*z* (%): 138 (9) $[M]^+$, 123 (20) $[C_9H_{15}]^+$, 96 (92) $[C_7H_{12}]^+$, 95 (47) $[C_7H_{11}]^+$, 81 (88) $[C_6H_9]^+$, 69 (27) $[C_5H_9]^+$, 68 (100) $[C_5H_8]^+$, 67 (78) $[C_5H_7]^+$.

2,3-*cis*,*trans*- or 2,3-*trans*,*cis*-2-Isopropenyl-1,3-dimethylcyclopentane (5a): The concentration of the isolated product was too low to calculate coupling constants and to assign the relative configuration. ^{1}H NMR (400 MHz, [D]$CHCl_3$, 25 °C, TMS): δ = 4.83 (m, 2H), 2.27 (m, 4H), 1,75 (s, 1H), 1.33 (s, 3H), 1.30 (s, 3H), 1.22 (m, 2H), 0.83 ppm (m, 6H); ^{13}C NMR (100 MHz, [D]$CHCl_3$, 25 °C, TMS): δ = 138.3 (C), 110.8 (=CH_2), 36.0 (cycl. CH), 31.0 (cycl. CH_2), 30.8 (cycl. CH_2), 24.8 (cycl. CH), 18.1 (CH_3), 17.0 ppm (=C−CH_3); MS (70 eV): *m*/*z* (%): 138 (9) $[M]^+$, 123 (24) $[C_9H_{15}]^+$, 96 (34) $[C_7H_{12}]^+$, 95 (21) $[C_7H_{11}]^+$, 83 (21) $[C_6H_{11}]^+$, 82 (39) $[C_6H_{10}]^+$, 81 (100) $[C_6H_9]^+$, 67 (46) $[C_5H_7]^+$, 55 (18) $[C_4H_7]^+$.

(1*S*,2*S*,3*R*)-2-Isopropenyl-1,3-dimethylcyclopentane (2,3-*cis*,*cis*-5; 5b): ^{1}H NMR (400 MHz, [D]$CHCl_3$, 25 °C, TMS): δ = 4.81 (s, 1H), 4.73 (s, 1H), 1.87 (m, 4H), 1.66 (s, 3H), 1.49 (t, 1H, ^3J = 9.9 Hz), 1.28 (m, 2H), 0.94 ppm (d, 6H, ^3J = 6.3 Hz); ^{13}C NMR (100 MHz, [D]$CHCl_3$, 25 °C, TMS, underlined values represent two C atoms with identical δ): δ = 145.5 (C), 111.5 (=CH_2), 64.4 (cycl. CH), 37.9 (cycl. CH), 32.2 (cycl. CH_2), 18.7 (CH_3), 17.6 (=C−CH_3); MS (70 eV): *m*/*z* (%): 138 (2) $[M]^+$, 123 (12) $[C_9H_{15}]^+$, 96 (29) $[C_7H_{12}]^+$, 95 (29) $[C_7H_{11}]^+$, 83 (100) $[C_6H_{11}]^+$, 82 (17) $[C_6H_{10}]^+$, 81 (33) $[C_6H_9]^+$, 69 (26) $[C_5H_9]^+$, 67 (27) $[C_5H_7]^+$, 55 (75) $[C_4H_7]^+$.

2,3-*cis*,*trans*- or 2,3-*trans*,*cis*-2-Isopropenyl-1,3-dimethylcyclopentane (5c): The concentration of the isolated product was too low to perform NMR spectroscopic studies. As a result of this fact, it was not possible to determine the relative structure (cf. text). MS (70 eV): *m*/*z* (%): 138 (5) $[M]^+$, 123 (21) $[C_9H_{15}]^+$, 96 (22) $[C_7H_{12}]^+$, 95 (21) $[C_7H_{11}]^+$, 83 (62) $[C_6H_{11}^+]$, 82 (25) $[C_6H_{10}]^+$, 81 (100) $[C_6H_9]^+$, 67 (40) $[C_5H_7]^+$, 55 (21) $[C_4H_7]^+$.

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[37] According to reference [13], the other transition states/intermediates are destabilized due to ecliptic arrangements of the methyl and terminal vinyl group of β-citronellene (**2**), which contributes to the cyclization process.

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