Fate of monoterpenes in near-critical water and supercritical alcohols assisted by microwave irradiation†‡

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The rearrangement of α- and β-pinene was studied under microwave irradiation in near-critical water and supercritical lower aliphatic alcohols, with the aim of identifying the pathway of α- and β-pinene isomerization. Generally, two pathways occur, pyrolysis on the one and acidolysis on the other hand, whereby acidolysis is predominant in the case of near-critical water and the second pathway is favored for experiments employing supercritical alcohols. The different behavior of these two structurally related solvents is attributed to the increased availability of protons if water is heated to 270 °C and 80 bar, thus enhancing the autoprotolysis of water. The application of alcohols instead furnished rearrangement products clearly attributed to thermal pyrolysis route by the formation of radical reaction intermediates.

Introduction

A small but heterogeneous class of natural products are the terpenes and terpenoids, which often are employed as major building blocks in the synthesis of high-valued chemicals.[1] In addition to the modification of the carbon skeleton by introducing heteroatoms (oxidation, epoxidation) or other functionalities (selective hydrogenation), terpenes and terpenoids offer the opportunity for performing interesting rearrangement reactions in the gaseous, liquid and supercritical phases.[2–5] Often the rearrangement of terpenes with constrained rings, *e.g.* α-pinene (**1**) or β-pinene (**2**, Chart 1), is focused on thermal (pyrolysis) and acid-catalyzed isomerizations (acidolysis). Without any catalyst under a high-temperature regime it is reported that **1** can easily be converted into limonene (**3**), alloocimene (**4**) as well as pyronenes (**5**) resulting from consecutive reactions of **4**.[2,3] Contrarily, on pyrolysis, **2** furnishes besides **3** and ψ-limonene (**7**), the acyclic hydrocarbon myrcene (**6**) as the main product in up to 85% yield.[2,3c,f,4,5a] Due to the formation of these products it is supposed that **1**, and respectively **2**, undergoes ring opening by forming a biradical intermediate, which undergoes fast rearrangement (*e.g.* retro-ene reaction) forming isomerization products.[2]

In presence of acidic or basic catalysts other types of isomerization are predominant. In case of **1** and **2**, the acid-catalyzed rearrangement results in an enlarged variety of products.[6,7] Performing the reaction under ambient conditions, compounds related to the *p*-menthadiene-structure are found: **3**, terpinolene (**8**), γ- (**9**) and α-terpinene (**10**). For the reactions, metal oxides, mineralic acids, metal salts or (ion-exchanged) zeolites are common catalysts.[1a,b,7] The formation of α-phellandrene (**11**), *p*-cymene (**12**), camphene (**13**), and β-phellandrene (**14**) is observed under special prerequisites concerning catalyst or reaction condition.[7f,h,l,8–11]

Commonly, pyrolysis and acidolysis reactions of terpenes are performed in the gas phase in order to control the residence time and to prevent bimolecular reactions furnishing undesirable polymers or dimers. In both cases, these gas phase reactions are accomplished under reduced- or high-pressure conditions,

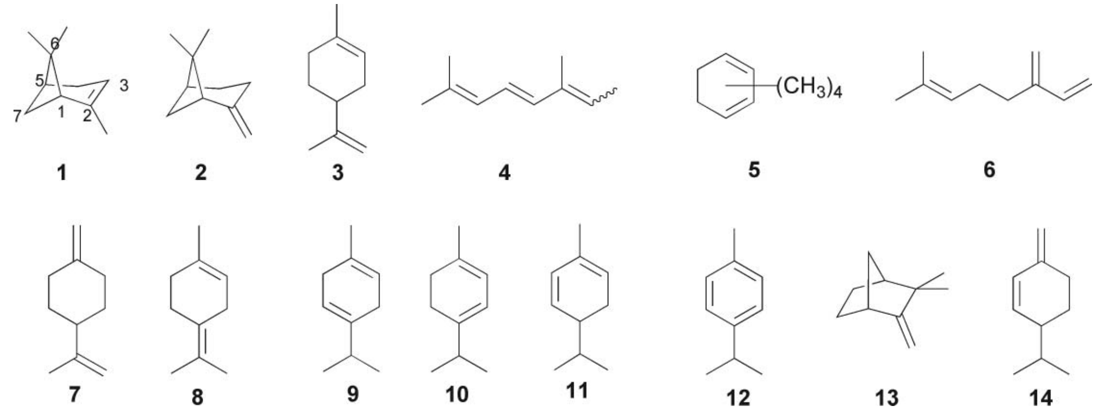

Chart 1

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Table 1 Dissipation factor tan δ,[15a] critical data (p_c, T_c), vapor pressure p_v,[15b] of water and different lower aliphatic alcohols as well as their equilibrium constants for autoprotolysis pK_{auto}[15c,d]

Alcohol	tan δ	p_c/bar	T_c/K	p_v/mbar[a]	pK_{auto}[a]
Water	0.132	220.6	647.1	32	14.995
Methanol	0.659	80.84	512.5	129	17.20
Ethanol	0.941	61.37	514.0	54	18.88
Propan-1-ol	0.757	51.69	536.8	20	19.43
Propan-2-ol	0.799	47.64	508.3	43	
Butan-1-ol	0.571	44.14	563.0	6.7	21.56
2-Methylpropan-1-ol	0.522	42.95	547.8	17	

[a] At 25 °C.

Table 2 Results of the rearrangement of α-pinene (**1**) and β-pinene (**2**) in near-critical water[a]

	α-Pinene (**1**)		β-Pinene (**2**)	
Compound	Yield (%)	Origin[b]	Yield (%)	Origin[b]
Limonene (**3**)	14	P, (A)	19	A
Alloocimene (**4**)	9	P	—	
Pyronene (**5**)	4	P	—	
Terpinolene (**8**)	20	A	23	A
γ-Terpinene (**9**)	24	A	24	A
α-Terpinene (**10**)	12	A	14	A
α-Phellandrene (**11**)	2	A	2	A
p-Cymene (**12**)	5	A	2	A
Camphene (**13**)	3	A	5	A
Unknown	7	?	10	?

[a] 250 μl pinene, 15 ml 0.03 M NaCl solution, 80 ml quartz vessel, heating: 10 min, reaction time: 60 min, cooling: 20 min, P_{max}: 1.2 kW, microwave: Synthos 3000. [b] A: acidolysis, P: pyrolysis.

allowing for the use of glass flasks or autoclaves made of stainless steel. Although it was shown recently that microwaves can be used as a tool for pyrolysis reactions,[12] the utilization of microwave irradiation to perform pyrolysis or acidolysis reactions with terpenes has not been reported yet. Within this work, a suitable method was investigated for the rearrangement of **1** and **2** using microwave irradiation[13] under high-temperature (<300 °C) and high-pressure (<80 bar) conditions. Thus, it was possible to generate near-critical water[14] and supercritical alcohols as reaction media for the transformation of the mentioned monoterpenes.

Results and discussion

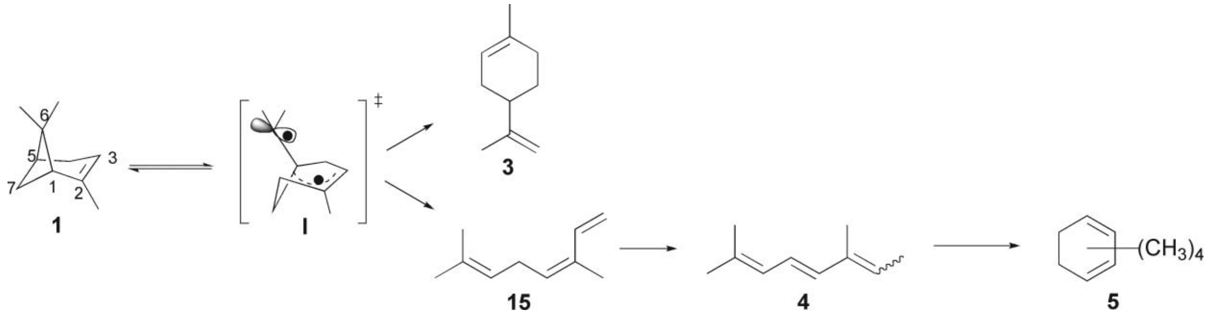
Comparison of the critical data for water and lower aliphatic alcohols[15] listed in Table 1 reveals great differences for both the critical pressure p_c and temperature T_c between these two structurally related class of molecules. Because of the experimental boundary conditions determined by the microwave apparatus used for the experiments (T_{lim} = 300 °C, p_{lim} = 80 bar; Synthos 3000; Anton Paar GmbH, Graz, Austria), it was not possible to perform experiments with supercritical water. In accordance to the work of Kremsner and Kappe in the field of microwave-assisted near-critical water generation, basic experiments approve the necessity of working with saline aqueous solutions instead of pure water, to achieve stable and reproducible reaction conditions as well as improved heat-up behavior (*cf.* ESI‡).[14a] Thus, experiments were conducted employing an 0.03 M NaCl solution.

Using lower aliphatic alcohols listed in Table 1 as solvents under the same experimental prerequisites (T_{lim} = 300 °C, p_{lim} = 80 bar) also, special experimental conditions have to be set up to avoid pressure and temperature instabilities when heating to the limiting parameters. In particular, when the alcohols undergo phase-transformation from liquid to gaseous or supercritical state, the energy uptake is distorted resulting in process instabilities. Facing and overcoming this problem was possible by employing passive heating elements made from silicon carbide into the reaction vessels (*cf.* ESI‡).[16] The application of alcoholic saline solutions is inappropriate since the saline residue (after evaporation of the solvent) might absorb the reactants and therefore adulterating the experimental outcomes.

Rearrangement of α-pinene and β-pinene in near-critical water

Experiments were conducted to study the behavior of α- (**1**) and β-pinene (**2**) under near-critical water conditions, whereby a discrete portion of the substrate (250 μl) was added to an aqueous solution of sodium chloride (15 ml, 0.03 M). This, under ambient conditions, bi-phasic mixture was exposed to microwave irradiation in quartz vessels, and heated up to 270 °C and 80 bar. After a heat-up period of 10 min, the conditions were kept constant for 60 min. After cooling the mixture to ambient temperature and work-up of the reaction mixture, the conversion (X) of both **1** and **2** was found to be quantitative. In the case of **1**, the resulting products indicate that both pyrolysis (**4**, **5**) and acidolysis reaction (**8–13**) took place (*cf.* Table 2), whereby the reaction of **2** under similar reaction conditions furnished the latter only.

In both cases, the majority of obtained product originates from the acidolysis reaction pathway. This is due to the fact that the activation energy for pyrolytic ring cleavage is higher than for the competitive reaction *via* carbocations (induced by addition of a proton to the double bond), resulting in a strong preference for the latter. This hypothesis is supported by the fact that thermal rearrangement normally required high temperatures (>300 °C) and short contact times in the case of flow systems or T of 200 °C and reaction times of >2 h if the reactions are carried out in batch system either under vacuum or high-pressure conditions.[2–5] In this case, 270 °C is not high enough to pyrolyze great amounts of **1** or **2**. Pyrolysis of **1** runs through a biradical reaction intermediate (**I**; Scheme 1), which, upon degenerative rearrangement, afforded racemic limonene (**3**; dipentene) and 3*Z*-ocimene (**15**) as primary pyrolysis products. The latter undergoes fast sigmatropic [1,5]H shift yielding alloocimene **4**, which cyclizes to form cyclohexadiene isomers **5**.[2b,3,17] The pyrolysis of **1** initially starts with the opening of the cyclobutane ring, forming the biradical intermediate **I** (Scheme 1). The radical is stabilized by the allylic system and furnishes the monocyclic retro-ene product **3** by a formal 1,5H shift in racemic form (dipentene). Dipentene formation is due to the mesomeric delocalization of one radical position as an allyl-type radical.[2b,3c,e,g] Furthermore, it is supposed that intermediate **I** yields the formal retro-[2 + 2]-cycloaddition product 3*Z*-ocimene (**15**) by complete ring opening. Due to selective formation of the *Z*-isomer, the molecule comprises an ideal structure for undergoing a sigmatropic [1,5]H shift to afford **4**.[3d,g,17] Due to this entropic and enthalpic favored rearrangement, the reaction from **15** to **4** is very fast, making it impossible to detect **15** in the reaction mixture yielding from pyrolysis of **1**.[2,3a–e,5] Conjugated triene **4** is able to undergo various electrocyclizations and sigmatropic group



Scheme 1 Formation of pyrolysis products from α-pinene (**1**).

Table 3 Results of the rearrangement of selected *p*-menthadienes in near-critical water[a]

	Yield (%)								
	3	**7**	**8**	**9**	**10**	**11**	**12**	**13**	Unknown
α-Pinene (incl. **3**)	16		23	28	14	2	6	3	8
α-Pinene (excl. **3**)	—		27	33	16	3	7	4	10
Limonene (**3**)	21	2	22	28	18	3	2	2	2
Terpinolene (**8**)	8	2	62	11	10	1	3	0	3
γ-Terpinene (**9**)	4	5	7	57	5	3	11	0	8
α-Terpinene (**10**)	2	3	8	18	44	1	19	0	5

[a] 250 µl α-pinene (**1**), 15 ml 0.03 M NaCl solution, 80 ml quartz vessel, heating: 10 min, reaction time: 60 min, cooling: 20 min, P_{max}: 1.2 kW, microwave: Synthos 3000.

transformations forming different tetramethylated cyclohexadienes **5**.[2,3a–e,5,18] The equality of the amounts of **3** (14%) formed through rearrangement of **1** with the summarized amounts of **4** and **5** (13%; Table 3) is an indicator that **3** mainly originates from pyrolysis and not from acidolysis. Kinetic pyrolysis experiments of **1** in the gas phase strongly indicate that the rate constants for competitive reactions yielding **3** and **15** (and its consecutive products) are almost equal.[2b,3d,e] For pyrolysis of **2** the ratio between pathways leading to **3**, acyclic **6**, and monocyclic **7** is approximately 2 : 17 : 1.[2,4e] Without the formation of **6** as major pyrolysis product, it can be concluded that pyrolysis does not take place for treatment of **2** under the herein presented conditions.§

Referring to **1**, the ratio of pyrolysis to acidolysis is 0.2, neglecting **3**, since this compound can arise from both reaction pathways. No pyrolysis occurs using **2** as the starting material. At elevated temperature, the ionic product of water is shifted to a higher value,[19] which leads to a higher concentration of protons available for chemical reactions, superposing the beneficial effect of higher *T* on the rate constant for thermal isomerization. Due to this behavior of water, it is not necessary to add any further catalyst for the acidic rearrangement of **1** or **2** in the present case. Another small but important fact is, that except for **12** the reaction almost exclusively yielded isomerization products. The formation of polymers or the hydration of **1** or **2** furnishing alcohols was not observed in all experiments. Additionally, no reaction with the reaction atmosphere (nitrogen, oxygen, argon, air) was detectable.

To identify the origin of the resulting products, **3** and **8–10** were treated separately in near-critical water under the same conditions as applied for **1** and **2**. The data compiled in Table 3 indicate that **3** is the most reactive *p*-menthadiene isomer, since it underwent isomerization to **8–10**. Contrarily, these compounds seem to be relatively stable under the conditions the reactions are carried out. The formation of *p*-cymene (**12**) as side reaction for the endocyclic isomers **9** and **10** is due to their tendency to form the thermodynamic stable aromatic. Important is also the fact that the isomerization of the monocyclic isomers yielded no traces of bicyclic products (**1**, **2**, and **13**).

Based on the experimental outcomes of the reactions of **1–3** and **8–10**, a general reaction scheme can be drawn (Scheme 2). With respect to Markovnikov's rule, a proton is added to the double bond of **1** or **2**, respectively, to form a triple-substituted carbocation (carbenium ion **II**; Scheme 2), which is stabilized by the neighboring methyl group by hyperconjugation. Interestingly, the present result supports the hypothesis that the formation of carbocation **II** (pinanyl cation) is an irreversible reaction, since neither in the case of the reaction of **1** nor **2** was an isomerization into the other observed.[7j] This is in contrast to previous studies, which indicate the existence of an equilibrium between **1** and **2** on treatment with acids or bases.[7e,9,20,21] The pinanyl cation is in equilibrium with the isobornyl cation (**IV**), whereby as intermediate structure the non-classical carbenium ion **III** (carbonium ion) can be formulated. Calculations on the B3LYP/6-31G(d) level of theory indicate a small energy difference between **II** and **IV**, accounting for these being real transition states and **III** is the global maximum on the reaction coordinate from **1** to **13**.[9] Despite the fact that calculations on the same level of theory indicate an increased stability of the bicyclic cations **II–IV** compared to the monocyclic menthenyl cation **V**,[9] the reaction preferably runs through this reaction pathway, probably due to entropic and enthalpic preference for an unsaturated less strained monocyclic ring system. Starting from **V**, an exocyclic deprotonation afforded limonene (**3**), whereas an endocylic loss of the proton furnishes terpinolene (**8**; Scheme 2). It has to be pointed out that the outcome of isomerization experiments with **3** and **8** indicate that the rearrangement of **3** to **8** runs through intermediate **V**, which is in contrast to the work of Comelli *et al.*, assuming **3** as an intermediate for the formation of **8–11**.[7j] By reprotonation of **8**, carbocation **VI** (terpinyl cation; Scheme 2) is formed, which is able to undergo two consecutive reactions: (i) γ-terpinene (**9**) is formed containing two isolate endocyclic double bonds (1,4-cyclohexadiene subsystem) and (ii) α-terpinene (**10**) is formed with

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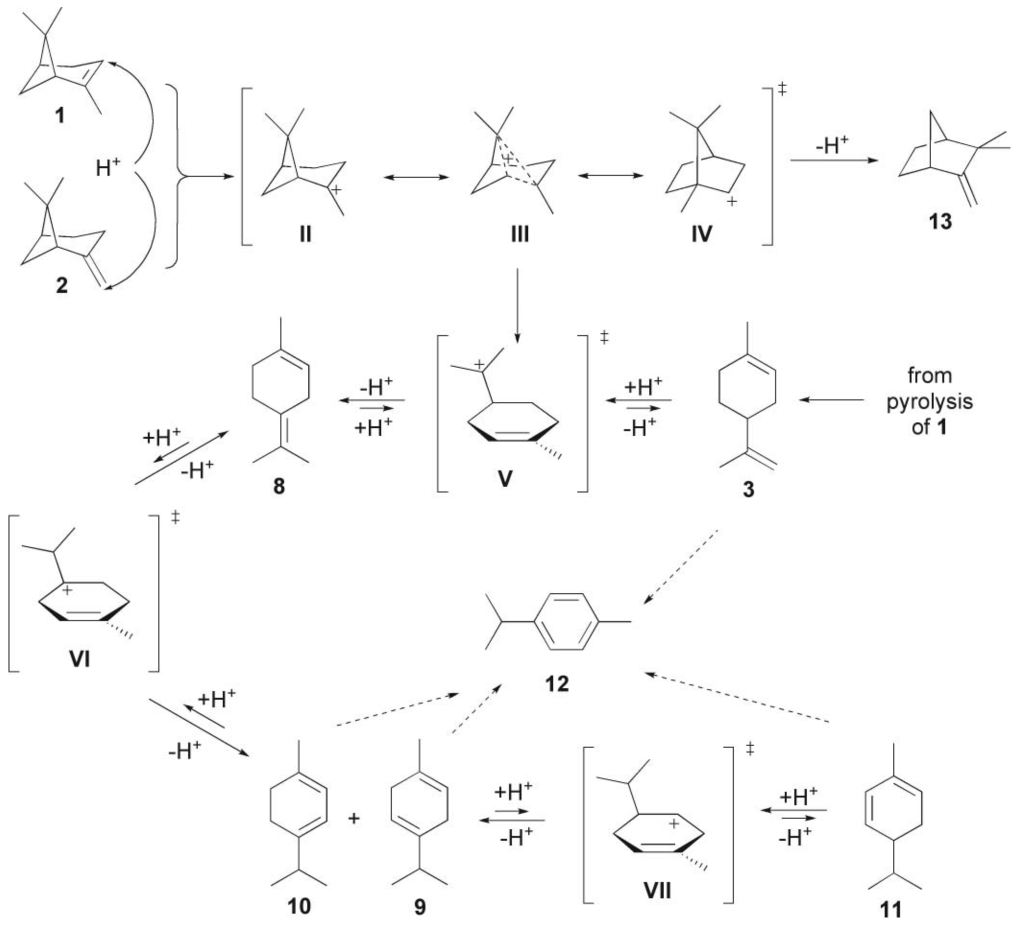
§ The lower activity of β-pinene **2** in the pyrolysis reaction compared to α-pinene **1** was also validated by comparative pyrolysis studies in the gas phase.[2,3b,g,4e] This effect is accounted to the higher thermodynamic stability of **2** due to the less strained bicyclic ring system in comparison with **1**.



Scheme 2 Acid-catalyzed rearrangement of α-pinene (**1**) and β-pinene (**2**) in near-critical water.

a conjugated double bond system (1,3-cyclohexadiene subsystem). Addition of a proton to **9** forms an intermediate carbocation **VII**, which undergoes deprotonation resulting in α-phellandrene (**11**). In the case of **9–11**, both double bonds are located in the ring system. Within the dehydrogenation of these compounds, *p*-cymene (**12**) is formed (Scheme 2). This reaction is known to proceed very effectively in the gas phase under the presence of acid catalysts like zeolites making this reaction an important industrial process, even when starting from **1** as substrate.[22]

Variation of reaction parameters for near-critical water isomerization of α-pinene

The time of the overall process was summarized by adding the time for heating, cooling, and the actual reaction time (eqn (1)). Within 10 min, the reaction mixture was heated up to 270 °C: t_H. The reaction time (t_R) itself is defined as the time the bulk reaction parameters T and p remain constant, in practice the time between up- and downstream heating or cooling processes, respectively (*cf.* ESI‡). After the reaction time follows a cool-down phase of 20 min duration (t_C).

$$t = t_H + t_R + t_C \qquad (1)$$

To obtain an overview of the reaction progress at different reaction times, the changes of selectivity S were investigated (Fig. 1), while varying the reaction time t_R from 0–60 min. In the case of treatment of **1**, the selectivities of compounds **4** and **5** were summarized and defined as pyrolysis products (S_{pyr}), whereas the selectivities for products **8–13** were summarized as acidolysis products (S_{acid}; eqn (2) and (3)). The selectivities of **2** and of the compounds which are unknown were not considered because the origin whether from pyrolysis or acidolysis is not possible to assign. Therefore the yield of **3** (Y_3) and unknown compounds (Y_u) were

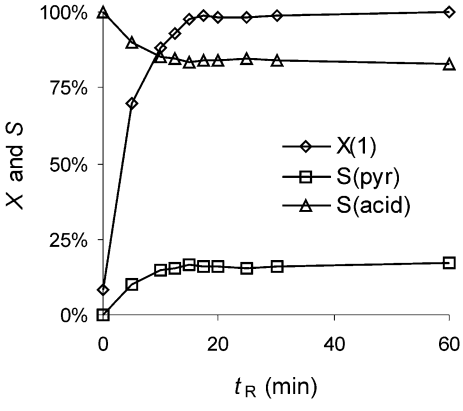


Fig. 1 Changing of selectivity of pyrolysis (S_{pyr}; *cf.* eqn (2)) and acidolysis (S_{acid}; *cf.* eqn (3)) and conversion of α-pinene (X_1) depending on reaction time t_R (eqn (1); 250 μl **1**, 15 ml 0.03 M NaCl solution, 80 ml quartz vessel, heating: 10 min, cooling: 20 min, P_{max}: 1.2 kW, microwave: Synthos 3000).

subtracted from the conversion of **1** (X_1) leading to the respective equations for S_{pyr} and S_{acid}.

$$S_{\text{pyr}} = \frac{Y_4 + Y_5}{X_1 - Y_3 - Y_u} \tag{2}$$

$$S_{\text{acid}} = \frac{\sum_{i=8}^{13} Y_i}{X_1 - Y_3 - Y_u} \tag{3}$$

Within the period of heating and cooling 10% of **1** were converted while only acidolysis products appeared (t_r: 0 min). Increasing of reaction time resulted in changing selectivity ratio of 5.7 in favor of S_{acid}, whereby the ratio itself remains constant after 10 min. The conversion of **1** was found to be quantitative after 15 min. The obtained results show that acidolysis is strongly preferred independently from the conditions the experiments have been performed at. As reported,[3,6,7e–h,j,l] pyrolysis reactions generally require much higher temperatures than acid-catalyzed rearrangement, due to the higher activation energies necessitated for the initiation of homolytic bond cleavage. Therefore, more acidolysis products were formed because temperatures of around 270 °C are not high enough for initial homolytic rupture of the bond between carbon atoms C1 and C6 (Scheme 2) initiating pyrolysis reactions of **1**.[2,3] Another fact counting against thermal isomerization *via* biradical intermediates is the fact that radical reactions are strongly disfavored if bimolecular reactions are able to take place. Due to high-pressure conditions, the probability for collisions between two reactant molecules or between cationic species (protons or proton-related species) and **1** or its products is much higher compared to thermal processes in the gas phase.

Related to the investigations of Kremsner and Kappe, a 0.03 M NaCl solution for the generation of near-critical water was applied so far.[14a] In order to investigate the effect of NaCl concentration on the conversion of **1** experiments with varied concentrations (0–0.05 mol l⁻¹ NaCl) have been performed (Table 4). Without any amounts of salt, water becomes transparent for microwave irradiation at higher temperature further affecting the energy uptake and therefore the maximal temperature T_{max} (220 °C) that can be reached under salt-free reaction conditions, thus resulting in conversions of 7 and 35% for **1** and **2**, respectively. By adding small amounts of NaCl (0.006 mol l⁻¹) to the reaction mixture the microwave absorption capacity of the bulk solvent can be improved significantly pointed out by higher T_{max} of 265 °C and therewith increased conversion of both pinenes. Further increase of NaCl concentration revealed only small effects on the conversion of **1** and also T_{max} remains constant. The conversion of **2** increases to nearly quantitative values by adding another amount of NaCl. These results show that the presence of small amounts of salt is essential for generating near-critical water under microwave radiation and therewith reaching high conversion of **1**. Instead of the 0.03 M NaCl solution, a lower concentrated NaCl solution is also practicable to receive adequate conversion.

Table 4 Effect of NaCl-concentration on the conversion of α-pinene (X_1) and β-pinene (X_2)[a]

	Concentration of NaCl solution/mol l⁻¹				
	0	0.006	0.015	0.03	0.05
T_{max}/°C[b]	222	262	262	265	261
X_1 (%)[c]	7	80	86	88	92
X_2 (%)[c]	35	65	92	98	98

[a] 250 µl pinene, 15 ml NaCl solution, 80 ml quartz vessel, heating: 10 min, reaction time: 15 min, cooling: 20 min, P_{max}: 1.2 kW, microwave: Synthos 3000. [b] Maximal temperature of the reactor from recorded data. [c] Product distribution is independent from conversion.

Table 5 Conversion of α-pinene (**1**) depending on the volume of **1** added to the solvent[a]

	Volume of **1**/ml			
	0.25	0.5	1	2
Ratio: reactant : solvent	0.017	0.033	0.067	0.133
T_{max}/°C[b]	267	266	268	266
X_1 (%)	85	72	68	68

[a] 15 ml 0.03 M NaCl solution, 80 ml quartz vessel, heating: 10 min, reaction time: 10 min, cooling: 20 min, P_{max}: 1.2 kW, microwave: Synthos 3000. [b] Maximal temperature of the reactor from recorded data.

Because the ratio of quartz vessel volume (80 ml) to reaction volume (15 ml) has to be constant in order to guarantee constant reaction conditions, it is not possible to vary the ratio by simply decreasing the amount of solvent. Nevertheless, increasing the amount of **1** during one reaction cycle would help to reduce waste and therefore improve the performance of the reaction considering terms of sustainability or green chemistry. Experiments were conducted performing the reaction with different amounts of **1** ranging from 0.25 to 2 ml. As demonstrated in Table 5, the increased amount of **1** shows only a small effect on the conversion of **1**. By doubling the amount of reactant (from 0.25 to 0.5 ml) the conversion of **1** decreases by about 15%. Four (1 ml) and eight times (2 ml) more reactant as used in former experiments is also practicable to receive moderate conversions of **1**, whereby it has to be mentioned that the product distribution remains constant for all experiments and no polymers are formed. Experiments have demonstrated that it is possible to reduce the ratio of solvent to substrate.

Rearrangement of α-pinene in supercritical alcohols

It has to be pointed out that the maximal temperature which can be achieved under the experimental prerequisites ($T_{\text{lim}} = 300$ °C, $p_{\text{lim}} = 80$ bar) in general depends on the applied alcohol (*cf.* Table 1 and ESI‡). Within the experiments it has been shown that the limiting factor is neither the temperature nor the power input, rather the pressure limit is reached first. According to theory of ideal gases (law of Boyle–Mariotte) volume and pressure are constrained variables. Increasing the free reaction volume (by decreasing the volume of heated alcohol) would consequently allow for the establishment of higher temperatures. However, basic experiments in this direction revealed that this interrelation is very complex. Therefore, the following experiments have been carried out using a constant reaction volume.

Fig. 2 pictures the results from the thermal isomerization of **1** using lower supercritical aliphatic alcohols as solvents (Table 1). Experimental outcomes revealed that besides the classical reactions expected for the thermal isomerization,[3,5] neither intermolecular reactions between reactants or rectant and solvent occurred, nor was the presence of products resulting from acidolysis route

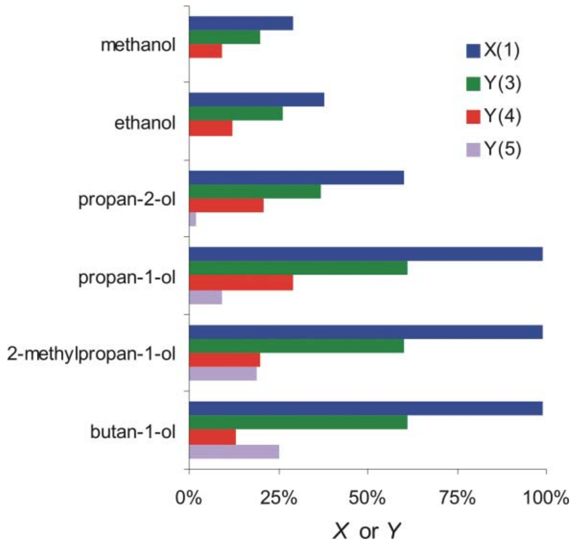


Fig. 2 Conversion of **1** and yield of **3–5** depending on the used alcohol (500 µl **1**, 30 ml alcohol, 80 ml quartz vessel; T_{lim} = 300 °C, p_{lim} = 80 bar, P_{lim} = 1.2 kW; heating: 10 min, reaction time: 60 min, cooling: 20 min, microwave: Synthos 3000).

(Scheme 2) observed. Pyrolysis in supercritical alcohols yielded the rearrangement products classified to the reaction pathway from biradical **1** in a 3 : 7 ratio in favor of the formation of **3** (Scheme 1). This is in clear contrast to the results observed when near-critical water was employed as the solvent (Table 2). Additionally the higher **3** : **4** ratio is contrary to the results from classical liquid or gas phase pyrolysis.[2,3d–g,5] The increase of limonene-selectivity through pyrolysis in supercritical media was recently described by Anikeev and coworkers for the use of water–ethanol mixtures (*p*: 120 bar).[23] The beneficial effect was accounted to the increased acidity of water due to change of its ion product.[19] However, in the present case, the presence of water can be ruled out, hence the higher limonene ratio has to be attributed to other circumstances. The independency of the product selectivity from the solvent applied is traced back to the fact that the reaction runs through a similar reaction intermediate, whose formation does not depend on the solvent properties/reaction environment and therefore ruling out an involvement of alcohol molecules or fragments in the rearrangement process.

As indicated in Fig. 2, the conversion of **1** strongly depends on the alcohol applied as solvent for the experiment: the higher the molar mass of the alcohol the higher the conversion is after 1 h of reaction time. Supercritical data for the alcohols listed in Table 1 revealed opposite trends: the higher the molar weight (i) the lower the critical pressure p_c is, and (ii) the higher the critical temperature T_c is, the higher the vapor pressure p_v is.[15b] Due to the lower p_v of the C_3- and C_4-alcohols, the external pressure limit (p_{lim}: 80 bar) is reached at a higher temperature level and also the existence of the supercritical state occurred earlier (reaction volume = constant). Due to the pressure–temperature dependency, the maximal temperatures T_{max} measured inside the reaction vessels are higher, which directly effects the reaction rate and therefore the conversion (Fig. 3). With the exception of butan-1-ol there is a linear correlation between T_{max} and conversion of **1**.

The alcohols used for the experiments proved to be inert under the high temperature and pressure regime. Prior to use, the alcohols were dried over molecular sieve before the reaction to avoid catalytic amounts of water. The absence of water was proved by determining residual water content by Karl–Fischer–Titration. Water is known to react as strong base, and as an acid, under near- and supercritical conditions, respectively, instead of a higher state of autoprotolysis.[14a,16a,19] Similar to water, alcohols may undergo autoprotolysis themself (Table 2). However, the equilibrium constants for these reactions are considerably low due to the disfavored formation of protonated alcohol species. By the loss of water, the protonated alcohols may form carbocations, which themselves are strong electrophiles and can undergo various reactions. Besides the formation of ethers also reaction with double bonds of **1** or its pyrolysis products **2–5** may occur. Both the formation of ethers and the formation of addition products can be ruled out, since the expected products have not been detected in the reaction mixtures (GC-MS, carbon mass balance for monoterpenes). This behavior is in contrast to the studies of Kamitanaka *et al.* and Horikawa *et al.* who reported addition of supercritical alcohols to styrene and aliphatic *n*-alkenes.[24] On the other hand, in a proton-rich medium, acid-catalyzed rearrangement products of **1** could be found, *e.g.*

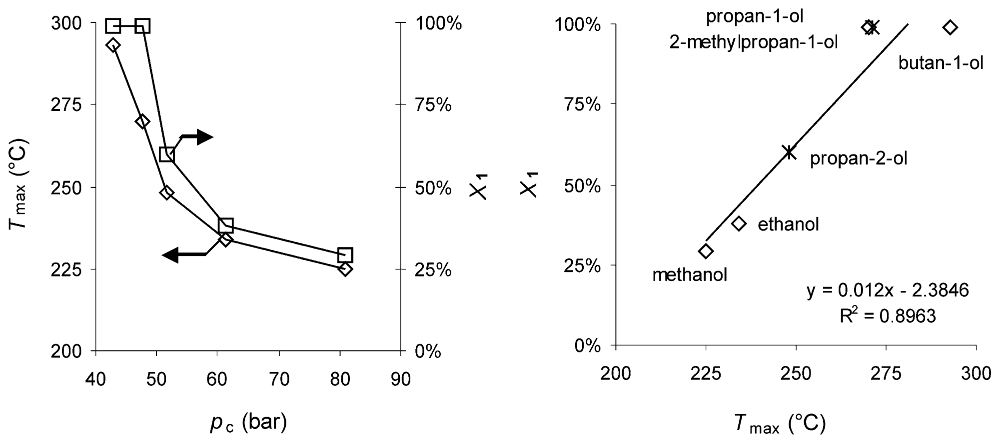


Fig. 3 Correlation between critical pressure p_c[15b] conversion of **1** (X_1; 500 µl **1**, 30 ml alcohol) and maximal temperature measured in the reaction vessel (T_{max}; left) and correlation between X_1 and T_{max} (right, squares = *n*-alcohols; 80 ml quartz vessel; T_{lim} = 300 °C, p_{lim} = 80 bar, P_{lim} = 1.2 kW; heating: 10 min, reaction time: 60 min, cooling: 20 min, microwave: Synthos 3000).

menthadienes.[7f,8,9,20,25] In the present case, only pyrolysis product of **1** can be found. Both, the absence of water and of acid-catalyzed rearrangement products of **1** imply that no protons are generated during the reaction. Thus, it can be concluded that the alcohols used as solvents for the isomerization of **1** under closed-vessel conditions are practically inert towards inter- and intramolecular reactions.

Conclusion

By using near-critical water or supercritical lower aliphatic alcohols generated under the influence of microwave irradiation in closed vessel reactors, it is possible to investigate pyrolysis and acidolysis reactions of terpenes. Comparison of the two solvent systems revealed significant differences in the experimental outcome regarding the isomerization of α- (**1**) and β-pinene (**2**). Since the improved availability of protons using near-critical water the reaction afforded mainly products of the *p*-menthane series, attributed to proton-catalyzed rearrangement mechanism, as the addition of other acid-catalyzing reactants like mineral acids, zeolites or heteropolyacids is not necessary. Within a reaction time of 15 min a quantitative conversion of **1** and **2** is achieved at temperatures of about 270 °C and a system pressure of 80 bar. Independently of both inert and non-inert conditions, the formation of polymers or oxidized products was not observed in any experiment. However, NaCl used for stable reaction condition shows no catalytic effect on the reaction mixture. Rearrangement of **1** afforded products resulting from acid-catalyzed rearrangement passing through cationic intermediates and thermal induced isomerization *via* biradical transition states, strongly disfavoring the latter route (5 : 1).

Regarding the pyrolysis of α-pinene (**1**) in supercritical alcohols typical compounds were also identified that were reported to yield from pyrolysis under classical conditions: limonene (**3**), alloocimenes (**4**), and pyronenes (**5**). Contrarily to earlier reports on the pyrolysis of **1**, the reaction favors that reaction route furnishing **2** over that one yielding **3** and **4**. Within the microwave-assisted heating of alcohols up to their critical parameters, the established pressure inside the quartz vessel is auto-generated depending on the applied solvent. In the case of methanol and ethanol, the pressure reaches its limitation (80 bar) with the consequence that the critical temperature can not be reached leading to low conversions of **1**. The higher alcohols are able to reach the supercritical state and resulting in the total conversion of **1**. The solvent itself is stable in the supercritical state and does not dehydrate or oxidize.

Experimental section

General

α-Pinene (**1**, 98%), β-pinene (**2**, 98%), limonene (**3**, 97%), terpinolene (**8**, 98%), γ-terpinene (**9**, 97%), and α-terpinene (**10**, 95%) were purchased from Sigma-Aldrich and used without further purification. Purity was determined by capillary gas chromatography. Water used for reaction has a purity of 99.9999% and a conductivity of $\leq 2\ \mu S\ cm^{-1}$. Analyses were carried out with a 6890 Series GC-MSD and a 6890 Series II GC-FID from Agilent Technologies. Products were identified by comparison with either retention times and/or mass spectra of pure reference compounds. GC-FID: HP 5, 30 m × 0.32 mm × 0.25 µm, 5 psi H_2; 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-MS: HP 5, 30 m × 0.32 mm × 0.25 µm, 7 psi He; 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 (70 eV).

Microwave system

The experiments were carried out in the microwave system Synthos 3000 (Anton Paar GmbH, Graz, Austria). The microwave oven is equipped with two magnetrons within a frequency of 2.45 GHz and an overall possible energy-input ranging from 0 to 1.4 kW. In the middle of the reaction space (*w*-*d*-*h*: 450 × 420 × 350 mm) a rotor is placed, which contains eight positions for quartz vessels. The 80 ml quartz vessels have a thickness of 0.8 cm and can be filled with maximal 60 ml of reaction solution. The vessels were closed by caps made of PTFE. The so prepared vessels were place in a security jacket made of polyetheretherketone PEEK. Then the vessels were placed into the rotor and this was closed with a security cap. The quartz vessels are approvable for pressure up to 80 bar and temperatures up to 300 °C. The pressure was determined by a hydraulic system while the cap of the vessels press against a stamp installed in the rotor. Temperature was determined by a gas-thermometer in only one quartz vessel. Additionally the temperature of all vessels was controlled by an IR-sensor. The power of the microwave irradiation could be controlled *via* a pressure-, temperature- or power-regulated program. In this case the power input was limited by temperature $T_{\text{lim}} = 300\ °C$, pressure $p_{\text{lim}} = 80$ bar, and power $P_{\text{lim}} = 1.2$ kW. For heating up to T_{lim} 10 min and for cooling down 20 min (pressurized air) were used.

Details concerning the heating behavior of near-critical water and supercritical alcohols under the experimental prerequisites are provided within the ESI.‡

Experimental procedure for conversion in near-critical water

To an aqueous solution of NaCl (15 ml, 0.03 M) saturated with nitrogen, α-pinene (1.57 mmol, 215 mg, 250 µl) was added into the quartz vessel equipped with a magnetic stirring bar. Four as-prepared vessels were placed into the rotor. The first reactor was equipped with a gas-thermometer. After closing the rotor with the security cap it was placed into the microwave oven. The predicted microwave program was started. After the reaction was finished, the mixture was extracted with ethyl acetate (15 ml). The organic phase was separated and analyzed by FID- and GC-MSD.

Experimental procedure for conversion in supercritical alcohol

To degassed and water-free alcohol (30 ml; *cf.* Table 1) α-pinene (3.15 mmol, 430 mg, 500 µl) was added into the quartz vessel equipped with a magnetic stirring bar and three passive heating elements (PHE, SiC, cylindrical *r*: 2.5 mm, *h*: 10 mm; Anton Paar GmbH). Four as-prepared vessels were placed into the rotor. The first reactor was equipped with a gas-thermometer. After closing the rotor with the security cap was placed into the microwave oven. The predicted microwave-program was started. After the reaction 1 ml of the reaction mixture was analyzed by FID- and GC-MSD.

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