

Thermal Behaviour of Selected C₁₀H₁₆ Monoterpenes

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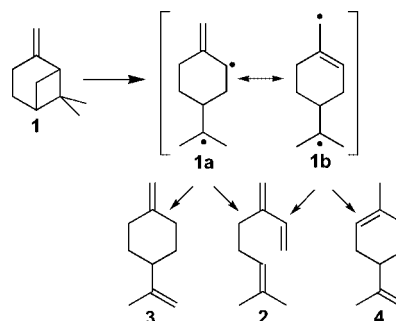
The presented work investigates the thermal behaviour of selected monoterpenes under various reactor temperatures and residence times (carrier gas, reactor inserts). In addition to the analysis of the liquid products by capillary GC and GC-MS, chemical derivatisation techniques (Diels–Alder reaction, hydrogenation) were used to identify the liquid-phase products. A thermal conversion of β -pinene (**1**), myrcene (**2**)

and limonene (**4**) in a reaction network is presented and the experimental evidence for the formation of pyrolysis products by a biradical pathway is discussed. The reaction network was modified based on the identification of additional C₁₀H₁₆ terpene isomers.

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Introduction

It is well known that β -pinene (**1**) is thermally converted into myrcene (**2**).^[1] This reaction exemplifies the chemistry of C₁₀H₁₆ terpene isomers and is also interesting from a mechanistic and thermodynamic viewpoint. Myrcene is an important raw material for the synthesis of terpene alcohols and aldehydes (e.g. citronellol and citral), which are relevant intermediates in the synthesis of vitamins A and E.^[2–4] Preliminary experiments revealed that in addition to myrcene (**2**) many other C₁₀H₁₆ monoterpenes are formed.^[5–7] The detailed reaction mechanism of this thermal rearrangement to C₁₀H₁₆ monoterpenes is not known. However, it seems that differences in the experimental setup and residence times are responsible for the contradicting yields and compositions of reaction products reported in the literature.^[5–9] Despite the fact that better analytical and technical methods have become available, very little work on the pyrolysis of **1** has been published in recent times.^[10–12] Most researchers do agree that the formation of the reaction products during the pyrolysis of **1** occurs via biradical intermediates (Scheme 1).^[8]



Scheme 1. Biradical reaction intermediates in the thermal transformation of β -pinene (**1**).

It is known that the pyrolysis of β -pinene (**1**) at temperatures above 400 °C leads to a multitude of products that arise from different parallel and consecutive reaction pathways. In addition to the open-chain main product **2**, monocyclic products like Ψ -limonene [*p*-mentha-1(7),8-diene (**3**)]^[13] and limonene (**4**) are also formed, see Scheme 1.^[1,14]

On the basis of our previous work experiences in the field of hydrocarbon pyrolysis,^[15–18] modern chromatographic techniques were combined with chemical methods to gain a closer insight into the reaction mechanism of such C₁₀H₁₆ terpene isomers. Herein we report on our results with the envisioned and implemented experimental setups for the thermal conversion of monoterpene hydrocarbons. These findings can serve as a basis for future investigations dealing with kinetic research and the trapping of transient intermediates.

Results and Discussion

In order to study the influence of various process parameters (carrier-gas flow, temperature) on the pyrolysis of **1**,

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a number of experiments were conducted (see Table 1). A comparison of the yields and selectivities of the collected liquid products indicates that the process parameters and other features connected with the experimental setup exhibit a tremendous influence.^[19]

Table 1. Process parameters of selected pyrolysis experiments ($T = 550\text{ }^{\circ}\text{C}$; substrate: β -pinene).

Experiment	1	2	3
Reactor	HCP empty ^[a]	HCP packed ^[b]	DGP ^[c]
Flow rate (N_2) [L/min]	0.15	0.15	1
Heated reactor volume [mL]	120	30	30
Average residence time ^[d] [s]	11.8	2.7	0.6
Substrate flow rate [mmol/min]	2.2	3.2	0.018
Substrate flow rate/total flow rate	25%	32%	360 ppm
Yield liquid products [%]	96	93	— ^[e]
β -Pinene in liquid product [%]	<5	<6	<0.01

[a] High-concentration pyrolysis, empty quartz tube, see the following text. [b] High-concentration pyrolysis, packed quartz tube, see Exp. Sect. [c] Dilution-gas pyrolysis, see the following text. [d] For the calculation of the average residence time, see Supporting Information. [e] Not measurable under our conditions.

The observed differences are due to variations in carrier gas and average residence times of the experimental setup employed. In the case of high-concentration pyrolysis (HCP), high substrate throughput was realised by fast and direct evaporation of the starting material. The substrate was passed through a heated evaporator (see Figure 1). It was shown in the experiments that high yields of liquid products and a nearly quantitative conversion of starting material are achieved by using a low carrier gas flow (Table 1).

Despite the fact that there were only minor differences in the experimental setup (Figures 1 and 2), the differences in the average residence times for the two sets of pyrolysis apparatus were significant (Table 1). In the case of dilution-gas pyrolysis (DGP), the average residence time can be de-

creased by realising a high carrier gas flow. The throughput was restricted to the flow rate of the carrier gas.

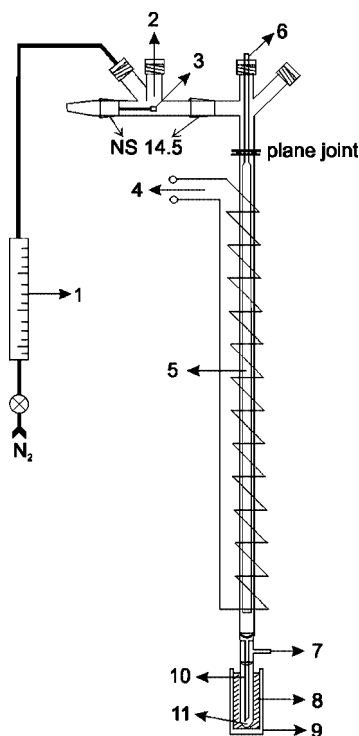


Figure 2. Schematic experimental setup for dilution-gas pyrolysis (DGP); 1 – rotameter for carrier gas, 2 – septum for dosing substrate, 3 – quartz ladle, 4 – electrical heating, 5 – quartz reactor, 6 – variable insert, 7 – exhaust for pyrolysis and carrier gas, 8 – coolant (liquid N_2), 9 – Dewar vessel, 10 – cold finger, 11 – liquid product collector.

Both pyrolysis techniques were comparable. A high throughput was realised by using HCP (packed quartz reactor), so that within short experimental times enough liquid products for further investigations were generated. On the

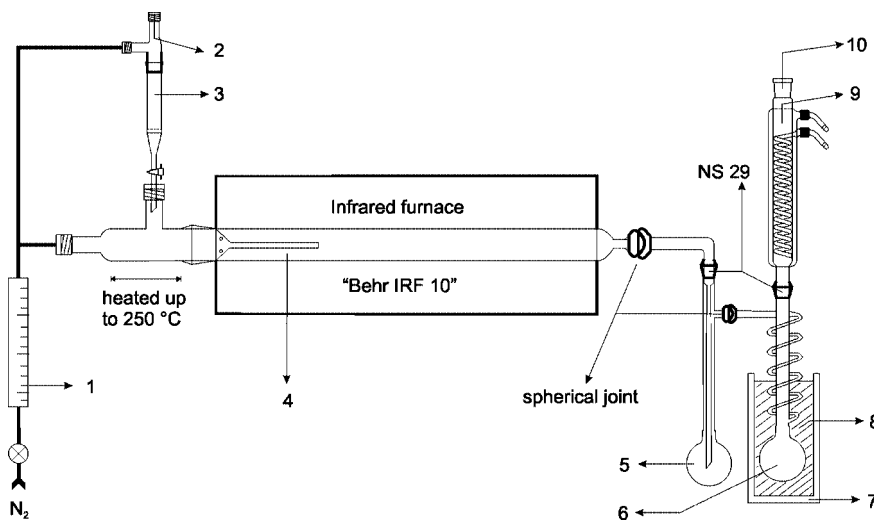


Figure 1. Schematic experimental setup for high-concentration pyrolysis (HCP); 1 – rotameter for carrier gas, 2 – septum for dosing substrate, 3 – substrate reservoir, 4 – quartz reactor, 5 – condenser 1 (air cooling), 6 – condenser 2 (cold trap), 7 – Dewar vessel, 8 – coolant (liquid N_2), 9 – jacketed coil condenser, 10 – exhaust for pyrolysis and carrier gas.

other hand, because of the small amounts of starting material required for the DGP experiments, this method was suitable for screening the chemistry of such hydrocarbons at elevated temperatures.

Because of the slow and continuous evaporation of the substrate and the low substrate concentration in the total gas flow, reproducible experimental conditions in the pyrolysis reactor were realised in the case of DGP. Thus, polymerisation reactions were also minimised. The residence time of the starting material was determined from the carrier gas velocity and the surface/volume ratio. The selectivity of myrcene (**2**) increases with increasing surface/volume ratio (Figure 3).

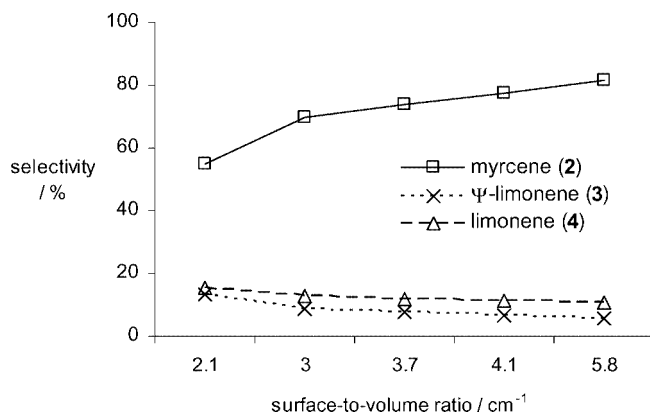


Figure 3. Selectivity of selected liquid products of β -pinene (**1**) pyrolysis depending on the surface/volume ratio (dilution-gas pyrolysis, $T = 500\text{ }^{\circ}\text{C}$, carrier gas: N_2 , flow rate: 1 L/min).

In further investigations using the reactor setup of DGP, compound **1** did not react below $350\text{ }^{\circ}\text{C}$ under the conditions investigated. Apparently, this temperature was too low to induce ring conversions. At $450\text{ }^{\circ}\text{C}$, no other side-product was formed, besides Ψ -limonene (**3**) and limonene (**4**), in noteworthy concentrations. Increasing the temperature to $650\text{ }^{\circ}\text{C}$ or even higher leads to the formation of aromatics and coke. Overall, the yield and selectivity of the target

product **2** decreased dramatically with increasing temperature, while it remained constant for the by-product limonene (Figure 4).

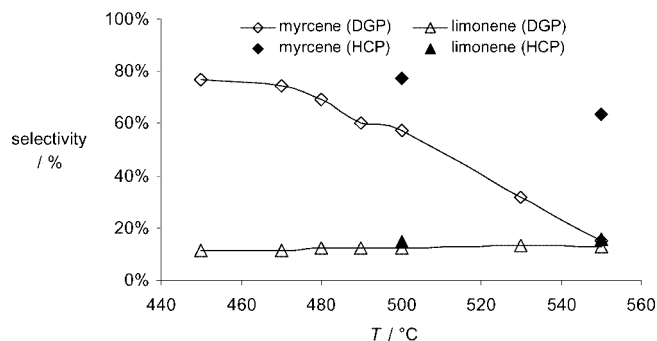


Figure 4. Selectivity for myrcene (**2**) and limonene (**4**) during the pyrolysis of β -pinene (**1**) as a function of the pyrolysis temperature and experimental setup, (carrier gas: N_2), HCP – high-concentration pyrolysis (packed quartz tube), DGP – dilution-gas pyrolysis.

The conversion to known and unknown β -pinene pyrolysis products, besides **2**, changes with rising temperature. In order to obtain larger amounts of liquid pyrolysis products for identification by chemical derivatisation, **1** was converted at $550\text{ }^{\circ}\text{C}$ using the HCP setup (packed quartz tube). Comparison with the results obtained from the DGP setup shows differences in the selectivity (Figure 4). The differences in product distribution resulted from the different carrier gas/substrate rates realised from both experimental setups (Table 1). On summarising these observations, it was concluded that myrcene (**2**) is preferentially formed if either a low residence time combined with a low flow rate and temperature ($450\text{ }^{\circ}\text{C}$), or longer residence times and higher temperatures ($550\text{ }^{\circ}\text{C}$) are realised.

The identification of the unknown products was rather difficult and required complex analytical approaches. For this purpose, a test mixture was prepared from readily available monoterpene hydrocarbons and analysed with GC-FID and GC-MS. Comparative gas chromatograms are depicted in Figure 5.

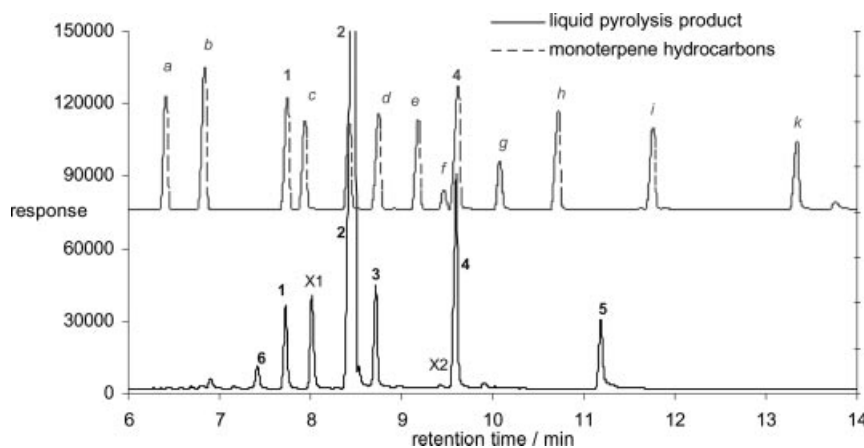


Figure 5. Comparison of gas chromatograms (GC-FID) of a test mixture containing monoterpene hydrocarbons and the liquid pyrolysis products of β -pinene; 1 – β -pinene, 2 – myrcene, 3 – Ψ -limonene, 4 – limonene, 5 – 5-ethylidene-1-methylcycloheptene (5-EMCHp), 6 – iridane-1(6),8-diene, X1 – unknown (M^+ : $m/z = 136$, $\text{C}_{10}\text{H}_{16}$), X2 – unknown (M^+ : $m/z = 134$, $\text{C}_{10}\text{H}_{14}$), a – α -pinene, b – camphene, c – *trans*-islimonene, d – α -phellandrene, e – α -terpinene, f – *p*-cymene, g – *trans*-ocimene, h – γ -terpinene, i – terpinolene, k – alloocimene.

Figure 5 shows that besides the target compound **2** and limonene (**4**), many other products were formed during the pyrolysis of **1**. Most of the products were identified as $C_{10}H_{16}$ isomers by GC-MS. Mass spectrometry also revealed one compound with a molar mass that is 2 units smaller than that of the starting material (X2, Figure 5). The structure has not yet been identified. However, initial data does not indicate aromatic structures like that found in *p*-cymene (4-methyl-1-isopropylbenzene). Combined results of GC-FID experiments and spectroscopic data (GC-MS) only provide evidence for the structures of $C_{10}H_{16}$ isomers. To extend these results, chemical derivatisation reactions were conducted.

In the first step, a Diels–Alder (DA) reaction was carried out in order to gain a closer look into the diversity of known and unknown hydrocarbon structures. Hydrocarbons containing a 1,3-diene system, such as compound **2** or α -phellandrene, undergo a DA reaction, thus making it an adequate instrument to characterise the mixture of pyrolysis products. Depending on the solvent and the dienophile, quantitative conversion was observed over a very short time range using **2** and α -phellandrene as the substrate. Similar reactions of liquid pyrolysis products revealed only one DA-active compound – myrcene (**2**). As a consequence of this result, the formation of monocyclic hydrocarbons with a 1,3-diene system (e.g. α -phellandrene, α -terpinene) by thermal rearrangement of **1** can be excluded (see Supporting Information).

The combination of GC-MS analyses and the heterogeneously catalysed hydrogenation of unsaturated hydrocarbons in ethyl acetate as the solvent is an established and powerful method for structural investigations. In order to obtain an overview of the possible hydrogenation products, pure compounds (**1**, **2** and **4**) were hydrogenated in addition to the liquid pyrolysis products received from HCP of hydrocarbon **1**.

Liquid-phase hydrogenation of compound **4** revealed that hydrogen addition takes place in two steps (Figure 6). In the first step, $C_{10}H_{18}$ hydrocarbons were formed by hydrogenation of the less hindered exocyclic double bond. Subsequently, the remaining double bond was reduced, and

thus a 3:1 mixture of *cis/trans*-*p*-menthane (4-methyl-1-isopropylcyclohexane) was obtained. These findings are in good agreement with results derived from the heterogeneous hydrogenation of the orange oil with PtO_2 as the catalyst.^[20] In a side reaction, *p*-cymene was formed. The oxidation of **4** to *p*-cymene under reducing reaction conditions can be explained by Pd-catalysed disproportionation reactions as reported in the literature.^[21]

In contrast to **4**, compound **2** is a triply unsaturated open-chain molecule containing one conjugated double-bond system. Similar to **4**, hydrogenation of **2** takes place stepwise producing several $C_{10}H_{18}$ and $C_{10}H_{20}$ hydrocarbons as intermediates (Figure 7). At the end of the hydrogen addition 2,6-dimethyloctane was formed.

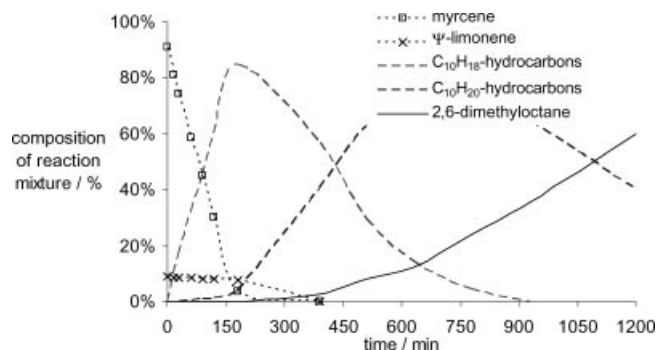
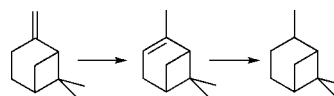


Figure 7. Liquid-phase hydrogenation of myrcene (**2**) in ethyl acetate at room temperature and atmospheric pressure as a function of reaction time (hydrogenation catalyst: Pd on a porous glass support).

When β -pinene (**1**) was used as the starting material, the hydrogenation catalyst isomerised the double bond of **1** in the first step, thus leading to α -pinene. A mixture of *cis*- and *trans*-pinane (2,6,6-trimethylbicyclo[3.1.1]heptane) was obtained after hydrogenation of α -pinene (Scheme 2). The



Scheme 2. Liquid-phase hydrogenation products of β -pinene (**1**) in ethyl acetate.

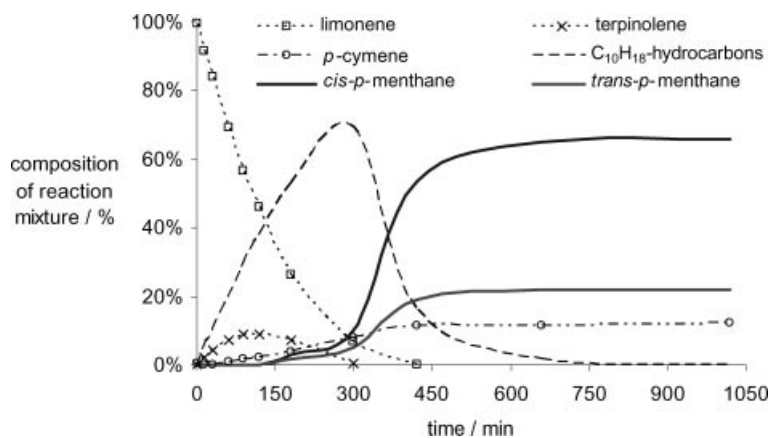
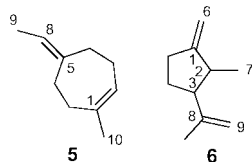


Figure 6. Liquid-phase hydrogenation of limonene (**4**) in ethyl acetate at room temperature and atmospheric pressure as a function of reaction time (hydrogenation catalyst: Pd on a porous glass support).

isomerisation of either pinene isomer into the other is a well-known and technically important reaction.^[22]

Our findings are in good agreement with research conducted on the hydrogenation of α -pinene.^[23] The hydrogenation of α -pinene is an important step in the technical synthesis of linalool. In situ reduction with hydrogen (Li/C₂H₅NH₂) gives a mixture of *cis*- (56–57%) and *trans*-pinane (43–44%).^[24] The heterogeneous hydrogenation leads to mixtures of pinane isomers with the *cis* selectivity ranging from 49 up to 99% depending on the catalyst (Pt/C, Pd/C or Ni), the H₂ pressure and the reaction temperature.^[24] Liquid-phase hydrogenation in ethyl acetate at ambient pressure and temperature with Pd on a porous glass support gave mixtures with a 75% *cis* selectivity.

After the hydrogenation of the liquid pyrolysis product derived from HCP of **1**, all hydrogenated products described above were identified in the reaction mixture, either by mass spectra (GC-MS) or by a comparison of the retention times of the pure compounds. Comparing the GC-MS data of the crude and hydrogenated pyrolysis mixture allowed for the identification of two other C₁₀H₁₆ hydrocarbons: 5-ethylidene-1-methylcycloheptene (**5**, 5-EMCHp) and iridane-1(6),8-diene (**6**) (Scheme 3).



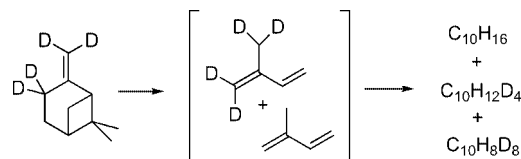
Scheme 3. Further thermal isomerisation products from β -pinene (**1**) pyrolysis [5-ethylidene-1-methylcycloheptene (**5**) and iridane-1(6),8-diene (**6**)].

In summary, the combined experimental studies (DA, hydrogenation reactions), comparison with the literature values, and the results of the GC-FID and GC-MS investigations allowed for the identification of the majority of the rearrangement products obtained from β -pinene pyrolysis. By a comparison with the reference compounds it can be ruled out that camphene and further menthadiene hydro-

carbons (e.g. α -phellandrene, α -terpinene, terpinolene) were formed during the thermal isomerisation of compound **1**.

As described in the literature,^[5–9] the thermal rearrangement of compound **1** leads to products **2–4**. Apparently, the conversion proceeds via biradical intermediates as shown in Scheme 1. A concerted mechanism (by cycloreversion of the cyclobutane ring in β -pinene) can be excluded, because of the product distribution and DA reactivity: in the case of such a concerted reaction, two DA-active compounds should have been observed.^[19] However, the liquid pyrolysis mixture yielded only one product with the 1,3-diene system – hydrocarbon **2**. Therefore, the initial reaction and thermal rearrangement of **1** must proceed via biradical intermediates.

It is also possible that the pyrolysis of hydrocarbon **1** progresses via lower molecular intermediates, e.g. isoprene (Scheme 4). This can be elucidated by pyrolysing 3,3,10,10-[²H₄]- β -pinene (β -pinene-D₄). Thermal conversion of β -pinene-D₄ would lead to a mixture of un-, tetra- and octadeuterated products (statistical distribution: D₀/D₄/D₈ = 1:2:1) if the reaction involved lower molecular fragments. It was shown that pyrolysis products with various amounts of deuterium (DGP of **1** and β -pinene-D₄ in a 1:1 ratio) were separated in GC analyses.^[25]



Scheme 4. Hypothetical reaction pathway via lower molecular intermediates.

The formation of un- and octadeuterated pyrolysis products was excluded, because the mass spectrum of the pyrolysis products of β -pinene-D₄ did not contain signals with m/z = 136 and 144 (Figure 8). A reaction pathway involving lower molecular reaction intermediates was thus ruled out. Therefore, the thermal gas-phase isomerisation of **1** pro-

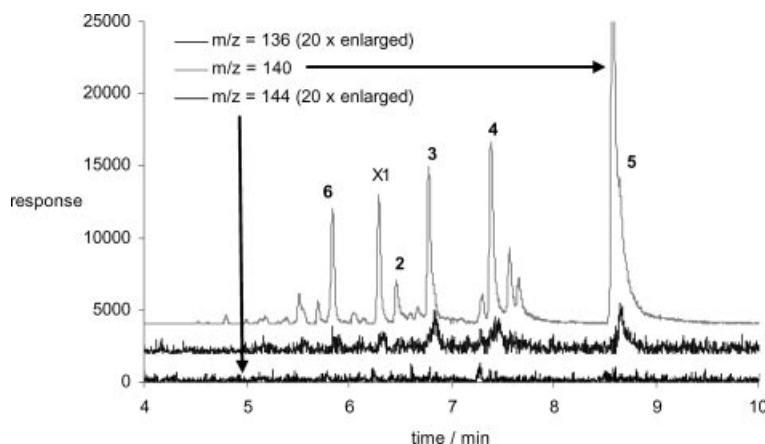
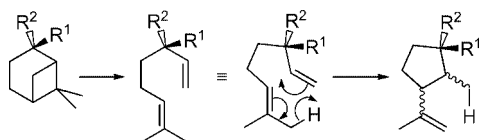


Figure 8. Selected ion chromatograms (GC-MSD) obtained from the dilution gas pyrolysis (DGP) of β -pinene-D₄, (T = 500 °C, carrier gas: N₂, flow rate: 1 L/min), **2** – myrcene-4,4,10,10-D₄, **3** – Ψ -limonene-2,2,7,7-D₄, **4** – limonene-6,6,7,7-D₄, **5** – 5-ethylidene-1-methylcycloheptene-4,4,6,6-D₄, **6** – iridane-1(6),8-diene-5,5,6,6-D₄, X1 – unknown (M^+ : m/z = 140, C₁₀H₁₂D₄).

ceeds by a monomolecular mechanism under the conditions investigated.

On the basis of these results, the formation of thermal isomerisation products of **1** must proceed via biradical intermediates. The formation of **3** and **4** from biradicals **1a** and **1b**, respectively (Scheme 1), can be explained by a [1,5]-(**3**) and [1,7]-H shift (**4**). Target product **2** was formed either from biradical **1a** or from **1b** by homolytic bond cleavage followed by (concerted) intramolecular radical recombination. Compounds **2–4** were directly formed from the substrate **1**, and are thus referred to as primary pyrolysis products (ppp).

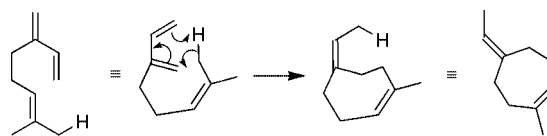
Furthermore, during the investigation of the thermal conversion of **1**, it was observed that the ppp undergo consecutive reactions. The pyrolysis products **5** and **6** were formed from target product **2**. The occurrence of **6** in connection with β -pinene pyrolysis was not found in the literature. It is known that pinene analogues (e.g. nopinone, pinane, pinan-2-ol) undergo cyclisation reactions involving open-chain intermediates (analogues of **2**) and lead to related substances as shown in Scheme 5.^[10,26–29] From a combination of mass spectra and hydrogenation experiments it was concluded that the thermal conversion product **6** was formed from primary pyrolysis product **2** by an ene reaction.



Scheme 5. Cyclisation of pinene analogues of the related cyclopentane derivatives by an ene reaction.

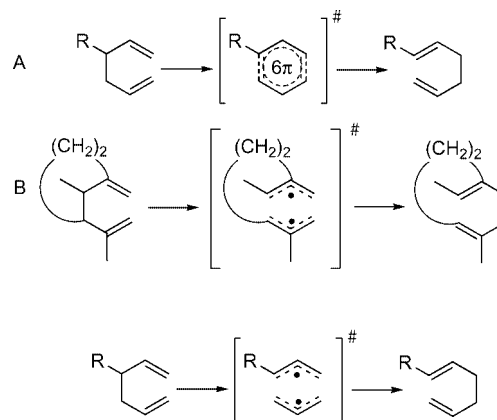
The formation of compound **5** (5-EMCHp), which was identified in the liquid pyrolysis-product mixture of substrate **1**, can be explained in different ways. According to the literature, 5-EMCHp is built from compound **2** by an ene reaction as depicted in Scheme 6.^[30]

Another possible reaction pathway leading to 5-EMCHp could be based on the Cope rearrangement (Scheme 7, A). In addition to the classical reaction pathway, a nonclassical



Scheme 6. Formation of 5-EMCHp by an ene reaction from myrcene.

Cope rearrangement of iridane-1(6),8-diene (**6**) via radical intermediates that are stabilised by allylic rearrangement could also lead to 5-EMCHp.



Scheme 7. Cope rearrangement (A) and formation of 5-EMCHp by a nonclassical Cope rearrangement (B) of iridane-1(6),8-diene, see ref.^[26]

Thermal isomerisation of iridane-1(6),8-diene to 5-EMCHp can be explained by the nonclassical pathway of the Cope rearrangement (Scheme 7).^[26] The unusual drawing of the starting molecule [iridane-1(6),8-diene] and the target 5-EMCHp in Scheme 7 illustrate the similarity between the classical and non-classical Cope rearrangements. Probably both reaction pathways participate in the formation of 5-ethylidene-1-methylcycloheptene (**5**).

The composition profile of the identified liquid pyrolysis products derived from **1** indicates a strong dependence concerning the reaction temperature for the DGP setup (Figure 9). On the one hand, increasing the temperature de-

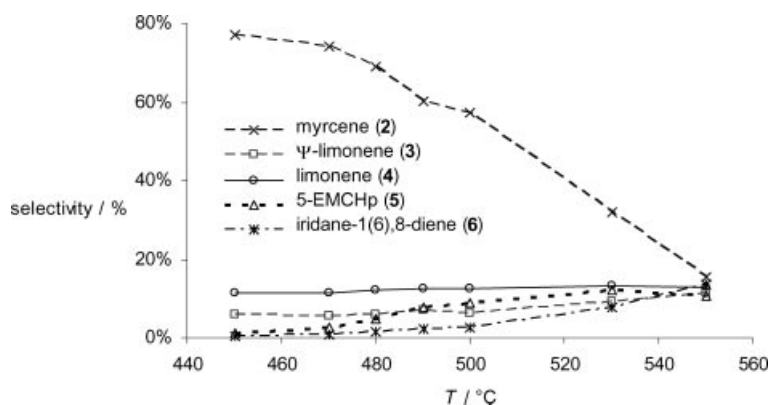


Figure 9. Selectivity of liquid pyrolysis products of β -pinene (**1**) as a function of the reaction temperature, (dilution-gas pyrolysis, carrier gas: N_2 , flow rate: 1 L/min).

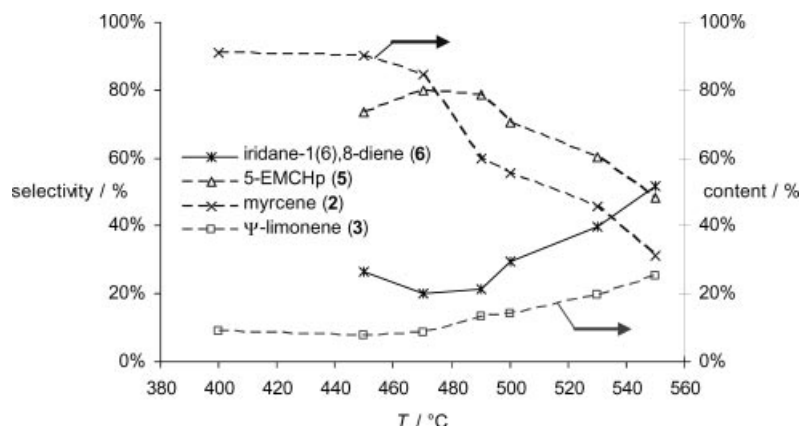


Figure 10. Content of myrcene (2) and Ψ-limonene (3) in the pyrolysis product and selectivities of compounds 5 and 6 as a function of the reaction temperature (dilution-gas pyrolysis, starting material: 2, carrier gas: N₂, flow rate: 1 L/min).

creased the amount of collected liquid pyrolysis products. On the other hand, the selectivity of the target product 2 decreased and approached the amount of the other products.

The results obtained from the pyrolysis of myrcene (2) and high-temperature pyrolysis of 1 are in agreement. Hydrocarbon 2 was not noticeably transformed until the reaction temperature reached 470 °C as shown in Figure 10, and the concentration decreased with increasing temperature. The selectivity, corrected for the conversion of 2, for the formation of 5 and 6 were in the same range as in the pyrolysis of 1.

The occurrence of Ψ-limonene (3) was also observed in the reaction of 1 at 450 °C. In contrast to the pyrolysis of 1, compound 3 is not a thermal isomerisation product of 2, but an inseparable impurity found in the starting material.

For the definite identification of 3, the reaction mixture of the myrcene pyrolysis was heated at 100 °C for 24 h. Under these reaction conditions, 2 dimerised by a DA reaction. Compound 3 was separated from the myrcene dimer by Kugelrohr distillation and was characterised by a combination of analytical methods based on GC, GC-MS and HPLC-NMR. Here it should be noted that the findings are in good agreement with results obtained from the pyrolysis of hydrocarbon 1 in a microreactor at 510 °C under normal pressure.^[12] The spectroscopic data are comparable with the data from the literature.^[31]

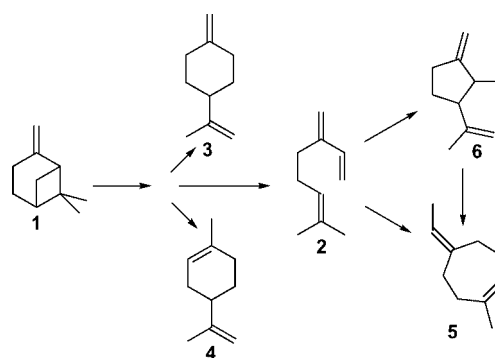
No conversion of limonene (4) was detected at 450 °C (Figures 3, 4 and 9). Hydrocarbon 4, like 2, seems to be thermodynamically stable under the experimental conditions investigated. Therefore, additional pyrolysis experiments were carried out at temperatures of 550 and 600 °C. Unconverted 4 was still found in the pyrolysis products at 550 °C. This observation additionally confirms the thermodynamic stability of 4. A temperature increase to 600 °C yielded monoaromatic products such as toluene or xylene.

Summary

Two efficient and complementary experimental setups were established for the investigation of the gas-phase be-

haviour of terpene hydrocarbons. It was shown that chemical derivatisation techniques were as effective as modern gas-chromatographic experiments. Together they provide the essential tools needed for the identification of the composition of hydrocarbon mixtures.

In agreement with previous results,^[5,8,10,27,30] the main products [myrcene (2), Ψ-limonene (3) and limonene (4)] from β-pinene pyrolysis were identified. The existence of 5-ethylidene-1-methylcycloheptene (5) was also confirmed.^[30] Within this investigation, a new substance in the thermal network of C₁₀H₁₆ hydrocarbons – iridane-1(6),8-diene (6) – was detected. The internal crosslink of products starting from β-pinene (1) is depicted in Scheme 8. It was shown that the formation of primary pyrolysis products (2–4) does not proceed by the concerted mechanism or via lower molecular weight fragments (isoprene). Rather, it appears to progress via joint biradical reaction intermediates. Secondary pyrolysis products (5, 6) were formed in consecutive reactions.



Scheme 8. Product network of β-pinene pyrolysis (legend: see Introduction and Scheme 3).

Considering the product distribution of β-pinene pyrolysis, a concerted reaction mechanism can be ruled out. The reaction proceeds through biradical intermediates. Additional experiments with other/additional carrier gases (H₂, D₂, toluene) or trapping methods (very low temperatures, spin traps) may yield further information on the bi-

radical reaction mechanism. On the basis of the pyrolysis findings, the chemical derivatisation and the gas chromatographic results presented within this paper, kinetic measurements are planned in order to gain further insight into the gas-phase behaviour of β -pinene.

Experimental Section

General Remarks: β -Pinene (**1**, ca. 99%), myrcene (**2**, ca. 80%) and limonene (**4**, ca. 97%) were purchased from Fluka. The purity was determined by capillary gas chromatography. Dichloromethane (DCM) was used for the dilution of liquid pyrolysis products. All other chemicals were readily available from commercial sources and were used without further purification. Analyses were carried out with a 6890 Series GC and 5890 Series II/5972 Series MSD GC from Agilent Technologies. Hexadecane (3 μ L) was used in all experiments as an internal standard. Products were identified by comparing either the retention time and/or mass spectra of pure reference compounds. GC-FID: HP 5, 30 m $\times$ 0.32 mm $\times$ 0.25 μ m, H_2 – 5 psi, program: 35 $^{\circ}$ C (hold 1 min), 4 K/min up to 80 $^{\circ}$ C, 4.5 K/min up to 90 $^{\circ}$ C, 35 K/min up to 280 $^{\circ}$ C (hold 3 min), injector temperature: 250 $^{\circ}$ C, detector temperature: 280 $^{\circ}$ C. GC-MSD: HP 5, 30 m $\times$ 0.32 mm $\times$ 0.25 μ m, He – 7 psi, program: 55 $^{\circ}$ C (hold 1 min), 5 K/min up to 150 $^{\circ}$ C, 20 K/min up to 280 $^{\circ}$ C (hold 5 min), injector temperature: 280 $^{\circ}$ C, EI (70 eV). NMR spectra were recorded with a Bruker Avance 200 MHz system (measurement frequency was 200 MHz for ^1H NMR and 50 MHz for ^{13}C NMR) in a 5-mm tube at room temperature. Measurements were carried out using trichloromethane- d_4 (CDCl_3) as solvent. IR spectra were measured with a Perkin–Elmer FT-IR spectrum 100 series device equipped with a universal ATR sampling accessory.

Pyrolysis: The investigated $\text{C}_{10}\text{H}_{16}$ hydrocarbons were pyrolysed over the temperature range 350–750 $^{\circ}$ C using two different experimental setups explained below and presented in Figures 1 and 2.

(a) Dilution-Gas Pyrolysis (DGP): Pyrolyses were carried out with an electrically heated quartz tube with a length of 50 cm and with a pyrolysis zone of approximately 20 cm (Figure 2).^[15] In all experiments, oxygen-free nitrogen with a purity of 99.999% was used as the carrier gas. Residence times were varied by either selecting different carrier gas flow rates (0.5, 1 and 1.2 L/min) or by variation of the surface/volume ratios of the reactor (see Supporting Information). The starting material was introduced onto a quartz ladle at the top part of the pyrolysis apparatus using a glass syringe (50 or 100 μ L). The starting material was carried along with the nitrogen stream into the reactor. Vaporisation of the starting material was supported by heating the ladle to 50 $^{\circ}$ C with a hot blast. Pyrolysis products were collected in a cold trap (liquid nitrogen) and were dissolved in 1 mL of DCM. The liquid products obtained were analysed by GC-FID and GC-MS using 3 μ L of hexadecane as an internal standard.

(b) High-Concentration Pyrolysis (HCP): The pyrolysis setup consists of three different structural elements: an evaporator, the pyrolysis reactor and a condenser. The evaporator is schematically depicted in Figure 1. In order to secure the complete and fast vaporisation of the starting material, the lower part of the evaporator was heated by an air fan up to 250 $^{\circ}$ C. Gaseous starting material was carried along with the nitrogen stream (0.15 L/min) into the reactor. The central piece of this experimental setup was the infrared furnace “IRF 10” (Behr Labortechnik GmbH, Düsseldorf, Germany), which was integrated into the setup consisting of an infra-

red-heated quartz reactor with an approximate length of 40 cm. The pyrolysis temperature was controlled with an Ni/CrNi thermocouple placed in the middle of the reactor. The temperature gradient (see Supporting Information) reveals that the pyrolysis occurred in a 20 cm long section of the whole reactor. In order to increase the reactor surface, the quartz tube was packed with small pieces of quartz glass calcinated in an air stream at 900 $^{\circ}$ C. The condenser system is shown in Figure 1. The second condenser was designed as a cold trap (liquid nitrogen) to allow for complete condensation of the pyrolysis products. A small amount of the product collected (50 μ L) was diluted in 1 mL of DCM and analysed by GC-FID and GC-MS after addition of 3 μ L of hexadecane as an internal standard. After every pyrolysis experiment with the HCP setup, the reactor was cleaned in an air stream at 900 $^{\circ}$ C.

Diels–Alder (DA) Reaction: The DA reactions were performed in two-necked flasks (100 mL) with reflux condensers and septums for sampling. Maleic anhydride (after purification by recrystallisation from chloroform) and tetracyanoethylene were used as dienophiles. Ethyl acetate (AcOEt), benzene and dichloromethane were used as solvents without further purification. The starting material (myrcene or α -phellandrene; 1.50 g, 11 mmol; 2 g in the case of the pyrolysis mixture) was dissolved in the solvent (AcOEt, benzene or DCM; 15 mL) together with hexadecane (200 μ L) as an internal standard. After adding the dienophile (12 mmol) and further solvent (15 mL), a sample (500 μ L) was taken from the reaction mixture. While refluxing for 2–4 h, samples were taken every 30 min and were analysed by GC-FID.

Hydrogenation: Liquid-phase hydrogenation was carried out in ethyl acetate as solvent. The purity of the hydrogen used was higher than 99.998%. The catalyst consisted of a porous glass support coated with palladium.

(a) Preparation of Catalyst: Silica was the main component (>95%) of the porous glass support TRISOPOR[®] (VitraBio GmbH, Steinach, Germany). In a round-bottom flask (100 mL), $\text{Pd}(\text{OAc})_2$ (20.2 mg, 0.09 mmol) was dissolved in dichloromethane (50 mL). The porous glass support (1 g) was added and the solvent was completely removed in vacuo. The coated glass was calcinated at 300 $^{\circ}$ C for 3 h (heating to 300 $^{\circ}$ C in 20 min) in the muffle furnace “mls 1200 pyro” (MLS GmbH, Leutkirch, Germany).

(b) Experimental Setup: In a Schlenk flask, the starting material (β -pinene, myrcene, limonene: 2.04 g, 15 mmol; 3 g in the case of the pyrolysis mixture) was dissolved together with hexadecane (200 μ L) as an internal standard in ethyl acetate (60 mL). After adding the catalyst (0.4 g), a sample (500 μ L) was taken. The flask was connected to the hydrogen reservoir by a plug valve and the reaction vessel was flushed with hydrogen (3 $\times$ 400 mL). Hydrogenation was carried out at room temperature and atmospheric pressure in a shaking apparatus “HS 501 digital” (IKA Labortechnik, Staufen, Germany). Every 30 min (after 180 min every 60 min) a sample (500 μ L) was taken. The hydrogenation process was observed by consumption of hydrogen and by analysing the samples with GC-FID and GC-MS (Figures 6 and 7). After the reaction was finished, the catalyst was filtered off, washed with ethyl acetate (2 $\times$ 5 mL) and dried at 105 $^{\circ}$ C before reusing it.

Synthesis

6,6-Dimethylbicyclo[3.1.1]heptan-2-one (Nopinone): Potassium permanganate (26.4 g, 0.17 mol) was added to a mixture of β -pinene (6 g, 44 mmol), aluminium oxide (60 g, 0.59 mol) and water (5 g, 0.28 mol). The mixture was transferred into a beaker (agate) with seven agate balls, inserted into a planetary ball mill “Pulverisette 5” (Fritsch GmbH, Idar-Oberstein, Germany) and milled at

300 rpm for 20 min. Subsequently, the reaction mixture was extracted with DCM (400 mL). After removal of the solvent, the crude product was purified by column chromatography (silica gel 40, 0.063–0.2 mm, Merck) using a mixture of ethyl acetate/*n*-hexane (1:3) as solvent. Yield: 3.4 g per beaker (56% based on β -pinene after purification). $n_D^{20} = 1.480$ [reference (1*R*)-(+)-nopinone: 1.479]. ¹H NMR (CDCl₃): δ = 0.85 (s, 3 H), 1.33 (s, 3 H), 1.59 (d, 1 H), 1.96–2.06 (m, 2 H), 2.24–2.25 (m, 1 H), 2.35–2.38 (dd, 1 H), 2.51–2.58 (m, 3 H) ppm. ¹³C NMR (CDCl₃): δ = 21.3, 21.9, 25.3, 25.7, 32.7, 40.2, 41.0, 57.7, 214.8 ppm. IR (ATR): $\tilde{\nu}$ = 2949, 2928, 2837 ($\nu_{\text{aliph. C-H}}$), 1706 ($\nu_{\text{C=O}}$), 1459 ($\delta_{\text{C-H}}$) cm⁻¹. MS (EI 70 eV, C₉H₁₄O): m/z (%) = 139 (0.9) [M⁺ + 1], 138 (8.6) [M⁺], 123 (16.5), 109 (26.3), 95 (40.8), 83 (100), 81 (37.3), 67 (23.1), 55 (41.4).

3,3,10,10-Tetradeuterio-6,6-dimethyl-2-methylenbicyclo[3.1.1]heptane (β -Pinene-D₄): In a three-necked flask (100 mL) with reflux condenser, gas inlet and septum, a mixture of methyltriphenylphosphonium bromide and sodium amide (13 g, 31.5 mmol; Fluka) was dissolved in dried DMSO-D₆ (15 mL; Aldrich). While stirring and flushing nitrogen through the mixture, nopinone (2.5 g, 18 mmol), dissolved in DMSO-D₆ was slowly added through a glass syringe. After complete addition, the reaction mixture was stirred at 50 °C for 4.5 h. The colour of the reaction mixture changed from pale yellow to auburn and sodium bromide precipitated. The reaction was monitored by taking samples and analysing them by GC-MS. The reaction was quenched with water (300 mL) and the mixture extracted with *n*-pentane (5 × 20 mL). The combined organic extracts were washed with water and dried with anhydrous sodium sulfate. The mixture was then washed with an NaHSO₃ solution and the solvent removed in vacuo. The crude product was purified by column chromatography (silica gel 40) using *n*-pentane as solvent. Yield: 1.74 g (69% based to nopinone). $n_D^{20} = 1.480$ [reference (–)- β -pinene: 1.479]. ¹H NMR (CDCl₃): δ = 0.73 (s, 3 H), 1.24 (s, 3 H), 1.40 (d, 2 H), 1.83 (s, 2 H), 1.97 (m, 1 H), 2.46 (m, 1 H) ppm. IR (ATR): $\tilde{\nu}$ = 2945, 2920, 2869 ($\nu_{\text{aliph. C-H}}$), 2299, 2200, 2101 ($\nu_{\text{aliph. C-D/C=D}}$), 1607 ($\nu_{\text{C=C}}$), 1457 ($\delta_{\text{C-H}}$), 720 (δ_{CH_2}), 684 (δ_{CD_2}) cm⁻¹. MS (EI 70 eV, C₁₀H₁₂D₄): m/z (%) = 141 (0.9) [M⁺ + 1], 140 (9.2) [M⁺], 125 (12.5), 97 (100), 96 (48.8), 95 (22), 81 (16.6), 79 (17.5), 69 (51.2).

Supporting Information (see footnote on the first page of this article): Mass spectra, properties of the reactor inserts used for the DGP setup, temperature gradient in the pyrolysis reactor of the HCP setup and calculation procedure for the average residence times.

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