Catalyst Epoxidation of 3-Carene and Limonene with Aqueous Hydrogen Peroxide, and Selective Synthesis of α-Pinene Epoxide from Turpentine

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Abstract: The epoxidation of turpentine (technical α-pinene), 3-carene, and limonene with aqueous hydrogen peroxide was studied in a new catalytic system employing manganese sulfate, salicylic acid, sodium bicarbonate, and acetonitrile, as a polar solvent. The proposed approach makes it possible to carry out a “chemical separation” of turpentine components, yielding valuable individual derivates of monoterpenes without the need to isolate individual monoterpenes reagents. Specific methods have been developed for the production of α-pinene epoxide, 3-carene epoxide, limonene diepoxide, as well as for two related compounds: 3-carene-5-one and 3-carene-2,5-dione.

Keywords: epoxidation; turpentine; α-pinene; α-pinene epoxide; 3-carene; 3-carene epoxide; limonene; limonene diepoxide; aqueous hydrogen peroxide

1. Introduction

An epoxidation reaction is one of the important methods for the functionalization of terpenes, with established industrial applications. Monoterpenes obtained from widely available and renewable raw plant materials are of particular interest, as they are starting compounds for the production of valuable synths. The most easily accessible natural monoterpenes are β-pinene, α-pinene 1, 3-carene 2, and limonene 3. The epoxides of these terpenes can be used for the synthesis of intermediates used in various fragrance, perfumery and pharmaceutical preparations [1,2], as well as in substances having a sweet taste [3]. Another promising use of α-pinene epoxide 4 is its transformation into pinocarveol and 3-pinanone [4]. Additionally, 3-carene epoxide 5 can be used to obtain carandiols [5]. One of the limonene epoxides has recently been used as a source of chirality in the synthesis of methylphosphonate oligonucleotides [6].

The epoxidation of β-pinene, α-pinene 1, 3-carene 2, and limonene 3 has been reviewed in the literature [7]. Currently, organic peracids and organic peroxides as double bond oxidizers are being more often replaced by ordinary aqueous hydrogen peroxide. This oxidizing agent is readily available, environmentally friendly, and practically waste-free. For sterically hindered α-pinene 1, low reactivity, low conversion, and low yield of epoxide 4 are often observed [7]. Different oxidizing agents may be used: oxygen with additives of cobalt (II) complexes [8,9], air as an oxygen source [10,11], sodium hypochlorite [12], meta-chloroperbenzoic acid [13], and hydrogen peroxide at various concentrations [13–17]. In at least one instance [14], epoxidation of α-pinene 1 was achieved by the action of 30% hydrogen peroxide (10 equivalents) in the presence of manganese sulfate (0.01 equiv.), and NaHCO₃ in an aqueous solution of dimethylformamide (DMF). The resulting yield of epoxide 4 was 54%, but the reaction times were significant and the isolation of the product challenging, as it requires a high-boiling solvent. A similar situation is described in another work [16]. Recently [18–23], other methods of epoxidation of α-pinene 1 have been described that rely, in particular, on catalysts immobilized on magnetic particles [21,22].
3-Carene 2 is usually referred to as an olefin that readily participates in the epoxidation reaction [7]. As oxidizing agents, it is possible to use peracetic acid [5,24] or hydrogen peroxide [5,15,17,25] at various concentrations and at different temperatures. In the oxidation of 3-carene 2 with 35% hydrogen peroxide in the presence of a rhenium catalyst at room temperature [25], the yield of 3-carene epoxide 5 was 75%. However, the required catalyst is expensive and hard to find, and the use of a toxic pyridine is clearly a drawback.

The oxidation of limonene 3 with hydrogen peroxide has received a lot of attention in the literature [7]. However, it should be noted that monoepoxidations, at the double bond in the ring and in the side chain, require difficult-to-find and expensive catalysts: molybdenum [26] and vanadium [27], respectively. Monoepoxidation of limonene has also been described [23,28–32]. The use of 60% hydrogen peroxide and of a conventional catalyst—chromatography grade aluminum oxide—leads to the formation of a mixture of both mono derivatives of limonene and its diepoxide—the reaction requiring the creation of an inert atmosphere [33]. Our interest was drawn to the epoxidation of limonene 3 by the action of 35% aqueous hydrogen peroxide in the presence of methyltrioxorhenium [1]. To obtain a 90% content of limonene diepoxide 8 in the reaction mixture, we employed a 3.4-fold molar amount of hydrogen peroxide and 1 molar percent of the catalyst was used; the reaction was carried out for 40 h at 0 °C.

In our previous communication [34], we studied the epoxidation of β-pinene with hydrogen peroxide in a reaction mixture containing water, sodium bicarbonate, and manganese salts. Methanol, DMF, and acetonitrile were used as the required polar organic solvents, and it was found that the reaction was accelerated by the addition of salicylic acid. Optimum epoxidation was obtained in the presence of acetonitrile, sodium bicarbonate, manganese sulfate, and salicylic acid during oxidation with 35%–38% aqueous hydrogen peroxide at 18–22 °C. A quantitative tandem 1H NMR-GLC method was also developed in order to determine the content of β-pinene and its labile epoxide. In this work, we extended the application of our catalytic system to other monoterpenes: α-pinene 1, 3-carene 2, and limonene 3. We also developed methods for the preparation of epoxides of these monoterpenes, and selectively obtained α-pinene 4 epoxide from turpentine.

2. Results and Discussion

Our objective was to develop a simple, economical, and technologically sound method to produce α-pinene epoxide 4. To this aim, we epoxidized turpentine (technical α-pinene 1), which contained ~75% of the main substance, according to the combined data obtained by GLC and gas chromatography-mass spectrometry [34]. The cost of the technical product is about two orders of magnitude lower than that of commercial α-pinene 1. The strategy to achieve this result consisted of setting up a gradual interaction of technical α-pinene 1 with 36% aqueous hydrogen peroxide in aqueous acetonitrile in the presence of a catalytic system, which included manganese sulfate, bicarbonate sodium and salicylic acid (Scheme 1). Hydrogen peroxide was used in a tenfold molar amount, and manganese sulfate was used in an amount of 2 percent molar amount relative to the loaded substrate. The products of interest—α-pinene epoxide 4, unreacted α-pinene 1, side monoterpenes and their oxidation products—were recovered from the reaction mixture using methylene chloride. After concentrating the extract, α-pinene epoxide 4 was isolated by vacuum distillation in 30% yield. The epoxidation system has a typical selectivity for epoxidation with peracids, so the usual selectivity is observed for α-pinene, namely 2,3-epoxy-cis-pinane 4 is formed. A fraction with a high content of α-pinene 1 was also isolated, which was then subjected to reoxidation using the above procedure. The composition of the reaction mixtures and the structures of the obtained compounds were determined by 1H NMR, GLC and gas chromatography-mass spectrometry, and by comparing the spectra with those described earlier in the literature [35].
Limonene diepoxide 8 was recovered from the partially evaporated reaction mixture with active and epoxidation proceeded exhaustively, with high yields of the desired diepoxides. The system was highly sensitive to the molar ratio of manganese sulfate relative to the loaded substrate. Although, in our work, we did not use the distillation residue containing valuable products of the transformation of β-pinene, 3-carene, and limonene; they can be separated using vacuum distillation or chromatography.

In addition to its simplicity, the proposed method for producing epoxide 4 offers two advantages: (i), the epoxidation of α-pinene 1 is achieved by the action of simple, cheap, and commercially available reagents, and (ii), inexpensive technical α-pinene is used as the starting compound. In the previous case, the epoxidation system has a typical selectivity for epoxidation with peracids, so the usual selectivity is observed for 3-carene, namely trans-3,4-epoxy-carane 5 is formed. Epoxide 5, together with traces of 3-carene 2 and by-products of allylic oxidation—3-carene-5-one 6 and 3-carene-2,5-dione 7 (Scheme 2)—were extracted with methylene chloride. The formation of compounds 6 and 7 was previously noted during the catalytic oxidation of 3-carene 2 in the presence of a cobalt catalyst [36]. The obtained extract was concentrated, and the 3-carene epoxide 5 was isolated by vacuum distillation with a yield of 47%. The 3-carene-5-one 6 and 3-carene-2,5-dione 7 were isolated from the distillation residue by C-18 reverse phase chromatography in 13% and 7% yields, respectively. The composition of the reaction mixtures and the structure of the obtained compounds were established on the basis of analysis by 1H NMR, GLC, and gas chromatography-mass spectrometry; the 1H NMR spectrum of epoxide 5 coincided with that published earlier [25].

Epoxidation of limonene 3 with 33% aqueous hydrogen peroxide was carried out in the presence of the same catalytic system, consisting of manganese sulfate (2 percent molar), sodium bicarbonate, and salicylic acid. The complete conversion of 3-carene 2 was achieved using approximately ten times the amount of hydrogen peroxide. As in the previous case, the epoxidation system has a typical selectivity for epoxidation with peracids, so the usual selectivity is observed for 3-carene, namely trans-3,4-epoxy-carane 5 is formed. Epoxide 5, together with traces of 3-carene 2 and by-products of allylic oxidation—3-carene-5-one 6 and 3-carene-2,5-dione 7 (Scheme 2)—were extracted with methylene chloride. The formation of compounds 6 and 7 was previously noted during the catalytic oxidation of 3-carene 2 in the presence of a cobalt catalyst [36]. The obtained extract was concentrated, and the 3-carene epoxide 5 was isolated by vacuum distillation with a yield of 47%. The 3-carene-5-one 6 and 3-carene-2,5-dione 7 were isolated from the distillation residue by C-18 reverse phase chromatography in 13% and 7% yields, respectively. The composition of the reaction mixtures and the structure of the obtained compounds were established on the basis of analysis by 1H NMR, GLC, and gas chromatography-mass spectrometry; the 1H NMR spectrum of epoxide 5 coincided with that published earlier [25].
Based on $^1$H NMR data, and by comparison with published data [37,38], the limonene diepoxide 8 obtained in our work consists of stereoisomers 1S,2R,4R,8S, 1S,2R,4R,8R, 1R,2S,4R,8S, and 1R,2S,4R,8R, which are present in the mixture in a ratio of 1.4:1.0:2.0:1.5. We did not observe any significant differences in the composition of the mixtures of limonene diepoxides from different syntheses. At the same time, enrichment in some isomers could be observed during distillation. We did not observe isomerization of isomers of limonene diepoxides into each other when they were kept with a catalytic system, or during distillation.

In conclusion, we have developed a catalytic system for the epoxidation of monoterpenes and synthesis of α-pinene epoxide 4, 3-carene epoxide 5, limonene diepoxide 8, as well as side compounds—3-carene-5-one 6 and 3-carene-2,5-dione 7. Optimal conditions with good synthetic results were obtained by allowing the monoterpene to interact with 33%-38% aqueous hydrogen peroxide in an aqueous solution of acetonitrile in the presence of a catalytic system at a temperature of 18–25 °C. A distinct advantage of the proposed method is the possible selective oxidation of turpentine with the isolation of valuable individual products, followed by a recovery of the distillation residue and repeated oxidation cycles in the same catalytic system.

3. Materials and Methods

$^1$H NMR spectra were recorded on a Bruker DRX-500 (Bruker BioSpin, Rheinstetten, Germany) and AV-400 spectrometers with an operating frequency of 500.13 MHz and 400.134 MHz for solutions in CDCl$_3$, using chloroform signals as an internal standard. GLC analysis was performed on a 7820A chromatograph (Agilent Technologies, Santa Clara, CA, US) with a flame ionization detector and an HP-5 capillary column (0.25 mm × 30 m × 0.25 μm), carrier gas helium, rate of 2 mL/min. Analysis by gas chromatography-mass spectrometry was performed on an Agilent 7890A instrument with an Agilent 5975C (Agilent Technologies, Santa Clara, CA, US) quadrupole mass detector, an HP-5MS quartz column (0.25 mm × 30 m × 0.25 μm), and an HP-5973N gas chromatography-mass spectrometer (Agilent Technologies) with a column HP-5MS.

Quantitative analysis by GLC was performed on an HP 5890 Series chromatograph (Hewlett-Packard Company, Palo Alto, CA, US) with a katharometer and an HP-5 capillary column, 30 m long, 0.53 mm inner diameter, and a stationary phase layer with a thickness of (block copolymer of dimethylpolysiloxane and phenylpolysiloxane) 2.65 μm; evaporator temperature 300 °C, detector temperature: 280 °C, initial column temperature 40 °C (2 min), heating at a rate of 5 deg/min up to 50 °C, 10 deg/min up to 70 °C, 20 deg/min up to 280 °C, isotherm at 280 °C, total analysis time: 26.5 min; carrier gas-helium, flow rate 5 mL/min, split ratio after the evaporator-10.

Technical α-pinene (76%), 3-carene (95%), limonene (95%), and commercial reagents were used. Solvents were prepared according to standard procedures.

$^1$H NMR and $^{13}$C NMR spectra for 8, $^1$H NMR spectra for 2, 5, 6, GLC-MS spectra for 4, 6, 7 are presented in Supplementary.

3.1. Preparation of α-Pinene Epoxide 4 in Aqueous Acetonitrile

The reaction was carried out in a glass reactor with a mechanical rotating stirrer, thermometer, and a dropping funnel with back pressure for supplying liquid with vigorous
stirring. The following reagents were loaded: 34.0 g (190 mmol) of turpentine (technical α-pi
nene 1) (according to combined GLC and gas chromatography-mass spectrometry analy
sis, it contained ~ 75% α-pinene 1, ~ 5% β-pinene, ~ 14% 3-carene 2, ~ 1% camphene, ~ 4% limonene 3), 250 mL acetonitrile, 0.6 g (4.0 mmol) anhydrous manganese sulfate, and 1.1 g (8.0 mmol) of salicylic acid. A mixture of 280 mL of 0.4 M sodium bicarbonate solution and 166 mL (2.0 mol) of 36% hydrogen peroxide was uniformly fed into the reactor over a period of 4 hours, maintaining a temperature between 20 and 25 °C. The mixture was stirred for an additional 2 h and subsequently treated with 100 mL methylene chloride 3 times. The extract was washed with water, dried, and the solvent was distilled off in vacuum (~ 20 mm Hg) at a temperature below 25 °C. A total of 31.5 g (>80%) of the crude product was obtained. Based on 1H NMR, GLC and gas chromatography-mass spectrometry analyses, the crude product contained 46% of α-pinene epoxide 4 and 32% of α-pinene 1. The distilled solvent containing trace amounts of α-pinene was used for extraction in the next cycle of epoxide 4 preparation.

The crude product was subjected to distillation with a reflux condenser at 10 mm Hg, with a cooled trap. Fraction 1 was distilled off at temperatures up to 75 °C (cube) and 40–50 °C (in vapors), fraction 2—at temperatures up to 90 °C (cube) and 50–70 °C (in vapors). The initial mixture (31.5 g) was fractioned as follows: fraction 1 (9.8 g) containing 62% of α-pinene 1 and 10% of α-pinene epoxide 4; fraction 2 (11.3 g) containing 85% of α-pinene epoxide 4, and the distillation residue (6.0 g). Fraction 1 was used in the next cycle for the preparation of epoxide 4; the distillation residue containing a number of valuable products of the transformation of β-pinene, 3-carene, and limonene was not used in this work. Repeated vacuum distillation under the same conditions of fraction 2 (11.3 g) yielded 8.5 g of the target product containing 93% of α-pinene epoxide 4. The total yield of epoxide 4 was 30%. The 1H NMR spectrum (CDCl3) δ, ppm comprised the following peaks: 0.92 s (3H, C8H3), 1.28 s (3H, C9H3), 1.34 s (3H, C10H3), 1.62 d (1H), 1.69–1.74 m (4H), and 3.03 dd (1H).

3.2. Preparation of 3-Carene Epoxide 5, 3-Carene-5-One 6 and 3-Carene-2,5-Dione 7 in Aqueous Acetonitrile

The reaction was carried out in a glass reactor with a mechanical, intensively rotating stirrer, thermometer and a nozzle for liquid supply with vigorous stirring. The following reagents were loaded: 2.30 g (16.0 mmol) of 95% 3-carene 2, 26.5 mL of acetonitrile, 0.048 g (0.32 mmol) of anhydrous manganese sulfate, and 0.088 g (0.64 mmol) of salicylic acid. A cooled mixture of 23.2 mL of 0.4 M sodium bicarbonate solution and 13.2 mL of 36% aqueous hydrogen peroxide was uniformly fed into the reactor over a period of 2 hours, maintaining the temperature between 18 and 22 °C. The mixture was stirred at this temperature for an additional 2 hours, and subsequently treated with 10 mL methylene chloride 3 times. The extract was washed with water, dried, and the solvent was then distilled off in a vacuum (~ 20 mm Hg) at a temperature below 25 °C. A total 2.19 g (~ 85%) of crude product was obtained. Based on 1H NMR, GLC, and gas chromatography-mass spectrometry analyses, the crude product contained 67% 3-carene epoxide 5, 1% 3-carene 2, 15% 3-carene-5-one 6, 8% 3-carene-2,5-dione 7 and 9% unidentified impurities. The distilled-off solvent containing traces of 3-carene 2 and epoxide 5 was used for extraction in the next cycle for preparing epoxide 5.

The crude product was subjected to distillation with a reflux condenser at 5 mm Hg, with a cooled trap. The initial mixture contained 67% of 3-carene epoxide 5. Epoxide 5 was distilled off at temperatures up to 90 °C (cube) and 45–60 °C (in vapors). A total of 1.16 g of the target product was obtained from the 2.19 g of the initial mixture. It contained 90% of epoxide 5, 2% of 3-carene 2, and unidentified compounds, as well as 0.91 g distillation residue. The 1H NMR spectrum of the target product corresponded to the spectrum of 3-carene epoxide 5. The 1H NMR spectrum (CDCl3) δ, ppm comprised the following peaks: 0.42 ddd (1H, C1H or C6H), 0.49 ddd (1H, C1H or C6H), 0.70 s (3H, C8H3), 0.98 s (3H, C9H3), 1.25 s (3H, C10H3), 1.47 dd (1H, C2H), 1.61 dt (1H, C2H), 2.11 dd
(1H, C2H), 2.26 ddd, (1H, C5H), and 2.80 t (1H, C4H). The total yield of 3-carene epoxide 5 per 3-carene 2 was 47%.

A fraction of the distillation residue (0.23 g) was subjected to C-18 reverse phase chromatography using a LiChrosorb®RP-18 (10 µm) column (MERCK KGAA, Darmstadt, Germany) (eluent-aqueous methanol, the gradient of methanol concentration varied from 35% to 55% by volume). The fractions from the GLC separations that contained individual compounds 6 and 7 were collected. Methanol was distilled off in a water-jet pump vacuum (~20 mm Hg) at room temperature, and the aqueous residue was extracted with diethyl ether. After the distillation of ether, 0.078 g of 3-carene-5-one 6 (yield 13%) and 0.043 g of 3-carene-2,5-dione 7 (yield 7%) were obtained. The structures of the products were confirmed by 1H NMR and gas chromatography-mass spectrometry. For 3-carene-5-one 6, the 1H NMR spectrum (CDCl3) δ, ppm comprised the following peaks: 0.72 m (1H, C1H), 1.02 s (3H, C8H3), 1.18 s (3H, C9H3), ~1.3 m (1H, C6H), 1.83 s (3H, C10H3), ~2.3 m (1H, C2H), ~2.6 m (1H, C2H), and 5.84 s (1H, C4H). For 3-carene-2,5-dione 7, the 1H NMR spectrum (CDCl3) δ, ppm comprised the following peaks: 1.28 s (6H, C8H3, C9H3), 1.95 s (3H, C10H3), 2.32 m (2H, C1H, C8H3), and 6.48 s (1H, C4H).

3.3. Preparation of Limonene Epoxide 8 in Aqueous Acetonitrile

The reaction was carried out in a glass reactor with a mechanical stirrer, a thermometer, and fittings for loading solid and liquid reagents with vigorous stirring.

The following reagents were loaded: 3.21 g (22.4 mmol) of 95% limonene, 41 mL of acetonitrile, 0.066 g (0.44 mmol) of anhydrous manganese sulfate, and 0.122 g (0.87 mmol) of salicylic acid. A cooled mixture of 30 mL of 0.4 M aqueous sodium bicarbonate solution and 21.5 mL of 33% aqueous hydrogen peroxide was uniformly fed into the reactor over a period of 3.5 hours, maintaining the temperature between 18 and 22 °C. The mixture was stirred at this temperature for another 15 min, and subsequently evaporated under vacuum at 25 °C, collecting the distillation in a cooled trap. The volume of the reaction mixture was decreased by a factor of 1.5. The evaporated reaction mixture was treated three times with 15 mL of methylene chloride. The extract was washed with water, dried, and the solvent subsequently distilled off under reduced pressure at a temperature of 25 °C, yielding 3.43 g (87%). Based on 1H NMR and GLC analyses, the product contained 95% limonene diepoxide 8 in the form of four spatial isomers. The 1H NMR spectrum (CDCl3) δ, ppm comprised the following peaks: 1.10 s, 1.11 s, 1.12 s, 1.13 s (3H, C10H3), 1.19 s (3H, C7H3), 2.34–2.50 m (2H, C9H2), and 2.82–2.92 m (1H, C2H). The azeotropic mixture of acetonitrile with water was distilled off from the reaction mixture and, to obtain limonene diepoxide, distilled methylene chloride was used in the subsequent cycles. Organic solvents may be reused in the procedures.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal11040436/s1, Figure S1: 1H-NMR compound 8, synthesis var1; Figure S2: 1H-NMR compound 8, synthesis var2 determination of the ratio of isomers; Figure S3: 1H-NMR compound 8, synthesis var1 determination of the ratio of isomers; Figure S4: 1H-NMR compound 8, synthesis var2; Figure S5: 13C-NMR compound 8, synthesis var1 domain 24.5ppm; Figure S6: 13C-NMR compound 8, synthesis var1; Figure S7: 13C-NMR compound 8, synthesis var2 domain 31ppm; Figure S8: 13C-NMR compound 8, synthesis var2; Figure S9: GLC-MS 3-carene allyl oxydation 1page CAR-3-EN-2-ONE; Figure S10: GLC-MS 3-carene allyl oxydation 2page CAR-3-EN-2-ONE; Figure S11: GLC-MS alpha-pinene epoxide distillated 1page; Figure S12: GLC-MS alpha-pinene epoxide distillated 2page; Figure S13: GLC-MS alpha-pinene epoxide mixture 1page; Figure S14: GLC-MS alpha-pinene epoxide mixture 2page; Figure S15: GLC-MS car-3-en-2,5-dione 1page; Figure S16: GLC-MS car-3-en-2,5-dione 2page; Figure S17: H-NMR 3-carene epoxide; Figure S18: H-NMR 3-carene; Figure S19: H-NMR of car-3-en-2-one; Figure S20: MS car-3-en-2-one from library.

Author Contributions: All authors have made substantive intellectual contributions to this study, at the conceptional and design levels, and pertaining to the acquisition, analysis, and interpretation of data. All authors participated in the drafting and revision of the manuscript, and all have approved
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