

Article

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

Vladislav V. Fomenko , Sergey S. Laev and Nariman F. Salakhutdinov

N.N. Vorozhtsov Novosibirsk Institute of Organic Chemistry Siberian Branch of RAS, 9 Lavrentiev Avenue, 630090 Novosibirsk, Russia; sergey@nioch.nsc.ru (S.S.L.); anvar@nioch.nsc.ru (N.F.S.)

* Correspondence: fomenko@nioch.nsc.ru; Tel.: +7-383-330-97-47

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 derivatives of monoterpenes without the need to isolate individual monoterpene 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



Citation: Fomenko, V.V.; Laev, S.S.; Salakhutdinov, N.F. Catalytic Epoxidation of 3-Carene and Limonene with Aqueous Hydrogen Peroxide, and Selective Synthesis of α -Pinene Epoxide from Turpentine. *Catalysts* **2021**, *11*, 436. <https://doi.org/10.3390/catal11040436>

Academic Editors:
Sébastien Leveneur, Vincenzo Russo,
Pasi Tolvanen, Brogini Gianluigi and
Victorio Cadierno

Received: 5 March 2021
Accepted: 25 March 2021
Published: 29 March 2021

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

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 synthons. 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 NaHCO_3 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].

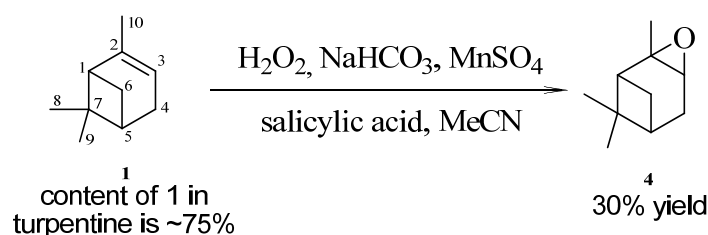
3-Carene 2 is usually referred to as an olefin that readily participates in the epoxidation reaction [7]. As oxidizing agents, it is possible to use peracetic acid [5,24] or hydrogen peroxide [5,15,17,25] at various concentrations and at different temperatures. In the oxidation of 3-carene 2 with 35% 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 methyltrioxorene [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

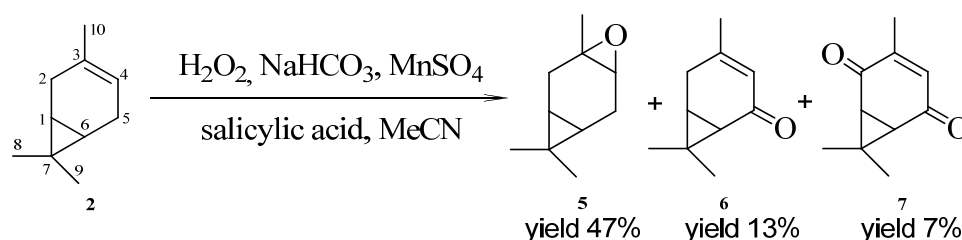
Our objective was to develop a simple, economical, and technologically sound method to produce α -pinene epoxide 4. To this aim, we epoxidized turpentine (technical α -pinene 1), which contained ~ 75% of the main substance, according to the combined data obtained by GLC and gas chromatography-mass spectrometry [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].



Scheme 1. Preparation of α -pinene epoxide 4 by epoxidation of α -pinene 1 of turpentine.

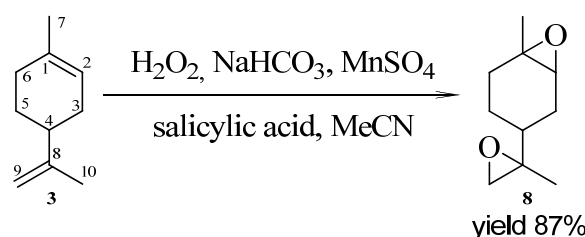
In addition to its simplicity, the proposed method for producing epoxide 4 offers two advantages: (i), the epoxidation of α -pinene 1 is achieved by the action of simple, cheap, and commercially available reagents, and (ii), inexpensive technical α -pinene is used as the starting compound. Although, 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.

Epoxidation of 3-carene 2 with 36% 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 most 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-caran 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].



Scheme 2. Oxidation of 3-carene 2 in a catalytic system consisting of manganese sulfate (2 mole percent), sodium bicarbonate, and salicylic acid in acetonitrile.

Epoxidation of limonene 3 with 33% aqueous hydrogen peroxide was carried out in the same catalytic system, using ten-fold molar amounts of hydrogen peroxide and two percent molar manganese sulfate relative to the loaded substrate. The system was highly active and epoxidation proceeded exhaustively, with high yields of the desired diepoxides. Limonene diepoxide 8 was recovered from the partially evaporated reaction mixture with methylene chloride, the extract was concentrated, and pure limonene diepoxide 8 was isolated in an 87% yield (Scheme 3) (purity was determined using ^1H NMR and GLC methods). The replacement of acetonitrile with DMF or methanol led to the appearance of monoepoxidation products in the reaction mixture, and the yield of diepoxide 8 decreased down to 55%.



Scheme 3. Preparation of limonene diepoxide 8 by epoxidation of limonene 3.

Based on ^1H 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

^1H 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 $\times$ 30 m $\times$ 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 $\times$ 30 m $\times$ 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.

^1H NMR and ^{13}C NMR spectra for 8, ^1H 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 -pinene 1) (according to combined GLC and gas chromatography-mass spectrometry analysis, 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 fractionated 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 (CDCl_3) δ , ppm comprised the following peaks: 0.92 s (3H, C^8H_3), 1.28 s (3H, C^9H_3), 1.34 s (3H, C^{10}H_3), 1.62 d (1H), 1.69–1.74 m (1H), 1.85–2.01 m (4H), and 3.03 dd (1H, C^3H).

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 (CDCl_3) δ , ppm comprised the following peaks: 0.42 ddd (1H, C^1H or C^6H), 0.49 ddd (1 H, C^1H or C^6H), 0.70 s (3H, C^8H_3), 0.98 s (3H, C^9H_3), 1.25 s (3H, C^{10}H_3), 1.47 dd, (1H, C^2H), 1.61 dt (1H, C^5H), 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, C⁶H), 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 var1 determination of the ratio of isomers; Figure S3: ¹H-NMR compound 8, synthesis var2 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 distilled 1page; Figure S12: GLC-MS alpha-pinene epoxide distilled 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

the current version to be published in *Catalysts* Journal. Supervision and project administration was made by N.F.S. All authors have read and agreed to the published version of the manuscript.

Funding: The research was supported by Russian Foundation for Basic Research (RFBR, grant 19-29-04011).

Acknowledgments: Authors would like to acknowledge the Multi-Access Chemical Research Center SB RAS for spectral and analytical measurements.

Conflicts of Interest: The authors declare no conflict of interest.

References

- De Villa, A.L.P.; De Vos, D.E.; De Montes, C.C.; Jacobs, P.A. Selective epoxidation of monoterpenes with methyltrioxorhenium and H_2O_2 . *Tetrahedron Lett.* **1998**, *39*, 8521–8524. [\[CrossRef\]](#)
- Fdil, N.; Romane, A.; Allaoud, S.; Karim, A.; Castanet, Y.; Mortreux, A. Terpenic olefin epoxidation using metals acetylacetonates as catalysts. *J. Mol. Catal. A* **1996**, *108*, 15–21. [\[CrossRef\]](#)
- Mori, K.; Kato, M. Synthesis and absolute configuration of (+)-hernandulcin, a new sesquiterpene with intensely sweet taste. *Tetrahedron Lett.* **1986**, *27*, 981–982. [\[CrossRef\]](#)
- Scheidl, F. Katalytische Umlagerungen von α -Pinen-epoxid in Gegenwart von Aluminium-alkoxiden. *Synthesis* **1982**, *9*, 728. [\[CrossRef\]](#)
- Watanabe, K.; Yamamoto, N.; Kaetsu, A.; Yamada, Y. Process for Producing 3,4-Caranediol. U.S. Patent 5608088A, 4 March 1997.
- Xu, D.; Rivas-Bascón, N.; Padial, N.M.; Knouse, K.W.; Zheng, B.; Vantourout, J.C.; Schmidt, M.A.; Eastgate, M.D.; Baran, P.S. Enantiodivergent Formation of C–P Bonds: Synthesis of P-Chiral Phosphines and Methylphosphonate Oligonucleotides. *J. Am. Chem. Soc.* **2020**, *142*, 5785–5792. [\[CrossRef\]](#) [\[PubMed\]](#)
- Bakhvalov, O.V.; Fomenko, V.V.; Salakhutdinov, N.F. Modern Methods of Epoxidation of α - and β -Pinenes, 3-Carene and Limonene. *Chem. Sustain. Dev.* **2008**, *16*, 633–691.
- Takai, T.; Hata, E.; Yoroze, K.; Mukaiyama, T. Cobalt(II) Complex Catalyzed Epoxidation of Olefins by Combined Use of Molecular Oxygen and Cyclic Ketones. *Chem. Lett.* **1992**, *21*, 2077. [\[CrossRef\]](#)
- Zhang, H.; He, J.; Lu, X.; Yang, L.; Wang, C.; Yue, F.; Zhou, D.; Xia, Q. Fast-synthesis and catalytic property of heterogeneous Co-MOF catalysts for the epoxidation of α -pinene with air. *New J. Chem.* **2020**, *44*, 17413–17421. [\[CrossRef\]](#)
- Martinez, H.; Amaya, A.A.; Paez-Mozo, E.A.; Martinez, F. Highly efficient epoxidation of α -pinene with O_2 photocatalyzed by dioxoMo(VI) complex anchored on TiO_2 nanotubes. *Microporous Mesoporous Mater.* **2018**, *265*, 202–210. [\[CrossRef\]](#)
- Lu, X.H.; Lei, J.; Wei, H.L.; Ma, X.T.; Zhang, T.J.; Hu, W.; Zhou, D.; Xia, Q.H. Selectively catalytic epoxidation of α -pinene with dry air over the composite catalysts of Co-MOR(L) with Schiff-base ligands. *J. Mol. Catal. A Chem.* **2015**, *400*, 71–80. [\[CrossRef\]](#)
- Elemans, J.A.A.W.; Bijsterveld, E.J.A.; Rowan, A.E.; Nolte, R.J.M. A host-guest epoxidation. *Chem. Commun.* **2000**, *24*, 2443–2444. [\[CrossRef\]](#)
- Majetich, G.; Hicks, R.; Sun, G.R.; McGill, P. Carbodiimide-Promoted Olefin Epoxidation with Aqueous Hydrogen Peroxide. *J. Org. Chem.* **1998**, *63*, 2564–2573. [\[CrossRef\]](#) [\[PubMed\]](#)
- Lane, B.S.; Burgess, K. A cheap, catalytic, scalable, and environmentally benign method for alkene epoxidations. *J. Am. Chem. Soc.* **2001**, *123*, 2933–2934. [\[CrossRef\]](#)
- Mouret, A.; Leclercq, L.; Muhlbauer, A.; Nardello-Rataj, V. Eco-friendly solvents and amphiphilic catalytic polyoxometalate nanoparticles: A winning combination for olefin epoxidation. *Green Chem.* **2014**, *16*, 269–278. [\[CrossRef\]](#)
- Pierri, L.; Gemenetzi, A.; Mavroggiorgou, A.; Regitano, J.B.; Deligiannakis, Y.; Louloudi, M. Biochar as supporting material for heterogeneous Mn(II) catalysts: Efficient olefins epoxidation with H_2O_2 . *Mol. Catal.* **2020**, *489*, 110946. [\[CrossRef\]](#)
- Cunningham, W.B.; Tibbetts, J.D.; Hutchby, M.; Maltby, K.A.; Davidson, M.G.; Hintermair, U.; Plucinski, P.; Bull, S.D. Sustainable catalytic protocols for the solvent free epoxidation and anti-dihydroxylation of the alkene bonds of biorenewable terpene feedstocks using H_2O_2 as oxidant. *Green Chem.* **2020**, *22*, 513–524. [\[CrossRef\]](#)
- Shi, Z.; Wu, C.; Wu, Y.; Liu, H.; Xu, G.; Deng, J.; Gu, H.; Liu, H.; Zhang, J.; Umar, A.; et al. Optimization of Epoxypinane Synthesis by Silicotungstic Acid Supported on SBA-15 Catalyst Using Response Surface Methodology. *Sci. Adv. Mater.* **2019**, *11*, 699–707. [\[CrossRef\]](#)
- Bermudez, J.H.; Rojas, G.; Benitez, R.B.; Franco, J.M. Easy Epoxidation of Monoterpenes from Common Starting Materials. *J. Braz. Chem. Soc.* **2020**, *31*, 1086–1092. [\[CrossRef\]](#)
- Charbonneau, L.; Foster, X.; Kaliaguine, S. Ultrasonic and Catalyst-Free Epoxidation of Limonene and Other Terpenes Using Dimethyl Dioxirane in Semibatch Conditions. *ACS Sustain. Chem. Eng.* **2018**, *6*, 12224–12231. [\[CrossRef\]](#)
- Payami, F.; Bezaatpour, A.; Eskandari, H. Excellent alkene epoxidation catalytic activity of macrocyclic-based complex of dioxo-Mo(VI) on supermagnetic separable nanocatalyst. *Appl. Organomet. Chem.* **2018**, *32*, e3986. [\[CrossRef\]](#)
- Akbarpour, S.; Bezaatpour, A.; Askarizadeh, E.; Amiri, M. Covalent supporting of novel dioxo-molybdenum tetradentate pyrrole-imine complex on Fe_3O_4 as high-efficiency nanocatalyst for selective epoxidation of olefins. *Appl. Organomet. Chem.* **2017**, *31*, e3804. [\[CrossRef\]](#)

23. Mirkhani, V.; Moghadam, M.; Tangestaninejad, S.; Bahramian, B. Polystyrene-bound imidazole as a heterogeneous axial ligand for Mn(salophen)Cl and its use as biomimetic alkene epoxidation and alkane hydroxylation catalyst with sodium periodate. *Appl. Catal.* **2006**, *311*, 43–50. [\[CrossRef\]](#)
24. Arbuzov, B.A. Research in the field of isomerization of terpene oxides. III. Isomerization of camphene, nopinene and 3-carene oxides in the Reformatsky reaction. *Russ. J. Gen. Chem.* **1939**, *9*, 255.
25. Saladino, R.; Neri, V.; Pelliccia, A.R.; Mincione, A.R. Selective epoxidation of monoterpenes with H₂O₂ and polymer-supported methylrheniumtrioxide systems. *Tetrahedron* **2003**, *59*, 7403–7408. [\[CrossRef\]](#)
26. Barlan, A.U.; Basak, A.; Yamamoto, H. Enantioselective Oxidation of Olefins Catalyzed by a Chiral Bishydroxamic Acid Complex of Molybdenum. *Angew. Chem. Int. Ed.* **2006**, *45*, 5849–5852. [\[CrossRef\]](#) [\[PubMed\]](#)
27. Nakagawa, Y.; Kamata, K.; Kotani, M.; Yamaguchi, K.; Mizuno, N. Polyoxovanadometalate-Catalyzed Selective Epoxidation of Alkenes with Hydrogen Peroxid. *Angew. Chem. Int. Ed.* **2005**, *44*, 5136–5141. [\[CrossRef\]](#) [\[PubMed\]](#)
28. Zhou, X.T.; Ji, H.B.; Xu, J.C.; Pei, L.X.; Wang, L.F.; Yao, X.D. Enzymatic-like mediated olefins epoxidation by molecular oxygen under mild conditions. *Tetrahedron Lett.* **2007**, *48*, 2691–2695. [\[CrossRef\]](#)
29. Resul MFMGFernandez, A.M.L.; Rehman, A.; Harvey, A.P. Development of a selective, solvent-free epoxidation of limonene using hydrogen peroxide and a tungsten-based catalyst. *React. Chem. Eng.* **2018**, *3*, 747–756. [\[CrossRef\]](#)
30. Charbonneau, L.; Foster, X.; Zhao, D.; Kaliaguine, S. Catalyst-Free Epoxidation of Limonene to Limonene Dioxide. *ACS Sustain. Chem. Eng.* **2018**, *6*, 5115–5121. [\[CrossRef\]](#)
31. Charbonneau, L.; Kaliaguine, S. Epoxidation of limonene over low coordination Ti in Ti-SBA-16. *Appl. Catal. A Gen.* **2017**, *533*, 1–8. [\[CrossRef\]](#)
32. Guidotti, M.; Psaro, R.; Batonneau-Gener, I.; Gavrilova, E. Heterogeneous Catalytic Epoxidation: High Limonene Oxide Yields by Surface Silylation of Ti-MCM-41. *Chem. Eng. Technol.* **2011**, *34*, 1924–1927. [\[CrossRef\]](#)
33. van Viet, M.C.A.; Mandelli, D.; Arends, I.W.C.E.; Schuchardt, U.; Sheldon, R.A. Alumina: A cheap, active and selective catalyst for epoxidations with (aqueous) hydrogen peroxide. *Green Chem.* **2001**, *3*, 243–246. [\[CrossRef\]](#)
34. Fomenko, V.V.; Bakhvalov, O.V.; Kollegov, V.F.; Salakhutdinov, N.F. Catalytic epoxidation of β -pinene with aqueous hydrogen peroxide. *Russ. J. Gen. Chem.* **2017**, *87*, 1675–1679. [\[CrossRef\]](#)
35. Tatarova, L.E.; Korchagina, D.V.; Volcho, K.P.; Salakhutdinov, N.F.; Barkhash, V.A. Reactions of Epoxides Prepared from Some Monoterpenes with Acetic Anhydride on Aluminosilicate Catalysts. *Russ. J. Org. Chem.* **2003**, *39*, 1076–1082. [\[CrossRef\]](#)
36. Galin, F.Z.; Kukovinets, O.S.; Shereshovets, V.V.; Safiullin, R.L.; Kukovinets, A.G.; Kabal'nova, N.N.; Kasradze, V.G.; Zaripov, R.N.; Kargapol'tseva, T.A.; Kashina, Y.A.; et al. Synthesis of 4 α -Hydroxy-6,6-Dimethyl-3-Oxabicyclo[3.1.0]hex-2-one from (+)-3-Carene. *Russ. J. Org. Chem.* **1996**, *32*, 1429–1432.
37. Carman, R.M.; Klika, K.D. Determination of the Enantiomeric Composition of Limonene and Limonene-1,2-epoxide in Lemon Peel by Multidimensional Gas Chromatography with Flame-Ionization Detection and Selected Ion Monitoring Mass Spectrometry. *Aust. J. Chem.* **1991**, *44*, 1803–1808. [\[CrossRef\]](#)
38. Soto, M.; Koschek, K. Diastereoisomeric diversity dictates reactivity of epoxy groups in limonene dioxide polymerization. *Express Polym. Lett.* **2018**, *12*, 583–589. [\[CrossRef\]](#)