

Ultrasonic and Catalyst-Free Epoxidation of Limonene and Other Terpenes Using Dimethyl Dioxirane in Semibatch Conditions

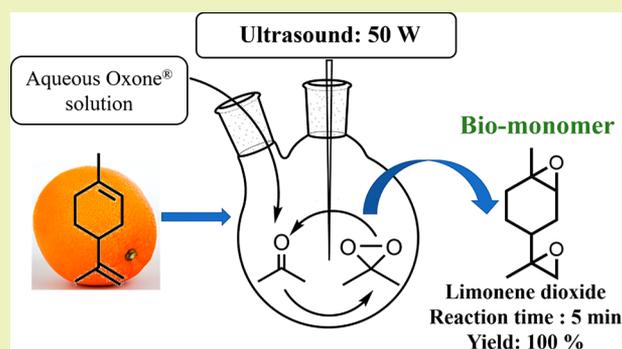
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Supporting Information

ABSTRACT: Limonene dioxide is a key intermediate molecule for the development of biobased polycarbonates or nonisocyanate polyurethanes. In this work the epoxidation of limonene to limonene dioxide using in-situ-generated dimethyl dioxirane as the oxidizing agent under both conventional agitation and ultrasound has been compared. The time required to completely convert limonene to limonene dioxide with 100% yield using ultrasound was only 4.5 min at room temperature. In comparison, when conventional agitation using a magnetic stirrer is used, the required time to reach a 97% yield of limonene dioxide was 1.5 h. The epoxidation of α -pinene has also been studied using both agitation techniques. Epoxidation of α -pinene to α -pinene oxide under ultrasound required only 4 min with an obtained yield of 100%, while in comparison with the conventional method the reaction time was 60 min. As for other terpenes, β -pinene was converted to β -pinene oxide in only 4 min whereas farnesol yielded 100% of the triepoxide in 8 min. Carveol, a limonene derivative, was converted to carveol dioxide with a yield of 98%. In the epoxidation reaction of carveol using dimethyl dioxirane the conversion was 100% in 5 min, but only 7,8-carveol oxide was produced.

KEYWORDS: Catalyst free, Ultrasound, Epoxidation process, Limonene, Limonene derivatives, Farnesol, Pinenes



INTRODUCTION

Biomass-based monomers are thought to be sustainable and renewable alternatives to traditional oil-based monomers.^{1–3} These new monomers will contribute to reduce our dependency on fossil carbon leading to a considerable reduction of CO₂ emissions in the atmosphere. Biomass-derived monomers may be classified into four different categories: oxygen-rich monomers (lactic acid, succinic acid), hydrocarbon monomers (bio-olefins), nonhydrocarbon monomer (carbon dioxide), and finally hydrocarbon-rich monomers (vegetable oils, fatty acids, terpenes).⁴ Terpenes, carbon-rich monomers mostly derived from essential oils, have been the subject of much scientific research. Considerable progress has been made in the field of terpenes-based monomers in order to produce biobased polymers.^{5–7} One of the most promising terpenes is limonene. Its annual production is around of 70 kt per year, mostly extracted from citrus peel wastes.^{8–10} Direct polymerization of limonene leads to low molecular weight polylimonene.¹¹ 1,2-Limonene oxide, the epoxidation product of limonene, is more promising and has been successfully used as a bio-monomer in combination with CO₂ in the presence of a catalyst, leading to the production of new green polycarbonates.^{7,10,12–15} Limonene dioxide, the double-epoxidation product of limonene, has attracted the attention of scientists since it has shown great potential for many applications in plastic industries. This monomer can be used for the development of epoxy resins or as a cross-linker. Limonene dicarbonate, the

product of the carbonation of limonene dioxide, has been successfully isolated in relatively good yield and is a very promising monomer to produce green polymers, nonisocyanate polyurethane.^{16–18} Finally, limonene dioxide can be converted by reacting the latter with a solution of ammonia in order to produce an aminoalcohol which can also be used in the production of isocyanate and phosgene-free polyhydroxyurethane.¹⁹ Given the importance of limonene dioxide for the production of new biobased polymers, it is crucial to develop a highly efficient epoxidation process in order to meet future industrial needs.

One of the most widely known methods for the epoxidation of olefins is the use of peracids in organic solvents, such as m-CPBA in CH₂Cl₂, also known as the Prilezhaev reaction.²⁰ Metal complexes are the most active catalysts for the epoxidation reaction.²¹ Different oxidizing agents can be used such as hydroperoxides, ClO⁻, and PhIO or molecular oxygen as oxygen source in the presence of such catalysts as supported metal oxides or organometallic complexes. The most employed metals are V, Mo, W, Ti, Mn, Cr, or Co.^{21,22} Hydrogen peroxide is a cheap and green epoxidizing agent that can be used in the presence of different types of catalysts including soluble metal oxides, metal oxides generated in situ, or organometallic

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complexes in the presence of organic solvents, mostly dichloromethane or DMF.²³ These techniques lead generally to high epoxide yields. From an environmental and health viewpoint these techniques are not essentially viable at industrial scales. Solvents such as dichloromethane or DMF and metal-based catalysts are rather toxic and are not considered environmentally friendly.^{21,24} Heterogeneous epoxidation of limonene using low-coordination titanium supported on silica using H₂O₂ as the oxidizing agent has attracted many scientists as an alternative, since it only produces a water molecule as a byproduct.^{25–35} Epoxidation of limonene to 1,2-limonene oxide by photocatalysis using low-coordination titanium and O₂ as the oxidation agent has also been studied.³⁶ However, this type of catalyst has shown a low yield of limonene dioxide which is a most promising biomonomer. The epoxide molecules are rather sensitive and can undergo ring opening with formation of diols in the presence of water in the hydrogen peroxide solution. Furthermore, limonene reacts with hydrogen peroxide leading to the formation of oxidation secondary products such as carveone, carveol, and perillyl alcohol. Finally, even with optimized pore structure and when working in anhydrous conditions, low-coordination titanium supported on silica was found to not be active enough for the double epoxidation of limonene to limonene dioxide.³⁷

Epoxidation of olefins by in-situ-generated dimethyl dioxirane (DMDO) by the reaction of acetone with potassium peroxy-monosulfate commercially known as Oxone, in semibatch conditions in the presence sodium bicarbonate as the buffer is not performed industrially. This epoxidation method is, however, rather green, fast, highly selective, and catalyst free, works at room temperature, and it is easy to separate the products from the reaction medium.^{21,38–48} Oxone is a cheap oxidizing agent, easy for storage, and a stable salt, and the only products generated are the epoxides, KSHO₄, acetone, sodium bicarbonate, and water. A greener approach for the double epoxidation of limonene has been achieved in the absence of any of catalyst using in-situ-generated DMDO at room temperature in acetone as both the ketone source and the solvent yielding 97% of limonene dioxide.⁴⁹ Epoxidation of limonene by in-situ-generated DMDO is a multiphasic process which requires strong agitation in order to enhance the DMDO mass transfer from the aqueous phase to the organic phase where the reaction takes place. To resolve that situation, ultrasonic agitation may be expected to considerably reduce the reaction time. In previous reports, epoxidation of various olefins was therefore performed under ultrasound in the presence of a catalyst, and the published results show a high yield of epoxides in only a few minutes, which is a considerable gain over conventional agitation using a magnetic stirrer or mechanical agitator.^{50–57} However, in the case of limonene, the obtained limonene dioxide yield was very low. This work aims at demonstrating the advantages of the use of ultrasound for the epoxidation reaction of limonene to produce limonene dioxide by using in-situ-generated DMDO as the oxidizing agent in the absence of any catalyst. In order to generalize this method, other terpenes such as α - and β -pinene, farnesol, and limonene derivatives such as carveol and carveone have also been epoxidized.

MATERIAL AND METHODS

Epoxidation of Terpenes under Semibatch Conditions Using in-Situ-Generated DMDO. A 125 mL glass flask was initially filled with 40 mL of acetone, 4.0 g of sodium bicarbonate, and 10 mmol of limonene (entry 1a). A 60 mL amount of an aqueous solution of 0.52 M

of Oxone was added using a syringe pump at a constant flowrate of 1 mL min⁻¹ when the reaction is carried out under conventional agitation and 10 mL min⁻¹ under ultrasound. The sonotrode used for the sonication was 7 mm in diameter (39 mm²) and 95 mm length (Hielscher). The ultrasound nominal power applied was 50 W with a frequency of 26 kHz. The 125 mL flask was immersed in a water bath in order to maintain the content at room temperature. The biphasic reaction medium was separated by liquid–liquid extraction using diethyl ether. The organic layer was dried on magnesium sulfate and evaporated on a rotary evaporator. Other terpenes such as α -pinene (entry 2a), β -pinene (entry 3a), (carveol entry 4a), carveone (entry 5a), and farnesol (entry 6a) were also epoxidized in the same epoxidation conditions as for limonene.

Characterization of the Reaction Medium. All reaction mixtures were analyzed using a CP-3800 gas chromatograph (Varian Inc.) equipped with a flame ionization detector (FID) and a Stabilwax column (30 m \times 0.53 mm \times 1 μ m) coupled with a 5 m guard column. The limonene conversion was determined using eq 1

$$\text{Conversion(\%)} = \frac{n_{o(\text{limonene})} - n_{f(\text{limonene})}}{n_{o(\text{limonene})}} \times 100 \quad (1)$$

The yield for limonene oxide and limonene dioxide was calculated using eq 2

$$\text{Yield(\%)} = \frac{n_{\text{epoxide}}}{n_{o(\text{limonene})}} \times 100 \quad (2)$$

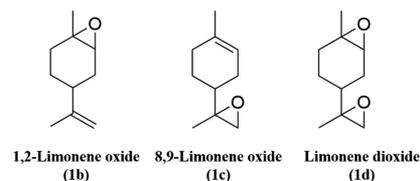
Both 1,2-limonene oxide and limonene dioxide standards were purchased from Sigma-Aldrich. Methoxybenzene was used as the internal standard. To ascertain the presence of limonene dioxide, α -pinene oxide (2b), or β -pinene oxide (3b) the reaction mixture composition was confirmed by GC-MS. The GC-MS was a Hewlett-Packard HP 5890 series GC system and MSD Hewlett-Packard model 5970. The GC-MS was equipped with a Zebtron ZB-SMS capillary column (30 m \times 0.25 mm \times 0.25 mm).

The yields for carveone, carveol, and farnesol oxides were determined by ¹H NMR using a Bruker 300 MHz NMR in deuterated chloroform. Their respective ¹H NMR spectra are available in the Supporting Information.

RESULTS AND DISCUSSION

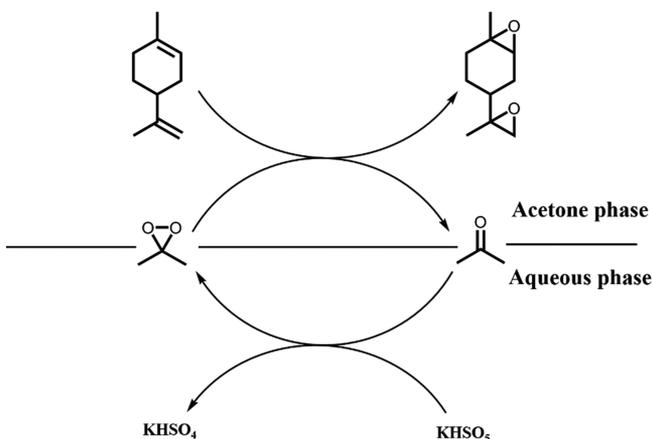
Optimization of Reaction Conditions for the Double Epoxidation of Limonene to Limonene Dioxide by DMDO under Ultrasound. Limonene was the model molecule used for optimization of reaction conditions for the synthesis of limonene dioxide by in-situ-generated DMDO under semibatch conditions coupled with ultrasound. The epoxidation reaction of limonene was expected to yield the different isomers represented on Scheme 1.

Scheme 1. Limonene Oxide Isomers



The epoxidation reaction by in-situ-generated DMDO is a multiphasic reaction comprising an organic phase, which is a mixture of acetone and limonene, an aqueous phase comprising an Oxone solution, which is added using a syringe pump at a constant flowrate in the reaction vessel, an aqueous acetone solution, and finally a solid phase composed of sodium bicarbonate as the buffer. The complete epoxidation process of limonene by DMDO is illustrated in Scheme 2.

Scheme 2. Limonene Epoxidation Process



KHSO_5 reacts in the aqueous phase by a nucleophilic attack, and one atom of oxygen is transferred to acetone, leading to the formation of DMDO and KHSO_4 . Following that step DMDO is transferred from the aqueous phase to the acetone phase, reacting with limonene, the latter being insoluble in water, and produces the limonene dioxide. The other product of DMDO reacting with limonene is acetone, which in our case is also the solvent of the reaction.

The epoxidation of limonene using in-situ-generated DMDO requires a strict control of the reaction conditions such as the flowrate of the aqueous solution of Oxone, the pH of the reaction medium, and the Oxone/limonene stoichiometric ratio. The effect of Oxone solution feed flowrate on the conversion and yield of limonene dioxide has been studied, and the results are reported in Figure 1.

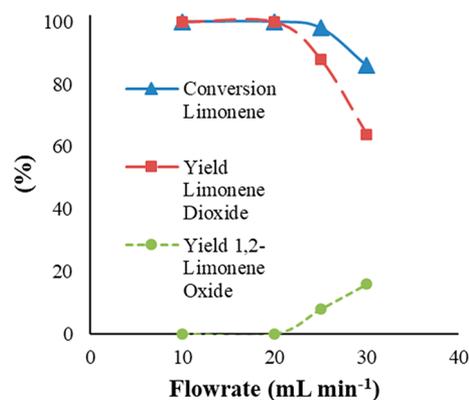
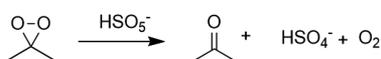


Figure 1. Effect of flowrate of the aqueous solution of Oxone on the conversion of limonene and limonene dioxide yield.

The maximum feed flowrate of the 0.52 M aqueous solution of Oxone for the epoxidation of limonene by DMDO generated in situ under ultrasound in order to obtain 100% of limonene dioxide yield should be 20 mL min⁻¹. At higher flowrate both conversion and yield start decreasing due to the catalytic decomposition of HSO_5^- by the already produced DMDO, with the reaction represented in Scheme 3.

Scheme 3. DMDO Decomposition by Oxone



The epoxidation of olefins by in-situ-generated DMDO as the oxidizing agent should be carried out over a narrow pH range between 7 and 9. At pH lower than 7 the oxidation of ketones by the Bayer–Villiger reaction was shown to be favored over the epoxidation of alkenes. By opposition, when the pH of the reaction medium is higher than 9, the auto-decomposition process of Oxone takes place, leading to a reduction in epoxide yield to only 12% or even less.⁴⁸ One of the easiest ways to maintain the pH of the reaction medium is to use sodium bicarbonate as the buffer in its solid form. The stability of sodium bicarbonate as the buffer of the reaction has been studied, and the results are presented in Figure 2.

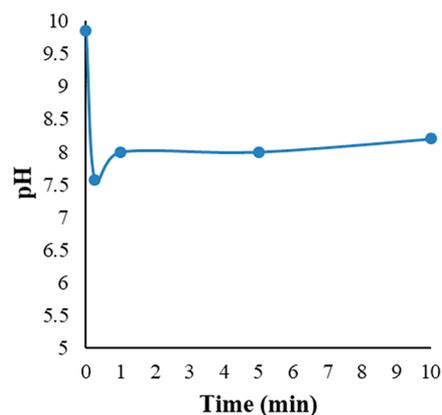


Figure 2. Stability of sodium bicarbonate as the buffer of the reaction.

The conditions for the test described in Figure 2 are 4 g of sodium bicarbonate, 40 mL of acetone, 60 mL of 0.52 aqueous Oxone solution under a flowrate of 20 mL min⁻¹ at room temperature, and 50 W of nominal ultrasound power for a reaction time of 10 min in the absence of limonene. Prior to adding the 0.52 M aqueous Oxone solution to the reaction vessel, the pH of the mixture of acetone with sodium bicarbonate is about 9.85. This is due to the low solubility of NaHCO_3 in acetone corresponding to 0.02 wt %.⁵⁸ After 15 s, the pH started to rapidly decrease to a value of 7.57, reaching 8.0 after only 1 min. After complete addition of the 0.52 M aqueous solution of Oxone, the pH of the mixture is relatively stable and is maintained at a value of 8. Finally, a mixture of 60 mL of 0.52 M aqueous solution of Oxone and acetone has slowly increased to a pH value of 8.2 after 10 min under ultrasound. The obtained experimental results are shown in Figure 2, indicating the stability of sodium bicarbonate as the buffer under ultrasound.

For stoichiometric considerations, an Oxone/limonene molar ratio of 2:1 is required to completely epoxidize the two unsaturations of limonene to limonene dioxide. This ratio was therefore optimized, and the results are reported in Table 1.

The results presented in Table 1 show that at a molar ratio of 2:1, the double epoxidation is not complete with a partial conversion of Oxone to epoxide of 86%, while at a molar ratio of 2.60:1, the two double bonds of limonene are completely epoxidized with a partial conversion of Oxone of 77%.

REACTION OF LIMONENE EPOXIDATION

The time evolutions of limonene conversion and epoxide yields were monitored with both conventional agitation using a magnetic stirrer and under ultrasound at optimized conditions, and the results are reported in Figure 3.

Table 1. Effect of the Total Amount of Oxone Fed to the Reactor at Constant Flowrate^a

Oxone/limonene ratio	pH of Oxone solution	conversion ^b (%)	1,2-limonene oxide yield ^b (%)	limonene dioxide yield ^b (%)	oxone conversion to epoxide (%)
2.00	1.43	99	24	75	86
2.60	1.30	100	0	100	77

^aA 10 mmol amount of limonene, 40 mL of acetone, 4 g of sodium bicarbonate, various amounts of Oxone dissolved in 60 mL of water were added to the flask at a constant flowrate of 20 mL min⁻¹, room temperature, and total reaction time 10 min. ^bLimonene conversion and yields were determined by GC-FID after purification.

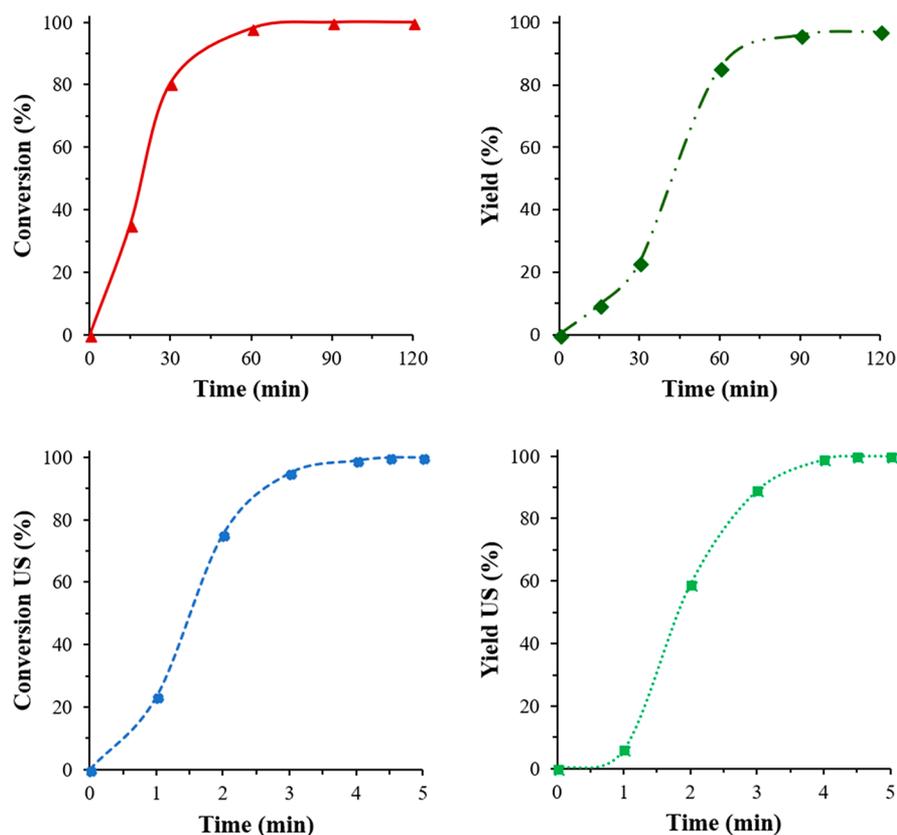


Figure 3. Time evolution of the conversion of limonene and the yield of limonene dioxide under conventional agitation and under ultrasound (US) (uncertainties on the conversion and yields are within 5%).

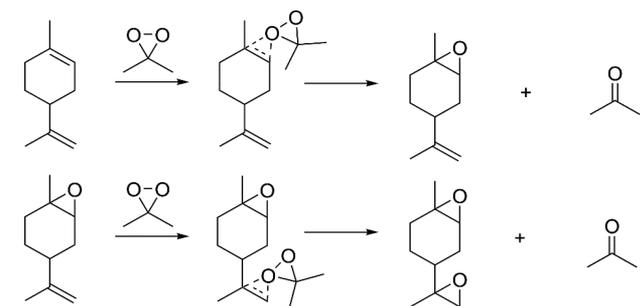
The time required to reach 100% conversion of limonene and 97% yield of limonene dioxide by conventional agitation is 90 min. This reaction time was considerably reduced to only 4.5 min under ultrasonic agitation, yielding 100% of limonene dioxide. Furthermore, no diol and no oxidation secondary products such as carvone or carveol by oxidation of the limonene ring were found in the reaction medium, which is not the case when H₂O₂ is used as the oxidizing agent. The only reaction intermediate detected by gas chromatography using in-situ-generated DMDO by both conventional and ultrasound agitation was the 1,2-limonene oxide.

The 8,9-limonene oxide isomer (see Scheme 2) was not detected as an intermediate in the reaction medium during the epoxidation of limonene to limonene dioxide by in-situ-generated DMDO using both conventional and ultrasonic agitation. The absence of 8,9-limonene is rather odd, since the 8,9-limonene oxide was detected when low-coordination titanium supported on silica was used as the catalyst using *tert*-butyl hydroperoxide as the oxidizing agent.³⁷ The absence of 8,9-limonene oxide isomer is not limited to the epoxidation of limonene under the present conditions using in-situ-generated DMDO in semibatch conditions. Michel et al. also observed the same phenomenon for the

same epoxidation reaction when hydrogen peroxide was used as the oxidizing agent catalyzed by methyltrioxorhenium (MTO) in homogeneous conditions at room temperature.⁵⁹ Under these conditions limonene was completely converted to 1,2-limonene oxide after 5 min of reaction time. Thereafter, the 1,2-limonene oxide was slowly reacted with hydrogen peroxide to produce limonene dioxide with a yield of 90% over a period of 24 h. Michel et al. mentioned that the only by-product was 1,2-limonene oxide.⁵⁹ On the basis of these observations, the epoxidation of limonene to limonene dioxide by in-situ-generated DMDO is considered to be a two-step successive reaction. This proposed reaction mechanism is represented in Scheme 4.

In kinetic terms, the 1,2 position of limonene is considered to be more reactive being trisubstituted than the 8,9 position which is disubstituted (see Scheme 2). In general, the trisubstituted double bond is epoxidized roughly 7 times faster than a disubstituted one. During the epoxidation process 1,2-limonene oxide is the first isomer formed by reaction of limonene with the already produced DMDO. Following this step the second epoxidation occurs, leading to the production of limonene dioxide. It is proposed that the first oxygen added to the 1,2 of the limonene position could induce a steric rearrangement, allowing the

Scheme 4. Epoxidation Mechanism of Limonene to Limonene Dioxide by DMDO



oxidizing agent to epoxidize the second unsaturation at position 8,9, thus producing the limonene dioxide. This hypothesis requires further investigations by theoretical calculations in order to reach a better understanding of the reaction intermediates.

■ EPOXIDATION OF α -PINENE AND OTHER TERPENES

On the basis of the results obtained for the epoxidation of limonene to limonene dioxide, the epoxidation α -pinene (2a) to α -pinene oxide (2b) was also studied (Scheme 5).

Scheme 5. Epoxidation of α -Pinene

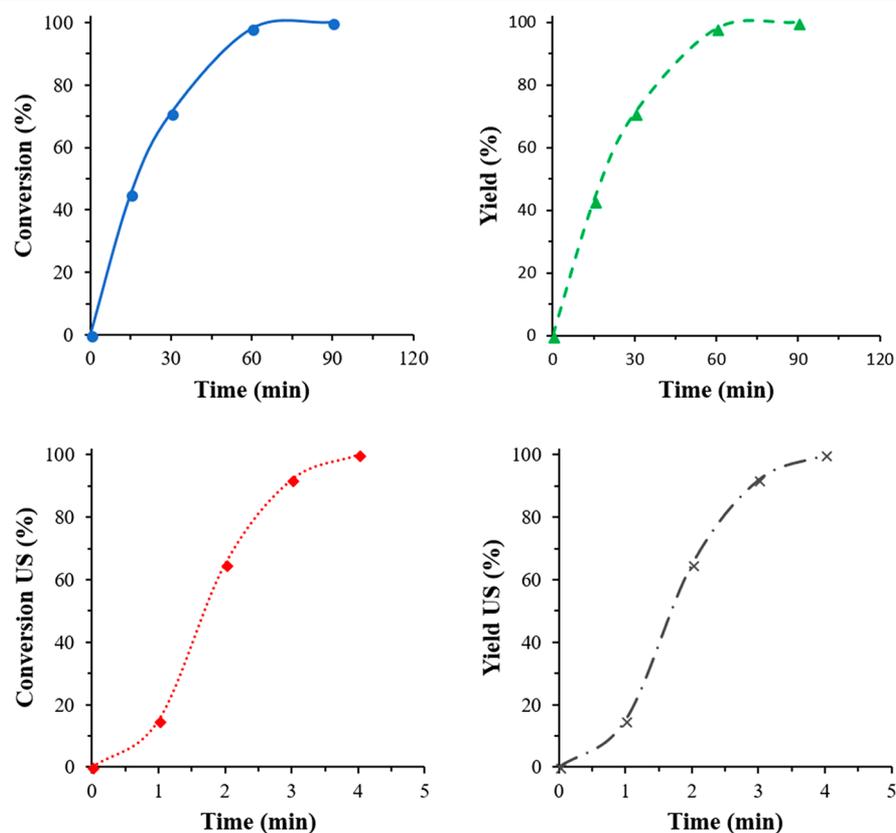
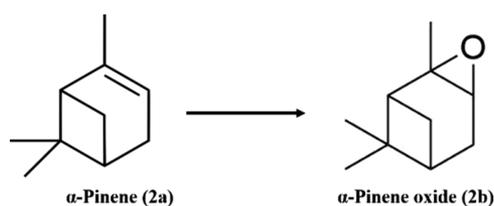


Figure 4. Time evolution of the conversion of α -pinene and yield of α -pinene oxide between conventional agitation and under ultrasound (US) (uncertainties on the conversion and yields are within 5%).

The epoxidation of α -pinene to α -pinene oxide has been performed under the same conditions optimized for the epoxidation of limonene. The obtained results are summarized in Figure 4.

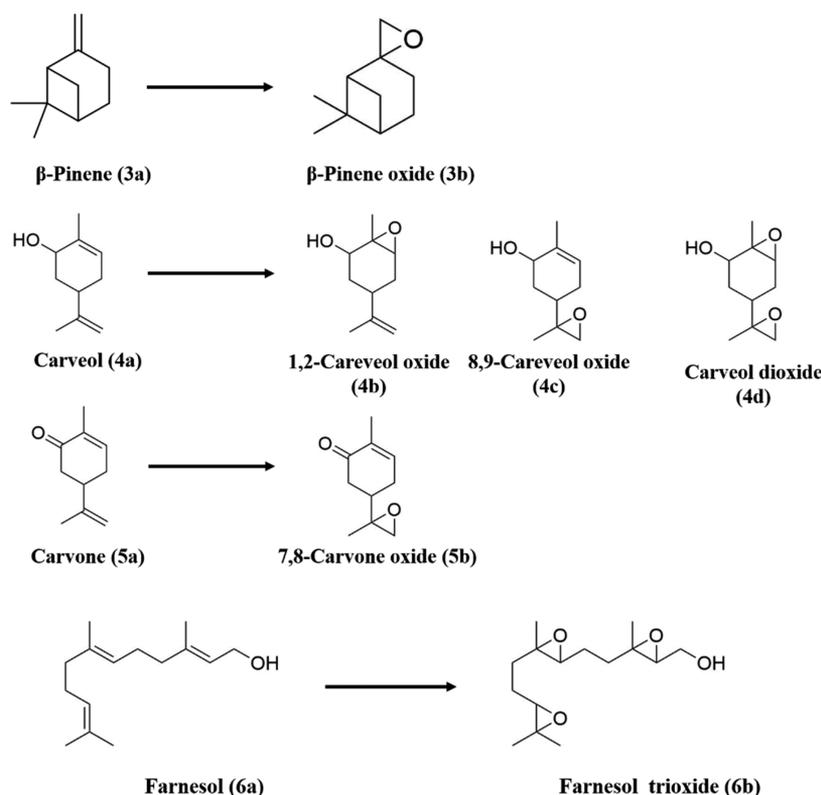
The results presented in Figure 4 show that for a conventional agitation the required time to completely convert α -pinene to α -pinene oxide is 60 min, allowing a yield of 100%. In comparison, when ultrasound is applied in the reaction medium, the time required is only 4 min to completely convert pinene, yielding 100% of pinene oxide. Furthermore, similar to the epoxidation of limonene, no oxidation products of the pinene ring such as verbenone and verbenol have been observed. The very significant effect of ultrasound on epoxidation reaction rates depicted in Figures 3 and 4 result from several factors. First, the interdependence of the mass transfer of the DMDO is greatly accelerated by the emulsifying effect of the acoustic wave through the intervention of the cavitation and microjets. Moreover, it may be hypothesized that the oxygen transfer from DMDO to the double bonds of terpenes is favored by the local temperature rise due to the cavitation.

Other terpenes were also epoxidized by in-situ-generated DMDO in semibatch conditions coupled with ultrasound. The different structures of the reactants and their epoxidation products are presented in Scheme 6.

The obtained results for the epoxidation of terpenes are summarized in Table 2.

β -Pinene, one of the most abundant terpenes in nature, was completely epoxidized with a yield of 100% of β -pinene oxide over only 4 min, similar to the required time for α -pinene. Farnesol, a sesquiterpene, bearing three unsaturations, has also been completely epoxidized (for ^1H NMR, see Supporting Information).

Scheme 6. Terpenes and Their Epoxidation Products

Table 2. Epoxidation of Natural Products Using in-Situ-Generated DMDO under Ultrasound^a

substrate	no. of instaurations	conversion ^b (%)	reaction time (min)	epoxides yield (%)
β -pinene (3a)	1	100	5	100
carveol (4a) ^c	2	100	6	>95
carvone (5a) ^{c,d}	2	100	6	100
farnesol (6a) ^c	3	100	8	100

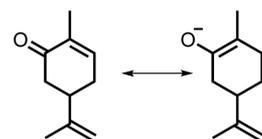
^aReaction conditions: 10 mmol of olefin (farnesol, 6.6 mmol), 40 mL of acetone, 4.0 g of sodium bicarbonate, 60 mL of 0.52 M Oxone solution under a flowrate of 20 mL min⁻¹, ultrasound power of 50 W, room temperature. ^bConversion was determined by GC-FID after purification. ^cYield was determined by ¹H NMR spectroscopy after purification. ^d100% of 8,9-carvone oxide; the double epoxidation did not occur.

The conversion of carveol was determined by GC-FID analysis and reached 100% with a yield of 99% of carveol dioxide. The minor by-products are the two monocarveol oxides (4b, 4c). Furthermore, the Oxone from the solution oxidized the alcohol function to ketone, converting carveol to carvone, the latter having been detected via ¹H NMR by the presence of small a peak with a chemical shift at 6.74 ppm (see Supporting Information).

Finally, epoxidation using in-situ-generated DMDO assisted by ultrasound reached its limitation when carvone was used as the substrate. Carvone has a carbonyl group at the beta position, reducing the electronic density of the double bond at position 1,2. Furthermore, this double bond is in resonance with the carbonyl group, which is represented in Scheme 7.

The ¹H NMR spectrum of carvone (see Supporting Information) displays one peak at 6.75 ppm corresponding to a multiplet of the β -proton of the enone moiety. The two ¹H NMR signals at $\delta = 4.75$ and 4.80 ppm are corresponding

Scheme 7. Resonance of the Carvone Double Bond



to the two geminal vinyl protons of the isopropenyl group. The two ¹H NMR spectra of carvone before and after the epoxidation reaction using DMDO were recorded (see Supporting Information). After 6 min of reaction, the two peaks at 4.75 and 4.80 ppm corresponding to the 7,8 position have completely disappeared but the peak at 6.75 is still there, allowing one to conclude to the formation of only one epoxide isomer. The same situation has also been observed when *meta*-chloroperbenzoic acid had been used as the oxidizing agent.⁶⁰ The results obtained for the epoxidation of carvone by in-situ-generated DMDO suggest that DMDO has an oxidizing capacity comparable to *m*-CPBA but in a greener way, being unable to epoxidize low electron density double bonds.

CONCLUSION

This work has shown the advantages of using ultrasonic agitation compared to traditional agitation for the epoxidation of limonene and other terpenes using in-situ-generated DMDO as the oxidizing agent. The main advantages of the procedure are the green aspect of the oxidizing agent and the reaction time reduction obtained by performing this oxidation under ultrasound agitation. This epoxidation method allowed reaching 100% conversion of limonene with a 100% yield of limonene dioxide in only 4.5 min compared to 90 min when traditional agitation is used. Furthermore, no oxidation products of limonene, such as carvone, carveol, and perrilyl alcohol, were found

in the reaction medium. The epoxidation of α -pinene under ultrasound required only 4 min, yielding 100% of α -pinene oxide without oxidation of the ring. Other terpenes such as β -pinene, farnesol, and carveol have also been oxidized, leading to very high epoxide yields. The only observed exception is for carveone, which was only converted to a 7,8 carveone oxide, a monoepoxide. Further work should consider performing this reaction in a continuous flow reactor which could be scaled up to industrial size.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b02578.

¹H NMR spectra before and after the epoxidation of limonene, carveone, carveol, and farnesol (PDF)

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Notes

The authors declare no competing financial interest.

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