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Stepwise and Microemulsions Epoxidation of Limonene by Dimethyldioxirane: A Comparative Study

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ABSTRACT: Limonene dioxide is recognized as a green monomer for the synthesis of a wide variety of polymers such as polycarbonates, epoxy resins, and nonisocyanate polyurethanes (NIPU). The developed green technologies for its synthesis over heterogeneous catalysts present a challenge in that the selectivity of limonene dioxide is rather low. Homogeneous epoxidation in the presence of dimethyldioxirane for limonene dioxide synthesis is a promising technology. This study reports the epoxidation of limonene by dimethyldioxirane (DMDO) using two approaches. The isolated synthesis of DMDO solution in acetone was followed by epoxidation of limonene in another reactor in 100% organic phase (stepwise epoxidation). Following this procedure, limonene dioxide could be produced with almost 100% conversion and yield. A second approach allowed using in situ generated in aqueous-phase DMDO to epoxidize the limonene forming a microemulsion with a solubilized surfactant in the absence of any organic solvent. The surfactants tested were hydrosulfate (CTAHS), bromide (CTAB), and chloride (CTAC) cetyltrimethylammonium. All these surfactants showed good stability of microemulsions at aqueous surfactant concentrations above their critical micellar concentrations (CMC). Stability is obtained at the lowest concentration when using CTAHS because of its very low CMC compared to CTAB and CTAC. The major advantages of epoxidation in microemulsions compared to DMDO stepwise epoxidation are the absence of an organic solvent (favoring a low reaction volume) and the very high oxygen yield of 60 to 70% versus 5% in a stepwise approach. The epoxides formed are easily separated from the aqueous medium and the surfactant by liquid−liquid extraction. Therefore, the developed in situ epoxidation process is a green technology conducted under mild conditions and convenient for large-scale applications.
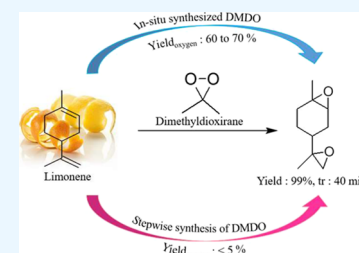
1. INTRODUCTION

The environmental and health restrictions on polymers formed from bisphenol A, phosgene, and epichlorohydrin that are usual components of fossil carbon-derived materials make the development of alternative polymers from biomass a great necessity.[1−3] Limonene, a most common terpene, is produced by more than 300 plants and available as a waste product from citrus juice industries. It is very competitive as an alternative green monomer because of its availability and low cost.[4−6] It is estimated that only orange juice industries could have produced more than 520 kilotons of R-(+)-limonene in 2014.[5] The quantity extracted and commercialized on the market does not exceed 90 kilotons per year; it is used in great part in the cosmetic, pharmaceutical, and food fields. This brings a major interest to valorize this abundant waste.

Several researchers have been interested in limonene as a monomer for the synthesis of renewable polymers, but most research on the polymerization of this natural diolefin in its crude form has resulted in polymers that do not have the desired properties (low glass transition temperature, low molecular weight, and/or low conversion) to compete with currently commercially available polyolefins.[7−9]

A more attractive approach is to functionalize limonene into an oxygenated intermediate that can produce a wide variety of more competitive polymers.[7,10−12] Specifically, 1,2-limonene oxide or limonene dioxide have all been identified as raw materials for the synthesis of green polymers such as nonisocyanate polyurethanes (NIPU) and green polycarbonates.[12−14] Studies have shown that by cycloaddition, limonene biscarbonate can be synthesized by the reaction of carbon dioxide with limonene dioxide, which in turn can react with polyfunctional amines to produce NIPUs with thermal and mechanical properties required from thermosetting or thermoplastic materials.[12,13,15] Also, poly(limonene carbonate) or poly(limonene biscarbonate) can be synthesized over a variety of catalysts forming green polycarbonates with properties that can compete with those of their petrochemical equivalents.[10,11,14,16] Given the importance of limonene dioxide for the synthesis of biobased polymers, the development of an epoxidation process addressing health and environmental issues is crucial.

Several green processes for limonene epoxidation are reported in the literature.[17−19] A tungsten-based polyoxometalate catalyst used with aqueous H_2O_2 as an oxidant was proposed for the solvent-free catalytic epoxidation of trisubstituted alkene bonds from a wide range of biorenewable terpene substrates.[19] 1,2-Limonene oxide was obtained in 95% yield after 1 h of reaction using 1 equiv of aqueous H_2O_2 (30%) at pH = 7, and no trace of limonene dioxide was detected under these conditions. Limonene dioxide was only obtained using 50% H_2O_2, 30 mol % Na_2SO_4, and toluene as the solvent in 69% yield after 7 h of reaction. Madadi et al. synthesized cobalt-substituted mesoporous SBA-16 catalysts for use in epoxidation with molecular oxygen.[20] Limonene epoxides were obtained using isobutyraldehyde as a co-reactant under very mild conditions in the presence of ethyl acetate as a green solvent. A conversion of 100% is achieved but the yield of limonene dioxide does not exceed 35%. In most cases, a high yield of limonene dioxide is a challenge for the heterogeneous epoxidation of limonene. The same challenge was observed when Charbonneau et al. epoxidized limonene over a Ti-SBA 16 catalyst.[21] The reaction was conducted at 75 °C in acetonitrile with a tert-butyl hydroperoxide (TBHP)/limonene molar ratio of 11/6. Limonene conversion reached 80% with a 1,2-limonene oxide selectivity of 79%, but no limonene dioxide was obtained.

Liquid-phase reactions in the absence of any heterogenous catalyst yielded almost 100% of limonene dioxide.[17,22−24] Very recently, the two-step stereoselective epoxidation of limonene without a catalyst was performed in the presence of N-bromosuccinimide.[22] The technique consists in a first step to perform di-bromohydration of the endocyclic and exocyclic bonds of limonene to form a dibromohydrin intermediate. The latter is added to a NaOH solution to form limonene dioxide. Thus, after 5 min of reaction, a 97% yield of trans-limonene dioxide was obtained using a molar ratio limonene/NBS of 1:2 at 60 °C by optimizing various parameters such as reaction temperature, molar ratio (limonene/N-bromosuccinimide (NBS)), and reaction time.[22] Another relevant technique for the liquid-phase epoxidation of limonene is the one-step epoxidation by in situ generation of dimethyldioxirane using oxone as the oxidant with excess acetone.[23] In this technique, the double epoxidation of limonene is carried out in semicontinuous fed mode at room temperature with a flow rate of 4 mL min^{-1} of aqueous oxone for a period of 45 min with a stoichiometric excess of 30% of oxone. A 97% yield of limonene dioxide is obtained. In a similar recent study, the effect of ultrasonic agitation on epoxidation was shown.[24] Limonene dioxide, α-pinene oxide, β-pinene oxide, farnesol trioxide, 7,8-carvone oxide, and carveol oxide were each obtained with 100% conversion and at least 97% yield during a reaction time of at least 1 h with magnetic stirring versus at most 8 min in the cases of ultrasonic stirring. The challenge of this process is that it involves a large amount of solvent and therefore a very high reaction volume and requires an excess of oxone. This makes it difficult to apply on a large scale.

Very recently, in a new study, the use of CTAHS as a surfactant to solubilize the hydrophobic terpene to be epoxidized by in situ dimethyldioxirane (DMDO) generation has been reported, and it allowed to exclude the presence of any additional organic solvent and this allowed to reduce considerably the amount of oxone necessary for the epoxidation of limonene and pinenes.[17] The present work consists in epoxidizing terpenes by DMDO using two different processes. The DMDO stepwise synthesis process, in which, as a first step, DMDO is synthesized and isolated in acetone in order to, in a second step, epoxidize terpenes in a 100% organic medium. A second process is the microemulsion allowing to epoxidize terpenes by in situ-generated aqueous-phase DMDO while testing the effect of other surfactants (CTAB and CTAC) in order to better disperse the hydrophobic terpenes to be epoxidized. This part of the work is based mainly on the optimization of the amount of acetone, surfactants, and sodium bicarbonate as the buffer. Finally, a comparison of the two processes will be discussed.

2. EXPERIMENTAL SECTION

2.1. Materials. The suppliers, characteristics, and structures of the main products used in this work are summarized in Table 1. The products were used directly without any preliminary purification.

Table 1. Main Products Used in the Present Work

Name	Structure	Case number (Purity)	Fournisseur
R-(+)-limonene		5989-27-5 (97%)	Sigma-Aldrich
α-pinene		80-56-8 (98%)	Sigma-Aldrich
β-pinene		18172-67-3 (97%)	Sigma-Aldrich
Triple Salt Oxone	$2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$	70693-62-8	Alfa Aesar
Cethyltrimethyl ammonium hydrogen sulfate	$CH_3(CH_2)_{14}CH_2-N^+-CH_3$ $^-O-S-OH$	68214-07-3 (98%)	Thermo Fisher Scientific
Cethyltrimethyl ammonium bromide	$H_3C(H_2C)_{15}-N^+-CH_3$ Br^-	57-09-0	Alfa Aesar
Cethyltrimethyl ammonium cloride	$CH_3(CH_2)_{14}CH_2-N^+-CH_3$ Cl^-	112-02-7	Alfa Aesar
Sodium bicarbonate	$NaHCO_3$	144-55-8 (99,7%)	Alfa Aesar

The substrates to be epoxidized are terpene compounds including limonene, alpha-pinene, and beta-pinene, with special attention to limonene. The oxygenating agent is the triple salt designated as oxone. It is important to remember that not all components of the latter are active. The active compound (oxygen generator) is potassium peroxymonosulfate, $KHSO_5$ (CAS number: 10058-23-8) (Scheme 1).

Scheme 1. Potassium Monoperoxysulfate (Active Component of Oxone)

(O = active oxygen)
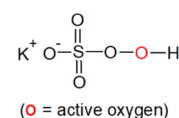
According to the manufacturer's information, the activity of the compound could decrease by 0.5% per month if stored under the recommended conditions. It is therefore recommended to use freshly purchased oxone for synthesis. Oxone in aqueous solution is strongly acidic. This acidity is regulated by using sodium bicarbonate in order to keep the reaction medium close to neutrality, favorable to epoxidation.

The effects of the surfactants CTAHS, CTAB, and CTAC on the epoxidation rate will be examined. All three surfactants have the same hydrocarbon chain (cetyltrimethyl ammonium), their difference being in the counterion. Their physico-chemical properties are different, and this could have an effect on the organic reaction.[25]

2.2. Methods. *2.2.1. Isolated Synthesis of DMDO and Epoxidation (Stepwise).* Several results on the production of DMDO to epoxidize olefins have been reported.[26–29] The method and conditions for the isolated synthesis of DMDO are almost identical in all these references. The method considered as a reference for the synthesis of DMDO in this study is that of Mikula et al.[26] The synthesis is carried out in a glass jacketed reactor of the AI R 20 L series with a cooler and pump, all provided by "Across International". The method was reproduced in the present work. To a vigorously stirred solution of sodium bicarbonate (2.5 kg) in water (4.125 L) and acetone (3 L) at 20 °C, potassium monoperoxy sulfate (oxone) was added in portions (5 × 0.81 kg) every 15 min. Simultaneously, a reduced pressure of 400 mbar was applied to avoid overpressure within the reactor caused by outgassing from the addition of oxone. The reactor is connected to a nitrogen gas stream as carrier gas. A condenser connected to a cryostatic temperature controller operating at −20 °C allowed collecting a yellow solution of dimethyldioxyran in acetone and recovering as a distillate, also cooled to −20 °C. The prepared solution is dried with magnesium sulfate. The product was immediately quantified by iodometric titration and stored in a freezer below −20 °C.

The freshly prepared DMDO solution was used without delay to epoxidize each of limonene, alpha-pinene, and beta-pinene. For this purpose, 1 mmol of limonene was reacted with 2.3 mmol of DMDO, 1 mmol of alpha-pinene with 1.2 mmol of DMDO, and 1 mmol of beta-pinene with 1.2 mmol of DMDO. All reactions were conducted at 0 °C to avoid evaporation of acetone from the DMDO solution. After 20 min of reaction, the acetone is evaporated under vacuum at room temperature and the resulting products are sent for quantification.

2.2.2. Determination of the DMDO Concentration in Acetone. Several methods are described in the literature to determine the concentration of dioxirane groups in DMDO solutions, including iodometric titration, methylphenyl sulfide or dimethyl sulfide oxidation, UV−visible technique, and NMR.[26,30–32] For our study, the concentration of dioxirane groups was determined by iodometric titration following the one proposed by Adam.[30] For this purpose, a 1 mL solution of dimethyldioxirane in acetone was added to a 2 mL solution of acetic acid and acetone with a molar ratio of 3:2. A 2 mL saturated aqueous solution of potassium iodide (KI) was then added with some dry ice to deaerate, and the resulting mixture was kept in the dark at room temperature for 10 min. The sample was diluted with 5 mL of distilled water. A 1 mL sample was titrated with 0.001 N aqueous sodium thiosulfate ($Na_2S_2O_3$) solution. The titration was repeated three times, resulting in dioxyrane concentrations of 0.06 to 0.07 mol/L.

2.2.3. Epoxidation in Microemulsions: In Situ-Synthesized DMDO for Expoxidation. All reactions were conducted under ambient conditions. The aqueous concentrations of surfactants were set at values close to their respective critical micellar concentrations (CMCs) (0.27, 0.90, and 1.40 mM, respectively, for CTAHS, CTAB, and CTAC). The aqueous concentration of oxone was 0.42 mol/L. The amount of

sodium bicarbonate was so that the final pH of the reaction medium was above 7. For this, a sodium bicarbonate/oxone molar ratio higher than or equal to 3 is required. Vigorous stirring and slow addition of the oxone are required for effective epoxidation.

The procedure of a typical test is as follows: in a 200 mL flask, 25 mL of distilled water, 33 mmol of sodium bicarbonate, and 5.4 mM CTAHS are mixed. In 4 mL of acetone, 6.2 mmol of limonene is dissolved and added to the flask. The whole mixture is stirred at 600 rpm. Oxone (10.5 mmol) or 6.5 g is added in 5 fractions in order to avoid the release of gas (i.e., 1.30 g every 5 min very slowly). At the end of the addition of oxone, the reaction is continued for another 20 min, which makes a total reaction time of 40 min. At the end of the reaction, the organic phase is separated with a separating funnel using ethyl diether as the extractant and dried with $MgSO_4$. The limonene epoxide is separated from the extractant using a rotary evaporator.

2.2.4. Extraction of Terpene Epoxide from the Aqueous Phase and Surfactant. In the case of terpene epoxidation in a 100% organic medium, that is, when DMDO is synthesized and isolated in acetone in order to epoxidize the terpene, the terpene epoxides are easily isolated using a rotary evaporator to remove the acetone. On the other hand, in the case of epoxidation in an aqueous medium by dispersing the terpene with a surfactant, the separation of the epoxide from the aqueous medium and the surfactant depends on the choice of the extractant. The extractant to be used must meet two criteria: solubilize the epoxides and not dissolve the surfactants (CTAHS, CTAB, and CTAC). The appropriate extractants are hexadecane, benzene, ethers, and so forth. Diethyl ether was chosen because of its low boiling point (34.6 °C). Indeed, at the end of the reaction, about 20 mL of diethyl ether is added to the reaction mixture, and the whole is put into a separating funnel. The two phases, organic and aqueous, are quite distinct: the epoxides dissolved spontaneously in the diethyl ether phase (organic phase) while the surfactant as well as the waste products from the oxone and the sodium bicarbonate are trapped in the aqueous phase. The organic phase was dried with $MgSO_4$ and filtered. Terpene epoxide was isolated after evaporation of diethyl ether and acetone using a rotary evaporator.

2.3. Characterization and Quantification of the Products of the Epoxidation Reaction. The samples were first analyzed by gas chromatography−mass spectrometry (GC−MS) to confirm the presence of limonene and pinenes epoxides. The GC−MS consisted of a Hewlett-Packard GC System HP 5890 series and Hewlett-Packard MSD Model 5970. The GC−MS system was equipped with a Zebron ZB-5MS capillary column (30 m × 0.25 mm × 0.25 mm). For quantitative analyses, measurements were then performed using a CP-3800 gas chromatograph (Varian Inc.) equipped with a flame ionization detector (FID) and coupled to a 5 m long Stabilwax column (30 m × 0.53 mm × 1 μm). The final products were quantified based on the calibration curves of the compounds identified by their retention time. Methyl benzoate is used as an internal standard. The conversion of terpenes and yield of terpene epoxides were calculated on the basis of chromatographic results using eqs 1 and 2, respectively.

$$\text{Conv}_{\text{terpene}}(\%) = \frac{n_{i(\text{terpene})} - n_{f(\text{terpene})}}{n_{i(\text{terpene})}} * 100 \qquad (1)$$

$$\text{Yield}_{\text{terpene epoxide}}\ (\%) = \frac{n_{(\text{tepene epoxide})}}{n_{i(\text{terpene})}} * 100 \quad (2)$$

The yields for limonene dioxide isomers were determined by ^{1}H NMR. The spectrum was recorded on a machine from Varian company, model Inova at 400 MHz, with 32 scans and a relaxation time of 2 s. Approximately, 10 mg of sample was diluted in approximately 1 g of CDCl$_3$. The isolated yield of each isomer is determined according to eq 3 after zooming and integrating the air (A) of each isomer peak.

$$\text{Yield}_{\text{Trans R}}\ (\%) = \frac{A_{\text{Trans R}}}{A_{\text{Trans R}} + A_{\text{Trans s}} + A_{\text{Cis R}} + A_{\text{Cis S}}} * 100 \quad (3)$$

3. RESULTS AND DISCUSSION

3.1. Stepwise Synthesis of DMDO and Subsequent Epoxidation.
The generated DMDO is in acetone solution. Several studies in the literature have reported that the epoxidation of olefins produced DMDO separately on a small scale.[26−29,33,34] Mikula et al. have developed their synthesis method using kilogram-scale reagents.[26] For optimal yield, this synthesis requires vigorous stirring, periodical slow addition of oxone, application of reduced pressure, and a condensation temperature of the DMDO solution below −20 °C.

The Mikula et al. procedure was reproduced using the double jacket reactor of the AI R 20 L series of "Across International". Initially, the whole quantities of water, acetone, and sodium bicarbonate necessary for the synthesis were admitted into the reactor and stirred vigorously (600 rpm). The oxone was added in small fractions. To avoid the overpressure related to the addition of the oxone, an initial reduced pressure of 400 mbar was applied in the reactor. The condensate was collected in the reflux condenser operating at −20 °C by cryostatic control. After 1 h 30 min of reaction, a 1.7 mL solution of DMDO is collected and quantified.

To avoid decomposition of the produced DMDO, it is necessary to store it in a freezer at temperatures around −20 °C. At room temperature, DMDO would spontaneously convert to acetone within a few days. Mikula et al. studied the decomposition of DMDO over a storage period of 23 months at −20 °C.[26] The freshly prepared DMDO was 72 mM. During the first 12 months, the product experienced a decrease in concentration to 40 mM, followed by a very small decrease over the next 11 months (38 mM). To avoid the loss, it is therefore advantageous to use freshly synthesized DMDO for the epoxidation reaction. The terpenes (limonene and pinenes) were then epoxidized (Scheme 2).

Limonene dioxide was synthesized in almost 100% yield over a reaction time of 20 min. The reaction is conducted at 0 °C to avoid undesirable thermal decomposition of DMDO to acetone. Under the same conditions, pinenes are also easily epoxidized with almost half the amount of DMDO compared to limonene because of their single double bond. The use of separately generated DMDO acetone solutions for the oxidation of various target molecules was reported by several authors.[35] The main advantage is the stoichiometric epoxidation of substrates in a 100% organic reaction medium. Near-neutral pH conditions must however be ensured.[36−38]

On the other hand, the DMDO isolated in acetone thus produced is in very low quantity compared to the quantities of

Scheme 2. DMDO Synthesis and Stepwise Epoxidation of Limonene and Pinenes
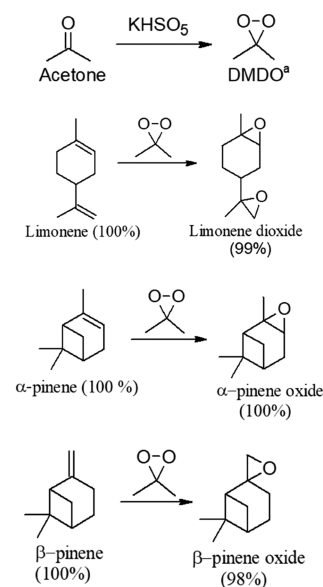
^{a}The yield of DMDO with respect to oxone is less than 5%.

reagents involved (especially the quantity of oxone). Table 2 summarizes some literature results compared to our result

Table 2. Synthesis of DMDO

ref	H$_2$O (L)	acetone (L)	oxone (kg)	n_{DMDO} (mol)	$\dfrac{\text{mol}_{\text{DMDO}}}{\text{kg}_{\text{oxone}}}$	T_C (°C)
29	0.25	0.192	0.12	0.015	0.125	−78
28	0.02	0.03	0.025	0.0016	0.064	dry ice
27	0.08	0.05	0.18	0.0052	0.028	dry ice
26	8.25	6	8.1	0.23	0.028	−40
this work	4.125	3	4.05	0.10	0.024	−20

concerning the employed reagents and the produced DMDO. In this regard, optimization studies estimated that when prepared beforehand as an acetone solution, the yield of DMDO with respect to potassium monoperoxysulfate (oxone) did not exceed 5%.[34] Moreover, it has been reported that condensation temperatures below −40 °C are necessary to improve the concentration of the DMDO in these solutions.[26] Some studies have mentioned that the application of trifluoroacetone (CF$_3$COCH$_3$), as a replacement for acetone (CH$_3$COCH$_3$), allowed the collection of dioxirane solutions in the parent ketone with concentrations 6 to 8 times higher than that in solutions usually obtained using the above described procedure.[39] These studies revealed, however, that the stability of the corresponding dioxirane is very low compared to that of DMDO; upon storage at −20 °C, the decomposition of this dioxirane is 6% after 48 h, and a loss of 30% for 120 h at 0 °C is observed. This decomposition led mainly to methyl trifluoroacetate (CF$_3$COOCH$_3$) and trifluoroacetic acid.[39] In contrast, the in situ application of DMDO precludes prior isolation and allows for a significantly improved yield relative to oxone. The following section will discuss the in situ DMDO epoxidation while discussing the effect of homogenization by different surfactants of the biphasic aqueous and organic reaction medium.

3.2. Epoxidation in Microemulsions: Effect of Different Surfactants and Comparative Study.

3.2.1. Background. Several previous studies have been conducted on the epoxidation of terpenes by in situ-generated DMDO.[17,23,24,35] In this technique, DMDO is generated at neutral pH as an intermediate after in situ reaction of acetone with potassium monoperoxysulfate $KHSO_5$, commercially available as oxone or caroat (Scheme 3). This DMDO route appears to allow

Scheme 3. Mechanism of DMDO Formation with Oxone
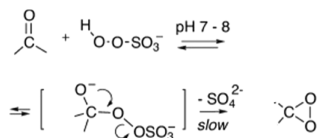
reaching very high oxygen yields for epoxidation compared to the stepwise application of DMDO. Scheme 4 illustrates the in situ epoxidation of terpene by DMDO.

**Scheme 4. Cycle of Terpene Epoxidation by In Situ DMDO Synthesis**
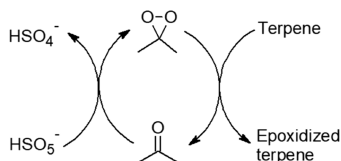
In an aqueous solution of oxone at near-neutral pH (pH = 7–8) and in the presence of acetone, the hydrogen sulfate anion (HSO_5^-) reacts with acetone to produce DMDO. A broad development of dioxirane chemistry on kinetic, stochimetric, and ^{18}O labeling data allowed to establish a mechanism of DMDO formation (Scheme 3).[40–42] According to some authors, there is additional formation of a hemiacetal intermediate, which evolves at the end to give DMDO.[38] Indeed, DMDO is known as an electrophilic oxygen transfer reagent, it can then be attacked by a variety of electron-rich substrates (terpene), yielding epoxidation products (epoxidized terpene) (Scheme 4); DMDO can also be simultaneously attacked by the hydrogen sulfate anion (HSO_5^-), giving the sulfate anion (HSO_4^-) and molecular oxygen (Scheme 5). Molecular oxygen may also result from

Scheme 5. Decomposition of DMDO by the Peroxymonosulfate Anion
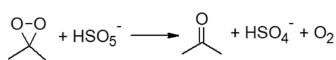
autodecomposition of oxone (Scheme 6). In some cases, as a result of phase incompatibility within the substrate, acetone is employed in large quantities serving as a phase transfer intermediate and also as an easily regenerated catalyst. These effects considerably deplete the oxygen yield; for example, for the complete epoxidation of limonene, an oxone/limonene ratio of 2.6 was required.[23] An oxone/limonene molar ratio

Scheme 6. Autodecomposition of Oxone
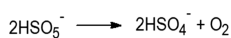
equal to 1 could suffice to completely epoxidize limonene stoichiometrically (the number of moles of active oxygen is equal to twice the number of moles of the oxone).

Indeed, in order to decrease the reaction volume, that is, to exclude the organic solvent and to minimize the loss of active oxygen, a surfactant can be used in order to use micellar catalysis; micellar catalysis in organic synthesis in general is widely defined in the literature.[43] Specifically for the case of the epoxidation of a hydrophobic terpene by DMDO in an aqueous medium, the oxone dissolves in the majority aqueous phase in which the hydrophobic terpene is epoxidized via DMDO. At an aqueous surfactant concentration above the CMC, micelles are formed in which the terpene is finely dispersed spontaneously; this forms a nearly homogeneous and indefinitely stable mixture. Acetone, in turn, is a compound that is both miscible in organic and aqueous media and is converted to DMDO by reaction with the oxone in the aqueous medium in order to migrate to the interface or within the micelle to epoxidize the terpene. With this in mind, the surfactant effect will be investigated in the case of aqueous phase epoxidation for concentrations before and after micelle formation. The application of a surfactant to disperse the hydrophobic terpene in aqueous medium could considerably reduce the acetone and oxone content as well as the reaction time to fully epoxidize a terpene. The distribution of terpene, oxone, surfactant, DMDO, and acetone within the micelle is shown in Scheme 7.[17]

Scheme 7. Epoxidation Reaction in Micellar Catalysis
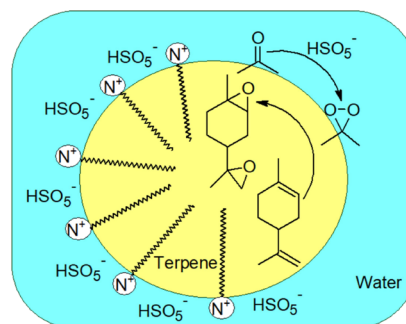
3.2.2. Optimization of the Reaction Conditions. Before testing the effect of CTAHS, CTAB, and CTAC for microemulsion stabilization of the biphasic reaction medium, the parameters such as reaction time, oxone/terpene molar ratio, and $NaHCO_3$/oxone molar ratio required for maintaining the pH close to neutrality and amount of acetone required were optimized. In a previous study, the reaction time and the oxone/terpene molar ratio were already optimized.[17] This part of the work will mainly consist of optimizing acetone and sodium bicarbonate as the buffer and testing and comparing the stability of three surfactant homologs (CTAHS, CTAB, and CTAC).

3.2.2.1. Optimization of the Amount of Sodium Bicarbonate as the Buffer. For an epoxidation reaction in using oxone, the presence of a buffer to maintain the reaction medium at a pH close to neutral is fundamental. A saturated aqueous solution of oxone has a pH below 2. The epoxidation reaction could possibly be carried out over the range of initial pH = 1.5 to 12. For an initial value of 1.5 to 8.6, the pH is adjusted with $NaHCO_3$; for pH values above 8.6, the pH is adjusted with NaOH. Figure 1 summarizes the results of the

epoxidation of limonene at different pH values. The reaction conditions are as described in the experimental part.
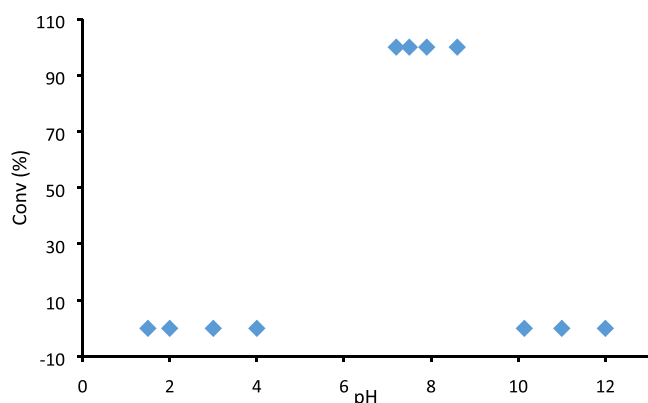

Figure 1. Conversion of limonene at different pH. See Table 3 for reaction conditions.

At very acidic or basic pH values, no conversion of limonene is observed. At pH = 7.2 to 8.6, the oxone has completely reacted. The amount of $NaHCO_3$ introduced in a saturated aqueous solution was optimized by measuring pH at various $NaHCO_3$/oxone ratios (Table 3). A minimal $NaHCO_3$/oxone ratio of 3 was required.

Table 3. Sodium Bicarbonate and pH Reaction Medium Effect on Limonene Conversion and LDO Yield[a]

n_{NaHCO_3}/n_{oxone}	pH[b]	conv$_{Lim}$ (%)	yield$_{LDO}$ (%)
4	7.90	100	98
3.5	7.60	100	99
3	7.20	100	98
2.5	6.4	76	53

[a]The reaction conditions are as described in the experimental part. At ambient temperature, 25 mL of distilled water, 0.05 g of CTAHS, and 6.2 mmol of limonene were diluted in 5 mL of acetone; 10.5 mmol of oxone or 6.5 g is added in five fractions (i.e., 1.30 g every 5 min very slowly). By varying the amount of sodium bicarbonate, the sodium bicarbonate/oxone ratio was established. [b]The pH is measured at the end of the reaction.

The major advantage of the epoxidation of limonene by DMDO lies in its high selectivity toward epoxides (Scheme 8).

Scheme 8. Epoxidation Products of Limonene by DMDO

Limonene   1,2 Limonene oxide   Limonene dioxide
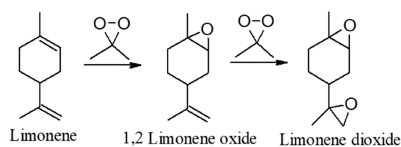
The application of CTAHS as a surfactant for this reaction is no exception. The only reaction intermediate is 1,2-limonene oxide. There was preferential attack of DMDO on the endocyclic double bond of limonene forming 1,2-oxide limonene first due to the electron-rich nature of the trisubstituted bond compared to the disubstituted exocyclic bond. No allylic epoxidation favoring the formation of carveol or carvone as in the case of epoxidation using hydrogen peroxide or tert-butyl hydroperoxide as the oxidant was

observed. Also, no secondary epoxidation by epoxide ring opening favoring diol formation was observed. Similarly, the NMR spectrum of the complete epoxidation of limonene shows no proton adjacent to a diol or ketone function. Details of the proton NMR analysis will be reported below. The NMR spectra of limonene before and after complete epoxidation are presented in the information sheet (appendix).

3.2.2.2. Optimization of the Amount of Acetone as the Catalyst Free Organic Solvent. Early work dealing with epoxidation reactions in the presence of a peracid had shown that the presence of a ketone accelerates the reaction.[38,44] This led to the discovery that in the presence of a ketone, the oxygen in the peracid passes through an intermediate, which is a dioxirane. Ketones have therefore been considered as catalysts for this type of reaction. Indeed, in addition to the use of a ketone and the aqueous oxone, the olefin is solubilized in an organic solvent, and therefore, the reaction is conducted in a biphasic medium.[45−47] On the other hand, the epoxidation reaction is possible even in the absence of an inert organic solvent; this has been discussed recently by Charbonneau et al.[23,24] The epoxidation reaction was carried out using exclusively acetone both to generate DMDO and as an organic solvent. Because of the high solubility of acetone in water, however, acetone is used in large quantities so that its concentration reaches its maximum equilibrium value. This leads to a large reaction volume and a low yield of active oxygen.

Very recently, a new epoxidation technique consisting of dispersing the hydrophobic terpene in the aqueous phase using a surfactant in order to exclude the organic solvent has been developed.[17] At very low surfactant concentrations above the CMC, micelles spontaneously form in which limonene is entrapped forming microemulsions. For this purpose, the use of an organic solvent or acetone in large quantities is no longer necessary. Acetone should be used in small quantities to act as a catalyst (in situ DMDO generator). To optimize the amount of acetone needed, the epoxidation reaction is carried out with different amounts of acetone while keeping the same reaction conditions. At this stage, the amount of surfactant is not optimized, and only CTAHS is tested as the surfactant. Figure 2 shows the results of the epoxidation of limonene with different amounts of acetone. The reaction sequence is as described in the experimental part.

Figure 2 shows the conversion and yield of limonene dioxide as a function of the amount of acetone. When the reaction is carried out without acetone (at the 0 mL acetone point), there is a low conversion of limonene without any formation of limonene dioxide. After the use of acetone, the conversion and yield increase exponentially with the amount of acetone. Only 4 mL of acetone was sufficient to completely convert limonene to limonene dioxide; this is equivalent to an acetone/water volume ratio of less than 1:5. The required oxone/alkene molar ratio is 1.6 for limonene (double unsaturation) and 0.9 for alpha-pinene (single unsaturation) for a reaction time of only 40 min.

In order to compare the efficiency of the microemulsion technique to other techniques used for epoxidation using oxone and acetone such as epoxidation in biphasic medium in the presence and without phase transfer catalyst (18-crown-6 or n-Bu4NHSO4) and epoxidation in the presence of excess acetone as a dioxirane generator and an alkene solubilizing solvent, the monosaturated terpene (alpha-pinene) is also epoxidized and the results are summarized in Table 4.
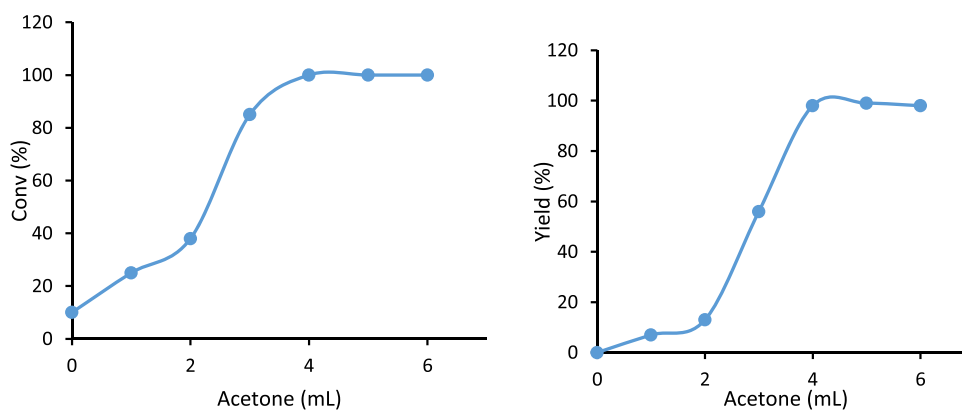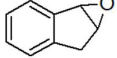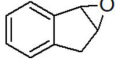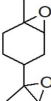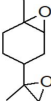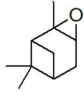
Figure 2. Limonene conversion and yield of limonene dioxide as functions of the amount of acetone. At ambient temperature, 25 mL of distilled water, 0.05 g of CTAHS, 33 mmol of sodium bicarbonate, and 6.2 mmol of limonene were diluted in different amounts of acetone; 10.5 mmol of oxone or 6.5 g is added in five fractions (i.e., 1.30 g every 5 min very slowly). The reaction was conducted as described in the Experimental Section.

Table 4. Results of Different In Situ DMDO Epoxidation Studies in Organic/Aqueous and 100% Aqueous Media for the Case with a Surfactant

Method	Epoxidized Alkene	Reaction time (hr)	Molar ratio oxone/alkene[c]	Conv (%)	Yield (%)	Reference
Benzene-H₂O 18-crown-6		3	2.3	80	98	[45]
Benzene-H₂O n-Bu₄NHSO₄		4	2.3	70	45	[45]
CH₂Cl₂-H₂O n-Bu₄NHSO₄		4	2.3	97	80	[45]
CH₂Cl₂-H₂O n-Bu4NHSO4		2	2	99,8		[46]
CH₂Cl₂-H₂O Free CTP		2	2	90		[46]
Acetone-H₂O Free CTP		1	2.6	100	100	[23,24]
H₂O-surfactant[a]		40 min	1.6[c]	100	98	This work
H₂O-surfactant[b]		40 min	0.9[c]	100	98	This work

[a]At ambient temperature, 25 mL of distilled water, 0.05 g of CTAHS, 33 mmol of sodium bicarbonate, 6.2 mmol of limonene diluted in 4 mL of acetone; 10.5 mmol of oxone or 6.5 g is added in five fractions (i.e., 1.30 g every 5 min very slowly). [b]25 mL of distilled water, 0.05 g of CTAHS, 16 mmol of sodium bicarbonate, 6.2 mmol of α-pinene diluted in 4 mL acetone, and 5.3 mmol of oxone added in five fractions. The reaction was conducted as described in the Experimental Section. [c]The molar number of active oxygen is equal to twice the molar number of the oxone according to the empirical formula of the oxone described in the Experimental Section.

For Table 4, as the aim of this work is a comparative study, a comparison of the present work (reaction in the microemulsion system) with previous studies is reported. From Table 4, the comparison variables such as the reaction time, amount of oxone, and the need for an organic solvent are compared side by side. For this purpose, more details of epoxidation chemistry in microemulsions are already reported in our former publications.[17,48] The present work is devoted much more on the comparison of processes using oxone as the oxidant through dimethyldioxirane.

Epoxidation technologies that solubilize the alkene to be epoxidized in an organic solvent for a two-phase reaction medium (benzene−H₂O, CH₂Cl₂−H₂O, or acetone−H₂O) require a volume of solvent that is generally equal to the volume of water needed to dissolve the oxone. This leads to a loss of active oxygen (excess oxone), as observed in most cases (Table 4). Indeed, an oxone/alkene molar ratio higher than 2

was required to completely epoxidize the monosaturated alkene over a high reaction time compared to the microemulsion (H_2O-surfactant) epoxidation technique. In contrast, in the case of microemulsion epoxidation, because the reaction is conducted without an organic solvent, replaced by minor amounts of surfactants, very high conversions and yields are achieved with only oxone/alkene molar ratios lower than 1 for alkene with one unsaturation (alpha-pinene) and 2 for alkene with double unsaturation (limonene). The reaction time is only 40 min. In the extensive literature available on the epoxidation of alkenes with oxone, the required oxone/alkene molar ratio was never less than 2. With the epoxidation reaction conditions at microemulsions, the use of the necessary oxone is reduced to at least 50%.

3.2.3. Effect of CTAHS, CTAB, and CTAC for DMDO In Situ Epoxidation. The importance of surfactant interactions at the aqueous phase-organic phase (terpene) interface for the in situ DMDO epoxidation reaction has been discussed previously.[17] Oxone is an aqueous oxidizing agent, and limonene is a hydrophobic substrate; thus, the oxygen must be transferred from the aqueous phase to the limonene. To this end, the application of a surfactant can effectively improve the dispersion of the hydrophobic terpene in the aqueous phase by promoting the formation of a microemulsion.

According to the literature, besides the presence of the oxidant and substrate, microemulsions are formed at specific compositions of water, oil, a surfactant, and a co-surfactant (usually an alcohol with an alkyl group between C_4 and C_8).[49−53] In the case of terpene epoxidation in the presence of in situ-generated DMDO, the formation of microemulsions involves only water, terpene, surfactant, and acetone at specific concentrations.[17]

To optimize the amount of surfactant required to microemulsify limonene, epoxidation reactions were conducted at different surfactant concentrations at values near the CMC at room temperature. Reaction tests were carried out under the same conditions while comparing the three homologs of cetyltrimethylammonium hydrogen sulfate (CTAHS), bromide (CTAB), and chloride (CTAC). Table 5 reports the CMCs of the different surfactants employed.

Table 5. CMC of Surfactants at 25 °C

surfactant	CMC (mM)	ref
CTAHS	0.27	25
CTAB	0.93	54,55
CTAC	1.40	54

Figure 3 displays the limonene conversion and LDO yield obtained in the series of epoxidation tests. The reaction conditions were as described in the Experimental Section. The double epoxidation of limonene occurs first after epoxidation of the endocyclic unsaturation as an intermediate, and then, the epoxidation of the exocyclic unsaturation is carried out to obtain the limonene dioxide. According to Figure 3, the most important phenomenon to consider for homogenization of the reaction medium is the use of the surfactant at a concentration above the CMC. At concentrations below the CMC (i.e., before micelle formation), no significant effect of surfactant concentration on conversion and yield was observed for all surfactants employed. The conversion of limonene is about 60% with a yield of limonene dioxide not exceeding 35% and the presence of limonene monoxide as the intermediate. The

CTAHS micelles form at a very low concentration (CMC of 0.27 mM) compared to the CTAB and CTAC micelles (0.93 and 1.40 mM, respectively).[25,54,55] The stabilities of these three surfactants are different. At only an aqueous phase concentration of CTAHS of 0.67 mM, conversion and yield of almost 100% are achieved; for CTAB, an aqueous phase concentration of 1.35 mM was sufficient to obtain the same results. This allows us to discover that CTAHS and CTAB homogenize the biphasic emulsion at concentrations very close to their respective CMC. On the other hand, for CTAC, conversions and yields of almost 100% could be reached only from the aqueous concentration of 5.4 mM.

For this epoxidation process, several advantages can be listed by comparing with stepwise DMDO epoxidation as listed in Table 6. For separate preparation of DMDO, the technique is very tedious and requires additional additives and steps, which are not necessary in the application of microemulsions. In the case of microemulsions, acetone acts as a catalyst and no organic solvent is needed. In addition, the amount of acetone required, the oxygen yield with respect to oxone, and the low reaction volume make the in situ technique under microemulsions certainly eligible for large-scale applications.

3.3. Stereoisomers of LDO. Generally, the epoxidation of chiral terpenes gives rise to several isomers regardless of the nature of the technology used.[19,56] Nonstereoselective epoxidation of the endocyclic unsaturation of limonene gives rise to a mixture of trans-limonene oxide and cis-limonene oxide.[19,20,56] After epoxidation of the exocyclic unsaturation to form limonene dioxide, there is the formation of an additional center of chirality at carbon C8. The number of diastereomers is then at a total of four (Scheme 9), among which 2 trans and 2 cis cannot be physically separated.[57,58] The importance of the reactivity of these cis and trans diastereomers is different when they are used as precursors in the formation of biosourced polymers.[14,56,59] These isomers are often quantified by chromatography using a chiral column or by proton NMR.[22,56,60−62]

As in our case, the limonene dioxide formed by in situ DMDO epoxidation reaction is a mixture of four isomers: two stereoisomers trans and cis, each of which has two enantiomers R and S (Scheme 9). The sample of this mixture of isomers was analyzed by proton NMR (Figure 4). The different proton NMR peaks of these four isomers were identified by comparison to the relative position of the peaks of the commercial LDO isomers and the peaks of the isolated isomers reported in literature.[57,59] From 1.17 to 1.22 ppm, the methyl proton bound to the carbon at position 7, due to its direct linkage to the ring, is identified by four peaks of varying intensities characterizing the quantities of the four isomers. The integration of each of these four peaks is used to estimate the quantities of different isomers of the LDO. According to the literature, the methyl proton bound to the carbon at position 10 is not affected by the different conformations of the isomers because of its exocyclic position.[57,59] This allowed its resonance to be identified by a single peak around 1.28 ppm. As in the literature, the appearance of peaks between 3.4 and 3.5 ppm indicates the presence of oxirane (epoxide).[63] This same quantification technique was used when LDO isomers were obtained by aerobic epoxidation using cobalt-substituted mesoporous SBA.[20] A 60:40 mixture of cis and trans LDO is obtained at proportions close to those in our study for the four isomers.[56] Epoxidation of limonene with a tungsten-based polyoxometalate catalyst using aqueous H_2O_2 as an oxidant
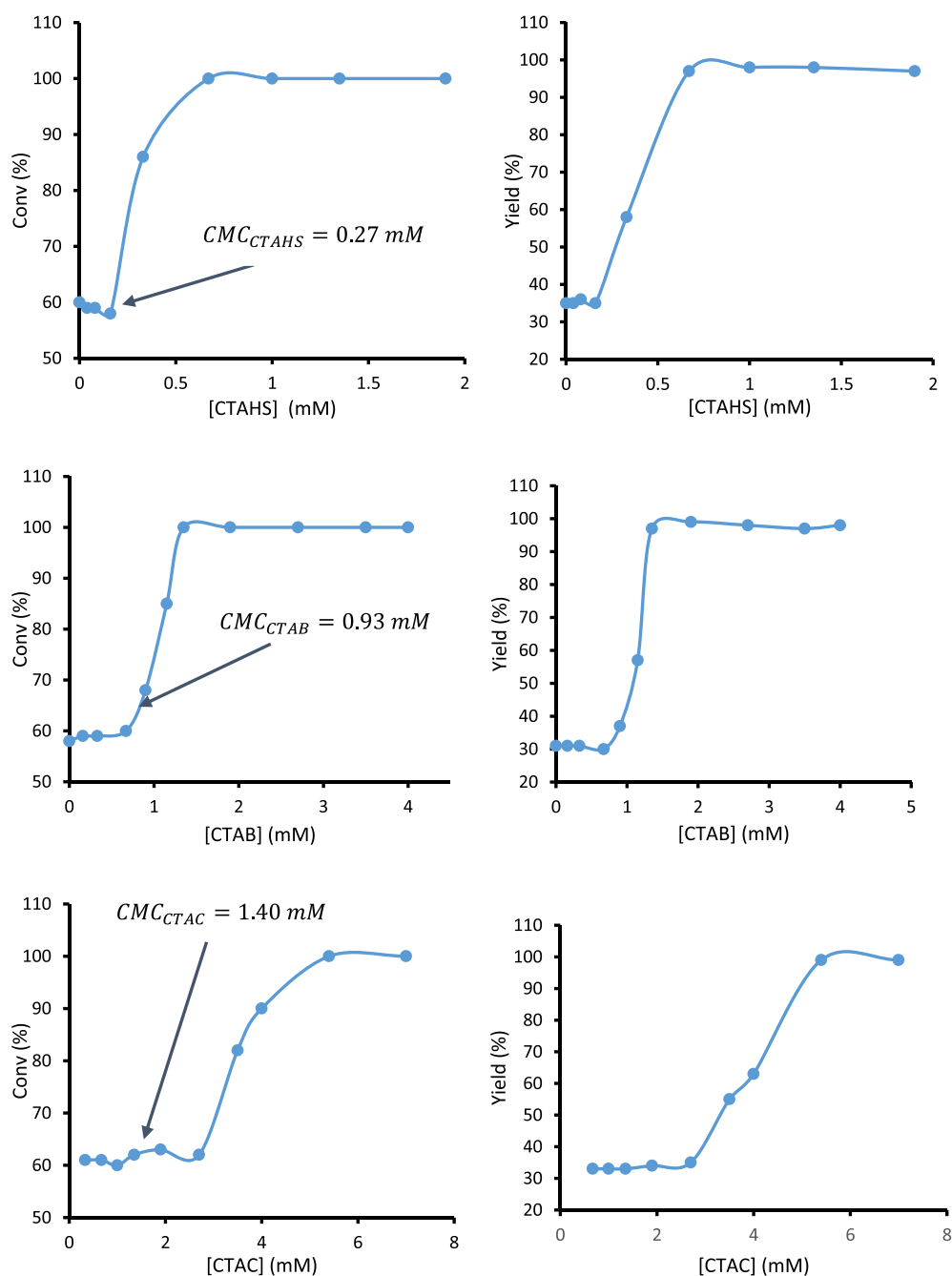
Figure 3. Limonene conversion and yield of limonene dioxide as function of surfactant concentration. Twenty-five milliliters of distilled water, the amount of surfactant is variable, 33 mmol of sodium bicarbonate, 6.2 mmol of limonene diluted in 4 mL of acetone; 10.5 mmol of oxone or 6.5 g is added in five fractions (i.e., 1.30 g every 5 min very slowly). The reaction was conducted as described in the Experimental Section.

also led to a mixture of the cis and trans isomers of 1,2-limonene oxide.[19] Quantification of these isomers using chromatography also gave a 57:43 ratio of cis and trans 1,2 limonene oxide, which is also a ratio close to the results of the present study.

4. CONCLUSIONS

This study investigated epoxidation processes using DMDO under two approaches. One approach is to synthesize DMDO separately and isolate it in acetone to epoxidize the terpene in a 100% organic medium. A second approach is the in situ epoxidation in the aqueous phase under the presence of

different surfactants to microemulsify the terpene. The objective was to compare the two processes. The epoxidation in stepwise synthesis of DMDO proved to be very tedious. Moreover, the conditions of DMDO synthesis and the quantities of reagents involved are not sufficient to warrant large-scale applications. Indeed, this isolated DMDO synthesis process is a promising route for minor scale epoxidations. On the other hand, according to the results listed in Table 2, the low yield of DMDO relative to the reagents involved and the very low condensation temperature are the main drawbacks of the process for large-scale application. Nevertheless, this approach could be useful in the case of epoxidation of

Table 6. Comparison of Stepwise and In Situ Microemulsion Technologies

	stepwise	in situ microemulsions
synthesis and epoxidation	two steps	one step
physical state of DMDO	isolated in acetone at $T < -20\ °C$	not required
additional reagents	gaseous and liquid N_2	not required
storage of DMDO	$T < -20\ °C$	not required
amount of acetone required	$40\ L_{acetone}/mol_{DMDO}$	$<1\ L_{acetone}/mol_{DMDO}$
$T°$ of epoxidation	$0\ °C$	ambient condition
oxygen number yield	<5%	60 à 70%
application at scale	not favorable	very favorable

Scheme 9. Isomers of LDO Obtained by Epoxidation with DMDO

Trans S 17 %	Trans R 22 %		Cis S 24 %	Cis R 37%
c	d	And	a	b
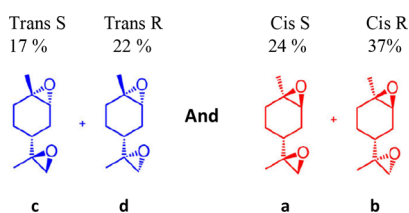
sensitive in aqueous media substrates.[28,35,38] On the other hand, epoxidation in the presence of in situ-generated DMDO by dispersing the terpene in the aqueous medium using a surfactant proved to be the most promising. The application of a very small amount of surfactant allowed to avoid using any organic solvent, and indeed, the hydrophobic terpene is perfectly dispersed in aqueous medium. Moreover, the reaction volume is very low compared to the conventional method involving the presence of an organic solvent. This resulted in terpene epoxides in almost 100% yield; the oxygen yield on the epoxides with respect to oxone reached up to 70%. The surfactants (CTAHS, CTAB, and CTAC) should be used above their CMCs. CTAHS showed stability at the lowest concentration due to its very low CMC. It should also be mentioned that this epoxidation technique is 100% green and conducted under mild conditions and can easily be scaled up to industrial scale. The waste generated at the end of the reaction is biodegradable.

■ ASSOCIATED CONTENT

ⓈⒾ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c02423.

Additional information on the H NMR analysis of limonene before and after epoxidation (PDF)

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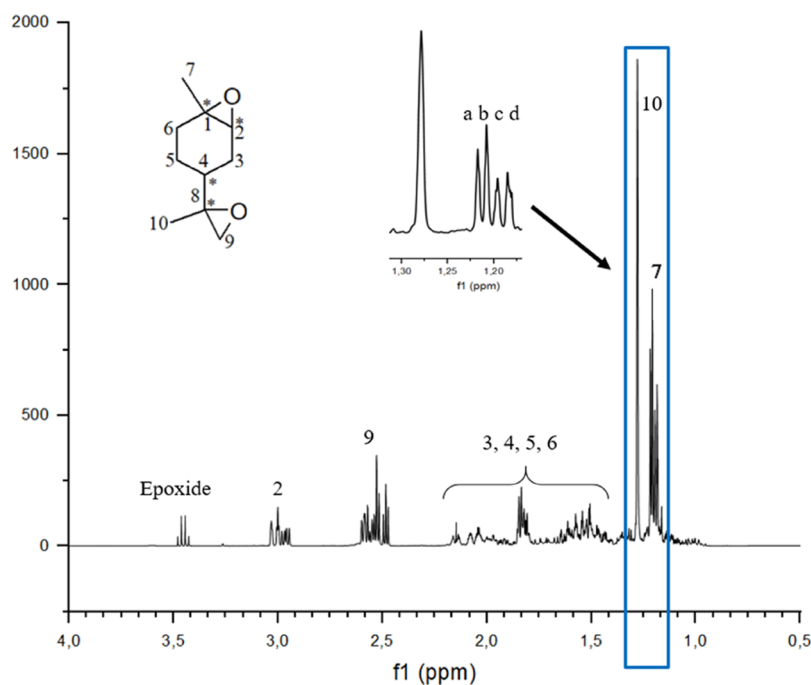Complete contact information is available at:
https://pubs.acs.org/10.1021/acsomega.2c02423

Notes

The authors declare no competing financial interest.

Figure 4. Proton NMR spectrum of LDO synthesized by reaction with DMDO.

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