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Sustainable green epoxidation of terpenes and other olefins by dioxirane generated from H_2O_2

Yacoub Mahamat Ahmat, *[a] Malak El Kaddouri,[ab] Louis Fradette[c]
and Serge Kaliaguine *[a]

This study examines the catalytic synergy between a nitrile and a ketone for the formation of dioxirane from hydrogen peroxide (H_2O_2) for the purpose of epoxidizing a wide variety of terpenes and other olefins. The influence of factors such as the amount of nitrile and ketone, the reaction time and the pH of the reaction medium on the conversion rate and epoxide yield is systematically evaluated to determine optimal conditions. Experimental findings reveal that under ambient conditions and at pH values above 11, nearly complete conversion and epoxide yields (~100%) are achieved across diverse terpene and other olefin substrates. The reaction process is simple and efficient, proceeding without any pre-synthesized solid catalyst, whereas readily available acetonitrile and acetone act as co-catalysts and can be recycled indefinitely, facilitating large-scale implementation. Complete substrate conversion and epoxide produced selectively, together with the use of low-cost raw materials that generate no waste, ambient reaction conditions and the perpetual recyclability of the reagents, makes this process more relevant than other epoxidation techniques and easier to implement on an industrial scale in response to the current industrial demand for epoxides.

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Sustainability spotlight

This work analyzes advances in the selective epoxidation of bio-olefins, highlighting the transition from classical stoichiometric oxidants to catalytic systems that employ greener oxidants and an improved green process. It provides mechanistic insights into active oxygen species formation and discusses strategies that enhance the activity, selectivity, and process efficiency. All reagents used in the process, including catalysts, are fully recyclable, very inexpensive, much less hazardous, and driven under ambient conditions, while no byproducts or waste is produced. This process is essential to reduce fossil olefin dependency and environmental impact in the polymer industry and support circular economy and green chemical manufacturing.

Introduction

The epoxidation of olefins is an important primary step in the production of a wide variety of high-value products in fine chemicals, polymers and pharmaceuticals.[1–5] The literature discusses a variety of epoxidation pathways, some of which are currently under development. The latter include homogeneous and heterogeneous catalytic pathways using molecular oxygen, hydrogen peroxide or other oxidizing agents.[5–10] From environmental considerations, molecular oxygen and hydrogen peroxide are considered the most desired oxidants as they generate no waste or only water. However, most of the catalytic pathways developed to date fail to meet all the essential criteria for an ideal epoxidation process, including high turnover numbers, excellent product selectivity, compatibility with environmentally benign solvents and catalyst stability with effective recovery and reusability.[11–13] For example, cyclic compounds bearing trisubstituted double bonds, such as limonene, α-pinene, terpinene and their epoxides, are chemically unstable in typical aerobic epoxidation media, promoting the formation of undesirable secondary oxidation products.[6] Additionally, some studies have observed a trade-off between selectivity and conversion, with higher conversion generally corresponding to lower selectivity.[14,15]

In response to these challenges, our recent research was focused on developing an efficient and sustainable method for terpene epoxidation. Our findings demonstrated that the dioxirane pathway represents one of the most promising and industrially viable routes for achieving highly selective terpene epoxidation.[16–18] Dioxirane is an oxidant usually formed from a ketone with oxone as the primary oxidant in an aqueous medium. This reaction medium was proven to generate the fewest secondary reactions with substrates and their corresponding epoxides, resulting in high selectivity toward the desired epoxide products. Beyond its outstanding selectivity, this pathway embodies the principles of green chemistry and offers significant potential for large scale implementation. The

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[a] *Department of Chemical Engineering, Laval University, Quebec City, Quebec, Canada. E-mail: Serge.Kaliaguine@gch.ulaval.ca; yacoub.mahamat-ahmat.1@ulaval.ca*

[b] *Euromed University of Fes, UEMF, Morocco*

[c] *Polytechnique Montreal, Montreal, Canada*

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high selectivity of this process to the target epoxide eliminates the need for post-epoxidation separation while employing low-cost and recyclable reagents.[16] In our previous investigations, we further demonstrated that the reaction can be carried out entirely in an aqueous medium without the use of organic solvents. This represents a major advancement in process sustainability and scalability. The only remaining drawback is the formation of sulfate waste $3KHSO_4 \cdot K_2SO_4$ from oxone by the reaction.[16]

To overcome this drawback and further enhance the environmental performance of the process, a more attractive option for generating dioxirane would be the *in situ* formation of this type of oxidant from hydrogen peroxide (H_2O_2) in the presence of a ketone. Oxone itself is synthesized from potassium hydroxide (KOH) and sulfuric acid (H_2SO_4) using H_2O_2 as the oxidant (Scheme 1).[19,20] Therefore, the direct generation of dioxirane from H_2O_2 represents a clean and promising alternative to the conventional oxone route. Since no persulfate would be generated in the reaction, the new route would produce no waste, and the liquid reagents involved in the reaction could be recyclable, further enhancing the process sustainability.

Building on this concept, Shi *et al.* developed a system for the *in situ* formation of a dioxirane from H_2O_2 for the asymmetric epoxidation of a series of olefins.[21,22] In their approach, both a ketone and a nitrile were required. A peroxyamine intermediate, which was formed through the reaction between the nitrile and H_2O_2, acted as an active oxidant, playing a role analogous to that of the peroxymonosulfate anion (HSO_5^-) in the conventional synthesis pathway. This intermediate subsequently reacted with the ketone to produce the oxidizing dioxirane species, which finally epoxidized the olefin. Scheme 1 provides a comparative description of these two pathways for the generation of dioxirane (exemplified here as dimethyldioxirane) to produce the epoxide.

This study aims at investigating in greater detail the synergistic effect between a nitrile and a ketone in the epoxidation of a series of olefins, mainly terpenes, using hydrogen peroxide as an oxidant, with the ultimate goal of developing an efficient process for synthesis of renewable and sustainable epoxides. Particular attention is given to the aspects of green chemistry, emphasizing the use of low-cost materials and operational simplicity, seeking full compliance with the twelve principles of green chemistry.

Materials and methods

Materials

All substrates subjected to epoxidation (R-(+)-limonene, (−)-α-pinene, (−)-β-pinene, 3-carene, α-terpinene, γ-terpinene, β-myrcene, carvone, carveol and styrene) were purchased from Sigma Aldrich with a purity of nearly 100%. The other products were purchased from Alfa Aesar. The oxidant used for the reaction was 30% hydrogen peroxide in aqueous solution. Potassium carbonate (K_2CO_3) was used to adjust the pH in order to conduct the reaction in a basic medium. Diethyl ether was used for liquid–liquid extraction due to its high affinity for epoxides and its low boiling point (34 °C). All products were used as received without any preliminary purification.

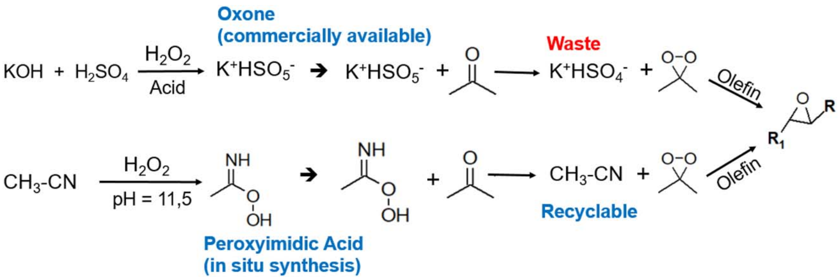
Methods

For a typical test, the epoxidation reaction was carried out under ambient conditions in a 250 ml round-bottom flask. The reaction mixture consisted of 15 ml of acetonitrile, 10 ml of acetone and 12 ml of aqueous potassium carbonate (K_2CO_3) solution (1 M), which were mixed thoroughly. Subsequently, 1 ml (6.2 mmol) of the substrate to be epoxidized (α-pinene) was added to the reaction mixture, followed by the addition of 1.8 ml (*i.e.*, 18 mmol) of 30% hydrogen peroxide. The mixture was stirred using a magnetic stirrer at 500 rpm for 2 hours.

At the end of the test, the reaction mixture was transferred to a separating funnel for liquid–liquid extraction. Approximately 50 ml of diethyl ether was added to the separating funnel containing the reaction mixture, resulting in the formation of two distinct phases. The lower phase is the aqueous phase, which was discarded, and the upper phase is the diethyl ether phase containing the epoxidized olefin. The organic phase was then recovered, dried using magnesium sulfate ($MgSO_4$) and transferred to a rotary evaporator to isolate the oxidized olefin. The final product was recovered for analysis to quantify the conversion of α-pinene and the corresponding epoxide yield.

Characterization

The reaction products were first identified by gas chromatography-mass spectrometry (GC-MS) to confirm the presence of terpene epoxides. The GC-MS comprised a Hewlett-Packard GC System HP 5890 series coupled to a Hewlett-Packard MSD Model 5970. The instrument was equipped with



Scheme 1 Comparison between the generation of dioxirane from oxone and directly from H_2O_2.

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a Zebron ZB-5MS capillary column (30 m × 0.25 mm × 0.25 mm).

For quantitative analysis, measurements were then conducted 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 was used as an internal standard. The conversion of terpenes and yield and selectivity of terpene epoxides were calculated on the basis of chromatographic results using eqn (1)–(3), respectively. The oxygen yield was calculated as the ratio of the number of oxygen atoms in the epoxidized olefin (N) to the number of moles of H_2O_2 used (eqn (4)).

$$\text{Conversion}_{\text{terpene}}\,(\%) = \frac{n_{\text{i(olefin)}} - n_{\text{f(olefin)}}}{n_{\text{i(olefin)}}} \times 100 \qquad (1)$$

$$\text{Yield}_{\text{terpene epoxide}}\,(\%) = \frac{n_{\text{(olefin epoxide)}}}{n_{\text{i(olefin)}}} \times 100 \qquad (2)$$

$$\text{Selectivity}_{\text{epoxide}}(\%) = \frac{n_{\text{epoxide}}}{n_{\text{i(olefin)}} - n_{\text{f(olefin)}}} \times 100 \qquad (3)$$

$$\text{Yield}_{\text{oxygen}}(\%) = \frac{N_{\text{oxygen in epoxide}}}{n_{H_2O_2}} \times 100 \qquad (4)$$

The ^{1}H-NMR spectra were recorded on a Varian Inova 400 MHz spectrometer using 32 scans and a relaxation time of 2 s. Approximately, 10 mg of each sample was dissolved in approximately 1 g of deuterated chloroform ($CDCl_3$).

Results and discussion

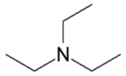
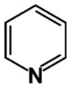
Traditionally, in order to form a dioxirane, the source used as an oxidant is a stable commercial form of potassium persulfate, oxone ($2KHSO_5 \cdot K_2SO_4 \cdot KHSO_4$).[20,23] The latter provides the active oxygen of the peroxymonosulfate anion (HSO_5^-) capable of reacting directly with a ketone to generate dioxirane. This method yields an effective and clean oxidizing intermediate. Several epoxidation studies have been carried out using this method of dioxirane *in situ* generation.[16]

It would, however, be particularly interesting if this dioxirane could be generated directly from H_2O_2 while maintaining the same reaction efficiency in terms of operational simplicity, conversion and epoxide yield.

According to preliminary tests, H_2O_2 alone was shown to not react directly with acetone to produce dimethyldioxirane. Based on the results summarized in Table 1, it was found to be necessary to use a nitrile that acts synergistically with the ketone to epoxidize the double bond. To demonstrate and confirm this catalytic synergy between a nitrile and a ketone in performing epoxidation through dioxirane generation in the presence of H_2O_2, a series of experiments were performed, and the results are summarized in Table 1.

According to the results summarized in Table 1, high epoxide conversions and yields are achieved only when both a nitrile and a ketone are used simultaneously (entries 1 and 2). The selectivity for alpha-pinene epoxide is always very high due to the absence or suppression of acid-catalyzed epoxide decomposition, which poses a challenge in the case of heterogeneous epoxidation using O_2 or H_2O_2. When only a nitrile is

Table 1 Synergistic effect of a nitrile and a ketone in epoxidation of α-pinene with H_2O_2[a]

Entry	Catalyst #1	Catalyst #2	Conv. (%)[b]	Yield (%)[c]	Selectivity (%)[d]
1	CH_3CN	CH_3COCH_3	100	96	96
2	CH_3CH_2CN	CH_3COCH_3	100	95	96
3	CH_3CN	—	2	—	—
4	CH_3CN	CH_3OH	12	8	66
5	CH_3CN	Ethyl acetate	5	—	—
6	—	CH_3COCH_3	3	—	—
7	Triethylamine 	CH_3COCH_3	4	—	—
8	 Pyridine	CH_3COCH_3	3	—	—
9	—	—	0	—	—

[a] Catalyst #1 (15 ml), catalyst #2 (10 ml), α-pinene (1 ml, 6.2 mmol), reaction time (2 h), H_2O_2 (30%; 1.8 ml, 18 mmol), K_2CO_3 (12 ml of 1 M solution), room temperature. [b] Calculated using eqn (1). [c] Calculated using eqn (2). [d] Calculated using eqn (3).

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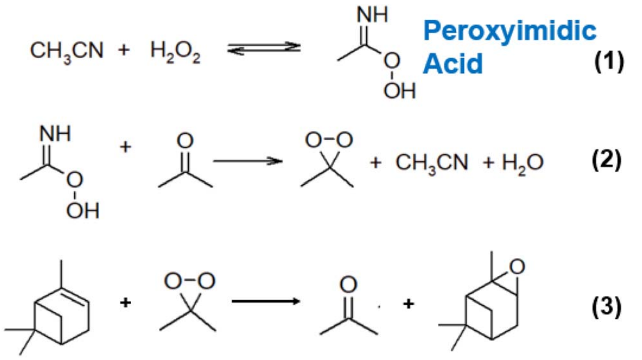


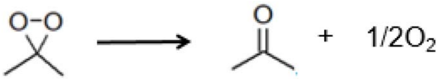
Scheme 2 Proposed successive reactions during epoxidation with H_2O_2 in the presence of the nitrile/ketone pair.

used, the conversion of α-pinene drops drastically to 2% (entry 3). To determine whether acetone plays a catalytic or solubilizing role in the reaction, another solvent with properties similar to acetone (methanol) was tested (entry 4). In this case, the conversion of α-pinene was only 12%. Similarly, when ethyl acetate was used, the conversion decreased to 5% (CH_3CN/ethyl acetate, entry 5).

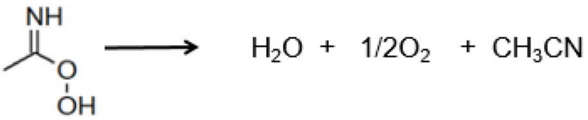
Furthermore, when the reaction was carried out in the absence of nitrile but in the presence of acetone, the conversion was limited to 3% (entry 6). To verify whether the presence of nitrile itself or simply a nitrogen-containing compound was required, additional tests were conducted using triethylamine and pyridine instead of acetonitrile (entries 7 and 8). In both cases, the conversion of α-pinene remained very low, confirming that the nitrile functionality plays a specific and essential role in the reaction mechanism. These observations strongly support the existence of a catalytic synergy between the nitrile and the ketone during the epoxidation process, which can be rationalized by the successive reactions illustrated in Scheme 2.

A test conducted in the absence of α-pinene allowed identification of acetonitrile as the product of reaction (2) instead of imidic acid. Reactions (1–3) were accompanied by decomposition reactions possibly of the three oxidizing agents (4–6), as indicated by gaseous oxygen evolution from the reaction medium.

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \qquad (4)$$

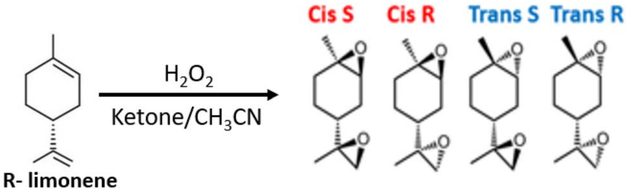


(5)



(6)

To further demonstrate that the reaction involves the presence of a ketone group that will form a dioxirane that reacts



Scheme 3 Epoxidation of R-limonene by a dioxirane to produce its chiral epoxides.

with the olefin to form the epoxide and to support the proposed mechanism (Scheme 2), we conducted new tests using a chiral ketone that we had previously studied, to determine whether a chiral yield could be achieved.[17] To do this, we used a chiral molecule, R-limonene (Scheme 3), while replacing acetone (which is not a chiral ketone) with the chiral ketone described in Table 2. The results are summarized in Table 2.

Indeed, according to the results in Table 2, when a chiral ketone was used instead of acetone (which is non-chiral), the yield of *trans*-limonene dioxide reached up to 92%. Only 5% of *cis*-limonene dioxide was formed. Whereas if acetone was used, a mixture of *cis* and *trans* was obtained with a *trans* yield of only 39%. In the absence of any ketone, the conversion was only 3%. This is sufficient evidence that the ketone group is indeed involved in the reaction through the formation of a dioxirane, which in turn acts to epoxidize the double bond.

Optimization of acetonitrile and ketone concentrations

Since it was confirmed that acetonitrile and acetone act synergistically in the formation of epoxides using H_2O_2 as the oxidant, a study was performed in which the amounts of acetonitrile and acetone were independently varied to assess their influence on the epoxidation reaction. The results for α-pinene conversion and epoxide yield are presented in Fig. 1. Optimal conversion (98%) and epoxide partial conversion (96%) were obtained when the volume of acetonitrile ranged between 15 and 20 ml. In contrast, both the conversion and yield decreased gradually when the acetonitrile volume exceeded 25 ml (Fig. 1). This behavior suggests that an excess of acetonitrile in the reaction medium promotes the catalytic decomposition of H_2O_2 into oxygen rather than its utilization for dioxirane formation. Consequently, the reduced availability of the active oxidizing species accounts for the observed decline in conversion and epoxide yield (Fig. 1).

To evaluate the effect of acetone, the amount of acetonitrile was kept constant at 15 ml to observe the variation in α-pinene conversion, and the epoxide yield was examined as a function of the amount of acetone. The results are shown in Fig. 2. Both the conversion and yield increased progressively with increasing amount of acetone, reaching nearly 100% at an acetone volume of 10 ml. Beyond this value, no decrease in the conversion or yield was observed, in contrast to the behavior noted for acetonitrile, where a decrease was observed starting at 25 ml.

To minimize the overall reaction volume of the reagents involved in the epoxidation reaction, a series of experiments were conducted, in which the volumes of acetonitrile, acetone

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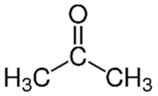
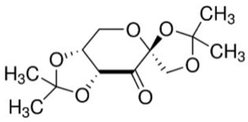
Table 2 Effect of the chiral ketone on the chiral yield of R-limonene dioxide[a]

Ketone catalyst				
Name	Structure	Conv. (%)	Yield of *trans* (%)	Yield of *cis* (%)
Catalyst free	—	3	—	—
Acetone		100	39	60
Chiral ketone		100	92	5

[a] Acetonitrile (15 ml), acetone (10 ml) or chiral ketone (2 g), R-limonene (0.5 ml, 3.1 mmol), reaction time (2 h), H_2O_2 (30%; 3.6 ml, 36 mmol), K_2CO_3 (12 ml of 1 M solution), room temperature.

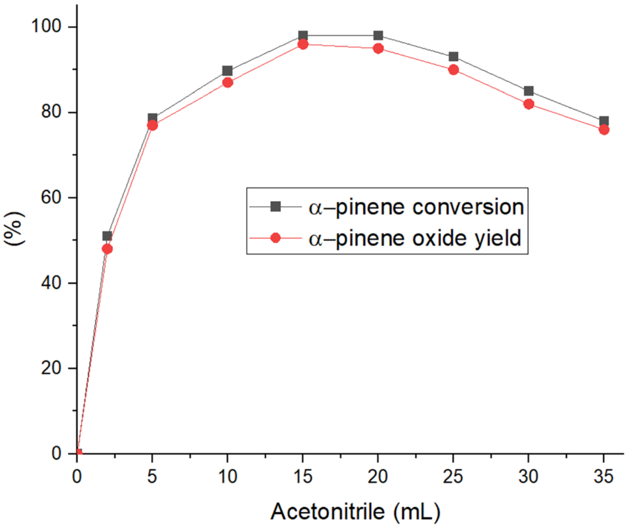


Fig. 1 Variation in α-pinene conversion and its epoxide yield as a function of the amount of acetonitrile. Reaction conditions: acetone (10 ml, 172 mmol), α-pinene (1 ml, 6.2 mmol), reaction time (2 h), H_2O_2 (1.8 ml, 18 mmol), K_2CO_3 (12 ml of 1 M solution), room temperature.

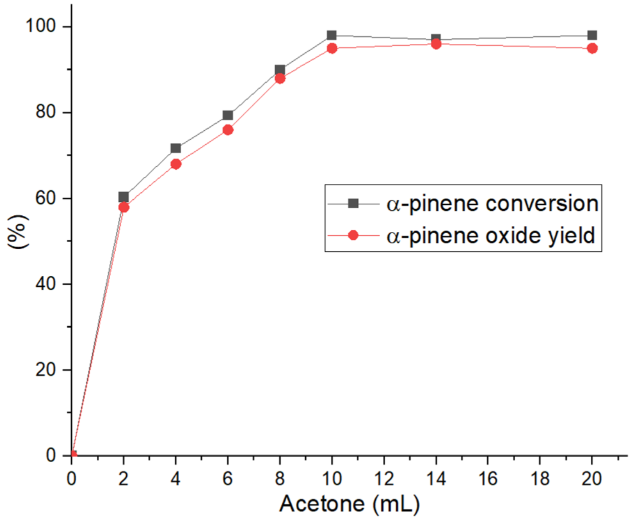


Fig. 2 Variation in α-pinene conversion and its epoxide yield as a function of the amount of acetone. Reaction conditions: acetonitrile (15 ml, 314 mmol), α-pinene (1 ml, 6.2 mmol), reaction time (2 h), H_2O_2 (1.8 ml, 18 mmol), K_2CO_3 (12 ml of 1 M solution), room temperature.

and water were systematically varied. The corresponding results are summarized in Table 3. When the total reaction volume that previously yielded nearly complete α-pinene conversion and epoxide formation (entry 1) was reduced by half (entry 2), both the conversion and yield decreased by approximately 10%. A further reduction of the reaction volume to one-third led to a reduction of approximately 25% in both conversion and the yield, resulting in values of 72% and 69%, respectively (entry 3, Table 3). Therefore, the reagent quantities used in entry 1 are considered as optimal values for achieving maximum conversion and epoxide yield.

In terms of mechanism, effectiveness, and scalability, reducing the reaction volume from 15/10 ml (acetonitrile/acetone) to 5/3.3 ml led to a decrease in α-pinene conversion from 98% to 72%, while the selectivity remained high (95–98%). It is our experience that the epoxidation reaction should be considered as competitive with oxidizing agent decomposition. A lower epoxide yield at full H_2O_2 conversion indicates the higher rate of this decomposition. It is likely that reducing the total volume, as indicated in Table 3, decreases the relative rate of epoxidation, for example, by decreasing the liquid–liquid interphase area.

Optimization of the reaction time

After optimizing the amounts of acetonitrile and acetone, the effect of reaction time on α-pinene conversion and the yield was evaluated. The results are presented in Fig. 3. Both the conversion and yield gradually increased with reaction time and

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Table 3 Effect of total reaction volume on the α-pinene conversion and epoxide yield[a]

Entry	$V_{acetonitrile}$ (mL)	$V_{acetone}$ (mL)	K_2CO_3 (mL)[b]	Conv. (%)[c]	Yield (%)[c]	Selectivity (%)[c]
1	15	10	12	98	96	98
2	7.5	5	6	87	86	98
3	5	3.3	3	72	69	95

[a] α-Pinene (1 ml, 6.2 mmol), reaction time (2 h), H_2O_2 (1.8 ml, 18 mmol), room temperature. [b] K_2CO_3 (1 M aqueous solution). [c] See the Characterization section for calculation.

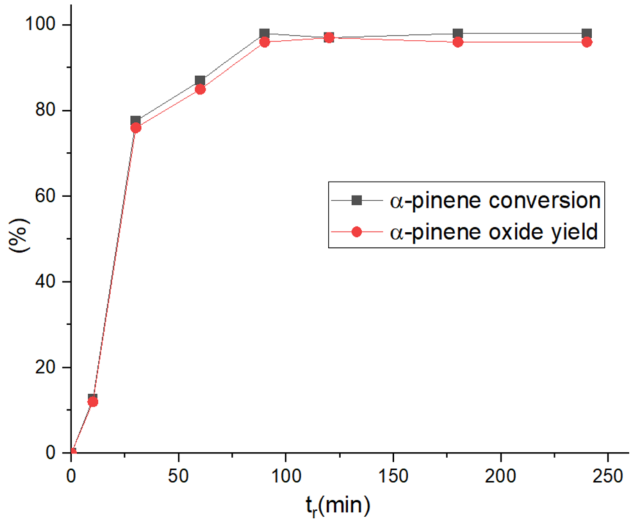


Fig. 3 Effect of reaction time on the α-pinene conversion and epoxide yield. Reaction conditions: acetonitrile (15 ml), acetone (10 ml), α-pinene (1 ml, 6.2 mmol), reaction time (2 h), H_2O_2 (1.8 ml, 18 mmol), K_2CO_3 (12 ml of 1 M solution), room temperature.

stabilized after approximately 90 minutes. The obtained α-pinene epoxide was stable in the reaction medium, and no decomposition was observed even when the reaction was extended to 4 hours. This shows that the reaction medium is chemically stable with respect to the epoxide formed. As shown in Fig. 3, the conversion of α-pinene to epoxide was very rapid, reaching nearly 80% within the first 30 minutes of reaction.

H_2O_2 concentration effect

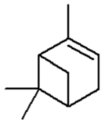
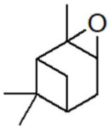
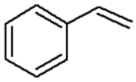
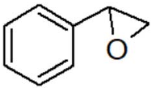
Table 4 shows the effect of hydrogen peroxide concentration on the conversion and epoxide yield. According to the results listed, it is observed that for the trisubstituted epoxide (alpha-pinene), a molar ratio of H_2O_2 to α-pinene of 3 was sufficient to achieve the total conversion and yield, whereas for styrene a ratio of 4 was required. This higher ratio is due to the greater nucleophilicity of the trisubstituted double bond in α-pinene compared to styrene.[24] Excess concentrations of H_2O_2 (3 for α-pinene and 6 for styrene) had no effect on the epoxides formed. The epoxides were obtained in a highly pure form, as shown in Fig. 4 and 5.

Effect of pH on the epoxidation reaction

The influence of pH on the epoxidation reaction was also evaluated based on the conversion to α-pinene and its epoxide yield. Potassium carbonate (K_2CO_3) was chosen to adjust the pH of the reaction medium. For this purpose, a series of 12 ml of aqueous K_2CO_3 solutions with different concentrations were prepared (column 2, Table 5). Each solution was used in a separate reaction under identical conditions, and the corresponding results are summarized in Table 5. The overall pH of the reaction mixture (pH_{whole}) was measured at the end of each experiment.

It can be observed that when the reaction was carried out without adding potassium carbonate, no epoxide was formed, indicating that α-pinene was not converted (entry 6). A sharp increase in both conversion and epoxide yield was observed as the aqueous concentration of K_2CO_3 increased, and nearly

Table 4 Effect of H_2O_2 concentration on the olefin conversion and yield[a]

Olefin	Epoxide	$n_{H_2O_2}/n_{Olefin}$	Conv. (%)	Yield (%)	Selectivity (%)	Entry
		2	71	70	99	1
		3	100	97	97	2
		4	100	97	97	3
		3	91	88	97	4
		4	100	97	98	5
		5	100	97	98	6

[a] Acetonitrile (15 ml), acetone (10 ml), olefin (1 ml, 6.2 mmol), reaction time (2 h), K_2CO_3 (12 ml of 1 M solution), room temperature.

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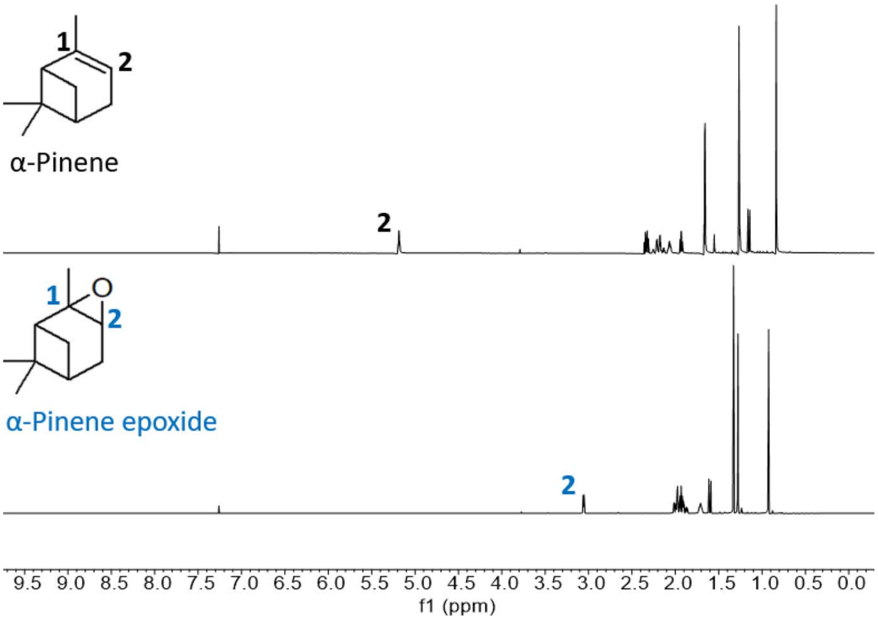

Fig. 4 Proton NMR spectrum of α-pinene and its corresponding epoxide.

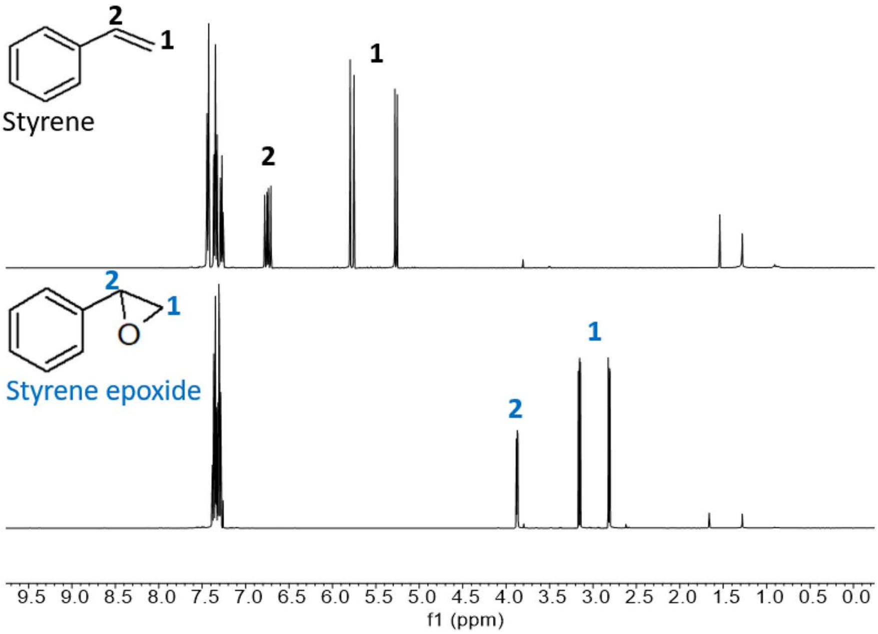

Fig. 5 Proton NMR spectrum of styrene and styrene epoxide obtained.

100% conversion and yield were achieved under strongly basic conditions, corresponding to a pH of 11.4 with a K_2CO_3 concentration of 1 M (entry 1).

The following explanation is based on the literature.[25–28] The positive effect of pH on α-pinene conversion and epoxide selectivity can be explained by the mechanism of peroxyimidic acid formation in the acetonitrile/H_2O_2 system. Under basic conditions, hydrogen peroxide is partially converted into the hydroperoxide anion (HOO^-), a more nucleophilic species that reacts readily with acetonitrile to form peroxyimidic acid, the active oxidant in Payne epoxidation. As the pH increases, the concentration of this oxidizing intermediate increases, leading to a higher epoxidation rate and thus greater α-pinene conversion *via* the dioxirane pathway. In addition, alkaline conditions suppress acid-catalyzed ring opening and rearrangement of α-pinene oxide, thereby improving epoxide selectivity. Consequently, both the conversion and selectivity increase markedly as the pH is increased from 6.0 to 11.4.

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Table 5 Influence of reaction pH on the α-pinene conversion and epoxide yield[a]

Entry	pH_{whole}	K_2CO_3 (M)[b]	Conv. (%)[c]	Yield (%)[c]	Selectivity (%)[c]	$Yield_{oxygen}$ (%)[c]
1	11.4	1	96	94	98	32
2	9.8	0.6	90	87	97	30
3	9	0.4	55	50	91	17
4	8	0.1	42	38	90	13
5	7.3	0.05	30	26	86	9
6	6	0	0	0	0	0

[a] Acetonitrile (15 ml), acetone (10 ml), α-pinene (1 ml, 6.2 mmol), reaction time (2 h), H_2O_2 (1.8 ml, 18 mmol), room temperature. [b] K_2CO_3 (12 ml of aqueous solution). [c] See the Characterisation section for calculation.

Comparison of different epoxidation techniques

To demonstrate the efficiency of the present epoxidation method employing dioxirane generated *in situ* from H_2O_2, with acetonitrile and acetone as co-catalysts, a comparative analysis was conducted against various reported epoxidation techniques, as summarized in Table 6. The comparison considers several key parameters, including the type of catalyst used, reaction temperature, reaction time, oxidant type and quantity, as well as the resulting conversion and epoxide selectivity.

Based on the conditions employed for the epoxidation of limonene and the corresponding results for conversion and epoxide selectivity, it can be observed that in most cases, achieving satisfactory performance often requires catalyst development, high temperatures and prolonged reaction times. In some cases, it is even necessary to use an oxidant such as *ter*-butyl hydroperoxide (TBHP), which is relatively expensive (entries 3–5). Under these conditions, both the conversion and yield tend to be lower, and in some cases, catalyst deactivation results in limited recyclability.

In contrast, the epoxidation technique presented in this work achieved complete substrate conversion and close to the maximum epoxide yield under ambient reaction conditions. The catalyst is indefinitely recyclable, the reaction time is three to twelve times shorter than the results reported in the literature and no waste is generated during the reaction. These advantages clearly demonstrate that this innovative method is more efficient and sustainable than previously reported ones.

Epoxidation of terpenes and other olefins

After systematically optimizing the reaction parameters for the epoxidation reaction by evaluating various factors such as the amount of acetonitrile and acetone, the concentration of potassium carbonate solution and the reaction time, a broad series of olefins, including terpenes, were epoxidized under these optimized conditions. The corresponding results are summarized in Table 7.

It can be observed that for all epoxidized olefins containing a single double bond, an H_2O_2/olefin molar ratio of 3 is more than sufficient to achieve nearly complete conversion and yield (entries 1, 2, 3, and 10). For olefins possessing two double bonds, doubling this molar ratio is necessary to reach full conversion and obtain higher yields (entries 4–6, 8, and 9). For the epoxidation of limonene, both monoepoxide and diepoxide products are formed, with yields of 60% and 38%, respectively (entry 4). In the case of β-myrcene, a terpene containing three double bonds (entry 9), only double epoxidation occurs, due to the conjugation of two of its double bonds. This observation is consistent with previously reported findings.[16,34] Some of the previously reported catalysts were able to epoxidize only one double bond of β-myrcene.[11,12,35] The epoxides produced at the end of the epoxidation reaction of all these olefins are almost pure, in contrast to those typically formed using most heterogeneous catalysts. In the case of epoxidation of corvone (entry 7), only the outer double bond was epoxidized. This is due to the presence of the ketone group, which forms a conjugated double bond with the endocyclic double bond, thereby preventing its epoxidation. This phenomenon was also been observed in previous studies.[36,37] For other olefins with two double bonds (entries 4–6, 8 and 9), double epoxidation is achieved by epoxidation of the endocyclic monoepoxide (Scheme 4), which is the first product formed during the reaction, due to the strong

Table 6 Comparison of different limonene epoxidation methods

Entry	Catalyst	T (°C)	t_r (h)	$\frac{n_{H_2O_2}}{n_{limonene}}$	Conv. (%)	Sel. (%)[a]	Ref.
1	CH_3CN–acetone	25	2	3	100	98	This work
2	Al_2O_3	80	10	5	92.2	80.4	5
3	Mo/Hf-MOF	70	24	TBHP	85	91	29
4	Mo-TUD-1	70	24	THBP	95	60	30
5	Ti-SBA-16	75	24	TBHP	80	79	31
6	$BW_{12}/Mo_{72}Fe_{30}$	75	6	3	89	58	32
7	W/SiO_2-Liq	90	6	2	55	56.4	33
8	$SiMo_{12}/Mo_{72}Fe_{30}$	75	6	3	92	46	32
9	W/SiO_2-Imp	90	6	2	68	63.2	33

[a] Monoepoxide and diepoxide of limonene.

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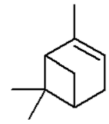
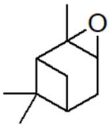
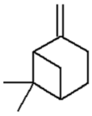
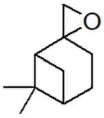
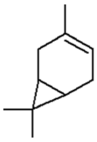
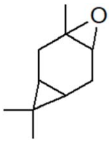
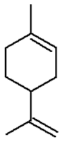
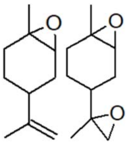
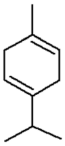
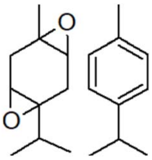
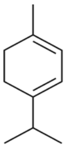
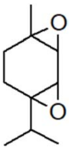
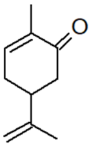
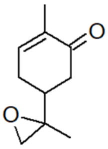
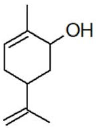
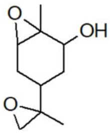
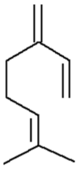
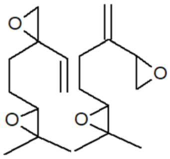
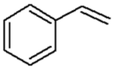
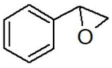
Table 7 Epoxidation of terpenes and other olefins under optimized conditions[a]

Entry	Olefin	Epoxide	$\frac{n_{H_2O_2}}{n_{\text{olefin}}}$[b]	Conv. (%)[b]	Yield (%)[c]	Selectivity (%)[c]	$\text{Yield}_{\text{oxygen}}$ (%)[c]
1			3	100	97	97	33
2			3	98	91	93	32
3			3	100	98	98	33
4			6	100	68/38[d]	98	
5			6	100	83/16[e]	83	28
6			6	100	85	85	29
7			3	100	97	97	33
8			6	100	96	96	33
9			6	100	100	100	33
10A			4	99	97	98	25
10B			3	91	88	97	33

[a] Acetonitrile (15 ml), acetone (10 ml), olefin (1 ml, 6.2 mmol), reaction time (2 h), K_2CO_3 (12 mL of 1 M solution), room temperature. [b] H_2O_2 (1.8 ml (18 mmol) for one double bond or 3.6 ml (36 mmol) for two or three double bonds). [c] See the Characterization section for calculation. [d] Diepoxide yield and *p*-cymene yield. [e] ^{1}H NMR analysis details are available in the SI.

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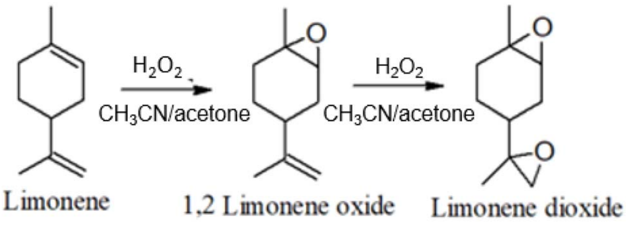
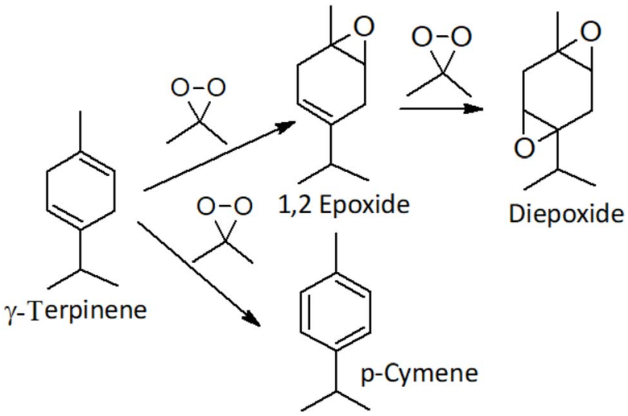


Scheme 4 Successive epoxidation of limonene to mono- and diepoxides.



Scheme 5 Products obtained by epoxidation of γ-terpinene (entry 5 of Table 7).

nucleophilicity of the double bond compared to the external one.[24] However, diepoxides cannot be formed without sufficient use of the oxidizing agent, which is hydrogen peroxide.

The exception is γ-terpinene (entry 5), which undergoes partial aromatization of its ring, resulting in the formation of *p*-cymene with a yield of 15% (Scheme 5). This side reaction has also been observed when performing epoxidation with dioxirane generated from oxone and following other epoxidation pathways.[16,38] Some studies have not confirmed this, but still show a relatively low yield of γ-terpinene epoxide compared to other epoxides; this could be related to the aromatization of the ring (yielding *p*-cymene).[7] Olefins other than terpenes such as styrene can also be efficiently epoxidized (entry 10), but a higher molar ratio was required, primarily due to the terminal and monosubstituted double bond.

Proposed reaction mechanism

As previously illustrated in Scheme 2, the epoxidation reaction proceeds through the formation of a reactive oxygen transfer species generated *in situ* from H_2O_2 in the presence of acetonitrile and acetone. Initially, acetonitrile activated H_2O_2 to form a peroxymidic acid intermediate, which subsequently oxidizes acetone to generate dioxirane. This dioxirane species is capable of transferring an oxygen atom to the olefinic substrate to yield the corresponding epoxide. During this process, acetone and acetonitrile are both regenerated, allowing the reaction to proceed catalytically without generating by-products. This synergistic sequence between the nitrile and ketone accounts for the high selectivity, complete conversion and environmentally benign nature of the epoxidation method.

Conclusion

This study reports the efficient epoxidation of terpenes and other olefins using dioxirane generated directly from H_2O_2 as the oxidant, highlighting the synergistic catalytic role of acetonitrile and acetone. The results demonstrate that the simultaneous presence of a nitrile and a ketone under strongly basic conditions (pH > 10) is essential for the reaction to proceed effectively. Acetone and acetonitrile recovery tests from the two phases obtained (both aqueous and organic) upon solvent extraction indicate that acetonitrile/acetone indeed act as homogeneous catalysts and are fully recovered after the reaction. After optimizing the reaction conditions, a broad range of olefins are successfully epoxidized with complete conversion and high yields under ambient conditions. All the reagents used in the reaction are of very low cost, readily available and can in principle be recycled indefinitely, while the process generated no waste.[7]

A comparative analysis with other reported epoxidation methods confirms that the proposed approach appears to be most relevant and effective in meeting the current industrial demand for epoxides. The sustainability and green aspect of this methodology are evidenced by the absence of toxic solvents, the use of recyclable acetone and acetonitrile as a pair of catalysts and the employment of hydrogen peroxide, an inexpensive, stable and environmentally benign oxidant widely used in industry. Moreover, the resulting epoxides are obtained in high purity and can be isolated simply by liquid–liquid extraction using diethyl ether, without the need for further purification.

Considering these advantages, the developed methodology represents a clean, economical and scalable process that aligns strongly with green chemical engineering principles and exhibits strong potential for industrial implementation.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

We declare that all data presented in the journal article are available upon request.

Supplementary information (SI): proton NMR spectra for most of the reagents studied in this work, both before and after the epoxidation reaction. After epoxidation, the protons adjacent to the epoxide groups appear at around 3 ppm. In contrast, before epoxidation, these protons adjacent to the double bonds are found beyond 4.5 ppm. See DOI: https://doi.org/10.1039/d6su00222f.

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