

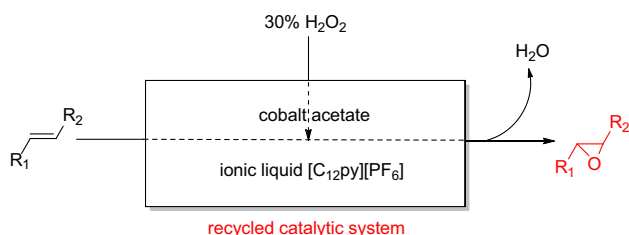
Efficient and convenient epoxidation of alkenes to epoxides with H_2O_2 catalyzed by $\text{Co}(\text{OAc})_2$ in ionic liquid $[\text{C}_{12}\text{py}][\text{PF}_6]$

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Abstract A simple, efficient, and eco-friendly procedure for the epoxidation of alkenes to epoxides with H_2O_2 catalyzed by $\text{Co}(\text{OAc})_2$ in ionic liquid $[\text{C}_{12}\text{py}][\text{PF}_6]$ has been developed. The reactions were carried out with alkene, $\text{Co}(\text{OAc})_2$ (0.1 mmol), $[\text{C}_{12}\text{py}][\text{PF}_6]$ (10 mL), and H_2O_2 (30 %, 11 mmol) at room temperature for 2–6 h. This atom-economical protocol affords the target products in good to high yields (88–98 %). The products can be separated by a simple extraction with organic solvent, and the catalytic system can be recycled and reused without loss of catalytic activity.

Graphical abstract A simple, efficient, and eco-friendly procedure for the epoxidation of alkenes to epoxides with H_2O_2 catalyzed by $\text{Co}(\text{OAc})_2$ in ionic liquid $[\text{C}_{12}\text{py}][\text{PF}_6]$ has been developed.



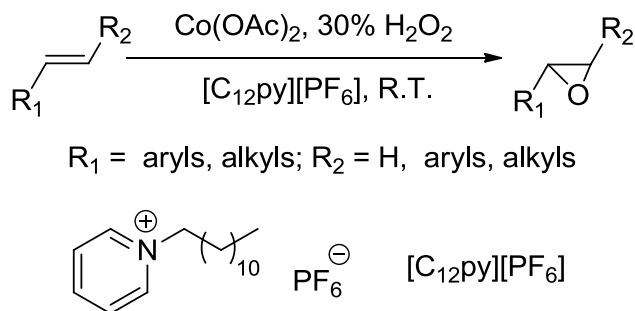
Keywords Epoxidation · Alkene · H_2O_2 · Cobalt acetate · Ionic liquid

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Introduction

Epoxides are important classes of chemicals used extensively for the preparation of a variety of fine or special chemicals such as natural products, drugs, polymer materials, etc., [1, 2]. Therefore, there has been tremendous interest in developing efficient methods for the synthesis of these molecules, and a well-known method constitutes the epoxidation of alkenes. Traditional methods for performing such a transformation generally involve the use of stoichiometric amount of the strongest oxidizing reagents (i.e., H_3PO_5 , peroxy acids, $\text{H}_2\text{WO}_4/\text{FAP}$, etc.) [3–5], and suffer from considerable drawbacks such as low yield, harsh or delicate reaction condition, and a large amount of waste by-products. Oxidation with NaClO [6, 7], PAA [8], TBHP [9, 10], PhIO [11, 12], NaIO_4 [13, 14], CHP [15], oxone [16–18], peracetic acid [19, 20], TADOOH [21], PPO [22], and other reagents [23–28] have also been developed for this conversion. However, these protocols are generally associated with one or more disadvantages, such as complex handling procedures, problematic side reactions, the use of expensive, toxic and moisture-sensitive reagents, long reaction times, low yields, and environmental concerns associated with the use of poorly manageable catalysts. Hydrogen peroxide (H_2O_2) is an economical, environmentally friendly and atom-efficient oxidant which leads to only water after the reaction [29]. This reagent has, however, high activation energy, making catalysis necessary [30], and a number of catalytic oxidation processes based upon the combination of transition metals or organocatalysts and H_2O_2 have been developed for such a conversion [31–37]. However, most of the procedures still suffered from the use of expensive reagents, difficulties in work-up, long reaction times, environmental hazards, waste control, etc. Consequently, search for new and environmentally benign synthetic methodologies



Scheme 1 Catalytic epoxidation of alkenes to epoxides

for epoxidation of alkenes that address these drawbacks remains to be of value and interest.

Ionic liquids (ILs) have attracted considerable attention during the past few years due, in some cases, to their favorable properties such as very low vapor pressure, wide liquid temperature range, good ionic conductivity, excellent electrochemical properties, and strong ability to dissolve many chemicals [38, 39]. Therefore, ILs have recently gained recognition of scholars from various fields such as chemical synthesis [40], analytical and separation science [41], electrochemistry [42], biocatalytic transformations [43], and catalysis [44, 45]. In continuation of our interest in exploring green oxidation reactions in ionic liquids, we report herein a new, efficient and environmentally friendly protocol for the epoxidation of alkenes to epoxides with H_2O_2 catalyzed by cobalt acetate ($Co(OAc)_2$) in ionic liquid *N*-dodecylpyridinium hexafluorophosphate ($[C_{12}py][PF_6]$) under mild conditions (Scheme 1). Furthermore, we demonstrate that the catalytic system can be recycled and reused without any significant loss of catalytic activity.

Experimental

Apparatus and reagents

All the chemicals were from commercial sources without any pretreatment. All reagents were of analytical grade. The ionic liquids were synthesized according to the literature procedure [39]. 1H NMR spectra and ^{13}C NMR spectra were recorded on a Bruker 500-MHz spectrometer using $DMSO-d_6$ as the solvent with tetramethylsilane (TMS) as an internal standard. GC analyses were performed on a Shimadzu-14B gas chromatography equipped with HP-1 capillary column (30 m, 0.25 mm, 0.25 μ m). Elemental analysis was performed on a Vario EL III instrument (Elementar Analysesensy Teme GmbH, Germany).

General procedure for epoxidation reactions

For a typical experiment, alkene (10 mmol), $Co(OAc)_2$ (1 mmol), and an aqueous solution of H_2O_2 (30 %, 11 mmol) were sequentially added to 10 mL of $[C_{12}py][PF_6]$. The obtained mixture was stirred vigorously at room temperature for the appropriate time (Table 2), the reaction progress was monitored by GC. Upon completion of the reaction, cyclohexane was used to extract the organic compounds (3×10 mL). The cyclohexane solution was washed with water (3×10 mL), and then dried over anhydrous Na_2SO_4 . The solvent was removed and the residue was distilled under vacuum to give the desired pure product. The rest of the ionic liquid and the catalyst were recovered by decantation of water produced in the reaction and concentration under vacuum. Fresh substrates were then recharged to the recovered catalytic system and then recycled under identical reaction conditions. The target substrates were characterized by NMR and Elemental analysis or compared with their authentic samples. Spectroscopic data for selected products are as follows.

2-Phenyloxirane (Table 2, entry 1)

Yield: 92 %; colorless oil; bp 193–195 °C/760 mm (Ref. [46] 192–194 °C/760 mm).

2-Ethyl-3-phenyloxirane (Table 2, entry 2)

Yield: 95 %; colorless oil; 1H NMR (500 MHz, $DMSO-d_6$): δ = 0.97 (t, 3H, CH_3), 1.54 (m, 2H, CH_2), 2.85 (m, 1H, CH), 3.78 (d, 1H, CH), 7.39–7.46 (m, 5H, Ar-H) ppm; ^{13}C NMR (500 MHz, $DMSO-d_6$): δ = 12.4, 23.1, 56.2, 62.7, 126.3, 127.8, 128.9, 137.6 ppm; anal. calcd for $C_{10}H_{12}O$: C, 81.01; H, 8.14; O, 10.77. Found: C, 81.04; H, 8.16; O, 10.80.

2-(*O*-Tolyl)oxirane (Table 2, entry 3)

Yield: 94 %; colorless oil; 1H NMR (500 MHz, $DMSO-d_6$): δ = 2.47 (s, 3H, CH_3), 2.83 (m, 2H, CH_2), 3.79 (m, 1H, CH), 7.23–7.41 (m, 4H, Ar-H) ppm; ^{13}C NMR (500 MHz, $DMSO-d_6$): δ = 18.5, 51.7, 54.3, 123.4, 124.9, 125.8, 128.4, 134.1, 138.7 ppm; anal. calcd for $C_9H_{10}O$: C, 80.53; H, 7.48; O, 11.89. Found: C, 80.56; H, 7.51; O, 11.92.

2-(2,4-Dimethylphenyl)oxirane (Table 2, entry 4)

Yield: 97 %; colorless oil; 1H NMR (500 MHz, $DMSO-d_6$): δ = 2.31 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 2.86 (m, 2H, CH_2), 3.81 (m, 1H, CH), 7.03–7.14 (m, 3H, Ar-H) ppm;

^{13}C NMR (500 MHz, DMSO- d_6): $\delta = 18.7, 22.6, 51.9, 54.1, 124.3, 125.5, 131.2, 132.8, 134.6, 139.5$ ppm; anal. calcd for $\text{C}_{10}\text{H}_{12}\text{O}$: C, 81.02; H, 8.14; O, 10.76. Found: C, 81.04; H, 8.16; O, 10.80.

2-(4-Methoxyphenyl)oxirane (Table 2, entry 5)

Yield: 98 %; colorless oil; ^1H NMR (500 MHz, DMSO- d_6): $\delta = 2.79$ (m, 2H, CH_2), 3.82 (m, 1H, CH), 3.89 (s, 3H, CH_3), 7.05 (m, 2H, Ar-H), 7.21 (m, 2H, Ar-H) ppm; ^{13}C NMR (500 MHz, DMSO- d_6): $\delta = 51.3, 54.5, 56.4, 117.4, 125.9, 131.6, 158.7$ ppm; anal. calcd for $\text{C}_9\text{H}_{10}\text{O}_2$: C, 71.95; H, 6.69; O, 21.28. Found: C, 71.98; H, 6.71; O, 21.31.

1,4-Di(oxiran-2-yl)benzene (Table 2, entry 6)

Yield: 96 %; colorless oil; ^1H NMR (500 MHz, DMSO- d_6): $\delta = 2.76$ (m, 2H, CH_2), 3.85 (m, 1H, CH), 7.24 (s, 4H, Ar-H) ppm; ^{13}C NMR (500 MHz, DMSO- d_6): $\delta = 50.7, 54.1, 124.5, 137.2$ ppm; anal. calcd for $\text{C}_{10}\text{H}_{10}\text{O}_2$: C, 74.02; H, 6.18; O, 19.71. Found: C, 74.06; H, 6.21; O, 19.73.

2-(4-Nitrophenyl)oxirane (Table 2, entry 7)

Yield: 90%; light yellow solid; ^1H NMR (500 MHz, DMSO- d_6): $\delta = 2.91$ (m, 2H, CH_2), 3.95 (m, 1H, CH), 7.68 (m, 2H, Ar-H), 8.13 (m, 2H, Ar-H) ppm; ^{13}C NMR (500 MHz, DMSO- d_6): $\delta = 51.7, 55.3, 56.4, 125.2, 126.8, 143.4, 149.2$ ppm; anal. calcd for $\text{C}_8\text{H}_7\text{NO}_3$: C, 58.13; H, 4.25; N, 8.46; O, 29.04. Found: C, 58.18; H, 4.27; N, 8.48; O, 29.06.

1-(2-(Oxiran-2-yl)phenyl)ethanone (Table 2, entry 8)

Yield: 88 %; colorless oil; ^1H NMR (500 MHz, DMSO- d_6): $\delta = 2.56$ (s, 3H, CH_3), 2.87 (m, 2H, CH_2), 3.89 (m, 1H, CH), 7.43–7.58 (m, 3H, Ar-H), 7.93 (m, 1H, Ar-H) ppm; ^{13}C NMR (500 MHz, DMSO- d_6): $\delta = 30.5, 52.1, 54.5, 123.7, 126.8, 129.3, 131.6, 134.2, 139.5, 200.7$ ppm; anal. calcd for $\text{C}_{10}\text{H}_{10}\text{O}_2$: C, 74.05; H, 6.18; O, 19.71. Found: C, 74.06; H, 6.21; O, 19.73.

2-Benzyloxirane (Table 2, entry 9)

Yield: 95 %; colorless oil; ^1H NMR (500 MHz, DMSO- d_6): $\delta = 2.51$ (m, 2H, CH_2), 2.63 (m, 2H, CH_2), 3.05 (m, 1H, CH), 7.25–7.43 (m, 5H, Ar-H) ppm; ^{13}C NMR (500 MHz, DMSO- d_6): $\delta = 40.3, 47.2, 55.7, 125.4, 127.8, 128.6, 137.7$ ppm; anal. calcd for $\text{C}_9\text{H}_{10}\text{O}$: C, 80.53; H, 7.48; O, 11.90. Found: C, 80.56; H, 7.51; O, 11.92.

(3-Propyloxiran-2-yl)methanol (Table 2, entry 10)

Yield: 97 %; colorless oil; ^1H NMR (500 MHz, DMSO- d_6): $\delta = 0.94$ (t, 3H, CH_3), 1.35–1.46 (m, 4H, CH_2CH_2), 2.54 (m, 1H, CH), 2.67 (m, 1H, CH), 3.62 (m, 2H, CH_2), 3.85 (brs, 1H, OH) ppm; ^{13}C NMR (500 MHz, DMSO- d_6): $\delta = 14.5, 21.4, 34.6, 54.9, 61.5, 65.2$ ppm; anal. calcd for $\text{C}_6\text{H}_{12}\text{O}_2$: C, 62.02; H, 10.36; O, 27.53. Found: C, 62.04; H, 10.41; O, 27.55.

7-Oxabicyclo[4.1.0]heptane (Table 2, entry 11)

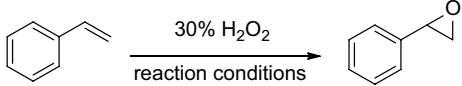
Yield: 98 %; colorless oil; bp 129–131 °C/760 mm (Ref. [46]) 128–130 °C/760 mm).

2-Isobutyloxirane (Table 2, entry 12)

Yield: 96 %; colorless oil; ^1H NMR (500 MHz, DMSO- d_6): $\delta = 0.93$ (dd, 3H, CH_3), 1.37 (t, 2H, CH_2), 1.69 (m, 1H, CH), 2.47 (m, 2H, CH_2), 2.62 (m, 1H, CH) ppm; ^{13}C NMR (500 MHz, DMSO- d_6): $\delta = 21.7, 25.6, 43.2, 49.5, 54.8$ ppm; anal. calcd for $\text{C}_6\text{H}_{12}\text{O}$: C, 71.92; H, 12.06; O, 15.95. Found: C, 71.95; H, 12.08; O, 15.97.

Results and discussion

The initial study was carried out using phenylethylene as the substrate to optimize the reaction conditions, and the results are summarized in Table 1. Initial reaction screening led to disappointing results in the absence of catalyst and ionic liquid, the reaction proceeded very slowly, and the yield was only 12 % after 24 h (Table 1, entry 1). The results mean that the oxidant H_2O_2 alone does not work effectively in the reaction. The effects of different ionic liquids, such as $[\text{C}_4\text{py}][\text{PF}_6]$, $[\text{C}_6\text{py}][\text{PF}_6]$, $[\text{C}_8\text{py}][\text{PF}_6]$, $[\text{C}_{10}\text{py}][\text{PF}_6]$, $[\text{C}_{12}\text{py}][\text{PF}_6]$, $[\text{C}_{12}\text{py}][\text{BF}_4]$, $[\text{C}_{12}\text{py}][\text{OTf}]$, and $[\text{C}_{12}\text{py}]\text{Br}$, were tested with $\text{Co}(\text{OAc})_2$ as catalyst in the reaction (Table 1, entries 2–9), it was observed that $[\text{C}_{12}\text{py}][\text{PF}_6]$ demonstrated the best performance (Table 1, entry 6). The different effects of ILs in the reaction may be attributed to their different characteristics of melting points. A review of the literature [47] shows that the kind of anion and the symmetry of cation are the two important factors giving the melting points, which would influence the different abilities of stabilizing and dissolving the oxidant H_2O_2 and the catalyst. Under the same conditions, the IL which stabilizes and dissolves them more easily will lead to a larger increase in the effective reactant concentration, which increases the encounter probabilities between the substrate and reactive

Table 1 Optimization of the conditions for epoxidation of phenylethylene with H₂O₂


Entry ^a	Ionic liquid	Catalyst	Time (h)	Yield (%) ^b
1	–	–	24	12
2	[C ₄ py][PF ₆]	Co(OAc) ₂	6	77
3	[C ₆ py][PF ₆]	Co(OAc) ₂	3	81
4	[C ₈ py][PF ₆]	Co(OAc) ₂	3	87
5	[C ₁₀ py][PF ₆]	Co(OAc) ₂	3	90
6	[C ₁₂ py][PF ₆]	Co(OAc) ₂	3	92
7	[C ₁₂ py][BF ₄]	Co(OAc) ₂	3	86
8	[C ₁₂ py][OTf]	Co(OAc) ₂	3	75
9	[C ₁₂ py]Br	Co(OAc) ₂	3	85
10	–	Co(OAc) ₂	8	71
11	[C ₁₂ py][PF ₆]	–	8	67
12	[C ₁₂ py][PF ₆]	WO ₃	8	75
13	[C ₁₂ py][PF ₆]	Fe(OAc) ₃	3	84
14	[C ₁₂ py][PF ₆]	Cu(OAc) ₂	6	71
15	[C ₁₂ py][PF ₆]	Mn(OAc) ₂	3	81
16	[C ₁₂ py][PF ₆]	FeBr ₃	3	79

^a The reactions were carried out with phenylethylene (10 mmol), catalyst (1 mmol), IL (10 mL), and H₂O₂ (30 %, 11 mmol) at room temperature

^b Isolated yield

species, and so the higher rate or yield of the reaction is observed. For a blank test (Table 1, entry 10), a lower yield of the product was obtained when the same reaction condition was used in the absence of ionic liquid. In addition, the catalyst is crucial for this reaction, and its lack leads to a much lower yield (Table 1, entry 11). Besides Co(OAc)₂, we also tried to use other types of catalysts in this model reaction (Table 1, entries 12–16), and the results showed that Co(OAc)₂ demonstrated the best performance in terms of yield and reaction rate. Therefore, the combination of H₂O₂, Co(OAc)₂ and [C₁₂py][PF₆] was chosen as the optimal conditions for further exploration.

In addition, the catalytic system could be typically recovered and reused for subsequent reactions with no appreciable decrease in yields and reaction rates (Fig. 1). The recycling process involved the removal of the product from the catalytic system, by a simple extraction with organic solvent. Fresh substrates were then recharged to the aqueous layer of catalytic system and the mixture was heated to react once again.

With these results in hand, we subjected other alkenes to the epoxidation reactions, and the results are listed in Table 2. It is clear that various types of aryl and alkyl alkenes can be successfully epoxidized to the corresponding

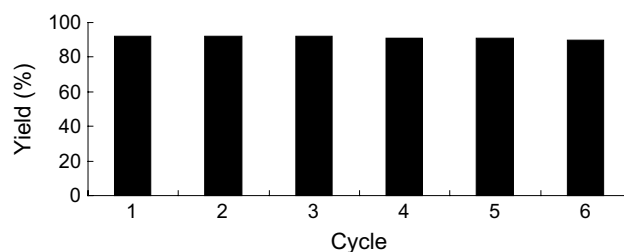


Fig. 1 Repeating reactions using recovered catalytic system. The reactions were carried out with phenylethylene (10 mmol), recovered catalytic system ([C₁₂py][PF₆], Co(OAc)₂), in the presence of H₂O₂ (30 %, 11 mmol) at room temperature for 3 h

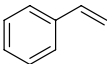

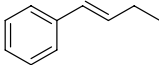
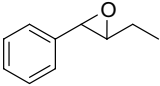
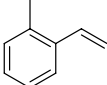

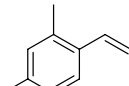
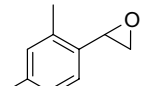
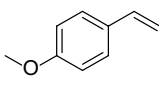
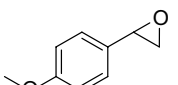
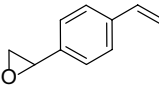
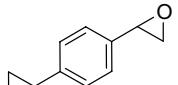
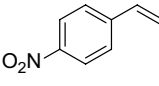
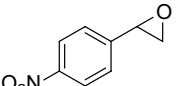
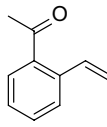
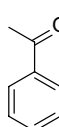
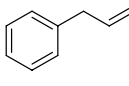
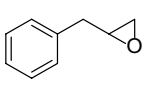
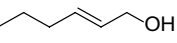
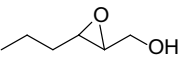


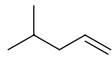
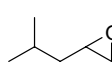
epoxides in good to high yields (Table 2, entries 1–12). Various functionalities such as alkyl, alkoxy, acetyl and nitro groups can tolerate the reaction. Surprisingly, the epoxidation of alkyl alkenes (Table 2, entries 10–12) to the corresponding epoxides is faster and more efficient than aryl alkenes (Table 2, entries 1–9). In addition, it was also observed that the electronic nature of the substituents on the aromatic ring has some impact on the reaction rate. Substrates with electron-withdrawing substituents (Table 2, entries 7 and 8) are less reactive than those with electron-donating substituents (Table 2, entries 3–6), and a decrease in the isolated yield or reaction rate.

The excellent results of the catalytic system suggest the epoxidation reaction has a particular reaction mechanism. According to the literatures [48, 49] and the observations in our reactions, taking the epoxidation of phenylethylene with H₂O₂ as an example, a possible mechanism is proposed (Scheme 2). In the reaction, the catalyst Co(OAc)₂ provides a source of Co(II) (1), which reacts with the oxidant H₂O₂ to form Co(III) = O (2). Then, 2 reacts with the substrate to form transition state 3. 3 then very rapidly affords Co(II) to yield the desired product. The Co(II) is then re-oxidized to Co(III) = O by H₂O₂ to complete the catalytic cycle. It looks like that the formation of 3 from 2 is the rate-determining step.

Conclusion

In conclusion, we have demonstrated an efficient and convenient epoxidation of alkenes to epoxides using H₂O₂/Co(OAc)₂ catalytic system in the ionic liquid [C₁₂py][PF₆]. A wide range of aryl and alkyl alkenes were found to be applicable to the catalytic system. Mild reaction conditions, simplicity of operation, high yields, stability, easy isolation of products, and excellent recyclability of the catalytic system are the attractive features of this methodology. The scope, definition of the mechanism and synthetic

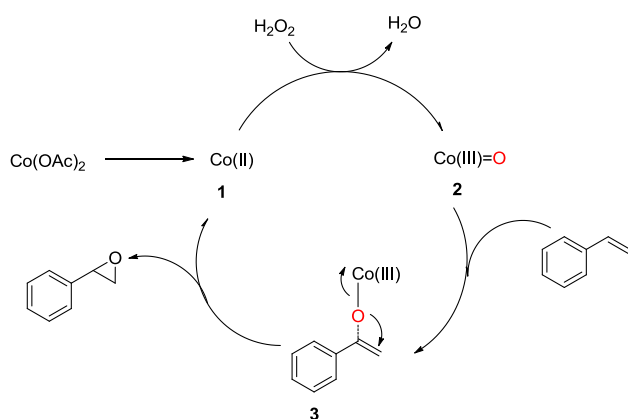
Table 2 Catalytic epoxidation of alkenes to epoxides

Entry ^a	Substrate	Product	Time / h	Yield / % ^b
1			3	92
2			3	95
3			3	94
4			3	97
5			3	98
6			3	96
7			6	90 ^c
8			6	88 ^c
9			3	95
10			2	97
11			2	98
12			2	96

^a Unless otherwise noted, the reactions were carried out with alkene (10 mmol), Co(OAc)₂ (1 mmol), [C₁₂py][PF₆] (10 mL), and H₂O₂ (30 %, 11 mmol) at room temperature

^b Isolated yield

^c The reaction was carried out at 50 °C



Scheme 2 Possible mechanism for the epoxidation of phenylethylene

application of this reaction are currently under study in our laboratory.

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