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Metal Catalyzed Oxidation Reactions of Alkenes Using Eco-Friendly Oxidants

Jay Soni, Pankaj Teli, Nusrat Sahiba, Ayushi Sethiya and Shikha Agarwal

Abstract

Oxidation of alkenes is an important reaction in academia, industry and science as it is used to develop epoxides, carbonyls, allylic compounds, 1,2-diols, etc. Metal catalyzed oxidation of alkenes has aroused as a significant tool in modern organic synthesis. Several techniques are available; however some of them suffer from few shortcomings viz. high cost, toxic nature, harsh reaction condition, solid waste generation, etc. In view of these drawbacks, green oxidants i.e. O_2 , H_2O_2 , TBHP, etc. have shown noteworthy prospects due to their nature, low cost, high atom economy and high sustainability in metal catalyzed reactions. This chapter highlights the metal catalyzed green oxidation of alkenes and shall provide new strategies for the functionalization and transformation of alkenes.

Keywords: Oxidation, alkenes, green oxidants, metal based catalysts, organic synthesis

1. Introduction

The carbon–carbon (C-C) bond is the fundamental unit of valuable organic molecules and possesses significant and diversified applications in nature. Alkenes are the copious portion of organic compounds that are produced abundantly from renewable resources and petrochemical feedstocks [1]. The unique reactivity profile of alkenes is responsible for the diversification and modification in the skeleton that makes them essential in organic synthesis. As a consequence, they have been implemented as starting materials in the synthesis of a wide range of organic chemical building blocks. Various types of molecules such as ethers, halo-ether, alcohol, diol, alkane, and halo compounds have been produced from alkenes via different chemical transformations like addition, substitution, oxidation, polymerization and so on.

Oxidation of alkenes is recognized as a powerful and straightforward tool for the construction of carbon–oxygen (C-O) bonds to develop epoxides, carbonyls, 1,2-diols, and allylic compounds, etc [2–4]. During the past decades, researchers paid much attention on this subject and several methodologies have been proposed to achieve the selective oxidation of alkenes. Several strong oxidizing agents like OsO_4 , RuO_4 , $NaIO_4$, CrO_2Cl_2 are used in stoichiometric amount for this purpose [5–9]. These protocols suffer from one or more drawbacks like expensive and toxic reagents, waste generation, low yields, harsh reaction conditions and many more.

The designing of mild, straightforward, and environmentally friendly methods of alkene oxidation has attracted continuous interest in organic chemistry. Because of these drawbacks, green oxidants i.e. O_2 , H_2O_2 , TBHP, and, even air have been used as green oxidants for sustainable and eco-friendly synthesis [10–15]. Recently, metal-catalyzed oxidation of alkenes has aroused as an important tool in modern organic synthesis [16–18]. Metal organic frameworks (MOFs) have porous and heterogeneous nature and are applied for the efficient catalytic synthesis in various reactions like condensations reactions, coupling reactions, Friedel–Crafts reactions, oxidations and so on [19–22]. Since this pioneering process was developed, the field has grown considerably and a range of metal-catalyzed oxidation reactions are routinely used in synthetic chemistry laboratories all over the world. In past years, scientists utilized various metals such as Pd, Mn, Mo, Se, Fe, etc. for the effective oxidation of alkenes [23–28]. The aforementioned results showed that new protocols and mechanisms of these transformations have been developed in past decades. The present chapter systematically summarizes the metal catalyzed green oxidation of alkenes and shall provide new strategies for the functionalization and transformation of alkenes along with their advantages and disadvantages.

2. Metal catalyzed oxidation of alkene

2.1 Copper catalyzed

An easy and practical strategy has been developed for the synthesis of allylic esters by the allylic oxidation of cyclic alkenes with several carboxylic acids in the presence of tert-butyl hydroperoxide as an oxidant and copper–aluminum mixed oxide as a catalyst (**Figure 1**) [29].

A copper(I)-catalyzed oxidation of alkenes into α -oxygenated ketones was introduced using molecular oxygen and N-hydroxyphthalimide (NHPI) or N-hydroxybenzotriazole (HOBt) at room temperature (**Figure 2**). The oxidation proceeded via radical forming process and the molecular oxygen got incorporated into the product, ketone [30]. The reaction worked well for both enynes and styrenes.

An effective strategy for esterification of unactivated C-H bonds (allylic and non-benzylic) of hydrocarbons using $CuBr_2$ with different carboxylic acids was developed by Zhou et al. Selectfluor (electrophilic fluorinating agent) was used as an oxidant for the reaction. The products were obtained in 17–80% yields via cross dehydrogenative coupling (**Figure 3**) [31].

The allylic oxidation of cyclohexene was catalyzed by copper–bisoxazoline employing copper complexes $Cu(MeCN)_4PF_6$, $(CuOTf)_2 \cdot PhH$, and $Cu(OTf)_2$ in acetonitrile or acetone as the solvents to obtain benzoic esters. Tert-butyl peroxybenzoate was used as an oxidant. The products were obtained in high yields with enantiomeric excess (<68% ee) (**Figure 4**) [32].

A study has been performed for the effect of acid and base on the oxidation of alkenes using palladium catalyst and O_2 as a sole oxidant in water as a solvent. The dihydroxylation occurred upon the oxidation in the presence of base while in the acidic medium, aldehydes and ketones were obtained by oxidative cleavage (**Figure 5**) [33].

A bis(sulfoxide) palladium catalyst (White catalyst) was applied to promote an intramolecular oxidative allylic cyclization to form biologically relevant tetracyclic flavonoids in the presence of benzoquinone as an oxidant (**Figure 6**) [34]. The reaction mechanism involved C-H activation and C-O bond formation. Both electron withdrawing and electron donating substituents provided products in high yields.

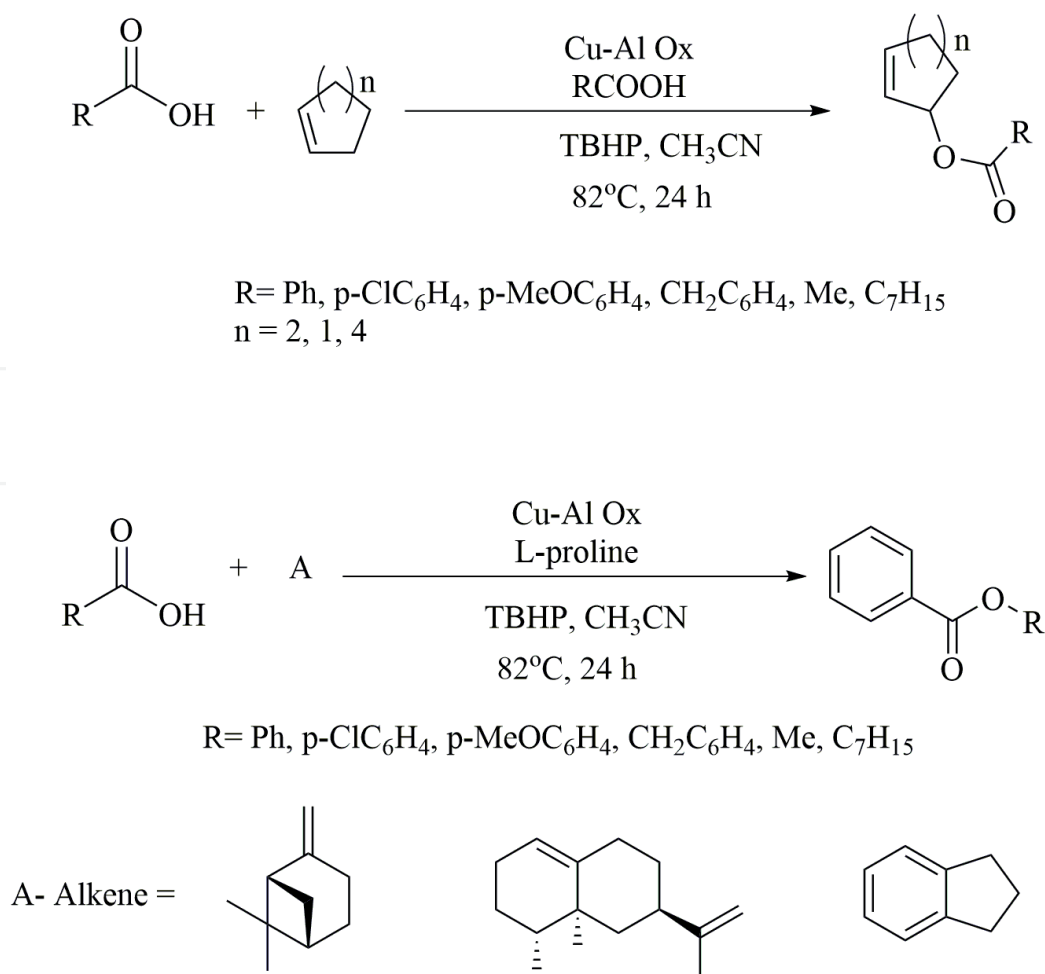


Figure 1.
Allylic oxidation of alkenes catalyzed by copper–aluminum mixed oxide

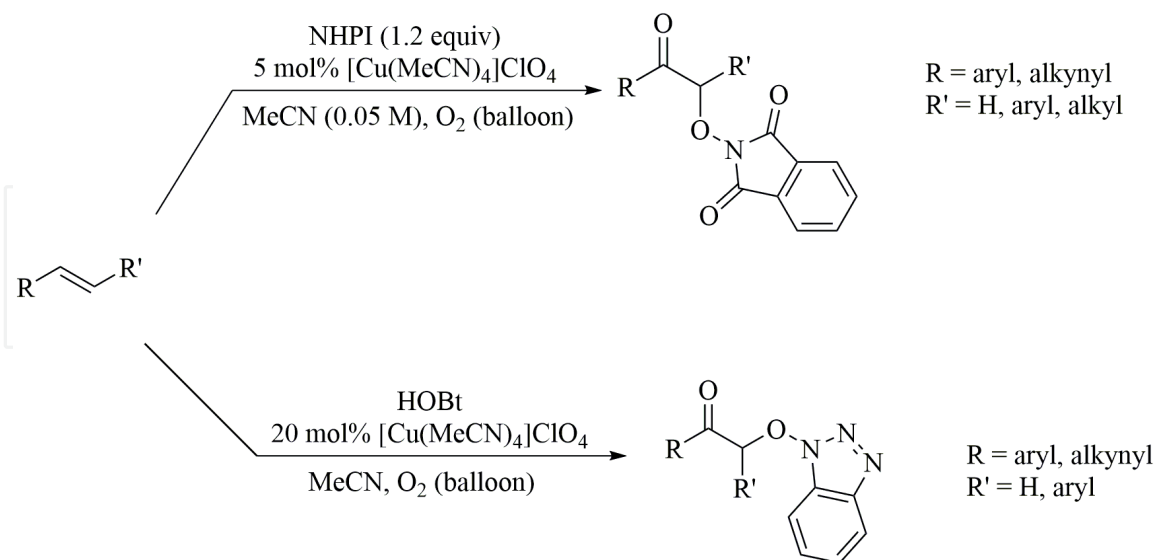


Figure 2.
Copper catalyzed oxidation of alkenes

Numerous catalytic systems have been developed for the selective formation of either linear or branched allylic oxidation products. The linear-selective allylic oxidation of alkenes was done via thioether ligand (**Figure 7, method a**). Furthermore, the scope of the reaction was similar to the method given firstly, by White. The reaction time was found slightly lesser in this method [35].

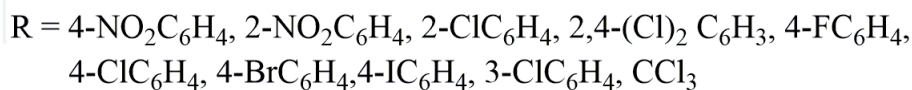
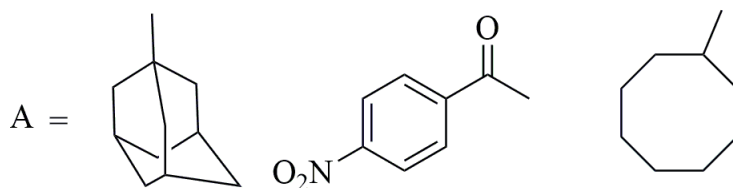
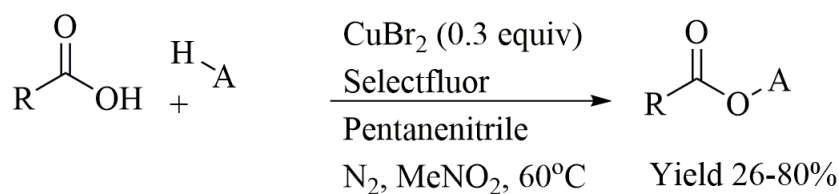


Figure 3.
Oxidation of cyclohexene using selectfluor

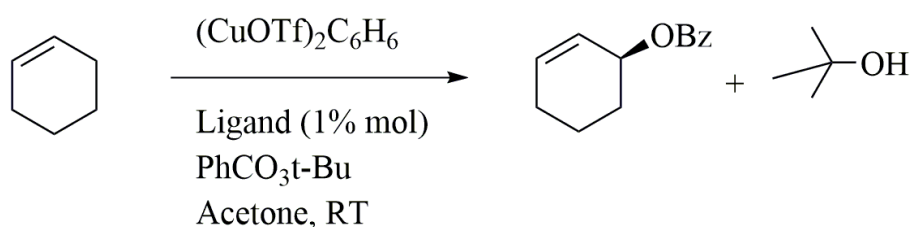


Figure 4.
Allylic oxidation of cyclohexene using (CuOTf)₂C₆H₆ palladium-catalyzed

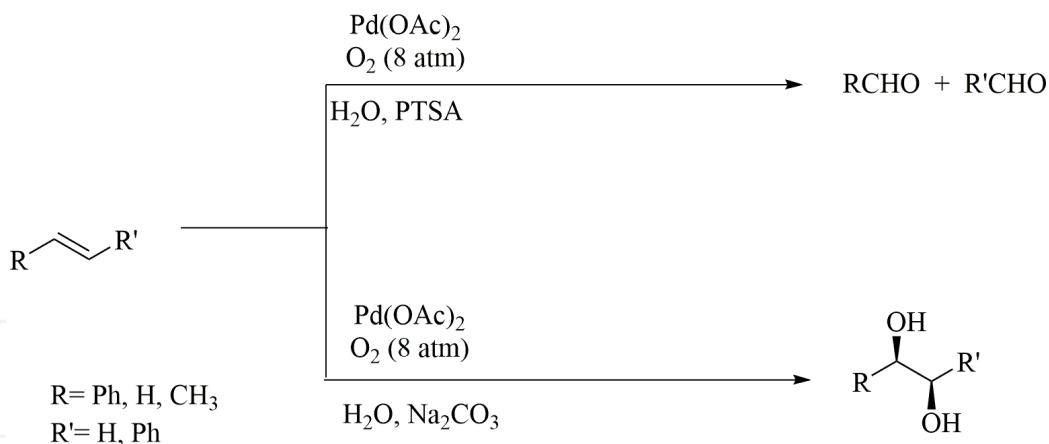


Figure 5.
Palladium-catalyzed direct oxidation of alkenes with molecular oxygen

The simple and inexpensive method was used for the synthesis of tetrahydrothiophenes which was highly active and linear-selective ligand using palladium-sulfide as catalyst (**Figure 7, method b**) [36].

The palladium-sulfide catalytic system was developed to achieve aerobic turn-over with 4,5-diazafluorenone ligand (**Figure 7, method c**). This system proved to be highly selective for linear allylic acetates with good yields and functional group tolerance [37].

Water, as a nucleophile was used in the allylic oxidation of alkenes to allylic alcohols using palladium chloride as a catalyst. Water and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was used as a co-oxidant in the reaction (**Figure 8**) [38].

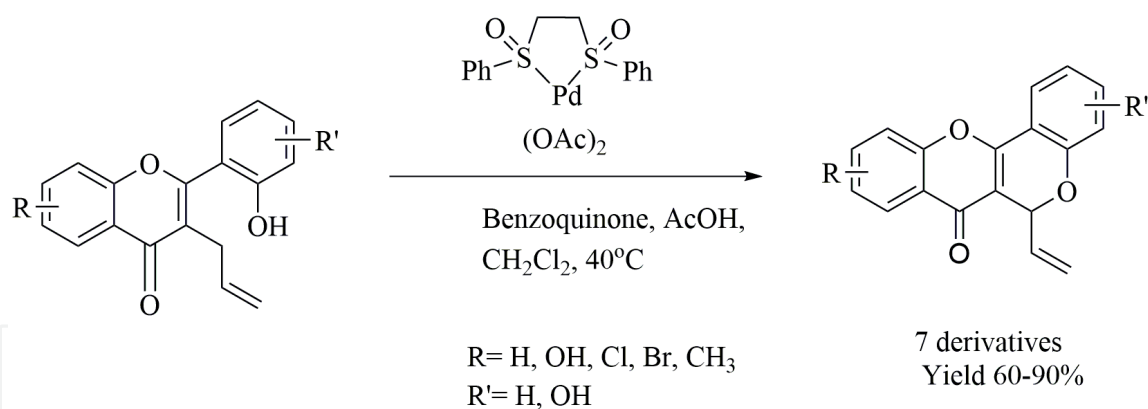


Figure 6.
 Synthesis of tetracyclic flavonoids by intramolecular oxidation allylic cyclization

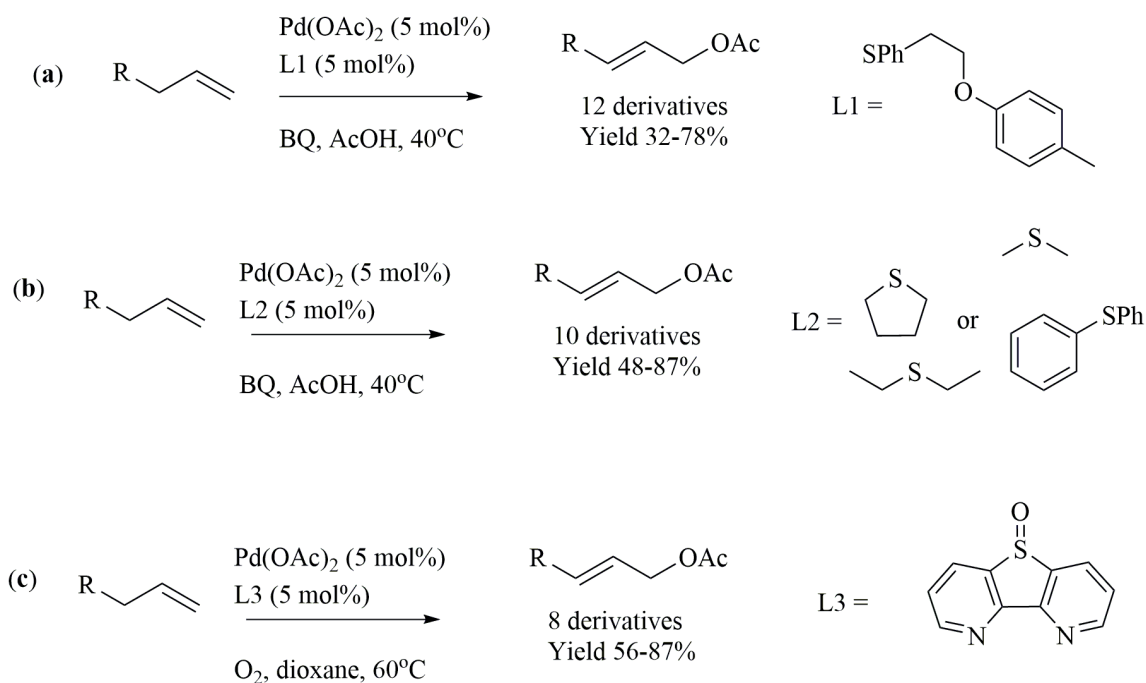
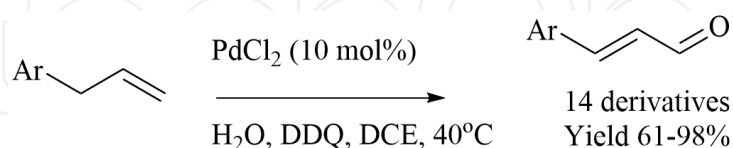


Figure 7.
 Catalyst system for liner-selective allylic oxidation.

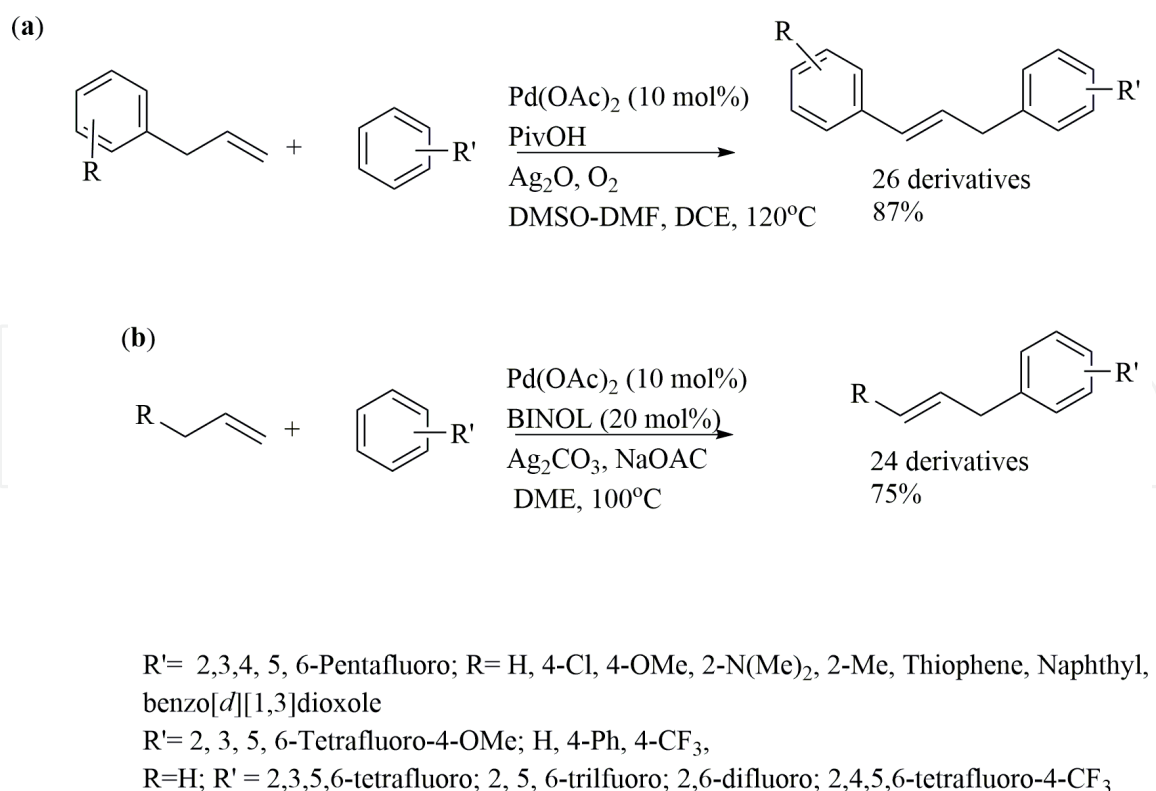


$\text{Ar} = \text{Ph, p-Me, p-Et, p-OMe, p-(t-Bu), 3,5 Methyl, o-Me}$

Figure 8.
 Synthesis of alkenyl aldehydes by allylic oxidation with water.

The obtained products were readily oxidized to (E)-alkenyl aldehydes in excellent yields using a second eq. of DDQ.

The allylic oxidation of alkenes with polyfluorobenzenes as nucleophiles was performed. The dehydrogenative coupling was achieved in the presence of silver additives to give the corresponding linear functionalised products in good yields (**Figure 9**) [39].

**Figure 9.**

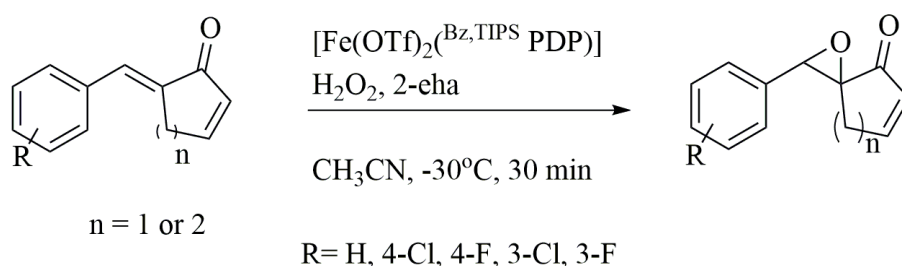
Allylic arylation with polyfluorobenzenes in the presence of silver additives.

The oxidation of unactivated alkenes resulted in a mixture of desired allylic arenes and Heck type products. A wide range of polyhalogenated nucleophiles was exemplified.

2.2 Iron catalyzed

Various iron catalysts were designed and employed for the oxidation of dienones using hydrogen peroxide as an oxidant and ethylhexanoic acid as an additive, necessary for controlling activation of the H₂O₂ at -30°C for 30 min. To optimize the reaction conditions, various solvents were examined like water, acetonitrile, THF, DMF, and toluene. Acetonitrile with 1–3 mol% of catalyst gave the best results for the reaction (**Figure 10**) [40].

A bifunctional iron nanocomposite catalyst was prepared and doped with N and P and employed for the direct oxidation of alkenes into ketones or 1,2-diketones *via* formation of an epoxide intermediate in the presence of TBHP as an oxidant in aqueous condition at mild temperature (**Figure 11**) [41].

**Figure 10.**

Oxidation of alkene using $[Fe(OTf)_2(Bz,TIPS PDP)]$.

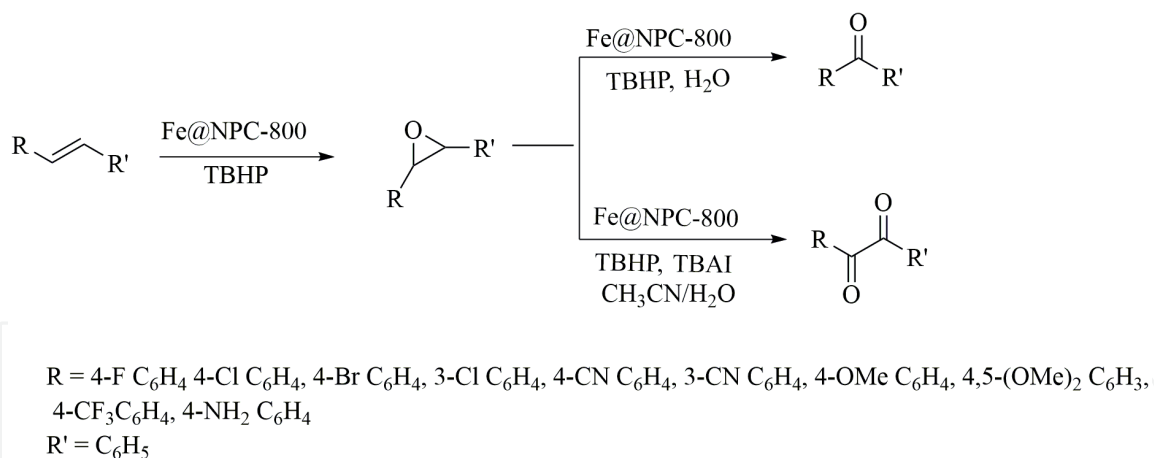


Figure 11.
 Oxidation of alkenes by bifunctional iron nanocomposite catalyst.

2.3 Ruthenium catalyzed

A convenient and effective method was developed for the oxidation of alkenes into α -diketones using ruthenium complex as a catalyst and TBHP as an oxidant. This pathway has several advantages like no requirement of additional ligands, highly functional group tolerance, mild reaction conditions and short reaction time (**Figure 12**) [42].

2.4 Chromium-catalyzed

Mesoporous chromium terephthalate MIL-101 was employed as a heterogeneous catalyst for the selective allylic oxidation of various alkenes in the presence of tert-butyl hydroperoxide as an oxidizing agent and provided α,β -unsaturated ketones. The catalyst MIL-101 was stable to chromium leaching and separated easily through the filtration and reused up to several cycles without any loss of catalytic activity [43].

The catalytic activities of Fe-MIL-101 and Cr-MIL-101 metal-organic frameworks were studied for the solvent-free oxidation of cyclohexene and α -pinene in the presence of molecular oxygen. Both catalysts were found effective for alkene oxidation at moderate temperature (40–60°C) and yielded allylic oxidation products. The Cr-MIL-101 afforded predominantly α,β -unsaturated ketones while Fe-MIL-101 produced mainly 2-cyclohexene-1-ol at 40°C after allylic oxidation of alkenes (**Figure 13**) [44].

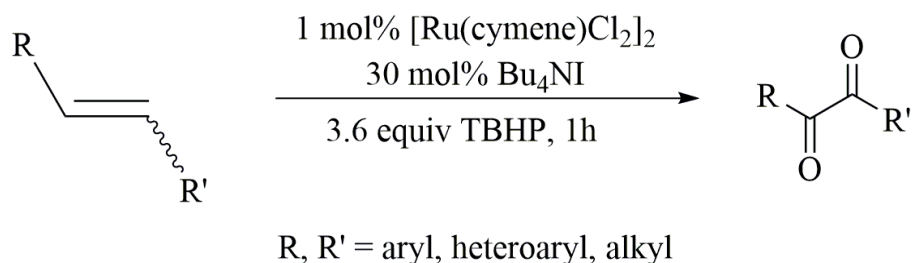


Figure 12.
 Ruthenium-catalyzed oxidation of alkenes at room temperature

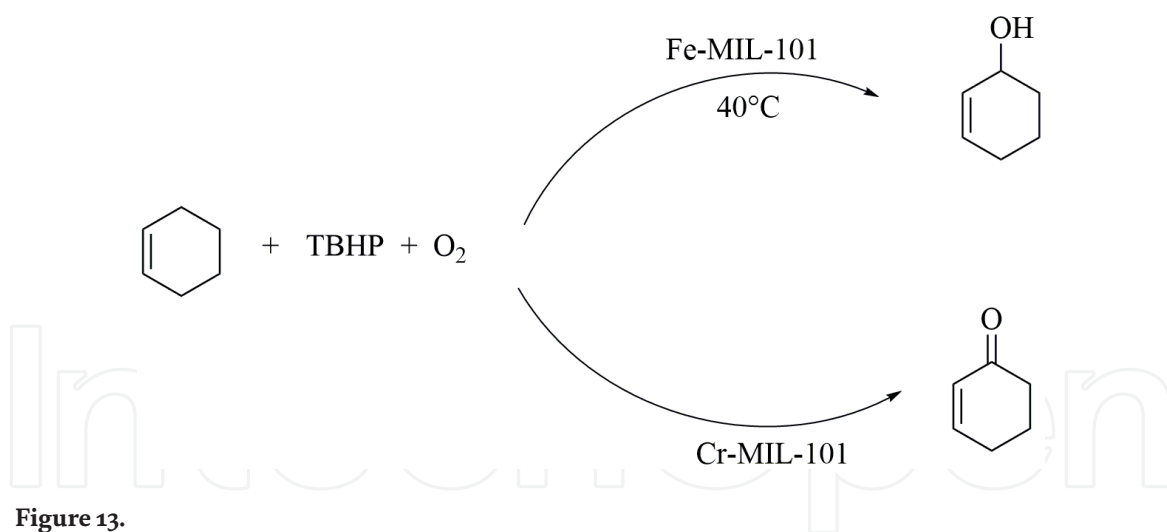


Figure 13.
Oxidation of alkenes using Fe-MIL-101 and Cr-MIL-101

2.5 Nickel catalyzed

An efficient pathway was explored for the synthesis of cyclic sulfamides through the selective oxidation of alkenes catalyzed by NiCl₂ or [Ni(acac)₂] in the mixture of DMF and sodium acetate at 40°C in inert conditions (**Figure 14**) [45].

2.6 Selenium catalyzed

Selenium can be used as a dopant to increase the surface area and total mesoporous volume of polymeric carbon nitride through its sublimation during the process of calcination. Shi and coworkers synthesized Se-doped polymeric carbon nitride (Se/PCN) from the calcination of melamine with Se powder and used it as a catalyst for the oxidation of β ionones in the presence of visible light (**Figure 15**) [46]. In place of H₂O₂ reagent, the authors employed water as the oxidant precursor that could produce the H₂O₂ oxidant via PCN-catalyzed photolysis of water [47, 48]. Catalyzed by doped Se, β -ionone could be oxidized into epoxide in moderate yield. The use of visible light as sustainable energy to drive the reaction is the advantage of the method.

Recently, selenium based catalysts were applied for the oxidation reactions under relatively mild conditions. The authors employed H₂O₂ as the green oxidant and the transition metal-free conditions avoided the metal residues in the product. Different from the reported selenium catalyzed oxidation reactions using diaryl diselenide or aryl selenic acid catalyst, 5 mol% of dialkyl diselenide, such as (PhCH₂Se)₂, (n-C₄H₉Se)₂, or (c-C₆H₁₁Se)₂ was used as the pre-catalyst, converting the alkene substrates into the related carbonyls in 30–74% yields in EtOH at 80–120°C (**Figure 16**) [49].

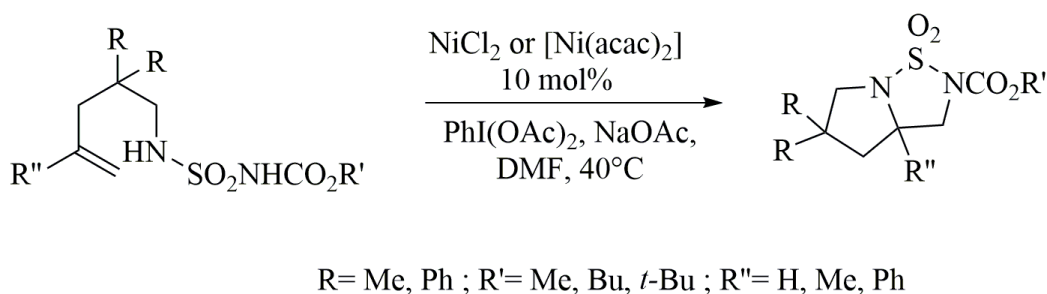


Figure 14.
Nickel catalyzed oxidation of alkenes

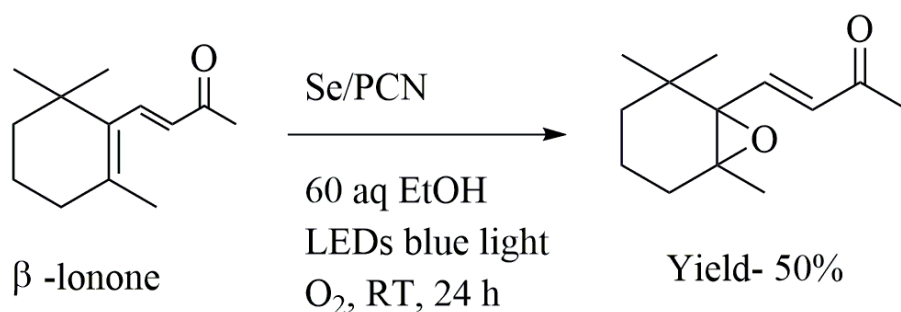


Figure 15.
Oxidation of β -ionone in the presence of Se/PCN

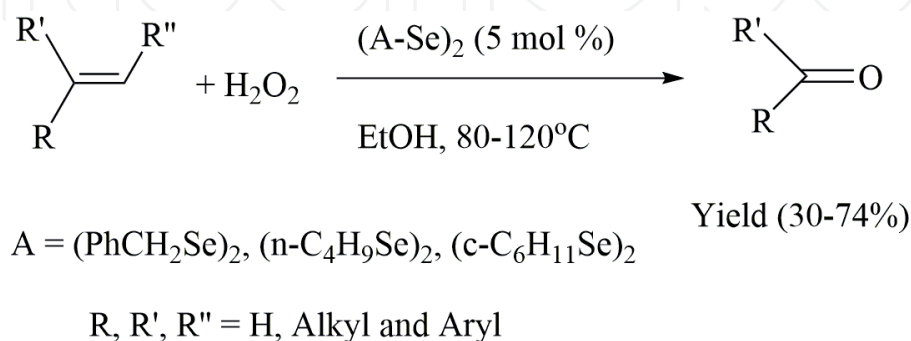
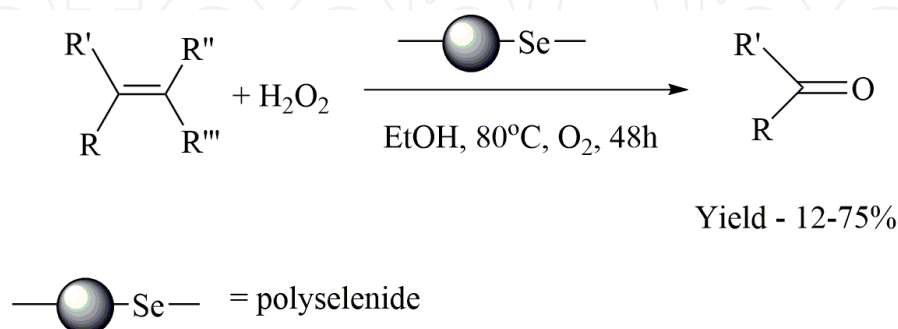


Figure 16.
Oxidation of alkene in the presence (RSe)₂ with H₂O₂

Selenization of dihalohydrocarbon with NaHSe (prepared via reduction of Se powder with NaBH₄ in situ) afforded polyselenide in just one step and it was found to be an efficient catalyst for alkene oxidative cracking reactions under mild conditions (**Figure 17**) [50].

The selenization of Fe₂O₃ afforded another convenient access to heterogeneous Se catalyst [51]. The developed method may be used at the industrial scale due to cheap and abundant nature of the support Fe₂O₃. The reaction mechanism involved attack of HSe⁻ anion on the iron positive centre of Fe = O and uploading of Se to produce Se/Fe₂O₃. It efficiently catalyzed the oxidative of alkenes in dimethyl



R = Ph, 2-ClC₆H₄, 4-ClC₆H₄, 3-ClC₆H₄, 2-MeC₆H₄, 3-MeC₆H₄, 4-MeC₆H₄
 R' = Ph, Me
 R'' = H, Me, CO₂Me, Ph
 R''' = H

Figure 17.
Oxidation of alkenes using polyselenide as a highly efficient catalyst

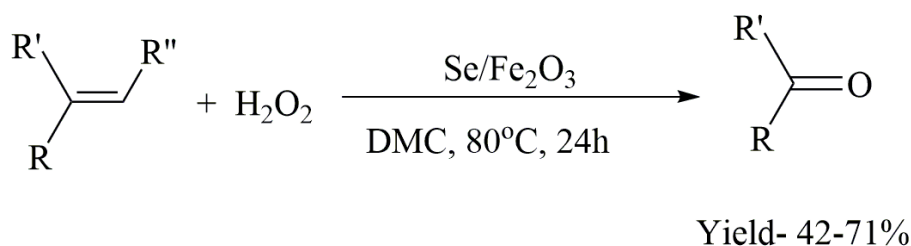


Figure 18.
Oxidation of alkenes in the presence of Se/Fe₂O₃

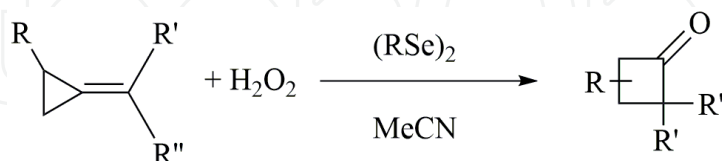


Figure 19.
Se-catalyzed oxidation of methylenecyclopropanes

carbonate (DMC) under mild reaction conditions (**Figure 18**). The synergistic effect of Se with Fe in the material, Se/Fe₂O₃ enhanced its catalytic activity [52].

The Se-catalyzed oxidation of methylenecyclopropanes (MCPs) generated oxidative ring expansion products, cyclobutanones instead of epoxides (**Figure 19**). This reaction may afford a direct access to cyclobutanone intermediates. The driving force for the conversion is the high ring strain of MCPs [53].

3. Metal based nano-particle catalyzed oxidation of alkenes

An eco-benign pathway was developed for the oxidation of alkenes to ketones using water as an oxidant and catalyst combination of dearomatized acridine-based PNP-Ru complex and indium(III) triflate. The present protocol showed good functional group tolerance. The pathway was highly advantageous over Wacker-type oxidation as no chemical oxidant was used and only hydrogen gas was liberated as the byproduct (**Figure 20**) [54].

A variety of mesoporous nanocomposites comprising of zirconium oxide and Keggin 12-phosphomolybdic acid compounds (ZrO₂-PMA) was synthesized through the application of evaporation-induced cooperative assembly method and were employed as an efficient catalyst for the oxidation of alkenes in the presence of hydrogen peroxide as an oxidant. ZrO₂ impregnated with nearly 37 wt% PMA exhibited significant activity for the oxidation of alkenes (**Figure 21**) [55].

Cobalt ferrite magnetic nanoparticles (CoFe₂O₄ NPs) were used as effective catalysts for the selective oxidation of alkenes into related aldehydes or epoxides in the presence of t-BuOOH as an oxidant and 1, 2-dichloroethane as a solvent. The catalyst was easily separated from the reaction medium using a magnet, and reused up to five consecutive cycles without any loss of activity (**Figure 22**) [56].

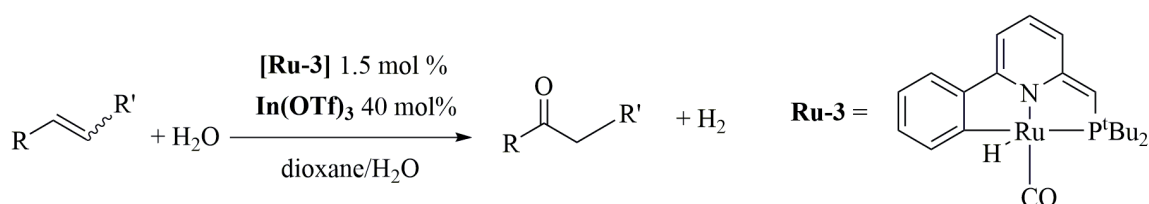


Figure 20.
Oxidation of alkenes by water

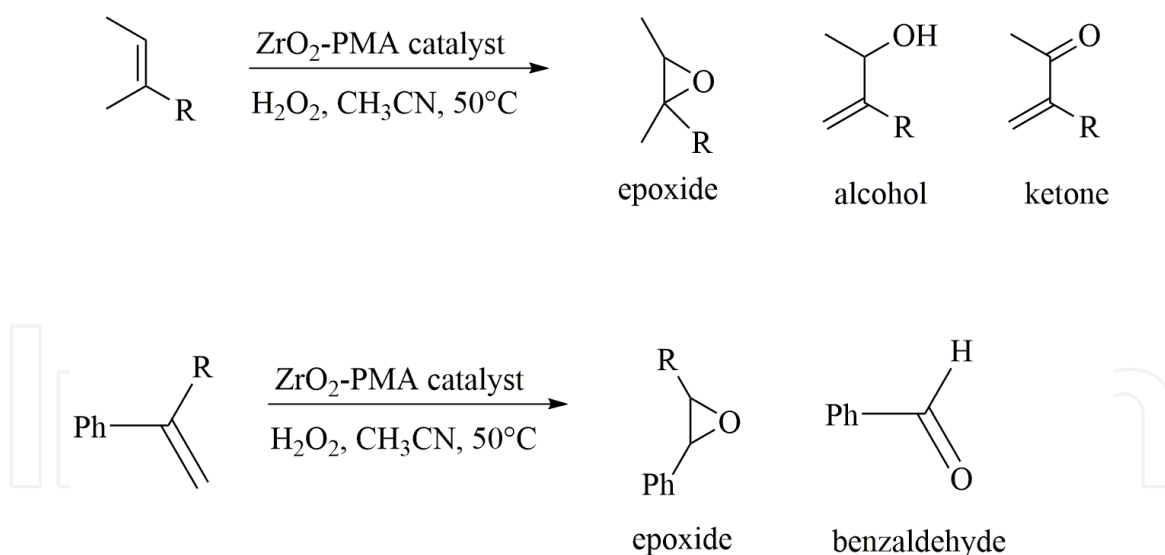


Figure 21.
Oxidation of alkenes by mesoporous zirconia-polyoxometalate nanocomposite materials

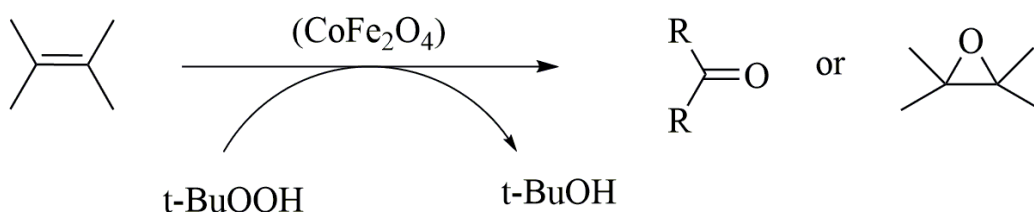


Figure 22.
Magnetic cobalt ferrite NPs as an efficient catalyst for oxidation of alkenes

A green method was developed for the oxidation of alkenes using chiral dicationic bisguanidinium in the presence of potassium permanganate at 60°C for 12–36 h. (**Figure 23**) [57].

An eco-friendly and highly efficient protocol was developed for the epoxidation of alkenes with m-chloroperbenzoic acid in the presence of $\text{Fe}_3\text{O}_4/\text{SiO}_2$ as a heterogeneous catalyst in DCM as solvent at mild reaction conditions in 4 h at RT. In addition, the prepared heterogeneous catalyst has some advantages such as easy preparation, reusability, handling and recovery, long-term stability as well as excellent yields (90–97%) in shorter reaction time (**Figure 24**) [58].

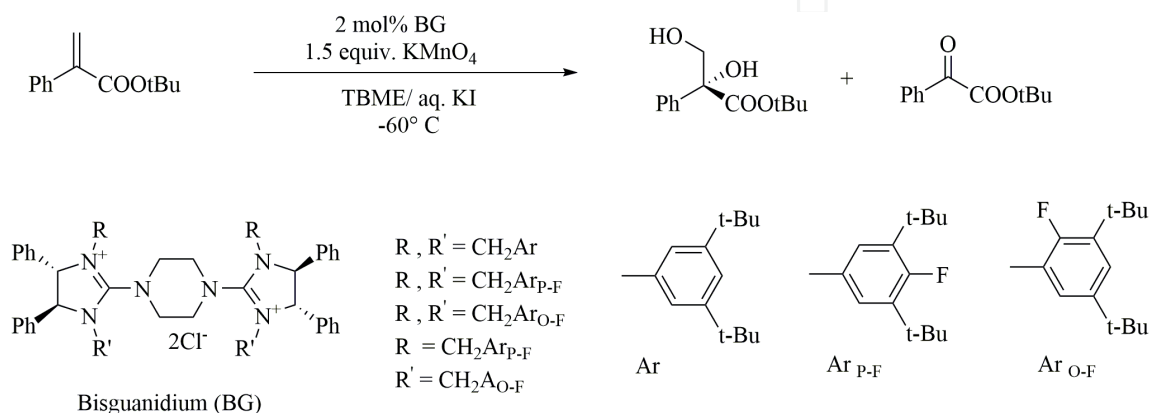


Figure 23.
Enantioselective oxidation of alkenes with potassium permanganate catalyzed by chiral Dicationic Bisguanidinium

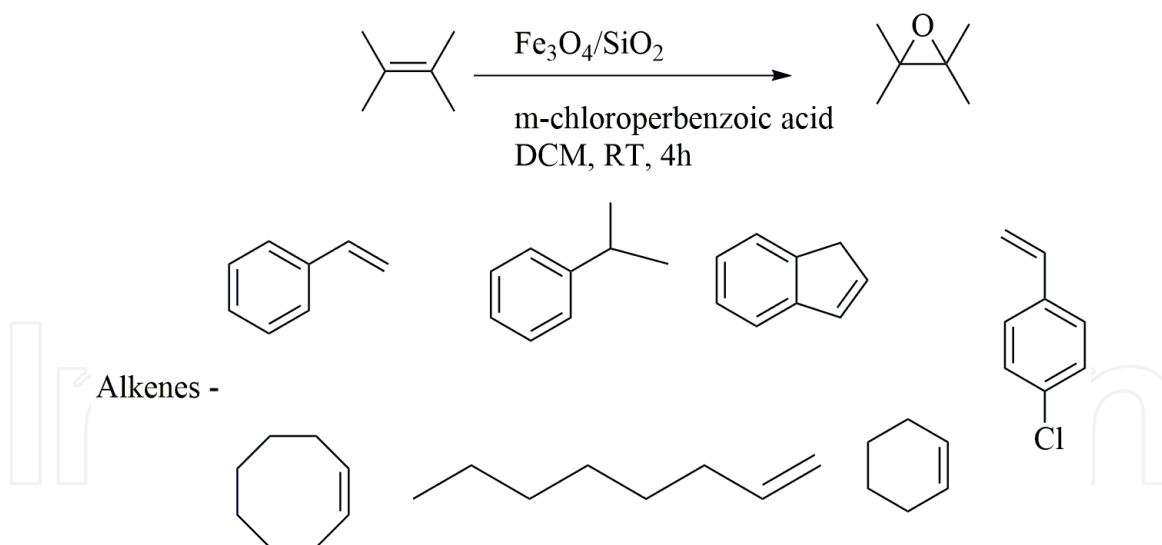


Figure 24.
Oxidation of alkenes in the presence of $\text{Fe}_3\text{O}_4/\text{SiO}_2$

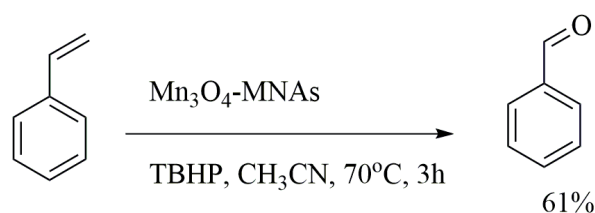


Figure 25.
Oxidation of styrene in the presence of Mn_3O_4 -MNAs with TBHP

Oxidation of styrene was done in the presence of mesoporous Mn_3O_4 nanoparticle (0.04 mmol) as catalyst and tert butyl hydroperoxide as mild oxidant with CH_3CN at 70°C for 3 h. Novel, simple, and high yield (67–91%) of products are the advantages of Mn_3O_4 -MNAs. The catalyst was recycled and reused up to five runs without a significant diminution in the catalytic efficiency (**Figure 25**) [59].

4. Applications

In this section, several cases were found that employed the copper-catalyzed allylic oxidation of olefins as an important step in the syntheses of synthetic products and pharmaceuticals. Some of the examples were exemplified by Nakamura and Nakada in their review on allylic oxidation reactions for the synthesis of natural products [60].

In 2009, Hayashi et al. produced the enantioselective synthesis of an O-protected 2-deoxystreptamine precursor, an amino-glycoside antibiotic, the same copper-catalyzed asymmetric desymmetrization procedure for the preparation of a chiral intermediate in the total synthesis of (–)-oseltamivir phosphate [61, 62].

The synthesis of steroids is one field where copper-catalyzed allylic oxidation has been more successful. The relatively inert steroid framework usually yielded the corresponding enone instead of an allylic alcohol. These types of phytosterol could have vivid applications in the field of medicine owing to their ability of modulating mitochondrial activity and their anti-inflammatory properties. Several examples of Kharasch–Sosnovsky reactions for the synthesis of steroids are available in the literature [63].

Barbacenic acid, a novel bisnorditerpene isolated from *Barbacenia flava*, was synthesized by a highly stereocontrolled route. The authors reported the allylic

oxidation on the silyl ether intermediate using TBHP in the presence of CuBr in benzene at 45°C under mild reaction conditions in 60% yield [64]. Moreover, oxidized alkenes were used in the synthesis of fine chemicals [65], arene reduction [66], and water repellency [67].

5. Conclusion

This chapter summarizes the recent strategies of the oxidation of alkenes *via* metal-based catalytic system. Various innovations have been implemented from time to time to increase the efficiency and sustainability of the protocols. This literature study demonstrated the potential of metal-based catalysts and nano-particle metal based catalysts in the oxidation of alkenes to produce different chemical entities such as carbonyl, 1,2-diol and allylic compounds. However, some challenges like low commercial applicability, less efficiency, low chemoselectivity control, over-oxidation, lack of knowledge and deeper understanding of mechanistic pathways are still present in this field. In this context, the improvement in industrially viability, efficiency and sustainability of synthetic pathways require innovation in both capability and strategy. The knowledge gained for the oxidation of alkenes from these studies along with their pros and cons will continue to enable advances in this area, which in turn shall lead to the advancement of new approaches.

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Conflict of interest


The authors declare no conflict of interest.

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