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Oxidation of Alcohols - A Mini Review

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Abstract: The oxidation of alcohols is a fundamental and widely employed transformation in organic chemistry. Over time, numerous oxidizing reagents have been developed to address the limitations of existing methods and to facilitate complex or selective oxidation reactions. This review provides a comprehensive overview of the development of various oxidizing agents used for alcohol oxidation. Additionally, the preparation, advantages, and limitations of these reagents are discussed, highlighting their applicability in modern synthetic chemistry.

Key words: Alcohol; Oxidation.

1 Introduction

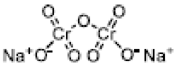
Alcohol oxidation is one of the most fundamental and widely utilized transformations in organic synthesis, playing a crucial role in the preparation of various carbonyl compounds. This selective oxidation process enables the synthesis of aldehydes, ketones, and carboxylic acids, depending on the type of alcohol and the reagents employed [1,2]. Both metal-based and nonmetal-based oxidizing agents have been extensively reported in the literature for the oxidation of primary, secondary, and tertiary alcohols, each offering distinct advantages in terms of selectivity and efficiency. Primary alcohols typically oxidize to aldehydes, which can undergo further oxidation to carboxylic acids. Secondary alcohols are commonly converted into ketones in a selective and straightforward manner. Tertiary alcohols, however, are generally resistant to oxidation due to the absence of an α-hydrogen, which is essential for the oxidation process. Nonetheless, tertiary diols, such as 1,2-diols, can undergo oxidation via an alternative mechanism, often leading to carbonyl compounds through carbon-carbon bond cleavage. This versatility in alcohol oxidation has made it an indispensable tool in both academic research and industrial applications.

This review offers a systematic overview of recent advances in alcohol oxidation, encompassing traditional metal-based reagents, emerging metal-free and catalytic systems, as well as electrochemical oxidation methods. By comparing their efficiency, selectivity, and sustainability, it provides valuable insights into the evolution of oxidation methodologies from conventional stoichiometric reagents to greener and more economical catalytic processes. Furthermore, it highlights the practical significance of these oxidation reactions in both industrial and academic research, enabling chemists to choose suitable strategies based on substrate type and desired functionality. Overall, this review seeks to bridge the gap between classical oxidation chemistry and modern sustainable approaches, underscoring the growing importance of environmentally friendly oxidation technologies in contemporary organic synthesis. A comprehensive summary of representative metal-based, nonmetal-based, and electrochemi-

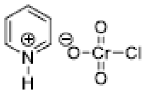
Chart 1

A. Metal-Based Oxidizing Agents

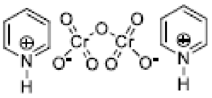
i. Chromium-based reagents



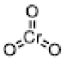
Sodium dichromate



Pyridinium chlorochromate

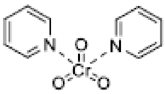


Pyridinium dichromate



, aq. H_2SO_4, Acetone

Jones reagent



Collins reagent ($CrO_3 \cdot 2Py$)

ii. Manganese-based reagents

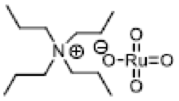
Potassium permanganate

$O=Mn=O$

Manganese dioxide (MnO_2)

Barium manganate $Ba(MnO_4)_2$

iii. Ruthenium-based reagent



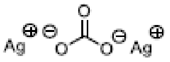
Tetrapropylammonium perruthenate

iv. Cerium-based reagent

$(NH_4)_2[Ce(NO_3)_6]$

Ceric ammonium nitrate

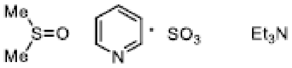
v. Argentum-based reagent



Fetizon's reagent

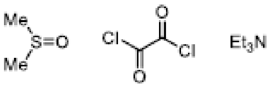
B. Nonmetal-Based Oxidizing Agents

i. Sulphur-based reagents

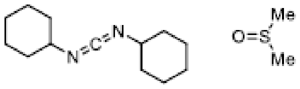


Parikh–Doering reagent

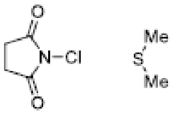
Albright–Goldman reagent



Swern reagent

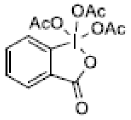


Pfitzner–Moffatt reagent

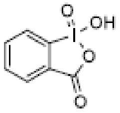


Corey Kim Reagent

ii. Hypervalent iodine reagents

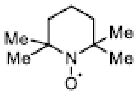


Dess–Martin periodinane (DMP)



2-Iodoxybenzoic acid (IBX)

iii. Nitroxyl radical



TEMPO (2,2,6,6-Tetramethylpiperidinyloxy)

iv. **Other oxidants- NaOCl,** Sodium Hypochloride, cal oxidation systems employed for the oxidation of alcohols is presented in **Chart 1**.

C. Electrochemical oxidation System

i. Using Nickel anode and Nickel cathode in a 0.5 M KOH Solution.

ii. Using carbon paper as the anode and nickel as the cathode in a solution of tetrabutylammonium tetrafluoroborate (nBu_4NBF_4) dissolved in a CH_3CN/H_2O mixture.

1. Oxidation of Alcohols using metal based oxidizing reagents

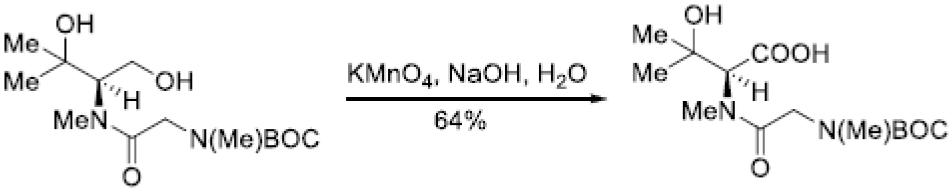
A. Potassium permanganate: Potassium permanganate ($KMnO_4$) is widely utilized in organic synthesis due to its strong oxidative properties, affordability, and ease of handling. It efficiently oxidizes primary alcohols to carboxylic acids and secondary alcohols to ketones under acidic, basic, or neutral conditions, Scheme 1 [3,6]. However, its reactivity is significantly lower in neutral media due to its limited solubility in water. To overcome solubility challenges and enhance reaction efficiency, various solvent systems have been explored. These include aqueous acetic acid, aqueous acetone, and biphasic systems such as ether-water, dichloromethane-water, and petroleum ether-water. Additionally, the use of organic co-solvents such as dioxane, pyridine, acetone, and *tert*-butanol (*t*-BuOH) has been employed to improve the solubility of alcohols in the reaction medium, thereby optimizing oxidation efficiency.

Menger and Lee et al. reported that solid $CuSO_4 \bullet 5H_2O$ can activate the oxidation potential of powdered $KMnO_4$. The $CuSO_4 \bullet 5H_2O/KMnO_4$ mixture efficiently oxidizes secondary alcohols to ketones, providing a milder reagent that is less reactive toward double bonds, Scheme 2 [7]. However, the oxidation of primary alcohols using this system proceeds very slowly. Moreover, this method does not demonstrate significant chemoselectivity in the oxidation of secondary alcohols in the presence of primary alcohols.

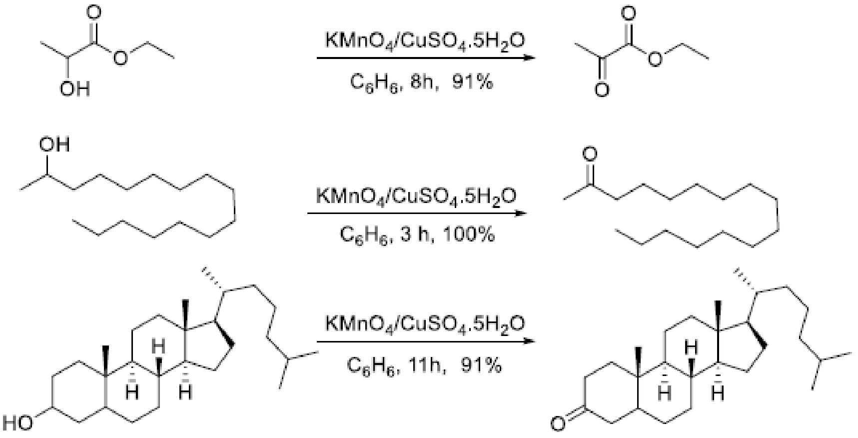
Despite its versatility, $KMnO_4$ has certain limitations in organic synthesis. Its high reactivity and harsh reaction conditions can lead to undesired side reactions, making it unsuitable for the oxidation of sensitive alcohols. Additionally, $KMnO_4$ readily reacts with a wide range of functional groups, including oximes, sulfides, thiols, and carbon-carbon double bonds. This lack of selectivity presents challenges in complex molecular systems.

B. Sodium dichromate: Sodium dichromate ($Na_2Cr_2O_7$) is a powerful oxidizing agent that efficiently converts primary alcohols to carboxylic acids and secondary alcohols to ketones under aqueous acidic conditions, Scheme 3 [8]. Like most chromium-based oxidants, it exhibits strong oxidative properties, particularly in low-pH environments. Selective oxidation of primary alcohols to aldehydes is challenging due to the harsh reaction conditions, including the exothermic nature of the process and the strong acidity required. In aqueous acidic media, aldehydes readily hydrate to form geminal diols, which are highly susceptible to further oxidation into carboxylic acids. However, aldehydes can be selectively obtained by using an excess amount of alcohol and rapidly removing the aldehyde via distillation using a fractionating column. Additionally, under highly acidic conditions, aldehydes and alcohols can react to form hemiacetals, which may further oxidize to esters as side products. Due to these factors, sodium dichromate is particularly valuable for the oxidation of primary alcohols to carboxylic acids and secondary alcohols to ketones.

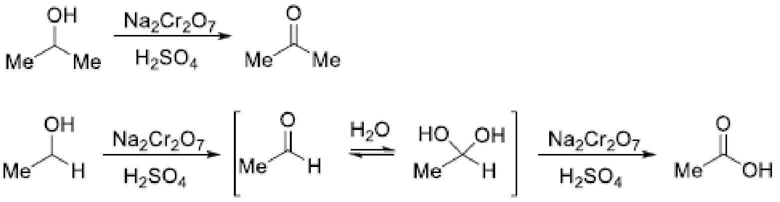
Since geminal diol formation in aqueous media hinders the selective oxidation of primary alcohols to aldehydes, researchers have explored non-aqueous oxidation methods. Gao et al. reported a solvent-free oxidation of primary alcohols



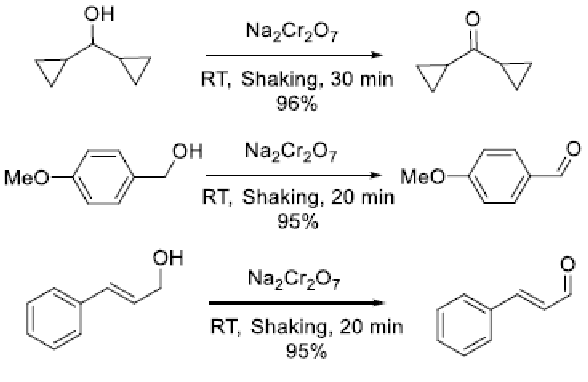
Scheme 1: Oxidation alcohols using $KMnO_4$ under basic medium



Scheme 2: Oxidation alcohols using $CuSO_4 \bullet 5H_2O/KMnO_4$



Scheme 3: Oxidation alcohols using $Na_2Cr_2O_7$ under aqueous acid medium



Scheme 4: Oxidation alcohols using $Na_2Cr_2O_7$ under solvent free condition

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to aldehydes using powdered $Na_2Cr_2O_7$ in a shaking machine at room temperature for 20 to 30 minutes, Scheme 4 [9]. This method also efficiently oxidizes secondary alcohols to ketones, offering a simple and effective alternative to traditional aqueous oxidation. The solvent-free nature of this approach reduces waste and minimizes side reactions, making it a more sustainable and practical method for selective alcohol oxidation.

C. Jones oxidation: The mixture of chromium trioxide and sulfuric acid in aqueous acetone, known as Jones reagent, is a highly effective oxidizing agent for primary and secondary alcohols, Scheme 5 [10]. In this reaction, chromium trioxide reacts with sulfuric acid to form chromic acid, which, in the presence of acetone and water, generates the active Jones reagent. Primary alcohols are directly oxidized to carboxylic acids, while secondary alcohols yield ketones at room temperature. Ali et al. reported silica gel supported Jones reagent is effective to stop the primary alcohol oxidation at aldehyde stage, Scheme 6 [11-12]. However, acid-sensitive alcohols are ineffective substrates due to the highly acidic nature of the reaction medium. Despite its effectiveness, a major drawback of the Jones oxidation method is the high toxicity of chromium compounds, which pose significant environmental and health hazards.

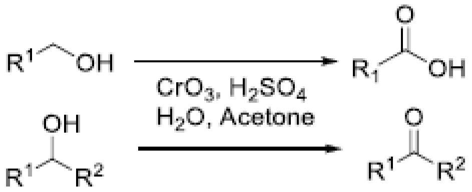
D. Pyridinium chlorochromate: Pyridinium chlorochromate (PCC) is a widely utilized, air-stable oxidizing reagent for the selective transformation of primary and secondary alcohols into their corresponding carbonyl compounds, Scheme 7 [13,14]. This yellow-orange, crystalline reagent is conveniently synthesized via the controlled addition of pyridine to a solution of chromium trioxide in 6M hydrochloric acid under low-temperature conditions, followed by filtration and isolation [13]. Stoichiometric amounts (typically 1.2 to 1.5 equivalents) of PCC efficiently oxidize a broad range of alcohols to aldehydes or ketones with high yields under mild and anhydrous conditions.

Due to its intrinsic acidity, PCC is less effective for the oxidation of acid-sensitive alcohols; however, the addition of sodium acetate (NaOAc) can mitigate this limitation, facilitating the oxidation of such substrates [13]. Addition of molecular sieves to the reaction mixture resultant increases the yield for the PCC oxidation of primary alcohol to aldehyde [15]. Comparative studies on various molecular sieves have revealed that the oxidation rate follows the order 5Å< 10Å< 4Å< 3Å. Alike Jones reagent and $Na_2Cr_2O_7$ the major drawback of the PCC is the high toxic nature of chromium.

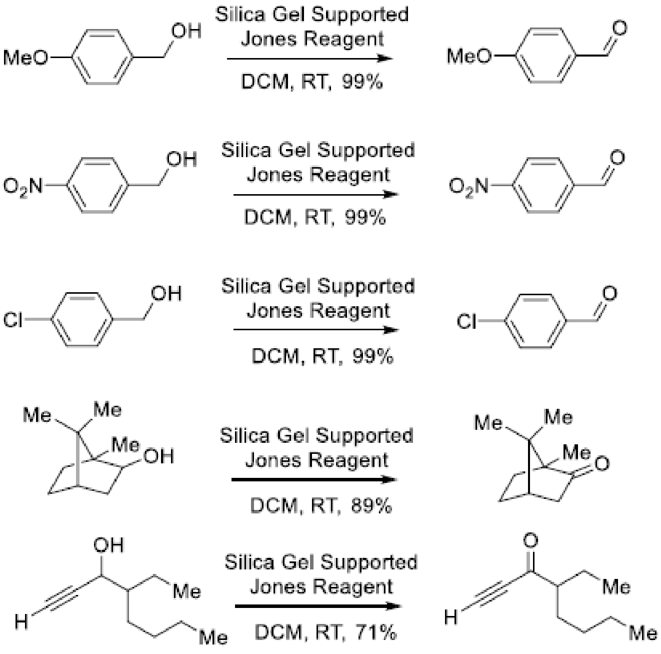
E. Collins reagent: Dipyridinechromium (VI) oxide is used for the oxidation of alcohols to carbonyl compounds [16,17]. It is prepared by the slow addition of chromium trioxide to anhydrous pyridine under cold conditions, followed by stirring at room temperature. After completion of the reaction and purification, free-flowing red crystals of Collins reagent are obtained with a yield of approximately 85–91%, Scheme 8 [17].

The reagent has low reactivity, requiring an excess amount to complete oxidation in a short duration, Scheme 9 [16]. However, this protocol is highly suitable for acid-sensitive alcohols. The reaction conditions can tolerate the protecting groups like O-trityl, O-silyl and epoxide, moity. The primary drawback of this reagent is excess amount that is up to 6 equivalent of reagent is some time required for complete oxidation. Toxicity of chromium is another serious drawback of this reagent.

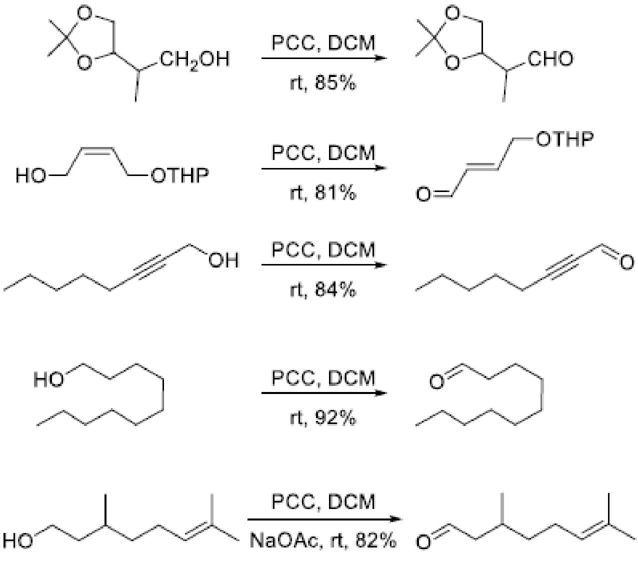
F. Pyridinium dichromate: Pyridinium dichromate (PDC) is a mild and selective oxidizing agent, easily prepared by adding pyridine to a concentrated solution of CrO_3 while keeping the reaction mixture ice-cold [18]. PDC is highly soluble in polar solvents such as water, DMSO, DMF,



Scheme 5: Oxidation alcohols using Jones reagent

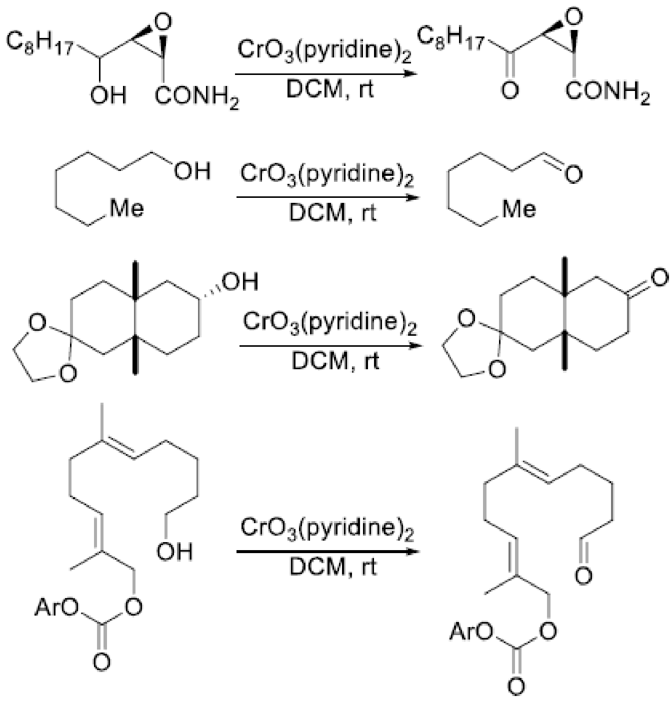


Scheme 6: Oxidation alcohols using Silica Gel Supported Jones reagent

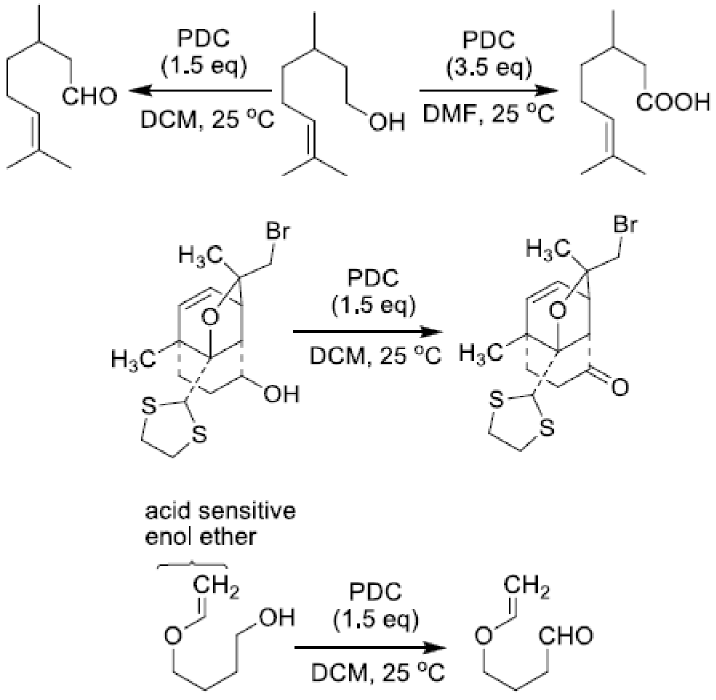


Scheme 7: Oxidation alcohols using PCC in DCM

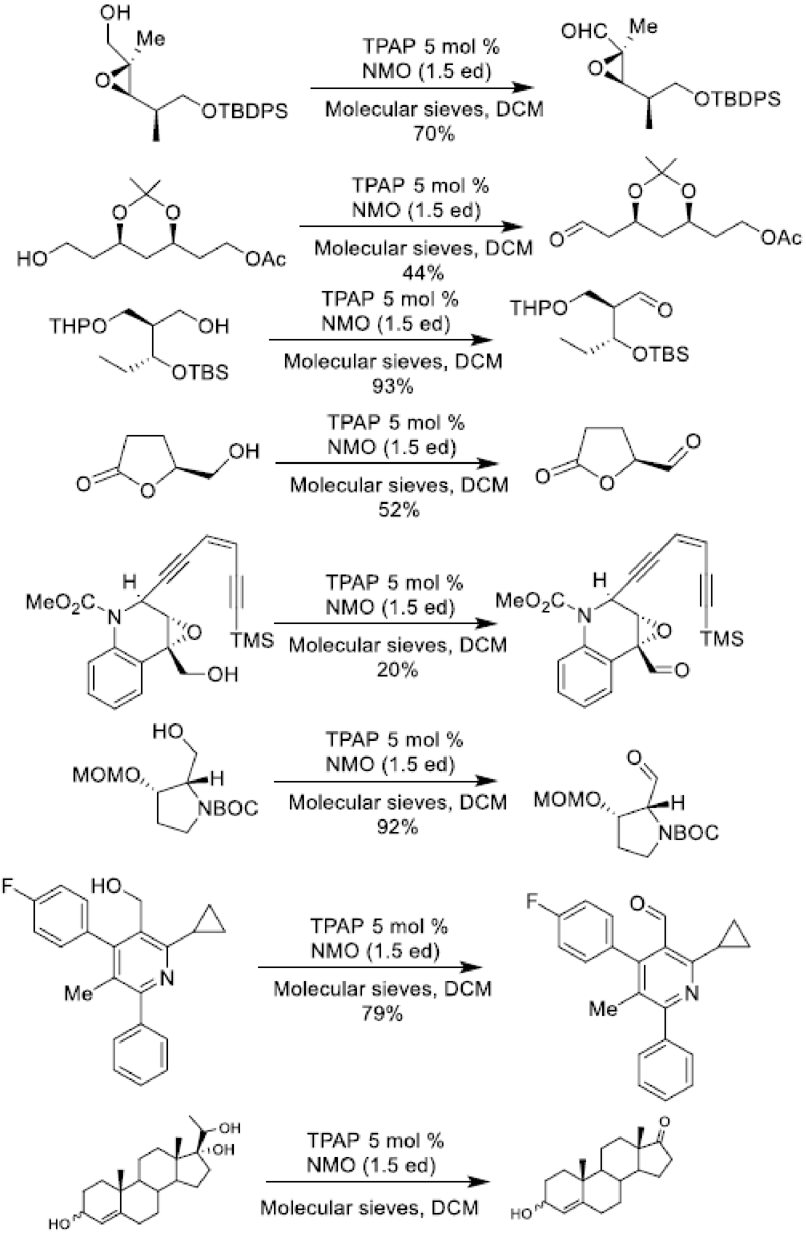
Scheme 8: Preparation of Collins reagent



Scheme 9: Oxidation of alcohol using Collins reagents

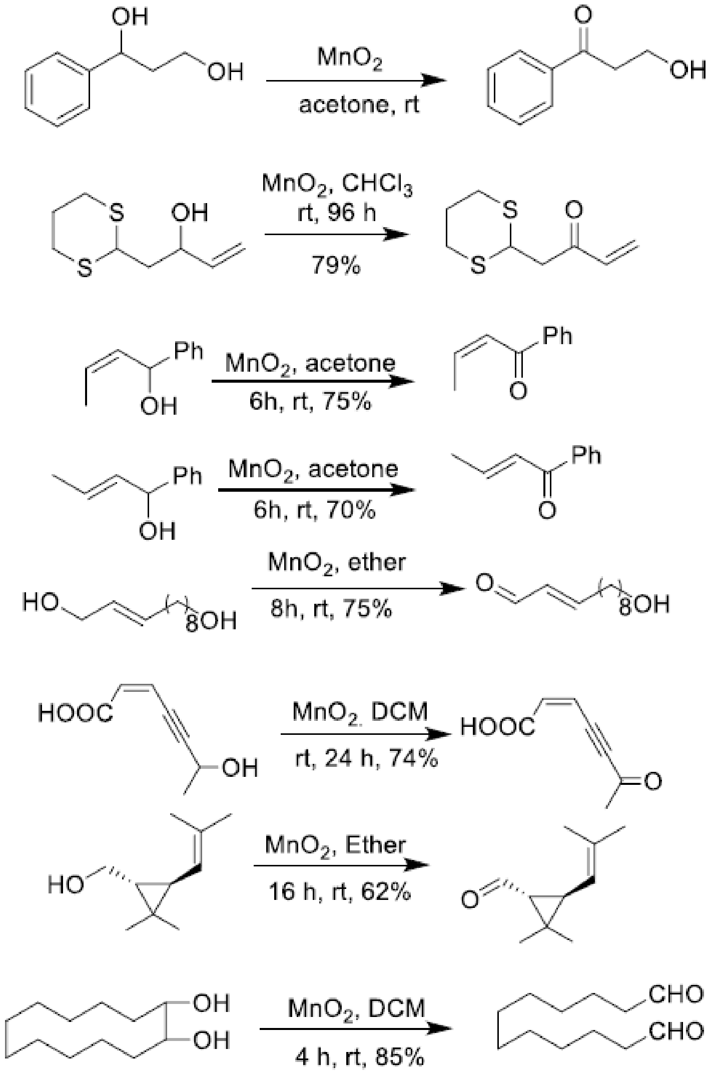


Scheme 10: Oxidation of alcohol using PDC

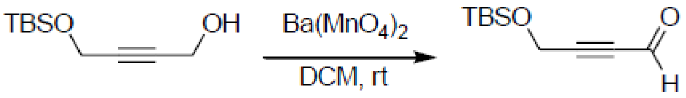


htbp

Scheme 11: Oxidation alcohol TPAP in presence of co-oxidant NMO



Scheme 12: Oxidation of allylic alcohol and 1,2-diol using MnO_2



Scheme 13: Oxidation of propergylic alcohol using $Ba(MnO_4)_2$

and dimethylacetamide, but less soluble in non-polar solvents like DCM, acetone, or chloroform, and unstable in acetonitrile. In oxidation reactions, PDC functions under nearly neutral conditions, making it less acidic than PCC. It efficiently oxidizes primary alcohols to aldehydes at 0^0C without significant over-oxidation, and can oxidize primary alcohols to carboxylic acids at 25^0C with 3.5 equivalents. Secondary alcohols are typically oxidized to ketones in DMF at low temperatures, while sensitive functional groups like thioacetals and enol ethers remain unaffected, Scheme 10. PDC in DCM can oxidize primary alcohols to aldehydes at room temperature with excellent yields, and secondary alcohols also undergo oxidation under similar conditions when combined with 0.4 equivalents of pyridiniumtrifluoroacetate, yielding excellent results. Here also the major drawback is the toxicity of Chromium.

G. Ley oxidation: TPAP (Tetrapropylammonium Perruthenate) is an air-stable, non-volatile, costly oxidizing agent used to convert primary alcohols to aldehydes and secondary alcohols to ketones, Scheme 11 [19,20]. It is used catalytically with NMO (N-Methylmorpholine-N-oxide) as a co-oxidant. The catalytic oxidation of TPAP in presence of co-oxidant NMO is known as Ley oxidation. The oxidation of alcohols under these reaction conditions does not lead to racemization at the stereogenic α-center. TPAP oxidation is highly selective, favoring primary alcohols over secondary ones, with tertiary alcohols remaining inert, and less hindered alcohols oxidizing faster than sterically hindered ones. It tolerates various functional groups, including ketals, epoxides, methylene cyclopropanes, double bonds, enediynes, MOM, MEM, BOM, DBS, THP, Trityl, OTMS, OTBS, esters, and lactones. Additionally, TPAP cleaves C-C bonds in 1,2-diols, regardless of their substitution pattern (primary-secondary, secondary-secondary, or secondary-tertiary diol), Scheme 11. Since water is a side product in the reaction, molecular sieves are used to remove water from the reaction mixture, ensuring efficient oxidation.

H. Manganese dioxide: Magnesium dioxide (MnO_2) is a highly chemoselective oxidant effective in oxidizing allylic, benzylic, or propargylic alcohols in the presence of saturated alcohols, Scheme 12 [21,22]. Activated MnO_2 can be prepared by reacting $MnSO_4$ with $KMnO_4$ under acidic or basic conditions [23] at elevated temperatures [24]. A more highly activated MnO_2 is obtained by reacting $MnCl_2$ with $KMnO_4$ at 60^0C for two hours and then leaving the mixture at room temperature overnight, followed by filtration, washing, and drying at 120-130^0C for 18 hours [24]. The choice of solvent plays a crucial role in the oxidation reaction, as MnO_2's activity significantly decreases in water, making oxidation of primary and secondary alcohols unsatisfactory. Polar solvents like DMF, DMSO, acetone, and ethyl acetate show similar deactivation of MnO_2, though to a lesser extent. Nonpolar solvents such as diethyl ether, petroleum ether, and benzene enhance the oxidizing activity, and higher temperatures can help overcome sluggish reactions in certain solvents. The MnO_2-to-substrate ratio varies depending on the mesoporous size of the MnO_2, ranging from 5:1 to 50:1. Additionally, cis-1,2-diols undergo C-C bond cleavage to form aldehydes or ketones, Scheme 12. Despite its advantages, the use of MnO_2 is limited by high reaction times, the need for excess reagent, and difficulty in obtaining highly activated MnO_2.

I. Barium Manganate: Barium manganate [$Ba(MnO_4)_2$] is an effective oxidizing agent with chemoselectivity similar to MnO_2, Scheme 13 [25]. It can be easily prepared by reacting $KMnO_4$, $BaCl_2$, NaOH, and KI in water within 15 minutes, followed by filtration, washing, and drying to obtain dark green crystals of $Ba(MnO_4)_2$. Unlike MnO_2, $Ba(MnO_4)_2$ does not require excess reagents for alcohol oxidation

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and does not necessitate special process for activation, making it a convenient and efficient oxidant for chemoselective oxidations.

J. Ceric ammonium nitrate: Ceric ammonium nitrate (CAN) is a commercially available chemoselective oxidizing agent for the oxidation of secondary alcohol in presence of primary alcohols, Scheme 14 [26,27]. Catalytic amount of CAN can oxidize secondary alcohol in presence of co-oxidant $NaBrO_3$. Primary alcohols are almost inert. However the double bond present in the substrate cannot tolerate CAN.

K. Fetizon's reagent: The Fetizon's reagent, consisting of silver carbonate (Ag_2CO_3) absorbed onto celite, is an efficient mild agent for converting alcohols into their corresponding carbonyl compounds, Scheme 15 [28,29]. This oxidation process is notably clean, with the products easily purified through simple filtration of silver metal. Allylic and benzylic alcohols are more reactive than secondary alcohols, which show slower oxidation under these conditions. Primary alcohols exhibit the least reactivity in this system, often requiring more stringent conditions for oxidation. Notably, hindered alcohols are inert under the Fertozon oxidation, demonstrating the reagent's selective reactivity. The simplicity of the reaction and ease of purification make Fertozon a valuable tool in organic synthesis for alcohol oxidation. The main drawback of the Fetizon's reagent is its high cost, which can make its use less economical for large-scale reactions. Additionally, an excess amount of the reagent is often required to achieve good yields, further increasing the overall cost and making it less efficient in terms of reagent usage.

2. Oxidation of Alcohols using non-metal based oxidizing reagents

A. Sodium hypochloride: Sodium hypochlorite (NaOCl), a commercially available oxidizing agent, is effective for oxidizing secondary alcohols in the presence of primary alcohols, Scheme 16 [30,31]. Typically, a solution of 1.86 M NaOCl (1.05 equivalents) is added dropwise to a diol solution in an aqueous acetic acid medium, yielding hydroxy ketones in good yields. However, if the oxidant is used in excess, side reactions can occur, leading to the formation of dimeric ester products as significant byproducts. Despite this, when controlled, NaOCl provides a straightforward and efficient method for selective oxidation of secondary alcohols.

B. (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl: 2,2,6,6- Tetramethylpiperidinyloxy (TEMPO) is a highly stable nitroxyl radical that serves as an efficient catalyst for alcohol oxidation when paired with co-oxidants like hypervalent iodine, hypochlorite, oxygen, bromite, or peroxy acids, Scheme 17 [32,33]. This catalytic method is particularly effective for oxidizing α-alkoxy or α-amino alcohols while preserving enantiomeric purity [33]. TEMPO-catalyzed oxidation is chemoselective, enabling the oxidation of primary alcohols in the presence of secondary alcohols, which are typically more resistant to oxidation. Under acidic conditions, secondary alcohols can also be successfully oxidized, although at a slower rate than primary alcohols.

C. Pfitzner Moffatt oxidation: In 1963 Moffatt and Pfitzner, reported a widely used method for oxidizing primary and secondary alcohols by activating DMSO with dicyclohexylcarbodiimide (DCC) and a catalytic amount of anhydrous phosphoric acid, Scheme 18 [34]. The use of strong acids slows down the reaction, making the moderately acidic conditions preferable. This methodology is highly useful due to

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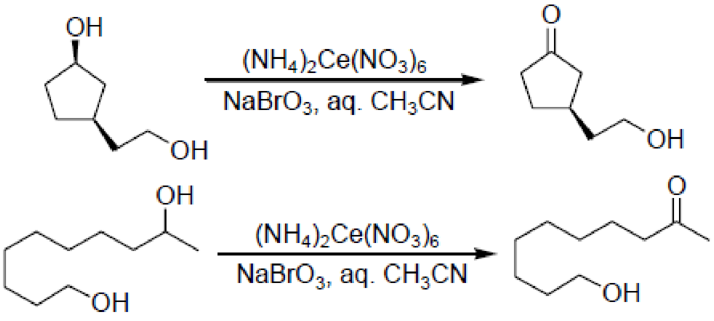
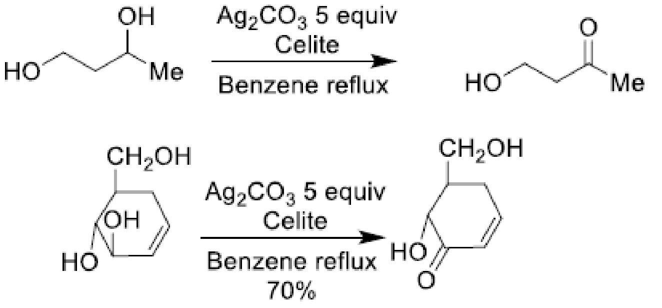
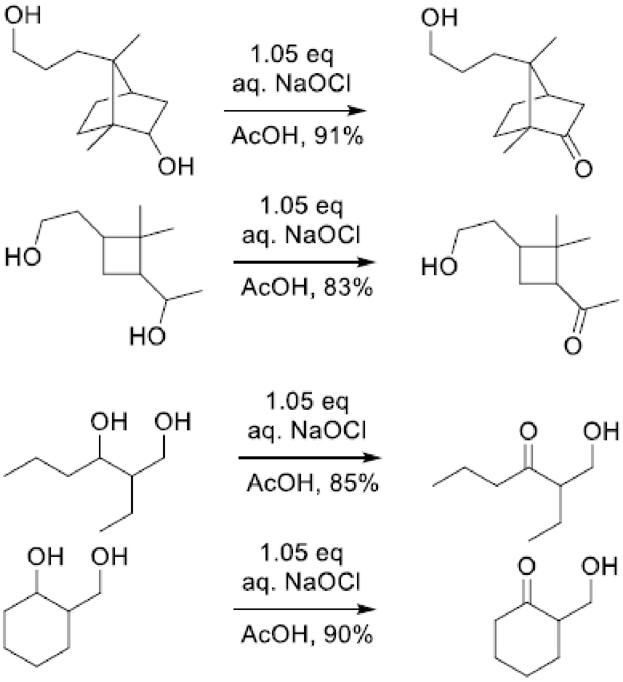


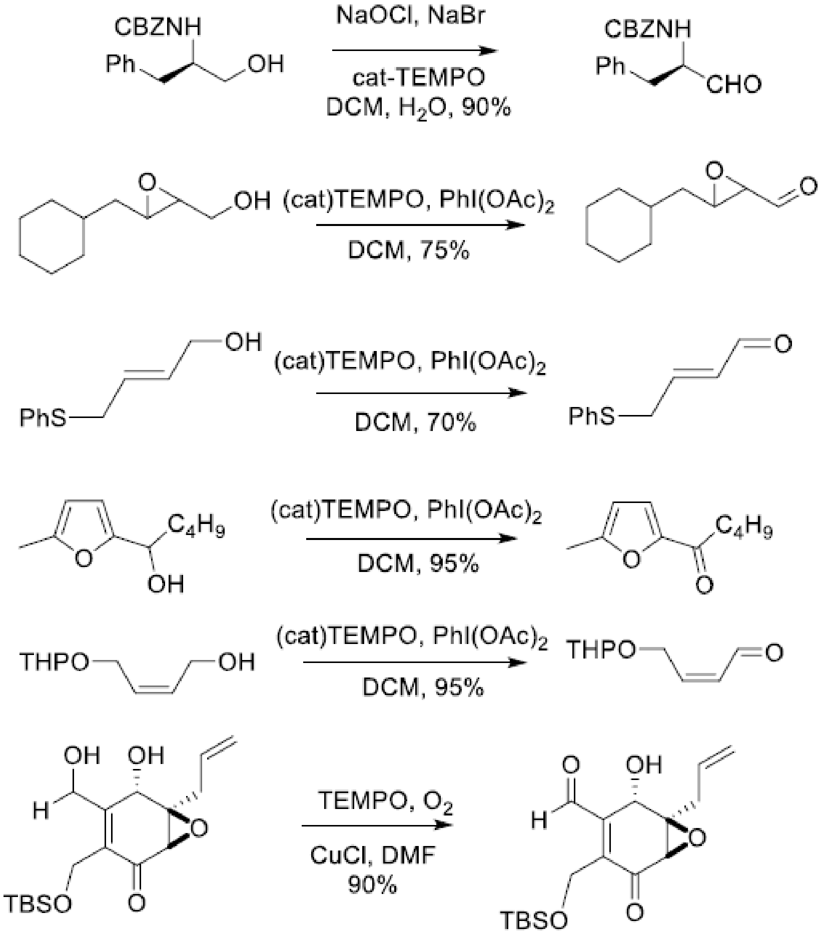
Scheme 14: Chemoselective oxidation of secondary alcohol using CAN



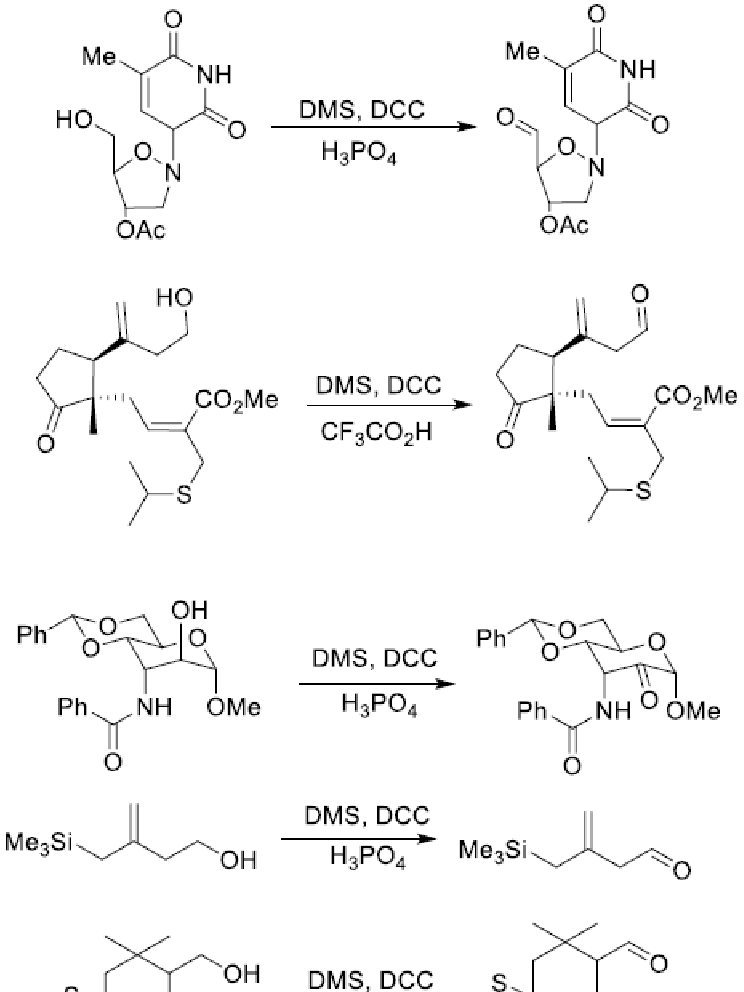
Scheme 15: Chemoselective oxidation of alcohol using Fetizon's reagent



Scheme 16: Chemoselective oxidation of secondary alcohol using NaOCl



Scheme 17: Oxidation of alcohol using Cat. TEMPO in presence of co-oxidant



Scheme 18: Oxidation of alcohol using DMSO and DCC

the affordability, ease of handling, and high yields of the reagents. Typically, an excess amount of DCC (around 3 equivalents or more) is used. However, the main drawback is the difficulty in removing the byproduct, dialkyl urea, and the excess DCC from the reaction mixture.

D. Albright Goldman oxidation: Later in the year 1965 Albright and Gold man documented another alcohol oxidation method by activating DMSO by acetic anhydride, Scheme 19 [35]. The reaction use to perform at room temperature. Highly sterically hindered hydroxides can be readily oxidized by this method.

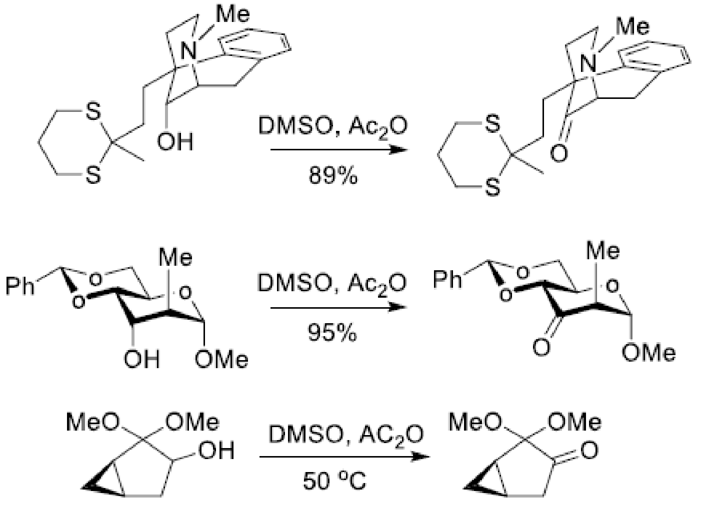
E. Parikh Doering oxidation: In 1967 Parikh and Doering reported another novel reagent for the oxidation of alcohol to carbonyl compound using DMSO and pyridine sulfur trioxide complex followed by the addition of triethyl amine at room temperature, Scheme 20 [36]. The main feature of this reagent is it cans oxidation of allylic alcohols to the corresponding carbonyl compounds very rapidly at room temperature within minutes.

F. Corey Kim oxidation: In 1972 Corey and Kim documented a effected alcohol oxidation reaction methodology by using N-chlorosuccnimide (NCS) and dimethylsulfide (DMS) which is known as Corey Kim oxidation, Scheme 21 [37]. NCS and DMS react to give S,S-dimethylsuccinimidosulfonium chloride insitu which react with alcohol in presence of base like trimethylamine give the corresponding aldehyde or ketone. Oxidation of Allylic and benzylic alcohols are ineffective for this transformation give allylic or benzylic chloride respectively. This reaction condition can tolerate a wide range of functional group.

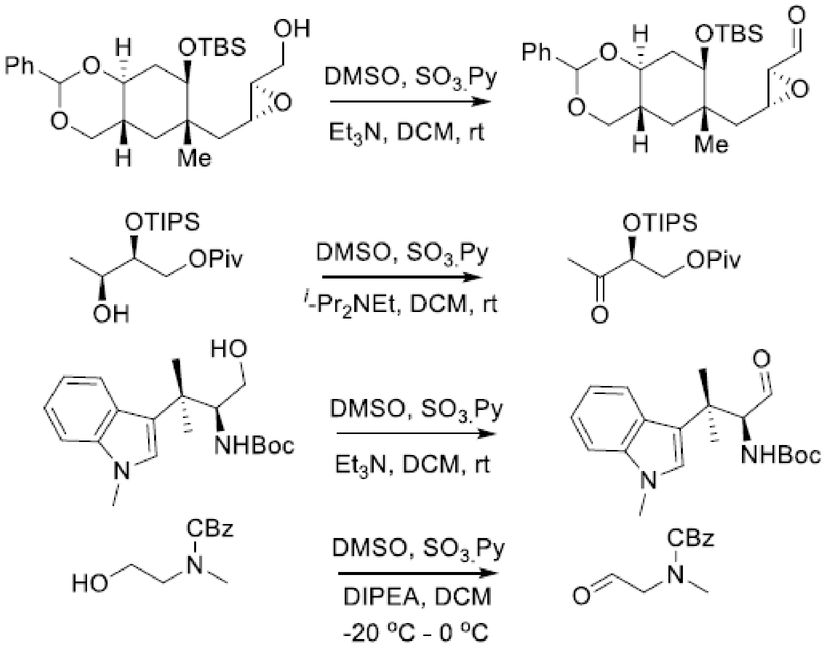
G. Swern Oxidation: Swern oxidation, one of the oldest and most effective methods for alcohol oxidation, was first reported by Swern et al. in 1976, utilizing trifluoroacetic anhydride (TFAA) to activate DMSO at temperatures below -50^{0}C, forming trifluoroacetoxydimethylsulfonium trifluoroacetate, which reacts with alcohols to produce alkoxydimethylsulfonium trifluoroacetates; these intermediates, in the presence of triethylamine, yield the corresponding carbonyl compounds, Scheme 22 [38]. In 1978, the same group introduced a more efficient activator, oxalyl chloride in dichloromethane (DCM) at -78^{0}C, generating chlorodimethylsulfonium chloride along with carbon dioxide and carbon monoxide as by products, which reacts rapidly with alcohols in the presence of Et_3N, allowing for the synthesis of sensitive carbonyl compounds like α-keto aldehydes and acylsilanes [39,40]. Extreme caution is required when activating DMSO with TFAA due to its violent reactivity, which can lead to explosions. To prevent Pummerer rearrangement, strict temperature control below -30^{0}C is essential. In contrast, the oxalyl chloride intermediate remains stable below -60^{0}C, making -78^{0}C the optimal reaction temperature. Notably, the efficiency of Swern oxidation remains unaffected by the steric hindrance of the hydroxyl group, further contributing to its broad applicability in organic synthesis.

H. Hypervalent Iodine compounds: IBX, a hypervalent iodine compound, was first discovered by Meyer and Hartmann in 1893 [41]. It can be synthesized from o-iodobenzoic acid using either potassium bromate ($KBrO_3$) in 2M sulfuric acid (H_2SO_2) at 60-65^{0}C [42] or oxone ($2KHSO_2 \bullet KHSO_4 \bullet K_2SO_4$) in water at 70^{0}C [43], Scheme 23. The former method provides a higher yield but with lower purity, whereas the latter offers better purity at the cost of reduced yield. Despite its potential, the synthetic applications of IBX remained unexplored until 1994 due to its insolubility in common organic solvents, including water.

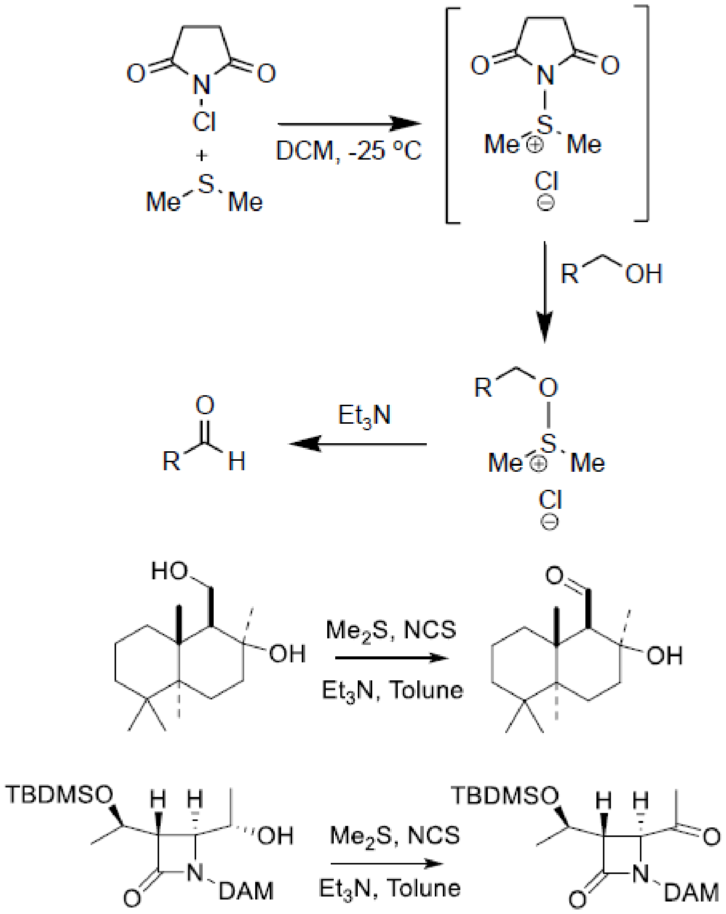
I. Dess Martin periodinane: In 1983,



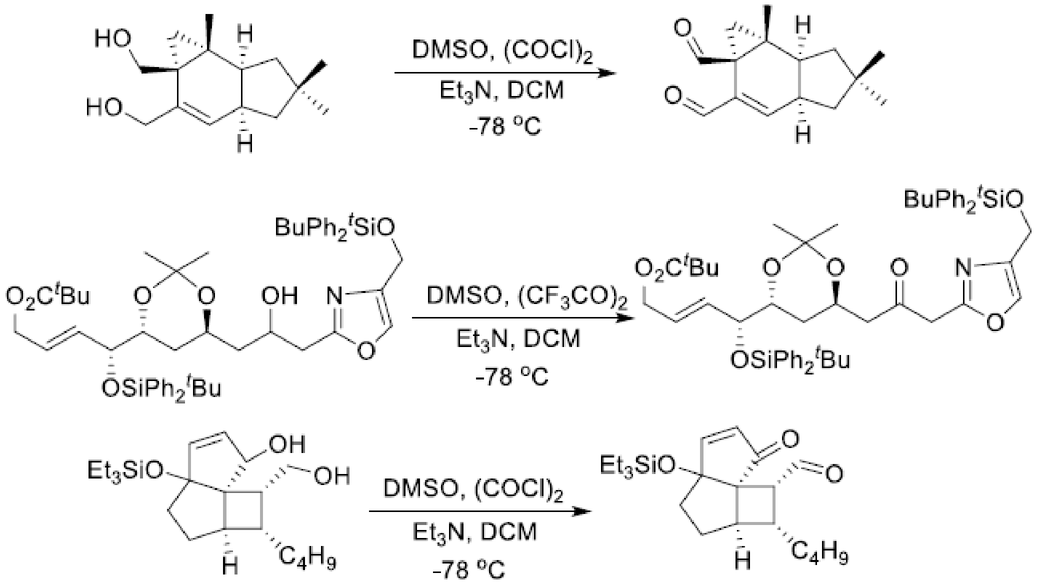
Scheme 19: Oxidation of alcohol using DMSO and Ac$_2$O



Scheme 20: Oxidation of alcohol using DMSO and Pyridine sulfur trioxide complex



Scheme 21: Oxidation of alcohol using Corey Kim reagent



Scheme 22: Oxidation of alcohol using DMSO and TFAA or $(COCl)_2$

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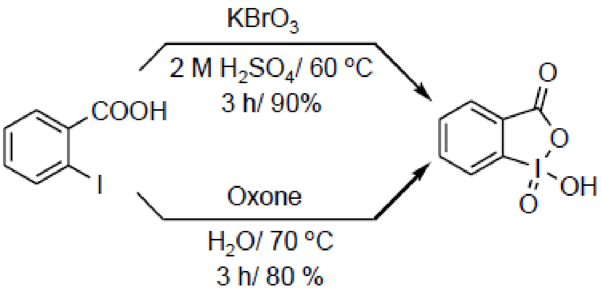
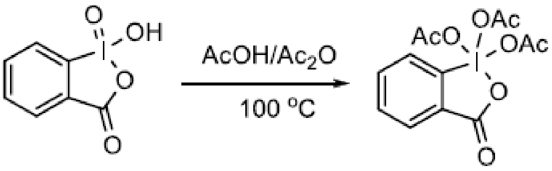


Scheme 23: Preparation of IBX form *o*-iodobenzoic acid



Scheme 24: Preparation Dess Martin Periodinane from IBX

Dess and Martin synthesized a novel 12-I-5 compound, commercially known as Dess-Martin Periodinane (DMP), from IBX [44]. The reaction involves IBX and acetic anhydride in an acetic acid medium at 100^0C, yielding DMP with an efficiency of 93%, Scheme 24.

Unlike IBX, DMP is soluble in common organic solvents such as chloroform, dichloromethane, and acetonitrile. It is a moisture-sensitive oxidizing agent, and 1.05 equivalents of DMP are sufficient to convert a wide range of alcohols to aldehydes at room temperature under inert conditions, Scheme 25. In the absence of an inert atmosphere, an excess of 30% reagent achieves the same yield. Notably, no further oxidation to carboxylic acids has been observed in any case.

J. 2-Iodoxy benzic acid: In 1994, Frigerio et al. reported the solubility of IBX in DMSO and demonstrated that 1.5 equivalents of IBX effectively oxidize a variety of alcohols to their corresponding carbonyl compounds at room temperature in a very short duration [45]. Additionally, 1,2-diols undergo oxidation to α-hydroxy ketones or 1,2-diketones without cleavage of the glycol bond, Scheme 26. Notably, this reaction does not require any special precautions, such as dry solvents or an inert atmosphere. Although IBX is insoluble in common organic solvents, Finney et al. demonstrated that alcohol oxidation can still be achieved in solvents such as ethyl acetate (EtOAc), chloroform ($CHCl_3$), 1,2-dichloroethane ($ClCH_2CH_2Cl$), acetone, acetonitrile (MeCN), and benzene at their respective reflux temperatures [46]. The oxidation was successfully carried out in the presence of 3 equivalents of IBX, and it was proposed that the reaction proceeds via a heterogeneous phase, Scheme 27. In all cases, the isolated yield of the carbonyl compounds was excellent. Although IBX is a well-known mild and selective oxidizing agent for converting primary alcohols to aldehydes, in 2002, Giannis et al. reported that IBX could further oxidize primary alcohols to carboxylic acids in the presence of *O*-nucleophiles such as 2-hydroxypyridine (HYP) and *N*-hydroxysuccinimide (NHS), Scheme 28 [47]. This reaction, conducted in DMSO at room temperature, provided an efficient and selective method for alcohol oxidation beyond the aldehyde stage.

In 2005, Vinod et al. conducted the first catalytic use of IBX in the presence of a co-oxidant such as oxone for the oxidation of primary and secondary alcohols,

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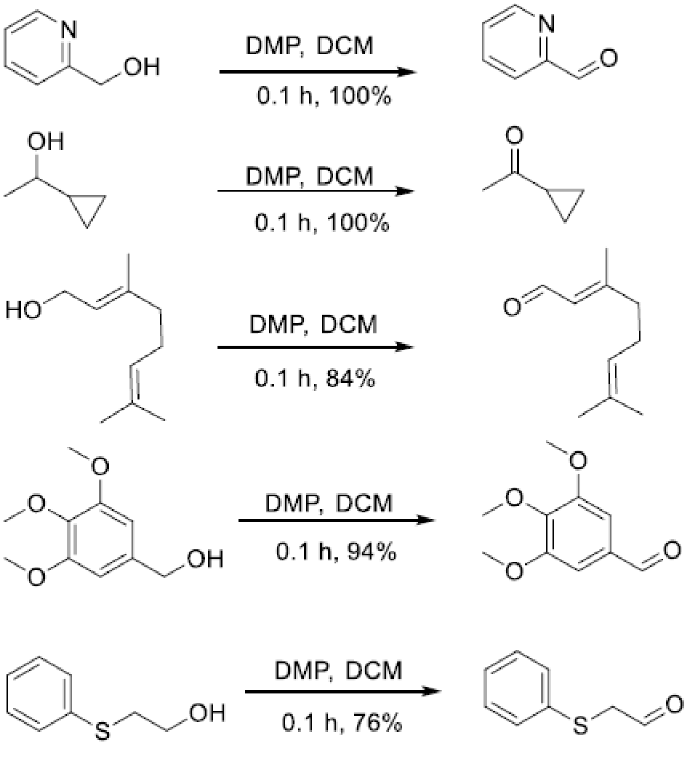
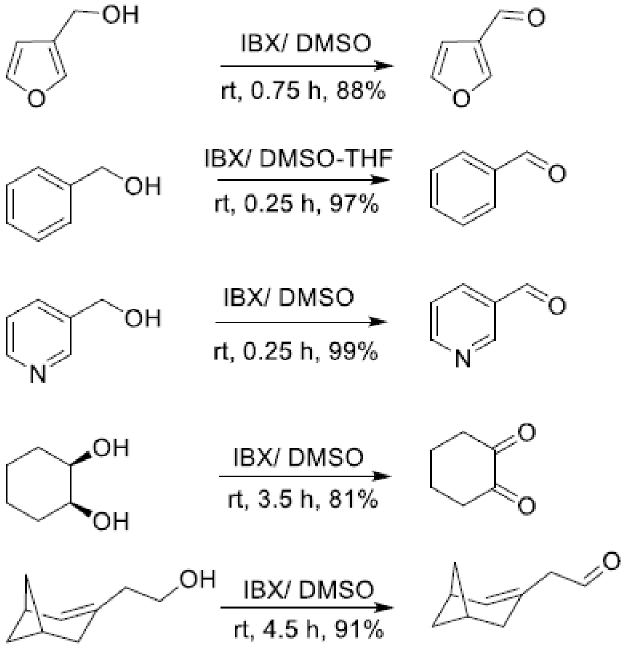


Scheme 25: Oxidation of alcohols using DMP



Scheme 26: Oxidation of alcohol using IBX in DMSO

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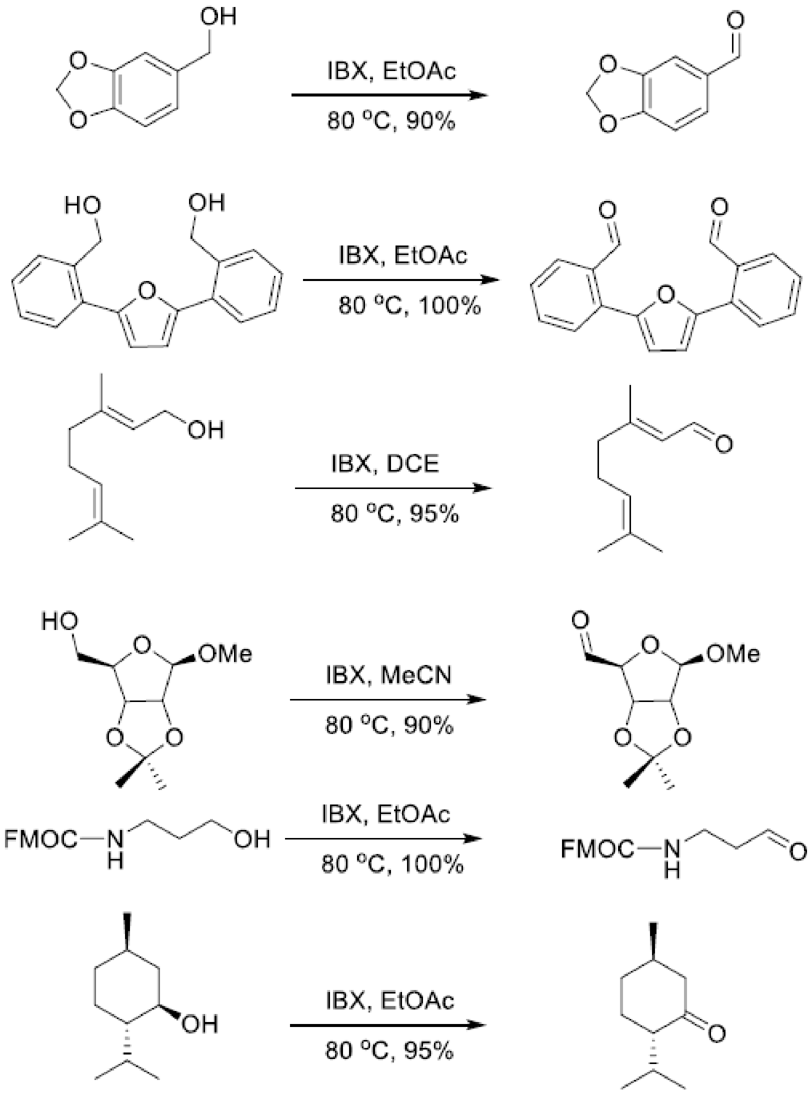
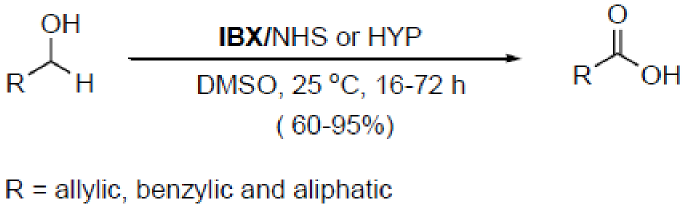
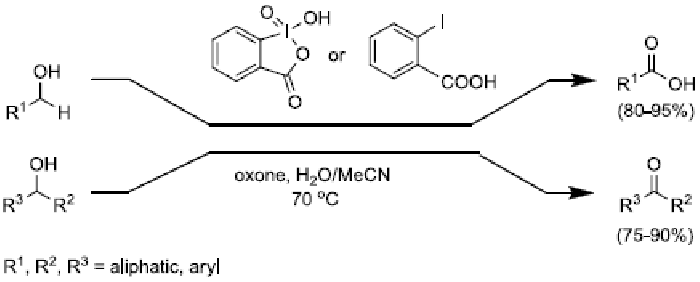


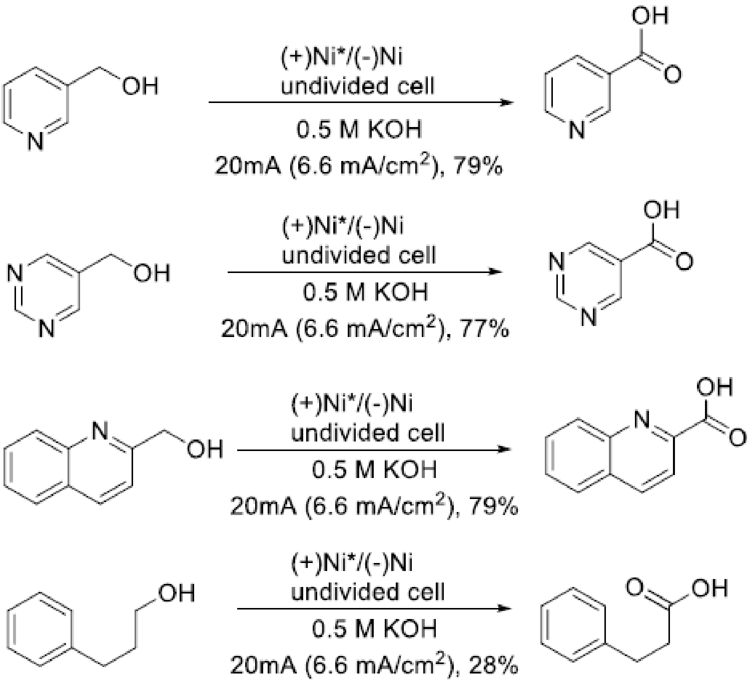
Scheme 27: Oxidation of alcohol using IBX in Common organic solvents



Scheme 28: Oxidation of alcohol to carboxylic acid using IBX



Scheme 29: Oxidation of alcohol using IBX as catalyst



Scheme 30: Electrochemical oxidation of alcohol to carboxylic acid

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Scheme 29 [48]. They demonstrated that IBX could be regenerated *in situ* from *o*-iodobenzoic acid (IBA) by oxone, allowing for an efficient and continuous oxidation process. Since oxone is known to oxidize aldehydes to their corresponding carboxylic acids, the oxidation of primary alcohols under these conditions results in carboxylic acids as the final products, while secondary alcohols are selectively converted to ketones. This catalytic system provides an efficient and sustainable approach to alcohol oxidation, reducing the need for stoichiometric amounts of IBX and expanding its practical applications in organic synthesis. IBX offers several advantages, including its eco-friendly nature, mild reaction conditions, easy availability, simple preparation, convenient storage, and high selectivity. In addition to its conventional stoichiometric use, catalytic methods for IBX oxidation have also been reported. Furthermore, IBX can be recycled by recovering it from the reaction mixture and reoxidizing it back to its active form, enhancing its sustainability and cost-effectiveness in organic synthesis. This recyclability further extends the practical utility of IBX in oxidation reactions, making it a valuable reagent in both academic and industrial applications.

3. Electrochemical Oxidation of Alcohols

Electrochemical oxidation of alcohols has gained significant attention in recent years as a sustainable and efficient alternative to conventional chemical oxidation methods. Traditional oxidation processes often rely on stoichiometric amounts of metal-based oxidants such as chromium-, manganese-, ruthenium-, cerium-, and silver-based reagents, which, although effective, generate considerable quantities of toxic and non-recyclable by products. The handling and disposal of these hazardous reagents pose serious environmental and safety concerns, limiting their large-scale industrial applicability. In contrast, electrochemical oxidation offers a greener and safer approach, where electrons serve as the clean oxidizing agents. This electrochemical strategy not only minimizes waste generation but also reduces process mass intensity (PMI), contributing to more sustainable reaction pathways. A notable advantage of these systems is the generation of molecular hydrogen (H_2) as the primary byproduct, which is environmentally benign and can be efficiently managed through controlled gas release techniques. Furthermore, the inherent tunability of electrochemical systems—through precise control of anodic potential, electrode material, and electrolyte composition—allows fine modulation of oxidation selectivity and efficiency. Such versatility enables the selective transformation of primary and secondary alcohols into their corresponding aldehydes or ketones under mild and environmentally friendly conditions. As a result, electrochemical oxidation of alcohols represents a promising platform for green and scalable synthetic chemistry, aligning closely with the principles of sustainable and safe chemical manufacturing.

Cantillo et al. developed a robust heterogeneous electrochemical strategy for the oxidation of primary alcohols to carboxylic acids using nickel anodes in alkaline aqueous media, Scheme 30 [49]. Upon contact with the alkaline solution, a layer of $Ni(OH)_2$ is formed on the nickel anode surface, which is subsequently converted in situ into catalytically active NiOOH. This NiOOH layer acts as an electron–proton transfer mediator (EPTM), efficiently promoting the oxidation of alcohols to carboxylic acids without the need for additional reagents or catalyst separation. The in situ generation of the NiOOH layer within the flow reactor ensures excellent structural stability and sustained catalytic performance. Moreover, the use of a three-step flow reactor cascade enables efficient gas management and high single-pass conversions. The system exhibits remark-

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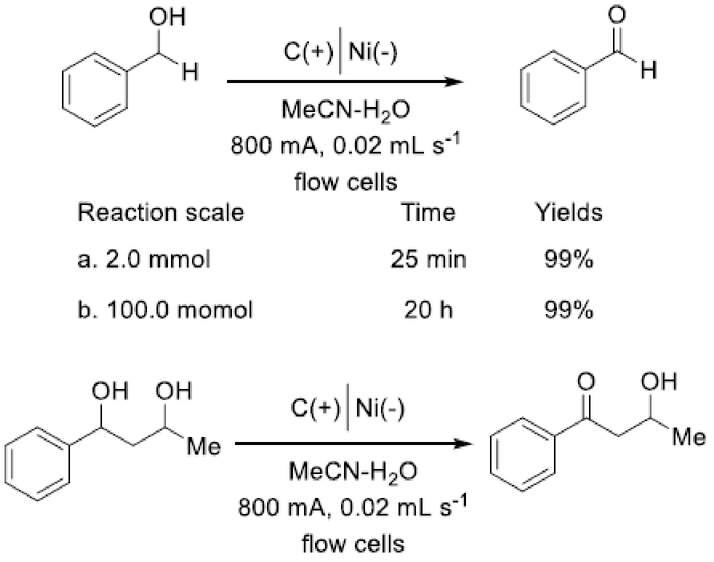

Scheme 31: Electrochemical oxidation of alcohol to aldehyde

able long-term operational stability, maintaining consistent conversion and selectivity for over 12 hours with minimal nickel leaching (∼21.3 μg L^{-1}), demonstrating its durability and suitability for industrial-scale applications.

Lie et al. reported electrochemical oxidation of alcohols using a flow electrolysis setup under controlled conditions [50]. In a typical procedure, alcohol substrate was combined with tetrabutylammonium tetrafluoroborate (nBu_4NBF_4) as the supporting electrolyte in a CH_3CN/H_2O (1:1, 30 mL) solvent mixture. The electrochemical cell consisted of carbon paper as the anode and a nickel plate as the cathode, each with an effective surface area of 1.6 cm^2. To eliminate any possible interference from atmospheric oxygen, the entire system was thoroughly purged with nitrogen prior to electrolysis. The reaction mixture was circulated through the flow electrochemical reactor at a rate of 0.10 mL s^{-1}. A constant current of 800 mA for at room temperature give the quantitative yield of aldehyde with electron rich aromatic alcohols product, Scheme 31. Electron deficient alcohols are not giving satisfactory results. Aliphatic alcohols are reluctant to convert carbonyl compound under this reaction condition. Hence show chemo selectivity, Scheme 31. High scale reaction also performed with satisfactory result with almost same yield but need more reaction time.

Despite its numerous advantages, the electrochemical oxidation of alcohols also faces several limitations. The reaction rate is often relatively slow, which can hinder its practical applicability and need to do under oxygen free condition. In many cases of primary alcohols, achieving selective oxidation to aldehydes is challenging, and the product selectivity is frequently unsatisfactory. Additionally, the process often requires expensive electrode materials, which increases the overall cost. Another significant drawback is the rapid deactivation or fouling of electrodes during the reaction, leading to reduced efficiency and poor reproducibility. These factors collectively limit the scalability of electrochemical alcohol oxidation for large-scale or industrial applications.

2 Conclusion

The oxidation of alcohols to carbonyl compounds is a cornerstone transformation in organic synthesis, with broad applications across pharmaceuticals, fine chemicals, and materials science. Over the years, numerous metal-based oxidizing reagents have been developed, each offering specific advantages in terms of selectivity, efficiency, and environmental impact. Traditional chromium-based reagents, such as PCC and PDC, continue to be widely employed due to their reliability; however, their toxicity and the challenges associated with waste disposal have prompted the search for greener alternatives.

Modern oxidation reagents, including TPAP, Dess–Martin periodinane (DMP), and DMSO-based systems, offer milder reaction conditions, improved functional group tolerance, and reduced environmental hazards. Nevertheless, challenges such as high cost, limited scalability, and the occurrence of side reactions still persist. The selection of an appropriate oxidation method thus depends on several factors, including substrate sensitivity, desired selectivity, and sustainability considerations.

In recent years, electrochemical oxidation has emerged as a transformative and sustainable alternative to traditional chemical oxidations. This approach utilizes electrons as clean redox mediators, eliminating the need for stoichiometric reagents and minimizing waste generation. Electrochemical methods provide high tunability, improved safety, and a reduced environmental footprint compared to conventional processes. Among these, heterogeneous electrocatalytic systems—particularly those employing nickel-based NiOOH-mediated oxidation—represent a significant advance toward scalable and environmentally benign oxidation chemistry. Despite ongoing challenges such as electrode fouling, sluggish kinetics, and limited substrate scope, continuous innovations in reactor design, electrode materials, and mechanistic insight are progressively addressing these limitations.

Among the oxidizing agents discussed, IBX has demonstrated the best overall performance, combining high efficiency, selectivity, environmental compatibility, catalytic reusability, and operational simplicity. Future research should focus on developing non-toxic, cost-effective, and eco-friendly oxidizing systems that maintain high catalytic efficiency and can be easily adapted for industrial use. The continued advancement of sustainable and recyclable oxidation technologies will not only enhance the efficiency and selectivity of oxidation processes but also contribute substantially to the broader objectives of green and sustainable chemistry.

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