

Applications of Transition Metal Perchlorates in Organic Functional Group Transformations

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Abstract: In view of the unique properties, like high solubility in most of the organic solvents, poor complexing ability, low charge density, stability under mild conditions and high electronegativity, transition metal perchlorates have been found to be highly effective catalysts/reagents in wide variety of functional group transformations leading to the synthesis of large number of important organic compounds. This review presents the recent applications of important transition metal perchlorates as safe catalysts/reagents for organic functional group transformations.

Keywords: Organic Synthesis, Reagents, Catalysts, Transition Metal Perchlorates.

INTRODUCTION

Over the years, use of transition metal perchlorates have been avoided by the chemists all over the world due to the fear that these may act as explosives [1], in view of their use during the world wars for the production of bombs and other explosive materials. But in recent years from the safety data sheets provided by the manufacturers it has been found that common metal perchlorates are stable under ordinary conditions of use and storage [2], e. g. As per National Fire Protection Association (NFPA), magnesium perchlorate is barely hazardous for health and can act as an oxidizing agent but is not explosive [3]. In last 2-3 decades this myth has been broken and more and more chemists has realized the potential of metal perchlorates as catalysts/reagents under mild conditions in organic synthesis. This renewed interest in applications of transition metal perchlorates is mainly because of the several unique properties possessed by these salts. These unique properties are high solubility in most of the organic solvents, poor complexing ability, low charge density, stability under mild conditions and high electronegativity. The recent developments and applications of transition metal perchlorates as promoters and catalysts for many important organic reactions are reviewed. The milder reaction conditions and their potential to act as Lewis acid contribute to an increased selectivity of the transformations. Transition metal Lewis acids are promising and interesting because the precursor is often structurally well-defined, steric and electronic ligand tuning to a particular reaction is easier. This review presents a general overview of more recent applications of transition metal perchlorates in organic functional group transformations. The important functional group transformations are:

RESULT AND DISCUSSION

1. Addition Reaction of Carbon-Carbon Double Bonds, Triple Bonds and Carbon-Hetero Double Bonds

Addition reactions are limited to chemical compounds that have multiply-bonded atoms, such as molecules with carbon-carbon

double bonds, i.e., alkenes, or with triple bonds, i.e., alkynes. Also included are molecules containing carbon - hetero double bonds like those with carbonyl (C=O) groups or those with imines (C=N) groups.

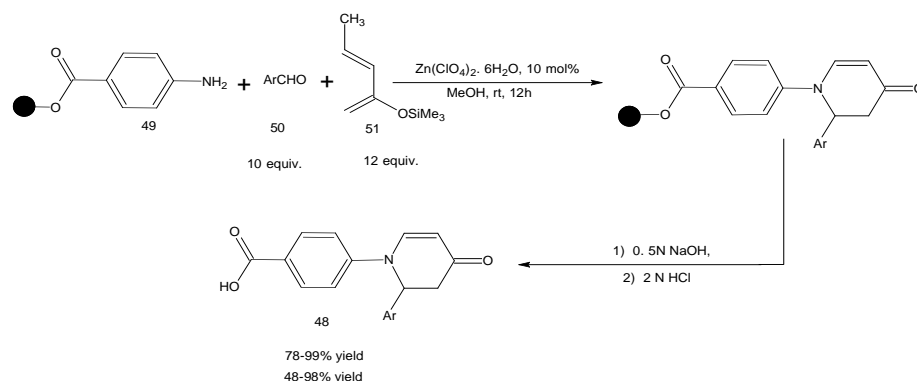
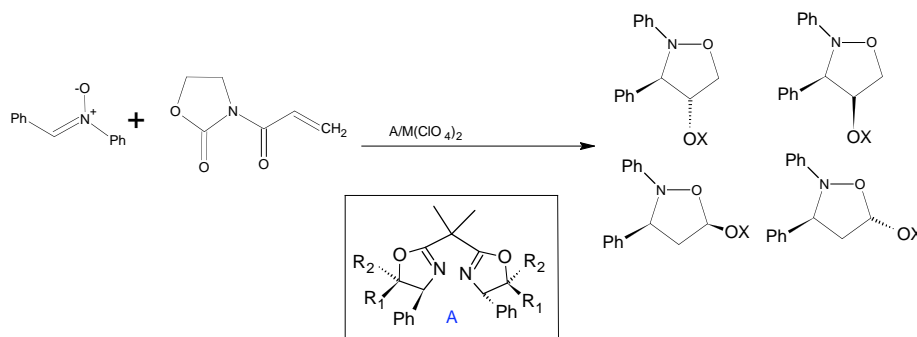
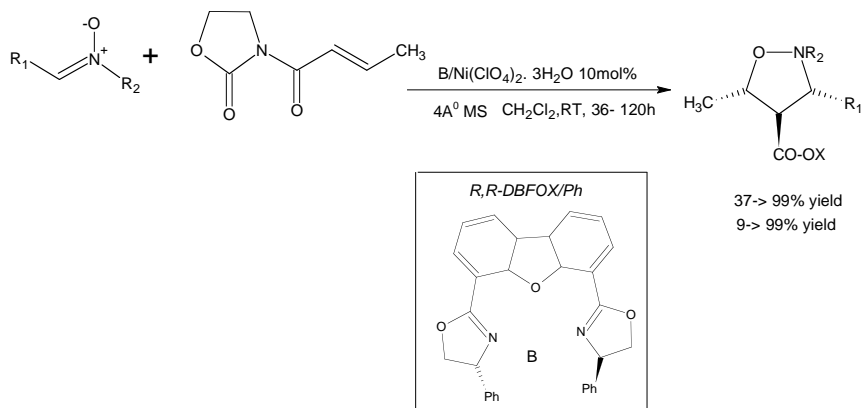
1.1. Diels-Alder reaction: The Diels-Alder reaction has become one of the most important cycloaddition reactions in organic synthesis, and some Diels-Alder reactions are unsuccessful because of the low reactivity of the reaction system. Lewis acid catalysts, high pressures and different solvents, can sometimes accelerate the reaction. For the synthesis of heterocyclic compounds, hetero-Diels-Alder reactions with nitrogen- or oxygen-containing dienophiles are particularly useful. The [4+2] cycloadducts derived from the cyclocondensation of N-protected α -aminoaldehydes with Danishefsky's diene represent useful building blocks for the construction of complex aminosugar antibiotics. H Guo *et al.* reported one-pot, three-component reaction for the construction of structurally diverse 2,3-dihydropyridin-4-ones on a soluble polymer support using $\text{Zn}(\text{ClO}_4)_2 \cdot 6(\text{H}_2\text{O})$ (Scheme 1) [4].

The proposed Aza Diels-Alder reaction involves either PEG-supported amines, aromatic aldehydes, and Danishefsky's diene, or PEG-supported aldehyde, aromatic amines, and Danishefsky's diene.

1.2. 1,3-dipolar cycloaddition: In recent years, De Simoni and co-workers have studied the use of Ph-bisoxazolines as chiral ligands for several perchlorates. In their more recent work [5] they found optimum conditions to obtain each of the four possible stereo isomers of 3,4-disubstituted isoxazolidines with good selectivity, through 1,3-cycloadditions between acryloyloxazolidinone and diphenylnitron (Scheme 2).

Kanemasa *et al.* proposed the complex derived from the (*R,R*)-4,6-dibenzofurandiyl-2,2-bis(4-phenyloxazoline) (*R,R*-DBFOX-Ph) ligand and $\text{Ni}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ as an excellent chiral Lewis acid catalyst in various 1,3-dipolar cycloadditions and conjugate additions. In the presence of the complex (*R,R*-DBFOX-Ph)ligand/ $\text{Ni}(\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ (10 mol%), for instance, 1,3-dipolar cycloadditions between nitrones and 3-(alk-2-enyl)-2-oxazolidinones occur with high diastereo- and enantioselectivities to give *trans*-3,4-isoxazolidines in high yields (Scheme 3) [6].

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**Scheme 1.** Diels-Alder Reaction.**Scheme 2.** 1,3-Dipolar Additions.**Scheme 3.** Synthesis of *trans*-3,4-isoxazolidines.

Although nickel perchlorate proved to be the best choice in various reactions, other perchlorates such as $Mg(ClO_4)_2$ and $Zn(ClO_4)_2 \cdot 6H_2O$ can also form very efficient chiral catalysts with (*R,R*-DBFOX-Ph) ligand. In fact, the first effective enantioselective 1,3-dipolar cycloaddition reactions between trimethylsilyldiazomethane and alkenes were achieved in the presence of these chiral complexes (Scheme 4) [7].

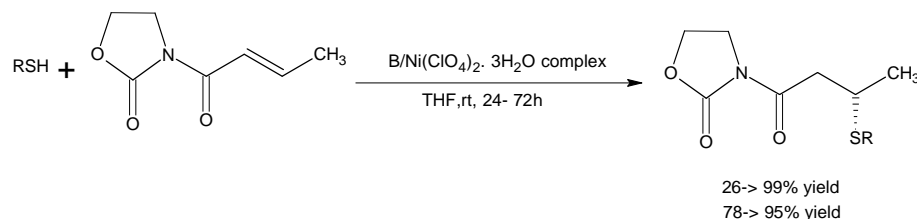
1.3. Michael addition reactions: The conjugate addition of an enolate-commonly derived from a β -dicarbonyl compound to an acceptor activated olefin such as methyl vinyl ketone results in a 1,5-dioxo constituted product [8] is known as the Michael reaction and it is among the most important C-C bond forming reactions. Traditional catalysts for this process are Bronsted bases such as tertiary amines, alkali alkoxides or hydroxides. However, the strongly basic conditions are often a limiting factor, since they can cause undesirable side and subsequent reactions. Therefore, a number of metal catalysts have been reported, which allow conversion

under milder conditions [9]. Michael addition reactions of nitromethane to 1-crotonoyl-3,5-dimethylpyrazoles was also studied using $Ni(ClO_4)_2 \cdot 3H_2O$ (Scheme 5).

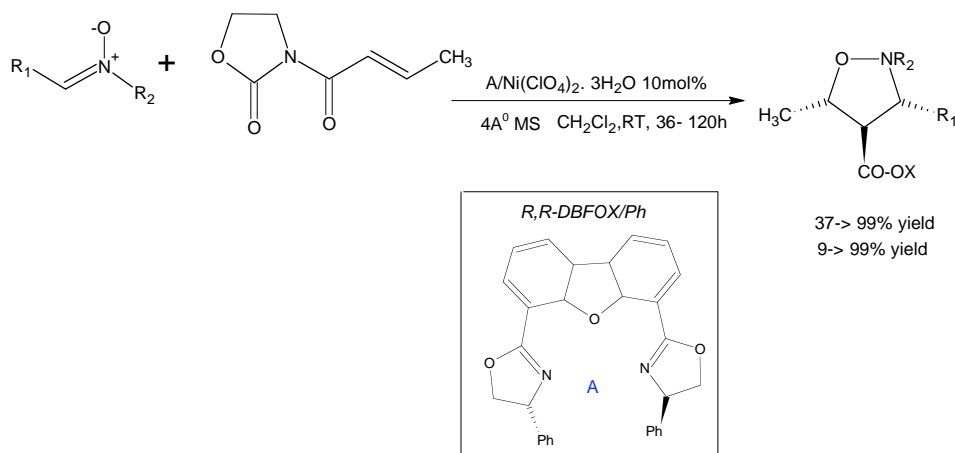
In this procedure, both α,β -unsaturated carbonyl acceptors as the electrophiles and nitromethane as the nucleophile are activated by catalytic amounts of chiral Lewis acid and amine catalysts, respectively [10]. The nitro adducts were generally obtained in very satisfactory yields and enantioselectivities, showing that the combined use of Lewis acid and amine catalysts works in a highly effective manner to accelerate Michael addition reactions with nitromethane. Analogously, [11] treatment of malononitrile with 3-(2-alkenyl)-2-oxazolidinones or 1-(alk-2-enyl)-4-bromo-3,5-dimethylpyrazoles can be doubly activated by the use of catalytic amounts (10 mol% each) of both (*R,R*-DBFOX-Ph)/ $Ni(ClO_4)_2 \cdot 3H_2O$ and an amine to give the Michael adducts in high chemical yields and with satisfactory enantioselectivities (Scheme 6).



Scheme 9. Zinc perchlorate catalyzed Michael Addition of thiols.



Scheme 10. Asymmetric conjugate Addition reactions.



Scheme 11. Chiral conjugate Additions.

tion of the complex **4** by coordination of the donor **1** to the metal center and activation through its Lewis acidity. The addition of the Michael acceptor results in the complex **5**, which is the catalytically active compound. It undergoes a conjugate addition via the intermediate **6**. Ligand exchange of the product complex **7** completes the catalytic cycle.

Conjugate addition of thiols to α,β -unsaturated ketones: Zinc perchlorate hexahydrate has been found to be a new and efficient catalyst for conjugate addition of thiols to α,β -unsaturated ketones under solvent-free conditions at room temperature (Scheme **9**) [13]

Reactions of aryl, aryl-alkyl, and alkyl thiols with cyclic and acyclic α,β -unsaturated ketones take place to afford compounds in good to excellent yields in short times. The rate of thiol addition is dependent on the electronic and steric natures of the enones and the thiols. When a substituent is present at the β -carbon of cyclic and acyclic α,β -unsaturated ketones, longer reaction times are required owing to the steric hindrance met by the conjugate addition. The addition of aryl thiols occurs more rapidly than that of alkyl ones.

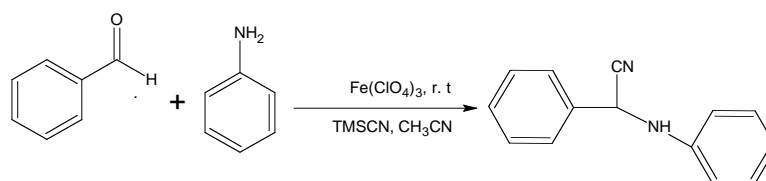
Kanemasa and co-workers was also employed the chiral catalyst (*R,R*-DBFOX-Ph) /Ni(ClO₄)₂·3H₂O carry out various asymmetric conjugate additions of nucleophiles to α,β -unsaturated carbonyl acceptors. They described the first examples of enantioselective thiol conjugate additions to 3-(alk-2-enoyl)-2-oxazolidinone cata-

lyzed by a chiral Lewis acid [14]. Among a variety of DBFOX/Ph complexes examined as chiral catalysts, the (*R,R*-DBFOX-Ph)/Ni(ClO₄)₂·3H₂O complex was exceptionally effective (Scheme **10**).

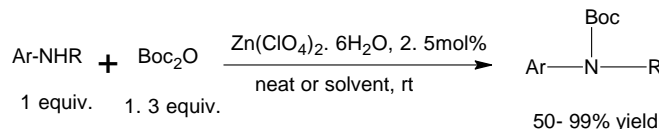
Although the complexes of DBFOX/Ph ligand of magnesium and zinc are also prepared by treatment with Mg(ClO₄)₂, Zn(ClO₄)₂·6H₂O, Zn(OTf)₂, or ZnI₂ showed satisfactory catalytic activity. On the other hand, metal complexes of the copper(II), iron(II), and manganese(II) ions perchlorates showed only a low catalytic activity.

1.4. Addition of nitrones to oxazolines: Kanemasa and co-workers used Ni(ClO₄)₂·3H₂O as an excellent chiral Lewis acid catalyst in various 1,3-dipolar cycloadditions and conjugate additions in which the complex derived from the (*R,R*)-4,6-dibenzofurandiyl-2,2-bis(4-phenyloxazoline) (*R,R*-DBFOX-Ph) ligand. In the presence of the complex **A**/Ni(ClO₄)₂·3H₂O (10 mol%), for instance, 1,3-dipolar cycloadditions between nitrones and 3-(alk-2-enoyl)-2-oxazolidinones occur with high diastereo- and enantioselectivities to give *trans*-3,4-isoxazolidines in high yields in 36-120h (Scheme **11**) [15].

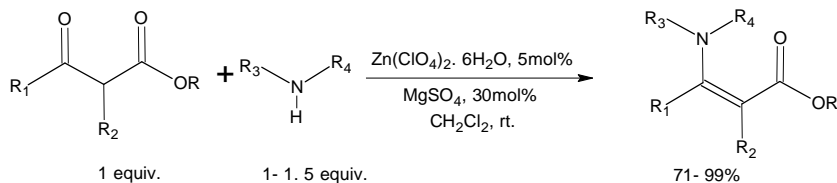
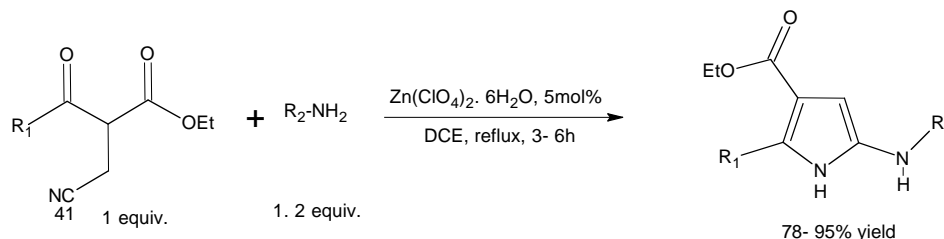
1.5. Strecker synthesis: The three component coupling of an amine, carbonyl compounds (generally an aldehyde) and either hydrogen cyanide or its alkaline metal cyanides to give α -



Scheme 12. Strecker Synthesis.



Scheme 13. Protection of amino group.

Scheme 14. Synthesis of N-substituted- β -enaminoesters).

Scheme 15. Synthesis of aminopyrroles via annulation reactions.

aminonitriles [16] constitutes an important indirect route in the synthesis of α -amino acids [17]. In the first step, the condensation of amine and carbonyl compound gives Schiff's base which undergoes nucleophilic addition to give α -aminonitriles. Ferric perchlorate acted as a mild Lewis acid might be a useful and inexpensive catalyst for the synthesis of α -aminonitrile. The reaction of aldehydes and amines with TMSCN in the presence of a catalytic amount of ferric perchlorate afforded the corresponding α -aminonitriles in acetonitrile as a solvent in high yields (Scheme 12) [18, 19].

1.6. Protection of arylamines as N-Boc derivatives: Protection of the amino group is often required during the synthesis of peptides, amino acids, and other natural products, so various reagents and methodologies by which to introduce this protection by use of Boc_2O have been developed over the years. Bartoli et al. exploited the high efficiency of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ in the protection of arylamines as N-Boc derivatives. Most of them require the presence of a base and work well only with alkylamines; the analogous reactions of primary and secondary arylamines proceed sluggishly, owing to their reduced nucleophilicity, and various side reactions can occur. The reactions proceed with the nucleophilic addition of the arylamine to carbonyl of Boc_2O . On the other hand, methods that use a Lewis acid catalyst to perform this protection are still rare. We reported the first example of an efficient protection methodology that employs $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, a simple and mild Lewis acid, as the catalyst (Scheme 13) [20].

The reaction works with primary and secondary aromatic amines under mild conditions and the protecting agent is used only in a small excess. Reaction rates and yields are governed by the

nucleophilicity of the amines. In particular, activated anilines give the Boc derivatives in very good yields, while deactivated substrates; on the other hand, give the protected derivatives with acceptable results in view of their low reactivity. The protection reaction is chemoselective: the amine is exclusively protected in the presence of amide, acid, indole, and thiol groups.

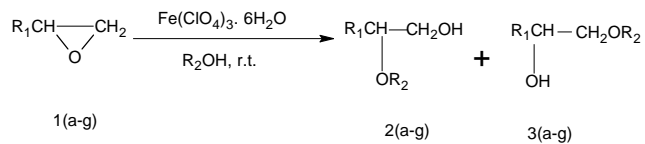
1.7. Condensation of primary and secondary amines with β -keto esters: $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ proved to be a very powerful catalyst for the condensation of primary and secondary amines with β -keto esters to give N-substituted β -enaminoesters (Scheme 14) [21] that can act as valuable intermediates for the synthesis of, for example, biologically active compounds. Even in this procedure, the addition of 30 mol % of MgSO_4 is required to improve yields. The catalyst can easily be recovered and recycled. Recently this technique is exploited for the stepwise synthesis of complex chiral piperidines [22] and tetrahydropyridines [23].

Peculiar reactivity pattern was observed when the starting β -keto ester bore a cyanomethyl group in the α -position (Scheme 15). In this particular case the addition of amine occurs on the CN triple bond rather than on the $\text{C}=\text{O}$, and a subsequent annulation reaction gives aminopyrroles using $\text{Zn}(\text{ClO}_4)_2 \cdot 6(\text{H}_2\text{O})$ [24].

2. EPOXIDATION

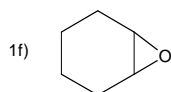
2.1. Opening of epoxides: Epoxidation of olefins followed by regioselective epoxide cleavage provides a powerful entry into specifically functionalized molecules β -alkoxy alcohols constitute an important class of organic compounds both because this type of functionality is often present in naturally occurring compounds and

because of their easy oxidation to α -alkoxy ketones or acids. Many reagents have been used in order to achieve the alcoholysis, hydrolysis and acetolysis of 1,2-epoxides under mild conditions [25-40]. Ring opening reaction of different classes of epoxides in primary, secondary and tertiary aliphatic alcohols in the presence of 0.01-0.05 molar equivalents of ferric perchlorate have been achieved (Scheme 16) [41].



R₁ or epoxide

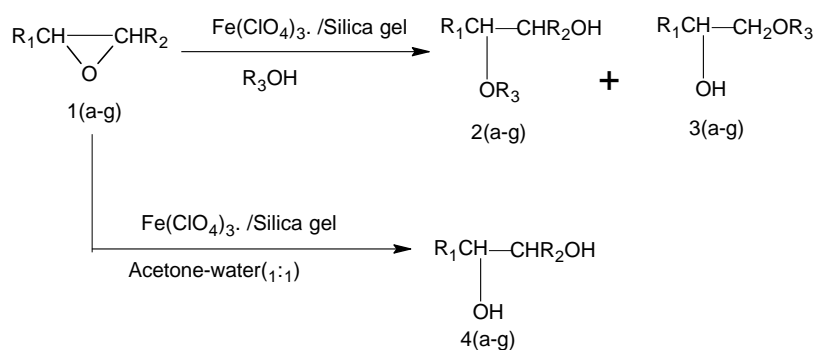
- 1a) Ph-
1b) PhOCH₂-
1c) (CH₃)₂CHOCH₂-
1d) CH₂=CH-CH₂-O-CH₂-
1e) ClCH₂-



1g) n-C₄H₉-

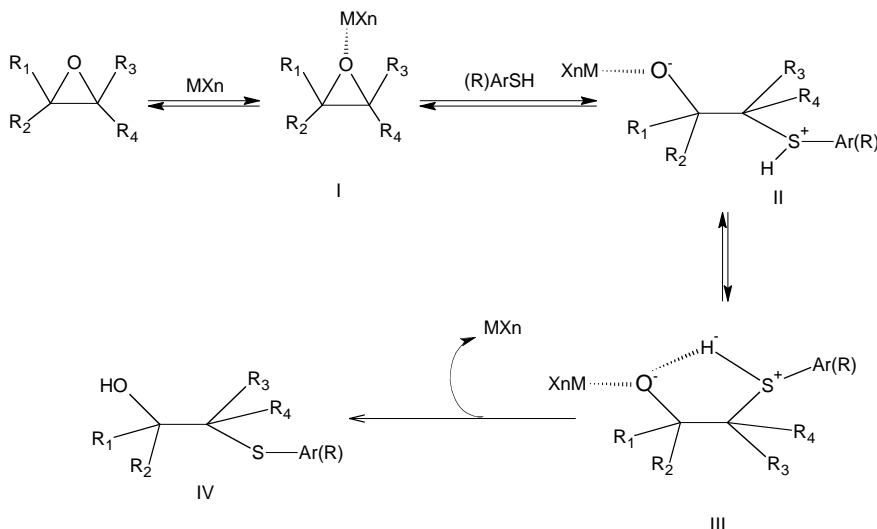
R₂ = Me, Et, n-Pr, i-Pr, t-Bu.

Scheme 16. Alcoholic epoxide ring opening.



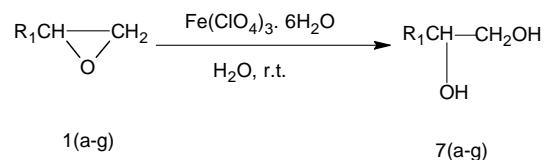
R₁ = Ph, R₂ = H (a); R₁⁺ R₂⁻ = -(CH₂)₄- (b); R₁ = Bu, R₂ = H (c); R₁ = ClCH₂, R₂ = H (d); R₁ = BuOCH₂, R₂ = H (e) R₁ = PhOCH₂, R₂ = H, (f); R₁ = CH₂-CHOCH₂, R₂ = H (g); R₃ = Me, Et, Pr, i-Pr, t-Bu

Scheme 18. Regioselective epoxide ring opening.



Scheme 19. Synthesis of sulfides from epoxides.

The reaction of epoxides with water was also preceded efficiently in the presence of 0.01-0.05 molar equivalents of ferric perchlorate (Scheme 17) [41].



Scheme 17. Aqueous epoxide ring opening.

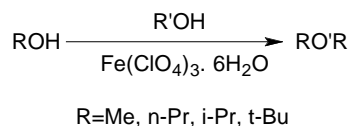
Ferric perchlorate hexahydrate on silica gel used for the ring opening of epoxides with primary, secondary, and tertiary alcohols and β -alkoxyalcohols were obtained in good and even excellent yields and high regioselectivity. Hydrolysis of epoxides has also been investigated in the presence of catalytic amounts of ferric perchlorate on silica gel. The reaction was carried out in a mixture of equal volumes of acetone and water, and it gave rise to vicinal diols in excellent yields (Scheme 18) [42].

Zinc perchlorate hexahydrate is found to be as a new and highly efficient catalyst for the synthesis of 2-hydroxysulfides by opening of epoxide rings with thiols under solvent free conditions. The catalytic activity of various group I/II metal perchlorates followed the order $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} >> \text{Mg}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} > \text{Ba}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O} >>>$

LiClO_4 . The $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ catalysed reaction of epoxides derived from cyclic and acyclic olefins with thiols afforded β -hydroxysulfides in high yields. Reaction with cycloalkene oxides led to stereoselective formation of the trans-2-hydroxysulfides (Scheme 19) [43].

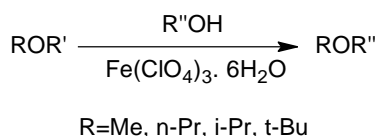
3. ETHERIFICATION/TRANSEETHERIFICATION

3.1. Conversion of alcohol to ethers: This common method for the conversion consists of the reaction of metal salt of alcohols with different alkylating agents in the presence of various catalysts [44-47]. The condensation of alcohols and their salts with aldehyde, olefins and alkyloxides [48], dialkyl phosphates [49] and alcohols [50, 51] have been reported. In the presence of ferric perchlorate as a catalyst, different kinds of allylic, secondary and tertiary benzylic alcohols can be subjected to solvolytic etherification in alcohols and bulky ethers were also synthesized in high yields (Scheme 20) [52].

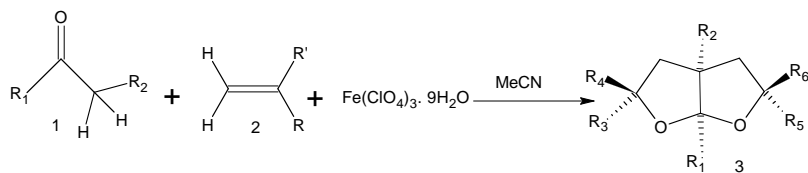


Scheme 20. Synthesis of epoxides.

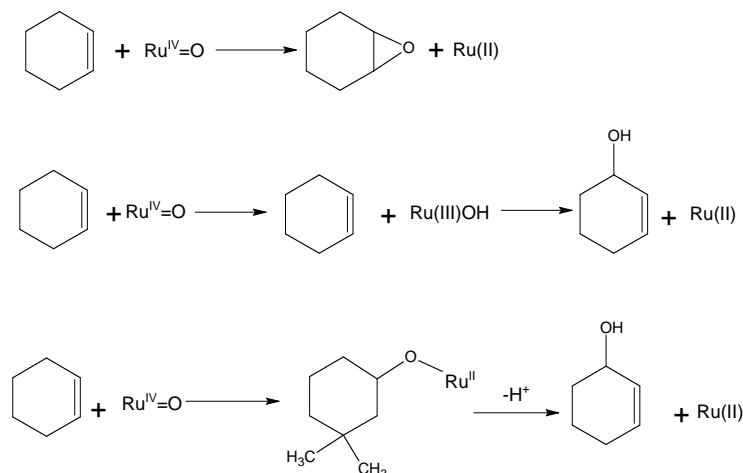
3.2. Transeetherification of ethers: Exchange of one alkoxy group to another for transeetherification is very rare for ethers [53]. Catalysts such as: p-toluenesulfonic acid [54], treatment of alkylaryl ethers with alkoxide ions [55], preparation of enol ethers by mercuric acetate [56] are some examples. Selective and efficient transeetherification of ethers has been carried out in the presence of ferric perchlorate successfully (Scheme 21) [57].



Scheme 21. trans-etherification.



Scheme 22. Oxidative cyclization of carbonyl compounds.



Scheme 23. Oxidation of alkenes.

4. OXIDATION REACTION

4.1. Aromatization of 1,4-DHP: The oxidation of the dihydropyridine ring is the main metabolic route for NADH mimics, exploring the reactions and mechanisms of these compounds, and utilizing them in a variety of synthetic reactions. The aromatization of 1,4-DHP is also one of the ubiquitous problems in organic chemistry, and several researchers have reported oxidation methods including chemical oxidation with ferric or cupric nitrates on a solid support [58], oxidation with ceric ammonium nitrate [59], ultrasound-promoted oxidation by clay-supported cupric nitrate [60], oxidation with pyridinium chlorochromate [61], oxidation with nitric acid [62], CuCl_3 [63], $\text{Mn}(\text{OAc})$ [64], voltammetric oxidation of 1,4-DHP in protic [65] and Pd/C in acetic acid [66].

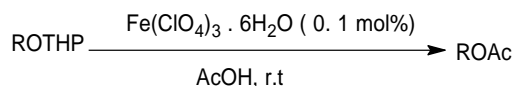
4.2. Oxidation of carbonyl compounds: In the presence of conjugated dienes carbonyl compounds (aldehydes and ketones) are oxidized into α,α -diaddition products using ferric perchlorate as a catalyst in acetonitrile (Scheme 22) [67].

4.3. Oxidation of alkenes: Oxidation of alkenes are also catalyzed by ruthenium(II) complexes containing coordinated perchlorate. ruthenium(II) perchlorate complexes $[\text{Ru}(\text{dppm})_3(\text{ClO}_4)]\text{ClO}_4$, $[\text{Ru}(\text{dppe})_3(\text{ClO}_4)]\text{ClO}_4$ and $[\text{Ru}(\text{dpae})_3(\text{ClO}_4)]\text{ClO}_4$ catalyze the selective homogeneous oxidation of alkenes with TBHP and H_2O_2 as oxidizing agents [68]. Oxidation of alkenes is also reported with above mentioned ruthenium(II) complexes containing coordinated perchlorate in the presence of cumene hydroperoxide (CHP) under homogeneous liquid phase. But linear alkenes like 1-heptene and 1-octene are not efficiently oxidized under these conditions (Scheme 23) [69].

4.4. Oxidation of ketones: Praveen Tondon *et al.* reported the oxidation of ketones by Ceric perchlorate catalysed by iridium(III). In search of economical and effective catalyst it was found that IrCl_3 , a sluggish catalyst in alkaline media, suppresses catalytic efficiency of osmium and ruthenium in aqueous perchloric acid medium in the oxidation of aliphatic ketones by ceric perchlorates [70].

5. SUBSTITUTION REACTION

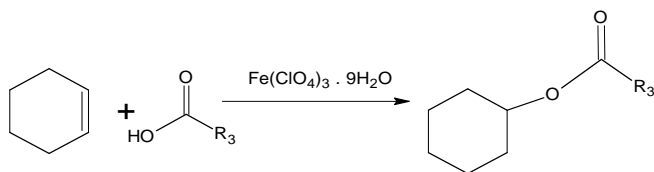
Deprotection of THP ethers: Although there are several methods for deprotection of THP ethers [71-74] and conversion of alcohols into acetates, methods for direct conversion of THP ethers to acetate are limited and even those suffer from serious drawbacks. The method available for the direct conversion of THP ethers to the corresponding acetates includes $\text{FeCl}_3/\text{Ac}_2\text{O}$, AcOH/AcCl , $\text{Ti}/\text{Ac}_2\text{O}$, bismuth salts, $\text{Cu}(\text{OTf})_2/\text{Ac}_2\text{O}$ and ZrCl_4 [75-78]. Ferric perchlorate in catalytic amounts can convert THP ethers directly and efficiently to the corresponding acetates in high yields in a one-pot reaction in the presence of acetic acid (Scheme 24) [79].



Scheme 24. Substitution Reaction.

6. ESTERIFICATION/TRANSESTERIFICATION

The esterifications and transesterifications are very important reactions in synthetic organic chemistry laboratories as well as academic laboratories for the preparation of polyesters from alcohols and acids or esters [80]. Selective esterification of carboxylic acids using aromatic and aliphatic alcohols is a useful organic reaction. The esters thus obtained are utilized to prepare fine chemicals used in the synthesis of drugs, food preservatives, solvents, perfumes, pharmaceuticals, plasticizers, and cosmetics [81-83]. Recently, Preyssler's anion catalyst, $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$ used for highly selective and efficient esterification of salicylic acid with some aliphatic and benzylic alcohols [84]. Also, an efficient transesterification of β -ketoesters using triphenylphosphine as catalyst has been described with various alcohols [85]. In 1992, Kumar [86] *et al.* reported the esterification of aliphatic acids using equivalent proportions of halide/alcohol/olefin in the presence of ferric perchlorate at room temperature (Scheme 25) [87-89].



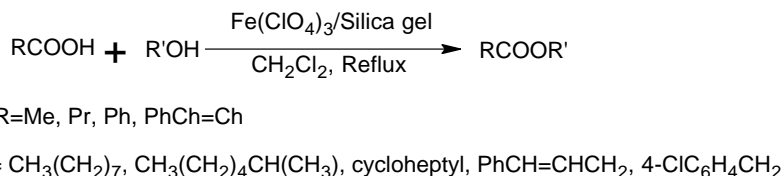
Scheme 25. Hydro-esterification of alkenes.

Substituted succinanic esters are obtained in good to excellent yields from succinanic acids by reaction with alcohols in the presence of ferric perchlorate [90]. Ferric perchlorate successfully has

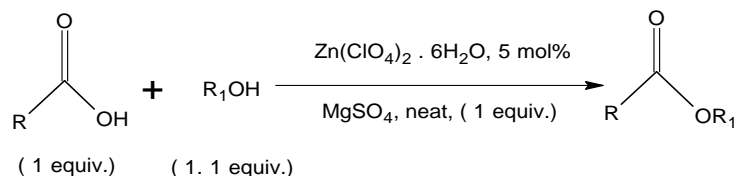
been used for the transesterification of ethyl acetate with alcohols and acids [91]. Adsorption of $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ onto chromatographic grade silica gel in the presence of alcohol (being used for esterification) produces a supported reagent, $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{ROH}/\text{SiO}_2$. This reagent has been found effective for the rapid and high yielding synthesis of esters, on grinding in the presence of carboxylic acids using pestle and mortar in the solid state [92]. The direct esterification with various acids and alcohols has been performed in dichloromethane. Reactions of acetic and butyric acids with saturated, cyclic, benzyl, and allyl alcohols were successfully run in the presence of 0.1-0.4 mole equivalent of Fe^{3+} in dichloromethane within 5-19 h. Similar reactions were also carried out with benzoic and cinnamic acids to obtain the corresponding esters in good or excellent yields (70-92%) using $\text{Fe}(\text{ClO}_4)_3 \cdot 6(\text{H}_2\text{O})$ (Scheme 26).

The system of $\text{Fe}(\text{ClO}_4)_3/\text{silica gel}$ has been used as a catalyst for acetylating and adsorption of $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ onto chromatographic grade silica gel in the presence of ethyl acetate (being used for transesterification) produces a supported reagent, $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{EtOAc}/\text{SiO}_2$. This reagent has been found effective for the rapid formation and high yield of esters via transesterification on grinding in the presence of alcohols/carboxylic acids using pestle and mortar in the solid state [93]. On the basis of these preliminary results we developed a method for the acylation of alcohols promoted by trace amounts of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.1-1 mol-%). The methodology is general and works with a large variety of substrates and anhydrides. The high efficiency of $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ allows reactions between poorly reactive substrates such as sterically hindered tertiary alcohols and aromatic anhydrides to be performed. All the reactions are carried out at a 1:1.05 alcohol/anhydride ratio at temperatures ranging from 20 to 70°C, with yields between 90 and 99% always being attained. These conditions are convenient both from a practical and from an economic point of view, since they avoid waste of reagents and allow a simple workup procedure. In terms of atom economy, however, this esterification process is still far from perfect. In fact, the reaction between almost equimolar amounts of a carboxylic acid and an alcohol should be the most straightforward and convenient way to prepare esters. We found [94] that $\text{Zn}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ efficiently catalyzes esterification between nearly equimolar amounts of carboxylic acids and alcohols when used at 80-100°C under SFCs in the presence of MgSO_4 (Scheme 27).

The reaction works without solvent at relatively low temperatures, and the catalyst can be filtered off, regenerated in oven at 60°C, and reused without loss of activity. Excellent results were obtained with a wide range of substrates, and various functionalities



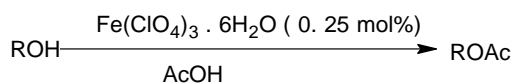
Scheme 26. Esterification by ferric perchlorate.



Scheme 27. Esterification by zinc perchlorate.

can tolerate the reaction conditions. To evaluate the application of the procedure to large-scale esterification, a reaction was scaled up to 100 mmol, giving almost the same results as the small-scale run (1 mmol).

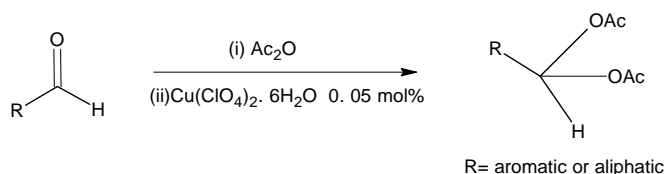
6.1. Acetylation of alcohols: Acetylation of alcohols is an important and routinely utilized transformation in organic chemistry [95]. Among the various protecting groups used for the hydroxyl group, acetyl is one of the most common groups used. This is due to its facile introduction, stability under acidic conditions and also the ease of removal by mild alkaline hydrolysis [96]. A variety of reagents catalyzed acetylation of alcohols with acetic anhydride in solvent has been reported. Lewis acids such as TaCl₅ [97], Cerium(III) triflate [98], Tin(IV) porphyrin [99], Mg(III) acetate [100], metallic Lewis acids [101], Zeolit HSZ-360 [102], Me₃SiOTf [103], Cu(OTf)₃ [104], Mg(Br)₂ [105], Sc(OTf)₃ [106], In(OTf)₃ [107], Bi(OTf)₃ [108], Vanadyl(IV)acetate [109], Iodine [110] lithium perchlorate [111] magnesium perchlorate [112] Zn(ClO₄)₂·6H₂O [113] HfCl₄·2THF [114] H₁₄[NaP₃W₃₀O₁₁₀] [115] have been used as catalysts for this transformation. Ferric perchlorate (0.25 mol%) is able to promote quantitative acetylation of alcohols and phenols using acetic acid as acetylating agent at room temperature in high yields (Scheme 28).



R = allyl-, aryl-, alkyl-, benzyl-, phenyl-, propargyl-

Scheme 28. Acetylation of alcohols.

6.2. Functional group protection: Copper perchlorate also acts as the efficient acetylation catalyst under solvent free conditions. In the case of acetylation of benzyl alcohol, 10 mmol of benzyl alcohol was added to the 1 equiv. of acetic anhydride followed by 0.05 mol % of Cu(ClO₄)₂·6H₂O. Yield of benzyl acetate with 99% purity was obtained. Among the aliphatic alcohols, primary, allylic, secondary, *tert*-propargylic and benzylic alcohols are used as substrates acetylated successfully using Cu(ClO₄)₂·6(H₂O). (Schemes 29) [116].

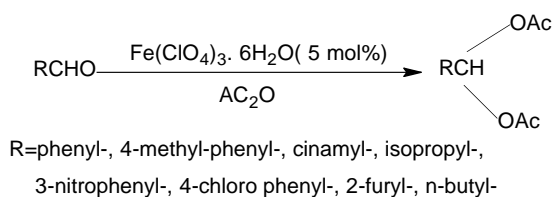


Scheme 29. Carbonyl Group Protection.

6.3. Acylation reaction: Zn(ClO₄)₂·6H₂O acts as acylation catalyst for poor nucleophilic phenols, alcohols and amines. The catalyst was found to be of general use with respect to other acylating agents such as propionic, *iso*-butyric, pivalic, benzoic and chloroacetic anhydrides. However, the rate of acylation was influenced by the steric and electronic factors of anhydrides and followed the order Ac₂O > (PhCO)₂O > (^tPrCO)₂O > (^tBuCO)₂O >> (ClCH₂CO)₂O [117]. With regard to the acylation of alcohols, Bartoli found [118] Zn(ClO₄)₂·6H₂O to be much more powerful than Mg(ClO₄)₂ and Bi(OTf)₃, the most active of the metal triflates [119]. The acylation of alcohols promoted by trace amounts of Zn(ClO₄)₂·6H₂O (0.1–1 mol-%). The methodology is general and works with a large variety of substrates and anhydrides. The high efficiency of Zn(ClO₄)₂·6H₂O allows reactions between poorly reactive substrates such as sterically hindered tertiary alcohols and

aromatic anhydrides to be performed. All the reactions are carried out at a 1:1.05 alcohol/anhydride ratio at temperatures ranging from 20 to 70 °C, with yields between 90 and 99% always being attained.

6.4. Preparation of 1,1-diacetate: Acylals [120] are synthetically useful protecting groups for carbonyl compounds due to their stability and they are also important building blocks for the synthesis of dyes in Diels-Alder reaction [121]. Since Knoevenagel and Clausen recognized that aldehydes could be transformed into the 1,1-diacetates with acetic anhydride in the presence of a catalytic amount of sulfuric acid, several modification of this transformation with a variety of reagents and catalysts have been developed. Some of them are AIPW₁₂O₄₀ [122], indium triflate [123], bismuth nitrate [124], chemoselective and convenient preparation of 1,1-diacetates from aldehydes, by solid lithium perchlorate [125] and many other catalysts were also reported and were given in the aforementioned references. An efficient, convenient and solvent-free out for preparation of 1,1-diacetates from aldehydes with catalytic amount of ferric perchlorate reported. These reactions have been performed using 5 mol% of the catalyst (Scheme 30).

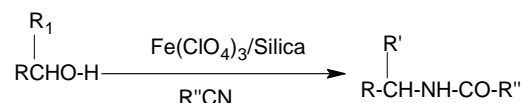


Scheme 30. Synthesis of diacetates.

When acetophenone-4-carbaldehyde used, smooth selective conversion of the aldehyde to the corresponding diacetate was observed while the ketone functionality remained intact.

7. AMIDATION

7.1. Ritter reaction: Among the applied acidic reagents for Ritter reaction the following are used: (CF₃SO₂)₂O [126], Ph₂CCl⁺SbCl⁶⁻ [127], BF₃·ET₂O [128], CoCl₂·Ac₂O [129] and Co(III)-DMG complex [130]. Ferric perchlorate hexahydrate supported on silica gel has been applied as a new and efficient reagent for one pot conversion of primary and secondary benzylic alcohols with nitriles to different substituted amides (Scheme 31) [131].

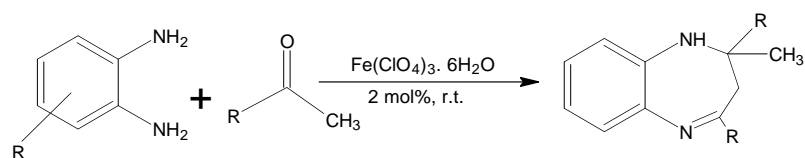
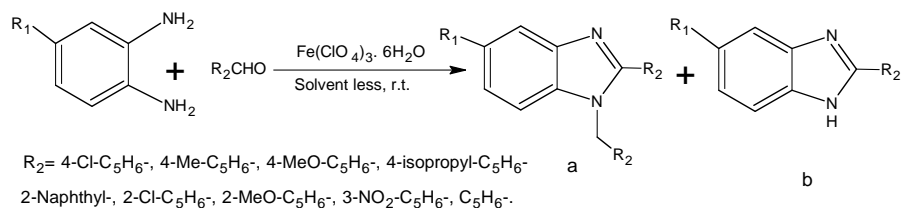
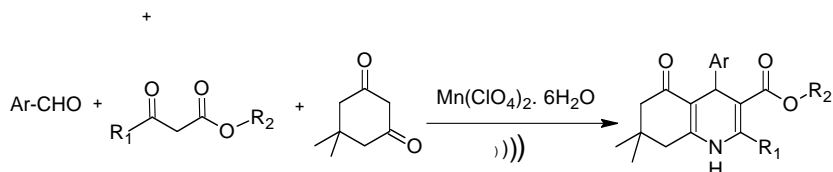


Scheme 31. Ritter Reaction.

Adsorption of Fe(ClO₄)₃·6H₂O onto chromatographic grade silica gel produces a supported reagent Fe(ClO₄)₃·6H₂O/SiO₂. This reagent has been found effective for the rapid and high yield regeneration of the carbonyl compounds from azines, oximes, semicarbazones, thiosemicarbazones and Schiff's base's on grinding in the solid state, using pestle and mortar [132].

8. POLYMERIZATION

8.1. Preparation of polypyrrole/polyethylene composite films: Electrically conductive polypyrrole/polyethylene composite films were prepared by the vapour-phase polymerization of pyrrole on porous polyethylene films containing FeCl₃ or Fe(ClO₄)₃ as a oxidants. It was found that the composite films have excellent mechanical properties compared to polypyrroles [133].

**Scheme 32.** Synthesis of 1,5-benzodiazepines.**Scheme 33.** Synthesis of benzamidazoles.**Scheme 34.** Synthesis of 1,4-DHP.

8.2. Synthesis of polypyrrole: polypyrrole has been synthesized using various oxidizing agents and examined as a positive electrode material. Polypyrrole has also synthesized on various conducting and nonconducting substrates using $\text{Fe}(\text{ClO}_4)_3$ as oxidizing reagent. By using PP nonwoven fabric as a substrate material, a high discharge capacity of 72 mA hg^{-1} was obtained. Polypyrrole synthesized on only one side of nonwoven fabric was able to be used as an electrode.

9. MUTICOMPONENT REACTIONS

9.1. Synthesis of benzodiazepines and benzimidazole derivatives: benzodiazepines are the interesting compounds because they belong to an important class of the pharmacologically preeminent 1,5-benzodiazepines which has been extensively used as anticonvulsant, antianxiety, analgesic, sedative, antidepressive, hypnotic and anti-inflammatory agent. A variety of catalysts such as $\text{BF}_3 \cdot \text{OEt}_2$ [134], $\text{PPA} \cdot \text{SiO}_2$ [135], $\text{MgO} \cdot \text{POCl}_3$ [136], $\text{Yb}(\text{Otf})_3$ [137], HO-Ac-microwave [138], $\text{SO}_4^{2-} \cdot \text{ZrO}_2$ [139], I_2 [140], InBr_3 [141], $\text{Ag}_3\text{PW}_{12}\text{O}_{40}$ [142], $[\text{L-proline}]_2\text{Zn}$ [143], solid acid [144] and ionic liquids [145, 146] have been employed to effect this transformation. Due to interesting applications of 1,5-benzodiazepines, we have recently reported a novel and efficient solvent-free process demonstrated for the synthesis of 1,5-benzodiazepines using ferric perchlorate as a catalyst (Scheme 32) [147].

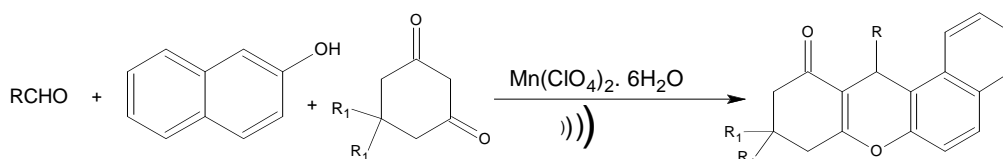
In recent years the preparation of benzimidazoles has also gained considerable attention [148-149]. The 2-aryl-1-arylmethyl-1H-1,3-benzimidazoles were obtained in good yields by the reaction of o-phenylenediamine derivatives with various aldehydes in the presence of ferric perchlorate in the absence of solvent at ambient temperature. The method has the ability to tolerate other functional groups such as methyl, methoxy, nitro and chloro groups (Scheme 33) [150].

9.2. Glycosylation reaction: α -C and N glycosylation reaction: Scandium(III)perchlorate acts as a novel catalyst for the organic synthesis. Hachiya and Kobayashi also reported the Scandium(III)perchlorate as a novel catalyst in the α -C- and N-glycosylation reactions (21) [151].

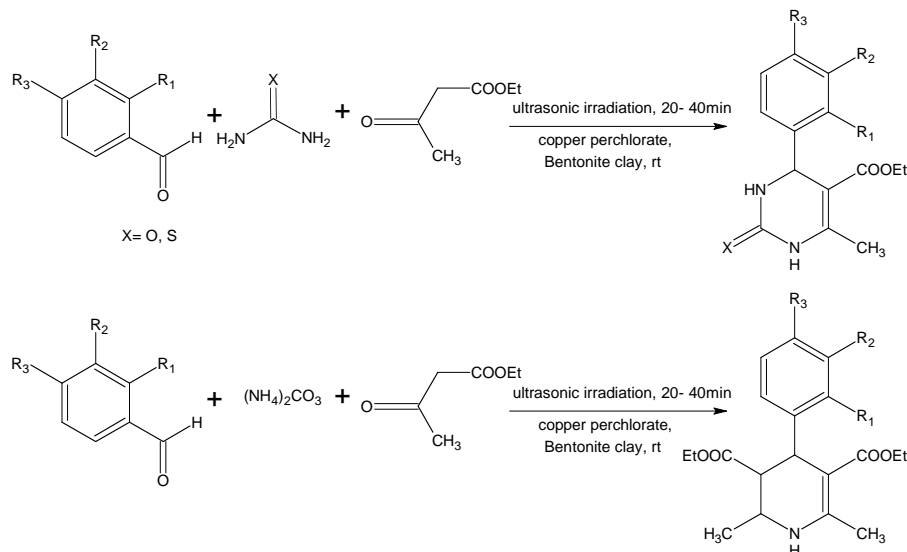
9.3. The synthesis of 4-substituted 1,4-dihydropyridine (1,4-DHP) nucleus is of great significance in synthetic organic chemistry due to its biological and pharmacological properties such as vasodilator, antihypertensive, bronchodilator, antithrombotic, hepatoprotective, antitumor, antimutagenic, geroprotective and antidiabetic agents [152]. So, the remarkable potential of novel 1,4-DHP and polyhydroquinoline derivatives as the source of valuable drugs and useful intermediate in organic chemistry is the main reason for its synthesis by different methodologies. Recently, several methods for the synthesis of polyhydroquinolines have been demonstrated by using molecular iodine [153], $\text{HClO}_4/\text{SiO}_2$ [154], $\text{Yb}(\text{OTf})_3$ [155], Baker's yeast [156], organo catalysts [157] and polymers [158, 159] Kumar *et al.* [160] reported the one pot synthesis of polyhydroquinoline derivatives using manganese perchlorate hydrate as a catalyst under ultrasonication Through the Hantzsch four component condensation (Scheme 34).

9.4. The synthesis of 12-Aryl or 12-Alkyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one Derivatives catalyzed by manganese perchlorate hydrate under ultrasonication via one pot three component reaction is also reported by Kumar *et al.* [161]. 12-Aryl or 12-Alkyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one have been synthesized by the condensation of aldehyde, 2-naphthol and 1,3-cyclohexadione or 5,5-dimethyl 1,3-cyclohexadione. Many reagents have been reported in the literature for this condensation including CAN [162] $\text{HBF}_4/\text{SiO}_2$ [163], $\text{HClO}_4/\text{SiO}_2$ [164], dodecatungstophosphoric acid [165], Sulfamic acid [166], Cyanuric Chloride [167]. The synthesis of 12-Aryl or 12-Alkyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one derivatives catalyzed by manganese perchlorate hydrate under ultrasonication via one pot three component reaction is shown in (Scheme 35).

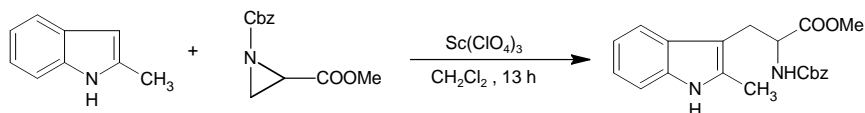
9.5. Hantzsch and Biginelli synthesis: Ferric perchlorate was found to be an efficient catalyst for the synthesis of 3,4-dihydropyrimidinones and thiones from an aldehyde, β -keto ester, urea and thiourea in acetonitrile. This new method has the advantages of being fully catalytic, good yields and requiring shorter reaction times as compared to the other catalysts used for this reaction [168-170]. Kumar *et al.* also reported the ultrasound promoted



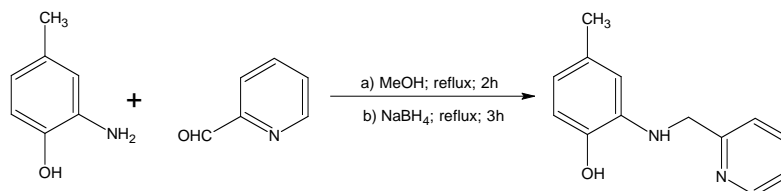
Scheme 35. Synthesis of substituted tetrahydrobenzo[α]xanthenones.



Scheme 36. Hantzsch and Biginelli synthesis.



Scheme 37. Synthesis of tryptophan derivatives.



Scheme 38. Synthesis of amines.

synthesis of substituted 1,2,3,4-tetrahydropyrimidine-2-ones and Hantzsch 1,4-dihydropyridines in dry media catalyzed by copper perchlorate (Scheme 36) [171].

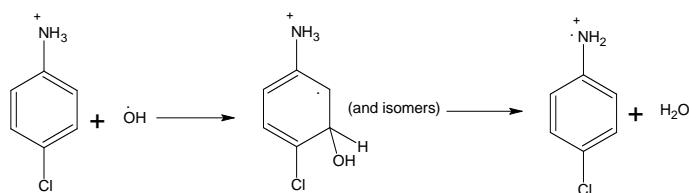
9.6. Synthesis of tryptophan derivatives: In the synthesis of optically active tryptophan derivatives, the Lewis acid-promoted coupling between indole and optically active serine-derived aziridine carboxylate is attractive because of flexibility and convergence. Scandium perchlorate has been found to be a superior Lewis acid to the previously reported Scandium triflate with respect to the yields as well as regioselectivity of aziridine ring opening (Scheme 37) [172].

9.7. Oxidative dehydrogenation of amine function to an imine group: The ligand (hpyramol=4-methyl-2-*N*-(2-pyridylmethyl)aminophenol) is found to undergo an oxidative dehydrogenation of its amine function to an imine group upon coordination with iron(II) chloride and manganese(II) perchlorate. The $\text{FeN}_2\text{O}_2\text{Cl}_2$ chromophore, while the manganese(II) ions in $[\text{Mn}(\text{ClO}_4)(\text{pyrimol})(\text{Hpyrimol})_2]$ are in distorted octahedral MnN_4O_2 environment with 2:1 ligand to metal ratio instead of 1:1 (Scheme 38) [173].

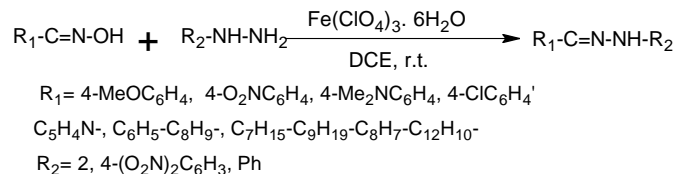
10. MISCELLANEOUS REACTIONS

10.1. Degradation of phenols and substituted phenols: Iron salts FeCl_3 and $\text{Fe}(\text{ClO}_4)_3$ promote degradation of phenols and substituted phenol. Certain solid metal oxides e.g. CuO and V_2O_5 are also capable promoting the aerobic photodegradation of phenols. Experiments with four different bioassay organisms (green algae *Chlorella vulgaris*, photobacteria *Benickea harveyi*, infusoria *tetrahymena pyriformis* and cladoceran organisms *daphnia magna*) have demonstrated that oxidative photodegradation of the 2,4,5-trichlorophenol solution promoted by FeCl_3 , $\text{Fe}(\text{ClO}_4)_3$ and V_2O_5 leads to complete or noticeable decrease in the toxicity of the solution in respect to all the organism except *tetrahymena pyriformis* [174].

10.2. Differentiation of organic sulfur forms in coal: various organic sulfur forms are differentiated in coal by stepwise oxidation with the mixture of perchloric acid and ferric perchlorate $\text{Fe}(\text{ClO}_4)_3$. Various organic sulfur compounds were oxidized with perchloric acid solution containing $\text{Fe}(\text{ClO}_4)_3$. And the amount of sulfate



Scheme 39. Mechanism of degradation of pollutants.



Scheme 40. Synthesis of aryl hydrazones.

formed during the reaction was measured. The compounds can be grouped into three categories according to their reactivity as follows. (1) Easily oxidized ones (2) less reactive ones (3) relatively stable ones. The organic sulfur in these coals could be differentiated into various groups according to their reactivities [175].

10.3. The degradation of a prototypical halogenoaromatic pollutants: The degradation of a prototypical halogenoaromatic pollutant, 4-chloroaniline, photoinduced by Fe(III) species, has been studied in acidic aqueous solution (pH 2-4) of $Fe(ClO_4)_3$ by means of product analysis and nanosecond transient absorption spectroscopy [176]. The degradation process is initiated by the attack of OH radicals on 4-CA, leading to radical cations, $4\text{-CA}^{\cdot+}$ as the major transient species. The formation of OH radicals, as found in several other studies [177-181]. The OH adducts are subsequently converted, by loss of H_2O , to $4\text{-CA}^{\cdot+}$ absorbing at 445nm, in a reaction whose rate increases with decreasing P_H . The overall sequence can be written as in reaction (Scheme 39).

10.4. Cyclosilylation reaction: $Cu(ClO_4)_2 \cdot 6H_2O$ has been found to be an efficient catalyst for cyclosilylation reaction of aldehydes in THF at room temperature with 1.0 mol% of the catalyst in short reaction time (mostly within 10 min.) [182].

10.5. Dicyanamides are hydrolyzed into amidocyanamide during its interaction with Cu(II) perchlorate and 2-pyridylcarbonyl-N,N-bis(2-pyridylmethyl)amine. The reaction of $Cu(ClO_4)_2$, 2-pyridylcarbonyl-N,N-bis(2-pyridylmethyl)amine (DPA-CO-py) and sodium dicyanamide (Nadca) in aqueous medium led to formation of three complexes: $\{[Cu(DPA)(\mu_{1.5}\text{-dca})-ClO_4]_n, [Cu_2(pic)(\mu_{1.3}\text{-H}_2\text{NCO-N-CN)}_2(H_2O)_2] \cdot 2H_2O$ and $Cu_2(pic)_2 \cdot H_2O$ [183].

10.6. Synthesis of Arylhydrazones: A convenient and practical method has also been developed for the synthesis of arylhydrazones in a one pot straightforward conversion of oximes, using ferric perchlorate as a catalyst (Scheme 40) [184].

CONCLUSION

The general use of perchlorates had for a long time been avoided, owing to the fear they could act as powerful oxidizers and explosives. Transition metal perchlorates are powerful and selective catalysts that can usually be employed under mild reaction conditions, at relatively low temperatures, and several functional groups are well tolerated. In several cases, transition metal perchlorates proved to be much more active than other commonly used Lewis acids, such as triflates, while at the same time being much less expensive. We believe a great number of acid catalyzed organic reactions can be performed by using these catalysts. Therefore, using

Transition metal perchlorate recommended for different purposes in organic chemistry which requires Lewis acid catalysis.

CONFLICT OF INTEREST

None.

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