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Hydrated Ferric Perchlorate, $Fe(ClO_4)_3.XH_2O$ in Organic Synthesis. A Short Review

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In this short review, we wish to present an overview of the applications of hydrated, ferric perchlorate, $Fe(ClO_4)_3.XH_2O$ as an available and inexpensive reagent amd catalyst in organic synthesis.

Keywords: Ferric perchlorate, Catalyst, Carbon-carbon cleavage and formation, Oxidation, Multi-component reaction

INTRODUCTION

Lewis acids accelerate a wide range of organic reactions by binding to and thereby activating reactants. This activation often results in rate increases of many orders of magnitude compared with the thermal reaction. The milder reaction conditions and the potential of the Lewis acid to act as template, both contribute to an increase in the selectivity of the transformations. Much attention has focused on the development of Lewis acid catalysts and on chiral Lewis acids for asymmetric synthesis. Important conditions for the catalytic, rather than stoichiometric, use of a Lewis acid are: (i) that activating bond-formation is reversible, and (ii) that Lewis acid-reactant binding is stronger than Lewis acid-product binding (to avoid product inhibition of the reaction).

Transition metal Lewis acids are promising and interesting because the precursor is often structurally well-defined and steric and electronic ligand tuning to a particular reaction is easier [1a]. In addition, there is current research and general interest in heterogeneous systems because of their importance in industry and in developing technologies [1b]. Heterogeneous organic reactions have proven useful to chemists in the laboratory as well as in the industrial context. These reactions are effected by the reagents immobilized on the porous solid supports and have advantages over the conventional solution phase reactions because of the good dispersion of active reagent sites, associated selectivity and easier work-up [1c]. Both ferric perchlorate and ferric perchlorate adsorbed on silica gel can be used for various organic functional group transformations as catalyst under homogeneous and heterogeneous conditions.

FERRIC PERCHLORATE

In recent years, ferric perchlorate has gained importance as versatile reaction medium for affecting various organic transformations. Ferric perchlorate is a versatile reagent in organic synthesis [2-6]. It is non-toxic, inexpensive, odorless and soluble in most of the organic solvents and is not explosive even when heated in solution. Ferric perchlorate is stable in solid state, but is caused fire or explosion when is heated and in contact with combustibles materials such as; wood, paper, organic substances and strong reducing agents.

Ferric perchlorate in most of the organic solvents has different oxidation potentials depending on the nature of the solvent in which it is dissolved. The oxidation potential of ferric perchlorate is 0.83 V in acetic acid and similar values are expected for other aliphatic acids. Also, the oxidation

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*Corresponding author. E-mail: mmh1331@yahoo.com potential of ferric perchlorate in methanol is 0.71 V [7]. Solutions of ferric perchlorate in alcohol, acetone and many other organic solvents are much more intensely yellow colored than aqueous solutions of comparable concentration and acidity [8]. Ferric perchlorate can be easily prepared in laboratory or commercially purchased from GFS Chemicals Company. Although there are different forms of ferric perchlorate ($Fe(ClO_4)_3.XH_2O$), in this review the attention has been mainly paied to $Fe(ClO_4)_3.\ 6H_2O$ and $Fe(ClO_4)_3.\ 9H_2O$.

Its hygroscopicity limits the scope of its laboratory applications. However, by applying $Fe(ClO_4)_3$ on silica gel a stable nonhygroscopic reagent is obtained that can be used without special precautions and attention [9].

Preparation of Ferric Perchlorate

Ferric perchlorate was prepared by the reaction of Fe $(OH)_3$ (1.0 g, 9.3 mmol) in perchloric acid (3.7 g, 37.2 mmol) in a one necked flask under reflux condition for 10 h. After cooling the mixture, ferric perchlorate was precipitated as pink crystals. Filtration of the solids followed by washing with 5 ml of perchloric acid gave the product in 85% yield. Product can be stored for a long time in a desicator under vacuum at room temperature; it should not be contact metallic equipments [2].

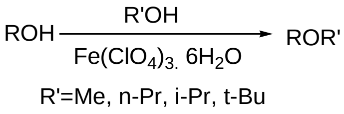
Preparation of Ferric Perchlorate on Silica Gel

A solution of 1.0 g of $Fe(ClO_4)_3$ in 10 ml of ethanol was added to a suspension of 10 g of silica gel (Merck, Kieselgel 40, 703230 mesh) in 30 ml of ethanol. The mixture was stirred for 30 min and the solvent evaporated under reduced pressure. The resulting brown powder was further dried in a vacuum drying cabinet at 60 ^{o}C and reduced pressure (20 mm Hg) [9].

FORMATION AND CLEAVAGE OF CARBON-OXYGEN BONDS

Ferric perchlorate has been used for the formation and cleavage of carbon-oxygen bonds of ethers, esters, alcohols, epoxides, tetrahydropyranyl ethers and acetals with reasonable versatility.

The common method for the conversion of alcohols to ethers consists of the reaction of metal salts of alcohols with different alkylating agents in the presence of various catalysts [10-14]. Condensation of alcohols or their salts with aldehydes, olefins and alkyloxides [18], dialkyl phosphates [19] and alcohols [20,21] have also been reported. However, some of these methods suffer from highly acidic or basic conditions or high costs of the reagents. 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 1) [22].

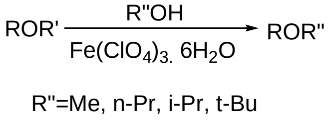


$$\mathrm{ROH} \xrightarrow[\mathrm{Fe(ClO_4)_{3.}\ 6H_2O}]{\mathrm{R'OH}} \mathrm{ROR'}$$

R'=Me, n-Pr, i-Pr, t-Bu

Scheme 1

Exchange of one alkoxy group to another for transetherification is very rare for ethers [23]. Catalysts such as: p-toluenesulfonic acid [24], treatment of alkylaryl ethers with alkoxide ions [25], preparation of enol ethers by mercuric acetate [26] are some examples. Selective and efficient transetherification of ethers has been carried out in the presence of ferric perchlorate successfully (Scheme 2) [27].



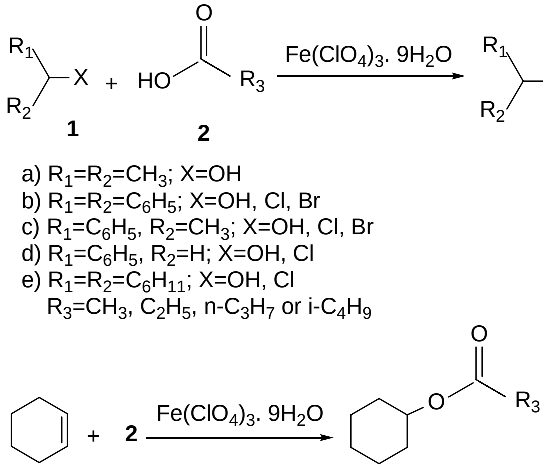
$$\mathrm{ROR'} \xrightarrow[\mathrm{Fe(ClO_4)_{3.}\ 6H_2O}]{\mathrm{R''OH}} \mathrm{ROR''}$$

R"=Me, n-Pr, i-Pr, t-Bu

Scheme 2

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 [28]. 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 [29-31]. Recently, Preyssler's anion catalyst, $[NaP_5W_{30}O_{110}]^{-14}$ used for highly selective and efficient esterification of salicylic acid with some aliphatic and benzylic alcohols [32]. Also, an efficient transesterification of β-ketoesters using triphenylphosphine has been described with various alcohols [33].

In 1992, Kumar [4] *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 3).



a) $R_1=R_2=CH_3$; X=OH
b) $R_1=R_2=C_6H_5$; X=OH, Cl, Br
c) $R_1=C_6H_5$, $R_2=CH_3$; X=OH, Cl, Br
d) $R_1=C_6H_5$, R_2=H; X=OH, Cl
e) $R_1=R_2=C_6H_{11}$; X=OH, Cl
$R_3=CH_3$, C_2H_5, n-C_3H_7 or i-C_4H_9

Scheme 3

Substituted succinanilic esters are obtained in good to excellent yields from succinanilic acids by reaction with alcohols in the presence of ferric perchlorate [34]. Ferric perchlorate has successfully been used for the transesterification of ethyl acetate with alcohols and acids [35].

Adsorption of $Fe(ClO_4)_3.6H_2O$ onto chromatographic grade silica gel in the presence of alcohol (being used for esterification) produces a supported reagent, $Fe(ClO_4)_3.6ROH/SiO_2$. 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 [36].

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 mol-equiv 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%) (Scheme 4). The system of $Fe(ClO_4)_3$/silica gel has been used as a catalyst for acetylating and formylating alcohols of various structure with ethyl acetate and ethyl formate (Scheme 5).

$$\text{RCOOH + R'OH} \xrightarrow[\text{CH}_2\text{Cl}_2\text{, reflux}]{\text{Fe(ClO}_4)_3\text{/Silica Gel}} \text{RCOOR'}$$

R=Me, Pr, Ph, PhCH=CH; R'= $CH_3(CH_2)_7$, $CH_3(CH_2)_4CH(CH_3)$, Cycloheptyl, $PhCH=CHCH_2$, Bn, 4-$ClC_6H_4CH_2$.

Scheme 4

$$\text{RCOOEt + R'OH} \xrightarrow[\substack{\text{ethyl acetate} \\ \text{or ethyl formate} \\ \text{reflux}}]{\text{Fe(ClO}_4)_3\text{/Silica Gel}} \text{RCOOR' + EtOH}$$

R=Me, H; R'= $CH_3(CH_2)_7$, $CH_3(CH_2)_4CH(CH_3)$, Cycloheptyl, Cyclooctyl, Bn, 4-$ClC_6H_4CH_2$, 4-$BrC_6H_4CH_2$, $C_6H_5CH=CH_2$.

Scheme 5

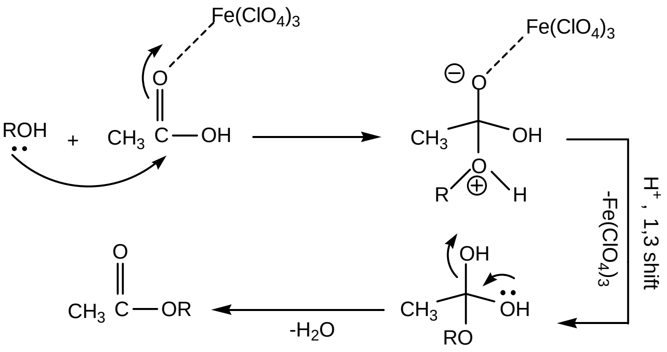
Adsorption of $Fe(ClO_4)_3.6H_2O$ onto chromatographic grade silica gel in the presence of ethyl acetate (being used for transesterification) produces a supported reagent, $Fe(ClO_4)_3.6EtOAc)/SiO_2$. This reagent has been found effective for the rapid formation and high yield of esters via transesterification on grinding in the presence of alcohols/carboxylic acids using pestle and mortar in the solid state [37].

Acetylation of alcohols is an important and routinely utilized transformation in organic chemistry [28]. 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, being stable in the acid reaction conditions and also ease of removal by mild alkaline hydrolysis [38]. A variety of reagents catalyzed acetylation of alcohols with acetic anhydride in solvent has been reported. Lewis acids such as $TaCl_5$ [39], Cerium(III) triflate [40], Tin(IV) porphyrin [41], Mg(III) acetate [42], metallic Lewis acids [43], Zeolit HSZ-360 [44], Me_3SiOTf [45], $Cu(OTf)_3$ [46], $Mg(Br)_2$ [47], $Sc(OTf)_3$ [48], $In(OTf)_3$ [49], $Bi(OTf)_3$ [50], Vanadyl(IV) acetate [51], Iodine [52] lithium perchlorate [53] magnesium perchlorate [54] $Zn(ClO_4)_2.6H_2O$ [55] $HfCl_4.2THF$ [56] $H_{14}[NaP_5W_{30}O_{110}]$ [57] 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 6). The plausible mechanism has been proposed for these reactions (Scheme 7) [58].

$$\text{ROH} \xrightarrow[\text{AcOH}]{\text{Fe(ClO}_4)_3\text{.6H}_2\text{O (0.25 mol\%)}} \text{ROAc}$$

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

Scheme 6



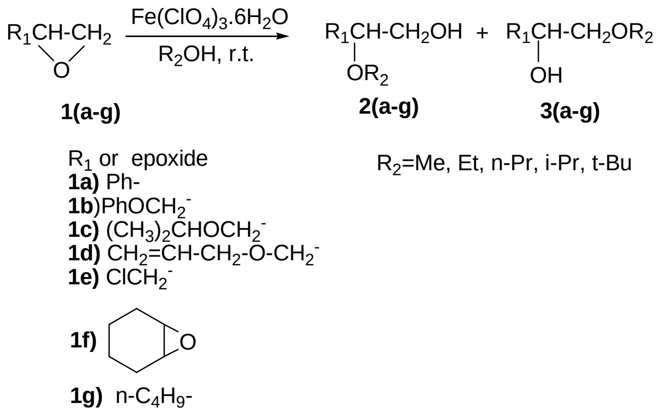
Scheme 7

Although there are several methods for deprotection of THP ethers [59-62] 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 include $FeCl_3/Ac_2O$, AcOH/AcCl, Ti/Ac_2O, bismuth salts, $Cu(OTf)_2/Ac_2O$ and $ZrCl_4$ [63-68]. 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 8) [69].

$$\text{ROTHP} \xrightarrow[\text{AcOH, r.t}]{\text{Fe(ClO}_4)_3\text{.6H}_2\text{O (1.0 mol\%)}} \text{ROAc}$$

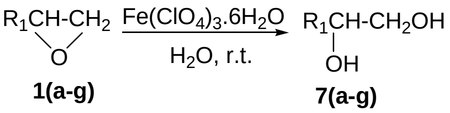
Scheme 8

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 [70] 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 [71]. Ring opening reaction of different classes of epoxides in primary, secondary and tertiary aliphatic alcohols in the presence of 0.01-0.0.5 molar equivalents of ferric perchlorate have been achieved (Scheme 9) [72].



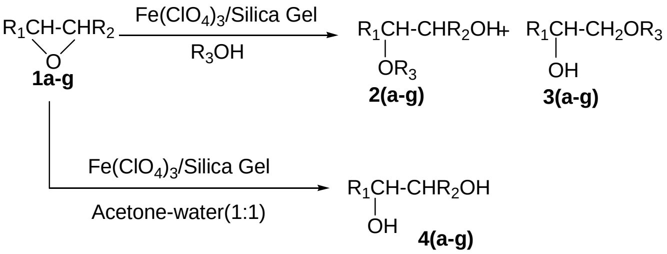
Scheme 9

The reaction of epoxides with water was also proceeded efficiently in the presence of 0.01-0.05 molar equivalents of ferric perchlorate (Scheme 10) [72].



Scheme 10

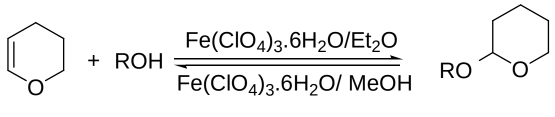
Ferric perchlorate hexahydrate on silica gel used for the ring opening of epoxides with primary, secondary, and tertiary alcohols and β-alkoxyalcohols were obtained in good and even excellent yields and high regioselectivity. Hydrolysis of epoxides have also been investigated in the presence of catalytic 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 11) [37].



R_1= Ph, R_2=H (a); R_1+R_2= -$(CH_2)_4$- (b);
R_1= Bu, R_2=H (c); R_1= $ClCH_2$, R_2= H (d);
R_1= $BuOCH_2$, R_2=H (e); R_1= $PhOCH_2$, R_2= H (f);
R_1= CH_2-$CHOCH_2$, R_2=H (g); R_3= Me, Et, Pr, i-Pr, t-Bu

Scheme 11

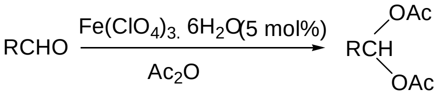
THP ethers can be easily prepared from a variety of hydroxyl containing compounds with DHP. Some efficient and commercially available reagents [73] and some readily available naturally occurring clays [74] have been utilized as efficient and versatile catalysts for this interconversion. Recently, the reaction was performed using acetonyl triphenyl phosphonium bromide supported on polystyrene [75]. Deprotection of THP ethers for regeneration of hydroxyl compounds usually entails rather harsh acidic conditions, which are rarely compatible with sensitive substrates [76]. All types of alcohols (primary, secondary, tertiary, benzylic, allylic and propargylic) were easily converted to THP ethers by the treatment of DHP with catalytic amounts of ferric perchlorate in Et_2O at an ambient temperature. The deprotection of THP ethers can be carried out under similar mild reaction conditions and with the same ease as the protection process (Scheme 12) [77].



Scheme 12

Acylals [78] 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 [79]. Since Knoevenagel [80] and Claussner [81] recognized that aldehydes could be transformed into the 1,1-diacetataes 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 $AlPW_{12}O_{40}$ [82], indium triflate [83], bismuth nitrate [84], chemoselective and convenient preparation of 1,1-diacetates from aldehydes, by solid lithium perchlorate [85] and many other catalysts are also reported and were given in the aforementioned references.

An efficient, convenient and solvent-free rout 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 (Scheme13).

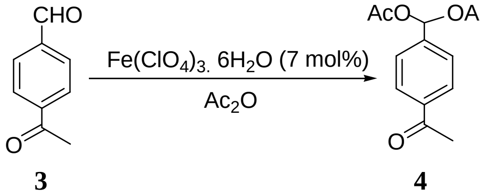


1 **2**

R = phenyl-, 4-methyl-phenyl-, cinamyl-, iso propyl-, 3-nitro phenyl-, 4-chloro phenyl-, 2-furyl-, n-butyl-

Scheme 13

When acetophenone-4-carbaldehyde used, smooth selective conversion of the aldehyde to the corresponding diacetate was observed while the ketone functionality remained intact (Scheme 14) [86].

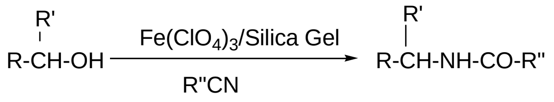


3 **4**

Scheme 14

FORMATION AND CLEAVAGE OF CARBON-NITROGEN BONDS

The reaction of carbonium ions with nitriles to form amides is known as the Ritter reaction [87]. Among the applied acidic reagents for Ritter reaction are: H_2SO_4 [88], $(CF_3SO_2)_2O$ [89] $Ph_2CCl^+SbCl_6^-$ [90], $BF_3.Et_20$ [91], Nafion-H [92], $CoCl_2$-Ac_2O [93] and Co(III)-DMG complex [94]. 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 15) [9].



$$R\text{-}\overset{R'}{CH}\text{-}OH \xrightarrow[R''CN]{Fe(ClO_4)_3/\text{Silica Gel}} R\text{-}\overset{R'}{CH}\text{-}NH\text{-}CO\text{-}R''$$

Scheme 15

Adsorption of $Fe(ClO_4)_3.6H_2O$ on chromatographic grade silica gel produces a supported reagent $Fe(ClO_4)_3.6H_2O/SiO_2$. 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 [95].

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 16) [96].

$$R^1\text{-}C{=}N\text{-}OH + R^2\text{-}NH\text{-}NH_2 \xrightarrow[DCE,\ r.t.]{Fe(ClO_4)_3.6H_2O} R^1\text{-}C{=}N\text{-}NH\text{-}R^2$$

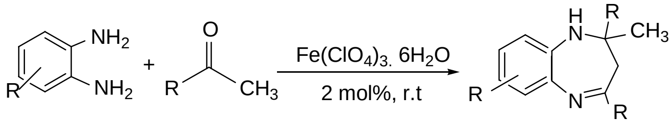
R^1= 4-$MeOC_6H_4$, 4-$O_2NC_6H_4$, 4-$Me_2NC_6H_4$, 4-ClC_6H_4, C_5H_4N-, C_6H_5-C_8H_9-, C_7H_{15}-C_9H_{19}-C_8H_7-$C_{12}H_{10}$-

R^2= 2,4-$(O_2N)_2C_6H_3$, Ph

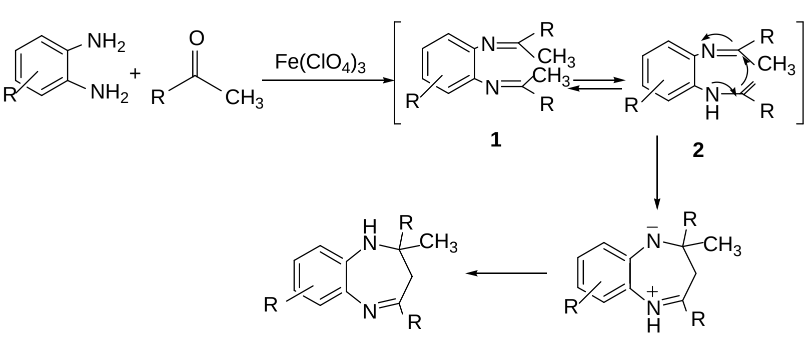
Scheme 16

Benzodiazepines are interesting compounds because they belong to an important class of the pharmacologically pre-eminent 1,5-benzodiazepines which have been extensively used as anticonvulsant, antianxiety, analgesic, sedative, antidepressive, hypnotic and anti-inflammatory agents [97-100].

A variety of catalysts such as $BF_3.OEt_2$ [101], $NaBH_4$ [102], PPA-SiO_2 [103], MgO-$POCl_3$ [104], $Yb(OTf)_3$ [105], Al_2O_3-P_2O_5 [106], HOAc-microwave [101-107], SO_4^{2-}-ZrO_2 [108], I_2 [109], $InBr_3$ [110], $Ag_3PW_{12}O_{40}$ [111], [L-proline]$_2$Zn [112], Solid acid [113] and ionic liquids [114,115] have been employed to affect this transformation. Due to interesting application 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 17). The mechanism of the reaction probably involves an intramolecular imine-enamine cyclization promoted by $Fe(ClO_4)_3$ as shown in Scheme 18 [116].



Scheme 17

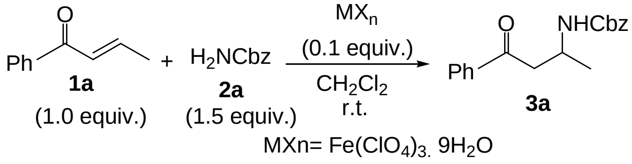


Scheme 18

In recent years the preparation of benzimidazoles has gained considerable attention [117-119]. The 2-aryl-1-arylmethyl-1*H*-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 19) [120].

Pyrazoles have a long history of applications in the pharmaceutical and agrochemical industry due to their herbicidal, fungicidal, insecticidal, analgesic, antipyretic and anti-inflammatory properties [121]. The synthesis of this eminent family of compounds has been previously reviewed [122]. These compounds were synthesized in mild conditions starting from 1,3-diketones and phenyl hydrazine in the presence ferric perchlorate hexahydrate and supported ferric perchlorate hexahydrate on silica gel as catalyst (Scheme 20) [123].

The *α*-amino carbonyl functionality is not only a segment of biologically important natural products but also a versatile intermediate for the synthesis of nitrogen-containing compounds such as 1,3-amino alcohols, *α*-amino ketones, *α*-amino acids, and *α*-lactams [124]. On the other hand, carbon-nitrogen bond formation between *α*,β-unsaturated carbonyl compounds and nitrogen nucleophiles (Aaza-Michael reaction) provides an alternative route to this functionality [124]. Catalytic activity of various transition metal salts has been surveyed in the reaction of phenyl propenyl ketone (**1a**) with benzyl carbamate (**2a**) in dichloromethane at room temperature. Among the metal salts tested, $Fe(ClO_4)_3$ was found to be the most effective (Scheme 21) [125].

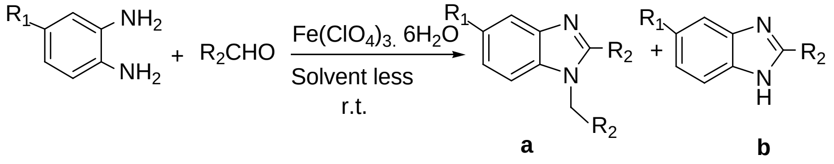


Scheme 21

FORMATION OF CARBON-CARBON BONDS

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 [126] is known as the Michael reaction and it is among the most important C-C bond forming reactions.

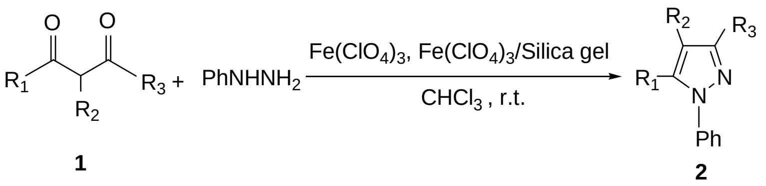
Traditional catalysts for this process are Brønstedt bases



R_1= H, CH_3, NO_2

R_2= 4-Cl-C_5H_6-, 4-Me-C_5H_6-, 4-MeO-C_5H_6-, 4-Isopropyl-C_5H_6-, 2-Naphthyl-, 2-Cl-C_5H_6-, 2-MeO-C_5H_6-, 3-NO_2-C_5H_6-, C_5H_6-,

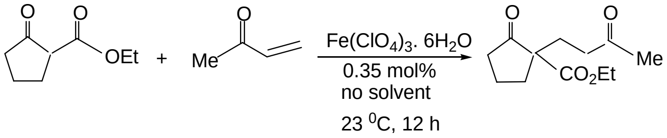
Scheme 19



a) R_1, R_2, R_3 = Ph, H, Ph **b**) R_1, R_2, R_3 = CH_3, Cl, CH_3 **c**) R_1, R_2, R_3 = CH_3, H, CF_3 **d**) R_1, R_2, R_3 = CH_3, H, OEt **e**) R_1, R_2, R_3 = CH_3, H, OMe **f**) R_1, R_2, R_3 = CH_3, H, CH_3

Scheme 20

such as tertiary amines, alkali alkaloxides 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 [127]. Ferric perchlorate catalyzed Michael reaction of β-esters with methyl vinyl ketone and methyl acrylate as acceptors has been investigated. With only 0.35 mol% of $Fe(ClO_4)_3$, quantitative conversions of ketoester with methyl vinyl ketone were obtained within 12 h to give the product in 99% yields after removal of the catalyst by simple filtration (Scheme 22) [128].

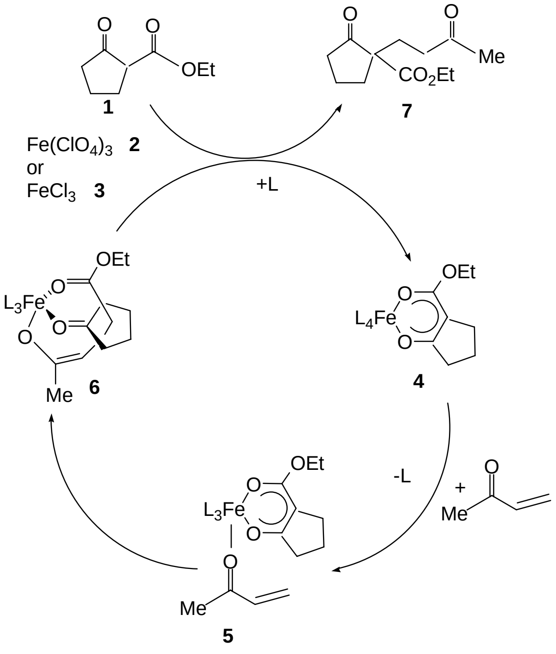


Scheme 22

The mechanism of Michael reaction catalyzed by ferric perchlorate has been proposed in Scheme 23. The first step is the formation 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 [128].

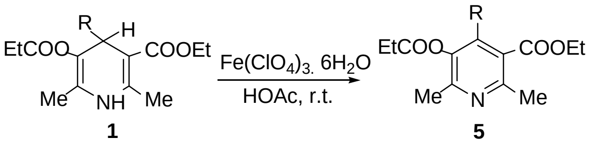
OXIDATION REACTIONS

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 [129], oxidation with ceric ammonium nitrate [130], ultrasound-promoted oxidation by clay- supported cupric nitrate [131], oxidation with pyridinium chlorochromate [132], oxidation with nitric acid [133], $RuCl_3$ [134], Mn(OAc) [131,135], voltammetric oxidation of 1,4-DHP in protic [136] and in aprotic media [137] and Pd/C in acetic acid [138].



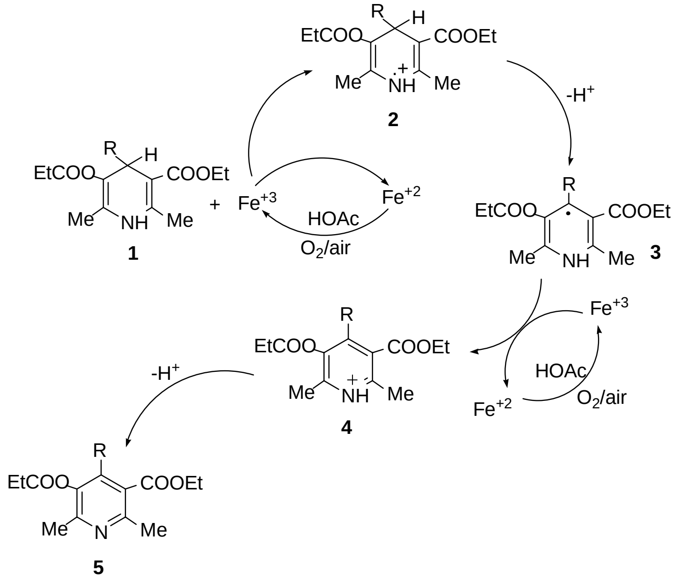
Scheme 23

Ferric perchlorate also oxidizes Hantzsch 1,4-DHPs in acetic acid [139e]. The catalytic oxidation of 1,4-DHP with ferric perchlorate mediated by acetic acid proceeds the pathways illustrated in Scheme 1. Presumably the oxidation of 1,4-DHPs is initiated by a single electron transfer to Fe(III) that produces Fe(II) and a radical cation which subsequently loses a proton to generate a radical **3**. With air present and because acid is used, Fe(II) goes back to Fe(III). This phenomenon has been already established [139k]. The regenerated iron(III) then oxidizes radical **3** to the protonated pyridine **4**. Ultimately the pyridinium species **4** loses a proton to give the desired pyridine derivative **5** (Schemes 24, 25).



R= H, CH_3, CH_3CH_2, Ph, 3-Nitro-Ph, 3-MeO-Ph,4-MeO-Ph, 2-Furyl, $(CH_3)_2CH$,

Scheme 24



Scheme 25

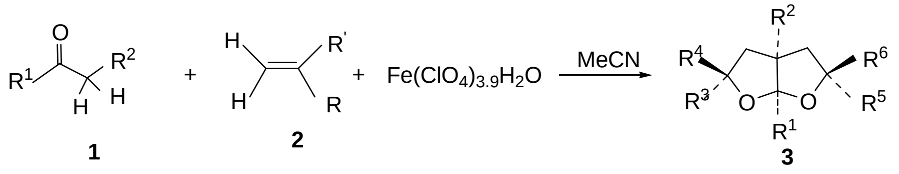
Ferric perchlorate nonahydrate in acetonitrile in the presence of conjugated dienes oxidizes carbonyl compounds (aldehydes and ketones) to α,α-diaddition products, hexahydrofuro[2,3-b]-furans **3**, in moderate yields. α,α-disubstituted ketones afforded the α,α-diaddition products 1,6-dioxaspiro[4,4]nonanes **4** or monoaddition products **6** and **7** (Scheme 26) . The isomer distribution and the influence of the reaction conditions are discussed based on selective oxidative deprotonation of the carbonyl compound by ferric perchlorate and addition of α-carbonyl alkyl radicals to conjugated olefins [140].

Electrically conductive polypyrrole/polyethylene composite films were prepared by the vapor-phase polymerization of pyrrole on porous polyethylene films containing $FeCl_3$ or $Fe(ClO_4)_3$ as oxidants. The conductivity of composite films increased by decreased polymerization temperature. The conductivity of the composite films was also a strong function of the oxidation potential of oxidant solutions which were impregnated into the polyethylene films prior to the polymerization of pyrrole. Maximum conductivity was obtained using short chain alcohols as solvents. It was found that the composite films have excellent mechanical properties compared to polypyrrole [141].

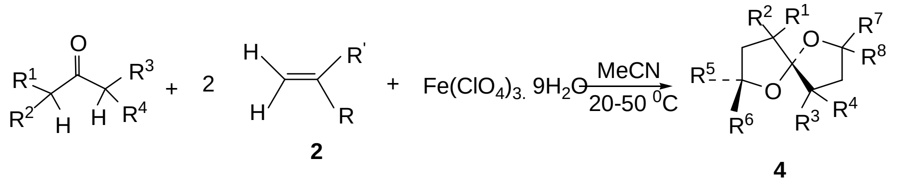
Polypyrrole has been chemically synthesized using various oxidizing reagents and examined as a positive electrode material. Physical properties, morphologies and electrochemical characteristics of polypyrrole were greatly influenced by the oxidizing reagent used for polymerization. In general, polypyrrole with a smaller particle size and a larger specific surface area showed better discharge performance than that with a larger particle size and a smaller specific surface area. Polypyrrole was also synthesized on various conducting and nonconducting substrates using $Fe(ClO_4)_3$ as an oxidizing reagent. By using PP non-woven fabric as a substrate material, a high discharge capacity of 72 mA h g^{-1} was obtained. Polypyrrole synthesized on only one side of PP non-woven fabric was able to be used as an electrode [142].

Iron salts, e.g., $FeCl_3$ and $Fe(ClO_4)_3$ promote degradation of phenol and substituted phenols if their aqueous solutions are irradiated in air, the substrate selectivity being low (i.e. the rates of degradation of different phenols are approximately equal), which is a valuable property of the proposed system from the ecological point of view. Certain solid metal oxides, e.g. CuO and V_2O_5, are also capable of promoting the aerobic photodegradation of phenols. However, metal oxides reveal very specific substrate selectivity. For example, CuO does not promote the degradation of unsubstituted phenol, while halogenated phenols are oxidized relatively rapidly. On the contrary, V_2O_5 oxidizes preferentially phenol and isomeric nitrophenols. These features reflect the difference in mechanisms operating in the cases of different oxides. Experiments with four different bioassay organisms (green algae Chlorella vulgaris, photobacteria Beneckea harveyi, infusoria Tetrahymena pyriformis and cladoceran organisms Daphnia magna have demonstrated that oxidative photodegradation of the 2,4,5-trichlorophenol solution promoted by $FeCl_3$, $Fe(ClO_4)_3$ and V_2O_5 leads to complete or noticeable decrease in the toxicity of the solution in respect to all the organisms except tetrahymena pyriformis. It may thus be concluded that the aerobic photodegradation of this poisonous pollutant under the action of the systems mentioned produces relatively harmless products [143].

Differentiation of organic sulfur forms in coal by stepwise oxidation with a mixture of perchloric acid and ferric perchlorate $Fe(ClO_4)_3$ was studied. Various organic sulfur compounds were oxidized with $HClO_4$ solution containing $Fe(ClO_4)_3$ and the amounts of sulfate formed during reaction were measured. The compounds can be grouped into three categories according to their reactivities as follows. (1) easily



	R^1	R^2		R	R'		R^1	R^2	R^3	R^4	R^5	R^6
1a	$-[CH_2]_4-$		2a	Ph	H	3a	$-[CH_2]_4-$		Ph	H	Ph	H
b	Et	Me	b	$CH=CH_2$	H	a'	$-[CH_2]_4-$		H	Ph	Ph	
c	Ph	Me				b	Et	Me	Ph	H	Ph	H
d	Me	Et				b'	Et	Me	H	Ph	Ph	H
e	H	Et				c	Ph	Me	Ph	H	Ph	H
f	H	$PhCH_2$				c'	Ph	Me	H	Ph	Ph	H
g	$-[CH_2]_2NMe[CH_2]-$					d	Me	Et	Ph	H	Ph	H
						d'	Me	Et	H	Ph	Ph	H
						e	H	Et	Ph	H	Ph	H
						e'	H	Et	H	Ph	Ph	H
						f	H	$PhCH_2$	Ph	H	Ph	H
						f'	H	$PhCH_2$	H	Ph	Ph	H
						g	$-[CH_2]_3NMe-$		Ph	H	Ph	H
						g'	$-[CH_2]_3NMe-$		H	Ph	Ph	H
						h	$-[CH_2]_4-$		$CH=CH_2$	$CH=CH_2$	$CH=CH_2$	H
						h'	$-[CH_2]_4-$		H		$CH=CH_2$	H



	R^1	R^2	R^3	R^4		R^1	R^2	R^3	R^4	R^5	R^6	R^7	R^8
1h	H	$-[CH_2]_4-$		Me	4a	H	$-[CH_2]_3-$		Me	Ph	H	Ph	H
i	H	Et	Me	Me	a'	H	$-[CH_2]_3-$		Me	H	Ph	Ph	H
					b	H	Et	Me	Me	Ph	H	Ph	H
					b'	H	Et	Me	Me	H	Ph	Ph	H

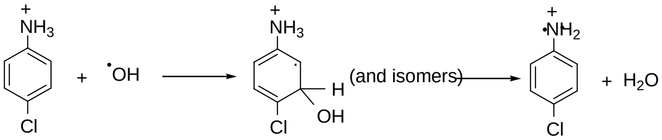
Scheme 26

oxidized ones, i.e. disulfides, for which almost all of the sulfur was converted to sulfate after oxidation, (2) less reactive ones, including aliphatic sulfides, aliphatic and aromatic thiols (20-30% of sulfur in these compounds was oxidized to sulfate), and (3) relatively stable ones, i.e. thiophenes and aromatic sulfides, from which no sulfate were formed. Samples of Illinois No. 6 and Bevier coals were also reacted with $HClO_4$ solutions containing increasing concentration of $Fe(ClO_4)_3$. The organic sulfur in these coals could be differentiated into various groups according to their reactivities [144].

The degradation of a prototypical halogenoaromatic pollutant, 4-chloroaniline, photoinduced by Fe(III) species, has been studied in acidic aqueous solutions (pH 2-4) of $Fe(ClO_4)_3$ by means of product analysis and nanosecond transient absorption spectroscopy [145]. The degradation process is initiated by the attack of OH radicals on 4-CA, leading to radical cations, 4-CA$^{\bullet+}$ as the major transient species. The formation of OH radicals, as found in several other studies [146-151].

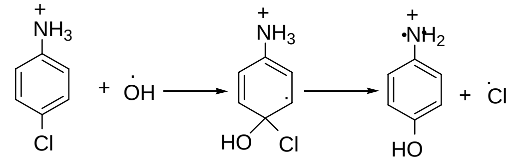
The OH adducts are subsequently converted, by loss of

H_2O, to 4-$CA^{\bullet+}$ absorbing at 445 nm, in a reaction whose rate increases with decreasing pH. The overall sequence can be written as in reaction (Scheme 27).



Scheme 27

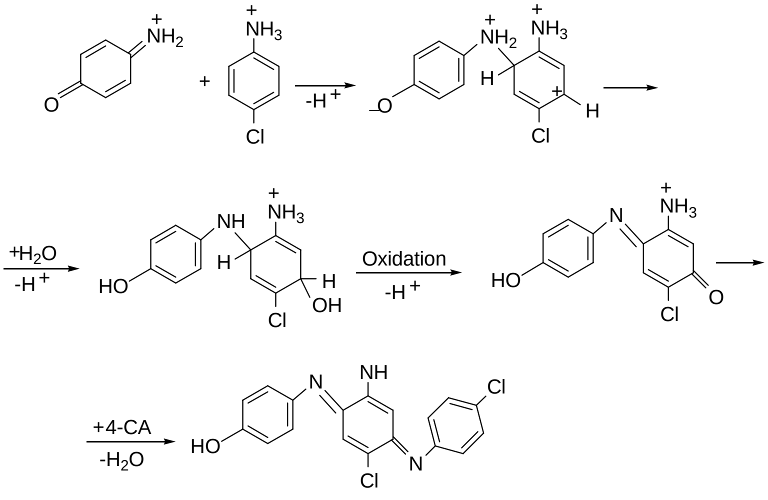
Several isomeric forms of the OH adduct can exist, depending on the site of attack of the OH radical on the molecule. In the case of 4-CA in acidic medium, containing The protonated amino substituent together with a second substituent in *p*-position, attack of OH on the *o*- and *m*-positions with respect to the amino group are expected to predominate. As an example, in this work has been considered, in a reaction (Scheme 28), the OH attack in *p*-position followed by elimination of a Cl atom, gives the experimentally observed product 4-aminophenol.



Scheme 28

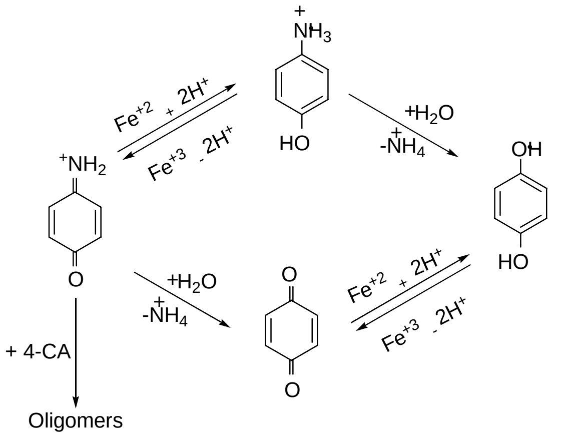
At high photon fluences, the decay of 4-$CA^{\bullet+}$ is dominated by second-order reactions; an accelerating effect of Fe(III) could be evidenced at low fluence. A large number of minor reaction intermediates could be detected by product analysis following continuous irradiation at λexc = 365 nm of aerated solutions, arising from ring substitution, ring opening and oligomerization processes. At higher concentration of 4-CA, the specificity of the degradation process increases; the oligomerization pathway becomes predominant and leads to three major oligomeric products, one of which could be unequivocally identified, while probable structures were proposed for the other two (Scheme 29).

The chemical nature of these products, as well as the observation of the *p*-benzoquinone/hydroquinone couple as the major photoproduct in deaerated solution, led to the proposal that *p*-benzoquinone monoimine is a key intermediate in the degradation of 4-CA. Direct oxidation of 4-$CA^{\bullet+}$ by Fe(III) is put forward as a possible explanation for its formation. Prolonged irradiation at λexc = 365 nm in the presence of oxygen leads to complete mineralization; the process is, however, complex due to the formation of light-absorbing aromatic intermediates on the one hand, and to the behavior of the Fe(III)/Fe(II) redox couple during irradiation on the other. Fe(III)-photoinduced oxidation of 4-CA is a fairly efficient process as long as the photoinducing Fe(III) species are not depleted. The further progress of the reaction requires the reoxidation of Fe(II) into Fe(III), which is accomplished in



Scheme 29

processes requiring both light and oxygen, probably by reactions of Fe(II) with photoinduced oxidizing radicals (Scheme 30).

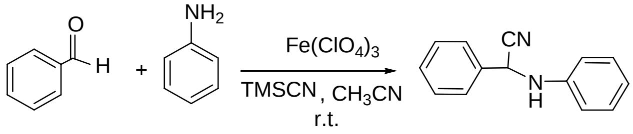


Scheme 30

MULTICOMPONENT REACTIONS

Some of the first multicomponent reactions can be traced back to the mid-late 1800's and include the Strecker synthesis [152] as well as the Biginelli [153] and Mannich [154] reactions. The three-component coupling of an amine, a carbonyl compound (generally an aldehyde) and either hydrogen cyanide or its alkaline metal cyanides to give α-aminonitriles [155] constitutes an important indirect route in the synthesis of α-amino acids [156].

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 31) [157a].



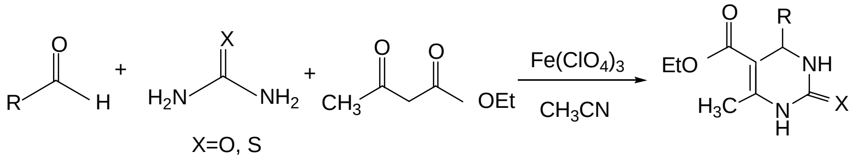
Scheme 31

An efficient synthesis of 3,4-dihydropyrimidinones and thiones using ferric perchlorate as the catalyst from an aldehyde, β-keto ester, and urea or thiourea in acetonitrile is described. Compared to the classical Biginelli reaction conditions, this new method consistently has the advantage of being fully catalytic, good yields and requiring short reaction times (Scheme 32) [158].

The mechanism of the Biginelli reaction has been reinvestigated in detail by Kappe [159]. He proposed and estabilified that the first step in this reaction, the acid catalyzed formation of an acyl imine intermediate **5** formed by reaction of the aldehyde with urea or thiourea is the key, rate determing step. Because of the **3d** empty orbital in iron, a complex can be formed and stabilized though coordination. In addition β-ketoester **3** also can be activated through a coordinative bond with FEP. Interception of the iminium ion by activated β-ketoester produces an open chain ureide **7** which is still coordinated and activated with $Fe(ClO_4)_3$. Hetrocyclization of **7** gives the corresponding pyrimidine ring with lose of ferric perchlorate and water. Our plausible mechanism is shown in Scheme 33.

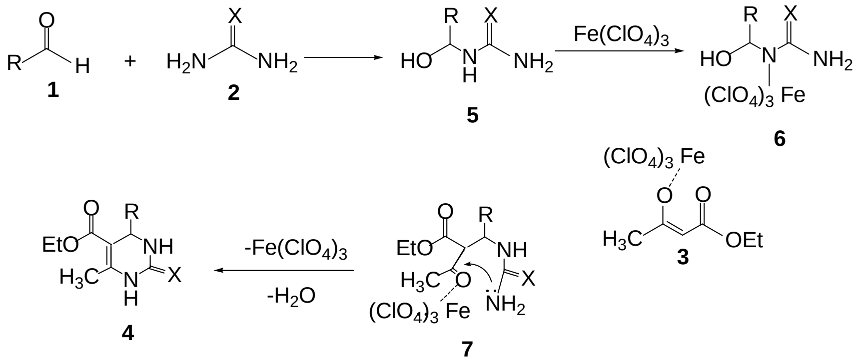
CONCLUDING REMARKS

In this review we have paid attention to ferric perchlorate and ferric perchlorate adsorbed on silica gel as reagents or catalysts for various organic reactions. Solid ferric perchlorate is potentially an explosive compound when it is heated and



1 2 3 4

Scheme 32



Scheme 33

contacted with combustibles materials. Therefore, it must be handled very cautiously. Ferric perchlorate and ferric perchlorate adsorbed on silica gel are great importance in terms of handeling, being inexpensive, non toxic, available and efficient for various organic transformations. We believe a great number of acid catalyzed organic reactions can be performed by using these catalysts. Therefore, using ferric perchlorate recommended for different purposes in organic chemistry which requires Lewis acid catalysis.

Abbreviations

Ferric Perchlorate	FEP
G. Frederick Smith	GFS
Tetrahydropyranyl	THP
3,4-Dihydro-2H-pyranpyran	DHP
1,4-Dihydropyridine	1,4-DHP
Nicotinamide Adenine Dinucleotide Phosphate	NADH
Trimethyl Silyl Cyanide	TMSCN
4-Chloroaniline	4-CA

REFERENCES

[1] a) H. Yamamoto, Lewis Acids in Organic Synthesis, Wiley-VCH, 2 (2001) 597; b) R.A. Sheldon, R.S. Downing, Appl. Catal. A. Gen. 189 (1999) 163; c) R.S. Varma, Green Chem. 1 (1999) 43.

[2] B. Kumar, H. Kumar, M. Singh, Indian J. Chem. 30B (1991) 460.

[3] B. Kumar, H. Kumar, B. Kaur, Indian J. Chem. 30B (1991) 869.

[4] B. Kumar, H. Kumar, A. Parmar Synth. Commun. 22 (1992) 1087.

[5] B. Kumar, H. Kumar, A. Parmar Indian J. Chem. 32B (1993) 292.

[6] A. Citterio, R. Sebastiano, M.C. Carvayal, J. Org. Chem. 56 (1991) 5335.

[7] E. Kotani, S. Kobayashi, Y. Ishii, S. Tobinaga, Chem. Pharm. Bull. 32 (1984) 4281.

[8] R.A. Horne, Phys. Chem. 62 (1958) 509.

[9] P. Salehi, A. Rostamian Motiagh, Synth. Commun. 30 (2000) 671.

[10] W.N. White, B.E. Norcross, J. Am. Chem. Soc. 83 (1961) 3265.

[11] E.M. Marks, D. Lipkin, B. Bettman, J. Am. Chem. Soc. 59 (1937) 946.

[12] W.T. Olson, H.F. Hipsher, C.M. Buess, I.A. Goodman, I. Hart, J.R. Lamneck, L.C. Gibbons, J. Am. Chem. Soc. 69 (1947) 2451.

[13] R.A. Dubios, Diss. Abstr. Bit. B. 37 (1976) 223.

[14] S.R. Sandier, Organic Functional Group Preparation, Academic Press, 1 (1986) 139.

[15] B.H. Shoemaker, C.E. Boord, J. Am. Chem. Soc. 53 (1931) 1505.

[16] S. Torii, S. Takagishi, T. Inokuchi, H. Okumoto, Bull. Chem. Soc. Jpn. 60 (1987) 775.

[17] C.D. Nenitzescu, V. Przemetzki, Chem. Ber. 69B (1936) 2706.

[18] H.C. Chitwood, B.T. Freure, J. Am. Chem. Soc. 68 (1964) 680.

[19] Y. Kashman, J. Org. Chem. 37 (1972) 912.

[20] N. Iranpoor, E. Mothaghineghad, Tetrahedron 50 (1994) 1859.

[21] N. Iranpoor, E. Mothaghineghad, Synth. Commun. 25 (1995) 2253.

[22] P. Salehi, N. Iranpoor, F.K. Behbahani, Tetrahedron 54 (1998) 943.

[23] N. Iranpoor, E. Mothaghineghad, Tetrahedron 50 (1994) 7299.

[24] E.F. Pratt, J.D. Draper, J. Am. Chem. Soc. 71 (1949) 2846.

[25] J.A. Zoltewiez, A.A. Sale, J. Org. Chem. 35 (1970) 3462.

[26] W.H. Watanabe, L.E. Conlon, J. Am. Chem. Soc. 79 (1957) 2828.

[27] P. Salehi, B. Seddighi, M. Irandoost, F.K. Behbahani, D.P. Tahmasbi, Synth. Commun. 30 (2000) 1743.

[28] [28] T.W. Green, P.G.M. Wuts, Protection Groups in Organic Synthesis, 3rd ed, Jhon Wiley & Sons. New York, 1999, p.150.

[29] Aromatic Chemicals, Perfumes and Flavour Technology, Sbp Board of Consultants and Engineers, Sbp Chemical Engineers Series No. 54 (Small Business Publications Delhi).

[30] E. Haslam, Tetrahedron 36 (1980) 2409.

[31] J. Aracil, M. Martinez, N. Sanchez, A. Corma, Zeolites 12 (1992) 233.

[32] F.F. Bamoharram, M.M. Heravi, M. Roshani, A.G. Jahangir, Applied Catalysis A: General 302 (2006) 42.

[33] J.S. Yadav, B.V.S. Reddy, A.D. Krishna, Ch. Suresh Reddy, A.V. Narsaiah, J. Mol. Catal. A: Chemical 261 (2007) 93.

[34] B. Kumar, A. Parmar H. Kumar, Indian J. Chem. B-Organic Chemistry Including Medicinal Chemistry 33 (1994) 698.

[35] B. Kumar, H. Kumar, A. Parmar, Indian J. Chem. B-Organic Chemistry Including Medicinal Chemistry 32 (1993) 292.

[36] a) A. Parmar, J. Kaur, R. Goyal, B. Kumar, H. Kumar, Synth. Commun. 28 (1998) 2821; b) A. Parmar, R. Goyal, B. Kumar, H. Kumar, Synth. Commun. 29 (1999) 139.

[37] P. Salehi, M.M. Khodaei, S.B. Ghareghani, A.R. Motlagh, Russ. J. Org. Chem. 39 (2003) 794.

[38] A.L. Pearson, W.J. Handbook Or Reagents For Organic Synthesis, Acetylating Agents and Protecting Groups, John Wiley & Sons, UK, 1999, pp. 9-16.

[39] S. Chandrasekhar, T. Roma Chander, M. Takhi, Tetrahedron Lett 39 (1998) 3263.

[40] R. Dalpazzo, A. De Nino, L. Maiuolo , A. Procopio, M. Nardi, G. Bartali, R. Romeo, Tetrahedron Lett. 44 (2003) 5621.

[41] M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpour Baltrork, R. Shabani, J. Mol. Catal. A: Chemical 219 (2004) 73.

[42] S. Gowda, K.M. Lokanatha Rai, J. Mol. Catal. A: Chemical 217 (2004) 27.

[43] S.G. Lee, J.H. Park, J. Mol. Catal. A: Chemical 194 (2003) 49.

[44] R. Ballini, G. Bosica, S. Carloni, L.Ciaralli, R. Maggi, G. Sortori, Tetrahedron Lett. 39 (1998) 6049.

[45] P.A. Procopiou, S.P.D. Baugh, S.S. Flack, G.G.A. Inglis, J. Org. Chem. 63 (1998) 2342.

[46] P. Saravanan, V.K. Singh, Tetrahedron Lett. 40 (1999) 2611.

[47] E .Vedejs, O. Dougulis, J. Org. Chem. 61 (1996) 5702.

[48] K. Ishehara, M. Kulata, H. Karihara, H. Yamamato, J. Am. Chem. Soc. 117 (1995) 4413.

[49] K.K. Chauhan, C.G. Frost, I. Love, D. Wait, Synlett (1999) 1743.

[50] M.D. Carrigan, R.S. Mohan, Synthesis 14 (2001) 2091.

[51] B.M. Choudary, M. Lakshmi, M. Kantan, V. Neeraja, T. Bandyopadhyay, P. Nassi. Reddy, J. Mol. Catal. A: Chemical 140 (1999) 25.

[52] P. Phukan, Tetrahedron Lett. 45 (2004) 4785.

[53] Y. Nakae, I. Kusati, T. Sato, Synlett 10 (2001) 1584.

[54] G. Bartoli, M. Bosco, R. Dalpozzo, E. Marcantoni, M. Massaccesi, S. Rinaldi, L. Sambri, Synlett (2003) 39.

[55] G. Bartoli, M. Bosco, R. Dalpozzo, E. Marcantoni, E. Massaccesi, L. Sambri, Eur. J. Org. Chem. (2003) 4611.

[56] J. Otera, Angew. Chem. Int. Ed. 1 (2001) 2044.

[57] M.M. Heravi, F.K. Behbahani, F.F. Bamoharram, J. Mol. Catal. A: Chemical 253 (2006) 16.

[58] M.M. Heravi, F.K. Behbahani, R. Hekmat Shoar, H.A. Oskooie, Cat. Commun.7 (2006) 136.

[59] A. Khan, S. Islam, L.H. Choudhurg, S. Ghosh,

Tetrahedron Lett. 45 (2004) 9617.

[60] Y.-G. Wang, X.-X. Wu, Z.-Y. Jiang, Tetrahedron Lett. 45 (2004) 2973.

[61] T. Ikawa, H. Sajiki, K. Hirota, Tetrahedron Lett. 60 (2004) 6189.

[62] I.E. Marko, A. Ates, B. Augustyns, A. Gautier, Y. Quesnel, L. Turet, M. Wiaux, Tetrahedron Lett. 40 (1999) 5613.

[63] B. Ganem, J.R.V.R. Small, J. Org. Chem. 39 (1974) 3728.

[64] M. Schwartz, R.M. Waters, Synthesis (1972) 567.

[65] S. Chandrasekhar, T. Ramachander, M.V. Reddy, M. Takhi, J. Org. Chem. 65 (2000) 4729.

[66] I. Mohammad Poor Baltork, A.R. Khosropour, Monatsch. Chem. 133 (2002) 189.

[67] K.L. Chandra, O. Saravanan, V.K. Singh, Tetrahedron Lett. 42 (2001) 5309.

[68] C.S. Reddy, G. Smith, S. Chandrasekhar, Tetrahedron Lett. 44 (2003) 4693.

[69] M.M. Heravi, F.K. Behbahani, R. Hekmat Shoar, H.A. Oskooie, J. Mol. Catal. A: Chemical 244 (2006) 8.

[70] T. Kino, H. Hatanaka, M. Hasshimoto, M. Nishisyma, T. Goto, M. Okuhara, M. Kohsaka, H. Aoki, H. Imanaka, J. Antibiot. 40 (1987) 1249.

[71] a) G.H. Posner, D.Z. Rogers, J. Am. Chem. Soc. 99 (1977) 8208; b) G.A. Olah, A.P. Fung, D. Meidar, Synthesis (1981) 280; c) C. Moberg, L. Rakos, L. Tome, Tetrahedron Lett. 3 (1992) 2191; d) N. Iranpoor, P. Salehi, Synthesis (1994) 1152; e) P. Stead, H. Marley, M. Mahmoudian, G. Webb, D. Noble, Y.T. Ip, E. Piga, T. Rossi, S. Roberts, M.J. Dawson, Tetrahedron Asymmerty 7 (1997) 2247; f) J. Xin, J. Suo, X. Zhang, Z. Zhang, New J. Chem. 24 (2000) 569; g) C.J. Salomon, Synlett (2001) 65; h) C. Jaramillo, J.L. Chiara, M. Martin-Lomas, J. Org. Chem. 59 (1994) 3135; i) C. Moberg, L. Rakos, L. Tottie, Tetrahedron Lett. 33 (1992) 2191; j) N. Iranpoor, T. Tarrian, Z. Movahedi, Synthesis (1996) 1473; k) N. Iranpoor, H. Adibi, Bull. Chem. Soc. Jpn. 73 (2000) 675; l) B.M. Choudary, Y. Sudha, Synth. Commun. 26 (1996) 2989; m) N. Iranpoor, M. Shekarriz, F. Shiriny, Synth. Commun. 28 (1998), 347; n) N. Iranpoor, I. Mohammadpoor Baltork, F. Shirini, Tetrahedron 47 (1991) 9861; o) B. Tamami, N. Iranpoor, M.A. Karimi Zarchi, Polymer 34 (1993) 2011; p) V. Mirkhani, S. Tangestaninejad, B. Yadollahi, L. Alipanah, Tetrahedron 59 (2003) 8213; q) M.L. Kantam, K. Aziz, K. Jeyalakshmi, P.R. Likhar, Catal. Lett. 89 (2003) 95; r) P. Salehi, B. Seddighi, M. Irandoost, F.K. Behbahani, Synth. Commun. 30 (2000) 2967.

[72] P. Salehi, B. Seddighi, M. Irandoost, F.K. Behbahani, Synth. Commun. 30 (2000) 2967.

[73] a) T. Neshiguchi, K. Karamine, J. Chem. Soc., Chem. Commun. (1990) 1776; b) T. Neshiguchi, S. Fuyrsahi, M. Kurodo, K. Kayesaki, M. Saiteh, J. Org. Chem. 63 (1998) 8183; c) S. Chandrasekhar, M. Takhi, R. Reddy, S. Maharatra, Tetrahedron 57 (2001) 4405; d) N. Deka, J.C. Sarma, J. Org. Chem. 66 (2001) 1947; e) N. Deka, J.C. Sarma, Synth. Commun. 30 (2000) 4435, and References Cited Therein; f) B.C. Ranu, M. Saha, J. Org. Chem. 59 (1994) 826; g) J.N. Canydo, A. Garcia, F. Lafont, D. Luna, J.M. Marenas, Synth. Commun. 24 (1994) 1345; h) S. Nak, R. Gaymath, B.K. Patel, Tetrahedron Lett. 42 (2001) 7679; i) A. Manar, T. Beregszaszi, Tetrahedron Lett. 37 (1996) 8597; L.C. Branco, C.A.M. Afonso, Tetrahedron 57 (2001) 4405; j) B.S. Babu, K.K. Balasubramanian, Tetrahedron Lett. 39 (1998) 9287; k) M.M. Heravi, F.K. Behbahani, R.H. Shoar, H.A. Oskooie, J. Mol. Catal. A-Chemical 244 (2006) 8; l) M.M. Heravi, P. Kazemian, H.A. Oskooie, M. Ghassemzadeh, J. Chem. Res. (S) (2005) 105; m) M.M. Heravi, F.K. Behbahani, H.A. Oskooie, R.H. Shoar. Tetrahedron Lett. 46 (2005) 2543; n) M.M. Heravi, H.A. Oskooie, L. Sangsefidi. M. Ghassemzadeh, K. Tabarhydar Phosphorus Sulfur And Silicon and the Related Elements 177 (2002) 2843; o) B. Mohajerani, M.M. Heravi, D. Ajami, Monatshefte Fur Chemie 132 (2001) 871; p) M.M. Heravi, D. Ajami, M. Ghassemzadeh Synthesis (1999) 393; q) M.M. Heravi, M. Haghighi, F. Derikvand, F.F. Bamoharram, Synth. Commun. 36 (2006) 3103.

[74] a) S. Hoyer, P. Laszlo, M. Orlonic, E. Pallo, Synthesis (1986) 65; b) B.P. Bandgaz, S.R. Jagtap, B. Aghade, P. Wadgaonkar, C.U. Deresh, R.S. Reddy, B. Pandey, Synthesis (1993) 1069; c) R. Balline, F. Bigi, S. Carloni, R. Maggi, G. Sartoni, Tetrahedron Lett. 38

(1997) 4169; d) I. Rodriguez, M.J. Clemant, S. Ilona, V. Fornes, A. Corma, J. Catal. 192 (2000) 44; e) K.R. Kleetstra, H. Vanbekkum, J. Chem. Res. (S) (1995) 26; f) M.M. Heravi, D. Ajami, M. Ghassemzadeh, Synth. Commun. 29 (1999) 1013; g) S. Chandrasekhar, M. Takhi, Y.R. Reddy, S. Maharatra, C. Rao, K.V. Reddy, Tetrahedron 53 (1997) 14997; h) A.S. Garare, D.P. Salde, M.S. Shengare, R.D. Wakharkar, Synth. Commun. 32 (2002) 1549.

[75] Y.S. Han, C.C. Lee, R.J. Chen, P.H. Szu, Tetrahedron 57 (2001) 5991.

[76] a) M. Miyashita, A. Yoshikoshi, P. Grieco, J. Org. Chem. 42 (1977) 3772; b) E.J. Corey, H. Niwa, J. Knolle, J. Am. Chem. Soc. 100 (1978) 1942; c) K. Bernardy, M.B. Floyd, J.F. Poletto, M.J. Weiss, J. Org. Chem. 44 (1979) 1438; d) Y. Ogawa, M. Shibasaki, Tetrahedron Lett. 25 (1984) 663; e) A. Fadel, J. Salaun, Tetrahedron 41 (1985) 1267; f) D. Gala, M. Steinman, R.S. Jaret, J. Org. Chem. 51 (1986) 4488; g) S. Kim, J.H. Park, Tetrahedron Lett. 23 (1987) 393; h) K.P. Nambiar, A. Mitra, Tetrahedron Lett. 35 (1994) 3033; i) K. Zimmermann, Synth. Commun. 25 (1995) 2959; j) A.S.-Y. Lee, F.-Y. Su, Y.-C. Liao, Tetrahedron Lett. 40 (1999) 1323; k) G.P. Ramanelli, C. Baronetti, H.J. Thomas, J.C. Autino, Tetrahedron Lett. 43 (2002) 7589; l) M.H. Habibi, S. Tangestaninejad, I. Mohammadpoor-Baltrok, V. Mirkhani, B. Yadollahi, Tetrahedron Lett. 57 (2001) 2851; m) M.M. Heravi, D. Ajami, M. Ghassemzadeh, Synth. Commun. 29 (1999) 1013.

[77] M.M. Heravi, F.K. Behbahani, H.A. Oskooie, R. Hekmat Shoar, Tetrahedron Lett. 46 (2005) 2543.

[78] J. J. Gregory, J. Chem. Soc. B (1970) 1201.

[79] a) B.B. Sinder, S.G. Amin, Synth. Commun. (1978) 117; b) I. Freeman, E.M. Karchetski, J. Chem. Eng. Data. 22 (1977) 335.

[80] E.J. Knoevenagel, Liebigs Ann. Chem. 402 (1905) 111.

[81] P. Claussner, Ber. Dtsch. Chem. Ges. 38 (1905) 2860.

[82] H. Firouzababi, N. Iranpoor, F. Nowrouz, K. Amani, Tetrahedron Lett. 44 (2003) 3951.

[83] R. Ghosh, S. Maiti, A. Chakraborty, R. Halder, J. Mol. Catal. A: Chemical 215 (2004) 49.

[84] D.H. Aggen, J.N. Arnold, P.D. Hayes, N.J. Smoter, R.S. Mohan, Tetrahedron 60 (2004) 3675.

[85] N. Ziyaei, N. Azizi, M.R. Saidi, J. Mol. Cat. A: Chemical 238 (2005) 138.

[86] M.M. Heravi, F.K. Behbahani, R. Hekmat Shoar, H.A. Oskooie, Mendeleev Commun, submitted.

[87] J.J. Ritter, P.P. Minieri, J. Am. Chem. Soc. 70 (948) 4045.

[88] a) J.A. Sanguigni, R. Levins, J. Med. Chem. 7 (1964) 573; b) F. Alonso Cermono, R.M. Obeso Caceres, Anal. Quim. 74 (1978) 778.

[89] A. Carcia Martinez, R. Martinez Alvarez, E. Teso Vilar, A. Garcia Fraile, M. Hanach, L.R. Subramanian, Tetrahedron Lett. 30 (1989) 581.

[90] a) D.H.R. Barton, P.D. Magnus, R.N. Young, J. Chem. Soc. Chem. Commun. (1973) 331; b) D.H. R. Barton, P.D. Magnus, J.A. Garbarino, R.N. Young, J. Chem. Soc. Perkin Trans. 1 (1974) 2101.

[91] H. Firouzabadi, A.R. Sardarian, H. Badparva, Synth. Commun. 24 (1994) 601.

[92] G.A. Olah, T. Yamato, S. Lyer, Mater. Chem. Phys. 17 (1987) 21.

[93] M. Mukhopadhyay, M.M. Reddy, G.C. Maikap, J. Iqbal, J. Org. Chem. 60 (1995) 2670.

[94] M. Mukhopadhyay, J. Iqbal, J. Org. Chem. 62 (1997) 1843.

[95] A. Parmar, R. Goyal, B. Kumar, H. Kumar, Indian J. Chem. B-Organic Chemistry Including Medicinal Chemistry 37 (1998) 941.

[96] H.A. Oskooie, M.M. Heravi, A. Sadnia, M. Safarzadegan, F.K. Behbahani, Mendeleev Commun., 17 (2007) 190.

[97] J. Krapcho, F.C. Turk, J. Med. Chem. 9 (1966) 191.

[98] L.H. Sternback, Angew. Chem. Int. Ed. Engl. 10 (1971) 34.

[99] L.O. Randall, B. Kappel, in: S. Garattini, E. Mussini, L.O. Randall (Eds.), Benzodiazepines, Raven Press, New York, 1973, pp. 27-51.

[100] H. Schutz, Benzodiazepines, Springer, Heidelberg, 1982.

[101] J.A. Herbert, H. Suschitzky, J. Chem. Soc. Perkin I (1974) 2657.

[102] H.R. Morales, A. Bulbarela, R. Contreras, Heterocycles 24 (1986) 135.

[103] D. Jung, T.W. Choi, Y.Y. Kim, I.S. Kim, Y.M. Park, Y.

G. Lee, Synth. Commun. 29 (1999) 1941.
[104] M.S. Balakrishna, B. Kaboudin, Tetrahedron Lett. 42 (2001) 1127.
[105] M. Curini, F. Epifano, M.C. Marcotullio, O. Rosati, Tetrahedron Lett. 42 (2001) 3193.
[106] B. Kaboadin, K. Navace, Heterocycles 55 (2001) 1443.
[107] M. Pozarentzi, J.S. Stephanatou, C.A. Tsoleridis, Tetrahedron Lett. 43 (2000) 1755.
[108] B.M. Reddy, P.M. Sreekanth, Tetrahedron Lett. 44 (2003) 4447.
[109] B.P. Bandgar, S.V. Bettigeri, N.S. Joshi, Synth. Commun. 34 (2004) 1447.
[110] J.S. Yadav, B.V.S. Reddy, S. P. Kumar, K. Nagaiah, Synthesis (2005) 480.
[111] J. S. Yadav, B.V.S. Reddy, N. Lingaiah, P.S. Saiprasad, Synthesis 6 (2004) 901.
[112] V. Sivamurugan, K. Deepa, M. Palanichamy, V. Murugesan, Synth. Commun. 34 (2004) 3833.
[113] M. Tajbakhsh, M.M. Heravi, B. Mohajerani, A.N. Ahmadi. J. Mol. Cata. A: Chemical 247 (2006) 213.
[114] D.V. Jarikote, S.A. Siddiqui, R. Rajagopal, K.V. Srinivasan, Tetrahedron Lett. 44 (2003) 1835.
[115] a) J.S. Yadav, B.V.S. Reddy, B. Eshwaraiah, K. Anuradha, Green Chem. 6 (2002) 592; b) D.V. Jarikote, S. Siddiqui, R. Rajagopal, T. Daniel, R.J. Lahoti, K.V. Srinivasan, Tetrahedron Lett. 44 (2003) 1835.
[116] M.M. Heravi, V. Zadsirjan, F.K. Behbahani, H.A. Oskooie, J. Mol. Catal. A: Chemical 259 (2006) 201.
[117] B. Sazen, D. Sames, Org. Lett. 5 (2003) 3607.
[118] J.C. Lewis, S.H. Wiedemann, R.G. Bergman, J.A. Ellman, Org. Lett. 6 (2004) 35.
[119] H. Matsushita, S.H. Lee, M. Joung, B. Clapham, K.D. Janda, Tetrahedron Lett. 45 (2004) 313.
[120] H.A. Oskooie, M.M. Heravi, A. Sadnia, F.K. Behbahani, F. Jannati, Chinese Chem. Lett. impress.
[121] a) B.J. Gaede, L. Mcdermott, J. Heterocycl. Chem. 30 (1993) 49; b) S. Ishii, K. Yagi, T. Umehara, M. Kudo, T. Nawamaki, S. Watanabe, Jap. Pat. 02, 129, 171, 1990; Chem. Abstr. 1990, 113, 172014; C) H. Shimori, T. Ishii, H. Yamazaki, Y. Yanasc, Y. Tanaka, Ger. Pat. 3, 713, 774, 1987; Chem. Abstr. 1988, 108, 112445; d) J.G. Buntaim, L.R. Hatton, D. Hawkins, C.J. Pearson, D.A. Roberts, Eur. Pat. Appl. 295, 117, 1988; Chem. Abstr. 1990, 112, 35845; e) G. Mcazza, G. Zanardi, J. Heterocycl. Chem. 30 (1993) 365.
[122] a) N. Hadad, J. Baron, Tetrahedron Lett. 43 (2002) 2171; b) K. Makino, H.S. Kim, Y. Kurasawa, J. Heterocycl. Chem. 35 (1998) 489; c) J. Elguero, Compr. Heterocycl. Chem. II 3 (1996) 1; d) K. Takagi, M. Hubert-Habart, J. Heterocycl. Chem. 33 (1996) 1003; e) N.R. El-Rayyes, N.A. Al-Awadi, Synthesis (1985) 1028; f) M.P. Sammes, A.R. Katritzky, in: Advances in Heterocyclic Chemistry, Vol. 34, Academic Press, 1983; G) L.C. Behr, R. Fusco, C.H. Jarboe, in: A. Weissberger (Ed.), The Chemistry of Heterocyclic Compounds, Interscience Publishers, John Wiley & Sons, New York, 1967.
[123] M.M. Heravi, T. Benmorad, F.K. Behbahani, H.A. Oskooie, Chinese Chem. Soc. Submitted.
[124] a) E. Juaristi, Enantioselective Synthesis of α-Amino Acids, Ed., Wiley-VCH, New York, 1997; b) G. Cardillo, C. Tomasini, Chem. Soc. Rev. (1996) 117; c) G.I. Georg (Ed.), The Organic Chemistry of α-Lactams, VCH Publishers, New York, 1993; d) F.F. Blicke, Org. React. 1 (1942) 303; e) M. Tramontini, Synthesis (1973) 703; f) M. Tramontini, L. Angiolini, Tetrahedron, 46 (1990) 1791; g) E.F. Kleinman, in: B.M. Trost, I. Fleming (Eds.), Comprehensive Organic Synthesis, Vol. 2, Pergamon, Oxford, 1991, p. 893; h) M. Arend, B. Westermann, N. Risch, Angew. Chem., Int. Ed. 37 (1998) 1044; i) M.E. Jung, in: B.M. Trost, I. Fleming (Eds.), Comprehensive Organic Synthesis, Vol. 4, Pergamon, Oxford, 1991, pp. 30-41 and references therein; j) S. Kobayashi, H. Ishitani, Chem. Rev. 99 (1999) 1069 and references therein.
[125] S. Kobayashi, K. Kakumoto, M. Sugiura, Org. Lett. 4 (2002) 1319.
[126] a) E.D. Bergmann, D. Ginsburg, R. Pappo, Org. React. 10 (1959) 179; b) D.A. Oare, C.H. Heathcock, in: E.L. Eliel, S.H. Wilen (Eds.), Topics in Stereochemistry, Vol. 19, Wiley Interscience, New York, 1989, pp. 227-407; c) P. Perlmutter, Conjugate Addition Reactions in Organic Synthesis, Tetrahedron Organic Chemistry Series, Vol. 9, Pergamon, Oxford, 1992.
[127] J. Christoffers, Eur. J. Org. Chem. (1998) 1259.
[128] S. Pelzar, T. Kauf, C. Van Wüllen, J. Christoffers, J.

Organometallic Chem. 684 (2003) 308.

[129] M. Balogh, I. Hermecz, Z. Meszaros, P. Laszlo, Helv. Chim. Acta. 67 (1984) 2270.

[130] J.R. Pfister, Synthesis (1990) 689.

[131] A. Maquestiau, A. Mayence, J. Eynde, Tetrahedron Lett. 32 (1991) 3839.

[132] J. Eynde, A. Mayence, A. Maquestiau, Tetrahedron 48 (1992) 463.

[133] R. Bocker, F.P. Guengerich, J. Med. Chem. 29 (1986) 1596.

[134] H. Mashraqui, K.A. Madhavi, Tetrahedron Lett. 39 (1998) 4895.

[135] S. Rajender, D.K. Varma, Tetrahedron Lett. 40 (1999) 21.

[136] J. Arguello, L.J. Nunez-Vergara, J.C. Sturm, J.A. Squella, Electrochim. Acta. 49 (2004) 4849.

[137] C. Lopez-Alarcon, L.J. Nunez-Vergara, J.A. Squella, Electrochim. Acta. 38 (2003) 505.

[138] N. Nakamichi, Y. Kawashita, M. Hayashi, Org. Lett. 4 (2002) 3955.

[139] a) M.M. Heravi, K. Bakhtiari, H.A. Oskooie, R. Hekmatshoar. Heterocyclic Commun. 12 (2006) 209-212 2006; b) M.M. Heravi, F. Derikvand, H.A. Oskooie, R. Hekmatshoar. J. Chem. Res. (S) (2006) 168; c) L. Fotouhi, S. Khaleghi, M.M. Heravi, Lett. Org. Chem. 3 (2006) 111; d) M.M. Heravi, F. Derikvand, H.A. Oskooie, R. Hekmatshoar. Synth. Commun. 36 (2006) 77; e) M.M. Heravi, F.K. Behbahani, H.A. Oskooie, R. Hekmatshoar. Tetrahedron Letters 46 (2005) 2775; f) M.M. Heravi, M. Ghassemzadeh, Phosphorus Sulfur and Silicon and the Related Elements 180 (2005) 347; g) M.M. Heravi, F. Dirkwand, H.A. Oskooie, M. Ghassemzadeh, Heterocyclic Commun. 11 (2005) 75; h) M.M. Heravi, F.S.S. Moosavi, Y.S. Beheshtiha, M. Ghassemzadeh, Heterocyclic Commun. 10 (2004) 415; i) M.M. Heravi, M. Ghassemzadeh, Heterocyclic Commun. 10 (2004) 465; j) M. Tajbakhsh, M.M. Heravi, A. Hosseini, A. Shahrezaiee, Phosphorus Sulfur and Silicon and the Related Elements 178 (2003) 773; k) Gmelin-Durrer. The Metallurgy of Iron, Vol. 3a, B, Verlag Chemie, 1971.

[140] A. Citterio, M.C. Carvajal, A. Mele, M. Nicolini, R. Santi, R. Sebastiano, J. Chem. Soc. Perkin Trans. 2 (1993) 1973.

[141] K. Kurachi, H. Kise, Polymer Journal 26 (1994) 1325.

[142] K. Nishio, M. Fujimoto, O. Ando, H. Ono, T. Murayama, J. Appl. Electrochem. 26 (1996) 425.

[143] G.B. Shulpin, M.M. Bochkova, G.V. Nizova, N.B. Kozlova, Applied Catalysis B-Environmental 12 (1997) 1.

[144] X. Zhou, C. Chriswell, Fuel Processing Technology, 46 (1996) 41.

[145] G. Mailhot, L. Hykrdová, J. Jirkovský, K. Lemr, G. Grabner, M. Bolte, Applied Catalysis B: Environmental 50 (2004) 25.

[146] P. Mazellier, J. Jirkovský, M. Bolte, Pestic. Sci. 49 (1997) 259.

[147] N. Brand, G. Mailhot, M. Bolte, Environ. Sci. Technol. 32 (1998) 2715.

[148] N. Brand, G. Mailhot, M. Bolte, Chemosphere 40 (2000) 395.

[149] G. Mailhot, N. Brand, M. Astruc, M. Bolte, Appl. Organomet. Chem.16 (2002) 27.

[150] C. Catastini, M. Sarakha, G. Mailhot, M. Bolte, Sci. Total Environ. 298 (2002) 219.

[151] W. Feng, D. Nansheng, Chemosphere 41 (2000) 1137.

[152] A. Strecker, Liebigs Ann. Chem. 75 (1850) 27.

[153] P. Biginelli, Ber. Dtsch. Chem. Ges. 24 (1891) 1317.

[154] C. Mannich, Kroschl, Arch. Phar. 250 (1912) 647.

[155] a) D. Enders, J.P. Shilvock, Chem. Soc. Rev. 29 (2000) 359; b) M. North, in: S.-I. Murahashi (Ed.), Science of Synthesis, Vol. 19, Thieme, Stuttgart, 2004, p. 285.

[156] R.O. Duthaler, Tetrahedron 50 (1994) 1539.

[157] a) H.A. Oskooie, M.M. Heravi, A. Sadnia, F. Jannati, F.K. Behbahani, Synth. Commun. 37 (2007) 1; b) H.A. Oskooie, M.M. Heravi, K. Bakhtiari, V. Zadsirjan, F.F. Bamoharram, Synlett (2006) 1768.

[158] a) M.M. Heravi, H.A. Oskooie, F.K. Behbahani, Russ. J. Org. Chem. Submitted; b) M.M. Heravi, F.K. Behbahani, V. Zadsirjan, H.A. Oskooie, Heterocyclic Commun., 12 (2006) 369; c) M.M. Heravi, K. Bakhtiari, F.F. Bamoharram, Cat. Commun. 7 (2006) 373; d) M.M. Heravi, F.F. Bamoharram, J. Mol. Catal. Chemical 242 (2005) 173; e) M. Tajbakhsh, M.M. Heravi, A.N. Ahmadi, J. Mol. Catal. Chemical 236 (2005) 216.

[159] C.O. Kappe, J. Org. Chem. 62 (1997) 7201.