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ADVANCEMENT IN LITHIUM PERCHLORATE CATALYZED SYNTHESIS OF ORGANIC MOLECULAR SCAFFOLDS

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ABSTRACT

Lithium perchlorate is a Lewis acid catalyst which activates a large number of organic reactions providing high yields with enhanced reaction rates. Moreover, it makes some of the reactions possible to proceed under solvent-free conditions which is an important aspect for the development of green chemistry. This paper canvasses the chemical literature on lithium perchlorate as a catalyst for organic synthesis of various molecular scaffolds.

KEYWORDS: Lithium perchlorate, catalyst, epoxides, alkylation, Friedel-Craft, Michael addition

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INTRODUCTION

Perchlorates are very strong oxidizing agents and have been reported to accelerate variety of slow organic reactions for the improvement of product yield. Lithium perchlorate ($LiClO_4$) is one of the widely used catalysts in organic synthesis[1]. However, it forms explosive mixtures with combustible organic or other oxidizable materials due to its high oxidation potential[2]. It has been reported as an efficient Lewis acid catalyst for organic synthesis with better results as compared to other perchlorates, such as magnesium perchlorate ($MgClO_4$) or zinc perchlorate ($ZnClO_4$), due to higher charge:size ratio and better co-ordination power of lithium ions[3]. Lithium perchlorate containing media has also been reported in several organic syntheses such as Diels-Alder cycloaddition (LPDE)[4], actualization ($LiClO_4$-trimethylsilylchloride)[5], aldol condensation ($LiClO_4$-trimethylsilyldiethylamine)[6], anodic coupling reaction ($LiClO_4$-nitromethane)[7], acylation ($LiClO_4$-bismuth triflate)[8], reductive amination (LDPE)[9], and N-alkyls ($LiClO_4$-nitromethane) reactions[10]. Moreover, it has been also used in investigating physico-chemical and spectroscopic properties[1]. It finds applications as catalyst in organic synthesis of several biologically active molecules such as pyrroloindoloquinazoline (antiviral)[11], piperidinones (p38MAP-kinase activation inhibitor)[12], aminohydroxylatedpiperidine (antineoplastic)[13], pyrimidinones(antibacterial)[14], azanucleosides (myelodysplastic syndromes)[7,15], sydnones (antimicrobial)[16], phosphonates (anticancer)[17], thiiranes (selective gelatinase inhibitors)[18], thiooxazolidinone (potassium channel opener)[3], oxadiazoles (antiinflammatory)[19]. Recently, Buriez *et al*. have been reported $LiClO_4$ as a supporting electrolyte for electrochemical grafting of a π-conjugated amino-ferrocifen drug complex over gold surface[20]. Masoud *et al*. reported preparation of composite polymer electrolyte using solution cast technique from polyethylene oxide (PEO) and $LiClO_4$ [21]. Choudhary *et al*. studied the effect of various blending methods used for the preparation of solid polymer electrolytes from polyethylene oxide (PEO) and $LiClO_4$ [22]. Very recently, Takahashi *et al.* have been reported disulphide bond formation in a tagged tripeptide using electrochemical phage-transfer anodic reaction in the presence of $LiClO_4$ and redox mediators (Et_4NBr, Bu_4NBr, PyHBr, NaBr, LiBr, NH_4Br *etc.*)[23]. Some of the functional group transformations catalysed by $LiClO_4$ are exemplified in Fig 1. Here, we reviewed the various finding for constructions of molecular scaffolds useful in synthetic chemistry using $LiClO_4$ as a catalyst. Moreover, we have tabulated some of vary important reactions of synthetic importance at the end of this paper.

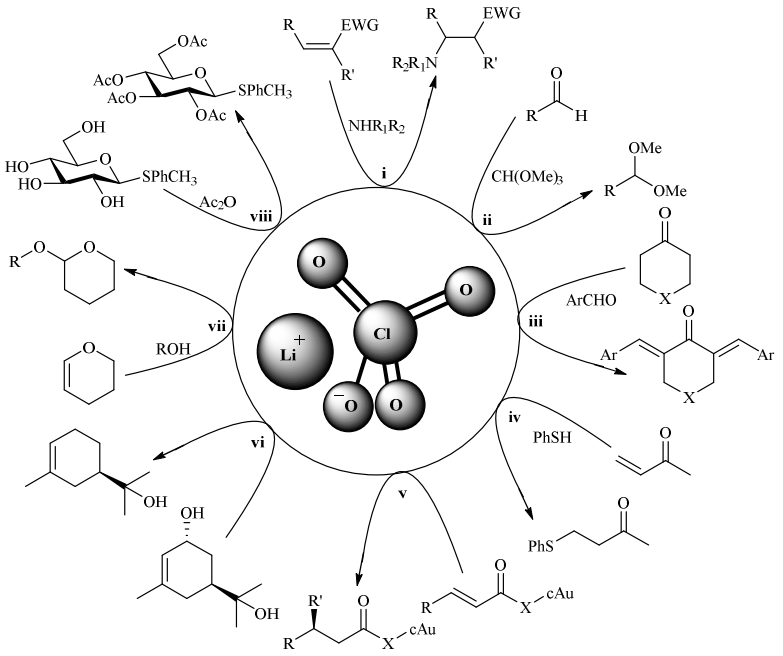


Figure 1
Schematic representation of functional group transformations catalyzed by lithium perchlorate (i-viii)[24-29].

Earlier, it has been documented that in $LiClO_4$ catalysed synthesis accelerated rate of reaction is associated with function of Li^+ ion as Lewis acid catalyst[4]. The fundamental mechanism adopted by $LiClO_4$ to catalyse the organic reactions is depicted in Fig 2. In this cycle, reactant R_1 and R_2 undergo catalytic reaction to give product with the help of the $LiClO_4$ catalyst. The first step of cycle starts with coordination of Lewis acid catalyst to a Lewis basic site of reactant R_1 and formation of reactant-catalyst complex with polarization of a part of the reactant molecule R_1. Generally, Lewis basic sites consist of one or more hetero-atoms such as oxygen and nitrogen. This polarization activates the reactant molecule R_1 for the actual organic transformation. In second step, reactant R_2 reacts with reactant R_1 at polar part within the complex. In third step, polarity and bond transition occurs and both reactants convert in the product P. In the final step, product P releases from Lewis-acid product complex by dissociation, leaving behind the catalyst to be reused for another cycle of the reaction. The overall catalytic efficiency is determined by the ease with which each of these steps proceeds[30,31].

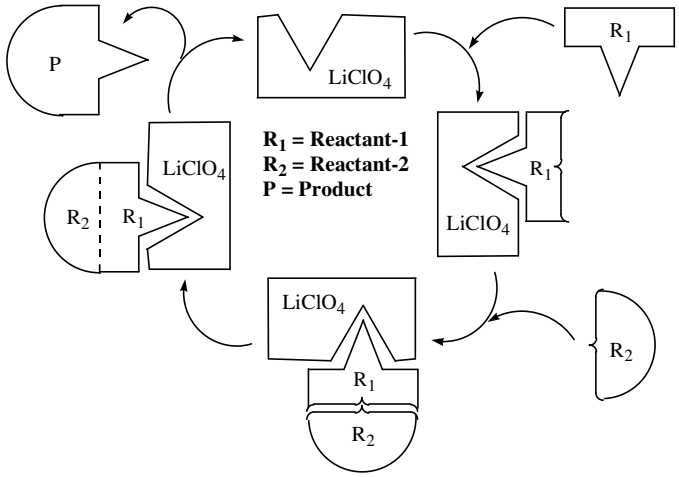


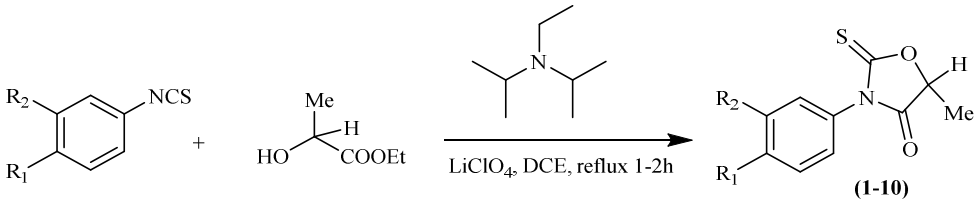
Figure 2
Mechanism of reaction catalyzed by $LiClO_4$.

1. Lithium perchlorate catalyzed synthesis

Lithium perchlorate has been reported as a highly efficient catalyst which is able to catalyse several chemical reactions for synthesis of thio-oxazolidinones, amines, thiiranes, oxadiazoles, *N*- or *C*-alkylated amines, acetylated sydnones, alkylphosphonates, halohydrins or *O*-acyl halohydrins, *O*-acylated diols, hydroxyazides, azanucleosides, imidazopyridinyl-pyrrolidinediones, imidazothiazolyl-pyrrolidinediones, piperidines, warfarin analogues, thioxotetrahydropyrimidinones, enones, 2-nitrophenylethylfurans, oxindoles, organic-inorganic hybrid membranes etc. Synthetic reactions of these molecules are described in following sections.

1.1 Synthesis of thio-oxazolidinones

Thio-oxazolidinones are heterocyclic in nature with nitrogen and oxygen in five-membered ring bridged with thion group[32]. They have been shown various biological activities *viz.* anticonvulsants, K^+ channel openers, antidiabetics *etc*[33-35]. Their analogues, oxazolidinones, are of the clinical significance *viz*. rivaroxaban, linezolid, eperezolid, posizolid, radezolid, torezolid *etc*.[36] and have been used as chiral auxiliaries in asymmetric synthesis to control the stereoselectivity[37]. Khatik *et al*. reported an efficient and convenient method for the synthesis of 5-methyl-3-aryl-2-thiooxazolidin-4-ones from aryl isothiocyanates and ethyl lactate in presence of DIPEA in dichloroethane (DCE) using catalytic amount of $LiClO_4$ (Scheme 1). In this reaction, the author reported that electron withdrawing groups increase the electrophilicity of aryl isothiocyanates providing better yields, whereas electron donating groups led to a longer reaction time with comparably lesser yields (Table **1**)[3,38].



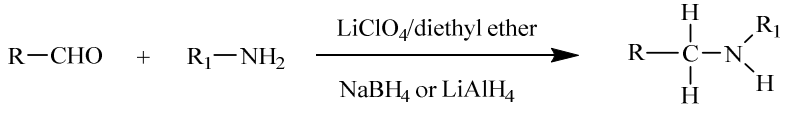
Scheme 1
LiClO$_4$ catalyzed synthesis of thio-oxazolidinones.

Table 1
Thio-oxazolidinones synthesized from aryl isothiocyanates and hydroxyl esters.

Entry	R_1	R_2	% Yield
1	Cl	H	90
2	Br	H	75
3	F	H	85
4	CN	H	80
5	H	NO_2	75
6	F	Cl	69
7	Cl	CF_3	72
8	Me	H	65
9	Me	Me	70
10	MeO	MeO	70

1.2 Synthesis of secondary and tertiary amines

Secondary and tertiary amines can be efficiently prepared by direct reductive amination of aldehydes and ketones with amines[39]. Direct reductive amination method involves the reaction between carbonyl compound and amine with suitable reducing agent in a one-pot operation. The carbonyl group initially reacts with ammonia or amine to form an imine, which then undergoes reduction in presence of hydrogen or hydride ion[40,41]. This method is highly advantageous over other imine synthesis methods due to wide commercial availability of substrates and mild reaction conditions. Several reagents which effect direct reductive amination include $NaBH(OAc)_3$[42,43], $Yb(OAc)_3$-(*S*)-α-MBA[44], $Zn(ClO_4)_2{\cdot}6H_2O$-$InCl_3$/Et_3SiH[45], ZSS-Pd nanoparticles[46], pyridine-BH_3[47], Pt-MoO_X/TiO_2[48], $ZnCl_2$-TMSOAc + $NaBH(OAc)_3$[49], Ir-f-Binaphane + H_2[50] *etc*. Recently, Pressnitz *et al.* have reported ω-transaminase catalysed asymmetric amination of cyclic ketones with enantiomeric excess upto > 99%[51]. Amines and their derivatives are used as building blocks for various organic substrates and also serve as biologically active compounds such as α-*N*-benzylamino acids[52], plasmochin[53], castanospermine and swainsonine[54], methamphetamine[55], and isofogamine[56]. Saidi *et al.* described reductive amination of aldehydes and primary or secondary amines with sodium borohydride or lithium aluminium hydride in the presence of lithium perchlorate in diethyl ether. Reaction with primary amines afforded corresponding secondary amines with good to excellent yields (Scheme 2)[9]. The solution of lithium perchlorate in diethyl ether produced iminium salt or an imine with aldehyde. Sodium borohydride and lithium aluminium hydride are both used as reducing agents but lithium aluminium hydride reduces other functional groups such as nitro, esters, epoxides *etc*[9,57]. Reduction of imines prepared *in-situ* afforded secondary amines in higher yields. Both reducing agents *viz.* sodium borohydride and lithium aluminium hydride provide similar yields (Table 2).

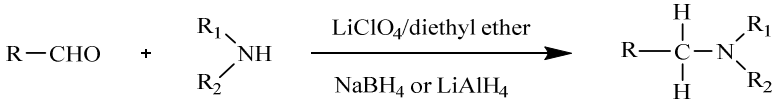


Scheme 2
LiClO$_4$ catalysed synthesis of secondary amines.

Table 2
Secondary amines synthesized by reductive amination of aldehydes.

Entry	R	R_1	$NaBH_4$ (% yield)	$LiAlH_4$ (% yield)
1	Ph	Ph	100	97
2	Ph	$CH(CH_3)CH_2CH_3$	97	98
3	Ph	$CH_2(CH_2)_3CH_3$	98	97
4	4-ClC_6H_4	$CH(CH_3)CH_2CH_3$	98	99
5	4-ClC_6H_4	Cyclohexyl	99	100
6	2,4-ClC_6H_3	$CH_2(CH_2)_3CH_3$	99	96
7	3-$NO_2C_6H_4$	Cyclohexyl	98	-
8	5-$NO_2C_6H_4$	$CH(CH_3)CH_2CH_3$	98	-
9	3-$NO_2C_6H_4$	$CH_2(CH_2)_3CH_3$	96	-
10	4-BrC_6H_4	$CH_2C_6H_5$	-	98
11	$CH_2CH{=}CHCH_3$	$CH_2C_6H_5$	62	52
12	2-Pyridyl	$CH_2C_6H_5$	94	-
13	2-Pyridyl	$CH_2(CH_2)_2CH_3$	90	-
14	$CH_2CH{=}CHC_6H_5$	Cyclohexyl	78	-
15	$CH_2CH_2CH_2C_6H_5$	$CH_2(CH_2)_3CH_3$	95	-
16	$CH_2CH_2CH_2C_6H_5$	$CH(CH_3)CH_2CH_3$	90	-
17	$CH_2CH(CH_3)_2$	$CH_2(CH_2)_3CH_3$	88	-

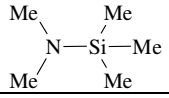
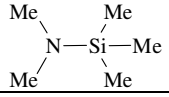
Scheme 3 represents the synthesis of tertiary amines via reaction of aldehydes and secondary amines. In this, iminium ions generated *in-situ* gave lower yields of tertiary amines compared to imines. The use of lithium aluminium hydride as reducing agent improves the yield by 10-20% as compare to sodium borohydride. However, there is decrease in the yield of tertiary amines as compared to secondary amines (Table 2 and 3). This may possibly due to steric hindrance between reactants, and more basicity of secondary amine reactants which may help in formation of coordination complex with Lewis acid. These facts decrease nucleophilicity of amines (Scheme 3)[57].



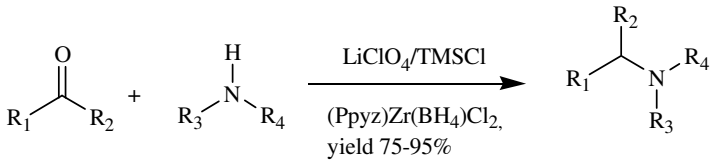
Scheme 3
$LiClO_4$ catalysed synthesis of tertiary amines.

Table 3
Tertiary amines synthesized by reductive amination of aldehydes.

Entry	R (Aldehyde)	Amine $NH(R_1)R_2$	$NaBH_4$ (% yield)	$LiAlH_4$ (% yield)
1	Ph		78	86
2	Ph		45	63
3	Ph		66	83
4	4-ClC_6H_4		72	82
5	4-ClC_6H_4		60	75
6	2,4-ClC_6H_3		79	91
7	3-$NO_2C_6H_4$		78	-
8	$CH_2C_6H_5$		76	88

9	$CH_2C_6H_5$		65	75
10	4-ClC_6H_4		-	58
11	4-BrC_6H_4		62	-
12	4-FC_6H_4		70	78
13	Ph		-	82
14	4-BrC_6H_4		81	-

Similarly, Heydari *et al*. have been reported synthesis of tertiary amines by $LiClO_4$ catalysed reductive amination of carbonyl compounds with different reducing agent (Scheme 4). The product was obtained in 75-95% of yield (Table 4)[58].

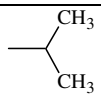
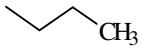
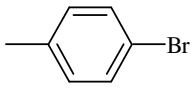
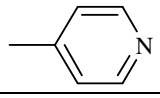
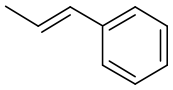
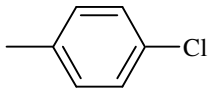
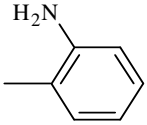
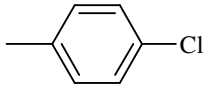
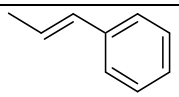
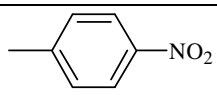


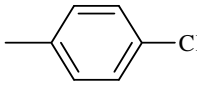
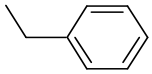
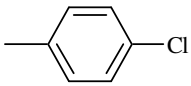
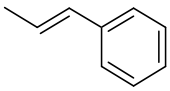
Scheme 4

$LiClO_4$ catalysed reductive amination with zirconium borohydride complex.

Table 4

Tertiary amines synthesized using $(Ppyz)Zr(BH_4)Cl_2$ as reducing agent.

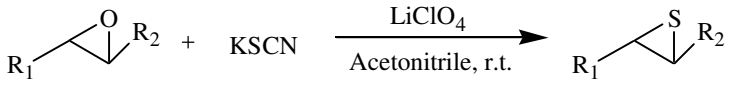
Entry	R_1	R_2	R_3	R_4	% Yield
1		H	Et	Et	87
2		H	Et	Et	90
3		H	Et	Et	75
4		H	Et	Et	80
5		H	Et	Et	82
6		H		H	90
7		H	Ph	H	95
8		H	Ph	H	92
9		H	Ph	H	90

10		H	Ph	H	90
11		Me	Ph	H	95
12	Ph	Me	Ph	H	84
13		H	*o*-TMS	H	89
14		H	H	NMe_2	80

In recent years, reductive amination has been used for chemical synthesis of various bioactive natural product such as (±)-coniine, (±)-anabasine, (±)-dihydropinidine, (±)-quinolizidines, (+)-tetraponerine T-3[59], (-)-lannotinidine B[60], pumiliotoxin C[61], (+)-preussin[62] and casuarine[63].

1.3 Synthesis of thiiranes

Thiiranes are the sulphur heterocycles with various biological activities such as selective gelatinase inhibitors, selective A1 adenosine receptor agonists, potential topoisomerase I inhibitors, estrogen synthetase inhibitors[18]. Recently, thiirane intermediates have been reported for the synthesis of thioglycosides. Thiiranes offer reactivity with nucleophiles having regioselectivity and stereoselectivity combined with the rich chemistry that a vicinal thiol group in the product provides[64]. Reddy *et al.* have been reported synthesis of thiiranes by reacting potassium thiocyanate with epoxides using catalytic amounts of lithium perchlorate and acetonitrile as solvent (Scheme 5)[65]. In this reaction, electron-releasing groups on the aromatic ring facilitate the formation of thiiranes whereas electron-withdrawing groups do not. Epoxides are the most convenient starting materials for preparation of simple thiiranes because of their ease of formation, wide reactivity, and ability to undergo regioselective ring-opening reactions, contributing largely to their synthetic value but require long reaction times and high temperature conditions. In the presence of catalytic amount of $LiClO_4$, reaction proceeds under mild conditions at higher reaction rates with excellent yield of products.



Scheme 5
$LiClO_4$ catalysed synthesis of thiiranes from epoxides.

The epoxide ring is almost a triangle shaped with bond angles of about 60° as compared to ether which has C-O-C bond angle about 120°. Thus, it has significant angular strain, also called von Baeyer strain, which determines its chemical reactivity[66]. Epoxides are highly reactive toward nucleophilic reagents. The nature of substituents at *p*-position of aromatic ring affects yield of product such as electron donating group (EDG) decreases yield of product (Table 5). The formation of thiiranes proceeds through the opening of epoxide ring by thiocyanate nucleophile and involve oxathiolan-2-ylideneamine anion (I) as an intermediate depicted below in Fig 3.

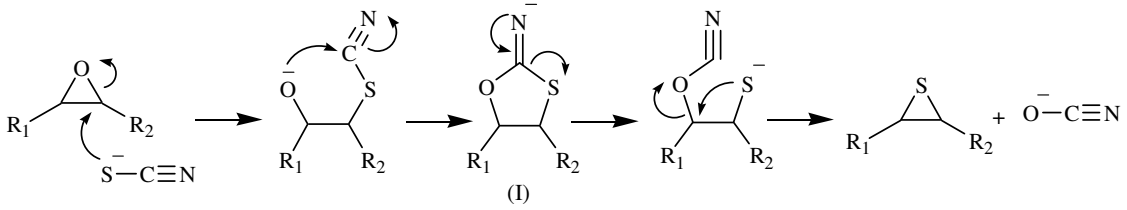
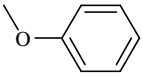
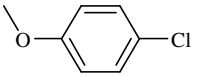
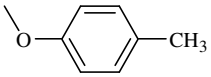
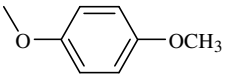
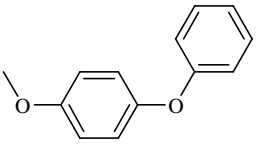
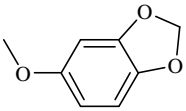
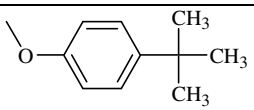
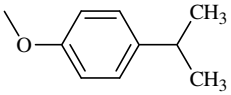
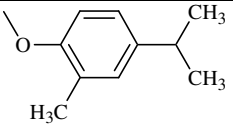
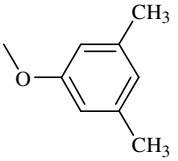
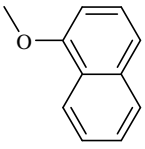
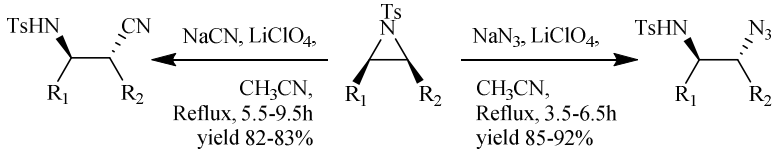


Figure 3
Mechanism of thiiranes formation from epoxides.

Table 5
Thiiranes synthesized from epoxides.

Entry	R_1	R_2	% Yield
1	Ph	H	90
2	Ph	Ph	85
3		H	95
4		H	90
5		H	85
6		H	78
7		H	75
8		H	72
9		H	80
10		H	83
11		H	80
12		H	92
13		H	85

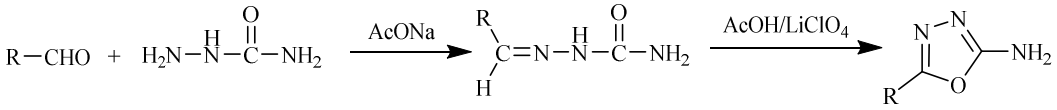
Similarly, Yadav *et al.* have been reported nucleophilic ring opening of activated aziridines with azide and cyanide nucleophiles in presence of $LiClO_4$ as a catalyst. The reaction found to afford β-azido and β-cyanoamines in yield 83-92% with high regioselectivity (Scheme 6)[67].



Scheme 6
$LiClO_4$ catalysed synthesis of β-azido and β-cyanoamines.

1.4 Synthesis of oxadiazoles

Oxadiazoles are five-membered heterocyclic compounds in which 1,3,4-oxadiazole cores have broad spectrum of biological activities such as antibacterial, antifungal, analgesic, anti-inflammatory, antiviral, anticancer, antihypertensive, anticonvulsant, and antidiabetic properties[68,69]. They have been also used in medicinal chemistry as bioisosteres for carboxylic acids, esters and carboxamides[70]. Examples of compounds containing the 1,3,4-oxadiazole moiety used in clinical medicine include raltegravir (antiretroviral drug) and zibotentan (anticancer agent)[68]. The electrophilic substitutions in oxadiazole ring carbon atom are very difficult because of relatively low electron density which can be attributed to electron withdrawal effect of the pyridine type nitrogen atom. However the attack of electrophiles occurs at nitrogen, if oxadiazole ring is substituted with electron-releasing groups[71]. Kumar *et al*. have been reported an efficient electrochemical method for the synthesis 5-substituted-2-amino-1,3,4-oxadiazoles using lithium perchlorate as supporting electrolyte (Scheme 7)[19]. The reaction was carried out by the treatment of semicarbazone and aromatic aldehydes at platinium electrode. The oxadiazoles obtained in very good yield, 75-96% (Table 6).

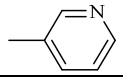
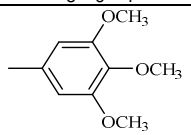
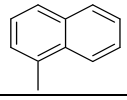
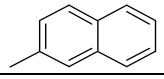


Scheme 7

$LiClO_4$ catalyzed synthesis of 5-substituted-2-amino-1,3,4-oxadiazoles.

Table 6

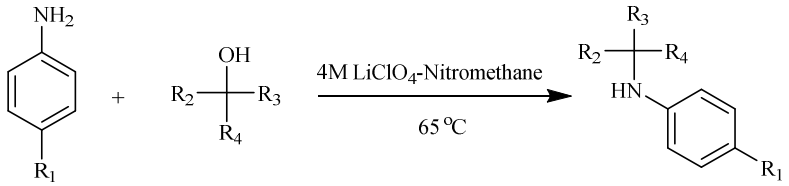
2-Amino-1,3,4-oxadiazoles synthesized from aldehydes and semicarbazone.

Entry	R	% Yield
1	2-BrC_6H_4	88
2	3-BrC_6H_4	96
3	4-BrC_6H_4	86
4	2-$NO_2C_6H_4$	92
5		79
6	CH_2Cl	75
7	$CHCl_2$	81
8	4-$CH_3C_6H_4$	85
9		92
10		87
11		86

1.5 Synthesis of N-alkylated anilines

Alkylanilines are important chemicals used as starting material in the industries for the production of dyes, pharmaceuticals and explosives[72-75]. Some of the useful alkylanilines include *N*-methylaniline (NMA), *N,N*-dimethylaniline (NNDMA) and toluidines[76,77]. Alkylanilines are conventionally synthesized by the alkylation of aniline in liquid phase using mineral acids as catalysts and alkyl halides or dimethyl sulphate as alkylating agents. But due to certain drawbacks these methods have been replaced by use of heterogeneous catalysts and relatively non-toxic alkylating agents such as methanol and dimethyl carbonate[78]. Zhou *et al.* reported synthesis of *N*-alkylated anilines by the reaction between substituted

aniline and diarylmethanols in the ratio of 1.5:1.0 at 65 °C in $LiClO_4$-nitromethane medium (Scheme 8). It was found from the reaction that diphenylmethanols with electron-withdrawing groups are less reactive than those with electron-donating groups[10].

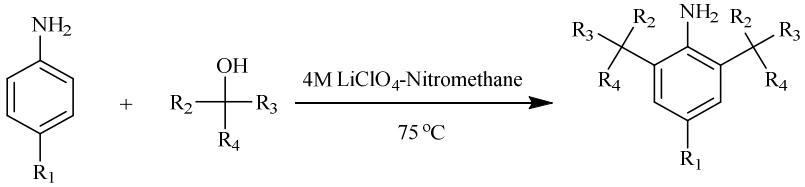


Scheme 8
$LiClO_4$ catalyzed N-alkylation of anilines.

Table 7
N-Alkylated anilines synthesized from anilines and alcohols.

Entry	R_1	R_2	R_3	R_4	% Yield
1	Cl	Ph	Ph	H	75
2	Cl	4-ClC_6H_4	Ph	H	68
3	Cl	4-BrC_6H_4	Ph	H	66
4	Cl	4-ClC_6H_4	4-$NO_2C_6H_4$	H	-
5	Cl	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	H	76
6	Cl	Ph	4-$OCH_3C_6H_4$	H	-
7	Cl	Ph	Me	H	53
8	Cl	Ph	Ph	Ph	61
9	H	Ph	Ph	H	54
10	Cl	Me	Me	H	-
11	Br	Ph	Ph	H	74

The reaction gives double Friedel-Craft alkylation product when ratio of substituted aniline and diarylmethanol is shifted from 1:1.5 to 1:2 at 75 °C (Scheme 9). The dialkylated anilines also obtained in very good yield, 70-99% (Table 8)[10].



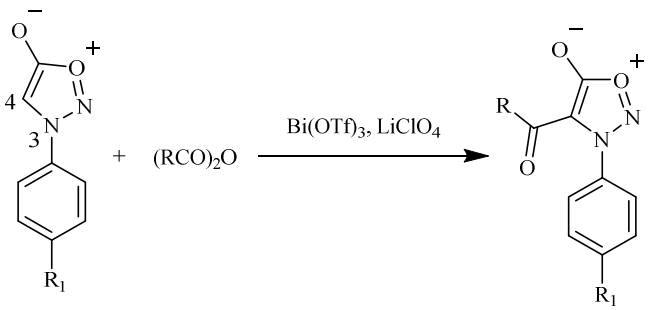
Scheme 9
$LiClO_4$ catalyzed double Friedel-Craft alkylation.

Table 8
Dialkyl anilines synthesized from anilines and diarylmethanol.

Entry	R_1	R_2	R_3	R_4	% Yield
1	Cl	Ph	Ph	H	99
2	Cl	4-ClC_6H_4	Ph	H	72
3	Cl	3-ClC_6H_4	Ph	H	73
4	Cl	4-BrC_6H_4	Ph	H	70
5	Cl	4-$CH_3C_6H_4$	4-$CH_3C_6H_4$	H	93
6	Cl	Ph	Ph	Ph	-
7	Cl	Ph	Ph	H	-
8	Me	Ph	Ph	H	78
9	NO_2	Ph	Ph	H	70

1.6 Friedel-Craft acylations of sydnones

Sydnones are mesoionic compounds with varying charge distribution on the ring according to their resonance form depending on their aryl substituents at the positions N(3) and C(4). Here, N(3) behaves as an electron-withdrawing substituent and C(4) shows as an electron-donating character to provide duality effect to the ring. The rupture of the sydnone rings via loss of a carbon dioxide molecule causes retention of the charges on the fragments which are called "azomethine-imines" resonance forms containing both positive and negative charges[79]. Sydnones possess many biological activities such as antibacterial, antineoplastic and anti-inflammatory agents. They also act as novel precursors for pyrazoles[80]. Mahoney *et al.* reported Friedel-Craft acylation reaction of phenylsydnone in the presence of bismuth triflate and lithium perchlorate (Scheme 10)[8]. The formation of product indicated a very strong effect of size of alkyl side chain in anhydrides as well as electron donating efficiency of substituents at *p*-position of phenyl and improvement in the yield by 19-28% (Table 9). Generally, electron withdrawing substituents at *p*-position slow down the reaction such as in case of $-NO_2$ substituent reaction could not complete even after 72 hrs. Similarly, Balaguer *et al.* also reported the synthesis of 4-acetyl-3-phenylsydnone using similar reaction conditions and reagents[81].



Scheme 10
$LiClO_4$-$Bi(OTf)_3$ catalysed acylation of 3-phenylsydnone.

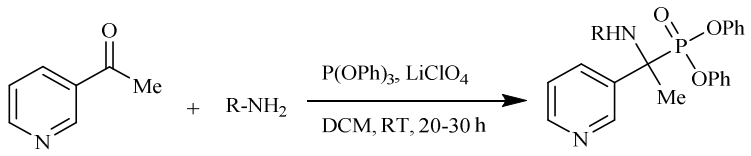
Table 9
4-Acetyl-3-phenylsydnone derivatives synthesized from phenylsydnones.

Entry	R	R_1	% Yield[a]
1	CF_3	H	-
2	CH_2CH_3	H	63
3	$CH_2CH_2CH_3$	H	73
4	$CH(CH_3)_2$	H	59
5[b]	CH_3	NO_2	-
6	CH_3	Cl	87
7	CH_3	Br	83
8	CH_3	CH_3	83
9[c]	CH_3	OCH_3	78

[a]Catalyst used at conc. of 25 mole %. [b]Incomplete reaction after 72 hrs also. [c]Reaction completed within 30 min.

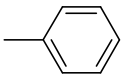
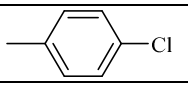
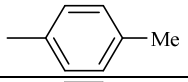
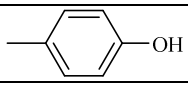
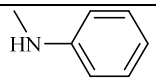
1.7 Synthesis of alkylphosphonates

Organic phosphonates are the important organic compounds containing $-PO_3H_2$ moiety attached to a carbon atom which is pH-dependent main structural feature of phosphonates. Besides being used in large number of technological applications of industrial and medicinal interest, phosphonates are also used in basic research in organic synthesis, construction of organic-inorganic hybrids and metal-containing coordination polymers[82]. Abdel-Megeed *et al.* reported the synthesis of diphenyl-1-(pyridine-3-yl)ethylphosphonates obtained from the reaction of 3-acetyl pyridine with aromatic amines and triphenylphosphite in the presence of lithium perchlorate as a catalyst in dichloromethane at room temperature (Scheme 11)[17].



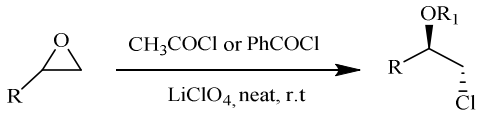
Scheme 11
$LiClO_4$ catalysed synthesis of diphenyl-1-(pyridine-3-yl)ethylphosphonates.

Table 10
Diphenyl-1-(pyridine-3-yl)ethylphosphonates synthesized from 3-acetyl pyridine.

Entry	R	% Yield
1		73
2		81
3		90
4		85
5		75

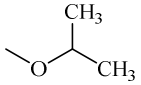
1.8 Nucleophilic ring opening of epoxides

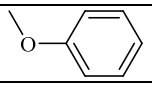
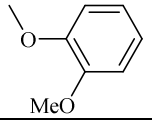
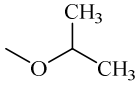
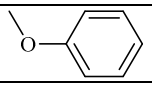
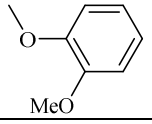
Epoxides are the three-membered heterocycles containing oxygen atom. Ring opening of epoxides can be brought with a large number of nucleophiles with stereoselectivity and regioselectivity[83,84]. Halohydrins are important class of compounds used for synthesis of various bioactive molecules or natural products and they can be synthesized by opening of epoxide ring with a nucleophile[85,86]. Azizi *et al.* have been reported ring opening of epoxides in the presence of catalytic amount of lithium perchlorate[87]. Scheme 12 represents the synthesis of acylated halohydrin synthesis through ring opening of epoxides with acid chloride *viz.* acetyl chloride or benzoyl chloride. Reactions of acid chloride were found to be completely regioselective with formation of one product due to preferred attack of nucleophile to less substituted carbon of epoxide (Table 11).



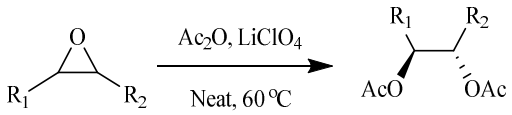
Scheme 12
$LiClO_4$ catalyzed ring opening of epoxides with acid chlorides.

Table 11
O-Acyl halohydrins synthesized from epoxides and acid chlorides.

Entry	R	R_1	% Yield
1	H	Ac	68
2	Me	Ac	76
3	Et	Ac	82
4	CH_2Cl	Ac	94
5	CH_2Br	Ac	80
6		Ac	86

7		Ac	89
8		Ac	90
9	CH_2Cl	COPh	82
10		COPh	90
11		COPh	84
12		COPh	90

The ring opening of epoxides with acetic anhydride in the presence of lithium perchlorate affords acetylated diols (Scheme 13)[87]. Acetic anhydride is generally considered to be less reactive due to higher stability of its intermediate carbocation. The amount of lithium perchlorate and temperature influences the reaction rate. However, products obtained in very good yield with 50 mol% lithium perchlorate at 60 °C (Table 12).



Scheme 13
$LiClO_4$ catalyzed ring opening of epoxide with acetic anhydride.

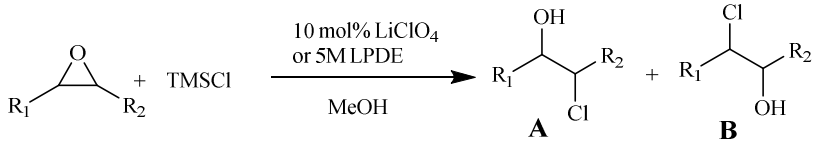
Table 12
Acetylated diols synthesized from epoxide and acetic anhydride.

Entry	R_1, R_2	% Yield
1	$-(CH_2)_4-$	76
2	n-C_2H_5, H	65
3	CH_2Cl, H	78
4	CH_2OPh, H	94
5	$CH_2OCH(CH_3)_2$, H	93
6	CH_2Br, H	68
7	Ph, H	66*

Reaction at room temperature.

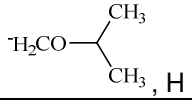
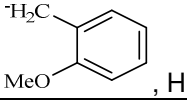
Scheme 14 represents the synthesis of chlorhydrins by reacting epoxides with trimethylsilyl chloride (TMSCl) in the presence of lithium perchlorate[87]. The same reaction when carried out in the presence of lithium perchlorate-diethyl ether medium provided similar results in terms of yield and regioselectivity. Both steric and electronic effects control regioselectivity in reactions of asymmetrical epoxides. These asymmetrical epoxides undergo cleavage by TMSCl with the attack at the less substituted carbon atom. However, in case of styrene oxide TMSCl preferably attacks at phenyl substituted carbon atom due to involvement of more stabilized carbocation as an intermediate. It is usually known that this type of SN2 reaction with chloride anion occurs through stereochemical inversion of center as a major product. However, in some cases it can also afford unexpected anti-chlorohydrin with retention of center[85,88]. Lithium perchlorate plays an important role in the ring opening of epoxides through the coordination of Li^+ with epoxide oxygen making the epoxide more susceptible to nucleophilic attack by TMSCl

(Table 13). It is followed by silylation of the oxygen atom and formation of the chlorohydrins. This method was found to be superior to other reported methods in literature in terms of the amount of the catalyst and TMSCl, preparation of catalyst, reaction time, temperature, requirement of solvent, products yields, and regioselectivity[89-92].



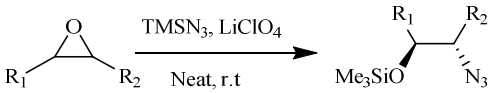
Scheme 14
$LiClO_4$ catalysed ring opening of epoxides with TMSCl.

Table 13
Chlorhydrins synthesized from epoxides.

Entry	R_1, R_2	% Yield[a]
1	Ph, H	82 (12:88)
2	CH_2CH_3, H	90 (80:20)
3	CH_2Cl, H	93 (90:10)
4	CH_2Br, H	90 (97:3)
5		96 (100:0)
6		97 (100:0)
7	CH_3, H	92 (82:18)
8	$-(CH_2)_4-$	90 (-)
9	$CH_2C_6H_5$, H	97 (100:0)

[a] *Values in parentheses indicates product A:B ratio.*

Scheme 15 represents the synthesis of *β*-hydroxyazides by reacting epoxides with trimethylsilylazide ($TMSN_3$) in the presence of lithium perchlorate. *β*-Hydroxyazides serves as an important precursor for the synthesis of *β*-aminoalcohols (used as *β*-adrenergic blockers), amino sugars and carbocyclic nucleosides[87].



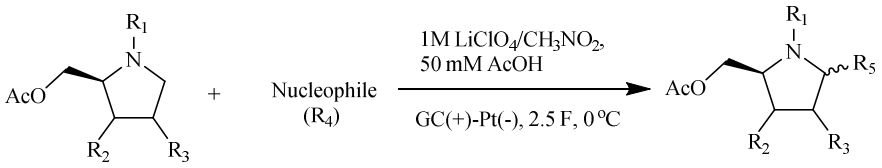
Scheme 15
$LiClO_4$ catalysed ring opening of epoxide with $TMSN_3$.

Table 14
β-Hydroxyazides synthesized from epoxide and $TMSN_3$.

Entry	R_1, R_2	% Yield
1	$-(CH_2)_4-$	45
2	n-C_2H_5, H	60
3	CH_2Cl, H	64
4	CH_2OPh, H	78
5	$CH_2OCH(CH_3)_2$, H	74
6	CH_2Br, H	60

1.9 Synthesis of azanucleoside derivatives

The nucleoside structure serves as an essential template for the development of therapeutically useful agents having antiviral activity, antitumor activity and treatment of pathologies induced by infections from HCMV, HSV, HIV, and HBV. Dideoxynucleoside analogues exhibit their antiviral activity by the competitive reversible inhibition of reverse-transcriptase (RT) and/or viral DNA chain termination[93]. Kim *et al.* have been reported coupling reaction by incorporating nucleophiles and nucleobases into prolinol derivatives (Scheme 16)[7]. Lithium perchlorate-nitromethane used as a catalyst to convert unactivated prolinol derivatives and nucleophile into iminium cation intermediates. This coupling reaction was carried out using glassy carbon anode and a platinum cathode at 0 °C. The yields of obtained coupling derivatives are given in Table 15.

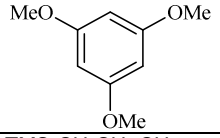
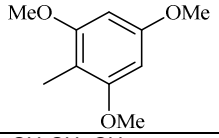


Scheme 16

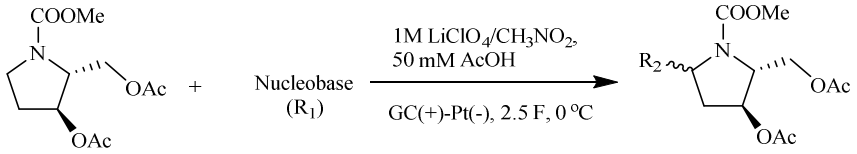
$LiClO_4$ catalyzed nucleophilic coupling of prolinols and nucleophiles.

Table 15

Nucleophilic coupling derivatives synthesized from prolinols.

Entry	R_1	R_2	R_3	R_4	R_5	% Yield
1	COOMe	H	H	TMS-$CH_2CH=CH_2$	-$CH_2CH=CH_2$	95
2	C(O)CO_2Me	H	H	TMS-$CH_2CH=CH_2$	-$CH_2CH=CH_2$	55
3	Ac	OAc	H	TMS-$CH_2CH=CH_2$	-$CH_2CH=CH_2$	71
4	Boc	OAc	H	TMS-$CH_2CH=CH_2$	-$CH_2CH=CH_2$	69
5	COOMe	OAc	H	HS-Ph	-S-Ph	71
6	COOMe	OAc	H			84
7	COOMe	H	OAc	TMS-$CH_2CH=CH_2$	-$CH_2CH=CH_2$	74

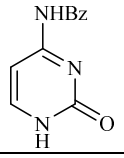
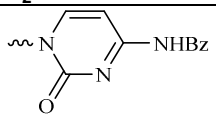
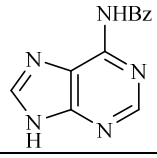
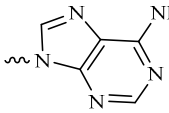
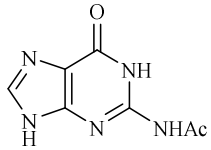
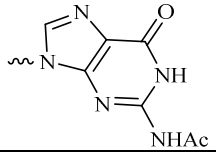
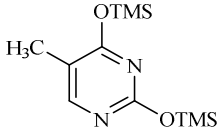
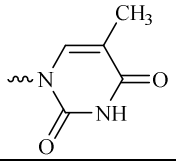
Scheme 17 represents the synthesis of azanucleoside derivatives by the reaction of prolinol derivatives with nucleobase in the presence of lithium perchlorate-nitromethane system[7]. The yields of synthesized azanucleosides are given in Table 16.



Scheme 17

$LiClO_4$ catalyzed coupling reaction of prolinols with nucleobases.

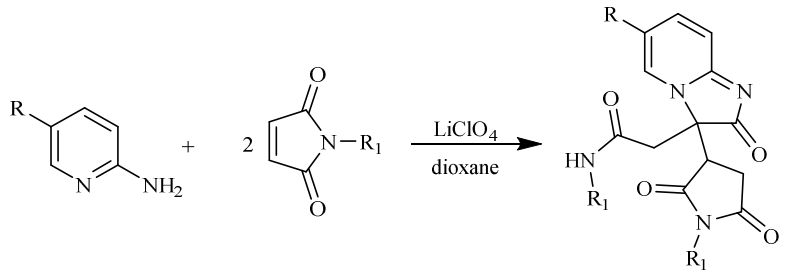
Table 16
Azanucleosides synthesized from prolinols and nucleobases.

Entry	R_1	R_2	% Yield[a]
1			52
2			54
3			44
4[b]			0

[a]*Compound 1-2 and 3 afforded α:β enomers in 1:1 and 2:3 ratios, respectively.* [b]*Product not obtained.*

1.10 Synthesis of (2-oxo-dihydro-imidazo[1,2-a]pyridin-3-yl)-pyrrolidine-2,5-diones

Matviiuk *et al.* reported the synthesis of double conjugate addition products using 2-aminopyridines with *N*-aryl maleimides under mild conditions in the presence of lithium perchlorate and dioxane (Scheme 18)[94]. Lithium perchlorate serves as an efficient Lewis acid catalyst in this reaction and in the absence of catalyst reaction fails to give double Michael addition product. The yields of obtained products are given in Table 17.

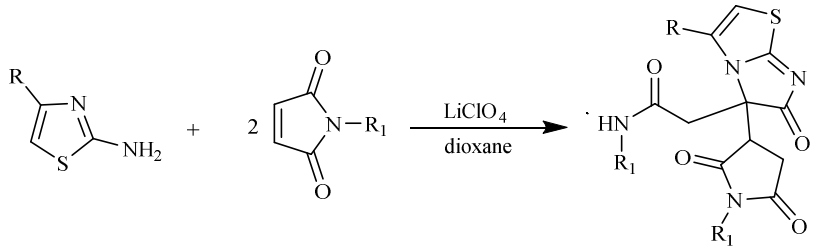


Scheme 18
$LiClO_4$ catalyzed double Michael addition of 2-aminopyridines and maleimides.

Table 17
(2-Oxo-dihydro-imidazo[1,2-a]pyridin-3-yl)-pyrrolidine-2,5-diones synthesized from 2-aminopyridines and maleimides.

Entry	R	R_1	% Yield
1	CH_3	C_6H_5	73
2	CH_3	4-$OCH_3C_6H_4$	68
3	CH_3	4-$CH_3C_6H_4$	62
4	Cl	4-$OCH_3C_6H_4$	50
5	Cl	C_6H_5	56

Similarly, reaction of 2-aminothiazoles with maleimides afforded (6-oxo-dihydro-imidazo[2,1-b]thiazol-5-yl)-pyrrolidine-2,5-dionesin the presence of catalytic amount of lithium perchlorate and dioxane (Scheme 19)[94].



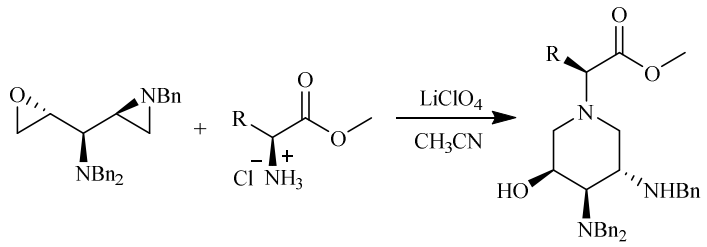
Scheme 19
LiClO4 catalyzed double Michael addition of 2-aminothiazoles and maleimides.

Table 18
(6-Oxo-dihydro-imidazo[2,1-b]thiazol-5-yl)-pyrrolidine-2,5-diones synthesized from 2-aminothiazoles and maleimides.

Entry	R	R_1	% Yield
1	H	4-$OCH_3C_6H_4$	80
2	C_6H_5	4-$OCH_3C_6H_4$	43

1.11 Synthesis of tri-substitutedpiperidines

The piperidine nucleus is abundant in naturally occurring alkaloids and synthetic compounds having certain biological and pharmacological properties. Thus, there is an immense interest in development of general methods for the enantioselective synthesis of piperidine derivatives[95]. Most of the piperidine precursors exist in chair conformation. Electron withdrawing groups (-NO_2, -CHO, -COR and -CONHPh), if introduced at the nitrogen atom affect the conformations of the heterocyclic rings and orientations of the substituents in 2,6-dialkyl- and 2,6-diaryl-substituted piperidines due to a strain in the normal chair conformation[96]. Ochoa-Teran *et al.* reported synthesis of enantiopure tri-substituted piperidines from chiral epoxyaziridine with α-amino esters catalyzed by lithium perchlorate (Scheme 20)[97].



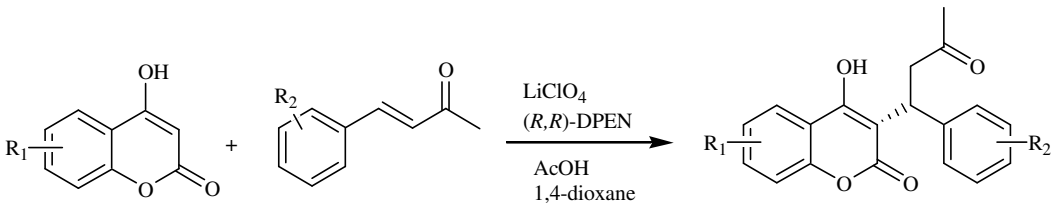
Scheme 20
LiClO4 catalysed synthesis of tri-substitutedpiperidines from epoxyaziridine and α-amino esters.

Table 19
Tri-substituted piperidines synthesized from epoxyaziridine and α-amino esters.

Entry	R	% Yield
1	Me	93
2	Bn	77
3	*i*-Bu	90
4	*i*-Pr	91
5	$CH_2CO_2CH_3$	75

1.12 Synthesis of warfarin analogues

Yang *et al*. have been reported asymmetric synthesis of warfarin analogues through Michael addition using 4-hydroxycoumarins and phenylbutenones in the presence of $LiClO_4$ and (*R*,*R*) diphenylethylenediamine (Scheme 21). $LiClO_4$ served as an excellent catalyst for an increase in reactivity and greater levels of stereoselectivity whereas 1,4-dioxane improved the enantioselectivity[98].



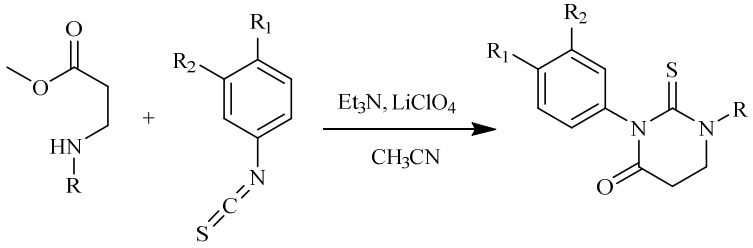
Scheme 21
$LiClO_4$ catalysed synthesis of warfarin analogues.

Table 20
Warfarin analogues synthesized from 4-hydroxycoumarins and phenylbutenones.

Entry	R_1	R_2	% Yield
1	H	*o*-OCH_3	52
2	H	*m*-OCH_3	64
3	H	*p*-CH_3	75
4	H	*p*-Cl	74
5	6-Cl	H	61
6	6-Cl	*o*-OCH_3	69
7	6-Cl	*p*-CH_3	62
8	6-Br	*o*-OCH_3	50

1.13 Synthesis of 3-aryl-2-thioxotetrahydropyrimidin-4-ones

3-Aryl-2-thioxotetrahydropyrimidin-4-ones belong to the class of heterocyclic compounds and have been reported for their biological activities such as antiatherosclerotic, anticancer, anticonvulsant and herbicidal activities[99-102]. Kumar *et al.* have been reported synthesis of 3-aryl-2-thioxotetrahydropyrimidin-4-ones via condensation of *β*-amino esters and aryl isothiocyanates in the presence of catalytic amount of $LiClO_4$ and triethylamine as a base (Scheme 22)[103]. The use of $LiClO_4$ resulted in excellent yield in short reaction time.



Scheme 22
$LiClO_4$ catalyzed synthesis of 3-aryl-2-thioxotetrahydropyrimidin-4(1H)-ones.

Table 21
3-Aryl-2-thioxotetrahydropyrimidin-4(1H)-ones synthesized fromβ-amino esters and aryl isothiocyanates.

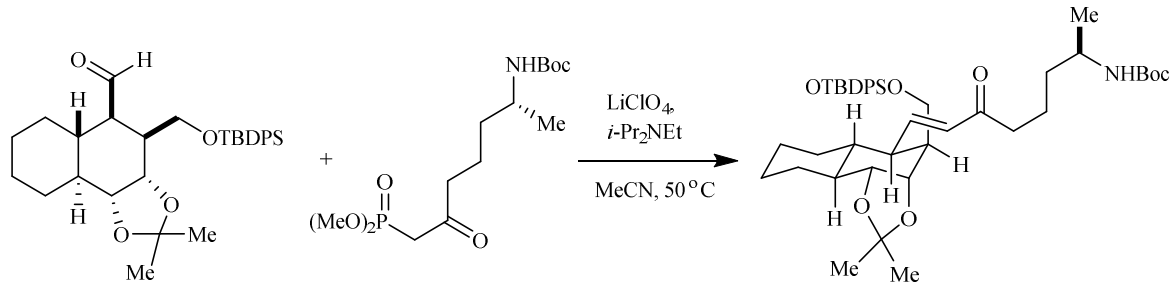
Entry	R	R_1	R_2	% Yield[a]
1	Et	Cl	CF_3	90
2	Et	CN	Cl	89
3	Et	CN	CF_3	88
4	Et	NO_2	CF_3	88
5	Et	Cl	H	87
6	Et	F	Cl	86
7	Et	H	NO_2	85
8	Bz	Cl	CF_3	84
9	Bz	CN	Cl	90
10	Bz	CN	CF_3	85
11	Bz	NO_2	CF_3	92
12	Bz	Cl	H	81
13	Bz	F	Cl	85
14	Bz	H	NO_2	84

15	α-MeBz	Cl	CF_3	80
16	α-MeBz	CN	Cl	86
17	α-MeBz	CN	CF_3	90
18	α-MeBz	NO_2	CF_3	88
19	α-MeBz	Cl	H	85
20	α-MeBz	F	Cl	75
21	α-MeBz	H	NO_2	70

[a]*Reaction time = 1.2-3.5h*

1.14 Synthesis of enones

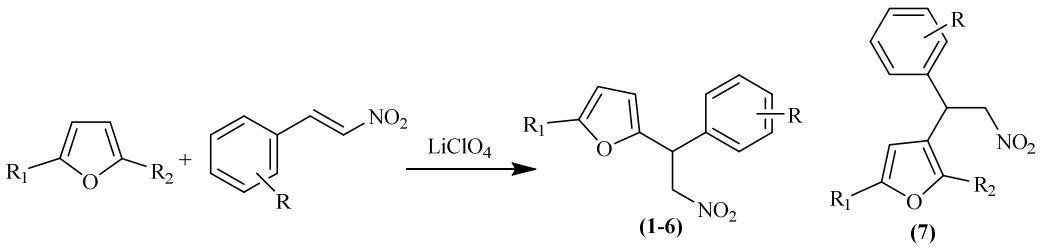
Evans *et al*. have been reported synthesis of enones using HWE olefination of aldehyde and (*R*)-*β*-ketophosphonate in the presence of lithium perchlorate and diisopropyl ethylamine in acetonitrile (Scheme 21)[104].



Scheme 23
Synthesis of enones by HWE olefination.

1.15 Synthesis of 2-(2-nitro-1-phenylethyl)furans

Furylnitroethanes are important substances which can be reduced to furylethanamines for incorporation into dopamine antagonists, platelet aggregation inhibitors and suppressor of appetite[105-107]. Recently, Stoermera *et al*. have been reported synthesis of 2-(2-nitro-1-phenylethyl)furans using Friedel-Crafts addition from furan and *β*-nitrostyrene in the presence of catalytic amount of lithium perchlorate in diethyl ether, where *β*-nitrostyrene functions as a Michael acceptor (Scheme 24)[108].



Scheme 24
$LiClO_4$ catalysed Friedel-Crafts addition.

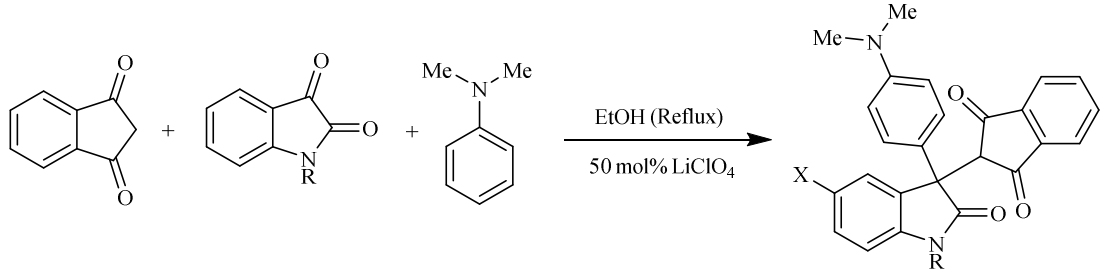
Table 22
2-(2-Nitro-1-phenylethyl)furans synthesized from furans and β-nitrostyrenes.

Entry	R_1	R_2	R	% Yield[a]
1	H	H	H	93
2	H	H	p-Cl	85
3	H	H	p-CH_3O	89
4	H	H	p-CH_3	94
5[b]	H	H	2,4-Cl_2	86
6	CH_3	H	H	90
7[c]	CH_3	CH_3	H	75

[a]*Reaction completes in 2-3 days.* [b] *Reaction completed in 0.25 day.*
[c] *Alkylation occurs at 3-position of furan, structure (7).*

1.16 Synthesis of unsymmetrical oxindoles

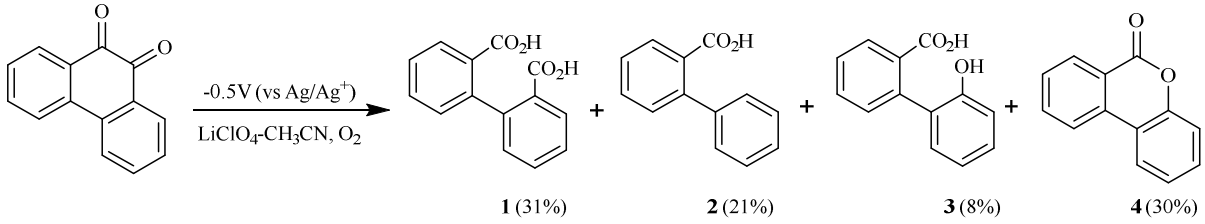
Ahadi *et al.* have been reported synthesis of unsymmetrical oxindoles using 1,3-indandion, *N,N*-dimethylaniline and isatin in the presence of catalytic amount of lithium perchlorate and ethanol (Scheme 25). The 10 mol% of lithium perchlorate in ethanol was found to be adequate for completion of the reaction while increasing or decreasing the amount from 10 mol% has no effect on improvement of the yield[109].



Scheme 25
Synthesis of unsymmetrical oxindoles.

1.17 Synthesis of aryl carboxylic acids

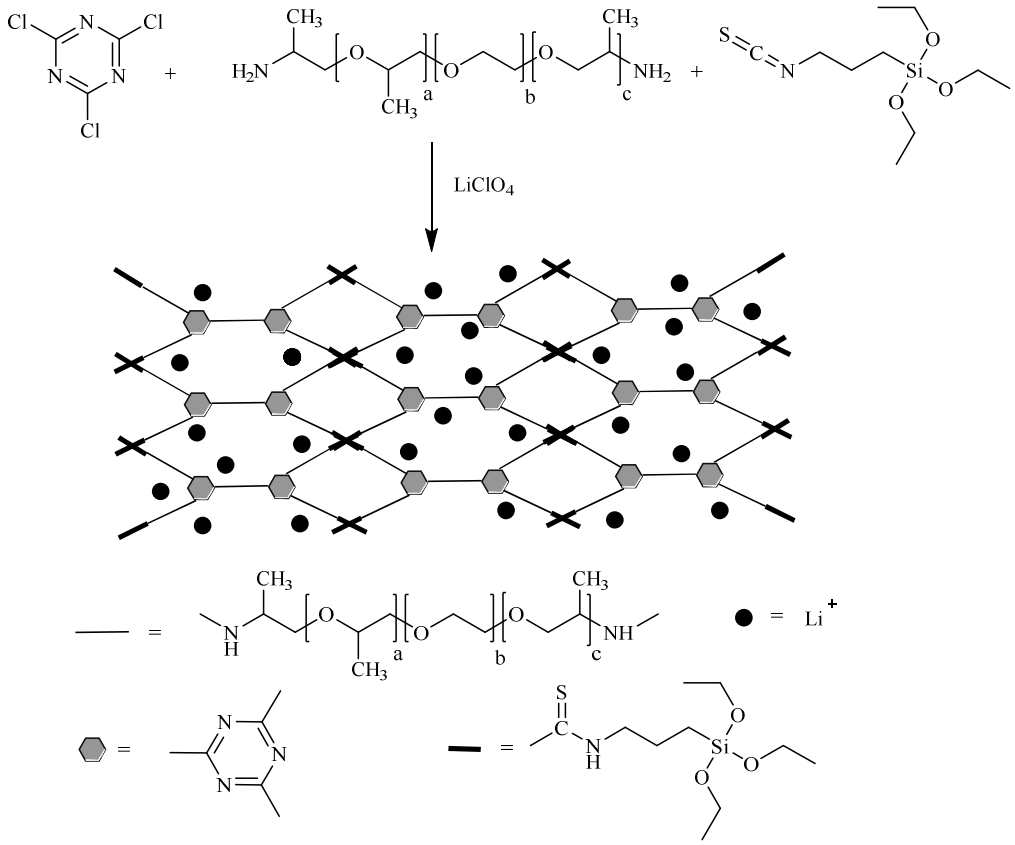
Aryl carboxylic acids are important class of aromatic compounds which have been used as bone resorption inhibitors, intermediates in polymer synthesis, starting materials for synthesis of neuropeptide FF receptor and orexin receptor antagonists. Recently, Batanero *et al.* have reported formation aryl carboxylic acids (**1-3**) by electrochemical reduction of 9,10-phenanthrenequinone using $LiClO_4$-acetonitrile as solvent-supporting electrolysis system (SSE) in the presence of oxygen (Scheme 26)[110]. This reaction involved formation of a dioxetane intermediate which also converted into dibenzopyranone (**4**) via Baeyer-Villiger/Dakin reaction.



Scheme 26
$LiClO_4$ catalysed formation of aryl carboxylic acids from 9,10-phenanthrenequinone.

1.18 Organic-inorganic hybrid electrolyte membranes

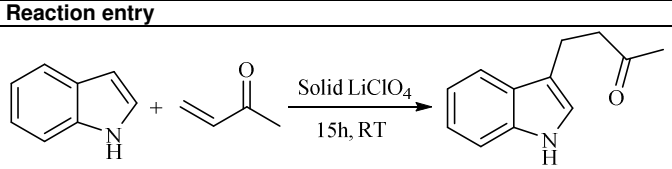
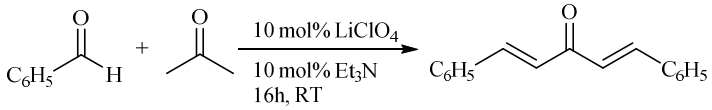
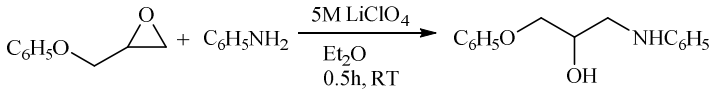
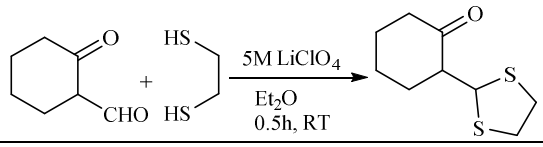
A hybrid material includes two moieties *i.e.* inorganic and organic, blended on the molecular scale. An organic moiety gets attached to the inorganic network, via its functional groups, modifying the silica network in the sol-gel process. Inorganic-organic hydrids are advantageous as they combine the different properties of both organic and inorganic components in one material. Sol-gel process is chemically related to an organic poly-condensation reaction which results in formation of a three-dimensional crosslinked network[111]. Wu *et al*. reported sol-gel process to obtain double core branched structure with organic-inorganic hybrid electrolyte membranes. This is based on reaction of tri-block copolymer poly(propylene glycol)-block-poly(ethylene glycol)-block-poly(propylene glycol)bis(2-amino propylether),3-isocyanatepropyltriethoxy-silane and central core 2,4,6-trichloro-1,3,5-triazine doped with $LiClO_4$ (Scheme 27)[112].

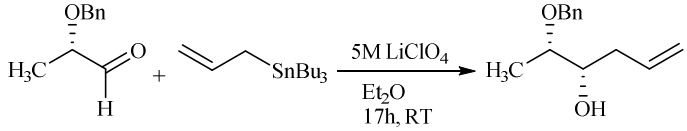
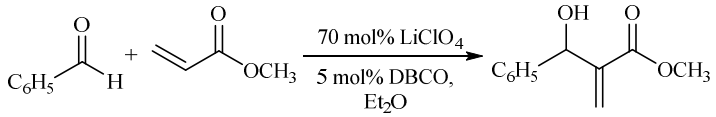
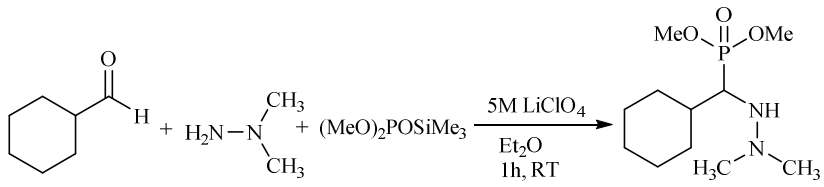
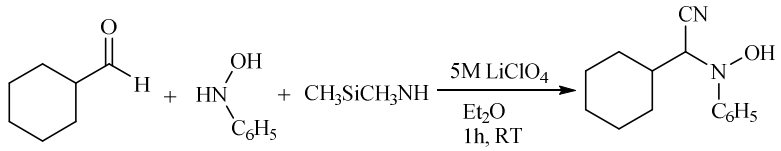
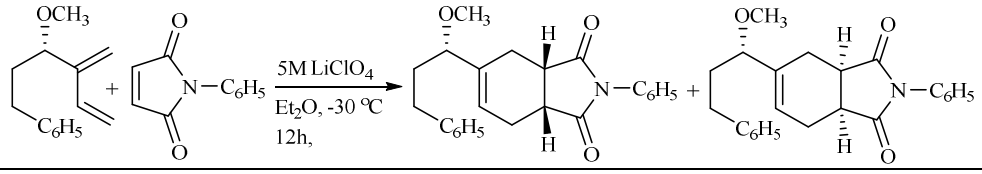
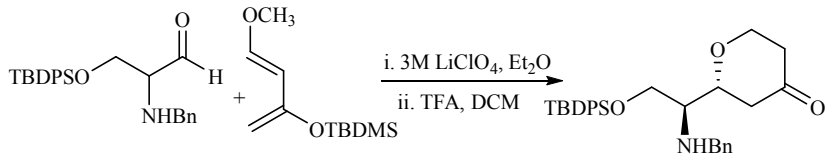
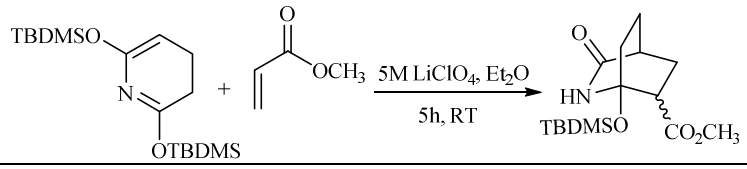
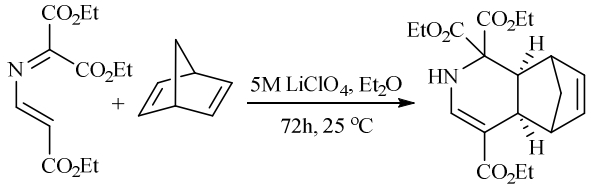
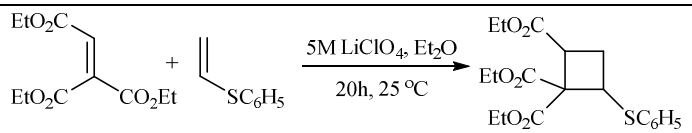
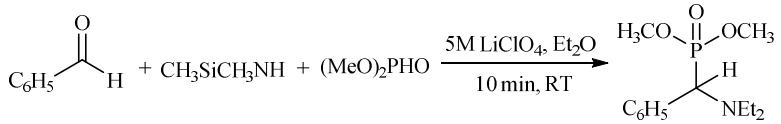
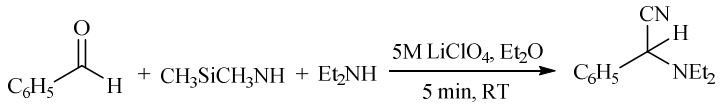


Scheme 27
Synthesis of organic-inorganic hybrid membrane.

The $LiClO_4$ has application in organic chemistry as a catalyst and supporting agent for variety of chemical reaction. For example, conjugated addition, aldol condensation, epoxide ring opening by poor nucleophiles and protection of aldehydes as dithioacetals (Sr. No. 1-4 in Table 23). Moreover, it has been successfully used in various chiral chemical synthesis as a catalyst such as chelation controlled addition, chiral Baylis-Hillman reaction, stereoselective cycloaddition, chiral cyanation and chiral phoshonation (Sr. No. 5-15 in Table 23).

Table 23
Miscellaneous reactions catalysed by $LiClO_4$.

Sr. No.	Reaction entry	Yield (%)	Ref.
1.		90	25
2.		91	113
3.		97	114
4.		80	115

5.		82	116
6.		72	117
7.		96	118
8.		92	119
9.		74	120
10.		79	121
11.		80	4, 122
12.		68	123
13.		72	124
14.		99	125
15.		94	126

CONCLUSION

Catalysts are important part of organic synthesis and frequently used in development of novel and improved synthetic strategies. They also play important role in advancement of environmentally benign organic synthesis. Lithium perchlorate is an easily available chemical that has been successfully used as a catalysts for synthesis of various bioactive molecules. Moreover, it is highly efficient catalyst for both achiral and chiral functional group transformation reactions. This study provides an important insight on lithium perchlorate catalyzed organic reactions which will be helpful for design and development of novel synthetic methodologies.

LIST OF ABBREVIATIONS

cAu	=	Chiral auxiliary
DCM	=	Dichloromethane
DIPEA	=	*N,N*-Diisopropylethylamine
EWG	=	Electron withdrawing group
HBV	=	Hepatitis B virus
HCMV	=	Human cytomegalovirus
HSV	=	Herpes simplex virus
HWE	=	Horner-Wadsworth-Emmons
LPDE	=	Lithium perchlorate-diethylether
(S)-α-MBA	=	(S)-α-Methylbenzylamine
NMA	=	*N*-Methylaniline
NNDMA	=	*N,N*-Dimethylaniline
TFA	=	Trifluoroacetic acid
TMSCl	=	Trimethylsilyl chloride
$TMSN_3$	=	Trimethylsilylazide
ZSS-Pd	=	Zwitterionic-Surfactant-Stabilized-Palladium
$(Ppyz)Zr(BH_4)Cl_2$	=	Zirconium borohydride-piperazine complexes

CONFLICT OF INTEREST

The authors report no conflicts of interest. The authors are responsible for the collection of material and writing of contents of this paper.

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