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# 1,4-Diazabicyclo[2.2.2]octane (DABCO) as a useful catalyst in organic synthesis

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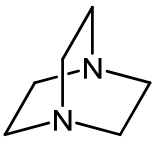
ABSTRACT

1,4-diazabicyclo[2.2.2]octane (DABCO) has been used in many organic preparations as a good solid catalyst. DABCO has received considerable attention as an inexpensive, eco-friendly, high reactive, easy to handle and non-toxic base catalyst for various organic transformations, affording the corresponding products in excellent yields with high selectivity. In this review, some applications of this catalyst in organic reactions were discussed.

## 1. Introduction

The interest in the field of organocatalysis has increased spectacularly in the last few years as a result of both the novelty of the concept and, more importantly, the fact that the efficiency and the selectivity of many organocatalytic reactions meet the standards of established organic reactions.

1,4-Diazabicyclo[2.2.2]octane (DABCO), a cage-like compound, is a small diazabicyclicmolecule with weak alkalescence, medium-hindrance. It has been widely used in organic synthesis reactions and can serve as a weak base and ligand (Scheme 1).



1,4-Diazabicyclo [2.2.2] octane (DABCO)

**Scheme 1**

DABCO is also used to adjust pH of the oxygen-sensitive resin to regulate the reaction rate in Flexplay time-limited DVDs. Antioxidants, such as DABCO are used to improve the lifetime of dyes. This makes DABCO useful in dye lasers and in mounting samples for fluorescence microscopy. DABCO has received considerable attention as an inexpensive, eco-friendly, high reactive, easy to handle and non-toxic base catalyst for various organic transformations, affording the corresponding products in excellent yields with high selectivity. The reactions are environmentally friendly and the catalyst can be recycled in some cases. DABCO has been reviewed by Yang Hua *et al*. recently [1]. In the following sections, some recent advances in the application of DABCO in organic synthesis will be discussed.

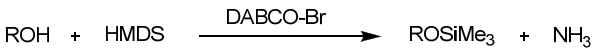
## 2. DABCO and functional group transformation

### *2.1. Protection of functional groups*

#### *2.1.1. Protection of hydroxyl groups*

##### *2.1.1.1. Silylation of hydroxyl Groups*

The protection and deprotection of functional groups are indispensable in the synthesis of polyfunctional compounds. In addition, several chemical conversions and multiple sequence syntheses are often required for the protection of hydroxyl groups. The silylation of alcohols and polyols is one of the most commonly used methods for their protection [2]. Many primary, secondary, tertiary alcohols and phenolic hydroxyl groups were effectively converted to their corresponding trimethylsilyl ethers using hexamethyldisilazane in the presence of catalytic amounts of DABCO-bromine under mild conditions at room temperature with short reaction times in good to excellent yields. Excellent chemoselective silylation of hydroxyl groups in the presence of other functional groups were also observed (Scheme 2). In comparison to other procedures reported in literature [3], its major advantage is that a very small amount of catalyst is enough to carry the procedure.




**Scheme 2**

##### *2.1.1.2. Acetal migration of 1,2:4,5-di-O-isopropylidene-D-fructopyranose*

More than 110 years ago Emil Fisher first described the formation of acetals from D-fructose and acetone [4]. Since then, the O-isopropylidene group has been extensively used in organic synthesis, especially in the field of carbohydrate chemistry. Acetal migration is a well-documented phenomenon, among which di-O-isopropylidene sugars are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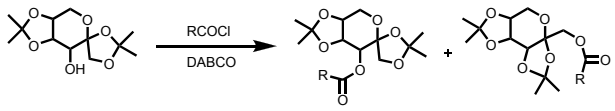
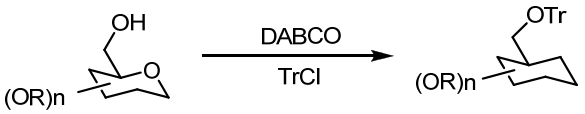
found to form thermodynamically favored isomers under acidic conditions (proton acids or Lewis acids) [5]. Acetal migration was observed when 1,2:4,5-di-O-isopropylidene-D-fructose was treated with various acyl chlorides in the presence of DABCO as a catalyst. 2,3:4,5-Di-O-isopropylidene-D-fructose derivatives were isolated as the only product in high to quantitative yields (Scheme 3). The used method had several advantages including mild conditions, good yields, and use of inexpensive catalyst [6].




**Scheme 3**

### 2.1.1.3. Protection of Carbohydrates

An efficient procedure for the regioselective tritylation of the primary hydroxyl group of aldohexopyranosides and nucleosides using trityl chloride in the presence of DABCO as a catalyst in dichloromethane has been developed. This method eliminates the need for the use of hazardous solvents such as pyridine and DMF for such reactions (Scheme 4) [7].

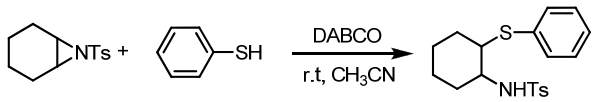



**Scheme 4**

### 2.1.2. Protection of amines

### 2.1.2.1. Ring-Opening Reactions of Aziridines with Amines or Thiols

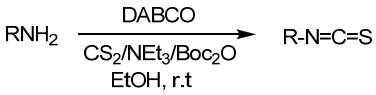
Ring-opening reactions of aziridines with nucleophiles provide a useful protocol in organic synthesis. Many reagents have recently been developed to realize the opening of the aziridine ring [8]. Efficient ring-opening of aziridines with various amines or thiols catalyzed by DABCO afforded the corresponding products in good to excellent yields under mild reaction conditions. 1 mol % of catalyst was also efficient in this reaction (Scheme 5). It is noteworthy that this reaction could be run under the air without loss of efficiency. The advantages of this method include good substrate generality, the use of air-stable, inexpensive DABCO as catalyst under mild conditions, and experimentally operational ease [9].




**Scheme 5**

### 2.1.2.2. Synthesis of isothiocyanates

Isothiocyanates constitute an important functional class in natural products and pharmaceutically active compounds [10]. Furthermore, isothiocyanates are widely applied as chemoselective electrophiles in bioconjugate chemistry because of their tolerance towards aqueous reaction conditions, and they are key intermediates in the synthesis of sulfur-containing heterocycles [11]. Alkyl and aryl amines are converted smoothly to the corresponding isothiocyanates via the dithiocarbamates in good to excellent yields using di-tert-butyl dicarbonate ($Boc_2O$) and DABCO as a catalyst. This reaction proceeds within 15 min with aliphatic and activated aromatic substrates; however, deactivated arylamines need longer reaction times for the complete formation of the dithiocarbamate in order to prevent side reactions such as Boc-protection of the amine or thiourea formation (Scheme 6). This method constitutes an interesting alternative in the synthesis of isothiocyanates (and thioureas) in complex synthetic sequences where a minimum work-up of the intermediate isothiocyanate should be carried out [12].

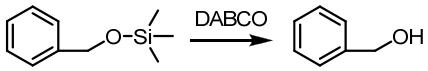



**Scheme 6**

## 2.2. Deprotection reactions

### 2.2.1. Deprotection of benzylic trimethylsilyl ethers

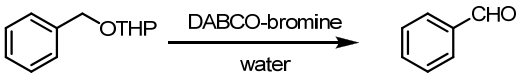
A trialkylsilyl group is one of the most common and widely used protecting groups [13]. This kind of protection was originally introduced to increase the volatility and stability of hydroxy groups and nowadays is applied in total and multistep syntheses in organic chemistry [14]. In this article, an expeditious and environmentally benign deprotection of benzylic-trimethylsilyl ethers using DABCO as a useful catalyst and microwave irradiation under solvent-free conditions is reported (Scheme 7). The salient features of this methodology are the mild reaction conditions, short reaction times, high yields, selectivity, and the absence of volatile and relatively expensive solvents [15].




**Scheme 7**

### 2.2.2. Oxidative Deprotection of THP and Silyl Ethers

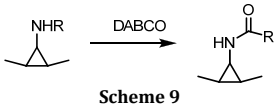
Silyl and THP (tetrahydropyranyl) ethers are extensively used as protective groups for alcohols in synthetic chemistry because of their low cost, efficiency of preparation, stability under the intended reaction conditions, and easy and selective removal [16]. DABCO–bromine complex is easily prepared frombromination of DABCO with liquid bromine at room temperature. It has been used as an oxidant for conversion of alcohols to their carbonyl compounds [17] (Scheme 8). This tetrameric DABCO–bromine complex (TDB) was utilized as a novel active bromine complex for the oxidative deprotection of THP and silyl ethers and semicarbazones to carbonyl compounds. The positive features of this method are ease of operation, excellent yields, and environmental consciousness [18].




**Scheme 8**

### 2.2.3. Deprotection of N-Alloc amines

A highly efficient one-pot deprotection coupling protocol of *N*-Alloc amino acids with activated *N*-Boc or *N*-Fmoc amino acids was developed in solution and on solid phase. DABCO was found to be especially effective for the deprotection of the *N*-Alloc group, resulting in short reaction times (10–20 min) and allowing the coupling of amino acids that are unstable in unprotected forms (Scheme 9) [19].

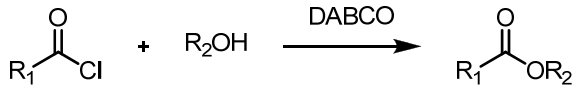



**Scheme 9**

### 2.3. Esterification reaction

#### 2.3.1. Preparation of esters and anhydrides

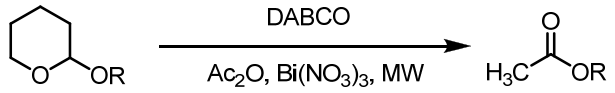
A manipulatively one-pot and rapid method for the synthesis of aliphatic and aromatic ester and anhydride from acid chloride and alcohol or potassium salt of carboxylic acid under solvent-free conditions is reported. The reaction has been carried out in excellent yield and short reaction time in the presence of DABCO under solvent-free conditions (Scheme 10). This work is a rapid and very convenient method for the synthesis of both symmetric as well as unsymmetric acid anhydride in excellent yields with high purity. By this method a variety of acid anhydrides such as aliphatic–aromatic, aliphatic–aliphatic and aromatic–aliphatic acid anhydride type can be readily prepared in short reaction time. This methodology is superior from point of view of yield, short reaction time and the easier work-up in comparison to the reported methods [20].




**Scheme 10**

#### 2.3.2. Conversion of Tetrahydropyranyl Ethers into Acetates

Acetylation of alcohols is an important transformation frequently used in organic synthesis. In this method, conversion of THP ethers into the corresponding acetates in the presence of bismuth(III) nitrate and DABCO as an effective co-catalyst under microwave irradiation without a solvent in high yields is described (Scheme 11) [21].




**Scheme 11**

#### 2.3.3. Preparation of Symmetrical Carboxylic Acid Anhydrides

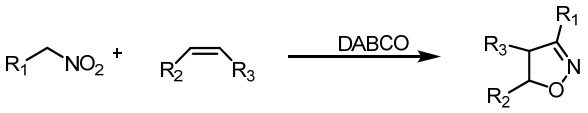
Carboxylic acid anhydrides are among the most important class of reagents used in organic synthesis [22,23]. They are the frequently preferred reactive acid derivatives for the preparation of esters, amides, and peptides [23]. Various types of carboxylic acids undergo rapid dehydration with DABCO/thionyl chloride ($SOCl_2$), under mild reaction conditions to afford symmetrical acid anhydrides in high isolated yields (Scheme 12) [24].


**Scheme 12**

## 3. DABCO in carbon-carbon coupling

### 3.1. Synthesis of isoxazolines

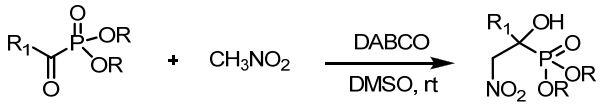
Isoxazolines appear in numerous medicinally active compounds and natural products of biological significance [25]. Additionally, they are valuable as synthetic intermediates [26] or protecting groups in organic synthesis [27] and commonly appear in ligands for asymmetric synthesis [28]. Activated nitrocompounds, in the presence of dipolarophiles using DABCO as an efficient catalyst undergo dehydration to afford directly isoxazoline derivatives (Scheme 13). The advantage of this method is simplicity. Experimental procedure and the reaction conditions are amenable to scale-up [29].




**Scheme 13**

### 3.2. Nitroaldol reaction of α-ketophosphonates

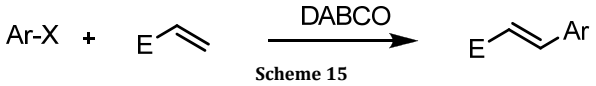
The nitroaldol (Henry) reaction of ketones and aldehydes has received a lot of attention in recent years [30]. Also, new developments in asymmetric nitroaldol reactions further enhanced their synthetic utility [31]. The use of α-ketophosphonates as the acceptors in the nitroaldol reaction has been known for some time [32]. An improved procedure for the nitroaldol reaction of α-ketophosphonates (both aryl and alkyl substituted) and nitromethane was achieved by using DABCO as a sterically hindered organic base catalyst (Scheme 14). This method is convenient to operate. Both α-aryl and α-alkyl substituted α-hydroxy-β-nitrophosphonates may be obtained in excellent yields with a simple operation in a short reaction time [33].




**Scheme 14**

### 3.3. Heck Reaction

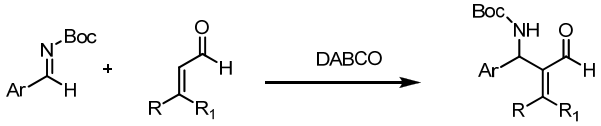
The Heck reaction is one of the most important methods in synthetic organic chemistry for the formation of C-C bonds [34]. $Pd(OAc)_2$/DABCO is an inexpensive and efficient catalytic system for the Heck reaction and provide products in high yields (Scheme 15) [35].




**Scheme 15**

### 3.4. Addition of α,β-unsaturated aldehydes to nitrostyrenes

Morita–Baylis–Hillman (MBH) reaction is an organocatalytic reaction involving the coupling of the α-position of activated alkenes with carbonyl electrophiles such as an aldehyde or ketone via the catalytic influence of nucleophilic species [36]. A novel proline and DABCO co-catalyzed reaction between unmodified α,β-unsaturated aldehydes and nitrostyrenes, which gives access to a-(1-aryl-2-nitro) ethyl-α,β-unsaturated aldehydes, is presented in Scheme 16. DABCO could either work as a base enabling the formation of a conjugated enamine and/or act as a nucleophile to generate an enamine intermediate [37].

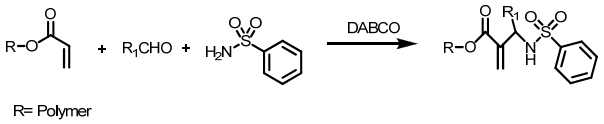



**Scheme 16**

### 3.5. Preparation of Sulfonamides

A new scaffold for combinatorial chemistry has been developed. In a three component reaction using polymer bound acrylic acid, aldehydes and sulfonamides under Baylis-Hillman reaction conditions, substituted 2-methylidene-3-aminoaryl

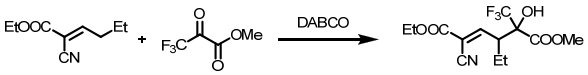
sulfonylpropionic acids using DABCO as a catalyst were synthesised. After cleavage from the solid support, the products were obtained in high purities (Scheme 17) [38].




**Scheme 17**

### *3.6. Carbonyl allylation of methyl trifluoropyruvate*

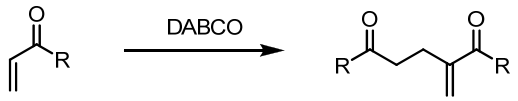
The carbonyl allylation of methyl trifluoropyruvate (MeTFP) with activated alkenes has been investigated in detail using organic base (DABCO) as a catalyst. This methodology will motivate more interests in the exploitation of carbonyl allylation catalyzed by organic bases (Scheme 18) [39].




**Scheme 18**

### *3.7. Dimerization of α,β-unsaturated ketones and nitriles*

α,β-Unsaturated ketones dimerize in the presence of catalytic amount of DABCO to produce the corresponding 2-methylene-1,5-diketones in good yields. Acrylonitrile provides the corresponding dimerized product (Scheme 19) [40].

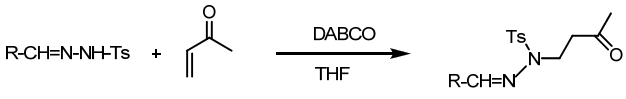



**Scheme 19**

## 4. Synthesis of DABCO-catalysed heterocyclic compounds

### *4.1. Reactions of hydrazones with activated olefins*

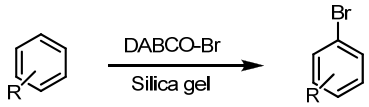
DABCO can catalyze aza-Michael addition reactions of hydrazones to activated olefins efficiently. In most cases, these aza-Michael addition reactions give the corresponding products in high yields under mild conditions (Scheme 20). The transformation is in contrast to the recently reported DABCO catalyzed aza-Baylis–Hillman reaction [41] and the reaction mechanism is different from phosphine Lewis base catalyzed Michael addition of alcohols to activated olefins [42]. Additionally, this finding can open new ways for the design of new reactions and synthesis of novel compounds by the organocatalysts in the future [43].




**Scheme 20**

### *4.2. Bromination of Various Organic Compounds*

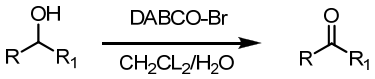
Tetrameric DABCO-bromine (TDB) is a powerful brominating agent but shows reasonable selectivity with certain substrates. TDB is a non-hygroscopic solid and is very stable at room temperature. It is not affected by ordinary exposure to light, air or water. It possesses ease of work-up. Stability of the reagent makes it a safe source of active bromine. The reagent is transformed during the reaction to the easily removable products and presents a convenient alternative to other amines. The selective bromination for activated aromatic compounds and alkenes using TDB is reported. Synthesis of α-bromo ketones and nitriles has also been achieved by using this reagent and the results are also reported. All products reported were obtained in good to excellent yields (Scheme 21) [44].




**Scheme 21**

### *4.3. Oxidation of alcohols*

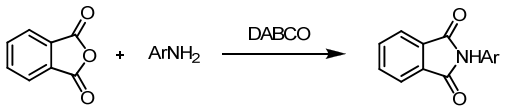
Alcohol oxidation yielding aldehydes and ketones is a chemical transformation of primary industrial importance in the fine chemicals industry as carbonyl compounds are precursors of a variety of valuable fine chemicals including fragrances, vitamins and drugs [45]. A tetrameric DABCO–bromine complex was synthesized, characterized and utilized as a novel active bromine complex for the oxidation of alcohols to carbonyl compounds (Scheme 22). This practical method has the advantages of mild reaction conditions, short reaction times, excellent yields of products, simple workup procedure, and low cost of catalyst [46].




**Scheme 22**

### *4.4. Synthesis of N-arylphthalimides*

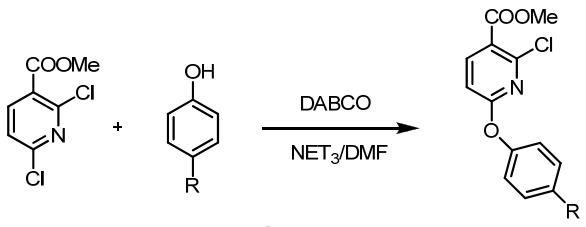
Phthalimides and *N*-substituted phthalimides are the compounds of an important class because they show interesting biological activities [47]. Solvent-free reactions between phthalic anhydride and aryl amines, catalyzed by DABCO in short reaction times and high yields were performed (Scheme 23). These reactions catalyzed by DABCO, do not require any solvent or solid support, and eliminate the need of stoichiometric amount of base [48].




**Scheme 23**

### *4.5. Nucleophilic Aromatic Substitution (SNAr) Reaction*

Exclusive formation of 6-aryloxy ethers from an SNAr reaction of methyl 2,6-dichloronicotinate with phenols catalyzed by DABCO is described. DABCO can regioselectively catalyze SNAr reaction in the presence of triethylamine in high yields (Scheme 24) [49].

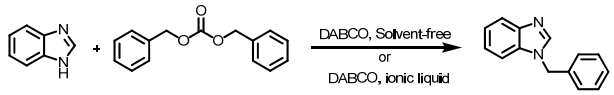



**Scheme 24**

### *4.6. Benzylation reaction*

DABCO can catalyze benzylation methodology for a variety of N-, O- and S-containing compounds utilizing dibenzyl carbonate (DBC) as an alkylating reagent. DABCO, acting as a nucleophilic catalyst, could effectively promote dibenzyl

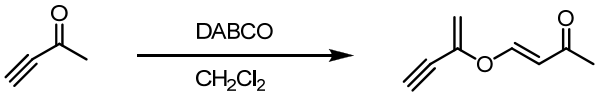
carbonate to behave as an alkylating reagent [50]. In this article, a novel, DABCO catalyzed benzylation methodology for a variety of N-containing compounds and a mercaptan utilizing DBC as the benzylating reagent is described (Scheme 25). These protocols avoid the use of toxic benzyl halides, eliminate the need of stoichiometric amount of base, and provide green processes for several important chemical transformations. In another article, by employing an ionic liquid as either a solvent or an additive, significant rate enhancement of the benzylation reaction can be accomplished using DABCO as a catalyst [51]. This methodology has the advantages of rapid reaction times, ease of operation and use of readily available ionic liquids. This could make this newly developed chemistry of general interest to organic chemists.




**Scheme 25**

### 4.7. Condensation of α-Acetylenic Ketones

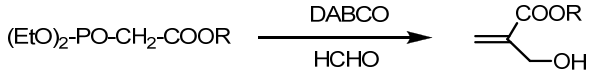
3-Butyn-2-one condenses with itself in the presence of DABCO as a catalyst to provide E-3-(1-buten-3-yn-2-oxy)-buten-2-one. Some advantages of this method are rapid reaction times and ease of operation (Scheme 26) [52].




**Scheme26**

### 4.8. Synthesis of alkyl α-(hydroxymethyl) acrylates

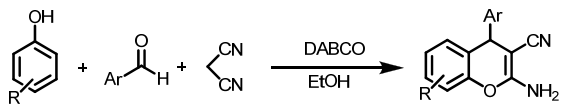
Alkyl α-(hydroxymethyl) acrylates are prepared in high yields on a synthetic scale by hydroxymethylation of the corresponding acrylates using aqueous formaldehyde in THF or DME as a solvent and DABCO as the catalyst. This communication reports an efficient and practical methodology for the synthesis of alkyl α-(hydroxymethyl) acrylates using DABCO as the catalyst in an aqueous medium (Scheme 27) [53].




**Scheme 27**

### 4.9. Synthesis of Naphthopyran Derivatives

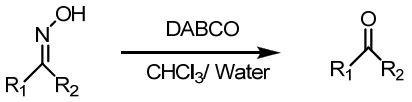
DABCO has been used as a mild and efficient catalyst for the synthesis of 2-amino-3-cyano naphthopyran derivatives via a one-pot three component reaction of aromatic aldehydes, naphthols, and malononitrile at room temperature. The short reaction times, easy workup, good to excellent yields, and mild reaction conditions make this domino Knoevenagel–Michael reaction both practical and attractive (Scheme 28) [54].




**Scheme 28**

### 4.10. Regeneration of Carbonyl Compounds

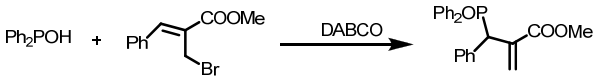
An efficient and convenient conversion of aldoximes and ketoximes to the corresponding carbonyl compounds with tetrameric DABCO–bromine complex is reported. This communication describes a simple, inexpensive, efficient, and convenient conversion of oximes to their carbonyl compounds using the TDB complex. This deprotection methodology of oximes finds wide application in organic synthesis because of the simplicity of workup and use of readily prepared oxidant under natural and mild conditions (Scheme 29) [55].




**Scheme 29**

### 4.11. Synthesis of 2-Methylene-3-phosphorylalkanoates

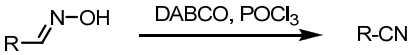
The Balyis–Hillman bromides react with secondary phosphine oxides or H-phosphonites in the presence of DABCO as a catalyst via an SN2-SN2' protocol to produce 2-methylene-3-phosphorylalkanoates under mild conditions in good yields (Scheme 30) [56].




**Scheme 30**

### 4.12. Preparation of Nitriles from Aldoximes

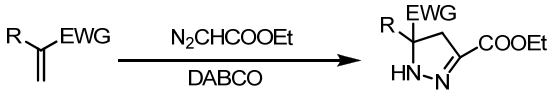
Nitriles have been used in organic synthesis for a long time as precursors of biologically active compounds such as antipecurnavirus tetrazole analogues [57]. The cyano group is a prominent functional motif found in several bioactive molecules and plays a significant role by hydrogen bonding to certain biological receptors [58]. In this method, a simple conversion of aldoximes to nitriles using DABCO—$POCl_3$ as an inexpensive and useful reagent was demonstrated (Scheme 31) [59].




**Scheme 31**

### 4.13. Synthesis of pyrazoles and pyrazolines

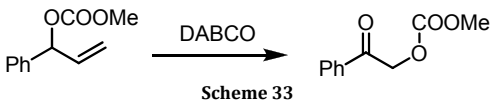
1,3-Dipolar cycloaddition of ethyl diazoacetate with various activated olefins using DABCO as a catalyst under solvent-free conditions at ambient temperature to afford 3,5-disubstituted pyrazolines and pyrazoles in moderate to good yields was reported (Scheme 32) [60].




**Scheme32**

### 4.14. Formation of 4-methoxy-1,3-dioxolan-2-ones

DABCO is a very effective catalyst in the formation of 4-methoxy-1,3-dioxolan-2-ones from the corresponding α-carbonatoaldehydes intermediates (Scheme 33) [61].

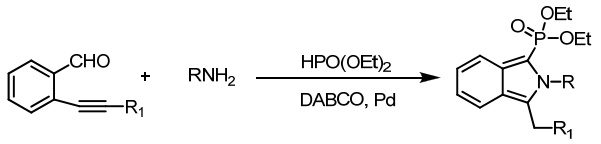



**Scheme 33**

### 4.15. Synthesis of isoindol-1-ylphosphonate derivatives

As a privileged fragment, the isoindole core is an ubiquitous subunit in many natural and synthetic products with remarkable biological activities. α-Amino(2-alkynylphenyl)

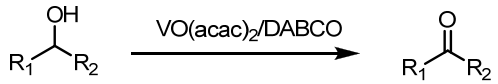
methylphosphonate, which was generated from 2-alkynyl benzaldehyde, amine, and diethyl phosphate, reacted with aryl iodide at room temperature in the presence of catalytic amount of DABCO in acetone, leading to the desired isoindol-1-ylphosphonate derivatives in good to excellent yields (Scheme 34) [62].




**Scheme 34**

### *4.16. Alcohol oxidation*

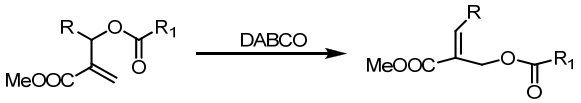
The catalytic conversion of alcohols to the corresponding aldehydes or ketones is a fundamental transformation in both laboratory and industrial synthetic chemistry [63]. A selective aerobic oxidation of alcohols into the corresponding aldehydes or ketones was developed by using two-component system $VO(acac)_2$/DABCO in the ionic liquid [bmim]$PF_6$, and the catalysts can be recycled and reused for three runs without any significant loss of catalytic activity. This catalytic system shows excellent selectivity toward oxidation of benzylic and allylic alcohols, and is notably not deactivated by heteroatom-containing (S, N) compounds. Most importantly, the newly developed catalytic system could also be recycled and reused for three runs without any significant loss of catalytic activity (Scheme 35) [64].




**Scheme 35**

### *4.17. Rearrangement of allylic esters*

The DABCO catalysed rearrangement of allylic esters in good yields (Scheme 36) [65].




**Scheme 36**

## 5. Conclusion

In this review, some applications of DABCO have been discussed. DABCO can be used as a base catalyst in various organic reactions and we believe that a great number of acid catalyzed organic reactions could be performed by using this catalyst. From the reported results, it can be concluded that DABCO is inexpensive, convenient, easy to handle, non toxic, easily available and efficient catalyst for various organic chemistry transformations. Thus, its use has been growing rapidly.

## Acknowledgements

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