

**1,4-DIAZABICYCLO[2.2.2]OCTANE
(DABCO)AS A USEFUL
CATALYST IN ORGANIC SYNTHESIS**

**A M.Sc. Dissertation Report By:
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**SCHOOL OF CHEMICAL SCIENCES
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April 2022**

1,4-Diazabicyclo[2.2.2]octane
(DABCO) As A Useful
Catalyst In Organic Synthesis

Submitted in Partial Fulfilment
Of
The Degree of M.Sc. (Organic Chemistry)

By

Bhalchandra A. Gaude

To the

School of Chemical Sciences
Goa University
Goa 403206
April 2022

DECLARATION

I hereby declare that the matter presented in this dissertation certified **"1,4-Diazabicyclo[2.2.2]octane (DABCO) As A Useful Catalyst In Organic Synthesis"** is the result of investigation carried out by me, under the supervision of Assistant Professor Dr. Sandesh Bugde and for the award of a degree.



Bhalchandra A. Gaude
20P0490029

CERTIFICATE

This is to certify that the dissertation entitled "**1,4-Diazabicyclo[2.2.2]octane (DABCO) As A Useful Catalyst In Organic Synthesis**" is bonified work carried out by Bhalchandra A. Gaude under my supervision in the partial fulfilment of the requirements for the award of degree of Master of Science in Chemistry at the School of Chemical Sciences, Goa University.



Dr. Sandesh Bugde
Project Guide



Prof. V.M.S. Verenkar
Dean of SCS,
Goa University

ACKNOWLEDGEMENT

It gives me an immense pleasure to present my dissertation topic
**“1,4-Diazabicyclo[2.2.2]octane (DABCO) As A Useful Catalyst In Organic
Synthesis.”**

I am very grateful to my project guide Dr. Sandesh Bugde, Assistant Professor at School of Chemical Sciences, Goa University, for his valuable guidance, encouragement and immense knowledge without which project would not have been successfully executed.

I extend my whole hearted thanks to Prof. V.M.S. Verenkar, Dean of School of Chemical Sciences, Goa University for ensuring us necessary facilities.

My deep sense of gratitude goes to all my friends for their support and cooperation all the way through my dissertation.

Last but not the least, I wish to thank my parents for their moral support throughout the project work particular and my studies in general.

CONTENTS

Sr. No.	Title	Page No.
I.	Introduction	1
II.	Literature Review	2-13
1.	A quaternary ammonium salt [H-dabco][AcO]: as a recyclable and highly efficient catalyst for the one-pot synthesis of β -phosphonomalonates	2
2.	Sonogashira reactions catalyzed by a new and efficient copper(I) catalyst incorporating N-benzyl DABCO chloride	2
3.	A facile synthesis of highly functionalized dihydrofurans based on 1,4-diazabicyclo[2.2.2]octane (DABCO) catalyzed reaction of halides with enones	3
4.	A new efficient synthesis of isothiocyanates from amines using di-tert-butyl dicarbonate	3
5.	An Efficient And Simple Procedure For Preparation Of Esters And Anhydrides From Acid Chlorides In The Presence Of 1,4-Diazabicyclo[2.2.2]Octane (DABCO) Under Solvent-Free Conditions	4
6.	Organocatalyzed nitroaldol reaction of α -ketophosphonates and nitromethane revisited	5
7.	Synthesis of N-arylphthalimides catalyzed by 1,4-diazabicyclo[2,2,2]octane [DABCO] in solventless system	5
8.	DABCO- and DBU-accelerated green chemistry for N-, O-, and S-benylation with dibenzyl carbonate	6
9.	DABCO-Catalyzed Efficient Synthesis of Naphthopyran Derivatives via One-Pot Three-Component Condensation Reaction at Room Temperature	6
10.	Synthesis of isoindol-1-ylphosphonate derivatives via Pd(0)-catalyzed reaction of α -amino (2-alkynylphenyl) methylphosphonate	7

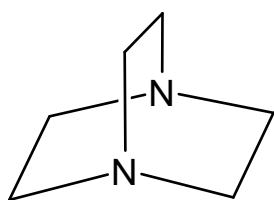
	with aryl iodide	
11.	The Baylis–Hillman chemistry in aqueous media: a convenient synthesis of 2-methylenealkanoates and alkanenitriles	8
12.	DABCO: An Efficient Organocatalyst in the Ring-Opening Reactions of Aziridines with Amines or Thiols	8
13.	DABCO Catalyzed Synthesis of Xanthene Derivatives in Aqueous Media	9
14.	Synthesis of Substituted Chromenes through the DABCO-Catalyzed Reaction of But-3-yn-2-one and Methyl Propiolate with Salicyl N-Tosylimines (DABCO=1,4-diazabicyclo[2.2.2]octane)	10
15.	Solvent-Free Green and Efficient One-Pot Synthesis of Dihydropyrano[3,2-c]chromene Derivatives	10
16.	Solvent-Free DABCO-Catalyzed One-Pot Conversion of Tetrahydropyranyl Ethers into Acetates by the Action of Bismuth(III) Nitrate under Microwave Irradiation	11
17.	DABCO-catalyzed Knoevenagel condensation of aldehydes with ethyl cyanoacetate using hydroxy ionic liquid as a promoter	11
18.	Aerobic, Chemoselective Oxidation of Alcohols to Carbonyl Compounds Catalyzed by a DABCO-Copper Complex under Mild Conditions	11
19.	DABCO-Mediated aza-Michael addition of 4-aryl-1,2,3-triazoles to cycloalkenones. Regioselective synthesis of disubstituted 1H-1,2,3-triazoles	12
20.	Stereoselective DABCO-Catalyzed Synthesis of (E)- α -Ethynyl- α,β -Unsaturated Esters from Allenyl Acetates	12
III.	Conclusion	14
IV.	References	15

INTRODUCTION

1,4-diazabicyclo[2.2.2]octane (DABCO), also known as triethylenediamine or TEDA, is a bicyclic organic compound with the formula $C_6H_{12}N_2$. This colourless solid is a highly nucleophilic tertiary amine base, which is used in many organic preparations as a good solid catalyst. DABCO has received considerable attention as an inexpensive, eco-friendly, highly reactive, easy to handle and non-toxic base catalyst for various organic transformations, and affording the corresponding products in excellent yields with high selectivity. DABCO catalyzes many reactions like Baylis-Hillman reaction, cycloaddition reactions, coupling reactions, Henry reaction, ring opening reactions etc. These reactions are environmentally friendly and the catalyst can be recycled in some cases.

DABCO is produced by thermal reactions of compounds of the type $H_2NCH_2CH_2X$ ($X=OH, NH_2,$ or NHR) in the presence of zeolitic catalysts. DABCO is 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. In chemical and biological defence, activated carbon impregnated with DABCO for use in filters for masks.

Structure:



Chemical Formula: $C_6H_{12}N_2$

IUPAC Name: 1,4-diazabicyclo[2.2.2]octane

Abbreviation: DABCO

Synonyms: Triethylenediamine, TEDA

Appearance: White crystalline powder

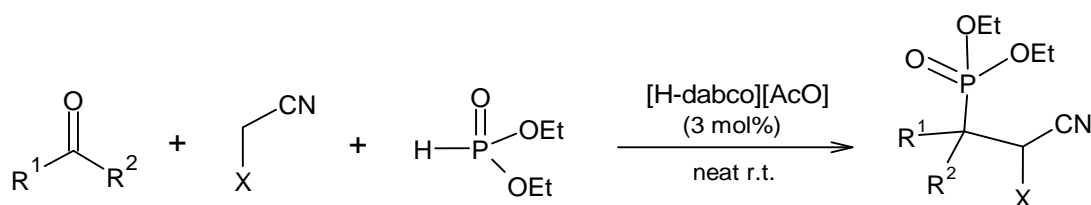
Molecular Weight: 112.18 g/mol

Melting point: 156 to 160 °C (429 to 433 K)

LITERATURE REVIEW

1. A quaternary ammonium salt [H-dabco][AcO]: as a recyclable and highly efficient catalyst for the one-pot synthesis of β -phosphonomalonates

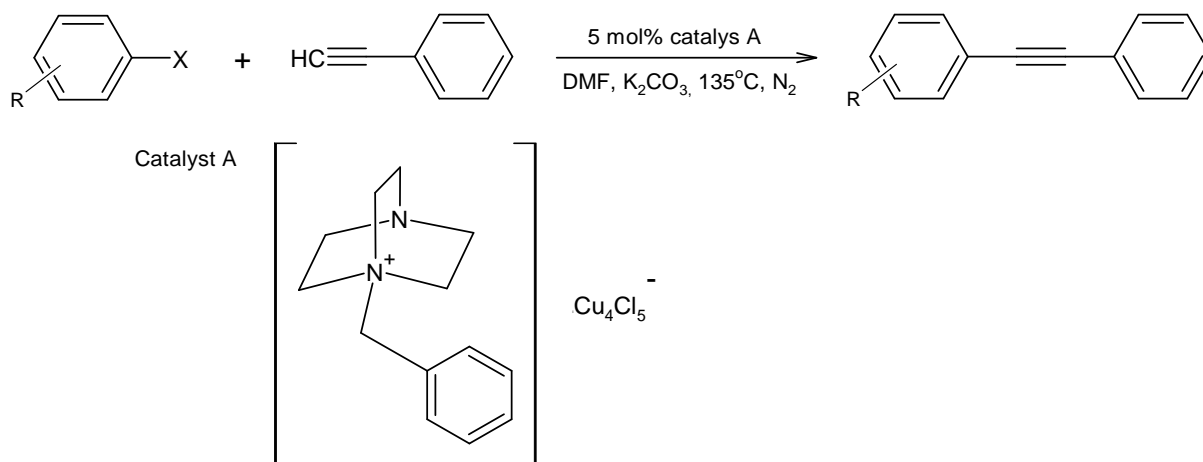
The paper includes DABCO-base quaternary ammonium salts (QASs) as highly efficient catalysts for the multi-component one-pot synthesis of β -phosphonomalonates via tandem Knoevenagel–phospha-Michael reaction. The reactions of aldehydes/ketones, active methylene compounds, and diethyl phosphite were performed under solvent-free conditions at room temperature. The catalyst could be easily recovered and reused at least for six times without activity loss. The desired products could be easily separated and purified by simple crystallization without any requirement of column chromatographic purification. It is a simple route to large scale synthesis of β -phosphonomalonates.¹



2. Sonogashira reactions catalyzed by a new and efficient copper(I) catalyst incorporating N-benzyl DABCO chloride

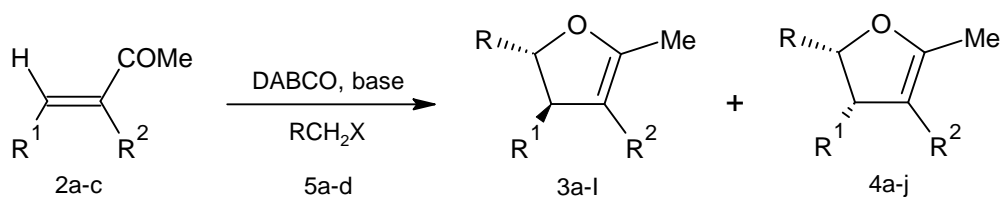
The paper reports on catalytic system of [N-benzyl DABCO]⁺[Cu₄Cl₅]⁻ (Catalyst A) as an efficient catalyst for palladium free Sonogashira cross-coupling reactions of aryl halides with phenylacetylene giving quantitative yields. The catalyst A is stable in air for several months and is insoluble in common organic solvents such as methanol, ethanol, acetonitrile and ethyl acetate, but is soluble in DMF. To optimize the reaction conditions a series of screening experiments were carried out for the cross-coupling of 4-iodonitrobenzene with phenylacetylene as a model reaction and the best results were obtained using N,N-dimethyl formamide (DMF) as solvent and K₂CO₃ (2 eq) as a base at 135°C. Under these conditions 4-nitro-1-phenylethynylbenzene was obtained as the desired product in 99% yield. Having optimized the reaction conditions, catalyst A was applied to the Sonogashira coupling of various aryl halides with phenylacetylene. Electron-poor aryl halides, in comparison to electron-rich aryl halides, gave better conversions in shorter reaction

times and a variety of substituted aromatic alkynes were prepared in good to excellent yields.²



3. A facile synthesis of highly functionalized dihydrofurans based on 1,4-diazabicyclo[2.2.2]octane (DABCO) catalyzed reaction of halides with enones

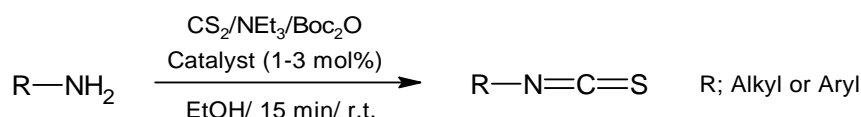
The paper reports on a synthetic route to form dihydrofurans 3 and 4 by treatment of halides 5 with electrophilic alkenes. It is a one-step catalytic process utilizing 1,4-diazabicyclo[2.2.2]octane (DABCO) as the catalyst. Stereoisomers of dihydrofuran 3 and 4 could be separated from one another on silica gel with petroleum ether–ethyl acetate as eluent and the isomers pair 3 and 4 could be readily transformed each other in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU)^{3h} in benzene.³



4. A new efficient synthesis of isothiocyanates from amines using di-tert-butyl dicarbonate

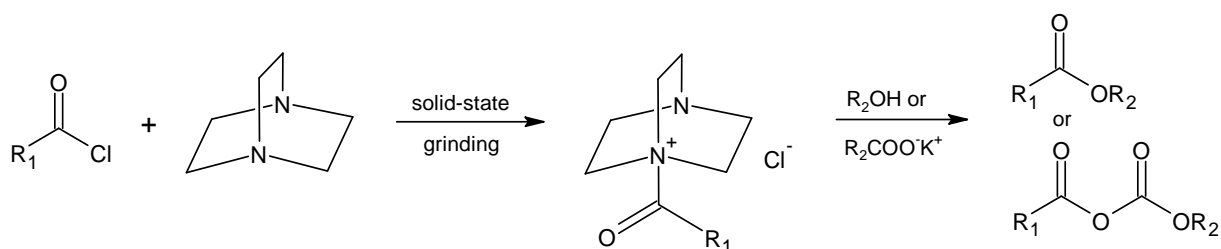
The paper suggests conversion of alkyl and aryl amines to the corresponding isothiocyanates via the dithiocarbamates in good to excellent yields using di-tert-butyl dicarbonate (Boc₂O) and 1–3 mol % of DMAP or DABCO as catalyst. Di-tert-butyl dicarbonate (Boc₂O) seemed a good candidate for the desulfurylation of the corresponding dithiocarbamate as this reagent may evolve CO₂ and COS during the

reaction, and residual carbon disulfide and tert-butanol together with the solvent should be removed easily by evaporation. A catalytic amount of DMAP or DABCO (1–3 mol %) increased the reaction rate significantly and one equivalent of triethylamine was needed for the stabilisation and complete formation of the dithiocarbamate. This method constitutes an interesting alternative in the synthesis of isothiocyanates as most of the byproducts are volatile, the work-up involves simple evaporation of the reaction mixture.⁴



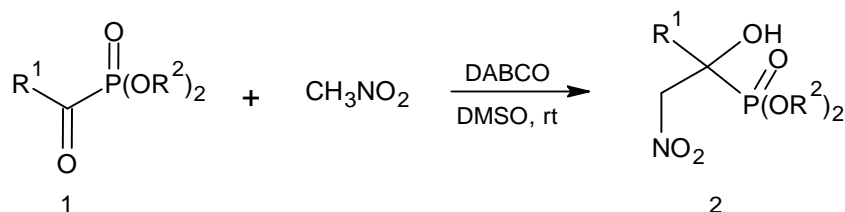
5. An Efficient And Simple Procedure For Preparation Of Esters And Anhydrides From Acid Chlorides In The Presence Of 1,4-Diazabicyclo[2.2.2]Octane (DABCO) Under Solvent-Free Conditions

The paper reports on a rapid method for one-pot synthesis of aliphatic and aromatic ester and anhydride from acid chloride and alcohol or potassium salt of carboxylic acid in the presence of 1,4-diazabicyclo[2.2.2]octane (DABCO) under solvent-free conditions. The effect of DABCO is to react with acid chloride to produce 1-aza-acyl-4-azoniabicyclo[2.2.2]octane chloride. This salt then reacts with alcohol or potassium salt of carboxylic acid to produce corresponding ester or anhydride. No selective esterification between primary, secondary alcohol and phenol was observed. The tertiary alcohols remained unchanged even the reaction mixture was heated at 70°C for 2 h. The catalyst (DABCO) could be reused again without significant decrease in its activity. The reaction has been carried out in excellent yield in short reaction time.⁵



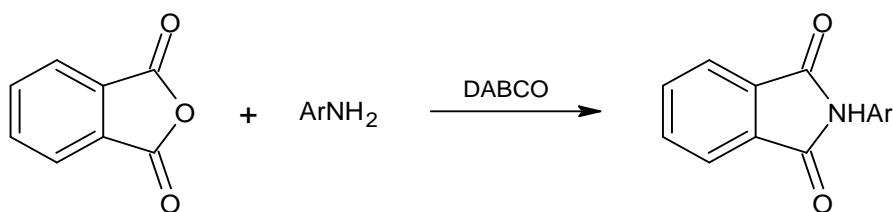
6. Organocatalyzed nitroaldol reaction of α -ketophosphonates and nitromethane revisited

The paper suggests an improved procedure for nitroaldol reaction of both aryl and alkyl substituted α -ketophosphonates with nitromethane catalyzed by DABCO in DMSO as a solvent at a room temperature. It was observed that the nitroaldol product is actually lowering the catalytic activity of DABCO (poisoning the catalyst). To overcome this poisoning problem, the DABCO catalyst was intentionally added in two portions (10 mol % each) with an interval of 30 min. Both α -aryl and α -alkyl substituted α -hydroxy- β -nitrophosphonates may be obtained in excellent yields with a simple operation and in a short reaction time.⁶



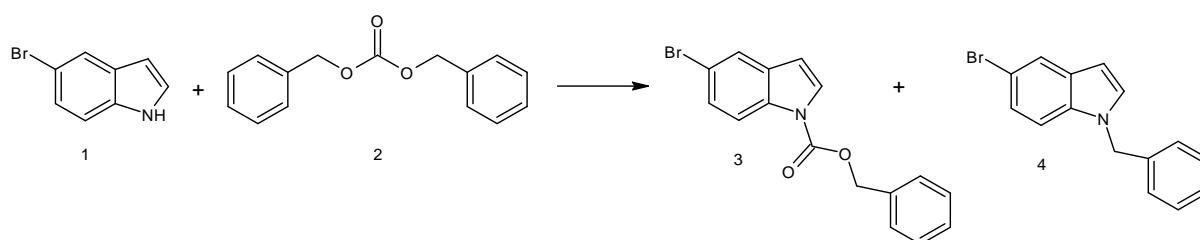
7. Synthesis of N-arylphthalimides catalyzed by 1,4-diazabicyclo[2,2,2]octane [DABCO] in solventless system

The paper reports on a green method for the facile formation of phthalimides, catalyzed by DABCO (1,4-diaza-bicyclo[2,2,2]octane) that involves grinding of phthalic anhydride, an appropriate aniline derivative using mortar and pestle. Without DABCO reaction does not proceed even under prolonged reflux in solvents. This solvent-free approach requires only a few minutes of reaction time and high yields is described.⁷

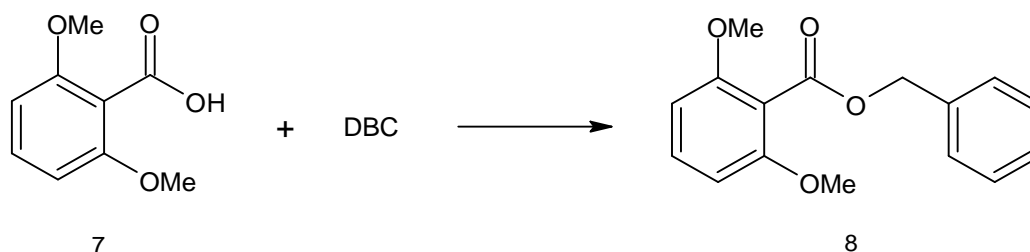


8. DABCO- and DBU-accelerated green chemistry for N-, O-, and S-benylation with dibenzyl carbonate

The paper includes benzylation of nitrogen, oxygen, or sulfur atoms with DBC (dibenzyl carbonate) as a benzylating reagent. Catalytic amounts of DABCO or DBU can accelerate this 'green' alkylation. The catalytic benzylation strategy was first evaluated by treating 5-bromoindole (1) with DBC (2) at 95°C in N,N-dimethylacetamide (DMA) using catalytic amounts (10 mol%) of DABCO. As revealed in Table 1, this reaction successfully afforded the desired 5-bromo- N-benzylindole (4) in 80% yield. Without DABCO, the same reaction generated only 5% of 4 over the same period of time.



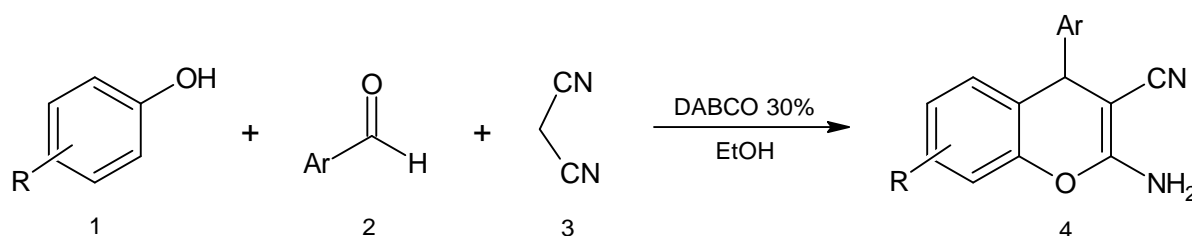
For the benzylation of a carboxylic acid with DBC, rate enhancement by DBU is also evident. Near quantitative (99%) conversion to the benzyl ester was achieved in 2h when 1.1 equiv. of DBU was employed in benzylation of 2,6-dimethoxybenzoic acid (7) with DBC. For the benzylation of aromatic acids, DBU was a superior catalyst to DABCO.



Presence of an electron-withdrawing group (NO₂) in the aromatic ring seems to enhance the benzylation rate. 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.⁸

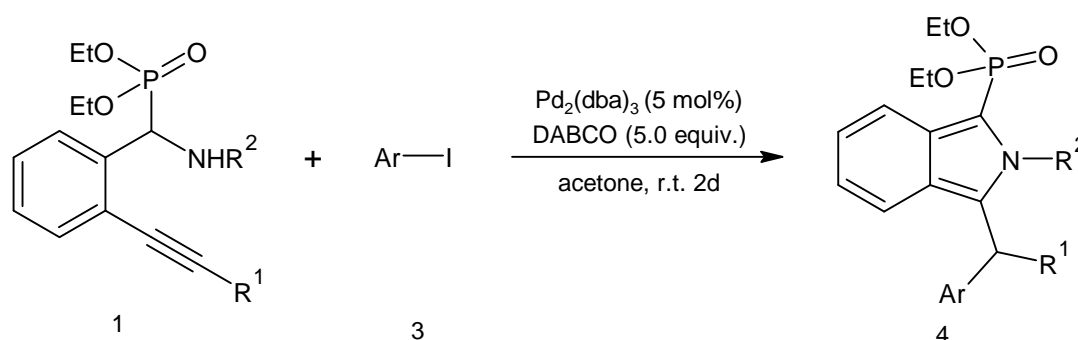
9. DABCO-Catalyzed Efficient Synthesis of Naphthopyran Derivatives via One-Pot Three-Component Condensation Reaction at Room Temperature

The paper includes DABCO-mediated three-component coupling of naphthols, aromatic aldehydes and malononitrile in ethanol at room temperature to afford 2-amino-3-cyano naphthopyran derivatives in good to excellent yields. The best yield was obtained with 0.3 equivalent of DABCO as catalyst. The reactions of aldehydes containing electron-donating groups show only a slightly slower reaction rate and lower yields than those containing electron-withdrawing groups. Reduced chemical yields was observed for both ortho-substituted benzaldehyde derivatives regardless of the electronic nature of the substituent. The short reaction times, easy workup, good to excellent yields, and mild reaction conditions make this domino Knoevenagel–Michael reaction both practical and attractive.⁹



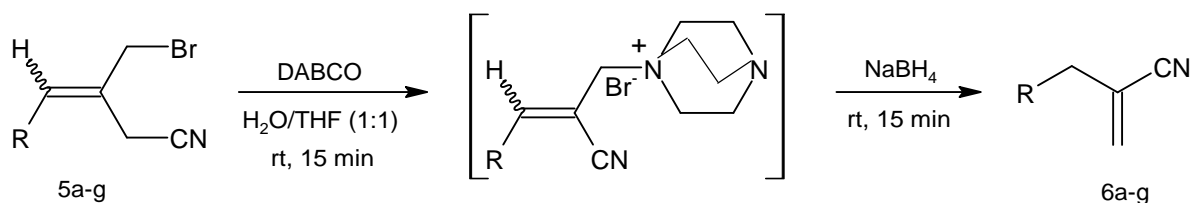
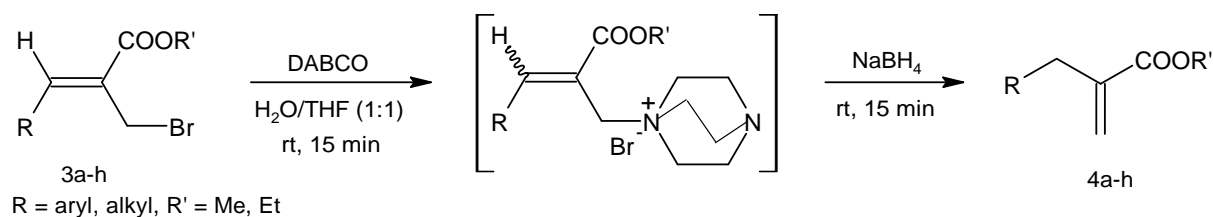
10. Synthesis of isoindol-1-ylphosphonate derivatives via Pd(0)-catalyzed reaction of α -amino (2-alkynylphenyl) methylphosphonate with aryl iodide

The paper suggests synthesis of isoindol-1-ylphosphonate derivatives via Pd(0)-catalyzed reaction of α -amino (2-alkynylphenyl) methylphosphonate with aryl iodide at room temperature in the presence of catalytic amount of Pd₂(dba)₃ and DABCO in acetone. Aryl iodides with electron-donating or electron-withdrawing group attached on the aromatic ring were all good partners in this transformation. The isoindol-1-ylphosphonate derivatives was obtained in good to excellent yields.¹⁰



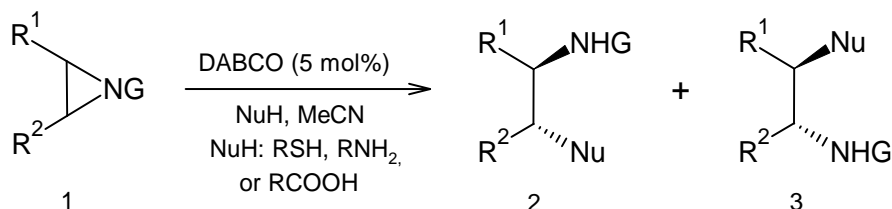
11. The Baylis–Hillman chemistry in aqueous media: a convenient synthesis of 2-methylenealkanoates and alkanenitriles

The paper reports on a synthesis of 2-methylenealkanoates and alkanenitriles via the regioselective nucleophilic addition (S_N2) of hydride ion from NaBH_4 to allyl bromides i.e. (2Z)-2-(bromomethyl)alk-2-enoates and 2-(bromomethyl)alk-2-enenitriles, derived from the Baylis–Hillman adducts, respectively, in the presence of DABCO in $\text{H}_2\text{O}/\text{THF}$ (1:1) at room temperature.¹¹



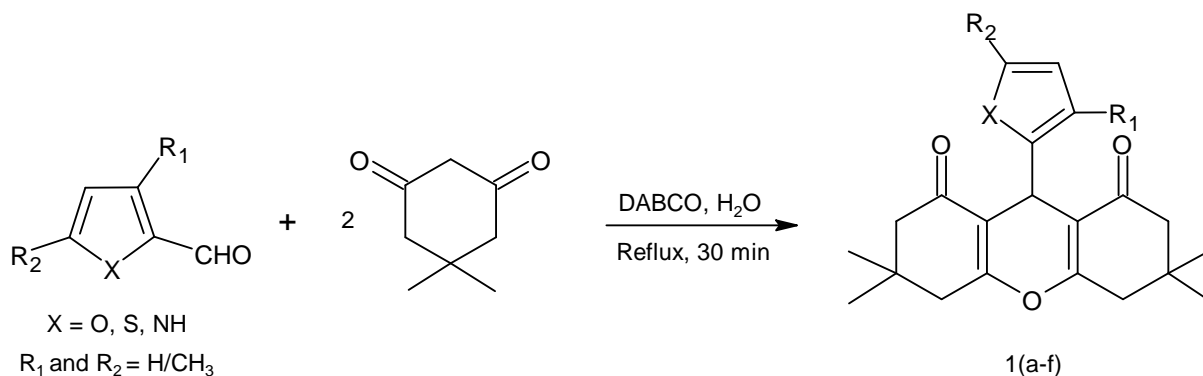
12. DABCO: An Efficient Organocatalyst in the Ring-Opening Reactions of Aziridines with Amines or Thiols

The paper reports on a 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. This reaction could be run under the air without loss of efficiency. In the case of unsymmetrically substituted aziridines 1c and 1d, completely regioselectivity with the attack of nucleophile on the less substituted aziridine carbon was observed.¹²

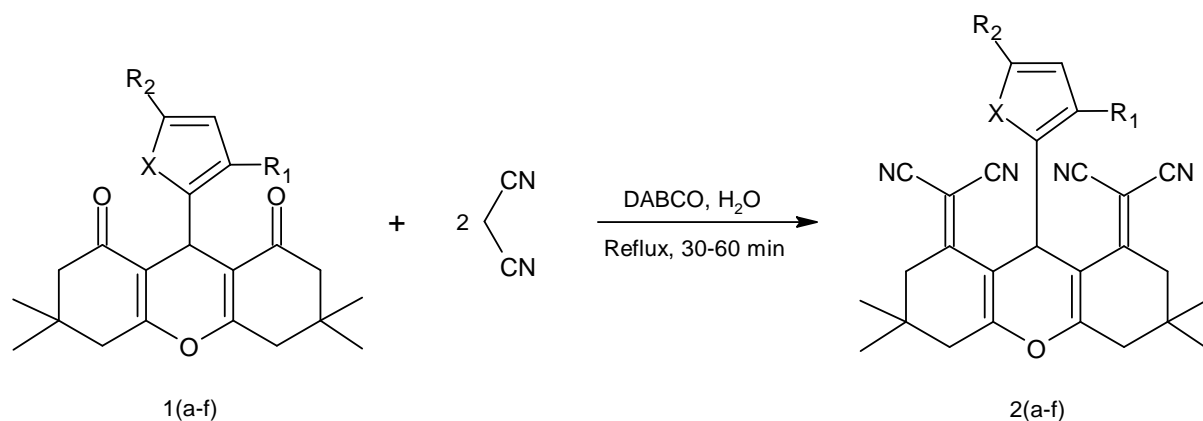


13. DABCO Catalyzed Synthesis of Xanthene Derivatives in Aqueous Media

The paper suggests condensation of heteroarylaldehyde, 5,5'-dimethyl-1,3-cyclohexanedione (dimedone), in the presence of catalytic amount of DABCO to produce a variety of 1,8-dioxooctahydroxanthenes derivatives 1(a-f). The reaction proceeds via the initial Knoevenagel, subsequent Michael, and final heterocyclization reactions.¹³

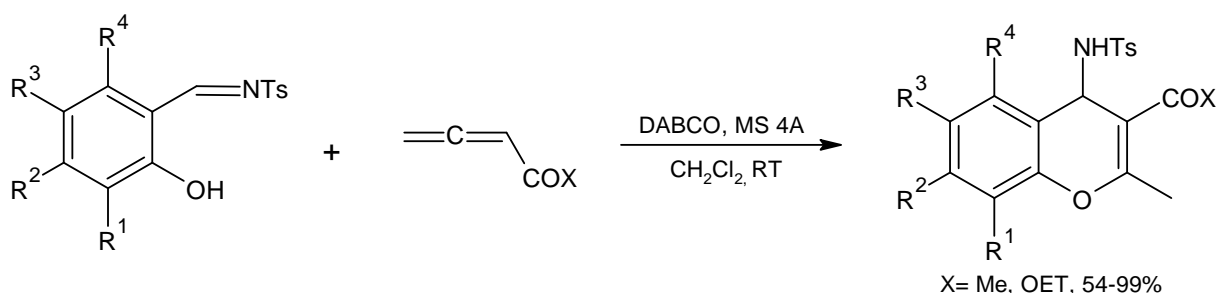


In order to optimize reaction conditions, a mixture of 3-methyl thienaldehyde (1 mmol), 5,5-dimethyl cyclohexane-1,3-dione (2 mmol) in H₂O was refluxed for an appropriate time as indicated by TLC using different amounts of DABCO (Table 1). The efficiency of the reaction is mainly affected by the amount of the catalyst. The optimal amount of the catalyst was 10mmol%, the higher amount of the catalyst did not increase the yield noticeably. The synthesized products 1(a-f) were further treated with malononitrile to obtain corresponding alkylidenes 2(a-f).¹³



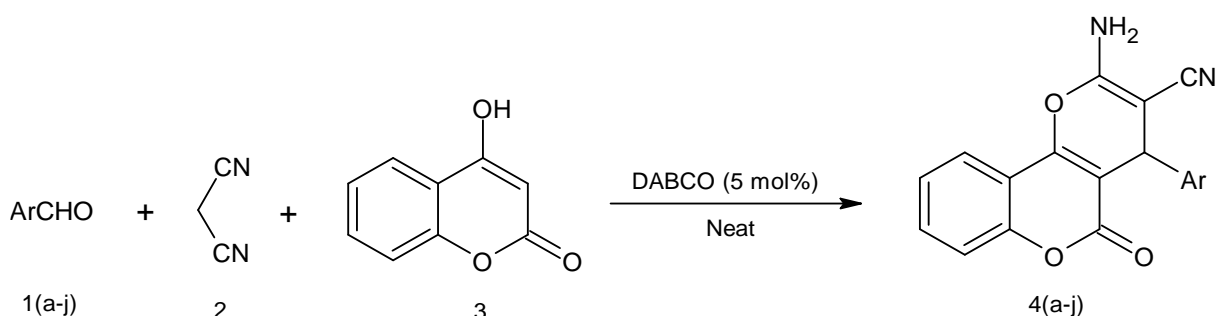
14. Synthesis of Substituted Chromenes through the DABCO-Catalyzed Reaction of But-3-yn-2-one and Methyl Propiolate with Salicyl N-Tosylimines (DABCO=1,4-diazabicyclo[2.2.2]octane)

The paper includes synthesis of highly functionalized chromenes by reaction of but-3-yn-2-one and methyl propiolate with salicyl N-tosylimines using DABCO=1,4-diazabicyclo[2.2.2]octane as a catalyst. The optimal reaction conditions for this reaction: 1.2 equivalents of but-3-yn-2-one 2a, 10 mol% of DABCO, and performing the reaction at room temperature (20°C) for 24 h. The reaction mechanism has been demonstrated based on the observations of ¹H NMR spectra.¹⁴



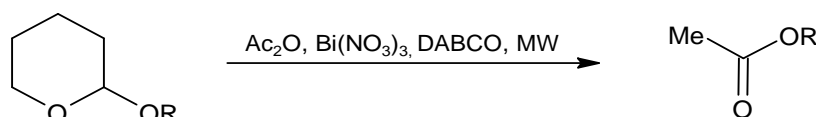
15. Solvent-Free Green and Efficient One-Pot Synthesis of Dihydropyrano[3,2-c]chromene Derivatives

The paper includes one-pot synthesis of dihydropyrano[3,2-c]chromene derivatives by the reaction of aromatic aldehydes, malononitrile, and 4-hydroxycoumarin catalyzed by DABCO in solventless conditions. When the reaction was carried out solvent-free neat condition at 100°C best results were obtained. The present method has the advantages of mild reaction conditions, short reaction times, easy isolation of products, and excellent yields.¹⁵



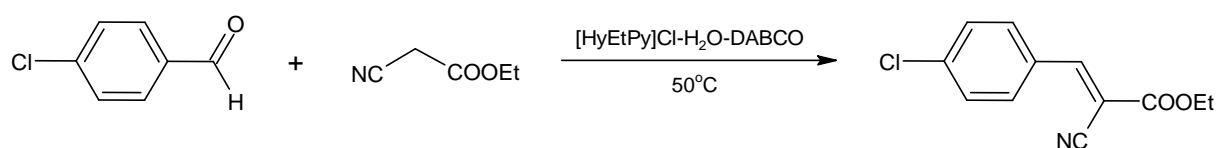
16. Solvent-Free DABCO-Catalyzed One-Pot Conversion of Tetrahydropyranyl Ethers into Acetates by the Action of Bismuth(III) Nitrate under Microwave Irradiation

The paper includes 1,4-diazabicyclo[2.2.2]octane (DABCO) as an effective co-catalyst in the direct conversion of THP ethers into the corresponding acetates in the presence of bismuth(III) nitrate under microwave irradiation. It requires no solvent and utilizes accessible, inexpensive, and nontoxic reagents and ensures high yields in short reaction time.¹⁶



17. DABCO-catalyzed Knoevenagel condensation of aldehydes with ethyl cyanoacetate using hydroxy ionic liquid as a promoter

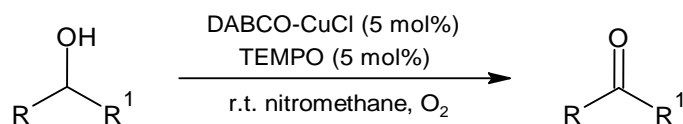
In this paper a protic-ionic-liquid solvent-catalyst system [HyEtPy]Cl-H₂O-DABCO was synthesised and used in the Knoevenagel condensation reaction of aromatic aldehydes with ethyl 2-cyanoacetate. This system showed better catalytic activity compared to other ionic liquid (IL) that had no hydroxyl group attached to the IL scaffold. At 50°C with 50% of H₂O and 20 mmol of DABCO, the Knoevenagel condensation promoted by the composite system proceeded well with good yield of product, and the solvent-catalyst system [HyEtPy]Cl-H₂O was recycled at least 6 times, showing no significant loss of activity.¹⁷



18. Aerobic, Chemoselective Oxidation of Alcohols to Carbonyl Compounds Catalyzed by a DABCO-Copper Complex under Mild Conditions

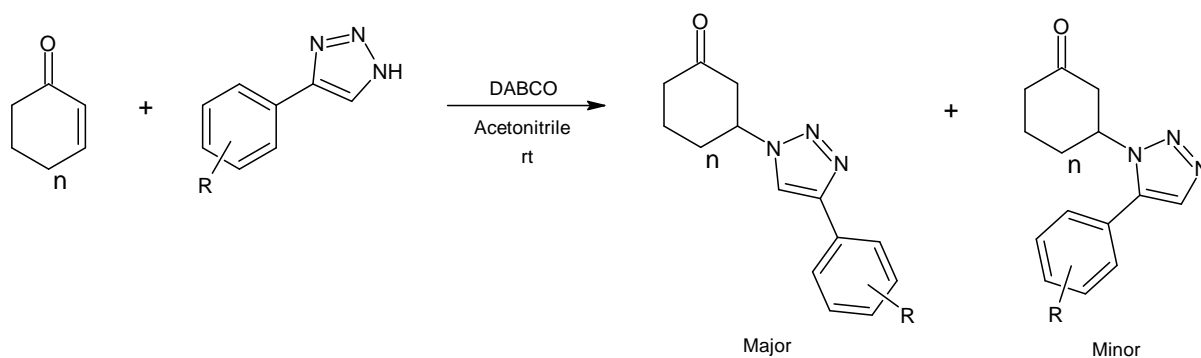
The paper includes selective oxidation of benzylic and allylic alcohols into the corresponding carbonyl compound using DABCO-copper(I) chloride complex (5 mol%) together with TEMPO (5 mol%) in nitromethane as solvent at room temperature where molecular oxygen acts as an ultimate, stoichiometric oxidant and water is the only by-product. Without DABCO the reaction gave only 9% yield, so it is

clear that the CuCl alone is not an active catalyst and DABCO is needed to increase its catalytic activity. Similarly, the oxidation reaction did not provide any oxidized product when the reaction was carried out without TEMPO. Solid state structure determination of DABCO-Cu complex shows that the Cu is in the Cu(II) oxidation state with trigonal bipyramidal geometry and exists in a linear polymeric structure due to strong hydrogen bonding.¹⁸



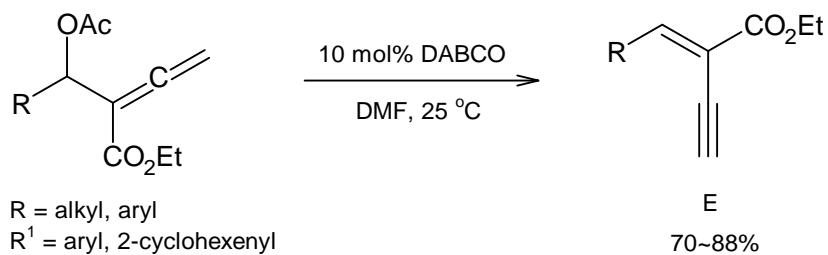
19. DABCO-Mediated aza-Michael addition of 4-aryl-1,2,3-triazoles to cycloalkenones. Regioselective synthesis of disubstituted 1H-1,2,3-triazoles

The paper includes DABCO-mediated synthesis of disubstituted 1,2,3-triazoles by aza-Michael reaction of 4-aryl-1,2,3-triazoles with 2-cycloalken-1-ones. The reactions were carried out in acetonitrile at room temperature to provide 1,4-disubstituted 1H-1,2,3-triazoles as major adducts and 1,5-disubstituted 1H-1,2,3-triazoles as minor adducts. The two regioisomers were separated by using column chromatography and the adducts were obtained in very good to excellent combined chemical yields.¹⁹



20. Stereoselective DABCO-Catalyzed Synthesis of (E)- α -Ethynyl- α,β -Unsaturated Esters from Allenyl Acetates

The paper includes the synthesis of (E)- α -ethynyl- α,β -unsaturated esters from allenyl acetates catalyzed by DABCO (0.1 equiv) in DMF at room temperature. Allenyl acetates were prepared from the reaction of aldehydes with organoindium reagent in situ generated from ethyl 4-bromobutynoate and indium in the presence of lithium iodide in DMF and subsequent acetylation.²⁰



CONCLUSION

1,4-diazabicyclo[2.2.2]octane (DABCO) is an highly efficient catalyst, a good nucleophile and base in numerous organic synthesis. DABCO has more advantages than other organic catalyst because it is non-toxic, inexpensive, eco-friendly, easy to handle, and thermally stable catalyst with simple experimental and isolation procedure. DABCO catalyzes many reactions like Baylis-Hillman reaction, Sonogashira reaction, oxidation reactions, ring opening reactions etc. Some of important organic compounds like Dihydrofurans, N-arylphthalimides, Chromenes, β -phosphonomalonates and derivatives of Naphthopyran, Xanthene etc., can be synthesised in excellent yield using DABCO as a catalyst. In some cases the DABCO catalyst can be recycled and reused without significant loss of activity.

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