

DABCO entrapped in agar-agar : A heterogeneous gelly catalyst for multi-component synthesis of 2-Amino-4H-Chromenes

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ABSTRACT

An efficient method for the multi-component synthesis of 2-amino-4H-chromenes by reaction of malanitrile with various aldehydes and phenols in the presence of gel entrapped DABCO as catalyst is reported.

Keywords : Multi-component reactions, Gel Entrapped Base Catalysts, Recyclability.

I. INTRODUCTION

The rapid assembly of molecular diversity utilizing multi-component reactions (MCRs) has received a great deal of attention, most notably for the speedy synthesis of novel molecular libraries¹. These methodologies are of particularly great utility when they lead to the formation of privileged medicinal and industrial scaffolds. 2-Amino-4H-chromene scaffolds are of significant medical relevance since they have widespread applications including antiviral², antimicrobial³, antiproliferative⁴, mutagenicity⁵, antitumor⁶, sex pheromone⁷ and central nervous system activity⁸. Looking at their importance from pharmacological and industrial point of view, several methods for the multi-component synthesis of 2-amino-4H-chromenes have been reported. These methods include both homogeneous as well as heterogeneous conditions, catalyzed by piperidine⁹, aqueous K₂CO₃¹⁰, triethylamine¹¹, basic ionic liquid¹², CATBr¹³, ammonium salt¹⁴, NaOH¹⁵, I₂/K₂CO₃¹⁶, TiCl₄¹⁷, InCl₃¹⁸ and heteropolyacid¹⁹ have been also employed. Although the literature on synthesis of 2-amino-4H-chromene enjoys a rich array of versatile methodologies, new efficient approaches can be valuable additions to the contemporary arsenal of synthetic strategies.

The concept of gel entrapped base catalysts (GEBs) combines the advantages of alkali and organic bases with those of heterogeneous supports²⁰. These catalysts are prepared by immobilization of alkali or organic bases by entrapping them in an aqueous gel matrix of agar-agar which is a polymer composed of repeating agarobiose units alternating between 3-linked β -D-galactopyranosyl (G) and 4-linked 3, 6-anhydro- α -L-galactopyranosyl (LA) units (**Fig.1**). This method reduces the amount of bases used and affords easy and efficient separation of products from the catalyst. Besides this, bases like alkalis when exposed to air, absorb moisture and are spoiled. On the contrary, the GEBs do not absorb moisture on exposure to air and remain intact. The use of GEBs in organic synthesis also provides excellent opportunity of recyclability and reusability which is seldom possible using bases alone as catalysts. However, despite their well recognized advantages, there have been only limited and sporadic

reports dealing with use of GEBCs in synthetic chemistry^{21, 22}. The interesting properties of GEBCs spurred us to tap their barely exploited potential in organic synthesis.

In our continued interest in the applications of novel catalysts in organic synthesis²³, we report herein the synthesis of 2-amino-4*H*chromenes of phenols, aldehydes and malanitrile in the presence of gel entrapped DABCO as a catalyst.

Results and Discussion

Initially, we focused our attention towards the synthesis of gel entrapped DABCO. A series of experiments were undertaken in which different concentrations of DABCO (5-25 %) were dissolved in a varying amount of agar-agar in water. After a considerable experimentation, we found that 20 % *w/w* of agar-agar aqua gel containing 10 % DABCO resulted in the formation of soft gel that served as GEBC in the present work. Gel entrapped DABCO was white jelly like substance that could be cut into pieces. The changes in physical nature of gel entrapped DABCO was studied in various solvents. The gel remained intact in ethanol, methanol, acetone, dichloromethane, toluene, 2-propanol and water.

Thermal behaviour of gel entrapped DABCO was studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (**Fig. 2**). The TGA/DSC curve revealed that the loss of water occurs initially upto ~150 °C and is accompanied with endothermic peak in DSC curve. The thermal decomposition of DABCO embedded polymer matrix occurs in two distinct steps giving approximately weight loss 11 % in each step. It is also revealed from the DSC curve that these processes are exothermic. The decomposition is completed at the temperature 510 °C.

Our next task was to demonstrate the catalytic activity of gel entrapped DABCO in the synthesis of 2-amino-4*H*chromenes (**Scheme 1**). As a trial case, equimolar mixture of phenol, benzaldehyde and malanitrile (5 mmol each) was stirred in the presence of 1 gm of various GEBCs in ethanol at ambient temperature till the completion of reaction as monitored by thin layer chromatography. The reaction proceeded efficiently yielding the corresponding 2-amino-4*H*-chromene 10 minutes. In order to check the generality of this methodology, a series of 2-amino-4*H*-chromenes were prepared by reaction of malanitrile with various phenols and aryl aldehydes. The results are summarized in (**Table 1**). With both electron-poor and electron-rich benzaldehydes, the corresponding products were obtained in good to excellent yields. The reaction of the sterically hindered 2-substituted benzaldehydes even gave higher yields highlighting the general applicability of the protocol. Further, we have also studied the reaction in absence of catalyst. It is worthy of note that in blank experiment no reaction was observed under similar conditions in the absence of gel entrapped DABCO. The striking feature of all the reactions was the isolation of products. It was interesting to observe that after specified time, the product precipitates out of the reaction mixture that can be isolated simply by filtration. The product obtained after sufficient washing with water was found to be practically pure. The identity of all the compounds was ascertained on the basis of IR, ¹H NMR, ¹³C NMR and mass spectroscopy data. The physical and spectroscopic data are in harmony with the proposed structures.

In the GEBCs, the reagent entrapped in the gel may leach into the solvent. To study the leaching of DABCO in solvent, 1 gm gel entrapped DABCO was stirred in 5 mL of ethanol at room temperature. The catalyst was filtered and water (3 mL) was added to the filtrate. The DABCO leached out was then determined by titrating against 0.1 N hydrochloric acid solution using methyl red as an indicator. It was observed that only 5 % DABCO leached out

from gel into ethanol. Using the amount of DABCO same as that leached out, the reaction between phenol, benzaldehyde and malanonitrile did not give quantitative yield of the corresponding product. This clearly demonstrated that catalysis was solely due to intact gel entrapped DABCO rather than leached DABCO.

The plausible mechanism for the formation of 2-amino-4*H*-chromenes using gel entrapped DABCO is shown in (Fig 3) Initially, the catalyst facilitates the formation of dicyanoolefin (5) by Knoevenagel condensation between aryl aldehyde and malanonitrile as well as generation of phenolate anion (6) from phenol. The addition of phenolate anion to dicyanoolefin results in the formation (7) which on cyclization furnishes imine (8) that results in the formation of 2-amino-4*H*-chromene (4 a-1).

The recovery and reuse of catalysts is highly preferable for the large scale operations and industrial point of view. To check the possibility of GEC recycling, the reaction of phenol, benzaldehyde and malanonitrile using gel entrapped DABCO in ethanol was studied. After completion of the reaction, the catalyst was separated from reaction mixture, washed with ethanol and reused in another reaction with identical substrates. The catalyst showed a remarkable recyclability as the corresponding yields started at 96 % and reached 90 % at fifth run (Fig. 3).

Experimental

Melting points were determined in an open capillary and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer FTIR spectrometer. The samples were examined as KBr discs ~5% w/w. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avon 300 MHz spectrometer using DMSO/CDCl₃ as solvent and TMS as internal reference. Mass spectra were recorded on a Shimadzu QP2010 GCMS with an ion source temperature of 280 °C. The thermal gravimetric analysis (TGA) curves were obtained by using the instrument STA 1500 in the presence of static air at a linear heating rate of 10 °C/min from 25 ° to 1000 °C. All chemicals were obtained from local suppliers and used without further purification.

Preparation of gel entrapped DABCO

To a boiling mixture of agar-agar (5 gm) in water (35 mL) was added a mixture of base (2.5 gm) in water (2.5 mL). The resultant solution was boiled with stirring for five minutes and cooled in ice bath to yield the desired gel entrapped DABCO catalyst.

*General procedure for the multi-component synthesis of 2-amino-4*H*-chromenes*

A mixture of phenol (5 mmol), aldehyde (5 mmol) and malanonitrile (5 mmol) was stirred in the presence of gel entrapped DABCO (1 gm) in 5 mL of ethanol at ambient temperature till the completion of the reaction as monitored by TLC. The resulting crude product was filtered off, washed with water and recrystallized from ethanol to afford pure products.

Spectral data of representative compounds

2-Amino-4-aryl-3-cyano-7-hydroxy-4*H*-chromene (4a): IR (KBr): ν 3429, 3211, 2193, 1651, 1505, 1447 cm⁻¹; ¹H NMR (300 MHz, DMSO): δ 4.50 (s, 1H), 6.40 (s, 1H, ArH), 6.48 (d, 1H, J=8.3 Hz, ArH), 6.80 (d, 1H, J=9.2 Hz, ArH), 6.85 (s, 2H, NH₂), 7.15-7.21 (m, 3H, ArH), 7.30 (t, 2H, J=7.1 Hz, ArH), 9.68 (s, 1H, ArOH); ¹³C NMR (75 MHz, DMSO): 57.74, 102.80, 112.69, 113.52, 121.00, 126.75, 127.75, 128.58, 129.84, 146.18, 149.24, 157.37, 160.30; MS (EI): m/z = 264 (M⁺).

2-Amino-3-cyno-4(phenyl)-4*H*-benzochromene(**4b**):IR (KBr): ν 3448, 3304, 3010, 2910,2204, 1649, 1633, 1550, 1450, 1375, 1267, 1100, 1022 cm^{-1} ; ^1H NMR (300 MHz, DMSO): δ 4.79 (s, 1H), 6.88 (brs, 2H, NH_2), 7.14 (d, 1H, $J=8.3$ Hz, ArH), 7.21-7.28(m, 5H, ArH), 7.45-7.56(m, 3H, ArH), 7.77 (d, 1H, $J=8.3$ Hz, ArH), 8.21(d, 1H, $J=8.3$ Hz, ArH) ; ^{13}C NMR (75 MHz, DMSO): 57.06, 78.61, 79.05, 79.49, 117.90, 121.36, 123.38, 124.08, 126.39, 126.65, 126.81, 127.14, 127.76, 128.04, 128.85, 133.14, 145.85, 160.45; MS (EI): $m/z = 298$ (M^+).

Conclusion

In conclusion, a novel and highly efficient methodology for the multi-component synthesis of 2-amino-4*H*-chromene by reaction of malanonitrile with various aldehydes and phenols in the presence of gel entrapped DABCO. The method offers several significant advantages, such as high conversions, easy handling, clean reaction profile and short reaction time, which make it a useful and an attractive addition to the existing methodologies.

Acknowledgements

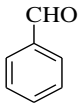
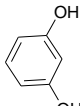
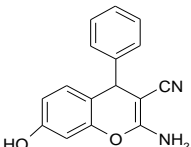
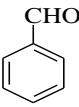
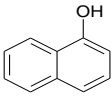
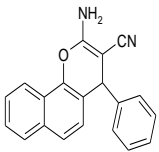
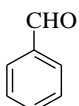
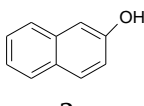
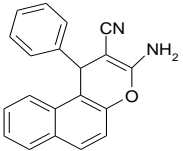
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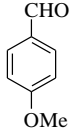
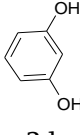
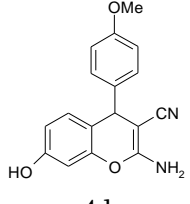
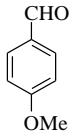
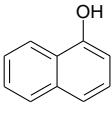
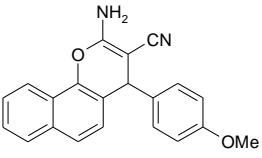
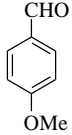
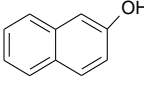
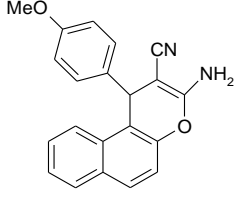
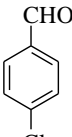
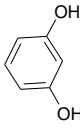
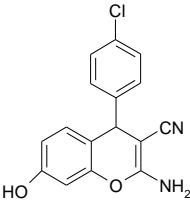
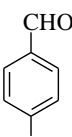
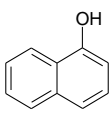
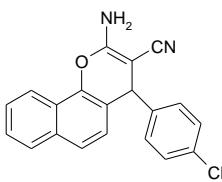
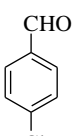
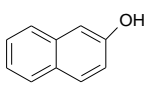
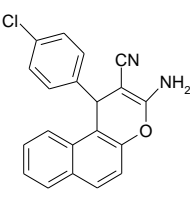
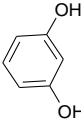
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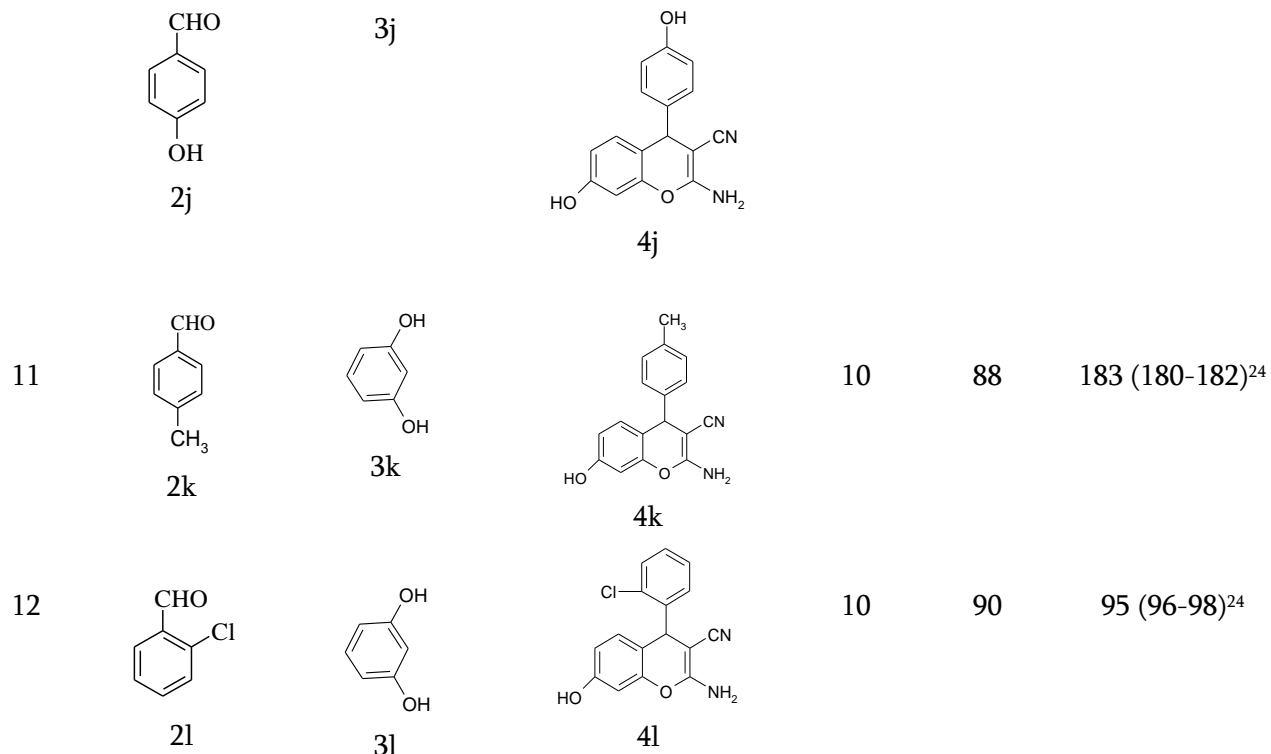
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Entry	Aldehyde	Phenol	Product	Time (Min)	Yield ^b (%)	M. P. (°C) ^c
1	 2a	 3a	 4a	10	96	235 (234-236) ²⁴
2	 2b	 3b	 4b	10	92	209 (210-211) ²⁵
3	 2c	 3c	 4c	10	93	280 (278-280) ²⁵

4	 2d	 3d	 4d	10	92	112 (112-114) ²⁴
5	 2e	 3e	 4e	10	90	191 (190-192) ²⁵
6	 2f	 3f	 4f	10	91	182 (182-183) ²⁵
7	 2g	 3g	 4g	10	89	158 (160-162) ²⁴
8	 2h	 3h	 4h	10	85	230 (231-232) ²⁵
9	 2i	 3i	 4i	10	86	205 (206-208) ²⁵
10		 		10	89	248 (248-250) ²⁴

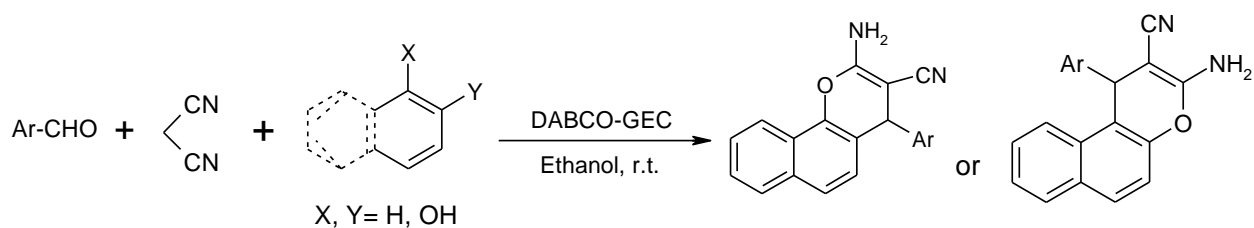


^aAll products were characterized by IR, ¹H NMR, ¹³C NMR and mass spectrometry.

^bIsolated yields.

^cLiterature values in parenthesis.

Table 1. Gel entrapped DABCOcatalyzed synthesis of 2-amino-4*H*-chromenes^a



Scheme 1: Multi-component synthesis of 2-amino-4*H*-chromenes using gel entrapped DABCO

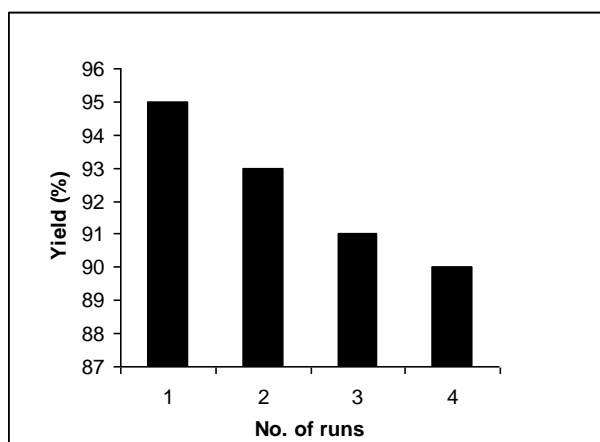


Fig. 3: Recyclic use of gel entrapped DABCO in of 2-amino-4*H*-chromene synthesis

Eco-friendly Synthesis of benzopyran Derivatives by Using Greener Catalysts

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ABSTRACT

A protocol has been developed for the efficient synthesis of structurally diverse tetrahydrobenzo[*b*]pyran via three-component reactions of dimedone, malanonitrile with various aldehydes and in the presence of gel entrapped NaOH as a catalyst.

Keywords : Gel Entrapped Base Catalyst, tetrahydrobenzo[*b*] pyran, recyclability

I. INTRODUCTION

Multicomponent reactions (MCRs) have attracted considerable attention owing to high synthetic efficiency, and, in many cases, the facile construction of novel molecular libraries. These methodologies are of particularly great utility when they lead to the formation of privileged medicinal scaffolds. Tetrahydrobenzo[*b*]pyrans are an important class of heterocyclic scaffolds in the field of drugs and pharmaceuticals. These compounds are widely used anti-coagulant, anti-cancer and anti-anginal spasmolytic agents.¹⁻⁴ In addition, they have been shown to act as cognitive enhancers, for the treatment of neurodegenerative disease, including Huntington's disease, amyotrophic lateral Sclerosis, Alzheimer's disease, AIDS associated dementia and Down's syndrome as well as for the treatment of Schizophrenia and myoclonus.^{5, 6} The polyfunctionalized benzopyrans are used as cosmetics, pigments and biodegradable agrochemicals.⁷ Other than their biological importance, some tetrahydrobenzo[*b*]pyrans have been widely used as photoactive materials.⁸ Looking at their importance from pharmacological and industrial point of view, several methods for the multi-component synthesis of tetrahydrobenzo[*b*]pyrans have been reported. These include both homogeneous as well as heterogeneous conditions, catalyzed by Na₂SeO₄, hexadecyldimethylbenzyl ammonium bromide,⁹ NaBr,¹⁰ tetra-methyl ammonium hydroxide (CH₃)₄ N⁺OH⁻,¹¹ TEBA,¹² KF-montmorillonite,¹³ KF-alumina,¹⁴ organocatalysts,¹⁵ acetic acid,¹⁶ diammonium hydrogen phosphate¹⁷ and hexadecyltrimethylammonium bromide.¹⁸ Microwaves¹⁹ and ultrasonic irradiation²⁰ have also been used to promote the reaction. Although the literature on synthesis of tetrahydrobenzo[*b*]pyrans enjoys a rich array of versatile methodologies, new efficient approaches can be valuable additions to the contemporary arsenal of synthetic strategies.

The concept of gel entrapped base catalysts (GEBs) combines the advantages of alkali and organic bases with those of heterogeneous supports.²¹ These catalysts are prepared by immobilization of alkali or organic bases by entrapping them in an aqueous gel matrix of agar-agar which is a polymer composed of repeating agarobiose units

alternating between 3-linked β -D-galactopyranosyl (G) and 4-linked 3, 6-anhydro- α -L-galactopyranosyl (LA) units. The use of GEBCs in organic transformations abates the amount of bases used and affords easy and efficient separation of products from the catalyst simply by filtration. Often, bases like alkalis absorb moisture when exposed to air and get spoiled. On the contrary, the GEBCs do not absorb moisture on exposure to air and remain intact. They also provide excellent opportunity of recyclability and reusability which is rarely possible using bases alone as catalyst. Further advantages of GEBCs include their ease of handling and being less corrosive. However, despite of their well recognized advantages, there have been only limited and sporadic reports dealing with the use of GEBCs in organic synthesis.²²

In continuation to our research work devoted to the development of green methodologies for MCRs.²³ we report herein an efficient synthesis of tetrahydrobenzo[*b*]pyrans from dimedone, malanonitrile and aryl aldehydes in the presence of Gel entrapped NaOH as a catalyst.

Results and Discussion

We focused our initial studies on synthesis of Gel entrapped NaOH (acronymed as GENaOH). A series of experiments were undertaken in which different concentrations of NaOH (5-25 %) were dissolved in a varying amount of agar-agar in water. After a considerable experimentation, we found that 20 % *w/w* of agar-agar aqua gel containing 10 % NaOH resulted in the formation of soft gel that served as GEBC in the present work. The GENaOH was light yellow jelly like substance that could be cut into pieces. The changes in physical nature of GENaOH were studied in different solvents. The GENaOH swelled in water and become soft. The nature of gel remained intact in organic solvents like ethanol, acetone, dichloromethane, toluene and isopropanol.

The TGA analysis of agar-agar and GENaOH are displayed in fig. The TGA profiles show three different weight losses at different temperatures. The first weight loss which occurs below 150 °C for GENaOH as well as agar could be due to removal of physisorbed or occluded water. The second step of decomposition which is initial above 240 °C in both agar-agar as well as GENaOH differed in their amount of respective weight losses (GENaOH ~8%, agar- agar 63.5% could be assigned to thermal decomposition of agar polymer was agar-agar. The decomposition of remaining polymer matrix is accompanied with ~21 % weight loss. Third step in the temperature range of 440-480°C. On the other hand the additional exothermic weight loss centered at 710 °C is observed and could be assigned the decomposition of carbonates frame if any. The entrapment of NaOH in gel matrix is evidenced by the comparatively large residual weight observed in the TGA profile of GENaOH than that of agar-agar.

In order to assess the catalytic activity of GENaOH in the synthesis of tetrahydrobenzo[*b*]pyrans (**Scheme 1**), an equimolar mixture of dimedone, malanonitrile and benzaldehyde (5 mmol each) was stirred in the presence of 1 gm of GENaOH in ethanol at ambient temperature till the completion of reaction as monitored by thin layer chromatography. The reaction proceeded efficiently yielding the corresponding tetrahydrobenzo[*b*]pyran in 91% yield in just 5-15 minutes. In order to check the generality of this methodology, a series of tetrahydrobenzo[*b*]pyrans were prepared by reaction of dimedone, malanonitrile with various aryl aldehydes. We were gratified to find that with both electron-poor and electron-rich benzaldehydes, the corresponding products were obtained in excellent yields. The reaction of the sterically hindered *o*-nitrobenzaldehyde even gave higher yields highlighting the general applicability of the protocol. The striking feature of all the reactions was the isolation of products. During the course of the reaction the product precipitates out and can be isolated simply by filtration. The product obtained after sufficient washing with water was found to be practically pure. The identity of all the compounds was ascertained on the basis of IR, ¹H NMR,

¹³C NMR and mass spectroscopy data. The physical and spectroscopic data are in consistent with the proposed structures.

It has been well established that in case of the GEBCs, the reagent trapped in the gel may leach into the solvent. To study the leaching of NaOH in solvent, 1 gm GENaOH was stirred in 5 mL of ethanol at room temperature. The GENaOH was filtered and water (3 mL) was added to the filtrate. The NaOH leached out was determined by titration with 0.1 N succinic acid solution using phenolphthalein as an indicator. The study revealed that only 3.91 % NaOH leached out from gel into ethanol. Using the amount of NaOH same as that leached out, the reaction between dimedone, malanonitrile and benzaldehyde did not gave quantitative yield of the corresponding product. This clearly demonstrated that catalysis was solely due to intact GENaOH rather than leached NaOH.

A proposed mechanism for the formation of tetrahydrobenzo[*b*]pyrans using GENaOH. The mechanism suggests that in step-1 Knoevenagel condensation takes place to form the α -cynocinnamonitrile derivative. In step-2 the active methylene of dimedone react with the electrophilic C=C double of α -cynocinnamonitrile giving the intermediate 6, which tautomerizes into 7. The latter is then cyclized by nucleophilic attack of the OH group on the cyano (CN) moiety, giving intermediate 8. Finally, the expected product 4 is afforded by tautomerization (8-4).

The use of catalyst is especially interesting when it can be used several times. To investigate the possibility of catalyst recycling, the reaction of dimedone, malanonitrile with benzaldehyde using GENaOH in ethanol was carried out. After completion of the reaction, the GENaOH was recovered by simple filtration, washed with ethanol and reused in another reaction with identical substrates. The catalyst could be reused for five runs without noticeable drop in the yield of product.

Experimental

Infrared spectra were recorded on a Perkin-Elmer FTIR spectrometer. The samples were examined as KBr discs ~5% w/w. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker Avon 300 MHz spectrometer using DMSO/CDCl₃ as solvent and TMS as internal reference. Mass spectra were recorded on a Shimadzu QP2010 GCMS with an ion source temperature of 280 °C. The thermal gravimetric analysis (TGA) curves were obtained by using the instrument STA 1500 in the presence of static air at a linear heating rate of 10 °C/min from 25 ° to 1000 °C. Melting points were determined in an open capillary and are uncorrected. All chemicals were obtained from local suppliers and used without further purification.

Preparation of gel entrapped NaOH

To a boiling mixture of agar-agar (20 Mg) in water (60 mL) was added a solution of NaOH (10 gm) in water (100 mL). The resultant solution was boiled with stirring for five minutes and cooled in ice bath to yield the desired GENaOH.

General procedure for the multi-component synthesis of tetrahydrobenzo[*b*]pyrans

A mixture of dimedone (5 mmol), malanonitrile (5 mmol) and aryl aldehyde (5 mmol) was stirred in the presence of GENaOH (1 gm) in 5 mL of ethanol at ambient temperature till the completion of the reaction as monitored by TLC. The resulting crude product was filtered off, washed with water and recrystallized from ethanol to afford the desired product.

Spectral data of representative compounds

2-Amino-3-cyano-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4-phenyl-4H-benzopyra: IR (KBr): ν 3396, 3323, 3213, 2961, 2199, 1976, 1660, 1371 cm⁻¹; ¹H NMR (300 MHz, DMSO-d₆): δ 1.05 (s, 3H), 1.12 (s, 3H), 2.21 (d, 1H), 2.22

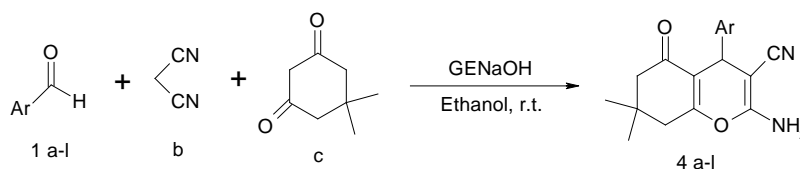
(d, 1H), 2.44 (s, 2H), 4.39 (s, 1H), 4.50 (s, 2H), 7.17-7.31 (m, 5H); ¹³C NMR (75 MHz, DMSO-d₆): 27.39, 28.92, 32.13, 35.88, 50.52, 59.03, 113.36, 120.03, 126.92, 127.50, 128.57, 144.78, 158.91, 162.73, 196.05; MS (EI): m/z = 294 (M⁺).

Conclusion

We have described a general and highly efficient procedure for the preparation of multi-component synthesis of tetrahydrobenzo[*b*]pyrans from dimedone, malanonitrile and aryl aldehydes in the presence of gel entrapped NaOH. The method offers several significant advantages, such as high conversions, easy handling, clean reaction profile, no energy consumption, high conversions, cost effective short reaction time and green methodology which make it a useful and an attractive addition to the existing methodologies.

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Scheme 1: GENaOH catalyzed multicomponent synthesis of tetrahydrobenzo[*b*]pyrans

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Review on Ferrites : Ferrite properties and its Applications

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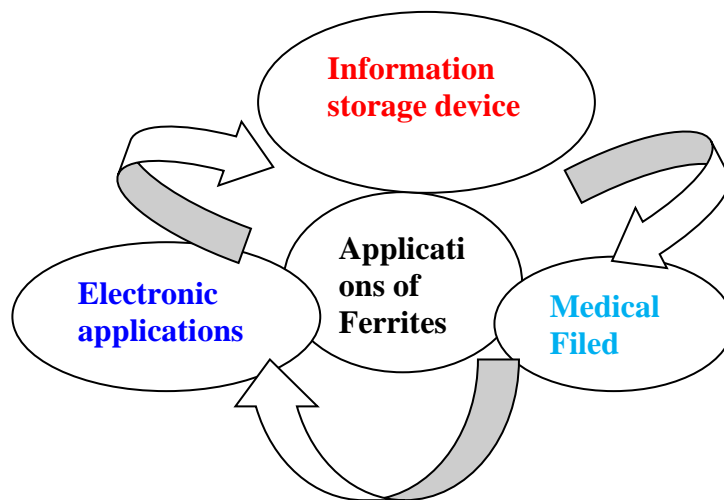
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ABSTRACT

Magnetic nanoparticles display awesome new phenomena which include superparamagnetism, excessive-field irreversibility, high saturation field, more anisotropy contributions, or shifted loops after field cooling, these phenomena rise up from finite size and ground results that dominate the magnetic behavior of character. Each ability software requires the magnetic nanoparticles to have extraordinary properties, as an example, in information storage applications, and other applications such as in electronics and medical fields

Keywords : Superparamagnetism, Excessive-Field Irreversibility, High Saturation Field, More Anisotropy Contributions, Shifted Loops, Field Cooling

Graphical Abstract:



I. INTRODUCTION

Inductive components for energy electronics are regularly exposed to symmetrical and asymmetrical square wave voltages. The usual method for predicting magnetic losses under such operating conditions is based entirely on a good generalization of the

Steinmetz equation. [1] Electrical resistivity of ferrite nanofibres enhances by reinforced soft magnetic composite and also used for applications [2] Structural and electrical properties of bismuth ferrite thin films enhances by annealing thin films with atmosphere [3] At 10 kHz, 1200 A/m, 25°C and 550 mT at 100°C saturation flux density and the power losses of a

MnZn ferrite polycrystalline material is reported [4] The properties of Mn–Zn ferrites by the doping of yttrium enhances the lattice constants and grain sizes to its maximum value and electromagnetic properties [5] The evaluation of things chargeable for the excessive–frequency shift of the complex permeability(mn) dispersion place in polymer composites of manganese–zinc(MnZn) ferrite, as well as to the growth in their thermo magnetic stability [6] As a function of frequency dielectric properties of $Mn_{0.4}Zn_{0.6}Fe_2O_4$ ferrites prepared by co-precipitation technique have been investigated [7] Inversion degree of spinels of solgel synthesized cobalt ferrites is achieved by adding excessive cations [8] co-precipitated Co–Zn and Mn–Zn ferrite particles in substituted by zinc improves structural and magnetic properties[9] Phase-pure metastable Mn-Zn ferrites were obtained as a result of low-temperature combustion synthesis from different fuels these Ferrite does not contain an extraneous non-magnetic phase (such as hematite), as evidenced by the absence of the characteristic peak for such a phase in XRD samples[10]

II. Result and Discussion

Atul Thakur et. al reported, Compressive stress due to changes in A-site and B-site Fe^{3+} ions due to grain size reduction. The migration of iron from the A-site to the B-site generates compressive stress in the nanoparticles due to the smaller distance between the B-site ions (0.292 nm) compared to the A-site ions (0.357 nm), the increased degree of inversion in nanometer ferrite may also contribute to compressive stress[11]. It can be reported by Bamzai that the material consists of several irregular cubic grains within the pure Mg ferrite and the aggregation of these grains increases with increasing Dy^{3+} ion concentration, It is also seen that it increases with further increase in Dy^{3+} [12]. It was observed that the dense particles of pure, Dy^{3+} ion-substituted were well crystallized into irregular shapes with large pores, it is

observed that the average particle size of these particles decreases with Dy^{3+} ion substitution, with the average size ranging from 1 to 4 μm , The value of magnetization increases with increasing value of applied magnetic field and saturates to a value of about 1000 Oer [12]. The atomic coordinate $x(=y=z)$ of oxygen atom is called the u parameter and the u parameter for sample L is 0.2608(2), which matches the parameter for sample H within experimental errors. If the oxygen atoms are arranged in ideal cubic close-packing and one-eighth of the tetrahedral and half of the octahedral interstices are occupied by transition metal atoms, then the u parameter is 0.25, denoted as A and B sites which affects in the projection is tilted slightly from [110] and when the u parameter exceeds 0.25, the oxygen atom moves away from the nearest A site in the [111] direction, increasing the size of the A site and decreasing the size of the B site[13].

A.V.Raut et al.reported that the value of dx increases with increasing zinc substitution and is attributed to the increase in mass overcoming the decrease in volume. H (dB less than dx) is attributed to pore formation during the synthesis process. the bulk density increases with increasing zinc substitution. This is due to the higher atomic weight of zinc (65.39 Ω) than the cobalt ion (58.93 Ω). The porosity (P%) of the zinc-substituted cobalt ferrite was estimated from the dx and dB values. it is also reported, that the (P%) decrease in within the increase in Zn substitution in is due to the increase in X-ray density of , with porosity values ranging from 22% to 19% [14].The saturation magnetization (M_s 465,628–5,316emu/g) exhibits size-dependent behavior. The presence of Zn at the octahedral site in the spinel lattice of cobalt ferrite causes spin canting, which causes the reduction of M_s . The correlation between decrease in crystal size and increase in tilt angle shows that M_s decreases by due to tilt rotation due to decrease in grain size[14]. Tulu Wegayehu Mammoa reported, that Co-ferrite materials synthesized using sol-gel auto combustion method by the substitution of manganese enhances

the structural, magnetic and electrical properties of ferrites, It was also observed that, the lattice parameters and the unit cell volume of the samples were almost reduced; and crystal size increased by and then decreased with increasing Mg content, while X-ray and apparent density decreased as Mg content increased, therefore, porosity increases with Mg concentration increases [15]. The results presented F. Ameen Ramiza et al indicate that the lattice parameter increases with increasing Mn ion content. The increase in lattice parameter can be attributed to the ionic radius of the ions. The lattice constant value of $ZnFe_2O_4$ was found to be 8.42 \AA , which is very consistent with the value obtained from the JCPDS map where $a = 8.44 \text{ \AA}$, while the lattice constant value of $MnFe_2O_4$ a was found to be 8.48 \AA [16]. The measured network parameters for all samples increased from 8.40 to 8.48 \AA . He also explained that, The X-ray density decreased linearly with the Mn concentration. The particle size of the samples was also affected by the manganese concentration. The smallest particle size ($6,198$) was obtained at $X=0.27$ when irradiated for 6 hours[16]. Radu George Ciocarlana et al. reported that, a new series of ferrite nanoparticles has been obtained, with different metals ($M_{0.25}Cu_{0.25}Mg_{0.5}Fe_2O_4$, where $M = Mn, Zn, Co, Ni$). The XRD diffraction patterns confirmed the phase purity and were used to determine the crystal size ($3-16$ nm). The activated surface of nanoparticles with OH and C-O groups was observed by FTIR spectroscopy and confirmed by XPS analysis. The magnetic properties show that the Co and Ni ferritic nanoparticles are superparamagnetic while the Zn and Mn ferrite nanoparticles are ferromagnetic[17]. Mamata Maisnam et al. explained that during the exchange, a local shift of the electrons is obtained in the direction of the applied field and this determines the polarization. At sufficiently low frequencies, since the interface polarization plays a dominant role, electrons jump to the grain boundary, and if the grain boundary resistance is high enough, the electrons accumulate at the boundary and generate a large

capacitance at high values of ϵ' at low frequencies. As the frequency increases, the superposition of electrons at the grain boundary decreases due to the reversal of the motion direction thereby reducing the polarization and thus leading to a lower value of ϵ' . In addition, ϵ' becomes very weak and almost constant beyond a certain frequency (50 kHz) indicating that in addition to this frequency of the external field, electron exchange between iron ions cannot follow the alternate field[18]. Ionic polarization and electron polarization contribute to the generation of at the very high frequency ($1012-1015$ Hz), which is beyond the scope of the present study[18]. The change of saturation magnetization as a function of Zn^{2+} ion concentration is explained by Mathur et al. The initial increase in the value of $4\pi M_s$ is attributed to the fact that at low concentrations, Zn^{2+} ions tend to flow preferentially to site A, resulting in an increased and only slight decrease in the magnetic moment of site B. magnetic field. the torque of position A, so the net magnetic torque increases. When the concentration of nonmagnetic Zn^{2+} ions exceeds $x = 0.3$, these ions also go to site B. He also reported Increasing the size of the particles results in a higher magnetic moment per unit volume. Figure 5 shows the change of Curie temperature of ferrite (both normal and hot pressed) with increasing Zn^{2+} ion concentration. The substitution of the opposite ions from Zn^{2+} leads to a change in the spin order from Yafet-Kittel (Y-K) type to Neel type. The energy required to compensate for rotational alignment in the Neel spinning order is greater than the energy required in the Y-K type spinning order, causing an increase in the Curie temperature. hot pressed ferrite has a higher Curie temperature than samples of the same composition normally prepared[19]. This is attributed to the higher density of magnetic ions in the low porosity hot-pressed samples, which requires higher energy for to compensate for spin alignment[19]. The decrease in loss and increase in permeability upon addition of cobalt could be explained by the effect of cobalt on anisotropy. The power loss, at constant frequency and

magnetic field strength, is determined by the temperature characteristic of the crystal isotropy (K_1) which governs the temperature characteristic of the magnetization at saturation[20]. K_1 represents the resistance of the energy barriers that the magnetic dipoles must overcome in order for them to leave their original orientation and align themselves in the direction of the external applied field. The anisotropy constant (K_1) depends on the crystal symmetry and interactions between ions occupying different sites of the lattice. When K_1 is small, it is easier to orient the magnetic dipoles in the favorable direction of the external magnetic field and then the magnetic permeability (μ_i) becomes higher and the power loss (P_v) decreases[20].

III. CONCLUSION

Ferrite has been researched and applied for more than years and is considered a technologies ranging from hard magnets to magnetic recordings and microwave devices. However, the advances in applications and manufacturing technologies over the past years of are impressive. Bulk ferrites remain a major group of magnetic materials, while nanostructured ferrites show impressive promise for applications in broader fields.

This examination showed that the neural network's preparation time is decreased drastically by utilizing a fuzzy rationale controller to adaptively fluctuate the learning parameters. At the point when this strategy is applied for the letter acknowledgment task, it yields a 92% exactness, which is a superior exhibition than the initially proposed approach, a Holland-style classifier. Also, this method can decrease the chance of overshooting and in some cases help the system escape a nearby least. The system's capacity to join during preparing and the last execution are reliant on the learning parameters. Our examination strengthens this reality, as our reproductions have shown that an "off-base" benefit of learning rate can prompt poor

letter acknowledgment precision. Besides, the approach is convenient, and can be practiced on other neural networks applications.

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