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Highly efficient green synthesis of the photochromic spironaphthoxazines using an eco-friendly choline hydroxide catalyst

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ABSTRACT

A greener route for the synthesis of the photochromic spironaphthoxazines employing a highly efficient, biodegradable and recyclable choline hydroxide catalyst in an aqueous medium has been described. This methodology offers diverse advantages such as mild reaction conditions, short reaction time (1 h), excellent yields (up to 91%), and operational simplicity that make it a useful and attractive option for the synthesis of the spironaphthoxazines. The choline hydroxide showed excellent catalytic performance until five recycles without significant loss of activity. The structures of synthesized spironaphthoxazines were deduced by their ¹H NMR spectra and melting points.

GRAPHICAL ABSTRACT



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KEYWORDS

Choline hydroxide; biodegradable; recyclable; spironaphthoxazines

Introduction

The spironaphthoxazine molecules are well-known to display photochromic and acidichromic properties. The spironaphthoxazines also exhibit high fatigue resistance and outstanding photo and pH stability.^[1] The reversible photochromism of these compounds is based on the interconversion between a closed spiro form, that is pale yellow or colorless, and open planar merocyanine form that is deeply colored.^[2] This phenomenon is due to the photochemical cleavage of the C(spiro)–O bond that led to the coplanarization of the two originally orthogonal heterocycles, leading to absorption at a longer wavelength owing to an extended π system in the merocyanine (MC) structure.^[3] In addition, the C(spiro)–O bond can also be broken by H⁺ to form a different type of

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Scheme 1. (a) Photo-induced and (b) proton-induced ring opening of spironaphthoxazine.

open form $(MC \cdot H)$.^[1,4] The open planar merocyanine structure returns back to the closed spiro form by spontaneous fading in the dark or upon irradiation with visible light (Scheme 1).^[5]

The spironaphthoxazines are T-type photo-switches in which the forward reaction is compelled by light and the regression happens spontaneously in the dark.^[6] The structural modification of these compounds enhances their fatigue resistance than those of spiropyrans.^[7] Spironaphthoxazines are employed in an extensive variety of applications like photochromic molecular switches,^[6,8] photo-responsive sunglasses and ophthalmic lenses,^[9] light filters, optical devices,^[2] optical memories, photo-control units for polymeric materials, in bipolar membranes and in liquid crystalline solvents.^[10]

A substantial amount of research has been undertaken for the synthesis of spironaphthoxazines. The most frequently used methods for the synthesis of spironaphthoxazine includes the application of diverse organic or inorganic bases like triethylamine,^[8,11] piperidine,^[8] NaOH,^[12] and KOH.^[6] All aforementioned hazardous bases produce spironaphthoxazines in little to reasonable yields as well as these procedures employed volatile, flammable and toxic organic solvents like ethyl alcohol, isopropyl alcohol, methyl alcohol, DMF, and DMSO. In the past few years, the growing environmental awareness in chemical research and industry led to practicing eco-friendly and sustainable techniques involving environmentally benign catalysts and evading hazardous organic solvents. Ionic liquids (ILs) are receiving extensive global attention and are being engaged widely in chemical conversions as green solvents and/or catalysts due to their exceptional properties such as solvation power, good catalytic activity, excellent recyclability, non-flammability, tunable solubility, and low volatility.^[13-16] Choline chloride (ChCl), a naturally occurring biocompatible compound belongs to the vitamin B family. It is well known commercially manufactured chicken feed additive. Choline hydroxide (ChOH) is an ionic liquid derived from Choline chloride.

ChOH has numerous advantages, viz. nontoxic, easily available, water soluble, biodegradable, reusable, strongly basic, good solvation power, inexpensive, and task-specific in various organic conversions.^[17–21]

In continuation of our endeavors in developing environmentally benign practices in organic synthesis,^[22-27] we herein present a highly efficient green synthesis of the



Scheme 2. General reaction for the synthesis of spironaphthoxazine.

| Notation | Product | Yield (%) ^a |
|----------|-----------|------------------------|
| SNO-1 | | 89 |
| SNO-2 | C N O O H | 87 |
| SNO-3 | | 83 |
| SNO-4 | | 84 |
| SNO-5 | | 91 |
| SNO-6 | | 88 |
| SNO-7 | | 87 |

Table 1. Yields of the synthesized spironaphthoxazine derivatives.

^alsolated yield.

photochromic spironaphthoxazines using an eco-friendly ChOH catalyst in an aqueous medium.

Results and discussion

A series of spironaphthoxazine derivatives (SNO-1 to SNO-7) have been synthesized using indolium iodide (1) and 1-nitroso-2-naphthol (2) in presence of choline hydrox-ide as a catalyst (Scheme 2 and Table 1).

In order to optimize the reaction conditions, a series of experiments employing varied conditions in terms of base catalyst, catalyst loading, reaction temperature and solvent for a model reaction of 1,2,3,3-Tetramethyl-3H-inol-1-ium iodide and 5-nitro-1-nitroso-2-naphthol were explored in detail as illustrated in Tables 2 and 3.

To ascertain the effect of the catalyst, the model reaction was first performed in water without any catalyst, which lead to no reaction progress, even after 24 h at $80 \degree C$ (Table 2, entry 1). After that, we tried the model reaction in the presence of different

| Entry | Catalyst | (mol%) | Reaction time (h) | Isolated yield (%) |
|-------|--|--------|-------------------|--------------------|
| 1 | Without catalyst | - | 24 | No reaction |
| 2 | КОН | 10 | 3 | 69 |
| 3 | NaOH | 10 | 3 | 67 |
| 4 | (CH ₃) ₄ N ⁺ OH ⁻ | 10 | 3.5 | 59 |
| 5 | Cs_2CO_3 | 10 | 3.5 | 63 |
| 6 | K ₂ CO ₃ | 10 | 3.5 | 58 |
| 7 | Na ₂ CO ₃ | 10 | 3.5 | 55 |
| 8 | DABCO | 10 | 6 | 59 |
| 9 | DBU | 10 | 6 | 52 |
| 10 | Piperidine | 10 | 4 | 55 |
| 11 | Et ₃ N | 10 | 4 | 53 |
| 12 | Pyridine | 10 | 5 | 45 |
| 13 | ChOH | 04 | 3 | 51 |
| 14 | ChOH | 06 | 2 | 67 |
| 15 | ChOH | 08 | 1.5 | 81 |
| 16 | ChOH | 10 | 1 | 91 |
| 17 | ChOH | 12 | 1 | 91 |

| Table 2. | Effect o | of various | bases on | the sy | ynthesis | of s | pirona | phthoxazine. |
|----------|----------|------------|----------|--------|----------|------|--------|--------------|
|----------|----------|------------|----------|--------|----------|------|--------|--------------|

Reaction conditions: Reaction of 1,2,3,3-tetramethyl-3H-indol-1-ium iodide (1 mmol) and 5-nitro-1-nitroso-2-naphthol (1 mmol), catalyst and water (3 mL) at 80°C.

Bold values indicates the finalized reaction conditions i.e. optimized conditions which gave best results.

organic bases (viz. tetramethylammonium hydroxide, 1,4-diazabicyclo[2.2.2]octane (DABCO), 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU), piperidine, triethylamine, pyridine) and inorganic bases (viz. KOH, NaOH, Cs₂CO₃, K₂CO₃, Na₂CO₃). The listed bases gave the desired product yields maximum up to 69% (Table 2, entry 2 to 12). In literature, a stoichiometric amount of these bases are used at high temperature. Further, they required longer reaction times and are non-recyclable. In order to overcome aforesaid difficulties, we turned our consideration toward recyclable ionic liquids. To our delight, ChOH as a catalyst gave the desired product with excellent yield of 91% within a short time (Table 2, entry 16). An excellent yield of the product was accomplished with choline hydroxide catalyst since it performs as a homogeneous catalyst in an aqueous medium which helps to increase the solubility of the reactants via hydrogen bonding and consequently increases the speed of the reaction. To decide the optimum catalyst loading, the model reaction was performed with varied mol % of ChOH at 80 °C (Table 2, entries 13–17). The reaction happened efficiently with 10 mol % of ChOH giving a single product in 91% yield (Table 2, entry 16). Increasing the quantity of ChOH further, displayed no significant enhancement in the yield or reaction rate.

Different solvents were screened for the model reaction, wherein reaction performance was found well in an aqueous medium (Table 3, entry 11). Later on the model reaction was carried at various temperatures ranging from 50 to 90 °C (Table 3, entries 8–12) and 80 °C was found to be the optimum temperature. Eventually, the optimized parameters for the model reaction are 1,2,3,3-Tetramethyl-3H-indol-1-ium iodide (1.0 mmol), 5-nitro-1-nitroso-2-naphthol (1.0 mmol) and ChOH (10 mol %) at 80 °C for 1 h in an aqueous medium.

Recyclability studies

In order to determine the industrial applicability of this procedure, the reaction of 1,2,3,3-Tetramethyl-3H-indol-1-ium iodide and 5-nitro-1-nitroso-2-naphthol catalyzed

| Entry | Solvent | Temperature (°C) | Reaction time (h) | lsolated yield (%) |
|-------|--------------------|---------------------|----------------------|-----------------------|
| 1 | Methanol | 65 | 4 | 64 |
| 2 | Ethanol | 79 | 4 | 61 |
| 3 | 1,2-dichloroethane | 84 | 5 | 43 |
| 4 | Dichloromethane | 40 | 5 | 35 |
| 5 | Chloroform | 61 | 5 | 33 |
| 6 | Tetrahydrofuran | 66 | 5 | 41 |
| 7 | toluene | 111 | 6 | 30 |
| 8 | Water | 50 | 4 | 37 |
| 9 | Water | 60 | 3 | 49 |
| 10 | Water | 70 | 2 | 61 |
| 11 | Water | 80 | 1 | 91 |
| 12 | Water | 90 | 1 | 91 |

Table 3. Influence of solvent and temperature on model reaction^a.

^aReaction conditions: Reaction of 1,2,3,3-tetramethyl-3H-inol-1-ium iodide (1 mmol), 5-nitro-1-nitroso-2-naphthol (1 mmol), ChOH (10 mol %) and solvent (3 mL).

Bold values indicates the finalized reaction conditions i.e. optimized conditions which gave best results.





by choline hydroxide was carried out on a larger scale (100 mmol) for the duration of 1 h. To our pleasure, the results were reproducible to that of a small scale (1 mmol) and 91% yield of the product was achieved. The recovery and reuse of a catalyst are highly desirable for a greener method. Thus, the recyclability of ChOH was investigated by using the above model reaction. After the accomplishment of the reaction (checked by TLC), the product was obtained by filtration. The catalyst in the form of filtrate reused in the next run without additional purification. In a test of five cycles, the catalyst could be reused without any significant loss of catalytic activity (Fig. 1).

FT-IR analysis

FT-IR is a great tool for determining forms of chemical bonds in a molecule by creating an infrared absorption spectrum resembling a molecular "fingerprint". For every chemical bond, there is a specific value of the wavelength of light absorbed (Fig. 2). With the aid of FT-IR spectroscopy, the fresh and recycled (after a 5th run) ChOH have been investigated. The relative study of the fresh and recycled ChOH demonstrates that there is no substantial alteration witnessed in the IR spectra of choline hydroxide. The protuberance at 3311 cm^{-1} is typical of O–H stretching vibration. The aliphatic C-H stretching vibration detected at 2957 cm^{-1} . The methyl deformation was witnessed at



Figure 2. FT-IR spectra of fresh and recycled ChOH.



Scheme 3. Proposed mechanism for formation of spironaphthoxazine catalyzed by ChOH.



Scheme 4. Synthesis of choline hydroxide (ChOH).

1477 cm⁻¹. The peak near 1359 cm^{-1} matches to stretching vibration of the C–N bond. The band at 1077 cm^{-1} agrees to C–O stretch in a primary alcoholic group. The C-H deformation of $-\text{CH}_{2-}$ group was detected around 951 and 881 cm⁻¹.

Based on the present investigational observations and literature reports,^[17,28] a possible mechanism for the reaction between 1,2,3,3-tetramethyl-3H-indol-1-ium iodide (i) and 1-nitroso-2-naphthol (iii) in presence of ChOH is shown in Scheme 3. The reaction began with the generation of 1,3,3-trimethyl-2-methyleneindolenine intermediate (ii) by deprotonation of (i) using choline hydroxide. An intermediate (v) was formed by an intermolecular cyclization of (ii) and (iii) catalyzed by ChOH. Finally, the catalyst will help an intermediate (v) to go through dehydration to yield spironaphthoxazine derivative. The significance of the alcoholic –OH group of choline hydroxide, we consider that it will form hydrogen bonding with nitroso group of 1-nitroso-2-naphthol (iii). This makes the nitroso group further electrophilic and prone to the nucleophilic attack by (ii).

Conclusion

In summary, a simple, time saving, efficient, economic and ecofriendly protocol for the synthesis of photochromic and thermochromic spironaphthoxazine was developed. This report first time claims the application of choline hydroxide for the synthesis of spironaphthoxazine derivatives. The catalyst shows good catalytic activity for the synthesis of spironaphthoxazine derivatives at mild reaction conditions. The catalyst could be reused for four consecutive cycles.

Experimental section

Materials and methods

All the required chemicals were purchased from s d Fine-Chem Limited and utilized without additional purification. The advancement of all reactions was checked by aluminum TLC plate, silica gel coated with fluorescent indicator F254 (Merck) identifying the spots with the help of UV light as a visualizing agent. ¹H NMR spectra were obtained on a 500 MHz instrument (Agilent NMR spectrometer) and 400 MHz (Bruker Ultrashield Plus NMR spectrometer) in CDCl₃ or DMSO-d₆ solvent at ambient temperature. We have mentioned the chemical shifts values on δ scale (ppm) relative to an internal standard tetramethylsilane [Si(CH₃)₄=0.00 ppm]. Infrared spectra were obtained with a JASCO-FT/IR 4100 LE ATR PRO450-S spectrometer. All the synthesized derivatives were analyzed by ¹H NMR spectra

and melting points. Melting points were recorded on standard melting point instrument bought from Sunder Industrial Product, Mumbai and are uncorrected.

General method for the preparation of choline hydroxide (ChOH)

The Choline hydroxide was prepared as per the literature.^[17] The solution of choline chloride (10 mmol), KOH (10 mmol) and methyl alcohol (15 mL) was heated at 60 °C for 12 h using continuous stirring. Solution was then cooled to rt and filtered later on to remove precipitated KCl. Eventually, the filtrate was concentrated by means of vacuum to get rid of methyl alcohol. The residue obtained was utilized without additional purification (Scheme 4).

General method for the synthesis of spironaphthoxazines

A mixture of indolium iodide 1 (1.0 mmol) and choline hydroxide (10 mol %) in water (3 mL) was stirred at 80 °C for 20 min. Then 1-nitroso-2-naphthol 2 (1.0 mmol) was added and the resulting mixture stirred at 80 °C for another 40 min. Then reaction mass was cooled to rt. The solid product was then filtered and washed with water. The synthesized product was finally purified using column chromatography technique (silica gel 100–200 mesh size) with ethyl acetate:hexane (05:95) as an eluent to give the desired spironaphthoxazine (Scheme 2 and Table 1).

Characterization data for selected spironaphthoxazine

SNO-1: 1,1,3-trimethyl-1,3-dihydrospiro[benzo[e]indole-2,3'-naphtho[2,1-b][1,4]oxazine]

Yield: 89%; Colorless solid; mp 123-124 °C. Reported mp 125 °C.

¹H NMR (500 MHz, DMSO-d₆) δ 8.499 (1H, d, J = 8.5 Hz, C10′–H), 7.968 (1H, s, C2′–H), 7.912 (1H, d, J = 8.6 Hz, C7′–H), 7.870–7.825 (3H, m, C6′–H, C8′–H, & C9′–H), 7.590 (1H, t, J = 8.3 Hz, C6–H), 7.418 (2 H, m, C4 & C5′–H), 7.243 (1H, t, J = 8.0 Hz, C5–H), 7.075 (1 H, d, J = 8.5 Hz, C7–H), 2.778 (3H, s, N–CH₃), 1.594 (3H, s, C1–CH₃), 1.472 (3H, s, C1–CH₃).

Full experimental details and data pertaining to the characterization of the compounds SNO-1 to SNO-7 using ¹H NMR and melting points are given in the Supplementary information.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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