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SYNTHESIS OF IONIC LIQUID CRYSTAL MATERIALS OF 3,4-DIHYDRO-3-PYRIDYL-2*H*-NAPHTHO [2,1-*e*] [1,3] OXAZINE DERIVATIVES

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ABSTRACT

Several 3,4-dihydro-3-pyridyl-2*H*-naphtho[2,1-*e*][1,3]oxazine derivatives were synthesized from 1-naphthol, various pyridines and formalin solution at room temperature. The six-membered oxazine skeleton was constructed via 1-benzyl-3-methyl imidazolium hydrogen sulphate [bnmim] [HSO_4] promoted Mannich type reaction.

Key words: 1,3-Oxazines, Ionic liquid, Mannich type reaction.

INTRODUCTION

The design of novel thermotropic liquid crystals as advanced functional materials involves selection of a suitable core fragment, linking group, and terminal functionality. However, anisometric rod-like or disk-like molecules used to be a fundamental prerequisite for conventional thermotropic liquid crystal formation, because steric packing considerations play an important role in this interesting state of soft matter.[1-5] Over many years, a large number of liquid crystalline compounds containing heterocyclic compounds have been synthesized.[6-8] This research field has grown even more in recent years, because of improvements in synthetic methodologies. Heterocycles are of great importance as core units in thermotropic liquid crystals owing to their ability to impart lateral and/or longitudinal dipoles combined with changes in the molecular shape.[9,10]

Multicomponent reactions (MCRs), defined as one pot reactions in which at least three functional groups join through covalent bonds, have been steadily gaining importance

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in synthetic organic chemistry.[11-14] Ionic liquids (ILs) have aroused considerable interest over the past decade due to their wide variety of properties. They can be used as solvents and reaction supports.[15-18] Various reactions have been reported recently using ionic liquid as a catalyst and reaction media.[19,20] The Mannich reaction has been widely used[21-23] to introduce oxazines. The 1,3-oxazine nucleus features prominently in many biologically important natural products and other bioactive molecules.[24-27] Naphthoxazine derivatives have exhibited therapeutic potential for the treatment of Parkinson's disease.[28,29]

Several methods for the preparation of 1,3-oxazine derivatives have previously been reported.[30-32] Few have been focused on the multicomponent reaction method. The present method is beneficial over previous reports due to its solvent-free condition. Our interest is to develop better protocols for the synthesis of biologically active heterocyclic molecules. We report have the synthesis of a series of 3,4-dihydro-3-pyridyl-2*H*-naphtho[2,1-*e*][1,3]oxazine derivatives using 1-naphthol, formalin and pyridine as substrates.

EXPERIMENTAL

The IR spectra were recorded on Bruker-IFS-66 FTIR instrument. NMR spectra were recorded on Varian Gemini 200 MHz instrument using tetramethylsilane as an internal standard in DMSO-d_6. Chemical shifts are expressed in ppm. The purity of the compounds was checked by TLC and spots were visualized in iodine vapour.

General procedure for the synthesis of compounds (4a-g)

A mixture of formalin (2.0 mmol), aromatic pyridine (1.0 mmol), 1-naphthol (1.0 mmol) and [bnmim] [HSO_4] (40 mol %) was stirred at room temperature. The reaction was monitored by TLC. After completion of reaction, reaction mixture was extracted with methylene dichloride (3 × 50 mL) and the insoluble ionic liquid [bnmim] [HSO_4] was directly recycled in subsequent runs. The organic layer was washed with water (2 × 10 mL); followed by brine (2 × 20 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The obtained product was purified by column chromatography on silica gel by hexane : ethyl acetate as eluent.

3,4-Dihydro-3-(pyridin-4-yl)-2H-naphtho[2,1-e][1,3]oxazine **(4a)**: IR: 1050 (C-O-C), 1198 (C-O-C); MS: m/z 263 (m + 1);

3,4-Dihydro-3-(pyridin-3-yl)-2H-naphtho[2,1-e][1,3]oxazine **(4b)**: MS: m/z 263 (m + 1);

3,4-Dihydro-3-(pyridin-2-yl)-2H-naphtho [2,1-e] [1,3] oxazine **(4c)**. MS : m/z 263 (m + 1);

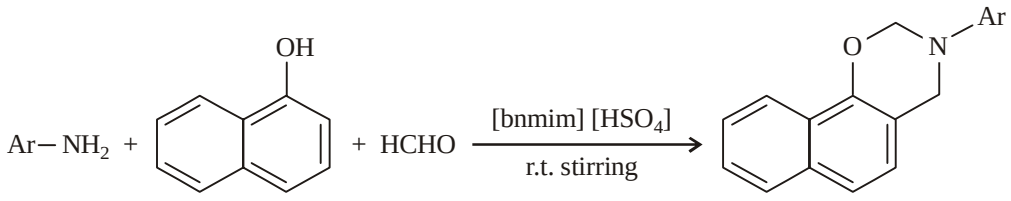
3,4-Dihydro-3-(6-methylpyridin-2-yl)-2H-naphtho[2,1-e][1,3]oxazine **(4d)**. MS: m/z 277 (m + 1);

3,4-Dihydro-3-(5-methylpyridin-2-yl)-2H-naphtho[2,1-e][1,3]oxazine **(4e)**. MS: m/z 277 (m + 1);

3,4-Dihydro-3-(4-methylpyridin-2-yl)-2H-naphtho[2,1-e][1,3]oxazine **(4f)**. MS: m/z 277 (m + 1);

3-(5-Chloropyridin-2-yl)-3,4-dihydro-2H-naphtho[2,1-e][1,3]oxazine **(4g)**. MS: m/z 298 (m + 1);

Scheme 1



(1a-g) **(2)** **(3)** **(4a-g)**

Ar = 4-Pyridyl, 3-Pyridyl, 2-Pyridyl, 2-(6-Methylpyridyl), 2-(5-Methylpyridyl), 2-(4-Methylpyridyl) and 2-(5-Chloropyridyl)

Table 1

Compound	Ar	Yield (%)	M. P. (°C)
4a	4-Pyridyl	63	68
4b	3-Pyridyl	75	72
4c	2-Pyridyl	74	76
4d	2-(6-Methylpyridyl)	72	80
4e	2-(5-Methylpyridyl)	68	86
4f	2-(4-Methylpyridyl)	69	88
4g	2-(5-Chloropyridyl)	76	91

Table 2: Spectral data of the compounds (4a-g)

Compd.	^{1}H NMR (DMSO-d_6, ppm)
4a	4.79 (s, 2H, -Ar-CH_2-N-), 5.43 (s, 2H,-O-CH_2-N-), 6.85-7.58 (m.9H), 8.42 (d, 1H);
4b	4.78 (s, 2H, -Ar-CH_2-N-), 5.42 (s,2H,-O-CH_2-N-) 6.84-7.56 (m, 8H), 8.40 (m, 2H);
4c	4.78 (s, 2H, -Ar-CH_2-N-), 5.41 (s, 2H,-O-CH_2-N-), 6.85-7.57 (m, 9H), 8.41(d, 1H);
4d	2.42 (s, 3H), 4.79 (s, 2H, -Ar- CH_2-N-), 5.42 (s, 2H,-O-CH_2-N-), 6.86-7.58 (m, 9H);
4e	2.39 (s, 3H), 4.77 (s, 2H, -Ar- CH_2-N-), 5.41 (s, 2H, -O-CH_2-N-), 6.85-7.58 (m, 8H), 8.40 (d, 1H);
4f	2.38 (s, 3H), 4.78 (s, 2H, -Ar- CH_2-N-), 5.42 (s, 2H,-O-VCH_2-N-), 6.86-7.59 (m, 8H), 8.41 (d, 1H);
4g	4.78 (s, 2H, -Ar- CH_2-N-), 5.42 (s, 2H,-O-CH_2-N-), 6.85-7.58 (m, 8H), 8.40 (d, 1H);

S, singlet; d, doublet ; dd, doublet of doublets; m, multiplet

RESULTS AND DISCUSSION

The synthesis of 3,4-dihydro-3-pyridyl-2*H*-naphtho[2,1-*e*] [1,3]oxazine derivatives promoted by ionic liquid as a catalyst has been reported **(Scheme 1)**. The reaction of pyridine (1 mmol), 1-naphthol (1 mmol) and formalin (2 mmol) at room temperature under stirring condition has been considered as the model reaction.

CONCLUSION

In conclusion, [bnmim] [HSO_4] used as a catalyst can readily be recycled. It can be used repeatedly for several times without appreciable loss in activity. Thia method is advantageous due to high conversion, short reaction time, clean reaction profile, simple experimental and workup procedures for the synthesis of **(4a-g)**.

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