Green Chemistry

Accepted Manuscript

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/greenchem

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Synthesis of 2-phenylnaphthalenes from styrene oxides using recyclable bronsted acidic $[HNMP]^+HSO_4^-$ ionic liquid

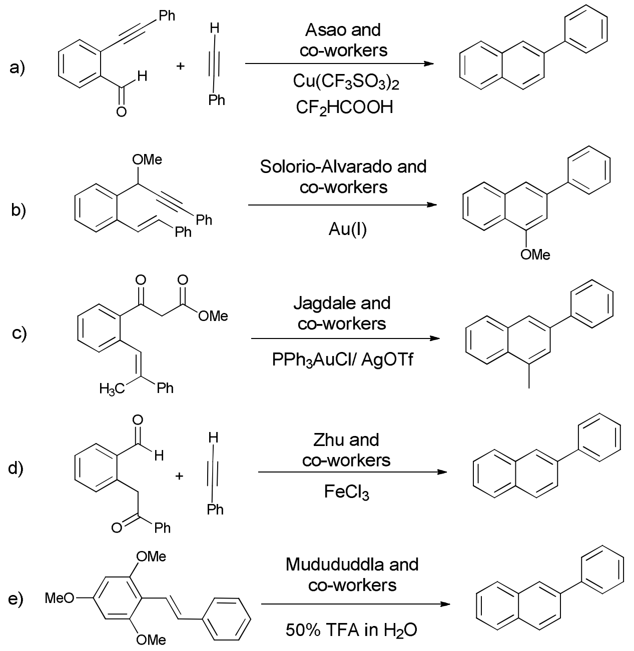
Kishor V. Wagh and Bhalchandra M. Bhanage*

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

This work reports novel and efficient protocol for the synthesis of 2-phenylnaphthalenes from styrene oxides using recylable ionic liquid. The ionic liquid *N*-methyl-2-pyrrolidone hydrogensulfate $[HNMP]^+HSO_4^-$ played a dual role of catalyst and solvent. It efficiently constructs 2-phenylnaphthalene and its derivatives in excellent yields with much simplicity in the operation. Present protocol has higher atom effeciency and wider substrate applicability. The $[HNMP]^+HSO_4^-$ has been effectively recycled up to five consecutive cycles without appreciable loss in its activity.

The naphthalene moiety is core structure of numerous organic compounds which exhibit diverse applications in medicinal and material chemistry.[1] For example, rifampicin/ rifamycin and gossypol are well known natural products having good biological activities. Moreover, naphthalene structural system also serve as key building block in many chemical and pharmaceutical industries.[2] Consequently, different strategies have been discribed for their regioselective synthesis in last few years. These strategies mainly involves Diels-Alder cycloaddition,[3] benzannulation,[4] and conjugate addition reactions.[5] Especially, the synthesis of 2-phenylnaphthalenes have gain significant attention because it display potent estrogen receptor (ER-b) agonistic activities.[6] Subsequently, a few indirect methods for the synthesis of 2-phenylnaphthalenes have also been reported including cross-coupling of functionalized starting materials like aryl halides,[7] aryl boron compounds,[8] and aryl Grignard reagents[9] with existing naphthalene core structures. Nevertheless, these protocols require functionalized naphthalene core as a prior precursor for their synthesis. Even though, there are some protocols reported for the direct synthesis of 2-phenylnaphthalenes from other starting precursors (Scheme 1).[10] Asao and co-workers reported the Lewis acid-catalyzed [4+2] benzannulation of *o*-alkynylbenzaldehydes and alkynes.[10a] Solorio-Alvarado and Echavarren demonstrated the cyclization of 1-(1-methoxy-3-phenylprop-2-yn-1-yl)-2-alkenylbenzenes in the presence of gold(I) as a catalyst.[10b] Jagdale and co-workers synthesized a naphthalenes using $Ph_3PAuCl/AgOTf$ (1:1) as a catalyst in DCE for the cyclization reaction of alkenyl *β*-keto esters.[10c] Zhu and co-workers reported the $FeCl_3$ catalyst for benzannulation of 2-alkylbenzaldehydes with alkynes.[10d] In 2014, Mudududdla and co-workers developed a method for preparation of the 2-phenylnaphthalenes using green solvent (water) and cheap catalyst.[10e] Although, these protocols were efficient for synthesis of substituted napthalenes, they requires use of expensive starting materials, organic solvents, transition metals, additives, either multiple steps. Hence, the development of simple and highly efficient solvent free protocol for the synthesis of 2-phenylnaphthalenes is still needed.

In current era, ionic liquids (ILs) have attracted considerable interest in the context of green media for synthesis.[11] The utilization of ILs as catalyst as well as solvent for numerious reactions has been reported.[12] ILs possess various attractive physicochemical properties such as low vapor pressure, non-volatility, non-flammability and thermal stability over a wide temperature range.[13] and make the possibility of enhancing the

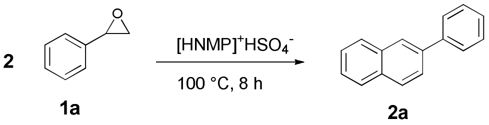


Scheme 1 Methods for preparation of 2-phenylnaphthalenes.

Department of Chemistry, Institute of Chemical Technology (Autonomous), Matunga, Mumbai- 400 019, India
** Corresponding author. Tel.: + 91- 22 3361 2601; Fax: +91- 22 3361 1020.*
E-mail address: bhalchandra_bhanage@yahoo.com, bm.bhanage@ictmumbai.edu.in (B. M. Bhanage).

† Electronic Supplementary Information (ESI) available: Characterization data of selected products. See DOI: 10.1039/b000000x/

reaction activity with selectivity.[14] Here, we have developed a novel, highly efficient, solvent free protocol as a supplement for the synthesise of 2-phenylnaphthalenes from styrene oxides by using a recyclable bronsted acidic $[HNMP]^+HSO_4^-$ ionic liquid as a catalyst as well as solvent (Scheme 2).



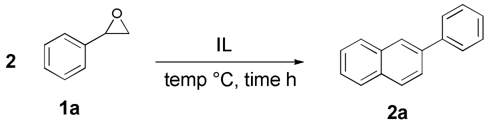
Scheme 2 Synthesis of 2-phenylnaphthalene.

Results and discussion

Initially, we have chosen the reaction of styrene oxide (**1a**) in ionic liquid which led to the formation of 2-phenylnaphthalene (**2a**) as a model reaction to optimise the various reaction parameters. The different reaction conditions such as catalyst study, solvent study, catalyst loading, reaction time and temperature were investigated for the model reaction (Table 1). In the beginning, various acidic catalysts such as montmorillonite K-10, *p*-toluene sulfonic acid, H_2SO_4, $Cu(OTf)_2$, $-SO_3H$ functionalized ionic liquid, $[HNMP]^+HSO_4^-$ and $[HMIM]^+HSO_4^-$ were screened (Table 1, entries 1-7), It was observed that among screened acid catalysts, $[HNMP]^+HSO_4^-$ was the most effective catalyst by providing desired product **2a** in 41% yield (Table 1, entry 6). Subsequently, when the reaction was carried out without catalyst, formation of **2a** was not observed (Table 1, entry 8). Next, we examined the effect of solvents for the synthesis of **2a** from **1a** (Table 1, entries 9-13). It was observed that among the solvent studied, DCE was found to be effective solvent providing **2a** in 50% yield (Table 1, entry 13). However, when the reaction was performed under solvent free condition, it provided **2a** in 61% yield (Table 1, entry 14). Hence, further studies were carried out using $[HNMP]^+HSO_4^-$ in absence of solvent. Furthermore, the effect of catalyst loading was also examined on the reaction yield. It was found that yield of **2a** was increases with increasing the catalyst loading from 2 mmol to 4 mmol (Table 1, entries 15-16). Whereas, on further increase in catalyst loading no siganificant increase in the yield of **2a** was observed. Subsequently, the effect of reaction time and temperature were also studied for the synthesis of **2a**, it was observed that 8 h was the minimum time required for the completion of reaction (Table 1, entries 19-20). During temperature study, it was observed that maximum yield of **2a** obtained at 100 °C (Table 1, entries 21-22). Whereas, on further decrease in temperature decrease in the yield of **2a** was observed. Hence, the optimized reaction condition for the synthesis of **2a** : **1a** (1 mmol), $[HNMP]^+HSO_4^-$ IL (4 mmol), 100 °C, 8 h.

Then the substrate scope for developed protocol was explored for the varity of substituted styrene oxide derivatives to furnish corresponding 2-phenylnaphthalene derivatives using optimized reaction conditions of model reaction (Table 2). The reaction of **1a** in ionic liquid $[HNMP]^+HSO_4^-$ provided the desired product **2a** in 80 % yield (Table 2, entry 1). It was found that the reaction of *p*-F, *p*-Cl, *m*-Cl, *p*-Br and *m*-Br substiuents on **1a** also provided the corresponding products **2b-2f** in good to excellent yields (Table 2, entries 2-6). Furthermore, the reaction of **1a** bearing electron donating substituents such as $–CH_3$, $-C(CH_3)_3$ also furnished the desired products **2g-2i** in excellent yields (Table 2, entries 7-9). However, the reaction of **1a** bearing *o*-halo substitutents provided the desired products **2j-2k** in low yields might be due to the steric effect (Table 2, entries 10 and 11).

Table 1 Optimisation for synthesis of 2-phenylnaphthalene[a]

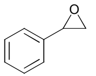
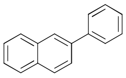
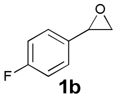
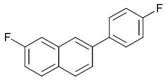
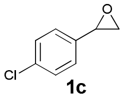
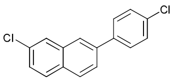
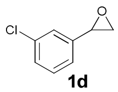
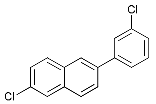
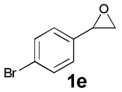
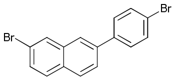
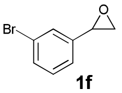
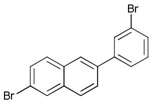
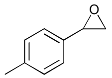
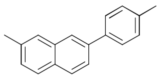
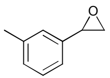
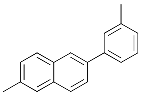
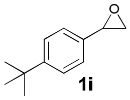
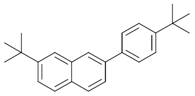
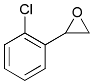
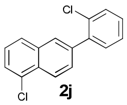
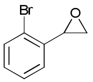
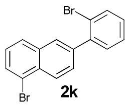


Entry	Catalyst	Solvent	*t* (h)	Temp (°C)	Conv. (%)[b]	Yield (%)[b]
Effect of catalyst						
1[c]	mont. k-10	toluene	12	110	32	25
2[d]	p-TSA	toluene	12	110	26	20
3[d]	H_2SO_4	toluene	12	110	08	Trace
4[d]	$Cu(OTf)_2$	toluene	12	110	00	N.D.
5	$-SO_3H$ functionalized IL	toluene	12	110	37	30
6	$[HNMP]^+HSO_4^-$	toluene	12	110	50	41
7	$[HMIM]^+HSO_4^-$	toluene	12	110	41	34
8	-	toluene	12	110	00	N.D.
Effect of solvent						
9	$[HNMP]^+HSO_4^-$	dioxane	12	110	44	38
10	$[HNMP]^+HSO_4^-$	cylohexane	12	110	35	28
11	$[HNMP]^+HSO_4^-$	CH_3CN	12	110	09	Trace
12	$[HNMP]^+HSO_4^-$	$CHCl_3$	12	110	51	43
13	$[HNMP]^+HSO_4^-$	DCE	12	110	59	50
14	$[HNMP]^+HSO_4^-$	-	12	110	71	61
Effect of catalyst loading						
15[e]	$[HNMP]^+HSO_4^-$	-	12	110	80	71
16[f]	$[HNMP]^+HSO_4^-$	-	12	110	90	82
Effect of time						
19[f]	$[HNMP]^+HSO_4^-$	-	8	110	90	82
20[f]	$[HNMP]^+HSO_4^-$	-	6	110	77	69
Effect of temperature						
21[f]	$[HNMP]^+HSO_4^-$	-	8	100	90	82
22[f]	$[HNMP]^+HSO_4^-$	-	8	90	78	70

[a] Reaction conditions: **1a** (1 mmol), catalyst (2 mmol), solvent (2 mL). [b] GC Conversion and Yield. [c] Catalyst (0.75 g). [d] 10 mol%. [e] Catalyst (3 mmol). [f] Catalyst (4 mmol). N.D. (not detected).

To further explore the practicability and commercial applications of the developed protocol. Here, we have examined the recovery and reusability of the present catalytic system for five times with model reaction (Fig 1). It was observed that catalyst was effective for the recyclability without much loss in its activity and the decrease in yield is might be due to handling loss during work up. For this we have also carried out the recovery wt.% of ionic liquid after each cycle and decrease in wt.% from 100% to 83% was observed (Fig. 1). As some of the reactions are ineffective on scale up, so we have carried out the model reaction on 3.0 mmol scale and it was found that catalyst was also effective on scale up for fresh and consecutive cycles (79%, 78%, 77%, 76%, 75% and 74%).

Table 2 Synthesis of 2-phenylnaphthalene derivatives^a

Entry	Styrene oxide	Product	Conv. (%)	Yield (%)^b
1	 **1a**	 **2a**	90	80
2	 **1b**	 **2b**	90	80
3	 **1c**	 **2c**	87	76
4	 **1d**	 **2d**	86	73
5	 **1e**	 **2e**	83	71
6	 **1f**	 **2f**	83	72
7	 **1g**	 **2g**	88	78
8	 **1h**	 **2h**	89	78
9	 **1i**	 **2i**	90	79
10	 **1j**	 **2j**	32	28^c
11	 **1k**	 **2k**	29	23^c

^{a} Reaction conditions: styrene oxide (1 mmol), $[HNMP]^+HSO_4^-$ (4 mmol), 100°C, 8 h. ^{b} Isolated yield. ^{c} GC Yield.

Here, we proposed a tentative mechanism for the present protocol[16,10e] (Scheme 3). The origin of catalytic activity in $[HNMP]^+HSO_4^-$ IL basically ascribed to bronsted acidic sites, which coordinates with oxygen atom of styrene oxide leading to the formation of **A**. Subsequently, the **A** opens to form **B** which on further rearrngement forms **C**. The **C** can isomerised into **D**. So, to investigate the reaction mechanism some control experiments have also been carried out. We have carried out the reaction of 1-phenyl acetaldehyde (**D**) and acetophenone (**H**) separately under the optimized reaction condition (Scheme 4). It was found that

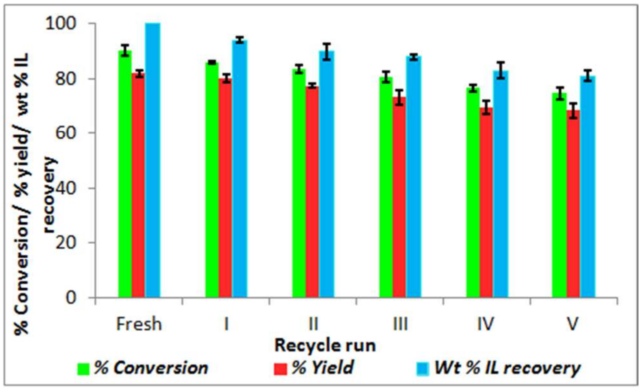
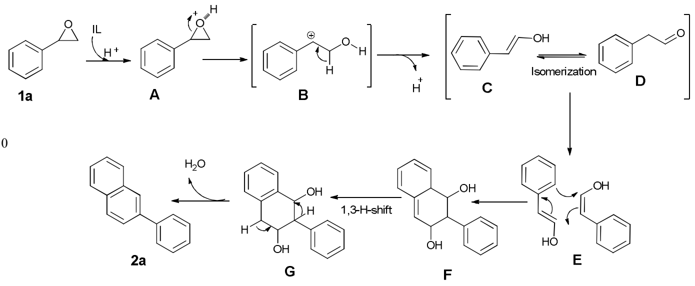
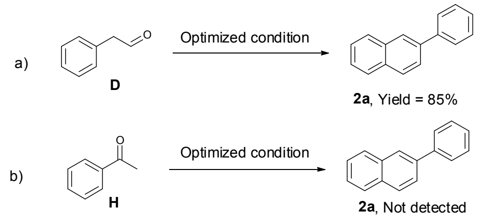


Fig 1 Catalyst recyclability study for model reaction. Reaction conditions: **1a** (1mmol), $[HNMP]^+HSO_4^-$ (4 mmol), 100 °C, 8 h. GC yield.

only **D** provided corresponding product **2a** in 85% yield, whereas **H** does not work which shows that the reaction may be proceeding through the ring opening of **1a** and isomerising into **D** during the course of reaction. Next, the **E** undergoes Diels-Alder reaction to form corresponding intermediate **F**. Subsequently, the intermediate **F** quickly rearranges through a 1,3-H-shift to **G**. Finally, the intermediate **G** undrgoes dehydration easily in the presence of $[HNMP]^+HSO_4^-$ catalyst furnishing the respective desire product **2a**.



Scheme 3 Plausible mechanism for synthesis of 2-phenylnaphthalenes from styrene oxides.



Scheme 4 Control experiments.

Conclusion

In summary, we have developed a simple, highly efficient and environmentally benign methodology for for the synthesis of 2-phenylnaphthalenes from styrene oxides by using $[HNMP]^+HSO_4^-$ ionic liquid. This is the first metal free, solvent free, additive free protocol for the synthesis of substituted napthalene derivatives with water as a green side product. The present protocol has good substrate scope with excellent yields as well as high selectivety and effectively recyled upto five consecutive cycles without any significant loss in its catalytic activity.

Experimental Section

All chemicals and reagents were purchased from firms of repute with their highest purity available and were used without further purification. For this study, ionic liquids were synthesized according to the procedures reported in the literature.[15] GC equipped flame ionization detector with a capillary column (Elite-1, 30 m × 0.32 mm × 0.25 µm) was carried out for gas chromatography analysis. GC-MS-QP 2010 instrument (Rtx-17, 30 m × 25 mm ID, film thickness 0.25 µm df) (column flow 2 mLmin^{-1}, 80 °C to 240 °C at 10°/min rise). Products were purified by flash chromatography on 60-120 mesh silica gels, SiO_2. ^1H and ^{13}C NMR spectra were recorded at 500 and 100 MHz in $CDCl_3$ as the solvent and TMS as an internal standard.

Procedure for synthesis of *N*-methyl-2-pyrrolidone hydrogen sulfate $[HNMP]^+HSO_4^-$ ionic liquid:

In a 250 mL round bottom flask with magnetic stirrer placed a 1-methyl-2-pyrrolidone (5 mol). Next, equimolar amount of concentrated sulphuric acid (98 wt%) was added drop wise slowly into the flask at room temperature and heated at 80 °C for 12 h. The mixture was then extensively washed with ether (3 × 10 mL) to remove unreacted residue and dried under vacuum by a rotary evaporator to get the viscous clear ionic liquid.

A typical experimental procedure for the synthesis of 2-phenylnaphthalenes from styrene oxides:

A mixture of **1a** (1 mmol), and $[HNMP]^+HSO_4^-$ (4 mmol) was stirred at 100 °C in a sealed 10 mL tube for 8 h. The progress of the reaction was monitored by gas chromatography. After the completion of reaction, it was cooled to room temperature. The reaction mixture was extracted with diethyl ether (3 × 8 mL) and the combined organic layers was washed with water (10 mL). The organic layer was dried over annhydrous Na_2SO_4 and evaporated under the reduced pressure to furnish the crude product. It was purified by column chromatography (silica gel, 60-120 mesh; petroleum ether) to give the corresponding product **2a** in 80% yield. The structure of the product was confirmed by GC-MS, ^1H NMR, ^{13}C NMR spectroscopic techniques. The purity of the compound was determined by GC-MS analysis.

Recyclability study

The reaction was carried out as mentioned above in model reaction procedure. However, after completion of reaction, the reaction mixture was extracted with diethyl ether (3 × 8 mL). Thus, the ionic liquid layer obtained was dried under reduced pressure for 2 h and directly used for next recycle run.

Acknowledgement

The author (KVW) is greatly thankful to the UGC (University Grant Commission, India) for providing the senior research fellowship (SRF).

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