Journal of Molecular Liquids 191 (2014) 137–141

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Short Communication

Room temperature ionic liquid choline chloride–oxalic acid: A versatile catalyst for acid-catalyzed transformation in organic reactions

Urmiladevi Narad Yadav, Ganapati Subray Shankarling *

Dyestuff Technology Department, Institute of Chemical Technology, Matunga, Mumbai 400 019, India

ARTICLE INFO

Article history:
Received 16 November 2013
Received in revised form 27 November 2013
Accepted 29 November 2013
Available online 14 December 2013

Keywords:
Choline chloride
Oxalic acid
Phenylhydrazone
Bis(indolyl)methane
Acidic ionic liquid
Solvent free synthesis

ABSTRACT

An efficient and facile synthesis of hydrazones, bis(indolyl)methanes and bis(4-hydroxycoumarin)methanes is facilitated by room temperature ionic liquid choline chloride–oxalic acid (ChCl:Ox). ChCl:Ox (10 mol%) efficiently catalyzes condensation of aldehydes with phenylhydrazine giving corresponding hydrazones in high yield (92–96%) within short reaction time of 3–5 min. Electrophilic cyclization reaction of indole and 4-hydroxy coumarin with aromatic aldehyde was effectively promoted by 30 mol% of ChCl:Ox giving corresponding bis(indolyl) arylmethanes and bis (4-hydroxycoumarin)methanes in good yield at room temperature. Procedure is very simple, solvent free and completely eliminates use of toxic acid catalyst. ChCl:Ox is biodegradable, can be recycled and reused without the loss of efficiency with respect to yield.

1. Introduction

Heterocycles such as phenylhydrazone, bis(indolyl)lmethane and bis(coumarin)methane derivatives have widespread application in the fields of biological and pharmacological sciences. Hydrazones have attracted the chemist as they are building blocks in the synthesis of compounds for applications in DSSC [1], NLO [2], medicinal chemistry [3–5] and synthesis of heterocycles such as oxadiazoles [6], bodipy [7], formazons [8] and thiadiazolidines [9]. Bis(indolyl)lmethanes and bis(coumarin)methanes show apoptosis and antiangiogenic activities [10–12]. Strepindole, member of bis(indolyl)methane family, is a potent genotoxic metabolite [13]. Bis(indolyl)methane is used as highly selective colorimetric and ratiometric fluorescent molecular chemosensors for Cu^{2+} cations [14] and F^- anions [15]. Versatile applications of these heterocycles have drawn attention of many scientists for their synthesis and to explore their property.

Synthesis of phenyl hydrazones involves reaction of carbonyl compound with phenyl hydrazine in the presence of acid catalyst such as PSSA [16] (poly styrene sulphonic acid), $Mg(ClO_4)_2$ [17], glac·CH_3COOH [18], and Bronsted and Lewis acid catalyst [19,20]. These acid catalysts are highly corrosive, unsafe to handle and pose severe threat to the environment. Hence several modifications for preparation of hydrazones are implemented such as design of new catalyst [21,22], zeolite [23], and use of different sources of energy like microwave [24], ultrasound [25] and ionic liquid [26].

Similarly, numerous reports on synthesis of bis(indolyl)methane has been reported using series of catalyst such as SO_4^{2-}/ZrO_2 [27], $SbCl_3$ [28], $(NH_4)H_2PW_{12}O_{40}$ [29], PEG-SO_3H [30], 3-methyl-1-sulfonic acid imidazolium chloride [31], camphor sulphonic acid or $ZrOCl_2 \cdot 8H_2O$ [32], $In(OTf)_3$ [33], and [bmim][MeSO4] [34]. A solvent free synthesis has been reported by Patil et al. which requires heating up to 80 °C and the reaction time ranges from 40 to 90 min [35]. But these reactions are encountered with drawbacks related to use of expensive catalyst and their reuse, high reaction temperature, multi-step synthesis of catalyst, stability and storage of catalyst, and use of organic solvents, tedious product isolation step, and long reaction hours.

In continuation of our research work [36–39] on the use of green catalyst for organic reaction we have carried out synthesis of hydrazones, bis(indolyl)methanes and bis(4-hydroxycoumarin)methanes using room temperature ionic liquid (RTIL) of choline chloride and oxalic acid (ChCl:Ox). Room temperature ionic liquids (RTILs) composed of choline chloride are synthesized by heating of two solids which forms eutectic mixture [40]. These eutectics are liquid at room temperature and are commonly called as 'deep eutectic solvents' or 'deep eutectic mixtures' [41–43]. We have explore the catalytic activity of ChCl:Ox for efficient synthesis and separation of aromatic and hetero-aromatic hydrazones, bis(indolyl)arylmethanes and bis(4-hydroxycoumarin)methanes.

---

* Corresponding author at: Department of Dyestuff Technology, Institute of Chemical Technology, N. P. Marg, Matunga, Mumbai 400 019, India. Tel.: +91 2233612708; fax: +91 22 33611020.
E-mail addresses: gsshankarling@gmail.com, gs.shankarling@ictmumbai.edu.in (G.S. Shankarling).

0167-7322/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.molliq.2013.11.036

2. Results and discussion

Reaction of phenylhydrazine with aldehydes such as benzaldehyde, p-nitrobenzaldehyde, and pyridine-3-carboxaldehyde yields the corresponding hydrazones either under neat conditions or in solvents. However, the conversion consumes 0.5–3 h in the absence of any catalyst at room temperature giving hydrazones in the range of 80–90% at room temperature. For the condensation of phenylhydrazine with less electrophilic aldehydes/ketones such as *N*, *N*-dimethyl-2-hydroxybenzaldehyde, 4-methoxybenzaldehyde, indole-3-carboxaldehyde, 4-methyl acetophenone, acetophenone and 4-bromoacetophenone no significant phenylhydrazone formation was observed when these substrates were treated with phenylhydrazine in absence of catalyst. Thus, we carried out the synthesis of phenylhydrazone derivatives with the above-mentioned substrate using ChCl:Ox as greener catalyst.

In order to study the catalytic efficiency of ChCl:Ox we used 4-methylacetophenone (1 mmol) as model substrate for reaction with phenyl hydrazine (1 mmol). The reaction was carried out in different sets of reaction conditions to find the most suitable parameters for hydrazone formation (Table 1).

Optimization result indicated that 10 mol% of ChCl:Ox was efficient to promote synthesis of hydrazone, further increase in mol% had no pronounced enhancement in yield indicating that the acidity requirement is well fulfilled by 10 mol% of catalyst. Conventional synthesis requires glacial acetic acid in refluxing ethanol; the yield obtained after 5 h is only 54%. Using biodegradable ChCl:Ox as catalyst affords 97% yield in just 5 min. Thus, the current process is highly efficient and simple as compared to other reported methodologies.

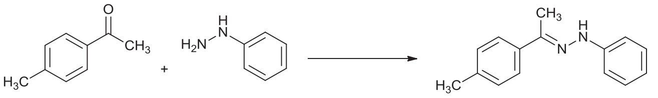
To elaborate the scope of ChCl:Ox as efficient catalyst, aldehydes and ketones with different electron donating and electron withdrawing substituents were investigated (Table 2). It was observed that reaction with electron withdrawing substituent (Table 2, entries 3b, 3c, 3d & 3k) was very fast which is due to high electrophilicity of carbonyl group induced by the substituent. Electron donating groups had pronounced effect on reaction rate. Electron donating group (Table 2, entry 3a, 3f, 3j) lowered the electrophilicity of carbonyl group and hence took longer reaction times to produce comparable yields to those obtained with simple and electron-withdrawing counterparts. Reaction with heterocycles such as acid sensitive furan-2-carboxaldehyde (3m), indole-3-carboxaldehyde (3n) and isatin (3o) occurred in short time of 3–5 min with 92–96%yield. The catalytic behavior of ChCl:Ox is well depicted in Scheme 1. The presence of ChCl:Ox catalyst results in enhanced polarization of carbonyl group through hydrogen bonding thereby assisting the reaction towards completion. Result in Table 2 summarizes the operational protocol for phenylhydrazone derivative synthesis thereby completely eliminating the drawbacks of use of organic solvents and toxic acid catalyst.

Mechanistic pathway (Scheme 1) indicates the catalytic role of ChCl:Ox. Electrophilicity of carbonyl group of aldehyde/ketone is increased by hydrogen bonding with acidic hydrogen of oxalic acid. An alcoholic hydroxyl group generated acts as base by donating a pair of electrons (oxygen lone pair) to form a covalent bond with H^+, thus acquiring a positive charge. Acid catalyzed dehydration occurs by exit of stable leaving group— $^+OH_2$. Finally protonation and deprotonation result in the formation of final product.

Since, bis(indoly)arylmethanes and bis(4-hydroxycoumarin)methanes are important intermediates for the synthesis of moiety with potential anticancer activities [10–12], we next planned to extend the application of ChCl:oxalic acid as a catalyst for their synthesis. 4-Methylbenzaldehyde and indole were chosen as model substrate for bis(indoly)methane synthesis. Reactions were carried out to optimize the mol% of catalyst required for reaction completion (Table 3). It is observed that in the presence of green catalyst like silica gel, amberlyst high temperature is required for reaction. In the presence of high temperature and acidic medium, polymerization of indole results in poor or low yield. However, by use of 30 mol% ChCl:oxalic cid, the reaction completes in 20 min at room temperature giving 98% conversion. High mol% of catalyst is required for bis(indolyl)methane synthesis as compared to hydrazones where 10 mol% of catalyst was sufficient for reaction conversion.

Different derivatives were synthesized in order to study the effect of various substituents over the yields. Nature of substituents on aldehyde and electron availability showed considerable effect in reaction time. Rate of electrophilic addition of indole with electron rich aldehyde (Table 4, 6a, 6b, 6c, & 6 k) was well facilitated giving high conversion

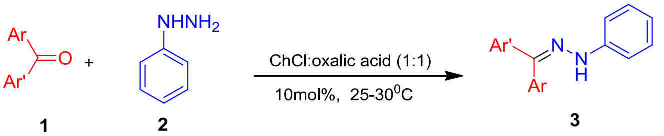
Table 1
Comparisons of ChCl:Ox catalyst with various homogeneous or heterogeneous catalysts in the condensation of 4-methyl acetophenone with phenylhydrazine.

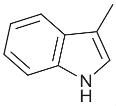
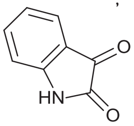


Sr. no.	Catalyst	Solvent	Reaction temp (°C)	Time	Yield (%)	Ref.
1.	glc.CH_3COOH	Ethanol	80	5 h	54	[44]
2.	glc.CH_3COOH	Glc.CH_3COOH	25	15 min	85	[45]
3.	[bbim]Br, 1 equiv.	–	28	4 min	93	[46]
4.	anhyd.Mg$(ClO)_4$, 5 mol%	Dichloromethane	20	2 h	95	[17]
5.	Conc.H2SO4, 2drops	Methanol	70	4 h	92	[47]
6.	ChCl:oxalic acid, 10 mol%	Ethanol	RT	10 min	94	–
7.	ChCl:oxalic acid, 10 mol%	Solvent free	RT	10 min	96	–
8.	ChCl:oxalic acid, 10 mol%	Solvent free	RT	5 min	95	–
9.	ChCl:oxalic acid, 5 mol%	Solvent free	RT	10 min	89	–
10	ChCl:oxalic acid, 15 mol%	Solvent free	RT	10 min	96	–

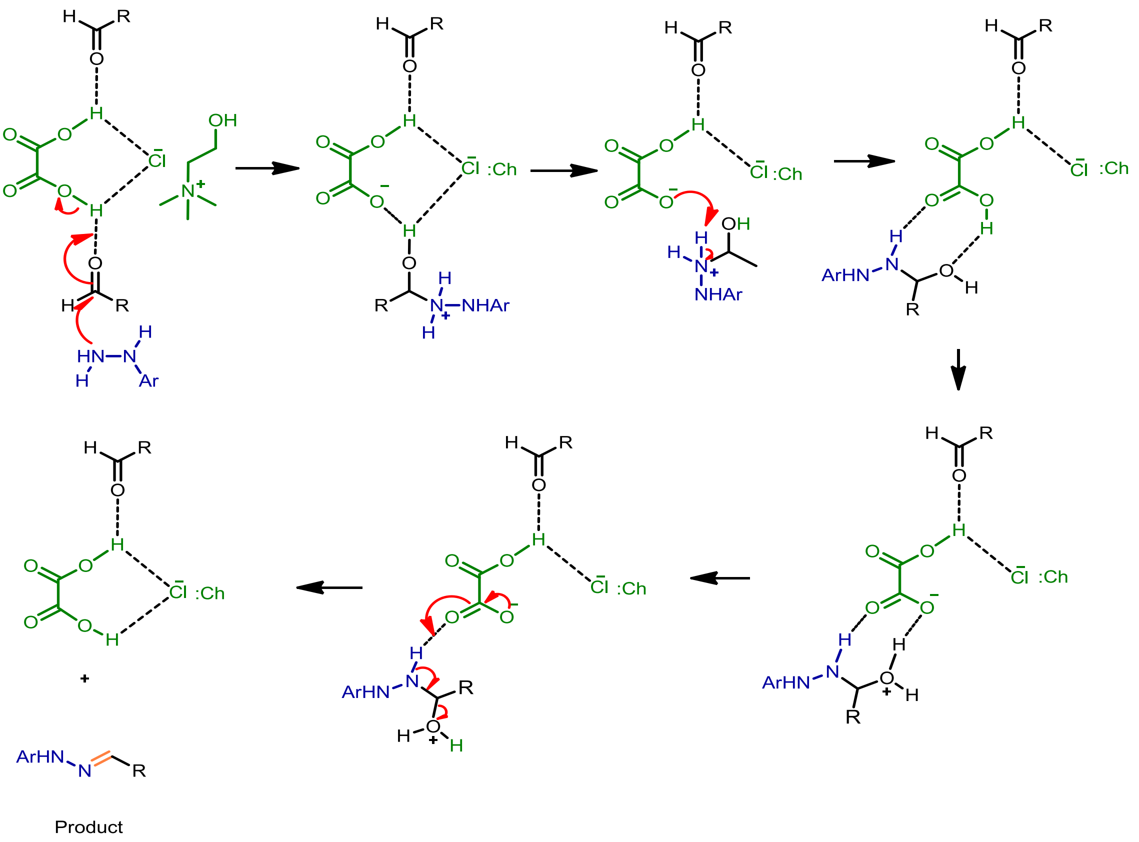
Reaction condition: 4-methylacetophenone:phenyl hydrazine 1:1 (mole ratio).

Table 2
Synthesis of various heterocyclic hydrazone derivative catalyzed choline chloride and oxalic acid ChCl:Ox.



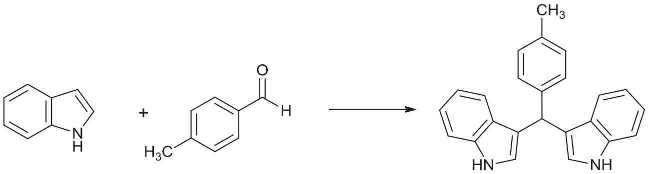
Product	Catalyst	Time (min)	Yield (%)
3a	$-p\text{-}OHC_6H_4$, $-H$	1	94
3b	$-p\text{-}NO_2C_6H_4$, $-H$	30 s	99
3c	$-p\text{-}FC_6H_4$, $-H$	30 s	96
3d	$-p\text{-}ClC_6H_4$, $-H$	30 s	98
3e	$-p\text{-}OCH_3C_6H_4$, $-H$	1	92
3f	$-p$-(N,N-diethyl)C_6H_4, $-H$	4	90
3g	$-m\text{-}(OC_6H_5)C_6H_4$, $-H$	2	91
3h	C_6H_5, $-H$	1	98
3i	C_6H_5, $-CH_3$	4	96
3j	$-p\text{-}CH_3C_6H_4$, $-CH_3$	5	95
3k	$-p\text{-}NO_2C_6H_4$, $-CH_3$	3	99
3l	$-p\text{-}BrC_6H_4$, $-CH_3$	4	94
3m	C_4H_3O, $-H$	2	94
3n	 , –H	3	92
3o		4	92

Reaction condition: aldehydes/ketone:phenyl hydrazine 1:1 (mole ratio), ChCl:Ox (10 mol%), and room temperature.



Scheme 1. Tentative reaction pathway for hydrazone synthesis catalyzed by ChCl:Ox.

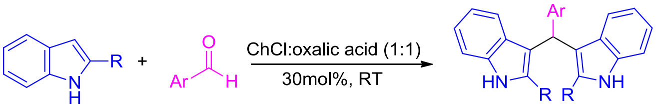
Table 3
Results of 3,3′-(*p*-tolylmethylene)bis(^{1}H-indole)synthesis using different catalyst and reaction conditions.



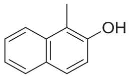
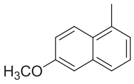
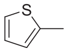
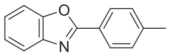
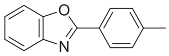
Sr. no.	Catalyst	Solvent	Reaction temp (°C)	Time	Yield (%)	Ref.
1.	SBA-15/SO_3H (70%)		70	24 h	62	[48]
2.	$KHSO_4$, 1 mmol	Methanol	RT	2 h	54	[49]
3.	$FeCl_3 \cdot 6H_2O$, 5 mol%	[omim] PF_6	RT	4 h	85	[50]
4.	–	[omim] BF_4	RT	4 h	91	[51]
5.	Amberlyst 15	–	80	2.5 h	96	[52]
6.	$La(NO_3)_3 \cdot 6H2O$, 5 mol%	–	20	2 h	98	[53]
7.	Silica gel	–	100	1 h	98	[54]
8.	Sodium dodecylsulfate	Water	RT	2.5 h	96	[55]
9	ChCl:oxalic acid, 30 mol%	Ethanol	RT	30 min	92	–
10.	ChCl:oxalic acid, 30 mol%	Solvent free	RT	20 min	98	–
11.	ChCl:oxalic acid, 20 mol%	Solvent free	RT	20 min	90	–
12.	ChCl:oxalic acid, 40 mol%	Solvent free	RT	10 min	97	–
13.	ChCl:urea	Solvent free	RT	30 min	NR	–

Reaction condition: 4-methylbenzaldehyde:indole (1:2) (mole ratio).

Table 4
Condensation of indole with various aromatic and heterocyclic aldehydes catalyzed by ChCl:Ox.

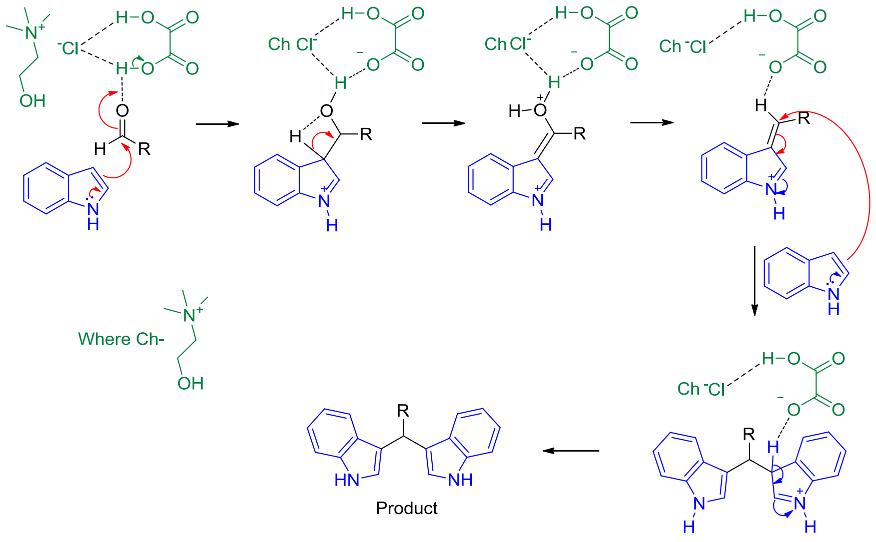


4 5 6

Product[a]	Ar	R	Time (in min)	Yield (%)[b]	M.P. (°C)
6a	– *p*-$CH_3C_6H_4$	– H	15	94	96–98
6b	– *p*-OHC_6H_4	– H	18	92	120
6c	– *p*-(N, N-CH_3)C_6H_4	– H	14	96	212–214
6d		– H	25	89	202
6e		– H	20	91	188
6f	– *m*-(OC_6H_5)C_6H_4,	– H	20	94	82–84
6g	– C_5H_4N	– H	24	88	136–138
6 h		– H	18	89	148
6i		– H	25	88	232
6j	– C_6H_5	– CH_3	10	95	242–244
6k	– *p*-$OCH_3C_6H_4$	– CH_3	18	96	210
6l	– *p*-$NO_2C_6H_4$, –H	– CH_3	20	93	242–244
6m		– CH_3	20	89	238

[a] Reaction conditions: indole (2 mmol), aldehyde (1 mmol), ChCl:Ox (30 mol%), and room temperature.

[b] Isolated yields. All products are characterized by IR and proton NMR.



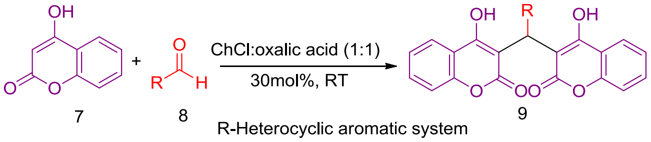
Scheme 2. A tentative mechanistic pathway for ChCl:oxalic acid (1:1) catalyzed synthesis of bis(indolyl)methanes.

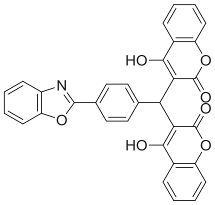
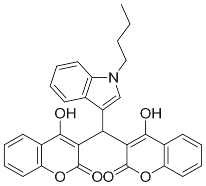
in short period. Electron withdrawing moiety like nitro group (6i), benzoxazole (6l) and pyridine (6g) consumed longer reaction times to produce comparable yields than those of their simple and electron-rich counterparts. Different bicyclic aldehydes of naphthalene series (6d & 6e) gave bis(indolyl)methane derivative in good yield, however the time required was more. The reason for lower reaction rate may be due to steric hindrance during the attack of second indole moiety (Scheme 2). We found that a number of heteroaromatic aldehydes (6h, 6i & 6m) afforded the corresponding bis(indolyl)methanes in good yields.

Encouraged by excellent results obtained using ChCl:Ox, we then investigated the scope for synthesis of bis(4-hydroxycoumarin)methanes using the same reaction condition. To our surprise ChCl:oxalic acid (1:1) was found to catalyze the reaction between 4-hydroxy coumarin and aldehyde very efficiently (Table 5). Novel derivatives were obtained within a time span of 20–25 min and are confirmed by FT-IR and ^{1}H NMR.

Table 5

Synthesis of bis(coumarin)methanes catalyzed by ChCl:Ox.



Product	Product[a]	Time (min)	Yield (%)[b]	M.P. (°C) observed
9a		25	96	250
9b		20	92	>300

[a] Reaction conditions: 4-hydroxy coumarin (2 mmol), aldehyde (1 mmol), ChCl:Ox (30 mol%), and room temperature.

[b] Isolated yields. All products are characterized by IR and H-NMR.

A reasonable mechanistic interpretation to explain the formation of the observed bis(indolyl)methanes might assume a reaction path as shown in Scheme 2. ChCl:oxalic acid (1:1) facilitates the reaction by making the carbonyl group electrophilic through hydrogen bonding. The reaction between ^{1}H of indole with aldehydes produces intermediate azafulvenium salts which further react with a second indole molecule to form the corresponding bis(indol-3-yl)methanes.

From economical and environmental points of view reuse of catalyst is extremely important hence a scale-up was set up. For hydrazone formation, scale-up batch for 50 g was carried using 4-methyl acetophenone and phenyl hydrazine as model substrate while for recyclability study of bis(indolyl)methane, indole, and 4-methylbenzaldehyde were taken as substrate. After completion of reaction as indicated on TLC water was added. Solid product was filtered out. ChCl:oxalic acid (1:1) was recovered by vacuum evaporation of water at 80 °C and dried over sodium sulfate. t was reused for the next cycles (Fig. 1). Recyclability study indicated that ChCl:oxalic acid (1:1) remains in high catalytic activity even after five successive runs.

3. Conclusion

In summary, ChCl:Ox proves to be a potential catalyst for the facile synthesis of phenylhydrazone derivatives, bis(indolyl)arylmethanes and bis(4-hydroxycoumarin)methanes. Additional catalyst and environmentally unfavorable volatile organic solvents have been completely avoided by adopting this strategy. The most attractive part of the methodology is its simple experimental procedure, high yield in short time

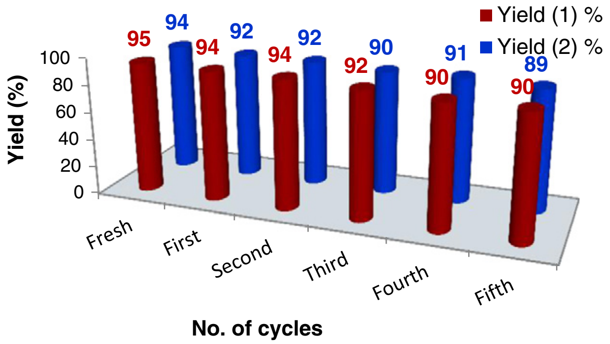


Fig. 1. Recyclability study, yield (1) refers to percentage of 4-methyl acetophenone phenylhydrazone product; yield (2) refers to percentage of 3,3′-(*p*-tolylmethylene) bis(^{1}H-indole) product.

and ease of product separation. The recyclability and biodegradability of catalyst make the process environmentally friendly and economically viable for the synthesis of various biologically and industrially important chemicals.

Acknowledgments

Authors are thankful to UGC-CAS for providing financial assistance and to the Institute of Chemical Technology, SAIF IIT-Bombay for recording IR and ^{1}H NMR.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.molliq.2013.11.036.

References

[1] G. Abdullah, A.I. Al-Sehemia, M.A. Abdullah, A.A. Yousry, Spectrochim. Acta A Mol. Biomol. Spectrosc. 91 (2012) 239.
[2] A.M. Asiri, N.A. Fatani, Dyes Pigments 72 (2007) 217.
[3] S.M. Sondhi, M. Dinodia, A. Kumar, Bioorg. Med. Chem. 14 (2006) 4657.
[4] M.R. Maurya, S. Agarwal, M. Abid, A. Azam, C. Bader, M. Ebel, Dalton Trans. (2006) 937.
[5] S.K. Sridhar, A. Ramesh, Biol. Pharm. Bull. 24 (2001) 1149.
[6] M. Dabiri, P. Salehi, M. Baghbanzadeh, M. Bahramnejad, Tetrahedron Lett. 47 (2006) 6983.
[7] O. Dilek, S.L. Bane, Tetrahedon Lett. 49 (2008) 1413.
[8] H. Tezcan, E. Uzluk, Dyes Pigments 75 (2007) 633.
[9] J. Motoyoshiya, M. Nishijima, I. Yarnamoto, H. Gotoh, J. Chem. Soc., Perkin Trans. 1 (1980) 576.
[10] S. Safe, S. Papineni, S. Chintharlapalli, Cancer Lett. 269 (2008) 326.
[11] S. Chintharlapalli, S. Papineni, S. Safe, Mol. Cancer Ther. 5 (2006) 1362.
[12] J. Hong, I. Samudio, S. Chintharlapalli, S. Safe, Mol. Carcinog. 47 (7) (2008) 492.
[13] T. Osawa, M. Namiki, Tetrahedron Lett. 24 (1983) 4719.
[14] R. Martinez, A. Espinosa, A. Tarraga, P. Molina, Tetrahedron 64 (2008) 2184.
[15] L. Wang, W. Wei, Y. Guo, J. Xu, S. Shao, Spectrochim. Acta A 78 (2011) 726.
[16] V. Polshettiwar, R.S. Varma, Tetrahedron Lett. 48 (2007) 5649.
[17] S.B. Chakraborti, Tetrahedron Lett. 45 (2004) 7641.
[18] J.R. Hwu, C.C. Lin, S.H. Chuang, K.Y. King, T.R. Su, S.C. Tsay, Bioorg. Med. Chem. 12 (2004) 2509.
[19] T.W. Greene, Protective Groups in Organic Synthesis, 1st edn John Wiley & Sons, New York, 1981.
[20] S. Ghadwal, M. Baruah, J.S. Sandhu, Synlett (1999) 1573.
[21] K. Niknam, A.R. Kiasat, S. Karimi, Synth. Commun. 35 (2005) 2231.
[22] A.R. Kiasat, F. Kazemi, K. Nourbakhsh, Phosphorus Sulfur Silicon Relat. Elem. 179 (2004) 563.
[23] A. Lalitha, K. Pitchumani, C. Srinivasan, Green Chem. (1999) 173.
[24] B.K. Banik, K.J. Barakat, W.R. Wagale, M.S. Manhas, A.K. Bose, J. Org. Chem. 64.
[25] A.C. Leite, D.M. Moreira, L.C. Coelho, F.D. Menezes, D.J. Brondani, Tetrahedron Lett. 49 (2008) 1538.
[26] D.V. Jarikote, R.R. Deshmukh, R. Rajagopal, R.J. Lahoti, T. Daniel, K.V. Srinivasan, Ultrason. Sonochem. 10 (2003) 45.
[27] B.M. Reddy, P.M. Sreekanth, L. Pandian, J. Mol. Catal. A Chem. 237 (2005) 93.
[28] M.A. Zolfigol, P. Salehi, M. Shiri, A. Sayadi, A. Abdoli, H. Keypour, M. Rezaeivala, K. Niknam, E. Kolvari, Mol. Divers. 12 (2008) 203.
[29] C. Karami, H. Ahmadian, M. Nouri, F. Jamshidi, H. Mohammadi, K. Ghodrati, A. Farrokhi, Z. Hamidi, Catal. Commun. 27 (2012) 92.
[30] J.V. Rani, V.K. Vani, V.C. Rao, Synth. Commun. 42 (2012) 2048.
[31] M.A. Zolfigol, A. Khazaei, A.R. Zare, A. Zare, Org. Prep. Proced. Int. 42 (2010) 95.
[32] S. Mishra, R. Ghosh, Indian J. Chem., Sect B 51B (2011) 1630.
[33] R. Nagarajan, P.T. Perumal, Tetrahedron 58 (2002) 1229.
[34] A.K. Chakraborti, S.R. Roy, D. Kumar, P. Chopra, Green Chem. 10 (2008) 1111.
[35] V.D. Patil, G.B. Dere, P.A. Rege, J.J. Patil, Synth. Commun. 41 (2011) 736.
[36] S.B. Phadtare, G.S. Shankarling, Green Chem. 12 (2010) 458.
[37] Y.A. Sonawane, S.B. Phadtare, B.N. Borse, A.R. Jagtap, G.S. Shankarling, Org. Lett. 12 (2010) 1456.
[38] P.M. Mahadev, K.J. Jarag, G.S. Shankarling, Green Chem. 13 (2011) 2130.
[39] B.S. Singh, H.R. Lobo, G.S. Shankarling, Catal. Commun. 24 (2012) 70.
[40] A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, V. Tambyrajah, Chem. Commun. (2003) 70.
[41] Q. Zhang, K.O. Vigier, S. Royer, F. Jerome, Chem. Soc. Rev. 41 (2012) 7108.
[42] C. Ruß, B. König, Green Chem. 14 (2012) 2969.
[43] E. Durand, J. Lecomte, P. Villeneuve, Eur. J. Lipid Sci. Technol. 115 (2013) 379.
[44] S.L. Dabb, B.A. Messerle, Dalton Trans. (2008) 6368.
[45] R.K. Yadlapalli, O.P. Chourasia, K. Vemuri, M. Sritharan, R.S. Perali, Bioorg. Med. Chem. Lett. 22 (2012) 2708.
[46] S.A. Siddiqui, R.N. Nadaf, R. Rajagopal, T. Daniel, R.J. Lahoti, K.V. Srinivasan, Synth. Commun. 34 (2004) 41.
[47] S.Y. Jadhav, S.P. Shirame, S.D. Kulkarni, S.B. Patil, S.K. Pasale, R.B. Bhosale, Bioorg. Med. Chem. Lett. 23 (2013) 2575.
[48] M.A. Naik, D. Sachdev, A. Dubey, Catal. Commun. 11 (2010) 1148.
[49] H.J. Kim, H. Lee, J.H. Lee, D.H. Choi, J.H. Jung, J.S. Kim, Chem. Commun. 47 (2011) 10918.
[50] S.J. Ji, M.F. Zhou, D.G. Gu, Z.Q. Jiang, T.P. Loh, Eur. J. Org. Chem. (2004) 1584.
[51] J.S. Yadav, B.V.S. Reddy, S. Sunitha, Adv. Synth. Catal. 345 (2003) 349.
[52] K. Singh, S. Sharma, A. Sharma, J. Mol. Catal. A Chem. 347 (2011) 34.
[53] J.P. Selvam, M. Srinivasulu, N. Suryakiran, V. Suresh, S.M. Reddy, Y. Venkateswarlu, Synth. Commun. 38 (2008) 1760.
[54] S.R. Mendes, S. Thurow, M.P. Fortes, F. Penteado, E.J. Lenardao, Diego Alves, G. Perin, R.G. Jacob, Tetrahedron Lett. 53 (2012) 5402.
[55] M.L. Deb, P.J. Bhuyan, Tetrahedron Lett. 47 (2006) 1441.