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Contents

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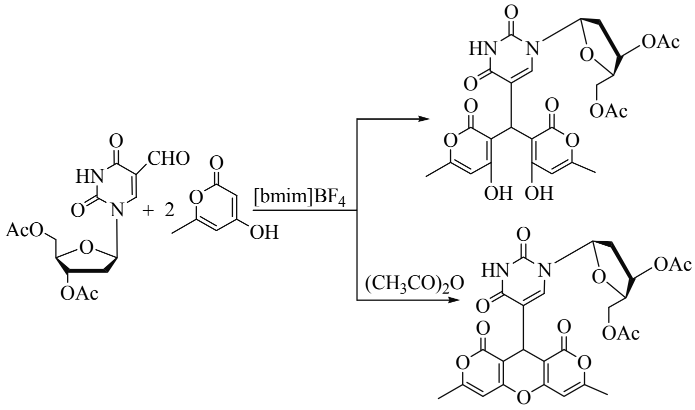

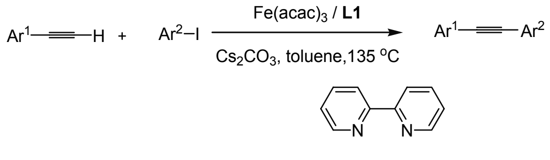

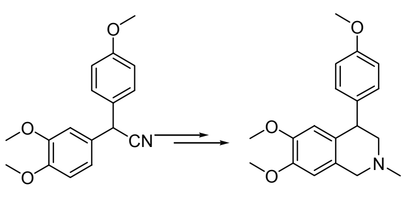

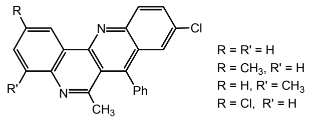

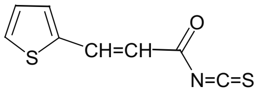

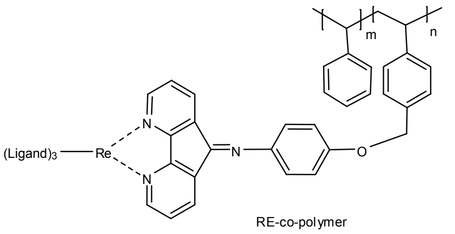

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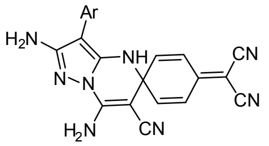
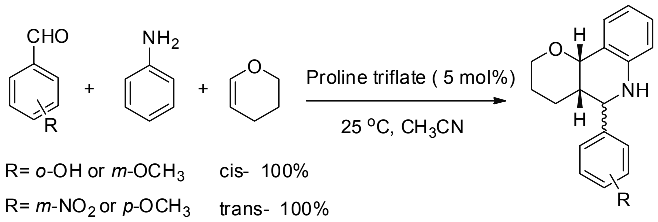
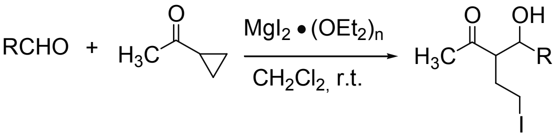
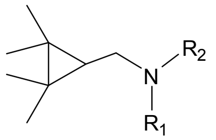
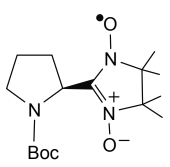


6









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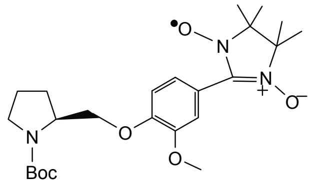

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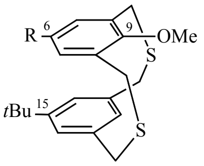

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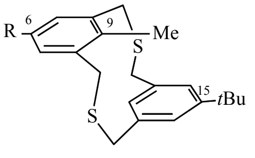

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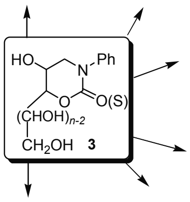

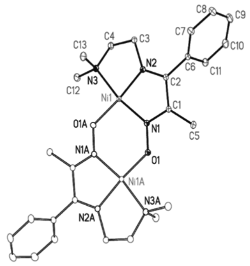

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A green protocol for synthesis of methylene dioximes promoted by an ionic liquid [bmim]BF_4

Hongjun Zang*, Yong Zhang, Meiling Wang and Bo-Wen Cheng

Department of Material Science and Chemistry Engineering, Tianjin Polytechnic University, Tianjin Municipal Key Laboratory of Fiber Modification and Functional Fiber, Tianjin 300160, P.R. China

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The ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim]BF_4, has been demonstrated to be an effective catalyst for synthesis of methylene dioximes. These reactions proceed with excellent yields under shorter reaction times than other reported methods. Furthermore, the ionic liquid [bmim]BF_4 can be recycled and reused without loss of catalytic activity.

Keywords: methylene dioximes, phase transfer catalyst, ionic liquid

In recent years, room-temperature ionic liquids (RTILs), new types of solvent for green chemistry, have been studied because they are stable, nonvolatile, and easy to recycle. Many important reactions have been carried out in ionic liquids.[1-5] Although many types of reactions have been investigated in ionic liquids, only a few examples of nucleophilic substitution reactions have been reported.[6-9] Nucleophilic displacement reactions are often carried out using phase transfer catalysts (PTC) to facilitate the reaction between the organic reactants and the inorganic ionic salts that provide the nucleophiles.[10] We envisaged the use of ionic liquids as catalysts would be advantageous in such a reaction as the synthesis of methylene dioximes.

Methylene dioximes are important chemicals useful as metal capturers, and anti-inflammatory and antibacterial agents.[11] The main synthetic route involves the use of phase transfer catalysts (PTCs) in the heterogenous reaction between oximes and dichloromethane. The synthesis of methylene dioximes involves alkylation of oximes with dichloromethane using either: (1) quaternary ammonium salt with 50% aqueous solutions of sodium hydroxide for 16 h,[12] (2) sodium hydroxide in combination with tetrabutylammonium bromide for 20 h,[13] (3) potassium superoxide in the presence of di-μ-chlorobis (2-methylallyl) dipalladium (II) catalyst for 72 h,[14,15] (4) potassium carbonate in combination with 18-crown-6 for 12 h under argon at 50 °C,[15] (5) sodium hydroxide in the presence of a low-molecular weight polyethylene glycol-400 (PEG-400) for 14–20 h,[16] (6) potassium hydroxide in combination with 18-crown-6 in acetonitrile at 70 °C,[17] (7) and sodium hydroxide in the presence of benzyldimethyl-tetradecylammonium chloride for 2–3.5 h.[18] However, some of these methods have not been entirely satisfactory, with disadvantages such as relatively long reaction times, low yield, high reaction temperature and using a catalyst that cannot be recycled. Therefore, the development of a simple, efficient, and environmentally benign method for the synthesis of methylene dioximes remains desirable.

As a continuation of our endeavours in green synthesis and using ionic liquids as a recyclable, eco-friendly catalysts,[19] we report here an efficient and environmentally friendly procedure for the preparation of methylene dioximes using ionic liquids as a substitute for phase transfer catalysis methods.

In our initial research, acetophenone oximes were selected as a representative reactant in order to optimise the reaction conditions. Reactions were carried out in different ionic liquids at room temperature under stirring. As shown in Table 1, the reaction proceeded efficiently in the ionic liquids [bmim]Br, [bmim]BF_4, [bmim]OH, [amim]Cl and [bmim]PF_6. The best reaction performance was delivered by [bmim]BF_4 (Table 1, Entry 3), which provided the product 3a in 96% yield in 30 min. Whereas in other reported methods,[12-18] to obtain the same yield needed 3.5 h. It was clear that synthesis of methylene dioximes using the ionic liquid as a catalyst was a quick and effective method. So [bmim]BF_4 was chosen for further study in this work.

Effects of reaction time on the yields of the products were also studied by prolonging the reaction time. When the reaction time was prolonged to 60 min, the compound **3a** (entries 2, 6, 8 and 10) was obtained in nearly 95% yield with different ionic liquids. The results showed that the reactions could proceed more efficiently with a prolonged reaction time.

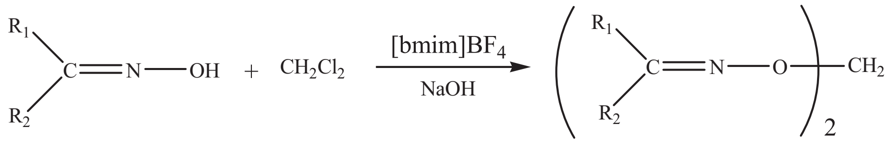
Table 1 The reaction of acetophenone oxime with dichloromethane in different ionic liquids at room temperature under stirring

Entry[a]	RTIL	Time/min	Yield/%[b]
1	[bmim]Br	30	87
2	[bmim]Br	60	94
3	[bmim]BF_4	30	96
4	[bmim]BF_4	30	94[c]
5	[bmim]OH	30	89
6	[bmim]OH	60	93
7	[amim]Cl	30	91
8	[amim]Cl	60	95
9	[bmim]PF_6	30	84
10	[bmim]PF_6	60	93

[a]Reaction conditions: 0.5 mmol acetophenone oxime, 3.5 mL dichloromethane, 0.1 mmol ionic liquid, 4 mmol sodium hydroxide

[b]Isolated yield.

[c][bmim]BF_4 was reused.



1 2 3

Scheme 1

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* Correspondent. E-mail: zanghongjun@tjpu.edu.cn

Table 2 Synthesis of methylene dioximes by [bmim]BF_4 with different alkalies

Entry	Time/min	Alkali	Yield/%[a]
1	30	NaOH	96
2	30	K_2CO_3	0
3	120	K_2CO_3	0
4	30	Na_2CO_3	0
5	120	Na_2CO_3	0
6	30	CH_3COONa	10
7	120	CH_3COONa	30
8	30	None	0
9	120	None	0

[a]Isolated yield.

Since the recovery and reuse of catalyst and solvent are highly preferable for a green process, we next investigated the reusability and recycling of the ionic liquid. After completion of the reaction, water was added into the reaction mixture, and the mixture was extracted by CH_2Cl_2. The water containing [bmim]BF_4 was evaporated under reduced pressure to recover the ionic liquid. The recycled [bmim]BF_4 (Table 1, entry 4) was reused in the reaction of acetophenone oxime with dichloromethane. The catalytic activity of did not show any significant decrease.

Simultaneously, the reaction of acetophenone oxime with dichloromethane was also performed in the presence of different alkalis such as NaOH, K_2CO_3, Na_2CO_3, CH_3COONa or without alkali in [bmim]BF_4 under the same reaction conditions (Table 2). The result showed that the reaction could not occur in the presence of potassium carbonate and sodium carbonate (Table 2, entries 2–5). Though in the presence of sodium acetate methylene dioximes could be obtained, the yield (only 10% and 30%) was lower than with sodium hydroxide (Table 2, entry 1). As shown in the Table 2 (entries 8, 9), the reaction did not occur without alkali. It showed that only in alkaline conditions, the reaction could be carried out. In the presence of strong base, the reaction was more easily carried out than with the weak base. These results revealed that [bmim]BF_4 combined with NaOH could effectively accelerate the reaction at room temperature under stirring.

With these results in hand, we turned our attention to the scope of the oximes in the reaction. The results were summarised in Table 3. For most of substrates, the reaction was completed at 20–30 min with high yields. whereas in reported methods,[12-18] the reaction was completed to need not less than 2 h with similar or lower yields. For example, compound **3e** was previously prepared in 90% yield within 3.5 h under ultrasonication,[18] whereas in the presence of [bmim]BF_4, **3e** was obtained in 93% yield in 30 min. The yield of **3e** was increased and the reaction time was shortened.

Experimental

Materials and instruments

Melting points were recorded on an electrothermal apparatus and were uncorrected. The ^1H NMR and ^{13}C NMR spectra were measured on a Bruker AVANCE 300 spectrometer using TMS as internal standard and $CDCl_3$ as solvent. IR spectra were measured with a BIO-RAD FTS3000 spectrometer. Mass spectra were obtained in ESI mode using a BrukerEsquire 3000 mass spectrometer. Elemental analyses were obtained using a Perkin–Elmer auto-analyser.

General procedure for the preparation of methylene dioximes

The oxime (**1**, 0.5 mmol) was dissolved in dichloromethane (**2**, 3.5 mL). [bmim]BF_4 (0.227 g, 0.1 mmol) and sodium hydroxide powder (0.160 g, 4 mmol) were added. The reaction mixture was stirred at room temperature for 30 min. The mixture was washed with water (10 mL) and extracted with CH_2Cl_2 (3.15 mL). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and evaporated to dryness *in vacuo*. The product was purified by chromatography on silica (200–300 mesh). Elution with a mixture of petroleum ether and ethyl acetate (20/1, V/V) afforded the methylene dioximes **3a–j**. All the known products **3a–g, 3j** were fully characterised by IR and ^1H NMR spectroscopy, and melting points, which were consistent with the literature data. The new compounds **3h–i** were identified by IR,^1H NMR, ^{13}C NMR, MS spectroscopy and elemental analysis.

3h: White solid; m.p. 162–164 °C. ν_{max} (KBr)/cm^{-1} 3417, 3053, 2941, 1649, 1518, 1044, 832. ^1H NMR (300 MHz, $CDCl_3$) 2.21 (s, 6H, CH_3), 3.80 (brs, 4H, NH_2), 5.80 (s, 2H, CH_2), 6.65 (d, $J = 8.9$ Hz, 4H, ArH), 7.51(d, $J = 8.9$ Hz, 4H, ArH). ^{13}C NMR (300 MHz, $CDCl_3$) 156.9, 147.8, 127.8, 126.9, 114.8, 99.2, 13.3. MS: *m/z* 335 $[M + Na]^+$, 313 $[M + 1]^+$. Anal. Calcd for $C_{17}H_{20}N_4O_2$: C 65.38, H 6.41, N 17.95. Found C 65.35, H 6.43, N 17.99%.

3i: White solid; m.p. 144–146 °C. ν_{max} (KBr)/cm^{-1} 3324, 2961, 1638, 1502, 1125, 811. ^1H NMR (300 MHz, $CDCl_3$) 2.99 (s, 12H, CH_3), 5.72 (s, 2H, CH_2), 6.68 (d, 4H, $J = 8.9$ Hz, ArH), 7.49 (d, 4H, $J = 8.9$ Hz, ArH), 8.12 (s, 2H, N=CH). ^{13}C NMR (300 MHz, $CDCl_3$) 151.6, 151.4, 128.7, 119.4, 111.7, 99.1, 40.2. MS: *m/z* 363 $[M + Na]^+$, 341 $[M + 1]^+$. Anal. Calcd for $C_{19}H_{24}N_4O_2$: C 67.06, H 7.06, N 16.47. Found C 67.03, H 7.08, N 16.46%.

The project was supported by the Tianjin National Natural Science Foundation (No. 07JCYBJC02200).

Table 3 Synthesis of methylene dioximes in ionic liquid [bmim]BF_4 in presence of NaOH

Entry	Oximes		Time/min	Yield[a]/%	M.p./°C (lit.)
	R_1	R_2			
3a	Ph	Me	30	96	95–97(94–96)[15]
3b	Ph	Ph	20	99	81–83(81–83)[15]
3c	—$(CH_2)_5$—		30	87	41–43(44–46)[15]
3d	—$(CH_2)_4$—		30	78	52–54(56–58)[15]
3e	4-$MeOC_6H_4$	Me	30	93	142–144(136–138)[15]
3f	4-$O_2NC_6H_4$	Me	20	97	147–150(158–160)[15]
3g	Me	Me	30	81	42–44(44)[14]
3h	4-$H_2NC_6H_4$	Me	30	94	162–164
3i	4-$(CH_3)_2NC_6H_4$	H	30	92	144–146
3j	2-$MeOC_6H_4$	H	20	97	91–94(98–99)[15]

[a]Isolated yield.

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