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Direct ionic liquid promoted organocatalyzed diazo-transfer reactions: diversity-oriented synthesis of diazo-compounds

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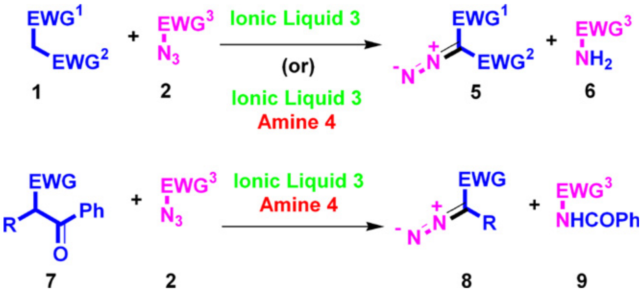
Abstract

A practical and novel ionic liquid promoted organocatalytic selective diazo-transfer process for the synthesis of highly substituted diazo-compounds in high yields is reported. The ionic liquid can be reused without affecting the reaction rates or yields over five runs.

Keywords: Amines; Cascade reactions; α-Diazo-compounds; Ionic liquids; Organocatalysis

1. Introduction

Diazo-compounds are of considerable importance in a variety of industries and research laboratories. As such, the development of new and more general green methods for their preparation is of significant interest.[1] Recently, ionic liquids have emerged as novel green reaction media for many organic transformations.[2] Surprisingly, to the best of our knowledge; there is no report on diazo-transfer reactions in ionic liquid. In this Letter, we present the synthesis of diazo-compounds in high yields via ionic liquid promoted organo-catalyzed diazo-transfer reactions as shown in Scheme 1.



Scheme 1. Direct ionic liquid promoted organocatalytic cascade diazo-transfer reactions.

Diazo-compounds **5** and **8** have been prepared by ionic liquid promoted organocatalytic diazo-transfer (DT) reactions using commercially available CH-acids **1**, azides **2**, and ionic liquids **3** (Scheme 1). Direct combination of an amine-catalyzed cascade amination/debenzoylation (A/DB) of highly substituted CH-acids **7** with azides **2** in ionic liquid **3** has been developed for the generation of diazo-compounds (α-diazo esters and α-diazo ketones) **8** as shown in Scheme 1. The diazo function is potentially a more valuable synthetic tool than the presently recognized because of its high reactivity, but its utility is limited by the scarcity of good methods for its production.

In continuation of our interest in the development of green cascade reactions through organocatalysis in ionic liquids,[3] we initiated our studies by screening a number of known ionic liquids **3** for the diazotization of dimedone **1a** with 1.0 equiv of *p*-toluenesulfonyl azide (**2a**) at room temperature as shown in Table 1. Interestingly, the ionic liquid [bmim]BF_4 resulted in good conversions and moderate yields of **5a** as shown in Table 1, entries 1 and 2. The ionic liquid, [bmim]OH also promoted the formation of

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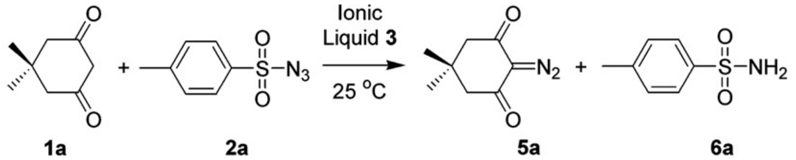
Table 1
Preliminary studies on the diazo-transfer reaction of CH-acid **1a** with **2a** in ionic liquids[a]



Entry	Ionic liquid	Ionic liquid (g)	Time (h)	Conversion[b] (%)	Yield **5a**[c] (%)
1[d]	[bmim]BF_4	1.2	5	>95	75
2[e]	[bmim]BF_4	1.2	5	>95	85
3[d]	[bmim]OH	0.3	1	>99	20
4[e]	[bmim]OH	0.3	1	>99	50
5[f]	[bmim]OH	0.3	1.5	>99	72
6[d]	**[bmim]Br**	**1.3**	**1**	**>99**	**96**

[a] Reactions were carried out in ionic liquid with 0.5 mmol each of **1a** and **2a**.
[b] Conversion is based on both TLC and ^1H NMR analysis.
[c] Yield refers to the column purified product.
[d] Diazo-compound **5a** was extracted from the ionic liquid with 30 mL of diethyl ether.
[e] Diazo-compound **5a** was extracted from the ionic liquid with 30 mL of ethyl acetate.
[f] Diazo-compound **5a** was extracted from the ionic liquid with 60 mL of ethyl acetate.

2-diazo-5,5-dimethyl-cyclohexane-1,3-dione **5a** with good conversions but poor to moderate yields as shown in Table 1, entries 3–5. Interestingly, [bmim]Br let to the formation of **5a** with excellent conversion and high yield (Table 1, entry 6). Both [bmim]BF_4 and [bmim]OH are good ionic liquids for the diazotization of CH-acid **1a** with **2a**; however, the isolation of diazo product **5a** from the ionic liquids was tedious possibly due to the strong interactions between **5a** and the ionic liquids, especially [bmim]OH. Interestingly, we did not encounter such isolation problems from [bmim]Br. We also reproduced the same results (Table 1, entry 6) with five different batches of [bmim]Br prepared from *N*-methylimidazole and *n*-butylbromide.[4] To increase the reaction rate and to investigate the effects of the azides **2a**–**e** and amines **4** on the diazotization reaction, we used the ionic liquids [bmim]Br and [bmim]BF_4 and screened a number of amines **4** as catalysts for the diazotization of CH-acid **1a** with 1.0 equiv of azides **2a**–**e** as shown in Table 2.

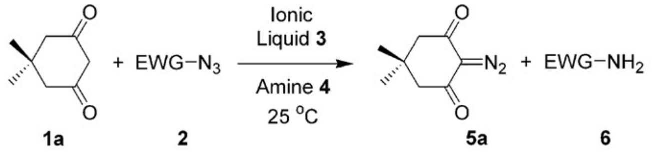
The diazo-transfer reaction of dimedone **1a** with TsN_3 **2a** in [bmim]BF_4 using 1.0 equiv of K_2CO_3 as a catalyst furnished the expected diazo product **5a** in 72% yield after 3 h (Table 2, entry 1). Interestingly, addition of 5 mol % of simple amines such as Et_3N, DBU, DABCO, DMAP, 4-pyrrolidin-1-yl-pyridine (PP), pyrrolidine, pyridine and *N*-methylimidazole (NMI) as catalyst in [bmim]BF_4 furnished the expected diazo product **5a** in 75–95% yields after 1.5–18 h as shown in Table 2, entries 2–9. Amongst these amines, DMAP and NMI showed promise as catalysts in [bmim]BF_4. To the best of our knowledge, there is no report on the diazo-transfer reactions catalyzed by DMAP and NMI. DMAP-catalyzed diazotization of **1a** with 1.0 equiv of MsN_3 **2b** in [bmim]BF_4 furnished the expected diazo product **5a** in 99% yield after 1 h as shown in Table 2, entry 11. The same reaction under DMAP-catalysis in [bmim]Br as a solvent furnished the diazo product **5a** in 99% yield after 0.5 h as shown in Table 2, entry 13. We also investigated the DMAP-catalyzed reaction of **1a** with the azides 4-$NO_2C_6H_4SO_2N_3$ (*p*NBSA) **2c**, 2-$NO_2C_6H_4SO_2N_3$ (*o*NBSA) **2d** and N_3CO_2Et **2e**, but the diazotization of the CH-acid was inferior compared to TsN_3 **2a** or MsN_3 **2b** as shown in Table 2, entries 14–16.

We also tested the DMAP-catalyzed diazo-transfer reaction of **1a** with TsN_3 **2a** in the conventional solvents CH_3CN and CH_2Cl_2; however, the diazotization of CH-acid was slightly less efficient compared to the reaction in [bmim]Br (Table 2, entries 17 and 18). The optimized conditions involved the addition of 1.0 equiv of MsN_3 **2b** to a mixture of CH-acid **1a** and 5 mol % of DMAP in 1.0 mL of [bmim]Br at 25 °C to furnish dione **5a** in 99% yield after 0.5 h (entry 13).

After successful demonstration of ionic liquid promoted DMAP-catalyzed diazo-transfer reaction of CH-acid **1a** with MsN_3 **2b**, we next focused on recycling the ionic liquid, as shown in Table 3. The ionic liquids, [bmim]BF_4 and [bmim]Br, could be recycled over five runs to produce diazo-compound **5a** without affecting significantly the reaction rate and yield (Table 3).

With an efficient method for the diazotization in hand, the scope of the self- and DMAP-catalyzed diazo-transfer reactions was investigated with various CH-acids **1a**–**q**. CH-acids **1a**–**q** were reacted with 1.0 equiv of MsN_3 **2b** catalyzed with or without 5 mol % of DMAP at 25 °C in [bmim]Br (Table 4). The diazo-compounds **5a**–**q** were obtained as single products in excellent yields, being even better than those from previous diazotization reactions performed in organic solvents under base catalysis.[5] Diazo products **5o** and **5p** are used for the preparation of diazabicyclo compounds[6] for the treatment of ischemia and hypoxia, emphasizing the value of this diazo-transfer approach in ionic liquids. Mechanistically, the rates of the diazotization reactions were accelerated by the ionic

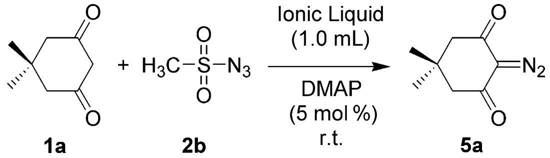
Table 2
Effect of the amine and azide on the ionic liquid promoted diazo-transfer reaction of dimedone **1a**[a]



Entry	EWG–N_3 **2** (1 equiv)	Ionic liquid **3**	Amine **4** (5 mol %)	Time (h)	Yield[b] (%) **5a**
1[c]	4-$CH_3C_6H_4SO_2N_3$ **2a**	[bmim]BF_4	—[e]	3	72
2[c]	**2a**	[bmim]BF_4	Et_3N	1.5	75
3[c]	**2a**	[bmim]BF_4	DBU	1.5	75
4[c]	**2a**	[bmim]BF_4	DABCO	3	78
5[c]	**2a**	[bmim]BF_4	DMAP	2	95
6[c]	**2a**	[bmim]BF_4	pp[f]	3	80
7[c]	**2a**	[bmim]BF_4	Pyrrolidine	2.5	82
8[c]	**2a**	[bmim]BF_4	Pyridine	18	83
9[c]	**2a**	[bmim]BF_4	NMI[g]	2	95
10[d]	**2a**	**[bmim]BF_4**	**DMAP**	**2**	**99**
11[d]	**$CH_3SO_2N_3$ 2b**	**[bmim]BF_4**	**DMAP**	**1**	**99**
12[d]	**2a**	**[bmim]Br**	**DMAP**	**0.5**	**98**
13[d]	**2b**	**[bmim]Br**	**DMAP**	**0.5**	**99**
14[d]	4-$NO_2C_6H_4SO_2$ N_3 **2c**	[bmim]Br	DMAP	1	85
15[d]	2-$NO_2C_6H_4SO_2N_3$ **2d**	[bmim]Br	DMAP	7	83
16[d]	$EtOCON_3$ **2e**	[bmim]BF_4	DMAP	3	60
17	**2a**	**CH_3CN**	**DMAP**	**1**	**94**
18	**2a**	**CH_2Cl_2**	**DMAP**	**2**	**90**

[a] Reactions were carried out in ionic liquid **3** (1.0 mL) with 1.0 equiv of **2** relative to **1a** (0.5 mmol) in the presence of 5 mol % of amine **4**.
[b] Yield refers to the column purified product.
[c] Diazo-compound **5a** was extracted from the ionic liquid with 30 mL of diethyl ether.
[d] Diazo-compound **5a** was extracted from the ionic liquid with 20 mL of diethyl ether and 16 mL of ethyl acetate.
[e] 1 equiv of K_2CO_3 was used.
[f] 4-Pyrrolidin-1-yl-pyridine.
[g] *N*-Methylimidazole.

Table 3
Recycling of ionic liquid solvent in the direct DMAP-catalyzed diazo-transfer reaction of CH-acid **1a** with methanesulfonyl azide **2b**[a]



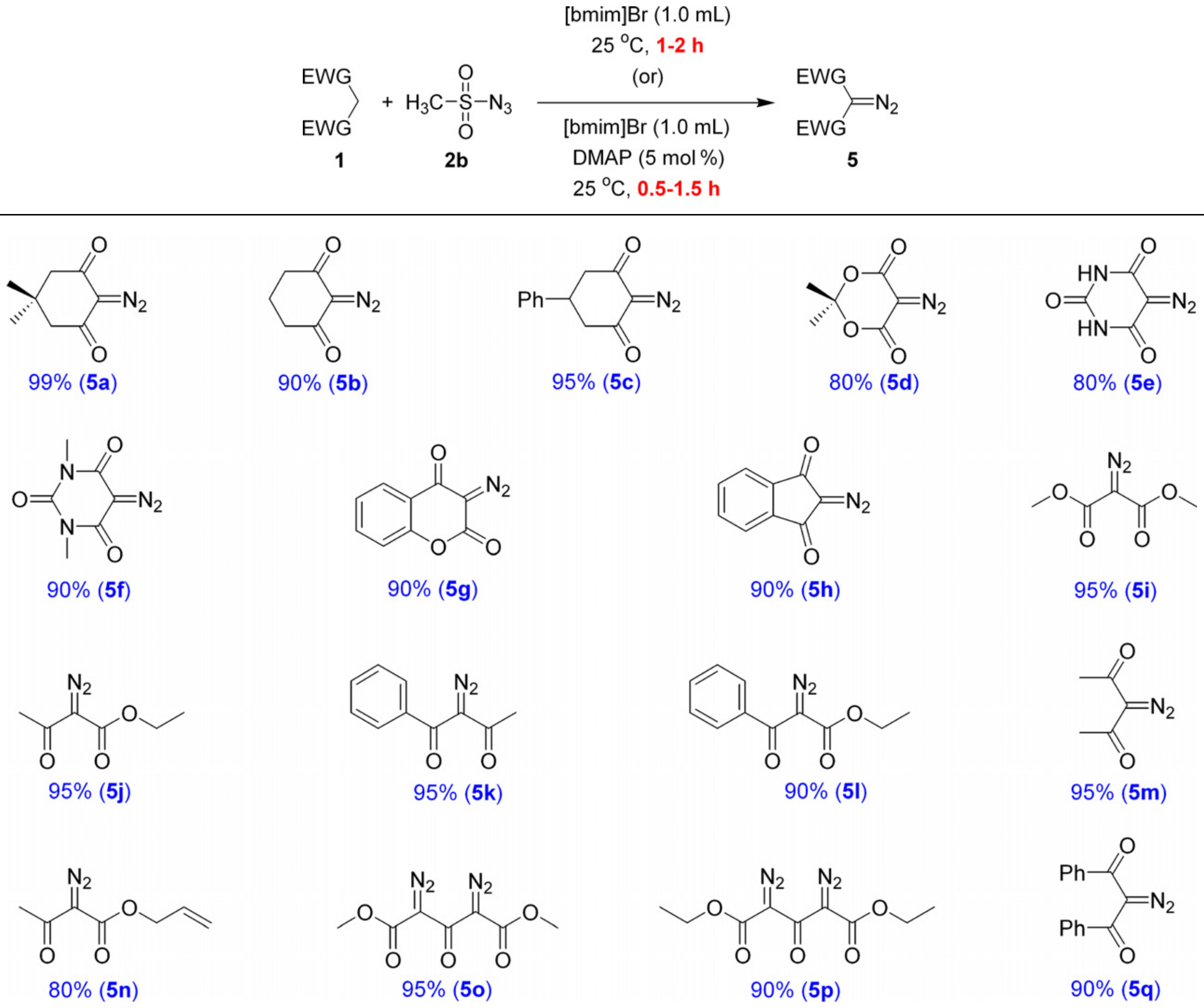
Run	[bmim]BF_4			[bmim]Br		
	Time (h)	Conversion[b] (%)	Yield **5a**[c,d] (%)	Time (h)	Conversion[b] (%)	Yield **5a**[c,d] (%)
1	1	>99	98	1	>99	99
2	2	>99	96	1.5	>99	97
3	3	>99	95	1.5	>99	97
4	3	>99	95	1.5	>99	96
5	3	>99	95	1.5	>99	95

[a] Reactions were carried out in ionic liquid with 0.5 mmol each of **1a**, **2b** and 5 mol % of DMAP.
[b] Conversion is based on both TLC and ^1H NMR analysis.
[c] Yield refers to the column purified product.
[d] Diazo-compound **5a** was extracted from the ionic liquid with 30 mL of diethyl ether.

liquid [bmim]Br, perhaps due to the basic nature of counter anion Br^-.

Next, we continued our investigation for the generation of highly functionalized diazo-compounds **8** under DBU-catalysis through the diazotization of CH-acids **7** via debenzoylation[7] (see Tables 5 and 6). Recently, Taber et al. reported that the DBU-catalyzed diazo-transfer reaction of highly functionalized CH-acids **7** with *p*NBSA **2c** proceeded with selective debenzoylation to provide the desired unsymmetrical α-diazo ketones and α-diazo esters

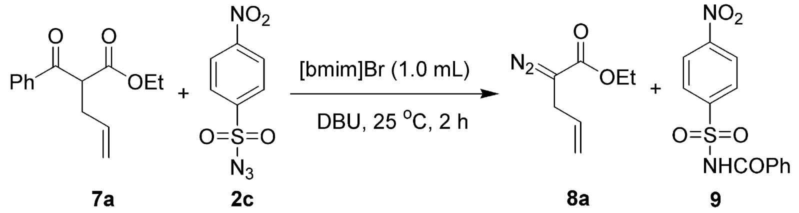
Table 4
Synthesis of diazo-compounds via cascade ionic liquid promoted DMAP-catalyzed diazo-transfer reactions of CH-acids **1a–q** with MsN_3 **2b**[a,b]



[a] Yield refers to the column purified product.

[b] Yields represent both DMAP- and non-DMAP-catalyzed reactions.

Table 5
Direct ionic liquid promoted DBU-catalyzed diazo-transfer reaction of highly substituted CH-acid **7a** with *p*NBSA **2c** via debenzoylation[a,b]



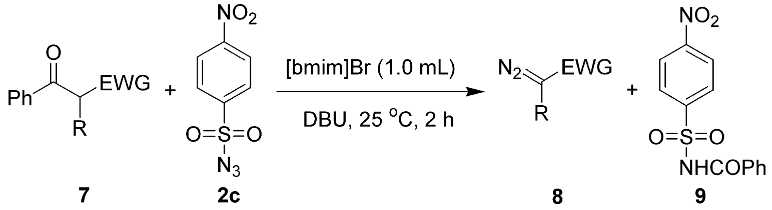
Entry	*p*NBSA **2c** (equiv)	DBU (equiv)	Yield **8a**[b] (%)
1	1	1	50
2	1	2	75
3	2	2	80

[a] See Section 2.

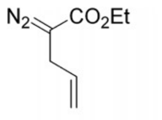
[b] Yield refers to the column purified product.

8 in CH_2Cl_2 with moderate to good yields.[7] Herein, we demonstrated the same reaction in [bmim]Br as a solvent at room temperature to furnish the unsymmetrical diazo-compounds **8** in high yields. Optimization in [bmim]Br

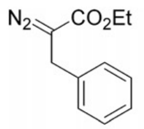
Table 6
The synthesis of diazo-compounds through cascade ionic liquid promoted DBU-catalyzed diazo-transfer reactions of highly functionalized CH-acids **7** with *p*NBSA **2c** via debenzoylation[a,b]



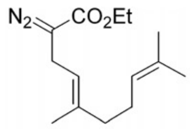
7 **2c** **8** **9**



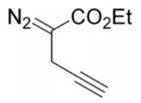
80% (**8a**)



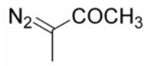
85% (**8b**)



85% (**8c**)



70% (**8d**)



85% (**8e**)

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[a] See Section 2.

[b] Yield refers to the column purified product.

revealed that 2.0 equiv each of DBU and *p*NBSA were required for the diazotization of CH-acid **7a** to furnish the unsymmetrical α-diazo ester **8a** in 80% yield after 2 h at 25 °C (Table 5, entry 3).

The results in Table 6 demonstrate the broad scope of this novel methodology covering a structurally diverse group of CH-acids **7a–e**. Cascade diazotization reaction of CH-acids **7a–e**, *p*NBSA **2c** and DBU furnished the α-diazo esters **8a–d** and α-diazo ketone **8e** in 70–85% yields (Table 6).

In conclusion, we have developed a metal-free, ionic liquid promoted synthesis of highly substituted symmetrical and unsymmetrical α-diazo ketones and α-diazo esters **5** and **8** from simple starting materials via diazotization reactions under amine catalysis. The ionic liquid promoted diazotization reaction proceeds in good yields with high selectivity using DMAP or DBU as the catalyst. Furthermore, we have demonstrated the recycling of the ionic liquids [bmim]BF_4 and [bmim]Br in the DMAP-catalyzed diazotization reactions. Further work is in progress to utilize [bmim]Br promoted diazo-transfer reactions in synthetic chemistry.

2. General experimental procedures for the ionic liquid promoted diazotization reactions

2.1. Self-catalyzed ionic liquid promoted diazotization reactions

Mesyl azide **2b** (0.5 mmol) was added to a solution of the corresponding CH-acids **1a–q** (0.5 mmol) in [bmim]Br (1.0 mL). The resulting reaction mixture was stirred at room temperature for the time indicated in Tables 1 and 4. The diazo-compounds **5a–q** were extracted from the ionic liquid with diethyl ether (25 mL) and ethyl acetate (15 mL). The combined organic layers were washed with water, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Pure products **5** were obtained by flash column chromatography (silica gel, mixture of hexane/ethyl acetate).

2.2. DMAP-catalyzed ionic liquid promoted diazotization reactions

Mesyl azide **2b** (0.5 mmol) was added to a solution of the corresponding CH-acid **1a–q** (0.5 mmol) and DMAP (5 mol %) in [bmim]Br (1.0 mL). The resulting reaction mixture was stirred at room temperature for the time indicated in Tables 2–4. The diazo-compounds **5a–q** were extracted from the ionic liquid with diethyl ether (25 mL) and ethyl acetate (15 mL). The combined organic layers were washed with water, dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. Pure products **5** were obtained by flash column chromatography (silica gel, mixture of hexane/ethyl acetate).

2.3. DBU-catalyzed ionic liquid promoted cascade diazotization reactions via debenzoylation

To 0.5 mmol of CH-acids **7a–e** and 1.0 mmol of *p*NBSA **2c** in an ordinary glass vial equipped with a magnetic stirring bar was added 1.0 mL of [bmim]Br, and then 1.0 mmol of DBU was added dropwise over 0.25 h and the reaction mixture was stirred at 25 °C for the time indicated in Tables 5 and 6. The α-diazo-compound **8** was extracted from ionic liquid with diethyl ether (25 mL) and ethyl acetate (15 mL). The combined organic layers were washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. Pure products **8** were obtained by flash column chromatography (silica gel, mixture of hexane/ethyl acetate).

Many of the diazo products **5** and **8** are commercially available or have been described previously, and their analytical data matched with literature values. New compounds were characterized on the basis of IR, ^{1}H and ^{13}C NMR data (see Supplementary data).

Acknowledgements

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Supplementary data

General experimental procedures, compound characterization and analytical data (IR, ^{1}H NMR and ^{13}C NMR) for all new compounds. Copies of the IR and ^{13}C NMR spectra of all new compounds. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2008.02.159.

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