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# NOVEL TASK-SPECIFIC IONIC LIQUIDS AS SOLVENTS FOR MICHAEL ADDITION OF METHYLENE ACTIVE COMPOUNDS TO CHALCONES WITHOUT ANY CATALYST

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# **GRAPHICAL ABSTRACT**

no catalyst,rt Solvent:[DBU][Lac]

R<sub>1</sub>=H, CN, CH<sub>3</sub>CO, CH<sub>3</sub>OCO, C<sub>2</sub>H<sub>5</sub>OCO R<sub>2</sub>=CN, COCH<sub>3</sub>, CO<sub>2</sub>CH<sub>3</sub>, CO<sub>2</sub>C<sub>2</sub>H<sub>5</sub>, NO<sub>2</sub> R<sub>3</sub>=H, Cl, CH<sub>3</sub>O, NO<sub>2</sub>, CH<sub>3</sub>

**Abstract** A convenient and facile method for Michael addition of methylene active compounds to chalcones has been developed by using 1,8-diazabicyclo [5.4.0]undec-7-enederived task-specific ionic liquids as reaction medium in the absence of any catalyst. This protocol could afford the Michael adducts in good to excellent yields in a short time, the workup is very simple, and the ionic liquid could be reused six times without significant loss of activity.

Keywords Methylene active compounds; Michael addition; recyclability; task-specific ionic liquid

## INTRODUCTION

Michael addition is one of the most simple, efficient, and atom-economical methodologies for carbon–carbon bond formation, which is central to organic synthesis. It is usually performed in organic solvents in the presence of strong bases that often lead to side reactions. Thus, many more efficient and milder catalysts, including 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD),<sup>[1]</sup> organic–inorganic hybrid catalysts supported on ordered porous structures,<sup>[2]</sup> monomeric La complexes on

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[DBU]X

 [DBU][Tfa]
 X=CF<sub>3</sub>COO

 [DBU][Ac]
 X=CH<sub>3</sub>COO

 [DBU][Lac]
 X=CH<sub>3</sub>CH(OH)COO

 [DBU][*n*-Pr]
 X=CH<sub>3</sub>CH<sub>2</sub>COO

 [DBU][*n*-Bu]
 X=CH<sub>3</sub>CH<sub>2</sub>COO

Figure 1. Structures of the DBU-derived ionic liquids.

apatite surfaces,<sup>[3]</sup> natural phosphate–doped catalyst,<sup>[4]</sup> SmI<sub>3</sub>,<sup>[5]</sup> and imidazolium ionic liquids<sup>[6]</sup> have been developed to catalyze this addition. Moreover, microwave<sup>[7]</sup> and ultrasounic irradiation<sup>[8]</sup> can be used to promote the Michael reaction. However, many of these methods suffer from some disadvantages, such as poor production yields, nonrecyclability of catalysts, and the involvement of some toxic organic solvents including dimethylformamide (DMF) and toluene.

In recent years, ionic liquid (ILs) used as catalysts or/and reaction media have been frequently investigated in organic transformations because of their advantages, such as stability, good solvating ability, nonflammability, variable polarity, and ease of workup.<sup>[9]</sup> However, related reports of using task-specific IL as catalyst as well as reaction solvent for carbon–carbon Michael addition is relatively rare.<sup>[10]</sup> Encouraged by the special, unique properties of ILs and their wide applications in organic synthesis,<sup>[9]</sup> a new type of task-specific ILs were developed through the neutralization of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) with five carbonyl acids, carboxyl acids, trifluoroacetic acid, acetic acid, lactic acid, *n*-propionic acid, and *n*-butyric acid (Fig. 1). These DBU-derived ionic liquids were successfully explored as catalysts for aza-Michael addition<sup>[11]</sup> and Knoevenagel condensation.<sup>[12]</sup> With our continuous efforts to establish simple and environmentally benign methods for organic transformation, herein we investigate Michael addition of methylene active compounds to chalcone with the novel task-specific DBU-base ionic liquids as catalysts as well as green solvents.

### **RESULTS AND DISCUSSION**

First, the Michael addition of malononitrile to chalcone was selected as a model reaction to establish the optimal reaction conditions. Traditional organic solvents DMF, acetone, toluene, and dichloromethane were used as reaction medium for the model reaction in the absence of any catalyst. The adduct yields are not satisfied even after 1 h of reaction (entries 1–4, Table 1). Inert imidazolium ILs were also exploited as solvents, and the reactions proceeded very slowly (entries 5 and 6, Table 1). Thus, our developed DBU-derived ILs were used as solvents without any

 Table 1. Influence of reaction solvents on the Michael reaction between malononitrile and chalcone without any catalyst<sup>a</sup>



Entry	Solvent	Amount of solvent (mL)	Reaction time (min)	Yield <sup>b</sup> (%)
1	DMF	2	60	21
2	Acetone	2	60	16
3	Toluene	2	60	13
4	CH <sub>2</sub> Cl <sub>2</sub>	2	60	6
5	[bmim]BF4	2	60	23
6	[bmim]PF <sub>6</sub>	2	60	43
7	[DBU][Ac]	2	20	82
8	[DBU][Lac]	2	20	85
9	[DBU][Tfa]	2	20	72
10	[DBU][n-Pr]	2	20	82
11	[DBU][ <i>n</i> -Bu]	2	20	77
12	[DBU][Lac]	0.5	20	35
13	[DBU][Lac]	1	20	73
14	[DBU][Lac]	5	20	85

<sup>*a*</sup>Reaction conditions: chalcone (1 mmol) and malononitrile (1 mmol) at rt. <sup>*b*</sup>Isolated yields.

catalyst (Fig. 2). The five ILs [DBU][Ac], [DBU][Lac], [DBU][Tfa], [DBU][*n*-Pr], and [DBU][*n*-Bu] were all suitable media for the reaction between malononitrile and chalcone (entries 6–11, Table 1), which shows the dual role of DBU-derived ILs as both reaction media and promotes. Among the five ILs, the yield obtained in [DBU][Lac] is greatest. Thus, [DBU][Lac] was selected for further experiments. Finally, the amount



Figure 2. The possible reaction route for chalcone and malonontrile.

of IL was also optimized. The yields in 0.5 mL and 1 mL were not so high, because the reaction mixture could not stir well enough (entries 12 and 13, Table 1). With the increase in the amount of [DBU][Lac], comparable product yield was obtained (Entry 13, Table 1). The optimal amount of [DBU][Lac] is 2 mL.

With optimized reaction conditions in hand, the Michael reactions of various methylene active ingredients, including ethyl cyanoacetate, ethyl acetoacetate, methyl acetoacetate, acetylacetone, dimethyl malonate, diethyl malonate, and nitromethane, were also investigated, and the products were isolated in good to excellent yields (>80% yield) (Table 2). Compared to the Michael additions of malononitrile to chalcone, the reactions of ethyl cyanoacetate, ethyl acetoacetate, methyl acetoacetate, acetylacetone, dimethyl malonate, and diethyl malonate with chalcone needed more reaction time with greater yields (entries 1–7, Table 2), which could be because the electron-withdrawing ability of the CN group is much stronger than that of carbonyl or carboxylic groups.

To extend the application scope of this protocol, the addition reactions of malononitrile to a series of substituted chalcones were also conducted, and the results in Table 2 show that the electron-donating groups at the aromatic ring, such as Cl, Me, and OMe prolonged the reaction time. However, compared with NO<sub>2</sub> at the aromatic ring, almost no side product was detected, leading to excellent product

**Table 2.** Results of Michael reaction between various active methylene compounds and chalcones under solvent-free conditions at room temperature<sup>a</sup>

$R_1$ $R_2$ + $R_3$ $R_1$ $R_2$ $R_3$ $R_1$ $R_2$ $R_3$ $R_$								
1		2			3			
Entry <sup>[17]</sup>	$R_1$	$R_2$	$R_3$	Product	Time (min)	$\mathbf{Yield}^{b} (\%)$		
1	CN	CN	Н	3a	5	85		
2	CN	$CO_2C_2H_5$	Н	3b	10	89		
3	CH <sub>3</sub> CO	COCH <sub>3</sub>	Н	3c	25	92		
4	CH <sub>3</sub> CO	$CO_2CH_3$	Н	3d	20	90		
5	CH <sub>3</sub> CO	$CO_2C_2H_5$	Н	3e	25	95		
6	CH <sub>3</sub> OCO	$CO_2CH_3$	Н	3f	40	93		
7	C <sub>2</sub> H <sub>5</sub> OCO	$CO_2C_2H_5$	Н	3g	40	92		
8	Н	$NO_2$	Н	3h	20	88		
9	CH <sub>3</sub> CO	COCH <sub>3</sub>	p-Cl	3i	50	81		
10	CH <sub>3</sub> CO	COCH <sub>3</sub>	p-CH <sub>3</sub> O	3j	400	95		
11	CH <sub>3</sub> CO	COCH <sub>3</sub>	p-NO <sub>2</sub>	3k	20	71		
12	CH <sub>3</sub> CO	COCH <sub>3</sub>	p-CH <sub>3</sub>	31	400	94		
13 <sup>c</sup>	CH <sub>3</sub> CO	COCH <sub>3</sub>	Н	3c	60	46		
14 <sup>d</sup>	CH <sub>3</sub> CO	COCH <sub>3</sub>	Н	3c	24h	85		

<sup>*a*</sup>Reaction conditions: methylene compounds (1.0 mmol), chalcones (1.0 mmol), and 2 mL [DBU][Lac] at rt.

<sup>b</sup>Isolated yield.

<sup>c</sup>Result from Ref. 13.

<sup>*d*</sup>Result from Ref. 14.

Entry	Reaction time (min)	Yield <sup>b</sup> (%)	
1	25	92	
2	25	89	
3	25	90	
4	40	92	
5	40	90	
6	40	87	

**Table 3.** Reuse of ionic liquid [DBU][Lac] as reaction media for the catalyst-free Michael reaction between acetyl acetone and chalcone<sup>a</sup>

<sup>*a*</sup>Reaction conditions: chalcone (1 mmol), acetyl acetone (1 mmol), and [DBU][Lac] (2 mL) without any catalyst at rt.

<sup>b</sup>Isolated yield.

yields (entries 9–12, Table 2). To demonstrate the advantages of this protocol, performance in [DBU][Lac] without catalyst was compared with other reported results (entries 3, 13, and 14, Table 2), using the reaction of acetylacetone and chalcone as a model. From both economic and environmental points of view, it is easy to conclude that the model reaction in [DBU][Lac] performed much better than those using reported methods.

Interestingly, a minor amount of side product benzene 4 was produced when the amount of malononitrile increased from 1.0 mmol to 2.0 mmol. Further, we raised the reaction temperature to  $50 \,^{\circ}$ C and prolonged the reaction time to 3 h. The side product became the major product, and the yield of benzene was 82% (Figure 2). The reason for the formation of benzene is the subsequent Knoevenagel condensation of Michael adduct **3a** with malonontirile, which is then involved in Thorpe–Ziegler cyclization, described in Ref. 15. The result may provide a green and efficient methodology for the preparation of benzene.

Finally, the recyclability of the IL [DBU][Lac] was studied using the reaction of acetyl acetone and chalcone as a model. The results are shown in Table 3. Upon the completion of the reaction, the reaction solution was extracted with ethyl acetate and purified by flash chromatography. The addition product was identified by <sup>1</sup>H NMR and <sup>13</sup>C NMR. The residual IL was washed with ethyl ether, dried under vacuum at 60 °C for 2 h, and reused for subsequent reactions. As shown in Table 3, the recovered IL could be used six times without obvious loss of promoting activity of the IL. After reusing the IL three times, the reaction time was prolonged because of some slight loss of IL in the workup process (entries 4–6, Table 3).

#### CONCLUSIONS

In conclusion, we have developed five task-specific ILs, [DBU][Lac], [DBU][Ac], [DBU][Tfa], [DBU][*n*-Pr], and [DBU][*n*-Bu]. The ILs were then used as reaction media as well as promoters for Michael addition of malononitrile to chalcone. Among the five ILs, [DBU][Lac] was found to be the most suitable for the reaction. Using [DBU][Lac] as solvent without any additional catalyst, various methylene active compounds were subjected to substituted chalcones, and good to excellent yields were obtained. This protocol also has some advantages, such as easy workup of

the reactions, excellent reaction selectivity, and good recyclability of the IL (reused six times without significant loss of activity).

## **EXPERIMENTAL**

All chemicals were purchased from Aldrich or Fluka. <sup>1</sup>H and <sup>13</sup>C NMR were recorded on a Bruker Avance DPX 400 spectrometer at 400 MHz and 100 MHz in CDCl<sub>3</sub> and D<sub>2</sub>O, respectively. Chemical shifts were reported in parts per million ( $\delta$ ), relative to the internal standard of tetramethylsilane (TMS). Melting points were determined using a YRT-3 apparatus. Elemental analysis was carried out on a Carlo Erba 1160. All reactions were monitored by thin-layer chromatography (TLC). Flash chromatography was performed on silica gel (100–200 mesh). All Michael adducts were purified through column chromatography and were characterized by NMR analysis and melting points.

# General Procedure for Preparation of Ionic Liquids [DBU][Lac], [DBU][Ac], [DBU][Tfa], [DBU][*n*-Pr], and [DBU][*n*-Bu]

DBU (6 mmol) was added to a 50-mL, three-necked flask cooled by an ice bath. Carboxylic acid (6 mmol) was then added dropwise at  $\leq$ 5 °C with thorough mixing. After dropwise addition and removal of the ice bath, the reaction mixture was stirred at room temperature for 24 h. The oil residue was dried in vacuo at 60 °C for 24 h to afford the desired ionic liquid as a light-yellow, viscous liquid.

## **Spectral Data of Novel Ionic Liquids**

**[DBU][Lac].** <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O):  $\delta = 3.93$  (q, 1H, J = 6.8 Hz, CH), 3.57–3.52 (m, 2H, 9-H), 3.47–3.44 (m, 2H, 11-H), 3.28–3..23 (m, 2H, 2-H), 2.73–2.70 (m, 2H, 6-H), 1.93–1.87 (m, 2H, 10-H), 1.67–1.54 (m, 6H, 3-H, 4-H, 5-H), 1.09 (d, 3H, J = 6.8 Hz, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O):  $\delta = 177.8$ , 165.5, 67.2, 53.4, 48.0, 36.7, 31.5, 28.4, 26.2, 23.7. Anal. calcd. for [DBU][Lac]: C, 59.35; H, 9.21; N, 11.49; O, 19.95. Found: C, 59.48; H, 9.15; N, 11.56; O, 19.81.

**[DBU][Ac].** <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O):  $\delta = 3.50-3.48$  (m, 2H, 9-H), 3.44–3.41 (m, 2H, 11-H), 3.23–3.20 (m, 2H, 2-H), 2.75–2.72 (m, 2H, 6-H), 1.89–1.83 (m, 2H, 10-H), 1.68–1.51 (m, 6H, 3-H, 4-H, 5-H), 1.63 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O):  $\delta = 174.4$ , 165.2, 53.1, 47.9, 37.8, 31.2, 28.6, 26.5, 25.1, 24.0, 19.5. Anal. calcd. for [DBU][Ac]: C, 62.10; H, 9.55; N, 13.11; O, 15.24. Found: C, 62.23; H, 9.50; N, 13.20; O, 15.07.

**[DBU][Tfa].** <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O):  $\delta = 3.55-3.42$  (m, 8H, 9-H, 11-H, 2-H), 2.79–2.77 (m, 2H, 6-H), 2.07–2.01 (m, 2H, 10-H), 1.76–1.70 (m, 6H, 3-H, 4-H, 5-H); <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O):  $\delta = 166.2$ , 118.4, 115.5, 54.3, 48.5, 38.0, 32.3, 28.9, 26.6, 23.8, 19.3. Anal. calcd. for [DBU][Tfa]: C, 49.54; H, 6.51; N, 10.45; F, 21.37; O, 12.13. Found: C, 49.62; H, 6.44; N, 10.52; F, 21.41; O, 12.01.

**[DBU][n-Pr].** <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O):  $\delta = 3.49-3.47$  (m, 2H, 9-H), 3.43–3.40 (m, 2H, 11-H), 3.23–3.21 (m, 2H, 2-H), 2.76–2.73 (m, 2H, 6-H), 1.92–1.88

(m, 2H, 10-H), 1.65–1.58 (m, 6H, 3-H, 4-H, 5-H), 1.50 (q, 3H, J=7.2 Hz, CH<sub>2</sub>), 0.90 (t, 3H, J=7.2 Hz, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O):  $\delta$ =177.1, 165.0, 53.0, 47.9, 44.8, 37.9, 30.7, 28.6, 26.5, 24.0, 19.5, 11.3. Anal. calcd. for [DBU][*n*-Pr]: C, 63.60; H, 9.88; N, 12.35; O, 14.17. Found: C, 63.69; H, 9.80; N, 13.38; O, 14.13.

**[DBU][n-Bu].** <sup>1</sup>H NMR (400 MHz, D<sub>2</sub>O):  $\delta = 3.50-3.48$  (m, 2H, 9-H), 3.43–3.41 (m, 2H, 11-H), 3.22–3.20 (m, 2H, 2-H), 2.76–2.75 (m, 2H, 6-H), 1.89–1.85 (m, 2H, 10-H), 1.84–1.81 (m, 2H,CH<sub>2</sub>), 1.65–1.57 (m, 6H, 3-H, 4-H, 5-H), 1.47–1.42 (m, 2H,CH<sub>2</sub>), 0.82 (t, 3H, J = 7.6 Hz, CH<sub>3</sub>); <sup>13</sup>C NMR (100 MHz, D<sub>2</sub>O):  $\delta = 176.4$ , 165.0, 53.0, 47.9, 37.9, 31.0, 29.3, 28.5, 26.5, 24.0, 23.2, 19.5, 14.4. Anal. calcd. for [DBU][*n*-Bu]: C, 64.88; H, 10.12; N, 11.58; O, 13.42. Found: C, 64.97; H, 10.06; N, 11.66; O, 13.31.

# General Procedure for Michael Reaction of Methylene Active Compounds with Chalcones

To a mixture of methylene active compounds (1 mmol) and chalcone (1 mmol) in a 10-mL flask equipped with a magnetic stirrer was added IL [DBU][Lac] (2 mL). The reaction mixture was stirred at room temperature for the desired time until the disappearance of the starting material, as monitored by TLC. Upon completion of the reaction, the mixture was extracted with ethyl acetate several times. The combined organic phase was concentrated through vacuum evaporation, and the resulting crude product was purified by silica column chromatography to give the desired product. These products are in good agreement with the spectral data in the literature. The IL [DBU][Lac] after extraction was dried in vacuo at 60 °C for 5 h. The recovered IL was then reused in subsequent reactions.

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