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DBU-Based Dicationic Ionic Liquids Promoted Esterification Reaction of Carboxylic Acid with Primary Chloroalkane Under Mild Conditions

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Abstract A series of DBU-based (DBU = 1, 8-diazabicyclo [5.4.0] undec-7-ene) dicationic ionic liquids with different anions were successfully synthesized by the reaction of DBU and 1, 6-dichlorohexane. Therein, the dicationic ionic liquid 1, 1′-(hexane-1, 6-diyl)bis(1, 8-diazabicyclo [5.4.0]undec-7-enium) dichlorine (**IL-1**) was successfully employed as an efficient catalyst in esterification reaction of carboxylic acids with primary chloroalkanes under mild conditions without any additional basic reagents. Moreover, the optimum catalyst could be efficiently reused for five times without any significant change on the catalytic effect. The improved protocol is not only efficient, but also green and pollution-free.

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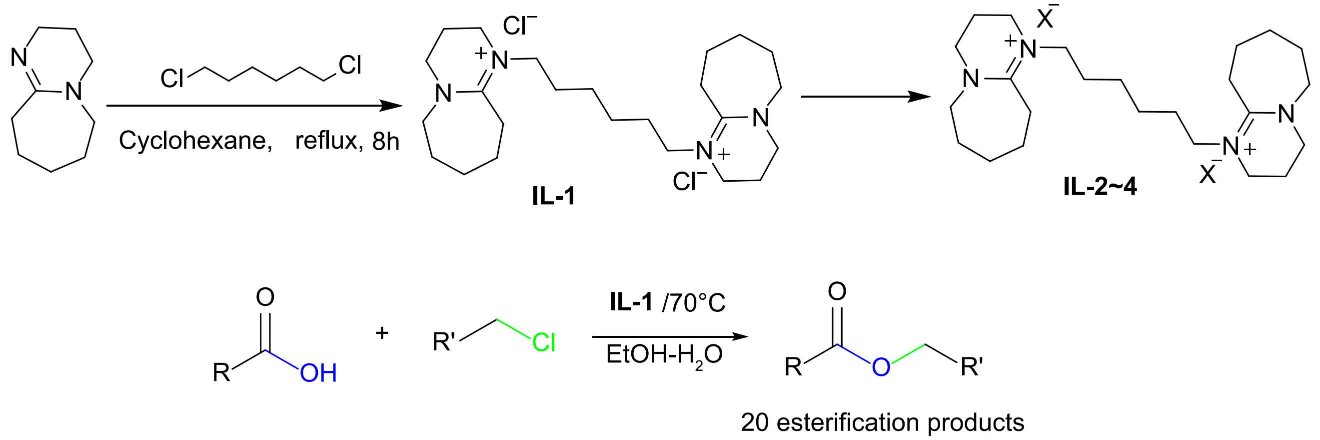
Graphical Abstract



Keywords DBU-based dicationic ionic liquids · Halides · Esterification reaction · Carboxylic acid · Primary chloroalkane

1 Introduction

Esters are widely used in chemical fields such as fragrances, polyester, plasticizer pharmaceutical [1, 2] natural products [3, 4] and etc. Therefore, esterification reaction has become one of the most frequently used reactions in organic chemistry. Wherein, in the presence of base, the reaction of carboxylic acids with halogenated alkanes is one of the main esterification methods. Compared with bromoalkanes and iodoalkanes, the utility of chloroalkane could reduce the cost of reaction and achieve the objective of atom economy besides low reaction activity. In addition, different kinds of bases such as K_2CO_3 [5], CsF [6], triethylamine (Et_3N) [7], hexamethylenetetramine (HMTA) [8], tetramethyl- ammonium hydroxide (TMAH) [9] have been tested and reported. Although these methods have showed efficient catalytic effect, some problems still need to be solved as environmental pollution, toxicity of base, high boiling point solvents as well as harsh reaction conditions. Therefore, it is necessary to develop an efficient and green strategy for esterification.

Some studies have showed that the ionic environment from ionic liquids (ILs) is helpful for the formation of reactive intermediates for different nucleophilic reactions [10, 11]. ILs are used as important reaction media for their various unique properties such as high thermal stability, nonvolatility, low vapour pressure, miscibility and reusability [12, 13]. These specific properties are dependent on their structure and compositions of ions, hence ILs are also mentioned as "designer solvents and/or catalysts" [14, 15]. The utility of ionic liquids not only greatly reduced the use of different hazardous and polluting organic solvents but also improved efficient catalytic activity. Compared with the monocationic ILs, the dicationic ILs showed better designability because different types of substrates could be used to form corresponding cationic part and different functional groups could be also introduced into the spacer [16–19], meanwhile, the anionic moiety might be consisted of different organic and inorganic components. So the dicationic ionic liquids exhibited a better application prospect [20]. Some applications of the dicationic ILs achieved better reaction effect in the esterification of carboxylic acids with primary chloroalkanes and the corresponding experimental results also indicated the ionic liquids' capability on solubility besides catalytic activity [21–24]. However, these catalytic systems still required the aid of basic reagents. So the requirement of basic dicationic ILs with high catalytic performance is obvious.

DBU as superbase was successfully synthesized into different monocationic type and dicationic type ionic liquids. Various property studies proved the advantages and uniqueness of DBU-based ionic liquids [25, 26]; meanwhile efficient catalytic activity was observed in different nucleophilic reactions as Knoevenagel condensation reaction [27], aza-Michael addition reaction [28], etc. During the investigation of this work, a series of DBU-based dicationic ILs were synthesized and applied to develop a facile, efficient and recyclable strategy for esterification of carboxylic acids and primary chloroalkanes under mild conditions without any additional basic reagents. The synthesized dicationic ILs not only acted as a catalyst, but also acted as a solubilizing agent for starting materials and products. Moreover, applicability and recyclability of the optimum catalytic system was also studied.

2 Experimental

2.1 General

All reagents and chemicals purchased from Aladdin or Alfa Company was of analytical grade and used without purification. And 1-ethyl-1,8-diazabicyclo [5.4.0]undec-7-enium chloride ([EtDBU]Cl), 1-butane-1,8-diazabicyclo [5.4.0]undec-7-enium chloride ([BuDBU]Cl), 1-hexane-1,8-diazabicyclo [5.4.0]undec-7-enium chloride ([HDBU]Cl), [1,1′-(ethyl-1,4-diyl)-bis(1,8- diazabicyclo[5.4.0]undec-7-ene)]dichlorine ($[C_2(DBU)_2]Cl$), [1,1′-(butane-1,4- diyl)-bis(1,8-diazabicyclo[5.4.0]undec-7-ene)]dichlorine($[C_4(DBU)_4]Cl$),1-hexy-l-(1,8-diazabicyclo[5.4.0]undec-7-enium)tetrafluoroborate ($[HDBU]BF_4$), tetrabutyl -ammonium acetate ([TBA][Ac]), 1-butyl-3-methylimidazolium proline ([bmim][Pro]) and 1,1′-Hexane-1,6-diylbis(3-methylpyridinium)dichlorine ($[C_6(Mpy)_2]Cl$) were obtained from commercial sources. The esterification reactions were monitored by TLC (silica gel). All the NMR spectra of synthesized ILs were characterized using D_2O or $CDCl_3$ as solvent at room temperature on a Bruker Avance-400 spectrometer. High resolution mass spectra were recorded on ThermoScientific XSeries^{II} ICP-MS mass spectrometer. The elemental analysis test was accomplished on a SPECTRO ARCOS elemental analyzer operation. And thermogravimetric analyses (TGA) of synthesized ILs was accomplished on Scinco TGA N-100 instrument with a heating rate of 10 °C/min^{-1} under nitrogen atmosphere. The pH values of the solutions of the catalytic system were tested using METTLER TOLEDO SevenCompact™ pH meter. All the esterification products were purified by column chromatography and characterized by ^{1}H-NMR spectroscopy.

2.2 Synthesis of DBU-Based Dicationic ILs

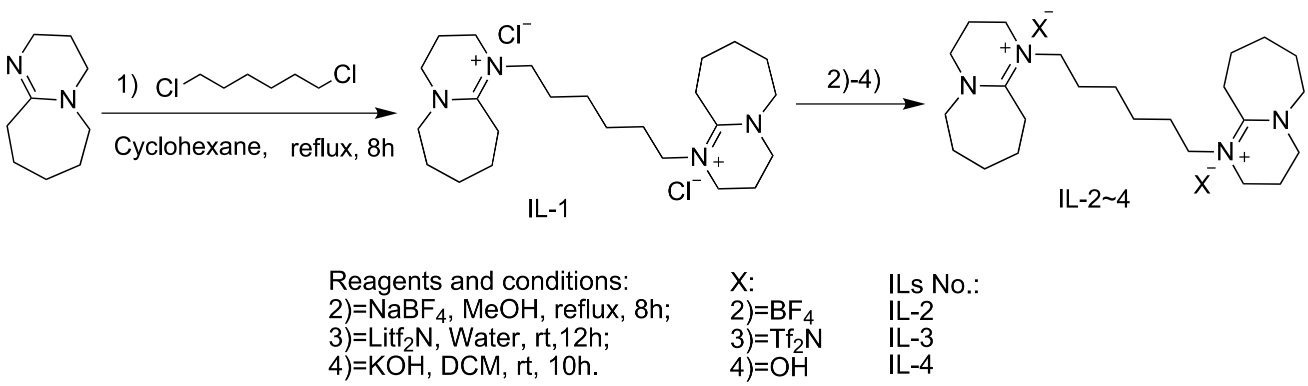
The specific synthetic procedures of DBU-based dicationic ILs were executed according to Scheme 1 and the details were as follows [29–31].

2.2.1 *Synthesis of 1, 1′-(hexane-1, 6-diyl)bis(1, 8-diazabicyclo [5.4.0]undec-7-enium) dichlorine (**IL-1**)*

DBU (68.88 mmol, 10.30 mL) and 1,6-dichlorohexane (34.44 mmol, 5.00 mL) were charged with 40 mL cyclohexane in a 100 mL two necked flask and stirred at room temperature, then raised to reflux temperature for 8 h in water bath under nitrogen atmosphere. White solid precipitate was formed. When the reaction was over, the white solid was collected by filtration, washed with ethyl acetate (3 × 10 mL) and dried under vacuum oven at 50 °C for 5 h. White solid; Yield 93%; ^{1}H NMR (400 MHz, D_2O) $\delta = 3.61–3.53$ (m, 4H), 3.45 (dq, $J = 12.7$, 6.1 Hz, 12H), 2.87–2.70 (m, 4H), 2.01 (t, $J = 5.9$ Hz, 4H), 1.66 (dtd, $J = 18.4$, 14.1, 12.0, 6.7 Hz, 16H), 1.38–1.28 (m, 4H); ^{13}C NMR (100 MHz, D_2O) $\delta = 166.4$, 54.6, 53.4, 48.8, 46.9, 28.1, 27.84, 27.8, 25.6, 25.5, 22.8, 19.7; FT-IR (KBr, cm^{-1}): 2927, 2863, 1617, 1467; HRMS calcd for (M-2Cl)/2: 194.1777; found: 194.1781. Elem. anal. calc. (%) for $C_{24}H_{44}Cl_2N_4$: C, 62.73; H, 9.65; Cl, 15.43; N, 12.19; found: C, 62.71; H, 9.66; Cl, 15.41; N, 12.22.

2.2.2 *Synthesis of 1, 1′-(hexane-1, 6-diyl)bis(1, 8-diazabicyclo[5.4.0] undec-7-enium) double tetrafluoroborate (**IL-2**)*

Sodium tetrafluoroborate (21.76 mmol, 2.39 g) was dissolved in 20 mL methanol and **IL-1** (10.88 mmol, 5 g) was added slowly into the flask under stirring. Then the mixture was refluxed for 8 h and sodium bromide was filtered off. Removed methanol on a rotary evaporator and dried the



Scheme 1 Synthesis of DBU-based dicationic ILs

obtained **IL-2** under vacuum oven at 60 °C for 3 h. White solid; Yield 87%; ^{1}H NMR (400 MHz, D_2O) $\delta = 3.66–3.53$ (m, 4H), 3.46 (dq, $J = 12.5$, 6.0 Hz, 12H), 2.88–2.72 (m, 4H), 2.01 (t, $J = 5.9$ Hz, 4H), 1.67 (dq, $J = 21.9$, 8.2, 7.2 Hz, 16H), 1.42–1.26 (m, 4H); 13C NMR (100 MHz, D2O) $\delta = 166.4$, 54.6, 53.4, 48.8, 46.9, 28.1, 27.9, 27.8, 25.6, 25.5, 22.8, 19.7; FT-IR (KBr, cm^{-1}): 2920, 2861, 1617, 1057; HRMS calcd for $(M\text{-}2BF_4)/2$: 194.1777; found: 194.2007. Elem. anal. calc. (%) for $C_{24}H_{44}B_2F_8N_4$: C, 51.27; H, 7.89; N, 9.96; found: C, 51.26; H, 7.90; N, 9.67.

2.2.3 *Synthesis of 1, 1'-(hexane-1, 6-diyl)bis(1, 8-diazabicyclo[5.4.0] undec -7-enium) double bis(triflic) imide (**IL-3**)*

Add bis (trifluoromethane) sulfonamide lithium salt (21.76 mmol, 6.25 g) into 30 mL deionized water. And **IL-1** (10.88 mmol, 5 g) was added slowly into the flask. Then the mixture was kept stirring for 12 h and new precipitate was formed. The target dicationic ionic liquid was filtrated, washed with deionized water and dried under a vacuum oven at 70 °C for 6 h. White solid, Yield 83%; 1H NMR (400 MHz, $CDCl_3$) $\delta = 3.81–3.25$ (m, 16H), 2.80 (d, $J = 24.4$ Hz, 4H), 2.09 (d, $J = 19.3$ Hz, 4H), 1.85–1.29 (m, 20H); 13C NMR (101 MHz, $CDCl_3$) $\delta = 166.7$, 121.5, 118.3, 55.3, 54.4, 49.1, 47.1, 28.5, 28.2, 28.0, 26.0, 25.8, 22.9, 19.8; FT-IR (KBr, cm^{-1}): 2948, 2865, 1620, 617; HRMS calcd for $(M\text{-}2Tf_2N)/2$: 194.1777; found: 194.1777. Elem. anal. calc. (%) for $C_{28}H_{44}F_{12}N_6O_8S_4$: C, 35.44; H, 4.67; N, 8.86; S, 13.51; found: C, 35.43; H, 4.66; N, 8.87; S, 13.52.

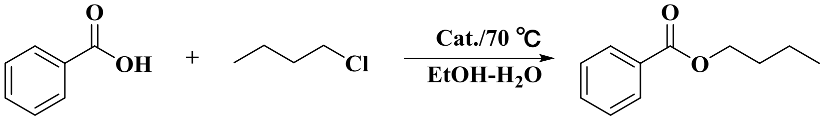
2.2.4 *Synthesis of 1, 1'-(hexane-1, 6-diyl)bis(1, 8-diazabicyclo[5.4.0]undec -7-enium) double hydroxyl (**IL-4**)*

After dissolving **IL-1** (10.88 mmol, 5 g) in 20 mL dichloromethane, potassium hydroxide (21.76 mmol, 1.22 g) was added into the solution. Then the mixture was kept stirring for 10 h at room temperature. The ion exchange process was completed; the mixture was filtered to remove the inorganic salt. After that, the residue obtained from removing dichloromethane was washed with ether and dried at 70 °C under vacuum for 5 h. White paste, Yield 83%; 1H NMR (400 MHz, D2O) $\delta = 3.61–3.54$ (m, 4H), 3.44 (dt, $J = 12.7$, 5.0 Hz, 12H), 2.90–2.68 (m, 4H), 2.01 (d, $J = 5.9$ Hz, 4H), 1.75–1.59 (m, 16H), 1.32 (d, $J = 3.9$ Hz, 4H); 13C NMR (100 MHz, D2O) $\delta = 166.4$, 54.6, 53.4, 48.8, 46.9, 28.1, 27.8, 27.8, 25.6, 25.5, 22.8, 19.7; FT-IR (KBr, cm^{-1}): 3370, 2936, 2854, 1616; HRMS calcd for (M-2OH)/2: 194.1777; found: 194.1777. Elem. anal. calc. (%) for $C_{24}H_{46}N_4O_2$: C, 68.20; H, 10.97; N, 13.26; found: C, 68.19; H, 10.98; N, 13.25.

2.3 Typical Procedure for Esterification Reaction

Carboxylic acids (1.00 mmol), primary chloroalkanes (1.20 mmol) and **IL-1** (0.30 mmol) were added respectively into a two necked flask equipped with 6 mL 50% aqueous ethanol solution under stirring, then raised the system temperature to 70 °C for a needed time in water bath. The progress of the reaction was monitored using thin layer

Table 1 Evaluation of the optimal catalysts and reaction temperature in the esterification reaction



Entry	Catalyst	Amount of catalyst (mol%)	T (°C)	Yield (%)[a]
1	–	–	70	–
2	IL-1	30	70	92
3	IL-2	30	70	84
4	IL-3	30	70	86
5	IL-4	30	70	88
6	IL-1	10	70	68
7	IL-1	20	70	81
8	IL-1	40	70	92
9	IL-1	30	50	74
10	IL-1	30	60	86
11	IL-1	30	80	92

Reaction conditions: benzoic acid (1.00 mmol), 1-chlorobutane (1.20 mmol), 50% aqueous ethanol solution (6 mL), reaction time 2 h

[a]Isolated yields

Table 2 Evaluation of the optimum solvent system in the esterification reaction

Entry	Solvent	Yield (%)[a]
1	H_2O	56
2	10% aqueous ethanol	64
3	20% aqueous ethanol	73
4	30% aqueous ethanol	81
5	40% aqueous ethanol	87
6	50% aqueous ethanol	92
7	60% aqueous ethanol	92

Reaction conditions: benzoic acid (1.00 mmol), 1-chlorobutane (1.20 mmol), 30 mol% of IL catalyst, solvent (6 mL), reaction time 2 h at 70 °C

[a] Isolated yields

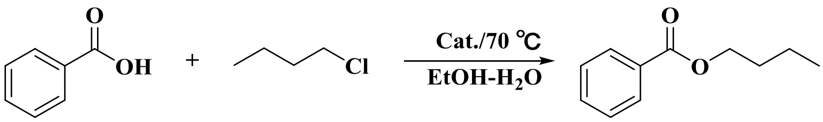
chromatography (TLC). When the reaction was over, the reactor was cooled down to room temperature. The mixture was diluted with water (10 mL) and extracted with ethyl acetate (3 × 5 mL), the extract was dried over anhydrous Na_2SO_4, filtered, and concentrated in a rotary evaporator to collect target product. Meanwhile, the reborn catalyst could be applied in the next cycle was after removing the solvent and dried at 80 °C under vacuum for 6 h. All the esterification products were further purified by column chromatography or distillation. The yields varied from 67 to 93% (Table 1).

3 Results and Discussion

3.1 Catalytic Study

Initially, the esterification reaction of benzoic acid with 1-chlorobutane was carried out as model reaction to evaluate the optimal IL catalyst as well as the reaction conditions and corresponding experimental results were summarized in Table 1. The experimental results indicated that there was no formation of product without catalyst (Table 1, entry 1). And good yields were obtained with DBU-based dicationic ILs as catalysts. It confirmed the efficient catalytic activity and solubilization of these catalysts. Compared with these synthesized catalysts, **IL-1** seemed to be with better catalytic activity and gave a high yield of 92% (Table 1, entries 2–5). After the optimum catalyst was confirmed, the amount of catalyst and the most appropriate reaction temperature was further explored. When the amount of **IL-1** was increased from 10.0 to 40.0 mol%, a high yield of 92% was obtained at 30.0 mol%, while a higher amount of catalyst didn't gave a higher yield (Table 1, entries 2, 6–8). Similarly, a high yield was obtained at 70 °C when the reaction temperature was

Table 3 Comparison results of the optimum catalyst with other catalysts

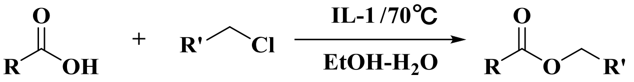


Entry	Catalyst	Amount of catalyst (mol%)	Yield (%)[a]
1	**IL-1**	30	92
2	DBU	30	74
3	([EtDBU]Cl)	60	61
4	([BuDBU]Cl)	60	64
5	[HDBU]Cl	60	67
6	$[C_2(DBU)_2]Cl$	30	85
7	$[C_4(DBU)_4]Cl$	30	89
8	$[HDBU]BF_4$	60	57
9	[TBA][Ac]	60	47
10	[bmim][Pro]	60	42
11	$[C_{6(}Mpy)_2]Cl$	30	61

Reaction conditions: benzoic acid (1.00 mmol), 1-chlorobutane (1.20 mmol), 50% aqueous ethanol solution (6 mL), 70 °C reaction time 2 h, 1-ethyl-1,8-diazabicyclo[5.4.0]undec-7-enium chloride ([EtDBU]Cl), 1-butane-1,8-diazabicyclo[5.4.0]undec-7-enium chloride ([BuDBU]Cl), 1-hexane-1,8-diazabicyclo[5.4.0] undec-7-enium chloride ([HDBU]Cl), [1,1′-(ethyl-1,4-diyl)-bis(1,8-diazabicyclo[5.4.0] undec-7-ene)]dichlorine ([C2(DBU)2]Cl), [1,1′-(butane-1,4-diyl)-bis(1,8-diazabicyclo[5.4.0]undec-7-ene)] dichlorine ([C4(DBU)4]Cl), 1-hexyl-(1,8-diazabicyclo [5.4.0]undec-7-enium)tetrafluoroborate ([HDBU]BF4), tetrabutylammonium acetate ([TBA][Ac]), 1-butyl-3-methylimidazolium proline ([bmim][Pro]). and 1,1′-hexane-1,6-diylbis (3-methylpyridinium) dichlorine ([C6(Mpy)2]Cl

[a] Isolated yields

Table 4 Esterification of carboxylic acids with chlorinated hydrocarbons



Entry	R	R′	Products	Time (h)	Yield (%)[a]
1	Ph–	$–CH_3$	$PhCOOCH_2CH_3$	2	94, 96[b], 97[c]
2	Ph–	$–CH_2CH_3$	$PhCOO(CH_2)_2CH_3$	2	93
3	Ph–	$–CH_2CH_2CH_3$	$PhCOO(CH_2)_3CH_3$	2	92
4	Ph–	$–CH(CH_3)_2$	$PhCOOCH_2CH(CH_3)_2$	2	52
5	Ph–	$–(CH_3)_3$	$PhCOOC(CH_3)_3$	2	29
6	Ph–	Ph–	$PhCOOCH_2Ph$	2	89
7	$4–NO_2– C_6H_4–$	$–CH_3$	$4–NO_2– C_6H_4COOCH_2CH_3$	2	95
8	$4–NO_2– C_6H_4–$	$–CH_2CH_2CH_3$	$4–NO_2– C_6H_4COO(CH_2)_2CH_3$	2	93
9	$3–Cl– C_6H_4–$	$–CH_3$	$3–Cl– C_6H_4COOCH_2CH_3$	2	87
10	$3–Cl– C_6H_4–$	$–CH_2CH_2CH_3$	$3–Cl– C_6H_4COO(CH_2)_3CH_3$	2	84
11	$2–HO– C_6H_4–$	$–CH_2CH_3$	$2–HO– C_6H_4COO(CH_2)_2CH_3$	2.5	67
12	$3,5–NO_2– C_6H_3–$	$–CH_3$	$3,5–NO_2– C_6H_3COOCH_2CH_3$	2.2	77
13	PhCH=CH–	$–CH_3$	$PhCH{=}CHCOOCH_2CH_3$	2.2	90
14	PhCH=CH–	$–CH_2CH_3$	$PhCH{=}CHCOO(CH_2)_2CH_3$	2.2	88
15	PhCH=CH–	$–(CH_2)_2CH_3$	$PhCH{=}CHCOO(CH_2)_3CH_3$	2.2	87
16	PhCH=CH–	Ph–	$PhCH{=}CHCOOCH_2Ph$	2.2	84
17[d]	$4–HOOC– C_6H_4–$	$–CH_3$	$1,4– C_6H_4 (COOCH_2CH_3)_2$	3	79
18[d]	$4–HOOC– C_6H_4–$	$–CH_2CH_2CH_3$	$1,4– C_6H_4 (COOCH_2CH_2CH_3)_2$	3	77
19[e]	Ph–	$–CH_2Cl$	$PhCOO(CH_2)_2OCOPh$	4	63
20[e]	Ph–	$–(CH_2)_5Cl$	$PhCOO(CH_2)_6OCOPh$	4	62
21	$–CH_3$	$–CH_2CH_2CH_3$	$CH_3COO(CH_2)_3CH_3$	3.8	67
22[d]	$HOOCCH_2–$	$–CH_3$	$CH_2(COOCH_2CH_3)_2$	4.2	65

All reactions were carried out on carboxylic acid (1.00 mmol), primary chloroalkane (1.20 mmol), **IL-1** (0.30 mmol), 50% aqueous ethanol solution (6 mL) at 70 °C

[a] Isolated yields

[b] The yield from bromoethane

[c] The yield from iodoethane

[d] The scale of chloroethane and chlorobutane was 2.20 mmol

[e] The scale of benzoic acid was 2.00 mmol

raised from 50 to 80 °C, and the yield had no increase at a higher temperature (Table 1, entries 2, 9–11).

Following, the optimum solvent system was investigated and the corresponding results were shown in Table 2. It could be observed that there was a significant increase on yield with addition of ethanol (Table 2, entries 1–7). A high yield of 92% was obtained in 50% aqueous ethanol solution, while the yield had no further increase in higher content of aqueous ethanol (Table 2, entries 6 and 7).

Under optimum reaction conditions, some other catalysts were screened and the corresponding experimental results were summarized in Table 3. It could be found that the recyclable catalyst **IL-1** has shown much better catalytic activity than DBU (Table 3, entries 1 and 2). Then, different type

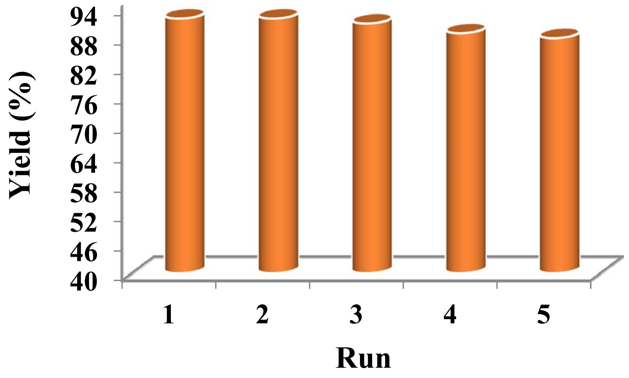


Fig. 1 Recyclability of the optimum catalytic system

Table 5 The pH values of every time in recycle experiments

Recycle time	0	1	2	3	4	5
pH[a]	8.59	8.59	8.59	8.57	8.45	8.21

Reaction conditions: benzoic acid (1.00 mmol), 1-chlorobutane (1.20 mmol), 50% aqueous ethanol solution (6 mL), 70 °C reaction time 2 h

[a] pH values were determined at 25 °C with the solution system containing **IL-1** of different recycle time

DBU-based ionic liquids catalysts were tested and the results confirmed a high catalytic performance of **IL-1** (Table 3, entries 1, 3–8). Meanwhile, the dicationic ionic liquids have showed better catalytic ability than monocationic ones. Moreover, some other traditional basic ionic liquids were found to be inferior to DBU-based ionic liquids on nucleophilic reaction especially esterification reaction (Table 3, entries 1, 9–11).

Since the optimum reaction conditions were determined, a variety of aromatic or aliphatic acids with different primary chloroalkanes were chosen as substrates for further study and the experimental results were presented in Table 4. Primarily, the experiments of aromatic acids with different substituents were executed. The reactions of benzoic acid gave good yields, whereas there was only a slight decrease of the yield with an increase in the length of chain alkanes (Table 4, entries 1–4). Compared to iodoethane (97%) and bromoethane (96%), chloroethane gave a slightly low yield (94%) (Table 4, entry 1). While compared to *n*-chlorobutane (92%), the yields of *sec*-butyl chloride and *tert*-butyl chloride decreased obviously to 52% and 29%, respectively (Table 4, entries 3–5). The esterification reactions of substituted benzoic acids with $–NO_2$, –OH and –Cl were also executed (Table 4, entries 7–12). It could be found the yields of nitrobenzoate (95%) and butyl nitrobenzoate (93%) were higher than the corresponding benzoic acid esterification products because of the presence of electron withdrawing groups (Table 4, entries 7, 8). Meanwhile, relatively lower yields of 3-chloro benzoic acid esterification products were obtained and the yields of ethyl chlorobenzoate and butyl chlorobenzoate were 87% and 84%, respectively (Table 4, entries 9, 10). Similar yields of 2-hydroxy and 3, 5-dinitro benzoic acid esterification products were obtained in 67 and 77%, respectively (Table 4, entries 11, 12). Then, good catalytic activity was also demonstrated in the esterification of cinnamic acid and the yields of two terephthalic acid esterification products were 79 and 77%, respectively (Table 4, entries 13–18). Besides, the reactions of benzoic acid with 1, 2-dichloroethane and 1, 6-dichlorohexane were proceed smoothly, and the desired diesters were obtained in the yields of 63 and 62%, respectively (Table 4, entries 19 and 20). Similarly, the aliphatic esterification products butyl acetate (67%) and diethyl malonate (65%) were also achieved in moderate yields (Table 4, entries 21 and 22). Thence, the protocol showed good catalytic activity for the esterification of different carboxylic acids and primary chloroalkanes under optimum reaction conditions.

3.2 Recyclability Test of the Optimum Catalytic System

A good recyclability of the catalytic system could not only make the reaction process much greener, but also realize economic feasibility and sustainable development. The recyclability test was studied using the model esterification reaction of benzoic acid with 1-chlorobutane under optimum conditions. When the reaction was over, the mixture was diluted with water (10 mL) and extracted with ethyl acetate (3×5 mL). And the catalyst was recovered after removing the solvent and dried at 80 °C under vacuum for 6 h. Then it could be treated as reborn catalyst and used in next run. As shown in Fig. 1, the yield of target product under optimum conditions didn't show significant change even after five runs, which indicated that the catalyst had almost no loss and the catalytic effect was less affected in recyclable catalytic system. Therefore, **IL-1** could be used as a stable and efficient catalyst for the esterification of the carboxylic acid and primary chloroalkane.

Moreover, the pH values of the recycle experiments were investigated and the results indicated pH value didn't change too much during the recyclability test (Table 5).

4 Conclusions

In conclusion, several DBU-based dicationic ILs with different anions were successfully synthesized and screened catalytic activity in esterification reaction of carboxylic acids with primary chloroalkanes under mild conditions without addition of any basic additives. The optimal protocol using **IL-1** as catalyst showed good catalytic effect with various substrates compared to traditional methods, and the after-treatment was simple. The catalyst was easy to be recycled, and the yields did not change significantly after reusing for five times.

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