

## Efficient Esterification of Ferrocenecarboxylic Acid in Ionic Liquids

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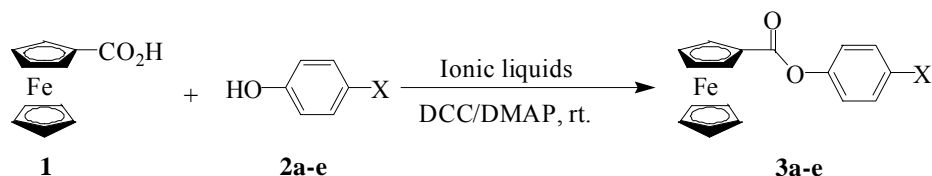
**Abstract:** An efficient esterification of ferrocenecarboxylic acid with substituted phenols has been achieved using DCC / DMAP protocol in ionic liquids. The corresponding esters are produced in high yields.

**Keywords:** Esterification, ferrocenecarboxylic acid, DCC / DMAP, ionic liquid.

The esterification of substituted phenols using anhydrides or acyl halides as the esterifying agent is one of the most routinely used transformation in organic synthesis. While this method was applied in the synthesis of ferrocenyl esters, the yield was poor mainly due to the decomposition of ferrocene ring under acidic condition. In order to avoid the decomposition, a mild reaction condition should be applied. In this paper, we describe the method for the esterification using 1, 3-dicyclohexylcarbodiimide (DCC)/ N,N-dimethylaminopyridine (DMAP) methodology<sup>1</sup>. However, this reaction is usually carried out in organic solvents, such as dichloroethane and benzene, whose toxic and hazardous properties limited the use of this reaction in industrial processes.

In recent years, ionic liquids have received great attention in chemistry because they have been shown to function as green reaction media<sup>2,3</sup>. With the desire to avoid the use of toxic organic solvent, we decided to carry out the esterification in ionic liquids, namely N-butyl-pyridinium bromide ([BPy][Br]) and N-hexyl-pyridinium bromide ([HPy][Br]). These ionic liquids were chosen for their good properties (such as stability, good capacity for organic substrates, *etc.*), the ease of preparation and in economic point of view.

**Scheme 1** Esterification of ferrocenylcarboxylic acid and substituted phenols

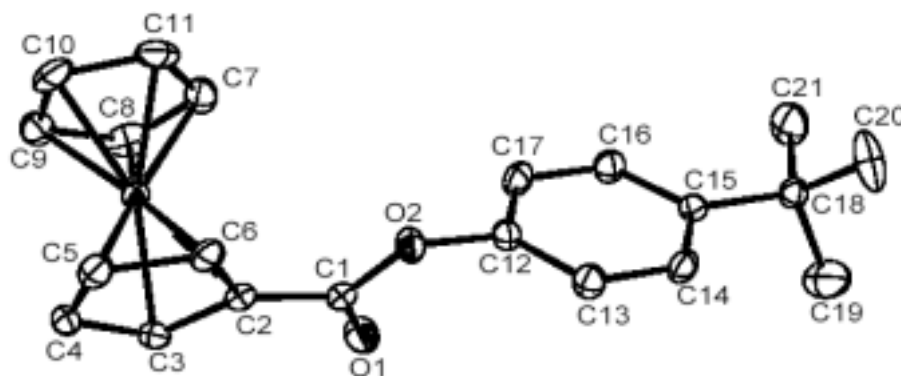


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**Table 1** Esterification of ferrocenylcarboxylic acid and substituted phenols in ionic liquids

Entry	Ionic liquid	X	Product	Yield % <sup>a</sup>
1	[BPy][Br]	H	<b>3a</b>	88, 86, 86, 84, 85 <sup>b</sup>
2	[HPy][Br]	H	<b>3a</b>	86
3	[BPy][Br]	t-Bu	<b>3b</b>	81
4	[HPy][Br]	t-Bu	<b>3b</b>	80
5	[BPy][Br]	OMe	<b>3c</b>	85
6	[HPy][Br]	OMe	<b>3c</b>	84
7	[BPy][Br]	NO <sub>2</sub>	<b>3d</b>	82
8	[HPy][Br]	NO <sub>2</sub>	<b>3d</b>	83
9	[BPy][Br]	Me	<b>3e</b>	89
10	[HPy][Br]	Me	<b>3e</b>	85

<sup>a</sup> Isolated yield; <sup>b</sup> Results for recycling reaction for five times.

**Figure 1** X-ray crystal structure of **3b**

The results are shown in **Table 1**. The products **3a-e** were characterized by IR, <sup>1</sup>H NMR and EA. The structure of **3b** was further confirmed by a single crystal X-ray crystallography<sup>4</sup>. It is known from **Table 1** that the yields were excellent. The recovered ionic liquids could be reused at least five runs without decrease in yield (**Table 1**, Entry 1).

Typical procedure was as follows: Ferrocenylcarboxylic acid (**1**, 0.46 g, 2 mmol), phenol (**2a**, 0.19 g, 2 mmol), 1, 3-dicyclohexylcarbodiimide (DCC) (0.45 g, 2.2 mmol), N,N-dimethylaminopyridine (DMAP) (0.05 g), ionic liquid ([BPy] [Br], 5 mL) were added into a 25 mL round bottom flask. Then the mixture was stirred at room temperature. The reaction process was monitored by thin layer chromatography (TLC). After completion of the reaction, the product was extracted with diethyl ether. The ether extracts were combined, washed with water and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removing ether under reduced pressure, the pure sample was obtained by recrystallization from ethanol to give **3a** (0.54 g, 88% yield), mp 120°C, <sup>1</sup>H NMR (CDCl<sub>3</sub>, δppm): 4.28 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.49 (s, 2H, C<sub>5</sub>H<sub>2</sub>H<sub>2</sub>), 4.88 (s, 2H, C<sub>5</sub>H<sub>2</sub>H<sub>2</sub>), 7.12-7.24 (m, 5H, ArH); IR (KBr, cm<sup>-1</sup>): 3099, 1719, 1591, 1487, 1454, 745, 691; Anal. Calcd. for C<sub>17</sub>H<sub>14</sub>FeO<sub>2</sub> C 66.70, H 4.61;

Found C 66.84, H 5.09.

We have established a practical process for the esterification of ferrocenylcarboxylic acid with substituted phenol in the presence of DCC/DMAP in ionic liquids. The reactions were usually completed within 24 hours at room temperature. In conclusion, the method is simple with high-yielding and environmentally friendly for the synthesis of the esters of ferrocenylcarboxylic acid. The ionic liquids have proved to be useful solvents in organic synthesis.

### References and Notes

1. B. Neises, W. Steglich, *Angew. Chem. Int. Ed.*, **1978**, *17*, 522.
2. P. Wasserscheid, W. Keim, *Angew. Chem. Int. Ed.*, **2000**, *39*, 3772.
3. R. Sheldon, *Chem. Commun.*, **2001**, 2399.
4. Crystal data for **3b**: C<sub>21</sub>H<sub>22</sub>FeO<sub>2</sub>, MW = 362.25, prism, space group *P2<sub>1</sub>/a*, *a* = 11.6361 (13), *b* = 10.8045 (10), *c* = 13.722 (2) Å,  $\beta$  = 95.489 (5), *V* = 1004.9 (3) Å<sup>3</sup>, *Z* = 4, *D<sub>c</sub>* = 1.401 g / cm<sup>3</sup>,  $\mu$  (MoK $\alpha$ ) = 8.87 cm<sup>-1</sup>, *F* (000) = 760.00. Crystal size 0.22 × 0.21 × 0.19 mm<sup>3</sup>, 3925 independent reflections (*R*<sub>int</sub> = 0.045), 13886 reflections collected. *R* = 0.043, *wR* = 0.086. Structure solution: direct methods (SHELX97); refinement method: full-matrix least-squares on *F*<sup>2</sup>.

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