

Tetramethylguanidium Lactate Ionic Liquid: Catalyst-free Medium for Michael Addition Reaction

LIANG Da-peng, XIN Xin, DUAN Hai-feng, YIN Yan-zhen,
GAO Han, LIN Ying-jie* and XU Jia-ning

Department of Organic Chemistry, College of Chemistry, Jilin University,
Changchun 130012, P. R. China

Abstract A catalyst-free, facile and efficient Michael addition reaction of active methylene compounds as well as nitromethane with chalcones catalyzed by guanidinium lactate ionic liquid was done. A series of chalcones, nitromethane, and active methylene compounds were converted smoothly to the corresponding products in high yields. The simple procedure, very mild conditions, high yields, and reuse of the IL without any loss of catalytic activity make this protocol considerably attractive for academic researches and practical applications.

Keywords Guanidinium lactate ionic liquid; Michael addition reaction; Chalcone; Active methylene compound

1 Introduction

The carbon-carbon bond formation and the functional group transformations are the most fundamental reactions for the construction of a molecular framework and hence represent a forefront of researches in organic chemistry^[1–6]. The Michael addition reaction is one of the most important carbon-carbon bond forming reactions^[7–10]. Normally, the additions of active methylene to α,β -unsaturated compounds are usually catalyzed by Lewis acids or strong bases, which usually result in undesirable side products^[11–13]. Thus, a number of mild reagents, such as *L*-proline^[14–17], K_2CO_3 ^[18], and Al_2O_3 ^[19,20] have been developed to catalyze the Michael addition reaction over the past few years.

During the last decade, air- and water-stable room temperature ionic liquids (ILs) have emerged as a green alternative to volatile and hazardous organic solvents^[21–26]. ILs usually consist of organic cations, such as imidazolium or pyridium species, and anion counterparts, such as AlX_4^- , BF_4^- , PF_6^- , $CF_3SO_3^-$ or $(CF_3SO_3)_2N^-$ etc.: Moreover, ILs are readily prepared and the properties can be easily adjusted by changing the anion or the alkyl groups attached to the cation. The modification of the structures of the cations or anions of ILs can result in some unique properties, which can alter the outcomes of various reactions. To date, ILs have been recognized as efficient and re-

cyclable reaction media for a variety of reactions.

Recently, these have been proved to be an efficient medium for the Michael addition reaction, where relatively long reaction time (22–100 h) is required or the reaction is catalyzed by an organic base to achieve a good yield. Yadav and Dell'Anna^[27,28] reported that $[bmim]BF_4$ is a good solvent for the reaction of acetylacetone or β -ketoesters with methyl vinyl ketone (MVK) and other enones catalyzed by $Ni(acac)_2$ or copper(II) triflate^[29], respectively.

Very recently, Mečiarová^[30] has described a novel catalyst-free Michael addition reaction in several ionic liquids.

In the past several years, our group^[31,32] has successfully used guanidinium ionic liquids as dual solvent-catalysts in the oxidation of alcohols, the nucleophilic substitution of alkyl halides, the Heck reaction, and the Knoevenagel condensation reactions. Herein is reported tetramethylguanidium lactate ionic liquid **1** (IL **1**, Fig. 1) used as dual solvent-catalyst for Michael addition (Scheme 1), and the results indicate that IL **1** is a good medium for catalyst-free Michael addition and that it can be recovered and reused without any loss of catalytic activity.

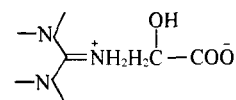
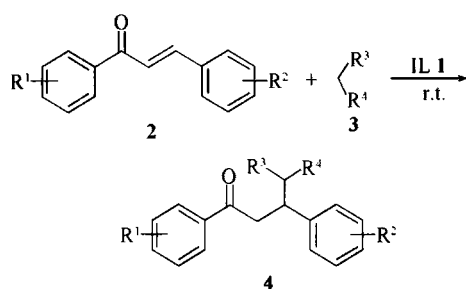


Fig. 1 Structure of guanidium lactate ionic liquid **1**

* Corresponding author. E-mail: linyj@jlu.edu.cn

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Scheme 1 Michael addition reaction of active methylene compounds with chalcones in IL 1

Table 1 Michael addition reaction of active methylene compounds with chalcones in IL 1 (Isolated yields)

Entry	Substrates						Time/h	Product	Yield(%)
	2	R ₁	R ₂	3	R ₃	R ₄			
1	2a	4-H	4-H	3a	COEt	COEt	3.3	4aa	99
2	2b	4-H	4-CH ₃	3a	COEt	COEt	3.4	4ba	99
3	2c	4-H	4-OCH ₃	3a	COEt	COEt	3.5	4ca	98
4	2d	4-H	2-OCH ₃	3a	COEt	COEt	5.0	4da	99
5	2e	4-H	2,3-O ₂ CH ₂	3a	COEt	COEt	4.6	4ea	99
6	2f	4-H	4-Cl	3a	COEt	COEt	4.2	4fa	98
7	2g	4-Cl	4-Cl	3a	COEt	COEt	4.5	4ga	99
8	2h	4-Cl	4-H	3a	COEt	COEt	4.0	4ha	98
9	2a	4-H	4-H	3b	COCH ₃	COCH ₃	2.4	4ab	85
10	2b	4-H	4-CH ₃	3b	COCH ₃	COCH ₃	3.1	4bb	84
11	2c	4-H	4-OCH ₃	3b	COCH ₃	COCH ₃	2.7	4cb	80
12	2d	4-H	2-OCH ₃	3b	COCH ₃	COCH ₃	3.0	4db	86
13	2e	4-H	2,3-O ₂ CH ₂	3b	COCH ₃	COCH ₃	2.0	4eb	92
14	2f	4-H	4-Cl	3b	COCH ₃	COCH ₃	1.2	4fb	90
15	2g	4-Cl	4-Cl	3b	COCH ₃	COCH ₃	2.0	4gb	83
16	2h	4-Cl	4-H	3b	COCH ₃	COCH ₃	1.5	4hb	87

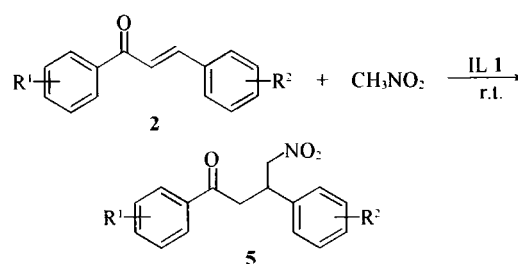
Encouraged by the above results, a series of chalcones 2 was then examined under identical conditions as described previously and the results are summarized in Table 1. To our delight, all reactions tested were complete within a short time and could afford the corresponding products in high yields under very mild conditions. When acetylacetone 3b was taken as a nucleophile to react with different chalcones, all reactions were completed soon and the addition products were obtained in high yields (Entries 10–16). It is worth noting that the reaction time of acetylacetone with chalcones was shorter than that of diethyl malonate, while the yields of the corresponding products were lower (Entries 1–16). Such results are mainly attributed to the stronger nucleophilic ability of acetylacetone in IL 1, which resulted in some side reactions and thus led to lower product yields.

Subsequently, nitromethane was also tested to react with chalcones in IL 1 (see Scheme 2); some results are shown in Table 2. In the presence of catalyst IL 1, the reactions of diethyl malonate, pentane-

2 Results and Discussion

In the primary experiment, diethyl malonate 3a was introduced as a nucleophile and chalcone 2a acted as a Michael accepter. When the reaction of compound 3a (2.0 mmol) and compound 2a (2.0 mmol) was conducted in IL 1 as the solvent without the addition of any catalyst, the reaction proceeded smoothly to completion at room temperature and afforded the Michael adduct 4a in a quantitative yield (Table 1, Entry 1).

2,4-dione, and nitromethane with chalcones proceeded smoothly. The possible catalytic mechanism of



Scheme 2 Michael addition reaction of nitromethane with chalcones in IL 1

Table 2 Results of Michael addition reaction of nitromethane with chalcones in IL 1 (Isolated yield)

Entry	2	Chalcone		Time/h	Product	Yield(%)
		R ₁	R ₂			
1	2a	4-H	4-H	0.33	5a	80
2	2b	4-H	4-CH ₃	0.23	5b	83
3	2c	4-H	4-OCH ₃	0.5	5c	82
4	2d	4-H	2-OCH ₃	0.25	5d	84
5	2e	4-H	2,3-O ₂ CH ₂	0.8	5e	76
6	2f	4-H	4-Cl	0.6	5f	79
7	2g	4-Cl	4-Cl	0.6	5g	80
8	2h	4-Cl	4-H	1.0	5h	81

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