



One-pot Green and Efficient Synthesis of Xanthenedione Derivatives using $[C_4(\text{mim})_2](\text{FeCl}_4)_2$ as a Magnetic Room Temperature Dicationic Ionic Liquid

BIJAN MOMBAINI GODAJDAR^{1*}, ALI REZA KIASAT² and ALI EZABADI³

¹Department of Chemistry, Islamic Azad University Omidyeh Branch, Omidyeh, Iran.

²Department of Chemistry, College of Science, Shahid Chamran University, Ahwaz, Iran.

³Department of chemistry, Faculty of Science, Islamic Azad University, Central Tehran Branch,

*Corresponding author E-mail: bmombini@gmail.com

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ABSTRACT

An easily prepared Fe (III)-derived Lewis acid ionic liquid, $[C_4(\text{mim})_2](\text{FeCl}_4)_2$, being comprised of dicationic ionic liquid cation and tetrachloroferrate anion, was found to be an efficient, recyclable catalyst for the synthesis of 1, 8-dioxooctahydroxanthenes by one-pot condensation reactions of dimedone/ 1, 3- cyclohexanedione with aromatic aldehydes under mild reaction conditions without utilization of additional organic solvent

Key words: Magnetic room temperature dicationic ionic liquid, 1, 8-dioxooctahydroxanthen, dimedone, Multi-component reactions, one-pot reaction.

INTRODUCTION

Xanthene derivatives are very important heterocyclic compounds and have been widely used as dyes fluorescent materials for visualization of bio-molecules and laser technologies due to their useful spectroscopic properties.¹ They have also been reported for their agricultural bactericide activity, photodynamic therapy, anti-inflammatory effect, and antiviral activity.²⁻⁵ Due to their wide range of applications, these compounds have received a great deal of attention in connection with their synthesis⁶⁻¹⁰.

Magnetic ILs not only have the excellent properties of IL but also exhibit an unexpectedly strong response to an additional magnet. These properties make magnetic ILs have more advantages and potential application prospects than conventional ILs in the fields of catalytic reactions, solvent effects and separation processes.¹¹ Although several types of magnetic ionic liquids have been created in recent years, there have been only a few reports about their applications as catalyst in chemical transformations.

In continuation of our work on the catalytic properties of magnetic ionic liquids,¹²⁻¹³ herein, we wish to report a simple, convenient and efficient method for the use of magnetic room temperature dicationic ionic liquid (MRTDIL) as catalyst for preparation of 1, 8- dioxo- octahydroxanthenes derivatives.

EXPERIMENTAL

Material and Methods

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. ¹H & ¹³C NMR spectra were recorded on a Bruker Advanced DPX 400 MHz instrument spectrometer using TMS as the internal standard in CDCl₃. IR spectra were recorded on a BOMEM MB-Series 1988 FT-IR spectrometer. Raman spectroscopy were recorded on a Bruker RFS 100/s Raman spectrometer. Aldehydes, and dimedone were purchased from Merck Company in high purity. Products were characterized by comparison of their physical and spectroscopic data with those of known samples.

Procedure for the preparation of [C₄(mim)₂][Cl₂](A)

1, 4-Dichlorobutane (1 mmol) was reacted with 1-methylimidazole (2 mmol), respectively, stirred in MeOH, refluxed for 24 h, and then precipitated from ethyl acetate to obtain the required product (white solid **1a**, yield 94%).

Procedure for preparation of [Pbmim][FeCl₄]₂ as a magnetic room temperature dicationic ionic liquid

[C₄(mim)₂](FeCl₄)₂, MRTDIL, was prepared by mixing crystal powder of [pbmim]Cl₂ (1 mmol) with anhydrous FeCl₃ (2 mmol) at room temperature for 3h, a dark brown liquid was obtained. The obtained MRTDIL was extracted with small amount of ethyl acetate. The solvent was evaporated and the resulting clear brown liquid was dried in vacuum oven at 60 °C for 24 h. The MRTDIL was obtained in high yield (89%).

General procedure for preparation of 1, 8-dioxo-octahydro-xanthenes (3a-I)

A mixture of dimedone/1, 3-cyclohexanedione (2 mmol), aromatic aldehyde (1 mmol) and MRTDIL (20% mol) was heated at 80 °C

for an appropriate time (Table 2). After completion of the reaction (TLC), the mixture was cooled to room temperature and washed with cooled water. The solid product was purified by crystallization from aqueous EtOH to afford products 3a-3m (Scheme 2).

All the products were fully characterized by spectroscopic data and their melting points are compared with reported values.

Spectral data

9-(phenyl)- 3,3,6,6-tetramethyl - 3,4,5,6,7,9- hexahydro-1H-xanthene-1,8-(2H)-dione (**3a**): ¹H NMR (CDCl₃, 400 MHz) δ: 1.02 (s, 6H), 1.13 (s, 6H), 2.19 (d, (2H, J = 16.2 Hz), 2.26 (d, 2H, J = 16.2 Hz), 2.50 (s, 4H), 4.78 (s, 1H), 7.12 (t, 1H, J = 7.2 Hz), 7.24 (t, 2H, J = 7.5 Hz), 7.32 (d, 2H, J = 7.6 Hz). ¹³C NMR (CDCl₃, 100 MHz) δ: 27.75, 29.69, 32.26, 32.61, 41.29, 51.18, 116.07, 126.76, 128.45, 128.80, 144.54, 162.70,

RESULTS AND DISCUSSION

The acidic MRTDIL catalyst was prepared according to previously reported (Scheme 1).¹³

Due to the paramagnetic nature of the [C₄(mim)₂](FeCl₄)₂, nuclear magnetic resonance technique could not be used to confirm its structure. Instead, UV spectra was used to characterize the [C₄(mim)₂](FeCl₄)₂ structure. The UV spectrum is shown in Figure 1. [C₄(mim)₂](FeCl₄)₂ spectra exhibited absorption bands in the visible region at 534, 620 and 680 nm which are characteristic for the FeCl₄⁻ anion. In order to be able to carry out preparation of 1, 8- dioxo- octahydroxanthenes derivatives in a more efficient way minimizing the time, temperature and amount of catalyst, the reaction of benzaldehyde, and dimedone was selected as model system to the effects of the catalyst at different reaction temperatures (25, 60, 80 and 100 °C) and the different amount of catalyst (0, 10, 20, 30, and 40% mol) were investigated. The reaction using 20% mol of MRTDIL at 80 °C proceeded in highest yield. Further increase in temperature to, 100 °C had little effect on the rate of reaction. Therefore, we kept the reaction temperature at 80 °C as optimal temperature.

This reaction was carried out without catalyst under solvent free conditions in order to establish the effectiveness of the catalyst. It was found that 1, 8- dioxo- octahydroxanthenes was not made after 1h of heating. The best results were obtained with 1: 2 ratio of benzaldehyde, dimedone, and 20% mol of MRTDIL after 10 min at 80 °C.

After optimizing the conditions, the generality of this process was demonstrated by the wide range of substituted aryl aldehydes to synthesize the corresponding products in excellent yields (Scheme 2, Table 1). As seen from Table 1, aromatic aldehydes having electron-donating as well as electron-withdrawing groups were uniformly transformed into the corresponding products in high yields within 10-15 min. Substituent on the aromatic ring had no obvious effect on yield or reaction time

under the above optimal conditions. Unlike some previously reported methods; the present method does not require toxic organic solvents to produce the 1,

8-dioxo-octahydroxanthene derivatives

The success of the above reactions prompted us to investigate the recyclability of catalyst. We carried out our study by using the reaction benzaldehyde with dimedone and under optimal conditions as a model study. For this aim, after completion of reaction (monitored by TLC), water was added to the reaction mixture and then the solid was isolated by filtration. The aqueous filtrate was then subjected to distillation at 80°C under reduced pressure (10 mmHg) for 4 h to recover the IL almost completely. The IL, thus recovered could be reused five times without loss of activity for the typical reaction (Fig 2).

Table 1: Synthesis of xanthenes derivatives

Entry	Ar	Product	R	Time (min)	Yield (%) ^a	M.P (°C)	
						Found	Reported ^{ref}
1	C ₆ H ₅	3a	CH ₃	10	92	203-204	204-205 ¹⁴
2	4-Cl-C ₆ H ₄	3b	CH ₃	10	90	230-232	230-231 ¹⁴
3	4-Br-C ₆ H ₄	3c	CH ₃	10	90	240-241	240-242 ¹⁵
4	2-Cl-C ₆ H ₄	3d	CH ₃	10	91	225-227	224-226 ¹⁴
5	3-Cl-C ₆ H ₄	3e	CH ₃	10	91	184-186	183-184 ¹⁴
6	4-NO ₂ -C ₆ H ₄	3f	CH ₃	10	89	222-223	222 ¹⁴
7	2-NO ₂ -C ₆ H ₄	3g	CH ₃	15	87	248-249	246-248 ¹⁴
8	3-NO ₂ -C ₆ H ₄	3h	CH ₃	15	89	171-173	170-172 ¹⁴
9	4-OCH ₃ -C ₆ H ₄	3i	CH ₃	15	88	241-243	242-244 ¹⁴
10	4-CH ₃ -C ₆ H ₄	3j	CH ₃	15	89	215-217	217-218 ¹⁴
11	4-CN-C ₆ H ₄	3k	CH ₃	15	90	218-220	230 ¹⁶
12	4-CN-C ₆ H ₄	3l	H	15	89	268-270	273-275 ¹⁷

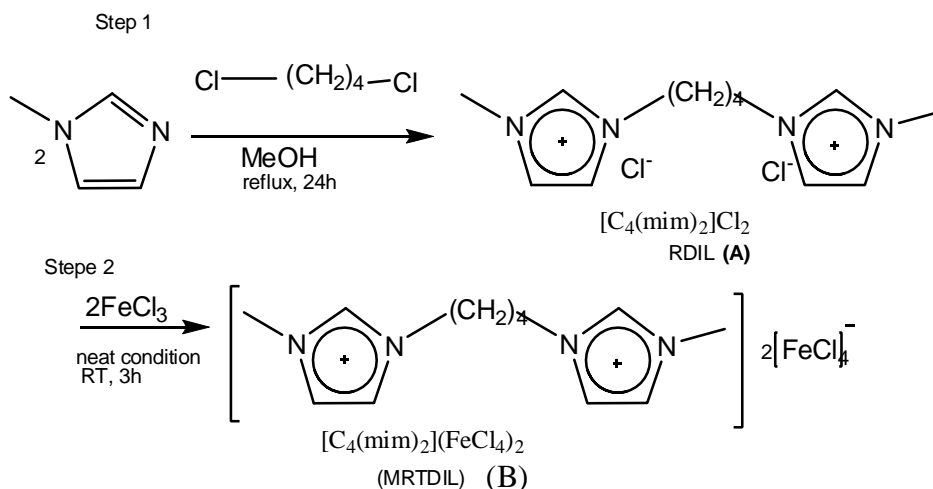
^aIsolated yield

Table 2: Comparison of results using MDIL catalyst with results obtained by other workers

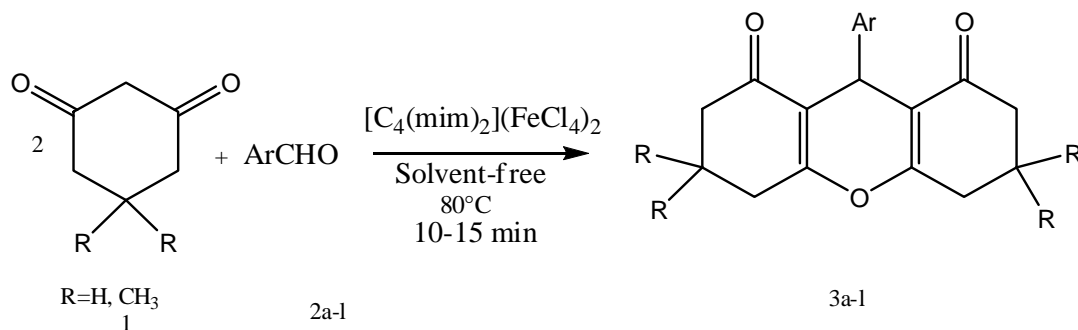
Catalyst	Conditions	Time (h)	Yield %	Rf
Silica sulfuric acid	Solvent- free/80°C	1-2.5	88-97	[9]
InCl ₃ .4H ₂ O	Ionic liquid/80°C	4-10	76-95	[6]
Fe ³⁺ -montmorillonite	EtOH(reflux)	6	84-96	[10]
NaHSO ₄ -SiO ₂	CH ₃ CN(reflux)	6	90-98	[7]
Amberlyst-15	CH ₃ CN(reflux)	5	90-96	[8]
[C ₄ (mim) ₂](FeCl ₄) ₂	Solvent-free/80°C	0.08- 0.25	87-91	-

The efficiency of MRTDIL (time, yield, reaction conditions) was compared with the efficiencies of other catalysts used in synthesis of 1,

8-dioxooctahydroxanthenes, the results are presented in Table 2. It is clear that the presented method is simpler, more efficient and less time consuming compared with other



Scheme 1: Synthesis of [C₄(mim)₂](FeCl₄)₂ as a magnetic room temperature dicationic ionic liuqid



Scheme 2: Synthesis of 1, 8-dioxo-octahydro-xanthenes

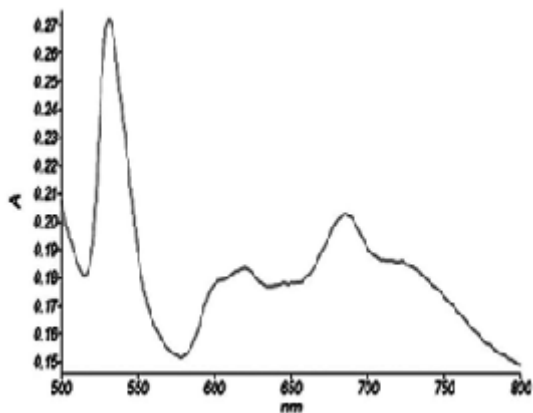


Fig. 1: Visible spectrum of [C₄(mim)₂](FeCl₄)₂

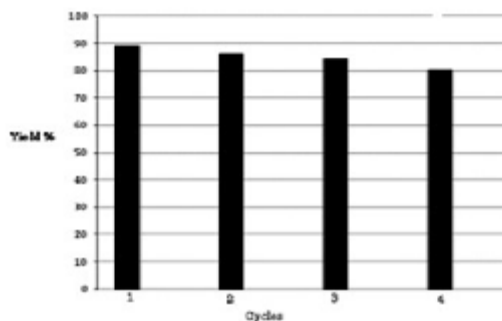


Fig. 2: Recyclability of the catalyst

CONCLUSION

In conclusion, we have successfully developed a simple and green catalytic procedure for the efficient synthesis of xanthenes using MRTDIL and under mild reaction conditions. MRTDIL can replace the ILs and other homogeneous catalysts with reasonable recovery

and reusability and therefore suitable for industrial applications.

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