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The Task Specific Ionic Liquid promoted reaction: An expeditious synthesis of privileged 1,8 - Dioxo-octahydroxanthene

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ABSTRACT

1,8 - Dioxo-octahydroxanthene were efficiently prepared by a recyclable carboxyl-functionalized [cmmim] [BF₄] Task Specific Ionic Liquid [TSIL] in aqueous media in high yield and the ionic liquid can be recycled at least 6 times without significant loss of activity.

Key words: Xanthenes, Task Specific Ionic Liquid, Recyclable Catalyst, Aqueous media.

INTRODUCTION

Xanthene derivatives have recently received great attention because of their wide range of therapeutic and biological properties[1]. Further they are very important class of compounds widely used in dyes, laser technology and in fluorescent materials [2]. The synthesis of xanthenediones usually condenses with appropriate active methylene carbonyl compounds and aldehydes catalyzed by organic and mineral acids, which often suffers from the disadvantages of long reaction times, harsh reaction conditions, toxicity and difficulty in product separation. In spite of potential utility of aforementioned routes for the synthesis of xanthene derivatives, many of these methods involve expensive reagents, strong acidic conditions, low yield and use of excess reagents/catalyst and toxic solvents. We disclosed herein, the new and efficient catalyst with high catalytic activity, short reaction time, recyclability and simple work-up under acidic and mild condition.

Ionic liquids have attracted extensive interest as excellent alternatives due to their favorable properties[3]. The use of ionic liquids as reaction medium and catalyst may offer a convenient solution to both the solvent emission and catalytic recycling problem. In the last few years, many innovative concepts have been created in utilizing the specific properties of specific ionic liquids

for special reactions and are called Task Specific Ionic Liquids (TSILs) [4]. Task-specific ionic liquids may be defined as ionic liquids in which a functional group is covalently tethered to the cation or anion of the ionic liquid [3b]. These TSILs can then act as reagents or catalysts in organic synthesis. They have also been referred as designer solvents as their physical and chemical properties could be adjusted by a careful choice of cation and anion.

Our recent interest has been in the development of new synthetic methods on using an alternative reaction media including TSILs, hydrotopes, biopolymers, enzymes [5]. Only few applications of 1-carboxymethyl-3-methylimidazolium cation functionalized Brønsted acidic ionic liquid is reported in literature such as Biginelli reaction [6], Mannich reaction [7], deoximation [8], and acetalization of aldehydes [9]. Recently, many synthetic methods for preparing xanthenedione compounds using different acidic ionic liquids have been reported [10]. To best of our knowledge, the synthesis of xanthenes involving catalytic amount of 1-carboxymethyl-3-methylimidazolium, are unprecedented, in aqueous medium. The reaction proceeds very fast and with high yielding using catalytic amount of ionic liquids and recovered task specific ionic liquid can be recycled many times without decrease of yield.

MATERIALS AND METHODS

Melting points were determined in open capillaries under air with an DBK programmable melting point apparatus. Reagent grade chemicals were purchased from a commercial source and used without further purification. IR spectra were recorded as KBr pellets in the 400-4000 cm^{-1} . ^1H -NMR spectra were recorded on Bruker 300 MHz.

Typical procedure for the preparation of carboxyl functionalized ionic liquid [cmmim][BF₄]

Chloroacetic acid (10 mmol) and 1-methylimidazole (10 mmol) was heated at 70-80°C in acetonitrile for 12 hrs. The solid thus obtained was filtered washed with acetonitrile and dried under vacuum for 4 hrs. at 50°C. The 1-carboxymethyl-3-methylimidazolium chloride was obtained as a white solid (95% yield). MP: -171-173°C (Lit-172-174°C) [7]. Chloride salt was stirred with NaBF₄ in acetonitrile overnight at RT. Solid filtered, washed with acetonitrile and removal of solvent under vacuum give [cmmim][BF₄] as yellow oil (90% yield).

General procedure for the synthesis of 1,8-Dioxo-octahydroxanthenes.

To a round bottom flask charged with aldehyde (10 mmol) dimedone or 1,3-cyclohexanedione (20 mmol) and 5 ml water under stirring, [cmmim][BF₄] (20 mol %) was added in the reaction mixture and then stirred for a certain time at 80°C. On completion of reaction (monitored by TLC), the crude product obtained was filtered, washed and recrystallized from ethanol to afford pure 1,8-dioxo-octahydroxanthenes. The products were identified by IR, ^1H NMR and physical data (mp) with those reported in the literature.

Spectral Data for Selected Compounds

1-carboxymethyl-3-methylimidazolium tetrafluoroborate [cmmim][BF₄]:

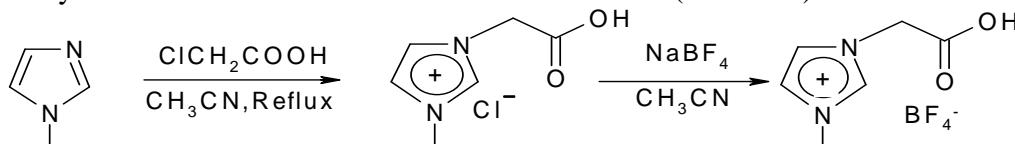
IR, ν_{max} : 1055, 1390, 1434, 1587, 1731, 2895, 3089, 3115 cm^{-1} . ^1H -NMR (300 MHz, D₂O) δ : 3.81 (s, 3H, CH₃), 4.90 (s, 2H, CH₂), 7.34-7.38 (d, 2H, J=5.23 Hz, CH=CH), 8.56 (s, 1H, CH=N).

3,3,6,6-Tetramethyl-9-(phenyl)-1,8-dioxo-octahydroxanthene (4b).

IR, ν_{\max} : 701, 745, 1143, 1201, 1360, 1465, 1669, 1687, 2976. 3039 cm^{-1} **$^1\text{H-NMR}$** (300MHz, CDCl_3) δ : 0.97 (s, 6H, 2 CH_3), 1.14 (s, 6H, 2 CH_3), 2.10-2.46 (m, 8H, 4 CH_2), 4.75(s, 1H, CH), 7.24-7.46 (m, 5H, ArH)

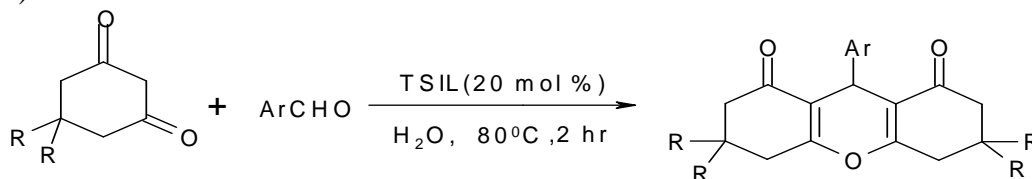
RESULT AND DISCUSSIONS

The synthesis of carboxyl functionalized task specific ionic liquid was prepared by reacting 1-methyl imidazole and chloroacetic acid in acetonitrile (scheme-1).



Scheme 1. Preparation of TSIL.

In order to find the optimum conditions for the formation of the products, the reaction of 1,3-cyclohexane dione and benzaldehyde was performed in presence of different solvents (scheme-2).



Scheme-2. The reaction of dimesone or or 1,3-cyclohexanedione with aldehyde catalyzed by TSIL.

Four reaction media were compared and the results were listed in *Table 1*.

Table 1-Reaction results in different media

Entry	Solvent	$t^{\circ}\text{C}$	T / hr	Yield %
1	DMSO	80	4	30
2	Ethanol	80	4	35
3	Ethanol :Water (1:1)	80	2	58
4	Water	80	2	85
5	Water	80	2	No reaction

The best result was obtained in presence of 20 mol %TSIL and water as solvent. It was found that the product was obtained in all solvents but yield is very low except water. It was found that almost no product was obtained in water in absence of catalyst [*Entry 5 Table 1*].

Based on the above investigation further reactions was carried using different aldehydes (Table-2) at 80°C and 20mol% catalyst for 2 hrs, the product 1,8 Dioxo-octahydroxanthenes could be obtained in high isolated yields (83-91%). The reaction procedure is demonstrated in Fig.1

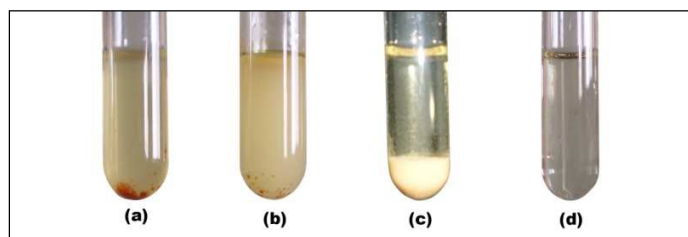


Fig 1. Reaction procedure of synthesis of 1,8 – Dioxo-octahydroxanthene.

a) TSIL + Reagents in H₂O at r. t. b) homogeneous phase at 80⁰C. c) solid product separated after completion of reaction d) filtrate containing TSIL after product separation.

When optimizing reaction condition the recycling performance of TSIL was investigated using the model reaction using benzaldehyde and 1,3-cyclohexanedione (figure-2).

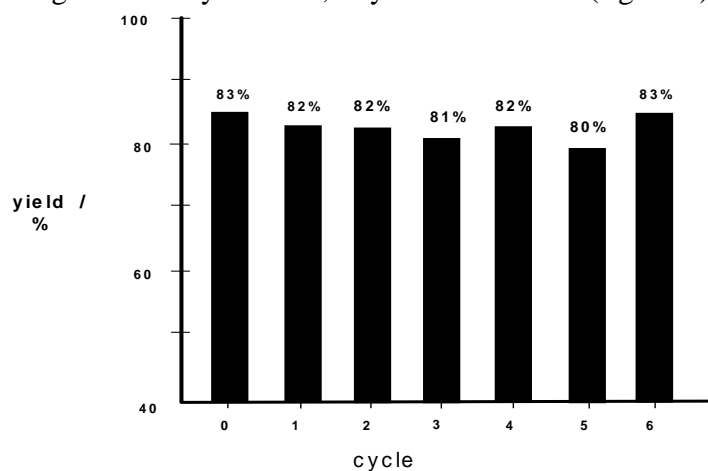


Fig 2. Recyclability performance of TSIL

After the separation of products, the catalyst containing water was reused in the next cycle without further purification. As shown in figure 2 the catalyst with solvent can be recycled at least 6 times without significant decrease of yields.

Table 2- TSIL catalyzed synthesis of 1,8-Dioxo-octahydroxanthenes. ^a

Entry	R	Ar	Product	Yield ^b	Mp/ ⁰ C[Ref.]
1	H	C ₆ H ₅	3a	83	267-268[11]
2	H	o-ClC ₆ H ₄	3b	91	248-250[11]
3	H	p-ClC ₆ H ₄	3c	89	293-285[11]
4	H	p-CH ₃ OC ₆ H ₄	3d	83	199-200[11]
5	H	p-BrC ₆ H ₄	3e	84	284-286[11]
6	CH ₃	o-ClC ₆ H ₄	4a	86	224-226[12]
7	CH ₃	C ₆ H ₄	4b	87	200-202[12]
8	CH ₃	p-HOC ₆ H ₄	4c	86	224-226[12]
9	CH ₃	p-ClC ₆ H ₄	4d	85	231-233[12]
10	CH ₃	o-NO ₂ C ₆ H ₄	4e	85	260-261[13]

^a All products were characterized by IR, ¹H-NMR and mass spectra.

^b Isolated yields after purification.

CONCLUSION

In conclusion, we have developed a simple efficient and green protocol for the synthesis of xanthene derivatives by use of carboxyl functionalized ionic liquid in water. The simple workup, short reaction time, mild reaction condition and recyclability of ionic liquid as catalyst are the prominent features of this new ionic liquid in organic transformations.

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