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Catalytic application of 3-methyl-1-sulfonic acid imidazolium tetrachloroferrate as nanostructured catalyst on the cross-aldol condensation reaction of cycloalkanones with aldehydes

Ardeshir Khazaei[a,*], Ahmad Reza Moosavi-Zare[b,*], Saeed Firoozmand[a]

[a]*Faculty of Chemistry, Bu-Ali Sina University, Hamedan, 6517838683, Iran*

[b]*Sayyed Jamaleddin Asadabadi University, Asadabad, 6541861841, I. R. Iran*

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Abstract

3-Methyl-1-sulfonic acid imidazolium tetrachloroferrate {[Msim]$FeCl_4$} as an efficient sulfur catalyst was prepared and applied, as an efficient catalyst, for the cross-aldol condensation reaction between cycloalkanones and arylaldehydes in order to give α,α′-bis(arylidene)cycloalkanones in high yields and short reaction times at 75 °C under solvent-free conditions.

Keywords: Sulfonic acid functionalized imidazolium salt; 3-methyl-1-sulfonic acid imidazolium tetrachloroferrate; cross-aldol condensation; α,α′-bis(arylidene)cycloalkanone; solvent-free.

Introduction

The cross-aldol condensation reaction has been widely used for carbon–carbon bond formation in organic transformations [1-3]. Cross-aldol condensation reaction of cycloalkanones with arylaldehydes giving α,α′-bis(arylidene)cycloalkanone [4], is very important because of its applications as precursor for the preparation of pyrimidine derivatives [5], and its intriguing biological activities such as antiangiogenic [6], quinine reductase inducer [7] and cholesterol-lowering properties [8,9]. For these reasons, search for finding an efficient, general and nonpolluting method for the preparation of α,α′-bis(arylidene)cycloalkanones is still needed.

Ionic liquids (ILs) have used as eco-friendly solvents, catalysts and reagents in organic synthesis, due to their significant properties such as low volatility, non-flammability, high thermal stability and ability to dissolve various materials [10,11]. For this reason, we have introduced sulfonic acid functionalized imidazolium salts (SAFIS) as a new category of ionic liquids and solid salts, and applied them as efficient catalysts and reagents in some organic synthesis [12-22].

In the continuation of our studies on the synthesis of acidic ionic liquids and acidic salts, we have reported 3-methyl-1-sulfonic acid imidazolium tetrachloroferrate {[Msim]$FeCl_4$} (Figure 1) as an efficient catalyst on the preparation of α,α′-bis(arylidene)cycloalkanones (Scheme 1).

*Corresponding author: Ahmad Reza Moosavi-Zare,
Tel: +98 (81) 33117804, Fax: +98 (81) 33117803
E-mail: moosavizare@yahoo.com, Khazaei_1326@yahoo.com

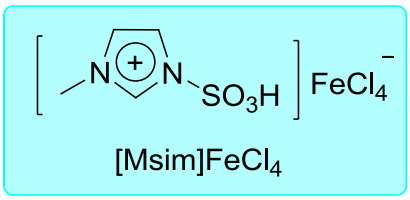
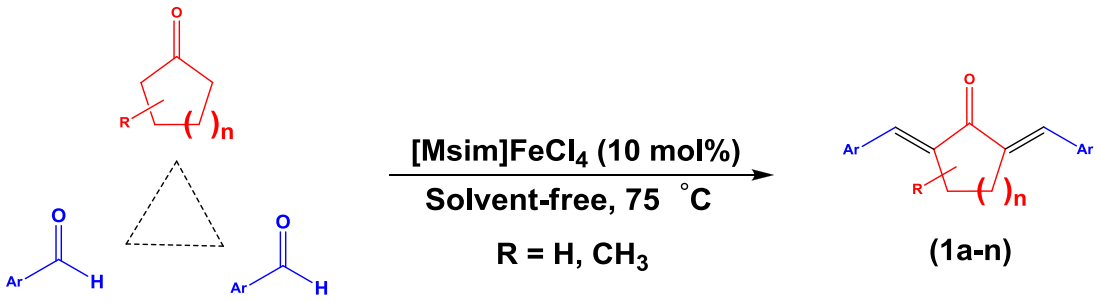


Figure 1. Structure of 3-methyl-1-sulfonic acid imidazolium tetrachloroferrate {[Msim]$FeCl_4$}



Scheme 1. The preparation of α,α′- bis(arylidene)cycloalkanones

Experimental

Materials and methods

All chemicals were purchased from Merck or Fluka Chemical Companies. The known products were identified by comparing their melting points and spectral data with those reported in the literature.

Procedure for the preparation of [Msim]$FeCl_4$

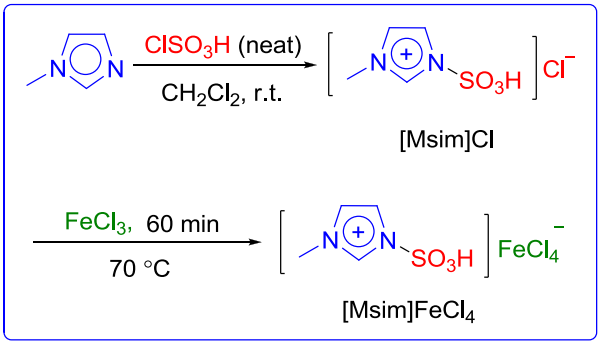
A round-bottomed flask (50 mL) was charged with 3-methyl-1-sulfonic acid imidazolium chloride (0.9931 g, 5 mmol), and then dry $FeCl_3$ (0.8042 g, 5 mmol) was added over a period of 5 min at 70 ºC. Then, the reaction mixture was stirred for 60 minutes at 70 ºC to give [msim]$FeCl_4$ as a green powder in 98 % yield [22].

General procedure for the synthesis of α,α'- bis(arylidene)cycloalkanones

To a well-ground mixture of cycloalkanone (1 mmol) and aldehyde (2 mmol) in a 10 mL round-bottomed flask connected to a reflux condenser, was added [msim]$FeCl_4$ (0.036 g, 10 mol%), and the resulting mixture was stirred in an oil-bath (75 °C). After completion of the reaction, as monitored by TLC, warm ethyl acetate was added to the reaction mixture to precipitate the catalyst. The catalyst was separated from reaction mixture by filtration. Then, ethanol (50%) was added drop wise to reaction mixture to precipitate the product. Finally, for further purification, the crude product was purified by recrystallization from ethanol (95%).

Results and discussion

Firstly, 1-methylimidazole in dry CH_2Cl_2 was reacted with chlorosulfonic acid at room temperature to afford 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl} as a viscous colorless oil [21]. Then, [Msim]$FeCl_4$ was produced by the reaction of [Msim]Cl with dry $FeCl_3$ at 70 °C (Scheme 2) [22].



Scheme 2. The synthesis of [Msim]$FeCl_4$

The morphology of [Msim]$FeCl_4$ was investigated by field emission scanning electron microscopy (FESEM). FESEM analysis of [Msim]$FeCl_4$ is displayed in Figure 2. As SEM image of the catalyst, indicating that the particles were synthesized in nano size.

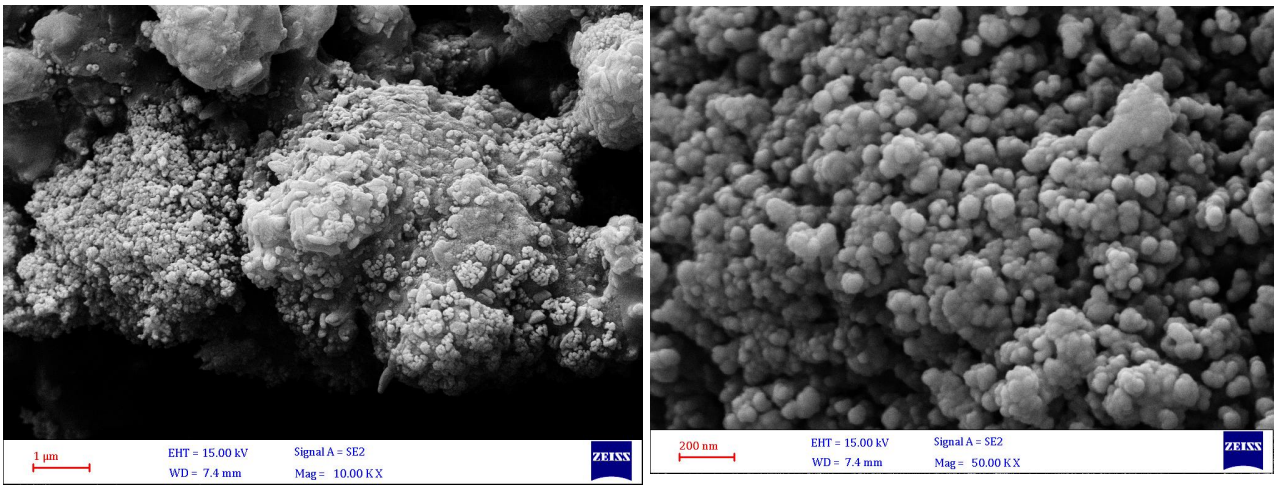


Figure 2. Field emission scanning electron microscopy (FESEM) of [Msim]$FeCl_4$

To optimize the reaction conditions, the condensation reaction of benzaldehyde and cyclohexanone as model reaction was studied using different amounts of [Msim]$FeCl_4$, at the range of 25-90 °C under solvent-free conditions. The results are given in Table 1. Table 1 indicates that 10 mol% of [Msim]$FeCl_4$ was sufficient to afford the product in high yields and in short reaction times at 75 °C (Table 1, Entry 4). No improvement in the reaction results was observed by increasing the amount of the catalysts and the temperature.

The model reaction was also examined in the persence of several solvents using 10 mol% of [Msim]$FeCl_4$ in comparision with solvent free-condition. The results were shown that solvent-free condition was the best condition in this reaction (Table 2, Entry 6).

Table 1. Effect of the catalyst amount and temperature on the reaction of benzaldehyde with cyclohexanone

Entry	Catalyst amount (g)	Temp. (℃)	Time (min)	Yield[a] (%)
1	-	75	1440	trace
2	1	75	60	15
3	5	75	30	60
4	10	75	25	91
5	15	75	25	91
6	10	25	1440	trace
7	10	50	90	85
8	10	60	45	87
9	10	80	25	91

[a]Isolated yield

Table 2. Effect of various solvents on the reaction of benzaldehyde with cyclohexanone, in the persence of $[Msim]FeCl_4$

Entry	Solvent	Temp. (°C)	Time (min)	Yield[a] (%)
1	THF	Reflux	60	45
2	EtOAc	Reflux	60	15
3	EtOH	Reflux	60	50
4	CH_2Cl_2	Reflux	60	20
5	n-Hexane	Reflux	60	10
6	-	75	25	91

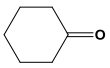
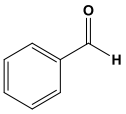
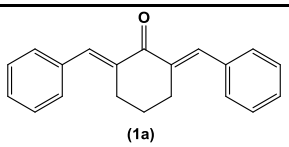
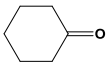
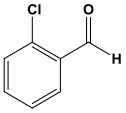
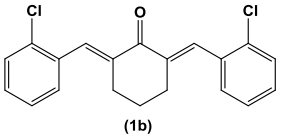
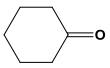
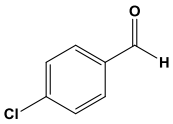
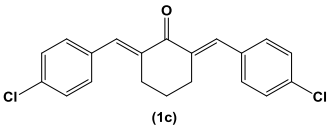
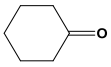
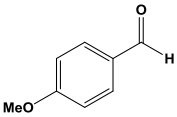
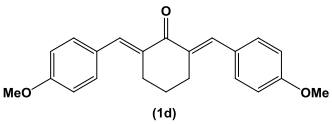
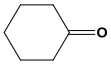
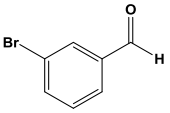
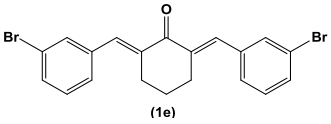
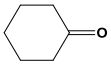
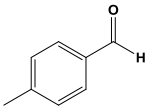
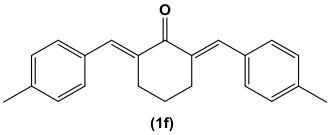
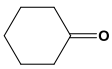
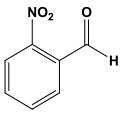
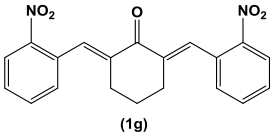
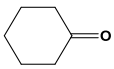
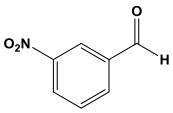
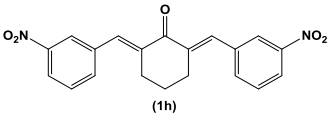
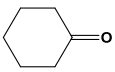
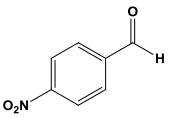
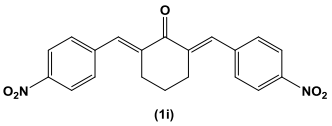
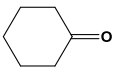
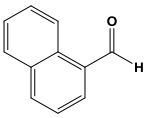
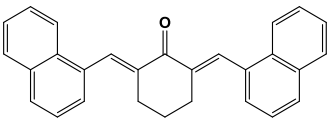
[a]Isolated yield

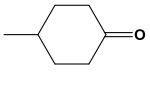
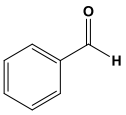
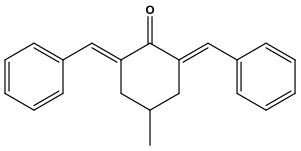
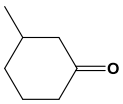
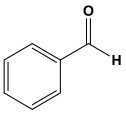
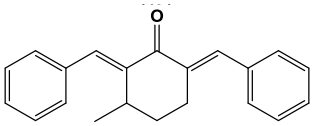
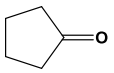
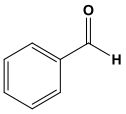
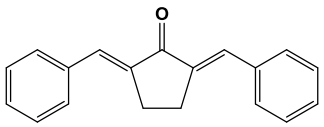
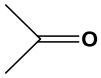
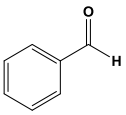
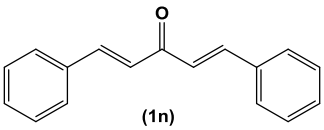
After optimization of the reaction conditions, the condensation of cycloalkanones such as cyclohexanone derivatives and cyclopentanone, with different arylaldehydes including benzaldehyde as well as aldehydes containing electron-withdrawing substituents, electron-releasing substituents or halogens was examined in the presence of $[Msim]FeCl_4$ at 75 °C in the absence of solvent, in order to assess the scope and the generality of the catalysts (Table 3). As it is shown in Table 3, it indicates that the expected products were synthesized in high yields and in short reaction times.

In a plausible mechanism (Scheme 3) which is supported by the literature [24-28], at first, cycloalkanone was activated by $[Msim]FeCl_4$ and converted to enol form and then reacted with activated aromatic aldehyde by acidic group of $[Msim]FeCl_4$ to give I after removing one molecule of H_2O. In the next step, I in enol form was reacted with another molecule of activated aromatic aldehyde to furnish the desired product after removing one molecule of H_2O.

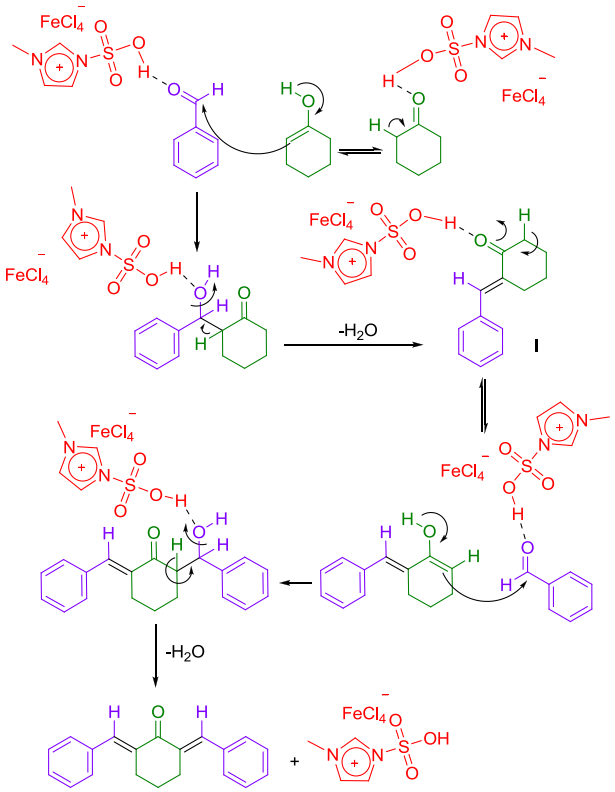
Reusability of the catalyst was also tested upon the condensation of cyclohexanone (1 mmol) with benzaldehyde (2 mmol). After completion of the reaction, as monitored by TLC, the reaction mixture extracted by dry ethyl acetate and separated from the catalyst after filtration. The catalyst was dried to reuse for another reaction. We observed that the catalytic activity of the catalyst was restored within the limits of the experimental errors for four successive runs (Figure 2).

Table 3. The solvent-free cross-aldol condensation of cycloalkanones from ketones and aromatic aldehydes using {[Msim]$FeCl_4$} at 75 ˚C

Entry	ketone	Aldehyde	Product	Time (min)	Yield[a] (%)	Mp °C (Lit.)
1			 (1a)	25	91	115-118 (115-118) [24]
2			 (1b)	21	92	101-103 (104-106) [25]
3			 (1c)	22	90	144-146 (144-146) [24]
4			 (1d)	18	95	162-164 (160-163) [24]
5			 (1e)	25	87	118-121 (118-119) [24]
6			 (1f)	22	92	166-169 (168-171) [24]
7			 (1g)	25	78	143-145 (151-154) [24]
8			 (1h)	25	85	188-190 (193-196) [24]
9			 (1i)	25	82	197-200 (208-210) [25]
10			 (1j)	15	90	208-211 (199-201) [26]

11				25	90	96-98 (97-99) [26]
12			 (1l)	25	80	116-119 (119-120) [27]
13			 (1m)	20	92	190-192 (188-191) [24]
14			 (1n)	30	70	108-111 (110-111) [28]

[a]Isolated yield



Scheme 3. The proposed mechanism for the synthesis of α,α′- bis(arylidene)cycloalkanones

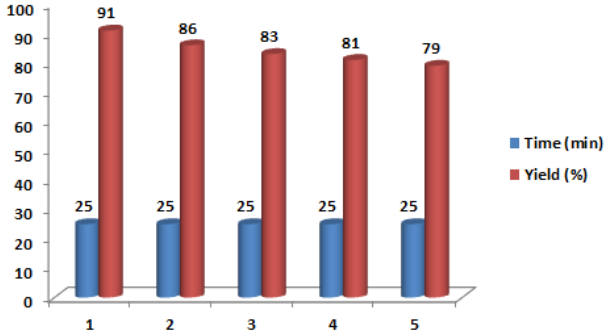


Figure 2. The condensation of cyclohexanone (1 mmol) with benzaldehyde (2 mmol) in the presence of the reused [Msim]$FeCl_4$

Conclusion

In this work, we have introduced 3-methyl-1-sulfonic acid imidazolium tetrachloroferrate {[Msim]$FeCl_4$}, as an efficient catalyst, for the cross-aldol condensation reaction between cycloalkanones and arylaldehydes to give α,α′- bis(arylidene)cycloalkanones in high yields and short reaction times at 75 °C under solvent-free conditions.

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