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Catalytic performance of a new Cu(II) Complex as an efficient and recyclable catalyst in the Synthesis of 1,8-dioxodecahydroacridines

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ABSTRACT

A novel Cu(II) complex of 3-hydroxy-2-naphtoic acid (CuL_2) has been studied for catalytic performance in the synthesis of 1,8-dioxodecahydroacridines. This efficient and eco-friendly catalyst has been utilized in a one-pot three-component condensation of dimedone, aromatic aldehydes and ammonium acetate under solvent and free-solvent conditions. This new heterogeneous catalyst has the advantages of being environmentally friendly, simple work-up and high yields character.

Keywords:3-hydroxy-2-naphtoic acid complex, decahydroacridine, solvent-free conditions, aromatic aldehyde.

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INTRODUCTION

During the recent years, synthesis of the Cu(II) complexes and their applications as catalyst have numerous been reported (Huang et al.2017), (Azam et al. 2017). Some of these complexes have been showed the biological properties such as antibacterial (Aktan et al. 2017), anticancer (Kesavan 2017) and antifungal (Liu et al. 2017).On the other hand, 1,8-dioxodecahydroacridines are the poly functionalized derivatives of 1,4-DHP. The most usual synthesis of these compounds include the three-component cyclocondensation of 1,3-cyclohexanedione or 5,5-dimethyl-1,3-cyclohexanedione (dimedone) with aromatic aldehydes and ammonium acetate or amines in the presence of a catalyst such as [Hmim]TFA(Dabiri et al. 2008), $B(C_6F_5)_3$ (Chandrasekhar et al. 2008), $Zn(OAc)_2$(Balalaie et al. 2009), L-proline (Venkatesan et al. 2008), Amberlyst-15(Das et al.2006), $CeCl_3.7H_2O$ (Fan et al. 2007), silica-bonded S-sulfonic acid (SBSSA)(Niknam et al. 2010)and silica-bonded *N*-propyl sulfamic acid (SBNPSA) (Rashedian, D. Saberi, K. Niknam et al. 2010), TBA (Davoodnia et al 2012), carbon base solid acid (CBSA)(Davoodnia et al. 2011), Brønsted acidic imidazolium salts (Shen et al. 2009) and MCM-41-SO_3H (Rostamizadeh et al. 2012).

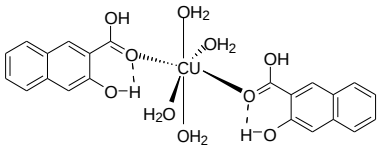

Figure 1: Structure of Catalyst CuL_2

Many of these methods suffer from some limitations such as long reaction times, drastic reactionconditions and low to moderate yields. During the course of our studies toward the development of new routes to the synthesis of heterocyclic compounds (Allameh et al. 2011), (Esmaeilzadeh et al. 2016), (Yasaghi et al. 2012), herein we report the catalytic effects Cu(II) complex (Figure 1) as lewis acidic catalyst in the synthesis of 1,8-dioxodecahydroacridines (Figure 2).

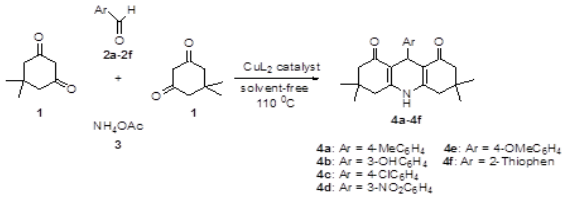

Figure 2: Catalytic synthesis of 1,8-dioxodecahydroacridines.

In order to find the optimal conditions, we first selected a model reaction including the synthesis of 4c. Therefore, a mixture of dimedone (2mmol), 4-Chlorobenzaldehyde (1mmol) and ammonium acetate (1mmol), in the presence of various amounts of the catalyst (CuL_2) was heated in different solvents and under solvent-free conditions (Table 1).

As can be seen, no product was produced in the absence of the catalyst even after 2h (Entry 1). The effects of reaction temperature and amount of catalyst on the output were investigated. The shortest time and best yield were achieved in the presence of 0.03g of the catalyst at 110 ℃ as optimal amount and temperature respectively (Table 1, Entry 8). The generality of this novel protocol was demonstrated by the wide range of aromatic aldehydes to synthesize the corresponding products in high to excellent yields (Table 2).

Table 1: Effect of amount of catalyst, solvent and temperature in the model reaction

Entry	Catalyst (g)	Solvent	Temp (°C)	Time (min)	Yield (%)
1	----	----	120	120	----
2	0.01	----	90	45	50
3	0.03	----	90	45	58
4	0.05	----	90	40	60
5	0.07	----	90	35	66
6	0.10	----	90	35	70
7	0.01	----	110	20	70
8	0.03	----	110	10	95
9	0.05	----	110	10	90
10	0.07	----	110	10	90
11	0.10	----	120	20	90
12	0.01	----	120	25	85
13	0.03	----	120	25	85
14	0.05	----	120	30	80
15	0.07	----	120	30	80
16	0.10	----	120	35	78
17	0.03	EtOH	Reflux	50	65
18	0.03	H_2O	Reflux	60	55
19	0.03	MeOH	Reflux	50	45
20	0.03	$CHCl_3$	Reflux	60	30

Table 2: Synthesis of 1,8-dioxodecahydroacridinesunder optimized conditions

Entry	Ar	Product	Yield (%)	Time (min)	Melting pint (°C)	
					Found	Reported
1	4-MeC_6H_4	4a	95	10	265-267	269-270(Davoodnia et al. 2011)
2	3-OHC_6H_4	4b	85	20	285-290	>302-304(Patil et al. 2014)
3	4-ClC_6H_4	4c	95	10	298-300	299-301(Davoodnia et al. 2011)
4	3-$NO_2C_6H_5$	4d	80	20	287-289	285-286(Patil et al. 2014)
5	4-$OMeC_6H_4$	4e	90	10	271-273	270-272(Davoodnia et al. 2011)
6	2-Thiophen	4f	80	15	296-298	296-297(Tu et al. 2009)

A plausible mechanism for the formation of products 4a-4f by using Cu (II) complex as catalyst is depicted in Figure 3. As shown, the complex can be active as a lewis acidic catalyst. Thus, we suggest that the cations Cu^{+2} are active as acid. The acidic cations lead to active the carbonyl groups in aldehydes (2) and dimedones (1) as electrophile and the rate of the reaction increases *via* the formation of the intermediates I, II. In continuation, the products 4 obtain after a cyclocondensation reaction between I and II.

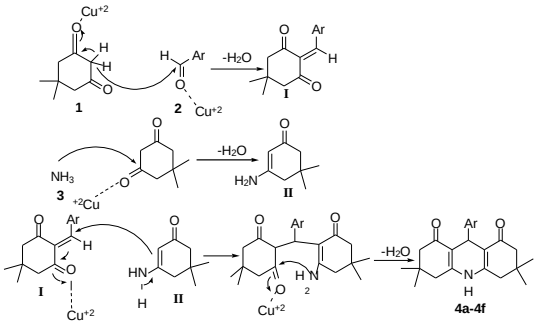

Figure 3: Plausible mechanism for the formation of 1, 8-dioxodecahydroacridines in the presence of Cu (II) complex as catalyst

MATERIALS AND METHODS

All chemicals were obtained from Merck Company and used as received.Melting points were determined on a SMP3 melting point apparatus. The IR spectra were obtained on a Tensor 27 Bruker spectrophotometer as KBr disks. The ^{1}H- NMR (300 MHz) spectra were recorded using Bruker 300 spectrometer. The compounds were indentified by the comparison of their physical and spectroscopic data with those of known compounds. The catalyst was prepared accordance with our previous work (Khoshdast et al. 2017), and the structure accuracy of the catalyst was characterized by FT-IR spectroscopy.

General procedure for the synthesis of1,8-dioxodecahydroacridinederivatives (4a-4f)

A mixture ofdimedone 1 (2mmol), aromatic aldehydes 2a-f (1 mmole), ammonium acetate 3 (1 mmole), and catalyst (CuL_2) (0.03 g) was heated in the oil bath at110°Cfor 10-20 min. After completion of reaction (monitored by TLC),the mixture was cooled to room temperature and then hot ethanol (10 mlit) was added. Due to the fact that the catalyst was insoluble in hot ethanol, it could therefore be recycled by a simple filtration. The separated catalyst reused in model reaction without appreciable reduction in the catalytic activity. The results of the first experiment and subsequent experiments were almost consistent in yields (95, 91 and 88%).

Selected Spectral data

3,3,6,6-tetramethyl-1,8-dioxo-9-(3-nitrophenyl)-decahydroacridine (4d)

^{1}H NMR (300 MHz, DMSO-d_6) δ:0.876 (s, 6H, $2CH_3$), 1.053 (s, 6H, $2CH_3$),1.994-2.521 (8H, $4CH_2$), 7.502-7.982 (4H, arom-H), 4.936 (s, 1H,CH), 9.504 (s, 1H, NH). IR (KBr disc) υ:1674(C= O), 1425,1528 (NO_2), 3187-3272(NH) cm^{-1}.

3,3,6,6-tetramethyl-1,8-dioxo-9-(4-methoxyphenyl)-decahydroacridine (4e)

^{1}H NMR (300 MHz, DMSO-d_6) δ: 0.875 (s, 6H, $2CH_3$), 1.050 (s, 6H, $2CH_3$), 2.011-2.527 (8H, $4CH_2$), 6.715-7.074 (4H, arom-H), 4.761 (s, 1H,CH), 9.265 (s, 1H, NH), 3.670 (s, 3H, CH3). IR (KBr disc) υ: 1644 (C= O), 1436, 1583 (NO_2), 3186-3273(NH) cm^{-1}.

RESULTS AND DISCUSSION

Treatment of dimedone,ammonium acetate and aromatic aldehydes in the presence of a catalytic amount of Cu(II) complex gave products which were identified as 1,8-dioxodecahydroacridines. All prouducts gave satisfactory spectral data inaccord with the assigned structures.

CONCLUSION

In conclusion, we used a Cu(II) complex for a cyclocondensation reaction of dimedone, aromatic aldehydes and ammonium acetate. The obtained results showed that the catalyst decreased the reaction time and increased the yields of the products. Also, one of the important advantages of the catalyst was easy separation without using hazardous solvents.

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