

Synthesis of open chain analogue of 1,8-dioxo-octahydroxanthene catalyzed by aluminosilicate MCM-41

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In this study, aluminosilicate MCM-41 has been found to be an efficient catalyst for reaction between different benzaldehyde derivatives and 5,5-dimethyl-1,3-cyclohexanedione to give open chain analogue of 1,8-dioxo-octahydroxanthene in excellent yields. No evidence for the formation of cyclization products was observed. The catalyst can be used several times after recovery.

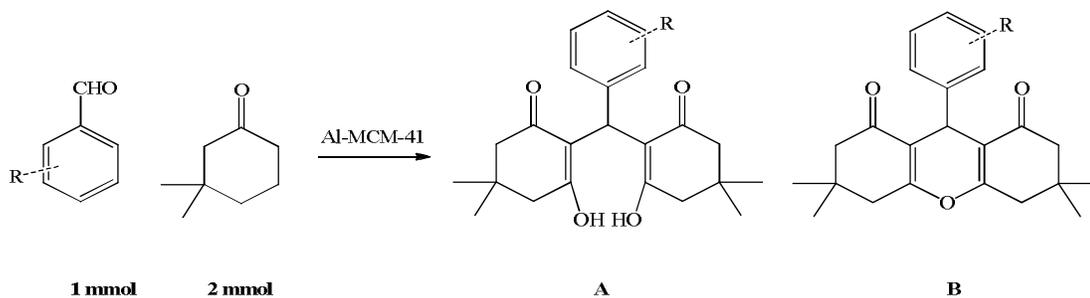
Keywords: Al-MCM-41; Mesoporous; Heterogenous catalyst; Multicomponent reaction

1. INTRODUCTION

Organic synthesis performed through multicomponent reactions (MCRs) is an attractive area of research in organic chemistry. Although most of the established MCRs do not require a catalyst, the search for new MCR products has resulted in an intensified effort to find catalysts and new catalyzed MCRs [1].

Recently, ordered mesoporous materials have been intensively studied with regard to technical applications as catalysts and catalyst supports [2]. The synthesis of the M41S family (MCM-41, MCM-48, MCM-50) of siliceous solids with sharply distributed pores of diameter in the mesoporous regime (20–100 Å) as well as highly specific surface of up to 1000 m²/g and a high thermal stability has greatly increased the range of heterogeneous catalytic applications [3]. Also, it is well known that by introducing aluminum inside the pore walls the catalytic activity increases and Al-MCM-41 shows remarkable acidic properties and has been found to catalyze several organic transformations [4,5].

In continuation of our previous research to develop new synthesis methodology with low impact environment effects [6-10], we decided to investigate the catalytic ability of Al-MCM-41 in multicomponent reactions by treatment of aryl aldehydes with 5,5-dimethylcyclohexane-1,3-dione (Scheme 1).



Scheme 1. Al-MCM-41 promoted synthesis of xanthene

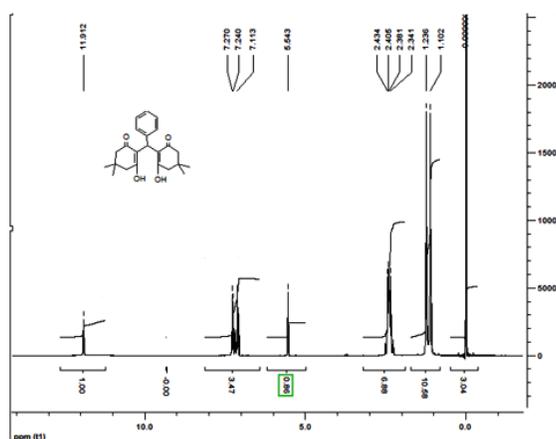
2. EXPERIMENTAL

Aluminosilicate MCM-41 was synthesized in our laboratory according to the reported procedure [11]. NMR spectra were recorded in DMSO on a Bruker Advance DPX 400 MHz instrument spectrometer using TMS as internal standard.

A mixture of benzaldehyde (1 mmol), 5,5-dimethyl-1,3-cyclohexanedione (2 mmol) and 100 mg Al-MCM-41 in 5 mL ethanol was stirred under reflux condition for appropriate time (table 1). After completion of the reaction that was monitored by TLC, the reaction mixture was cooled, filtered and concentrated to give desired product. The solid crude products were recrystallized from ethanol.

3. RESULTS AND DISCUSSION

First, the reaction condition including solvent, amount of catalyst and temperature was optimized. Thin layer chromatography analysis of the reaction mixture showed completion of the reaction when the conversion of benzaldehyde (1 mmol) and 5,5-dimethyl-1,3-cyclohexanedione (2 mmol) was carried out on ethanol under reflux condition and Al-MCM-41 (0.1 g) as host nanoreactor. The ^1H NMR spectra of the product indicate the formation of dihydroxy compound and no cyclization product was obtained even if the reaction time was extended to 12 h. It exhibits two singlet resonances for the non-equivalent methyl groups at $\delta=1.10$ and 1.23 ppm. Also, the proton on methylene bridge and hydroxyl groups appear at $\delta =5.54$ and 11.91 ppm, respectively (Scheme 2).

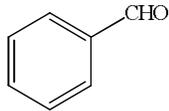
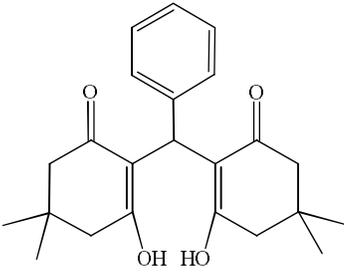
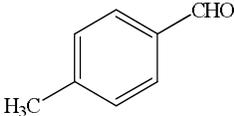
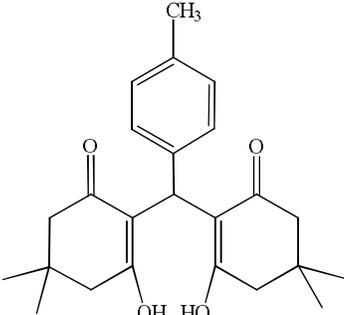
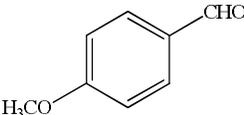
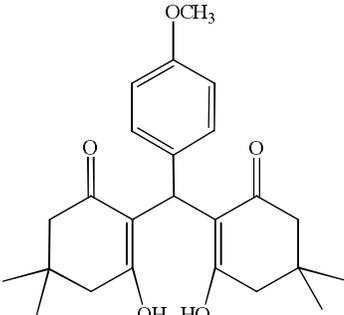
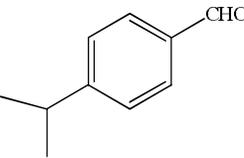
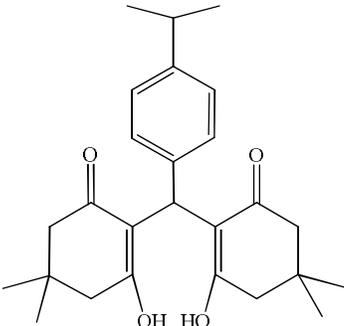


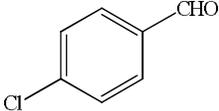
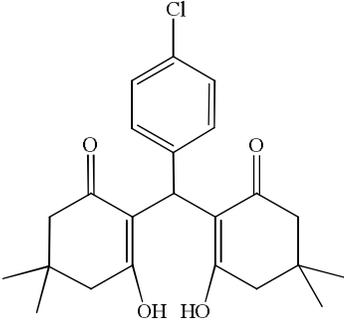
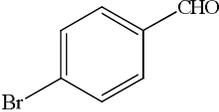
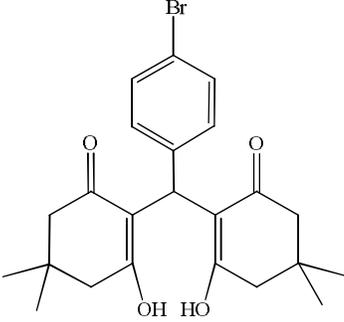
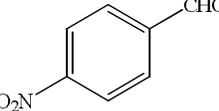
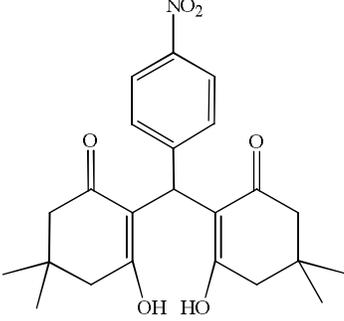
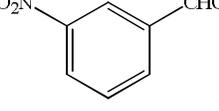
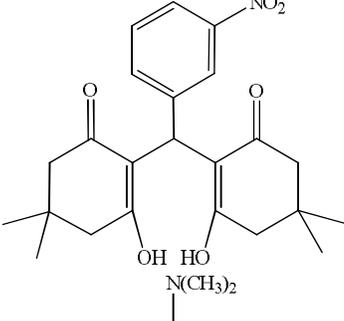
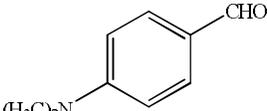
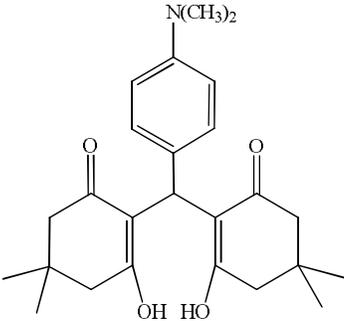
Scheme 2.

Scheme 2. ^1H NMR spectra of open chain analogue of 1,8-dioxo-octahydroxanthene

As shown in table 1 the reaction worked well with a range of aromatic aldehyde containing electron donating group for example OCH₃ or N(CH₃)₂ and electron-withdrawing group for example NO₂ or Br, giving open chain analogue of 1,8-dioxo-octahydroxanthene derivatives in 87–94% yields.

Table 1. Preparation of open chain analogue of 1,8-dioxo-octahydroxanthene using Al-MCM-41 as catalyst

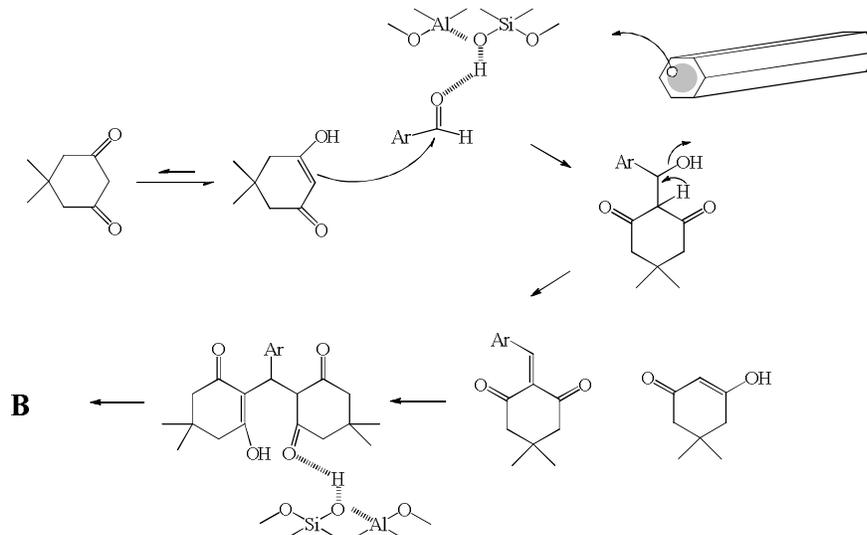
Entry	Aldehyde	Product	Time (h)	Yield (%) ^a
1			1	94
2			2	90
3			2.5	85
4			2.5	87

5			2.0	88
6			2	88
7			3	90
8			2.5	89
9			2	94

A plausible mechanism to rationalize this transformation is illustrated in Scheme 3. The catalyst was easily recovered by simple filtration, washed with ethanol and dried at 110 °C for 15

min before using for another time. No thermal or mechanical degradation was observed when recycled several time.

In conclusion, we have developed a convenient method for the synthesis of open chain analogue of 1,8-dioxo-octahydroxanthenes utilizing Al-MCM-41. The simple experimental work-up, high yields and applications of inexpensive catalysts are the advantages of the present method.



Scheme 3. Proposed mechanism

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