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SULPHONATED MCM-41 AS AN EFFICIENT AND REUSABLE CATALYST FOR THE SYNTHESIS OF 14-ARYL-14H-DIBENZO[A,J]XANTHENES UNDER SOLVENT-FREE CONDITION

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ABSTRACT

A simple and efficient method has been developed for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes from condensation of aromatic aldehydes and β-naphthol under microwave irradiation in the presence of catalytic amount of sulphonated MCM-41 in solvent-free condition. The silent features of present method are easy handling, stability, reusability and eco-friendliness of the catalyst, high yields, short reaction time, simple experimental and work up procedure.

Keywords: *Sulphonated MCM-41, dibenzenoxanthene, solvent-free, microwave irradiation*

INTRODUCTION

Xanthenes and its derivatives attracted special attention of organic chemist because these heterocycles are biologically active with potential applications as anti-inflammatory[1], antibacterial[2], and antiviral agents[3]. In addition, the compound used as dyes[4], in laser technologies[5], and in fluorescent materials[6].

As a result of their importance from industrial, biological and synthetic point of view, many synthetic methods have been reported for the synthesis of xanthenes such as cyclocondensation between 2-hydroxyaromatic aldehydes and 2-tetralone[7], cyclodehydrations[8] and intramolecular phenyl carbonyl reaction of aldehydes with β-naphthol by dehydration[9]. Very recently several catalysts have been used for this reaction includes sulphamic acid[10], iodine[11], aluminium hydrogen sulphate[12], dipyridine cobalt chloride[13], selectflour[14], and alum[15]. However, some of these methods suffer from one or more drawbacks such as strong acidic condition, long reaction times, low yield of the products, tedious work-up, and need to use excess amount of reagent. Thus, there is a need to develop a simple, efficient and rapid procedure for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes.

The use of solid acid catalysts has gained importance in organic synthesis due to several advantages such as operational simplicity, non-toxicity, reusability, low cost, and easy isolation after completion of the reaction.

Organic synthesis in absence of solvent is a powerful tool for the generation of structurally diverse molecules, due to their special activity, the ease of set-up and work-up, arising great interest[16]. Moreover, solvent free reactions relatively are faster, taking just a contact with each other. This aspect coupled with the low cost of running a reaction without solvent and not needed special equipment, could become a decisive factor in industry.

The application of microwave irradiation to the combinatorial chemistry becomes a powerful tool in accelerating the pace of library synthesis[17]. Domestic microwave oven is most popularly used in synthesis, because of its low cost and ready availability. Our results show that the effect of microwave irradiation on the reaction studied was a shortening of the reaction times and a smooth increase in the yields. However, specially fabricated mono-mode microwave reactors provide homogeneous heating, temperature control, and more importantly improved safety features. Major aim of this integrated technology is to exploit high degree of molecular diversity throughout organic synthesis to rapid access greatly expanded drug-like compound collection without tedious or time-consuming processes[18].

EXPERIMENTAL

All chemicals were purchased from Merck, Aldrich and Rankem chemical companies and used without further purification. The uncorrected melting points of compounds were taken in an open capillary in a paraffin bath. The progress of the reaction was monitored by TLC (Thin Layer Chromatography). IR spectra were recorded on Perkin-Elmer FT spectrophotometer in KBr disc. ^{1}HNMR spectra were recorded on Varian NMR spectrometer. Model Mercury Plus (300 MHz) and the chemical shifts are given in ppm relative to signal for TMS as an internal standard. Microwave irradiation was carried out in a microwave oven (BPL, 800T, 2450 MHz) with power output of 800 W.

Synthesis of the MCM-41

For the synthesis of MCM-41 chemical was used, tetraethyl orthosilicate as silica source (TEOS, Merck India. Ltd), cetyl trimethyl ammonium bromide as template (CTABr, SD Fine chemicals, India), HCl (Merck India. Ltd) for maintain pH. The MCM-41 was synthesized according to established procedure[19]. In a typical synthesis 6.89 gm of CTABr dissolved in a warm 140 ml of deionised (30-40°C) water and to this solution 20.18 mL of tetraethyl orthosilicate was added dropwise with constant stirring at room temperature gel was obtained stirred it for 2 h. After that, the pH of the resulting gel was adjusted by 1M HCl from 12.5 to 8.5. After 2 h stirring, the resulting gel was poured into Teflon bottle, and heated at 100°C for 24 h. white solid was obtained, then filtered, washed with deionised water and dried at 60°C over night. The template was removed by the calcination at 500°C for 7 h with a heating rate 2.5 $^\circ$C/min.

Synthesis of sulphonated MCM-41

To a magnetically stirred solution of calcined MCM-41 (5g, 27.7mmol) in dichloromethane (20 mL), chlorosulphonic acid (1g, 9 mmol) was added dropwise at 0°C during 2 h. After completion of addition, the mixture was stirred for 2 h until HCl was removed from reaction vessel. Then, the mixture was filtered and washed with acetonitrile (20 mL) and dried at room temperature to obtain sulphonated MCM-41.

Characterization of MCM-41 materials

XRD data were recorded on Rigaku Miniflex instrument Cu-Kα radiation (1.5404 A^0) in the range 1.5 to 10. The XRD patterns of MCM-41 are shown in Fig.**1.** The sample exhibits an intense signal at about $2\theta = 2.1^0$ due to (1 0 0) plane and weak signal between 3.5 and 6.0^0 due to (1 1 0), (2 0 0), and (2 1 0) planes, these peaks are typical of MCM-41 materials[20]. In Fig.**2** after sulphation of MCM-41 showed weaker peaks of (1 0 0), (1 1 0), and (2 0 0) planes indicating that long-range order of MCM-41 are decreased after modification. In Table **4** decrease of the value of d-spacing and unit cell parameter of sulphonated MCM-41 was observed due to the incorporation of sulphate groups. This suggests that sulphate group have been successfully immobilized in the pore of MCM-41.

General procedure for the synthesis of 14-aryl-14H-dibenzo[a, j]xanthenes

The mixture of aromatic aldehyde (1 mmol), β-naphthol (2 mmol) and sulphonated MCM-41 (1 mol %) was taken in a 50 ml Borosil beaker. The reaction mixture was mixed properly with the help of glass rod and then irradiated in a microwave oven operating power (720 W) for 2-4 min. The progress of reaction was monitored by TLC, after completion of the reaction; the content was cooled to room temperature and diluted with $CHCl_3$ (2 × 10 mL). The content was filtered and the solid material was washed with $CHCl_3$ (2 × 10 mL). The solvent evaporated under reduced pressure to give crude product, which is recrystallized from ethanol to afford the pure product **3(a-l)** in excellent yield. The products **3 (a-l)** were confirmed by comparisons with authentic samples, IR, ^{1}H NMR, spectra and melting points.

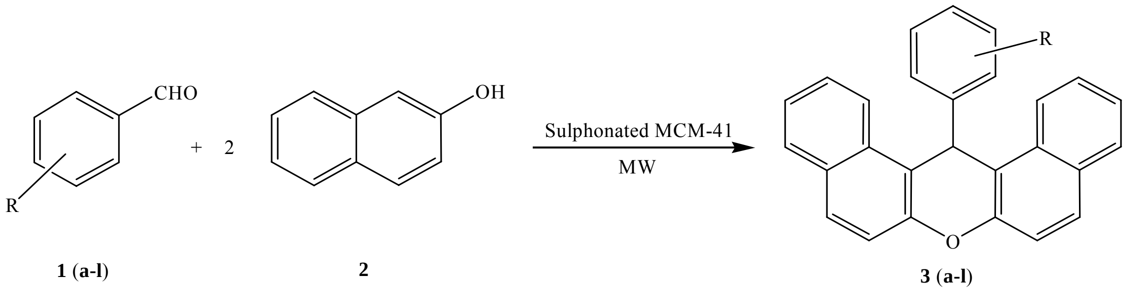
RESULTS AND DISCUSSION

In continuation of our work to develop a new synthetic methodology[21], herein, we would like to report an efficient and rapid method for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes from the condensation of aromatic aldehydes with β-naphthol in the presence of catalytic amount of sulphonated MCM-41 using microwave irradiation under solvent-free condition. Initially, we have carried out a model reaction of benzaldehyde with β-naphthol using sulphonated MCM-41 (1 mol %), without solvent, under microwave irradiation operating at 720 W powers. The reaction proceeded smooth and was completed within 2 min with 96 % yield. Encouraged by this result we turned our attention was directed towards the various substituted aldehydes reacted, rapidly with β- naphthol to give corresponding 14-aryl-14H-dibenzo[a,j]xanthenes derivatives.

To determine the role of sulphonated MCM-41, the same reaction was carried out in the absence of catalyst; the desired product was not formed after 20 min. This result indicates that sulphonated MCM-41 exhibits a high catalytic activity in this transformation.

The reusability of the catalyst is important for the large scale operation and industrial point of view. Therefore, the recovery and reusability of sulphonated MCM-41 was examined. The catalyst can be separated and reused after washing with ethyl acetate and drying at 60°C. The reusability of the catalyst was investigated in the reaction of benzaldehyde with β-naphthol **3a** in the presence of 1 mol % sulphonated MCM-41. From Table **2** shows that the catalyst can be used five times without significant loss of activity.

We have compared our results with other literature procedures, and are described in Table **3**. The data presented in this table shows the promising feature of this method in terms of shorter reaction time and excellent yields of products are achieved.



Scheme-1

Table-1: Synthesis of 14-aryl-14-H-dibenzo[a,j]xanthene derivatives in presence of sulphonated MCM-41 as a catalyst under microwave irradiation[a].

Product	R	Time (min)	Yield(%)[b]	M.P. (°C) Found	Reported
3a	H	2	96	181-182	182[12]
3b	2-Cl, 4-Cl	3	91	228-229	228[12]
3c	3-Cl	3	88	171-173	173[12]
3d	4-Cl	2.3	90	284-286	288[12]
3e	4-OH	2.3	87	140-142	140[13]
3f	4-Me	3	92	227-228	228[13]
3g	3-NO_2	3	89	213-215	213[13]
3h	4-NO_2	3	91	310-311	312[13]
3i	4-OMe	3	89	203-205	205[13]
3j	4-F	3	92	237-238	238[13]
3k	2-OMe	4	91	255-257	258[13]
3l	3-Br	2.5	87	188-190	190[13]

[a]All products were characterized by their physical constant, comparison with authentic samples, IR and ^1H NMR spectroscopy. [b]Yields based upon starting aldehyde.

Table-2: Recovery and reuse of sulphonated MCM-41 in the reaction of benzaldehyde with β-naphthol under microwave irradiation. (Table **1,** entry **3a**)

Run no.	**Yield (%)^a**
1	94
2	93
3	92
4	90
5	90

^{a}Isolated Yield

Table-3: Comparisons of some other reported procedure with the present method for the synthesis of 14-phenyl-14H-dibenzo[a, j]xanthene (Table **1,** entry **3a**)

Entry	**Catalyst**	**Conditions**	**Time**	**Yield(%)**	**Reference**
1	Sulphamic acid	Solvent free; heat (125°C)	8 h	93	[9]
2	Iodine	Solvent free; heat (90°C)	2.5 h	90	[10]
3	Aluminium hydrogen sulphate	Solvent free; heat (90°C)	31 min	90	[11]
4	Selectfluor^{TM}	Solvent free; heat (125°C)	8 h	93	[13]
5	Sulphonated MCM-41	Solvent free; MW (720 W).	2 min	96	Present

Table-4:XRD results of MCM-41 and sulphonated MCM-41 catalyst.

Samples	**d_{100} spacing (A^0)**	**Unit cell parameter a_0 (A^0)**
MCM-41	42.64	49.24
Sulphonated MCM-41	41.24	47.62

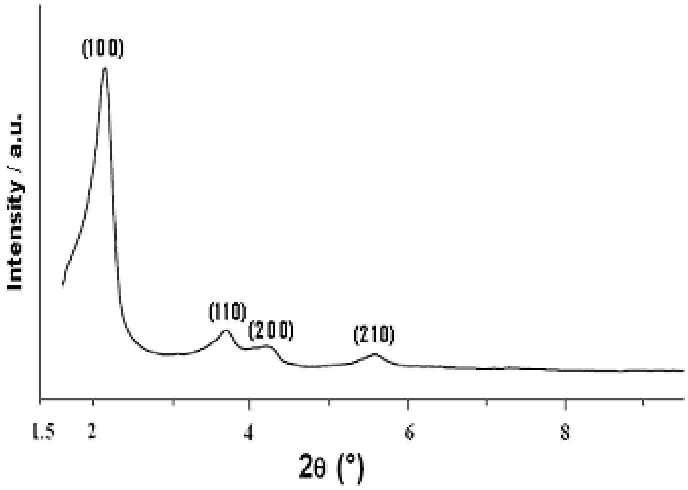


Fig.1 Powder X-ray diffraction of MCM-41

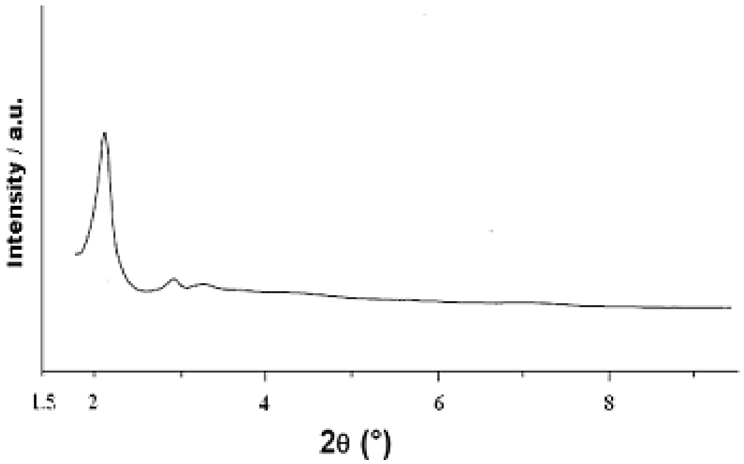


Fig. 2 Powder X-ray diffraction of sulphonated MCM-41.

Spectral data of representative compound

14-(4-Nitrophenyl)-14H-dibenzo[a,j]xanthene (Table 1, entry 3h). Yellow solid: mp. 312°C. IR (KBr) 3402, 3056, 1590, 1520, 1352, 1245, 1142, 807, 746 cm^{-1}. ^{1}H NMR 300 MHz, $CDCl_3$) d = 7.52 (s, 1H), 7.12-8.54 (m, 16H). Anal. Calcd. for $C_{27}H_{17}NO_3$: C, 80.38; H, 4.25; N, 3.47. Found: C, 80.28, H, 4.23, N, 3.55.

CONCLUSIONS

In conclusion, we have investigated the sulphonated MCM-41 as an mild and efficient catalyst for the synthesis of substituted 14-aryl-14H-dibenzo[a,j]xanthenes under solvent-free conditions using microwave irradiation. The remarkable advantages offered by this method are: catalyst is inexpensive, non-toxic, easy handling and reusable, simple work-up procedure, short reaction time, high yields of product with better purity and green aspect by avoiding toxic catalyst and hazardous solvent.

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