Application of Sulfonic Acid Functionalized Nanoporous Silica (SBA-Pr-SO_3H) in the Green One-pot Synthesis of Polyhydroacridine Libraries

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ABSTRACT: *1,8-Dioxo-decahydroacridines have been synthesized by the three-component reaction of aromatic aldehydes, aromatic amines (or ammonium acetate), and dimedone in the presence of sulfonic acid functionalized nanoporous silica (SBA-Pr-SO_3H) under solvent-free conditions. Excellent yields, short reaction times, mild reaction conditions, and easy work-up procedures are advantages of this green method.*

KEY WORDS: *Acridine derivatives, Nano-reactor, Functionalized mesoporous materials, Dimedone.*

INTRODUCTION

Multi-Component Reactions (MCRs) have recently appeared as powerful alternatives to more traditional strategies, mainly by means of their operational simplicity and high atom economy [1-4]. The current literature reveals that 1,4-dihydropyridine derivatives exhibit interesting biological activities such as anti-microbial [5], anti-viral [6], anti-HIV [7], and anti-cancer [8, 9] activities. Acridines and their derivatives as polyfunctionalized 1,4-dihydropyridines, have been found to possess a wide spectrum of biological activities [10, 11], but recent research has mainly focused on their utility as anticancer [12], antitumor [13], and anti-Alzheimer's disease drugs [14]. In the literature some methods are available for the synthesis of acridine compounds containing 1,4-dihydropyridines, from the reaction of dimedone, aldehydes and ammonium acetate or different substituted anilines via traditional heating in organic solvents [15], using ionic liquids [16], or microwave/ H_2O [17], and in the presence of different catalysts such as TEBAC/H_2O [18], silica-bonded s-sulfonic acid [19], *p*-dodecyl benezenesulfonic acid [20], amberlyst-15 [21], $CeCl_3.7H_2O$ [22], tris(pentafluorophenyl) borane [23], HY zeolite [24], and PEG-400/ CAN [25].

Mesoporous materials have been receiving considerable attention in recent years because of their

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potential application as catalysts [26], supports [27], adsorbents [28] as well as nano-reactors [29]. The SBA-15 is new nanoporous silica with hexagonal structure, high surface area, large pore size, great pore wall thickness, and high thermal stability. It has been functionalized with different groups to produce highly active and selective catalysts [30, 31]. Integration of acidic functional groups (e.g., SO_3H) into SBA-15 has also been explored to produce promising solid acids [32]. Recently, there has been an increasing number of reports about the applications of these materials as catalysts in chemical transformations [33-36].

In continuation of our work on the application of heterogeneous solid catalysts in multi-component synthesis of heterocyclic compounds [37-40], herein we want to report the synthesis of acridinedione derivatives in the presence of sulfonic acid functionalized SBA-15 (SBA-Pr-SO_3H).

EXPERIMENTAL SECTION

All chemicals were obtained commercially and used without further purification. IR spectra were recorded from KBr disk using a FT-IR Bruker Tensor 27 instrument. Melting points were measured by using the capillary tube method with an electro thermal 9200 apparatus. The ^{1}H NMR (500 MHz) was run on a Bruker DPX, 500 MHz. GC-Mass analysis was performed on a GC-Mass model: 5973 network mass selective detector, GC 6890 Agilent. SEM analysis was performed on a Philips XL-30 field-emission scanning electron microscope operated at 16 kV while TEM was carried out on a Tecnai G^2 F30 at 300 kV.

Synthesis and functionalization of SBA-15

The nanoporous compound SBA-15 was synthesized and functionalized according to our previous report [38] and the modified SBA-Pr-SO_3H was used as nanoporous solid acid catalyst in the following reaction.

General procedure for the synthesis of 1,8-dioxo-decahydroacridine derivatives 4a-h

The SBA-Pr-SO_3H (0.02 g) was activated in vacuum at 100 °C and then after cooling to room temperature, dimedone **1** (2 mmol, 0.28 g), aromatic aldehyde **2** (1 mmol), and aryl amine or ammonium acetate **3** (1.2 mmol) were added to it. The mixture was heated under solvent-free condition for an appropriate time while the reaction was monitored by TLC. After completion of the reaction, the crude product was dissolved in hot ethanol and then the catalyst was removed by filtration. The pure product was obtained by cooling of filtrate. The catalyst was washed subsequently with diluted acid solution, distilled water and then acetone, dried under vacuum and re-used for several times without loss of significant activity.

3,3,6,6-Tetramethyl -9-(2-methoxyphenyl) -1,8-dioxo-decahydroacridine (4a)

IR (KBr): 3314, 3285, 2953, 1638, 1589, 1485, 1366, 1225, 1143 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.86 (s, 6H, $2CH_3$), 1.01 (s, 6H, $2CH_3$), 2.07 (d, *J* = 16.5 Hz, 2H, CH_2), 2.17 (d, *J* =16.6 Hz, 2H, CH_2), 2.29 (d, *J* = 16.5 Hz, 2H, CH_2), 2.36 (d, *J* = 16.6 Hz, 2H, CH_2), 3.77 (s, 3H, OCH_3), 5.20 (s, 1H, CH), 6.20 (s, 1H, NH), 6.74-6.81 (m, 1H, ArH), 7.04-7.22 (m, 1H, ArH), 7.23 (d, *J* = 8.7 Hz, 1H, ArH), 7.39 (d, *J* = 8.7 Hz, 1H, ArH) ppm. MS: m/z (%) 380 [M$^+$], 363, 349, 296, 273, 217.

3,3,6,6-Tetramethyl -9-(2,3-dimethoxyphenyl) -1,8-dioxo-decahydroacridine (4c)

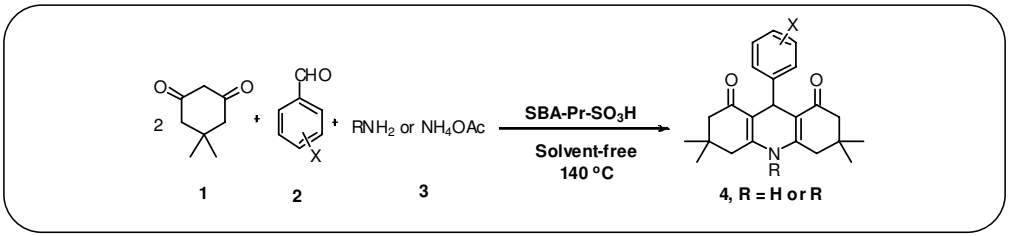
IR (KBr): 3283, 2959, 1640, 1614, 1487, 1364, 1225, 1143 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.99 (s, 6H, $2CH_3$), 1.09 (s, 6H, $2CH_3$), 2.18 (d, *J* = 16.5 Hz, 2H, CH_2), 2.20 (d, *J* = 16.6 Hz, 2H, CH_2), 2.30 (d, *J* = 16.5 Hz, 2H, CH_2), 2.36 (d, *J* = 16.6 Hz, 2H, CH_2), 3.73 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 5.32 (s, 1H, CH), 6.35 (s, 1H, NH), 6.74-6.76 (m, 1H, ArH), 7.20 (d, *J* = 8.7 Hz, 1H, ArH), 7.26 (d, *J* = 8.7 Hz, 1H, ArH) ppm. MS: m/z (%) 410 [M$^+$], 379, 323, 295, 273, 217.

3,3,6,6-Tetramethyl -9-(4-nitrophenyl) -1,8-dioxo-octahydroxanthene (5a)

IR (KBr): 3448, 2958, 1637, 1578, 1488, 1363, 1341, 1221, 1145 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.00 (s, 6H, $2CH_3$), 1.11 (s, 6H, $2CH_3$), 2.18 (d, *J* = 17.6 Hz, 2H, 2 × CH), 2.35 (d, *J* = 16 Hz, 2H, 2 × CH), 2.47 (d, *J* = 16 Hz, 2H, 2 × CH), 2.63 (d, *J* = 17.6 Hz, 2H, 2 × CH), 4.07 (s, 1H, CH), 7.49 (d, *J* = 8.8 Hz, 2H, ArH), 7.54 (d, *J* = 8.8 Hz, 2H, ArH) ppm. MS: m/z (%) 395 [M$^+$].

3,3,6,6-Tetramethyl -9-(2-methoxyphenyl) -1,8-dioxo-octahydroxanthene (5b)

IR (KBr): 2954, 1661, 1623, 1421, 1426, 1360, 1250 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.97 (s, 6H, $2CH_3$),1.1 (s, 6H, $2CH_3$), 2.12 (d, *J* = 17.6 Hz, 2H, 2 × CH),



Scheme 1

2.15 (d, *J* = 16 Hz, 2H, 2 × CH), 2.20 (d, *J* = 16 Hz, 2H, 2 × CH), 2.36 (d, *J* = 17.6 Hz, 2H, 2 × CH), 3.78 (s, 3H, CH_3O), 4.86 (s, 1H, CH), 6.78-7.10 (m, 2H, ArH), 7.42 (d, *J* = 8.8 Hz, 2H, ArH) ppm. MS: m/z (%) 380 [M^+].

3,3,6,6-Tetramethyl -9-(4-hydroxyphenyl) -1,8-dioxo-octahydroxanthene (5c)

IR (KBr): 3399, 2960, 1653, 1615, 1421, 1365, 1225, 1197 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$): δ 1.00 (s, 6H, $2CH_3$), 1.1 (s, 6H, $2CH_3$), 2.17 (d, *J* = 17.6 Hz, 2H, 2 × CH), 2.23 (d, *J* = 16 Hz, 2H, 2 × CH), 2.26 (d, *J* = 16 Hz, 2H, 2 × CH), 2.46 (d, *J* = 17.6 Hz, 2H, 2 × CH), 4.68 (s, 1H, CH), 7.12 (d, *J* = 8.8 Hz, 4H, ArH) ppm. MS: m/z (%) 366 [M^+].

RESULTS AND DISCUSSION

In this paper, the synthesis of 1,8-dioxo-decahydroacridine derivatives **4** through the three-component condensation of dimedone **1**, aromatic aldehydes **2**, and nitrogen source like ammonium acetate or aromatic amines **3** in the presence of SBA-Pr-SO_3H as an efficient nanoparticle with acidic properties has been studied (Scheme 1). For finding the best reaction conditions, at first, we investigated the effects of solvents on this synthesis. The reaction of dimedone **1**, 4-methoxybenzaldehyde **2b** and ammonium acetate **3** was selected as the reaction model. Among the different conditions such as H_2O, EtOH, MeCN, H_2O/EtOH, and solvent-free condition, it was found that solvent-free condition results in the highest yield in a reasonable time (Table 1). Therefore, the evaluation of this reaction was made under solvent-free condition at 140 °C for the synthesis of 1,8-dioxo-decahydroacridines **4a-h** and the results are summarized in Table 2. Surprisingly, contrary to our expection, in the case of aromatic amines such as 4-nitroanioline, 2-nitroaniline, and 4-bromoaniline, 1,8-dioxo-octahydroxanthenes **5a-c** were obtained as the major products. A wide range of aromatic aldehydes containing both electron-donating and electron-withdrawing groups have been used in this reaction and in all cases, high yields of products were obtained. It was reported that in the absence of the catalyst the product was obtained in low yield (30%) [41].

A proposed mechanism for the synthesis of decahydroacridines **4a-h** is outlined in Scheme 2. At first, the acid catalyst changes aldehyde **2** into the convenient electrophile via protonation of carbonyl group which then, condenses with one molecule of dimedone **1** in a fast Knoevenagel condensation to produce intermediate **6**. Simultaneously, the condensation of another molecule of dimedone **1** with amine **3** gives the enamine intermediate **7** which reacts to intermediate **6** via Michael addition reaction to produce the adduct product **8**. Finally, after an intramolecular cyclization followed by dehydration, the compound **8** is converted to the expected product **4**.

In this procedure, SBA-Pr-SO_3H plays a crucial role in accelerating the reaction. The reaction takes place in the pores of SBA-Pr-SO_3H which acts as a nano-reactor (Fig. 1). After completion of reaction, the crude product was dissolved in hot EtOH and SBA-Pr-SO_3H was easily filtrated from the reaction mixture. The catalyst washed subsequently with diluted acid solution, distilled water and then acetone, dried under vacuum and re-used for several times without significant loss of activity. The reusability of the catalyst was investigated under optimized conditions for the synthesis of the model compound **4b**. As it is shown in Fig. 2, the process of recycling was completed four times and no significant decrease in activity was observed. The yields for the four runs were found to be 92%, 86%, 79%, and 71%, respectively.

Table 1: The effects of different conditions on the synthesis of 4b.

Entry	Solvent	Time (h)	Yield (%)
1	H_2O	5	43
2	EtOH	5	34
3	EtOH/ H_2O (1:1)	5	48
4	CH_3CN	3	57
5	Neat	25 min	92

Table 2: The synthesis of 1,8-dioxo-decahydroacridines 4 in the presence of SBA-Pr-SO_3H.

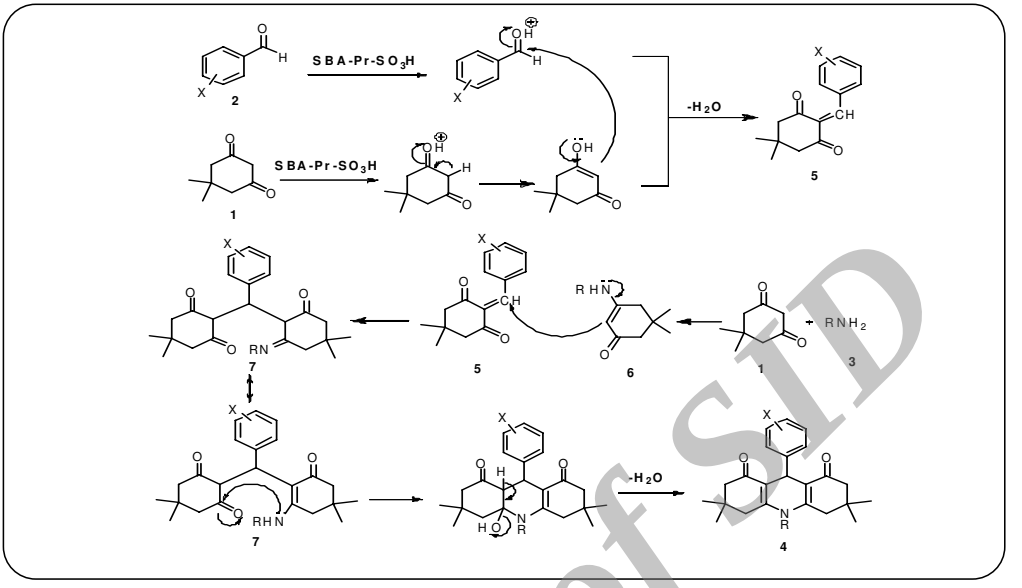
Entry	Product	Time (min)	Yield (%)	Mp (°C)	Mp (L)
1	4a	25	70	287-290	294-296 [42]
2	4b	25	92	304-307	298-300 [43]
3	4c	25	59	316-318	324-326 [42]
4	4d	25	59	292-294	296-297 [43]
5	4e	25	62	298-301	296-298 [44]
6	4f	25	77	316-320	318-320 [22]
7	4g	25	66	290	290-291 [45]
8	4h	25	58	249-251	260-262 [46]
9	5a	40	59	227-231	225-227 [47]
10	5b	45	90	192-195	190-191 [48]
11	5c	40	63	245-248	245-250 [47]

The efficiency of various catalysts in the synthesis of 1,8-dioxo-decahydroacridines **4** has been compared in Table 3. Short reaction times and high yield of products and, in contrast with other existing methods, demonstrated that SBA-Pr-SO_3H acts as an efficient nano-reactor in this reaction.

The SBA-15 as a new nanoporous silica can be prepared by using commercially available triblock copolymer pluronic P126 as a structure directing agent [51]. The sulfonic acid functionalized SBA-15 was usually synthesized through direct synthesis or post-grafting [52, 53]. A schematic illustration for the preparation of SBA-Pr-SO_3H was shown in Fig. 3. At First, the calcined SBA-15 silica was functionalized with (3-mercaptopropyl) trimethoxysilane (MPTS) and then, the thiol groups were oxidized to sulfonic acid by hydrogen peroxide.

The surface of the catalyst was analyzed by different methods such as TGA, BET and other methods which were demonstrated that the organic groups (propyl sulfonic acid) were immobilized into the pores [38].

Fig. 4 illustrates the SEM and TEM images of SBA-Pr-SO_3H. SEM image (Fig. 4, a) shows uniform particles about 1µm which the same morphology was observed for SBA-15. It can be concluded that morphology of the solid



Scheme 2

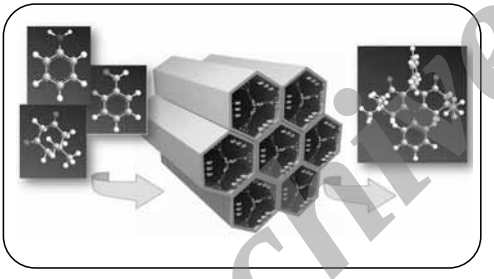


Fig. 1: SBA-Pr-SO_3H acts as a nano-reactor.

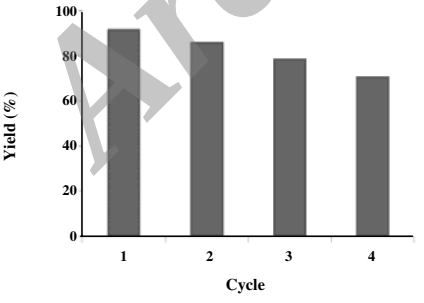


Fig. 2: Reusability of SBA-Pr-SO_3H in the synthesis of compound 4b.

was saved without change during the surface modifications. On the other hand, the TEM image (Fig. 4, b) reveals the parallel channels, which resemble the pores configuration of SBA-15. This indicates that the pore of SBA-Pr-SO_3H was not collapsed during two steps reactions.

CONCLUSIONS

In conclusion, an efficient methodology for Hantzsch reaction using SBA-Pr-SO_3H as a nano-reactor was introduced. SBA-15 functionalized with Brönsted sulfonic sites shows the favorable acidity to activate the substrate molecules to obtain 1,8-dioxo-decahydroacridines in excellent yield. The catalyst could be recovered and reused for several reaction cycles without noticeable loss of reactivity. Mild reaction condition, simplicity of the procedure, and short reaction times are the significant advantages of this methodology.

Acknowledgements

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Table 3: Comparison of different conditions in the synthesis of 1,8-dioxo-decahydroacridines.

Entry	Catalyst	Solvent	Condition	Time (h)	Yield	Year	Ref
1	TEBAC[a]	H_2O	Reflux	4-8	90-98	2006	[18]
2	[Hmim]TFA[b]	—	Heating	4-7	78-89	2008	[16]
3	HY-Zeolite	EtOH	Reflux	2.5-3.5	70-90	2009	[24]
4	SDS[c]	H_2O	Reflux	6-20	56-72	2009	[49]
5	SBSSA[d]	EtOH	Reflux	1-4.5	84-96	2010	[19]
6	SBNPSA[e]	EtOH	Reflux	2-5	86-93	2010	[50]
7	CAN[f]	PEG-400	Heating	3.5-4	93-98	2010	[25]
8	SBA-Pr-SO_3H	—	Heating	25min	58-92	This work	

a) Triethylbenzylammonium chloride. b) 1-Methylimidazolium triflouroacetate. c) Sodium 1-dodecanesulfonic. d) Silica-bonded S-sulfonic acid. e) Silica bonded N-propyl sulfamic acid. f) Ceric ammonium nitrate.

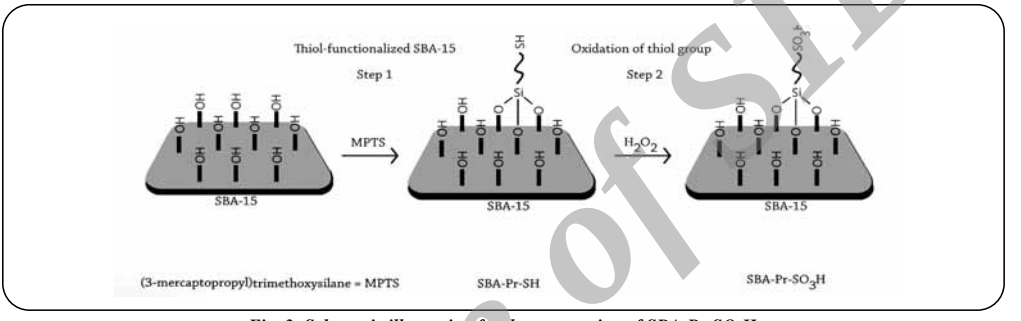

Fig. 3: Schematic illustration for the preparation of SBA-Pr-SO_3H.

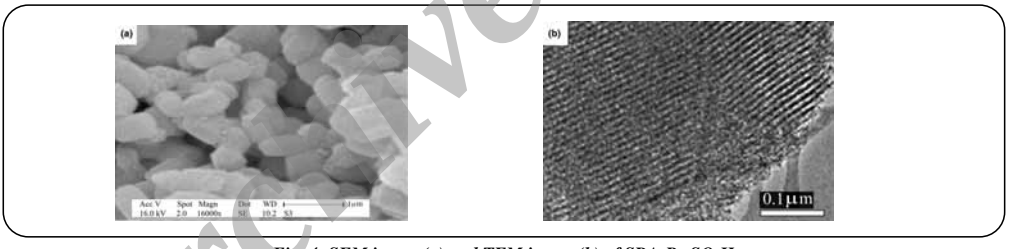

Fig. 4: SEM image (a) and TEM image (b) of SBA-Pr-SO_3H.

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