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New and Efficient Solventless Synthesis of 14-aryl-14H-dibenzo[a,j]xanthene Derivatives with Chemisorbed bis(hydrogen sulphate)benzene (SiO_2-BHSB)

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Abstract

Our method exhibited a shorter reaction time and higher yield compared to the results of other groups. This suggests that our approach is not only environmentally friendly but also highly efficient. Our results demonstrate the potential of using SiO2-BHSB as a catalyst for 14-aryl-14Hdibenzo-[a,j]xanthenes synthesis. In summary, our study highlights the advantages of using a heterogeneous catalyst, SiO2-BHSB, for the synthesis of 14-aryl-14Hdibenzo-[a,j]xanthenes. Our method offers a simple and green approach without the need for toxic solvents. The catalyst demonstrated good catalytic activity, easy recoverability, and reusability for several runs without loss in activity. The results of our study provide a promising avenue for the development of new strategies for 14-aryl-14Hdibenzo-[a,j]xanthenes synthesis,.

Keywords: 14-aryl or alkyl-14-H-dibenzo[a,j]xanthene, SiO_2-BHSB

Introduction

Dibenzo[a,j]xanthene are the prominent class of xanthene; it is a pentacyclic ring system where pyran forms the central part and is fused with four benzene rings [1], it is an essential oxygen-containing heterocyclic moiety shows different types of biological activities like antiviral, anti-plasmodial, having biological importance like both sensitizers in photodynamic therapy to localize and control tumors cells [2-3] even in the development of Antileishmanial Agents [4], furthermore xanthene used for generation of hydrogen peroxide five also xanthene derivatives such as Benzo-xanthene have properties like antibacterial and anti-inflammatory moreover used in laser technology and extensively used in dyes [6-7].

By taking into consideration of the importance of this compound, some recent development in 14-aryl or alkyl-14-H-dibenzo[a,j]xanthene has been done from *β*-naphthol and aryl aldehydes by using different catalytic systems; such as nanocatalyst like Nano Nickel-Cobalt Ferrite [8], Fe_3O_4@Agar-Ag as nanocatalyst [9], ZrO_2 nanoparticles [10], Sulfonated starch nanoparticles [11]. Some environmentally attractive ionic liquids to approach towards green chemistry like Bronsted acidic di-cationic ionic liquid [12], $[(Et)_3$ N-H]$FeCl_4$ ionic liquid [13], Some researchers done by using biological catalyst like glycine [14], Supramolecular *β*-Cyclodextrin [15], SO_4^{2-}/SnO_2-Fly Ash, bifunctional catalyst using microwave-assisted reaction [16], Some nanoparticle coated catalyst like Sulphated-PWA-supported MCM-41 coated Nickel ferrite [17], ultrasonic irradiation system by Fe_3O_4 @SiO_4-$SnCl_4$ [18], some transition metal-Pd Catalysed Formal [3+3] Annulation of Benzylic *gem*-Diacetates [19], H-Zeolite [20], $CuSO_4 \cdot 5H_2O$ [21], iodine catalyzed cyclization [22], some acid such as Polystyrene Sulfonic Acid [23]. These are the various catalytic system used for the synthesis of 14-aryl-14H-dibenzo[a, xanthenes. Indisputably, some of these procedures are good in view of reactivity. However, these synthetic procedures are hindered by the unavailability of complex catalytic material [24].

In latterly years, surface synthetic organic chemistry is gaining much appreciation due to its more surface area, recyclability, stability, selectivity, and low toxicity. The use of catalysts on solid supports has attained appreciable importance. It helps both in the purification process and in the prevention of reaction residues hence, it achieves solvent-free conditions in addition to support by providing surface to the reaction [25-26].

In this report, we have reported use of SiO_2–BHSB in the synthesis of 14-aryl or 14H-dibenzo[a,j]xanthenes at room temperature [27]. SiO_2-supported acid catalysts have received widespread attention nowadays due to its efficiency, recyclability, and uniqueness of high efficiency. Thus, This reaction is a more suitable green approach towards the synthesis of 14-aryl or 14H-dibenzo[a,j]xanthenes to attain a higher yield of the product.

Experimental

All chemicals were available and purchased from Sigma Aldrich and alfa aesar. The catalyst was synthesized according to the literature. Melting points were recorded on a Veego melting point apparatus VMP-CM. The IR spectra were obtained using a Nicolet impact 410 FTIR spectrometer using the KBr pellet technique. The H^1NMR (400 MHz) spectra were recorded with a Bruker DRX-400 spectrometer.

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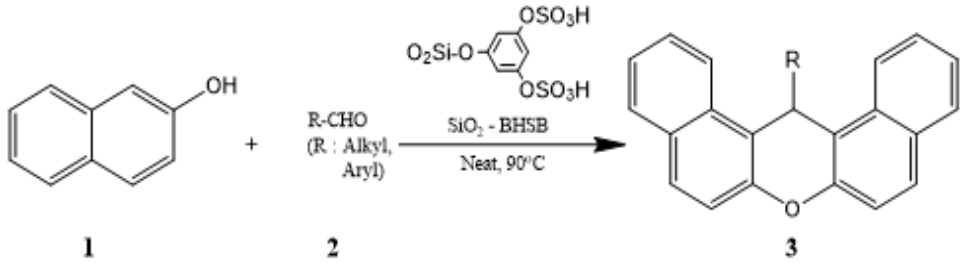


Fig 1: Synthesis of silica chemisorbed bis(hydrogensulhato)benzene (SiO_2-BHSB)

Synthesis of SiO_2-BHSB was achieved in three steps, by the necessary modifications in the literature procedures [28].

Step-I: Synthesis of Silica Chloride (SiO2-Cl) [28]

To a vigorously stirring, ice cold mixture of oven dried silica gel (100–200 mesh, 10 g) and dichloromethane (50 mL) into a round bottom flask (250 mL) equipped with water condenser and a calcium chloride guard tube, cold thionyl chloride (10 g) was added drop wise, the mixture is further stirred at room temperature for 24 h. The unreacted thionyl chloride and solvent were removed under reduced pressure, obtained light gray particles of silica chloride (SiO_2-Cl) are flame dried and immediately stored in a previously weighed airtight glass bottle. The yield of so obtained SiO_2-Cl was found 10.380 g and it can be used for months without decrease in its activity. The silica chloride (SiO_2-Cl) being a moisture sensitive compound, it gets covered into original silica gel when it comes in contact with moisture. Therefore it needs to be stored in an airtight glass bottle. The amount of chloride in the SiO_2-Cl sample was determined using the simple acid–base titration, in which the liberated HCl from silica chloride (100 mg) in 50mL deionized water was titrated against the standardized alkali solution. About 1.666 milli-equivalent chloride was found per gram of SiO_2-Cl sample.

Step-II, Synthesis of SiO_2-Phloroglucinol

Silica chloride (SiO_2-Cl, 8.30 mmol) from step-I and phloroglucinol (7.5 mmol) were stirred in dry CH_2Cl_2 (30 mL) taken into a round bottom flask equipped with a drying tube (Scheme 3, step-II). Evolving HCl bubbles from the reaction mixture indicate progress of the reaction. After 2 h of stirring, the resulting silica bound phloroglucinol (SiO_2-Phgl) was filtered at the pump, washed with CH_2Cl_2 (30 mL), dried at 60–70 ºC and weighed. A 5.520 g yield of SiO2-Phgl was obtained.

Step-III, Synthesis of silica chemisorbed bis(hydrogen sulphate)benzene (SiO_2-BHSB)

A 10% solution of chlorosulfonic acid (15 mmol) in CH_2Cl_2 was added drop wise to a magnetically stirring, cold suspension of SiO_2-phloroglucinol (7.5 mmol) in CH_2Cl_2 (30 mL) with the help of constant dropping funnel. The immediately evolving HCl gas was trapped by a NaOH scavenger assembly arranged along. After completion of addition, the mixture was stirred for further 2 h, the resulting suspension was filtered at a pump, washed thrice with methanol and once with distilled water in order to remove even a last fraction of an unreacted or physisorbed chlorosulfonic acid. The filtered brown solid was dried at 60 ºC for 6 h, resulted free flowing particles were weighed 6.240 g as a final yield and stored in a glass bottle. The formation of SiO_2-BHSB was examined by qualitative as well as quantitative analytical methods.

General Procedure for the Synthesis of 14-aryl-14H-dibenzo[a,xanthenes

A mixture of 2-naphtol (1 mmol), aromatic aldehyde (2 mmol) and SiO_2–BHSB (2.5 mol%) as a catalyst was added and stirred in a flask. The mixture was heated at 90 °C for an appropriate period of time (**Scheme 1)**, as mentioned in **Table 2**. After completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature. The crude product was heated in ethyl acetate, and the catalyst was removed by filtration. The pure product was obtained by cooling of the filtrate. Some of the products are known compounds. New compounds were characterized by IR and NMR spectroscopy. Their melting points are compared with reported values in literature. The recovered catalyst from the reaction mixture was washed with ample ethanol, dried at 60 ºC, After drying, it can be reused without a noticeable loss of reactivity.

Spectroscopic Data of Representative Compounds

14-phenyl-14H-dibenzo[a,j]xanthene 3a: White solid, IR (KBr, cm−1): νmax = 3074, 3020, 2924, 1623, 1590, 1512, 1454, 1400, 1251, 1077, 961, 826, 802, 742 cm^{-1} ; 1H NMR (250 MHz, $CDCl_3$): δ = 6.48 (s, 1H, CH), 6.97 (t, J = 7.5 Hz, 1H, ArH), 7.13 (t, J = 7.5 Hz, 2H, ArH), 7.39 (t, J = 7.5 Hz, 2H, ArH), 7.45–7.59 (m, 6H, ArH), 7.79 (t, J = 8.5 Hz, 4H, ArH), 8.40 (d, J = 8.5 Hz, 2H, ArH) ppm.

Results and Discussion

In this paper, the condensation of β-naphtol and various aldehydes in the presence of a SiO_2–BHSB as a heterogeneous catalyst for the preparation of 14-aryl or alkyl-14Hdibenzo[a,j]xanthenes has been studied (Scheme 1). We initially investigated the catalytic activity of SiO_2–BHSB in the synthesis of benzoxanthenes under different reaction conditions. The solvent effect in the condensation of benzaldehyde and β-naphthol in the presence of SiO_2–BHSB as a model has been studied. As shown in Table 1, among the tested solvents, such as ethanol, methanol, CH_3CN, 1,2-dichloroethane, $CHCl_3$ and a solvent-free system, the best result was obtained after 20 min under solvent-free conditions in excellent yield (98%). Therefore, this reaction was developed with other aldehydes, and the results are summarized in Table 2. The time of reaction was within 18-40 min, and high yields of 14-aryl or alkyl-14H-dibenzo[a,j]xanthenes were obtained. After completion of the reaction (monitored by TLC), the crude product was dissolved in hot ethyl acetate, the heterogeneous solid catalyst was removed easily by simple filtration and, after cooling of the filtrate, the pure crystals of products were obtained. The catalyst can be reactivated by simple washing, then reused without noticeable loss of reactivity. The new products were characterized by IR and NMR spectroscopy. Melting points are compared with reported values in literature.

The suggested mechanism for the SiO_2–BHSB catalyzed transformation is shown in Figure 2. Concerning the reaction mechanism, we suggest that, initially a carbocation be formed and then aryl-or alkyl-methane is naphthol prepared, which then undergo dehydration to give the final product.

Table 1: Synthesis of 14-phenyl-14H-dibenzo[a,j]xanthene 3a in the presence of SiO_2 – BHSB in different solvents

Entry	Solvent	Temperature (°C)	Time(h)	Yield (%)
1	Solvent free	90	20 min	97
2	Methanol	90	10	45
3	Acetonitrile	90	10	41
4	Water	90	20	23
5	Tetrahydrofuran	90	12	34
6	Dichloromethane	90	12	70

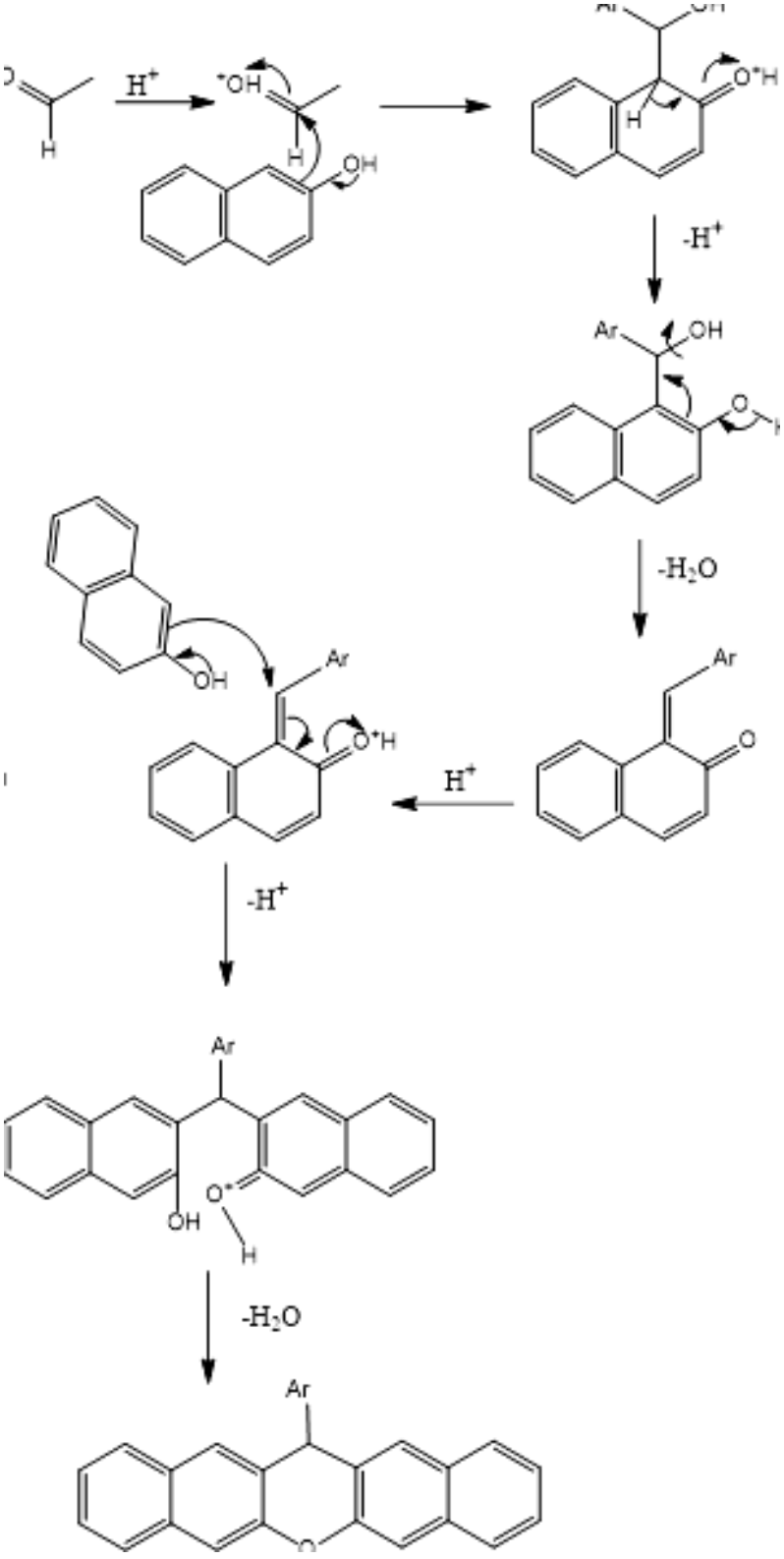
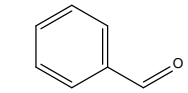
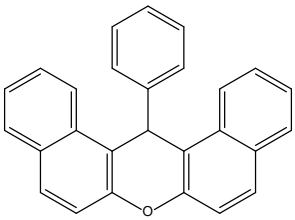
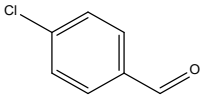
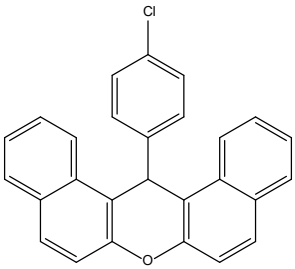
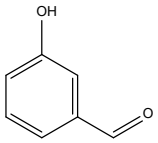
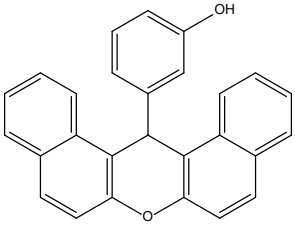
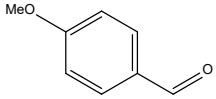
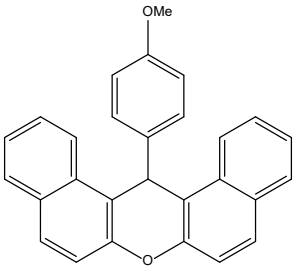
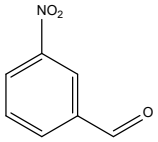
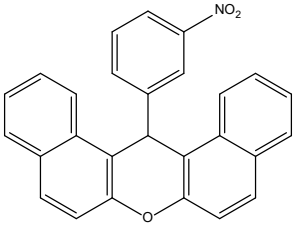
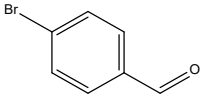
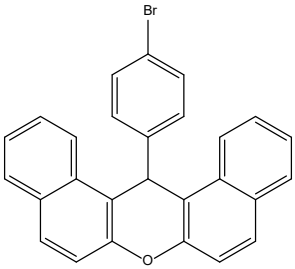
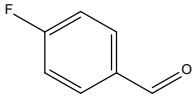
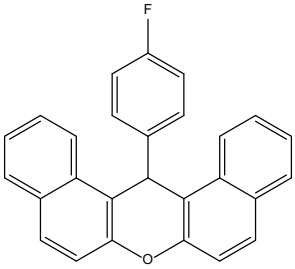
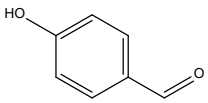
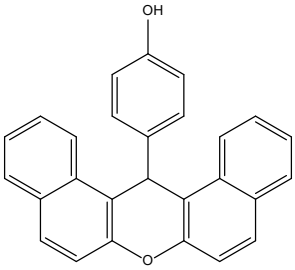
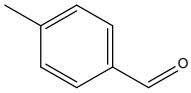
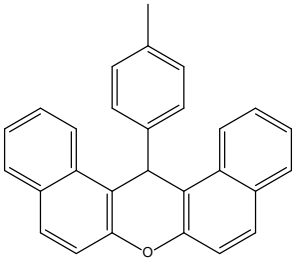
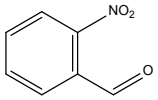
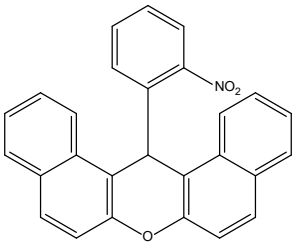
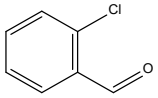
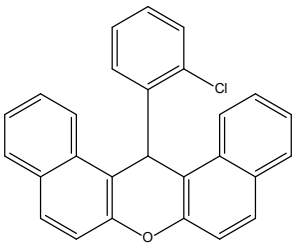
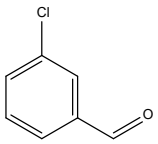
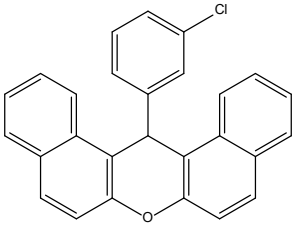
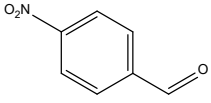
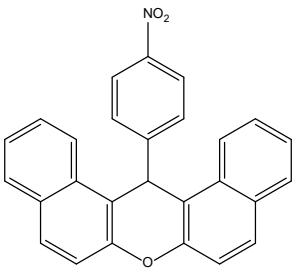
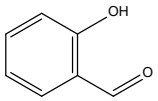
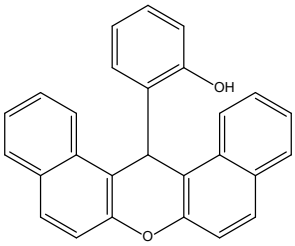
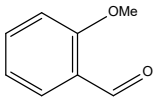
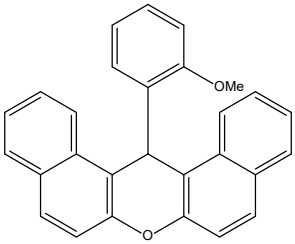


Fig 2: Possible mechanism of present reaction.

Table 2: Preparation of 14-aryl-14H-dibenzo[a,j]xanthene's using SiO_2 – BHSB (2.5 mol %) as catalyst

Entry	Aldehyde (1)	Product (3)	Time (min)	Yield (%)	Melting point (°C)
a			20	98	182-183
b			24	97	288-289
c			35	93	240-242
d			30	98	205
e			35	98	210
f			33	90	299-301
g			18	98	238

h			35	97	140
i			34	97	225
j			22	96	291
k			25	93	173
l			38	95	286-283
m			40	97	311
n			40	92	180

o			24	95	164

Conclusion

Our findings revealed a simple synthesis of 14-aryl-14H-dibenzo-[a,j]xanthenes using SiO_2-BHSB as an efficient catalyst. The attractive features of this protocol are simple procedure, short reaction time, high yields, simple workup, reusability of the catalyst and non-chromatographic purification of products, i.e. simple recrystallization from ethyl acetate. In the field of benzoxanthene synthesis, this approach could make a valuable contribution.

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