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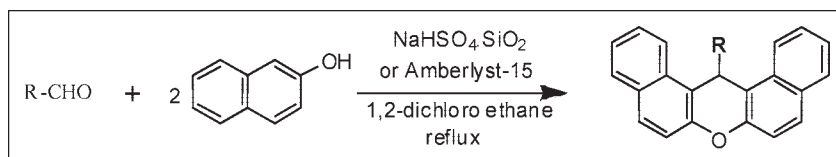
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Silica supported sodium hydrogen sulfate (NaHSO<sub>4</sub>·SiO<sub>2</sub>) or amberlyst-15 acts as an efficient heterogeneous catalyst for the preparation of 14-alkyl and aryl-14-H-dibenzo[*a,j*]xanthenes with various aldehydes and β-naphthol in dichloroethane solvent in excellent yields. Synthesis of three new compounds are reported using this methodology. Recyclable nature of the amberlyst-15 catalyst was also studied and the catalyst can be reused.

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## INTRODUCTION

Xanthenes and Benzoxanthenes are important class of heterocyclic compounds and they possess diverse range of biological properties such as antiviral [1], antibacterial [2], anti-inflammatory [3] activities, as well as in photodynamic therapy [4]. Benzoxanthenes have also been investigated for agricultural bactericide activity for antagonism of the paralyzing action of zoxazolamine [5]. In addition, these compounds have wide applications in dyes [6] and in laser technologies [7] because of their useful spectroscopic properties. These compounds can also be employed as pH sensitive fluorescent materials for visualization of biomolecules [8].

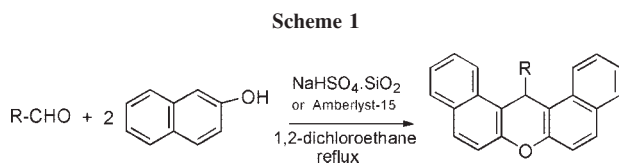
Many synthetic routes have been developed for the synthesis of xanthenes and benzoxanthenes, such as γ-alkylations to the heteroatom [9], trapping of benzyne by phenols [10], cyclocondensation between 2-hydroxy aromatic aldehydes, 2-tetralone [11], intramolecular phenyl carbonyl coupling reactions of benzaldehydes and acetophenones [12], reaction of β-naphthol with formamide [13], carbon monoxide [14], and 2-naphthol-1-methanol [15].

The reaction procedure has been improved by reacting β-naphthol with aldehydes under microwave irradiation [16] and using various acid catalysts [17]. Recently, our group reported using polyaniline based solid acid catalyst for the preparation of dodecahydroxanthenes [18]. In continuation of our research work, in this article we

have used silica supported sodium hydrogen sulfate (NaHSO<sub>4</sub>·SiO<sub>2</sub>) or amberlyst-15, an efficient heterogeneous acid catalyst for the preparation of 14-Alkyl and Aryl-14-H-dibenzo[*a,j*]xanthenes with various aldehydes and β-naphthol in dichloroethane solvent (Scheme 1). Recyclable nature of the amberlyst-15 catalyst was also studied.

## RESULTS AND DISCUSSION

Product was not obtained when benzaldehyde (1 mmol) was reacted with β-naphthol (2 mmol) in 1,2-dichloroethane (5 mL) under reflux conditions for 24 h. However, with the use of Amberlyst-15 (20 wt % with respect to aldehyde) as catalyst yielded dibenzoxanthene in 93% yield in 2 h. Almost same yield (92%) was obtained with the use of silica supported sodium hydrogen sulfate as catalyst. Both catalysts are not soluble in organic solvents and act as heterogeneous catalysts. We have also examined this condensation reaction using different catalysts such as Amberlite IR-120 (H<sup>+</sup> form), Montmorillonite K-10, and Indion-236. However, very low yield (<15%) was obtained even for longer reaction time. This may be because of the acidic nature of these catalysts, *i.e.* these catalysts show less acidic character for this reaction. To evaluate the efficiency of this methodology, the catalytic activity of Amberlyst-15 and silica supported sodium hydrogen sulfate was studied



for various aldehydes with  $\beta$ -naphthol and the yields are reported in Table 1. The products were obtained within 2 to 4 h in excellent yields and generally, both catalysts provided almost the same yield (Table 1).

We observed that the reactivity of aromatic aldehydes with  $\beta$ -naphthol is higher when compared with the aliphatic aldehydes in terms of yields and reaction time (Table 1). Furfural undergoes condensation smoothly with  $\beta$ -naphthol in 2.5 h with good yield (entry no. 15, Table 1). 4-Dimethylaminobenzaldehyde and pyridine-4-carbaldehyde did not react to give dibenzoxanthenes and it may be due to the presence of basic nitrogen in the system (Table 1). Amberlyst-15 can be recovered by simple filtration and can be reused after activation by treatment with HCl.

In conclusion, we have described a simple, clean, efficient, and environmental friendly method for the synthesis of biologically active heterocyclic compound, dibenzoxanthenes using two different inexpensive and nonhazardous catalysts  $\text{NaHSO}_4 \cdot \text{SiO}_2$  and Amberlyst-15. We feel that this method is a valid contribution to the existing methodologies.

## EXPERIMENTAL

All chemicals were of research grade and were used as obtained from Aldrich and Fluka. The reactions were carried out in a round-bottomed flask of 25 mL capacity at reflux temperature in an efficient fume hood. Analytical thin layer chromatography was performed with E. Merck silica gel 60F glass plates and flash chromatography using E. Merck silica gel (60–120 mesh). Melting points were determined on a MEL-TEMP II melting point apparatus and were uncorrected. NMR spectra were recorded of Gemini 200 MHz Varian instrument and Avance 300 MHz Bruker UX 300 FT NMR. All NMR data were obtained in  $\text{CDCl}_3$  solution and chemical shifts ( $\delta$ ) were given in ppm relative to TMS and are compared with the reported literature values. Mass spectra were recorded on VG Micromass 7070 H (EI), VG Autospec (FAB) using  $\text{Cs}^+$  ion gun, MNBA as a matrix, Applied Biosystems QSTAR XL High resolution mass spectrometer, Thermofinnigan ESI ion trap mass spectrometer and GC-MS instruments. Elemental analyses were performed using a Vario-EL elemental analyzer.

**Typical procedure for the preparation of dibenzoxanthenes.** In a typical procedure, a mixture of aldehyde (1 mmol),  $\beta$ -naphthol (2 mmol), 1,2-dichloroethane (5 mL), and  $\text{NaHSO}_4 \cdot \text{SiO}_2$  (100 mg) (Method A) or Amberlyst-15 (20 wt % with respect to aldehyde) (method B) was stirred at reflux for the appropriate time according to Table 1. The progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was filtered off and the organic

solvent was evaporated by reduced pressure. The crude products were subjected to column chromatography (silica gel 5% EtOAc in hexane) to afford the pure products. All products were characterized by  $^1\text{H}$  NMR, mass spectral data and compared with the reported spectral and physical data for known compounds (entry numbers 1–9, 11–13).

The recovered catalyst (Amberlyst-15) was reused (after treatment with HCl) four more times for the condensation reaction between benzaldehyde and  $\beta$ -naphthol following the above procedure for 2 h in each case the corresponding product furnishes with a yield of 93, 92, 92, and 91%.

Selected analytical data of three new representative dibenzoxanthenes are given below.

**14-(3,4-dimethoxyphenyl)-14H-ibenzo[*a,j*]xanthene (entry 10).** Wheatish solid; mp 186–188°C. IR (KBr): 3065, 1681, 1590, 1269, 1239, 1135, 1019, 815, 746  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.35 (d, 2H), 7.35–7.81 (m, 10H), 7.08 (dd, 1H), 6.83 (d, 1H), 6.62 (d, 1H), 6.4 (s, 1H), 3.68 (s, 3H), 3.64 (s, 3H);  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  154.36, 148.95, 148.6, 147.45, 137.58, 131.32, 130.98, 128.68, 128.64, 126.64, 126.56, 124.10, 122.6, 122.25, 117.78, 117.30, 111.68, 110.77, 55.85, 55.51, 37.29; HRMS (ESI) Calcd for  $\text{C}_{29}\text{H}_{23}\text{O}_3$  [ $\text{M} + \text{H}$ ] $^+$  419.1647, found 419.1633; *Anal.* Calcd for  $\text{C}_{29}\text{H}_{23}\text{O}_3$ : C, 83.23; H, 5.30; Found: C, 83.17; H, 5.38.

**14-Heptyl-14H-dibenzo[*a,j*]xanthene (entry 14).** Off-white solid; mp 74–76°C. IR (KBr): 2922, 2850, 1589, 1458, 1397, 1241, 810, 741  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.25 (d, 2H), 7.9 (d, 2H), 7.75 (d, 2H), 7.6 (t, 2H), 7.42 (t, 2H), 7.3 (d, 2H), 5.55 (s, 1H), 2.02 (m, 2H), 1.1–0.85 (m, 10 H), 0.7 (t, 3H);  $^{13}\text{C}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.9, 131.4, 131.0, 128.8, 128.1, 126.5, 124.0, 122.4, 117.5, 116.7, 35.9, 31.7, 31.0, 29.7, 29.0, 24.8, 22.4, 14.0. HRMS (ESI) Calcd for  $\text{C}_{28}\text{H}_{29}\text{O}$  [ $\text{M} + \text{H}$ ] $^+$  381.2218, found 381.2217; *Anal.* Calcd for  $\text{C}_{28}\text{H}_{29}\text{O}$ : C, 88.38; H, 7.42; Found: C, 88.41; H, 7.35.

**Table 1**

Synthesis of dibenzoxanthene derivatives using heterogeneous catalysts.

Entry	R	Time(h)	Yield <sup>a</sup> (%)	
			Method A	Method B
1	$\text{C}_6\text{H}_5$	2	92	93
2	4- $\text{ClC}_6\text{H}_4$	1.5	91	90
3	4- $\text{FC}_6\text{H}_4$	2	96	94
4	4- $\text{BrC}_6\text{H}_4$	3	92	94
5	4- $\text{O}_2\text{NC}_6\text{H}_4$	3	91	90
6	4- $\text{H}_3\text{CC}_6\text{H}_4$	2	92	93
7	$\text{H}_3\text{CCH}_2\text{CH}_2$	4	81	82
8	$(\text{CH}_3)_2\text{CHCH}_2$	2	85	83
9	$\text{CH}_3(\text{CH}_2)_3\text{CH}_2$	4	87	88
10	3,4- $(\text{OCH}_3)_2\text{C}_6\text{H}_2$	4	85	86
11	3- $\text{O}_2\text{NC}_6\text{H}_4$	2.5	91	90
12	4- $\text{OHC}_6\text{H}_4$	4	80	82
13	4- $\text{H}_3\text{COC}_6\text{H}_4$	3	90	90
14	$\text{H}_3\text{C}(\text{CH}_2)_5\text{CH}_2$	4	82	83
15	2- $\text{C}_4\text{H}_3\text{O}$	2.5	81	84
16	4- $\text{C}_5\text{H}_4\text{N}$	24	–	–
17	4- $\text{N}(\text{CH}_3)_2\text{C}_6\text{H}_4$	24	–	–

Method A =  $\text{NaHSO}_4 \cdot \text{SiO}_2$ ; Method B = Amberlyst-15.

<sup>a</sup> Isolated yields.

**14-(2-Furyl)-14H-dibenzo[*a,j*]xanthene (entry 15).** Reddish solid; mp 217–219°C. IR (KBr): 3059, 2923, 1621, 1590, 1245, 1146, 813, 737 cm<sup>-1</sup>. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ = 8.33 (d, 2H), 7.82–7.39 (m, 10H), 7.13 (d, 1H), 6.6 (s, 1H), 6.03 (m, 1H), 5.75 (d, 1H); <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ 156.8, 149.2, 141.2, 129.2, 128.6, 126.8, 126.2, 124.6, 124.4, 122.8, 118.0, 114.2, 110.3, 106.6, 31.6; HRMS: (ESI) Calcd for C<sub>25</sub>H<sub>17</sub>O<sub>2</sub> [M+ H]<sup>+</sup> 349.1228, found 349.1230; *Anal.* Calcd for C<sub>25</sub>H<sub>17</sub>O<sub>2</sub>: C, 86.19; H, 4.63; Found: C, 86.26; H, 4.61.

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