Research Article

Synthesis of 14-Aryl-14H-dibenzo[a,j]xanthene Derivatives Using H-Zeolite A as an Efficient and Reusable Catalyst under Solvent-Free Condition

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H-Zeolite A is an efficient, excellent, and reusable catalyst for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthene derivatives by one-pot synthesis of β -naphthol with various aromatic aldehyde derivatives under solvent-free condition. The synthesized zeolite H-Zeolite A was characterized by XRD, SEM, and FT-IR. The synthesized products were characterized by FT-IR and $^1\text{H-NMR}$ spectra. Simple workup procedure, short reaction time, high yield, and reusability of the catalyst are the characteristic features of these reactions.

1. Introduction

The homogenous acid catalysts such as AlCl_3 , HCl , and H_2SO_4 are used for organic reactions carried out in industries and laboratories. However the above-mentioned homogeneous acid catalysts have some disadvantages such as toxicity, corrosivity, expensive cost, and large amount of wastes. So in order to overcome these limitations, new solid acids such as zeolites, clays, and acidic resins have been tested [1–4]. However, xanthenes and their derivatives are very important organic reactions as they contain both therapeutic and biological properties such as anti-inflammatory [5], antiviral [6] antibacterial [7], antileukemic [8], insecticidal [9], antifungal [10], free radical scavenging activity [11], antimycobacterial [12], antiparasitic [13–15], antitumor [13], apoptotic effects [16], antiproliferative [17], antimalarial [18], antioxidant [19], and anticancer [20]. In addition, xanthene derivatives such as 14-aryl-14H-dibenzo[a,j]xanthenes are of great importance as they retain pharmaceutical and industrial properties. The compounds formed are widely used as leucodye [21], in laser technology [22], and in fluorescent materials [23]. However, a number of synthetic methods have been reported in the literature for the synthesis of xanthene derivatives in the presence of various catalysts such as $\text{AcOH-H}_2\text{SO}_4$ [24], P-TSA [25],

sulfamic acid [26], molecular iodine [27], silica sulfuric acid [28], heteropoly acids [29], Amberlyst-15 [30], cyanuric chloride [31], NaHSO_4 [32], nano- TIO_2 [33], $\text{Al}(\text{HSO}_4)_3$ [34], InCl_3 [35], $\text{Yb}(\text{OTf})_3$ [36], and cellulose H_2SO_4 [37]. However these above-mentioned methods have some limitations such as long reaction time, expensive reagents, strong acidic condition, and a very low yield. So, in order to overcome these limitations, the discovering of new and efficient catalyst with high catalytic efficiency, short reaction time, and reusability is used for the preparation of xanthenes. The main purpose of this study is to utilize the H-Zeolite A as an efficient catalyst for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthene derivatives.

2. Experimental

2.1. Synthesis of Zeolite A. Zeolite A was prepared by dissolving 0.723 g of sodium hydroxide in 80 mL distilled water which was then divided into two equal volumes in polypropylene bottles. To first half add 8.258 g sodium aluminate and mix gently in capped polypropylene bottle until it becomes clear. To the second half add 15.4 g sodium metasilicate and mix gently in capped polypropylene bottle until it becomes clear. Now the silicate solution was poured into

SCHEME 1: One-pot synthesis of xanthene derivatives in the presence of H-Zeolite LTA under solvent-free condition.

aluminate solution quickly and a thick gel was formed. The polypropylene bottle was kept in oven at 99°C for 4 h. The resulting mixture was washed and centrifuged until $\text{pH} \leq 9$ and dried at 110°C. The sample was ground into powder and calcined at 500°C for 4 h in order to remove water and organic precursors.

2.2. Conversion of Zeolite A into H Form. Zeolite A was converted into H form by the following procedure: 9.0 g of Zeolite A, 7.23 g of NH_4Cl , and 13.80 mL of distilled water were mixed with 0.1 M hydrochloric acid solution to reach pH 4. The mixture was stirred at 60°C for 6 h. Then the material was filtered and washed with distilled water. After the removal of chlorides, the resulting material, NH_4 -zeolite, was placed in an oven at 60°C for 24 h. The ammonium form of Zeolite A was converted into the H form by calcinations over 60 min at 500°C.

2.3. General Procedure for the Synthesis of 14-Aryl-14H-dibenzo[a,j]xanthene. A mixture of 2-naphthol (1 mmol, 0.144 g), aldehydes (1 mmol), and catalyst H-Zeolite A (0.05 g) in a 25 mL round conical flask was heated in an oil bath (paraffin oil) at 100°C for appropriate time (as shown in Scheme 1). The progress of the reaction was monitored by TLC (*n*-hexane: ethyl acetate, 3:1). After completion of the reaction, mixture was cooled to room temperature. Then the product was washed with ethyl acetate and filtered to remove catalyst. After removal of the solvent, the solid product was obtained and was further recrystallized for ethanol to afford the pure xanthene derivatives.

3. Characterization

3.1. The Synthesized Zeolite A Was Characterized by XRD, FT-IR, and SEM Techniques and the Reaction Products Were Characterized by FT-IR and ^1H -NMR

3.1.1. X-Ray Diffraction (XRD). For X-ray diffraction, the samples were sieved in an ABNT number 200 (0.074 mm) sieve and then placed in an aluminum sample holder for X-ray diffraction assays, using Shimadzu XRD 6000 equipment. The operational details of the technique were set as follows: copper $\text{K}\alpha$ radiation at 40 KV/30 mA, with a goniometer speed of 2°/min and a step of 0.02° in the 2θ range scanning from 10° to 70° for Na-LTA and 2θ range scanning from 0° to 80° for H-LTA.

3.1.2. Scanning Electron Microscopy (SEM). Surface micrographs of H form of Zeolite A were obtained by SEM instrument. Scanning electron micrograms of these materials

were taken at 10,000x magnifications to understand their surface morphology and to get the clear view of crystals.

3.1.3. Fourier Transform-Infrared Spectroscopy (FT-IR). For FT-IR analysis, the H form Zeolite A sample and reaction products were subjected to physical treatment in accordance with the KBr method, which consists of mixing 0.007 g of the sample and 0.1 g KBr and grinding and pressing the solid mixture to 5 tons for 30 s in order to form a pellet that allows the passage of light. The H form of Zeolite A and its reaction products was performed using an infrared spectrophotometer Shimadzu FT-IR in the wavelength ranging from 500 to 4500 cm^{-1} .

3.1.4. Nuclear Magnetic Resonance (NMR) Spectroscopy. ^1H -NMR spectra were obtained on Bruker 400 MHz spectrophotometer with CDCl_3 as solvent using tetramethylsilane (TMS) as an internal standard; the chemical shift values are in δ .

3.1.5. Spectra Data of Products. 14-Phenyl-14H-dibenzo[a,j]xanthene: pale yellow solid; FT-IR (KBr, cm^{-1}): 3677, 1247, 947. ^1H -NMR (CDCl_3): 6.56 (s, 1H, CH), 6.98–7.02 (2H, d, Ar-H), 7.90–8.03 (4H, m, Ar-H), 8.08–8.71 (9H, m, Ar-H), 8.72–8.75 (2H, d, Ar-H) (Table 5, entry 1, Figures 4 and 5).

14-(4-Chlorophenyl)-14H-dibenzo[a,j]xanthene: brown solid; FT-IR (KBr, cm^{-1}): 3658, 1401, 814. ^1H -NMR (CDCl_3): 7.92 (s, 1H, CH), 7.84–7.7 (3H, m, Ar-H), 7.70–7.68 (2H, d, Ar-H), 7.46–7.43 (3H, m, Ar-H), 7.37–7.33 (3H, m, Ar-H), 7.26 (s, 1H, CH), 7.16–7.07 (3H, m, Ar-H) (Table 5, entry 2, Figures 6 and 7).

14-(3-Nitrophenyl)-14H-dibenzo[a,j]xanthene: yellow solid; FT-IR (KBr, cm^{-1}): 3655, 3120, 1527, 1400, 814. ^1H -NMR (CDCl_3): 8.07 (s, 1H, CH), 8.49–8.47 (2H, d, Ar-H), 8.21–8.20 (2H, d, Ar-H), 7.71–7.67 (3H, m, Ar-H), 7.61–7.59 (2H, d, Ar-H), 7.43 (s, 1H, Ar-H), 7.35–7.32 (2H, d, Ar-H), 7.26–7.10 (3H, m, Ar-H), 6.84 (s, 1H, CH) (Table 5, entry 5, Figures 8 and 9).

14-(4-Hydroxyphenyl)-14H-dibenzo[a,j]xanthene: pink solid; FT-IR (KBr, cm^{-1}): 3679, 3151, 1513, 1400, 1160, 815, 606. ^1H -NMR (CDCl_3): 7.83–7.75 (5H, m, Ar-H), 7.69–7.67 (2H, d, Ar-H), 7.45–7.42 (3H, m, Ar-H), 7.36–7.32 (3H, m, Ar-H), 7.26 (s, 1H, OH), 7.18–7.12 (3H, m, Ar-H), 6.99–6.97 (2H, d, Ar-H) (Table 5, entry 6, Figures 10 and 11).

4. Results and Discussion

The X-ray diffraction pattern of Zeolite-A and its H form is shown in Figure 1. In the X-ray diffraction pattern it is shown that degree of crystallinity is very high and all the materials are crystalline in nature without any amorphous

SCHEME 2: The concerned reaction for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthenes.

FIGURE 1: X-ray diffraction patterns of Zeolite A and its H form.

FIGURE 2: SEM image of H form of Zeolite A.

FIGURE 3: FT-IR pattern of H form of Zeolite A.

phase. The sharp peak 2θ value for calcined Zeolite A and its H form is 24.5 which is easily observed. Further confirmation from Figure 1 shows that the powder X-ray diffraction pattern of H form Zeolite A is similar to the diffraction pattern of its parent Zeolite A. There is no doubt that there is small difference in crystalline peaks between these two because during the formation of H form some impurities are present in ammonium salt. The SEM morphology of H-form Zeolite A is expressed in Figure 2. The SEM image of H-form Zeolite A shows that particles appear to have a cuboidal shape with extraordinary crystal edges and the particle size ranges between 2 and 5 microns. The FT-IR spectrum of H-form Zeolite A is shown in Figure 3. FT-IR spectrum shows absorption bands at 450 cm^{-1} which is attributed to Si, Al-O band, and those at 1000 cm^{-1} and 750 cm^{-1} are, respectively, attributed to asymmetric and symmetric stretches of the zeolite framework. A band for the OH group is clearly observed at 3400 cm^{-1} . We have created an excellent and highly efficient method for the synthesis of 14-aryl-14H-dibenzo[a,j]xanthene derivatives from the reaction of 2-naphthol, various derivatives of aromatic aldehydes, and catalyst H-Zeolite A (0.05 g or 5 mol%) under solvent-free condition at 100°C , so the concerned reaction was carried out between 4-chlorobenzaldehyde and 2-naphthol as shown in Scheme 2.

FIGURE 4: ^1H -NMR spectrum of 14-phenyl-14H-dibenzo[a,j]xanthene.

FIGURE 5: FT-IR spectrum of 14-phenyl-14H-dibenzo[a,j]xanthene.

FIGURE 6: ^1H -NMR spectrum of 14-(4-chlorophenyl)-14H-dibenzo[a,j]xanthene.

FIGURE 7: FT-IR spectrum of 14-(4-chlorophenyl)-14H-dibenzo[a,j]xanthene.

FIGURE 8: ¹H-NMR spectrum of 14-(3-nitrophenyl)-14H-dibenzo[a,j]xanthene.

FIGURE 9: FT-IR spectrum of 14-(3-nitrophenyl)-14H-dibenzo[a,j]xanthene.

FIGURE 10: ^1H -NMR spectrum of 14-(4-hydroxyphenyl)-14H-dibenzo[a,j]xanthene.

FIGURE 11: FT-IR spectrum of 14-(4-hydroxyphenyl)-14H-dibenzo[a,j]xanthene.

TABLE 1: Effect of different solvents on the reaction between 4-chlorobenzaldehyde and 2-naphthol.

Entry	Solvent	Catalyst (g)	Time	Yield (%)
1	Ethanol	0.05	50 min	67
2	Methanol	0.05	50 min	73
3	CHCl_3	0.05	50 min	64
4	Solvent-free	0.05	15 min	95

To select reaction conditions, first the effect of solvents on the rate of reaction for the synthesis of 14-(4-chlorophenyl)-14H-dibenzo[a,j]xanthene by two-component reaction of 4-chlorobenzaldehyde and 2-naphthol in the presence of catalyst H-Zeolite A (0.05 g) under various solvents is shown in Table 1.

It was detected that the best result was obtained when reaction was carried out under solvent-free condition (Table 1, entry 4). The reaction was over within 15 minutes and the reaction product was obtained in a 95% yield. Next the study was carried out to determine the effect of amount of catalyst H-Zeolite A. The reaction was carried out by varying different amount of catalyst. The best yield was obtained with 0.05 g of the catalyst. Further increase in the amount of catalyst in the above-mentioned reaction did not have any significant change in the reaction product shown in Table 2.

The reason is that the additional acid sites cause no effect because the reactants may reduce sufficient sites to bind with. Hence we used weight of catalyst (0.05 g) for the rest of the reactions. The reusability of the catalyst was clarified in the synthesis of 14-(4-chlorophenyl)-14H-dibenzo[a,j]xanthene. After each run, the catalyst was recovered, washed with solvents, namely, chloroform and ethyl acetate, dried in an

TABLE 2: Effect of different amount of catalyst on the reaction between 4-chlorobenzaldehyde and 2-naphthol.

Entry	Catalyst (g)	Solvent	Time (min)	Temp (°C)	Yield (%)
1	0.01	Solvent-free	35	100	54
2	0.02	Solvent-free	30	100	66
3	0.03	Solvent-free	25	100	79
4	0.04	Solvent-free	20	100	84
5	0.05	Solvent-free	15	100	95
6	0.06	Solvent-free	15	100	95

TABLE 3: Effect of recyclability of H-Zeolite A for the synthesis of 14-(4-chlorophenyl)-14H-dibenzo[a,j]xanthene.

Entry	Yield (%)
1st run	95
2nd run	93
3rd run	90
4th run	89

TABLE 4: Comparison of H-Zeolite A for the synthesis of 14-(4-chlorophenyl)-14H-dibenzo[a,j]xanthene.

Entry	Catalyst	Condition	Time (h)	Yield (%)	Ref.
1	H ₂ SO ₄	AcoH/80°C	73	60	[24]
2	Silica H ₂ SO ₄	S.f./80°C	15–120 min	80–96	[28]
3	Amberlyst-15	S.f./125°C	0.5–2	80–94	[30]
4	Yb(OTf) ₃	(13py) Bf ₄	5–7	80–95	[36]
5	NaHSO ₄	S.f./90°C	0.5–1	74–91	[32]
6	Cellulose H ₂ SO ₄	S.f./110°C	1.5–3	81–97	[37]
7	H-Zeolite A	S.f./100°C	15–35 min	94–98	This work

S.f.: solvent free.

oven at 100°C for 2 h before use, and tested for its activity in the consecutive runs with no fresh catalyst added. The catalyst was tested for four runs as shown in Table 3.

The small reduction in the catalytic activity is mainly due to the loss of the catalyst structure during recovery process. To show the advantages of H-Zeolite A in comparison with some other reported catalysts, we found that some results for the synthesis of 14-(4-chlorophenyl)-14H-dibenzo[a,j]xanthene shown in Table 4 indicate that H-Zeolite A is an excellent catalyst with respect to reaction time and yield compared to previously reported literature.

To study the scope of the reaction we utilized various derivatives of aromatic aldehydes to evaluate this procedure. The reaction time and % yield of the products are shown in Table 5.

The electronic effect and the nature of substituents have a strong effect on the yield of the products. Benzaldehyde and other aromatic aldehydes having electron-withdrawing and electron-donating group were used and reacted to give the corresponding xanthene derivatives. In

all these above-mentioned cases the yield was excellent and electron-withdrawing groups were strongly more effective than electron-donating group.

5. Conclusion

In conclusion, an excellent and highly efficient method for the preparation of 14-aryl-14H-dibenzo[a,j]xanthene derivatives has been obtained by the condensation of 2-naphthol with various aromatic aldehydes using the reusable H-Zeolite A as a solid acid heterogeneous catalyst under solvent-free condition. Simple workup procedure, short reaction time, high yield, and reusability of the catalyst are the characteristic features of these reactions.

Competing Interests

The authors declare no conflict of interests regarding this manuscript.

TABLE 5: One-pot synthesis of different xanthene derivatives catalyzed by H-Zeolite A.

Entry	Aldehydes	Product	Time	Yield (%)	m.p. (°C)	Ref.
1			17	96	182-183	183 [31, 38]
2			15	97	287-288	288 [31, 38]
3			25	95	254-255	255 [31]
4			35	92	310-311	311 [31]
5			35	92	211-212	211 [39]

TABLE 5: Continued.

Entry	Aldehydes	Product	Time	Yield (%)	m.p. (°C)	Ref.
6			32	90	138–140	140 [40]

m.p.: melting point.

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