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Xanthan sulfuric acid: An efficient biodegradable solid acid catalyst for the synthesis of 14-aryl-14*H*-dibenzo[*a,i*]xanthene-8,13-diones

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ABSTRACT

Xanthan sulfuric acid (XSA) is employed as a recyclable catalyst for the synthesis of 14-Aryl-14H-dibenzo[a,i]xanthene-8,13-diones. These syntheses were performed by the condensation of 2-hydroxynaphthalene-1,4-dione, aromatic aldehydes and 2-naphthol. This methodology is mild, high yielding, green and the catalyst could be easily recycled.

Keywords: 14-Aryl-14H-dibenzo[a,i]xanthene-8, 13-diones; aldehyde; synthesis; biodegradable; Xanthan sulfuric acid.

INTRODUCTION

Henna leaves, Lawsonia inermis is the principal source for natural dye. 2-Hydroxy 1,4- naphthoquinone is known for the past 4000 years, found in many natural products and has been employed as a synthetic intermediate for the preparation of numerous heterocyclic compounds with interesting biological properties such as antitumor, antibacterial, antifungal and anti inflammatory agents [1-3]. Compounds containing heterocyclic quinone group represent an important class of biologically active molecules [4]. Furthermore, these heterocycles display useful spectroscopic properties and are used as dyes [5], in laser technologies [6] and as fluorescent materials for the visualization of biomolecules [7]. A number of xanthene dyes are extracted naturally from soil and plants, such as Indigofera longeracemosa [8]. The biological processes involved with antitumoral activity of quinones are DNA intercalation, bioreductive alkylation of biomolecules, and generation of oxy radicals through redox cycling [9-12].

In view of broad biological activities, we are interested to develop novel heterocyclic fused quinines. Thus, the development of new and simple synthetic methods for the efficient preparation of 14-Aryl-14H-dibenzo[a,i]xanthene-8, 13-dione is an interesting challenge. Number of acidic catalysts has been used for organic synthesis. Some of these methods suffer from severe drawbacks, including use of large amounts of expensive reagents and catalysts, low yield, long reaction times, special apparatus, and tedious workup procedures, which necessitate the development of an alternative route for the synthesis of these biologically active molecules.

Recently, the direction of science and technology has been shifting more towards eco-friendly, natural product resources and reusable catalysts. Thus, natural biopolymers are attractive candidates in the search for such solid support catalysts. [13] Xanthan and its derivatives [14-15], have some unique properties, which make them attractive alternatives for conventional organic or inorganic supports for catalytic applications. Among different

biopolymers, Xanthan is the most abundant bacterial exopolysaccharide in the world, which is produced through fermentation and it has been widely studied during the past decades, as it is a biodegradable material and a renewable resource. Unlike other gums, it is very stable under a wide range of temperatures and pH values. Recently, sulfonated xanthan has been utilized as a biopolymeric solid support acid catalyst for the synthesis of α-amino nitriles. [16] This polymer has unlimited availability as a renewable agro-resource and is biodegradable. Xanthan sulfuric acid can be easily prepared by the reaction of Xanthan with chlorosulfonic acid; the number of acidic (H^+) sites in the Xanthan sulfuric acid determined by acid-base titration was 0.6 meq/g.

MATERIALS AND METHODS

Melting points were determined in open capillaries and are uncorrected. The progress of the reaction was monitored by TLC and visualized with UV light. IR spectra (KBr) were recorded on Shimadzu FTIR model 8010 spectrometer and the ^{1}H NMR spectra was measured on a Varian Gemini 200-MHz spectrometer using TMS as internal standard. The C, H, and N analysis of the compound was done on a Carlo Erba model EA1108. Mass spectra were recorded on a Jeol JMS D-300 spectrometer.

Typical procedure for the preparation of 14-Aryl-14H-dibenzo[a,i]xanthene-8, 13-diones

A mixture of 2-hydroxynaphthalene-1,4-dione (1 mmol),2-naphthol (1mmol), aldehyde (1 mmol) and Xanthan sulfuric acid (0.08 g) in ethanol(5 mL) was stirred at 50 ^{0}C for appropriate time, as shown in Table 1. After completion of the reaction (conformed over TLC), the reaction mixture was filtered and washed with ethyl acetate (10 ml) to separate the catalyst. Then the filtrate was evaporated under reduced pressure to afford a pure product. Further purification was followed by crystallization from ethanol.

Spectral Data

14-Phenyl-14H-dibenzo[a,i]xanthene-8, 13-dione (4a)

Orange powder, m.p. >300 ^{o}C (Lit.[17] 319-320 ^{0}C); IR (KBr, cm^{-1}): 3022, 1695, 1652, 1573; ^{1}H NMR (DMSO-d_6): δ 5.82 (1H, s, CH of pyran ring), 7.09-8.26 (15H, m, ArH); MS (m/z): 388 (M^+); Anal. Calcd. for $C_{27}H_{16}O_3$: C, 83.49; H, 4.15. Found: C, 83.38; H, 4.18.

14-(2-Chlorophenyl)-14*H*-dibenzo[a,i]xanthene-8, 13-dione (4b)

Yellow powder, m.p. 280 ^{0}C (Lit.[17] 281-282 ^{0}C); IR (KBr): 3069, 1665, 1635, 1590, cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 6.19 (s, 1H, CH of pyran ring), 7.08-8.29 (m, 14H); MS (m/z): 422 (M^+); Anal. calcd for $C_{27}H_{15}ClO_3$: C 76.69, H 3.58; found: C 76.76, H 3.47.

14-(3-Nitrophenyl)-14H-dibenzo[a,i]xanthene-8, 13-dione (4c)

Yellow powder, m.p. >300 ^{o}C (Lit.[17] 304-305 ^{0}C); IR (KBr, cm^{-1}): 3071, 1697, 1654, 1525; ^{1}H NMR (DMSO-d_6) δ: 6.09 (1H, s, CH of pyran ring), 7.49-8.27 (14H, m, ArH); MS (m/z): 433 (M^+); Anal. Calcd. for $C_{27}H_{15}NO_5$: C, 74.82; H, 3.49; N, 3.23. Found: C, 72.75; H, 3.41; N, 3.17.

14-(4-Nitrophenyl)-14*H*-dibenzo[a,i]xanthene-8, 13-dione (4d)

Yellow powder, m.p. >300 ^{o}C (Lit. [17] 332-333 ^{0}C); IR (KBr): 3079, 1666, 1635, 1591, cm^{-1}; ^{1}H NMR (DMSO-d_6) δ: 6.10 (s, 1H, CH of pyran ring), 7.39-8.25 (m, 14H); MS (m/z): 433 (M^+); Anal. calcd for $C_{27}H_{15}NO_5$: C 74.82, H 3.49, N 3.23; found: C74.88, H 3.35, N 3.21.

14-(4-Chlorophenyl)-14H-dibenzo[a,i]xanthene-8, 13-dione (4e)

Yellow powder, m.p. >300 ^{o}C (Lit.[17] 305-306 ^{0}C); IR (KBr, cm^{-1}): 2933, 1701, 1661, 1577; ^{1}H NMR (DMSO-d_6) δ 5.80 (1H, s, CH of pyran ring), 7.21-8.29 (14H, m, ArH); MS (m/z): 422 (M^+); Anal. Calcd. for $C_{27}H_{15}ClO_3$: C, 76.69; H, 3.58. Found: C, 76.59; H, 3.55.

14-(3,4-Dichlorophenyl)-14H-dibenzo[a,i]xanthene-8, 13-dione (4f)

Yellow powder, m.p. 262-263 ^{0}C (Lit. [17] 260-261 ^{0}C); IR (KBr: 3030, 1681, 1599, 1561, cm^{-1}; ^{1}H NMR (DMSO-d_6) δ: 5.91 (s, 1H, CH of pyran ring), 7.31-8.17 (m, 13H), MS (m/z): 457 (M^+); Anal. calcd for $C_{27}H_{14}Cl_2O_3$: C 70.91, H 3.09; found: C 70.99, H 3.19

14-(2,4-Dichlorophenyl)-14H-dibenzo[a,i]xanthene-8,13-dione (4g)
Yellow powder, m.p. >300 ^{0}C (Lit. [17] 301-302 ^{0}C); IR (KBr): 3046, 1666, 1635, 1592, cm^{-1}; ^{1}H NMR (DMSO-d_6) δ 6.10 (s, 1H, CH of pyran ring), 7.08-8.22 (m, 13H); MS (m/z): 457 (M^+); Anal. calcd for $C_{27}H_{14}Cl_2O_3$: C 70.91, H 3.09; found: C 70.88, H 3.10.

14-(4-Methylphenyl)-14H-dibenzo[a,i]xanthene-8, 13-dione (4h)
Orange powder, m.p. 254-255 ^{0}C (Lit.[17] 255-256 ^{0}C); IR (KBr, cm^{-1}): 2934, 1701, 1669, 1572; ^{1}H NMR (DMSO-d_6) (δ ppm): 2.11 (3H, s, CH_3), 5.86 (1H, s, CH of pyran ring), 7.02-8.28 (14H, m, ArH). MS (m/z): 402 (M^+); Anal. Calcd. for $C_{28}H_{18}O_3$: C, 83.57; H, 4.51. Found: C, 83.59; H, 4.42.

14-(4-Methoxyphenyl)-14H-dibenzo[a,i]xanthene-8, 13-dione (4i)
Yellow powder, m.p. 281-282 ^{0}C (Lit.[17] 279-280 ^{0}C); IR (KBr, cm^{-1}): 2952, 1699, 1665, 1585; ^{1}H NMR (DMSO-d_6) (δ ppm): 3.65 (3H, s, OCH_3), 5.96 (1H, s, CH of pyran ring), 6.85-7.99 (14H, m, ArH). MS (m/z): 418 (M^+); Anal. Calcd. for $C_{28}H_{18}O_4$: C, 80.37; H, 4.34.Found: C, 80.36; H, 4.30.

14-(2-Hydroxy-3-methoxylphenyl)-14H-dibenzo[a,i]xanthene-8, 13-dione (4j)
Yellow powder, m.p. >300 ^{0}C; IR (KBr, cm^{-1}): 2948, 1685, 1666, 1555; ^{1}H NMR (DMSO-*d6*) δ 3.86 (3H, s, OCH_3), 5.71 (1H, s, CH of pyran ring), 6.69-8.09 (14H, m, ArH). MS (m/z): 434 (M^+); Anal. Calcd. for $C_{28}H_{18}O_5$: C, 77.41; H, 4.18. Found: C, 77.37; H, 4.31.

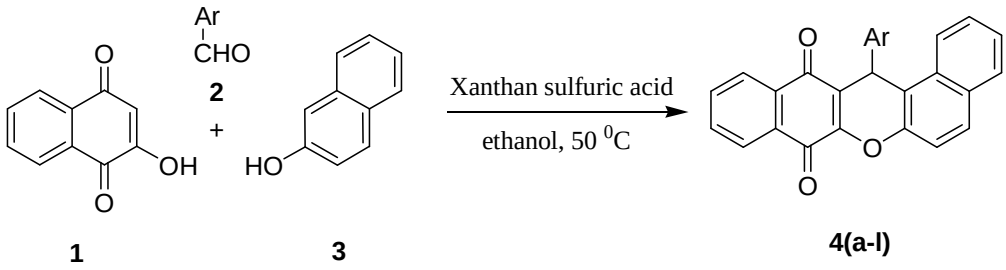
14-(3,3,4-Trimethoxylphenyl)-14H-dibenzo[a,i]xanthene-8, 13-dione (4k)
Yellow powder, m.p. >300 ^{0}C; IR (KBr, cm^{-1}): 2938, 1701, 1673, 1594; ^{1}H NMR (DMSO-*d6*) δ 3.63 (9H, s, OCH_3), 5.99 (1H, s, CH of pyran ring), 6.51-7.99 (20H, m, ArH). MS (m/z): 478 (M^+); Anal. Calcd. for $C_{30}H_{22}O_6$: C, 75.30; H, 4.63. Found: C, 75.24; H, 4.69.

14-(2-Naphthyl)-14H-dibenzo[a,i]xanthene-8, 13-dione (4l)
Orange powder, m.p. >300 ^{0}C; IR (KBr, cm^{-1}): 2938, 1679, 1635, 1570; ^{1}H NMR (DMSO-d_6) δ 5.97 (1H, s, CH of pyran ring), 7.25-8.29 (17H, m, ArH). MS (m/z): 438 (M^+); Anal. Calcd. for $C_{31}H_{18}O_3$: C, 84.92; H, 4.14. Found: C, 84.90; H, 4.10.

RESULTS AND DISCUSSION

In continuation of our earlier studies on the synthesis of heterocyclic compounds by using new reagents [18-19] and also In view of the current trends in catalytic processes, there is merit in developing a truly catalytic method for the formation of 14-Aryl-14H-dibenzo[a,i]xanthene-8, 13-diones. Now, we have found that the reaction can be conveniently performed under neutral and mild conditions in the presence of a catalytic amount of Xanthan sulfuric acid.

We now report here the synthesis of 14-Aryl-14H-dibenzo[a,i]xanthene-8, 13-diones by the reaction of 2-hydroxynaphthalene-1,4-dione , 2-naphthol, aldehyde and Xanthan sulfuric acid, (Schme-1).



Scheme-1: synthesis of 14-Aryl-14H-dibenzo[a,i]xanthene-8, 13-diones by using xanthan sulfuric acid as a solid acid catalyst

Table 1: Synthesis of 14-Aryl-14H-dibenzo[a,i]xanthene-8,13-diones with Xanthan sulfuric acid

Entry	Aldehyde	Product	Time (min)	Yield(%) [a]
1	benzaldehyde	4a	30	95
2	2 chlorobenzaldehyde	4b	30	91
3	3-nitrobenzaldehyde	4c	35	94
4	4-nitrobenzaldehyde	4d	35	95
5	4-chlorobenzaldehyde	4e	40	92
6	3,4 dichlorobenzaldehyde	4f	30	89
7	2,4 dichlorobenzaldehyde	4g	45	87
8	4-methylbenzaldehyde	4h	35	92
9	4–methoxybenzaldehyde	4i	35	90
10	2–hydroxyl 3-methoxybenzaldehyde	4j	30	93
11	2,3,4 tri methoxybenzaldehyde	4k	35	94
12	Naphthaldehyde	4l	30	95

[a] Yields refer to pure solid products; all products were characterized by spectral data

We examined the effect of the amount of catalyst in this reaction. The best results were obtained using higher amount of catalyst (95%). Using lower amounts of catalyst resulted in lower yields, in the absence of catalyst the yield of the product was found to be very low (Table-2).

Table-2: Influence of the catalytic amounts of Xanthan sulfuric acid [a]

Entry	Catalyst(grams)	Time (min)	Yield(%) [b]
1	None	120	Trace
2	0.01	30	25
3	0.02	30	55
4	0.06	30	78
5	0.08	30	95
6	0.08	60	95

Reaction conditions: [a] Mixture of 2-hydroxynaphthalene-1,4-dione (1 mmol),2-naphthol (1mmol), benzaldehyde (1 mmol) and Xanthan sulfuric acid in ethanol was stirred at 50 ^0C [b] isolated yield

The reusability of the catalyst was checked by separating the Xanthan sulfuric acid from the reaction mixture by simple filtration, dried in an oven (50mm Hg pressure) at 60 ^oC for 3h prior to use in the other reaction. The recovered catalyst can be reused at least three additional times in subsequent reactions without significant decrease in product yield (Table 3).

Table-3: The effect of reusability of catalyst on yield [a].

Run	Cycle	Yield(%) [b]
1	0	95
2	1	93
3	2	88
4	3	81

Reaction conditions: [a] Mixture of 2-hydroxynaphthalene-1,4-dione (1 mmol),2-naphthol (1mmol), benzaldehyde (1 mmol) and Xanthan sulfuric acid (0.08 g) in ethanol was stirred at 50 ^0C.
[b] Yields refer to the pure isolated recovered catalyst.

CONCLUSION

In conclusion, we are reporting that Xanthan sulfuric acid is an efficient and reusable catalyst for the synthesis of 14-Aryl-14H-dibenzo[a,i]xanthene-8, 13-diones derivatives. The present protocol provides easy work-up procedure, cost efficiency, providing reusability of the catalyst with excellent yields, and it is non-toxic, which makes this method a valid contribution to the existing methodologies.

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