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Short communication

# Solvent-free synthesis of aryl-14*H*-dibenzo[*a*,*j*]xanthenes and 1,8-dioxo-octahydro-xanthenes using silica sulfuric acid as catalyst

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**Abstract**

A simple and efficient method for the synthesis of aryl-14*H*-dibenzo[*a*,*j*]xanthenes and 1,8-dioxo-octahydro-xanthenes using silica sulfuric acid as a reusable eco-friendly catalyst under solvent-free conditions is described.

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*Keywords:* Xanthenes; Solvent-free; Silica sulfuric acid; Naphthol; Reusable catalyst

## 1. Introduction

Xanthenes and benzoxanthenes have received much attention because of their wide range of therapeutic and biological properties, such as antibacterial [1], antiviral [2], and anti-inflammatory activities [3]. Furthermore, these compounds have emerged as sensitizers in photodynamic therapy [4] and are used as leuco-dyes [5] and in laser technology [6].

Many procedures have been disclosed to synthesize xanthenes and benzoxanthenees, including cyclodehydration [7], trapping of benzynes by phenols [8] as well as the cyclocondensation of 2-hydroxy aromatic aldehydes and 2-tetralone [9]. Furthermore, the synthesis of 14*H*-dibenzo[*a*,*j*]xanthene and its analogous can be prepared by reaction of 2-naphthol with 2-naphthol-1-methanol [10], formamide [11] and carbon monoxide [12]. However, many of these methods suffer drawbacks including long reaction times, unsatisfactory yield, harsh reaction conditions and an excess of reagents and catalysts.

Recently, silica sulfuric acid has been used as an efficient heterogeneous catalyst for many organic transformations [13] because of its low cost, ease of preparation [14], recycling and ease of handling; in addition, the catalyst can conveniently be separated by simple filtration.

## 2. Experimental

Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Mass spectra were recorded on a Finnigan-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. $^{1}H$ and $^{13}C$ NMR spectra were recorded on a Bruker DRX-300 Avance spectrometer at 300.13 and 75.47 MHz, respectively. IR spectra were recorded on a Bomem MB-Series FT-IR spectrophotometer. The chemicals used in this work were purchased from Fluka (Buchs, Switzerland).

### *2.1. Typical procedure for the preparation of aryl-14H-dibenzo[a,j]xanthenes (**3**)*

A mixture of 2-naphthol (1 mmol), aldehyde (0.5 mmol) and silica sulfuric acid (0.03 g) was heated at 80 °C.

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The reaction was monitored by TLC. After completion, the mixture was washed with $CHCl_3$ (10 ml) and filtered to recover the catalyst. The solvent was evaporated and the crude product recrystallized from EtOH to afford pure **3**.

### *2.2. Typical procedure for the preparation of 1,8-dioxo-octahydro-xanthenes (5)*

The procedure was similar to that described for **3** with the exception that 2-naphthol was replaced with 5,5-dimethyl-1,3-cyclohexanedione.

All the products are known compounds and were characterized by IR and NMR spectroscopic data and their melting points are compared with reported values.

*Spectral data for compound **3c***: m.p. 286–288 °C; IR (KBr) ($\nu_{max}$, $cm^{-1}$): 3033, 1618, 1580; $^1H$ NMR ($CDCl_3$): $\delta_H$ 6.48 (1H, s, CH), 7.10–8.34 (16H, m, Arom.); $^{13}C$ NMR ($CDCl_3$): $\delta_C$ 37.37, 116.73, 118.02, 122.40, 124.37, 126.92, 128.64, 128.91, 129.09, 129.49, 131.04, 131.24, 132.07, 143.46, 148.66; MS (*m/z*, %) 392 (25), 281 (100), 252 (45), 75 (34).

*Compound **3d***: m.p. 296–298 °C; IR (KBr) ($\nu_{max}$, $cm^{-1}$): 3030, 1624, 1586; $^1H$ NMR ($CDCl_3$): $\delta_H$ 6.47 (1H, s, CH), 7.25–8.34 (16H, m, Arom.); $^{13}C$ NMR ($CDCl_3$): $\delta_C$ 37.46, 116.64, 118.02, 120.21, 122.39, 124.38, 126.93, 128.91, 129.12, 129.88, 131.03, 131.23, 131.58, 143.98, 148.65; MS (*m/z*, %) 437 (20), 281 (100), 252 (40), 75 (15).

## 3. Results and discussion

Herein, a simple, efficient and high-yielding method for the synthesis of xanthene derivatives using silica sulfuric acid as a reusable eco-friendly catalyst under solvent-free conditions (Scheme 1) is described.

In terms of the amount of catalyst required for the reaction of 4-chloro-benzaldehyde (**2c**) and 2-naphthol (**1**) to afford **3c** under solvent-free conditions at 80 °C, as can be seen from Fig. 1, best results were obtained using 0.03 g of catalyst.

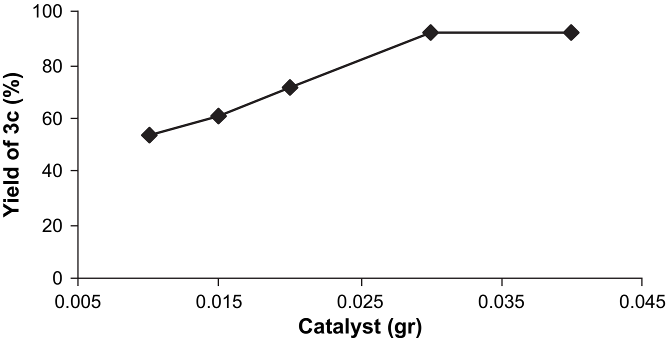
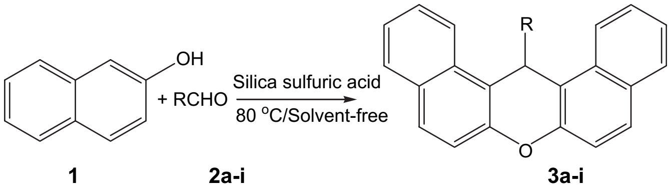


Fig. 1. Effect of catalyst on the synthesis of **3c** (reaction conditions: 4-chlorobenzaldehyde (1 mmol), 2-naphthol (2 mmol), 80 °C, 30 min).



Scheme 1.

As the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthene was recently reported by Shaterian et al. using silica sulfuric acid under solvent-free conditions at 125 °C [15], the optimum temperature was also examined using the reaction of 4-chloro-benzaldehyde (**2c**) and 2-naphthol (**1**) in the presence of the optimum quantity of silica sulfuric acid under solvent-free conditions. As can be seen from Table 1, it was possible to carry out the reaction at the much lower temperature, 80 °C, in similar yield.

The reaction of various aromatic aldehydes (**2a–i**) and 2-naphthol (**1**) in the presence of the optimum quantity of silica sulfuric acid under solvent-free conditions at 80 °C resulted in the formation of the 14-aryl-14*H*-dibenzo[*a*,*j*]xanthene (**3a–i**) (Scheme 1). Several functionalities present in the aryl aldehydes such as halogen, methoxy and nitro group were tolerated. In all the cases the corresponding benzoxanthenes were obtained in good/excellent yield after 15–120 min (Table 2).

In these experiments the product was isolated by filtration and the catalyst could then be reused together with fresh reagents in further reactions. Thus, recyclization of the catalyst was possible without significant loss of catalytic activity (Table 2, entry **3c**). In the absence of silica sulfuric acid, the products were obtained in low yield (<30%) after long reaction times (6–8 h) under solvent-free conditions at 80 °C.

However, the reaction conducted with 1-naphthol instead of 2-naphthol did not afford any product.

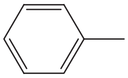
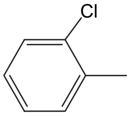
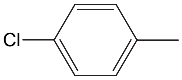
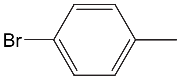
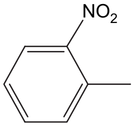
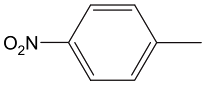
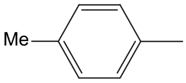
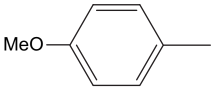
Table 3 compares the efficiency of the silica sulfuric acid catalyst with the efficiency of other catalysts in the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthene obtained by other workers. It is clear from Table 2 that the current method is simpler, more efficient and less time-consuming for the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthene derivatives.

Table 1
Effect of temperature on the synthesis of **3c**[a]

| Temperature/°C | Yield/% |
|---|---|
| 60 | 74 |
| 80 | 92 |
| 100 | 91 |
| 125 | 90 |

[a] 4-Chloro-benzaldehyde (1 mmol), 2-naphthol (2 mmol), catalyst (0.03 g), 30 min.

Table 2
Synthesis of benzoxanthenes

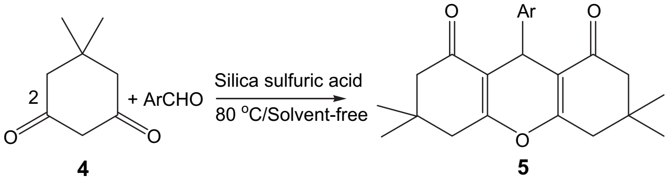
| **3** | R | Time/min | Yield/%$^a$ |
|---|---|---|---|
| **a** |  | 45 | 89 |
| **b** |  | 30 | 92 |
| **c** |  | 30 | 92 (87, 83, 80)$^b$ |
| **d** |  | 30 | 87 |
| **e** |  | 15 | 96 |
| **f** |  | 40 | 89 |
| **g** |  | 60 | 94 |
| **h** |  | 45 | 86 |
| **i** |  | 120 | 80 |

[a] Isolated yields.
[b] Isolated yields after recycling of catalyst.

Encouraged by these results, we carried out the reaction of 5,5-dimethyl-1,3-cyclohexanedione (**4**) instead of 2-naphthol (**1**) with various aromatic aldehydes under solvent-free conditions at 80 °C, which afforded 1,8-dioxo-octahydro-xanthene derivatives (**5**) in excellent yields within a short period of time (Scheme 2, Table 4).

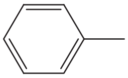
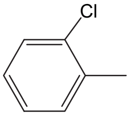
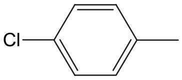
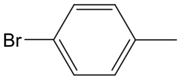
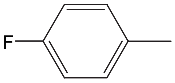
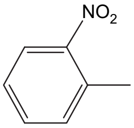
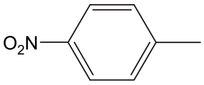
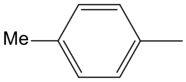
Table 3
Comparison of results using silica sulfuric acid catalyst with results obtained by other workers

| Catalyst | Conditions | Time/min | Yield/% | Ref. |
|---|---|---|---|---|
| Silica sulfuric acid | Solvent-free/80 °C | 0.25–2 | 80–94 | – |
| Selectfluor | Solvent-free/125 °C | 6–12 | 90–95 | [7c] |
| *p*-Toluene sulfonic acid | Solvent-free/125 °C | 2.5–6 | 80–96 | [7d] |
| *p*-Toluene sulfonic acid | 1,2-Dichloroethane (reflux) | 15–24 | 85–95 | [7d] |
| $I_2$ | Solvent-free/90 °C | 2–5 | 85–95 | [7e] |
| Sulfamic acid | Solvent-free/125 °C | 6–12 | 90–95 | [7f] |
| Amberlyst-15 | Solvent-free/125 °C | 0.5–2 | 80–94 | [7h] |



Scheme 2.

Table 4
Synthesis of 1,8-dioxo-octahydro-xanthenes

| **4** | Ar | Time/h | Yield/%$^a$ |
|---|---|---|---|
| **a** |  | 1 | 97 |
| **b** |  | 2.5 | 94 |
| **c** |  | 1.5 | 94 |
| **d** |  | 2.5 | 97 |
| **e** |  | 2 | 92 |
| **f** |  | 1 | 91 |
| **g** |  | 1.5 | 91 |
| **h** |  | 2.5 | 88 |

[a] Isolated yields.

## 4. Conclusions

A simple, efficient and ‘green’ method for the synthesis of xanthenes using silica sulfuric acid under solvent-free conditions has been developed, which affords short reaction times, excellent yields and utilization of an inexpensive and reusable catalyst.

## Acknowledgement

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