# Antimony (III) acetate as a versatile and efficient catalyst for synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes at room temperature

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Antimony (III) acetate was used in the one-pot three-component synthesis of biologically active 14-aryl-14*H*-dibenzo[*a,j*] xanthenes from the condensation between arylaldehydes and β-naphthol under solvent-free conditions at ambient temperature. This methodology has a number of advantages such as, short reaction time, easy work-up and high yields.

**Keywords:** $Sb(OAc)_3$, 14-aryl-14*H*-dibenzo[*a,j*]xanthenes, solvent-free condition

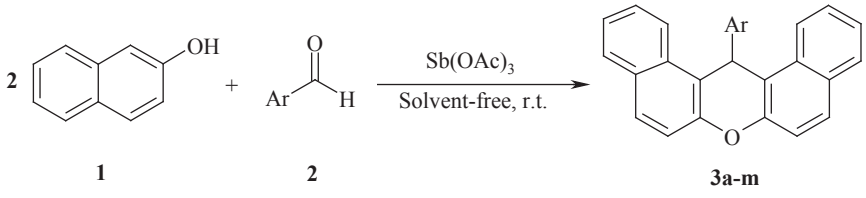
14-Aryl(alkyl)-14*H*-dibenzo[*a,j*]xanthenes are important biologically active heterocyclic compounds with anti-viral,[1] anti-inflammatory[2] and anti-bacterial[3] activities. Thus a broad utility range has made xanthenes prime synthetic candidates thereby accentuating the need to develop newer synthetic routes for scaffold manipulation of xanthene derivatives.

Several methods have been reported for the synthesis of benzoxanthenes, such as the cyclocondensation reaction of 2-hydroxyaromatic aldehydes and 2-tetralone,[4] the reaction of benzaldehyde and acetophenone[5] and the condensation of β-naphthol with alkyl or aryl aldehydes. The latter synthetic method can be promoted by many Brønsted acid catalysts such as: $H_2SO_4$, HCl, *p*-toluenesulfonic acid, sulfamic acid, methanesulfonic acid, $H_3PO_4$ or $HClO_4$ at 0 °C in acetic acid, ionic liquids, heteropolyacids, silica sulfuric acid, cyanuric chloride, LiBr, $CoPy_2Cl_2$, $Yb(OTf)_3$, $Sc[N(SO_2C_8F_{17})_2]_3$, $NaHSO_4$, $Al(HSO_4)_3$, bismuth(III)chloride, $ZrO(OTf)_2$, ruthenium chloride hydrate, silica supported perchloric acid, $P_2O_5/Al_2O_3$ and silica chloride.[6–11] Though different approaches have been reported, there are many limitations, such as the use of expensive and excess amounts of catalysts, elevated temperatures, long reaction times, hazardous organic solvents and reagents, and low yields. Hence, the development of novel methods for the synthesis of functionalised biologically active 14-aryl(alkyl)-14*H*-dibenzo[*a,j*]xanthenes is of great importance because of their potential biological and pharmaceutical activities. We have developed an efficient procedure for the one-pot three-component synthesis of biologically active 14-aryl-14*H*-dibenzo[*a,j*]xanthenes in the presence of antimony(III)acetate as a solid phase acidic catalyst, under solvent-free conditions at an ambient temperature (Scheme 1).

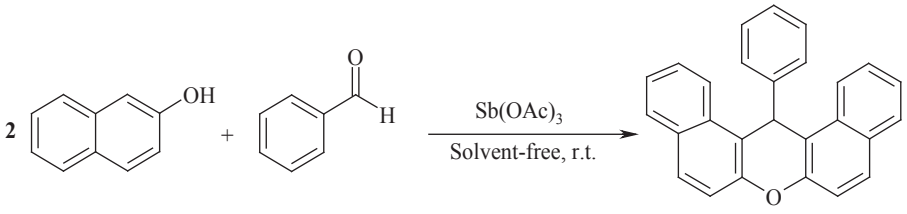
## Result and discussions

We have investigated the synthesis of 14-aryl-14*H*-dibenzo[*a,j*] xanthenes in the presence of antimony(III)acetate as catalyst. First, the reaction of benzaldehyde (1 mmol) with 2-naphthol (2 mmol) was chosen as a model system (Scheme 2). Initially a control experiment confirmed that the reaction did not proceed in the absence of a catalyst (Table 1, entry 1). The model reaction was then performed in the presence of different catalysts and solvents at different temperatures.

We have carried out a model study with benzaldehyde (1 mmol) and 2-naphthol (2 mmol) using $Sb(OAc)_3$ (0.02 g) as catalyst at room temperature. In order to establish the better catalytic activity of $Sb(OAc)_3$, we have compared the reaction using other catalysts at room temperature and for 15 min. The results are listed in Table 1. The results show that $Sb(OAc)_3$ is a more efficient catalyst with respect to the reaction time and exhibits broad applicability giving products in similar or better yield (Table 1, entry 16).




**Scheme 1** Synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes in the presence of antimony(III)acetate as catalyst.




**Scheme 2** Synthesis of 14-phenyl-dibenzo[*a,j*]xanthenes in the presence of $Sb(OAc)_3$ as catalyst.

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**Table 1** Evaluation of the activity of different catalysts and $Sb(OAc)_3$ for the condensation of benzaldehyde and 2-naphthol

| Entry | Catalyst | Time/min | Yield/%[a] |
|---|---|---|---|
| 1 | – | 15 | 5 |
| 2 | $H_2SO_4$ | 15 | 55 |
| 3 | HCl | 15 | 60 |
| 4 | *p*-TSA | 15 | 52 |
| 5 | Sulfamic acid | 15 | 73 |
| 6 | $BF_3.SiO_2$ | 15 | 85 |
| 7 | Silica/sulfuric acid | 15 | 60 |
| 8 | LiBr | 15 | 44 |
| 9 | $CoPy_2Cl_2$ | 15 | 62 |
| 10 | $Yb(OTf)_3$ | 15 | 30 |
| 11 | $NaHSO_4$ | 15 | 45 |
| 12 | $Al(HSO_4)_3$ | 15 | 67 |
| 13 | $BiCl_3$ | 15 | 24 |
| 14 | $ZrO(OTf)_2$ | 15 | 45 |
| 15 | $P_2O_5/Al_2O_3$ | 15 | 50 |
| 16 | $Sb(OAc)_3$ | 15 | 92 |

[a]Isolated yield.

**Table 2** Optimisation amount of $Sb(OAc)_3$ on the reaction of condensation of benzaldehyde and 2-naphthol under solvent-free at ambient temperature

| Entry | Catalyst/g | Time/min | Yield/%[a] |
|---|---|---|---|
| 1 | 0.04 | 5 | 96 |
| 2 | 0.03 | 10 | 95 |
| 3 | 0.02 | 15 | 92 |
| 4 | 0.01 | 20 | 92 |

[a]Isolated yield.

**Table 3** Effect of the solvent on the reaction between benzaldehyde and 2-naphthol using $Sb(OAc)_3$

| Entry | Solvent | Temperature/°C | Yield/%[a] |
|---|---|---|---|
| 1 | $CHCl_3$ | Reflux | 10 |
| 2 | EtOH | Reflux | 70 |
| 3 | $CHCl_3$ | 25 | – |
| 4 | EtOH | 25 | 5 |
| 5 | $CHCl_3$ | 60 | 30 |
| 6 | EtOH | 60 | 50 |
| 7 | Solvent-free | 25 | 92 |

[a]Isolated yield.

In order to determine the optimum quantity of $Sb(OAc)_3$ the reaction of benzaldehyde and 2-naphthol was carried out at room temperature using different quantities of $Sb(OAc)_3$ (Table 2). $Sb(OAc)_3$ (0.02 g) gave an excellent yield in 15 min (Table 2, entry 3).

The above reaction was also examined in various solvents (Table 3). The results indicated that different solvents affected the efficiency of the reaction. Most solvents required a longer time and gave moderate yields, and the best results were obtained when solvent-free conditions were used (Table 3, entry 7).

To study the scope of the reaction, a series of aromatic aldehydes catalysed by $Sb(OAc)_3$ (0.02 g) were studied. The results are shown in Table 4. In all cases, aromatic aldehydes substituted with either electron-donating or electron-withdrawing groups underwent the reaction smoothly and gave the products in excellent yields.

The compounds **3a**–**m** were characterised by $^1$H NMR and IR spectroscopy and elemental analyses. Spectral data were compared with the literature data.[12–16]

In summary, we have developed a mild, highly efficient method for synthesis of biologically active 14-aryl-14*H*-dibenzo[*a,j*]xanthenes in the presence of antimony(III)acetate as a solid phase acidic catalyst. The method requires a simple work-up, is inexpensive and gives excellent yields.

## Experimental

All chemicals were purchased from commercial suppliers and were used without any purification. All products were identified by their spectra and physical data. Melting points were measured by using the capillary tube method with an Electrothermal 9100 apparatus. IR spectra were recorded on a Shimadzu spectrometer 883 (KBr pellets, Nujol mulls, 4000–400 $cm^{-1}$). $^1$H NMR spectra were recorded on a Bruker-Avance DRX 400 spectrometer using TMS as an external standard.

*Preparation of 14-aryl or alkyl-14H-dibenzo[*a,j*]xanthenes catalysed by antimony(III)acetate*

A mixture of β-naphthol (2 mmol), arylaldehyde (1 mmol) and antimony(III)acetate (0.02 g) was ground in a mortar for 15 min under solvent-free conditions at room temperature. The progress of the reaction was monitored by TLC. After completion of the reaction, the crude solid product was dissolved in $CH_2Cl_2$. The mixture was filtered to separate the catalyst. The catalyst was washed with (2 × 5 mL) $CH_2Cl_2$. The recovered catalyst was dried *in vacuo* and used in subsequent catalytic runs. Products were obtained by removal of the $CH_2Cl_2$ solvent under reduced pressure.

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**Table 4** Synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes using $Sb(OAc)_3$ as catalyst

| Entry | Ar | Product | Time/min | Yield/% | M.p./°C | |
|---|---|---|---|---|---|---|
| | | | | | Found | Reported |
| 1 | $C_6H_5$ | **3a** | 15 | 92 | 181–183 | 184–186 [12] |
| 2 | 2-$NO_2$–$C_6H_4$ | **3b** | 2 | 97 | 216–218 | 215–217 [14] |
| 3 | 3-$NO_2$–$C_6H_4$ | **3c** | 2 | 98 | 207–209 | 210–211 [13] |
| 4 | 4-$NO_2$–$C_6H_4$ | **3d** | 2 | 98 | 313–315 | 311–312 [12] |
| 5 | 4-OH-3-OMe–$C_6H_3$ | **3e** | 6 | 95 | 206–208 | 206–207 [16] |
| 6 | 4-OMe–$C_6H_4$ | **3f** | 4 | 96 | 205–207 | 203–205 [13] |
| 7 | 4-Br–$C_6H_4$ | **3g** | 8 | 92 | 291–293 | 297–298 [12] |
| 8 | 2-Cl–$C_6H_4$ | **3h** | 2 | 98 | 211–213 | 214–216 [13] |
| 9 | 3-Cl–$C_6H_4$ | **3i** | 30 | 90 | 208–210 | 210–212 [15] |
| 10 | 4-Cl–$C_6H_4$ | **3j** | 30 | 90 | 292–294 | 289–290 [13] |
| 11 | 4-OH–$C_6H_4$ | **3k** | 30 | 90 | 132–134 | 135–136 [14] |
| 12 | 4-COH–$C_6H_4$ | **3l** | 2 | 97 | 258–259 | 252–255 [15] |
| 13 | 2-OMe–$C_6H_4$ | **3m** | 2 | 98 | 215–217 | 214–216 [13] |

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