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Facile One-Pot Synthesis of Tetrahydrobenzo[a]xanthene-11-one and Aryl-14*H*-dibenzo[a,j]xanthene

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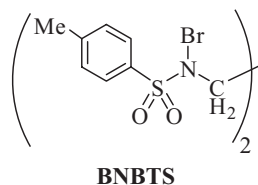
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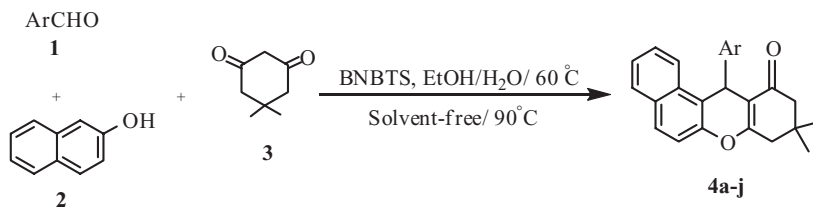
In recent years, xanthenes and benzoxanthenes have been of great interest because they have been found to possess useful biological activities such as anti-inflammatory,¹ antiviral,² and antibacterial activities.³ They also are being utilized as antagonists for the paralyzing action of zoxazolamine,⁴ in photodynamic therapy,⁵ as leuco-dyes in laser technology,⁶ and as pH-sensitive fluorescent materials for visualization of biomolecules.⁷ Several methods have been reported for the synthesis of xanthene derivatives by the condensation of β -naphthol with aldehydes and of β -naphthol, aldehydes and dimedone catalyzed by $\text{BF}_3 \cdot \text{SiO}_2$,⁸ $\text{Sr}(\text{OTf})_2$,⁹ $\text{NaHSO}_4 \cdot \text{SiO}_2$,¹⁰ $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$,¹¹ $\text{NH}_4\text{H}_2\text{PO}_4/\text{SiO}_2$,¹² Amberlyst-15,¹³ and *p*-TSA.¹⁴ However, many of these procedures suffer from harsh reaction conditions, long reaction times, and difficult work-up.

In continuation of our interest in the application of *N,N'*-dibromo-*N,N'*-1,2-ethanediyl bis(*p*-toluenesulfonamide) [BNBTS]^{15,16} in organic synthesis,^{17,18} we report here a convenient method for the preparation of tetrahydrobenzo[a]xanthene-11-ones (**4**) in solution and under solvent-free conditions (*Scheme 1*).



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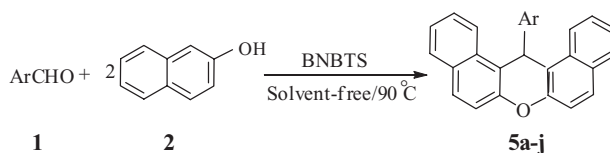


- a) Ar = C₆H₅ b) Ar = *p*-CH₃C₆H₄ c) Ar = *p*-CH₃OC₆H₄ d) Ar = *p*-ClC₆H₄ e) Ar = *p*-NO₂C₆H₄
 f) Ar = *m*-NO₂C₆H₄ g) Ar = *o*-ClC₆H₄ h) Ar = 2-HO-5-BrC₆H₃ i) Ar = *p*-HOC₆H₄ j) Ar = *o*-CH₃OC₆H₄

Scheme 1

Among the solvents screened such as chloroform, ethylene chloride, toluene and aqueous ethanol, the latter (70:30) proved to be the best (*Table 1*). No by-products were detected under either conditions (in solution or under solvent-free conditions).

Similarly, dibenzo[*a,j*]xanthenes (**5a-j**) were obtained by the condensation of aromatic aldehydes with two equivalents of β -naphthol under solvent-free conditions (*Scheme 2*, *Table 2*); however, only poor yields (30–40%) were obtained when this reaction was performed in solution.

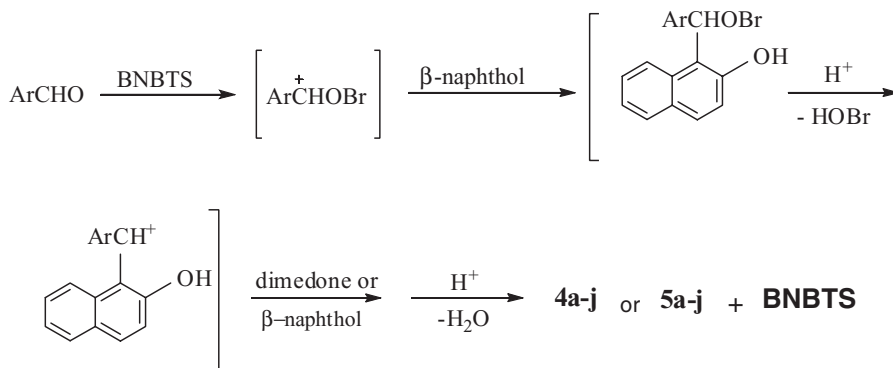


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Scheme 2

In both cases, the reaction of aldehydes substituted with either electron-donating or electron-withdrawing groups proceeded smoothly and gave the expected compounds in high yields. However, aliphatic aldehydes gave very low yields (15–20%) of the corresponding products **4** and **5**. Since BNBTS contains bromine atoms attached to nitrogen atoms, it is likely that it releases Br⁺ *in situ*, which acts as a catalyst in the reaction medium.^{15,17} Therefore, the mechanism shown in *Scheme 3* can be suggested for this conversion.^{9,10,13} Although the yields and reaction times using other reagents are approximately the same (*Table 2*), BNBTS is an inexpensive and mild catalyst which reacts under homogeneous conditions. BNBTS is re-usable (after evaporation of ethanol) and after four runs, the catalytic activity of the BNBTS was only reduced to about 35%.

In conclusion, we have introduced the novel catalytic reagent *N,N'*-dibromo-*N,N'*-1,2-ethanediylyl*bis*(*p*-toluenesulfonamide) [BNBTS] as the activator for the reaction between aldehydes and β -naphthol under solvent-free conditions and for the reaction of aldehydes, β -naphthol and dimedone in solution or under solvent-free conditions. All the products were characterized by their melting points, IR, ¹H NMR and ¹³C NMR spectroscopic data.



Scheme 3

Short reaction times, high yields, a reusable and inexpensive catalyst and easy work-up are the advantages of this method.

Experimental Section

Substrates, solvents and other chemicals were purchased from Fluka, Merck and Aldrich chemical companies. The progress of the reactions was monitored by TLC (SiO₂-*n*-hexane:acetone). IR spectra (KBr) were recorded on a Shimadzu Fx-90 infrared spectrophotometer and the NMR spectra were obtained on a JEOL 90 MHz spectrometer using TMS as the internal standard. BNBS was prepared according to our previously reported procedure.^{15,16}

Table 1
Yields and mps of Tetrahydrobenzoxanthenes catalyzed by BNBS.^a

Cmpd	Solvent-free		In Solution ^b		mp. (°C)	lit. mp. (°C)
	Yield (%)	Time (min)	Yield (%)	Time (min)		
4a	93	92	90	100	147–149	151–153 ⁹
4b	90	80	92	120	174–176	176–178 ²⁰
4c	93	25	90	30	203–205	204–205 ⁹
4d	97	93	92	60	178–180	180–182 ⁹
4e	88	60	86	50	177–179	178–180 ²⁰
4f	87	95	87	190	170–172	168–170 ⁹
4g	95	45	90	60	175–177	179–180 ²⁰
4h	97	20	92	20	265–267	266–268 ²⁰
4i	92	52	90	60	227–229	223–225 ¹⁰
4j	95	42	91	87	158–160	163–165 ²⁰

a) Products were characterized from their physical properties, by comparison with authentic samples, and by spectroscopic methods. b) In 70:30 ethanol-water.

Table 2
Yields and mps of Aryl-14*H*-dibenzo[xanthenes catalyzed by BNBTS.^a

Cmpd	Solvent-free		mp. (°C)	<i>lit.</i> mp. (°C)
	Yield (%)	Time (min)		
5a	90	24	180–182	183 ⁸
5b	88	70	224–226	228 ⁸
5c	87	120	208–209	204 ⁸
5d	96	50	283–285	286–288 ⁸
5e	95	90	308–310	310 ⁸
5f	93	74	215–217	213 ¹⁹
5g	90	100	198–200	203–205 ⁸
5h	89	76	295–297	296–298 ⁸
5i	89	45	138–140	140 ¹¹
5j	90	65	261–263	260 ⁸

a) Products were characterized from their physical properties, by comparison with authentic samples, and by spectroscopic methods.

Preparation of Aryl Tetrahydrobenzo[*a*]xanthen-11-ones (4a–j) under Solvent-free Conditions. General Procedure

A mixture of the aldehyde (2 mmol), 2-naphthol (0.28 g, 2 mmol), 5,5-dimethylcyclohexane-1,3-dione (0.31 g, 2.2 mmol) and BNBTS (0.1 g, 0.2 mmol) was stirred using a magnetic stirrer at 90°C. The progress of the reaction was monitored by TLC (SiO₂-*n*-hexane:acetone [8:2]). After completion of the reaction, ethanol (15 mL) was added, stirred (6–7 min) and cooled. The precipitated product was collected and recrystallized from methanol. Evaporation of the filtrate under reduced pressure gave BNBTS, characterized by its mp. 92–94°C, in nearly quantitative yield.

Preparation of Aryl Tetrahydrobenzo[*a*]xanthen-11-ones (4a–j) in Solution. General Procedure

A mixture of the aldehyde (2 mmol), 2-naphthol (0.28 g, 2 mmol), 5,5-dimethylcyclohexane-1,3-dione (0.31 g, 2.2 mmol), ethanol/water (2 mL) and BNBTS (0.1 g, 0.2 mmol) was stirred using a magnetic stirrer at 60°C. The progress of the reaction was monitored by TLC (*n*-hexane:acetone [8:2]). After completion of the reaction, the solution was cooled. The precipitated product was collected and recrystallized from methanol. Evaporation of the filtrate under reduced pressure gave BNBTS, characterized by its mp. 92–94°C, in nearly quantitative yield.

Preparation of Aryl 14*H*-Dibenzo[*a*]xanthen-11-ones (5a–j) under Solvent-free Conditions. General Procedure

A mixture of the aldehyde (2 mmol), 2-naphthol (0.57 g, 4 mmol) and BNBTS (0.1 g, 0.2 mmol) was stirred using a magnetic stirrer at 90°C. The progress of the reaction was monitored by TLC (*n*-hexane:acetone [8:2]). After completion of the reaction, ethanol (15

mL) was added and stirred (6–7 min) and cooled. The precipitated product was collected and recrystallized from methanol. Evaporation of the filtrate under reduced pressure gave BNBTs, characterized by its mp. 92–94°C, in nearly quantitative yield.

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