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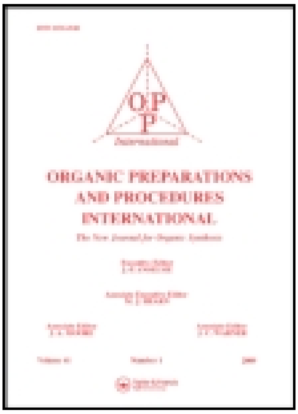

Organic Preparations and Procedures International: The New Journal for Organic Synthesis

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/uopp20

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

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Published online: 01 Oct 2010.

To cite this article: Ramin Ghorbani-Vaghei & Seyedeh Mina Malaekehpoor (2010) Facile One-Pot Synthesis of Tetrahydrobenzo[a]xanthene-11-one and Aryl-14H-dibenzo[a.j]xanthene, Organic Preparations and Procedures International: The New Journal for Organic Synthesis, 42:5, 494-498, DOI: 10.1080/00304948.2010.514802

To link to this article: http://dx.doi.org/10.1080/00304948.2010.514802

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Organic Preparations and Procedures International, 42:494–498, 2010

ISSN: 0030-4948 print
DOI: 10.1080/00304948.2010.514802

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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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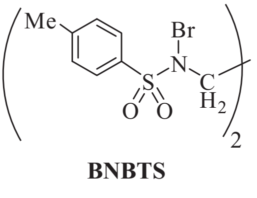
In recent years, xanthenes and benzoxanthenes have been of great interest because they have been found to possess useful biological activities such as anti-inflammatory,[1] antiviral,[2] and antibacterial activities.[3] They also are being utilized as antagonists for the paralyzing action of zoxazolamine,[4] 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 $BF_3.SiO_2$,[8] $Sr(OTf)_2$,[9] $NaHSO_4.SiO_2$,[10] $H_{14}[NaP_5W_{30}O_{110}]$,[11] $NH_4H_2PO_4/SiO_2$,[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*).



BNBTS

Submitted June 4, 2009.

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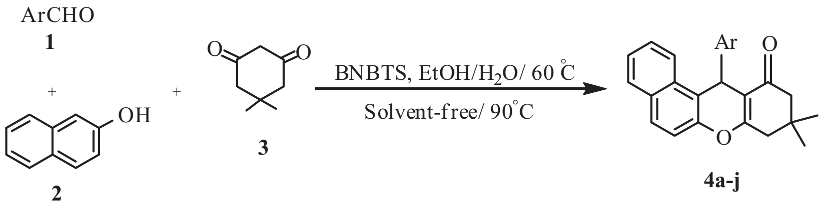
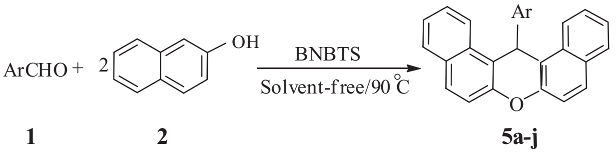


a) Ar = C_6H_5 b) Ar = p-$CH_3C_6H_4$ c) Ar = p-$CH_3OC_6H_4$ d) Ar = p-ClC_6H_4 e) Ar = p-$NO_2C_6H_4$
f) Ar = m-$NO_2C_6H_4$ g) Ar = o-ClC_6H_4 h) Ar = 2-HO-5-BrC_6H_3 i) Ar = p-HOC_6H_4 j) Ar = o-$CH_3OC_6H_4$

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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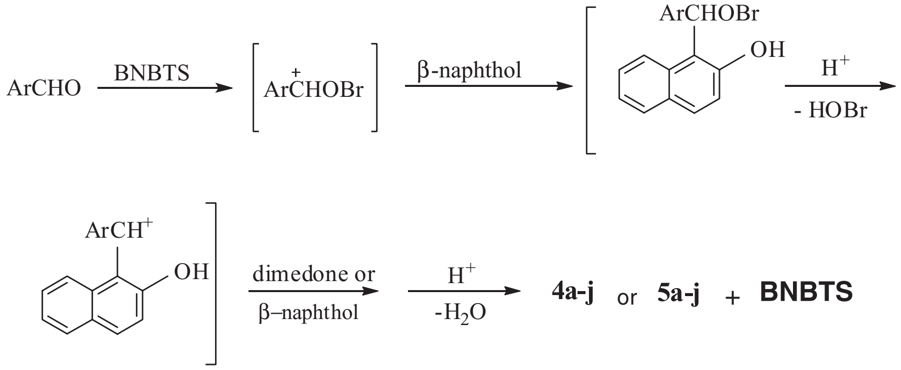
Scheme 2

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-ethanediyl*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, ^{1}H NMR and ^{13}C 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 (SiO_2-*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. BNBTS was prepared according to our previously reported procedure.[15,16]

Table 1

Yields and mps of Tetrahydrobenzoxanthenes catalyzed by BNBTS.[a]

	Solvent-free		In Solution[b]			
Cmpd	Yield (%)	Time (min)	Yield (%)	Time (min)	mp. (°C)	*lit.* mp. (°C)
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*-dibenzoxanthenes catalyzed by BNBTS.[a]

Cmpd	Solvent-free Yield (%)	Time (min)	mp. (°C)	*lit.* mp. (°C)
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 (SiO_2-*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 14H-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.

Acknowledgement

We are thankful to Bu-Ali Sina University, Center of Excellence and Development of Chemical Methods (CEDCM) for financial support.

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