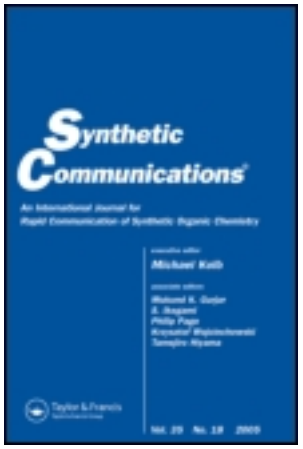


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Green Approaches for the Synthesis of 12-Aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-ones in Aqueous Media and Under Microwave Irradiation in Solventless Conditions

Jitender M. Khurana [a], Anshika Lumb [a], Archana Pandey [a] & Devanshi Magoo [a]

[a] Department of Chemistry, University of Delhi, Delhi, India

Accepted author version posted online: 17 Nov 2011.Version of record first published: 27 Feb 2012.

To cite this article: Jitender M. Khurana , Anshika Lumb , Archana Pandey & Devanshi Magoo (2012): Green Approaches for the Synthesis of 12-Aryl-8,9,10,12-tetrahydrobenzo[a]xanthen-11-ones in Aqueous Media and Under Microwave Irradiation in Solventless Conditions, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 42:12, 1796-1803

To link to this article: http://dx.doi.org/10.1080/00397911.2010.544832

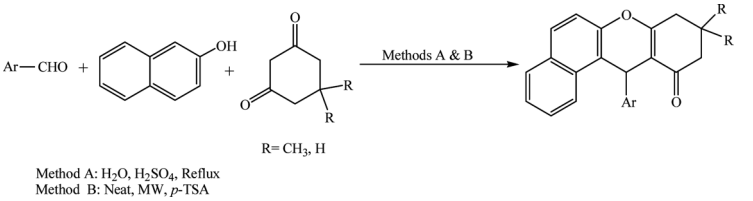
Synthetic Communications®, 42: 1796–1803, 2012

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2010.544832

GREEN APPROACHES FOR THE SYNTHESIS OF 12-ARYL-8,9,10,12-TETRAHYDROBENZO[*a*]XANTHEN-11-ONES IN AQUEOUS MEDIA AND UNDER MICROWAVE IRRADIATION IN SOLVENTLESS CONDITIONS

Jitender M. Khurana, Anshika Lumb, Archana Pandey, and Devanshi Magoo
Department of Chemistry, University of Delhi, Delhi, India

GRAPHICAL ABSTRACT



Abstract *Convenient and environmentally benign procedures have been reported for the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one derivatives by multi component condensation reactions of aromatic aldehydes with β-naphthol and cyclic 1,3-dicarbonyl compounds, namely, dimedone and cyclohexane-1,3-dione. The three-component condensation has been successfully achieved in one pot by refluxing the components in water and is efficiently catalyzed by sulfuric acid. The condensation has also been achieved by irradiating the components in the presence of a catalytic amount of* para-*toluene sulfonic acid under neat conditions with microwaves. The green methodologies defined herein avoid the severe conditions posed by the older existing methods and prove to be efficient in terms of good yields, operational simplicity, easy workup, and short reaction time.*

Keywords Cyclohexane-1,3-dione; dimedone; microwave; water; xanthene

INTRODUCTION

Among diverse families of dyes, xanthene and benzoxanthene derivatives hold a prominent position because of their useful photochemical and photophysical properties.[1] Xanthenes and the related condensed ring system variants have been used as dyes,[2] food colorants,[3] and fluorescent materials for visualization of biomolecular assemblies.[4] Particularly, carboxy-functionalized fluorescein[5] and rhodamine[6]

Received October 12, 2010.
Address correspondence to Jitender M. Khurana, Department of Chemistry, University of Delhi, Delhi 110007, India. E-mail: jmkhurana@chemistry.du.ac.in

dyes, which share a common xanthene-based skeleton, have become increasingly important as conjugated fluorescent markers of biologically active compounds.

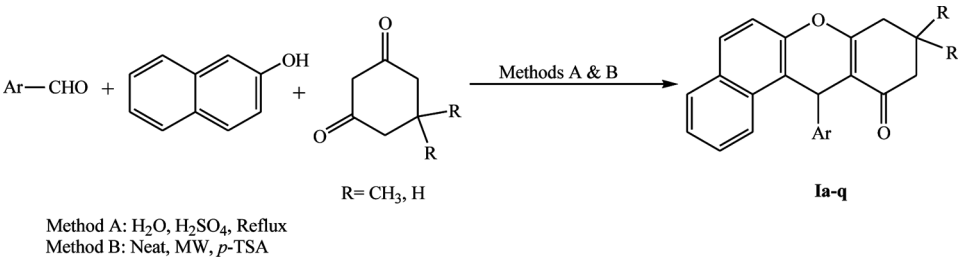
The xanthene- and benzoxanthene-based derivatives are also being used to develop polymer photoimaging systems, which have numerous applications primarily in the print and electronic industry.[7] Xanthene dyes are also utilized in fabricating dye-doped materials with interesting applications in holography, optical computing, and holographic interferometry.[8] Furthermore, benzoxanthene derivatives are important components of biologically active heterocycles. They are known to display pharmacological properties such as antibacterial,[9] anti-inflammatory,[10] and antiviral activities.[11] Because of a wide utility range of xanthene derivatives, there has been a significant impetus in developing newer synthetic routes for scaffold manipulation of these structural motifs. Recent reports on the synthesis of tetrahydrobenzo[*a*]xanthen-11-ones describe the reaction of aldehydes and β-naphthol with cyclic 1,3-dicarbonyl compounds in the presence of catalysts such as strontium triflate[12] and $NaHSO_4 \cdot SiO_2$[13] under reflux in halogenated solvents for long hours. $InCl_3$, P_2O_5,[14] and TBAF[15] have also been employed to bring about the cyclocondensation reaction. These synthetic methods afforded good yields but have limitations of long reaction times, harsh reaction conditions, and use of toxic solvents and often expensive catalysts. Consequently, there is scope for developing improved and environmentally benign methodologies for the synthesis of these benzoxanthene derivatives.

Because of the ubiquitous use of toxic reagents, chemicals, and volatile, flammable organic solvents, the concept of "green chemistry" has gained phenomenal impetus. It emphasizes the development of environmentally clean synthesis, eliminating the use of hazardous reagents, chemicals, and solvents. In this regard, organic synthesis in aqueous media is rapidly gaining importance. Because of its green credentials, safety, and economy, water has emerged as a promising alternative solvent in the arena of organic synthesis.[16] Also, considerable attention has been drawn to reactions carried out under solvent-free conditions. This solventless synthesis with exposure to microwaves[17] has the associated benefits of shorter reaction time, simple experimental setup, and efficient workup procedures.

In conjunction with our continuing efforts to explore new reactions for synthesis of heterocyclic compounds,[18] we embarked upon environmentally benign strategies to explore the possibility of synthesizing tetrahydrobenzo[*a*]xanthene-11-one derivatives by one-pot condensation of aromatic aldehydes, β-naphthol, and cyclic 1,3-dicarbonyl compounds in aqueous media using H_2SO_4 as catalyst and under microwave irradiation in neat conditions using catalytic *para*-toluenesulfonic acid (*p*-TSA).

RESULTS AND DISCUSSION

We report herein efficient and green approaches for the synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-ones derivatives by one-pot, three-component condensation of aromatic aldehydes, β-naphthol, and cyclic 1,3-dicarbonyl compounds catalyzed by H_2SO_4 in water as the solvent under reflux conditions and also under microwave irradiation using *p*-TSA as catalyst in solventless conditions (Scheme 1).



Scheme 1. Synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-ones.

To achieve optimum reaction conditions, we initially investigated the reaction of 4-chlorobenzaldehyde (1.0 mmol), β-naphthol (1.0 mmol), and 5,5-dimethylcyclohexane-1,3-dione (dimedone) (1.2 mmol) in different media in the presence of acid catalysts such as HCl, HNO_3, CH_3COOH, and H_2SO_4. The best result was obtained when the reaction was carried out in water in the presence of a catalytic amount of sulfuric acid (0.1 mmol) under reflux conditions. The reaction underwent completion in 3 h, yielding 88% of 12-(4-chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*] xanthene-11-one (**1**) after a simple workup. Repeating the reaction under similar conditions using HNO_3 as the catalyst resulted in a mixture of products while reactions with HCl and CH_3COOH resulted in sluggish and incomplete reactions with only a trace amount of the product. In the absence of any catalyst, we did not observe any product formation even after 10 h of reflux. Reactions using a catalytic amount of H_2SO_4 in CH_3CN under reflux resulted in a mixture of products while the reaction in tetrahydrofuran (THF) resulted in an incomplete reaction with an inferior yield (41%) of **1**. Thus catalytic H_2SO_4 in water under reflux was chosen as the optimum system to extend the protocol. Subsequent reactions of variously substituted aromatic aldehydes with β-naphthol and dimedone were carried out under these conditions. The reactions proceeded smoothly for different aldehydes to afford the corresponding xanthene derivatives in excellent yields. The results have been summarized in Table 1 (method A, entries 1–12).

The protocol was further extended by exploring the cyclocondensation of various aldehydes and β-naphthol with another cyclic 1,3-dicarbonyl compound (i.e., cyclohexane-1,3-dione). The reaction of 4-chlorobenzaldehyde (1.0 mmol), β-naphthol (1.0 mmol), and cyclohexane-1,3-dione (1.2 mmol) in water using 10 mol% of H_2SO_4 as catalyst under similar conditions yielded 89% of 12-(4-chlorophenyl)-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (**1 m**) after 3 h. Other substituted benzaldehydes also underwent successful condensation with β-naphthol and cyclohexane-1,3-dione, giving good yields of corresponding xanthene derivatives (Table 1, method A, entries 13–17).

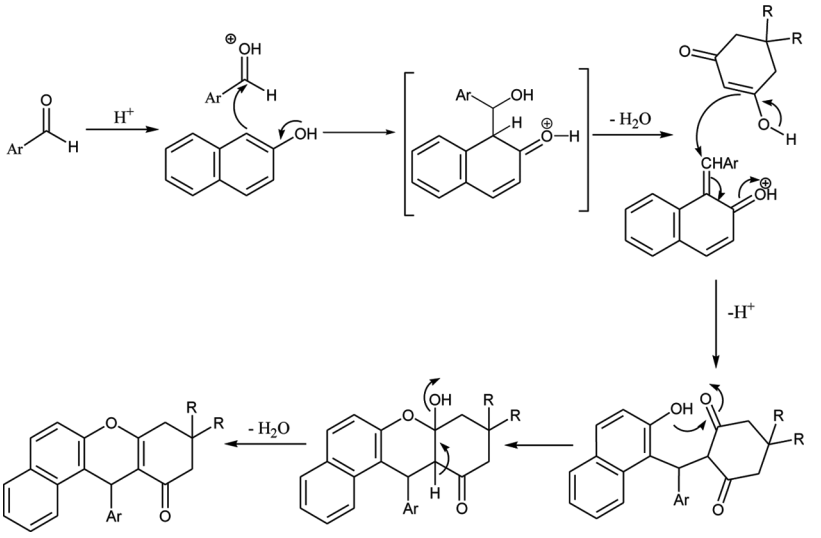
We decided to further explore these reactions under neat conditions with exposure to microwave irradiation. The control reactions of 4-chlorobenzaldehyde, β-naphthol, and dimedone mixed with a catalytic amount of H_2SO_4 under neat conditions led to charring of the components. Therefore, we attempted the reaction using solid acid catalyst *p*-TSA. A neat reaction mixture of 4-chlorobenzaldehyde, β-naphthol, and dimedone with varying amounts of *p*-TSA was exposed to

Table 1. Synthesis of tetrahydrobenzo[*a*]xanthene-11-ones by condensation of aldehydes, β-naphthol, and dimedone/cyclohexane-1,3-dione

				Method A[a]		Method B[b]			
Entry	Ar	R	Product	Time (h)	Yield (%)	Time (min)	Yield (%)	Mp (°C)	Lit. mp (°C)
1	4-ClC_6H_4	CH_3	**1a**	3	88	5.0	83	184–186	180–182[14]
2	4-BrC_6H_4	CH_3	**1b**	3	89	4.5	84	180–182	183–184[18g]
3	4-FC_6H_4	CH_3	**1c**	3	91	5.5	83	180–182	185–186[14]
4	4-$CH_3OC_6H_4$	CH_3	**1d**	3.5	86	4.0	82	202–204	204–205[14]
5	4-$CH_3C_6H_4$	CH_3	**1e**	3.5	87	4.5	80	174–176	176–178[14]
6	C_6H_5	CH_3	**1f**	3	88	6.0	84	150–152	151–153[14]
7	2,4-$Cl_2C_6H_3$	CH_3	**1g**	3	88	4.5	83	176–178	178–180[14]
8	2-Naphthyl	CH_3	**1h**	3	91	5.0	84	230–232	231–233[15]
9	2-BrC_6H_4	CH_3	**1i**	3	84	4.0	81	166–168	169–170[15]
10	3-BrC_6H_4	CH_3	**1j**	3	89	4.5	82	170–172	169–171[18g]
11	4-$NO_2C_6H_4$	CH_3	**1k**	2.5	90	4.0	85	178–180	178–180[14]
12	4-OH C_6H_4	CH_3	**1l**	3.5	85	5.0	85	210–212	213–214[12]
13	4-ClC_6H_4	H	**1m**	3	89	5.0	84	206–208	208–209[12]
14	C_6H_5	H	**1n**	3	88	5.5	81	204–206	202–203[18g]
15	2-BrC_6H_4	H	**1o**	3	89	5.0	80	234–236	235–237[15]
16	4-$NO_2C_6H_4$	H	**1p**	3	90	4.5	81	240–242	246–247[18g]
17	3-ClC_6H_4	H	**1q**	3	89	5.0	84	204–206	204–206[18g]

[a]Method A: reaction in water under reflux, H_2SO_4 (0.1 mmol).

microwaves (120 °C, 100 W). The best result was obtained using 2 mol% of the catalyst after exposure for 5 min, yielding 83% of the desired xanthene derivative 12-(4-chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-one (**1a**). Greater amount of the catalyst (2.5 mol%) did not aid the reaction significantly, and



Scheme 2. Proposed pathway for the synthesis of **1**.

no reaction was observed in the absence of the catalyst. Also, the reaction of 4-chlorobenzaldehyde and β-naphthol with cyclohexane-1,3-dione under similar conditions yielded 84% of the corresponding xanthene derivative 12-(4-chlorophenyl)-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (**1 m**) in 4.5 min. The generality of the optimized protocol (i.e., catalytic *p*-TSA) under neat conditions with microwave irradiation (method B) was checked by carrying out the reactions of different substituted aromatic aldehydes with β-naphthol and dimedone or cyclohexane-1,3-dione, which yielded the corresponding products in good to excellent yields under these conditions. These results have been compiled in Table 1.

A plausible mechanism for the formation of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one derivatives (**1a–q**) in the presence of acid catalysts is proposed in Scheme 2. Our aim was to strategize the in situ trapping of the *o*-QM intermediate with the carbon nucleophile, a facile synthesis of the desired xanthene derivatives, which was successful under the conditions described.

CONCLUSION

In conclusion, we have reported efficient and environmentally benign methodologies for the synthesis of tetrahydrobenzo[*a*]xanthene-11-ones by using catalytic sulfuric acid in water under reflux and by microwave irradiation under neat conditions in the presence of catalytic *p*-TSA. The methods offer several advantages in terms of operational simplicity, easy workup, short reaction time, and good yields of pure product, thus circumventing the problems posed by previous protocols.

EXPERIMENTAL

The reactions in microwave were carried out on the CEM Discover system (Model No. 908010, manufactured by CEM Company in USA, with vertically focused infrared [IR] temperature control system, maximum microwave power of 300 W, frequency @ 2.455 GHz) in vials (10 mL) sealed with a septum with a stirring option. Melting points were recorded on a Tropical Labequip apparatus and Khera digital melting-point apparatus and are uncorrected. IR spectra were recorded on Perkin-Elmer FTIR-1710 instrument. NMR spectra were recorded on Bruker Avance Spectrospin at 300 MHz and 400 MHz using tetramethylsilane (TMS) as the internal standard. Fast atom bombardment (FAB) mass spectra were recorded on a Jeol SX 102/Da-600 mass spectrometer using argon/xenon as the FAB gas and a KC-455-TOF mass spectrometer (Micromass, Manchester, UK).

Preparation of Compounds 1a–q Under Conventional Heating Conditions (Method A)

A mixture of aldehyde (1.0 mmol), β-naphthol (1.0 mmol), 5,5-dimethyl-1,3-cyclohexanedione (dimedone) or 1,3-cyclohexanedione (1.2 mmol), H_2SO_4(0.1 mmol), and 10 mL of water was stirred magnetically under reflux for appropriate time as mentioned in Table 1. The progress of the reaction was monitored by thin-layer chromatography (TLC) using petroleum ether/ethyl acetate (85:15; v/v) as eluent. After completion of the reaction, the reaction mixture was allowed to cool to room

temperature. The precipitate formed was collected by filtration at pump, washed well with water–ethanol (1:1, v/v), and dried. The crude product was recrystallized from ethanol to yield pure 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-one derivatives. The product was identified by mp, IR, NMR, and mass spectra.

Preparation of Compounds 1a–q Under MW Conditions (Method B)

In a 10-mL vial, aldehyde (1.0 mmol), β-naphthol (1.0 mmol), and dimedone or 1,3-cyclohexanedione (1.2 mmol) were mixed thoroughly and *p*-TSA (2 mol%) was added. The vial was sealed with a cap containing a septum. The loaded vial was then placed into the cavity of the microwave reactor and heated at 100 W and 100 °C for 4–6 min (as indicated by thin-layer chromatography, TLC) (Table 1). The mixture was cooled to room temperature and quenched with 5 mL of water. The precipitate formed was collected by filtration at pump, washed with water–ethanol (1:1 v/v), and dried. The crude product was recrystallized from ethanol to yield pure xanthen-11-one derivative.

Representative Analytical Data

12-(4-Chlorophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-one (1a). White solid, mp 178–180 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.90$ (d, $J = 8.3$ Hz, 1H, Ar), 7.76–7.80 (m, 2H, Ar), 7.36–7.46 (m, 2H, Ar), 7.32 (d, $J = 8.9$ Hz, 1H, Ar), 7.26–7.28 (m, 2H, Ar), 7.12–7.15 (m, 2H, Ar), 5.67 (s, 1H, CH), 2.56 (s, 2H, CH_2), 2.31 (d, $J = 16.3$ Hz, 1H, CH), 2.24 (d, $J = 16.3$ Hz, 1H, CH), 1.12 (s, 3H, CMe), 0.96 (s, 3H, CMe); IR (ν_{max} cm^{-1}) (KBr): 2956, 1648, 1596, 1374, 1224, 1185; MS (ESI): m/z calc. for $C_{25}H_{21}ClO_2$, 388; found (%) = 388 [$(M)^+$, 90], 390 [32].

12-(4-Bromophenyl)-9,9-dimethyl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-one (1b). White solid, mp 183–184 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.89$ (d, $J = 8.3$ Hz, 1H, Ar), 7.76–7.80 (m, 2H, Ar), 7.38–7.45 (m, 2H, Ar), 7.26–7.33 (m, 3H, Ar), 7.20–7.23 (m, 2H, Ar), 5.66 (s, 1H, CH), 2.56 (s, 2H, CH_2), 2.31 (d, $J = 16.3$ Hz, 1H, CH), 2.24 (d, $J = 16.3$ Hz, 1H, CH), 1.12 (s, 3H, CMe), 0.96 (s, 3H, CMe); ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 196.8$, 164.0, 147.7, 143.7, 131.5, 131.3, 131.2, 130.1, 129.1, 128.5, 127.1, 125.0, 123.4, 120.1, 117.0, 116.9, 113.7, 50.8, 41.4, 34.2, 32.2, 29.3, 27.1; IR (ν_{max} cm^{-1}) (KBr): 2955, 1652, 1596, 1373, 1228, 1185; MS (FAB): m/z calc. for $C_{25}H_{21}BrO_2$, 432; found (%) = 433 [$(M + H)^+$, 88], 435 [$(M + 2 + H)^+$, 90].

9,9-Dimethyl-12-(4-methylphenyl)-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-one (1e). White solid, mp 176–178 °C; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.0$ (d, $J = 8.4$ Hz, 1H, Ar), 7.33–7.77 (m, 2H, Ar), 7.40–7.44 (m, 1H, Ar), 7.32–7.37 (m, 2H, Ar), 7.20–7.30 (m, 2H, Ar), 6.96 (d, $J = 8.0$ Hz, 2H, Ar), 5.66 (s, 1H, CH), 2.54 (s, 2H, CH_2), 2.30 (d, $J = 16.2$ Hz, 1H, CH), 2.23 (d, $J = 16.2$ Hz, 1H, CH), 2.19 (s, 3H, CH_3), 1.10 (s, 3H, CMe), 0.98 (s, 3H, CMe); ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 196.8$, 163.7, 147.7, 141.8, 135.6, 131.5, 131.4, 128.9, 128.6, 128.3, 128.2, 126.9, 124.8, 123.6, 117.9, 117.0,114.4, 50.9, 41.4, 34.2, 32.2, 29.2, 27.2, 20.9; IR

(ν_{max} cm^{-1}) (KBr): 2950, 1649, 1597, 1372, 1228, 1185; MS (FAB): m/z calc. for $C_{26}H_{24}O_2$ 368; found (%) = 369 [M + H$^+$, 90].

12-(4-Chlorophenyl)-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (1m). White solid, mp 206–208 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.87$ (d, $J = 7.8$ Hz, 1H, Ar), 7.76–7.79 (m, 2H, Ar), 7.24–7.45 (m, 5H, Ar), 7.13 (d, $J = 8.4$ Hz, 2H, Ar), 5.71 (s, 1H, CH), 2.60–2.79 (m, 2H, CH_2), 2.32–2.51 (m, 2H, CH_2), 1.91–2.12 (m, 2H, CH_2); IR (ν_{max} cm^{-1}) (KBr): 2962, 1647, 1593, 1374, 1231, 1189; MS (ESI): m/z calc. for $C_{23}H_{17}ClO_2$ 360; found (%) = 361 [M + H]$^+$.

12-Phenyl-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (1n). White solid, mp 204–206 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.95$ (d, $J = 8.1$ Hz, 1H, Ar), 7.74–7.78 (m, 2H, Ar), 7.03–7.44 (m, 8H, Ar), 5.73 (s, 1H, CH), 2.59–2.79 (m, 2H, CH_2), 2.31–2.50 (m, 2H, CH_2), 1.91–2.08 (m, 2H, CH_2); IR (ν_{max} cm^{-1}) (KBr): 2955, 1647, 1593, 1372, 1229, 1188; MS (ESI): m/z calc. for $C_{23}H_{18}O_2$ 326; found (%) = 326 [M$^+$, 92].

12-(2-Bromophenyl)-8,9,10,12-tetrahydrobenzo[*a*]xanthen-11-one (1o). White solid, mp 235–237 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.28$ (d, $J = 8.4$ Hz, 1H, Ar), 7.72–7.76 (m, 2H, Ar), 7.34–7.50 (m, 3H, Ar), 7.17–7.30 (m, 2H, Ar), 7.0–7.1 (m, 1H, Ar), 6.89–7.0 (m, 1H, Ar), 5.97 (s, 1H, CH), 2.53–2.83 (m, 2H, CH_2), 2.23–2.46 (m, 2H, CH_2), 1.93–2.16 (m, 2H, CH_2); ^{13}C NMR (300 MHz, $CDCl_3$): $\delta = 196.8$, 165.7, 147.5, 144.1, 133.3, 131.8, 131.7, 131.3, 129.1, 128.3, 127.8, 127.6, 127.0, 124.9, 123.4, 117.8, 115.0, 37.1, 35.3, 27.8, 20.3; IR (ν_{max} cm^{-1}) (KBr): 2957, 1652, 1595, 1371, 1227, 1189; MS (FAB): m/z calc. for $C_{23}H_{17}BrO_2$ 404; found (%) = 405 [(M + H)$^+$, 99], 407 [(M + 2 + H)$^+$, 99].

ACKNOWLEDGMENTS

A. L. thanks the University of Delhi for the award of UTA and D. M. thanks the Council for Scientific and Industrial Research, New Delhi, India, for the grant of junior and senior research fellowships.

REFERENCES

1. Neckers, D. C.; Valdes-Aguilera, O. M. Photochemistry of the xanthene dyes. *Adv. Photochem.* **1993**, *18*, 315–394.
2. Banerjee, A.; Mukherjee, A. K. Chemical aspects of santalin as a histological stain. *Stain Technol.* **1981**, *56*, 83–85.
3. Heitz, J. R. Pesticidal applications of halogenated xanthene dyes. *Phytoparasitica* **1997**, *25*, 89–92.
4. Knight, C. G.; Stephens, T. Xanthene-dye-labelled phosphatidylethanolamines as probes of interfacial pH studies in phospholipid vesicles. *Biochem. J.* **1989**, *258*, 683–687.
5. Rossi, F. M.; Kao, J. P. Y. Practical method for the multigram separation of the 5- and 6-isomers of carboxyfluorescein. *Bioconjugate Chem.* **1997**, *8*, 495–497.
6. Noelting, E.; Dziewoński, K. Zur Kenntniss der Rhodamine. *Chem. Ber.* **1905**, *38*, 3516–3527.
7. Monroe, B. M.; Weed, G. C. Photoinitiators for free-radical-initiated photoimaging systems. *Chem. Rev.* **1993**, *93*, 435–448.

8. Manivannan, G.; Leelere, P.; Semal, S.; Changkakoti, R.; Renotte, Y.; Lion, Y.; Lessard, R. A. Photobleaching of xanthene dyes in a poly(vinyl alcohol) matrix. *Appl. Phys. B* **1994**, *58*, 73–77.
9. Hideo, T.; Teruomi, J. (Sankyo Co.) Benzopyrano[2,3-*b*]xanthene derivatives. Jpn Patent 56005480, 1981.
10. Poupelin, J. P.; Saint-Ruf, G.; Foussard-Blanpin, O.; Marcisse, G.; Uchida-Ernouf, G.; Lacroix, R. Synthesis and anti-inflammatory properties of bis(2-hydroxy-1-naphthyl)-methane derivatives, 1: Monosubtituted derivatives. *Eur. J. Med. Chem.* **1978**, *13*, 67–71.
11. Lambert, R. W.; Martin, J. A.; Merrett, J. H.; Parkes, K. E. B.; Thomas, G. J. Preparation of pyrimidine nucleosides as thymidine kinase inhibitors and virucides. PCT International. Appl. WO Patent 9706178, 1997.
12. Li, J.; Tang, W.; Lu, L.; Su, W. Strontium triflate–catalysed one-pot condensation of β-naphthol, aldehydes, and cyclic 1,3-dicarbonyl compounds. *Tetrahedron Lett.* **2008**, *49*, 7117–7120.
13. Das, B.; Laxminarayana, K.; Krishnaiah, M.; Srinivas, Y. An efficient and convenient protocol for the synthesis of novel 12-aryl- or 12-alkyl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-one derivatives. *Synlett* **2007**, 3107–3112.
14. Nandi, G. C.; Samai, S.; Kumar, R.; Singh, M. S. An efficient one-pot synthesis of tetrahydrobenzo[*a*]xanthene-11-one and diazabenzo[*a*]anthracene-9,11-dione derivatives under solvent-free condition. *Tetrahedron* **2009**, *65*, 7129–7134.
15. Gao, S.; Tsai, C. H.; Yao, C.-F. A simple and green approach for the synthesis of tetrahydrobenzo[*a*]xanthene-11-one derivatives using tetrabutyl ammonium fluoride in water. *Synlett.* **2009**, 949–954.
16. (a) Lindstorm, U. M. Stereoselective organic reactions in water. *Chem. Rev.* **2002**, *102*, 2751–2722; (b) Li, C. J.; Chen, L. Organic chemistry in water. *Chem. Soc. Rev.* **2006**, *35*, 68–82; (c) Dallinger, D.; Kappe, C. O. Microwave-assisted synthesis in water as solvent. *Chem. Rev.* **2007**, *107*, 2563–2591.
17. Gupta, M.; Paul, S.; Gupta, R. General characteristics and applications of microwaves in organic synthesis. *Acta Chim. Slov.* **2009**, *56*, 749–764.
18. (a) Khurana, J. M.; Kukreja, G.; Bansal, G. Desulfurization of thioureas, benzimidazoline-2-thiones, and 1,3-dihydro-1,3-diaryle-2-thioxopyrimidine-4,6(2*H*,5*H*)-diones with nickel boride at ambient temparature. *J. Chem. Soc. Perkin Trans. 1* **2002**, 2520–2524; (b) Khurana, J. M.; Kukreja, G. Nickel boride–mediated reductive desulfurization of 2-thioxo-4(3*H*)-quinazolinones: A new synthesis of quinazolin-4(3*H*)-ones and 2,3-dihydro-4(1*H*)-quinazolinones. *J. Heterocycl. Chem.* **2003**, *40*, 677–679; (c) Khurana, J. M.; Agrawal, A.; Kukreja, G. A novel two-step synthesis of 3,4-dihydro-4-oxo-5*H*-pyrano[2,3-*d*]pyrimidines. *Heterocycles* **2006**, *68*, 1885–1892; (d) Khurana, J. M.; Arora, R.; Satija, S. 7,11-Diaryl-2,4-diazospiro[5.5]undecane-1,5,9-triones: A new series of spiroheterocycles. *Heterocycles* **2007**, *71*, 2709–2716; (e) Khurana, J. M.; Sharma, V. A novel synthesis of 2-substitued 2*H*-imidazo[1,5-*b*]isoquinoline-1,5-diones by in situ desulfurization. *Chem. Heterocycl. Compd.* **2008**, *44*, 309–313; (f) Khurana, J. M.; Kumar, S. Tetrabutylammonium bromide (TBAB): A neutral and efficient catalyst for the synthesis of biscoumarin and 3,4-dihydropyrano[*c*]chromene derivatives in water and solvent-free conditions. *Tetrahedron Lett.* **2009**, *50*, 4125–4127; (g) Khurana, J. M.; Magoo, D. pTSA-catalysed one-pot synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-ones in ionic liquid and neat conditions. *Tetrahedron Lett.* **2009**, *50*, 4777–4780; (h) Khurana, J. M.; Magoo, D. Efficient one-pot syntheses of 2*H*-indazolo[2,1-*b*]phthalazine-triones by catalytic H_2SO_4 in water–ethanol or ionic liquid. *Tetrahedron Lett.* **2009**, *50*, 7300–7303.