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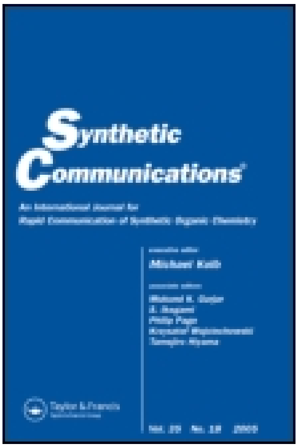

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Aldonitrones as Aldehyde Equivalents: An Efficient, Green, and Novel Protocol for the Synthesis of 1,8-Dioxo-octahydroxanthenes

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ALDONITRONES AS ALDEHYDE EQUIVALENTS: AN EFFICIENT, GREEN, AND NOVEL PROTOCOL FOR THE SYNTHESIS OF 1,8-DIOXO-OCTAHYDROXANTHENES

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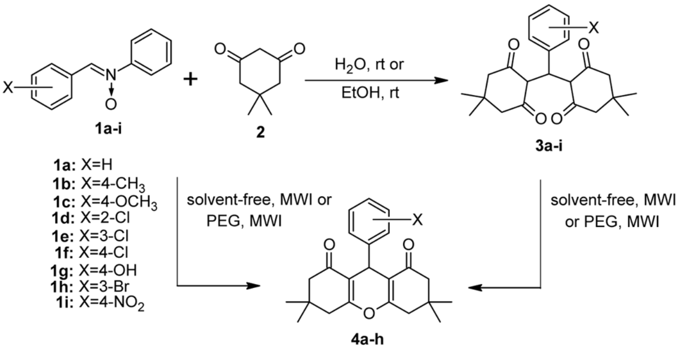
GRAPHICAL ABSTRACT



Abstract *A novel, self-catalyzed, solvent-free, microwave-enhanced, green, and efficient protocol for the synthesis of 1,8-dioxo-octahydroxanthenes and bis-5,5-dimethyl-1,3-cyclohexanediones by condensing aldo-nitrones (imine oxide) and dimedone (5,5-dimethyl-1,3-cyclohexanedione) under microwave irradiation is disclosed. Product formation (viz. xanthenes and bis-5,5-dimethyl-1,3-cyclohexanediones) is dependent on reaction conditions. The entire process is green and sustainable in terms of solvents, chemicals, reaction procedure, and yields. A plausible reaction mechanism of this reaction is also proposed.*

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Keywords Bis-5,5-dimethyl-1,3-cyclohexanediones; dimedone (5,5-dimethyl-1,3-cyclohexanedione); 1,8-dioxo-octahydroxanthenes; microwave irradiation (MWI); nitrones; solvent-free

INTRODUCTION

Nitrones (imine oxides) are reputed 1,3-dipoles and have been extensively explored for the synthesis of five-membered heterocycles by combining them with several types of multiple bonds.[1] Apart from this major utility, their general

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chemistry has been little studied.[1c] There are few reports of successful 1,3-additions of nitrones.[2] In contrast, their counterpart imines have been extensively explored to expose their utility as aldehyde equivalent.[3]

Within oxygen heterocycles, xanthenes gained much attention because of their numerous applications in medicinal chemistry and material science such as antiviral,[4] antibacterial,[5] and anti-inflammatory activities.[6] They also act as sensitizers in photodynamic therapy (PDT) for destroying the tumor cells.[7] Xanthenes are further used in the dye industry,[8] as antagonists for the paralyzing action of zoxazolamine,[9] as pH-sensitive fluorescent materials for visualization of biomolecules,[10] in biodegradable agrochemicals,[11] in cosmetics and pigments,[12] and in laser technology because of their spectroscopic properties.[13] Furthermore, xanthenes-based dyes are extracted naturally from soil and from plants such as *Indigofera longeracemosa.*[14]

Because of these extensive utilities of these molecules, the search for efficient, facile synthesis of these molecules continues to attract much attention, and to achieve this goal several catalysts have been used, such as Yb(PFO)$_3$,[15] SmCl$_3$,[16] p-dodecylbenzenesulfonic acid,[17] para-toluencesulfonic acid (pTSA),[18] methanesulfonic acid,[19] sulfamic acid,[20] Amberlyst-15,[21] NaHSO$_4$SiO$_2$ or WO$_3$/ZrO$_2$,[22] diammoniumhydrogen phosphate,[23] HClO$_4$-SiO$_2$,[24] HClO$_4$-SiO$_2$ and PPA-SiO$_2$,[25] Yb(OTf)$_3$,[26] InCl$_3 \cdot 4H_2O$,[27] silica-bonded N-propyl sulfamic acid (SBNPSA),[28] β-cyclodextrin,[29] Dowex 50w,[30] cyanuric chloride,[31] polyaniline-p-toluenesulfonate,[32] ZrOCl$_2 \cdot 8H_2O$,[33] H$_3$PW$_{12}$O$_{40}$,[34] proline triflate,[35] LiBr,[36]TiO$_2$/SO$_4^{2-}$,[37] ionic liquids,[38] and ultrasound irradiation[39]. Some of these already reported procedures are not very efficient, require expensive catalyst and harsh reaction conditions, and leave harmful waste on workup. There is still scope for development of a green, sustainable process.

The present protocol is the first ever use of aldo-nitrones for the preparation of 1,8-dioxo-octahydroxanthenes and bis-5,5-dimethyl-1,3-cyclohexanediones using various environmentally benign reaction conditions. This reaction plausibly proceeds via addition–elimination pathway followed by cyclization to afford the desired products in very good to excellent yields.

RESULTS AND DISCUSSION

Initially, a series of nitrones was prepared using a variety of aldehydes and hydroxyl amine as per already reported methods.[40] A mixture of freshly prepared N-phenyl-N-phenylmethylidenamine oxide (10 mmol) **1a** and 5,5-dimethyl-1,3-cyclohexanedione (20 mmol) **2** was stirred under different reaction conditions (Table 1). In the absence of solvents, the reaction did not proceed up to 15 h (Table 1, entry 1). Among solvents, distilled water and ethyl alcohol only accelerated the reaction in a minimum reaction time at ambient temperature (Table 1, entry 4,5) and afforded **3a** in 86 and 90% yields respectively. Under these reaction conditions, only bis-5,5-dimethyl-1,3-cyclohexanedione products were obtained (Table 2) instead of cyclized product **4** (Scheme 1).

Following the same reaction procedure, a variety of nitrones **1a–i** were reacted with 5,5-dimethyl-1,3-cyclohexanedione in water and EtOH at ambient temperature with similar success. Nitrones bearing electron-withdrawing **1d–f, 1h–i** and donating

Table 1. Reaction of **1a** and **2** under different solvents[a]

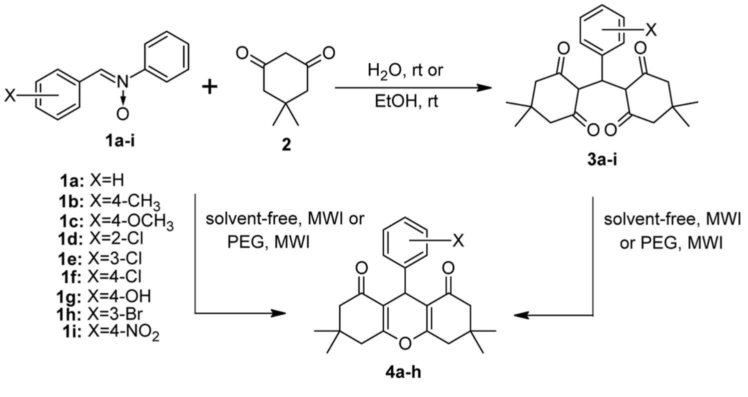
Entry	Solvent	Time (h)	Yield (%)
1	No solvent	15	–
2	EtOAc	9	56
3	PEG	5	45
4	H_2O	3	86
5	EtOH	1	90
6	$CHCl_3$	14	39
7	Toluene	13	12

[a] Reaction conditions: **1** (10 mmol), **2** (20 mmol), and solvent (10 mL) stirred at rt. PEG stands for polyethylene glycol.

Table 2. Synthesis of bis-5,5-dimethyl-1,3-cyclohexanedione **3a–i** at ambient temperature

			Time (h)		Yield (%)		
Entry	Aldo-nitrone	Product[a]	A	B	A	B	Melting point (°C)
1	**1a**	**3a**	3.0	1.0	86	90	192–194[25]
2	**1b**	**3b**	4.0	1.5	88	91	139–141[16]
3	**1c**	**3c**	4.5	2.0	85	88	146–148[25]
4	**1d**	**3d**	3.5	1.5	85	90	196–197[36d]
5	**1e**	**3e**	3.5	1.5	87	92	185–187[25]
6	**1f**	**3f**	3.0	1.0	91	93	143–144[36d]
7	**1g**	**3g**	4.5	2.0	86	91	188–190[16]
8	**1h**	**3h**	3.0	2.0	89	90	203–204[37]
9	**1i**	**3i**	4.0	2.0	88	90	188–190[25]

[a] The products were characterized by comparison of their melting points and spectral (IR, ^1H NMR) data with those of authentic samples. A and B stand for reaction conditions H_2O, rt and EtOH, rt, respectively.



Scheme 1. Synthesis of xanthenes **4a–h** and bis-5,5-dimethyl-1,3-cyclohexanediones **3a–i**.

Table 3. Effects of solvent variations under MWI[a]

Entry	Solvent	Time (min)	Yield **4a** (%)
1	Solvent free	2.0	84
2	H_2O	2.0	82
3	H_2O–EtOH (50:50)	2.0	80
4	PEG	0.5	89
5	PEG–H_2O (50:50)	2.0	84

[a] Reaction conditions: A mixture of **1** (10 mmol), **2** (20 mmol), and solvent (5 mL) was irradiated under MWI.

group **1b–c** on the aldehyde ring did not have significant effect either on rate of reaction or on yields of bis-products **3a–i** (Table 2).

Further, the same reaction was investigated under microwave irradiations (Prolabo Microwave Module Synthwave S-402) using different reaction conditions (Table 3). Interestingly, in all cases reaction of N-phenyl-N-phenylmethylidenamine oxide **1** and 5,5-dimethyl-1,3-cyclohexanedione **2** under microwave irradiations (Scheme 1) afforded only 1,8-dioxo-octahydroxanthenes **4a–h**, in almost comparable yields and reaction time (Table 3).

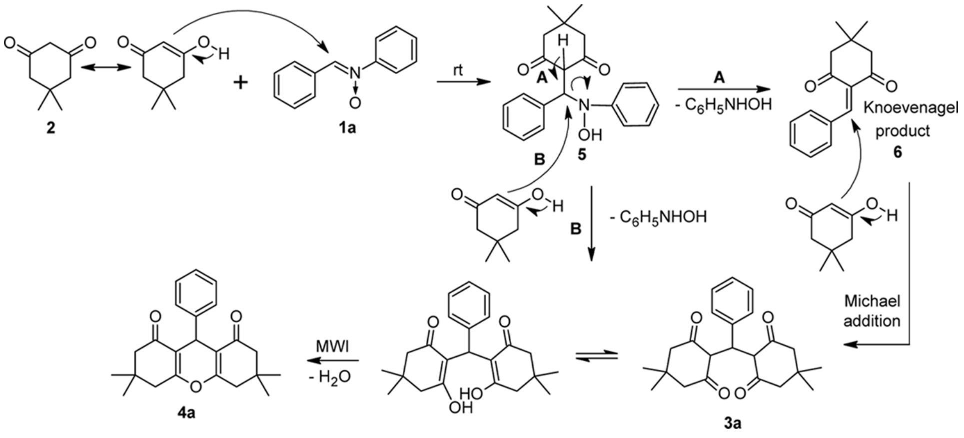
As per current awareness of green and sustainable chemistry, reaction conditions were optimized as condensation of N-phenyl-N-phenylmethylidenamine oxide **1a** and 5,5-dimethyl-1,3-cyclohexanedione **2** was carried out under microwave irradiations without any solvent or catalyst to afford product **4a** in a fraction of a minute (Table 4). This procedure is fairly large in scope and is extendable to several nitrones **1b–i** to obtain xanthenes **4a–h** (for other details, see Table 4).

In further study of this investigation, when bis-5,5-dimethyl-1,3-cyclo hexanediones **3a–h** were subjected to microwave irradiations for 1–2 min in the presence of polyethylene glycol and solvent-free conditions, cyclized products were obtained **4a–h** in good to excellent yields.

Table 4. Synthesis of 1,8-dioxo-octahydroxanthenes under MWI

			Time (min)		Yield %		
Entry	Aldo-nitrone	Product[a]	A	B	A	B	Melting point (°C)
1	**1a**	**4a**	2.0	0.5	84	89	205–206[37a]
2	**1b**	**4b**	2.5	1.0	86	90	216–217[37a]
3	**1c**	**4c**	3.0	1.5	84	88	241–243[37a]
4	**1d**	**4d**	2.0	0.5	88	92	226–228[37a]
5	**1e**	**4e**	2.0	0.5	86	91	190–192[25]
6	**1f**	**4f**	2.0	1.0	87	92	230–233[33]
7	**1g**	**4g**	2.5	1.0	87	91	246–248[37a]
8	**1i**	**4h**	3.0	1.5	85	90	221–223[37a]

[a] The products were characterized by comparison of their melting points and spectral (IR, ^{1}H NMR) data with those of authentic samples. A and B stand for reaction conditions solvent-free, MWI and PEG, MWI, respectively.



Scheme 2. Plausible reaction mechanism for the syntheses of **3a–i** and **4a–h**.

A plausible mechanism for this reaction could be via nucleophilic attack of **2** onto electron-deficient imino carbon of nitrone **1**, yielding intermediate **5**, which after elimination can follow two routes (as shown in Scheme 2). This unstable intermediate can adopt two routes, **A** and **B**. In route **A** the Knoevenagel product of 5,5-dimethyl-1,3-cyclohexanedione (viz., 2-benzylidene-5,5-dimethylcyclohexane-1,3-dione **6**) is formed via a simple addition–elimination reaction, in which one molecule of **2** adds to aldehydic carbon of nitrone **1** with elimination of phenlhydroxylamine followed by nucleophilic addition of a second molecule of **2** in a Michael way to afford **3a** (Scheme 2). In route **B**, without the formation of any Knoevenagel product **6**, nucleophilic addition of the second molecule of **2** occurs on intermediate **5**, followed by elimination of phenylhydroxylamine to afford **3a**, Which undergoes dehydration under microwave heating to afford **4a** (Scheme 2).

Overall, this reaction seems to be self-catalyzed as nitrones are highly polar. Facile addition of dimedone could take place on these with concommittant elimination of phenlhydroxylamine. In this sequence, one can presume that either basicity of the eliminated base or acidity of the dimidione is responsible for the autocatalysis.

CONCLUSION

In summary, the present protocol is an efficient, green, sustainable, convenient, and mild strategy for the synthesis of 1,8-dioxo-octahydroxanthenes and bis-5,5--dimethly-1,3-cyclohexanedione derivatives. The method reported herein, in contrast to earlier ones, does not employ any toxic or expensive catalysts or stringent reaction conditions and is free of any corrosive or unwanted by-products. Desired products are obtained in very good to excellent yields.

EXPERIMENTAL

Melting points were determined in open capillaries and are uncorrected. Reagent-grade chemicals were purchased from a commercial source and used without further purification. The reactions were carried out in Prolabo Microwave Module Synthwave S-402 (preliminary experiments were carried out in a domestic microwave oven). Infrared (IR) spectra were recorded in KBr discs on a Perkin-Elmer 240C analyzer. ^{1}H NMR spectra were recorded on a Bruker Avance II 400 NMR spectrometer using tetramethylsilane (TMS) as internal standard. Elemental analysis were recorded on a Vario Micro V1.9.6 analyzer. The progress of the reaction was monitored by thin-layer chromatography (TLC) using silica gel G (Merck).

Typical General Methods

Synthesis of bis-5,5-dimethyl-1,3-cyclohexanedione (3a–i). A mixture of nitrone (10 mmol) **1**, 5,5-dimethyl-1,3-cyclo-hexandione (20 mmol) **2**, and distilled water (10 ml) or ethyl alcohol (10 ml) was stirred at ambient temperature for an appropriate time (see Table 2). Reaction progress was monitored via TLC. After reaction completion, the crude product was precipitated out in aqueous media and in ethyl alcohol precipitates formed on addition of cold water. The obtained product was filtered, dried, and (for further purification) recrystallized from ethanol.

Synthesis of 1,8-dioxo-octahydroxanthenes (4a–h). A mixed reaction mixture of nitrone (10 mmol) and 5,5-dimethyl-1,3-cyclo-hexandione (20 mmol) using solvent-free or polyethylene glycol (5 mL) was irradiated in an Erlenmeyer flask under microwave irradiations for an appropriate time (see Table 4). Reaction progress was monitored via TLC. After reaction completion, the reaction mass was cooled and stirred with cold water (10 mL) for 15 min. The obtained product was filtered, dried, and (for further purification) recrystallized from ethanol.

Representative Spectral Data

Compound 3a. IR (KBr): 3063, 2962, 1593, 1448, 1372 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 11.90 (s, 1H, OH), 11.59 (s, 1H, OH), 7.28–7.10 (m, 5H, ArH), 5.54 (s, 1H, CH), 2.48–2.17 (m, 8H, 4 CH_2), 1.26 (s, 6H, 2 CH_3), 1.10 (s, 6H, 2 CH_3). Anal. calcd. for $C_{23}H_{28}O_4$: C,74.97; H, 7.66. Found: C, 75.01 H, 7.60.

Compound 4a. IR (KBr): 3312, 2957, 1662, 1626, 1466, 1362 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29–7.26 (m, 2H, ArH), 7.23–7.19 (m, 2H, ArH), 7.11–7.07 (m, 1H, ArH), 4.74 (s, 1H, CH), 2.46 (s, 4H, 2 CH_2), 2.25–2.21 (d, 2H, CH_2), 2.18–2.14 (d, 2H, CH_2) 1.10 (s, 6H, 2 CH_3), 0.98 (s, 6H, 2 CH_3). Anal. calcd. for $C_{23}H_{26}O_3$: C, 78.83; H, 7.48. Found: C, 78.99 H, 7.31.

Supporting Information

Full experimental details, IR, ^{1}H NMR, and elemental analyses with literature references for all compounds are provided online.

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REFERENCES

1. (a) Padwa, A. (Ed.). *1,3-Dipolar Cycloaddition Chemistry*; Wiley-Interscience: New York, 1984; (b) Torssell, K. B. G. *Nitrile Oxides, Nitrones, and Nitronate in Organic Synthesis*; VCH: New York, 1988; (c) Banerji, A.; Sengupta, P. Recent studies on 1,3-dipolar cycloadditions of nitrones. *J. Ind. Inst. Sci.* **2001**, *81*, 313.
2. (a)Okino, T.; Hoashi, Y.; Takemoto, Y. Thiourea-catalyzed nucleophilic addition of TMSCN and ketene silyl acetals to nitrones and aldehydes. *Tetrahedron Lett.* **2003**, *44*, 2817–2821; (b) Murahashi, S.-I.; Imada, Y.; Kawakami, T.; Harada, K.; Yonemushi, Y.; Tomita, N. Enantioselective addition of ketene silyl acetals to nitrones catalyzed by chiral titanium complexes: Synthesis of optically active α-amino acids. *J. Am. Chem. Soc.* **2002**, *124*, 2888.
3. (a) Chiba, R.; Oriyama, T. A highly stereoselective Knoevenagel reaction of *N*-tosylimines with active methylene compounds in DMSO. *Chem. Lett.* **2008**, *37*, 1918–1219; (b)Mekheimer, R. A.; Al-Zaydi, K. M.; Al-Shamary, A.; Sadek, K. U. Solar thermochemical reactions IV: Unusual reaction of nitrones with acetonitrile derivatives induced by solar thermal energy. *Green Sustainable Chem.* **2011**, *1*, 176–181; (c)Patai, S. *The Chemistry of the Carbon-Nitrogen Double Bond;* London: Interscience, 1970.
4. Andrieux, B. J.; Plat, M. New total synthesis of bikaverin. *Tetrahedron Lett.* **1992**, *33*, 2805–2806.
5. Chatterjee, S.; Iqbal, M.; Kauer, J. C.; Mallamo, J. P.; Senadhi, S.; Mallya, S.; Bozyczko-Coyne, D.; Siman, R. Xanthene derived potent nonpeptidic inhibitors of recombinant human calpain I. *Bioorg. Med. Chem. Lett.* **1996**, *6*, 1619–1622.
6. Chibale, K.; Visser, M.; Schalkwyk, D. V.; Smith, P. J.; Saravanamuthu, A.; Fairlamb, A. H. Exploring the potential of xanthene derivatives as trypanothione reductase inhibitors and chloroquine potentiating agents. *Tetrahedron* **2003**, *59*, 2289–2296.
7. Zarei, A.; Hajipour, A. R.; Khazdooz, L. The one-pot synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a,j*]xanthenes catalyzed by P_2O_5/Al_2O_3 under microwave irradiation. *Dyes Pigm.* **2010**, *85*, 133–138.
8. Banerjee, A.; Mukherjee, A. K. Chemical aspects of santalin as a histological stain. *Stain Technol.* **1981**, *56*, 83–85.
9. Saint-Ruf, G.; Hieu, H. T.; Poupelin, J. P. The effect of dibenzoxanthenes on the paralyzing action of zoxazolamine. *Naturwissenschaften* **1975**, *62*, 584–585.
10. Knight, C. G.; Stephenes, T. Xanthene-dye-labelled phosphatidylethanolamines as probes of interfacial pH: Studies in phospholipid vesicles. *Biochem. J.* **1989**, *258*, 683–687.
11. (a) Hafez, E. A. A.; Elnagdi, M. H.; Elagamey, A. G. A.; El-Taweel, F. M. A. A. Nitriles in heterocyclic synthesis: Novel synthesis of benzo[c]coumarin and of benzo[c]pyrano[3,2-c]quinoline derivatives. *Heterocycles* **1987**, *26*, 903; (b) Abdel-Galil, F. M.; Raid, B. Y.; Sherif, S. M.; Elnagdi, M. H. Activated nitriles in heterocyclic synthesis: A novel synthesis of 4-azoloyl-2-aminoquinolines. *Chem. Lett.* **1982**, 1123–1126.
12. Ellis, G. P. The chemistry of heterocyclic compounds. In *Chromenne, Chromanes, and Chromone*, vol. 2; A. Wessberger, and E. C. E. Taylor (Eds.) John Wiley: New York, 1977; pp. 13.
13. Dabiri, M.; Baghbanzadeh, M.; Nikcheh, M. S.; Arzroomchilar, E. Eco-friendly and efficient one-pot synthesis of alkyl- or aryl-14*H*-dibenzo[*a,j*]xanthenes in water. *Bioorg. Med. Chem. Lett.* **2008**, *18*, 436–438.

14. Licudine, P. J. A.; Kawate, M. K.; Li, Q. X. Method for the analysis of phloxine B, uranine, and related xanthene dyes in soil using supercritical fluid extraction and high-performance liquid chromatography. *J. Agric. Food Chem.* **1997**, *45*, 766–773.
15. Sundar, C. S.; Rao, K. U. M.; Reddy, N. B.; Reddy, M. V. N.; Prasad, S. S.; Reddy, C. S. Ytterbium perfluorooctanoate [Yb(PFO)$_3$]: A novel and efficient catalyst for the synthesis of tetrahydrobenzo[a]xanthene-11-ones under microwave irradiation. *Catal. Sci. Technol.* **2012**, *2*, 1382–1385.
16. Ilangovan, A.; Malayappasamy, S.; Muralidharan, S.; Maruthamuthu, S. A highly efficient green synthesis of 1, 8-dioxooctahydroxanthenes. *Chem. Centr. J.* **2011**, *5*, 81.
17. Jin, T. S.; Zang, J. S.; Xiao, J. C.; Wang, A. Q.; Li, T. S. Clean synthesis of 1,8-dioxooctahydroxanthene derivatives catalyzed by *p*-dodecyl benezenesulfonic acid in aqueous media. *Synlett* **2004**, 866–870.
18. Khosropour, A. R.; Khodaei, M. M.; Moghannian, H. A facile, simple, and convenient method for the synthesis of 14-alkyl or aryl-14-*H*-dibenzo[a,j]xanthenes catalyzed by *p*TSA in solution and solvent-free conditions. *Synlett* 2005, 955–958.
19. Bhattacharya, A. K.; Rana, K. C. Microwave-assisted synthesis of 14-aryl-14-*H*-dibenzo[a.j]xanthenes catalyzed by methanesulphonic acid under solvent-free condition. *Mendeleev Commun.* **2007**, *17*, 247–248.
20. Rajitha, B.; Kumar, B. S.; Reddy, Y. T. Sulfamic acid: A novel and efficient catalyst for the synthesis of aryl 14H dibenzo[a.j]xanthenes under conventional heating and microwave irradiation. *Tetrahedron Lett.* **2005**, *46*, 8691–8693.
21. Das, B.; Thirupathi, P.; Mahender, I. Amberlyst-15: An efficient reusable heterogeneous catalyst for the synthesis of 1,8-dioxooctahydroxanthenes and 1,8-dioxo-decahydroacridines. *J. Mol. Catal. A: Chem.* **2006**, *247*, 233–239.
22. Nagarapu, L.; Baseeruddin, M.; Kumari, N. V. Efficient synthesis of aryl 14-H dibenzo[a.j]xanthenes using $NaHSO_4SiO_2$ or 5% WO_3/ZrO_2 as heterogeneous catalysts under conventional heating in a solvent-free media. *Synth. Commun.* **2007**, *37*, 2519–2525.
23. Darviche, F.; Balalaie, S.; Chadegani, F. Diammonium hydrogen phosphate as a neutral and efficient catalyst for synthesis of 1,8-dioxooctahydroxanthene derivatives in aqueous media. *Synth. Commun.* **2007**, *37*, 1059–1066.
24. Bigdeli, M. A.; Heravi, M. M.; Mahdavinia, G. H. Silica-supported perchloric acid ($HClO_4$-SiO_2): A mild, reusable, and highly efficient heterogeneous catalyst for the synthesis of 14-aryl or alkyl-14-*H*-dibenzo[a, j]xanthenes. *J. Mol. Catal. A: Chem.* **2007**, *275*, 25–29.
25. Kantevari, S.; Bantu, R.; Nagarapu, L. $HClO_4$-SiO_2- and PPA-SiO_2-catalyzed efficient one-pot Knoevenagel condensation, Michael addition, and cyclodehydration of dimedone and aldehydes in acetonitrile, aqueous, and solvent-free conditions: Scope and limitations. *J. Mol. Catal. A: Chem.* **2007**, *269*, 53–57.
26. Su, W.; Yang, D.; Jin, C. Yb(OTf)$_3$-catalyzed condensation reaction of β-naphthol and aldehyde in ionic liquids: A green synthesis of aryl-14H-dibenzo[a,j]xanthenes. *Tetrahedron Lett.* **2008**, *49*, 3391–3394.
27. Fan, X. S.; Li, Y. Z.; Zhang, X. Y. $InCl_3 \cdot 4H_2O$-promoted green preparation of xanthenedione derivatives in ionic liquids. *Can. J. Chem.* **2005**, *83*, 16–20.
28. Rashedian, F.; Saberi, D.; Niknam, K. Silica-bonded N-propyl sulfamic acid: A recyclable catalyst for the synthesis of 1,8-dioxo-decahydroacridines, 1,8-dioxo-octahydroxanthenes, and quinoxalines. *J. Chin. Chem. Soc.* **2010**, *57*, 998.
29. Kokkirala, S.; Sabbavarapu, N. M.; Yadavalli, V. D. N. β-Cyclodextrin-mediated synthesis of 1,8-dioxooctahydroxanthenes in water. *Eur. J. Chem.* **2011**, *2*, 272–275.
30. Shakibaei, G. I.; Mirzaei, P.; Bazgir, A. Dowex-50 W-promoted synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthene and 1,8-dioxo-octahydroxanthene derivatives under solvent-free conditions. *Appl. Catal. A: Gen.* **2007**, *325*, 188–192.

31. Zhang, Z. H.; Tao, X. Y. 2,4,6-trichloro-1,3,5-triazine-promoted synthesis of 1,8-dioxo-octahydroxanthenes under solvent-free conditions. *Aus. J. Chem.* **2008**, *61*, 77–79.
32. John, A.; Yadav, P.; J. P.; Palaniappan, S. Clean synthesis of 1,8-dioxo-dodeca hydroxanthene derivatives catalyzed by polyaniline-*p*-toluenesulfonate salt in aqueous media. *J. Mol. Catal. A: Chem.* **2006**, *248*, 121–125.
33. Lu, H. Y.; Li, J. J.; Zhang, Z. H. $ZrOCl_2.8H_2O$ a highly efficient catalyst for the synthesis of 1,8-dioxo-octahydroxanthene derivatives under solvent- free conditions. *Appl. Organometal. Chem.* **2009**, *23*, 165–169.
34. Karthikeyana, G.; Pandurangana, A. Heteropolyacid ($H_3PW_{12}O_{40}$) supported MCM-41: An efficient solid acid catalyst for the green synthesis of xanthenedione derivatives. *J. Mol. Catal. A: Chem.* **2009**, *311*, 36–45.
35. Li, J.; Lu, L.; Su, W. A new strategy for the synthesis of benzoxanthenes catalyzed by proline triflate in water. *Tetrahedron Lett.* **2010**, *51*, 2434–2437.
36. Kumar, D.; Sandhu, J. S. Efficient, solvent-free, microwave-enhanced Condensation of 5,5-dimethyl-1,3-cyclohexanedione with aldehydes and Imines using LiBr as inexpensive, mild catalyst. *Synth. Commun.* **2010**, *40*, 510–517.
37. Jin, T.-S.; Zhang, J.-S.; Wang, A.-Q.; Li, T.-S. Solid-state condensation reactions between aldehydes and 5,5-dimethyl-1,3-cyclohexanedione by grinding at room temperature. *Synth. Commun.* **2005**, *35*, 2339–2345.
38. (a) Kang, H.; Hu, Y.; Huang, H.; Wei, P. Condensation of 1,3-cyclohexanedione with aromatic aldehydes catalyzed by acidic ionic liquids. *Heterocycl. Commun.* **2008**, *14*, 223–227; (b) Ma, J. J.; Wang, C.; Wu, Q. H.; Tang, R. X.; Liu, H. Y.; Li, Q. An efficient green synthesis of xanthenedione derivatives promoted by acidic ionic liquid. *Heteroatom. Chem.* **2008**, *19*, 609–611; (c) Fang, D.; Gong, K.; Liu, Z. L. Synthesis of 1,8-dioxo-octa hydroxanthenes catalyzed by acidic ionic liquids in aqueous media. *Catal. Lett.* **2009**, *127*, 291–295; (d) Suresh; Kumar, D.; Sandhu, J. S. An efficient green protocol for the production of 1,8-dioxo-octahydroxanthenes in Triethylammonium acetate (TEAA) a recyclable Inexpensive ionic liquid. *Rasayan. J. Chem.* **2009**, *2*, 937–940.
39. (a) Venkatesan, K.; Pujari, S. S.; Lahoti, R. J. An efficient synthesis of 1,8-dioxoocta hydro-xanthene derivatives promoted by a room temperature ionic liquid at ambient conditions under ultrasound irradiation. *Ultrason. Sonochem.* **2008**, *15*, 548–553; (b) Sudha, S.; Pasha, M. A. Ultrasound assisted synthesis of tetrahydrobenzo[c]xanthene-11-ones using CAN as catalyst. *Ultrason. Sonochem.* **2012**, *19*, 994–998.
40. Hamer, J.; Macaluso, A. Nitrones. *Chem. Rev.* **1964**, 473–495.