

A Novel Green Synthesis of 1, 8-Dioxo-Octahydro Xanthenes by Using Ionic Liquid

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Abstract:

By using ionic liquid as a solvent synthesis of 1, 8-dioxo-octahydro Xanthenes derivatives having so many special advantages as environmental friendly, very easy to work up and gives good yield.

Keywords: Dimedone, 1, 8-dioxo-octahydro Xanthenes, ionic liquid, aldehydes.

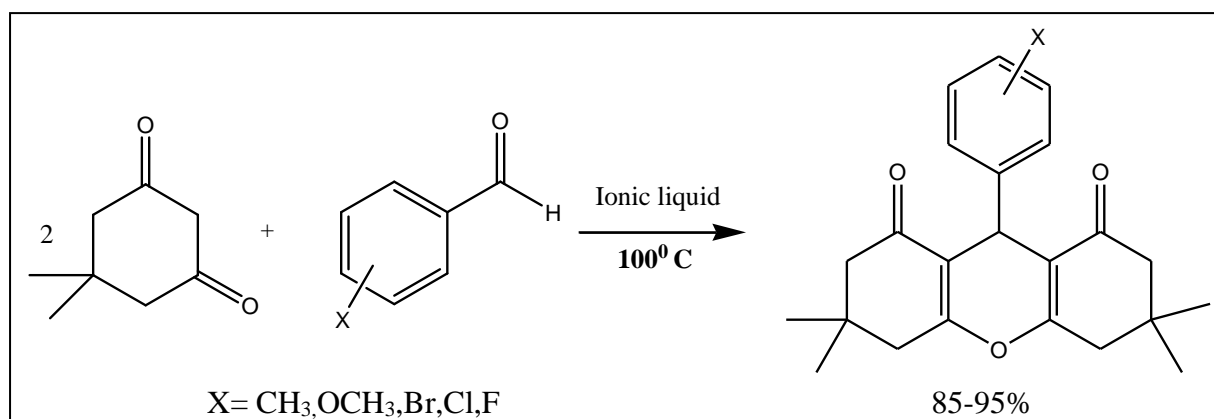
Introduction:

In the last so many decades the chemists are interested in synthesizing xanthenes derivatives as they shows pharmacological and pharmaceutical activities as antiviral¹, antibacterial², anti-inflammatory³. these are used as antagonists for paralyzing the action of zoxazolamine⁴ also in photodynamic therapy. these xanthene and benzoxanthene derivatives shows prominent framework in different synthetic as well as natural products and show its prominent position^{6,7}.

Xanthenes diones are likewise special structural units constituting various natural products⁸ and also used as synthons as inherent activity of their inbuilt pyran ring⁹. These are useful precursors for many organic compounds¹⁰ and in dyes¹¹ also in laser technologies¹² and pH-sensitive fluorescent materials for the visualization of biomolecules assemblies¹³.

One of the very famous methods reported for synthesis of xanthene diones involves condensation of aromatic aldehydes with 1,3 cyclohexanedione (dimedone). The various catalyst has been reported for synthesis of 1,8 dioxo octahydro xanthenes are NSPVPC, [Et₃NC₄SO₃H] [HSO₄] / Al₂O₃, polyaniline, p-toulene sulfonate¹⁴⁻¹⁷, alumina sulfuric acid, CAN, [BMIm] [BF₄] Mg(BF₄)₂, [Et₃N-SO₃H]Cl, DABCO, SmCl₃, Cellulose sulfonic acid¹⁸⁻²³, heteropolyacid MCM-41, TBAHS²⁴⁻²⁸, tetra methyl guanidium trifluoroacetate, [DDPA] [HSO₄], [TMPSA] [HSO₄], TFA, trichlor isocyanuric acid²⁹⁻³³, SbCl₃/SiO₂, InCl₃/P₂O₅, p-dodecyl benzene sulfonic acid³⁴⁻³⁷.

Most of these methods have advantages and disadvantages taking consideration the weakness as long reaction time, hazardous catalyst, low yield and hazardous solvents. To overcome all these problems we have developed efficient method of synthesis of 1,8 di oxo octahydro xanthenes using ionic liquids. In recent years these ionic liquids having useful alternative for conventional organic solvents which are hazardous also they possess negligible vapour pressure, chemical stability and ease of recovery³⁸. In recent years chemist giving much attention for context of green synthesis.



Scheme : green Synthesis of 1,8-dioxo-octahydroxanthenes using ionic liquids

General Procedure :

To a mixture of aldehyde (1mmol) 5,5-dimethyl 1,3 cyclohexanedione or dimedone (2mmol) and 1-ethyl 3-methyl imidazolium chloride/ZnCl₂ (.85ml) ionic liquid was added in 50 ml round bottom flask and is stirred at 100^o C on heating magnetic stirrer. The progress of the reaction was monitored by TLC after completion of the reaction the reaction mixture was cooled to room temperature and water (5ml) added, solid separated was filtered off. then the crude product was recrystallised from ethanol to give the pure product. The ionic liquid was recovered and reused for three times.

Spectral Data:

3,3,6,6-tetramethyl-9-(4-chloro phenyl)- 1,8 –dioxo-octahydro xanthene: (entry 1)

IR (cm⁻¹) : 3030,2963,2952,1679,1661,1469,1361,1198,1166,1003,852. ¹H NMR: 7.717-7.24 (dd, 4H), 4.71(s, 1H), 2.46 (s, 4H), 2.18(q, 4H), 1.10(s, 6H), 0.98(s, 6H). ¹³C NMR : 191.10, 157.17, 137.45, 126.79, 124.53, 122.97, 110.03, 45.45, 35.61, 26.96, 26.22, 24.03, 22.05. m/z 385.2(M+1) , 273.2

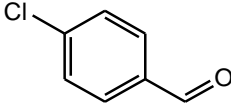
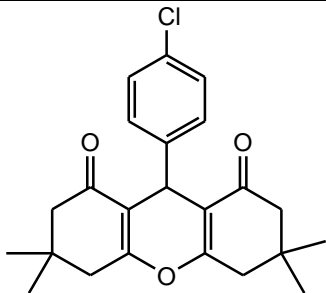
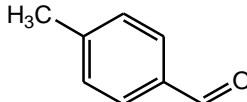
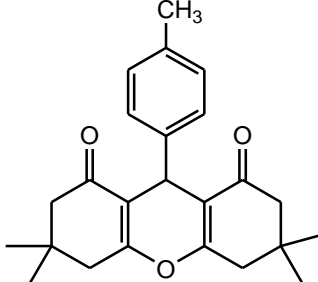
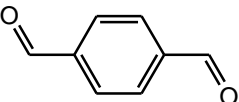
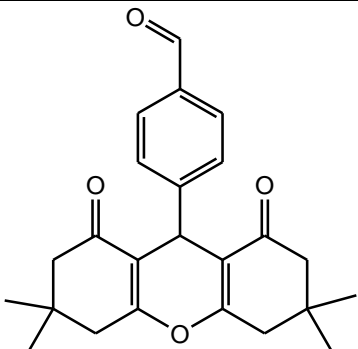
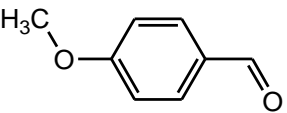
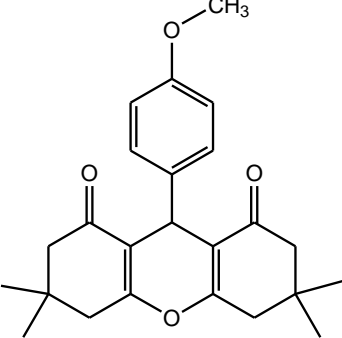
3,3,6,6-tetramethyl-9-(4-methyl phenyl)- 1,8 –dioxo-octahydro xanthene: (entry 2)

IR(cm⁻¹): 3036, 2959, 2873, 1663, 1623, 1359, 1197, 1164, 1139, 1000, 842. ¹H NMR: 7.17 (d,2H), 7.01 (d, 2H), 4.71 (s, 1H), 2.45 (s, 4H), 2.24 (s, 3H), 2.18 (q, 4H), 1.09 (s, 6H), 0.99 (s, 6H). ¹³C NMR: 196.4, 162.0, 141.1, 135.7, 128.7, 128.2, 115.7, 50.7, 40.8, 32.2, 31.4, 29.2, 27.3, 21.0 .m/z 365.3 (M+1), 273.2

9,9'-(1,4-phenylene)bis(3,3,6,6-tetramethyl-3,4,5,6,7, 9-hexahydro-1H-xanthene-1,8 (2H)-dione (Entry 3) IR (cm⁻¹): 2957, 2871, 1665, 1620, 1365, 1201, 1167, 1144, 1005, 590. 1H NMR: 7.07 (s, 4H), 4.70 (s, 2H), 2.42 (s, 8H), 2.17 (s, 8H), 1.07 (s, 12H), 0.97 (s, 12H). m/z: 13C NMR: 196.4, 162.4, 141.7, 127.9,115.7, 50.8, 40.8, 32.2, 30.1, 28.9, 27.7. m/z: 645.4 (M + Na), 273.2.

3,3,6,6-tetramethyl-9-(4-methoxy-phenyl)-1,8-dioxo- octahydroxanthene (Entry 4) IR (cm⁻¹): 3059, 2958, 2876, 1665, 1626, 1511, 1462, 1357, 1260, 1193, 1109, 1031, 841, 569. 1H NMR: 7.18 (d, 2H), 6.75 (d, 2H), 4.69 (s, 1H), 3.73 (s, 3H), 2.45 (s, 4H),1.09 (s, 6H), 0.99 (s, 6H). 13C NMR: 196.5, 162.0, 157.9, 136.4, 129.3, 115.7, 113.4, 55.1, 50.7, 40.8, 32.2, 30.9, 29.2, 27.3. m/z: 381.2, 273.2.

Table : An efficient synthesis of 1,8-dioxoxanthenes using ionic liquids

Sr. No.	Aldehyde	Product	Time (hr)	Yield (%)	m.p. (°c)
1 216				1.20	91
2 217				1.35	90
3				1.30	79 315
4				1.32	87 244

All the products were characterized by IR, Mass, NMR, ^{13}C NMR and comparison of their melting point with those of the authentic samples.

Result and discussion :

Reaction in between dimedone and 4-chloro benzaldehyde in presence of ionic liquid was studied as good reaction. All study was carried out at optimum temperature to carry similar type of reaction and various aldehydes. The reaction between aryl aldehyde and dimedone gives excellent yield very well also giving excellent yield in respect to 1,8 dioxo-octahydroxanthene.

For evaluation the scope of reaction of 1,8 dioxo-octahydro xanthenes were prepared by reaction of dimedone and aromatic aldehydes under optimized condition. In all cases aromatic aldehyde with electron donating or electron withdrawing substituent reacted efficiently and with dimedone to yield cyclocondensation products in high yield over short reaction time. The structures of isolated products was assigned based on their spectral analysis also by taking their melting points. Also ionic liquids in this case are reused for upto 3 times with excellent yields without loss in reactivity.

Conclusion:

In short we have reported simple, convenient, one-pot procedure for synthesis of different types of xanthene derivatives using ionic liquid. The ionic liquid used can also be easily recovered.

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