

MANGANESE PERCHLORATE CATALYZED EFFICIENT GREENER SONOCHEMICAL SYNTHESIS OF ARYL-14-H-DIBENZO [α ,j] XANTHENES AND 4-SUBSTITUTED 2H-CHROMEN-2-ONES

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Abstract: Hydrated manganese perchlorate under ultrasonic irradiation is found to be an efficient, greener protocol for the synthesis of Aryl-14-H-dibenzo [α ,j] xanthenes and 4-substituted 2H-Chromen-2-ones. The present methodology offers momentous improvement over various options for the synthesis of Aryl-14-H-dibenzo [α ,j] xanthenes and 4-substituted 2H-Chromen-2-ones with regard to yield of the product, reaction time, simplicity in operation and green aspects by avoiding toxic solvents and high temperature.

Keywords: Manganese Perchlorate hydrate, Ultrasound irradiation, Aryl-14-H-dibenzo [α ,j] xanthenes, 4-substituted 2H-Chromen-2-ones.

Introduction

Coumarin and xanthenes have shown a greater potential in organic chemistry due to their wide range of biological and therapeutic activities¹⁻². The important applications of Xanthenes and coumarins are their use as antibacterial, antiviral, anti-inflammatory activities³⁻⁵, dyes and in fluorescent material⁶. Recently the synthesis of benzoxanthenes has been achieved by the reaction of aldehyde and β -naphthol by dehydration in presence of catalyst, such as $\text{Fe}(\text{HSO}_4)_3$ ⁷, Heteropolyacids⁸, Ionic liquid⁹, Polytungstozincate acid¹⁰, Sodium lauryl sulphate¹¹, Molecular iodine¹², DOWEX-50W¹³, Alum¹⁴, Cellulose sulfuric acid¹⁵, InCl_3 ¹⁶. Classically the processes consist of the condensation of phenols with β -ketoester in the presence of a variety of reagents and give good yield of 4-substituted coumarins¹⁷. Several catalysts have been used in the Von Pechmann reaction including $\text{H}_2\text{SO}_4/\text{SiO}_2$ ¹⁸, Benzoyl Sulfonic acid¹⁹, Keggin heteropolyacids²⁰, PW AI-MCM-41²¹, Graphite/Montmorillonite K10²², Sulfated zirconia²³, HCl ²⁴, Bismuth nitrate²⁵, Nafion resins/Silica nanocomposites²⁶, Amberlite Ion-exchange resin²⁷. Drawbacks of these methods are that Some of the catalysts used for the synthesis of Aryl-14-H-dibenzo [α ,j] xanthenes and 4-substituted 2H-Chromen-2-ones are harsh or hazardous, or have to be used in considerable excess²⁷, Some are not efficient in terms of time (up to several hours^{11, 14, 19, 24, 27}), yield²⁰⁻²² or lead to the formation of side product (Table I, Table II). These shortcomings certainly demand the search for a safe, more convenient and efficient method. An increasing environmental consciousness in chemical research and industry, challenges for the sustainable environmental calls for clean procedure²⁸. Ultrasound-assisted organic synthesis (UAOS) as a

green synthetic approach is a powerful technique that is being used more and more to accelerate the organic reactions²⁹. UAOS can be extremely efficient and it is applicable to a broad range of practical synthesis. The notable features of the ultrasound approach and the use of transition metal perchlorates³⁰ as catalysts for the organic synthesis enhanced reaction rates, formation of purer product in high yields and considered a processing aid in terms of energy conservation and waste minimization which compared with traditional methods, this technique is more convenient taking green chemistry concepts into account³¹. In order to expand the applications of ultrasound in combination with heterogeneous catalysts in the synthesis of heterocyclic compounds, we wish to report a general, efficient and eco-friendly method for the synthesis of Aryl-14-H-dibenzo [α ,j] xanthenes and 4-substituted 2H-Chromen-2-ones.

Table: 1 Activity of the catalysts in the synthesis of Aryl-14-H-dibenzo [α ,j] xanthenes

Entry	catalyst	Temp. (°C)	Reaction time (h)	Yield (%)	References
1	Fe(HSO ₄) ₃	Reflux	0.40-1.2	70-95	7
2	Heteropolyacids	100	1-1.5	80-94	8
3	Ionic liquid	100	0.50-0.60	78-96	9
4	PTC (sodium lauryl sulphate)	100	2-3	88-93	11
5	Dowex-50W	100	1-1.5	78-91	13
6	Alum	100	3-4	80-91	14
7	Cellulose sulfuric acid	110	1.5-3	81-95	15

Table: 2 Activity of the catalysts in the synthesis of 4-substituted 2H-Chromen-2-ones.

Entry	catalyst	Temp. (°C)	Reaction time (h)	Yield (%)	References
1	H ₂ SO ₄ /silica gel	120	0.50-1.5	73-92	18
2	Benzylsulfonic acid	150	20	50-86.2	19
3	Keggin heteropoly acid	25	0.40-1.5	20-75	20
4	Al MCM-41	150	2-12	60-79	21
5	Graphite/Montmorillonite	130	0.5-0.12	62-75	22
6	Sulfated zirconia	150	0.5-0.20	78-85	23
7	HCl	60	4	94	24
8	Nafion/resin	Reflux	2	86-74	27
9	Amberlyst	120	2	86-91	28

Experimental

All melting points recorded are uncorrected; IR spectra were recorded using KBr pellets on a Perkin–Elmer spectrophotometer, NMR spectra on AL-300F (Bruker) FT NMR spectrophotometer using tetramethylsilane (TMS) as internal standard. Sonication was performed in ELMA, Transonic T 310/H Ultrasonic cleaner (with a frequency of 35 KHz), Hans Schmidbauer GmbH and Co., and Germany. The reactions were performed in open vessels.

General Procedure for synthesis of 4-substituted 2H-chromen-2-ones

To a mixture of substituted Phenol (10mmol) and ethyl acetoacetate (10mmol) added Manganese perchlorate hydrate (1.0 mol %) and reaction mixture was exposed to ultrasound irradiation (Scheme I). The progress of reaction was followed by TLC. After completion of the reaction, the

reaction mixture was poured on crushed ice and stirred for 5 min. The solid precipitated was filtered off and recrystallized from ethanol to afford pure product. The formation of products was confirmed by comparing the melting points, IR and NMR data with authentic samples and literature data.

6-methoxy-4-methyl-2H-chromen-2-One(1d). Mp.164-165°C. IR(KBr, cm⁻¹) 2935, 1683, 1626, 1485, 1238, 1187, 804. ¹H NMR (300 MHz, CDCl₃): δ 2.41 (3H, s), 3.89 (3H, s), 6.36 (1H, s), 7.15 (1H, d, *J* = 9.1 Hz), 7.26 (1H, s), 7.35 (1H, d, *J* = 9.1 Hz). ¹³C NMR (75MHz, CDCl₃): δ 18.4, 56.1, 108.3, 115.3, 117.4, 119.7, 120.2, 146.9, 153.2, 155.4, 160.1.

7-Ethoxy-4-methyl-2H-chromen-2-one(1e). Mp.115-117°C. IR(KBr, cm⁻¹) 2942, 1681, 1618, 1497, 1239, 1168, 817. ¹H NMR (300 MHz, CDCl₃): δ 1.24 (3H, t, *J* = 6.4Hz), 2.31 (3H, s), 4.12 (2H, q, *J* = 6.4Hz), 6.38 (1H, s), 7.16(1H, d, *J* = 9.4 Hz), 7.62 (1H, s), 7.35 (1H, d, *J* = 9.1 Hz). ¹³C NMR (75MHz, CDCl₃): δ 15.7, 18.6, 66.1, 108.7, 110.1, 118.2, 119.7, 126.2, 146.2, 153.7, 156.8, 162.3.

7, 8-Dihydroxy-4-methyl-2H-chromen-2-one(1h). Mp.240-241°C. IR(KBr, cm⁻¹) 3417, 3223, 1676, 1620, 1585, 1443, 1156, 811. ¹H NMR (300 MHz, CDCl₃): δ 2.37 (3H, s), 6.12 (1H, s), 6.86 (1H, d, *J* = 8.6 Hz), 7.11 (1H, d, *J* = 8.6 Hz). ¹³C NMR (75MHz, CDCl₃): 18.4, 109.8, 112.1, 112.7, 116.1, 131.8, 143.5, 149.6, 154.1, 160.3.

General Procedure for synthesis of aryl-14-H-dibenzo [a,j]xanthenes

To a mixture of aldehyde (1mmol), and 2-naphthol (2mmol) added Manganese perchlorate hydrate (1.0 mol %) and reaction mixture was exposed to ultrasound irradiation (Scheme II). The progress of reaction was followed by TLC. After the completion of reaction, the reaction mixture was diluted with ethyl alcohol and stirred for 10 minutes at 80°C. The residue was filtered hot and kept at room temperature and the resulting crystalline product was collected by filtration. The product formed was recrystallized from ethanol. The formation of products was confirmed by comparing the melting points, elemental analysis IR and NMR data with authentic samples and literature data

4-(4-Chlorophenyl)-14H-dibenzo[a,j]xanthene (2c) Mp 289-290°C. IR (KBr, cm⁻¹): 3133, 1618, 1590, 1450, 1225, 1105, 820, 776; ¹H NMR (CDCl₃): δ 6.50 (s, 1H), 7.07-8.31 (m, 16H); ¹³C NMR (75 MHz, CDCl₃): δ 36.7, 117.8, 118.5, 124.2, 125.5, 127.9, 129.2, 129.5, 130.1, 130.5, 131.5, 131.6, 131.8, 145.3, 148.8.

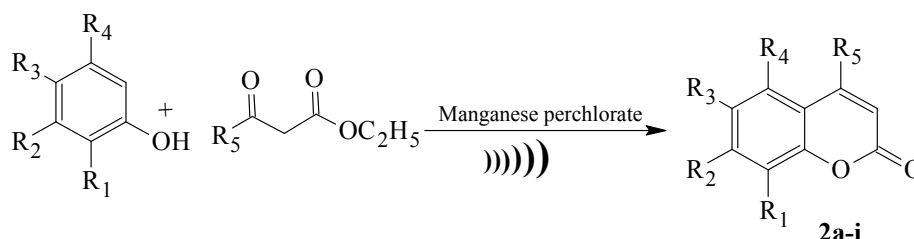
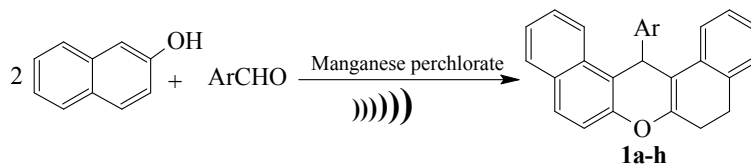
14-(4-Hydroxyphenyl)-14H-dibenzo[a,j]xanthene (2g) Mp 137-138°C IR (KBr, cm⁻¹): 3400, 1581, 1511, 1405, 1250, 1241, 814; ¹H NMR (CDCl₃): δ 4.95 (br s, 1H, OH), 6.42 (s, 1H CH), 6.58-8.39 (m, 16H); ¹³C NMR (75 MHz, CDCl₃): δ 37.5, 115.8, 117.6, 118.4, 123.3, 124.6, 127.6, 129.2, 129.3, 129.9, 131.4, 131.9, 137.9, 149.2, 154.2.

14-(2-Nitrophenyl)-14H-dibenzo[a,j]xanthene (2h) Mp 215-217°C. IR (KBr, cm⁻¹): 3400, 3056, 1593, 1522, 1351, 1240, 1142, 807, 746; ¹H NMR (CDCl₃): δ 7.52 (s, 1H), 7.10-8.54 (m, 16H); ¹³C NMR (75 MHz, CDCl₃): δ=32.7, 118.0, 118.3, 123.2, 124.5, 125.1, 125.3, 127.7, 128.0, 129.3, 129.6, 129.9, 130.6, 132.2, 132.6, 134.4, 141.2, 147.5, 149.8;

14-(3-Fluorophenyl)-14H-dibenzo[a,j]xanthene (2i) Mp 258-259°C IR (KBr, cm⁻¹): 3153, 1594, 1403, 1240, 1206, 1067, 817, 745; ¹H NMR (CDCl₃): δ 6.51(s, 1H), 6.72-8.35 (m, 16H); ¹³C NMR (75 MHz, CDCl₃): δ 38.2, 113.8 and 90, 114.0 (*J*_{C-F} 21.5Hz), 115.4, 115.8 (*J*_{C-F} 21.5 Hz), 117.2, 118.2, 122.7, 124.31, 124.32 (*J*_{C-F} 2.8 Hz) 124.7, 127.3, 129.3, 129.5, 130.1, 130.2 (*J*_{C-F} 8.3Hz), 131.4, 131.7 (*J*_{C-F} 19.4 Hz), 147.8, 147.9 (*J*_{C-F} 6.2 Hz), 149.2, 161.7, 165.1.

Results and Discussion

In order to enlarge the application of ultrasound irradiation and the use of heterogeneous catalyst in synthesis of heterocyclic compounds and in continuation of our work to develop new and eco-friendly synthetic methodologies, we here in report an efficient and eco-friendly procedure for synthesis of aryl-14-H-dibenzo[α , j] xanthenes (**Scheme-1**) & 4-substituted 2H-chromen-2-ones (**Scheme-2**) in presence of Manganese perchlorate hydrate as catalyst under ultrasound irradiation at 35 kHz.



Initially, to optimize the amount of catalyst required in these reactions, reactants were reacted under ultrasound irradiation in presence of 0, 0.1, 0.5, 0.8, 1.0 mol% of Manganese perchlorate hydrate. The best results were obtained using 1.0 mol% catalyst for the synthesis of 4-substituted 2H-chromen-2-ones and aryl-14-H-dibenzo[α , j] xanthenes (Table 3,5). To verify the effect of ultrasound irradiation on these methods for synthesis of aryl-14-H-dibenzo[α , j] xanthenes and 4-substituted 2H-chromen-2-ones was done in presence of 1.0 mol% of Manganese Perchlorate hydrate with or without ultrasound irradiation. The generality of this process was demonstrated by wide range of substituted aryl phenols to synthesize 4-substituted 2H-chromen-2-ones and various aldehyde to synthesize aryl-14-H-dibenzo[α , j] xanthenes in high to excellent yields (Table 4, 6). The high yield transformations were carried out without any significant amount of undesirable side products. It was found that use of ultrasound radiations lead to faster reaction and higher yields as compared to without ultrasonication. Unlike some previously reported methods this method does not require toxic organic solvents to produce aryl-14-H-dibenzo [α , j] xanthenes & 4-substituted 2H-chromen-2-ones.

Table: 3 Effect of amounts of catalyst $Mn(ClO_4)_2 \cdot 6H_2O$ with or without sonication for synthesis of 7-hydroxy-4-methyl-2H-chromen-2-on

Entry	$ClO_4)_2$ %	With Sonication		Without Sonication	
		Yield (%)	Time(min.)	Yield (%)	Time(min.)
1.	0	Nil	300	Nil	400
2.	0.1	5	225	2	400
3.	0.5	35	150	20	350
4.	0.8	50	140	35	350
5.	1.0	87	80	55	350

Table: 4 Mn(ClO₄)₂. 6H₂O catalyzed synthesis of 2H-chromen-2-ones under ultrasound irradiation

Entry	Products	R ₁	R ₂	R ₃	R ₄	R ₅	Time (min)	Yield (%)	M.Pt. (Lit mp.) (°C)	Ref.
1.	1a	H	OH	H	H	Me	80	87	185-186(185-186)	38
2.	1b	H	OH	H	OH	Me	75	85	285-286(286-287)	38
3.	1c	H	OMe	H	H	Me	70	82	162-163(160-161)	38
4.	1d	H	H	OMe	H	Me	75	85	164-165(161-163)	38
5.	1e	H	OEt	H	H	Me	65	84	114-117(115-117)	38
6.	1f	H	Me	H	H	Me	75	84	132-135(133-134)	38
7.	1g	H	H	H	H	Me	80	78	81-82(80-81)	38
8.	1h	OH	OH	H	H	Me	65	75	240-241(240-242)	38

Table: 5 Effect of amounts of catalyst Mn(ClO₄)₂. 6H₂O with or without sonication for Synthesis of 14-(4-Chloro-phenyl)-14H-dibenzo [a,j]xanthene.

Entry	Mn (ClO ₄) ₂ mol%	With Sonication		Without Sonication	
		Yield (%)	Time(min.)	Yield (%)	Time(min.)
1.	0	Nil	325	Nil	400
2.	0.1	35	310	10	400
3.	0.5	45	220	28	350
4.	0.8	75	150	45	350
5.	1.0	89	120	47	350

Table 6 Mn(ClO₄)₂.6H₂O catalyzed synthesis of 14-H-dibenzo[a,j]xanthenes under ultrasound irradiation.

Entry	Products	Ar	Time (min)	Yield (%)	M.Pt. (Lit.mp.) (°C)	Ref.
1.	2a	Ph	120	89	183-184(185)	37
2.	2b	4-OMePh	110	85	204-205(204)	37
3.	2c	4-ClPh	120	86	289-290(289)	37
4.	2d	4-NO ₂ Ph	110	85	312-313(310)	37
5.	2e	3-NO ₂ Ph	110	82	209-210(211)	37
6.	2f	4-FPh	115	89	238-240(239)	37
7.	2g	4-OHPh	115	83	137-138(140)	37
8.	2h	2-NO ₂ Ph	120	89	215-217(214)	37
9	2i	3-FPh	115	91	258-260(258-259)	36

Conclusion

We describe here in Manganese Perchlorate hydrate catalyzed highly efficient, one pot, green protocol for synthesis of aryl-14-H-dibenzo [a,j]xanthenes & 4-substituted 2H-chromen-2-ones under ultrasound irradiation in excellent yields. The present methodology gives several advantages such as simple procedure, easy work up and clean reaction profile, use of inexpensive catalyst, use of green solvents and milder reaction conditions.

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