Research Article

Novel $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ -Catalysed One-Pot Multicomponent Synthesis of 9,10-Dihydro-8H-benzo[a]xanthen-11(12H)-one Derivatives

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A simple and efficient protocol for the synthesis of highly substituted xanthenes is developed through the condensation of β -naphthol, aldehydes, and cyclic 5,5-dimethylcyclohexane-1,3-dione with zirconium oxychloride octahydrate as a catalyst via multicomponent condensation strategy. The present method gives good to excellent yields of substituted 9,10-dihydro-8H-benzo[a]xanthen-11(12H)-one derivatives.

1. Introduction

Xanthenes and benzoxanthenes are biologically important drug intermediates. They are cited as active oxygen heterocycles possessing antibacterial. Research on xanthenes, especially benzoxanthenes, has emerged in organic synthesis due to their wide range of biological and therapeutic properties like antiviral [1], antibacterial [2], and anti-inflammatory activities [3], as well as in photodynamic therapy [4] and as antagonists of the paralyzing action of zoxazolamine [5]. Xanthenes are also available from natural sources. Popularly known, Santalin pigments have been isolated from a number of plant species [6]. Furthermore, due to their useful spectroscopic properties, they are used as dyes [7], in laser technologies [8], and in fluorescent materials for visualization of biomolecules [9]. Many procedures are disclosed to synthesize xanthenes and benzoxanthenes like cyclodehydrations [10], trapping of benzyne by phenols [11], alkylations of hetero atoms [12], and cyclocondensations between 2-hydroxy aromatic aldehydes and 2-tetralone [13]. Benzaldehydes and acetophenones bearing tethered carbonyl chains underwent the intermolecular phenyl-carbonyl

coupling reactions in the presence of samarium diiodide and hexamethylphosphoramide to afford xanthenes [14]. In addition, 14H-dibenzo[a,j]xanthenes and related products are prepared by reaction of β -naphthol with form amide [15], 1-hydroxy methyl-naphthalen-2-ol [16], and carbon monoxide [17].

Initially, we investigated the condensation reaction of β -naphthol, benzaldehyde, and 5,5-dimethylcyclohexane-1,3-dione using different Lewis acids catalysts and conditions such as $\text{La}(\text{OTf})_3$, ZnCl_2 , AlCl_3 , and $\text{Sr}(\text{OTf})_3$ [18]. However, many of these reagents or catalysts are expensive, harmful, and difficult to handle especially on a large scale.

2. Experimental

2.1. Materials and Instruments. All reagents were purchased from Merck. Aldehydes were distilled before use. Melting points were determined using a Linkman HF591 heating stage, used in conjunction with a TC92 controller, and uncorrected. NMR spectra were recorded using either a Bruker DRX500 machine at room temperature. ^1H , ^{13}C

NMR, and ^{19}F NMR spectra were measured using $\text{DMSO}-d_6$ as solvent. CHN analyses were performed on Exeter Analytical Inc. Model C-400 CHN Analyzer. Mass spectra were obtained using a Micromass LCT machine in ES or EI mode. Infrared spectra were measured on a Perkin Elmer Paragon 100 FT-IR spectrometer. All the reactions were monitored by TLC using 0.25 mm silica gel plates (Merck 60F₂₅₄) UV indicator.

2.2. Typical Procedure for Synthesis of 9,9-Dimethyl-12-phenyl-9,10-dihydro-8H-benzo[a]xanthen-11(12H)-one (4a). A mixture of β -naphthol (1.0 mmol), benzaldehyde (1.1 mmol), and 5,5-dimethylcyclohexane-1,3-dione was added to zirconium oxychloride octahydrate (0.2 mmol) in ethanol (2 mL). The mixture was stirred at room temperature for the given times (Table 2). The progress of the reaction was monitored by TLC. After completion of the reaction water was added and the product was extracted with ethyl acetate (3 $\times$ 10 mL). The organic layer was dried (MgSO_4) and evaporated, and the crude product was purified by column chromatography by using ethyl acetate and hexane (7:3) to provide the pure product. The filtrate was concentrated under reduced pressure and dried at 100°C to recover the catalyst for subsequent use.

2.3. Selected Spectra

9,9-Dimethyl-12-phenyl-9,10-dihydro-8H-benzo[a]xanthen-11(12H)-one (4a). White crystals mp 202–203°C; yield: 97%; FT-IR (KBr, cm^{-1}) 3062, 3023, 2953, 1647, 1550, 1443, 1367, 1234; ^1H NMR (CDCl_3 δ ppm): 1.1 (3H, s, CH_3), 1.26 (3H, s, CH_3), 2.23 (2H, dd, $^1J = 4.0$ Hz, $^2J = 17.0$ Hz), 2.57 (2H, dd, $^1J = 2.5$ Hz, $^2J = 17.5$ Hz), 5.67 (1H, s, CH), 7.04 (1H, t, $J = 7.5$ Hz, Ar-H), 7.13 (2H, t, Ar-H), 7.35–7.40 (5H, m, Ar-H), 7.78 (2H, t, Ar-H), 7.99 (1H, d, Ar-H). ^{13}C NMR (CDCl_3 δ ppm): 26.1, 28.3, 28.7, 31.2, 33.7, 40.4, 49.9, 113.2, 116.0, 116.6, 122.6, 123.8, 125.2, 125.9, 127.2, 127.2, 127.3, 127.3, 127.8, 130.4, 130.4, 143.7, 146.7, 162.8, 195.9; (EI) found: M^+ , 354.1632, $\text{C}_{25}\text{H}_{22}\text{O}_2$ requires M^+ , 354.1611; LRMS m/z (EI): 354 (M^+ , 70%), 277 ($\text{M}-\text{C}_6\text{H}_5$, 65%); elemental analysis: found (%): C, 84.87; H, 6.31. Calcd for $\text{C}_{25}\text{H}_{22}\text{O}_2$: C, 84.72; H, 6.26.

12-(4-Fluorophenyl)-9,9-dimethyl-9,10-dihydro-8H-benzo[a]xanthen-11(12H)-one (4i). White crystals mp 196–197°C; yield: 97%; FT-IR (KBr, cm^{-1}) 3053, 3028, 2953, 1640, 1583, 1435, 1373, 1228; ^1H NMR (CDCl_3 δ ppm): 1.18 (3H, s, CH_3), 1.33 (3H, s, CH_3), 2.31 (2H, dd, $^1J = 3.5$ Hz, $^2J = 17.5$ Hz), 2.64 (2H, dd, $^1J = 2.5$ Hz, $^2J = 17.5$ Hz), 5.23 (1H, s, CH), 7.32 (1H, t, $J = 8.0$ Hz, Ar-H), 7.52 (2H, t, Ar-H), 7.62–7.76 (5H, m, Ar-H), 8.14 (2H, t, $J = 8.0$ Hz, Ar-H); ^{13}C NMR (CDCl_3 δ ppm): 26.1, 28.3, 28.7, 31.2, 33.7, 40.4, 49.9, 113.2, 116.0, 116.6, 122.6, 123.8, 125.2, 125.9, 127.2, 127.2, 127.3 (d, $^2J_{\text{CF}} = 14.98$ Hz, C-3), 127.8 (d, $^1J_{\text{CF}} = 250.32$ Hz, C-4), 130.4, 130.4, 143.7, 146.7, 162.8, 195.9; ^{19}F NMR (CDCl_3 δ ppm): –64.19; (EI) found: M^+ , 372.2103, $\text{C}_{25}\text{H}_{21}\text{FO}_2$ requires M^+ , 372.1503; LRMS m/z (EI): 372 (M^+ , 45%), 277 ($\text{M}-(4-\text{FC}_6\text{H}_5)$, 75%); elemental

analysis: found (%): C, 80.71; H, 5.72. Calcd for $\text{C}_{25}\text{H}_{21}\text{FO}_2$: C, 80.62; H, 5.68.

12-(2-Fluorophenyl)-9,9-dimethyl-9,10-dihydro-8H-benzo[a]xanthen-11(12H)-one (4j). White crystals mp 231–232°C; yield: 95%. FT-IR (KBr, cm^{-1}) 3073, 3056, 2906, 1662, 1534, 1423, 1372, 1230, cm^{-1} ; ^1H NMR (CDCl_3 δ ppm): 1.18 (3H, s, CH_3), 1.29 (3H, s, CH_3), 2.11 (2H, dd, $^1J = 3.0$ Hz, $^2J = 18.0$ Hz), 2.31 (2H, dd, $^1J = 2.5$ Hz, $^2J = 17.5$ Hz), 5.06 (1H, s, CH), 7.08 (1H, t, $J = 8.0$ Hz, Ar-H), 7.32 (2H, t, Ar-H), 7.59–7.83 (5H, m, Ar-H), 8.14 (2H, t, $J = 8.0$ Hz, Ar-H); ^{13}C NMR (CDCl_3 δ ppm): 25.4, 27.8, 29.1, 30.2, 35.3, 42.2, 48.2, 112.7, 115.2, 117.4, 121.7, 124.2, 125.8, 126.6, 127.8, 127.9, 129.5 (d, $^2J_{\text{CF}} = 14.95$ Hz, C-3), 130.2 (d, $^1J_{\text{CF}} = 251.76$ Hz, C-2), 131.8, 136.5, 140.5, 148.5, 161.9, 193.6; ^{19}F NMR (CDCl_3 δ ppm): –73.23; (EI) found: M^+ , 372.3110, $\text{C}_{25}\text{H}_{21}\text{FO}_2$ requires M^+ , 372.1503; LRMS m/z (EI): 372 (M^+ , 35%), 277 ($\text{M}-(2-\text{FC}_6\text{H}_5)$, 84%); elemental analysis: found (%): C, 80.71; H, 5.72. Calcd for $\text{C}_{25}\text{H}_{21}\text{FO}_2$: C, 80.62; H, 5.68.

9,9-Dimethyl-12-(4-(trifluoromethyl)phenyl)-9,10-dihydro-8H-benzo[a]xanthen-11(12H)-one (4k). White crystals mp 227–228°C; yield: 97%; FT-IR (KBr, cm^{-1}) 3098, 3043, 2923, 1673, 1555, 1465, 1343, 1223, cm^{-1} . ^1H NMR (CDCl_3 δ ppm): 1.31 (3H, s, CH_3), 1.52 (3H, s, CH_3), 2.27 (2H, dd, $^1J = 2.5$ Hz, $^2J = 16.0$ Hz), 2.43 (2H, dd, $^1J = 2.5$ Hz, $^2J = 17.0$ Hz), 5.43 (1H, s, CH), 7.20 (1H, t, $J = 7.5$ Hz, Ar-H), 7.43 (2H, t, Ar-H), 7.59–7.83 (5H, m, Ar-H), 8.14 (2H, t, $J = 8.0$ Hz, Ar-H); ^{13}C NMR (CDCl_3 δ ppm): 25.1, 28.3, 29.5, 32.9, 34.4, 46.3, 49.1, 110.9, 116.1, 119.2, 123.4, 124.7, 125.2, 126.1, 127.2, 127.3, 128.3, 130.2, 131.8, 133.3, 135.35 (q, $^1J_{\text{CF}} = 251.9$ Hz, CF_3), 136.5, 140.5, 148.5, 161.9, 193.6; ^{19}F NMR (CDCl_3 δ ppm): –112.32; (EI) found: M^+ , 422.2130, $\text{C}_{26}\text{H}_{21}\text{F}_3\text{O}_2$ requires M^+ , 422.1523; LRMS m/z (EI): 422 (M^+ , 25%), 277 ($\text{M}-(4-\text{CF}_3\text{C}_6\text{H}_5)$, 72%); elemental analysis: found (%): C, 80.05; H, 5.23. Calcd for $\text{C}_{26}\text{H}_{21}\text{F}_3\text{O}_2$: C, 73.92; H, 5.01.

12-([1,1'-Biphenyl]-4-yl)-9,9-dimethyl-9,10-dihydro-8H-benzo[a]xanthen-11(12H)-one (4l). White crystals mp 214–215°C; yield: 91%; FT-IR (KBr, cm^{-1}) 3086, 3039, 2909, 1680, 1543, 1436, 1352, 1231, cm^{-1} ; ^1H NMR (CDCl_3 δ ppm): 1.27 (3H, s, CH_3), 1.39 (3H, s, CH_3), 2.10 (2H, dd, $^1J = 3.0$ Hz, $^2J = 17.5$ Hz), 2.28 (2H, dd, $^1J = 3.0$ Hz, $^2J = 17.5$ Hz), 5.08 (1H, s, CH), 7.11 (3H, m, Ar-H), 7.42 (2H, t, Ar-H), 7.21 (2H, t, $J = 7.5$ Hz, Ar-H), 7.42 (1H, t, Ar-H), 7.59–7.83 (5H, m, Ar-H), 8.14 (2H, t, $J = 7.5$ Hz, Ar-H); ^{13}C NMR (CDCl_3 δ ppm): 23.7, 24.9, 27.9, 31.3, 32.4, 41.3, 43.4, 110.7, 113.3, 116.6, 120.3, 121.3, 121.9, 122.4, 123.5, 125.3, 126.8, 129.1, 129.9, 130.2, 130.0, 131.4, 132.0, 133.8, 134.2, 135.6, 141.6, 145.6, 146.7, 168.5, 192.1; (EI) found: M^+ , 430.2109, $\text{C}_{31}\text{H}_{26}\text{O}_2$ requires M^+ , 422.1523; LRMS m/z (EI): 430 (M^+ , 15%), 277 ($\text{M}-(\text{C}_6\text{H}_5\text{C}_6\text{H}_4)$, 63%); elemental analysis: found (%): C, 86.32; H, 5.98. Calcd for $\text{C}_{31}\text{H}_{26}\text{O}_2$: C, 86.48; H, 6.09.

12-(Furan-2-yl)-9,9-dimethyl-9,10-dihydro-8H-benzo[a]xanthen-11(12H)-one (4o). White crystals mp 245–246°C; yield: 97%; FT-IR (KBr, cm^{-1}) 3060, 3046, 2943, 1672, 1539, 1482,

TABLE 1: Screening of the catalyst and solvent for the reaction of β -naphthol, benzaldehyde, and 5,5-dimethylcyclohexane-1,3-dione catalyzed by $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}^a$.

Entry	Catalyst (mol%)	Solvent/condition	Time (h)	Yield ^b (%)
1	20	Water/80°C	10	—
2	20	THF/Reflux	10	—
3	20	CH_3CN /Reflux	10	<10
4	20	CH_3NO_2 /Reflux	10	15
5	20	CHCl_3 /Reflux	10	15
6	20	DMF/80°C	10	55
7	20	CH_2Cl_2 /Reflux	10	65
8	20	(bmim) BF_4 /Reflux	5	75
9	20	None/80°C	10	20
10	20	$\text{CH}_3\text{CH}_2\text{OH}$ /rt	4	85
11 ^c	20	$\text{CH}_3\text{CH}_2\text{OH}$/Reflux	1	92, 93, 92, 92, 91
12	10	$\text{CH}_3\text{CH}_2\text{OH}$ /Reflux	10	80
12	30	$\text{CH}_3\text{CH}_2\text{OH}$ /Reflux	4	92
10	none	$\text{CH}_3\text{CH}_2\text{OH}$ /Reflux	10	Nil

^aReaction conditions: β -naphthol (1.0 mmol), benzaldehyde (1.0 mmol), and 5,5-dimethylcyclohexane-1,3-dione (1.1 mmol), zirconium oxychloride catalyst.

^bIsolated yield.

^cCatalyst was reused five times.

TABLE 2: Synthesis of xanthenes in the presence of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$.

Entry	R	Product	Time (h)	Yield ^a (%)
1	C_6H_5	4a	1	92
2	<i>p</i> - $\text{CH}_3\text{C}_6\text{H}_4$	4b	2	85
3	3- CH_3 -4- CH_3 - C_6H_3	4c	3	82
4	<i>p</i> - $\text{CH}_3\text{OC}_6\text{H}_4$	4d	2	85
5	<i>p</i> - ClC_6H_4	4e	1	95
6	<i>p</i> - $\text{NO}_2\text{C}_6\text{H}_4$	4f	1	96
7	<i>o</i> - $\text{NO}_2\text{C}_6\text{H}_4$	4g	1	90
8	<i>p</i> - ClC_6H_4	4h	1	95
9	<i>p</i> - FC_6H_4	4i	0.5	97
10	<i>o</i> - FC_6H_4	4j	0.5	95
11	<i>p</i> - $\text{CF}_3\text{C}_6\text{H}_4$	4k	0.5	97
12	<i>p</i> -(C_6H_5) C_6H_4	4l	1	91
13	CH_3CH_2	4m	4	75
14	2-Thiophene	4n	5	80
15	2-Furan	4o	5	82

^aIsolated yield.

1362, 1231, cm^{-1} ; ^1H NMR (CDCl_3 δ ppm): 1.24 (3H, s, CH_3), 1.35 (3H, s, CH_3), 2.36 (2H, dd, $^1J = 2.5$ Hz, $^2J = 17.5$ Hz), 2.42 (2H, dd, $^1J = 2.5$ Hz, $^2J = 17.5$ Hz), 5.26 (1H, s, CH), 7.21 (1H, t, $J = 7.0$ Hz, Furyl-H), 7.33 (1H, t, $J = 7.5$ Hz, Furyl-H), 7.42 (1H, t, $J = 7.0$ Hz, Furyl-H), 7.5. ^{13}C NMR (CDCl_3 δ ppm): 23.2, 24.4, 28.8, 29.6, 32.5, 40.2, 46.2, 114.9, 116.2, 119.4, 121.7, 124.2, 125.8, 126.6, 127.8, 127.9, 129.5, 131.8, 136.5, 140.5, 148.5, 161.9, 193.6; (EI) found: M^+ , 344.1911, $\text{C}_{23}\text{H}_{20}\text{O}_3$ requires M^+ , 344.1421; LRMS m/z (EI): 344 (M^+ , 34%), 267 (M -(Furyl),

48%); elemental analysis: found (%): C, 80.33; H, 5.63, 5.98. Calcd for $\text{C}_{23}\text{H}_{20}\text{O}_3$: C, 80.21; H, 5.85.

3. Results and Discussion

In continuation of our efforts towards the development of novel methodologies under green chemical approaches herein we report a mild, efficient, and facile one-pot synthesis of multisubstituted xanthen derivatives for the first time by the multicomponent reaction of β -naphthol, benzaldehyde, and 5,5-dimethylcyclohexane-1,3-dione using zirconium oxychloride octahydrate as a Lewis acid catalyst (Scheme 1). The side reactions were not observed in our work. However, the corresponding of (**4a-j**) were the major products, when $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was employed as the catalyst, hence, showing good chemoselectivity.

In order to determine the most appropriate choice of catalyst and solvent system for this $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ catalyzed synthesis of substituted xanthenes, we examined the above reaction in several catalyst amounts and solvents (Table 1). The results indicate that different solvents affected the efficiency of the reaction. Acetonitrile, nitromethane, and chloroform catalyst afforded low yields (Table 1, entries 3–5), while when water and tetrahydrofuran with were used as solvents, no products were detected (Table 1, entries 1 and 2). The use of solvents such as DMF, dichloromethane, and [bmim] BF_4 could improve the yields (Table 1, entries 6–8). In particular, the reaction could be carried out under solvent-free condition and gave moderate yield (Table 1, entry 9); finally, when ethanol under reflux with 20 mol% catalyst was used, the yield increased to 92% better than any other solvents examined here. The catalytic activity of the recycled $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was also examined. $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ could be reused five times for the reaction without noticeable loss of activity (Table 1, entry 11).

In order to determine the scope of this reaction, we have synthesized differently substituted xanthenes by varying differently substituted aldehydes including both electron-donating and electron-withdrawing groups. It is observed that the reaction gave good yields of products with faster reaction rate when the aldehyde bearing electron-withdrawing group is used compared to the aldehydes with electron-donating groups. The corresponding results are tabulated in Table 2.

On the basis of the above results, this process was then extended to heterocyclic and aliphatic aldehydes. Propionaldehyde, thiophene-2-carbaldehyde, and furan-2-carbaldehyde afforded the corresponding products (**4m**, **4n**, **4o**) in 75%, 80%, and 82% yields, respectively (Table 2, entries 13–15). Compared with aromatic aldehydes, heterocyclic or aliphatic aldehydes afforded relatively lower yields of the corresponding **4** (Table 2).

A tentative mechanism for the formation of derivatives **4** is proposed in Scheme 2. By referring to the literature [19], we supposed that the reaction may proceed via the *ortho*-quinone methides intermediate **5**, which was formed by the nucleophilic addition of β -naphthol to aldehyde with $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$. Subsequent substitution of the oxygen

SCHEME 1

SCHEME 2: Proposed mechanism for the condensation reaction of aldehydes, β -naphthol, and 5,5-dimethylcyclohexane-1,3-dione.

atom, which was coordinated by zirconium oxychloride, with 5,5-dimethylcyclohexane-1,3-dione **1** afforded **6**. Then compounds **6** eliminated one molecule of H_2O and afforded title product **4**. All the products were characterized by ^1H , ^{13}C NMR, IR, and mass spectra and compared with authentic samples.

4. Conclusion

We have developed a one-pot multicomponent reaction for the synthesis of 9,10-dihydro-8H-benzo[a]xanthene-11(12H)-one derivatives catalyzed by zirconium oxychloride in excellent yields. This method includes the use of recyclable catalyst,

mild reaction conditions, easy work-up, good chemoselectivity, high yields, and cleaner reaction profiles.

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