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Bismuth Nitrate Catalysed Convenient Synthesis of 1,8-Dioxo-Octahydro xanthene Derivatives

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ABSTRACT

Synthesis of wide variety of substituted 1, 8-dioxo-octahydro xanthene derivatives from reacting various Benzaldehydes with 5, 5-dimethyl-1,3-cyclohexane-dione via Bismuth Nitrate [$Bi(NO_3)_3$ $5H_2O$] Catalysed reaction is described. The present methodology offers several significant advantages such as high yields, short reaction times, simple operation and convenient work-up.

Keywords: Benzaldehydes, 5,5-dimethyl-1,3-cyclohexane-dione, Bismuth Nitrate, EtOH, 1,8-dioxo-octahydroxanthene.

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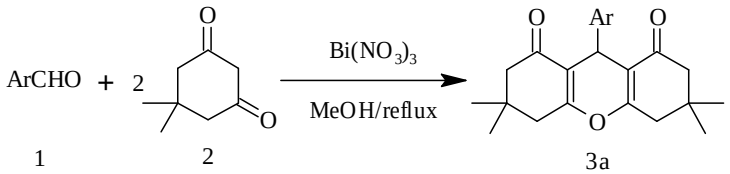
INTRODUCTION

Xanthene dyes importance has been well recognized at all hands because of their wide range of biological and pharmaceutical characteristics such as bactericidal activity, anti-inflammatory [1]. A variety of these xanthene derivatives are widely used as the physicochemical properties of the dyes vary widely and different combination of properties is possible. These include absorption and emission maximum of chromophoric system, polarity and micro environmental dependence of the fluorescence for diverse applications [2] and also these compounds widely used as leuco-dye [3], in laser technology [4] and in fluorescent materials [5]. Xanthene's derivatives are parent compounds of a large number of naturally occurring and synthetic derivatives, and occupy a prominent position in medicinal chemistry, considerable attention has been directed towards the synthesis of compound containing xanthenedione nucleus, constitute a structural unit in a number of natural products and have been used as versatile synthons because of the inherent reactivity of the inbuilt pyran ring, and possessing a wide variety of biological properties [6]. Furthermore, these compounds have recently received great attention because of their wide range of therapeutic and biological properties, such as antibacterial [7], antiviral [8], and anti-inflammatory activities [9]. The several reports have been advancing in which xanthenediones derivatives were obtained through condensation of aldehyde and dimedone under various conditions [9-11]. The

development of a simple, highly efficient methodology for synthesis of xanthenes remains desired. In the quest for developing a less toxic, potential green catalyst, we thought of using bismuth nitrate for this reaction. We are particularly interested in bismuth nitrate, because it is not much expensive and can be easily available in our laboratory and it is a wide variety of utility in different chemical transformations, like addition of amines, imidazoles and thiols to enones [12]. Our team have described the synthetic utility of $Bi(NO_3)_3$ as a catalyst in the synthesis of indole heterocycles [13]. Here our report is a simple and efficient method for the synthesis of 1, 8-dioxo-octahydroxanthene using $Bi(NO_3)_3$ as a catalyst. And this $Bi(NO_3)_3$ is insoluble in common organic solvents, it can be filtered off after the reaction and is suited for recycling.

Scheme 1: **The synthetic strategy for the construction of 1,8-dioxo-octa hydroxanthene**



Scheme-1

Table 1: Screening of the catalytic activity of Bismuth Nitrate [$Bi(NO_3)_3$] for the synthesis of xanthenediones at reflux temperature.

Entry	Solvent	Amount of Catalyst	Time / h	Yield / %[a]
1	MeOH	15% $BiNO_3$	3.50	93
2	EtOH	15% $BiNO_3$	3.50	90
3	CH_2Cl_2	20% $BiNO_3$	1.30	82
4	Toluene	20% $BiNO_3$	4.00	78
5	CH_3CN	20% $BiNO_3$	2.00	90
6	DMF	20% $BiNO_3$	4.30	72
7	THF	20% $BiNO_3$	6.45	60
8	EtOH	20% $BiNO_3$	2.00	90
9	MeOH	25% $BiNO_3$	2.00	90
10	MeOH	20% $BiNO_3$	2.00	(93,85,80)[b]
11	H_2O	20% $BiNO_3$	15.00	30
12	MeOH/ H_2O	20% $BiNO_3$	2.00	90
13	EtOH/ H_2O	20% $BiNO_3$	2.00	90

[a] Isolated yields

[b] The same catalyst recovered and reused for each of the three runs

In this communication we report the synthesis of substituted xanthenediones via the condensation of aldehyde with dimedone using $Bi(NO_3)_3$ as a catalyst in methanol (Scheme 1, Table 1). In order to study catalytic activity of Bismuth Nitrate in aqueous alcohol, acetonitrile and various solvents, the condensation of various benzaldehydes and dimedone under various conditions has been investigated

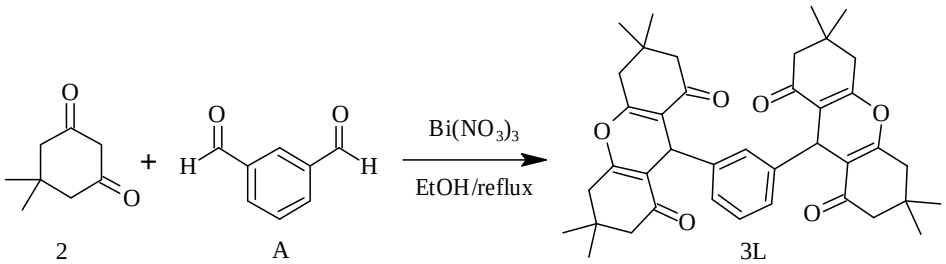
RESULTS AND DISCUSSION

We examined the catalytic activity of $Bi(NO_3)_3$ in different reaction media to investigate the solvent effect on reaction in the synthesis of xanthene diones, condensation of various benzaldehydes and dimedone, the results are summarized in the Table 1 and exemplify that polar solvents such as MeOH and EtOH are better solvents than non-polar ones. Although the reaction proceeds in water, the isolated yields are very low (≤30%) (Table 1, entry 11). Also, we examined the reaction in an

alcohol / water system. Remarkably, the condensation proceeded smoothly in MeOH / H_2O (1 / 1, *v/v*), EtOH / H_2O (1 / 1, *v/v*) system and afforded the desired product in good yield (90%) (Table 1, entries 12, 13). However MeOH was found to be best for the catalytic reaction at reflux temperature in terms of yield and reaction time, the best results were achieved by carrying out the reaction at reflux temperature to afford substituted xanthenediones in 90-93% yield respectively. Further we set out to establish the optimal amount of $Bi(NO_3)_3$, finding that reaction with a 15 mol% catalyst loading gave a 93% yield after 3.5 hr (entry 1), however the best result (93%) corresponds to the use of 20 mol % catalyst (entry 10) and the reaction time reduced to 120 min. The increasing amount of the catalyst did not change the reaction time whereas isolated yield was found to be less in nature (entry 9). Another advantage is the use of $Bi(NO_3)_3$ was that it could be easily recovered and recycled in subsequent reactions without significant decrease in the activity of the catalyst, (Table 1, entry 10**,** 1st run 93%, 2nd run 85% and 3rd run 80%). which was easily separated by simple extraction and filtration.

Encouraged by the above results, via similar reaction condition we replaced the isophthalaldehyde instead of aromatic aldehyde. We optimized the amount of catalyst for condensation reaction of 5,5-dimethyl-1,3-cyclohexanedione and isophthalaldehyde A to give structurally complex bis-xanthenedione 3L (Table-2, Entry-3L), as shown in (Scheme-2).

Scheme 2: **The synthetic strategy for the construction of bis-xanthenedione**



2 A 3L

Scheme 2

Table 2: Synthesis of Xanthenediones promoted by Bismuth Nitrate at reflux temperature

Sl. No.	Aldehydes	Time (%)	Yields (%)	MP °C
3a	PhCHO	1.55	93	197-199
3b	4-$MeOC_6H_4CHO$	2.00	91	239-241
3c	3-$MeOC_6H4CHO$	2.00	91	227-229
3d	4-FC_6H_4CHO	1.50	95	223-225
3e	2-ClC_6H_4CHO	2.50	91	226-228
3f	3-ClC_6H_4CHO	1.50	95	183-185
3g	4-ClC_6H_4CHO	1.50	95	233-235
3h	4-BrC_6H_4CHO	1.50	95	235-237
3i	2-$NO_2C_6H_4CHO$	2.50	75	261-263
3j	3-$NO_2C_6H_4CHO$	1.50	80	146-148
3k	4-$NO_2C_6H_4CHO$	1.50	80	224-226
3L	Isophthalaldehyde	2.00	88	235-237

CONCLUSION

Finally we conclude that, the synthesis of xanthenediones derivatives were obtained through condensation of aldehydes and dimedone, the reaction was successfully carried out in presence of catalytic amount of reusable Bismuth Nitrate at reflux temperature. This method offers several significant advantages, such as high

conversions, easy handling, cheaper catalyst, cleaner reaction profiles, short reaction time, and the reaction conditions are environmental friendly and might be amenable for up-scaling.

EXPERIMENTAL

All the melting points were recorded in open capillaries. The purity of the compounds was checked by TLC on silica gel and they were purified by column chromatography. ^{1}H NMR spectra were recorded on a Bruker-300 Hz spectrometer using *TMS* as an internal standard. IR spectra were obtained using a FTS-135 spectrometer instrument. The compounds 3a–3L are known, their identity were proven by means, comparison of their melting points and spectral data with the reported data to be found in literature [14,15].

Synthesis of Xanthenediones

To a mixture of 1.0 mmol benzaldehyde 1 and 2 mmol dimedone 2 in 10 cm^3 methanol, 0.5mg $Bi(NO_3)_3$ (0.10 mmol) was added. The reaction mixture was refluxed on water bath for the appropriate time. The reaction was monitored by TLC. After completion of reaction, the reaction mixture was filtered to remove the catalyst and washed with 3cm^3 of acetone. Then the clear filtrate was poured into 50 cm^3 water and extracted with ethyl acetate (3 x 10 cm^3). And dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure. The residue, thus obtained was purified by column chromatography using silica gel (60-120 mesh) and eluted with petroleum ether:ethyle acetate to afford xanthenediones. Similarly remaining compounds were purified by using the above procedure.

Spectral Data

9-Aryl-3,3,6,6-tetramethyltetrahydroxanthene-1,8-dione (3a):
M.P.=201-203^{o}C; ^{1}H NMR (300MHz, $CDCl_3$); δ = 7.24-7.00 (5H, m), 4.69 (1H, s), 2.40(4H, s), 2.20-2.07(4H, m),1.04(6H, s), 0.93 (6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 196.1, 162.1, 143.9, 128.2, 127.8, 126.1, 115.4, 50.5, 40.6, 31.9, 31.6, 29.0, 27.1; IR (KBr) 2959, 1662, 1467, 1361, 1199, 1165, 1141, 1003, 891, 798, 742, 700, 661 cm^{-1}.

9-(4-Methoxy-phenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-2*H*-xanthene-1,8-dione (3b):
M.P.=239-241^{o}C; ^{1}H NMR (300MHz, $CDCl_3$) δ.= 7.18 (1H, d, *J* = 8.0 Hz), 6.73(1H, d, *J* = 8.0Hz), 4.67(1H,s), 3.71(3H, s), 2.43(4H, s), 2.24-2.11(4H, m), 1.07(6H, s), 0.97(6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 195.3, 163.0,156.9, 136.4, 126.2, 113.7, 113.4, 55.0, 50.7, 40.8, 32.1, 30.9,29.2, 27.3; IR (KBr) 3460, 2956, 1667, 1511, 1462, 1359, 1259, 1194, 1032, 841, 729, 568 cm^{-1}.

9-(3-Methoxy-phenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-2*H*-xanthene-1,8-dione (3c):
M.P.=227-229^{o}C; ^{1}H NMR (300MHz, $CDCl_3$) δ = 7.18(1H, d, *J* = 8.0 Hz), 6.73 (1H,d, *J* = 8.0 Hz), 4.67(1H,s), 3.71(3H, s), 2.43(4H, s), 2.24-2.11(4H, m), 1.07(6H, s), 0.97(6H, s); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 195.3, 161.0, 157.9, 136.4, 124.2, 115.7, 111.4, 55.0, 50.7, 40.8, 32.1, 30.9, 28.2, 27.3; IR (KBr) 3460, 2956, 1667, 1511, 1462, 1359, 1259, 1194, 1032, 841, 729, 568 cm^{-1}.

9-(4-fluorophenyl)-3,3,6,6-tetramethyl-3,4,6,7-tetrahydro-2*H*-xanthene-1,8(5H,9H)-dione (3d). M.P.=223-225 ^{o}C;^{1}HNMR(300MHz, $CDCl_3$) δ = 1.04(s, 6H, $2CH_3$), 1.11(s,6H, $2CH_3$), 2.14-2.46 (m, 8H, $4CH_2$), 4.77(s, 1H, CH), 7.31(d, *J*=8.4Hz, 2H, ArH), 7.65(d, *J*=8.4 Hz, 2H, ArH).; ^{13}CNMR ($CDCl_3$, 75MHz): δ = 196.14, 163.73, 162.46, 146.64, 129.31, 124.20, 115.23, 115.18, 113.35, 50.70, 40.83, 31.68, 29.14,27.30; IR (KBr,cm^{-1}): 2961,2873, 1660, 1624, 1590, 1485, 1450, 1361, 1241, 1201, 1165, 1140, 1003, 930, 769, 696, 575.

9-(2-Chloro-phenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-2*H*-xan thene-1,8-dione (3e):
M.P.=226-228^{o}C; ^{1}H NMR (300MHz, $CDCl_3$) δ=7.20-7.11 (4H,m), 4.29 (1H, s), 2.24(4H, s), 2.15-2.00(4H,m), 1.58(6H, s), 0.97(6H, s); ^{13}C NMR(75MHz, $CDCl_3$) δ = 196.7, 163.0, 141.0, 130.0, 130.1, 129.2, 114.9, 51.1, 41.1,32.4, 31.7, 29.9, 27.1; IR(KBr) 2955, 1660, 1467, 1362,1197, 1163, 1008, 846, 713, 666, 565 cm^{-1}

9-(3-clorophenyl)-3,3,6,6-tetramethyl-3,4,6,7-tetrahydro-2*H*-xanthene-1,8(5H,9H)-dione(3f). M.P.=183-185 ^{o}C; ^{1}H NMR (300MHz, $CDCl_3$) d: 1.02 (s, 6H, 2 CH_3), 1.12 (s, 6H, 2 CH_3), 2.30–2.49 (m, 8H, 4 CH_2), 4.74 (s, 1H, CH), 7.11–7.25 (m, 4H, ArH) ; ^{13}C NMR (75 MHz, $CDCl_3$) δ 195.3, 162.7, 157.3, 135.9, 126.2, 113.7, 112.9, 55.0, 50.7, 40.8, 32.1, 30.9, 29.2,

27.3; IR (KBr):.3030, 1685, 1660, 1620, 1490, 1475, 1365, 1200, 1170, 1136, 1090, 1010, 1000, 850, 840 cm^{-1}.

9-(4-Chloro-phenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-2*H*-xan thene-1,8-ione (3g): M.p=229-231°C; ^{1}H NMR (300MHz, $CDCl_3$) δ = 0.98 (s, 6H, 2 CH_3), 1.10(s, 6H, $2CH_3$), 2.22–2.50 (m, 8H, $4CH_2$), 4.64 (s, 1H, CH), 7.26–7.42 (m, 4H, ArH); (75 MHz, $CDCl_3$) δ = 195.3, 162.7, 157.3, 135.9, 126.2, 113.7, 112.9, 55.0, 50.7, 40.8, 32.1, 30.9,29.2, 27.3 ;IR (KBr):. 3030, 2980, 1680, 1660, 1620, 1490, 1480, 1360, 1200, 1170, 1140, 1092, 1011, 1000, 851, 839 cm^{-1}.

9-(4′-Bromo-phenyl)-3,3,6,6-tetramethyl-3,4,5,6,7,9-hexahydro-2*H*-xanthene-1,8-(2h)-dione(3h): M.P.=235-37°C; ^{1}HNMR (300MHz, $CDCl_3$) δ = 1.00 (s,6H, $2CH_3$), 1.12 (s, 6H, $2CH_3$), 2.16-2.48 (m, 8H, $4CH_2$), 4.72 (s, 1H, CH), 7.18 (d, *J* = 8.4Hz, 2H, ArH), 7.35 (d, *J* = 8.4 Hz, 2H, ArH). ^{13}C NMR (75 MHz, $CDCl_3$) δ = 197.0, 161.9, 143.0, 131.8, 130.1, 127.1, 114.9, 50.7, 40.9, 31.1, 31.5, 28.9, 27.3IR (KBr): 2953, 2878, 1679, 1662, 1625, 1487, 1470, 1362 cm^{-1}.

3,3,6,6-Tetramethyl-9-(2-nitro-phenyl)-3,4,5,6,7,9-hexahydro-2*H*-xan thene-1,8-dione (3i):
M.P.=261-263°C; ^{1}H NMR(300MHz, $CDCl_3$)δ = 7.70 (1H, d, *J* = 8.1Hz),7.40-7.06(3H,m),5.48 (1H,s),2.43(4H,s),2.21-2.06 (4H,m),1.07(6H,s), 1.04(6H,s); ^{13}CNMR (75MHz, $CDCl_3$) δ= 196.2,162.9,150. 8, 149.7, 131.9, 127.9, 127.3, 124.5, 115.6, 50.4, 40.7, 32.1, 31.9, 29.0, 28.8, 27.4; IR (KBr): 2956, 1640, 1531, 1463, 1377, 1235, 1196, 1024, 914, 732, 653, 575 cm^{-1}.

3,3,6,6-Tetramethyl-9-(3-nitro-phenyl)-3,4,5,6,7,9-hexahydro-2*H*-xan thene-1,8-dione (3j):
M.P.=146-148°C; ^{1}HNMR (300MHz, $CDCl_3$) δ = 7.68(1H,d, *J*=8.1Hz), 7.44-7.08 (3H,m), 5.16(1H,s), 2.63(4H,s), 2.11-2.07(4H,m), 1.12(6H,s), 1.10 (6H,s); ^{13}CNMR (75MHz, $CDCl_3$) δ= 196.2, 162.9, 150.8, 149.7, 131.9, 127.9, 127.3, 124.5, 115.6, 50.4, 40.7, 32.1, 31.9, 29.0, 28.8, 27.4; IR(KBr): 2956, 1640, 1531, 1463, 1377, 1235, 1196, 1024, 914, 732, 653, 575 cm^{-1}.

3,3,6,6-Tetramethyl-9-(4-nitro-phenyl)-3,4,5,6,7,9-hexahydro-2*H*-xan thene-1,8-dione (3k):
M.P.=224-226°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.07 (2H, d, *J* = 8.4 Hz), 7.45 (2H, d, *J* =8.4 Hz), 4.81 (1H, s), 2.47(4H, s), 2.27-2.11 (4H, m), 1.10 (6H, s), 0.97 (6H,s); ^{13}C NMR(75 MHz, $CDCl_3$) δ 196.2, 162.9, 151.4, 146.5, 129.3, 123.4, 114.5, 50.6, 40.8, 32.3, 32.2, 29.6, 29.2, 27.2; IR (KBr) 2957, 1660, 1515, 1465, 1357, 1199, 1164, 1005, 864, 734, 564 cm^{-1}

Bis(1,8-dioxo-octahdroxanthene)(3L):
M.P.=236-38°C; ^{1}HNMR (300MHz, $CDCl_3$) δ = 1.10(12H, s, 3H), 1.38 (12H,s, CH3), 2.15-2.21 and 2.18-2.25 (8H, 2d, *J* = 16.00 Hz, 16.00Hz, 4CH2), 2.398-2.442 and 2.511-2.555 (8H, 2d, *J* = 17.6 Hz, 17.6 Hz, 4CH2), 4.68 (2H,s,), 7.04-7.26 (4H,m, Ar-H).; ^{13}C NMR (100MHz, $CDCl_3$): δ = 27.68 (4 CH3), 29.35 (4CH3), 31.42 (2C-3, 2C-6), 32.32 (2C-9), 40.92 (4 C-4,C-5), 50.91 (4C-2, C-7), 115.66 (4C=C), 126.55 (Ar-C), 127.95 (Ar-C), 128.39 (Ar-C), 143.74 (2,Ar-C), 162.53 (C= C), 196.60 (4 C=O) ppm; IR (KBr): 2957, 2879, 664, 1457, 1368, 1203, 1158, 779 cm^{-1}.

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