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An efficient synthesis of thiocoumarin catalysed by triethylamine under solvent free conditions

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ABSTRACT

An efficient synthesis of thiocoumarin has been developed by the reaction of easily accessible *â*-oxodithioesters and salicylaldehyde derivatives in the presence of mild, nonnucleophilic base, triethylamine under solvent free conditions. The mild reaction conditions, high yields, operational simplicity and shorter reaction period illustrate the good synthetic utility of this method.

KEYWORDS

Coumarins;
β-oxodithioesters;
Triethylamine;
High yields;
Solvent free.

INTRODUCTION

Coumarins are among the best known oxygen heterocycles and are present abundantly as a structural motif in numerous naturally occurring products including edible vegetables and fruits[1]. Synthesis of these compounds by simple and effective methods is interesting because of its wide range of applications such as fixatives in food and cosmetics, optical brightening agents and dispersed fluorescent and laser dyes[2]. Interest in their chemistry continues unabated because they display a remarkable array of biochemical and pharmacological actions such as anti-HIV[3a,b], anticoagulation[3c], antibiotic[3d], anticancer[3e], antiinflammatory[3f,g], antioxidant[3h] and antitumor activity[3i].

Synthesis of coumarin involving different types of catalyst such as $AlCl_3$[4], exchange resins[5], Zn/I_2[6], p-TsOH[7], $InCl_3$[8], Tellurium[9] have been developed. However, the reports[10] on the synthesis of chromene-2-thiones are limited and suffer with many drawbacks. It is therefore of utmost importance that the synthesis of thiocoumarin and its derivatives should be achieved by a simple and effective method.

Recently, triethylamine has emerged as a powerful catalyst for the synthesis of various heterocycles such as ethyl 4-cyano-2-hydroxy-2-methyl-5-oxopyrrolidine-3-carboxylat[11], Oxathiolanes[12], benzopyrano[3,4-c]pyrrolidines[13] and furo[3,4-*d*]-1,3-thiazoles[14].

To the best of our knowledge, there was no report yet available on synthesis of thiocoumarin in the presence of triethylamine. In this paper, we report herein the catalytic activity of triethylamine in the synthesis of thiocoumarin by condensation of *â*-oxodithioesters and salicylaldehyde derivatives under solvent free conditions.

EXPERIMENTAL

Materials and methods

Reagents were commercially purchased from Aldrich and used without further purification. Commercial solvents were used after distillation. Melting points are uncorrected and were determined in capillary tubes

on an apparatus containing silicon oil. The IR spectra were recorded on a Perkin Elmer 983 spectrometer in KBr pellets with absorption given in cm^{-1}. ^1H and ^{13}C NMR spectra were recorded respectively on a Varian EM-390 (300 MHz and 75.5 MHz) spectrometer using $CDCl_3$ as solvent. The Chemical shifts (äppm) and the coupling constants (Hz) are reported in the standard fashion with reference to internal tetramethyl silane (TMS). The MS spectra were recorded on a Jeol JMSD-300 spectrometer. Masses (MS) are reported in unit of mass over charge (m/z), the molecular or base peaks and relative intensities are indicated by (M) and (%) respectively. Elemental analyses were performed on a Carlo Erba's108 microanalyzer.

General procedure for the synthesis of compound (5a-m): Salicyldehyde/substituted salicylaldehyde (2.5 mmol), *â*-oxodithioester (2.5 mmol), and triethylamine (10 mol %) were heated at 90°C with stirring for 30-45min. Then the progress of the reaction was monitored by thin layer chromatography. After completion of the reaction, water was added, and the product was extracted with ethyl acetate. After the organic layer was dried (Na_2SO_4) and evaporated, the residue was recrystallized by ethyl acetate and hexane to afford pure yellow crystals of thiocoumarins **(5a-m)**.

3-Benzoyl-2*H*-chromene-2-thione (5a)

m.p.170-171°C, (lit. [10a] m.p. 169-170 °C); IR (KBr): 1246, 1604, 1663, 3031, 3053 cm^{-1}; ^1H NMR: δ 7.36-7.42 (m, 1H), 7.46-7.57 (m, 3H), 7.59-7.62 (m, 3H), 7.67-7.71 (m, 1H), 7.93-7.96 (m, 2H); ^{13}C NMR:δ 116.8, 119.9, 125.9, 128.6, 128.7, 129.6, 133.3, 133.5, 133.9, 135.7, 139.1, 157, 192.3, 193.5; EIMS *m/z* 266 (M^+). Anal. Calcd for $C_{16}H_{10}O_2S$: C, 72.16; H, 3.78; S, 12.04. Found: C, 72.31; H, 3.62; S, 11.95.

3-(4-Methoxybenzoyl)-6-bromo-2*H*-chromene-2-thione (5b)

m.p. 207-208°C. (lit. [10d] m.p. 208-209°C); IR (KBr): 1236, 1593, 1643, 3051 cm^{-1}; ^1H NMR: δ 3.8 (s, 3H), 6.87 (d, *J* = 6.6 Hz, 2H), 7.33 (d, *J* = 6.6Hz, 1H), 7.41 (s, 1H), 7.27-7.67 (m, 2H), 7.83 (d, *J* = 6.6Hz, 2H); ^{13}C NMR: δ 55.7, 114.2, 118.3, 118.6, 121.5, 128.3, 130.5, 131.3, 132.4, 135.7, 140.4, 155.7, 164.5, 190.3, 193.0; EIMS *m/z* 375 (M^+). Anal. Calcd for $C_{17}H_{11}BrO_3S$: C, 54.41; H, 2.95; S, 8.55. Found: C, 54.46; H, 2.95; S, 8.55.

3(4-Methylbenzoyl)-8-methoxy-2*H*-chromene-2-thione (5c)

m.p. 164-165°C. (lit. [10d] m.p.163-165°C); IR (KBr): 1277, 1604, 1659, 3058 cm^{-1}; ^1H NMR: δ 2.42 (s, 3H), 4.05 (s, 3H), 7.13-7.32 (m, 5H), 7.56 (s, 1H), 7.85 (d, *J* = 6.3Hz, 2H); ^{13}C NMR: δ 21.9, 56.3, 114.5, 119.5, 120.7, 125.8, 129.5, 129.8, 133.2, 133.4, 139.7, 145.1, 146.8, 192.0, 192.9; EIMS *m/z* 312 (M^+). Anal. Calcd for $C_{18}H_{16}O_3S$: C, 69.21; H, 5.16; S, 10.26. Found: C, 69.27; H, 5.13; S, 10.28.

3-(4-Chlorobenzoyl)-6-bromo-2*H*-chromene-2-thione (5d)

m.p. 194-196°C. (lit. [10d] m.p.195-196°C); IR (KBr):1235, 1587, 1663, 3053cm^{-1}; ^1H NMR: δ 7.43-7.55 (m, 3H), 7.74-7.87 (m, 5H); ^{13}C NMR: δ 118.5, 118.7, 121.3, 129.1, 129.2, 130.6, 130.9, 132.1, 133.8, 136.1, 139.7, 155.8, 190.7, 192.7; EIMS *m/z* 377 (M^+). Anal. Calcd for $C_{16}H_8BrClO_2S$: C, 50.62; H, 2.12; S, 8.45. Found: C, 50.69; H, 2.07; S, 8.47.

3(2-Acetylthiophene)-8-methoxy-2*H*-chromene-2-thione (5e)

m.p. 165-167°C. (lit. [10d] m.p.165-167°C); ^1H NMR: δ 3.83 (s, 3H), 6.75-6.79 (m, 2H), 7.07 (t, 1H), 7.25 (s, 1H), 7.40-7.42 (m, 1H), 7.65 (d, *J* = 3.9Hz, 1H), 7.83 (d, *J* = 2.7 Hz, 1H); ^{13}C NMR: δ 56.3, 111.5, 119.7, 120.2, 121.3, 125.1, 128.1, 134.7, 135.6, 138.7, 143.3, 144.7, 146.4, 185.7, 192.8; EIMS *m/z* 302 (M^+). Anal. Calcd for $C_{15}H_{10}O_3S_2$: C, 59.58; H, 3.33; S, 21.21. Found: C, 59.55; H, 3.33; S, 21.18.

3-(Furan-2-oyl)-8-methoxy-2H-chromene-2-thione (5f)

mp 169-171 °C. (lit. [10b] m.p.169-170°C); IR (KBr): 1170, 1257, 1559, 1601, 1659, 2929 cm^{-1}. ^1H NMR: δ 4.02 (s, 3H), 6.57 (dd, *J* = 1.5, 1.8 Hz, 1H), 7.29-7.11 (m, 4H), 7.59 (s, 1H), 7.62 (d, *J*=6.3 Hz, 1H), ^{13}C NMR: δ 56.3, 112.8, 114.7, 119.6, 120.1, 120.5, 125.7, 133.7, 138.4, 146.7, 147.5, 151.7, 179.7, 192.5: EIMS m/z 287 (M^+). Anal. Calcd for $C_{15}H_{10}O_4S$: C, 62.93; H, 3.52. Found: C, 62.69; H, 3.31.

3-(4-Acetylpyridine)-2*H*-chromene-2-thione (5g)

m.p.180-181°C. (lit.[10d] m.p.179-181°C); ^{1}H NMR: δ 7.66-7.81 (m, 4H), 7.99-8.01 (d, *J* = 6Hz, 1H), 8.16- 8.19 (d, *J* = 6.6Hz, 1H), 8.29-8.35 (m, 1H), 8.51 (s, 1H), 8.82-8.85 (m, 1H); ^{113}C NMR: δ 115.1, 116.5, 121.7, 122.1, 127.3, 129.3, 129.4, 130.7, 135.8, 142.3, 150.9, 192.2; EIMS *m/z* 267 (M^+). Anal. Calcd for $C_{15}H_9NO_2S$: C, 67.40; H, 3.39; N, 5.24; S, 12.00. Found: C, 67.39; H, 3.37; N, 5.31; S, 11.99.

3-Benzoyl-8-ethoxy-2H-chromene-2-thione (5h)

m.p. 163-165°C. (lit.[10b] m.p.164-165°C); IR (KBr): 1166, 1235, 1459, 1565, 1663, 2855, 2925 cm^{-1}. ^{1}H NMR: δ 1.53 (t, 3H). 4.27 (q, 2H), 7.10-7.18 (m, 2H), 7.26 (d, *J* = 6.3 Hz, 1H), 7.46 (t, 2H), 7.59 (s, 2H), δ 7.93 (d, *J* =7.2 Hz, 2H), ^{13}C NMR: δ 14.7. 65.1, 115.9, 119.5, 120.7, 125.7, 128.7, 129.5, 133.7, 133.9, 135.7, 139.4, 146.1, 147.2, 192.3, 192.9; EIMS (m/z): 311 (M^+). Anal. Calcd for $C_{18}H_{14}O_3S$: C, 69.66; H, 4.55. Found: C, 69.79; H, 4.49.

3-(4-Methylbenzoyl)-6-nitro-2H-chromene-2-thione (5i)

m.p. 233-235°C. (lit.[10b] m.p. 233-234°C); IR (KBr): 1153, 1291, 1547, 1607, 1663, 3725 cm^{-1}. ^{1}H NMR: δ 2.43 (s, 3H). 7.25-7.28 (m, 2H), 7.59-7.65 (m, 2H), 7.83 (d, *J* = 8.1 Hz, 2H), 8.49-8.47 (m, 2H), ^{13}C NMR: δ 21.8, 117.6, 120.1, 123.9, 127.4, 129.6, 129.8, 130.9, 132.5, 141.2, 144.6, 145.7, 159.3, 190.7, 192.1; EIMS (m/z): 326 (M^+). Anal. Calcd for $C_{17}H_{11}NO_4S$: C, 62.76; H, 3.41; N, 4.31. Found: C, 62.65; H, 3.35; N, 4.45.

3-(Thien-2-oyl)-6-bromo-2H-chromene-2-thione (5j)

m.p. 201-203°C. (lit.[10b] m.p. 202-203°C); IR (KBr): 1162, 1235, 1549, 1602, 1639, 3055 cm^{-1}. ^{1}H NMR: δ 7.13 (t, 1H), 7.37 (d, *J* = 8.7 Hz, 1H), 7.50 (s, 1H), 7.65 (d, *J* = 3.3 Hz, 1H), 7.69-7.78 (m, 3H), ^{13}C NMR: δ 118.3, 118.5, 121.2, 128.4, 130.7, 131.1, 131.2, 135.1, 135.9, 139.6, 142.6, 155.7, 183.7, 192.3; EIMS (m/z): 352 (M^+). Anal. Calcd for $C_{14}H_7BrO_2S_2$: C, 47.87; H, 2.01. Found: C, 47.63; H, 2.32.

3-(Furan-2-oyl)-6-bromo-2H-chromene-2-thione (5k)

m.p. 197-198°C. (lit.[10b] m.p. 198-199°C); IR (KBr): 1174, 1240, 1363, 1461, 1553, 1639, 3118 cm^{-1}. ^{1}H NMR: δ 6.61-6.59 (m, 1H). 7.28 (d, *J* = 3.3 Hz, 1H), 7.39 (d, *J* = 8.7 Hz, 1H), 7.51 (s, 1H), 7.65 (s,1H), 7.75-7.71 (m, 2H), ^{13}C NMR: δ 112.9, 118.3, 118.4, 120.2, 121.2, 130.6, 131.5, 135.9, 138.8, 147.6, 151.7, 155.7, 179.0, 192.3.

3(4-Chlorobenzoyl)-8-methoxy-2*H*-chromene-2-thione (5l)

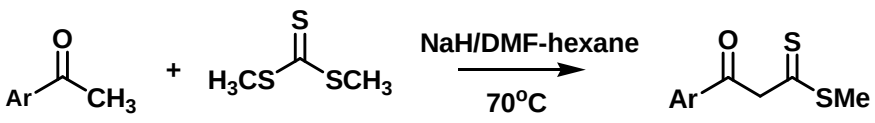
m.p. 173-175°C (lit.[10b] mp 174-175°C); ^{1}H NMR: δ 3.95 (s, 3H), 7.07-7.14 (m, 2H), 7.19-7.25 (m, 1H), 7.36 (d, *J* = 5.4 Hz, 2H), 7.55 (s, 1H), 7.77 (d, *J* = 6.3Hz, 2H); ^{13}C NMR: δ 56.3, 114.7, 119.7, 120.8, 125.9, 129.1, 130.7, 134.1, 134.1, 139.1, 140.3, 146.8, 147.1, 191.3, 192.8; EIMS *m/z* 330 (M^+). Anal. Calcd for $C_{17}H_{11}ClO_3S$: C, 61.73; H, 3.35; S, 9.69. Found: C, 61.55; H, 47; S, 9.59

3(4-Methoxybenzoyl)-8-methoxy-2*H*-chromene-2-thione (5m)

m.p. 141-143°C. (lit.[10d] mp 140-142°C); IR (KBr): 1274, 1593, 1651, 3051 cm^{-1}; ^{1}H NMR: δ 3.80 (s, 3H), 3.92 (s, 3H), 6.85 (d, *J* = 6.6 Hz, 2H), 7.04-7.11 (m, 2H), 7.19-7.24 (m, 1H), 7.48 (s, 1H), 7.83 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR: δ 55.6, 56.3, 114.1, 114.42, 119.5 120.7, 125.8, 128.6, 132.2, 133.3, 139.8, 146.8, 146.9, 164.3, 190.9, 193.0; EIMS *m/z* 326 (M^+). Anal. Calcd for $C_{18}H_{14}O_4S$: C, 66.24; H, 4.32; S, 9.82. Found: C, 66.25; H, 4.31; S, 9.85.

RESULTS AND DISCUSSION

The desired β-oxodithioesters[15] 3a-g (TABLE 1)

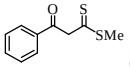
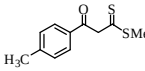
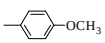
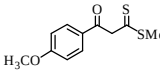
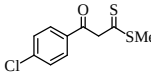
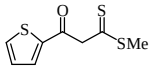
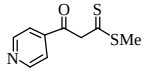
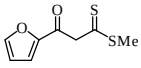


(1a-g) (2) (3a-g)

Scheme 1 : Synthesis of β-oxodithioesters

were synthesized in good yields by stirring ketones **(1)** with (*S,S*)-dimethyl trithiocarbonate **(2)** in the presence of NaH in DMF-hexane (1:4) mixture at room temperature (Scheme 1, TABLE -1).

TABLE 1 : Synthesis of diverse secondary amines via reductive amination of different aldehydes catalyzed by molecular iodine[a]

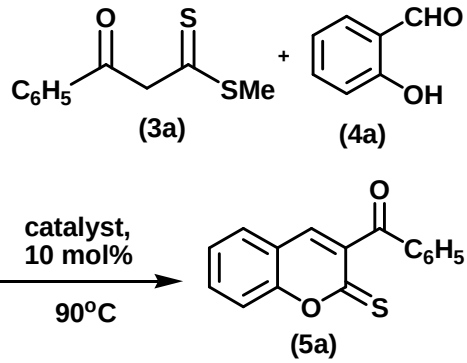
Entry	Ar	Dithioesters	Mp(°C)	Yield[a] (%)
1		 3a	57-58	72
2		 3b	54-55	75
3		 3c	74-75	73
4		 3d	72-73	71
5		 3e	49-50	55
6		 3f	71-72	57
7		 3g	51-52	59

[a]**Yield of isolated product**

To establish the reaction conditions for the triethylamine catalyzed Knoevenagel condensation, the reaction of salicylaldehyde (2.5 mmol) with *β*-oxodithioesters (2.5 mmol) was taken as model reaction (entry 1, TABLE 3). Our initial experiment focused on optimizing the reaction conditions by taking various amounts of triethylamine in the range of 5-15 mol% and temperatures in the range of 80-100°C. It was observed that only 10 mol% of triethylamine could effectively catalyzed the reaction at 90°C in 30 mins. An increase in the catalyst showed no substantial improvement in the yield, though a slight improvement in the reaction time was observed.

To evaluate the scope of this catalytic system, different base catalysts were used guided by the template reaction of salicylaldehyde **(4a)** and *β*-oxodithioester **(3a)**. Triethylamine was found to be the best catalyst, giving the highest yield of the product under a short duration of 30 min. The pure products are obtained by simply recrystallisation with ethanol. It was also observed that piperidine, pyrrolidine and morpholine gave good yields of the product but it requires longer heating (1.5-3.5h) while NaOH, NaOEt and NaOMe gave poor yields of the desired products with longer heating (4.5-6.5h) and the reaction is not clean, requires chromatographic separation (TABLE 2). Prominent among the advantages of this new procedure are easy workup, good yields, short reaction times, and operational simplicity.

TABLE 2 : Evaluation of different catalytic systems in optimization of the coumarin synthesis[a]



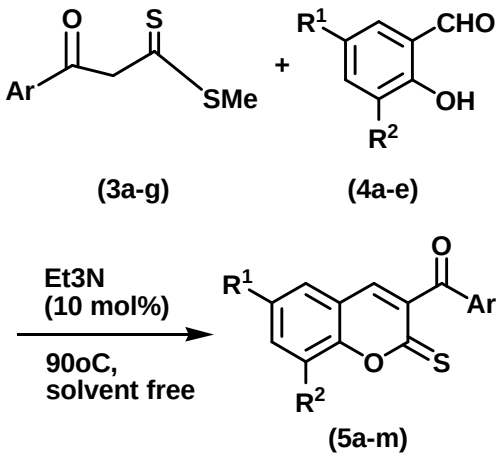
Entry	Catalyst	Time	Yield[b](%)
1	Triethylamine	30min	95
2	Pyrollidine	3h	73
3	Morpholine	3.5h	67
4	Piperidine	1.5h	91
5	NaOH	4.5h	55
6	NaOMe	6h	43
7	NaOEt	6.5h	39

[a]**salicylaldehyde 4a (2.5 mmol), β-oxodithioesters 3a (2.5 mmol), catalyst (10 mol %);** [b]**isolated yield.**

It is noteworthy to mention that using different solvents such as DMSO, DMF, THF, and acetonitrile did not improve the yields and thus we have optimized the reaction condition at 90°C for 30 min without any solvent. After optimizing the reaction condition, the same process was successfully extended to different *β*-oxodithioesters **(3b-g)** and different substituted 2-hydroxy benzaldehydes to afford coumarin **(5b-m)** in good to excellent yields. The results are summarized in TABLE 3.

The reaction proceeds smoothly in a short time and the methodology was found equally facile in all the aryl and heteroaryl *β*-oxodithioesters. All products are known compounds, which were characterized by IR and ^{1}H NMR, ^{13}C NMR spectral data and their mps compared with literature reports.

TABLE 3 : Triethylamine catalyzed preparation of coumarins[a]



Entry	Ar	R^1	R^2	Product	Yield[b](%)
1	Ph	H	H	5a	96
2	4-$MeOC_6H_5$	Br	H	5b	86
3	4-MeC_6H_5	H	OMe	5c	93
4	4-ClC_6H_5	Br	H	5d	90
5	2-thienyl	H	OMe	5e	89
6	2-furyl	H	OMe	5f	91
7	4-pyridyl	H	H	5g	87
8	Ph	H	OEt	5h	90
9	4-MeC_6H_5	NO_2	H	5i	83
10	2-thienyl	Br	H	5j	87
11	2-furyl	Br	H	5k	95
12	4-ClC_6H_5	H	OMe	5l	96
13	4-$MeOC_6H_5$	H	OMe	5m	93

[a]**Reaction conditions: 3 (2.5 mmol), 4 (2.5 mmol), triethylamine (10mol %), 90°C, 30-45min;** [b]**Isolated yield.**

CONCLUSION

In conclusion, we have successfully demonstrated triethylamine catalysed synthesis of thiocoumarins under solvent free conditions. The mild reaction conditions, high yields, operational simplicity and shorter reaction period illustrate the good synthetic utility of this new method.

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