JOC Notes

Application of β-Oxodithioesters in Domino and Multicomponent Reactions: Facile Route to Dihydropyrimidines and Coumarins

Okram Mukherjee Singh* and Nepram Sushuma Devi

Department of Chemistry, Manipur University, Canchipur-795003, India

ok_mukherjee@yahoo.co.in

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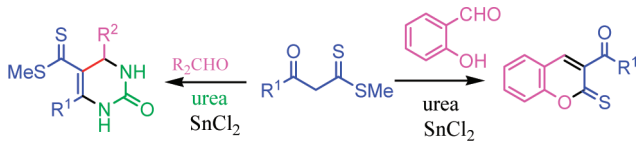

A facile route to hitherto unknown 5-methylmercaptothiocarbonyl-4-aryl-3,4-dihydropyrimidin-2(1*H*)-ones and substituted 2*H*-chromene-2-thiones has been developed. $SnCl_2$-catalyzed cyclocondensation of β-oxodithioesters with a variety of readily accessible aldehydes and urea affords the dihydropyrimidinones. The methodology involves the three-component Biginelli reaction. On the other hand, substituted salicylaldehyde and β-oxodithioesters reacted under the same condition to afford the substituted 2*H*-chromene-2-thiones in high yields.

Domino processes and multicomponent reactions (MCRs), in an environmentally benign and atom-economic fashion, play important roles in organic synthesis, especially for the synthesis of bioactive heterocycles.[1] Polyfunctionalized dihydropyrimidines are prepared by a multicomponent reaction that was first reported by Biginelli in 1893, involving a one-pot condensation of an aldehyde, β-ketoester, and urea under strongly acidic conditions.[2] Considerable interest in this transformation has steadily increased over the past decade[3] owing to their remarkable pharmacological properties such as calcium channel modulatory activity,[4a,b] inhibiting the platelet activating factor,[4c] and selectively antagonizing the human R1A receptors,[4d] to name a few. This has led to the development of several new methods[5] for promoting the Biginelli reaction, including solid phase reactions[6a−c] and microwave irradiation.[6d]

The Lewis acid-catalyzed Biginelli reaction has also achieved considerable success. The use of a number of catalysts such as BF_3Et_2O,[7a] $FeCl_3·6H_2O$,[7b] LiBr,[7c] $ZnCl_2$,[7d] $BiCl_3$,[7e] $LaCl_3·7H_2O$,[7f] $Mn(OAC)_3·2H_2O$,[7g] $InCl_3$,[7h] $Cu(OTf)_2$,[7i] lanthanide triflates,[7j] $ZrCl_4$,[7k] Yb^{III} resin,[7l] $CeCl_3·7H_2O$,[7m] $LiClO_4$,[7n] $RuCl_3$,[7o] SmI_2,[7p] $Sr(OTf)_2$,[7q] $La(OTf)_3$, or $Yb(OTf)_3$ in the presence of a chiral Yb catalyst[7r] has been reported to be effective for this one-pot reaction.

However, to our knowledge the new methodologies in all these reported methods use only the β-ketoesters such as ethyl acetoacetate or methyl acetoacetate and variations are designed only in the structures of the substituted aldehydes. As a result, the structures of known dihydropyrimidines either in improved yields or by the application of new techniques are always reported.[7a−r] We are reporting herein the application of β-oxodithioesters[8] in Biginelli reactions under solvent-free conditions to synthesize the hitherto unreported dihydropyrimidinones in excellent yields. Also described herein is an expedient synthesis of a novel series of coumarines using β-oxodithioesters as an unprecedented substrate for the Knovenagel type of cyclocondensation.

β-Oxodithioesters **3** are generally prepared by reacting any active methylene compound with CS_2 in the presence of a suitable base followed by alkylation with either dimethylsulfate or methyl iodide. This method gives poor yields and also mixtures of dithioesters and ketene dithioacetals. Thus improved yields of β-oxodithioesters are obtained by treating active methylene compounds **1** with (*S*,*S*)-dimethyl trithiocarbonate

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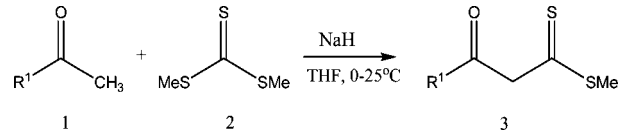
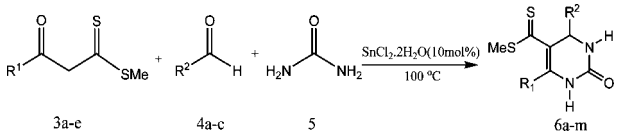
SCHEME 1. Synthesis of β-Oxodithioesters



1 2 3

TABLE 1. $SnCl_2$ Catalyzed Multicomponent Reaction: Preparation of Dihydropyrimidines[a]

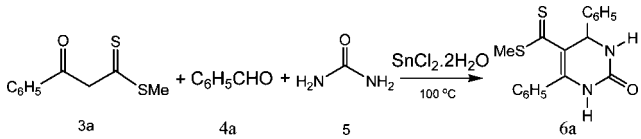


3a-e 4a-c 5 6a-m

entry	R^1	R^2	yield (%)[b]	product
1	C_6H_5	C_6H_5	75	**6a**
2	C_6H_5	4-$CH_3OC_6H_4$	75	**6b**
3	C_6H_5	4-ClC_6H_4	72	**6c**
4	4-$CH_3OC_6H_5$	C_6H_5	71	**6d**
5	4-$CH_3OC_6H_4$	4-$CH_3OC_6H_4$	73	**6e**
6	4-$CH_3OC_6H_4$	4-ClC_6H_4	80	**6f**
7	4-ClC_6H_4	C_6H_5	75	**6g**
8	4-ClC_6H_4	4-$CH_3OC_6H_4$	82	**6h**
9	4-ClC_6H_4	4-ClC_6H_{54}	76	**6i**
10	4-$CH_3C_6H_4$	C_6H_5	70	**6j**
11	4-$CH_3C_6H_4$	4-$CH_3OC_6H_4$	73	**6k**
12	4-$CH_3C_6H_4$	4-ClC_6H_4	75	**6*l***
13	CH_3	C_6H_5	70	**6m**

[a] Reaction conditions: **3** (1.0 mmol), **4** (1.0 mmol), **5** (1.0 mmol), $SnCl_2$ (10 mol %), 100 °C, 1.0−5.0 h. [b] Isolated yield

SCHEME 2. Synthesis of 5-Methylmercaptothiocarbonyl-4,6-diphenyl-3,4-dihydropyrimidin-2(1*H*)-one



3a 4a 5 6a

2[9] in the presence of NaH (Scheme 1). We have been using these β-oxodithioesters **3** extensively as the precursors of ketene *S*,*S*-, *N*,*S*-, and *N*,*N*-acetals.[10]

The reaction of benzaldehyde **4a**, urea **5**, and β-oxodithioester **3a** was first tested with use of 20 mol % stannous chloride as the catalyst at room temperature. After 20 min the whole reaction mixture forms a paste that made it impossible to continue the stirring under room temperature. It was then warmed to 100 °C, when the paste turned to a homogeneous liquid. Stirring was continued at this temperature for 1 h (monitored by TLC). The reaction went smoothly and the corresponding dihydropyrimidine **6a** was obtained in 75% yield (Table 1, entry 1). The yield was still as high as 75% even when the amount of $SnCl_2$ was reduced from 20 mol % to 10 mol % (Scheme 2).

The same process was successfully extended to a wide range of structurally varied aldehydes **4b**,**c**, urea **5**, and β-oxodithioesters **3b**−**e** to afford the corresponding hitherto unreported dihydropyrimidinones **6b**−**m** in good yields (Table 1). The use of 5 mol % of catalyst caused a slight decrease in the yield.

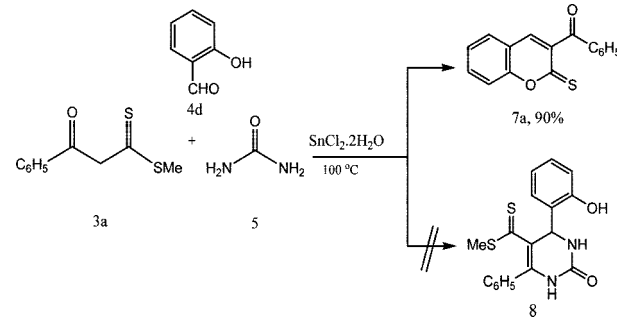
To evaluate the scope of this catalytic system, the range of metal salts was extended to various metal halides guided by the template reaction of benzaldehyde **4a**, urea **5**, and β-oxodithioester **3a**. $SnCl_2$ was found to be the best catalyst, giving the highest yield of the product under a short duration of 1 h. It was also observed that $ZnCl_2$ and $FeCl_3$ gave good yields of the product, while $MgCl_2$, $BiCl_3$, and $LaCl_3$ gave poor yields of the desired products (Table 2).

TABLE 2. Evaluation of Different Catalytic Systems in Optimization of the Dihydropyrimidine Synthesis[a]

entry	catalyst	time (h)	yield (%)
1	$SnCl_2$	1	75
2	$ZnCl_2$	3	55
3	$FeCl_3$	2	65
4	$AlCl_3$	6	40
5	$CuBr_2$	6	40
6	CuI_2	6	45
8	$MgCl_2$	12	10
9	$BiCl_3$	10	15
	$10LaCl_3$	8	10

[a] Benzaldehyde **4a** (5.0 mmol), urea (5.1 mmol), catalyst (10 mol %), β-oxodithioester **3a** (5.0 mmol).

SCHEME 3. $SnCl_2$-Catalyzed Reaction of Salicylaldehyde with β-Oxodithioester and Urea



A control experiment in the absence of the catalyst provided no product. Moreover, 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 100 °C for 1 h under solvent-free condition. Electronic variation on aryl aldehydes caused no appreciable changes in the efficiency of the condensations.

Next we evaluated the scope of this process by employing *o*-hydroxybenzaldehyde in the multicomponent reaction. Previously, we were expecting the formation of the corresponding *o*-hydroxyphenyl-substituted dihydropyrimidine **8.** Replacement of these β-oxodithioesters by β-ketoesters such as methyl acetoacetate and ethyl acetoacetate yielded the corresponding *o*-hydroxyaryl-substituted dihydropyrimidines under similar conditions. Literature reports[6] also support the obtention of dihydropyrimidines from β-ketoesters (methyacetoacetate/ethylacetoacetate), salicylaldehyde, and urea under these similar Biginelli cyclocondensations.

Surprisingly, during our investigations, we could not trace any such dihydropyrimidines **8** and only the coumarins **7** were obtained exclusively in good yields (Scheme 3). The structures were confirmed by spectroscopic and analytical data.[11] The absence of nitrogen in the CHN analyses gave us a clue to the structural elucidation of the respective hitherto unknown coumarins, which were confirmed by the mass data. In our final series of experiments we set out to examine the synthesis of

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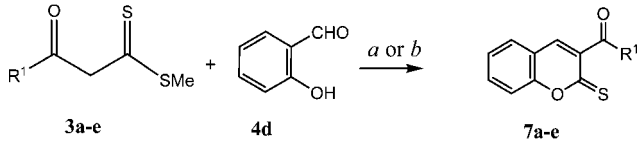
(11) The structures of all the new compounds were confirmed with the help of spectral and analytical data.

TABLE 3. Synthesis of 2*H*-Chromene-2-thiones from *β*-Oxodithioesters and Salicylaldehyde[a,b]



entry	R^1	yield (%)[c]	Yield (%)[d]	product
1	C_6H_5	90	70	**7a**
2	4-$CH_3OC_6H_4$	95	72	**7b**
3	4-ClC_6H_4	90	70	**7c**
4	4 -$CH_3C_6H_4$	95	75	**7d**
5	CH_3	80	72	**7e**

[a] Reaction conditions: **3** (1.0 mmol), **4** (1.0 mmol), **5** (1.0 mmol), $SnCl_2$ (20 mol %), 100 °C, 1.0−5.0 h. [b] Reaction conditions: **3** (1.0 mmol), **4** (1.0 mmol), $SnCl_2$ (20 mol %), 100 °C, 1.0−5.0 h. [c] Isolated yields in the presence of urea. [d] Isolated yields in the absence of urea

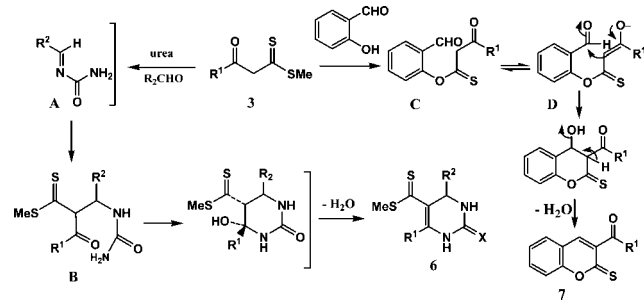
chromenes in the absence of urea. Thus salicylaldehyde **4d** and *β*-oxodithioesters **3** in the absence of urea were submitted to $SnCl_2$-catalyzed intramolecular ring cyclizations. The same chromene compounds **7a**−**e** were obtained with lower yields. The role of urea in these transformations is not very clear, even though higher yields of chromenes are obtained in their presence. Probably the combination of urea with the catalyst enhanced the domino process through the formation of the imino complex of the aldehyde functionality.

The coumarin synthesis was optimized by stirring the mixture of *β*-oxodithioester, *o*-hydroxybenzaldehyde, and urea at 100 °C in the presence of a catalytic amount of $SnCl_2$ (20 mol %) for a certain period of time required to complete the reaction (TLC). The reaction mixture was then poured into crushed ice, and the solid product was separated, filtered, and recrystallized from ethanol. To study the generality of this process, a few examples illustrating this novel and general method for the synthesis of chromenes were studied and are summarized in Table 3. As can be seen from Table 3, various *β*-oxodithioesters **3a**−**e** were treated with salicylaldehyde **4d** to give the corresponding coumarins **7a**−**e** in good to excellent yields.

Coumarins constitute an important class of oxygen heterocycles possessing a wide range of biological activities[12] such as antifungal, antihypertensive, antioxidant, anti-inflammatory, and antimicrobial activity.[13] They are abundant in numerous naturally occurring products, including edible vegetables and fruits.[14]

On the basis of all the results obtained, a plausible mechanism for the synthesis of 5-methylmercaptothiocarbonyl-4-aryl-3,4-dihydropyrimidin-2(1*H*)-ones **6** and substituted 2*H*-chromen-2-thiones **7** is presented in Scheme 4. For dihydropyrimidines, the first step in this reaction, the acid-catalyzed formation of an acyl imine intermediate **A** formed by reaction of the aldehyde with urea, is the key rate-limiting step. Interception of the

SCHEME 4. Plausible Mechanism for the Synthesis of Dihydropyrimidines 6 and Chromenes 7 from *β*-Oxodithioesters 3



iminium ion by *β*-oxodithioester **3** produces an open-chain ureide **B** that subsequently cyclizes to the dihydropyrimidinones **6**. For coumarins, the overall transformation commences from the condensation product **C** of *β*-oxodithioester **3** and *o*-hydroxy benzaldehyde, mediated by $SnCl_2$, to generate enolate **D**, which participates in subsequent intramolecular aldol condensation to give **7**.

In conclusion, we have successfully demonstrated the synthetic applications of *β*-oxodithioesters in multicomponent reactions to synthesize the hitherto unreported 5-methylmercaptothiocarbonyl-4-aryl-3,4-dihydropyrimidin-2(1*H*)-ones and also 2*H*-chromen-2-thiones. A particularly attractive feature of this approach is that depending on the structure of aldehydes, two important bioactive heterocycles can be synthesized from the same *β*-oxodithioester under the same reaction conditions. Both the reaction approach avoiding the use of solvent and the ready availability of a wide range of substrates from cheap starting materials make this new strategy highly attractive in diversity oriented synthesis.

Experimental Section

General Procedure for Synthesis of Dihydropyrimidine-2(1*H*)-ones 6. A mixture of aldehyde (5 mmol), urea (5 mmol), *β*-dithioester (5 mmol), and $SnCl_2$ (0.4 mmol, 20 mol %) was heated at 100 °C with stirring for 1−4 h. Water (30 mL) was then added and the mixture extracted with chloroform (20 mL). The organic layer was dried with anhydrous Na_2SO_4 and evaporated. The crude product was subjected to column chromatography on SiO_2, using increasing amounts of ethyl acetate in petroleum ether as eluent. All new compounds were fully characterized by spectroscopy, mass spectrometry, and elemental analysis.

5-Methylmercaptothiocarbonyl-4,6-diphenyl-3,4-dihydropyrimidin-2(1*H*)-one (6a): Bright yellow powder. Mp 198−200 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 2.30 (s, 3H), 5.87 (d, J = 2.7 Hz, 1H), 6.32 (s, 1H, NH), 7.28−7.44 (m, 10H), 7.61 (s, 1H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ ppm) 20.5, 60.9, 119.4, 127.2, 128.1, 128.2, 128.7, 128.8, 129.9, 134.6, 136.5, 141.7, 152.6, 227.0; IR (KBr) (ν max, cm^{-1}) 1226, 1629, 1700, 3084, 3198 cm^{-1}; MS *m*/*z* 340 (M^+). Anal. Calcd for $C_{18}H_{16}N_2OS_2$: C, 63.50; H, 4.74; N, 8.23; S, 18.84. Found: C, 63.58; H, 4.79; N, 8.30; S, 18.74.

5-Methylmercaptothiocarbonyl-4-(4-methoxyphenyl)-6-phenyl-3,4-dihydropyrimidin-2(1*H*)-one (6b): Bright yellow powder. Mp 182−183 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 2.31 (s, 3H), 3.79 (s, 3H), 5.83 (d, J = 2.1 Hz, 1H), 6.17 (s, 1H, NH), 6.83 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 7.37−7.46 (m, 5H), 8.07 (s, 1H, NH); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ ppm) 20.4, 55.2, 60.4,113.9, 119.6,128.2, 128.4, 128.8, 129.8, 134.1, 134.6, 136.2, 152.7, 159.3, 227.2; IR (KBr) (ν max, cm^{-1}) 1244, 1610, 1691, 3095, 3213 cm^{-1}; MS *m*/*z* 370 (M^+). Anal. Calcd for $C_{19}H_{18}N_2O_2S_2$:

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C, 61.60; H, 4.90; N, 7.56; S, 17.31. Found: C, 61.50; H, 4.84; N, 7.53; S, 17.44.

General Procedure for the Synthesis of 2*H*-Chromene-2-thiones 7: Method A: In the Absence of Urea. Salicyldehyde (2.5 mmol), β-dithioester (2.5 mmol), and $SnCl_2$ (0.4 mmol, 20 mol %) were heated at 100 °C with stirring for 1 h. Then 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 products **7**. In cases where further purification was required, the crude products were subjected to column chromatography on SiO_2, using increasing amounts of ethyl acetate in hexanes as eluent.

Method B: In the Presence of Urea. A mixture of salicyldehyde (5 mmol), β-dithioester (5 mmol), urea (5 mmol) and $SnCl_2$ (0.4 mmol, 20 mol %) was heated at 100 °C with stirring for 1 h. After cooling, the reaction mixture was poured into cold water. The solid was suction filtered, washed with cold water (20 mL), filtered, and recrystallized from ethyl acetate or ethanol to afford pure product. Selected physical data for compounds follow.

3-Benzoyl-2*H*-chromene-2-thione (7a): Yellow crystals. Mp 170−171 °C. ^{1}H NMR (300 MHz, CDCl3, δ ppm) 7.37−7.42 (m, 1H), 7.45−7.56 (m, 3H), 7.59−7.66 (m, 3H), 7.68−7.71 (m, 1H), 7.94−7.96 (m, 2H); ^{13}C NMR(75.5 MHz, $CDCl_3$, δ ppm) 116.7, 119.9, 125.9, 128.6, 128.7, 129.6, 133.2, 133.6, 133.9, 135.6, 139.1, 157, 192.3, 193.6; IR (KBr) (ν max, cm^{-1}) 1246, 1604, 1662, 3032, 3052 cm^{-1}; MS *m*/*z* 266 (M^+). Anal. Calcd for $C_{16}H_{10}O_2S$: C, 72.16; H, 3.78; S, 12.04. Found: C, 72.10; H, 3.72; S, 11.84.

3-(4-Methoxybenzoyl)-2*H*-chromene-2-thione (7b): Yellow crystals. Mp 187−189 °C. ^{1}H NMR (300 MHz, $CDCl_3$, δ ppm) 3.85 (s, 3H), 6.93 (d, J = 8.7 Hz, 2H), 7.36−7.43 (m, 1H), 7.53−7.71 (m, 4H), 7.89 (d, J = 8.7 Hz, 2H); ^{13}C NMR (75.5 MHz, $CDCl_3$, δ ppm) 55.5, 114, 116.7, 120, 125.9, 128.4, 128.6, 132.2, 133, 133.2, 139.5, 157, 164.3, 190.8, 193.8; IR (KBr) (ν max, cm^{-1}) 1242, 1597, 1654, 3018, 3055 cm^{-1}; MS *m*/*z* 296 (M^+). Anal. Calcd for $C_{17}H_{12}O_3S$: C, 68.90; H, 4.08; S, 10.82. Found: C, 68.88; H, 3.98; S, 10.79.

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Supporting Information Available: Full experimental details and spectroscopic data (copies of ^{1}H and ^{13}C NMR). This material is available free of charge via the Internet at http://pubs.acs.org.

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