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Facile synthesis of substituted dihydro-1,4-dithiins and -1,4-dithiepins from α-oxo ketene cyclic dithioacetals

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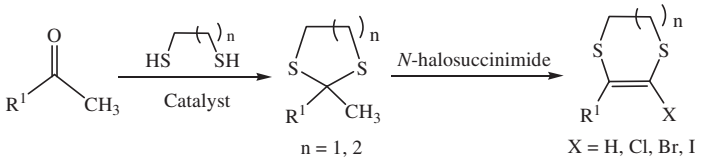
Abstract—A novel and facile synthesis of substituted 2,3-dihydro-1,4-dithiins and 6,7-dihydro-5*H*-1,4-dithiepins based on the reactions of α-bromo/hydroxy ketones with α-oxo ketene cyclic dithioacetals has been developed. A general mechanism for the reactions is proposed.

Thioacetals have been extensively investigated as carbonyl protection groups and versatile intermediates in the synthesis of multi-functional complex molecules and natural products.[1,2] To date, a variety of methods are available for the preparation of thioacetals from carbonyl compounds or *O*,*O*-acetals with thiols employing various acidic catalysts.[3,4] However, the high stability of thioacetals makes their deprotection requiring drastic conditions or toxic reagents such as mercury salts, heavy metals, ceric ammonium nitrate (CAN), SeO_2, or $Pb(OAc)_4$.[5–7] Recently, a number of Lewis acids such as $Bi(NO_3)_3$, clay–$Fe(NO_3)_3$, and some nonmetallic reagents including the oxide of nitrogen, triethyloxonium tetrafluoroborate, and methyl fluorosulfonate have also been applied for the selective deprotection of dithioacetals.[8–10] During the course of these studies, a range of ring-expansion reactions of 1,3-dithiolanes and 1,3-dithianes to produce substituted dihydro-1,4-dithiins and -1,4-dithiepins had been achieved in the presence of $TeCl_4$, WCl_6, $MoCl_5$, SiO_2–Cl, *o*-iodoxybenzoic acid, *m*-chloroperbenzoic acid, 2,4,6-trichloro-1,3,5-triazine, halogens (Br_2 and Cl_2), or *N*-halosuccinimides (NBS, NCS, and NIS) (Scheme 1).[11–13] Indeed, 2,3-dihydro-1,4-dithiins were reported to undergo oxidation easily, affording dienophiles for the convenient use in Diels–Alder reactions.[14] Also, 2,3-dihydro-1,4-dithiins have proven to be useful precursors to mimic cis-configurated double bonds, in the preparation of simple alkenes and other unsaturated compounds as well.[15] Additionally, some derivatives of the dihydro-1,4-dithiins and -1,4-dithiepins show activities as nonpeptide antagonists of human Galanin Hgal-1 receptor.[16]

Recently, we developed a novel thioacetalization reaction using nonthiolic odorless cyclic ketene dithioacetals, for example, 2-(2-chloro-1-(1-chloroethenyl)-2-propenylidene)-1,3-dithiane and 3-(1,3-dithian-2-ylidene)pentane-2,4-dione, as 1,3-propanedithiol equivalents.[17] During the course of our studies on the thioacetalization of α-bromo/hydroxy carbonyl compounds using 2-(1,3-dithiolan/dithian-2-ylidene)-3-oxobutanoic acids **1a/1b** as dithiol equivalents, surprisingly, we found that the



Scheme 1.

Keywords: Acetyl chloride; 2,3-Dihydro-1,4-dithiins; 6,7-Dihydro-5*H*-1,4-dithiepines; α-Oxo ketene cyclic dithioacetals.
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main products were substituted dihydro-1,4-dithiins and -1,4-dithiepins. We herein wish to report the new findings on these investigations.

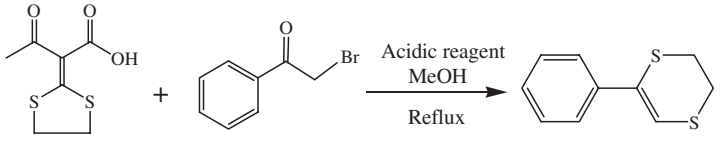
There are many reports including some review articles available regarding the synthesis and application of α-oxo ketene dithioacetals.[18] According to the procedure described in the literature,[19] ethyl 2-(1,3-dithiolan/dithian-2-ylidene)-3-oxobutanoate were prepared from ethyl 3-oxobutanoate, carbon disulfide, 1,2-dibromoethane/1,3-dibromopropane in the presence of K_2CO_3 in nearly quantitative yields (99%). They were then converted into **1a** and **1b** via a hydrolysis process, respectively.[18] It is worth noting that compounds **1a** and **1b** are odorless solids and stable under ambient atmosphere. Also they are associated with some synthetic advantages including simple procedure, mild conditions, high yields and commercial starting materials without foul smell.

The initial study was performed on the reaction between **1a** and 2-bromo-1-phenylethanone **2a** (Table 1, entry 1) via a very simple procedure described as following: **1a** (1.0 mmol), **2a** (1.0 mmol), methanol (10 mL), and acetyl chloride (1.5 mmol) were added into a flask equipped with a condenser. The mixture was heated to reflux and stirred for about 10 h when **2a** was consumed as indicated by TLC. The reaction mixture was cooled to ambient temperature and neutralized with 10% aq $NaHCO_3$. After extractive work-up, chromatography over silica gel (eluent: petroleum ether) afforded a pure product in 56.5% yield, which was identified as 5-phenyl-2,3-dihydro-1,4-dithiin **3a** (mp: 59–61 °C).

To optimize the yield of **3a**, a range of reactions between **1a** and **2a** were carried out under various conditions, and some results are summarized in Table 1. Apparently, the amount of acetyl chloride affects the rate of the cleavage of **1a** and the subsequent reaction with **2a** in methanol (entries 1–4). The reaction rate is significantly speeded up when increasing the feed ratio of acetyl chloride/**1a**. It appears that there might be a critical ratio for the reaction, in other words, the reaction rate changes very slightly beyond the ratio. The high reaction rate is attained when the reaction proceeds with a 1:5 molar ratio of **1a**/acetyl chloride (entry 3). An appropriately excess of **1a** to **2a** can result in slightly higher yield (entries 3 and 5). The reaction can proceed in ethanol to afford **3a** (entry 7), but fails in benzene, THF, or CH_2Cl_2 (entries 8–10). For the comparison with acetyl chloride, other acidic reagents such as HCl(aq) and H_3PO_4 were selected and employed in the novel reactions (entries 11 and 12). The results reveal that acetyl chloride is the most effective reagent among those examined. It should be mentioned that only very faint odor of dithiol can be perceived during both reaction and work-up process.

Under the conditions described in Table 1 (entry 5), a range of reactions were performed on a variety of α-bromo ketones **2** with compounds **1a** and **1b**.[20] All reactions proceed smoothly under the essentially mild acidic conditions to afford the corresponding substituted dihydro-1,4-dithiins and -1,4-dithiepins **3b**–**k** in good yields, and some results are listed in Table 2. The results exhibit the scope and generality of the reaction with respect to different α-bromo ketones **2**. To extend the scope of this novel protocol, the reactions of **1** with other carbonyl compounds were examined. To our delight, when 2-hydroxy-1,2-diphenylethanone was subjected to identical conditions, the substituted dihydro-1,4-dithiins and -1,4-dithiepins **3l** and **3m** were obtained in 72.5% and 70.1% yields, respectively (Table 2, entries 12 and 13). Therefore, we present here a convenient and facile protocol for the synthesis of dihydro-1,4-dithiins and -1,4-dithiepins. To the best of our knowledge, this method

Table 1. Reactions between 2-(1,3-dithiolan-2-ylidene)-3-oxobutanoic acid **1a** and 2-bromo-1-phenylethanone **2a**

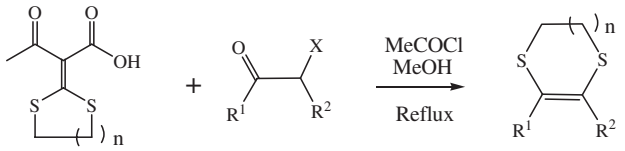


1a **2a** **3a**

Entry	Acidic reagent	**1a**/**2a**/Acidic reagent[a]	Solvent (h)	Time (h)	Yield (%)[b]
1	CH_3COCl	2:2:3	MeOH	10.0	56.5
2	CH_3COCl	1:1:3	MeOH	8.0	58.1
3	CH_3COCl	1:1:5	MeOH	5.0	58.2
4	CH_3COCl	1:1:10	MeOH	4.5	59.4
5	CH_3COCl	1.2:1:5	MeOH	5.0	60.1
6	CH_3COCl	2:1:5	MeOH	5.0	61.3
7	CH_3COCl	1.2:1:5	EtOH	8.0	47.7
8	CH_3COCl	1.2:1:5	Benzene	5.0	0
9	CH_3COCl	1.2:1:5	THF	5.0	0
10	CH_3COCl	1.2:1:5	CH_2Cl_2	5.0	0
11	HCl(aq)	1.2:1:5	MeOH	5.0	26.8
12	H_3PO_4	1.2:1:5	MeOH	5.0	0

[a] Molar ratio.
[b] Isolated yields after silica gel chromatography.

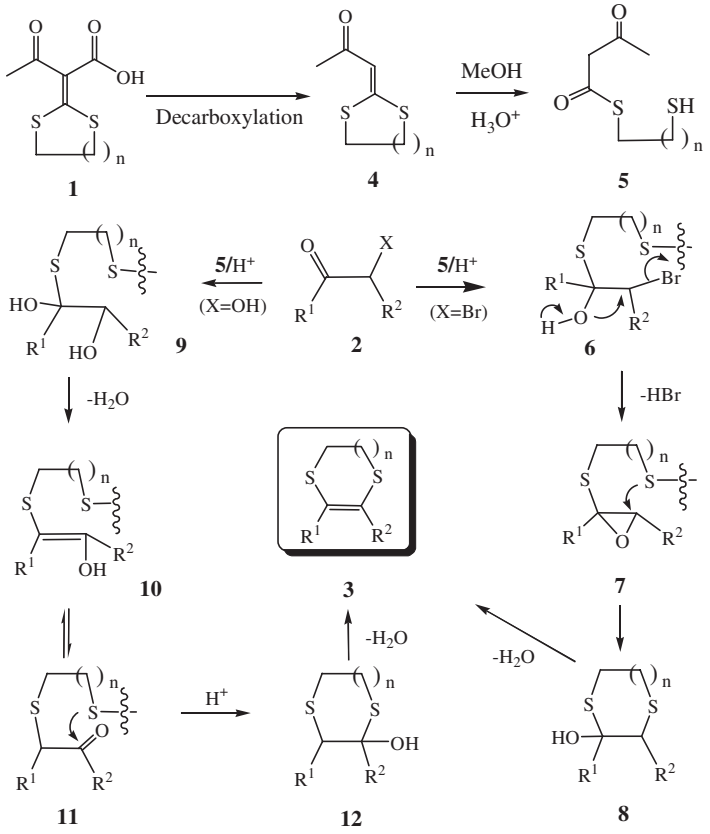
Table 2. The reactions of α-bromo/hydroxy ketones **2** with 2-(1,3-dithiolan/dithian-2-ylidene)-3-oxobutanoic acids **1**



1 **2** **3**

Entry	Substrates **1**, **2**				Time (h)	Product **3**	Mp (°C)	Yield[a] (%)
	n	X	R^1	R^2				
1	1	Br	Ph	H	5.0	**3a**	59–61	60.1
2	2	Br	Ph	H	5.5	**3b**	Oil	63.7
3	1	Br	4-ClPh	H	6.0	**3c**	71–73	60.9
4	2	Br	4-ClPh	H	5.0	**3d**	69–71	54.8
5	1	Br	4-CH_3Ph	H	6.5	**3e**	57–59	61.5
6	1	Br	4-CH_3OPh	H	6.0	**3f**	76–78	64.5
7	2	Br	4-CH_3OPh	H	5.0	**3g**	56–58	65.6
8	1	Br	4-Biphenyl	H	4.5	**3h**	103–105	63.9
9	2	Br	4-Biphenyl	H	3.5	**3i**	106–108	64.8
10	1	Br	Naphenyl	H	4.5	**3j**	81–83	80.3
11	2	Br	Naphenyl	H	3.5	**3k**	66–68	79.8
12	1	OH	Ph	Ph	6.5	**3l**	96–98	72.5
13	2	OH	Ph	Ph	7.5	**3m**	134–136	70.1

[a] Isolated yields over silica gel chromatography.



1 **4** **5** **9** **2** **6** **10** **3** **7** **11** **12** **8**

Scheme 2. A mechanism proposed for the reaction of **1** with **2**.

is the first example of a one-step synthesis of 2,3-dihydro-1,4-dithiins and 6,7-dihydro-5*H*-1,4-dithiepins directly from carbonyl compounds without using dithiols.

On the basis of the results together with our previous finding,[17] a mechanism was proposed as depicted in Scheme 2. The reaction starts from the generation of HCl based on the esterification of acetyl chloride with

MeOH. Prompted by HCl generated, compound **1** undergoes decarboxylation to give a ketene dithioacetal **4**. With the attacks by methanol and H_2O, **4** is transformed into a thiol-bearing intermediate **5**, which reacts with α-bromo/hydroxy ketones **2**. Most likely the mechanism for α-bromo ketones is different from that for α-hydroxy ketones although they are finally converted into the same compounds of type **3**.

In summary, a facile one-step synthesis of substituted dihydro-1,4-dithiins and -1,4-dithiepins **3** based on the reactions of α-bromo/hydroxy ketones **2** with α-oxo ketene cyclic dithioacetals **1a** and **1b** has been developed. This novel protocol is associated with simple procedure, mild conditions, and good yields, especially in relation to recent environmental concerns. Further investigations of the scope of the reaction and application are in progress.

Acknowledgments

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20. General procedure for the preparation of **3** between **1** and **2** (**3a** as an example): **1a** (1.2 mmol), **2a** (1.0 mmol), methanol (10 mL), and acetyl chloride (0.36 mL, 5 mmol) were added into a flask equipped with a condenser. The mixture was heated to reflux and stirred for about 5 h when **2a** was consumed as indicated by TLC. The reaction mixture was cooled down to ambient temperature and neutralized with 10% aq $NaHCO_3$. After extractive workup, separation was carried out over silica gel chromatography (eluent: petroleum ether–diethyl ether = 90:1, v/v) to give **3a** as a white solid. (yield: 60.1%, mp: 59–61 °C).
5-Phenyl-2,3-dihydro-1,4-dithiine **3a**, white solid, mp: 59–61 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ: 3.22–3.25 (m, 2H), 3.29–3.33 (m, 2H), 6.39 (s, 1H), 7.30 (m, 3H), 7.40 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 26.6, 27.6, 113.1, 126.7, 127.1, 128.5, 133.4, 138.7; IR (KBr, neat): 3070, 2972, 1687, 1643, 1597, 1493, 1241, 1142, 762 cm^{-1}; Anal. Calcd for $C_{10}H_{10}S_2$: C, 61.81; H, 5.19. Found: C, 61.71; H, 5.22.

2-Phenyl-6,7-dihydro-5*H*-1,4-dithiepine **3b**, colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ: 2.20–2.25 (m, 2H), 3.56–3.64 (m, 4H), 6.11 (s, 1H), 7.25–7.30 (m, 3H), 7.46–7.49 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 30.4, 31.0, 32.4, 118.0, 127.3, 127.7, 127.9, 128.1, 129.2, 135.2, 141.2; IR (KBr, neat): 3063, 2922, 1676, 1578, 1487, 1276, 1156, 749 cm^{-1}; Anal. Calcd for $C_{11}H_{12}S_2$: C, 63.41; H, 5.81. Found: C, 63.52; H, 5.77.

5-(4-Chlorophenyl)-2,3-dihydro-1,4-dithiine **3c**, white solid, mp: 71–73 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ: 3.41–3.46 (m, 4H), 6.38 (s, 1H), 7.30 (d, $J = 8.0$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H); IR (KBr, neat): 3010, 2923, 1669, 1567, 1484, 1286, 1089, 787 cm^{-1}; Anal. Calcd for $C_{10}H_9ClS_2$: C, 52.50; H, 3.97. Found: C, 52.58; H, 3.92.

2-(4-Chlorophenyl)-6,7-dihydro-5*H*-1,4-dithiepine **3d**, white solid, mp: 69–71 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ: 2.20–2.24 (m, 2H), 3.57–3.64 (m, 4H), 6.08 (s, 1H), 7.24 (d, $J = 8.0$ Hz, 2H), 7.41 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 30.2, 30.8, 32.5, 118.6, 128.2, 128.5, 133.6, 133.8, 139.6; IR (KBr, neat): 2920, 1614, 1536, 1482, 1301, 790 cm^{-1}; Anal. Calcd for $C_{11}H_{11}ClS_2$: C, 54.42; H, 4.57. Found: C, 54.51; H, 4.53.

5-*p*-Tolyl-2,3-dihydro-1,4-dithiine **3e**, white solid, mp: 57–59 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ: 2.34 (s, 3H), 3.22–3.24 (t, $J = 4.0$ Hz, 2H), 3.30–3.31 (t, $J = 4.0$ Hz, 2H), 6.34 (s, 1H), 7.12 (d, $J = 8.0$ Hz, 2H), 7.32 (d, $J = 8.0$ Hz, 2H); IR (KBr, neat): 3021, 2918, 1643, 1552, 1451, 1384, 781 cm^{-1}; Anal. Calcd for $C_{11}H_{12}S_2$: C, 63.41; H, 5.81. Found: C, 63.51; H, 5.76.

5-(4-Methoxyphenyl)-2,3-dihydro-1,4-dithiine **3f**, white solid, mp: 76–78 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ: 3.20–3.22 (t, $J = 4.0$ Hz, 2H), 3.28–3.32 (t, $J = 4.0$ Hz, 2H), 3.81 (s, 3H), 6.27 (s, 1H), 6.84–6.87 (q, $J = 8.0$ Hz, 2H), 7.08–7.45 (q, $J = 8.0$ Hz, 2H); IR (KBr, neat): 2959, 1605, 1505, 1251, 789; Anal. Calcd for $C_{11}H_{12}OS_2$: C, 58.89; H, 5.39. Found: C, 58.76; H, 5.45.

2-(4-Methoxyphenyl)-6,7-dihydro-5*H*-1,4-dithiepine **3g**, white solid, mp: 56–58 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ: 2.18–2.22 (m, 2H), 3.53–3.57 (m, 2H), 3.58–3.65 (m, 2H), 3.80 (s, 3H), 6.01 (s, 1H), 6.82 (d, $J = 8.0$ Hz, 2H), 7.42 (d, $J = 8.0$ Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): 30.7, 31.3, 32.6, 55.6, 113.7, 116.5, 128.9, 134.0, 135.6, 159.8; IR (KBr, neat): 3027, 2955, 1601, 1494, 1453, 1236, 766 cm^{-1}; Anal. Calcd for $C_{12}H_{14}OS_2$: C, 60.46; H, 5.92. Found: C, 60.57; H, 5.85.

5-(4-Diphenyl)-2,3-dihydro-1,4-dithiine **3h**, white solid, mp: 103–105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ: 3.25–3.27 (t, $J = 4.0$ Hz, 2H), 3.31–3.34 (t, $J = 4.0$ Hz, 2H), 6.46 (s, 1H), 7.34–7.61 (m, 9H); IR (KBr, neat): 3070, 2971, 1687, 1596, 1493, 1449, 1241, 761 cm^{-1}; Anal. Calcd for $C_{16}H_{14}S_2$: C, 71.07; H, 5.22. Found: C, 71.16; H, 5.18.

2-(4-Diphenyl)-6,7-dihydro-5*H*-1,4-dithiepine **3i**, white solid, mp: 106–108 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ: 2.22–2.25 (m, 2H), 3.58–3.66 (m, 4H), 6.18 (s, 1H), 7.33–7.59 (m, 9H); IR (KBr, neat): 3029, 2918, 1675, 1531, 1481, 1299, 762 cm^{-1}; Anal. Calcd for $C_{17}H_{16}S_2$: C, 71.78; H, 5.67. Found: C, 71.66; H, 5.73.

5-(Naphthalen-2-yl)-2,3-dihydro-1,4-dithiine **3j**, white solid, mp: 81–83 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ: 3.28–3.30 (t, $J = 4.0$ Hz, 2H), 3.35–3.37 (t, $J = 4.0$ Hz, 2H), 6.55 (s, 1H), 7.41–7.46 (m, 2H), 7.56 (d, $J = 8.0$ Hz, 1H), 7.78–7.83 (m, 3H), 7.91 (s, 1H); IR (KBr, neat): 3052, 2922, 1627, 1559, 1460, 1284, 7.53 cm^{-1}; Anal. Calcd for $C_{14}H_{12}S_2$: C, 68.81; H, 4.95. Found: C, 68.69; H, 5.01.

2-(Naphthalen-2-yl)-6,7-dihydro-5*H*-1,4-dithiepine **3k**, white solid, mp: 66–68 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ: 2.24–2.28 (m, 2H), 3.62–3.65 (m, 2H), 3.67–3.69 (m, 2H), 6.25 (s, 1H), 7.43–7.49 (m, 2H), 7.62 (d, 1H), 7.79–7.83 (m, 3H), 7.96 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): 30.4, 31.0, 32.5, 118.7, 125.4, 126.0, 126.1, 126.2, 127.4, 127.6, 128.1, 132.9, 133.1, 135.2, 138.5; IR (KBr, neat): 3051, 2907, 1626, 1533, 1450, 1299, 742 cm^{-1}; Anal. Calcd for $C_{15}H_{14}S_2$: C, 69.72; H, 5.46. Found: C, 69.63; H, 5.50.

5,6-Diphenyl-2,3-dihydro-1,4-dithiine **3l**, white solid, mp: 96–98 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ: 3.41–3.47 (m, 4H), 7.12–7.22 (m, 10H); IR (KBr, neat): 3055, 2920, 1647, 1572, 1443, 698 cm^{-1}; Anal. Calcd for $C_{16}H_{14}S_2$: C, 71.07; H, 5.22. Found: C, 71.18; H, 5.16.

2,3-Diphenyl-6,7-dihydro-5*H*-1,4-dithiepine **3m**, white solid, mp: 134–136 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ: 2.17–2.21 (m, 2H), 3.74–3.79 (m, 4H), 7.13–7.24 (m, 10H); IR (KBr, neat): 2929, 1646, 1563, 1442, 695 cm^{-1}; Anal. Calcd for $C_{17}H_{16}S_2$: C, 71.78; H, 5.67. Found: C, 71.66; H, 5.72.