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Rongalite® and base-promoted cleavage of disulfides and subsequent Michael addition to α,β-unsaturated ketones/esters: an odorless synthesis of β-sulfido carbonyl compounds

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ABSTRACT

A highly practical method to access β-sulfido carbonyl compounds was developed, which could be conducted without any expensive reagent, special apparatus/technique, and no requirement of metal catalysts. β-Sulfido carbonyl compounds were formed at room temperature, in short time and with high chemoselectivity in good to excellent yields. A plausible mechanism for the role of Rongalite®, as a promoter for the cleavage of disulfides generating thiolate anions that then undergo facile thia-Michael addition to α,β-unsaturated ketones and esters is proposed.

1. Introduction

The β-sulfido carbonyl compounds are important building blocks in the synthesis of natural and pharmacological compounds.[1] Various approaches toward the synthesis of β-sulfido carbonyl compounds have been explored during the past years. One of the most common approaches for the synthesis of β-sulfido carbonyl compounds is thia-Michael addition of thiols to α,β-unsaturated carbonyl compounds, which provides a great strategy for chemoselective protection of the olefinic double bond of conjugated enones.[2] Thus, there have been constant efforts toward the development of methodologies for thia-Michael addition in the presence of various promoting agents.[3] Alternatively, the reactions conducted in ionic liquids[4] and using water as the medium[5] have been investigated. However, the use of highly volatile and unpleasant smelling free thiols leads to serious environmental, safety problems and also limits the use of these methods for large-scale operations in all the reported methods. Besides the drawback of these methodologies are associated with undesirable side reactions owing to the oxidation of thiols. In order to minimize or eliminate the encountered problems, a range of odorless protocols has also been reported. The use of long-chain alkyl thiols or substituted thiophenols with a trimethylsilyl moiety as odorless substrates has been reported for this purpose.[6] The highlight of this methodology is no free thiols involved in the reaction. However, these odorless procedures often suffer from certain drawbacks, such as cost of some catalysts, long reaction time, use of strong alkaline media, and limited substrate scope.

The cleavage of disulfide bond could lead to interesting products by the reaction of the resulting nucleophilic sulfur[7] species to a variety of organic substrates. Studies directed toward the cleavage of disulfide bonds in proteins is an important determinant in understanding the structural activity and structural domains of proteins, which would help in the design and development of new therapeutic agents and the conversion of large proteins into smaller fragments that are more amenable for sequencing.[8] The sulfur–sulfur bond in organic disulfides may be cleaved by nucleophilic, electrophilic, and radical processes. Several transition metal complexes have also been shown to cleave sulfur–sulfur bond in organic disulfides.[9]

In 2000, Chandrasekaran and co-workers[10] have discovered that the tandem sulfur transfer/reduction/Michael addition strategy for the synthesis of β-sulfido carbonyl compounds mediated by benzyltriethylammonium tetrathiomolybdate for 4 h to 10 h in acetonitrile. Later, Ranu and Mandal have reported that InI-promoted[11a,b]

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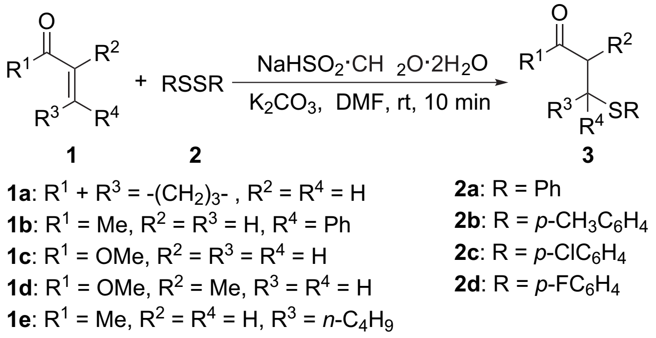
Michael addition of thiolate anions to conjugated carbonyl compounds for 1.5–5 h under reflux THF or In-TMSCl-promoted[11c] for 4.5–6 h in CH_3CN under sonication. For the synthesis of β-sulfido carbonyl compounds from thia-Michael addition of disulfides to α,β-unsaturated carbonyl compounds, very little attention was paid to it.[12] From a synthetic point of view, the development of an improved, facile procedure using less expensive and more sustainable promoter has remained a highly desirable goal.

As a continuing interest in developing novel synthetic routes for the formations of carbon–carbon and carbon–heteroatom bonds,[13] we expected to apply the sulfite/base system in the thia-Michael addition to α,β-unsaturated ketones and esters. Herein, we wish to report a highly practical method to access β-sulfido carbonyl compounds by Rongalite® (sodium formaldehyde sulfoxylate, $NaHSO_2{\cdot}CH_2O{\cdot}2H_2O$ as an inexpensive reagent)-promoted cleavage of disulfides and subsequent thia-Michael addition to α,β-unsaturated ketones and esters under mild reaction conditions (Scheme 1).



Scheme 1. Rongalite®-promoted thia-Michael addition.

2. Results and discussion

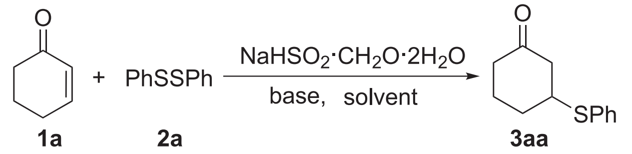
Initial studies focused on the screening of the solvents, bases as well as Rongalite® loading with the reaction of cyclohex-2-enone **1a** and phenyl disulfide **2a** as the model reaction at room temperature. The results are listed in Table 1.

Through the screening process, trace target product was detected in the presence of a series of solvents such as 1,4-dioxane, toluene, HMPA, and $CH_3CH_2NO_2$. However, we were delighted to find that the yield could be improved to 32% or 47% when the combination of Cs_2CO_3 and DMSO or DMF was employed at room temperature, respectively (Table 1, entries 1–6). Encouraged by these promising results, we further optimized the reaction conditions, such as bases, the amount of Rongalite® loading, and bases (Table 1, entries 7–19).

Next, different experiments were carried out by varying the amount of Rongalite® (Table 1, entries 11–15). Increasing the amount of Rongalite® to 4 equiv resulted in excellent yield. No target product was detected in the absence of Rongalite® and both starting materials were recovered in quantitative, which also further proved that Rongalite® do play an important role in this reaction (Table 1, entry 16). On the other hand, among the bases tested, K_2CO_3 afforded best yield under these conditions (Table 1, entries 7–11). We also examined the effect of the amount of K_2CO_3, the target product was not observed without K_2CO_3, increasing the amount of K_2CO_3 to 2 equiv resulted in excellent yield.

With optimal conditions in hand, the reaction of various cyclic and acyclic α,β-unsaturated carbonyl compounds with disulfides was examined to explore the scope of the reaction and the results are summarized in Table 2. In all cases, Rongalite®-promoted reactions proceeded smoothly and gave the corresponding products in good to excellent yields.

Table 1
Screening conditions for the thia-Michael addition reaction of cyclohex-2-enone with 1,2-diphenyldisulfide[a]



Entry	Rongalite® (equiv)	Solvent	Base	Yield[b] (%)
1	2	1,4-Dioxane	Cs_2CO_3	trace
2	2	Toluene	Cs_2CO_3	trace
3	2	HMPA	Cs_2CO_3	trace
4	2	$CH_3CH_2NO_2$	Cs_2CO_3	trace
5	2	DMSO	Cs_2CO_3	32
6	2	DMF	Cs_2CO_3	47
7	4	DMF	Cs_2CO_3	73
8	4	DMF	$KF{\cdot}2H_2O$	trace
9	4	DMF	Et_3N	12
10	4	DMF	K_3PO_4	trace
11	4	DMF	K_2CO_3	89
12	5	DMF	K_2CO_3	89
13	3	DMF	K_2CO_3	77
14	2	DMF	K_2CO_3	67
15	1	DMF	K_2CO_3	13
16	—	DMF	K_2CO_3	NR
17	4	DMF	K_2CO_3	97[c]
18	4	DMF	K_2CO_3	97[d]
19	4	DMF	none	NR

NR=No reaction.

[a] All reactions were run with cyclohex-2-enone **1a** (0.4 mmol), phenyl disulfide **2a** (0.2 mmol), $NaHSO_2{\cdot}CH_2O{\cdot}2H_2O$, and base (1 equiv) in 3 mL of solvent at room temperature for 10 min.

[b] Isolated yields.

[c] 2 equiv of K_2CO_3.

[d] 3 equiv of K_2CO_3.

As shown in Table 2, the substitution groups on the aromatic ring associated with disulfides had little effect on the yields. It is observed that the corresponding products were obtained in excellent yields by the reaction of electron-rich disulfide, such as *p*-tolyl disulfide **2b** with various Michael acceptor **1**(**a**–**e**) (Table 2, entries 2, 6, 10, 14, and 18) under optimal conditions. In contrast, the yields were decreased slightly when less nucleophilic disulfide, such as *p*-fluorophenyl disulfide **2e** was used under the same conditions (Table 2, entries 4, 8, 12, 16, and 20). A little decrease in the product yield was observed in reaction with various using benzalacetone (**1b**) as Michael acceptor (Table 2, entries 5–8). In the case of Michael acceptor, such as methyl acrylate (**1c**), the product was formed in good yields (Table 2, entries 9–12).

Moreover, we further investigated α-substituted Michael acceptor methyl methacrylate (**1d**) (Table 2, entries 13–16) and β-substituted Michael acceptor oct-3-en-2-one (**1e**) (Table 2, entries 17–20) could react with various disulfides rapidly afford good yields.

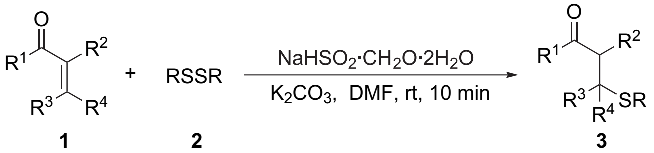
Next, the chemoselective addition reaction in the presence of unprotected reactive functional groups, such as $-NH_2$ also proved to be successful. The corresponding product of **3ce** was obtained in 94% yield (Scheme 2).

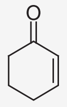
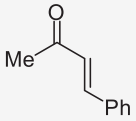
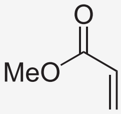
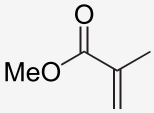
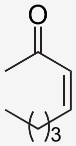
Furthermore, the present route to β-sulfido carbonyl compounds was successfully applied to a large scale reaction. For instance, the thia-Michael addition of cyclohex-2-enone **1a** (1.92 g) to phenyl disulfide **2a** (2.18 g) promoted by Rongalite® provided the desired product **3aa** in 98% yield (Table 2, entry 1).

According to the previous proposed mechanism,[14] a tentative mechanism for the formation of β-sulfido carbonyl compounds was proposed in Scheme 3. Rongalite® can be readily decomposed into HCHO and HSO_2^- anion (**A**). Intermediate (**A**) then reacts with RSSR

Table 2

Rongalite®-promoted cleavage of disulfides followed by thia-Michael addition[a]



Entry	Acceptor **1**	R (Disulfide **2**)	Product	Yield[b] (%)
1	 **1a**	6C_6H_5 (**2a**)	**3aa**	97 (98)[c]
2		*p*-$(CH_3)C_6H_4$ (**2b**)	**3ab**	98
3		*p*-$(Cl)C_6H_4$ (**2c**)	**3ac**	94
4		*p*-$(F)C_6H_4$ (**2d**)	**3ad**	87
5	 **1b**	C_6H_5 (**2a**)	**3ba**	92
6		*p*-$(CH_3)C_6H_4$ (**2b**)	**3bb**	93
7		*p*-$(Cl)C_6H_4$ (**2c**)	**3bc**	90
8		*p*-$(F)C_6H_4$ (**2d**)	**3bd**	83
9	 **1c**	C_6H_5 (**2a**)	**3ca**	96
10		*p*-$(CH_3)C_6H_4$ (**2b**)	**3cb**	98
11		*p*-$(Cl)C_6H_4$ (**2c**)	**3cc**	95
12		*p*-$(F)C_6H_4$ (**2d**)	**3cd**	88
13	 **1d**	C_6H_5 (**2a**)	**3da**	94
14		*p*-$(CH_3)C_6H_4$ (**2b**)	**3db**	96
15		*p*-$(Cl)C_6H_4$ (**2c**)	**3dc**	93
16		*p*-$(F)C_6H_4$ (**2d**)	**3dd**	88
17	 **1e**	C_6H_5 (**2a**)	**3ea**	94
18		*p*-$(CH_3)C_6H_4$ (**2b**)	**3eb**	93
19		*p*-$(Cl)C_6H_4$ (**2c**)	**3ec**	90
20		*p*-$(F)C_6H_4$ (**2d**)	**3ed**	84

[a] All reactions were run with α,β-unsaturated ketones/esters **1** (0.4 mmol), disulfides **2** (0.2 mmol), $NaHSO_2 \cdot CH_2O \cdot 2H_2O$ (0.8 mmol), and K_2CO_3 (0.4 mmol) in 2 mL of DMF at room temperature for 10 min.

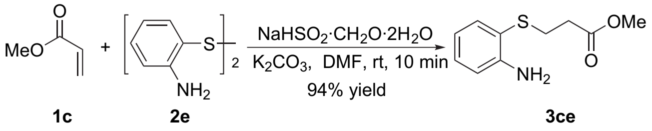
[b] Isolated yields.

[c] The reaction was run with cyclohex-2-enone **1a** (20 mmol, 1.92 g), phenyl disulfide **2a** (10 mmol, 2.18 g), $NaHSO_2 \cdot CH_2O \cdot 2H_2O$ (40 mmol), and K_2CO_3 (20 mmol) in 10 mL of DMF at room temperature for 10 min.

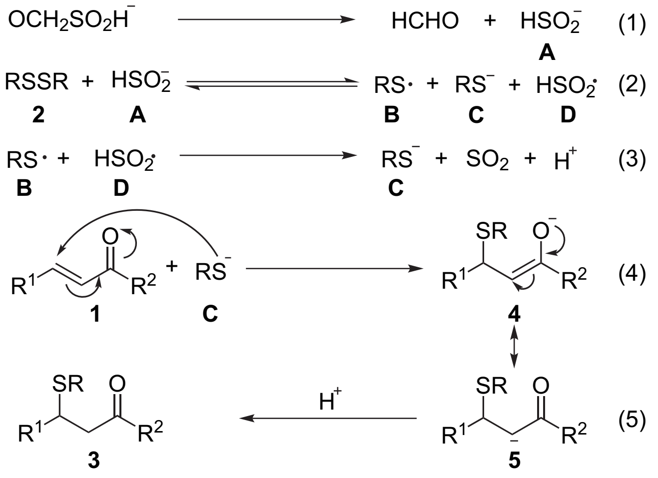
(**2**) to generate two radical intermediates (**B** and **D**) and an anion (**C**). The radical (**B**) can also be converted into thiolate anion (**C**) by reacting with intermediate (**D**). Finally, the 1,4-addition of the thiolate anion (**C**) to the β-position of the Michael acceptor (**1**) affords the target product.

3. Conclusion

In summary, we have developed a highly practical and operationally simple method by the Rongalite® and base-promoted cleavage of disulfides and subsequent odorless thia-Michael addition in good to excellent yields under mild reaction conditions. Compare to reported methodologies, the important features of this methodology are broad substrates scope, high yielding, no requirement of metal catalysts, reasonably rapid reaction rate, and especially in a scaled-up synthesis. Efforts to explore the detailed mechanism and further applications of the present system in other transformations using disulfide as a reaction partner are ongoing in our group.



Scheme 2. Rongalite®-promoted chemoselective addition reaction.



Scheme 3. A tentative mechanism for the formation of β-sulfido carbonyl compounds.

4. Experimental section

4.1. General

Chemicals and solvents were either purchased or purified by standard techniques. Melting points were uncorrected and recorded on Digital Melting Point Apparatus WRS-1B. IR spectra were recorded on a AVATAR 370 FI-Infrared Spectrophotometer. NMR spectroscopy was performed on both a Bruck-300 spectrometer operating at 300 MHz (^1H NMR) and 75 MHz (^{13}C NMR). TMS (tetramethylsilane) was used as an internal standard and $CDCl_3$ was used as the solvent. Mass spectrometric analysis was performed on GC–MS analysis (SHIMADZU GCMS-QP2010). Elemental analysis was determined on a Carlo-Erba 1108 instrument.

4.2. General procedure for synthesis of synthesis of β-sulfido carbonyl compounds

A mixture of α,β-unsaturated ketones/esters **1** (0.4 mmol), disulfide **2** (0.2 mmol), Roganlite® (4 equiv), and K_2CO_3 (2 equiv) in DMF (2 mL) was stirred at room temperature for 10 min. The mixture washed with water and extracted with ethyl acetate. The organic phase was separated and dried over anhydrous sodium sulfate, filtered and the solvent was evaporated under vacuum. The residue was purified by flash column chromatography (ethyl acetate or hexane/ethyl acetate) to afford the desired product **3**.

*4.2.1. 4-(p-Fluorophenylthio)-4-phenylbutan-2-one (**3bd**).* (Table 2, entry 8). ^1H NMR (30 MHz, $CDCl_3$) δ: 7.28–7.18 (m, 7H), 6.94–6.88 (m, 2H), 4.60 (t, J=7.3 Hz, 1H), 3.04 (dd, J=7.8 Hz, J=1.0 Hz, 2H), 2.09 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 205.5, 162.9 (d, $^1J_{C-F}$=246.6 Hz), 141.0, 136.2 (d, $^3J_{C-F}$=8.3 Hz), 128.9, 128.6, 127.8, 127.6, 116.1 (d, $^2J_{C-F}$=21.6 Hz), 49.3, 49.0, 30.9; MS (EI, 70 eV) m/z (%): 274(M^+, 5), 147 (22), 43 (100). Anal. Calcd for $C_{16}H_{15}FOS$: C, 70.05; H, 5.51. Found: C, 70.11; H, 5.46.

*4.2.2. Methyl-3-(p-fluorophenylthio)propanoate (**3cd**).* (Table 2, entry 12). ^1H NMR (300 MHz, $CDCl_3$) δ: 7.41–7.36 (m, 2H), 7.03–6.98 (m, 2H), 3.67 (s, 3H), 3.11 (t, J=7.3 Hz, 2H), 2.59 (t, J=7.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 172.2, 162.3 (d, $^1J_{C-F}$=245.6 Hz), 133.5 (d, $^3J_{C-F}$=8.0 Hz), 130.1 (d, $^4J_{C-F}$=3.2 Hz), 116.3 (d, $^2J_{C-F}$=21.8 Hz), 51.9, 34.3, 30.5; MS (EI, 70 eV) *m*/*z* (%): 214(M$^+$, 100), 127 (53), 141 (69), 154 (46). Anal. Calcd for $C_{10}H_{11}FO_2S$: C, 56.06; H, 5.17. Found: C, 56.10; H, 5.22.

*4.2.3. Methyl-3-(p-fluorophenylthio)butanoate (**3dd**).* (Table 2, entry 16). ^{1}H NMR (30 MHz, $CDCl_3$) δ: 7.40–7.36 (m, 2H), 7.03–6.97 (m, 2H), 3.66 (s, 3H), 3.23–3.16 (m, 1H), 2.91–2.84 (m, 1H), 2.68–2.61 (m, 1H), 1.25 (d, *J*=7.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 175.4, 162.2 (d, $^1J_{C-F}$=245.5 Hz), 133.4 (d, $^3J_{C-F}$=8.0 Hz), 130.6, 116.2 (d, $^2J_{C-F}$=21.8 Hz), 52.0, 39.8, 38.9, 16.9; MS (EI, 70 eV) *m*/*z* (%): 228(M$^+$, 57), 141 (100), 45 (42). Anal. Calcd for $C_{11}H_{13}FO_2S$: C, 57.87; H, 5.74. Found: C, 57.74; H, 5.77.

*4.2.4. 4-(p-Tolylthio)octan-2-one (**3eb**).* (Table 2, entry 18). ^{1}H NMR (30 MHz, $CDCl_3$) δ: 7.31 (d, *J*=8.1 Hz, 2H), 7.11 (d, *J*=8.0 Hz, 2H), 3.52–3.48 (m, 1H), 2.68–2.61 (m, 2H), 2.33 (s, 3H), 2.12 (s, 3H), 1.56–1.26 (m, 6H), 0.89 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 207.1, 137.6, 133.3, 130.6, 129.9, 49.2, 44.2, 34.5, 30.8, 29.2, 22.6, 21.3, 14.1; MS (EI, 70 eV) *m*/*z* (%): 250(M$^+$, 30), 124 (100), 43 (87). Anal. Calcd for $C_{15}H_{22}OS$: C, 71.95; H, 8.86. Found: C, 72.01; H, 8.89.

*4.2.5. 4-(p-Chlorophenylthio)octan-2-one (**3ec**).* (Table 2, entry 19). ^{1}H NMR (30 MHz, $CDCl_3$) δ: 7.35–7.24 (m, 4H), 3.56–3.52 (m, 1H), 2.67–2.64 (m, 2H), 2.13 (s, 3H), 1.57–1.25 (m, 6H), 0.87 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 206.7, 133.7, 133.4, 133.3, 129.2, 49.0, 44.1, 34.6, 30.8, 29.1, 22.6, 14.1; MS (EI, 70 eV) *m*/*z* (%): 270 (M$^+$, 12), 144 (32), 109 (16), 43 (100). Anal. Calcd for $C_{14}H_{19}ClOS$: C, 62.09; H, 7.07. Found: C, 62.12; H, 7.13.

*4.2.6. 4-(p-Fluorophenylthio)octan-2-one (**3ed**).* (Table 2, entry 20). ^{1}H NMR (30 MHz, $CDCl_3$) δ: 7.42–7.37 (m, 2H), 7.01–6.95 (m, 2H), 3.47–3.43 (m, 1H), 2.65–2.60 (m, 2H), 2.11 (s, 3H), 1.53–1.24 (m, 6H), 0.86 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 206.8, 162.6 (d, $^1J_{C-F}$=246.1 Hz), 135.5 (d, $^3J_{C-F}$=8.1 Hz), 129.3, 116.1 (d, $^2J_{C-F}$=21.5 Hz), 49.1, 44.8, 34.5, 30.8, 29.1, 22.6, 14.1; MS (EI, 70 eV) *m*/*z* (%): 254(M$^+$, 18), 128 (44), 43 (100). Anal. Calcd for $C_{14}H_{19}FOS$: C, 66.11; H, 7.53. Found: C, 62.08; H, 7.59.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.02.001.

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