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Odorless Thioacetalization Reagent 2-[1,3]Dithian-2-Ylidene-3-Oxo-Bu and Its Chemoselectivity

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Odorless Thioacetalization Reagent 2-[1,3] Dithian-2-Ylidene-3-Oxo-Butanamide and Its Chemoselectivity

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ABSTRACT

2-[1,3]Dithian/dithiolan-2-ylidene-3-oxo-butanamide **2a/2b** were synthesized and investigated in the thioacetalization reaction of aldehydes/ketones **3**. The experiments revealed that **2a** could be used as a nonthiolic, odorless 1,3-propanedithiol equivalent in the conversion of aldehydes/ketones into the corresponding dithianes **4**, however, **2b** was less effective. Moreover, the chemoselectivity of the thioacetalization of **3** in the presence of **2a** is discussed.

Key Words: Carbonyl compounds; Chemoselectivity; α-oxo ketene dithioacetals; 1,3-propanedithiol equivalent.

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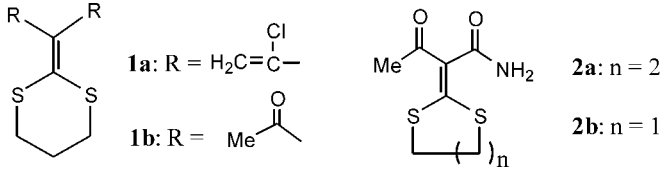
INTRODUCTION

Thioacetals have been extensively investigated as carbonyl protection groups and versatile intermediates in the synthesis of multifunctional complex molecules and natural products.[1,2] To date, there are many methods reported for the preparation of thioacetals from carbonyl compounds or *O,O*-acetals with thiols employing various acid catalysts such as protonic acids, Lewis acids, and solid acids.[3,4] However, the traditional methods suffer from the use of volatile, foul-smelling, low molecular weight thiols that lead to serious safety and environment problems. To resolve these problems, some attempts have been made to develop odorless substitutes for these noxious thiols.[5–7] Generally, an alkyl chain of over 12 carbon atoms in a thiol is crucial in reducing the offending smell. Therefore, a range of odorless or faintly smelling thiols has been developed by increasing alkyl chain length of thiol or introducing the trialkylsilyl group into the benzene ring of benzyl mercaptan and benzenethiol.[5] Incorporation of 1,3-propanedithiol functions within linear and cross-linked copolymeric reagents[6] or conversion of the thiol to its odorless dithioester have been reported and applied in organic synthetic chemistry.[7] However, there is no mention about the chemoselectivity of the thioacetalization in the above work. Moreover, the multistep process of preparation, the high cost of catalysts, and the toxicity of some precursors limit the further utilization of the thiol reagents or their equivalents.

Our laboratory has been engaging in the synthesis and application of ketene dithioacetals for over a decade.[8] Recently, we developed novel nonthiolic, odorless 1,3-propanedithiol equivalents based on cyclic ketene dithioacetals, e.g., **1a** and its precursor **1b** (Sch. 1).[9] In the presence of **1a** or **1b**, the thioacetalization of a range of aldehydes and ketones has been achieved under mild conditions along with high chemoselectivity. These results encourage us to believe that a wide range of known and/or unknown cyclic ketene dithioacetals might be used as dithiol equivalents in thioacetalization if appropriate conditions are employed. With the expectation of obtaining efficient and practical thioacetalization reagents, we investigated α-oxo cyclic ketene dithioacetals, 2-[1,3]dithian-2-ylidene-3-oxo-butanamide **2a**,



Scheme 1.

and its analogue **2b** (Sch. 1) as dithiol equivalents in the thioacetalization with the selected aldehydes and ketones **3**.

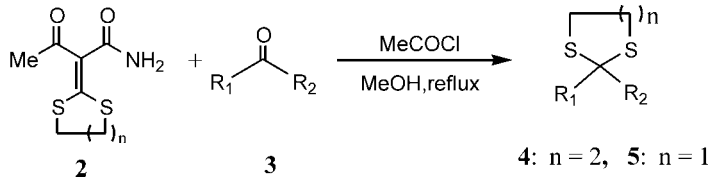
RESULTS AND DISCUSSION

Thioacetalization of Carbonyl Compounds 3 with 2

Extensive work on the synthesis and application of α-oxo ketene dithioacetals has been reported elsewhere.[8,10] According to the procedure described in literature,[11] α-oxo ketene dithioacetals **2a** and **2b** can be readily prepared from 3-oxo-butanamide, carbon disulfide, and 1,3-dibromopropane/1,2-dibromoethane in the presence of K_2CO_3 in good yields (80%). It is noteworthy that both **2a** and **2b** are odorless solids and stable under ambient atmosphere, and they are associated with some synthetic advantages, such as simple procedure, mild conditions, high yields, and commercial starting materials without foul smell.

In our previous work,[9b] the production of HCl by addition of acetyl chloride to reagents **1b** in dry methanol has proved to be a convenient way to achieve the thioacetalization of a range of aldehydes and ketones. Therefore, in the present work we also selected acetyl chloride as catalyst and methanol as reaction medium to investigate the thioacetalization of selected aldehydes and ketones **3** with **2**.

The reactions between the selected carbonyl compounds **3** and **2** proceeded via a very simple procedure (Sch. 2); preparation of **4a** from the reaction between **2a** and **3a** was described as an example (Table 1, entry 1): **3a** (1.0 mmol), **2a** (1.0 mmol), methanol (10 mL), and acetyl chloride (0.18 mL, 2.5 mmol) were added into a flask equipped with a condenser. The mixture was heated to reflux and stirred for about 120 min as indicated by TLC for a complete reaction. The resulting mixture was then allowed to cool down to room temperature and neutralized with aqueous $NaHCO_3$ (10%). After extractive work-up, separation was carried out over silica gel



2 **3** **4**: n = 2, **5**: n = 1

Scheme 2. Thioacetalization of carbonyl compounds **3** with **2**.

Table 1. Thioacetalization of carbonyl compounds **3** with **2a**/**2b**.

Entry	Substrate **3**	R_1	R_2	Product **4**[a]	Time (min)	Yield (%)[b]
1	**3a**	Ph	H	**4a**	120	76
2	**3b**	4-CH_3Ph	H	**4b**	165	80
3	**3c**	4-Cl Ph	H	**4c**	150	90
4	**3d**	4-NO_2 Ph	H	**4d**	110	95
5	**3e**	3-NO_2 Ph	H	**4e**	130	92
6	**3f**	2-Furyl	H	**4f**	60	70
7	**3g**	2-Thiophene	H	**4g**	70	90
8	**3h**	$(CH_2)_4$		**4h**	76	77
9	**3i**	$(CH_2)_5$		**4i**	110	82
10	**3j**	Et	Me	**4j**	200	78
11	**3k**	Ph	Me	**4k**	250	90
12	**3l**	4-Cl Ph	Me	**4l**	280	94
13	**3m**	4-NO_2 Ph	Me	**4m**	180	93
14	**3n**	Ph	Ph	**4n**	360	92
15	**3a**	Ph	H	**5a**	720	40 (56)
16	**3d**	4-NO_2 Ph	H	**5d**	960	35 (59)
17	**3m**	4-NO_2 Ph	Me	**5m**	960	11 (85)
18	**3n**	Ph	Ph	**5n**	360	0 (98)

[a]All products were characterized by ^{1}H NMR and IR spectra.
[b]Isolated yields by column chromatography over silica gel, the data in bracket are the recoveries of compounds **3**.

chromatography (eluent: petroleum ether : ethyl acetate = 60 : 1, v/v) to give a pure product in 76% yield, which was identified as dithioacetal **4a**. It is worth mentioning that nearly no free 1,3-propanedithiol is released within the reaction system because only a very faint smell of thiol can be perceived during both the reaction process and the work-up process. Following the above procedure, a range of selected carbonyl compounds with different chemical structures were converted into the corresponding dithioacetals **4** in good-to-high yields (up to 95%); some of the results are summarized in Table 1 (entries 1–14). The presented results exhibit the scope and generality of the thioacetalization with respect to the different carbonyl compounds, i.e., aromatic, aliphatic, and heterocyclic aldehydes or ketones. It is worth noting that the reaction rates for the thioacetalization with aromatic aldehydes are slightly faster in comparison to that with the corresponding aromatic ketones, as can be seen in Table 1 by comparing entries 3 and 12 or entries 4 and 13. This difference should be attributed to the steric effect from the chemical structures of the aromatic aldehydes and ketones. That is the

reason why the protection of the sterically hindered aromatic ketone **3n** (entry 14) needs even more long reaction time.

We next investigated **2b**, the analogue of **2a**, in the thioacetalization of the selected carbonyl compounds **3** under the same procedure described above (Sch. 2); some of the results are also summarized in Table 1 (entries 15–18). It is worth noting that the selected carbonyl compounds, except the sterically hindered aromatic ketone **3n** (entry 18), could be converted into the corresponding dithiacetals **5** in the presence of **2b**. However, the conversions are too low, even though the reactions proceeded for more than 12h under reflux temperature. The results indicate that **2b** is much less effective as a practical thioacetalization reagent under the studied conditions. The different results achieved from the thioacetalization with **2a** and that with **2b** might stem from the differences of the rigidity and the steric effect of their bis(alkylthio) groups, which deserves further investigation.

Chemoselectivity of the Thioacetalization

The difference of the reactivities between aldehyde and ketone suggest that the thioacetalization might be used for the selective protection of these groups, namely, provide a convenient route for the protection of an aldehyde in the presence of a ketone. Then several reactions of **2a** with the different mixtures of aromatic aldehyde (or aliphatic ketone) and aromatic ketone were carried out under the above reaction conditions. In all the cases, the feed molar ratio of reactant aromatic aldehyde (or aliphatic ketone), aromatic ketone, and thioacetaliztion reagent **2a** was kept constant at 1 : 1 : 1. Some of the results are summarized in Table 2. As shown in Table 2, the chemoselectivity of the thioacetalization of carbonyl compounds depended on the reactivity differences among the reactant carbonyl compounds. In some cases (entries 1–4), chemoselective protection

Table 2. Chemoselectivity of thioacetalization of **3** in the presence of **2a**.

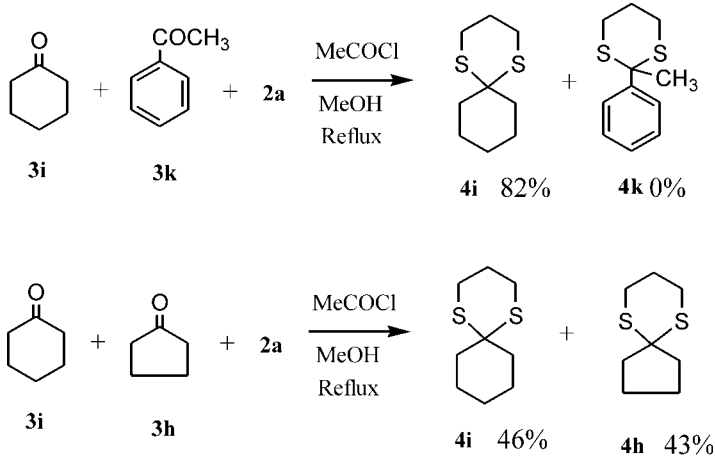
Entry	Substrate **3**	Product **4**[a]	Time (min)	Yield (%)[b]
1	**3a/3k**	**4a**	180	75 (96)
2	**3d/3m**	**4d**	150	81 (97)
3	**3i/3k**	**4i**	140	82 (96)
4	**3j/3k**	**4j**	300	77 (95)
5	**3h/3i**	**4h/4i**	300	43/46

[a]All products were characterized by ^{1}H NMR and IR spectra.
[b]Isolated yields by column chromatography over silica gel, the data in bracket are the recovery of the unreacted compounds **3**.

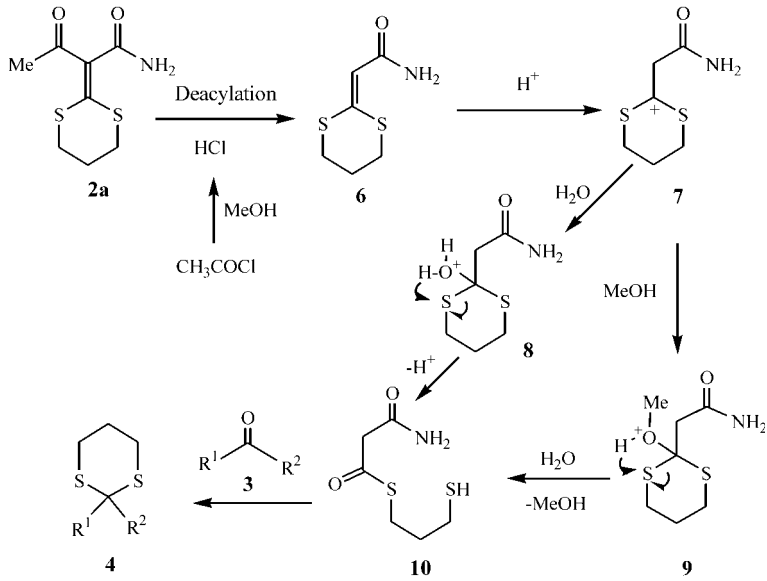
was achieved in which the reactant carbonyl compounds showed obviously different reactivities. For example, the reaction of **3i**/**3k**/**2a** was performed under the same procedure described above (Sch. 3, entry 2). Subsequently, thioacetal **4i** was obtained in 82% yield, while starting material **3k** was almost completely recovered back (96%), and thioacetal **4k** was even not detectable. However, in the case of **3h**/**3i**/**2a** (Sch. 3, entry 5), mixed dithioacetals **4h** and **4i** were obtained, meanwhile both unreacted **3h** and **3i** were detected. According to their ^{1}H NMR spectra, the ratio of **4h** and **4i** is 1 : 1.1. The yields for **4h** and **4i** were obtained as 43% and 46%, respectively. The results reveal that the reactivity difference between cyclohexanone and cyclopentanone is not big enough for the selective protection under the studied conditions. Nevertheless, the present work has well demonstrated that the thioacetalization of carbonyl compounds **3** in the presence of **2a** exhibits significantly high chemoselectivity, providing selective protection of aromatic aldehyde or aliphatic ketone from an aromatic ketone.

Mechanism of the Thioacetalization

To investigate the mechanism of the thioacetalization reaction, one more reaction was carried out. The mixture of **3e** (1.0 mmol), **2a** (1.0 mmol), and acetyl chloride (0.18 mL, 2.5 mmol) in methanol (10 mL) was stirred at reflux temperature for 40 min. Then the reaction mixture was allowed to cool down to room temperature and neutralized with 10% aqueous K_2CO_3.



Scheme 3. Chemoselectivity of thioacetalization of **3** in the presence of **2a**.



Scheme 4. A proposed mechanism for the thioacetalization of carbonyl compounds **3** with **2a**.

From this system, thioacetal **4e** and intermediate **10** (Sch. 4) were obtained in 41% and 24% yields, respectively, while starting materials **2a** and **3e** were recovered in 30% and 52% yields, respectively. In our recent studies on the carbon-carbon cleavage of α-acyl ketene dithioacetals, the deacylation was found to occur very easily and usually under acidic conditions.[12,13] On the basis of the obtained results combined with our previous studies,[9,12,13] a mechanism for the thioacetalization is proposed as shown in Sch. 4. The reaction commences from the generation of HCl based on the esterification between acetyl chloride and methanol. Catalyzed by the released HCl, α-oxo ketene dithioacetal **2a** undergoes deacylation to give ketene dithiolacetal **6**. Followed by the addition of proton to its carbon-carbon double bond, ketene dithiolacetal **6** is converted into a carbon cation **7**, which is stablized by the electron donating bis(alkylthio) groups. With the attacks by H_2O or methanol, the carbon cation **7** leads to the formation of the intermediate **10** through the intermediates **8** or **9**. Finally, a transthioacetalization reaction takes place between the intermediate **10** and carbonyl compound **3** to give the corresponding dithioacetals **4**. It is obvious that 3-amino-3-oxopropanoic acid and its methyl ester are generated as by-products in our present studies. These compounds are more easily removed during the extractive work-up

process than acetylacetic acid and its methyl ester, as described in our previous work.[9b] The results provide a convenient way to isolate the by-products from the resulting reaction mixture. Additionally, these by-products are very useful because they can be used as precursors for the synthesis of ketene dithioacetals. Meanwhile, 3-amino-3-oxopropanoic acid, its methyl ester and compound **2a** as well might buffer the reaction medium and hence increase the reaction yields, especially in the cases of the acid-sensitive substrates. Actually, in the case of **3f**, the yield was increased to around 10% compared with the corresponding result in our earlier work.[9b] Further applications of the novel thiol equivalent reagent in other organic reactions and the recycling of the by-products are currently under investigation in our laboratory.

CONCLUSIONS

In summary, a promising, efficient, and practical thioacetalization reagent, 2-[1,3]dithian-2-ylidene-3-oxo-butanamide **2a**, has been developed. In the presence of the nonthiolic, odorless 1,3-propanedithiol equivalent **2a**, a wide range of selected carbonyl compounds were converted into the corresponding dithioacetals **4**, and the relatively slow reaction rate of aromatic ketones allows chemoselective protection of an aromatic aldehyde or aliphatic ketone from an aromatic ketone. This thioacetalization associated with its mild reaction conditions, simple procedure, high yields, and perfect chemoselectivity provides a very efficient and convenient protocol for the syntheses of thioacetals and chemoselective protection of carbonyl compounds as dithianes in academia and industry.

EXPERIMENTAL

General

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. ^{1}H-NMR spectra were recorded at 25°C on a Varian INOVA500 (500 MHz) spectrometer in $CDCl_3$ and TMS as internal standard. Mass spectra were obtained on a Hewlett-Packard GC 6890/MS 5973 spectrometer. IR spectra (KBr) were recorded on a Magna-560 FTIR spectrophotometer in the range of 400–4000 cm^{-1}. Elemental analyses were measured on a PE-2400 analyzer (Perkin-Elmer).

Typical Procedure for Dithioacetals 4 and 5

3a (1.0 mmol), **2a** (1.0 mmol), methanol (10 mL), and acetyl chloride (0.18 mL, 2.5 mmol) were added into a flask equipped with a condenser. The mixture was heated to reflux and stirred for about 120 min as indicated by TLC for a complete reaction. The reaction mixture was allowed to cool down to room temperature and neutralized with aqueous $NaHCO_3$ (10%). After extractive work-up, separation was carried out over silica gel chromatography (eluent: petroleum ether : ethyl acetate = 60 : 1, v/v) to give dithioacetal **4a** as a white solid in 76% yield.

This procedure was followed by all the reactions listed in Tables 1 and 2. All the dithioacetals **4** and **5** listed in Tables 1 and 2 are known compounds, and their spectroscopic data (^{1}H NMR and IR) and elemental analyses are in good agreement with that in the literature.

Intermediate **10**: ^{1}H NMR (500 MHz, $CDCl_3$): 1.40 (1H, t, J = 8 Hz, SH), 1.91 (2H, m, CH_2 CH_2SH), 2.60 (2H, m, CH_2SH), 3.03 (2H, t, J = 7 Hz, CH_2SC), 3.55 (2H, s, CH_2CO), 5.91 (1H, broad, NH_2), 6.7 (1H, broad, NH_2); IR (cm^{-1}): 3429, 3331, 3188, 2927, 2556, 1673,1384, 1262, 1189, 1016; MS m/z [M^+]: 193.

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