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Thioacetalization of aldehydes and ketones in SDS micelles

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Aromatic aldehydes have been successfully converted into their corresponding dithioacetal, dithiolane and dithiane derivatives in excellent yields with thiol (benzyl thiol and thiophenol), 1,2-ethanedithiol and 1,3-propanedithiol using trichloroacetic acid in sodium dodecyl sulfate micelles. The same procedure is applicable to ketones, but they need more time to be converted into their thioacetals.



Keywords: thioacetalization; thioacetals; thiol; surfactant; sodium dodecyl sulfate; trichloroacetic acid

1. Introduction

One of the biggest challenges in modern chemistry is to find environmentally friendly processes while carrying out already known chemical reactions. Recently, organic reactions in water have

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received much attention, because water is a cheap, safe, noninflammable and environmentally benign solvent (1). In many cases, due to hydrophobic effects, using water as a solvent not only accelerates reaction rates but also enhances reaction selectivities, even when the reactants are sparingly soluble or insoluble in it (2). However, organic solvents are still used instead of water because most organic substrates are not soluble in water and, therefore, water cannot function as a reaction medium. A possible new way to improve the solubility of substrates is to use surface-active compounds that can form micelles (3). The driving force of micelle formation is the elimination of the contact between the alkyl chains and water. Surfactants are frequently employed in order to perform reactions in water (4, 5).

The protection of carbonyl groups as dithioacetals is a common and popular practice in organic chemistry (6). The importance of thioacetals is due in part to their inherent stability under usual acidic or basic conditions and also because of their behavior as masked acyl anions or methylene functions (7). In this view, there have been continued improvements in the methods of preparation of thioacetals (8-11).

Although most of the methods provide good yields, still some of them require the use of expensive and toxic reagents or catalysts, result in unwanted side reactions, offer poor selectivity when applied to mixtures of aldehydes and ketones and require the use of organic solvents always. In this respect, we are interested in introducing a green process to overcome these limitations.

As part of our continued activities in this area (12), herein, we report a new protocol that employs trichloroacetic acid (TCA) as an efficient Bronsted catalyst in the thioacetalization of a variety of aldehydes and ketones in aqueous micellar media, using sodium dodecyl sulfate (SDS) as a surfactant to assist in solubilizing the organic substrates (Scheme 1).



Scheme 1. Protection of carbonyl compounds.

2. Results and discussion

At the outset, loading of SDS and TCA was studied using the reaction of benzaldehyde with 1,2-ethanedithiol in H₂O at 25°C. As shown in Table 1, thioacetalization proceeded smoothly in the presence of 25 mol% of SDS (4 ml, critical micellar concentration (CMC) = 8.1×10^{-3} M) (13) and 1 mmol of TCA (Entry 1). Further decreases in the loading of SDS dropped the yield of the product significantly (Entries 2 and 3). In order to show the role of micellar SDS, the same reaction was examined in the presence of 1 mmol of TCA. As can be seen, this reaction remained incomplete and only 40% of the desired product was obtained after 3 h (Entry 4).

In order to check the effect of other surfactants, we studied the effect of different micellar media on the thioacetalization of benzaldehyde with 1,2-ethanedithiol. Among the micellar solutions examined, SDS turned out to be the most efficient micellar medium, leading to the desired product in 96% yield after 53 min at 25°C. Our observations showed that similar reactions in the presence

	—СНО + Н	5	\longrightarrow s
Entry	SDS (mmol)	TCA (mmol)	Yield% ^b
1	0.25	1	96
2	0.07	1.5	80
3	0.05	2	50
4	0	1	40 ^c

Table 1. Effect of the loading of SDS and TCA.^a

Notes: ^aReaction conditions: the reactions were performed with benzaldehyde (1 mmol) and 1,2-ethanedithiol (1.1 mmol) for 53 min, at 25°C.

^bIsolated yield.

^cIsolated yield after 3 h.

of cetyltrimethylammonium bromide as a cationic micelle and Triton X-100 as a neutral micelle at their CMCs did not proceed to completion even after 3 h and the desired product was obtained in 70% and 75% yields, respectively.

SDS is a surfactant, and the surfactant used in water can make organic materials soluble, and it is stable in water, so it can solve the drawback of the reactions in water. SDS has been used in a number of organic reactions as a good catalyst (14). SDS is an emulsifying agent, which catalyzes the reactions and forms the stable colloidal particles in the presence of the substrates in water and this colloid formation plays an important role in the acceleration of the reactions (Figure 1).

To demonstrate the generality of this method, we next investigated the scope of this reaction under the optimized reaction conditions, and the results are summarized in Table 2. Accordingly, dithioacetals, 1,3-dithiolanes and 1,3-dithianes have been obtained by the reaction of thiol (benzyl thiol and thiophenol), 1,2-ethanedithiol and 1,3-propanedithiol, respectively, in the presence of TCA in SDS micelles. Various types of aromatic aldehydes carrying either electron-donating or -withdrawing substituents afford high product yields with high purity with exception of the electron-withdrawing nitro group, which has a slightly longer reaction time. The protection of heteroaromatic and α , β -unsaturated aldehydes was also carried out under similar reaction conditions. In each case, the corresponding thioacetals were obtained in excellent yields. The acid-sensitive



Figure 1. Micelle-promoted thioacetalization of aldehydes and ketones in water in the presence of TCA.

	R HS	$\rightarrow \mathbb{R}^{R} (S)_{n} \circ \mathbb{R}^{S-Ar} (S)_{n} \circ$					
Entry	Product	Yield% ^b (t/min)	(Ref.)	Entry	Product	Yield% ^b (t/min)	(Ref.)
1	S S	96 (53)	(10a)	11	MeO-SPh SPh	96 (70)	(8d)
2	MeO	96 (36)	(10a)	12	O ₂ N-S-Ph S-Ph	96 (6 h)	(11c)
3	но-	95 (16)	(10a)	13	SPh SPh	93 (45)	(9a)
4	O ₂ N-S	90 (3 h)	(10a)	14	O ₂ N-SPh SPh	94 (6 h)	(8d)
5	CI-S	96 (25)	(11e)	15	S	89 (45)	(11e)
6	N S	92 (30)	(15)	16	S S	50 (8 h)	(11a)
7	⊂ S S	96 (25)	(10a)	17	S S	50 (6 h)	(11a)
8	⟨S⟩	92 (62)	(11c)	18	S S	60 (7 h)	(11a)
9	но-	94 (15)	(11d)	19	S	60 (10 h)	(11a)
10	0 ₂ N	86 (4 h)	(11d)	20	S S S	82 (5 h)	(11a)

Table 2. Protection of carbonyl compounds as dithioacetals, 1,3-dithiolanes and 1,3-dithianes.^a

Notes: ^aThe products were characterized by comparison of their spectroscopic and physical data with those of the authentic samples synthesized by reported procedures. ^bYields refer to pure isolated products.

2-furaldehyde can also be protected to the desired 1,3-dithiolane derivatives without any difficulty. This method does not work properly for aliphatic aldehydes and always gives a mixture of products that are not identified. It is worth mentioning that the same procedure is applicable to ketones at 70° C (Entries 16–20).

In general, aldehydes react much faster than ketones with thiols to yield the corresponding thioacetals. It is also worth nothing that in these conditions, thioacetalization of both cyclic and acyclic ketones proceeded well to produce the corresponding 1,3-dithiolanes in moderate to good yields. We have also observed that a sterically hindered ketone such as camphor can be protected as thioacetal in 60% yield (Entry 19) with a longer reaction time.

Furthermore, the relatively slow reaction rate of ketones allows chemoselective protection of aldehydes in the presence of ketones, making this an important tool in synthetic organic chemistry. For instance, when an equimolar mixture of benzaldehyde and acetophenone was allowed to react with 1,2-ethanedithiol in the presence of TCA/SDS system, only the 1,3-dithiolane derivative of the benzaldehyde was obtained (Scheme 2). This observation shows that the presented method is potentially applicable for chemoselective conversion of aldehydes to the corresponding thioacetals in the presence of ketone functions in multi-functional molecules.



Scheme 2. Reagents and conditions: molar ratio of substrates to TCA (1:1:1) in the presence of 25 mol% of SDS in H_2O at 25°C.

3. Conclusion

In conclusion, we have developed a highly selective, efficient and green process for the chemoselective thioacetalization of a variety of aldehydes and ketones in aqueous micellar media. The current methodology has many advantages such as (i) operational simplicity, (ii) good to excellent yields, (iii) easy availability, (iv) excellent chemoselectivity, (v) the use of water as a reaction medium and (vi) low cost, which make it a valid contribution to the existing processes in the field of thioacetalization of aldehydes and ketones. Efforts to expand the scope of this reaction in green solvents and deprotection of thioacetals are currently underway in our laboratory.

4. Experimental

SDS and TCA as well as all the thiol and carbonyl compounds employed as substrates are commercial products (Merck Chemical Company) and were used without further purification. Melting points (mp) were determined in a capillary tube. ¹H NMR spectra were recorded on a Bruker-200 NMR spectrometer using TMS as the internal standard.

4.1. General procedure

To a solution of SDS (25 mol%, 0.07 g) in H₂O (4 ml), an aldehyde (1 mmol), thiol (2.2 mmol) or dithiol (1.2 mmol) and TCA (1 mmol, 0.16 g) were added. The mixture was stirred at 25°C. The progress of the reaction was monitored by TLC until the aldehyde was consumed (Table 2). Then, K_2CO_3 (0.5 mmol, 0.07 g) was added to the reaction mixture to precipitate dodecyl sulfate and filtered. The product was then extracted with ethyl acetate (4 × 10 ml). Concentration of the organic layer under reduced pressure and purification of residue by passing through silica gel furnished the respective thioacetal in excellent yields. An identical procedure was employed using TCA (1 mmol, 0.16 g) and SDS (25 mol%, 0.07 g) for the thioacetalization of ketones at 70°C.

All the products are known compounds and characterized easily by comparison with authentic samples (¹H NMR, mp).

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