

SHORT COMMUNICATION

Efficient thioacetalisation of carbonyl compounds

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The thioacetalisation of a variety of heterocyclic, aromatic, and aliphatic carbonyl compounds (1 mmol) with ethane-1,2-dithiol (1 mmol) using silica sulphuric acid (SSA) is presented as an efficient heterogeneous catalyst under mild and solvent-free conditions at 60 °C. The thioacetals were formed within a short reaction time (1–34 min) and isolated with 90–98 % yield following an extractive procedure and chromatography on silica gel. The competitive protection reaction between aldehyde and ketone with ethane-1,2-dithiol afforded the protected derivatives of benzaldehyde and acetophenone with 92 % and 8 % yields, respectively, indicating some selectivity.

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Keywords: silica sulphuric acid (SSA), heterogeneous catalyst, thioacetalisation, chemoselectivity, carbonyl compounds, 1,2-ethanedithiol

The protection of carbonyl groups as dithioacetals is a common and popular practice in organic chemistry (Wuts & Greene, 2006; Kocienski, 1994), since they are quite stable under basic or acidic conditions. Among the different carbonyl-protecting groups, 1,3-dithianes, 1,3-oxathiolanes, and 1,3-dithiolanes have long been used as protective groups, and act as an acyl- anion equivalent in carbon–carbon bond-forming reactions (Eliel & Morris-Natschke, 1984; Gröbel & Seebach, 1977; Bulman Page et al., 1989). They are generally prepared by Brønsted or Lewis acid-catalysed condensation of carbonyl compounds with thiols or dithiols, in the presence of strong acid catalysts such as AlCl₃ (Ong, 1980), LnCl₃ (Garlaschelli & Vidari, 1990), ZnCl₂ (Evans et al., 1977), TiCl₄ (Kumar & Dev, 1983), WCl₆ (Firouzabadi et al., 1998), InCl₃ (Muthusamy et al., 2001), In(OTf)₃ (Muthusamy et al., 2002), Sc(OTf)₃ (Kamal & Chouhan, 2002a, 2003), Bi(NO₃)₃ (Komatsu et al., 1995), VO(OTf)₂ (De, 2005), and Ce(OTf)₃ (Kumar et al., 2010). A number of milder procedures employing lithium salts (Firouzabadi et al., 1999a, 1999b; Saraswathy & Sankararaman, 1994; Tietze et al., 2000; Yadav et al., 2001), NiCl₂ (Khan et al., 2003), CoCl₂

(De, 2004), NBS (Kamal & Chouhan, 2002b), silica gel-supported sulphamic acid (Aoyama et al., 2013), and I₂ (Samajdar et al., 2001) have also been reported for this purpose. Many of these protocols suffer from drawbacks such as requiring harsh reaction conditions and stoichiometric amounts of catalysts, the use of expensive reagents and/or chlorinated organic solvents and, in some instances, strong acidic reagents. Recently, a number of solid-supported reagents have also been used for the thioacetalisation of various types of carbonyl compounds, e.g. ZrCl₄–SiO₂ (Patney & Margan, 1996), SOCl₂–SiO₂ (Kamitori et al., 1986), CoBr₂–SiO₂ (Patney, 1994), TaCl₅–SiO₂ (Chandrasekhar et al., 1997), Cu(OTf)₂–SiO₂ (Anand et al., 1999), NaHSO₄–SiO₂ (Das et al., 2005), and I₂–natural phosphate (Zahouily, 2005). Interestingly, only a few of these methods have demonstrated chemoselective protection of aldehydes in the presence of ketones (Ong, 1980; Muthusamy et al., 2001; Kamal & Chouhan, 2002a, 2002b, 2003; Karimi & Seradj, 2000).

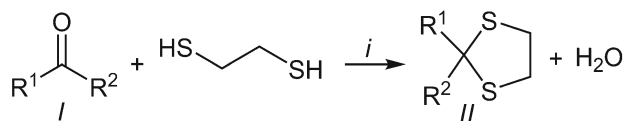
However attractive these reagents may be, to the best of our knowledge there is only one report on the application of silica sulphuric acid (SSA) in the thioac-

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Table 1. Thioacetalisation of carbonyl compounds in the presence of SSA

Entry	R ¹	R ²	Time/min		Yield/%	
			A ^a	B ^b	A ^a	B ^b
1	Phenyl	H	5	3	95	96
2	4-Bromophenyl	H	2	–	98	–
3	4-Chlorophenyl	H	4	–	97	–
4	4-Nitrophenyl	H	3	14	98	74
5	3-Nitrophenyl	H	3	16	94	76
6	4-Methoxyphenyl	H	1	4	98	97
7	2-Methoxyphenyl	H	2	5	98	94
8	3-Bromophenyl	H	12	–	85	–
9	4-Methylphenyl	H	7	6	90	94
10	4-Hydroxyphenyl	H	1	5	95	94
11	4-Dimethylaminophenyl	H	3	–	90	–
12	4-Formylphenyl	H	3	–	70	–
13	1-Hydroxy-2,6-dimethoxyphenyl	H	3	–	96	–
14	Thiophen-2-yl	H	1	–	90	–
15	2-Furyl	H	3	17	70	98
16	3-Indolyl	H	12	–	90	–
17	2-Phenylethen-1-yl	H	3	4	98	95
18	Phenyl	CH ₃	34	10	90	5
19	Benzyl	CH ₃	20	–	98	–

a) Reaction conditions in present work (A): carbonyl compound (1.0 mmol), ethane-1,2-dithiol (1.0 mmol), SSA (0.1 g), 60 °C; b) reported (Pourmousavi & Kazemi, 2012) reaction conditions (B): carbonyl compound (2.0 mmol), ethane-1,2-dithiol (2.4 mmol), SSA (0.02 g), ambient temperature.

**Fig. 1.** Thioacetalisation of carbonyl compounds. Reaction conditions: *i*) SSA, 60 °C; for R¹ and R², see Table 1.

etalisation of carbonyl compounds (Pourmousavi & Kazemi, 2012). As a continuation of our studies on the application of SSA in organic synthesis (Habibi et al., 2013a, 2013b, 2013c), the utilisation of SSA as a heterogeneous acid catalyst is here reported for the highly chemoselective thioacetalisation of a variety of carbonyl compounds using ethane-1,2-dithiol under solvent-free conditions at 60 °C (Fig. 1). The results are compared with those obtained by Pourmousavi and Kazemi (2012) for analogous thioacetalisation of several identical carbonyl compounds at ambient temperature.

Solvents and reagents were obtained from commercial sources (Aldrich, Merck) and used without purification. Column chromatography was performed on silica gel (60–120 mesh). SSA was prepared according to the method previously reported (Zolfigol, 2001; Pourmousavi & Kazemi, 2012).

General procedure for synthesis of 2-R¹-2-R²-1,3-dithiolanes (II)

SSA (0.1 g) was added to a mixture of corresponding carbonyl compound (R¹R²C=O, *I*) (1.0 mmol)

and ethane-1,2-dithiol (0.094 g, 1.0 mmol) and the reaction mixture was stirred at 60 °C under solvent-free conditions. After the appropriate time (disappearance of starting carbonyl compound was monitored by TLC), the reaction mixture was diluted with CH₂Cl₂ (DCM, 20 mL), filtered and the filtrate washed with water (15 mL). The organic layer was dried with anhydrous MgSO₄, filtered and concentrated under reduced pressure affording the crude product which was purified by chromatography on a short silica gel column using EtOAc/hexane (φ_r = 1 : 4) as the eluent to afford the corresponding thioacetal (*II*). The reaction was carried out with various aldehydes such as benzaldehyde (Table 1, entry 1), aromatic aldehydes containing electron-withdrawing and electron-donating substituents (entries 2–13), heterocyclic aldehydes (entries 14–16), α,β -unsaturated aldehydes (entry 17), and ketones (1-phenylethan-1-one (acetophenone), entry 18; 1-phenylpropan-2-one, entry 19). The products were characterised by their physical and spectral data and a comparison with authentic samples.

First, the solvent effect and catalytic activity of SSA for the thioacetalisation of 4-chlorobenzaldehyde with ethane-1,2-dithiol at 60 °C were investigated. It was found that the products under solvent-free conditions were very clean and the reactions were completed much more rapidly than reactions using solvents. The relevant results are summarised in Table 2. It can be seen that, under solvent-free reaction conditions, 4-chlorobenzaldehyde afforded 2-(4-chlorophenyl)-1,3-dithiolane (Table 2, entry 6) within 4 min with a 97 %

Table 2. Solvent effect on thioacetalisation of 4-chlorobenzaldehyde^a

Entry	Solvent	Time/min	Conversion/%
1	<i>n</i> -hexane	33	70
2	CH ₃ CN	15	90
3	CH ₂ Cl ₂	7	90
4	CHCl ₃	5	80
5	MeOH	5	65
6	no solvent	4	97

a) Reaction conditions: 4-chlorobenzaldehyde (1.0 mmol), ethane-1,2-dithiol (1.0 mmol), SSA (0.1 g), 60 °C.

yield. In this respect, other starting aldehydes and ketones were allowed to react under the solvent-free conditions.

To examine the selectivity of thioacetalisation in the competitive protection of aldehyde and ketone, a mixture of benzaldehyde (1 mmol), acetophenone (1 mmol) and ethane-1,2-dithiol (1 mmol) in the presence of SSA (0.1 g) was allowed to react at 60 °C for 5 min. Examination of the isolated and purified reaction products revealed that 2-phenyl-1,3-dithiolane (protected benzaldehyde) and 2-methyl-2-phenyl-1,3-dithiolane (protected acetophenone) were formed with 92 % and 8 % yields, respectively. This observation indicates that this method is potentially applicable in the chemoselective conversion of aldehydes to the corresponding thioacetals in the presence of ketones.

It should also be noted that the thioacetalisation of a conjugated aldehyde takes place chemoselectively and the C=C bond remains intact during the reaction (Table 1, entry 17). In addition, ketones produce the corresponding 1,3-dithioacetals with very good to excellent yields but the reaction requires a longer time (Table 1, entries 18, 19, reaction conditions A) and higher temperature (Table 1, entry 18; 60 °C in A versus ambient temperature in B) than with aldehydes.

Some benefits of the thioacetalisation presented us-

ing SSA-like solvent-free versus solvent conditions (entries 2–4, 6, 9–11), short versus longer reaction time (entries 4, 6, 9–11), equimolar versus higher amounts of reactants (entries 2–11), no toxicity (entries 5, 8), availability, preparation, recycling, and easy storage of the catalyst compared with other methods are summarised in Table 3.

In conclusion, it was found that SSA efficiently catalyses the dithioacetalisation of a variety of carbonyl compounds under solvent-free conditions. The simplicity, mild reaction conditions and chemical selectivity represent several advantages over many existing methods.

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Table 3. Comparison of catalytic effect of various catalysts and reaction conditions in thioacetalisation of benzaldehyde

Entry	Solvent	Catalyst/g	T/°C	Time/min	Yield/%	Mole ratio ^a	Reference
1	–	SSA/0.1	60	5	95	1 : 1	Present work
2	DCM	CoBr ₂ -SiO ₂ /2	rt	10	99	10 : 12–30	Patney, 1994
3	DCM	ZrCl ₄ -SiO ₂ /1	rt	1	98	10 : 12–30	Patney & Margan, 1996
4	Benzene ^b	SOCl ₂ -SiO ₂ /0.2	rt	300	100	1 : 1.1	Kamitori et al., 1986
5	–	I ₂ -natural phosphate/0.3	rt	3	90	2 : 2.1	Zahouily et al., 2005
6	Hexane	Sulphamic acid-SiO ₂ /0.3	rt	120	99	2 : 2.4	Aoyama et al., 2013
7	– ^c	P ₂ O ₅ -Al ₂ O ₃ /0.2 ^d	rt	1	92	2 : 2.4	Zarei et al., 2009
8	–	H ₂ SO ₄ -silica/0.02	rt	3	96	2 : 2.4	Pourmousavi & Kazemi, 2012
9	DCM	SiO ₂ -AlCl ₃ /0.4 ^d	reflux	72	95	1 : 1.1–1.2	Tamami & Borujeny, 2003
10	DCM	Polystyrene-AlCl ₃ /0.25 ^d	reflux	210	98	1 : 1.1–1.2	Tamami & Borujeny, 2003
11	DCM	Polystyrene-FeCl ₃ /0.4 ^d	reflux	245	91	1 : 1.1–1.2	Tamami & Borujeny, 2003

a) Carbonyl compound/ethane-1,2-dithiol mole ratio; b) under nitrogen; c) under microwave irradiation (900 W); d) amount given in mmol; rt means ambient temperature.

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