ARTICLE

OBC
www.rsc.org/obc

Chemoselective thioacetalisation and transthioacetalisation of carbonyl compounds catalysed by tetrabutylammonium tribromide (TBATB)†

Sarala Naik, Rangam Gopinath, Mousumi Goswami and Bhisma K. Patel*
Indian Institute of Technology, Guwahati, Guwahati, 781 039, Assam, India.
E-mail: patel@iitg.ernet.in; Fax: +91-361-2690762; Tel: +91-361-2582307

Received 20th February 2004, Accepted 1st April 2004
First published as an Advance Article on the web 11th May 2004

Thioacetals and thioketals of various aldehydes and ketones were obtained directly from carbonyl compounds or by a transthioacetalisation process from cyclic *O,O*-acetals in the presence of dithiols and a catalytic amount of tetrabutylammonium tribromide (TBATB). Chemoselective thioacetalisation of aromatic aldehydes containing an electron-donating group in the presence of an aldehyde containing an electron-withdrawing group, aldehydes in the presence of ketones, aliphatic cyclic ketones in the presence of aromatic ketones and less hindered ketones in the presence of more hindered ketones have been achieved. A cyclic acetal containing an electron-donating group has been chemoselectively transthioacetalised in the presence of an acetal having an electron-withdrawing substituent. These selectivities are due to the intrinsic reactivity of the substrate themselves and are independent of the catalyst and reaction conditions. Shorter reaction times, mild reaction conditions, stability of acid sensitive protecting groups, high efficiencies, facile isolation of the desired products and the catalytic nature of the reagent are the attractive features of the present method.

Introduction

Acetals, oxathioacetals and thioacetals are the most widely used groups for masking a carbonyl compound. During a multi-step synthetic process the acetal and thioacetal protected carbonyl groups are resistant to attack by various reagents such as nucleophilic, basic, oxidizing, catalytic and hydride reducing agents.[1] Inspite of the difficulties associated with their removal, thioacetals are most often used because of their greater stability towards acidic conditions as compared to corresponding *O,O*-acetals and *O,S*-acetals. In addition to serving as a protecting group for carbonyl compounds, thioacetals are widely used as precursors for acylanion equivalents and masked methylene functions in carbon–carbon bond forming reactions.[2] Moreover *S,S*-acetals can be used as intermediates for the conversion of the carbonyl functions to the parent hydrocarbons by reductive desulfurisation.[3] Some of these approaches have been used extensively for the synthesis of several natural products.[4]

The preparation of dithioacetals has generally been achieved by the condensation of carbonyl compounds with thiols or dithiols in presence of protic acids, Lewis acids and supported reagents. A comprehensive list of methods and reagents has been compiled and reviewed.[1a,b,5] Some other methods which are either not reviewed or some recently reported use Lewis acids,[6] metal triflates,[7] lithium salts,[8] supported reagents,[9] and other miscellaneous reagents.[10] In addition, a variety of other reagents such as methylthiotrimethylsilane,[11] bis (diisobutylaluminium)-1,2-ethanedithiolate,[12] polyphosphoric acid trimethylsilyl esters,[13] 2-chloro-1,2,3-dithioborolane,[14] 2,2-dimethyl-2-sila-1,3-dithiane/$BF_3{\cdot}Et_2O$[15] have been developed for this purpose. Recently, thioacetalisation of carbonyl compounds has been achieved using a surfactant-type Brønsted acid in an aqueous medium[16] and by an exchange reaction from 2,2-dimethyl-1,3-dithiolane catalysed by solid acidic catalysts.[17] Despite numerous methods reported in the literature, some of the problems of the existing methods are difficulties in work-up, isolation, requirement of inert atmosphere, harsh reaction conditions, expensive and stoichiometric reagents, incompatibility with other protecting groups and failure to protect deactivated and hindered substrates.

Molecules bearing multiple carbonyl groups are frequently encountered and in those cases, the carbonyl group being modified must be differentiated from the other carbonyls and from acetals and ketals, which can also be considered as members of the carbonyl family. One of the problems associated is poor selectivity when applied to a mixture of aldehyde and ketone. Recently, several methods have been reported for the chemoselective thioacetalisation between aldehydes and ketones.[5,6e–f,7a–b,8b–d,9b,10f–j,18] However, there are only a few methods known for the chemoselective thioacetalisation between ketones[5,6e,7a–b,8d,10f,18,19] and between aldehydes[6e,18] but, none of the reported methods describe the chemoselective thioacetalisation of a carbonyl compound with different dithiols. Chemoselective transthioacetalisation between different acetals has not been reported at all. Thus, selective thioacetalisation of carbonyl compounds are of great synthetic value. However, the development in this area demands a synthetic methodology satisfying all the above-mentioned criteria and also not only chemoselectivities between aldehydes and ketones but also between different aldehydes and different ketones. It is also important to understand what governs the selectivity, is it the intrinsic reactivity of the substrates or catalyst or reaction conditions?

Results and discussion

Recently tetrabutylammonium tribromide (TBATB), a stable orange crystalline solid has emerged as an efficient reagent for various organic transformations as reported by us[20] and by others.[21] It has been prepared in an environmentally benign way using tetrabutylammoniumbromide, 30% H_2O_2 and catalytic quantity of V_2O_5.[20e] As a part of this continuing programme we wish to utilise this reagent for an efficient thioacetalisation of carbonyl compounds and transthioacetalisation of *O,O*-acetals. When used in stoichiometric amounts this reagent is reported to unmask thioacetal.[21d] However, using a catalytic quantity (0.02 equiv.) it acts as a promoter for thioacetalisation of aldehydes and thioketalisation of ketones.

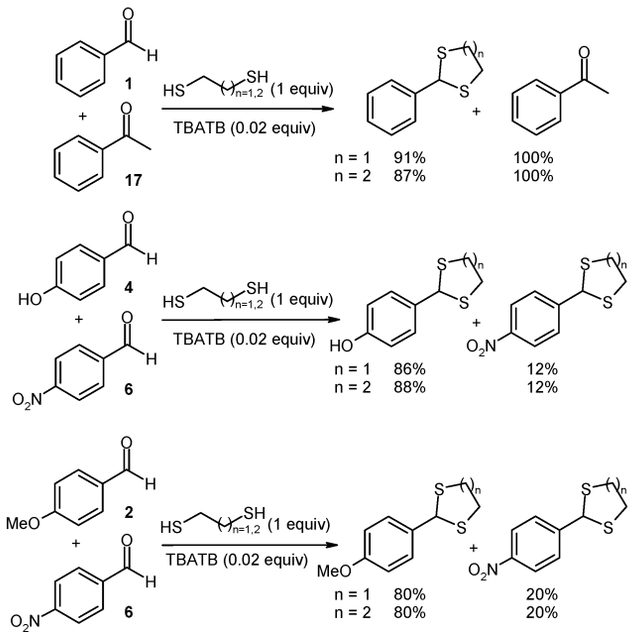
† Dedicated to Professor Subramanian Ranganathan on the occasion of his 70th birthday.

DOI: 10.1039/b402648a

Table 1 Thioacetalisation[a] of carbonyl compounds

Entry	R^1	R^2	Time/h	X_1 [b,c]	X_2 [b,c]
1	Ph	H	0.08	96	96
2	*p*-(OMe)C_6H_4	H	0.08	87	84
3	*o*-(OH)C_6H_4	H	0.50	95	95
4	*p*-(OH)C_6H_4	H	0.50	97	94
5	*o*-(NO_2)C_6H_4	H	1.50	45	30
6	*p*-(NO_2)C_6H_4	H	1.50	70	70
7	*p*-(Cl)C_6H_4	H	1.00	80[d]	79[d]
8	*p*-$N(CH_3)_2C_6H_4$	H	1.00	81[d]	75[d]
9	3,4-di (OMe)C_6H_3	H	1.00	90	80
10	*p*-(OAc)C_6H_4	H	1.00	70	70
11	*p*-(OBz)C_6H_4	H	1.00	72	68
12	*p*-(OBn)C_6H_4	H	1.00	85	83
13	*p*-(Oallyl)C_6H_4	H	1.00	77	70
14	Furyl	H	1.00	70	80
15	PhCH=CH	H	0.25	88	81
16	Cyclohexanone	—	0.50[e]	75	75
17	Ph	CH_3	1.00[e]	90	85
18	Ph	Ph	3.00[e]	79[d]	82[d]

X_1 = 1,3-dithiolane, X_2 = 1,3-dithiane. [a] Reactions were monitored by TLC/GC. [b] Confirmed by comparison with IR and ^1H NMR of the authentic sample. [c] % Isolated yield. [d] Based on the recovery of starting material. [e] 0.1 equiv. of TBATB was used.



Scheme 1 Chemoselective thioacetalisation.

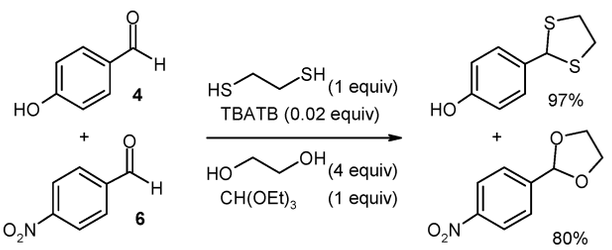
The experimental procedure for thioacetalisation is remarkably simple and does not require the use of dry solvents and inert atmosphere or reflux conditions. To a stirred solution of carbonyl compound and 1,2-ethanedithiol or 1,3-propanedithiol in THF was added a catalytic quantity of TBATB (0.02 equiv.) and the mixture was left stirred at room temperature. The versatility of the process has been proved with a wide range of aldehydes and ketones with various stereo-electronic factors as shown in Table 1. The role of TBATB is not clear but it is most likely that it reacts with dithiol similar to alcohols[20a–d,22] to generate HBr, which may activate the carbonyl group by protonation at the carbonyl oxygen for further reaction. In a control experiment, when benzaldehyde was treated with a catalytic quantity of 48% HBr (0.02 equiv.) instead of TBATB and 1,2-ethanedithiol, benzaldehyde 1,3-dithiolane was obtained in good yield (95%).

Under these conditions, a wide range of aldehydes and ketones containing electron-donating, electron-withdrawing, conjugated and hindered groups could all be transformed to the corresponding 1,3-dithiolanes and 1,3-dithianes in good yields. As can be seen from Table 1, most of the substrates gave excellent yields of the corresponding dithioacetals. Aldehydes containing electron-donating groups such as *o*-hydroxybenzaldehyde **3** and *p*-hydroxybenzaldehyde **4** gave excellent yields of the corresponding products. However, aldehydes containing electron-withdrawing substituents such as *o*-nitrobenzaldehyde **5** and *p*-nitrobenzaldehyde **6** gave poor yields of the corresponding dithioacetals. A variety of functional groups such as *O*-acetyl, *O*-benzoyl, *O*-benzyl, *O*-allyl and double bonds were found to be quite stable during the reactions. The compatibility of the methodology was demonstrated by the regioselective thioacetalisation of unsaturated aldehydes in good yields as shown in the case of aldehydes **13** and **15**. Importantly, no other side products, *viz*. bromination were observed. Ketones **16**–**18** reacted slowly under the given condition giving poor yields. However, a better yield was obtained by using (0.1 equiv.) of the reagent.

This difference in reactivity of the aldehydes and the ketones suggest that the method can be useful for the selective protection of aldehydes. When dithiol (1 equiv.) was added to an equimolar mixture of an aldehyde **1** and a ketone **17** (Scheme 1) it was observed that in this mixture, the aldehyde formed the dithiolane and dithiane whilst the ketone was almost completely recovered. Similar chemoselectivity was observed in the thioacetalisation of benzaldehyde **1** over acetophenone **17** with other catalysts such as $BF_3{\cdot}Et_2O$, NBS, I_2 and with HBr. The selectivity remained unaltered even when the reaction was performed at different temperatures (−10 °C and 80 °C) and with different solvents ($CHCl_3$, Et_2O, toluene and CH_3CN) using TBATB as the catalyst. This is because of the higher ground state energy and lower transition state for aldehydes as compared to the higher ground state stabilization and higher activation energy for ketones as explained for acetalisation reactions.[20a] Thus in this case the selectivity is due to the intrinsic reactivity of the substrates and is independent of the catalyst, solvent and reaction temperature.

Selective protection of one aliphatic aldehyde in the presence of another has been addressed only twice in the literature.[6e,18] Realizing the sharp contrast in the reactivity of *p*-hydroxybenzaldehyde **4** over *p*-nitrobenzaldehyde **6** we decided to make selective thioacetalisation our objective. Thus, in a competitive reaction between *p*-nitrobenzaldehyde **6** and *p*-hydroxybenzaldehyde **4** the later was thioacetalised (Scheme 1). This selectivity is in sharp contrast to the selectivities obtained in the acetalisation of carbonyl compounds,[20a,23] where a substrate containing an electron-withdrawing group such as *p*-nitrobenzaldehyde **6** reacts preferentially over a substrate having an electron-donating group, *p*-hydroxybenzaldehyde **4**. In an analogous reaction between *p*-methoxybenzaldehyde **2** and *p*-nitrobenzaldehyde **6** the former was thioacetalised preferentially (Scheme 1). Here again the selectivity is independent of the catalysts ($BF_3{\cdot}Et_2O$, NBS, I_2 and HBr), solvents ($CHCl_3$, Et_2O, toluene and CH_3CN) and the reaction temperature (−10 °C and 80 °C). Not surprisingly the reactions were found to be slower at lower temperature (−10 °C). In our previous work pertaining to acetalisation [20a] we have argued that due to lower electron density around the carbonyl carbon of *p*-nitrobenzaldehyde **6** compared to *p*-hydroxybenzaldehyde **4** the former is more susceptible to nucleophilic attack by diols for acetalisation. Unfortunately, the same logic could not be extended to the thioacetalisation process in spite of a similarity in the reaction mechanism. One plausible explanation is that the stabilisation of filled sulfur orbitals towards thiocarbenium ions predominates over the effects due to electron-donating and electron-withdrawing groups present in the aromatic ring. A second explanation could be due to a higher molecular orbital coefficient at the carbonyl carbon of *p*-hydroxybenzaldehyde **4**, the sulphur nucleophile with its larger orbital overlaps efficiently satisfying the Bürgi–Dunitz trajectory of 107° for a favourable nucleophilic attack. Thus, in aldehydic substrates

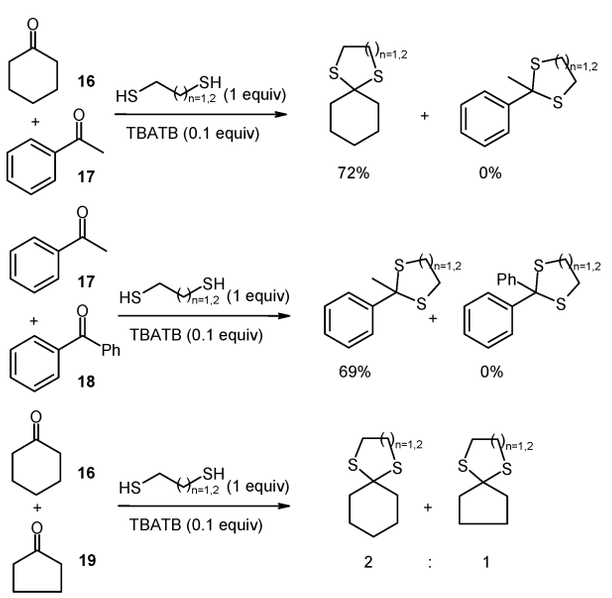
containing both electron-donating and electron-withdrawing groups, for the selective protection at the electron rich aldehydic carbonyl site thioacetalisation process is preferred and for the protection at the electron-deficient aldehydic carbonyl acetalisation is desirable. This assumption of ours is evident from the following competitive experiment (Scheme 2). When an equimolar mixture of *p*-hydroxybenzaldehyde **4** and *p*-nitrobenzaldehyde **6** was reacted with an equimolar mixture of 1,2-ethanedithiol, 1,2-ethanediol and triethylorthoformate, TBATB (0.01 equiv) in THF, *p*-hydroxybenzaldehyde **4** was completely thioacetalised whereas *p*-nitrobenzaldehyde **6** was acetalised to 35% with the rest being starting material. It may be mentioned here that for the complete acetalisation of *p*-nitrobenzaldehyde, 4 equivalents of the diol is necessary.[20a] When the above competitive reaction was performed with 1,2-ethanediol (4 equiv.) and 1,2-ethanedithiol (1 equiv.) a complete chemoselective thioacetalisation of *p*-hydroxybenzaldehyde and acetalisation of *p*-nitrobenzaldehyde (80%) was observed with the rest being starting materials as shown in Scheme 2.



Scheme 2 Chemoselective acetalisation and thioacetalisation.

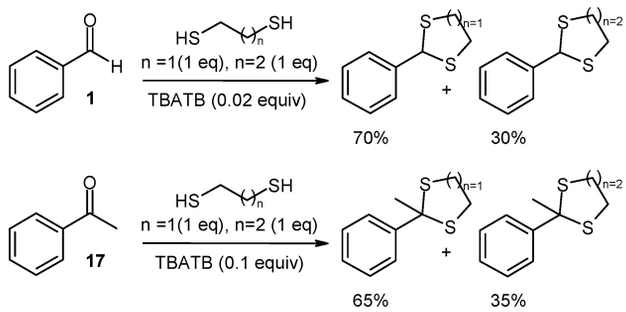
There have been reports of selective thioketalisation of aliphatic ketones over aromatic ketones.[5,6e,7a–b,8d,10f,18,19] By employing our methodology aliphatic cyclic ketones could be preferentially thioketalised over aromatic ketones as demonstrated for cyclohexanone **16** and acetophenone **17**. Further, it was observed that the less hindered aromatic ketone acetophenone **17** could be selectively thioketalised in the presence of a hindered aromatic ketone, benzophenone **18** employing the present protocol (Scheme 3). This method was then used for the selective protection of a six membered aliphatic ketone **16** as a thioketal in the presence of a five membered aliphatic ketone **19** (Scheme 3). Thus this methodology will be useful for selective protection of a six membered aliphatic ketone in the presence of a five membered aliphatic ketone.[6e,7a–b,8d,10f,18,19]

Recently, we have reported a competitive reaction between different diols for the same carbonyl compound and have found



Scheme 3 Chemoselective thioketalisation.

good degrees of selectivities. The apparent order of acetal formation for different carbonyl groups is: aldehyde-1,3-dioxanes > aldehyde-1,3-dioxolanes > ketone-1,3-dioxolanes > ketone-1,3-dioxanes.[20a] This prompted us to investigate whether any preferential formation of a particular thioacetal or thioketal exists for a carbonyl group when reacted with an equimolar mixture of dithiols. When benzaldehyde **1** was reacted in the presence of both 1,2-ethanedithiol and 1,3-propanedithiol in equimolar amounts, the ratio of 1,3-dithiolane over 1,3-dithiane was found to be 7 : 3. When the same competitive reaction was carried out with acetophenone **17**, a similar selectivity was observed as shown in Scheme 4. Thus, 1,3-dithiolane formations are preferred both for aldehydes and ketones compared to 1,3-dithiane. However, during the acetalisation process the preferences obtained were different, aldehyde preferring 1,3-dioxanes and ketones 1,3-dioxolanes.[20a] Thus from the present study the apparent order of thioacetal and thioketal formation of different carbonyl groups is: aldehyde-1,3-dithiolane > aldehyde-1,3-dithiane > ketone-1,3-dithiolane > ketone-1,3- dithiane.



Scheme 4 Chemoselective thioacetalisation/ketalisation.

Transthioacetalisation

Protection followed by deprotection and subsequent reprotection with a different protecting group is usual practice in a multi-step synthesis as demanded by their stability under the reaction conditions in subsequent steps. Thus, a direct method for this transformation avoiding the intermediate step of going back to the parent functionality is gaining more importance in order to improve the overall synthetic efficiency. Transthioacetalisation of acetal is a useful transformation for the preparation of *S,S*-acetals and in comparison with thioacetalisation of carbonyl compounds, it is faster and cleaner. The reactions are faster because the reactive intermediate oxocarbenium is rapidly generated by the protonation of one of the oxygen atoms of the acetal, which leaves *via* anchimeric assistance from the other oxygen attached to the same carbon whereas thioacetalisation of the carbonyl is initiated by coordination to a protic acid. Catalysts such as 5 M $LiClO_4$,[8d] WCl_6,[10e] trichloroisocyanuric acid[10g] and I_2[10f] are known to be active both towards thioacetalisation and transthioacetalisation processes.[8d,10e,g,j] A number of other acidic reagents such as $MgBr_2$,[24] $TeCl_4$,[25] $ZrCl_4$,[26] $SiO_2/SOCl_2$[27] and neutral koaline clay[28] have also been reported for this purpose. Very recently it has been achieved using ionic liquids under solvent free conditions[29] and using $InCl_3$.[30] None of the reported methods describe chemoselective transthioacetalisation between acetals and ketals and between different acetals. In this context we have explored TBATB as the catalyst for the chemoselective transthioacetalisation. A lower quantity of TBATB (0.01 equiv.) was used as compared to direct thioacetalisation from the corresponding carbonyls. In a typical reaction, to cyclic 1,3-dioxolane or 1,3-dioxane (1 equiv.) and 1,2-ethanedithiol or 1,3-propanedithiol (1 equiv.) in acetonitrile was added a catalytic amount of TBATB (0.01 equiv.) which was stirred at room temperature for a certain period of time. The results are summarised in Table 2. All the reactions were

Table 2 Transthioacetalisation[a] of 1,3-dioxolane

Entry	R^1	R^2	Time/h	X_1[b,c]	X_2[b,c]
1a	Ph	H	0.08	99	98
2a	*p*-(OMe)C_6H_4	H	0.08	98	94
4a	*p*-(OH)C_6H_4	H	0.08	97	99
5a	*o*-(NO_2)C_6H_4	H	0.75	82	89
6a	*p*-(NO_2)C_6H_4	H	0.33	84	85
7a	*p*-(Cl)C_6H_4	H	0.08	93	94
14a	Furyl	H	0.08	95	96
15a	PhCH=CH	H	0.08	83	89
16a	Cyclohexanone	—	0.08	92	90
17a	Ph	CH_3	0.08	89	91

X_1 = 1,3-dithiolane, X_2 = 1,3-dithiane. [a] Reactions were monitored by TLC/GC. [b] Confirmed by comparison with IR and ^{1}H NMR of the authentic sample. [c] % Isolated yield.

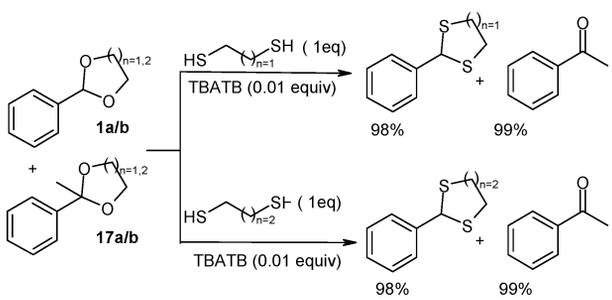
Table 3 Transthioacetalisation[a] of 1,3-dioxane

Entry	R^1	R^2	Time/h	X_1[b,c]	X_2[b,c]
1b	Ph	H	0.08	93	94
2b	*p*-(OMe)C_6H_4	H	0.08	95	94
4b	*p*-(OH)C_6H_4	H	0.08	97	97
5b	*o*-(NO_2)C_6H_4	H	0.75	82	89
6b	*p*-(NO_2)C_6H_4	H	0.33	85	84
7b	*p*-(Cl)C_6H_4	H	0.08	98	99
14b	Furyl	H	0.08	96	95
15b	PhCH=CH	H	0.08	83	90
16b	Cyclohexanone	—	0.08	89	92
17b	Ph	CH_3	0.08	91	89

X_1 = 1,3-dithiolane, X_2 = 1,3-dithiane. [a] Reactions were monitored by TLC/GC. [b] Confirmed by comparison with IR and ^{1}H NMR of the authentic sample. [c] % Isolated yield.

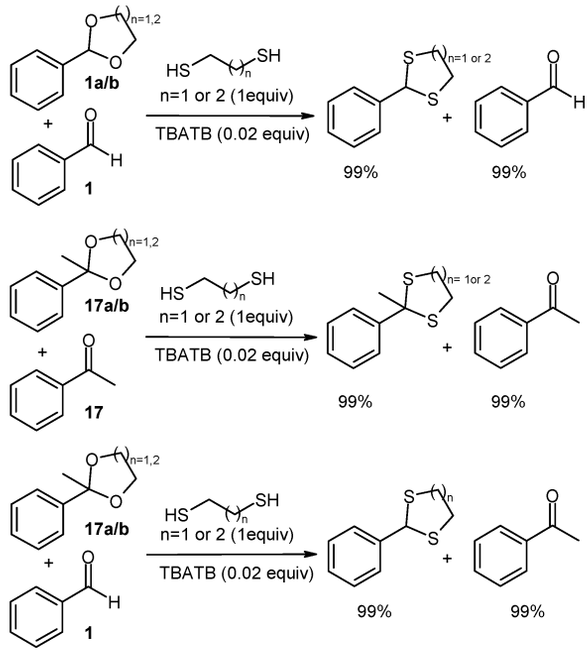
complete in less than 5 minutes giving excellent yields of products. A wide range of structurally varied cyclic *O,O*-acetals underwent transthioacetalisation either with 1,2-ethanedithiol or 1,3-propanedithiol to furnish the corresponding *S,S*-acetals in nearly quantitative yields. During the process no parent carbonyl compound could be detected by gas chromatographic analysis of the reaction mixture. It is worth mentioning that direct thioacetalisation of aromatic aldehydes containing electron-withdrawing groups such as *o*-nitrobenzaldehyde **5** and *p*-nitrobenzaldehyde **6** gave poor yields, whereas transthioacetalisation of acetals **5a** and **6a** gave excellent yields of the corresponding thioacetals. Substrates containing double bonds remained unscathed by this process. Aromatic acetals and ketals smoothly underwent transthioacetalisation and transthioketalisation as shown in Tables 2 and 3.

High chemoselectivity of the method is demonstrated by competitive reactions between an acetal and a ketal. When an equimolar mixture of an acetal **1a** or **1b** (1 equiv.) and a ketal **17a** or **17b** (1 equiv.) was allowed to react with either 1,2-ethanedithiol or 1,3-propanedithiol (1 equiv.) and a catalytic amount of TBATB (0.01 equiv.) in acetonitrile at ambient temperature, a nearly quantitative yield of the thioacetal was obtained with a trace amount of ketal (< 2%) and during the process the acetophenone ketal was deprotected to acetophenone **17** (Scheme 5).



Scheme 5 Chemoselective transthioacetalisation and deketalisation.

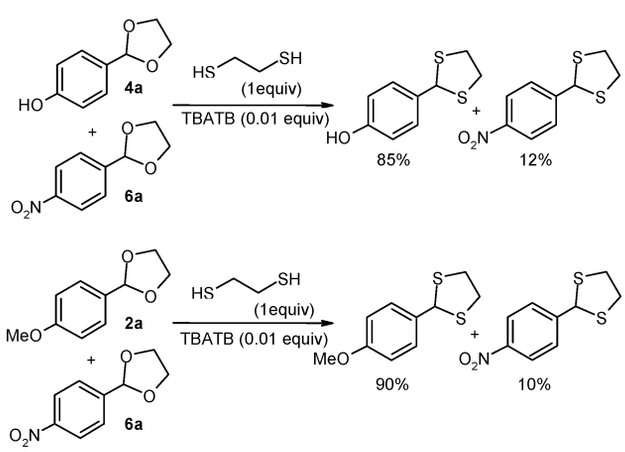
Acetals and ketals are much more reactive towards transthioacetalisation and transthioketalisation compared to the direct thioacetalisation and thioketalisation of the corresponding carbonyl compounds. Chemoselective catalytic activity of the catalyst is demonstrated by transthioacetalisation and transthioketalisation of an acetal or a ketal in the presence of an aldehyde or a ketone. In a competitive reaction, cyclic acetals of benzaldehyde **1a** or **1b** and acetophenone **17a** or **17b** were preferentially protected in the presence of benzaldehyde **1** and acetophenone **17** respectively in quantitative yields (Scheme 6).



Scheme 6 Chemoselective transthioacetalisation and transthioketalisation.

However, attempts to carry out chemoselective transthioketalisation of ketals **17a** or **17b** over aldehyde **1** failed inspite of the higher reactivity of the ketals towards transthioketalisation and during the process, the ketal **17a** or **17b** was deprotected to ketone **17** and aldehyde was thioacetalised as shown in Scheme 6.

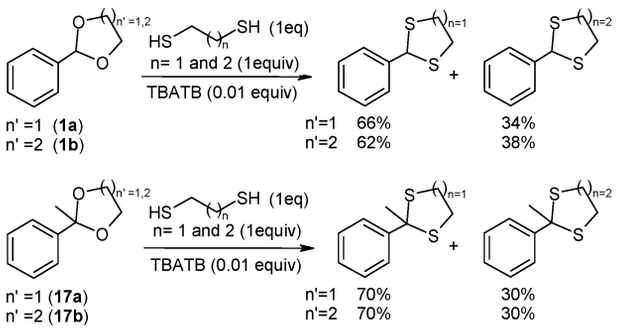
The preferential transthioacetalisation of an acetal containing an electron-donating substituent **2a** and **4a** over an acetal containing an electron-withdrawing group **6a** is demonstrated in Scheme 7. This observation is consistent with preferential thioacetalisation of *p*-hydroxybenzaldehyde **4** over *p*-nitrobenzaldehyde **6** (Scheme 1). In an analogous competitive reaction, the 1,3-dioxolane of *p*-methoxybenzaldehyde **2a** has



Scheme 7 Chemoselective transthioacetalisation.

been preferentially transthioacetalised in the presence of the 1,3-dioxolane of *p*-nitrobenzaldehyde **6a**. It has been found that the acetal of *p*-nitrobenzaldehyde is much more stable compared to the acetal of *p*-hydorxybenzaldehyde.[31]

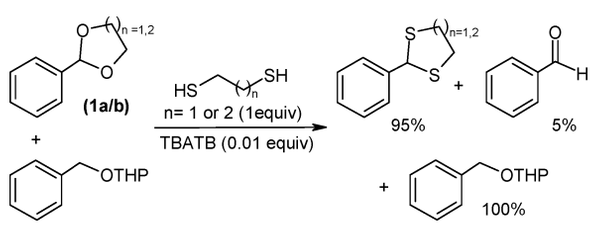
The preferential formation of 1,3-dithiolane over 1,3-dithiane was also observed during transthioacetalisation and transketalisation as demonstrated in the competitive reaction shown in Scheme 8.



Scheme 8 Chemoselective transthioacetalisation and transthioketalisation.

When aldehyde-1,3-dioxolane **1a** or aldehyde-1,3-dioxane **1b** were reacted with an equimolar mixture of 1,2-ethanedithiol or 1,3-propanedithiol, acetals preferentially form 1,3-dithiolanes, an observation consistent with the preferential formation of 1,3-dithiolane in a competitive reaction directly from an aldehyde (Scheme 4). In a similar competitive reaction with ketals **17a** or **17b** a higher percentage of 1,3-dithiolane was obtained (Scheme 8).

Further the chemoselectivity of the method was demonstrated by competitive reaction between a symmetrical acetal **1a** and an unsymmetrical acetal such as the THP ether of benzyl alcohol. The former was preferentially thioacetalised over the latter (Scheme 9). It is not surprising since unsymmetrical acetals such as THP ethers are much more stable under acidic conditions as compared to the symmetrical acetals.[31]



Scheme 9 Chemoselective transthioacetalisation of symmetrical acetal.

Conclusion

In conclusion, various aldehydes and ketones were protected as their thioacetals and thioketals under mild reaction conditions in the presence of a catalytic amount of TBATB. By using this method a particular carbonyl group can be selectively blocked in the presence of another such as between aldehydes and ketones, between two aldehydes and two ketones. Transthioacetalisation of *O,O*-acetals and *O,O*-ketals was also achieved using this catalyst. In comparison with the existing methods using many acidic catalysts, this method is very general, simple, high-yielding, environmentally friendly and oxygen and moisture tolerant. In terms of selectivity and efficiency this procedure is superior to many of the reported methods where oxidants as well as strong acids are used. Due to the mild reaction conditions, a number of functional groups, albeit being capable of reacting with TBATB remain intact.

Experimental

General remarks

All the reagents were commercial grade and purified according to the established procedures. Organic extracts were dried over anhydrous sodium sulfate. Solvents were removed in a rotary evaporator under reduced pressure. Silica gel (60–120 mesh size) was used for column chromatography. Reactions were monitored by TLC on silica gel 60 F_{254} (0.25 mm). NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 with tetramethylsilane as the internal standard for ^{1}H (200, 300 and 400 MHz) or $CDCl_3$ or DMSO-d_6 solvent as the internal standard for ^{13}C (50, 75 and 100 MHz). Melting points were recorded on a Buchi B-545 melting point apparatus and are uncorrected. IR spectra were recorded in KBr or neat on a Nicolet Impact 410 spectrophotometer. Gas liquid chromatography was performed in HP-6890 using a crossed-linked methylsilicone gum capillary column (30 m × 0.32 mm × 0.25 μm) fitted with FID. The following thioacetals and thioketals derived from parent aldehydes and ketones have been reported in the literature: 1,3-dithiolanes **1**–**2**, **4**, **10**,[10i] **3**, **5**,[32] **6**,[8d] **7**,[8d] **8**,[5] **9**,[8d] **13**,[30] **14**,[32] **15**,[8d] **16**,[10g] **17**,[8d] **18**,[32] **19**[18] and 1,3-dithianes **1**–**2**, **4**, **5**, **10**–**13**, **15**,[10i] **3**,[28] **6**–**7**,[10g] **9**,[33] **14**,[18] **16**,[7b] **17**,[10g] **18**,[9f] **19**,[34] and **8**.[35]

General procedure for preparation of cyclic thioacetals and thioketals. To a solution of carbonyl compound (5 mmol) in THF (5 mL) and 1,2-ethanedithiol or 1,3-propanedithiol (5.5 mmol) was added tetrabutylammonium tribromide (0.1 mmol). The homogeneous reaction was left at room temperature and the progress of the reaction mixture was monitored by TLC and GC. After completion of the reaction, the reaction mixture was poured into saturated $NaHCO_3$ solution (10 mL) and the product was extracted with ethyl acetate (2 × 25 mL). The organic layer was separated, dried over anhydrous sodium sulfate and concentrated. Further purification was achieved by a flash column chromatography and products were identified by comparison of their NMR, IR, GC, and GC co-injection with authentic samples prepared by known methods.

General procedure for transthioacetalisation. To a mixture of 1,3-dioxolane or 1,3-dioxane (2 mmol) and 1,2-ethanedithiol or 1,3-propanedithiol (2.2 mmol) in acetonitrile (2 mL) was added tetrabutylammonium tribromide (0.04 mmol). The homogeneous reaction was left at room temperature and the progress of the reaction was monitored by TLC and GC. After completion of the reaction, the reaction mixture was poured into saturated $NaHCO_3$ solution (10 mL) and the product was extracted with ethyl acetate (2 × 25 mL). The organic layer was separated, dried over anhydrous sodium sulfate and concentrated. Further purification was achieved by flash column chromatography and products were identified by comparison of their NMR, IR, GC, and GC coinjection with authentic samples prepared by known methods.

Chemoselective thioacetalisation of aldehydes in the presence of ketones. To the mixture of benzaldehyde **1** (1 mmol), acetophenone **17** (1 mmol) and 1,2-ethanedithiol or 1,3-propanedithiol (1 mmol) in THF was added tetrabutylammonium tribromide (0.02 mmol). The homogeneous reaction was left at room temperature. The percentages of products formed at different times were determined by gas liquid chromatography.

Chemoselective thioacetalisation of *p*-hydroxybenzaldehyde 4 in the presence of *p*-nitrobenzaldehyde 6. To the mixture of *p*-hydroxybenzaldehyde **4** (2 mmol), *p*-nitrobenzaldehyde **6** (2 mmol) and 1,2-ethanedithiol or 1,3-propanedithiol (2 mmol) in THF (2 mL) was added tetrabutylammonium tribromide

(0.04 mmol). The homogeneous reaction was left at room temperature. The percentages of products formed at different times were determined by gas liquid chromatography.

Chemoselective acetalisation of *p*-nitrobenzaldehyde 6 and thioacetalisation of *p*-hydroxybenzaldehyde 4. To an equimolar (1 mmol each) mixture of *p*-hydroxybenzaldehyde **4** and *p*-nitrobenzaldehyde **6** in THF (2 mL) was added 1,2-ethanedithiol (1 mmol) and 1,2-ethanediol (4 mmol) followed by triethylorthoformate (1 mmol) and TBATB (0.02 mmol). The homogeneous reaction was left at room temperature. The percentages of products formed at different times were determined by gas liquid chromatography.

Chemoselective ketalisation of different ketones. To an equimolar (1 mmol each) mixture of two ketones and 1,2-ethanedithiol or 1,3-propanedithiol (1 mmol) in THF (2 mL) was added tetrabutylammonium tribromide (0.1 mmol). The homogeneous reaction was left at room temperature. The percentages of products formed at different times were determined by gas liquid chromatography.

Chemoselective thioacetalisation and thioketalisation of aldehydes and ketones with dithiols. To an equimolar mixture of 1,2-ethanedithiol and 1,3-propanedithiol (1 mmol each) in THF (2 mL) was added an aldehyde or a ketone (1 mmol) followed by TBATB (0.02 mmol for aldehyde and 0.1 mmol for ketone). The homogeneous reaction was left at room temperature. The percentages of products formed at different times were determined by gas liquid chromatography.

Chemoselective transthioacetalisation of acetals (1,3-dioxolane or 1,3-dioxane) in the presence of ketals (1,3-dioxolane or 1,3-dioxane). To the mixture of acetal (1 mmol), ketal (1 mmol) and 1,2-ethanedithiol or 1,3-propanedithiol (1 mmol) in acetonitrile (2 mL) was added tetrabutylammonium tribromide (0.01 mmol). The homogeneous reaction was left at room temperature. The percentages of products formed at different times were determined by gas liquid chromatography.

Chemoselective transthioacetalisation of acetal (1,3-dioxolane or 1,3-dioxane) in the presence of aldehyde and transthioketalisation of ketal (1,3-dioxolane or 1,3-dioxane) in the presence of ketone. To the mixture of acetal or ketal (1 mmol) and its corresponding carbonyl compound (1 mmol) and 1,2-ethanedithiol or 1,3-propanedithiol (1 mmol) in acetonitrile (2 mL) was added tetrabutylammonium tribromide (0.01 mmol). The homogeneous reaction was left at room temperature. The percentages of products formed at different times were determined by gas liquid chromatography.

Chemoselective transthioacetalisation and transthioketalisation of acetals (1,3-dioxolane or 1,3-dioxane) and ketals (1,3-dioxolane or 1,3-dioxane) with dithiols. To an equimolar mixture of acetal or ketal (1 mmol) 1,2-ethanedithiol and 1,3-propanedithiol (1 mmol each) in acetonitrile (2 mL) was added tetrabutylammonium tribromide (0.01 mmol). The homogeneous reaction was left at room temperature. The percentages of products formed at different times were determined by gas liquid chromatography.

Chemoselective transthioacetalisation of symmetrical acetal in the presence of an unsymmetrical acetal. To an equimolar mixture of benzaldehyde acetal (1,3-dioxolane or 1,3-dioxane), tetrahydropyranyl ether of benzylalcohol and 1,2-ethanedithiol or 1,3-propanedithiol (1 mmol) in acetonitrile (2 mL) was added tetrabutylammonium tribromide (0.01 equiv.). The homogeneous reaction was left at room temperature. The percentages of products formed at different times were determined by gas liquid chromatography.

Phenyl-1,3-dithiolane (1X$_1$). ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.34 (m, 2H), 3.50 (m, 2H), 5.64 (s, 1H), 7.30 (m, 3H), 7.47 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 40.4, 56.1, 127.0, 128.3, 128.8, 138.4.

Phenyl-1,3-dithiane (1X$_2$). ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.91 (m, 1H), 2.17 (m, 1H), 2.80–3.20 (m, 4H), 5.16 (s, 1H), 7.31 (m, 3H), 7.46 (m, 2H).

4-Methoxyphenyl-1,3-dithiolane (2X$_1$). ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.32 (m, 2H), 3.46 (m, 2H), 3.79 (s, 3H), 5.63 (s, 1H), 6.83 (d, 2H, J = 8.8 Hz), 7.45 (d, 2H, J = 8.8 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 40.3, 55.3, 56.1, 113.8, 129.2, 132.0, 159.3.

4-Methoxyphenyl-1,3-dithiane (2X$_2$). ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.59–1.86 (m, 2H), 2.72–2.89 (m, 4H), 3.66 (s, 3H), 4.99 (s, 1H), 6.72 (d, 2H), 7.24 (d, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 24.0, 31.2, 49.7, 54.3, 113.0, 127.9, 130.3, 158.5.

2-Hydroxyphenyl-1,3-dithiolane (3X$_1$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.10 (m, 2H), 3.50 (m, 2H), 5.82 (s, 1H), 6.85 (m, 2H), 7.20 (d, 1H), 7.32 (d, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 39.7, 54.0, 117.2, 120.3, 121.8, 129.7, 129.9, 154.9.

2-Hydroxyphenyl-1,3-dithiane (3X$_2$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.91 (m, 1H), 2.20 (m, 1H), 2.92 (m, 2H), 3.07 (m, 2H), 5.40 (s, 1H), 6.33 (s, 1H), 6.88 (m, 2H), 7.25 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.3, 32.0, 47.6, 117.6, 121.2, 124.1, 129.6, 130.5, 154.7.

4-Hydroxyphenyl-1,3-dithiolane (4X$_1$). ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.24–3.49 (m, 4H), 5.63 (s,1H), 6.75 (d, 2H, J = 8.4 Hz), 7.34 (d, 2H, J = 8.4 Hz), 7.54 (s, 1H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 38.9, 54.6, 114.1, 128.2, 130.4, 155.8.

4-Hydroxyphenyl-1,3-dithiane (4X$_2$). ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.93 (m, 1H), 2.16 (m, 1H), 2.89 (m, 2H), 3.05 (m, 2H), 4.80 (s, 1H), 5.12 (s, 1H), 6.78 (m, 2H), 7.34 (m, 2H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 25.0, 32.2, 50.7, 115.6, 129.2, 131.4, 155.6.

2-Nitrophenyl-1,3-dithiolane (5X$_1$). ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.92 (m, 2H), 3.12 (m, 2H), 5.88 (s, 1H), 7.43 (m, 1H), 7.61(m, 1H), 7.87 (m, 2H).^{13}C NMR (50 MHz, $CDCl_3$) δ 39.7, 50.4, 124.4, 128.3, 130.2, 133.1, 136.9, 148.1.

2-Nitrophenyl-1,3-dithiane (5X$_2$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.99 (m, 1H), 2.20 (m, 1H), 2.93 (m, 2H), 3.13 (m, 2H), 5.89 (s, 1H), 7.44 (m, 1H), 7.62 (m, 1H), 7.88 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.0, 29.7, 32.3, 46.0, 124.8, 129.1, 130.8, 133.5.

4-Nitrophenyl-1,3-dithiolane (6X$_1$). ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.37–3.57 (m, 4H), 5.65 (s, 1H), 7.67 (d, 2H, J = 8.7 Hz), 8.15 (d, 2H, J = 8.7 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 40.9, 55.3, 124.1, 129.2, 147.8, 149.1.

4-Nitrophenyl-1,3-dithiane (6X$_2$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.96 (m, 1H), 2.23 (m, 1H), 2.95 (m, 2H), 3.08 (m, 2H), 5.23 (s, 1H), 7.66 (d, 2H), 8. 21 (d, 2H).^{13}C NMR (50 MHz, $CDCl_3$) δ 24.7, 31.7, 50.3, 123.9, 128.9, 146.1, 147.6.

4-Chlorophenyl-1,3-dithiolane (7X$_1$). ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.42 (m, 4H), 5.59 (s, 1H), 7.27 (d, 2H, J = 8.8 Hz), 7.44 (d, 2H, J = 8.8 Hz).^{13}C NMR (50 MHz, $CDCl_3$) δ 40.2, 55.3, 128.4, 129.2, 133.5, 134.9.

4-Chlorophenyl-1,3-dithiane (7X$_2$). ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.01 (m, 1H), 2.50 (m, 1H), 2.99 (m, 4H), 5.13 (s, 1H), 7.38 (m, 4H).^{13}C NMR (50 MHz, $CDCl_3$) δ 24.9, 31.9, 50.5, 128.9, 129.2, 134.1, 137.6.

4-(N,N'-dimethyl)phenyl-1,3-dithiolane (8X$_1$). ^{1}H NMR (200 MHz, $CDCl_3$) δ 2.99 (s, 6H), 3.33 (m, 2H), 3.51 (m, 2H), 5.65 (s, 1H), 6.66 (d, 2H, J = 9 Hz), 7.39 (d, 2H, J = 9 Hz). ^{13}C NMR (50 MHz, $CDCl_3$) δ 40.1, 40.6, 56.5, 112.3, 128.8.

4-(N,N'-dimethyl)phenyl-1,3-dithiane (8X$_2$). ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.91 (m, 1H), 2.16 (m, 1H), 2.80–3.10 (m, 10H), 5.11 (s, 1H), 6.67 (d, 2H, J = 9 Hz), 7.33 (d, 2H, J = 9 Hz).^{13}C NMR (50 MHz, $CDCl_3$) δ 25.1, 32.3, 40.5, 50.9, 112.3, 128.5.

3,4-Dimethoxyphenyl-1,3-dithiolane (9X$_1$). ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.38 (m, 4H), 3.76 (s,3H), 3.81 (s, 3H), 5.50 (s, 1H), 6.85 (m, 3H).^{13}C NMR (50 MHz, $CDCl_3$) δ 40.1, 55.9, 110.7, 110.8, 120.2, 131.9, 148.8.

3,4-Dimethoxyphenyl-1,3-dithiane (9X$_2$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.94 (m, 1H), 2.16 (m, 1H), 2.90 (m, 2H), 3.05 (m, 2H), 3.86 (s, 3H), 3.89 (s, 3H), 5.13 (s, 1H), 6.82 (d, 1H, J = 8.4 Hz), 7.02 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.0, 32.1, 51.1, 55.8, 110.7, 111.0, 119.9, 131.6, 148.9.

4-Acetoxyphenyl-1,3-dithiolane (10X$_1$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.28 (s, 3H), 3.34 (m, 2H), 3.47 (m, 2H), 5.62 (s, 1H), 7.02 (d, 2H, J = 8.4 Hz), 7.52 (d, 2H, J = 8.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.1, 40.1, 55.6, 121.5, 129.0, 137.8, 150.2, 169.3.

4-Acetoxyphenyl-1,3-dithiane (10X$_2$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.92 (m, 1H), 2.15 (m, 1H), 2.27 (s, 3H), 2.88 (m, 2H), 3.04 (m, 2H), 5.15 (s, 1H), 7.05 (d, 2H, J = 8.4 Hz), 7.47 (d, 2H, J = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.0, 24.9, 31.9, 50.6, 121.7, 128.9, 136.6, 154.4, 169.2.

4-Benzoylphenyl-1,3-dithiolane (11X$_1$). Mp 102 °C. IR (KBr) 1736, 1603, 1506, 1270, 1200, 1173, 1068, 1025 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.36 (m, 2H), 3.50 (m, 2H), 5.66 (s, 1H), 7.16 (d, 2H), 7.53 (m, 5H), 8.19 (d, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.2, 55.7, 121.6, 122.5, 128.5, 129.1, 130.1, 133.6, 137.8, 151.2, 165.0. Anal. calcd for $C_{16}H_{14}O_2S_2$: C, 63.54; H, 4.67. Found: C, 63.60; H, 4.71%.

4-Benzoylphenyl-1,3-dithiane (11X$_2$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.93 (m, 1H), 2.16 (m, 1H), 2.90 (m, 2H), 3.06 (m, 2H), 5.19 (s, 1H), 7.19 (d, 2H), 7.41 (m, 1H), 7.51 (m, 3H), 7.64 (m, 1H), 8.18 (d, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.0, 32.0, 50.6, 121.9, 122.5, 128.5, 129.0, 130.1, 133.6, 136.7, 150.7, 164.9.

4-Benzyloxyphenyl-1,3-dithiolane (12X$_1$). Mp 92 °C. IR (KBr) 2916, 1609, 1512, 1251, 1251, 1173, 1013 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.28 (m, 2H), 3.46 (m, 2H), 5.02 (s, 2H), 5.61 (s, 1H), 6.89 (d, 2H, J = 8.4 Hz), 7.35 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.1, 56.0, 70.0, 114.7, 127.3, 127.9, 128.5, 129.1, 132.1, 136.8, 158.5. Anal. calcd for $C_{16}H_{16}OS_2$: C, 66.63; H, 5.59. Found: C, 66.68; H, 5.57%.

4-Benzyloxyphenyl-1,3-dithiane (12X$_2$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.91 (m, 1H), 2.14 (m, 1H), 2.88 (m, 2H), 3.03 (m, 2H), 5.03 (s, 2H), 5.12 (s, 1H), 6.92 (d, 2H, J = 8.5 Hz), 7.37 (m, 7H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.0, 32.1, 50.7, 70.0, 114.9, 127.4, 127.9, 128.5, 128.9, 131.5, 136.8, 158.7.

4-O-allylphenyl-1,3-dithiolane (13X$_1$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.34 (m, 2H), 3.50 (m, 2H), 4.52 (m, 2H), 5.30 (m, 2H), 5.62 (s, 1H), 6.03 (m, 1H), 6.87 (m, 2H), 7.42 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.1, 55.9, 68.8, 114.6, 117.7, 129.0, 129.4, 131.9, 133.1, 158.3.

4-O-allylphenyl-1,3-dithiane (13X$_2$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.95 (m, 1H), 2.16 (m, 1H), 2.91 (m, 2H), 3.05 (m, 2H), 4.53 (m, 2H), 5.12 (s, 1H), 5.29 (m, 1H), 5.40 (m, 1H), 6.04 (m, 1H), 6.87 (d, 2H), 7.38 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 25.0, 32.1, 50.7, 68.8, 114.8, 117.7, 128.9, 130.0, 131.4, 133.1, 158.6.

2-Furyl-1,3-dithiolane (14X$_1$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.30 (m, 2H), 3.44 (m, 2H), 5.62 (s, 1H), 6.28 (m, 2H), 7.36 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 39.1, 47.4, 107.0, 110.3, 142.5, 154.2.

2-Furyl-1,3-dithiane (14X$_2$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.97 (m, 1H), 2.12 (m, 1H), 2.94 (m, 4H), 5.22 (s, 1H), 6.34 (m, 1H), 6.40 (m, 1H), 7.36 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 25.0, 30.0, 41.8, 107.6, 110.4, 142.0, 151.5.

Cinnamyl-1,3-dithiolane (15X$_1$). ^{1}H NMR (200 MHz, $CDCl_3$) δ 3.27 (m, 4H), 5.12 (d, 1H), 6.00 (dd, 1H), 6.52 (d, 1H), 7.26 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 39.8, 52.0, 126.8, 128.0, 128.7, 129.4, 130.1, 136.2.

Cinnamyl-1,3-dithiane (15X$_2$). ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.88 (m, 1H), 2.11 (m, 1H), 2.88 (m, 4H), 4.80 (d, 1H), 6.25 (dd, 1H), 6.74 (d, 1H), 7.39 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 25.1, 30.1, 47.6, 125.9, 126.6, 128.0, 128.5, 133.3, 136.0.

1,4-Dithia-spiro[4,5]-decane (16X$_1$). ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.41 (m, 2H), 1.62 (m, 4H), 2.00 (m, 4H), 3.28 (s, 4H). ^{13}C NMR (50 MHz, $CDCl_3$) δ 25.0, 26.2, 38.3, 42.9, 69.2.

1,5-Dithia-spiro[5,5]-undecane (16X$_2$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.47 (m, 2H), 1.62 (m, 4H), 2.03 (m, 6H), 2.85 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.9, 25.7, 25.8, 26.0, 37.8, 50.2.

2-Methylphenyl-1,3-dithiolane (17X$_1$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.14 (s, 3H), 3.40 (m, 4H), 7.21 (m, 1H), 7.30 (m, 2H), 7.74 (d, 2H, J = 7.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 33.8, 40.2, 68.5, 126.7, 127.0, 127.9, 145.8.

2-Methylphenyl-1,3-dithiane (17X$_2$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.79 (s, 3H), 1.93 (m, 2H), 2.69 (m, 4H), 7.25 (m, 1H), 7.37 (m, 2H), 7.93 (d, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 24.5, 27.9, 32.7, 53.8, 126.9, 127.6, 128.4, 143.7.

2,2-Diphenyl-1,3-dithiolane (18X$_1$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.39 (s, 4H), 7.27 (m, 6H), 7.59 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.1, 127.2, 127.9, 128.2, 144.6.

2,2-Diphenyl-1,3-dithiane (18X$_2$). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.97 (m, 2H), 2.75 (m, 4H), 7.31 (m, 6H), 7.67 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 24.4, 29.3, 127.5, 128.3, 129.3, 142.4.

Acknowledgements

S. N., R. G. and B. K. P. acknowledges the support of this research to DST New Delhi and CSIR 01(1688)/00/EMR-II and M. G. to IIT Guwahati. Thanks are due to RSIC, Lucknow and IIT Kanpur, for providing NMR spectra.

References

1 (*a*) T. W. Greene, P. G. M. Wuts, *Protective Groups in Organic Synthesis*, 3rd edn, Wiley & Sons, New York, 1999; (*b*) P. J. Kocieński, *Protecting Groups*, Georg Thieme Verlag, New York, 1994; (*c*) F. A. J. Meskens, *Synthesis*, 1981, 501; (*d*) M. Schelhaas and H. Waldmann, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 2056.

2 (*a*) E. J. Corey and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 1965, **4**, 1075; (*b*) E. J. Corey and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 1965, **4**, 1077; (*c*) E. J. Corey and D. Seebach, *J. Org. Chem.*, 1966, **31**, 4097; (*d*) D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 239; (*e*) D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 639; (*f*) D. Seebach, *Synthesis*, 1969, 17; (*g*) B.-T. Gröbel and D. Seebach, *Synthesis*, 1977, 357; (*h*) E. L. Eliel and S. S. Morris–Natsche, *J. Am. Chem. Soc.*, 1984, **106**, 2937; (*i*) J. E. Lynch, E. L. Eliel and S. S. Morris-Natsche, *J. Am. Chem. Soc.*, 1984, **106**, 2943; (*j*) P. C. B. Page, M. B. van Niel and J. C. Prodger, *Tetrahedron*, 1989, **45**, 7643; (*k*) K. Utimoto, A. Nakamura and S. Motsubara, *J. Am. Chem. Soc.*, 1990, **112**, 8189; (*l*) *Comprehensive Organic Synthesis*, ed. B. M. Trost, Pergamon, New York, 1991, vol. 3, ch. 1.3; (*m*) *Comprehensive Organic Synthesis*, ed. B. M. Trost, Pergamon, New York, 1991, vol. 1, ch. 2.3; (*n*) G. R. Petti and E. E. van Tamelene, *Org. React.*, 1962, **12**, 356.

3 R. K. Olsen, and J. O. Currier Jr., *The Chemistry of the Thiol Group* ed. S. Patai, John Wiley & Sons, New York, 1974, part 2, p. 519.

4 (*a*) Y. Mori, Y. Kohchi and M. Suzuki, *J. Org. Chem.*, 1991, **56**, 631; (*b*) S. D. Rychnovsky, *Chem. Rev.*, 1995, **95**, 2021; (*c*) A. B. Smith III, S. M. Condon and J. A. McCauley, *Acc. Chem. Res.*, 1998, **31**, 35.

5 A. K. Banerjee and M. S. Laya, *Russ. Chem. Rev.*, 2000, **69**, 947.

6 (*a*) L. F. Fieser, *J. Am. Chem. Soc.*, 1954, **76**, 1945; (*b*) W. E. Truce and F. E. Roberts, *J. Org. Chem.*, 1963, **28**, 961; (*c*) B. S. Ong, *Tetrahedron Lett.*, 1980, **21**, 4225; (*d*) V. Kumar and S. Dev, *Tetrahedron Lett.*, 1983, **24**, 1289; (*e*) M. A. Ceschi, L. de. A. Felix and C. Peppe, *Tetrahedron Lett.*, 2000, **41**, 9695; (*f*) S. Muthusamy, S. A. Babu and C. Gunanathan, *Tetrahedron Lett.*, 2001, **42**, 359.

7 (*a*) S. Muthusamy, S. A. Babu and C. Gunanathan, *Tetrahedron*, 2000, **58**, 7897; (*b*) A. Kamal and G. Chouhan, *Tetrahedron Lett.*, 2002, **43**, 1347; (*c*) E. J. Corey and K. Shimoji, *Tetrahedron Lett.*, 1983, **24**, 169; (*d*) H. Firouzabadi, B. Karimi and S. Eslami, *Tetrahedron Lett.*, 1999, **40**, 4055.

8 (*a*) L. F. Tietze, B. Weigand and C. Wulff, *Synthesis*, 2000, 69; (*b*) J. S. Yadav, B. V. S. Reddy and S. K. Pandey, *Synlett*, 2001, 238; (*c*) H. Firouzabadi, N. Iranpoor and B. Karimi, *Synthesis*, 1999, 58; (*d*) V. G. Saraswathy and S. Sankararaman, *J. Org. Chem.*, 1994, **59**, 4665.

9 (*a*) G. A. Olah, S. C. Narang, D. Meidar and G. F. Salem, *Synthesis*, 1981, 282; (*b*) Y. Kamitori, M. Hojo, R. Masuda, T. Kimura and T. Yoshida, *J. Org. Chem.*, 1986, **51**, 1427; (*c*) H. K. Patney, *Tetrahedron Lett.*, 1991, **32**, 2259; (*d*) H. K. Patney, *Tetrahedron*

Lett., 1994, **35**, 5717; (*e*) S. Chandrasekhar, M. Takhi, Y. R. Reddy, S. Mohapatra, C. R. Rao and V. K. Reddy, *Tetrahedron*, 1997, **53**, 14997; (*f*) A. Lalitha, K. Pitchumani and C. Srinivasan, *Green Chem.*, 1999, 173; (*g*) N. Deka and J. C. Sarma, *Chem. Lett.*, 2001, 794.

10 (*a*) H. Hauptmann and M. M. Campos, *J. Am. Chem. Soc.*, 1950, **72**, 1405; (*b*) J. R. Williams and G. M. Sarkisian, *Synthesis*, 1974, 32; (*c*) B. S. Ong and T. H. Chan, *Synth. Commun.*, 1977, **7**, 283; (*d*) P. C. B. Page, J. C. Prodger and D. Westwood, *Tetrahedron*, 1993, **49**, 10355; (*e*) H. Firouzabadi, N. Iranpoor and B. Karimi, *Synlett*, 1998, 739; (*f*) S. Samajdar, M. K. Basu, F. F. Backer and B. K. Banik, *Tetrahedron Lett.*, 2001, **42**, 4425; (*g*) H. Firouzabadi, N. Iranpoor and H. Hazarkhani, *J. Org. Chem.*, 2001, **66**, 7527; (*h*) A. Kamal and G. Chouhan, *Synlett*, 2002, 474; (*i*) A. T. Khan, E. Mondal, P. R. Sahu and S. Islam, *Tetrahedron Lett.*, 2003, **44**, 919; (*j*) H. Firouzabadi, N. Iranpoor and H. Hazarkhani, *Synlett*, 2001, 1641; (*k*) N. Srivastava, S. K. Dasgupta and B. K. Banik, *Tetrahedron Lett.*, 2003, **44**, 1191.

11 D. A. Evans, K. G. Grimm and L. K. Truesdale, *J. Am. Chem. Soc.*, 1975, **97**, 3229.

12 T. Satho, S. Uwaya and K. Yamakawa, *Chem. Lett.*, 1983, 667.

13 M. Kakimoto, T. Seri and Y. Imai, *Synthesis*, 1987, 164.

14 D. R. Morton and S. J. Hobbs, *J. Org. Chem.*, 1979, **44**, 656.

15 J. A. Soderquist and E. I. Miranda, *Tetrahedron Lett.*, 1986, **27**, 6305.

16 S. Kobayashi, S. Iimura and K. Manabe, *Chem. Lett.*, 2002, 10.

17 B. Pério and J. Hamelin, *Green Chem.*, 2000, **2**, 252.

18 T. Sato, J. Otera and H. Nozaki, *J. Org. Chem.*, 1993, **58**, 4971.

19 D. A. Evans, L. K. Truesdale, K. G. Grimm and S. L. Nesbitt, *J. Am. Chem. Soc.*, 1977, **99**, 5009.

20 (*a*) R. Gopinath, Sk. J. Haque and B. K. Patel, *J. Org. Chem.*, 2002, **67**, 5842; (*b*) S. Naik, R. Gopinath and B. K. Patel, *Tetrahedron Lett.*, 2001, **42**, 7679; (*c*) R. Gopinath and B. K. Patel, *Org. Lett.*, 2000, **2**, 4177; (*d*) U. Bora, G. Bose, M. K. Chaudhuri, S. S. Dhar, R. Gopinath, A. T. Khan and B. K. Patel, *Org. Lett.*, 2000, **2**, 247; (*e*) M. K. Chaudhuri, A. T. Khan, B. K. Patel, D. Dey, W. Kharmawophlang, T. R. Lakshmiprabha and G. C. Mandal, *Tetrahedron Lett.*, 1998, **39**, 8163.

21 (*a*) E. Mondal, P. R. Sahu, G. Bose and A. T. Khan, *Tetrahedron Lett.*, 2002, **43**, 2843; (*b*) G. Bose, P. M. Bhujarbarua, M. K. Chaudhuri, D. Kalita and A. T. Khan, *Chem. Lett.*, 2001, 290; (*c*) G. Bose, E. Mondal, A. T. Khan and M. J. Bordoloi, *Tetrahedron Lett.*, 2001, **42**, 8907; (*d*) E. Mondal, G. Bose and A. T. Khan, *Synlett*, 2001, 785; (*e*) E. Mondal, G. Bose and A. T. Khan, *Synlett*, 2001, 785.

22 S. Kajigaeshi, T. Kakinami and T. Hirakawa, *Chem. Lett.*, 1987, 627.

23 Unpublished results.

24 J. H. Park and S. Kim, *Chem. Lett.*, 1989, 629.

25 H. Tani, K. Masumoto and T. Inamasu, *Tetrahedron Lett.*, 1991, **32**, 2039.

26 H. Firouzabadi, N. Iranpoor and B. Karimi, *Synlett*, 1999, 319.

27 H. Firouzabadi, N. Iranpoor, B. Karimi and H. Hazarkhani, *Synlett*, 2000, 263.

28 G. K. Jnaneshwar, N. B. Barhate, A. Sudalai, V. H. Deshpande, R. D. Wakharkar, A. S. Gajare, M. S. Shingare and R. Sukumar, *J. Chem. Soc., Perkin Trans. 1*, 1998, 965.

29 B. C. Ranu, A. Das and S. Samanta, *J. Chem. Soc., Perkin Trans. 1*, 2002, 1520.

30 (*a*) B. C. Ranu, A. Das and S. Samanta, *Synlett*, 2002, 727; (*b*) A. Kamal and A. Chouhan, *Tetrahedron Lett.*, 2003, **44**, 3337.

31 R. Gopinath, A. R. Paital and B. K. Patel, *Tetrahedron Lett.*, 2002, **43**, 5123.

32 R. V. Anand, P. Sarvanan and V. K. Singh, *Synlett*, 1999, 415.

33 A. F. Patrocinio and P. J. S. Moran, *J. Organomet. Chem.*, 2000, **603**, 220.

34 B. Pandey, S. Y. Bal, U. R. Khire and A. T. Rao, *J. Chem. Soc., Perkin Trans. 1*, 1990, 3217.

35 L. Qun, C. Guangbo, Y. Haifeng, L. Yingchun, Z. Jingping and Q. D. Dewen, *J. Org. Chem.*, 2003, **63**, 9148.