Pergamon

Tetrahedron 58 (2002) 7897–7901

TETRAHEDRON

Indium triflate: a mild Lewis acid catalyst for thioacetalization and transthioacetalization

Sengodagounder Muthusamy,* Srinivasarao Arulananda Babu and Chidambaram Gunanathan

Silicates and Catalysis Discipline, Central Salt and Marine Chemicals Research Institute, Bhavnagar 364 002, India

Received 26 April 2002; revised 1 July 2002; accepted 25 July 2002

Abstract—Protection of a variety of carbonyl compounds as thioacetals using indium triflate, a mild Lewis acid catalyst, was achieved at ambient temperature in very good yield. Transthioacetalization of oxyacetals into thioacetals was also achieved in an excellent yield. A mixture of carbonyl compound and its respective oxyacetal was also completely converted into thioacetal in the presence of indium triflate.

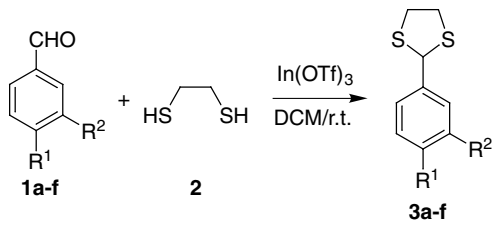
1. Introduction

Protection and deprotection of reactive functional groups are essential steps in the synthesis of polyfunctional compounds.[1] The protection of carbonyl compounds as thioacetals is a frequently encountered synthetic step for the preparation of many important natural/unnatural organic compounds including multifunctional complex molecules.[2] The recognition of thioacetals is due in part to their inbuilt stability over usual acidic or basic conditions and also because of their behavior as masked acyl anions or methylene functions.[3] Further, the use of thioacetals as blocking groups has enabled a new strategy for the electrophilic substitution on the carbonyl compound. In this view, there have been continued improvements in the methods of synthesis of thioacetals. Commonly, these compounds are prepared by protic or Lewis acid-catalyzed condensation of carbonyl compounds with thiols.[1] Lewis acid catalysts such as, $ZnCl_2$,[4] $LnCl_3$,[5] $FeCl_3/SiO_2$,[6] $AlCl_3$,[7] $ZrCl_4/SiO_2$,[8] $TeCl_4$,[9] $SnCl_2$,[10] $SiCl_4$,[11] $TiCl_4$,[12] $BF_3{\cdot}OEt_2$[13] etc. have been used for this purpose. Reagents such as I_2/alumina,[14] $Cu(OTf)_2/SiO_2$,[15] magnesium or zinc triflate,[16] $InCl_3$,[17a] amberlyst-15,[18a] thionyl chloride[18b] adsorbed on silica gel, lithium perchlorate,[19a] bis(diisobutylaluminium)-1,2-ethanedithiolate[19b] and ceric ammonium nitrate[20] have also found favor.

Indium triflate[21] is a mild Lewis acid, which has attracted little attention as a catalyst. Recently, we have shown that the O–H insertion reaction of α-diazo carbonyl compounds to various alcohols is facilitated in the presence of $In(OTf)_3$.[21a] To the best of our knowledge, indium triflate has not been used for thioacetalization or transthioacetalization. We herein report an efficient and mild method for thioacetalization and transthioacetalization at ambient temperature using indium triflate as a catalyst.

2. Results and discussion

The protection of a variety of aldehydes and ketones with ethane-1,2-dithiol in the presence of indium triflate was carried out at ambient temperature. Additionally, we carried out the transthioacetalization of oxyacetals and thioacetalization of a mixture of an oxyacetal and its parent carbonyl compound. The details are presented in the following sections.



Scheme 1.

Table 1. Thioacetalization of aldehydes in the presence of $In(OTf)_3$

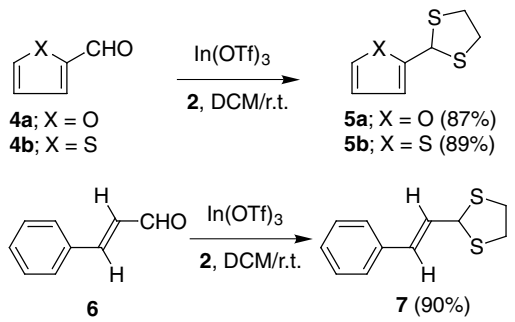
Aldehyde	Thioacetal	R^1	R^2	Time (min)	Yield[a] of **3** (%)
1a	**3a**[b]	OH	OMe	8	84
1b	**3b**[b]	OH	H	9	85
1c	**3c**	OMe	H	6	95
1d	**3d**	Me	H	8	93
1e	**3e**	H	H	8	89
1f	**3f**	NO_2	H	35	86

[a] Yields (unoptimized) based on the starting aldehydes.
[b] Reaction was carried out using methanol as a solvent.

Keywords: carbonyl compounds; indium triflate; thioacetalization; transthioacetalization.

* Corresponding author. Tel.: +91-278-567760; fax: +91-278-567562; e-mail: salt@csir.res.in

0040–4020/02/$ - see front matter
PII: S0040-4020(02)00897-9



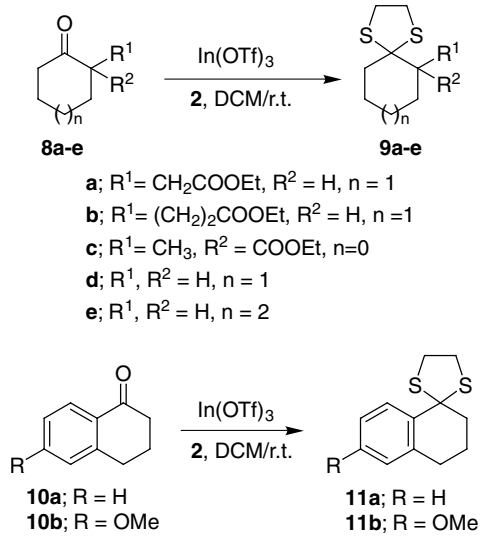
Scheme 2.

2.1. Thioacetalization of aldehydes

To a mixture of an equimolar amount of the aldehyde **1a** and ethane-1,2-dithiol was added 8 mol% of indium triflate and stirred at room temperature for 8 min. Concentration followed by column chromatographic purification of the crude reaction mixture afforded product **3a** in 84% yield. The reaction was repeated with various aldehydes **1b**–**f** containing electron-withdrawing and electron-donating substituents (Scheme 1, Table 1). The protection of heteroaromatic (**4a**,**b**) and α,β-unsaturated (**6**) aldehydes was also carried out under similar reaction conditions and the results are summarized in Scheme 2. In each case the corresponding thioacetals were obtained in good yield.

2.2. Thioacetalization of ketones

The reaction of an equimolar amount of ketone **8a** with

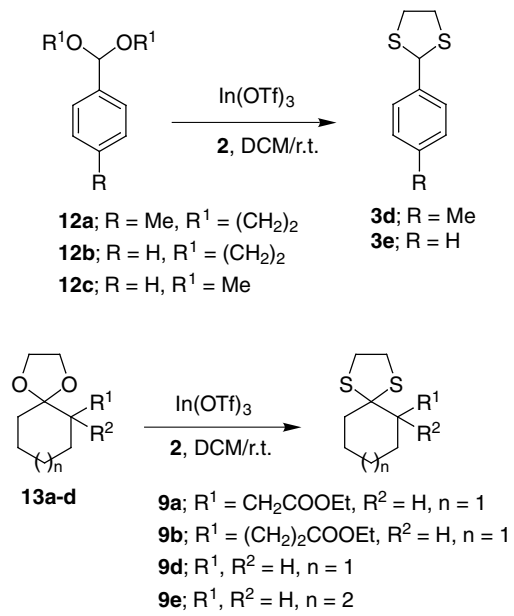


Scheme 3.

Table 2. Thioacetalization of ketones in the presence of $In(OTf)_3$

Ketone	Thioacetal	Time (h)	Yield[a] (%)
8a	**9a**	2.5	91
8b	**9b**	2.5	93
8c	**9c**	3.5	87
8d	**9d**	1.5	92
8e	**9e**	1.5	90
10a	**11a**	4.5	89
10b	**11b**	4.0	94

[a] Yields (unoptimized) based on the starting ketones.



Scheme 4.

Table 3. Transthioacetalization of oxyacetals

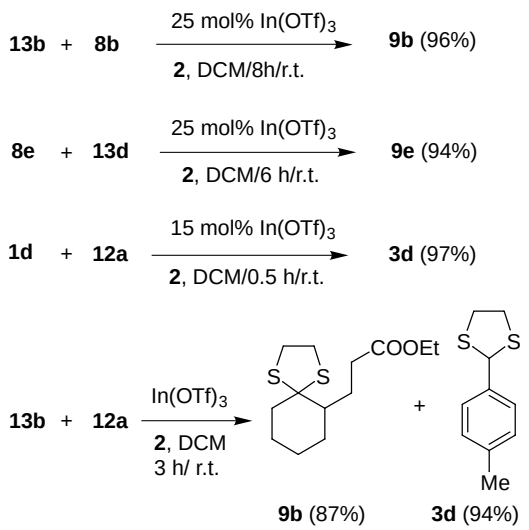
Oxyacetal	Thioacetal	Time (min)	Yield[a] (%)
12a	**3d**	10	90
12b	**3e**	8	89
12c	**3e**	5	92
13a	**9a**	240	92
13b	**9b**	270	90
13c	**9d**	150	88
13d	**9e**	150	93

[a] Yields (unoptimized) based on the starting oxyacetals.

ethane-1,2-dithiol in dry DCM was carried out in the presence of 10 mol% of indium triflate as described earlier to afford product **9a** in 91% yield. This reaction was generalized using various mono- and disubstituted cycloalkanones to afford the corresponding thioacetals **9a**–**e** in very good yield (Scheme 3, Table 2). This reaction was extended to other cyclic ketones such as α-tetralones under similar experimental conditions to afford the respective thioacetals **11a**,**b** in good yield (Scheme 3, Table 2).

2.3. Transthioacetalization of oxyacetals

A mixture of the oxyacetal **12a** and ethane-1,2-dithiol was allowed to react in the presence of indium triflate (15 mol%) for 10 min at room temperature. The reaction mixture was worked-up and purification of the crude reaction mixture afforded product **3d** in 90% yield (Scheme 4, Table 3). This reaction revealed that transthioacetalization of the oxyacetal **12a** into **3d** occurred swiftly in a clean manner without any side product. Similarly, transthioacetalization of the oxyacetal **12b** and the hemiacetal **12c** derived from aromatic aldehydes was also performed to furnish thioacetal **3e** in very good yield. Consequently, we were interested to execute a similar reaction using oxyacetals prepared from ketones. For this purpose, we carried out the reaction of **13a** with **2** in the presence of indium triflate for 4 h to afford product **9a** in 92% yield (Scheme 4, Table 3). This reaction exposed that an oxyacetal of ketone can also be converted

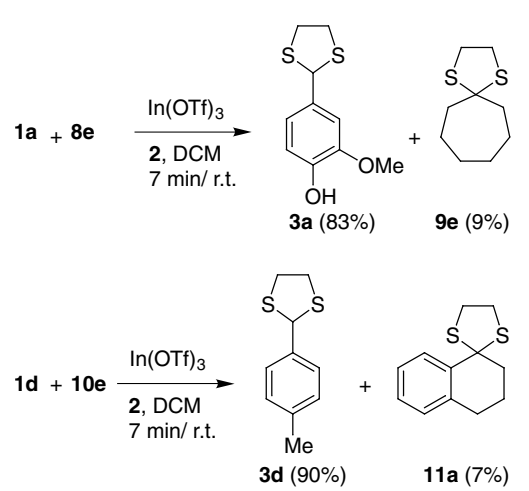


Scheme 5.

efficiently into a thioacetal in the presence of indium triflate. In order to generalize this transthioacetalization reaction, we carried out the reactions of various oxyacetals derived from ketones **13b–d** with **2** in the presence of indium triflate (25 mol%) to afford the respective products in good yield. Use of five or less mol% of indium triflate catalyst for transthioacetalization of oxyacetals derived from ketone required long reaction times (~35 h).

2.4. Transthioacetalization of a mixture of an oxyacetal and its parent carbonyl compound

It has been reported[19] that a mixture of an oxyacetal and ketone with **2** afforded only the transthioacetalization product. To test this theory, we carried out the reaction of the oxyacetal **13b** (1 equiv.) and ketone **8b** (1 equiv.) with an excess amount of thiol **2** (2.1 equiv.) in the presence of indium triflate (25 mol%). Purification of the reaction mixture afforded product **9b** in 96% yield and no detectable amount of the starting materials remaining in the reaction mixture. This reaction revealed that the oxyacetal **13b** as well as its parent ketone **8b** were converted simultaneously into thioacetal **9b** in good yield. Subsequently, we performed further experiments on the mixture of oxyacetals and carbonyl compounds, which also yielded good conversion into thioacetals; the results are summarized in Scheme 5.



Scheme 6.

2.5. Competitive thioacetalization of aldehydes and ketones

In order to check the chemoselectivity of the thioacetalization reaction, equimolar quantities of aldehyde **1a**, ketone **8e** and ethane-1,2-dithiol were allowed to react in the presence of 10 mol% of indium triflate for 7 min at ambient temperature. Immediate work-up and purification of the crude reaction mixture afforded products **3a** and **9e**, respectively. In a similar manner, the reaction of aldehyde **1d** and ketone **10a** with ethane-1,2-dithiol was carried out to afford products **3d** and **11a**, respectively (Scheme 6). These reactions provided the thioacetals from aldehydes preferentially.

In summary, we have shown that $In(OTf)_3$ can be effectively employed for the protection of carbonyl compounds as their thioacetals in good yield at ambient temperature in a mild manner. Moreover, transthioacetalization of oxyacetals in the presence or absence of their parent carbonyl compounds was also achieved in an excellent yield using indium triflate.

3. Experimental

Melting points are uncorrected. IR spectra were recorded on a Perkin–Elmer Spectrum GX FT-IR spectrophotometer. ^1H NMR, ^{13}C NMR spectra were recorded on a Bruker Avance DPX 200 (200 and 50.3 MHz, respectively) spectrometer and referenced to TMS. Carbon types were determined from DEPT ^{13}C NMR experiments. Elemental analyses were performed on a Perkin–Elmer Model 2400 analyzer. Thin layer chromatography was performed on silica/alumina plates and components were visualized by observation under iodine or by sulfuric acid charring. Column chromatography was performed on neutral alumina/silica gel. Preparation of oxyacetals of carbonyl compounds were carried out according to the general procedure using ethylene glycol in the presence of catalytic amount of 4-toluenesulfonic acid.[1a]

3.1. General procedure for the indium triflate-catalyzed conversion of carbonyl compounds or oxyacetals into thioacetals

To a solution of carbonyl compound or an oxyacetal (1 mmol) and ethane-1,2-dithiol (1.1 mmol) in dry DCM (5 mL) was added 8–10 mol% of indium triflate. The reaction mixture was stirred at room temperature under an inert atmosphere and monitored by TLC until the disappearance of starting carbonyl compound or an oxyacetal. After the appropriate period, the reaction mixture was diluted with DCM (10 mL) and water (15 mL) was added. The organic phase was separated and the aqueous layer was washed with DCM (10 mL). Concentration of the combined organic layer under reduced pressure afforded the crude product, which was purified by neutral alumina/silica gel column chromatography to afford the corresponding product.

3.2. General procedure for the indium triflate-catalyzed thioacetalization of a mixture of an oxyacetal and its parent carbonyl compound

To a solution of carbonyl compound (1 mmol), oxyacetal (1 mmol) and ethane-1,2-dithiol (2.1 mmol) in dry DCM (15 mL) was added 10–25 mol% of indium triflate. The reaction mixture was stirred at room temperature under an inert atmosphere. The reaction was monitored by TLC, which showed initially the formation of the respective carbonyl compound as well as dithiol. The reaction was continued until the disappearance of starting material and carbonyl compound was indicated. After the appropriate period, the reaction mixture was diluted with dichloromethane (15 mL) and washed with water (15 mL). The organic phase was separated and the aqueous layer was washed with DCM (15 mL). Concentration of the organic fractions under reduced pressure afforded the crude product, which was further purified by neutral alumina/silica gel column chromatography to afford the respective thioacetal.

3.3. Procedure for the competitive thioacetalization of aldehydes and ketones

To a mixture of aldehyde **1a** (1 mmol), ketone **8e** (1 mmol) and ethane-1,2-dithiol (1 mmol) in analytical grade methanol (8 mL) was added 10 mol% of indium triflate. The reaction mixture was stirred at ambient temperature for 7 min. Concentration in vacuum furnished the crude mixture which was then dissolved in dry dichloromethane and worked-up as described above to afford thioacetals **3a**, **9e** in 83 and 9% yields, respectively. Similarly, the reaction of an aldehyde **1d** and ketone **10a** in dichloromethane was carried out to afford the thioacetals **3d**, **11a** in 90 and 7% yields, respectively.

All new compounds gave satisfactory spectral data in accordance to their proposed structures and known compounds gave consistent data with the literature report.

3.3.1. 4-(1,3-Dithiolan-2-yl)-2-methoxyphenol 3a. Colorless solid, mp 100–102°C ($CHCl_3$/petroleum ether); [Found: C, 52.80; H, 5.21; S, 28.15. $C_{10}H_{12}S_2O_2$ requires C, 52.60; H, 5.29; S, 28.09%]; ν_{max} (KBr) 3400, 1597, 1509, 1449, 1425, 1268, 1227 cm^{-1}; δ_H (200 MHz, CD_3CN) 7.07 (1H, s, arom-*H*), 6.98 (1H, d, *J*=8.0 Hz, arom-*H*), 6.81 (1H, d, *J*=8.0 Hz, arom-*H*), 5.89 (1H, s, O*H*), 5.60 (1H, s, C*H*), 3.81 (3H, s, OCH_3), 3.50–3.23 (4H, m); δ_C (50.3 MHz, CD_3CN) 147.0 (*quat*-C), 146.0 (*quat*-C), 131.8 (*quat*-C), 121.6 (=*C*H), 114.6 (=*C*H), 110.9 (=*C*H), 57.2 (*C*H), 56.4 (O*C*H_3), 40.6 (*C*H_2).

3.3.2. 4-(1,3-Dithiolan-2-yl)phenol 3b.[18b] Colorless solid, mp 115–117°C ($CHCl_3$/petroleum ether, lit.[18b] mp 116°C); δ_H (200 MHz, CD_3CN) 7.54 (1H, s, O*H*), 7.34 (2H, d, *J*=8.4 Hz, arom-*H*), 6.75 (2H, d, *J*=8.4 Hz, arom-*H*), 5.63 (1H, s, C*H*), 3.49–3.24 (4H, m); δ_C (50.3 MHz, CD_3CN) 155.8 (*quat*-C), 130.4 (*quat*-C), 128.2 (=*C*H), 114.1 (=*C*H), 54.6 (*C*H), 38.9 (*C*H_2).

3.3.3. 4-Methoxyphenyl-1,3-dithiolane 3c.[18b,19a,22a] Colorless solid, mp 60–62°C ($CHCl_3$/petroleum ether, lit.[19a] mp 59–60°C); δ_H (200 MHz, $CDCl_3$) 7.40 (2H, d, *J*=8.6 Hz, arom-*H*), 6.78 (2H, d, *J*=8.6 Hz, arom-*H*), 5.59 (1H, s, C*H*), 3.66 (3H, s, OCH_3), 3.42–3.14 (4H, m); δ_C (50.3 MHz, $CDCl_3$) 159.3 (*quat*-C), 131.9 (*quat*-C), 129.2 (=*C*H), 113.8 (=*C*H), 56.1 (*C*H), 55.3 (O*C*H_3), 40.3 (*C*H_2).

3.3.4. 4-Methylphenyl-1,3-dithiolane 3d.[14a,15,18b] Colorless solid, mp 55–57°C ($CHCl_3$/petroleum ether, lit.[14a] mp 56–58°C); δ_H (200 MHz, $CDCl_3$) 7.37 (2H, d, *J*=7.2 Hz, arom-*H*), 7.06 (2H, d, *J*=7.2 Hz, arom-*H*), 5.58 (1H, s, C*H*), 3.40–3.17 (4H, m), 2.27 (3H, s, CH_3); δ_C (50.3 MHz, $CDCl_3$) 138.2 (*quat*-C), 137.8 (*quat*-C), 129.7 (=*C*H), 128.4 (=*C*H), 56.7 (*C*H), 40.8 (*C*H_2), 24.6 (*C*H_3).

3.3.5. Phenyl-1.3-dithiolane 3e.[18a,19a] Thick oil; δ_H (200 MHz, $CDCl_3$) 7.37–7.33 (5H, m, arom-*H*), 5.56 (1H, s, C*H*), 3.41–3.37 (4H, m); δ_C (50.3 MHz, $CDCl_3$) 138.4 (*quat*-C), 128.8 (=*C*H), 128.3 (=*C*H), 126.9 (=*C*H), 56.1 (*C*H), 40.4 (*C*H_2).

3.3.6. 2-(4-Nitrophenyl)-1,3-dithiolane 3f.[14b,22b] Pale yellow solid, mp 70–72°C ($CHCl_3$/petroleum ether, lit.[22a] mp 67–69°C); 8.15 (2H, d, *J*=8.7 Hz, arom-*H*), 7.67 (2H, d, *J*=8.7 Hz, arom-*H*), 5.65 (1H, s, C*H*), 3.57–3.37 (4H, m); δ_C (50.3 MHz, $CDCl_3$) 149.1 (*quat*-C), 147.8 (*quat*-C), 129.2 (=*C*H), 124.1 (=*C*H), 55.3 (*C*H), 40.9 (*C*H_2).

3.3.7. 2-(1,3-Dithiolan-2-yl)furan 5a.[18a,b] Thick oil; δ_H (200 MHz, $CDCl_3$) 7.32 (1H, t, *J*=4 Hz, =C*H*), 6.26 (2H, d, *J*=4 Hz, =C*H*), 5.60 (1H, s, C*H*), 3.40–3.18 (4H, m); δ_C (50.3 MHz, $CDCl_3$) 154.6 (*quat*-C), 142.6 (=*C*H), 110.6 (=*C*H), 107.2 (=*C*H), 47.7 (*C*H), 39.3 (*C*H_2).

3.3.8. 2-Thien-2-yl-1,3-dithiolane 5b. Thick oil; [Found: C, 44.79; H, 4.34; S, 51.19. $C_7H_8S_3$ requires C, 44.64; H, 4.28; S, 51.07%]; ν_{max} (neat) 3100, 2964, 2921, 1651, 1429, 1269 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 7.17 (1H, d, *J*=4 Hz, =C*H*), 7.00 (1H, d, *J*=4 Hz, =C*H*), 6.84 (1H, t, *J*=4 Hz, =C*H*), 5.88 (1H, s, C*H*), 3.41–3.24 (4H, m); δ_C (50.3 MHz, $CDCl_3$) 147.8 (*quat*-C), 127.1 (=*C*H), 126.2 (=*C*H), 126.1 (=*C*H), 51.3 (*C*H), 40.5 (*C*H_2).

3.3.9. (*E*) 2-(2-Phenylethenyl)-1,3-dithiolane 7.[14b,19a] Pale yellow solid, mp 57–59°C ($CHCl_3$/petroleum ether, lit.[19a] mp 58–59°C); δ_H (200 MHz, $CDCl_3$) 7.45–7.19 (5H, m, arom-*H*), 6.50 (1H, d, *J*=15.5 Hz, =C*H*), 6.20 (1H, dd, J_1=15.5 Hz, J_2=8.9 Hz, =C*H*), 5.22 (1H, d, *J*=8.9 Hz, =C*H*), 3.60–3.20 (4H, m); δ_C (50.3 MHz, $CDCl_3$) 136.2 (*quat*-C), 130.1 (=*C*H), 129.4 (=*C*H), 128.7 (=*C*H), 128.0 (=*C*H), 126.8 (=*C*H), 52.0 (*C*H), 39.8 (*C*H_2).

3.3.10. Ethyl 1,4-dithiaspiro[4.5]dec-6-ylacetate 9a. Thick oil; [Found: C, 55.48; H, 7.70; S, 24.80. $C_{12}H_{20}S_2O_2$ requires C, 55.35; H, 7.74; S, 24.63%]; ν_{max} (neat) 2978, 2929, 2856, 1730, 1443, 1373, 1287, 1172 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 4.12 (2H, q, *J*=7.0 Hz, OCH_2), 3.24–3.18 (4H, m), 3.09–2.99 (1H, m), 2.34–1.50 (8H, m), 1.35–1.15 (2H, m), 1.25 (3H, t, *J*=7.0 Hz, CH_3); δ_C (50.3 MHz, $CDCl_3$) 173.3 (*C*OO), 74.0 (*quat*-C), 60.6 (O*C*H_2), 45.8 (*C*H_2), 44.9 (*C*H), 39.6 (*C*H_2), 39.3 (*C*H_2), 38.4 (*C*H_2), 32.6 (*C*H_2), 26.2 (*C*H_2), 25.4 (*C*H_2), 14.6 (*C*H_3).

3.3.11. Ethyl 3-(1,4-dithiaspiro[4.5]dec-6-yl)propionate 9b. Colorless oil; [Found: C, 56.82; H, 8.15; S, 23.19. $C_{13}H_{22}S_2O_2$ requires C, 56.89; H, 8.08; S, 23.37%]; ν_{max} (neat) 2929, 2855, 1734, 1445, 1333, 1170 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 4.05 (2H, q, J=7.0 Hz, OCH_2), 3.21–3.08 (4H, m), 2.41–2.09 (4H, m), 1.89–1.76 (2H, m), 1.56–1.35 (5H, m), 1.22–0.97 (2H, m), 1.18 (3H, t, J=7.0 Hz, CH_3); δ_C (50.3 MHz, $CDCl_3$) 173.9 (*C*OO), 74.8 (*quat*-C), 60.5 (O*C*H$_2$), 47.7 (*C*H), 45.5 (*C*H$_2$), 39.5 (*C*H$_2$), 39.3 (*C*H$_2$), 32.9 (*C*H$_2$), 31.2 (*C*H$_2$), 27.7 (*C*H$_2$), 26.2 (*C*H$_2$), 25.1 (*C*H$_2$), 14.6 (*C*H$_3$).

3.3.12. Ethyl 6-methyl-1,4-dithiaspiro[4.4]nonane-6-carboxylate 9c. Thick oil; [Found: C, 53.77; H, 7.45; S, 26.11. $C_{11}H_{18}S_2O_2$ requires C, 53.62; H, 7.36; S, 26.03%]; ν_{max} (neat) 2970, 2928, 1727, 1461, 1371, 1282 cm^{-1}; δ_H (200 MHz, $CDCl_3$) 4.14 (2H, q, J=7.0 Hz, OCH_2), 3.26–3.24 (4H, m), 2.54–2.36 (3H, m), 1.80–1.55 (3H, m), 1.41 (3H, s, CH_3), 1.27 (3H, t, J=7.0 Hz, CH_2CH_3); δ_C (50.3 MHz, $CDCl_3$) 175.5 (*C*OO), 77.9 (*quat*-C), 60.8 (O*C*H$_2$), 58.0 (*quat*-C), 44.7 (*C*H$_2$), 40.2 (*C*H$_2$), 39.7 (*C*H$_2$), 35.9 (*C*H$_2$), 22.8 (*C*H$_2$), 20.4 (*C*H$_2$), 14.5 (*C*H$_3$).

3.3.13. 1,4-Dithiaspiro[4.5]decane 9d.[14b,22c] Thick oil; δ_H (200 MHz, $CDCl_3$) 3.29–3.25 (4H, m), 2.02–1.96 (4H, m), 1.68–1.57 (4H, m), 1.44–1.41 (2H, m); δ_C (50.3 MHz, $CDCl_3$) 69.2 (*quat*-C), 43.3 (*C*H$_2$), 38.8 (*C*H$_2$), 26.6 (*C*H$_2$), 25.4 (*C*H$_2$).

3.3.14. 1,4-Dithia-spiro[4.6]undecane 9e.[18a,22d] Thick oil; δ_H (200 MHz, $CDCl_3$) 3.29–3.25 (4H, m), 2.20–2.16 (4H, m), 1.60–1.57 (8H, m); δ_C (50.3 MHz, $CDCl_3$) 72.3 (*quat*-C), 46.5 (*C*H$_2$), 39.3 (*C*H$_2$), 29.0 (*C*H$_2$), 26.1 (*C*H$_2$).

3.3.15. 3′,4′-Dihydro-2′*H*-spiro[1,3-dithiolane-2,1′-naphthalene] 11a.[15] Thick oil; δ_H (200 MHz, $CDCl_3$) 7.95–7.90 (1H, m, arom-*H*), 7.15–6.94 (3H, m, arom-*H*), 3.60–3.35 (4H, m), 2.80–2.71 (2H, m), 2.40–2.35 (2H, m), 2.04–1.95 (2H, m); δ_C (50.3 MHz, $CDCl_3$) 139.5 (*quat*-C), 137.7 (*quat*-C), 131.3 (=*C*H), 129.1 (=*C*H), 127.7 (=*C*H), 126.5 (=*C*H), 69.2 (*quat*-C), 44.3 (*C*H$_2$), 41.3 (*C*H$_2$), 29.9 (*C*H$_2$), 23.3 (*C*H$_2$).

3.3.16. 6′-Methoxy-3′,4′-dihydro-2′*H*-spiro[1,3-dithiolane-2,1′-naphthalene] 11b.[14b] Colorless solid, mp 85–87°C (petroleum ether); δ_H (200 MHz, $CDCl_3$) 7.85 (1H, d, J=8.8 Hz, arom-*H*), 7.74 (1H, dd, J_1=8.8 and J_2=2.2 Hz, arom-*H*), 6.47 (1H, s, arom-*H*), 3.73 (3H, s, OCH_3), 3.58–3.33 (4H, m), 2.77–2.70 (2H, m), 2.38–2.33 (2H, m), 2.02–1.94 (2H, m); δ_C (50.3 MHz, $CDCl_3$) 158.9 (*quat*-C), 139.2 (*quat*-C), 132.7 (=*C*H), 131.2 (*quat*-C), 113.5 (=*C*H), 112.8 (=*C*H), 69.2 (*quat*-C), 55.7 (O*C*H$_3$), 44.5 (*C*H$_2$), 41.2 (*C*H$_2$), 30.4 (*C*H$_2$), 23.3 (*C*H$_2$).

Acknowledgements

This research was supported by CSIR (Young Scientist Scheme), New Delhi. We thank Dr P. K. Ghosh, Director and Dr R. V. Jasra, Head of the Discipline, for their encouragement shown in this work. S. A. B. and C. G. thank CSIR, New Delhi for a fellowship.

References

1. (a) Greene, T. W. *Protective Groups in Organic Synthesis*. Wiley: New York, 1981. (b) Loewenthal, H. J. E. In *Protective Groups in Organic Chemistry*. McOmie, J. F. W., Ed.; Plenum: New York, 1973; pp 323–402.
2. Kunz, H.; Waldmann, H. *Comprehensive Organic Synthesis*, Trost, B. M., Fleming, I., Eds.; Pergamon: New York, 1991; Vol. 6, pp 677–681.
3. (a) Corey, E. J.; Seebach, D. *J. Org. Chem.* **1966**, *31*, 4097. (b) Seebach, D. *Synthesis* **1969**, 17. (c) Groebel, B.-T.; Seebach, D. *Synthesis* **1977**, 357. (d) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239. (e) Page, P. C. B.; van Niel, M. B.; Prodger, J. *Tetrahedron* **1989**, *45*, 7643.
4. Truce, W. E.; Roberts, F. E. *J. Org. Chem.* **1963**, *28*, 961.
5. Garlaschelli, L.; Vidari, G. *Tetrahedron Lett.* **1990**, *31*, 5815.
6. Patney, H. K. *Tetrahedron Lett.* **1991**, *32*, 2259.
7. Ong, B. S. *Tetrahedron Lett.* **1980**, *21*, 4225.
8. Patney, H. K.; Margan, S. *Tetrahedron Lett.* **1996**, *37*, 4621.
9. Tani, H.; Masumoto, K.; Inamasu, T. *Tetrahedron Lett.* **1991**, *32*, 2039.
10. Das, N. B.; Nayak, A.; Sharma, R. P. *J. Chem. Res. (S)* **1993**, 242.
11. Ku, B.; Oh, D. Y. *Synth. Commun.* **1989**, *19*, 433.
12. Kumar, V.; Dev, S. *Tetrahedron Lett.* **1983**, *24*, 1289.
13. Fieser, L. F. *J. Am. Chem. Soc.* **1954**, *76*, 1945.
14. (a) Firouzabadi, H.; Iranpoor, N.; Hazarkhani, H. *J. Org. Chem.* **2001**, *66*, 7527. (b) Deka, N.; Sarma, J. C. *Chem. Lett.* **2001**, 749 and references cited therein.
15. Anand, R. V.; Saravanan, P.; Singh, V. K. *Synlett* **1999**, 415.
16. Corey, E. J.; Shimoji, K. *Tetrahedron Lett.* **1983**, *24*, 169.
17. (a) Muthusamy, S.; Babu, S. A.; Gunanathan, C. *Tetrahedron Lett.* **2001**, *42*, 359. (b) Muthusamy, S.; Babu, S. A.; Gunanathan, C. *Synth. Commun.* **2001**, *31*, 1205.
18. (a) Perni, R. B. *Synth. Commun.* **1989**, *19*, 2383. (b) Kamitori, T.; Hojo, K.; Masuda, R.; Kimura, T.; Yoshida, T. *J. Org. Chem.* **1986**, *51*, 1427.
19. (a) Saraswathy, V. G.; Sankararaman, S. *J. Org. Chem.* **1994**, *59*, 4665. (b) Satoh, T.; Uwaya, S.; Yamakawa, K. *Chem. Lett.* **1983**, 667.
20. Mandal, P. K.; Roy, S. C. *Tetrahedron* **1995**, *51*, 7823.
21. (a) Muthusamy, S.; Babu, S. A.; Gunanathan, C. *Tetrahedron Lett.* **2002**, *43*, 3133. (b) Loh, T.-P.; Hu, Q.-Y.; Tan, K.-T.; Cheng, H.-S. *Org. Lett.* **2001**, *3*, 2669. (c) Gadhwal, S.; Sandhu, J. S. *J. Chem. Soc., Perkin Trans. 1* **2000**, 2827. (d) Miyai, T.; Onishi, Y.; Baba, A. *Tetrahedron* **1999**, *55*, 1017. (e) Ali, T.; Chauhan, K. K.; Frost, C. G. *Tetrahedron Lett.* **1999**, *40*, 5621.
22. (a) Jo, S.; Tanimoto, S.; Oida, T.; Okano, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1434. (b) Patney, H. K. *Tetrahedron Lett.* **1991**, *32*, 413. (c) Reid, E. E.; Jelinek, A. *J. Org. Chem.* **1950**, *15*, 448. (d) Ho, T.-L.; Wong, W. L. *Can. J. Chem.* **1972**, *50*, 3740.