

# Neutral Lithium Triflate (LiOTf) Efficiently Catalyzes Chemoselective Preparations of Cyclic and Acyclic Dithioacetals from Carbonyl Compounds, Acylals, and O,O-Cyclic and Open-Chain Acetals under Solvent-Free Conditions

Habib Firouzabadi,\* Shahram Eslami, and Babak Karimi

Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran

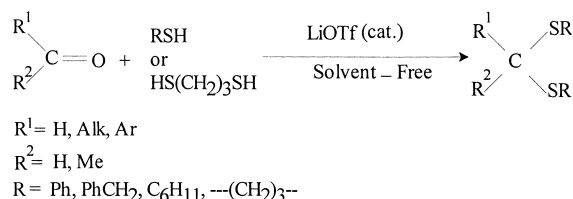
(Received May 1, 2001)

An efficient and chemoselective preparation of cyclic and acyclic thioacetals from carbonyl compounds, cyclic and acyclic acetals and acylals in the presence of catalytic amounts of neutral lithium triflate and thiols under solvent-free conditions is described.

Dithioacetals are among the most important and popular protective groups for carbonyl functions in organic synthesis.<sup>1</sup> Moreover, they have been widely used as precursors of acyl anion equivalents<sup>2</sup> or masked methylene functions.<sup>3</sup> The methods that have been reported for the preparation of dithioacetals from carbonyl compounds generally involving catalysis by protic acids, supported and solid acids, Lewis acids, and some silicon reagents, suffer from harsh or highly acidic conditions.<sup>4,5</sup> Therefore, the development of new methods for preparing these compounds from carbonyl functions or their derivatives in the presence of a neutral catalyst<sup>6</sup> is of practical importance. We have recently introduced LiBr as a potential neutral catalyst for an exceptional chemoselective preparation of 1,3-dithianes from some aldehydes.<sup>7</sup> LiBr is a highly hygroscopic compound, which puts some limitation on its use. A recent report describes the thioacetalization of carbonyl compounds in 2 and 0.23 molar solutions of LiClO<sub>4</sub> in Et<sub>2</sub>O.<sup>8</sup> Solvent-free reactions have found widespread interest and applications in organic reactions from different angles.<sup>9</sup> In a continuation of our studies in this area, we now report on new applications of LiOTf,<sup>10</sup> as an effective neutral catalyst, for the efficient preparation of dithioacetals from carbonyl compounds, acylals, and open-chain and cyclic acetals under solvent-free conditions. This catalyst had previously been used for the aminolysis of oxiranes<sup>11</sup> and glycosylation reactions.<sup>12</sup>

## Results and Discussion

Lithium trifluoromethanesulfonate (LiOTf) was prepared according to known procedure. Several washings of LiOTf powder with absolute ether produced an almost neutral compound (the pH of an aqueous solution of 0.1 M of the pre-washed LiOTf with absolute ether was ~6.9–7). In our previous report,<sup>10</sup> the pH of an aqueous solution of 0.1 M of LiOTf was reported to be 6.5–6.6. An effective thioacetalization of benzaldehyde with 1,3-propanedithiol,  $\alpha$ -toluenethiol, benzenethiol, and cyclohexanethiol was performed well under solvent-free conditions at 90 °C in the presence of a 0.05 molar



Scheme 1.

ratio of LiOTf. Substituted benzaldehydes were also efficiently converted to their corresponding 1,3-dithianes under similar reaction conditions (Scheme 1, Table 1, entries 1–7). Both saturated and  $\alpha,\beta$ -unsaturated aldehydes were also converted to 1,3-dithianes in good-to-excellent yields (Table 1, entries 8–10), whereas LiBr has been an ineffective catalyst, and the substrates remained intact after prolonged reaction times.<sup>7</sup> The efficient dithioacetalization of cyclohexanone and 4-phenyl-2-butanone, by this method, clearly shows the strong catalytic activity of LiOTf in comparison with LiBr (Table 1, entries 11, 12). However, under similar reaction conditions, the dithioacetalization of acetophenone was not successful, and gave the corresponding 1,3-dithiane in 15% yield after 19 h at 110 °C (Table 1, entry 13). We have minimized the amount of the organic solvent used for extracting the products by using a small continuous extractor apparatus in order to make this method a user-friendly procedure. In these reactions, lithium ion can act as a Lewis acid (hard acid), and by coordination to the carbonyl oxygen (hard base) it can activate the carbonyl functionality for further manipulation. However, by IR studies, such an interaction has been established for the benzaldehyde carbonyl stretching frequency in a 5 molar ethereal solution LiClO<sub>4</sub>.<sup>6</sup>

LiOTf, under solvent-free conditions, is a highly chemoselective catalyst for dithioacetalization reactions. This has been shown by several competitive reactions between aldehydes and ketones (Table 2, entries 1–3) and between ketones (Table 2, entry 4). The results clearly show that LiOTf can be considered as a useful substitute for the potentially explosive

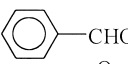
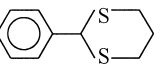
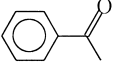
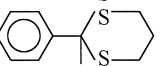
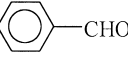
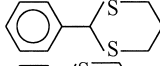
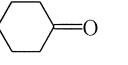
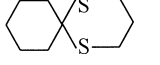
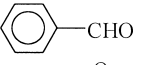
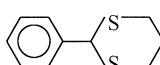
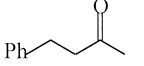
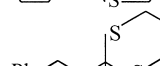
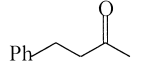
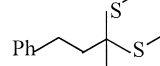
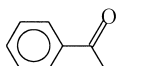
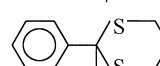
Table 1. Transformation of Carbonyl Compounds to their Corresponding Cyclic and Acyclic Dithioacetals with LiOTf under Solvent-Free Conditions

| Entry | R <sup>1</sup>                                                                    | R <sup>2</sup> | RSH<br>or<br>HS(CH <sub>2</sub> )SH | Subst./Thiol/LiOTf | Time<br>h          | Yield <sup>a)</sup><br>% |
|-------|-----------------------------------------------------------------------------------|----------------|-------------------------------------|--------------------|--------------------|--------------------------|
| 1     | Ph                                                                                | H              | -(CH <sub>2</sub> ) <sub>3</sub> -  | 1:1.1:0.05         | 0.1                | 99                       |
| 2     | Ph                                                                                | H              | Ph                                  | 1:2.1:0.05         | 1.2                | 90                       |
| 3     | Ph                                                                                | H              | PhCH <sub>2</sub>                   | 1:2.0:0.05         | 0.5                | 92                       |
| 4     | Ph                                                                                | H              | C <sub>6</sub> H <sub>11</sub>      | 1:2.1:0.05         | 0.8                | 99                       |
| 5     | 4-MeOC <sub>6</sub> H <sub>4</sub>                                                | H              | -(CH <sub>2</sub> ) <sub>3</sub> -  | 1:1.1:0.05         | 0.1                | 98                       |
| 6     | 4-ClC <sub>6</sub> H <sub>4</sub>                                                 | H              | -(CH <sub>2</sub> ) <sub>3</sub> -  | 1:1.1:0.05         | 0.2                | 96                       |
| 7     | 4-NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub>                                   | H              | -(CH <sub>2</sub> ) <sub>3</sub> -  | 1:1.1:0.1          | 0.2                | 85                       |
| 8     | PhCH=CH                                                                           | H              | -(CH <sub>2</sub> ) <sub>3</sub> -  | 1:1.1:0.05         | 0.1                | 98                       |
| 9     | Me <sub>2</sub> C=CH(CH <sub>2</sub> ) <sub>2</sub> C(Me)=CH                      | H              | -(CH <sub>2</sub> ) <sub>2</sub> -  | 1:1.1:0.05         | 0.8                | 97                       |
| 10    | MeC=CH(CH <sub>2</sub> ) <sub>2</sub> CH(Me)CH <sub>2</sub>                       | H              | -(CH <sub>2</sub> ) <sub>2</sub> -  | 1:1.1:0.05         | 3 <sup>b),c)</sup> | 94                       |
| 11    |  |                | -(CH <sub>2</sub> ) <sub>3</sub> -  | 1:1.5:0.2          | 0.6                | 96 <sup>d)</sup>         |
| 12    | PhCH <sub>2</sub> CH <sub>2</sub>                                                 | Me             | -(CH <sub>2</sub> ) <sub>3</sub> -  | 1:1.7:0.2          | 4.5                | 95 <sup>d)</sup>         |
| 13    | Ph                                                                                | Me             | -(CH <sub>2</sub> ) <sub>3</sub> -  | 1:1.7:0.3          | 19                 | 15 <sup>c),d)</sup>      |

a) Isolated yields. b) GC yields based on *n*-heptane as an internal standard. c) NMR yields.

d) Reactions were performed at 110 °C.

Table 2. Selective Dithioacetalization of Carbonyl Compounds with 1,3-Propanedithiol in the Presence of LiOTf as Catalyst under Solvent-Free Conditions

| Entry | Substrate                                                                           | Product                                                                             | Subst./Thiol/LiOTf | Time<br>min | Product <sup>a)</sup><br>% |
|-------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------|-------------|----------------------------|
| 1     |  |  | 1:1:1.1:0.05       | 10          | 100                        |
|       |  |  |                    |             | 0                          |
| 2     |  |  | 1:1:1.1:0.05       | 4           | 96                         |
|       |  |  |                    |             | 4                          |
| 3     |  |  | 1:1:1.1:0.05       | 2           | 98                         |
|       |  |  |                    |             | 10                         |
| 4     |  |  | 1:1:1.7:0.2        | 270         | 84                         |
|       |  |  |                    |             | 4                          |

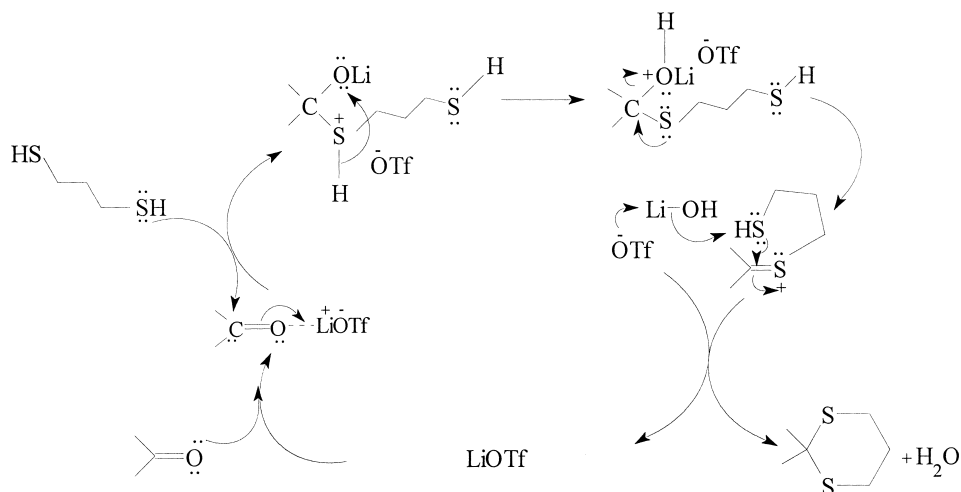
a) Product ratios based on NMR and GC analysis.

LiClO<sub>4</sub><sup>6,8</sup> and the highly hygroscopic LiBr<sup>7</sup> for the selective dithioacetalization of carbonyl compounds.

We have also proposed a reaction pathway that shows the

catalytic behavior of LiOTf for the dithioacetalization of carbonyl compounds (Scheme 2).

The direct transformation of masked carbonyl groups to oth-



Scheme 2.

Table 3. Transformation of Acetals, and Acylals to their Corresponding Cyclic 1,3-Dithianes with 1,3-Propanedithiol and LiOTf as Catalyst under Solvent-Free Conditions

| Entry | R <sup>1</sup>                                  | R <sup>2</sup> | R <sup>3</sup>                     | Subst./Thiol/LiOTf | Time | Yield <sup>a)</sup> |
|-------|-------------------------------------------------|----------------|------------------------------------|--------------------|------|---------------------|
|       |                                                 |                |                                    |                    | h    | %                   |
| 1     | Ph                                              | H              | Me                                 | 1:1.1:0.05         | 0.1  | 98                  |
| 2     | 4-MeC <sub>6</sub> H <sub>4</sub>               | H              | Et                                 | 1:1.1:0.05         | 0.1  | 96                  |
| 3     | 4-ClC <sub>6</sub> H <sub>4</sub>               | H              | Et                                 | 1:1.1:0.05         | 0.25 | 95                  |
| 4     | 4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> | H              | Et                                 | 1:1.1:0.1          | 0.25 | 90                  |
| 5     | PhCH=CH                                         | H              | Et                                 | 1:1.1:0.05         | 0.1  | 95                  |
| 6     | CH <sub>3</sub> (CH <sub>2</sub> ) <sub>5</sub> | H              | Et                                 | 1:1.1:0.05         | 0.3  | 94                  |
| 7     |                                                 |                | Et                                 | 1:1.5:0.2          | 0.5  | 96                  |
| 8     | PhCH <sub>2</sub> CH <sub>2</sub>               | Me             | Et                                 | 1:1.7:0.2          | 1.2  | 95 <sup>b)</sup>    |
| 9     | Ph                                              | Me             | Et                                 | 1:1.7:0.3          | 5.5  | 92 <sup>b)</sup>    |
| 10    | Ph                                              | H              | -(CH <sub>2</sub> ) <sub>3</sub> - | 1:1.3:0.3          | 1    | 95                  |
| 11    | 4-MeC <sub>6</sub> H <sub>4</sub>               | H              | -(CH <sub>2</sub> ) <sub>3</sub> - | 1:1.3:0.3          | 0.1  | 98                  |
| 12    | 4-ClC <sub>6</sub> H <sub>4</sub>               | H              | -(CH <sub>2</sub> ) <sub>3</sub> - | 1:1.3:0.3          | 5    | 95                  |
| 13    | 4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> | H              | -(CH <sub>2</sub> ) <sub>3</sub> - | 1:1.3:0.3          | 6.5  | 85                  |
| 14    | PhCH=CH                                         | H              | -(CH <sub>2</sub> ) <sub>3</sub> - | 1:1.3:0.3          | 2.3  | 92                  |
| 15    |                                                 |                | -(CH <sub>2</sub> ) <sub>3</sub> - | 1:1.5:0.3          | 1    | 92                  |
| 16    | Ph                                              | Me             | -(CH <sub>2</sub> ) <sub>3</sub> - | 1:1.7:0.3          | 50   | 92 <sup>b)</sup>    |
| 17    | Ph                                              | Ph             | -(CH <sub>2</sub> ) <sub>3</sub> - | 1:1.7:0.4          | 62   | trace               |
| 18    | 2,5-MeOC <sub>6</sub> H <sub>3</sub>            | H              | -(CH <sub>2</sub> ) <sub>3</sub> - | 1:1.1:0.2          | 2    | 95                  |
| 19    | 2-MeOC <sub>6</sub> H <sub>4</sub>              | H              | -(CH <sub>2</sub> ) <sub>3</sub> - | 1:1.1:0.2          | 4    | 94                  |
| 20    |                                                 | H              | -(CH <sub>2</sub> ) <sub>3</sub> - | 1:1.2:0.2          | 8    | 94                  |
| 21    | PhCH=CH                                         | H              | -Ac                                | 1:1.1:0.2          | 8    | 92                  |
| 22    | Ph                                              | H              | -Ac                                | 1:1.1:0.2          | 20   | 91                  |
| 23    | C <sub>10</sub> H <sub>7</sub>                  | H              | -Ac                                | 1:1.1:0.2          | 0    | 92                  |
| 24    | 4-BrC <sub>6</sub> H <sub>4</sub>               | H              | -Ac                                | 1:1.1:0.2          | 30   | 91                  |

a) Isolated yields. b) Reaction was performed at 110 °C.

er chemically different protected groups is sometimes of value in the total synthesis of complex organic molecules. The transformations would be of more practical importance if they were accompanied by high chemoselectivity. For this purpose we have investigated the direct conversion of open-chain and cyclic acetals, and acylals to the corresponding dithioacetals in the presence of thiols and catalytic amounts of LiOTf at 90–

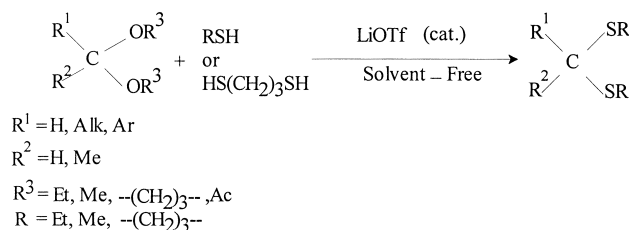
110 °C under solvent-free conditions. Our results show that the conversions proceeded very well with excellent yields (Scheme 3, Table 3). To the best of our knowledge, the presented method is the first example of an efficient functional group transformation of open-chain and cyclic acetals, and acylals to their corresponding dithioacetals under solvent-free and neutral conditions.

The chemoselectivity of the catalyst for the formation of 1,3-dithianes from chemically different masked carbonyl functions is demonstrated in Table 4. The catalyst showed high chemoselectivity, and discrimination between different func-

tional groups was efficiently observed.

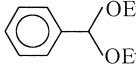
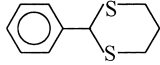
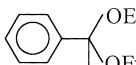
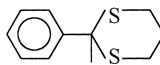
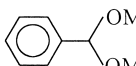
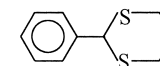
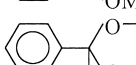
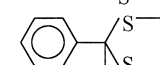
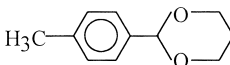
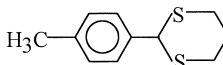
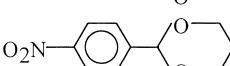
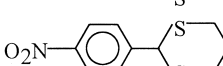
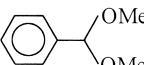
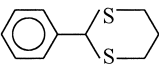
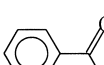
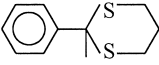
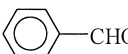
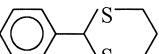
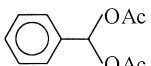
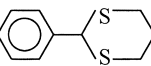
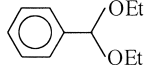
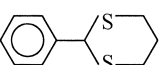
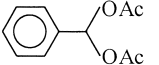
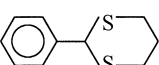
The noticeable difference between the rates of transthioacetalization of benzaldehyde dimethyl acetal [PhCH(OMe)<sub>2</sub>] (6 min, which carries two electron-donating-OMe groups), and benzylidene diacetate [PhCH(OAc)<sub>2</sub>] (20 h, which carries two electron-withdrawing-OAc groups) resembles the generation of a carbonium ion-type species in the reaction pathway. The carbocationic center is thus easily attacked by the thiol to form the dithioacetal (Scheme 4). The resonance forms presented in the scheme clearly show that intermediate I is much more stable than intermediate II. We believe that this difference in stability affects the rates of the reactions.

**Conclusion.** The catalytic nature of the method, neutrality of the catalyst, solvent-free reaction conditions, fast reaction

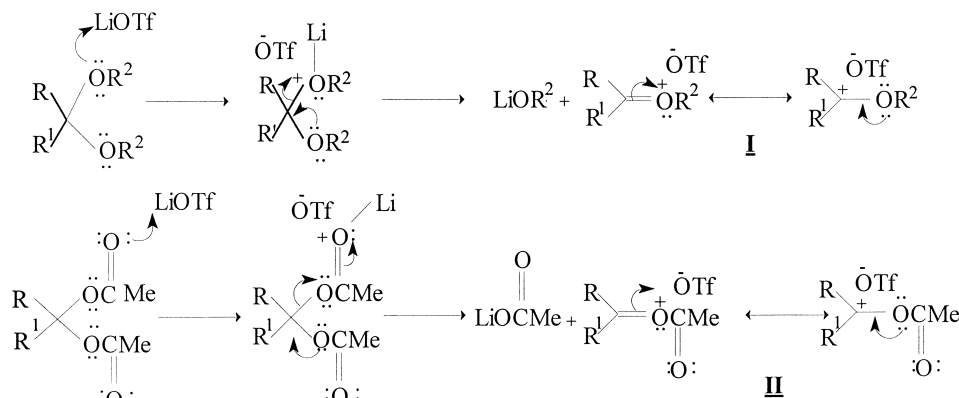


Scheme 3.

Table 4. Selective Transdithioacetalization of Acetals and Acylals with 1,3-Propanedithiol and LiOTf as Catalyst under Solvent-Free Conditions

| Entry | Substrate                                                                           | Product                                                                             | Subst./Thiol/LiOTf | Time<br>min | Product <sup>a)</sup><br>% |
|-------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|--------------------|-------------|----------------------------|
| 1     |    |    | 1:1:1.1:0.05       | 10          | 100                        |
|       |    |    |                    |             | 0                          |
| 2     |   |   | 1:1:1.1:0.05       | 10          | 100                        |
|       |  |  |                    |             | 0                          |
| 3     |  |  | 1:1:1.1:0.3        | 25          | 90                         |
|       |  |  |                    |             | 10                         |
| 4     |  |  | 1:1:1.1:0.05       | 10          | 100                        |
|       |  |  |                    |             | 0                          |
| 5     |  |  | 1:1:1.1:0.05       | 5           | 98                         |
|       |  |  |                    |             | 7                          |
| 6     |  |  | 1:1:1.1:0.05       | 10          | 98                         |
|       |  |  |                    |             | 0                          |

a) Product ratios based on NMR and GC based on *n*-heptane as internal standard.



Scheme 4.

rates, easy work-up, high chemoselectivity of the method, and high yields of the products are worth mentioning as advantages of the presented method.

### Experimental

**General.** All chemicals were either prepared in our laboratories or were purchased from Fluka and Merck Companies. Because the products are known compounds, the elemental analyses are not given in the text. Most of the products were purified by column chromatography on silica gel 60 Mesh ASTM or recrystallization from appropriate solvents and identified by comparisons of their mp, IR, NMR, and mass spectra with those reported for authentic samples. The progress of the reactions was followed by TLC using silica-gel polygrams SIL G/UV 254 plates or by GC using a Shimadzu gas chromatograph GC-14A, equipped with a flame-ionization detector and a glass column packed with DC-200 stationary phase and nitrogen as the carrier gas. NMR spectra were run on a Bruker Avance DPX 250 MHz instrument. Mass spectra were recorded by GCMS-QP 1000 EX at 20 eV (Shimadzu).

**General Procedure for the Functional Group Transformation of Carbonyl Compounds, Acetals, and Acylals to the Corresponding 1,3-Dithianes.** To a stirred mixture of the carbonyl compound/acetal/acylal (10 mmol) and dithiol (11–17 mmol) or monothiol (21 mmol), anhydrous LiOTf (0.5–3 mmol) was added. The mixture was heated at 90 °C (or 110 °C for ketones) while stirring was continued, and the progress of the reaction was followed by TLC. After completion of the reaction,  $\text{CH}_2\text{Cl}_2$  (20 mL) was added to the mixture and was continuously extracted by a continuous extractor. The resulting mixture was washed successively with a 10% NaOH solution ( $2 \times 5$  mL), brine (5 mL), and water (10 mL). The organic layer was separated and dried over anhydrous  $\text{Na}_2\text{SO}_4$ . Evaporation of the solvent under reduced pressure gave an almost pure product. Further purification was achieved by column chromatography on silica gel or recrystallization from an appropriate solvent to give the desired product(s) in good-to-excellent yield(s) (Table 1, and 3). The resulting 1,3-dithianes were known compounds<sup>3f,i,4d,6</sup> and were easily characterized by a comparison of their physical data with those of authentic samples (spectroscopic data, mp). However, some spectroscopic data for some of the isolated 1,3-dithianes (Table 3, entries 3, 18, 19, 20, 24) are given below:

**2-(2,5-Dimethoxyphenyl)-1,3-dithiane:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250 MHz)  $\delta$  1.91–2.15 (m, 2H), 2.81–3.18 (m, 4H), 3.67 (s, 3H), 3.75 (s, 3H), 5.60 (s, 1H), 6.74 (s, 2H), and 7.09 (s, 1H).  $^{13}\text{C}$

NMR ( $\text{CDCl}_3$ , 62.90 MHz)  $\delta$  25.69, 33.55, 44.23, 56.15, 56.85, 112.55, 114.44, 114.93, 128.58, 149.99, and 154.29.

**2-(2-Methoxyphenyl)-1,3-dithiane:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250 MHz)  $\delta$  1.84–2.08 (m, 2H), 2.79–3.06 (m, 4H), 3.74 (s, 3H), 5.61 (s, 1H), 6.78 (d, 1H), 6.90 (t, 1H), 7.16 (t, 1H), and 7.50 (d, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 62.90 MHz)  $\delta$  25.75, 32.81, 44.04, 56.16, 111.17, 121.42, 127.73, 129.56, 129.81, and 155.83.

**2-(4-Bromophenyl)-1,3-dithiane:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250 MHz)  $\delta$  1.86–2.11 (m, 2H), 2.81–3.03 (m, 4H), 5.05 (s, 1H), 7.32 (d, 2H), and 7.41 (d, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 62.90 MHz)  $\delta$  25.38, 32.30, 51.07, 122.73, 129.95, 132.22, and 138.50.

**2-(4-Methylphenyl)-1,3-dithiane:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250 MHz)  $\delta$  1.65 (s, 3H), 1.92–2.30 (m, 2H), 2.77–2.96 (m, 4H), 5.08 (s, 1H), 7.16 (d, 2H), and 7.28 (d, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 62.90 MHz)  $\delta$  21.59, 25.52, 32.54, 51.59, 128.00, 129.80, 136.57, and 138.60.

**2-(5-Methylfuryl)-1,3-dithiane:**  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 250 MHz)  $\delta$  1.87–2.14 (m, 2H), 2.27 (s, 3H), 2.85–2.96 (m, 4H), 5.14 (s, 1H), 5.88 (d, 2H), and 6.21 (d, 2H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 62.90 MHz)  $\delta$  14.41, 25.65, 30.77, 42.88, 106.98, 108.34, 150.16, and 152.39.

The authors are thankful to the Shiraz University Research Council for the partial support of this work.

### References

- 1 a) T. W. Greene and P. G. M. Wuts, "Protective Groups in Organic Synthesis," 2nd ed, Wiley, New York (1991), pp. 178–207. b) P. J. Kocienski, "Protective Groups," ed by R. Enders and B. M. Trost, Thieme, Stuttgart (1994).
- 2 a) E. J. Corey and D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **4**, 1075, 1077 (1965). b) D. Seebach, *Angew. Chem., Int. Ed. Engl.*, **8**, 639 (1969). c) B. T. Grobel and D. Seebach, *Synthesis*, **1977**, 357. d) G. R. Pettit and E. E. Van Tamelen, *Org. React.*, **12**, 356 (1962).
- 3 For leading references for dithioacetalization of carbonyl compounds see: a) L. Garlaschelli and G. Vidari, *Tetrahedron Lett.*, **31**, 5815 (1990). b) H. Hauptmann and M. Moura Campos, *J. Am. Chem. Soc.*, **72**, 1405 (1950). c) D. Seebach and M. Kolb, *Chem. Ind. (London)*, **1974**, 687. d) B. S. Ong, *Tetrahedron Lett.*, **21**, 4225 (1980). e) V. Kumar and S. Dev, *Tetrahedron Lett.*, **24**, 1289 (1983). f) B. Ku and D. Y. Oh, *Synth. Commun.*, **19**, 433 (1989). g) B. S. Ong and T. H. Chan, *Synth. Commun.*, **7**, 283 (1977). h) E. J. Corey and K. Shimoji, *Tetrahedron Lett.*, **24**, 169

- (1983). i) P. K. J. Chowdhury, *Chem. Res. (Synop.)*, **1993**, 124. j) N. B. Das, A. Nayak, and R. P. Sharma, *J. Chem. Res. (Synop.)*, **1993**, 242. k) N. Komatsu, M. Uda, and H. Suzuki, *Synlett.*, **1995**, 984. l) P. Kumar, R. S. Reddy, A. P. Singh, and B. Pandey, *Tetrahedron Lett.*, **33**, 825 (1992). m) D. Villemin, B. Labiad, and M. Hammadi, *J. Chem. Soc., Chem. Commun.*, **1992**, 1192. n) J. Taleiwa, H. Horiuchi, and S. Vemura, *J. Org. Chem.*, **60**, 4039 (1995). o) G. A. Olah, S. C. Narang, D. Meidar, and G. F. Salem, *Synthesis*, **1981**, 282. p) A. K. Maiti, K. Basu, and P. Bhattacharyya, *J. Chem. Res. (Synop.)*, **1995**, 108. q) H. K. Patney, *Tetrahedron Lett.*, **32**, 2259 (1991). r) H. K. Patney and S. Margan, *Tetrahedron Lett.*, **37**, 4621 (1996). s) Y. Kamitori, M. Hojo, R. Masuda, T. Kimura, and T. Yoshida, *J. Org. Chem.*, **51**, 1427 (1986). t) P. Kumar, R. S. Reddy, A. P. Singh, and B. Pandey, *Synthesis*, **1993**, 67.
- 4 For leading references for transdithioacetalization of acetals see: a) J. H. Park and S. Kim, *Chem. Lett.*, **1989**, 629. b) H. Tani, K. Masumoto, T. Inamasu, and H. Suzuki, *Tetrahedron Lett.*, **32**, 2039 (1991). c) H. Firouzabadi, N. Iranpoor, and B. Karimi, *Synlett.*, **1998**, 739. d) G. K. Jnaneshwara, 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. e) H. Firouzabadi, N. Iranpoor, and B. Karimi, *Synlett*, **1999**, 319.
- 5 For dithioacetalization of carbonyl compounds and transdithioacetalization of acetals under neutral reaction conditions see: V. G. Saraswathy and S. Sankararaman, *J. Org. Chem.*, **59**, 4665 (1994).
- 6 H. Firouzabadi, N. Iranpoor, and B. Karimi, *Synthesis*, **1999**, 58.
- 7 L. F. Tietze, B. Weigand, and C. Wulff, *Synthesis*, **2000**, 69.
- 8 K. Tanaka and F. Toda, *Chem. Rev.*, **100**, 1025 (2000).
- 9 H. Firouzabadi, B. Karimi, and S. Eslami, *Tetrahedron Lett.*, **40**, 4055 (1999).
- 10 J. Auge and F. Leroy, *Tetrahedron Lett.*, **37**, 7715 (1996).
- 11 A. Lubineau and B. Drouillat, *J. Carbohydrate Chem.*, **16**, 1179 (1997).
- 12 S. J. Kobisen and F. H. Westheimer, *J. Am. Chem. Soc.*, **101**, 5985 (1979).
-