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# A mild and efficient method for the protection of carbonyl compounds as oxathiolanes, dithiolanes and dithianes catalyzed by molybdenyl acetylacetonate

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**Abstract**—Carbonyl compounds have been successfully converted into their corresponding oxathiolane, dithiolane and dithiane derivatives in excellent yields with 2-mercaptoethanol, 1,2-ethanedithiol and 1,3-propanedithiol using a catalytic amount of molybdenyl acetylacetonate.

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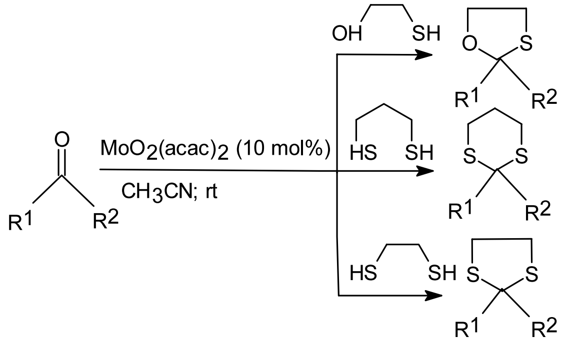
One of the major challenging problems during multistep syntheses is to protect a carbonyl functionality from nucleophilic attack until its electrophilic nature can be exploited. For this reason, the protection of carbonyl groups remains a crucial challenge to organic chemists. Among carbonyl protecting groups, 1,3-oxathiolanes, 1,3-dithiolanes and 1,3-dithianes constitute an important class of compounds as acyl anion equivalents[1] or masked methylene functions in carbon–carbon bond forming reactions. In addition to this, these substrates are versatile[2] due to their ease of preparation and also to their stability under basic or mildly acidic conditions. Some of the catalysts reported for the preparation of 1,3-oxathiolanes and 1,3-dithiolanes which have greatly enriched the science of methodology of synthetic organic chemistry are HCl,[3] PTSA,[4] $BF_3$–$OEt_2$,[5] $SO_2$,[6] $ZnCl_2$,[7] TMSCl–NaI,[7] TMSOTf,[8] $AlCl_3$,[9] $TiCl_4$,[10] $LaCl_3$,[11] $SiCl_4$,[12] $Cu(OTf)_2$–$SiO_2$,[13] $ZrCl_2$–$SiO_2$,[14] $WCl_6$,[15] 5 M $LiClO_4$/$Et_2O$(LPDE)[16] and $TaCl_5$–$SiO_2$[17] etc., but many of these procedures are associated with certain limitations such as low yields, harsh reaction conditions, longer reaction times and costly reagents as well as inconvenience in handling the reagents. So milder, simpler and more efficient alternatives are still desirable.

It has been observed recently that there has been a tremendous upsurge of interest in the protection of different reactive functionalities. We wish to report here a mild and efficient method for the protection of carbonyl compounds as 1,3-oxathiolanes, 1,3-dithiolanes and 1,3-dithianes using a catalytic quantity (10 mol%) of molybdenyl acetylacetonate in good to excellent yields (Scheme 1).

Although molybdenum catalyzed epoxidation of double bonds and oxidation of alcohols to carbonyl compounds[18] is well documented in the literature, to our knowledge there has been no investigation into the protection of carbonyl groups molybdenum reagents. Thus, various cyclic and acyclic carbonyl compounds were subjected to the protection reaction[19] using 2-mercaptoethanol, 1,2-ethanedithiol or 1,3-propanedithiol in



**Scheme 1.**

*Keywords*: carbonyl compounds; 2-mercaptoethanol; 1,2-ethanedithiol; 1,3-propanedithiol; molybdenyl acetylacetonate; oxathiolane; dithiolane; dithiane.

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**Table 1.** $MoO_2(acac)_2$ catalyzed protection of carbonyl compounds as oxathiolanes, dithiolanes or dithianes

| Entry | Substrate | Reagent | Time (h) | Yield (%)[a] |
|---|---|---|---|---|
| 1 | Benzaldehyde | $HSCH_2CH_2OH$ | 4.0 | 86 |
| 2 | *p*-Methoxybenzaldehyde | $HSCH_2CH_2OH$ | 3.0 | 82 |
| 3 | *p*-Chlorobenzaldehyde | $HSCH_2CH_2OH$ | 4.0 | 94 |
| 4 | Cinnamaldehyde | $HSCH_2CH_2OH$ | 3.5 | 92 |
| 5 | 3,4-Dimethoxybenzaldehyde | $HSCH_2CH_2OH$ | 4.5 | 86 |
| 6 | 3-Methoxy-4-benxyloxybenzaldehyde | $HSCH_2CH_2OH$ | 4.5 | 86 |
| 7 | Piperonal | $HSCH_2CH_2OH$ | 4.0 | 88 |
| 8 | Cyclopentanone | $HSCH_2CH_2OH$ | 3.5 | 94 |
| 9 | Cyclohexanone | $HSCH_2CH_2OH$ | 3.5 | 96 |
| 10 | Indanone | $HSCH_2CH_2OH$ | 4.0 | 81 |
| 11 | α-Tetralone | $HSCH_2CH_2OH$ | 4.0 | 80 |
| 12 | 1-Hexanal | $HSCH_2CH_2OH$ | 3.0 | 89 |
| 13 | 2-Hexanone | $HSCH_2CH_2OH$ | 3.0 | 88 |
| 14 | Furfural | $HSCH_2CH_2OH$ | 4.0 | 87 |
| 15 | Benzaldehyde | $HSCH_2CH_2SH$ | 1.5 | 95 |
| 16 | *p*-Methoxybenzaldehyde | $HSCH_2CH_2SH$ | 2.0 | 96 |
| 17 | *p*-Chlorobenzaldehyde | $HSCH_2CH_2SH$ | 2.0 | 98 |
| 18 | *p*-Nitrobenzaldehyde | $HSCH_2CH_2SH$ | 4.0 | 97 |
| 19 | Indanone | $HSCH_2CH_2SH$ | 3.5 | 90 |
| 20 | Cyclopentanone | $HSCH_2CH_2SH$ | 3.0 | 88 |
| 21 | Benzaldehyde | $HSCH_2CH_2CH_2SH$ | 3.0 | 94 |
| 22 | *p*-Methoxybenzaldehyde | $HSCH_2CH_2CH_2SH$ | 4.0 | 97 |
| 23 | *p*-Chlorobenzaldehyde | $HSCH_2CH_2CH_2SH$ | 4.5 | 81 |
| 24 | Cyclohexanone | $HSCH_2CH_2CH_2SH$ | 3.0 | 85 |
| 25 | 1-Hexanal | $HSCH_2CH_2CH_2SH$ | 3.5 | 78 |

[a] Yields refer to isolated pure products.

the presence of a catalytic amount of molybdenyl acetylacetonate [$MoO_2(acac)_2$; 10 mol%] in acetonitrile at room temperature to yield the corresponding 1,3-oxathiolanes, 1,3-dithiolanes or 1,3-dithianes in excellent yields, and the results are summarized in Table 1. All the products were characterized by spectroscopic analysis and also by comparison of the data obtained with those of authentic samples.

In conclusion, we have developed a mild and efficient method for the protection of carbonyl compounds as the corresponding oxathiolane, dithiolane and dithiane derivatives in excellent yields with 2-mercaptoethanol, 1,2-ethanedithiol and 1,3-propanedithiol using a catalytic amount of molybdenyl acetylacetonate.

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## References

1. (a) Lynch, J. E.; Eliel, E. L. *J. Am. Chem. Soc.* **1984**, *106*, 2943; (b) Eliel, E. L.; Morris, Natsche, S. S. *J. Am. Chem. Soc.* **1984**, *106*, 2937; (c) Utimoto, K.; Nakamura, A.; Molsubara, S. *J. Am. Chem. Soc.* **1990**, *112*, 8189.
2. (a) Corey, E. J.; Seebach, D. *J. Org. Chem.* **1966**, *31*, 4097; (b) Eliel, E. L.; Morris-Natschke, S. *J. Am. Chem. Soc.* **1984**, *106*, 2937.
3. Ralls, J. W.; Dobson, R. M.; Reigel, B. *J. Am. Chem. Soc.* **1949**, *71*, 3320.
4. Djerssi, C.; Gorman, M. *J. Am. Chem. Soc.* **1953**, *75*, 3704.
5. Wilson, G. E., Jr.; Huang, M. G.; Schloman, W. W., Jr. *J. Org. Chem.* **1968**, *33*, 2133.
6. Burezyk, B.; Kortylewticz, Z. *Synthesis* **1982**, 831.
7. Yadav, V. K.; Fallis, A. G. *Tetrahedron Lett.* **1988**, *29*, 897.
8. Ravindranathan, T.; Chavan, S. P.; Dantale, S. W. *Tetrahedron Lett.* **1995**, *36*, 2285.
9. Ong, B. S. *Tetrahedron Lett.* **1980**, *21*, 4225.
10. Kumar, V.; Dev, S. *Tetrahedron Lett.* **1983**, *24*, 1289.
11. Garlaschelli, L.; Vidari, G. *Tetrahedron Lett.* **1990**, *31*, 5815.
12. Ku, B.; Oh, D. Y. *Synth. Commun.* **1989**, *19*, 433.
13. Anand, R. V.; Sarvanan, P.; Singh, V. K. *Synlett* **1999**, 413.
14. Patney, H. K.; Margan, S. *Tetrahedron Lett.* **1996**, *37*, 4621.
15. Firouzabadi, H.; Iranpoor, N.; Karimi, B. *Synlett* **1998**, 739.
16. Saraswathy, V. G.; Geetha, V.; Sankararaman, S. *J. Org. Chem.* **1994**, *52*, 4665.
17. Chandrasekhar, S.; Takhi, M.; Reddy, Y. R.; Mohapatra, S.; Rao, C. R.; Reddy, K. V. *Tetrahedron* **1997**, *53*, 14997.
18. (a) Lorber, C. Y.; Pauls, I.; Osborn, J. A. *Bull. Soc. Chim. Fr.* **1996**, *133*, 755; (b) Maignien, S.; Ait-Mohand, S.; Muzart, J. *Synlett* **1996**, 439 and references cited therein.
19. **A typical procedure**: To a stirred mixture of benzaldehyde (106 mg; 1.0 mmol) and 1,2-ethanedithiol (113 mg; 1.2

mmol) in acetonitrile (1 mL) was added dry molybdenyl acetylacetonate (22 mg; 10 mol%) at room temperature under argon. The reaction mixture was stirred at room temperature for 4 h, diluted with diethyl ether (20 mL), washed thoroughly with water (2×5 mL) and brine (2× 5mL), then dried ($Na_2SO_4$). Evaporation of the solvent under reduced pressure afforded a product which was purified by column chromatography over silica gel (25% ethyl acetate in petroleum ether) to afford pure 2-phenyl-1,3-oxathiolane (142 mg, 86%). IR ($\nu_{max}$, KBr) 2869, 1492, 1454, 1265, 1230, 1195, 1062, 1018, 972 $cm^{-1}$; $^1H$ NMR (300 MHz, $CDCl_3$) $\delta$ 3.15–3.31 (m, 2H), 3.90–3.98 (m, 1H), 4.49–4.55 (m, 1H), 6.06 (s, 1H), 7.29–7.41 (m, 3H), 7.45–7.49 (m, 2H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ 33.9, 71.8, 86.9, 126.5, 128.3, 128.5, 139.1.