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# A Facile and Efficient Procedure for the Transdithioacetalization of 1,1-Diacetates Using $POCl_3$-Montmorillonite as Catalyst

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## ABSTRACT

A rapid and efficient method for the transdithioacetalization of 1,1-diacetates with 1,2-dithioglycol was described in good to excellent yield catalyzed by $POCl_3$-montmorillonite.

*Key Words:* Transdithioacetalization; 1,1-Diacetates; $POCl_3$-montmorillonite; Thioacetals.

Protection of carbonyl groups as thioacetals are quite often a necessary requirement in the synthesis of multiple functional organic molecules.[1]

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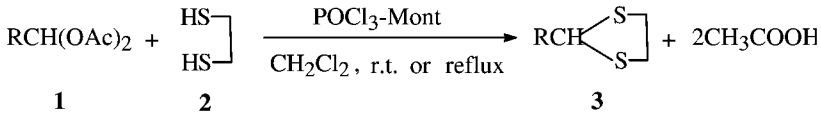
Thioacetals are quite stable toward a wide variety of reagents and are also useful in organic synthesis as acyl carbanion equivalents in C—C bond forming reactions. Moreover, S,S-acetals could be used as intermediates for the conversion of the carbonyl function to parent hydrocarbons.[3] In the literature, several types of lewis acid[4–8] catalysts were introduced previously for the preparation of thioacetals from carbonyl compounds. Mixed reagent systems[9–12] have also been developed for the formation of thioacetals. As a faster and cleaner reaction compared with thioacetalization of cabonyl compounds, transthioacetalization of acetals is a useful transformation for the preparation of S,S-acetals that have been reported in the literature.[13] However, many of these reported methods require long reaction times, stoichiometric use of expensive and hazardous reagent and lack general applicability. After a literature survey, we found that the transthioacetalization of 1,1-diacetate has also been reported,[14] but only a few kinds of diacetates are studied. In this article, we have introduced $POCl_3$-mont as an efficient catalyst for the transthioacetalization of 1,1-diacetates (Scheme. 1).

When various types of aromatic 1,1-diacetates **1** are heated with 1,2-dithioglycol **2** in refluxing dichloromethane or at room temperature in the presence of $POCl_3$-mont, the corresponding dithiolanes **3** are obtained in good to excellent yield. The result is summarized in Table 1.

From Table 1, we found that 1,1-diacetates of benzaldehyde and cinnamaldehyde and with electron-donating groups (**1a**, **1g**, **1b**, **1c**, and **1j**) were easily converted to the corresponding dithiolanes at room temperature in the presence of $POCl_3$-mont. Howerery, 1,1,-diacetates with electron-withdrawing group (**1d**, **1e**, **1f**, **1h**, and **1i**) take longer reaction time at room temperature; therefore, complete conversion of the reactions need in refluxing temperature. For example, the transthioacetalization of **1f** need 45 min in dichloromethane at room temperature under catalyst of $POCl_3$-mont and give the corresponding yield 83%, when it is proceeded in refluxing $CH_2Cl_2$ only need 15 min and the yield is 90% (as shown in Table 1). It is pointed out that **1h** and **1i** provide poor conversion rate ($<40\%$) at room temperature for the time 2 hr, whereas over 72% yield were obtained in refluxing $CH_2Cl_2$ for 60 min, possibly due to the strong electron withdrawing nitro substituent.

In summary, we have developed a facile and efficient procedure for the transthioacetalization of 1,1-diacetates with 1,2-dithiaglycol under the catalyst




*Scheme 1.*

***Table 1.*** Transdithioacetalization of 1,1-diacetates catalyzed by $POCl_3$-mont.

| Entry | Substrate | Product | Solvent | Tep. (°C) | Time (min) | Yield (%)[a] |
|---|---|---|---|---|---|---|
| 1 | $PhCH(OAc)_2$ **1a** | $PhCH(SCH_2)_2$ **3a** | $CH_2Cl_2$ | r. t. | 15 | 96 |
| 2 | $4\text{-}MeC_6H_4CH(OAc)_2$ **1b** | $4\text{-}MeC_6H_4CH(SCH_2)_2$ **3b** | $CH_2Cl_2$ | r. t. | 15 | 95 |
| 3 | $4\text{-}MeOC_6H_4CH(OAc)_2$ **1c** | $4\text{-}MeOC_6H_4CH(SCH_2)2$ **3c** | $CH_2Cl_2$ | r. t. | 10 | 95 |
| 4 | $4\text{-}ClC_6H_4CH(OAc)_2$ **1d** | $4\text{-}ClC_6H_4CH(SCH_2)_2$ **3d** | $CH_2Cl_2$ | reflux | 10 | 94 |
| 5 | $3\text{-}ClC_6H_4CH(OAc)_2$ **1e** | $3\text{-}ClC_6H_4CH(SCH_2)_2$ **3e** | $CH_2Cl_2$ | reflux | 5 | 97 |
| 6 | $2,4\text{-}Cl_2C_6H_3CH(OAc)_2$ **1f** | $2,4\text{-}Cl_2C_6H_3CH(SCH_2)_2$ **3f** | $CH_2Cl_2$ | reflux | 15 | 90 |
| 7 | $PhCH{=}CHCH(OAc)_2$ **1g** | $PhCH{=}CHCH(SCH_2)_2$ **3g** | $CH_2Cl_2$ | r. t. | 10 | 98 |
| 8 | $4\text{-}O_2NC_6H_4CH(OAc)_2$ **1h** | $4\text{-}O_2NC_6H_4CH(SCH_2)_2$ **3h** | $CH_2Cl_2$ | reflux | 60 | 74 |
| 9 | $3\text{-}O_2NC_6H_4CH(OAc)_2$ **1i** | $3\text{-}O_2NC_6H_4CH(SCH_2)_2$ **3i** | $CH_2Cl_2$ | reflux | 60 | 72 |
| 10 | $3,4\text{-}(OCH_2O)C_6H_3CH(OAc)_2$ **1j** | $3,4\text{-}(OCH_2O)C_6H_3CH(SCH_2)_2$ **3j** | $CH_2Cl_2$ | r. t. | 15 | 97 |

[a]Isolated yields.

of $POCl_3$-mont. For this method has operational simplicity, high yield, short reaction time and using a reusable catalyst.

## EXPERIMENTAL

The $POCl_3$-mont catalyst was obtained by mixing $POCl_3$ and montmorillonite clays in $CH_2Cl_2$ then solvent was removed under reduced pressure and finally stored in desiccator until use. The products were characterized by $^1H$ NMR spectra and comparison of their melting or boiling points with literature values.

### General Procedure for the Transthioacetalization of 1,1-Diacetate

A mixture of 1,1-diacetate 1. (2.00 mmol, synthesized as described previously[15]), $HSCH_2CH_2SH$ (2.4 mmol), $CH_2Cl_2$ (8 mL), and $POCl_3$-mont (150 mg) was stirred in refluxing $CH_2Cl_2$ or at room temperature for the time indicated in Table 1. The reaction was monitored by TLC. After completion of the reaction, $CH_2CI_2$ (10 mL) was added to the reaction mixture and the $POCl_3$-mont was filtered off. The catalyst was washed with $CH_2Cl_2$ ($2 \times 8$ mL); after that, the filtrate was washed with 5% HCl (15 mL), 5% $NaHCO_3$ (15 mL) and brine ($2 \times 15$ mL) successively and dried with $MgSO_4$. The solvent was evaporated under reduced pressure, and residue was chromatographed on silica gel (petroleum-ether as eluent) to give the corresponding dithiolanes **3** (Table 1). $^1H$ NMR spectra were determined in D-chloroform solution on a FT-NMR Bruker 300 (300 MHz), and reported in $\delta$ ppm using tetramethylsilane as the standard.

**4-$MeOC_6H_4CH(SCH_2)_2$ 3c**

$\delta_H$ 3.30–3.45 [4H, m, 4-$CH_3OC_6H_4CH$ ($SC\mathbf{H}_2)_2$], 3.80[3H, s, 4-$CH_3OC_6H_4CH(SCH_2)_2$], 5.60[1H, s, 4-$CH_3OC_6H_4C\mathbf{H}(SCH_2)2$], 6.87–7.47[4H, m, 4-$CH_3OC_6\mathbf{H}_4CH(SCH_2)_2$].

**4-$ClC_6H_4CH(SCH_2)_2$ 3d**

$\delta_H$, 3.30–3.60 [4H, m, 4-$ClC_6H_4CH(SC\mathbf{H}_2)_2$], 5.60[1H,s, 4-$ClC_6H_4C\mathbf{H}$ $(SCH_2)_2$], 7.30–7.50 [4H, m, 4-$ClC_6\mathbf{H}_4CH$ $(SCH_2)_2$].

**PhCH═CHCH(SCH$_2$)$_2$ 3g**

$\delta_H$ 3.22–3.42 [4H, m, $C_6H_5CH$═$CHCH$ (SC**H**$_2$)$_2$], 5.22 [1H, d, $C_6H_5$-$CH$═$CHC$**H**(SCH$_2$)$_2$], 6.15–6.22[1H, dd, $C_6H_5CH$═$CHCH$ (SC**H**$_2$)$_2$], 6.52[1H, d, $C_6H_5C$**H**═$CHCH$ (SCH$_2$)$_2$], 7.22–7.46 [5H, m, $C_6$**H**$_5$-$CH$═$CHCH$ (SCH$_2$)$_2$].

**4-O$_2$NC$_6$H$_4$CH(SCH$_2$)$_2$ 3h**

$\delta_H$3.35–3.60 [4H, m, 4-$NO_2C_6H_4CH$ (SC**H**$_2$)$_2$], 5.60 [1H, s, 4-$NO_2C_6H_4C$**H** (SCH$_2$)$_2$], 7.67–8.15 [4H, m, 4-$NO_2C_6$**H**$_4$CH (SCH$_2$)$_2$].

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