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Preyssler-type heteropoly acid: A new, mild and efficient catalyst for protection of carbonyl compounds

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Abstract

Preyssler-type heteropoly acid is introduced as a new, mild and efficient catalyst for protection of a variety of carbonyl compounds with 1,3-propane dithiol.

Keywords: Preyssler-type heteropoly acid; Protection; Carbonyl groups; 1,3-Propanedithiol

The protection of carbonyl compounds as dithioacetals is an important sequence in multi-step preparation of many important organic compounds including multifunctional complex molecules [1,2]. Moreover, the electrophilic properties of carbonyl group in aldehydes and ketones can be a good choice to be attacked by a nucleophile at the site. Thus, one of the most popular methods for protection of carbonyl groups is to convert them into their corresponding dithioacetals [3].

There are many methods in the literature for the protection of carbonyl compounds as dithioacetals using various catalysts or stoichiometric reagents [3]. However, most of these procedures have some restrictions such as low yields of the products, long reaction times, harsh reaction conditions, difficulties in work-up and the requirement for an inert atmosphere. Therefore, the search for alternative methods that can overcome these drawbacks is desirable.

In the past three decades, the broad utility of heteropoly acids (HPAs) as solid acids and multi-electron oxidation catalysts in solution as well as in the solid state for a wide variety of synthetic and industrial organic useful transformations like alcohol dehydration, alkylation, and esterification has been demonstrated [4–10].

On the other hand, precise control of the acidity in a small-scale reaction with usual corrosive any strong acid is extremely difficult. Considering the reversible nature of some processes in organic syntheses, low yield in reaction with pervious usual strong liquid acid is expected. So Preyssler-type heteropoly acid ($H_{14}NaP_5W_{30}O_{110}$) has been introduced as an efficient alternative. The advantages of Preyssler acid as a solid acid catalyst may include large number of balanced protons, strong acidity, high hydrothermal stability, and wide pH range stability in solution [10,11]. A few of researchers have investigated the catalytic performances of Preyssler-type heteropoly acid in a number of organic synthesis processes [12–15].

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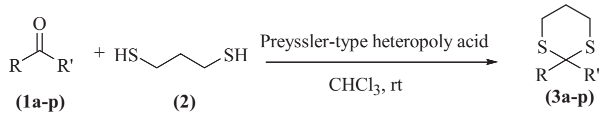


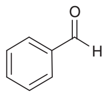
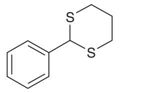
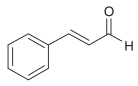
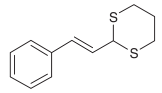
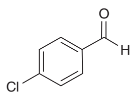
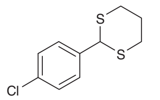
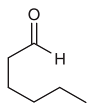
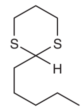
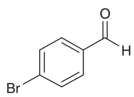
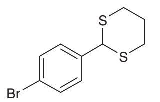
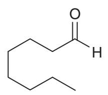
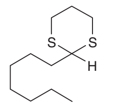
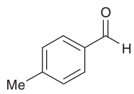
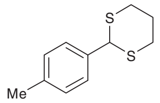
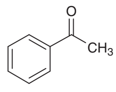
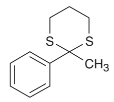
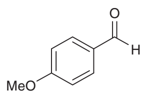
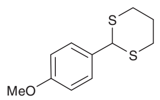
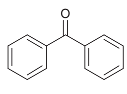
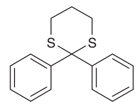
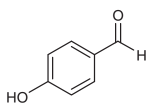
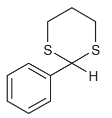
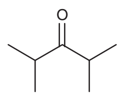
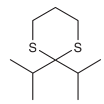
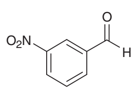
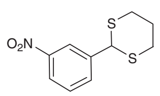
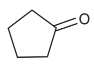
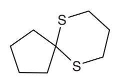
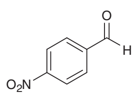
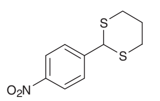
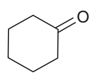
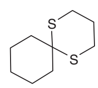
Scheme 1.

Within our ongoing research program to develop new synthetic methodologies [16–20], we proposed that Preyssler-type heteropoly acid might be a useful catalyst for thioacetalization of carbonyl compounds. In this paper, we wish to report a simple and easy method for chemoselective thioacetalization of various aromatic and aliphatic aldehydes and ketones using Preyssler-type heteropoly acid as a new and efficient catalyst, depicted in Scheme 1.

The Preyssler-type heteropoly acid was prepared and characterized according to the previously published method [21] and then the reaction of 1,3-propanedithiol (**2**) with benzaldehyde (**1a**) as a model reaction was performed in different solvents and different catalytic amount of Preyssler acid. On the basis of the reaction times and yields, $CHCl_3$ and 0.1 mol% of the catalyst was selected as the most suitable reaction conditions.

Various aldehydes and ketones (**1a–1p**) used as substrates to react with 1,3-propanedithiol (**2**). The results in Table 1 clearly demonstrate that protecting of carbonyl compounds using 1,3-propanedithiol as protection reagent in

Table 1
Protection of different aldehydes and ketones as their corresponding 1,3-dithianes by reaction with 1,3-propanedithiol.[a]

Entry	Substrate	Time (min)	Product	Yield[b] (%)	Entry	Substrate	Time (min)	Product	Yield[b] (%)
1a		5		96	**1i**		5		90
1b		10		92	**1j**		15		87
1c		10		90	**1k**		15		80
1d		5		95	**1l**		25		92
1e		2		96	**1m**		40		83
1f		2		95	**1n**		45		87
1g		10		85	**1o**		30		90
1h		20		80	**1p**		20		90

[a] Reaction conditions as explained in the experimental procedure and the products are characterized from their spectral data.
[b] Isolated yields.