

SHORT COMMUNICATION

Efficient thioacetalisation of carbonyl compounds

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Received 4 February 2013; Revised 18 April 2013; Accepted 1 May 2013

The thioacetalisation of a variety of heterocyclic, aromatic, and aliphatic carbonyl compounds (1 mmol) with ethane-1,2-dithiol (1 mmol) using silica sulphuric acid (SSA) is presented as an efficient heterogeneous catalyst under mild and solvent-free conditions at 60 °C. The thioacetals were formed within a short reaction time (1–34 min) and isolated with 90–98 % yield following an extractive procedure and chromatography on silica gel. The competitive protection reaction between aldehyde and ketone with ethane-1,2-dithiol afforded the protected derivatives of benzaldehyde and acetophenone with 92 % and 8 % yields, respectively, indicating some selectivity.

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Keywords: silica sulphuric acid (SSA), heterogeneous catalyst, thioacetalisation, chemoselectivity, carbonyl compounds, 1,2-ethanedithiol

The protection of carbonyl groups as dithioacetals is a common and popular practice in organic chemistry (Wuts & Greene, 2006; Kocienski, 1994), since they are quite stable under basic or acidic conditions. Among the different carbonyl-protecting groups, 1,3-dithianes, 1,3-oxathiolanes, and 1,3-dithiolanes have long been used as protective groups, and act as an acyl- anion equivalent in carbon–carbon bond-forming reactions (Eliel & Morris-Natschke, 1984; Gröbel & Seebach, 1977; Bulman Page et al., 1989). They are generally prepared by Brønsted or Lewis acid-catalysed condensation of carbonyl compounds with thiols or dithiols, in the presence of strong acid catalysts such as AlCl₃ (Ong, 1980), LnCl₃ (Garlaschelli & Vidari, 1990), ZnCl₂ (Evans et al., 1977), TiCl₄ (Kumar & Dev, 1983), WCl₆ (Firouzabadi et al., 1998), InCl₃ (Muthusamy et al., 2001), In(OTf)₃ (Muthusamy et al., 2002), Sc(OTf)₃ (Kamal & Chouhan, 2002a, 2003), Bi(NO₃)₃ (Komatsu et al., 1995), VO(OTf)₂ (De, 2005), and Ce(OTf)₃ (Kumar et al., 2010). A number of milder procedures employing lithium salts (Firouzabadi et al., 1999a, 1999b; Saraswathy & Sankararaman, 1994; Tietze et al., 2000; Yadav et al., 2001), NiCl₂ (Khan et al., 2003), CoCl₂

(De, 2004), NBS (Kamal & Chouhan, 2002b), silica gel-supported sulphamic acid (Aoyama et al., 2013), and I₂ (Samajdar et al., 2001) have also been reported for this purpose. Many of these protocols suffer from drawbacks such as requiring harsh reaction conditions and stoichiometric amounts of catalysts, the use of expensive reagents and/or chlorinated organic solvents and, in some instances, strong acidic reagents. Recently, a number of solid-supported reagents have also been used for the thioacetalisation of various types of carbonyl compounds, e.g. ZrCl₄–SiO₂ (Patney & Margan, 1996), SOCl₂–SiO₂ (Kamitori et al., 1986), CoBr₂–SiO₂ (Patney, 1994), TaCl₅–SiO₂ (Chandrasekhar et al., 1997), Cu(OTf)₂–SiO₂ (Anand et al., 1999), NaHSO₄–SiO₂ (Das et al., 2005), and I₂–natural phosphate (Zahouily, 2005). Interestingly, only a few of these methods have demonstrated chemoselective protection of aldehydes in the presence of ketones (Ong, 1980; Muthusamy et al., 2001; Kamal & Chouhan, 2002a, 2002b, 2003; Karimi & Seradj, 2000).

However attractive these reagents may be, to the best of our knowledge there is only one report on the application of silica sulphuric acid (SSA) in the thioac-

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