

Short Communication

Synthetic Methods, III [1]: Sulfated Zirconia Catalyzed Thioacetalization of Carbonyl Compounds

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Summary. Sulfated zirconia effectively catalyzes the reaction of carbonyl compounds with 1,2-ethanedithiol or thiophenol to afford the corresponding dithioacetals as useful organosulfur synthons. Isolation of pure products in high yields by simple filtration and evaporation is an important feature of this method.

Keywords. Carbonyl compounds; Catalysis; Sulfated zirconia; Thioacetalization.

Synthetische Methoden, 3. Mitt.: Thioacetalisierung von Carbonylverbindungen mit $ZrO_2SO_4^{2-}$
(Kurze Mitt.)

Zusammenfassung. ZrO_2/SO_4^{2-} katalysiert die Reaktion von Carbonylverbindungen mit 1,2-Ethandiol oder Thiophenol zu den als Organoschwefelsynthonsen wertvollen entsprechenden Dithioacetalen. Ein wichtiges Merkmal der Methode ist die einfache Isolierung der Produkte in guten Ausbeuten durch Filtration und Entfernung des Lösungsmittels.

Introduction

The protection of carbonyl group as thioacetals is frequently a necessary requirement in the manipulation of multifunctional organic molecules [2]. Thioacetals are also useful in organic synthesis as acyl carbanion equivalents [3]. In general, thioacetals have been prepared by protic acid or *Lewis* acid catalyzed condensation of carbonyl compounds with thiols [4–14]. However, many of these methods suffer from harsh conditions, expensive reagents, slow reaction rates, poor yields when applied to hindered and aromatic ketones, and sometimes cumbersome extraction procedures. Consequently, there seems to be a need to develop new reagents for this reaction.

In recent years, there has been considerable interest in the catalysis of organic reactions by solid superacid catalysts being potential alternatives to other strong acids which are environmentally undesirable [15]. Of the several solid superacid

catalysts, sulfated zirconia ($\text{SO}_4^{2-}/\text{ZrO}_2$) exhibits the highest acid strength ($\text{H}_0 < -16.04$) [16–18]. It can be prepared easily by sulfate treatment of zirconium hydroxide followed by calcination and has been found to be a useful catalyst in a variety of reactions [19–23].

Results and Discussion

We report herein the usefulness of sulfated zirconia as an efficient heterogenous catalyst for the thioacetalization of carbonyl compounds (Scheme). The results are presented in Tables 1 and 2. The work-up procedure is exceedingly simple and involves merely a filtration. Sulfated zirconia is recovered and reactivated for reuse by calcination at 650°C . This procedure of thioacetalization appears to be quite general as both aldehydes and ketones were smoothly converted into thioacetals in excellent yields (Table 1) and almost in pure form. All products have been characterized by ^1H NMR spectroscopy.

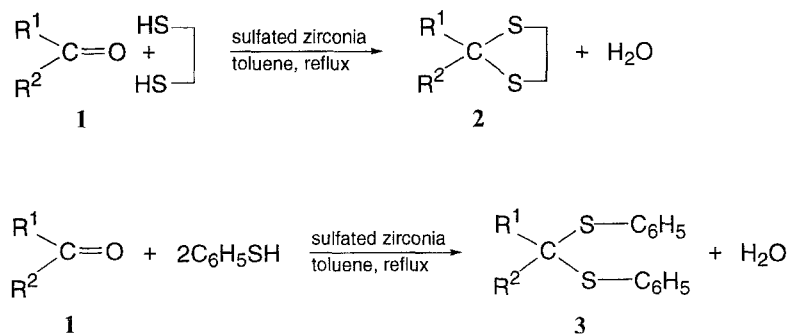
This thioacetalization method is a useful alternative to existing procedures. Furthermore, it is advantageous because of the ease of separation, high yields, short reaction times, and recyclability of the catalyst.

Experimental

Sulfated zirconia was supplied by MEL Chemicals, England; it was calcinated at 650°C in a furnace for 3 h and then cooled under nitrogen. This catalyst was then used directly for the reaction. Melting points were determined by the open-capillary method and are uncorrected. ^1H NMR spectra were recorded on a Perkin-Elmer 90 MHz NMR spectrometer (chemical shifts in δ , ppm) using *TMS* as internal standard.

General Procedure of Thioacetalization

A mixture of the carbonyl compound (10 mmol), 1,2-ethanedithiol (10 mmol) or thiophenol (20 mmol), and sulfated zirconia (100 mg) in toluene was stirred under reflux for the specified time (Table 1). Water formed was removed azeotropically. The reaction was monitored by TLC. After completion of the reaction, the mixture was filtered, and the catalyst was washed with ether (4×10 ml). The solvent was removed under reduced pressure to afford the products in high yields and in almost pure form.



Scheme

Table 1. Sulfated zirconia catalyzed thioacetalization of carbonyl compounds (cf. Scheme)

R^1	R^2	Product	Reaction time (min)	Yield (%)	m.p. b.p./torr
Furfuryl	H	2a	30	93	80/5
C_6H_5	H	2b	40	95	185/5
4-Cl- C_6H_4	H	2c	25	94	59
4-Me- C_6H_4	H	2d	35	93	56
4-MeO- C_6H_4	H	2e	80	91	61
4-NO ₂ - C_6H_4	H	2f	20	93	68
Cyclopentyl		2g	85	90	107/15
Cyclohexyl		2h	70	92	54
C_6H_5	CH ₃	2i	125	94	131/3
C_6H_5	C_6H_5	2j	150	90	104
Furfuryl	H	3a	25	92	110/760
4-Cl- C_6H_4	H	3b	45	96	64
4-Me- C_6H_4	H	3c	40	97	54
4-MeO- C_6H_4	H	3d	85	97	72
2-NO ₂ - C_6H_4	H	3e	40	93	84

Table 2. ¹NMR data of products (CDCl₃, TMS)

	δ (ppm); J (Hz)
2a	3.21 (s, 4H), 5.60 (s, 1H), 6.20 (d, 2H), 7.18 (t, 1H)
2b	3.23 (s, 4H), 5.61 (s, 1H), 7.45 (m, 5H)
2c	3.75 (s, 2H, S-CH ₂), 3.85 (s, 2H, S-CH ₂), 6.20 (s, 1H, C-H), 8.10 (d, 2H, $J = 5$ Hz, Ar-H), 8.30 (d, 2H, $J = 5$ Hz, Ar-H)
2d	2.33 (s, 3H, Ar-CH ₃), 3.36 (s, 2H, S-CH ₂), 3.40 (s, 2H, S-CH ₂), 5.60 (s, 1H, C-H), 7.23 (d, 2H, $J = 4$ Hz, Ar-H), 7.40 (d, 2H, $J = 4$ Hz, Ar-H)
2e	3.37 (s, 2H, S-CH ₂), 3.43 (s, 2H, S-CH ₂), 3.80 (s, 3H, OCH ₃), 5.57 (s, 1H, C-H), 6.80 (d, 2H, $J = 4.5$ Hz, Ar-H), 7.40 (d, 2H, $J = 4.5$ Hz, Ar-H)
2f	3.75 (s, 2H, S-CH ₂), 3.83 (s, 2H, S-CH ₂), 6.22 (s, 1H, C-H), 8.50 (s, 2H, $J = 4$ Hz, Ar-H), 9.02 (s, 2H, $J = 4$ Hz, Ar-H)
2g	2.1 (m, 8H, cyclopentyl), 3.40 (s, 4H, 2 × S-CH ₂)
2h	2.17 (m, 10H, cyclohexyl), 3.45 (s, 4H, 2 × S-CH ₂)
2i	1.7 (s, 3H, CH ₃), 3.30 (s, 4H, 2 × S-CH ₂), 7.28 (m, 5H, Ar-H)
2j	3.8 (s, 4H, 2 × S-CH ₂), 7.40 (s, 10H, Ar-H)
3a	6.1 (s, 1H, C-H), 7.2–7.4 (m, 13H, Ar-H)
3b	6.2 (s, 1H, C-H), 7.3–7.6 (m, 14H, Ar-H)
3c	2.32 (s, 3H, Ar-CH ₃), 5.9 (s, 1H, C-H), 7.1–7.3 (m, 14H, Ar-H)
3d	3.81 (s, 3H, O-CH ₃), 5.8 (s, 1H, C-H), 7.0–7.2 (m, 14H, Ar-H)
3e	6.1 (s, 1H, C-H), 7.1–7.3 (m, 14H, Ar-H)

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