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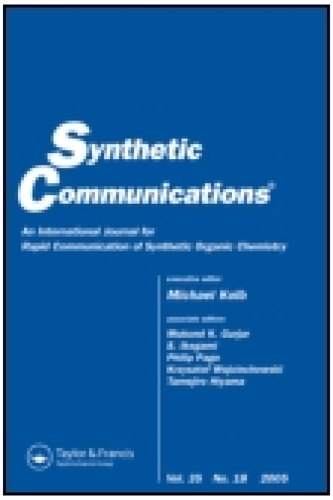

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Immediate and Efficient Oxidative Deprotection of Dithioacetals to Carbonyl Compounds by Zinc Dichromate Trihydrate ($ZnCr_2O_7 \cdot 3H_2O$)

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ABSTRACT

Zinc dichromate trihydrate ($ZnCr_2O_7 \cdot 3H_2O$) is an efficient oxidizing agent for the immediate deprotection of 1,3-dithianes, 1,3-dithiolanes, and dibutyl dithioacetals to their corresponding carbonyl compounds in non-aqueous and aprotic conditions at room temperature.

Key Words: Zinc dichromate trihydrate; Oxidative deprotection; 1,3-Dithianes; 1,3-Dithiolanes; Dibutyl dithioacetals; Thioacetals; Carbonyl compounds.

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INTRODUCTION

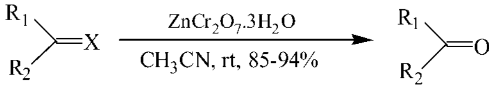
Chemical manipulation of complex polyfunctional molecules often requires the sequential protection and deprotection of various functionalities. The electrophilic nature of the carbonyl groups is the dominant nature of their extensive chemistry. One of the major challenging problems during many multi-step syntheses is how to protect a carbonyl from nucleophilic attack until its electrophilic properties can be exploited. For this reason the protection and deprotection of the carbonyl group remain crucial challenges to organic chemists. Due to the stability of 1,3-dithioacetals[1] towards various reagents and reaction conditions and their wide applications as acyl anion equivalents for carbon–carbon bond forming reactions, 1,3-dithioacetals have attained a position of prominence in the area of carbonyl group protections.[2] Therefore, as with most protecting groups, development of new methods for deprotection of dithioacetals into their corresponding carbonyl compounds have attracted many attentions.[3] (For a review see Ref.[3j].) Metal coordination, alkylation, and oxidation are three general strategies which can be used for this purpose. However, each of the reported procedures suffer from at least one of the following drawbacks; requiring drastic conditions, multi-step processes, tedious work-up, long reaction times, low yields, and use of expensive reagents. Thus, an improved alternative procedure for this important transformation is of practical value and appreciated by synthetic organic chemists.

Zinc dichromate trihydrate ($ZnCr_2O_7 \cdot 3H_2O$) which is easily prepared by the reaction of $ZnCO_3$ with CrO_3 in an acidic solution is a stable, cheap, and easily handed compound.[4] Recently, we have reported $ZnCr_2O_7 \cdot 3H_2O$ as an efficient oxidizing agent for the oxidation of alcohols, oxidative deprotection of 1,3-dioxalanes, and oximes to their corresponding carbonyl compounds and preparation of α-ketophosphonates by the oxidation of α-hydroxyphosphonates.[5]

In this paper, we have applied $ZnCr_2O_7 \cdot 3H_2O$ as an efficient oxidizing agent for the immediate deprotection of various types of dithioacetals to their corresponding carbonyl compounds in non-aqueous and aprotic conditions at room temperature (Sch. 1).

RESULTS AND DISCUSSION

Oxidative deprotection of 2-phenyl-1,3-dithiolane (**1a**) as a model compound was studied in several solvents including CH_3CN, CH_2Cl_2, $CHCl_3$, CCl_4, and C_6H_6 using $ZnCr_2O_7 \cdot 3H_2O$ (2 equiv.) as an oxidant. We found that CH_3CN was a suitable solvent for this purpose. Various types of aromatic 1,3-dithianes and 1,3-dithiolanes with electron-releasing and



1 **2**

X=$-S(CH_2)_3S-$, $-S(CH_2)_2S-$, $-(SBu)_2$

R_1=Ph, alkyl

R_2=Ph, alkyl, H

Scheme 1.

electron-withdrawing groups (**1a–n**), aliphatic 1,3-dithianes and 1,3-dithiolanes (**1o–q**) and dibutyl dithioacetals (**1r, s**) were cleanly and immediately deprotected to their corresponding carbonyl compounds in 85–94% yields in CH_3CN at room temperature with 2–2.2 equiv. of $ZnCr_2O_7 \cdot 3H_2O$ (Table 1).

In conclusion, we have introduced $ZnCr_2O_7 \cdot 3H_2O$ as an easily prepared, cheap, stable oxidant for the fast and high yielding deprotection of various types of dithioacetals to their corresponding carbonyl compounds. Mild reaction conditions and easy work-up of the reaction mixture are also worthy of mention for the presented method.

EXPERIMENTAL

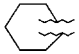
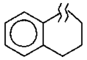
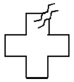
$ZnCr_2O_7 \cdot 3H_2O$ and dithioacetals were prepared according to the known procedures.[1,4] Yields refer to isolated products. The purity determination of the products were accomplished by TLC on silica gel polygram SIL G/UV 254 plates or GLC on a Shimadzu Model GC-8A instrument with a flame ionization detector and a column of 15% carbowax 20 M/chromosorb-W acid washed 60–80 mesh. All products were characterized by comparison of their spectral and physical data with those of authentic samples. Boiling points of the products were determined under atmospheric pressure unless otherwise indicated in the table.

General Procedure

To a solution of dithioacetals (**1**, 1 mmol) in dry CH_3CN (5 mL), $ZnCr_2O_7 \cdot 3H_2O$ (0.67–0.74 g, 2–2.2 mmol) was added. The resulting mixture was stirred at room temperature. Immediate reaction occurred. Silica gel (1 g) was added to the reaction mixture and the solvent was evaporated under reduced

Table 1. Deprotection of thioacetals by $ZnCr_2O_7 \cdot 3H_2O$ in CH_3CN at room temperature.

Substrate **1**	R_1	R_2	X	Oxidant/ substrate	Yield[a] (%)	B.p. (760 mmHg) or m.p.	Reported [6] b.p.760 (mmHg) or m.p.
a	Ph	H	$-S(CH_2)_3S-$	2/1	85	175	179
b	Ph	H	$-S(CH_2)_2S-$	2/1	85	175	179
c	$4\text{-}ClC_6H_4$	H	$-S(CH_2)_3S-$	2/1	90	46	47.5
d	$4\text{-}ClC_6H_4$	H	$-S(CH_2)_2S-$	2/1	88	46	47.5
e	$4\text{-}MeC_6H_4$	H	$-S(CH_2)_3S-$	2/1	92	109[b]	106[b]
f	$4\text{-}MeC_6H_4$	H	$-S(CH_2)_2S-$	2/1	90	109[b]	106[b]
g	$4\text{-}BrC_6H_4$	H	$-S(CH_2)_3S-$	2/1	88	70	67
h	$4\text{-}NO_2C_6H_4$	H	$-S(CH_2)_3S-$	2/1	90	104	107
i	$4\text{-}MeOC_6H_4$	H	$-S(CH_2)_3S-$	2/1	88	130[c]	134[c]
j	Ph	Ph	$-S(CH_2)_3S-$	2.2/1	94	49	47.8
k	$4\text{-}ClC_6H_4$	Me	$-S(CH_2)_3S-$	2.2/1	93	230	232
l	$4\text{-}ClC_6H_4$	Me	$-S(CH_2)_2S-$	2.2/1	90	236	232

m	Ph	Me	$-S(CH_2)_3S-$	2.2/1	94	199	202
n	Ph	Et	$-S(CH_2)_3S-$	2.2/1	92	214	217.5
o			$-S(CH_2)_2S-$	2/1	85	160	155.4
p			$-S(CH_2)_3S-$	2.2/1	92	114[d]	115[d]
q			$-S(CH_2)_3S-$	2.2/1	88	198	196
r	Ph	H	$(-SBu)_2$	2/1	88	175	179
s	$2\text{-}ClC_6H_4$	H	$(-SBu)_2$	2/1	88	208	211.9

[a] Isolated yields. All the reactions were occurred immediately.

[b] Boiling points were determined at 10.

[c] Boiling points were determined at 12 mmHg.

[d] Boiling points were determined at 6 mmHg.

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pressure. The resulting powder was poured on a silica gel pad (3-cm thick) and washed with *n*-hexane/EtOAc (5 : 1) (3 × 30 mL). The desired product (**2**) was isolated in excellent yields (85–94%) after the evaporation of the solvent.

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