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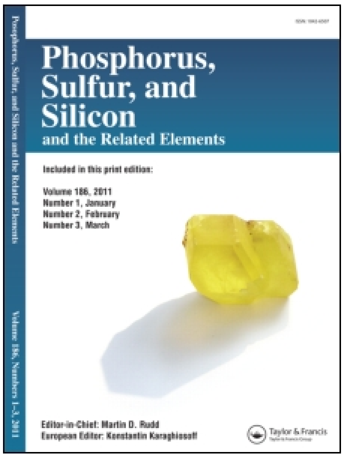

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Trichloroisocyanuric Acid, as an Industrial Chemical, Promotes Transthioacetalization of Diacetals of 2,2-Bis (Hydroxymethyl)-1,3-propanediol and Cleavage of Thioacetals

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TRICHLOROISOCYANURIC ACID, AS AN INDUSTRIAL CHEMICAL, PROMOTES TRANSTHIOACETALIZATION OF DIACETALS OF 2,2-BIS (HYDROXYMETHYL)-1,3-PROPANEDIOL AND CLEAVAGE OF THIOACETALS

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Trichloroisocyanuric acid has been used as a mild, efficient, and new catalyst for transthioacetalization of diacetals of 2,2-bis (hydroxymethyl)-1,3-propanediol in CH_2Cl_2 at room temperature. A clean, easy, and general method for efficient deprotection of thioacetals to their corresponding carbonyl compounds using trichloroisocyanuric acid/silica gel and water system also is described.

Keywords: Deprotection; diacetals of 2,2-bis (hydroxymethyl)-1,3-propanediol; transthioacetalization; thioacetals; trichloroisocyanuric acid

INTRODUCTION

Protection of carbonyl compounds as dithioacetals (1,3-dithiolanes, 1,3-dithianes, and acyclic thioacetals) is an indispensable part of the synthesis of many polyfunctional molecules. Moreover, thioacetals often serve as precursors of acyl anion equivalents displaying reactivity umpolung and masked methylene function.[1–4] Although, they have been prepared generally by condensation of carbonyl compounds with dithiols, transthioacetalization has gained attention as the method of choice for this purpose.[5–10]

Conversion of thioacetals under mild reaction conditions into carbonyl compounds also is the most frequently used procedure in multi

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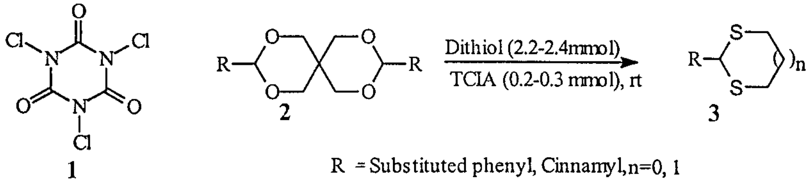
step organic synthesis.[1–4] Recently, we have introduced some mild, efficient, and chemoselective catalysts for thioacetalization and transthioacetalization reactions.[11–13] In this article we report transthioacetalization of diacetals of 2,2-bis (hydroxymethyl)-1,3-propanediol and cleavage of thioacetals with trichloroisocyanuric acid (TCIA) under mild reaction conditions.

RESULTS AND DISCUSSION

(a) Transthioacetalization of Diacetals of 2,2-Bis (hydroxymethyl)-1,3-propanediol Catalyzed by Trichloroisocyanuric Acid (TCIA, 1)

Acetals are one of the most useful and versatile protecting groups for carbonyl functions and the most popular ones are 1,3-dioxolanes and 1,3-dioxanes, because of their relative stabilities.[14–16] These compounds are usually liquid and their purifications and their handlings are difficult. In recent years, attention has been paid to the synthesis of diacetals of 2,2-bis (hydroxymethyl)-1,3-propanediol. These are crystalline compounds with sharp melting points,[17–21] therefore their isolation and identifications are an easy process. Direct transformation of these substances to other classes of compounds has not yet been reported in the literature.

Literature survey shows that TCIA, a cheap industrial chemical has found little applications in functional group transformation.[22–26] Recently, this compound has been used for the conversion of alcohols into their corresponding alkyl chlorides, oxidation of sulfides into sulfoxides, and oxidative coupling of thiols and selenols.[27–30] Recently we have used TCIA as a mild catalyst for thioacetalization and transthioacetalization reactions.[31] Now, we report that TCIA catalyzes efficient conversion of diacetals of 2,2-bis (hydroxymethyl)-1,3-propanediol into the 1,3-dithiolanes and 1,3-dithianes in CH_2Cl_2 at room temperature (Scheme 1, Table I).



SCHEME 1

As shown in Table I, a wide variety of diacetals with electron-withdrawing and releasing groups were cleanly and easily converted

TABLE I Transthioacetalization of Acetals of 2,2-Bis(hydroxymethyl)-1,3-propanediol in the Presence of TCIA with 1,3-Propanedithiol and Ethanedithiol in CH_2Cl_2 at Room Temperature

Entry	R	n	TCIA (mmol)	Time (h)	Yield %[a]
2a	Ph	0	0.2	1.5	95
2b	Ph	1	0.2	2	94
2c	4-CH_3-C_6H_4	0	0.2	1.5	95
2d	4-CH_3-C_6H_4	1	0.2	1.5	96
2e	4-CH_3O-C_6H_4	1	0.2	1	94
2f	3-CH_3O-C_6H_4	1	0.2	1	95
2g	2,4,6-$(CH_3)_3$-C_6H_2	1	0.2	1.5	90
2h	4-Br-C_6H_4	0	0.3	2	92
2i	4-Br-C_6H_4	1	0.3	2	93
2j	4-Cl-C_6H_4	1	0.3	2.5	94
2k	3-NO_2-C_6H_4	1	0.3	3.5	92
2l	Cinnamyl	0	0.2	1.5	95
2m	Cinnamyl	1	0.2	1.5	92

[a]Isolated yields.

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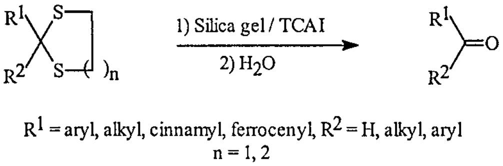
into the 1,3-dithianes and 1,3-dithiolanes under mild reaction conditions in excellent yields.

(b) Solvent-Free Deprotection of Thioacetals with Silica Gel/TCIA System

Deprotection of thioacetals into the corresponding parent molecules is one of the most frequently used procedure in multistep organic synthesis.[1–4] Literature review shows that conversion of S, S-acetals to carbonyl compounds may be achieved by one of two pathways: (a) acidic or transition metal ions hydrolysis (such as Ti^{4+}, Cu^{2+}, Ag^{+}, Hg^{2+}, Cd^{2+}) and (b) oxidative(chemical, photolytic and electrolytic processes) or alkylative hydrolysis.[1–4] Recently reported methods are: use of $GaCl_3/H_2O$,[32] $Bi(NO_3)$, $5H_2O/O_2$,[33] SeO_2/AcOH,[34] $(PhSeO)_2O$,[35] $Fe(phen)_3^{3+}$,[36] $SbCl_5$/aq. $NaHCO_3$,[37] N-fluoro-2,4,6-trimethylpyridinum triflate/water,[38] zirconium sulfophenyl phosphonate,[39] clayan and clayfen,[40,41] oxide of nitrogen,[42] natural kaolinitic clay.[43] Some of the above methods have its own merits and some drawbacks, such as toxicity to the environment, expensive reagent, difficult preparation, and use of expensive equipments. Very recently preparation and cleavage of thioacetals has been reviewed.[44]

On the other hand, trichloroisocyanuric acid (**1**)/$AgNO_3/CH_3CN/H_2O$ system has been used for deprotection of thioacetals by Olah and his coworkers.[45] In this procedure large excess of $AgNO_3$ (4.5 equiv.) and

1(4 equiv.) has been used in aqueous CH_3CN (75%) for the deprotection of thioketals. Now we report a cheap, high yielding, and convenient procedure for the deprotection of thioacetals and thioketals to the corresponding carbonyl compounds with (**1**)/silica gel system at room temperature in the absence of solvent (Scheme 2, Table II).



SCHEME 2

By this procedure, the expensive $AgNO_3$ has been omitted and the amount of trichloroisocyanuric acid (**1**) has been decreased from 4 to 1.5 equivalents per mole of the substrates. The reaction was completed after a few minutes by grinding the substrates and **1** with silica gel followed by the addition of a few drops of H_2O. The method shows general applicability for the deprotection of thioacetals and thioketals as well. Ring-enlargement reactions of thioketals derived from carbonyl compounds with enolizable hydrogens have not been observed by this method.[46]

In conclusion, in this study, we introduced a new useful application for trichloroisocyanuric acid (TCIA) an industrial chemical that catalyzes efficiently conversion of diacetals of 2,2-bis (hydroxymethyl)-1,3-propanediol into the 1,3-dithiolanes and 1,3-dithianes in CH_2Cl_2 at room temperature. We have also shown that TCIA as a reagent is able to effect deprotection of thioacetals and thioketals to the corresponding carbonyl compounds in the presence of silica gel in the absence of solvent at room temperature. Expensive $AgNO_3$ formerly used by Olah and his coworkers for this purpose has been eliminated in this procedure and the amount of trichloroisocyanuric acid has been decreased from 4 to 1.5 equivalents per mole of the substrates. Yields of the isolated products are usually excellent by these methods.

EXPERIMENTAL

Typical Procedure for Transthioacetalization of Diacetals of 4-Toluylaldehyde

To a stirred solution of the diacetal of 4-toluylaldehyde (0.75 g, 2.5 mmol), 1,2-ethanedithol (0.5 ml, 5.5 mmol) in CH_2Cl_2 (25 ml) and trichloroisocyanuric acid (0.12 g, 0.5 mmol) was added. After completion

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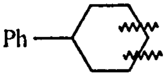
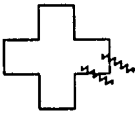
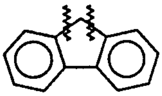
TABLE II Deprotection of Cyclic and Acyclic Thioacetals and Thioketals

No	R^1	R^2	n	Yield (%)[a,b,47]
1	Ph	H	1	95
2	Ph	H	2	95
3	4-$(CH_3)C_6H_4$	H	1	92
4	4-$(CH_3)C_6H_4$	H	2	91
5	4-$(CH_3O)C_6H_4$	H	1	90
6	3-$(CH_3O)C_6H_4$	H	2	92
7	2-$(CH_3)C_6H_4$	H	2	94
8	3-$(CH_3)C_6H_4$	H	2	94
9	4-$(Br)C_6H_4$	H	2	90
10	4-$(Cl)C_6H_4$	H	2	90
11	PhCH=CH	H	1	92
12	PhCH=CH	H	2	92
13	$Ph(CH_3)CH$	H	1	95
14	$PhCH_2CH_2$	CH_3	2	94
15	Ph	CH_3	1	96
16	Ph	CH_3	2	95
17	4-$(Cl)C_6H_4$	CH_3	2	90
18	4-$(CH_3)C_6H_4$	CH_3	2	92
19	Ph	Ph	1	94
20	Ph	Ph	2	92
21	3,4-$(CH_3O)_3C_6H_3$	CH_3	2	94
22	$PhCH_2$	CH_2CH_3	1	95
23	$PhCH_2$	CH_2CH_3	2	91
24			2	90
25			2	89
26			2	91
27	-(CH2)$_5$-		2	95
28	Ferrocenyl	CH_3	2	75

[a] Isolated yields.

[b] Structures are confirmed by IR, ^1H-NMR, ^{13}C-NMR, mp/bp.

of the reaction (1.5 h, TLC) the reaction mixture was quenched with an aqueous solution of NaOH (10%, 25 ml). Then CH_2Cl_2 (2 × 15 ml) was added to the resulting reaction mixture. The organic layer was separated, washed with H_2O (2 × 100 ml), dried ($MgSO_4$), and filtered. Evaporation of the solvent in vacuo gave 2-(4-toluyl)-1,3-dithiolane (0.94 g, 95%), (white needles) which crystallized from petroleum ether, m.p. 56–8°C (uncorrected); ^{1}H-NMR ($CDCl_3$, 250 MHz) $\delta = 2.38$ (s, 3H) 3.28–3.45 (m, 4H), 5.60 (s, 1H), 7.11 (d, 2H), 7.40 (d, 2H); ^{13}C-NMR ($CDCl_3$, 63 MHz) $\delta = 21.09$, 40.16, 56.11, 127.79, 129.12, 137.10, 137.78 MS (20 eV) m/z (relative intensity) 196 (M^+, 68.9), 168 (M^+ - $CH_2{=}CH_2$, 25.4), 153 (100), 135 (83.6), 91 (57.5), 45 (99.3), CHN analysis: %C (Cald.; 61.17, Found; 61.20), %H (Cald.; 6.16, Found; 6.14).

Typical Procedure for Dethioacetalization of 2,2-Diphenyl-1,3-dithiane under Solvent-Free Conditions

A mixture of 2,2-diphenyl-1,3-dithiane (0.54 g, 2 mmol), trichloroisocyanuric acid (0.69 g, 3 mmol) and silica gel (2 g) was ground in a mortar for 3 min. Then H_2O was added dropwise (10–15 drops) with stirring. The resulting mixture was continuously extracted in a small continous extractor with a mixture of n-hexane/EtOAc (5 ml, 5:1). Evaporation of the solvent in vacuo gave the benzophenone (0.33 g, 92%), white needle crystals from absolute ethanol m.p. 46–48°C (lit[46]: 47–49°C).

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