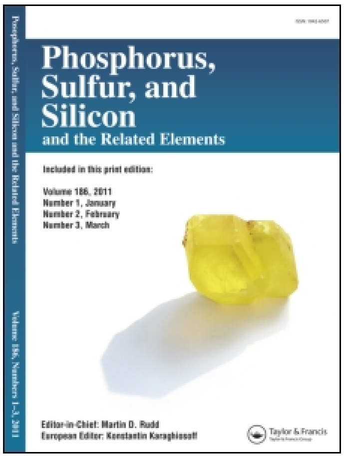

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Silica Chloride (SiO_2-Cl) Promotes Highly Efficient Transformation of Acylals to Dithianes, Dithiolanesm, and Oxathiolanes

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SILICA CHLORIDE (SiO_2-Cl) PROMOTES HIGHLY EFFICIENT TRANSFORMATION OF ACYLALS TO DITHIANES, DITHIOLANESM, AND OXATHIOLANES

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Acylals react with 1,3-propanedithiol, 1,2-ethanedithiol and 2-mercaptoethanol in the presence of silica chloride to give 1,3-dithianes, 1,3-dithiolanes and 1,3-oxathiolanes in excellent yields in CH_2Cl_2 at room temperature. It has been observed that acylals were more reactive than their aldehydes but less reactive than acetals and ketals. Also aliphatic acylals survive under these conditions.

Keywords: Acylals; dithiane; dithiolane; geminal diacetate; oxathiolane; silica chloride

INTRODUCTION

A vast number of methods are available for the preparation of acylals [1–6] or geminal diacetates, from aldehydes, in different reaction conditions. Acylals are readily available, even in large quantities. These compounds are stable to oxidation and can be used for the selective protection of aldehydes, and also as starting materials for Diels-Alder cycloaddition reactions.[7] However, the chemistry of geminal diacetates has been little explored and is mostly focused on the deprotection reactions,[8–13] and stability of the acylals in acidic and basic conditions. Significant transformations of acylals have been studied only in a few cases in the presence of carbanions.[14] Very recently, the reactivity of acylals toward Gringard and organolithium reagents has been also reported.[15]

The limited knowledge about the chemical properties of acylals encouraged us to study the chemical reactions of this class of compounds from different views. Recently, we have paid attention to introduce

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new methods for efficient protection of carbonyl groups by their transformation to acetals or thioacetals and also transacetalization and transthioacetalization reactions under mild reaction conditions.[16-19] Very little attention has been paid to silica chloride as a potential heterogeneous inorganic polymeric bed in organic reactions.[20-21] We have recently found that silica chloride is able to catalyze highly efficient transdithioacetalization of acetals.[22]

RESULTS AND DISCUSSIONS

In this article, we report that silica chloride is able to promote transformation of acylals to dithianes, dithiolanes, and oxathiolanes in CH_2Cl_2 at room temperature with high efficiency. To the best of our knowledge, this is the first report for these useful transformations in the literature (see Figure 1 and Table I).

Chemoselectivity of the method is important in organic reactions. Therefore, by using competitive reactions between very basic molecules, we have shown that silica chloride is a chemoselective catalyst for the reactions studied and presented in this paper. A mixture of phenylmethanediol diacetate (**1a**) and acetophenone (**3**) in the presence of the catalyst in CH_2Cl_2 was caused to react with an equimolar amount of 1,3-propane dithiol. The diacetate was preferentially transformed into its 1,3-dithiane in a quantitative yield whereas the ketone remained intact. Phenylmethanediol diacetate (**1a**) in the presence of benzaldehyde dimethyl acetal (**4**) remained intact although benzaldehyde dimethyl acetal (**4**) was almost exclusively converted to the corresponding 1,3-dithiane (Figure 2).

We have observed that acyclic acetal derived from acetophenone (5) in the presence of 4-chlorophenyl methanediol diacetate (1l) was converted to its dithiolane in 98% whereas 5 was converted to its dithiolane in only 10% yield. Cyclic acetal from 4-chloroacetophenone as its 1,3-oxolane (6) in the presence of 1l shows also a very good selectivity in reacting

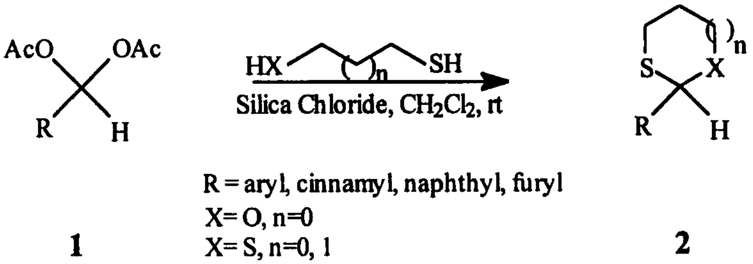

FIGURE 1

TABLE I Transformation of Acylals to Dithianes, Dithiolanes and Oxathiolanes Catalyzed by SiO_2-Cl in CH_2Cl_2

Entry	Substrate	R	X	n	SiO_2-Cl (g)[a]	Time (h)	Yield %[b]
1	1a	C_6H_5	S	1	0.5	3	92[20]
2	1b	4-Me-C_6H_4	S	1	0.5	1.25	94
3	1c	4-Br-C_6H_4	S	1	0.6	4.5	90
4	1d	2-MeO-C_6H_4	S	1	0.5	0.5	92
5	1e	2,5-diMeO-C_6H_3	S	1	0.5	0.25	95
6	1f	5-Me-Furyl	S	1	0.5	0.75	94
7	1g	Cinammyl	S	1	0.5	0.75	92
8	1h	1-Naphthyl	S	1	0.5	3.25	93
9	1i	4-NO_2-C_6H_4	S	1	1.0	4.0[c]	85
10	1j	C_6H_5	S	0	0.5	3.15	90
11	1k	4-Cl-C_6H_4	S	0	0.6	4.0	91
12	1l	2-MeO-C_6H_4	S	0	0.5	0.5	92
13	1m	Cinammyl	S	0	0.5	0.75	90
14	1n	C_6H_5	O	0	0.5	3.5	89
15	1o	2-MeO-C_6H_4	O	0	0.5	0.5	90
16	1p	4-Me-C_6H_4	O	0	0.5	1.5	90
17	1q	4-Cl-C_6H_4	O	0	0.6	4.25	89

[a] Silica chloride used for 1 mmol of the substrate.

[b] ^{1}HNMR and ^{13}CNMR are given for some products in the experimental section.

[c] Reaction was performed in refluxing CH_3CN.

with 2-mercaptoethanol. The 1,3-oxolane (6) was converted in 85% to its oxathiolane whereas (11) was converted to its oxathiolane in only 15%. The diacetate (1b) in the presence of oxathiolane (7) remained intact also the oxathiolane was converted exclusively to its 1,3-dithiolane while reacting with 1,2-ethanedithiol (Figure 2).

The difference in reactivities between acylals and acetals, ketals and oxathiolanes can be described by considering the nature of the carbocationic intermediates (**8**, **9** in Figures 3 and 4) derived from the above substrates during the reactions. The carbocations derived from acetals, ketals and oxathiolanes are stabilized as either an oxonium or a sulfonium ion (**8**, Figure 3). Carbocation derived from acylals can also be considered as an oxonium ion (**9**, Figure 4). This ion is hardly stable because of the presence of —OAc and SiO— groups in the vicinity of the oxonium ion intermediate, that should be formed during the progress of the reaction.

Aliphatic acylals survive and do not undergo transthioacetalization under similar reaction conditions. Aromatic aldehydes in the presence of aryl acylals (unsubstituted) do not show reasonable chemoselectivity.

In summary, this is the first report that is presented for the transformation of acylals to dithianes, dithiolanes, and oxathiolanes and also a new application of silica chloride in organic synthesis. The mild

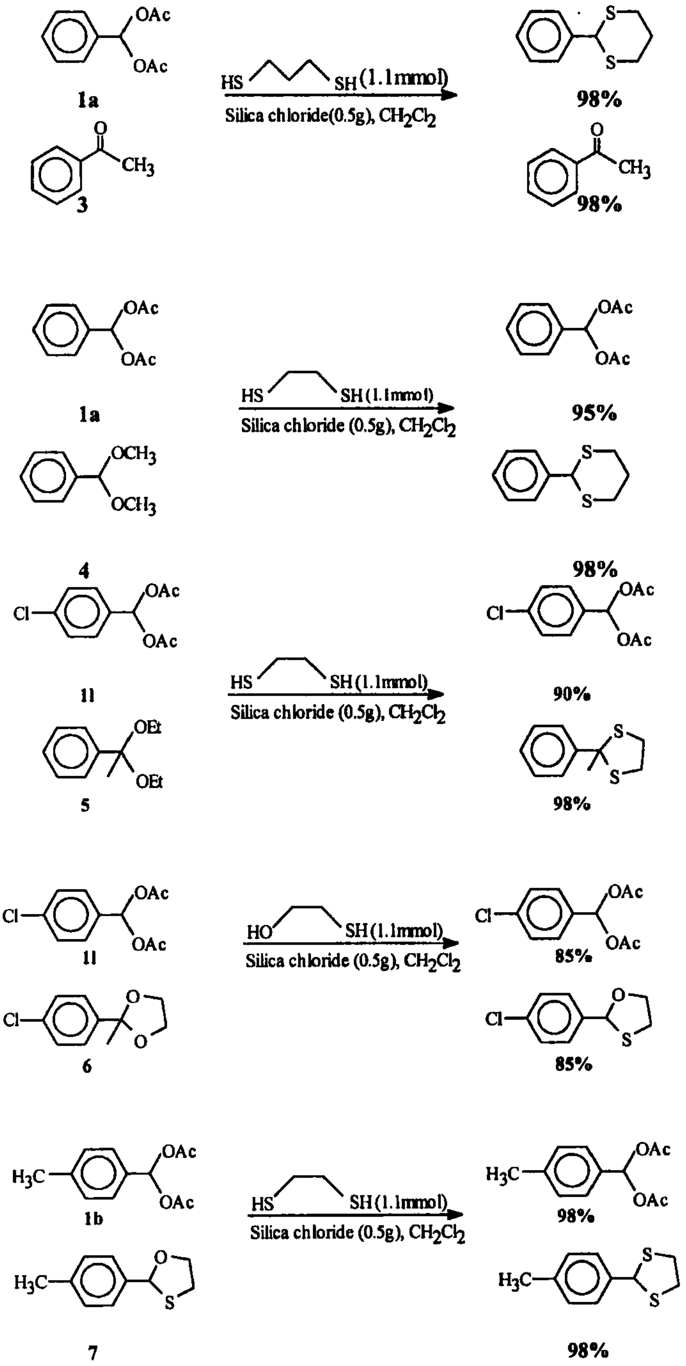
OAc
OAc
1a
3
CH3
HS SH(1.1mmol)
Silica chloride(0.5g), CH2Cl2
S
S
98%
CH3
98%
1a
4
OCH3
OCH3
HS SH(1.1mmol)
Silica chloride (0.5g), CH2Cl2
95%
98%
Cl
11
5
OEt
OEt
HS SH(1.1mmol)
Silica chloride (0.5g), CH2Cl2
90%
98%
11
6
O
O
HO SH(1.1mmol)
Silica chloride (0.5g), CH2Cl2
85%
85%
H3C
1b
7
HS SH(1.1mmol)
Silica chloride (0.5g), CH2Cl2
98%
98%

FIGURE 2

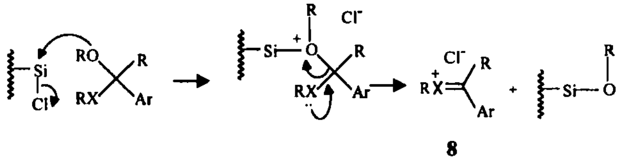

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FIGURE 3

reaction conditions, high yields of the products, availability of the cheap reagent, easy work-up and selectivity of the reactions are the strong practical features of the presented method.

EXPERIMENTAL

General Procedure for Transdithioacetalization of Acylals to Dithianes and Dithiolanes

To a solution of gem diacetate **1** (5 mmol), 1,3-propanedithiol or 1,2-ethanedithiol (5.5–6 mmol) in CH_2Cl_2 (25 ml), chlorinated silica gel (SiO_2Cl)[22] (2.5 g) was added and the resulting mixture was stirred at room temperature for the appropriate time (Table I). After completion of the reaction (TLC, CCl_4/EtOAc, 5/1) the mixture was quenched with aqueous NaOH (10%, 10 ml). Then CH_2Cl_2 (50 ml) was added and the organic layer was washed with an aqueous solution of NaOH (10%, 50 ml) and then with H_2O (2 x 25 ml). The organic layer was separated and dried over anhydrous $MgSO_4$ and filtered. Evaporation of the solvent *in vacuo* gave the desired pure products in excellent yields (Table I).

General Procedure for Transformation of Acylals to Oxathiolanes

To a solution of gem diacetate **1** (5 mmol), 2-mercaptoethanol (6–6.5 mmol) in CH_2Cl_2 (25 ml), silica chloride (2.5 g) was added and the

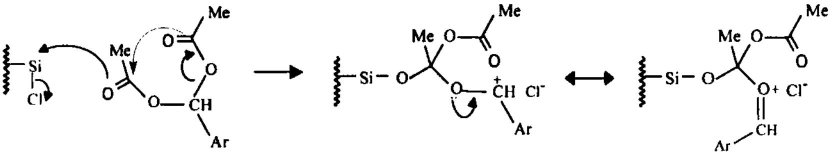

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FIGURE 4

resulting mixture was stirred at room temperature. After completion of the reaction (TLC) the mixture was quenched with aqueous NaOH (10%, 10 ml). Then CH_2Cl_2 (50 ml) was added and the organic layer was washed with an aqueous solution of NaOH (10%, 50 ml) and then with H_2O (2 × 25 ml). The organic layer was separated and dried over anhydrous $MgSO_4$ and filtered. Evaporation of the solvent *in vacuo* gave the desired products in good yields (Table I). Further purification was performed by distillation under vacuum.

2(4-Bromo phenyl)-1,3-dithiane (**2c**); ^{1}H-NMR ($CDCl_3$, 250MHz) $\delta = 1.91$ (m, 1H), 2.07 (m, 1H), 2.92 (m, 4H), 5.04 (s, 1H), 7.33 (d, 2H), 7.46 (d, 2H); ^{13}C-NMR ($CDCl_3$, 63MHz) $\delta = 26.80$, 32.30, 51.07, 122.73, 129.95, 132.22, 138.51.

2(2-Methoxy phenyl)-1,3-dithiane (**2d**); ^{1}H-NMR ($CDCl_3$, 250MHz) $\delta = 1.89$ (m, 1H), 2.05 (m, 1H), 2.76 (m, 2H), 2.93 (m, 2H), 3.69 (s, 3H), 5.61 (s, 1H), 6.77 (d, 1H), 6.90 (t, 1H), 7.12 (m, 1H), 7.47 (d, 1H); ^{13}C-NMR ($CDCl_3$, 63MHz) $\delta = 25.75$, 32.81, 43.99, 56.16, 111.18, 121.42, 128.71, 129.56, 129.81, 155.83.

2(2,5-Dimethoxy)-1,3-dithiane (**2e**): ^{1}H-NMR ($CDCl_3$, 250MHz) $\delta = 1.91$ (m, 1H), 2.10(m, 1H), 2.81 (m, 2H), 3.01 (m, 2H), 3.75 (s, 3H), 3.79 (s, 3H), 5.60 (s, 1H), 6.81 (s, 2H), 7.26 (s, 1H); ^{13}C-NMR ($CDCl_3$, 63MHz) $\delta = 25.69$, 33.55, 44.23, 56.15, 56.85, 112.55, 115.01, 122.38, 149.99, 114.93, 154.29.

2(5-Methyl furyl)-1,3-dithiane (**2f**): ^{1}H-NMR ($CDCl_3$, 250MHz) $\delta = 1.90$–2.15 (m, 2H), 2.27 (s, 3H), 2.90 (m, 4H), 5.28 (s, 1H), 5.89 (d, 1H), 6.22 (d, 1H); ^{13}C-NMR ($CDCl_3$, 63MHz) $\delta = 14.41$, 26.69, 30.04, 42.88, 108.34, 110.81, 150.16, 152.39.

2-Cinnamyl-1,3-dithiane (**2g**); ^{1}H-NMR ($CDCl_3$, 250 MHz) $\delta = 1.76$–2.01 (m, 2H), 2.71–2.80 (m, 4H), 4.69(d, 1H), 6.16 (d of d, 1H), 6.67 (d, 1H), 7.12–7.25 (m, 5H); ^{13}C-NMR ($CDCl_3$, 63MHz) $\delta = 25.60$, 30.39, 53.95, 120.05, 127.37, 128.99, 133.78, 136.48, 138.11.

2(2-Methoxy phenyl)-1,3-dithiolane (**2l**); ^{1}H-NMR ($CDCl_3$, 250MHz) $\delta = 3.06$–3.35 (m, 4H), 3.78 (s, 3H), 5.99 (s, 1H), 6.78 (d, 1H), 6.86 (t, 1H), 7.12 (m, 1H), 7.63 (d, 1H); ^{13}C-NMR ($CDCl_3$, 63MHz) $\delta = 39.78$, 49.47, 56.03, 110.86, 121.00, 128.50, 129.20, 129.61, 156.95.

2(4-Methyl phenyl)-1,3-oxathiolane (**2p**); ^{1}H-NMR ($CDCl_3$, 250MHz) $\delta = 2.30$ (s, 3H) 3.00 (m, 1H), 3.12 (m, 1H), 3.92 (m, 1H), 4.26 (m, 1H), 5.03 (s, 1H), 6.97 (d, 2H), 7.32 (d, 2H); ^{13}C-NMR ($CDCl_3$, 63MHz) $\delta = 21.66$, 32.86, 72.25, 87.47, 127.10, 129.98, 130.14, 130.27.

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