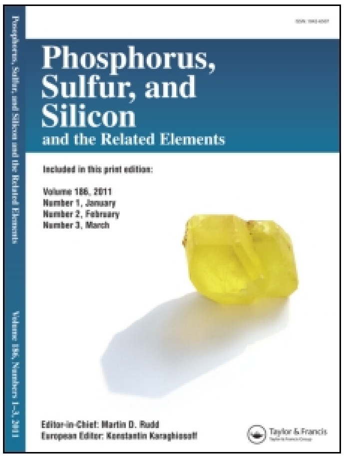

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New Applications of Solid Silica Chloride (SiO_2 -Cl) in Organic Synthesis. Efficient Preparation of Diacetals of 2,2-Bis(Hydroxymethyl)-1,3-propanediol from Different Substrates and Their Transthioacetalization Reactions. Efficient Regeneration of Carbonyl Compounds from Acetals and Acylals

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NEW APPLICATIONS OF SOLID SILICA CHLORIDE (SiO_2-Cl) IN ORGANIC SYNTHESIS. EFFICIENT PREPARATION OF DIACETALS OF 2,2-Bis(HYDROXYMETHYL)-1,3-PROPANEDIOL FROM DIFFERENT SUBSTRATES AND THEIR TRANSTHIOACETALIZATION REACTIONS. EFFICIENT REGENERATION OF CARBONYL COMPOUNDS FROM ACETALS AND ACYLALS

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A new application of solid silica chloride, an easily available and efficient catalyst for the preparation of diacetal of 2,2-bis-(hydroxymethyl)-1,3-propanediol from aldehydes, acetals, acylals, and oximes, is described. Transthioacetalization of diacetals of 2,2-bis-(hydroxymethyl)-1,3-propanediol into their corresponding 1,3-dithianes and 1,3-dithiolanes in the presence of silica chloride is presented. Efficient regeneration of carbonyl compounds from their corresponding acetals, ketals, diacetals, and acylals in the presence of this catalyst also is described.

Keywords: Acetals; acylals; carbonyl compounds; oximes; silica chloride; transthioacetalization

Solid supports have found wide applications in organic reactions from different views.[1] They mostly facilitate the work-up of the reaction mixtures and usually high selectivity accompanied with high yields of the products is observed. Silica gel is one of the extensively used support for different purposes in organic chemistry.[2] Modified silica supports for functional group transformation also is of interest. Silica chloride has been reported to be an efficient reagent for the selective thioacetalization of carbonyl compounds and transformation of sulfoxides to thioethers.[3] Literature survey shows that less attention

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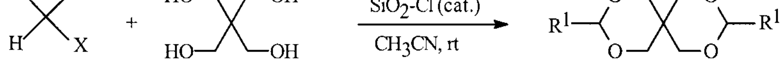
has been paid to silica chloride as a potential heterogeneous inorganic polymeric bed in organic reactions. Recently we paid attention to silica chloride in functional group transformation reactions and reported a new procedure for the preparation of high capacity SiO_2-Cl.[4a] We have applied this heterogeneous catalyst for efficient transdithioacetalization of acetals, transformation of acylals into thioacetals, dehydration of *tert*-benzylic alcohols to their olefins, and dethioacetalization of thioacetals into their carbonyl compounds and transformation of silyl and THPethers to their iodides, ring-expansion annelation and ring-expansion-chlorination of cyclic thioacetals.[4a–f] Solid SiO_2-Cl recently has been used as an efficient catalyst for tetrahydropyranylation of hydroxy functional groups.[4e] In this article we report further applications of this high capacity solid SiO_2-Cl in some important functional group transformations.

A) PREPARATION OF DIACETALS OF 2,2-Bis-(HYDROXYMETHYL)-1,3-PROPANEDIOL FROM DIFFERENT SUBSTRATES AND THEIR TRANSTHIOACETALIZATION REACTIONS

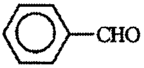
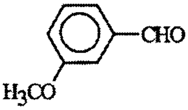
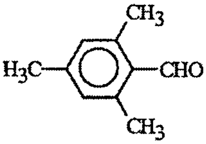
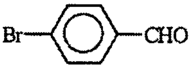
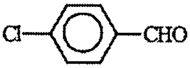
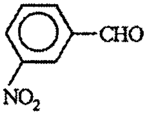
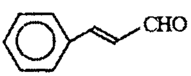
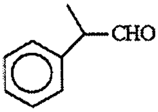
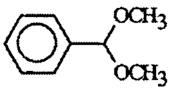
Carbonyl functional groups often play important roles in the synthesis of complex organic molecules, and a great deal of synthetic work has been done on the protection and masking of carbonyl compounds.[5] Acetals are one of the most useful and versatile protecting groups for carbonyl functions and the most popular ones are 1,3-dioxolanes and 1,3-dioxanes because of their relative stability.[6] They usually are liquid and their purification and handling is difficult. In recent years, attention has been paid to the synthesis of diacetals of 2,2-bis (hydroxymethyl)-1,3-propanediol, which are crystalline substances and have sharp melting points.[7] We now report on the efficient and high yielding preparation of diacetals of 2,2-bis-(hydroxymethyl)-1,3-propanediol from aldehydes and their cyclic and open-chain O,O-acetals, oxathioacetals, acylals, and oximes catalyzed by SiO_2-Cl at room temperature in CH_3CN (Scheme 1, Table I). However, ketones do not react under similar



R^1 = aryl,cinnamyl
X = -OMe, -OEt, -OAc
XX = $-O(CH_2)_3O-$, $-O(CH_2)_2S-$, =NOH

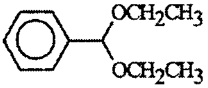
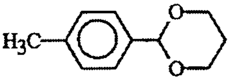
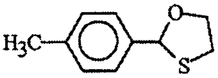
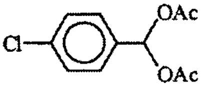
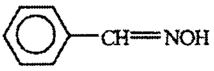
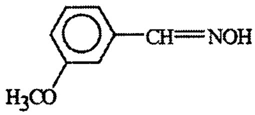
SCHEME 1

TABLE I Synthesis of Diacetals of 2,2-Bis-(hydroxymethyl)-1,3-propanediol from Different Substrates Using SiO_2-Cl as a Catalyst in CH_3CN at Room Temperature

Substrate[a]		Yield[b] %	^{1}H-NMR ($CDCl_3$, 250 MHz, δ) and some of the ^{13}C-NMR ($CDCl_3$, 62.90 MHz, δ)
	(**1a**)	95	3.75 (2H, d), 3.85 (4H, m), 4.88 (2H, d), 5.44 (2H, s), 7.52 (10H, m)
	(**1b**)	96	2.33 (6H, s), 3.67 (2H, d), 3.80 (4H, m), 4.81 (2H, d), 5.42 (2H, s), 7.18 (4H, d), 7.38 (4H, d)
	(**1c**)	95	3.69 (2H, d), 3.81 (6H, s), 3.86 (4H, m), 4.86 (2H, d), 5.40 (2H, s), 6.97 (4H, d), 7.42 (4H, d)
	(**1d**)	96	3.60 (2H, d), 3.82 (6H, s), 3.84 (4H, m), 4.85 (2H, d), 5.39 (2H, s), 6.90 (2H, d), 7.07 (4H, d), 7.24 (2H, t). ^{13}C-NMR ($CDCl_3$, 50 MHz) $\delta = 32.91, 56.11, 70.92, 71.42, 102.43, 111.74, 115.53, 118.88, 130.48, 140.08, 160.06$.
	(**1e**)	89	2.21 (6H, s), 2.45 (12H, s), 3.52 (2H, d), 3.74 (4H, m), 4.92 (2H, d), 5.71 (2H, s), 6.79 (4H, s). ^{13}C-NMR ($CDCI_3$, 50 MHz) $\delta = 20.98, 21.38, 32.91, 71.14, 73.09, 102.59, 130.41, 130.92$ 137.12, 138.86.
	(**1f**)	94	3.39 (2H, d), 3.59 (4H, m), 4.38 (2H, d), 5.14 (2H, s), 7.08 (4H, d), 7.22(4H, d).
	(**1g**)	95	3.53 (2H, d), 3.79 (4H, m), 4.79 (2H, d), 5.41 (2H, s), 7.35 (4H, d), 7.41(4H, d).
	(**1h**)	95	3.70 (2H, d), 3.84 (4H, m), 4.80 (2H, d), 5.50 (2H, s), 7.49 (2H, d), 7.77 (2H, d), 8.13 (2H, t), 8.29 (2H, d).
	(**1i**)	96	3.49 (2H, d), 3.70 (4H, m), 4.68 (2H, d), 5.05 (2H, d), 6.20 (2H, d of d), 6.75 (2H, d), 7.32 (10H, m). ^{13}C-NMR ($CDCl_3$, 50 MHz) $\delta = 32.85, 70.62, 71.13, 101.87, 125.49, 127.30, 128.73, 129.02, 134.16, 136.33$
	(**1j**)	85	1.58 (6H, d), 3.10 (2H, m), 3.33 (2H, d), 3.58 (4H, m), 4.63 (4H, d), 7.39 (10H, m). ^{13}C-NMR ($CDCl_3$, 50 MHz) $\delta = 16.07, 16.34, 64.29, 65.70, 105.45, 126.99, 128.70, 143.06$.
	(**1k**)	96	3.75 (2H, d), 3.85 (4H, m), 4.88 (2H, d), 5.41 (2H, s), 7.52 (10H, m)

(*Continued on next page*)

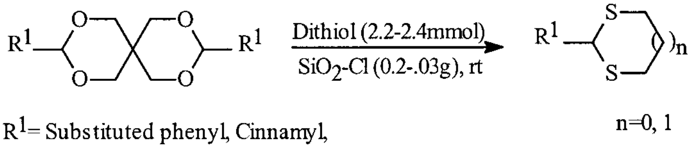
TABLE I Synthesis of Diacetals of 2,2-Bis-(hydroxymethyl)-1,3-propanediol from Different Substrates Using SiO$_2$-Cl as a Catalyst in CH$_3$CN at Room Temperature *(Continued)*

Substrate^a		Yield^b %	^{1}H-NMR (CDCI$_3$, 250 MHz, δ) and some of the ^{13}C-NMR (CDCl$_3$, 62.90 MHz, δ)
	(**1l**)	95	3.75 (2H, d), 3.85 (4H, m), 4.88 (2H, d), 5.45 (2H, s), 7.52 (10H, m)
	(**1m**)	94	2.36 (6H, s), 3.71 (2H, d), 3.88 (4H, m), 4.88 (2H, d), 5.45 (2H, s), 7.20 (4H, d), 7.38 (4H, d)
	(**1n**)	92	2.33 (6H, s), 3.67 (2H, d), 3.80 (4H, m), 4.81 (2H, d), 7.18 (4H, d), 7.38 (4H, d)
	(**1o**)	90	3.53 (2H, d), 3.79 (4H, m), 4.79 (2H, d), 5.41 (2H, s), 7.35 (4H, d), 7.41 (4H, d)
	(**1p**)	79	3.58 (2H, d), 3.78 (4H, m), 4.82 (2H, d), 5.38 (2H, s), 7.42 (10H, m)
	(**1q**)	77	3.60 (2H, d), 3.82 (6H, s), 3.84 (4H, m), 4.85 (2H, d), 5.39 (2H, s), 6.90 (2H, d), 7.07 (4H, d), 7.24 (2H, t)

^{a}The ratios of SiO$_2$-Cl: subs.: diol were 0.3 g: 1 mmol: 0.55–0.6 mmol.
^{b}Isolated yields.

reaction conditions and remained almost intact in the reaction mixtures. Therefore, this method easily can be used for the selective protection of aldehydes in the presence of ketones. Ketals in the presence of this catalyst under similar reaction conditions were deprotected easily to their corresponding ketones rather than undergo transacetalization reactions with 2,2-bis-(hydroxymethyl)-1,3-propanediol.

Transthioacetalization of diacetals of 2,2-bis-(hydroxymethyl)-1,3-propanediol with 1,3-propanedithiol and ethanedithiol also was achieved very easily using this catalyst at room temperature in CHCl$_3$



SCHEME 2

TABLE II Transthioacetalization of Acetals of 2,2-Bis(hydroxymethyl)-1,3-propanediol in the Presence of SiO_2-Cl with 1,3-Propane and 1,3-Ethanedithiol in $CHCl_3$ at Room Temperature

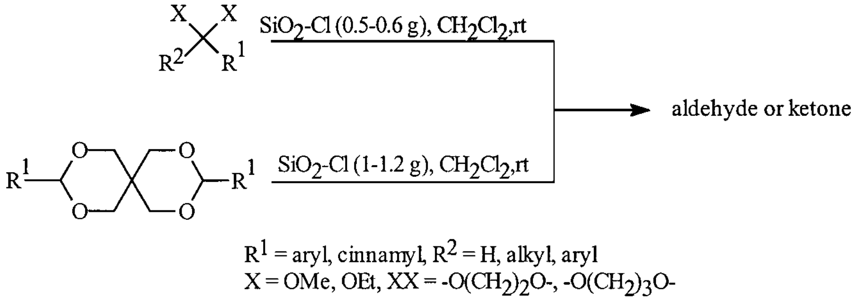
Entry	R^1	n	SiO_2-Cl (g)	Time (min)	Yield %[a]
4a	Ph	0	0.2	15	95
4b	Ph	1	0.2	20	94
4c	4-CH_3-C_6H_4	0	0.2	15	95
4d	4-CH_3-C_6H_4	1	0.2	15	96
4e	4-CH_3O-C_6H_4	1	0.2	10	94
4f	3-CH_3O-C_6H_4	1	0.2	10	95
4g	2,4,6,-$(CH_3)_3$-C_6H_2	1	0.2	20	90
4h	4-Br-C_6H_4	0	0.3	25	92
4i	4-Br-C_6H_4	1	0.3	25	93
4j	4-Cl-C_6H_4	1	0.3	30	94
4k	3-NO_2-C_6H_4	1	0.3	50	92
4l	Cinnamyl	1	0.2	15	95
4m	Ph(CH_3)CH	1	0.2	25	92

[a] Isolated yields.

(Scheme 2, Table II). All reactions cleanly proceeded under mild reaction conditions to give the corresponding 1,3-dithianes and 1,3-dithiolanes in excellent yields.

B) DEPROTECTION OF ACETALS

Acetals are one of the most useful and versatile protecting groups in organic syntheses. They found widespread applications in the protection of carbonyl, hydroxyl, and diol functions.[6] In this study, we paid attention to high yielding regeneration of carbonyl groups from their acetals under mild reaction conditions. A plethora of methods are reported for this purpose such as aqueous acid hydrolysis,[5] K-10 in a aqueous methanol,[8] and nonaqueous methods including $TeCl_4$,[9] $[Ru(CH_3CN)_3(triphos)](OTf)_2$,[10] silica-supported guanidinium chloride/acetyl chloride,[11] $SiCl_4$/NaI,[12] K-10 montmorileonite,[13] DDQ,[14] Ph_3P/CCl_4,[15] $SnCl_2{\cdot}2H_2O$,[16] $CuSO_4$-SiO_2,[17] WC_{16},[18] trimethylsilyl bis(fluorosulfuryl)imide,[19] and CAN.[20] Synthetic importance of this transformation is the attention to and introduction of new methods that show selectivity; being mild and using simple and easily available catalysts. In this study we report that silica chloride is able to convert various types of acetals and ketals (dimethyl, diethyl, cyclic acetals, and diacetals of pentaerythritol) to the corresponding carbonyl compounds under mild reaction conditions (Scheme 3, Table III).



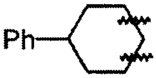
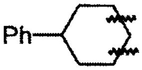
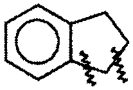
SCHEME 3

As shown in Table III, a variety of acyclic acetals (entries 1–6) of structurally different carbonyl compounds as well as cyclic dioxolanes of aldehydes (entries 7–10) can be cleanly deprotected at room temperature using 0.5–0.6 g of silica chloride in dry CH_2Cl_2. On the other hand, cleavage of cyclic dioxolanes derived from aromatic and aliphatic ketones was also achieved in dry CH_2Cl_2 in the presence of 0.5–0.6 g of silica chloride (entries 11–18). Diacetal of 2,2-bis-(hydroxymethyl)-1,3-propanediol derived from aldehydes were successfully deprotected into their corresponding aldehydes in excellent yields (entries 19–23). Diacetals of 2,2-bis-(hydroxymethyl)-1,3-propanediol derived from ketones are unstable compounds and have not been reported yet; therefore, we could not study their behavior in the presence of silica chloride.

C) REGENERATION OF ALDEHYDES FROM ACYLALS UNDER MILD REACTION CONDITIONS

Regeneration of aldehydes from their diacetates (acylals) under mild conditions, with high yields and selectivity, is a useful chemical transformation. A literature survey reveals that a variety of methods are available for this purpose.[21] Some of the reported procedures have its own merit and also its own drawbacks. Some require the use of strong acids which other functional groups in the molecule may not tolerate, some need long reaction times and provide low yields. In some other reported methods, the use of microwave oven is obligatory that may not be available in any laboratories. Very recently, $AlCl_3$ in refluxing CH_3CN has been used for the efficient regeneration of aldehydes from acylals.[22] $AlCl_3$ suffers from being a strong Lewis acid and may affect sensitive functional groups in refluxing CH_3CN. We recently reported that silica chloride promotes highly efficient transformation of acylals into 1,3-dithiolanes, 1,3-dithianes and 1,3-oxathiolanes under mild reaction conditions.[4b] Now we report efficient deprotection of aryl and

TABLE III Deprotection of Acetals and Ketals with SiO_2-Cl

Entry	R^1	R^2	X, XX	SiO_2-Cl (g)	Time (min)	Yield (%)[a,b,c]
1	Ph	H	OMe	0.5	15	95
2	Ph	H	OEt	0.5	10	93
3	*p*-MeC_6H_4	H	OEt	0.5	10	94
4	*p*-ClC_6H_4	H	OEt	0.6	20	91
5	*p*-$NO_2C_6H_4$	H	OEt	0.6	40	88
6			OEt	0.5	15	98
7	*p*-MeC_6H_4	H	$-OCH_2CH_2O-$	0.5	20	90
8	*p*-$MeOC_6H_4$	H	$-OCH_2CH_2O-$	0.5	25	94
9	PhCH=CH	H	$-OCH_2CH_2O-$	0.5	15	96
10	n-C_6H_{13}	H	$-OCH_2CH_2O-$	0.6	30	81
11	Ph	Me	$-OCH_2CH_2O-$	0.5	10	94
12	*p*-ClC_6H_4	Me	$-OCH_2CH_2O-$	0.5	30	89
13	*p*-PhC_6H_4	Me	$-OCH_2CH_2O-$	0.5	10	88
14	$PhCH_2CH_2$	Me	$-OCH_2CH_2O-$	0.6	35	91
15			$-OCH_2CH_2O-$	0.6	30	85
16			$-OCH_2CH_2O-$	0.5	15	90
17				1.1	30	85
18	Ph	Et	$-OCH_2CH_2O-$	0.5	20	92
19	Ph	H	$C(CH_2O-)_4$	1	20	90
20	*p*-MeC_6H_4	H	$C(CH_2O-)_4$	1	15	92
21	*p*-$MeOC_6H_4$	H	$C(CH_2O-)_4$	1	15	94
22	PhCH=CH	H	$C(CH_2O-)_4$	1	10	95
23	*p*-ClC_6H_4	H	$C(CH_2O-)_4$	1.1	40	93

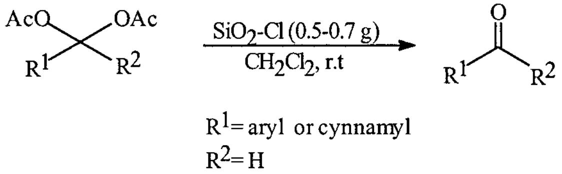
[a] The yields refer to isolated pure products.

[b] Benzaldehyde was isolated as its 2,4-nitrophenylhydrazine derivative.

[c] Isolated yield.

allyl acylals in CH_2Cl_2 at room temperature in the presence of this catalyst (Scheme 4, Table IV).

4-Nitrobenzylidene diacetate, which usually resists deprotection reactions under nonsolvolytic conditions, was deprotected in refluxing CH_3CN after 90 min in a good yield in the presence of silica chloride (entry 8, Table IV). Phenolic acetates also were deprotected easily in the presence of this catalyst and this is demonstrated by the reaction of acetyl salicylaldehyde diacetate (entry 9, Table IV). Phenolic ethers survived under similar reaction conditions (entries 3–5, Table IV).



SCHEME 4

A furanoid acylal (entry 10, Table IV) also was converted to its corresponding aldehyde without polymerization in the presence of silica chloride. Aliphatic acylals remain unreacted even in refluxing CH_3CN.

The selectivity of the method is demonstrated by the following reactions. 4-Methylbenzylidene diacetate was converted to its carbonyl compound almost exclusively in the presence of 0.5 g of silica chloride in dry CH_2Cl_2 at room temperature whereas, phenylethylidene diacetate remained almost intact. 4-Methylbenzylidene diacetate preferentially was converted to the corresponding aldehyde in the presence of 4-methylbenzaldehyde 1,3-dithiane under similar reaction conditions (Scheme 5).

In summary, in this study, we have presented some new applications of silica chloride as an efficient catalyst or reagent, which work under nonhydrolytic conditions for the deprotection of benzylic and

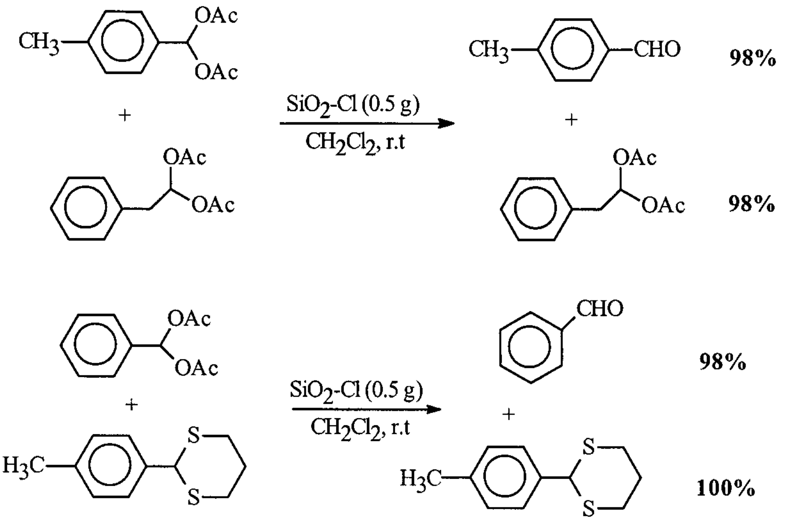
TABLE IV Deprotection of Acylals by SiO_2-Cl in CH_2Cl_2 at Room Temperature

Entry	Substrate	Time (min)	SiO_2-Cl (g)	Yield %[a]
1	$PhCH(OAc)_2$	30	0.5	91[b]
2	4-H_3C-C_6H_4-$CH(OAc)_2$	15	0.5	92
3	4-H_3CO-C_6H_4-$CH(OAc)_2$	20	0.5	94
4	2-CH_3O-C_6H_4-$CH(OAc)_2$	20	0.5	95
5	2,5-di-CH_3O-C_6H_4-$CH(OAc)_2$	15	0.5	95
6	4-Br-C_6H_4-$CH(OAc)_2$	40	0.6	90
7	4-Cl-C_6H_4-$CH(OAc)_2$	60	0.7	90
8	4-NO_2-C_6H_4-$CH(OAc)_2$	90	0.7[c]	80
9	2-OAc-C_6H_4-$CH(OAc)_2$	70	0.6	87
10	5-CH_3-Furyl-$CH(OAc)_2$	30	0.5	91
11	1-Naphthyl-$CH(OAc)_2$	30	0.5	92
12	$PhCH{=}CHCH(OAc)_2$	30	0.5	95

[a] Isolated yield.

[b] Benzaldehyde was isolated as its 2,4-dinitrophenylhydrazine derivative.

[c] Reaction was performed in refluxing CH_3CN in the presence of 0.7 g of the catalyst.



SCHEME 5

allylic acylals and also a wide variety of acetals and ketals. We also have introduced facile and high yielding preparation of diacetals of 2,2-bis-(hydroxymethyl)-1,3-propanediol from aldehydes, acetals, oxathioacetals, acylals, and oximes in the presence of this heterogeneous catalyst in excellent yields at room temperature. Transthioacetalization of the diacetals successfully was achieved in excellent yields by this method. The yields of the reactions were excellent and work-up of the reaction mixtures was easy and not time-consuming. High chemoselectivity, facile work-up, easily available and cheap silica chloride, high rates, and yields of the reactions are the strong practical points of the presented method.

EXPERIMENTAL

General

Silica chloride was prepared in a quantitative yield according to our previously reported procedure[4] by the reaction of thionyl chloride and silica gel. Silica chloride is a grayish and stable powder that should be stored in the absence of moisture. IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer. ^{1}H-NMR and ^{13}C-NMR spectra were run on a Bruker Avance DPX 250 MHz instrument. Mass spectra were run on a Shimadzu GC MS-QP 1000 EX. Products are known and they were identified by the comparison of their spectral and physical data with those reported for authentic samples.

General Procedure for Preparation of Diacetal of 2,2-Bis-(hydroxymethyl)-1,3-propanediol

To a solution of an aldehyde (5 mmol) in CH_3CN (25 ml), 2,2-bis-(hydroxymethyl)-1,3-propanediol (3 mmol) and silica chloride (1.5 g) were added. The resulting mixture was stirred at room temperature. After completion of the reaction (12–14 h), the solvent was evaporated in vacuo. Then CH_2Cl_2 (75 ml) was added to the mixture and washed with an aqueous solution of NaOH (10%, 25 ml) and H_2O (3×25 ml). The organic layer was separated and dried over anhydrous $MgSO_4$ and filtered. Evaporation of the solvent in vacuo gave the desired product in good to excellent yields. Further purification was achieved by recrystallization in an appropriate solvent (Table I).

Transthioacetalization of Diacetal of 2,2-Bis-(hydroxymethyl)-1,3-propanediol; A Typical Procedure

To a solution of 4-bromobenzaldehyde (0.37 g, 2 mmol) in $CHCl_3$ (25 ml), 1,3-propanedithiol (2.2 mmol) and silica chloride (0.6 g) were added. The resulting mixture was stirred at room temperature for 25 min. After completion of the reaction (monitored by TLC) the reaction was quenched with an aqueous solution of NaOH (10%, 25 ml). Then $CHCI_3$ (25 ml) was added into the mixture and the organic layer was separated and washed with H_2O (2×25 ml). The organic layer was dried over anhydrous $MgSO_4$ and filtered. Evaporation of the solvent in vacuo gave the pure 4-bromo-1,3-dithiane (0.53 g, 92%) as white needle crystals from petroleum ether; m.p 92–94°C (uncorrected); ^1H-NMR ($CDCl_3$, 250 MHz) $\delta = 1.89$–2.12 (m, 2H), 2.82–3.03 (t, 4H), 5.04 (s, 1H), 7.33 (d, 2H), 7.46 (d, 2H) ppm; ^{13}C-NMR ($CDCl_3$, 63 MHz) $\delta = 26.80$, 32.30, 51.07, 122.73, 129.95, 132.22, 138.51 ppm; MS (20 eV) m/z (relative intensity) 276 ($M^+ + 2$, 37.3), 274 (M^+ 35.4), 201 (M^+-SC_2H_4, 32.7), 130 (14.6), 105 (40.2), 74 (45.8), 45 (100), CH analysis: %C (calculated = 43.64, found = 43.60), %H (calculated = 4.03, found = 4.10) (Table II, entry **4i**).

General Procedure for Deprotection of Acetals with SiO_2-Cl

To a solution of acetal (2 mmol) in dry CH_2Cl_2 (10 ml) SiO_2-Cl (0.5–1.1 g) was added. The resulting mixture was stirred at room temperature and the progress of the reaction was monitored by TLC. After completion of the reaction (10–40 min), the reaction was quenched with 10% NaOH aqueous solution (15 ml) and extracted with CH_2Cl_2 (3 × 30 ml). The organic layer was washed with saturated NaCl solution (2 × 15 ml) and water (15 ml) and dried over anhydrous Na_2SO_4. Evaporation of the solvent under reduced pressure gave almost pure product. Further purification was achieved by column chromatography on silica gel or recrystallization from an appropriate solvent to give the desired product in good to excellent yields (Table III).

General Procedure for Deprotection of Acylals in the Presence of Silica Chloride

To a solution of acylal (1 mmol) in dry CH_2Cl_2 (25 ml), silica chloride (0.5–0.7 g) was added and the resulting mixture was stirred at room temperature for the appropriate reaction time. After completion of the reaction (TLC), silica gel (1 g) was added to the reaction mixture and the solvent was evaporated under reduced pressure. To the resulting powder an extra amount of silica gel (2 g) was added and the solid mixture was washed with petroleum ether (b.p. 60–80°C)/EtOAc (5:1) (75 ml) and filtered. The solvent was evaporated on a rotary evaporator to afford the desired aldehyde in excellent yields. The partially volatile aldehydes were isolated as their 2,4-dinitrophenyl hydrazine derivatives (Table IV).

REFERENCES

[1] (a) A. McKillop and D. W. Young, *Synthesis*, 401 (1979); (b) A. Cornelis and P. Laszlo, *Synthesis*, 909 (1985).

[2] (a) E. Keinan and Y. Mazur, *J. Org. Chem.*, **43,** 1020 (1978); (b) D. M. Tal, E. Keinan, and Y. Mazur, *Tetrahedron*, **37,** 4327 (1981); (c) F. D. Onofrio and A. Scettri, *Synthesis*, 1159 (1985); (d) F. Chávez, S. Suárez, and M. A. Díaz, *Synth. Commun.*, **24,** 2325 (1994); (e) T. Nishiguchi and C. Kamio, *J. Chem. Soc. Perkin Trans. I*, 707 (1989).

[3] (a) Y. Kamitori, M. Hojo, R. Masuda, T. Kimura, and T. Yoshida, *J. Org. Chem.*, **51,** 1427 (1986); (b) F. Mohanazadeh, A. R. Momeni, and Y. Ranjbar, *Tetrahedron Lett.*, 6127 (1994).

[4] (a) H. Firouzabadi, N. Iranpoor, B. Karimi, and H. Hazarkhani, *Synlett.*, 263 (2000); (b) H. Firouzabadi, N. Iranpoor, and H. Hazarkhani, *Phosphorus, Sulfur, and Silicon* **176,** 165 (2002); (c) H. Firouzabadi, N. Iranpoor, H. Hazarkhani, and B. Karimi, *Synth. Commun.* (in press); (d) H. Firouzabadi, N. Iranpoor, H. Hazarkhani, and B. Karimi, *J. Org. Chem.* **67,** 2572 (2002); (e) H. Firouzabadi, N. Iranpoor, and H. Hazarkhani, *Tetrahedron Lett.* (in press); (f) N. Ravindranath, C. Ramesh, and B. Das, *Synlett.*, 1777 (2001).

[5] T. W. Greene and P. G. M. Wuts, *Protective Groups in Organic Synthesis* (Wiley, New York, 1991), pp. 178–186.

[6] (a) H. Firouzabadi, N. Iranpoor, and B. Karimi, *Synlett.*, 321 (1999); (b) D. J. Kalita, R. Borah, and C. Sarma, *Tetrahedron Lett.*, **39,** 4573 (1998); (c) R. Ballini, G. Bosiva, B. Frullanti, R. Maggi, G. Sartori, and F. Schroer, *Tetrahedron Lett.*, **39,** 1615 (1998); (d) B. Karimi, H. Seradje, and G. R. Ebrahimain, *Synlett.*, 1456 (1999); (e) B. Karimi and A. Miri Ashtiani, *Chem. Lett.*, 1199 (1999).

[7] (a) T. S. Jin, T. S. Li, Z. H. Zhang, and Y. J. Yuan, *Synth. Commun.*, **29,** 1601 (1999); (b) C. D. Wang, X. Z. Shi, and R. J. Xie, *Synth. Commun.*, **27,** 2517 (1997); (c) X. Chen, Y. T. Xu, and C. X. Jin, *Hecheng Huaxue*, **5,** 212 (1997); (d) E. Bograchov, *J. Am. Chem. Soc.*, **72,** 2265 (1950); (e) Y. Peng, X. Song, and X. Qian, *Synth. Commun.*, **31,** 3735 (2001).

[8] J. Asakura, M. J. Robins, Y. Asaka, and T. H. Kim, *J. Org. Chem.*, **61,** 9026 (1996).

[9] H. Tani, T. Inamasu, K. Masumoto, R. Tamura, H. Shimizu, and H. Suzuki, *Phosphorus, Sulfur, and Silicon*, **67,** 261 (1992).

[10] S. Ma and L. M. Venanzi, *Tetrahedron Lett.*, **34,** 8071 (1993).

[11] P. Gros, P. L. Perchec, and J. P. Senet, *J. Chem. Res. (S)*, 196 (1995).

[12] S. S. Elmorsy, M. V. Bhatt, and A. Pelter, *Tetrahedron Lett.*, **33,** 1657 (1992).

[13] E. C. L. Gautier, A. E. Graham, A. McKillop, S. P. Standen, and R. J. K. Taylor, *Tetrahedron Lett.*, **38,** 1881 (1997).

[14] (a) K. Tanemura, T. Suzuki, and T. Horaguchi, *J. Chem. Soc. Chem. Commun.*, 979 (1992); (b) A. Oku, M. Kinugasa, and T. Kamada, *Chem. Lett.*, 165 (1993).

[15] C. Johnstone, W. J. Kerr, and J. S. Scott, *J. Chem. Soc. Chem. Commun.*, 341 (1996).

[16] K. L. Ford and E. J. Roskamp, *J. Org. Chem.*, **58,** 4142 (1993).

[17] G. M. Caballero and E. G. Gros, *Synth. Commun.*, **25,** 395 (1995).

[18] H. Firouzabadi, N. Iranpoor, and B. Karimi, *J. Chem. Research (S)*, 664 (1998).

[19] G. Kaur, A. Trehan, and S. Trehan, *J. Org. Chem.*, **63,** 2365 (1998).

[20] A. Ates, A. Gautier, B. Leroy, J. M. Plancher, Y. Quesnel, and I. E. Markó, *Tetrahedron Lett.*, **40,** 1799 (1999).

[21] (a) S. V. Lieberman and R. Connor, *Org. Syn.*, **2,** 441 (1951); (b) S. M. Tsang, E. H. Wood, and J. R. Johnson, *Org. Syn.*, **3,** 641 (1955); (c) K. S. Kochhar, B. S. Bal, R. P. Deshpande, S. N. Rajadhyaksha, and H. W. Pinnick, *J. Org. Chem.*, **48,** 1765 (1983); (d) C. Narayana, S. Padmanabhan, and G. W. Kabalka, *Tetrahedron Lett.*, **31,** 6977 (1990); (e) R. S. Varma, A. K. Chatterjee, and M. Varma, *Tetrahedron Lett.*, **34,** 3207 (1993). (f) D. Villemin and B. Martin, *J. Chem. Research (S)*, 146 (1994); (f) E. R. Pérez, A. L. Marrero, R. Pérez, and M. A. Autle, *Tetrahedron Lett.*, **36,** 1779 (1995); (g) T. S. Li, Z. H. Zhang, and C. G. Fu, *Tetrahedron Lett.*, **38,** 3285 (1997); (h) T. S. Jin, Y. R. Ma, Z. H. Zhang, and T. S. Li, *Synth. Commun.*, **27,** 3379 (1997); (i) Y. Y. Ku, R. Patel, and D. Sawick, *Tetrahedron Lett.*, **34,** 8037 (1993); (j) P. Cotelle and J. P. Catteau, *Tetrahedron Lett.*, **33,** 3855 (1992).

[22] I. Mohammadpoor-Baltork and H. Alian, *J. Chem. Research (S)*, 272 (1999).