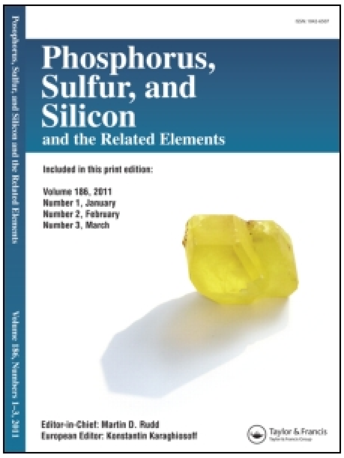

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NEW APPLICATIONS OF SOLID SILICA CHLORIDE (–SiO_2Cl): EFFICIENT OXIDATION OF CYCLIC THIOACETALS, TMS, TBDMS, AND THP ETHERS TO THEIR CARBONYL COMPOUNDS BY SOLID SILICA CHLORIDE/$KMnO_4$ SYSTEM

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Solid silica chloride/$KMnO_4$ system oxidizes effectively aromatic and aliphatic cyclic thioacetals (1,3-dithiolanes, 1,3-dithianes) and silyl and pyranyl ethers into their corresponding carbonyl compounds in dry CH_3CN at room temperature in high yields. Over-oxidation of aldehydes to carboxylic acids has not been observed by this system. In the absence of silica chloride, $KMnO_4$ in dry CH_3CN is an ineffective reagent for these oxidations.

Keywords: Carbonyl compounds; oxidations; potassium permanganate; silica chloride; silyl ethers; tetrahydropyranyl ethers; thioacetals

The use of permanganate as an oxidant in organic chemistry goes back to Kekule's and Werner's era. It was used for the *cis* hydroxylation of carbon-carbon double bonds. Since then this oxidant has been used extensively for varieties of oxidation reactions. Permanganate is one of the most cited oxidant in chemical reactions and in addition to its uses in laboratories it is used industrially for the preparation of organic compounds. The major drawback of using permanganate, especially for large-scale operations, is the formation of manganese dioxide as a solid waste coproduct in the process of the reaction. Recently, a chemical process has been invented by which this solid waste can be easily recycled to produce permanganate. Today, by this recycling process, permanganate is considered as a green and versatile laboratory reagent and an industrial oxidant.[1] Potassium permanganate also has been used

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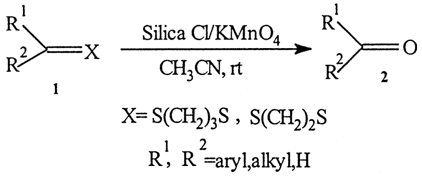
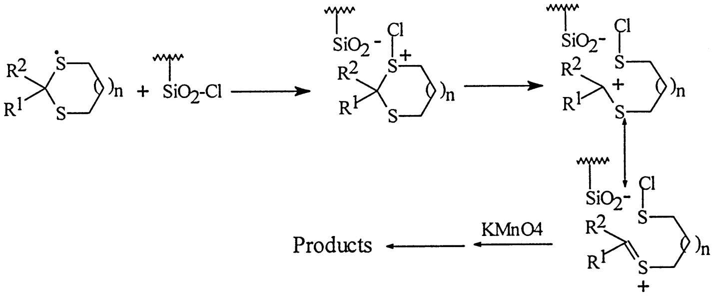
for some functional group transformations in the presence of Lewis acids[2] such as ferric chloride, zinc chloride, and boron trifluoride in polar solvents.

Recently, we have looked at the preparation of high capacity silica chloride and explored its synthetic utility as a catalyst and also as a reagent in organic reactions.[3] The advantages of using silica chloride as an alternative to TMSCl, thionyl chloride, oxalyl chloride, etc. are: a) its very low vapor pressure, which is not harmful to the respiratory system and to the eyes; b) its lower moisture sensitivity; c) its lack of corrosion to damage reaction vessels and apparatus; d) its easy handling for the large scale operations; and e) its easy isolation from the reaction mixture. With these significant practical aspects of silica chloride and $KMnO_4$ in mind, now we report that a combination of solid silica chloride and $KMnO_4$ provides an effective oxidizing system for the mild and highly selective oxidation of cyclic thioacetals(1,3-dithiolanes and 1,3-dithiones) and silyl and tetrahydropyranyl ethers into their carbonyl compounds in dry CH_3CN at room temperature in high yields (Schemes 1 and 2). By this oxidation system, cyclic thioacetals (1,3-dithiolanes and 1,3-dithianes) derived from aromatic aldehydes and ketones were cleanly converted into their aldehydes and ketones in excellent yields at room temperature (Table I, entries 1–20).



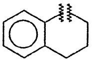
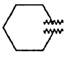
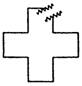
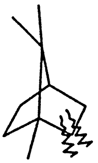
SCHEME 1



SCHEME 2

1,3-Dithiolanes and 1,3-dithianes derived from aliphatic carbonyl compounds were oxidized smoothly to regenerate their corresponding carbonyl compounds in good yields (Table I, entries 21–23). Oxidation of cinnamyl 1,3-dithiolane and its corresponding 1,3-dithiane proceeded

TABLE I Oxidation of Cyclic Thioacetals (1,3-Dithianes and 1,3-Dithiolanes) with Silica Chloride/$KMnO_4$ System in Dry CH_3CN to their Carbonyl Compounds

Entry	R^1	R^2	X	Time (min.)	Yield (%)[a,b,c]
1	Ph	H	–S$(CH_2)_2$S–	15	85[d]
2	Ph	H	–S$(CH_2)_3$S–	20	85[d]
3	4-Cl–C_6H_4	H	–S$(CH_2)_2$S–	25	87
4	4-Cl–C_6H_4	H	–S$(CH_2)_3$S–	20	90
5	4-CH_3–C_6H_4	H	–S$(CH_2)_2$S–	20	91
6	4-CH_3–C_6H_4	H	–S$(CH_2)_3$S–	20	90
7	4-Br–C_6H_4	H	–S$(CH_2)_2$S–	25	90
8	4-NO_2–C_6H_4	H	–S$(CH_2)_2$S–	35	92
9	4-CH_3O–C_6H_4	H	–S$(CH_2)_2$S–	15	91
10	4-CH_3O–C_6H_4	H	–S$(CH_2)_3$S–	20	89
11	Cinnamyl	H	–S$(CH_2)_2$S–	15	85[e]
12	Cinnamyl	H	–S$(CH_2)_3$S–	17	86[e]
13	Ph	Ph	–S$(CH_2)_2$S–	5	90
14	Ph	Ph	–S$(CH_2)_3$S–	5	91
15	4-Cl–C_6H_4	Me	–S$(CH_2)_2$S–	10	85
16	4-Cl–C_6H_4	Me	–S$(CH_2)_3$S–	10	92
17	Ph	Me	–S$(CH_2)_2$S–	5	92
18	Ph	Me	–S$(CH_2)_3$S–	5	90
19	Ph	Et	–S$(CH_2)_2$S–	7	92
20			–S$(CH_2)_2$S–	5	90
21			–S$(CH_2)_2$S–	15	81
22			–S$(CH_2)_2$S–	10	88
23			–S$(CH_2)_2$S–	10	87

[a] Yields refer to isolated products.

[b] GC purity > 96%.

[c] Structures were determined by IR, ^{1}HNMR, ^{13}CNMR, and m.p./b.p.

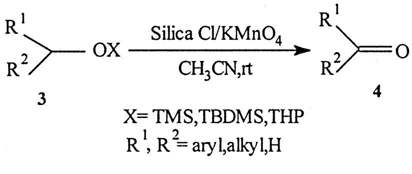
[d] Benzaldehyde was isolated as its 2,4-dinitrophenylhydrazine derivative.

[e] Benzaldehyde was isolated.

smoothly with the cleavage of the carbon-carbon double bond to give benzaldehyde in 88% yield (Table I, entries 11, 12). In the reactions we have studied for this purpose, overoxidation of aldehydes to their corresponding carboxylic acids was not observed. We observed that $KMnO_4$ in the absence of silica chloride was not an effective oxidant for the conversion of thioacetals to their corresponding carbonyl compounds.

We have found that the sequence of the addition of silica chloride and $KMnO_4$ is very crucial in the reactions. Solid silica chloride should be added first to the reaction mixture and then the appropriate amounts of solid $KMnO_4$ should be added to the mixture to bring the reaction to completion. Even though the detail of the mechanism of this oxidation reaction is obscure to us but by considering the sequence of the addition of silica chloride first, we can propose a pathway in which the chlorine atom of silica chloride is attacked by the nucleophilic sulfur atom of thioacetals to generate a sulfonium chloride intermediate that undergoes immediate carbon-sulfur cleavage to produce a resonance stabilized carbocationic species. This highly reactive intermediate can easily react with $KMnO_4$ to produce the desired carbonyl compound (Scheme 2).

Conversion of silyl and tetrahydropyranyl ethers to their carbonyl compounds under mild conditions is also of practical importance therefore we also studied these reactions by this new oxidation system (Scheme 3).



SCHEME 3

First, oxidation of benzyltrimethylsilyl ether with the silica chloride/$KMnO_4$ system in dry CH_3CN at room temperature was studied. The reaction proceeded smoothly and benzaldehyde was produced in high yield without further oxidation to benzoic acid (Table II, entry 1). The sequence of the addition of silica chloride and $KMnO_4$ was also important in this reaction. Solid silica chloride should be added first to the solution of the substrate in dry CH_3CN and then addition of $KMnO_4$ brought the reaction to completion. We applied similar reaction conditions for the oxidation of some other primary benzylic and

TABLE II Oxidation of TMS, TBDMS, and THP Ethers with the Silica Chloride/$KMnO_4$ System in Dry CH_3CN to their Carbonyl Compounds

			Time (min.)			Yield (%)[a,b,c]		
Entry	R^1	R^2	THP	TMS	TBDMS	THP	TMS	TBDMS
1	Ph	H	2	5	30	88[d]	88	85
2	4-Cl—C_6H_4	H	7	5	35	90	91	88
3	4-CH_3—C_6H_4	H	5	15	35	91	89	90
4	4-Br—C_6H_4	H	7	17	45	90	91	91
5	2-NO_2—C_6H_4	H	10	25	120	88	89	85
6	4-CH_3O—C_6H_4	H	5	10	30	91	90	90
7	Cinnamyl	H	5	15	30	85[e]	82[e]	83[e]
8	Ph	Ph	5	20	20	90	92	92
9	Ph	Me	5	20	25	92	92	91
10	Ph	Et	7	20	27	90	91	90
11	$Ph(CH_2)_2$	H	10	70	100	87	85	87
12	$Ph(CH_2)$	H	10	10	20	90	90	75
13	C_7H_{15}	H	30	120	150	70	71	70
14	C_6H_{13}	Me	30	120	140	75	70	60

[a] Yields refer to isolated products.

[b] GC purity > 96%.

[c] Structures were determined by IR, ^{1}HNMR, ^{13}CNMR, m.p./b.p.

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

[e] Benzaldehyde was isolated.

aliphatic silyl ethers to their corresponding aldehydes in good to excellent yields (Table II, entries 1–6). Oxidation of secondary benzylic and aliphatic trimethylsilyl ethers progressed easily to their corresponding ketones in high to excellent yields (Table II, entries 8–10). Cinnamyl trimethylsilyl ether oxidation was accompanied by the oxidation of carbon-carbon bond to afford benzaldehyde in 85% yield (Table II, entry 7). We also studied oxidative deprotection of *tert*-butyldimethylsilyl ethers (TBDMS ethers), which are more stable than their trimethylsilyl analogs by this oxidation system in dry CH_3CN. (Scheme 3, Table II). Primary and secondary benzylic TBDMS ethers also were oxidized easily to their corresponding aldehydes and ketones in good to excellent yields (Table II, entries 1–10). The carbon-carbon double bond of cinnamyl TBDMS ether was cleaved to give benzaldehyde in 82% yield (Table III, entries 7). Primary and secondary aliphatic TBDMS ethers were cleanly oxidized to their corresponding aldehydes and ketones by this oxidation system (Table II, entries 11–14).

Finally, we have studied oxidation of tetrahydropyranyl ethers by silica chloride and $KMnO_4$ in dry CH_3CN at room temperature under similar reaction conditions used for the oxidation of silyl ethers.

Our results show that THP ethers were oxidized effectively to their carbonyl compounds. Various types of primary and secondary aromatic tetrahydropyranyl ethers substituted with electron-releasing and electron-withdrawing groups (Table II, entries 1–11) were converted easily to their corresponding carbonyl compounds in high yields. Oxidation of cinnamyl tetrahydropyranyl ether also was accompanied with the cleavage of the carbon-carbon double bond to give benzaldehyde in 83% yield (Table II, entries 7).

In conclusion, in this study we have introduced a new oxidizing system in which $KMnO_4$ as a green oxidant and easy handling solid silica chloride has been used for the effective oxidation of cyclic thioacetals, silyl, and pyranyl ethers to their carbonyl compounds in dry CH_3CN at room temperature. By this method, overoxidation of aldehydes to their carboxylic acids has not been observed.

GENERAL

All the products are known and commercially available compounds. Therefore, their physical data are not given. The products were purified by column or plate chromatography on silica gel, when necessary, the purity determination of the products was accomplished by GC on a Shimadzu model GC-14A instrument or by TLC on silica gel polygram SIL G/UV 254 plates. The IR spectra were recorded on a Perkin Elmer 781 spectrophotometer. The NMR spectra were recorded on a Bruker advance DPX 250 MHz spectrometer.

Oxidatrion of Cyclic Thiacetals, Silyl, and Pyranyl Ethers with the Silica Chloride/$KMnO_4$ System

General Procedure

To a solution of the substrate (1 mmol) in dry CH_3CN (5 mL) silica chloride (0.5 g for silyl ethers, 0.6 g for pyranyl ethers, and 1 g for cyclic thioacetals) was added and then $KMnO_4$ (0.158 g, 1 mmol for silyl ethers, 0.189 g, 1.2 mmol for pyranyl ethers, and 0.474 g, 3 mmol for cyclic thioacetals); the resulting mixture was stirred at room temperature for the appropriate reaction time (Tables I–IV). The progress of the reaction was monitored by TLC and GC. After completion of the reaction, the solvent was evaporated under reduced pressure. The resulting solid mixture was added to a silica gel pad (3 cm thick) and was washed with a mixture of hexanes/EtOAc (5:1, 3 × 20 mL). The filtrates were combined and the solvent was evaporated under reduced pressure to afford the desired products in good to excellent yields (Table I–IV). The quantity of the aldehydes with high vapor pressures were determined by their conversion into their 1,4-dinitrophenylhydrazone derivatives.

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