



## High yielding oxidative deprotection of silyl and pyranyl ethers to their corresponding carbonyl compounds with strontium manganate in the presence of aluminum chloride in solution and under neat conditions

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### ABSTRACT

Strontium manganate (SrMnO<sub>4</sub>) in presence of aluminum chloride (AlCl<sub>3</sub>) is an efficient reagent for the high yielding oxidative deprotection of aromatic and aliphatic silyl and pyranyl ethers in to their corresponding carbonyl compounds, in solution and under solvent free conditions.

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### KEYWORDS

Strontium manganate;  
Aluminum chloride;  
Net condition;  
Oxidative deprotection;  
Tetrahydropyranyl ethers.

### INTRODUCTION

Hydroxy group is one of the most abundant functional groups in organic molecules and its protection is important in multi-step synthesis. Transformation of hydroxy functional groups into their silyl and pyranyl ethers is a common way for their protection during the total synthesis of complex organic molecules<sup>[1-3]</sup>. Regeneration of protected group to the original functional group or its oxidized form is a useful transformation. This transformation has been under attention and varieties of methods have been reported by investigators. The reported methods include; Tris [trinitratoceric (IV)] paraperiodate ([NO<sub>3</sub>)<sub>3</sub>Ce]·H<sub>2</sub>IO<sub>6</sub><sup>[4]</sup>, Fe(NO<sub>3</sub>)<sub>3</sub>·1.5N<sub>2</sub>O<sub>4</sub> and Cu(NO<sub>3</sub>)<sub>2</sub>·N<sub>2</sub>O<sub>4</sub><sup>[5]</sup>, Silver and sodium bromate in the presence of aluminum chloride<sup>[6]</sup>, 2,3-Dechloro-5,6-dicyanoquinone (DDQ)<sup>[7,8]</sup>, Ceric ammonium nitrate (CAN)<sup>[9]</sup>, N-bromosuccinimide (NBC)<sup>[10]</sup>, Potassium permanganate in the presence of lewis acids<sup>[11]</sup>, Nitrosonium tetra fluoroborate (NO<sup>+</sup>BF<sub>4</sub>)<sup>[12]</sup>, Bis[trinitratoceric (IV)] Chromato [(NO<sub>3</sub>)<sub>3</sub>Ce]<sub>2</sub>CrO<sub>4</sub>

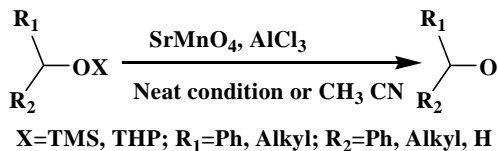
<sup>[13]</sup>, Jones reagent (CrO<sub>3</sub> / H<sub>2</sub>SO<sub>4</sub> / Acetone)<sup>[14-16]</sup>, Zinc chlorochromate nonahydrate (ZCCNH)<sup>[17]</sup>, bis (triphenylsilyl) chromate[(ph<sub>3</sub>sio)<sub>2</sub>cro<sub>2</sub>]<sup>[18]</sup>, Pyridinium fluorochromate (PFC)<sup>[19]</sup>, Trimethyl-Silylchlorochromate [ClCrO<sub>2</sub>(osiMe<sub>3</sub>)]<sup>[20]</sup>, Collins reagent (CrO<sub>3</sub>·2py)<sup>[21]</sup>, Pyridinium chlorochromate (PCC)<sup>[22,23]</sup>, 3-Carboxy pyridinium chlorochromate (CPCC)<sup>[24]</sup>, Alumina supported chromium (VI) oxide<sup>[25]</sup> and Pyridinium dichromate (PDC)<sup>[20]</sup>.

Some of the reported procedures for the oxidation of silyl and pyranyl ethers suffer at least from one of the following disadvantages: Using expensive reagents<sup>[4,13]</sup>, high acidity of the media<sup>[14-16]</sup>, requiring long reaction times<sup>[18,19]</sup>, dangerous procedure for their preparation<sup>[21-24]</sup>, and difficult procedure<sup>[18]</sup>. Therefore, efficient and one-pot direct oxidation of silyl and tetrahydropyranyl ethers under mild and solvent-free conditions can be considered as a useful procedure for further manipulation of the hydroxy functionality in organic synthesis.

In this paper, we report a new efficient method for deprotection of various types of silyl and pyranyl ethers

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into their corresponding carbonyl compounds in solution and under solvent-free conditions using strontium manganate and aluminium chloride as an easily prepared, stable and a cheap reagent (SCHEME 1, TABLES 1 and 2).



SCHEME 1

TABLE 1: Oxidative deprotection of trimethyl silyl ethers to their corresponding carbonyl compounds with SrMnO<sub>4</sub>/AlCl<sub>3</sub>

Entry	Substrate <sup>a</sup>	Product	Yield% <sup>b</sup> Time/min	
			Solution <sup>c</sup>	Solvent-free <sup>c</sup>
1	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OTMS	C <sub>6</sub> H <sub>5</sub> CHO	95(15)	90(90)
2	2-ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OTMS	2-ClC <sub>6</sub> H <sub>4</sub> CHO	96(20)	91(90)
3	3-MeOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OTMS	3-MeOC <sub>6</sub> H <sub>4</sub> CHO	93(15)	90(90)
4	4-ClC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OTMS	4-ClC <sub>6</sub> H <sub>4</sub> CHO	97(15)	90(90)
5	4-MeOC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OTMS	4-MeOC <sub>6</sub> H <sub>4</sub> CHO	94(15)	92(90)
6	2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> OTMS	2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CHO	98(15)	92(60)
7	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OTMS	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub> CHO	93(20)	84(120)
8	4-Me <sub>2</sub> CHC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OTMS	4-Me <sub>2</sub> CHC <sub>6</sub> H <sub>4</sub> CHO	97(20)	88(90)
9	C <sub>6</sub> H <sub>5</sub> CH=CH <sub>2</sub> OTMS	C <sub>6</sub> H <sub>5</sub> CH=CHO	94(15)	88(60)
10	PhCH=CH <sub>2</sub> OTMS	PhCH=CHCHO	97(15)	92(90)
11	C <sub>6</sub> H <sub>5</sub> CH(OMe) <sub>2</sub>	C <sub>6</sub> H <sub>5</sub> (Me) <sub>2</sub> CO	94(20)	89(90)
12	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH(OMe)	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CO	93(20)	85(90)
13	2-C <sub>4</sub> H <sub>9</sub> SCH <sub>2</sub> OTMS	2-C <sub>4</sub> H <sub>9</sub> SCHO	96(15)	87(90)

TABLE 2: Oxidative deprotection of THP-ethers to their corresponding carbonyl compounds with SrMnO<sub>4</sub>/AlCl<sub>3</sub>

Entry	Substrate <sup>a</sup>	Product	Yield% <sup>b</sup> (Time/min)	
			Solution <sup>c</sup>	Solvent-free <sup>c</sup>
1	C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> OTHP	C <sub>6</sub> H <sub>5</sub> CHO	95(15)	92(60)
2	2-O <sub>2</sub> N C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OTHP	2-O <sub>2</sub> N C <sub>6</sub> H <sub>4</sub> CHO	98(20)	92(60)
3	3-O <sub>2</sub> N C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OTHP	3-O <sub>2</sub> N C <sub>6</sub> H <sub>4</sub> CHO	95(20)	91(60)
4	4-O <sub>2</sub> N C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OTHP	4-O <sub>2</sub> N C <sub>6</sub> H <sub>4</sub> CHO	96(15)	91(60)
5	3-MeO C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OTHP	3-MeO C <sub>6</sub> H <sub>4</sub> CHO	98(15)	92(16)
6	4-MeO C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OTHP	4-MeO C <sub>6</sub> H <sub>4</sub> CHO	98(15)	93(60)
7	4-Br C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OTHP	4-Br C <sub>6</sub> H <sub>4</sub> CHO	99(15)	96(60)
8	4-Cl C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OTHP	4-Cl C <sub>6</sub> H <sub>4</sub> CHO	98(15)	95(60)
9	2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CH <sub>2</sub> OTHP	2,4-Cl <sub>2</sub> C <sub>6</sub> H <sub>3</sub> CHO	99(15)	96(60)
10	4-Me <sub>2</sub> CHC <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OTHP	4-Me <sub>2</sub> CHC <sub>6</sub> H <sub>4</sub> CHO	98(20)	92(75)
11	4-Me <sub>3</sub> C C <sub>6</sub> H <sub>4</sub> CH <sub>2</sub> OTHP	4-Me <sub>3</sub> C C <sub>6</sub> H <sub>4</sub> CHO	97(20)	93(75)
12	PhCH=CH-CH <sub>2</sub> OTHP	PhCH=CH-CHO	98(15)	92(60)
13	C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )CH(OMe)	C <sub>6</sub> H <sub>5</sub> (CH <sub>3</sub> )CO	96(15)	90(60)
14	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CH(OMe)	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CO	98(20)	93(60)
15	n-C <sub>7</sub> H <sub>15</sub> CH <sub>2</sub> OTHP	n-C <sub>7</sub> H <sub>15</sub> CHO	96(20)	92(75)
16	3-C <sub>5</sub> H <sub>4</sub> NCH <sub>2</sub> OTHP	3-C <sub>5</sub> H <sub>4</sub> NCHO	98(20)	92(60)
17	9-C <sub>14</sub> H <sub>9</sub> CH <sub>2</sub> OTHP	9-C <sub>14</sub> H <sub>9</sub> CHO	87(25)	80(90)

<sup>a</sup>THP=Tetrahydropyranyl. <sup>b</sup>Isolated yields. <sup>c</sup>Substrate:SrMnO<sub>4</sub>:AlCl<sub>3</sub> = 1:1:1

Primary and secondary benzylic trimethylsilyl ethers were oxidized easily to the corresponding aldehydes and ketones in good to excellent yields (TABLE 1, Entries, 1-9, 11-12). Cinnamyl trimethylsilyl ether was oxidized to cinnamaldehyde in 92-97% yields. (TABLE 1, entry 10).

Through this study, we have found the oxidative deprotection of trimethylsilyl ethers with SrMnO<sub>4</sub>/AlCl<sub>3</sub> in solutions were transformed faster than under neat conditions.

We have also studied oxidative deprotection of tetrahydropyranyl ethers of various alcohols with SrMnO<sub>4</sub>/AlCl<sub>3</sub> in solution and under solvent free conditions (SCHEME 1, TABLE 2). By this procedure, various types of aromatic tetrahydropyranyl ethers with electron-releasing and electron-withdrawing groups (TABLE 2, Entries 1-11) were converted to their corresponding carbonyl Compounds (80-98%). Primary aliphatic THP-ether was also oxidized to the corresponding aldehyde in 92-96% yields (TABLE 2, Entry 15).

Oxidative deprotection THP-ethers of primary and secondary alcohols with this reagent in solution and reflux conditions were performed. In these transformations we have not seen any over oxidation of aldehydes to their corresponding carboxylic acids.

In conclusion, the paper describes an efficient method for oxidative deprotections of trimethylsilyl- and tetrahydropyranyl ethers. Short reaction times, heterogeneous reaction conditions, excellent yields, easy workup and offer significant improvements over many existing methods.

## EXPERIMENTAL

### Preparation of strontium manganate (SrMnO<sub>4</sub>)

In a round-bottomed flask (250 ml) equipped with a magnetic stirrer and a condenser, a warm solution of potassium manganate (0.05 mol) in distilled water (60 ml) was prepared. To this solution, strontium hydroxide (0.05 mol) was added and the mixture was stirred for 0.5h. The reaction mixture was filtered and the solid material was washed with distilled water. The resulting crystals were dried in a desiccator under vacuo to afford strontium manganate in 87% yield. Found: Sr, 41.96% calcd for SrMnO<sub>4</sub>: Sr, 42.42%<sup>[27]</sup>.

### General procedure for oxidative deprotection of trimethylsilyl and THP-ethers in solution

In a round-bottomed flask (50 ml) equipped with a magnetic stirrer and a condenser, a solution of trimethylsilyl or THP ethers (1 mmol) in CH<sub>3</sub>CN (10 ml) was

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prepared.  $\text{SrMnO}_4$  (1 mmol) and  $\text{AlCl}_3$  (1mmol) was added to the solution and the mixture was refluxed for 15-25min. The Progress of the reaction was followed by TLC (eluent: n-hexane / EtOAc:5/1). The reaction mixture was filtered and the solid material was filtered and the solid material was washed with  $\text{CH}_3\text{CN}$  (15 ml). The Filtrate was evaporated and the resulting crude material was purified by column chromatography on silica gel to afford the pure product. (TABLES 1,2).

### General procedure for oxidative deprotection of trimethylsilyl and THP ethers under net conditions

A mixture of trimethylsilyl or THP ethers (1 mmol)  $\text{SrMnO}_4$  (1mmol) and  $\text{AlCl}_3$  (1 mmol) were heated on an oil bath ( $70^\circ\text{C}$ ) for 60-120 min. The progress of the reaction was followed by TLC (eluent: n- hexane / EtOAc:5/1) After completion of the reaction, the mixture was cooled to room temperature and extracted with  $\text{Et}_2\text{O}$  ( $\times 15$  ml). The solvent was evaporated and the resulting crude material was purified by column chromatography on silica gel to afford the pure products (TABLES 1, 2).

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