

High Yielding Oxidative Deprotection of Silyl and Pyranyl Ethers to Their Corresponding Carbonyl Compounds with Strontium Manganate in the Presence of Aluminium Chloride in Solution and Under Solvent-Free Conditions

Mostafa GHOLIZADEH^{1,*}, I. MOHAMMADPOOR BALTORK²

¹*Department of Chemistry, Tarbiat Moallem University of Sabzevar, Sabzevar-IRAN
e-mail: m_gholizadeh@sttu.ac.ir.*

²*Department of Chemistry, Isfahan University, Isfahan 81746-73441, IRAN
e-mail: Imbaltork@sci.ui.ac.ir*

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Strontium manganate (SrMnO₄) in the presence of aluminium chloride (AlCl₃) is an efficient reagent for the high yielding oxidative deprotection of aromatic and aliphatic silyl and pyranyl ethers into their corresponding carbonyl compounds, in solution and under solvent-free conditions.

Key Words: Strontium manganate, aluminium chloride, solvent-free conditions, 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.^{1–3} Regeneration of the protected group to the original functional group or its oxidized form is a useful transformation. The latter has been the focus of attention and a variety of methods have been reported. The reported methods include tris [trinitratoceria(IV)] paraperiodate ([NO₃)₃Ce]₃.H₂IO₆,⁴ Fe(NO₃)₃.3/2N₂O₄ and Cu(NO₃)₂.N₂O₄,⁵ silver and sodium bromate in the presence of aluminum chloride⁶, 2,3-dechloro – 5,6-dicyanoquinone (DDQ),^{7,8} ceric ammonium nitrate (CAN),⁹ N-bromosuccinimide (NBC),¹⁰ potassium permanganate in the presence of Lewis acids,¹¹ nitrosonium tetrafluoroborate (NO⁺BF₄⁻),¹²

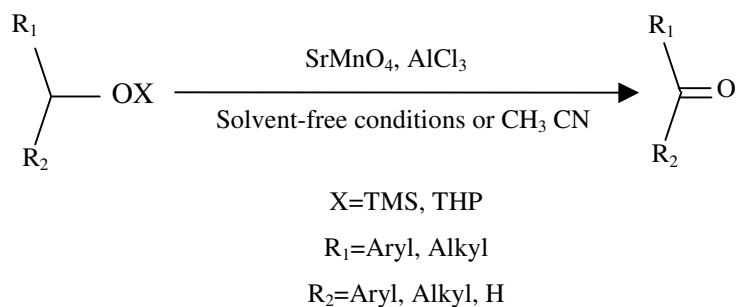
*Corresponding author

Bis[trinitratocerium(IV)]chromato $[(\text{NO}_3)_3\text{Ce}]_2\text{CrO}_4$,¹³ Jones reagent ($\text{CrO}_3/\text{H}_2\text{SO}_4/\text{acetone}$),^{14–16} zinc chlorochromate nonahydrate (ZCCNH)¹⁷, bis(triphenylsilyl) chromate $[(\text{Ph}_3\text{SiO})_2\text{CrO}_2]$,¹⁸ pyridinium fluoro-chromate (PFC),¹⁹ trimethyl – silylchlorochromate $[\text{ClCrO}_2(\text{osiMe}_3)]$,²⁰ Collins reagent ($\text{CrO}_3 \cdot 2\text{py}$),²¹ pyridinium chlorochromate (PCC),^{22,23} 3-carboxypyridinium chlorochromate (CPCC),²⁴ alumina supported chromium(VI) oxide²⁵ and pyridinium dichromate (PDC),²⁰ polyvinylpyrrolidone-bromine complex²⁸ N-hydroxyphthalimide (NHPI) and lipophilic Co(II) complexes,²⁹ a polymer supported on peroxy tungstate tungstate complex³⁰ and so on, silica gel supported on Dess-Martin periodinane,³¹ and 4-aminobenzoic acid supported on silica gel.³²

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,^{4,13} high acidity of the media,^{14–16} requiring long reaction times,^{18,19} dangerous procedure for their preparation,^{21–24} and difficult procedure.¹⁸ Therefore, efficient and 1-pot direct oxidation of silyl and tetrahydropyranyl ethers under mild and solvent-free conditions can be considered a useful procedure for further manipulation of the hydroxy functionality in organic synthesis.

We have reported previously the oxidation of benzylic and allylic alcohols and also oxidative cleavage some of these oximes into their corresponding carbonyl compounds with strontium manganate in the presence of aluminum chloride.²⁷

In this paper, we report a new efficient method for deprotection of various types of silyl and pyranyl ethers into their corresponding carbonyl compounds in solution and under solvent-free conditions using strontium manganate and aluminum chloride as an easily prepared, stable, and inexpensive reagent (Scheme 1, Tables 1 and 2).



Scheme 1. Oxidative deprotection of TMS- and THP-ethers to their corresponding carbonyl compounds under the following conditions:

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 and 11 and 12). Cinnamyl trimethylsilyl ether was oxidized to cinnamaldehyde in 92%-97% yields (Table 1, Entry 10).

Results of the study showed that the oxidative deprotection of trimethylsilyl ethers with $\text{SrMnO}_4/\text{AlCl}_3$ in solutions transformed faster than under solvent-free conditions.

Table 1. Oxidative deprotection of trimethyl silyl ethers to their corresponding carbonyl compounds with SrMnO₄/AlCl₃.

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

^aTMS=-SiMe₃, ^bIsolated yields. ^cSubstrate: SrMnO₄:AlCl₃ = 1:1:1.

We have also studied oxidative deprotection of tetrahydropyranyl ethers of various alcohols with SrMnO₄/AlCl₃ 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 of THP-ethers of primary and secondary alcohols with this reagent in solution and reflux conditions was performed. In these transformations we have not observed 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, and easy work-up offer significant improvements over many existing methods.

Experimental

Preparation of Strontium Manganate (SrMnO₄)

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 0.5 h. The reaction mixture was filtered and the solid material was washed with distilled water. The resulting crystals were dried in a desiccator under vacuum to afford strontium manganate in 87% yield. Found: Sr, 41. 96% calcd for SrMnO₄: Sr, 42.42%.²⁷ It is a bench-top reagent and should be stable for a long time. We used the aluminum chloride as an activator of SrMnO₄.

Table 2. Oxidative deprotection of THP-ethers to their corresponding carbonyl compounds with SrMnO₄/AlCl₃

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

^aTHP=Tetrahydropyranyl. ^bIsolated yields. ^cSubstrate: SrMnO₄: AlCl₃ = 1:1:1.

General Procedure for the Oxidative Deprotection of Trimethylsilyl and THP-ethers in Solution

In a round-bottomed flask (50 mL) equipped with a magnetic stirrer and a reflux condenser was placed a solution of TMS- or THP-ethers (1 mmol) in CH₃CN (10 mL). SrMnO₄ (1 mmol) and AlCl₃ [freshly sublimed] (1 mmol) were added to the solution and the mixture was refluxed for 15-25 min. The progress of the reaction was followed by TLC (eluent: n-hexane/EtOAc 5:1). The reaction mixture and the solid material were filtered and the solid material was washed with CH₃CN (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 and 2).

General procedure for the Oxidative Deprotection of Trimethylsilyl and THP ethers under Solvent-Free Conditions

A mixture of TMS- or THP-ethers (1 mmol) SrMnO₄ (1 mmol) and AlCl₃ [freshly sublimed] (1 mmol) was heated on an oil bath (70 °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 Et₂O (2 × 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 and 2).

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