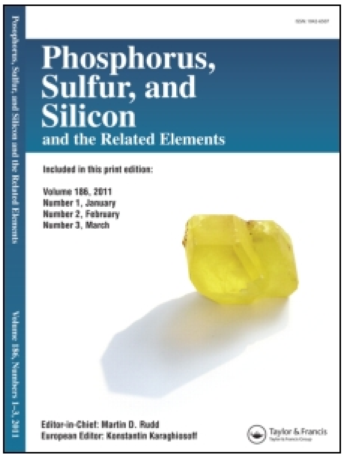

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ZINC CHLOROCHROMATE NONAHYDRATE [Zn(ClCrO$_3$)$_2$.9H$_2$O] IS A USEFUL REAGENT SOLUTION OXIDATIVE DEPROTECTION FOR THE SOLVENT-FREE AND IN OF TRIMETHYL- AND TERT-BUTYLDIMETHYLSILYL ETHERS

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ZINC CHLOROCHROMATE NONAHYDRATE [$Zn(ClCrO_3)_2.9H_2O$] IS A USEFUL REAGENT FOR THE SOLVENT-FREE AND IN SOLUTION OXIDATIVE DEPROTECTION OF TRIMETHYL- AND TERT-BUTYLDIMETHYLSILYL ETHERS

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Primary and secondary tert-butyldimethylsilyl and trimethylsilyl ethers are oxidized to their corresponding carbonyl compounds with zinc chlorochromate nonahydrate (ZCCNH) in dichloromethane or under solvent free conditions in good yields. For comparison, we have also studied the reactions with pyridinium chlorochromate (PCC) under similar reaction conditions.

Keywords: Zinc chlorochromate nonahydrate; Pyridinium chlorochromate; Oxidative deprotection; Oxidation; Silyl ethers; Solvent-free

INTRODUCTION

Direct oxidative deprotection of silyl ethers is of practical importance and varieties of methods are available in the chemical literature.[1] TMS and TBDMS groups are the two most encountered silyl moieties which are used for masking hydroxyl groups in the course of the total synthesis of complex organic molecules.[2] Literature search shows that oxidative cleavage of the TBDMS ethers even under harsh reaction conditions is difficult[1a,3].

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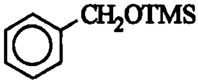
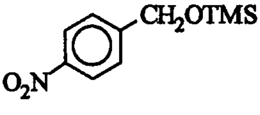
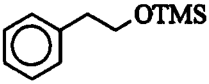
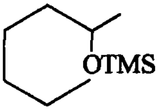
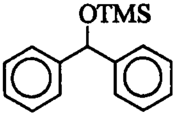
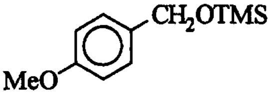
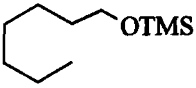
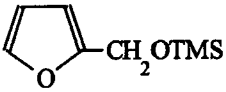
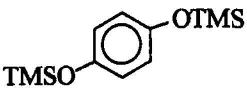
In this report we have paid attention to the oxidative deprotection of TBDMS and TMS ethers using zinc chlorochromate nonahydrate (ZCCNH)[1b], a newly developed oxidizing agent, in CH_2Cl_2 or under neat condition .Through this study, we have also compared the results of the oxidative deprotection of the silyl ethers with ZCCNH with those obtained by pyridinium chlorochromate (PCC) oxidation.[4]

RESULTS AND DISCUSSION

Both reagents are effective oxidants for the transformation of TMS ethers ($1_{a\text{-}i}$) to the corresponding carbonyl compounds under solvent-free conditions (Table I). Oxidation of some TMS ethers in solutions are reported earlier with ZCCNH and PCC[1a,b,1,3] or we have investigated in our laboratories during the progress of this work. For comparison, we have also summarized the results in solution in Table I.

TABLE I Comparison of Oxidative Deprotection of TMS Ethers to Their Corresponding Carbonyl Compounds with Zinc Chlorochromate Nonahydrate (ZCCNH) and Pyridinium Chlorochromate (PCC) under Solvent-Free Conditions and in Solution

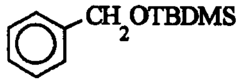
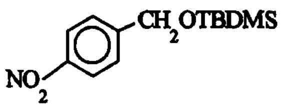
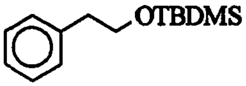
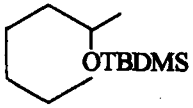
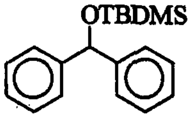
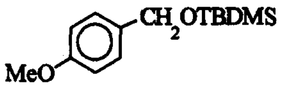
		Solvent-Free		*In Solution*	
	Substrate	*Oxid/Subst(h) Yield*[a]		*Oxid/Subst(h) Yield*[a]	
		(ZCCNH)	*(PCC)*	*(ZCCNH)*	*(PCC)*
1		0.5(-)[b]80	4(0.25)95	0.5(0.25)85	4(1.5)90
2		1(-)[b]85	6(1)10	2(3.4)87[20]	6(2)77
3		1(-)[b]84	10(0.5)80	1(0.25)80	10(2)86

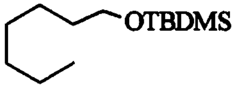
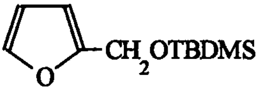
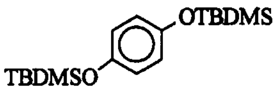
		Solvent-Free		*In Solution*	
	Substrate	*Oxid/Subst(h) Yield*[a]		*Oxid/Subst(h) Yield*[a]	
		(ZCCNH)	*(PCC)*	*(ZCCNH)*	*(PCC)*
4		1.2(-)[b]74[c]	10(0.7)80[c]	1.2(0.25)95	10(1)71
5		0.8(-)[b]95	5(0.3)93	1(0.25)93	5(0.5)87
6		0.4(-)[b]95	3(0.17)98	0.4(0.8)89	4(0.5)88
7		1.2(-)[b]76[c]	10(0.5)75[c]	1.2(0.8)93	10(1)87
8		0.8(-)[b]85	5(0.08)70	0.8(0.2)73	5(0.2)57
9		1.5(-)[b]100	6(0.2)89	1(1)90[20].	-(2)99

a) Isolated yields after column chromatography or as 2,4-dinitrophenylhydrazone derivative.
b) Reactions occurred immediately.
c) GC yield.

Direct oxidation of tert-butyldimethylsilyl (TBDMS) ethers is a difficult task[11] and we have studied the use of ZCCNH, as an oxidant, for this purpose in CH_2Cl_2. Surprisingly, the transformation proceeded smoothly in less than lh and the corresponding carbonyl compounds were isolated in good to high yields. *tert-Butyldimethylsilyl* ethers are stable to PCC in solution even in the presence of added potassium fluoride.[3] Oxidation of tert-butyldimethylsilyl ethers with ZCCNH and PCC under neat conditions was also studied. ZCCNH is an effective oxidant in the absence of solvent for this purpose and the carbonyl compounds are produced in 70–88% yields in a few minutes at room temperature (Table II).

TABLE II Comparison of Oxidative Deprotection of tert-Butyldimethylsilyl (TBDMS) Ethers with Zinc Chlorochromate Nonahydrate (ZCCNH) and Pyridinium Chlorochromate (PCC) under Solvent-Free Conditions and in Solution

		Solvent-Free		*In Solution*	
	Substrate	*Oxid/Subst(h) Yield*[a]		*Oxid/Subst(h) Yield*[a]	
		(ZCCNH)	*(PCC)*	*(ZCCNH)*	*(PCC)*
1		5.5(0.17)83	8.5(0.8)85	7(0.5)80	10(5)-[b]
2		6.5(0.1785	10(2)-b	10(0.5)78	15(3)90
3		6(-)[b]74	10(1)10	8(0.5)80	15(3)84
4		6.2(0.17)73[c]	10(3)10[c]	8(0.6)75[c]	10(3)90[c]
5		7.2(0.17)87	10(1)80	9(-)76	10(4)70
6		4.5(-)[b]88	7(0.7)90)	5.5(0.3)90	10(5)90

	Substrate	*Solvent-Free*		*In Solution*	
		Oxid/Subst(h) Yield[a]		*Oxid/Subst(h) Yield*[a]	
		(ZCCNH)	*(PCC)*	*(ZCCNH)*	*(PCC)*
7		6.1(0.17)70[c]	10(2.5)5[c]	8(0.5)78[c]	-
8		-[b]	-[b]	10(1.5)50	-[b]
9		-[b]	-[b]	10(0.25)80	-[b]

a) Isolated yields after column chromatography or as 2,4-dinitrophenylhydrazone derivative.
b) Reactions occurred immediately.
c) GC yield.

Generally, ZCCNH is a more effective reagent than PCC for conversion of TBDMS ethers to their corresponding carbonyl compounds either in solution or in the absence of solvent (Table II).

Conclusion

Zinc chlorochromate nonahydrate (ZCCNH) an easily prepared and a cheap reagent is a useful oxidant for the efficient oxidative deprotection of highly stable tert-butyldimethylsilyl ethers to their corresponding carbonyl compounds in good yields. The reactions proceed under mild reaction conditions in solution and also in the absence of solvent. Generally, ZCCNH is a more effective reagent than PCC for the oxidative transformation of TBDMS ethers. Both ZCCNH and PCC transform TMS ethers to the carbonyl compounds effectively in the absence of solvents and in solution. Over-oxidation of the products is not observed by the presented methods.

EXPERIMENTAL

General: Products were characterized by comparison of their physical data with those of authentic samples. All yields refer to isolated products unless otherwise indicated. IR spectra were recorded on a Perkin Elmer 781. Mass spectra were recorded on a Shimadzu GCMC-QP 1000 EX. TLC accomplished the purity determination of the products on silica gel polygram SILG/UV 254 plates or GLC on a Shimadzu GC-14A instrument. CH_2Cl_2 was dried and predistilled. The yields of the partially volatile carbonyl compounds were determined by both GLC or as their 2,4-dinitrophenylhydrazone derivatives.

Oxidative Deprotection of 4-Nitrobenzyl-tert-butyldimethylsilyl Ether with $Zn(ClCrO_3)_2.9H_2O$ (ZCCNH) in CH_2Cl_2 to 4-Nitrobenzaldehyde: a Typical Precedure for the Direct Oxidation of TBDMS Ethers to Their Corresponding Carbonyl Compounds

To a solution of 4-nitrobenzyl-tert-butyldimethylsilyl ether (0.267 g, 1 mmol) in CH_2Cl_2 (10 ml) in a round-bottom flask (25 ml) equipped with a magnetic stirrer, $Zn(ClCrO_3)_2.9H_2O$ (4.98 g, 10 mmol) was added and the resulting mixture was stirred vigorously for 0.5 h. The progress of the reaction was monitored by TLC. Solvent was evaporated on a rotary evaporator and the residue was applied on a silica gel pad and was eluted with petroleum ether/acetone (8/1). The solvent was evaporated and to the resulting residue, CH_3OH (3×5 ml) was added and the resulting mixture was evaporated until the mixture was free form tert-butyldimethylsilane. The desired product was isolated in 78% yield, 0.118 g, mp 105–106°C [lit, mp 106°C] (entry 2, Table II).

Oxidative Deprotection of 4-Nitrobenzyltrimethylsilyl Ether with Pyridinium Chlorochromate (PCC) to 4-Nitrobenzaldehyde Under Solvent-Free Conditions: a Typical Procedure for the Direct Oxidation of TMS Ethers to their Corresponding Carbonyl Compounds

A mixture of 4-nitrobenzyltrimethylsilyl ether (0.226 g, 1 mmol) and PCC (1.3 g, 6 mmol) was prepared and was magnetically agitated for 1h. at room temperature. To the resulting mixture Et_2O (30 ml) was added and filtered through a silica gel pad (4 g). The filter cake was washed further with an extra amount of Et_2O (20 ml). The combined filtrates were evaporated and the resulting residue was further purified by column chromatography on silica gel and eluted with petroleum ether/acetone (8/1) to afford the desired aldehyde in a quantitative yield, mp 105–106°C [Lit.[24] 106°C] (entry 2, Table I).

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