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Deprotection and Direct Oxidative Deprotection of Trimethylsilyl Ethers to their Corresponding Alcohols and Carbonyl Compounds with Tris[trinitratocerium(IV)] Paraperiodate, $[(NO_3)_3Ce]_3.H_2IO_6$, in an Aprotic Solvent

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Deprotection and Direct Oxidative Deprotection of Trimethylsilyl Ethers to their Corresponding Alcohols and Carbonyl Compounds with Tris[trinitratocerium(IV)] Paraperiodate, $[(NO_3)_3Ce]_3.H_2IO_6$, in an Aprotic Solvent

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Abstract: Deprotection of structurally different trimethylsilyl ethers to their corresponding alcohols has been achieved in refluxing benzene in the presence of tris[trinitratocerium(IV)] paraperiodte in a few minutes. This reagent has also been used successfuly for the direct oxidation of trimethylsilyl ethers to their corresponding carbonyl compounds. Benzylic double bonds are prone to cleavage reactions with this method.

Protection of functional groups is of vital importance in the synthesis of structurally complex molecules with multiple functionality. Hydroxy group is one of the most abondant functional groups in organic molecules and its controlled manupulation is very important in multi-step syntheses. One of the versatile and useful methods for the protection of hydroxy groups is their transformation to their trialkylsilyl ethers.[1]

Regeneration of the protected group to the original functional group under mild and aprotic condition is a useful achievement in organic synthesis.

Conversion of silyl ethers to their alcohols is usually proceeded either under protic and aqueous conditions[2] or in the presence of fluoride ion in water. Both of these conditions are not safe for the aqueous and acid sensitive compounds and the aqueous work-up makes the isolation of the water soluble compounds a difficult process.[3-5]

Methylammounium fluoride(MAF) recently has been reported as a deprotecting agent for trialkylsilyl ethers which does not need water for the work-up of the reaction mixture, but this method suffers very seriously from long reaction times (1 to 7 days).[5] Polymer supported ammonium fluorid, which is reported very recently, seems to be more reactive for the deprotection of trialkylsilyl ethers, and only few hours are needed for the reaction to proceed to its completion.[6]

Attention has been paid recently to oxidative deprotection of trialkylsilyl ethers which is a useful transformation in organic synthesis. New methods for this purpose have been developed and introduced in chemical literature[7-10]. The reported methods usually suffer from drawbacks such as; protic condition, tedious work-up, long reaction times, unavailability of the reagents and aqueous reaction conditions.

Recently we have reported a method ($AgBrO_3$ or $NaBrO_3$ in the presence of $AlCl_3$) which deprotects and oxidizes trimethylsilyl ethers efficiently in aprotic solvents and under non-aqueous conditions.[11]

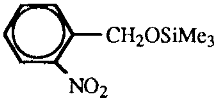
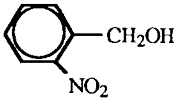
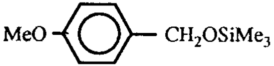
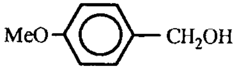
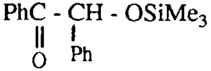
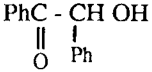
Table 1. Comparision of Some of the Results Obtained by the Oxidations with ($[(NO_3)_3Ce]_3.H_2IO_6$) (1) with Some of those Reported by $CrO_3.H_2SO_4$ (2), N-Bromosuccinimides (3) and Bis(triphenylsilyl) Chromate (4).

Entry	Substrate	Yield%			
		(1)	(2)	(3)	(4)
1	$PhCH_2OSiMe_3$	85	-	87	-
2	$4\text{-}MeOC_6H_4CH_2OSiMe_3$	90	-	70	-
3	$Ph_2CHOSiMe_3$	55	82	72	98

Now in this communication we report that tris[trinitratocerium(IV)] paraperiodate ($[(NO_3)_3Ce]_3.H_2IO_6$) a previously reported oxidizing agent[12,14] is able either to oxidize trimethylsilyl ethers to their carbonyl compounds or to deprotect directly the silyl ethers to their corresponding alcohols. In order to show the oxidizing ability of this reagent we have compared some of the results with some of those reported in the literature (Table 1)[7,8,10,13].

The pathway of the reactions is quite dependent upon the reaction times and also the equivalent amounts of the reagent. Deprotection occurs at the begining of the reactions and the mixture should be worked-up within the first few minutes, otherwise it goes further and only carbonyl compounds are isolated. Reactions do not usually work easily at room temperature and should be performed under reflux conditions in benzene. During the oxidation of silyl ethers with benzylic double bonds the complete cleavage of C=C was observed. The results are summerized in Tables 2 and 3.

Table 2. Deprotection of Silyl Ethers with $[(NO_3)_3Ce]_3 . H_2IO_6$ (T.T.C.P.P.) in Refluxing Benzene.

Entry	Substrate	Product	Oxidant/Substrate	Reation Time (min.)	Yield%
1	$PhCH_2OSiMe_3$	$PhCH_2OH$	2	5	87
2	$Ph_2CHOSiMe_3$	Ph_2CHOH	4.5	15	90
3			3.5	15	90
4			2	5	45
5	 $\underset{\underset{O}{\|}}{PhC}-\underset{\underset{Ph}{\mid}}{CH}-OSiMe_3$	 $\underset{\underset{O}{\|}}{PhC}-\underset{\underset{Ph}{\mid}}{CH}\ OH$	3.5	30	95
6	$PhCH{=}CH\text{-}CH_2OSiMe_3$	$PhCH{=}CHCH_2OH$	3.5	5	93

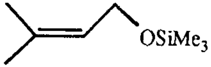
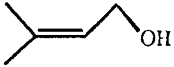
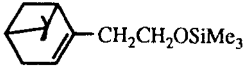
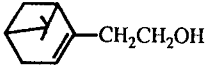
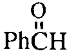
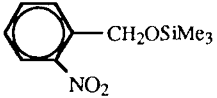
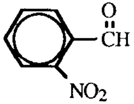
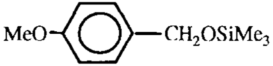
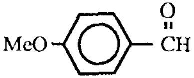
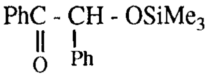
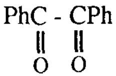
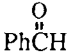
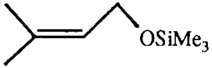
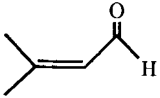
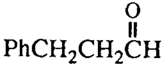
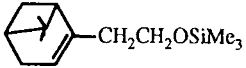
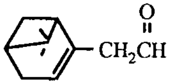
7			3.5	Immediately	95
8	$PhCH_2CH_2CH_2OSiMe_3$	$PhCH_2CH_2CH_2OH$	5	15	90
9			5	10	85

Table 3. Oxidative Deprotection of Silyl Ethers with $[(NO_3)_3Ce]_3.H_2IO_6$ in Refluxing Benzene.

Entry	Substrate	Product	Oxidant / Substrate	Reation Time (hr.)	Yield%
1	$PhCH_2OSiMe_3$	 $\mathrm{Ph\overset{\overset{O}{\|}}{C}H}$	2	0.33	85
2	$Ph_2CHOSiMe_3$	Ph_2CO	4.5	3	55
3			5	4.5	55
4			3	3.5	90
5	 $\mathrm{Ph\underset{\underset{O}{\|}}{C}-\underset{\underset{Ph}{\vert}}{C}H-OSiMe_3}$	 $\mathrm{Ph\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}Ph}$	3.5	3.5	90

6	$PhCH{=}CH\text{-}CH_2OSiMe_3$	 $PhC(=O)H$	5	5	85
7			3.5	0.33	80
8	$PhCH_2CH_2CH_2OSiMe_3$	 $PhCH_2CH_2C(=O)H$	5	3.3	83
9			5	3	80

EXPERIMENTAL

The reagent was prepared by the previously reported method.[12,14]

General Procedure for the Deprotection of Trimethylsilyl Ethers with $[(NO_3)_3Ce]_3 . H_2IO_6$ in Benzene.

A solution of silyl ether(1 mmol .) in benzene (5 ml) was treated with 2-5 molar equivalents of reagent and the reaction mixture was refluxed for 0-30 min. The progress of the reaction was monitored by TLC or GLC. The reaction mixture was filtered and the solid residue was washed with benzene several times (3x15 ml). Evaporation of the solvent, followed by column chromatography on silica gel, gave the corresponding alcohol in good to high yields. The product of each reaction was identified by its refractive index (n_D) or mp, IR and NMR spectra and their comparison with those reported for the authentic samples.[15-17]

General Procedure for the Oxidative Deprotection of Trimethylsilyl Ethers with $[(NO_3)_3Ce]_3 . H_2IO_6$ in Benzene.

A solution of silyl ether (1 mmol) in benzene (5 ml) was treated with 2-5 molar equivalents of reagent and the reaction mixture was refluxed for 0.33-5 hr. The progress of the reaction was monitored by TLC or GLC. The reaction mixture was filtered and the solid residue was washed by benzene several times (3x15 ml). Evaporation of the solvent, followed by colunm chromatography on silica gel, gave the corresponding carbonyl compounds in good to high yields. The product of each reaction was identified by its refractive index (n_D) or mp, IR and NMR spectra and their comparison with those reported for the authentic samples.[15-17]

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