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Zirconium hydroxide chromate ($Zr_4(OH)_6(CrO_4)_5(H_2O)_2$): A useful reagent for the oxidation of silyl ethers to theirs corresponding carbonyl compounds

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ABSTRACT

Zirconium hydroxide chromate ($Zr_4(OH)_6(CrO_4)_5(H_2O)_2$) can be used as stable, mild and efficient oxidizing reagent for oxidative-deprotection of silyl ethers to the corresponding carbonyl compounds.

KEYWORDS

Zirconium hydroxide chromate;
Oxidative deprotection;
Silyl ethers;
Carbonyl compound.

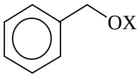
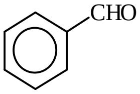
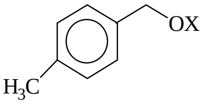
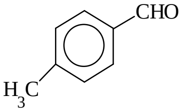
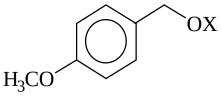
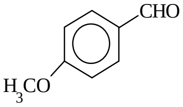
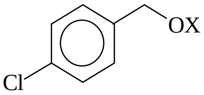
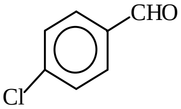
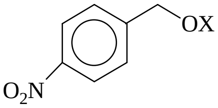
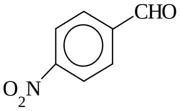
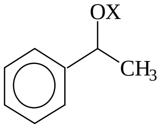
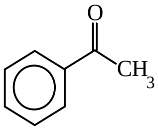
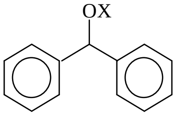
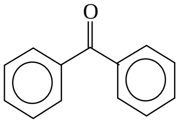
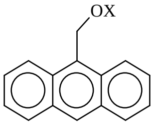
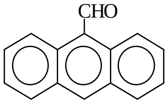
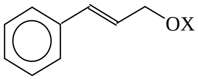
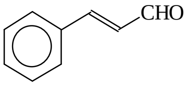
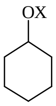
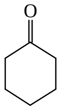
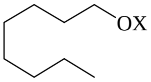
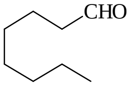
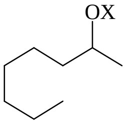
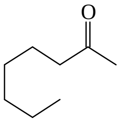
INTRODUCTION

Hydroxy group is one of the most abundant functional group in organic molecules and its protection is important in multi-step synthesis. One of the versatile and useful methods for the protecion of hydroxy groups is their transformation to their trimethylsilyl (TMS) and *tert*-butyldimethylsilyl (TBDMS) ethers[1].

Regeneration of protected group to the original functional group or its oxidized form is a useful transformation. There are some methods available for the conversion of silyl ethers to their original functional group[2]. Some of these methods were performed under protic and aqueous conditions, which are not safe for the acid sensitive molecules especially in the aqueos solution. Direct oxidation of silyl ethers is more important in organic synthesis. Nitrosonium tetrafluoroborate ($NO^+BF_4^-$)[3], 2,3-Dicholoro-5,6-dicyanoquinone (DDQ)[4], cerric ammonium nitrate (CAN)[5], silver and sodium bromate ($AgBrO_3$, $NaBrO_3$)[6], tris[trinitratocerium (IV)] paraperiodate (TTCPP) [$((NO_3)_4Ce)_3H_2IO_6$][7] and NBS[8] are some examples of the reagents which can be used for the direct oxidation of silyl ethers. Among the reagent which can be used for the direct oxidation of silyl ethers, chromium based oxidants are the most widely used reagents. Trimethylsilyl chlorochromate [$ClCrO_2(OSiMe_3)$][9], bis (triphenylsilyl)chromate [$\{Ph_3SiO)_2CrO_2$][10], Collin's reagent (CrO_3. 2Py)[11], Jones reagent (CrO_3/ H_2SO_4/ acetone),[12] Pyridinum dichromate (PDC)[12,13], Zinc chlorochromate nonahydrate (ZCCNH)[14], zinc dichromate trihydrate (ZDC)[15], bis[trinitratocerium (IV) chromate (BTNCC) [$((NO_3)_3Ce)_2CrO_4$] in benzene[16], 3-carboxypyridinium chlorochromate (CPCC)[17] and pyridinium chlorochromate (PCC)[18] are chromium based oxidants which have been used for this purpose.

Liu *et al.* have reported that *tert*-butyldimethylsilyl ethers are stable to PCC in solution even in the presence of added potassium fluoride[19,20] but pyridinium dichromate (PDC) in combination with

TABLE 1: oxidation of silyl ether with ZHC

Entry	Silyl ethers	x	Product	Time (min)	Yiled^a %
1		TMS TBDMS		40 100	90 85
2		TMS TBDMS		40 100	88 85
3		TMS TBDMS		30 90	90 90
4		TMS TBDMS		150 240	85 80
5		TMS TBDMS		12(h) 15(h)	85 80
6		TMS TBDMS		40 160	92 90
7		TMS TBDMS		60 160	90 90
8		TMS TBDMS		60 130	85 85
9		TMS TBDMS		120 180	80 80
10		TMS TBDMS		No Reaction	
11		TMS TBDMS		No Reacton	
12		TMS TBDMS		No Reaction	

a: Yields refer to isolated products and 2,4-dinitrophenyl-hydrazine derivative. Structures are confirmed by R, ^{1}H-NMR, mp and bp,

chlorotrimethylsilane ($ClSiMe_3$)[21] and Jones reagent, CrO_3/H_2SO_4/acetone[12] oxidizes *tert*-butyldimrthylsilyl ethers to the corresponding carbonyl compounds.

However, most of the reported methods suffer at least from one the following disadvantage: 1) cost of preparation, 2) long reaction time, 3) high acidity of the media, 4) dangerous procedure for their preparation, 5) aqueous condition, 6) low yield, 7) tedious work up. Therefore search for new oxidizing agents for such functional group transformation are still in demand.

In continuation of our study to explore new applications of zirconium hydroxide chromate[22] ($Zr_4(OH)_6(CrO_4)_5(H_2O)_2$) (ZHC), we found that this compound is a useful, stable and efficient reagent for oxidative-deprotection of silyl ethers to their corresponding carbonyl compound. (TABLE 1)

Zirconium hydroxide chromate which is a red octahedral crystal was prepared easily in compound from the $K_2Cr_2O_7$, $Zr(NO_3)_4$ and CrO_3. [23]

Primary and secendary benzylic trimethylsilyl ethers are oxidized to the corresponding aldehyde and ketone in good to excellent yields (Entries1-7).

Cinnamyl trimethylsilyl ether gave cinnamyl aldehyde without the cleavage of the carbon-carbon double bond in 80% yield (Entry 9).

Zirconium hydroxide chromate in CH_3CN converted primary and secondary benzyl *tert*-buthyldimethyl silyl ethers hardly to carbonyl compounds with low yields (TABLE 1).

Oxidation of *tert*-butyldimethylsilyl ethers proceeded hardly than the oxidation of trimethylsilyl ethers (TABLE 1). Primary and secendary benzylic *tert*-butyldimethylsilyl ethers are oxidized to the corresponding aldehyde and ketone in good to excellent yields (Entries1-7).

4-nitrobenzylic trialkylsilyl ether oxidizes to its corresponding aldehyde at higher time and 80- 85% yield (Entry 5).

Saturated primary and secondary trimethylsilyl and *tert*-butyldimethylsilyl ethers did not converted to the corresponding carbonyl compounds under this condition (Entries 10-12).

The reactions are relatively clean with no tar formation and no over oxidation to carboxylic acids.

The lower acidity of this reagent in comparison with other chromates, easy preparation, stability, reactivety, chemoselectivety and easy work-up make zirconium hydroxide chromate a versatile and a practical reagent for the oxidation of organic compounds.

EXPERIMENTAL

($Zr_4(OH)_6(CrO_4)_5(H_2O)_2$) (2-2.5 mmol) was added to a solution of trialkylsilyl ethers (1 mmol) in CH_3CN (5 mL). The resulting mixture was stirred at reflux. The progress of the reaction was monitored by TLC. After completion of the reaction, silica gel (1gr) was added to the reaction mixture and the solvent was evaporated under reduced pressure. The resulting material was added on silica gel pad (3 cm thick). The filter cake was washed with n-hexane/ ethyl acetate (5:1, 200 mL) and the filtrate was concentrate evaporated to afford the desired product in excellent yield.

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