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Oxidative Deprotection of Tetrahydropyranyl Ethers to Carbonyl Compounds with Montmorillonite K-10 Supported Bis(trimethylsilyl) Chromate under Non-aqueous Conditions†

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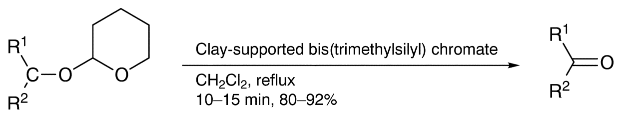
A variety of tetrahydropyranyl ethers are oxidized to the corresponding carbonyl compounds in excellent yields by montmorillonite K-10 supported bis(trimethylsilyl) chromate in dichloromethane at room temperature.

Tetrahydropyranylation is one of the most frequently used processes to protect hydroxy groups.[1] Because of the remarkable stability of tetrahydropyranyl ethers toward a variety of conditions such as strongly basic media, reactions involving Grignard reagents and lithium alkyls, reduction with hydride, oxidation, oxidative alkylation and acylation reactions, *etc*., tetrahydropyranylation is one of the methods of choice to protect a hydroxy group in a multi-step organic synthesis.[2] Many catalysts have already been proposed for the tetrahydropyranylation of alcohols and the cleavage of tetrahydropyranyl ethers to the parent alcohols.[3,4] Direct oxidation of tetrahydropyranyl ethers to their carbonyl compounds is a useful practical achievement. This oxidation is rather rare in the literature.[5,6] Consequently introduction of new methods and inexpensive reagents for such a functional group transformation is still in demand.

Recently we have introduced montmorillonite K-10 supported bis(trimethylsilyl) chromate for oxidation[7,8] and oxidative deprotection of trimethylsilyl ethers.[9] We now report a new and convenient method for the oxidative deprotection of tetrahydropyranyl ethers to their carbonyl compound in high to excellent yields using montmorillonite K-10 supported bis(trimethylsilyl) chromate. At room temperature this reagent is able to convert primary and secondary tetrahydropyranyl ethers to their corresponding aldehydes and ketones (Scheme 1, Table 1).



Scheme 1

Overoxidation of oxidative deprotection of primary tetrahydropyranyl ethers was not observed. Tetrahydropyranyl cinnamyl ether was oxidatively deprotected to cinnamaldehyde in excellent yield. In this reaction the formation of benzaldehyde was not observed, showing that the carbon–carbon double bond is not prone to cleavage with this reagent.

In order to investigate whether THP ethers are directly oxidized or initially cleaved to the corresponding alcohols and oxidized to carbonyl compounds we attempted to oxidize some corresponding alcohols under the same reaction conditions, when we found that the oxidation of alcohols is very fast compared to THP ethers. However we could observe such alcohol intermediates by TLC or GLC. Thus we could conclude that THP ethers are first cleaved to alcohols and then converted *via* fast reactions to the final products. It is also noteworthy that with nsupported bis(trimethylsilyl) chromate no reaction takes place at all.

In conclusion the present methodology offers an attractive and efficient method for the direct oxidation of tetrahydropyranyl ethers to their carbonyl compounds.

Experimental

Supported montmorillonite K-10 was prepared by the reported method.[7,9] Yields refer to isolated product. Products were identified by comparison of their physical data. THP ethers were prepared according to described procedures.[3,4,10].

Oxidative Deprotection of Tetrahydropyranyl Ethers. General Procedure.—In a round-bottomed flask (50 ml) equipped with a condenser and a magnetic stirrer a solution of THP ether (1 mmol) in CH_2Cl_2 (15 ml) was prepared. Supported montmorillonite K-10, bis(trimethylsilyl) chromate [0.8 g, equivalent to 1.2 mmol of chromium(VI) oxidant] was added to this solution and refluxed for 10–25 min. Reaction progress was monitored by GLC or TLC (eluent hexane–ethyl acetate 8:2). After completion of the reaction, the mixture was filtered and solid material was washed with CH_2Cl_2. The filtrates were combined and evaporated. The resulting crude material was further purified on a silica gel plate or silica gel column with appropriate eluent to afford the corresponding carbonyl compound (Table 1).

Table 1 Oxidative deprotection of THP ethers with montmorillonite K-10 supported bis(trimethylsilyl) chromate in CH_2Cl_2 at reflux temperature

Entry	Substrate	*t*/min	Product	Yield(%)	Mp/°C [Bp/°C (Torr)] Found	Reported[11]
1	$PhCH_2OTHP$	10	PhCHO	92	175–176/760	178–179/760
2	$4\text{-}MeC_6H_4CH_2OTHP$	10	$4\text{-}MeC_6H_4CHO$	90	58–59	59–61
3	$2\text{-}NO_2\text{-}5\text{-}MeC_6H_3CH_2OTHP$	25	$2\text{-}NO_2\text{-}5\text{-}MeC_6H_3CHO$	88	65–66	66–67
4	PhCH(Me)OTHP	25	PhCOMe	82	200–201/760	202/760
5	$Ph_2CHOTHP$	25	PhCOPh	85	47–48	49–51
6	$PhCH{=}CHCH_2OTHP$	25	PhCH=CHCHO	80	247–248/760	248/760
7	CyclohexylTHP	25	Cyclohexanone	82	154–155/760	155/760
8	2-Me-CyclohexylTHP	20	2-Me-Cyclohexanone	85	164–165/760	165/760
9	(−)-MenthylTHP	20	(−)-Methone	82	208–210/760	208–210/760

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