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Note

Desilylative Oxidation of Alkyl Trimethylsilyl Ethers with Pyridinium Fluorochromate

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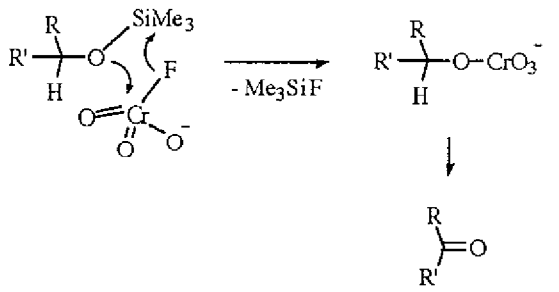
Direct conversion of alkyl trimethylsilyl ethers to carbonyl compounds is accomplished using PFC in dichloromethane at room temperature. For a similar oxidation of *t*-butyldimethylsilyl ethers the PCC-*n*-Bu_4NF combination may be employed.

INTRODUCTION

Pyridinium fluorochromate (PFC) has approximately the same capability as pyridinium chlorochromate (PCC) in oxidation of organic compounds.[1] Owing to its lower acidity, PFC is the oxidizing agent of choice for alcohols containing acid sensitive functionalities. Although it has been reported that primary *t*-butyldimethylsilyl ethers survive the oxidation conditions,[2] we wished to determine whether it is possible to convert trimethylsilyl ethers to carbonyl compounds directly with PFC. The rationale behind our study was that the $FCrO_3^-$ anion may still be able to use its bound fluorine to attack the less hindered silicon atom of a TMS ether. We envisioned the process may even involve a pairwise group exchange (Eq. 1), leading to the chromate ester from a TMS ether upon elimination of Me_3SiF. Decomposition of the chromate ester completes the desilylative oxidation.



(1)

A subsequent investigation indeed upheld our expectation. Thus, we have submitted TMS ethers of primary and secondary alcohols, and allylic alcohols to PFC and obtained the carbonyl products (Table 1). We also confirmed the inertness of TBS ethers. Benzyl *t*-butyldimethylsilyl ether underwent extremely slow oxidation (0% after 4 h), if at all. Accordingly, it is possible to oxidize a TMS ether in the presence of a TBS ether.

Table 1. Conversion of TMS-ethers to Carbonyl Compounds

Alcohol	Carbonyl Compound	Yield(%)
Menthol	Menthone	82
Cholesterol	4-Cholesten-3-one	70
trans-Piperitol	Piperitone	92
Geraniol	Citral	85
Benzyl alcohol	Benzaldehyde	72

Desilylative oxidation of *t*-butyldimethylsilyl ethers can be performed with a combination of reagents, such as PCC and tetra-*n*-butylammonium fluoride, albeit in surprisingly lower yields. The latter provides an active fluoride ion to cleave such ethers[3] for the oxidation in situ. Thus, we observed the latter protocol gave 4-cholesten-3-one in 45% yield from cholesteryl TMS ether (vs. 70% with PFC) and benzaldehyde from benzyl TBS ether in 38% yield. Note that with this prolonged reaction time PFC also effects the oxidation in 20% yield.

We have attempted a desilylative oxidation of 2-trimethylsilylmethylpyridine, hoping to obtain 2-pyridinecarbaldehyde. However, only protodesilylation was observed. 2-Picoline was the only detectable product.

EXPERIMENTAL SECTION

Generation of Carbonyl Compounds from Trimethylsilyl Ethers

General Procedure

A solution of a TMS ether (10 mmol) in CH_2Cl_2 (3 mL) was added all at once to a magnetically stirred suspension of pyridinium fluorochromate (20 mmol) in the same solvent (2 mL). Progress of the oxidation was monitored by TLC. When all the starting material disappeared (usually 4-5 h) the mixture was filtered through a pad of Celite, the solvent was removed by rotary evaporation, and the residue was purified by chromatography over silica gel to furnish the pure product which was identified by IR and NMR spectrometry.

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Key Words

Oxidation; Pyridinium fluorochromate.

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