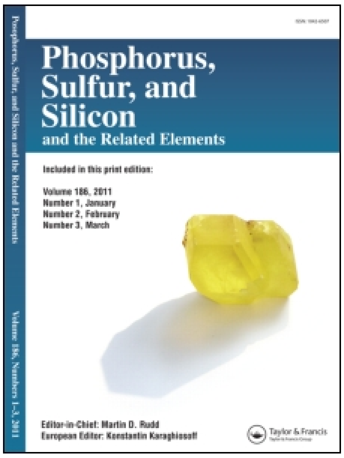

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2,6-Dicarboxypyridinium Fluorochromate: A Mild and Efficient Reagent for Oxidative Deprotection of Trimethylsilyl Ethers to Their Corresponding Carbonyl Compounds

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Deprotection of trimethylsilyl ethers to their parent aldehydes and ketones in high yields has been carried out using 2,6-dicarboxypyridinium fluorochromate under mild conditions.

Keywords 2,6-Dicarboxypyridinium fluorochromate; deprotection; oxidative; trimethylsilyl ethers

INTRODUCTION

The protection of certain functional groups and the deprotection of the protected drivatives constitute important processes in synthetic organic chemistry in polyfunctional molecules, including the total synthesis of natural products. Thus, a large number of protective groups have been developed along with numerous methods for their removal.[1–5]

Conversion of the hydroxy function to trimethylsilyl ether is one of the most useful and convenient methods for the protection of this functional group.[6–8] Direct oxidation of trimethylsilyl ethers to their corresponding carbonyl compounds has found considerable attention during recent years.[9–10]

However, some of the reported methods show limitations such as the use of expensive reagents, a long reaction time, low yields of the

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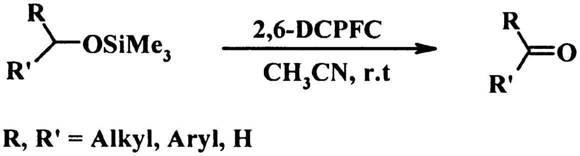
products, and tedious work-up. Therfore, the introduction of new methods and inexpensive reagents for such functional group transformation is still in demand.

RESULTS AND DISCUSSION

As a part of our program related to developing new oxidation methods, we wish to report here a new, simple, and general procedure that can be used for the oxidative deprotection of trimethylsilyl ethers to their corresponding carbonyl compounds under nonaqueous conditions at room temperature.[11] 2,6-dicarboxypyridinium fluorochromate (2,6-DCPFC) is a new, rapid, and efficient reagent for this purpose (Scheme 1).



SCHEME 1

This reagent is easily and cheaply prepared from pyridine 2,6-dicarboxylic acid, 40% aq. hydrofluoric acid, and chromium (VI) oxide in a molar ratio of 1:1.5:1. This compound is nonhygroscopic and an air-stable reagent that can be stored in a polythene bag for longer periods without decomposition. It is soluble in polar solvents such as acetonitrile and acetone; slightly soluble in THF, chloroform, and dichloromethane; and insoluble in benzene, *n*-hexane, and carbon tetrachloride. The chromium content of the reagent was determined by atomic absorption. Also, elemental analysis (C, H, N) were performed and the experimental and calculated results are in a very good agreement.

The effect of solvent in the oxidation reaction was evaluated by carrying out the oxidation in a series of solvents with varying polarity. Deprotection of benzaldehyde trimethylsilyl ether with a 1:1 ratio was carried out in dichloromethane, chloroform, tetrahydrofuran, n-hexane, and acetonitrile at room temperature. The results are presented in Table I.

A wide variety of trimethylsilyl ethers such as benzylic, allylic, and aliphatic have been converted to their corresponding carbonyl compounds using this reagent at room temperature (Table II).

It is noteworthy that, unlike other oxidative hydrolytic methods, the major drawback of overoxidation of the resulting aldehydes

TABLE I Oxidative Deprotection of Benzaldehyde Trimethylsilyl Ether in Different Solvents Using 2,6-DCPFC at Room Temperature

Entry	Solvent	Reaction period (min)	Yield (%)[a]
1	CH_3CN	5	99
2	$CHCl_3$	90	70
3	CH_2Cl_2	90	74
4	n-C_6H_{12}	90	15
5	THF	90	35

[a] Yields refer to isolated products.

is not observed under the reaction conditions. Interestingly the α, β-unsaturated derivatives underwent deprotection very efficiently without affecting the olefinic bond and the reaction is essentially chemoselective (Table II, entry 14). Furthermore, functional groups such as chloro, methoxy, nitro, and alkyl also were inert to this reagent and no byproduct formation was observed (Table II, entries 3–10).

In order to show the efficiency of this method, we have compared some of the results with relevant results reported in the literature[9,10]

TABLE II Oxidative Deprotection of Trimethylsilyl Ethers With 2,6-DCPFC in CH_3CN at Room Temperature

Entry	Substrate	Time (min)	Product[a]	Yield (%)[b]
1	$C_6H_5CH_2OSiMe_3$	5	C_6H_5CHO	99
2	$(C_6H_5)_2CHOSiMe_3$	5	$(C_6H_5)_2CO$	100
3	o-$ClC_6H_4CH_2OSiMe_3$	6	o-ClC_6H_4CHO	98
4	p-$ClC_6H_4CH_2OSiMe_3$	6	p-ClC_6H_4CHO	97
5	m-$MeOC_6H_4CH_2OSiMe_3$	7	m-$MeOC_6H_4CHO$	95
6	p-$MeOC_6H_4CH_2OSiMe_3$	6	p-$MeOC_6H_4CHO$	96
7	o-$MeOC_6HCH_2OSiMe_3$	5	o-$MeOC_6H_4CHO$	96
8	p-$MeC_6H_4CH_2OSiMe_3$	6	p-MeC_6H_4CHO	96
9	p-$NO_2C_6H_4CH_2OSiMe_3$	12	p-$NO_2C_6H_4CHO$	92
10	$C_6H_5CH(p\text{-}CIC_6H_4)OSiMe_3$	7	$C_6H_5C(p\text{-}CIC_6H_4)O$	95
11	$C_6H_5CH_2CH_2CH_2OSiMe_3$	14	$C_6H_5CH_2CH_2CHO$	86
12	$CH_3\ (CH_2)_7OSiMe_3$	30	$CH_3\ (CH_2)_6CHO$	82
13	α-tetralol trimethylsilyl ether	11	α-tetralon	94
14	$C_6H_5CH{=}CHCH_2OSiMe_3$	7	Cinnamaldehyde	93

[a] All of the products were characterized by comparing them with known compounds and their IR and ^1H NMR showed physical and spectral data in accordance with their expected structure and with authentic samples.

[b] Yields refer to isolated products.

TABLE III Comparison of Some of the Results Obtained by the Oxidative Deprotection of Trimethylsilyl Ethers With 2,6-DCPFC[a] With Some of Those Obtained by QFC[9,b] and BTPPC[10,c]

Entry	Reagent	Substrate	Time (min)	Conditions	Yield (%)
1	2,6-DCPFC	p-$NO_2C_6H_4CH_2OSiMe_3$	12	CH_3CN, r.t.[d]	92
		$(C_6H_5)_2CHOSiMe_3$	5		100
2	QFC	p-$NO_2C_6H_4CH_2OSiMe_3$	90	CH_3CN, r.t.	89
		$(C_6H_5)_2CHOSiMe_3$	70		93
3	BTPPC	p-$NO_2C_6H_4CH_2OSiMe_3$	420	CH_3CN, reflux	90
		$(C_6H_5)_2CHOSiMe_3$	18		95

[a] 2,6-Dicarboxypyridinium fluorochromate.
[b] Quinolinium fluorochromate.
[c] Benzyltriphenylphosphonium chlorate.
[d] Room temperature.

(Table III). As indicated in Table III, 2,6-DCPFC compared to the other reagents performs this transformation in a higher yield, shorter reaction times, and milder conditions.

In conclusion, 2,6-dicarboxypyridinium fluorochromate is a mild, efficient, and inexpensive reagent for the one-pot oxidative deprotection of trimethylsilyl ethers to their corresponding carbonyl compounds in nonaqueous conditions.

EXPERIMENTAL

Products were isolated and their physical data were compared with those of known samples. Solvent was freshly distilled. Trimethylsilyl ethers were prepared according to the described procedure.[12]

Preparation of 2,6-DCPFC

To a solution of 2 g (0.02 mol) of CrO_3 in 1.0 mL of water in a polyethylene beaker, 1.5 mL (0.03 mol) of 40% HF was added with stirring. An orange-red solution was obtained. The reaction mixture was then cooled in an ice bath (−5°C) and 3.342 g (0.02 mol) of pyridine and 2,6-dicarboxylic acid were added portion-wise with stirring. When an orange crystalline compound separated out, this was filtered under vacuum using a polyethylene funnel, washed with petroleum ether (3 × 10 mL), rapidly dried in a vacuum desicator, and finally stored in a polyethylene bag. The yield of 2,6-DCPFC was 5.28 g (92%).

General Procedure for the Oxidative Deprotection of Trimethylsilyl Ethers with 2,6-DCPFC

In a round-bottomed flask (50 mL) equipped with a magnetic stirrer, a mixture of the substrate (1 mmol) in CH_3CN (5 mL) and 2,6-DCPFC (1 mmol) was placed. The reaction mixture was stirred at room temperature for the specified time (Table II). The progress of the reaction was monitored by TLC. After the reaction was completed, the mixture was filtered and the solid material was washed with diethyl ether (2 × 10 mL). The combined filtrate was evaporated under reduced pressure to afford an almost pure carbonyl compound in 82–100%. If necessary, the products were further purified on a silica-gel plate or silica-gel column with an appropriate eluent.

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