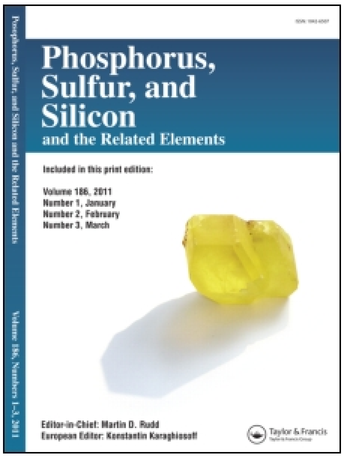

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QUINULINIUM FLUOROCHROMATE $C_9H_7NHCrO_3F$: AN EFFICIENT AND CONVENIENT REAGENT FOR THE OXIDATIVE DEPROTECTION OF TRIMETHYLSILYL ETHERS IN NON-AQUEOUS CONDITIONS

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Primary and secondary trimethylsilyl ethers are efficiently converted to their carbonyl compound using quinolinium fluorochromate in nonaqueous conditions.

Keywords: Deprotection; oxidative; quinoliniumfluoro chromat; trimethylsilyl ether

The protection of certain functional groups and the deprotection of the protected derivatives 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 method for the protection of this functional group.[6–8] Direct oxidation of trimethylsilyl ethers to their corresponding carbonyl compound has found considerable attention during recent years.[9–20]

However, some of the reported methods show limitation such as use of expensive reagents, long reaction time, low yields of the products, and tedious work-up. Therfore, the introduction of new methods and

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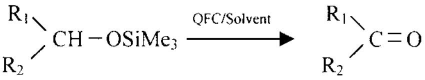
inexpensive reagents for such functional group transformation is still in demand.

RESULTS AND DISCUSSION

We report here a new and efficient method for the cleavage of trimethylsilyl ethers using quinoliniumfluoro chromat. This reagent recently has been used for the oxidation of alcohols.[21] For this purpose, first, we have studied the oxidative deprotection of benzyltrimethylsilyl ether to benzaldehyde with this reagent in common organic solvent, such as MeCN, CH_2Cl_2, $CHCl_3$, THF and n-hexane. The experimental results show that MeCN is a suitable solvent for these oxidations (Scheme 1) (Table I).



SCHEME 1

When a variety of trimethylsilyl ethers were treated with quinoliniumfluoro chromat, the corresponding carbonyl compound were obtained in excellent yields (Table II).

It is important to note that the reaction medium was almost neutral, so that some of the sensitive functionalities such as the carbon-carbon double bond remained intact (Table II, entry 15).

In conclusion quinoliniumfluoro chromat is a mild, efficient, and inexpensive reagent for the one-pot oxidative deprotection of trimethylsilyl ethers to the corresponding carbonyl compound in nonaqueous condition.

TABLE I Oxidative Deprotection of Benzyltrimethylsilyl Ether in Different Solvents Using QFC at 25°C

Entry	Solvent	Time (h)	Yield (%)[a,b]
1	CH_2Cl_2	2	45
2	$CHCl_3$	2	35
3	THF	2	30
4	c-C_6H_{12}	2	45
5	CH_3CN	0.6	92

[a] Yields refer to isolated products as their 2,4-dinitro phenylhydrazones.

[b] Substrate/oxidant (1/1).

TABLE II Oxidative Deprotection of Trimethylsilyl Ethers with QFC in CH_3CN at 25°C

Entry	Substrate	Time (h)	Products	Yield (%)[a]
1	$C_6H_5CH_2OTMS$	0.6	C_6H_5CHO	92
2	$(C_6H_5)_2CHOTMS$	1.6	$(C_6H_5)_2CO$	93
3	o-$ClC_6H_4CH_2OTMS$	0.8	o-ClC_6H_4CHO	89
4	p-$ClC_6H_4CH_2OTMS$	0.75	p-ClC_6H_4CHO	92
5	m-$MeOC_6H_4CH_2OTMS$	0.8	m-$MeOC_6H_4CHO$	93
6	p-$MeOC_6H_4CH_2OTMS$	0.5	p-$MeOC_6H_4CHO$	94
7	o-$MeOC_6H_4CH_2OTMS$	0.8	o-$MeOC_6H_4CHO$	94
8	$C_6H_5CH(p\text{-}ClC_6H_4)OTMS$	1.2	$C_6H_5C(p\text{-}ClC_6H_4)O$	95
9	p-$MeC_6H_4CH_2OTMS$	1.5	p-MeC_6H_4CHO	91
10	$C_6H_5CH_2CH_2CH_2OTMS$	1.2	$C_6H_5CH_2CH_2CHO$	90
11	p-$NO_2C_6H_4CH_2OTMS$	1.5	p-$NO_2C_6H_4CHO$	89
12	m-$NO_2C_6H_4CH_2OTMS$	1.4	p-$NO_2C_6H_4CHO$	92
13	$CH_3(CH_2)_7OTMS$	1.7	$CH_3(CH_2)_6CHO$	85
14	$CH_3(CH_2)_6OTMS$	1.6	$CH_3(CH_2)_5CHO$	86
15	$C_6H_5CH{=}CHCH_2OTMS$	0.7	$C_6H_5CH{=}CHCHO$	94

[a] Isolated yields.

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. QFC was prepared according to the literature.[21]

General Procedure for the Oxidative Deprotection of Trimethylsilyl Ethers with QFC

Trimethylsilyl ethers (1 mmol) was added to a stirred suspension of QFC (0.249 g, 1 mmol) in CH_3CN (15 ml). The reaction mixture was stirred at room temperature for 0.5–1.7 h. The progress of the reaction was monitored by TLC (eluent:hexane/ethyl acetate, 10:1). After the reaction was complete the mixture was filtered, and the solid material was washed with diethyl ether several times. The combined filtrate was evaporated under reduced pressure and the resulting crude material was purified on a silica-gel plat or silica-gel column with an appropriate eluent. Pure compounds were obtained in 85–94% yields (Table II).

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