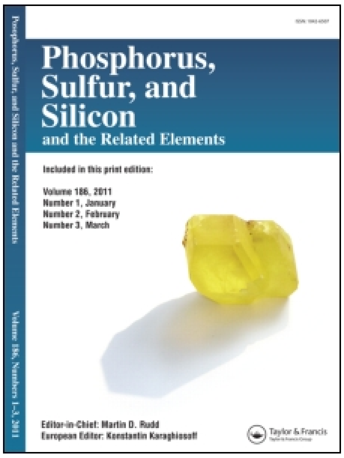

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Quinolinium Fluorochromate: An Efficient and Convenient Reagent for Oxidative Cleavage of Thioacetals to Their Parent Carbonyl Compounds

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Deprotection of thioacetals to their parent carbonyl compounds in high yields has been carried out using quinolinium fluorochromate under mild conditions.

Keywords Aldehydes; deprotection; ketones; thioacetals; quinolinium fluorochromate

INTRODUCTION

Thioacetals are used frequently to protect carbonyl compounds in the course of the total synthesis of organic compounds, and hence several reagents have been developed for their deprotection.[1,2] Despite the availability of many reagents and procedures for deprotection into their parent carbonyl compounds, most reagants are usually not straightforward. Therefore, considerable efforts have been directed towards developing mild and selective methods for thioacetal deprotection. Typically, most of these methods require the use of protic or lewis acids and a large number of these methods require drastic conditions or toxic reagents such as mercuric[3] and Fe (III) reagents or heavy metal salts.[4]

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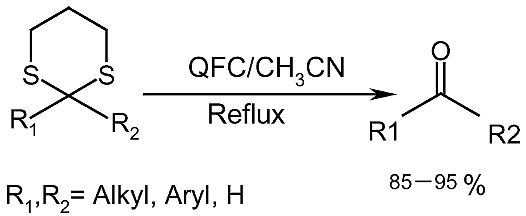
Thioacetals also have been deprotected by the combined use of molecular oxygen and catalytic amounts of $Bi(NO_3)_3.5H_2O$.[5] Recently, some nonmetallic reagents, such as trimethyloxonium tetrafluoroborate,[6] methylfluorosulphonate,[7] and oxides of nitrogen,[8] also have been used for deprotection. Usually, these methods are expensive and require multistep operations.

RESULTS AND DISCUSSION

Herein we wish to report an extremely mild method for the deprotection of thioacetals to the corresponding carbonyl compounds with Quinolinium Fluorochromate (QFC, Scheme 1). This reagent recently has been used for the oxidation of alcohols,[9] the deprotection of trimethylsilyl ethers,[10] the oxidative cleavage of oximes and phenylhydrazones,[11] the conversion of thioamides and thioureas to their oxygen analogues,[12] and the oxidation of thiols to disulfides,[13] and it has certain advantages over similar oxidizing agents. The results obtained with QFC are satisfactory and suggest that this new reagent is a valuable addition to the existing oxidizing agents.

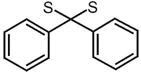
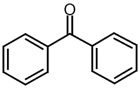
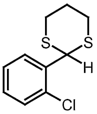
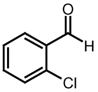
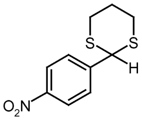
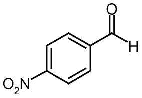
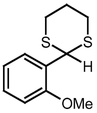
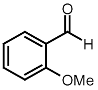
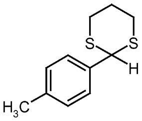
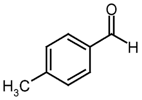
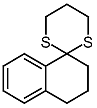
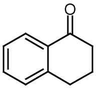
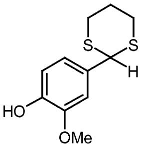
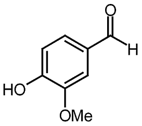
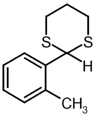
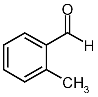
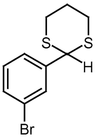
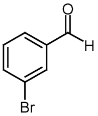
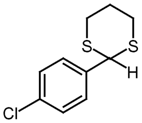
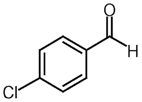


SCHEME 1

Our experiments show that thioacetals are converted to their corresponding aldehydes and ketones in a suitable solvent. Further oxidation of aldehydes to their carboxylic acids are not observed. Furthermore, functional groups, such as chloro, boromo, methoxy, nitro, and alkyl, also were inert to this reagent and no byproduct formation was observed (Table I).

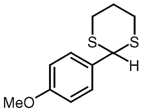
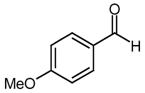
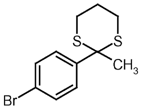
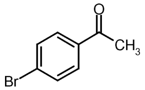
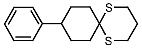
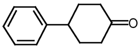
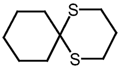
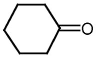
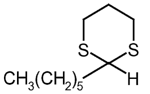
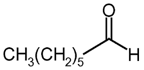
The effect of solvent in the oxidation reaction was evaluated by carrying out the oxidation in a series of solvents with varying polarity. Deprotection of 2-chlorobenzaldehyde thioacetal with QFC in a 1:2.5 ratio was carried out in dichloromethane, chloroform, tetrahydrofuran, cyclohexan, dioxane, and acetonitril at reflux temperature. The results are presented in Table II. As indicated in this table, acetonitril was found to be the best choice for this transformation. This probably is due to greater solubility of the reagent in this solvent.

TABLE I Oxidative Deprotection of Thioacetals With QFC in CH_3CN at Reflux Temperature

Entry	Substance	Time (h)	Product	Yields[a] %
1		4.5		90
2		4		92
3		4.5		85
4		3.5		92
5		2.5		87
6		2		95
7		4		91
8		3		94
9		2.5		93
10		4		91

(Continued on next page)

TABLE I Oxidative Deprotection of Thioacetals With QFC in CH_3CN at Reflux Temperature *(Continued)*

Entry	Substance	Time (h)	Product	Yields[a] %
11		3.5		94
12		2.5		95
13		4		90
14		4		85
15		4		88

[a]Yields refer to isolated products.

In conclusion, we have developed a mild method for the regeneration of carbonyl compounds from thioacetal that possess significant advantages over the existing methods, such as having simple procedure, a high yield, and mild conditions.

EXPERIMENTAL

Products were isolated and their physical data were compared with those of known samples. Solvent was freshly distilled. Thioacetals[14] and QFC[10] were prepared according to the described procedures.

TABLE II Oxidative Deprotection of 2-Chlorobenzaldehyde Thioacetal in Diffrent Solvents Using QFC at a Reflux Temperature

Entry	Solvent	Reaction Period (h)	Yields(%)[a]
1	CH_2Cl_2	3	15
2	$CHCl_3$	4	20
3	THF	3	10
4	c-C_6H_{12}	4	5
5	Dioxane	5	30
6	CH_3CN	4	92

[a]Yields refer to isolated products.

General Procedure for the Regeneration of Carbonyl Compounds from Thioacetals

Thioacetal (1 mmol) was added to a stirred suspension of QFC (0.622 g, 2.5 mmols) in acetonitril (15 mL). The reaction mixture was stirred at reflux temperature for 2–4.5 h. The progress of the reaction was monitored by TLC (eluent: CH_2Cl_2/CCl_4, 1:1). After completion of the reaction, the mixture was filtered and the solid material was washed with diethylether. The combined filtrate was evaporated under reduced pressure to give almost pure products in a 85–95% yield (Table I). If necessary, the products were purified further on a silica-gel plate or silica-jel column with an appropriate eluent.

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