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Tetramethylammonium fluorochromate(VI): a new and efficient oxidant for organic substrates

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Abstract—Tetramethylammonium fluorochromate(VI), $(CH_3)_4N^+CrO_3F^-$ (TMAFC), was prepared and used for quantitative oxidation of several organic substrates. This new compound is more efficient and has certain advantages over similar oxidizing agents in terms of the amount of oxidant and solvent required, short reaction times and high yields. © 2003 Published by Elsevier Science Ltd.

The oxidation of organic substrates in aprotic solvents, under mild and neutral conditions, is important in modern organic synthesis. Therefore, the search for new oxidizing agents is of interest to synthetic organic chemists. Many such reagents have been developed in recent years with some success.[1] In particular, there is continued interest in the development of new chromium(VI) reagents for the effective and selective oxidation of alcohols, under mild conditions. Of the large number of 'mild' chromium based oxidizing agents available, many prove impractical when the reactions are performed on a large (mol) scale,[2] although in recent years, significant improvements have been achieved by the use of new oxidizing agents.[3–5] Examples are: pyridinium chlorochromate,[6] pyridinium dichromate,[7] pyridinium fluorochromate[8] and 2,2′-bipyridinium chlorochromate.[9] Tetramethylammonium fluorochromate (TMAFC) was synthesized with the belief that this reagent could be used for the oxidation of organic substrates. There were two primary incentives for selection of $(CH_3)_4N^+$ as the counter ion. Firstly, quaternary ammonium ions are often used as phase transfer catalysts. This could make TMAFC a more efficient and stronger oxidizing agent.[10,11] Secondly, quaternary ammonium ions are used as crystal growing agents. Hence using this counter ion, improves the quality of the TMAFC crystals.[12]

TMAFC was prepared inside a glove box purged with argon. Chromium(VI) oxide (1.07 g, 10.7 mmol) was dissolved in dry acetonitrile (25 ml) in a polyethylene beaker and a stoichiometric amount of tetramethylammonium fluoride (1 g, 10.7 mmol) was added with stirring at room temperature. Within 5 min a clear orange solution formed which upon refrigerating, gave solid TMAFC, which was isolated by filtration. The solid was washed with dry isopropanol and diethyl ether, and dried under vacuum for 1 h. The solid was dissolved in acetonitrile and slow evaporation (1 week) furnished suitable crystals of TMAFC. Satisfactory elemental analysis was obtained. $(CH_3)_4N[CrO_3F]$: calcd: C, 24.85; H, 6.21; N, 7.25, found: C, 24.52; H, 6.42; N, 7.21%. IR, UV/vis, ^{19}F, ^{1}H NMR and single-crystal X-ray diffraction analysis were all consistent with the TMAFC structure.

This work provides a useful new oxidant for organic chemists. The chemistry of TMAFC has been explored as an oxidizing agent (Scheme 1, Table 1).

$$RCR'HOH + (CH_3)_4N[CrO_3F] \longrightarrow RCR'O + (CH_3)_4N[CrO_2F] + H_2O$$

Scheme 1.

Keywords: oxidant; chromium(VI) reagents; tetramethylammonium fluorochromate(VI); oxidation; organic substrates.

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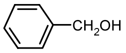
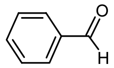
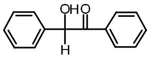
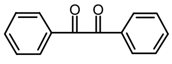
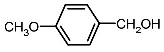
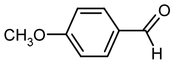
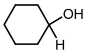
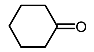
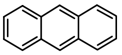
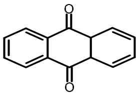
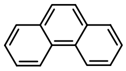
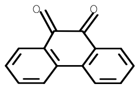
Table 1. Oxidation of alcohols **1** and polycyclic arenes **3** with TMAFC, PFC[a] and IQFC[b]

		TMAFC					PFC		IQFC	
Substrate		Substrate /Oxidant Ratio	Time (min)	Product		Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)
1a	n-C_3H_7-OH	1/1	200	**2a**	n-C_2H_5-CHO	90	210	90	NR[c]	NR
1b	n-C_4H_9-OH	1/1	120	**2b**	n-C_3H_7-CHO	98	120	94	NR	NR
1c		1/1	40	**2c**		95	45	90	60	91
1d		1/1	120	**2d**		98	150	98	180	98
1e		1/1	50	**2e**		95	50	90	NR	NR
1f		1/1	125	**2f**		98	210	89	240	90
3a		1/2	33	**4a**		98	150	68	300	72
3b		1/2	45	**4b**		98	240	68	360	51

[a] Pyridinium fluorochromate(VI)
[b] Isoquinolinium fluorochromate(VI)
[c] NR: Not Reported

In order to examine the oxidative ability of TMAFC the following typical procedure was employed: In a small-scale experiment TMAFC (1 mmol) was suspended in methylene chloride (ca. 2 ml) and an alcohol (l mmol in 0.5–1.5 ml of CH_2Cl_2) was rapidly added at room temperature and the resulting mixture stirred vigorously for the appropriate time (Table 1). The molar ratio of substrate to oxidant was 1:1 in the case of alcohols **1** and 1:2 in the case of polycyclic arenes **3**. The solution became homogeneous briefly before the black-brown reduced reagent precipitated. The progress of the reactions were monitored by TLC and UV/visible spectrophotometry (at 352 nm). Analysis of the reaction mixture for the corresponding carbonyl compound was accomplished by the procedure reported in earlier papers.[8,13] The above procedure may be carried out on 1–100 g scales without any problem.

Table 1 summarizes the products, yields and times of reaction of TMAFC with various substrates. The oxidative effect of TMAFC on polycyclic rings appears more pronounced than alcohols (Table 1). This could be due to the interaction of π electrons with the quaternary cation as suggested by Felder[14] and Pullman.[15] The probable importance of such interactions in biological recognition processes has been emphasized by Dougherty et al. on the basis of a number of observations made by their group and others.[16] Granier et al.[17] have already linked higher reactivities with the extent of symmetry about the Cr for $MCrO_3F$ (M = K, Rb, Cs and NH_4). They concluded that the inequality between the Cr–O and the Cr–F bonds is responsible for higher reactivity. Interestingly, our X-ray data clearly demonstrate such inequality. The reason for this inequality is due to the CH···F hydrogen bond that forms between the methyl hydrogen of the cation and the fluoride atom of the anion. This type of hydrogen bonding in tetramethylammonium salts has been studied by Harmon.[18] TMAFC appears to be a stronger reagent than others; this could be due to its lower symmetry.

It has also been found that this reagent has certain advantages over similar oxidizing agents in terms of amounts of oxidant and solvent required, and especially in the short reaction times required and in higher product yields[8,19,20] (Table 1).

Because of the stability and solubility of TMAFC, reactions can be performed at room temperature and the separation of the products is facile. During the reactions, the color of the oxidant changes from orange to brown, providing visual means for ascertaining the progress of the oxidation. The mechanism for the present oxidation is still unclear. However, we assume that the mechanism of oxidation is similar to that of other fluorochromates. In addition this oxidant and the oxidation conditions can be used for the synthesis of highly functionalized molecules.

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