

Microwave Assisted Oxidation of Organic Substrates Using Tetramethylammonium fluorochromate (TMAFC)

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An efficient and mild methodology for oxidation of some organic compound is described using tetramethylammonium fluorochromate (TMAFC) under microwave irradiation.

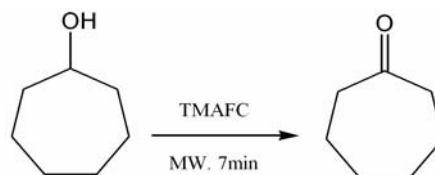
The oxidation of organic substrates in aprotic solvents, under mild and neutral conditions, is important in modern organic synthesis. Therefore, the search for new oxidizing agents is of interest to synthetic organic chemists. Many such reagents have been developed in recent years with some success.¹ 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 fluorochromate⁸, 2,2'-bipyridinium chlorochromate⁹, tripropylammonium fluorochromate¹⁰ and tetramethylammonium fluorochromate (TMAFC)¹¹. On the other hand in recent years organic reactions assisted by microwave irradiation have gained special attention. The chief features of the microwave reactions are the enhanced selectivity, much improved reaction rates, milder reaction conditions and formation of cleaner products. These reactions are especially appealing as they can be carried out in open vessels thus avoiding the risk of development of high pressures in addition to the associated case of manipulation. In continuation of our ongoing work on development of highly efficient oxidation protocols, we observed that the oxidation of alcohols with tetramethylammonium fluorochromate (VI) (TMAFC) under microwave irradiation could be carried out much more quickly than using conventional techniques.

Tetramethylammonium fluorochromate (TMAFC) was prepared by the reported method.¹¹

In a small-scale experiment TMAFC (1 mmol) was suspended in dichloromethane (*ca.* 2 ml) and an alcohol (1 mmol in 0.5 to 1.5 ml of CH₂Cl₂) was rapidly added at room temperature and the resulting mixture stirred vigorously for the appropriate time. The mixture was irradiated for the time indicated in the table by microwave radiation (3.67 GHz, 300W) (Table 1). The molar ratio of substrate to oxidant was 1:1 in the case of alcohols and 1:2 in the case of polycyclic arenes. The solution became homogeneous briefly before the black-brown reduced reagent precipitated. The progresses 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.^{8,12} The above procedure may be carried out on 1-100 g scales without any problem.

Tetramethylammonium fluorochromate in dichloromethane oxidizes primary and secondary alcohols to the corresponding aldehydes or ketones in high yields under microwave irradiation.



The versatility of the procedure was further demonstrated by the oxidation of some natural products such as menthol and the sugar derivative 1, 2 : 5, 6 – di – O – isopropylidene – α – D – glucufuranose, in to the corresponding ketones respectively.

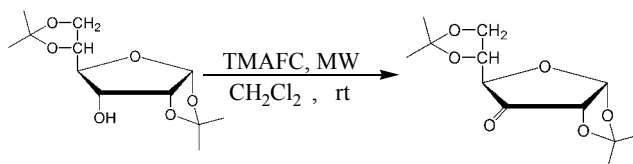


Table 1 summarizes the products, yields and times of reaction of TMAFC with various substrates. TMAFC chose as an oxidant, because it has been proven to be a useful oxidant in some reactions including the oxidation of alcohols. TMAFC as an oxidant is a very well suited reagent for microwave synthesis, because as an ionic and magnetically retrievable material, it carries a benefit of efficient conversion of electromagnetic energy into a heat according to the dielectric heating mechanism. Granier *et al.*¹³ have already linked higher reactivities with the extent of symmetry about the Cr for MCrO₃F (M= K, Rb, Cs and NH₄). 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 have been studied by Harmon.¹⁴ TMAFC appears to be a stronger reagent than others; this could be due to its lower symmetry. It has been found also 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.^{8,11,15,16}

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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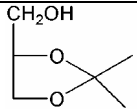
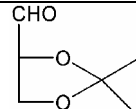
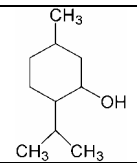
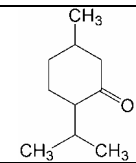
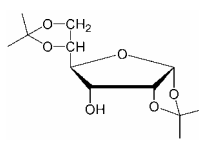
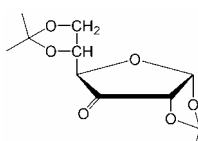
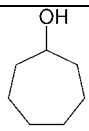
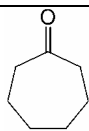
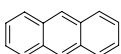
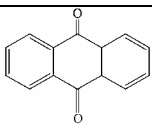
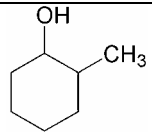
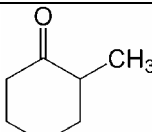
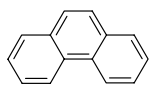
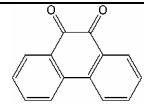
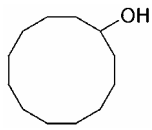
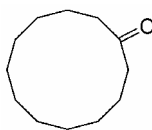
Substrate	Time (Min)	Product	Yield %	Substrate	Time (Min)	Product	Yield %
$\text{CH}_3(\text{CH}_2)_4\text{CH}_2\text{OH}$	3	$\text{CH}_3(\text{CH}_2)_4\text{CHO}$	95		15		89
$\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{OH}$	11	$\text{CH}_3(\text{CH}_2)_6\text{CHO}$	95		6		95
2- $\text{CH}_3(\text{CH}_2)_9\text{CH}_2\text{OH}$	8	2- $\text{CH}_3(\text{CH}_2)_9\text{CHO}$	92		13		92
	7		92		15		98
	10		90		23		90
	16		98				

Table 1. Oxidation of some organic substrates with TMAFC under microwave radiation

