

## SHORT COMMUNICATION

### MICROWAVE-ASSISTED OXIDATION OF ALCOHOLS AND POLYARENES WITH TETRAMETHYLAMMONIUM FLUOROCHROMATE

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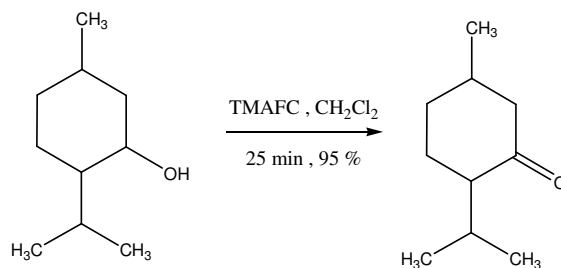
**ABSTRACT.** An efficient and mild method for the oxidation of alcohols and polyarenes is described using tetramethylammonium fluorochromate (TMAFC) under microwave irradiation.

**KEY WORDS:** Oxidation, Alcohols, Polyarenes, Microwave irradiation

## INTRODUCTION

The oxidation of alcohols to carbonyl compounds is a fundamental transformation in organic chemistry since carbonyl compounds are widely used as intermediates both in manufacturing and research [1]. Although the oxidation of organic compounds under non-aqueous conditions has become an effective technique for modern organic synthesis [2], the methods still suffer some disadvantages including the cost of preparation, long reaction time, and tedious work-up procedures. In recent years, oxidation processes have received much attention, especially in the search for selective and environmentally friendly oxidants [3, 4].

Recently, using reactants adsorbed on inorganic supports and microwave activation, Varma *et al.* [5] have published several examples of oxidation reactions of alcohols to carbonyl compounds as well as sulfides to sulfoxides and sulfones. Under similar conditions (KMnO<sub>4</sub> adsorbed on alumina), Loupy *et al.* [6] have converted aromatic hydrocarbons to aromatic ketones; whereas Palombi *et al.* [7] oxidised alcohols using *t*-butyl hydroperoxide supported on zeolites. In the present paper we report a fast and facile microwave accelerated oxidation of primary alcohols to aldehydes and secondary alcohols to ketones (Scheme 1).



Scheme 1

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The oxidation reactions of some alcohols and polyarenes by TMAFC using conventional heating have been reported earlier by us [8].

### EXPERIMENTAL

Experiments were carried out in closed vessel multi mode Microsynth Milstone laboratory microwave oven using a 900 Watts Westpointe microwave operating at 3.67 GHz with an internal volume of 0.9 m. All the experiments had good reproducibility by repeating the experiments in same conditions.

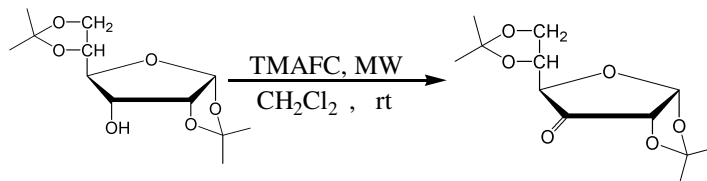
Tetramethylammonium fluorochromate (TMAFC) was prepared by the reported method [8]. In a small-scale experiment TMAFC (1 mmol) was suspended in dichloromethane (ca. 2 mL) and an alcohol (1 mmol in 0.5 to 1.5 mL of  $\text{CH}_2\text{Cl}_2$ ) was rapidly added at room temperature and the resulting mixture stirred vigorously for the appropriate time. The mixture was irradiated for the time indicated in Table 1 by microwave radiation (3.67 GHz, 300 W). The molar ratio of substrate to oxidant was 1:1 in the case of alcohols and 1:2 in the case of polycyclic arenes (anthracene and phenanthrene). The solution became homogeneous briefly before the black-brown reduced reagent precipitated. The progresses of the reactions were monitored by TLC and UV/Visible spectrophotometer (at 352 nm). Analysis of the reaction mixture for the corresponding carbonyl compound was accomplished by the procedure reported in earlier papers. [9, 10]. The above procedure may be carried out on 1-100 g scales without any problem.

### RESULTS AND DISCUSSION

TMAFC was used for the oxidation of some alcohols and polycyclic arenes under microwave irradiation in  $\text{CH}_2\text{Cl}_2$  as solvent. This method offers some advantages in term of simplicity of performance, simple operation condition, no side product formation, very low reaction time and a wide range of substrates can be converted to their corresponding aldehydes and ketones. In addition, the reduced reagent  $(\text{CH}_3)_4\text{N}^+\text{CrO}_2\text{F}^-$  can also be recycled after oxidation.

TMAFC is very good reagent for the oxidation based on quaternary ammonium halochromates. In our research on oxidation processes, we chose TMAFC as an oxidant, because it has been proven to be a useful oxidant in some reactions including the oxidation of alcohols [8]. 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 heat according to the dielectric heating mechanism.

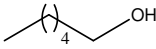
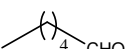
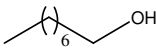
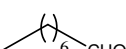
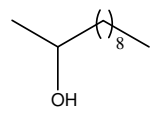
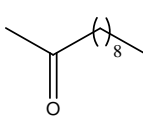


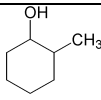
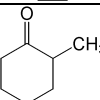
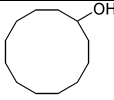
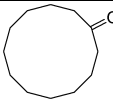
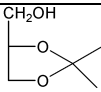
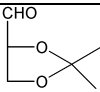
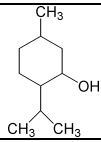
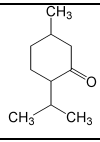
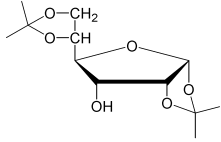
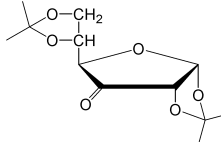
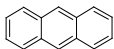
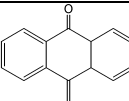
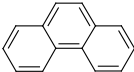
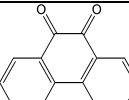
The versatility of the procedure was further demonstrated by the oxidation of some natural products such as menthol and the sugar derivative 1,2,5,6-di-O-isopropylidene- $\alpha$ -D-glucofuranose, in to the corresponding ketones respectively (Scheme 2).



Scheme 2

Table 1 summarizes the products, yields and times of reaction of TMAFC with various alcohols and polyarenes.

Table 1. Oxidation of some alcohols and polyarenes with tetramethylammonium fluorochromate: TMAFC.

Substrate	Time (min)	Product	Yield%
	6		95
	11		95
	13		92
	17		92
	15		90
	16		98
	15		89
	25		95
	13		92
	20		98
	23		90

The carbonyl compounds were obtained with satisfactory yield and in a short time (Table 1) as compare to articles that published earlier by us [8].

The primary alcohols were turned into the desired aldehydes without over oxidizing them to carboxylic acids. The reactivity of the secondary alcohols seems to be slightly lower, but the addition of higher amount of the oxidant did not increase the yield of desired ketones. It seems that oxidation is also efficient for the oxidation of polycyclic arenes such as anthracene and phenanthrene in microwave irradiation with compare to conventional heating.

### CONCLUSION

In conclusion, we have described a highly efficient microwave-induced modification of conventional heating procedure for the oxidation of alcohols that allows for the rapid synthesis of aldehydes or ketones.

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### REFERENCES

1. Trost, B.M. *Comprehensive Organic Synthesis (Oxidation)*, Vol. 7, Pergamon: New York; **1991**.
2. Hudlicky, M. *Oxidations in Organic Chemistry*, ACS Monographs 186, ACS: Washington, DC; **1990**.
3. (a) Sato, K.; Aoki, M.; Noyori, R. *Science* **1998**, 281, 1646. (b) Sato, K.; Aoki, M.; Tagaki, J.; Noyori, R. *J. Am. Chem. Soc.* **1997**, 119, 12386.
4. (a) Varma, R.S.; Saini, R.K. *Tetrahedron Lett.* **1998**, 39, 1481. (b) Varma, R.S.; Dahiya, R. *Mol. Online* **1998**, 2, 82. (c) Varma, R.S.; Dahiya, R. *Tetrahedron Lett.* **1998**, 39, 1307. (d) Varma, R.S.; Saini, R.K.; Dahiya, R. *Tetrahedron Lett.* **1997**, 45, 7823.
5. (a) Varma, R.S.; Dahiya, R. *Tetrahedron Lett.* **1997**, 38, 2023. (b) Varma, R.S.; Saini, R.K.; Meshram, H.M. *Tetrahedron Lett.* **1997**, 38, 6525. (c) Varma, R.S.; Saini, R.K.; *Tetrahedron Lett.* **1998**, 39, 1481. (d) Varma, R.S.; Saini, K.S.; Dahiya, R. *Tetrahedron Lett.* **1997**, 38, 7823. (e) Varma, R.S.; Saini, K.S.; Dahiya, R. *J. Chem. Res. (S)* **1998**, 120.
6. Qussaid, A.; Loupy, A. *J. Chem. Res. (S)* **1997**, 342
7. Palombi, L.; Bonadies, F.; Scettri, A. *Tetrahedron* **1997**, 53, 15867.
8. Mahjoub, A.R.; Ghammami, S.; Kassae, M.Z. *Tetrahedron Lett.* **2003**, 44, 4555.
9. Bhattacharjee, M.N.; Chaudhuri, M.K.; Dasgupta, H.S.; Roy, N. *Synthesis* **1982**, 588.
10. Piancatelli, G.; Scettri, A.; Auria, M.D. *Synthesis* **1982**, 245.