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Oxidation of Alcohols with Tripropylammonium Fluorochromate, $(C_3H_7)_3NH[CrO_3F]$ Under Microwave Irradiation

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An efficint and mild methodology for oxidation of alcohols is described, using tripropylammonium fluorochromate $(C_3H_7)_3NH[CrO_3F]$, under microwave irradiation. The easy procedure, simple wake-up, short reaction time and excellent yields are another advantages of this reagent.

Key Words: Tripropylammonium fluorochromate, Microwave, Irradiation, Alcohol, Oxidation.

INTRODUCTION

The oxidation of organic substrates in aprotic solvents, under mild and neutral conditions, is important in modern organic synthesis. Amoung them the oxidation of alcohols plays an important role in organic synthesis and since carbonyl compounds are widely used as intermediates both in manifactury an libratory. Therefore, the search for new oxidizing agents is of interest to synthetic organic chemists[1,2]. 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], 2,2'-bipyridinium chlorochromate[9], tripropylammonium fluorochromate[10] and tetramethylammonium fluorochromate[11]. On the other hand in recent years organic reactions assisted by microwave irradiation have gained special attention. The main 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 procedures, we observed that the oxidation of alcohols with tripropylammonium fluorochromates (TriPAFC) under microwave irradiation could be carried out much more quickly than using conventional techniques.

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EXPERIMENTAL

CrO_3 (Merck, P.A.) was used without further purification. Solvents were purified by standard methods. Infrared spectra were recorded as KBr disks on a Shimadzu model 420 spectrophotometer. The UV/Visible measurements were made on an Uvicon model 922 spectrometer. Proton, ^{13}C, ^{19}F NMR were carried out on a Bruker AVANCE DRX 500 spectrometer at 500, 125, 470.66 MHz. All the chemical shifts are quoted in ppm using the high-frequency positive convention; ^1H and ^{13}C NMR spectra were referenced to external $SiMe_4$ and ^{19}F NMR spectra to external $CFCl_3$. Chromium was estimated iodometrically. In the case of the reduced product of the oxidant, chromium was determined after oxidizing with acidic peroxodisulfate ($K_2S_2O_8$) solution. The relative concentrations of carbon, hydrogen and nitrogen were obtained from the Microanalytical laboratories, Department of Chemistry, OIRC, Tehran. Melting points were measured on Electrothermal 9100 melting point apparatus. A Microsynth Milstone laboratory microwave oven has been used.

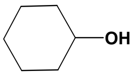
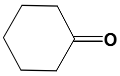
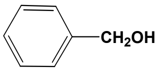
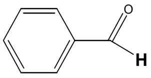
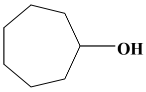
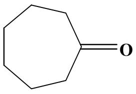
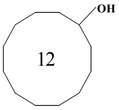
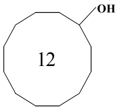
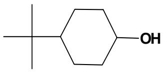
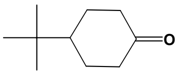
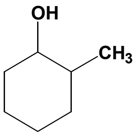
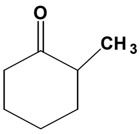
Synthesis of tripropylammonium fluorochromate (TriPAFC), $(C_3H_7)_3NH$ $[CrO_3F]$: A 1 g (10 mmol) sample of chromium(VI) oxide, CrO_3 and 0.9 mL (20 mmol) of 40 % hydrofluoric acid were added to 20 mL of water in a 100 mL polyethylene beaker with stirring. After 5-7 min the homogeneous solution was cooled to *ca.* 0-2 °C. To the resultant clear orange solution, tripropylamine (1.4 mL, 10 mmol) was added dropwise with stirring over a period of 0.5 h and stirring was continued for 0.5 h at -4 °C. The precipitated yellowish-orange solid was isolated by filtration on a polyethylene funnel, washed with petroleum ether (3 × 60 mL) and dried in vacuum for 2 h at room temperature Yield: (98 %); m.p. 142 °C, $C_9H_{22}NO_3FCr$: Calcd. (%) C, 41.05; H, 8.35; N, 5.31 Found (%) C, 41.22; H, 8.46; N, 5.02. IR (KBr, cm^{-1}): 904 $\nu_1(A_1)$ or $\nu(CrO_3)$, 647 $\nu_2(A_1)$ or $\nu(Cr\text{-}F)$, 949 $\nu_4(E)$ or $\nu(CrO_3)$, Electronic absorption at 22321 cm^{-1}, corresponded to $^1A_2 \rightarrow {}^1E$ (ε = 140 M^{-1} cm^{-1}); 28729 cm^{-1} to $^1E \rightarrow {}^1E$ (ε = 667 M^{-1} cm^{-1}) and 35951 cm^{-1} to $^1A_2 \rightarrow {}^1E$ (ε = 1287 M^{-1} cm^{-1}). UV/Visible, ^{13}C NMR, ^1H NMR and ^{19}F NMR were all consistent with the TriPAFC structure. The above procedure can be scaled up to larger quantities, if desired. The pH of 0.01 M solution of TriPAFC in water was 3.3.

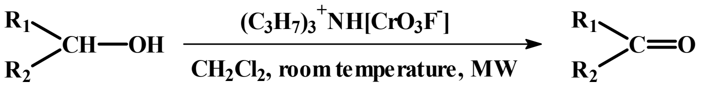
General procedure: In a typical reaction, 1 mmol of hexanol was dissolved in 2 mL of CH_2Cl_2 in a 150 mL conical flask and treated with 1.5 mmol of TriPAFC. The reaction mixture was then irradiated in the microwave oven (operation at 2.45 GHz, 200W) for 4 min at ambient procedure. On completion of the reaction (monitored by TLC). Quenched with 0.5 mL of methanol. The mixture was filtered through a short pad of silica gel with ethyl acetate and the solvent evaporated to yield hexanal in 89 % yield. No side products were observed to be formed. All the products were characterized by IR, NMR (^1H and ^{13}C). Mass spectra and direct comparison with authentic samples.

RESULTS AND DISCUSSION

The results obtained with tripropylammonium fluorochromates under microwave radiations are quite satisfactory. Tripropylammonium fluorochromates in dichloromethane under microwave radiations oxidizes primary and secondary alcohols to the corresponding aldehydes or ketones in high yields (Table-1).

TABLE-1
OXIDATION OF ALCOHOLS AND POLYCYCLIC ARENES WITH TriPAFC UNDER MICROWAVE CONDITION

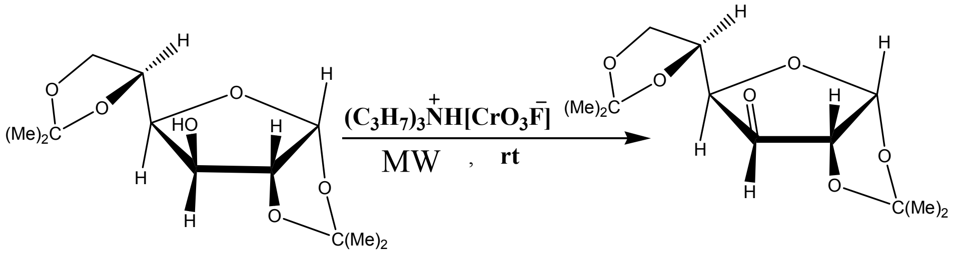
	Substrate	Product	TriPAFC	
			Time (min)	Yield (%)
1	n-C_3H_7-OH	n-C_2H_5-CHO	5	90
2	n-C_4H_9-OH	n-C_3H_7-CHO	4	90
3	n-C_5H_{11}-OH	n-C_4H_9-CHO	4	90
4	n-C_6H_{13}-OH	n-C_5H_{11}-CHO	4	89
5	n-$C_{11}H_{23}$-OH	n-$C_{10}H_{21}$-CHO	2	90
6	2-C_3H_7-OH	2-C_3H_6O	5	90
7	2-C_8H_{17}-OH	2-C_8H_{16}O	5	92
8			14	90
9			2	98
10			3	90
11			4	94
12			24	90
13			5	90



$$R_1R_2CH{-}OH \xrightarrow[CH_2Cl_2,\ room\ temperature,\ MW]{(C_3H_7)_3{}^{+}NH[CrO_3F^{-}]} R_1R_2C{=}O$$

Scheme-I

Tripropylammonium fluorochromates in dichloromethane also oxidize anthracene and phenanthrene to anthraquinone and phenanthraquinone in 66 and 63 % yields under microwave radiations respectively. This reagents work as efficiently as activated manganese dioxide or Collins reagent[12]. The reaction of triphenylphosphine with TriPAFC (molar ratio of PPh_3: TriPAFC = 1:1.1) in acetonitrile were carried out at room temperature and triphenylphosphine oxide was obtained in a quantitative yield. This provides a clear-cut example of an oxygen transfer reaction involving TriPAFC and the result may also be useful in defining other related reactions. Tripropylammonium fluorochromates have also been used for oxidation of carbohydrates such as 1, 2: 5, 6 -Di-O- isopropylidine -α-D-glucofuranose to its relative ketosuga like as pyridinium chlorochromate[13] by use of the equimolar ratio of the reagent. The data of the oxidation under microwave radiations show the chief features of the microwave reactions that are the enhanced selectivity, much improved reaction rates, milder reaction conditions and formation of cleaner products.



Scheme-II

Tripropylammonium fluorochromates are easily prepared in high yields from chromium(VI) oxide, tripropylamine and aqueous hydrofluoric acid (HF) in a convenient molar ratio. The bright orange crystalline reagent can be stored in polyethylene containers for long periods without decomposition. The IR spectrum of the reagents are similar to that of other fluorochromates[14]. Tripropylammonium fluorochromates is soluble in water, dimethylformamide, acetonitrile and acetone; it is less soluble in dichloromethane and only sparingly soluble in benzene, carbon tetrachloride, chloroform and hexane.

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