

Note

Trimethylammonium fluorochromate (TriMAFC): A convenient new and mild reagent for oxidation of organic substrates

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Trimethylammonium fluorochromate (TriMAFC) is easily synthesized by addition of a trimethylamine to an aqueous solution of CrO₃ and HF and used for quantitative oxidation of several organic substrates. This reagent is a versatile reagent for the effective and selective oxidation of organic substrates, in particular for alcohols, under mild conditions.

Keywords: Chromium(VI) reagents, trimethylammonium fluorochromate, oxidation, organic substrate

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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. In particular, there is continued interest in the development of new chromium(VI) reagents for the effective and selective oxidation of organic substrates, in particular alcohols, under mild conditions. In recent years, significant improvements were achieved by the use of new oxidizing agents¹⁻³, such as 3-carboxypyridinium chlorochromate⁴, pyridinium fluorochromate⁵, quinolinium dichromate⁶, caffeinilium chlorochromate⁷, quinolinium chlorochromate⁸, isoquinolinium fluorochromate⁹ and tetramethylammonium fluorochromate¹⁰. We have now investigated the synthetic potential of trimethylammonium fluorochromate, C₃H₁₀CrFNO₃, (TriMAFC) and found that this reagent has certain advantages over similar oxidizing agents in terms of

amounts of oxidant and solvent required, easier working up and high yields (**Scheme I**). Further, trimethylammonium fluorochromate does not react with acetonitrile, which is a suitable medium for studying kinetics and mechanism.

Results and Discussion

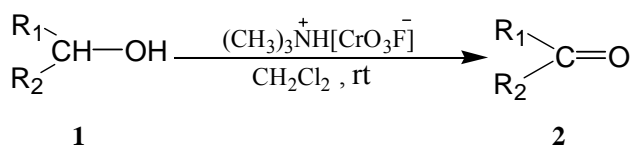
The results obtained with trimethylammonium fluorochromate are very satisfactory and show the new reagent as a valuable addition to the existing oxidizing agents. Trimethylammonium fluorochromate in dichloromethane oxidizes primary (**1a-h**) and secondary alcohols (**3a-i**) to the corresponding aldehydes (**2a-h**) or ketones (**4a-i**) in high yields (**Table I**).

Trimethylammonium fluorochromate also oxidizes anthracene **5a** and phenanthrene **5b** to anthraquinone **6a** and phenanthraquinone **6b** in 65% and 62% yields, respectively. This reagent works as efficiently as activated manganese dioxide or Collins reagent¹¹. The reaction of triphenylphosphine **7a** with TriMAFC (molar ratio of PPh₃-TriMAFC; 1:1.1) in acetonitrile was carried out at room temperature and triphenylphosphine oxide **8a** was obtained in a quantitative yield. This provides a clear-cut example of an oxygen transfer reaction involving TriMAFC, and the result may also be useful in defining other related reactions.

Trimethylammonium fluorochromate is easily prepared in 86% yield from chromium(VI) oxide, trimethylamine and aqueous 40% hydrofluoric acid in a molar ratio of 1:1:2. The bright orange crystalline reagent can be stored in polyethylene containers for long periods without decomposition. The chromium(VI) content may be easily determined iodometrically. The IR spectrum is similar to that of other fluorochromates¹². Trimethylammonium fluorochromate is soluble in water, dimethylformamide, acetonitrile, acetone and dichloromethane; it is only sparingly soluble in benzene, carbon tetrachloride, chloroform and hexane.

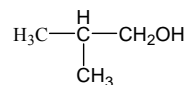
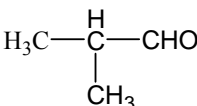
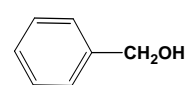
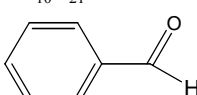
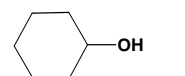
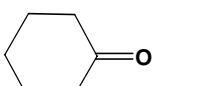
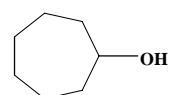
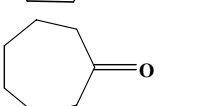
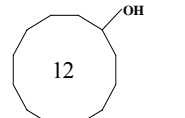
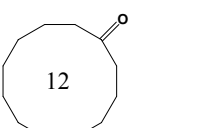
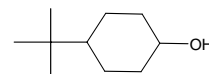
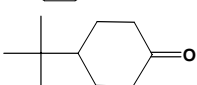
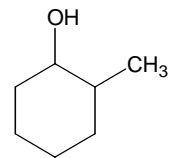
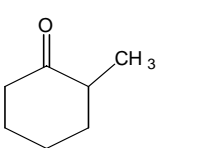
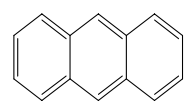
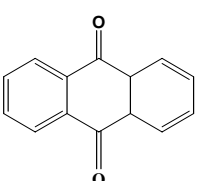
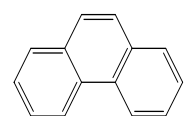
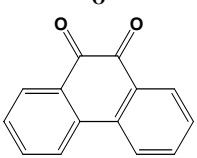
Experimental Section

CrO₃ (Merck, P.A.) was used without further purification. Solvents were purified by standard methods. IR spectra were recorded as KBr disks on a



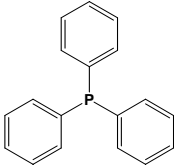
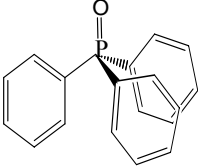
Scheme I

Table I — Oxidation of alcohols and polycyclic arenes with TriMAFC

Substrate		Substrate /Oxidant ratio	Time (min)	Product		Yield (%)	b.p./m.p. °C
<i>n</i> -C ₃ H ₇ -OH	1a	1/1	182	<i>n</i> -C ₂ H ₅ -CHO	2a	90	48-50
<i>n</i> -C ₄ H ₉ -OH	1b	1/1	165	<i>n</i> -C ₃ H ₇ -CHO	2b	90	74-75
<i>n</i> -C ₅ H ₁₁ -OH	1c	1/1	97	<i>n</i> -C ₄ H ₉ -CHO	2c	92	102
<i>n</i> -C ₆ H ₁₃ -OH	1d	1/1	115	<i>n</i> -C ₅ H ₁₁ -CHO	2d	90	129-31
	1e	1/1	64		2e	92	63-64
<i>n</i> -C ₈ H ₁₇ -OH	1f	1/1	160	<i>n</i> -C ₇ H ₁₅ -CHO	2f	95	170-72
<i>n</i> -C ₁₁ H ₂₃ -OH	1g	1/1	54	<i>n</i> -C ₁₀ H ₂₁ -CHO	2g	90	110-13
	1h	1/1	42		2h	92	177-79
2-C ₃ H ₇ -OH	3a	1/1	84	2-C ₃ H ₆ O	4a	90	55-57
3-C ₇ H ₁₅ -OH	3b	1/1	172	3-C ₇ H ₁₄ O	4b	90	146-48
2-C ₈ H ₁₇ -OH	3c	1/1	161	2-C ₈ H ₁₆ O	4c	90	172-73
2-C ₁₁ H ₂₃ -OH	3d	1/1	42	2-C ₁₁ H ₂₂ O	4d	90	230-34
	3e	1/1	7hr		4e	80	154-56
	3f	1/1	46		4f	92	179-81
	3g	1/1	75		4g	92	50-61
	3h	1/1	13h		4h	90	47-50
	3i	1/1	169		4i	90	162-63
	5a	1/2	4h		6a	65	284-85
	5b	1/2	4h		6b	62	208-10

— Contd

Table I — Oxidation of alcohols and polycyclic arenes with TriMAFC — *Contd*

Substrate	Substrate /Oxidant ratio	Time (min)	Product	Yield (%)	b.p./m.p. °C
 7a	1/1.1	4	 8a	97	156-57

Shimadzu model 420 spectrophotometer; UV/Visible spectra on a Uvicon model 922 spectrometer; and ^1H , ^{13}C and ^{19}F NMR spectra on Bruker AVANCE DRX 500 spectrometer at 500, 125, 470.66 MHz. All the chemical shifts are quoted in δ , ppm using the high-frequency positive convention; ^1H and ^{13}C NMR spectra were referenced to external TMS 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 ($\text{K}_2\text{S}_2\text{O}_8$) solution. The percent composition of carbon, hydrogen and nitrogen were obtained from the Microanalytical Laboratories, Department of Chemistry, OIRC, Tehran.

Preparation of trimethylammonium fluorochromate (TriMAFC), $\text{C}_3\text{H}_{10}\text{CrFNO}_3$. Chromium(VI) oxide (1g, 0.01 mole) was dissolved in water in a polyethylene beaker and 40 % hydrofluoric acid (0.9 mL, 0.02 mole) was added with stirring at 0°C . To the resultant clear orange solution, trimethylamine (0.8 mL, 0.01 mole) was added dropwise with stirring over a period of 0.5 hr and stirring was continued for another 0.5 hr at 0°C . The precipitated orange solid was separated by filtration, washed with pet. ether (3×60 mL) and dried *in vacuo* for 2 hr at room temperature, yield 1.53 g (86%), m.p. 126°C . Anal. Calcd for $\text{C}_3\text{H}_{10}\text{CrFNO}_3$: C, 20.11; H, 5.58; N, 7.82. Found: C, 20.08; H, 5.64; N, 7.69%; IR (KBr): 912 (A_1) or (CrO_3), 636 (A_1) or (Cr-F), 950 (E) or (CrO_3) cm^{-1} ; UV/Visible, ^{13}C NMR, ^1H NMR and ^{19}F NMR were all consistent with the TriMAFC structure. The above procedure can be performed on a 250g scale without any difficulty.

General procedure for oxidation of organic substrates. To a stirred suspension of trimethylammonium fluorochromate (2.5 g) in dichloromethane (generally 5 mL), a solution of the substrate in the minimum amount of dichloromethane was added dropwise, the molar ratio of substrate to the oxidant

being 1:1 in the case of alcohols (**1,3**) and 1:2 in the case of arenes **5** (**Table I**). The mixture was refluxed for the time indicated in **Table I** [The completion of the reaction is followed by UV/Visible and TLC using ether/pet. ether (60:40) as eluant]. The mixture was diluted with ether (1:1, vol/vol) and filtered through a short column of silica gel to give a clear solution. The solution was evaporated and the residual product purified by distillation, recrystallization or column chromatography. The progress of the reactions was also monitored and checked by UV/Visible spectrophotometry. The amount of the oxidant during the reaction was measured spectrophotometrically at 350 nm. A very small magnetic stirrer was designed at the cell (10 mm quartz cell) compartment just in the bottom of sample cell in the spectrophotometer to stir up the solution under study in cell. The reaction mixtures remained homogeneous in the solvent system used.

Reaction of TriMAFC with triphenylphosphine.

The reaction was performed under nitrogen atmosphere in a dry 100 mL round bottomed flask and under efficient stirring. To a vigorously stirred solution of triphenylphosphine (1.50 g, 5.70 mmoles) in acetonitrile (35 mL), TriMAFC (1.12 g, 6.27 mmoles) was added in two instalments in about one minute, maintaining the substrate - oxidant ratio at 1:1.1. An exothermic reaction set in instantaneously, and was complete in 5 min. The solution was cooled and the mother liquor and the washings, after separation of reduced TriMAFC product by centrifugation, were filtered through a short silica gel column (7×2 cm^2). The contents of the column were thoroughly washed with ether (3×35 mL) and filtered. The combined filtrates were evaporated on a steam-bath, and the product was characterized as triphenylphosphine oxide by elemental analyses and IR spectral studies, yield 1.54 g (97%), m.p. 155°C (lit.⁵ m.p. $156-57^\circ\text{C}$).

Acknowledgement

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