# Tripropylammonium Fluorochromate (TriPAFC): A Convenient New Reagent for Oxidation of Organic Substrates

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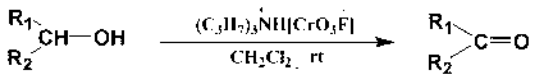
The search for new oxidizing agents is of interest to synthetic organic chemists. Many such reagents have been developed in recent years with some success. In particular, there is continued interest in the development of new chromium(VI) reagents for the effective and selective oxidation of organic substrates, in particular alcohols, under mild conditions. In recent years, significant improvements were achieved by the use of new oxidizing agents,[1-3] such as 3-carboxypyridinium chlorochromate,[4] pyridinium fluorochromate,[5] quinolinium dichromate,[6] caffeinilium chlorochromate,[7] quinolinium chlorochromate,[8] isoquinolinium fluorochromate[9] and tetramethylammonium fluorochromate.[10] We have now investigated the synthetic potential of tripropylammonium fluorochromate, $C_9H_{22}CrFNO_3$, (TriPAFC) and we have 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. Further, tripropylammonium fluorochromate does not react with acetonitrile, which is a suitable medium for studying kinetics and mechanism.

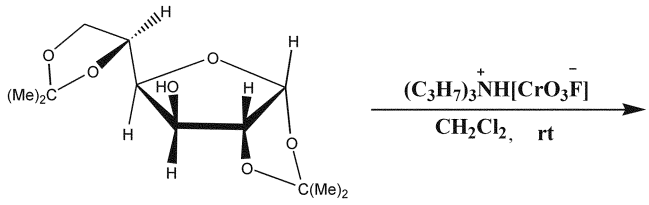
The results obtained with tripropylammonium fluorochromate are very satisfactory and shows the new reagent as a valuable addition to the existing oxidizing agents. Tripropylammonium fluorochromate in dichloromethane oxidizes primary (**1a-h**) and secondary alcohols (**3a-i**) to the corresponding aldehydes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



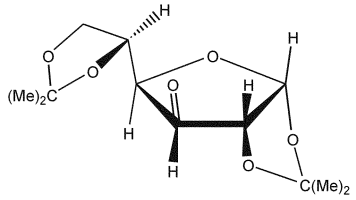

**1** **2**

Tripropylammonium fluorochromate in dichloromethane also oxidizes anthracene (**5a**) and phenanthrene (**5b**) to anthraquinone (**6a**) and phenanthraquinone (**6b**) in 70% and 65% yields respectively. This reagent works as efficiently as activated manganese dioxide or Collins reagent.[11] The reaction of triphenylphosphine (**7a**) with TriPAFC (molar ratio of $PPh_3$ : TriPAFC = 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 TriPAFC, and the result may also be useful in defining other related reactions.

Tripropylammonium fluorochromate has also been used for oxidation of carbohydrates such as 1,2: 5,6-Di-O-isopropylidine-$\alpha$-D-Glucofuranose (**9a**) to its relative ketosugar (**10a**) as pyridinium dichromate,[12] but in 92% yield, in 115 minutes and by use of the equimolar ratio of the reagent.




**9a**




**10a**

Tripropylammonium fluorochromate is easily prepared in 95% yield from chromium(VI) oxide, tripropylamine and aqueous 40% hydrofluoric acid in a molar ratio of 1 : 1 : 1.5. 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 fluorochromates.[13] Tripropylammonium fluorochromate is soluble in water, dimethylformamide, acetonitrile, acetone and dichloromethane; it is only sparingly soluble in benzene, carbon tetrachloride, chloroform and hexane.

## Experimental Section

**Preparation of tripropylammonium fluorochromate, (TriPAFC), $C_9H_{22}CrFNO_3$.** Chromium(VI) oxide (15.0 g, 0.150 mol) was dissolved in water in a polyethylene beaker and 40% hydrofluoric acid (11.3 mL, 0.225 mol) was added with stirring at 0 °C. To the resultant clear orange solution,

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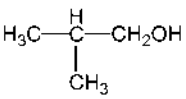
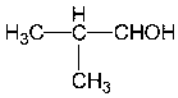
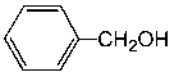
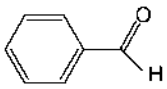
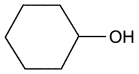
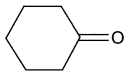
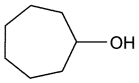
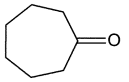
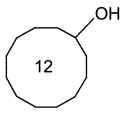
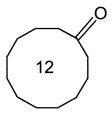
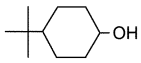
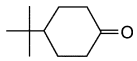
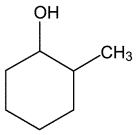
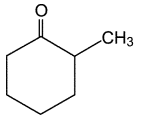
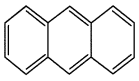
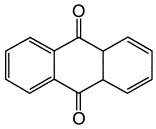
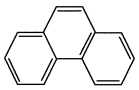
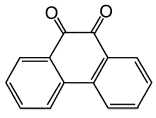
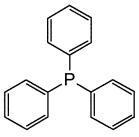
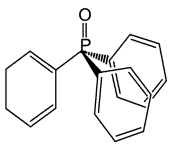
**Table 1**. Oxidation of alcohols and polycyclic arenes with TriPAFC

| | Substrate | Substrate/ Oxidant Ratio | Time (min) | | Product | Yield (%) | M.P. (°C) | B.P. (°C) |
|---|---|---|---|---|---|---|---|---|
| **1a** | *n*-$C_3H_7$-OH | 1/1 | 160 | **2a** | *n*-$C_2H_5$-CHO | 90 | | 48-50 |
| **1b** | *n*-$C_4H_9$-OH | 1/1 | 150 | **2b** | *n*-$C_3H_7$-CHO | 90 | | 74-75 |
| **1c** | *n*-$C_5H_{11}$-OH | 1/1 | 98 | **2c** | *n*-$C_4H_9$-CHO | 92 | | 102 |
| **1d** | *n*-$C_6H_{13}$-OH | 1/1 | 105 | **2d** | *n*-$C_5H_{11}$-CHO | 90 | | 129-131 |
| **1e** |  | 1/1 | 50 | **2e** |  | 92 | | 63-64 |
| **1f** | *n*-$C_8H_{17}$-OH | 1/1 | 98 | **2f** | *n*-$C_7H_{15}$-CHO | 90 | | 170-172 |
| **1g** | *n*-$C_{11}H_{23}$-OH | 1/1 | 47 | **2g** | *n*-$C_{10}H_{21}$-CHO | 90 | | 110-113 |
| **1h** |  | 1/1 | 39 | **2h** |  | 92 | | 177-179 |
| **3a** | 2-$C_3H_7$-OH | 1/1 | 64 | **4a** | 2-$C_3H_6O$ | 90 | | 55-57 |
| **3b** | 3-$C_7H_{15}$-OH | 1/1 | 155 | **4b** | 3-$C_7H_{14}O$ | 90 | | 146-148 |
| **3c** | 2-$C_8H_{17}$-OH | 1/1 | 160 | **4c** | 2-$C_8H_{16}O$ | 90 | | 172-173 |
| **3d** | 2-$C_{11}H_{23}$-OH | 1/1 | 60 | **4d** | 2-$C_{11}H_{22}O$ | 90 | | 230-234 |
| **3e** |  | 1/1 | 7h | **4e** |  | 90 | | 154-156 |
| **3f** |  | 1/1 | 50 | **4f** |  | 90 | | 179-181 |
| **3g** |  | 1/1 | 75 | **4g** |  | 94 | 50-61 | |
| **3h** |  | 1/1 | 10h | **4h** |  | 90 | 47-50 | |
| **3i** |  | 1/1 | 160 | **4i** |  | 90 | | 162-163 |
| **5a** |  | 1/2 | 4h | **6a** |  | 70 | 284-285 | |
| **5b** |  | 1/2 | 4h | **6b** |  | 65 | 208-210 | |
| **7a** |  | 1/1.1 | 5 | **8a** |  | 98 | 156-157 | |

tripropylamine (28.3 mL, 0.150 mol) was added dropwise with stirring to this solution over a period of 0.5 h and stirring was continued for 0.5 h at 0 °C. The precipitated orange solid was isolated by filtration, washed with petroleum ether (3 × 60 mL) and dried in vacuum for 2 h at room temperature. Yield: 37.5 g (95%); mp 142 °C. $C_9H_{22}CrFNO_3$: Calc. C, 41.06; H, 8.36; N, 5.32 Found: C, 40.85; H, 8.13; N, 5.26. I.R. (KBr): 908 $cm^{-1}$ $\nu_1(A_1)$ or $\nu(CrO_3)$, 646 $cm^{-1}$ $\nu_2(A_1)$ or $\nu$(Cr-F), 951 $cm^{-1}$ $\nu_4(E)$ or $\nu(CrO_3)$ $cm^{-1}$. UV/Visible, $^{13}C$ NMR, $^1H$ NMR and $^{19}F$ NMR were all consistent with the TriPAFC structure. The above procedure can be performed on a 250 g. scale without any difficulty.

**General procedure for oxidation of organic substrates:** To a stirred suspension of tripropylammonium fluorochromate (2.7 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**) (See Table). The mixture was refluxed for the time indicated in the table. [The completion of the reaction is followed by UV/Visible and TLC using ether/petroleum 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 homogenous in the solvent system used.

**Reaction of TriPAFC 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 1.50 g (5.72 mmol) of triphenylphosphine in 35 mL of acetonitrile, 1.65 g (6.29 mmol) of TriPAFC 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 TriPAFC 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: 1.56 g (98%), mp: Found. 155 °C (Lit. mp. 156-157 °C).

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