

# Triethylammonium Fluorochromate—A New, Mild, Stable, and Inexpensive Chromium(VI) Oxidant\*

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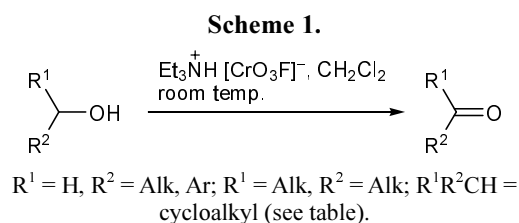
**Abstract**—Triethylammonium fluorochromate was prepared and was used to quantitatively oxidize a number of organic substrates. Triethylammonium fluorochromate is a versatile reagent ensuring effective and selective oxidation of organic compounds, in particular of alcohols, under mild conditions.

Oxidation of organic substrates in aprotic solvents under mild and neutral conditions is an important process in modern organic synthesis. Therefore, search for new oxidants attract attention of organic chemists. Many reagents have been developed in the recent years and used with some success. In particular, there exists persistent interest in the development of new chromium(VI) reagents for effective and selective oxidation of organic substrates, e.g., alcohols, under mild conditions. Such new oxidants [1–3] as 3-carboxypyridinium chlorochromate [4], pyridinium fluorochromate [5], quinolinium dichromate [6], caffeinium chlorochromate [7], quinolinium chlorochromate [8], isoquinolinium fluorochromate [9], and tetramethylammonium fluorochromate [10] should be noted.

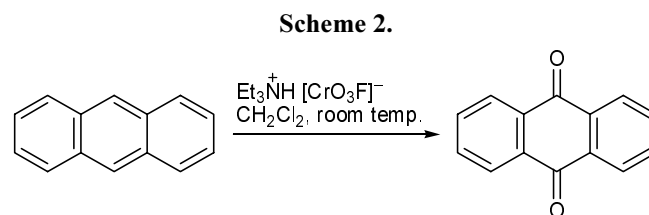
In the present work we studied the synthetic potential of a new chromium(VI) reagent, triethylammonium fluorochromate ( $(C_2H_5)_3NH^+ CrO_3F^-$  (TEAFC). This reagent is more advantageous than the known analogs as regards the amount of oxidant, solvent requirements, easy working up, and product yield. Furthermore, triethylammonium fluorochromate does not react with acetonitrile which is a convenient solvent for studying kinetics and mechanism.

The results obtained with the use of triethylammonium fluorochromate are quite satisfactory, and they

show that the proposed reagent is a valuable addition to the existing oxidants. Triethylammonium fluorochromate in methylene chloride oxidizes primary and secondary alcohols to the corresponding aldehydes and ketones in high yields (Scheme 1, see table). Under analogous conditions, anthracene and phenanthrene are oxidized to 9,10-anthraquinone and 9,10-phenanthrenequinone, respectively, in 68 and 65% yield (Scheme 2). The reagent works as effectively as does activated manganese dioxide or Collins reagent [11].



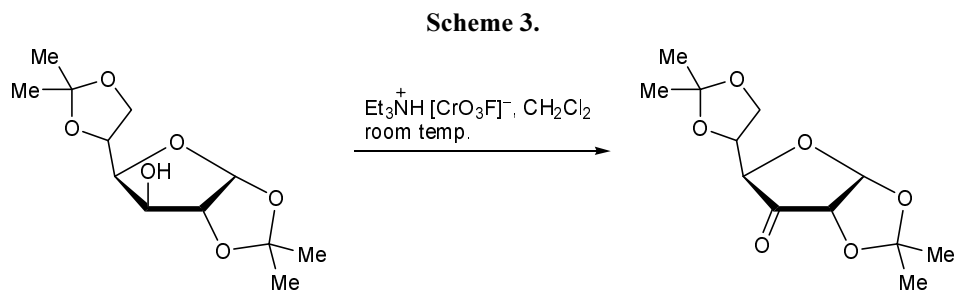
\* The text was submitted by the authors in English.



The reaction of triphenylphosphine with triethylammonium fluorochromate (molar ratio  $PPh_3:TEAFC = 1:1.1$ ) was carried out in acetonitrile at room temperature. As a result, triphenylphosphine oxide was obtained in quantitative yield. This reaction provides a bright example of an oxygen-transfer process involving TEAFC.

Triethylammonium fluorochromate was also used to oxidize carbohydrates. In particular, the corresponding oxo derivative was obtained from 1,2:5,6-di-*O*-isopropylidene- $\alpha$ -D-glucofuranose (Scheme 3); unlike the oxidation with pyridinium chlorochromate [12], in our case the reaction occurs with equimolar amounts of the reactants and is complete in 120 min (yield 94%).

Triethylammonium fluorochromate is easily prepared in 92% yield from chromium(VI) oxide, triethylamine, and 40% aqueous hydrofluoric acid at a molar



ratio of 1:1:1.5. The bright orange crystalline substance can be stored in a polyethylene container for a long time without appreciable decomposition. The concentration of chromium(VI) can be determined by iodometric titration. The IR spectrum of triethylammonium fluorochromate is similar to the spectra of other fluorochromates [13]. The reagent is soluble in water, dimethylformamide, acetonitrile, and acetone, less soluble in methylene chloride, and poorly soluble in benzene, carbon tetrachloride, and hexane.

### EXPERIMENTAL

The IR spectra were recorded on a Shimadzu Model 420 spectrometer in KBr. The electron absorption spectra were measured on a Uvicon Model 922 spectrophotometer. The  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra were obtained on a Bruker Avance DRX 500 instrument at 500, 125, and 470.66 MHz, respectively; the chemical shifts were measured relative to tetramethylsilane ( $^1\text{H}$ ,  $^{13}\text{C}$ ) or  $\text{CFCl}_3$  ( $^{19}\text{F}$ ) as internal reference.

#### Oxidation of alcohols and polycyclic aromatic hydrocarbons with triethylammonium fluorochromate

Substrate	Substrate–oxidant molar ratio	Reaction time, min	Product	Yield, %	bp, °C
1-Propanol	1:1	188	Propanal	90	48–50
1-Butanol	1:1	170	Butanal	90	74–75
1-Pentanol	1:1	100	Pentanal	92	102
1-Hexanol	1:1	110	Hexanal	90	129–131
2-Methyl-1-propanol	1:1	70	2-Methylpropanal	92	63–64
1-Octanol	1:1	164	Octanal	95	170–172
1-Undecanol	1:1	50	Undecanal	90	110–113
Phenylmethanol	1:1	40	Benzaldehyde	92	177–179
2-Propanol	1:1	70	Acetone	90	55–57
3-Heptanol	1:1	160	3-Heptanone	88	146–148
2-Octanol	1:1	165	2-Octanone	90	172–173
2-Undecanol	1:1	40	2-Undecanone	90	230–234
Cyclohexanol	1:1	7 h	Cyclohexanone	85	154–156
Cycloheptanol	1:1	40	Cycloheptanone	92	179–181
Cyclododecanol	1:1	80	Cyclododecanone	92	50–61 <sup>a</sup>
4- <i>tert</i> -Butylcyclohexanol	1:1	13.5 h	4- <i>tert</i> -Butylcyclohexanone	90	47–50 <sup>a</sup>
2-Methylcyclohexanol	1:1	177	2-Methylcyclohexanone	90	162–163
Anthracene	1:2	4 h	9,10-Anthraquinone	68	284–285 <sup>a</sup>
Phenanthrene	1:2	4 h	9,10-Phenanthrenequinone	65	208–210 <sup>a</sup>
Triphenylphosphine	1:1.1	5	Triphenylphosphine oxide	97	156–157 <sup>a</sup>

<sup>a</sup> Melting point.

Chromium(VI) oxide (Merck) was used without additional purification. Solvents were purified by standard procedures.

**Triethylammonium fluorochromate.** Chromium trioxide, 15.0 g (0.15 mol), was dissolved in water in a polyethylene beaker, the solution was cooled to 0°C, and 11.25 ml (0.225 mol) of 40% hydrofluoric acid was added under stirring. Triethylamine, 20.90 ml (0.15 mol), was then added dropwise over a period of 30 min under stirring to the resulting orange solution, and the mixture was stirred for an additional 30 min at 0°C. The orange solid was filtered off, washed with petroleum ether (3 × 60 ml), and dried for 2 h under reduced pressure at room temperature. Yield 30.5 g (92%), mp 176°C. IR spectrum (KBr),  $\nu$ ,  $\text{cm}^{-1}$ : 908 (CrO<sub>3</sub>), 640 (Cr–F), 952 (CrO<sub>3</sub>). The electron absorption and <sup>13</sup>C, <sup>1</sup>H, and <sup>19</sup>F NMR spectra were consistent with the assumed structure. Found, %: C 31.84; H 7.02; N 5.98. C<sub>6</sub>H<sub>16</sub>CrFNO<sub>3</sub>. Calculated, %: C 32.57; H 7.23; N 6.33. The above procedure can be performed on a ~250-g scale with no difficulties.

**General procedure for oxidation of organic substrates with triethylammonium fluorochromate.**

A solution of an organic compound in a minimal volume of methylene chloride was added dropwise under stirring to a suspension of 2.43 g of triethylammonium fluorochromate in methylene chloride (usually 5 ml). The substrate-to-oxidant molar ratio was 1:1 for alcohols and 1:2 for aromatic hydrocarbons (see table). The mixture was then heated under reflux for a time indicated in table. The progress of reactions was monitored by spectrophotometry at a wavelength corresponding to the oxidant ( $\lambda$  350 nm; the reaction was carried out in a 10-mm spectrophotometric cell equipped with a very small magnetic stirrer) or by thin-layer chromatography using diethyl ether–petroleum ether (40:60) as eluent. When the reaction was complete, the mixture was diluted with an equal volume of diethyl ether and filtered through a short column charged with silica gel. The solvent was removed from the filtrate, and the residue was purified by distillation, crystallization, or column chromatography.

**Oxidation of triphenylphosphine with triethylammonium fluorochromate.** The reaction was carried out in a 100-ml round-bottom flask in a nitrogen atmosphere under efficient stirring. Triethylammonium fluorochromate, 1.39 g (6.28 mmol), was added in two

portions over a period of 1 min to a solution of 1.5 g (5.7 mmol) of triphenylphosphine in 35 ml of acetonitrile (substrate-to-oxidant ratio 1:1.1). An exothermic reaction set in instantaneously and was complete in 5 min. The solution was cooled, the reduced oxidant was separated by centrifugation, and the liquid phase and the washings were passed through a short column (7 × 2 cm) charged with silica gel. The column was additionally washed with diethyl ether (3 × 35 ml), the combined filtrates were evaporated on a water bath, and the residue was identified as triphenylphosphine oxide by elemental analysis and IR data. Yield 1.5 g (97%), mp 155°C; published data: mp 156–157°C.

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