Pyridinium Fluorochromate; A New and Efficient Oxidant for Organic Substrates

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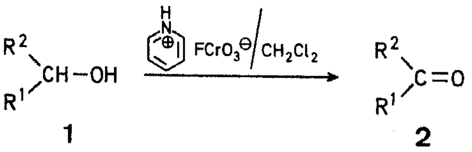
There is continued interest in the development of new chromium(VI) reagents[1-5] for the effective and selective oxidation of organic substrates, in particular alcohols, under mild conditions. Of the large number of "mild" oxidizing agents available many prove impractical when the reactions are performed on a larger (mol) scale. In recent years, significant improvements were achieved by the use of new oxidizing agents such as pyridinium chlorochromate[2,3], pyridinium dichromate[4], and 2,2'-bipyridinium chlorochromate[5]. We have now investigated the synthetic potential of pyridinium fluorochromate, $C_5H_5NHCrO_3F$, and we have found that this reagent has certain advantages over similar oxidizing agents in terms of amounts of oxidant and solvent required, short reaction times, and high yields. Further, pyridinium fluorochromate does not react with acetonitrile which is a suitable medium for studying oxidation kinetics and mechanism. The acidity of pyridinium fluorochromate (pH of a 0.01 molar solution: 2.45) is less pronounced than that of pyridinium chlorochromate (pH of a 0.01 molar solution: 1.75). The results hitherto obtained with pyridinium fluorochromate are very satisfactory and suggest the new reagent as a valuable addition to the existing oxidizing agents.

Pyridinium fluorochromate in dichloromethane oxidizes primary (**1a-d**) and secondary alcohols (**1e**) to the corresponding aldehydes or ketones (**2**) in high yields; the reagent has also been successfully applied to the oxidation of benzoin (**1g**) and a tricyclic allylic alcohol (**1f**) to benzil (**2g**) and a tricyclic enone (**2f**), respectively.



Pyridinium fluorochromate in dichloromethane also oxidizes anthracene (**3a**) and phenanthrene (**3b**) to anthraquinone (**4a**)

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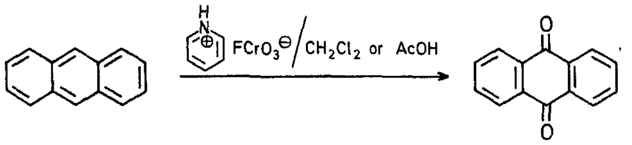
and phenanthrene-9,10-quinone (**4b**) in 68% and 52% yields, respectively. To our knowledge, these yields are higher than those obtained by other oxidizing agents under mild conditions and they may even be raised to 98% and 72% by using acetic acid as reaction medium.



3 a **4 a**

The attempted analogous oxidation of naphthalene so far led only to ~25% of oxidation product.

Pyridinium fluorochromate is easily prepared in 93-94% yield from pyridine, aqueous 40% hydrofluoric acid, and chromium(VI) oxide in a molar ratio of 1 : 1.5 : 1. The orange crystalline reagent can be stored in sealed polythene bags for long periods without decomposition. The chromium(VI) content may be easily determined iodometrically. The molar conductance of the reagent in water (see procedure) suggests an uni-uni valent electrolytic nature in accordance with the formula shown; this fact may account for the stability of the compound. The I.R. spectrum is similar to that of potassium fluorochromate[6,7]. Pyridinium fluorochromate is soluble in water, dimethylformamide, and acetone; it is less soluble in dichloromethane and only sparingly soluble in benzene, carbon tetrachloride, chloroform, and hexane.

Pyridinium Fluorochromate(VI), $C_5H_5NHCrO_3F$:

Chromium(VI) oxide (CrO_3; 15.0 g, 0.15 mol) is dissolved in water (25 ml) in a polythene beaker and 40% hydrofluoric acid (11.25 ml, 0.225 mol) is added with stirring at room temperature. Within 5 min, a clear orange solution results. To this solution, pyridine (12.3 ml, 0.15 mol) is added slowly with stirring. The mixture is heated on a steam bath for ~15 min, then cooled to room temperature, and allowed to stand for 30-35 min. The bright orange, crystalline pyridinium fluorochromate is isolated by filtration, pressed between the folds of filter paper, and dried in vacuo for ~1 h; yield: 27.9 g (93.5%); m.p. 106-108 °C.

$C_5H_6CrFNO_3$	calc.	C 30.16	H 3.04	Cr 26.12	F 9.54	N 7.04
(199.1)	found	30.12	3.07	26.17	9.58	6.96

I.R. (KBr): $\nu = 908$ (ν_1), 640 (ν_2), 340 (ν_3), 952 (ν_4), 373 (ν_5), 262 (ν_6) cm^{-1}.

Molar conductance of a 0.001 molar solution of pyridinium fluorochromate in water: $\Lambda_M(25\,°C) = 128\ ohm^{-1}\ cm^2\ mol^{-1}$.

The above procedure can be performed on a 200 g scale without any difficulty.

Oxidation of Organic Substrates (1, 3) with Pyridinium Fluorochromate; General Procedure:

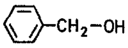
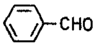
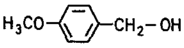
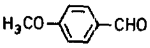
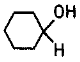
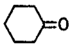
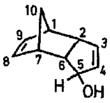
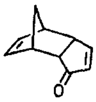
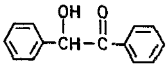
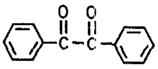
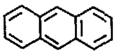
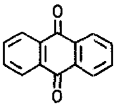
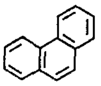
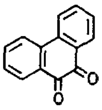
The reaction is carried out in a dry round-bottom flask fitted with reflux-condenser and efficient stirrer. To a vigorously stirred suspension of pyridinium fluorochromate (generally 10 g) in dichloromethane (generally 18 ml), a solution of the substrate in a small amount of dichloromethane is added all at once, the molar ratio of substrate to oxidant being 1 : 1.25-1.5 in the case of alcohols (**1**) and 1 : 2.5 in the case of polycyclic arenes (**3**) (see Table). The mixture is stirred for the time indicated in the Table [The progress of the reaction may be followed by T.L.C. on silica gel using benzene/ethyl acetate (90/10) as eluent]. The mixture is diluted with ether (1/1 vol/vol) and filtered through a short column of silica gel to give a clear solution. This solution is evaporated and the residual product purified by distillation, recrystallization, or column chromatography.

The above procedure may be carried out on 1-100 g scales without any problem.

4-Oxotricyclo[5.2.1.0^{2,6}]deca-3,8-diene (2f); Typical Procedure:

In a 250 ml round-bottom flask fitted with reflux condenser and stirrer is placed a suspension of pyridinium fluorochromate (16.15 g, 81.2 mmol) in dichloromethane (30 ml). To this, a solution of 4-hydroxytricyclo[5.2.1.0^{2,6}]deca-3,8-diene[17] (**1f**; 8.0 g, 54.05 mmol) in dichloromethane (40 ml) is added with vigorous stirring which is continued for 90 min. The reaction is monitored by T.L.C. on silica gel using benzene/ethyl acetate (90/10) as eluent. To the resultant mixture, dry ether (100

Table. Oxidation of Alcohols (**1**) and Polycyclic Arenes (**3**) with Pyridinium Fluorochromate

Substrate	Substrate/ Oxidant [mol/mol]	Solvent	Reaction time	Product[a]	Yield [%]	m.p. or b.p./torr [°C]	
						found	reported
1a n-C_4H_9–OH	1/1.5	CH_2Cl_2	2 h	**2a** n-C_3H_7–CHO	94	b.p. 74°/760	b.p. 75°/760[10]
1b n-C_7H_{15}–OH	1/1.5	CH_2Cl_2	1 h	**2b** n-C_6H_{13}–CHO	84	b.p. 152°/760	b.p. 153°/760[12]
1c 	1/1.25	CH_2Cl_2	45 min	**2c** 	90	b.p. 63°/10	b.p. 62°/10[8]
1d 	1/1.25	CH_2Cl_2	50 min	**2d** 	90	b.p. 248°/760	b.p. 249.5°/760[9]
1e 	1/1.5	CH_2Cl_2	3.5 h	**2e** 	89	b.p. 153-154°/760	b.p. 155.4°/760[11]
1f 	1/1.5	CH_2Cl_2	1.5	**2f** 	92-93	m.p. 79-80°	m.p. 80°[14]
1g 	1/1.5	CH_2Cl_2	2.5	**2g** 	98	m.p. 95°	m.p. 95°[13]
3a 	1/2.5 1/2.5	CH_2Cl_2 AcOH	4 h 1.5 h	**4a** 	68 98	m.p. 274°	m.p. 275°[15]
3b 	1/2.5 1/2.5	CH_2Cl_2 AcOH	5 h 2 h	**4b** 	52 72	m.p. 205°	m.p. 206.5-207.5°[16]

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[a] The purity of the liquid products was found to be >98% by G.L.C. analysis.

ml) is added and the mixture is filtered through a short silica gel column (7 cm × 2 cm^2). The contents of the column are thoroughly washed with ether (3 × 40 ml) and filtered. The combined filtrates are evaporated on a steam bath and the oily residue, which solidifies on standing, is recrystallized from pentane; yield of colorless crystalline **2f**: 7.3 g (92%); m.p. 79-80 °C (Ref.[14], m.p. 80 °C).

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