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Short Communication

4-Benzylpyridinium Fluorochromate: An Efficient and Selective Oxidant for Organic Substrates

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Summary. A new chromium(VI) reagent, 4-benzylpyridinium fluorochromate, was prepared and used for oxidation of various organic substrates under solvent-free conditions. The reagent selectively converts primary benzylic alcohols to their corresponding carbonyl compounds in the presence of primary aliphatic alcohols.

Keywords. Oxidant; 4-Benzylpyridinium fluorochromate; Oxidation; Alcohols.

Introduction

Over the years, partial oxidation has been one of the fundamental procedures in synthetic organic chemistry. It not only finds application in basic research and pharmaceutical industries, but also is regarded as a core technology for converting petroleum-based materials or biomass-based feedstocks to useful chemicals. Although a wide variety of oxidants, catalysts, and reaction systems have been developed yet, Cr(VI) based oxidants are extensively used owing to their commendable performance under mild conditions with high efficiency in amounts ranging from stoichiometric to a large excess [1–9]. Some of the important reagents are pyridinium chlorochromate [1], pyridinium bromochromate [2], pyridinium fluorochromate [3], imidazolium fluorochromate [4], isoquinolinium fluorochromate [5], quinaldinium fluorochromate [6], quinolinium fluorochromate [7], 3,5-dimethylpyrazolium fluorochromate [8], and 2,6-dicarboxypyridinium fluorochromate [9]. However, most of them suffer from at least one of the following drawbacks: high acidity, no selectivity, hygroscopicity, photosensitivity, and tedious work-up procedures. Therefore, the search for new oxidizing reagents is still a pressing need.

In continuation of our studies on the development of new chromium(VI) reagents allowing oxidations to be performed under different conditions [6, 10–14], herein we introduce a new reagent, 4-benzylpyridinium fluorochromate (**1**), which can be used for the oxidative transformation of various alcohols and oximes into the corresponding carbonyl compounds selectively under solvent-free conditions.

Results and Discussion

4-Benzylpyridinium fluorochromate (**1**) can be easily prepared in good yield (86%) from 4-benzylpyridine, 40% hydrofluoric acid, and chromium(VI) oxide in a molar ratio of 1:1.5:1. The bright-orange crystalline reagent can be stored in a sealed polythene bag for long periods without decomposition. The structure of **1** was confirmed by elemental analysis, IR (KBr), UV-Vis, ^{1}H NMR spectra, and single-crystal X-ray diffraction analysis (Fig. 1). The infrared absorption frequencies for the fluorochromate group at $\bar{\nu} = 931$, 879, and 603 cm^{-1} of **1** are attributable to $\bar{\nu}_{asym}$ (Cr=O), $\bar{\nu}_{sym}$ (Cr=O), and $\bar{\nu}$ (Cr–F). Figure 1 shows the structure and the atomic numbering scheme for **1**. Thus, the X-ray structure determi-

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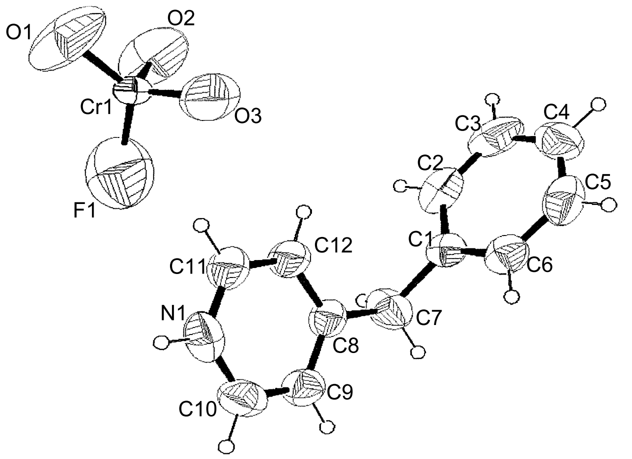

Fig. 1. The structure of **1**, with 50% probability displacement ellipsoids, showing the atomic numbering scheme

nation revealed an ionic structure consisting of $C_{12}H_{11}NH^+$ and CrO_3F^- ions.

The reagent **1** is soluble in *DMSO* and *DMF*, sparingly soluble in acetone, dichloromethane, acetonitrile, and water, and insoluble in carbontetrachloride, benzene, ether, and chloroform. These results are indicative of the ionic nature of **1**. The reagent melts at 113–114°C. The compound is diamagnetic as tested by means of magnetic susceptibility measurement. It is a 1:1 electrolyte ($\Lambda_M = 127\,\mathrm{mho\,cm^2\,mol^{-1}}$, in acetonitrile). The *pH* value of a 0.01 M aqueous solution of **1** was found to be 3.15. Thus, the acidity of **1** is less pronounced than that of *PCC*, *PFC*, and *QFC* [1, 3, 7].

The chemistry of **1** was explored as an oxidizing agent, and Table 1 summarizes the products, yields, and times of the oxidation reactions with various substrates under solvent-free conditions. In the oxidation of different types of primary alcohols (Entries 1–8) with **1** no overoxidation to carboxylic acids was observed. Cinnamyl alcohol (Entry 6) was oxidized to the corresponding α,β-unsaturated aldehyde, and no trace of benzaldehyde was detected. Obviously, **1** can not cleave the double bond of cinnamyl alcohol. Benzoin (Entry 13) was oxidized to benzil with no bond cleavage, but benzil was obtained in low yield. No oxidation products were obtained with anthracene and phenanthrene (Entries 14, 15) even for long reaction times. Oxidative deoximation of benzaldoxime by **1** gave benzaldehyde almost quantitatively (Entry 16). The selectivity of **1** was indicated by a remarkable rapid oxidation of primary benzylic and allylic alcohols (Entries 1–6) relative to aliphatic primary and secondary alcohols (Entries 8–11) and also to secondary benzylic alcohols (Entries 12, 13). Thus, treatment of 4-methoxybenzyl alcohol (1 mmol) and 1-octanol (1 mmol) with **1** (3 mmol) for 40 min

Table 1. Oxidation of alcohols, aromatic hydrocarbons, and oximes using **1** under solvent-free conditions at room temperature

Entry	Substrate	Oxidant/Substrate (molar ratio)	Time/min	Yield/%[b]
1	Benzyl alcohol	1.5	5	95
2	4-Methylbenzyl alcohol	1.5	8	87
3	4-Chlorobenzyl alcohol	1.5	8	79
4	4-Methoxybenzyl alcohol	1.5	5	88
5	4-Nitrobenzyl alcohol	1.5	25	79
6	Cinnamyl alcohol	1.5	9	87
7	Citronellol	1.5	130	75
8	1-Octanol	1.5	360	77
9	Cyclohexanol	1.5	70	77
10	4-*tert*-Butylcyclohexanol	1.5	200	82
11	Menthol	1.5	130	76
12	Benzhydrol	1.5	60	76
13	Benzoin	1.5	30[a]	57[c]
14	Anthracene	1.5	1440[a]	NR[d]
15	Phenanthrene	1.5	1440[a]	NR[d]
16	Benzaldoxime	2	8	98
17	Cyclohexanone oxime	2	35	68
18	Cyclopentanone oxime	2	45	75
19	Benzoin oxime	2	60	52

[a] At 70°C; [b] yields refer to isolation of 2,4-*DNP* derivatives; [c] yield of isolated pure carbonyl compound for benzil; [d] no reaction

leads to 100% oxidation to 4-methoxybenzaldehyde while 1-octanol can be recovered unchanged.

In conclusion, the easily prepared new reagent **1** has a number of advantages in terms of selectivity, lower acidity, stability, and yield of product. These advantages make this reagent a useful addition to the category of reagents used for the oxidation of organic substrates.

Experimental

Preparation of 4-Benzylpyridinium Fluorochromate

CrO_3 (10 g, 0.1 mol) was dissolved in H_2O (15 cm^3) in a polythene beaker and 40% HF (8.7 cm^3, 0.15 mol) was added with stirring at room temperature. To this solution 0.1 mol 4-benzylpyridine (16.7 cm^3) were added in a dropwise manner. The bright-orange crystalline solid thus formed was filtered off and dried under vacuum for 1 h. The solid was dissolved in H_2O and slow evaporation (2 d) furnished suitable crystals of **1**. Yield 86%; mp 113–114°C. ^{1}H NMR (200 MHz, *DMSO*-d$_6$): $\delta = 4.1$ (s), 7.25 (m), 7.75 (d), 8.75 (s); calcd, for $C_{12}H_{11}NHCrO_3F$: C 49.84, H 4.18, N 4.84, Cr 17.98; found: C 50.02, H 4.39, N 5.02, Cr 17.50%.

X-ray diffraction data were collected at 293(2) K on a Stoe IPDS-2 diffractometer using Mo K_α radiation, $\lambda = 0.71073$ Å. The compound crystallizes in the monoclinic system with unit cell dimensions $a = 8.3060$ (14), $b = 5.9663$ (7), $c = 25.257$ (4) Å, $\beta = 95.747$ (13)°, $V = 1245.4(3)$ Å^3, and Z = 4. Crystallographic data, tables of atomic coordinates and thermal parameters, and full lists of bond lengths and angles were deposited at the Cambridge Crystallographic Data Centre, CCDC No. 612004. Copies of this information may be obtained from the director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk).

General Procedure for Oxidation Under Solvent-Free Conditions

The oxidant **1** (0.434 g, 1.5 mmol) was added to the substrate (1 mmol) in a mortar. Starting materials were instantly mixed and then stored for the appropriate period either at room temperature with grinding or in an oven without any further agitation (Table 1). The progress of the reaction was monitored by dissolving a sample in CH_2Cl_2 and using TLC on silica gel (*n*-hexane:ethyl acetate = 2:1). Upon completion of the reaction, extraction with Et_2O (3×25 cm^3) and evaporation of the solvent gave the corresponding carbonyl compounds.

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References

[1] Corey EJ, Suggs JW (1975) Tetrahedron Lett **16**: 2647

[2] Narayanan N, Balasubramanian TR (1986) Indian J Chem **25B**: 228

[3] Bhattacharjee MN, Chaudhuri SK, Dasgupta HS, Roy N (1982) Synthesis **7**: 588

[4] Pandurangan A, Arabindoo B, Murugesan V, Rojkumar GA (1999) Indian J Chem **38B**: 99

[5] Srinivasan R, Stanley P, Balasubramanian K (1997) Synth Commun **27**: 2057

[6] Değirmenbaşı N, Özgün B (2004) Monatsh Chem **135**: 407

[7] Murugesan V, Pandurangan A (1997) Indian J Chem **31B**: 377

[8] Bora U, Chadhuri MK, Dey D, Kalita D, Kharmawphlang W, Mandal GC (2001) Tetrahedron **57**: 2445

[9] Tajbakhsh M, Hosseinzadeh R, Sadatshahabi M (2005) Synth Commun **35**: 1547

[10] Değirmenbaşı N, Özgün B (2002) Monatsh Chem **133**: 1417

[11] Değirmenbaşı N, Özgün B (2006) G U J Sci **19**: 9

[12] Özgün B, Değirmenbaşı N (1999) Synth Commun **29**: 763

[13] Özgün B, Değirmenbaşı N (1996) Synth Commun **26**: 3601

[14] Şendil K, Özgün B (2006) Phosphorus Sulfur and Silicon **18**: 959