Monatshefte für Chemie 137, 1529–1533 (2006)
DOI 10.1007/s00706-006-0549-2

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Dipyrazinium Tri(fluorotrioxochromate): An Efficient Oxidant for Organic Substrates

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Received May 8, 2006; accepted May 19, 2006

Summary. The first polymeric halotrioxochromate, dipyrazinium tri(fluorotrioxochromate), was prepared and used for quantitative oxidation of several organic substrates. This novel compound is more efficient than, and has certain advantages over, its monomeric analogues in terms of the amount of oxidant required, reaction times, and yields.

Keywords. Oxidant; Dipyrazinium tri(fluorotrioxochromate); Oxidation; Organic substrates.

Introduction

Organic reactions were found to occur efficiently in solid state. There is an increasing interest in the use of environmentally benign conditions [1, 2], and particularly solvent-free procedures [3]. Avoiding organic solvents during the reactions in organic synthesis leads to a clean, efficient, and economical technology. In solid state reactions, work-up is considerably simplified, cost is reduced, increased amounts of reactants can be used in the same equipment, and reactivities and sometimes selectivities are enhanced without dilution [4]. Organic solid- state reactions are usually carried out by keeping a mixture of finely powdered reactant and reagent at room temperature. In some cases, these reactions are accelerated by heating and grinding of the reaction mixture using a mortar and pestle [5]. Partial oxidations of organic substrates have always been very important in modern organic synthesis. The oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones is a fundamental area that is encountered at all levels of organic synthesis. Therefore, the search for new oxidizing agents is of interest to synthetic organic chemists [6], and for this purpose no other reagent could be as popular, as useful, and as successful as the chromium based reagents have been.

Though there are some limitations of chromium reagents in terms of environmental antagonism, the popularity of such reagents does not seem to diminish

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because their performance under mild conditions with high efficiency and cost-effectiveness weigh far over their limitations. Thus, chromium based oxidizing agents have been extensively worked on leading to the development of a number of reagents, many of which have become quite popular and performing well as oxidizing agents [7–13]. However, most of these reagents that have been developed so far suffer from at least one of the drawbacks such as high acidity, photosensitivity, instability, tedious work-up procedures, or requirement of large excess of reagent.

In our previous studies we have reported the preparation of new dichromates and halotrioxochromates with various heteroaromatic bases [14–19]. In continuation we aimed to prepare pyrazinium fluorochromate with the belief that this reagent could be used for the oxidation of organic substrates. But an interesting reaction has been observed which resulted in the formation of dipyrazinium tri (fluorotrioxochromate) (**1**). Though it was found previously that with organic bases it is possible to prepare polychromates [20, 21] to the best of our knowledge the occurrence of polymeric halotrioxochromates has not been reported before. This work provides such a novel oxidant, which can be used for the oxidative transformation of various alcohols, oximes, and anthracene into the corresponding carbonyl compounds under solvent-free conditions.

Results and Discussion

Dipyrazinium tri(fluorotrioxochromate) (**1**), can be easily prepared in a good yield (80%) from pyrazine, 40% hydrofluoric acid, and chromium(VI) oxide in a molar ratio of 1:1:1. The dark red crystalline reagent can be stored in a sealed polythene

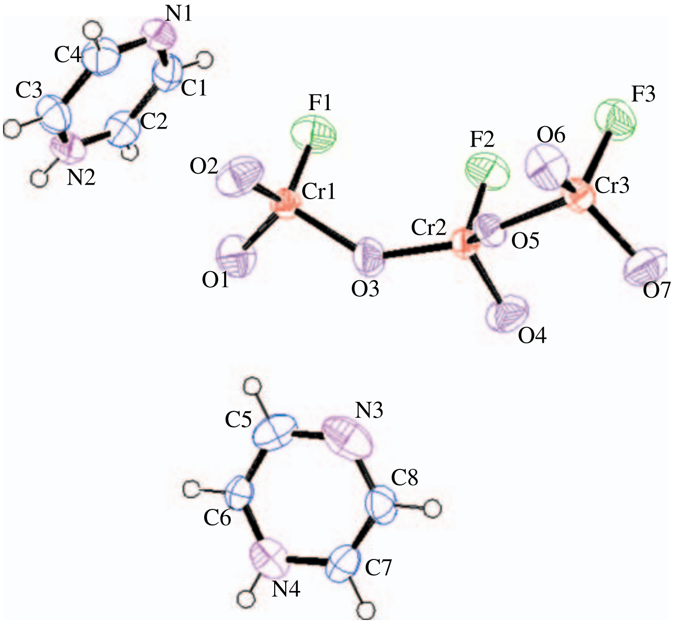

Fig. 1. The structure of **1**, with 50% probability displacement ellipsoids, showing the atomic numbering scheme

bag for long periods without decomposition; **1** is also moisture-insensitive. The structure of **1** was confirmed by elemental analysis, IR (KBr), UV/Vis, ^{1}H NMR spectra, and single-crystal X-ray diffraction analysis (see Fig 1). The infrared absorption frequencies for the tri(fluorotrioxochromate) group at $\bar{\nu} = 944$, 889, 771, and 617 cm^{-1} of **1** are attributable to $\bar{\nu}_{asym}$(Cr=O), $\bar{\nu}_{sym}$(Cr=O), $\bar{\nu}$(Cr–O–Cr), and $\bar{\nu}$(Cr–F). Figure 1 shows the structure and the atomic numbering scheme for **1**. X-Ray structure determination revealed an ionic structure consisting of $C_4H_5N_2H^+$ and $Cr_3O_7F_3{}^{2-}$ ions.

The reagent **1** is soluble in *DMF*, water, and *DMSO*; sparingly soluble in benzene and ethylacetate; and insoluble in ether, toluene, acetonitrile, dichloromethane, and chloroform. These results are indicative of the ionic nature of **1**. The reagent decomposes at 210°C. The compound is paramagnetic as tested by means of magnetic susceptibility measurement. The *pH* value of 0.01 *M* aqueous solution of **1** was found to be 3. Thus, the acidity of **1** is less pronounced than that of *PCC*, *PFC*, and *QFC* [7, 9, 12].

This compound provides a useful new oxidant for synthesis. 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, 3–6) with **1** no overoxidation to carboxylic acids was observed. Cinnamyl alcohol (Entry 3) was oxidized to the corresponding α,β-unsaturated aldehyde, and no trace of benzaldehyde could be detected. Obviously, **1** cannot cleave the double bond of cinnamyl alcohol. Oxidative deoximation of benzaldoxime and benzoinoxime by **1** gave the corresponding carbonyl compounds in very high yields (Entries 10, 11). Finally, oxidation of anthracene gave anthraquinone in excellent yield (Entry 9).

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

Entry	Substrate	Product	Oxidant/Subst. (mole ratio)	Time/min	Yield[b]/%
1	1-Octanol	Octanal	0.6	14	95
2	Cyclohexanol	Cyclohexanone	0.6	8	92
3	Cinnamyl Alcohol	Cinnamaldehyde	0.6	15	90
4	Benzyl Alcohol	Benzaldehyde	0.6	7	98
5	4-Methoxybenzyl Alcohol	4-Methoxybenzaldehyde	0.6	10	95
6	4-Methylbenzyl Alcohol	4-Methylbenzaldehyde	0.6	5	94
7	Benzoin	Benzil	0.6	30[a]	97[c]
8	Benzhydrol	Benzophenone	0.6	25	93
9	Anthracene	Anthraquinone	0.8	23[a]	92[c]
10	Benzaldoxime	Benzaldehyde	0.8	20	85
11	Benzoin oxime	Benzoin	0.8	12	87

[a] At 70°C; [b] yields refer to isolation of 2,4-*DNP* derivatives; [c] yield of isolated pure carbonyl compound for benzil and antraquinone

Table 2. Oxidation of some alcohols and oximes by **1** in comparison with other oxidants under solvent-free conditions at room temperature

Substrate	Reagent	Oxidant/Subst. (mole ratio)	Time/min	Yield/%	Ref.
Benzyl Alcohol	**1**	0.6	7	98	
Cyclohexanol		0.6	8	92	
Benzaldoxime		0.8	20	85	–
Benzoin oxime		0.8	12	87	
Benzyl Alcohol	*PCC*[a]	1	15	96	[23]
Benzaldoxime		2	120	80	
Benzoin oxime		2	210	80	
Benzyl Alcohol	*QxFC*[b]	1.5	120	95	[14]
Cyclohexanol		1.5	45	72	
Benzyl Alcohol	*PFC*[c]	1	10	93	[22]
Cyclohexanol		1	15	86	
Benzyl Alcohol	*2,6-DCPFC*[d]	1.5	4	92	[10]
Cyclohexanol		1.5	20	89	

[a] Pyridinium chlorochromate; [b] quinoxalinium fluorochromate; [c] pyridinium fluorochromate; [d] 2,6-dicarboxypyridinium fluorochromate

The mole ratio between the organic substrate and the oxidation agent is an important parameter with respect to the practical value of an oxidation reagent. In this study, mole ratios between oxidant and the organic substrates were 0.6:1 and 0.8:1. This is a significant advantage of the reagent. In addition this reagent has certain advantages over its monomeric analogues in terms of lower acidity, higher stability, and especially shorter reaction times required and higher product yields (Table 2).

In conclusion, these advantages make this reagent a useful addition to the category of reagents used for the oxidation of organic substrates.

Experimental

Preparation of Dipyrazinium tri(fluorotrioxochromate)

CrO_3 (20 g, 0.2 mol) was dissolved in H_2O (40 cm^3) in a polyethylene beaker and 40% HF (11.3 cm^3, 0.23 mol) was added with stirring at room temperature. 0.2 mol pyrazine (13.5 g) dissolved in 50 cm^3 water were added to the above solution in a dropwise manner. The mixture was kept at room temperature for 2 h. The dark red crystalline solid thus formed was filtered off and dried under vacuum for 1 h. The solid was dissolved in water and slow evaporation (2 d) furnished suitable crystals of **1**. Yield 80%; Mp 210°C (dec); ^{1}H NMR (200 MHz, D_2O): $\delta = 8.6$ (s); Calcd for $(C_4H_4N_2H)_2Cr_3O_7F_3$: C 19.70, H 2.06, N 11.42, Cr 31.01; found: C 19.17, H 2.05, N 11.49, Cr 30.58%.

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 $a = 5.3221$ (4), $b = 10.6158$ (10), $c = 13.7344$ (10) Å, $\beta = 91.459$ (6)°, $V = 775.72$ (11) Å^3, and $Z = 2$. 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. 600254. 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** (0.290 g or 0.390 g; 0.6 or 0.8 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 2). The progress of the reaction was monitored by dissolving a sample in CH_2Cl_2 and using TLC on silica gel (*n*-hexane:ethylacetate = 2:1). Upon completion of the reaction, extraction with Et_2O ($3 \times 25\,cm^3$) and evaporation of the solvent gave the corresponding carbonyl compounds.

Acknowledgements

The authors are thankful to the Research Foundation of Gazi University for supporting this study.

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