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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

PYRIDINIUM SULFONATE CHLOROCHROMATE (VI), $C_5H_5NSO_3H$ $[CrO_3Cl]$ (PSCC): A NEW REAGENT FOR OXIDATION OF ORGANIC SUBSTRATES

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Online publication date: 16 August 2010

To cite this Article Kassae, M. Z. and Bekhradnia, A. R.(2004) 'PYRIDINIUM SULFONATE CHLOROCHROMATE (VI), $C_5H_5NSO_3H$ $[CrO_3Cl]$ (PSCC): A NEW REAGENT FOR OXIDATION OF ORGANIC SUBSTRATES', Phosphorus, Sulfur, and Silicon and the Related Elements, 179: 10, 2025 — 2028

To link to this Article: DOI: 10.1080/10426500490473555

URL: <http://dx.doi.org/10.1080/10426500490473555>

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PYRIDINIUM SULFONATE CHLOROCHROMATE (VI), $C_5H_5NSO_3H [CrO_3Cl]$ (PSCC): A NEW REAGENT FOR OXIDATION OF ORGANIC SUBSTRATES

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(Received January 27, 2004; accepted March 16, 2004)

A fast, mild, and reasonable oxidizing agent, pyridinium sulfonate chlorochromate (VI), $C_5H_5NSO_3H [CrO_3Cl]$ (PSCC) is synthesized. Its reactions with primary, secondary, benzylic, and allylic alcohols under very mild conditions give the corresponding carbonyl compounds. These are obtained with relatively short reaction times. The oxidant/substrate ratios of 1:1 are employed.

Keywords: Carbonyl compounds; oxidation of alcohols

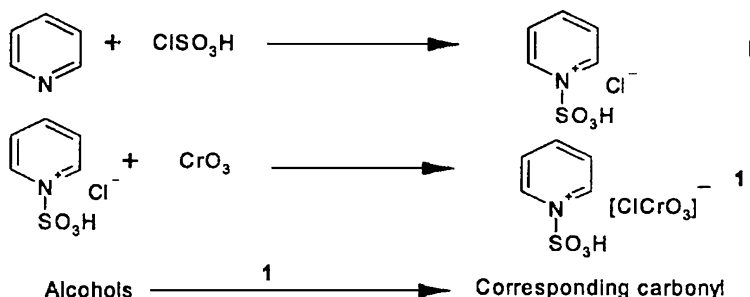
INTRODUCTION

The value of mild oxidation of alcohols to their corresponding aldehydes is evident.^{1–4} Many reagents and methods have been reported that carry out this fundamental transformation. Among these, chromium (VI)-based oxidizing agents have become quite popular. Typical examples are: the Collins reagent,⁵ chromium trioxide-3,5-dimethyl-pyrazole complex,⁶ pyridinium chlorochromate,⁷ pyridinium dichromate,⁸ 2,2'-bipyridinium chlorochromate,⁹ and 3,5 dimethylpyrazolium fluorochromate (VI).¹⁰

In this article a novel, highly efficient, and widely applicable method for fast and mild oxidation of alcohols to their corresponding aldehydes is reported. First, pyridinium sulfonate chloride (**I**) is prepared via addition of chlorosulfonic acid to pyridine in chloroform.¹¹ Consequently, pyridinium sulfonate chlorochromate (VI), $C_5H_5NSO_3H$

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[CrO₃Cl] (PSCC) is synthesized through the reaction of CrO₃ with aqueous **I** (Scheme 1). This is done using a molar ratio of 1:1. An excellent yield of PSCC is obtained. PSCC is soluble in dichloromethane, acetonitrile, and chloroform. Its melting point is 65°C.



SCHEME 1

RESULTS AND DISCUSSION

PSCC readily oxidizes primary, allylic, benzylic, and secondary alcohols to their corresponding carbonyls. Also, anthracene is oxidized to 9,10-anthraquinone (Table I).

TABLE I ¹H NMR and GC Analyses of Oxidation of Organic Substrates with Pyridinium-1-sulfonate Chlorochromate

Entry	Substrates	Products	Yield% (by ¹ H NMR and GC)
1	Allyl alcohol	Acrolein	80
2	Anthracene	9,10-Anthraquinone	57
3	p-Methoxybenzyl alcohol	p-Methoxybenzaldehyde	95
4	Benzyl alcohol	Benzaldehyde	91
5	Furfuryl alcohol	Furfural	55
6	1-Pentanol	1-Pentanal	65
7	1-Butanol	1-Butanal	60
8	Ethylene glycol	Glyoxal	50
9	Isobutanol	2-Methylpropanal	65
10	Isopropyl alcohol	Acetone	68
11	2-Butanol	2-Butanone	66
12	2-pentanol	2-Pentanone	69

EXPERIMENTAL

Preparation of PSCC

Chlorosulfonic acid (23 ml) is added dropwise to a stirred solution of pyridine (64 ml) in chloroform (100 ml) at -5°C . The reaction mixture is stirred at the same temperature for 20 min. Pyridinium sulfonate chloride is formed as a white solid and separated. This solid (4.25 g) is dissolved in 2 ml of water, and CrO_3 (2 g) is added and stirred for 30 min at room temperature. An orange-red solution is obtained. The reaction mixture is then cooled in an ice bath ($0-5^{\circ}\text{C}$). The yield of $\text{C}_5\text{H}_5\text{NSO}_3\text{H} [\text{CrO}_3\text{Cl}]$ is found to be 91%. The extent of the oxidation is determined via proton nuclear magnetic resonance (^1H NMR) and gas chromatography (GC) (Table I).

General Experimental Procedure for the Application of PSCC as an Oxidizing Agent

To a stirred solution of PSCC (5 mmole) in CH_2Cl_2 (10 ml), a solution of alcohol (5 mmole) in CH_2Cl_2 (10 ml) is added in one portion. Stirring is continued for 30 min to give a yellow solution. The progress of the reaction is monitored by thin layer chromatography (TLC) (ethyl acetate-hexane (1:9)). After completion of the reaction, dry diethyl ether (50 ml) is added to the reaction mixture.

The whole mass is shaken well. The organic layer is decanted, and the residue is washed with dry diethyl ether (3×20 ml). The combined organic layers are passed through a short pad of celite. This is to trap the reduced chromium. The product of oxidation is also washed thoroughly with diethyl ether (3×10 ml). The solvent is removed in a rotavapor under reduced pressure.*

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* ^1H NMR, ^{13}C NMR, IR, and UV spectra were entirely consistent with the assigned structure of PSCC. Selected data are as follows: ^1H NMR (90 MHz, CH_3CN): $\delta = 7.9$ (m, 2H, *m*-CH), 8.5 (m, 1H, *p*-CH), 8.8 (m, 2H, *o*-CH), ^{13}C NMR (90 MHz, CH_3CN): $\delta = 127.33$ (2C, *m*-CH), 141 (1C, *p*-CH), 178 (2C, *o*-CH); IR $\nu(\text{KBr})$: 954 (s, Cr-O), 921 (s, Cr-O), 435 (m, Cr-Cl), 1150–1250 (s, $-\text{SO}_3$) 1440–1640 (originating due to the pyridinium sulfonate cation); UV(CH_3CN): 350–400 (CrCl), 256–260 (originating due to the pyridinium sulfonate cation).

Elemental analysis data for the PSCC is found as follows: Cr, 17.6%; C, 20.5%; N, 4.80%; H, 1.95%. Calculated: Cr, 17.65%; C, 20.37%; N, 4.75%; H, 1.83%.

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