

Synthesis and characterization of two new triphenylphosphonium halochromates, $(C_6H_5)_3PH[CrO_3X]$, ($X=F, Br$)

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Abstract

Two new mild oxidizing agents, triphenylphosphonium fluorochromate (TriPPFC), triphenylphosphonium bromochromate (TriPPBC), have been easily prepared. These reagents are suitable for oxidizing various primary and secondary alcohols to their corresponding carbonyl compounds. TriPPFC and TriPPBC have many advantages over similar oxidizing agents including: ease of preparation, involving, simple cationic exchange; high yields of the oxidized species; short reaction times; good selectivity; lower oxidant/substrate ratio and lower solvent requirement.

Keywords: Chromium(VI), triphenylphosphonium fluorochromate, triphenylphosphonium bromochromate, oxidation, organic substrate, alcohols

Introduction

By far the most commonly used method for the synthesis of aldehydes and ketones are the oxidation of alcohols. Many new oxidative methods have been described over the 30 last years. Significant improvements are achieved in the development of new Cr(VI) based oxidizing agents, such as: the Collins reagents,¹ chromium trioxide-3,5-dimethylpyrazole complex,² pyridinium chlorochromate (PCC),³ pyridinium dichromate (PDC),⁴ 2,2'-bipyridinium chlorochromate (BiPCC),⁵ pyridinium fluorochromate (PFC)⁶⁻⁹ quinolinium fluorochromate,¹⁰ quinolinium chlorochromate,¹¹ and 3,5-dimethylpyrazolium fluorochromate (DmpzHFC)¹². Industrial demands have led many workers to search for more ideal oxidants with a number of specifications including: lower cost, higher yields, better selectivity, milder neutral conditions, easier preparations, high solubility, less toxicity, and short reaction times. Even though,

numerous oxidants for oxidation of alcohols are already reported, the growing demand for new oxidants of alcohols made us carry out the synthesis of triphenylphosphonium fluorochromates (TriPPFC), triphenylphosphonium bromochromates (TriPPBC).

Results and Discussion

TriPPFC and TriPPBC are non-hygroscopic, air-stable but moderately light-sensitive solids which should be protected from light during preparation and storage. The structures of the reagents were confirmed by elemental analysis, infrared spectra and UV-Visible spectroscopy. The infrared absorption frequencies for fluorochromate group in TriPPFC found and assigned as: 877 cm^{-1} $\nu_1(A_1)$ or $\nu(\text{CrO}_3)$, 640 cm^{-1} $\nu_2(A_1)$ or $\nu(\text{Cr-F})$, 947 cm^{-1} $\nu_4(E)$ or $\nu(\text{CrO}_3)\text{ cm}^{-1}$.

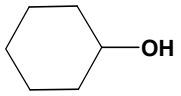
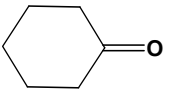
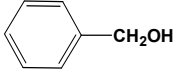
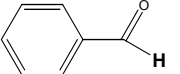
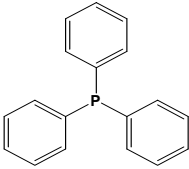
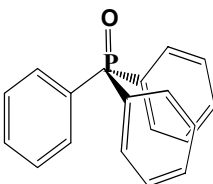
The infrared absorption frequencies for bromochromate group at 945 and 913 cm^{-1} in triphenylphosphonium bromochromate are attributable to $\nu_{\text{asym}}(\text{Cr-O})$, $\nu_{\text{sym}}(\text{Cr-O})$ and $\nu(\text{Cr=O})$, respectively. These assignments are in accord with those found for other bromochromate and fluorochromates.¹³⁻¹⁵

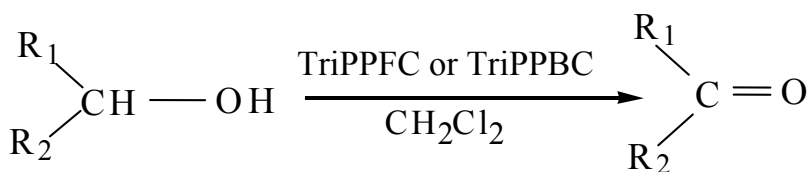
These reagents are soluble in dimethylformamide and dimethyl sulfoxide, sparingly soluble in dichloromethane, acetonitrile and chloroform and insoluble in benzene, toluene, ether, nitrobenzene and ethyl acetate. These results are indicative of the ionic nature of these compounds. The compounds are diamagnetic.

Different primary and secondary alcohols were subjected to oxidations with TriPPFC and TriPPBC in dichloromethane. These oxidations take place under mild and quantitative conditions giving excellent yields (Table 1).

Table 1. Oxidations via TriPPBC and TriPPF

Substrate	Product	TriPPBC		TriPPFC	
		Time (min)	Yield (%)	Time (min)	Yield(%)
1 $\text{CH}_3(\text{CH}_2)_2\text{OH}$	$\text{CH}_3\text{CH}_2\text{CHO}$	170	88	160	90
2 $(\text{CH}_3)_2\text{CHOH}$	$(\text{CH}_3)_2\text{CO}$	150	90	150	90
3 $\text{CH}_3(\text{CH}_2)_3\text{OH}$	$\text{CH}_3(\text{CH}_2)_2\text{CHO}$	130	86	100	88
4 $\text{H}_3\text{C}-\underset{\text{OH}}{\underset{ }{\text{C}}}-\text{CH}_2\text{CH}_3$	$\text{H}_3\text{C}-\underset{\text{O}}{\underset{ }{\text{C}}}-\text{CH}_2\text{CH}_3$	120	90	180	92

5	$\text{CH}_3(\text{CH}_2)_4\text{OH}$	$\text{CH}_3(\text{CH}_2)_3\text{CHO}$	130	85	100	88
6	$\text{CH}_3(\text{CH}_2)_7\text{OH}$	$\text{CH}_3(\text{CH}_2)_6\text{CHO}$	120	82	180	84
7			250	91	255	93
8			30	94	35	96
9			5	90	5	92



Scheme 1

The corresponding aldehyde and ketone products can then be easily isolated by simple filtration and evaporation of the solvent. Yields obtained using TriPPFC and TriPPBC are mostly higher than other similar reported reagents in the literature, while both reagents ratios as well as reaction times are lower (Table 1).

Experimental Section

General Procedures. Triphenylphosphonium Bromide and chromium trioxide were obtained from Fluka (Buchs, Switzerland). Melting points are measured on an Electrothermal 9100 apparatus. Elemental analyses (C, H, and N) were performed using a Heraeus CHN-O-Rapid analyzer. Infrared spectra were recorded as KBr disks on a Shimadzu model 420 spectrophotometer. The UV/Visible measurements were made on an Uvicon model 922

spectrometer. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were measured on a BRUKER-DRX500 AVANCE instrument.

Triphenylphosphonium bromochromate(VI), $(\text{C}_6\text{H}_5)_3\text{PH}[\text{CrO}_3\text{Br}]$, TriPPBC. A solution of chromium trioxide (1 g, 10 mmol) in dry acetonitrile (25 ml) was cooled to 0°C and a stoichiometric amount of triphenylphosphonium Bromide (3.43 g, 10 mmol) was added under stirring at room temperature. Within 30 min, a clear orange solution formed which upon refrigerating gave solid TriPPBC, which was isolated by filtration. The solid was washed with hexane and dried under vacuum for 1 h (4.03 g, 91% yield). IR. $\text{C}_{18}\text{H}_{16}\text{BrCrO}_3\text{P}$: Calcd. %C, 48.75; %H, 3.61. Found: %C, 50.58; %H, 3.72. (KBr): 913cm^{-1} $\nu_1(\text{A}_1)$ or $\nu(\text{CrO}_3)$, 940cm^{-1} $\nu_4(\text{E})$ or $\nu(\text{CrO}_3)$. UV/Visible was all consistent with the TriPPBC structure. Electronic at 452 nm, Corresponding to $1a_2 \rightarrow 11e$ ($\epsilon = 50 \text{ M}^{-1} \text{ cm}^{-1}$); 363 nm to $10e \rightarrow 11e$ ($\epsilon = 346 \text{ M}^{-1} \text{ cm}^{-1}$); and 270 nm to $a_1 \rightarrow e$ ($\epsilon = 1112 \text{ M}^{-1} \text{ cm}^{-1}$).

Triphenylphosphonium fluorochromate (VI), $(\text{C}_6\text{H}_5)_3\text{PH}[\text{CrO}_3\text{F}]$, TriPPFC. To a solution of CrO_3 (1g 10 mmol) in 12 ml water, placed in a 100 ml polyethylene beaker, 9 ml (20 mmol) 40% aqueous HF was added over a period of 0.5 h and stirring was continued for 0.5 h at 0°C . A clear orange solution is obtained. Triphenylphosphonium Bromide (3.43 g, 10 mmol) is added portion-wise, with stirring. An orange soft-solid, in a greenish liquid is obtained. To this mixture, 30 ml CH_2Cl_2 are added. The orange organic phase is decanted and the solvent is distilled off. A reddish orange gel is separated and stored in the refrigerator (3.74 g, 98% yield). $\text{C}_{18}\text{H}_{16}\text{CrFO}_3\text{P}$: Calcd. %C, 56.54; %H, 4.18. Found: %C, 58.60; %H, 4.35. IR. (KBr): 877 cm^{-1} $\nu_1(\text{A}_1)$ or $\nu(\text{CrO}_3)$, 640 cm^{-1} $\nu_2(\text{A}_1)$ or $\nu(\text{Cr-F})$, 947 cm^{-1} $\nu_4(\text{E})$ or $\nu(\text{CrO}_3)$ cm^{-1} . UV/Visible $^{13}\text{C-NMR}$ and $^1\text{H-NMR}$ were all consistent with the TriPPFC structure. Electronic absorption at 450 nm^{-1} , corresponding to $1a_2 \rightarrow 9e$ ($\epsilon = 86 \text{ M}^{-1} \text{ cm}^{-1}$); 363 nm^{-1} to $8e \rightarrow 9e$ ($\epsilon = 460 \text{ M}^{-1} \text{ cm}^{-1}$); and 280 nm^{-1} to $12a_1 \rightarrow 9e$ ($\epsilon = 910 \text{ M}^{-1} \text{ cm}^{-1}$).

General procedure for oxidation of alcohols with TriPPFC and TriPPBC

To a stirred suspension of TriPPFC or TriPPBC (1 mmol) in dichloromethane (25 ml), a solution of the substrate (1 mmol) in the minimum amount of dichloromethane was added drop wise (Table I). The progress of the reaction is monitored by TLC and UV/Vis spectrophotometry. Filtration and evaporation of solvent furnished the product. The molar ratios of substrate to oxidants were 1:1. The solution became homogeneous briefly before the black-brown reduced reagent precipitated. The products are purified by distillation, crystallization or columns.

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