

Methyltriphenylphosphonium Halochromates, [Me(Ph)₃P][CrO₃X] (MTriPPXC) (X= F, Cl, Br): the Three New, Mild and Stable Oxidants for Organic Substrates

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ABSTRACT

Methyltriphenylphosphonium Halochromates (MTriPPXC) were prepared and used for oxidation of alcohols under mild conditions. These new compounds are more efficient and have certain advantages over similar oxidizing agents in terms of the amount of oxidants, short reaction times, and high yields. Methyltriphenylphosphonium Halochromates, Me(Ph)₃PCrO₃X (MTriPPXC) (X= F, Cl, Br) are easily synthesized by the reaction of Methyltriphenylphosphonium with an aqueous solution of CrO₃ and HX in a 1:1:2 mole ratio. The reactions were carried out in solution, under mild and acid-free conditions.

Key Words: Chromium(VI), Methyltriphenylphosphonium Fluorotrioxochromate, Methyltriphenylphosphonium Chlorotrioxochromate, Methyltriphenylphosphonium Bromotrioxochromate, Oxidation, Organic substrate, Alcohols.

1. INTRODUCTION

Of the large number of "mild" chromium based oxidizing agents available, many have proven to be impractical when the reactions are performed on a large (mol) scale [1], although in recent years, significant improvements have been achieved by the use of new oxidizing agents [2-4]. Examples are pyridinium fluorochromate [5], chromium trioxide-3,5-dimethylpyrazole complex [6], 3-carboxypyridinium chlorochromate [7], 4-benzylpyridinium fluorochromate [8], quinoxalium fluorochromate (QxFC) [9], tetramethylammonium fluorochromate [10], tripropylammonium fluorochromate [11] and tributylammonium chlorochromate [12]. These reagents may all be used for the oxidation of alcohols to corresponding aldehydes and ketones. This manuscript introduces Methyltriphenylphosphonium Halochromates (VI) (MTriPPXC), (X=F, Cl, Br) for the oxidation of alcohols to their corresponding aldehydes and ketones, under mild conditions.

2. EXPERIMENTAL

Methyltriphenylphosphonium bromide and chromium trioxide were obtained from Fluka (Buchs, Switzerland). Melting points are measured on an Electrothermal 9100 apparatus. Infrared spectra were recorded as KBr disks on a Shimadzu model 420 spectrophotometer. The UV/Visible measurements were made on an Uvicon model 922 spectrophotometer. Proton, ¹³C and ¹⁹F NMR were carried out on a Bruker AVANCE DRX 500 spectrometer at 500, 125, 470.66 MHz. All the chemical shifts are quoted in ppm using the high-frequency positive convention; Chromium was estimated iodometrically. In the case of the reduced product of the oxidant, chromium was determined after oxidizing with acidic peroxodisulfate (K₂S₂O₈) solution.

2.1. Preparation of Methyltriphenylphosphonium Fluorochromates, MTriPPFC

A 1g (10 mmol) sample of chromium (VI) oxide, CrO₃, and 9 ml (20 mmol) of 40% hydrofluoric acid were

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added to 20 ml of water in a 100 ml polyethylene beaker with stirring. After 5-7 min the homogeneous solution was cooled to 0 °C. To the resultant clear orange solution, Methyltriphenylphosphonium bromide (14 ml, 100 mmol) was added portion-wise, with stirring to this solution over a period of 0.5 h and stirring was continued for 0.5 h at 0 °C. The solid was washed with hexane and dried under vacuum for 1 h. IR. (KBr): 909 cm^{-1} $\nu_1(\text{A}_1)$ or $\nu(\text{CrO}_3)$, 644 cm^{-1} $\nu_2(\text{A}_1)$ or $\nu(\text{Cr-F})$, 944 cm^{-1} $\nu_4(\text{E})$ or $\nu(\text{CrO}_3)$ cm^{-1} . UV/Visible $^{13}\text{C-NMR}$, $^1\text{H-NMR}$ and $^{19}\text{F-NMR}$ were all consistent with the MTriPPFC structure. Electronic absorption at 450 nm, corresponding to $1a_2 \rightarrow 9e$ ($\epsilon = 136 \text{ M}^{-1} \text{cm}^{-1}$); 363 nm to $8e \rightarrow 9e$ ($\epsilon = 354 \text{ M}^{-1} \text{cm}^{-1}$); and 273 nm to $12a_1 \rightarrow 9e$ ($\epsilon = 1083 \text{ M}^{-1} \text{cm}^{-1}$).

2.2. Preparation of Methyltriphenylphosphonium Chlorochromates, MTriPPCC

To a solution of 1g (0.01 mol) CrO_3 in 25 ml water, placed in a 100 ml beaker, hydrochloric acid (15 ml, 0.298 mol) 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. Methyltriphenylphosphonium bromide (3.5 g, 0.01 mol) is added portion-wise, with stirring. A reddish orange solid is separated and stored in the refrigerator IR. (KBr): 903 cm^{-1} $\nu_1(\text{A}_1)$ or $\nu(\text{CrO}_3)$, 946 cm^{-1} $\nu_4(\text{E})$ or $\nu(\text{CrO}_3)$ and 432 cm^{-1} $\nu_2(\text{A}_1)$ or $\nu(\text{Cr-Cl})$. UV/Visible $^{13}\text{C-NMR}$ and $^1\text{H-NMR}$ were all consistent with the MTriPPCC structure. Electronic at 450 nm, Corresponding to $1a_2 \rightarrow 9e$ ($\epsilon = 80 \text{ M}^{-1} \text{cm}^{-1}$); 363 nm to $8e \rightarrow 9e$ ($\epsilon = 478 \text{ M}^{-1} \text{cm}^{-1}$); and 274 nm to $12a_1 \rightarrow 9e$ ($\epsilon = 1324 \text{ M}^{-1} \text{cm}^{-1}$).

2.3. Preparation of Methyltriphenylphosphonium Bromochromates, MTriPPBC

A solution of chromium trioxide (1 g, 0.01 mol) in dry acetonitrile (25 ml) was cooled to 0°C and a stoichiometric amount of Methyltriphenylphosphonium Bromide (3.57 g, 0.01 mol) was added under stirring at room temperature. Within 1h, a clear orange solution formed which upon refrigerating gave solid MTriPPBC, which was isolated by filtration. The solid was washed with hexane and dried under vacuum for 1 h. IR. (KBr): 908 cm^{-1} $\nu_1(\text{A}_1)$ or $\nu(\text{CrO}_3)$, 944 cm^{-1} $\nu_4(\text{E})$ or $\nu(\text{CrO}_3)$. UV/Visible $^{13}\text{C-NMR}$ and $^1\text{H-NMR}$ were all consistent with the MTriPPBC structure. Electronic at 452 nm, corresponding to $1a_2 \rightarrow 9e$ ($\epsilon = 78 \text{ M}^{-1} \text{cm}^{-1}$); 363 nm to $8e \rightarrow 9e$ ($\epsilon = 499 \text{ M}^{-1} \text{cm}^{-1}$); and 270 nm to $12a_1 \rightarrow 9e$ ($\epsilon = 1350 \text{ M}^{-1} \text{cm}^{-1}$).

2.4. Oxidation of Alcohols: General Method

In a small-scale experiment MTriPPXC were suspended in methylene chloride (*ca.* 2 ml) and an alcohol (1 mmol in 0.5 to 1.5 ml of CH_2Cl_2) were rapidly added at room temperature and the resulting mixture stirred vigorously for the appropriate time (Table 1). The molar ratios of substrate to oxidants were 1:1 in the case of alcohols. The solution became homogeneous briefly before the black-brown reduced reagent precipitated. The progresses of the reactions were monitored by TLC and UV/Visible spectrophotometry (at 363 nm). Analysis of the reaction mixture for the corresponding carbonyl

compound was accomplished by the procedure reported in earlier papers [5-10].

3. DISCUSSION AND CONCLUSIONS

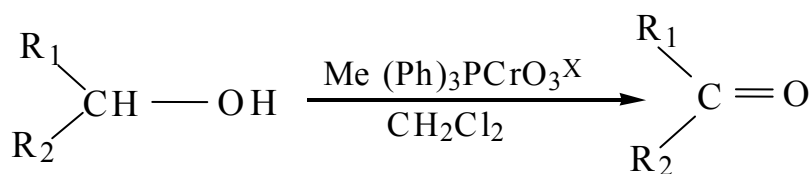
MTriPPXC are easily prepared, with a relatively excellent yield. The structure and formula of MTriPPXC are determined and confirmed by using UV/Visible, IR, $^{13}\text{C-NMR}$, $^1\text{H-NMR}$ and $^{19}\text{F-NMR}$ (for MTriPPFC) spectroscopies. MTriPPFC, MTriPPCC and MTriPPBC are prepared by two different methods. MTriPPFC and MTriPPCC are prepared by the reaction of chromium(VI) oxide, related acid and Methyltriphenylphosphonium bromide. MTriPPBC prepared by a direct addition reaction that is between chromium (VI) oxide and Methyltriphenylphosphonium bromide without any use of acid. The orange crystalline reagents could be stored in polyethylene containers for long periods without decomposition.

Organic chemists must often choose from hundreds of oxidizing agents and reaction conditions to perform a desired oxidation without affecting other functional groups present or causing side reactions. Oxidations of primary alcohols to aldehydes without further oxidation to carboxylic acids is difficult to accomplish with oxidizing agents in aqueous solution because small amounts of aldehyde hydrates, which are in equilibrium with the aldehyde, are readily oxidized to the corresponding carboxylic acids. The results obtained with MTriPPFC, MTriPPCC and MTriPPBC are very satisfactory and shows that these new reagents as valuable additions to the existing oxidizing agents. MTriPPFC, MTriPPCC and MTriPPBC in dichloromethane oxidize primary and secondary alcohols to the corresponding aldehydes or ketones in high yields (Scheme 1, Table 1).

MTriPPFC, MTriPPCC and MTriPPBC, have also been used for oxidation of carbohydrates such as 1, 2: 5, 6 - Di-O-isopropylidene- α -D-Glucofuranose to its relative ketosugar as pyridinium dichromate, by use of the equimolar ratio of the reagents (Scheme 2).

The reaction of triphenylphosphine with MTriPPXC (molar ratio of PPh_3 : MTriPPXC = 1:1.1) in acetonitrile were carried out at room temperature and triphenylphosphine oxide were obtained in quantitative yields. This provides a clear-cut example of an oxygen transfer reaction involving MTriPPXC.[10-12] Because of the stability and solubility of MTriPPFC, MTriPPCC and MTriPPBC, reactions can be performed at room temperature and the separation of the products is facile. During the reactions, the color of the oxidants change from orange to brown, providing visual means for ascertaining the progress of the oxidation. The mechanisms for the present oxidations are still unclear. However we assume that the mechanisms of oxidations are similar to that of other halochromates. In addition these oxidants and the oxidation conditions can be used for the synthesis of highly functionalized molecules.

Scheme 1



Scheme 2

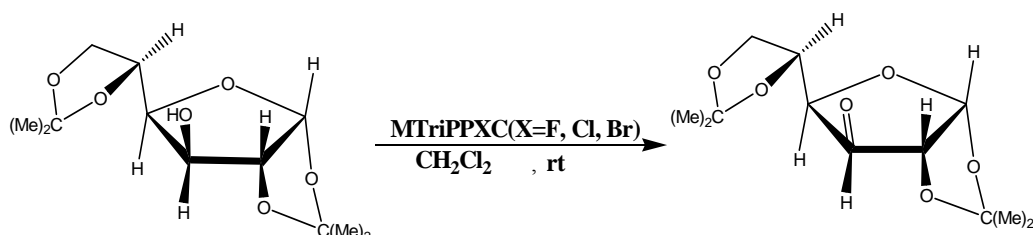
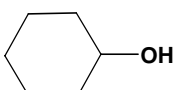
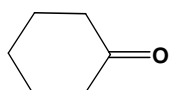
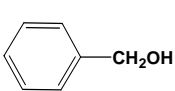
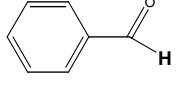
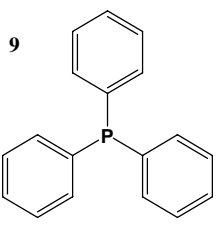
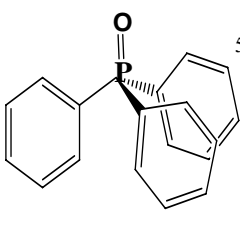


Table 1. Oxidation of alcohols and polycyclic arenes with MTriPPXC (X= F, Cl, Br)

Substrate	Product	MTriPPFC		MTriPPCC		MTriPPBC		
		Time (min)	Yield (%)	Time (min)	Yield (%)	Time (min)	Yield (%)	
1	n-C3H7-OH	n-C2H5-CHO	120	92	133	90	150	88
2	2-C3H7-OH	2-C2H5-CHO	128	90	140	92	135	85
3	n-C4H9-OH	n-C3H7-CHO	120	94	130	93	130	91
4	2-C4H9-OH	n-C3H7-CHO	100	94	105	92	113	83
5	n-C5H11-OH	n-C4H9-CHO	90	89	95	88	98	87
6	n-C8H17-OH	n-C7H15-CHO	70	88	84	86	90	85
7			4h	90	5h	88	7h	87
8			35	96	40	95	40	94
9			5	94	5	92	5	90

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