

Mild and Efficient Reagents for Oxidation of Alcohols: [MeOCH₂(Ph)₃P]⁺[CrO₃X][−], (X=F, Cl)

Amir Lashgari^{*1} and Shahriar Ghammamy

¹Department of Chemistry, Faculty of Science, Imam Khomeini International University, Qazvin, Iran

*Corresponding email: ikiu2014@gmail.com

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ABSTRACT

Two fast, mild, and reasonable oxidizing agents, methoxymethyltriphenylphosphonium halochromates (VI), [MeOCH₂(Ph)₃P]⁺[CrO₃X][−] (MMTriPPXC) are synthesized. The preparations of methoxymethyltriphenylphosphonium halochromates are new and efficient reagents for the oxidation of primary and secondary alcohols to their corresponding carbonyl compounds in dichloromethane at ambient temperature. These are obtained with relatively short reaction times. The oxidants/substrates ratios of 1:1 are employed.

Key words: chromium(VI), methoxymethyltriphenylphosphonium, fluorotrioxochromate, methoxymethyltriphenylphosphonium chlorotrioxochromate, oxidation, organic substrate.

INTRODUCTION

Oxidation of organic compounds under non aqueous and aprotic conditions is an important reaction in synthetic organic chemistry. For this purpose different Cr(VI) based oxidants are reported in the literature [1-10]. Thus a milder, more selective and inexpensive reagent is still in demand. Extensive work has led to the development of a good number of these oxidants such as the Collins reagent [11], chromium trioxide-3,5-dimethylpyrazole complex [12], 2,2'-bipyridinium chlorochromate (BIPCC) [13], 3,5-dimethylpyrazolium fluorochromate [14], 2,6-dicarboxypyridinium chlorochromate [15,16], *N*-methylpiperidinium chlorochromate [17], tetramethylammonium fluorochromate(VI) (TMAFC) [18], and *N*-methylbenzylammonium fluorochromate(VI) (MBAFC) [19]. These reagents may all be used for the oxidation of alcohols to corresponding aldehydes and ketones. This manuscript introduces methoxymethyltriphenylphosphonium halochromates (MMTriPPXC) that are new promising phosphonium reagents with improved efficiency, selectivity and durability, for the oxidation of alcohols to their corresponding aldehydes and ketones, under mild conditions.

EXPERIMENT

Chemicals and instrumentation

Methoxymethyltriphenylphosphonium chloride and chromium trioxide were obtained from Fluka (Buchs, Switzerland). Chromium was estimated iodometrically. In the case of the reduced product of the oxidant, chromium was determined after oxidizing with acidic potassium peroxodisulfate (K₂S₂O₈) solution. The percent composition of elements was obtained from the Microanalytical Laboratories, Department of Chemistry, OIRC, and Tehran. Melting points are measured on an Electrothermal 9100 apparatus and are

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uncorrected. Analysis of $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and $^{19}\text{F NMR}$ spectra was measured on a BRUKER-DRX500 AVANCE instrument. The UV-Vis measurements were made on an Uvicon model 922 spectrometer. All separations and quantization of alcohols and aldehydes were performed using a Philips 4410 gas Chromatograph. Include for FTIR analysis (Shimadzu FTIR QP89500, sample was analysed using NaCl plate or thin film).

Preparation of methoxymethyltriphenylphosphonium fluorochromate (VI) (MMTriPPCF) $[\text{MeOCH}_2(\text{Ph})_3\text{P}]^+[\text{CrO}_3\text{F}]^-$

A 1.0 g (10 mmol) sample of chromium (VI) oxide, CrO_3 , and 9ml (20 mmol) of 40% hydrofluoric acid were 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, Methoxymethyltriphenylphosphonium Chloride (3.42g, 10 mmol) was added to this solution over a period of 30min and stirring was continued for 30min at 0 °C. The solid was washed with hexane and dried under vacuum for 1 h. $\text{C}_{20}\text{H}_{20}\text{FCrO}_4\text{P}$: Calculated. %C, 56.33; %H, 4.69. Found: %C, 58.46; %H, 4.87. IR. (KBr): 900 cm^{-1} $\nu_1(\text{A}_1)$ or $\nu(\text{CrO}_3)$, 630 cm^{-1} $\nu_2(\text{A}_1)$ or $\nu(\text{Cr-F})$, 940 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 MMTriPPCF structure. Electronic absorption at 450 nm, corresponding to $1a_2 \rightarrow 9e$ ($\epsilon = 157\text{ M}^{-1}\text{ cm}^{-1}$); 363 nm to $8e \rightarrow 9e$ ($\epsilon = 512\text{ M}^{-1}\text{ cm}^{-1}$); and 274 nm to $12a_1 \rightarrow 9e$ ($\epsilon = 1272\text{ M}^{-1}\text{ cm}^{-1}$).

Preparation of methoxymethyltriphenylphosphonium chlorotrioxochromate (VI) (MMTriPPCC) $[\text{MeOCH}_2(\text{Ph})_3\text{P}]^+[\text{CrO}_3\text{Cl}]^-$

Methoxymethyltriphenylphosphonium chlorotrioxochromate, can be easily prepared in excellent yield from the reaction of CrO_3 with Methoxymethyltriphenylphosphonium chloride in acetonitrile in a molar ratio of 1:1. To a solution of (1g 10 mmol) CrO_3 in was dissolved in acetonitrile in a beaker and methoxymethyltriphenylphosphonium chloride (3.42 g, 10 mmol) was added dropwise with stirring over a period of 30min and stirring was continued for 30min at 0 °C. A clear orange solution is obtained. An orange soft-solid, in a greenish liquid is obtained. To this mixture, 30 ml CH_2Cl_2 is added. The orange organic phase is decanted and the solvent is distilled off. A reddish orange gel is separated and stored in the refrigerator. $\text{C}_{20}\text{H}_{20}\text{ClCrO}_4\text{P}$: Calculated. %C, 54.23; %H, 4.51. Found: %C, 56.89; %H, 4.72. IR. (KBr): 900 cm^{-1} $\nu_1(\text{A}_1)$ or $\nu(\text{CrO}_3)$, 430 cm^{-1} $\nu_2(\text{A}_1)$ or $\nu(\text{Cr-Cl})$, 944 cm^{-1} $\nu_4(\text{E})$ or $\nu(\text{CrO}_3)$. $^{13}\text{C-NMR}$ and $^1\text{H-NMR}$ were all consistent with the MMTriPPCC structure. UV/Visible: Electronic transition at 448 nm, Corresponding to $1a_2 \rightarrow 9e$ ($\epsilon = 273\text{ M}^{-1}\text{ cm}^{-1}$); 363 nm to $8e \rightarrow 9e$ ($\epsilon = 635\text{ M}^{-1}\text{ cm}^{-1}$); and 271 nm to $12a_1 \rightarrow 9e$ ($\epsilon = 1512\text{ M}^{-1}\text{ cm}^{-1}$).

Oxidation of alcohols: General Method

A solution of the alcohol in the minimum amount of dichloromethane (25 ml) is added dropwise at room temperature to a stirred suspension of methoxymethyltriphenylphosphonium halochromates (0.01 mol). The progresses of the reactions are monitored by TLC and UV/Vis spectrophotometry (at 363 nm). The mixture were stirred and refluxed for the time indicated in the Table 1. At room temperature, diluted with CH_2Cl_2 and filtered. 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. Products are characterized by comparison with authentic samples (NMR, IR, TLC and mp/bp measurement).

RESULT AND DISCUSSION

Primary and secondary alcohols are converted to their corresponding carbonyl compounds in good to high yields. Further oxidation of aldehydes to their carboxylic acids was not observed. Under the same conditions alcohols are selectively oxidized to their corresponding carbonyl compounds.

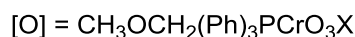
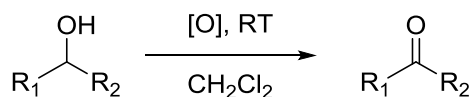
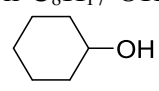
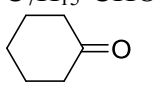
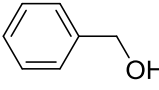
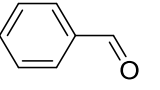
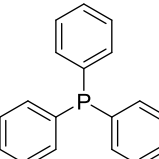
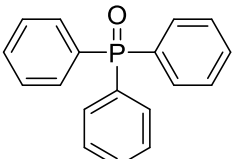


Figure 1. The oxidation of secondary alcohols at room temperature.

The selectivity of methoxymethyltriphenylphosphonium halochromates(VI) (MMTriPPXC) $[\text{MeOCH}_2(\text{Ph})_3\text{P}]^+[\text{CrO}_3\text{X}]^-$, (X=F, Cl) (MMTriPPXC) are well demonstrated through their oxidation of benzyl alcohol (yield of product: 92 and 94% respectively), in the presence of equimolar amounts of 2-phenylethyl alcohol (no product detected). Neither carboxylic acids overoxidation products nor other by-products are formed upon oxidation of alcohols via MMTriPPXC reagents. Different primary and secondary alcohols were subjected to oxidations with methoxymethyltriphenylphosphonium halochromates (VI) (MMTriPPXC) in dichloromethane (Figure 1). These oxidations take place under mild and completely ordinary conditions and giving excellent yields (Table 1).

Table 1. Oxidations via MMTriPPCC and MMTriPPFC

	Substrate	Product	MMTriPPCC		MMTriPPFC	
			Time (min)	Yield (%)	Time (min)	Yield (%)
1	n-C ₃ H ₇ -OH	n-C ₂ H ₅ -CHO	120	90	120	92
2	2-C ₃ H ₇ -OH	2-C ₂ H ₅ -CHO	95	92	90	94
3	n-C ₄ H ₉ -OH	n-C ₃ H ₇ -CHO	90	88	90	92
4	2-C ₄ H ₉ -OH	2-C ₃ H ₇ -CHO	85	88	80	90
5	n-C ₅ H ₁₁ -OH	n-C ₄ H ₉ -CHO	100	90	85	91
6	n-C ₈ H ₁₇ -OH	n-C ₇ H ₁₅ -CHO	90	86	80	88
7			1.5 h	96	1h	95
8			60	92	48	94
9			4	90	4	90

MMTriPPXC and the results may also be useful in defining other related reactions. The reactions of triphenylphosphine with MMTriPPXC in acetonitrile were carried out at room temperature and triphenylphosphine oxide was obtained in quantitative yields. These provide a clear-cut example of oxygen transfer reaction involving MMTriPPXC (Figure 2).

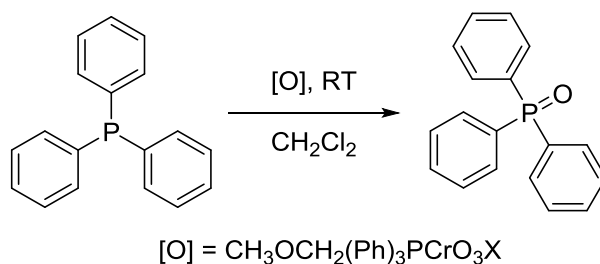


Figure 2. The oxidation of Triphenylphosphine at room temperature.

CONCLUSION

Methoxymethyltriphenylphosphonium fluorochromate was prepared from chromium(VI) oxide, methoxymethyltriphenylphosphonium chloride and aqueous HF in a mole ratio of 1:1:2. But, methoxymethyltriphenylphosphonium chlorochromate was easily prepared from the reaction of chromium(VI) oxide and methoxymethyltriphenylphosphonium chloride without any use of acid. The bright orange crystalline reagents could be stored in polyethylene containers for long periods without decomposition. The IR spectra are similar to that of the other halochromates [20-25]. Methoxymethyltriphenylphosphonium halochromates are soluble in water, dimethylformamide, acetonitrile, acetone and dichloromethane. They are only sparingly soluble in benzene, carbon tetrachloride, chloroform and hexane. Moreover, functional groups such as methoxy and methyl attached on the phenyl ring are inert to these reagents. In addition, we have shown that these reagents do not oxidize a variety of other substrates, including diphenyl sulfide, thiophenol, 3,5-dimethoxyphenol, 2-benzyl-3,4-dihydro-2H-pyran, benzyloxytrimethylsilane, N-methyl-2-phenylthioacetamide and sodium 2-hydroxyiminomalonate. The results obtained with methoxymethyltriphenylphosphonium halochromates are very satisfactory and show the new reagents to be valuable additions to existing oxidizing agents.

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