

Synthesis of Triphenylmethylphosphonium Chlorochromate as A Mild and Selective Reagent for Oxidation of Alcohols

A.R. Hajipour^{a,b,*}, L. Khazdooz^a and A.E. Ruoho^b

^aPharmaceutical Research Laboratory, College of Chemistry, Isfahan University of Technology, Isfahan 84156, Iran

^bDepartment of Pharmacology, University of Wisconsin Med. Sch. 1300 University Avenue, Madison, 53706-1532, WI, USA

(Received 4 September 2005, Accepted 1 November 2005)

Triphenylmethylphosphonium chlorochromate was synthesized from triphenylmethyl bromide and chromium(VI) oxide in HCl 6 N and used as an efficient and selective reagent for oxidation of alcohols to their corresponding aldehydes or ketones derivatives in refluxing acetonitrile in good to excellent yields.

Keywords: Alcohols, Aldehydes, Ketones, Oxidation, Triphenylmethylphosphonium chlorochromate

INTRODUCTION

Oxidation in modern organic chemistry is one of the most important reactions. Classic reagents like manganese dioxide (MnO₂), potassium permanganate (KMnO₄), chromium trioxide (CrO₃), potassium chromate (K₂CrO₄), and potassium dichromate have been used in literature [1]. Some new reagents have also been reported [2-11]. Most of the previous oxidants suffer at least from one of the following disadvantages: 1) long reaction time, 2) hygroscopicity, 3) high acidity, 4) instability, 5) no selectivity and dangerous procedure for preparation, 7) tedious work-up procedures, 8) photosensitivity, 9) high cost of preparation, 10) low yields of products, 11) over oxidation to carboxylic acids. The most widely employed transition metal oxidant is Cr(VI) in aqueous solution depending upon concentration and pH. In dilute solution, the monomeric acid chromate ion is present, and as the concentration increases, the dichromate ion dominates. It is believed that in oxidation of alcohols, a part of the substrate

is oxidized *via* a free radical intermediate resulting from oxidation by Cr(VI). This scheme also includes Cr(V) as a participant in the mechanism [12].

EXPERIMENTAL

General

All yields refer to isolated products. Products were characterized by comparison with authentic samples (¹H NMR, IR and GC spectrum, melting and boiling point, TLC). ¹H NMR spectra was recorded on a 250 MHz in DMSO-d₆, IR spectra on a FT-IR_680plus and GC spectra on a GC-14A Shimadzu.

Preparation of Triphenylmethylphosphonium Chlorochromate

To a solution of triphenylmethylphosphonium bromide (10 mmol, 3.57 g) in water (25 ml) was added a solution of CrO₃ (10 mmol, 0.99 g) in HCl 6 N (15 ml) under stirring at room temperature until an orange precipitate was formed. After 30 min stirring, the mixture was filtered, washed with water

*Corresponding author. E-mail: haji@cc.iut.ac.ir

Table 1. Oxidation of Alcohols by $\text{Ph}_3\text{PMeClCrO}_3$ in Refluxing Acetonitrile^{a,b}

Substrate (2)	Product (3)	Time (min)	Yield (%)
PhCH ₂ OH	PhCHO	10	85
3-MeOC ₆ H ₄ CH ₂ OH	3-MeOC ₆ H ₄ CHO	10	89
4-MeOC ₆ H ₄ CH ₂ OH	4-MeOC ₆ H ₄ CHO	10	90
3,4-(MeO) ₂ C ₆ H ₃ CH ₂ OH	3,4-(MeO) ₂ C ₆ H ₃ CHO	10	90
2,5-(MeO) ₂ C ₆ H ₃ CH ₂ OH	2,5-(MeO) ₂ C ₆ H ₃ CHO	10	91
2-OHC ₆ H ₄ CH ₂ OH	2-OHC ₆ H ₄ CHO	10	88
2-ClC ₆ H ₄ CH ₂ OH	2-ClC ₆ H ₄ CHO	10	80
4-ClC ₆ H ₄ CH ₂ OH	4-ClC ₆ H ₄ CHO	10	80
4-BrC ₆ H ₄ CH ₂ OH	4-BrC ₆ H ₄ CHO	15	84
3-NO ₂ C ₆ H ₄ CH ₂ OH	3-NO ₂ C ₆ H ₄ CHO	180	72
4-NO ₂ C ₆ H ₄ CH ₂ OH	4-NO ₂ C ₆ H ₄ CHO	180	75
PhCHOHPh	PhCOPh	5	90
PhCHOHCOPh	PhCOCOPh	10	95
1-hexanol	1-hexanal	150	0
1-Octanol	1-Octanal	150	0
2-Ethyl-1-hexanol	2-Ethyl-1-hexanal	150	0
Cyclohexanol	Cyclohexanone	100	0

^aSubstrate/Oxidant (1:1). ^bYields based on the isolated pure products after chromatography.

CONCLUSIONS

In conclusion, in this study we have introduced a new and mild reagent for oxidation of different types of alcohols in refluxing acetonitrile. The stability, easy preparation, mildness of the reagent, straightforward work-up, mild reaction conditions, high yields of the products and the reaction under non-aqueous condition make this reagent a useful method for oxidize of alcohols.

ACKNOWLEDGEMENTS

We gratefully acknowledge the funding support received for this project from the Isfahan University of Technology (IUT), IR Iran (ARH) and Grant GM 33138 (AER) from the National Institutes of Health, USA. Further financial support from Center of Excellency in Chemistry Research (IUT) is gratefully acknowledged.

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