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

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Triphenylmethylphosphonium chlorochoromate 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 chlorochoromate

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) hygroscopisity, 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 Chlorochoromate

To a solution of triphenylmethylphosphonium bromide (10 mmol, 3.57 g) in water (25 ml) was added a solution of CrO_3 (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

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(2 ×15 ml), and dried at room temperature (3.93 g, 95.4% Yield); m.p.: 128-130 °C; IR (KBr): 3053, 2970, 1900, 1586, 1495, 1484, 1437, 1115, 997, 945, 787, 741, 686 cm⁻¹.

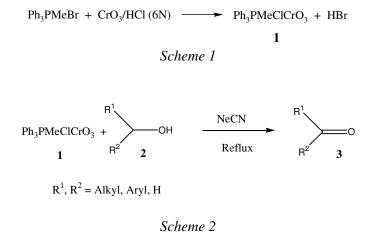
Oxidation of Benzyl Alcohol with Triphenylmethylphosphonium Chlorochoromate to Benzaldehyde

In a round-bottomed flask (25 ml), equipped with a reflux condenser and a magnetic stirrer, a solution of benzyl alcohol (1 mmol, 0.11 g) and triphenylmethylphosphonium chlorochoromate (1 mmol, 0.41 g) in acetonitrile was added and refluxed for 10 min. The reaction was monitored by TLC (EtOAC/n-Hexane 10:90). The reaction mixture was cooled to room temperature and the solid was then separated through a short pad of silica gel and washed with acetonitrile (5 ml). The solvent was evaporated and the resulting crude material was purified by column chromatography on silica gel using a mixture of ethyl acetate and n-hexane as eluent (10:90). Pure benzaldehyde was obtained in 85% yield (0.09 g).

RESULTS AND DISCUSSION

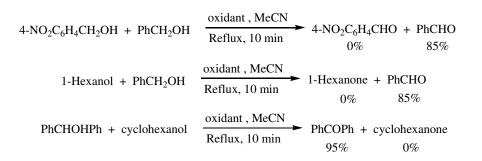
In continuous to our previous works [11,13], here we introduce an efficient, mild, selective and rapid method for selective oxidation of alcohols to their corresponding aldehydes or ketones with triphenylmethylphosphonium chlorochoromate (1). This reagent was readily prepared in high yield by adding a solution of CrO_3 in HCl (6 N) into a stirring solution of $Ph_3P^+MeBr^-$ and continued to stir for 30 min at room temperature. Filtration and drying the precipitates produced an orange powder (Scheme 1).

This reagent is soluble in acetonitrile, N,N-



dimethylformamide and slightly soluble in ethyl acetate. The advantages of this oxidant are included: 1) in oxidation an excess amount of reagent do not need, 2) short reaction time, 3) no further oxidation to the corresponding carboxylic acids, 4) high selectivity, 5) by using excess amount of reagent oxidation of producing aldehyde to the carboxylic acid is occuring, 6) no Lewis acids catalyst need, 7) reaction under non-aqueous condition (Scheme 2).

In comparison to benzylic alcohols, oxidation of aliphatic alcohols with this reagent did not occurred at all even by using excess oxidizing agent (2 molar ratio) and longer reaction time. The electron donor substituted groups on benzene ring of alcohols, accelerate the reaction and the acceptors groups have the opposite effect. The secondary alcohols in compare to the primary give more yields in shorter times (Scheme 3 and Table 1).



Scheme 3

A Mild and Selective Reagent for Oxidation of Alcohols

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

Table 1. Oxidation of Alcohols by Ph₃PMeClCrO₃ in Refluxing Acetonitrile^{a,b}

^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.

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