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N-Methyl Piperidinium Chlorochromate Adsorbed on Alumina: A New and Selective Reagent for the Oxidation of Benzylic Alcohols to their Corresponding Carbonyl Compounds

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Summary. N-Methyl piperidinium chlorochromate adsorbed on alumina oxidizes a wide variety of benzylic alcohols to the corresponding carbonyl compounds.

Keywords. N-Methyl piperidinium chlorochromate; Oxidation; Benzylic alcohols; Carbonyl compounds.

Introduction

Oxidation of alcohols to carbonyl compounds is a fundamental type of reaction encountered at all levels and aspects of organic synthesis [1]. Oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones is often accomplished using chromium IV [2], manganese reagents [3], and oxalyl chloride/*DMSO* [4]. A large number of catalytic systems employing a metal complex associated with a peroxo species have been described for the oxidation of alcohols to the corresponding carbonyl compounds [5], but these reagents are in most cases relatively expensive and rarely commercially available. Pyridinium chlorochromate in dichloromethane [6] is a versatile oxidizing reagent of high efficiency; however, work-up of the reaction mixture is tedious [7].

Results and Discussion

Reagents adsorbed on mineral supports have gained popularity in organic synthesis due to their selectivity and their simplicity of manipulation [8]. In continuation of our program to develop methodologies using solid supports [9], we report a very facile method of oxidation of primary and secondary alcohols employing N-methyl piperidinium chlorochromate (*MPPC*) adsorbed on alumina.

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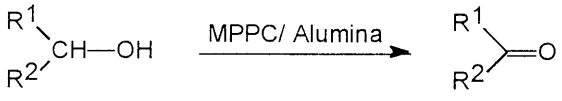
The reagent is inexpensive and easily prepared by reaction of N-methyl piperidine with chromium trioxide in 6 *N* hydrochloric acid. *MPPC* is soluble in polar solvents such as dioxane and acetone and insoluble in chloroform, benzene, and hexane. The oxidizing reagent can be stored at least for three months without losing its activity. The *pH* of a 0.01 *M* aqueous solution of *MPPC* is 1.85, which is quite close to that reported for pyridinium chlorochromate (1.75) and lower than that reported for zinc chlorochromate monohydrate (2.3) [10].

Preliminary investigations demonstrated that some primary and secondary alcohols (1 mmol) can be oxidized to the corresponding aldehydes and ketones with *MPPC* (2 mmol). We observed conversions up to 65%; additional oxidizing agent failed to drive the reaction to completion. The moderate yields can presumably be attributed to difficulties with the work-up of the reaction mixture.

The concept of utilizing reagents adsorbed on inert inorganic supports for oragnic reactions is well documented [8, 9] and has been applied especially to chromium compounds [9a–f,j]. *MPPC* adsorbed on alumina provides a particular environment capable of enhancing the reactivity of several reactants. Perhaps neutral alumina modifies the mildly acidic character of piperidinium chlorochromate. Among the various solid supports examined such as montmorillonite K-10, silica gel, and alumina, the latter turned out to work best. This reagent is easily prepared by adding alumina to an aqueous solution of *MPPC* followed by evaporation to dryness on a rotary evaporator. The yellow-orange solid can be stored at room temperature and in light at least for three months. The reaction is simply performed by stirring an excess of oxidant with alcohol in *e.g.* dioxane. The products can be easily isolated by mere filtration and removal of solvent. Interestingly, this adsorbed reagent is effective only in oxidizing primary and



Scheme

Table 1. Oxidation of benzylic alcohols with *MPPC* adsorbed on alumina in dioxane

R^1	R^2	Reaction time / min	Yield[a] / %
C_6H_5	H	100	93
m-ClC_6H_4	H	119	89
p-ClC_6H_4	H	75	91
p-BrC_6H_4	H	60	92
m-OHC_6H_4	H	80	96
C_6H_5	C_6H_5	120	80
p-ClC_6H_4	C_6H_5	125	81
C_6H_5	CH_3	110	89
C_6H_5CO	C_6H_5	720	75
o-$NH_2C_6H_4$	H	240	83

[a] Yields refer to isolation of *DNPH* derivatives

secondary benzylic alcohols (Table 1) and therefore can be used for selective oxidation of benzylic alcohols in the presence of other hydroxy groups.

In conclusion, a safe oxidant on solid support, which is a good alternative to pyridinium chlorochromate, is introduced. It has all the advantages of pyridinium chlorochromate and, in addition, is selective for benzylic alcohols.

Experimental

All oxidation products are known and were identified by comparison of their physical and spectroscopic data with those of authentic samples. Yields refer to isolation of the 2,4-dinitrophenylhydrazones (*DNPH*). N-Methylpiperidine was obtained commercially.

Preparation of N-methyl piperidinium chlorochromate adsorbed on alumina

To a solution of 20 g CrO_3 (0.2 mol) in 36.8 g 6 *N* HCl (0.22 mol) at 40°C, 19.8 g N-methylpiperidine (0.2 mol) were added within 15 min. The resulting solution was stirred at 10°C for 2 h by which time a yellow-orange solid precipitated. Isolation of this material and drying gave *MPPC* (found: C 30.10, H 5.70, N 5.60, Cr 21.9%; calcd.: C 30.64, H 6.00, N 5.96, Cr 22.1%). Reheating of the above *MPPC* suspension to 40°C resulted in a homogeneous solution. Alumina (100 g, 100–200 mesh) was then added while stirring at 40°C. After evaporation under reduced pressure, the yellow-orange solid was dried in vacuum. *MPPC* and *MPPC*/alumina can be preserved for at least 3 months in air and at room temperature without losing their activity.

Oxidation of benzylalcohol

1 g of the above reagent (2 mmol) was added to a solution of 0.147 g benzylalcohol (1 mmol) in 10 cm^3 of dioxane. The reaction mixture was stirred for 100 min at room temperature. After completion of the reaction (monitored by TLC) the solid was filtered off and washed with 10 cm^3 of $CHCl_3$. The combined filtrates were evaporated and vacuum distilled to give 83% benzaldehyde.

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