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GUANIDINIUM CHLOROCHROMATE, A NEW, EFFICIENT, AND MILD OXIDIZING AGENT FOR BENZYLIC AND OTHER ALCOHOLS TO CARBONYL COMPOUNDS IN WATER AND ORGANIC SOLVENTS

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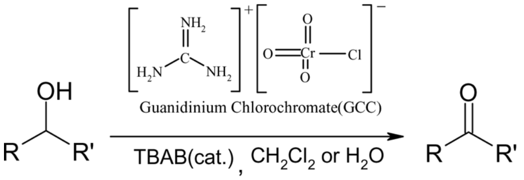
GRAPHICAL ABSTRACT



$R' =$ Ar/ CH_3; R= H/ Ar/ CH_3

Abstract *Guanidinium chlorochromate (GCC) has been first reported as a new oxidizing agent for the oxidation of a series of benzylic and a number of other aliphatic and aromatic alcohols to carbonyl compounds and quinones respectively in water in the presence of a phase-transfer catalyst and also in an organic solvent such as methylenechloride.*

Keywords Carbonyl compounds; guanidinium chlorochromate (GCC); oxidation

INTRODUCTION

Oxidation reactions are very important in organic synthesis. Many methods and oxidizing agents have been discovered for oxidation, but development and modification of known reagents have been studied in recent years.[1] Many important reviews have highlighted the discovery and use of such oxidizing agents, some of which are strong and some of which are mild. Manganese- and chromium-based compounds are classic in nature, and their oxides and different complexes have been developed for many successful oxidations. Chromium-based oxidizing agents such as chromium trioxide-pyridine,[2] Jones reagent ($CrO_3/CH_3COCH_3/H_2SO_4$),[3] pyridinium chlorochromate (PCC),[4] pyridinium dichromate (PDC),[5] 1,1,3,3-tetramethylguanidinium dichromate (TMGDC), pyridinium fluorochromate,[6] benzyltrimethylammonium fluorochromate, tributylammonium chlorochromate,

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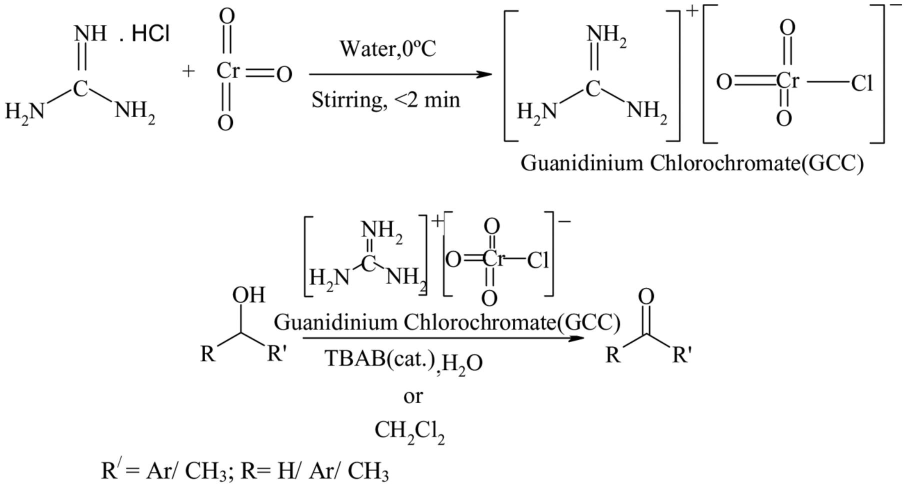
methyltriphenylphosphonium halochromates, poly[N-(4-pyridinium dichromate)-*p*-styrene sulfonamide],[7] and also ceric ammonium nitrate[8] have been reported and are widely used. Still the demand of new oxidizing agents that are either soluble in water or organic solvents is increasing. Co(I) oxidations[9] are also effective in very mild conditions for oxidation of benzylic alcohols to aldehydes, which we have developed. The other mild oxidants developed are dimethylsulfoxide–N,N′-dicyclohexylcarbodiimide (DMSO–DCC),[10] DMSO–Ac_2O,[11] DMSO–P_4O_{10},[12] DMSO–oxalyl chloride or trifluoroacetic anhydride (TFAA),[13] hypervalent iodine, and Oppenauer oxidation.[14]

We herein report the development of another novel oxidizing agent, guanidinium chlorochromate (GCC), whose acidity is somewhat less than that of pyridinium chlorochromate as guanidine is a stronger base than pyridine, and the solubility of GCC is more in water, although it is soluble in dimethylformamide (DMF), DMSO, acetone, and acetonitrile. A phase-transfer catalyst like *t*-butylammonium bromide increases its applicability for both water-soluble or insoluble alcohol substrates.

The new oxidizing reagent, GCC, was prepared (Scheme 1) by treatment of equivalent amounts of guanidinium hydrochloride and chromium trioxide in water at 0 °C instantaneously by stirring with a glass rod. The reagent is stable at room temperature, moderately light sensitive in solution state, but fairly light stable in solid phase. Infrared (IR) spectrum showed peaks at 3454, 1652, 1558, 946, and 902 cm^{-1}.

This new reagent is more water soluble and versatile for any benzylic-type alcohols (either water-soluble or insoluble benzylic alcohols by addition of a phase-transfer catalyst for oxidation to carbonyl compounds) (Scheme 1). GCC in water is also found to be very effective for secondary alcohols (Table 1). However, the small-chain primary alcohols like propanol and butanol are converted to the corresponding acids in aqueous medium. When the oxidation is performed in



Scheme 1. Preparation of GCC and oxidation of alcohols to carbonyl compounds.

Table 1. Oxidation of alcohols (**1**–**13**) by guanidinium chlorochromate (GCC)[a]

Entry	Substrate	Product	Yield (%)	Mp/bp (°C) found (reported)
1	Benzyl alcohol	Benzaldehyde	94	178 (178)
2	Isopropanol	Acetone	93	56
3	Cyclohexanol	Cyclohexanone	95	155.6 (156)
4	Benzoin	Benzil	97	94 (95)
5	1,1-Diphenyl methanol	Benzophenone	98	48 (48)
6	1-Phenyl ethanol	Acetophenone	94	200 (202)
7	4-Hydroxy benzyl alcohol	4-Hydroxy-benzaldehayde	83	116 (116)
8	4-Nitrobenzyl alcohol	4-Nitro-benzaldehayde	95	104 (103–106)
9	1-(*p*-Nitro phenyl) ethanol	*p*-Nitroacetophenone	93	76 (76)
10	9-Fluorinol	9-Fluorinone	75	82 (83)
11	Vanillyl alcohol	Vanillin	92	82 (83)
12	Furfuryl alcohol	Furfuraldehyde	94	164 (162)
13	1-Butanol[b]	1-Butanal	90	74 (75)

[a] Small-chain aliphatic alcohols such as propanol and butanol are converted to the acids, and long-chain alcohols such as palmityl alcohols are almost unreactive.

[b] Reaction is performed in methylenechloride solvent.

methylenechloride as solvent, short-chain primary alcohols (e.g., 1-butanol) is oxidized to 1-butanal in good yield, but the reagent is not suitable for the oxidation of primary long-chain saturated alcohols (e.g., palmityl alcohol).

Final confirmation of the structure of the new oxidizing agent GCC was established by single-crystal x-ray structure.[15] The single crystal was developed by slow evaporation of the acetone–water (70:30) solution of GCC. The single-crystal x-ray structure of GCC is shown below (Fig. 1). The ORTEP diagram shows that the unit cell contains $C(NH_2)_3^+$ (symmetrical protonated guanidinium cation) and $ClCrO_3^-$ anion as a stable salt. In Fig. 1(b), the short hydrogen bonds between the hydrogen atoms of the guanidinium cation and the oxygen atoms of the chlorochromate anion

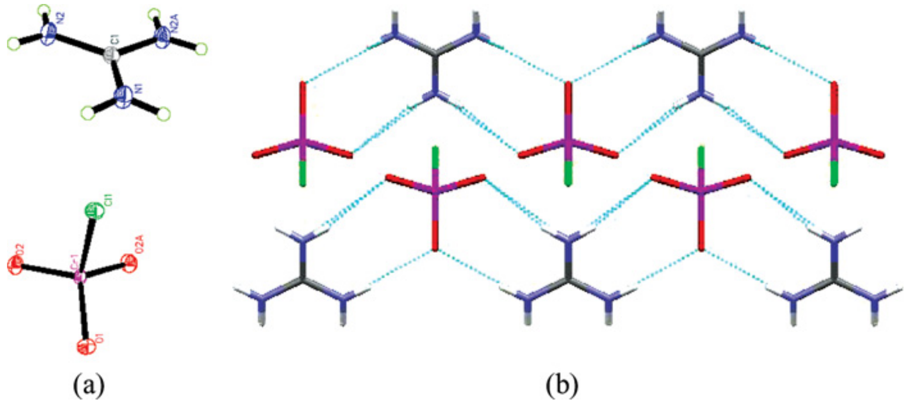


Figure 1. (a) ORTEP diagram (evaluated from single-crystal x-ray study) of GCC; (b) wavelike structure along crystallographic *b* axis. Hydrogen bonds are shown as dashed lines.

are shown where an alternate array of the respective cation and anion form a wavelike network.

Thus the oxidizing reagent, GCC, is found to be very successful in the oxidation of benzylic and other alcohols to carbonyl compounds.

In conclusion, in this study we have reported the development of a new and mild reagent for the oxidation of different types of alcohols, mainly in aqueous or binary phase. The stability, easy preparation, mildness of the reagent, straightforward workup, mild reaction condition, and good yield of the respective oxidation product make this reagent useful for oxidization of alcohols to carbonyl compounds. During the reactions, the color of the oxidant changes from orange to blackish brown, providing a visual means of ascertaining the progress of the reaction.

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