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Imidazolium Bromo chromate: a new and efficient reagent for Oxidation of aliphatic alcoholic compounds

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Abstract

The new chromium (VI) oxidizing reagent imidazolium bromo chromate (IBC) was prepared and characterized. The IBC has been found to be stable and an efficient solid reagent which can be easily prepared in good yield. It act as an efficient brominating agent for hydroxylated aromatic compounds as well as good oxidizing agent for the conversion of alcohols to carbonyl compounds with good yield.

Keywords- Imidazolium bromo chromate, Oxidation: Alcohols

Introduction

Chromium was discovered in 1798 by the French chemist Vauquelin[1]. It is a transition element located in group VI-B of the periodic table having a ground state electronic configuration of (Ar) $3d^5$ $4s^1$. Chromium is one of the most widely distributed heavy metal and is the twenty-first abundant element in the earth's crust.

Chromium (VI) complexes are among the most interesting transition metal complexes that have great attention over the past decades. Due to their appealing catalytic and oxidizing properties, they have been widely explored since the very beginning of organic chemistry. The topic remains of current interest as exemplified by the huge number of reactions involving the use of chromium (VI) reagents. Moreover, a plethora of chromium reagents and procedures have been proposed and described extensively. The main objective of present study is to synthesis of new chromium (VI) reagent for the oxidation of different organic substrates and encourage its various contributions to the important and exciting field of synthetic organic chemistry.

Brominated aromatic compounds are valuable intermediates in organic synthesis and they have been used widely industrially important products and biologically active substrate as Antitumor, Antifungal, Antibacterial, Antineoplastic and Antiviral compounds2-3

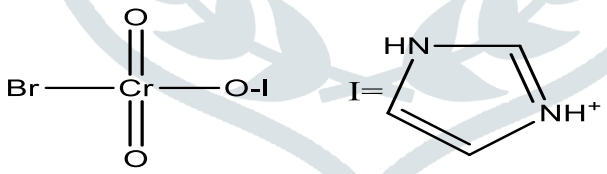
The oxidation of alcohols is the important basic reaction in organic chemistry and most commonly used method for the synthesis of aldehydes and ketones. Therefore, the search for new oxidizing agent is of interest to synthetic organic chemists.

In recent years some chromium (VI) reagents for the effective and selective oxidation of alcohols under mild conditions have been developed with some success4. Some of reagents like pyridinium dichromate5, pyridinium fluorochromate6, quinolinium chlorochromate7, quinolinium fluorochromate8, imidazolium chlorochromate9, prolinium chlorochromate10, caffelinillium chlorochromate11, are reported as oxidizing agents while some reagents like pyridinium bromochromate12, benzimidazolium bromochromate13, quinoxalinium bromochromate14 works as oxidizing as well as good brominating agent.

Oxidation states of chromium metal includes Cr+2, Cr+3, Cr+6 which are stable states whereas Cr+4 and Cr+5 are unstable in water and they form Cr+3 and Cr+6. Cr+6 is used as oxidant for various reactions. Chromium (VI) exists as acetochromate ion in presence of 97% acetic acid15. New chromium species are formed on adding anions like Cl-, Br-, F-, and So4 2- anions. The chemistry of chromium (VI) complexes has advantage in both synthetic organic chemistry and medicinal field because of its high reactivity. Nowdays, the deveiopment of new and versatile chromium (VI) reagents16-21 for oxidizing organic molecules is of great interests and studied extensively. Oxides and oxyacid's of Cr (VI) are powerful oxidants and chromic esters have been proposed as intermediates in Cr(VI) oxidations.

Preparation of Imidazolium bromochromate : This was synthesized[6] by taking 20g (0.2 mol) of chromium trioxide in water (25ml), cooled to 0^0C. To this solution, 47% HBr (38ml, 0.21mol) was added slowly with constant stirring. The content were cooled to 0^oC. and then Imidazole (14gm 0.2 mol) was added over 15-20 min. to give a brown solid. The reaction mixture was chilled for 4-5 hr. The dark brown crystals were then filterwd and dried. The product was recrystallized from aqueous acetic acid (40:60 v/v) its purity was checked by TLC and confirmed by melting point and mass analysis.

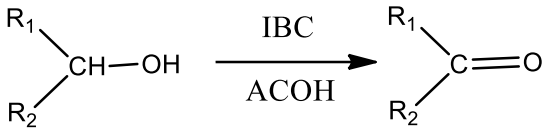
Structural formula for IBC is



imidazolium bromochromate

Oxidation of alcohols by IBC: A study of oxidative behavior of IBC with primary and secondary alcohol in acetic acid was undertaken (Scheme 1) and the results are presented in table 1. The results of oxidation obtained with IBC are satisfactory in comparison with other reagent considering the amount of oxidant, acidity, percentage yield and reaction time, respectively.

Reaction



Scheme-1

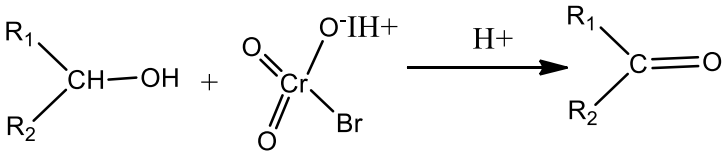
Table 1

Oxidation of alcohols by Imidazolium bromochromate

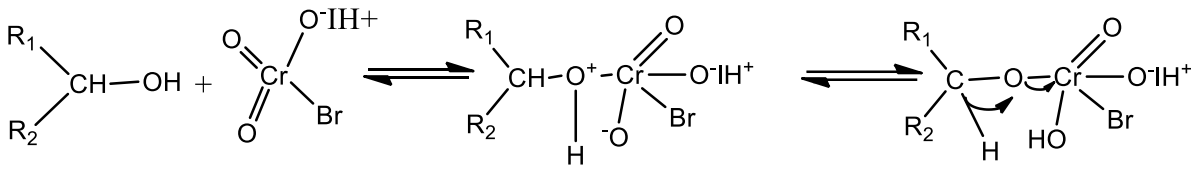
Sr. No.	Starting material	Product	B.P.(0C) (Lit)
1	n-Hexyl alcohol	1-Hexanal	129 (130) [23]
2	Isobutyl alcohol	2-Butanone	79 (82) [23]
3	n-Butyl alcohol	1-Butanal	74 (75) [23]
4	Benzyl alcohol	Benzaldehyde	180 (179) [23]
5	n-Propyl alcohol	Propanal	50 (49) [23]
6	Isopropyl alcohol	Acetone	55 (56) [23]
7	Amyl alcohol	1-Pentanal	105 (104) [23]
8	Isoamyl alcohol	2-Pentanone	101 (102) [23]

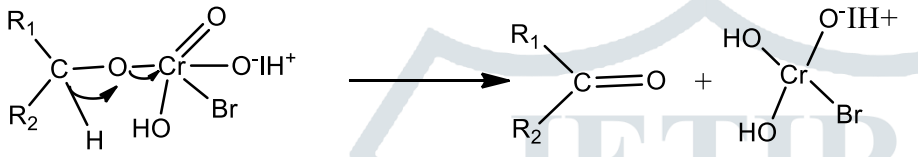
Probable reaction mechanism of oxidation of alcohols

Reaction



Mechanism





Experimental

General procedure for oxidation of alcohols: To a solution of substrate (0.01 mol) in acetic acid (15ml) Imidazolium bromochromate (0.264g, 1mmol) was added and the mixture was stirred magnetically for 2-3 h. The progress of reaction was monitored by TLC. After completion of reaction, reaction mixture was distilled by circulation of ice cold water through condenser, extracted with ether and filtered through silica column. Finally it was washed with ether. On evaporation of ether product is obtained.22

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