

Imidazolium Bromochromate: A New Efficient reagent for Bromination and Oxidation

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Abstract— The recently developed reagent, Imidazolium bromochromate (IBC), not only demonstrates high efficiency as an oxidant for alcohols but also serves as an effective brominating agent for aromatic compounds.

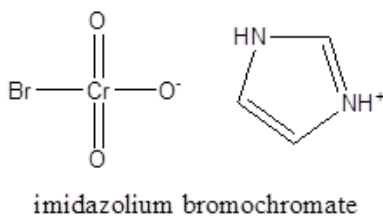
Index Terms— IBC, Oxidation, Bromination

I. INTRODUCTION

Chromium (VI) reagents find extensive applications in organic chemistry, particularly in the oxidation of alcohols to carbonyl compounds¹. There remains a sustained interest in advancing new chromium (VI) reagents to enable efficient and selective oxidation of organic substrates under mild conditions. Recent years have witnessed notable advancements through the introduction of novel oxidizing agents such as pyridinium chlorochromate²(PCC), pyridinium fluorochromate³(PFC), Quinolinium chlorochromate⁴(QCC), quinolinium dichromate⁵ and quinolinium fluorochromate⁶(QFC).

Here, we present a novel reagent, imidazolium bromochromate (IBC) (C₃H₅BrCrN₂O₃). Besides its efficacy as an oxidant, IBC demonstrates utility in the bromination of aromatic compounds. The obtained results with IBC are promising, indicating its value as a significant addition to the existing chromium (VI) reagents.

Structural formula for IBC is



Imidazolium bromochromate is conveniently synthesized from imidazole, 47% hydrobromic acid, and chromium (VI) oxide in a 1:1:1 molar ratio. IBC appears as a mustard-gray, non-hygroscopic, and moderately light-sensitive solid, necessitating protection from light during preparation and storage. Its structure was confirmed through elemental analyses and an IR (KBr) spectrum, revealing characteristic bands at 950, 749 (Cr-stretching vibration of BrCrO₃ ion), 700, 350, 260, and 230 cm⁻¹.

In imidazolium bromochromate, (CrO₃,Br)⁻ exists as the ionic form, with its vibrational spectrum aligning closely with that anticipated for the (CrO₃Br)⁻ ion, as inferred from a comparison with (CrO₃F)⁻ in KCrO₃F and (CrO₃Cl)⁻ in KCrO₃Cl. The molar conductance of IBC in water at 30°C is measured at 1.20 x 10⁻³ mho cm⁻¹. Notably, the acidity of IBC, with a pH of 3.57 for a 0.01 M solution, is less pronounced compared to pyridinium bromochromate and PCC, with pH values of 3.35 (for a 0.03 M aqueous solution) and 1.75 (for a 0.01 M solution), respectively.

IBC dissolves readily in dimethylformamide and dimethylsulphoxide, with limited solubility observed in dichloromethane and chloroform, while it remains insoluble in benzene, toluene, ether, nitrobenzene, and ethyl acetate. Oxidation experiments were conducted in dichloromethane, while bromination reactions were performed in acetic acid solution using IBC. The findings from the bromination studies are outlined in Table 1.

Table 1- Bromination of Aromatic Compounds by IBC

Substrate	Product	Solvent	Time (h)	Yield (%)

				(%)
Anisole	4-	HO	4	94
	Bromoanisole	AC		
Acetanilide	4-	HO	4	89
	Bromoacetanilide	AC		
Benzanilide	4-	HO	4	76
	Bromobenzanilide	AC		
Acetophenone	3-	HO	4	46
	Bromoacetophenone	AC		
4-Nitroacetophenone	4-Nitro-3-bromoacetophenone	HO	4	52
		AC		
4-Bromoacetophenone	4,3-Dibromoacetophenone	HO	4	51
		AC		

IMIDAZOLIUM BROMOCHROMATE (IBC)

The preparation and the uses of the polymer supported reagents in the oxidation and bromination of organic compounds are under way

IBC oxidises alcoholic compounds to the corresponding carbonyl compounds The Experimental Details and the result are given in Table 2.

II. EXPERIMENTAL

Melting points were determined in open capillaries on a digital melting point apparatus and are not corrected Mass spectra were recorded in a Q-TOF MICROMASS (ESI_MS) by SAIF, Panjab University Chandigarh, NMR an Bruker Advanced Neo 500 MHz instrument. All reagents and solvents are of reagent grade.

1 Preparation of imidazolium bromochromate:

A solution of chromium trioxide (20 g. 0.2 mol) in water (25 mL) was cooled to 0°C and to this was added 47% aqueous hydrobromic acid (23.5 ml. 0.2 mol) slowly with vigorous stirring imidazole (13.6 g. 0.2 mol) was then added dropwise during 15 min to afford a mustard gray powder. The reaction mixture was cooled for 2 hr The resulting mustard gray solid was collected on a sintered glass funnel and washed with ether, kept under suction until moderately dry. and

placed under vacuum pump pressure until a dry powder, 147°C dec. Yield 36.9 g (70%)
Found; 14.3, H,2.01, Br,32.8, Cr,20.8, Calc: C, 14.47; H, 2.02; Br, 32.09; Cr, 20.88;

Table 2- Oxidation of Alcohols by IBC in Dichloromethane

Substrate	Product	Time (hr)	Yield (%)
n-propyl alcohol	Propanal	4	68
Iso-propyl alcohol	Propanone	4-5	63
Amyl Alcohol	Pentanal	4	68
n-Hexyl alcohol	1-Hexanal	4	67
Cyclohexanol	Cyclohexanone	4	48
Octanol	Octanal	4	52
Cinnamyl Alcohol	Cinnamaldehyde	4	82
Benzyl Alcohol	Benzaldehyde	5	72

The reaction was carried out with 2 equiv. of IBC at reflux temp. All reactions were carried out in flasks blackened from the outside to prevent any photochemical reaction b. Yield was based on 2,4-dimophenylhydrazone derivative identified by melting point. The yields refer to non-optimised reaction conditions.

IMIDAZOLIUM BROMOCHROMATE

2) Bromination: General method

To a suspension of IBC (5.2 g. 0.02 mol) in acetic acid (25 ml) was added the substrate (0.01 mol) dissolved in a small amount of acetic acid. The reaction mixture was heated on a water-bath with occasional stirring The completion of the reaction was evidenced from change in the colour of the contents to green. The reaction mixture was poured into water (100 ml), extracted with ether, the ethereal extract washed with aqueous NaHCO₃, and water, dried, filtered and solvent removed. The product was purified by distillation or recrystallisation

3)Oxidation of alcohols: General method

To IBC (0.015 mol) in CH₂Cl₂ (25 ml) was added the alcohol (0.01 mol) dissolved in a small amount of the solvent. The mixture was refluxed for 1 to 4 he cooled to room temperature, diluted with CH₂Cl₂, and filtered

Evaporation of the solvent furnished the product which was isolated as a 2,4- dinitrophenylhydrazone.

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