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Imidazolium bromo chromate: A new and efficient reagent for bromination of hydroxy aromatic compounds

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Abstract

A new Cr (VI) oxidizing agent Imidazolium Bromo chromate (IBC) has been used as an efficient and selective nuclear brominating agent for aromatic hydroxyl acetophenones, aldehyde, phenols as well as a brominating agent for unsaturated aromatic compounds. IBC has been found to be an efficient solid reagent that can be easily prepared in good yield.

Keywords: Imidazolium Bromo chromate; Bromination: Hydroxylated aromatics; Oxidation: Alcohols.

1. Introduction

Brominated aromatic compounds are valuable intermediates in organic synthesis and they have been used widely in industrial important products and biologically active substrates as antitumor, antifungal, antibacterial, and antiviral compounds (1, 2). Molecular bromine in acetic acid or chloroform and KBr plus KBrO₃ in an aqueous solution are good brominating agents for organic substrates, but molecular bromine is hazardous and its vapors are irritating. Moreover, aqueous KBr-KBrO₃ cannot be used for many substrates since they are insoluble in water. Both brominating agents cause nuclear as well as side-chain bromination. Therefore, the search for new reagents is of interest to synthetic organic chemists. The present paper reports the use of imidazolium bromo chromate (IBC) in acetic acid as a selective brominating agent for hydroxyl aromatic and unsaturated aromatic compounds. The hydroxyl aromatic or unsaturated aromatic compounds and IBC were dissolved in a minimum amount of glacial acetic acid and the reaction mixture was heated on a water bath with constant heating. Completion of the reaction was checked by TLC and the color of the reaction mixture (Green) acts as an indicator monitoring the progress of the reaction. The time required for the reaction was 25-45 minutes. The contents were then poured into water. The brominated products obtained were recrystallized from aqueous ethanol. The structures of the products were confirmed by IR, and ¹H NMR and by comparing their melting points with those of samples prepared by known literature methods. (Table 1). [3-5] Bromination of aromatic compounds by IBC has the following advantages: the procedure is simple; the isolation of the product is easy; the IBC reagent is easy to handle, can be weighed, and has no hazardous effect, of bromine. Chemical Apparatus and Material: General: All reagents and solvents are reagent grade. Melting point were determined in open capillaries on an Electrothermal 9100 apparatus and are not corrected. All products were identified by comparison of their spectral and physical data with those of known sample. The purity of product has been checked by TLC. IR spectra were recorded in KBr on a Bruker. ¹H NMR spectra were recorded on Bruker Advance Neo 500 MHz NMR spectrometer in DMSO as solvent and TMS as in internal standard. Mass analysis was carried out on Waters Q-T of MICROMASS (ESI-MS).

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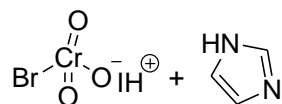


Figure 1 Structural Formula of IBC

Probable reaction and mechanism for bromination of IBC

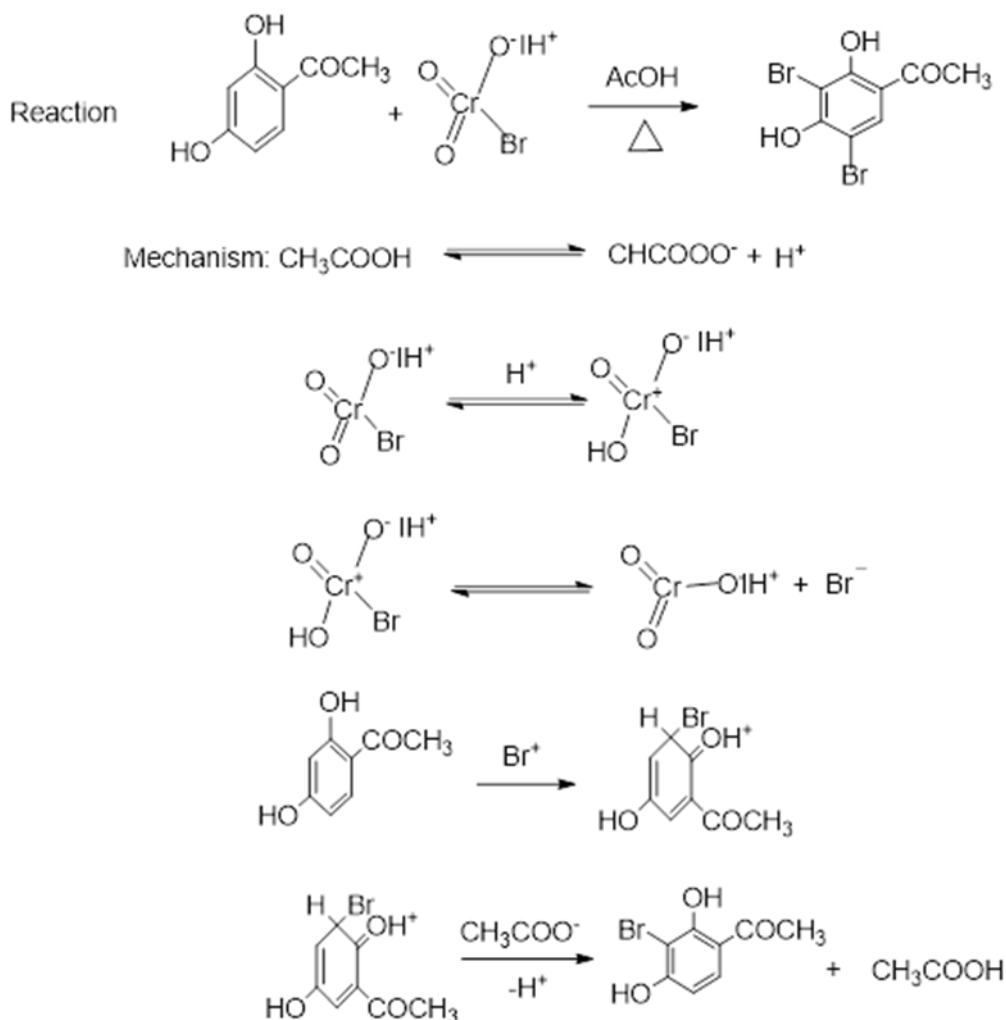


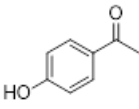
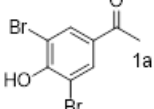
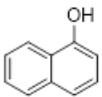
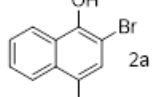
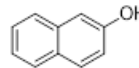
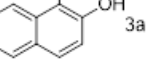
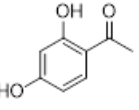
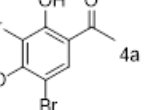
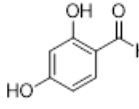
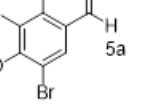
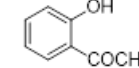
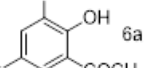
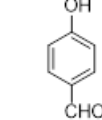
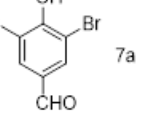
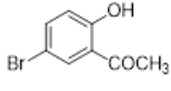
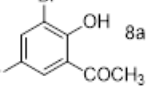
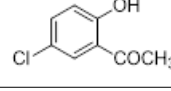
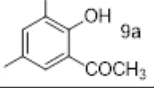
Figure 2 Reaction Mechanism of Bromination of IBC

Preparation of Imidazolium Bromo chromate: This was synthesized⁶ by taking 20g (0.2 mol) of chromium trioxide in water (25ml), cooled to 0°C. To this solution, 47% HBr (38ml, 0.21mol) was added slowly with constant stirring. The content was cooled to 0°C. 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 filtered 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.

A typical procedure for bromination: A mixture of 4-hydroxyacetophenone (1.35 gm 0.01mol) and IBC (2.48 gm 0.01mol) in glacial acetic acid (8-10 ml) was heated on water bath for few minutes. After the reaction was completed (TLC and when a green color were appeared in reaction mixture). The content was poured with ice-cold water. The solid thus obtained was filtered and washed with water and recrystallized in aqueous ethanol.

Bromination of hydroxyl aromatic compounds by IBC: Bromination of hydroxyl aromatic compounds with IBC in acetic acid is studied and summarized in Table 1. The IBC is an found to be an efficient brominating agent for hydroxyl aromatic compounds. Selected spectroscopic data.

Table 1 Bromination of Hydroxyl Aromatic Compounds by Imidazolium Bromo Chromate

| Entry | Reactant | Product | M.P. | Yield % |
|-------|---|---|--------------|---------|
| 1. |  |  | 180 (10) | 80 |
| 2. |  |  | 103 (10, 11) | 90 |
| 3. |  |  | 89 (10, 11) | 80 |
| 4. |  |  | 181 (10, 11) | 81 |
| 5. |  |  | 164 (10, 11) | 83 |
| 6. |  |  | 108 (10, 11) | 91 |
| 7. |  |  | 180 (10, 11) | 82 |
| 8. |  |  | 108 (10, 11) | 85 |
| 9. |  |  | 80 (10, 11) | 84 |

Imidazolium bromo chromate: IR (KBr) : (cm^{-1}) γ_{max} : 3147, 1585, 1562, 1419, 942, 759, 652 & 466 cm^{-1} ^1H NMR (DMSO δ_{ppm}): 7.75 (s,1H), 7.70 (s,1H), 6.97 (s,1H), 7.10 (s 1H), 7.0 (s 1H); mass for $\text{C}_3\text{H}_5\text{BrCrN}_2\text{O}_4$: m/z 265(100%), 264 (12%), 261 (5%) Elem. Anal. Calc. for $\text{C}_3\text{H}_5\text{BrCrN}_2\text{O}_4$: C,14.47; H,2.02; Br,32.09; Cr, 20.88; N, 11.25; O,19.28; found C,14.42; H,2.04; Br,32.05; Cr, 20.85; N, 11.21; O,19.25

2-Hydroxy-3,5-dibromo acetophenones 6a: IR (cm^{-1}) γ_{max} : 3110 (O-H), 1645 (C=O), 1460

(C=C); ^1H NMR (DMSO δ_{ppm}): 2.66 (s, 3H, COCH_3), 7.85 (s, 1H, 6 Ar-H), 7.84 (s, 1H, 4Ar-OH), 13.06 (s, 1H, Ar-H); Anal. calcd. for $\text{C}_8\text{H}_6\text{Br}_2\text{O}_2$: C, 32.65; H, 2.04; Br, 54.42. Found C, 32.45; H, 2.05; Br, 54.32.

2-Hydroxy-3-dibromo, 5-chloro Aceto phenones 9a: IR (cm^{-1}) γ_{max} : 3115 (O–H), 1630 (C=O), 1430 (C=C); ^1H NMR (DMSO δ_{ppm}): 2.56 (s, 3H, COCH_3), 7.96 (s, 2H, 6 Ar–H), 7.94 (s, 1H, 4Ar–OH), 13.06 (s, 1H, Ar–OH); Anal. calcd for $\text{C}_8\text{H}_6\text{BrClO}_2$: C, 33.68; H, 2.10; Br, 28.07. Found C, 33.55; H, 2.08; Br, 27.09.

4-Hydroxy-3,5-dibromoacetophenones 1a: IR (cm^{-1}) γ_{max} : 3100 (O–H), 1660 (C=O), 1580 (C=C); ^1H NMR (DMSO δ_{ppm}): 2.56 (s, 3H, COCH_3), 8.30 (s, 2H, 3&6 Ar–H), 6.21 (s, 1H, Ar–OH); Anal. Calcd. for $\text{C}_8\text{H}_6\text{Br}_2\text{O}_2$: C, 32.65; H, 2.04; Br, 54.42. Found C, 32.55; H, 1.98; Br, 54.61.

2-4-Dihydroxy-3,5-dibromoacetophenones 4a: IR (cm^{-1}) γ_{max} : 3300 (O–H), 1610 (C=O), 1460 (C=C); ^1H NMR (DMSO δ_{ppm}): 7.88 (s, H, COCH_3), 6.25 (s, H, 4Ar–H), 13.32 (s, 1H, 2Ar–OH); Anal. calcd. for $\text{C}_8\text{H}_6\text{Br}_2\text{O}_3$: C, 30.96; H, 1.93; Br, 51.61. Found C, 30.85; H, 1.97; Br, 51.72.

2. Conclusion

A newer and highly efficient Oxidizing agent Imidazolium Bromo chromate (IBC) has been explored for the enhanced, and more selective brominating agent for various aromatic compounds. Again, we have opened new avenues towards brominating agent in this area with positive future prospectus.

Compliance with ethical standards

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Disclosure of conflict of interest

Authors have no conflict of interest.

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