

## Isoquinolinium bromochromate; new, efficient and stable reagent for oxidation of aromatic amines and phenols

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**Abstract :** The new chromium(VI) oxidizing reagent isoquinolinium bromochromate (IQBC) was prepared and characterized. This new compound has been found to be an efficient reagent for oxidation of primary amines and phenols. The oxidation of primary amines and phenols with isoquinolinium bromochromate proceeded smoothly to afford corresponding azobenzenes and quinones in good to excellent yield. The synthesized isoquinolinium bromochromate is more ideal reagent, with number of specifications including higher yield, mild conditions and easy preparation. The results obtained with isoquinolinium bromochromate are satisfactory and suggest that this new reagent is valuable addition to the existing chromium(VI) reagents.

**Keywords :** Isoquinolinium bromochromate, oxidation, anilines, phenols.

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### Introduction

Azobenzenes have been widely utilized as dyes and analytical reagents<sup>1</sup>. They can also be utilized as a material of non-linear optics, optic information storing material in laser disk and dyes with oil solubility in photochromy in modern technology<sup>2,3</sup>. Natural products having a benzoquinone structure show biologically important properties such as cardio-vascular, antitumour, antibacterial, antigerminative and antiprotozoan activities<sup>4</sup>.

Some benzoquinones such as trimethyl-*p*-benzoquinone and 2,3-dimethoxy-5-methyl-*p*-benzoquinone are especially valuable starting materials for the synthesis of vitamin-E and coenzyme Q and therefore, possess immense medicinal importance<sup>5</sup>.

In recent years some chromium(VI) reagents for the effective and selective oxidation of alcohols under mild conditions have been developed with some success<sup>6</sup>. Some of reagents like pyridinium chlorochromate<sup>7</sup>, pyridinium dichromate<sup>8</sup>, pyridinium fluorochromate<sup>9</sup>, quinolinium chlorochromate<sup>10</sup>, quinolinium fluorochromate<sup>11</sup>, imadazolium chlorochromate<sup>12</sup>, prolinium chlorochromate<sup>13</sup>, caffeinilium chlorochromate<sup>14</sup>, are reported as oxidizing agent while some reagents like pyridinium

bromochromate<sup>15</sup>, benzimidazolium bromochromate<sup>16</sup>, quinoxalinium bromochromate<sup>17</sup> work as oxidizing as well as good brominating reagents. However, most of these reagents have been developed so far suffer from at least one of the drawbacks such as high acidity, photosensitivity, instability, tedious workup procedure or requirement of large excess of reagents.

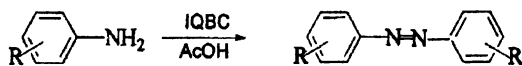
The main interest here is to develop bromochromate reagent, which can be used as oxidizing reagent, herein we first time report the synthesis and application of isoquinolinium bromochromate as more ideal reagent, with number of specification including lower cost, higher yield, better selectivity, mild conditions and easy preparation. The results obtained with isoquinolinium bromochromate are satisfactory and suggest that this new reagent is valuable addition to the existing chromium(VI) reagents.

Isoquinolinium bromochromate can be easily prepared in good yield. It is quite stable when stored in dry condition and it acts as oxidizing agents for the conversion of primary amines to symmetrical azobenzenes and phenols to quinones. The oxidation of substituted anilines to azobenzenes with variety of reagents such as phenyliodoacetate<sup>18</sup>, sodium hypochloride<sup>19</sup> and manganese dioxide<sup>20</sup> has been reported. The variety of oxidi-

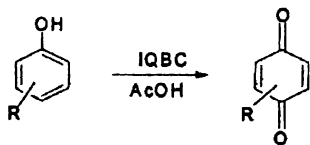
zing systems such as hydrogen peroxide and methyloxorhenium(VII)<sup>21</sup>, ceric ammonium nitrate<sup>22</sup>, sensitized photo oxidation method<sup>23</sup>, chromium silicate and hydrogen peroxide<sup>24</sup>, molecular oxygen catalyzed by a mixture of cobalt and manganese salt of *p*-amino benzoic acid<sup>25</sup> and hydrogen peroxide in presence of cobalt(II) and manganese(II) acetate<sup>26</sup> used for oxidation phenols to quinones.

The structure of the reagent was confirmed by elemental analysis and IR spectra. The IR absorption frequencies for bromochromate group at 1014, 945 and 767  $\text{cm}^{-1}$  in isoquinolinium bromochromate are attributed to  $\nu_{\text{asym}}(\text{Cr}-\text{O})$ ,  $\nu_{\text{sym}}(\text{Cr}-\text{O})$  and  $\nu(\text{Cr}=\text{O})$  respectively. These assignments are in accord with those found for other bromochromate and fluorochromate<sup>27,28</sup>. It is soluble in dichloromethane, acetonitrile, chloroform and insoluble in benzene, toluene, nitrobenzene and ethyl acetate, these results are indicative of ionic nature of reagent.

A study of oxidative behavior of IQBC with primary amines and phenols in acetic acid was undertaken (Schemes 1 and 2) and the results are presented in Table 1. The results of oxidation obtained with IQBC are very satisfactory in comparison with other reagents considering the amount of oxidant, acidity, percent yield and reaction time respectively. The reagent was conveniently prepared, non hygroscopic, easy to handle and can be weighed easily. Apart from being an efficient oxidant, IQBC can be used as an efficient reagent for bromination of aromatic compounds<sup>29</sup>.



Scheme 1



Scheme 2

In conclusion, easy preparation of reagent, no catalyst, mild conditions, good reaction yields of products and less reaction time make IQBC a good reagent for oxidation of primary amines and phenols. Since reagent

is solid it can be easily weighed and has no hazardous effect.

## Experimental

All reagents and solvents are of reagent grade. Melting points 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 was checked by TLC. IR spectra were recorded in KBr on Perkin-Elmer spectrophotometer.  $^1\text{H}$  NMR spectra were recorded on Gemini 300 MHz in  $\text{CDCl}_3$  as solvent and TMS as an internal standard.

### Preparation of isoquinolinium bromochromate :

A solution of chromium trioxide (10 g, 0.1 mol) in water (15 ml) was cooled at 0 °C and to this 47% aqueous hydrobromic acid (17 ml, 0.1 mol) was slowly added with vigorous stirring. To this resulting solution isoquinoline (13 ml, 0.1 mol) was added and cooled for 2 h. The resulting yellow orange colored solid was collected on sintered glass funnel and recrystallised by ethyl alcohol, m.p. 105–107 °C, yield 84% (Found : C, 34.92; H, 2.53; N, 4.48. Calcd. for  $[\text{C}_9\text{H}_7\text{NHCrO}_3\text{Br}(\text{iso})]$  : C, 34.83; H, 2.58; N, 4.51%).

### General procedure for oxidation of anilines and phenols :

To a solution of substrate (1 mmol) in acetic acid (5 ml) isoquinolinium bromochromate (0.308 g, 1 mmol) was added and the mixture was stirred magnetically for two hours at room temperature. The progress of reaction was monitored by TLC. After completion of reaction mixture was diluted with cold water and extracted with ether. On evaporation of ether, the product was obtained, which was further purified by crystallization.

### Selected spectroscopic data :

Azobenzene, IR  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) : 2990, 1565, 1556, 1455 (KBr);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 7.35–7.82 (m). 4,4'-Dichloroazobenzene, IR  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) : 2994, 1611, 1571, 1460 (KBr);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 7.25–7.76 (m). 3,3'-Dimethylazobenzene, IR  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) : 3007, 2985, 1608, 1560, 1555 (KBr);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 2.26 (6H, s,  $\text{CH}_3$ ), 7.35–7.82 (8H, m). 1,4-Benzoquinone, IR  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) : 3010, 1650, 1317, 1070, 1460, 900 (KBr);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 6.78 (s). 2-Methyl-1,4-benzoquinone, IR  $\nu_{\text{max}}$

Table 1. Oxidation of aromatic amines and phenols by isoquinolinium bromochromate

Entry	Substrate	Product	Yield (%)	M.p. (°C) (lit.)
1	Aniline	Azobenzene	90	67 (68) <sup>30</sup>
2	3-Methylaniline	3,3'-Dimethylazobenzene	84	54 (54-56) <sup>30</sup>
3	2-Methoxyaniline	2,2'-Dimethoxyazobenzene	75	144 (143-145) <sup>30</sup>
4	4-Ethoxyaniline	4,4'-Diethoxyazobenzene	80	159 (157-159) <sup>30</sup>
5	4-Chloroaniline	4,4'-Dichloroazobenzene	77	186 (185) <sup>30</sup>
6	4-Bromoaniline	4,4'-Dibromoazobenzene	70	204 (205) <sup>30</sup>
7	2-Chloroaniline	2,2'-Dichloroazobenzene	74	136 (137) <sup>30</sup>
8	Phenol	1,4-Benzoquinone	76	116 (115-117) <sup>31</sup>
9	2-Methylphenol	2-Methyl-1,4-benzoquinone	71	69 (68-70) <sup>31</sup>
10	2,6-Dimethylphenol	2,6-Dimethyl-1,4-benzoquinone	85	73 (72) <sup>31</sup>
11	Catechol	1,2-Benzoquinone	84	61 (60-70) <sup>31</sup>
12	1-Naphthol	1,4-Naphthoquinone	83	127 (128.5) <sup>31</sup>
13	2-Chlorophenol	2-Chloro-1,4-benzoquinone	67	57 (57) <sup>31</sup>
14	Hydroquinone	1,4-Benzoquinone	78	113 (114-117) <sup>31</sup>

( $\text{cm}^{-1}$ ) : 3030, 1656, 1340, 1090, 930 (KBr);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 2.0 (3H, s), 6.3-6.81 (3H, m). 2,6 Dimethyl-1,4-benzoquinone, IR  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) : 3020, 1651, 1300, 1070, 930 (KBr);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 1.9 (6H, s), 6.5 (2H, s). 1,4-Naphthoquinone, IR  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) : 3030, 1648, 1320, 1075, 1080, 915 (KBr);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) 7 (2H, s), 7.6-8.2 (4H, s).

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