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Quinoxalinium Bromochromate– A New and Efficient Reagent for Oxidation of Alcohols and Bromination of Aromatic Compounds

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ABSTRACT

The new mild chromium (VI) oxidizing agent, quinoxalinium bromochromate (QxBC), was prepared and characterized. This new compound is effective in the oxidation of alcohols and in the bromination of aromatic compounds.

Keywords: Quinoxalinium Bromochromate, Oxidation, Alcohols, Bromination

1. INTRODUCTION

The oxidation of organic substrates in aprotic solvents, under mild and neutral conditions, is important in modern organic synthesis. Therefore, the search for new oxidizing agents is of interest to synthetic organic chemists. Many such reagents have been developed in recent years with some success (1). In particular, there is continued interest in the development of new chromium (VI) reagents for the effective and selective oxidation of alcohols, under mild conditions. Some of the important entries in the list of reagents are pyridinium chlorochromate (PCC) (2), pyridinium dichromate (PDC) (3), pyridinium fluorochromate (PFC) (4), pyridinium bromochromate (PBC) (5), quinolinium chlorochromate (QCC) (6), quinolinium fluorochromate (QFC) (7), prolinium chlorochromate (8) and caffeinilium chlorochromate (9). Over several years our group has been involved in developing bromochromate reagents allowing oxidation and bromination (10). However, most of these reagents that have been developed so far suffer from at least one of the drawbacks such as high acidity, photosensitivity, instability, tedious work-up procedures, or requirement of large excess of reagent.

Therefore, the search for a preminent new reagent persisted which has now led to the synthesis of quinoxalinium bromochromate, $C_8H_6N_2HCr0_3Br$, (QxBC).

2. EXPERIMENTAL

Melting points were determined in open capillaries on an Electrothermal 9200 apparatus and are not corrected. IR spectra were recorded on a MATTSON 1000 FTIR spectrophotometer, ^{1}NMR spectra on VARIAN EM360L 60 MHz instrument. All reagents and solvents are of reagent grade.

2.1. Preparation of quinoxalinium bromochromate

A solution of chromium trioxide (20 g; 0.2 mol) in water (25 mL) was cooled to 0°C and to this 47% aqueous hydrobromic acid (23.5 mL; 0.2 mol) was slowly added with vigorous stirring. To this resulting solution quinoxaline (27 g; 0.2 mol) was added and then cooled for 2 h. The resulting mustard yellow 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, E.n: 108-110 °C, Yield 83 % (52 g).
Anal: Calc. for $C_8H_6N_2HCr0_3Br$ C, 30.89; H, 2.27; N, 9.01; Cr, 16.72 %
Found C, 30.96; H, 2.38; N, 9.19; Cr, 16.65 %.

2.2. Oxidation of alcohols: General Method

To QxBC (0.015 mol) in CH_2Cl_2 (25 mL) was added the alcohol (0.01 mol) dissolved in a small amount of the solvent. The mixture was stirred for 4-4.5 h at room temperature, diluted with CH_2Cl_2 and filtered. Evaporation of the solvent furnished the product, which was isolated as a 2,4-dinitrophenylhydrazone derivative.

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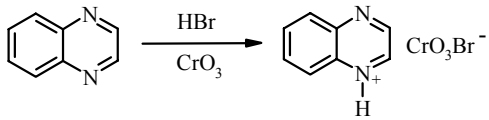
2.3. Bromination: General Method

To a suspension of QxBC (6.22 g, 0.02 mol) in acetic acid (25 mL) was added the subsrate (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 was washed with aqueous $NaHCO_3$ and water, dried (Na_2SO_4), filtered and the solvent was removed. The product was purified by distillation or recrystallization.

3. RESULTS AND DISCUSSION

Quinoxalinium bromochromate can be easily prepared in good yield, quite stable when stored dry and in the absence of light, and is active as oxidizing agents for the conversion of alcohols to carbonyl compounds, and as brominating agents of aromatic compounds. The new bromochromate complex is produced in good yield (83 %) by the addition of aqueous solution of CrO_3 to the quinoxaline; the use of 47% HBr with CrO_3 causes the formation of bromochromate species.



QxBC is a mustard yellow, non-hygroscopic, air-stable but moderately light-sensitive solid which should be protected from light during preparation and storage. The structure of the reagent was confirmed by elemental analysis and infrared spectra. The infrared absorption frequencies for bromochromate group at 945, 913 and 750 cm^{-1} in quinoxalinium bromochromate and is attributable to ν_{asym}(Cr-0), ν_{sym}(Cr-0) and ν(Cr=O), respectively. These assignments are in accord with those found for pyridinium bromochromate (PBC) (11).

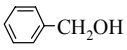
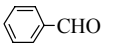
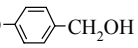
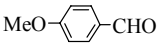
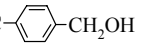
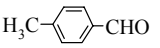
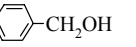
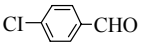
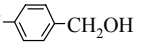
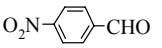
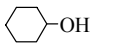
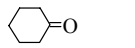
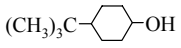
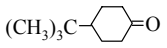
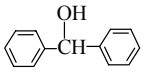
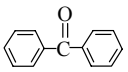
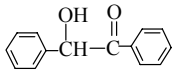
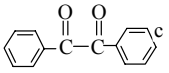
It is soluble in dimethyl formamide and dimethylsulphoxide, sparingly soluble in dichloromethane, acetonitrile and chloroform and insoluble in benzene, toluene, ether, nitrobenzene and ethyl acetate. These results are indicative of the ionic nature of QxBC. The compound is diamagnetic. It is a 1:1 electrolyte (Λ_M=130 mho cm^2 mol^{-1}, in acetonitrile) showing a pH value of 2.18 (0.01 M aqueous solution). The pH of 0.01 M solution of PCC was found to be 1.75 (2). Thus, the acidity of QxBC is less pronounced than that of PCC.

A study of the oxidative behavior of QxBC with primary and secondary alcohols in dichloromethane was undertaken. The results are presented in Table 1. The results of oxidation obtained with QxBC are very satisfactory in comparison with its companion reagents like naphthyridinium dichromate (NapDC) (12), PCC (2), quinolinium dichromate (QDC) (13) and PDC (3) in considering the amount of oxidant, acidity, percent yield and reaction time respectively.

We have also carried out the bromination reactions in acetic acid solution of QxBC. The results of the bromination studies by QxBC are summarised in Table 2. QxBC is more efficient in the bromination of aromatic compounds than side-chain bromination. The results of bromination obtained with QxBC are comparable with its companion reagents like QnBC (10d) and 4-(Dimethylamino)pyridinium bromochromate (DMAPBC) (16).

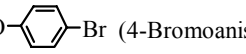
In conclusion, the lower acidity of this reagent, the ready preparation, its stability, nonhygroscopicity, the ease of the work up of the reaction mixture, reasonable yields of products and reaction time make quinoxalinium bromochromate a versatile and practical reagent for the oxidation of alcohols, a good brominating agent for aromatic compounds and a useful addition to the presently available bench reagents in organic synthesis. Bromination of aromatic compounds by QxBC has also the following advantages: QxBC reagent is easy to handle, can be weighed and has no hazardous effect.

Table 1. Oxidation of Alcohols by QxBC in Dichloromethane[a]

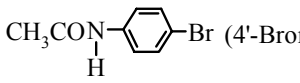
	Substrate	Product	Yield (%)[b]	2,4-DNP (m.p.°C) Obs.	Lit.[14]
1.	$CH_3(CH_2)_6CH_2OH$	$CH_3(CH_2)_6CHO$	45	104-106	106
2.			70	236-237	237
3.			73	253-254	254
4.			68	231-232	233
5.			51	264-265	265
6.			50	318-320	320
7.			53	160-162	162
8.			42	155-156	156
9.			65	237-238	238
10.			67	93-95	95

[a] The reaction was carried out with 1.5 equiv of QnBC 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-dinitrophenylhyrazone derivative identified by melting point (except for the benzil whose melting point was taken in directly). The yields refer to non-optimised reaction conditions.
[c] Confirmed by IR, ^{1}H-NMR.
IR(KBr): υ (cm^{-1})= 3066, 1679, 1658, 1592, 1577, 1450, 1220, 919, 718, 700, 685.
^{1}H NMR(CCl_4): δ (ppm)= 7.50-8.00 (m, 10H)

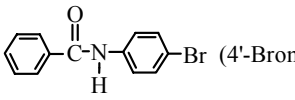
Spectral data for compounds 2a-2f (Table 2)

2a.  (4-Bromoanisole)

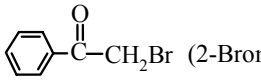
IR(KBr): υ (cm^{-1})= 3002, 2956, 2944, 2836, 1587, 1498, 1454, 1248, 1172, 1110, 1078, 1039, 995, 829, 692, 600, 511.
^{1}H NMR($CDCl_3$): δ (ppm)= 3.91 (s, 3H); 7.52-7.01(dd, 4H).

2b.  (4'-Bromoacetanilide)

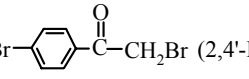
IR(KBr): υ (cm^{-1})= 3304, 3032, 2919, 2837, 1672, 1600, 1590, 1500, 1400, 1380, 1178, 1079, 1000, 970, 821, 750, 700, 607, 516.
^{1}H NMR(CCl_4): δ (ppm)= 2.12 (s, 3H); 7.20-7.28 (m, 4H)

2c.  (4'-Bromobenzanilide)

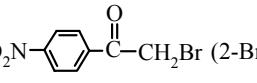
IR(KBr): υ (cm^{-1})= 3339, 3054, 1661, 1589, 1411, 1196, 946, 893, 750, 714, 509.
^{1}H NMR($CDCl_3$): δ (ppm)= 7.29-7.74 (m, 9H)

2d.  (2-Bromoacetophenone)

IR(KBr): υ (cm^{-1})= 3054, 2964, 1683, 1646, 1598, 1492, 1450, 960, 887, 684, 525.
^{1}H NMR($CDCl_3$): δ (ppm)= 4.51 (s, 2H); 7.53-7.69 (m, 5H).

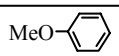
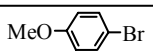
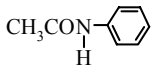
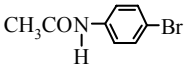
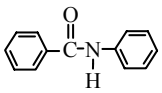
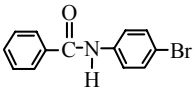
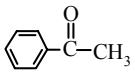
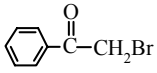
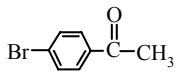
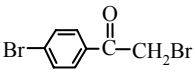
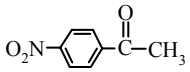
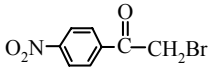
2e.  (2,4'-Dibromoacetophenone)

IR(KBr): υ (cm^{-1})= 3000, 2967, 2918, 2834, 1700, 1584, 1560, 1480, 1460, 1080, 720, 506.
^{1}H NMR(CCl_4): δ (ppm)= 4.40 (s, 2H); 7.71-7.92 (dd, 4H)

2f.  (2-Bromo-4'-nitroacetophenone)

IR(KBr): υ (cm^{-1})= 3100, 2915, 2867, 1700,1600, 1519, 1460, 1340, 1200, 1000, 860, 751, 690, 516.
^{1}H NMR(CCl_4): δ (ppm)=4.50 (s, 2H); 8.19-8.41 (dd, 4H)

Table 2. Bromination Reactions of Some Selected Aromatic Compounds with QxBC[a].

	Substrate (1)	Product[b] (2)	Time (h)	Yield(%)[c]	m.p/ b.p. °C Obs.	Lit.[15]
a.			4	64	221	223
b.			3	61	167-168	169
c.			4	60	200-202	202
d.			5	35	49-50	51
e.			7	30	109-110	110
f.			9	27	99-101	101

[a] Brominations were carried out in acetic acid with a substrate to oxidant ratio 1:2.
[b] All products were identified by comparison of their physical and spectral data with those of authentic samples.
[c] Isolated yields.

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