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*Short Communication*

# Tetrapropylammonium bromochromate and tetrabutylammonium bromochromate $[NR_4]CrO_3Br$, (R= Pr, Bu): two new and efficient reagents for oxidation of alcohols

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**Tetrapropylammonium bromochromate (VI), $[N(Pr)_4]CrO_3Br$, TPABC and tetrabutylammonium bromochromate (VI), $[N(Bu)_4]CrO_3Br$, TBABC were prepared and used to quantitatively oxidizing of a number of organic substrates. These reagents are versatile reagents for the effective and selective oxidation of organic substrates, in particular for alcohols, under mild conditions.**

**Key words:** Chromium (VI), reagent, tetrapropylammonium bromochromate, tetrabutylammonium bromochromate, oxidation, organic substrates, alcohols.

## INTRODUCTION

Organic chemists must often choose from hundreds of oxidizing agents and reaction conditions to perform a desired oxidation without affecting other functional groups present or causing side reactions. Therefore, the search for new oxidizing agents is of interest to synthetic organic chemists. In recent years, significant improvements were achieved by the use of new oxidizing agents, (Maier et al., 1999; Bhandari et al, 2001; Meenahshisundaram and Soctaungam, 2001; Heravi et al., 1999; Chaubey et al. 2003; Bhattacharjee et al., 1982; Jeyanthi et al., 2002; Shirini et al., 2003; Srinivasan et al., 1997) such as tetramethylammonium fluorochromate (Mahjoub et al., 2003), 2,2'- bipyridinium chlorochromate, (Corey and Fleet, 1973), tributylammonium chlorochromate (Ghammamy and SeyedSadjadi, 2005), and 3,5-Dimethl-pyrazolium fluorochromate (Bhattacharjee et al., 1987). 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 reagents. Therefore, the search for permanent new reagents persisted which have now led to the synthesis of tetra-propylammonium bromochromate (VI), $[N(Pr)_4]CrO_3Br$, TPABC and tetrabutylammonium bromochromate (VI), $[N(Bu)_4]CrO_3Br$, TBABC.

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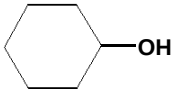
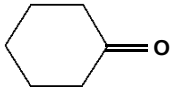
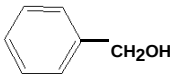
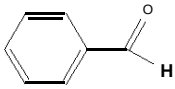
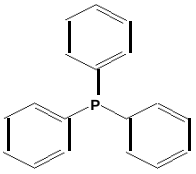
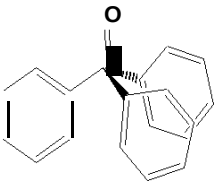
## EXPERIMENTAL

All reagents and solvents are of reagent grades. $^1H$ and $^{13}C$ NMR spectra were recorded using Bruker DRX-500 in $CD_3CN$ solutions. IR spectra were recorded using a Shimadzu IR- 420 spectrometer. The UV/Visible measurements were made on an Uvicon model 922 spectrometer. Melting points were obtained on an Electro-thermal 9100 apparatus. All separations and quantization of alcohols and aldehydes were performed using a Philips 4410 gas Chromatograph.

### Preparation of Tetrapropylammonium bromochromate, $[N(Pr)_4]CrO_3Br$

Chromium (VI) oxide (1 g, 10 mmol) was dissolved in dry actonitrile (25) in a beaker and a stoichiometric amount of tetrapropylammonium Bromide (2.66 g, 10 mmol) was added under stirring at room temperature. Within 5 min, a clear orange solution formed which upon refrigerating gave solid TPABC, which was isolated by filtration. The solid was washed with hexane and dried under vacuum

**Table 1.** Oxidations via TBABC and TPABC.

| Substrate | Product | TBABC | | TPABC | |
|---|---|---|---|---|---|
| | | Time (min) | Yield (%) | Time (min) | Yield (%) |
| n-$C_3H_7$-OH | n-$C_2H_5$-CHO | 130 | 90 | 120 | 88 |
| *2*-$C_3H_7$-OH | *2*-$C_2H_5$-CHO | 120 | 90 | 132 | 87 |
| n-$C_4H_9$-OH | n-$C_3H_7$-CHO | 100 | 89 | 95 | 85 |
| 2-$C_4H_9$-OH | 2-$C_3H_7$-CHO | 95 | 93 | 90 | 91 |
| n-$C_5H_{11}$-OH | n-$C_4H_9$-CHO | 97 | 87 | 104 | 86 |
| n-$C_8H_{17}$-OH | n-$C_7H_{15}$-CHO | 70 | 84 | 68 | 83 |
|  |  | 145 | 94 | 155 | 89 |
|  |  | 35 | 96 | 30 | 95 |
|  |  | 5 | 92 | 5 | 90 |

for 1 h. $C_{12}H_{28}BrCrO_3N$: Cacld. %C, 39.93; %H, 7.65. Found: %C, 40.14; %H, 8.01. IR. (KBr): 844$cm^{-1}$ $\nu_1(A_1)$ or $\nu(CrO_3)$, 948$cm^{-1}$ $\nu_4(E)$ or $\nu(CrO_3)$ . UV/Visible was all consistent with the TPABC structure. Electronic absorption at 452 nm, corresponding to $1a_2$ 9e ( = 161 $M^{-1}$ $cm^{-1}$); 363 nm to 8e 9e ( = 737 $M^{-1}$ $cm^{-1}$); and 261 nm to $12a_1$ 9e ( = 1683 $M^{-1}$ $cm^{-1}$).

**Preparation of tetrabutylammonium bromochromate, $[N(Bu)_4]CrO_3Br$**

Tetrabutylammonium bromochromate(IV), $[N(Bu)_4]CrO_3Br$ was prepared by dissolving Chromium (VI) oxide (1 g, 10 mmol) in MeCN and addition of this solution to a solution of tetrabutylammonium Bromide (3.22 g, 10 mmol) in MeCN under stirring at room temperature until an orange precipitate was formed. After 2 h stirring, the mixture was filtered. The solid was washed with hexane and dried under vacuum for 1 h. $C_{16}H_{36}BrCrO_3N$: Cacld. % C, 45.508; %H, 8.532. Found: %C, 46.40; %H, 8.91. IR. (KBr): 895$cm^{-1}$ $_1(A_1)$ or $(CrO_3)$, 949$cm^{-1}$ $_4(E)$ or $(CrO_3)$. UV/Visible $^{13}$C-NMR and $^1$H-NMR were all consistent with the TBABC structure. Electronic absorption at 454 nm, corresponding to $1a_2$ 9e ( = 130 $M^{-1}$ $cm^{-1}$); 363 nm to 8e 9e ( = 670$M^{-1}$ $cm^{-1}$); and 260nm to $12a_1$ 9e ( =1622 $M^{-1}$ $cm^{-1}$).

**Oxidation of alcohols: general method**

Tetraalkylammonium bromochromate (10 mmol) is added in one portion, to a stirred solution of each alcohol (25 ml) in $CH_2Cl_2$, at room temperature. The progresses of the reactions are monitored by TLC and UV/Vis spectrophotometry (at 363 nm). The mixture were stirred and refluxed for the time indicated in the Table 1 at room temperature, diluted with $CH_2Cl_2$ and filtered. Evaporation of solvent furnished the product. The molar ratio of substrate to oxidants was 1:1. The solution became homogeneous briefly before the black-brown reduced reagent precipitated. Products are characterized by comparison with authentic samples (NMR, IR, TLC and mp/bp measurement).

## RESULTS AND DISCUSSION

Tetraalkylammonium bromochromates could be easily prepared in good yield, quite stable when stored dry and in the absence of light, and are active as oxidizing agents for the conversion of alcohols to carbonyl compounds.

$[N(Bu)_4]CrO_3$ Br and $[N(Pr)_4]CrO_3Br$ were prepared by the reaction of relative salts with $CrO_3$ in 1:1 ratio in the acetonitrile solvent. (Scheme 1).

$$R_4NBr + CrO_3 \longrightarrow R_4N[CrO_3Br] \quad \text{in that } (R=C_3H_7, C_4H_9)$$

**Scheme 1**

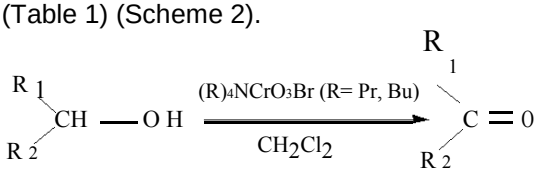
They have been found that these reagents have certain advantages over similar oxidizing agents in terms of the amounts of oxidants and solvent required, and especially in the short reaction times required and in the higher yields of the product (Table 1).

The nature of the solvent does not appear to be particularly critical. Hydrocarbons, benzene, ethers and chlorinated hydrocarbons are equally effective, the practical choice being oriented by the solubility of the pro- ducts and the desired reaction temperature. The chromium (VI) contents easily determined iodometrically. The IR spectra of TBABC and TPABC are similar to that of other bromochromates (Harmon et al., 1974). The IR spectrum of the $CrO_3Br^-$ ion has been the subject of several publications

(Harmon et al., 1974; Nakamoto, 1978). The $XY_3Z$ ions have six infrared active vibrations.These infrared active vibrations are $_1(A_1)$ or $(XY_3)$, $v_2(A_1)$ or $(XZ)$, $_3(A_1)$ or $(XY_3)$, $_4(E)$ or $(XY_3)$, $_5(E)$ or $(XY_3)$ and $_6(E)$ or $_r(XY_3)$. In TBABC and TPABC, $_1(A_1)$ or $(XY_3)$, and $_4(E)$ or $(XY_3)$ are seen at 895 and 949 $cm^{-1}$, 844 and 948 $cm^{-1}$ respectively.

In conclusion, the ready preparation of these reagents, their stability, nonhygroscopicity, the ease of the work up of the reaction mixtures, reasonable yields of products and reaction time make tetraalkylammonium bromo-chromates versatile and practical reagents for the oxidation of alcohols and useful additions to the presently available bench reagents in organic synthesis. TBABC and TPABC reagents are easy to handle, could be weighed and have no hazardous effects.

Tetraalkylammonium bromochromates in dichloro- methane also oxidize primary and secondary alcohols, respectively, the corresponding aldehydes or ketones in high yields (Table 1) (Scheme 2).




**Scheme 2**

During the reactions, the color of the oxidants change from orange to brown, providing visual means for ascertaining the progress of the oxidations. The results obtained with tetraalkylammonium bromochromates are very satisfactory and show the new reagents as valuable addition to the existing oxidizing agents.

Tetraalkylammonium bromochromates are soluble in water, dimethylformamide, acetonitrile and acetone; they are less soluble in dichloromethane and only sparingly soluble in benzene, carbon tetrachloride, chloroform and hexane.

The $^1H$ and $^{13}C$ NMR spectra data of the compounds in $CD_3CN$ solvent confirm the proposed structures of the new reagents especially show the cationic parts. Important peaks in the $^1H$ and $^{13}C$ NMR spectra of each compound are discussed.

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