Synthesis and Reactions of Two New Tetramethylammonium Halochromates (TMAXC) (X= Cl, Br): Stable, Mild, Efficient and Inexpensive Chromium (VI) Oxidation Reagents

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Abstract: Oxidation of primary and secondary alcohols to the corresponding carbonyl compounds (aldehydes and ketones) can be accomplished by using Tetramethylammonium Chlorotrioxochromate (TMACC) and Tetramethylammonium Bromotrioxochromate (TMABC) that abbreviated as Tetramethylammonium Halochromates (TMAXC) as the oxidizing agents. These new compounds are more efficient and have certain advantages over similar oxidizing agents in terms of the amount of oxidants and solvent required, short reaction times and high yields. These compounds were characterized by FT-IR and UV/Visible techniques.

Key words: Chromium (VI) · Tetramethylammonium Chlorotrioxochromate · Tetramethylammonium Bromotrioxochromate · Oxidation · Organic Substrate · Alcohols · FT-IR and UV/Visible Techniques

INTRODUCTION

Of the large number of mild chromium based oxidizing agents available, many have proven to be impractical when the reactions are performed on a large (mol) scale [1]. There are continued interest in the development of new chromium (VI) reagents for the effective and selective oxidation of organic substrates, in particular alcohols, under mild conditions. Therefore, the search for new oxidizing agents are of interests to synthetic organic chemists. Many such reagents have been developed with some success [2], pyridinium chlorochromate [3], quinolinium chlorochromate [4], isoquinolinium chlorochromate [5], prolinium chlorochromate [6], caffeinilium chlorochromate [7], isoquinolinium chlorochromate [8], 2,2′-bipyridinium chlorochromate [9], 3,5-dimethylpyrazolium fluorochromate [10], tetramethylammonium fluorochromate [11], tripropylammonium fluorochromate [12] and tributylammonium chlorochromate [13]. These reagents may all be used for the oxidation of alcohols to corresponding aldehydes and ketones. Tetramethylammonium Chlorotrioxochromate (TMACC) and Tetramethylammonium Bromotrioxochromate (TMABC) that abbreviated as Tetramethylammonium Halochromates (TMAXC) were synthesized and found that these reagents have certain advantages over similar oxidizing agents in terms of amounts of oxidants and solvent required, easier working up and high yields.

Experimental Details: CrO₃ (Merck, p.a.) was used without further purification. Solvents were purified by standard methods [11-13]. Melting points were determined in open capillaries on an Electro thermal 9200 apparatus and are not corrected. The UV/Visible measurements were made on an Unicam model 922 spectrophotometer. Infrared spectra were recorded as KBr disks on a Shimadzu model 420 spectrophotometer. 'H and 13C-nmr were recorded on a Broker AVANCE DRX 500 spectrometer at 500 and 125 MHz, respectively. All the chemical shifts are quoted in ppm using the high-frequency positive convention; 1H and 13C-nmr spectra were referenced to external SiMe₄. Chromium was estimated iodometrically. In the case of the reduced products of the oxidants, chromium was determined after oxidizing with acidic potassium peroxodisulfate (K₂S₂O₈) solution. The percent composition of elements was obtained from the Micro analytical Laboratories, Department of Chemistry, OIRC, Tehran.

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Fig. 1: FTIR spectrum of tetramethylammonium chlorotrioxochromate (KBr Disk).

Fig. 2: UV/Vis spectrum of tetramethylammonium chlorotrioxochromate.

Fig. 3: ¹H-NMR spectrum of tetramethylammonium chlorotrioxochromate.

Synthesis of Tetramethylammonium Chlorotrioxochromate: Chromium(VI) oxide (0.44 g, 4.4 mmol) was dissolved in acetonitrile in a beaker with stirring at 0°C. To the resultant clear orange solution, tetramethylammonium chloride (0.48 g, 4.4 mmol) was added over a period of 30 min and stirring was continued for 30 min at 0°C. After these times, a clear orange solution formed which upon refrigerating gave solid TMACC, which was isolated by filtration. The solid was washed with hexane and dried under vacuum for 1 h. mp152°C. Found: C, 23.52; H, 5.88; N, 6.82. IR (KBr): 907 cm⁻¹ ν(e), 948 cm⁻¹ νs(CrO₃) (Figure 1). UV/Visible C-NMR and ¹H-NMR were all consistent with the TMACC structure. Electronic absorption at 450 nm, corresponding to 1a₁→9e (ε = 156 M⁻¹ cm⁻¹); 363 nm to 8e→9e (ε = 942 M⁻³ cm⁻³); and 283 nm to 12a₁→9e (ε = 1506 M⁻¹ cm⁻¹) (Figures 2,3).

Synthesis of Tetramethylammonium Bromotrioxochromate: Chromium(VI) oxide (1 g, 10 mmol) was dissolved in dry acetonitrile (20) in a beaker and a stoichiometric amount of tetramethylammonium Bromide (1.54 g, 10 mmol) was added under stirring at room temperature. Within 5 min, a clear orange solution formed which upon refrigerating gave solid TMABC, which was isolated by filtration. The solid was washed with hexane and dried under vacuum for 1 h. mp. 300°C. Found: C, 19.54; H, 4.84; N, 5.65. IR (KBr): 901 cm⁻¹ ν(A₁) or ν(CrO₃), 949 cm⁻¹ νs(E) or ν(CrO₃) (Figure 4). UV/Visible was all consistent with the TMABC structure. Electronic absorption at 451 nm, corresponding to 1a₁→9e (ε = 180 M⁻¹ cm⁻¹); 364 nm to 8e→9e (ε = 732 M⁻³ cm⁻³); and 262 nm to 12a₁→9e (ε = 1454 M⁻¹ cm⁻¹) (Figure 5).
Fig. 4: FTIR spectrum of Tetramethylammonium bromotrioxochromate (KBr Disk).

Fig. 5: UV/Vis spectrum of Tetramethylammonium bromotrioxochromate.

Table 1: Oxidations via TMACC and TMABC.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product</th>
<th>TMACC</th>
<th>TMABC</th>
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<td></td>
<td></td>
<td>Time (min)</td>
<td>Time (min)</td>
</tr>
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<td>n-C₆H₁₆-OH</td>
<td>n-C₆H₁₆-CHO</td>
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General Procedure for Oxidation of Organic Substrates:
To tetramethylammonium Halo chromates (0.001 mol) in CH2Cl2 (25 ml) were added the alcohol (0.001 mol) dissolved in a small amount of the solvent at room temperature. The mixture were stirred and refluxed for the time indicated in the Table 1 at room temperature, diluted with CH2Cl2 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. The progresses of the reactions were monitored by TLC and UV/Vis spectrophotometry.

RESULTS AND DISCUSSION
Tetramethylammonium chlorochromate and tetramethylammonium bromochromate are easily prepared from the reaction of chromium (VI) oxide and related tetramethyammonium halide in molar ratio of 1:1 in acetonitrile. The results obtained with tetramethylammonium halochromates are very satisfactory and show that the new reagents to be valuable additions to the existing oxidizing agents.

Tetramethylammonium halochromates in dichloromethane oxidize primary and secondary alcohols to the corresponding aldehydes or ketones in high yields respectively, (Table 1) (Scheme 1).

Scheme 1:

Tetramethylammonium halo chromates have also been used for oxidation of carbohydrates such as 1, 2: 5, 6 -Di-O- isopropylidine –á-D-Glucofuranose to its relative ketosugar like as pyridinium chlorochromate [14].but in high yield and by use of the equimolar ratio of the reagents (Scheme 2).

Scheme 2:


