Synthesis and Reactions of Triethylammonium Halochromate(IV), (C$_2$H$_5$)$_3$NH[CrO$_3$](X=F, Cl)

Reagents and Oxidation of Alcohols

Under Microwave Irradiation

Shahriar Ghammamy, a,b* Vahideh Jalalat, b Zahra Javanshir, c Fahmideh Shabani, c Razieh Shakeri, b and Zahra Shokri Aghbolagh b, d

aDepartment of Chemistry, Islamic Azad University, Ardabil Branch, Ardabil, Iran.
bDepartment of Chemistry, Faculty of Science, Imam Khomeini International University, Qazvin, Iran.
cMember of Young Researchers Club, Islamic Azad University, Ardabil Branch, Ardabil, Iran.
dMember of Young Researchers Club, Islamic Azad University, Qazvin, Iran.

E-mail: shghamami@yahoo.com, shghamami@ikiu.ac.ir

Received date: August 25, 2010

Abstract

Triethylammonium halochromates are easily synthesized by addition of triethylamine to aqueous solutions of CrO$_3$ and HX (X=F, Cl), and show ability in the oxidation of alcohols to their corresponding aldehydes and ketones under microwave irradiation.

Keywords: Alcohols, oxidation, triethylammonium halochromates, synthesis, microwave, reagents

1. Introduction

There is continued interest in the development of new chromium(VI) reagents for the effective and selective oxidation of alcohols, under mild conditions. Of the large number of “mild” chromium based oxidizing agents available, many prove impractical when the reactions are performed on a large (mol) scale, although in recent years, significant improvements have been achieved by the use of new oxidizing agents. Some examples are: pyridinium chlorochromate, pyridinium dichromate, pyridinium fluorochromate, 2,2'-bipyridinium chlorochromate, triethylammonium fluorochromate and tetraethyiammonium fluorochromate (TEAFC). In continuation of our ongoing work on development of highly efficient oxidation protocols, we observed that the oxidation of alcohols with triethylammonium halochromates (VI) (TriEAXC) (X=F, Cl) under microwave irradiation could be carried out much faster than using conventional techniques.
2. Results and Discussion

Different primary and secondary alcohols were subjected to oxidations with triethylammonium halochromate in dichloromethane (Scheme 1). This oxidation take place under mild and completely heterogeneous conditions giving excellent yields (Table 1). The corresponding aldehyde and ketone products can then be easily isolated by simple filtration and evaporation of the solvent. Yield obtained using TriEAHC (X=F, Cl) are mostly higher than those reported in the literature, while both reagent ratio and reaction times are lower (Table 1, Scheme 1).

The versatility of the procedure was further demonstrated by the oxidation of some natural products such as menthol and the sugar derivative 1, 2 : 5, 6 - di - O - isopropylidene – α – D - glucofuranose, in to the corresponding ketones respectively (Scheme 2).

(Table 1) summarizes the products, yields and times of reaction of TriEAHC with various substrates. TriEAHC chose as oxidants, because they have been proven to be useful oxidants in some reactions including the oxidation of alcohols. TriEAHC as oxidants are very well suited reagents for microwave synthesis, because as ionic and magnetically retrievable materials, they carried benefit of efficient conversion of electromagnetic energy into a heat according to the dielectric heating mechanism.12,13

3. Experimental

Typical Procedure: CrO3 (Merck, P.A.) was used without further purification. Solvents were purified by standard methods. Infrared spectra were recorded as KBr disks on a Shimadzu model 420 spectrophotometer. The UV/Visible measurements were made on an Uvicon model 922 spectrometer. Proton, 13C, 19F NMR (for TriEAFC) were carried out on a Bruker AVANCE DRX 500 spectrometer at 500, 125, 470.66 MHz. All the chemical shifts are quoted in ppm using the high-frequency positive convention; 1H and 13C NMR spectra were referenced to external SiMe4 and 19F NMR spectra to external CFCl3. Chromium was estimated iodometrically. In the case of the reduced product of
Table 1. Oxidation of alcohols and polycyclic arenes with TriEAHC under microwave condition.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Product</th>
<th>TriEAFC</th>
<th>TriEACC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Time (min)</td>
<td>Yield (%)</td>
</tr>
<tr>
<td>1</td>
<td>n-C3H7-OH</td>
<td>8</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>n-C4H9-OH</td>
<td>7</td>
<td>90</td>
</tr>
<tr>
<td>3</td>
<td>n-C5H11-OH</td>
<td>5</td>
<td>90</td>
</tr>
<tr>
<td>4</td>
<td>n-C6H13-OH</td>
<td>5</td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td>n-C11H23-OH</td>
<td>3</td>
<td>90</td>
</tr>
<tr>
<td>6</td>
<td>2-C3H7-OH</td>
<td>7</td>
<td>90</td>
</tr>
<tr>
<td>7</td>
<td>2-C6H17-OH</td>
<td>8</td>
<td>92</td>
</tr>
<tr>
<td>8</td>
<td></td>
<td>20</td>
<td>90</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td>2</td>
<td>100</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>3</td>
<td>90</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>5</td>
<td>92</td>
</tr>
<tr>
<td>12</td>
<td></td>
<td>40</td>
<td>90</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>7</td>
<td>90</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>10</td>
<td>70</td>
</tr>
</tbody>
</table>

The oxidant, chromium, was determined after oxidizing with acidic peroxodisulfate (K2S2O8) solution. The relative concentrations of carbon, hydrogen and nitrogen were obtained from the Microanalytical laboratories, Department of Chemistry, OIRC, Tehran. Melting points were measured on an Electrothermal 9100 melting point apparatus. A Microsynth Milstone laboratory microwave oven has been used.

**Synthesis of Triethylammonium Fluorochromate (TriEAFC), (C3H2)3NH[CrO3F]**. A 1 g (10 mmol) sample of chromium (VI) oxide, CrO3, and 0.9 ml (20 mmol) of 40% hydrofluoric acid were added to 20 ml of water in a 100
ml polyethylene beaker with stirring. After 5-7 min the homogeneous solution was cooled to ca. 2°C. To the resultant clear orange solution, triethylamine (14ml, 10 mmol) was added dropwise with stirring to this solution over a period of 0.5 h and stirring was continued for 0.5 h at -4°C. The precipitated yellowish-orange solid was isolated by filtration on a polyethylene funnel, washed with petroleum ether (3 × 60 ml) and dried in vacuum for 2 h at room temperature. Yield: (88%).

**Synthesis of Triethylammonium Chlorochromate (TriEACC), (C$_2$H$_5$)$_3$NH[CrO$_3$Cl]**. Chromium(VI) oxide (1 g, 10 mmol) was dissolved in water in a beaker and hydrochloric acid (0.251 ml, 15 mmol) was added with stirring at 0 °C. To the resultant clear orange solution, triethylamine (0.059 gr, 10 mmol) was added dropwise with stirring to this solution over a period of 0.5 h and stirring was continued for 0.5 h at -4°C. The precipitated orange solid was isolated by filtration, washed with anhydrous ether (3×60 ml) and dried in vacuum for 2 h at room temperature. Yield: 54%.

**4. Conclusion**

Triethylammonium halochromates show ability in the oxidation of alcohols to their corresponding aldehydes and ketones under microwave irradiation. Different primary and secondary alcohols were subjected to oxidations with triethylammonium halochromate in dichloromethane. This oxidation take place under mild and completely heterogeneous conditions giving excellent yields. TriEAHC as oxidants are very well suited reagents for microwave synthesis, because as ionic and magnetically retrievable materials, they carried benefit of efficient conversion of electromagnetic energy into a heat according to the dielectric heating mechanism.

**Acknowledgement**

The authors would like to thank Dr Mahjoub for valuable discussions.

**References and Notes**