

Communication

Bis(trimethylsilyl)chromate Catalyzed Oxidations of Alcohols to Aldehydes and Ketones with Periodic Acid

Karim Asadollah *, Majid M. Heravi *, Rahim Hekmatshoar and Soma Majedi

Department of Chemistry, School of Sciences, Azzahra University, Vanak, Tehran, Iran

* Authors to whom correspondence should be addressed; E-mails: k_assadollah@yahoo.com (Karim Asadollah); mmh1331@yahoo.com (Majid M. Heravi)

Received: 15 February 2007; in revised form: 19 March 2007 / Accepted: 23 March 2007 / Published: 5 May 2007

Abstract: A facile, selective and high yielding bis(trimethylsilyl) chromate (BTSC) catalyzed selective oxidation of alcohols to aldehydes and ketones with periodic acid is reported.

Keywords: Oxidation; BTSC; Carbonyl compounds; Periodic acid.

Introduction

The selective oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones is a fundamental transformation in synthetic organic chemistry [1]. A plethora of reagents are available for this interconversion, but most of these reagents, which are often expensive and toxic, must be used in stoichiometric quantities.

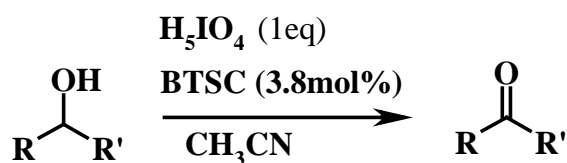
Some of the most applicable, efficient and on the other hand most notorious and hazardous reagents used in oxidations are chromium based chemicals. The utility of chromium (VI) reagents in the oxidative transformation is compromised due to their inherent toxicity (they are cancer-causing suspects) and other problems such as difficulties in preparation and handling of its complexes, susceptibility to ignition and explosivity, difficulties in terms of product isolation and waste disposal, etc. [2]. Consequently, from both the environmental and economical points of view catalytic oxidative transformations are thus promising and valuable and those employing less hazardous chromium reagent in catalytic amounts are particularly attractive. Accordingly, several methods have been

recently reported for the catalytic oxidation of primary and secondary alcohols to carbonyl compounds using a variety of catalysts [3].

Results and Discussion

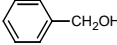
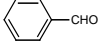
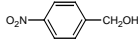
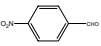
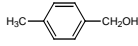
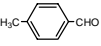
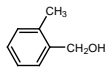
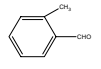
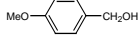
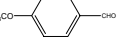
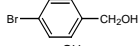
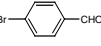
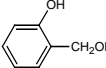
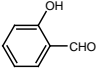
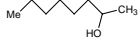
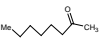
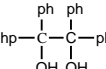
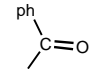


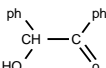
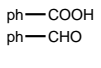
Our laboratory has been engaged in the exploration of practical green chemistry procedures that eliminate or minimize the use of hazardous substances which are dangerous to human life and environments [4] but necessary for chemical reactions. We are also interested in oxidative transformations, especially those which involve user friendly oxidative reagents and catalysts [5]. Although we have previously reported bistrimethylsilyl chromate (BTSC) as a versatile reagent for various oxidative transformations [6] and it is being used routinely in organic synthesis, the need to use an excess or at least a stoichiometric amount of BTSC to perform the oxidations is a drawback, due to all the known disadvantages of chromium based compounds. Therefore, new oxidation protocols that only require catalytic amounts of chromium based reagents and generate less chromium waste are still in much demand. In this communication, we wish to report a BTSC catalyzed oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones with H_5IO_6 in high yields using only 3.8% mol of the catalyst (Scheme 1).

Scheme 1.



Bis(trimethylsilyl)chromate was prepared following the reported procedure [6a] from hexamethyldisiloxane and CrO_3 in dichloromethane. The oxidation reaction was conducted by refluxing benzyl alcohol (1 equiv.), BTSC (3.8 mol %), periodic acid (1 equiv.). The progress of the reaction was monitored by TLC. Upon the completion of the reaction the solvent was evaporated to dryness and the crude product was directly subjected to column chromatography using a small pad of silicagel and a 9:1 mixture of pet. ether-ethyl acetate as eluent to afford benzaldehyde in almost quantitative yield. To establish the generality of method various alcohols including aromatic, aliphatic, benzylic, primary and secondary were oxidized to the corresponding carbonyl compounds in high yields. The results are summarized in Table 1. No overoxidation products (to carboxylic acid) were observed. It is worthwhile to mention that in the presence of alkyne (propargyl alcohol) and alkene (cinnamyl alcohol) groups this protocol for oxidation of hydroxyl groups to carbonyl groups did not work. Oxidation of hexanol to hexanal (entry 10) took 4 h to complete. Furthermore the oxidation of benzopinacol (entry 9) gave benzophenone and the oxidation of pinacol gave a complicated mixture. Benzoin (entry 11) afforded a mixture of benzoic acid (45%) and benzaldehyde (37%).

Table 1. Oxidations of alcohols to aldehydes and ketones with BTSC/H₅IO₆.

| Entry | Compound | Product | Solvent | Temp(°C) | Time(h) | Yield ^b (%) | m.p or b.p.(°C) | |
|-------|---|---|--------------------|----------|---------|---------------------------|--------------------|-------|
| | | | | | | | Found | Lit. |
| 1 |  |  | CH ₃ CN | 40-50 | 1 | 96 | 179 ^c | 181 |
| 2 |  |  | CH ₃ CN | 80 | 3 | 80 | 106 | 104 |
| 3 |  |  | THF | 60 | 3 | 91 | 204-5 | 202 |
| 4 |  |  | CH ₃ CN | 50-60 | 3 | 82 | 200 ^c | 200-3 |
| 5 |  |  | THF | 50-60 | 2 | 96 | 248 ^c | 248 |
| 6 |  |  | THF | 50 | 3 | 87 | 67 | 65 |
| 7 |  |  | THF | 60 | 3 1/2 | 79 | 196-7 ^c | 194 |
| 8 |  |  | CH ₃ CN | 80 | 4 1/2 | 83 | 172-3 | 170 |
| 9 |  |  | THF | 60 | 2 | 86 | 48 | 47 |
| 10 |  |  | CH ₃ CN | 80 | 4 | 81 | 131 | 129 |
| 11 |  |  | CH ₃ CN | 80 | 2 1/2 | 82 | 121 | 118 |

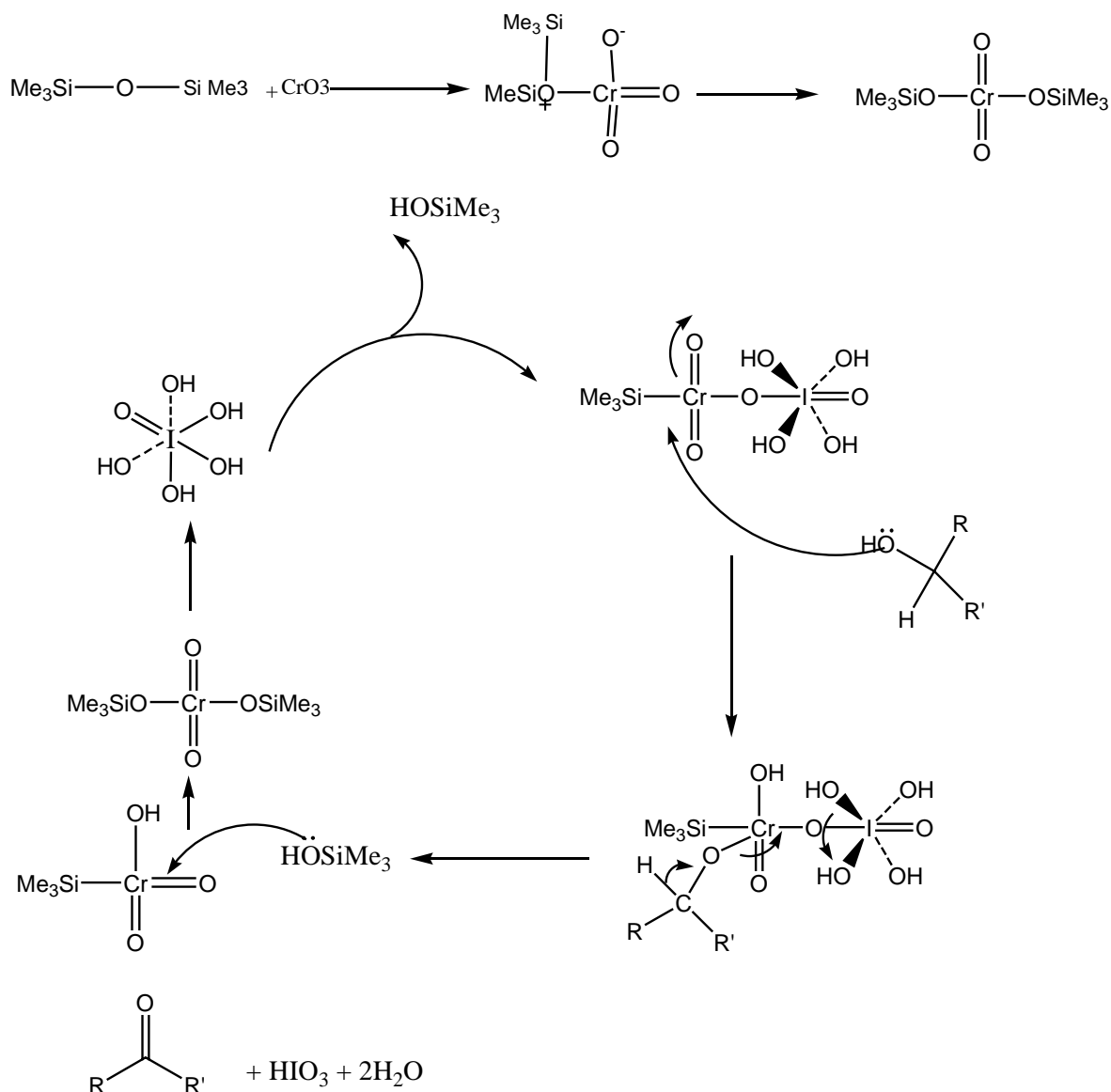
a) All reactions were conducted in CH₃CN except for entries 3, 5 and 9 which were done in THF.

b) Yields are based on GC analysis. The products were characterized by comparison of their IR with those of authentic samples and their boiling points and melting points with those reported in CRC Handbook of Chemistry.

c) Boiling point, CRC Handbook of Chemistry.

It is noteworthy to mention that in this reaction no addition of water is required, in contrast to the CrO₃/H₅IO₆ oxidation [7]. The yield of the oxidation of benzyl alcohol to benzaldehyde (96%), relative to the amount of BTSC used, clearly shows the catalytic nature of this reaction. A plausible mechanism is illustrated in Scheme 2. The only shortcoming of this method is the lack of reactivity of aliphatic alcohols. However, we took advantage of this apparent disadvantage to show the selectivity of the protocol for the selective oxidation of benzylic alcohol in the presence of hexanol. Benzyl alcohol was selectively oxidized in 1 h to benzaldehyde in 90% yield in the presence of hexanol without detection of hexanal.

Scheme 2.



In continuation of our ongoing program to develop the use of solventless systems for environmentally benign synthetic protocols utilizing microwave irradiation [8], we examined the use of this procedure for oxidation of benzyl alcohols in a solventless system. No conversion was observed.

Conclusions

In summary, we have developed an effective and versatile catalytic system for the selective oxidation of various types of alcohols to carbonyl compounds. Primary alcohols can be oxidized to the corresponding aldehydes without any appreciable overoxidation to the corresponding carboxylic acids. This method for oxidation of alcohols offers a simple protocol, and is much less hazardous when compared to other conventional chromium oxidations currently used. Due to the simplicity and environmentally friendly conditions, this methodology should find utility in organic synthesis.

Experimental

General

All products were known and their physical and spectroscopic data were compared with those of authentic samples.

Oxidation of benzyl alcohol: Typical procedure

Benzyl alcohol (1 mmol), periodic acid (1.05 mmol) and BTSC (3.8 mol%) were refluxed in acetonitrile (5 mL). The progress of reaction was monitored by TLC, using a 9:1 mixture of pet. ether-ethyl acetate as eluent. Upon the completion of the reaction, the solvent was evaporated to dryness. To the crude product ethyl acetate (10 mL) was added and the solution was washed with 10 mL of 1:1 brine-water. The organic layer was separated, dried over Na₂SO₄ and evaporated to dryness. The residue was directly passed through a small silica gel column to afford benzaldehyde in 96% yield.

Acknowledgments

We are grateful for the partial financial support from Azzahra Research Council.

References and Notes

1. Hudlicky, M.; *Oxidation in Organic Chemistry*; American Chemical Society: Washington, DC **1990**.
2. Varma, R. S.; Saini, R. K. Wet alumina supported chromium (VI) oxide: Selective oxidation of alcohols in solventless system. *Tetrahedron Lett.* **1998**, *39*, 1481-1482.
3. (a) Velusamy, S.; Srenvasan, A.; Punniyamurthy, T. Copper (II) catalyzed selective oxidation of primary alcohols to aldehydes with atmospheric oxygen. *Tetrahedron Lett.* **2006**, *47*, 923-926; (b) Herrerias, C. I.; Zhang, T. Y.; Li, Ch. Catalytic oxidations of alcohols to carbonyl compounds by oxygen under solvent-free and transition-metal-free conditions. *Tetrahedron Lett.* **2006**, *47*, 13-17; (c) Mardani, H. R.; Golchobian, H. Effective oxidation of benzylic and aliphatic alcohols with hydrogen peroxide catalyzed by a manganese(III) Schiff-base complex under solvent-free conditions. *Tetrahedron Lett.* **2006**, *47*, 2349-2352; (d) Farhadi, S.; Afshari, M.; Maleki, M.; Babazadeh, Z. Photocatalytic oxidation of primary and secondary benzylic alcohols to carbonyl compounds catalyzed by H₃PW₁₂O₄₀/SiO₂ under an O₂ atmosphere. *Tetrahedron Lett.* **2005**, *46*, 8483-8486; (e) Hunsen, M. Pyridinium chlorochromate catalyzed oxidation of alcohols to aldehydes and ketones with periodic acid. *Tetrahedron Lett.* **2005**, *46*, 1651-1653.
4. (a) Heravi, M. M.; Behbahani, F. K.; Bamoharram, F. F. H-14[NaP₅W₃₀O₁₁₀]: A heteropoly acid catalyzed acetylation of alcohols and phenols in acetic anhydride. *J. Mol. Catal. A. Chem.* **2006**, *253*, 16-19; (b) Heravi, M. M.; Bakhtiari, Kh.; Bamoharram, F. F. An efficient and chemoselective synthesis of acylals from aromatic aldehydes and their regeneration, catalyzed by 12-molybdo-phosphoric acid. *Catal. Commun.* **2006**, *7*, 499-501; (c) Heravi, M. M.; Bakhtiari,

- Kh.; Bamoharram, F. F. 12-Molybdophosphoric acid: A recyclable catalyst for the synthesis of Biginelli-type 3,4-dihydropyrimidine-2(1H)-ones. *Catal. Commun.* **2006**, *7*, 373-376; (d) Bamoharram, F. F.; Heravi, M. M.; Roshani, M.; Tawakoli, N. A catalytic method for synthesis of δ -butyrolactone, ϵ -caprolactone and 2-cumaranone in the presence of Preyssler's anion, $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{(14-)}$, as a green and reusable catalyst. *J. Mol. Catal. A. Chem.* **2006**, *252*, 90-95; (e) Heravi, M. M.; Motamedi, Siefi, N, Bamoharram, F. F. Catalytic synthesis of 6-aryl-1H-pyrazolo[3,4-d]pyrimidin-4[5H]-ones by heteropolyacid: H-14 $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ and $\text{H}_3\text{PW}_{12}\text{O}_{40}$. *J. Mol. Catal. A.* **2006**, *249*, 1-3; (f) Bamoharram, F. F.; Heravi, M. M.; Roshani, M. Jahangiri, M.; Gharib, A. Preyssler catalyst, $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{(14-)}$: A green, efficient and reusable catalyst for esterification of salicylic acid with aliphatic and benzylic alcohols. *Applied Cat. A.* **2006**, *302*, 42-47; (g) Oskooei, H. A.; Heravi, M. M.; Bakhtiari, Kh, Zadsirjan, V. H-14 $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ as an efficient catalyst for the one-pot synthesis of alpha-amino nitriles. *Synlett*, **2006**, *11*, 1768-1770; (h) Heravi, M. M.; Derikvand, F.; Haghigi, M. "On water": Rapid Knoevenagel condensation using sodium pyruvate. *Lett. Org. Chem.* **2006**, *3*, 297-299; (i) Heravi, M. M.; Derikvand, F.; Oskooie, H. A.; Hekmatshoar, R. Zeofen: a user friendly agent for oxidation of the Hantzsch 1,4-dihydro-pyridines. *J. Chem. Res.* **2006**, *3*, 168-169; (j) Fotouhi, L.; Nematolahi, D.; Heravi, M. M.; Tamari, E. An efficient electrochemical method for a unique synthesis of new derivatives of 7H-thiazolo[3,2-b]-1,2,4-triazin-7-one. *Tetrahedron Lett*, **2006**, *47*, 1713-1716.
5. (a) Heravi, M. M.; Derikvand, F.; Ghassemzadeh, M. Tetrameric DABCO-bromine complex: A novel reagent for regeneration of carbonyl compounds from aldoximes and ketoximes. *Synth Commun.* **2006**, *36*, 581-585; (b) Heravi, M. M.; Derikvand, F.; Ghassemzadeh, M.; Neumuller, B. Synthesis, characterization and structure of a tetrameric DABCO-bromine complex: a novel oxidizing agent for oxidation of alcohols to carbonyl compounds. *Tetrahedron Lett.* **2005**, *46*, 6243-6245; (c) Heravi, M. M.; Mirza Aghajan, Z. Microwave-assisted oxidation of alcohols using wet alumina supported ammonium chlorochromate in solventless system. *Naturforsch.* **1999**, *54*, 815-817; (d) Heravi, M. M.; Ajami, D.; Tabar hydra, K.; Ghassemzadeh, M. Remarkable fast microwave-assisted zeolite HZSM-5 catalyzed oxidation of alcohols with chromium trioxide under solvent-free conditions. *J. Chem. Res.* **1999**, *5*, 334-335; (e) Heravi, M. M. Ajami, D.; Aghapoor, K.; Ghassemzadeh, M. 'Zeofen', a user-friendly oxidizing reagent *Chem. Commun.* **1999**, *89*, 833-834; (f) Heravi, M. M.; Ajami, D.; Ghassemzadeh, M. Wet alumina supported chromium (VI) oxide: A mild, efficient and inexpensive reagent for oxidative deprotection of trimethylsilyl and tetrahydropyranyl ethers in a solventless system. *Synthesis*, **1999**, *3*, 393-394.
6. (a) Heravi, M. M.; Derikvand, F.; Oskooei, H. A.; Hekmatshoar, R. Silica gel-supported bis(trimethylsilyl) chromate: Oxidation of 1,4-dihydropyridines to pyridines. *Synth. Commun.* **2006**, *36*, 77-82; (b) Heravi, M. M.; Ajami, D. Oxidative deprotection of tetrahydropyranyl ethers to carbonyl compounds with montmorillonite K-10 supported bis(trimethylsilyl) chromate under non-aqueous conditions. *J. Chem. Res.* **1998**, *718-719*; (c) Heravi, M. M.; Ajami, D.; Tabar-Heydar, K.; Mojtahedi, M. M. Direct oxidative deprotection using montmorillonite supported bis-(trimethylsilyl)chromate. *J. Chem. Res.* **1998**, *9*, 620-621; (d) Heravi, M. M.; Ajami, D.; Tajbakhsh, M.; Ghassemzadeh, M. Clay supported bis-(trimethylsilyl)-chromate: An efficient reagent for oxidative deoxygenation. *Monatsh. Chem.* **2000**, *131*, 1109-1113; (e) Heravi, M. M.; Ajami, D. Clay supported bis(trimethylsilyl)chromate: Oxidative deprotection of

- tetrahydropyranyl ethers under solvent-free conditions using microwaves. *Monatsch. Chem.* **1999**, *130*, 709-712; (f) Khaleghi, Sh.; Heravi, M. M.; Derikvand, F. Bis(trimethylsilyl) chromate: An efficient reagent for cleavage of phenylhydrazones. *Phosphorus Sulfur Silicon* **2006**, *181*, 227-231.
7. Zhao, M.; Li, J.; Song, Z.; Desmond, R.; Taschaen, D. M.; Grabowski, E. J. J.; Reider, P. A novel chromium trioxide catalyzed oxidation of primary alcohols to the carboxylic acids. *Tetrahedron Lett.* **1998**, *39*, 5323-5326.
 8. (a) Heravi, M. M.; Beheshtiha, Y. S.; Ghasemzadeh, M.; Hekmat Shoar, R.; Sarmadi, N. Solid state deoxygenation with clay supported ammonium chlorochromate: Regeneration of carbonyl compounds using microwaves in a solventless system. *Monatsh. Chem.* **2000**, *31*, 187-190; (b) Heravi M. M.; Rajabzadeh, G.; Bamoharram, F. F.; Seifi, N. An eco-friendly catalytic route for synthesis of 4-amino-pyrazolo[3,4-d]pyrimidine derivatives by Keggin heteropolyacids under classical heating and microwave irradiation. *J. Mol. Catal. A: Chem.* **2006**, *256*, 238-241.
 9. Kim, S. S.; Nehru, K.; Kim, S. S.; Kim, D. W.; Jung, H. C. A Mild and Highly Efficient Oxidation of Sulfides to Sulfoxides with Periodic Acid Catalyzed by FeCl₃. *Synthesis* **2002**, *17*, 2484-2486.
 10. Kim, S. S.; Nehru, K. A Mild and Efficient Oxidation of Alcohols to Carbonyl Compounds by Periodic Acid Catalyzed by 2,2,6,6-Tetramethylpiperidiny-1-oxyl. *Synlett* **2002**, *4*, 616-617.

Sample availability: Samples of the compounds presented in this paper are available from the authors.

© 2007 by MDPI (<http://www.mdpi.org>). Reproduction is permitted for noncommercial purposes.