Trichloroisocyanuric Acid/KBr as a Catalytic System for the Chemoselective Oxidation of Benzylic and Secondary Alcohols

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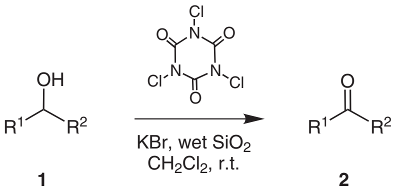
Abstract: Chemoselective oxidation of benzylic and secondary alcohols were proceeded by using a catalytic amount of KBr in the presence of trichloroisocyanuric acid and wet SiO_2 under mild and heterogeneous conditions with excellent yields.

Key words: trichloroisocyanuric acid, benzylic and secondary alcohols, chemoselective oxidation

The oxidation of alcohols into the corresponding aldehydes or ketones is one of the most important functional group transformations in organic synthesis. Many oxidizing reagents have been traditionally employed in order to accomplish this transformation.[1–19] From an economic and environmental viewpoint, catalytic oxidation processes are thus valuable, and those employing metal-free catalysts are particularly attractive.[13,14,18,20]

The aim of this work was two-fold: (a) to overcome the limitations and drawbacks of the reported methods such as over oxidation, tedious work-up, acidic media, transition metals and safety problems;[15–17] (b) to develop this procedure as a highly useful technique, especially for industry and it has many advantages: reduced pollution, low costs, chemoselectivity and simplicity in process and handling (these factors are especially important in industry).

In continuation of our studies in this regard,[21] we have found that trichloroisocyanuric acid,[22] an inexpensive commercially available reagent primarily used as a disinfectant and deodorant, has found little application in organic chemistry.[23] On the basis of abovementioned facts and our interest in the use of heterogeneous systems in organic reactions,[24] herein we report a very mild, simple, cheap and chemoselective method for the general oxidation of alcohols to the corresponding carbonyl compounds using trichloroisocyanuric acid and a catalytic amount of KBr in the presence of wet SiO_2 in dichloromethane. Different types of benzylic and secondary alcohols (**1**) were subjected to the oxidation reaction in the presence of trichloroisocyanuric acid (**I**), catalytic amount of KBr (**II**) and wet SiO_2 in dichloromethane at room temperature (Scheme 1, Table 1).



Scheme 1

For showing the chemoselectivity of the described system some competitive reactions were design. A mixture of equal amounts of primary and secondary alcohols was subjected to oxidation in the presence of reagents under the conditions given in Table 1 (Scheme 2). Tetraphenylethylene glycol was converted into benzophenone with good yield (Table 1, Entry 9). This observation is in close agreement with our previously reported data.[21] When a mixture of cyclohexanol and *n*-octanol was allowed to react under the described conditions, the former oxidized to cyclohexanone in 100% conversion and the latter gave *n*-octanal in trace conversion. A similar result was obtained in the oxidation of 1-indanol and 2-phenyl ethanol, affording 1-indanone and 2-phenyl ethanal in 100% and trace conversions, respectively. These studies clearly reveal that this method can be applied for the chemoselective oxidation of secondary alcohols in the presence of primary hydroxy groups. Although these results are in contrast to the data reported by Giacomelli et al. (in that work, the reported catalyst was TEMPO),[18] they are in close agreement with the data reported by Konwar et al.[1]

Also, we observed that the secondary hydroxyl group in 1-phenyl-1,2-ethanediol was selectively oxidized into the corresponding ketone (Scheme 3; Table 1, entry 12).

A plausible mechanism for the oxidation is shown in Scheme 4 based on literature,[25] our observations and obtained results, catalytic activity of KBr (Scheme 5) and in situ generation of HOCl by the use of trichloroisocyanuric acid in the presence of water.[22c,26,27] The oxidation of bromide ion by HOCl would give hypobromous acid[25] and subsequent oxidation of alcohols affords aldehydes and ketones.

In conclusion, chemoselectivity, the cheapness and availability of the reagents, easy and clean work-up and high yields make this method attractive for chemists. We believe that the present methodology could be an important addition to the existing methodologies.

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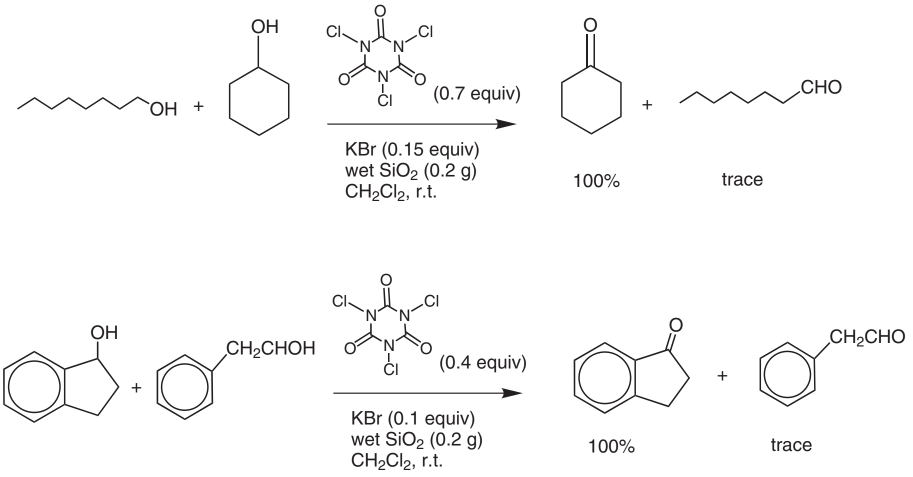
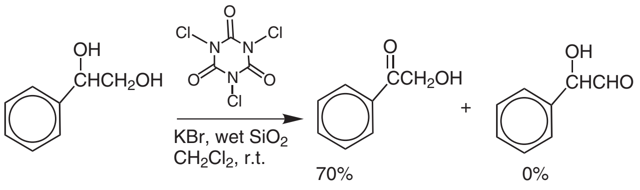


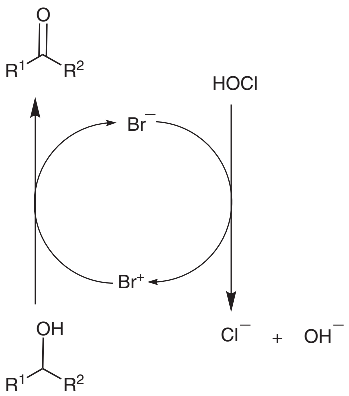
Scheme 2



Scheme 3

Oxidation of 4-Bromobenzyl Alcohol to 4-Bromobenzaldehyde: Typical Procedure

KBr (0.0142 g, 0.12 mmol) was added to a solution of 4-bromobenzyl alcohol (0.187 g, 1 mmol) and wet SiO_2 (0.2 g) in CH_2Cl_2 (10 mL), followed by addition of trichloroisocyanuric acid (0.093 g, 0.4 mmol). The resulting reaction mixture was stirred at r.t. for 75 min (the progress of the reaction was monitored by TLC) and then filtered. The residue was washed with CH_2Cl_2 (20 mL). Anhyd Na_2SO_4 (1 g) was added to the filtrate and filtered off after 20 min. CH_2Cl_2 was removed. The yield was 0.173 g (94%).



Scheme 5

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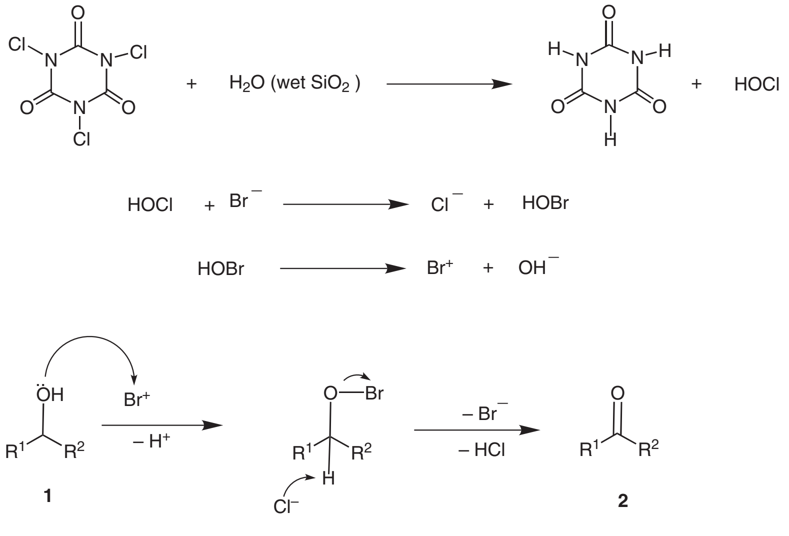

Scheme 4

Table 1 Oxidation of Alcohols **1** to the Corresponding Carbonyl Compounds **2**[a]

Entry	Substrate[b] **1**	Product **2**	Reagent and catalyst/substrate (mmol)[b]		Time (h)	Yield (%)[c]
			I	**II**		
1	Benzyl alcohol	Benzaldehyde	0.4	0.1	0.75	93
2	4-Bromobenzyl alcohol	4-Bromobenzaldehyde	0.4	0.12	1.25	94
3	2,4-Dichlorobenzyl alcohol	2,4-Dichlorobenzaldehyde	0.6	0.15	1.25	96
4	4-Nitrobenzyl alcohol	4-Nitrobenzaldehyde	2	0.35	48	50[d]
5	4-Methylbenzyl alcohol	4-Methylbenzaldehyde	0.4	0.1	0.5	90
6	1-Indanol	1-Indanone	0.4	0.1	0.25 (5)[e]	98
7	2-Phenyl ethanol	2-Phenyl ethanal	0.7	0.15	28	trace
8	Benzhydrol	Benzophenone	0.4	0.15	2	97
9	Tetraphenylethyleneglycol	Benzophenone	2.7	0.4	48	80[c]
10	2-Menthol	2-Menthon	0.7	0.15	3	96
11	Cyclododecanol	Cyclododecanone	0.7	0.15	1.25	98
12	1-Phenylethan-1,2-diol	1-Phenyl-2-hydroxy ethanone	0.6	0.15	3.75	70[d,f]
13	1-Cyclohexyl ethanol	1-Cyclohexyl ethanone	0.4	0.1	1	82
14	Cyclohexanol	Cyclohexanone	0.7	0.15	1.5	95[d,f]
15	2-Pentanol	2-Pentanone	0.4	0.15	0.75	100[d,f]
16	1-Octanol	1-Octanal	0.7	0.15	4	trace
17	1-Pentanol	1-Pentanal	0.7	0.15	5	trace

[a] Conditions: combination of trichloroisocyanuric acid (**I**) and wet SiO_2 (50%) in the presence of a catalytic amount of KBr (**II**) in CH_2Cl_2 at r.t.
[b] Wet SiO_2:substrate (0.2 g:1 mmol).
[c] Isolated yields.
[d] Conversion.
[e] Without KBr.
[f] GC yields.

Reference

(1) Gogoi, P.; Sarmah, G. K.; Konwar, D. *J. Org. Chem.* **2004**, *69*, 5153; and references cited therein.
(2) Bressette, A. R.; Glover, L. C. IV *Synlett* **2004**, 738.
(3) Fernandes, R. A. *Synlett* **2003**, 741.
(4) Salehi, P.; Firouzabadi, H.; Farrokhi, A.; Gholizadeh, M. *Synthesis* **2001**, 2273.
(5) Mahjoub, A. R.; Ghammami, S.; Kassaee, Z. *Tetrahedron Lett.* **2003**, *44*, 4555.
(6) Yamato, T.; Shinoda, N. *J. Chem. Res., Synop.* **2002**, 400.
(7) (a) Firouzabadi, H.; Iranpoor, N.; Hazarkhani, H. *Phosphorus, Sulfur Silicon Relat. Elem.* **2003**, *178*, 149. (b) Firouzabadi, H.; Iranpoor, N.; Amani, K. *Synthesis* **2003**, 408; and references cited therein.
(8) Sakuratani, K.; Togo, H. *Synthesis* **2003**, 21.
(9) Tashiro, A.; Mitsuishi, A.; Irie, R.; Katsuki, T. *Synlett* **2003**, 1868.
(10) Kim, S. S.; Kim, D. W. *Synlett* **2003**, 1391.
(11) Velusamy, S.; Punniyamurthy, T. *Org. Lett.* **2004**, *6*, 217.
(12) Hanasaka, F.; Fujita, K.; Yamaguchi, R. *Organometallics* **2004**, *23*, 1490.
(13) Gilhespy, M.; Lok, M.; Baucherel, X. *Chem. Commun.* **2005**, 1085.
(14) Wu, X.; Ma, L.; Ding, M.; Gao, L. *Synlett* **2005**, 607.
(15) Mori, K.; Hara, T.; Mizaugaki, T.; Ebitani, K.; Kaneda, K. *J. Am. Chem. Soc.* **2004**, *126*, 10657.
(16) Chhikara, B. S.; Tehlan, S.; Kumar, A. *Synlett* **2005**, 3041.
(17) Velusamy, S.; Ahmed, M.; Punnigamurthy, T. *Org. Lett.* **2004**, *6*, 4812.
(18) Luca, L. D.; Giacomelli, G.; Porcheddu, A. *Org. Lett.* **2001**, *3*, 3041.
(19) Pillai, V. R.; Sahle-Demessie, E. *Green Chem.* **2004**, *6*, 161.
(20) (a) Gogoi, P.; Sarmah, G. K.; Konwar, D. *J. Org. Chem.* **2004**, *69*, 5153. (b) Wang, N.; Liu, R.; Chen, J.; Liang, X. *Chem. Commun.* **2005**, 5322. (c) Ferreira, P.; Hayes, W.; Phillips, E.; Rippon, D.; Tasang, S. C. *Green Chem.* **2004**, *6*, 310.

(21) (a) Zolfigol, M. A.; Shirini, F.; Mohammadpoor-Baltork, I.; Ghorbani-Choghamarani, A.; Hajami, M.; Sedaghat, A. M. *Mendeleev Commun.* **2005**, 113. (b) Mirjalili, B. F.; Zolfigol, M. A.; Bamoniri, A.; Zarei, A. *Bull. Korean Chem. Soc.* **2003**, *24*, 400. (c) Shirini, F.; Zolfigol, M. A.; Khaleghi, M. *Bull. Korean Chem. Soc.* **2003**, *24*, 1021. (d) Shirini, F.; Zolfigol, M. A.; Mallakpour, B.; Mallakpour, S. E.; Hajipour, A. R. *Aust. J. Chem.* **2001**, *54*, 405. (e) Mirjalili, B. F.; Zolfigol, M. A.; Bamoniri, A.; Zaghaghi, Z. *J. Chem. Res., Synop.* **2003**, 273. (f) Mirjalili, B. F.; Zolfigol, M. A.; Bamoniri, A.; Zaghaghi, Z.; Hazar, A. *Acta Chem. Slov.* **2003**, *50*, 563. (g) Shirini, F.; Zolfigol, M. A.; Khaleghi, M. *Phosphorus, Sulfur Silicon Relat. Elem.* **2003**, *178*, 2107. (h) Iranpoor, N.; Firouzabadi, H.; Zolfigol, M. A. *Bull. Chem. Soc. Jpn.* **1998**, *71*, 905. (i) Shirini, F.; Zolfigol, M. A.; Torabi, S. *Lett. Org. Chem.* **2005**, *2*, 398.

(22) (a) Zolfigol, M. A.; Ghorbani Choghamarani, A.; Hazarkhani, H. *Synlett* **2002**, 1002. (b) Zolfigol, M. A.; Madrakian, E.; Ghaemi, E.; Mallakpour, S. *Synlett* **2002**, 1633. (c) Zolfigol, M. A.; Ghaemi, E.; Madrakian, E. *Synlett* **2003**, 191. (d) Zolfigol, M. A.; Madrakian, E.; Ghaemi, E. *Synlett* **2003**, 2222. (e) Mohammadpoor-Baltork, I.; Zolfigol, M. A.; Abdollahi-Alibeik, M. *Synlett* **2004**, 2803. (f) Zolfigol, M. A.; Azarifar, D.; Maleki, B. *Tetrahedron Lett.* **2004**, *45*, 2181.

(23) For a recent review on the use of trichloroisocyanuric acid, see: (a) Tilstam, U.; Weinmann, H. *Org. Process Res. Dev.* **2002**, *4*, 384. (b) Ye, J.; Wang, Y.; Liu, R.; Zhang, G.; Zhang, Q.; Chen, J.; Liang, X. *Chem. Commun.* **2003**, 2714. (c) Ye, J.; Wang, Y.; Chen, J.; Liang, X. *Adv. Synth. Catal.* **2004**, *346*, 691; and references cited therein. (d) Firouzabadi, H.; Iranpoor, N.; Hazarkhani, H. *Synlett* **2001**, 1641. (e) Xiog, Z. X.; Huang, N. P.; Zhong, P. *Synth. Commun.* **2001**, *31*, 245. (f) Mendonça, G. F.; Sanseverino, A. M.; Mattos, M. C. S. D. *Synthesis* **2003**, 45. (g) Synlett Spotlight 132: Barros, J. *Synlett* **2005**, 2115.

(24) (a) Zolfigol, M. A. *Tetrahedron* **2001**, *57*, 9509. (b) Zolfigol, M. A.; Torabi, M.; Mallakpour, S. E. *Tetrahedron* **2001**, *57*, 8381. (c) Zolfigol, M. A.; Shirin, F.; Ghorbani Choghamarani, A.; Mohammadpoor-Baltork, I. *Green Chem.* **2002**, *4*, 562. (d) Zolfigol, M. A.; Madrakian, T.; Ghaemi, E.; Afkhami, A.; Azizian, S.; Afshar, S. *Green Chem.* **2002**, *4*, 611.

(25) Koo, B. S.; Lee, C. K.; Lee, K. J. *Synth. Commun.* **2002**, *32*, 2115; and references cited therein.

(26) Budavari, S.; O'Neil, M. J.; Smith, A.; Heckelman, P. E. *The Merck Index*, 11th Ed.; Merck & CO Inc.: Whitehouse Station, New Jersey, **1989**, 8993.

(27) Zolfigol, M. A.; Ghaemi, E.; Madrakian, E.; Ghorbani Choghamarani, A. *Mendeleev Commun.* **2006**, 41.