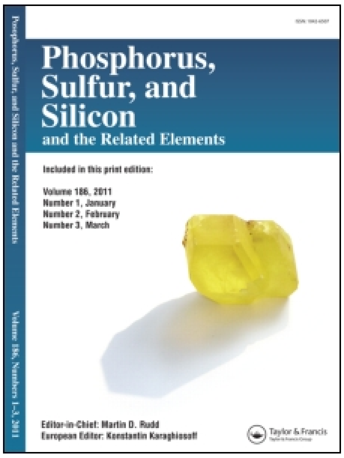

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Efficient Oxidation of Alcohols with KBrO 3 in the Presence of Silica Chloride and Wet SiO 2

Farhad Shirini[a]; Mohammad Ali Zolfigol[b]; Mahroo Khaleghi[a]
[a] Guilan University, Rasht, Iran [b] Bu-Ali Sina University, Hamadan, Iran

To cite this Article Shirini, Farhad , Zolfigol, Mohammad Ali and Khaleghi, Mahroo(2003) 'Efficient Oxidation of Alcohols with KBrO 3 in the Presence of Silica Chloride and Wet SiO 2', Phosphorus, Sulfur, and Silicon and the Related Elements, 178: 10, 2107 — 2110

To link to this Article: DOI: 10.1080/713744572

URL: http://dx.doi.org/10.1080/713744572

Phosphorus, Sulfur, and Silicon, 178:2107–2110, 2003

ISSN: 1042-6507 print / 1563-5325 online
DOI: 10.1080/10426500390221555

EFFICIENT OXIDATION OF ALCOHOLS WITH $KBrO_3$ IN THE PRESENCE OF SILICA CHLORIDE AND WET SiO_2

Farhad Shirini,[a] *Mohammad Ali Zolfigol,*[b]
and Mahroo Khaleghi[a]
Guilan University, Rasht, Iran[a] *and Bu-Ali Sina University, Hamadan, Iran*[b]

(Received February 13, 2003; accepted March 25, 2003)

Alcohols were oxidized to their corresponding carbonyl compounds with $KBrO_3$ in the presence of silica chloride and wet SiO_2, in solution and under solvent free conditions.

Keywords: Oxidation of alcohols; silica chloride; solution; solvent free conditions

The total syntheses of complex molecules demand new methods in different areas of organic chemistry. Therefore, the development of reagents is always rewarding to synthetic organic chemists.

Oxidation is one of the most important classes of reactions in synthetic organic chemistry and the development of new oxidizing agents and the modification of known reagents have been studied actively in recent years.[3,4]

The most powerful oxidation state of bromine is ($+5^5$). Bromates have been used for oxidation of a variety of inorganic compounds under aqueous conditions. However, a literature search shows that bromates have not found many applications as oxidizing agents in the field of organic synthesis. To the best of our knowledge only a few reports are available that deal with oxidation of organic compounds with bromate ion in either strong acidic or basic solution using sodium or potassium bromates.[6–8]

In connection with our ongoing research program directed toward the development of new oxidizing agents,[9–12] herein we report an efficient

The authors acknowledge the financial support of this work by the Guilan University Research Council.

Address correspondence to Farhad Shirini, Department of Chemistry, Faculty of Science, Guilan University, Rasht, Iran. E-mail: shirini@guilan.ac.ir

method for the oxidation of alcohols in solution and under solvent free conditions with $KBrO_3$ in the presence of silica chloride and wet SiO_2 (Scheme 1, Table I). Yields and reaction times are given in Table I. Overoxidation of the products using this method was not observed.

$$R_1R_2CHOH \xrightarrow{\text{A or B}} R_1R_2CO$$

A: $KBrO_3$/ Silica chloride/ wet SiO_2, Solvent Free, 80 °C.

B: $KBrO_3$/ Silica chloride/ wet SiO_2, n-Hexane, reflux.

SCHEME 1

As shown in Table I, there are appreciable differences between the results obtained in solution and those in solvent free conditions. Thus, by omiting the solvent, in addition to the ease of the work-up procedure, the reaction time was reduced and the need for sovent is avoided. This method is not suitable for the oxidation of allylic alcohols (Table I, entry 14).

It should be noted that oxidation did not proceed using $KBrO_3$ or silica chloride or wet SiO_2 alone even after prolonged heating.

In conclusion the ready availability and low cost of the reagents, the simple and clean work-up and the high product yields make this method a useful addition to the present methodologies for the oxidation of alcohols.

EXPERIMENTAL

Oxidation of 2-Bromobenzyl Alcohol Under Solvent-Free Conditions. A Typical Procedure

To a mixture of silica chloride (0.3 g), wet SiO_2 [(SiO_2/H_2O: 50% w/w), 0.2 g] and $KBrO_3$ (0.167 g, 1 mmol), was added 2-bromobenzyl alcohol (0.187 g, 1 mmol). The resultant mixture was heated in an oil bath (80°C) for 6 min. The progress of the reaction was monitored by TLC. The reaction mixture was triturated with CH_2Cl_2 (10 mL) and then filtered. Anhydrous $MgSO_4$ was added to the filterate which was filtered after 10 min. Evaporation of the solvent followed by column chromatography on silica gel gave 2-bromobenzaldehyde in 95% yield.

Oxidation of 1-Phenylpropan-2-ol in n-Hexane. A Typical Procedure

In a round-bottomed flask (10 mL) equipped with a condenser and a magnetic stirrer a mixture of silica chloride (0.3 g), wet

TABLE I Oxidation of Alcohols to Their Corresponding Carbonyl Compounds in n-Hexane or Under Solvent-Free Conditions

			Solvent-free oxidation		Oxidation in solution	
Entry	Substrate	Product[a]	Time (min)	Yield (%)[b]	Time (min)	Yield (%)[b]
1	$PhCH_2OH$	PhCHO	15	90	20	85
2	$2\text{-}BrC_6H_4CH_2OH$	$2\text{-}BrC_6H_4CHO$	6	95	8	90
3	$2\text{-}ClC_6H_4CH_2OH$	$2\text{-}ClC_6H_4CHO$	5	85	15	86
4	$4\text{-}CH_3OC_6H_4CH_2OH$	$4\text{-}CH_3OC_6H_4CHO$	4	90	20	90
5	$4\text{-}(Me)_3CC_6H_4CH_2OH$	$4\text{-}(Me)_3CC_6H_4CHO$	8	92	65	85
6	PhCH(OH)Ph	PhCH(OH)Ph	5	87	20	85
7	PhCH(OH)COPh	PhCOCOPh	10	85	110	86
8	$PhCH(OH)CH_2OH$	PhCOCHO	20	82	180	80
9	$PhCH_2CH_2CH_2OH$	$PhCH_2CH_2CHO$	25	92	150	80
10	$PhCH_2CH(OH)CH_3$	$PhCH_2COCH_3$	23	90	70	90
11	$CH_3(CH_2)_6CH_2OH$	$CH_3(CH_2)_6CHO$	5	85	10	90
12	cyclohexanol	cyclohexanone	5	90	15	86
13	4-methylcyclohexanol	4-methylcyclohexanone	10	86	15	85
14	$PhCH{=}CHCH_2OH$	$PhCH{=}CHCHO$	10	—[c]	20	—[c]

[a] Products were characterized by their physical constants, comparison with authentic samples and IR and NMR spectroscopy.

[b] Isolated yield.

[c] Mixture of products.

SiO_2[SiO_2/H_2O:50% w/w), 0.2 g], $KBrO_3$ (0.167 g, 1 mmol) and 1-phenylpropan-2-ol (0.136 g, 1 mmol) in hexane (5 ml) was prepared and refluxed for 70 min. The progress of the reaction was monitored by TLC. The reaction mixture was filtered and the residue was washed with CH_2Cl_2(15 mL). Anhydrous $MgSO_4$ was added to the filterate and filtered after 10 min. Evaporation of the solvent followed by column chromatography on silica gel gave phenylpropan-2-one in 90% yield.

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