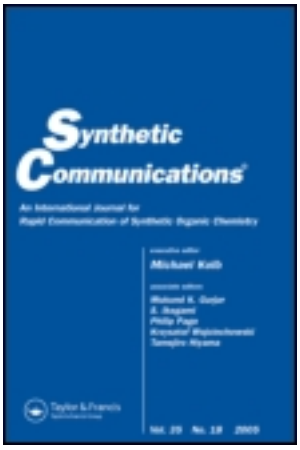

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$KBrO_3/ZrClO_2 \cdot 8H_2O$: An Efficient Reagent System for the Oxidation of Alcohols

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$KBrO_3/ZrClO_2 \cdot 8H_2O$: An Efficient Reagent System for the Oxidation of Alcohols

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Abstract: $KBrO_3$ in the presence of $ZrOCl_2 \cdot 8H_2O$ can be used as an effective oxidizing agent for the conversion of alcohols to their corresponding carbonyl compounds. All reactions were performed under mild and completely heterogeneous conditions in good to high yields.

Keywords: Alcohols, heterogeneous conditions, $KBrO_3$, oxidation, $ZrOCl_2 \cdot 8H_2O$

Sodium bromate and potassium bromate are commercially available, very stable solids that can be handled much more easily than liquid bromine or hypobromous acid solutions. Oxidation with bromates results in bromide ion formation, which can be safely treated or recycled. Thus, such oxidations are recognized as friendly to the environment, compared with the traditional metal-containing reagents such as chromate, permanganate, and cerium salts.

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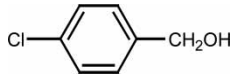
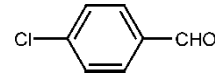
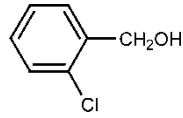
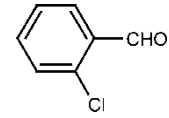
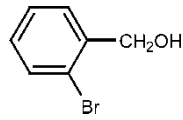
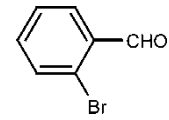
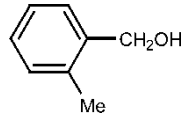
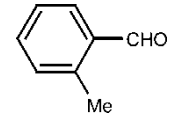
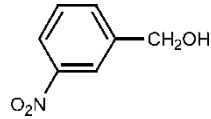
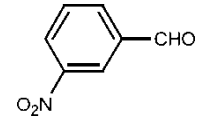
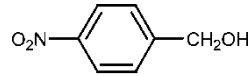
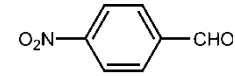
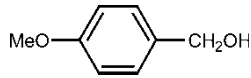
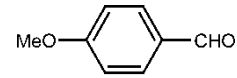
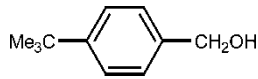
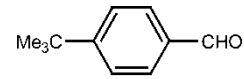
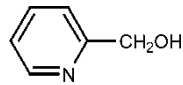
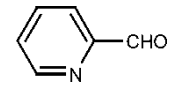
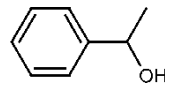
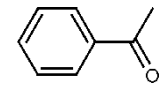
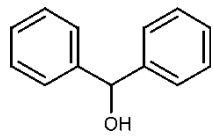
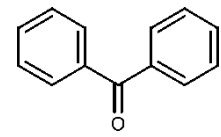
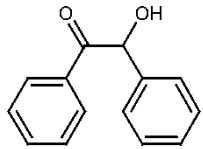
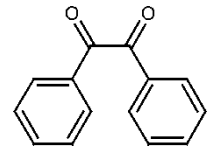
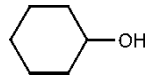
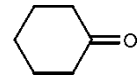
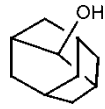
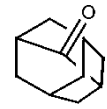
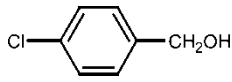
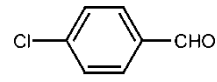
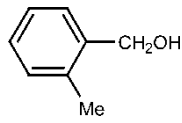
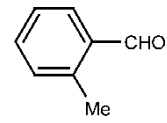
Table 1. Oxidation of alcohols using $KBrO_3$ in the presence of $ZrOCl_2 \cdot 8H_2O$[a]

Entry	Substrate	Product	Time (h)	Yield (%)
1			0.22	92
2			0.75	90
3			0.2	87
4			0.33	85
5			0.83	85
6			4	90
7			0.17	70
8			0.17	85
9			0.42	75
10			0.1	95
11			0.42	95

(*continued*)

Table 1. Continued

Entry	Substrate	Product	Time (h)	Yield (%)
12			1.75	90
13	$PhCH_2CH(OH)CH_3$	$PhCH_2COCH_3$	0.5	70
14	$PhCH(CH_3)CH_2OH$	$PhCH(CH_3)CHO$	1	80
15			0.5	92
16			2.5	90
17			1	—[b]
18			1	—[c]

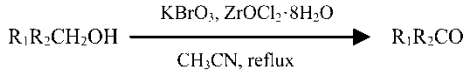
[a]Isolated yields.

[b]Reaction was performed in the presence of $ZrOCl_2$ and the starting material was recovered at the end of the reaction.

[c]Reaction was performed in wet acetonitrile and the starting material was recovered at the end of the reaction.

However, because of the disadvantages such as overoxidation, bromination, oxidative bromination, and need for strongly acidic or basic media, only a few reports are available that deal with oxidation of organic compounds using sodium or potassium bromates.[1–3]

In continuation with our ongoing research program directed toward the development of new oxidizing agents,[4–7] herein we report that $KBrO_3$ as a cheap and readily available reagent is able to oxidize alcohols to their corresponding carbonyl compounds in the presence of $ZrOCl_2 \cdot 8H_2O$. All reactions were performed under completely heterogeneous conditions in good to high yields (Table 1, Scheme 1). Overoxidation of the products was not observed by this method.



Scheme 1.

It should be noted that the progress of the reaction strongly depends on the presence of H_2O in the structure of $ZrOCl_2 \cdot 8H_2O$. This can be shown through comparing oxidation of 4-chlorobenzyl alcohol using $KBrO_3$ in the presence of $ZrOCl_2 \cdot 8H_2O$ and $ZrOCl_2$ (Table 1, entries 1, 17). On the basis of these results, we thought that the effect of $ZrOCl_2 \cdot 8H_2O$ on the acceleration of the reaction may only be related to the presence of H_2O, so that the presence of the other part of the molecule is not important. Lack of the progress of the reaction in wet acetonitrile disproved this hypothesis (Table 1, entry 18).

To show the oxidizing ability of this method, we have compared some of the results with some of those reported in the literature (Table 2).[8,9]

In conclusion, the cheapness and availability of the reagents, easy and clean isolation procedure, good to high yields of the products, and the heterogeneous nature of the reaction conditions all make the proposed method attractive for large-scale applications. We believe that our method can be a useful addition to the existing methods.

EXPERIMENTAL

All of the products were characterized by comparison of their physical and spectral data with those of known samples. All yields refer to isolated products.

General Procedure for the Oxidation of Alcohols

To a solution of alcohol (1 mmol) in CH_3CN (5 mL) were added $KBrO_3$ (2 mmol, 0.334 g) and $ZrOCl_2 \cdot 8H_2O$ (0.5 mmol, 0.161 g) and the mixture was refluxed for the appropriate time (Table 1). The progress of the reaction

Table 2. Comparison of our results with those of crosslinked poly-vinyl-pyridine supported ferric dichromate (2)[8] and Chromic Acid on Amberlist A-26 (3)[9]

		Yield % (h)		
Entry	Substrate	(1)	(2)	(3)
1	1-Phenyl ethanol	95 (0.1)	35 (1)	—
2	Cyclohexanol	92 (0.5)	70 (8)	77 (3)

was monitored by TLC (eluent: CCl_4/Et_2O, 6:1). After completion of the reaction, the mixture was filtered and the solid material was washed with CH_3CN (10 mL). The solvent was evaporated and the crude product was purified by chromatography on silica gel using appropriate eluent. The pure products were obtained in good to high yields (Table 1).

ACKNOWLEDGMENT

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REFERENCES

1. Kajigashi, S.; Nakagawa, T.; Nagasaki, N.; Yamasaki, H. Oxidation of alcohols and ethers using sodium bromate-hypobromic acid system. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 747.
2. Narayana, S.; Srinivasan, V. S. Facile regeneration of carbonyl compounds from semicarbazones by potassium bromate. *J. Chem. Soc., Perkin Trans. 2* **1986**, 1557.
3. Shirini, F.; Zolfigol, M. A.; Khaleghi, M. Efficient oxidation of alcohols with $KBrO_3$ in the presence of silica chloride and wet SiO_2. *Phosphorous, Sulfur Silicon Relat. Elem.* **2003**, *178*, 2107.
4. Shirini, F.; Zolfigol, M. A.; Azadbar, M. R. Oxidation of benzyl alcohols under mild and heterogeneous conditions. *Russian J. Org. Chem.* **2001**, *37*, 1600.
5. Shirini, F.; Zolfigol, M. A.; Pourhabib, A. $ZrCl_4$/wet SiO_2 promoted oxidation of alcohols by $(NH_4)_2Cr_2O_7$ in solution and under solvent free conditions. *J. Chem. Res., Synop.* **2001**, 476.
6. Shirini, F.; Zolfigol, M. A.; Abedini, M.; Salehi, P. Oxidation of alcohols using $(NH_4)_2Cr_2O_7$ in the presence of $Al(HSO_4)_3$ and wet SiO_2. *Mendeleev Commun.* **2003**, 265.
7. Shirini, F.; Tajik, H.; Jalili, F. Polymer supported reagents: Oxidative selection between alcohols. *Synth. Commun.* **2001**, *31*, 2885.
8. Tamami, B.; Firouzabadi, H.; Lakouraj, M. M.; Mahdavian, A. Poly (vinylpyridine) supported versus unsupported ferric dichromate in oxidation of different organic compounds. *J. Polymer Sci. Tec.* **1994**, *3*, 82.
9. Cainelli, G.; Cardillo, G.; Orena, M.; Sandri, S. Polymer supported reagents. Chromic acid on an anion exchange resin. A simple and practical oxidation of alcohols to aldehydes and ketones. *J. Am. Chem. Soc.* **1976**, *98*, 6738.