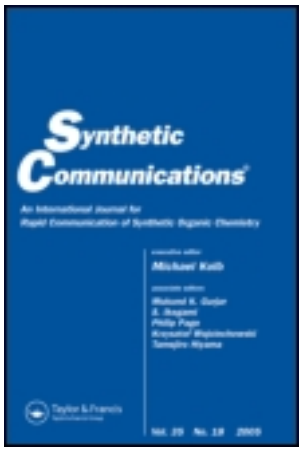


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

HIGHLY SELECTIVE OXIDATION OF PRIMARY AND SECONDARY BENZYLIC ALCOHOLS BY $KMnO_4/ZrOCl_2\ 8H_2O$ IN DIETHYL ETHER

Habib Firouzabadi [a], Mahmood Fakoorpour [a] & Hassan Hazarkhani [a]

[a] Department of Chemistry, College of Sciences, Shiraz University, Shiraz, 71454, Iran

Published online: 09 Nov 2006.

To cite this article: Habib Firouzabadi , Mahmood Fakoorpour & Hassan Hazarkhani (2001) HIGHLY SELECTIVE OXIDATION OF PRIMARY AND SECONDARY BENZYLIC ALCOHOLS BY $KMnO_4/ZrOCl_2\ 8H_2O$ IN DIETHYL ETHER, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 31:24, 3859-3862, DOI: 10.1081/SCC-100108237

To link to this article: http://dx.doi.org/10.1081/SCC-100108237

SYNTHETIC COMMUNICATIONS, 31(24), 3859–3862 (2001)

HIGHLY SELECTIVE OXIDATION OF PRIMARY AND SECONDARY BENZYLIC ALCOHOLS BY $KMnO_4/ZrOCl_2 \cdot 8H_2O$ IN DIETHYL ETHER

Habib Firouzabadi,* Mahmood Fakoorpour, and Hassan Hazarkhani

Department of Chemistry, College of Sciences,
Shiraz University, Shiraz 71454, Iran

ABSTRACT

Zirconyl chloride octahydrate-potassium permanganate is used for highly selective and efficient oxidation of primary and secondary benzylic alcohols to the corresponding carbonyl compounds under mild condition. Over-oxidation of aldehydes to carboxylic acids and damage to carbon–carbon double bond is not observed by this method.

Potassium permanganate has long been used as an oxidant for a variety of organic functional groups,[1,2] either in aqueous or non-aqueous media. Nevertheless, potassium permanganate has found relatively little application in the oxidation of alcohols to aldehydes and ketones, especially for the oxidation of primary alcohols to aldehydes. Precautions, in such cases, must be taken that aldehyde is not further oxidized to the carboxylic acid.

*Corresponding author. Fax: Int. (071) 20027; E-mail: firouzabadi@chem.susc.ac.ir

One way to halt oxidation is by distillation of the aldehyde as it is formed.[3] In order to control the oxidation power of MnO_4^- anion, modifications have been devised and reported.[1,4–6]

Heterogeneous oxidation of unsaturated primary and secondary alcohols by permanganate mixed with solid support, such as copper sulfate pentahydrate is reported. By this procedure, primary alcohols are converted to their carboxylic acids in high yields.[7] Solid sodium permanganate monohydrate has also been used for the oxidation of primary alcohols to their carboxylic acids.[8]

Now, we wish to report that zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$) is a suitable support for the highly selective and high yield oxidation of benzylic, aryl allylic alcohols by $KMnO_4$ in diethyl ether at room temperature (Table, Scheme 1).

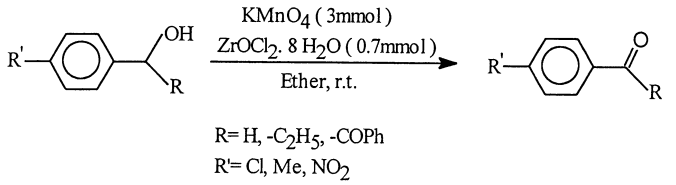
Oxidation of primary and secondary benzylic alcohols in the presence of saturated ones, shows high selectivity of the presented method. We have shown this selectivity in a single molecule bearing benzylic and saturated hydroxyl functional groups (Scheme 2). Vicinal diols, benzylic silyl and THP ethers remain unreacted in the presence of $KMnO_4/ZrOCl_2 \cdot 8H_2O$. Water of hydration of zirconyl chloride plays a crucial role in the activity of the solid support. We have observed that when $ZrOCl_2 \cdot 8H_2O$ was left in an oven at 140°C overnight the rate of the reaction dropped drastically.

Table. Oxidation of Alcohols by $KMnO_4/ZrOCl_2 \cdot H_2O$ in Et_2O at Room Temperature

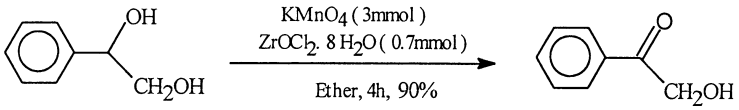
Alcohol	Oxidant/ Promoter[a] Ratio	Time (h)	Product	Yield (%)
$PhCH_2OH$	2–3/0.7	3.5	PhCHO[b]	95
4-H_3C-C_6H_4-CH_2OH	2–3/0.7	3.5	4-CH_3-C_6H_4-CHO	93
4-H_3CO-C_6H_4-CH_2OH	2–3/0.7	3	4-CH_3O-C_6H_4-CHO	94
4-Cl-C_6H_4-CH_2OH	2–3/0.7	3.5	4-Cl-C_6H_4-CHO	94
4-Br-C_6H_4-CH_2OH	2–3/0.7	3.5	4-Br-C_6H_4-CHO	92
4-$HOCH_2$-C_6H_4-CH_2OH	3–4/0.7	5.5	4-OHC-C_6H_4-CHO	90
9-Hydroxymethyl anthracene	2–3/0.7	6	9-Anthraldehyde	85
$PhCH(OH)CH_2CH_3$	3–4/0.7	4.5	$PhCOCH_2CH_3$	95
PhCH(OH)Ph	3–4/0.7	4.5	PhCOPh	94
PhCH(OH)COPh	2–3/0.7	6	PhCOCOPh	91
$PhCH{=}CHCH_2OH$	3–4/0.7	12	PhCH=CHCHO	90
PhCH=CHCH(OH)Ph	2–3/0.7	6	PhCH=CHCOPh	92

[a]Oxidant/promoter ratio per one mmol of substrate. [b]Benzaldehyde was isolated as its 2,4-dinitrophenylhydrazine derivative.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016



Scheme 1.



Scheme 2.

This observation is in agreement with that reported for oxidation by $KMnO_4/CuSO_4 \cdot 5H_2O$.[7]

In conclusion, in this investigation we have presented a new method for the highly efficient and selective oxidation of benzylic alcohols with $KMnO_4$ in diethyl ether.

EXPERIMENTAL

General Procedure. To a solution of alcohol (10 mmol) in Et_2O (25 mL) was added $KMnO_4/ZrOCl_2 \cdot 8H_2O$ (20–30 mmol/0.7 mmol). The resulting mixture was stirred at room temperature for the appropriate reaction time (monitored by TLC, table). After completion of the reaction, the reaction mixture was filtered through a silica-gel pad and the filter cake was further washed with Et_2O (2×10 mL). The ethereal solutions were combined together and evaporated to give the desired product in good to excellent yield (table). Further purification was accomplished by column chromatography packed with silica gel with the appropriate solvent.

ACKNOWLEDGMENTS

The authors are grateful to National Research Council of I.R. for grant No. 464 and Shiraz University Research Council for the partial support of this work.

REFERENCES

1. Fatiadi, A.J. Synthesis **1987**, 85.
2. a) Hudlicky, M. *Oxidation in Organic Chemistry*, American Chemical Society, Washington, DC, 1990, b) Augustine, R.L.; Dekker, M. *Oxidation*, New York, 1969.
3. Vogel, A.R., *Vogel's Textbook of Practical Organic Chemistry*, 5th ed., Longman Scientific and Technical, 1989.
4. Firouzabadi, H.; Vessal, B.; Naderi, M. Tetrahedron Lett. **1982**, 1847.
5. Firouzabadi, H.; Sardarian, A.R.; Naderi, M.; Vessal, B. Tetrahedron **1984**, *40*, 500.
6. Firouzabadi, H.; Mottaghinejad, E.; Seddighi, M. Synthesis **1989**, 378.
7. Noureldin, N.A.; Lee, D.J. J. Org. Chem. **1982**, *47*, 2790.
8. Menger, F.M.; Lee, C. Tetrahedron Lett. **1981**, 1655.

Received in the Netherlands February 10, 2001