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HIGHLY SELECTIVE OXIDATION OF PRIMARY AND SECONDARY BENZYLIC ALCOHOLS BY $\text{KMnO}_4/\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ IN DIETHYL ETHER

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HIGHLY SELECTIVE OXIDATION OF PRIMARY AND SECONDARY BENZYLIC ALCOHOLS BY $\text{KMnO}_4/\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ IN DIETHYL ETHER

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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.

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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 ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$) 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).

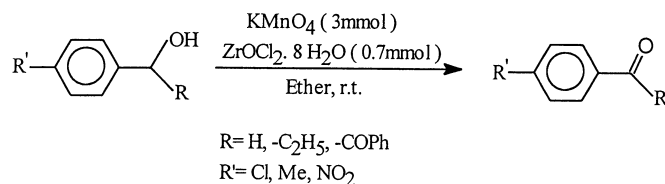
Oxidation of primary and secondary benzylic alcohols in the presence of saturated ones, shows high selectivity of the presented method. We have shown this selectivity in a single molecule bearing benzylic and saturated hydroxyl functional groups (Scheme 2). Vicinal diols, benzylic silyl and THP ethers remain unreacted in the presence of $\text{KMnO}_4/\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$. Water of hydration of zirconyl chloride plays a crucial role in the activity of the solid support. We have observed that when $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ was left in an oven at 140°C overnight the rate of the reaction dropped drastically.

Table. Oxidation of Alcohols by $\text{KMnO}_4/\text{ZrOCl}_2 \cdot \text{H}_2\text{O}$ in Et_2O at Room Temperature

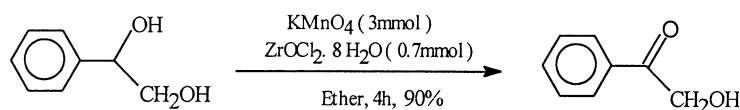
Alcohol	Oxidant/ Promoter ^a Ratio	Time (h)	Product	Yield (%)
PhCH_2OH	2-3/0.7	3.5	PhCHO^b	95
$4\text{-H}_3\text{C-C}_6\text{H}_4\text{-CH}_2\text{OH}$	2-3/0.7	3.5	$4\text{-CH}_3\text{-C}_6\text{H}_4\text{-CHO}$	93
$4\text{-H}_3\text{CO-C}_6\text{H}_4\text{-CH}_2\text{OH}$	2-3/0.7	3	$4\text{-CH}_3\text{O-C}_6\text{H}_4\text{-CHO}$	94
$4\text{-Cl-C}_6\text{H}_4\text{-CH}_2\text{OH}$	2-3/0.7	3.5	$4\text{-Cl-C}_6\text{H}_4\text{-CHO}$	94
$4\text{-Br-C}_6\text{H}_4\text{-CH}_2\text{OH}$	2-3/0.7	3.5	$4\text{-Br-C}_6\text{H}_4\text{-CHO}$	92
$4\text{-HOCH}_2\text{-C}_6\text{H}_4\text{-CH}_2\text{OH}$	3-4/0.7	5.5	$4\text{-OHC-C}_6\text{H}_4\text{-CHO}$	90
9-Hydroxymethyl anthracene	2-3/0.7	6	9-Anthraldehyde	85
$\text{PhCH(OH)CH}_2\text{CH}_3$	3-4/0.7	4.5	$\text{PhCOCH}_2\text{CH}_3$	95
PhCH(OH)Ph	3-4/0.7	4.5	PhCOPh	94
PhCH(OH)COPh	2-3/0.7	6	PhCOCOPh	91
$\text{PhCH=CHCH}_2\text{OH}$	3-4/0.7	12	PhCH=CHCHO	90
PhCH=CHCH(OH)Ph	2-3/0.7	6	PhCH=CHCOPh	92

^aOxidant/promoter ratio per one mmol of substrate. ^bBenzaldehyde was isolated as its 2,4-dinitrophenylhydrazine derivative.





Scheme 1.



Scheme 2.

This observation is in agreement with that reported for oxidation by KMnO₄/CuSO₄·5H₂O.⁷

In conclusion, in this investigation we have presented a new method for the highly efficient and selective oxidation of benzylic alcohols with KMnO₄ in diethyl ether.

EXPERIMENTAL

General Procedure. To a solution of alcohol (10 mmol) in Et₂O (25 mL) was added KMnO₄/ZrOCl₂·8H₂O (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 Et₂O (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.

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