Oxidation of Alcohols by Zinc manganate

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Summary: Zinc manganate has been found to be a convenient reagent for the oxidation of primary and secondary alcohols to the corresponding carbonyl compounds, and also the oxidation of allylic alcohols to the isomerically pure products in good yields.

Several oxidizing agent have been developed\textsuperscript{1-6}; in this paper, we report a new oxidizing agent, zinc manganate, for the oxidation of alcohols to the corresponding carbonyl compounds.

Reagent handling is very easy and doesn't need special treatment for its activation. On the basis of results obtained so far, this reagent obviously qualifies as an important addition to the present methodology\textsuperscript{1-6}. 
Preparation of zinc manganate, ZnMnO₄, readily available and stable compound, was done by treatment of solutions of potassium permanganate with zinc chloride in the presence of potassium iodide at 80°C for twenty minutes⁷.

Zinc manganate has been found to be a convenient reagent for the oxidation of primary and secondary alcohols to the corresponding carbonyl compounds. The reaction proceeded quite well at room temperature in dichloromethane (Table 1).

**Table 1: Oxidation of primary and secondary alcohols.**

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>Product</th>
<th>time(h)</th>
<th>yield*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃(CH₂)₄CH₂OH</td>
<td>CH₃(CH₂)₄CHO</td>
<td>72</td>
<td>75</td>
</tr>
<tr>
<td>HC = CCH₂OH</td>
<td>HC = CCHO</td>
<td>24</td>
<td>78</td>
</tr>
</tbody>
</table>

* Products were characterized by comparison with authentic samples (i.r. spectrum, n.m.r. spectrum, and glpc, ov1 glass column).

In addition, zinc manganate has been found to be a convenient reagent for the oxidation of allylic alcohols to the isomerically pure products in good yields. It was found that yields of α,β-unsaturated aldehydes from their corresponding allylic alcohols in the presence of zinc
manganate are typically equal or greater than manganese dioxide \(^8\) (Table 2).

\[
\begin{align*}
\text{R}^1_1 \text{C} &= \text{C} \quad \text{ZnMnO}_4 \quad \text{CH}_2\text{Cl}_2 / R.T. \\
\text{R}^2_2 \text{CH}_3 \text{OH} & \quad \text{C} \quad \text{CHO}
\end{align*}
\]

Table 2: Oxidation of allylic alcohols.

<table>
<thead>
<tr>
<th>R(^1)</th>
<th>R(^2)</th>
<th>Time (h)</th>
<th>Yield %</th>
<th>E : Z*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(_3)</td>
<td>CH(_3)CH(_2)</td>
<td>24</td>
<td>81</td>
<td>100:0</td>
</tr>
<tr>
<td>CH(_3)CH(_2)</td>
<td>CH(_3)</td>
<td>24</td>
<td>80</td>
<td>0:100</td>
</tr>
<tr>
<td>CH(_3)</td>
<td>H</td>
<td>24</td>
<td>82</td>
<td>0:100</td>
</tr>
</tbody>
</table>

* The isomeric ratio was determined by glpc (glass capillary column, SE-54, 30 m).

Experimental

PREPARATION OF ZINC MANGANATE:

Separate solutions of potassium permanganate (1 mole), zinc chloride (1 mole), sodium hydroxide (1 mole) and potassium iodide (0.12 mole) were prepared in distilled water and added together. The reaction mixture was stirred while being heated for 20 minutes; it was then filtered with suction, and the solid material was washed until the color of permanganate was not observed in the filtrate. The resulting dark brown crystals were dried in a desiccator (CaCl\(_2\)) for 24 hours, and were dried by azeotropic removal of water with dry benzene. It was then filtered with suction, and solid dry zinc manganate was collected and stored.
PREPARATION OF (E)-3-METHYL-2-PENTENAL

To a magnetically stirred solution of 0.60 g (6 mmol) of (E)-3-methyl-2-penten-1-ol in 45 ml of dichloromethane, 6.64 g (36 mmol) of dry powdered zinc manganese was added at room temperature. The reaction mixture was stirred for 24 h and then filtered. The filter cake was washed with dichloromethane. Filtrate and washings were combined and brought to dryness. The residue was chromatographed: elution from silica gel with 30% dichloromethane-70% hexane followed by evaporation of solvents, gave 0.486 g (4.86 mmol, 81% yield) of a colourless product. IR (neat): 1690 (s) and 1635 (m) cm\(^{-1}\); NMR (CDCl\(_3\), internal TMS), \(\delta\): 1.08 (t, J=7.5 Hz, 3 H), 2.17 (s, 3 H), 2.19 (q, J=7.5 Hz, 2 H), 5.83 (d, J=8 Hz, 1 H), and 9.99 ppm (d, J=8 Hz, 1 H); high-resolution MS calculated (m/z) for C\(_6\)H\(_{12}\)O: 100.0889; found: 100.0893.

Similarly, oxidation of (Z)-3-methyl-2-penten-1-ol afforded the corresponding aldehyde in 80% yield: IR(neat) 1985(s) and 1640(m) cm\(^{-1}\); NMR (CDCl\(_3\), internal TMS), \(\delta\): 1.17 (t, J=7.5 Hz, 3 H), 1.97 (s, 3 H), 2.63 (q, J=7.5 Hz, 2 H), 5.83 (d, J=8 Hz, 1 H) and 9.97 ppm (d, J=8 Hz, 1 H); high-resolution MS: calculated (m/z) for C\(_6\)H\(_{12}\)O: 100.0889; found: 100.0869.

Acknowledgements:

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REFERENCES