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Alcohol oxidation

Alcohol oxidation is an important organic reaction.

The indirect oxidation of primary alcohols to carboxylic acids normally proceeds via the corresponding aldehyde, $R-CH_{2}OH \xrightarrow{[O]} R-C'_{H} \xrightarrow{H_{2}O} R-C'_{H} \xrightarrow{OH} [O] \xrightarrow{O} R-C'_{OH}$ primary alcohol aldehyde aldehyde hydrate carboxylic acid

Mechanism of oxidation of primary alcohols to carboxylic acids via aldehydes and aldehyde hydrates

which is transformed via an **aldehyde hydrate** (R-CH(OH)₂) by reaction with water. The oxidation of a primary alcohol at the aldehyde level is possible by performing the reaction in absence of water, so that no aldehyde hydrate can be formed.

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Oxidation to aldehydes

Oxidation of alcohols to aldehydes is partial oxidation; aldehydes are further oxidized to carboxylic acids. Conditions required for making aldehydes are heat and distillation. In aldehyde formation, the temperature of the reaction should be kept above the boiling point of the aldehyde and below the boiling point of the alcohol.

Reagents useful for the transformation of primary alcohols to aldehydes are normally also suitable for the oxidation of secondary alcohols to ketones. These include:

 Chromium-based reagents, such as Collins reagent (CrO₃·Py₂), PDC or PCC.



 [O]= chromium-based reagent, activated DMSO, hypervalent iodide compound, TPAP or TEMPO

R¹= alkyl or aryl substituent R²= hydrogen, alkyl or aryl substituent

Oxidation of alcohols to aldehydes and ketones

- <u>Sulfonium species</u> known as "activated <u>DMSO</u>" which can result from reaction of DMSO with <u>electrophiles</u>, such as <u>oxalyl chloride</u> (Swern oxidation), a <u>carbodiimide</u> (Pfitzner-Moffatt <u>oxidation</u>) or the complex SO₃·Py (Parikh-Doering oxidation).
- Hypervalent iodine compounds, such as <u>Dess-Martin periodinane</u> or <u>2-lodoxybenzoic acid</u>.
- Catalytic <u>TPAP</u> in presence of excess of <u>NMO</u> (Ley oxidation).
- Catalytic <u>TEMPO</u> in presence of excess <u>bleach</u> (NaOCI) (Oxoammonium-catalyzed oxidation).

Catalytic Redox-active copper complex in the presence of oxygen at room temperature.

Allylic and benzylic alcohols can be oxidized in presence of other alcohols using certain selective oxidants such as manganese dioxide (MnO_2) .

Oxidation to ketones

Reagents useful for the oxidation of secondary alcohols to ketones, but normally inefficient for oxidation of primary alcohols to aldehydes, include chromium trioxide (CrO₃) in a mixture of sulfuric acid and acetone (Jones oxidation) and certain ketones, such as cyclohexanone, in the presence of aluminium isopropoxide (Oppenauer oxidation). Another method is oxoammonium-catalyzed oxidation. Additionally, sodium hypochlorite (or household bleach) in acetone has been reported for efficient conversion of secondary alcohols in the presence of primary alcohols (Stevens oxidation).^[2]

Oxidation to carboxylic acids

The direct oxidation of primary alcohols to carboxylic acids can be carried out using

- Potassium permanganate (KMnO₄);
- Jones oxidation;
- PDC in DMF;
- Heyns oxidation;
- Ruthenium tetroxide (RuO₄);
- or TEMPO.

Diol oxidation

Alcohols possessing two hydroxy groups located on adjacent carbons —that is, 1,2-diols— suffer oxidative breakage at a carbon-carbon bond with some oxidants such as sodium periodate (NaIO₄) or lead tetraacetate (Pb(OAc)₄), resulting in generation of two carbonyl groups. The reaction is also known as glycol cleavage.



R= alkyl, aryl or hydrogen

Oxidative breakage of carbon-carbon bond in 1,2-diols

References

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primary alcohol

carboxylic acid

[O]= KMnO₄, Jones oxidation, PDC in DMF, Heyns oxidation, RuO₄ or TEMPO Oxidation of primary alcohols to carboxylic acids

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This page was last edited on 16 August 2020, at 08:55 (UTC).

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