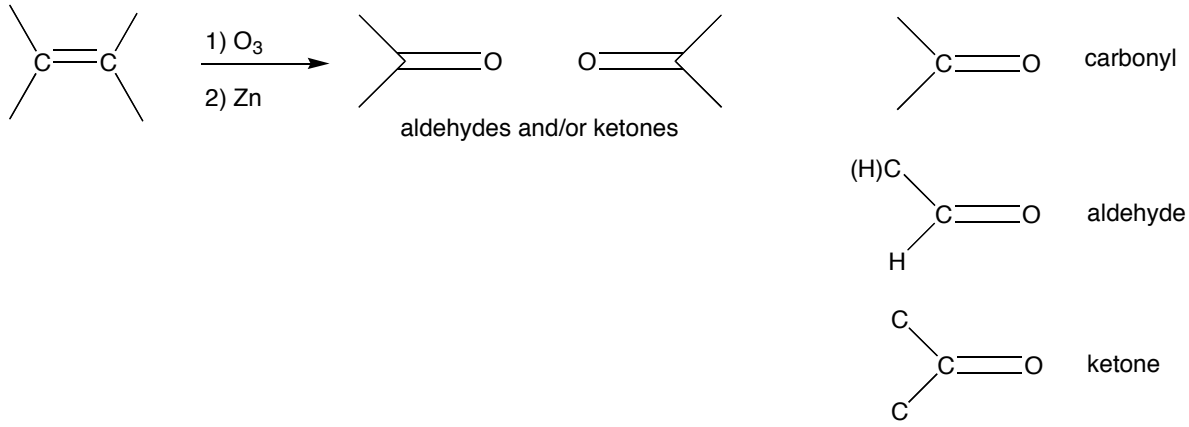
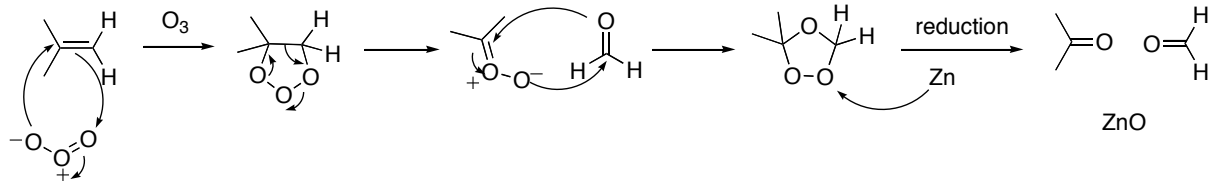
Review: Ozonolysis

Ozone (O_3) – colourless gas, "electrical" smell

General scheme:

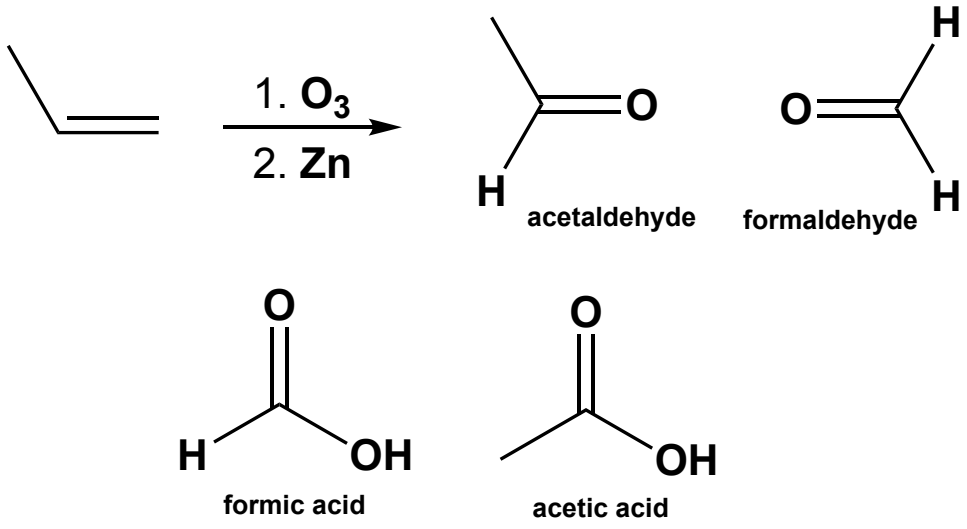


Mechanism:



aside: zinc oxide is commonly found in strong sunscreens

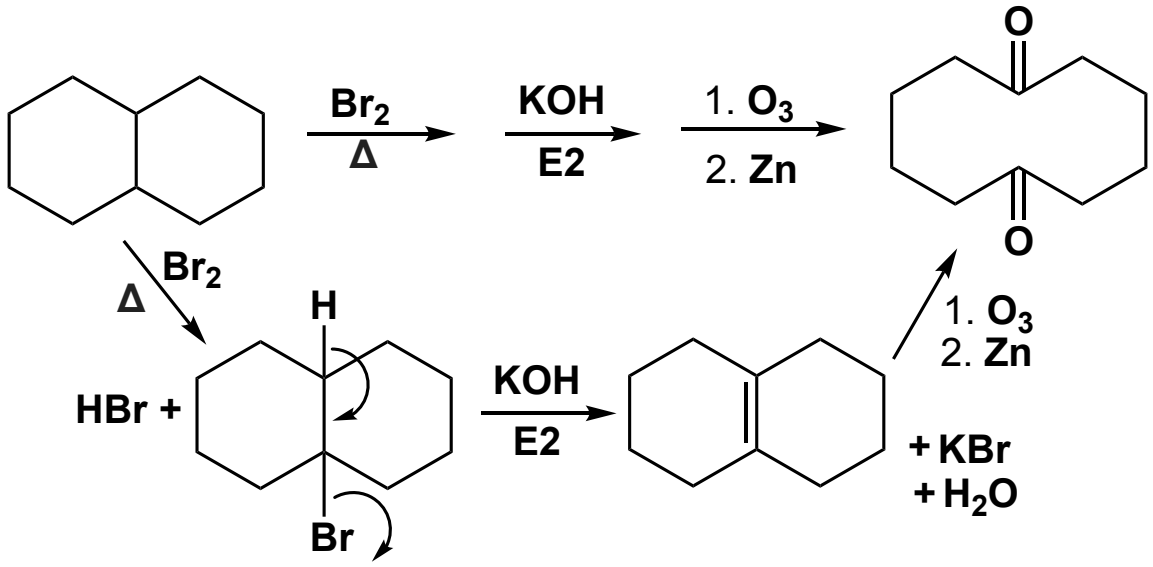
Example 1



formaldehyde – cadaver preservation

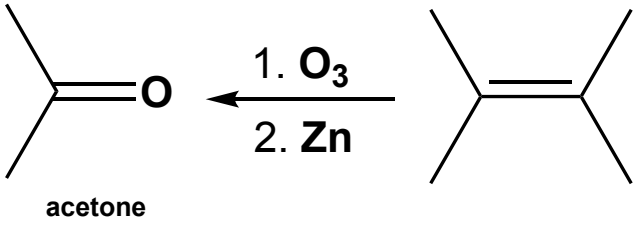
Example 2

question taken from a final examination



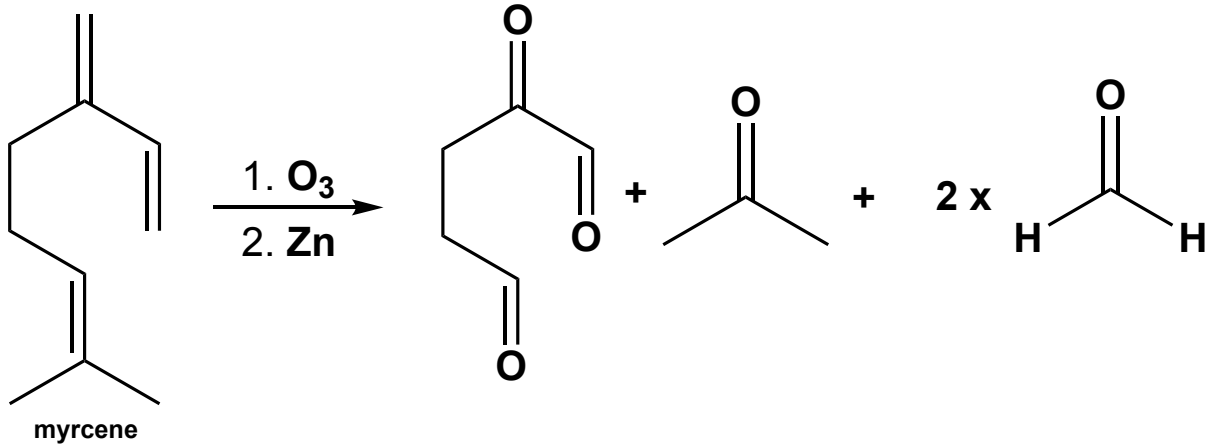
Example 3

If you were given ozonlysis of a molecule to make acetone, how would you make it?



acetone

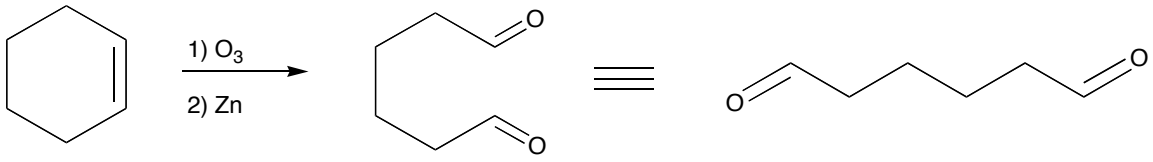
Example 4



myrcene

aside: 2 isoprene units make up myrcene, making this a monoterpene

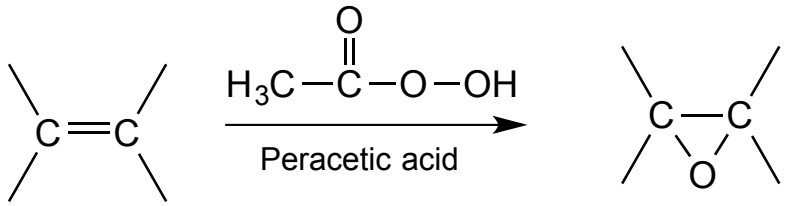
Example 5



Epoxidation

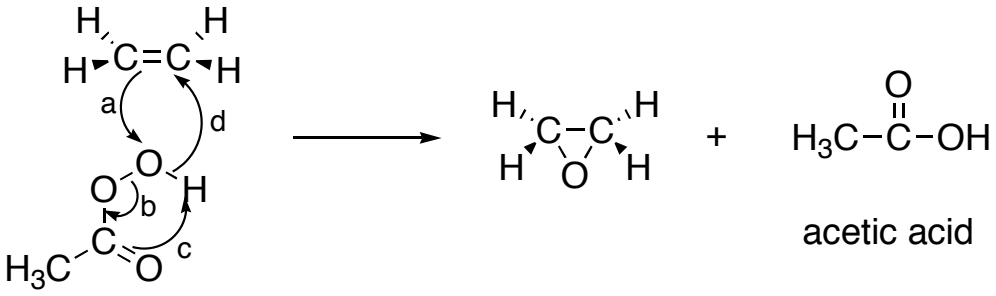
- concerted reaction: all bonds break and form at the same time
- stereospecific: the stereochemistry of the products is determined by the starting material

General scheme



SYN addition

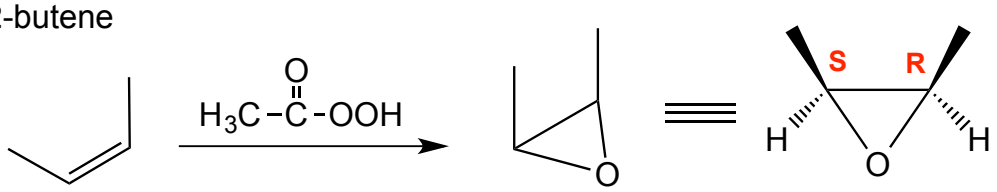
Mechanism:



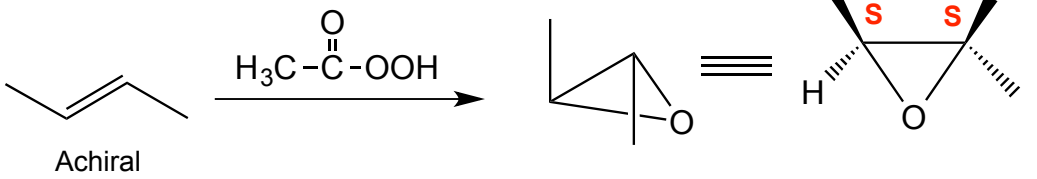
Peracetic acid (epoxidizing reagent) is NOT the same as acetic acid (product of this reaction; also a component of vinegar).

Example 1

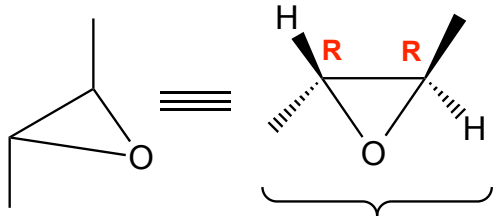
Cis-2-butene



Trans-2-butene



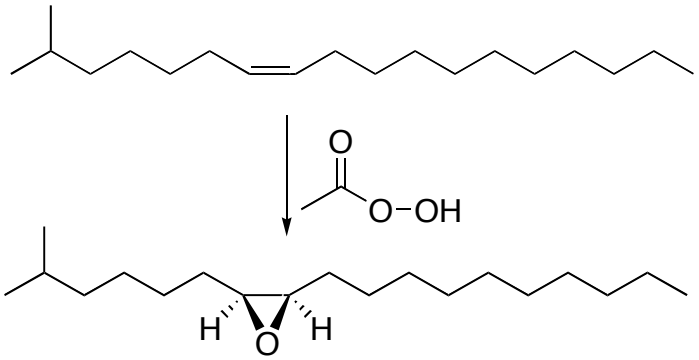
Achiral



Enantiomers
(1:1) Racemic mixture

Cis-2-butene product: a meso compound
Trans-2-butene product: a racemate

Example 2



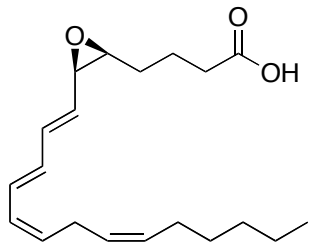
- Done by Adolf Butenandt

Gypsy moth sex pheromone

- The epoxide formed is a compound called disparlure
- Results in 50:50 mixture, but only the one shown is the active pheromone
- Pheromones (pherein horman – to carry excitement), chemical messengers

Do humans produce epoxides? *Yes, we do.*

Example 3



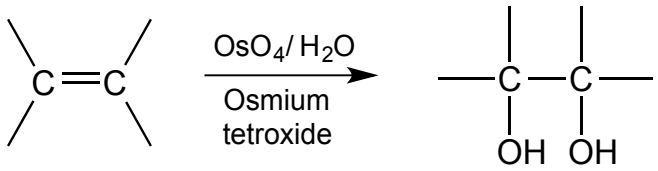
Leukotriene A4 -
- substance (chemical messenger) that mediates anaphylaxis (allergic reaction, asthma)

- First isolated by 2 Swedish scientists using ram testes

Dihydroxylation of Alkenes

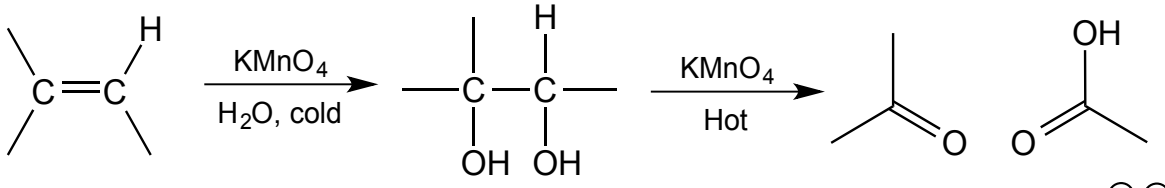
- this is a stereospecific, syn addition
- 2 hydroxyl groups added to the same side of a double bond

General scheme

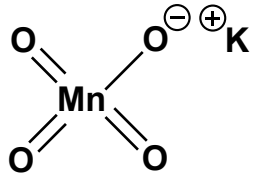


A glycol

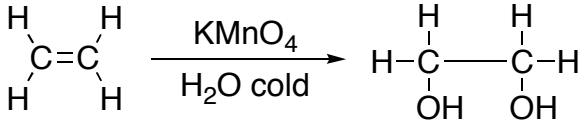
SYN addition
Stereospecific



$KMnO_4$ = Potassium permanganate, strong purple solution in water



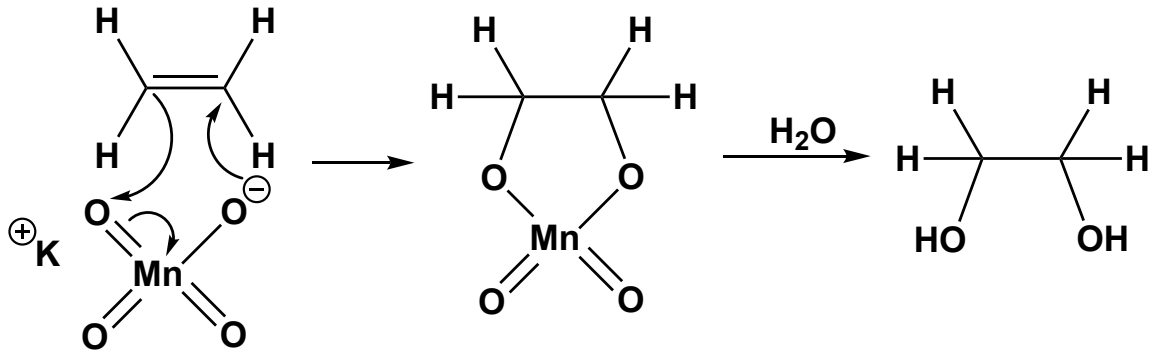
Example 1:



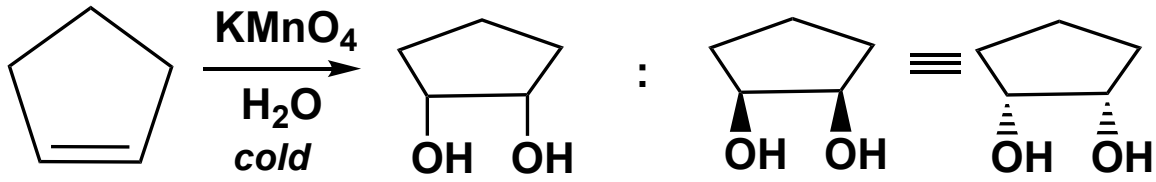
ethylene glycol

- MnO_2 is a side product which is a brown colour and needs to be removed

Mechanism

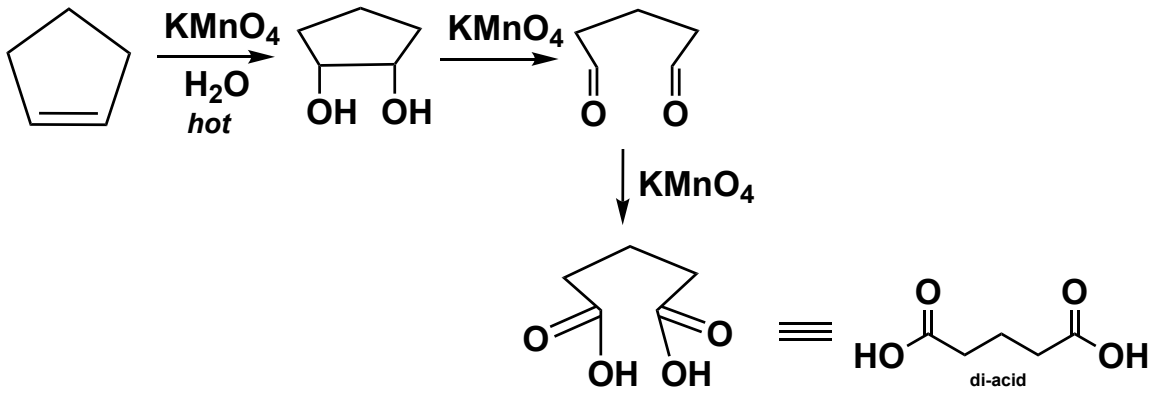


Example 2



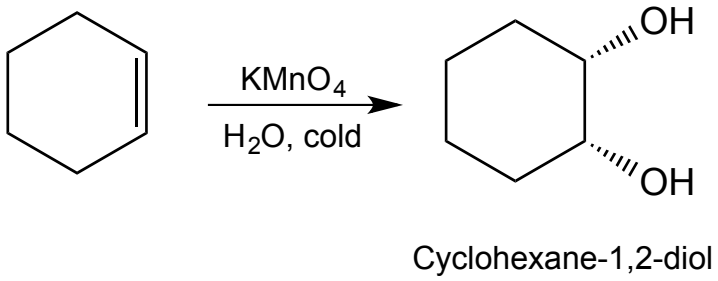
In cold conditions (room temperature or below), the reaction stops at the diol.

Example 3



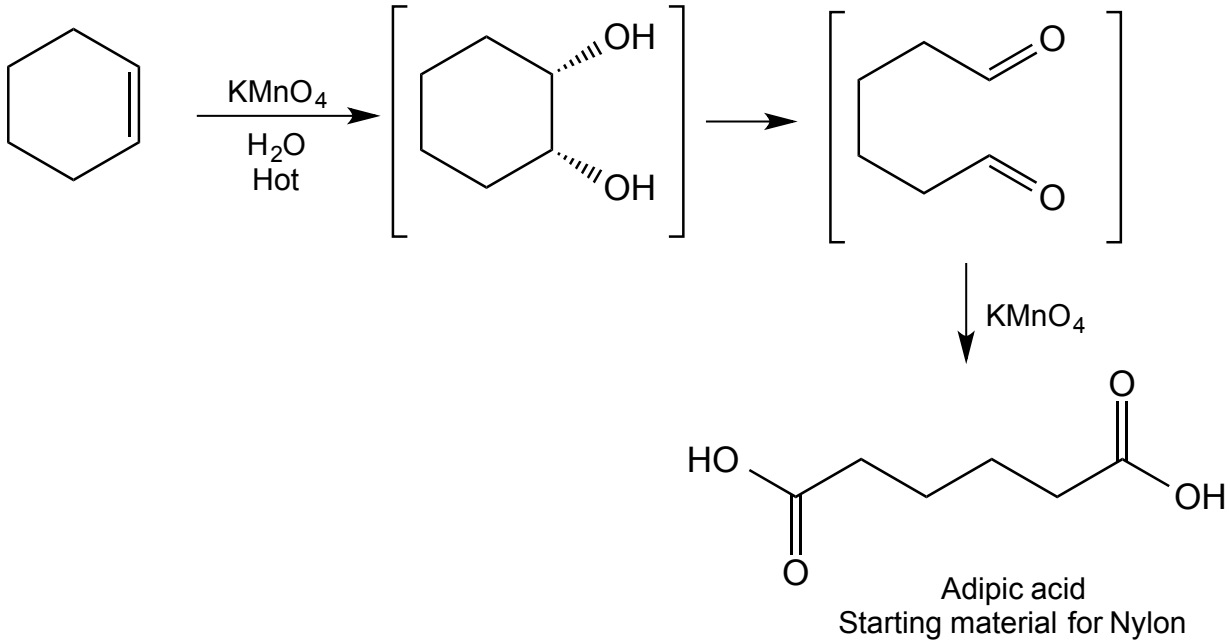
Hot potassium permanganate will not stop oxidation at the diol. It can break C-C bonds to form the corresponding carboxylic acids from the original alkene.

Example 4



Cyclohexane-1,2-diol

Example 5

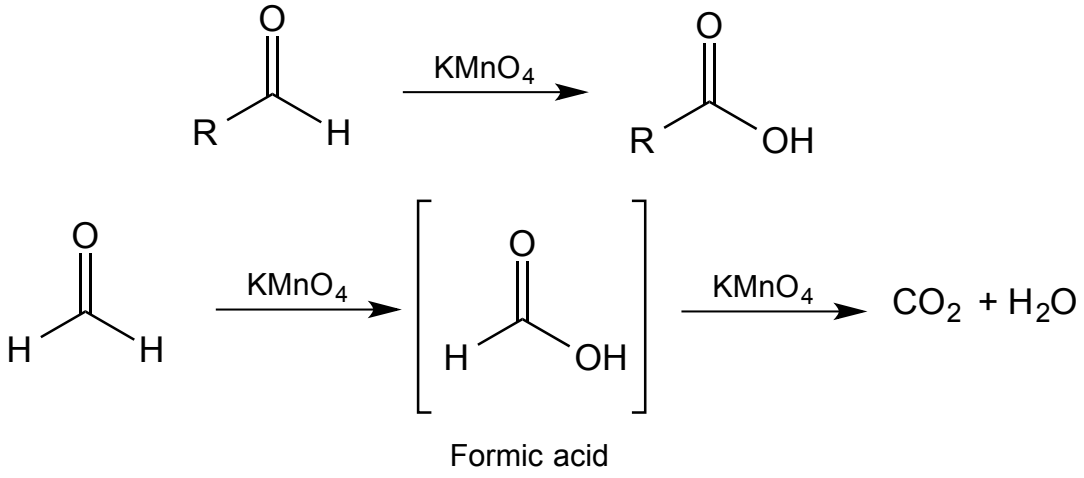


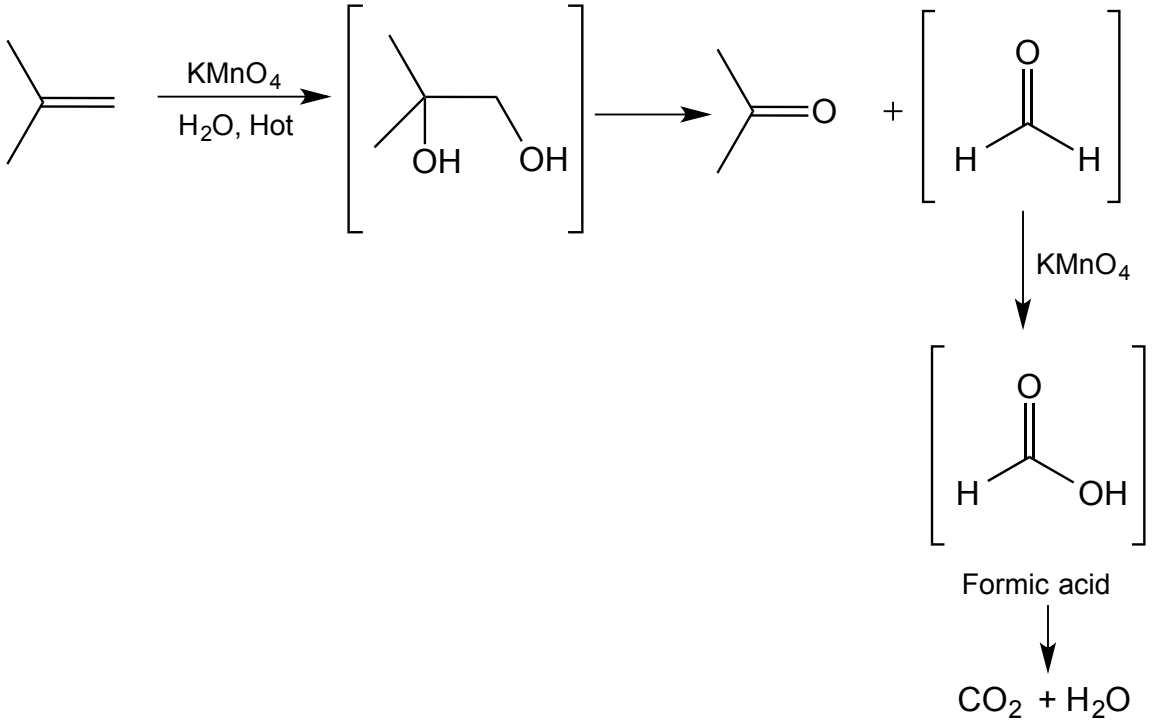
Adipic acid
Starting material for Nylon

Note: if cold, the reaction would stop at the cyclohexane-1,2-diol as in example 4.

Example 6

In $KMnO_4$ aldehydes get oxidized to carboxylic acids, and formaldehyde to H_2O/CO_2





if ketone (carbon on both sides) = the reaction stops here
if aldehyde (carbon on one side, hydrogen on the other) = reaction continues to alcohol
if formaldehyde (hydrogen on both sides) = reaction continues to carbon dioxide & water