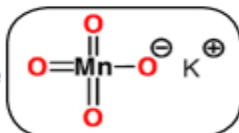


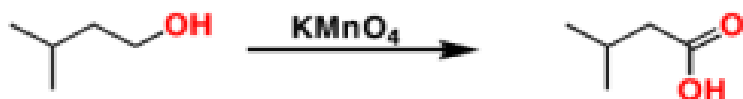
KMnO₄
Potassium permanganate



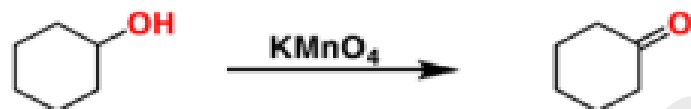
What it's used for: This strong oxidizing agent will oxidize primary alcohols (and aldehydes) to carboxylic acids, secondary alcohols to ketones, form diols from alkenes, and oxidatively cleave carbon-carbon bonds. It will also oxidize C-H bonds adjacent to aromatic rings.

Similar to: K₂Cr₂O₇, OsO₄, O₃

Example 1: Oxidation - conversion of primary alcohols to carboxylic acids



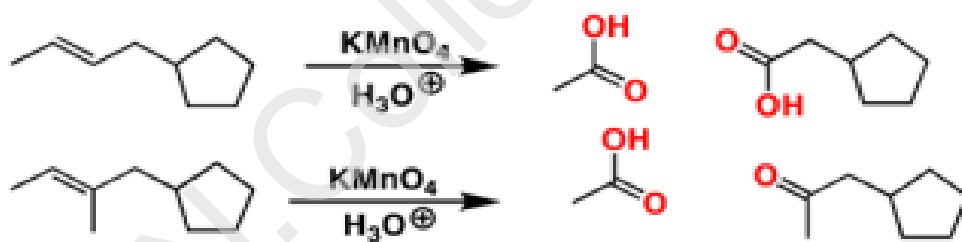
Example 2: Oxidation - conversion of secondary alcohols to ketones



Example 3: Oxidation - conversion of aldehydes to carboxylic acids

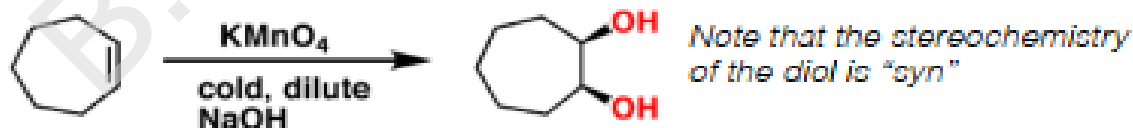


Example 4: Oxidative cleavage - conversion of alkenes to ketones / carboxylic acids

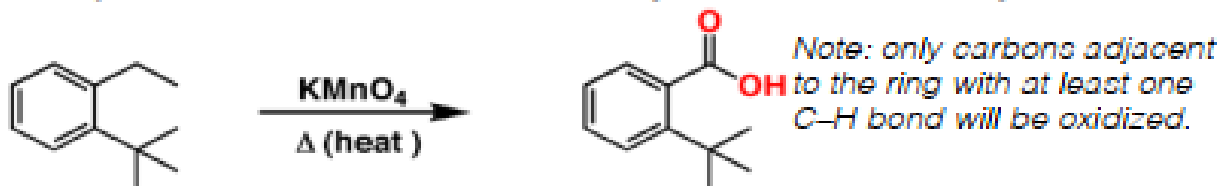


note: ketone

Example 5: Dihydroxylation - conversion of alkenes to vicinal diols

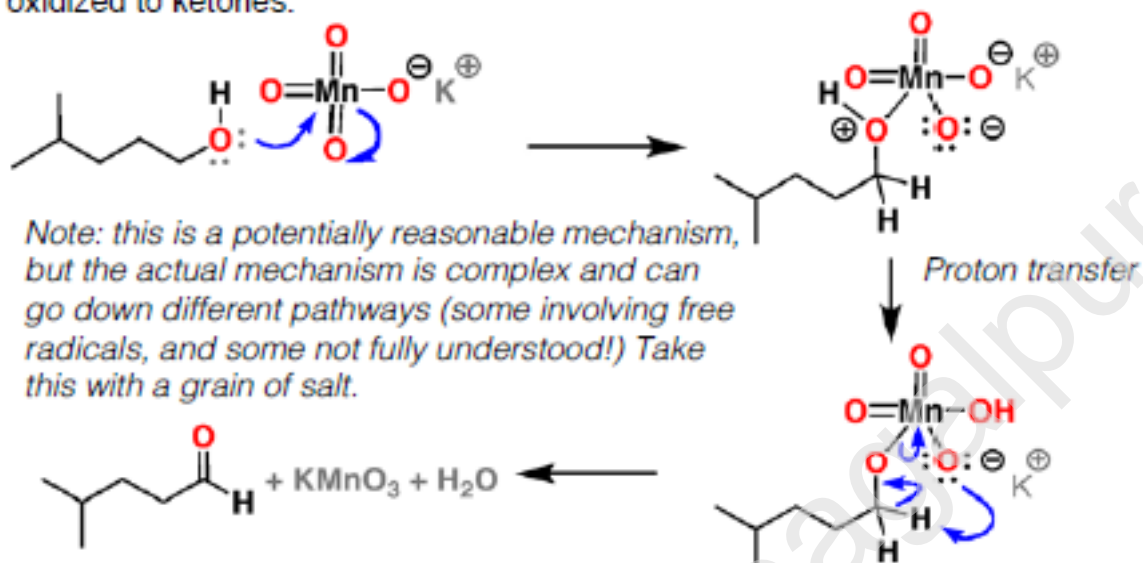


Example 6: Oxidation - conversion of alkylaromatics to carboxylic acids



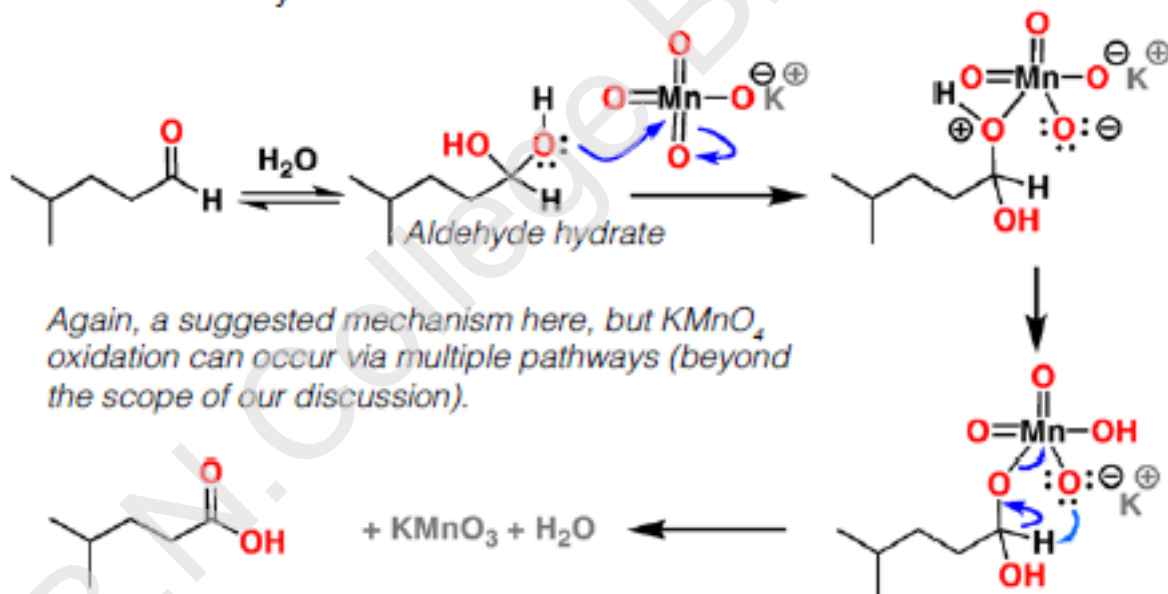
How it works: *Oxidation of primary and secondary alcohols*

Primary alcohols are oxidized to carboxylic acids; secondary alcohols are oxidized to ketones.



Note: this is a potentially reasonable mechanism, but the actual mechanism is complex and can go down different pathways (some involving free radicals, and some not fully understood!) Take this with a grain of salt.

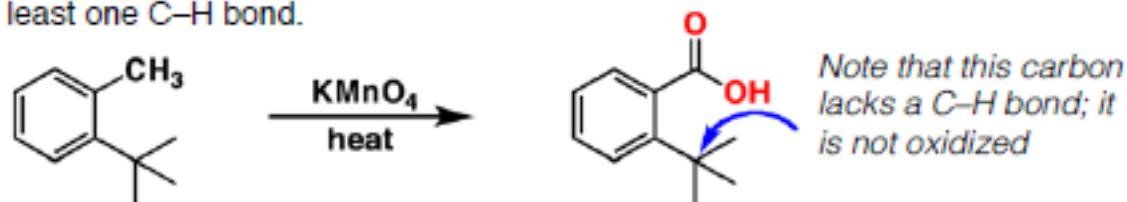
Aldehydes are not stable under these reaction conditions and will be further oxidized to carboxylic acids



Again, a suggested mechanism here, but KMnO_4 oxidation can occur via multiple pathways (beyond the scope of our discussion).

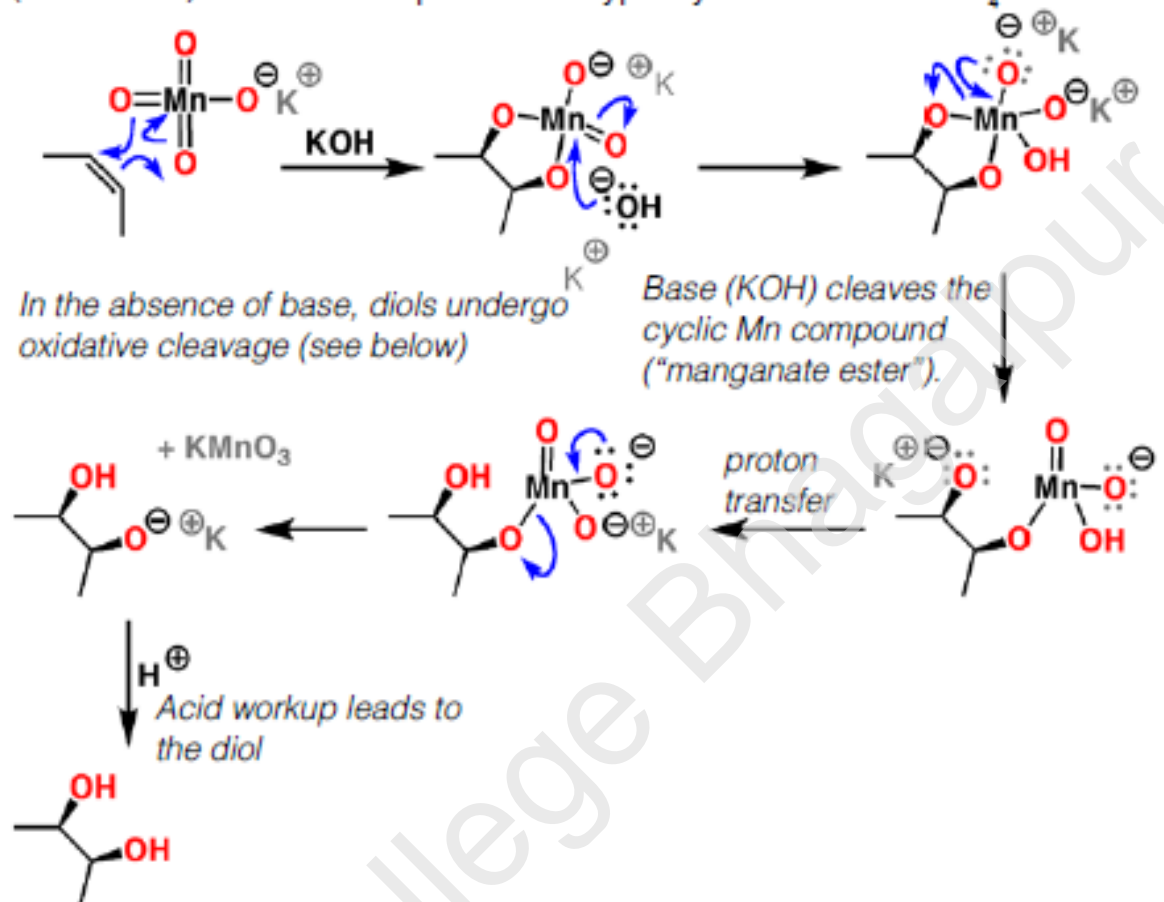
How it works: *Oxidation of aromatic side chains*

The mechanism for side chain oxidation is complex (involves free radicals) and not completely understood. It requires that the carbon adjacent to the arene have at least one C-H bond.



How it works: *Dihydroxylation of alkenes*

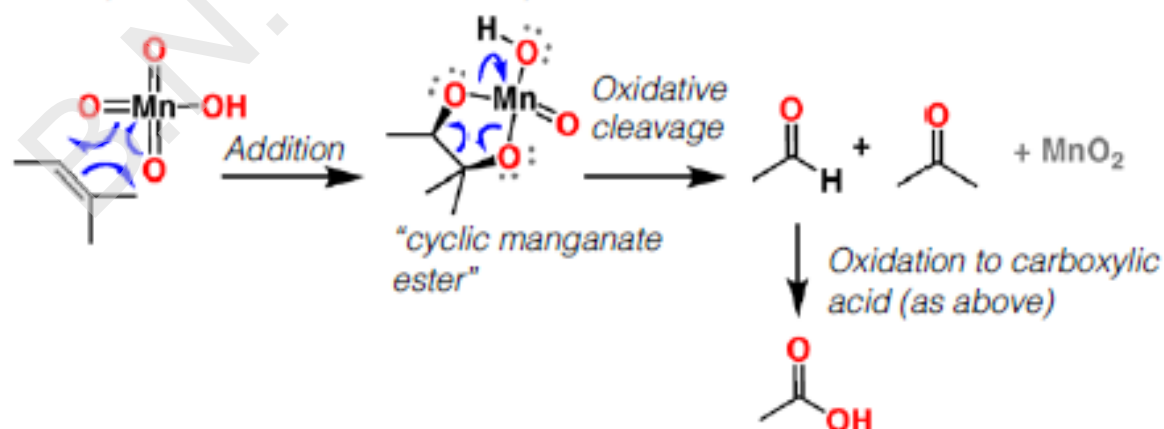
Under cold, dilute basic conditions, KMnO_4 will convert alkenes into 1,2-diols (vicinal diols). Yields for this process are typically lower than for OsO_4 .



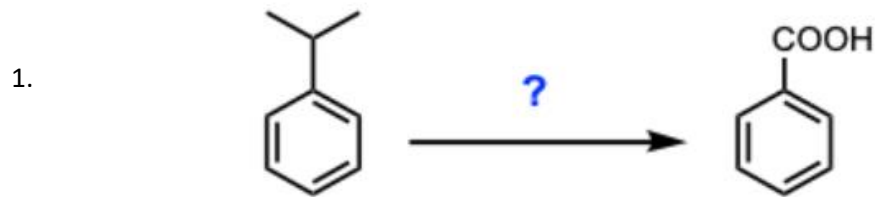
How it works: *Oxidative cleavage of alkenes*

Under acidic conditions vicinal diols undergo oxidative cleavage.

KMnO_4 is protonated to give HMnO_4 and adds to the alkene as above:

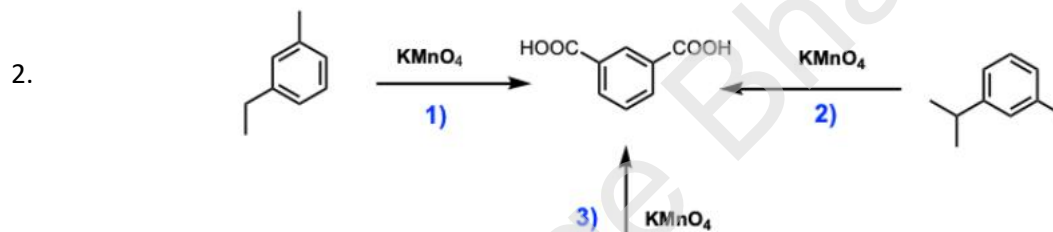


Examples:



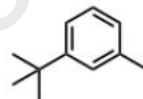
Choose a suitable reagent to carry out this reaction :

- a) NaBH₄
- b) H₂ , Pd-C
- c) KMnO₄
- d) H₂SO₃



Which of the reactions 1) - 3) is correct?

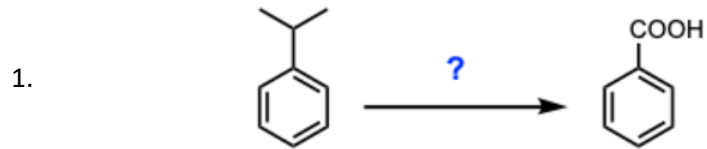
- a) 1)
- b) 2)
- c) 3)
- d) 1) and 2)
- e) all are correct



3. One the isomers outlined in the parentheses (ortho- , meta- and para-) reacted with the excess of KMnO₄ forming compound X which on heating loses one molecule of water giving a product with molecular formula C₈H₄O₃. Determine which isomer was used and the structure of compound X and the final product.

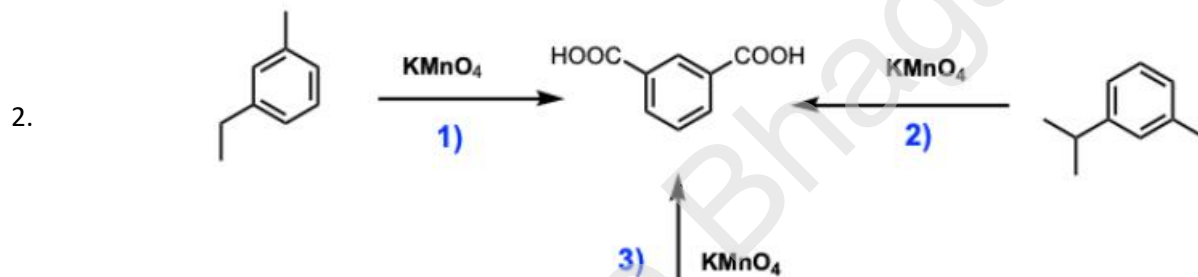


Hints:



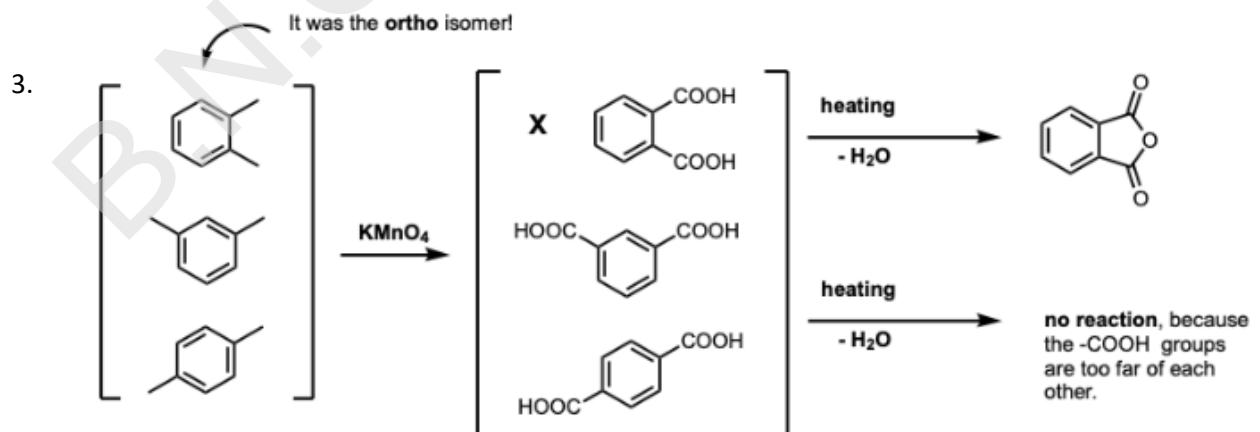
Choose a suitable reagent to carry out this reaction :

- a) NaBH₄
- b) H₂, Pd-C
- c) KMnO₄**
- d) H₂SO₃

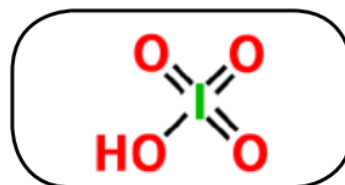


Which of the reactions 1) - 3) is correct?

- a) 1)
- b) 2)
- c) 3)
- d) 1) and 2)**
- e) all are correct



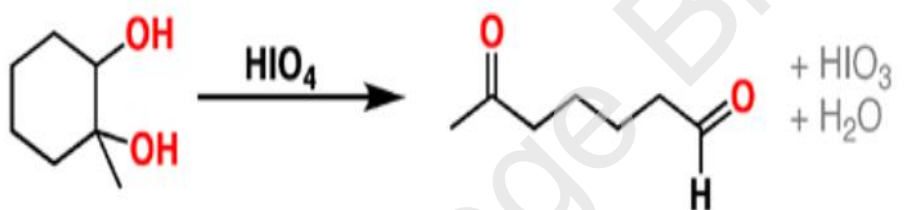
HIO_4 Periodic acid



What it's used for: Periodic acid is a strong oxidizing agent. It is most commonly used for the oxidative cleavage of 1,2-diols (vicinal diols) to give aldehydes and ketones.

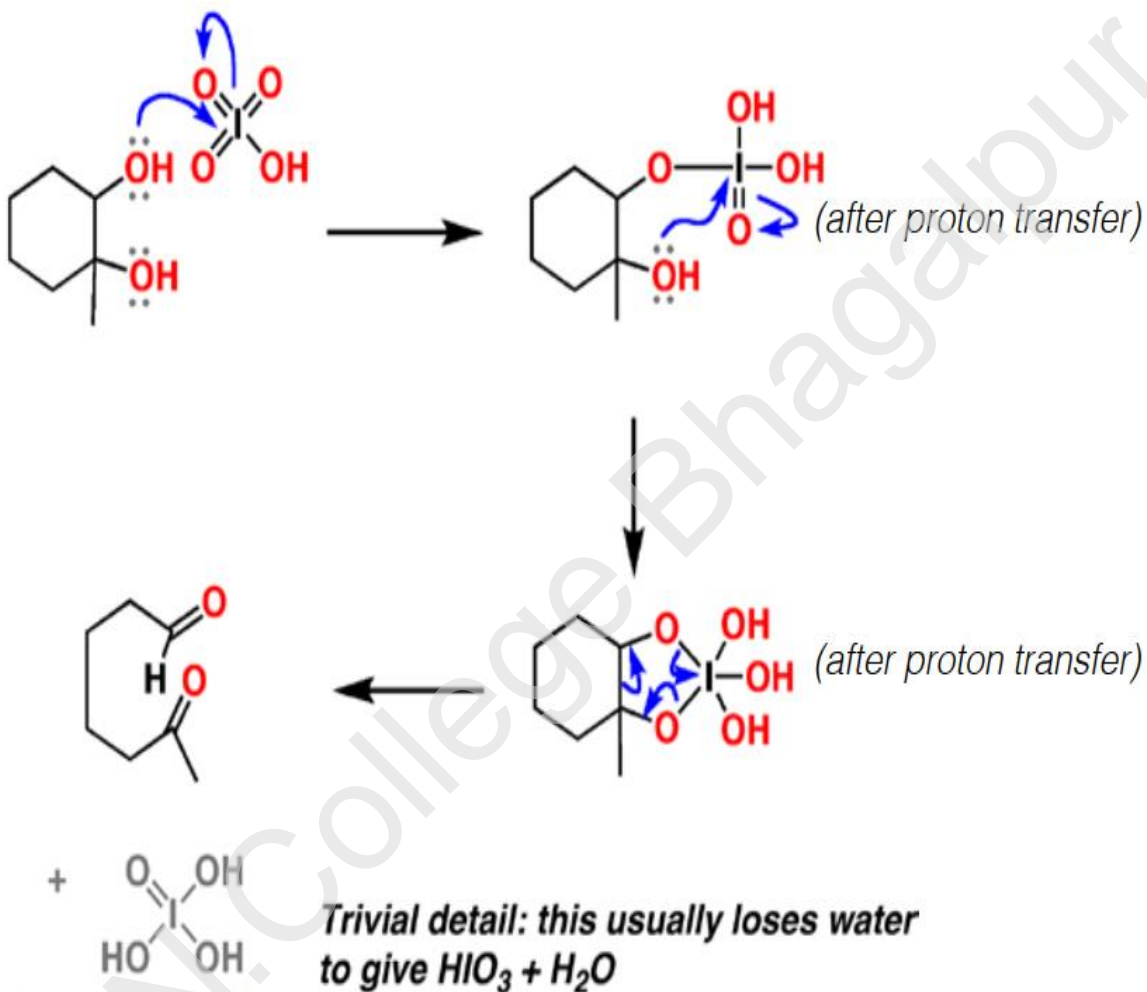
Similar to: Sodium periodate (NaIO_4), Lead (IV) acetate [$\text{Pb}(\text{OAc})_4$]

Example 1: Cleavage of diols to give aldehydes/ketones



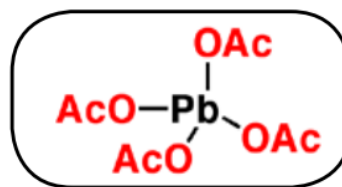
How it works: *Cleavage of diols to give aldehydes/ketones*

Periodic acid is a strong oxidizing agent. Similar to $\text{Pb}(\text{OAc})_4$, it can cleave 1,2-diols (vicinal diols) to give the corresponding aldehydes or ketones.



Notice how iodine starts in the (VII) oxidation state and goes to (V) (it has been reduced)

Pb(OAc)₄
Lead tetraacetate

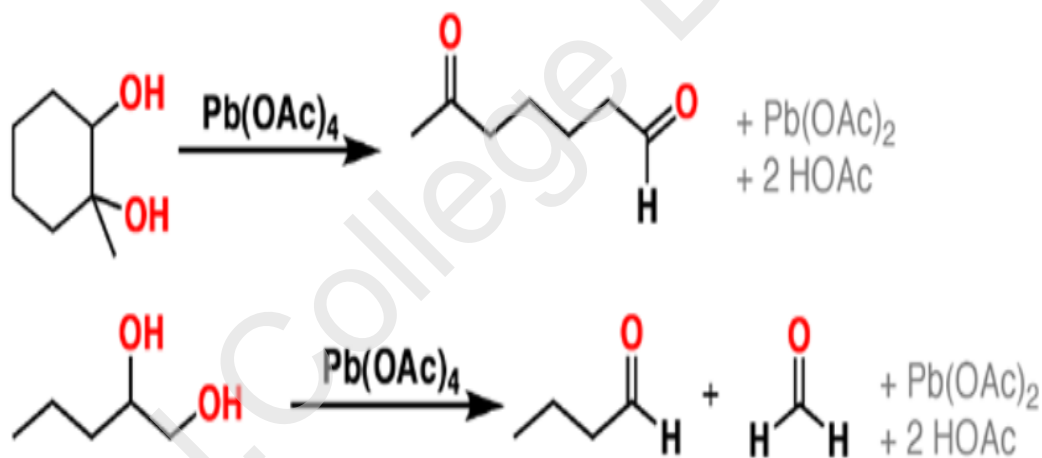


Also known as: Lead (IV) acetate

What it's used for: Lead tetraacetate will cleave 1,2-diols (vicinal diols) into aldehydes/ketones, similar to NaIO₄ and HIO₄.

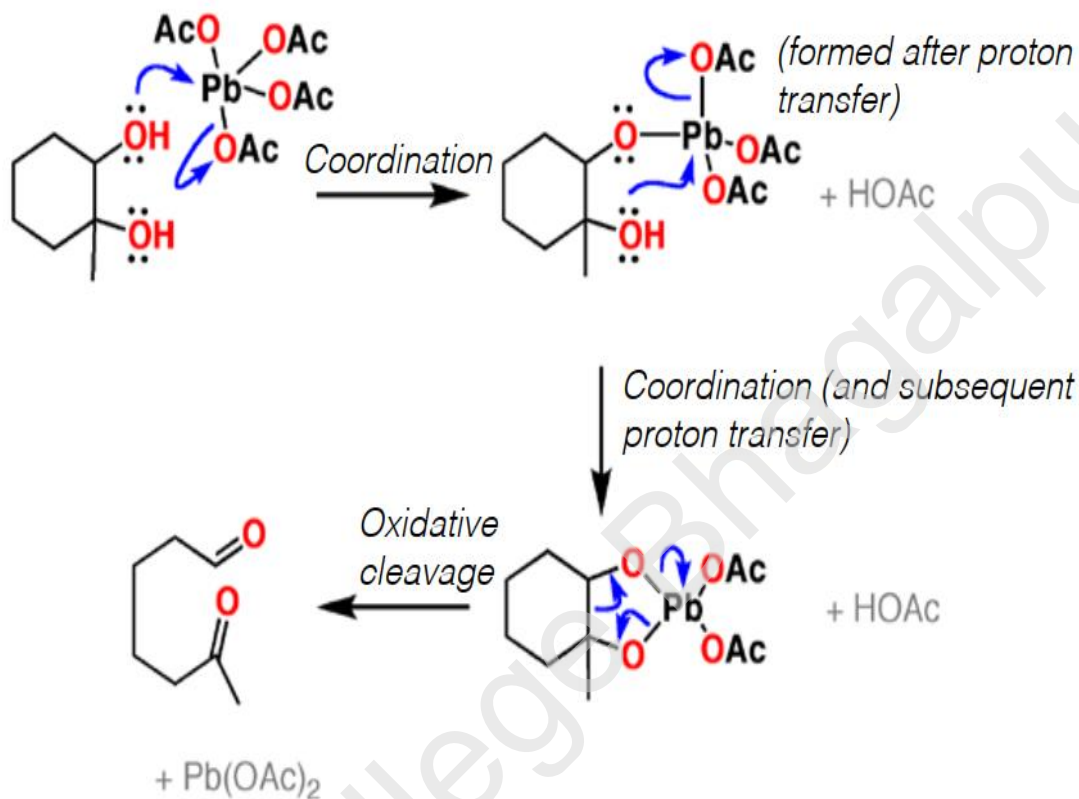
Similar to: Sodium periodate (NaIO₄), periodic acid (HIO₄).

Example 1: Oxidative cleavage - conversion of diols to aldehydes / ketones.



How it works: *Cleavage of diols to aldehydes/ketones*

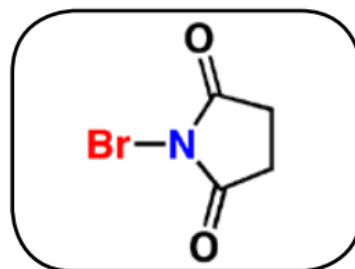
Lead (IV) acetate is an oxidizing agent. It works by coordinating to the 1,2-diol and then breaking the carbon-carbon bond in a cyclic mechanism:



Note that Pb(IV) has been reduced to Pb(II). The acetate groups are liberated as acetic acid.

NBS

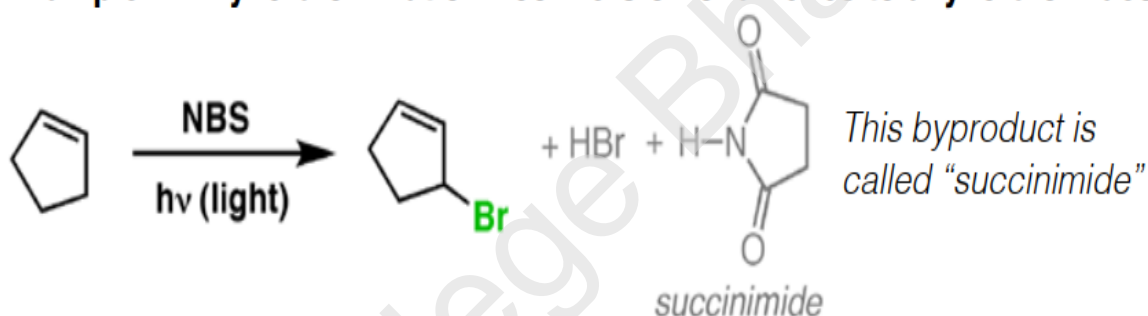
N-Bromosuccinimide



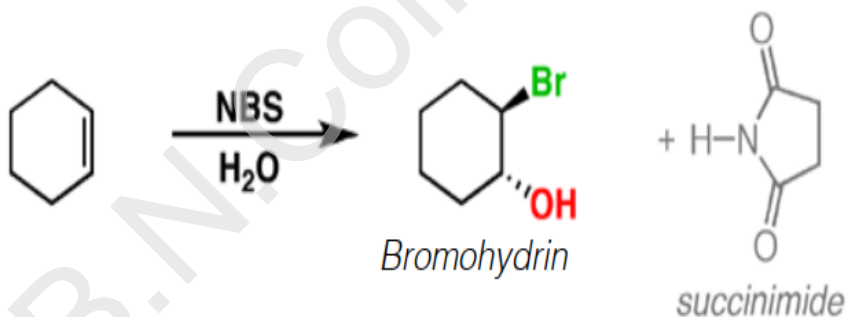
What it's used for: NBS is a source of reactive, electrophilic bromine. It is often used for allylic bromination and in formation of halohydrins from alkenes. Since it is a crystalline solid it is more convenient to use than liquid elemental Br_2 .

Similar to: Br_2 , NCS (N-chlorosuccinimide), NIS (N-iodosuccinimide)

Example 1: Allylic bromination - conversion of alkenes to allylic bromides



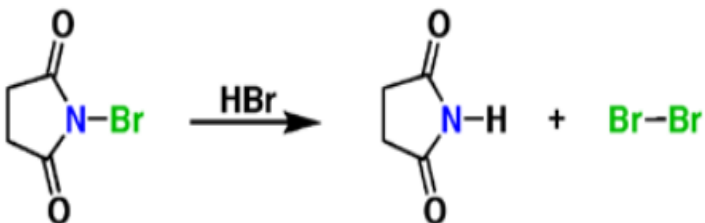
Example 2: Conversion of alkenes to bromohydrins



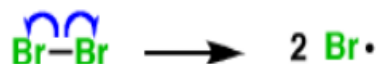
How it works: *Allylic bromination*

NBS provides a constant, low concentration of Br_2 , which is formed when HBr (from propagation step 1) reacts with NBS. This is useful because the low concentration of Br_2 prevents dibromination of the double bond from occurring.

Generation of Br_2



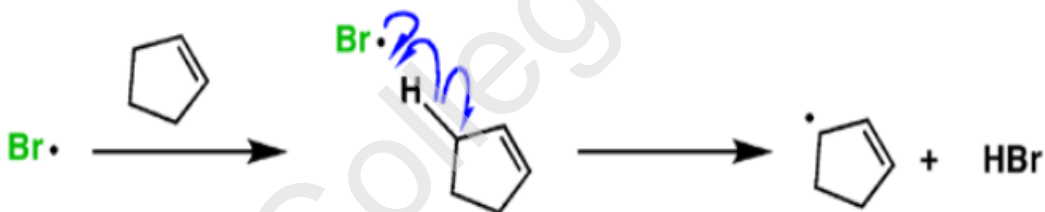
Initiation step



When bromine is heated or treated with light, homolytic cleavage of the $\text{Br}-\text{Br}$ bond results in the formation of two bromine radicals.

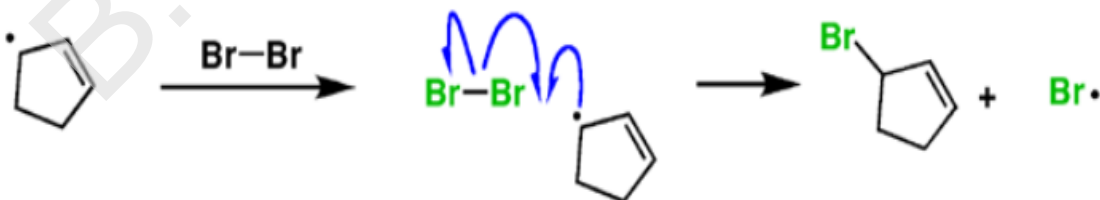
Propagation step 1

In the first propagation step, the bromine radical removes a hydrogen from the allylic carbon, giving a resonance-stabilized free radical.



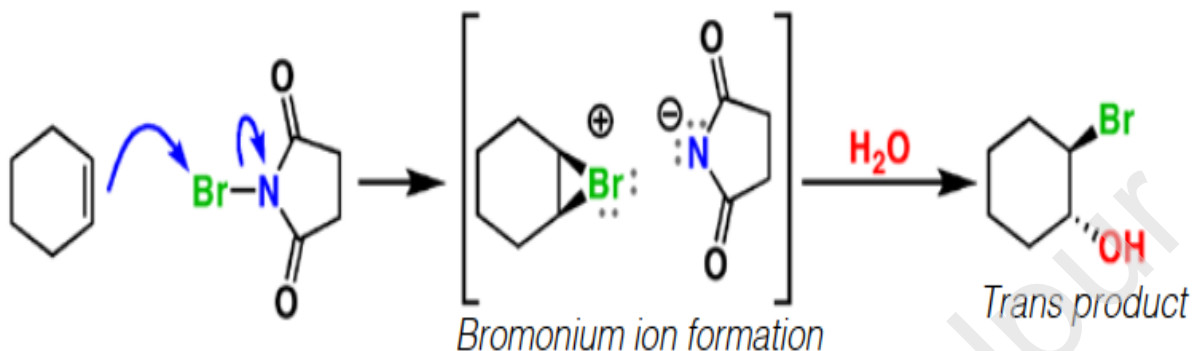
Propagation step 2

In the second propagation step, the allylic radical reacts with Br_2 , giving the allylic bromide and regenerating a new Br radical. This continues the catalytic cycle.

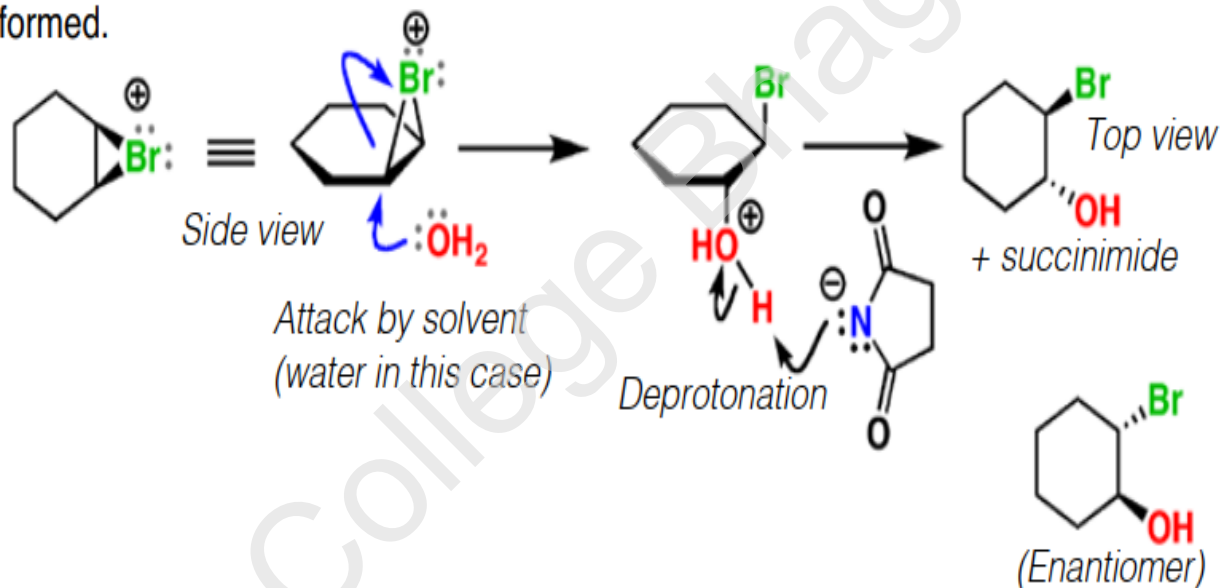


How it works: *Halohydrin formation*

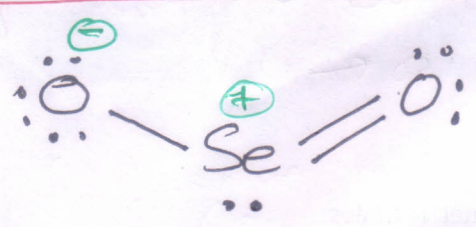
As with Br_2 , alkenes treated with NBS will form bromonium ions:



The trans product is formed exclusively due to attack of nucleophile on the face opposite the bromonium ion. Note - in this case a 1:1 mixture of enantiomers is formed.

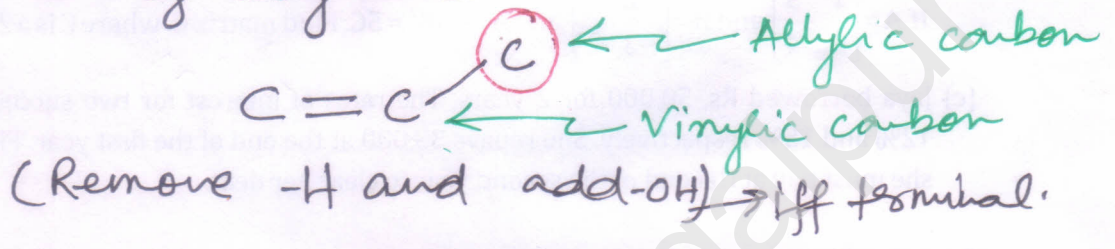


Selenium Dioxide SeO₂



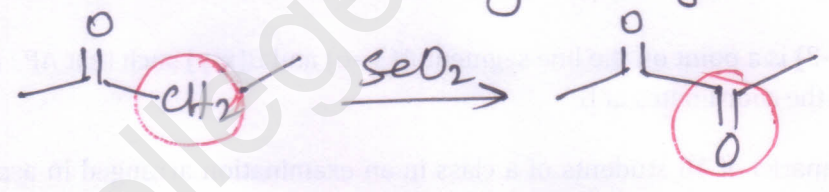
→ Selenium dioxide is an important oxidising agent.

→ Oxidation of allylic carbon

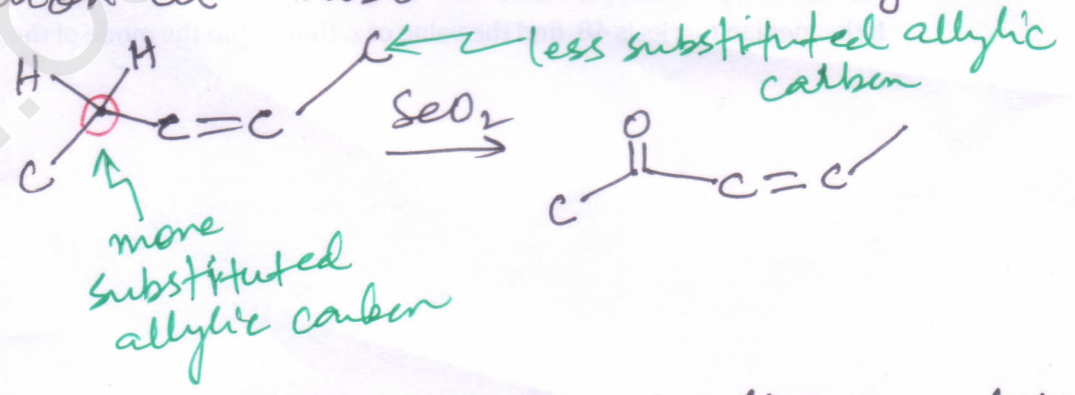


→ Oxidation of active methylene group.
(having acidic H)

generally -CH₂ group attached to carbonyl groups are active methylene group.



→ Oxidation at most substituted allylic carbon.



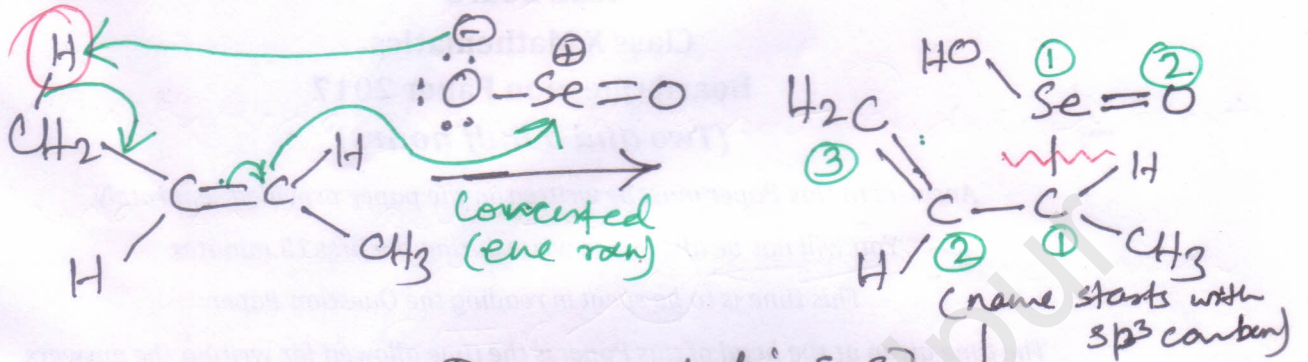
→ Oxidation with E-selectivity (trans product → major)

→ Oxidation inside the ring will be preferred.

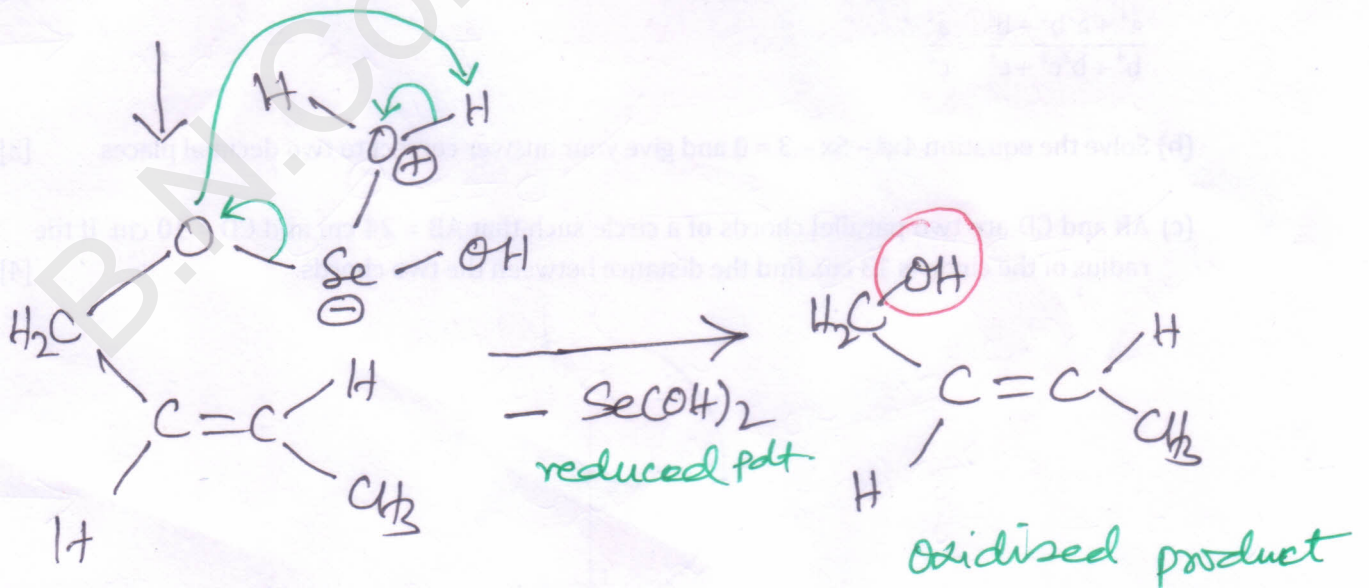
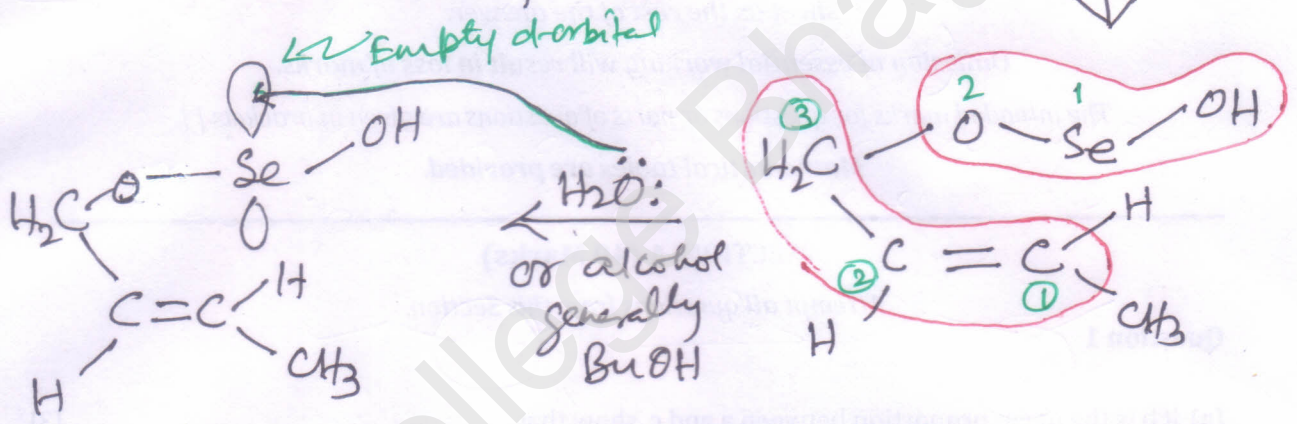
→ If two double bonds are there, ~~more~~ allylic carbon corresponding to e⁻ rich alkene will ^{get} oxidised.

Mechanism: (out of the syllabus)

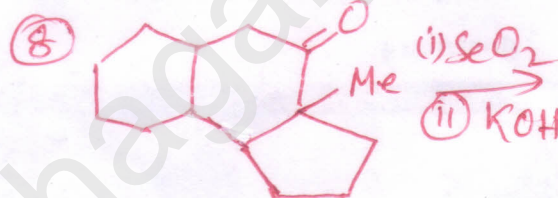
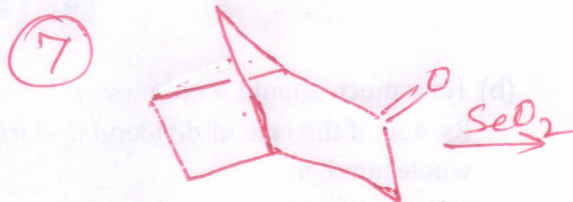
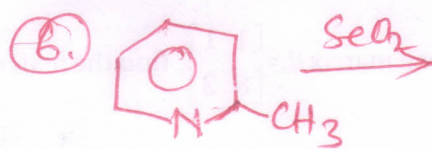
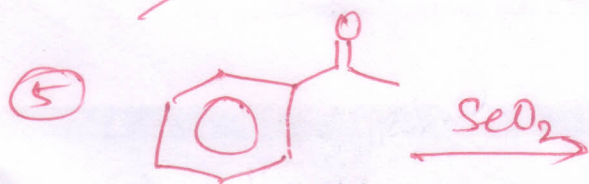
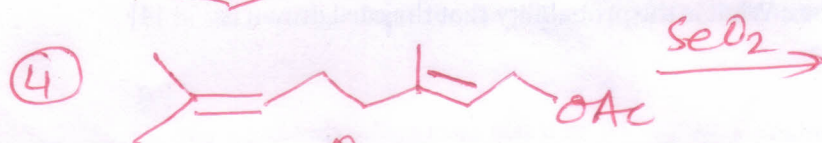
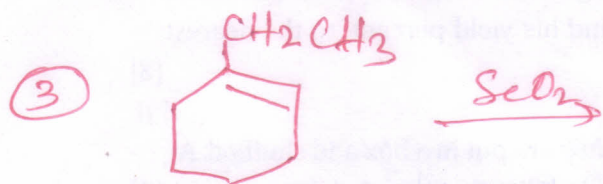
→ Ene reaction followed by [2,3] sigmatropic reaction.



In sigmatropic [2,3], we break bond b/w 1 & 2 and forms a bond b/w 2 & 3



Questions



B.N.College Bhagalpur