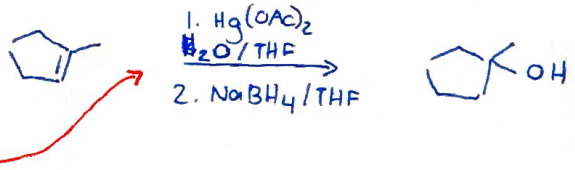
Alkene Reactions II

Last time: carbon-halogen bonds

Today: synthesis of alcohols

Oxymercuration - demercuration

Summary:



- Markovnikov orientation
- Anti addition
- ~100% yields
- No rearrangements ☺
- Also works with ROH instead of H_2O

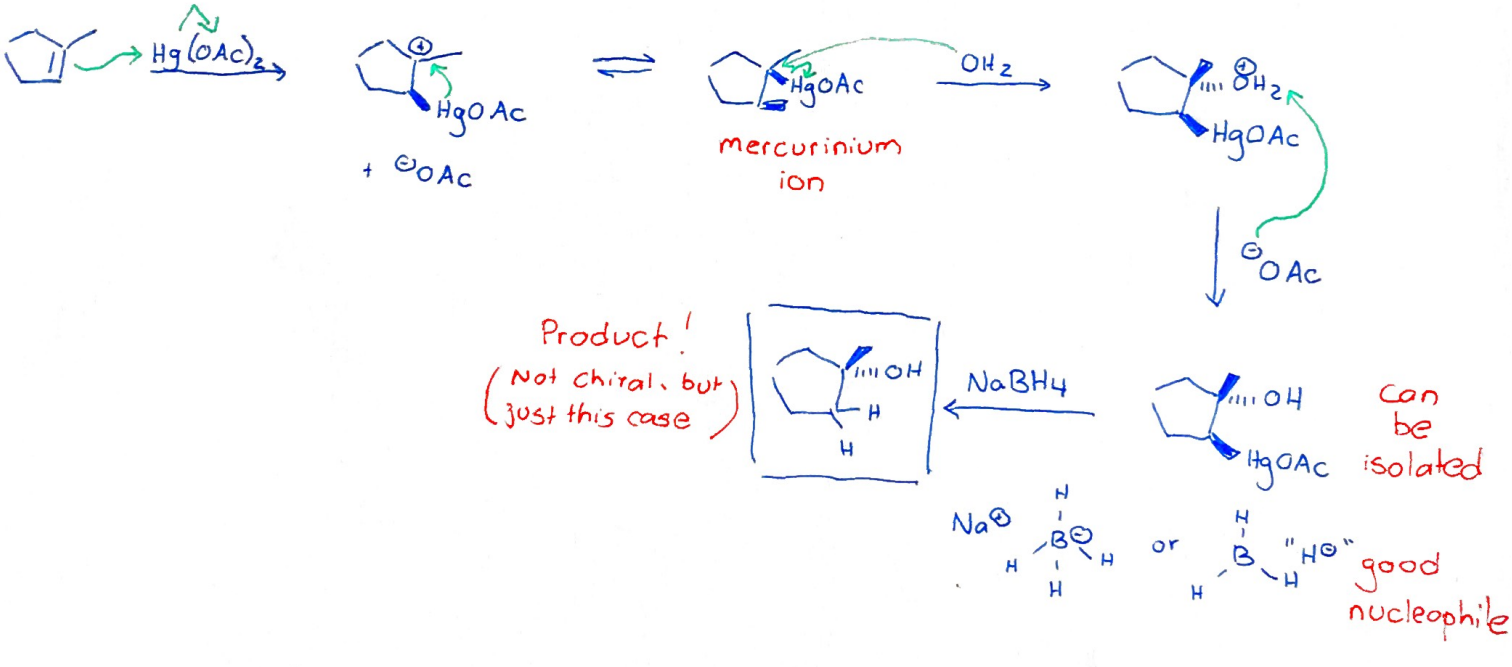
This notation means two rxns were carried out

THF = Tetrahydrofuran ≡  used as solvent

$Hg(OAc)_2$ is electrophilic

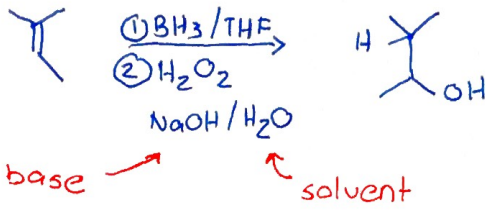
$^{\ominus}OAc$ = acetate ≡  ∴ $Hg^{2+}(^{\ominus}OAc)_2$

How does this happen? Know for exam!



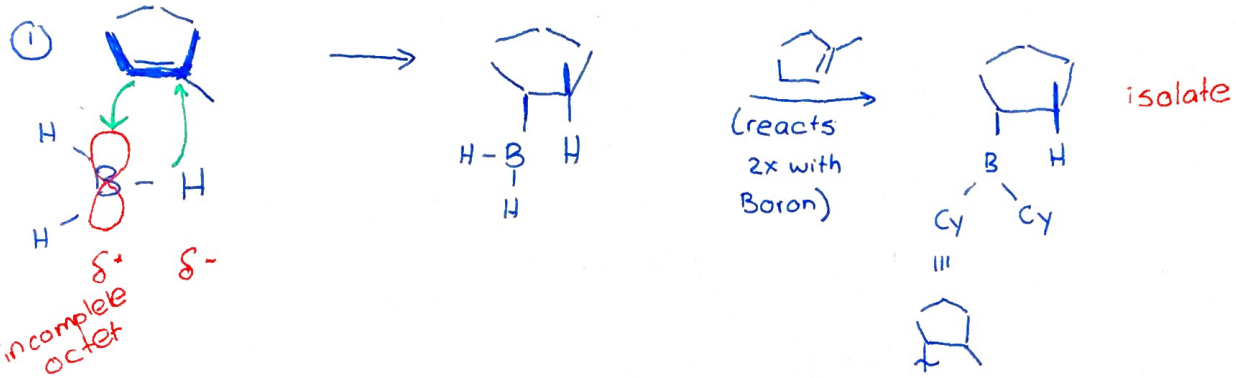
Hydroboration - Oxidation

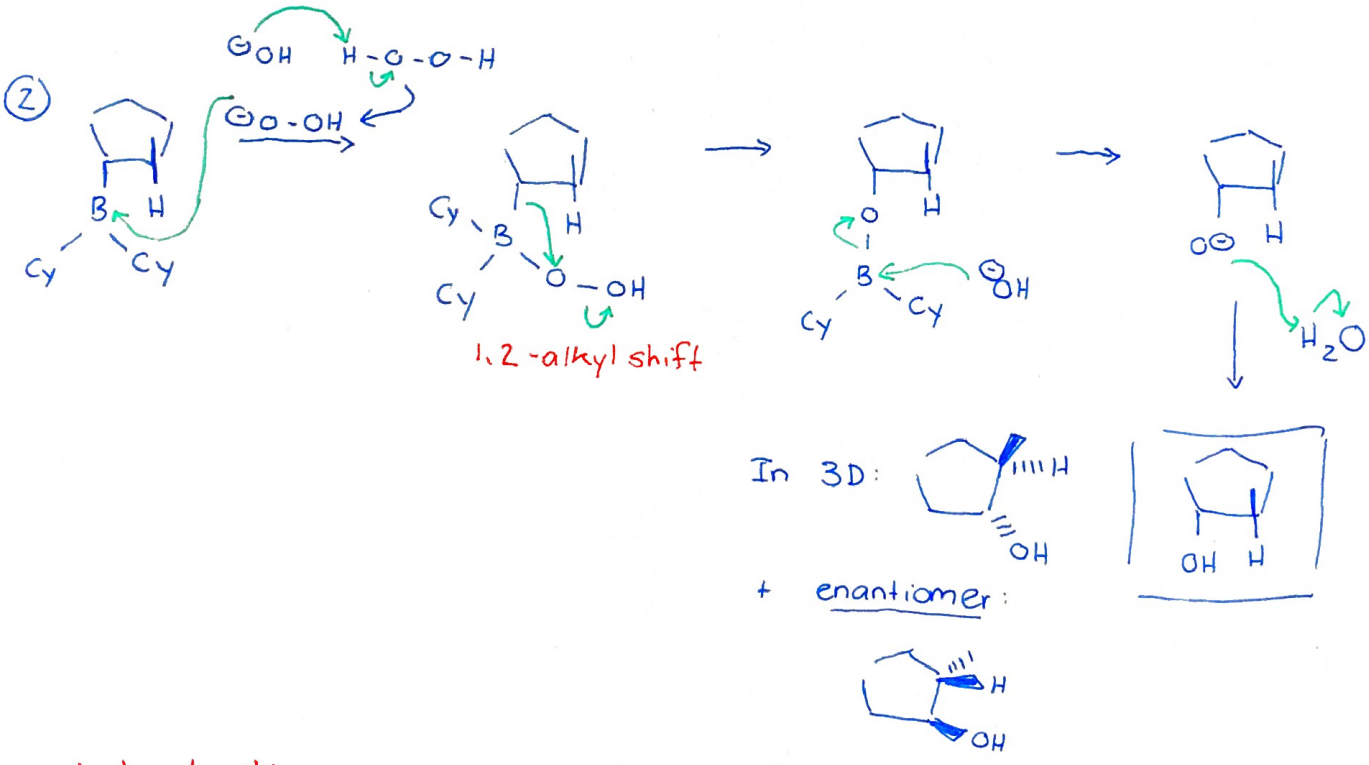
Summary:



- Anti-Markovnikov orientation **
- No rearrangements ☺
- syn addition

How? Use  as an example again.

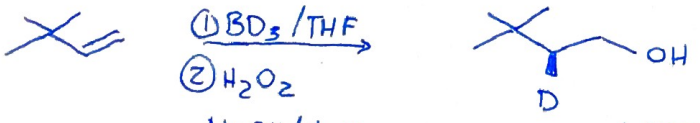
① 

② 

In 3D:

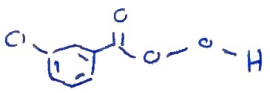
+ enantiomer:

What about:



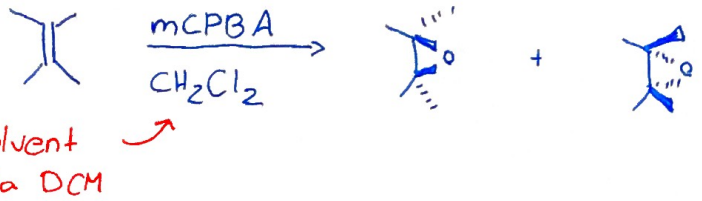
+ enantiomer

Epoxidation



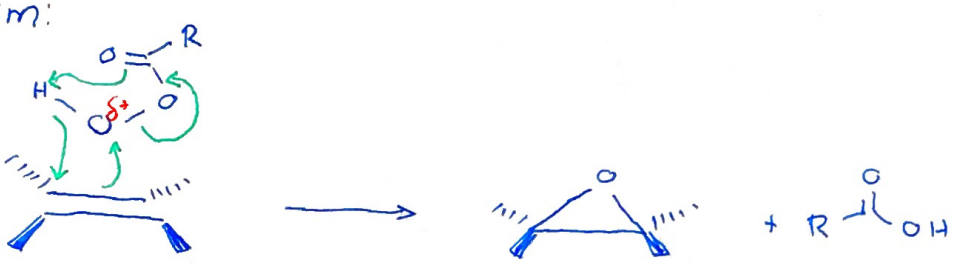
meta-chloroperoxybenzoic acid

Summary:



• Syn addition

Mechanism:



Example with α-pinene
(smells like rosemary)

Sterics (

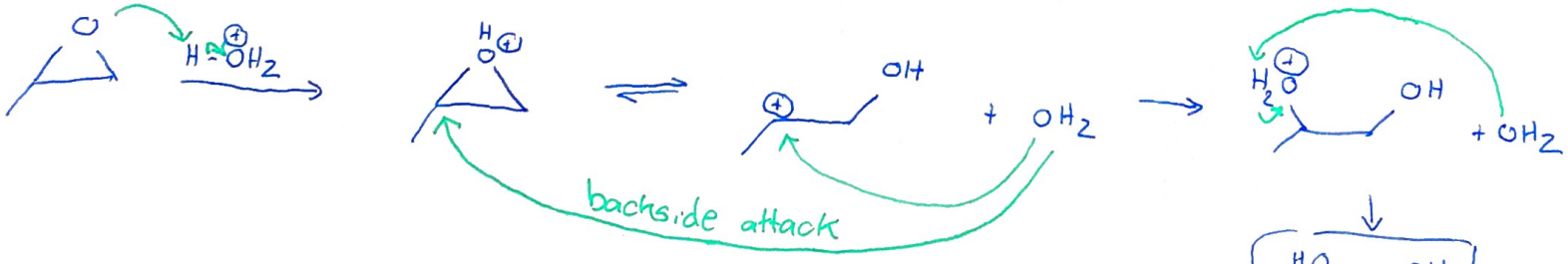
stereospecific – bottom addition only

Epoxides are highly reactive in nucleophilic ring openings

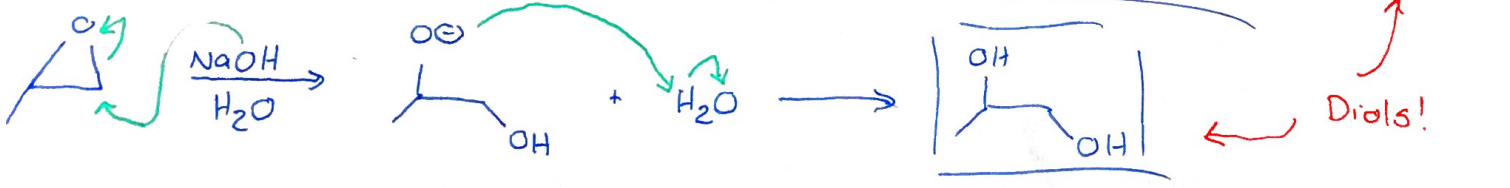
Why?

• polar covalent bonds
• relief of ring strain

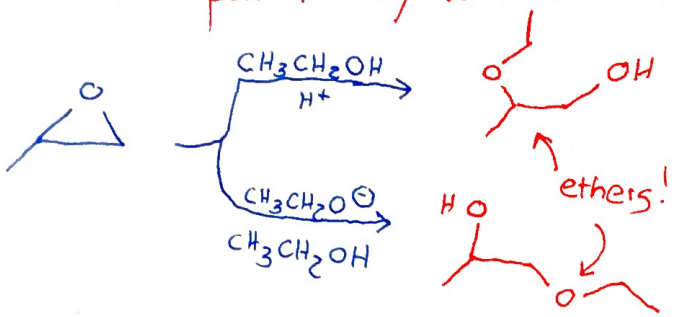
Acidic conditions – nucleophilic attack on more substituted carbon



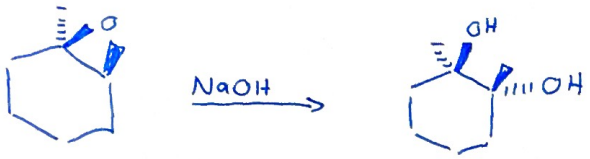
Basic conditions — nucleophilic attack on less substituted carbon



Can't tell apart? Try with other nucleophile:

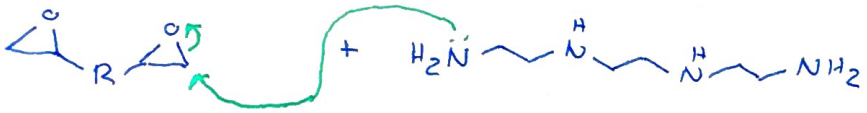


Ring opening epoxides with a base yields trans 1,2-diols!



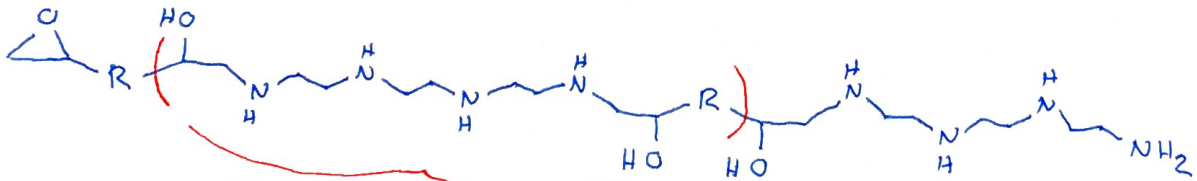
trans 1,2-diol
anti addition

Epoxy glues are also formed by ring opening epoxides



epoxy resin
typically low molecular weight "pre polymers"

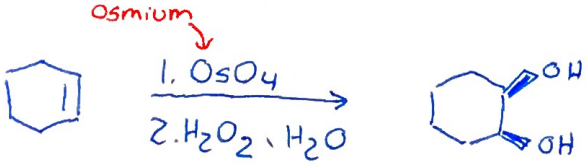
TETA
a typical hardener or curing agent



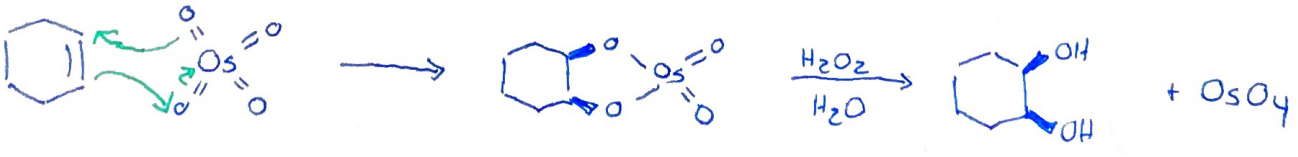
repeat unit of a polymer

some of the strongest adhesives known!

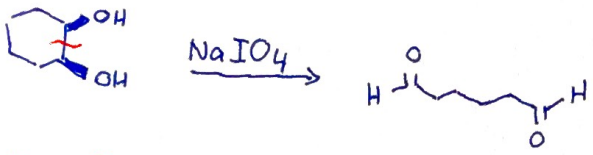
What about cis 1,2-diols? New approach needed.



How?

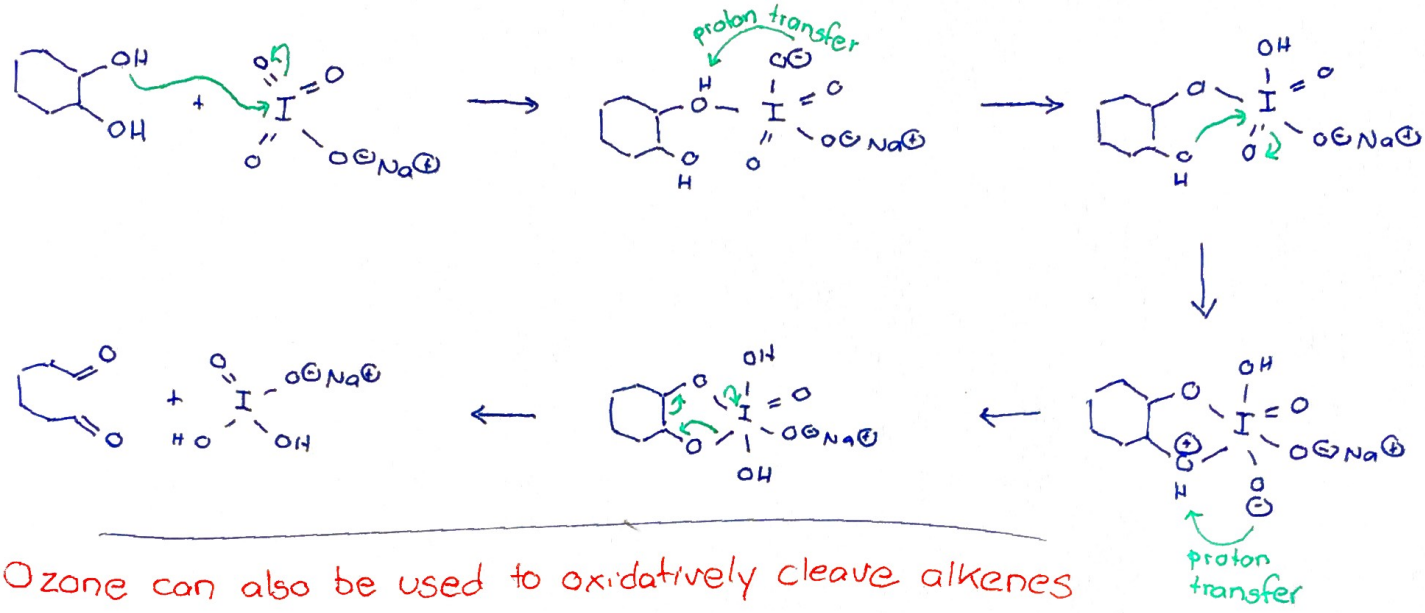


Oxidative Cleavage Reactions



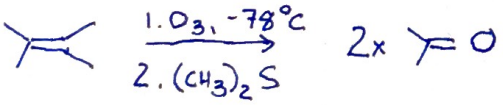
forms aldehydes or ketones

How?



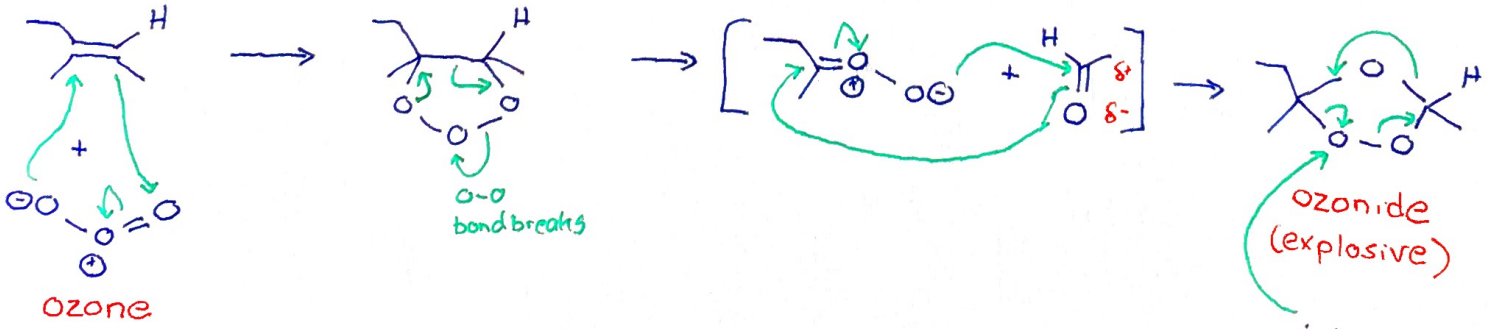
Ozone can also be used to oxidatively cleave alkenes

Ozonolysis summary:

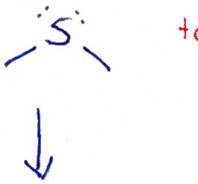


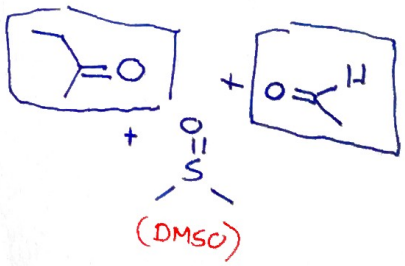
aldehydes and ketones

Mechanism:

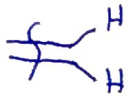
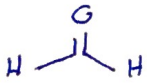
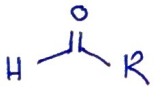
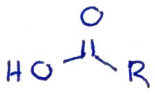
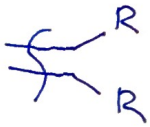
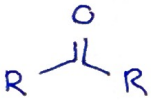
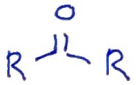


[reminder: resonance structures!]

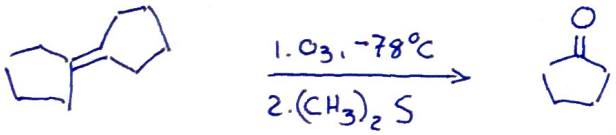


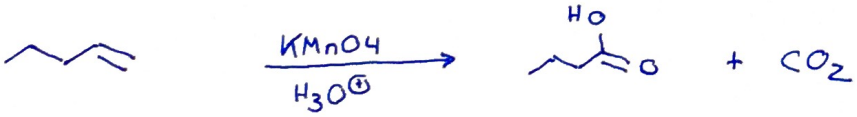


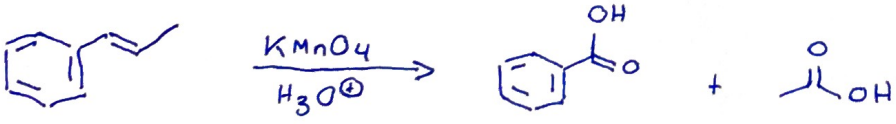
Oxidative Cleavage Summary

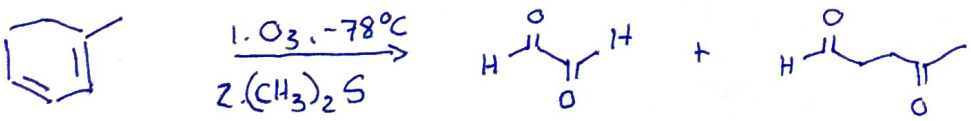
Substrate:	1. O_3, -78°C 2. $(CH_3)_2S$	Vigorous Oxidation $KMnO_4$, H_3O^+
	 aldehydes	$O=C=O$ (bubbles)
		 carboxylic acids!
	 ketones	 ketones

Examples:

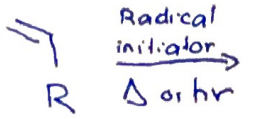




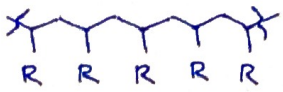




Radical Polymerization

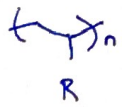


monomer



polymer

abbreviated:

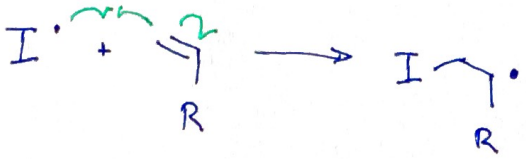


repeat unit

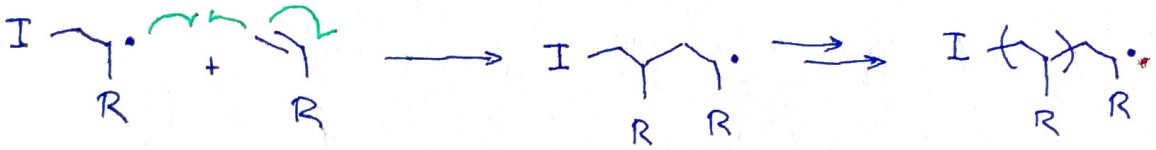
n = number of repeat units

How?

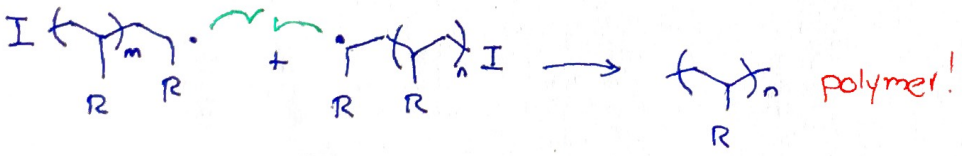
① Initiation:



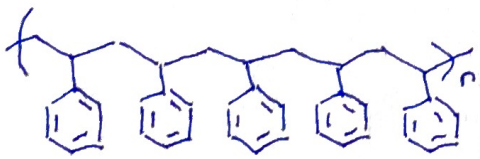
② Propagation:



③ Termination:



What is the monomer of:



① Find the repeat unit

② Make double bond

styrene