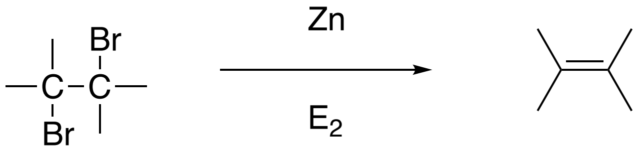
CHEM 261 Nov 25, 2021

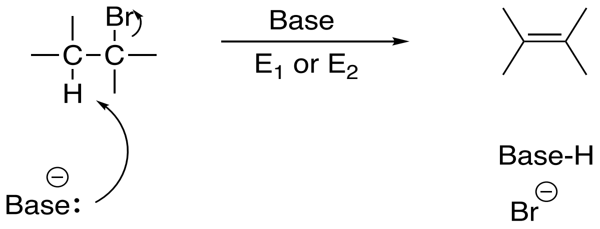
RECALL: Elimination reactions

Types of Elimination Reactions:

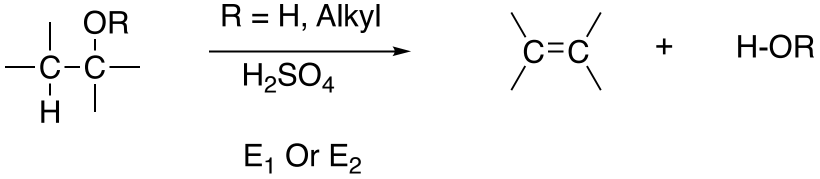
1) Dehalogenation (Removal of X_2, X = halide)



2) Dehydrohalogenation



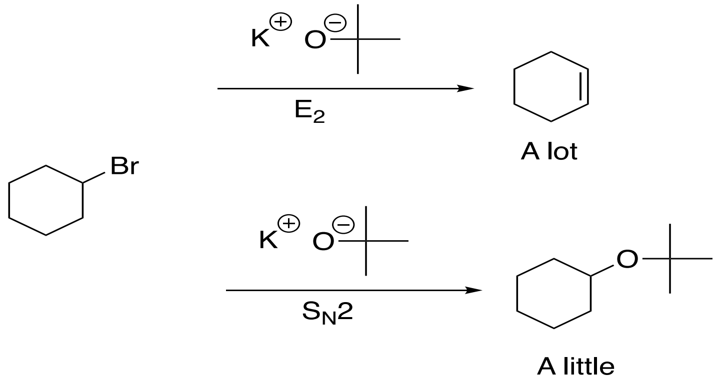
3) Dehydration



E_2 Reaction (E=Elimination)**:**

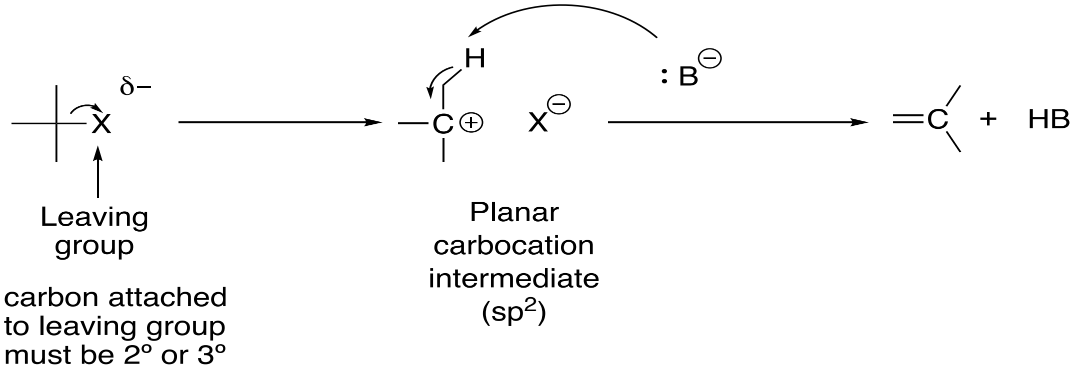
- Rate depends on two concentrations
- Stereospecific
- Concerted (bonds being formed and broken at the same time)
    - No intermediate
- Anti-periplanar geometry

Example: bulky nucleophiles/bases favour elimination

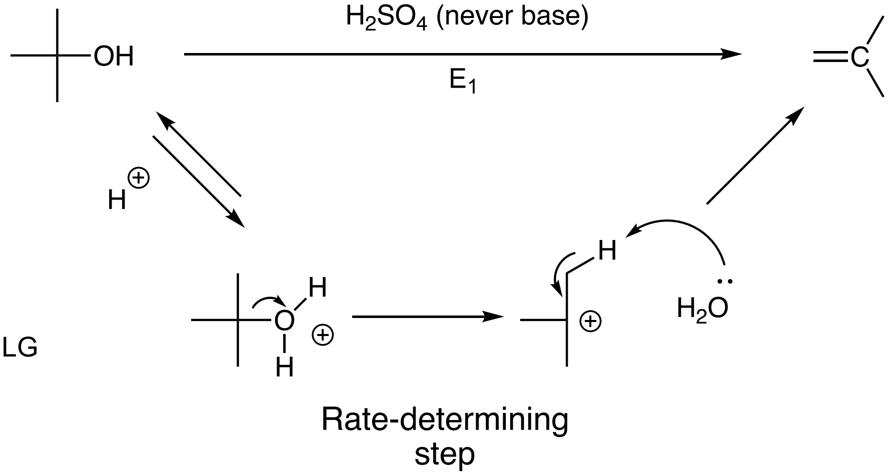


E_1 Reaction:

- Rate depends on one concentration
- Not concerted (carbocation intermediate)
- Not stereospecific
- Favoured with leaving group being 3º



Example #1: Dehydration



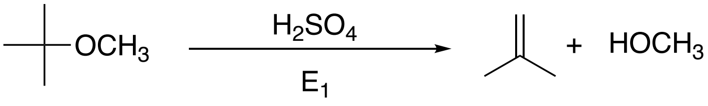
$\overset{\ominus}{OH}$
$\overset{\ominus}{OR}$ Not LG

HOH
HOR LG

LG = Leaving Group

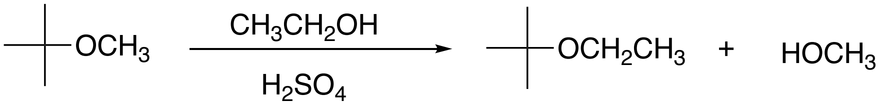
Example #2:

E_1



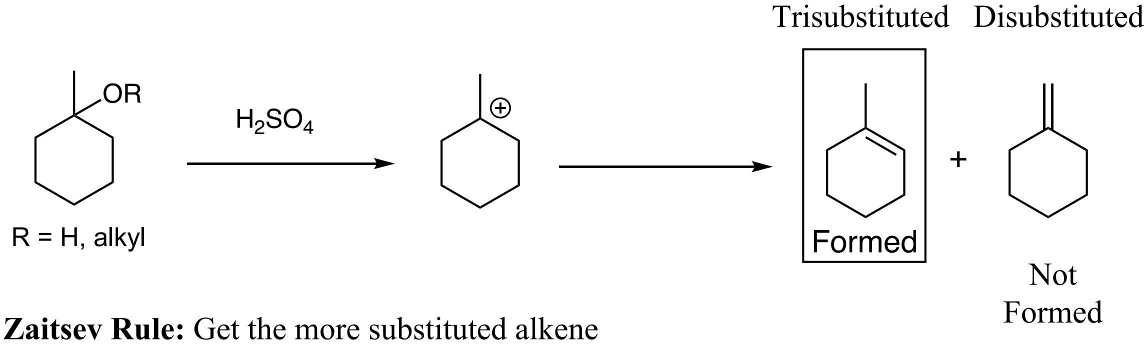
vs.

S_N1



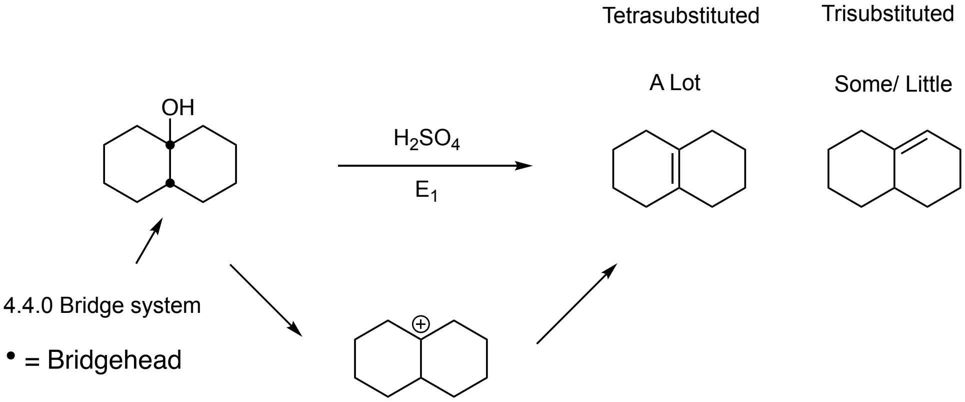
Substitution	vs.	Elimination:
- Low Temp		- High Temp
- Weaker Base		- Stronger Conditions
- Dilute H^+		- Conc. H^+
- Leaving group on 1° carbon		- 2°, 3°
- Small Nucleophile		- Large Nucleophile

Example #2: Dehydration or Removal of HOR



Zaitsev Rule: Get the more substituted alkene

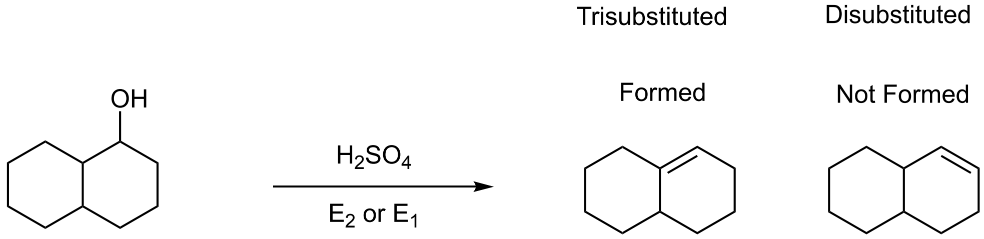
Example #3: Dehydration



Zaitsev Rule: Get the more substituted alkene

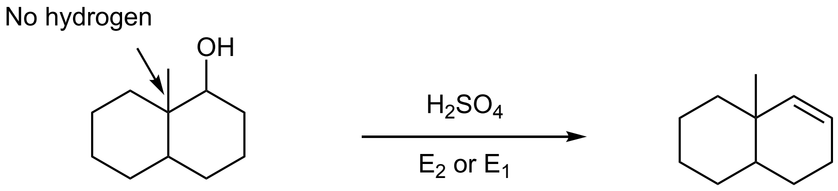
Bredt Rule: Bridged alkenes are only okay if one of the bridges is a “zero” (0) bridge in small rings <9 ; If a bicyclic ring system has all bridges > 0 carbons, then there cannot be an alkene on a bridgehead.

Example #4: Dehydration

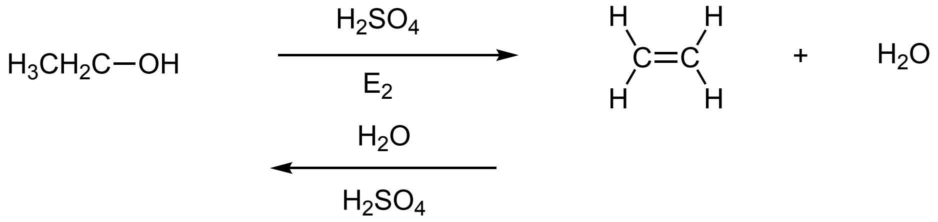


Zaitsev Rule: Get the more substituted alkene

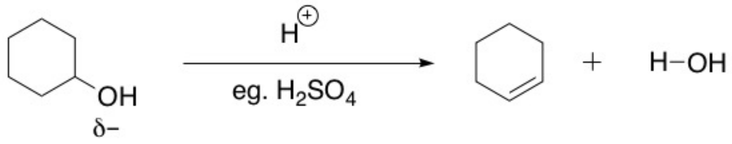
Example #5: Dehydration

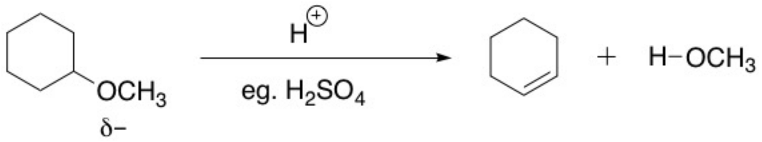


Example #5: E₂ Dehydration



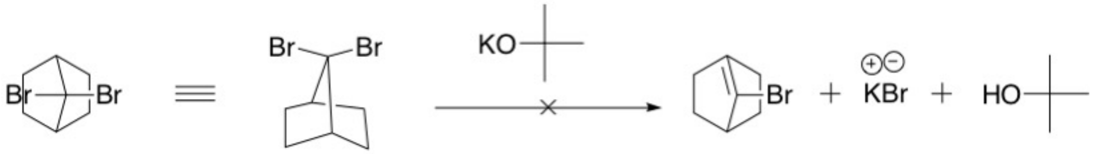
Elimination reactions:





-OH and -OCH_3 are bad leaving groups and so these reactions would not occur spontaneously without an acid catalyst.

To determine whether an elimination can occur, ask yourself three questions:



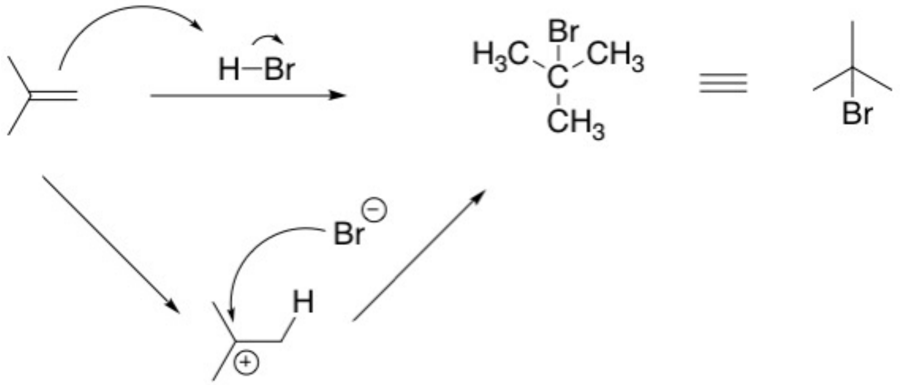
1. Is there a good leaving group present?
   Eg. Yes, Br is a good leaving group

2. Is there a hydrogen on the carbon next to the carbon containing the leaving group?
   Eg. Yes, on the bridge-heads on either side of the carbon containing the Br.

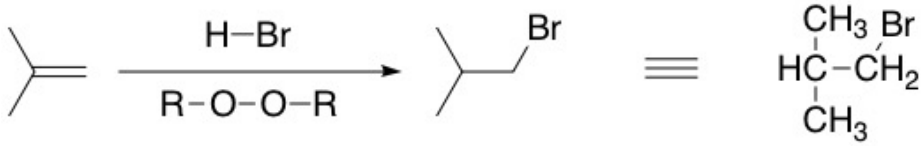
3. Is Bredt's Rule being followed?
   Eg. No, if a double bond was being formed, it would be at a bridge-head and Bredt's rule states that a double bond cannot be formed at a bridge-head if the rings are small and all bridges >0. (double bond too strained)

Substitution would likely not occur either as the electrophilic site is hindered (tertiary carbon).

Addition Reactions

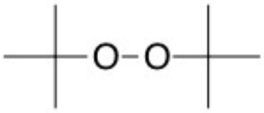


For alternate regiochemistry (addition of Br onto the less substituted carbon) need dialkyl peroxide



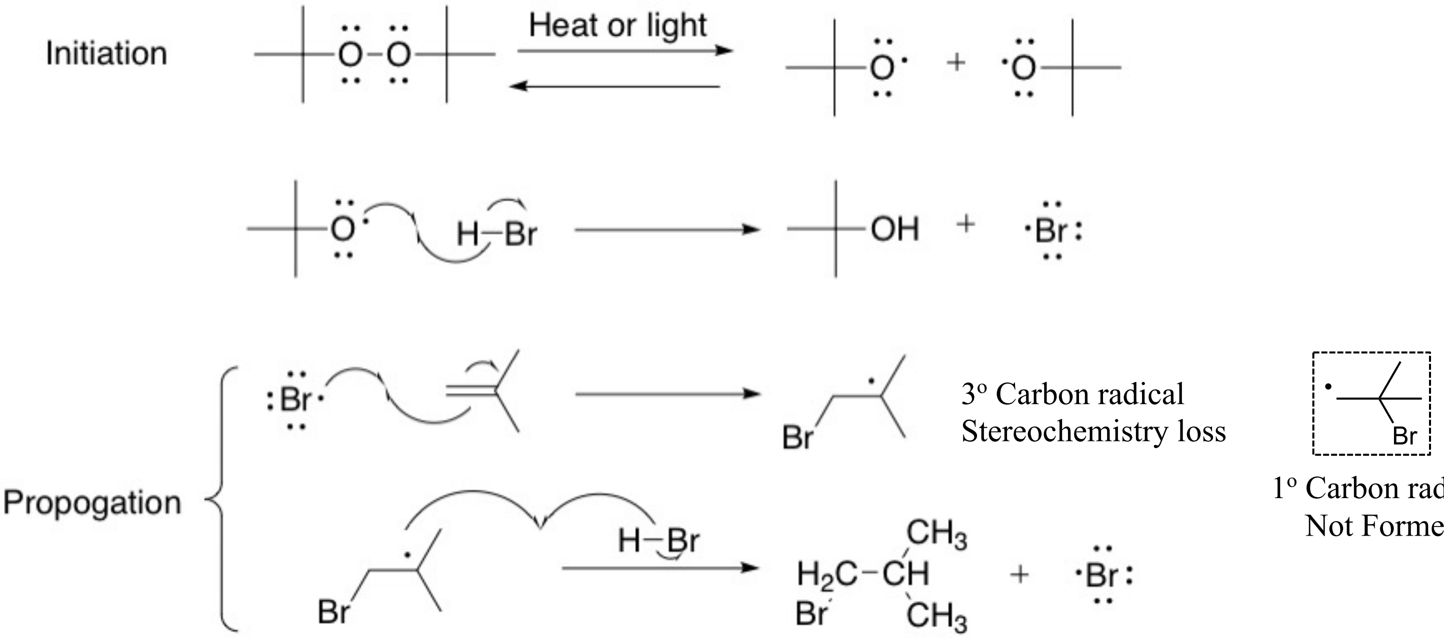
Examples of peroxides

Tert-butyl peroxide



Hydrogen peroxide HO–OH

Radical mechanism

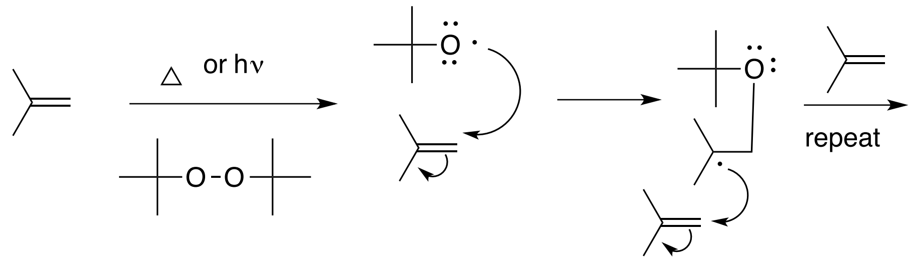


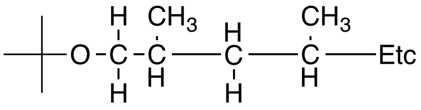
3° Carbon radical
Stereochemistry loss

1° Carbon radical
Not Formed

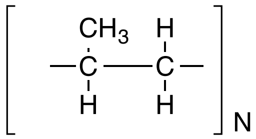
Termination – Combination of any two radicals

Example without HBr – a polymerization reaction occurs





polypropylene



shorthand notation for polypropylene

Note more stable radical (in this case tetiary) is always formed by addition onto double bond

There is a termination step (not shown) that ends this polymerization. It requires combination of 2 radicals. It could be two growing chain radicals meeting or it could be from peroxide. If less peroxide is used the polymer chain will be longer.

Polymers
Poly = many
Meros = parts

Examples of Biopolymers

1. Polysaccharides
   - polymers of sugars

2. Proteins and peptides
   - polymers of amino acids

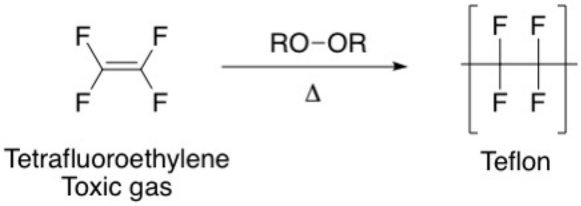
3. Nucleic acid polymers (DNA and RNA)
   - polymers of nucleotides

4. Fats and polyketides
   - polymers of fatty acids

5. Polyisoprenoids/ terpenoids
   - polymers of isoprene

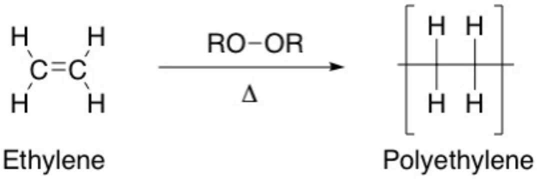
Polymer formation

Teflon

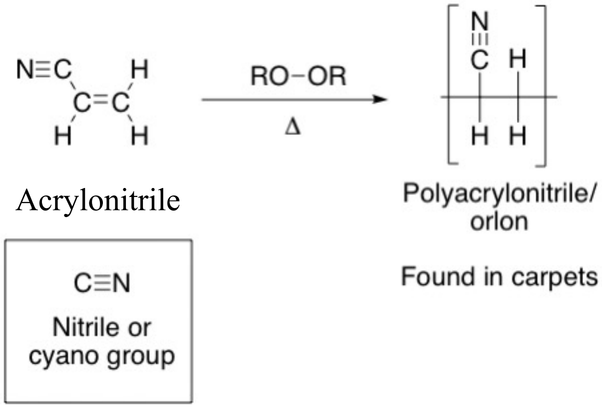


Many polymers degrade into their components if heated enough, and can further decompose.

Polyethylene

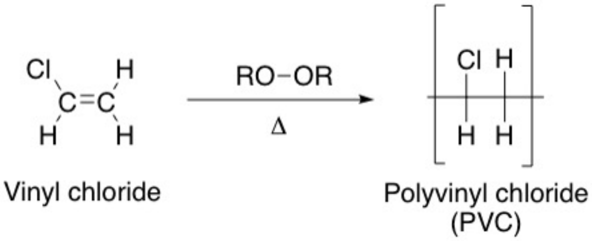


Polyacrylonitrile



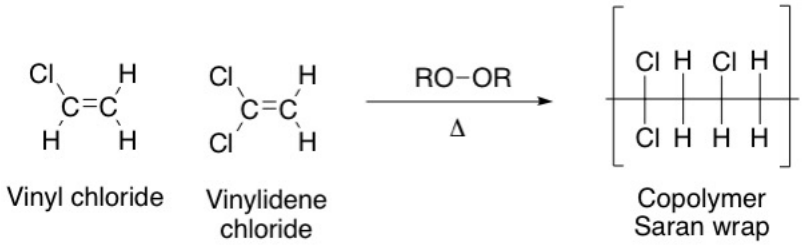
Polyacrylonitrile can form HCN if it is heated to decomposition.

Polyvinyl chloride



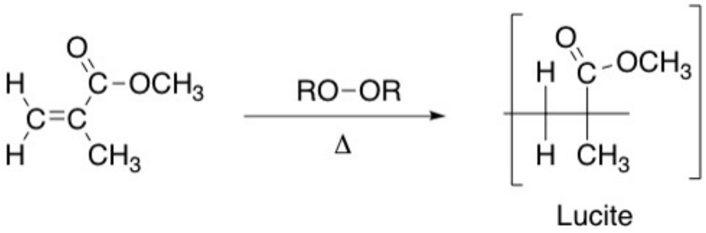
Such polymers containing chloride can form HCl if decomposed.

Copolymers

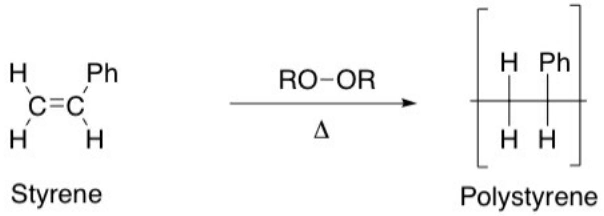


Copolymers are composed of two different subunits.

Lucite

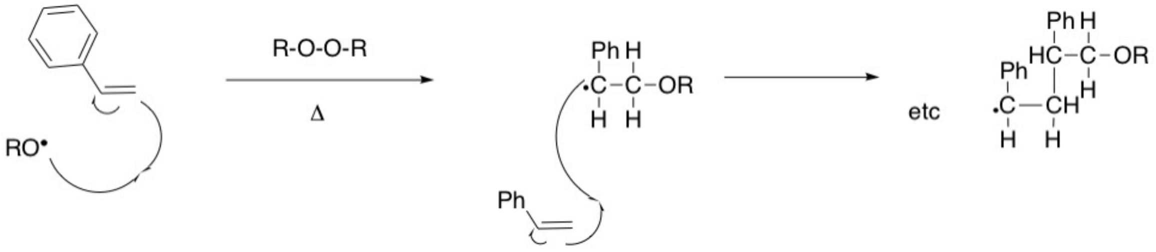


Polystyrene

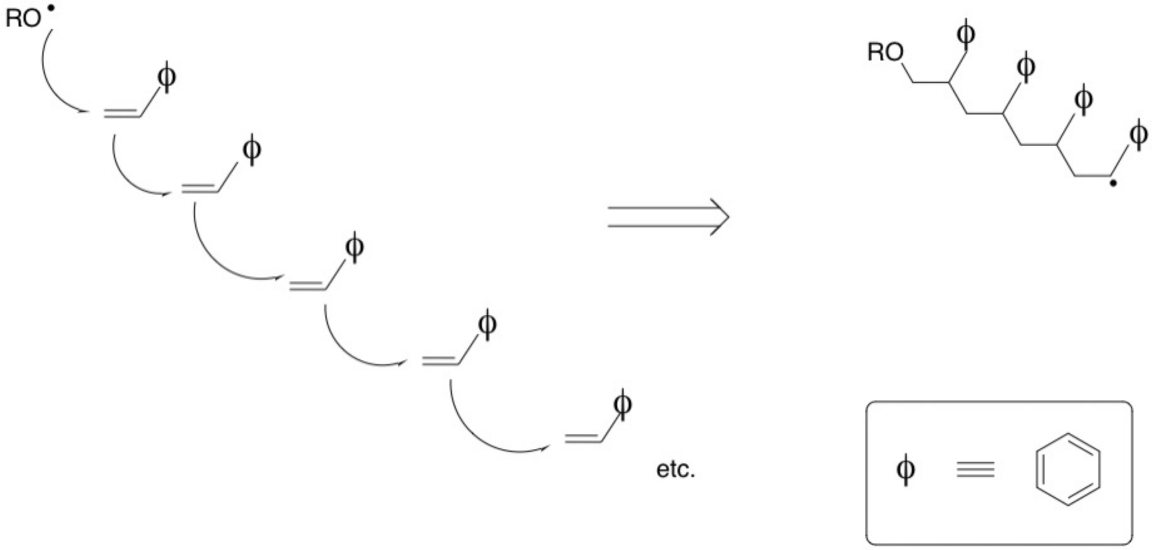


phenyl group is Ph

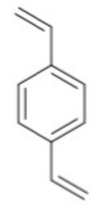
Example: Mechanism of polystyrene formation



Short-hand for mechanism of polystyrene formation



Divinyl benzene can be added as a cross-linker so chains link on both of its double bonds This make the copolymer more solid (as you encounter in many products) – typically about one part in 100 to one part in 6 of divinylbenzene may be added



Divinylbenzene