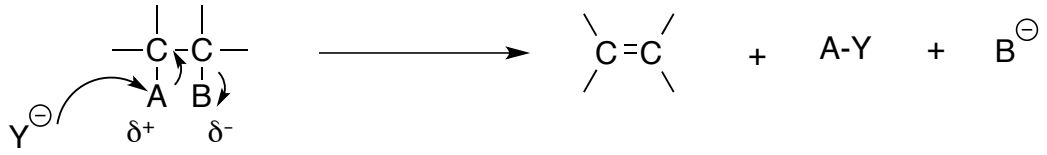
Recall:

Elimination reaction



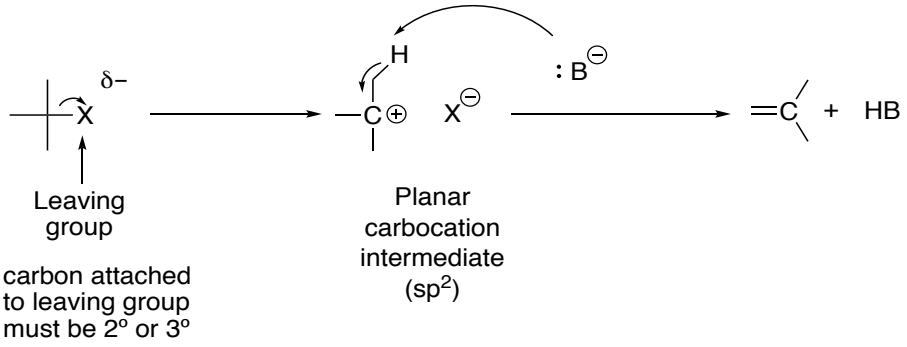
2 Types of Mechanisms: E_1 and E_2

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

- Rate depends on two concentrations
- Stereospecific
- Concerted (bonds being formed and broken at the same time)
  - No intermediate
- follows Zaitsev Rule: most substituted alkene will be the major product
- Anti-periplanar geometry
- 1º, 2º, 3º, but especially primary and secondary

E_1 Reaction:

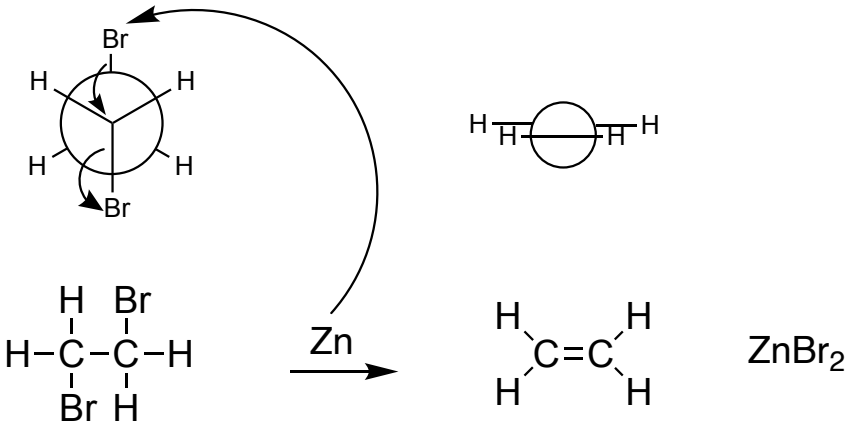
- Rate depends on one concentration
- Not concerted (carbocation intermediate)
- Not stereospecific, needs high temoeratures
- Favored with leaving group being 3º



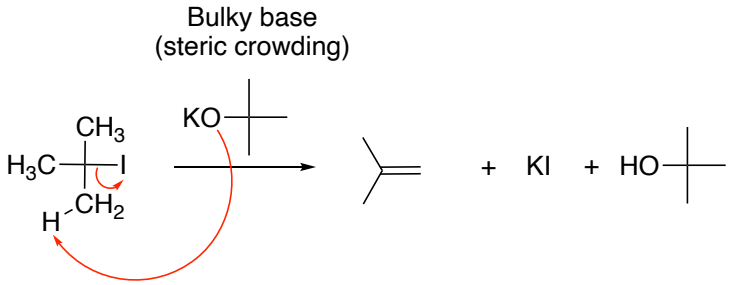
Example:

Dehalogenation

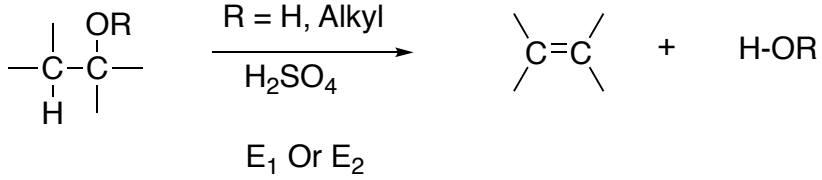
Example 1:



Example 2: Dehydrohalogenation



3) Dehydration



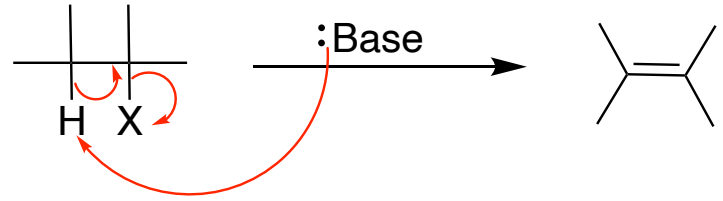
Bredt Rule: Bridged alkenes are only okay if one of the bridges is a "zero" (0) bridge in small rings <9

<u>Dehydration</u>

-OH and -OR are not leaving groups, but H-OH and H-OR are okay (they can leave favoured by heat or strong acid)

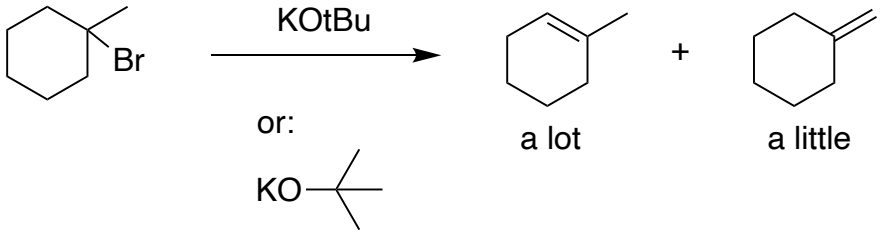
Dehydrohalogenation

Zaitsev Rule: Get the more substituted alkene

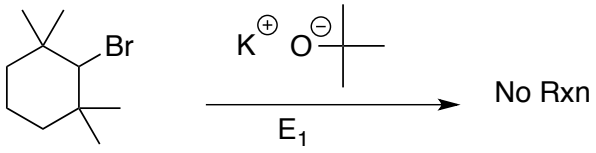


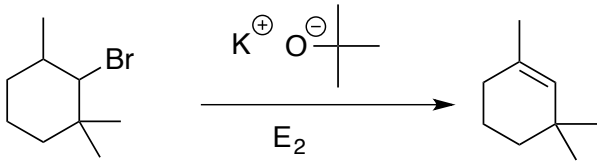
X= Cl, Br, I

Example 1:



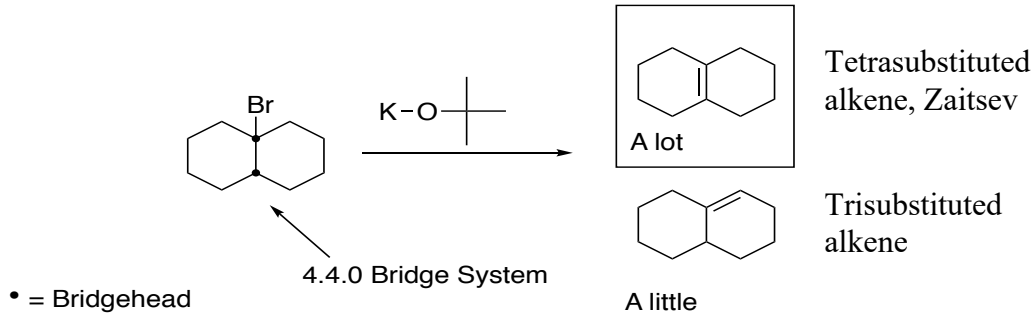
Example 2:



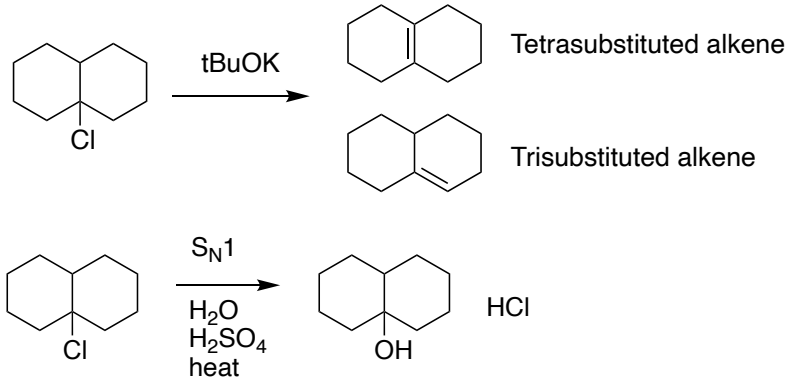


need hydrogen on adjacent carbon for loss of HBr

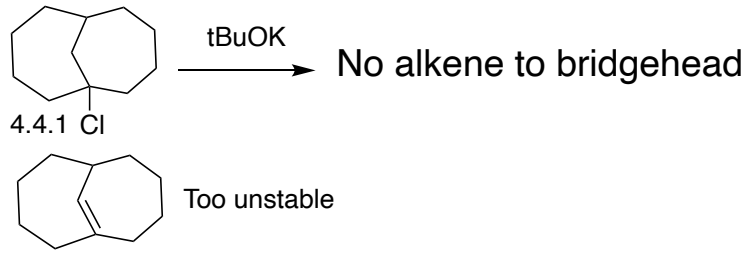
Example 3:



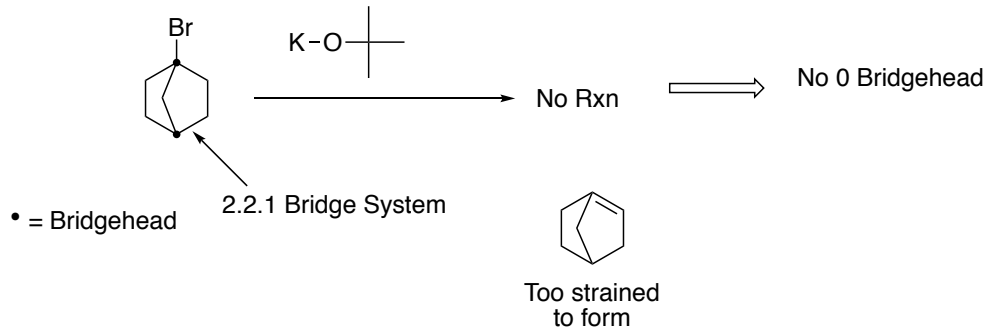
Example 4:



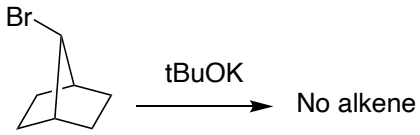
Example 5:



Example 6:

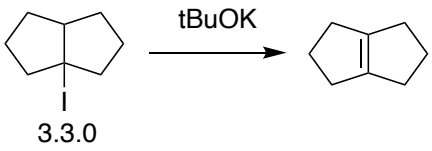


Example 7:

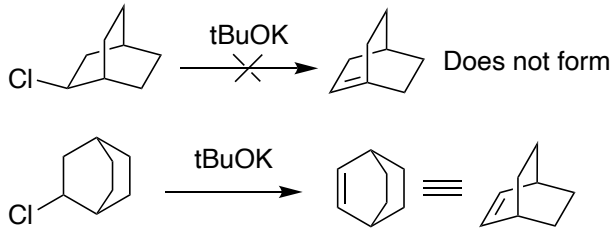


(too unstable – will not form according to Bredt's rule

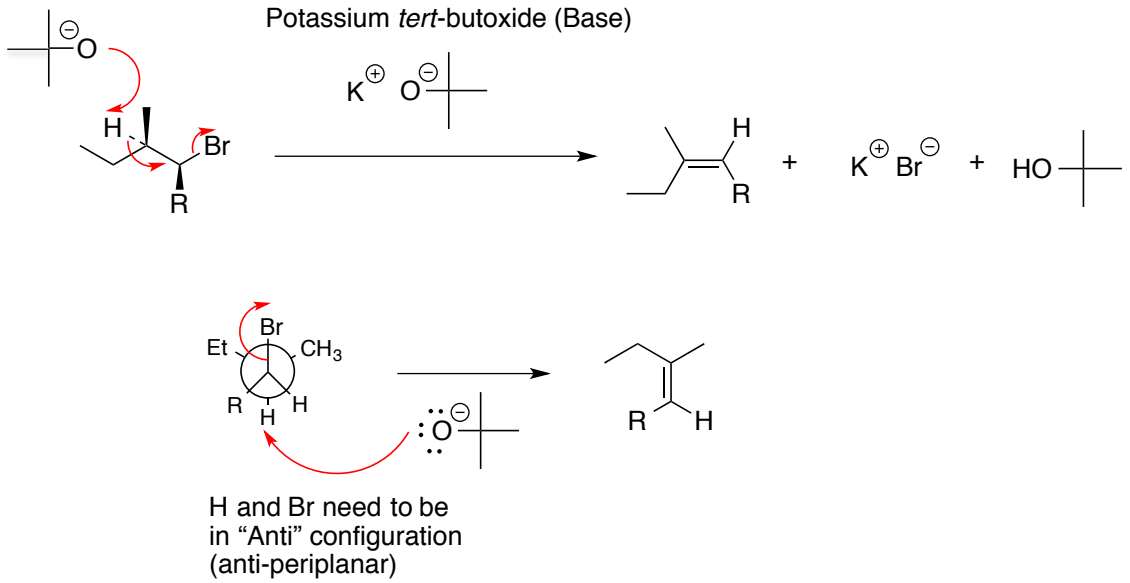
Example 8:



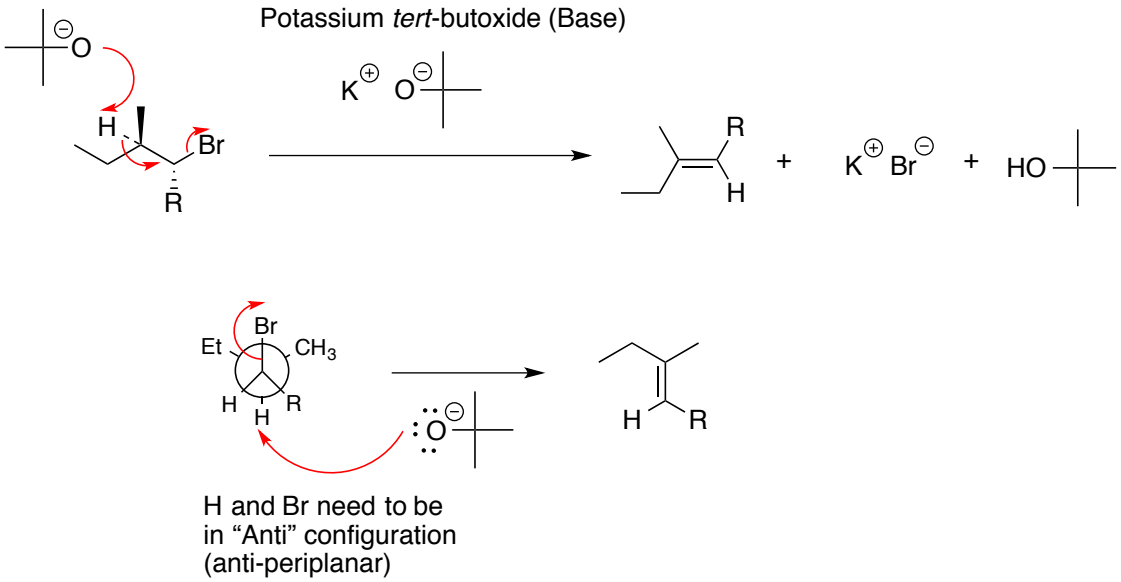
Example 9:



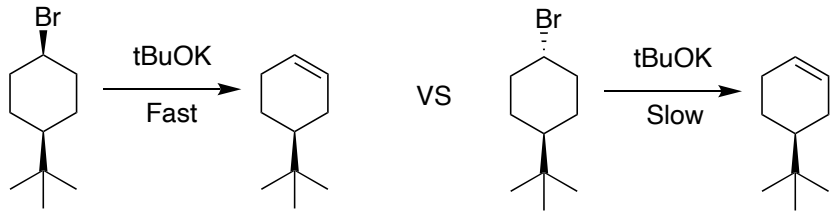
Example 10 A:



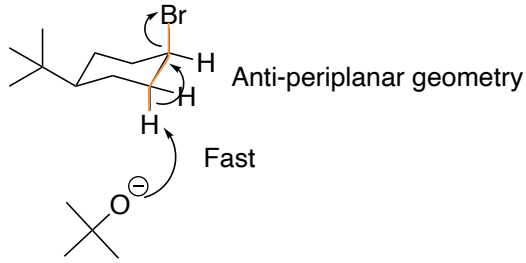
Example 10 B: Start with different stereochemistry get different product stereochemistry (a diastereomer)

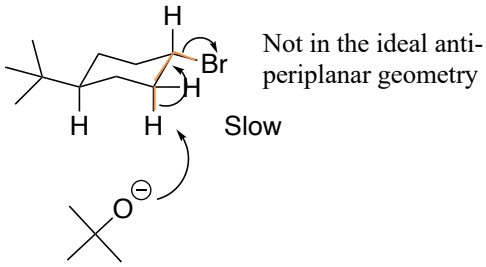


Example 11:



The *tert*-butyl group must be placed in the equatorial position

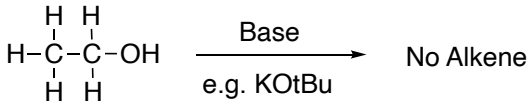


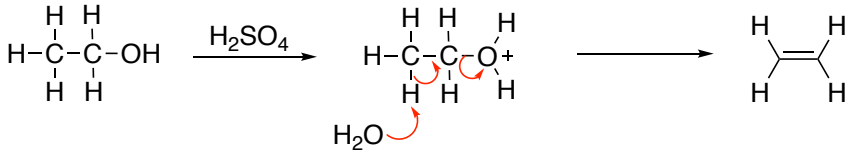


Dehydration

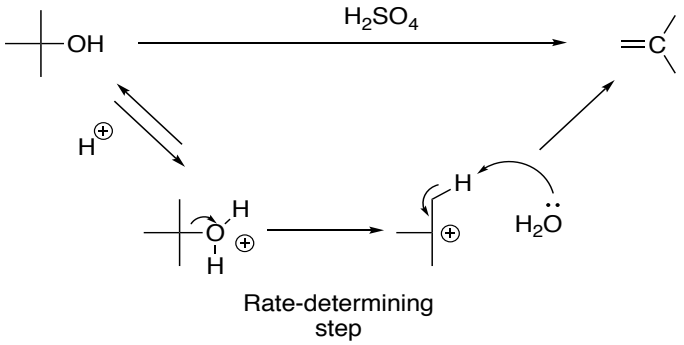
-OH and -OR are not leaving groups, but H-OH and H-OR are okay (they can leave favoured by heat or strong acid)

Example 1:

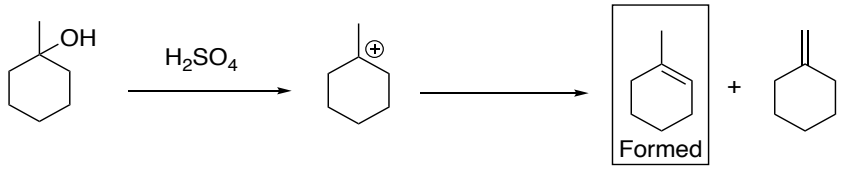




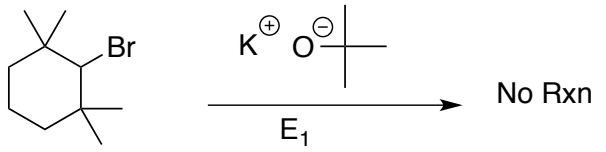
Example 2:

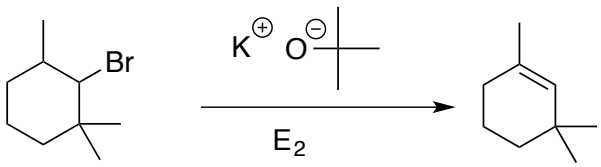


Example 3:

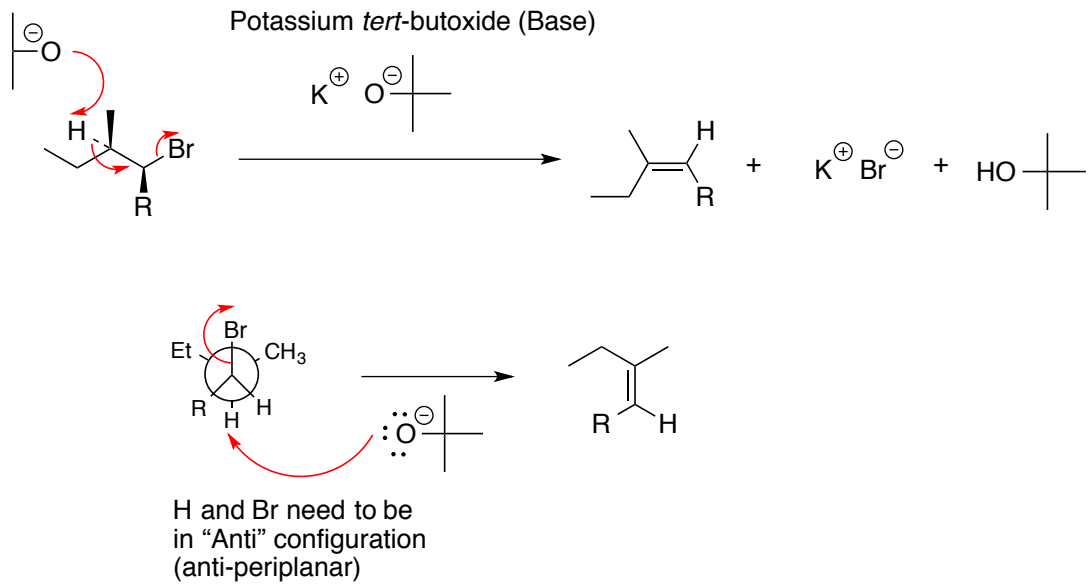


Example 4:

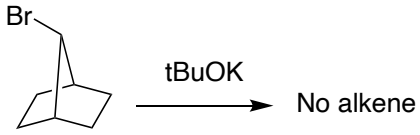




Example 5:



Example 6:



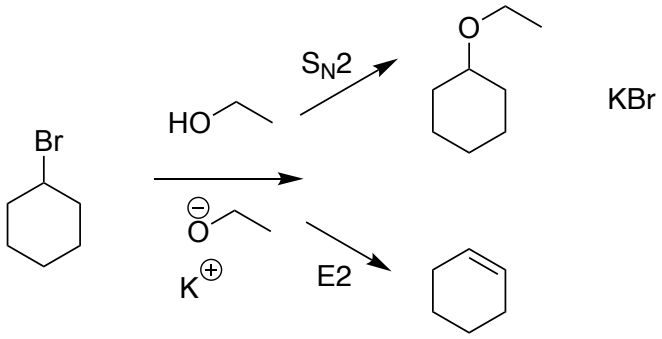
(too unstable – will not form according to Bredt's rule

Elimination vs Substitution

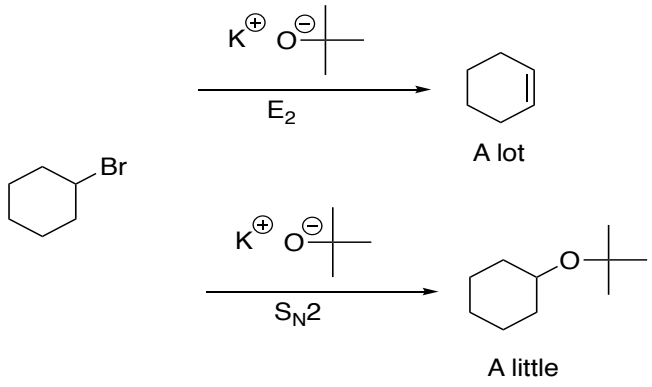
Substitution	vs.	**Elimination**
- Low Temp		- High Temp (Heat)
- Weaker Base		- Stronger Base
- Dilute H^+		- Conc. H^+
- Leaving group on 1° carbon		- 2°, 3°
- Small Nucleophile		- Large Nucleophile

Note: HO-H, HOR are leaving groups but requires strong acid (H^+) such as H_2SO_4

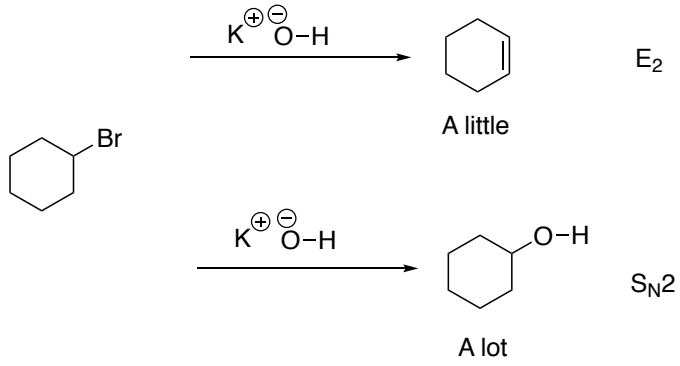
Example 7:



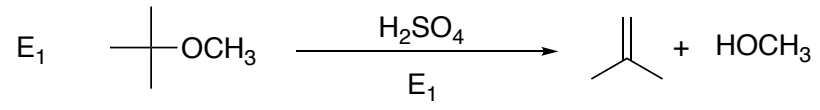
Example 8A: bulky nucleophiles/bases favor elimination



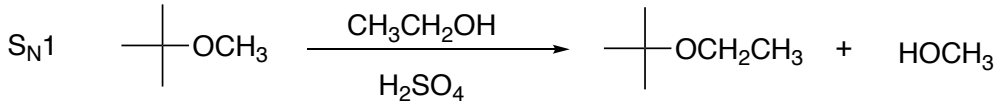
Example 8B: small nucleophiles/bases favor substitution



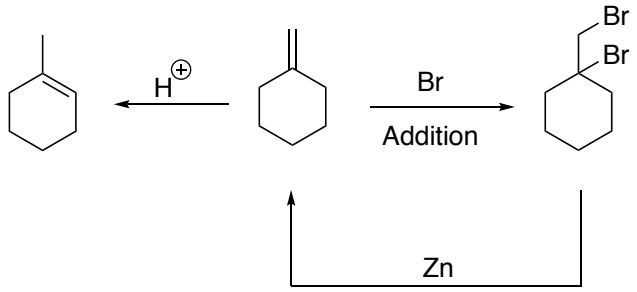
Example 9A:



vs.



Example 9B:



Due to mechanism of Zn, the double bond is stuck at less substituted end.

Double bond can go to more substituted if it is left in acid

Polymers
Poly = many
Meros = parts

Natural Polymers (Biopolymers)

1. Polysaccharides
   - polymers of sugars (e.g. cellulose, glycogen)

2. Proteins and peptides
   - polymers of amino acids

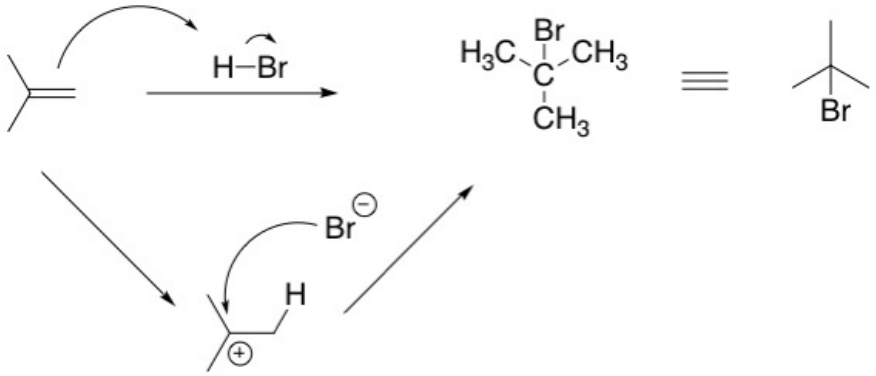
3. Nucleic acid polymers (DNA and RNA)
   - polymers of nucleotides

4. Fats and polyketides
   - polymers of fatty acids

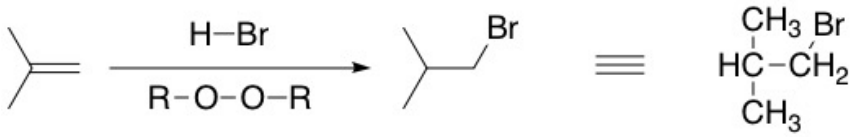
5. Polyisoprenoids/terpenoids
   - polymers of isoprene (i. e. natural compound rubber)

<u>Recall</u>:

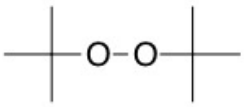
Addition Reactions of Alkenes (Markovnikov addition)



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



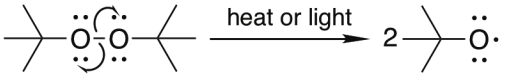
Examples of peroxides

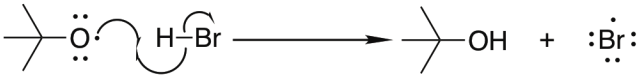
Tert-butyl peroxide 

Hydrogen peroxide HO–OH

Radical mechanism

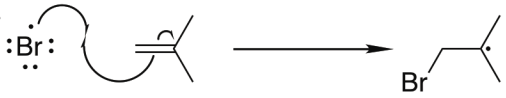
Initiation



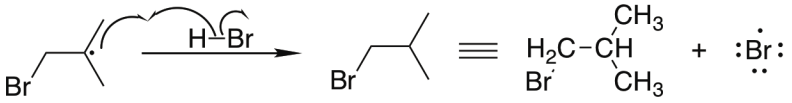


O-Br bond is not strong as both atoms are electron withdrawing elements. Therefore, *tert*-butyl alcohol is formed

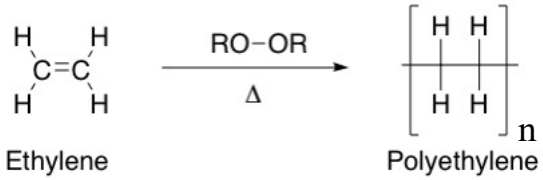
Propagation



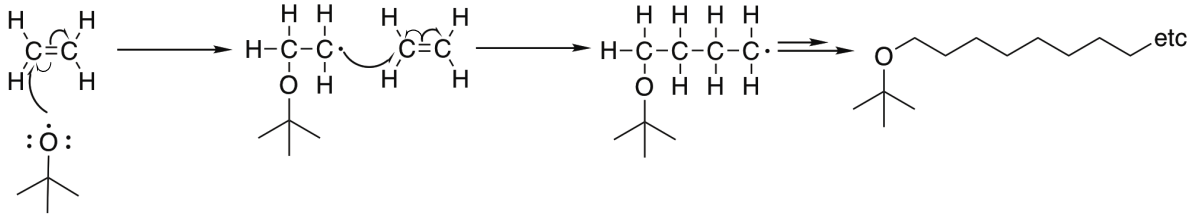
Radical forms on that carbon with the maximum number of alkyl groups attached: radicals are electron deficient and electron-donating substituents stabilize them



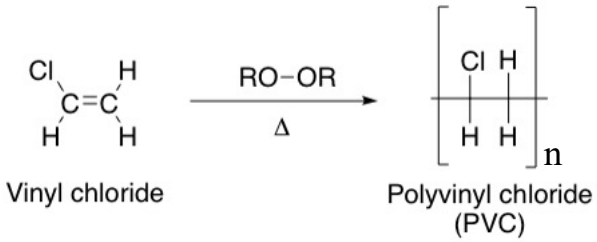
Polyethylene



Mechanism:

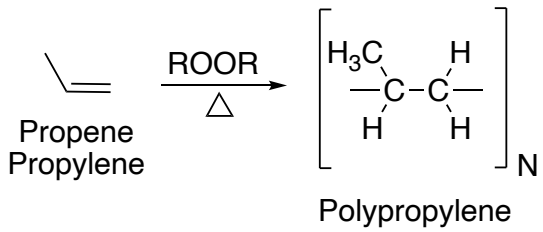


Polyvinyl chloride

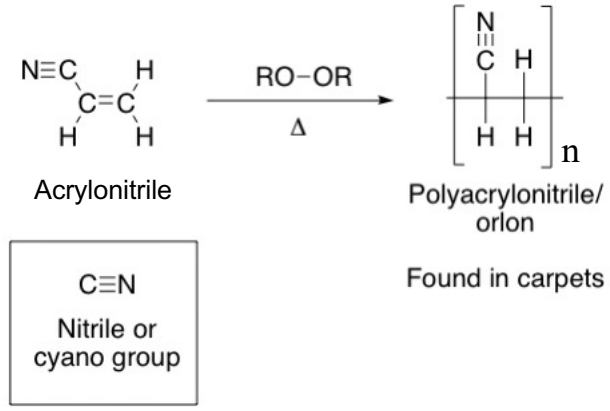


Such polymers containing chloride can form HCl if decomposed.

Polypropylene

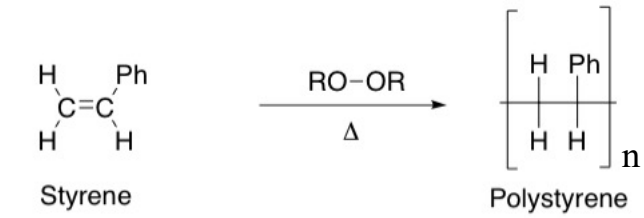


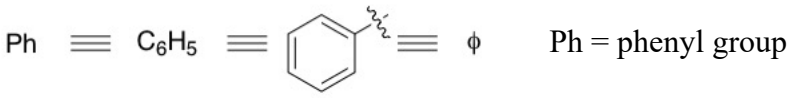
Polyacrylonitrile



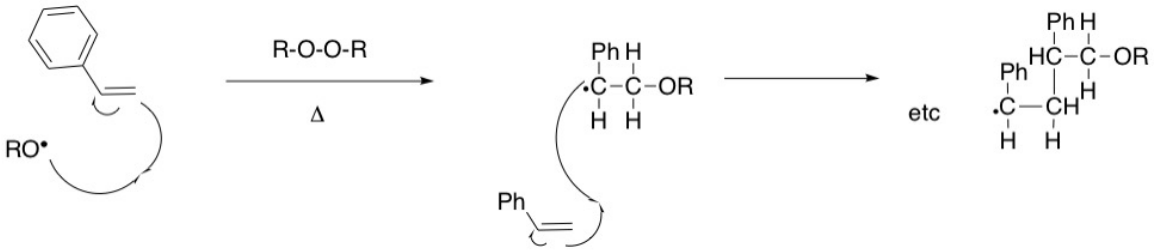
Polyacrylonitrile can form HCN if it is heated to decomposition.

Polystyrene

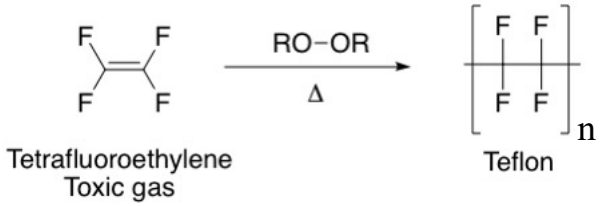




Example: Mechanism of polystyrene formation

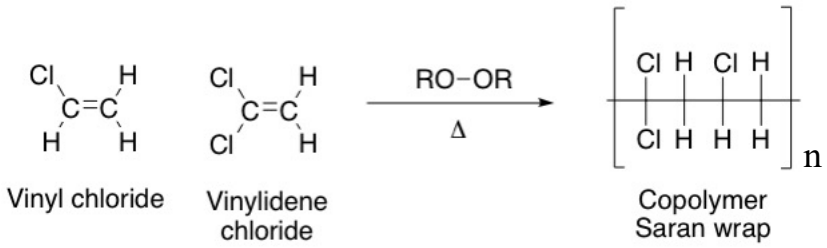


Teflon (Polytetrafluoroethylene)



Teflon is very unreactive and does not adhere substances
Many polymers degrade into their components if heated enough, and can further decompose.

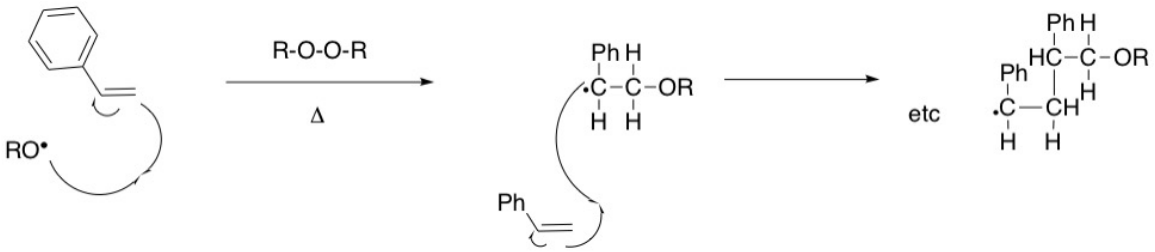
Copolymers



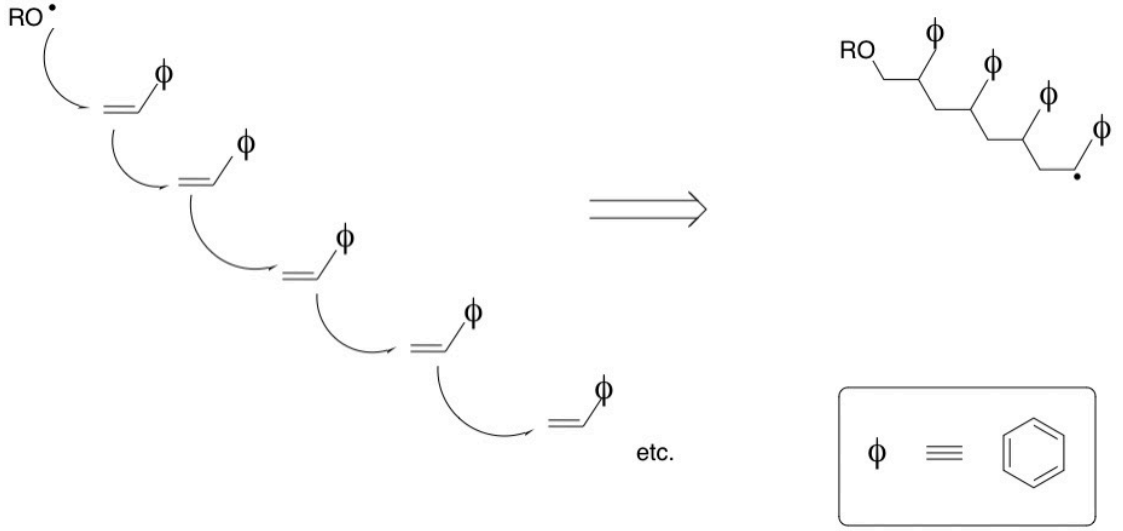
Copolymers are composed of two different subunits.

Cross-linked polymers

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