Additions to Alkenes

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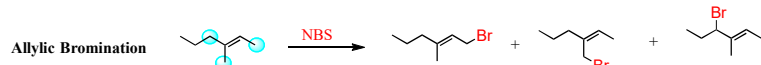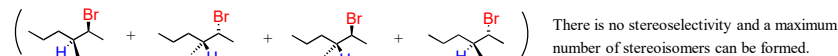**Addition of Hydrogen halide (HX)**

HX
X = F, Cl, Br. I
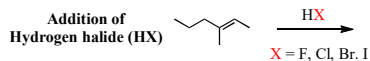
The reaction goes through a regioselective formation of a carbocation. This is the **Markovnikov's rule** stating that the **proton binds to the less substituted carbon** because by doing so the more substituted/stable carbocation is formed. The halide can attack the carbocation from both faces, thus a mixture of enantiomers is produced.
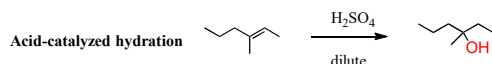
2°   3° carbocation more stable   Enantiomers

* Notice that an alkene with a chiral center will produce a mixture of **diastereomers.**

Radical Addition of HBr

HBr
ROOR
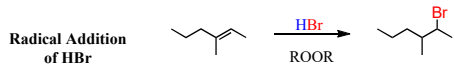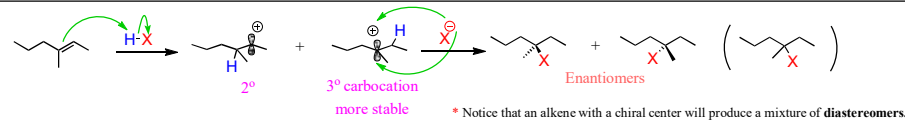
Only HBr works for Anti-Markovnikov addition. The reaction goes through a radical mechanism with syn and anti additions.

There is no stereoselectivity and a maximum number of stereoisomers can be formed.
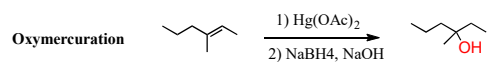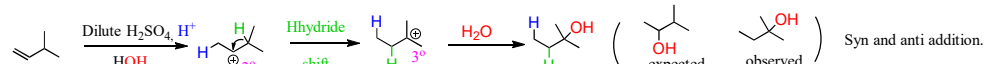

Allylic Bromination

NBS

NBS is used to brominate the **allylic position** of the double bond. So, for the regiochemistry of the bromination, you can simply identify the allylic positions and place the bromine there.
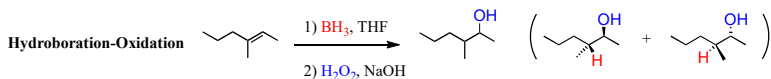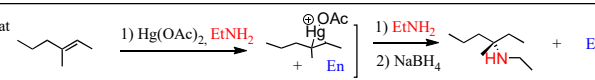
However, **the reaction is not as straightforward!** It involves resonance-stabilization of the allylic radicals and other regioisomers are also formed. In addition, the lack of stereochemical control makes **predicting all the possible products quite difficult.** You can check https://www.chemistrysteps.com/allylic-bromination/ for more details.


Acid-catalyzed hydration

H_2SO_4
dilute

Acid-catalyzed hydration follows the **Markovnikov's rule.** However, **rearrangements** are possible because of the carbocation intermediates.

Dilute H_2SO_4 H^+ / HOH   Hhydride shift H_2O expected   observed   Syn and anti addition.


Oxymercuration

1) $Hg(OAc)_2$
2) NaBH4, NaOH

Same product as acid-catalyzed hydration. The main **reason for using Oxymercuration is preventing possible rearrangements** that happen during acid-catalyzed hydration.
The mechanism goes through a **three-membered ring** which can react with **other nucleophiles** such as alcohols, amines and thiols.

1) $Hg(OAc)_2$, $EtNH_2$ 1) $EtNH_2$ 2) $NaBH_4$ + En

Hydroboration-Oxidation

1) BH_3, THF
2) H_2O_2, NaOH

Unlike H_2SO_4 and $Hg(OAc)_2$, **Hydroboration**-Oxidation is used for **Anti-Markovnikov** hydroxylation. **Hydroboration is a concerted, syn addition**, so the **H** and **OH** appear on the **same side** in the product. For better stereoselectivity, bulky dialkylboranes such as 9-BBN (R_2BH general formula) are used.

1) BH_3, THF   2) H_2O_2, NaOH
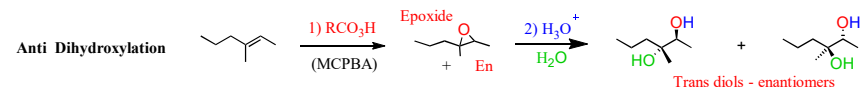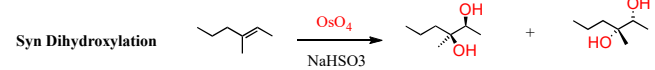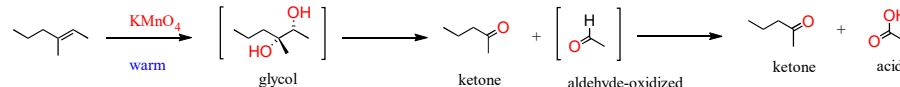

Ozonolysis

1) O_3
2) Me_2S
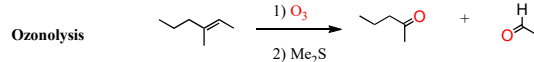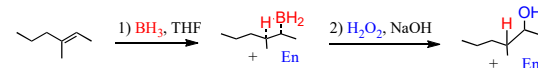
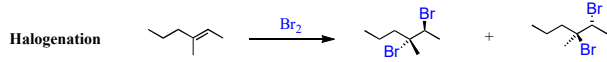Like for any other exercise, numbering the carbon chain will help a lot!
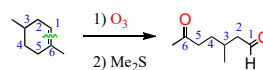
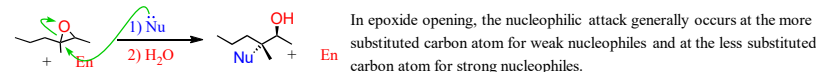To predict the structure of starting alkene, connect the two carbons of carbonyl with a double bond:

connect

Syn Dihydroxylation
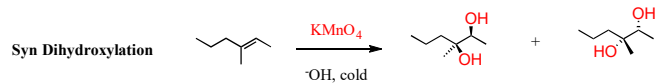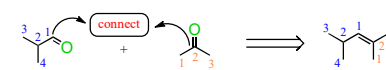
$KMnO_4$
⁻OH, cold

The **syn dihydroxylation** with $KMnO_4$ works only at **lowered temperatures**. If **heat** is applied, the **double bond is cleaved:**

$KMnO_4$ / warm   glycol   ketone   aldehyde-oxidized   ketone   acid

Syn Dihydroxylation

OsO_4
NaHSO3

Anti Dihydroxylation

1) RCO_3H Epoxide
(MCPBA)
+ En

2) H_3O^+
H_2O

Trans diols - enantiomers

An **epoxide** is a strained **three-membered, cyclic ether** that can be reacted with many other nucleophile since epoxides are very reactive.

1) Nu
2) H_2O

In epoxide opening, the nucleophilic attack generally occurs at the more substituted carbon atom for weak nucleophiles and at the less substituted carbon atom for strong nucleophiles.
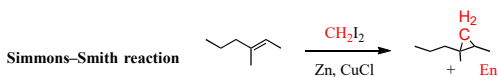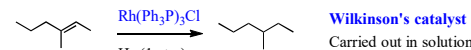

Halogenation

Br_2

Stereochemistry is the key in halogenation of a double bond. A three-membered ring intermediate (**bridged halonium ion**) is formed upon addition of the first halogen and the second one can only add from the opposite side. Thus, **trans enantiomers** formed by **anti** addition.

Br_2 + En

Halohydrin Formation

Br_2
H_2O
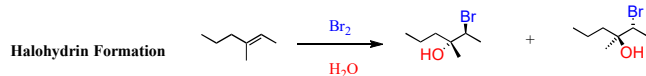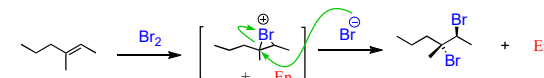
Same mechanism as bromination. Only the bridgedhalonium ion is **attacked by the water here**.
Key point for **regiochemistry**: the **water attacks the more substituted carbon** of the ring.
Key point for **stereochemistry**: the **Br and OH are trans** since H_2O attacks from the opposite side.

H_2O + En

Hydrogenation

H_2
Pd/C

Enantiomers
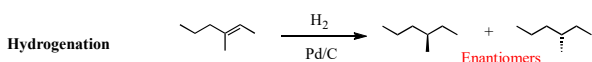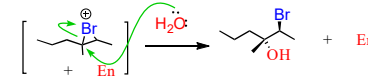
Other catalysts such as Pt or Ni can also be used for **catalytic hydrogenation** of alkenes. It is a **syn addition.**
For **homogeneous** reactions, **Wilkinson's catalyst** is used instead of metals.

$Rh(Ph_3P)_3Cl$
H_2 (1 atm)

Wilkinson's catalyst
Carried out in solution

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Simmons–Smith reaction

CH_2I_2
Zn, CuCl
+ En

It is a stereospecific reaction and depending on the configuration of the alkene, cis or trans product is obtained:

CH_2I_2 / Zn, CuCl   (Z) → Cis CH_2I_2 / Zn, CuCl   (E) → Trans

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Doing practice problems is the only way to learn - https://www.chemistrysteps.com/category/organic-chemistry/addition-reactions-of-alkenes/