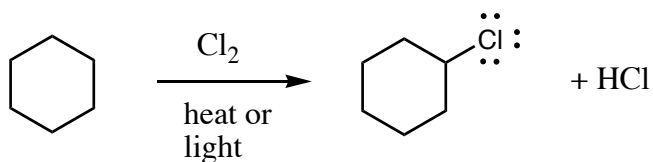


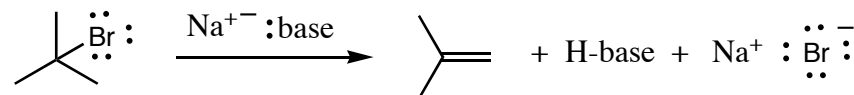
Halogenation of Alkanes - Ch 4, 8



- radical mechanism (write on back of card)
- only works with Cl_2 and Br_2
- usually results in multiple products
 exceptions: when all carbons are the same (as above)
 when one carbon forms a more stable radical (3° , benzyl, or allyl)



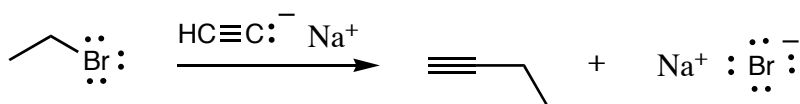
E2 Reaction of Alkyl Halides - Ch 8, 9



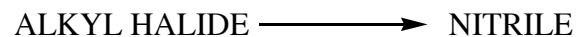
- E2 mechanism (write on back of card)
- only works with 2° and 3° alkyl halides
- with 2° alkyl halides, use $(\text{CH}_3)_3\text{COK}$ to avoid $\text{S}_{\text{N}}2$ reactions
- must have a strong base (usually alkoxide)
- constitutional isomers may form if more than one β hydrogen is available
- anti elimination: when both carbons are stereocenters, only one stereoisomer is formed



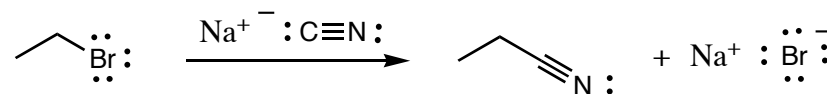
$\text{S}_{\text{N}}2$ Reaction of Alkyl Halides with Acetylide Anions - Ch 8, 11



- $\text{S}_{\text{N}}2$ mechanism (write on back of card)
- alkyl halides must be 1° to avoid E2 reactions
- internal alkynes may be formed by using terminal alkynes which have been deprotonated with NaH or NaNH_2



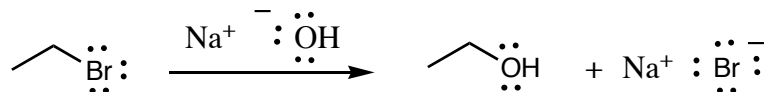
$\text{S}_{\text{N}}2$ Reaction of Alkyl Halides with Cyanide - Ch 8, 22



- $\text{S}_{\text{N}}2$ mechanism (write on back of card)
- alkyl halides must be 1° to avoid E2 reactions

ALKYL HALIDE \longrightarrow ALCOHOL

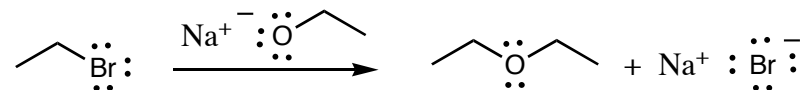
S_N2 Reaction of Alkyl Halides with Hydroxide - Ch 8, 12



- S_N2 mechanism (write on back of card)
- alkyl halides must be 1° to avoid E2 reactions

ALKYL HALIDE, \longrightarrow ETHER
ALCOHOL

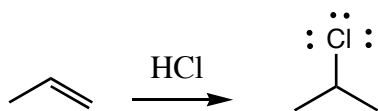
S_N2 Reaction of Alkyl Halides with Alkoxides - Ch 8, 14



- S_N2 mechanism (write on back of card)
- alkyl halides must be 1° to avoid E2 reactions
- alkoxides are formed by reacting alcohols with NaH, Na (methyl, 1°) or K (2°)
- 3° alcohols cannot be used as they are too bulky to react in S_N2 mechanisms

ALKENE \longrightarrow ALKYL HALIDE

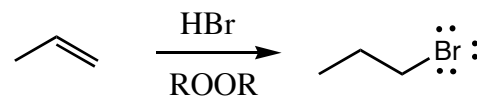
Addition Reaction of HX to an Alkene - Ch 9



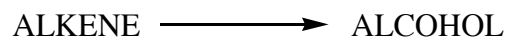
- carbocation mechanism (write on back of card)
- HCl, HBr, and HI may be used
- subject to rearrangements
- halogen goes to the more substituted side of the C=C
- all possible stereoisomers are formed

ALKENE \longrightarrow ALKYL HALIDE

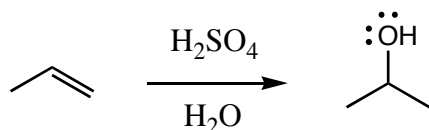
Addition Reaction of HX to an Alkene with Organic Peroxide - Ch 9



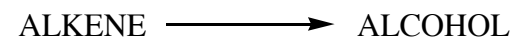
- radical mechanism (write on the back of card)
- only HBr may be used (HCl, HI go by carbocation mechanism)
- not subject to rearrangements
- halogen goes to the less substituted side of the C=C
- all possible stereoisomers are formed



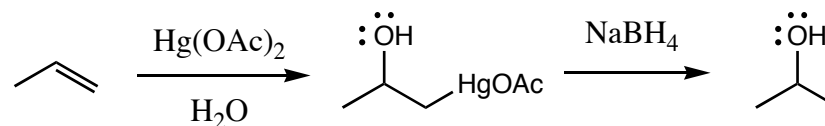
Acid Catalyzed Addition of Water to an Alkene - Ch 9



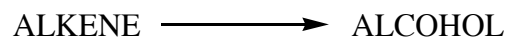
- carbocation mechanism (write on back of card)
- acid is catalytic; it must have a non-nucleophilic conjugate base - phosphoric acid may also be used
- subject to rearrangements
- OH goes to the more substituted side of the C=C
- all possible stereoisomers are formed



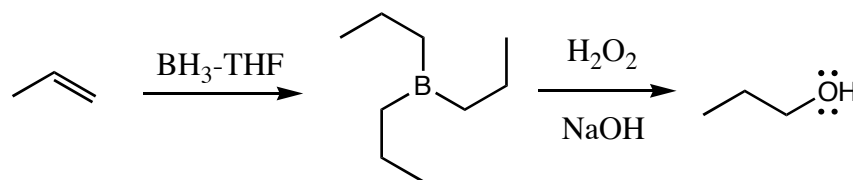
Addition of Water to an Alkene by Oxymercuration-reduction - Ch 10



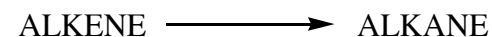
- reaction takes place in two steps
- not subject to rearrangements
- OH goes to the more substituted side of the C=C
- all possible stereoisomers are formed



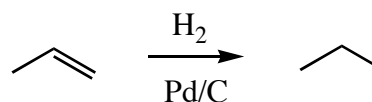
Addition of Water to an Alkene by Hydroboration-oxidation - Ch 10



- reaction takes place in two steps
- only 1/3 equivalent of borane-THF is needed
- not subject to rearrangements
- OH goes to the less substituted side of the C=C
- H and OH are added to the same side (syn addition)



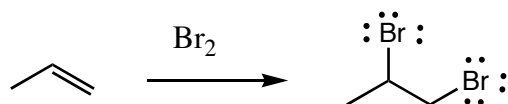
Hydrogenation of an Alkene - Ch 10



- excess hydrogen is always present (all C=C react)
- palladium is catalytic; other metals such as platinum or rhodium may be used
- the metal catalysts are pyrophoric (must be handled with care)

ALKENE \longrightarrow VICINAL DIHALIDE

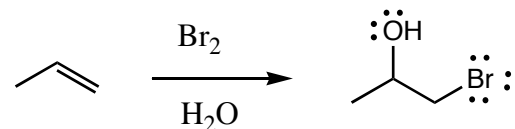
Addition of X_2 to an Alkene - Ch 10, 11



- bromonium ion mechanism (write on back of card)
- Cl_2 , Br_2 , or I_2 may be used
- not subject to rearrangements
- halogens added to opposite sides of the $C=C$ (anti addition)

ALKENE \longrightarrow HALOHYDRIN

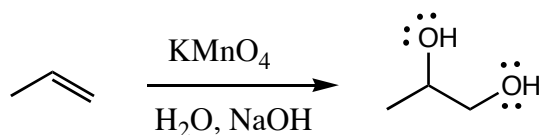
Addition of X and OH to an Alkene - Ch 10



- bromonium ion mechanism (write on back of card)
- Cl_2 , Br_2 , or I_2 may be used
- not subject to rearrangements
- OH goes to the more substituted side of the $C=C$
- OH and X added to opposite sides of the $C=C$ (anti addition)

ALKENE \longrightarrow VICINAL DIOL

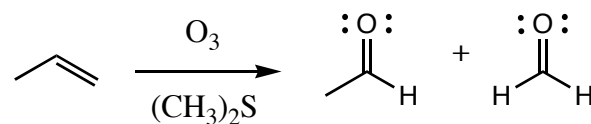
Addition of OH to Both Sides of an Alkene - Ch 10



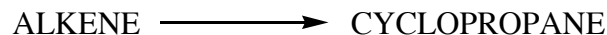
- product is also called a glycol
- OsO_4 , H_2O_2 may also be used (fewer side reactions)
- not subject to rearrangements
- OH 's are added to the same side of the $C=C$ (syn addition)

ALKENE \longrightarrow ALDEHYDE, KETONE, or $COOH$

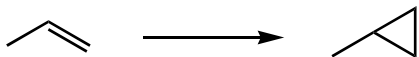
Cleavage of an Alkene by Ozonolysis - Ch 10, 17, 20



- formation of aldehyde or ketone depends on how many C 's are attached to each C of the $C=C$
- when hydrogen peroxide is used in place of dimethyl sulfide, aldehydes are oxidized to carboxylic acids
- cyclic alkenes give dicarbonyl compounds
- if both sides are identical, only one product is formed



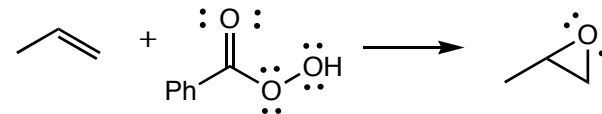
Addition of a Carbene to an Alkene to form a Cyclopropane - Ch 10



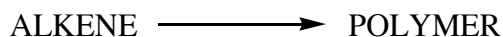
- reagents: 1) CH_2N_2 (diazomethane), heat
carbene mechanism (write on back of card)
- 2) CH_2I_2 , Zn/Hg (Simmons-Smith reaction)
gives fewer side products
- 3) CHCl_3 , $(\text{CH}_3)_3\text{COK}$
carbene mechanism (write on back of card)
two of the halogens remain attached
- not subject to rearrangements
- new carbon is added to the same side of the $\text{C}=\text{C}$
(syn addition; "cis stays cis & trans stays trans")



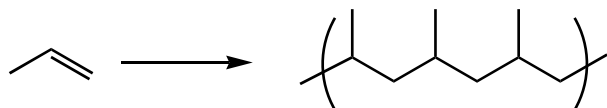
Addition of Oxygen to an Alkene to form an Epoxide - Ch 10



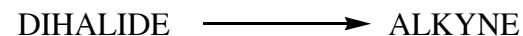
- reagent is a peroxy acid and may be abbreviated PhCO_3H
- not subject to rearrangements
- oxygen is added to the same side of the $\text{C}=\text{C}$
(syn addition; "cis stays cis & trans stays trans")



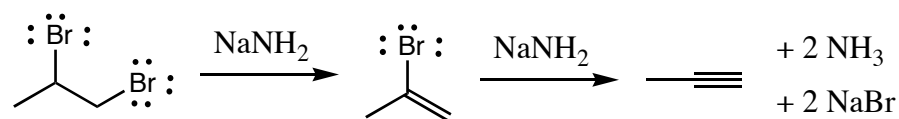
Addition of an Alkene to Another Alkene to form a Polymer - Ch 10



- reagents: 1) H_2SO_4
carbocation mechanism (write on the back of card)
- 2) ROOR , light or heat
radical mechanism (write on the back of card)
- carbocation mechanism is subject to rearrangements, radical mechanism is not
- all possible stereoisomers are formed



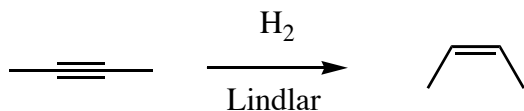
Double Elimination of a Dihalide to form an Alkyne - Ch 11



- vicinal or geminal dihalides can be used in this reaction
- a much stronger base (NaNH_2) is needed for the elimination of the vinyl halide
- KOH may also be used if the temperature is increased to 200°K
- cumulated alkenes may form, but alkynes will predominate
- if a terminal alkyne is formed, water is needed to protonate the acetylide ion that forms in the presence of the base

ALKYNE \longrightarrow CIS ALKENE

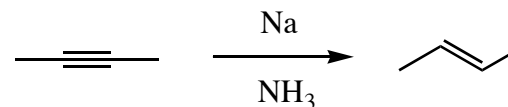
Hydrogenation of an Alkyne to form a Cis Alkene - Ch 11



- Lindlar catalyst contains Pd/BaSO₄, quinoline and/or lead acetate
- H's are added to the same side of the triple bond
- only way to make the cis alkene exclusively

ALKYNE \longrightarrow TRANS ALKENE

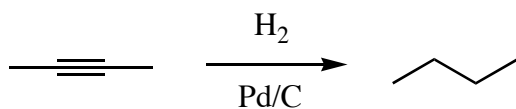
Reduction of an Alkyne to a Trans Alkene - Ch 11



- radical mechanism (write on back of card)
- good way to make trans alkenes exclusively

ALKYNE \longrightarrow ALKANE

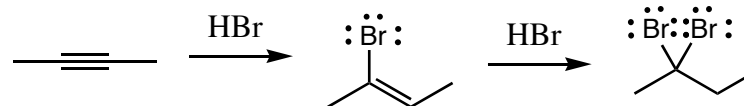
Hydrogenation of an Alkyne to an Alkane - Ch 11



- cannot be stopped at the alkene stage with these reagents

ALKYNE \longrightarrow VINYL HALIDE or DIHALIDE

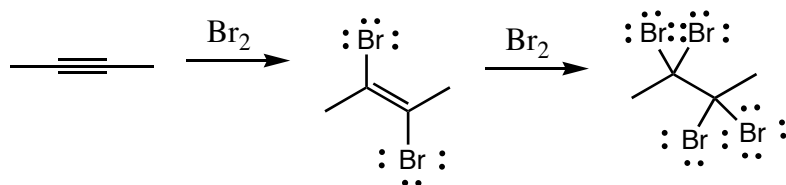
Addition of 1 or 2 eq of HX to an Alkyne - Ch 11



- HCl, HBr, and HI can be used
- halogen goes to the more substituted side of terminal alkynes unless ROOR is added
- both halogens are added to the same carbon
- anti addition is usually observed (X and H are trans)

ALKYNE \longrightarrow VINYL DIHALIDE or TETRAHALIDE

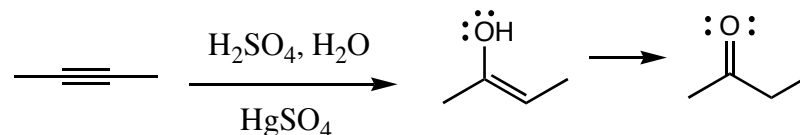
Addition of 1 or 2 eq of X_2 to an Alkyne - Ch 11



- Cl_2 , Br_2 , or I_2 may be used
- anti addition is usually observed (X's are trans)

ALKYNE \longrightarrow KETONE

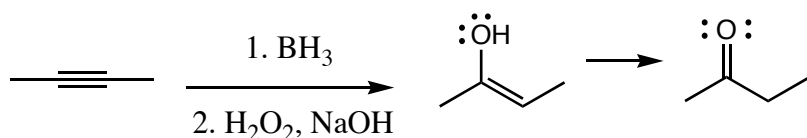
Addition of Water to an Alkyne (Hydration) - Ch 11



- $NaBH_4$ is not needed (unlike alkene reaction)
- an enol is initially formed; it tautomerizes to a ketone
- the OH (then $C=O$) goes to the more substituted side
- if the alkyne is not symmetrical, two products are formed

ALKYNE \longrightarrow ALDEHYDE or KETONE

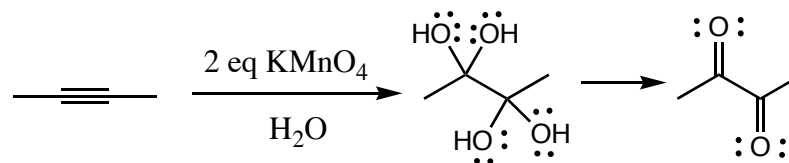
Addition of Water to an Alkyne (Hydration) - Ch 11



- terminal alkynes require a sterically hindered borane such as disiamyl borane or dicyclohexyl borane
- an enol is initially formed; it tautomerizes to a $C=O$ the OH (then $C=O$) goes to the less substituted side
- terminal alkynes form aldehydes; internal alkynes form ketones
- if the alkyne is not symmetrical, two products are formed

ALKYNE \longrightarrow DIKETONE

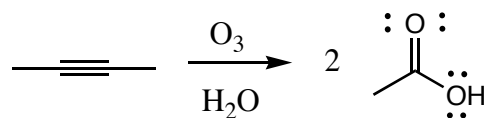
Oxidation of an Alkyne to form a Diketone - Ch 11



- tetraol is initially formed; hydrates equilibrate to $C=O$'s
- reaction must be kept cool and neutral, or the the diketone may react further

ALKYNE \longrightarrow 2 COOH'S

Cleavage of an Alkyne by Ozonolysis - Ch 11



- no dimethyl sulfide or hydrogen peroxide is needed
- unsymmetrical alkynes give two products