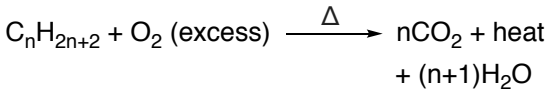
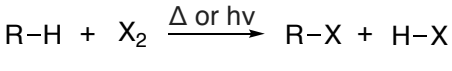
Reactions of Alkanes

Combustion of alkanes



— Without heat, no reaction

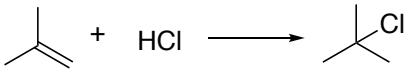
Radical Halogenation



— R = alkyl
— X = Cl, Br

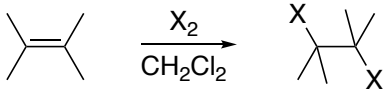
Reactions of Alkenes

Addition of HX



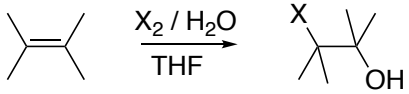
— X = Cl, Br, I
— Via carbocation
— Markovnikov orientation

Addition of Halogens (X_2)



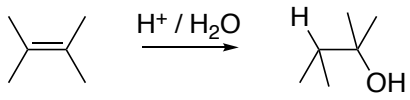
— X = Br_2, Cl_2, also ICl or BrCl
— Halonium ion intermediate
— Trans product

Halohydrin formation



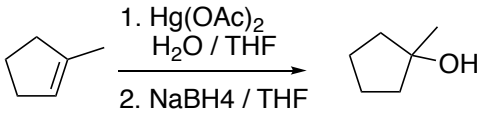
— X = Br_2, Cl_2, I_2
— Trans product
— Modification: NBS/H_2O/solvent (or NCS orv8u NIS)
— Can use nucleophiles besides H_2O (R-OH, R-CO_2H)

Addition of Water



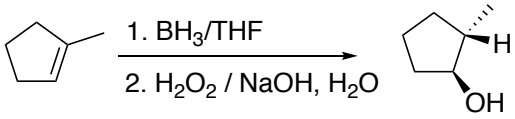
- Acid catalyst
- Nucleophiles besides H_2O (i.e. MeOH, H_2S, etc.)

Oxymercuration-Demurcuration



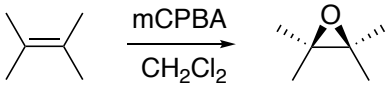
- Mercurinium ion intermediate
- No carbocation rearrangement
- Uses water to make alcohols
- Uses alcohols (R-OH) to make ethers

Hydroboration (no mechanism)



- Anti-markovnikov
- Syn addition of H_2O

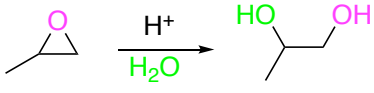
Epoxidation



- Stereoselective if starting material has steric hindrance
- Concerted addition of mCPBA

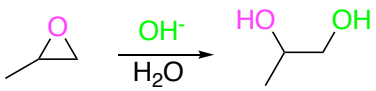
Ring-opening of epoxides

Acidic



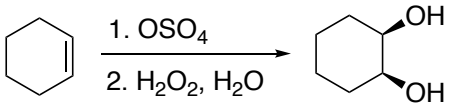
- Step 1: protonate O
- Step 2: nucleophilic attack
- Diol product

Basic



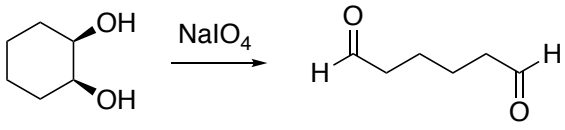
- Step 1: nucleophilic attack at less hindered carbon
- Step 2: protonate O
- Diol product

Hydroxylation



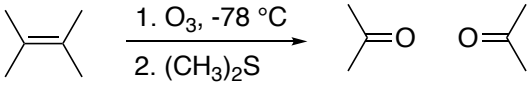
- Cis 1,2-diol

Oxidative cleavage (no mechanism)



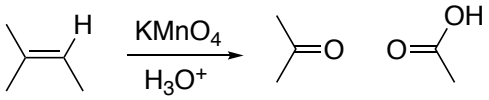
- Aldehyde
- Concerted decomposition

Ozonolysis (no mechanism)

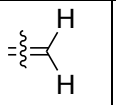
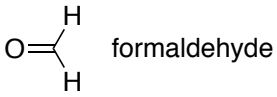
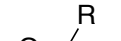
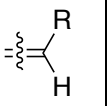
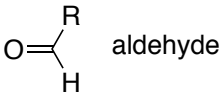
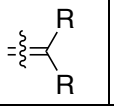
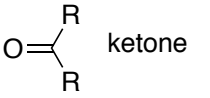
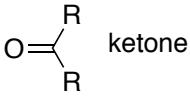


- Break double bond, insert carbonyl
- End groups stay the same

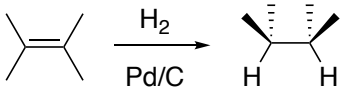
Vigorous oxidation (no mechanism)



- Break double bond, insert carbonyl
- End Hs get oxidized

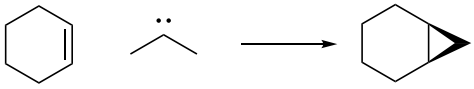
	Ozonolysis	Vigorous Oxidation
	 formaldehyde	 carbon dioxide
	 aldehyde	carboxylic acid
	 ketone	 ketone

Hydrogenation



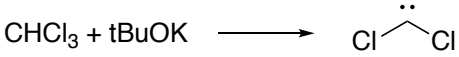
— Reduction to alkane
— Syn addition of H_2

Addition of Carbenes (no mechanism)

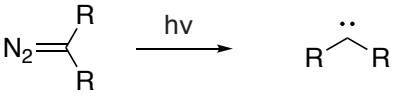


— Highly reactive
— Neutral
— Unfilled octet

Generating Carbenes (no mechanism)

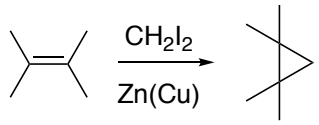


— Dichlorocarbene only



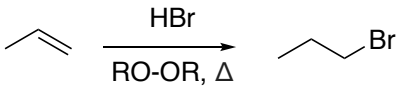
— More generalizable

Simmons-Smith cyclopropanation (no mechanism)



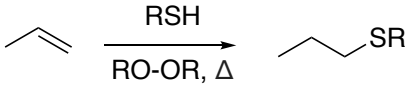
— No carbene intermediate

HBr/peroxides



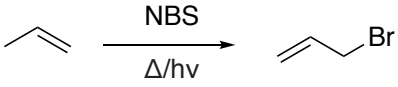
— Anti-Markovnikov
— Only HBr, not HI or HCl
— Radical mechanism

Thiol-ene reaction



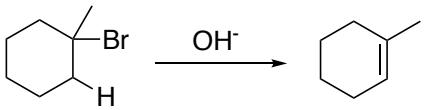
— Anti-Markovnikov addition of SR
— Radical mechanism

Allylic Bromination (no mechanism)

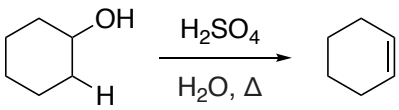


— Radical mechanism
— Electrons from C-H bond instead of double bond

Forming alkenes



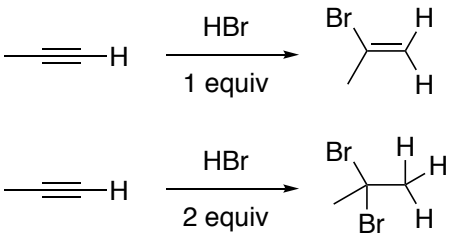
— Elimination
— More substituted C=C



— Elimination of H_2O
— Need heat

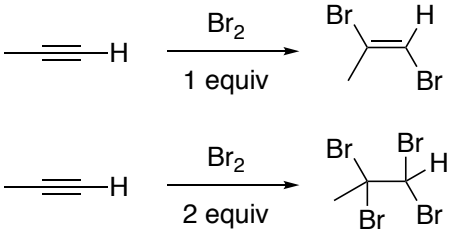
Reactions of Alkynes

Addition of HX to alkynes



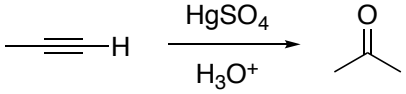
— Markovnikov addition
— Similar to alkenes
— Carbocation stability

Addition of X_2 to alkynes



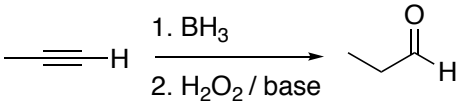
— Trans addition
— Similar to alkenes

Addition of H_2O via oxymercuration



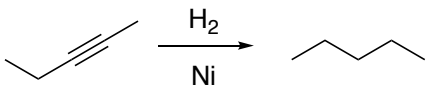
— Ketone generation
— Keto-enol tautomerization (acidic)
— No analogous demurcuration step

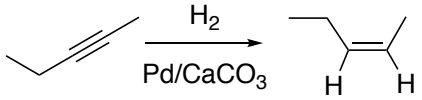
Hydroboration of alkynes (no mechanism)



— Aldehyde generation
— Tautomerization (basic)

Addition of H_2 (using a catalyst) (no mechanism)

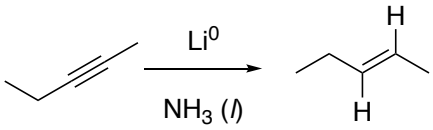




- Catalyst: Ni, Pt, Pd, PtO
- Reduced to alkane
- No reaction without catalyst

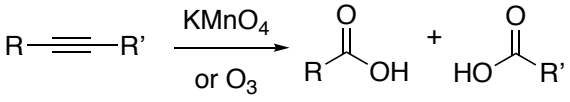
- Lindlar's catalyst
- Z isomer (Hs add cis)

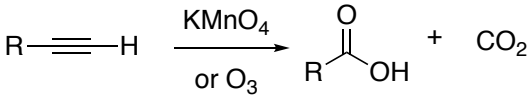
Dissolving metal reduction (no mechanism)



- E isomer (Hs add trans)

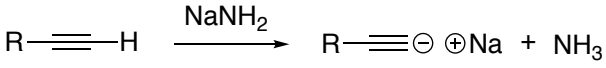
Oxidative cleavage (no mechanism)

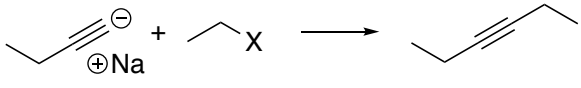


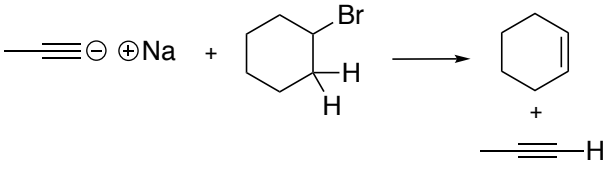


- Break alkyne to form carboxylic acids

Alkynes as nucleophiles

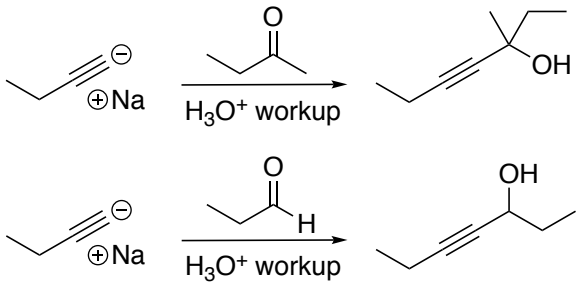






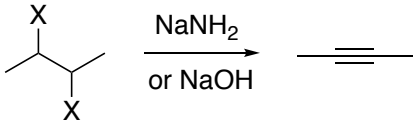
- Can act as a nucleophile with 1° alkyl halides
- Acetylides can act as a base with 2° and 3° R-X

Acetylides with carbonyl compounds

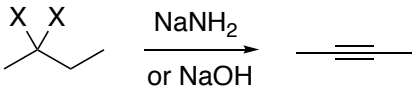


— First form acetylide
— Need acidic workup

Synthesis of alkynes

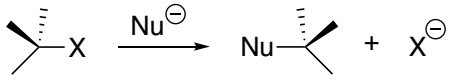


— Dehydrohalogenation of vicinal dihalides



— Dehydrohalogenation of geminal dihalides

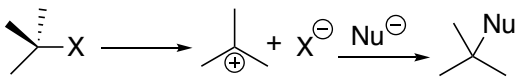
S_N2



X = leaving group

— 1 step process
— Bimolecular RDS
— Backside attack
— Inversion of stereochem
— Filled orbital of nucleophile interacts with antibonding orbital on carbon

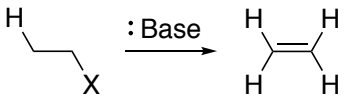
S_N1



X = leaving group

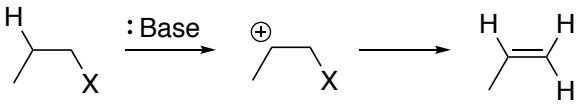
— 2 step process
— Unimolecular RDS
— Carbocation planar intermediate
— Filled orbital of nucleophile interacts with antibonding orbital on carbon

E2



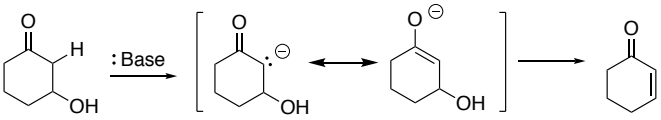
— 1 step process
— Bimolecular RDS
— Antiperiplanar H and LG

E1



— 2 step process
— Unimolecular RDS (carbocation)
— No antiperiplanar requirement
— Selectivity: E > Z, Saytzeff product

E1cB

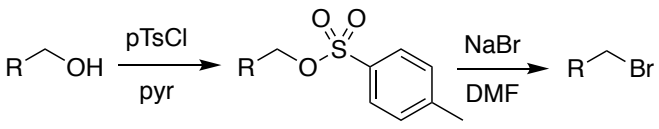


— 2 step process
— Resonance stabilized carbanion
— Carbanion adjacent to C=O, poor LG

Reactions of Alcohols

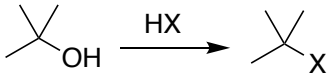
Forming alkyl halides

From alcohols via S_N2



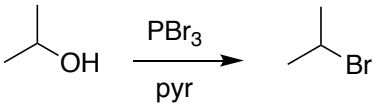
— Make O a better leaving group
— Can use any nucleophile for S_N2 step
— 1° or 2° alcohols

From alcohols by protonation



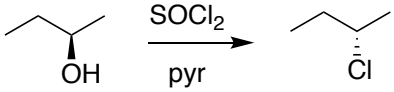
- Make O a better leaving group
- S_N1 mech
- 3° alcohols, allylic, benzylic

From alcohols using PX_3 via S_N2



- PCl_3, PBr_3, $P+I_2$
- ROH = $-CH_3$ > 1° > 2°
- Make O a better LG

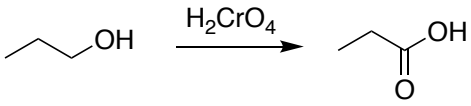
From alcohols using $SOCl_2$



- Net S_N2 process
- ROH = 1°, 2°
- Make O a better LG

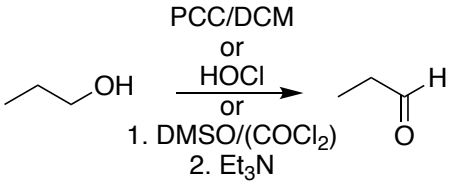
Oxidation of alcohols

Vigorous oxidation



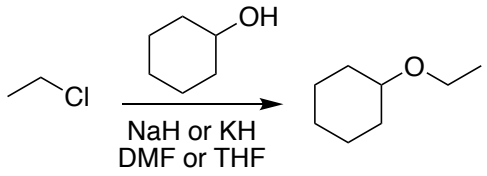
- 1° → carboxylic acid
- 2° → ketone
- 3° → no reaction

Mild oxidations



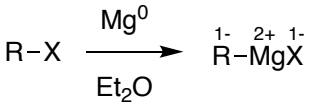
- 1° → aldehyde
- 2° → ketone
- 3° → no reaction
- DMSO/($COCl_2$)/Et_3N = Swern oxidation

Willamson-Ether Synthesis

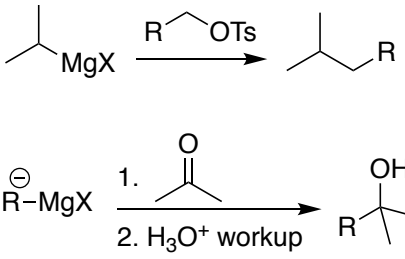


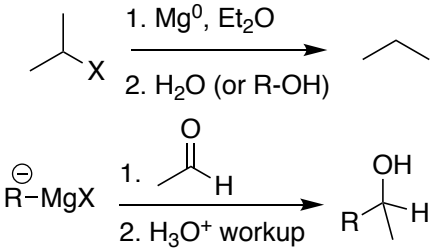
- 1° R-X, ok for 2°
- Strong base
- Aprotic polar solvent
- S_N2-like mechanism

Grignard Reagents



- Organometallic compounds
- R = 1°, 2°, 3° RX, alkenyl, aryl, benzylic
- X = Cl, Br, I
- Makes alkanes

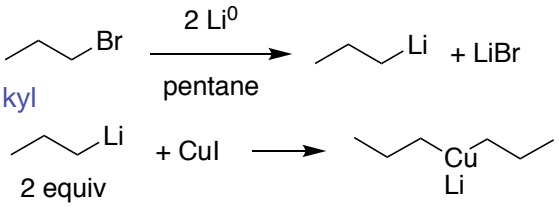




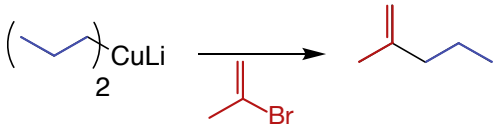
Gilman Reagents

R-X for organometallic reagent

R =
Methyl
Primary Alkyl
Aryl
Vinyl
Allyl



- 2 steps

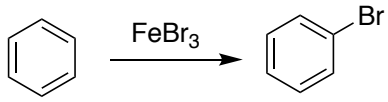


R'-X for coupling reaction

R' =
Methyl
Primary Alkyl
Aryl
Vinyl
Allyl

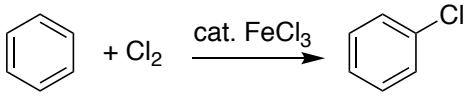
Electrophilic Aromatic Substitution

Bromination of Benzene



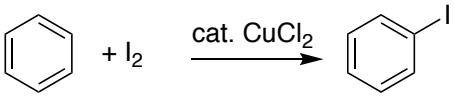
- Br activated as a good electrophile
- RDS = breaking aromaticity
- Resonance stabilized carbocation

Chlorination of Benzene



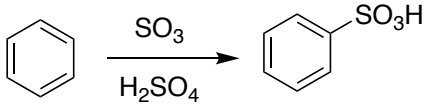
- Same mechanism as bromination

Iodination of Benzene



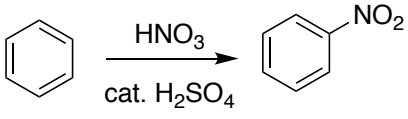
- Same mechanism as bromination

Sulfonation of Benzene



- SO_3 activated as a good electrophile

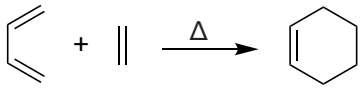
Nitration of Benzene



- NO_2 activated as a good electrophile

Pericyclic Reactions

Diels Alder



- [4+2] cycloaddition
- diene: s-cis
- EWG on dienophile increases reactivity
- Endo product preferred