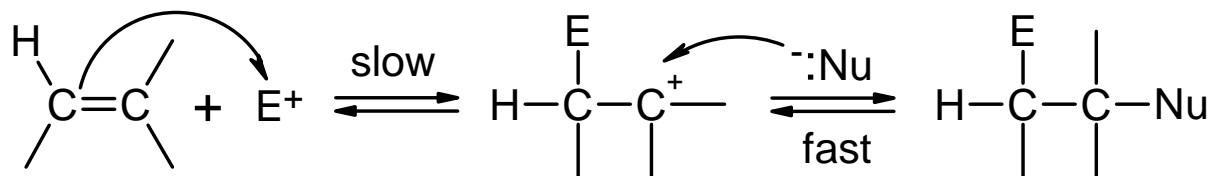


Chapter 11 (Electrophilic) Addition Reactions

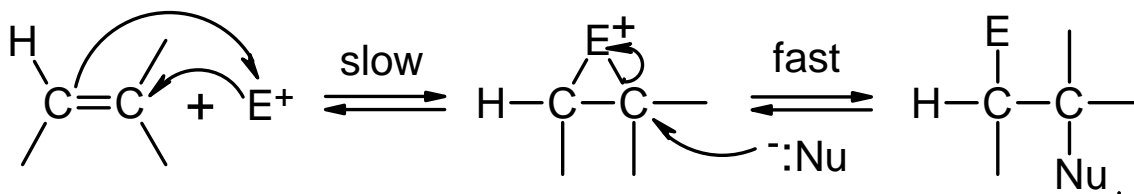
□ What to master

- ◆ Predicting the Products of Addition Reactions of Alkenes: Mechanism, Regiochemistry & Stereochemistry
- ◆ Predicting the Products of Addition Reactions of Alkynes: Mechanism, Regiochemistry & Stereochemistry
- ◆ Recognizing When Rearranged Products Occur
- ◆ Predicting How the Rate of Addition Varies with Structure
- ◆ Predicting the Addition Products of Conjugated Dienes
- ◆ Using Addition Reactions to Synthesize Target Compounds

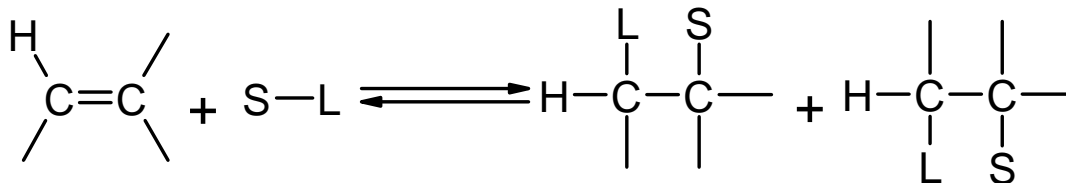
Chapter 11 (Electrophilic) Addition Reactions



regioselective
non-stereoselective



regioselective
stereoselective



regioselective
stereoselective
(concerted)

Addition of Hydrogen Halides: Halides

□ hydrogen halides: $\text{H}^+\text{-X}^-$; [📖 406 bottom](#)

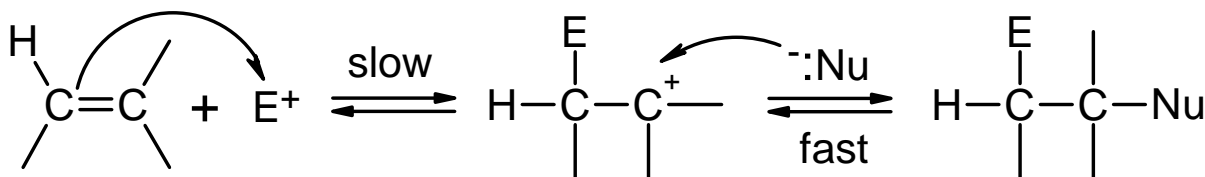
◆ unsymmetrical alkenes: regioselectivity, [📖 407 top](#)

○ Markovnikov's rule: mechanism, [📖 408 top](#) & [📖 408-9](#)

◆ non-stereoselective & rearrangement: [📖 410](#) & [411](#)

◆ alkynes: monohaloalkenes and dihaloalkanes, [📖 411 mid](#)

◆ *practice*: [📖 409-412 Practice 11.1](#), [Problems 11.3](#) & [11.4](#)



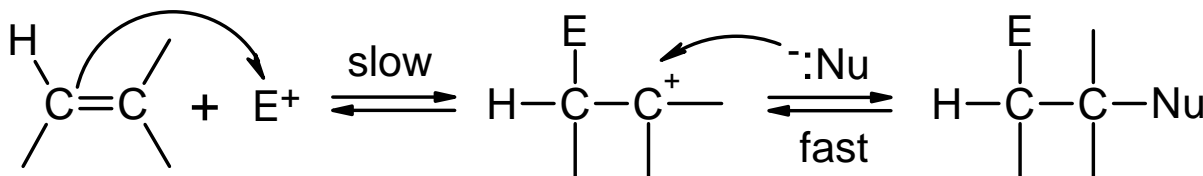
Addition of Water (Hydration): Alcohols

□ non-nucleophilic strong acid in H₂O: [📖 412 bottom](#)

◆ non-stereoselective & rearrangement: [📖 412 & 413](#)

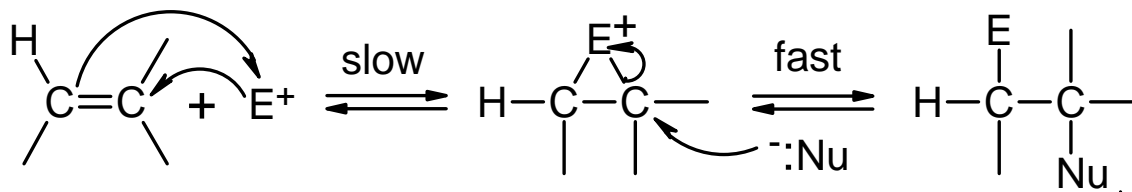
○ the exact reverse of E1 for acid-catalyzed dehydration

◆ *practice*: [📖 413 Problems 11.5 & 11.6](#)



Addition of Halogen (Cl₂/Br₂): 1,2-Dihalides

- dihaloalkanes: unsaturation test (Br₂), [📖 414 top](#)
- ◆ bromonium ion intermediate: concerted; [📖 415 Figure 11.1](#)
 - stereospecific anti attack of Br⁻ (S_N2) at the more substituted carbon (S_N1) but racemates: [📖 416 Fig. 11.2](#) & [📖 417 Fig. 11.3](#)
- ◆ relative rates of alkenes: [📖 417 Table 11.1](#)
- ◆ **alkynes**: *trans*-dihaloalkenes, [📖 418 middle](#)
- ◆ *practice*: [📖 418-9 Problems 11.7, 11.8 & 11.9](#)



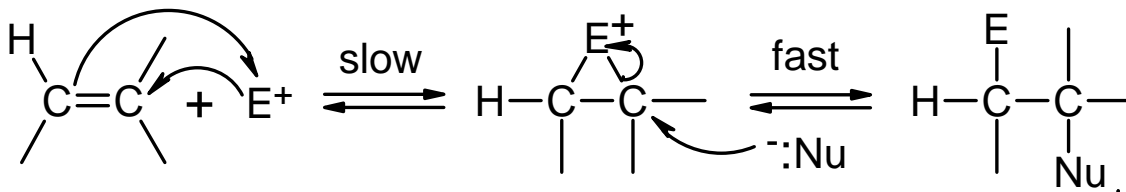
Formation of Halohydrins: β -Haloalcohols

□ Halonium attacked by H_2O (solvent): [📖 419](#)

◀ ◆ stereospecific & regioselective: $\text{S}_{\text{N}}2$ (anti) & $\text{S}_{\text{N}}1$ (more stable C^+); [📖 420 Figure 11.4](#)

◆ industrial applications: epoxide (EO), MTBE; [📖 422](#)

◆ *practice*: [📖 421 Practice 11.3](#), [📖 421 Problems 11.10 & 11.11](#)



Oxymercuration-Reduction: Alcohols

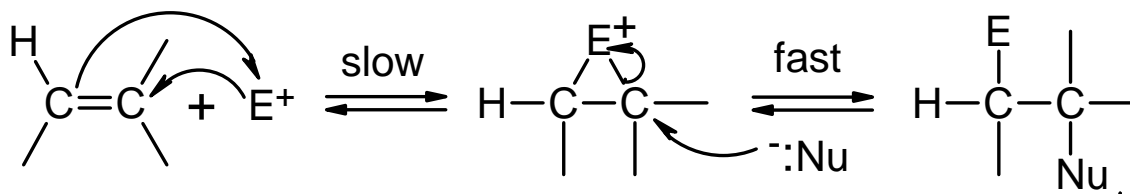
□ Selective hydration:  [423-4](#) [Figure 11.5](#)

◆ $\text{Hg}(\text{OAc})_2$ in H_2O followed by NaBH_4 reduction








◆ no rearrangement: Markovnikov product,  [423 bottom](#)

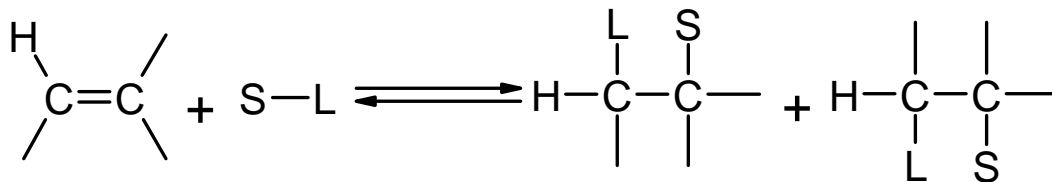
◆ **alkynes**: ketones - tautomer of enol;  [424-5](#) [Fig. 11.6](#)

◆ *practice*:  [425-6 Problems 11.13 & 11.14](#)



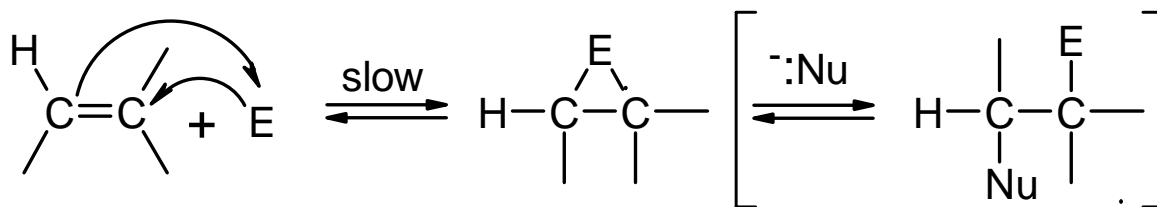
Hydroboration-Oxidation: Alcohols

- anti-Markovnikov hydration: concerted;  [426-7](#) [Fig. 11.7](#)
- ◆ borane: $\text{BH}_3 \equiv \text{H}_2\text{B}^{\delta+}-\text{H}^{\delta-}$, $[(\text{BH}_3)_2/\text{BH}_3 \cdot \text{THF}]$;  [426-7](#)
- ◆ regioselectivity: B to the less hindered carbon,  [428](#) [Fig. 11.8](#)
- ◆ **alkynes**: ketones / aldehydes;  [430](#) & [431-2](#)
 - monohydroboration of terminal alkynes: aldehyde with $\text{R}_2\text{B-H}$
- ◆ asymmetric hydroboration: chiral borane;  [433](#) [Focus On](#)
- ◆ *practice*:  [429](#) & [432](#) [Practice 11.4](#) & [11.5](#);  [429-432](#)
[Problems 11.15](#), [16](#), [17](#), [18](#), [19](#)



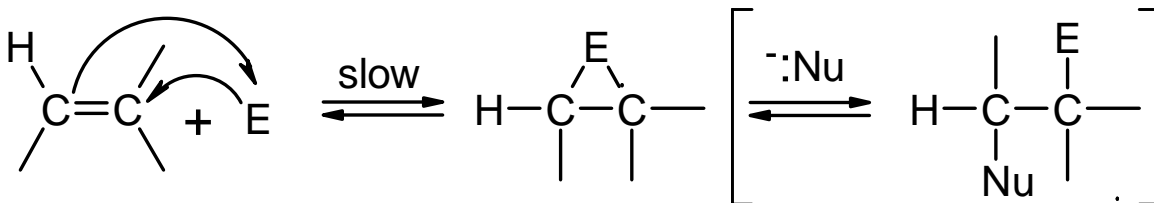
Addition of Carbenes: Cyclopropanes

- Reactive electrophile & neutral: $R_2C:$, [📖 435 bottom](#)
 - ◆ concerted reactions: [stereospecific formation](#) of cyclopropane
 - ◆ how to make carbenes: in-situ formation
 - diazomethane (CH_2N_2) & heat/light/ Cu^{2+} : [📖 436 top & middle](#)
 - α -elimination of haloform: CHX_3 & base; [📖 436 bot & 437 top](#)
 - carbenoid: CH_2I_2 & $Zn(Cu)$, (Simmons-Smith reaction); [📖 437 mid](#)
 - ◆ *practice*: [📖 437 Problem 11.22](#)



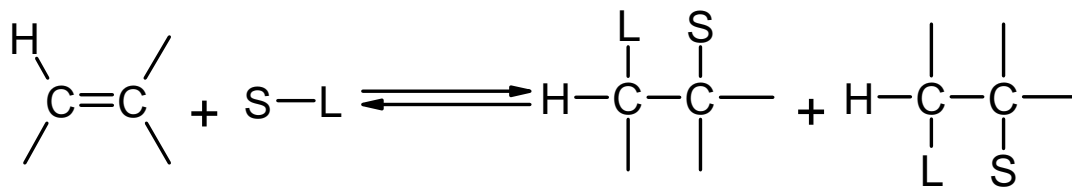
Epoxidation (Addition of Oxygen Atom)

- per(oxy)carboxylic acids as electrophilic oxygen atoms
 - ◆ concerted mechanism: stereospecific; [📖 438 middle & top](#)
 - ◆ other peroxyacids & reactions: [📖 438 bottom & 439 top](#)
 - ◆ *practice*: [📖 439 Problem 11.23](#)



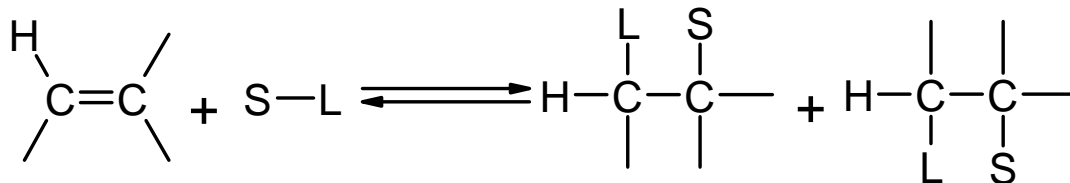
Dihydroxylation (Addition of Diols)

- addition of OsO_4 (KMnO_4) with Na_2SO_3 (NaOH in H_2O)
 - ◆ concerted addition: *syn*-1,2-diols; [📖 439 bottom & 440 top](#)
 - ◆ KMnO_4 & catalytic osmylation: [📖 440 middle & bottom](#)
 - ◆ *practice*: [📖 440 Problem 11.24](#)



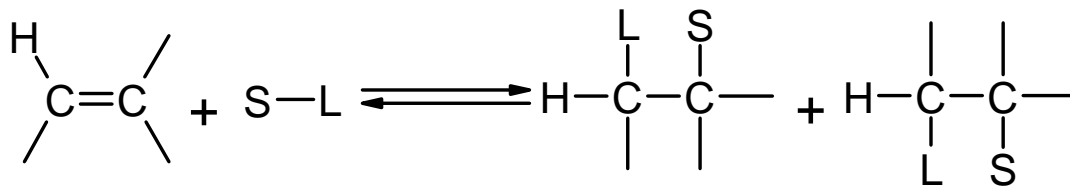
Ozonolysis (Addition of Ozone & Cleavage)

- ozone as a 1,3-dipole: $^-O-O-O^+$; [📖 441 bottom](#)
- ◆ concerted addition (pericyclic reactions): ozonides
- ◆ reductive cleavage with Me_2S : ketone/aldehyde; [📖 441-2](#)
- ◆ structural identification: C_5H_{10} ; [📖 443 top](#)
- ◆ *practice*: [📖 443 Prac. 11.6](#), [📖 442-3 Problems 11.26 & 27](#)



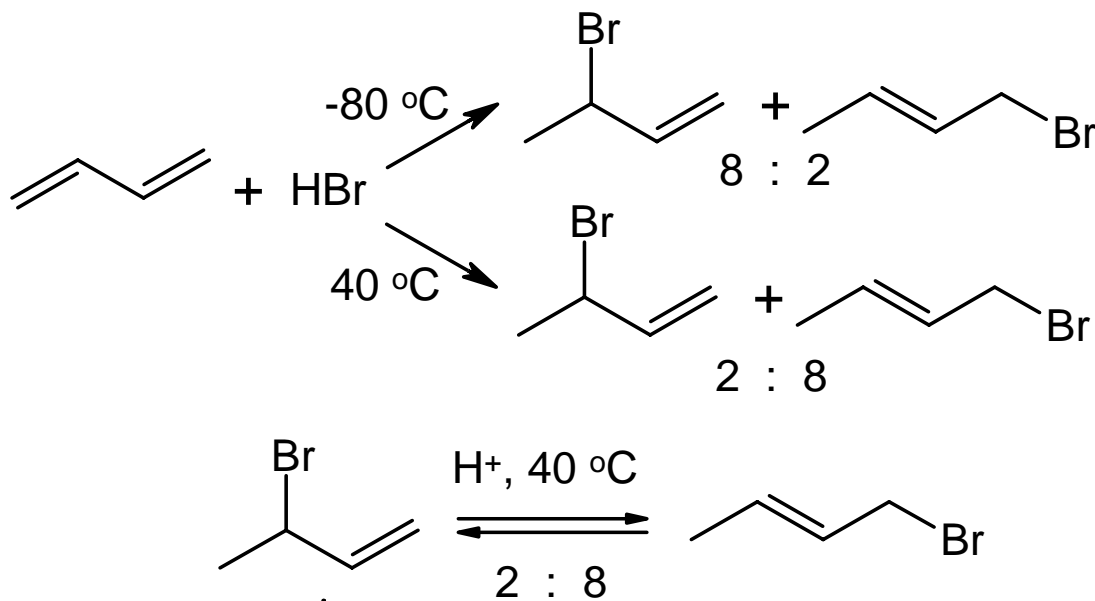
Catalytic Hydrogenation (Addition of H₂)

- Activation with heterogeneous catalysts: [📖 444 Fig. 11.9](#)
 - ◆ cleavage of H—H & π -bond of alkene: **generally syn addition**
 - ◆ alkenes & alkynes: more reactive than arenes & carbonyls (ketones, esters, carboxylic acids, aldehydes); [📖 445 middle](#)
 - ◆ partial reduction of alkynes: Lindlar catalyst; [📖 445 bottom](#)
 - ◆ asymmetric hydrogenation: chiral ligands; [📖 449-50 Focus On](#)
 - ◆ *practice*: [📖 446 Problem 11.28](#)



Addition to Conjugated Dienes

- 1,2- vs 1,4-addition: [📖 446 middle](#)
 - ◆ unstable carbocations with other additions: [📖 447](#)
- kinetic vs thermodynamic products: [📖 448 Fig. 11.10](#)



Synthetic Planning of Target Materials

- Retrosynthetic analysis: backward; [📖 451 top](#)
- ◆ synthesis of *Z*-alkene from acetylene: [📖 451 middle](#)
- ◆ synthesis of 2-heptanone from acetylene: [📖 451 bottom](#)
 - a retrosynthesis & a synthetic scheme: [📖 451 bottom](#) & [452 top](#)
- ◆ *meso*-2,3 butanediol from a starting compound with not more than 3 carbons: [📖 452 top](#)
- ◆ *practice*: [📖 452](#) & [453](#) Problem 11.31

공부하는 방법

“그저 익숙하도록 읽는 것뿐이다. 글을 읽는 사람이, 비록 글의 뜻은 알았으나, 만약 익숙하지 못하면 읽자마자 곧 잊어버리게 되어, 마음에 간직할 수 없을 것은 틀림없다.

이미 읽고 난 뒤에, 또 거기에 자세하고 익숙해질 공부를 더한 뒤라야 비로소 마음에 간직할 수 있으며, 또 흐뭇한 맛도 있을 것이다.” - 퇴계 이황 (금장태 著)

