

# Chapter 5. Polar Addition & Elimination Reactions

- Reverse of one another: [📖 473 bottom](#)
  - ◆ hydration of alkenes & dehydration of alcohols: [📖 474 top](#)
  - ◆ microscopic reversibility: identical reaction pathways; **intermediates & TS for either reaction**; [📖 475 Fig. 5.1](#)
- Polar addition: generalized mechanisms
  - ◆ **kinetics, regioselectivity & stereochemistry**
  - ◆ bimolecular electrophilic additions:  $\text{Ad}_{\text{E}2}$ ; [📖 475 bottom](#)
    - carbocation formation free of  $\text{Y}^-$  or as an intimate ion pair
    - a bridged cationic intermediate: *anti*
  - ◆ termolecular electrophilic addition:  $\text{Ad}_{\text{E}3}$ ; [📖 476 top](#)
    - concerted transfer of  $\text{E}^+$  &  $\text{Y}^-$ : *anti*

## ❖ Addition of Hydrogen Halides (I)

□ Regioselectivity: Markovnikov's rule; [📖 477 mid.](#)

◆ more stable carbocation: HX; **TS resembles RDS**

○ order of reactivity: HI > HBr > HCl

○ anti-Markovnikov addition: HBr; **radical mechanism**

□ kinetics of HBr/HCl addition to isolated alkenes

◆ rate =  $k[\text{alkene}][\text{HX}]^2$ , Ad<sub>E</sub>3, *anti* addition: [📖 478 & 479](#)

○ temp. & solvent-dependent: mostly *syn* at -78 °C in CH<sub>2</sub>Cl<sub>2</sub>

◆ kinetics of HBr/HCl addition to aryl conjugated alkenes

○ rate =  $k[\text{alkene}][\text{HX}]$ , Ad<sub>E</sub>2, *syn* addition: [📖 479 middle](#)

◆ conjugated dienes: 1,2-addition via ion-pair; [📖 481 top](#)

○ thermodynamic stability: aryl conjugation; [📖 481 middle](#)

## ❖ Addition of Hydrogen Halides (II)

- Rearranged products: [📖 480 top](#)
  - ◆ discrete & faster formation of more stable carbocations
    - by hydride or alkyl shift:  $A_{\text{D}}\text{E}3$  mechanism: [📖 480 middle](#)
  - ◆ HX with norbornene: *exo* isomer; [📖 481 bottom](#)
    - HBr: ~50% rearranged product; symmetrical bridged ion
    - HCl: unequal distribution of isomers; faster ion-pair collapse before the bridged ion achieves symmetry; [📖 482 top](#)
- Salt effect: increased C-X bond; LiBr,  $\text{Bu}_4\text{N}^+\text{Cl}^-$ 
  - ◆ competing reactions in nucleophilic solvents: [📖 480 bottom](#)

## ❖ Acid-Catalyzed Hydration

- The more highly substituted alcohol: [📖 483 middle](#)
  - ◆ general acid catalysis: RDS is the protonation step
    - normal solvent isotope effect:  $k_{\text{H}_2\text{O}/\text{D}_2\text{O}} = 2\sim 4$
    - $\sigma^+$ : R=Ar & increased rate with an ERG; [📖 484 Table 5.1](#)
    - no  $^2\text{H}$  loss or exchange at the early stage: [📖 483 top](#)
  - ◆ the nature of carbocation depends on the solvent: [📖 484](#)
    - weaker acid (acetic acid-HBr):  $\text{Ad}_{\text{E}}3$  & stereospecific *anti*; via an alkene-acid complex
    - stronger acid (triflic acid):  $\text{Ad}_{\text{E}}2$  & not stereospecific; formation of discrete carbocation intermediates ([rearrangement](#))
  - ◆ related reactions: hydrolysis of enol ethers; [📖 485 middle](#)

## ❖ Addition of Halogens (I)

□  $\text{rate} = k_1[\text{olefin}][\text{Br}_2] + k_2[\text{olefin}][\text{Br}_2]^2 + k_3[\text{olefin}][\text{Br}_2][\text{Br}^-]$

◆ in MeOH & excess Br<sup>-</sup>:  $k_3$ , [Br<sub>2</sub>] complex; [📖 486 top](#)

◆ in nonpolar solvents:  $k_1$  &  $k_2$ , [📖 486 bottom](#)

○ plausible 2nd order & 3rd order mechanisms

◆ styrenes:  $\rho = -4.8$  with  $\sigma^+$  constants; highly ionic TS

◆ reversibility of the bromonium ion: [📖 491 top](#)

◆ summary of the bromination mechanism: [📖 492 top](#)

□ Chlorination:  $\text{rate} = k[\text{olefin}][\text{Cl}_2]$ ; [📖 487 Table 5.2](#)

◆ larger increase in reactivity with more substituted alkenes

◆ competitive elimination of H<sup>+</sup> after migration: **greater positive charge due to weaker bridging by chlorine**; [📖 494 top](#)

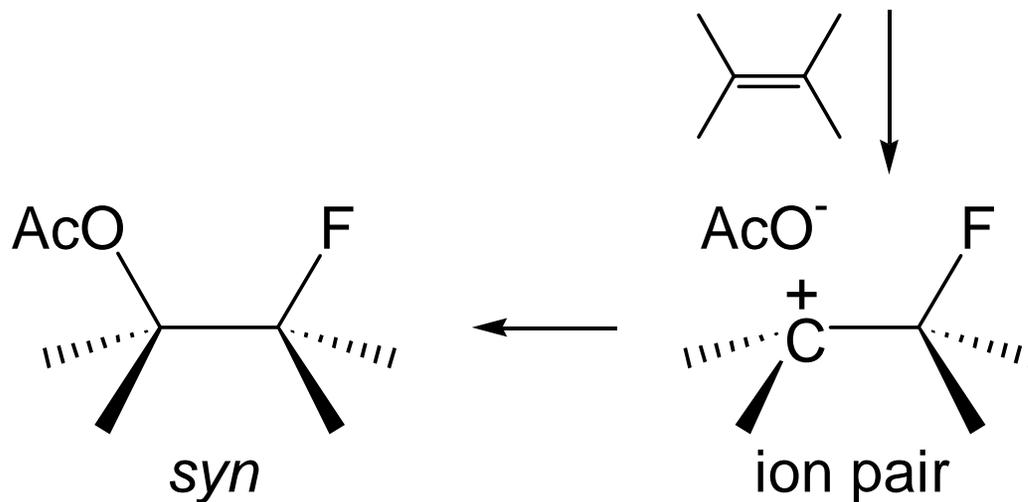
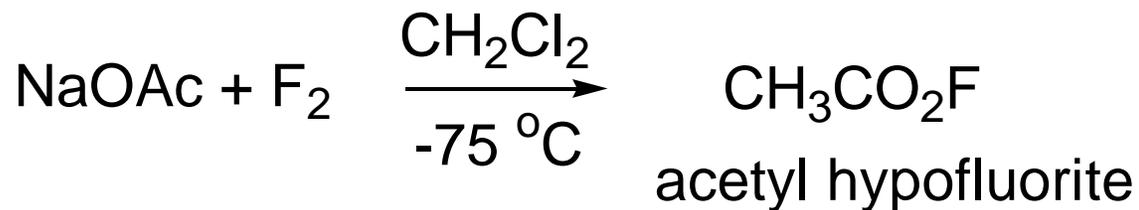
## ❖ Addition of Halogens (II)

- Stereochemistry: *anti* vs *syn*;  488 [Table 5.3](#)
- ◆ Br<sub>2</sub>: [bridged ion vs ion pair](#); isolated vs conjugated alkenes
  - R = alkyl or aryl with EWGs vs R = aryl with EDGs
- ◆ Cl<sub>2</sub>: low selectivity due to poor bridging ability of Cl
  - less polarizable & likely to become positively charged
- ◆ other reactions: Br<sub>3</sub><sup>-</sup> & halohydrins;  [491-2](#)
- Evidences for the bridged bromonium ions
  - ◆ NMR spectrum in superacid conditions:  [489-90](#)
  - ◆ X-ray structure of sterically hindered ions:  490 [Fig. 5.2](#)

## ❖ Addition of Halogens (III)

- Fluorination: violent reactions with  $F_2$ ; mixtures
  - ◆ mild fluorinating agents:  $XeF_2$ ,  $AcOF$ , dilute  $F_2$  at low temp.
    - *syn* product from collapse of the ion pair: [📖 496 middle](#)
- Iodination: easily reversible to alkenes; *anti*
- Conjugated dienes: 1,2- vs 1,4-adduct & *anti* vs *syn*
  - ◆  $Br_2$ : 1,4-*syn* addition via ionic intermediate; [📖 496 bottom](#)
  - ◆ mild  $pyr \bullet Br_2 / Br_3^-$ : 1,2-*anti* addition via  $Ad_E3$ ; [📖 497 top](#)

## ❖ Stereochemistry of Fluorination



*no bridged fluoronium ion involved*



## ❖ Sulfenylation

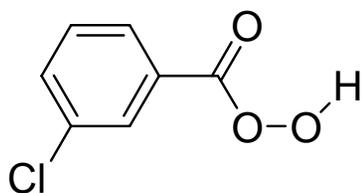
- Sulfenylation: bridged intermediates; [📖 498 bottom](#)
- ◆ sulfenylating reagents: [📖 498 Scheme 5.1](#)
- ◆ less electrophilic & better bridging: less rate increase ( $10^2$  times) with [2,3-dimethyl-2-butene](#) than  $\text{Cl}_2$  ( $10^6$ )/ $\text{Br}_2$  ( $10^7$ )
- ◆ regioselectivity: substrate & reagent; [📖 500 Table 5.4](#)
  - often *anti*-Markovnikov addition **due to steric factors**
  - electrophilic  $\text{CF}_3\text{CH}_2\text{SX}$ : Markovnikov & *anti*; [📖 500 middle](#)

# ❖ Selenenylation

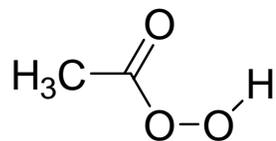
- Selenenylation: bridged seleniraniums; [📖 501 mid.](#)
  - ◆ rate-acceleration by ERG-Ar: concerted addition/ionization
  - ◆ selenenylating reagents: [📖 498 Scheme 5.1](#)
  - ◆ rate-enhancing: alkyl groups; [📖 502 Table 5.5](#)
    - phenyl: rate-retarding; steric & stabilized alkene
  - ◆ regioselectivity: anti-Markovnikov; [📖 501 bottom](#)
    - rearrangement to the thermodynamic Markovnikov product
    - styrene: the Markovnikov product
  - ◆ stereoselectivity: *anti* & diaxial; [📖 502-3](#)
  - ◆ utility of selenide intermediates: [📖 501 top](#)

## ❖ Epoxidation with Peroxides

- Concerted mechanism: syn addition; [📖 504 middle](#)
- ◆ common epoxidizing reagents: [mCPBA etc.](#)
- ◆ faster rate: strained/ERG-alkenes & EWG-peroxy acids
  - $k_{\text{norbornene}} = 2 k_{\text{cyclopentene}}$ ,  $k_{\text{trans-cyclooctene}} = 90 k_{\text{cyclohexene}}$
  - Aryl-conjugated alkene: stabilized & less reactive
- ◆ stereoselectivity: less hindered face; [📖 505 top](#)
  - hydroxy-directing effect: H-bonding; [📖 505 middle](#)
  - inductive effects: *syn*-EWG vs *anti*-ERG; [📖 506 bottom](#)
- ◆ DMDO: (in-situ) preparation & reactions; [📖 509 top](#)
  - more reactive to *Z*-alkenes: [📖 510 top](#)
  - more nucleophilic than peroxyacids: [📖 510-511](#)



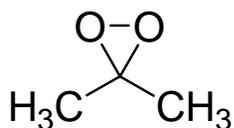
MCPBA



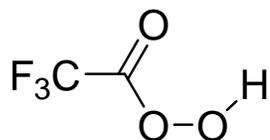
peroxyacetic acid



Oxone  
(potassium  
peroxymonosulfate)



dimethyldioxirane  
(DMDO)



peroxytrifluoroacetic acid



## ❖ Transformations of Epoxides (Oxiranes)

- Ring-opening: steric/electronic; [📖 511 bottom](#)
  - ◆ basic conditions: less substituted carbons (steric)
  - ◆ acidic conditions: degree of the C-O rupture; [📖 512 top](#)
    - pH-rate profile: stable with weak base; [📖 512 middle](#)
  - ◆ cyclohexene epoxides: regio/stereospecific; [📖 514 bottom](#)
    - via cations: not stereospecific but regiospecific; [📖 513 bottom](#)
    - reaction conditions: catalyzed/uncatalyzed; [📖 514 top](#)
  - ◆ propylene oxide with HBr: anti-Markovnikov; [📖 515 top](#)
    - possible reversal of regioselectivity with a stabilized cation intermediate

## ❖ Electrophilic Addition with Metal Ions

- Formation of alkene-metal ion complex: [📖 515 mid.](#)
- ◆  $\text{Hg}^{2+}$ : stable mercurinium ions; [📖 517 top](#)
  - alkene reactivity: steric hindrance to  $\text{Hg}^{2+}$ ; [📖 516 Table 5.6](#)
  - reagent activity:  $\text{Hg}(\text{O}_2\text{CCF}_3)$ ,  $\text{Hg}(\text{ClO}_4)_2 > \text{Hg}(\text{OAc})_2 \gg \text{HgCl}_2$
  - styrene:  $\rho = -3.16$ ; a cationic character
  - regioselectivity: Markovnikov addition
    - but at the sterically less hindered position: [📖 516 middle](#)
  - *anti* addition: acyclic/monocyclic alkenes; [📖 517 bottom](#)
  - *syn* addition: bicycles, group transfer from  $\text{Hg}^{2+}$ ; [📖 518 top](#)
    - remote attack from polar groups: [📖 518 mid](#) & [📖 518 mid](#)
- ◆ argentation: reversible complex formation; [📖 520 bottom](#)
  - analysis & separation of alkenes, no intermolecular Nu attack

## ❖ Hydroboration and Functionalization

- Concerted syn electrophilic addition: [📖 522 top](#)
  - ◆ reagent reactivity vs stability: [📖 521 bottom](#)
  - ◆ less hindered & more e<sup>-</sup>-rich site: [📖 523 Table 5.7](#)
  - ◆ [less hindered face](#) & higher selectivity with bulky reagents
  - ◆ rearrangement to terminal sites: > 160 °C; [📖 525 middle](#)
    - intramolecular migration via e<sup>-</sup>-poor  $\pi$ -complex: [📖 526 bottom](#)
    - thermodynamic control: [📖 525-6](#)
  
- Concerted migration of the R: functionalization
  - ◆ hydroxylation ([📖 527-8](#)), amination ([📖 528-9](#))
  - ◆ enantioselective hydroboration: chiral boranes; [📖 530](#)

## ❖ Comparison of Electrophilic Additions

- Correlation between reactivity & IP:  532 [Fig. 5.7](#)
  - ◆ protonation: substitution degree at the more substituted C
    - the major factor: carbocation stability
  - ◆ bromination: total No of substituents; symmetrical bridge
  - ◆ sulfenylation/selenenylation: less sensitive to substitution
  - ◆ epoxidation: similar to bromination but a reduced slope
  - ◆ mercuration: carbocation-like but a large steric effect
  - ◆ hydroboration: dominant steric effect and less e<sup>-</sup> demand
- Polar addition intermediates:  534 [Figure 5.8](#)
  - ◆ electronic/steric control: regio-/stereoselectivity

## ❖ Polar Addition to Alkynes (I)

- Basic mechanisms: via a complex; [📖 538 top](#)
- Addition of HCl: vinyl cation (*sp*); [📖 539 top](#)
  - ◆ aryl alkynes: mainly *syn*, Ad<sub>E</sub>2; stabilized by aryl groups
  - ◆ alkyl alkynes: Ad<sub>E</sub>2 ([📖 540](#)) or Ad<sub>E</sub>3 ([📖 539](#), added X<sup>-</sup>)
- Hydration: ketones via vinyl cations; [📖 540 top](#)
  - ◆ solvent isotope effect: rate-determining protonation step
- Chlorination of aryl alkynes: vinyl cations; [📖 540 bot](#)
  - ◆ phenylacetylene:  $\rho = -4.2$  with  $\sigma^+$  constants; [vinyl cation](#)
  - ◆ rate =  $k[\text{alkyne}][\text{Cl}_2]$ ; nonstereospecific; solvent capture

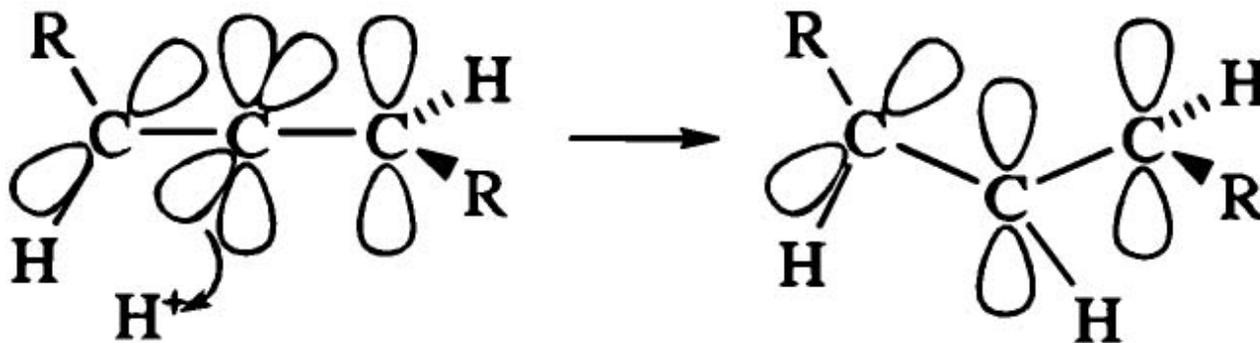
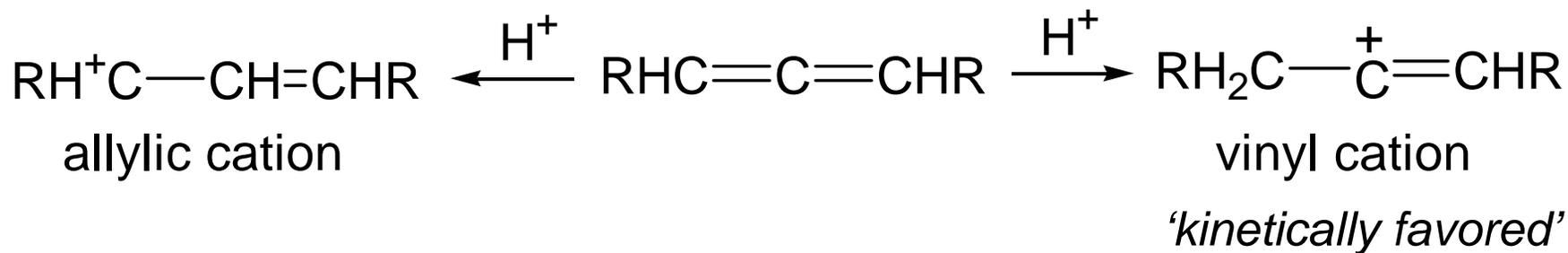
## ❖ Polar Addition to Alkynes (II)

- Chlorination of alkyl alkynes: [📖 541 top](#)
  - ◆ disubstituted: *anti* via bridged ions; very fast ( $k_{\text{di}}/k_{\text{mono}} = \sim 100$ )
  - ◆ monosubstituted: *syn*; short lifetime for the vinyl cation pair
- Bromination: alkyne-Br<sub>2</sub> complex; [📖 541 bottom](#)
  - ◆ aryl alkynes: not stereospecific via a vinyl cation (Ad<sub>E</sub>3)
    - *anti*: EWG on aryl rings (bridged) & added Br<sup>-</sup> salts
  - ◆ alkyl alkynes: *anti* with Ad<sub>E</sub>3; [📖 542 middle](#)
- Mercuration: *E* or *Z*-addition; to ketones, [📖 544 mid](#)
- Reactivity of alkynes and alkenes: [📖 537 Table 5.10](#)
  - ◆ vinyl cations: 10-15 kcal higher than alkyl cations
  - ◆ bridged ions with a double bond: very strained

## ❖ Addition to Allenes

- Vinyl cation: kinetically favored; [📖 545 middle](#)
  - ◆ twisted allyl cations: 36-38 kcal higher than vinyl cations
  - ◆ RDS: protonation step to the vinyl cation
- Addition of HX: vinyl halides; [📖 545-6](#)
  - ◆ geminal dihalides with 2 HX: stabilized by the 1<sup>st</sup> halogen
- Addition of H<sub>2</sub>O: ketones via enols; [📖 546 middle](#)
- Addition of X<sub>2</sub>/Hg<sup>2+</sup>: bridged ions; [📖 546 middle](#)
  - ◆ nucleophilic attack at the terminal carbon

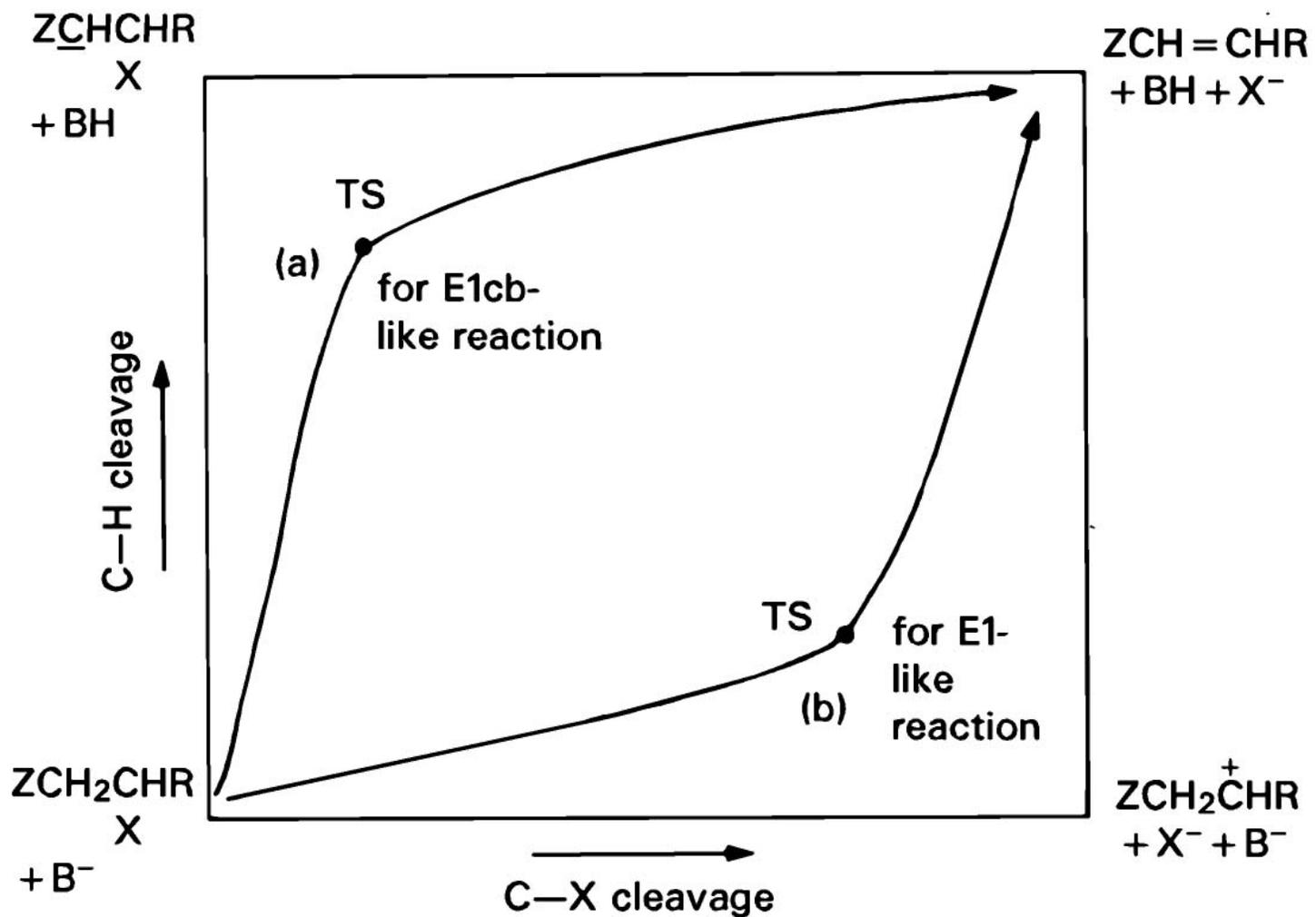
## ❖ Mechanism in Allenes: Vinyl vs Allylic Cation



## ❖ Polar Elimination Reactions: Mechanisms

- Classification of elimination modes: [📖 547 top](#)
  - ◆ relative to X:  $\alpha$ -,  $\beta$ -,  $\gamma$ -elimination; [📖 548 Scheme 5.2](#)
- Limiting mechanisms of  $\beta$ -eliminations: [📖 548-9](#)
- Variable (E2) TS theory:  $\text{CH}_3\text{CH}_2\text{X}$ ; [📖 549 Fig. 5.11](#)
  - ◆ 2-/3-D potential energy diagrams: [📖 550 Fig. 5.12](#)
  - ◆ change of TS: substituent effects (Z or R); [📖 551 Fig. 5.13](#)
- SAR (structure-[re]activity relationship): E1 / E1cb
  - ◆ EDG / EWG, more / less substitution, good / poor leaving group, solvents with high / low  $\gamma$ , stronger & harder bases (E1 over  $\text{S}_{\text{N}}1$ ) / stronger bases: [📖 548-9 Schemes 5.3-5.4](#)

# ❖ Change of TS in Eliminations: Substituents



## ❖ Regiochemistry of Eliminations

### □ E2 via an 'E1-like' TS: regioselectivity of E1

◆ E1 TS (RDS) resembles the carbocation:  555 [Fig. 5.14](#)

○ the more stable carbocation: hyperconjugation giving the more substituted alkene: the Saytzeff product / rule;  555 [middle](#)

### □ E2 via an 'E1cb-like' TS: regioselectivity of E1cb

◆ E1cb TS (RDS): significant bond between H & base

○ low  $\Delta E_a$ : easier removal of H; less hindered & more acidic  $\beta$ -H (kinetic acidity), stronger/bulky bases (the Hofmann rule)

### □ Concerted E2: significant C=C bond at TS

◆ more substituted alkenes & (anti)periplanar conformations

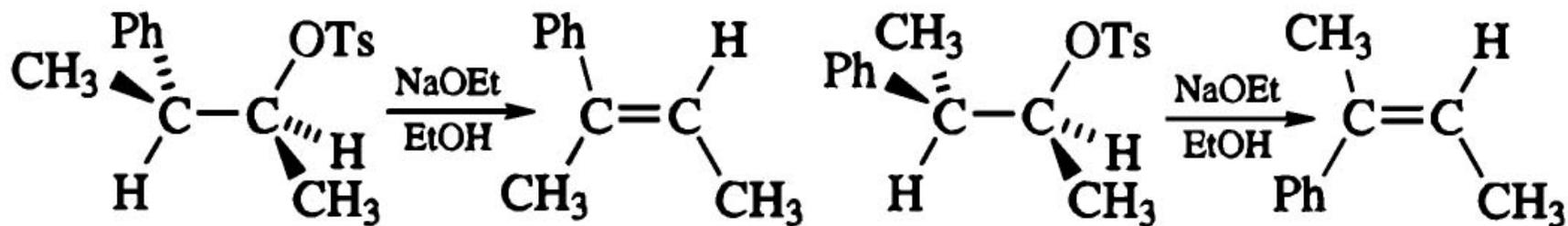
◆ effects of leaving groups, base strength & bulkiness: 

557-8 [Table 5.11](#), [5.12](#) & [5.13](#),  [557 & 558](#)

## ❖ Stereochemistry of E2 Eliminations

- Periplanar conformation: *anti* & *syn*; [📖 558 bottom](#)
- ◆ cyclics: mostly *anti* in cyclohexanes; [📖 560 middle](#)
  - 90% *syn* for 4-ring; 50% *syn* for 5-ring
  - *syn* elimination: no *anti* conformation possible; [📖 561 top](#)
- ◆ acyclics: usually *anti* favored; stereospecific, [📖 559 top](#)
  - competitive *syn* elimination possible: [📖 559 mid](#) & [Table 5.14](#)
  - *syn* elimination in acyclic systems: [📖 560 Table 5.15](#)
    - poor X, longer chain, nonpolar solvent, strong base
    - an ion pair: less *syn* with crown ethers; [📖 561 bottom](#)
    - steric effect: [📖 562 bottom Table](#) & [📖 563 top](#)
- ◆ Z-selectivity: arene sulfonates; [📖 563 middle](#)

## ❖ *Anti* Elimination in Acyclic Compounds



## ❖ Dehydration of Alcohols

- Acid-catalyzed elimination: E1; [📖 563 bottom](#)
  - ◆ reverse of acid-catalyzed hydration: cation intermediates
    - reactivity:  $3^\circ > 2^\circ \gg 1^\circ$  alcohols
    - more substituted alkenes predominant
    - rearranged products: [📖 564 top](#)
    - secondary kinetic isotope effect at  $\beta$ -position: [📖 564 middle](#)

## ❖ Eliminations Not Involving C-H Bonds (I)

□ Vicinal dibromides: *anti* with NaI; [📖 564-5](#)

◆ lower selectivity with Zn/Cr: nonstereospecific formation of [an organometal intermediate](#)

□ Acid-catalyzed deoxymercuration: [📖 566 bottom](#)

◆  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_2\text{HgI}$ :  $10^{11}$  faster than  $\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$

○ bridged  $\text{Hg}^+$ : faster with the *trans* isomer; [📖 566 bottom](#)

◆ other metals:  $\text{IHg} \sim \text{Ph}_3\text{Pb} \sim \text{Ph}_3\text{Sn} > \text{Ph}_3\text{Si}$  ( $10^6$  slower)  $> \text{H}$

○ weaker bond energies:  $\text{Hg-C } 27 < \text{Pb-C } 31 < \text{Sn-C } 54 < \text{Si-C } 60 < \text{H-C } 96 \text{ kcal/mol}$

○ stabilized  $\beta$ -cation via a bridged ion or e-donation: [📖 566 top](#)

## ❖ Eliminations Not Involving C-H Bonds (II)

- Elimination of  $\beta$ -hydroxysilanes/tins: [📖 566 middle](#)
  - ◆ *anti* elimination under acidic conditions
- Elimination of  $\beta$ -halo/carboxysilanes: [📖 566-7](#)
  - ◆ *anti* elimination under basic conditions: [📖 567 top](#)
  - ◆  $\beta$ -sulfonyloxysilanes: mild conditions; [📖 567 middle](#)
- Vinyl silanes/stannanes: substitution; [📖 567 bottom](#)
  - ◆ activated olefins & *anti* addition to silanes
- Allyl silanes/stannanes: active  $E^+$ ; [📖 568](#)
  - ◆ allyl anion equivalents: rearrangement of double bonds