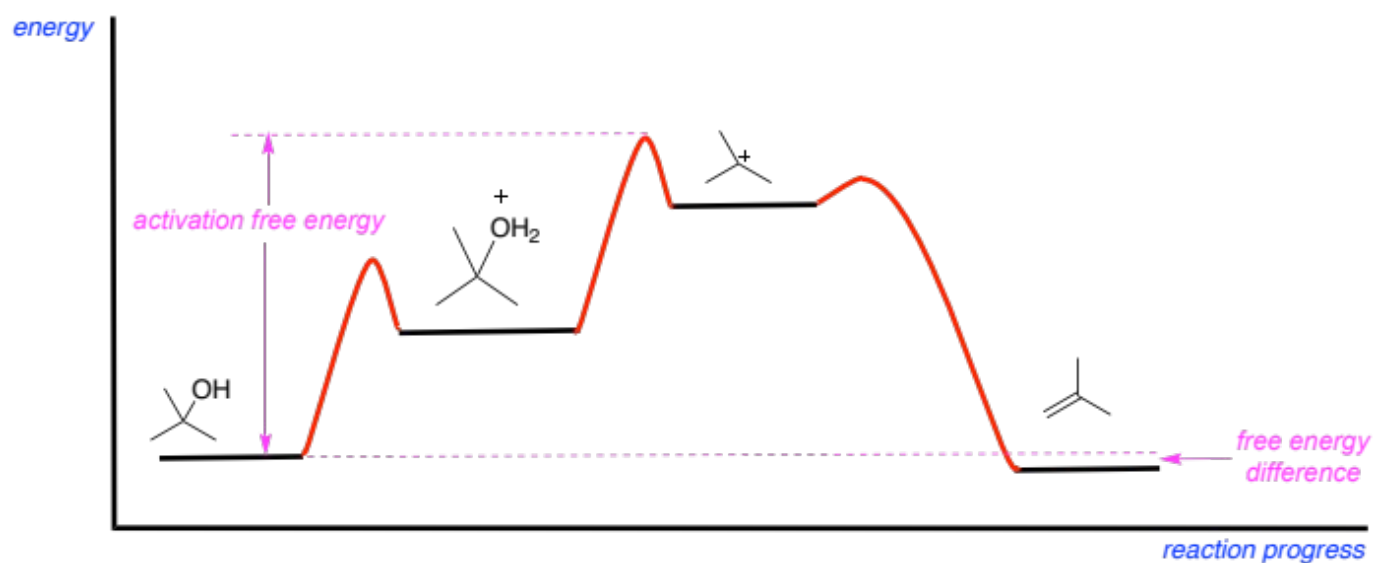
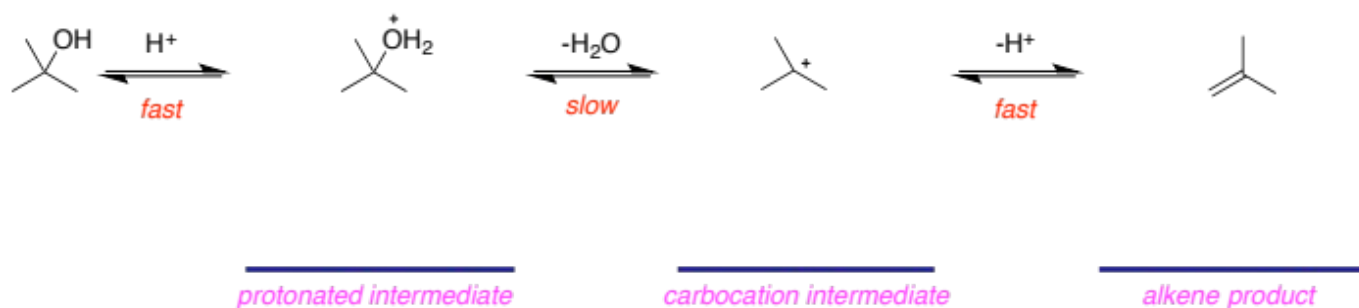


# Elimination Reactions To Form Alkenes

from chapter(s) \_\_\_\_\_ in the recommended text

## A. Introduction

## B. E1 Mechanisms



## Kinetics

the rate of the reaction above *is* proportional to starting material

rate is proportional to  $[^t\text{BuOH}]$  rate =  $k [^t\text{BuOH}]$

Mathematically, the rate of a reaction is approximately given by which of the following equations **C** and **D**.

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

**A**

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

**B**

$$k = Ae^{-E_a/RT}$$

**C**

$$\ln k = \ln A - E_a/RT$$

**D**

Using a reference text, define the following terms:

$\Delta G^\ddagger$  = Gibbs energy of activation units kiloJoules (kJ)

$\Delta S^\ddagger$  = entropy of activation units Joules\*(Kelvin)<sup>-1</sup> (J/K)

$\Delta H^\ddagger$  = enthalpy of activation units kiloJoules (kJ)

$\Delta G^\circ$  = Gibbs free energy per mole of reaction at standard conditions (298 K, 100 kPa, 1M Reactant/Product) units kiloJoules (kJ)

$\Delta S^\circ$  = Entropy per mole of reaction at standard conditions units Joules\*(Kelvin)<sup>-1</sup> (J/K)

$\Delta H^\circ$  = Enthalpy per mole of reaction at standard conditions units kiloJoules (kJ)

T = absolute temperature measured in Kelvin

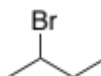
R = universal gas constant units Joules\*(Kelvin)<sup>-1</sup>\*(moles)<sup>-1</sup>

A = pre-exponential factor which is a constant representing the empirical relationship between rate coefficient and temperature unique to the chemical reaction

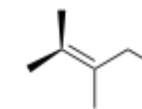
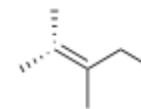
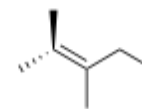
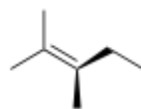
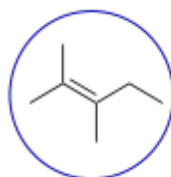
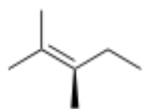
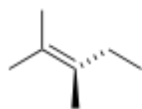
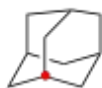
$E_a$  = activation energy for the reaction

The difference between  $\Delta G^\ddagger$  and  $E_a$  is  $E_a$  is more analogous to  $\Delta H^\ddagger$  which considers the thermodynamic form of the rate equation, while  $\Delta G^\ddagger$  is the difference between the ground state of reactant and transition peak with respect to both  $\Delta S^\ddagger$  and  $\Delta H^\ddagger$ .

## Carbocation Stability

Rates of E1 reactions tend to *increase**most stable**least stable**fastest*

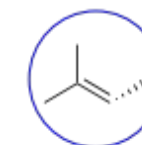
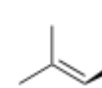
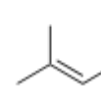
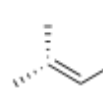
Bredt's Rule

*slowest*adamantane below is  $sp^3$ -hybridized so it has ideal dihedral angles of  $\sim 109^\circ$ All the carbons in adamantane have *the same* hybridization states.the adamantane carbocation shown involves *more* ring and bond strain.resembles the configuration around the alkene in *adamantene*; this *is not* a stable conformation.

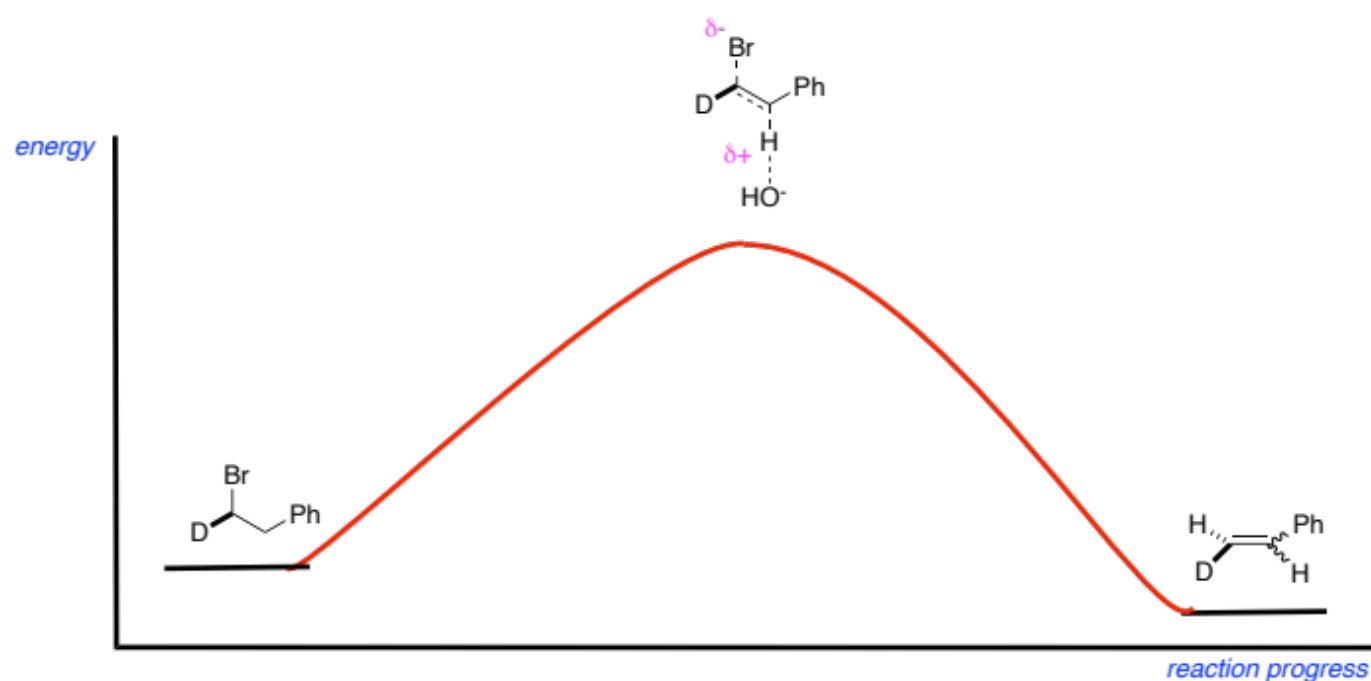
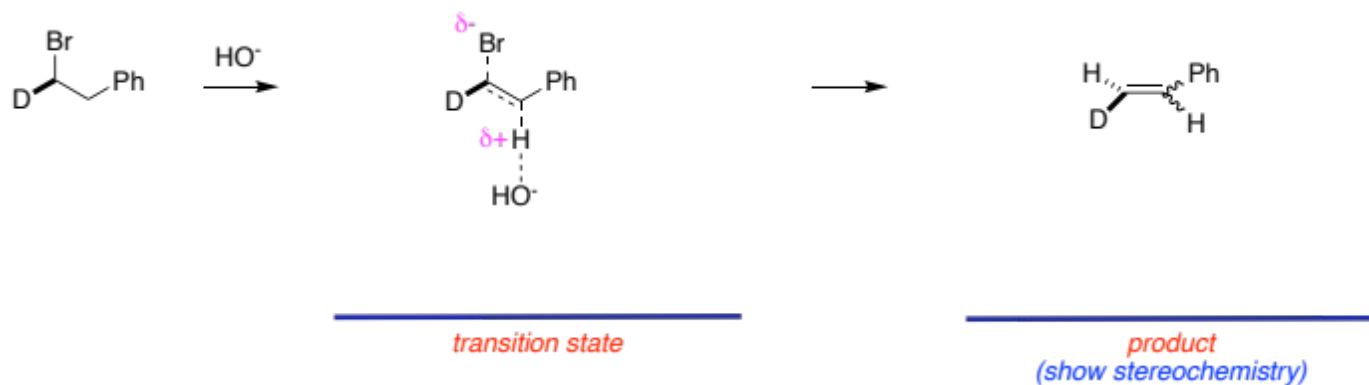
adamantane

adamantane  
cation

adamantene

E1 eliminations that result in formation of adamantene *are not* favorable.

### C. E2 Mechanisms



### Kinetics

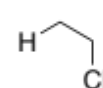
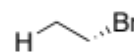
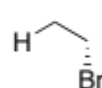
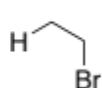
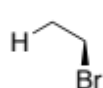
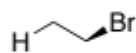
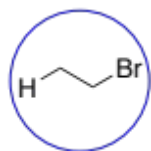
rate is proportional to  $[\text{DCHBrCH}_2\text{Ph}] [\text{OH}^-]$

rate =  $k [\text{DCHBrCH}_2\text{Ph}] [\text{OH}^-]$

Doubling the amount of base *doubles* rates of E2 eliminations.

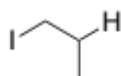
## Stereoselectivity

that puts two substituents on *different* sides and *perpendicular*.



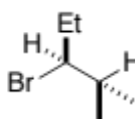

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*syn-periplanar*  
*EtCl*



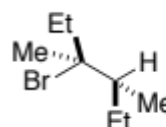

---

*anti-periplanar*  
*1-iodopropane*




---

*anti-periplanar*  
*EtBrHCCHMe<sub>2</sub>*



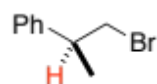

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*anti-periplanar*  
*EtMeHCCBrMeEt*

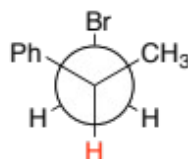



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*anti-periplanar*  
*ethyl iodide*



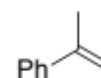
*..... can be represented as*




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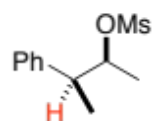
*complete Newman projection*

base  
→

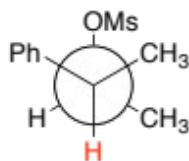



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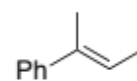
*show alkene product*



..... can be represented as

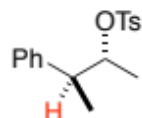


base  
→

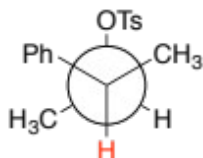


complete Newman projection

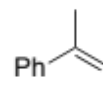
show alkene product



..... can be represented as

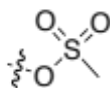


base  
→

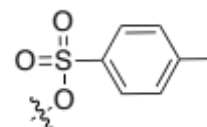


complete Newman projection

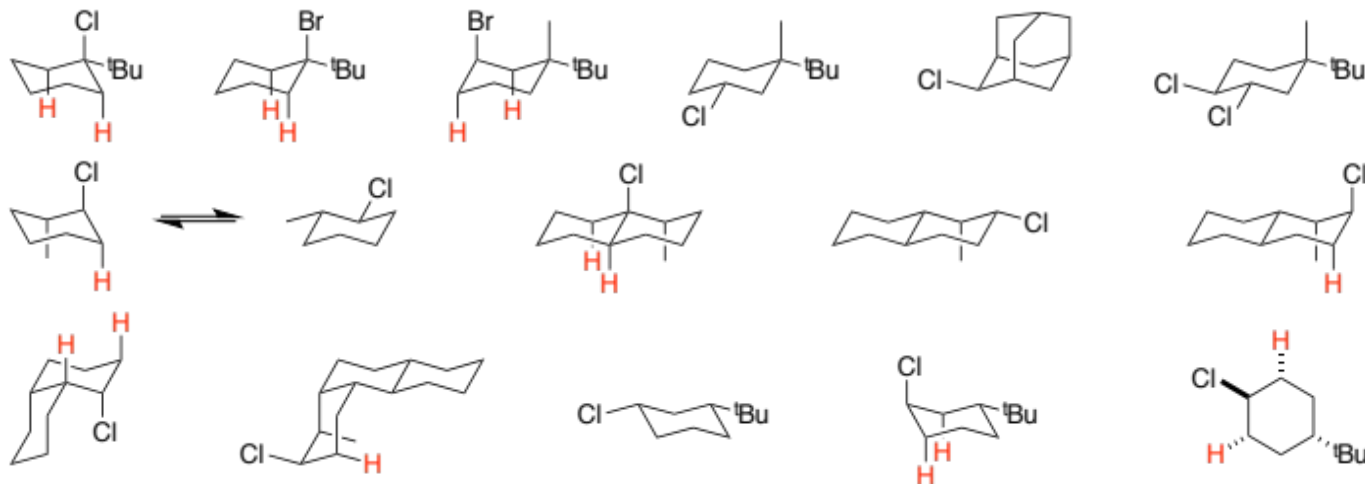
show alkene product



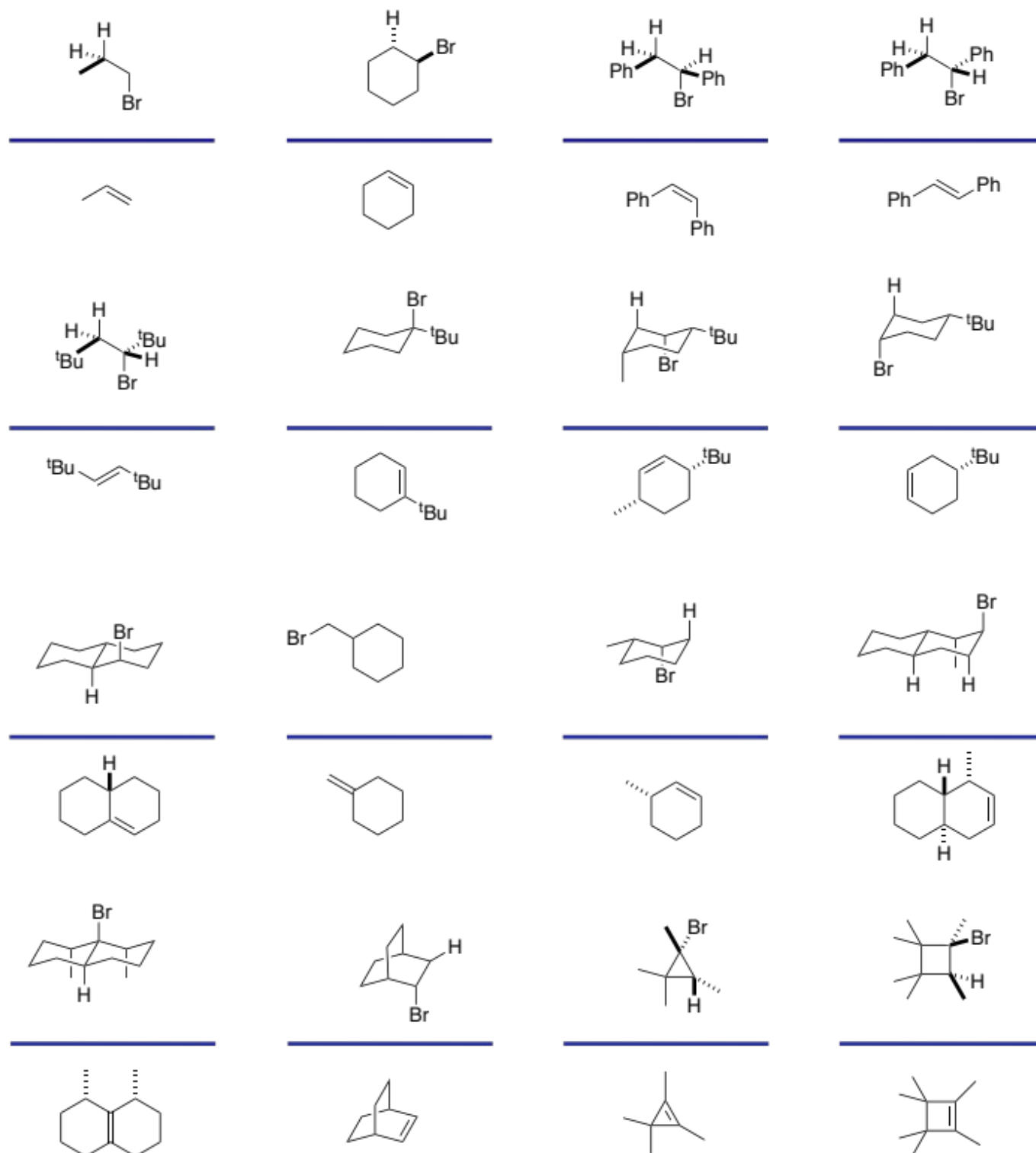
mesyl group, -OMs



tosyl group, -OTs



hydrogen that is being deprotonated and the leaving group are *anti*-periplanar.



## D. Factors That Favor E1, E2, S<sub>N</sub>1, or S<sub>N</sub>2

### Basicity vs Nucleophilicity

- (i) strongly basic character of Y<sup>-</sup> will increase the rate of E2 relative to E1 reactions and it will tend to favor E2 over nucleophilic substitution reactions;
- (ii) weakly basic character of Y<sup>-</sup> will retard the rate of E2 relative to E1 reactions and it will tend to favor E1 over nucleophilic substitution reactions;
- (iii) less basic character of Y<sup>-</sup> will not affect the rate of E1 eliminations, but it will not favor E2 over E1 mechanisms; and,
- (iv) strongly nucleophilic character of Y<sup>-</sup> will increase the rate of S<sub>N</sub>2 relative to S<sub>N</sub>1 reactions and it will tend to increase the rates of S<sub>N</sub>2 over elimination reactions.

the likelihood of preferential E2 *increases* with the base strength.

### Nucleophilicity

- (i) S<sub>N</sub>1 relative to S<sub>N</sub>2 reactions; and,
  - (ii) E1 over E2
- 
- (i) S<sub>N</sub>2 relative to S<sub>N</sub>1 reactions;
  - (ii) E2 over E1 reactions.

The following order is approximate. It varies with the HOMO/LUMO match of the nucleophile with the electrophile.

N <sub>3</sub> <sup>-</sup>	CN <sup>-</sup>	I <sup>-</sup>	MeO <sup>-</sup>	NH <sub>3</sub>	H <sub>2</sub> O	Cl <sup>-</sup>	
<i>most nucleophilic</i>						<i>least nucleophilic</i>	
NH <sub>2</sub> <sup>-</sup>	HO <sup>-</sup>	PhO <sup>-</sup>	NH <sub>3</sub>	H <sub>2</sub> O	Cl <sup>-</sup>		
<i>most basic</i>						<i>least basic</i>	

*because HCl the strongest acid, then H<sub>3</sub>O<sup>+</sup> then NH<sub>4</sub><sup>+</sup> then PhOH (marginally) then H<sub>2</sub>O then NH<sub>3</sub>*



## Temperature (and Entropy)

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$$

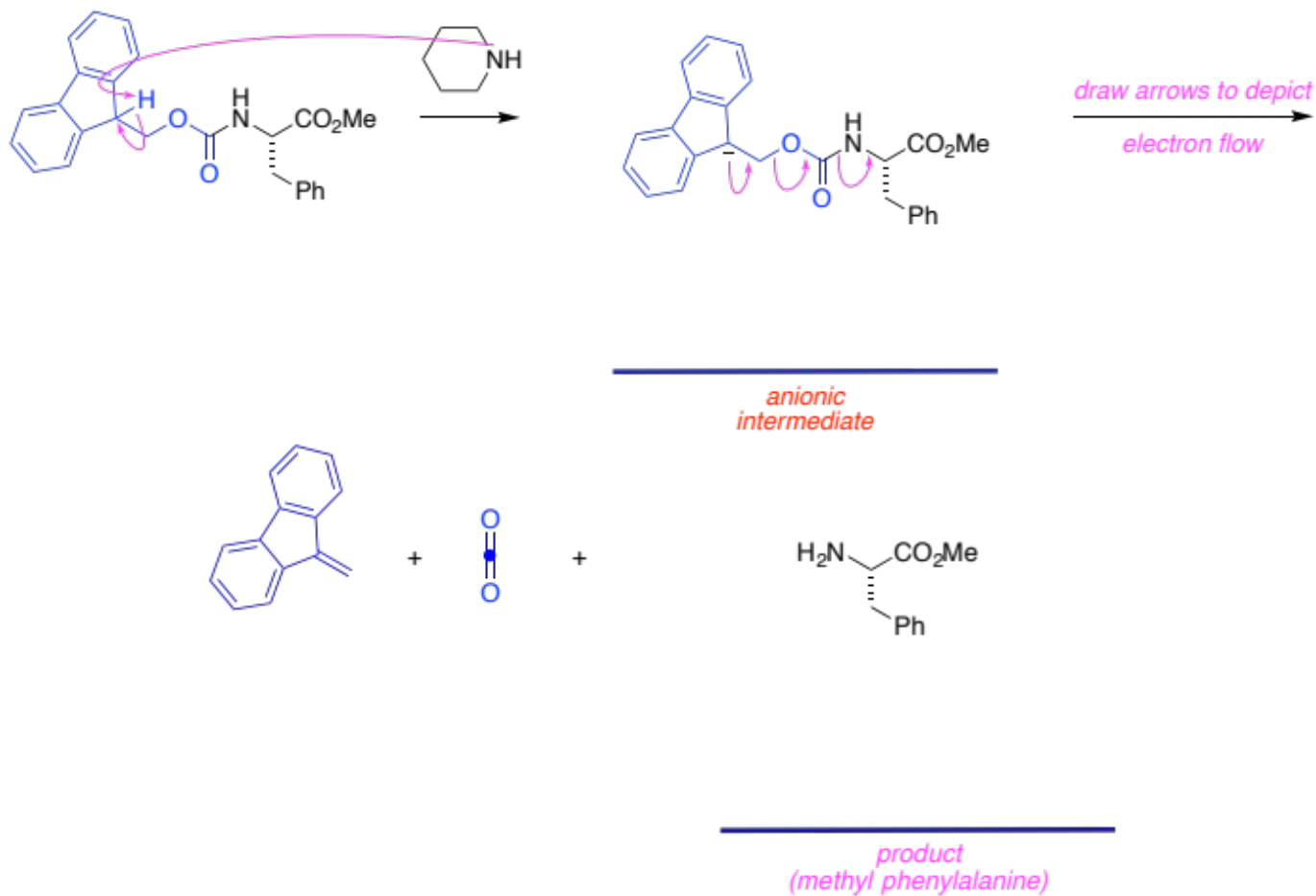
rate determining transition states in *E2* and *S<sub>N</sub>2* over *E1* and *S<sub>N</sub>1* reactions.

Low temperatures therefore tend to favor *E2* and *S<sub>N</sub>2* over *E1* and *S<sub>N</sub>1* reactions.

High temperatures therefore tend to *E1* and *S<sub>N</sub>1* over *E2* and *S<sub>N</sub>2* reactions.

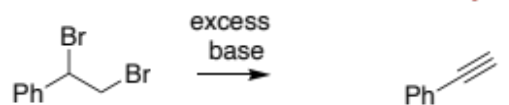
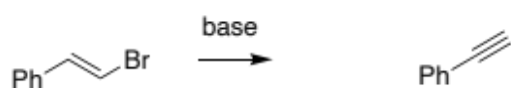
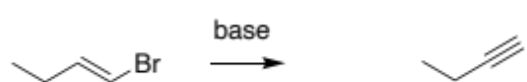
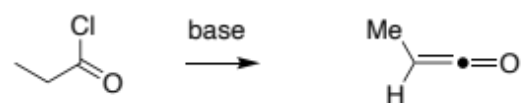
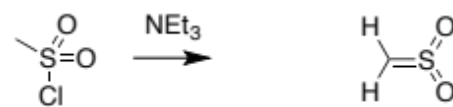
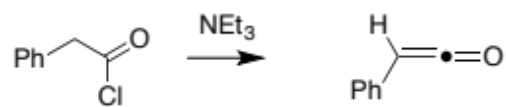
## E. E1cB

removal of 9-fluorenyloxymethyl groups, *ie* *Fmoc* used to protect amines as *carbamates*.



Fluorenyl anions formed in this protection process have 14 e, and are therefore *aromatic*.

## F. Eliminations To Give Allenes, Alkynes, Ketenes And Sulfenes




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*ketene*

---

*sulfene*

---

*ketene*

---

*alkyne*

---

*alkyne*

---

*alkyne*