

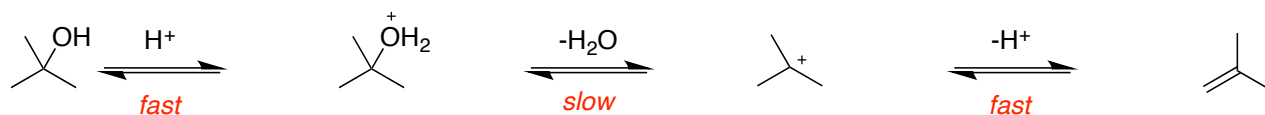
Elimination Reactions To Form Alkenes

from chapter(s) _____ in the recommended text

A. Introduction

.

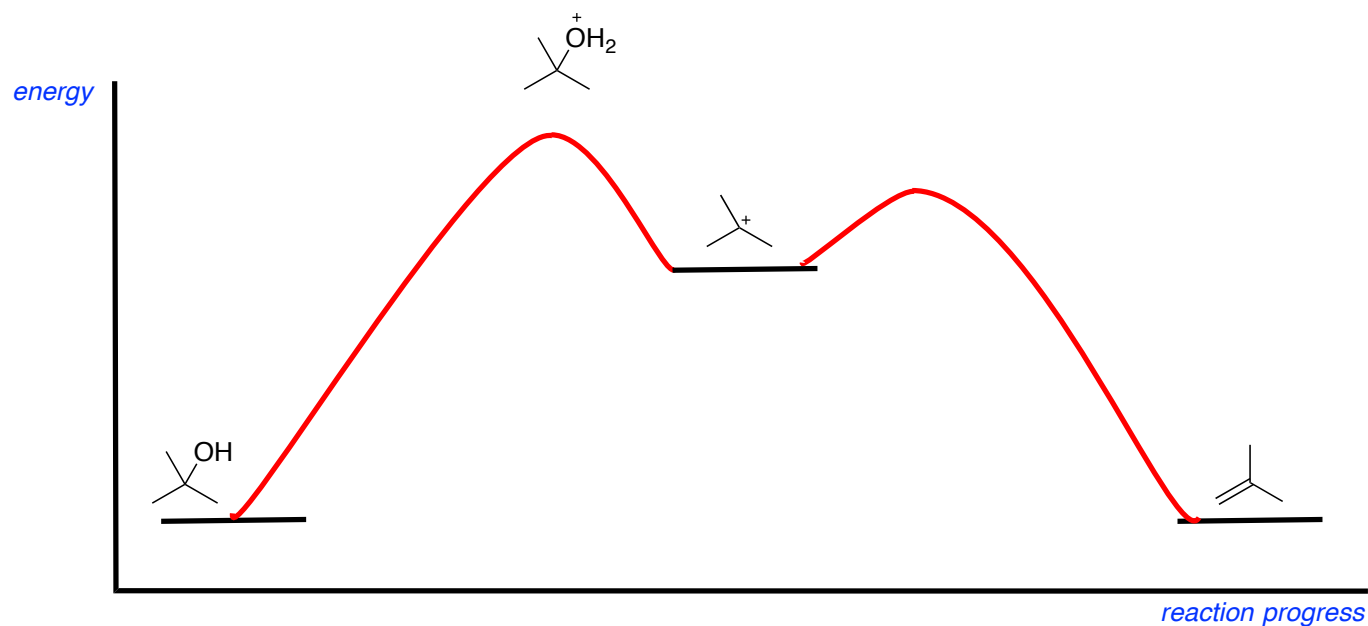
B. E1 Mechanisms



protonated intermediate

carbocation intermediate

alkene product



Kinetics

rate is proportional to

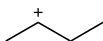
$[\text{tBuOH}]$

rate =

$k [\text{tBuOH}]$

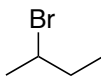
Carbocation Stability

Rates of E1 reactions tend to *increase*



most stable

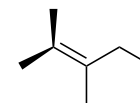
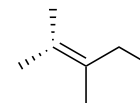
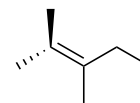
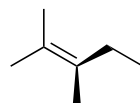
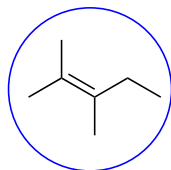
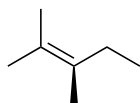
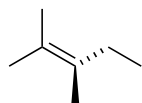
least stable



fastest

slowest

Bredt's Rule



sp^3 so it has ideal dihedral angles of about 109

the same

more

is not



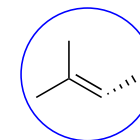
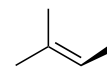
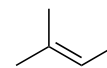
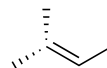
adamantane



adamantane cation

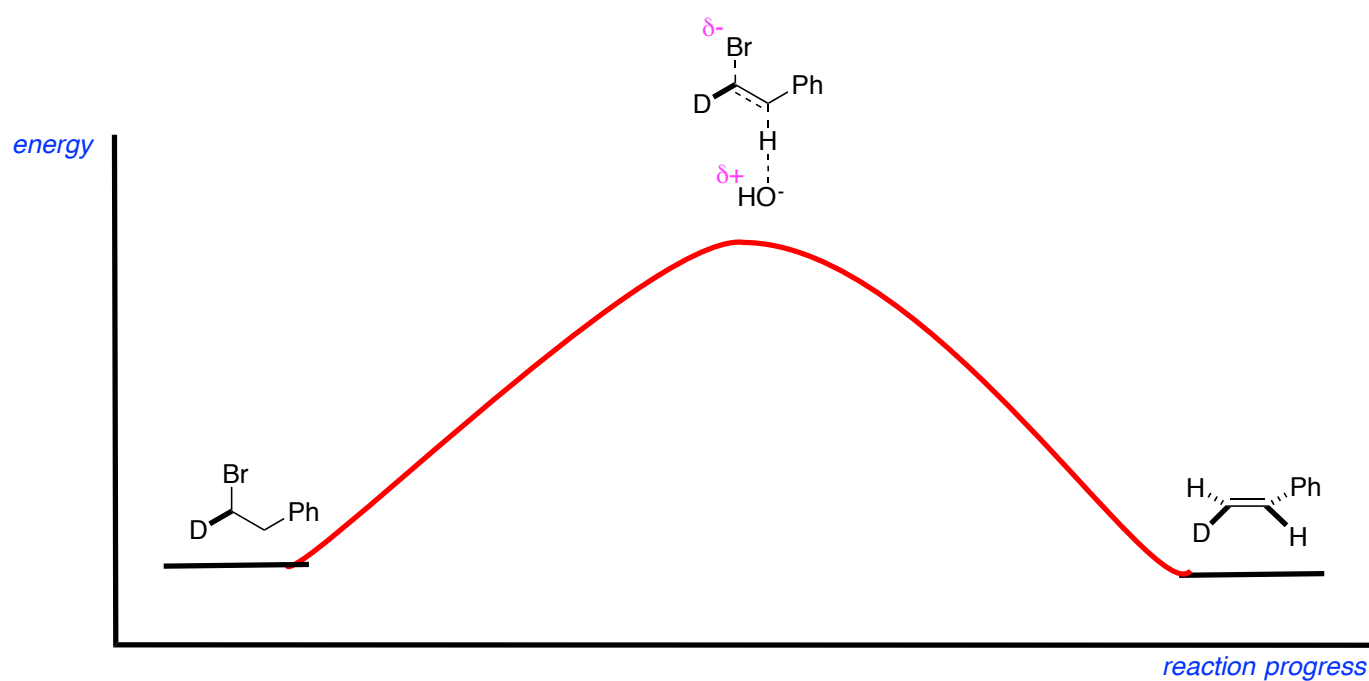
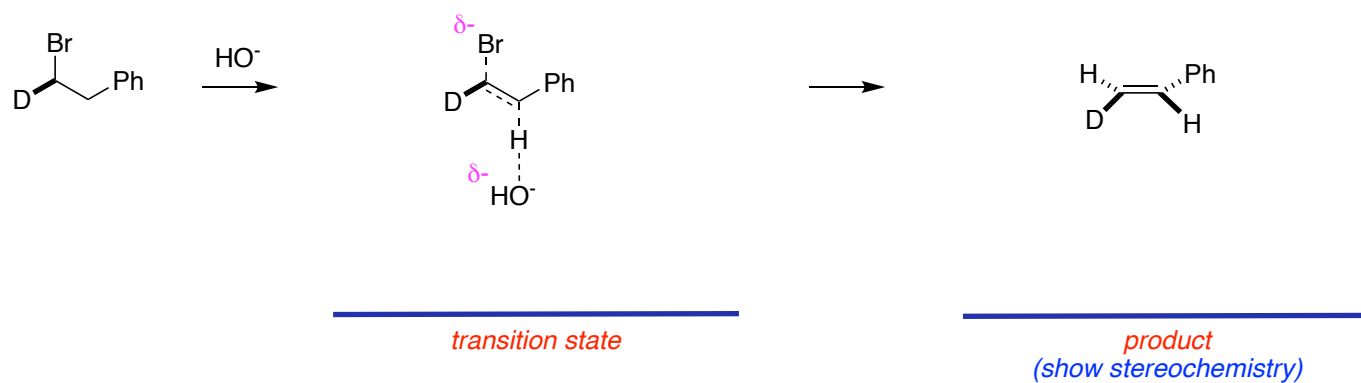


adamantene



are not favorable.

C. E2 Mechanisms



Kinetics

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

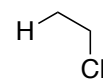
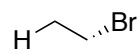
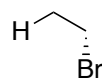
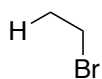
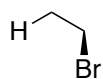
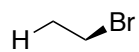
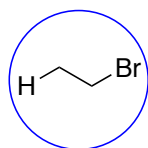
rate = $k [\text{DCHBrCH}_2\text{Ph}] [\text{OH}^-]$

doubles

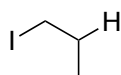
Stereoselectivity

different

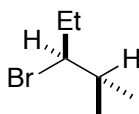
perpendicular.



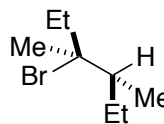
*syn-periplanar
EtCl*



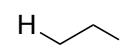
*anti-periplanar
1-iodopropane*



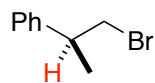
*anti-periplanar
EtBrHCCHMe₂*



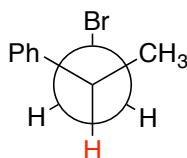
*anti-periplanar
EtMeHCCBrMeEt*



*anti-periplanar
ethyl iodide*

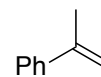


*..... can be
represented as*

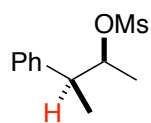


*complete Newman
projection*

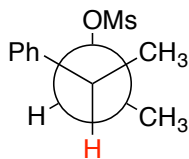
base



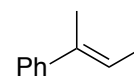
show alkene product



..... can be represented as

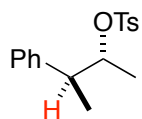


base
→

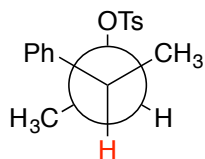


complete Newman projection

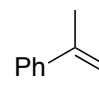
show alkene product



..... can be represented as



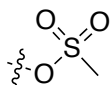
base
→



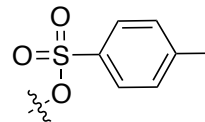
complete Newman projection

show alkene product

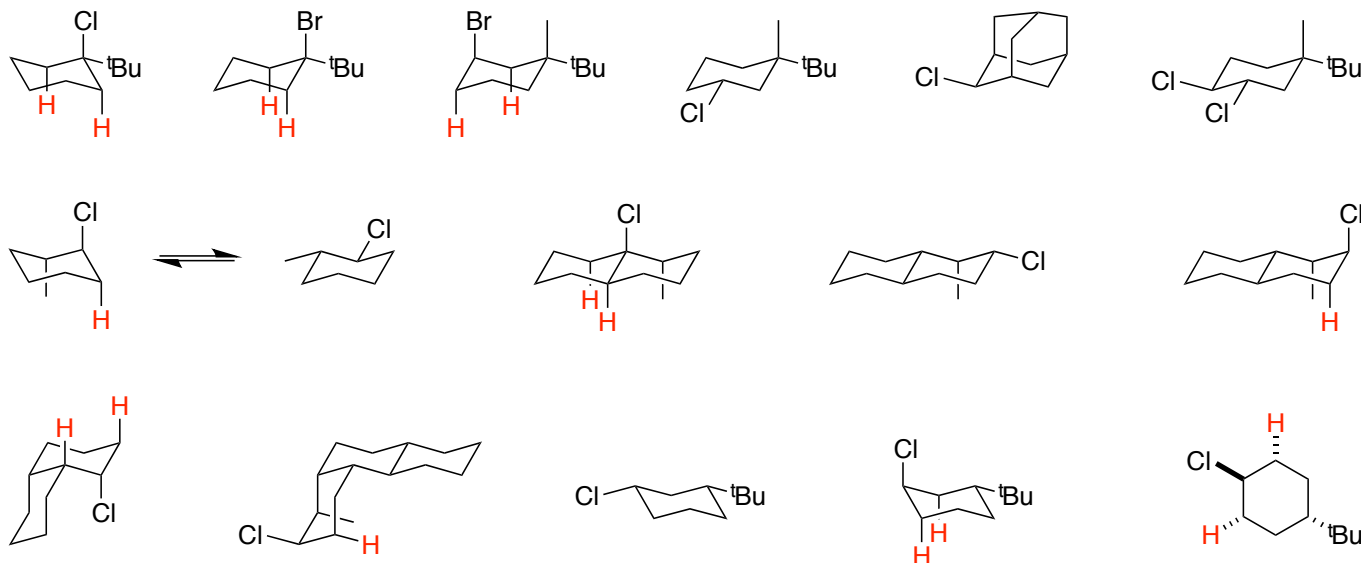
Show structures for:

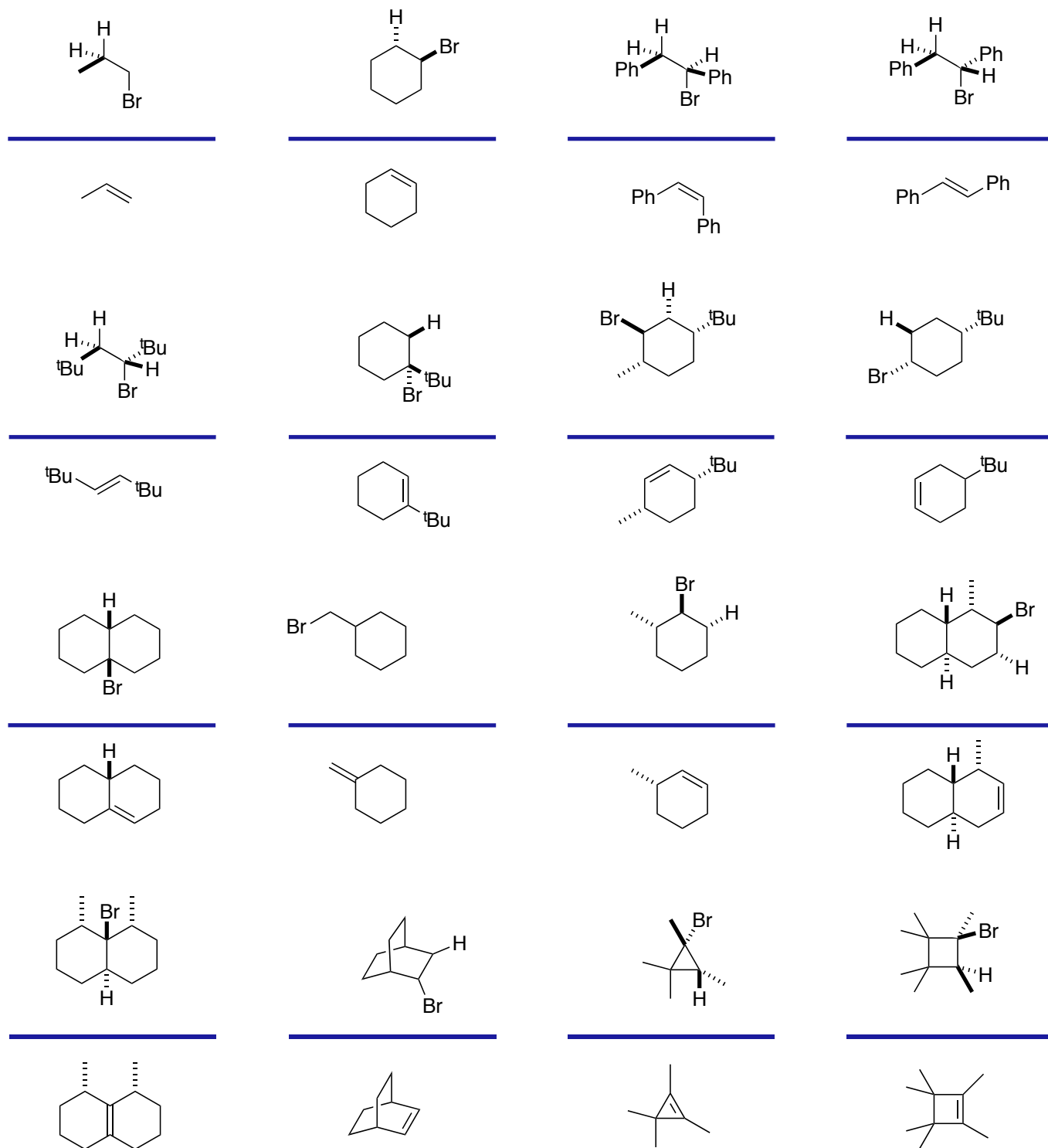


mesyl group, -OMs



tosyl group, -OTs



anti-periplanar.

D. Factors That Favor E1, E2, S_N1, or S_N2

Basicity vs Nucleophilicity

- (i) E2 relative to E1 reactions and it will tend to favor E2
- (ii) E2 relative to E1 favor E1
- (iii) will not will not
- (iv) S_N2 relative to S_N1 S_N2

increases

Nucleophilicity

- (i) S_N1 relative to S_N2 reactions; and,
- (ii) E1 over E2

- (i) S_N2 relative to S_N1 reactions;
- (ii) E2 over E1 reactions.

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

N₃⁻ CN⁻ I⁻ MeO⁻ NH₃ H₂O Cl⁻

most nucleophilic

least nucleophilic

NH₂⁻ HO⁻ PhO⁻ NH₃ H₂O Cl⁻

most basic

least basic

because HCl the strongest acid, then H₃O⁺ then NH₄⁺ then PhOH (marginally) then H₂O then NH₃

Temperature (and Entropy)

E2 and S_N2 over E1 and S_N1.

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

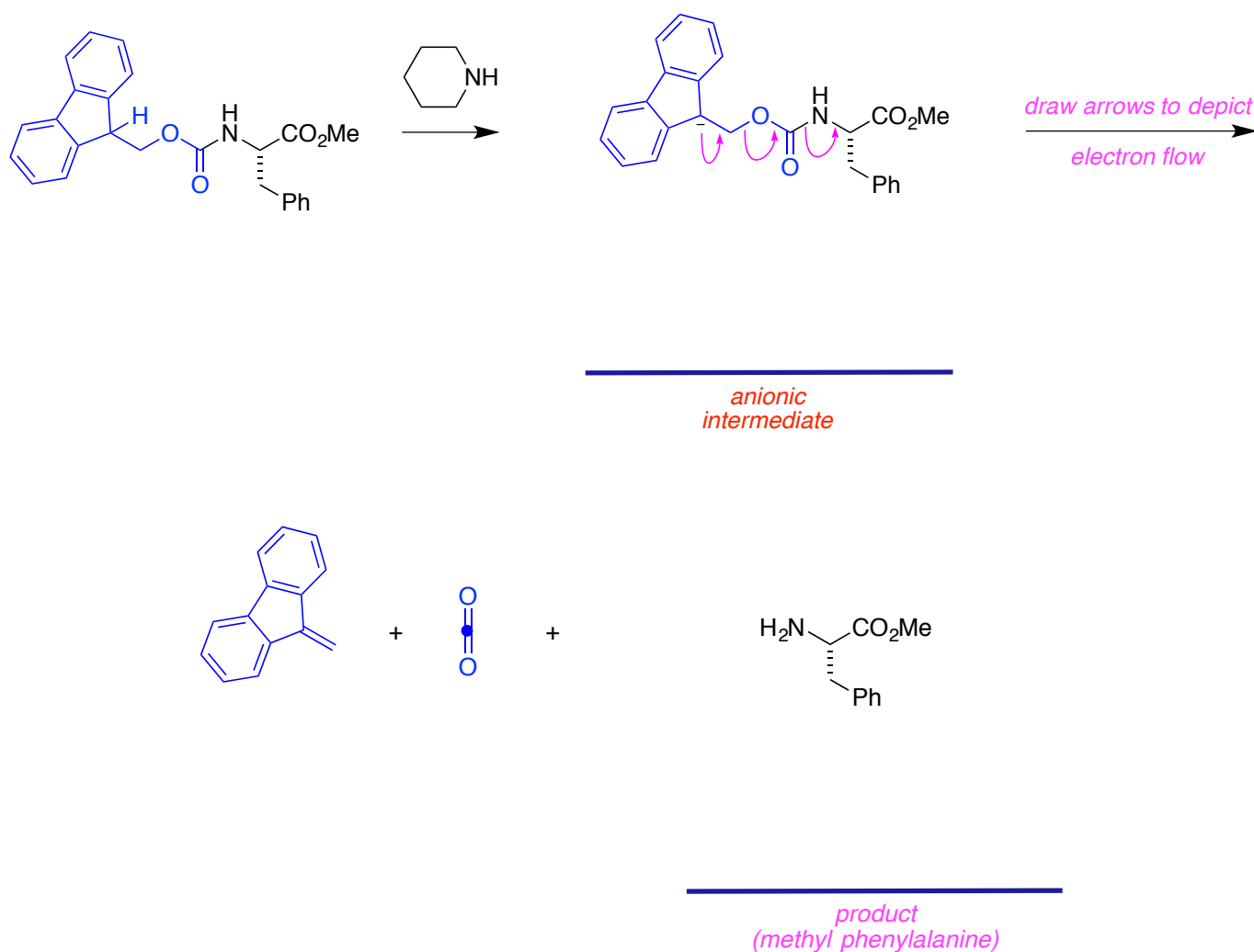
E2 and S_N2 over E1 and S_N1 reactions.

E1 and S_N1 over E2 and S_N2 reactions.

E. E1cB

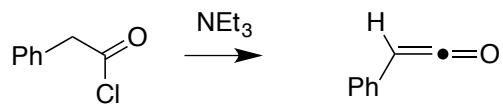
Fmoc

carbamates.

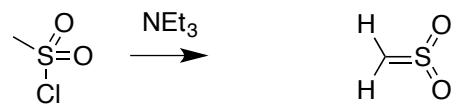


14 πe,
aromatic.

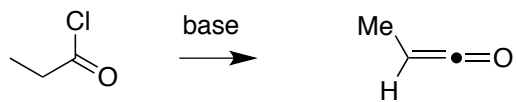
F. Eliminations To Give Allenes, Alkynes, Ketenes And Sulfenes



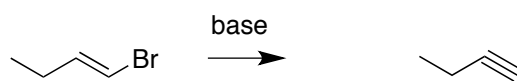
ketene



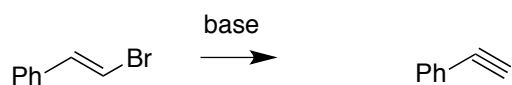
sulfene



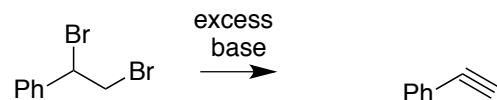
ketene



alkyne



alkyne



alkyne