

# Elimination Reactions To Form Alkenes

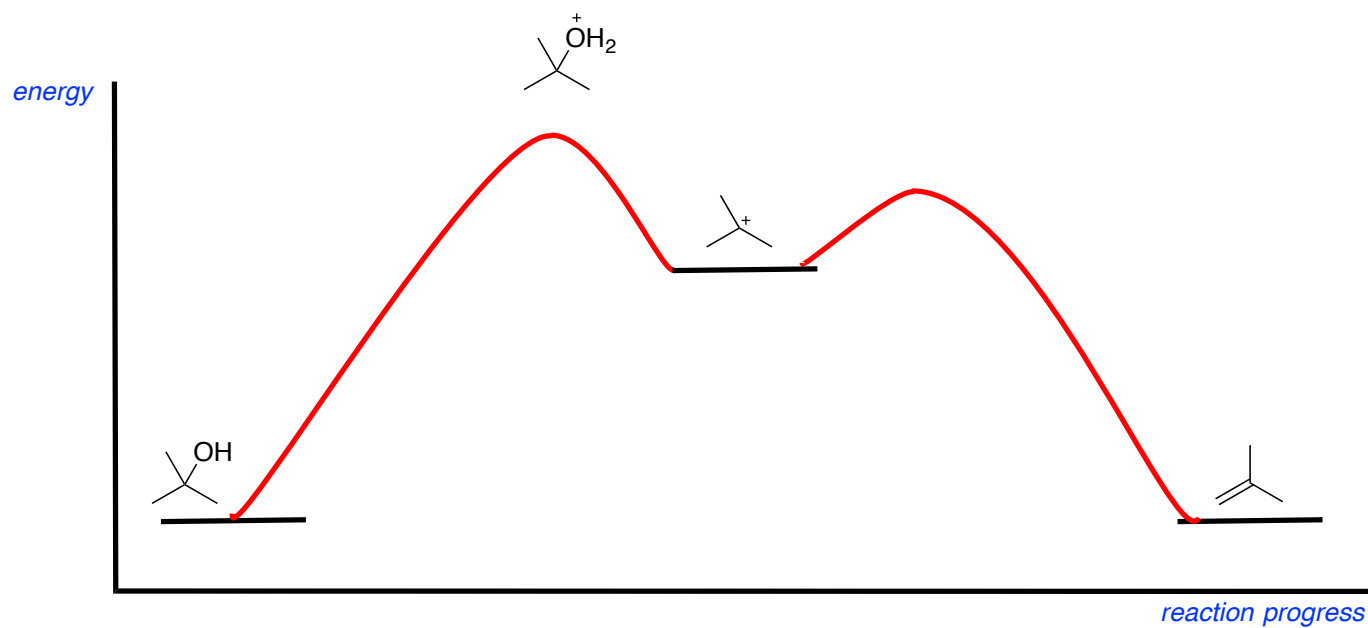
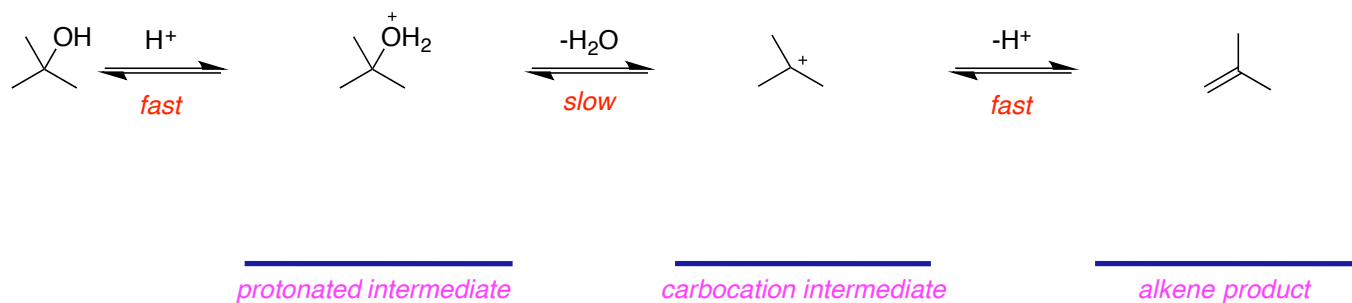
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from chapter(s) \_\_\_\_\_ in the recommended text

## A. Introduction

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## B. E1 Mechanisms



### Kinetics

rate is proportional to

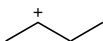
$[\text{tBuOH}]$

rate =

$k [\text{tBuOH}]$

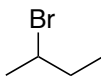
Carbocation Stability

Rates of E1 reactions tend to increase



most stable

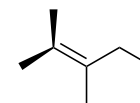
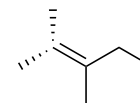
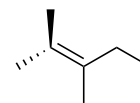
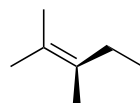
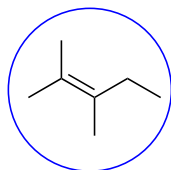
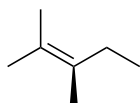
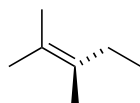
least stable



fastest

slowest

### Bredt's Rule

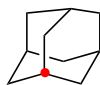


$sp^3$  so it has ideal dihedral angles of about 109

the same

more

is not



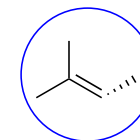
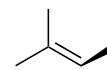
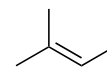
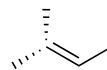
adamantane



adamantane  
cation

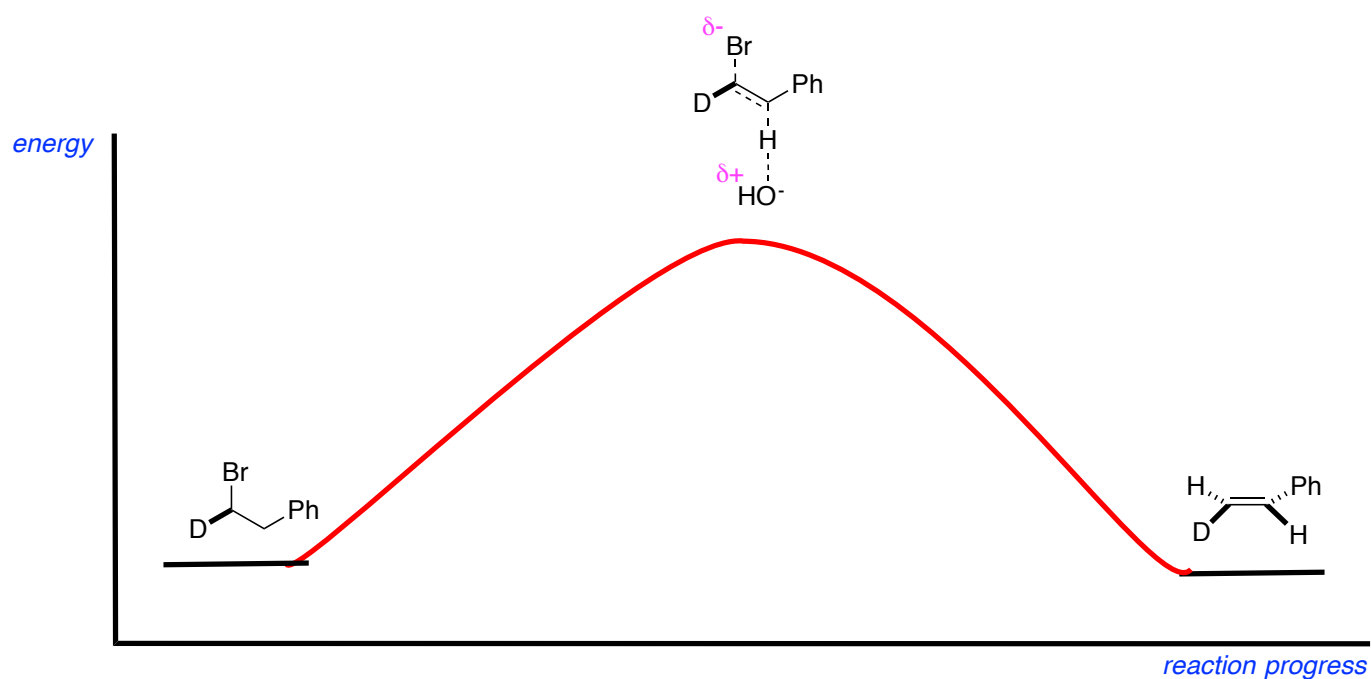
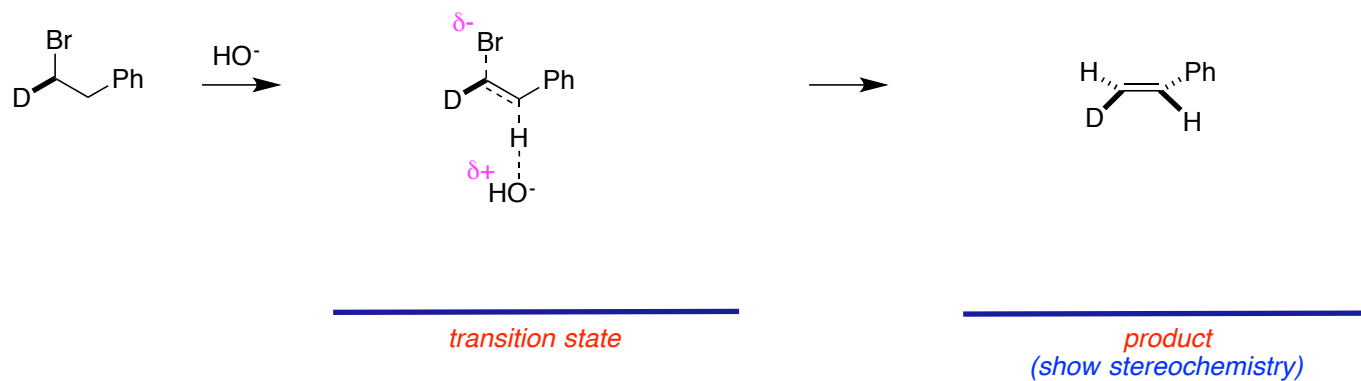


adamantene



are not favorable.

## C. E2 Mechanisms



### Kinetics

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

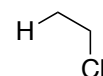
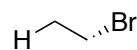
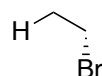
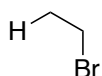
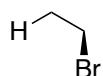
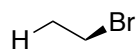
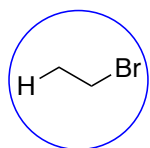
rate =  $k [\text{DCHBrCH}_2\text{Ph}] [\text{OH}^-]$

doubles

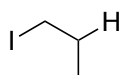
Stereoselectivity

different

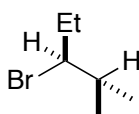
perpendicular.



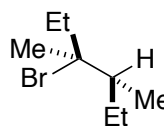
*syn-periplanar  
EtCl*



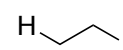
*anti-periplanar  
1-iodopropane*



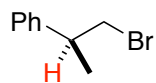
*anti-periplanar  
EtBrHCCHMe<sub>2</sub>*



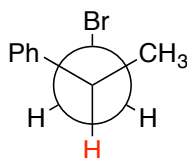
*anti-periplanar  
EtMeHCCBrMeEt*



*anti-periplanar  
ethyl iodide*

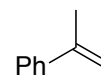


*..... can be  
represented as*

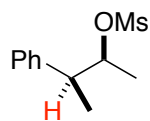


*complete Newman  
projection*

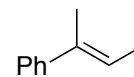
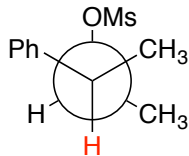
base  
→



*show alkene product*

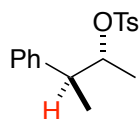


..... can be represented as

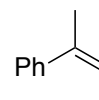
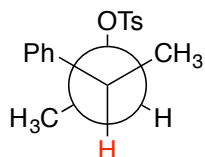


complete Newman projection

show alkene product



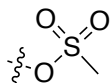
..... can be represented as



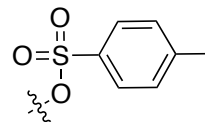
complete Newman projection

show alkene product

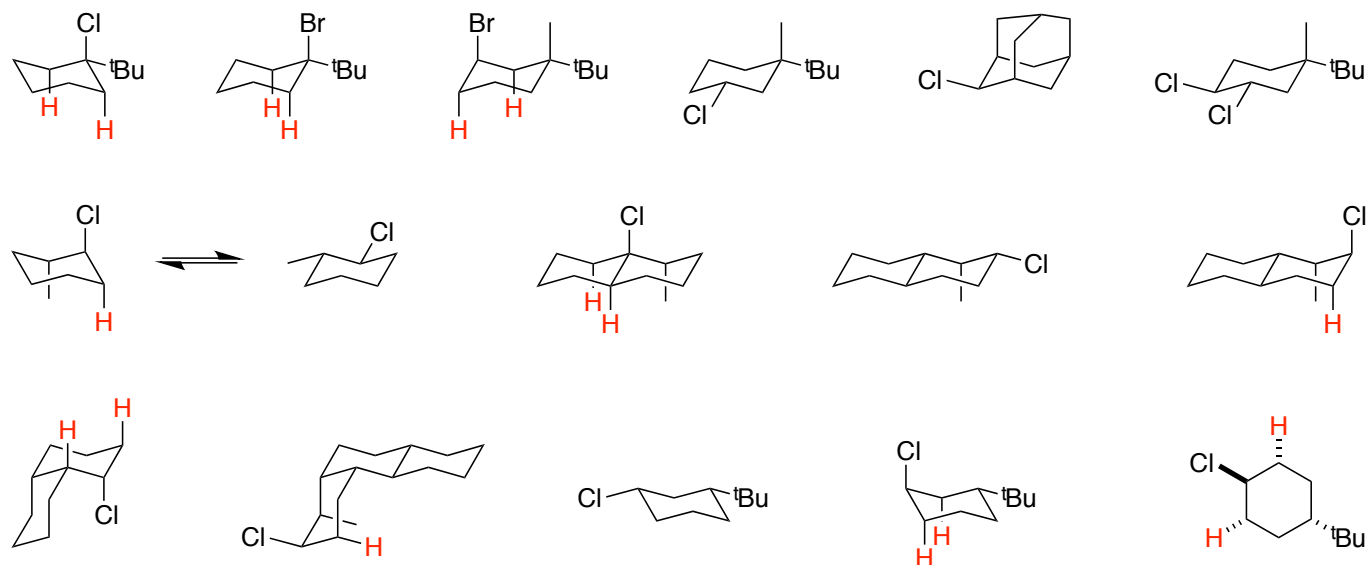
Show structures for:



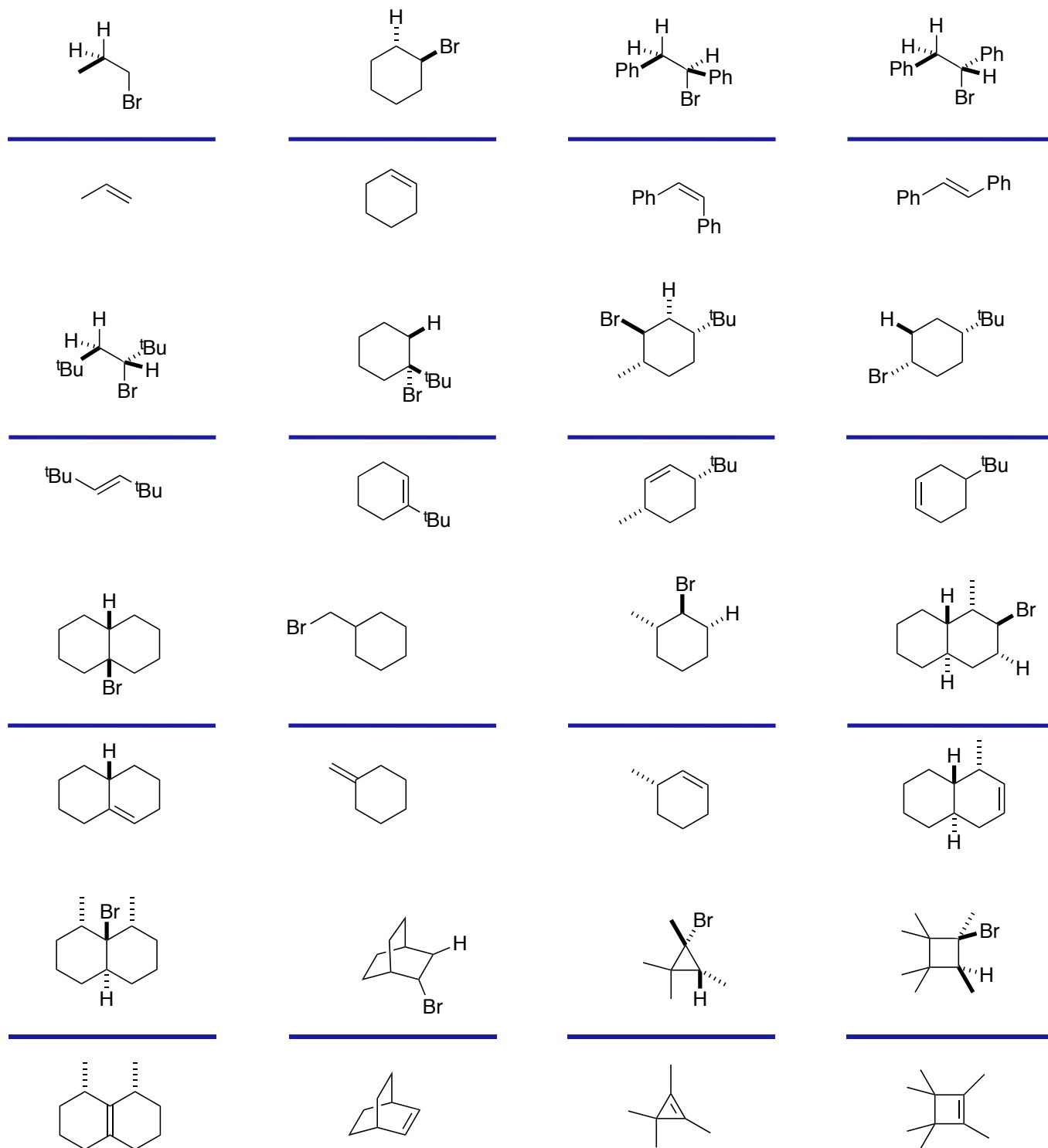
mesyl group, -OMs



tosyl group, -OTs



*anti*-periplanar.



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

### 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<sub>N</sub>2 relative to S<sub>N</sub>1 S<sub>N</sub>2

increases

### 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.

CN<sup>-</sup>                      N<sub>3</sub><sup>-</sup>                      I<sup>-</sup>                      Cl<sup>-</sup>                      MeO<sup>-</sup>                      NH<sub>3</sub>                      H<sub>2</sub>O

---

*most nucleophilic*

*least nucleophilic*

OH<sup>-</sup>                      Cl<sup>-</sup>                      PhO<sup>-</sup>                      NH<sub>2</sub><sup>-</sup>                      NH<sub>3</sub>                      H<sub>2</sub>O

---

*most basic*

*least basic*



## Temperature (and Entropy)

E2 and S<sub>N</sub>2 over E1 and S<sub>N</sub>1.

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

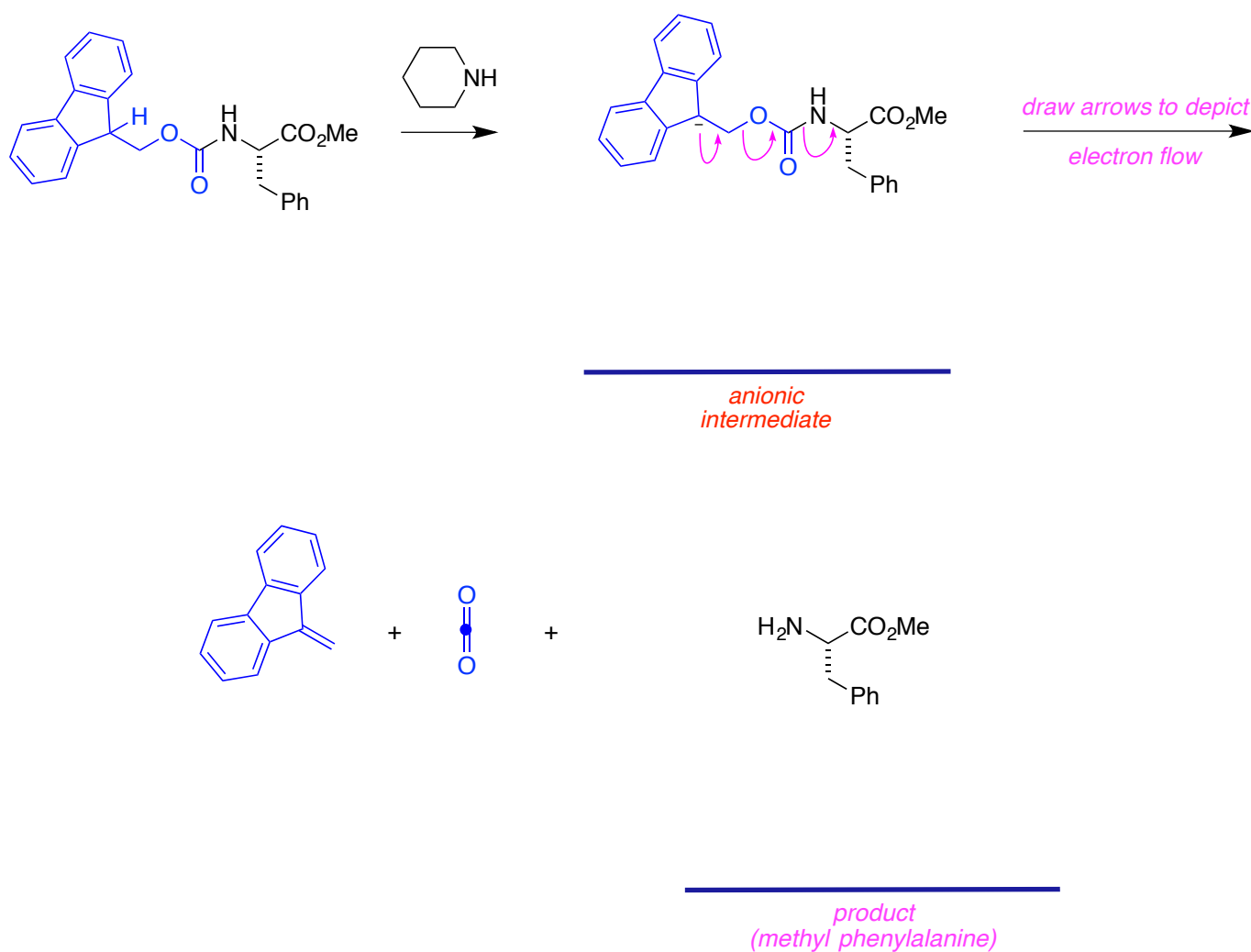
E2 and S<sub>N</sub>2 over E1 and S<sub>N</sub>1 reactions.

E1 and S<sub>N</sub>1 over E2 and S<sub>N</sub>2 reactions.

## E. E1cB

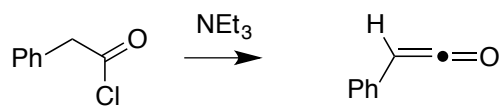
Fmoc

carbamates.



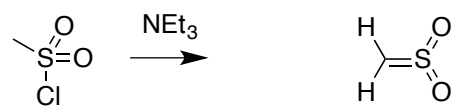
14  $\pi$ e,  
aromatic.

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



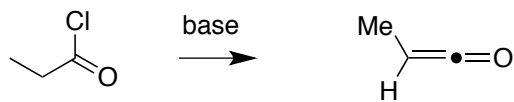

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*ketene*



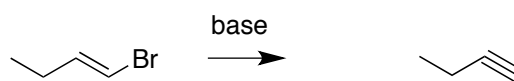

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*sulfene*



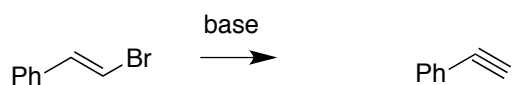

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*ketene*



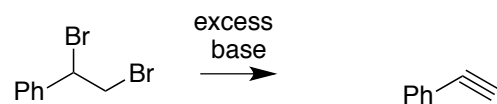

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*alkyne*




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*alkyne*




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*alkyne*