Chemistry 233
Chapter 6 Problem Set

Nucleophiles and Electrophiles

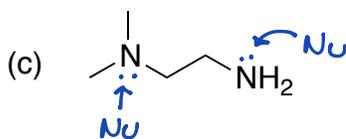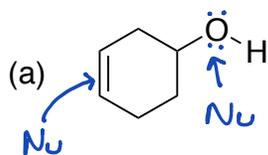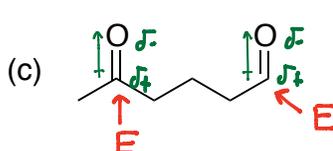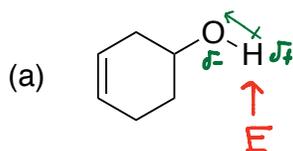1) Identify all of the nucleophilic centers in each of the following compounds:
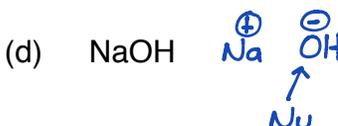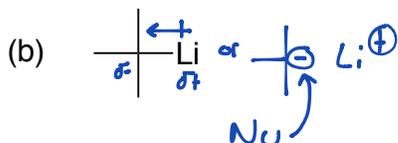
2) Identify all of the electrophilic centers in each of the following compounds:

Note: Despite polarization in the bond, we generally don't consider a carbon bonded to an OH as electrophilic
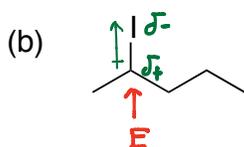
Arrow Pushing and Reaction Mechanisms

3) Identify which arrow pushing pattern is utilized in the following reactions:

(a) Leaving Group — Loss of a Leaving Group

(b) Proton transfer

(c) Nucleophilic Attack

(d)

~H
Hydride
Shift

H (don't have to show the H)
Carbocation
rearrangement

(e)

E

Nu

+

Nucleophilic
Attack

(f)

~CH₃
methyl
Shift

Carbocation
rearrangement

(g)

Ph $\diagup$ OSO₂CH₃

Leaving group

$\longrightarrow$

Ph—⊕

+

⊖OSO₂CH₃

Loss of a
Leaving Group

(h)

Nu

E

Nucleophilic
Attack
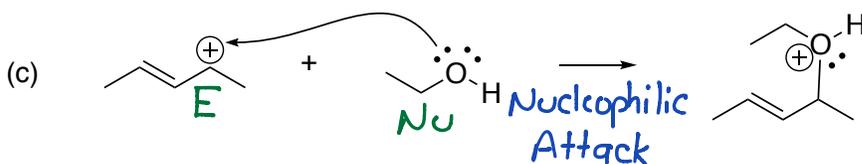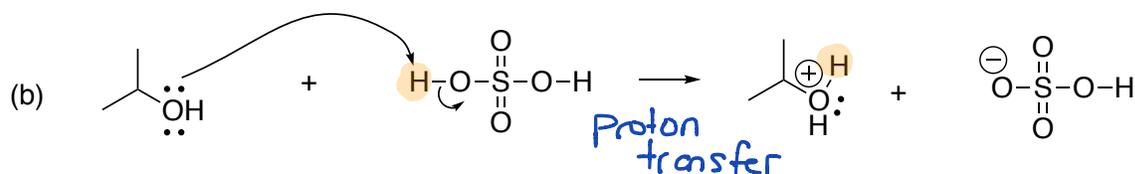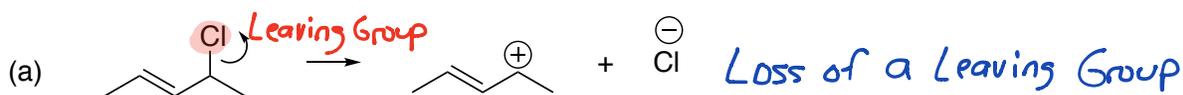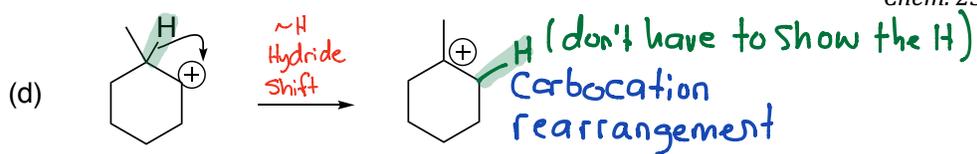
4) Identify the electron flow pattern in each step of the complete reaction mechanisms shown below.
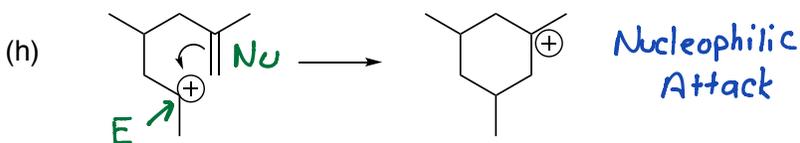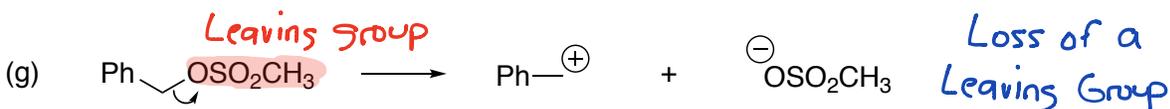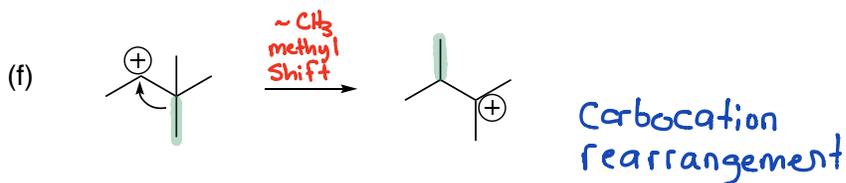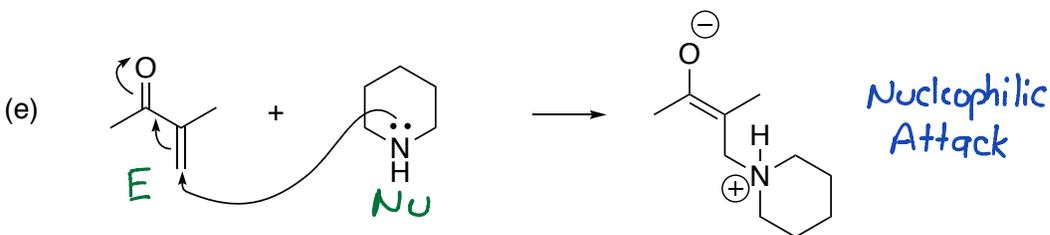
(a)

OH

Nu
attack

$\xrightarrow{\substack{\text{Loss} \\ \text{of} \\ \text{L.G.}}}$

Proton
Transfer

+ HO—

(b)

$\xrightarrow{\substack{\text{Loss} \\ \text{of} \\ \text{L.G.}}}$

+ I⊖

$\xrightarrow{\substack{\text{Carbocation} \\ \text{rearr.}}}$

OH

Nu
attack

Na OH

Proton
Transfer

Na⁺ + H₂O +
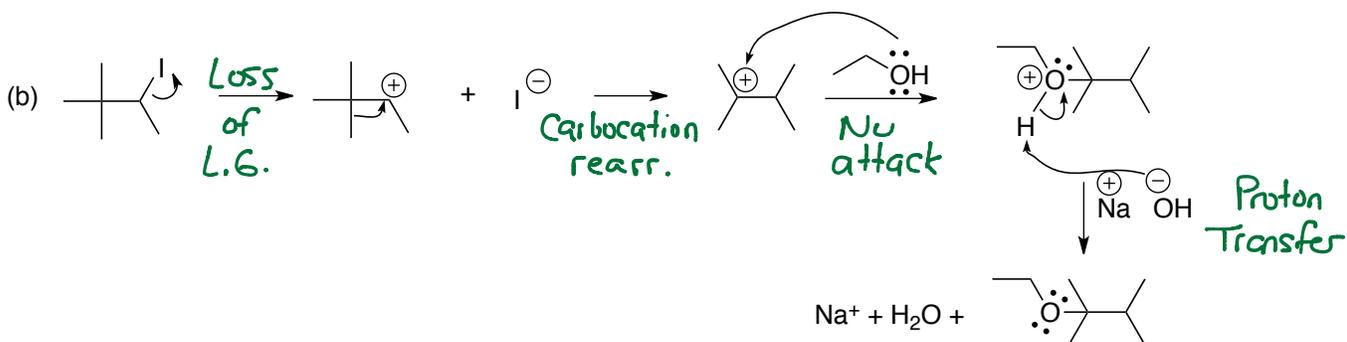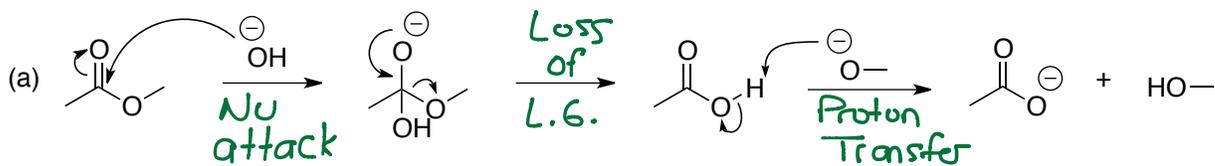
5) Draw curved arrows to accomplish the following transformations. *Hint: it may help to draw in lone pairs.*

(a) [structure with Br, Cl⁻, curved arrows] → [isopropyl chloride structure] + Br⁻   or   [Br structure] → [carbocation + Cl⁻] → [Cl structure]

(b) [structure with Br] → [carbocation ⊕] + Br⁻   →(Cl⁻)→   [structure with Cl]

(c) [cyclopentane with H and I, O⁻ base structure] → [cyclopentene] + [structure with OH]
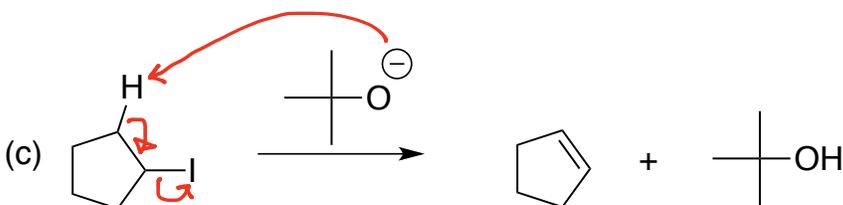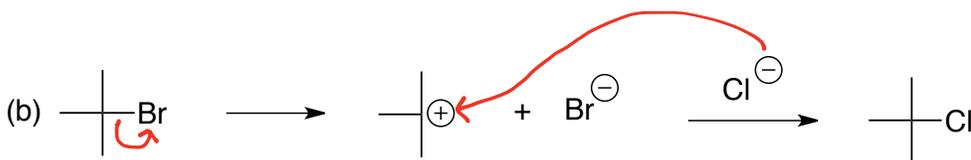
6) Predict if the following carbocations will rearrange. If so, draw the rearrangement product.

(a) [cyclohexane cation, 2°] —yes→ [ring-contracted 3° cation]

(b) [cyclohexyl cation, 2°]   No

(c) [methylenecyclohexane cation, 2°] —yes→ [2° allylic cation]
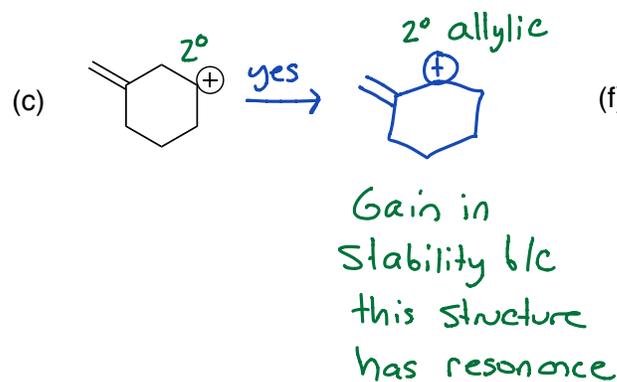
Gain in
Stability b/c
this structure
has resononce

(d) [cyclopentane cation, 2°] —yes→ [two products]

methyl   or   alkyl shift
Shift   from bond in ring

(e) [3° cation structure]   No

Rearrangement would give
another 3° ⊕ (No gain)

(f) [branched cation] —yes→ [rearranged cation]

Hydride shift is
preferred over
methyl shift.

Reaction Coordinate Diagrams

7) Consider the two energy diagrams shown below:

E_a
G
ΔG
Rxn
(a)

E_a
G
ΔG
Rxn
(b)
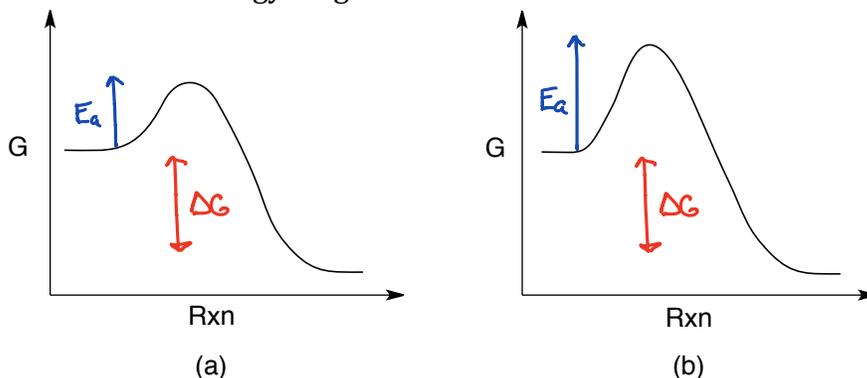
(a) Which of the two reactions will occur at a faster rate?

(a) Smaller activation energy (E_a)

(b) Compare the value of ΔG for both reactions.

Both have the same ΔG.

(c) At equilibrium, which reaction, if either, will favor product?

Both have -ΔG & will favor product

(d) At equilibrium, which reaction, if either, will contain a higher concentration of product?

Same ΔG = Same amount of product at equilibrium.

8) Consider the following reaction that is thermodynamically favored. Draw a reaction coordinate diagram that represents the reaction.

OCH_3 + Cl → OCH_3 + Cl

SM   P

E
Sm
P
Rxn
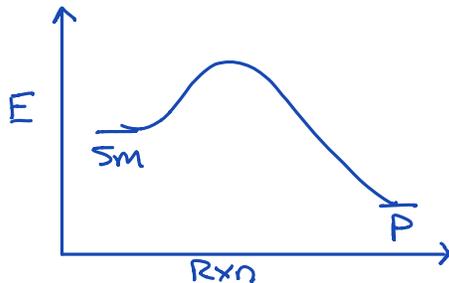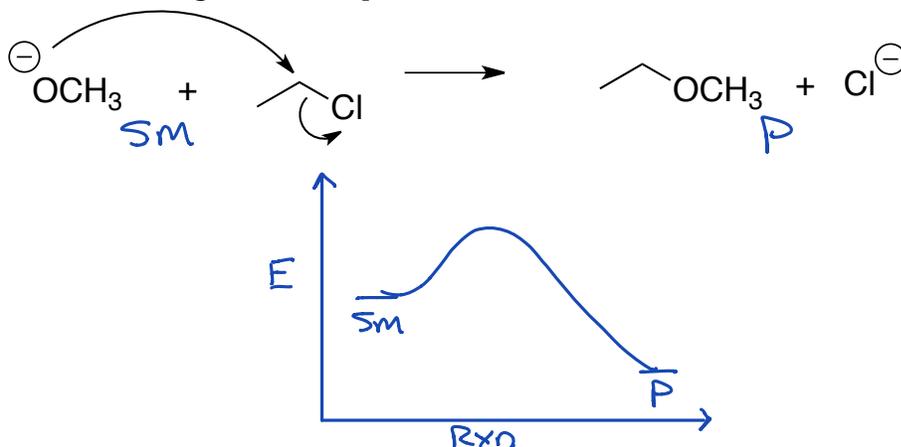
9) Draw a reaction coordinate diagram for a reaction that is exergonic (exothermic), has two intermediates, and the rate-determining step is the second step.

Step2 (RDS)
Step 1
Step 3
E
I1
I2
Sm
P
Rxn
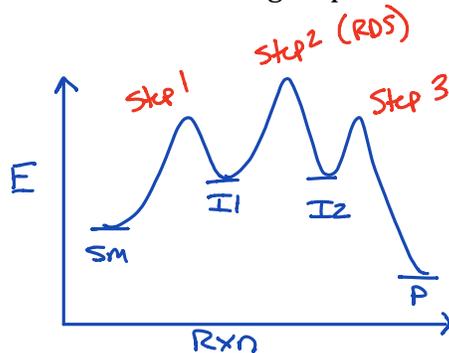
Exergonic = P lower E than SM

I's should be higher E than SM & P