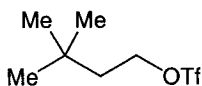Out of 20 pts.

Key

3pts.

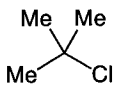## Problem Set #5, 5.12 Spring 2003
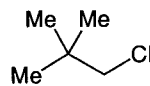### Due Monday, March 31, 4pm

1. a) Rank the following series of molecules based on reactivity in an S_N2 reaction (NaI/acetone).
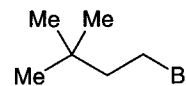   (1= fastest S_N2, 4= slowest S_N2)

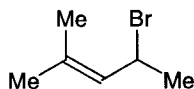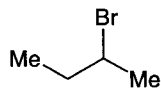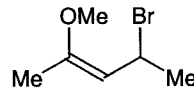| Me Me	Me Me	Me Me	Me Me
Me⟍⟍OTf	Me⟍⟍Cl	Me⟍⟍Cl	Me⟍⟍Br
1	4	3	2

b) Rank the following series of molecules based on reactivity in an S_N1 reaction (EtOH/heat).
   (1= fastest S_N1, 4= slowest S_N1)

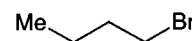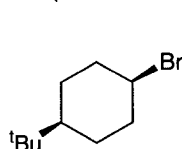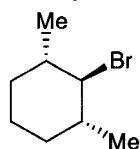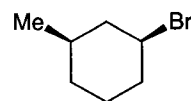| Me Br	Br	OMe Br	
Me⟍⟍Me	Me⟍⟍Me	Me⟍⟍Me	Me⟍⟍Br
2	3	1	4

c) Rank the following series of molecules based on reactivity in an E2 reaction (NaO^{i}Pr/ ^{i}PrOH).
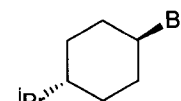   (1= fastest E2, 4= slowest E2)

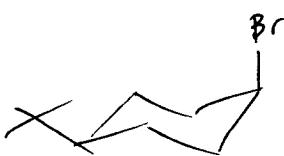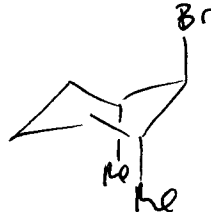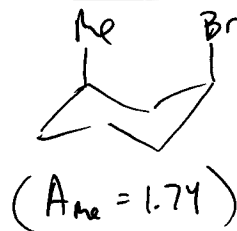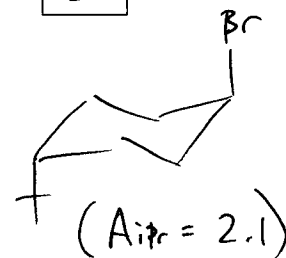|	Me	Me	
Br, ^{t}Bu	Br, ''Me	Me, Br	Br, ^{i}Pr
1	4	2	3

"locked axial"

"no a·f.p. Hs"

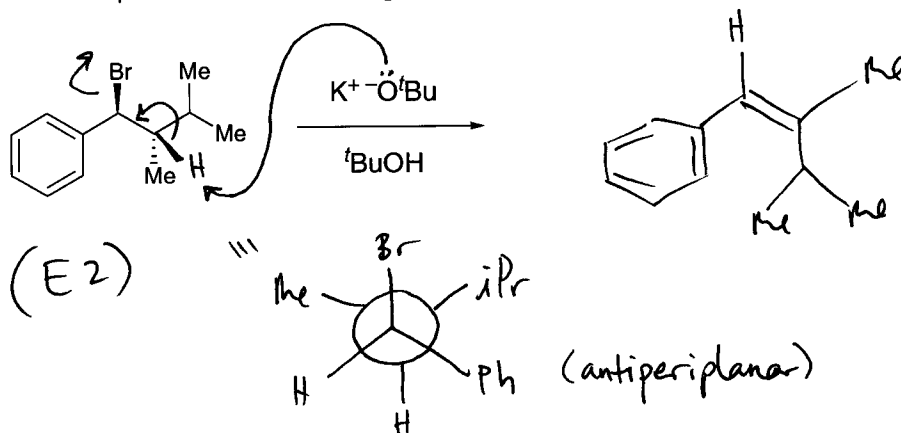$(A_{Me} = 1.74)$

$(A_{iPr} = 2.1)$

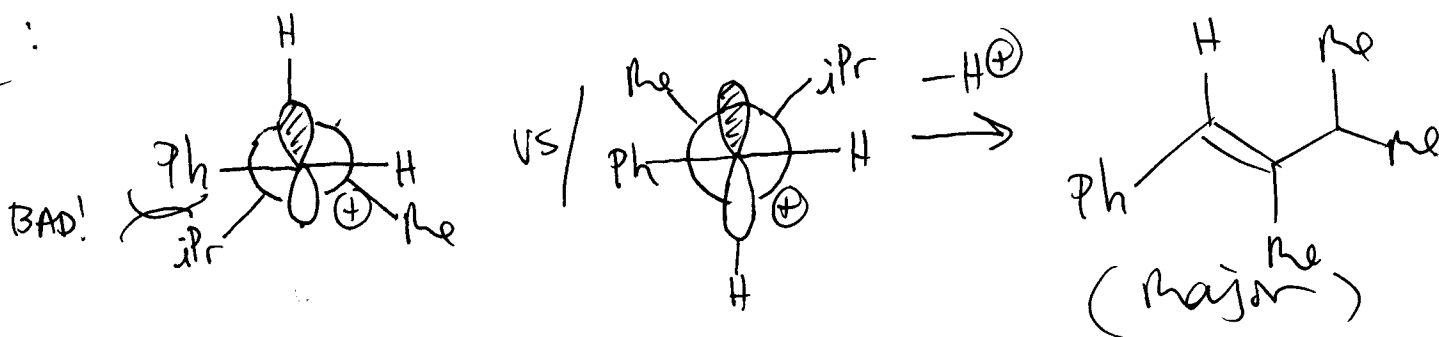**2. a)** Predict the product of the following reaction, and provide the mechanism for its formation.

K+ ⁻O^tBu / ^tBuOH

(E2)

(antiperiplanar)

b) Draw a picture of the transition state for the above reaction. Pay attention to stereochemistry!

$Br^{\delta -}$ ... $\delta^- OtBu$
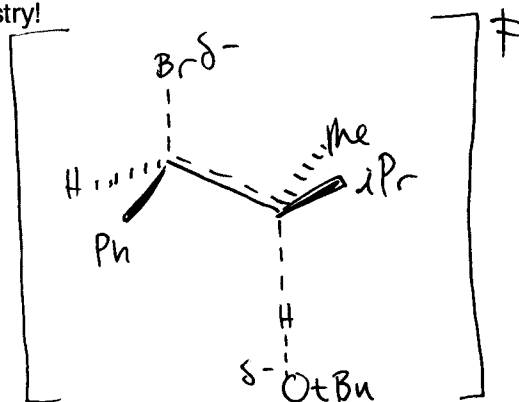
c) If the same molecule were heated in diisopropylamine ($^iPr_2NH$), would you expect the same product that you drew in part **a**? Why or why not?

No! Heating the molecule from part a in diisopropylamine would result in an E1 elimination. Because E1 eliminations go through a planar carbocation, both alkene isomers can form. In general, the most stable isomer results from an E1 elimination. (Phenyl on the same side as the methyl, not the isopropyl.)

E1:

BAD!

vs/

−H⊕

(major)

3 pts.

3. Predict the products of the following **substitution** reactions, and specify whether each proceeds by **S$_N$1** or **S$_N$2**. Pay attention to stereochemistry.

a)

MeOH
Δ
S$_N$1

+

(enantiomers)

b)

KCN
DMF
S$_N$2

c)

NaI
acetone, Δ
S$_N$2

d)

H$_2$O
Δ
S$_N$1
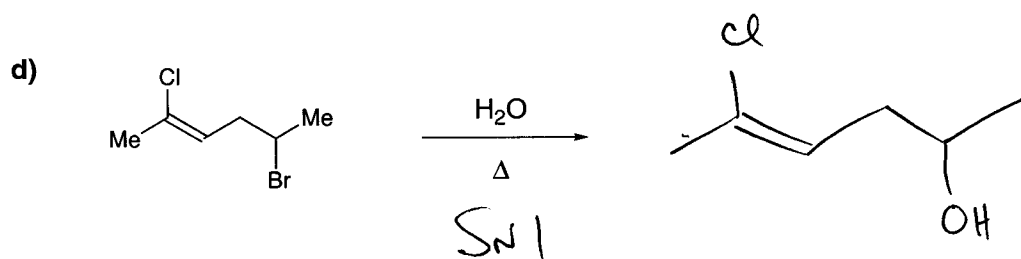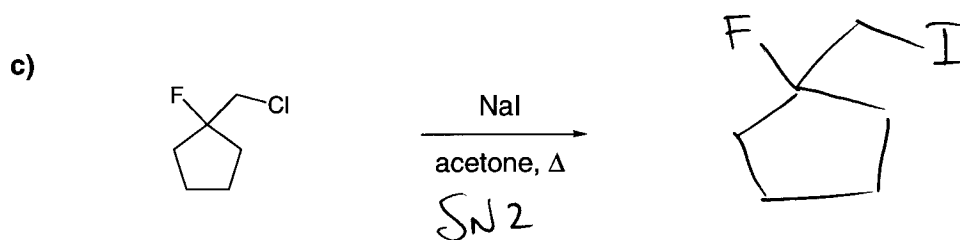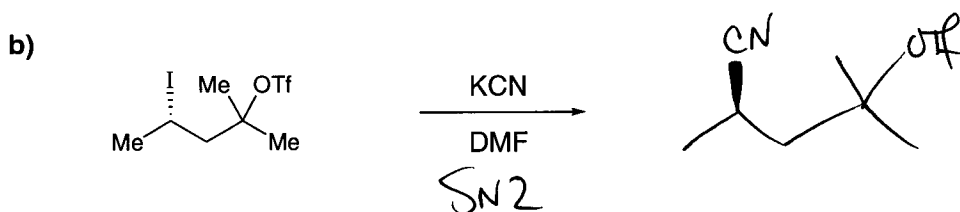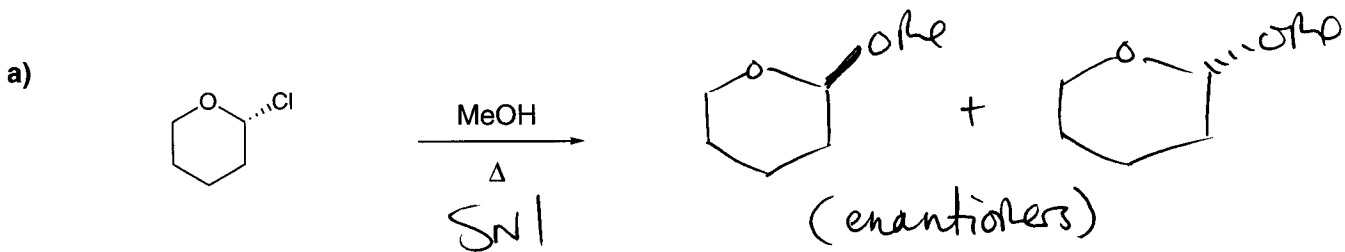
Note: Some of these conditions would also cause elimination products to form. In this problem, we are only focusing on the substitution products.

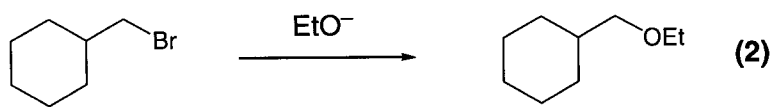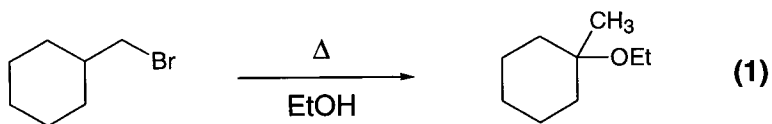**4.** The reaction conditions are very important in determining what products are obtained in elimination reactions. Predict the **major** products of the following **elimination** reactions.
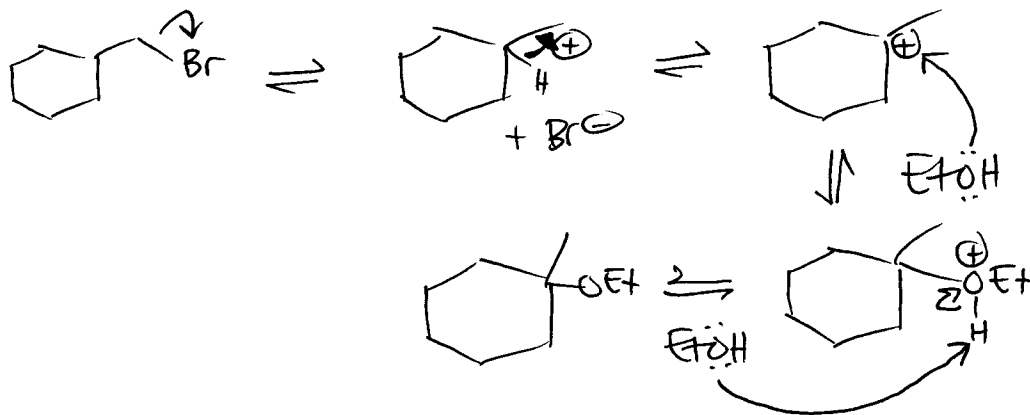

Li$^+$ $^-$N^{i}Pr$_2$

"bulky"

Br, Me

Na$^+$ $^-$NH$_2$

"small"

Na$^+$ $^-$OMe

(only one a.p.p. H)

Br

Me

MeNH$_2$, Δ

(E1)

Et$_3$N, Δ

(E1)

Br

Me

Na$^+$ $^-$OMe

"small"

K$^+$ $^-$O^{t}Bu

"bulky"
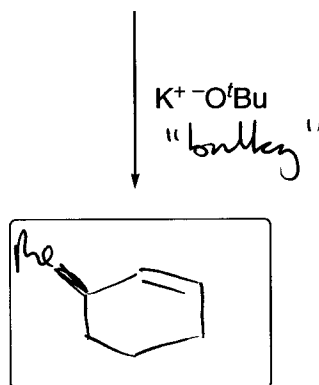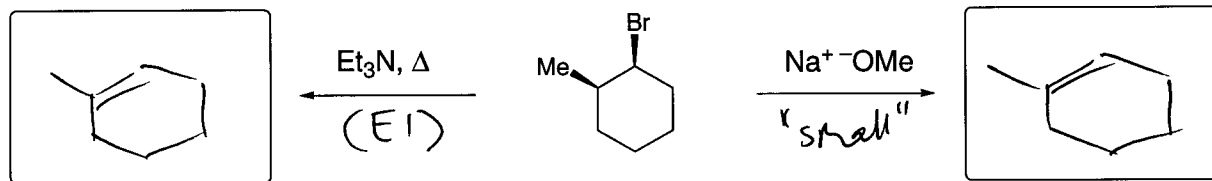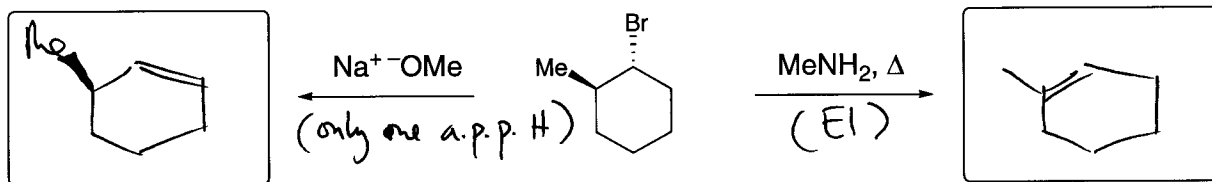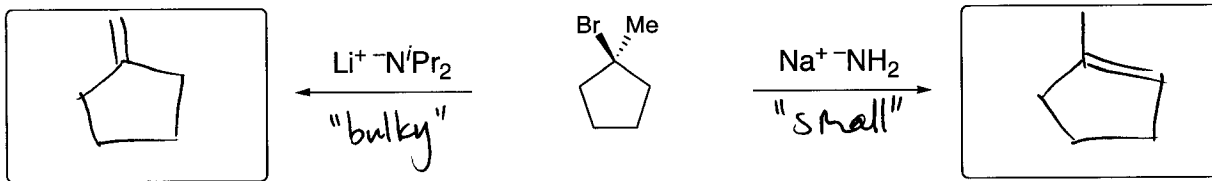
5. (Bromomethyl)cyclohexane undergoes the following two reactions:

$$\text{(cyclohexyl-CH}_2\text{Br)} \xrightarrow[\text{EtOH}]{\Delta} \text{(cyclohexyl with } CH_3, \text{ OEt)} \quad \textbf{(1)}$$

$$\text{(cyclohexyl-CH}_2\text{Br)} \xrightarrow{EtO^-} \text{(cyclohexyl-CH}_2\text{OEt)} \quad \textbf{(2)}$$
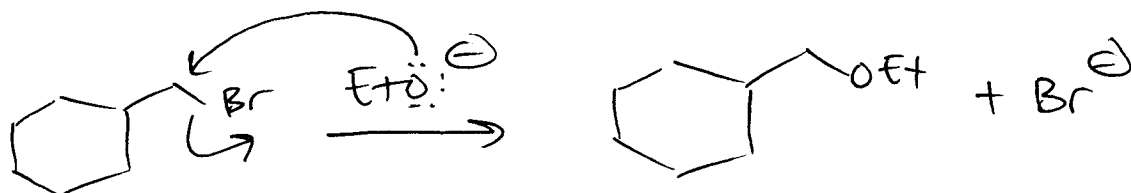
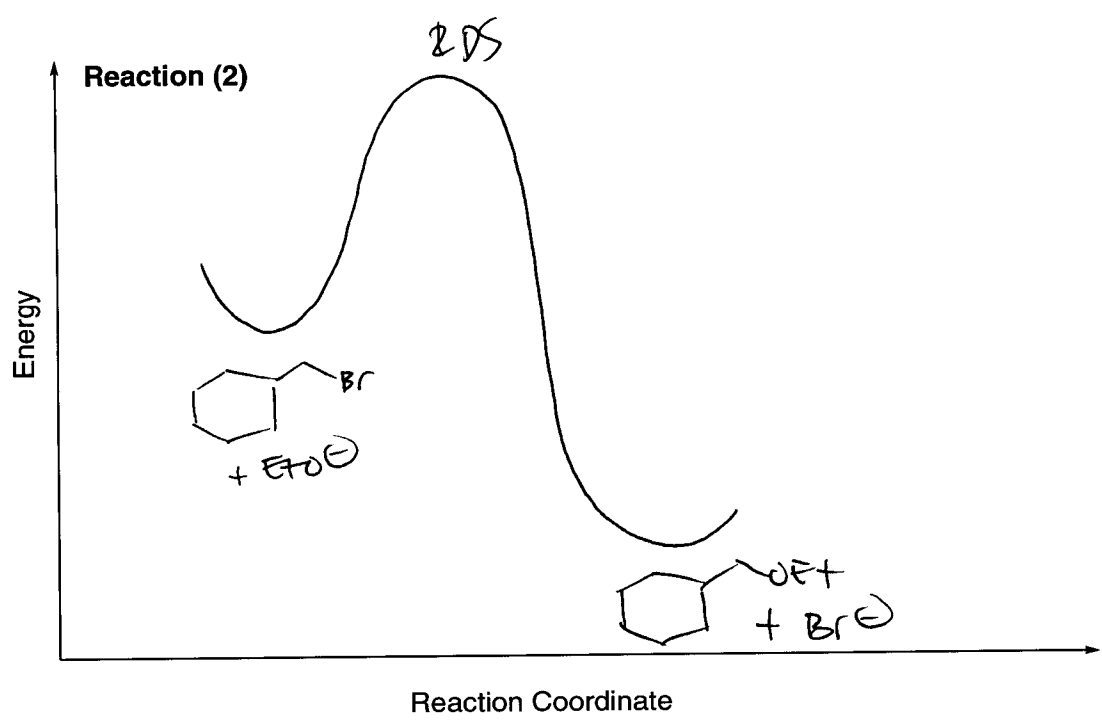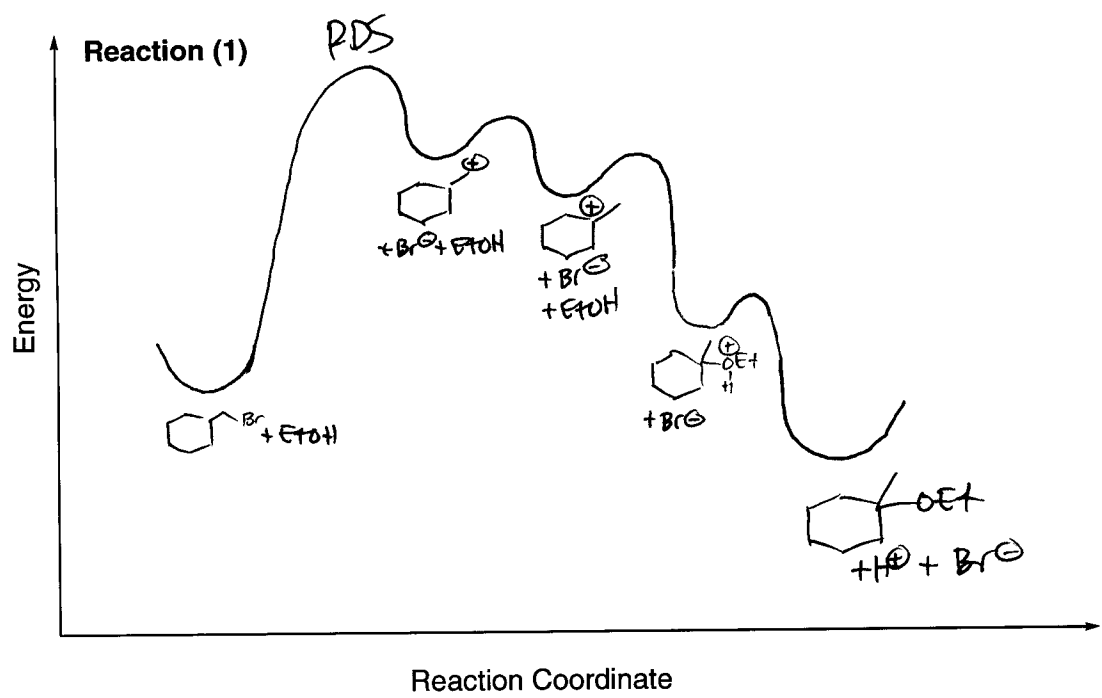**a)** Provide a **detailed** mechanism for reaction **(1)**. SN1 !

b) Provide a **detailed** mechanism for reaction **(2)**. SN2 !

c) Draw reaction-energy diagrams for the reactions on the previous page. Clearly label starting materials, intermediates, products, and the rate-determining step for each reaction.

Reaction (1)

Energy

Reaction Coordinate

Reaction (2)

Energy

Reaction Coordinate

6. The mechanism of the following reaction involves mechanistic steps that you are already familiar with. Provide a detailed mechanism.