1) Circle the best answer to each of the following questions. (25 pts)

1a. Which of the following reaction mechanisms is least likely to be observed in sterically hindered substrates?
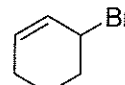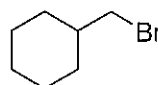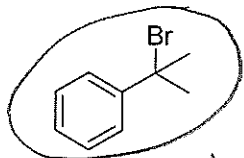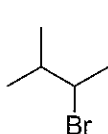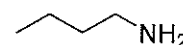
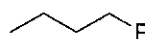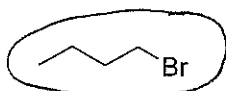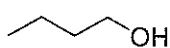E1   E2   (S$_N$2)   S$_N$1   All equally likely

1b. Which of the following substrates would react **fastest** in an S$_N$1 reaction?

CH$_3$Br
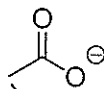
3°, benzylic

1c. Which of the following substrates would react **fastest** as an **electrophile** in an S$_N$2 reaction?

OH   Br   F   NH$_2$

best leaving group

1d. Which base would most likely react through an E2 mechanism with the substrate shown in the box?

substrate

CH$_3$CH$_2$OH   H$_2$O   Br$^\ominus$
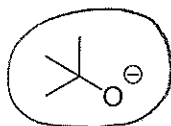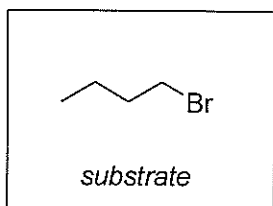
Strong, sterically hindered

all are weak

1e. Which of these would react *fastest* in an S$_N$2 mechanism with sodium cyanide?

(CH$_3$Br)   Br   Br   Br   Br
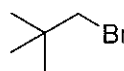
least hindered

2.   Predict the major organic product of each of the following reactions. Show stereochemistry where appropriate. **Put your answer in the box for credit.** (24 pts)
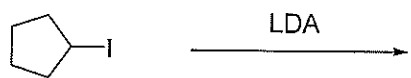

LDA

$E2$

NaI

acetone

S_N2

inversion

H_2SO_4 (aq)

Δ
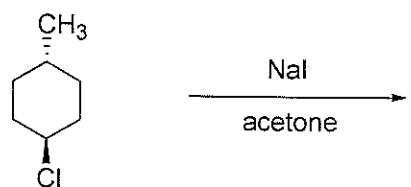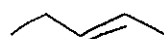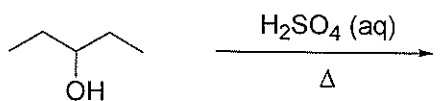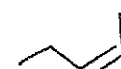
dehydration –
$E1$

also OK
(we hadn't
talked about
stereoselectivity
in E1 yet)

Br_2

hν

1. TsCl, pyr
2. NaN_3, DMF

CH_3OH

Show major
substitution product
ONLY

$O CH_3$

$CH_3 \ddot{O} H$

$1L$

$CH_3\overset{\oplus}{:O:}$ H $\longleftarrow$ $CH_3 \ddot{O} H$ $O CH_3$
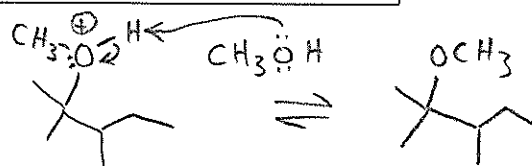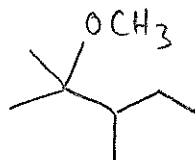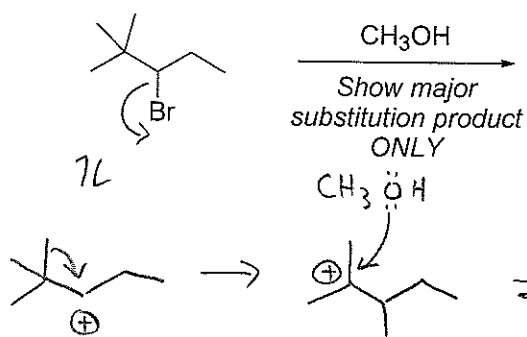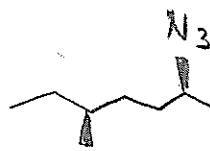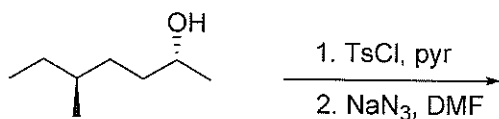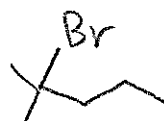
3.   For each of the three reactions shown below, circle the letter that corresponds to the energy diagram at the bottom of the page that most accurately represents the reaction. You can use your knowledge of the mechanistic steps involved in each reaction even if you have not seen an energy diagram for that particular reaction. *Consider each reaction in the forward direction, from left to right.* (15 pts)

Reaction		Choices
(CH₃)₃C–OH + HCl → (CH₃)₂C=CH₂		A B C **(D)** E F
CH₃CH₂CH₂CH₂–F + NaBr / DMSO → CH₃CH₂CH₂CH₂–Br		A **(B)** C D E F
Ph–CHBr–CH₃ + H₂O → Ph–CHOH–CH₃		A B **(C)** D E F

Energy diagrams A, B, C (top row) and D, E, F (bottom row), each with "energy ↑" on the y-axis and "reaction →" on the x-axis.

Mechanisms:

$$(CH_3)_3C\text{–}\overset{..}{\underset{..}{O}}H \xrightarrow{\;H\text{–}Cl\; fast\;} (CH_3)_3C\text{–}\overset{+}{\underset{..}{O}}H_2 \xrightarrow{\; slow, RDS \;} \overset{H}{\underset{H_2\overset{..}{O}\; fast}{}} \; (CH_3)_2C=CH_2$$

In SN2, weaker base displacing stronger base is endothermic

$$CH_3CH_2CH_2CH_2\text{–}F \;\;\; Br^{\ominus} \longrightarrow \;\;\; CH_3CH_2CH_2CH_2\text{–}Br$$

$$Ph\text{–}CHBr\text{–}CH_3 \xrightarrow{\; slow, RDS \;} Ph\text{–}CH^{+}\text{–}CH_3 \xrightarrow{\; H_2\overset{..}{O}\; fast \;} \xrightarrow{\; H_2\overset{..}{O}\; fast \;} Ph\text{–}CHOH\text{–}CH_3$$

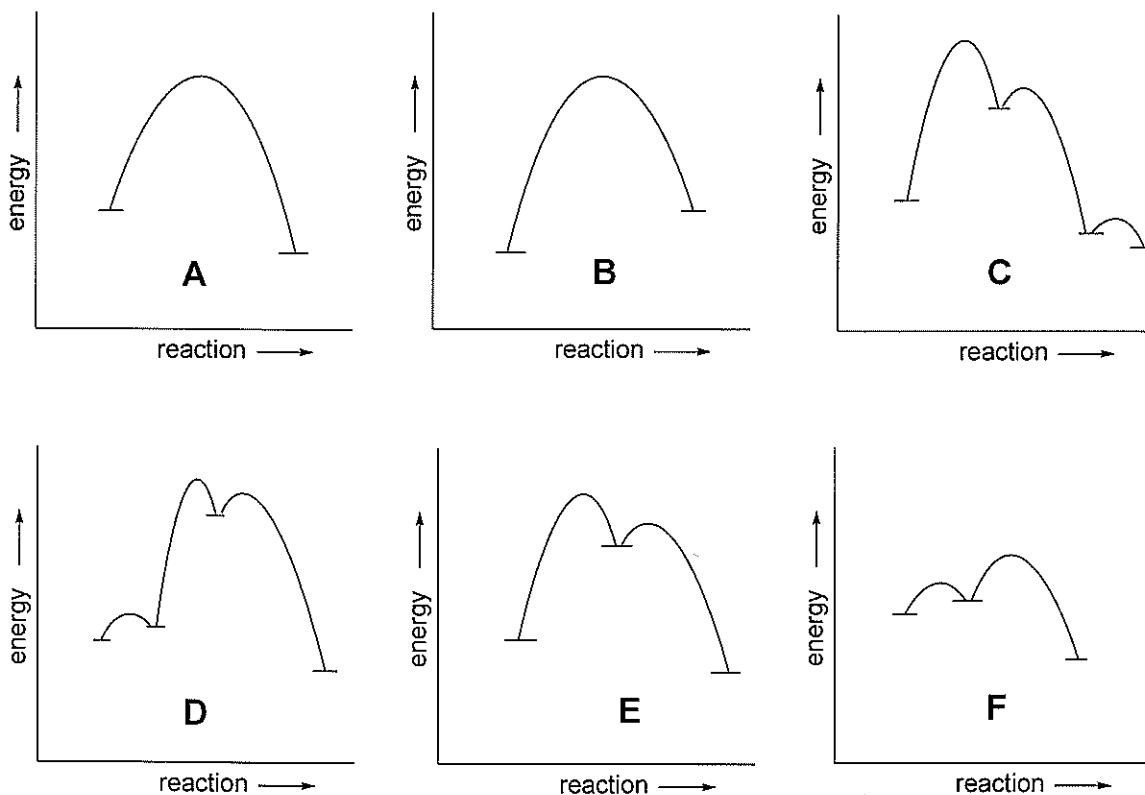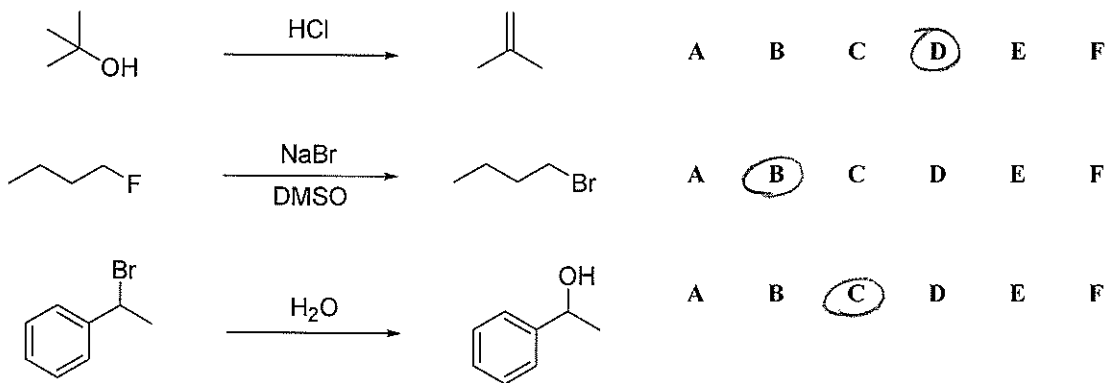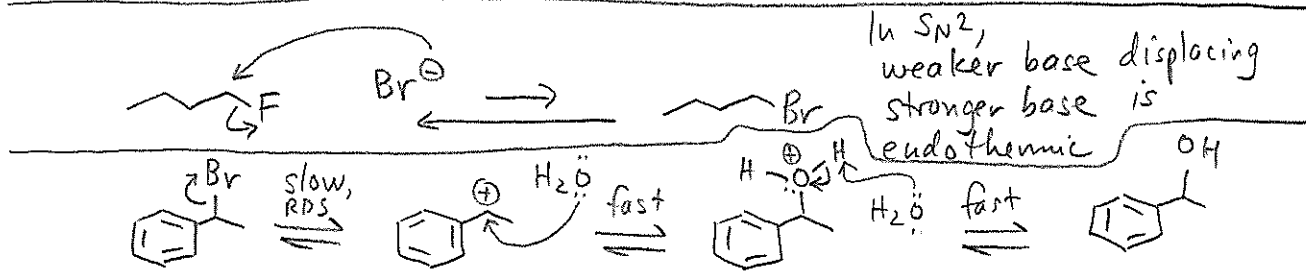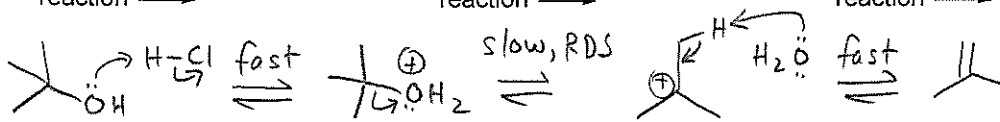4.   Predict the products of each of the following S_N1 reactions. Show stereochemistry in your structures at all asymmetric carbons. Then identify the correct stereochemical r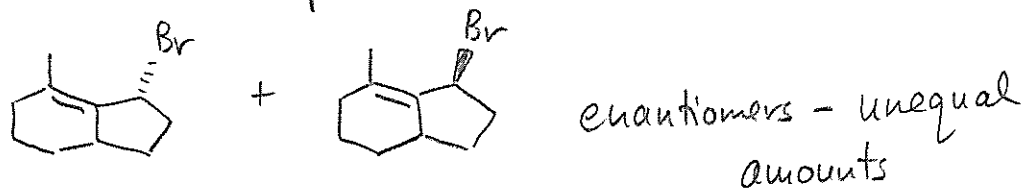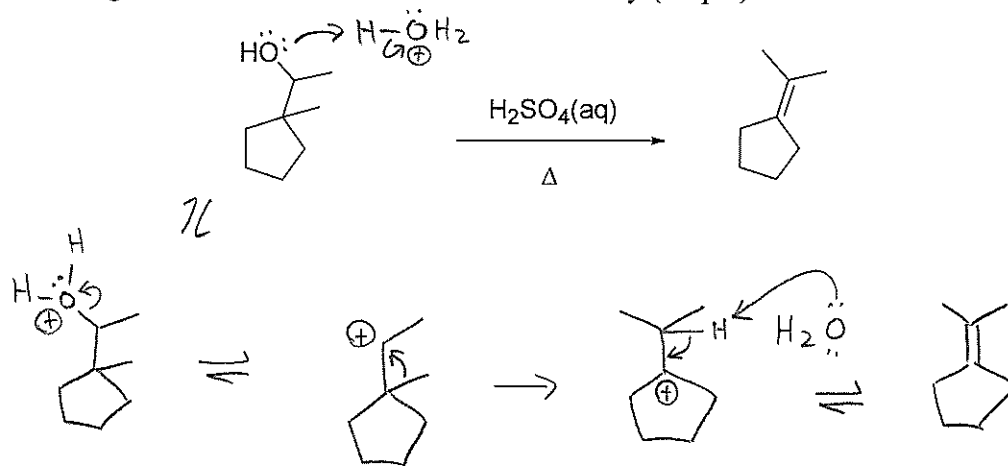elationship between the structures (enantiomers or diastereomers) and whether they are formed in equal amounts or unequal amounts by circling the correct terms (16 pts).

(circle one)   ENANTIOMERS   (DIASTEREOMERS)

(circle one)   Equal amounts   (Unequal amounts)

(circle one) (ENANTIOMERS)   DIASTEREOMERS

(circle one)   Equal amounts   (Unequal amounts)

Also OK for this problem:

enantiomers — unequal amounts
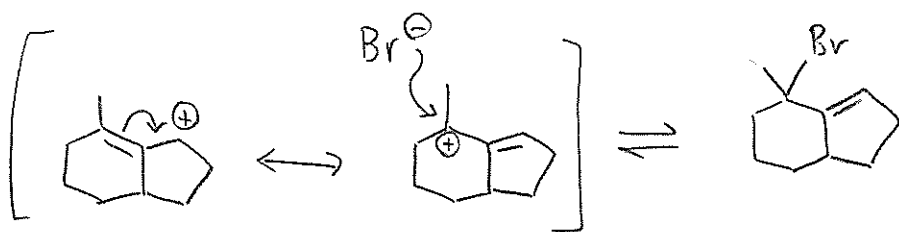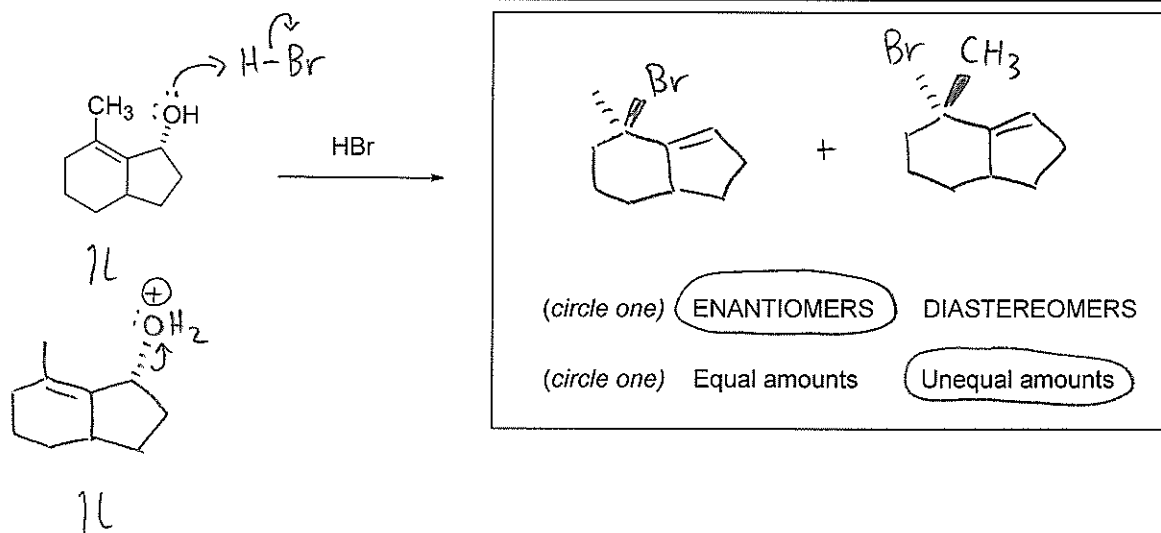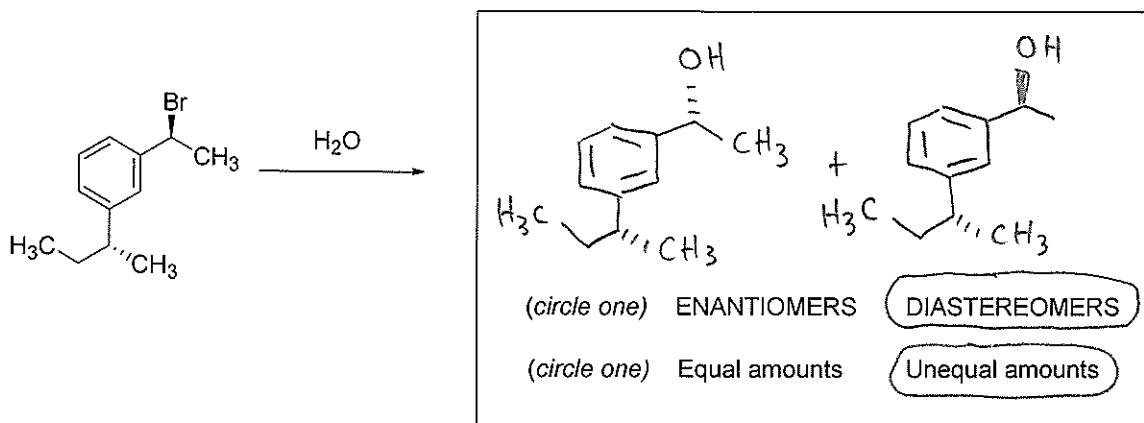
5a. Draw an arrow-pushing mechanism showing the conversion of the starting material to the product. Include all curved arrows, necessary lone pairs and non-zero formal charges. Be sure to draw all structures clearly (10 pts).

5b. Draw an arrow-pushing mechanism showing the conversion of the starting material to the product. Include all curved arrows, necessary lone pairs and non-zero formal charges. Be sure to draw all structures clearly (10 pts).