

Name: \_\_\_\_\_ Perm number: \_\_\_\_\_

Question	Your score
1) (100 pts)	
2) (20 pts)	
3) (35 pts)	
4) (25pts)	
5) (20 pts)	
<b>Total (200 pts)</b>	

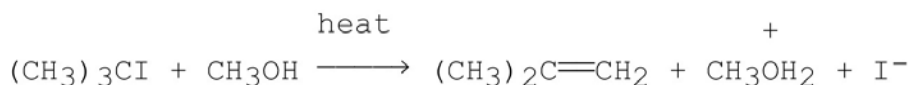
1. MULTIPLE CHOICE. Choose the one alternative that best completes the statement or answers the question (50 pts).

- 1) (-)-Mandelic acid has a specific rotation of  $-158^\circ$ . What would be the specific rotation of a solution which contains 40% (-)-mandelic acid and 60% (+)-mandelic acid?  
 A)  $+32^\circ$       B)  $-32^\circ$       C)  $+63^\circ$       D)  $-63^\circ$       E)  $+95^\circ$

1) A

- 2) Consider the following experimental data for the rate of the reaction given below:

2) B



Experiment #1	[Alkyl Halide]	[Base]	Rate
1	0.01	0.01	1
2	0.02	0.01	2
3	0.01	0.02	1

What is the mechanism for the reaction?

- A) first order,  $\text{S}_{\text{N}}1$   
 B) first order,  $\text{E}1$   
 C) first order,  $\text{S}_{\text{N}}2$   
 D) first order,  $\text{E}2$   
 E) none of the above
- 3) Which of the following is the electronic configuration of the element Fe (atomic number 26)?
- A)  $1s^2 2s^2 2p^8 3s^2 3p^6 4s^2 3d^6$   
 B)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4d^6$   
 C)  $1s^2 2s^2 2p^6 3s^2 3p^8 3d^6$   
 D)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 4p^6$   
 E)  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$
- 4) If an acyclic alkane hydrocarbon contains n carbon atoms, how many hydrogen atoms must it also contain?

3) E

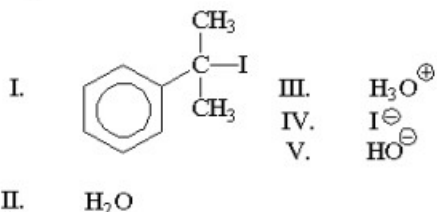
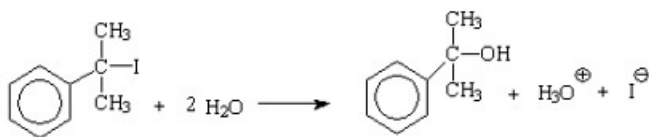
4) E

- A)  $n + 2$   
 B)  $n - 2$   
 C)  $n$   
 D)  $2n$   
 E)  $2n + 2$

B

5) What is the nucleophile in the reaction shown below?

5)         



A) I                  B) II                  C) III                  D) IV                  E) V

6) What is the strongest intermolecular force present in liquid ethanol?

6)         

- A) ion-dipole
- B) dipole-dipole, specifically hydrogen bonding
- C) ion-ion
- D) dipole-dipole, but not hydrogen bonding
- E) induced dipole-induced dipole

7) Which of the following is the rate law for  $\text{S}_{\text{N}}1$  mechanisms?

7)         

- A) Rate =  $k[\text{Alkyl Halide}]$
- B) Rate =  $k[\text{Nucleophile}]$
- C) Rate =  $k[\text{Alkyl Halide}][\text{Nucleophile}] + k_2[\text{Alkyl Halide}]$
- D) Rate =  $k[\text{Alkyl Halide}][\text{Nucleophile}]$
- E) Rate =  $k_1[\text{Alkyl Halide}] + k_2[\text{Nucleophile}]$

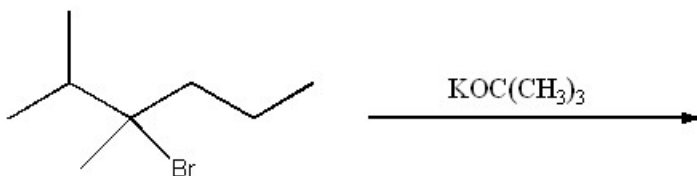
8) Excluding the horizontal node which is coincident with the molecular plane, how many nodes are present in  $\Psi_4$  of the 1, 3, 5-hexatriene  $\pi$  system?

8)         

- A) 6                  B) 0                  C) 4                  D) 3                  E) 5

9) What is the major organic product of the following reaction?

9)         



- A) 2,3-dimethyl-2-hexene
- B) 2-isopropyl-1-pentene
- C) (E)-2,3-dimethyl-3-hexene
- D) (Z)-2,3-dimethyl-3-hexene
- E) 2,3-dimethyl-1-hexene

10) The hydrolysis of *tert*-butyl chloride proceeds more rapidly in a solvent mixture which is 70% water/30% acetone than in one which is 30% water/70% acetone. Why?

10)         

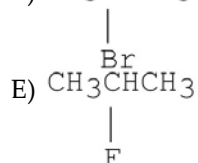
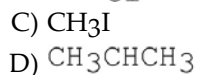
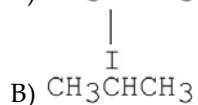
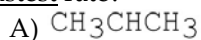
- A) The transition state in the carbocation formation step is better stabilized in the more polar solvent mixture.
- B) The solvent which contains a greater percentage of water is less polar, and this destabilizes the *tert*-butyl chloride.
- C) The reaction proceeds by an  $\text{S}_{\text{N}}1$  mechanism wherein the rate is increased by increasing the concentration of the nucleophile water.
- D) The reaction proceeds by an  $\text{S}_{\text{N}}2$  mechanism wherein the rate is increased by increasing the concentration of the nucleophile water.

A

E) none of the above

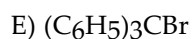
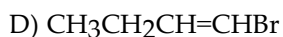
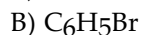
11) Which of the following alkyl halides undergoes E1 reactions with the fastest rate?

11) A



12) Which of the following bromides reacts readily via an  $\text{S}_{\text{N}}2$  reaction with  $\text{NaN}_3$ ?

12) C



13) The  $K_{\text{eq}}$  for the interconversion for the two chair forms of methylcyclohexane at  $25^\circ\text{C}$  is 18. What % of the chair conformers feature an axial methyl group?

13) E

A) 25

B) 75

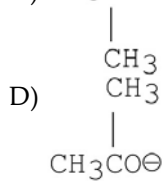
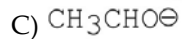
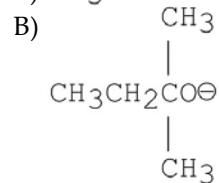
C) 95

D) 50

E) 5

14) Which of the following bases gives the highest anti-Zaitsev product in E2 reactions when reacted with 2-bromo-2, 3-dimethylbutane?

14) B



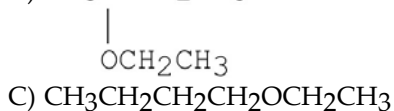
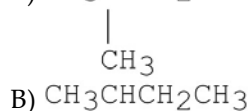
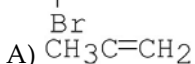
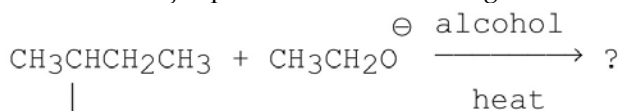
15) Protic and aprotic solvents are very similar as solvents except for their

15) B

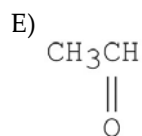
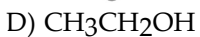
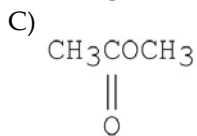
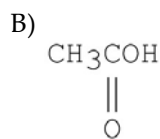
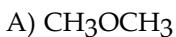
A) dielectric constant.

B) ability to stabilize anions by hydrogen bonding.

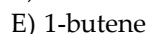
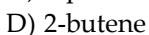
- C) ability to stabilize cations by hydrogen bonding.  
 D) polarity.  
 E) ability to stabilize cations with unshared pairs of electrons.
- 16) Which conformer is at a local energy minimum on the potential energy diagram in the chair-chair interconversion of cyclohexane?
- A) boat  
 B) fully eclipsed  
 C) half-chair  
 D) twist-boat  
 E) planar
- 17) What is the major product of the following reaction?



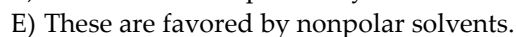
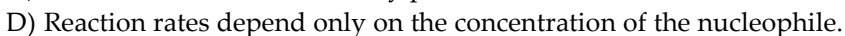
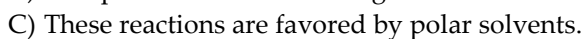
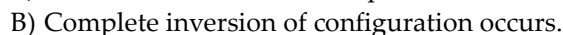
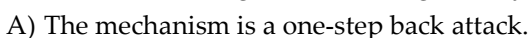
- 18) Which of the following is the strongest acid?



- 19) Which of the following is capable of exhibiting cis-trans isomerism?



- 20) Which of the following statements is generally true for  $\text{S}_{\text{N}}1$  reactions?



- 21) Which sequence of reagents works best to convert 3-hexene to 3-hexyne?

16) D

17) E

18) B

19) D

20) C

21) C

- A) 1. HCl 2. NaNH<sub>2</sub>
- B) 1. NaNH<sub>2</sub> 2. HI 3. H<sub>3</sub>O<sup>+</sup>
- C) 1. Br<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub> 2. NaNH<sub>2</sub> (excess)
- D) 1. BH<sub>3</sub>·THF 2. HO<sup>-</sup>, H<sub>2</sub>O<sub>2</sub> 3. NaNH<sub>2</sub>
- E) 1. Cl<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub> 2. NaCN (excess)



22) Assuming no other changes, what is the effect of doubling only the concentration of the nucleophile in the above reaction?

22) E

- A) triples the rate
- B) quadruples the rate
- C) doubles the rate
- D) rate is halve
- E) no change

23) The specific rotation of optically pure (*R*)-*sec*-butyl alcohol is -13.52°. An optically pure sample of (*R*)-*sec*-butyl bromide was converted into the corresponding *sec*-butyl alcohol via an S<sub>N</sub>2 reaction. What is the specific rotation of the product, assuming 100% yield?

23) E

- A) zero
- B) -13.52°
- C) between 0° and -13.52°
- D) between 0° and +13.52°
- E) +13.52°

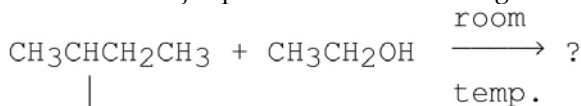
24) Which of the following correctly describes the relative nucleophilicities of methoxide and *tert*-butoxide?

24) C

- A) These alkoxides have essentially the same nucleophilicities since the negative charge in both is localized on an oxygen atom.
- B) *tert*-Butoxide is more nucleophilic because it is more basic.
- C) Methoxide is more nucleophilic because the nucleophilicity of *tert*-butoxide is diminished by steric effects.
- D) *tert*-Butoxide is more nucleophilic because it contains three methyl groups which increase the charge on its oxygen by donating electron density.
- E) none of the above

25) What is the major product of the following reaction?

25) A



- A)  $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CH}_3$
- B)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_3$
- C)  $\text{CH}_3\text{C}=\text{CH}_2$
- D)  $\text{CH}_3\text{CH}=\text{CHCH}_3$
- E)  $\text{CH}_2=\text{CHCH}_2\text{CH}_3$

26) Which of the following contributes to make ΔG° more negative?

26) D

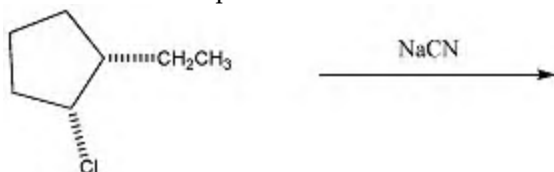
- A) a more positive  $\Delta H^\circ$
- B) a larger rate constant
- C) use of a catalyst
- D) a more positive  $\Delta S^\circ$
- E) none of the above

27) When 1-pentanol is heated with HCl/ZnCl<sub>2</sub>, 1-chloropentane is the major organic product. This reaction proceeds through an \_\_\_\_\_ mechanism, and \_\_\_\_\_ is produced as a byproduct.

- A) S<sub>N</sub>1, H<sub>2</sub>
- B) S<sub>N</sub>2, H<sub>2</sub>
- C) S<sub>N</sub>2, H<sub>2</sub>O
- D) S<sub>N</sub>1, H<sub>2</sub>O
- E) E2, H<sub>2</sub>

27) C

28) What mechanism predominates in the reaction below?



- A) S<sub>N</sub>2
- B) E1
- C) S<sub>N</sub>1 without rearrangement
- D) E2
- E) S<sub>N</sub>1 with rearrangement

28) A

29) What type of isomers are CH<sub>3</sub>CH<sub>2</sub>OCH<sub>3</sub> and CH<sub>3</sub>CH<sub>2</sub>CH<sub>2</sub>OH?

- A) stereochemical
- B) conformational
- C) configurational
- D) symmetrical
- E) constitutional

29) E

30) Starting with 2-butene, which of the following is the best method for preparing 2-butyne?

- A) Br<sub>2</sub>/CCl<sub>4</sub>; 2NaNH<sub>2</sub>
- B) HBr; NaNH<sub>2</sub>
- C) Br<sub>2</sub>/CCl<sub>4</sub>; Zn/H<sup>+</sup>; H<sub>2</sub>/Ni
- D) HBr; Zn/H<sup>+</sup>; H<sub>2</sub>/Ni
- E) HBr; H<sub>2</sub>/Ni; Zn/H<sup>+</sup>

30) A

31) Which of the following is/are the main product(s) of the following reaction?



- A) CH<sub>2</sub>CH=CHCH<sub>3</sub>  
|  
Br
- B) CH<sub>2</sub>CH<sub>2</sub>CH=CH<sub>2</sub>  
|  
Br
- C) CH<sub>3</sub>CHCH=CH<sub>2</sub>  
|  
Br
- D) A and B

31) E

E) A and C

32) Which of the following is least likely to be found in the product mixture which results when 2-iodopentane reacts with sodium ethoxide in ethanol?

- A) 1-pentene
- B) (Z)-2-pentene
- C) (E)-2-pentene
- D) 1-ethoxypentane
- E) 2-ethoxypentane

32) D

33) How many asymmetric centers are present in a molecule of 2,4,6-trimethylheptane?

- A) 0
- B) 1
- C) 2
- D) 3
- E) 4

33) A

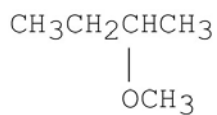


34) Assuming no other changes, what is the effect of doubling both the alkyl halide and the nucleophile concentrations in the above reaction?

- A) no change
- B) quadruples the rate
- C) triples the rate
- D) rate is halved
- E) doubles the rate

34) B

35) When (S)-2-bromobutane undergoes an S<sub>N</sub>2 reaction with CH<sub>3</sub>O<sup>-</sup>, the product is the compound shown below. What is/are the configuration(s) of the product(s) obtained from this reaction?



- A) S only
- B) R only
- C) a mixture of enantiomers with more S than R
- D) a mixture of enantiomers with more R than S
- E) equal mixture of R and S

35) B

36) Which of the following is the best leaving group?

- A) Cl<sup>-</sup>
- B) F<sup>-</sup>
- C) Br<sup>-</sup>
- D) HO<sup>-</sup>
- E) I<sup>-</sup>

36) E

37) Among the compounds water, 1-butyne, 2-butyne, and ethane, which are stronger acids than ammonia?

- A) 1-butyne and 2-butyne
- B) water and ethane
- C) water and 1-butyne
- D) 1-butyne and ethane

37) C

38) In the S<sub>N</sub>1 hydrolysis mechanism of (CH<sub>3</sub>)<sub>3</sub>CBr, there are \_\_\_\_\_ elementary steps, \_\_\_\_\_ distinct transition states, and \_\_\_\_\_ distinct intermediates.

- A) 3, 3, 2
- B) 2, 2, 2
- C) 2, 2, 3
- D) 2, 3, 2
- E) 3, 2, 3

38) A

39) What is the major product from the acid-catalyzed hydration of 2-methyl-2-pentene?

39) D

- A) 2-methyl-1-pentanol
- B) 2-methyl-3-pentanol
- C) 2-methylpentane
- D) 2-methyl-2-pentanol
- E) 1-methoxypentane

40) In the addition of hydrogen bromide to alkynes in the absence of peroxides, which of the following species is believed to be an intermediate?

40) D

- A) bromonium ion
- B) vinyl anion
- C) vinyl radical
- D) vinyl cation
- E) carbene

Key: 1) A 2) B 3) E 4) E 5) B 6) B 8) D 9) B 10) A 11) A 12) C 13) E 14) B 15) B 16) D 17) E 18) B 19) D 20) C 21) C 22) E 23) E 24) C 25) A 26) D 27) C 28) A 29) E 30) A 31) E 32) D 33) A 34) B 35) B 36) E 37) C 38) A 39) D 40) D

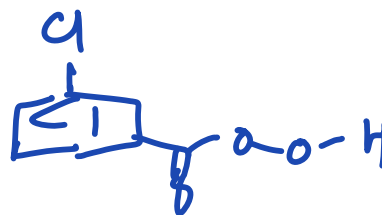
## 2. Structures and Nomenclature (20 pts)

1) Draw a structure for each of the following names (2 pts/each)

a) allyl bromide



b) *m*-CPBA



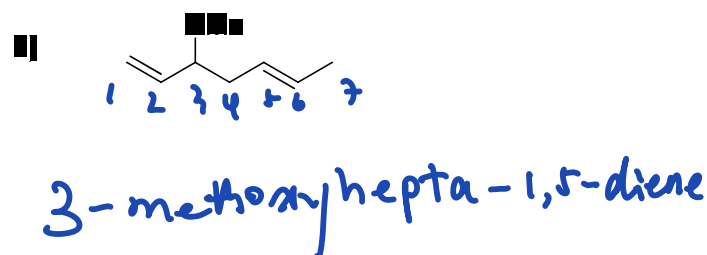
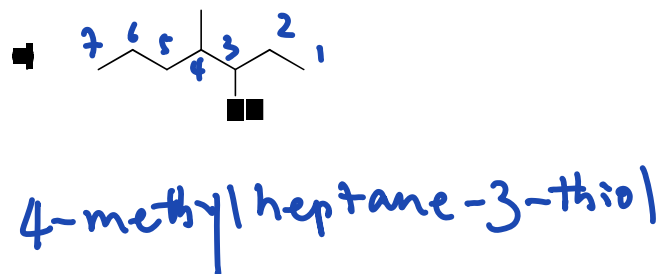
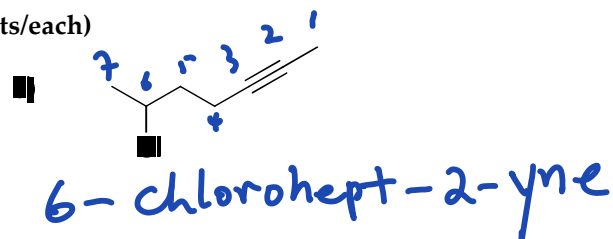
c) tert-butyl alcohol



d) methyl ethyl sulfide

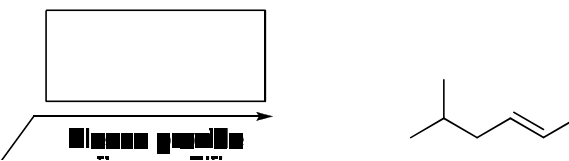
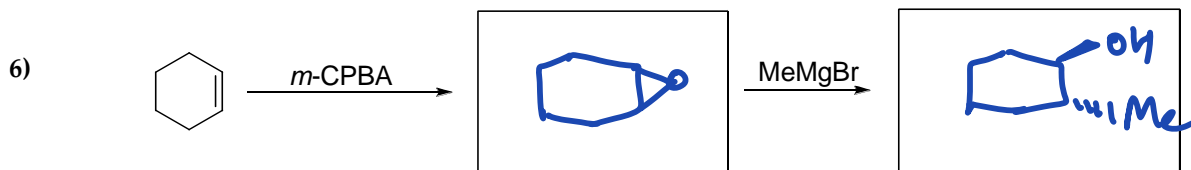
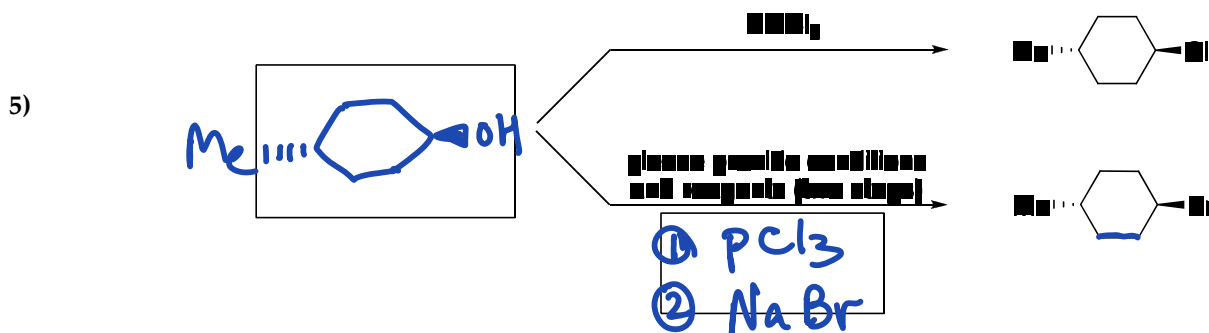
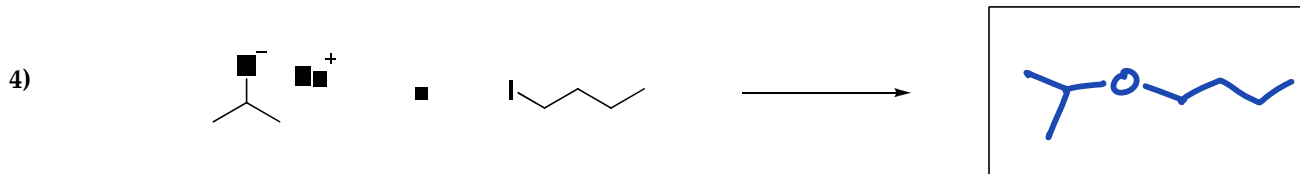
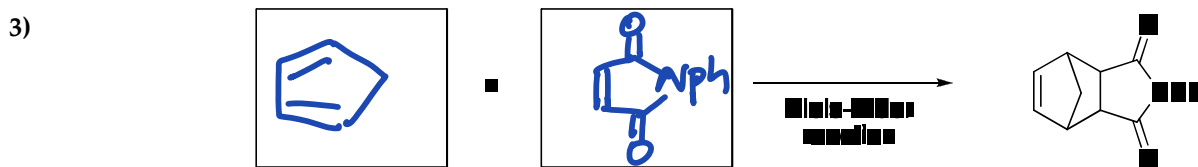
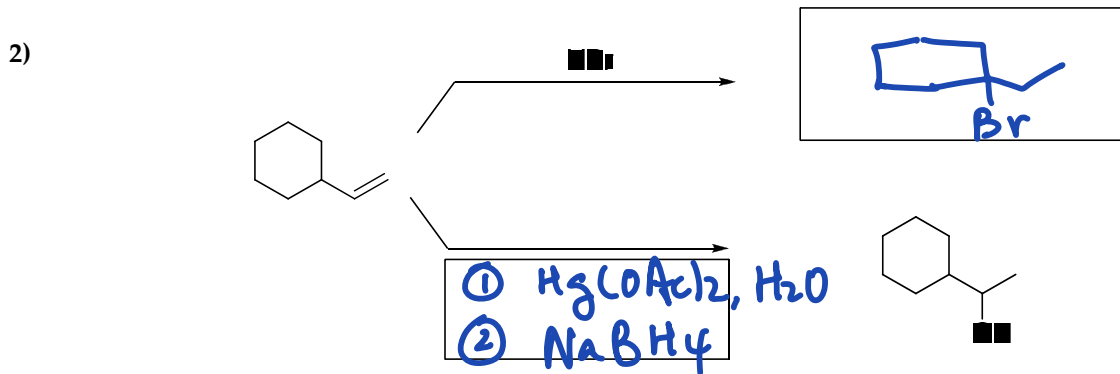
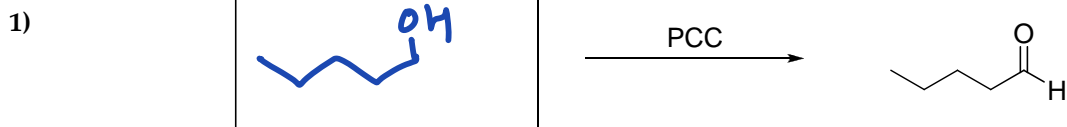


2) Name the following compounds according to the IUPAC rule (3 pts/each)

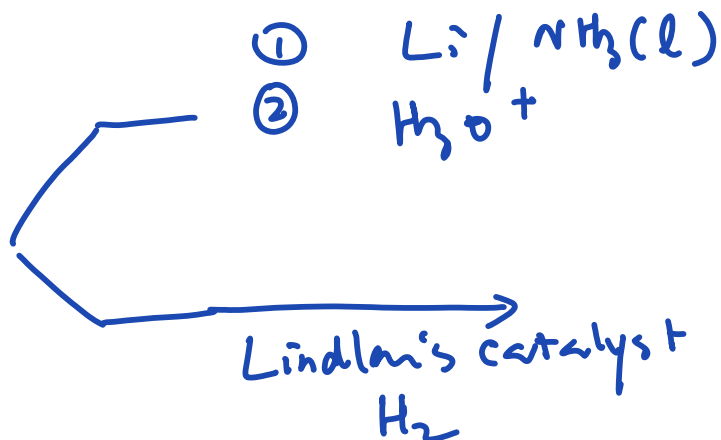




3. Please complete the following reactions by either providing starting material(s), product(s) and/or the necessary reaction conditions (35 pts)

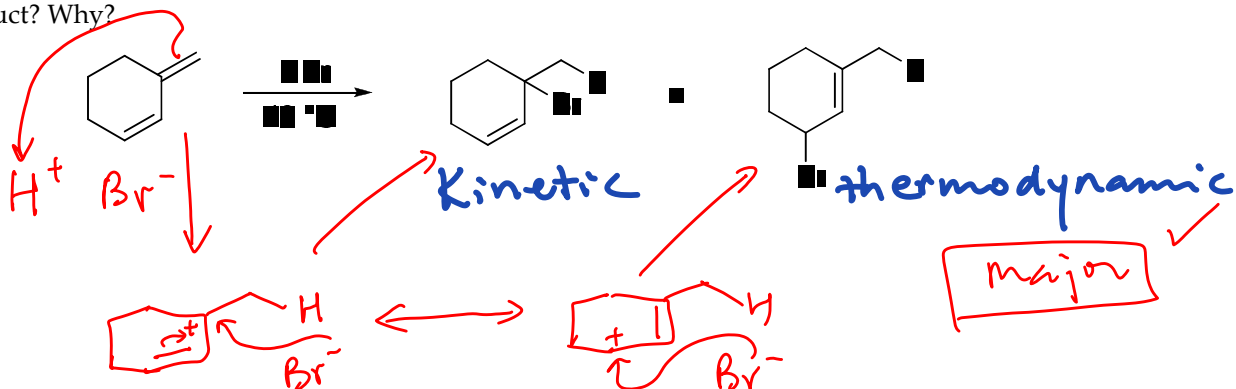


7)

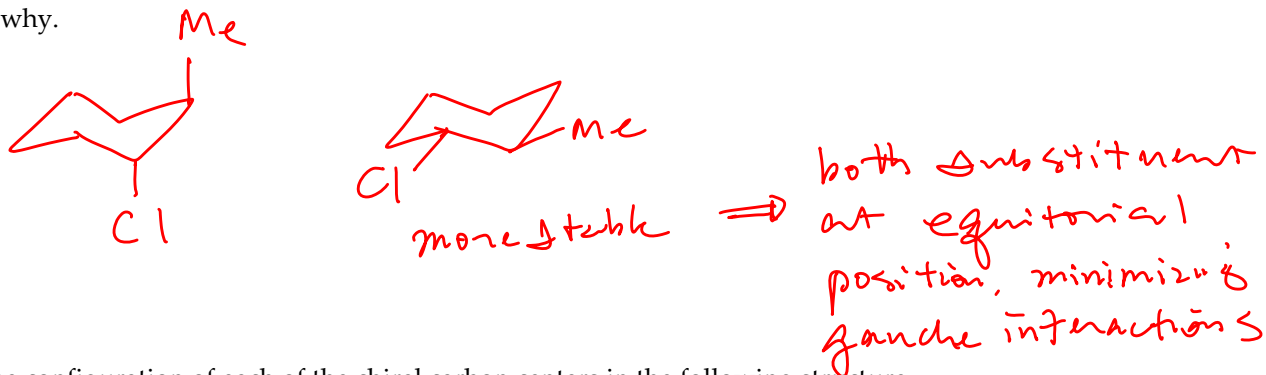


4. Answers the question briefly (25 pts)

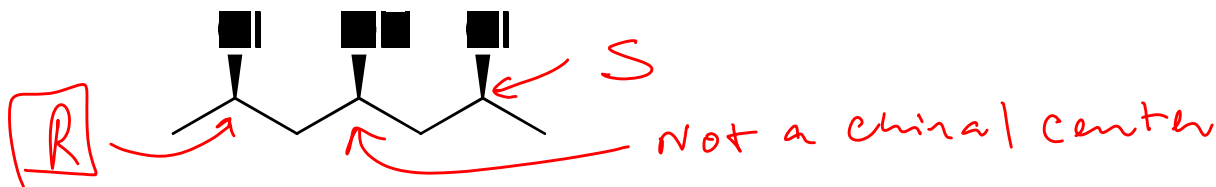
1) For the following reaction, which product is the kinetic product and which one thermodynamic? Use electron-pushing arrows to outline the reaction mechanism(s) for their formations. Under the indicated reaction conditions, which one is the major product? Why?



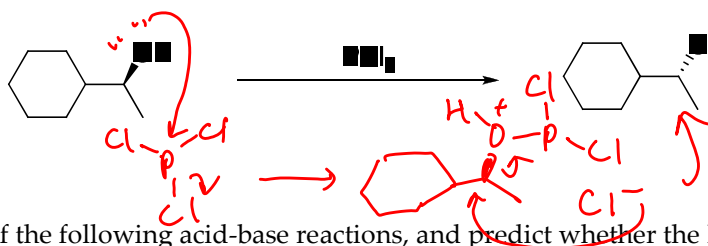
2) Please draw the two chair conformers of *trans*-1-methyl-2-chlorocyclohexane and indicate which one is more stable and briefly explain why.



3) Please indicate the configuration of each of the chiral carbon centers in the following structure.

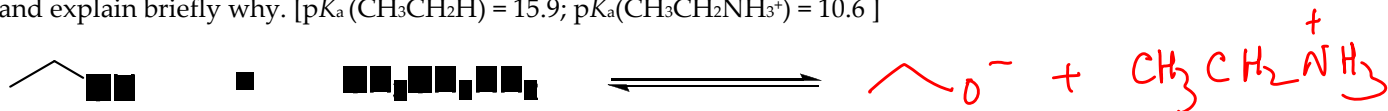


4) Please use electron-pushing arrows to describe the reaction mechanism of the following reaction:



5) Give the products of the following acid-base reactions, and predict whether the  $K_{\text{eq}} >$ ,  $=$  or  $< 1$  based on the  $\text{pK}_a$  value

given and explain briefly why. [ $pK_a(\text{CH}_3\text{CH}_2\text{H}) = 15.9$ ;  $pK_a(\text{CH}_3\text{CH}_2\text{NH}_3^+) = 10.6$ ]



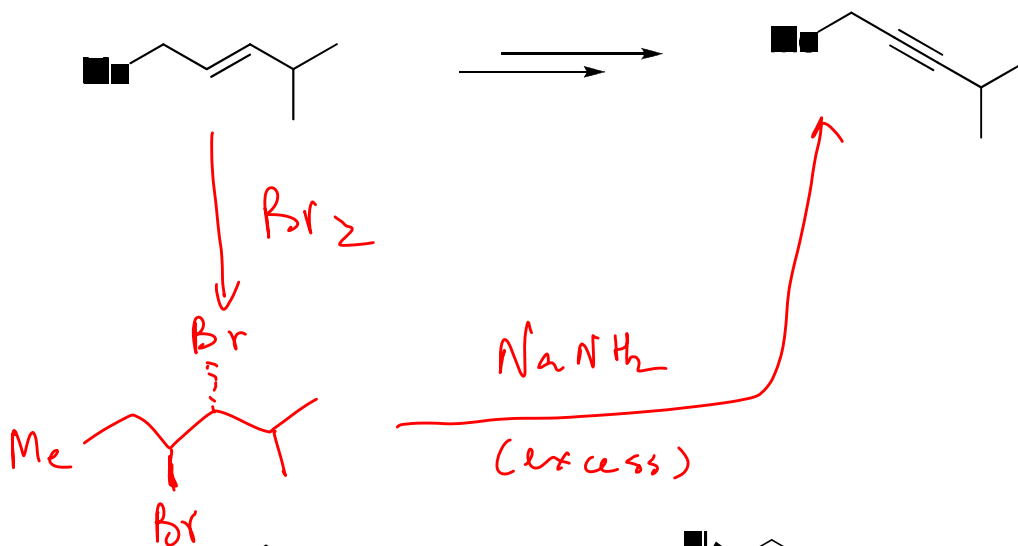
$$\log K_{eq} = pK_a(\text{product}) - pK_a(\text{reactant}) = 10.6 - 15.9 = -5.3$$

$$K_{eq} < 1$$

because  $\text{CH}_3\text{CH}_2\text{NH}_3^+$  is a stronger acid than  $\text{CH}_3\text{CH}_2\text{OH}$

5. Please provide a reasonable synthetic sequence to achieve the preparation of the desired product using the designated starting material. You can use any reagent and solvent (20 pts).

a)



b)

