

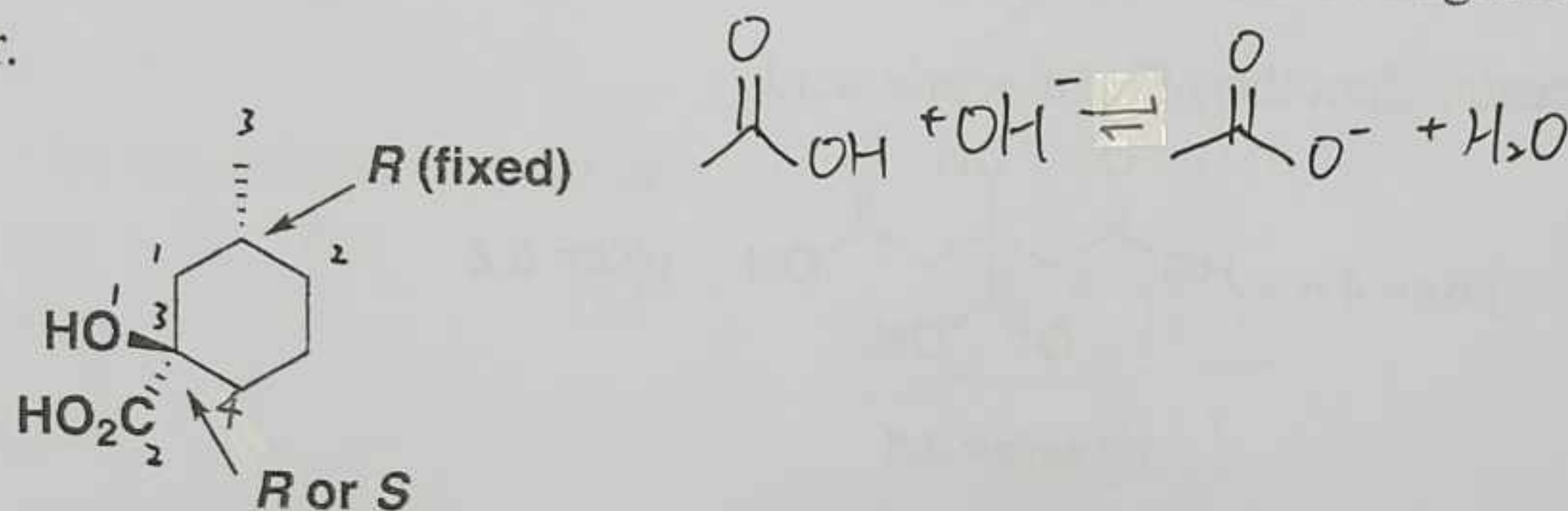
(B) Organic Chemistry (I), The First Mid-Term Examination, 17 Oct 2023

Total score: 110 points, total 3 pages

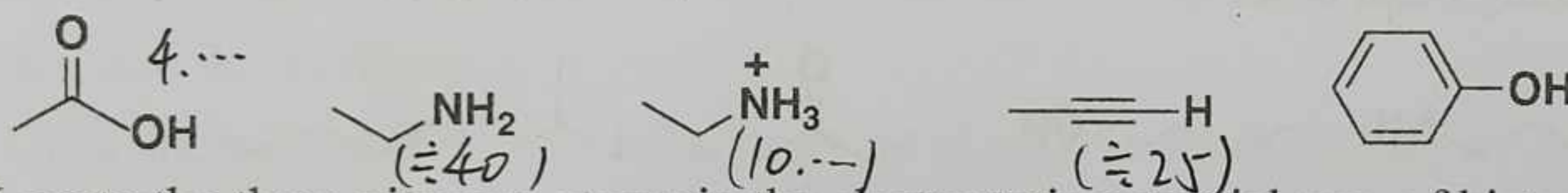
Name: 黃子安 Department: 化學系 NO. 111023066

1. (3%) The specific rotation of (*R*)-(+)-glyceraldehyde is +8.7. If the observed specific rotation of a mixture of (*R*)-glyceraldehyde and (*S*)-glyceraldehyde is +1.4, what percent of glyceraldehyde is present as the *R* enantiomer?

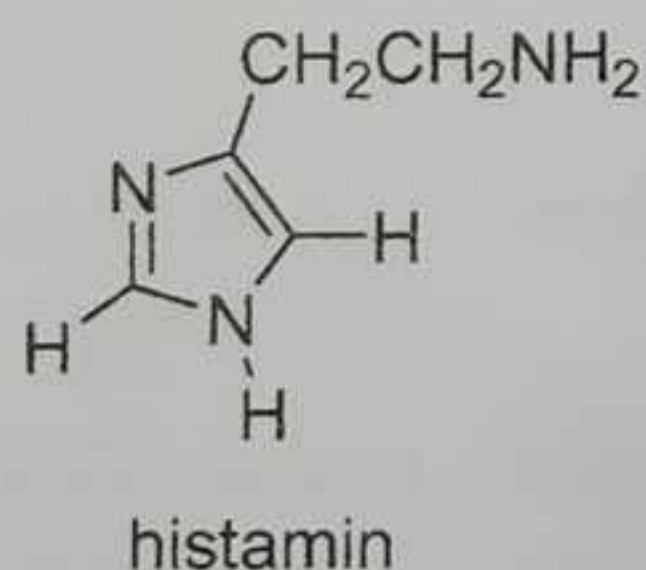
2. (6%) Draw the most stable chair conformer and indicate the configuration of any asymmetric center.



3. (3%) Which of the following compounds can OH^- remove a proton in a reaction that favors product formation? H_2O ($\text{pK}_a \approx 15.7$)

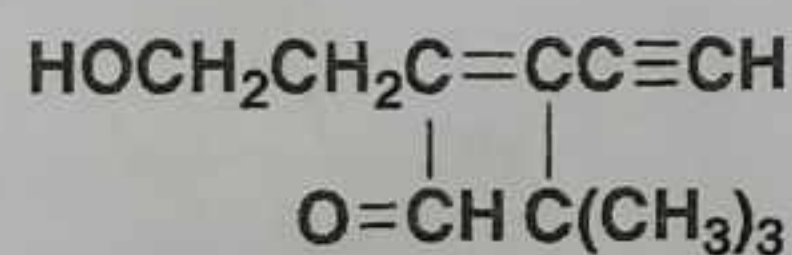


4. (3%) Locate the three nitrogen atoms in the electrostatic potential map of histamine, the compound that causes the symptoms associated with the common cold and with allergic responses. Which of the nitrogen atom is the most basic? Explain its greater basicity.

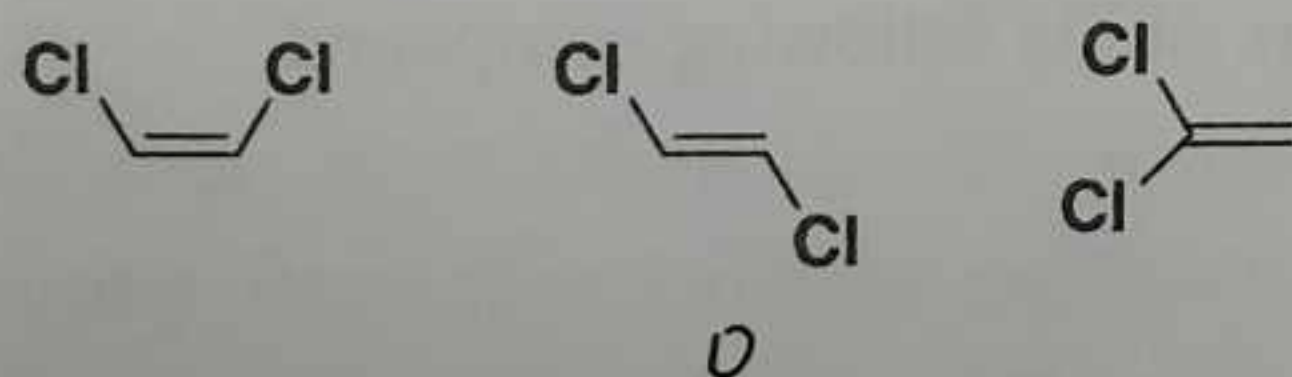


5. (2%) Draw the structure of N_3^- and shows approximate bond angle.

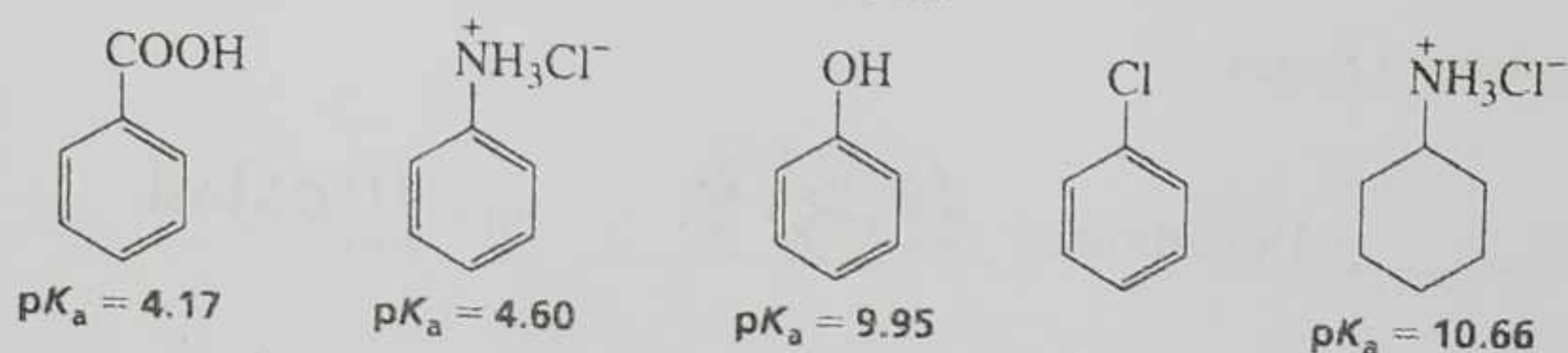
6. (2%) Draw the *Z* isomer of



7. (3%) Rank the following compounds from highest dipole moment to lowest dipole moment:

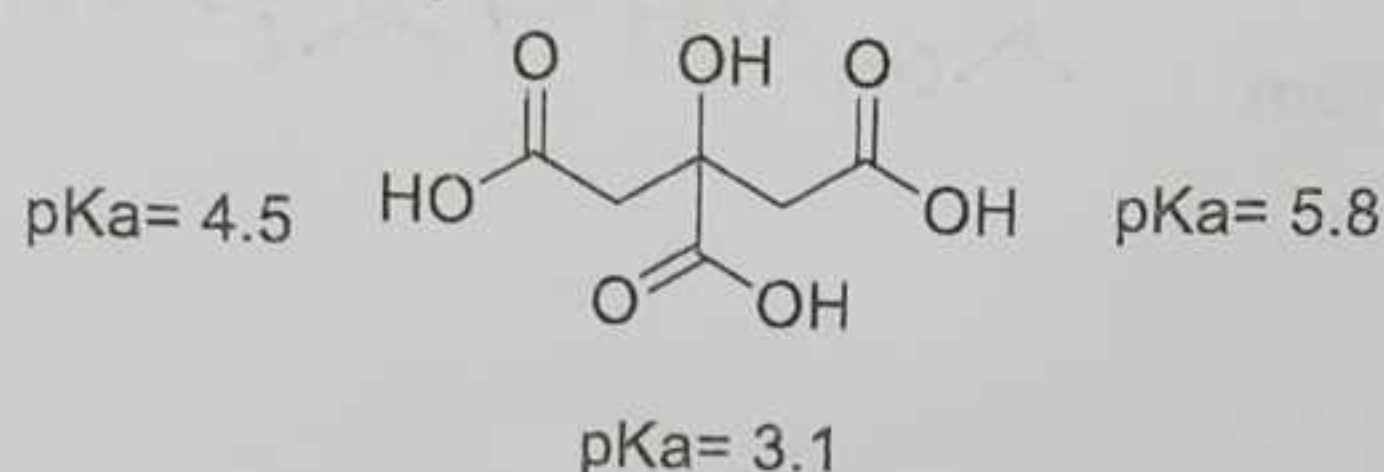


8. (5%) How could you separate a mixture of the following compounds. The reagents available to you are water, ether, 1.0 M HCl, and 1.0 M NaOH.



9. (4%) Citrus fruit are rich in citric acid, a compound with three COOH groups. Explain the following:

- The first pKa (for the COOH group in the center of molecule) is lower than the pKa of acetic acid.
- The third pKa is greater than the pKa of acetic acid.



10. (3%) The boiling points of HF, H₂O, and NH₃ are 20 °C, 100 °C, and -33 °C. They all form hydrogen bonds. Why the boiling points are so different?

11. (3%) List the boiling point order

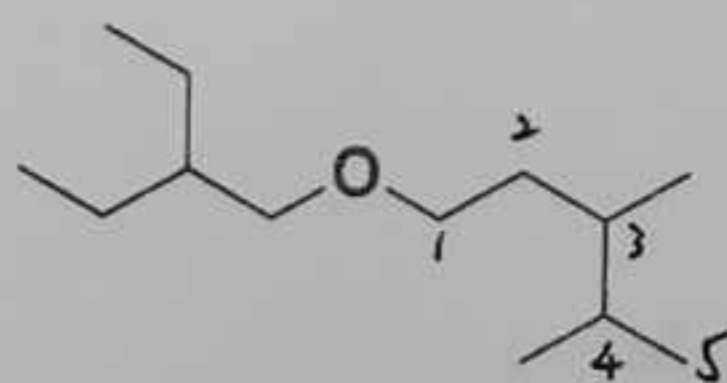


12. (14%) Explain the following terms or provide an example of them.

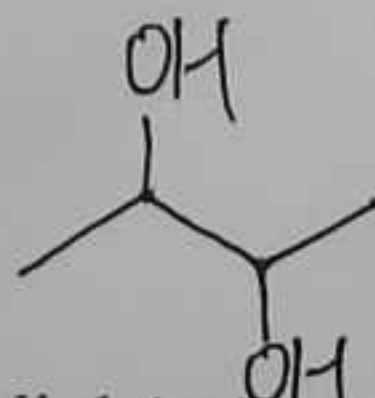
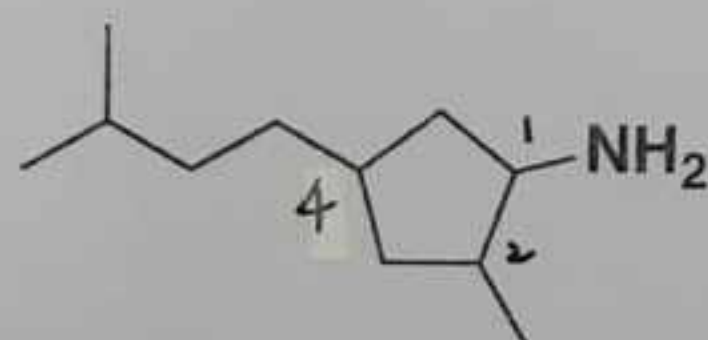
- stereocenter
- asymmetric center
- specific rotation
- gauche interaction
- 1,3-diaxial interaction
- racemic mixture
- enantiomeric excess

13. (12%) Name the compound (IUPAC name) or draw the structure.

a.



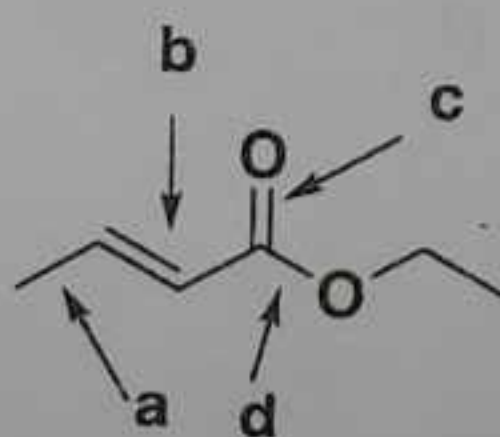
b.



- Draw the erythro enantiomers of 2,3-butanediol (using Fischer projection).
- Draw the *cis*-fused chair form structure of the following compound.

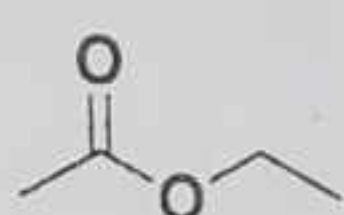


14. (3%) Order the bond length of a, b, c and d.

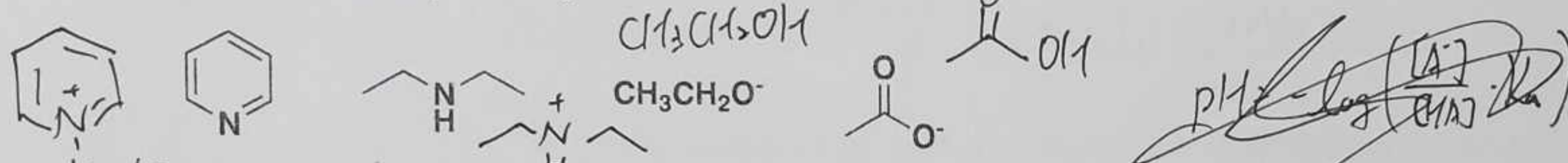


$$pH = -\log\left(\frac{[HA]}{[A^-]} \cdot K_a\right) = pK_a - \log\frac{[HA]}{[A^-]} \Rightarrow pK_a = pH + \log\frac{[HA]}{[A^-]}$$

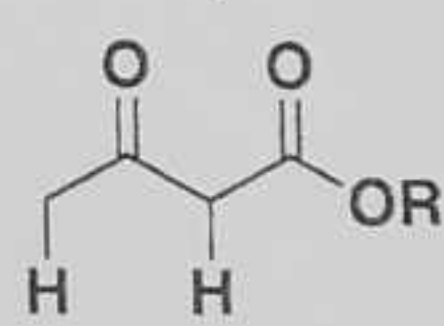
15. (2%) Indicate which atom that is most apt to be protonated and explain.



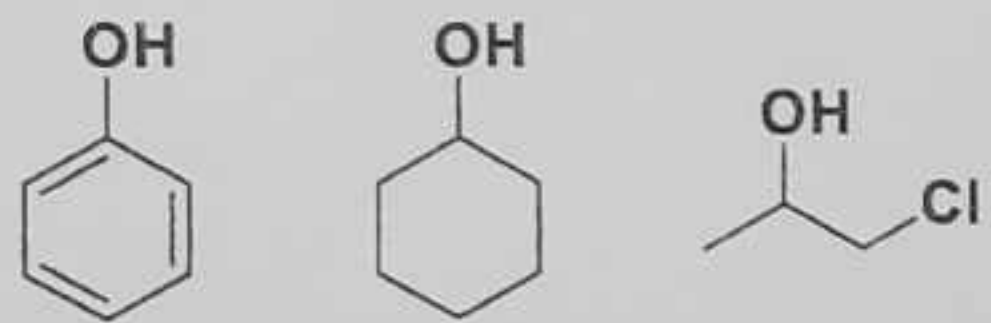
16. (4%) Order the basicity and explain.



17. (2%) Which proton is more acid?



18. (3%) Order the acidity and explain.

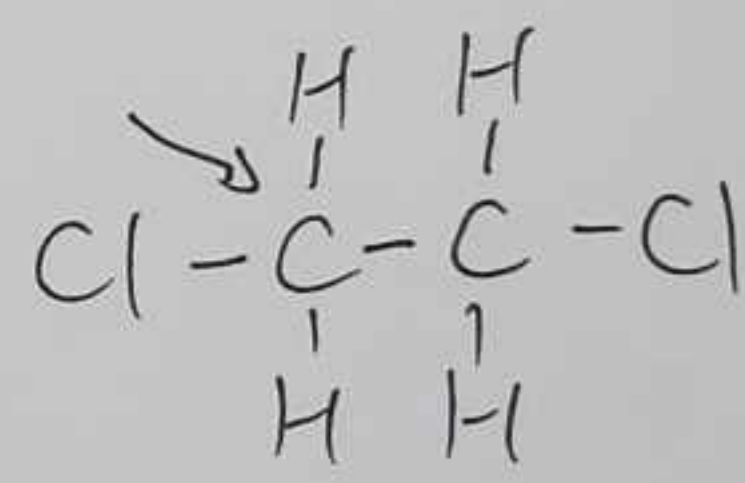


Handwritten notes for question 18:

$$\Rightarrow pH = pK_a - \log\frac{[A^-]}{[HA]}$$

$$\Rightarrow [H^+] = \frac{[A^-][H^+]}{[HA]} K_a$$

$$K_a = \frac{[A^-][H^+]}{[HA]}$$



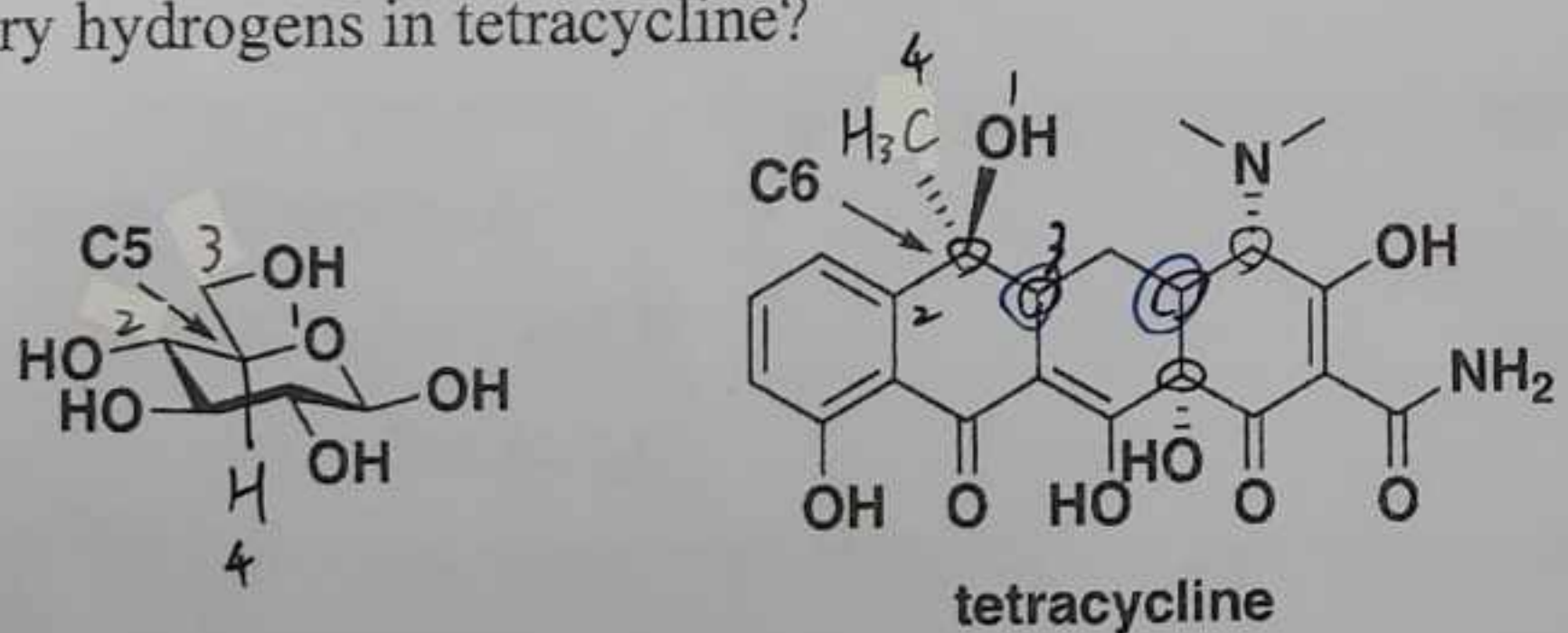
19. (5%) Draw a potential energy diagram for rotation about the C-C bond of 1,2-dichloroethane through 360°, starting with the least stable conformer. The anti-conformer is 1.2 kcal/mol more stable than a gauche conformer. The eclipsed conformers have two energy barriers, 5.2 kcal/mol and 9.3 kcal/mol.

20. (3%) Draw the most stable chair form structure of *cis-tert*-butyl-3-methylcyclohexane.

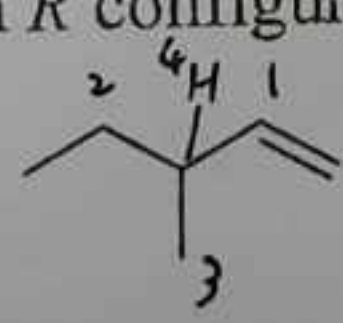
21. (3%) Please use molecular orbital to explain why the staggered conformer of ethane is more stable than its eclipsed conformer.

22. (4%) If you are carrying out a reaction that produces hydroxide ion. For the reaction to take place at a constant pH, it will be buffered at pH = 4.2. Would it be better to use a formic acid/formate buffer or an acetic acid/acetate buffer? (The pKa of formic acid = 3.75 and the pKa of acetic acid = 4.76).

23. (12%) Indicate the carbon configurations of C5 and C6. How many asymmetric carbons and tertiary hydrogens in tetracycline?



24. (6%) The following compound contains an asymmetric carbon with R configuration. Draw its steric struct using perspective formulas and Fischer projection.

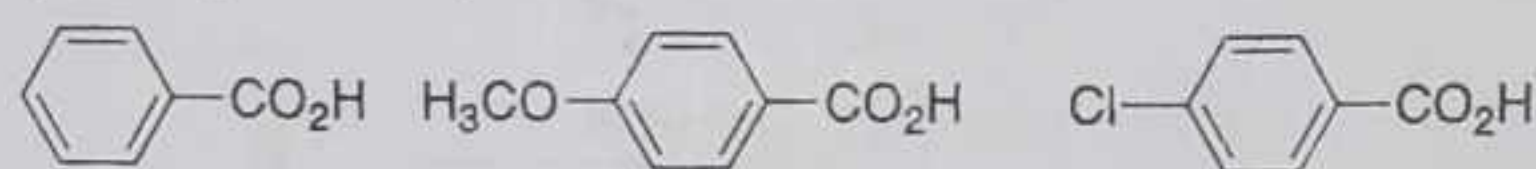


(B) Organic Chemistry (I); The Second Mid-Term Examination; 2 Dec 2022

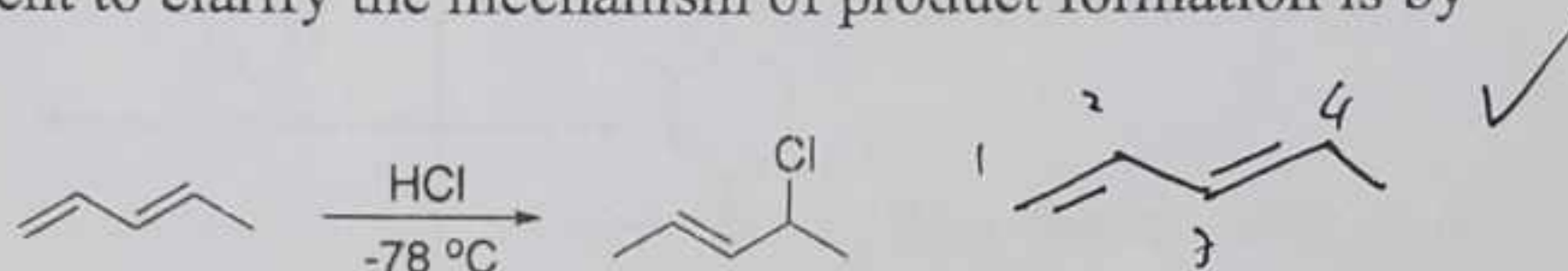
Name: 黃子竣 Department: 化學系 NO. 111023066

Total score: each answer 3%, total 110 %

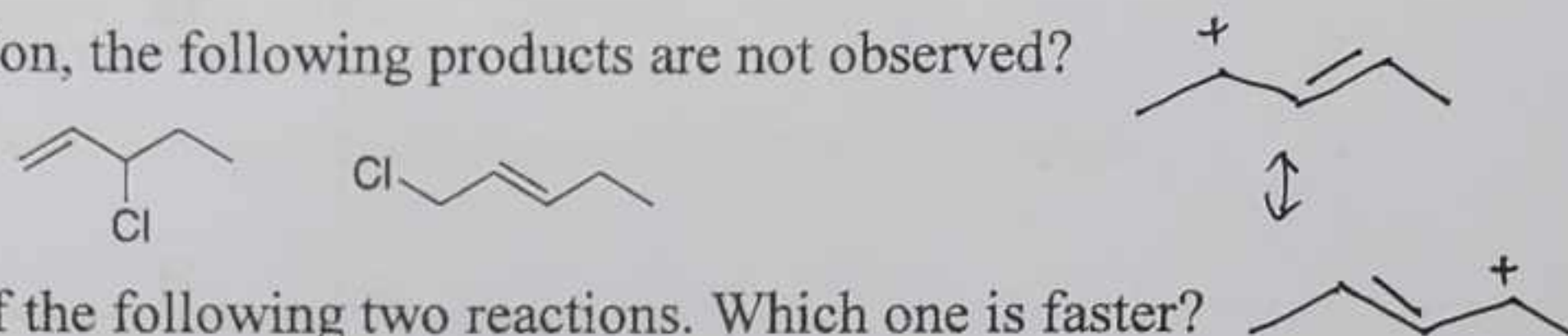
1. Order the acidity and provide your reasons.



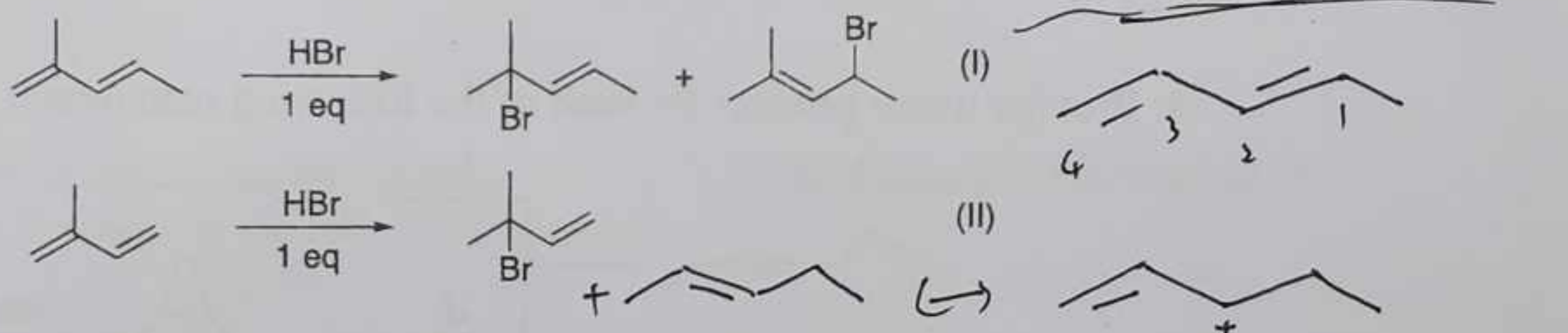
2. (a) The reaction of HCl with 1,3-pentadiene under -78°C gives 4-chloro-2-pentene. Please design an experiment to clarify the mechanism of product formation is by 1,2 or 1,4 addition.



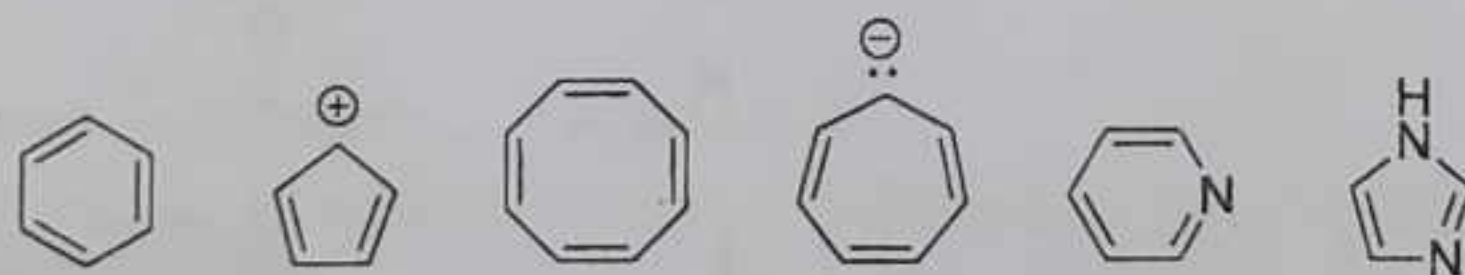
(b) Why, in the above reaction, the following products are not observed?



3. Comparison the reactivity of the following two reactions. Which one is faster? Why?

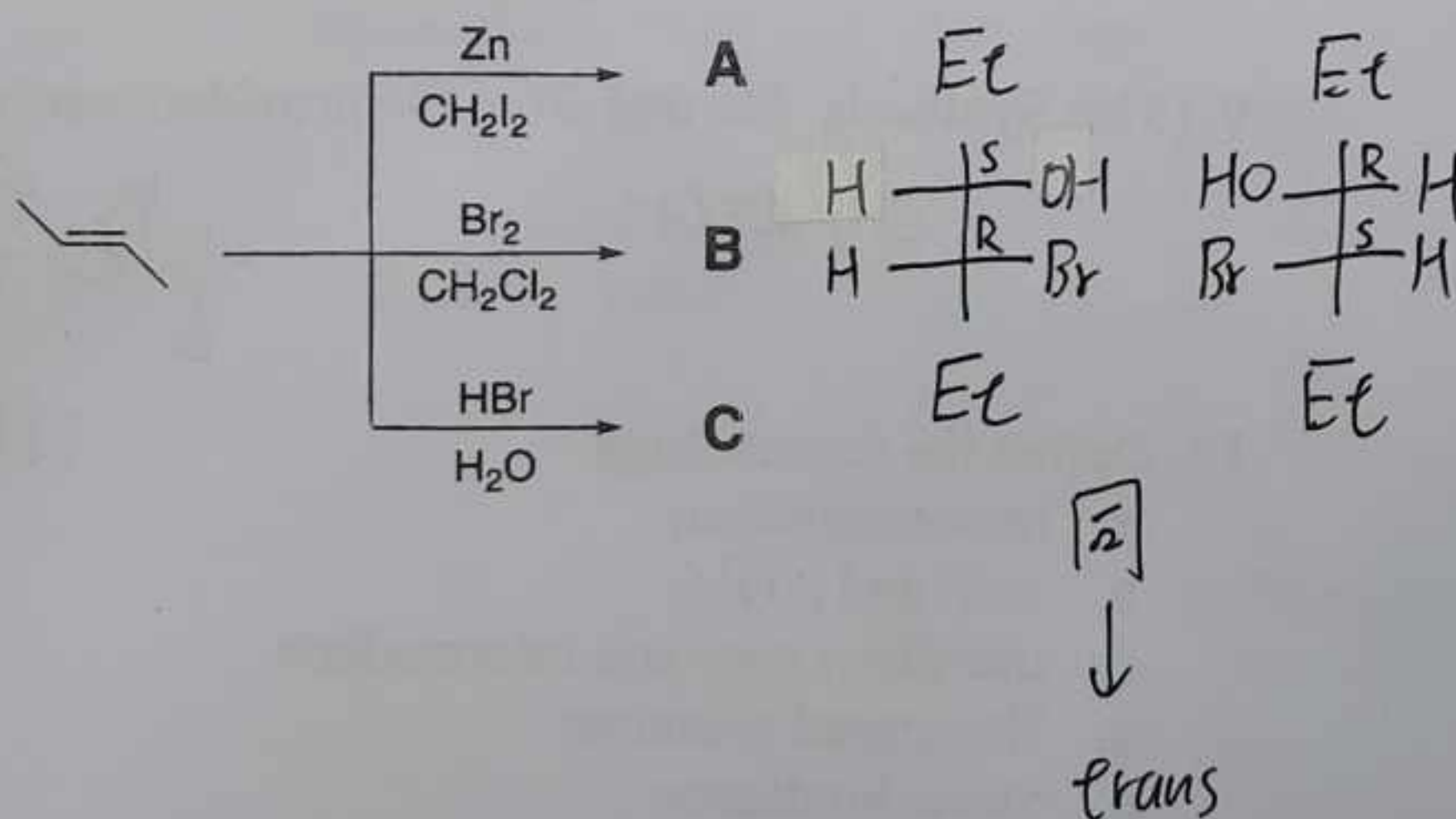


4. Which of the following structures are planar structures?

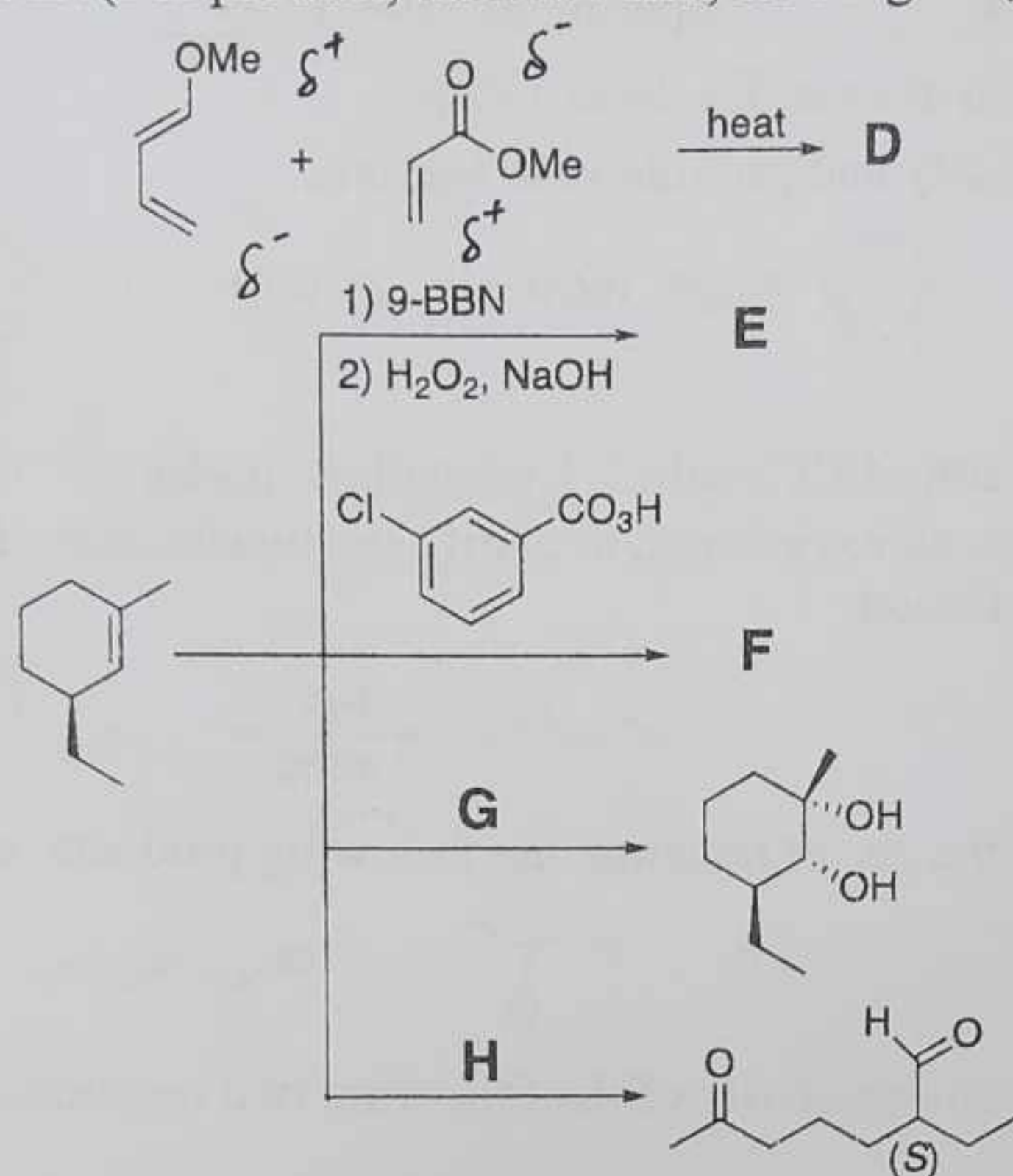


5. Starting with ethyne, describe how the following compounds can be synthesized. (3*S*,4*R*)-4-bromo-3-hexanol and (3*R*,4*S*)-4-bromo-3-hexanol (as a racemic mixture)

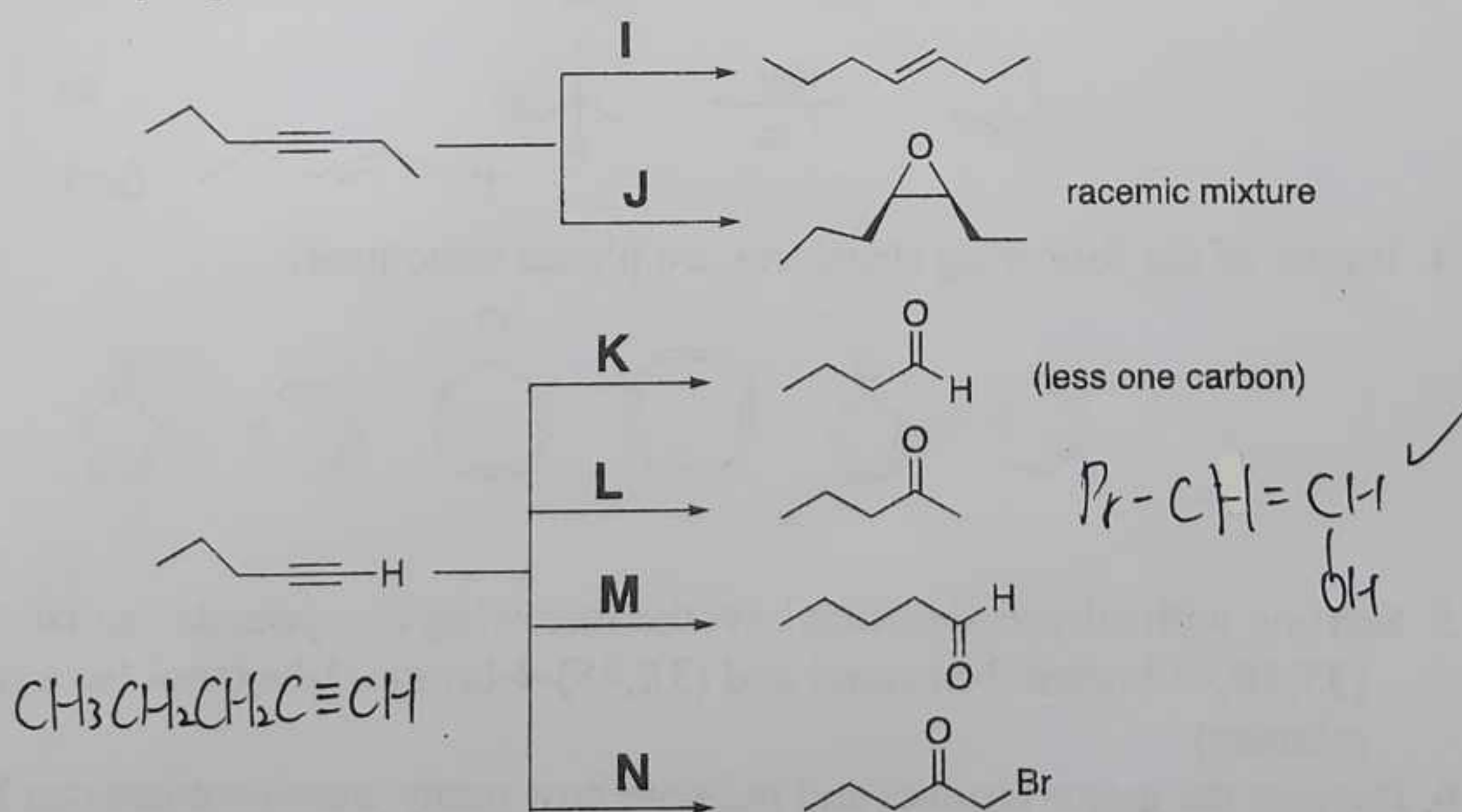
6. Provide the major product and indicate how many stereoisomers can be obtained.



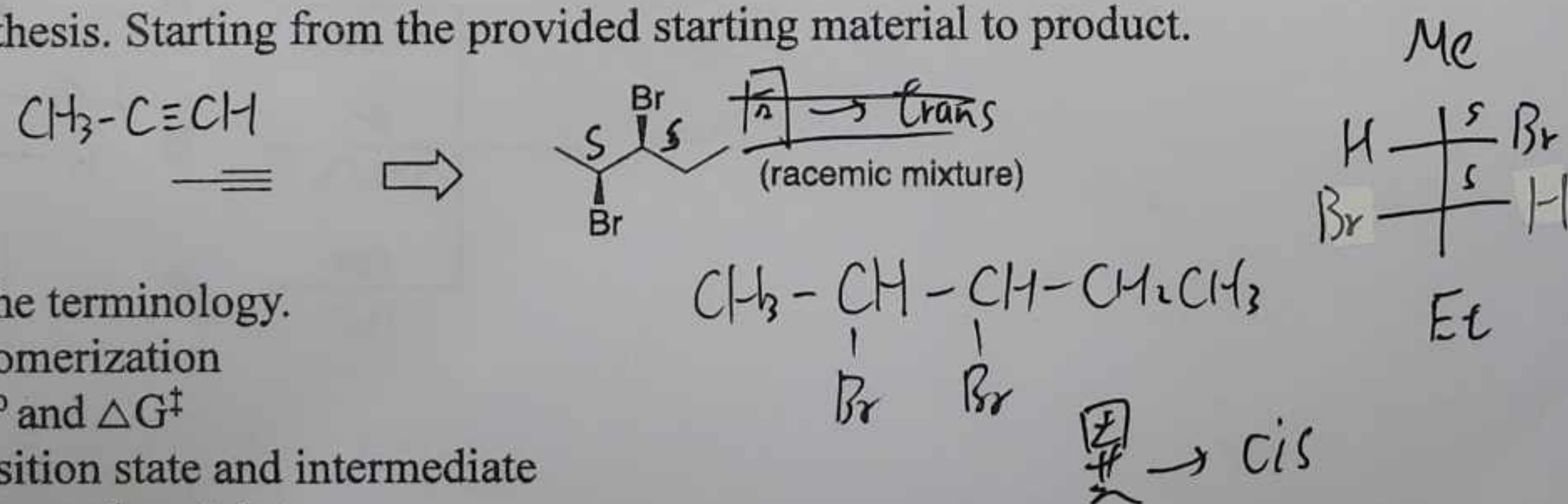
7. Provide the suitable reagents or major product (indicate the stereochemistry) of the following reactions. (For product, each 2% and, for reagents, each 3%)



8. Provide major product for each of the following reactions.



9. (5%) Synthesis. Starting from the provided starting material to product.

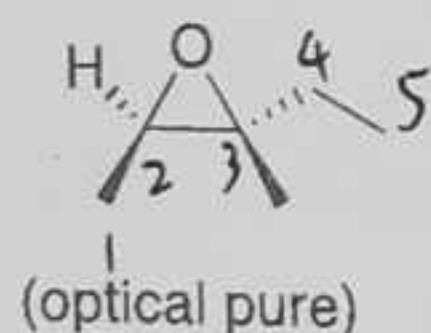


10. Define the terminology.

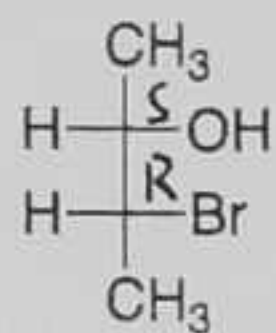
- tautomerization
- ΔG° and ΔG^\ddagger
- transition state and intermediate
- Hammond postulate
- Steric hindrance

11. Give the IUPAC name (include *R* and/or *S* configuration) of

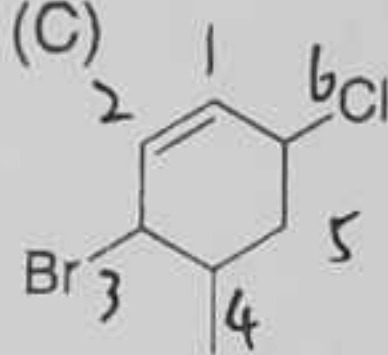
(A)



(B)



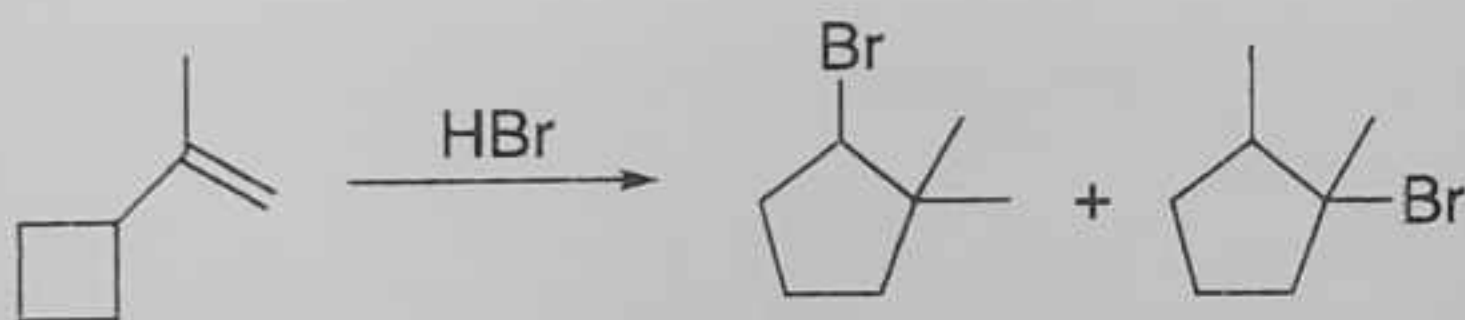
(C)



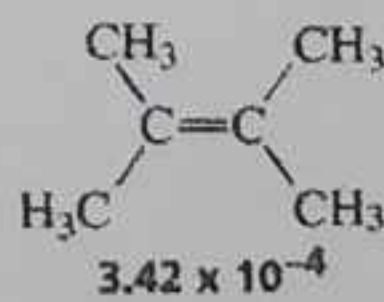
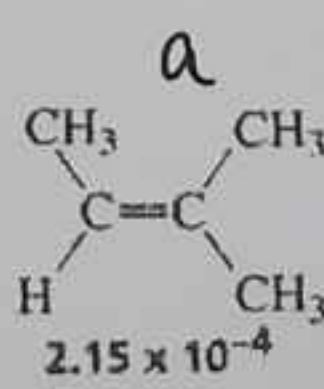
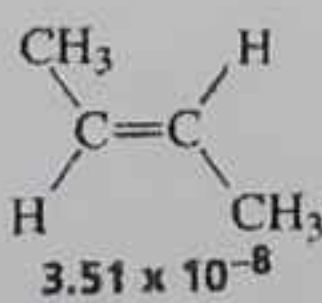
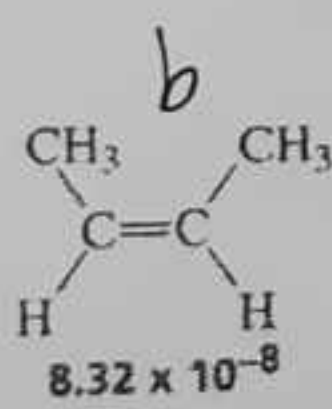
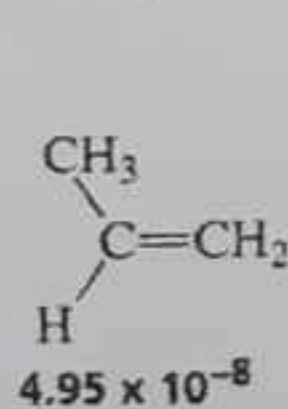
12. The olefin reacts with Br_2 in the presence of excess amount of water (co-solvent) to halohydrin as the major product. The water can be replaced by alcohol. However, when the water is replaced by ether, this reaction is not conducive to product formation. Explain.

13. Alkynes are less stable than alkenes at room temperature. Why the reactivities of alkenes toward to HBr are higher than those of alkynes?

14. Propose a mechanism for the following reaction and explain why does the rearrangement occur.



15. The second-order rate constant (in units of $\text{M}^{-1}\text{s}^{-1}$) for acid-catalyzed hydration at 25°C is given for each of the following alkenes:



- Comparison the stability of 2-methyl-2-butene and (*Z*)-2-butene. Provide your reason(s).
- Explain why 2-methyl-2-butene react faster than (*Z*)-2-butene in acid-catalyzed hydration.

16. Explain why more substituted alkenes are more stable.

17. Please draw the HOMO and LUMO molecular orbitals of 1,3-butadiene.