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

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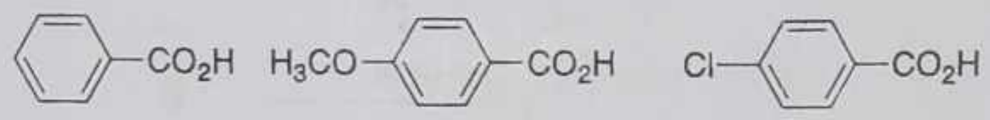
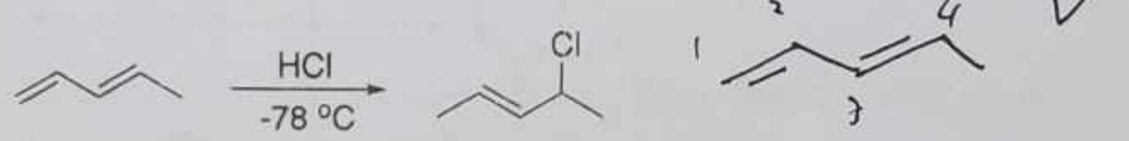
Total score: each answer 3%, total 110 %

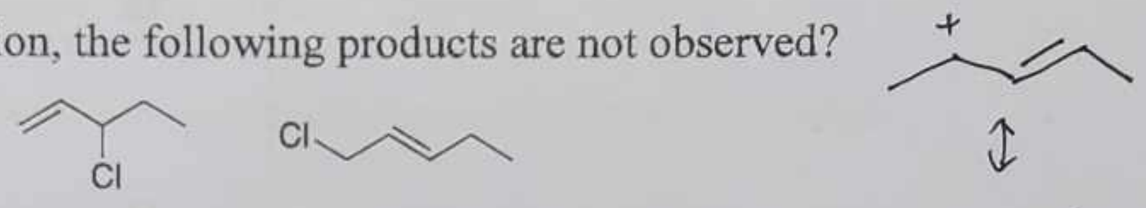
1. Order the acidity and provide your reasons.



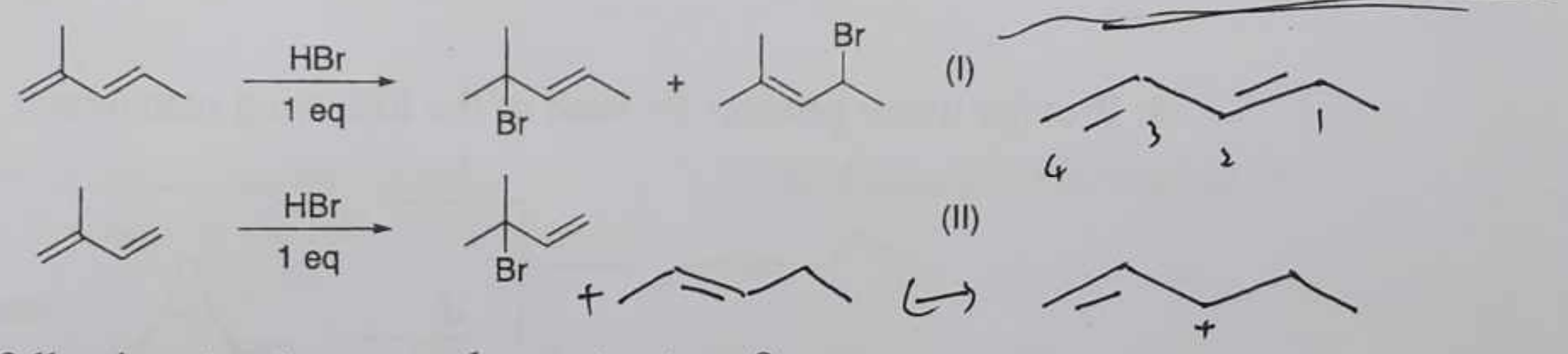
2. (a) The reaction of HCl with 1,3-pentadiene under -78 °C gives 4-chloro-2-pentene. Please design an experiment to clarify the mechanism of product formation is by 1,2 or 1,4 addition.



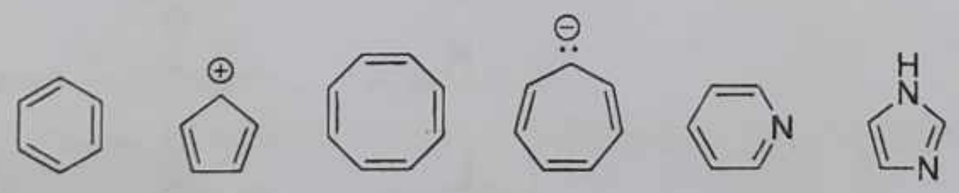
(b) Why, in the above reaction, the following products are not observed?



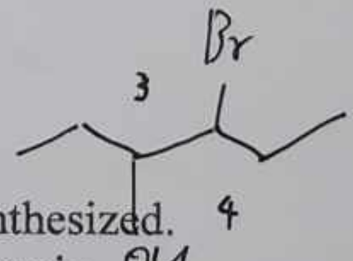
3. Comparison the reactivity of the following two reactions. Which one is faster? Why?



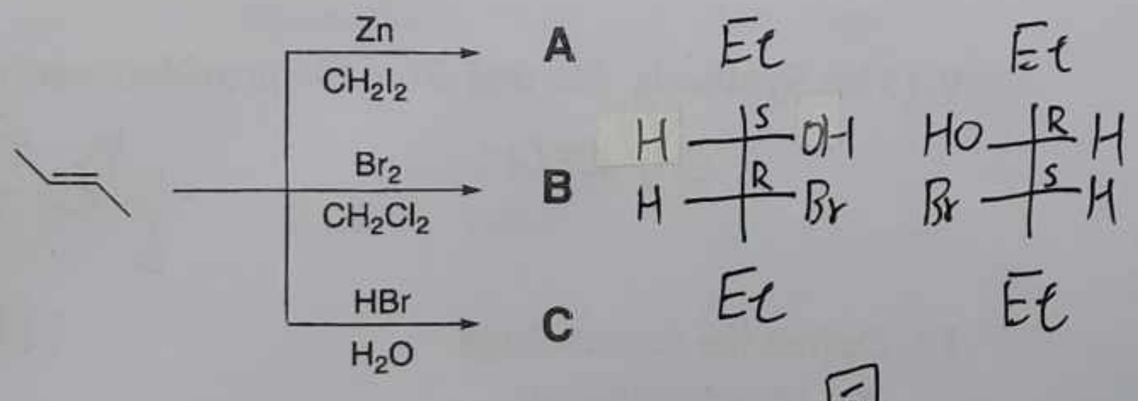
4. Which of the following structures are planar structures?



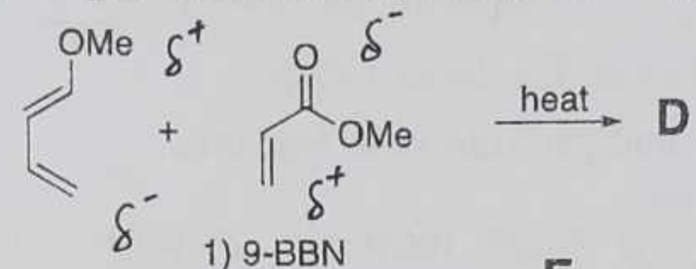
5. Starting with ethyne, describe how the following compounds can be synthesized. (3*S*,4*R*)-4-bromo-3-hexanol and (3*R*,4*S*)-4-bromo-3-hexanol (as a racemic mixture)



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

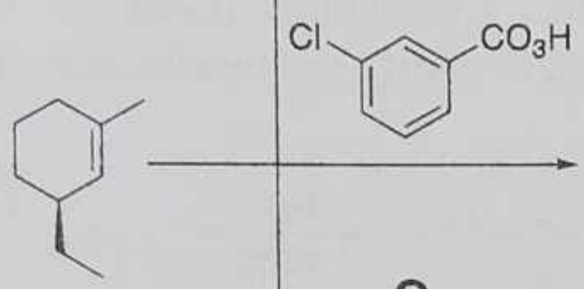


7. Provide the suitable reagents or major product (indicate the stereochemistry) of the following reactions. (For product, each 2% and, for reagents, each 3%)



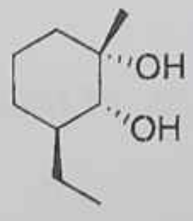
heat → **D**

1) 9-BBN
2) H_2O_2, NaOH → **E**

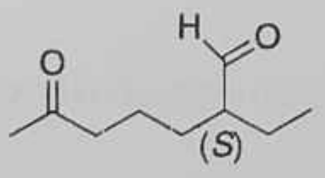


F

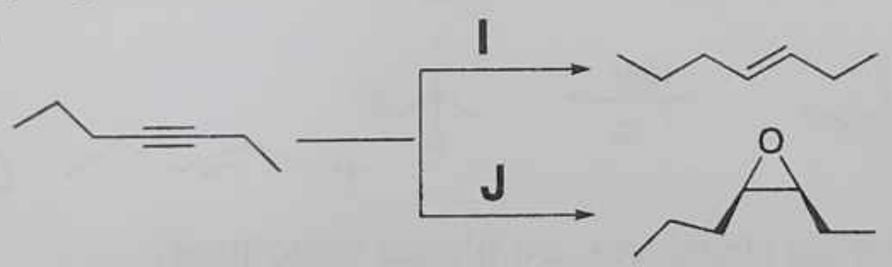
G

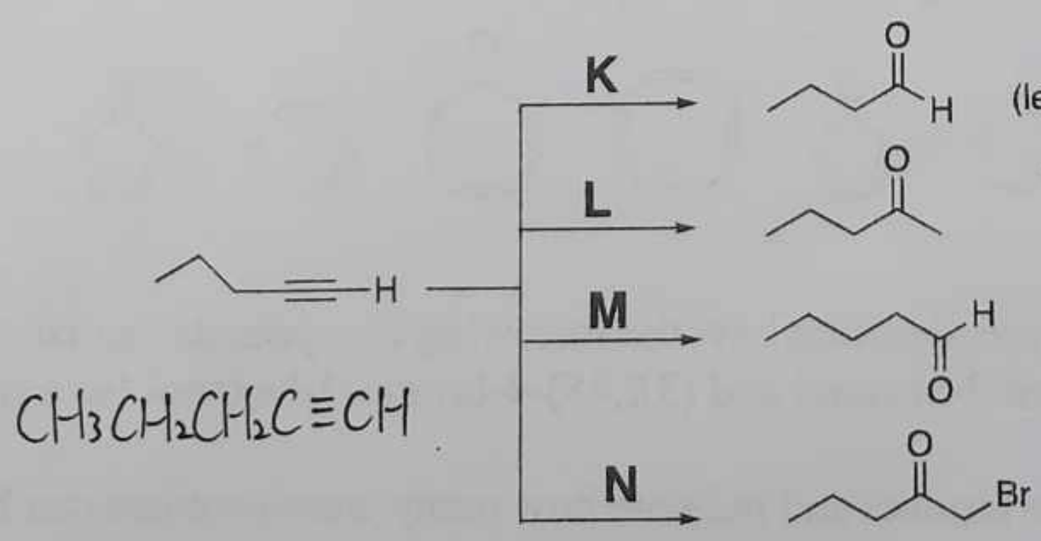


H



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

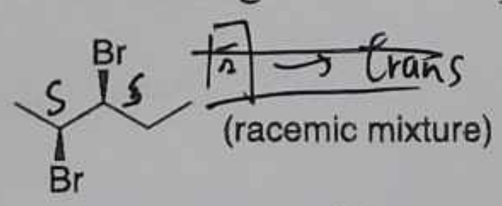




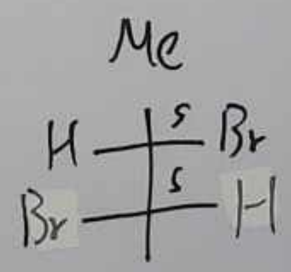
$Pr-CH(OH)-CH=CH_2$ ✓

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

$CH_3-C\equiv CH$ ⇨



~~trans~~ → cis



10. Define the terminology.
   a. tautomerization
   b. $\triangle G^{o}$ and $\triangle G^{\ddagger}$
   c. transition state and intermediate
   d. Hammond postulate
   e. Steric hindrance

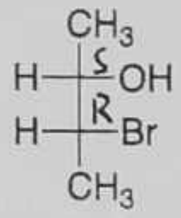
$CH_3-CH(Br)-CH(Br)-CH_2CH_3$

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

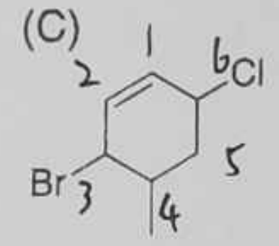
(A)

(optical pure)

(B)



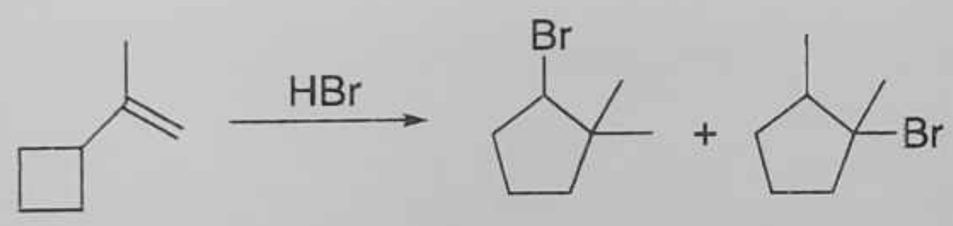
(C)



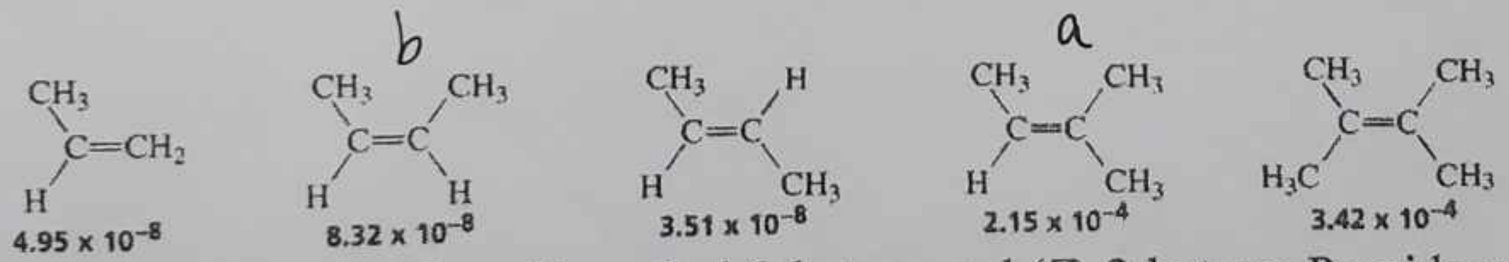
12. The olefin reacts with Br_2 in the presence of excess amount of water (co-solvent) to halohydrin as the major product. The water can be replaced by alcohol. However, when the water is replaced by ether, this reaction is not conducive to product formation. Explain.

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 $M^{-1}s^{-1}$) for acid-catalyzed hydration at 25 °C is given for each of the following alkenes:



4.95 x 10^{-8} 8.32 x 10^{-8} 3.51 x 10^{-8} 2.15 x 10^{-4} 3.42 x 10^{-4}

a. Comparison the stability of 2-methyl-2-butene and (*Z*)-2-butene. Provide your reason(s).

b. 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.