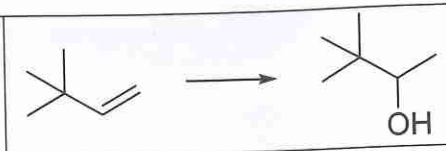


SQ-3. What are the best reagents to complete this transformation?



(A)  $\text{H}_2\text{O}/\text{H}^+$

(B)  $\text{BH}_3/\text{THF}$  followed by  $\text{H}_2\text{O}_2/\text{OH}^-$

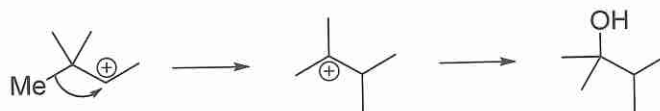
(C)  $\text{Hg}(\text{OAc})_2/\text{H}_2\text{O}$  followed by  $\text{NaBH}_4/\text{OH}^-$

(D)  $\text{HBr (aq)}$  followed by  $\text{OH}^-$

**Knowledge Required:** (1) Markovnikov's Rule. (2) Hydration of alkenes involving oxymercuration/demercuration and hydroboration/oxidation. (3) Carbocation rearrangements. (4) Regioselective reactions.

**Thinking it Through:** In solving this problem, you first identify what atoms add to the alkene to yield the final product. In this reaction, you note that  $\text{H}$  and  $\text{OH}$  add. Next, you consider what regioselectivity the reaction follows and that this addition reaction yields a Markovnikov product, i.e. where the  $\text{H}$  adds to the side of the alkene with the most hydrogens.

Given the choice of reagents in the answer options, you recall that while the reagents in choices (A), (B), and (C) all yield alcohols, only choices (A) and (C) lead to Markovnikov additions. To consider which of these two choices is preferred, you notice the high level of branching on carbon-3, (i.e. the carbon next to the alkene). The addition reaction of  $\text{H}_2\text{O}/\text{H}^+$  to an alkene involves a carbocation intermediate. For choice (A), the intermediate will undergo a 1,2-methyl shift resulting in a rearrangement, forming a more stable carbocation and a different product:

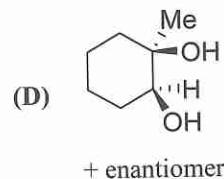
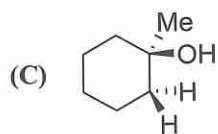
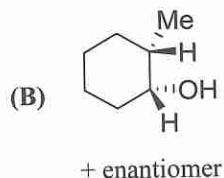
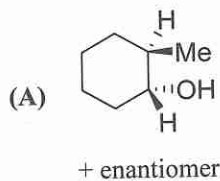
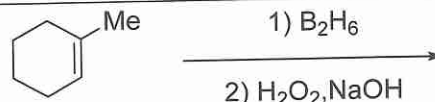


Choice (C) is correct because it is the only answer that leads to the correct product. Oxymercuration gives a Markovnikov product but does not involve carbocation formation and therefore no rearrangement will occur.

Choice (A) is not correct because after a 1,2-methyl shift, a different product forms. Choice (B) is not correct because hydroboration/oxidation results in an *anti*-Markovnikov product. Choice (D) is not correct because the reagents will produce a mixture of substitution and elimination products.

**Practice Problems:** PQ-8, PQ-9, PQ-10, and PQ-11

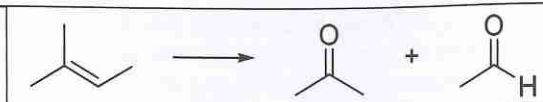
SQ-4. Predict the major product(s) of this reaction.



**Knowledge Required:** (1) Hydration of alkenes involving oxymercuration/demercuration and hydroboration/oxidation. (2) Regioselective reactions. (3) Stereospecific reactions.



SQ-6. Which reagents will yield these products?



- (A)  $\text{KMnO}_4/\text{OH}$  followed by an acid wash with heat  
 (B)  $\text{KMnO}_4/\text{OH}$  followed by a water wash, keep reaction cold  
 (C)  $\text{O}_3/\text{Me}_2\text{S}$   
 (D)  $\text{OsO}_4/\text{NMO}/\Delta$

**Knowledge Required:** (1) Oxidation of alkenes to form *syn*-diols. (2) Oxidation resulting in molecular cleavage.

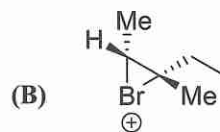
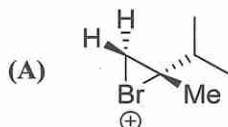
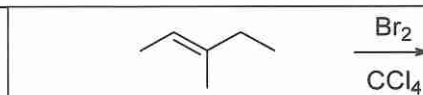
**Thinking it Through:** In solving this problem, you first note that each of these reagents oxidize alkenes. To figure out which reagent is used, you recall the favored products for each set of reagents. When the reagents in choices (B) and (D) react with alkenes, both form *syn*-diols. Given the reagents in choices (A) versus (C), you recall that ozonolysis ( $\text{O}_3/\text{Me}_2\text{S}$ ) of alkenes results in the formation of ketones and aldehydes; whereas, with heat,  $\text{KMnO}_4$  will oxidize alkenes to ketones and carboxylic acids.

Choice (C) is the correct answer because ozonolysis results in ketone and aldehyde products.

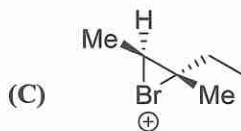
Choices (B) and (D) are not correct because these reagents yield *syn*-diols. Choice (A) is not correct because with heat, the oxidative products are ketones and carboxylic acids.

**Practice Problems:** PQ-15, PQ-16, and PQ-17

SQ-7. Which is an intermediate for this reaction?



+ enantiomer



+ enantiomer



**Knowledge Required:** (1) Addition reactions utilizing  $\text{X}_2$ . (2) Stereospecific reactions.

**Thinking it Through:** In solving this problem, you recall that the reaction of an alkene with  $\text{Br}_2$  forms a bromonium ion as an intermediate. All of the possible answers show a bromonium ion. Next you identify differences among the answers and note that choices (B) and (C) each show the bromine adding to the carbons involved in the double bond of the starting material. You recall that the bromonium ion forms by adding to the carbons in the double bond. You remember that this reaction involves a stereospecific addition where the bridge forms *syn*. Only choice (C) retains the stereochemistry from the alkene with the two methyl groups remaining *cis*.

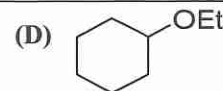
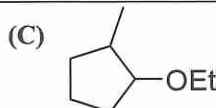
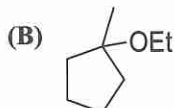
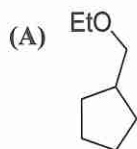
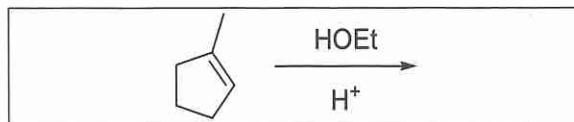
Therefore, choice (C) is correct.

Choices (A) and (D) are not correct because they would involve a rearrangement of the molecule. Choice (B) is not correct because it would require a change in stereochemistry of the alkene substituents.

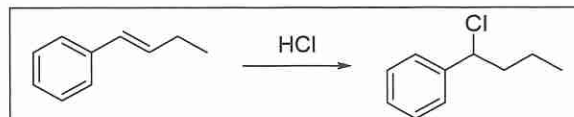
**Practice Problems:** PQ-18, and PQ-19

## Practice Questions (PQ)

PQ-1. What is the major product of this reaction?

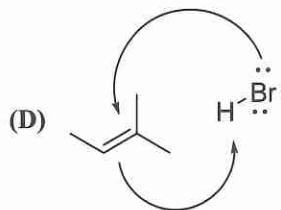
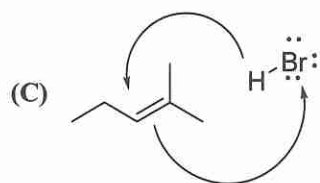
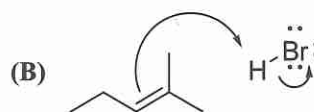
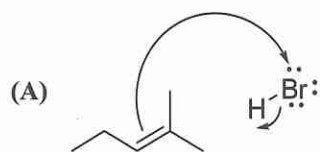
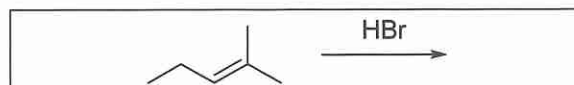


PQ-2. Why does this reaction selectively form this product?

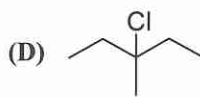
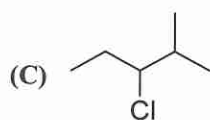
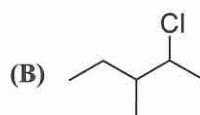
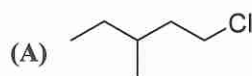
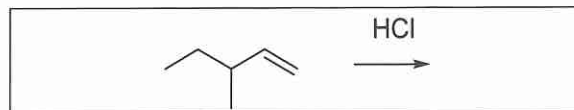


- (A) The benzene ring sterically hinders the reaction.
- (B) The chlorine has an electronic attraction for the benzene ring.
- (C) The carbocation intermediate is stabilized through resonance
- (D) The alternative product undergoes a rearrangement reaction.

PQ-3. What is a step in the mechanism of this reaction?

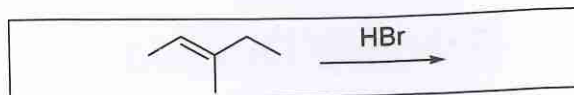


PQ-4. What is the major product of this reaction?





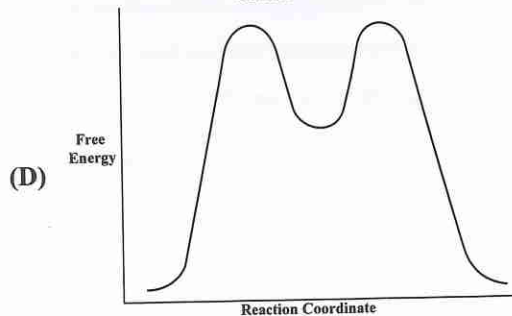
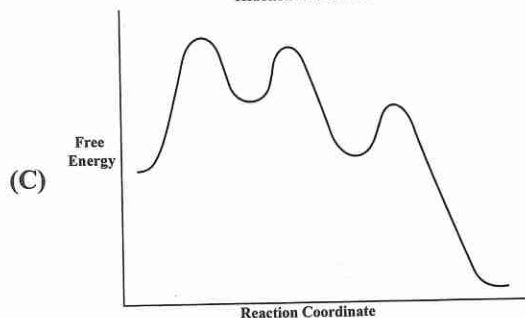
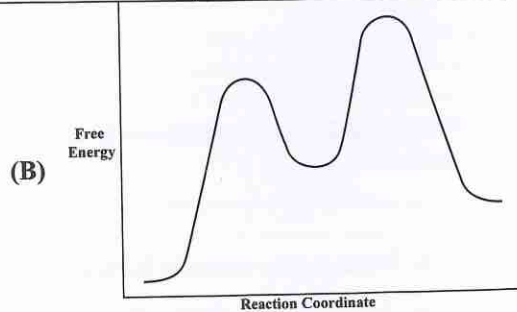
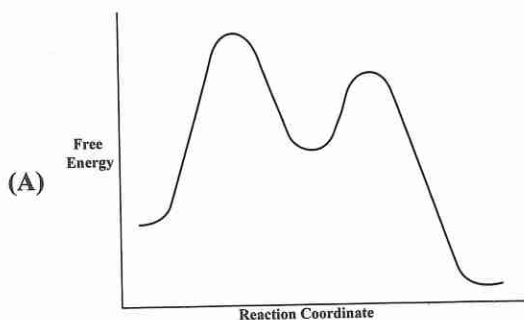
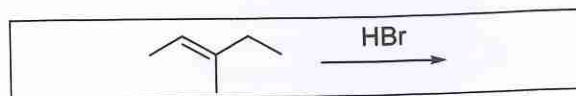
PQ-5. What characterizes the product(s) formed from this reaction?



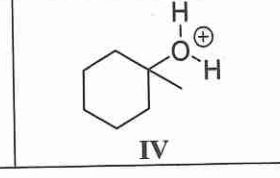
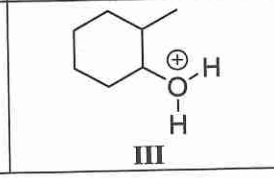
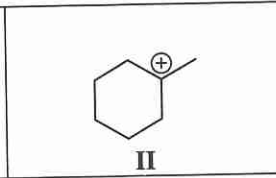
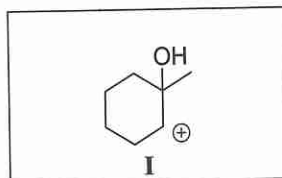
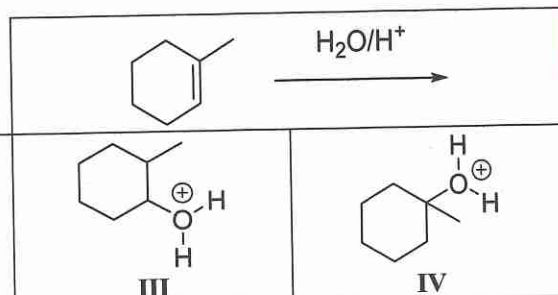
- (A) a mixture of enantiomers  
(C) an achiral molecule

- (B) a racemic mixture  
(D) a mixture of diastereomers

PQ-6. Which energy diagram is consistent with this reaction?



PQ-7. What is/are intermediate(s) for this reaction?



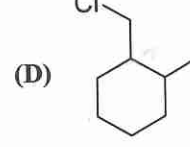
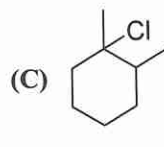
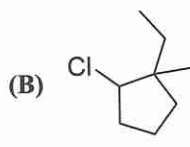
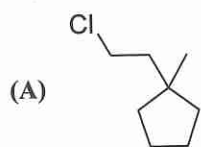
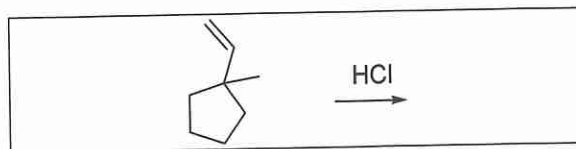
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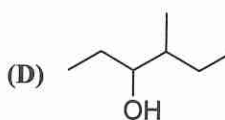
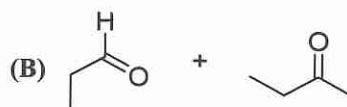
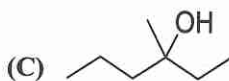
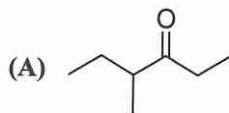
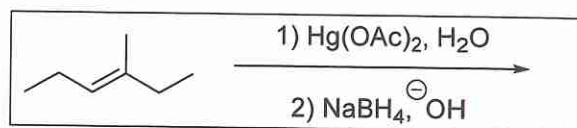
(C) II and IV

(D) only III

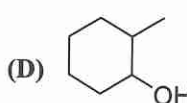
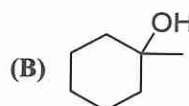
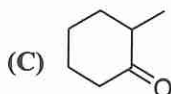
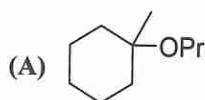
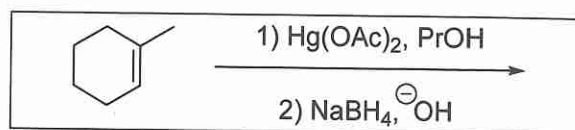
PQ-8. Which product results from this addition reaction?



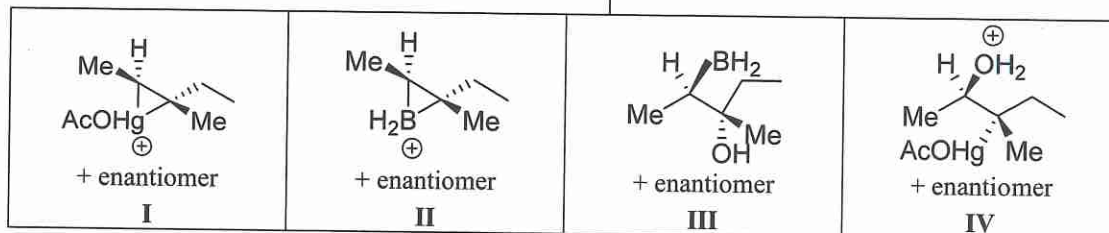
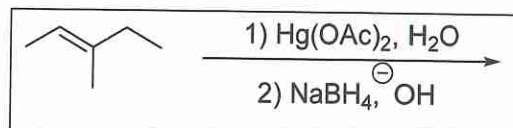
PQ-9. What is the product(s) of this reaction?



PQ-10. What is the product of this reaction?



PQ-11. What are intermediates to this reaction?



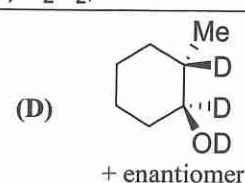
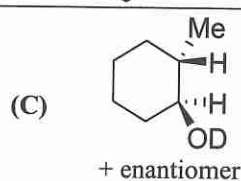
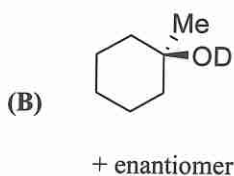
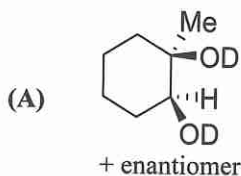
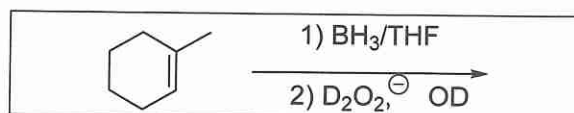
(A) only I

(B) I and IV

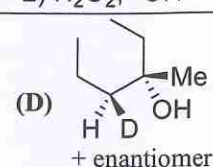
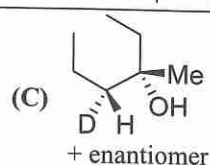
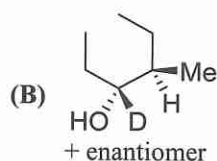
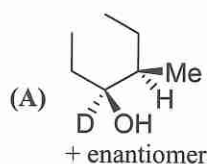
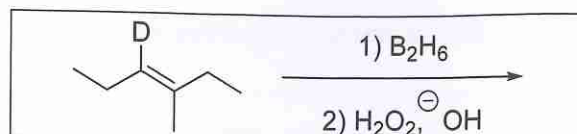
(C) only II

(D) II and III

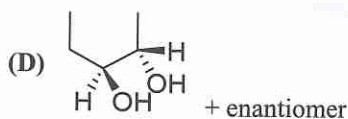
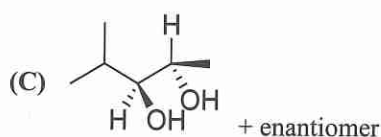
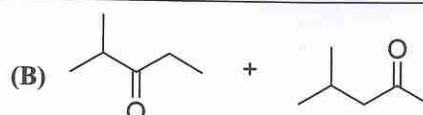
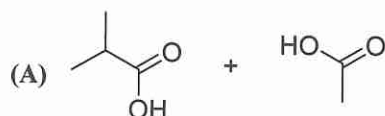
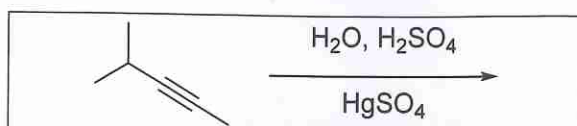
PQ-12. What are the products of this reaction?



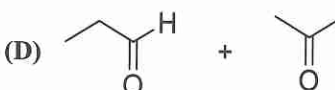
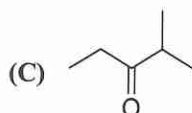
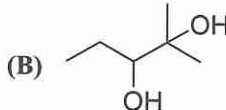
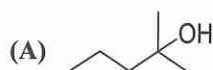
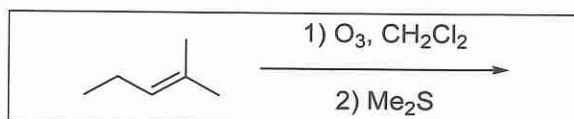
PQ-13. What are the products of this reaction?



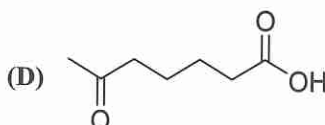
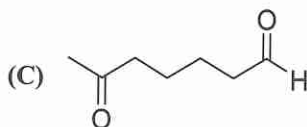
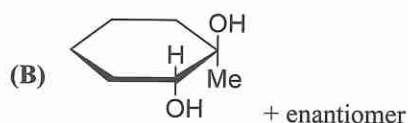
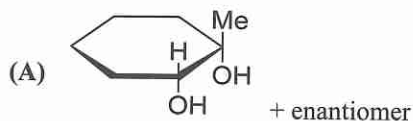
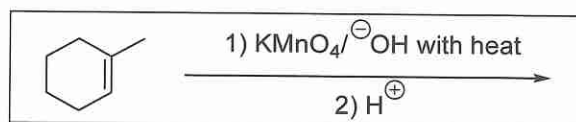
PQ-14. What are the major products of this reaction?



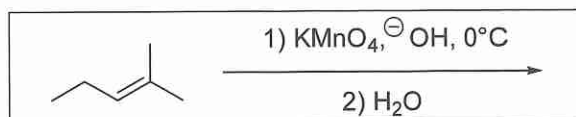
PQ-15. What is/are the product(s) of this reaction?



PQ-16. What is/are the product(s) of this reaction?

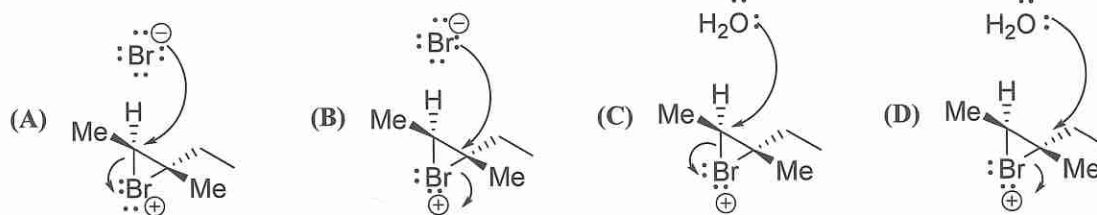
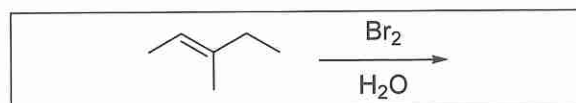


PQ-17. How is this reaction characterized?

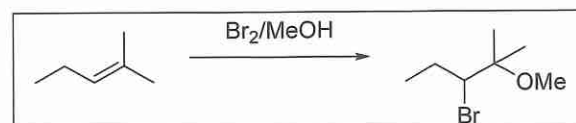


- (A) only regioselective
- (B) both regioselective and stereospecific
- (C) only stereospecific
- (D) neither regioselective nor stereospecific

PQ-18. Which reaction step occurs in this reaction mechanism?

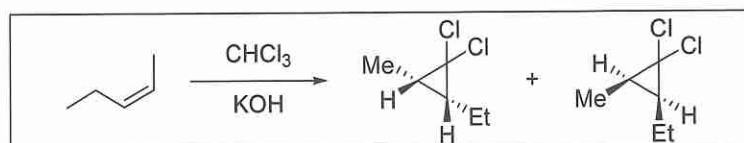


PQ-19. Why is the product shown the preferred constitutional isomer of this reaction?



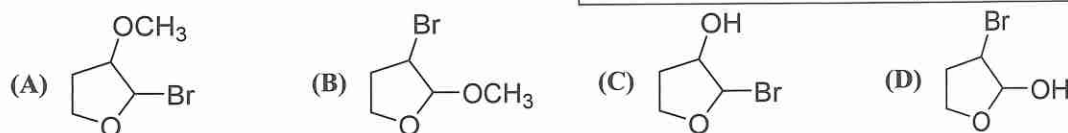
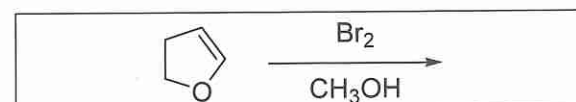
- (A) The nucleophile attacks the more stable carbocation formed during a Markovnikov addition.
- (B) The nucleophile attacks the carbon with the largest  $\delta^+$  charge.
- (C) Steric hindrance inhibits the nucleophile attack on the other carbon.
- (D) The bromonium bridge forces an *anti*-addition of the nucleophile.

PQ-20. How is this reaction characterized?

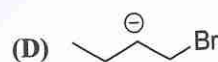
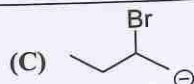
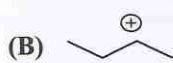
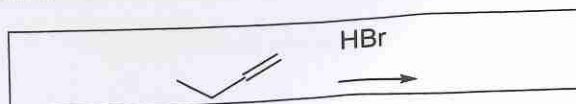


- (A) both regioselective and stereospecific
- (B) only regioselective
- (C) only stereospecific
- (D) neither regioselective nor stereospecific

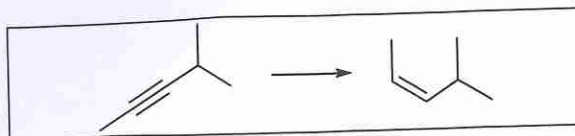
PQ-21. What is the product of this reaction?



PQ-22. What is an intermediate of this reaction?



PQ-23. Which reagents complete this reaction?



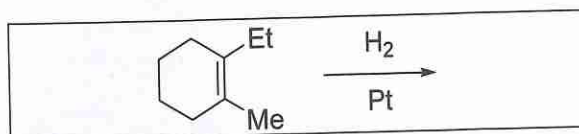
(A) Li, EtNH<sub>2</sub> followed by NH<sub>4</sub>Cl

(C) H<sub>2</sub>/Lindlar's catalyst

(B) H<sub>2</sub>/Pt

(D) H<sub>2</sub>O<sub>2</sub>, <sup>-</sup>OH

PQ-24. Which term best describes the product(s) of this reaction?



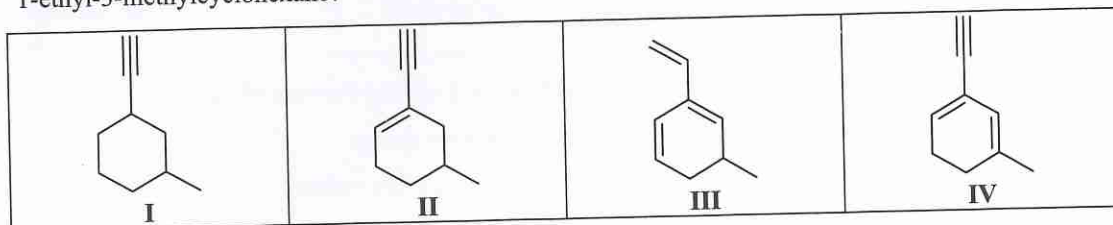
(A) single optically active compound

(C) mixture of diastereomers

(B) meso compound

(D) racemic mixture

PQ-25. Which molecule(s) require(s) exactly 3 moles of H<sub>2</sub> in the presence of Pt to yield 1-ethyl-3-methylcyclohexane?



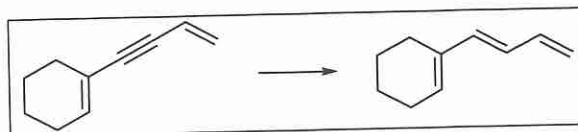
(A) only I

(B) only II

(C) II and III

(D) III and IV

PQ-26. What are the best reagents to complete this reaction?



(A) H<sub>2</sub>/Pt

(C) H<sub>2</sub>/Lindlar's catalyst

(B) NaBH<sub>4</sub>, MeOH

(D) Li, EtNH<sub>2</sub>, -78°C followed by NH<sub>4</sub>Cl wash