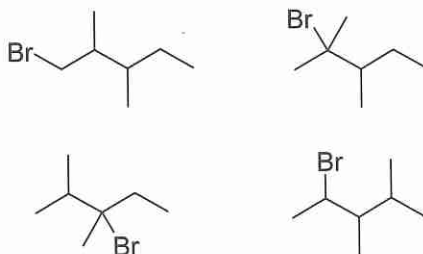


**SQ-7.** Which compound would give only one alkene product when treated with sodium methoxide and heat?

- (A) 1-bromo-2,3-dimethylpentane      (B) 2-bromo-2,3-dimethylpentane  
(C) 3-bromo-2,3-dimethylpentane      (D) 2-bromo-3,4-dimethylpentane

**Knowledge Required:** (1) Nomenclature of alkyl halides. (2) Elimination reaction products.

**Thinking it Through:** You know that strong bases such as sodium methoxide, when reacted with alkyl halides in the presence of heat give alkene functional group products through elimination pathways. Because the choices are all given as their IUPAC names, you know to translate these into structures.



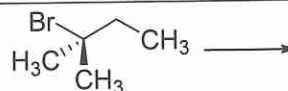
You know that bimolecular elimination pathways (E2 reactions) proceed with strong Brønsted-Lowry bases removing a hydrogen atom beta, or two carbons away, from the bromide leaving group. You realize that this question is not asking for the major product, which would be governed by whether the base was hindered or unhindered, but instead is looking for a starting material that will produce only one product. You realize that you are therefore looking for a starting material with only ONE source of  $\beta$ -hydrogen atoms.

Choice (A) is the correct response because the removal of the  $\beta$  hydrogen and bromide leaving group generates only one possible alkene product.

Choices (B) and (D) are not correct because there are two unique sets of hydrogen atoms beta to the bromide leaving group in each. Choice (C) is not correct because there are three unique sets of hydrogen atoms beta to the bromide leaving group.

**Practice Problems:** PQ-23 and PQ-24

**SQ-8.** Each condition would promote an elimination pathway with this reaction EXCEPT one. What is the EXCEPTION?



- (A) increase in temperature      (B) dissolution in nonpolar solvent  
(C) addition of a base which is also a poor nucleophile      (D) addition of a strong base

**Knowledge Required:** (1) Conditions and mechanism for elimination mechanistic pathways.

**Thinking it Through:** You recall that elimination reactions take place when alkyl halides are added to conditions which remove hydrogen atoms and lose halide leaving groups. Both unimolecular (E1) and bimolecular (E2) mechanism pathways are possible, usually determined by the strength of the added Brønsted-Lowry base. You also know that temperature variations have the ability to effect elimination reactions, higher temperatures will drive elimination pathways in preference to the substitution alternatives.

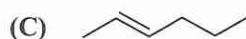
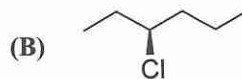
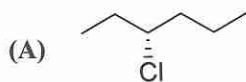
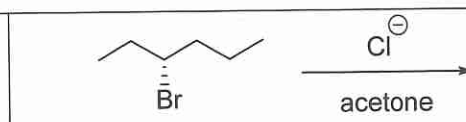
Choice (B) is the correct. Dissolution of alkyl halide in non-polar solvents does not favor an elimination.

Choices (C) and (D) are not correct. They involve the addition of bases where deprotonation and loss of a leaving group is possible (dehydrohalogenation), resulting in elimination products. Choice (A) is not correct. It involves the addition of heat, which can increase the likelihood of elimination reactions due to increasing the entropy of the reaction, making  $\Delta G$  more negative for elimination.

**Practice Problems:** PQ-25 and PQ-26



SQ-9. What is the product of this reaction?

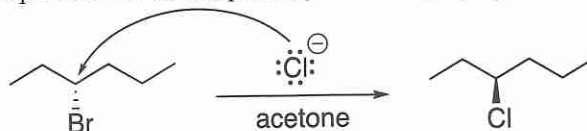
**Knowledge Required:** (1) Deciding on the mechanistic pathway between  $S_N1$ ,  $S_N2$ , E1 and E2 reactions.

**Thinking it Through:** As you complete the review of substitution and elimination reactions, a key step to any of these questions is to correctly identify which of the four potential mechanisms will produce the major product. Though heat and solvent choice can certainly vary the outcome, it is good to have a guide to the most common outcomes of these reactions.

You recall that both the nature of substrate ( $1^\circ$ ,  $2^\circ$ , or  $3^\circ$ ) will play a role as will the nature and strength of the nucleophile/base. The table below provides a good guide for general outcomes of these reactions in absence of changes in heat and solvents:

Type of alkyl halide	Poor Nu; Weak base	Good Nu; Weak base	Good Nu; Moderate base	Good Nu; strong unhindered base	Poor Nu; strong hindered base
$1^\circ$ unbranched	$S_N2$	$S_N2$	$S_N2$	$S_N2$	E2
$1^\circ$ branched	$S_N2$	$S_N2$	$S_N2$	E2	E2
$2^\circ$	$S_N1$	$S_N2$	$S_N2$	E2	E2
$3^\circ$	$S_N1$	$S_N1$	E2	E2	E2
Example Nu/Bases	water or alcohol	halides	$^-CN$ , $^-N_3$ , $^-SH$	unhindered alkoxides, hydroxide	LDA and $t\text{-BuO}^-$

You note that in this prompt, the reaction is that of a secondary alkyl halide with a weak base/good nucleophile (i.e.,  $Cl^-$ ) and thus will proceed via an  $S_N2$  pathway as the major product.



Choice (B) is correct. This is the  $S_N2$  product, including the correct stereochemical outcome.

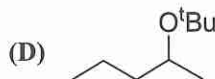
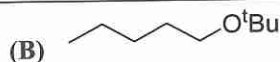
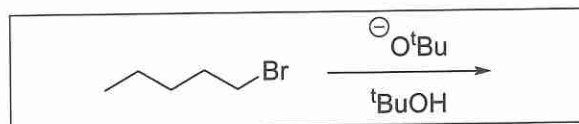
Choice (A) is not correct. Though this appears to be a substitution product, the stereochemistry is incorrect.

Choices (C) and (D) are not correct. These are the elimination products, which would be minor products.

**Practice Problems:** PQ-27, PQ-28, PQ-29 and PQ-30

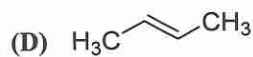
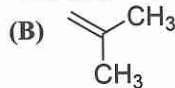
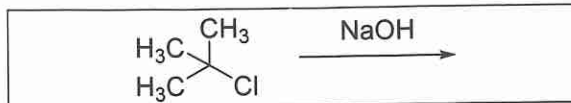
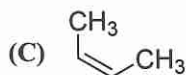
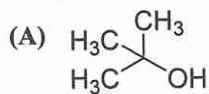
## Practice Questions (PQ)

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

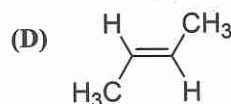
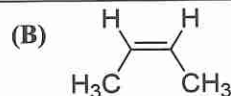
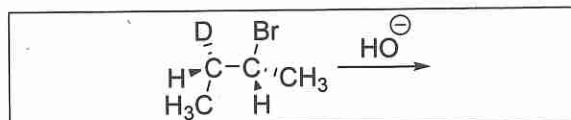
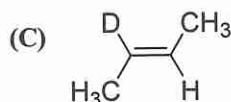
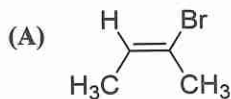




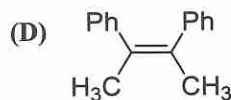
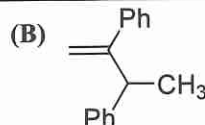
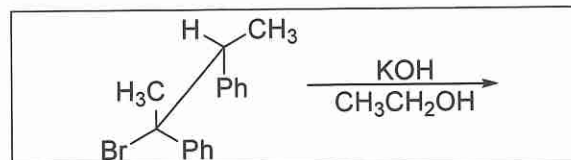
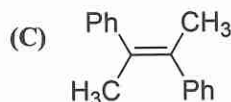
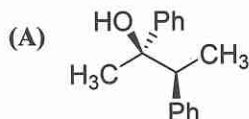
PQ-2. What is the product of this reaction?



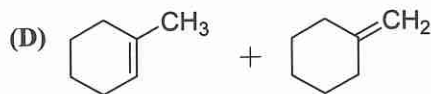
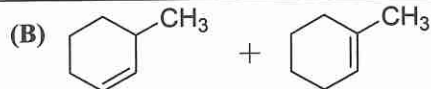
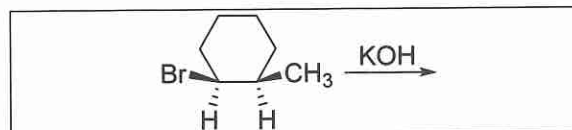
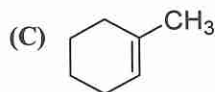
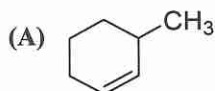
PQ-3. Which is a likely product of this reaction?



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

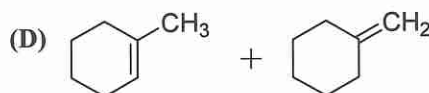
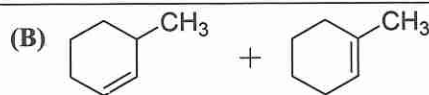
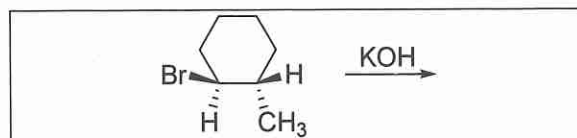
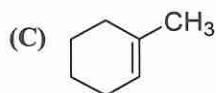
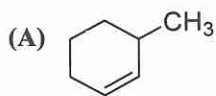


PQ-5. What is/are the possible product(s) of dehydrohalogenation of *cis*-1-bromo-2-methylcyclohexane?

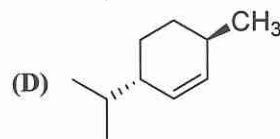
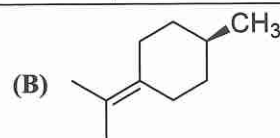
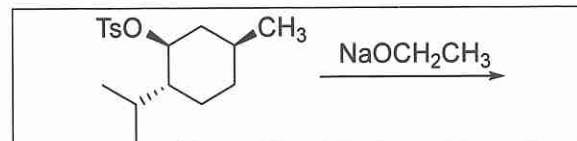
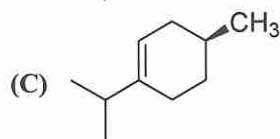
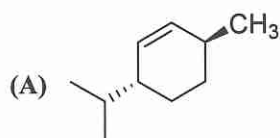




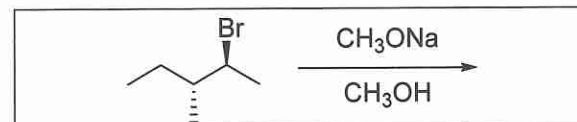
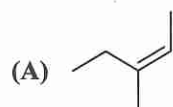
PQ-6. What is/are the possible product(s) of dehydrohalogenation of *trans*-1-bromo-2-methylcyclohexane?



PQ-7. Which product would suggest that a bimolecular elimination (E2) mechanism is occurring?



PQ-8. What is the major product of this reaction?



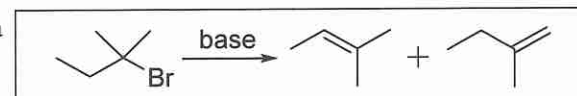
PQ-9. When 2-bromo-2-methylbutane is treated with a base, a mixture of 2-methyl-2-butene and 2-methyl-1-butene is produced; when potassium hydroxide is the base, 2-methyl-1-butene accounts for 45% of the product mixture. However, when potassium *tert*-butoxide is the base, 2-methyl-1-butene accounts for 70% of the product mixture. What percent of 2-methyl-1-butene would be in the mixture if potassium propoxide were the base?

(A) Less than 45%

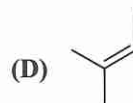
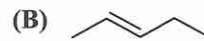
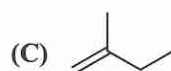
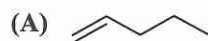
(C) Between 45% and 70%

(B) 45%

(D) More than 70%



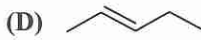
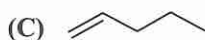
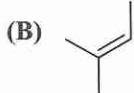
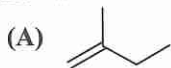
PQ-10. What would be the major product of the dehydrohalogenation of 2-chloropentane by KOH?



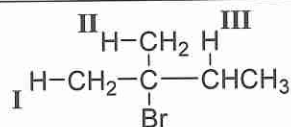
PQ-11. Zaitsev's rule states that

- (A) the order of reactivity of alcohols in dehydration reactions is  $3^\circ > 2^\circ > 1^\circ$ .
- (B) an equatorial substituent in cyclohexane results in a more stable conformation than if that substituent were axial.
- (C) E2 reactions occur only if the  $\beta$  hydrogen and leaving group can assume an anti-periplanar arrangement.
- (D) when a reaction forms an alkene, and several possibilities exist, the more (or most) stable isomer is the one which predominates.

PQ-12. What would be the major product of the dehydrohalogenation of 3-chloropentane by KOH?



PQ-13. In the dehydrohalogenation of 2-bromo-2-methylbutane with potassium hydroxide, which hydrogen atom is preferentially abstracted?



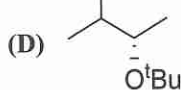
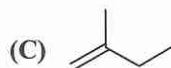
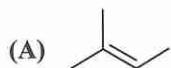
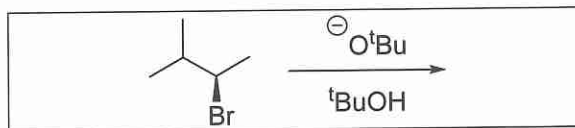
(A) I

(B) II

(C) III

(D) I or II

PQ-14. What is the major product of this reaction?



PQ-15. What would be the first step in the dehydration reaction of cyclohexanol in sulfuric acid?

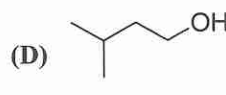
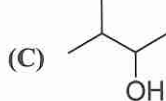
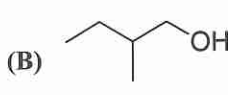
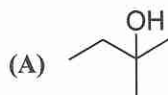
(A) loss of hydroxide

(B) loss of proton by the alcohol

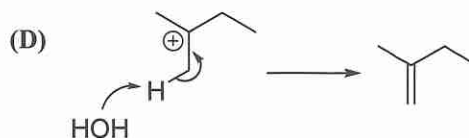
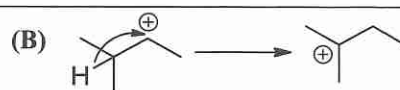
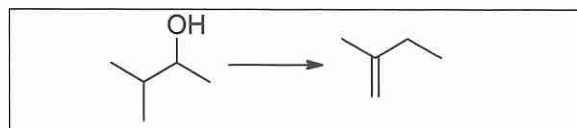
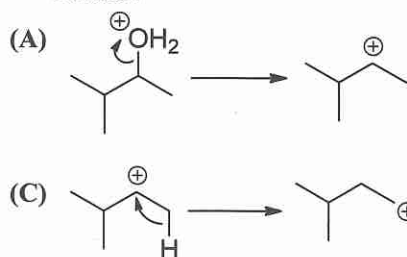
(C) formation of a sulfite ester

(D) protonation of the alcohol

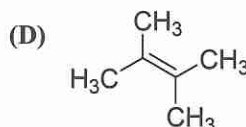
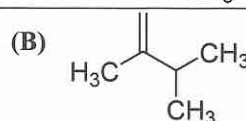
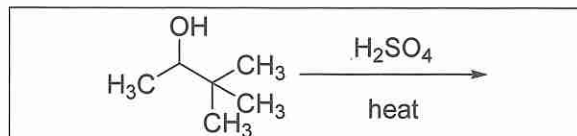
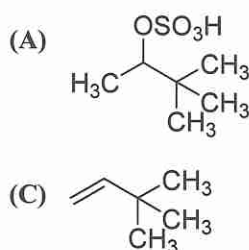
PQ-16. Which molecule is dehydrated fastest in concentrated  $\text{H}_2\text{SO}_4$ ?



**PQ-17.** Which step is NOT reasonable in the mechanism to describe the formation of 2-methyl-1-butene by dehydration of 3-methyl-2-butanol?



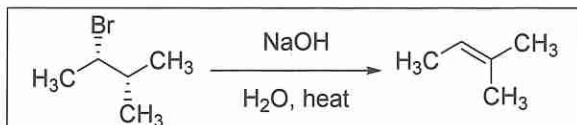
**PQ-18.** What is the major product of this dehydration reaction?



**PQ-19.** Why would concentrated hydrobromic acid be an inappropriate catalyst for the dehydration of alcohols?

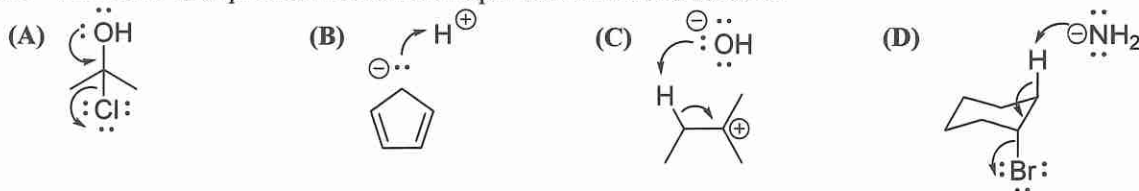
- (A) HBr is too weakly acidic to protonate the alcohol.
- (B) The conjugate base,  $\text{Br}^-$ , is a good nucleophile, and it would attack the carbocation to form an alkyl bromide.
- (C) HBr is strongly acidic, so the water molecule would not be a good leaving group after protonation of the alcohol.
- (D) HBr would be more likely to promote rearrangement of the carbocation intermediate.

**PQ-20.** What effect will reducing the volume of  $\text{H}_2\text{O}$  by half have on the reaction rate?



- (A) reaction rate will double
- (B) reaction rate will reduce by half
- (C) reaction rate will quadruple
- (D) no effect on the rate of this reaction

**PQ-21.** What is an example of a mechanistic step involved in an E2 reaction?



**PQ-22.** In a unimolecular elimination (E1) reaction, the correct order of mechanistic steps is

- (A) dissociation of the leaving group, then deprotonation at the  $\beta$  position  
 (B) simultaneous dissociation of the leaving group and deprotonation of the  $\beta$  position  
 (C) association of the nucleophile/base, then dissociation of the leaving group  
 (D) deprotonation at the  $\beta$  position, then dissociation of the leaving group

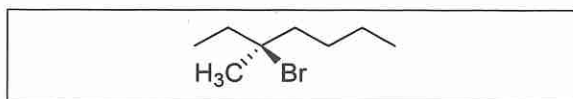
**PQ-23.** How many alkene products, including *E/Z* isomers, can form from the E2 elimination of the compound?

(A) 2

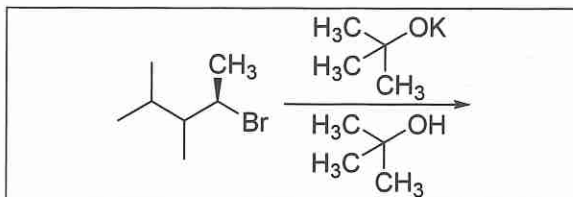
(B) 3

(C) 4

(D) 5



**PQ-24.** What is the major product of this reaction?



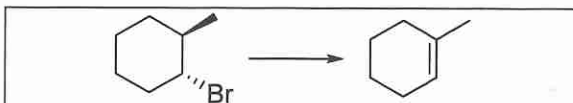
(A) 2,3-dimethyl-2-pentene

(C) *E*-3,4-dimethyl-2-pentene

(B) 3,4-dimethyl-1-pentene

(D) *Z*-3,4-dimethyl-2-pentene

**PQ-25.** Which reagents best accomplish this transformation?



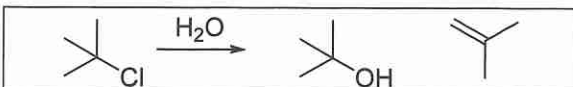
(A)  $\text{CH}_3\text{ONa}$

(C)  $\text{POCl}_3$ , pyridine

(B)  $\text{CH}_3\text{OH}$ , heat

(D)  $\text{H}_3\text{C}-\text{C}(\text{CH}_3)_2-\text{OK}$

**PQ-26.** What solvent results in the fastest rate for this reaction?



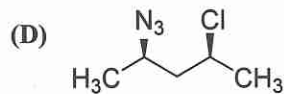
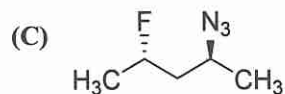
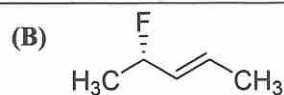
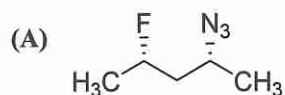
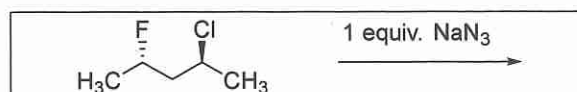
(A) hexanes

(B) acetone

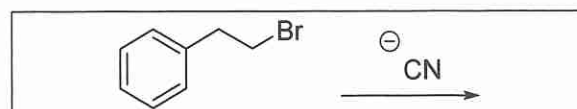
(C) methylene chloride

(D) water

PQ-27. What is the product of this reaction?



PQ-28. What is the expected major reaction pathway for this reaction?



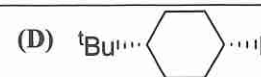
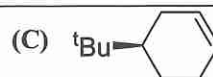
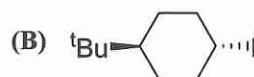
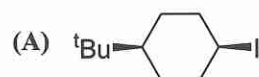
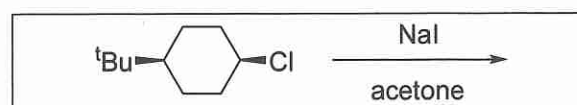
(A) E1

(B) E2

(C) S<sub>N</sub>2

(D) S<sub>N</sub>1

PQ-29. What is the major product of this reaction?



PQ-30. What is the major product of this reaction?

