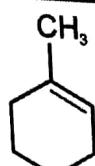
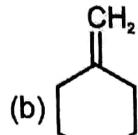
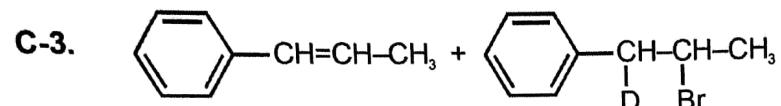


Organic Reaction Mechanisms-IV

- B-6.** (a)  (b) 

C-1. The compound must have acidic β -hydrogen and a relatively poor leaving group.

C-2. In E1cB mechanism carbanion is formed as intermediate and 1st step is reversible.



PART - II

- | | | | | |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| A-1. (B) | A-2. (D) | A-3. (A) | A-4. (B) | A-5. (A) |
| A-6. (B) | A-7. (B) | A-8. (C) | B-1. (C) | B-2. (D) |
| B-3. (A) | B-4. (C) | B-5. (A) | B-6. (B) | B-7. (A) |
| B-8. (B) | C-1. (B) | C-2. (C) | C-3. (B) | C-4. (A) |

PART - III

1. (B) 2. (A \rightarrow p,r) ; (B \rightarrow q,s) ; (C \rightarrow s) ; (D \rightarrow t)

EXERCISE – 2

- | | | | | |
|-----------------|---------|--------|--------|---------|
| PART - I | | | | |
| 1. (D) | 2. (D) | 3. (C) | 4. (D) | 5. (A) |
| 6. (A) | 7. (C) | 8. (B) | 9. (A) | 10. (C) |
| 11. (C) | 12. (C) | | | |

PART - II

- | | | | | |
|---|------|------|------|-------|
| 1. 23 | 2. 6 | 3. 5 | 4. 5 | 5. 3 |
| 6. 32 [Molecular Weights (P – Q) = 114 – 82 = 32] | | | 7. 3 | 8. 78 |

PART - III

- | | | | | |
|-----------|-----------|---------|-----------|-----------|
| 1. (ABCD) | 2. (BCD) | 3. (AD) | 4. (ABCD) | 5. (ABD) |
| 6. (ABCD) | 7. (ABCD) | 8. (BD) | 9. (CD) | 10. (ABC) |

PART - IV

- | | | | | |
|--------|--------|--------|--------|--------|
| 1. (B) | 2. (C) | 3. (C) | 4. (A) | 5. (C) |
| 6. (D) | 7. (C) | 8. (D) | | |

EXERCISE – 3

PART - I

1. $(X) = \overset{\cdot}{C}O_2$; $(Y) = CH_2 = CH - \overset{\cdot}{C}(=O) - O - H$; $(Z) = CH_2 = CH - \overset{\cdot}{C}H_2 - OH + H_2O$ 2. (A)

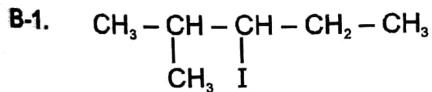
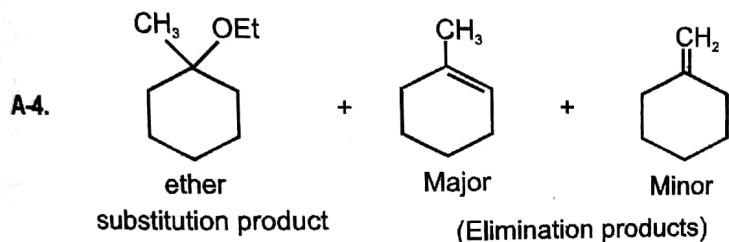
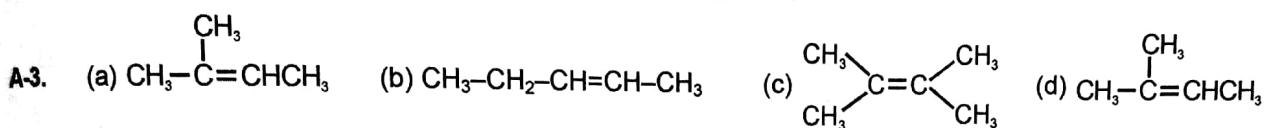
- | | | | |
|---------|---------|--|---------|
| 3. (D) | 4. (C) | 5. (A) - q ; (B) - q ; (C) - r, s ; (D) - p, s | 6. (D) |
| 7. (A) | 8. (C) | 9. 5 | 11. (B) |
| 12. (A) | 13. (A) | 10. (D) | 16. (4) |

PART - II

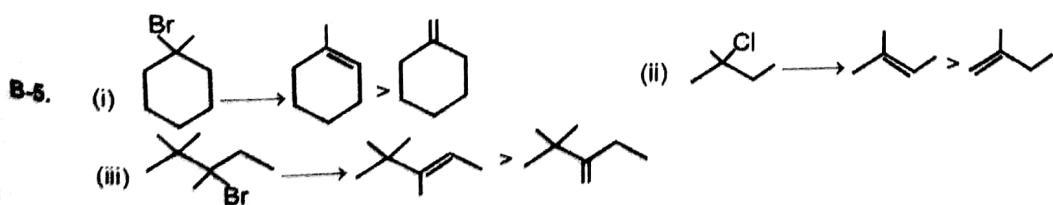
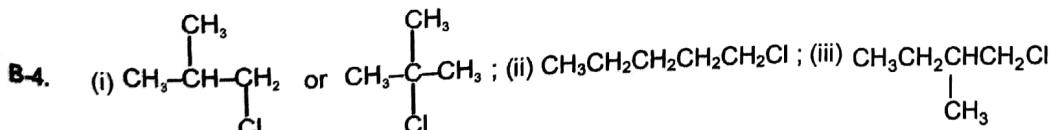
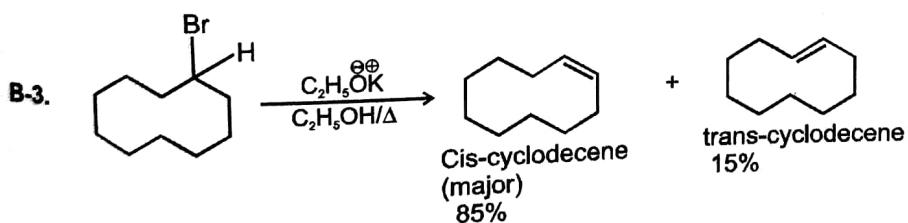
- | | | | | |
|--------|---------|--------|--------|---------|
| 1. (2) | 2. (1) | 3. (3) | 4. (3) | 5. (3) |
| 2. (2) | 7. (1) | 8. (2) | 9. (3) | 10. (4) |
| 3. (1) | 12. (4) | | | |

Answers**EXERCISE - 1****PART - I**

- A-1. In basic condition very poor leaving group -OH will eliminate but in acidic medium -OH will be converted into -OH_2^+ which is very good leaving group.
- A-2. 1° carbocation $\text{R}-\overset{\oplus}{\text{CH}_2}$ would rearrange and 2-alkene would result. Even if 1-alkene is also formed but, it would tend to rearrange in acidic medium to 2-alkene.

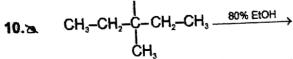
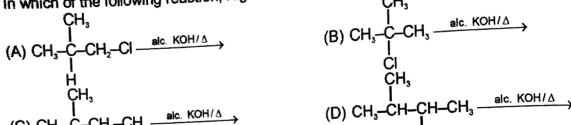


B-2. $t\text{-BuO}^-$ is bulky base so Hoffmann product is formed as major product.



Organic Reaction Mechanisms-IV

9. In which of the following reaction, regioselectivity can be observed.



What is / are true about above reaction?

- (A) Major product is given by S_N1 reaction.
 (B) Through E1 mechanism 3 alkenes are formed.
 (C) 3-Methylpentan-3-ol is also formed as one of the product.
 (D) Fractional distillation of elimination products will give two fractions.

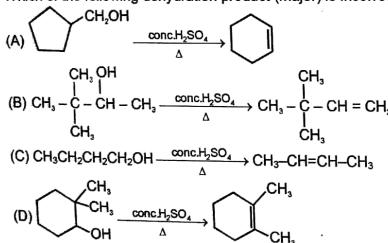
PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

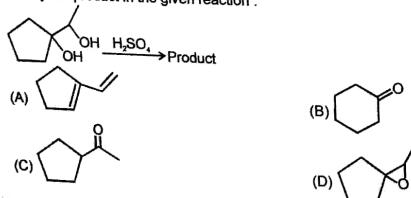
Comprehension # 1

Alcohols undergo acid catalysed elimination reactions to produce alkenes. Because water is lost in the elimination, this reaction is called dehydration reaction. Secondary and tertiary alcohols always give E1 reaction in dehydration. Primary alcohols whose β-carbon is branched also give E1 reaction. The reactivity of alcohol for elimination reaction is tertiary alcohol > Secondary alcohol > Primary alcohol.

1. Which of the following dehydration product (major) is incorrect ?



2. Identify the product in the given reaction :



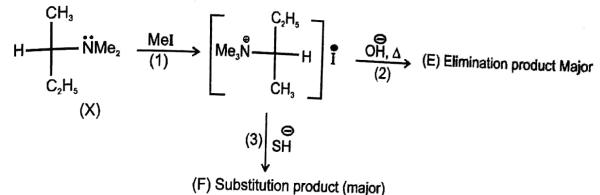
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Organic Reaction Mechanisms-IV

Comprehension # 2



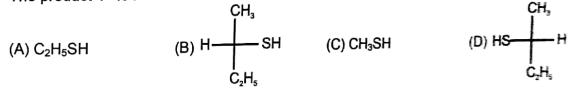
3. The incorrect statement about step-1 is :

- (A) It is S_N2 reaction
 (B) Only one transition state is formed in this reaction
 (C) Walden inversion has occurred at reactant 'X'
 (D) The reaction has molecularity two

4. The product 'E' is :

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

5. The product 'F' is :



Comprehension # 3

Answer Q.6, Q.7 and Q.8 by appropriately matching the information given in the three columns of the following table.

Observe the three columns in which column-1 represents reactants, column-2 represents reaction conditions while column-3 represents products.

Column-1	Column-2	Column-3
(I)		(P)
(II)		(Q)
(III)		(R)
(IV)		(S)

6. The bimolecular reaction is represented by :

- (A) (IV), (iii), (Q) (B) (I), (ii), (S) (C) (III), (ii), (P) (D) (II), (i), (R)

7. The dehydration reaction is represented by :

- (A) (III), (ii), (R) (B) (III), (iv), (P) (C) (I), (ii), (S) (D) (IV), (iii), (R)

8. The unimolecular nucleophilic substitution is represented by :

- (A) (II), (iii), (Q) (B) (I), (iv), (S) (C) (IV), (iv), (Q) (D) (IV), (iii), (Q)

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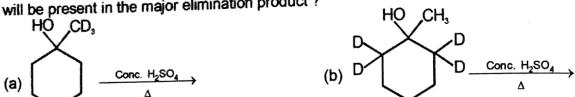
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Organic Reaction Mechanisms-IV

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

1. 'X' is a smallest optically active alkanol. On dehydration it can form Y number of alkenes (including stereoisomers). On reaction with Lucas reagent it forms Z number of alkyl halides (including stereoisomers). Report your answer as [Z Y].

2. If the starting material is labelled with deuterium as indicated, predict how many total deuterium atoms will be present in the major elimination product?



3. The total number of alkenes possible by dehydrobromination of 3-bromo-3-methylhexane using alcoholic KOH is :

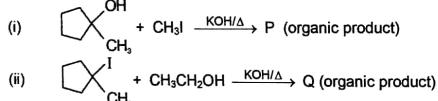
4. In the given reaction : $\text{CH}_3\text{CH}(\text{Ph})\text{CH}_2\text{CH}_3 \xrightarrow[\Delta]{\text{conc. H}_2\text{SO}_4}$ Alkenes

Total number of alkenes (Including stereo isomers) formed will be

5. $\text{Ph}-\overset{\text{OH}}{\underset{\text{Br}}{\text{C}}} \xrightarrow[\Delta]{\text{Alc. KOH}}$ Alkenes

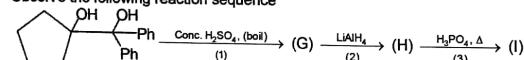
the total number of possible alkenes in this elimination reaction is.

6. The difference of molecular weights of the major products P and Q form at the following reactions is



7. Rearrangement of carbon skeleton of substrate is possible in which of the following reactions ? S_N1, S_N2, E1, E2, E1CB, S_N2Th, S_N2Ar, EAS (Electrophilic aromatic substitution), electrophilic addition on alkenes, free radical substitution of alkanes.

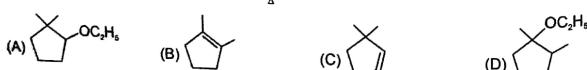
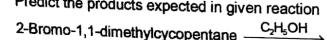
8. Observe the following reaction sequence



Calculate molecular mass [W] of product I and report your answer as N, where N = W ÷ 3.

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. Predict the products expected in given reaction



Organic Reaction Mechanisms-IV

2. Which of the following order is/are correct for the rate of E2 reaction ?

- (A) 5-Bromocycloheptene > 4-Bromocycloheptene
(B) 2-Bromo-1-phenylbutane > 3-Bromo-1-phenylbutane
(C) 3-Bromocyclohexene > Bromocyclohexane
(D) 3-Bromo-2-methylpentane > 2-Bromo-4-methylpentane

3. Which of the following statement(s) is/are true about the following eliminations ?

- (I) (II)
(A) Hoffmann product is major product in I.
(C) Hoffmann product is major product in II.
(B) Saytzeff product is major product in I.
(D) Saytzeff product is major product in II

4. In which reaction product formation takes place by Hoffmann rule ?

- (A) $\text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}_3 \xrightarrow[\Delta]{\text{t-BuO}^+ \text{K}^+}$ (B) $\text{CH}_3-\text{CH}_2-\text{CH}-\text{CH}_3 \xrightarrow[\Delta]{\text{CH}_3\text{CH}_2\text{OK}}$
Br F
(C) $\text{CH}_3-\text{CH}_2-\text{CH}-\overset{\oplus}{\text{N}}\left(\text{CH}_3\right)_2\text{CH}_3 \xrightarrow[\Delta]{\text{OH}^-}$ (D) $\text{CH}_3-\text{CH}_2-\text{CH}-\overset{\oplus}{\text{S}}\left(\text{CH}_3\right)_2\text{CH}_3 \xrightarrow[\Delta]{\text{OH}^-}$

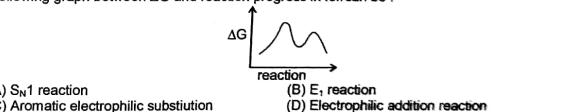
5. Which of the following compounds can give E1cB reaction ?

- (A) CF_3CHCl_2 (B) $\text{C}_6\text{H}_5-\text{CH}-\text{CH}_2\text{F}$ (C) $\text{CH}_3\text{CH}_2-\text{CH}_2\text{Br}$ (D) $\text{C}_6\text{H}_5-\text{CH}-\text{CH}_2\text{-CHO}$
NO₂

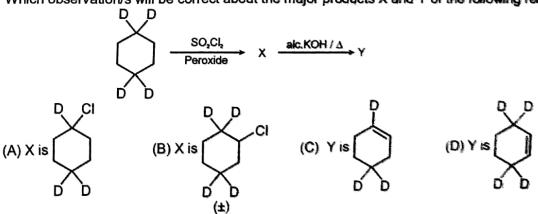
6. Which of the following statement(s) is/are correct

- (A) E2 is a concerted reaction in which bonds break and new bonds form at the same time in a single step.
(B) Order of reactivity of alkyl halides towards E2 dehydrohalogenation is found to be $3^\circ > 2^\circ > 1^\circ$
(C) In E2 reaction both β hydrogen and leaving group should be antiperiplanar
(D) In E2 elimination different stereoisomer (diastereomer) converts into different stereo product.

7. Following graph between ΔG and reaction progress is for/can be :



8. Which observation/s will be correct about the major products X and Y of the following reaction.

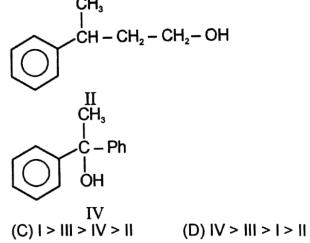
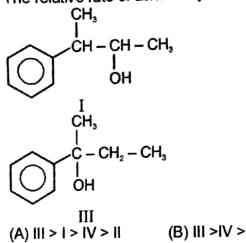


Exercise-2

Marked Questions may have for Revision Questions.

PART - I : ONLY ONE OPTION CORRECT TYPE

1. The relative rate of acid catalysed dehydration of following alcohols would be :

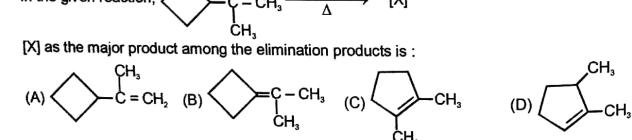


- (A) III > I > IV > II (B) III > IV > I > II (C) I > III > IV > II (D) IV > III > I > II

2. Which one of the following compound undergoes E1 reaction most readily ?



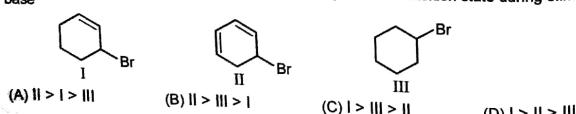
3. In the given reaction, [X] as the major product among the elimination products is :



4. Intermediates for both the steps are respectively ?

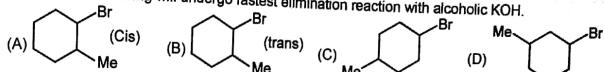
- (A) Carbocation & No intermediate (B) No intermediate & carbocation
 (C) Carbocation & carbanion (D) Carbocation & carbocation

5. Arrange the following in decreasing order of stability of their transition state during elimination by strong base

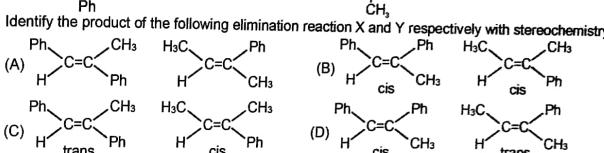


- (A) II > I > III (B) II > III > I (C) I > III > II (D) I > II > III

6. Which of the following will undergo fastest elimination reaction with alcoholic KOH.

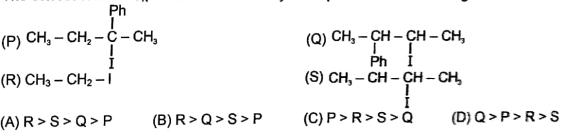


7. Identify the product of the following elimination reaction X and Y respectively with stereochemistry :



8. Which mechanism has different reactivity order of alkyl halides (1° , 2° , 3°) than others :
 (A) S_N1 (B) S_N2 (C) E1 (D) E2

9. The correct order of S_N2 / E2 ratio for the % yield of product of the following halide is :



- (P) R > S > Q > P (Q) R > Q > S > P (C) P > R > S > Q (D) Q > P > R > S

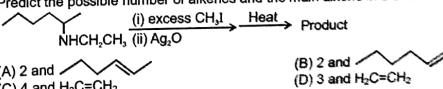
10. (I) (Reactant)
 In this reaction I and II are,

- (A) Enantiomers (B) Structure isomers
 (C) Geometrical isomers (D) Identical compounds

11. Select the incorrect option for the following statements.

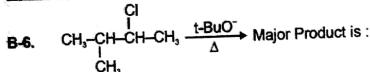
- (A) Bimolecular elimination of alkyl halides is a stereospecific reaction.
 (B) In S_N2 reaction a single isomer is the only product.
 (C) Alcohol dehydrate in strongly basic conditions by E1 mechanism.
 (D) 3-hydroxypropanal dehydrates in strong basic condition by E1cb mechanism.

12. Predict the possible number of alkenes and the main alkene in the following reaction.

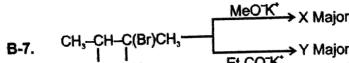


- (A) 2 and (B) 2 and
 (C) 4 and (D) 3 and

Organic Reaction Mechanisms-IV



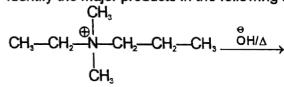
- (A) $\text{CH}_3-\text{C}=\text{CH}-\text{CH}_3$ (B) $\text{CH}_3-\text{CH}-\text{CH}=\text{CH}_2$ (C) $\text{CH}_2=\text{C}-\text{CH}_2-\text{CH}_3$ (D) $\text{CH}_3-\text{CH}-\text{CH}-\text{CH}_3$



X and Y are respectively :

- (A) $\begin{array}{c} \text{CH}_3-\text{C}=\text{C}-\text{CH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$ and $\begin{array}{c} (\text{CH}_3)_2\text{CH}-\text{C}=\text{C}-\text{H} \\ | \quad | \\ \text{CH}_3 \quad \text{H} \end{array}$
(B) $\begin{array}{c} \text{CH}_3-\text{C}=\text{C}-\text{CH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{H} \end{array}$ and $\begin{array}{c} \text{CH}_3-\text{C}=\text{C}-\text{CH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$
(C) Both $\begin{array}{c} \text{CH}_3-\text{C}=\text{C}-\text{CH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$
(D) Both $\begin{array}{c} \text{H} \quad \text{C}=\text{C} \\ | \quad | \\ \text{H} \quad \text{CH}_3 \end{array}$

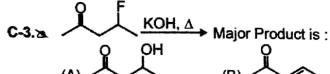
B-8. Identify the major products in the following reaction ?



- (A) $\text{CH}_3-\text{CH}=\text{CH}_2$ (B) $\text{CH}_2=\text{CH}_2$ (C) $\text{CH}_3\text{CH}_2-\overset{\oplus}{\text{N}}-\text{OH}$ (D) $\text{C}_2\text{H}_5-\text{OH}$

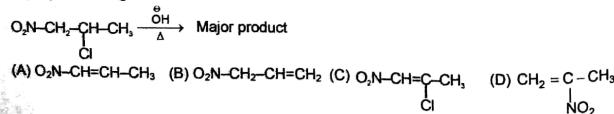
Section (C) : Unimolecular elimination by conjugate base (E1cB)

- C-1. Reaction intermediate of E1cB reaction is :
(A) Carbocation (B) Carbanion (C) Benzyne (D) Free radical
C-2. D-exchange is observed in :
(A) E1 (B) E2 (C) E1cB (D) none of these



- (A) $\text{O} \text{---} \text{C}(\text{OH})-\text{CH}_2-\text{CH}_2-\text{Br}$ (B) $\text{O} \text{---} \text{C}(\text{CH}_2)-\text{CH}_2-\text{Br}$ (C) $\text{O} \text{---} \text{C}(\text{CH}_2)=\text{CH}_2$ (D) $\text{O} \text{---} \text{C}(\text{CH}_2)-\text{CH}_2-\text{Br}$

C-4. Major product of given reaction is-



Organic Reaction Mechanisms-IV

PART - III : MATCH THE COLUMN

1. Match List I (Reaction) with List II (Type of reaction) and select the correct answer using the code given below the lists :

	List I		List II
(P)		(1)	S _N 1
(Q)		(2)	S _N 2
(R)		(3)	E1
(S)		(4)	E2

Codes :
P Q R S
(A) 4 2 1 3
(C) 3 1 2 4

(B) 2 4 3 1
(D) 2 1 4 3

2. Match reactions written in List-I with their mechanism in List-II.

	List-I		List-II
(A)	$\text{Ph}-\text{CH}_2-\text{CH}_2-\text{Br} \xrightarrow{\text{aq. KOH}} \text{Ph}-\text{CH}(\text{OH})-\text{CH}_2 + \text{Ph}-\text{CH}=\text{CH}_2$	(p)	S _N 1
(B)	$\text{Ph}-\text{CH}_2-\text{CH}_2-\text{Br} \xrightarrow[\Delta]{\text{EtONa}} \text{Ph}-\text{CH}_2-\text{CH}_2-\text{OEt} + \text{Ph}-\text{CH}=\text{CH}_2$	(q)	S _N 2
(C)	$\text{Ph}-\text{CH}_2-\text{CH}_2-\text{Br} \xrightarrow[\Delta]{\text{EtO/EtOD}} \text{Ph}-\text{CH}=\text{CH}_2$	(r)	E ₁
(D)	$\text{Ph}-\text{CH}_2-\text{CH}_2-\text{Br} \xrightarrow[\Delta]{\text{EtO/EtOD}} \text{Ph}-\text{CH}=\text{CH}_2 + \text{Ph}-\text{CD}_2-\text{CH}_2\text{Br}$	(s)	E ₂
			(t) E1cB

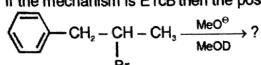
Organic Reaction Mechanisms-IV

Section (C) : Unimolecular elimination by conjugate base (E1cB)

C-1. What are the essential conditions for any reaction to show E1cB mechanism ?

C-2. If ethanol containing EtOD is used as solvent, then deuterium exchange take place in E1cB mechanism. Why ?

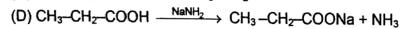
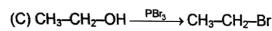
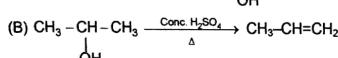
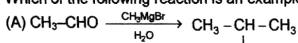
C-3. If the mechanism is E1cB then the possible products will be :



PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Unimolecular eliminaiton reaction (E1)

A-1. Which of the following reaction is an example of elimination reaction :



A-2. Correct statement for E1 Reaction is :

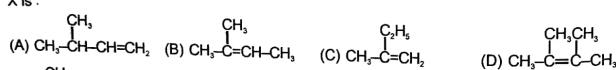
- (A) It is a two step process.
(B) Rearrangement is possible.
(C) Good leaving group favours
(D) All of these

A-3. Intermediate formed during E1 reaction is –

- (A) Carbocation (B) Carbanion (C) Free radical (D) Carbene

A-4. $\text{CH}_3\text{-CH}-\text{CH}-\text{CH}_3 \xrightarrow{\text{EtOH}/\Delta} \text{Major elimination product X.}$

X is :

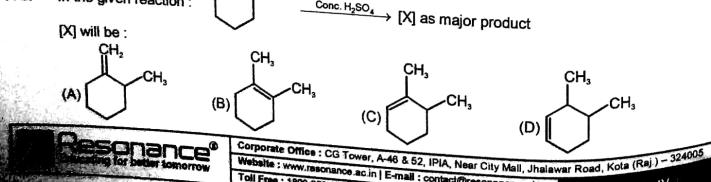


A-5. $\text{CH}_3\text{-}\underset{\substack{| \\ \text{OH}}}{\text{C}}\text{-CH}_2\text{-CH}_3 \xrightarrow[\Delta]{\text{Conc. H}_2\text{SO}_4} \text{Major Product}$

Major product is :



A-6. In the given reaction :



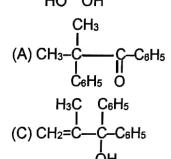
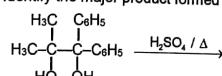
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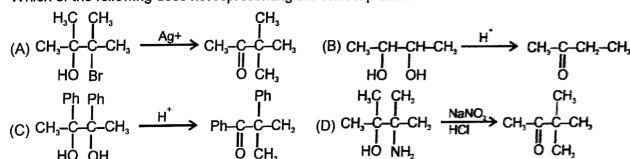
ADV ORM IV

Organic Reaction Mechanisms-IV

A-7. Identify the major product formed in the following reaction



A-8. Which of the following does not representing the correct product



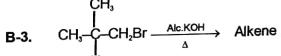
Section (B) : Bimolecular elimination reaction (E2)

B-1. Correct statement for E2 Reaction is :

- (A) It is a two step process.
(B) It is an unimolecular reaction
(C) Strong base favours
(D) Carbanion is formed during the reaction

B-2. Intermediate of E2 reaction is –

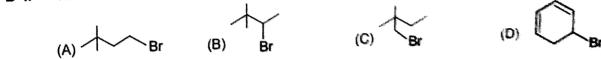
- (A) Carbocation
(B) Carbanion
(C) Free radical
(D) Intermediate is not Formed



Alkene is –



B-4. Which of the following cannot undergo E2 reaction ?



B-5. 2-Chlorobutane on treatment with alcoholic KOH/Δ gives major product :

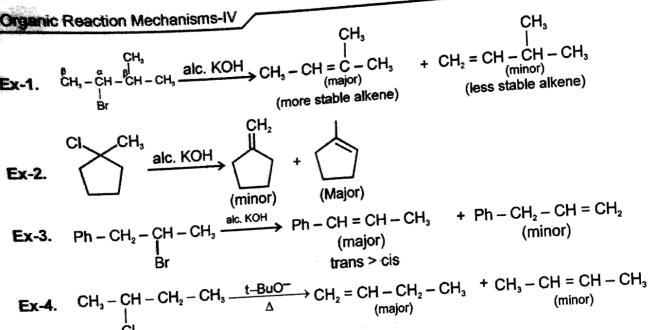
- (A) 2-Butene (B) 1-Butene (C) 2-Butanol (D) 1-Butyne

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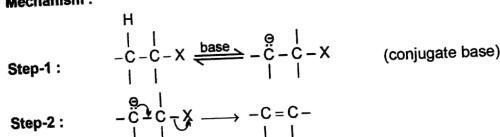
Organic Reaction Mechanisms-IV



Section (C) : Unimolecular elimination by conjugate base (E1cB)

In the E1cB, H leaves first and then the X. This is a two step process, the intermediate is a carbanion.

Mechanism :

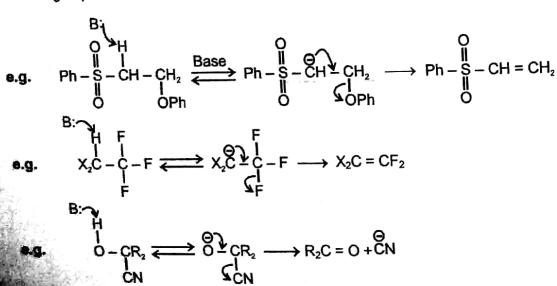


Remarks :

First step consists of the removal of a proton (H^\oplus) by a base generating a carbanion.

In second step carbanion loses a leaving group to form alkene.

Condition: For the E1cB, (i) substrate must be containing acidic hydrogens and (ii) poor leaving groups.



Organic Reaction Mechanisms-IV

Exercise-1

Marked Questions may have for Revision Questions.

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Unimolecular elimination reaction (E1)

A-1. Why dehydrogenation of alcohol takes place in acidic medium generally but not in basic medium.

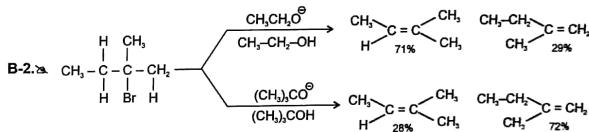
A-2. 1° alcohols are poor starting material for synthesis of 1-Alkene. Explain ?

A-3. Predict the major product of the acid catalysed dehydration of the following alcohols :
(a) $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}_2\text{CH}_3$ (b) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$
(c) $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}(\text{CH}_3)_2$ (d) $(\text{CH}_3)_2\text{CCH}_2\text{OH}$

A-4. When 1-Bromo-1-methylcyclohexane is heated in ethanol for an extended period of time, three products result: one ether and two alkenes. Predict the products of this reaction, and propose a mechanism for their formation. Also, mention the major elimination product.

Section (B) : Bimolecular elimination reaction (E2)

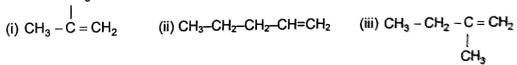
B-1. A halide with formula $\text{C}_6\text{H}_5\text{J}$ is found to give two isomeric alkenes 2-methyl-2-pentene and 4-methyl-2-pentene on dehydrohalogenation with alcoholic KOH. Suggest its structure.



Explain why more alkylated alkene is formed predominantly if base is $\text{CH}_3\text{CH}_2\text{O}^\ominus$, while less alkylated alkene is obtained majorly when t-BuO^\ominus base is used.

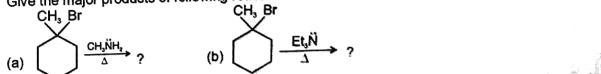
B-3. Bromocyclohexane on heating with ethanolic KOH, produces two alkenes. Write the two products also mention the major one.

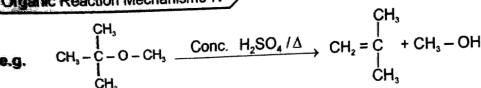
B-4. Which alkyl chloride would yield following pure alkene on reaction with alcoholic KOH ?



B-5. Predict all the alkenes that would be formed by dehydrohalogenation of the following alkyl halides with sodium ethoxide in ethanol and identify the major alkene :
(i) 1-Bromo-1-methylcyclohexane (ii) 2-Chloro-2-methylbutane
(iii) 2, 2, 3-Trimethyl-3-bromopentane.

B-6. Give the major products of following reaction :





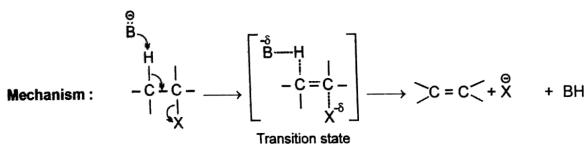
Section (B) : Bimolecular elimination reaction (E2)

(1) E2 Reaction of Alkyl halide :

Dehydrohalogenation is the elimination of a hydrogen and a halogen from an alkyl halide to form an alkene. Dehydrohalogenation can take place by E1 and E2 mechanism.

Reagent

(i) Hot alcoholic solution of KOH or $\text{EtO}^- / \text{EtOH}$ (ii) NaNH_2 (iii) $\text{t-BuO}^- \text{K}^+$ in t-BuOH



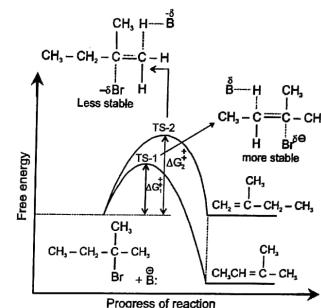
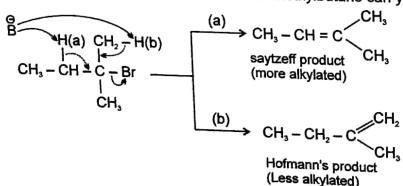
Characteristics of E2 reaction :

1. This is a single step, bimolecular reaction
2. It is a second order reaction
3. Kinetics \rightarrow Rate $\propto [R-X][Base]$
4. Rearrangement is not possible
5. For the lower energy of activation, transition state must be stable
6. E2 follows a concerted mechanism
7. The orientation of proton & leaving group should be antiperiplanar
8. Here β -H is eliminated by base hence called β elimination
9. Positional orientation of elimination \rightarrow In most E1 and E2 eliminations where there are two or more possible elimination products, the product with the most highly substituted double bond will predominate. This rule is called the saytzeff or zaitsev rule.

Rearactivity towards E2 \rightarrow R-I $>$ R-Br $>$ R-Cl $>$ R-F

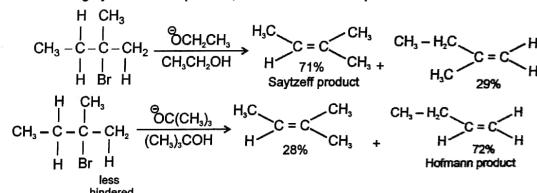
Rate of E2 reaction $= 3^\circ \text{ Alkylhalide} > 2^\circ \text{ Alkylhalide} > 1^\circ \text{ Alkylhalide}$

For example : Dehydrohalogenation of 2-bromo-2-methylbutane can yield two products.

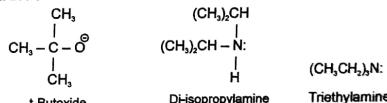


Formation of the Hoffmann product

Bulky bases can also accomplish dehydrohalogenations that do not follow the Saytzeff rule. Due to steric hindrance, a bulky base abstracts a less hindered proton, often the one that leads to formation of the least highly substituted product, called the Hoffmann product.

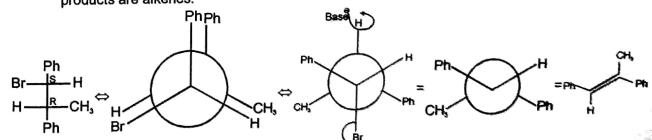


Bulky base :



Stereospecific E2 reactions

The E2 is stereospecific because it normally goes through an anti periplanar transition state. The products are alkenes.



Organic Reaction Mechanisms-IV

Characteristics of E1 reaction :

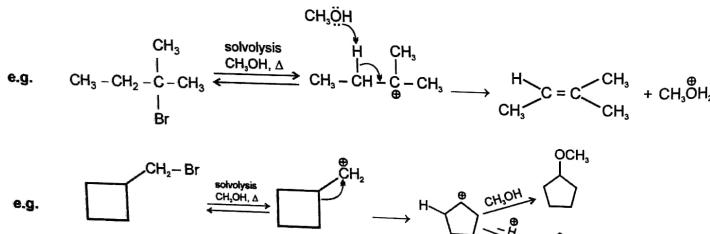
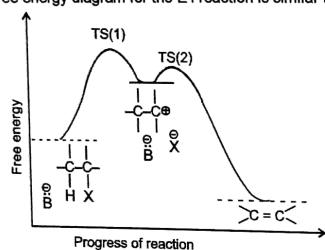
- (i) It is unimolecular, two step process.
- (ii) It is a first order reaction.
- (iii) Reaction intermediate is carbocation, so rearrangement is possible.
- (iv) In the second step, a base abstracts a proton from the carbon atom adjacent to the carbocation, and forms alkene.

Rate of E1 = 3° Alcohol > 2° Alcohol > 1° Alcohol.

Rate of reaction \propto stability of carbocation

- (v) Kinetics : Rate \propto [Alkyl halide]
Rate = k [Alkyl halide]

(vi) Energetics : The free energy diagram for the E1 reaction is similar to that for the S_N1 reaction.

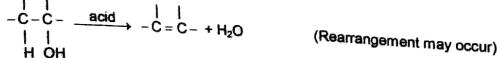


(2) E1 Reaction of Alcohols :

Dehydration requires an acidic catalyst to protonate the hydroxyl group of the alcohol and convert it to a good leaving group. Loss of water, followed by loss of proton, gives the alkene. An equilibrium is established between reactants and products. For E1 mechanism reagents are :

(i) H₃PO₄ / Δ

(ii) H₂SO₄ / 160°



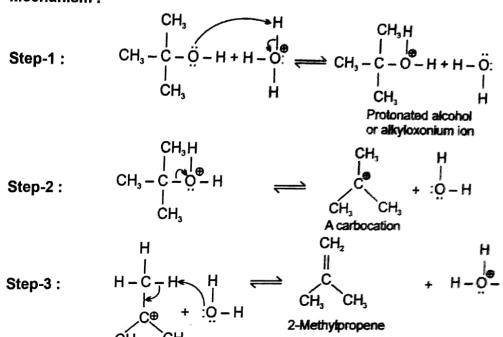
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ADV ORM IV 2

Organic Reaction Mechanisms-IV

Mechanism :



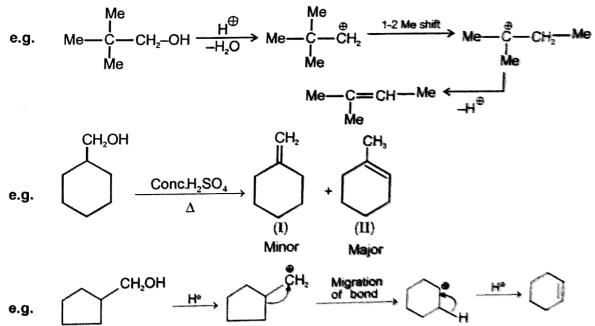
Remarks :

In first step, an acid-base reaction a proton is rapidly transferred from the acid to one of the unshared electron pairs of the alcohol.

In second step the carbon oxygen bond breaks. The leaving group is water molecule.

Finally, in third step the carbocation transfers a proton to a molecule of water. The result is the formation of hydronium ion and an alkene.

Reactivity of ROH : 3° > 2° > 1°



(3) E1 Reaction of Ether :

Elimination is not a favourable reaction for ether, but however few reactions have been observed.

E1 Elimination takes place via formation of stable carbocation.

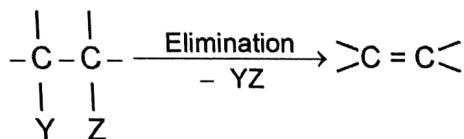
Ether undergoes dehydration reaction in the presence of conc. H₂SO₄ / Δ .

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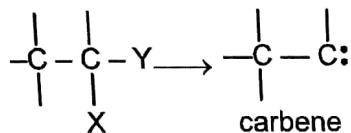
Organic Reaction Mechanisms-IV

Elimination reactions:

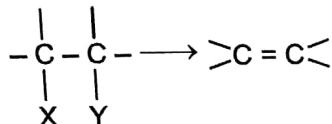
In an elimination reaction two atoms or groups (YZ) are removed from the substrate and generally resulting into formation of π bond.



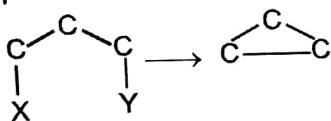
α -elimination : When two groups are lost from the same carbon atom to give a carbene (or nitrene). This is also called 1,1-elimination.



β -elimination : When two groups are lost from adjacent atoms so that a new π bond is formed. This is also called 1,2-elimination.



γ -elimination : It is also called 1,3-elimination. In this a three membered ring is formed.



Type of β -elimination reactions : There are three types of elimination reactions

(I) E1 (II) E2 (III) E1cB

Section (A) : Unimolecular eliminaiton reaction (E1)

Proton and leaving group depart in two different step.

- (a) First step : Slow step involves ionisation to form carbocation
- (b) Second step : Abstraction of proton

(1) E1 Reaction of Alkyl halides :

Mechanism :

