CHAPTER 5

Aliphatic Hydrocarbons (Alkenes)

INTRODUCTION

- Alkenes are the acyclic hydrocarbons in which the unsaturation is double bond between carbon atoms (C=C)
- Alkenes are also known as olefins (i.e., oleum, oil + fines, forming) because lower alkene react with halogens to form dihalides which are oily substance.
- General formula of alkenes is C_nH_{2n} (n = 2, 3, 4, 5, ...).
- Hybridisation of unsaturated carbon is sp^2.
- Bond angle of sp^2 carbon is 120° and geometry is trigonal planar.
- Nature of bonding

Bond	Bond length	Bond energy
C=C	1.34 Å	142 kcal/mole
=C–H	1.10 Å	106 kcal/mole

- The following table gives the types of isomerism alkenes show with the minimum number of carbon required for that isomerism.

Isomerism	Minimum number carbon
Chain isomerism	4
Position isomerism	4
Functional isomerism	3
Ring chain isomerism	3
Geometrical isomers	4
Optical isomerism	6

- Cumulated polyene having even number of double bonds that has $=C\begin{smallmatrix} \diagup a \\ \diagdown b \end{smallmatrix}$ system at both ends can exhibit optical isomerism but cannot exhibit geometrical isomerism.
- Cumulated polyene having odd number double bonds that has $=C\begin{smallmatrix} \diagup a \\ \diagdown b \end{smallmatrix}$ system at both ends can exhibit geometrical isomerism but cannot exhibit optical isomerism

PHYSICAL PROPERTIES

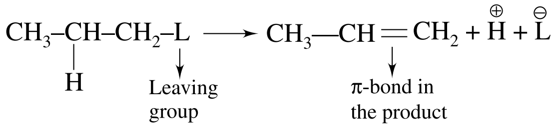
- Alkenes are colourless and odourless.
- Alkenes are insoluble in water and soluble in organic solvents.
- Physical state:

  C_2–C_4 ⟶ gaseous
  C_5–C_{15} ⟶ liquid
  C_{16} and above ⟶ solid like wax

- Boiling point and Melting point $\propto$ Molecular weight
- B.P. and M.P. decrease with increase in branches in alkene
- Melting points of *cis* isomers are lower than *trans* isomers, because *cis* isomer is less symmetrical than *trans*, and therefore *trans* isomer packs more tightly in the crystal lattice and hence have a higher melting point.
- Boiling points of *cis* isomers are higher than *trans* isomers because *cis*-alkenes has greater polarity (Dipole moment) than trans one.
- Alkenes are lighter than water.

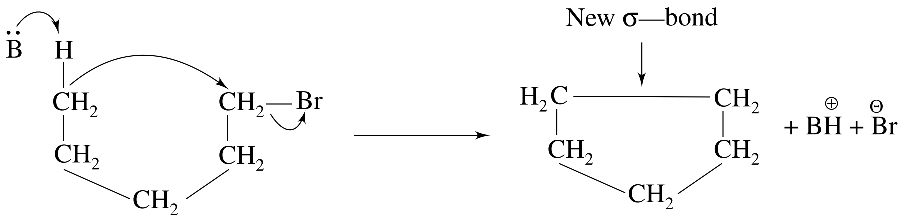
ELIMINATION REACTIONS

The most common type of elimination reaction is one in which two fragments are removed from a substrate to produce a modified substrate and two small units. One of these fragments is usually the leaving group of the substrate. Elimination usually produces a new pi-bond in the modified substrate (1).



$$CH_3-\underset{\underset{H}{|}}{CH}-CH_2-\underset{\underset{\text{Leaving group}}{\downarrow}}{L} \longrightarrow CH_3-\underset{\underset{\pi\text{-bond in the product}}{\downarrow}}{CH=CH_2}+\overset{\oplus}{H}+\overset{\ominus}{L} \qquad ...(1)$$

In some elimination reactions (but very uncommon) a new sigma-bond is produced instead of a pi-bond.

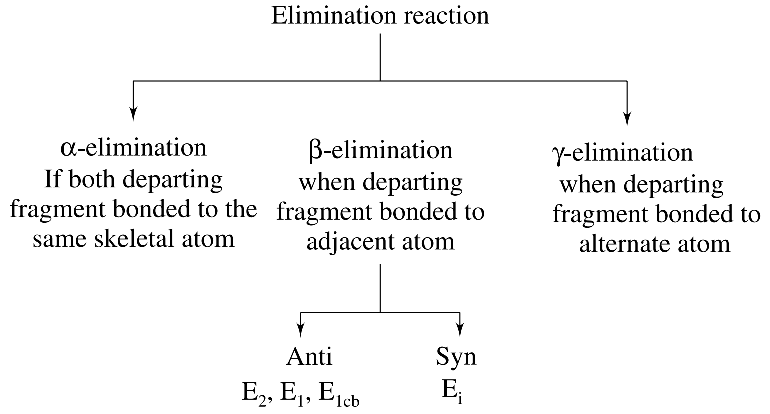


...(2)

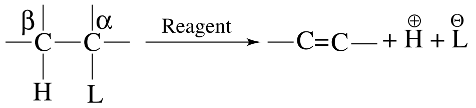
Elimination reactions occur when the compounds have nucleophilic group as a leaving group. The leaving groups responsible for elimination reaction are:

$$\text{Leaving groups are } X, OH, OR, \overset{\oplus}{N}_2, N_3, H_2\overset{\oplus}{O}, \overset{\oplus}{N}R_3 \text{ and } \overset{\oplus}{S}R_2$$

Classification of elimination reaction:



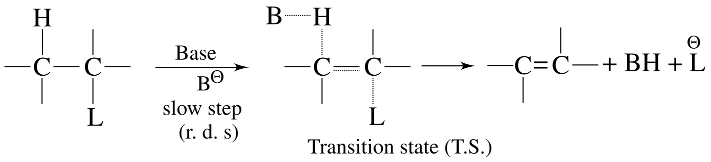
β **elimination:** Such elimination reaction is which removal of one fragment (leaving group) from α. Carbon & other fragment (mostly H-atom) from β Carbon is known as β-elimination reaction



$$-\underset{H}{\overset{\beta|}{C}}-\underset{L}{\overset{|\alpha}{C}}- \xrightarrow{\text{Reagent}} -C{=}C- + \overset{\oplus}{H} + \overset{\ominus}{L}$$

Types of β-elimination

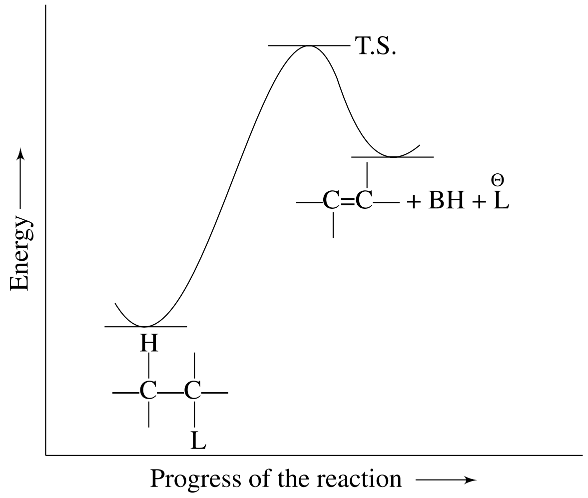
(i) **E_2 (bi molecular elimination reaction)**



$$-\underset{|}{\overset{H}{\overset{|}{C}}}-\underset{L}{\overset{|}{C}}- \xrightarrow[\text{slow step (r. d. s)}]{\text{Base } B^{\ominus}} -\overset{B\cdots H}{C}\text{=}\underset{L}{C}- \longrightarrow -C{=}C- + BH + \overset{\ominus}{L}$$

Transition state (T.S.)

Energy Profile

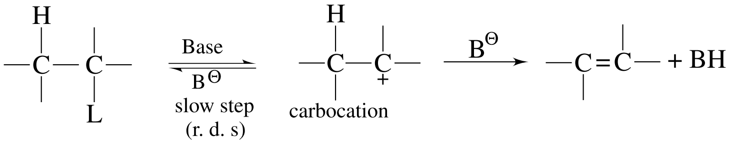


Important Points

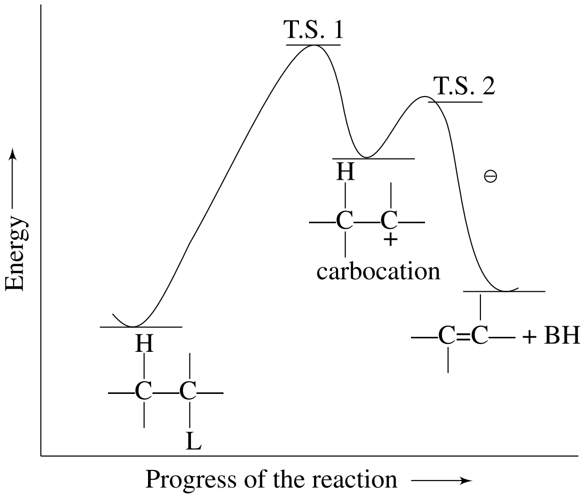
1. One-step reaction
2. No intermediate forms, product formation taking place by formation of TS
3. Strong base needed to remove hydrogen as proton from β carbon
4. Follows the second order kinetics: Rate = K [Substrate] [base]

5. In most of cases major product is Saytzeff and in few cases the major product is Hofmann
6. Stereospecific and stereoselective
7. Reactivity order 3° > 2° > 1°
8. Branching at α and β-carbons and the presence of electron-withdrawing group on the carbon increases the rate of reaction
9. In a polar solvent the rate decreases
10. With increasing concentration and basicity of the added base, the rate increases
11. As the temperature increases, the rate increases
12. E_2 reactions compete with SN_2 reactions

E_1 (Unimolecular elimination reaction)



Energy Profile

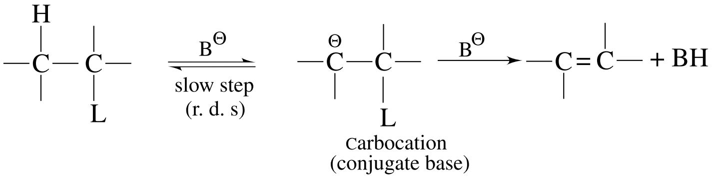


Important Points:

1. Two-step reaction
2. Carbocation as reaction intermediate
3. In the second step the hydrogen leaves as proton from the carbocation
4. Weak base is needed in second step to remove hydrogen as proton
5. Follows the first order kinetics: Rate = K [Substrate]
6. Major product of the reaction is Saytzeff product
7. Non-stereospecific and non-stereoselective
8. Reactivity order 3° > 2° > 1°
9. Any structural feature that stabilises the carbocation will increase the rate; thus, branching at α and β-carbons increases the rate
10. Polar protic solvents increase rate
11. The concentration and the basicity of the solvent have no effect on the rate
12. As the temperature increases, the rate increases
13. E_1 reactions compete with SN_1 reactions

E1cb (Unimolecular elimination reaction with respect to conjugate base)

Elcb mechanism is limited to substrates that can stabilise the carbanion intermediate, i.e., β-carbon should contain carbonyl, nitro, cyano, sulphonyl, or other carbanion stabilising group.



Important Points:

1. Two-step reaction
2. Carbanion as reaction intermediate
3. The leaving group leaves the carbanion either as an anion or as a neutral group
4. Strong base is needed to remove hydrogen as proton in the first step
5. Follows the second order kinetics: Rate = K [Substrate] [Base]
6. Major product of reaction obtain by Hofmann elimination
7. Non-stereospecific and non-stereoselective
8. Reactivity order 3° > 2° > 1°
9. Any structural feature that stabilises the intermediate carbanion will increase the rate; presence of an α-aryl group shifts a β-elimination toward Elcb pathway
10. Polar aprotic solvent increases the rate
11. With increasing concentration and basicity of the added base, the rate increases
12. As the temperature increases, the rate increases

Direction of Elimination

- When all β-hydrogens are not equal, more than one type of alkenes is formed.
- Elimination, in which the most substituted alkene is the major product, is known as Saytzeff elimination and the rule is known as **Saytzeff rule**.
- Elimination, in which the least substituted alkene is the major product, is known as Hofmann elimination and the rule is known as **Hofmann rule**.

Hofmann elimination reaction takes place in the following four cases.

(i) When the base is bulky
(ii) When the leaving group is a poor leaving group, such as F, $\overset{\oplus}{N}R_3$ and $\overset{\oplus}{S}R_2$
(iii) When the alkyl halide contains one or more double bonds at β-carbon
(iv) Steric hindrance at γ-carbon

Trick - In terms of β-hydrogen, saytzeff rule **Poorer became poorer**

Stereochemistry of Elimination Reaction:

Optically active substrates, in which α and β carbons are chiral, give stereoselective as well as stereospecific products. Geometry of alkene depends on the configuration of the substrate, as described in the following section.

Stereochemistry of elimination can be remember by the following two words:

(I) CAR where
    C means *cis* (or *Z*) alkene
    A means *anti* elimination
    R means racemic mixture (or threo form)
  (i) Erythro form (or meso form) gives *E* or *trans* alkene, upon *anti* eliminations
  (ii) Threo form (or d or *l* form) gives *Z* or *cis* alkene, upon *anti* eliminations

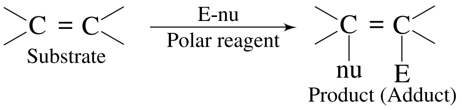
(II) CSM where

C means *cis* alkene
S means *syn* elimination
M means meso form (or erythro form)

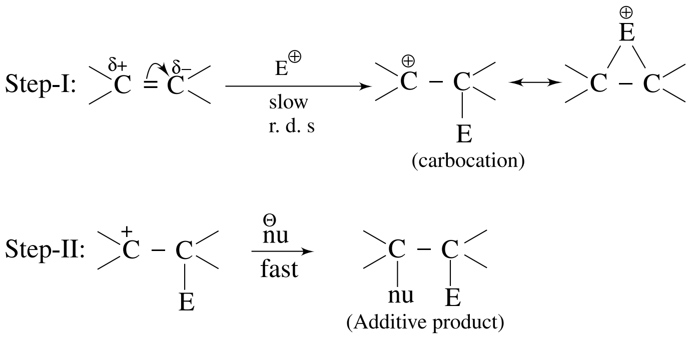
(i) Erythro form (or meso form) gives *Z* or *cis* alkene, upon *syn* elimination
(ii) Threo form (or *d* or *l* form) gives E or *trans* alkene, upon *syn* elimination

ELECTROPHILIC ADDITION REACTION TO CARBON–CARBON DOUBLE BOND:

- To introduce the mechanism of electrophilic addition, let us consider the following general reaction.



Mechanism



Important Points

- It is a two-step process
- Breaking of π-bond of carbon–carbon double bond is achieved by electrophile (E^+) in slow step; so it is known as electrophilic addition reaction (E.A.R)
- Intermediate is carbocation so re-arrangement, ring expansion, etc., takes place
- Rate law:

$$\frac{dx}{dt} = k[\text{Alkene}][E^+]$$

- It is a second order reaction
- Rate of E.A.R ∝ stability of carbocation
- It is a stereospecific reaction
- Major product given by Markovnikov's rule

Markovnikov's rule

Markovnikov's rule can be used in those alkenes which fulfil the following conditions:

(i) Both alkene and reagent must be unsymmetrical
(ii) Substituent(s) present on doubly bonded carbon(s) should only be +I group(s)
(iii) If phenyl group is present on doubly bonded carbon, then both doubly bonded carbons should be substituted by phenyl group

This rule states that electrophilic part of an unsymmetrical reagent attaches itself to that double bonded carbon atom which has more number of hydrogen atoms and negative part goes to that doubly bonded carbon which bears less number of hydrogen atoms.

Or

In terms of hydrogen Markovnikov's rule is: '**Richer becomes richer**'

Advanced Markovnikov's Rule:

Formation of a more stable carbocation takes place by the addition of the electrophilic part of unsymmetrical reagent on unsymmetrical alkene.

Note:

(i) A reaction in which two or more constitutional isomers could be obtained as product but one of them predominates, is called a **regioselective reaction.** Thus, ionic addition of unsymmetrical reagents to unsymmetrical alkenes is a regioselective reaction.

(ii) It is important to remember that whenever a reaction leads to the formation of a carbocation you must check its structure for the possibility of rearrangement etc.

Stereochemistry of Addition Reactions

Stereochemistry of addition reaction depends upon two factors:

(i) Whether both electrophile and the nucleophile will join themselves of the two double bonded carbons from the same side (*syn* addition) of the double bond or from the opposite sides (*anti* addition).

(ii) The geometrical orientation of the two parts of the addendum $\overset{\oplus}{E}$ and $\overset{\oplus}{N}$ to each other.

Selection of stereoisomer

Profile 1: When both alkene and reagent are symmetrical

Alkene	Reagent	Major addition product
Cis	*Syn*	Meso
Cis	*Anti*	Racemic mix
Trans	*Syn*	Racemic mix
Trans	*Anti*	Meso

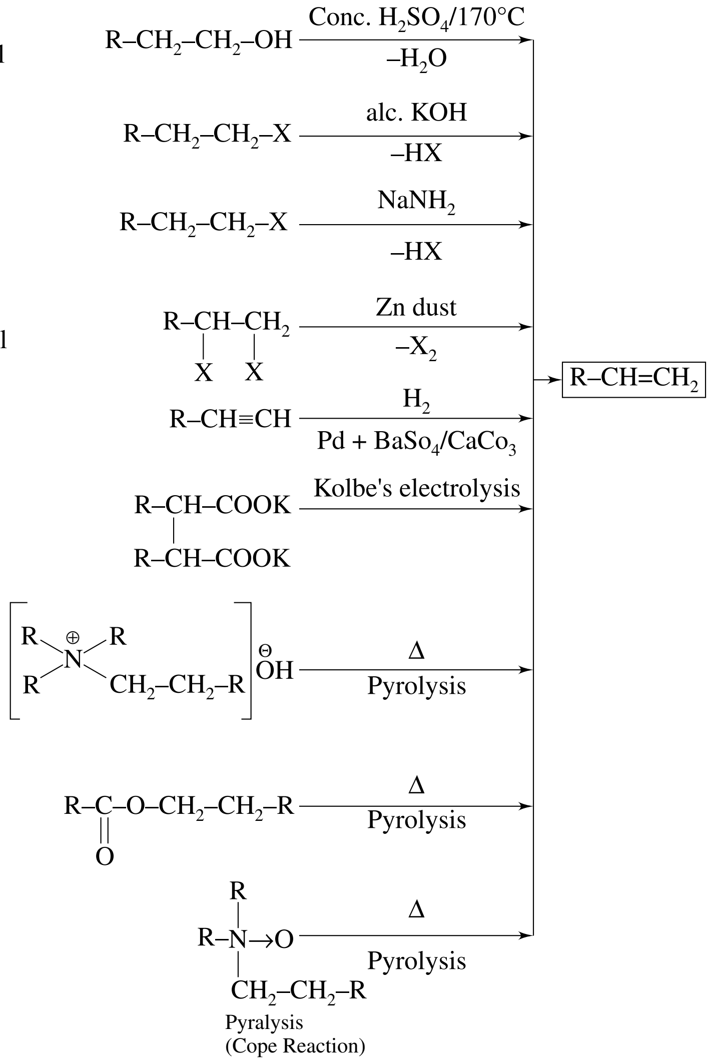
Profile 2: Either alkene or reagent or both unsymmetrical

Alkene	Reagent	Major addition product
Cis	*Syn*	Erythro
Cis	*Anti*	Threo
Trans	*Syn*	Threo
Trans	*Anti*	Erythro

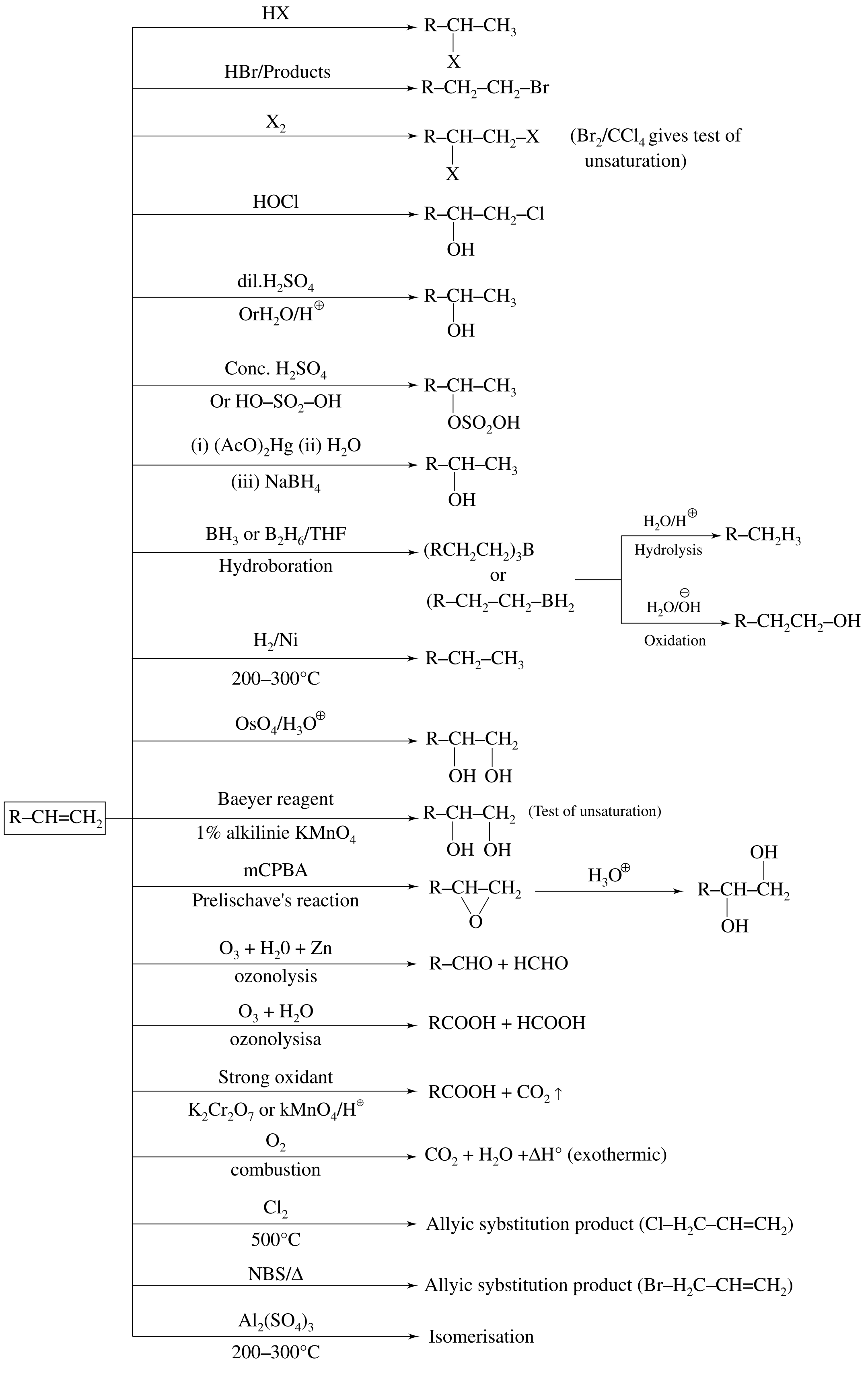
Note: From left to right → Major addition product

From right to left → Major β-elimination product

METHOD OF PREPARATION

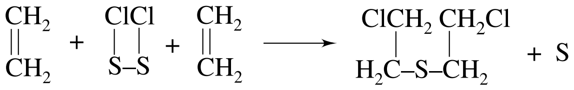


CHEMICAL PROPERTIES OF ALKENES



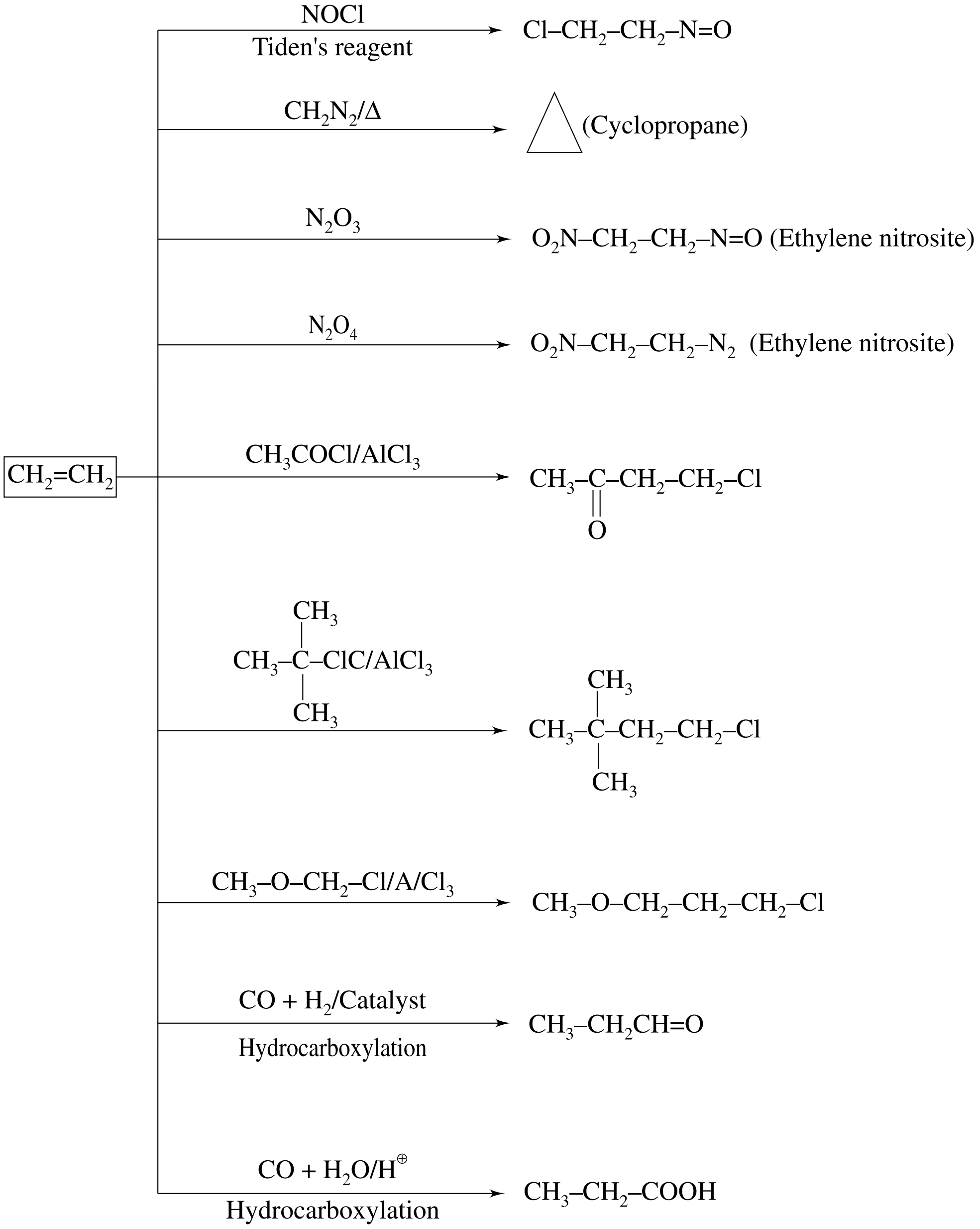
SPECIAL POINTS:

- Ethene is used in the artificial ripening of fruits
- Water solution of sodium or potassium salt of succinic acid on electrolysis gives ethane at anode
- Ethene reacts with sulphur monochloride (S_2Cl_2) to form poisonous mustard gas (β, β-dichloro diethyl sulphide), gas is used a war gas (Used in the World War I)



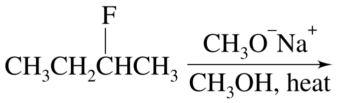
$$\begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} + \begin{matrix}Cl\;Cl\\ |\;\;\;|\\ S{-}S\end{matrix} + \begin{matrix}CH_2\\ \|\\ CH_2\end{matrix} \longrightarrow \begin{matrix}ClCH_2\;CH_2Cl\\ |\qquad\;\;|\\ H_2C{-}S{-}CH_2\end{matrix} + S$$

- Some other reactions of ethene are:



SOLVED EXAMPLE

1. In the reaction



$$CH_3CH_2\overset{\overset{F}{|}}{C}HCH_3 \xrightarrow[CH_3OH,\ heat]{CH_3O^-Na^+}$$

the major product formed is

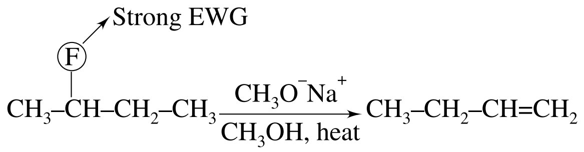
(1) $CH_3CH_2CH(OCH_3)CH_3$

(2) $CH_3CH=CHCH_3$

(3) $CH_3CH_2CH=CH_2$

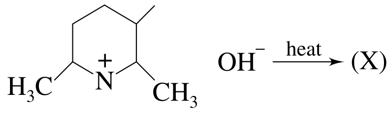
(4) $CH_3CH_2CH_2OCH_3$

Sol. **[3]**

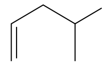


→ It is E_1cb reaction thus major product obtained by Hoffmann elimination hence1-butene (major)

2. In the reaction



the organic product (X) is

(1)


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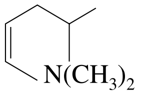

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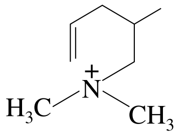

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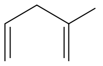
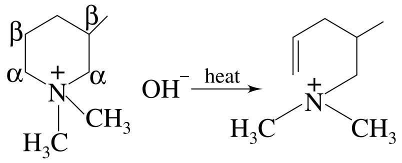


Sol. **[3]**

Pyrolysis of Quaternary ammonium hydroxide takes place according to Hoffman rule.



Hoffmann elimination

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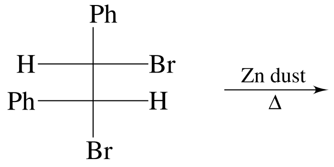
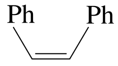


(1)


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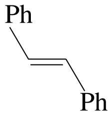

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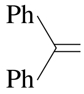

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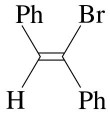
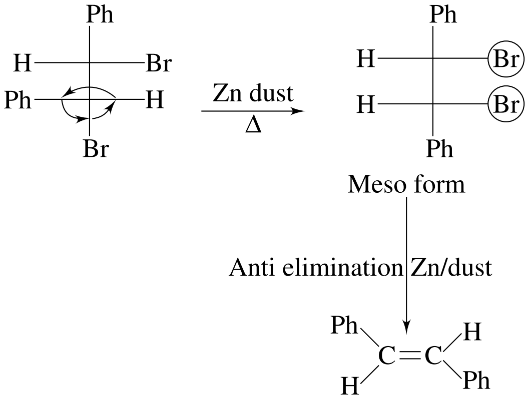


Sol. **[2]**

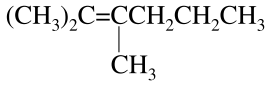


Concept form *Trans* form

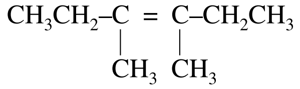
Meso upon *anti* elimination gives *trans* isomer as the major product (refer key concept).

4. A hydrocarbon C_8H_{16} on oxidation with a hot acidified solution of $KMnO_4$ forms 2-butanone and isobutyric acid. The hydrocarbon is

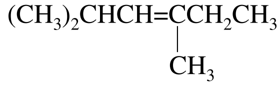
(1) $(CH_3)_2C=C(CH_2CH_3)_2$

(2)


$$(CH_3)_2C=\underset{\underset{CH_3}{|}}{C}CH_2CH_2CH_3$$

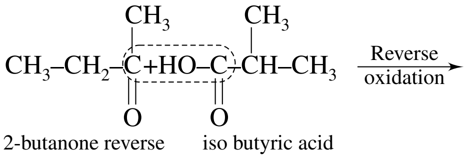
(3)


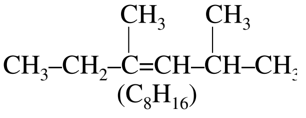
$$CH_3CH_2\text{–}\underset{\underset{CH_3}{|}}{C} = \underset{\underset{CH_3}{|}}{C}\text{–}CH_2CH_3$$

(4)


$$(CH_3)_2CHCH=\underset{\underset{CH_3}{|}}{C}CH_2CH_3$$

Sol. **[4]**





$$CH_3\text{–}CH_2\text{–}\overset{\overset{CH_3}{|}}{C}=CH\text{–}\overset{\overset{CH_3}{|}}{C}H\text{–}CH_3$$

(C_8H_{16})

5. An unsaturated hydrocarbon on reductive ozonolysis gives two molecules of propanedial $[CH_2(CHO)_2]$ and no other carbon compound. The hydrocarbon is

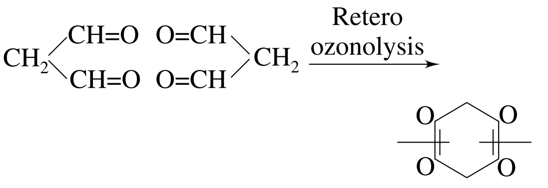
(1) hexa-2,4-diene

(2) cyclohexa-1,3-diene

(3) cyclohexa-1-4-diene

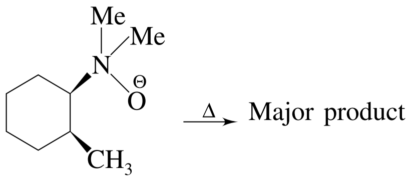
(4) 1,2-dimethylcyclobutene

Sol. **[3]**

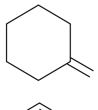


Cyclohexa-1,4-diene

6.



(1)



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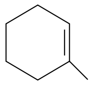
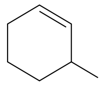


(3)

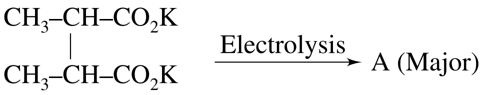


(4) None of these

Sol. **[3]**

It's Cope reaction. Hoffmann elimination takes place.

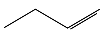
7.



$$\begin{array}{l} CH_3\text{–}CH\text{–}CO_2K \\ \quad\ | \\ CH_3\text{–}CH\text{–}CO_2K \end{array} \xrightarrow{\text{Electrolysis}} \text{A (Major)}$$

Major product (A) of the above reaction

(1)



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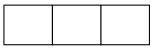
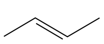
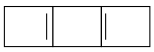


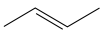
(3)



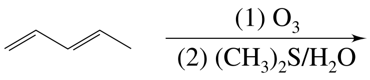
(4)



Sol. **[3]**

 (trans will be major) by Kolbe electrolysis

8.



Which of the following is not formed in the above reaction?

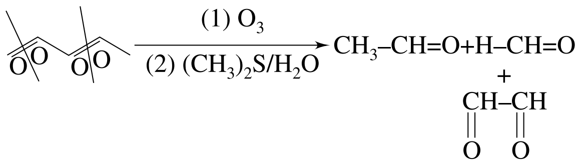
(1) HCHO

(2) CH_3CHO

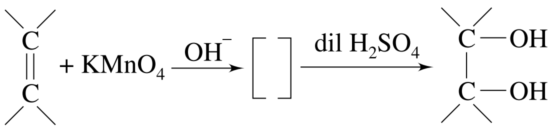
(3) Glyoxal

(4) CH_3CH_2CHO

Sol. **[4]**



9. In the oxidation of alkenes with a dilute $KMnO_4$ solution followed by acidification with dilute H_2SO_4 to give diol



The OH group comes from

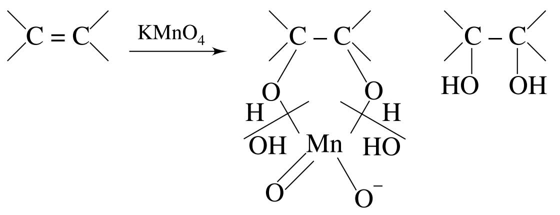
(1) NaOH

(2) H_2O

(3) $KMnO_4$

(4) H_2SO_4

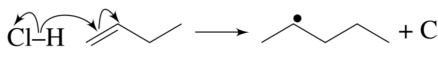
Sol. **[3]**



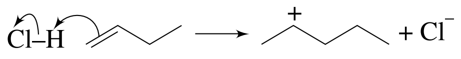
This mechanism indicates that OH group came from $KMnO_4$.

10. Which of the following most accurately describes the first step in the reaction of hydrogen chloride with 1-butene?

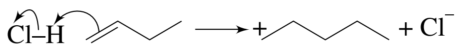
(1)



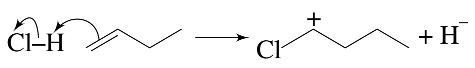
(2)



(3)



(4)



Sol. **[2]**

Attack on alkene by H–Cl takes place in such a way that most stable carbocation is formed as reaction intermediate.

11. In the addition reaction

$CH_3OCH = CHF + HCl \longrightarrow$

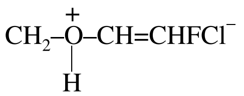
the major product obtained is

(1) CH_3OCH_2CHClF

(2) $CH_3OCH(Cl)CH_2F$

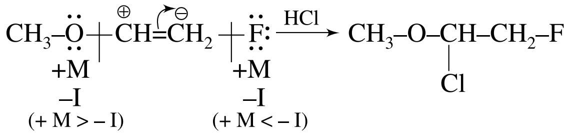
(3) $ClCH = CHF$

(4)

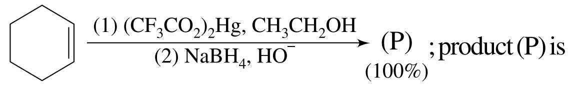


$$CH_2\text{–}\overset{+}{\underset{\underset{H}{|}}{O}}\text{–}CH{=}CHFCl^-$$

Sol. **[2]**

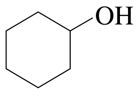


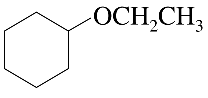
$$CH_3-\ddot{\underset{..}{O}}-\overset{\oplus}{C}H=\overset{\ominus}{C}H_2-\ddot{\underset{..}{F}}: \xrightarrow{HCl} CH_3-O-\underset{\displaystyle Cl}{CH}-CH_2-F$$

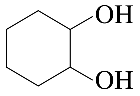
12. 

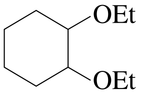
$\xrightarrow[\text{(2) } NaBH_4,\ HO^-]{\text{(1) } (CF_3CO_2)_2Hg,\ CH_3CH_2OH}$ (P) (100%) ; product (P) is

Cyclohexene

(1) 

(2) 

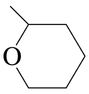
(3) 

(4) 

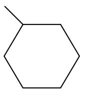
Sol. **[2]**

Alkoxymercuration–De-mercuration reaction according to Markownikoff rule.

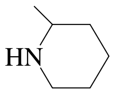
13. Rank the following in the increasing order of rate of reaction with HBr.



(P)



(Q)



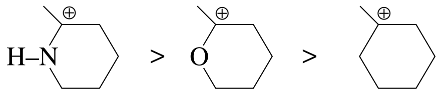
(R)

(1) R > P > Q (2) R > Q > P

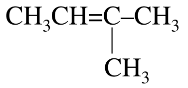
(3) P > R > S (4) P > S > R

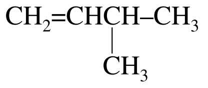
Sol. **[1]**

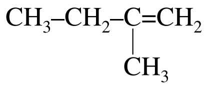
Formation of carbocation is the rate determining step.
Thus Rate of E.A.R. ∝ Stability of carbocation

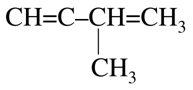


14. A hydrocarbon reacts with HI to give (X) which on reacting with aqueous KOH forms (Y). Oxidation of (Y) gives 3-methyl-2-butanone. The hydrocarbon is

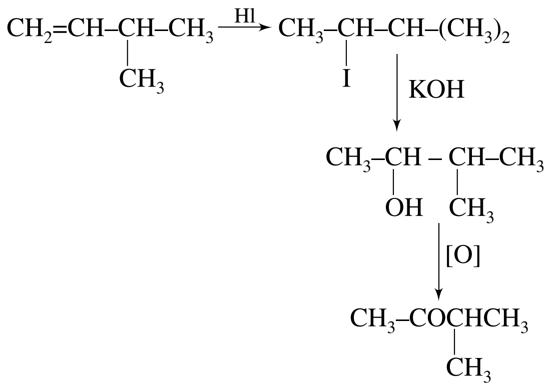
(1)  $CH_3CH=\underset{\displaystyle CH_3}{C}-CH_3$

(2)  $CH_2=CH\underset{\displaystyle CH_3}{CH}-CH_3$

(3)  $CH_3-CH_2-\underset{\displaystyle CH_3}{C}=CH_2$

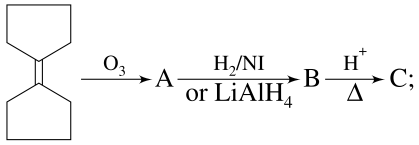
(4)  $CH=C-\underset{\displaystyle CH_3}{CH}=CH_3$

Sol. **[2]**

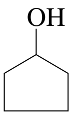


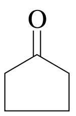
$$CH_2=CH-\underset{\displaystyle CH_3}{CH}-CH_3 \xrightarrow{HI} CH_3-\underset{\displaystyle I}{CH}-CH-(CH_3)_2 \xrightarrow{KOH} CH_3-\underset{\displaystyle OH}{CH}-\underset{\displaystyle CH_3}{CH}-CH_3 \xrightarrow{[O]} CH_3-CO\underset{\displaystyle CH_3}{CH}CH_3$$

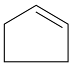
3-methyl-2-butanone

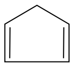
15. 

$\xrightarrow{O_3}$ A $\xrightarrow[\text{or } LiAlH_4]{H_2/NI}$ B $\xrightarrow[\Delta]{H^+}$ C; product (C) of the reaction is

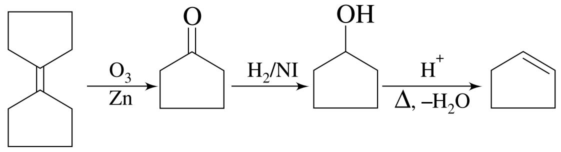
(1) 

(2) 

(3) 

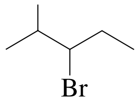
(4) 

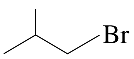
Sol. **[3]**

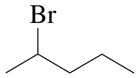


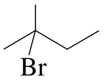
EXERCISE 1

1. Which alkyl bromide will yield only one alkene upon E_2 elimination?

(1) 

(2) 

(3) 

(4) 

2. Consider the following conversion

$C_6H_5CH_2CH_3 \xrightarrow{(P)}$ Product $\xrightarrow{(Q)} C_6H_5CH=CH_2$

Ethylbenzene Styrene

The reagents (P) and (Q) that should be employed are respectively

(1) $SOCl_2$ and H_2O

(2) SO_2Cl_2 and KOH/C_2H_5OH

(3) Cl_2, hv and $H_2O|KOH$

(4) $SOCl_2$ and KOH/C_2H_5OH

3. $\underset{[A]}{CH_3CH_2Cl} \xrightarrow[KOH]{alc.} [B] \xrightarrow{HCl} [C] \xrightarrow[KOH]{aq.} \underset{[D]}{C_3H_8O}$

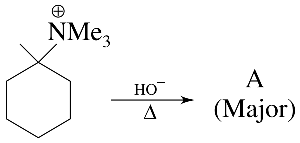
[A] will be

(1) 1-chloro propane

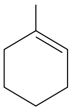
(2) 2-chloro propane

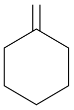
(3) Both of these

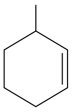
(4) None of these

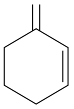
4. 

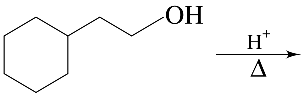
Major product is:

(1) 

(2) 

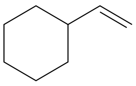
(3) 

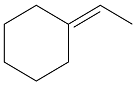
(4) 

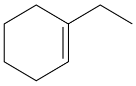
5. 

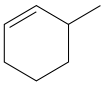
A is the major product,

So A is:

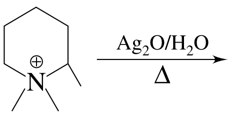
(1) 

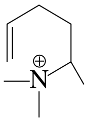
(2) 

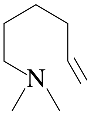
(3) 

(4) 

6. Which of the following is correct for the given reaction?



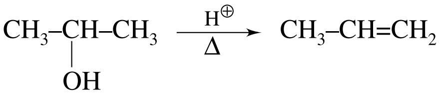
(1) Major product of reaction is 

(2) Major product of reaction is 

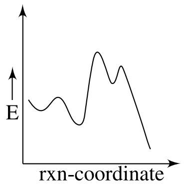
(3) Syatzeff alkene is the major product of the reaction

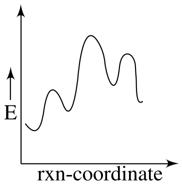
(4) Reaction is unimolecular

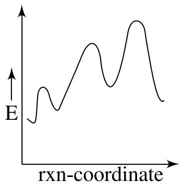
7. The energy profile of the given reaction

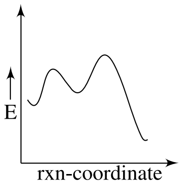


$CH_3\text{–}\underset{\displaystyle\overset{|}{OH}}{CH}\text{–}CH_3 \xrightarrow[\Delta]{H^{\oplus}} CH_3\text{–}CH{=}CH_2$

(1) 

(2) 

(3) 

(4) 

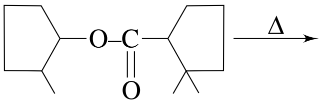
8. Which of the following will give the best yield of 2-pentene on reaction with C_2H_5ONa/C_2H_5OH?

(1) 2-Iodopentane

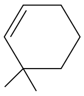
(2) 2-Bromopentane

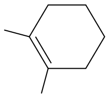
(3) 3-Iodopentane

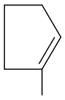
(4) All equally satisfactorily

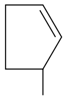
9. 

An alkene (major)

(1) 

(2) 

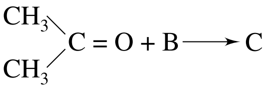
(3) 

(4) 

10. Consider the following reactions

$Ph_3P^+CH_3CH_2Br \longrightarrow A$

$A + C_2H_5ONa \longrightarrow B$

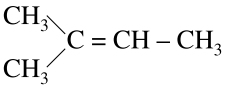


$(CH_3)_2C = O + B \longrightarrow C$

The final product is

(1) $Ph_3P^+CH_2CH_3Br^-$

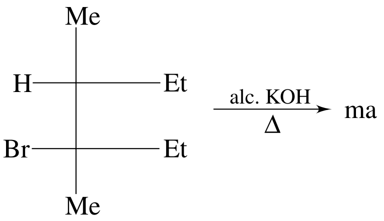
(2) $Ph_3P = CH - CH_3$

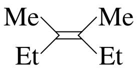
(3) 

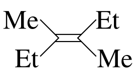
$(CH_3)_2C = CH - CH_3$

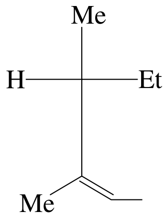
(4) 

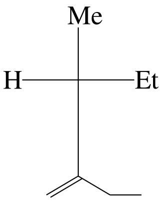
$(CH_3)_2CH - CH = CH_2$

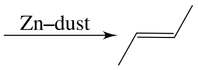
11. 

(1) 

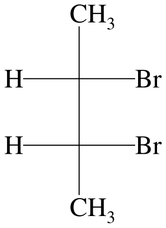
(2) 

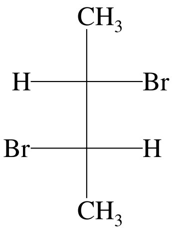
(3) 

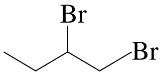
(4) 

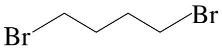
12. (p) 

Compound (p) is:

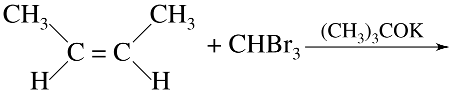
(1) 

(2) 

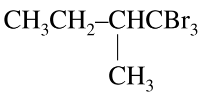
(3) 

(4) 

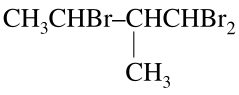
13. Consider the following reaction



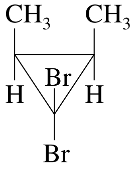
The product obtained in the reaction is

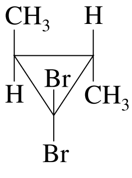
(1) 

$CH_3CH_2\text{–}\underset{\underset{CH_3}{|}}{C}HCBr_3$

(2) 

$CH_3CHBr\text{–}\underset{\underset{CH_3}{|}}{C}HCHBr_2$

(3) 

(4) 

14. Ethylene on reaction with Br_2 in methanol forms

(1) 1,2-dimethoxyethane

(2) 1-bromo-2-methoxyethane

(3) 1, 2-dibromoethane

(4) a mixture of (2) and (3)

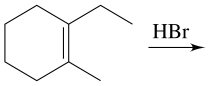
15. Cis-2, 3-Diphenyl-2-butene is allowed to react with H_2 in the presence of palladium catalyst. The major product will be

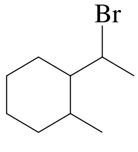
(1) meso-2, 3-diphenylbutane

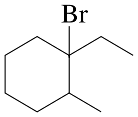
(2) (+)-2, 3-diphenylbutane

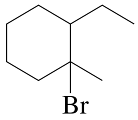
(3) (–)-2, 3-diphenylbutane

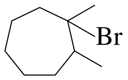
(4) (±)-2, 3-diphenylbutane

16.  Major product. Major product is:

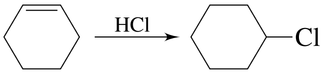
(1) 

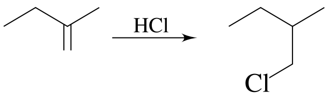
(2) 

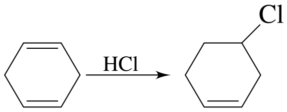
(3) 

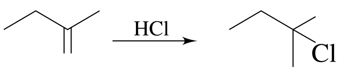
(4) 

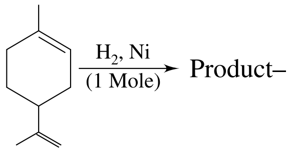
17. Which reaction will occur at the fastest rate?

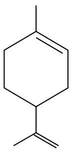
(1) 

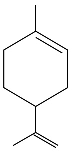
(2) 

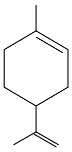
(3) 

(4) 

18. 

(1) 

(2) 

(3) 

(4) No reaction

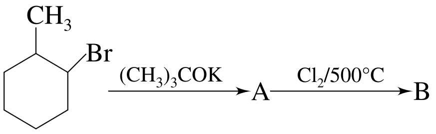
19. 3-Phenylpropene ($C_6H_5CH_2CH = CH_2$) when subjected to oxymercuration–demercuration process produces

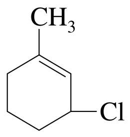
(1) $C_6H_5CH_2CHOCHCH_2OH$

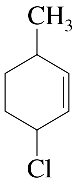
(2) $C_6H_5CH_2CH_2CH_2OH$

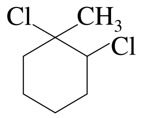
(3) $C_6H_5CHOHCH = CH_2$

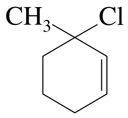
(4) $C_6H_5CH_2CHOHCH_3$

20. 

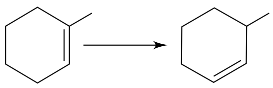
(1) 

(2) 

(3) 

(4) 

21. Which reagent is best to perform the following transformation?



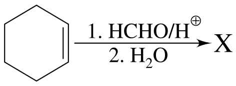
(1) HBr, NaOH, $C\overset{\ominus}{O}K^{\oplus}$

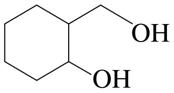
(2) HBr, R–O–O–R, hν, OH–(alc)

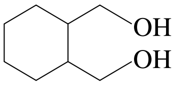
(3) BH_3.THF, NaOH – H_2O_2, ThO_2

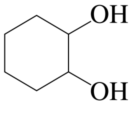
(4) Br_2, NaOH

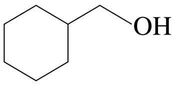
22. In the given reaction



(1) 

(2) 

(3) 

(4) 

23. The major product in the reaction

$CH_2 = CHCl + HOCl \longrightarrow$

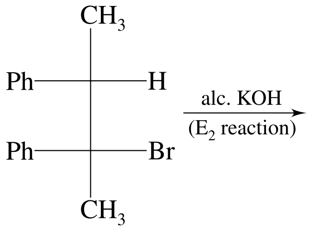
is

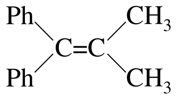
(1) $HOCH_2–CHCl_2$

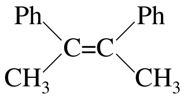
(2) $CH_2Cl–CH(Cl)OH$

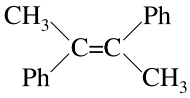
(3) CH_2ClCHO

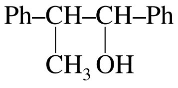
(4) $ClOCH_2–CH_2Cl$

24.  Major product of the reaction is:

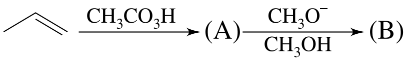
(1) 

(2) 

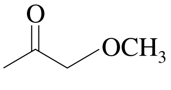
(3) 

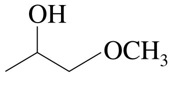
(4) 
$\underset{CH_3}{\underset{|}{Ph–CH}}–\underset{OH}{\underset{|}{CH}}–Ph$

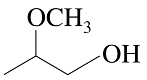
25. Consider the following sequence of reaction.

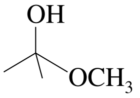


The product (B) is

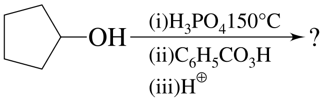
(1) 

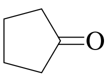
(2) 

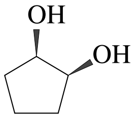
(3) 

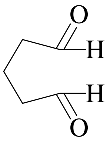
(4) 

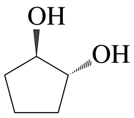
26. What will be the chief product from the following reaction sequence?

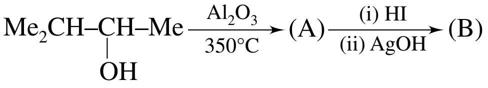


(1) 

(2) 

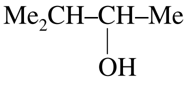
(3) 

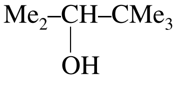
(4) 

27. 
$Me_2CH–\underset{OH}{\underset{|}{CH}}–Me \xrightarrow[350°C]{Al_2O_3} (A) \xrightarrow[(ii)\ AgOH]{(i)\ HI} (B)$

Product (B) of above reaction:

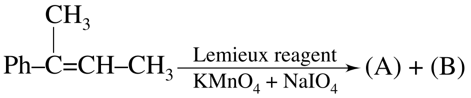
(1) $Me_2C(OH)CH_2Me$

(2) 
$Me_2CH–\underset{OH}{\underset{|}{CH}}–Me$

(3) 
$Me_2–\underset{OH}{\underset{|}{CH}}–CMe_3$

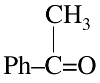
(4) $HO–CH_2–(CH_2)Me$

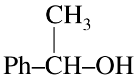
28.



$$\mathrm{Ph{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CH_3 \xrightarrow[KMnO_4\,+\,NaIO_4]{Lemieux\ reagent} (A) + (B)}$$

Which of the following compounds are (A) and (B) in this order?

(I)  $\mathrm{Ph{-}\overset{CH_3}{\overset{|}{C}}{=}O}$ (II) $CH_3CH{=}O$

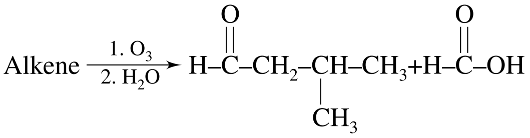
(III) $CH_3{-}COOH$ (IV)  $\mathrm{Ph{-}\overset{CH_3}{\overset{|}{C}H}{-}OH}$

(V) CH_3CH_2OH (VI) PhCOOH

(1) I, II (2) I, III

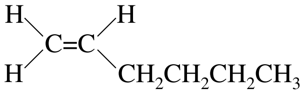
(3) III, VI (4) IV, V

29. Which alkene will undergo the following reaction?

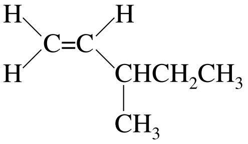


$$\mathrm{Alkene \xrightarrow[2.\ H_2O]{1.\ O_3} H{-}\overset{O}{\overset{\|}{C}}{-}CH_2{-}\underset{CH_3}{\underset{|}{C}H}{-}CH_3 + H{-}\overset{O}{\overset{\|}{C}}{-}OH}$$

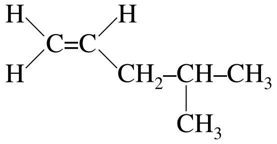
(1)



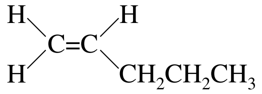
(2)



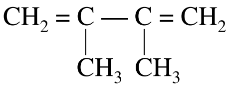
(3)



(4)



30. One mole of a hydrocarbon on ozonolysis yields one mole of glyoxal and two moles of formaldehyde. The hydrocarbon is

(1)  $\mathrm{CH_2 = \underset{CH_3}{\underset{|}{C}} — \underset{CH_3}{\underset{|}{C}} = CH_2}$

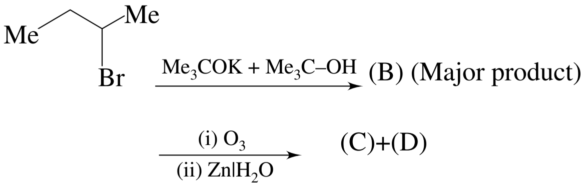
(2) $CH_2 = CH - CH = CH_2$

(3) $CH_2 = CH - CH_2 - CH = CH_2$

(4) $CH_3CH = C = CH_2$

EXERCISE 2

1.



The products (C) and (D) are:

(1) Methanal + Propanal

(2) Propanoic acid + CO_2

(3) 2 mol ethanoic acid

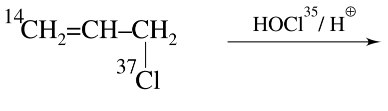
(4) 2 mol ethanal

2. The racemic-2-3-dibromopentane on reaction with KI in acetone gives:

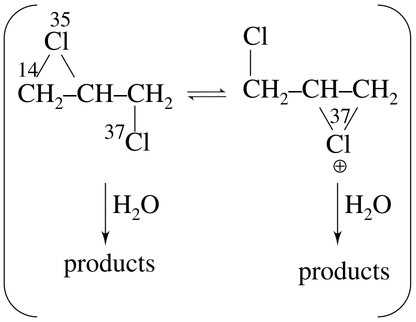
(1) *E*-Pent-2-ene (2) *Z*-Pent-2-ene

(3) Both (1) and (2) (4) None of these

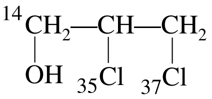
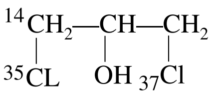
3. Observe the following reaction

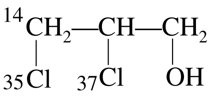
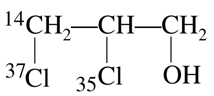


$$\mathrm{^{14}CH_2{=}CH{-}\underset{^{37}Cl}{\underset{|}{C}H_2} \xrightarrow{HOCl^{35}/\,H^{\oplus}}}$$

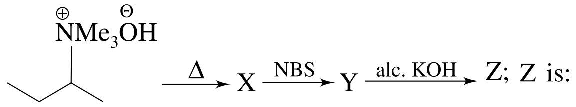


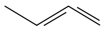
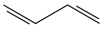
Which of the following cannot be the product?

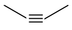
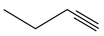
(1)  $\mathrm{\underset{OH}{\underset{|}{^{14}CH_2}}{—}\underset{_{35}Cl}{\underset{|}{CH}}{—}\underset{_{37}Cl}{\underset{|}{CH_2}}}$ (2)  $\mathrm{\underset{^{35}CL}{\underset{|}{^{14}CH_2}}{—}\underset{OH}{\underset{|}{CH}}{—}\underset{_{37}Cl}{\underset{|}{CH_2}}}$

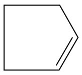
(3)  $\mathrm{\underset{_{35}Cl}{\underset{|}{^{14}CH_2}}{—}\underset{_{37}Cl}{\underset{|}{CH}}{—}\underset{OH}{\underset{|}{CH_2}}}$ (4)  $\mathrm{\underset{^{37}Cl}{\underset{|}{^{14}CH_2}}{—}\underset{_{35}Cl}{\underset{|}{CH}}{—}\underset{OH}{\underset{|}{CH_2}}}$

4.

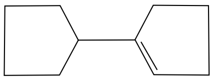
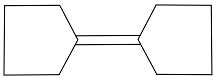


(1)  (2) 

(3)  (4) 

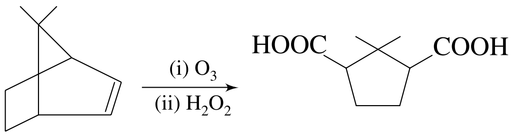
5.  $\xrightarrow{\text{Conc. } H_2SO_4}$ (B) Product (B) is:

(A)

(1)  (2) 

(3) Both (1) and (2) (4) None of these

6. Consider the following ozonolysis reaction



The correct statement about the above product formed is:

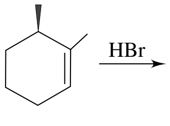
(1) it is a racemic mixture

(2) a pure enantiomer

(3) it is meso form of isomer

(4) it has a pseudochiral carbon

7. The products(s) of the following reaction can best be described as:

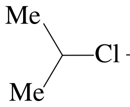


(1) A racemic mixture

(2) A single enantiomer

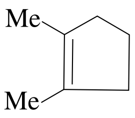
(3) A pair of diastereomers

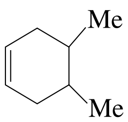
(4) An achiral molecule

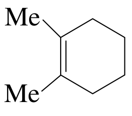
8.  $\xrightarrow{\text{Na+ether}}$ (B) $\xrightarrow[Cl_2+hv]{\text{2 mol}}$

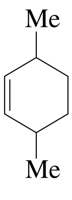
(C) $\xrightarrow[\text{Alc. KOH}]{\text{2 mol}}$ (D) $\xrightarrow[\Delta]{CH_2=CH_2}$ (E)

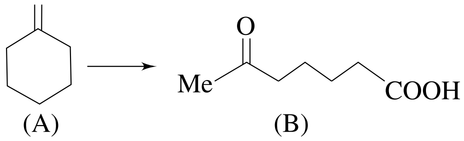
The final product (E) is:

(1) 

(2) 

(3) 

(4) 

9. 

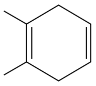
The above conversion can be carried out by which process?

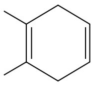
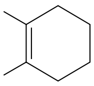
(1) **i.** HBr + Peroxide
  ii. Me_3CO, Δ
  iii. O_3/H_2O

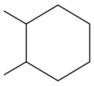
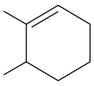
(2) **i.** HBr
  ii. C_2H_5O, Δ
  iii. O_3/H_2O

(3) **i.** HI
  ii. MeO, Δ
  iii. O_3/Zn-acid

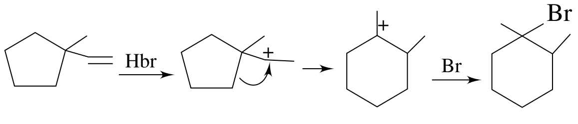
(4) **i.** HCl + Peroxide
  ii. Aq. KOH
  iii. $O_3/Zn\text{-}H_2O$

10.  $\xrightarrow[\text{1 mole}]{H_2/Hi}$ Major Product is:

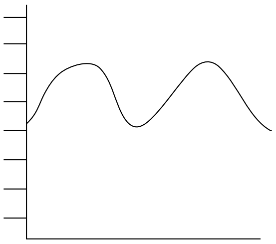
(1)  (2) 

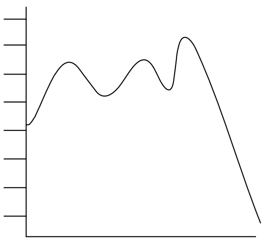
(3)  (4) 

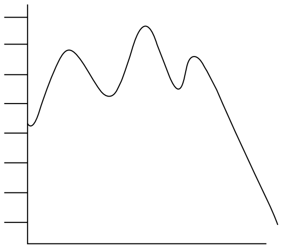
11. Consider the following rearrangement reaction:

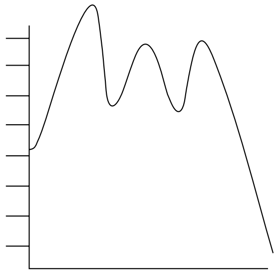


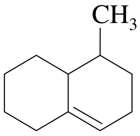
Which of the following reaction coordinates best represents the overall reaction? (Note: the units are arbitrary)

(1) 

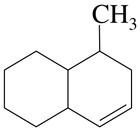
(2) 

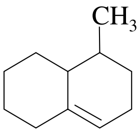
(3) 

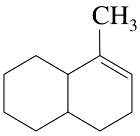
(4) 

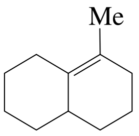
12. 

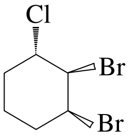
$\xrightarrow[2.\ H_2O_2/OH^{\ominus}]{1.\ BH_3/THF}$ (A) 5 $\xrightarrow[\Delta]{H^{\oplus}}$ (B) The product (B) is:

(1) 

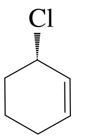
(2) 

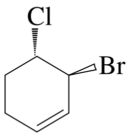
(3) 

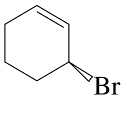
(4) 

13. 

$\xrightarrow{Zn,\ \Delta}$ Major product:

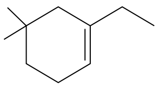
(1) 

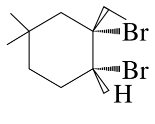
(2) 

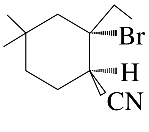
(3) 

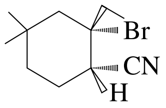
(4) None of these

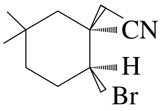
14. Give the major product of the following reaction

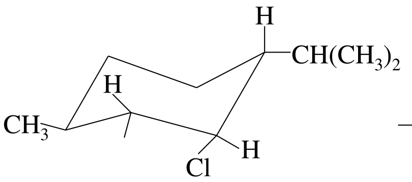

$\xrightarrow{BrCN}$

(1) 

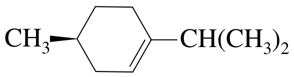
(2) 

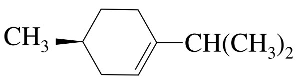
(3) 

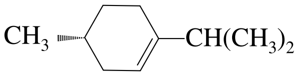
(4) 

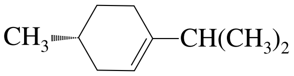
15. 

$\xrightarrow{EtO^{\ominus}}$ (A) + (B)

(I) 

(II) 

(III) 

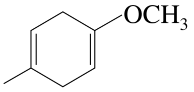
(IV) 

Correct code of Answer is

(1) A → I, B → II (2) A → I, B → III

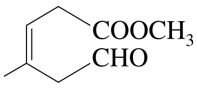
(3) A → III, B → IV (4) A → III, B → II

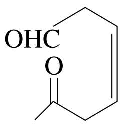
16. In the reaction

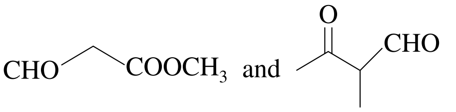


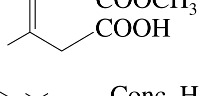
$\xrightarrow[1\ Mole]{O_3}$ I $\xrightarrow{Zn/H_2O}$ II

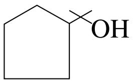
The final product (II) formed in major amount is

(1) 

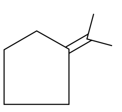
(2) 

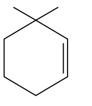
(3) 

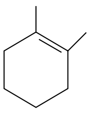
(4) 

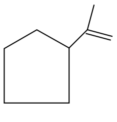
17. 

$\xrightarrow[\Delta]{Conc.\ H_2SO_4}$

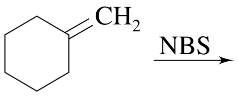
(1) 

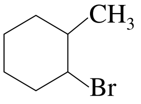
(2) 

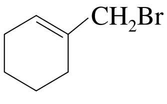
(3) 

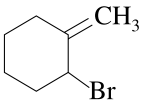
(4) 

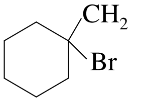
18. The major product formed in the following reaction is:



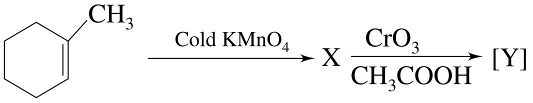
(1) 

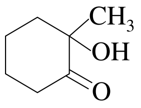
(2) 

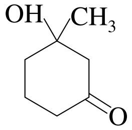
(3) 

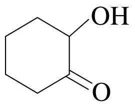
(4) 

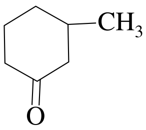
19. What is the compound 'Y' in the following sequence of reactions?

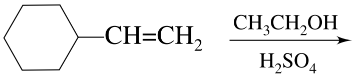


(1) 

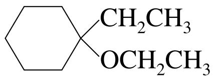
(2) 

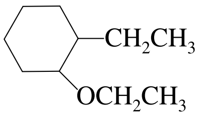
(3) 

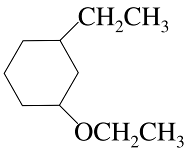
(4) 

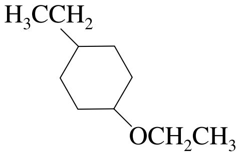
20. 

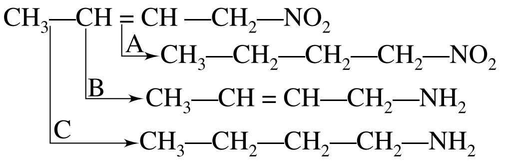
Identify the product

(1) 

(2) 

(3) 

(4) 

21. 

$CH_3—CH=CH—CH_2—NO_2$

$\xrightarrow{A} CH_3—CH_2—CH_2—CH_2—NO_2$

$\xrightarrow{B} CH_3—CH=CH—CH_2—NH_2$

$\xrightarrow{C} CH_3—CH_2—CH_2—CH_2—NH_2$

A, B and C are respectively–

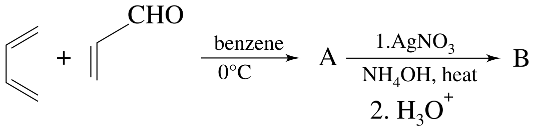
(1) A = Raney Ni, H_2, B = Sn/HCl, C = NH_2-NH_2, H_2O_2

(2) A = NH_2-NH_2, H_2O_2, B = Sn/HCl, C = Raney Ni, H_2

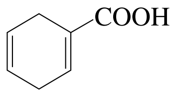
(3) A = Sn/HCl, B = Raney Ni, H_2 , C = NH_2-NH_2, H_2O_2

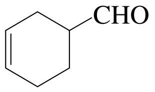
(4) A = NH_2-NH_2, H_2O_2, B = Raney Ni, C = Sn/HCl

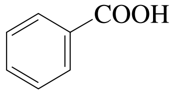
22. Consider the following sequence of reaction

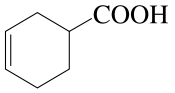


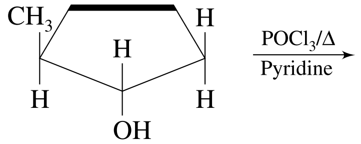
The structure of the end product (B) is:

(1) 

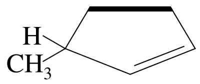
(2) 

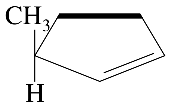
(3) 

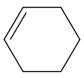
(4) 

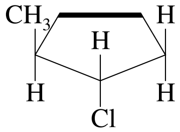
23. 

Major product of the reaction is:

(1) 

(2) 

(3) 

(4) 

24. In the reaction

Cis-$CH_2=CH(CH_2)_2CH=CH–COOCH_3$ + Br_2(1 mole) $\xrightarrow{CCl_4}$

The major product obtained is:

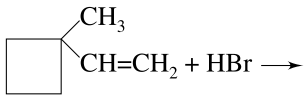
(1) meso-$CH_2=CH(CH_2)_2CHBrCHBrCOOCH_3$

(2) (±) cis-$CH_2BrCHBr(CH_2)_2CH=CHCOOCH_3$

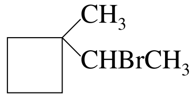
(3) (±)-$CH_2=CH(CH_2)_2CHBrCHBrCOOCH_3$

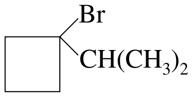
(4) (±)-cis-$CH_2=CH–\underset{Br}{C}H–\underset{Br}{C}H–CH=CHCOOCH_3$

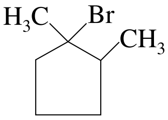
25. In the reaction

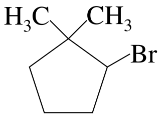


the major product formed is:

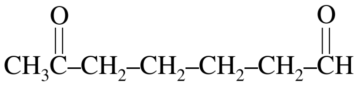
(1) 

(2) 

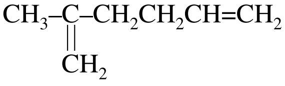
(3) 

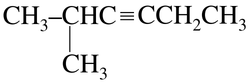
(4) 

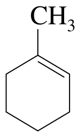
26. On catalytic hydrogenation, an organic compound $X(C_7H_{12})$ absorbs 1 mol of hydrogen and yields a compound C_7H_{14}. On ozonolysis and subsequent treatment with Zn/H_2O, the compound

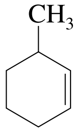

$CH_3\overset{\overset{O}{\|}}{C}-CH_2-CH_2-CH_2-CH_2-\overset{\overset{O}{\|}}{C}H$

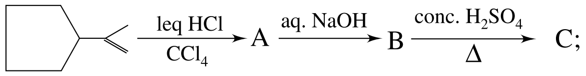
is obtained. The structure of X is

(1) 
$CH_3-\underset{\underset{CH_2}{\|}}{C}-CH_2CH_2CH=CH_2$

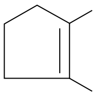
(2) 
$CH_3-\underset{\underset{CH_3}{|}}{C}HC\equiv CCH_2CH_3$

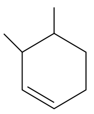
(3) 

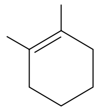
(4) 

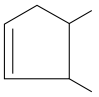
27. 

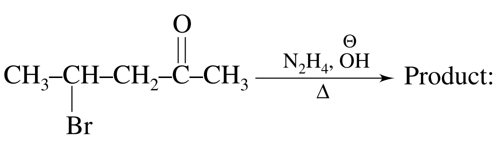
C is:

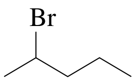
(1) 

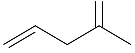
(2) 

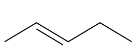
(3) 

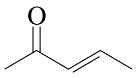
(4) 

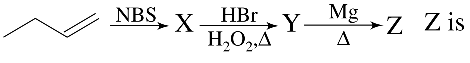
28. 
$CH_3-\underset{\underset{Br}{|}}{C}H-CH_2-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\Delta]{N_2H_4,\ \overset{\ominus}{O}H}$ Product:

(1) 

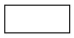
(2) 

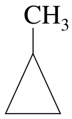
(3) 

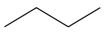
(4) 

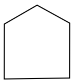
29. 

Z is

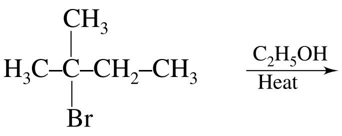
(1) 

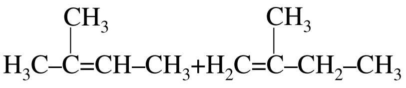
(2) 

(3) 

(4) 

30. Consider the following reaction,


$H_3C-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-CH_2-CH_3 \xrightarrow[\text{Heat}]{C_2H_5OH}$


$H_3C-\overset{\overset{CH_3}{|}}{C}=CH-CH_3+H_2C=\overset{\overset{CH_3}{|}}{C}-CH_2-CH_3$

(I) (II)

The correct statement concerning I and II is

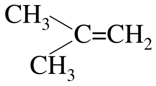
(1) I is the major product as it is formed at faster rate than II

(2) II is the major product as it is formed at faster rate than I

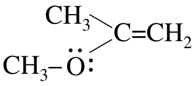
(3) I is major product as it is more stable than II

(4) I and II are formed in comparable amounts

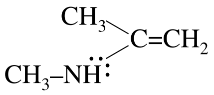
31. Arrange the following reactions in decreasing order of electrophilic addition reaction towards HCl:



(P)



(Q)

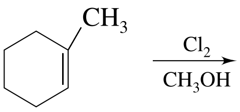


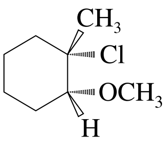
(R)

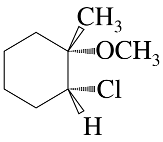
(1) P > Q > R (2) Q > R > P

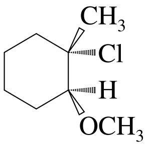
(3) R > Q > P (4) P = Q = R

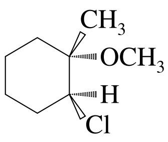
32. Which of the following is major product of reaction shown below?



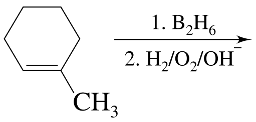
(1) 

(2) 

(3) 

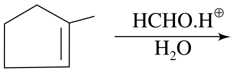
(4) 

33. 1-Methylcyclohexene is allowed to react with B_2H_6. The product is hen treated with H_2O_2 and NaOH. The reaction is

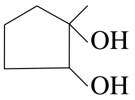


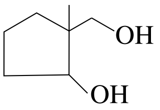
The product formed is

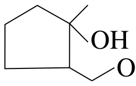
(1) 1-methylcyclohexanol
(2) 2-methylcyclohexanol
(3) (±) trans-2-methylcyclohexanol
(4) (±) cis-2-methylcyclohexanol

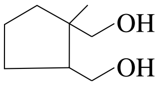
34. 

Major product:

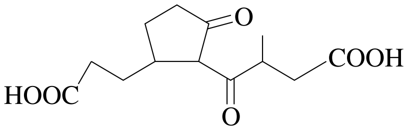
(1) 

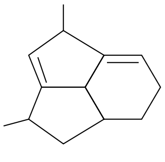
(2) 

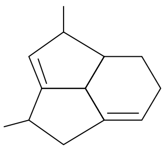
(3) 

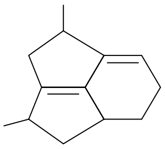
(4) 

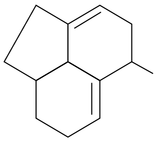
35. Which molecule will give the following dicarboxylic acid upon treatment with acidic solution of $KMnO_4$?



(1) 

(2) 

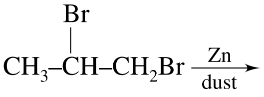
(3) 

(4) 

EXERCISE 3

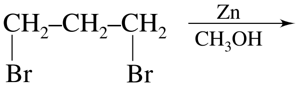
One and More Than One Option Correct Type Questions

1. Which of the following reactions result in formation of an alkene?

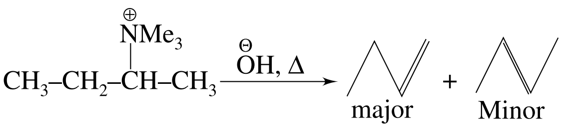
(1) 
$\overset{Br}{CH_3–CH}–CH_2Br \xrightarrow[\text{dust}]{Zn}$

(2) $CH_3–CH_2–CHBr_2 \xrightarrow[Na/\Delta]{\text{Ether}}$

(3) $CH_3–CH_2–CHBr_2 \xrightarrow[\text{(ii) } NaNH_2/\Delta]{\text{(i) Alc. KOH}}$

(4) 
$\underset{Br}{CH_2}–CH_2–\underset{Br}{CH_2} \xrightarrow[CH_3OH]{Zn}$

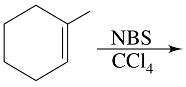
2. For the reaction

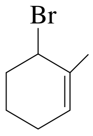


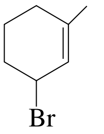
choose the correct statements:

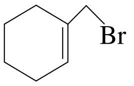
(1) The reaction is E_2
(2) Hoffmann product is major product
(3) Transition state has carbanion like character
(4) Transition state has carbocation like character

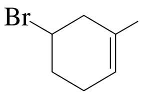
3. Which of the following are formed in the given reaction?



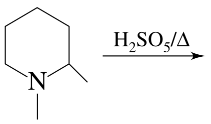
(1) 

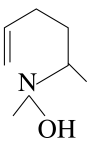
(2) 

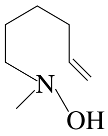
(3) 

(4) 

4. Which of the following statements are correct for the given reaction?

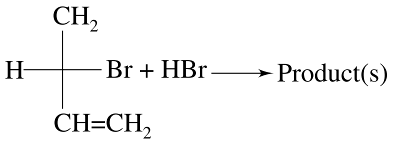


(1) Major product of reaction is 

(2) Major product of reaction is 

(3) Syatzeff alkene is major product of reaction
(4) Reaction is intramolecular elimination

5. Consider the following addition reaction on a pure enantiomer of the shown bromoalkene.



What is/are true regarding products of the above reaction?

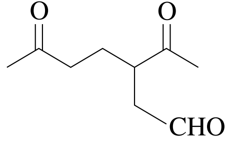
(1) Four stereoisomers of products are formed

(2) A pair of enantiomers and a meso-dibromide is formed

(3) Only a pair of diastereomers is formed

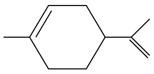
(4) One of the products is meso-dibromide

6. A hydrocarbon X ($C_{10}H_{16}$) upon catalytic hydrogenation gives 4-methyl-1-isopropyl cyclohexane. Also X upon ozonisation followed by hydrolysis in the presence of Zn gives CH_2O and



The correct statement(s) concerning X is/are

(1) Structure of X is

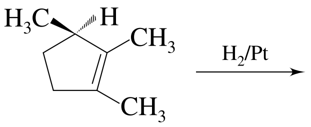


(2) X has two chiral carbons

(3) X has one chiral carbon

(4) With excess of HCl, X gives racemic dichloride

7. The compound given below is chiral. What would be the outcome of catalytic hydrogenation of a pure enantiomer of this compound?



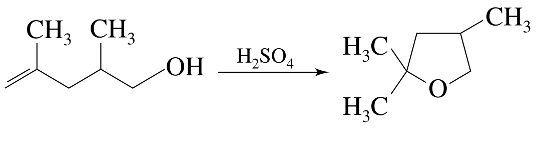
(1) A pair of enantiomers in equal amount would be produced

(2) A pair of diastereomers in unequal amounts would be produced

(3) A pair of enantiomers in unequal amounts would be produced

(4) A pair of diastereomers in equal amount would be produced

8. Consider the following reaction



Which of the following is/are true statement/s?

(1) Reaction initiates by protonation of –OH followed by formation of carbocation

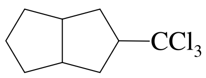
(2) Reaction is initiated at C=C forming a tertiary carbocation

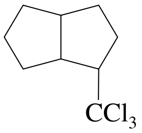
(3) Here intramolecular reaction is favoured by entropy of reaction

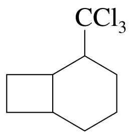
(4) The same reaction can also be accomplished using NaOH as catalyst

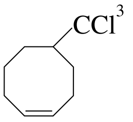
9. What products are expected in the following reaction?

1.0 equivalent

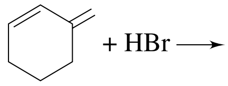
(1) 

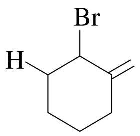
(2) 

(3) 

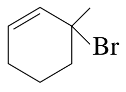
(4) 

10. Predict the product(s) in the following reaction

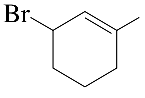


(1) 

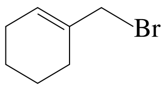
Kinetic

(2) 

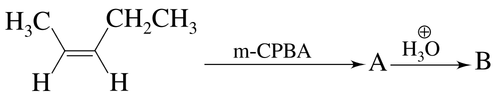
Kinetic

(3) 

Thermodynamic

(4) 

Thermodynamic

11. 

Choose the correct statements regarding above reaction

(1) Product A is optically active

(2) The conversion of alkene to product B is a stereospecific reaction

(3) Product B has achiral molecules

(4) Formation of 'A' is *syn* addition reaction

Assertion and Reason Type Question

(1) If both (A) and (R) are correct and (R) is the correct explanation for (A)

(2) If both (A) and (R) are correct and (R) is not the correct explanation

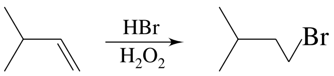
(3) If (A) is correct and (R) is incorrect

(4) If (A) is incorrect and (R) is correct

12. **Statement-I:** cis-2-butene with cold, dilute, alkaline $KMnO_4$ gives meso-2,3-butanediol.

Statement-II: In alkaline solution, under cold condition, $KMnO_4$ acts as a mild oxidising agent.

13. **Statement-1:**



Statement-2: Reaction completes via free radical mechanism and initially ·Br attach with alkene to form more stable free radical.

14. **Statement-I:** 2-bromobutane with $(CH_3)_3COK$ in tertiary butanol gives 1-butene as major product.

Statement-II: Very strong base $(CH_3)_3COK$ in tertiary butanol brings about E2 elimination reaction.

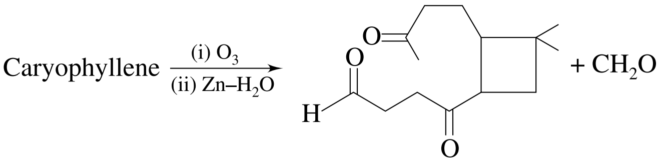
15. **Statement-I:** In reductive ozonolysis, dimethylsulphide is better reducing reagent than Zn-H_2O.

Statement-II: $(CH_3)_2S$ bring about homogeneous catalysis

Comprehension Type Question

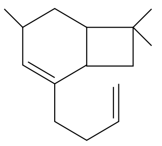
Comprehension (Q. 16 and 17)

Caryophyllene ($C_{15}H_{24}$) contains a six membered ring and on ozonolysis gives the following product.

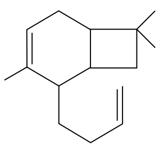


16. The structure of caryophyllene is

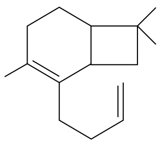
(1)



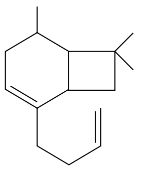
(2)



(3)

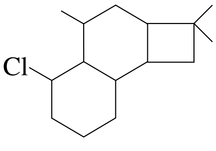


(4)

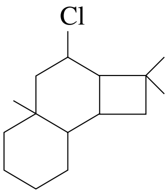


17. If caryophyllene is treated with 1.0 mole of HCl, a ring closure reaction takes place to form monochloride. What is the most likely product of this reaction?

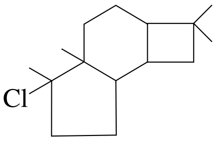
(1)



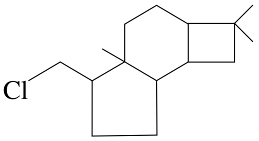
(2)



(3)



(4)

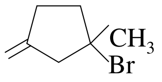


Comprehension (Q. 18–20)

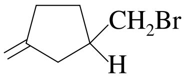
An organic compound X ($C_7H_{11}Br$) shows optical isomerism as well as decolourises brown colour of bromine water solution. X on treatment with HBr in the absence of a peroxide forms a pair of diastereomers, both of them are optically active. Also, X with C_2H_5ONa in C_2H_5OH gives a single product Y (C_7H_{10}). Y on treatment with ozone followed by reduction with $(CH_3)_2S$ given 1, 3,-cyclopentanedione as one product.

18. The structure of compound X is

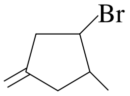
(1)



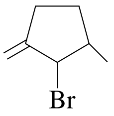
(2)



(3)



(4)



19. The correct statement regarding product(s) formed by the reaction of X with HBr in the presence of H_2O_2 is

(1) Only a pair of enantiomers is formed

(2) Only a pair of diastereomers is formed

(3) Two pairs of enantiomers are formed

(4) A meso product is formed

20. The correct statement concerning product(s) formed when Y is treated with excess of HCl is

(1) A pair of enantiomers is formed in equal amount

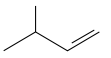
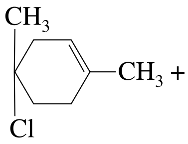
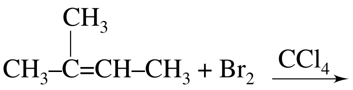
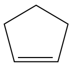
(2) Two pairs of diastereomers are formed

(3) Only a meso-dichloride is formed

(4) Only one pair of diastereomers is formed

Column Matching Type Question

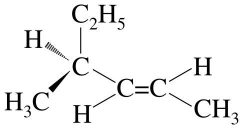
21. Consider the reaction in Column-I and match with the properties of products form Column-II

	Column-I		**Column-II**
(1)	 + HCl ⟶	(P)	Racemic mixture of products
(2)	 + HCl ⟶	(Q)	Pair of stereoisomers
(3)	 $CH_3-\overset{CH_3}{\overset{\vert}{C}}=CH-CH_3 + Br_2 \xrightarrow{CCl_4}$	(R)	Involve a 2° carbocation
(4)	 $+ Cl_2 - H_2O \longrightarrow$	(S)	Involve a 3° carbocation

Codes

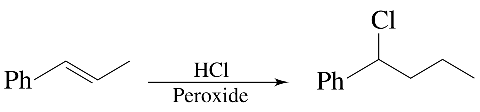
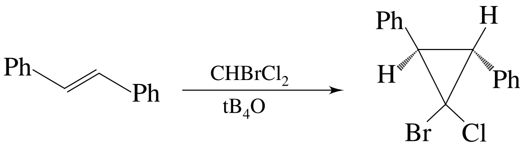
	A	**B**	**C**	**D**
(1)	P, Q, R, S	Q, S	P, Q	P, Q
(2)	S	R, S	Q	P, Q
(3)	S	R, S	P, Q, R	Q, R
(4)	R, S	P, S	Q, S	P

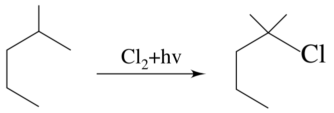
22. Match the alkenes in Column-I with the stereochemistry of addition product(s) obtained with Br_2/CCl_4 in presence of $FeBr_3$ in Column-II.

	Column-I		**Column-II**
(A)	*cis*-2-butene	(P)	Racemic mixture of products
(B)	*trans*-2-butene	(Q)	Meso product
(C)	*cis*-2-pentene	(R)	Meso cyclic bromonium ion
(D)		(S)	Pair of diastereomers of product

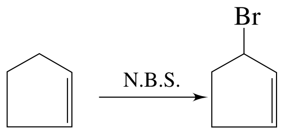
	A	**B**	**C**	**D**
(1)	P	Q, R	R	S
(2)	P, R	Q	P	S
(3)	S	R	P	Q, S
(4)	R, S	S	Q, R	P

23.

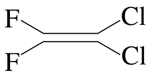
	Column-I **(Reactant, reagent, and product)**		**Column-II** **(Intermediate involved)**
(a)		(p)	Carbene
(b)		(q)	Free radical

(c) 

(r) Carbanion

(d) 

(s) Carbocation

(e) $F_3C–CHCl_2 \xrightarrow{\text{Et ONa + EtOH}}$ 

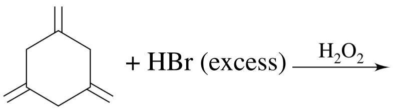
(1) a → s; b → p; c → q; d → q; e → r
(2) a → p; b → r; c → q; d → p; e → s
(3) a → p; b → s; c → r; d → p; e → q
(4) a → s; b → q; c → r; d → s; e → p

Single Digit Integer Type Question

24. If 3-bromo-4-methyl hexane is treated with ethanolic KOH solution, how many different alkenes would be formed?

25. If a racemic mixture of 3-methyl-1-pentene is treated with HCl, how many different chloropentane (important products only) would be formed?

26. Consider the following reaction

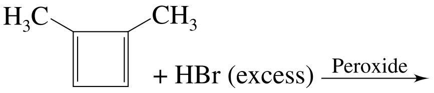


How many different products would be formed?

27. A mixture containing all the stereoisomers of 3, 4, 5-trimethyl cyclopentene is treated with O_3 followed by Zn-hydrolysis, how many different isomers of products would result?

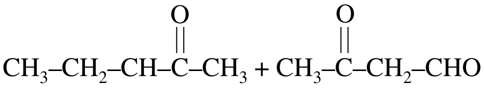
28. Cyclobutene when refluxed in presence of potassium metal, evolve hydrogen gas and an aromatic system is formed. How many pi-electrons are involved in the above formed aromatic system?

29. Consider the following reaction



How many different products (including stereoisomers) would be formed?

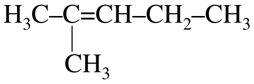
30. $\underset{X}{\text{Alkene(s)}} + O_3 \xrightarrow[H_2O]{Zn} CH_3–CHO +$



$$CH_3–CH_2–CH–\overset{\overset{O}{||}}{C}–CH_3 + CH_3–\overset{\overset{O}{||}}{C}–CH_2–CHO$$

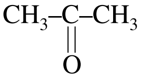
How many different isomers of alkene (X) can give the above reaction?

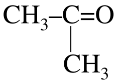
EXERCISE 4

1. The compound 

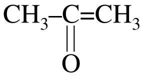
$$H_3C–\underset{\underset{CH_3}{|}}{C}=CH–CH_2–CH_3$$

$\xrightarrow{\text{Vigorous oxidation}}$ product, here product is **[AIEEE-2002]**

(1) CH_3COOH &  $CH_3–\underset{\underset{O}{||}}{C}–CH_3$

(2) $CH_3–CH_2–COOH$ &  $CH_3–\underset{\underset{CH_3}{|}}{C}=O$

(3) $CH_3–CH_2–COOH$ only

(4) HCOOH &  $CH_3–\underset{\underset{O}{||}}{C}=CH_3$

2. During dehydration of alcohols to alkenes by heating with conc. H_2SO_4 the initiation step is **[AIEEE-2003]**

(1) elimination of water
(2) formation of an ester
(3) protonation of alcohol molecule
(4) formation of carbocation

3. Which one of the following has the minimum boiling point? **[AIEEE-2004]**

(1) n-Butane (2) 1-Butyne
(3) 1-Butene (4) Isobutane

4. Reaction of one molecule of HBr with one molecule of 1, 3-butadiene at 40°C given predominantly **[AIEEE-2005]**

(1) 1-bromo-2-butene thermodynamically controlled conditions
(2) 3-bromobutene under kinetically controlled conditions
(3) 1-bromo-2-butene under kinetically controlled conditions
(4) 3-bromobutene thermodynamically controlled conditions

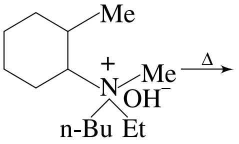
5. Acid catalysed hydration of alkenes except ethane leads to the formation of– **[AIEEE-2005]**

(1) secondary or tertiary alcohol
(2) primary alcohol
(3) mixture of secondary and tertiary alcohols
(4) mixture of primary and secondary alcohols

6. Elimination of bromine from 2-bromobutane results in the formation of **[AIEEE-2005]**

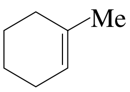
(1) predominantly 2-butene
(2) equimolar mixture of 1 and 2-butene
(3) predominantly 2-butyne
(4) predominantly1-butene

7.

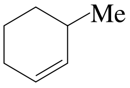


The alkene formed as a major product in the above elimination reaction is **[AIEEE-2006]**

(1) $CH_2 = CH_2$ (2)



(3)



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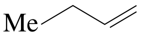


8. In the following sequence of reactions, the alkene affords the compound 'B'

$CH_3CH = CHCH_3 \xrightarrow{O_3} A \xrightarrow[Zn]{H_2O} B$. The compound B is **[AIEEE-2008]**

(1) CH_3COCH_3 (2) $CH_3CH_2COCH_3$
(3) CH_3CHO (4) CH_3CH_2CHO

9. Ozonolysis of an organic compound gives formaldehyde as one of the products. This confirms the presence of **[AIEEE-2011]**

(1) two ethylenic double bonds
(2) vinyl group
(3) an isopropyl group
(4) an acetylenic triple bond

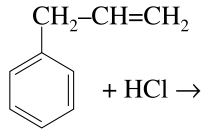
10. Ozonolysis of an organic compound 'A' produces acetone and propionaldehyde in equimolar mixture. Identify 'A' from the following compounds: **[AIEEE-2011]**

(1) 1-Pentene (2) 2-penetene
(3) 2-Methyl-2-pentene (4) 2-Methyl-1-pentene

11. 2-Hexyne gives trans-2-hexene on treatment with– **[AIEEE-2012]**

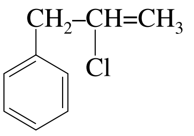
(1) Li/NH_3 (2) $Pd/BaSO_4$
(3) $LiAIH_4$ (4) Pt/H_2

12. Given

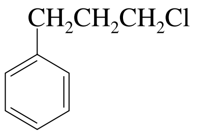


$+ HCl \rightarrow X$, X is **[JEE Main Online-2013]**

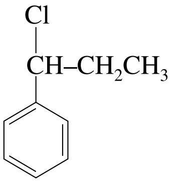
(1)



(2)



(3)



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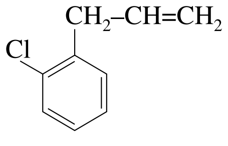


13. The addition of HI in the presence of peroxide catalyst does not follow anti Markovnikov's rule because **[JEE main Online-2013]**

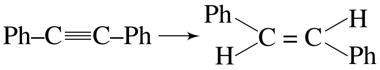
(1) HI is a strong reducing agent
(2) HI bond is too strong to be broken homolytically
(3) I atom combines with H atom so give back HI
(4) iodine atom is not reactive enough to add across a double bond

14. In the hydroboration–oxidation reaction of propene with diborane, H_2O_2 and NaOH, the organic compound formed is: **[JEE Main Online-2014]**

(1) CH_3CH_2OH (2) $CH_3CHOHCH_3$
(3) $CH_3CH_2CH_2OH$ (4) $(CH_3)_3COH$

15. The reagent needed for converting

[JEE Main Online-2014]



(1) Cat. Hydrogenation (2) H_2/Lindlar Cat.

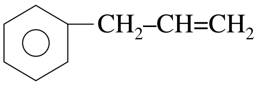
(3) Li/NH_3 (4) $LiAlH_4$

16. The gas liberated by the electrolysis of Dipotassium succinate solution is

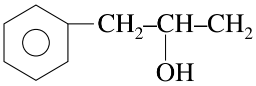
[JEE Main Online-2014]

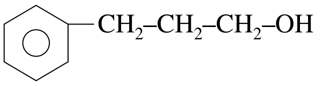
(1) Ethane (2) Ethyne

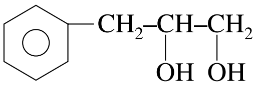
(3) Ethene (4) Propene

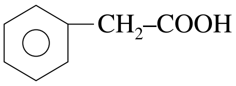
17.  on mercuration–demercuration produces the major product

[JEE Main Online-2014]

(1) 

(2) 

(3) 

(4) 

18. In the presence of peroxide, HCl and HI do not give anti-Markownikoff's addition to alkenes because

[JEE Main Online -2014]

(1) One of the steps is endothermic in HCl and HI

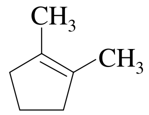
(2) Both HCl and HI are strong acids

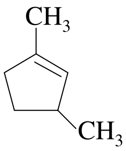
(3) HCl is oxidising and the HI is reducing

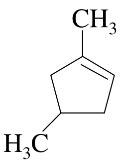
(4) All the steps are exothermic in HCl and HI

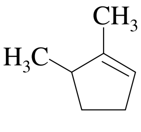
19. Which compound would give 5-Keto-2-methyl hexanal upon ozonolysis?

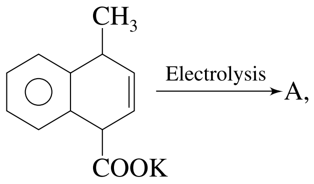
[JEE Main-2015]

(1) 

(2) 

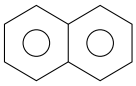
(3) 

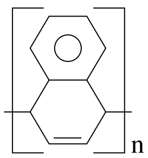
(4) 

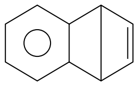
20. 

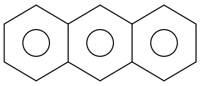
[JEE Main Online-2015]

A is:

(1) 

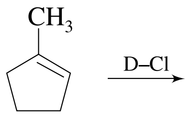
(2) 

(3) 

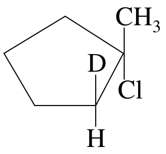
(4) 

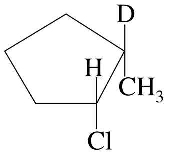
21. What is the major product expected from the following reaction?

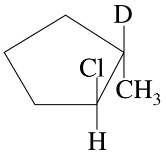
[JEE main Online-2015]

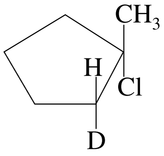


where D is an isotope of hydrogen.

(1) 

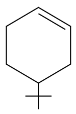
(2) 

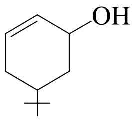
(3) 

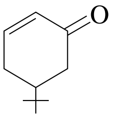
(4) 

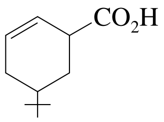
22. The product of the reaction given below is:

[JEE main-2016]

(1) 

(2) 

(3) 

(4) 

23. The reaction of propene with HOCl (Cl_2 + H_2O) proceeds through the intermediate:

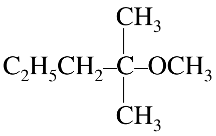
[JEE Main-2016]

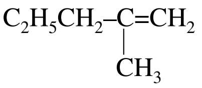
(1) HC_3–CH^+–CH_2–OH (2) CH_3–CH^+–CH_2–Cl

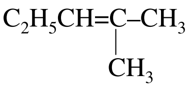
(3) CH_3–CH(OH)–H_2^+ (4) CH_3–CHCl–H_2^+

24. 2-chloro-2-methylpentane on reaction with sodium methoxide in methanol yields

[JEE Main-2016]

(I) 
$C_2H_5CH_2-\underset{CH_3}{\overset{CH_3}{C}}-OCH_3$

(II) 
$C_2H_5CH_2-\underset{CH_3}{C}=CH_2$

(III) 
$C_2H_5CH=\underset{CH_3}{C}-CH_3$

(1) Both I and III (2) Only III

(3) Both I and II (4) All of these

25. Cyclohexene is best prepared from cyclohexanol by which of the following?

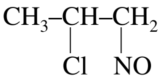
[IIT-2005]

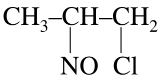
(1) conc. H_3PO_4 (2) conc. $HCl/ZnCl_2$

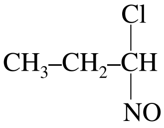
(3) conc. HCl (4) conc.HBr

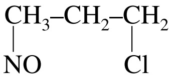
26. $CH_3-CH=CH_2 + NOCl \longrightarrow P$; Identity the adduct.

[IIT-2006]

(1) 
$CH_3-\underset{Cl}{CH}-\underset{NO}{CH_2}$

(2) 
$CH_3-\underset{NO}{CH}-\underset{Cl}{CH_2}$

(3) 
$CH_3-CH_2-\underset{NO}{\overset{Cl}{CH}}$

(4) 
$\underset{NO}{CH_3}-CH_2-\underset{Cl}{CH_2}$

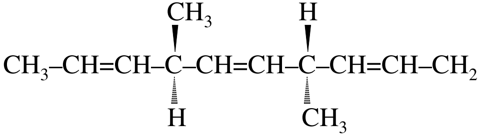
27. The number of stereoisomers obtained by bromination of trans-2-butene is

[IIT-2007]

(1) 1 (2) 2

(3) 3 (4) 4

28. The number of optically active products obtained from the complete ozonolysis of the given compound, is **[IIT Advance-2012]**

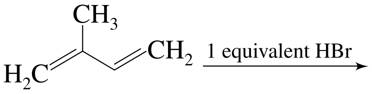

$CH_3-CH=CH-\underset{H}{\overset{CH_3}{C}}-CH=CH-\underset{CH_3}{\overset{H}{C}}-CH=CH-CH_2$

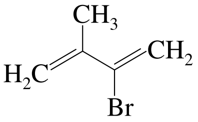
(1) 0 (2) 1

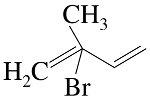
(3) 2 (4) 4

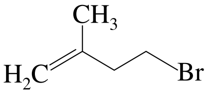
29. In the following reaction, the major product is

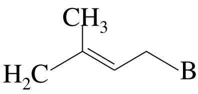
[JEE Advance-2015]



(1) 

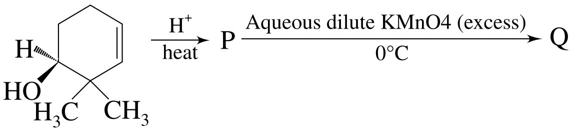
(2) 

(3) 

(4) 

30. The number of hydroxyl group(s) in Q is

[JEE Advance-2015]



ANSWER KEY

EXERCISE # 1

1. (2)	2. (2)	3. (3)	4. (2)	5. (3)
6. (2)	7. (2)	8. (3)	9. (4)	10. (3)
11. (2)	12. (1)	13. (3)	14. (4)	15. (1)
16. (3)	17. (4)	18. (3)	19. (4)	20. (4)
21. (3)	22. (1)	23. (2)	24. (3)	25. (2)
26. (4)	27. (1)	28. (1)	29. (3)	30. (2)

EXERCISE # 2

1. (1)	2. (3)	3. (4)	4. (2)	5. (3)
6. (3)	7. (3)	8. (3)	9. (2)	10. (2)
11. (4)	12. (3)	13. (3)	14. (2)	15. (1)
16. (1)	17. (3)	18. (2)	19. (1)	20. (1)
21. (2)	22. (4)	23. (2)	24. (2)	25. (3)
26. (3)	27. (3)	28. (3)	29. (2)	30. (3)
31. (3)	32. (3)	33. (3)	34. (3)	35. (4)

EXERCISE # 3

1. (1,2)	2. (1,2,3)	3. (1,2,3)	4. (2,4)	5. (3,4)
6. (1,3,4)	7. (2)	8. (2,3)	9. (2,3,4)	10. (2,3)
11. (1,2,4)	12. (2)	13. (1)	14. (2)	15. (3)
16. (3)	17. (1)	18. (2)	19. (4)	20. (2)
21. (1)	22. (2)	23. (1)	24. (6)	25. (5)
26. (3)	27. (4)	28. (6)	29. (8)	30. (8)

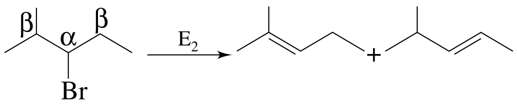
EXERCISE # 4

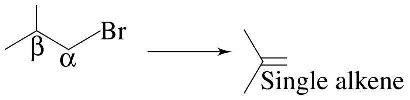
1. (2)	2. (3)	3. (4)	4. (1)	5. (1)
6. (1)	7. (1)	8. (3)	9. (2)	10. (3)
11. (1)	12. (3)	13. (4)	14. (3)	15. (3)
16. (3)	17. (1)	18. (1)	19. (2)	20. (1)
21. (1)	22. (2)	23. (2)	24. (4)	25. (1)
26. (1)	27. (1)	28. (1)	29. (4)	30. (4)

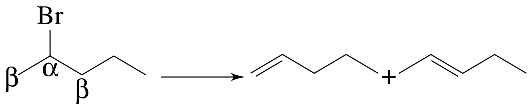
HINT AND SOLUTION

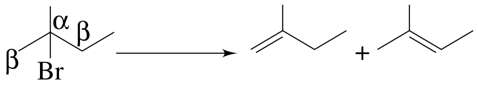
EXERCISE # 1

1. [2]

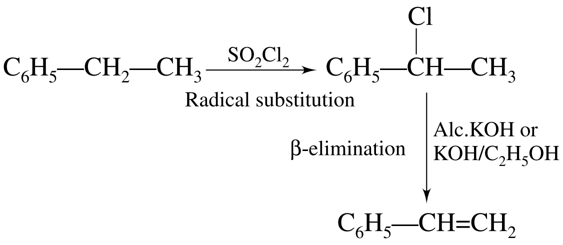






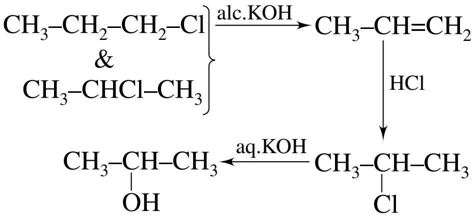


2. [2]



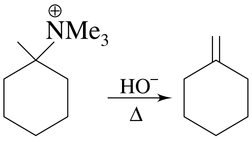
$$C_6H_5{-}CH_2{-}CH_3 \xrightarrow[\text{Radical substitution}]{SO_2Cl_2} C_6H_5{-}\overset{\displaystyle Cl}{\overset{|}{C}H}{-}CH_3 \xrightarrow[\text{Alc.KOH or KOH/}C_2H_5OH]{\beta\text{-elimination}} C_6H_5{-}CH{=}CH_2$$

3. [3]



$$\left.\begin{array}{l}CH_3{-}CH_2{-}CH_2{-}Cl\\ \qquad\&\\ CH_3{-}CHCl{-}CH_3\end{array}\right\} \xrightarrow{\text{alc.KOH}} CH_3{-}CH{=}CH_2 \xrightarrow{HCl} CH_3{-}\underset{\underset{\displaystyle Cl}{|}}{CH}{-}CH_3 \xrightarrow{\text{aq.KOH}} CH_3{-}\underset{\underset{\displaystyle OH}{|}}{CH}{-}CH_3$$

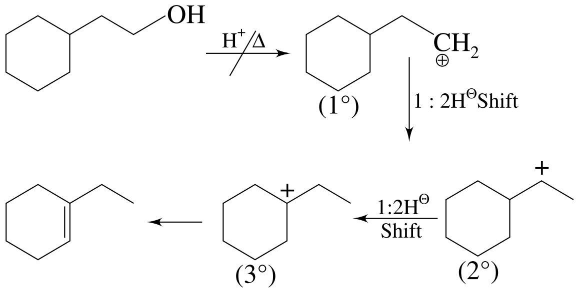
4. [2]



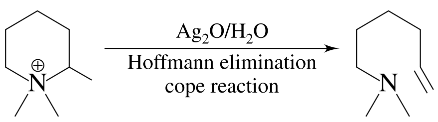
Hoffmann elimination

Pyrolysis of QAH takes place by Hoffmann rule

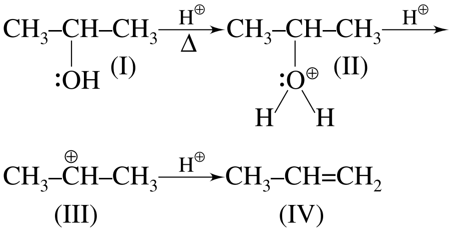
5. [3]



6. [2]

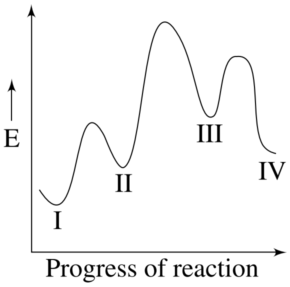


7. [2]



$$CH_3{-}\underset{\underset{\displaystyle :OH}{|}}{CH}{-}CH_3\ (I) \xrightarrow[\Delta]{H^{\oplus}} CH_3{-}\underset{\underset{\displaystyle H\ \ \ H}{:\overset{|}{O}^{\oplus}}}{CH}{-}CH_3\ (II) \xrightarrow{H^{\oplus}}$$

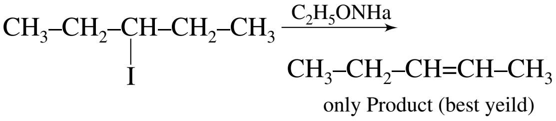
$$CH_3{-}\overset{\oplus}{C}H{-}CH_3\ (III) \xrightarrow{H^{\oplus}} CH_3{-}CH{=}CH_2\ (IV)$$



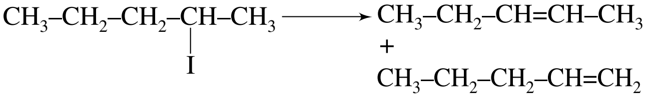
8. [3]

(i) Reactivity of β-elimination in alkyl halide
R – I > R – Br > R – Cl

(ii) If halide same
Reactivity ∝ stability of alkene

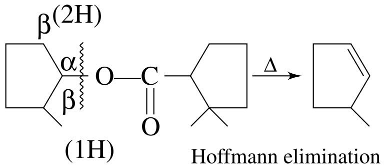


$$CH_3{-}CH_2{-}\underset{\underset{\displaystyle I}{|}}{CH}{-}CH_2{-}CH_3 \xrightarrow{C_2H_5ONHa} \underset{\text{only Product (best yeild)}}{CH_3{-}CH_2{-}CH{=}CH{-}CH_3}$$



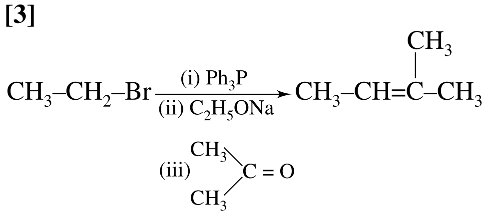
$$CH_3{-}CH_2{-}CH_2{-}\underset{\underset{\displaystyle I}{|}}{CH}{-}CH_3 \longrightarrow \begin{array}{l}CH_3{-}CH_2{-}CH{=}CH{-}CH_3\\ +\\ CH_3{-}CH_2{-}CH_2{-}CH{=}CH_2\end{array}$$

9. [4]



Hoffmann elimination

10. [3]

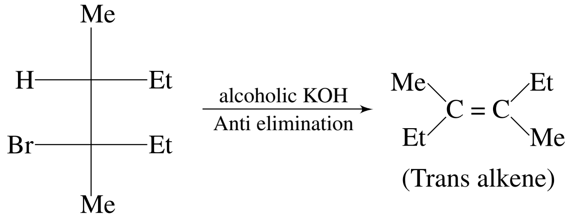


$$CH_3–CH_2–Br \xrightarrow[\text{(ii) } C_2H_5ONa]{\text{(i) } Ph_3P} CH_3–CH=\overset{\overset{\displaystyle CH_3}{|}}{C}–CH_3$$

$$\text{(iii) } (CH_3)_2C=O$$

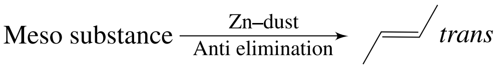
Witting reaction

11. [2]

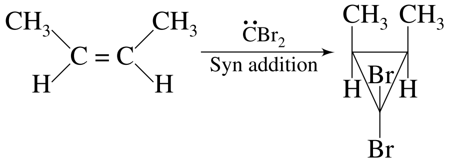


Erythero [EAT] (refer key concept)

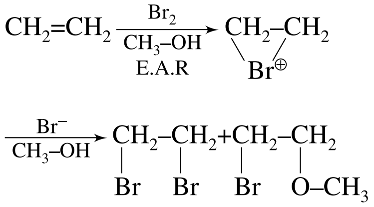
12. [1]



13. [3]



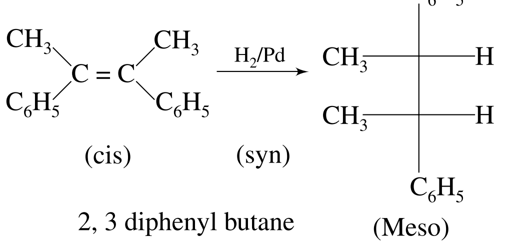
14. [4]



$$CH_2=CH_2 \xrightarrow[\text{CH}_3\text{–OH}\ \text{E.A.R}]{Br_2} \underset{\diagdown\ Br^{\oplus}\ \diagup}{CH_2–CH_2}$$

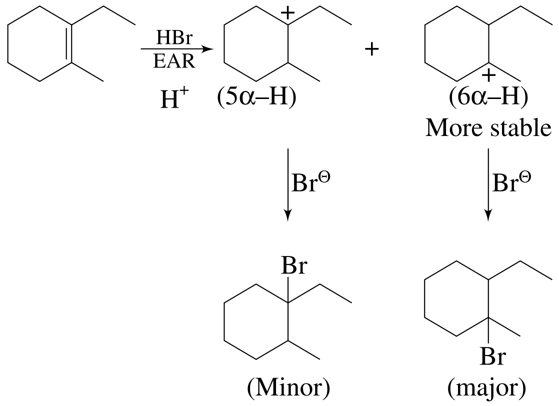
$$\xrightarrow[CH_3–OH]{Br^-} \underset{Br}{\underset{|}{CH_2}}–\underset{Br}{\underset{|}{CH_2}}+\underset{Br}{\underset{|}{CH_2}}–\underset{O–CH_3}{\underset{|}{CH_2}}$$

15. [1]



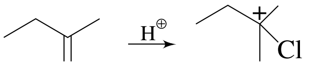
2, 3 diphenyl butane (Meso)

16. [3]



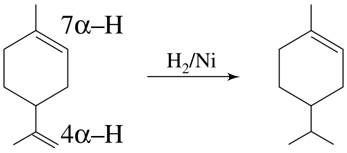
17. [4]

Rate of E.A.R α Stability of carbocation



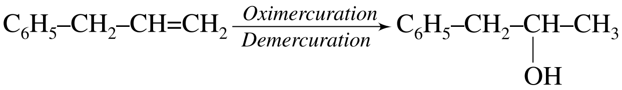
3° carbocation (most stable)

18. [3]



$$\text{Reactivity of alkene} \propto \frac{1}{\text{stability of alkene}} \propto \frac{1}{\alpha - H}$$

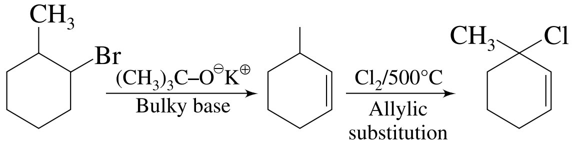
19. [4]



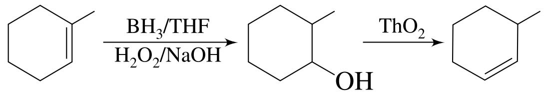
$$C_6H_5–CH_2–CH=CH_2 \xrightarrow[\textit{Demercuration}]{\textit{Oximercuration}} C_6H_5–CH_2–\underset{OH}{\underset{|}{CH}}–CH_3$$

Overall OMDM is Hydration, according to Markownikoff rule

20. [4]



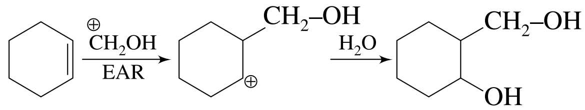
21. [3]



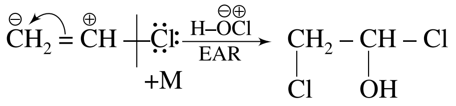
Hydration via anti-Markownikoff addition

22. [1]

$H-CH=O \xrightarrow{H^{\oplus}} \overset{\oplus}{C}H_2-OH$



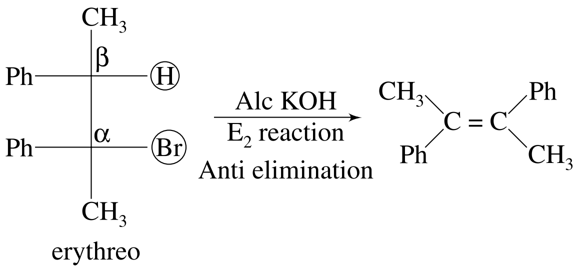
23. [2]



$\overset{\ominus}{C}H_2=\overset{\oplus}{C}H-\ddot{Cl}: \xrightarrow[EAR]{\overset{\ominus\oplus}{H-OCl}} \underset{Cl}{CH_2}-\underset{OH}{CH}-Cl$

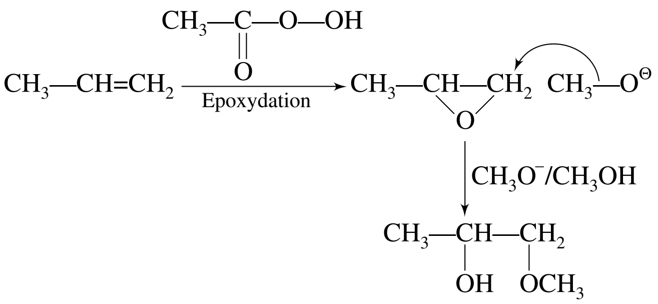
+M

24. [3]



Trick ⟶ EA(T) ⟶ *trans* (refer Key concept)

25. [2]

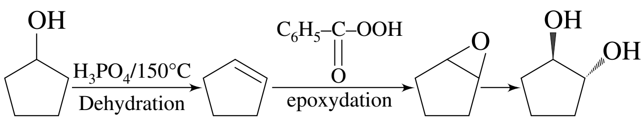


$CH_3-CH=CH_2 \xrightarrow[Epoxydation]{CH_3-\underset{O}{\overset{\|}{C}}-O-OH} CH_3-CH-CH_2\ (epoxide)\quad CH_3-O^{\ominus}$

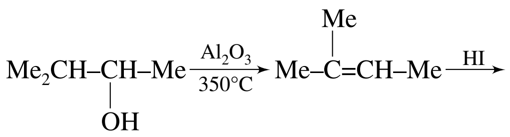
$\xrightarrow{CH_3O^-/CH_3OH} CH_3-\underset{OH}{CH}-\underset{OCH_3}{CH_2}$

Nucleophile attach at least steric centre

26. [4]

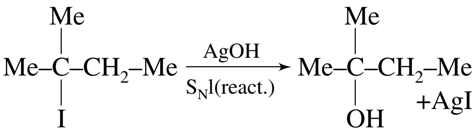


27. [1]



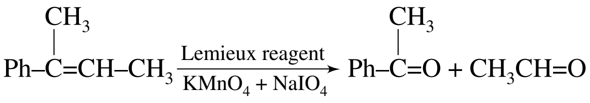
$Me_2CH-\underset{OH}{CH}-Me \xrightarrow[350°C]{Al_2O_3} Me-\overset{Me}{C}=CH-Me \xrightarrow{HI}$

Al_2O_3 is dehydrating agent.



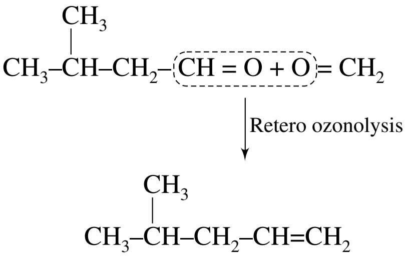
$Me-\overset{Me}{\underset{I}{C}}-CH_2-Me \xrightarrow[S_N1(react.)]{AgOH} Me-\overset{Me}{\underset{OH}{C}}-CH_2-Me + AgI$

28. [1]



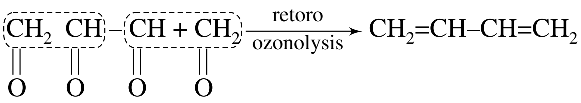
$Ph-\overset{CH_3}{C}=CH-CH_3 \xrightarrow[KMnO_4+NaIO_4]{Lemieux\ reagent} Ph-\overset{CH_3}{C}=O + CH_3CH=O$

29. [3]



$CH_3-\overset{CH_3}{CH}-CH_2-CH=O+O=CH_2 \xrightarrow{Retero\ ozonolysis} CH_3-\overset{CH_3}{CH}-CH_2-CH=CH_2$

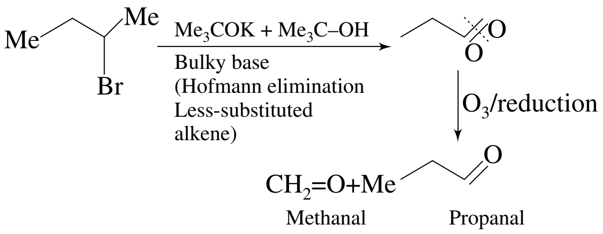
30. [2]



$\underset{O}{CH_2}\ \underset{O}{CH}-\underset{O}{CH}+\underset{O}{CH_2} \xrightarrow[ozonolysis]{retoro} CH_2=CH-CH=CH_2$

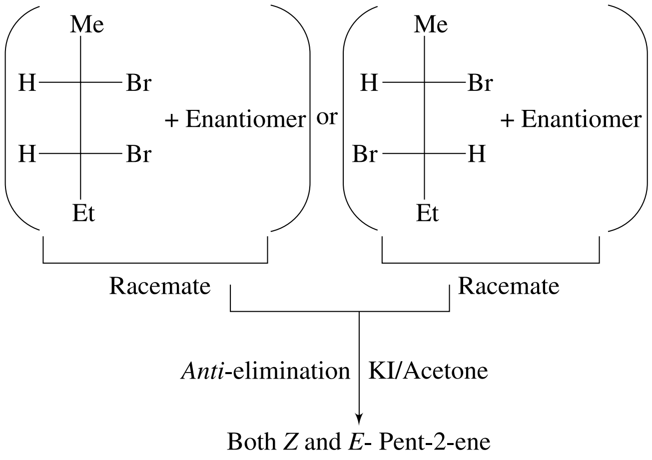
EXERCISE # 2

1. [1]

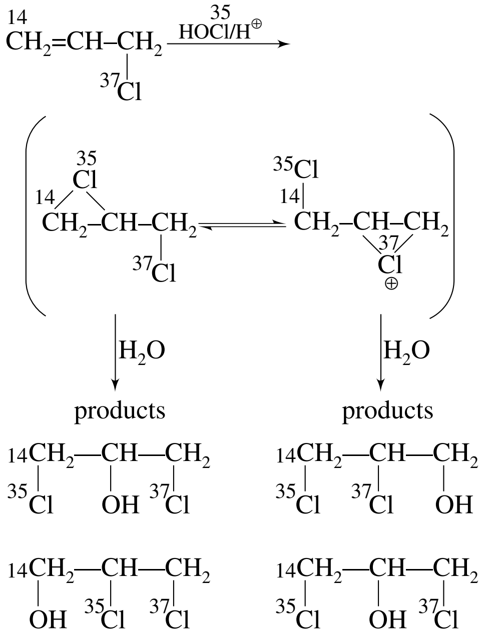


2. [3]

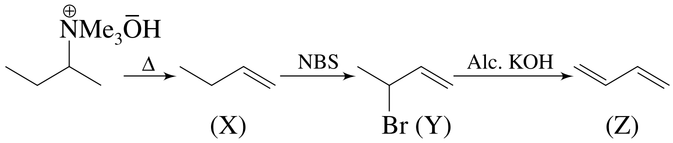
2, 3-dibromopentane, meso isomer is not possible, since two terminal groups are different.



3. [4]

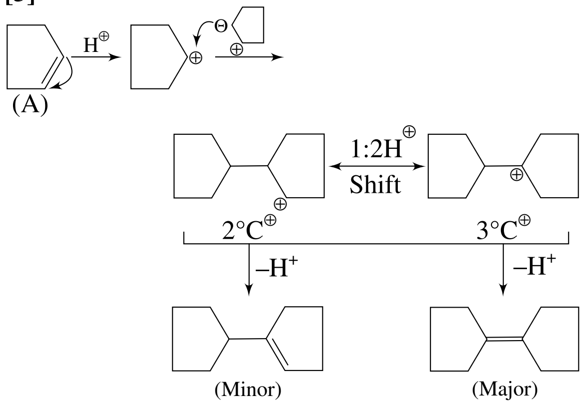


4. [2]



Hoffmann elimination

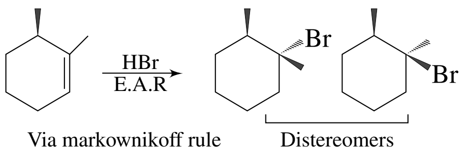
5. [3]



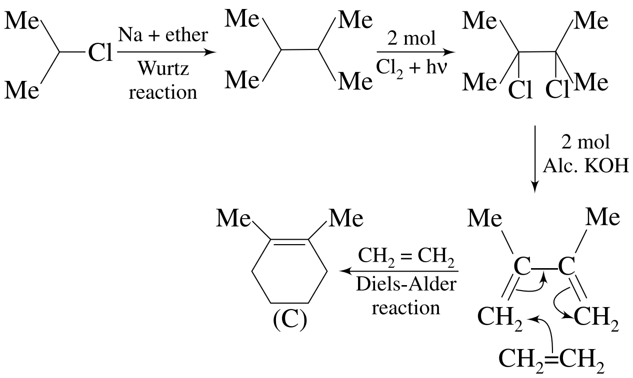
6. [3]

Product has 2 chiral C but POS present and also the two–COOH will come on the same side giving meso form of diacid

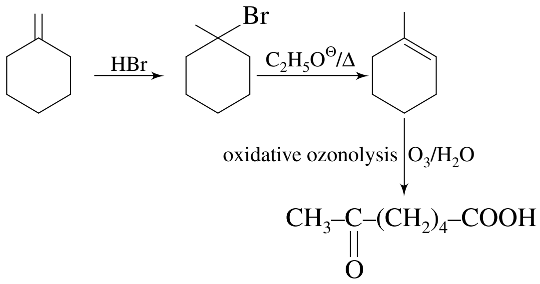
7. [3]



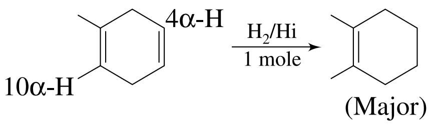
8. [3]



9. [2]

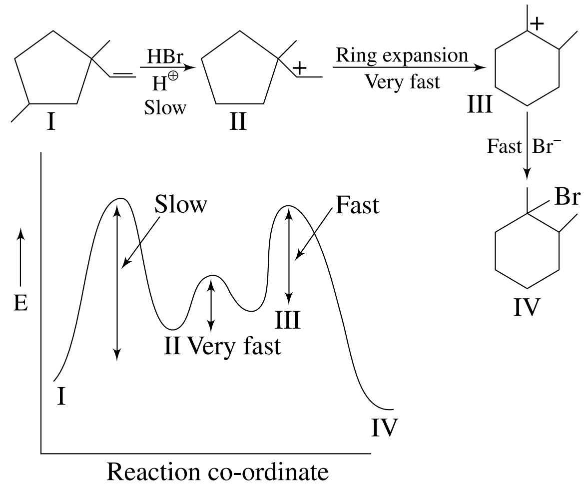


10. [2]

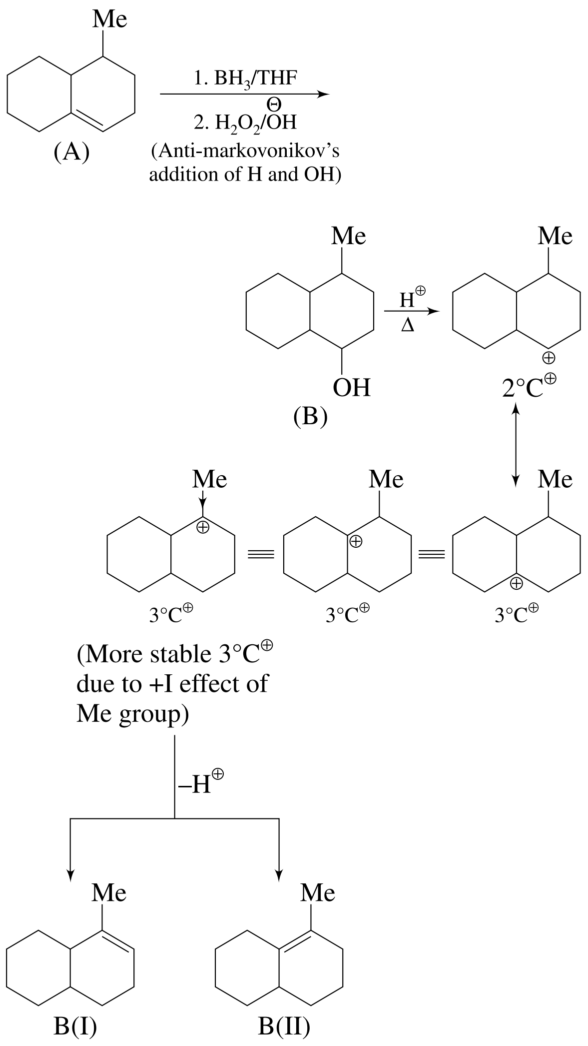


Reactivity of alkene $\frac{1}{\text{stability of alkene}} \propto \frac{1}{\alpha - \text{H}}$

11. [4]



12. [3]

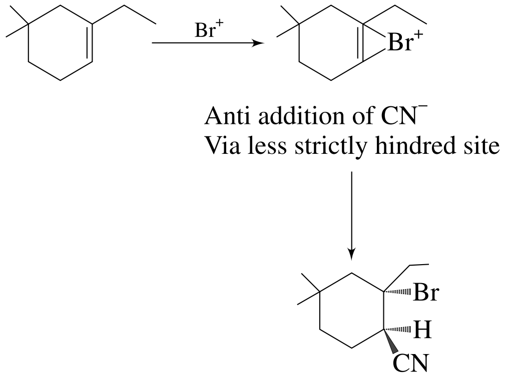


Out of B(I) and B(II), B(I) is more likely to be formed because in B(II) double bond is joined to two rings (exocyclic bond) and, hence, is not so stable.

13. [3]

Anti-elimination takes place

14. [2]



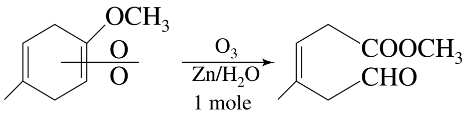
15. [1]

E_2-elelmation reaction takes place.

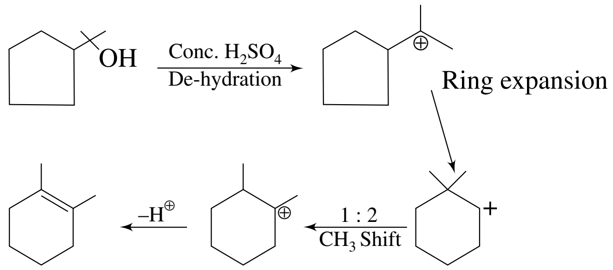
Syatzeff product obtained by anti-elimination

16. [1]

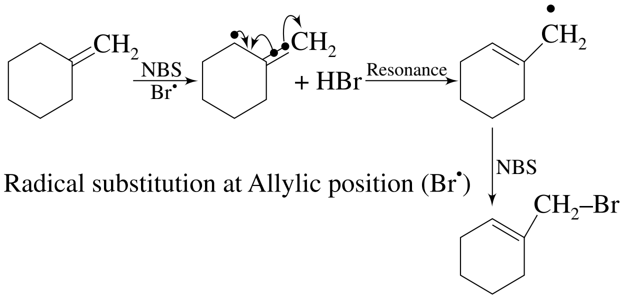
+M favours ozonolysis



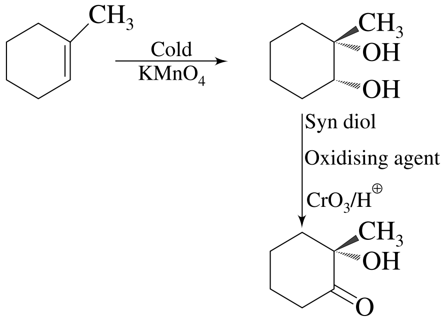
17. [3]



18. [2]



19. [1]



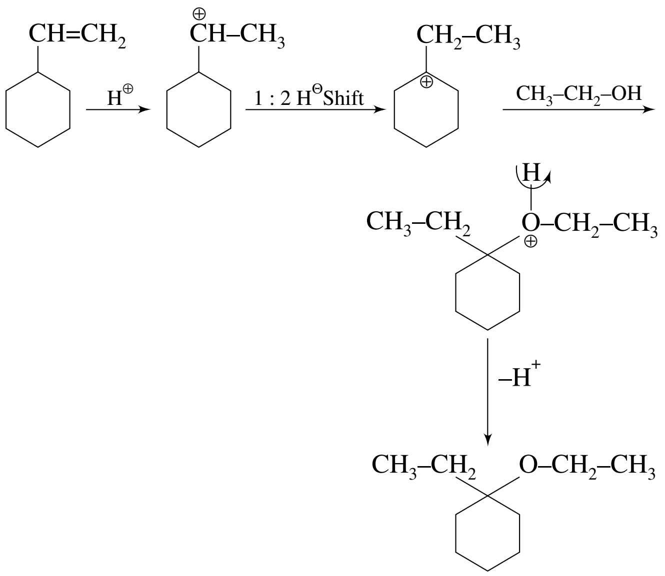
3° alcohol do not give oxidation reaction

20. [1]

→ E.A.R

→ Markownikoff rule applies

$H_2SO_4 \rightarrow H^{\oplus} + HSO_4^{\ominus}$



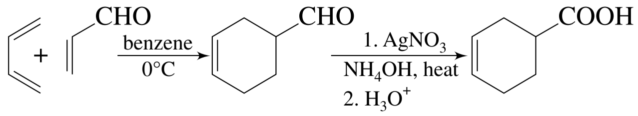
21. [2]

$NH_2–NH_2/H_2O_2$ only reduce C = C

Sn + HCl only reduce – NO_2

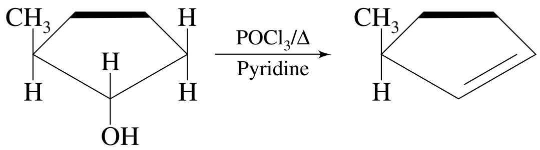
Raney Ni reduces C = C and – NO_2 Both

22. [4]



Diel's-Alder After reaction 1:4 addition

23. [2]

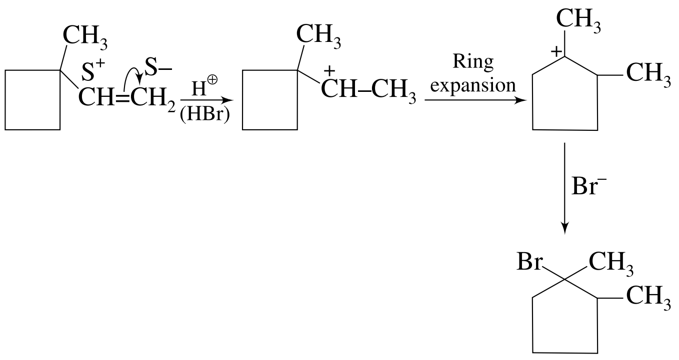


With bulky reagent Hoffmann elimination takes place.

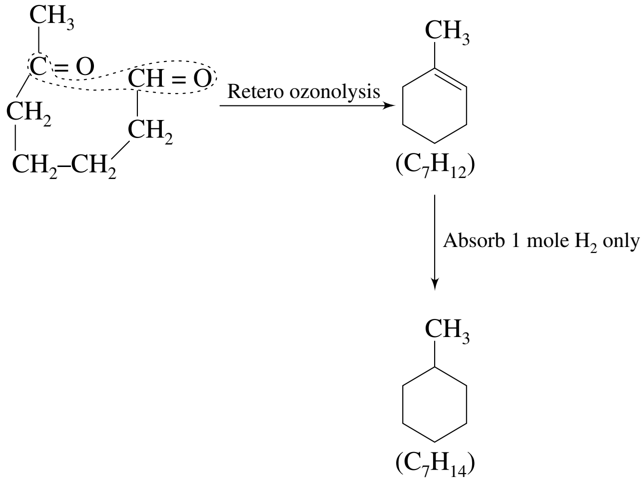
24. [2]

Cis alkene + *Anti* reagent ⇒ Racemic mixture

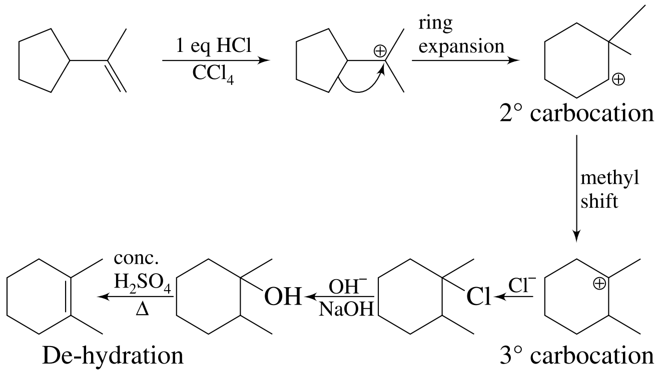
25. [3]



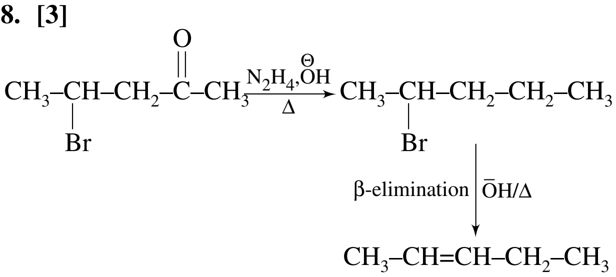
26. [3]



27. [3]

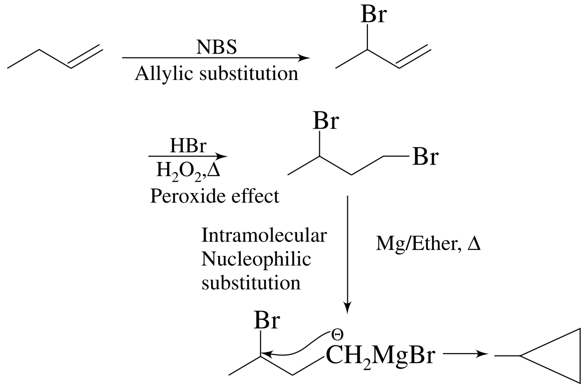


28. [3]



→ Wolf–Kishner reduction followed by β-elimination (De-hydrohalogenation) takes place simultaneously

29. [2]



30. [3]

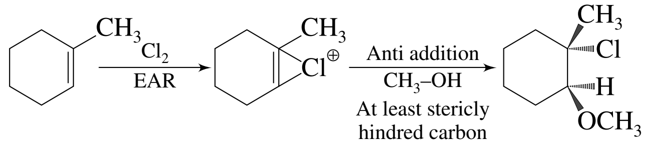
This is an example of E_1 reaction hence more stable alkene is obtained as major product. So that alkene (I) is formed as the major product because it is more substituted and thus more stable than alkene (II).

31. [3]

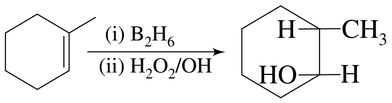
Rate of E.A.R ∝ stability of $-\overset{|}{\underset{|}{C}}{}^{\oplus}-$ ∝ ERG ∝ $\dfrac{1}{EWG}$

$\underset{+M}{-NH-CH_3} > \underset{+M}{-OCH_3} > \underset{+M}{-CH_3}(ERG\downarrow)$

32. [3]



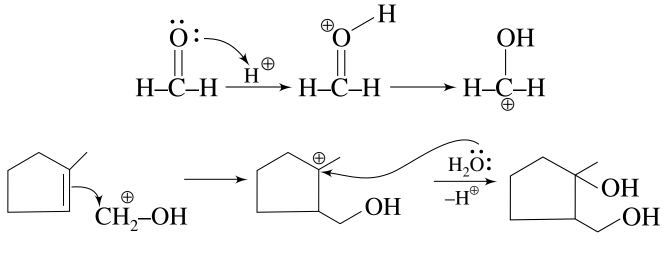
33. [3]



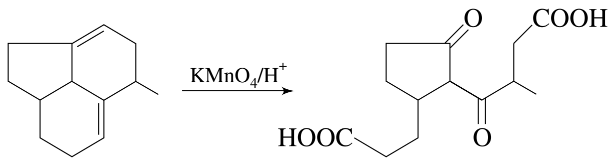
(±) *trans*-2-methylcyclohexanol

Syn addition via Anti-Markownikoff addition

34. [3]

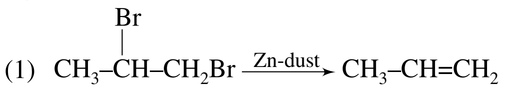


35. [4]



EXERCISE # 3

1. [1, 2]

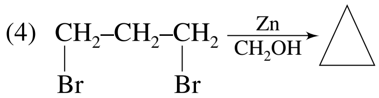


(1) $CH_3-\overset{\overset{\large Br}{|}}{CH}-CH_2Br \xrightarrow{\text{Zn-dust}} CH_3-CH=CH_2$

(2) $CH_3-CH_2-CHBr_2 + Na \xrightarrow[\Delta]{Et_2O}$

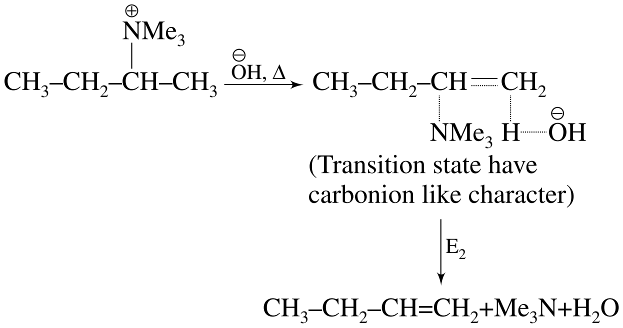
$CH_3-CH_2-CH=CH-CH_2-CH_3$

(3) $CH_3-CH_2-CHBr_2 \xrightarrow[\text{(ii) } NaNH_2/\Delta]{\text{(i) Alc. KOH}} CH_3-C\equiv CH$



(4) $\underset{\underset{\large Br}{|}}{CH_2}-CH_2-\underset{\underset{\large Br}{|}}{CH_2} \xrightarrow[CH_2OH]{Zn}$

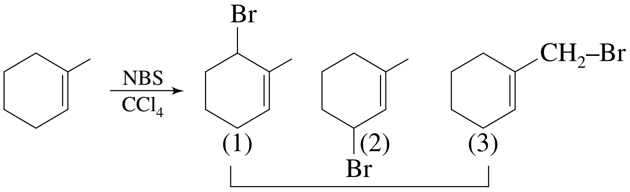
2. [1, 2, 3]



$CH_3-CH_2-CH=CH_2+Me_3N+H_2O$

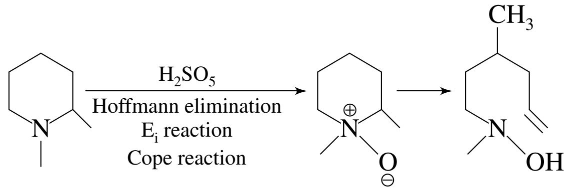
Hoffmann prouct

3. [1, 2, 3]

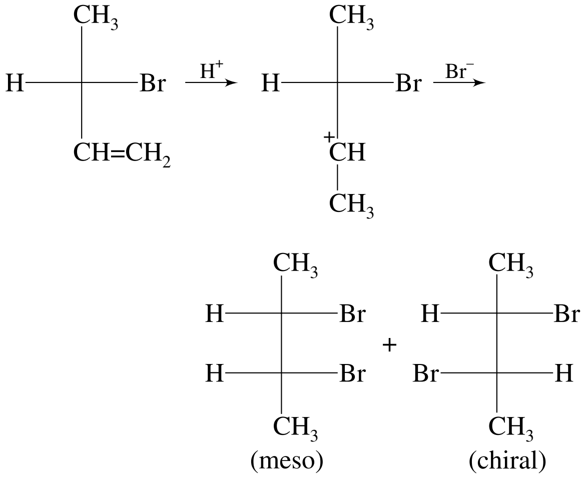


Allylic substituted product

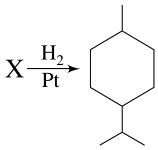
4. [2, 4]



5. [3, 4]

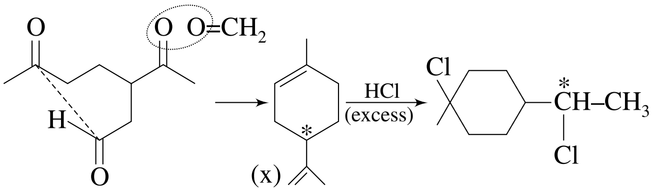


6. [1, 3, 4]



Therefore, X has a six membered ring.]

Connecting ozonolysis product to form a six membered ring gives structure of X as



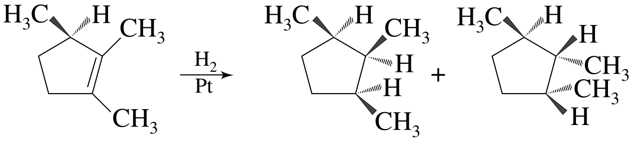
It has a chiral carbon

It has one chiral carbon (racemic mix)

Chiral carbon is produced through carbocation and racemic mixture would be formed

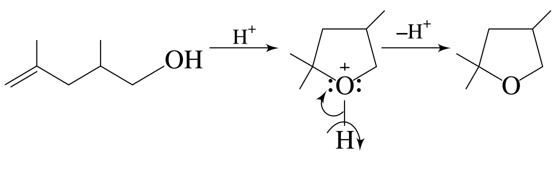
7. [2]

Catalytic hydrogenation occur with *syn*-orientation in the present case hydrogenation would be slightly more favoured from the side opposite to the methyl group at chiral carbon.

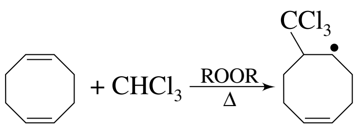


More favoured

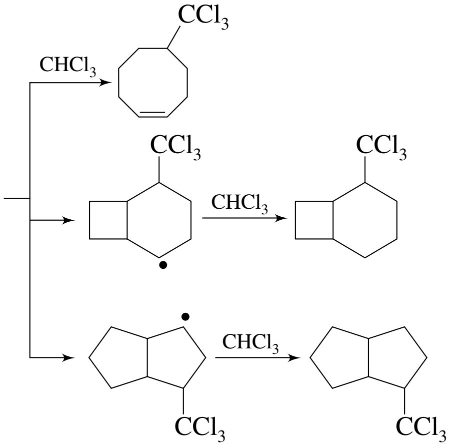
8. [2, 3]



9. [2, 3, 4]

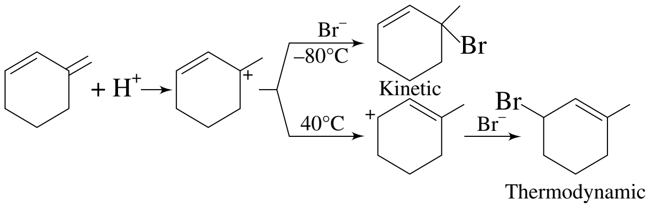


1.0 equivalent

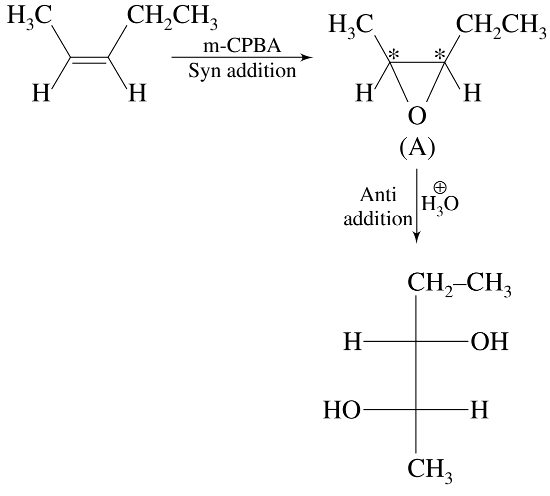


10. [2, 3]

Electrophilic addition occur at 1,2-position under kinetically controlled condition while at 1, 4-position under thermodynamically controlled condition



11. [1, 2, 4]

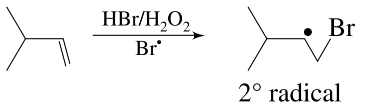


(chiral molecule)

12. [2]

It is true that in cold, alkaline condition, KMnO4 acts as mild oxidising agent but the reason for the formation of meso diol is syn hydroxylation via a cyclic intermediate.

13. [1]



2° radical
(more stable)

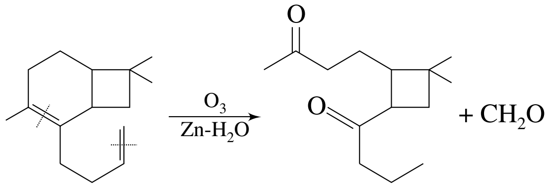
14. [2]

The bulky base $(CH_3)_3COK$ brings about E-2 elimination by abstracting hydrogen from less hindered β-carbon giving less substituted alkene as major product.

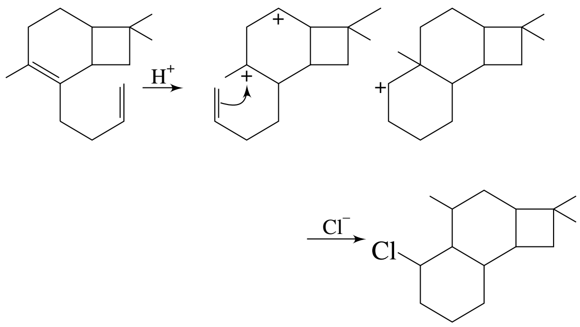
15. [3]

$(CH_3)_2S$ is better reducing agent, reduces ozonide to corresponding carbonyls and itself oxidised into $(CH_3)_2SO$ which is a common organic solvent. It does not reduce carbonyls products further.

16. [3]



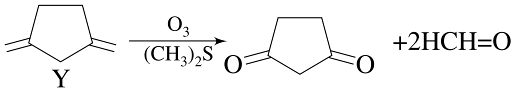
17. [1]



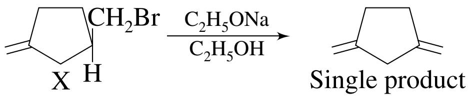
18. [2] **19. [4]** **20. [2]**

[18–20]

Y upon ozonolysis followed by work-up with $(CH_3)_2S$ gives 1,3-cyclopentanedione, it must be

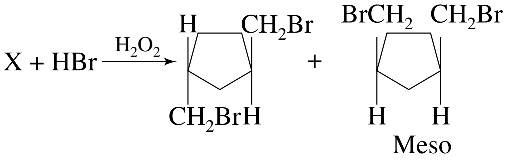


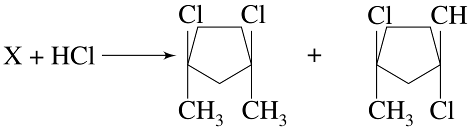
Y is obtained as single dehydrobromination product, X must be



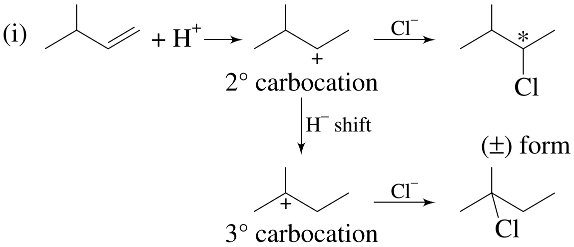
Single product

Also,

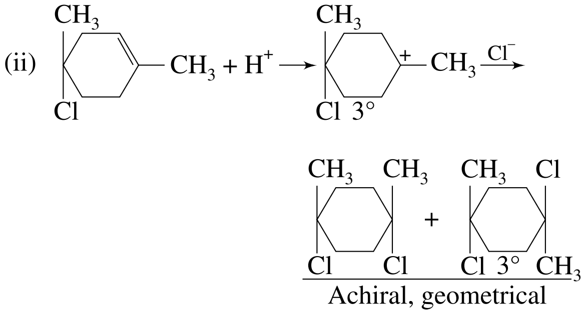




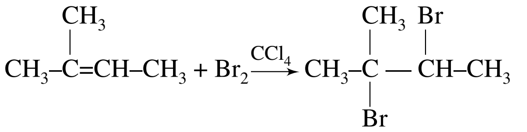
21. [1]



(i) → (P,Q,R,S)



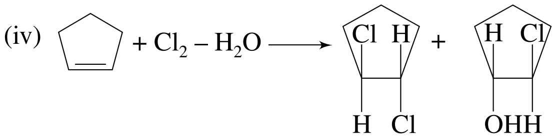
(ii) → (P,S)

(iii) 

$$CH_3-\overset{CH_3}{C}=CH-CH_3 + Br_2 \xrightarrow{CCl_4} CH_3-\underset{Br}{\overset{CH_3}{C}}-\overset{Br}{CH}-CH_3$$

(Chiral = racemic mixture)

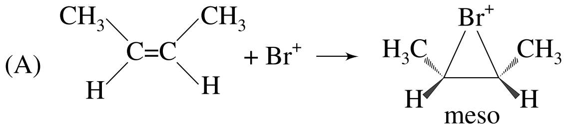
(iii) → (P,Q)



(Racemic mixture)

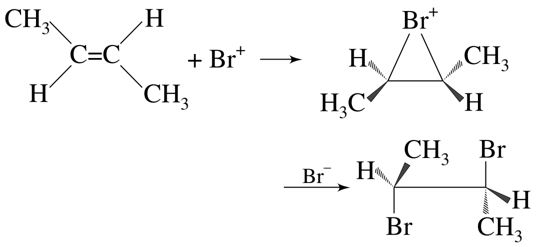
(iv) → (P,Q)

22. [2]

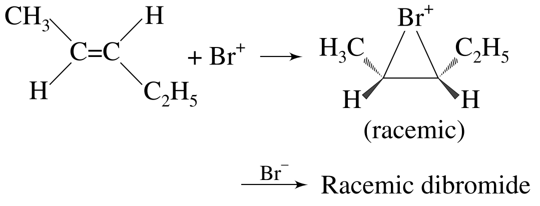


$\xrightarrow{Br^+}$ Racemic dibromide

(B)



(C)

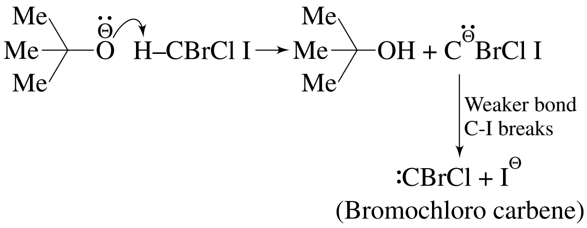


(D) Two *anti*-dibromides are formed in equal amounts but presence of an additional chiral carbon makes the two products diastereomers.

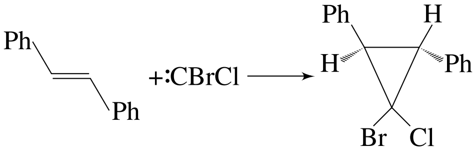
23. [1]

(a → s) HCl with peroxide does not undergo anti-Markovnikov's addition unlike HBr + peroxide, so reaction does not proceed by free-radical mechanism but by carbocation.

(b → p) Proceed via carbene mechanism.



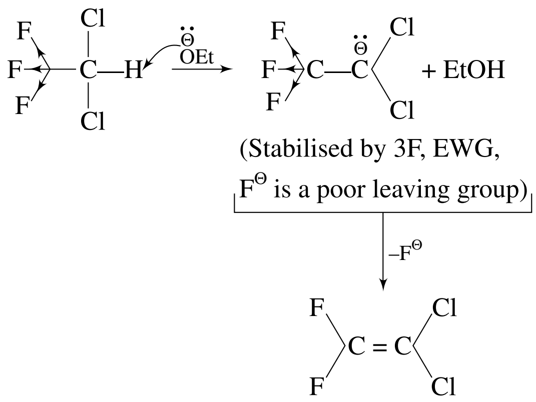
It is a stereospecific and stereoselective reaction; trans reactant gives trans product.



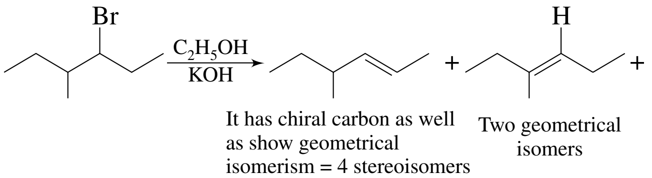
(c → q) Proceeds via free-radical mechanism.

(d → q) proceeds via free-radical mechanism.

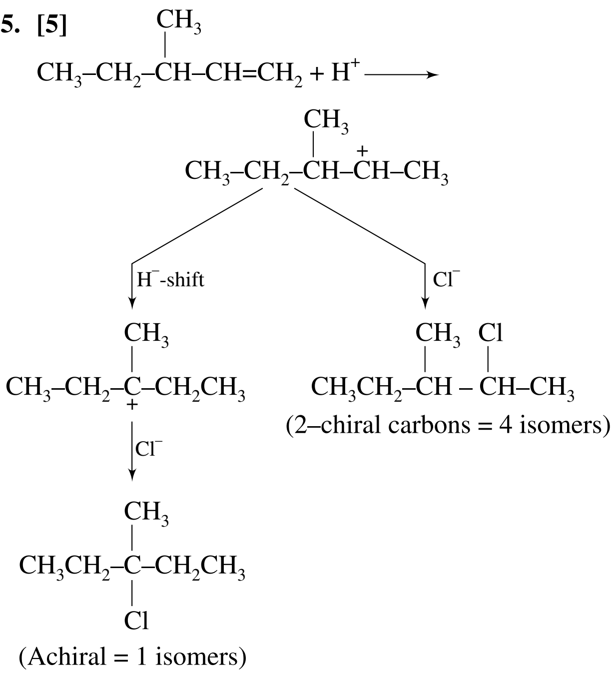
(e → r) It is an example of E_1 CB (elimination unimolecular via conjugate base) and proceeds via carbanion mechanism. EWG (electron-withdrawing group) and poor leaving, three F atoms stabilise the carbanion.



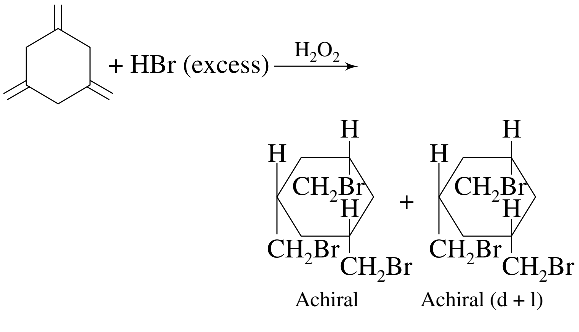
24. [6]



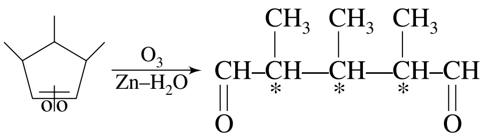
25. [5]



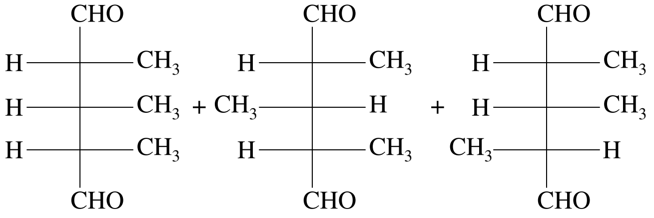
26. [3]



27. [4]

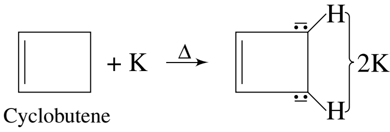


Chiral C = 3
(including 1 pseudo chiral carbon)



Meso Meso (d + l)

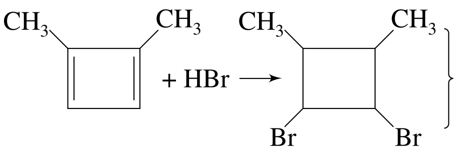
28. [6]



Cyclobutene

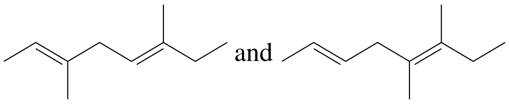
Aromatic dianion
(It has 6 delocalised pi-electrons)

29. [8]



Two meso and 3 pairs of enantiomers = 8 isomers

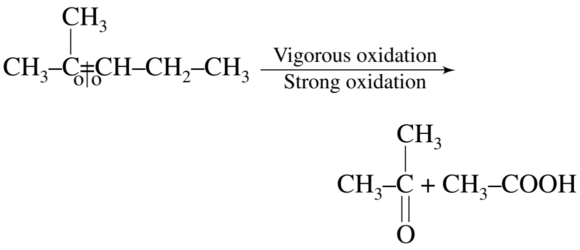
30. [8]



Both of the above dienes are capable of showing geometrical isomerism at both of their double bonds. Therefore, four stereoisomers exist for each of them.

EXERCISE # 4

1. [2]



$$\text{CH}_3\text{–}\overset{\text{CH}_3}{\overset{|}{\text{C}}}\text{=CH–CH}_2\text{–CH}_3 \xrightarrow[\text{Strong oxidation}]{\text{Vigorous oxidation}} \text{CH}_3\text{–}\underset{\text{O}}{\underset{\|}{\overset{\text{CH}_3}{\overset{|}{\text{C}}}}} + \text{CH}_3\text{–COOH}$$

2. [3]

$$\text{R–O–H} \xrightarrow[\text{H}^{\oplus}]{\text{Reduction}} \text{R–}\overset{\oplus}{\ddot{\text{O}}}\text{–H}_2 \longrightarrow \text{R}^{\oplus}$$

Initiation step
(Proto nation of alcohol)

3. [4]

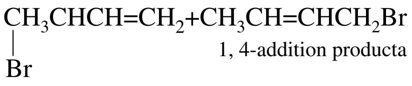
boiling point ∝ polarity

- Since alkanes are less polar, they have lesser boiling point than alkene and alkyne.
- In isomeric alkane (b. pt.) $\propto \dfrac{1}{\text{branching}}$

Thus isobutane has least boiling point

4. [1]

$\text{CH}_2\text{=CHCH=CH}_2 + \text{HBr} \longrightarrow$



$$\underset{\text{Br}}{\underset{|}{\text{CH}_3\text{CH}}}\text{CH=CH}_2 + \text{CH}_3\text{CH=CHCH}_2\text{Br}$$

1, 4-addition producta

1, 2-addition product

Addition is through the formation of allylic carbocation,

$$\text{CH}_2\text{=CH}\overset{\oplus}{\text{C}}\text{HCH}_3 \longleftrightarrow \text{CH}_3\text{CH=CH}\overset{\oplus}{\text{C}}\text{H}_2$$

(2° allylic)
(more stable)

(1° allylic)
(less stable)

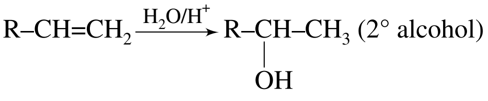
Under mild conditions (temperature = – 80°C) kinetic product is the 1, 2-addition product and under vigorous conditions, (temperature = 40°C) thermodynamic product is the 1, 4-addition product.

Thus, 1-bromo-2-butene is the product under given condition.

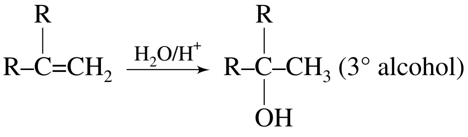
5. [1]

$$\text{CH}_2\text{=CH}_2 \xrightarrow{\text{H}_2\text{O/H}^+} \text{CH}_3\text{–CH}_2\text{–OH}$$

1° alcohol



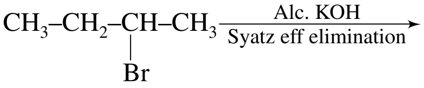
$$\text{R–CH=CH}_2 \xrightarrow{\text{H}_2\text{O/H}^+} \text{R–}\underset{\text{OH}}{\underset{|}{\text{CH}}}\text{–CH}_3 \text{ (2° alcohol)}$$



$$\text{R–}\overset{\text{R}}{\overset{|}{\text{C}}}\text{=CH}_2 \xrightarrow{\text{H}_2\text{O/H}^+} \text{R–}\underset{\text{OH}}{\underset{|}{\overset{\text{R}}{\overset{|}{\text{C}}}}}\text{–CH}_3 \text{ (3° alcohol)}$$

Except ethene other alkene will give secondary or tertiary alcohol

6. [1]



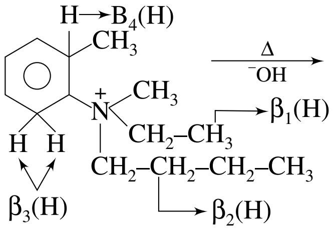
$$CH_3-CH_2-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow[\text{Syatz eff elimination}]{\text{Alc. KOH}}$$

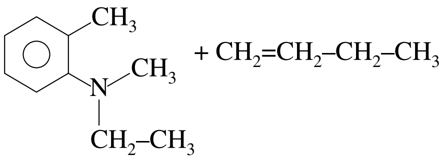
$$\underset{\substack{\text{2-butene}\\ \text{major}}}{CH_3-CH = CH-CH_2} + \underset{\substack{\text{1-butene}\\ \text{minor}}}{CH_3-CH_2-CH=CH_2}$$

7. [1]

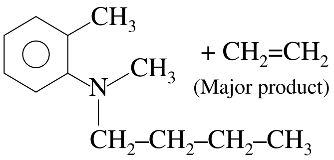
Compounds bearing a quaternary nitrogen atom bonded to four alkyl groups when heated in the presence of base like OH^- undergo E_2 elimination with the formation of less substituted alkene as a major product with the loss of β-H atom.

This type of elimination is called Hofmann elimination.





(Minor product)



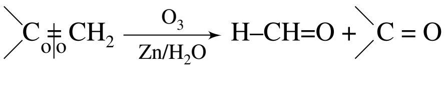
Hence, $CH_2=CH_2$ will be a major product.

8. [3]

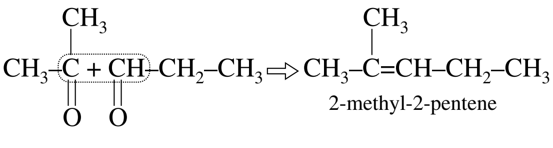
$$CH_3-CH\overset{}{=}CH-CH_3 \xrightarrow[Zn/H_2O]{O_3} 2CH_3-CH=O$$

(Ozonolysis)

9. [2]



10. [3]

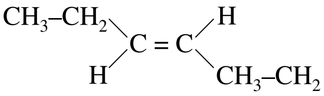


$$CH_3-\underset{\underset{O}{\|}}{\overset{\overset{CH_3}{|}}{C}} + \underset{\underset{O}{\|}}{CH}-CH_2-CH_3 \Rightarrow CH_3-\overset{\overset{CH_3}{|}}{C}=CH-CH_2-CH_3$$

2-methyl-2-pentene

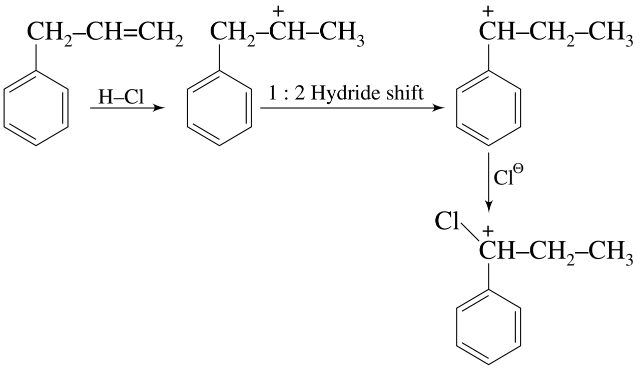
11. [1]

$$CH_3-CH_2-CH=CH-CH_2-CH_3 \xrightarrow[\text{Birch reduction}]{Li/NH_3}$$



Trans-2-hexene

12. [3]



13. [4]

Factual

14. [3]

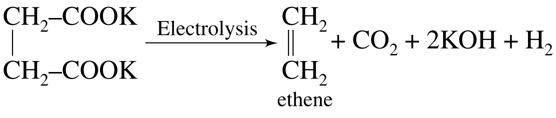
$$CH_3-CH=CH_2 \xrightarrow[H_2O_2/NaOH]{B_2H_6/THF} CH_3-CH_2-CH_2-OH$$

Trick → AMK addition of $H^+/\bar{O}H$ (Hydration)

15. [3]

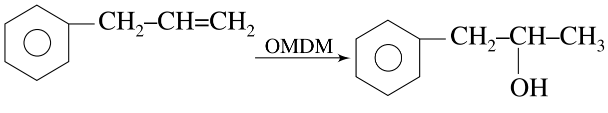
Li/NH_3 (Birch reduction) achieved vig., anti addition.

16. [3]



$$\begin{array}{l}CH_2-COOK\\ |\\ CH_2-COOK\end{array} \xrightarrow{\text{Electrolysis}} \underset{\text{ethene}}{\begin{array}{c}CH_2\\ \|\\ CH_2\end{array}} + CO_2 + 2KOH + H_2$$

17. [1]

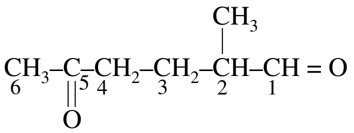


Hydration according to M.K rule

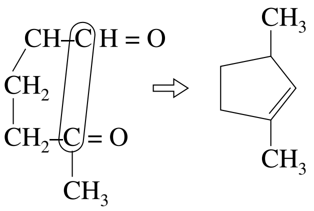
18. [1]

Factual

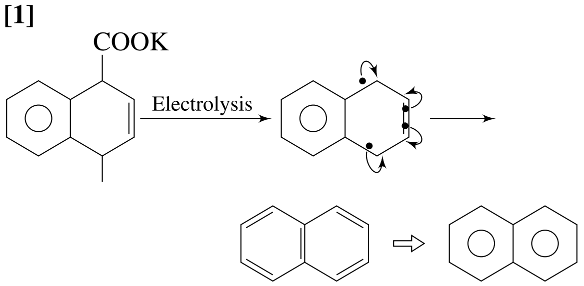
19. [2]



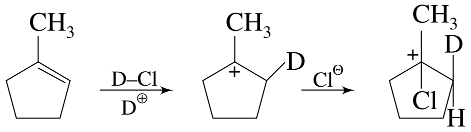
$\underset{6}{CH_3}-\underset{\underset{O}{\|}}{\overset{5}{C}}-\underset{4}{CH_2}-\underset{3}{CH_2}-\underset{2}{\overset{\overset{CH_3}{|}}{CH}}-\underset{1}{CH}=O$



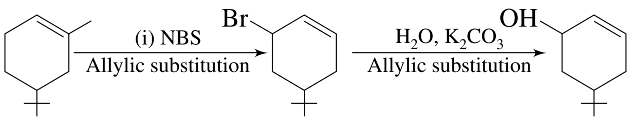
20. [1]



21. [1]



22. [2]

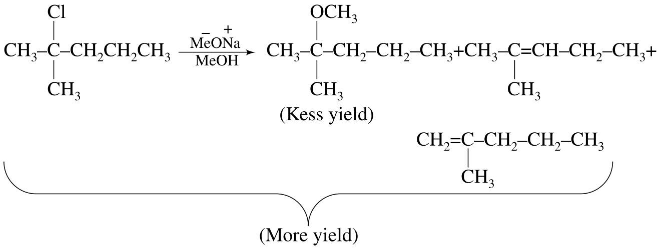


23. [2]

$CH_3-\overset{\oplus}{C}H=CH_2 \xrightarrow[E.AR]{\overset{-}{HO}/\overset{\oplus}{Cl}} CH_3-\overset{+}{C}H-CH_2-Cl$

24. [4]

($\bar{O}Me$) in polar solvent (MeOH) gives elimination products over substitution products but all products are possible in different yields.



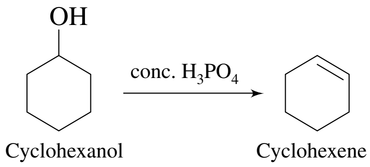
$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Cl}{|}}{C}}-CH_2CH_2CH_3 \xrightarrow[MeOH]{Me\overset{-}{O}\overset{+}{Na}} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OCH_3}{|}}{C}}-CH_2-CH_2-CH_3+CH_3-\underset{\underset{CH_3}{|}}{C}=CH-CH_2-CH_3+CH_2=\underset{\underset{CH_3}{|}}{C}-CH_2-CH_2-CH_3$

(Kess yield)

(More yield)

25. [1]

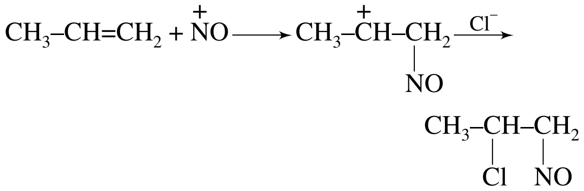
Cyclohexanol, on treatment with concentrated H_3PO_4 undergo acid catalysed dehydration giving cyclohexene.



26. [1]

NOCl undergoes electrophilic addition on alkene as

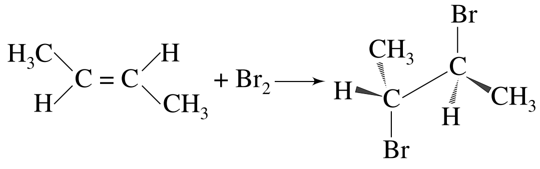
$NOCl \longrightarrow {}^{+}N=O + Cl^{-}$



$CH_3-CH=CH_2+\overset{+}{N}O \longrightarrow CH_3-\overset{+}{\underset{\underset{NO}{|}}{C}H}-CH_2 \xrightarrow{Cl^{-}} CH_3-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{NO}{|}}{CH_2}$

27. [1]

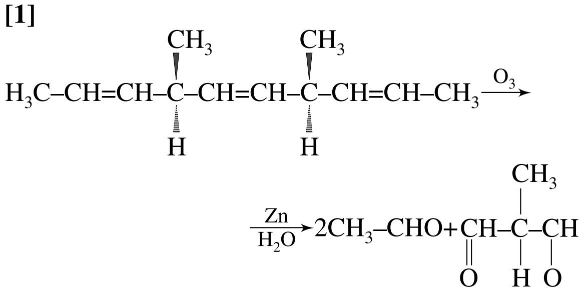
Br_2 undergoes *anti* addition on C = C bonds as:



(meso isomer)

Trick→TAM (refer Key concept)

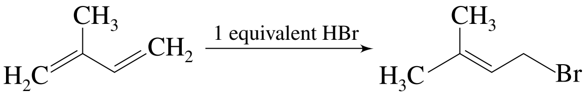
28. [1]



Since, none of the above dial is chiral, no optically active product is obtained.

29. [4]

1:4 addition takes place



30. [4]