11. ALKENES AND ALKYNES

UNSATURATED HYDROCARBONS

Contain carbon-carbon double or triple bonds (more hydrogen can be added).

1. INTRODUCTION OF ALKENES

Introduction - Structure and Bonding

- Alkenes are also called olefins, contain a carbon-carbon double bond.
- General formula: C_nH_{2n} (for one double bond)
- Suffix = – ene

Calculating Degrees of Unsaturation

1. An acyclic alkene has the general structural formula C_nH_{2n-2}.
2. Cycloalkanes also have the general formula C_nH_{2n}.
3. Each π-bond or ring removes two hydrogen atoms from a molecule and this introduces on degree of unsaturation.
4. The number of degrees of unsaturation for a given molecular formula can be calculated by comparing the actual number of H atoms in a compound and the maximum number of H atoms possible.
5. This procedure gives the total number of rings and or π bonds in a molecule.

2. NOMENCLATURE OF ALKENES

IUPAC Nomenclature of Alkenes

Step 1: Identify and name the longest continuous chain of C atoms which contains the double bond(s) (# C + -ene).

Step 2: Number the longest chain so that the C's joined by the double bond have the lowest numbers possible. If the double bond has the same position starting from either end, use the positions of the substituents to determine the beginning of the chain.

Step 3: Locate the double bond by the lower numbered C-atom joined by the double bond (e.g. 1-butene).

Step 4: Locate and name attached groups.

Step 5. Combine the names for the attached groups and the longest chain into the name.

If there is more than one double bond:

- A **counting prefix** (di-, tri-, tetra-, etc.) is placed immediately in front of the suffix **–ene** to indicate the number of double bond (diene, triene, tetraene, etc.).
- Usually, an ''a" is placed before the counting prefix to make pronunciation easier (e.g. butadiene).
- The starting position of each double bond is indicated by the lower number, separated by commas (e.g. 1, 3-butadiene).
- For cycloalkenes, the ring is named as **cyclo–** + #C + **-ene**; one of the carbons of the double bond must be numbered ''1".

Nomenclature of Alkenes

Some alkene or alkenyl substituents have common names.

The simplest alkene, $CH_2 = CH_{2n}$ named in the IUPAC system as ethene, is often called ethylene.

Illustration 1: Name of the following as substituted derivatives of ethylene. **(JEE MAIN)**

a. $CH_3 - CH = CH - CH_3$ b. $Cl_2C = CHCl$ c. $(CH_3)_2C = CH_2$

d. $(CH_2 = CH)_2C = CH_2$ e. $(CH_2 = CH) - CH = CH - (CH = CH_2)$

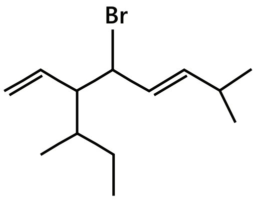
Sol: When both the carbons contain same substituents use the symmetrical (sym) and when both substituents are on the same C atom use unsymmetrical (unsym)

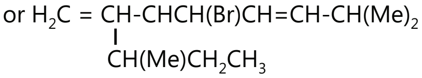
a. Sym-Dimethyl ethylene b. Trichloroethylene c. unsym-Dimethyl ethylene

d. unsym-Divinyl ethylene e. sym-Divinyl ethylene

Illustration 2: Write the IUPAC names of the following.

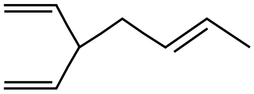
a.





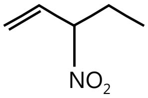
or $H_2C = \underset{\displaystyle CH(Me)CH_2CH_3}{CH}\text{-}CHCH(Br)CH{=}CH\text{-}CH(Me)_2$

b.



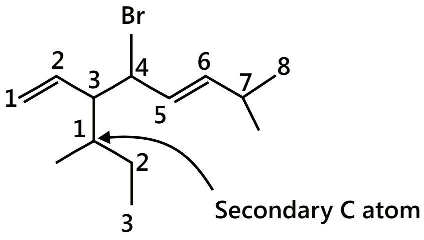
or $(H_2C = CH)_2CHCH_2CH = CHCH_3$

c.



or $CH_3CH = C(NO_2)CH_2CH_3$ **(JEE ADVANCED)**

Sol: (a)

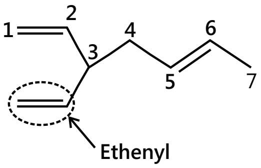


4-Bromo-3-(1-methylpropyl)-7-methyl-1, 5-octadiene

Or

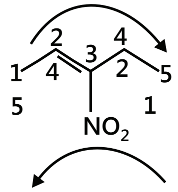
4-Bromo-3-(sec-butyl)-7-methyl-1, 5-octadiene

(b)



Choose the longest chain with two (C = C). There (C = C) cannot be taken into a single chain 3-Ethenyl-1, 5-heptadiene.

(c)



3-Nitro-pent-2-ene

3. HYBRIDIZATION OF ALKENES

1. When a carbon is connected to three other atoms (that is, one of the bonds is a double bond), the molecules are modelled by combining the 2s and two of the 2p-orbitals to produce **three sp^2-orbitals**.
2. Since only two of 2p orbitals where hybridized, there is one leftover p orbital in an sp^2-hybridized carbon atom.

Introduction – Structure and Bonding

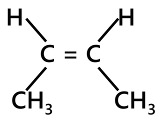
Recall that the double bond consists of a π -bond and a σ -bond.

Each carbon is sp^2 hybridized and trigonal planar, with bond angles of approximately 120°.

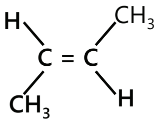
4. ISOMERIZATION

Geometric Isomers in Alkenes

1. Free rotation is not possible around double bonds, therefore there are two different forms of 2-butene, which are **geometric isomers** of each other.
2. The prefix **cis-** is used when the two arms of the longest chain are on the **same side** of the double bond; the prefix **trans**- is used when they are on **opposite sides** of the double bond.
3. Geometric isomers can have drastically different chemical and physical properties.



cis-2-butene

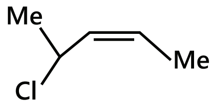


trans-2-butene

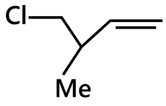
Illustration 3: Which of the following do not show G.I.?

(JEE MAIN)

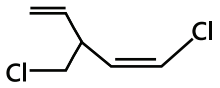
a.



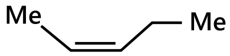
b.



c.

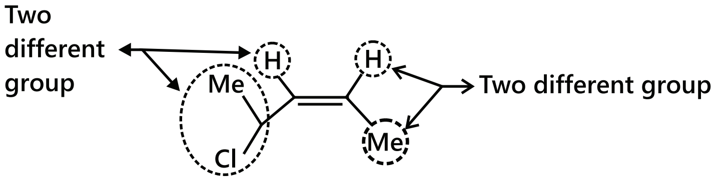


d.



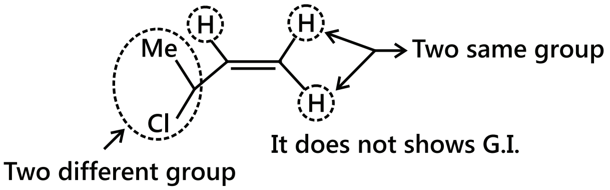
Sol: In order to show Geometrical isomerism, the alkene must contain different substituents.

(a)



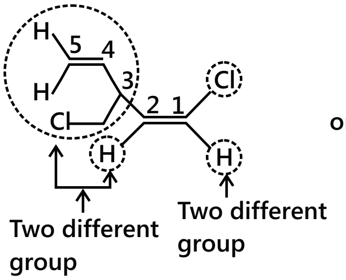
Its show G.I.

(b)

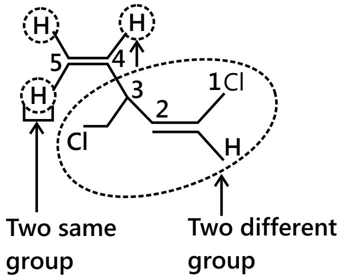


Option (b) does not show G.I

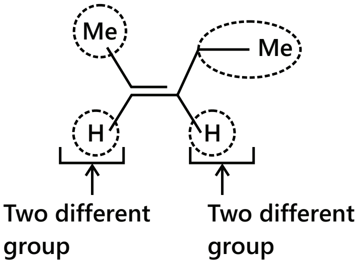
(c) Option (c) show G.I. at the double bond between $C_1 - C_2$ but does not show G.I. at the double bond between $C_4 - C_5$.



or



(d)

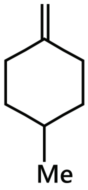


Shows G.I

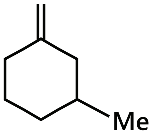
Shows G.I

Illustration 4: From the following G.I. shown by:

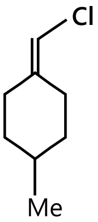
(a)



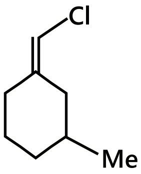
(b)



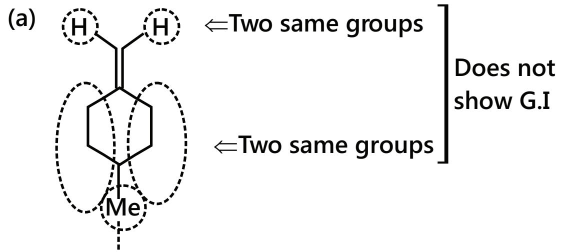
(c)

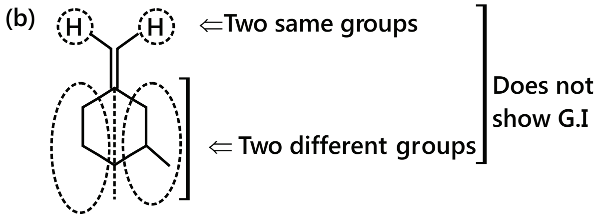


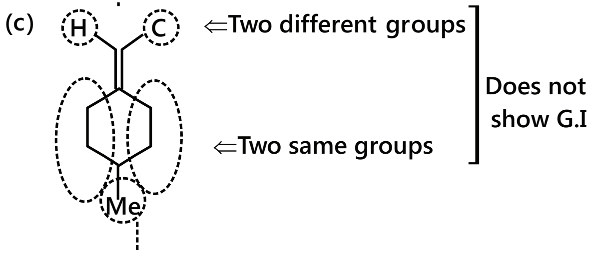
(d)

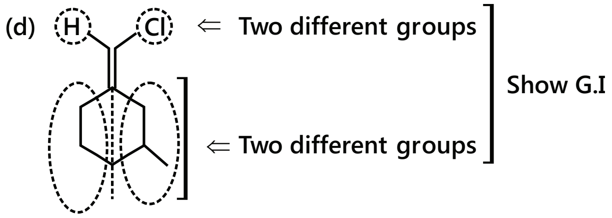


Sol: In order to show Geometrical isomerism the alkene must contain different substituents .i.e. the substituents on both the carbon bearing double bonds must have different substituents. **(JEE ADVANCED)**



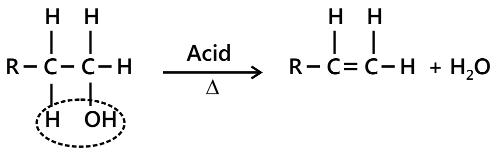






5. PREPARATION OF ALKENES

5.1 Dehydration of alcohols



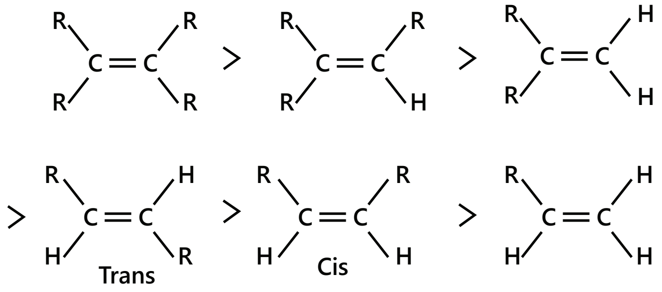
$$\mathrm{R-\underset{H}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-H \xrightarrow[\Delta]{Acid} R-\overset{H}{C}=\overset{H}{C}-H + H_2O}$$

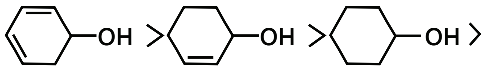
Ease of dehydration of alcohols: 3° > 2° > 1°, because the alkenes formed are more stable.

Various dehydrating agents can be used for the dehydration of alcohols:

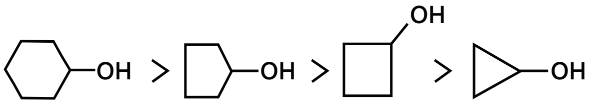
1. Conc. H_2SO_4 at 443 – 453 K (170 – 180°C) acts as Lowry Bronsted acid $H^{\oplus}$ donor.
2. H_3PO_4 (Phosphoric acid at 470 K).
3. Al_2O_3 at 633 K (380°C) acts as a Lewis acid.
4. Heating with P_2O_5 or P_4O_{10} (phosphorous pentoxide).
5. Heating with $POCl_3$ (phosphorous oxychloride) + pyridine.
6. Heating with $KHSO_4$.

Stability order of alkene: More substituted alkenes is more stable (due to hyperconjugation).



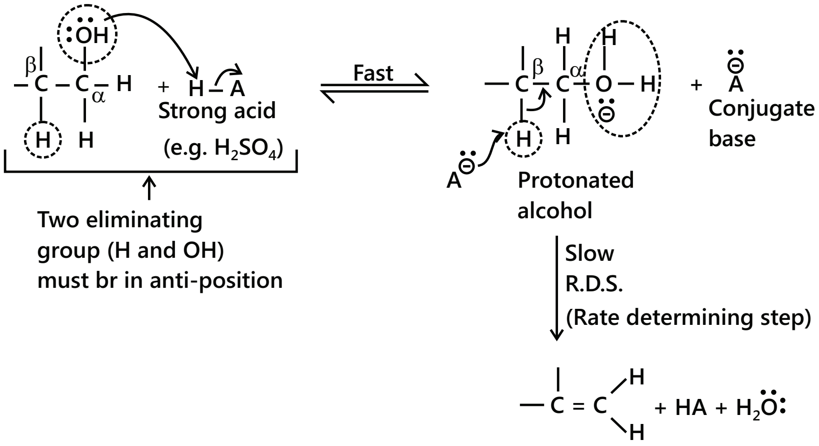


(Stabilisation by extended conjugation)



(Due to ring stability)

Mechanism of dehydration of 1° alcohols: E_2 mechanism



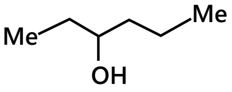
1. The first step in the dehydration of 1° alcohols is protonation.
2. The second step is the attack of C_B (conjugated base) at –proton(-OH_2^+) and the elimination of protonated hydroxyl group (a good leaving group) takes place simultaneously to form double bond.

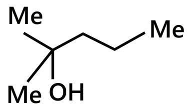
   $$\text{Rate}=k\left[\overset{\ominus}{\ddot{A}}\right]\text{[protonated alcohol]}$$

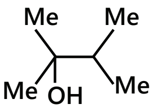
3. Kinetics of the reaction is of the second order and bimolecular.
4. Two eliminating groups (i.e., H and OH groups) must be in anti-position.
5. Reaction is stereospecific and stereo selective (or regioselective).
6. No rearrangement takes place.

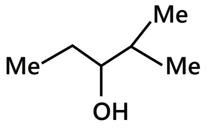
Illustration 5: Arrange the following alcohols in the decreasing order of their ease of dehydration with H_2SO_4.

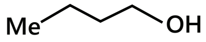
(JEE MAIN)

a.


b.


c.


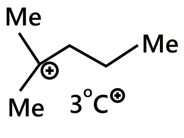
d.


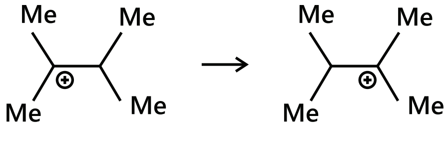
e.


Sol: Order of stability of carbocation: 3°>2°>1°

Depending upon the formation of carbocation we can explain the order of reactivity.

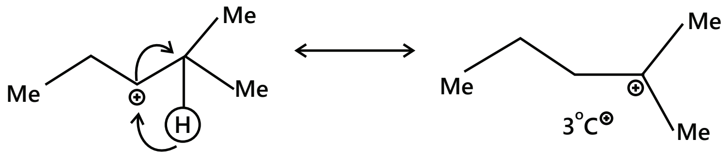
We can see that options (b) and (c) are 3° alcohols, since dehydration of alcohol proceeds through the formation of carbocation, we have to take into consideration the stability of carbocation. 3° carbocation in (c) is more stable due to resonance and gives a more substituted alkene.

(b)


(c)


Remaining (a) and (d) both are 2° alcohols , 2° carbocation can be stabilized to 3° via 1, 2-$H^{\ominus}$ shift and gives a more substituted alkene

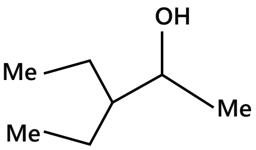
(d)



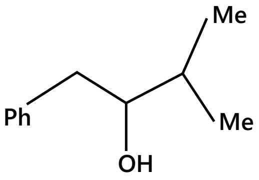
So, the order of dehydration is: (c) > (b) > (d) > (a) > (e)

Illustration 6: Give the products of the reaction with conc. H_2SO_4 of: **(JEE ADVANCED)**

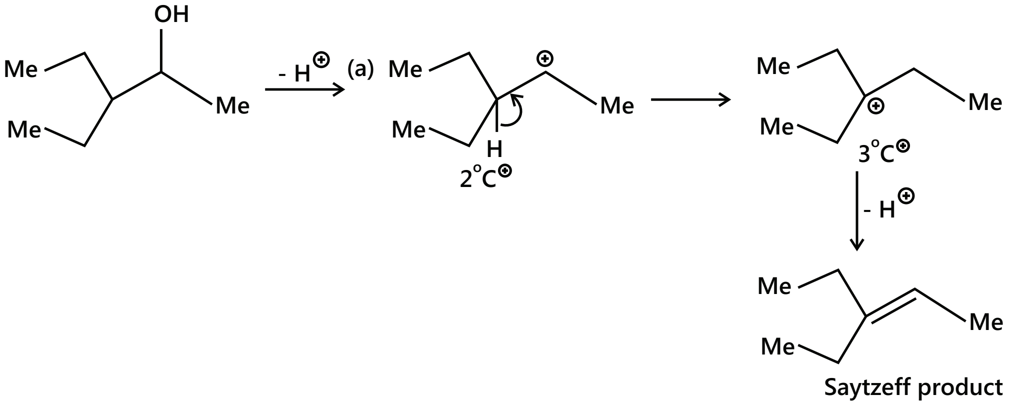
(a)



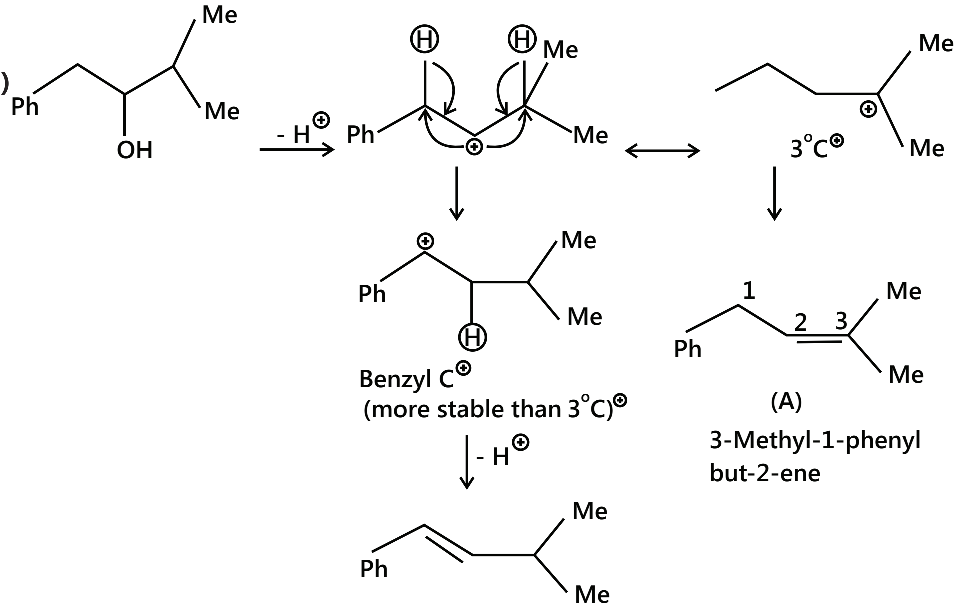
(b)



Sol: **(a)**



(b)

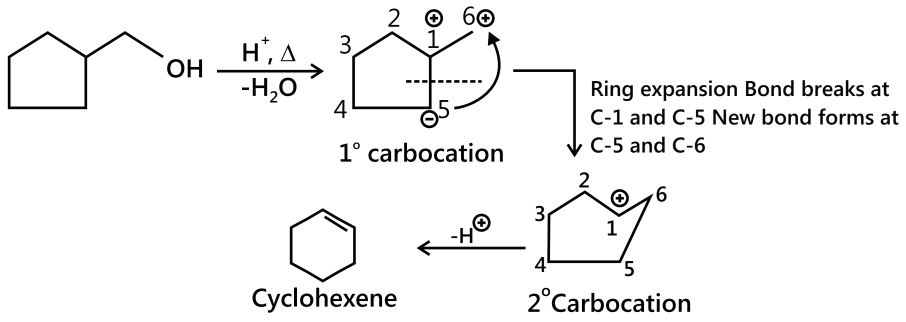


5.2 Rearrangement and Ring Expansion

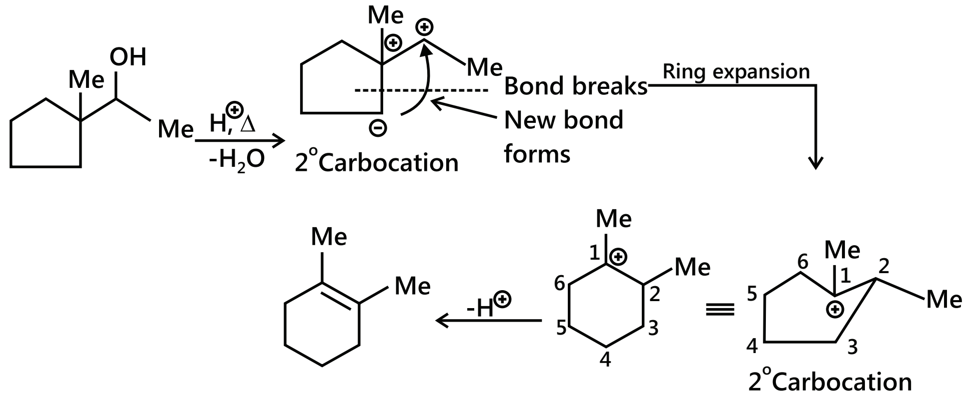
Rearrangement results in the substitution, elimination, and ring expansion or ring contraction. In case of cyclic alcohols, whenever a carbocation is formed outside, the next C atom of a ring, ring expansion may take place, if a relief in the ring strain occurs.

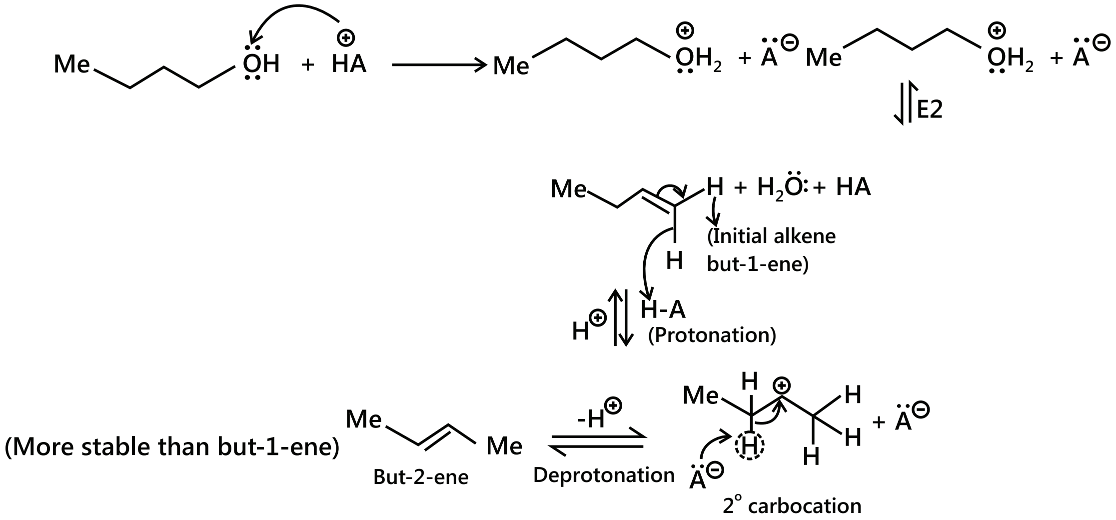
Examples of Ring Expansion:

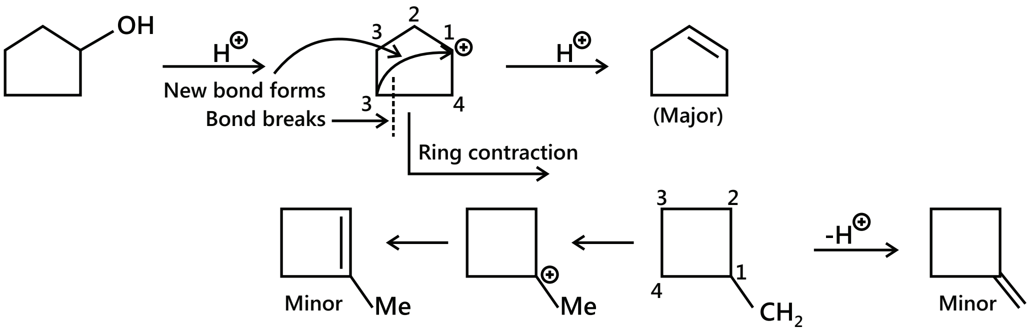
1.



2.







Whenever a carbocation is formed on the ring, ring contraction takes place. But in this case, ring strain is not relieved (because higher homologue cyclic ring has to change to lower one), however, the products corresponding to ring contraction are formed in smaller amounts.

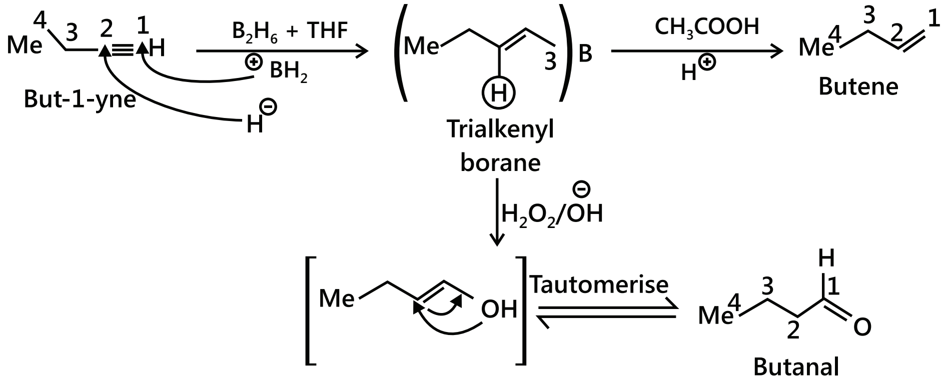
5.3 From Alkynes

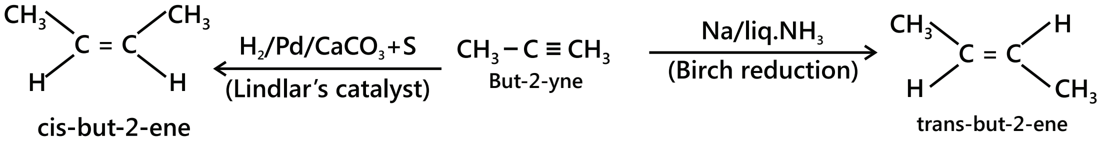
1. By partial reduction of alkynes. The catalytic hydrogenation of alkynes to alkenes occurs faster than that of alkenes to alkanes. Therefore, by using a specific catalyst, it is possible to stop the reduction to give cis-or trans-alkenes depending upon the nature of the catalyst used.

(i) Cis-alkenes are formed by hydrogenation in presence of (i) Pd/$BaSO_4$ or $CaCO_3$ poisoned with $PbCO_3$ or Lindlar's catalyst(quinolone) (ii) B_2H_6 in THF/ ether+ CH_3COOH.

(ii) Trans-alkenes are formed by hydrogenation in presence of Na+liq.NH_3(Birch reduction)

(a) With terminal alkyne.





(b) With internal alkynes:

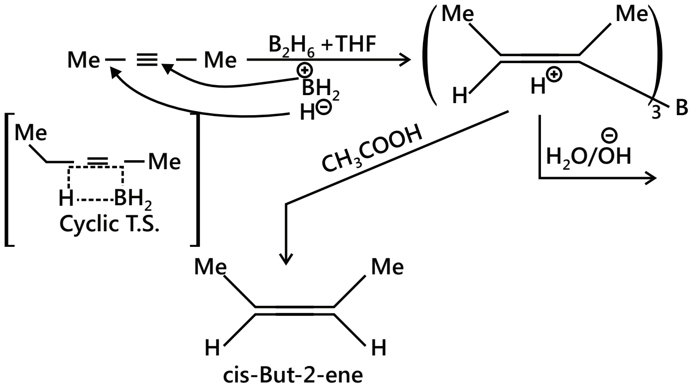
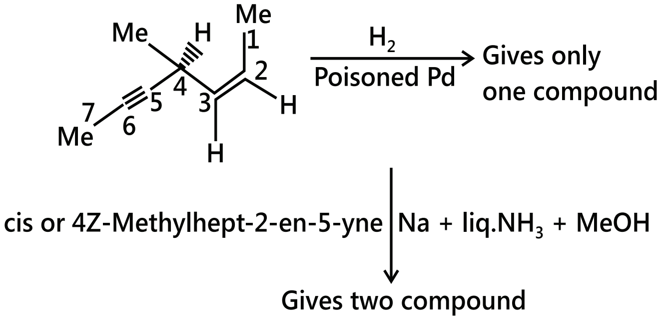


Illustration 7: Explain **(JEE ADVANCED)**



Sol: Here the reactant contains a chiral center hence it is optically active. On reduction with palladium it produces cis product hence the chirality is lost thus it is optically inactive. (Carbon contains two of the same groups)

On birch reduction Trans addition takes place thus product is trans and it is optically active. It gives two product d and l.

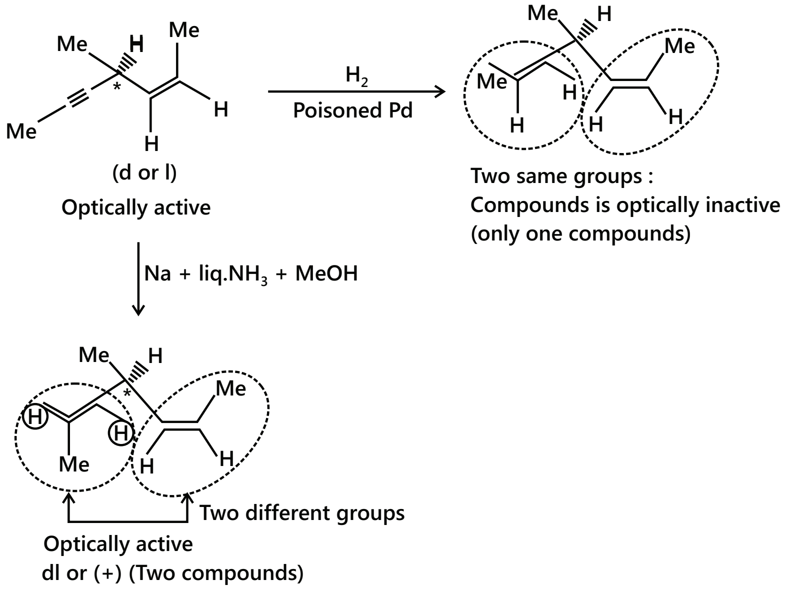
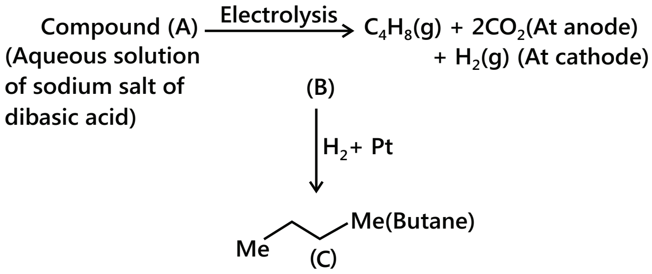


Illustration 8: Identify A and B

(JEE MAIN)



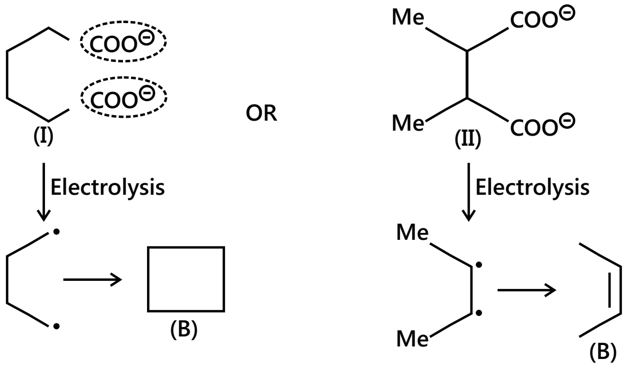
Gas (B) gives test for unsaturation, i.e. it decolourises Br_2 water and aq. $KMnO_4$ solution.

Sol: From the given data it appears that the starting compound contains 6 carbon in its backbone. (Since product formed is butene (4 carbon) and 2 molecule of CO_2 (2 carbon).

Thus the compound (A) should be 6 C-atom dibasic acid (four C atoms of (B) or (C) and two (COOH) groups.

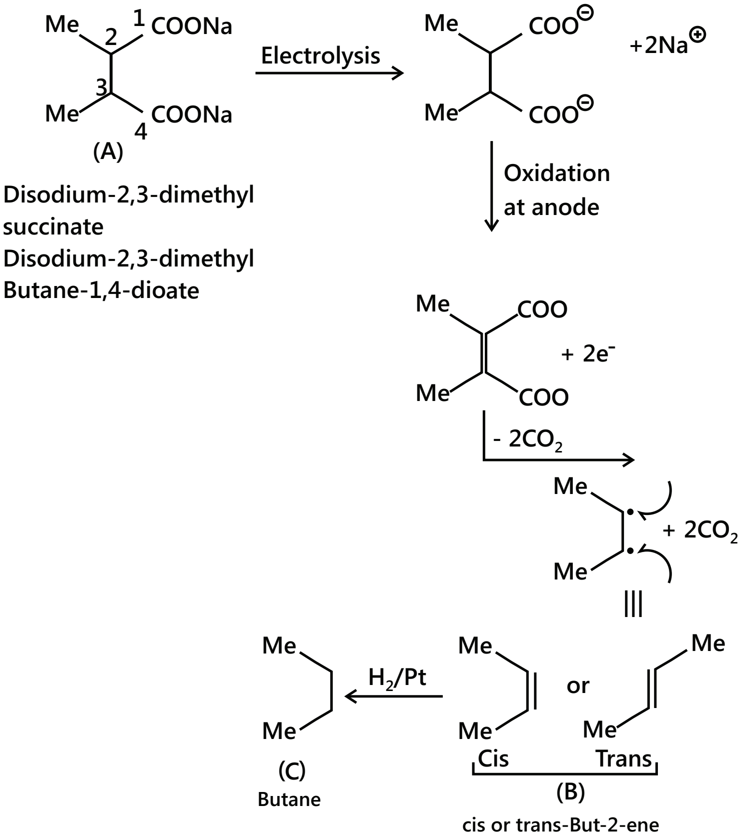
The first step is Kolbe's Electrolysis which proceeds through free radical mechanism.

The two possible structure of the dibasic acids are as follows:



As given B gives test for unsaturation, therefore, (A) can be (II).

Possible reaction is as follows:

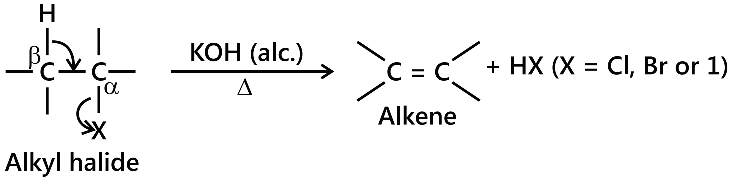


At the cathode, the reduction of H_2O takes place (since reduction potential of H_2O > reduction potential of Na^+ ion).

$$H_2O + e^{\Theta} \rightarrow \overset{\Theta}{O}H + 1/2H_2(g)$$

5.4 From Alkyl Halides

From alkyl halides or haloalkanes: Alkyl halides on heating with a strong base such as sodium ethoxide or concentrated alcoholic solution of potassium hydroxide undergo dehydrohalogenation to give alkenes.



E.g. $\overset{\beta}{C}H_3\overset{\alpha}{C}H_2 - I + KOH\,(alc.) \xrightarrow{353\text{-}363\ K} CH_2 = CH_2 + KI + H_2O$

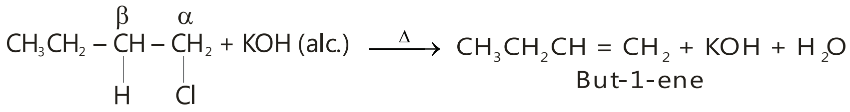
Iodoethane (Ethyl iodide) — Ethene (Ethylene)

$CH_3\overset{\beta}{C}H_2 - \overset{\alpha}{C}H_2 - Br + KOH\,(alc.) \xrightarrow{353\text{-}363\ K} CH_3CH = CH_2 + KBr + H_2O$

1-Bromopropane (n-Propyl bromide) — Propene (Propylene)

This process of the removal of a molecule of a halogen halide (HCl, HBr or HI) from a haloalkane to form an alkene is called dehydrohalogenation. Dehydrohalogenation is an example of an elimination reaction. Since, in this reaction, a hydrogen is removed from β-carbon and halogen from the α-carbon, therefore, it is called β-elimination reaction. The ease of dehydrohalogenating of alkyl halides having the same alkyl group but different halogens is: iodides > bromides > chlorides while for isomeric alkyl halides having the same halogen but different structures is: tertiary > secondary > primary. Thus, a tertiary alkyl iodide is most reactive.

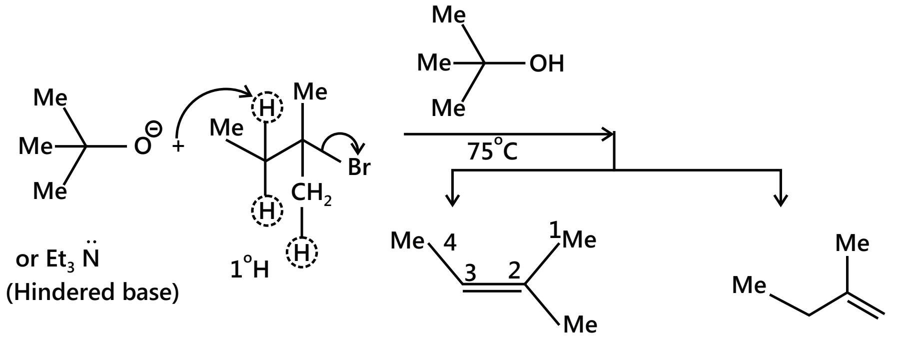
Saytzeff rule: Depending upon the structure, alkyl halides may give one or more isomeric alkenes. For example, dehydrohalogenation of 1-chlorobutane gives only one alkene, i.e., but-1-ene since only one type of β-hydrogen is available on the left side of the molecule.



$$CH_3CH_2-\underset{H}{\overset{\beta}{CH}}-\underset{Cl}{\overset{\alpha}{CH_2}} + KOH\,(alc.) \xrightarrow{\Delta} \underset{\text{But-1-ene}}{CH_3CH_2CH=CH_2} + KOH + H_2O$$

1-Chlorobutane

1. When a bulky base is used, e.g. potassium tert-butoxide in tert-butyl alcohol or $Et_3\ddot{N}$, for the dehydrohalogenation of RX, the less-substituted alkene (Hofmann product) is favoured.



2-Methyl-but-2-ene (27.5%) More substituted

2-Methyl-but-1-ene (72.5%) Less substituted

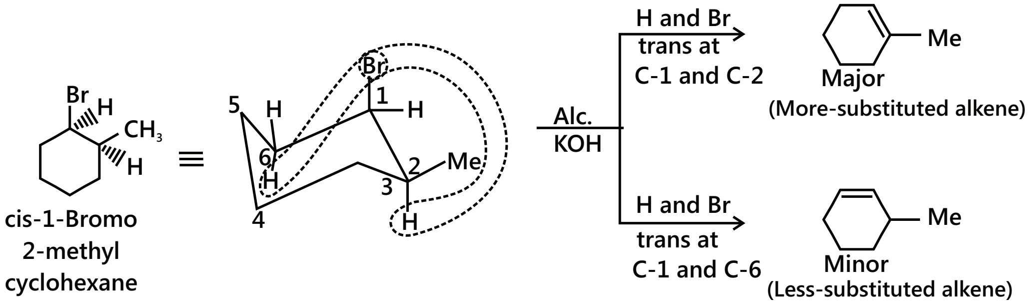
It is due to the steric hindrance of the bulky base. The large tert-butoxide ion finds difficulty in removing one of the internal 2° H atoms because of greater steric hindrance (or crowding) at that site in the transition state (T.S.). It removes one of the more exposed 1°H atoms of the methyl group and gives less-substituted alkene, i.e. follows Hofmann's rule.

If the RX contains one or more double bonds, then the Saytzeff product is not formed, instead a product containing a conjugated double bond is formed rather than containing an isolated double bond, since conjugated double bonds are more stable than isolated double bonds.

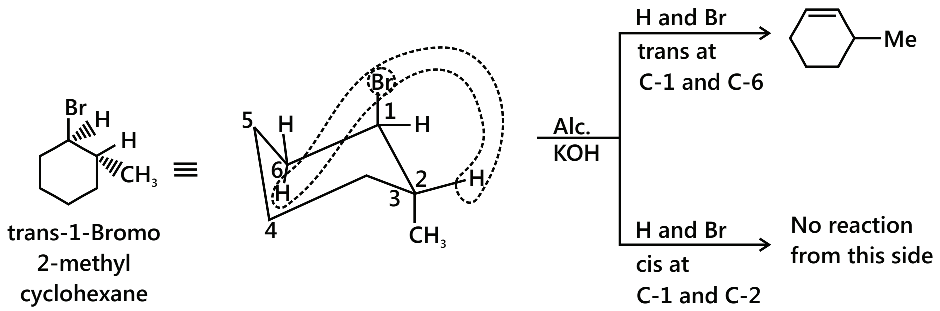
When the more substituted alkene obtained by Saytzeff rule is sterically hindered, the less-substituted alkene is formed in a major amount.

Stereo chemical requirement: For E_2 dehydrohalogenation, two eliminating groups must be in trans position and must yield anti-elimination reaction.

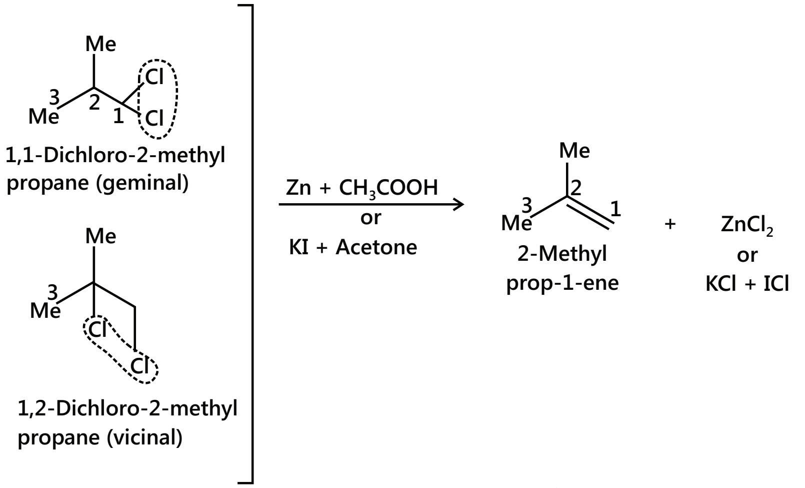
(i) Anti-elimination can occur in two ways with cis-isomer.

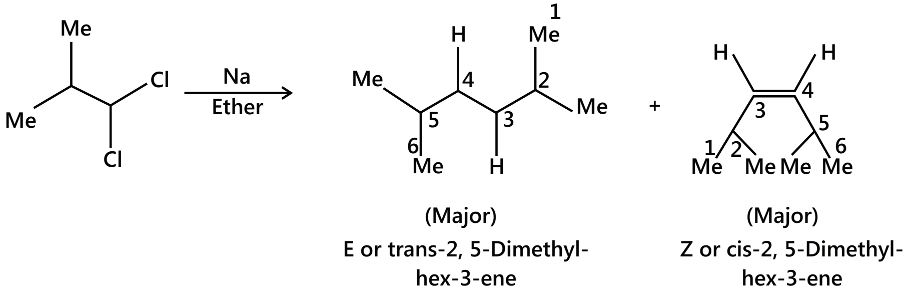


(ii) Anti-elimination can occur in one way with the trans- isomer.



Dehalogenation Geminal (1, 1-dihalogen) and vicinal (1, 2-dihalogen) derivatives of alkane with (Zn dust + EtOH or CH_3COOH) or KI + acetone or (Na + ether) give alkene.

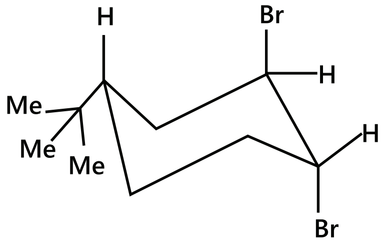


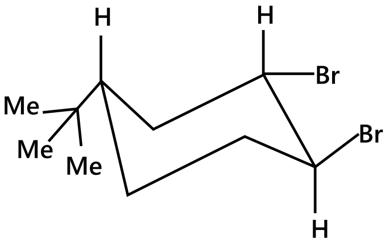


E_2 Dehalogenation is anti

Reaction is stereospecific

Note: The presence of tert-butyl group on equatorial position does not allow the flipping of the equatorial Br to axial Br.





A forms alkene B does not.

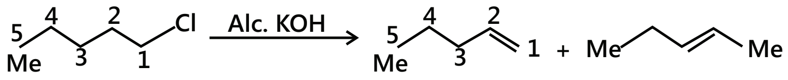
Illustration 9: Identify all the possible alkenes that would be formed on the dehydrohalogenation of the following organic halides with alcoholic KOH. Also, identify the major alkene.

(a). 1-Chloropentane (b). 2-Chloropentane (c). 2-Chloro-2-methyl butane **(JEE ADVANCED)**

Sol: Identify the carbocation that is going to form during the reaction and accordingly predict the product (minor and major).

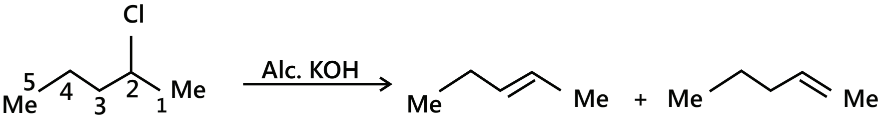
Order of stability of carbocation – tert> sec>primary.

(a)



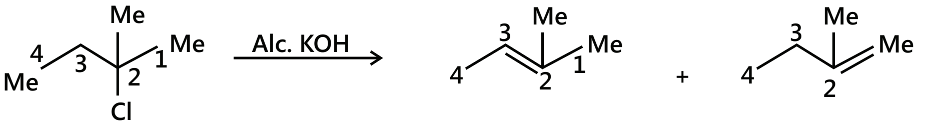
Pent-1-ene (Minor) Pent-2-ene (Major)

(b)



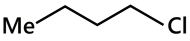
Pent-2-ene (Major) Pent-1-ene (Minor)

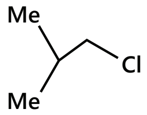
(C)

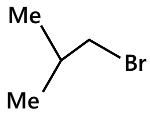


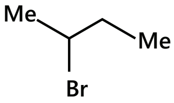
2-Methyl but-2-ene (Major) 2-Methyl but-1-ene (Minor)

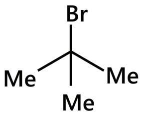
Illustration 10: Predict the order of reactivity of the following compounds in dehydrohalogenation. **(JEE MAIN)**

I. 

II. 

III. 

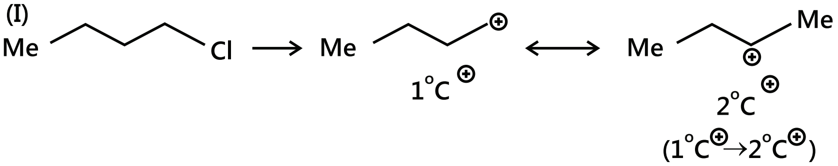
IV. 

V. 

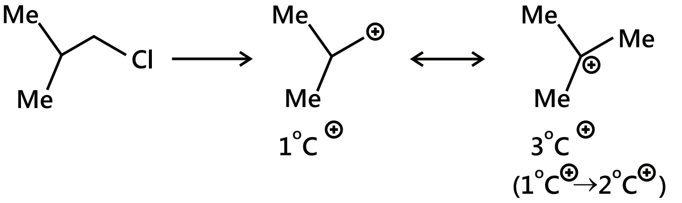
Sol: Order of formation of carbocation is 3° > 2° > 1°

Correct order of reactivity is (V) > (III) > (II) > (IV) > (I)

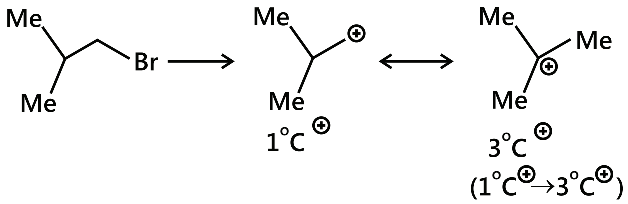
(I)



(II)

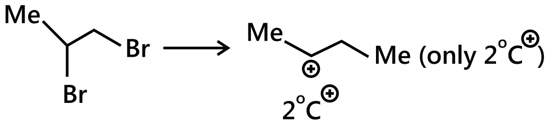


(III)



(II) and (III) both involves formation of tertiary carbocation but ease of formation of carbocation in (III) is more than in (II), because the reactivity order of RX is RI > RBr > RCl > RF due the leaving group order of $I^{\ominus} > Br^{\ominus} > Cl^{\ominus} > F^{\ominus}$

(IV)



(V)

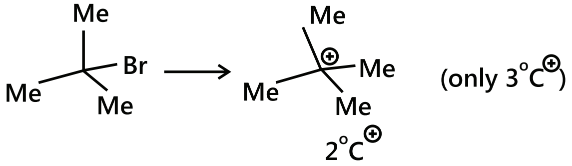
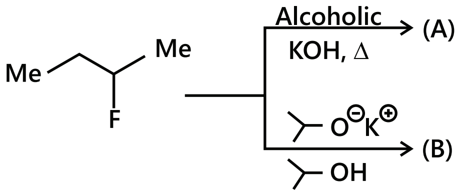
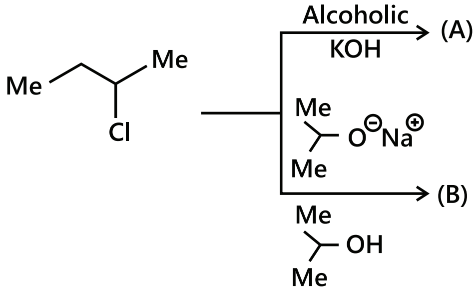


Illustration 11: Given the major and minor products of the following reactions.

a.

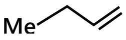


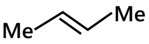
b.

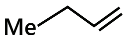


(JEE ADVANCED)

Sol: Depending upon the base used, predict the product. If the bulky base is used, the Hoffmann product (less substituted alkene, less stable) will predominate. If the non- bulky base is used, Saytzeff product (more substituted, more stable) will predominate.

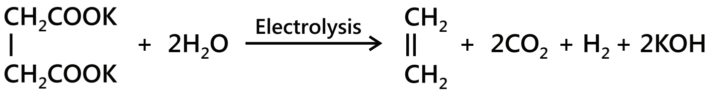
(a) Here RX is RF, thus less-substituted alkene (Hofmann elimination) is formed, irrespective of whether the base is bulky or non-bulky. Both (A) and (B) are same. 

(b) (A) Base used is non bulky thus the Saytzeff product is formed (More-substituted alkene) 

(B) Base used is bulky thus the Hofmann product is formed (Less-substituted alkene) 

5.5 Kolbe's Electrolytic Method

Electrolysis of sodium or potassium salts of saturated dicarboxylic acids gives alkenes. For example,

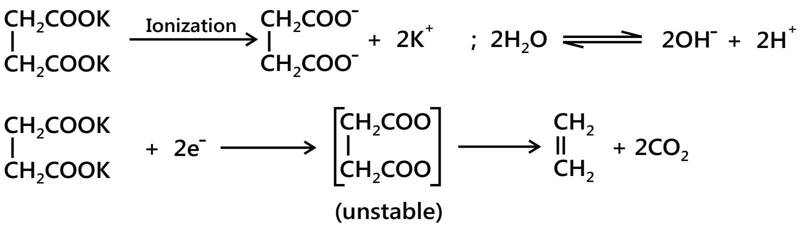


$$\begin{matrix} CH_2COOK \\ | \\ CH_2COOK \end{matrix} + 2H_2O \xrightarrow{\text{Electrolysis}} \begin{matrix} CH_2 \\ || \\ CH_2 \end{matrix} + 2CO_2 + H_2 + 2KOH$$

Pot. succinate   Ethylene

The reaction is believed to occur by the following steps:

At anode:



$$\begin{array}{l}CH_2COOK\\|\\CH_2COOK\end{array} \xrightarrow{\text{Ionization}} \begin{array}{l}CH_2COO^-\\|\\CH_2COO^-\end{array} + 2K^+ \quad ; \; 2H_2O \rightleftharpoons 2OH^- + 2H^+$$

$$\begin{array}{l}CH_2COOK\\|\\CH_2COOK\end{array} + 2e^- \longrightarrow \underset{\text{(unstable)}}{\left[\begin{array}{l}CH_2COO\\|\\CH_2COO\end{array}\right]} \longrightarrow \begin{array}{c}CH_2\\||\\CH_2\end{array} + 2CO_2$$

At cathode. Since the electrode potential of H^+ ions is much higher than that of K^+ ions, therefore, H^+ ions are preferentially reduced to produce H_2 while K^+ ions remain in the solution.

$$2H^+ + 2e^- \longrightarrow [2H] \longrightarrow H_2$$

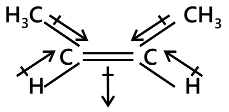
6. PHYSICAL PROPERTIES OF ALKENES

1. Only weak Vander Waals interactions, have low melting points and boiling points which increases with increased in surface area as the number of carbon increases.
2. Alkenes are soluble in organic solvents and insoluble in water.
3. Cis-2-Butene has a higher boiling point {4°C} than trans-2-butene {1°C} because in cis isomer, two C-C bond dipoles rain force each other yielding a small net molecular dipole.
4. Range of physical states: $\leq 4C's - \text{gases}, 5-17\,C's - \text{liquid}, \geq 18\ C's - \text{solids}$.
5. Less dense than water as a result floats on water. Flammable and non-toxic.

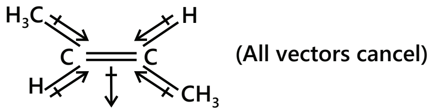
6.1 Boiling Point

Boiling points of all these hydrocarbons increase with the increase in the carbon content; for each added $-CH_2-$) group, boiling point rises from 20°C to 30°C. Because of the presence of π-bonds, these molecules are slightly polar and, hence, have a higher boiling points than those of the corresponding alkanes.

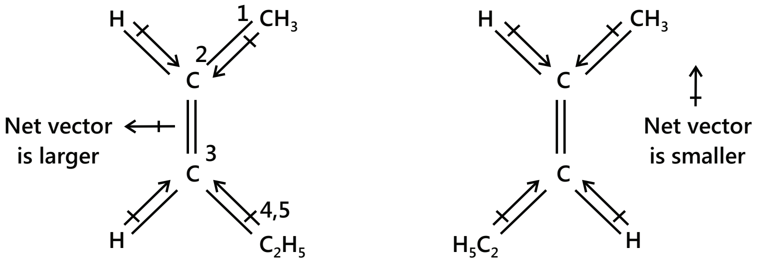
In alkenes that show geometrical isomerism, generally boiling point of cis form is higher than the trans form due to the high polarity of the cis isomer compared to its trans isomer.



Net dipole
It shows dipole moment
(Hence, slightly polar)
b.p. (277 K)



Dipole moment = 0
(Non-polar)
b.p. (274 K)



cis-Pent-2-ene
(A)

trans-Pent-2-ene
(B)

Dipole moment of (A) > Dipole moment of (B)
(A) is more polar than (B)
b.p. of > b.p. of (B)

In alkenes that show geometrical isomers, trans forms have higher melting points than cis forms because the more symmetrical trans forms pack closely in the crystal lattice.

Similarly, out of o^-, m^- and p-xylenes, the p-isomers that are most symmetrical have the highest melting point.

6.2 Solubility

The solubility in non-polar solvents are in the following order: alkanes > alkenes > alkynes. Alkanes and alkynes are thereby, only very slightly soluble in water (with alkynes being slightly more soluble than alkenes). The densities of alkenes and alkynes are lower than that of water.

Illustration 12: i. Predict the more stable alkene of each pair.

ii. For which pairs could you use ΔH_h°?

iii. For which pairs could you use ΔH_C° to determine their relative stabilities?

I. (a) 2-Methyl-pent-2-ene

(b) 2,3-Dimethyl-but-2-ene ΔH_C°

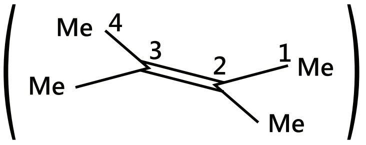
II. (c) Hexene (d) cis-Hex-3-ene

III. (e) trans-Hex-2-ene (f) 2-Methyl-pent-2-ene

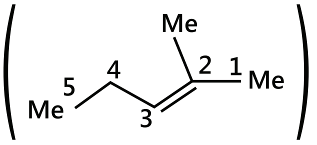
IV. (g) cis-Hex-3-ene (h) trans-Hex-3-ene **(JEE MAIN)**

Sol:

(I)



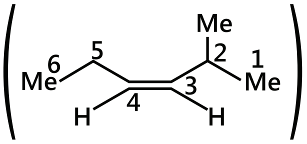
is more stable than (a)



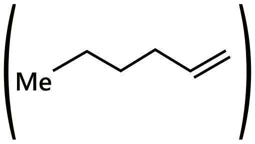
(tetra-substituted) **(tri-substituted)**

ΔH_h° cannot be used because the same alkane is not produced on hydrogenation. So, ΔH_C° is used to determine the relative stabilities of the alkene pairs because on complete combustion, the alkene requires same moles of O_2 and produces same moles of CO_2 and H_2O (same formula: C_6H_{12}).

(II)



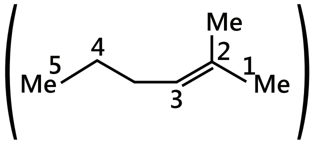
is more stable than (c)



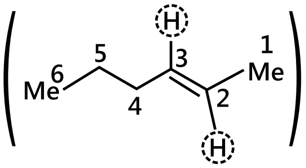
(Di-substitued) **(Mono-substitued)**

ΔH_h° is used to determine the relative stabilities of the alkene pair because on hydrogenation two alkenes would yield the same alkane.

(III)



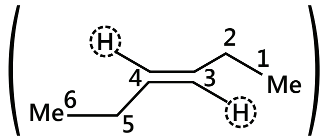
is more stable than (e)



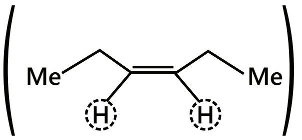
(Tri-substituted) **(Di-substitued)**

ΔH_C° is used, since it will not produce the same alkane on hydrogenation but on combustion alkene requires same moles of O_2 and produces same moles of CO_2 and H_2O (same formula: C_6H_{12}).

(IV)



is more stable than (g)



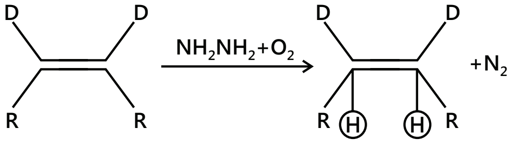
7. REACTIONS OF ALKENES

7.1 Hydrogenation of Alkenes

Hydrogenation of alkenes can be carried out by the following reagents:

1. Pt or Pd or Ni or PtO_2
2. Pd + C or Pt + C (C ⇒ charcoal), Wilkinson's catalyst $[RhCl(Ph_3P)_3]$ Chlorotris (triphenyl phosphine) rhodium (I)
3. $NaBH_4 + AlCl_3$ in diglyme (solvent)
4. $NaBH_4 + PtCl_2$

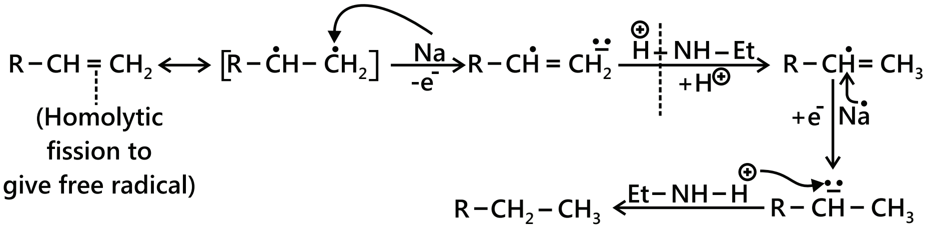
Hydrazine $(NH_2NH_2 + O_2)$



5. Birch Reduction: Birch reduction (alkali metals, such as Na and K in liquid $NH_3 + EtOH$ or MeOH), Mechanism of only terminal (C = C) bond to (C – C) bond:

$$NH_2-H + HO-Et \longrightarrow Ⓗ - \dot{N}H - Et + H_2O$$

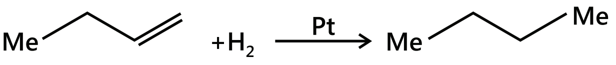
Source of H atom is from liquid NH_3. If ND_3 is used, D atom will be added.



Heat of hydrogenation: The energy released when one mole of alkenes is hydrogenated with H_2 is called the heat of hydrogenation.

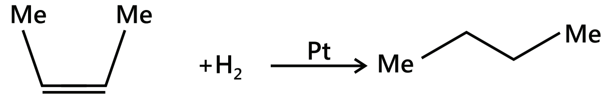
More negative the heat of hydrogenation of an alkene, less stable is the alkene. So, the stability order is as follows:

Trans-But-2-ene > cis-But-2-ene > But-1-ene



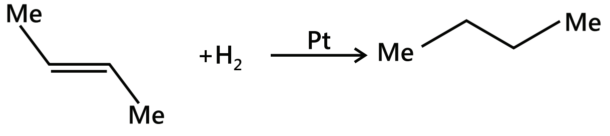
But-1-ene

ΔH° = -127 kJ mol^{-1}



cis-But-2-ene

ΔH° = -120 kJ mol^{-1}

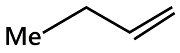


trans-But-2-ene

ΔH° = -115 kJ mol^{-1}

Heat of Combustion: When the hydrogenation of the alkene does not give the same alkane, the heat of combustion is used to measure their relative stabilities. More negative the value of ΔH_C°, less stable is the compound or vice versa.

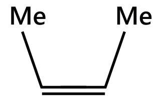
I.



$+ 6O_2 \longrightarrow 4CO_2 + 4H_2O \qquad \Delta H_c^\circ = -2720\ kJ\ mol^{-1}$

But-1-ene

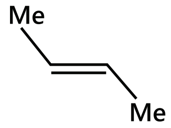
II.



$+ 6O_2 \longrightarrow 4CO_2 + 4H_2O \qquad \Delta H_c^\circ = -2710\ kJ\ mol^{-1}$

cis-But-2-ene

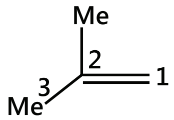
III.



$+ 6O_2 \longrightarrow 4CO_2 + 4H_2O \qquad \Delta H_c^\circ = -2705\ kJ\ mol^{-1}$

trans-But-2-ene

IV.



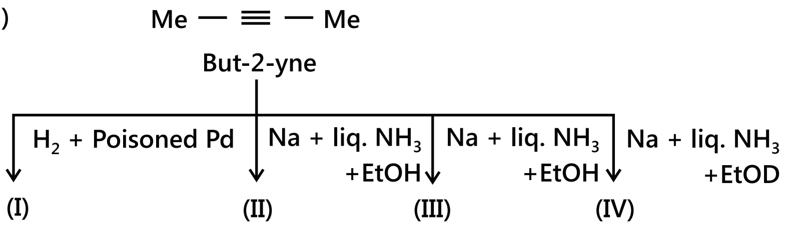
$+ 6O_2 \longrightarrow 4CO_2 + 4H_2O \qquad \Delta H_c^\circ = -2700\ kJ\ mol^{-1}$

2-Methylprop-1-ene

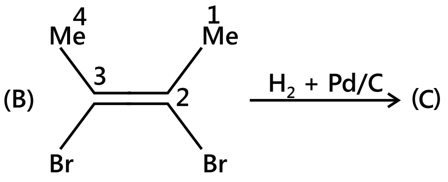
Although each isomer mentioned above (I – IV) consumes 6 moles of O_2 and produces 4 moles of CO_2 and 4 moles of H_2O, the comparison of ΔH_C° shows that (IV) is most stable among the four isomers because it evolves the least heat. Thus, the order of stability is: (IV) > (III) > (II) > (I).

Illustration 13: Give the products with their stereoisomers, if any. **(JEE ADVANCED)**

(a)

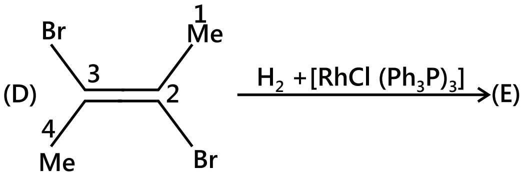


(b)



cis-2,3-Dibromo-but-2-ene

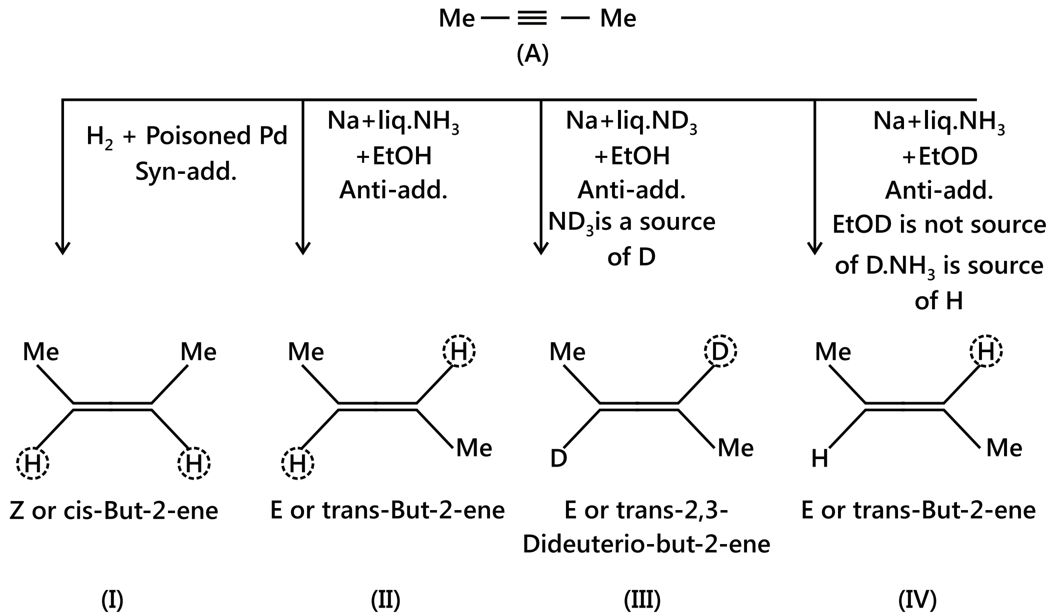
(c)



trans-2,3-Dibromo-but-2-ene

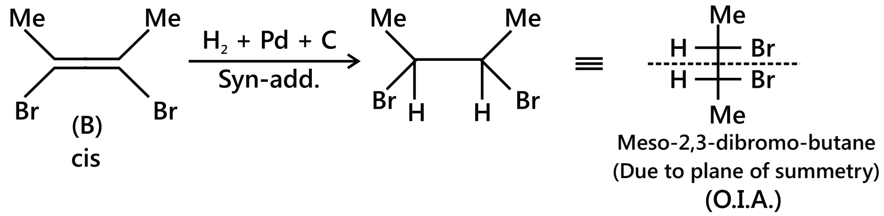
Sol: Identify the reducing agent used for the different reaction. Depending upon the type of reducing agent used and addition of hydrogen predict the formation of stereoisomer.

(a)

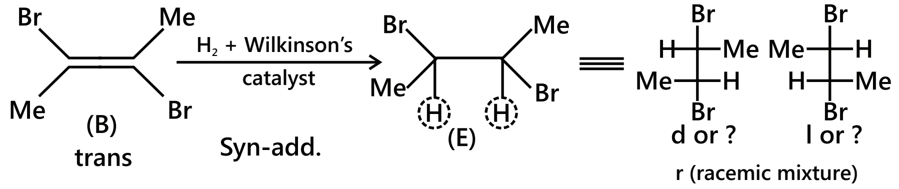


(b) **Note:** Metal + H_2 does not reduce (R – X) to (R – H) but reduced (Ar – X) to (Ar – H).

Reactant is cis + mechanism of addition is syn → product is meso.



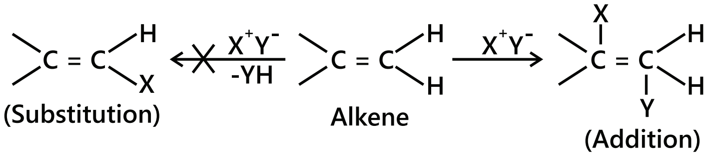
(c) Reactant is trans + mechanism of addition is syn → product is dl or (±) or racemic.



7.2 Electrophilic Addition Reactions

In electrophilic addition reactions of alkenes, a π bond is broken and two new σ bonds are formed. Formation of an electron deficient electrophile is the driving force for this reaction. This electrophile form a covalent bond with π electrons of alkene and the positive charge is transferred to the remaining doubly bonded carbon.

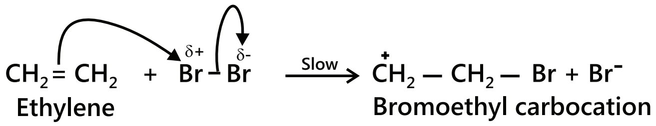
In second step of E.A.R. positively charged intermediate combine with electron rich anion to form the second covalent bond. That is one weak π bond is broken and two strong σ bonds are formed.



Let us illustrate the mechanism of electrophilic addition reactions by taking the example of addition of Br_2 to ethylene. The reaction occurs by a two-step ionic mechanism as discussed below:

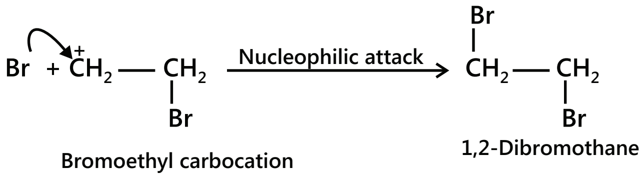
Step-1: Bromine molecule is nonpolar but when it comes close to an ethylene molecule, the π-electrons of the double bond begin to repel the electron pair holding the two bromine atoms together in the bromine molecule. As a result, the bromine molecule gets polarized. The positive end of this bromine dipole behaves as an electrophile and is attracted by the π-electrons of the ethylene molecule to form a π-complex* which subsequently gives the carbocation and the bromide ion. This step is slow and hence is the rate determining step of the reaction.

This step can simply be represented as



$$CH_2 = CH_2 + \overset{\delta+}{Br} - \overset{\delta-}{Br} \xrightarrow{\text{Slow}} \overset{+}{C}H_2 - CH_2 - Br + Br^-$$

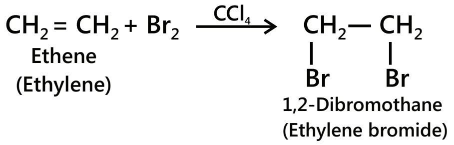
Step-2: The carbocation formed in **step-1** being a reactive chemical species immediately undergoes a nucleophilic attack by the bromide ion present in the solution forming the addition product. This step is fast and hence does not affect the rate of the reaction.



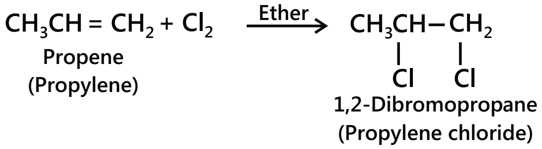
$$Br + \overset{+}{C}H_2 - \underset{Br}{CH_2} \xrightarrow{\text{Nucleophilic attack}} \underset{}{\overset{Br}{CH_2}} - \underset{Br}{CH_2}$$

7.3 Addition of X_2

Addition of halogens: Halogens such as chlorine and bromine readily add to alkenes to form 1, 2-dihaloalkanes. For example,



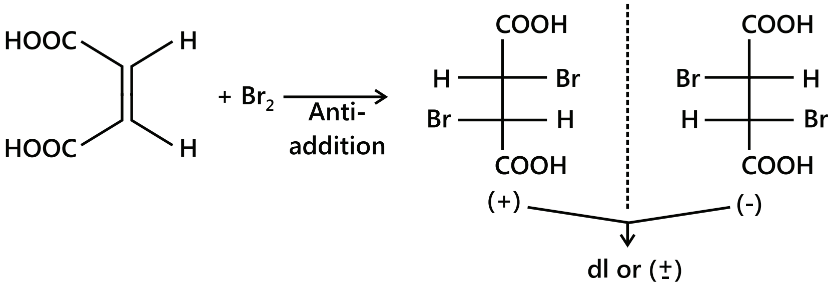
$$CH_2 = CH_2 + Br_2 \xrightarrow{CCl_4} \underset{Br}{CH_2} - \underset{Br}{CH_2}$$



$$CH_3CH = CH_2 + Cl_2 \xrightarrow{\text{Ether}} CH_3\underset{Cl}{CH} - \underset{Cl}{CH_2}$$

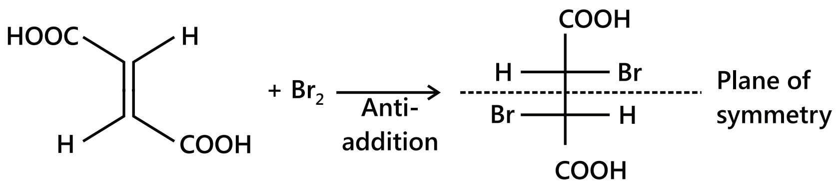
During the addition of bromine to alkenes, bromine loses its orange red colour, since the dibromide formed is colourless. This reaction is, therefore, used as a **test for unsaturation in organic compounds.** Reactivity order: $F_2 > Cl_2 > Br_2 > I_2$ (because the $E_{activation}$ order is: $F_2 < Cl_2 < Br_2 < I_2$).

Reactant cis (with two same groups) + mechanism of addition of Br_2 is anti (with two same groups) $\Rightarrow$ product is dl or (±) of racemic. Reactant is trans + mechanism of addition of Br_2 is anti $\Rightarrow$ product is meso. Similarly, maleic acid (cis) + Br_2 (anti-addition) $\rightarrow$ dl product.



dl or (±)
2,3-Dibromobutan-1,4-dioic acid

Fumaric acid (trans) $+Br_2$ (anti-addition) → Meso product



(trans)

Meso-2,3-dibromobutan-1,4-dioic acid

7.4 Addition of HX

Addition of halogen halides. Mono-haloalkanes or alkyl halides are formed when alkenes react with halogen halides (HCl, HBr, HI),

Alkyl halide

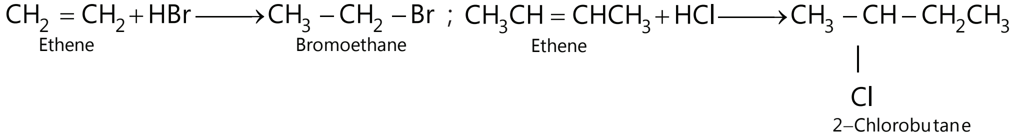
e.g. $\underset{\text{(Ethylene)}}{\underset{\text{Ethene}}{CH_2{=}CH_2}} + HBr \longrightarrow \underset{\text{(Ethyl bromide)}}{\underset{\text{Bromoethane}}{CH_3-CH_2Br}}$

The order of reactivity of halogen halides in this reaction is: HI > HBr > HCl. This order of reactivity can be explained on the basis of bond dissociation energies of the halogen halides; lower the bond dissociation energy, more reactive is the halogen halide ;

HI (300 kJ mol^{-1}) > HBr (360 kJ mol^{-1}) > HCl (430 kJ mol^{-1})

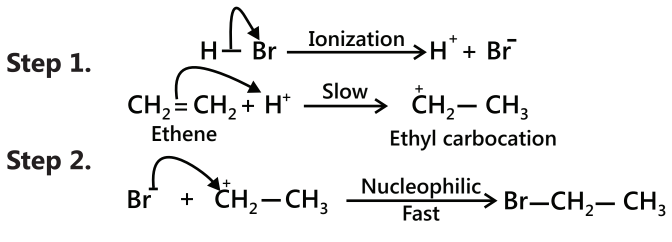
The actual product formed, however, depends upon whether the alkene is symmetrical or unsymmetrical as discussed below:

(i) Addition to symmetrical alkenes. When the alkene is symmetrical only one product is theoretically possible. For example,



$$\underset{\text{Ethene}}{CH_2=CH_2}+HBr \longrightarrow \underset{\text{Bromoethane}}{CH_3-CH_2-Br}\ ;\ \underset{\text{Ethene}}{CH_3CH=CHCH_3}+HCl \longrightarrow \underset{\text{2–Chlorobutane}}{CH_3-\underset{\underset{\displaystyle Cl}{|}}{CH}-CH_2CH_3}$$

Mechanism: Like the addition of halogen, addition of halogen halides to alkenes is also an electrophilic addition reaction and occurs by the following two steps:



Step 1.

$$H-Br \xrightarrow{\text{Ionization}} H^+ + Br^-$$

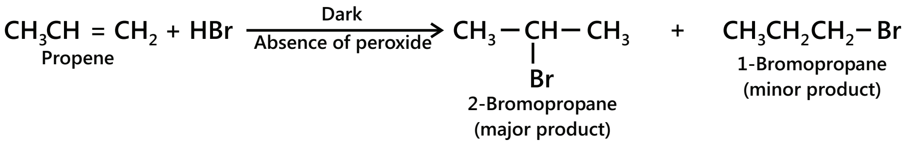
$$\underset{\text{Ethene}}{CH_2=CH_2} + H^+ \xrightarrow{\text{Slow}} \underset{\text{Ethyl carbocation}}{\overset{+}{C}H_2-CH_3}$$

Step 2.

$$Br^- + \overset{+}{C}H_2-CH_3 \xrightarrow[\text{Fast}]{\text{Nucleophilic}} Br-CH_2-CH_3$$

Ethyl carbocation Bromoethane

(ii) Addition to unsymmetrical alkenes: When the alkene is unsymmetrical, two products are theoretically possible. For example, the addition of HBr to propene in the dark and in the absence of peroxides can, in principle, give two products. But experimentally, it has been found that under these conditions, the major product is 2-bromopropane and the minor product is 1-bromopropane.

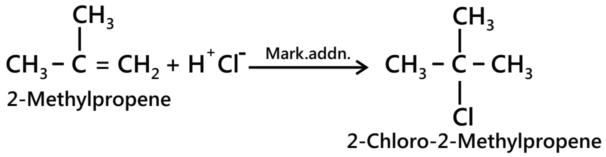


$$CH_3CH=CH_2 + HBr \xrightarrow[\text{Absence of peroxide}]{\text{Dark}} \underset{\substack{\text{2-Bromopropane}\\\text{(major product)}}}{CH_3-\underset{\displaystyle Br}{\underset{|}{C}H}-CH_3} + \underset{\substack{\text{1-Bromopropane}\\\text{(minor product)}}}{CH_3CH_2CH_2-Br}$$

Propene

Markovnikov's rule: The rule states that: "The addition of unsymmetrical reagents such as HX, H_2O, HOX, etc. to unsymmetrical alkenes occurs in such a way that the negative part of the addendum (i.e., adding molecule) goes to that carbon atom of the double bond which carries lesser number of hydrogen atoms."

For example,



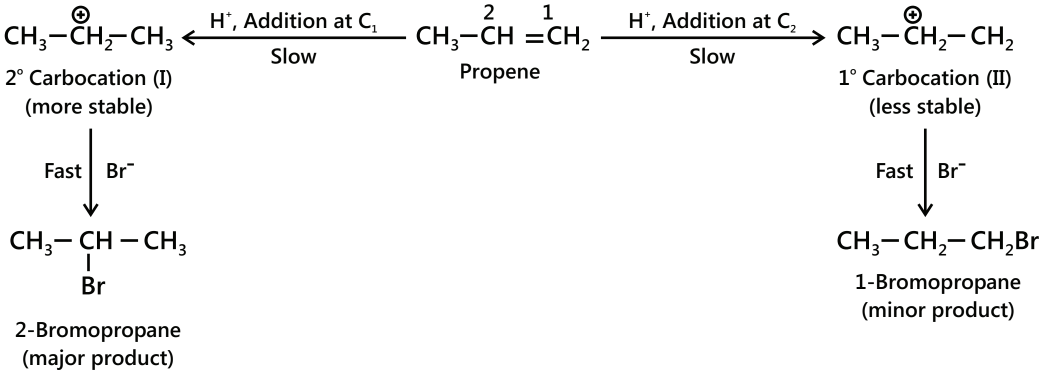
$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2 + H^+Cl^- \xrightarrow{\text{Mark.addn.}} CH_3-\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3$$

2-Methylpropene

2-Chloro-2-Methylpropene

Theoretical explanation of Markovnikov's rule: The addition of hydrogen halides to alkenes is an electrophilic addition reaction. Thus, during the addition of HBr to propene, the first step involves the addition of a proton. This addition, in principle, can occur in two ways. If the proton adds on the terminal carbon atom of the double bond, a 2° carbocation (I) is formed and if addition occurs on the middle carbon atom. a 1° carbocation (II) is produced.

Since, a 2° carbocation (I) is more stable than 1° carbocation (II), therefore, carbocation (I) is predominantly formed. This carbocation then rapidly undergoes nucleophilic attack by the Br^- ion forming 2-bromopropane as the major product. Thus, Markovnikov's addition occurs through the more stable carbocation intermediate.



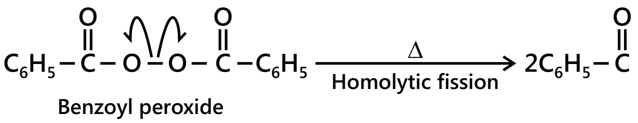
Peroxide effect: It should be noted that Markovnikov's rule is not always followed. In the presence of peroxides such as benzoyl peroxide ($C_6H_5CO-O-O-COC_6H_5$), the addition of HBr (but not of HCl or HI) to unsymmetrical alkenes takes place contrary to Markovnikov's rule. This is known as **Peroxide effect** or **Kharasch effect**. Thus,

$$\underset{\substack{\text{Propene}\\\text{(Propylene)}}}{CH_3CH=CH_2} + HBr \xrightarrow[\text{Anti-Mark.add.}]{(C_6H_5COO)_2,\ \Delta} \underset{\substack{\text{1-Bromopropane}\\\text{(n-Propyl bromide)}}}{CH_3CH_2CH_2Br}$$

Mechanism: The addition of HBr to alkenes in presence of peroxides occurs by a free radical mechanism. It consists of the following three steps.

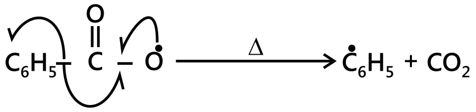
(a) Initiation.

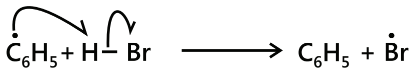
(i)



$$\underset{\text{Benzoyl peroxide}}{C_6H_5-\overset{\displaystyle O}{\overset{\|}{C}}-O-O-\overset{\displaystyle O}{\overset{\|}{C}}-C_6H_5} \xrightarrow[\text{Homolytic fission}]{\Delta} 2C_6H_5-\overset{\displaystyle O}{\overset{\|}{C}}$$

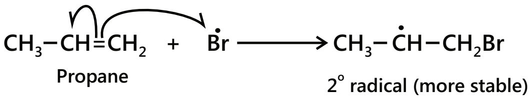
(ii)

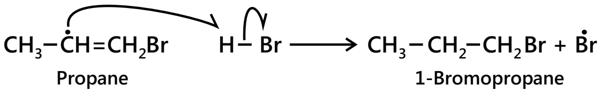


(iii) 

(b) Propagation: It consists of two steps.

During the first step, a Br^- adds to the double bond in such a way so as to give the more stable free radical. In the second step, the free radical thus produced abstracts a H from HBr to complete the addition.

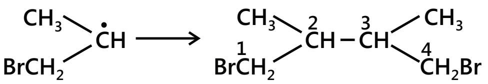
(i) 

(ii) 

(c) Termination:

(i) $2Br \longrightarrow Br_2$

(ii) $CH_3-CH-CH_2Br+Br \longrightarrow \underset{\text{1,2–Dibromopropane}}{CH_3-CHBr-CH_2Br}$

(iii) 

1,4-Dibromo-2,3-dimethylbutane

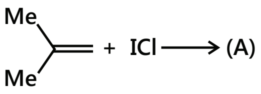
HCl, HF and HI do not obey Peroxide effect. Only HBr does WHY?

X in HX	ΔH (in kJ/mole)	
	(i) $X + CH_2 = CHCH_3 \longrightarrow XCH_2-CH-CH_3$	(ii) $XCH_2-CHCH_3+HX \longrightarrow XCH_2-CH_2CH_3+X$
F	–209	+159
Cl	–101	+27
Br	–42	–37
I	+12	–104

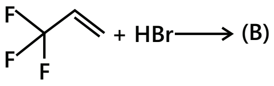
In HBr, both the steps being exothermic, it obeys the peroxide effect.

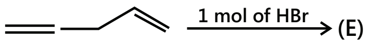
From the above data, it is clear that only with HBr, both the steps are exothermic and hence the peroxide effect is observed. With HCl or HF, the peroxide effect is not observed because the second step involving the reaction of carbon radical with HCl or HF is endothermic. Further, the peroxide effect is also not observed with HI because the first step involving the addition of iodine radical to alkenes is endothermic.

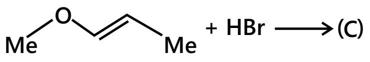
Illustration 14: Complete following reactions: **(JEE MAIN)**

(a) 

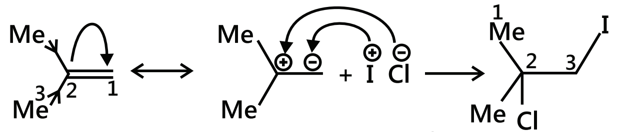
(d) 

(b) 

(e) 

(c) 

Sol: (a)

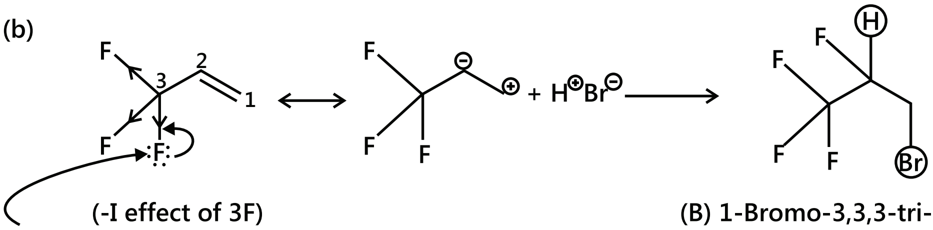


[+I effect of two (me) groups]
2-Methyl but-1-ene
or
Isobutylene

So $Cl^{\ominus}$ and $I^{\oplus}$
(Markovnikov's addition)

(A)
2-Chloro-3-iodo-2-methyl propane

(b)



(-I effect of 3F)
(3,3,3-Trifluoroprop-1-ene)

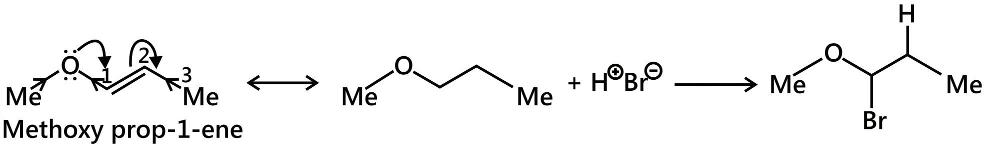
(B) 1-Bromo-3,3,3-tri-fluoroprpane

F is highly electronegative in nature. Due to the –I effect of three F atoms, addition is anti-Markovnikov's (negative part of the reagent is adding to the C atom containing more number of H atoms).

The resonance effect (+R effect) from the lone pair e^-s of F atoms is not operative because lone pair e^- s and double bond are not in conjugation.

So the –I effect of F atoms is operative and, hence, the electromeric effect of double bond takes place from C_1 to C_2.

(c)

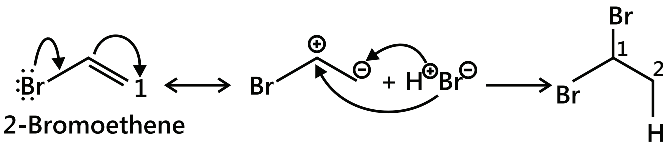


Methoxy prop-1-ene
or
Propenyl methyl ether

Methoxy-1-bromo-propane
or
1-Bromopropyl methyl ether

Here, +R effect is more operative than –I effect of O atom, since the lone pair on oxygen and double bond are in conjugation. Moreover, R > I, so Markovnikov's addition takes place.

(d)

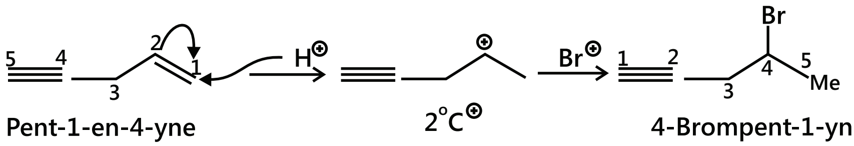


2-Bromoethene

(D) 1,1-Dibromethane

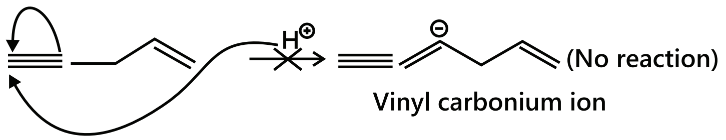
(Same explanation as in part (c) above)

(e)



Pent-1-en-4-yne

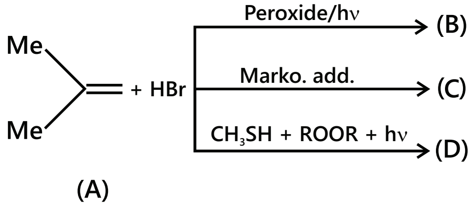
4-Brompent-1-yne
(E)



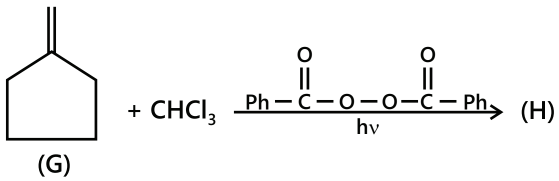
Since, alkyl carbonium ion is more stable than vinyl carbonium ion, alkene reacts at a faster rate than alkynes towards FA.

Illustration 15: Complete the following reaction: **(JEE ADVANCED)**

(a)

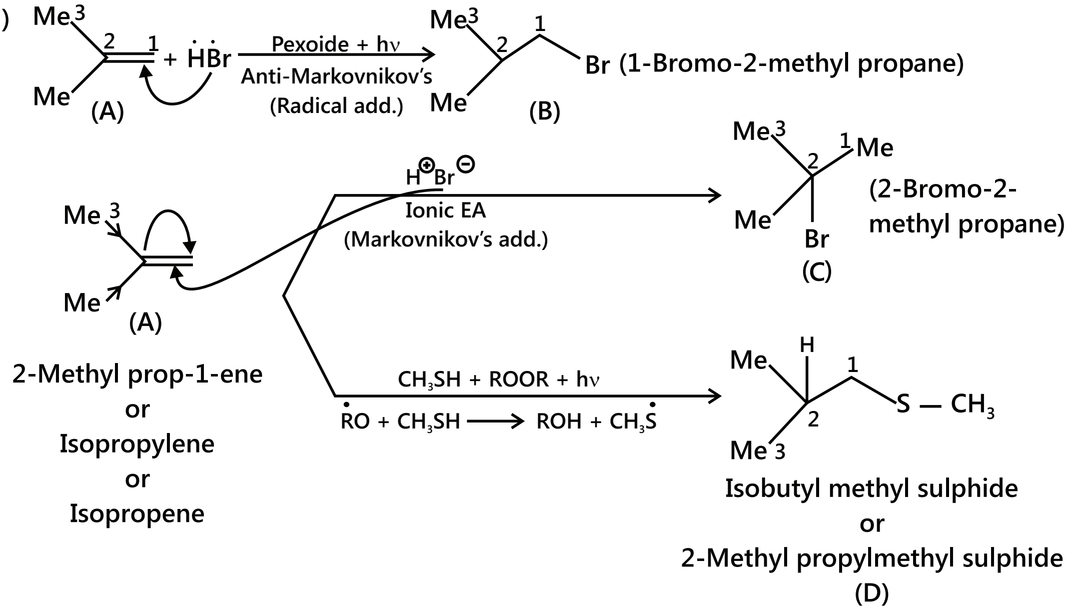


(b)

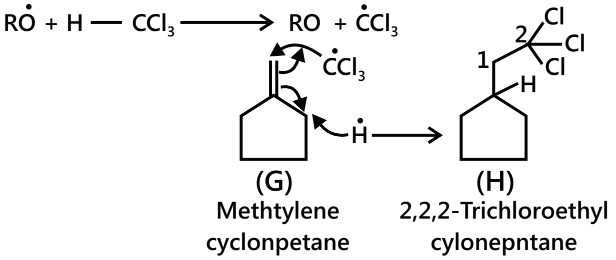


Sol: It is an example of free radical mechanism.

(a)



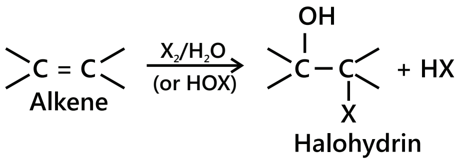
(b)



7.5 Addition of HOX

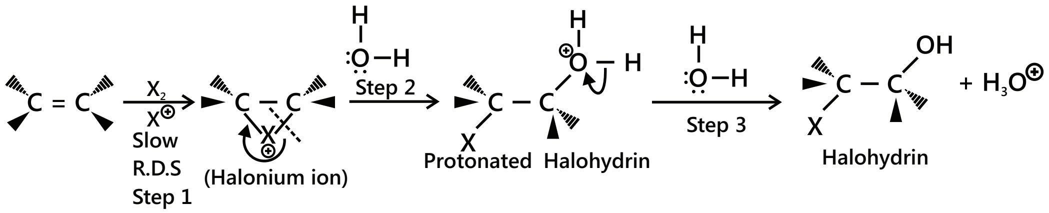
Addition of the elements of hypohalous acids (HOX where X = Cl, Br or I) – Halohydrin formation. Chlorine and bromine in the presence of water readily add to alkenes to form the corresponding halohydrins.

$X_2 + H_2O \longrightarrow HOX + HX$



$$>C = C< \xrightarrow[\text{(or HOX)}]{X_2/H_2O} >\underset{}{\overset{OH}{\overset{|}{C}}} - \underset{\underset{X}{|}}{C}< + HX$$

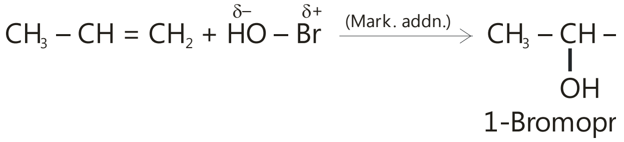
Mechanism:



For example,

$$\underset{\text{Ethene (Ethylene)}}{CH_2=CH_2} \xrightarrow[\text{(or HOCl)}]{Cl_2/H_2O} \underset{\text{2-Chloroethanol (Ethylene chlorohydrin)}}{HO-CH_2-CH_2-Cl+HCl}$$

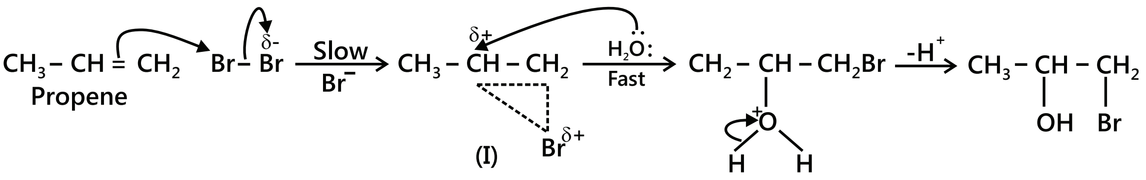
The overall reaction involves the addition of the elements of hypohalous acid $(\overset{\delta-}{HO}-\overset{\delta+}{X})$ in accordance with Markovnikov's rule.



$$CH_3-CH=CH_2+\overset{\delta-}{HO}-\overset{\delta+}{Br} \xrightarrow{\text{(Mark. addn.)}} \underset{\text{1-Bromopr}}{CH_3-\underset{OH}{\underset{|}{CH}}-}$$

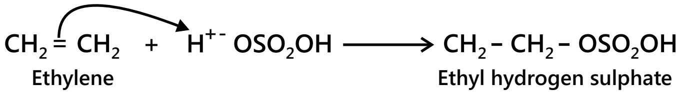
The order of reactivity of different hypohalous acids, i.e., X_2/H_2O (HOX) is:

$$Cl_2/H_2O(HOCl) > Br_2/H_2O(HOBr) > I_2/H_2O(HOI)$$

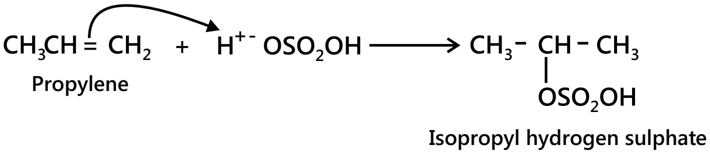


7.6 Addition of H_2O (Indirect)

Addition of sulphuric acid – Indirect hydration of alkenes. Cold, conc. H_2SO_4 adds to alkenes to form alkyl hydrogen sulphates. In the case of unsymmetrical alkenes, addition occurs in accordance with Markovnikov's rule.



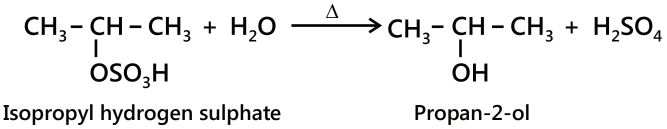
$$\underset{\text{Ethylene}}{CH_2=CH_2} + H^{+-}OSO_2OH \longrightarrow \underset{\text{Ethyl hydrogen sulphate}}{CH_2-CH_2-OSO_2OH}$$



$$\underset{\text{Propylene}}{CH_3CH=CH_2} + H^{+-}OSO_2OH \longrightarrow \underset{\text{Isopropyl hydrogen sulphate}}{CH_3-\underset{OSO_2OH}{\underset{|}{CH}}-CH_3}$$

Importance. Alkyl hydrogen sulphates on boiling with water, undergoes hydrolysis to produce alcohols.

For example,



$$\underset{\text{Isopropyl hydrogen sulphate}}{CH_3-\underset{OSO_3H}{\underset{|}{CH}}-CH_3} + H_2O \xrightarrow{\Delta} \underset{\text{Propan-2-ol}}{CH_3-\underset{OH}{\underset{|}{CH}}-CH_3} + H_2SO_4$$

Thus, alkenes can be converted into alcohols as follows:

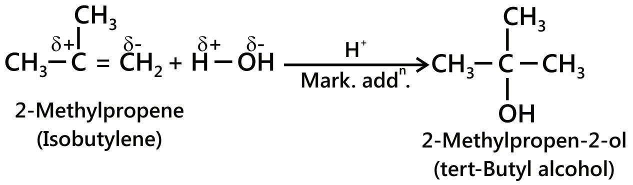
$$\underset{\text{Ethene}}{CH_2=CH_2} \xrightarrow[\text{(ii) } H_2O,\Delta]{\text{(i) Conc. } H_2SO_4 \text{ (cold)}} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

This overall two-step conversion of an alkene first into alkyl hydrogen sulphate followed by hydrolysis with boiling water to form alcohols is called the **indirect hydration of alcohols**.

7.7 Addition of H_2O (Direct)

Addition of water – Direct hydration of alkenes. Hydration means the addition of water. Ordinarily, water does not add directly to most of alkenes. However, some reactive alkenes do add water in the presence of mineral acids to form alcohols. The addition occurs in accordance with Markovnikov's rule.

For example,



$$CH_3-\overset{\overset{CH_3}{|}}{\overset{\delta+}{C}}=\overset{\delta-}{C}H_2+\overset{\delta+}{H}-\overset{\delta-}{OH}\xrightarrow[\text{Mark. add}^n.]{H^+}CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

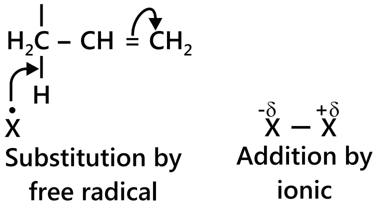
2-Methylpropene
(Isobutylene)

2-Methylpropen-2-ol
(tert-Butyl alcohol)

7.8 Allylic Substitution

Alkenes mainly show two types of reactions:

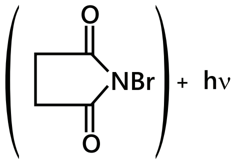
1. Addition reaction (by ionic attack) and 2. Substitution reaction (by free-radical attack).

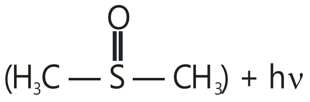


Substitution by free radical

Addition by ionic

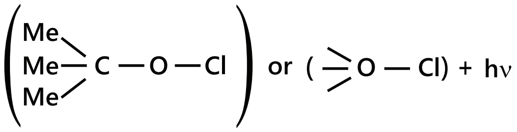
Allylic halogenations can be carried out by the following reagents:

1. Cl_2 at high temperature (773 K) or Br_2 at 400 K.
2. NBS (N-bromosuccinimide)  + hν
3. With NBS + DMSO (dimethyl sulphoxide)



$(H_3C-\overset{\overset{O}{\|}}{S}-CH_3)+h\nu$ addition of OH^- and $Br^{\oplus}$ takes place at double bond (addition reaction).

4. Cl_2SO_2 (sulfuryl chloride) ⇒ allylic chlorination
5. t-Butyl hypochlorite

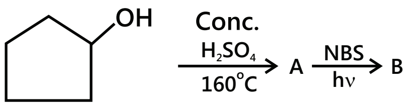


⇒ **allylic chlorination**

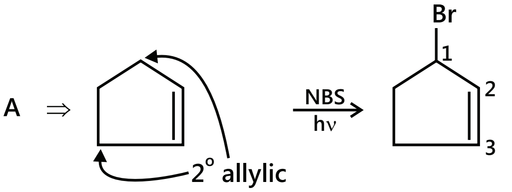
The relative rate of abstraction of hydrogen:

3° allylic > 2° allylic > 1° allylic > 3° > 2° > 1° > methyl > vinylic

Illustration 16: Complete the following reaction: **(JEE MAIN)**

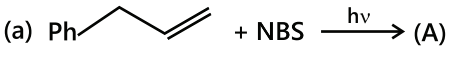


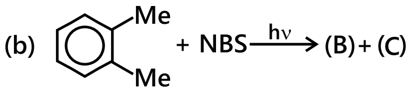
Sol:

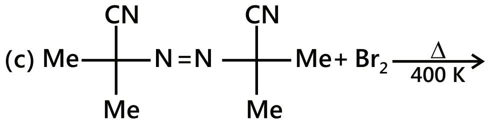


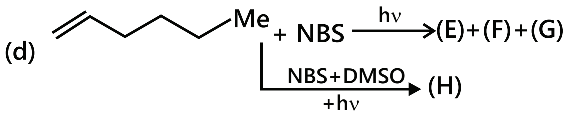
Cyclopent-1-ene 1-Bromocyclopent-2-ene

Illustration 17: Give the products of the reactions given below **(JEE ADVANCED)**

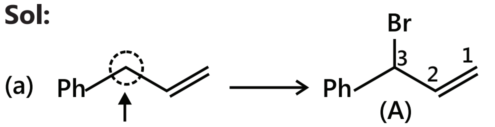






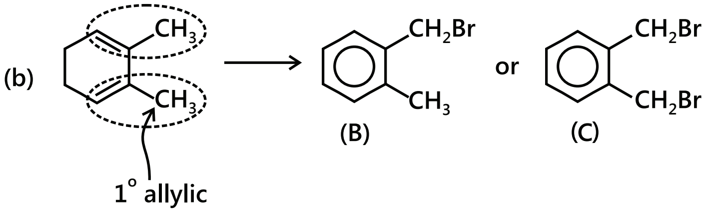


Sol:

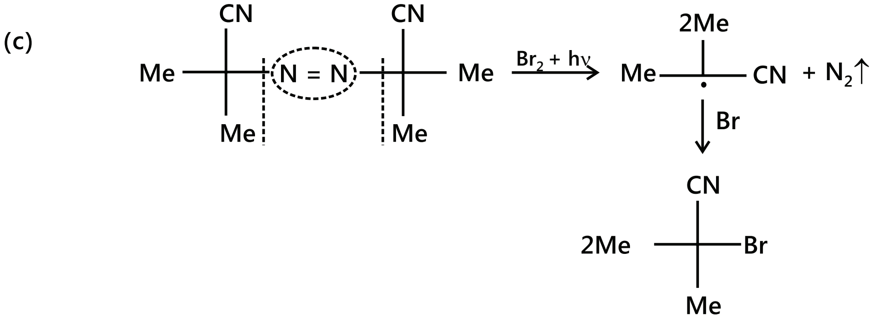


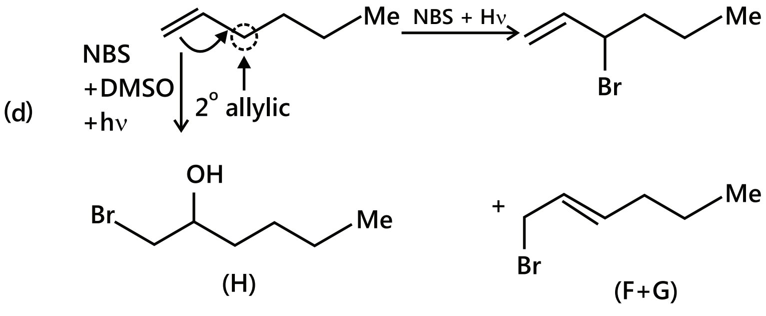
(A)

(3-Bromo-3-phenyl-1-ene)



(B) (C)



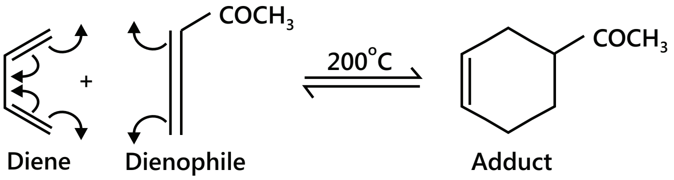


(H)

(F+G)
(cis and trans)

7.9 Diels Alder Reaction

A conjugate diene (with S-cis conformation) is treated with alkene or alkyne called a dienophile. The Diels-Alder reaction is insensitive to the presence or absence of solvents and catalysts. For example,

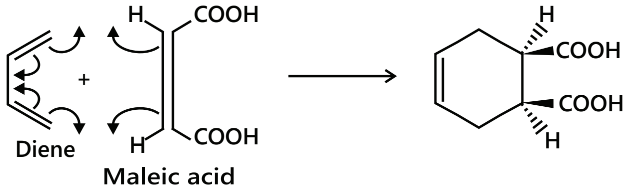


Mechanism: It takes place by concerted mechanism called pericyclic reaction. In a concerted mechanism, breaking and formation of bonds takes place simultaneously.

The reaction proceeds faster when the dienophiles have e⁻ withdrawing groups, such as (—COOH), (—COOR), (—CHO), (—NO_2), and (—CN), and dienes have e⁻ donating groups such as (Me), (Et), etc. So, 1, 3-butadiene is less reactive than its mono-, di-, and trimethyl derivatives.

These reactions are stereospecific, i.e., maleic acid give cis and fumaric acid gives trans isomers, both by cis-addition.

Mechanisms: cis-additions



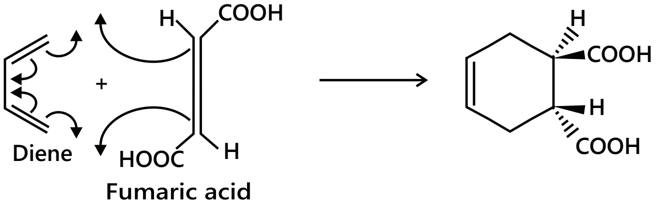
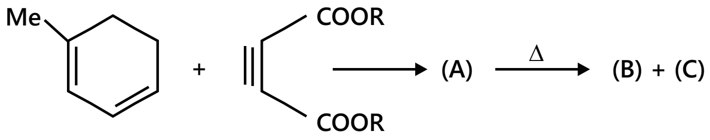
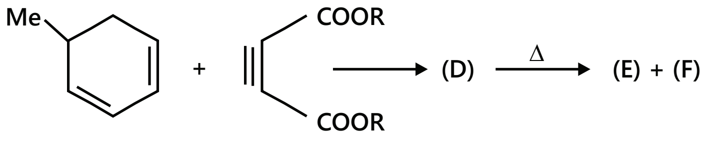


Illustration 18: Complete the following reactions:

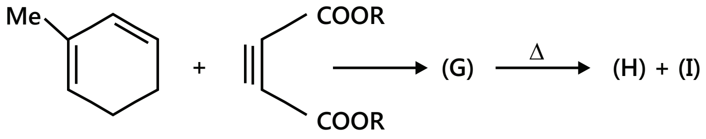
(a)



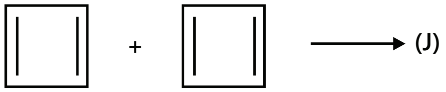
(b)



(c)

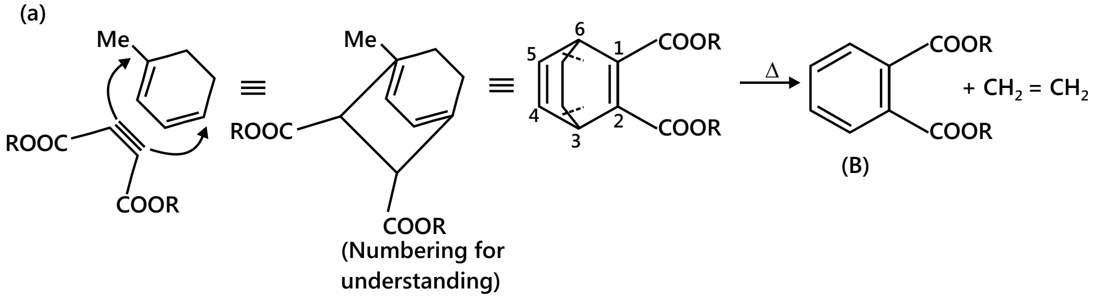


(d)

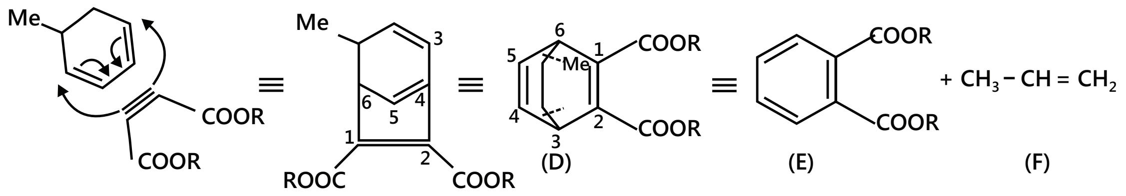


Sol: These are examples of Diels alder reaction. Diene and dienophile combine to form new ring. The mechanism is concerted type (Bond breaking and bond making takes place simultaneously)

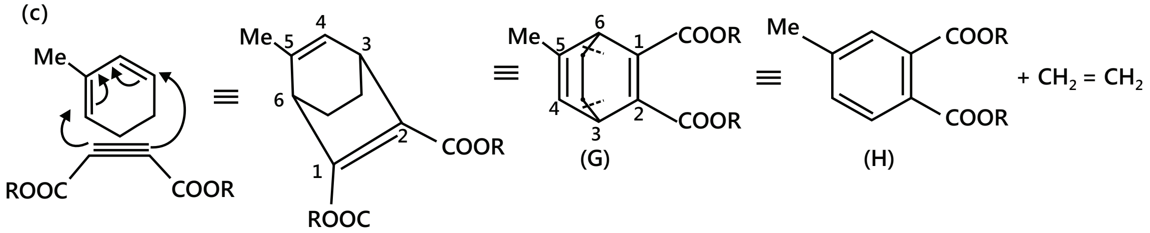
(a)



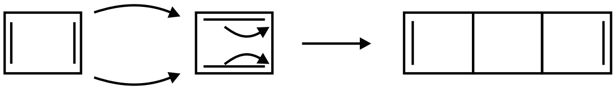
(b)



(c)

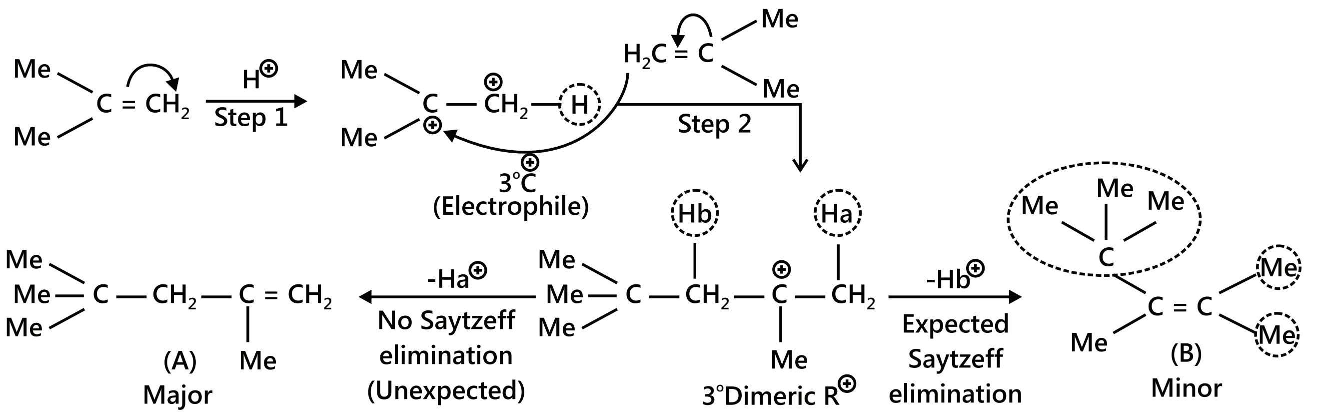


(d)



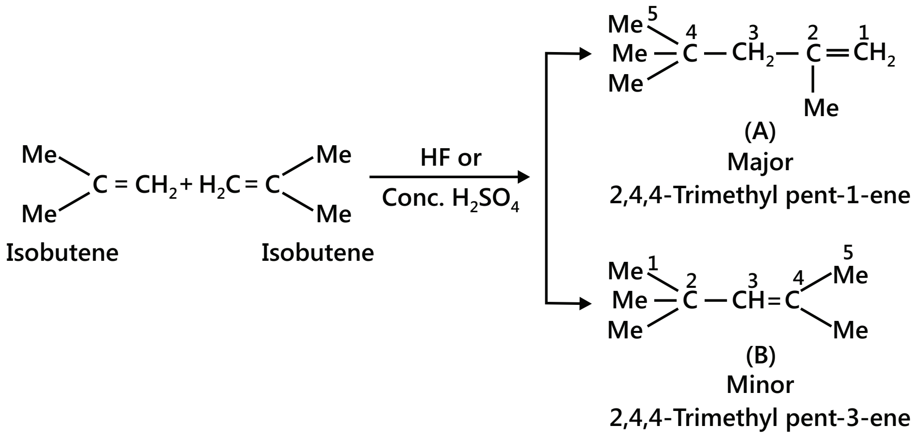
7.10 Dimerisation

Mechanism:



(B) is sterically hindered because the bulky t-butyl group is cis to Me group

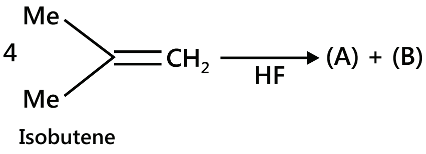
Alkene in the presence of HF or conc. H_2SO_4 or H_3PO_4 gives two alkenes (C_8H_{16}).



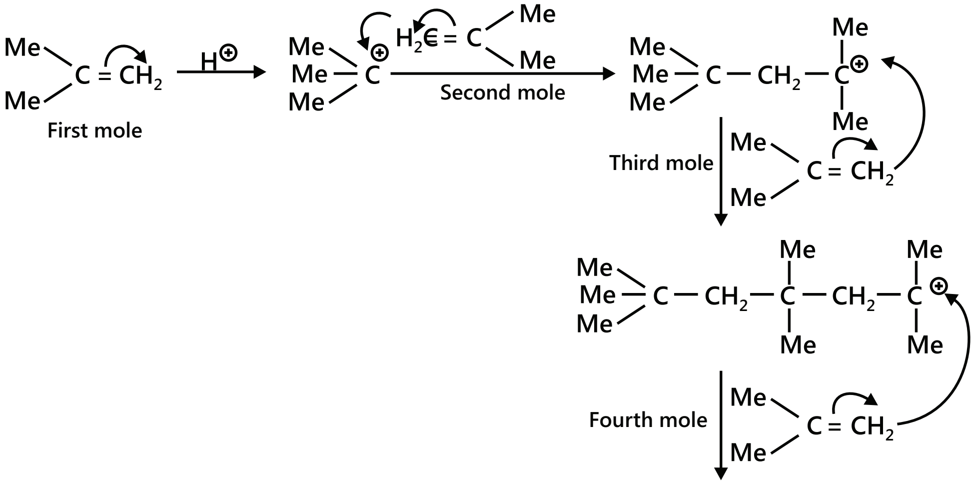
HCl, HBr, and HI cannot be used as acid catalysts. An acid catalyst must have a weak nucleophilic conjugate base to avoid addition of HX to the (C = C) bond. $Cl^{\ominus}$, $Br^{\ominus}$ and $I^{\ominus}$, the conjugate bases of HCl, HBr, and HI, respectively; are good nucleophiles that bind to alkyl carbocation; whereas $F^{\ominus}$, the conujugate base of HF, is a weak nucleophile and does not bind to alkyl carbocation.

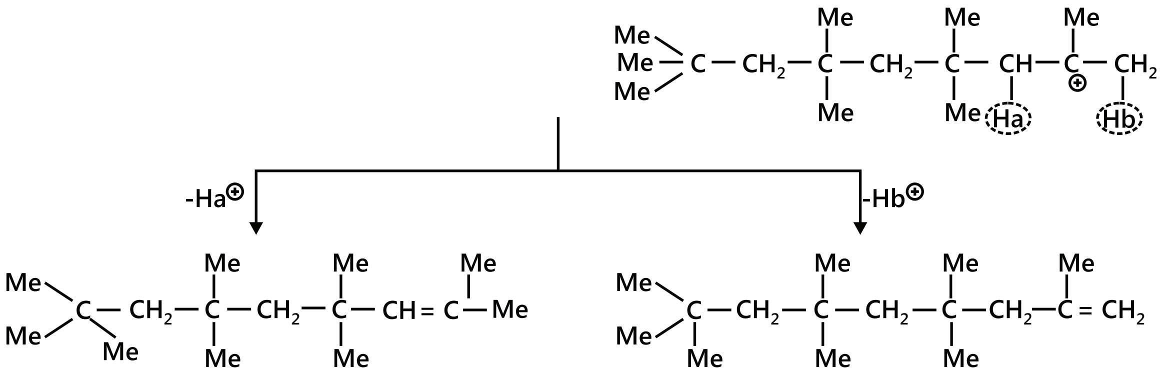
BF_3 with a little amount of H_2O can also be used to initiate the dimerisation or polymerisation of an alkene only at 73K. It is due to the information of strong Bronsted acid ($BF_3 + H_2O \rightleftharpoons HBF_3 \cdot OH$), which provides $H^{\oplus}$ to alkene to form the $R^{\ominus}$.

Illustration 19: Complete the following reaction:



Sol:



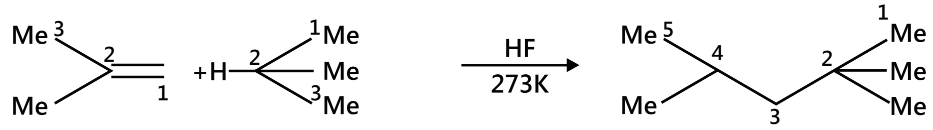


(A)
(Minor)
(Sterically hindered)

(B)
(Major)

7.11 Alkylation

Alkylation is the addition of alkene to alkane in the presence of H_2SO_4 or HF at 273 K.

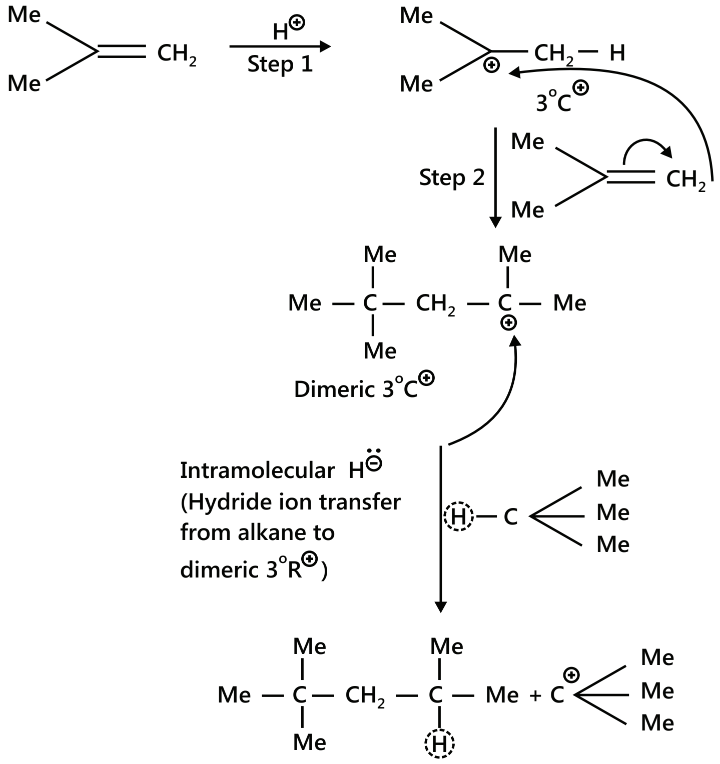


2-Methylprop-1-ene
or
(isobutene)
or
isobutylene)

2-Methyl propane
or
(tert-butane)

2,2,4-Trimethyl pentane

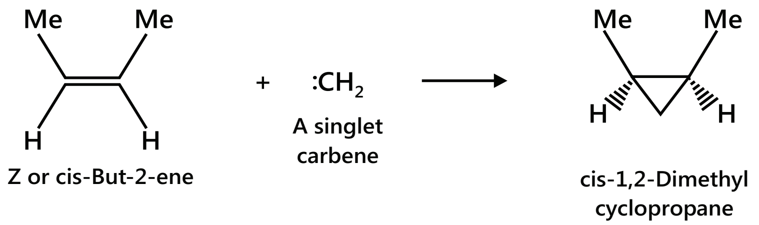
Mechanism:



The propagation step is the chain reaction that continues when Me_3C^+ adds to a molecule of isobutene to form the same 3^oR^+, which accepts as H^- (hydride ion) from another alkane molecule.

7.12 Carbene Insertion to Alkenes

Alkenes react with carbenes in the presence of light to give a cyclic compound.



The carbene is e^--deficient and adds to the e^- rich -bond to give a cyclopropane ring.

Stereochemistry of Carbene: The addition of a singlet carbene $(\uparrow\bullet CH_2\bullet\downarrow)$ is both stereospecific and stereoselective and syn, while the addition of a triplet carbene $(\uparrow\bullet CH_2\bullet\downarrow)$ is non-stereospecific and non-stereoselectively.

Diazomethane generates singlet carbene but in the presence of inert N_2, the singlet carbene collides with N_2 molecules and loses energy to give the carbene having the lower energy triplet.

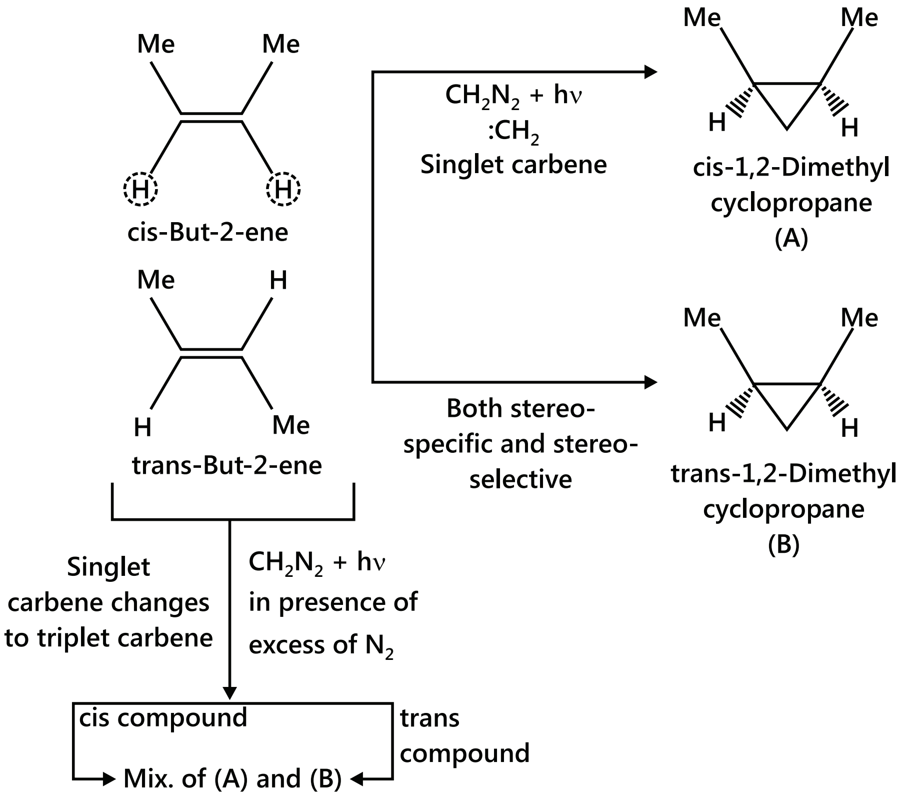


Illustration 20: Give the product of the following:

(a) Cyclohexane + CH_2N_2 + hv

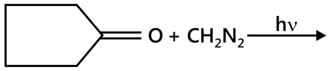
(b) Trans-2-Butene + $CHCl_3$ + KOH

(c) Cis-2-Butene + $HCBr_2Cl$ + KOH

(d) Trans-2-Butene + $HCBr_2Cl$ + KOH

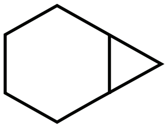
(e) 3-Methylcyclopentene + CH_2I_2 + Zn/Cu (couple) (Simmons-Smith reaction)

(f)



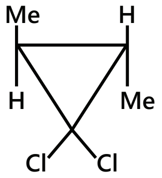
Sol:

(a)



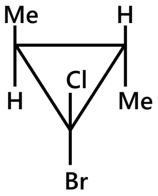
Bicyclo [4.1.0] heptane

(b)



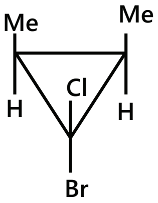
trans-1,2-Dimethyl 3,3-dichloro cyclopropane

(c)

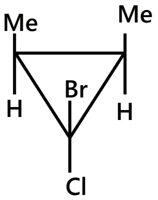


trans-2,3-Dimethyl-1-chlorobromo cyclopropane (Each halogen is cis to one Me and trans to other)

(b)

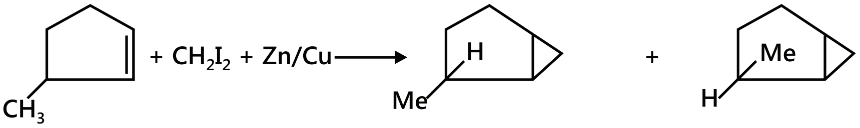


cis-1,2-Dimethyl-cis-1-chlorobromo-cyclopropane



cis-2,3-Dimethyl-trans-1-chlorobromo-cyclopropane

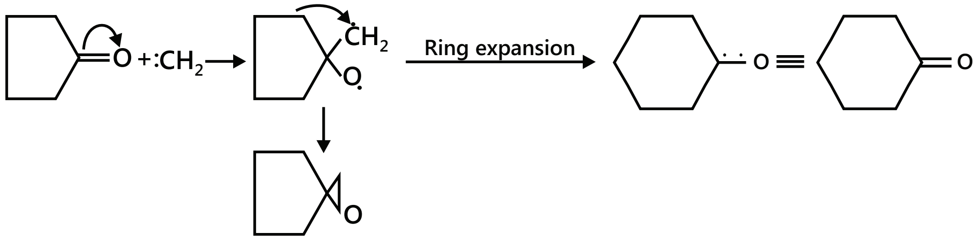
(e) Two diastereomers are obtained:



exo-2-Methyl-bicyclo [3.1.0] hexane

endo

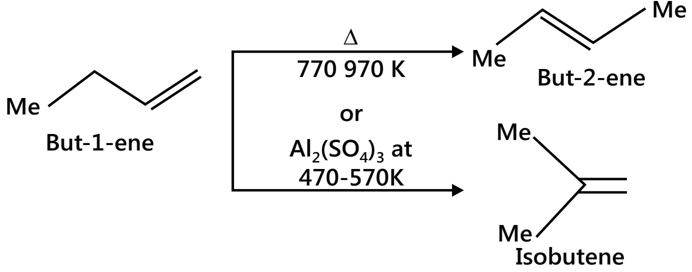
(f) By this method 7- to 10-memberd cyclic ring can be prepared.



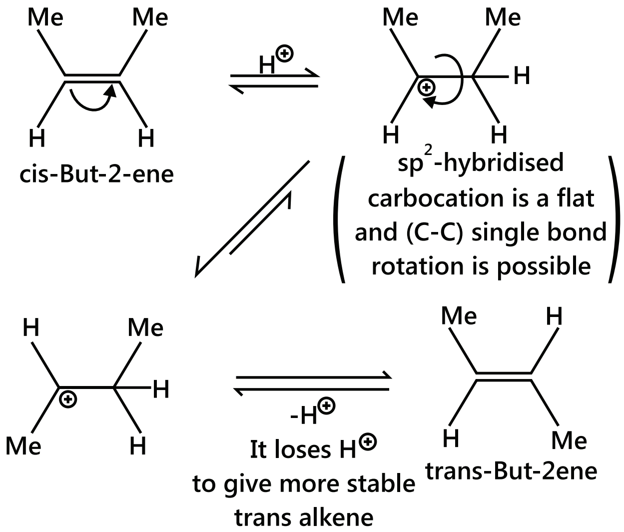
Small amount

7.13 Isomerisation and the Shifting of Double Bond

Shifting of double bond (centre of the chain) or migration of methyl group takes place when heated at 770-970K or when heated with a catalyst $Al_2(SO_4)_3$ at 470-570K.



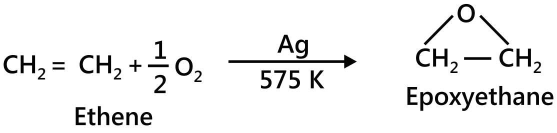
When either a cis or trans alkene is placed in a strong acid solution, each of them is converted to a mixture of 76% of trans and 24% of the cis-isomer. The ratio of isomers is thermodynamically or equilibrium controlled.

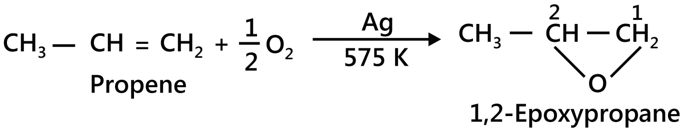


7.14 Oxidation Reactions

1. **Complete oxidation with oxygen or air – Combustion:** All combustion reactions are highly exothermic in nature. For example, $CH_2 = CH_2 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$: + $\Delta_C H = -1411$ kJ mol^{-1}k.
2. **Controlled oxidation with oxidising agent** gives different products:

   (i) Oxidation with oxygen: Alkenes react with O_2 in the presence of silver as a catalyst to form epoxy alkanes or epoxides. For example,





7.14.1 Hydroxylation

Alkenes are oxidised to 1,2-diols with any of the following reagents:

(a) **Cold alkaline or aqueous $KMnO_4$ solution:** It is also called Baeyer's reagent. It is a test for unsaturation for both alkenes and alkynes. The pink colour of $KMnO_4$ is discharged and the black-brown precipitate of MnO_2 is obtained, and alkenes are converted to diols.

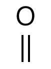
(b) **OsO_4 (osmium tetraoxide)** in pyridine or ether solution followed by the reaction with Na_2SO_3/H_2O or $NaHSO_3/H_2O$ converts alkene to diols and OsO_4 to Os metal.

(c) **With catalytic amount of OsO_4 in H_2O_2**: With the reagents (a), (b) and (c), the addition of two (—OH) groups takes place by syn-addition (or cis-addition) and is called **syn-hydroxylation**.

Anti Hydroxylation with the following reagents :

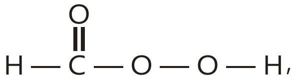
(d) **Peroxy acid followed by the hydrolysis with H_2O:**

For example,

i. 

$Ph-\overset{\overset{O}{||}}{C}-O-O-H$

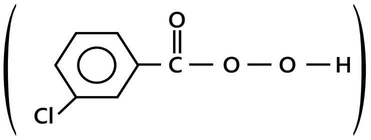
Peroxybenzoic acid

, ii. 

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

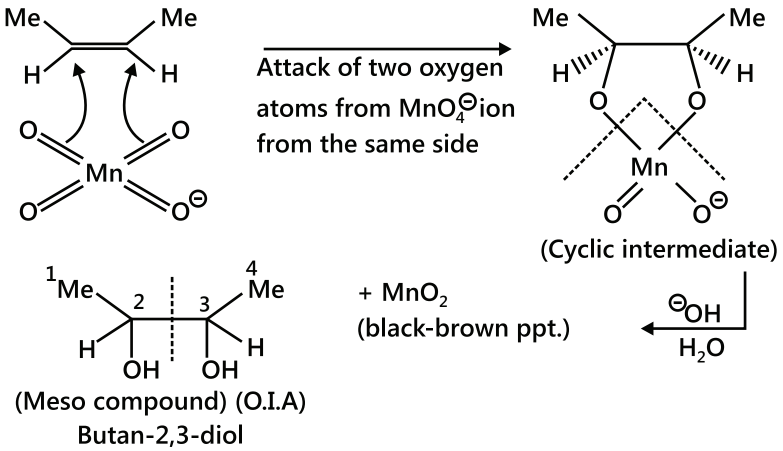
, peroxymethanoic acid or peroxyformic acid, and

iii. MCPBA (m-chloroperbenzoic acid)

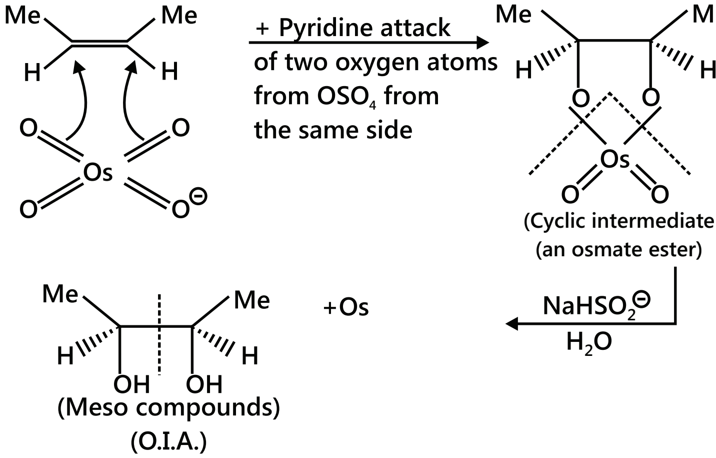


Mechanism of syn hydroxylation:

i.

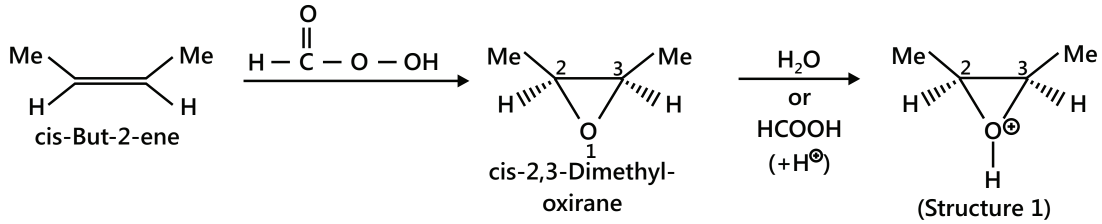


ii.

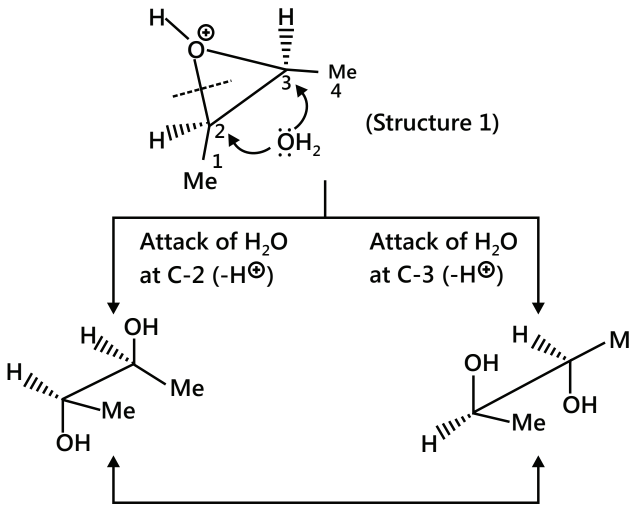


Mechanism of Anti-hydroxylation

I.



II.



Enantiomer
Product is dl or (±) or
rancemic-Butane-2,3-diol

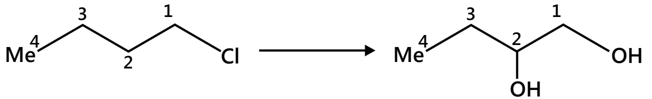
For syn hydroxylation,

	Reactant	Reagent mechanism	Product
1.	Cis (with two same groups)	Syn (with two same (—OH) groups)	Meso
2.	Trans (with two same groups)	Syn (with two same (—OH) groups)	(±) or racemate
3.	Cis or trans (with two different groups)	Syn (with two same (—OH) groups)	(±) or racemate

For anti-Hydroxylation,

	Reactant	Reagent mechanism	Product
1.	Cis (with two same groups)	Anti (with two same (—OH) groups)	(±) or racemate
2.	Trans (with two same groups)	Anti (with two same (—OH) groups)	Meso
3.	Cis or trans (with two different groups)	Anti (with two same (—OH) groups)	(±) or racemic

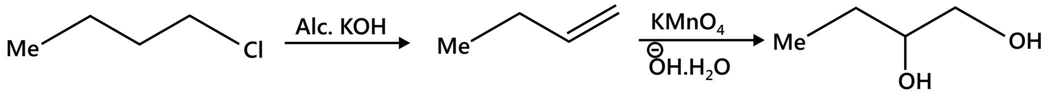
Illustration 21: Convert



1-Chlorobutane

Propane-1,2diol

Sol: First the compound undergoes dehydrohalogenation reaction to form an unsaturation. This on treatment with aq.KMnO$_4$ gives diol.



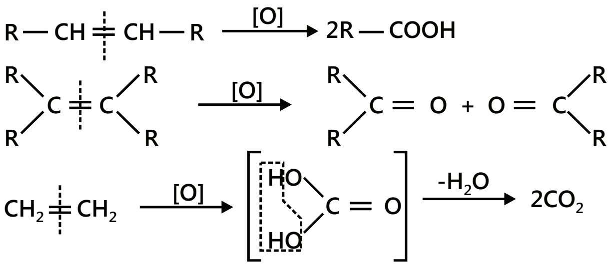
7.14.2 Cleavage

A. Oxidative cleavage

Alkenes are oxidatively cleaved by any of the following reagents:

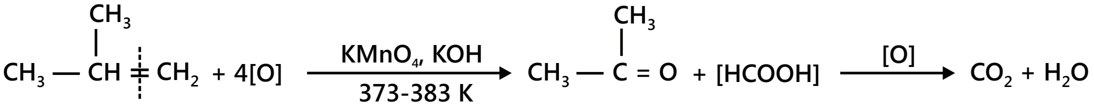
1. Hot alkaline KMnO$_4$ solution followed by acidification

2. Hot acidic $KMnO_4$ solution.
3. Hot acidic $K_2Cr_2O_7$ solution.



Carbonic acid

With terminal alkenes, one of the products is always methanoic acid (formic acid) with on further oxidation gives $CO_2 + H_2O$. For example,



$$CH_3-\overset{\overset{CH_3}{|}}{CH}=CH_2 + 4[O] \xrightarrow[373\text{-}383\ K]{KMnO_4,\ KOH} CH_3-\overset{\overset{CH_3}{|}}{C}=O + [HCOOH] \xrightarrow{[O]} CO_2 + H_2O$$

2-Methylpropene (Isobutylene)

Propanone (Acetone)

With non-terminal alkenes, carboxylic or ketones or both of these are obtained depending upon the nature of the alkene. For example.

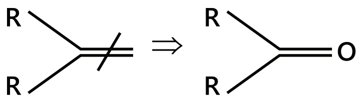
$$CH_3CH_2CH=CHCH_3 + 4[O] \xrightarrow[373\text{-}383\ K]{KMnO_4,\ KOH} CH_3CH_2COOH + HOOCCH_3$$

Pent-2-ene

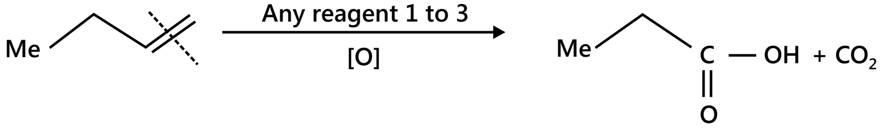
Propanoic acid (Propionic acid)

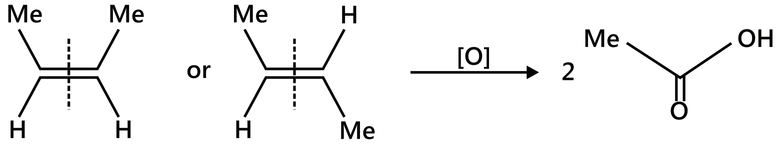
Ethanoic acid (Acetic acid)

Rules of oxidation:

$CH_2 \neq \Rightarrow$	CO_2
$R-CH \neq \Rightarrow$	$R-COOH$
$R_2C=CH_2$	

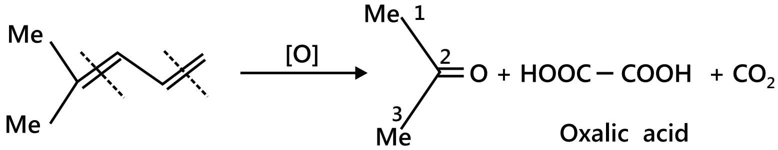
The oxidative cleavage of alkenes is used to establish the position or location of the double bond and the structure of the alkene chain or ring.





cis

trans



Acetone
or
Propan-2-one

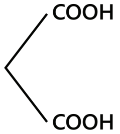
Oxalic acid
or
Ethane-1,2-dioic acid

Illustration 22: Compound (A) (C_6H_8) $\xrightarrow{[O]}$ Malonic acid only. Identify compound (A).

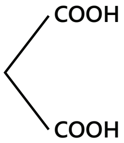
Sol: First, calculate the degree of unsaturation.

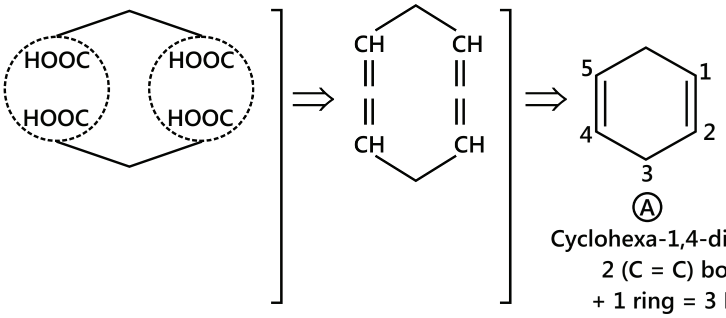
$$\text{D.U.} = \frac{(2n_C + 2) - n_H}{2} = \frac{(2 \times 6 + 2) - 8}{2} = 3^\circ$$

Structure of malonic acid is ⇒



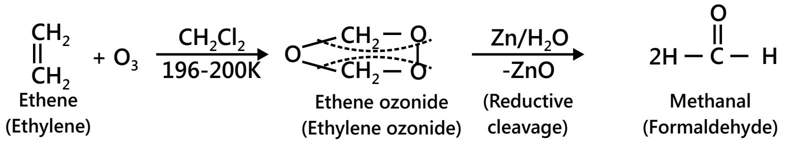
It is a 3C-atom dibasic acid, but compound (A) has six C atoms. So, 2 mol are joined with each other.

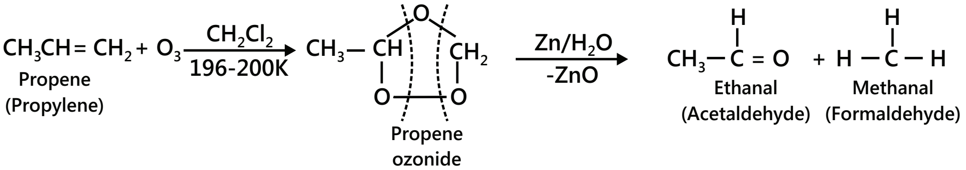




Cyclohexa-1,4-diene
2 (C = C) bonds
+ 1 ring = 3 D.U.

B. Ozonolysis (Oxidation with ozone): When ozone is passed through a solution of an alkene in some inert solvent such as CH_2Cl_2, $CHCl_3$ or CCl_4 at a low temperature (196-200K), it oxidises alkenes to ozonides. Ozonides are unstable and explosive compounds. Therefore, they are not usually isolated but are reduced, in situ, with Zn dust and water or H_2/Pd to give aldehydes or ketones or a mixture of these (reductive cleavage) depending upon the structure of the alkene.

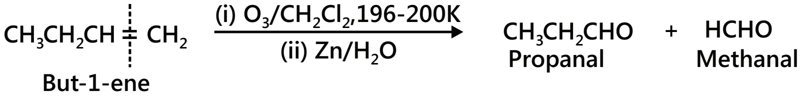


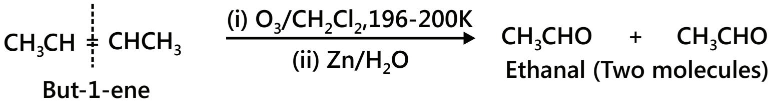


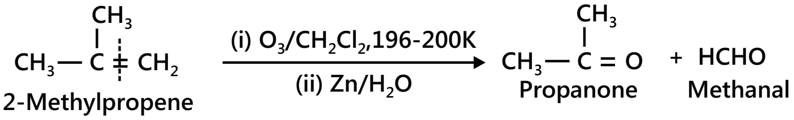
However, if the ozonide are decomposed only with water, the H_2O_2 produced during the reaction oxidises the initially formed aldehydes to the corresponding acids (oxidative cleavage).

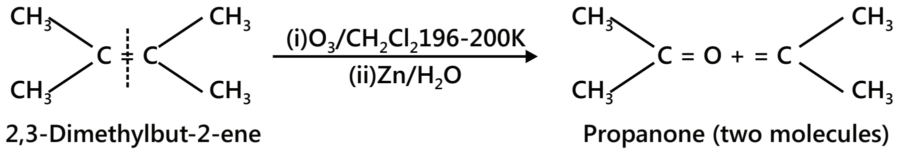
This two-step conversion of an alkene into an ozonide followed by its reductive cleavage to yield carbonyl compounds is called ozonolysis.

Importance: Ozonolysis is a versatile method for locating the position of a double bond in an unknown alkene gives the same combination of aldehydes and or/ketones. Therefore, this method that has been extensively used in the past for structure elucidation of alkenes.









Reagents used for reducive and oxidative ozonoylsis

Reduction of ozonide (Reductive ozonolysis)

(a) Zn-acid
(b) H_2 + Catalyst (Ni, Pt, Pd)
(c) Me_2S (Dimethyl sulphide)
(d) Ph_3P (Triphenyl phosphine)
⇓
It gives aldehyde and ketone

(e) LAH or $NaBH_4$
⇓
It gives alcohols from aldehyde and ketones

Oxidation of ozonide (Oxidative ozonolysis)

(f) H_2O
(g) Ag_2O
(h) H_2O_2
(i) $KMnO_4/NaIO_4$
(j) H_2O
(HCO_3H, $PhCO_3H$)
⇓
Aldehyde give acids and ketones do not change

For example:

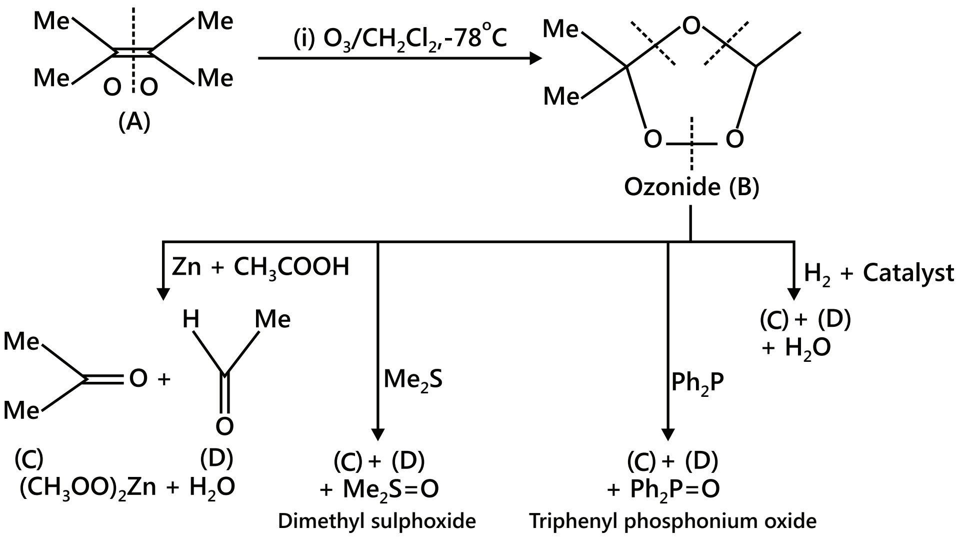


Illustration 23: Identify the compounds (A), (B), and (C). **(JEE MAIN)**

Compound (A) (C_8H_{12}) $\xrightarrow[\text{of } H_2/Pd]{\text{1 mol}}$ (B) (C_8H_{14})
Does not show
Stereoisomerism
$\downarrow$ O_3/Ph_3P
Symmetrical diketone
(C) ($C_8H_{12}O_2$)

Sol: First calculate degree of unsaturation for A,B and C

D.U. in (A) = $\frac{(2n_C+2)-n_H}{2}=\frac{(2\times8+2)-12}{2}=3^{\circ}$; D.U. in (B) = $\frac{(2n_C+2)-n_H}{2}=\frac{(2\times8+2)-14}{2}-2^{\circ}$

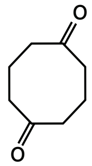
D.U. in (C) = $\frac{(2\times8+2)-12}{2}=3^{\circ}$

In compound (C), Degree of Unsaturation is 3°. Out of three, two are due to diketone.

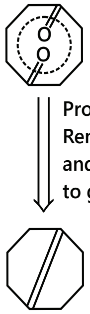
So, one D.U. in compound (C) is due to either one (C = C) bond or one ring of eight C atoms.

One (C = C) bond is not possible because after ozonolysis of (A), the double bond cannot be left behind. So (C) is 8C ring with two $(-\overset{\overset{O}{\|}}{C}-)$ groups at the symmetric position.

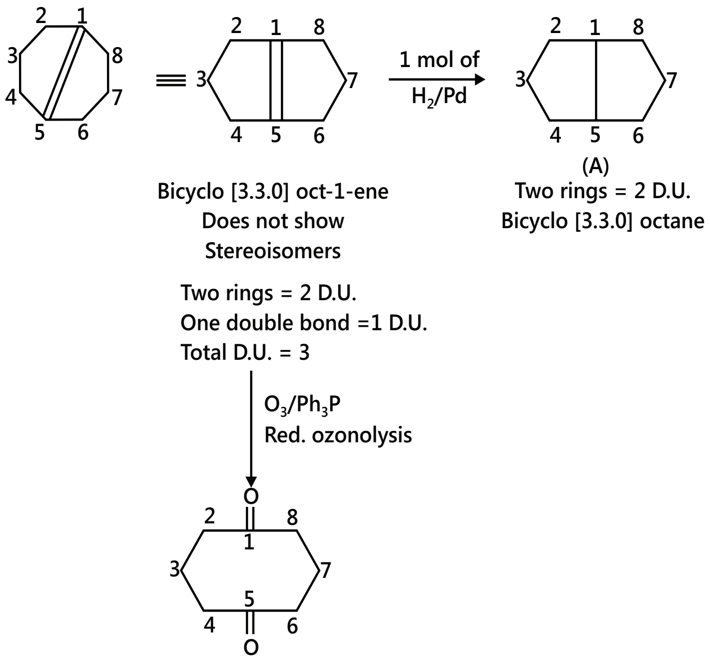
C ⇒



or



Proceed reverse,
Remove O atoms
and join the double bond
to get (A)



Bicyclo [3.3.0] oct-1-ene
Does not show
Stereoisomers

Two rings = 2 D.U.
One double bond =1 D.U.
Total D.U. = 3

(A)
Two rings = 2 D.U.
Bicyclo [3.3.0] octane

(C) Cyclooctane
Symmetrical diketone

One Ring = 1 D.U.
Two $(-\overset{\overset{O}{\|}}{C}-)$ gps = 2.D.U.
Total D.U. = 3

8. USES OF ALKENES

(i) Lower members of the family are used as fuel and illuminants.

(ii) Alkenes and substituted alkenes upon polymerisation form a number of useful polymers such as polythene, PVC, teflon, orlon, etc.

(iii) Ethene is employed for the preparation of ethyl alcohol and ethylene glycol (anti-freeze).

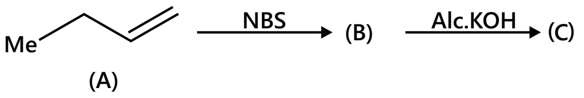
(iv) Ethylene is used for artificial ripening of green fruits.

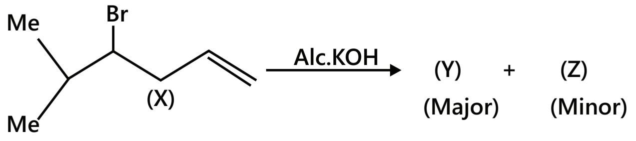
(v) Ethylene is also used in oxygen ethylene flame for cutting and welding of metals.

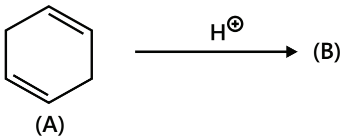
Solved Examples

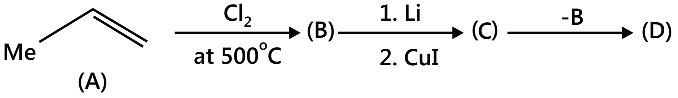
JEE Main/Boards

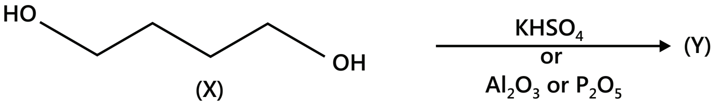
Example 1: Complete the following reactions:

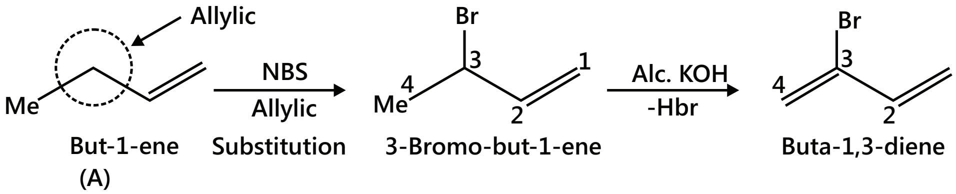
(a)


(b)


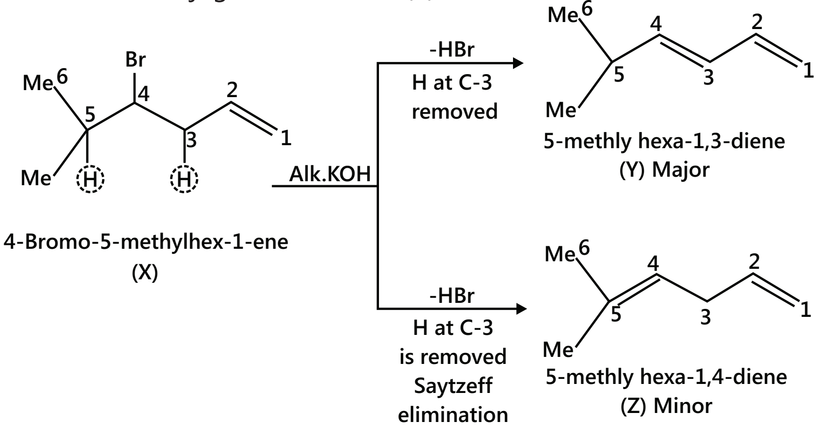
(c)


(d)


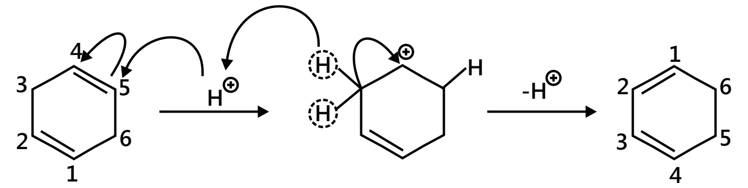
(e)


Sol: (a)


(b) (Z) is formed by Saytzeff's elimination, but the product (Y) is formed in major amount because product (Y) is a more stable conjugate diene than (Z), isolated diene



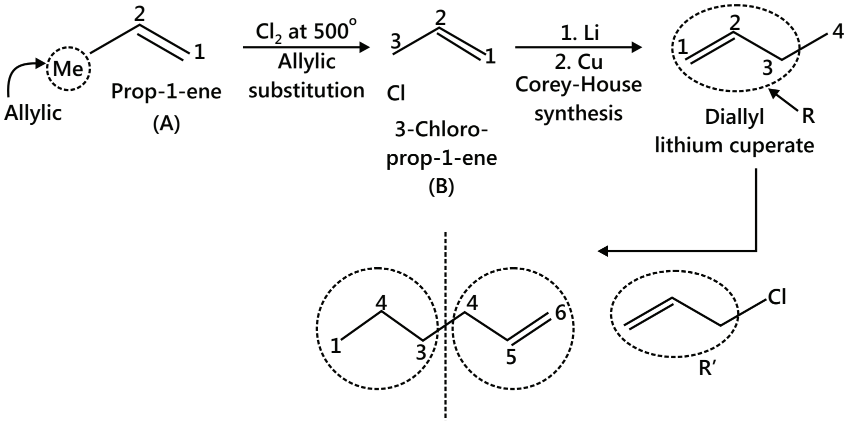
(c)



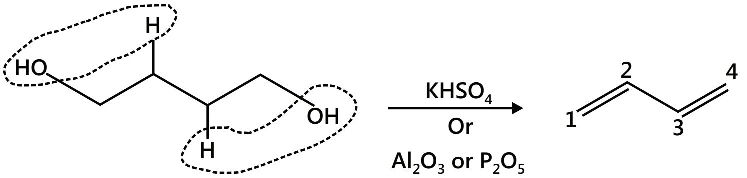
Less stable isolated diene (A) Cyclohexa-1,4-diene

More stable conjugated diene (B) Cyclohexa-1,3-diene

(d)



(e)

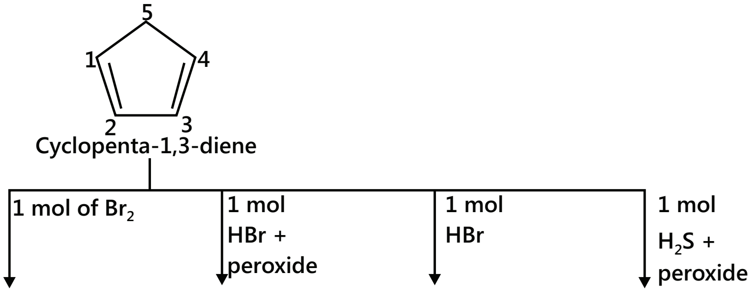


(X) Butan-1,4-diol

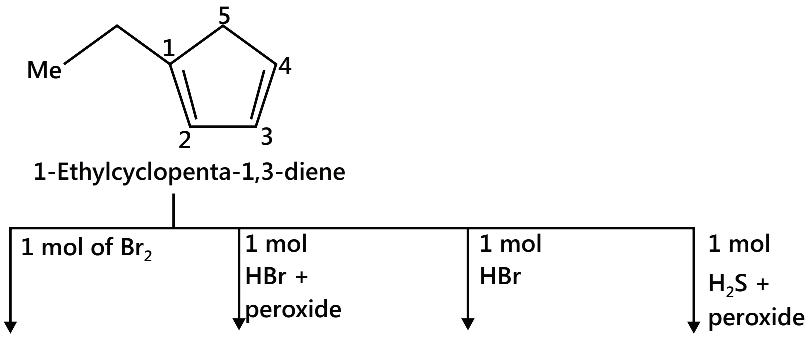
(Y) Butan-1,3-diene

Example 2: Give the major products (not stereoisomers) of the following:

(a

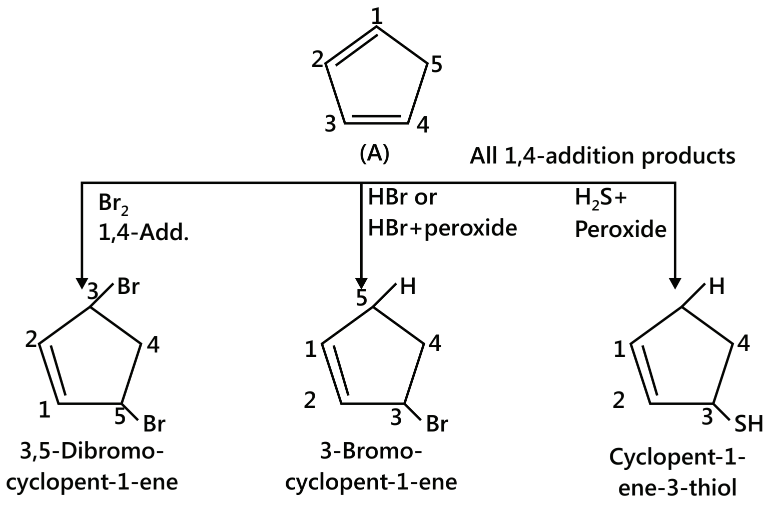


(b)

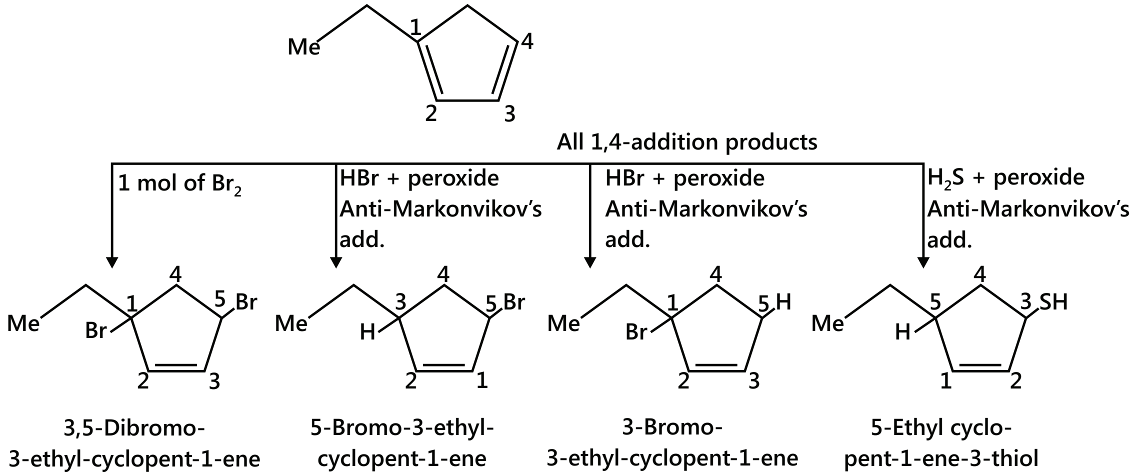


Sol:

(a)

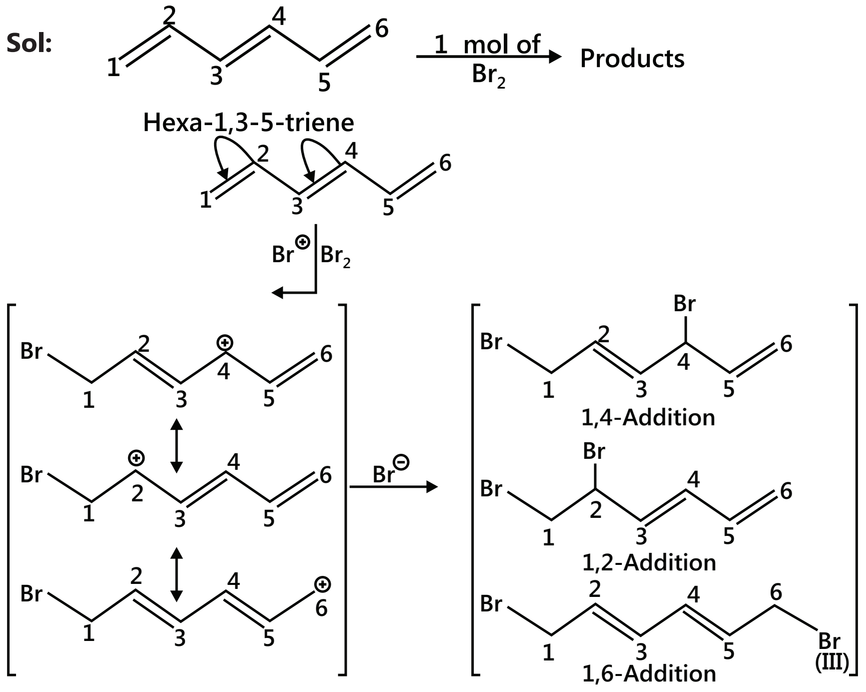


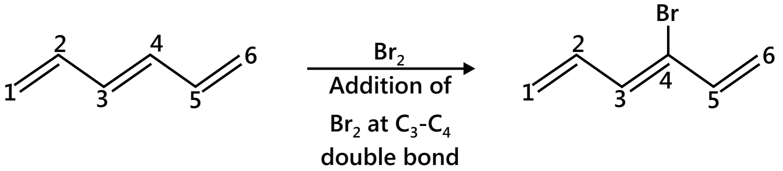
(b)



Example 3: Write all the possible structures and give the structure of the products that are thermodynamically favoured.

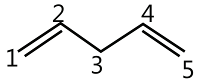
Sol:



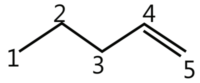


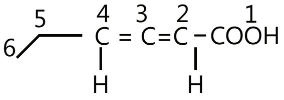
More stable Products (II and III, conjugate dienes) are thermodynamically favoured products than I and IV (isolated dienes)

Example 4: Distinguish between the given pairs.

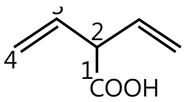
(a)

(A)

and

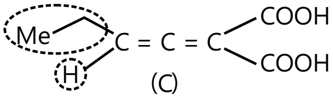

(B)

(b)

(C)

and


(D)

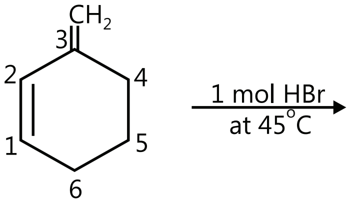
Sol: (a) Compounds (A) and (B) are distinguished chemically by quantitative catalytic hydrogenation. Since compound (A) has two double bond whereas compound (B) has only one double bond .Compound (A) will require 2 moles of H_2 for 1 mole of (A) while (B) will requires 1 mole of H_2 per mole of (B).



(b) Allene (C) with different groups on each of the double bonds is optically active and can be resolved into its enantiomers.

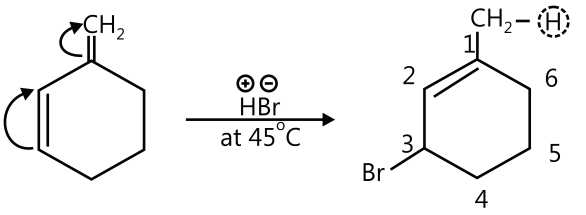
Compound (D) is conjugate diene and does not show optical isomerism.

Example 5: Give the major and minor products.

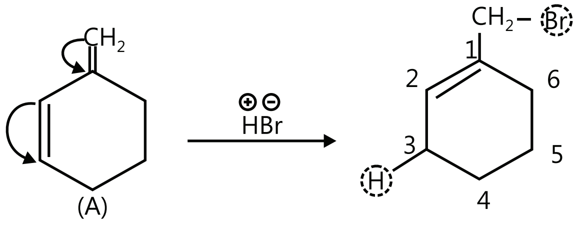


(A)
3-Methylenecyclohex-1-ene

Sol: At high temperature (45°C), 1, 4-addition products is more favourable.

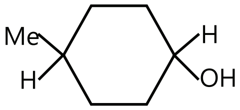


(B) (major)
3-Bromo-1-methyl-
cyclohex-1-ene

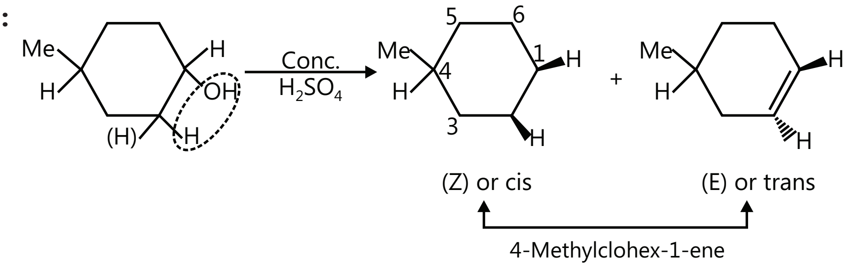


(C) (major)
1-Bromo-1-methyl-
cyclohex-1-ene

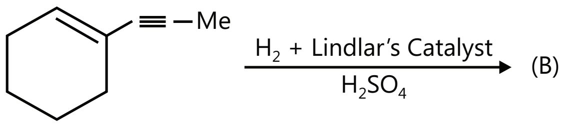
Example 6: Dehydration of (A) with conc. H_2SO_4 gives a compound that exists in two isomeric forms. Give the structures of both the isomers.


(A)

Sol:

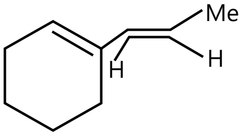


Example 7:

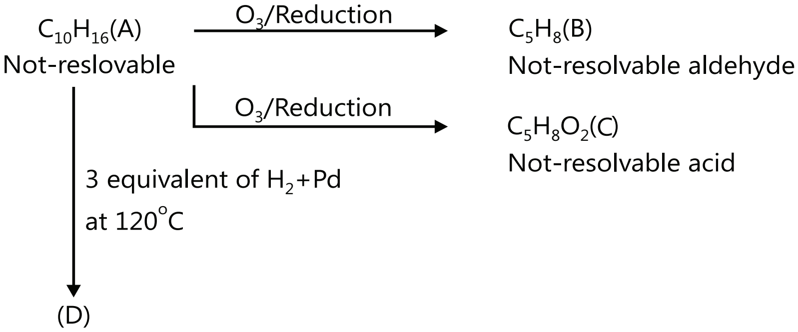


(A)

Sol: Addition of H atom by Lindlar's catalyst is a syn-addition. It reduces (C ≡ C) bond to (C = C) bond so the product (B) is

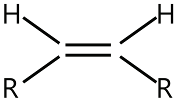


Example 8:



Write all the possible structures of (A), (B) and (C).

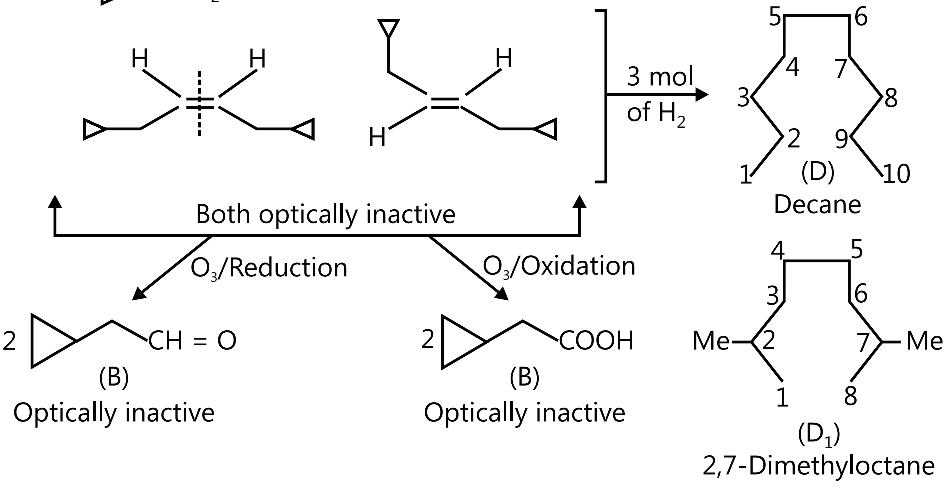
Sol: Since the reductive and oxidative ozonolysis products are different, the alkene of the type

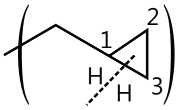


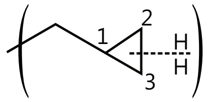
is possible

If R = (▷— CH_2)— , the possible structures of (A) can be:

R = (▷— CH_2)— , the possible structures of (A) can be :



(D) is obtained when ($C_1 - C_3$) bond breaks 

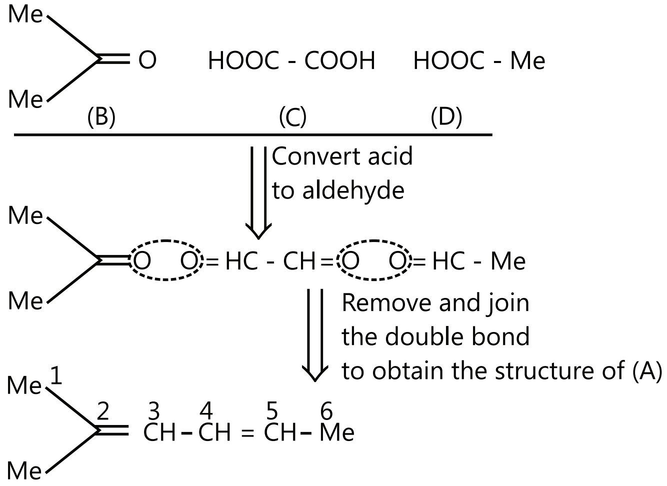
(D_1) is obtained when ($C_2 - C_3$) bond  breaks during hydrogenation of (A).

Example 9: Give the number of stereoisomers of (A) in the following reactions.

(a) $(A)\ (C_7H_{12}) \xrightarrow{O_3/\text{oxidation}} \underset{(B)}{\text{Acetone}} + \underset{(C)}{\text{Oxalic acid}} + \underset{(D)}{\text{Acetic acid}}$

(b) $(A)\ (C_8H_{14}) \xrightarrow{O_3/\text{oxidation}} \underset{(B)}{\text{Butane-2-one}} + \underset{(C)}{\text{Oxalic acid}} + \underset{(D)}{\text{Acetic acid}}$

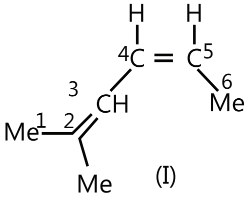
Sol:

(a) 

(A) (C_7H_{12})

Here Compound (A) shows G.I around C_4 — C_5 double bond (since the two groups around C-4 and C-5 are different) but do not show G.I around C_2 — C_3 double bond because the two groups around C-2 are the same.

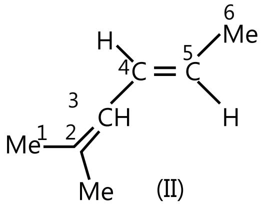
Number of stereoisomers for (A) — 2



(I)

4Z-2-Methylhexa-2,4-diene

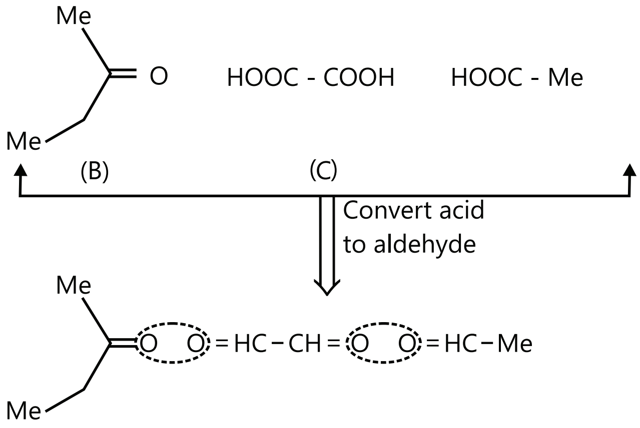
and

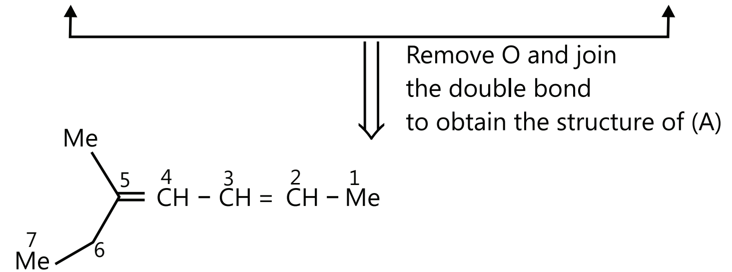


(II)

4E-2-Methylhexa-2,4-diene

(b) Proceed in the same manner as in (a)





(A) (C_8H_{18})

(5-Methylhepta-2,4-diene)

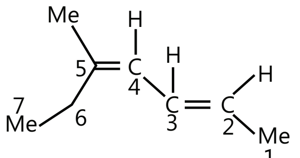
(A) shows geometrical isomers around both (C_2 — C_3) and (C_4 — C_5) double bonds (two of the groups around these double bonds are different)

Moreover, terminal groups (—CH_3) and (—C_2H_5), around C_2 and around C_5, respectively, are different.

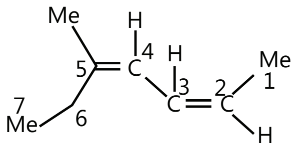
Number of G.I. when the terminal groups are different = 2^n, where n is the number of double bonds (two double bonds).

G.I. = 2^2 = 4

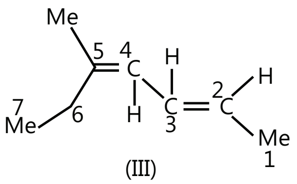
Number of stereoisomers of (A) = 4



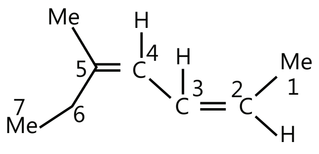
(I)
(2Z,4Z)



(II)
(2E,4Z)



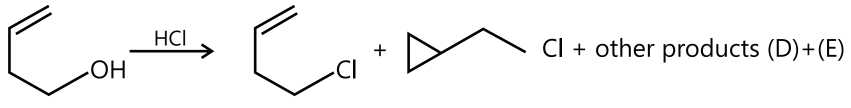
(III)
(2Z,4E)



(IV)
(2E,4E)

Example 10: Explain the formation of the products giving the structures of the intermediates.

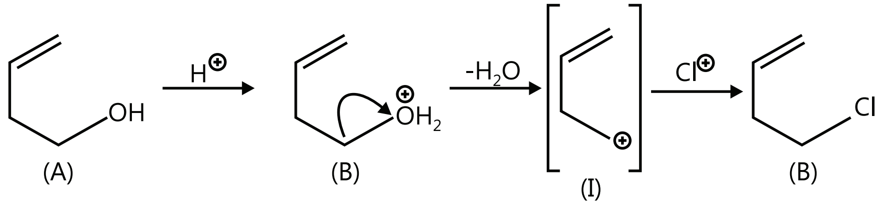
(a)



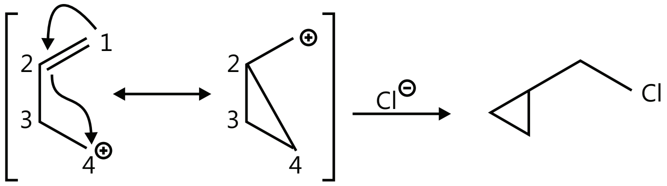
(A) (B)

Sol:

(a)

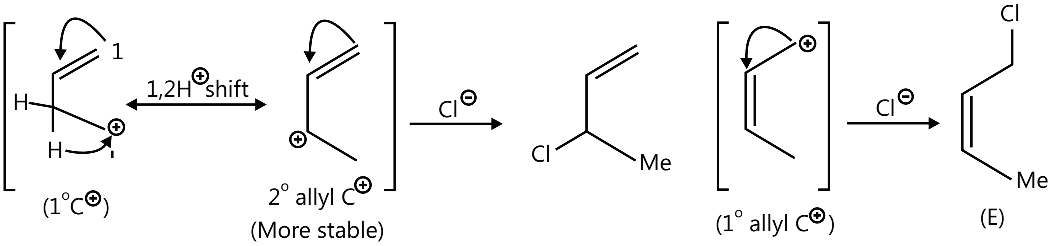


In this reaction presence of double bond influences the reaction pathway and unusual product may also be formed. Due to the presence of e⁻-rich double bond, the intermediate (I) carbocation may also involve intra-molecular rearrangement to form a three membered cyclic ring as shown below:

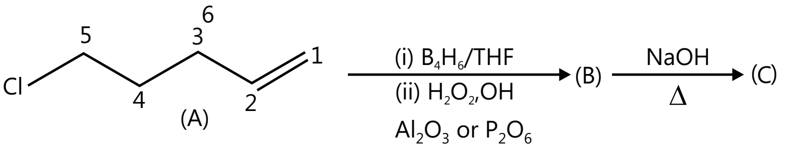


(I) (C)

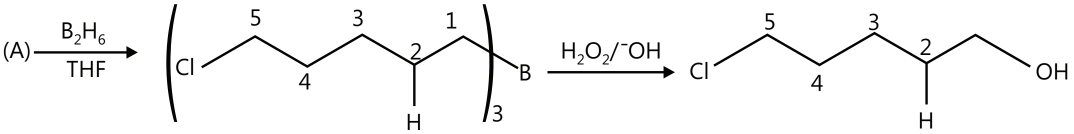
Other products can be obtained due to carbocation (I) rearrangement.



Example 11: Complete the following reaction:

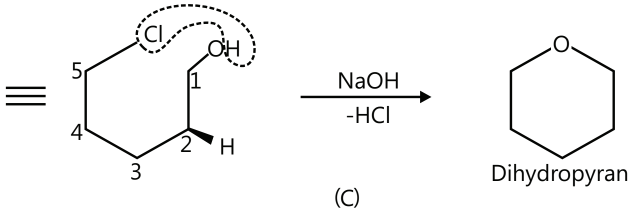


Sol: It is an example of hydroboration-oxidation reaction, it is used in the formation of alcohol from an alkene. It follows anti-Markovnikov's rule, and the addition of H and OH is syn (cis)(addition of H and BH_2 takes place from the same side)



(5-Chloropentane-1-ol)

(B)



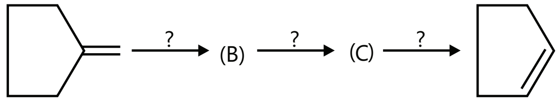
(C)

Dihydropyran

JEE Advanced/Boards

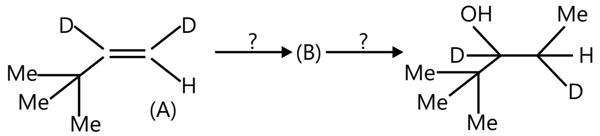
Example 1: Complete the following reaction with appropriate reagents.

(a)



(A) (D)

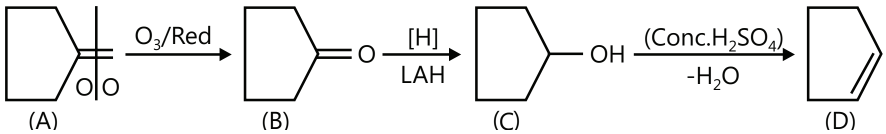
(b)



Sol: (a) Compound (D) Contains a (C = C) bond in the ring, Double bond can be obtained by the dehydration of alcohol.So, (C) is an alcohol.Alcohol (C) is obtained by the reduction of (>C = 0) using reducing agent like LAH.

∴ So (B) contains a keto group (>C = O) , (> C = O) group can be obtained from (A) by ozonolysis.

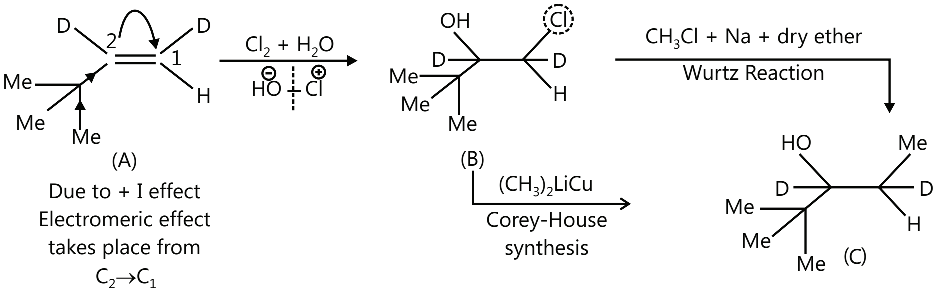
The different steps are as follows:



(b) **Proceeding reverse:** (Retrosynthetic approach)

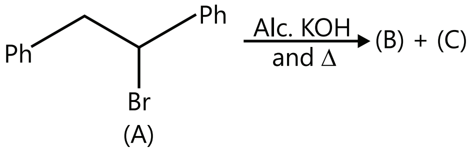
Compound (D) contains one Me and one –OH group. It can be obtained by adding (Cl_2+ H_2O) (HOCl) to (A).

Thus compound (B) will have one OH and one Cl group; now one Me group can be added to (B) by Corey-House synthesis or Wurtz reaction of (B).

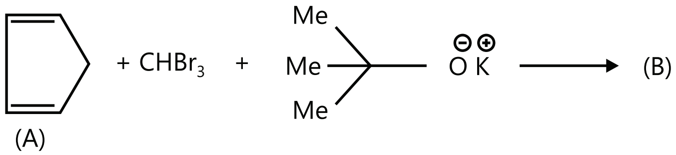


Example 2: Complete the following reactions:

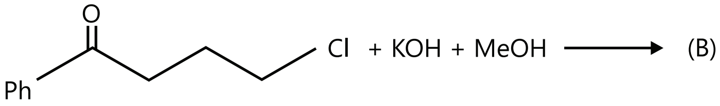
(a)



(b)

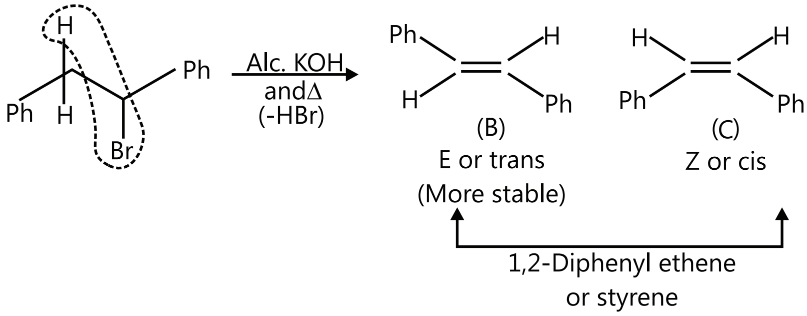


(c)

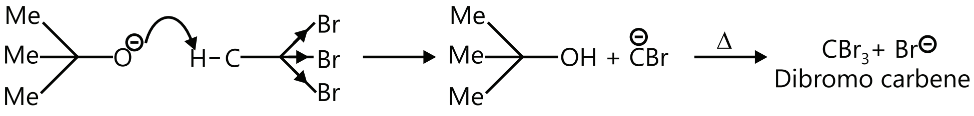


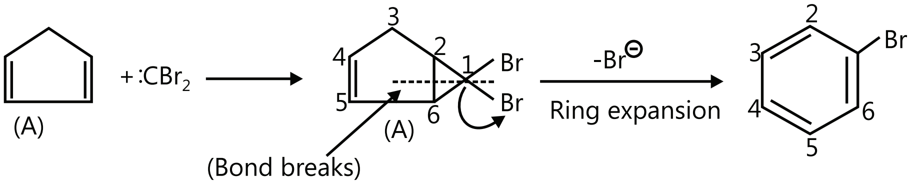
Sol:

(a)

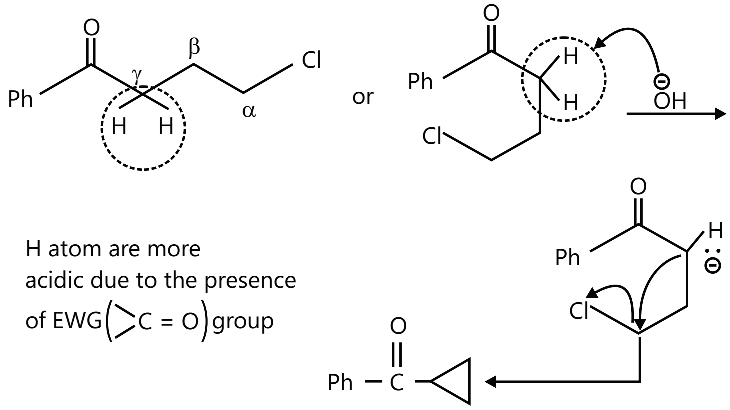


(b)





(c) It is an example of -elimination.



H atom are more acidic due to the presence of EWG ($>C=O$) group

Example 3: Identify the products in the following reactions giving their stereoisomers (if any).

(a) (A)$Me^{1}-{}^{2}\equiv{}^{3}-{}_{4}\,{}^{5}Me \xrightarrow{D_2\text{+ Poisoned Pd}}$ (B) $\xrightarrow{H_2+Pt}$ C (No. of isomers)

(b) (B)(from Problem A)$\xrightarrow[\text{reagent}]{\text{Baeyer's}}$ (D) + (E) (Colour of precipitate)

(c) (B) $\xrightarrow{PhCO_3H+H_2O}$ (D)

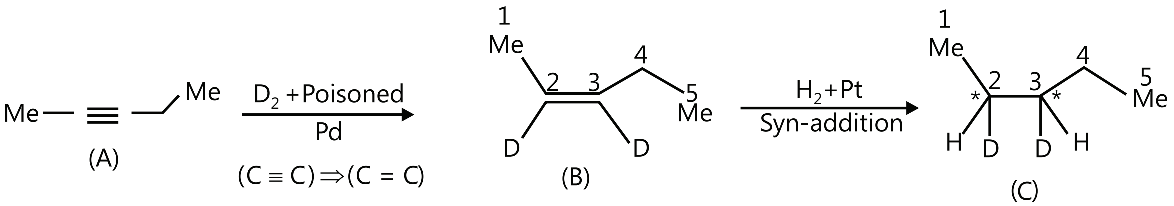
(d) (A) $\xrightarrow{Na+liq.\ ND_3+EtOH}$ (F) $\xrightarrow[\text{or}]{Alk.KMnO_4}$ (D)

$OSO_4/NaHSO_3$

$PhCO_3H/H_2O$

Sol:

(a)



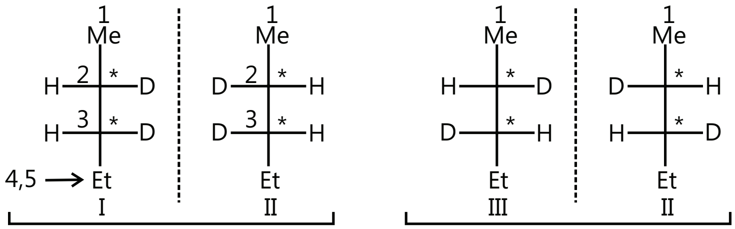
(C)

2Z-2,3-Dideuteropent-2-ene
or
2Z-2,3-Di-d-pent-2-ene

2,3-Dideuteropentane
or
2,3-Di-d-pentane

Since Addition of D_2 by (D_2+Pd) is a syn addition Compound (B) is a cis compound and the addition of H_2 + Pt is also syn. But (B) has two different (R) groups (Me and Et), so the product (C) will not be Meso but a racemic compound.

Compound (C) contains two chiral carbon, thus the number of optical isomers will be $2^2 = 4$ (two pairs of enantiomer). These are:



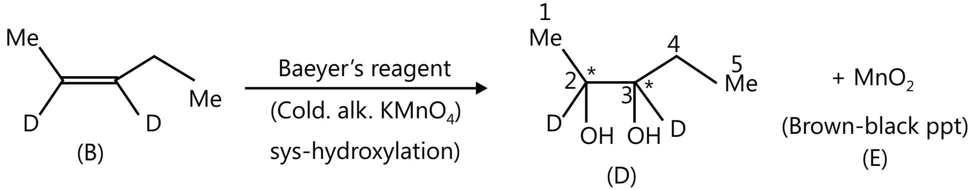
Racemate

Racemate

Pairs of enantiomers: I and II; III and IV (I, III); (I, IV); (II, III),

Pairs of diastereomers: (II, IV)

(b)



(B)

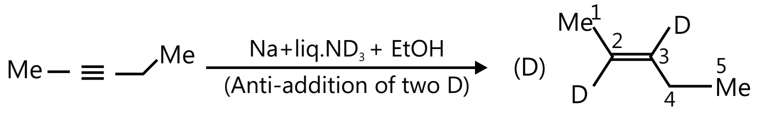
cis-Compound
with two different
R group

(D)
2,3-Dideutentropent-2,3-diol
or
2,3-Di-d-pent-2,3-diol

[Two chiral centres; four stereoisomers as in (a)]

(c) (B) cis-Compound with two different R group $\xrightarrow[\text{Anti-hydroxylation}]{PhCO_3H + H_2O}$ (D) [As in (b)]

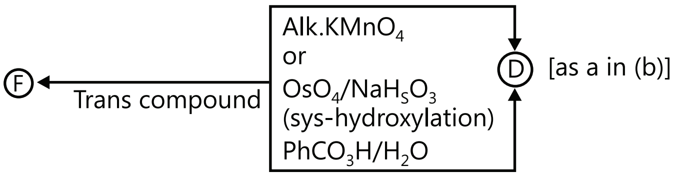
(d)



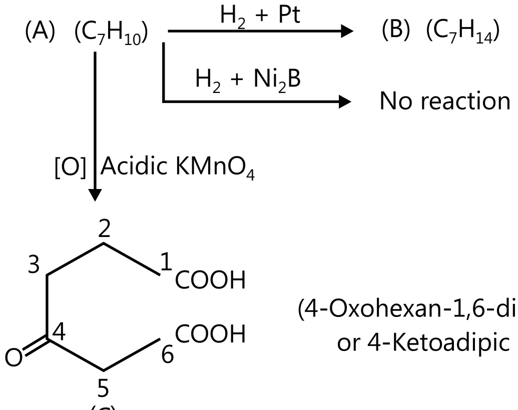
(A)

(trans or E)

(2E-2,3-Deuteropent-2-ene)
or
2E-2,3-Di-d-pent-2-ene



Example 4: Identify (A), (B) and (C) in the following reaction.



(C)

(4-Oxohexan-1,6-dioic acid)
or 4-Ketoadipic acid)

Sol: First of all we have to calculate degree of unsaturation:

$$\text{D.U. in (A)} = \frac{(2n_C + 2) - n_H}{2} = \frac{(7 \times 2 + 2) - 10}{2} = 3^\circ$$

D.U. in (B) = $\frac{(7\times2+2)-14}{2}=1^{\circ}$

Since (A) does not react with P-2 or Brown catalyst (Ni_2B) that reduces alkyne to alkene

Therefore, (A) does not contain (C ≡ C) bond.

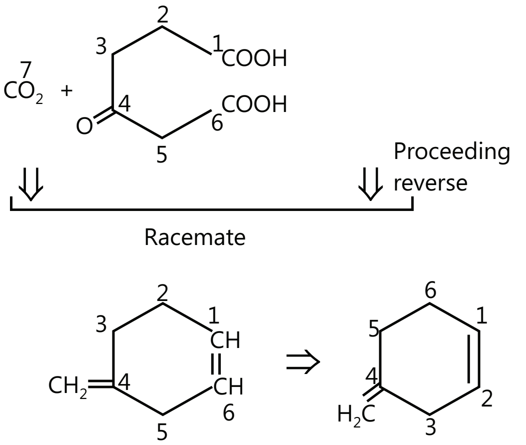
As we have calculated, (B) has 1.D.U., it must be a ring (because after hydrogenation of (A) no double bond will be left)

From the above data it appears that, (A) has one ring and two (C = C) bonds; hence, (A) is a diene.

$$\left.\begin{array}{l}\text{Total number of C atoms in (A)=7}\\ \text{Total number of C atoms in (C)=6}\end{array}\right]\text{one C atoms is lost as } CO_2$$

Possible structure of (A) are as follows:

i.

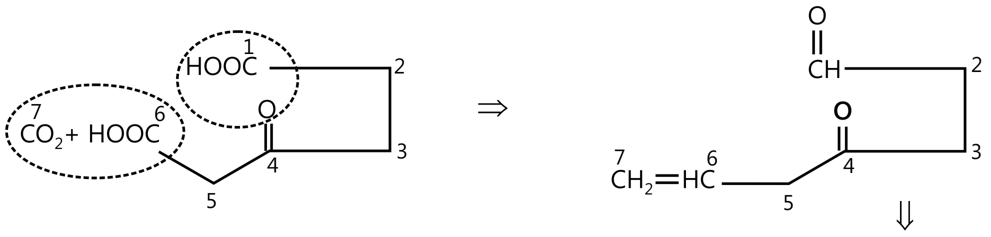


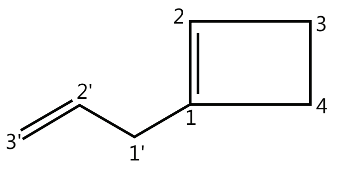
(I)

(4-Methyl cyclohexene)

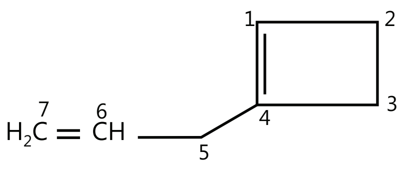
ii. Other two possibilities of the combination are as follows:

(a) $(\overset{1}{C}OOH)$ Groups combines with $(\overset{4}{C}=H)$ group and $\overset{7}{C}O_2$ combination with $(\overset{6}{C}OOH)$.





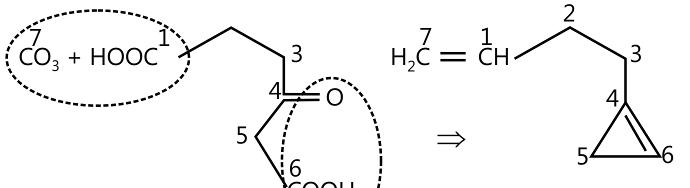
≡



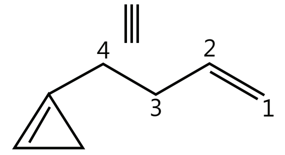
(II)
(Numbering in accordance with naming)
1-(prop-2-enyl)cyclobut-1-ene
or
1-Allyl cyclobutene

(II)
(Numbering in accordance with problem)

(b) $\overset{6}{\text{(COOH)}}$ Groups combines with (C=O) group and CO_2 is in combination with $\overset{1}{\text{(COOH)}}$



(Numbering in accordance
with problem)

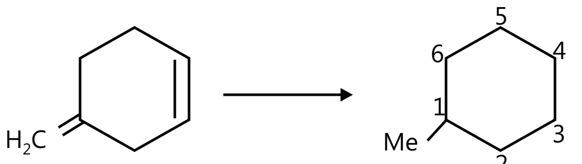


(Numbering in accordance
with naming)
(4-(Cyclopropenyl)but-1-ene)

Structure III is not possible, because on hydrogenation (A) gives (B) (C_7H_{14}), i.e., it absorbs 2 mol of H_2, whereas III will absorb 3 mol of H_2.

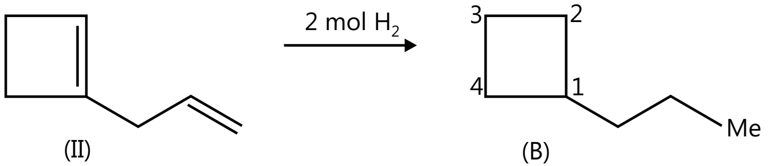
Because of highly strained ring Structure III is unlikely.

Two possible structures are as :-



(I)

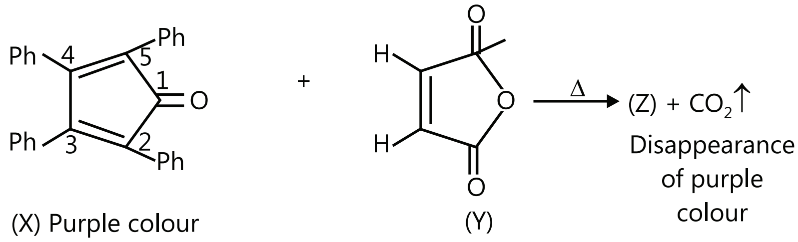
(B)
(C_7H_{14}) (1-Methyl cyclohexane)



(II)

(B)
1-Propyl-cyclobutane

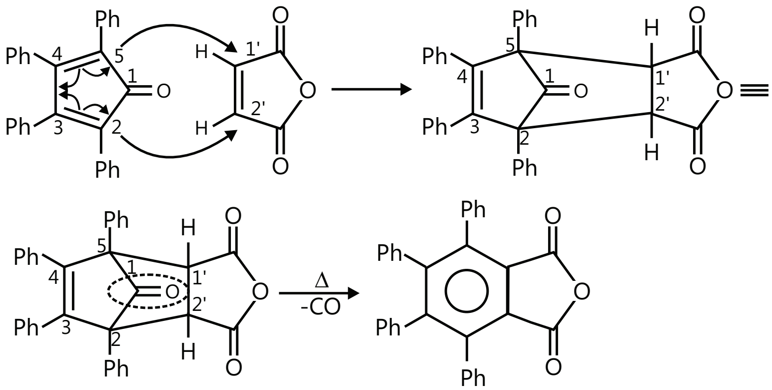
Example 5: Complete the following reactions:



(X) Purple colour
2,3,4,5,-Tetraphenyl cyclopenta-
2,4-dien-1-one

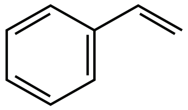
(Y)
Maleic
anhydride

Sol: It is an example of Diels Alder reaction. The mechanism is a concerted type (bond breaking and bond making takes place simultaneously)

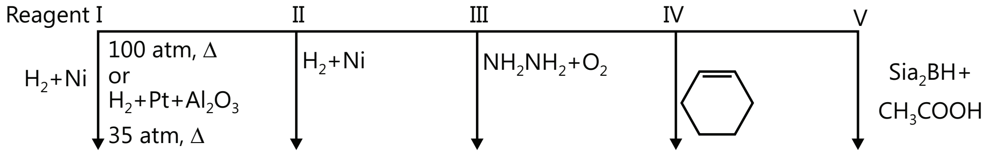


(Z)
(Colourless
compound)

Example 6: Identify (A) to (H)

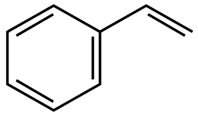


(A)

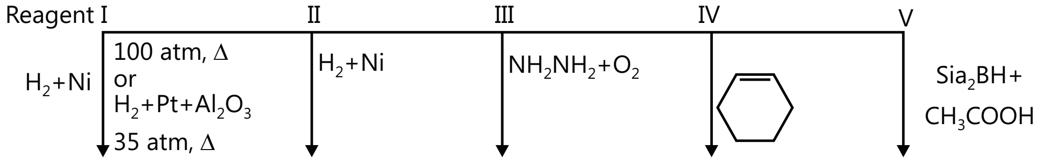


(B) (C) (D) + (E) (gas) (F) + (G) (H)

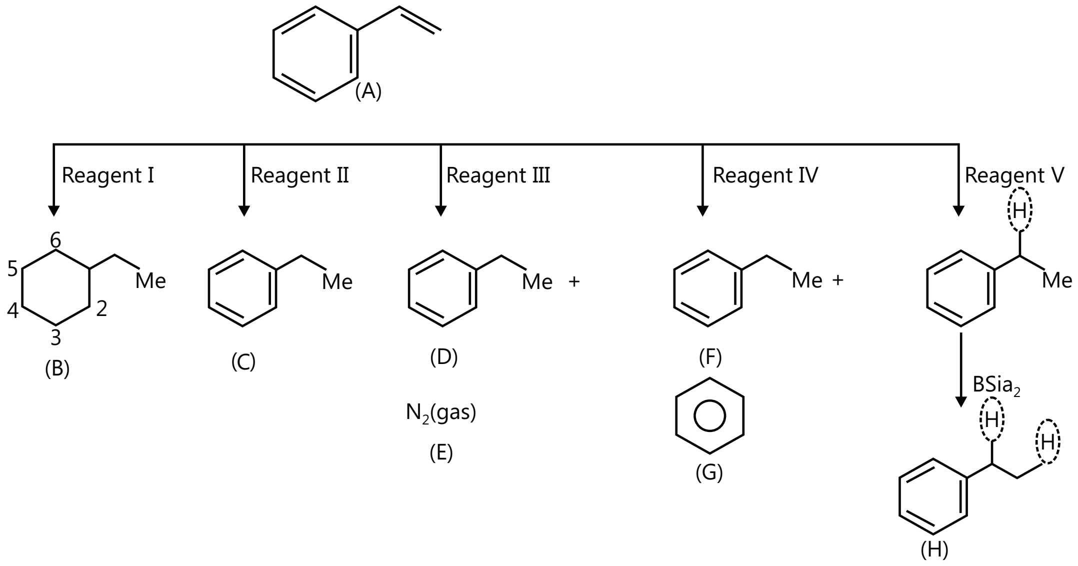
Sol:



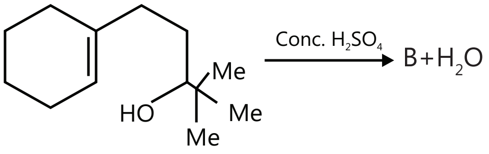
(A)



(B) (C) (D) + (E) (gas) (F) + (G) (H)

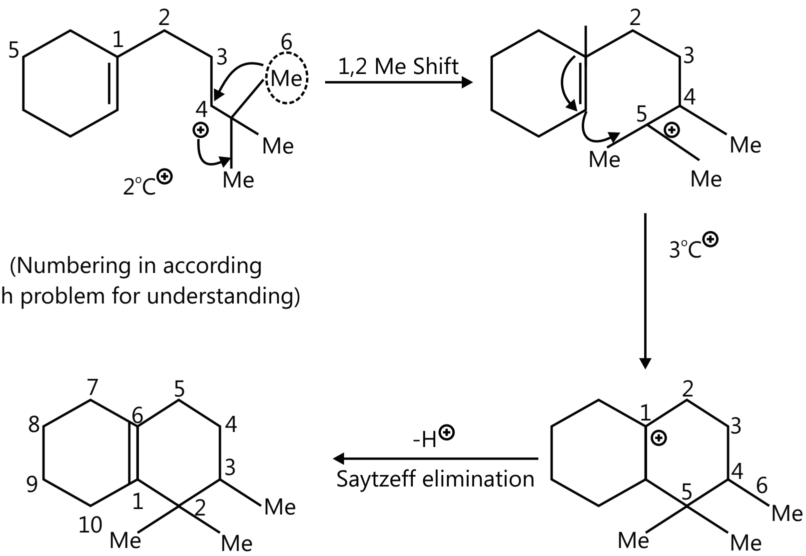


Example 7: Write the product with its mechanism.



(A)

Sol:

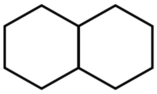


(Numbering in according with problem for understanding)

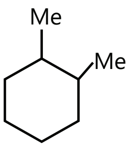
2,2,3-Trimethyl bicyclo [4.4.0] dec-1-ene

Example 8: Which of the following show G.I.?

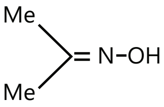
(a)



(b)

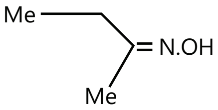


(c)



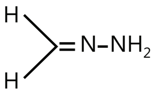
$(Me)_2C{=}N{-}OH$

(d)



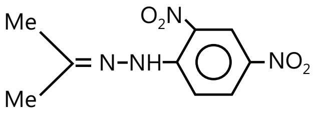
$CH_3CH_2(Me)C{=}N.OH$

(e)



$H_2C{=}N{-}NH_2$

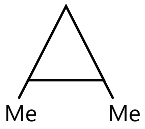
(f)



$(Me)_2C{=}N{-}NH{-}C_6H_3(NO_2)_2$

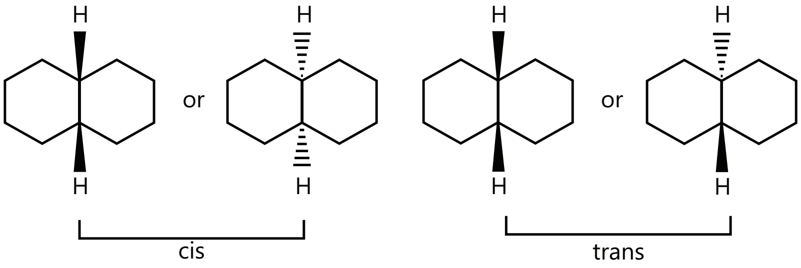
(g) Ph – N = N – Ph

(h)



Sol: In order to show geometrical isomerism the alkene must contain different substituents i.e. the substituents on both the carbon bearing double bond must have different substituents

(a) It shows G.I.

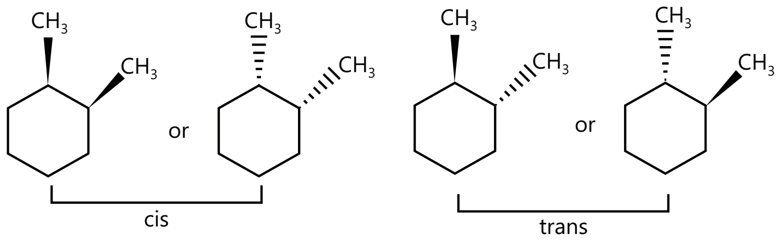


(i) Two atoms on the dotted line (.........................) means that the groups are below the plane of the ring.

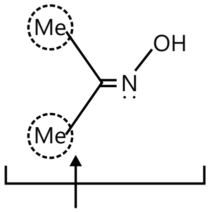
(ii) Two atoms on the bold lines (**.........................**) means that the groups are above the plane of the ring.

(iii) One atom on the dotted line (.........................) means that one group is below and another is above the plane of the ring.

(b) It shows G.I.

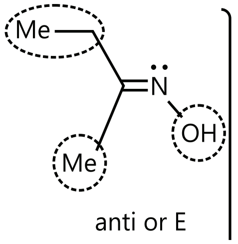


(c) It does not show G.I.



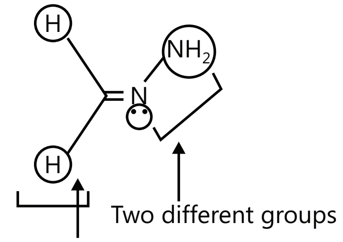
Two same groups

Priority of C_2H_5 > CH_3 and OH > LP of e s



Two higher priority group on the same side, on two different C atom of the double bond

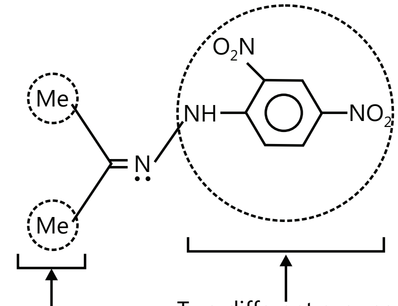
(e) It does not show G.I



Two different groups

Two same groups

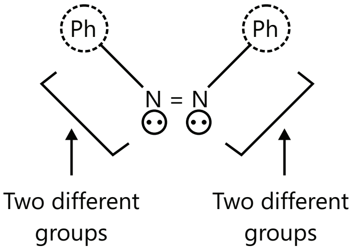
(f) It does not show G.I

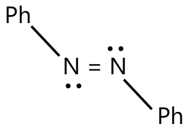


Two same groups

Two different groups

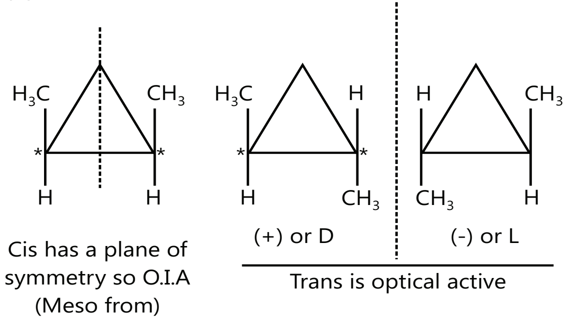
(g) It shows G.I.





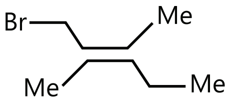
anti or E

(h) It shows G.I.

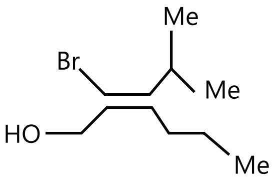


Example 9: Give IUPAC name to each of the following using E or Z designations.

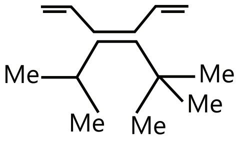
(A)



(B)

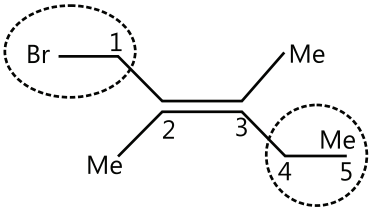


(C)



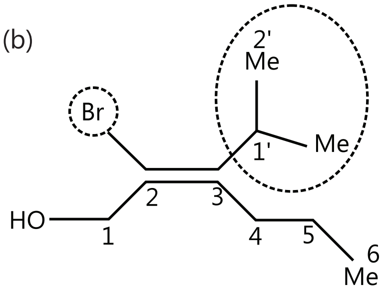
Sol:

(a)



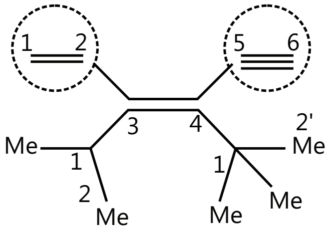
Two higher priority groups on opposite side,1E,
1-Bromo-2,3-dimethyl pent-2-ene

(b)



Priority of (-Br) > (-CH_2OH) and [$(CH_3)_2CH$-]>(-C_3H_7).
Two higher priory groups on the same side.
2Z,2-Bromo-3-(1-methyl ethyl) hex-2-en-1-ol

(c)



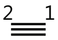
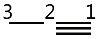
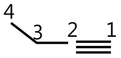
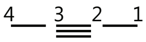
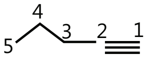
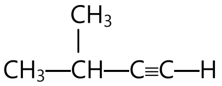
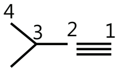
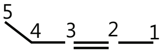
Priority of HC ≡ C- > $(CH_3)_3C$- > CH_2=CH-B> $(CH_3)_2CH$-
Two higher priority groups on the same side.
3Z,3-(1-methyl ethyl)-4-(1-1-Dimethyl ethyl)-hexa-1,3-dine-5-yne

ALKYNES

1. INTRODUCTION

1.1 Nomenclature

Alkynes are unsaturated hydrocarbons that contain (C≡C) bond. Their general formula is C_nH_{2n-2}.

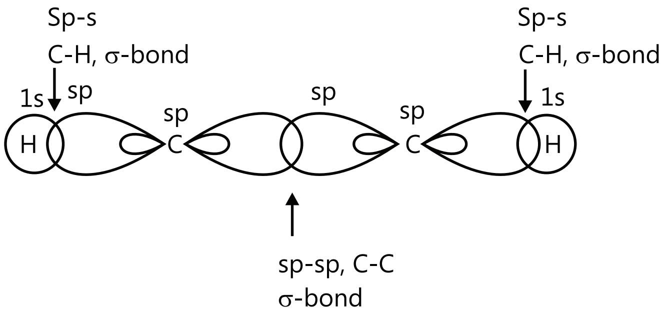
Condensed	Stick	Bond line	IUPAC name	Common or trivial name
C_2H_2	H—C≡C—H		Ethyne	Acetylene
C_3H_4	$H_3C—C≡C—H$		Propyne	Methylacetylene
C_4H_6	$CH_3—CH_2—C≡CH$ $CH_3—C≡C—CH_3$	 	But-1-yne But-2-yne	Ethylacetylene Dimethy lacetylene
C_5H_8	$CH_3—CH_2—CH_2—C≡C—H$		3-Methyl-but-1-yne	Propylacety lene
	or  $CH_3—CH(CH_3)—C≡C—H$		3-Methyl-but-1-yne	Isopropyl-acetylene
	or $CH_3—CH_2—C≡C—CH_3$		Pent-2-yne	Ethyl methylacetylene

1.2 Structure

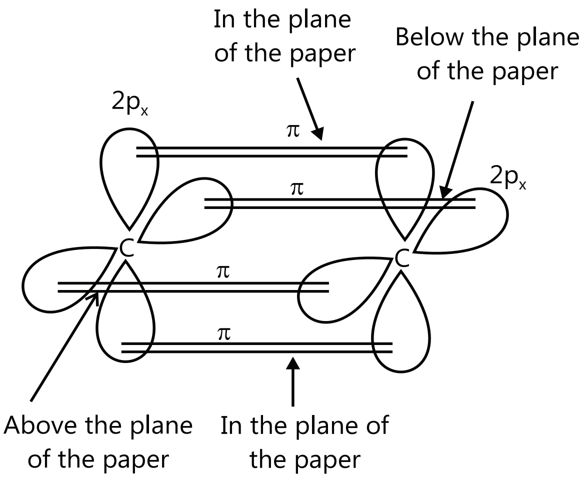
Each carbon atom of ethyne is sp-hybridized. One sp-hybridized orbital of each carbon undergoes head on overlap with sp-hybrisized orbital of another carbon to form a sp-sp, C-C, σ-bond. The second sp-hybridized orbital of each carbon overlaps along the internuclear axis with 1 s-orbital of each of the two hydrogen atoms forming two sp-s, C—H, σ-bonds. Each carbon is now left with two unhybridized p-orbitals ($2p_x$ and $2p_y$) which are perpendicular to each other as well as to the plane of the C—C sigma bond.

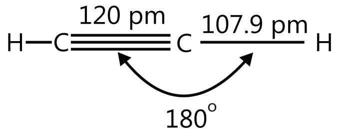
The two $2p_x$– orbitals, one on each carbon, are parallel to each other and hence overlap sideways to form a π-bond. Similar overlap between $2p_y$– orbitals, one on each carbon, results in the formation of a second π-bond as shown in figure.

(a)



(b)





Carbon-carbon triple bond consists of one strong σ-bond and two weak π-bonds. The total strength of C ≡ C bond in ethyne is 823 kJ mol^{-1}. It is stronger than the C = C bond of ethane (599 kJ mol^{-1}) and C – H bond of ethane (348 kJ mole^{-1}). Further, due to the smaller size of sp-orbitals (as compared to sp^2 and sp^{3-}) and sideways overlap of p-orbitals, the carbon-carbon bond length in ethyne is shorter (120 pm) than those of C = C (134 pm) and C–C (154 pm).

1.3 Isomerism in Alkynes

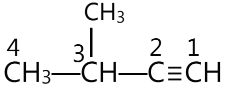
(i) Position isomerism. The first two members, i.e., ethyne and propyne exist in one form only. However, butyne and higher alkynes exhibit position isomerism due to the different position of the triple bond on the carbon chain. For example,

$CH_3—CH_2—C≡CH$ $\qquad$ $CH_3—C≡C—CH_3$

But-1-yne $\qquad$ But-2-yne

(ii) Chain isomerism. Alkynes having five or more carbon atoms show chain isomerism.

$CH_3—CH_2—CH_2—C≡CH$



$\overset{4}{C}H_3—\overset{3}{C}H(CH_3)—\overset{2}{C}≡\overset{1}{C}H$

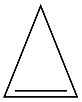
(iii) Functional isomerism: Alkynes are functional isomers of dienes

$\overset{4}{C}H_3 — \overset{3}{C}H_2 — \overset{3}{C} ≡ \overset{1}{C}H$ $\qquad$ $\overset{1}{C}H_2 = \overset{2}{C}H — \overset{3}{C}H = \overset{4}{C}H_2$

But-1-yne $\qquad$ Buta-1,3-diene

(iv) Ring chain isomerism: Alkynes show ring chain isomerism with cycloalkenes. For example,

$CH_3—C≡CH$ and



are ring chain isomers.

Propyne $\qquad$ Cyclopropene

2. PREPARATION OF ALKYNES

2.1 From Calcium Carbide

Alkynes are prepared by the following general methods.

1. **By the action of water on calcium carbide:** Ethyne (acetylene) is prepared in the laboratory as well as on a commercial scale by the action of water on calcium carbide.

   $CaC_2 + 2H_2O \rightarrow HC{\equiv}CH + Ca(OH)_2$

   Calcium carbide   Ethyne (Acetylene)

   Calcium carbide needed for the purpose is manufactured by heating limestone (calcium carbonate) with coke in an electric furnace at 2275 K.

   $CaCO_3 \xrightarrow{2275K} CaO + CO_2$

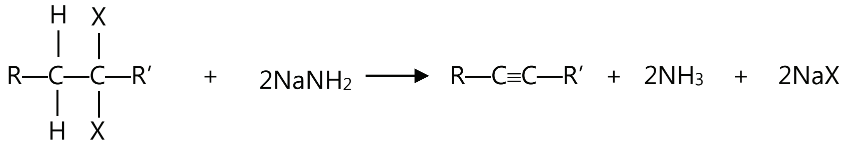
   $CaO + 3C \xrightarrow{2275K} CaC_2 + CO$

2. **Procedure:** Lumps of calcium carbide are placed on a layer of sand in a conical flask fitted with a dropping funnel and a delivery tube. The air present in the flask is replaced by oil gas since acetylene forms an explosive mixture with air. Water is now dropped from the dropping funnel and the acetylene gas thus formed is collected over water.

3. **Purification:** Acetylene gas prepared by the above method contains impurities of hydrogen sulphide and phosphine due to the contamination of CaS and calcium phosphide in calcium carbide. Phosphine is removed by passing the gas through a suspension of bleaching powder. Pure acetylene is finally collected over water.

2.2 Double Dehydrohalogenation of Dihalides

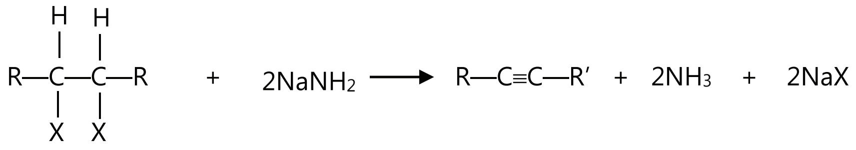
Double dehydrohalogenation of a geminal dihalide



$$R-\overset{H}{\underset{H}{C}}-\overset{X}{\underset{X}{C}}-R' + 2NaNH_2 \longrightarrow R-C{\equiv}C-R' + 2NH_3 + 2NaX$$

Geminal dihalide   Sodium amide   Alkyne   Ammonia   Sodium halide

Double dehydrohalogenation of a vicinal dihalide



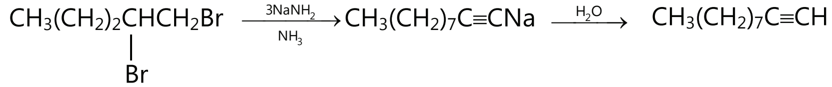
$$R-\overset{H}{\underset{X}{C}}-\overset{H}{\underset{X}{C}}-R + 2NaNH_2 \longrightarrow R-C{\equiv}C-R' + 2NH_3 + 2NaX$$

Vicinal dihalide   Sodium amide   Alkyne   Ammonia   Sodium halide

The most frequent application of these procedures are in the preparation of terminal alkynes. Since the terminal alkyne product is acidic enough to transfer a proton to the amide anion. One equivalent of base in addition to the two equivalents required for double dehydrohalogenation is needed. Adding water or acid after the reaction is complete converts the sodium salt to the corresponding alkyne.

1. $(CH_3)_3CCH_2CHCl_2 \xrightarrow[NH_3]{3NaNH_2} (CH_3)_3CC{\equiv}CNa \xrightarrow{H_2O} (CH_3)_3\ CC{\equiv}CH$

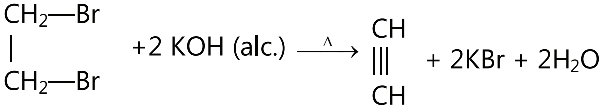
1,1-Dichloro-3,3-Dimethylbutane — Sodium salt of alkyne product (not isolated) — 3,3-Dimethyl-1-butyne (56-60%)

2. 

$CH_3(CH_2)_2\underset{\displaystyle Br}{\underset{|}{C}}HCH_2Br \xrightarrow[NH_3]{3NaNH_2} CH_3(CH_2)_7C{\equiv}CNa \xrightarrow{H_2O} CH_3(CH_2)_7C{\equiv}CH$

1,2-Dibromodecane — Sodium salt of alkyne Product (not isolated) — 1-Decyne (54%)

Double dehydrohalogenation to form terminal alkynes may also be carried out by heating geminal and vicinal dihalides with potassium ter-butoxide in dimethyl sulfoxide. By heating with alcoholic solutio`n of KOH



$$\begin{matrix} CH_2{-}Br \\ | \\ CH_2{-}Br \end{matrix} + 2\ KOH\ (alc.) \xrightarrow{\Delta} \begin{matrix} CH \\ ||| \\ CH \end{matrix} + 2KBr + 2H_2O$$

1,2-Dibromodecane (Ethylene dibromide) — Acetylene

CONCEPTS

Misconception: The reaction, in fact, occurs in two steps and each step involves the loss of a molecule of HBr as shown below:

$BrCH_2{-}CH_2Br + KOH\ (alc.) \xrightarrow{\Delta} CH_2{=}CHBr + KBr + H_2O$

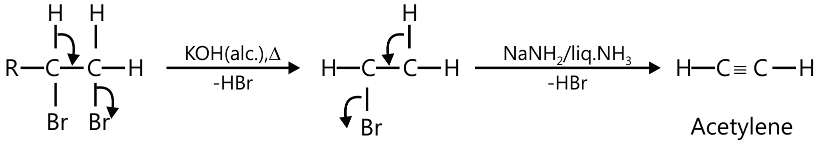
Ethylene dibromide — Vinyl bromide

$CH_2{=}CH{-}Br + KOH\ (alc.) \xrightarrow{\Delta} CH{\equiv}CH{+}KBr{+}H_2O$

Vinyl bromide — Acetylene

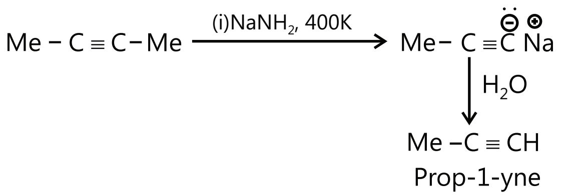
Aman Gour (JEE 2012, AIR 230)

Explanation: In ethylene dibromide, Br is present on a saturated carbon atom. Therefore. Like alkyl halides, it is a reactive molecule. Consequently, on heating with alcoholic KOH, it readily eliminates a molecule of HBr to form vinyl bromide in good yield. In contrast, due to the presence of Br on a doubly bonded carbon atom, vinyl bromide is a highly unreactive molecule and hence on heating with alcoholic KOH, it does not easily lose a molecule of HBr to form acetylene. Thus, with alcoholic KOH, the yield of acetylene is low. Therefore, to obtain acetylene in fairly good yield from vinyl bromide, a much stronger base than alcoholic KOH such as $NaNH_2$ in liquid NH_2 is usually used. Thus, dehydrohalogeneation of ethylene dibromide to acetylene is preferably carried out in the following two stages.



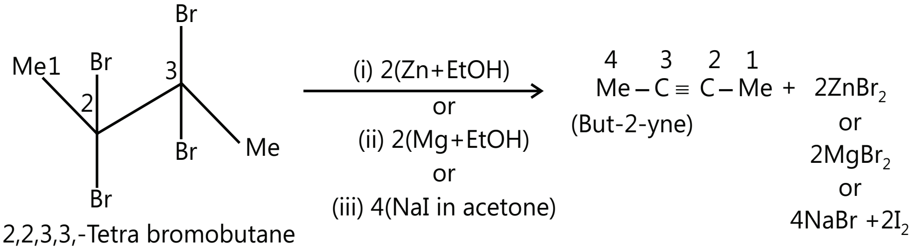
Vicinal dihalide — Vinyl bromide

With a strong base ($\overset{\Theta}{NH_2}$), isomerisation also taken place to give terminal alkyne.



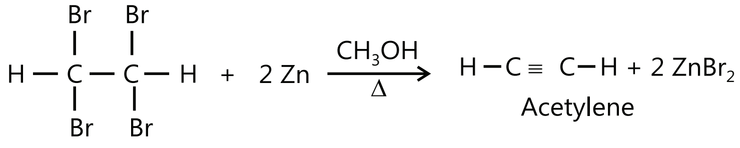
$$\begin{tikzcd}[column sep=large] \mathrm{Me-C\equiv C-Me} \arrow[r, "\text{(i)}NaNH_2\text{, 400K}"] & \mathrm{Me-C\equiv \overset{\ominus}{\ddot{C}}\,\overset{\oplus}{Na}} \arrow[d, "H_2O"] \\ & \mathrm{Me-C\equiv CH} \\ & \text{Prop-1-yne} \end{tikzcd}$$

Dehalogenation of tri/tetra halides



2,2,3,3,-Tetra bromobutane

3. **By dehalogenation of tetrahalides.:** Tetrahaloalkanes when heated with zinc dust in methanol undergo dehalogenation to yield alkynes. For example



$$\mathrm{H-\underset{Br}{\overset{Br}{\underset{|}{\overset{|}{C}}}}-\underset{Br}{\overset{Br}{\underset{|}{\overset{|}{C}}}}-H} + 2\,\mathrm{Zn} \xrightarrow[\Delta]{CH_3OH} \underset{\text{Acetylene}}{\mathrm{H-C\equiv C-H}} + 2\,\mathrm{ZnBr_2}$$

1,1,2,2-Tetrabromoethane

2.4 Dehalogenation of Haloforms

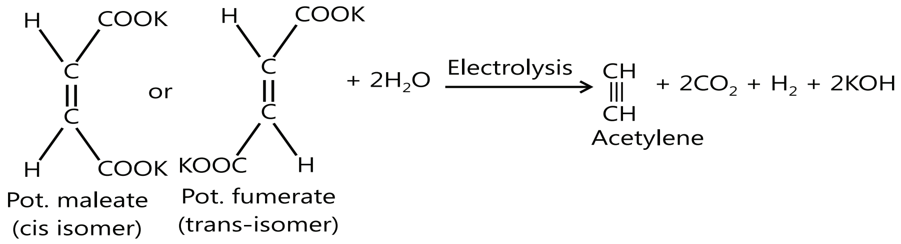
By dehalogenation of haloforms: Chloroform and iodoform on heating with silver powder undergo dehalogenation to form ethyne.

$$\underset{\text{Chloroform}}{\mathrm{CH}}\boxed{\mathrm{Cl_3} + 6\,\mathrm{Ag} + \mathrm{Cl_3}}\underset{\text{Chloroform}}{\mathrm{CH}} \xrightarrow{\Delta} \underset{\text{Ethyne}}{\mathrm{HC\equiv CH}} + 6\,\mathrm{AgCl}$$

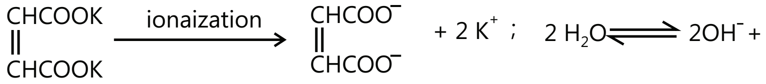
$$\underset{\text{Iodoform}}{\mathrm{CH}}\boxed{\mathrm{I_3} + 6\,\mathrm{Ag} + \mathrm{I_3}}\underset{\text{Iodoform}}{\mathrm{CH}} \xrightarrow{\Delta} \underset{\text{Ethyne}}{\mathrm{HC\equiv CH}} + 6\,\mathrm{AgI}$$

2.5 Kolbe's Electrolytic Reaction

Kolbe's electrolytic reaction: Acetylene can be prepared by electrolysis of a concentrated solution of sodium or potassium salt of maleic acid or fumaric acid. Thus,

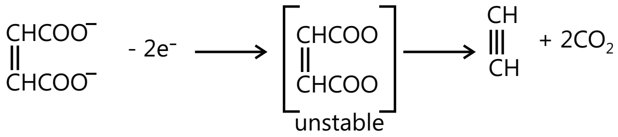


This reaction is called Kolbe's electrolytic reaction and is believed to occur by the following steps:



$$\begin{array}{c}\mathrm{CHCOOK}\\ \|\\ \mathrm{CHCOOK}\end{array} \xrightarrow{\text{ionaization}} \begin{array}{c}\mathrm{CHCOO^-}\\ \|\\ \mathrm{CHCOO^-}\end{array} + 2\,\mathrm{K^+}\ ;\quad 2\,\mathrm{H_2O} \rightleftharpoons 2\mathrm{OH^-} +$$

At anode:

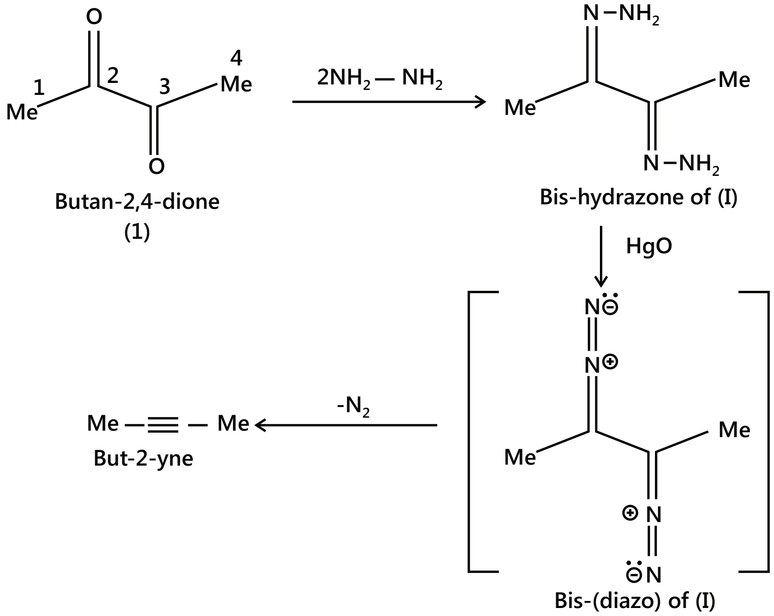


$$\begin{array}{c} CHCOO^- \\ \| \\ CHCOO^- \end{array} - 2e^- \longrightarrow \left[\begin{array}{c} CHCOO \\ \| \\ CHCOO \end{array}\right]_{\text{unstable}} \longrightarrow \begin{array}{c} CH \\ ||| \\ CH \end{array} + 2CO_2$$

At cathode: $2H^+ + 2e^- \longrightarrow [2H] \longrightarrow H_2$

2.6 From α-diketo

α- Diketone reacts with hydrazine ($NH_2 - NH_2$) to give bis-hydrazone which on oxidation with HgO gives unstable bis(diazo) compound which decomposes to give alkyne.



2.7 Industrial Method

$$2CH_4(g) \xrightarrow{1773\ K} CH{\equiv}CH(g) + 3H_2(g)$$

The reaction is highly endothermic, yet the optimum time for this reaction is 0.01 second.

$\Delta n = n_P - n_R = 4 - 2 = 2$ mol, and this causes a significant increase in ΔS. At this high temperature, the $T\Delta S$ term in the equation $\Delta G = \Delta H - T\Delta S$ predominates, making ΔG = –ve , although ΔH = +ve.

But ΔH_f° for C_2H_2 = +227 k mol^{-1} shows that acetylene is thermodynamically unstable, explodes readily, and gets converted into its elements.

$C_2H_2(g) \longrightarrow 2C(s) + H_2(g)$, $\Delta H^\circ = -227$ kJ $mole^{-1}$

2.8 Berthelot Synthesis

Mearcellin Berthelot synthesized acetylene from its elements (carbon and hydrogen) by striking an electric arc between two electrodes in an atmosphere of H_2 gas.

$2C + H_2 \rightleftharpoons CH \equiv CH(g)$

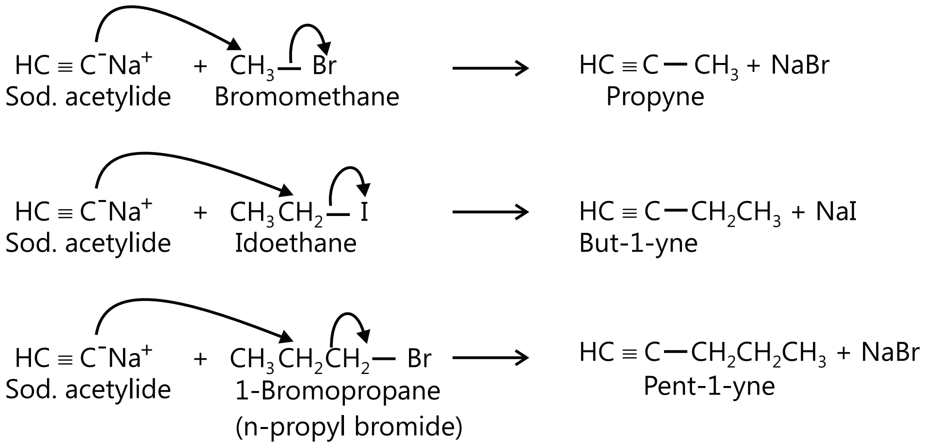
Acetylene

2.9 Higher Alkynes from Acetylene

Synthesis of higher alkynes from acetylene: Acetylene is first treated with sodium metal at 475K or with sodamide in liquid ammonia at 196 K to form sodium acetylide. This upon treatment with alkyl halides gives alkyne.

For example:

$$\underset{\text{Ethyne(Acetylene)}}{HC \equiv CH} + NaNH_2 \xrightarrow{\text{Liq.}NH_3\text{,196K}} \underset{\text{Sodium acetylide}}{HC \equiv C^-Na^+} + NH_3$$



$$\underset{\text{Sod. acetylide}}{HC \equiv C^-Na^+} + \underset{\text{Bromomethane}}{CH_3-Br} \longrightarrow \underset{\text{Propyne}}{HC \equiv C-CH_3} + NaBr$$

$$\underset{\text{Sod. acetylide}}{HC \equiv C^-Na^+} + \underset{\text{Idoethane}}{CH_3CH_2-I} \longrightarrow \underset{\text{But-1-yne}}{HC \equiv C-CH_2CH_3} + NaI$$

$$\underset{\text{Sod. acetylide}}{HC \equiv C^-Na^+} + \underset{\text{(n-propyl bromide)}}{\underset{\text{1-Bromopropane}}{CH_3CH_2CH_2-Br}} \longrightarrow \underset{\text{Pent-1-yne}}{HC \equiv C-CH_2CH_2CH_3} + NaBr$$

An analogous sequence usually terminal alkynes as starting material yields alkynes of the type RC = CR′.

$$\underset{\text{2–Methy–1–Pentyne}}{(CH_3)_2CHCH_2C \equiv CH} \xrightarrow[NH_3]{N_2NH_3} (CH_3)_2CHCH_2C \equiv CNa \xrightarrow{CH_3Br} \underset{\text{5–Methyl–2–Hexyne–181\%}}{(CH_3)_2CHCH_2C \equiv CCH_3}$$

Dialkylation of acetylene can be achieved by carrying out the sequence twice.

$$\underset{\text{Acetylene}}{HC \equiv CH} \xrightarrow[\text{2.}CH_3CH_2Br]{\text{1.NaOH,}NH_3} HC \equiv CCH_2CH_3 \xrightarrow[\text{2.}CH_3Br]{\text{1.NaOH,}NH_3} \underset{\text{2–Pentyne(81\%)}}{CH_3C \equiv CCH_2CH_3}$$

3. PROPERTIES OF ALKYNES

(i) No cis-trans isomerism: The sp hybrid orbitals are linear, ruling out cis-trans stereoisomers in which substituents must be on different sides of the multiple bond.

(ii) Bonds: Bond length decreases in the following order: Alkane > Alkene > Alkyne

Bond length order: $-\underset{sp^3}{C}-H > =\underset{sp^2}{C}-H > \equiv\underset{sp}{C}-H$

Bond Strength order: $\equiv\underset{sp}{C}-H > =\underset{sp^2}{C}-H > -\underset{sp^3}{C}-H$

As a general rule 'more the s – character of hybrid orbitals used by an atom, closer are the bonding electrons to the atom and shorter and stronger is any of its σ-bonds'.

(iii) Solubility and Dipole moment

Decreasing solubility in H_2O: Alkynes > Alkenes > Alkanes

Alkynes are slightly more soluble in H_2O because they are somewhat more polar.

The dipole moment of alkyne is greater than those in alkene because (C — C) sp bond is more polarized than (C — C) sp^2 bond: this is because C with more s character is more electronegative.

Dipole moment of but-1-yne is 0.8 D and that of but-1-ene is 0.3 D.

Due to a slightly high polarity and dipole moment of alkynes than those of alkenes (and of alkenes higher than alkane) boiling point of alkynes > alkenes > alkanes, with the same number of C atoms.

They go from gases to liquids to solids with increasing molecular weights. There is a little difference in boiling points of these hydrocarbons with similar C skeletons.

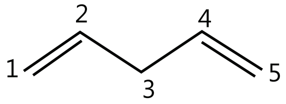
(iv) Smell: All alkynes are odourless except acetylene which has a garlic smell due to the presence of impurity, phosphine.

(v) Physical state: The first three members are gases, the next eight are liquids, and the rest are solids.

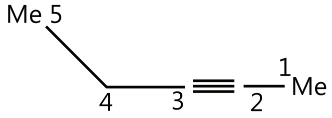
(vi) Melting and Boiling points: The m.p. and b.p. of alkynes are slightly higher than those of the corresponding alkenes and alkanes. This is probably due to the presence of a triple bond, alkynes have linear structures and hence their molecules can be more closed packed in the crystal lattice as compared to those of corresponding alkenes and alkanes.

(vii) Densities: Densities of alkynes like those of alkenes and alkanes increase as the molecular size increases. However, they are all lighter than water, since densities lie in the range 0.69 – 0.77 g/cm^2.

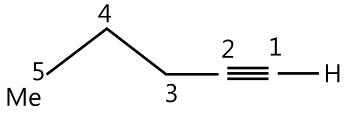
(viii) Stability: Alkynes are less stable than isomeric dienes as is evident from their heat of formation (ΔH_f°) values.



(1,4-Pentadiene) +106.0 kJ mol-1



(Pent-2-yne) +129.0 kJ mol-1



(Pent-2-yne) +144.5 kJ mol-1

(ix) Reactivity: However, alkynes are less reactive than the corresponding alkenes towards electrophilic addition (EA) reaction (except catalytic hydrogenation), even though they contain two π-bonds. This is due to:

(a) Greater EN of sp-hybridised C atom of alkynes than sp^2 –hybridised C atom of alkenes which hold the π - electrons of alkynes more tightly.

(b) Greater delocalisation of π -electrons in alkynes (because of cylindrical nature of their π -electrons cloud) than in alkenes. As a result, π -electrons of alkynes are less easily available for addition reaction than those of alkenes. So alkynes are less reactive than alkenes towards electrophilic addition reaction.

Catalytic hydrogenation, however, is an exception: Alkenes are adsorbed on the surface of catalyst only when the plane of π-bond approaches perpendicularly. In alkynes because of the cylindrical nature of π-bonds, approach by hydrogen along the axis of the cylinder is more effective and thus transition state in alkynes is less strained. So alkynes react faster than alkenes with H_2.

(x) Acidity of alkynes:

Terminal alkynes are more acidic than alkenes because alkyne C-atoms are sp hybridized and electrons in an s-orbital are more tightly held than in a p-orbital also s-electrons are closer to the nucleus.

Furthermore, since the sp orbital has more s character (50% s) than sp^2 (33% s) or sp^2 orbital (25% s), the electrons in sp orbital are more tightly held by the nucleus than electrons in sp^2 or sp^3 orbital.

In another words, sp-hybridised C is more EN than sp^2, or sp^3-hybridised C atom. Due to this greater EN, the electrons of (C — H) bonds are displaced more towards the C atom than towards the H atom. Therefore, the H-atom is less tightly held by the C atom and hence can be removed as a proton (H$^+$ ion) by a strong base and consequently terminal alkynes behave as acids.

$$R - C \equiv C - H + \text{strong base} \longrightarrow R - C \equiv \overset{\ddot{\ominus}}{C} - \text{Base} - H$$

As a rule, as the s character decreases from sp to sp^2 to sp^3 hybridised C atom, the acidic character of hydrocarbons decreases in the following order.

$$Me - HC = O \longleftrightarrow Me - C^{\oplus}H - O^{\ominus}$$

4. REACTIONS OF ALKYNES

4.1 Acidic Character

(i) Formation of alkali metal acetylides: Ethyne and other terminal alkynes (Alkynes in which the triple bond is at the end of the carbon chain) or 1-alkynes react with strong bases such as sodium metal at 475 K or sodamide in liquid ammonia at 196 K to form sodium acetylides with evolution of H_2 gas.

$$\underset{\substack{\text{Ethyne}\\\text{(Acetylene)}}}{2HC \equiv CH} + 2Na \xrightarrow{475K} \underset{\substack{\text{Monosodiume ethynide}\\\text{(monosodium acetylide)}}}{2HC \equiv C^{-}Na^{+}} + H_2$$

$$\underset{\text{(A terminal alkyne)}}{R-C \equiv CH} + NaNH_2 \xrightarrow[196K]{Liq. NH_3} \underset{\text{(A sod. alkynide)}}{R-C \equiv C^{-}Na^{+}} + NH_3$$

During these reactions, the acetylenic hydrogen is removed as a proton to form stable carbanions (acetylide ions) Sodium acetylide is decomposed by water regenerating acetylene. This shows that water is a stronger acid than acetylene and thus displaces acetylene from sodium acetylide.

$$\underset{\text{(Monosodium acetylide)}}{HC \equiv C^{-}Na^{+}} + H_2O \longrightarrow \underset{\text{(Acetylene)}}{HC \equiv CH} + NaOH$$

(ii) Formation of heavy metal acetylides: Acetylenic hydrogens of alkynes can also be replaced by heavy metal ions such as Ag^+ and Cu^+ ions. For example. When treated with ammoniacal silver nitrate solution (Tollen's reagent), alkynes form a white precipitate of silver acetylides.

$$\underset{\text{Ethyne}}{CH \equiv CH} + \underset{\text{Tollens reagent}}{2[Ag(NH_3)_2]^{+}OH^{-}} \longrightarrow \underset{\text{Disilver ethynide}}{AgC = CAg} + 2H_2O + 4NH_3$$

$$\underset{\text{(Terminal alkyne)}}{R-C \equiv CH} + \underset{\text{Tollens reagent}}{[Ag(NH_3)_2]^{+}OH^{-}} \longrightarrow \underset{\substack{\text{Silver alkynide}\\\text{(White ppt.)}}}{R-C \equiv C-Ag} + H_2O + 2NH_3$$

Similarly, with ammoniacal cuprous chloride solution, terminal alkynes form red ppt. of copper acetylides.

$$\underset{\text{(Ethyne)}}{HC \equiv CH} + 2[Cu(NH_3)_2]^{+}OH^{-} \longrightarrow \underset{\text{Dicopper ethynide}}{CuC \equiv CCu} + 2H_2O + 4NH_3$$

$$\underset{\text{(Terminal alkyne)}}{R-C \equiv CH} + \underset{\text{Tollens reagent}}{[Cu(NH_3)_2]^{+}OH^{-}} \longrightarrow \underset{\substack{\text{Monocopper alkynide}\\\text{(Red ppt.)}}}{R-C \equiv C-Cu} + H_2O + 2NH_3$$

Unlike alkali metal acetylides are not decomposed by water. They can however, be decomposed with dilute mineral acids to regenerate the original alkynes.

$$\underset{\text{(Disilver acetylide)}}{AgC \equiv CAg} + 2HNO_3 \longrightarrow \underset{\text{Acetylene}}{HC \equiv CH} + 2AgNO_3$$

$$\underset{\text{(Dicopper acetylide)}}{CuC \equiv CCu} + 2HCl \longrightarrow \underset{\text{Acetylene}}{HC \equiv CH} + 2CuCl$$

(iii) Formation of alkynyl Grignard reagents: Acetylne and other terminal alkynes react with Grignard reagents to form the corresponding alkynyl Grignard reagents. For example.

$$\underset{\text{(Acetylene)}}{HC \equiv CH} + \underset{\text{Grignard reagent}}{RMgX} \xrightarrow[Ether]{Dry} \underset{\substack{\text{Acetylenic}\\\text{Grignard reagent}}}{HC \equiv CMgX} + \underset{\text{Alkane}}{RH}$$

$$\underset{\text{Terminal alkyne}}{R'-C \equiv CH} + \underset{\text{Grignard reagent}}{RMgX} \xrightarrow[Ether]{Dry} \underset{\text{Alkynyl Grignard reagent}}{R'-C \equiv CMgX} + \underset{\text{Alkane}}{RH}$$

Alkynyl Grignard reagents like usual Grignard reagents can be used to prepare a variety of organic compounds.

Importance: The formation of metal acetylides can be used:

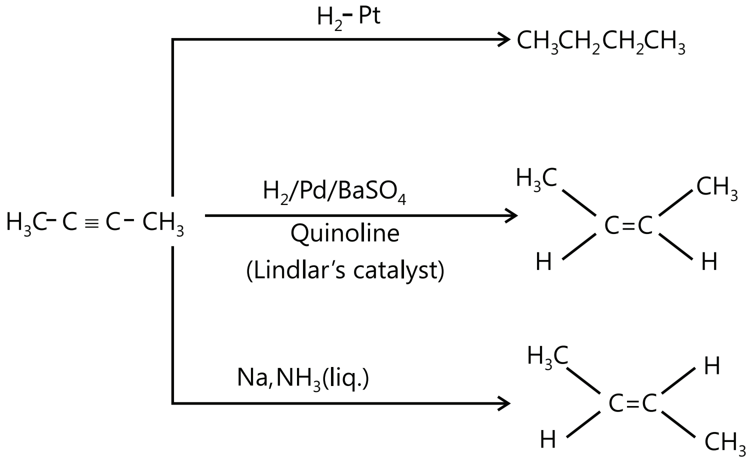
(a) For the separation and purification of terminal alkynes from non-terminal alkynes, alkanes and alkenes.

(b) To distinguish terminal alkynes from non-terminal alkynes or alkenes.

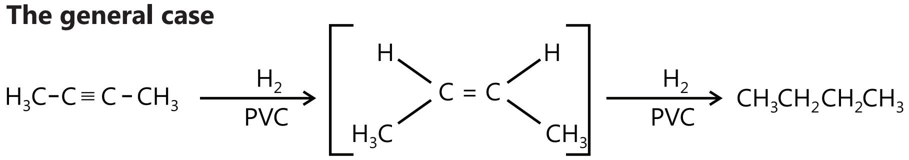
4.2 Hydrogenation / Reduction

$RC \equiv CR' + 2H_2 \xrightarrow{cat} RCH_2CH_2R'$ Catalyst = Pt, Pd, Ni or Rh

Alkene is an intermediate



The general case



The reaction takes place on the surface of Pt or Pd. Since the addition is twice, it is hard to see the syn addition.

But the reaction can be stopped at the alkene stage by using the following reagents.

(a) H_2 + Pd + $BaSO_4$ + S or quinoline in boiling xylene (called Lindlar's catalyst). In this case, reaction proceeds via syn addition of H_2.

(b) H_2 + P-2 or Brown catalyst (H_2 + Ni + B) or (H_2 + Ni_2B). It also proceeds via syn addition of H_2.

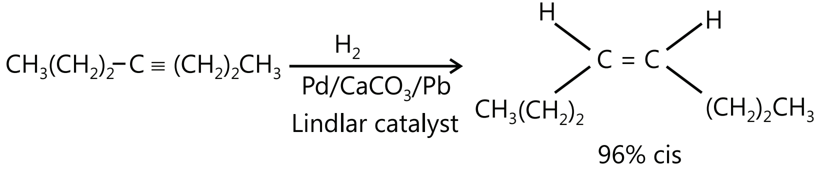
(c) Alkali metals (Na, K, Cs) + liq. NH_3 and C_2H_5 OH (It is called Birch reduction). It proceeds via anti-addition of H_2.

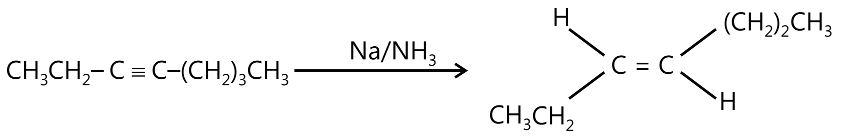
(d) $LiAlH_4$(LAH). It reduces $(C \equiv C)$ to (C = C) via anti addition of H_2; does not reduce (C = C) to (C — C) bond; reduces (C=C) to (C —C) only when the phenyl group is attached to the -C atom of the double bond.

(E.g. $Ph-\overset{\beta}{CH}=\overset{\alpha}{CH}-CH_3$ to $Ph-CH_2-CH_2-CH_3$)

Reduction of alkynes to (Z) – alkenes

Lindlar's catalyst: Pd, quinoline, Pb and $CaCO_3$ poisons the metal catalyst. So that the H_2 adds only to the alkyne. Not reactive enough for alkenes.





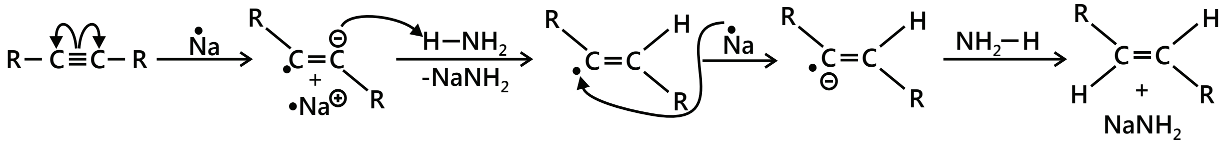
98% trans

Reduction of alkynes to (E) – alkenes. Reaction via Na radical dissolved in liquid NH_3.

$Na^{\bullet} + NH_3 \rightarrow Na^+ + e^- [NH_3]_n$

Solvated electron

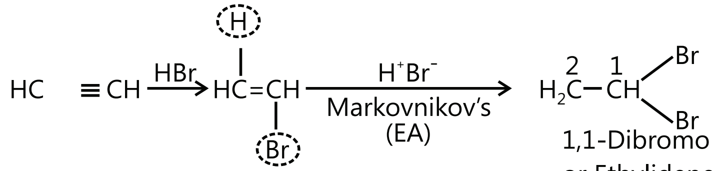
Mechanism of Na/NH_3 reductions: $Na^+ \xrightarrow{-33°C} Na^+ + NH_3(e^-)$



4.3 Addition of X_2

Like alkenes, 1 mol of alkynes adds 2 moles of halogens and proceeds via anti-addition of halogens, and orange or brown colour of Br_2 is discharged (test for unsaturation)

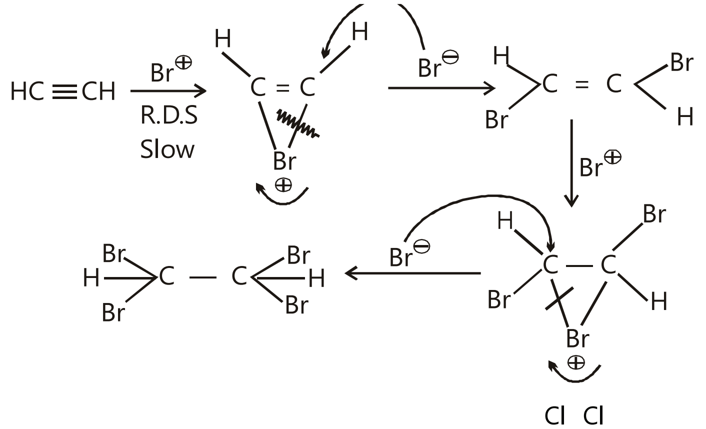
(I)

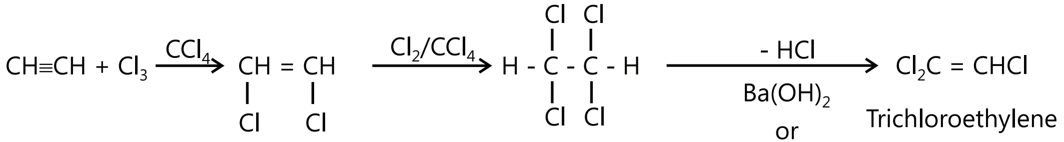


1,1-Dibromo ethane
or Ethylidene bromide

Mechanism:

Like alkenes it proceed via the formation of intermediate cyclic bromonium ion. First, electrophile (Br⊕) add and then the addition of nucleophile (Br⊖) from anti-position take place. That is why this reaction is called EA (electrophilic addition) reaction. The reaction is stereospecific (attack by electrophile in a specific manner).



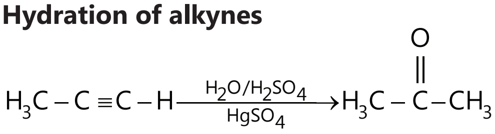


Westron or 1,1,2,2,-tetrachloro ethane or acetylene tetrachloride

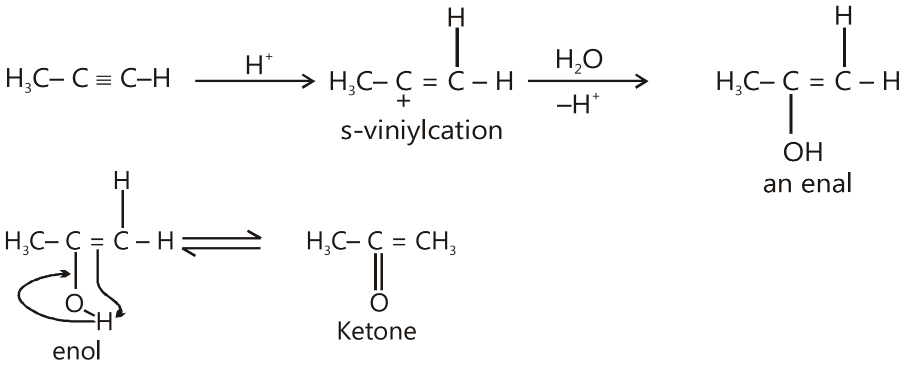
Trichloroethylene or westrosol

4.4 Addition of Water

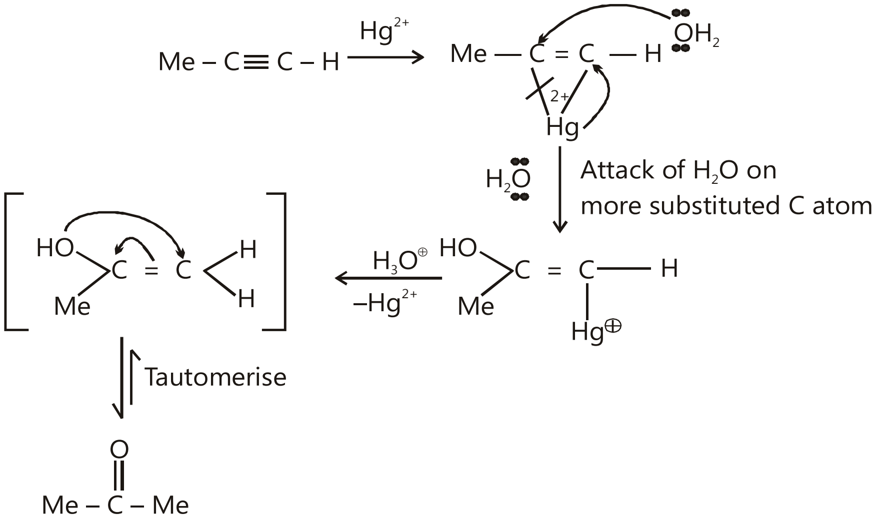
Hydration of alkynes



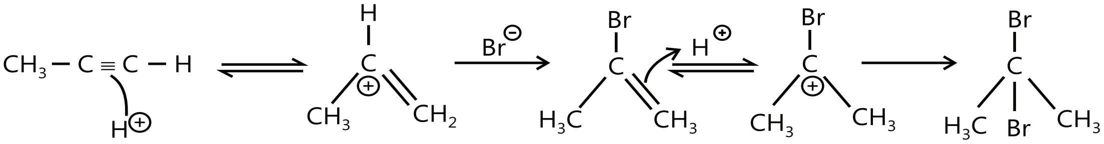
$$H_3C-C\equiv C-H \xrightarrow[HgSO_4]{H_2O/H_2SO_4} H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$



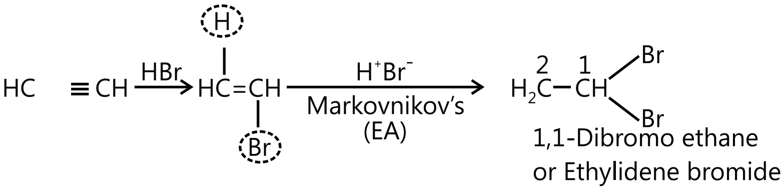
(Oxymercuration-demercuriation of triple bond)



4.5 Addition of HX

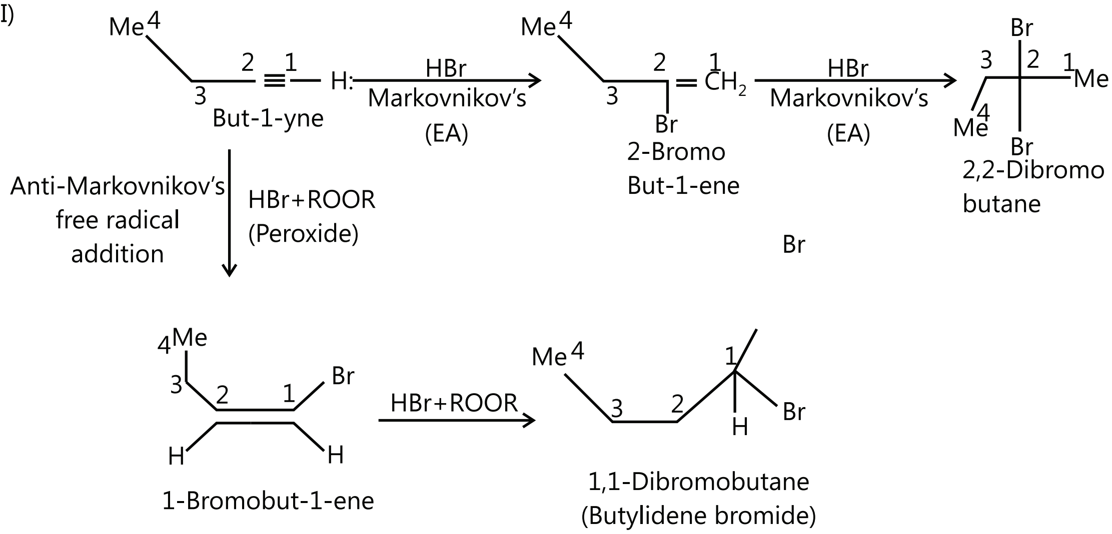


(I)



1,1-Dibromo ethane
or Ethylidene bromide

(II)



CONCEPTS

The order of reactivity of HX is HI > HBr > HCl > HF

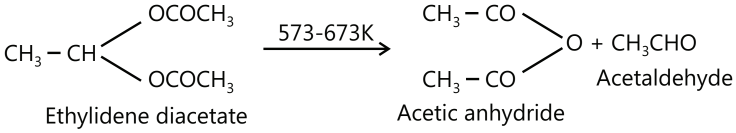
Aishwarya Karnawat (JEE 2012 AIR 839)

4.6 Addition of Acids

Addition of carboxylic acids: When acetylene is passed into warm acetic acid in presence of mercury salts, first vinyl acetate and then ethylidene diacetate is formed.

$$\underset{\text{Acetylene}}{HC\equiv CH}+\underset{\text{Acetic acid}}{CH_3COO-H}\xrightarrow[353K]{Hg^{2+}}\underset{\text{vinyl acetate}}{H_2C=CH-OCOCH_3}\xrightarrow[Hg^{2+}]{CH_3COOH}\underset{\text{Ethylidene discetate}}{CH_3-CH(OCOCH_3)_2}$$

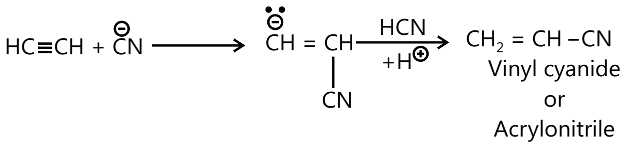
Vinyl acetate is used for the manufacture of vinyl resin. Ethylidene diacetate, when heated rapidly to 573-673K, gives acetic anhydride and acetaldehyde.



$$\underset{\text{Ethylidene diacetate}}{CH_3-CH\begin{matrix}OCOCH_3\\OCOCH_3\end{matrix}}\xrightarrow{573\text{-}673K}\underset{\text{Acetic anhydride}}{\begin{matrix}CH_3-CO\\CH_3-CO\end{matrix}\!\!>O}+\underset{\text{Acetaldehyde}}{CH_3CHO}$$

4.7 Addition of HCN

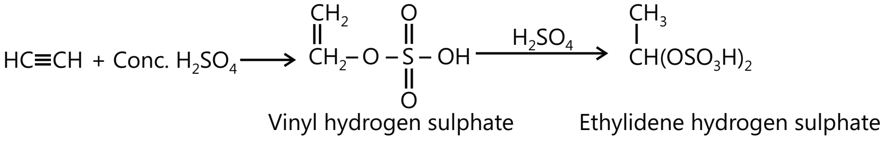
The reaction is nucleophilic addition (NA) initiated by CN^- from NaCN.



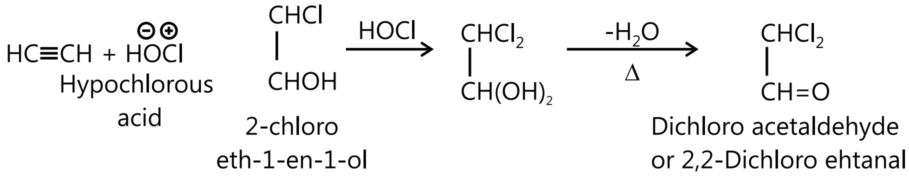
$$HC\equiv CH+\overset{\ominus}{C}N\longrightarrow \overset{\ominus\,\cdot\cdot}{C}H=\underset{\displaystyle CN}{\underset{|}{CH}}\xrightarrow[+H^{\oplus}]{HCN}CH_2=CH-CN$$

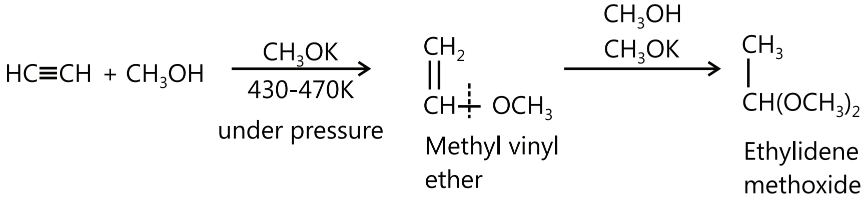
Vinyl cyanide
or
Acrylonitrile

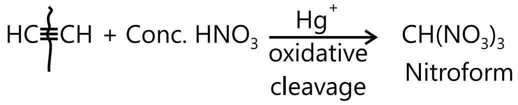
4.8 Addition to Other Compounds



$$HC\equiv CH+\text{Conc. }H_2SO_4\longrightarrow \underset{\text{Vinyl hydrogen sulphate}}{\overset{\displaystyle CH_2}{\overset{\|}{CH_2}}-O-\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}-OH}\xrightarrow{H_2SO_4}\underset{\text{Ethylidene hydrogen sulphate}}{\overset{\displaystyle CH_3}{\overset{|}{CH(OSO_3H)_2}}}$$

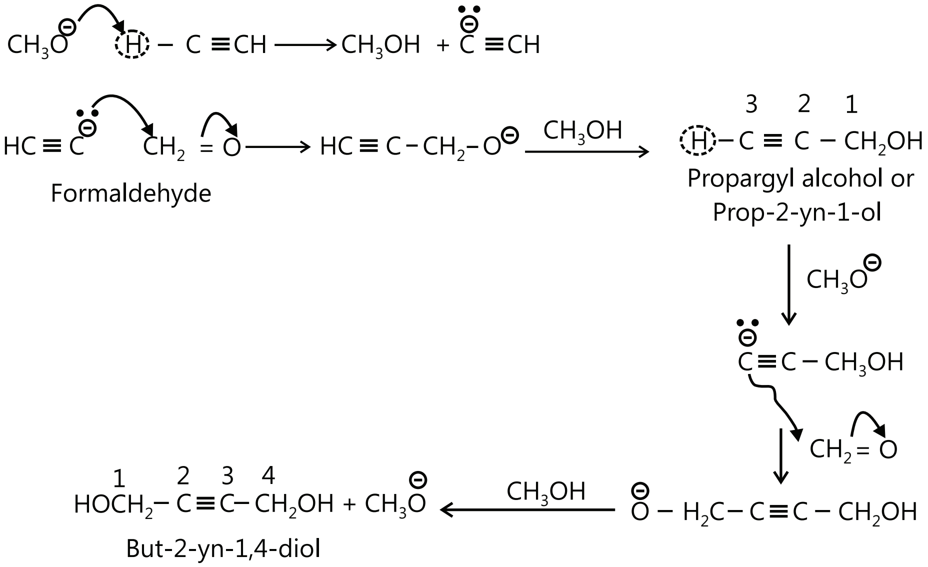






4.9 Ethyne + Methanal

The addition of ethyne to unsaturated link like (>C = O) is called ethinylation. Acetylene or terminal alkyne containing ≡ CH (a methine H-atom) reacts with a carbonyl group (>C = O) in the presence of sodium or potassium alkoxide (RONa or ROK) or $NaNH_2$ to give alkyndiol with a small amount of alkyneol.



4.10 Nucleophilic Addition

Because of the greater electronegativity of the sp-hybridized carbons as compared to sp^2 hybridized carbons, alkynes are more susceptible to nucleophilic addition reactions than alkenes.

For example, when acetylene is passed into methanol at 433-473 K in presence of a small amount (1-2%) of potassium methoxide under pressure, methyl vinyl ether is formed.

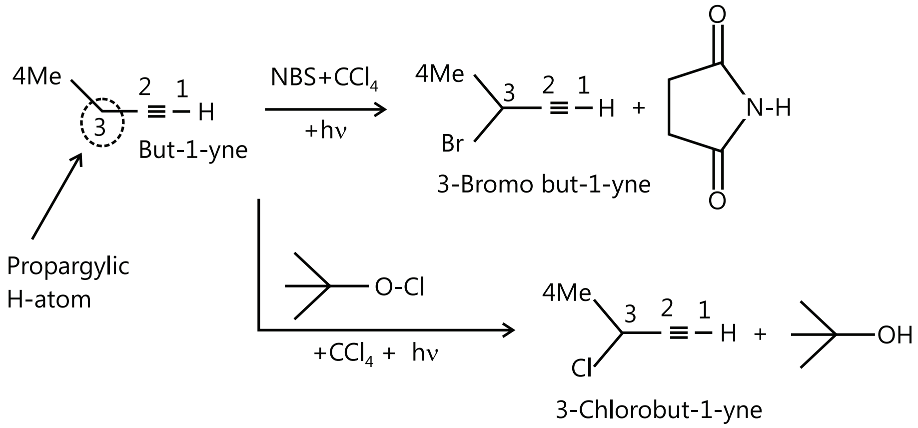
$$\underset{\text{Acetylene}}{HC \equiv CH} + \underset{\text{Methanol}}{CH_3O-H} \xrightarrow[433-473K]{CH_3O^-K^+} \underset{\text{Methyl vinyl ether}}{CH_2 = CH-OCH_3}$$

$$\underset{\text{Acetylene}}{HC \equiv CH} + \underset{\text{Methanol}}{CH_3O-H} \xrightarrow[433-473K]{CH_3O^-K^+} \underset{\text{Methyl vinyl ether}}{CH_2 = CH-OCH_3}$$

Methyl vinyl ether is used for making polyvinyl ether plastics.

4.11 Propargylic Halogenation

Alkenes undergo allylic substitution with NBS, whereas alkynes undergo propargylic halogenation with NBS, Cl_2SO_2 (sulfuryl chloride). Me_3COCl(t-butyl hypchlorite), and Cl_2 at 500°C.

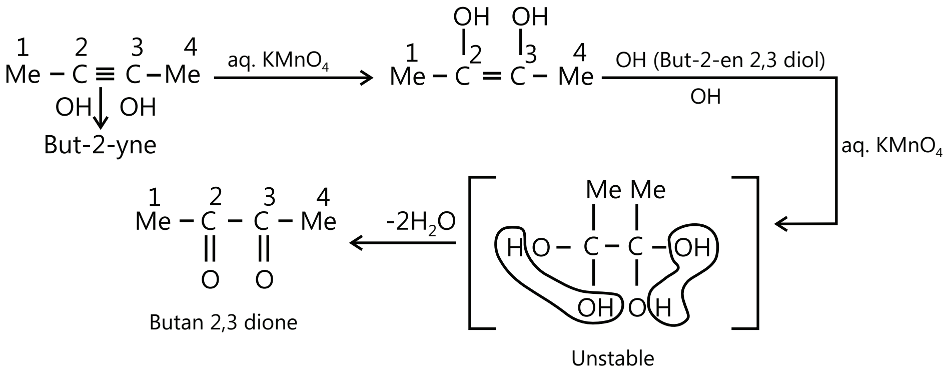


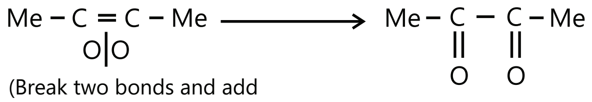
Reaction proceeds via free radical mechanism to give propargylic radical, which is stabilized by resonance via extended π-bonding.

4.12 Hydroxylation of Alkynes

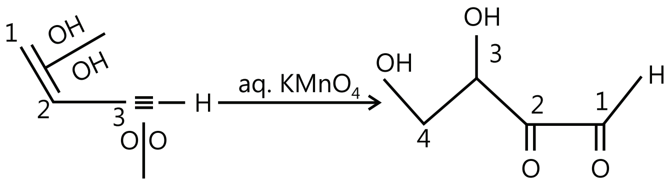
Hydroxylation of alkyne with aqueous or neutral $KMnO_4$ solution (Baeyer's reagent) test for unsaturation)

Pink colour of $KMnO_4$ is discharged and brown black precipitate of MnO_2 is obtained. This reaction converts alkynes first to enediols and then further gives tetraols, which being unstable lose H_2O to give diketones.





(Break two bonds and add O atom on both sides)



But-1-en-3-yne

3,4-Dihydroxy-2-oxo butan-1-al

4.13 Oxidation Reactions

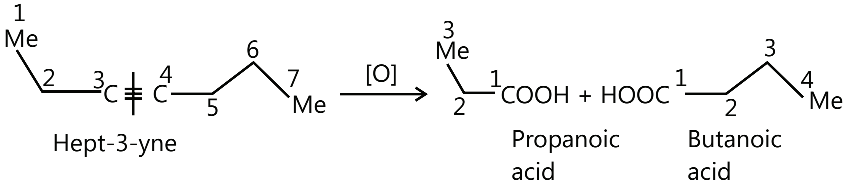
4.13.1 Oxidative Cleavage

(a) Alkynes are oxidatively cleaved in alkaline or acidic conditions at higher temperature, as mentioned.

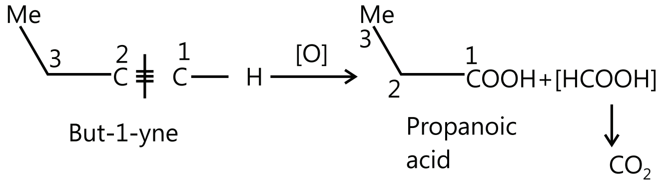
$$R-C\not\equiv \Longrightarrow R-COOH$$

$$H-C\not\equiv \Longrightarrow [H-COOH] \Longrightarrow CO_2$$

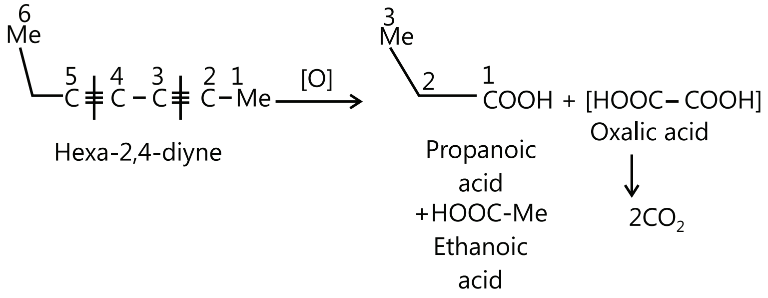
(i)



(ii)



(iii)

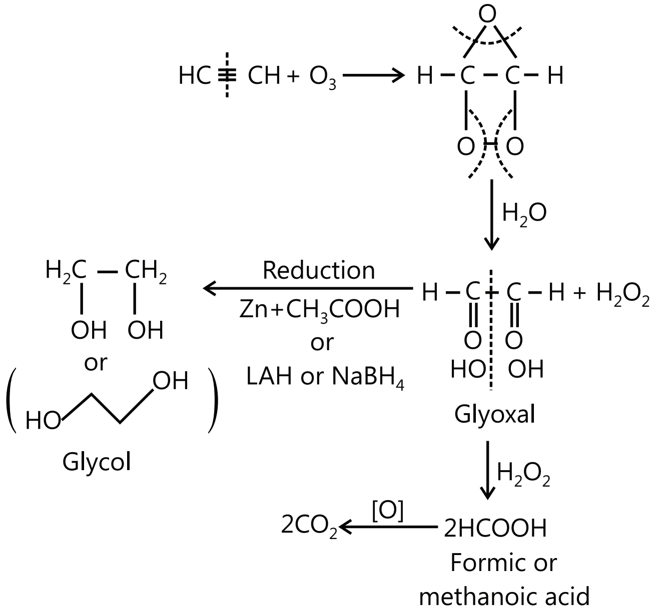


CrO_3 in CH_3COOH oxidizes alkenes but does not affect alkynes

4.14 Ozonolysis of Alkynes

Alkyne form ozonides with O_3 and are decomposed by H_2O to give diketones, which are then oxidised by H_2O_2 or $KMnO_4/NaIO_4$ or peracids; given acids, and on reduction with metal / acid, LAH, or $NaBH_4$ give diols.

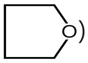
(i)

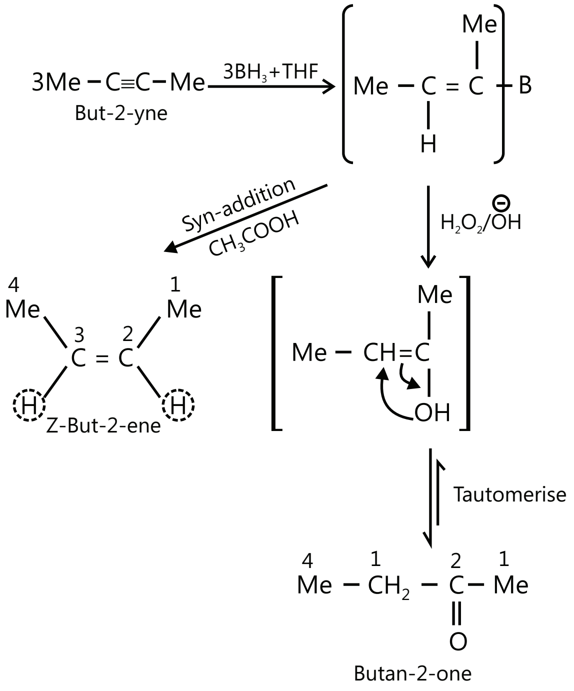


Terminal alkynes give HCOOH as one of the products which is further oxidized to CO_2

These oxidative cleavage reactions are rarely used for synthesis because alkynes are not readily available. They are used to locate the position of a triple bond in an alkyne.

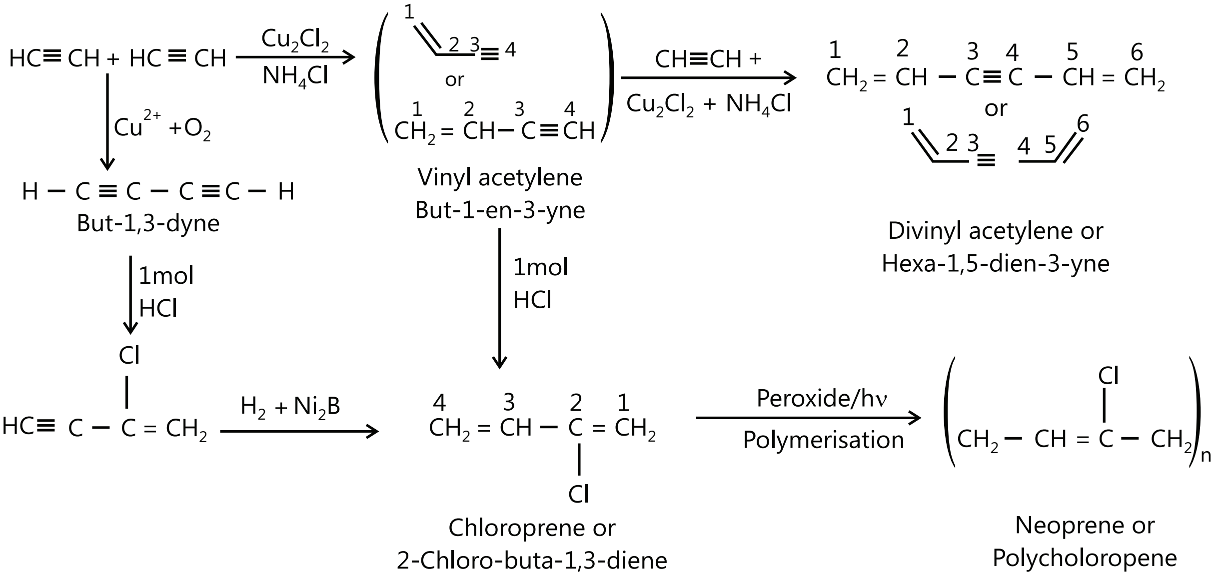
4.15 Hydroboration of Alkynes

- Terminal alkynes of HBO reaction give aldehyde, whereas internal alkynes give ketone.
- Alkynes react with BH_3 or B_2H_6 complexed with THF (tetrahydrofuran ) to give trivinyl borane, which upon subsequent treatment with alkaline H_2O_2 gives alcohols corresponding to anti-Markovnikov's addition of H_2O to alkynes, which on tautomerisation give corresponding aldehydes or Ketones.
- If trivinyl borane is treated with acid(CH_3COOH), it gives cis-alkene (proceeds via syn-addition of H_2).

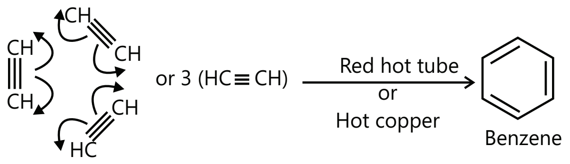


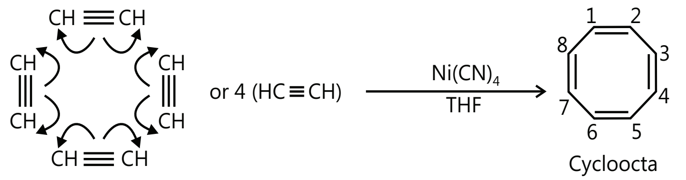
4.16 Polymerisation

1. Linear Polymerisation



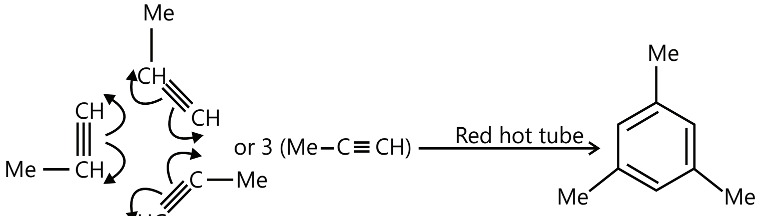
2. Cyclic Polymerisation





Cycloocta
1,3,5,7 tetra-ene

3. Propyne



1,3,5-Trimethyl benzene or Mesitylene

4.17 Isomerization

When alkynes are heated with $NaNH_2$ in an inert solvent such as kerosene oil or paraffin oil, they undergo isomerization. i.e. 2-alkynes isomerize to 1-alkynes and vice versa.

$$\underset{\text{But-2-yne}}{CH_3C{=}CCH_3}\xrightarrow[\text{inertsolvent, heat}]{NaHH_2\text{ in}}\underset{\text{But-1-yne}}{CH_3CH_2C{=}CH};\underset{\text{But-1-yne}}{CH_3CH_2C{=}CH}\xrightarrow[\text{inertsolvent, heat}]{NaHH_2\text{ in}}\underset{\text{But-2-yne}}{CH_3C{=}CCH_3}$$

Uses of alkynes

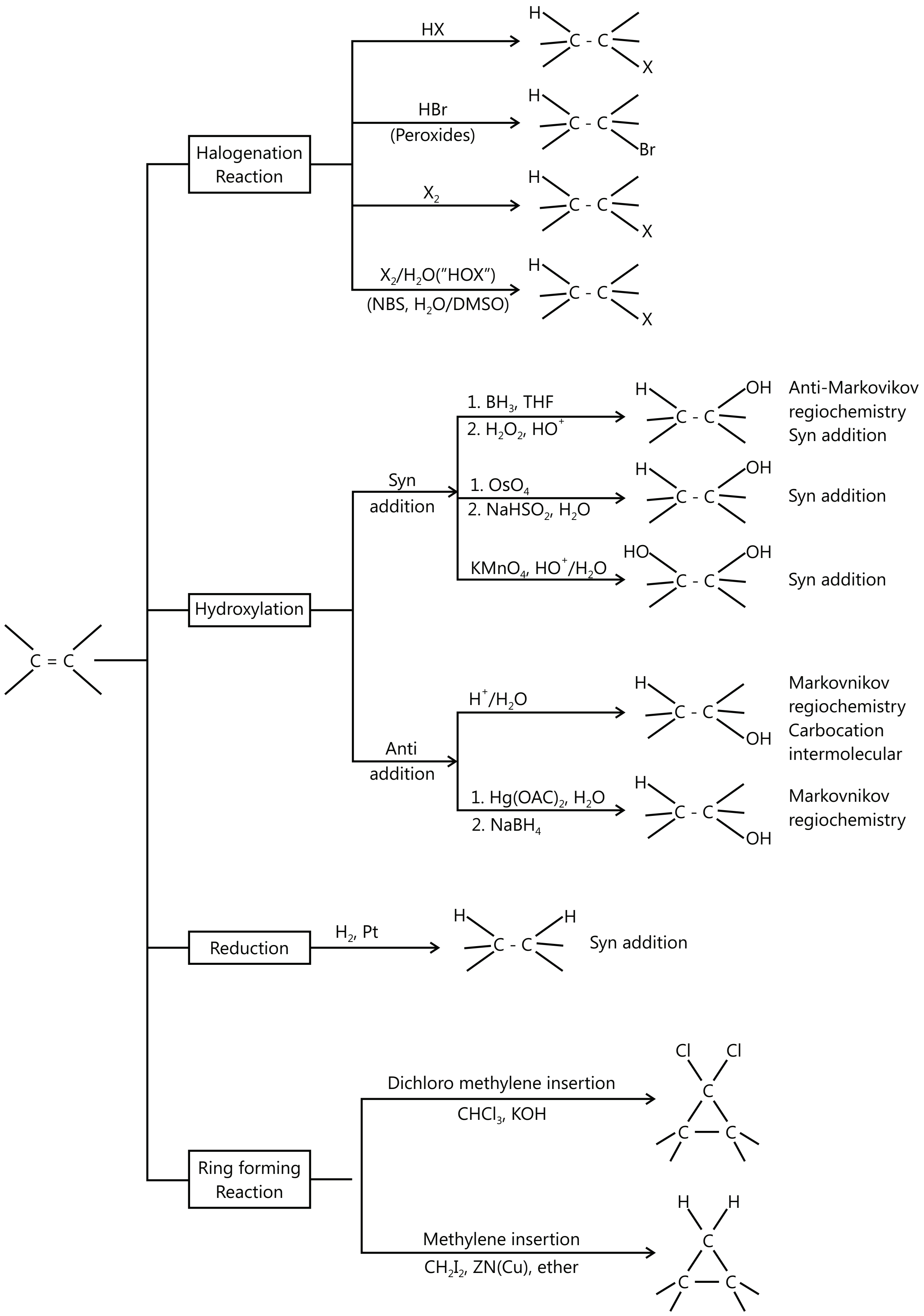
- **(i)** Acetylene and its derivatives are widely used in synthetic organic chemistry for synthesis of cis-and trans-alkenes, methyl ketones etc.
- **(ii)** Oxyacetylene flame is used for cutting and welding of metals.
- **(iii)** Acetylene is used as illuminant in hawker's lamp and in light houses.
- **(iv)** Acetylene is used for the ripening of fruits and vegetables.
- **(v)** Acetylene is used for manufacture of ethyl alcohol, acetaldehyde, acetic acid, vinyl plastics, synthetic rubbers such as Buna N and synthetic fibers such as Orlon.

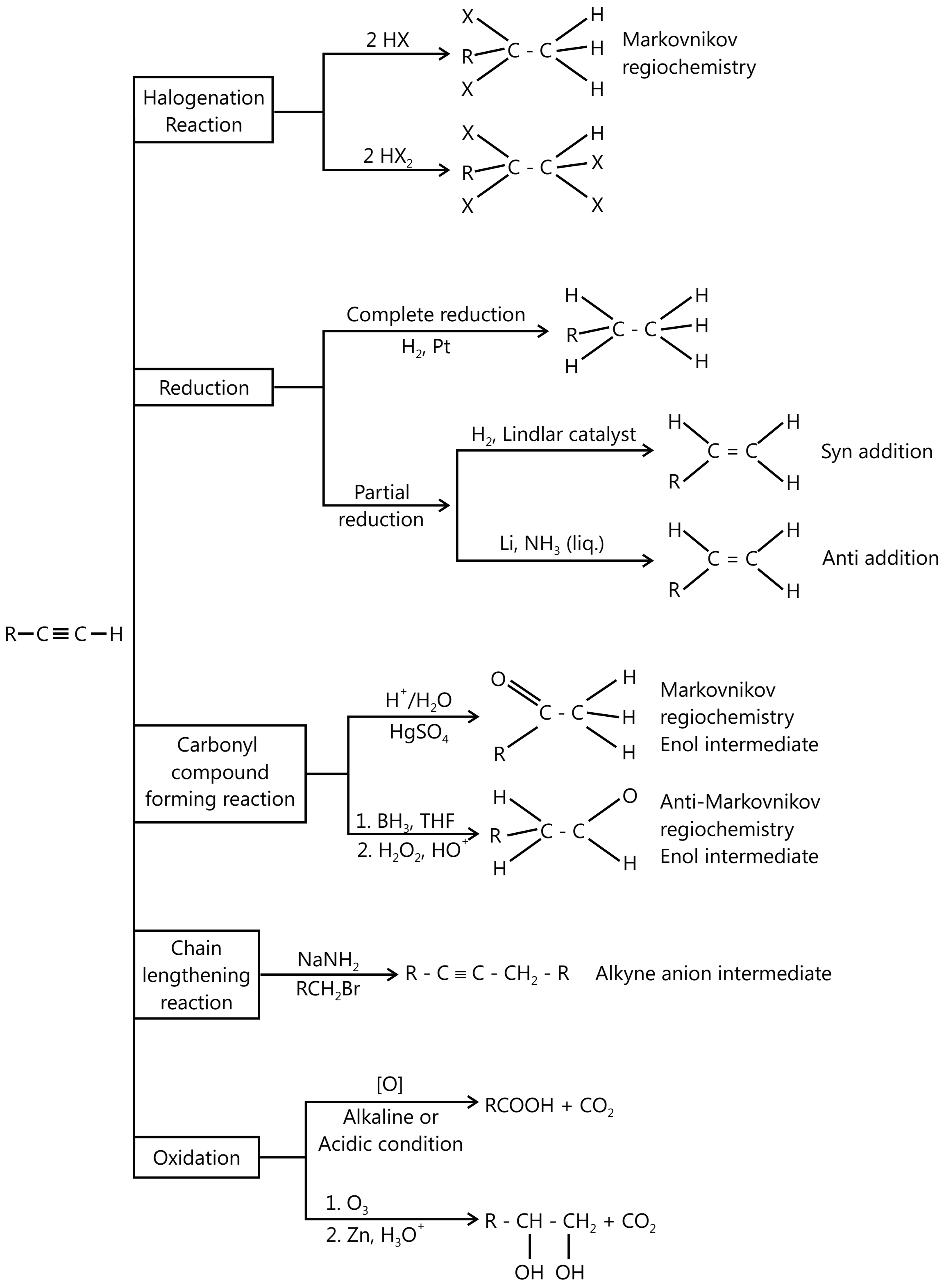
CONCEPTS

Difference between Alkenes and Alkynes

	Test	**Alkene**	**Alkyne**
1.	Flame observed on comnustion	Luminous	Smoky
2.	Br_2/CCl_4 solution	Orange colour is discharged	Orange colour is discharged
3.	Cold aq. or alkaline $KMnO_4$ solution (Baeyer's reagent)	Pink colour is discharged with the formation of diol compound	Pink colour is discharged with the formation of dicarbonyl compound
4.	Ammoniacal AgNO3 solution [Ag(NH3)2]+ (Tollens reagent)	No action	Whote ppt. of silver alkynide (given by only terminal alkynes)
5.	Ammoniacal CuCl solution	No action	Red ppt. of copper acetylide (given by only terminal alkynes)
6.	Reactivity towards electrophilic addition reaction (e.g. HX, X_2)	Alkenes are more reactive than alkynes	
7.	Reactivity towards catаytic	Alkynes are more reactive than alkenes	
8.	Reactivity towards nuclephilic addition reaction (e.g. CN^+)	Alkynes are more reactive than alkenes	

POINTS TO REMEMBER

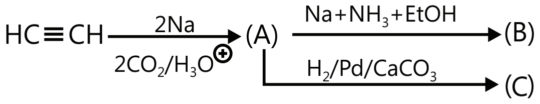


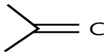

R—C≡C—H
Halogenation Reaction
2 HX
Markovnikov regiochemistry
2 HX2
Reduction
Complete reduction
H2, Pt
Partial reduction
H2, Lindlar catalyst
Syn addition
Li, NH3 (liq.)
Anti addition
Carbonyl compound forming reaction
H+/H2O
HgSO4
Markovnikov regiochemistry
Enol intermediate
1. BH3, THF
2. H2O2, HO+
Anti-Markovnikov regiochemistry
Enol intermediate
Chain lengthening reaction
NaNH2
RCH2Br
R - C ≡ C - CH2 - R
Alkyne anion intermediate
Oxidation
[O]
Alkaline or Acidic condition
RCOOH + CO2
1. O3
2. Zn, H3O+
R - CH - CH2 + CO2
OH OH

Solved Examples

JEE Main/Boards

Example 1: Identify A to C.



Sol: It is an example of ethinylation (addition of ethyne to unsaturated link like  group).

First step is the reaction with the sodium metal to form disodium acetylide with evolution of hydrogen gas.

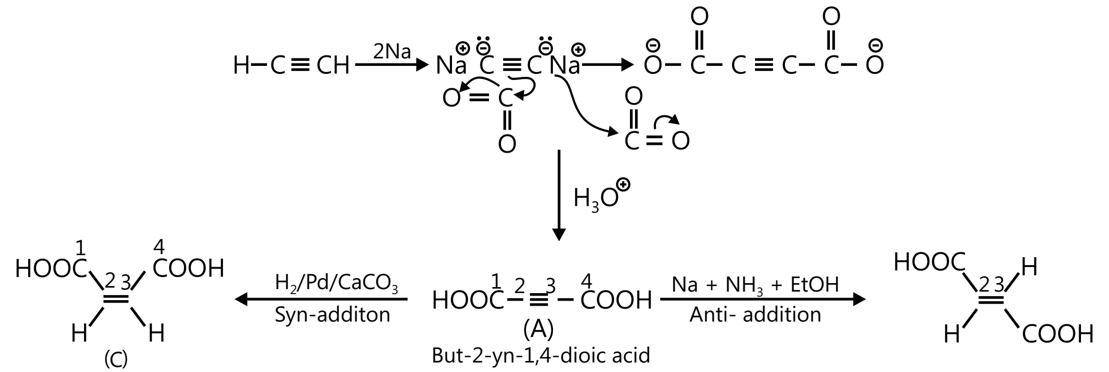
This reaction shows the acidic character of alkynes.

During this step acetylenic hydrogens are removed as a proton to form stable carbanion.

Now the carbanion reacts with two moles of carbon dioxide and forms an adduct which on treatment with acid yields acid.

Next step is reduction using Lindlar Catalyst (H_2/Pd-$CaCO_{3)}$ the addition is syn.

On treatment with (NH_3+EtOH) trans product is formed thus the addition is anti.

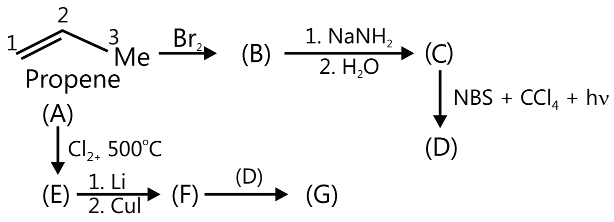


(C)
Maleic acid or
cis-But-2-en-1,4-dioic acid

(A)
But-2-yn-1,4-dioic acid

Fumaric acid (B) or
trans-But-2-en-1,4-dioic acid

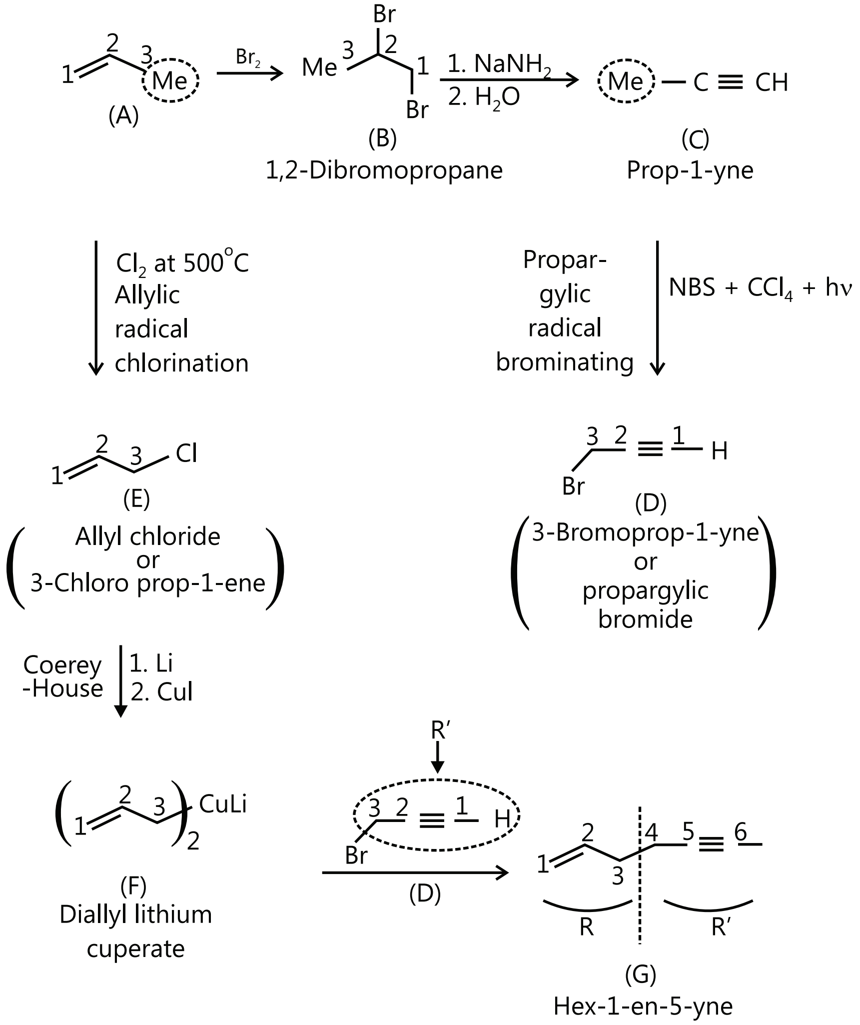
Example 2: Identify B to G.



Sol:

- Addition of Br_2 across double bond forms 1,2-dibromo propane.
- This on treatment with soda lime undergoes double dehalogenation to form an alkyne
- Now alkyne on the treatment with a brominating agent (NBS- N-Bromosuccinimide) and CCl_4 as a solvent in presence of light.
- On the other side, the first step is Allylic chlorination using Cl_2 at 500 °C.

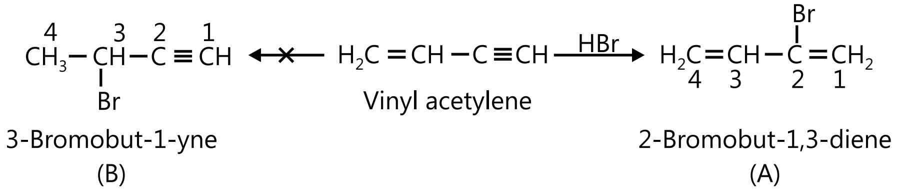
- The reaction proceeds through radical formation.
- Now Allyl chloride undergoes chain lengthening reaction to form Hex-1-en-5-yne.
- The reaction is known as Corey house synthesis



Example 3: Alkenes are more reactive than alkynes towards electrophilic addition reaction, yet vinyl acetylene reacts with 1 mole of HBr at triple bond. Explain why.

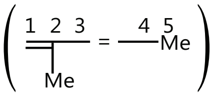
Sol:

- Alkynes are less stable than isomeric diene.
- Compound (A) is a conjugate diene whereas compound (B) is an alkyne.
- As heat of formation of diene is less than the heat of formation of alkyne, Vinyl acetate reacts with 1 mole of HBr to form a conjugate diene and formation of compound (B) is not favoured.

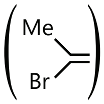


$$\underset{\text{3-Bromobut-1-yne (B)}}{\overset{4}{C}H_3-\underset{\underset{Br}{|}}{\overset{3}{C}H}-\overset{2}{C}\equiv\overset{1}{C}H} \xleftarrow{\times} \underset{\text{Vinyl acetylene}}{H_2C=CH-C\equiv CH} \xrightarrow{HBr} \underset{\text{2-Bromobut-1,3-diene (A)}}{\underset{4}{H_2C}=\underset{3}{CH}-\underset{2}{\overset{\overset{Br}{|}}{C}}=\underset{1}{CH_2}}$$

The product A (Conjugated diene) is more stable than B (an alkyne)

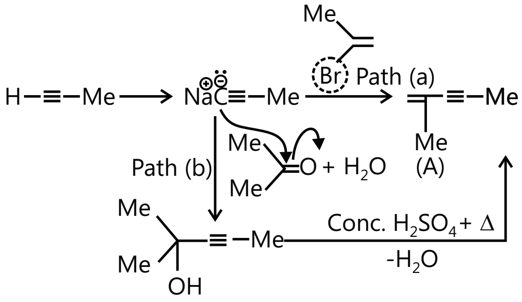
Example 4: There are two path (a) and (b) For the preparation of a compound (a) 

(2-methylpent-1-en-3-yne), which path is correct and why? Also name the paths (a) and (b). Path (a)

Sol: Path (b) is correct because in path (a) compound 

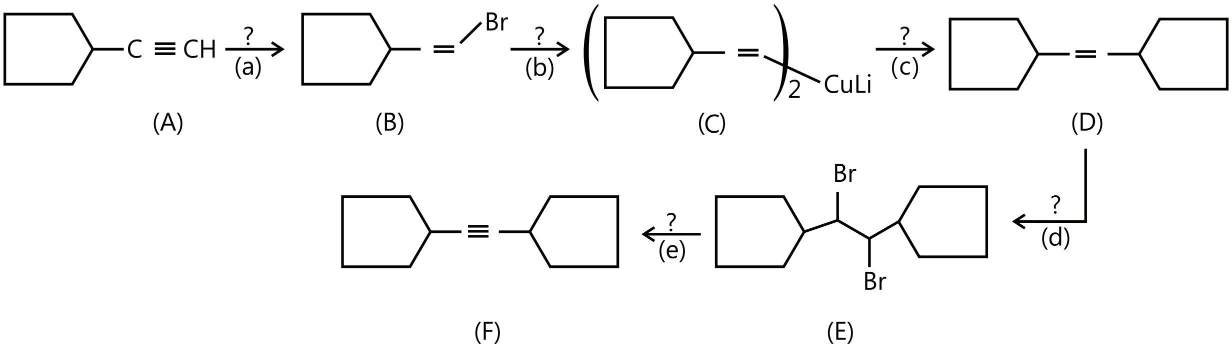
vinyl halide which is not reactive, so the reaction does not occur.

Path (a) is the alkylation of alkyne, whereas path (b) is propinylation (type of ethinylation), i.e., addition of propyne to unsaturated link like (> C = O) group.



JEE Advanced/Boards

Example 1: Complete the following missing reagents

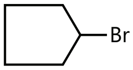


Sol: (i)

(a) HBr + Peroxide

First step is addition of HBr, it takes place according to Markovnikov's rule.

(b) (1) Li (2) CuI (Corey – House): Second step is Corey House synthesis.

(c) 

Third step is the reaction with alkyl halide.

(d) Br_2/CCl_4

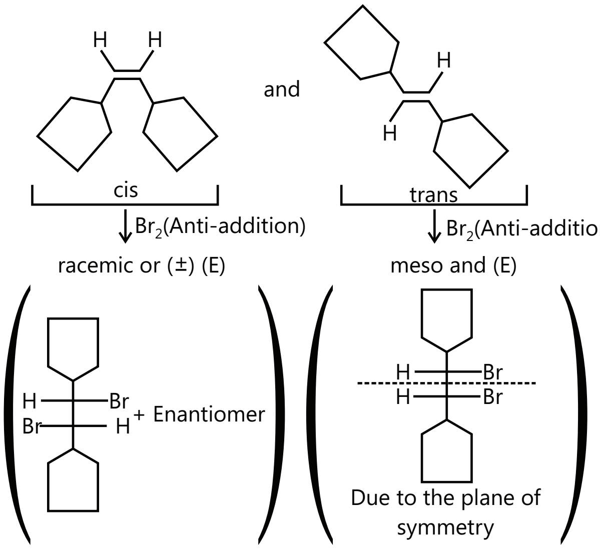
Bromination using Br_2 and CCl_4 as a solvent

(e) KOH(s), at 473 K

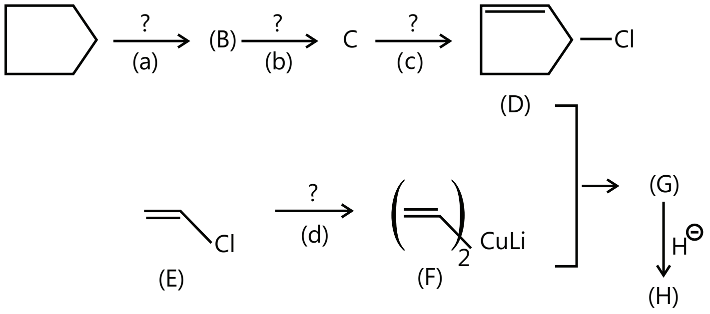
Last step is double dehalogenation using base like KOH at 473 K

(ii) Cis compound on addition with Br_2 (Anti addition) forms a racemic mixture or enantiomer.

Trans compound on addition with Br_2 (Anti addition) produces Meso compound (it contains plane of symmetry)

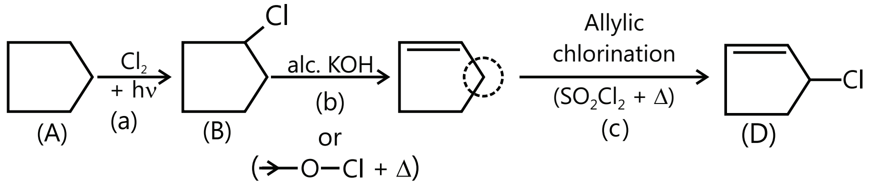


Example 2: Convert the following

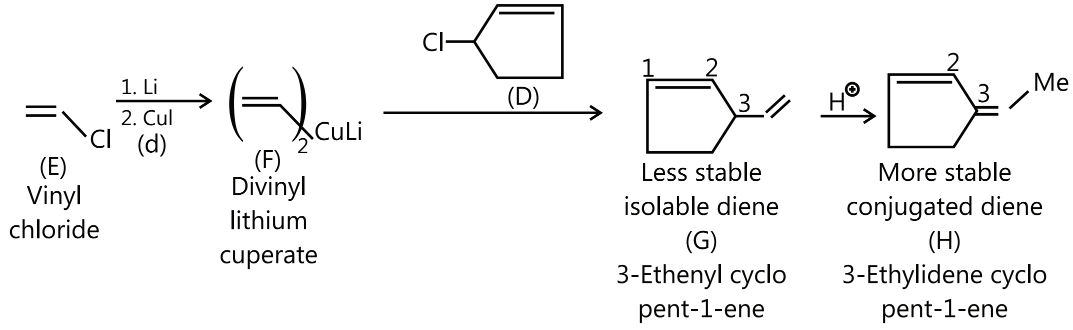


Sol:

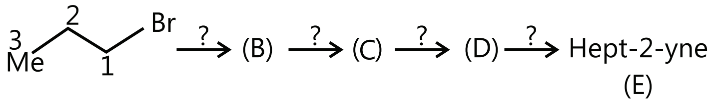
(a)



(b)

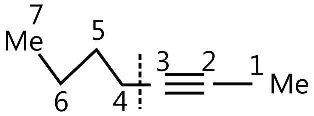


Example 3: Convert the following.



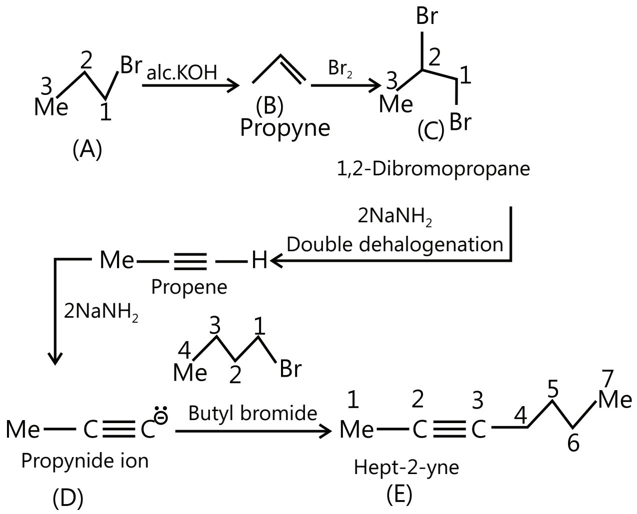
Write the structure of (E).

Sol: The structure of E is



First prepare 3C – atom alkyne $(Me-C\equiv C-H)$ from (A) and then react 4C – atom RX with alkynide ion to get (E).

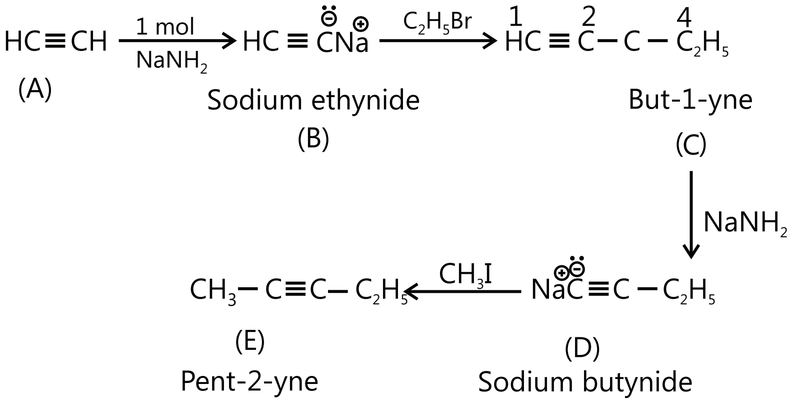
Reaction:



Example 4: Complete the following:

$$\underset{\substack{\text{Ethyne}\\ \text{(A)}}}{HC\equiv CH}\xrightarrow[NaNH_2]{\text{1 mol}}B\xrightarrow{C_2H_5Br}C\xrightarrow{NaNH_2}D\xrightarrow{CH_3I}(E)$$

Sol:



$$\underset{\text{(A)}}{HC\equiv CH}\xrightarrow[NaNH_2]{\text{1 mol}}\underset{\substack{\text{Sodium ethynide}\\ \text{(B)}}}{HC\equiv \overset{\ominus}{C}\overset{\oplus}{Na}}\xrightarrow{C_2H_5Br}\underset{\substack{\text{But-1-yne}\\ \text{(C)}}}{H\overset{1}{C}\equiv \overset{2}{C}-C-\overset{4}{C_2H_5}}$$

$$\xrightarrow{NaNH_2}\underset{\substack{\text{(D)}\\ \text{Sodium butynide}}}{\overset{\oplus}{Na}\overset{\ominus}{C}\equiv C-C_2H_5}\xrightarrow{CH_3I}\underset{\substack{\text{(E)}\\ \text{Pent-2-yne}}}{CH_3-C\equiv C-C_2H_5}$$

JEE Main/Boards

Exercise 1

Q.1 What are alkenes? Discuss briefly the various methods used for the preparation of alkenes. Describe with a labelled diagram the laboratory preparation of ethane from ethanol.

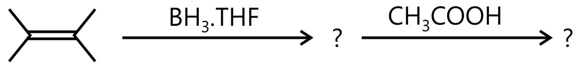
Q.2 Write the major products of the hydrocarbon and oxidation of:

(A) 1-Ethyl cyclopentene

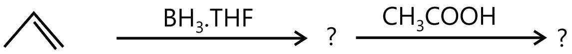
(B) Methylene cyclopentene

Q.3 Give the missing compounds in the following:

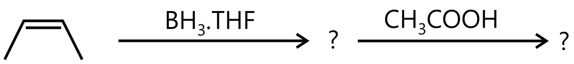
(A)



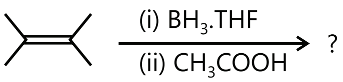
(B)



(C)



(D)



Q.4 Complete the following equation:

(A) $CH_3C \equiv CCH_3 \xrightarrow[Pt]{H_2} (A)$

$\xrightarrow[Pt]{H_2} CH_3CH_2CH_2CH_3$

(B) $CH_3-C \equiv CCH_3 \xrightarrow{Na + C_2H_5OH}$

(B) + $NaOC_2H_5$

Q.5 Give an account of physical and chemical reactions of alkenes.

Q.6 What are alkynes? How are they prepared in the laboratory?

Q.7 Give an account of physical properties and chemical reactions of alkynes.

Q.8 (A) Starting with any alkyne, prepare ethyl cyclohexyl ethyne.

(B) Starting with cyclohexyl ethyne, prepare acetyl cyclohexane.

Q.9 (A) Complete the following reactions:

$CH_3COCH_3 \xrightarrow{NaNH_2} A \xrightarrow{C_2H_2} B$

$\xrightarrow{H^+} C \xrightarrow[Pd]{H_2(1\,\text{equiv})} D \xrightarrow[400°C]{Al_2O_3\,,\,\Delta} E$

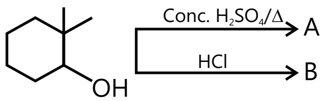
(B) Complete the following reactions:

$CH_3-C\equiv CH \xrightarrow[CH_2CH_2Br]{NaNH_2} A$

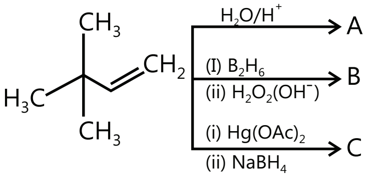
$\xrightarrow[\text{Lindlar's catalyst}]{H_2} B \xrightarrow[Zn(Cu)]{CH_2I_2} C$

Q.10 Predict the product of the following:

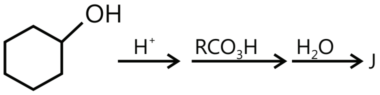
(A)



(B)



(C)

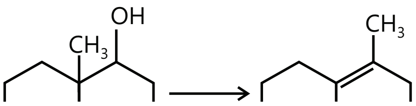


Q.11 (A) Give reasons for the following:

When 1-penten-4-yne is treated with HBr in equimolecular proportion, the addition takes place on double bond and not on triple bond yielding thereby the product

$CH_3CH(Br)CH_2C\equiv CH$.

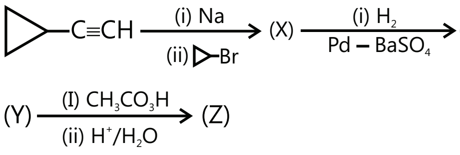
(B) Provide a suitable mechanism for the following reaction.



Q.12 Three isomeric alkenes A, B and C, (C_5H_{10}) are hydrogenated to yield 2-methylbutane A and B gave the same 3° ROH on oxymercuration-demercuration B and C give different 1° ROH's on hydroboration-oxidation supply the structures of A, B and C.

Q.13 3,3-dimethyl-1-butene and HI react to give two products, $C_6H_{13}I$. On reaction with alc. KOH one isomer, (1) gives back 3,3-dimethyl-1-butene the other (J) gives an alkene that is reductively ozonized to give $Me_2C{=}O$. Give the structures of (I) and (J) and explain the formation of the latter.

Q.14 Identify X, Y and Z in the following sequence of reaction giving stereo chemical structure wherever possible.



Exercise 2

Single Correct Choice Type

Q.1 On heating CH_3COONa with soda lime the gas evolved will be

(A) C_2H_2 (B) CH_4 (C) C_2H_6 (D) C_2H_4

Q.2 The addition of Br_2 to trans-2-butene produces

(A) (+) 2, 3-dibromobutane

(B) (–) 2, 3-dibromobutane

(C) rac -2, 3-dibromobutane

(D) meso -2,3-dibromobutane

Q.3 Isomers which can be interconverted through rotation around a single bond are

(A) Conformers (B) Diastereomers

(C) Enantiomers (D) Positional isomers

Q.4 The olefin, which on ozonolysis gives CH_3CH_2CHO and CH_3CHO

(A) But-1-ene (B) But-2-ene

(C) Pent-1-ene (D) Pent-2-ene

Q.5 Which of the C — C bond is strongest?

(A) Formed by sp^3–sp^3 hybridised carbon atoms (as in alkanes)

(B) Formed by sp^2–sp^2 hybridised carbon (as in alkenes)

(C) Formed by sp–sp hybridised carbon atoms (as in alkynes)

(D) None of these

Q.6 End product of the following sequence is:

$$CaO + C \xrightarrow{\text{Heat}} (A) \xrightarrow{H_2O} (C) \xrightarrow[H_2SO_4]{Hg^{2+}} (C)$$

(A) Ethanol (B) Ethyl hydrogen sulphate

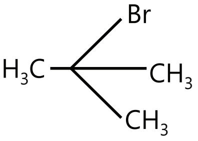
(C) Ethanal (D) Ethylene glycol

Q.7 The treatment of C_2H_5MgI with water produces

(A) Methane (B) Ethane

(C) Ethanal (D) Ethanol

Q.8 When isobutene is brominated, the percentage of



would be

(A) 0% (B) 83% (C) 10% (D) 100%

Q.9 Propene can be converted into 1-propanol by oxidation. Which set of the reagents is used to effect the conversion?

(A) OsO_4 — $CHCl_3$ (B) O_3/Zn — H_2O

(C) Alkaline and cold $KMnO_4$ (D) B_2H_6 and alk. H_2O_2

Q.10 In the following sequence of reactions, identify the product (d)

$$CH \equiv CH \xrightarrow{HBr} (A) \xrightarrow{HBr} (B) \xrightarrow{alk.KOH} (C) \xrightarrow{NaNH_2} (D)$$

(A) Ethanol (B) Ethyne

(C) Ethanal (D) Ethene

Q.11 Which one is highly unstable?

(A) $CH_2{=}CH{-}OH$ (B) $CH_2{=}CH{-}Cl$

(C) $CH_2{=}CH{-}CH_2{-}Cl$ (D) $CH_3{-}C{\equiv}CH$

Previous Years' Questions

Q.1 Marsh gas mainly contains ***(1980)***

(A) C_2H_2 (B) CH_4 (C) H_2S (D) CO

Q.2 Which of the following will decolourise alkaline $KMnO_4$ solution? ***(1980)***

(A) C_3H_8 (B) CH_4 (C) CCl_4 (D) C_2H_4

Q.3 The compound 1,2-butadiene has ***(1983)***

(A) Only sp-hybridised carbon atoms

(B) Only sp^2-hybridised carbon atoms

(C) Both sp and sp^2-hybridised carbon atoms

(D) sp, sp^2 and sp^3-hybridised carbon atoms

Q.4 When propyne in treated with aqueous H_2SO_4 in presence of $HgSO_4$, the major product is ***(1983)***

(A) Propanal (B) Propyl hydrogen sulphate

(C) Acetone (D) Propanol

Q.5 Bayer's reagent is ***(1984)***

(A) Alkaline permanganate solution

(B) Acidified permanganate solution

(C) Neutral permanganate solution

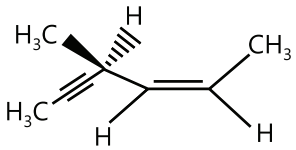
(D) Aqueous bromine solution

Q.6 Acidic hydrogen is present in ***(1985)***

(A) Ethyne (B) Ethene

(C) Benzene (D) Ethane

Q.7 Hydrogenation of the adjoining compound in the presence of poisoned palladium catalyst gives ***(2001)***



(A) An optically active compound

(B) An optically inactive compound

(C) A racemic mixture

(D) A diastereomeric mixture

Q.8 The reaction of propene with HOCl proceeds via the addition of ***(2001)***

(A) H^+ in the first step

(B) Cl^+ in the first step

(C) OH^- in the first step

(D) Cl^+ and OH^- single step

Q.9 In the presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti Markownikoff's addition to alkenes because ***(2001)***

(A) Both are highly ionic

(B) One is oxidising and the other is reducing

(C) One of the steps is endothermic in both the cases

(D) All the steps are exothermic in both the cases

Q.10 Which of the following compound will exhibit geometrical isomerism? ***(2015)***

(A) 1-Phenyl-2-butene

(B) 3-Phenyl-1-butene

(C) 2-Phenyl-1-butene

(D) 1,1-Diphenyl-1-propane

Q.11 The reaction of propene with HOCl (Cl_2 + H_2O) proceeds through the intermediate : ***(2016)***

(A) $CH_3 - CH^+ - CH_2 - Cl$ (B) $CH_3 - CH(OH) - CH_2{+}$

(C) $CH_3 - CHCl - CH_2$ (D) $CH_3 - CH^+ - CH_2 - OH$

Q.12 The major organic compound formed by the reaction of 1, 1, 1-trichloroethane with silver powder is ***(2014)***

(A) Acetylene (B) Ethene

(C) 2-Butyne (D) 2-Butene

Q.13 In the reaction,

$CH_3COOH \xrightarrow{LiAlH_4} A \xrightarrow{PCl_5} B \xrightarrow{Alk.KOH} C$

the product C is ***(2014)***

(A) Acetaldehyde (B) Acetylene

(C) Ethylene (D) Acetyl chloride

Q.14 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 ***(2008)***

(A) CH_3CH_2CHO (B) CH_3COCH_3

(C) $CH_3CH_2COCH_3$ (D) CH_3CHO

Q.15 The hydrocarbon which can react with sodium in liquid ammonia is ***(2008)***

(A) $CH_3CH_2CH_2C \equiv CCH_2CH_2CH_3$

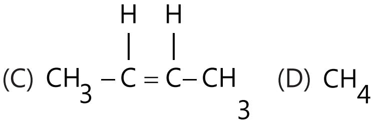
(B) $CH_3CH_2C \equiv CH$

(C) $CH_3CH \equiv CHCH_3$

(D) $CH_3CH_2C \equiv CCH_2CH_3$

Q.16 The treatment of CH_3MgX with $CH_3C\equiv C-H$ produces *(2008)*

(A) $CH_3-CH\equiv CH_2$ (B) $CH_3C\equiv C-CH_3$



(C) $CH_3-\overset{H}{\overset{|}{C}}=\overset{H}{\overset{|}{C}}-CH_3$ (D) CH_4

Q.17 The alkene that exhibits geometrical isomerism is: *(2009)*

(A) Propene (B) 2-methyl propene

(C) 2-butene (D) 2- methyl -2- butane

Q.18 One mole of a symmetrical alkene on ozonolysis gives two moles of an aldehyde having a molecular mass of 44 u. The alkene is *(2010)*

(A) Propene (B) 1–butene

(C) 2–butene (D) Ethene

Assertion and Reason Type

Read the following questions and answer as per the direction given below:

(A) Statement-I is true; statement-II is true;

statement-II is a correct explanation of statement-I.

(B) Statement-I is true; statement-II is true; statement-II is not the correct explanation of statement-I.

(C) Statement-I is true; statement-II is false.

(D) Statement-I is false; statement-II is true.

Q.19 Statement-I: Addition of Br_2 to 1-butene gives two optical isomers.

Statement-II: The product contains one asymmetric carbon. *(1998)*

Q.20 Statement-I: 1-butene on reaction with HBr in the presence of a peroxide produces 1 bromobutane.

Statement-II: It involves the formation of a primary radical. *(2000)*

Q.21 Statement-I: Dimethyl sulphide is commonly used for the reduction of an ozonide of an alkene to get the carbonyl compound.

Statement-II: It reduces the ozonide giving water soluble dimethyl sulphoxide and excess of it evaporates. **(2000)**

Q.22 Statement-I: Addition of bromine to trans-2-butene yields meso-2, 3-dibromo butane.

Statement-II: Bromine addition to an alkene is an electrophilic addition.

JEE Advanced/Boards

Exercise 1

Q.1 Compound (X) (C_5H_8O) does not appreciably react with Lucas reagent at room temperature but gives a precipitate with silver nitrate (ammoniacal). With Me Mg Br, 0.42gms of (X) gives 22400 mL of CH_4 at STP. Treatment of H_2 in the presence of Pt catalyst followed by boiling with excess HI, gives n-pentane. Suggest the structure for (X) and write equations involved.

Q.2 Compound (A) C_5H_{10} decolourizes Br_2. When (A) is treated with hot $KMnO_4$, two acids (B) and (C) are formed. When (B) is treated with soda lime, methane is formed. When (C) is heated with soda lime ethane is formed. What are the structure of (A), (B) and (C).

Q.3 An organic compound (A) C_6H_{12} is treated with Cl_2 in the presence of CCl_4 gives (B) $C_6H_{12}Cl_2$. Compound (B) on treatment with alcoholic KOH followed by $NaNH_2$ resulting in the formation of compound (C) C_6H_{10}. Compound (C) on treatment with H_2 (gas) over platinum forms 2-methyl pentane. Compound (C) gives ammoniacal $AgNO_3$ test. Ozonolysis of (A) gives two aldehydes (D) and (E) where E is acetaldehyde. Identify A, B, C, D and E.

Q.4 A hydrocarbon (A) is treated with excess of HCl. A dihalogen derivative (B) is formed. Compound (B) on treatment with aqueous KOH gives C. Compound (C) can be obtained by heating calcium salt of 2-methyl propanoic acid with calcium acetate what are A, B and C?

Q.5 $CF_3CH=CH_2+HBr\xrightarrow{AlBr_3}X$

Q.6 An organic compound (A) C_9H_{12} gave (B) $C_8H_6O_4$ on oxidation by alkaline $KMnO_4$. (B) on heating does not form anhydride. Also (B) reacts with Br_2 in the presence of iron to give only one monobromo derivative (C). $C_8H_5BrO_4$. What are A, B and C.

Q.7 A hydrocarbon (A) C_9H_{10} adds Cl_2 to give (B) $C_9H_{10}Cl_2$. Hydrolysis of (B) gives (C) $C_9H_{12}O_2$. Oxidation of (A) gave two acids identified as benzoic acid and acetic acids. What are A, B and C?

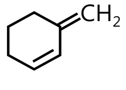
Q.8 An organic compound (A) $C_9H_{10}Br_2$ forms $C_9H_{11}OBr$ with caustic soda solution the later is resistant to further action of alkali. (B) on treating with H_2SO_4 converts into (C) with on ozonolysis gives ethanal and another compound (D). Identify (A) to (D) and give reactions.

Q.9 An organic compound (A) C_6H_{10}, on reduction first gives (B) C_6H_{12} and finally (C) C_6H_{14}. (A) on ozonolysis followed by hydrolysis gives two aldehydes (D) C_2H_4O and (E), $C_2H_2O_2$. Oxidation of (B) with $KMnO_4$ gives the acid (F) $C_4C_8O_2$. Determine the structures of (A) to (F) with proper reasoning.

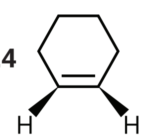
Q.10 An organic compound (A) of molecular formula C_5H_8 when treated with Na in liquid ammonia followed by reaction with n-propyl iodide yields (B) C_8H_{14}. (A) gives a ketone $C_5H_{10}O$ when treated with dil. H_2SO_4 and $HgSO_4$. (B) on oxidation with alkaline. $KMnO_4$ gives two isomeric acids (D) and (E) $C_4H_8O_2$. Give structures of compounds (A) to (D) with proper reasoning.

Q.11 An organic compound (A) C_8H_6, on treatment with dil. H_2SO_4 containing mercuric sulphate gives a compound (B), which can also be obtained from a reaction of benzene with acid chloride in the presence of anhydrous $AlCl_3$. The compound (B) when treated with iodine in aq. KOH, yields C and a yellow compound (D). Identify A, B, C and D with justification.

Q.12 An organic compound A (C_5H_8) on hydrogenation gives compound B(C_5H_{12}). Compound A on ozonolysis gives formaldehyde and 2-ketopropanal. Deduce structure of compound A.

Q.13 What are the possible products from 1,4-addition of HBr on 

Draw all possible carbocations and state which carbocation is more stable

Q.14 

$+CH_2=CH–CH=CH_2$

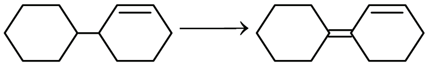
A Predict the structure of A and explain.

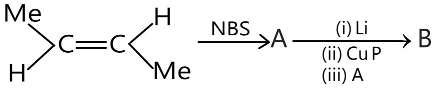
Q.15 A hydrocarbon (P) of the formula C_8H_{10}, on ozonolysis, gives compound Q ($C_4H_6O_2$) only. The compound (Q) can also be obtained from an alkyl bromide, R (C_3H_5Br) upon treatment with Mg in dry ether, followed by CO_2 and acidification. Identify (P), (Q) and (R) and give equations for the reactions.

Q.16 Two isomeric alkyl bromides (A) and (B) have molecular formula $C_5H_{11}Br$. (A) on treatment with alcoholic KOH gives two isomers (C) and (D) of formula C_5H_{10}. (C) on ozonolysis gives formaldehyde and 2-methylpropanal. (B) with alcoholic KOH gives (D) and (E). Catalytic hydrogenation of (C), (D) and (E) gives (F) C_5H_{12}. Identify (A) to (F).

Q.17 How would you bring about the following conversion.

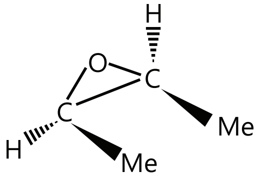
(i) 1, 3-Butadiene to racemic - 1, 4-dibromo -2, 3-dideutrobutene

(ii) 

(iii) 

(iv) Z-2, 3-Dideutero-2-butene to racemic-erythro-2-Bromo-2,3-Didenterobutane

(v) 1-Methyl cyclopentene to trans-2-Methyl cyclopentane

(vi) 

to (S, S) – Glycol + R, S Glycol

Q.18 A compound (A) has C = 85.7%, H = 14.3%. Its molecular weight is 70. It does not react with Cl_2 in dark but gave a substitution product C_5H_9Cl in presence of light. What is (A)?

Q.19 An organic compound (A) C_6H_{10} does not react with ammoniacal $AgNO_3$ but on reduction first gives (B) C_6H_{12} and then (C) C_6H_{14}. (A) on ozonolysis gives two aldehydes C_2H_4O (D) and $C_2H_2O_2$ (E). Oxidation of (B) with alkaline $KMnO_4$ gives acid (F) $C_3H_6O_2$. What are (A) of (F)?

Q.20 Two isomeric organic compounds (A) and (B) on reduction with Zn-Cu couple give n-butane. On treating

(A) and (B) with Na and ether separately, n-octane (C) and 3, 4-diemthylhexane (D) are formed but if a mixture of (A) and (B) reacts with Na and ether, one more product (E) in addition to (C) and (D) is

Exercise 2

Single Correct Choice Type

Q.1 A sample of 1.79 mg of a compound of molar mass 90g mol^{-1} when treated with CH_3MgI releases 1.34 mL of a gas at STP. The number of active hydrogen in the molecule is

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

Q.2 Reaction of Br_2 on ethylene in presence of NaCl gives

(A) $BrCH_2$-CH_2Br (B) $ClCH_2$-CH_2Br

(C) Both of these (D) None of these

Q.3 The reaction conditions leading to the best yield of C_2H_5Cl are

(A) $C_2H_6\text{(excess)} + Cl_2 \xrightarrow[\text{light}]{\text{UV}}$

(B) $C_2H_6 + Cl_2 \xrightarrow[\text{room temp.}]{\text{dark}}$

(C) $C_2H_6 + Cl_2\text{(excess)} \xrightarrow[\text{light}]{\text{UV}}$

(D) $C_2H_6 + Cl_2 \xrightarrow[\text{light}]{\text{UV}}$

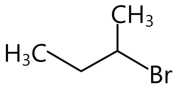
Q.4 The treatment of $CH_3C(CH_3)=CHCH_3$ with $NaIO_4$ or boiling $KMnO_4$, produces

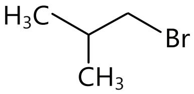
(A) $CH_3COCH_3 + CH_2O$ (B) $CH_3CH_2CHO + CH_3CHO$

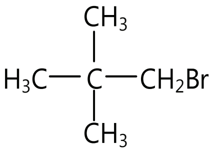
(C) $CH_3COCH_3 + CO_2$ (D) $CH_3COCH_3 + HCOOH$

Q.5 What is the chief product obtained when n-butane is treated with bromine in the presence of light at 130°C?

(A) 

(B) 

(C) 

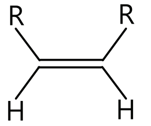
(D) 
$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-CH_2Br$

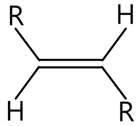
Q.6 Addition of halogen acid (HX) is least in

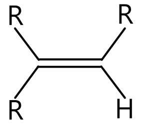
(A) $CH_2=CHCl$ (B) $CH_2=CH_2$

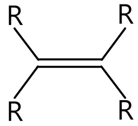
(C) $CH_3–CH=CH_2$ (D) $(CH_3)_2C=CH_2$

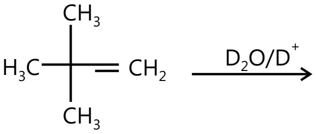
Q.7 Which of the following alkene will react fastest with H_2 under catalytic hydrogenation condition?

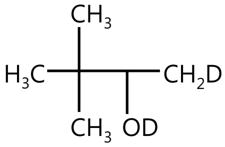
(A) 

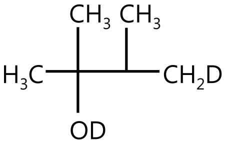
(B) 

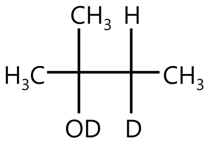
(C) 

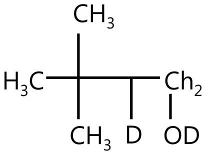
(D) 

Q.8 Products of the reaction. 
$H_3C-\overset{CH_3}{\underset{CH_3}{}}=CH_2 \xrightarrow{D_2O/D^+}$

(A) 
$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-\underset{OD}{C}-CH_2D$

(B) 
$H_3C-\overset{CH_3}{\underset{OD}{C}}-\overset{CH_3}{C}-CH_2D$

(C) 
$H_3C-\overset{CH_3}{\underset{OD}{C}}-\overset{H}{\underset{D}{C}}-CH_3$

(D) 
$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-\underset{D}{C}-\underset{OD}{Ch_2}$

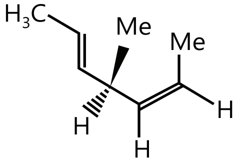
Q.9 The C–H bond length is longest in

(A) C_2H_2 (B) C_2H_4 (C) C_2H_6 (D) $C_2H_2Br_2$

Q.10 Point out (A) in the given reaction sequence:

$$(A) \xrightarrow{O_3/H_2O} (B) \xrightarrow{\Delta} 2CH_3COOH + CO_2$$

Q.11 Hydrogenation of the compound



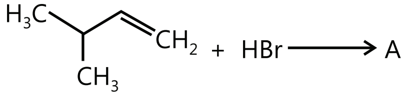
In the presence of poisoned palladium catalyst gives:

(A) An optically active compound

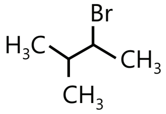
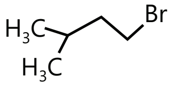
(B) An optically inactive compound

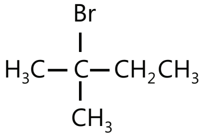
(C) A racemic mixture

(D) A diastereomeric mixture

Q.12 

(Predominant). A is

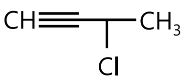
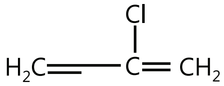
(A)  (B) 

(C) 
$H_3C-\overset{Br}{\underset{CH_3}{C}}-CH_2CH_3$ (D) Non of these

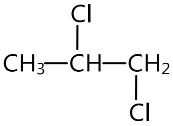
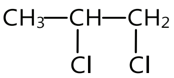
Q.13 Identify (B) in the following sequence of reactions

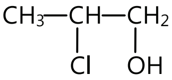
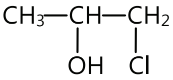
$CH\equiv CH \xrightarrow{Cu_2Cl_2+NH_4Cl} (A) \xrightarrow{HCl} (B)$

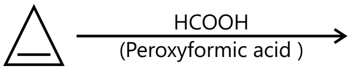
(A) CH_3CH_2Cl (B) $CH_2=CH\text{-}CH_2CH_2Cl$

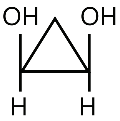
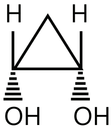
(C) 
$CH\equiv\underset{Cl}{C}-CH_3$ (D) 
$H_2C=\overset{Cl}{C}=CH_2$

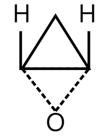
Q.14 $CH_3-CH=CH_2 \xrightarrow{Cl_2-H_2O}$ Z . Z may be

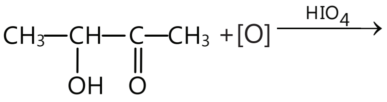
(A) 
$CH_3-\overset{Cl}{CH}-\underset{Cl}{CH_2}$ (B) 
$CH_3-\underset{Cl}{CH}-\underset{Cl}{CH_2}$

(C) 
$CH_3-\underset{Cl}{CH}-\underset{OH}{CH_2}$ (D) 
$CH_3-\underset{OH}{CH}-\underset{Cl}{CH_2}$

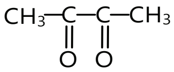
Q.15  Z. Z may be

(A)  (B) 

(C)  (D) Non of these

Q.16 
$CH_3-\underset{OH}{CH}-\underset{\underset{O}{\|}}{C}-CH_3+[O]\xrightarrow{HIO_4}$ Z.Z may be

(A) CH_3-CHO (B) CH_3-COOH

(C) 
$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-CH_3$ (D) None of these

Q.17 Which one of the following heptanols can be dehydrated to hept-3-ene only?

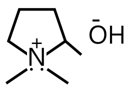
(A) Heptan-3-ol (B) Heptan-4-ol

(C) Heptan-2-ol (D) Heptan-1-ol

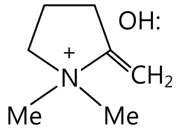
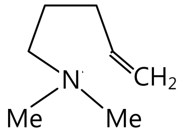
Q.18 Aqueous solution of potassium propanoate is electrolysed. Possible organic products are:

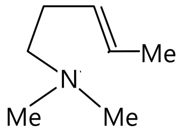
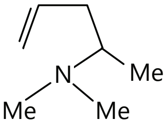
(A) n-Butane (B) $C_2H_5COOC_2H_5$

(C) CH_3-CH_3 (D) $CH_2=CH_2$

Q.19 

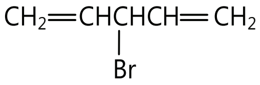
The above compound undergoes elimination on heating to yield which of the following products?

(A)  (B) 

(C)  (D) 

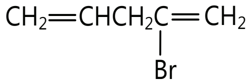
Multiple Correct Choice Type

Q.20 $CH_2=CHCH_2CH=CH_2 \xrightarrow{NBS}$ A, A can be

(A) 
$CH_2=CH\underset{Br}{CH}CH=CH_2$

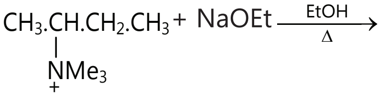
(B) $CH_2=CHCH=CH-CH_2Br$

(C) $CH_2=CHCH_2CH=CHBr$

(D) 
$CH_2=CHCH_2\underset{Br}{C}=CH_2$

Q.21 Which of the following elimination reactions will occur to give but-1-ene as the major product?

(A) $CH_3.CHCl.CH_2.CH_3 + KOH \xrightarrow{EtOH}$

(B) 
$CH_3.\underset{\underset{+}{N}Me_3}{CH}.CH_2.CH_3+NaOEt\xrightarrow[\Delta]{EtOH}$

(C) $CH_3.CH_2.CHCl.CH_3+Me_3CO^-K^+\xrightarrow{\Delta}$

(D) $CH_3.CH_2.CHOH.CH_3+conc.H_2SO_4$

Q.22 Select true statement(s):

(A) I_2 does not react with ethane at room temperature even though I_2 is more easily cleaved homolytically than the other halogens.

(B) Regiochemical outcome of a free radical addition and an electrophilic addition reaction on propene is identical.

(C) The rate of bromination of methane is decreased if HBr is added to the reaction mixture.

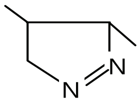
(D) Allylic chloride adds halogens faster than the corresponding vinylic chloride.

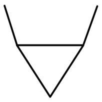
Q.23 An alkene on ozonolysis yields only ethanal. There is an isomer of this which on ozonolysis yields:

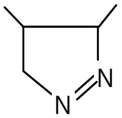
(A) Propanone	(B) Ethanal
(C) Methanal	(D) Only propanal

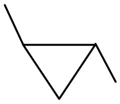
Q.24 $CH_3–CH=CH–CH_3 + CH_2N_2 \xrightarrow[\Delta]{} A$

A can be

(A)


(B)


(C)


(D)


Q.25 Which of the following will give same product with HBr in presence or absence of peroxide.

(A) Cyclohexene

(B) 1-methylcyclohexene

(C) 1, 2-dimethylcyclohexene

(D) 1-butene

Q.26 The ionic addition of HCl to which of the following compounds will produces a compound having Cl on carbon next to terminal.

(A) $CH_3.(CH2)_3.CH=CH_2$	(B) $CH_3.CH=CH_2$
(C) $CF_3.CH=CH_2$	(D) $CF_3.CH=CH_2$

Q.27 Which is/are true statements/reactions?

(A) $Al_4C_3 + H_2O \longrightarrow CH_4$

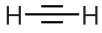
(B) $CaC_2 + H_2O \longrightarrow C_2H_2$

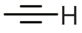
(C) $Mg2C_3 + H_2O \longrightarrow CH_3C≡CH$

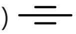
(D) $Me_3C–H + KMnO_4 \longrightarrow Me_3C–OH$

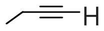
Q.28 $C \xrightarrow[H_2O_2/OH^-]{BH_3/THF} A \xrightarrow[H_2SO_4]{HgSO_4} B$

B and C are identical when A is –

(A)


(B)


(C)


(D)


Assertion Reasoning Type

Each of the questions given below consists of two statements, an assertion (A) and reason (R). Select the number corresponding to the appropriate alternative as follows:

(A) If both Assertion and Reason are true and Reason is the correct explanation of Assertion .

(B) If both Assertion and Reason are true but Reason is not the correct explanation of Assertion .

(C) If Assertion is true but Reason is false.

(D) If Assertion is false but Reason is true.

Q.29 Assertion: In α,β-unsaturated compounds with C=C and C=O conjugated, attack of nucleophile takes place on C=C.

Reason: The C=O bond is stronger than C=C.

Q.30 Assertion: Alkyl iodides are more reactive than alkyl chlorides for elimination reactions.

Reason: I– is a better leaving group than Cl–

Q.31 Assertion: $CH_3CH_2^-$ is a stronger base than F–.

Reason: The negative charge density on carbon is greater than the negative charge density of F–.

Q.32 Assertion: $CH_3–C≡C–CH_3$ is more reactive than CH≡CH towards HCl.

Reason: The carbocation formed is more stable in the case of $CH_3–C≡C–CH_3$ than CH≡CH.

Q.33 Assertion: CH≡CH reacts with HCl in the presence of $HgCl_2$ while $CH_2=CH_2$ does not.

Reason: There is more unsaturation in CH≡CH than in $CH_2=CH_2$.

Comprehension Type (34-36)

n-Butane is produced by mono bromination of ethane followed by Wurtz reaction, as follows

(i) $CH_3CH_3 \xrightarrow[h\nu]{Br_2} CH_3CH_2–Br$

(ii) $CH_3CH_2Br \xrightarrow{Na} CH_3CH_2CH_2CH_3 + CH_2{=}CH_2 + CH_3{-}CH_3 + NaBr$

Mechanism: $Na \rightarrow Na^+ + e^-$;

$CH_3CH_2Na + CH_3CH_2Br \rightarrow$

$CH_3CH_2CH_2CH_3 + CH_2{=}CH_2 + CH_3{-}CH_3$

$CH_3CH_2Br \rightarrow CH_3\dot{C}H_2 + \dot{Br}$

$CH_3\dot{C}H_2 + e^- \rightarrow CH_3CH_2^{\bullet}$

Q.34 The amount of ethyl bromide required to prepare 55g of butane would be

(A) 106.72 (B) 206.72 (C) 20.67 (D) 2.067

Q.35 If the yield of n-butane was 85%, then the actual amount of ethyl required to produce 55g of n-butane would be

(A) 2.432g (B) 24.32g (C) 243.2g (D) 0.2432g

Q.36 The other products which could be formed

(A) $CH_2{=}CH_2$ (B) $CH_3CH_2CH_3$

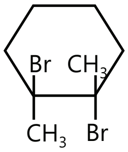
(C) CH_4 (D) $CH_3CH_2CH_2{-}CH_2{-}CH_3$

Comprehension Type (36-38)

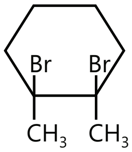
The functional group in alkenes is C–C double bond which is made of one σ-bond and one π-bond. The weaker π-bond would tend to attract the electrophile and convert itself to a stable carbonium ion which reacts with nucleophile remainder to form the addition product. The addition reaction of alkenes is stereo specific as well as stereoselective. i.e., the isomeric alkenes react differently with same addendum to give stereochemically different products. Where addition of HBr proceeds through carbocation formation and hence racemisation is expected. With low concentration of Br_2 in vapour phase substitution predominates over addition.

Q.37 Reaction of 1,2-dimethylcyclohexene with bromine water gives the product

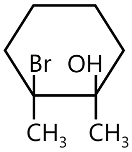
(A)



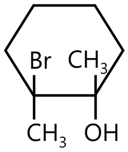
(B)



(C)



(D)



Q.38 $^{14}CH_3{-}CH{=}CH_2 \xrightarrow[\text{high temperature}]{Br_2\text{/low conc.}}$

Product of the above reaction is

(A) $Br{-}^{14}CH_2{-}CH{=}CH_2$ (B) $^{14}CH_2{=}CH{-}CH_2{-}Br$

(C) Both (a) and (b) (D) None of these

Q.39 Trans-2-butene when reacts with Br_2, the product formed is

(A) Racemic mixture (B) Meso form

(C) Optically pure (D) No specific stereochemistry

Match the Columns

Q.40 Match the entries in column I with entries in column II

Column I	**Column II**
(A) $CH_3{-}C{\equiv}C{-}CH_3$ cis-2-butene	(p) $Na/NH_3(l)$
(B) $CH_3{-}C{\equiv}C{-}CH_3 \longrightarrow$ trans-2-butene	(q) $H_2/Pd/BaSO_4$
(C) $CH_3C{\equiv}C{-}CH_3 \longrightarrow$ 1-Butyne	(r) Alc. KOH, Δ
(D) $CH_3{-}CH_3{-}C{\equiv}CH \longrightarrow$ 2-Butyne	(s) $NaNH_2$, Δ

Q.41 Match List-I with List-II and select the correct answer

List I (Reaction)	**List II (Reagents)**
(A) $CH_3{-}CH{=}CH_2 \rightarrow CH_3{-}CHBr{-}CH_3$	(p) HBr
(B) $CH_3{-}CH{=}CH_2 \rightarrow CH_3{-}CH_2{-}CH_2Br$	(q) Br_2
(C) $CH_3{-}CH{=}CH_2 \rightarrow BrCH_2{-}CH{=}CH_2$	(r) HBr/Peroxide
(D) $CH_3{-}CH{=}CH_2 \rightarrow CH_3{-}CHBr{-}CH_2Br$	(s) NBS

Q.42 Match the column

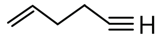
Column I	**Column II**
(A) $RCOONa \xrightarrow{\text{Electrolysis}} R{-}R$	(p) Corey-House reaction
(B) $R{-}CH_2{-}COOH \xrightarrow[\Delta]{\text{Soda Lime}} R{-}CH_3$	(q) Kolbe electrolysis
(C) $RCOOH \xrightarrow[\text{(ii) } Cl_2/\Delta]{\text{(i) } AgNO_3} R{-}Cl$	(r) Oakwood degradation

Previous Years' Questions

Q.1 $(CH_3)_3CMgCl$ on reaction with D_2O produces ***(1997)***

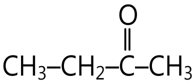
(A) $(CH_3)_3CD$ (B) $(CH_3)_3OD$

(C) $(CD_3)_3CD$ (D) $(CD_3)_3OD$

Q.2 In the compound,  the C2–C3 bond is of the type ***(1999)***

(A) sp–sp^2 (B) sp^3–sp^3 (C) sp–sp^3 (D) sp^2–sp^3

Q.3 The product(s) obtained via oxymercuration ($HgSO_4$ + H_2SO_4) of 1-butyne would be

(A)  $CH_3-CH_2-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$ (B) $CH_3-CH_2-CH_2-CHO$

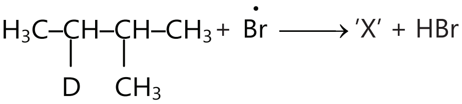
(C) $CH_3-CH_2-CHO + HCHO$

Q.4 Identify a reagent from the following list which can easily distinguish between 1-butyne and 2-butyne. ***(2002)***

(A) Bromine, CCl_4 (B) H_2, Lindlar catalyst

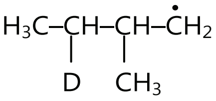
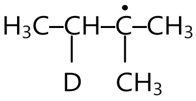
(C) Dilute H_2SO_4, $HgSO_4$ (D) Ammoniacal $CuCl_2$ solution

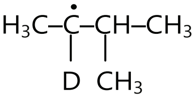
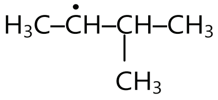
Q.5 Consider the following reaction



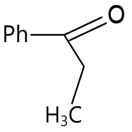
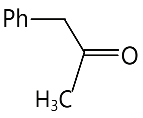
$H_3C-\underset{\displaystyle D}{\underset{|}{C}H}-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_3 + \overset{\bullet}{Br} \longrightarrow \text{'X'} + HBr$

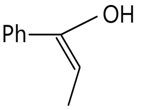
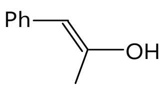
Identify the structure of the major product X ***(2002)***

(A)  $H_3C-\underset{\displaystyle D}{\underset{|}{C}H}-\underset{\displaystyle CH_3}{\underset{|}{C}H}-\overset{\bullet}{C}H_2$ (B)  $H_3C-\underset{\displaystyle D}{\underset{|}{C}H}-\underset{\displaystyle CH_3}{\underset{|}{\overset{\bullet}{C}}}-CH_3$

(C)  $H_3C-\underset{\displaystyle D}{\underset{|}{\overset{\bullet}{C}}}-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_3$ (D)  $H_3C-\overset{\bullet}{C}H-\underset{\displaystyle CH_3}{\underset{|}{C}H}-CH_3$

Q.6 $Ph-C\equiv C-CH_3 \xrightarrow[H^+]{Hg^{2+}}$ A ; A is ***(2003)***

(A)  (B) 

(C)  (D) 

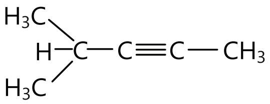
Comprehension Based Questions (Q.7 & 8)

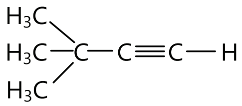
An acyclic hydrocarbon P, having molecular formula C_6H_{10}, gave acetone as the only organic product through the following sequence of reactions, in which Q is an intermediate organic compound.

Q.7 The structure of compound P is

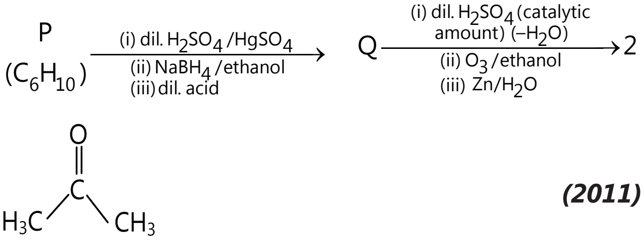
(A) $CH_3CH_2CH_2CH_2—C\equiv C—H$

(B) $H_3CH_2C—C\equiv C—CH_2CH_3$

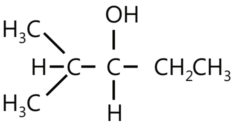
(C) 

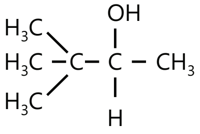
(D) 

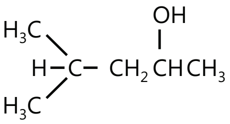
Q.8 The structure of the compound Q is



(2011)

(A) 

(B) 

(C) 

(D) $CH_3CH_2CH_2CH(OH)CH_2CH_3$

Q.9 Give reasons for the following in one or two sentences: ***(1983)***

(i) Methane does not react with chlorine in dark.

(ii) Propene reacts with HBr to give isopropyl bromide but does not give n-propyl bromide.

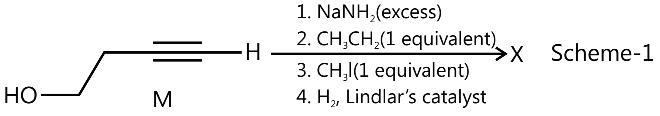
Q.10 Following statements are true, only under some specific conditions. Write the condition for each sub question in not more than two sentences:

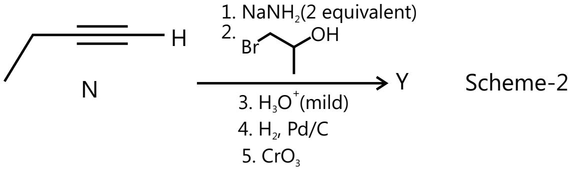
(i) 2-methyl propene can be converted into isobutyl bromide by hydrogen bromide

(ii) Ethyne and its derivatives will give white precipitate with ammoniacal silver nitrate solution. ***(1984)***

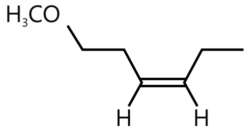
Paragraph for Questions 11 and 12

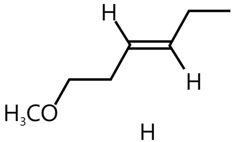
Schemes 1 and 2 describe sequential transformation of alkynes M and N. Consider only the major products formed in each step for both schemes.

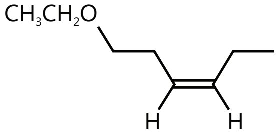


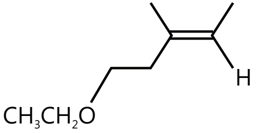


Q.11 The product X is ***(2014)***

(A) 

(B) 

(C) 

(D) 

Q.12 The correct statement with respect to product Y is ***(2014)***

(A) It gives a positive Tollens test and is a functional isomer of X.

(B) It gives a positive Tollens test and is a geometrical isomer of X.

(C) It gives a positive iodoform test and is a functional isomer of X.

(D) It gives a positive iodoform test and is a geometrical isomer of X.

Questions

JEE Main/Boards

Exercise 1

Q.3 Q.8 Q.13 Q.15 (b)
Q.20 (a)

Exercise 2

Q.1 Q.7 Q.9 Q.14
Q.28

Previous Years' Questions

Q.10 Q.13

JEE Advanced/Boards

Exercise 1

Q.1 Q.8 Q.13 Q.18 Q.21

Exercise 2

Q.5 Q.9 Q.14 Q.22 Q.26

Previous Years' Questions

Q.6 Q.8

Answer Key

JEE Main/Boards

Exercise 2

Single Correct Choice Type

Q.1 B **Q.2** C **Q.3** A **Q.4** D **Q.5** C **Q. 6** C
Q.7 B **Q.8** D **Q. 9** D **Q.10** B **Q.11** A

Previous Years' Questions

Q.1 B **Q.2**.D **Q.3** D **Q.4** C **Q.5** A **Q.6** A **Q 7** B
Q.8 B **Q.9** C **Q.10** A **Q.11** A **Q.12** D **Q.13** C **Q.14** D
Q.15 B **Q.16** D **Q.17** C **Q.18** C **Q.19** A **Q. 20** B **Q.21** A
Q.22 B

JEE Advanced/Boards

Exercise 2

Single Correct Choice Type

Q.1 C **Q.2** C **Q.3** A **Q.4** B **Q.5** B,C **Q.6** B **Q.7** D
Q.8 B **Q.9** C **Q.10** C **Q.11** B **Q.12** C **Q.13** D **Q.14** D
Q.15 C **Q.16** A **Q.17** B **Q.18** A **Q.19** B

Multiple Correct Choice Type

Q.20 A,B **Q.21** B,C **Q.22** A,C,D **Q.23** A,C **Q.24** A,B,C,D **Q.25** A,C **Q.26** A,B,D
Q.27 A,B,C,D **Q.28** A,C

Assertion Reasoning Type

Q.29 B **Q.30** A **Q.31** A **Q.32** A **Q.33** B

Comprehension Type

Q.34 A **Q.35** A **Q.36** A **Q.37** D **Q.38** C **Q.39** B

Match the Columns

Q.40 A → q; B → p; C → s; D → r **Q.41** A → p; B → r; C → s; D → q **Q.42** A → q; B → r; C → s; D → p

Previous Years Questions

Q.1 A **Q.2** D **Q.3** A **Q.4** D **Q.5** B **Q.6** A **Q.7** D
Q.8 B **Q.11** A **Q.12** C

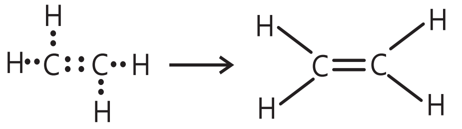
Solutions

JEE Main/Boards

Exercise 1

Sol 1: Alkenes are substances which contain less hydrogen than the maximum quantity of hydrogen which a carbon atom can have

Structure:-



Preparation of Alkenes:-

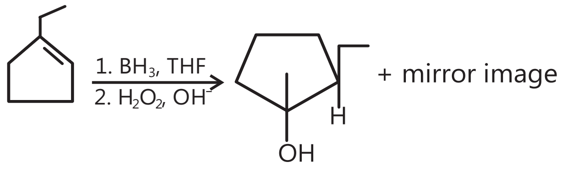
(1) Dehydrohalogenation of Alkyl halide

(2) Dehyration of Alcohols

(3) Dehalogenation of vicinal dihalides

(4) Dehalogenation of geminal dihalide

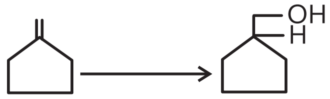
Sol 2: (A)



trans additon

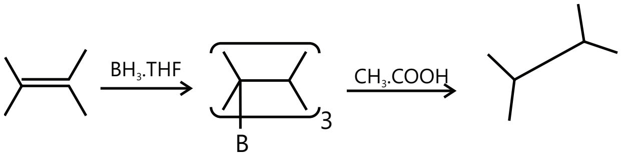
∴ Recemic mixture

(B)

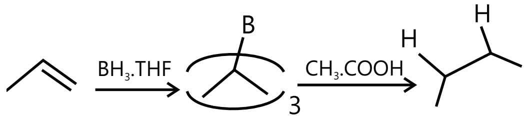


Antimarkov's addition

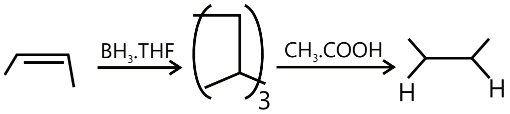
Sol 3: (A)



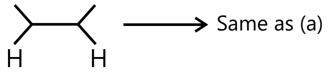
(B)



(C)

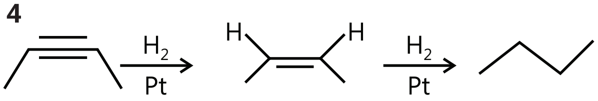


(D)

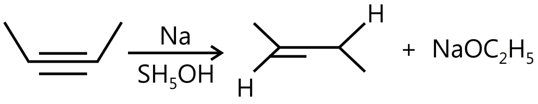


Sol 4

(A)



(B)



Sol
5: Physical properties: Refer theory pg.26

Chemical properties: Refer theory pg.29

Sol 6: Alkynes:-

In the family of hydrocarbon alkynes are the most unsaturated one with C≡C bond and are highly reactive.

Preparation:-

(1) Dehydrohalogenation

(2) From tetradehalogenation

(3) From haloform

(4) Kolbe's electrolytic decarboxylation

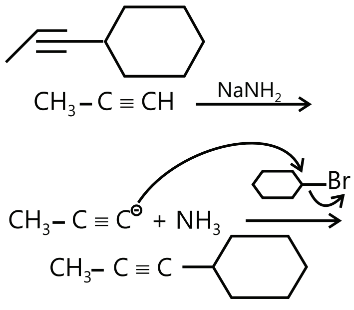
(5) Berthlot's reaction

Sol 7: Physical properties: Refer theory pg.42

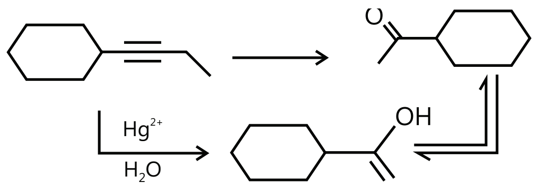
Chemical properties: Refer theory pg.44

Sol 8:

(A)

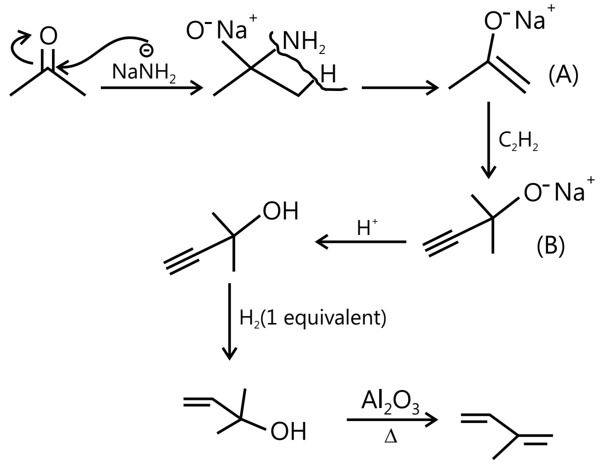


(B)

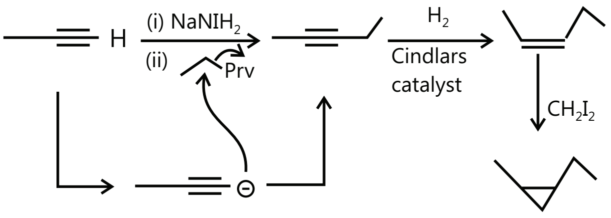


Sol 9:

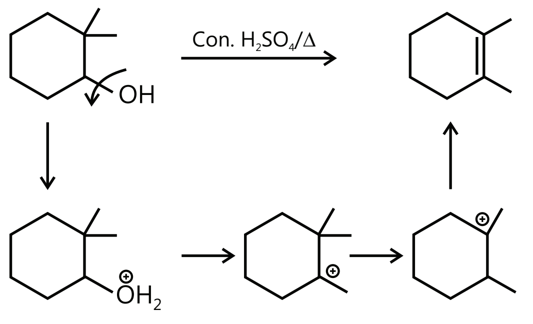
(A)

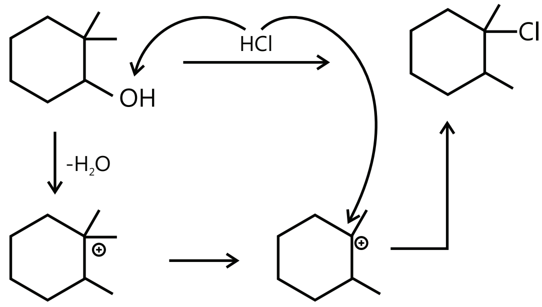


(B)

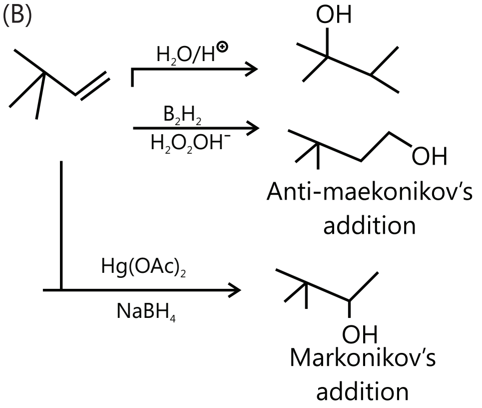


Sol 10: (A)

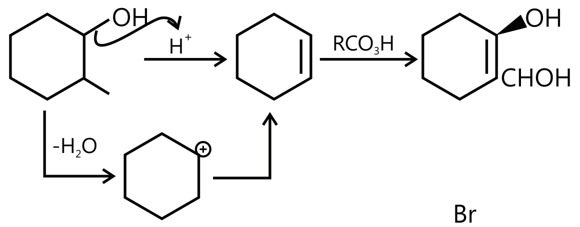




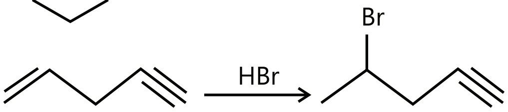
(B)



(C)

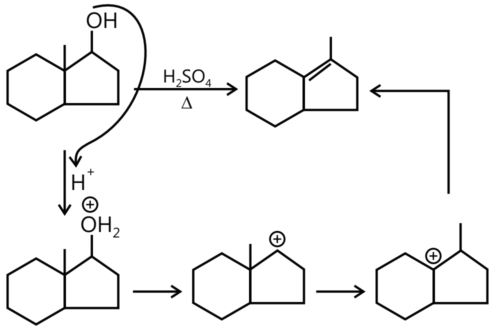


Sol 11: (A)

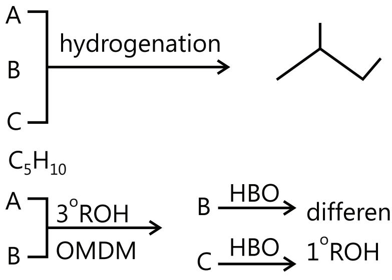


Doubled bonds are more electron donating than triple bond because of difference in electronegativity and because of which first addition will takes place on double bond rather than triple bond.

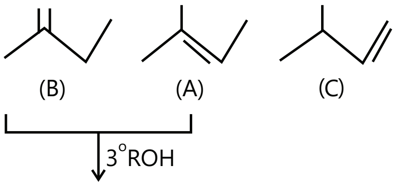
(B)

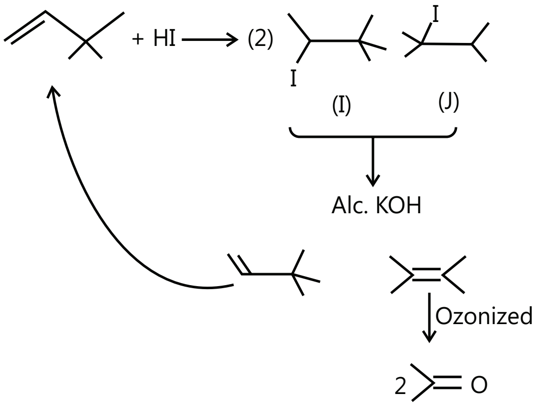


Sol 12:

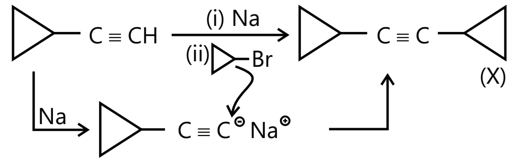


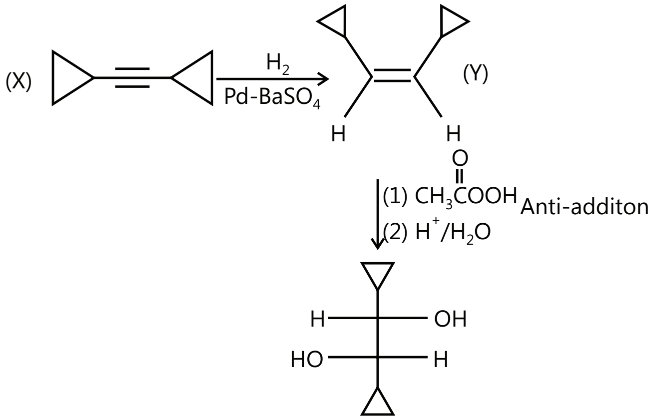
Sol 13:





Sol 14

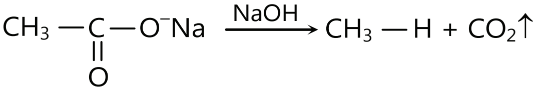




Exercise 2

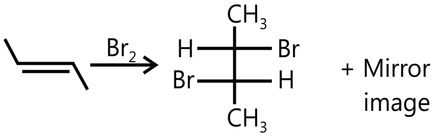
Single Correct Choice Type

Sol 1: (B) Dicarboxylation of acid ion



$$CH_3-\underset{\underset{O}{\|}}{C}-O^{-}Na \xrightarrow{NaOH} CH_3-H + CO_2\uparrow$$

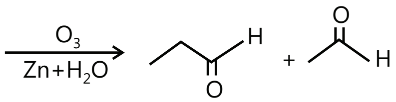
Sol 2: (C)

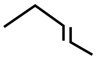


Recemic mixture

Sol 3: (A) Definition of conformers.

Sol 4: (D) Olefin

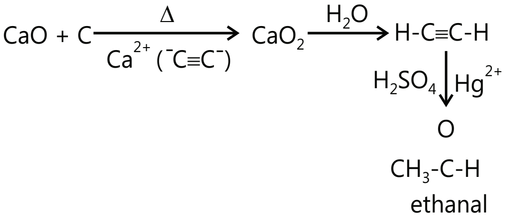




pent-2-ene

Sol 5: (C) C ≡ C is strongest because it is shortest and more orbitals are overlapping.

Sol 6: (C)



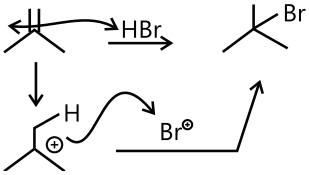
$$\begin{tikzcd}[column sep=small] CaO + C \arrow[r, "\Delta", "Ca^{2+}({}^{-}C{\equiv}C^{-})"'] & CaO_2 \arrow[r, "H_2O"] & H\text{-}C{\equiv}C\text{-}H \arrow[d, "H_2SO_4"', "Hg^{2+}"] \\ & & CH_3\text{-}\overset{O}{C}\text{-}H \end{tikzcd}$$

ethanal

Sol 7: (B) $C_2H_3MgI \xrightarrow{H_2O} C_2H_6$

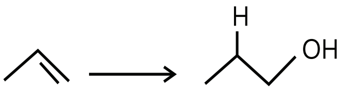
Abstracts acidic hydrogen.

Sol 8: (D)



only product

Sol 9: (D)



Anti Markonikov's addition

Sol 10: (B)

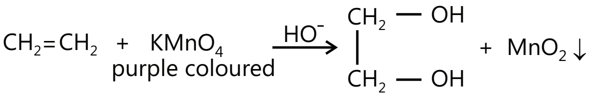
$$\begin{tikzcd} HC \equiv CH \arrow[r, "HBr"] & H_2C \equiv CH-Br \arrow[d, "Alc.\ KOH"] \\ & HC \equiv CH \end{tikzcd}$$

Sol 11: (A) Enol form is not net stable as keto is much more stable.

Previous Years' Questions

Sol 1: (B) Methane is produced due to the decay of vegetables or animal organisms present in swamps and marsh, by the action of bacteria. Due to this method of formation, methane is also known as marsh gas.

Sol 2: (D) Unsaturated compounds which contain C=C or C≡C, decolourises the purple colour of alkaline $KMnO_4$ solution.



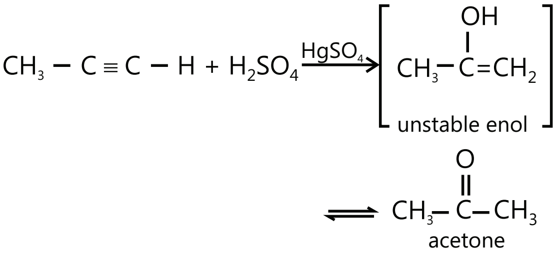
$$\underset{\text{purple coloured}}{CH_2{=}CH_2 + KMnO_4} \xrightarrow{HO^{-}} \begin{matrix} CH_2-OH \\ | \\ CH_2-OH \end{matrix} + MnO_2\downarrow$$

Sol 3: (D) Structural formula of 1, 2-butadiene is:

$$H_2C{=}C{=}CH{-}CH_3$$

↑ ↑ ↑ ↑

Sol 4: (C) Alkynes undergo Markownikoff's addition of water in presence of $H_2SO_4/HgSO_4$:



$$CH_3-C\equiv C-H + H_2SO_4 \xrightarrow{HgSO_4} \left[\underset{\text{unstable enol}}{CH_3-\overset{\overset{\displaystyle OH}{|}}{C}=CH_2}\right] \rightleftharpoons \underset{\text{acetone}}{CH_3-\overset{\overset{\displaystyle O}{||}}{C}-CH_3}$$

Sol 5: (A) Bayer's reagent is cold, dilute, alkaline perman-ganate solution, used to detect presence of olefinic bonds.

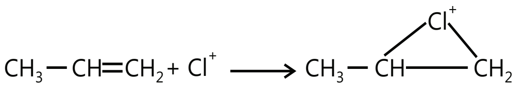
Sol 6: (A) Terminal alkynes are slightly acidic, forms salt with very strong base like Na, $NaNH_2$ etc.

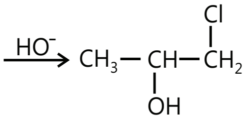
$$\underset{\text{ethyne}}{H-C\equiv C-H} + Na \xrightarrow{} H-C\equiv C^-Na^+ + \frac{1}{2}H_2\uparrow$$

Sol 7: (B) Hydrogenation with poisoned palladium brings about cis hydrogenation of alkyne and does not affect double bonds:

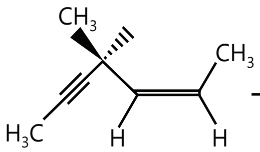
Sol 8: (B)

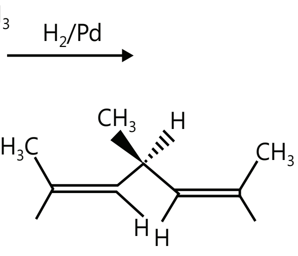
$HOCl \longrightarrow HO^- + Cl^+$





$$\xrightarrow{HO^-} CH_3-\underset{\underset{\displaystyle OH}{|}}{CH}-\overset{\overset{\displaystyle Cl}{|}}{CH_2}$$





meso-compound
(optically inactive)

i.e. Reaction is initiated by Cl^+(Chloronium ion electrophile).

Sol 9: (C) In addition of HBr to an alkene, in presence of peroxide, both the propagation steps are exothermic:

$$HBr + HO^{\bullet} \rightarrow H_2O + Br^{\bullet}$$

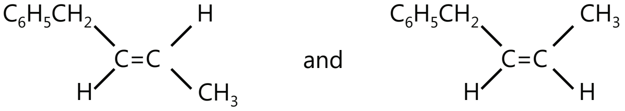
Propagation

$$\begin{cases} CH_3-CH=CH_2+Br^{\bullet} \rightarrow CH_3-\dot{C}H-CH_2Br \quad \Delta H<0 \\ CH_3-\dot{C}H-CH_2Br+HBr \rightarrow CH_3-CH_2-CH_2Br+Br^{\bullet} \quad \Delta H<0 \end{cases}$$

In case of addition of HCl and HI, one of the propagation step is endothermic, reaction fail to occur.

Sol 10: (A)

$C_6H_5CH_2{=}CHCH_3$ has two geometrical isomers



Trans

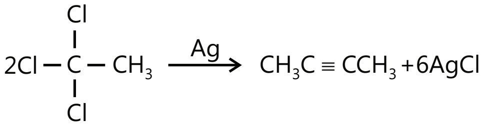
Cis

So it is 1-Phenyl-2-butene

Sol.11: (D) $CH_3-CH^+-CH_2-Cl$

Sol 12: (A)

$$\begin{tikzcd} CH_3COOH \arrow[r, "LiAlH_4"] & CH_3CH_2OH \arrow[d, "PCl_3"] & \text{'A'} \\ & CH_3CH_2Cl \arrow[d, "\text{Alc. KOH}"] & \text{'B'} \\ & CH_2{=}CH_2 & \text{'C'} \end{tikzcd}$$

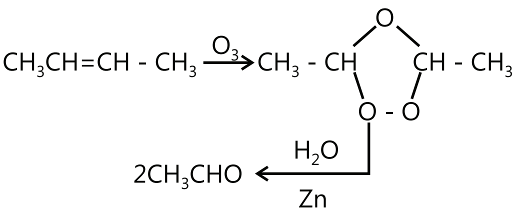


$$2Cl-\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}-CH_3 \xrightarrow{Ag} CH_3C\equiv CCH_3+6AgCl$$

1, 1, 1- Trichloroethane

Sol 13: (C)

Sol 14: (D)



Sol 15: (B)

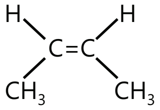
$$CH_3CH_2CH_2\equiv CH \xrightarrow[\Delta]{Na/Liq.NH_3} CH_3CH_2C\equiv\overset{\ominus}{C}Na^{\oplus}$$

It is a terminal alkyne, having acidic hydrogen.

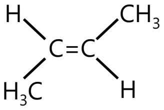
Note: Solve it as a case of terminal alkynes, otherwise all alkynes react with Na in liq. NH_3

Sol 16: (D) $CH_3-MgX+CH_3-C\equiv C-H\rightarrow CH_4$

Sol 17: (C)



Cis



Trans

Sol 18: (C) 2–butene is symmetrical alkene

$$CH_3-CH=CH-CH_3\xrightarrow[Zn/H_2O]{O_3}2.CH_3CHO$$

Molar mass of CH_3CHO is 44 u.

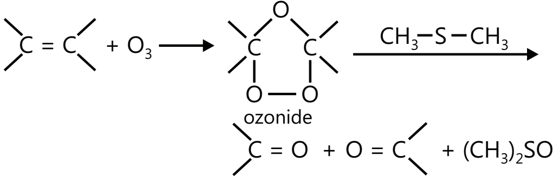
Sol 19: (A)

$$CH_3-CH_2-CH=CH_2+B\,r^{\bullet}\rightarrow CH_3-CH_2-\underset{\text{a secondary radical}}{\dot{C}H}-CH_2Br$$

Therefore, Statement I is correct but Statement II is incorrect.

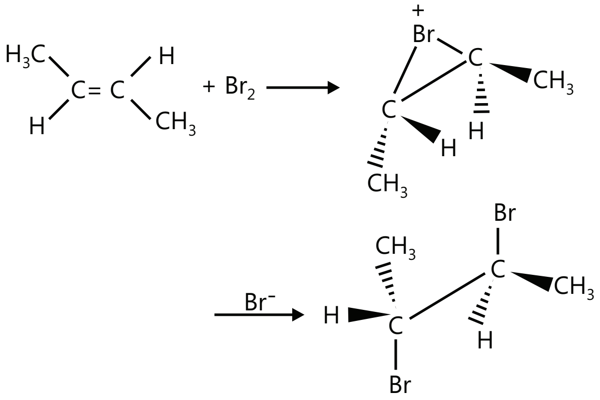
Sol 20: (B) Both Statement I and Statement II are correct and Statement II is correct explanation of Statement I.

Sol 21: (A)



Both Statement I and Statement II are correct and Statement II is correct explanation of Statement I.

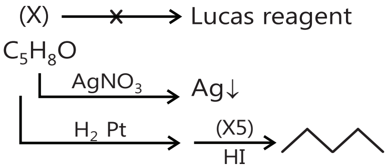
Sol 22: (B) Statement I is correct. Statement II is also correct. Meso form of the product is due to anti addition of Br on cyclic bromonium ion intermediate, hence Statement II is not correct explanation of Statement II.



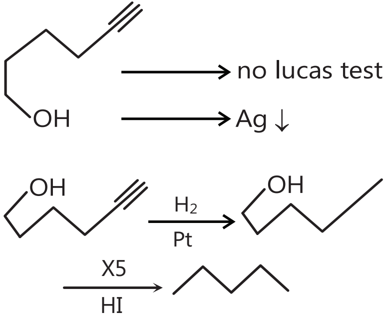
JEE Advanced/Boards

Exercise 1

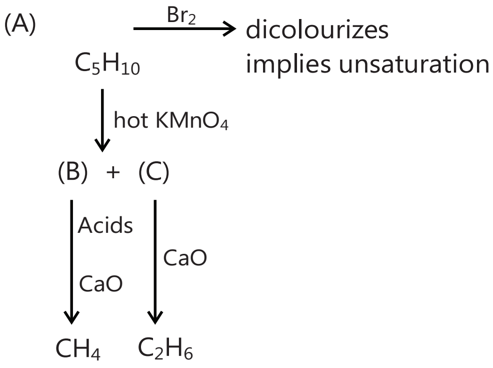
Sol 1:

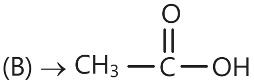


Degree of unsaturation : 2

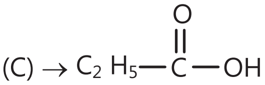


Sol 2:



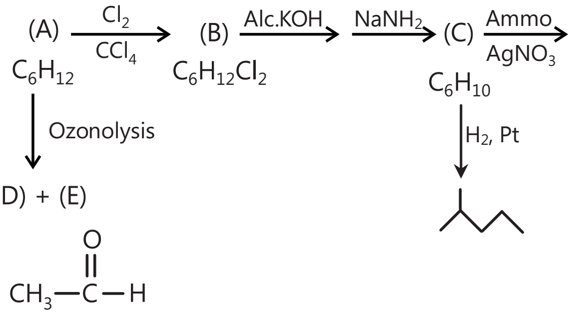


$$(B)\rightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

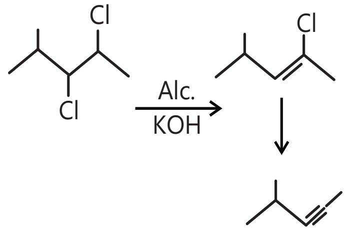


$$(C)\rightarrow C_2H_5-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Sol 3:

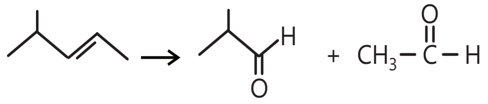


(B)

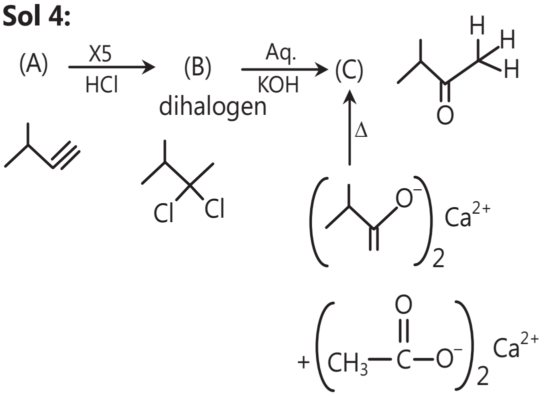


(C) terminal alkyne

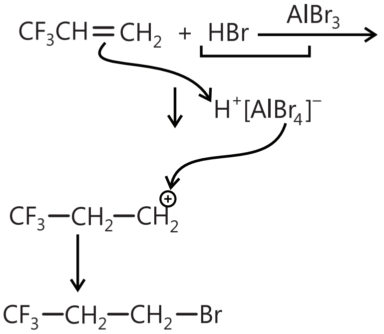
(D) + (E)



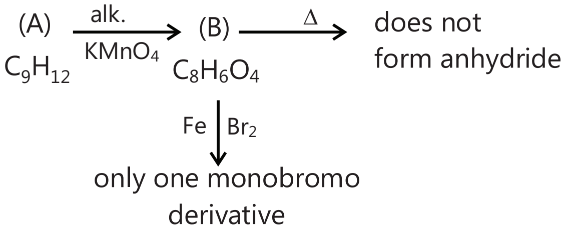
Sol 4:



Sol 5:



Sol 6:

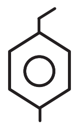


Degree of unsaturation of (A) = 4

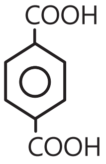
So it should contain benzene ring

In the compound (B) both –COOH should be at para position to give only one bromination product

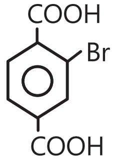
(A)



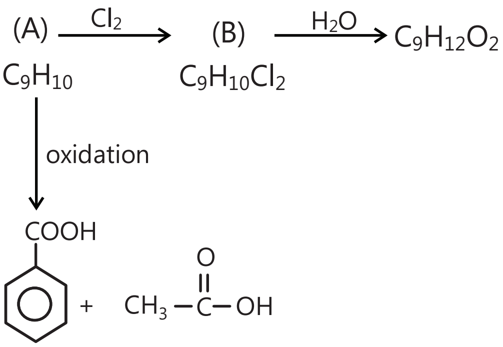
(B)



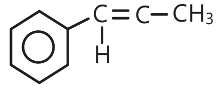
(C)



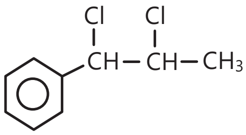
Sol 7:



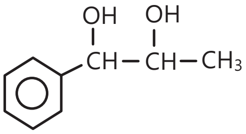
(A)



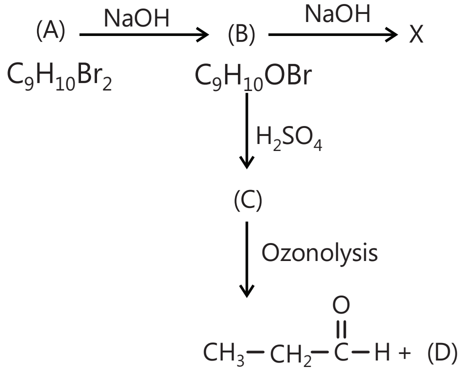
(B)



(C)



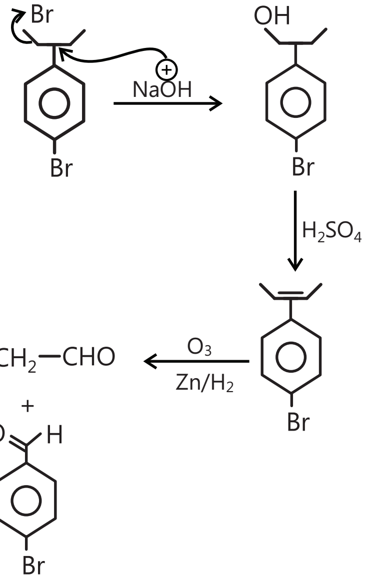
Sol 8:



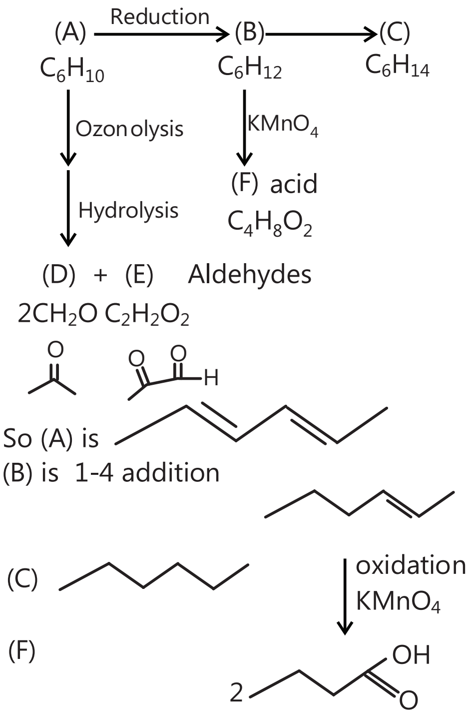
Since only one –Br is hydrolysed

∴ One is attached to alkyl group and other one to aryl group.

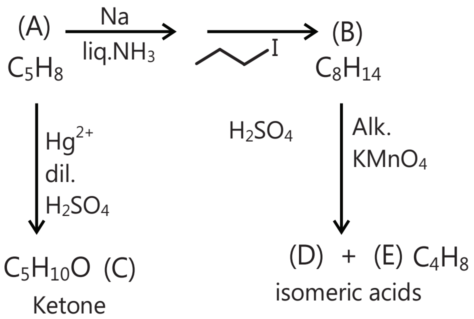
(A)



Sol 9:



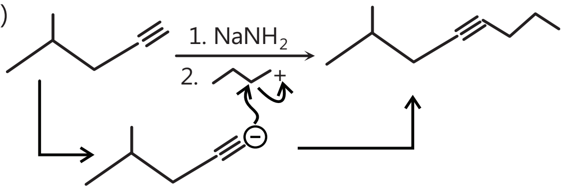
Sol 10:



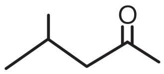
Degree of unsaturation of (A) = 2

∴ Alkyne. Terminal alkyne because formation of (B) and branched because formation of ketone (C)

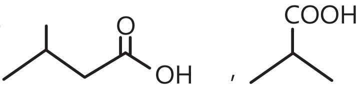
(A)



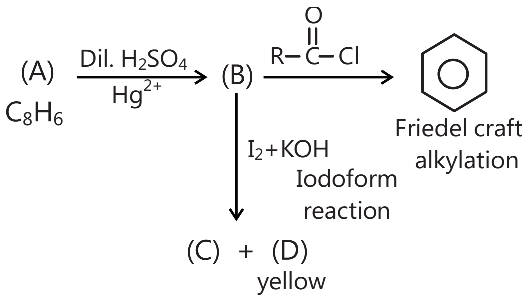
(C)



(D),(E)

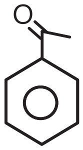


Sol 11:

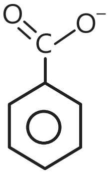


For reaction (B) → (C) it is iodoform so (D) → CHI_3 yellow precipitate and (B) should have acetyl ketone.

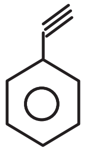
(B)



(C)

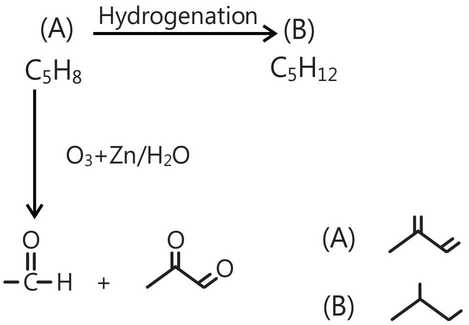


(A)

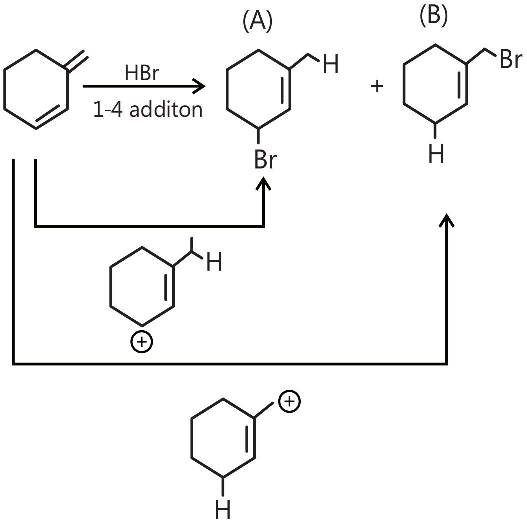


OMDM for alkyne give ketone

Sol 12:



Sol 13:

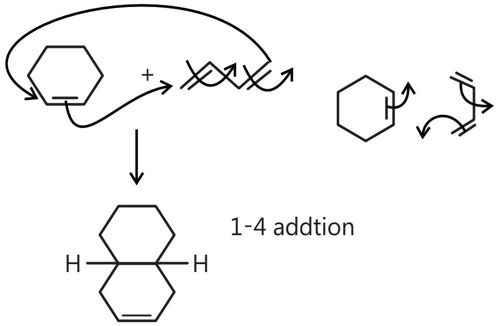


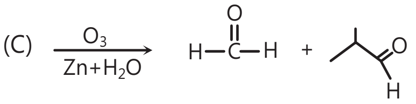
Compound (A) carbocation is more stable resonance is in both the compounds but

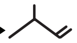
(A) have 3 α – H

(B) have 0 α – H

Sol 14:





∴ (C) →


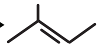
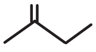
$(B) \xrightarrow[KOH]{Alc.} (D) + (E)$

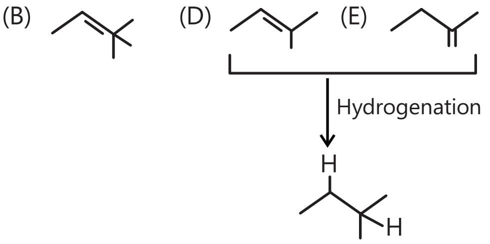
(C), (D), (E)

↓ Catalytic hydrogenation

C_5H_{12}

∴ (D) is isomer of (C)

∴ (D) →

not

because will not get by isomeric alkyl bromide of (B)

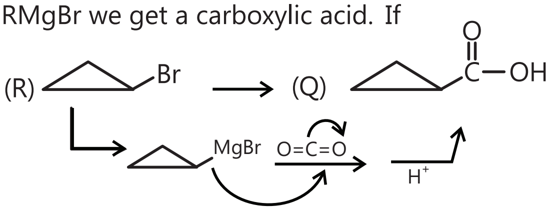


Sol 15:

(P) $\xrightarrow[Zn/H_2O]{O_3}$ (Q) $\xleftarrow[2.\ CO_2, H^+]{1.\ Mg/Et_2}$ C_3H_5Br

C_8H_{10} ← symmetric compound; $C_4H_6O_2$ only

Q is an acid because after reaction with CO_2, H^+ of RMgBr we get a carboxylic acid. If



∴ (P)

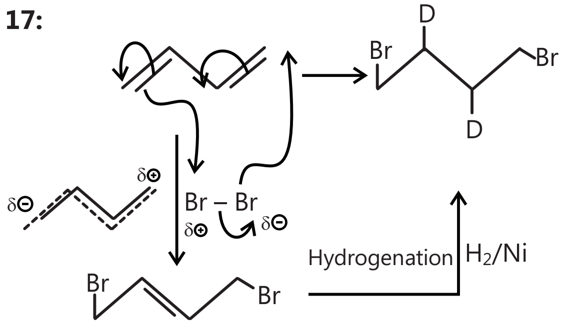

to satisfy the degree of unsaturation of (P) alkyl group must be cyclic.

Sol 16: (A), (B) $C_5H_{11}Br$

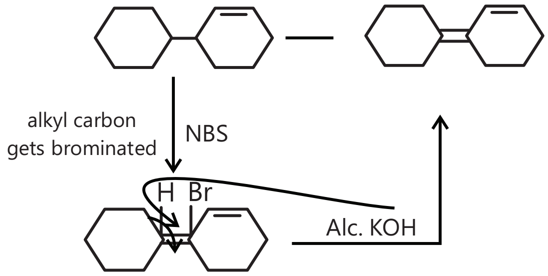
isomeric alkyl bromides (A) $\xrightarrow[KOH]{alc.}$ (C) + (D) isomers C_5H_{10}

Sol 17:

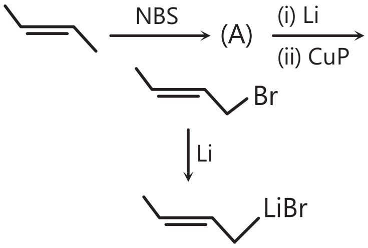
(i)



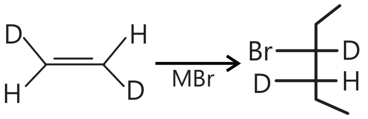
(ii)



(iii)

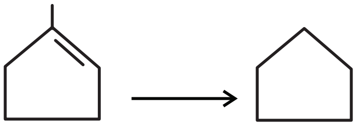


(iv)

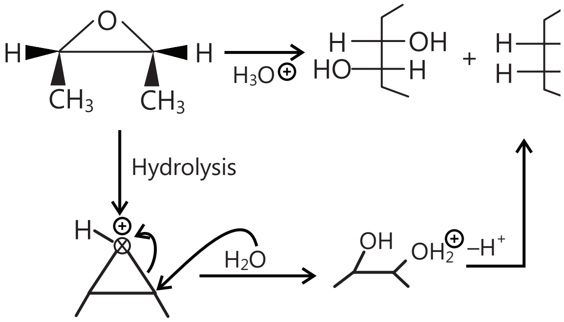


Anti-addition

(v)



(vi)



Sol 18: $(A) \xrightarrow[h\nu]{Cl_2} C_5H_9Cl$

C = 85.7%; h = 14.3%

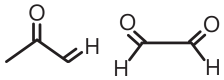
total molecular weight = 70

$C_5H_{10} \longrightarrow$ 

Sol 19:

$$\begin{tikzcd} (A)\ C_6H_{10} \arrow[r, "Amm.", "AgNO_3"'] \arrow[d, "Reduction"] & (X)\ \text{Not a terminal Alkyne} \\ (B)\ C_6H_{12} \arrow[r, "Alk.", "KMnO_4"'] \arrow[d] & (F)\ C_3H_6O_2 \\ (C)\ C_6H_{14} & \end{tikzcd}$$

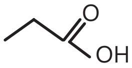
$$(A) \xrightarrow[Zn+H_2O]{O_3} \underset{C_2H_4O}{(D)} + \underset{C_2H_2O_2}{(E)}$$



(A) 

(B)  1-4 addition

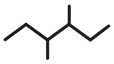
(C) 

(F) 

Sol 20: (A) + (B)
isomers

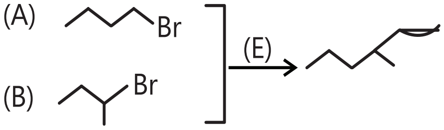
↓ Zn-Cu

$(A) \xrightarrow{Na/Ether}$  (C)

$(B) \xrightarrow{Na/Ether}$  (D)

But mixture gives (E)

Na/Ether is Wurtz reaction and dimerise the alkyl bromide so they are symmetric.



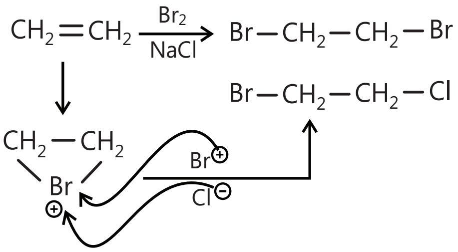
Exercise 2

Single Correct Choice Type

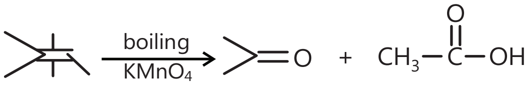
Sol 1: (C) Releases 1.34 mL of a gas at STP

∴ 3 moles of CH_4

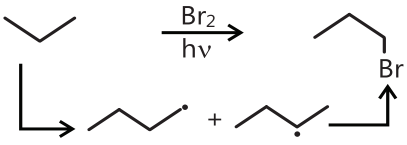
∴ 3 active α - H hydrogen.

Sol 2: (C) 

Sol 3: (A) $\underset{(X5)}{C_2H_6} + Cl_2 \xrightarrow{h\nu} C_2H_5Cl$

Sol 4: (B) 

Oxidative cleavage

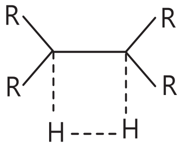
Sol 5: (B,C) 

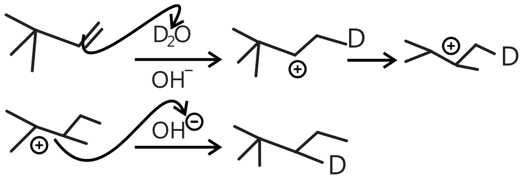
more stable

Sol 6: (B) Carbon is least stable in $\begin{array}{c} CH_3-\overset{\oplus}{C}H_2 \\ \uparrow \\ CH_2=CH_2 \end{array}$

∴ Addition will be least $CH_2=CH_2$

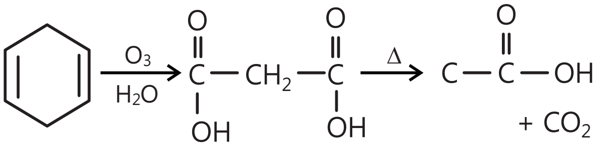
Sol 7: (D) Stability of complex that forms during reaction with H_2



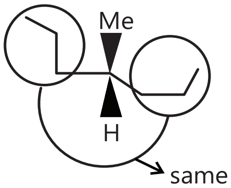
Sol 8: (B) 

Sol 9: (C) C-C-H is sp^3 hybridised, hence 's' character is less, So bond length in C-H is longest

Sol 10: (C)

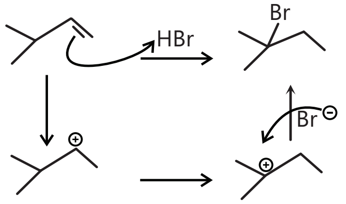


Sol 11: (B) Hydrogenate product

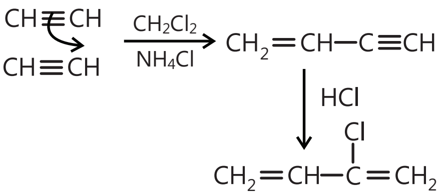


∴ optically inactive compound.

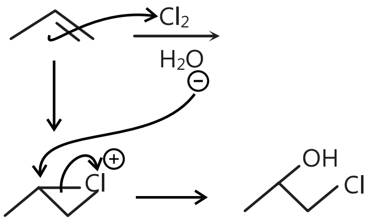
Sol 12: (C)



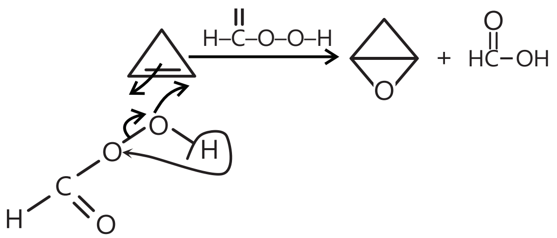
Sol 13: (D)



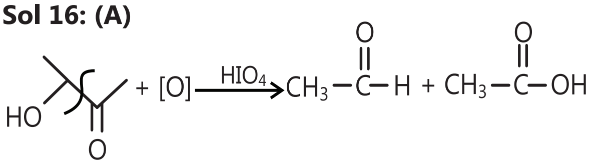
Sol 14: (D)



Sol 15: (C)



Sol 16: (A)



Sol 17: (B)

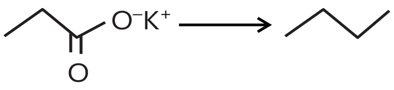
$$CH_3CH_2CH_2CH(OH)CH_2CH_2CH_3 \xrightarrow[-H_2O]{\text{Dehydration}}$$

(Heptan–4–ol)

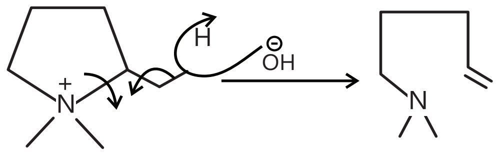
$$CH_3CH_2CH=CHCH_2CH_2CH_3$$

(Hept–3–ene)

Sol 18: (A)

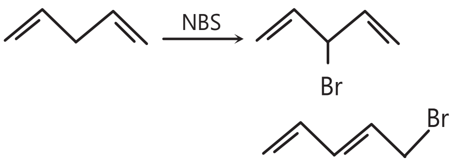


Sol 19: (B)



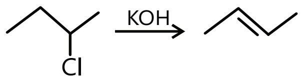
Multiple Correct Choice Type

Sol 20: (A,B)

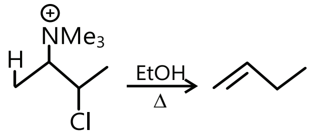


Sol 21: (B,C)

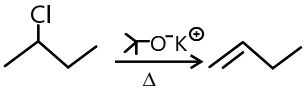
(A)



(B)

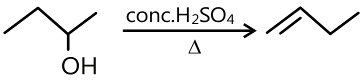


(C)



less hindered –H will get abstracted

(D)



Sol 22: (A,C,D) but the reaction will be reversible since C–I is very week.

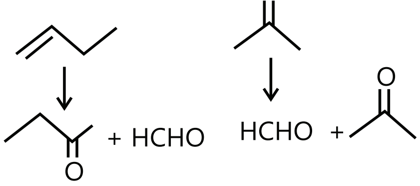
(B) × (C) ✓ (D) more stable system

Sol 23: (A,C)

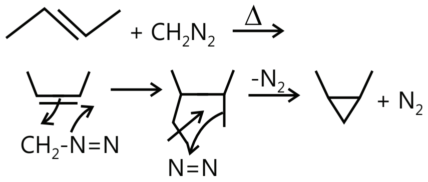
Alkane $\xrightarrow{\text{ozonolysis}}$ CH_3-CHO

Alkene :

Isomers :

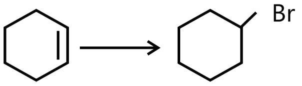


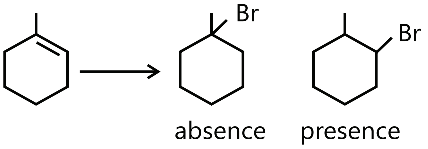
Sol 24: (A,B,C,D)

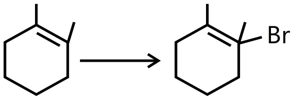


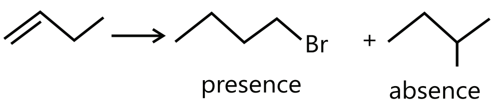
Same for trans form.

Sol 25: (A,C)

(A)


(B)


(C)


(D)


Sol 26: (A,B,D)

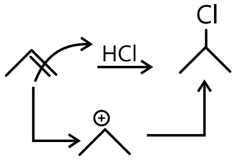
(A) $CF_3-CH_2-CH_2-CH_2-CH{=}CH_2$

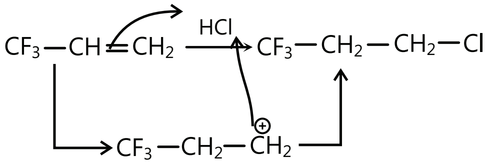
$$\downarrow HCl$$

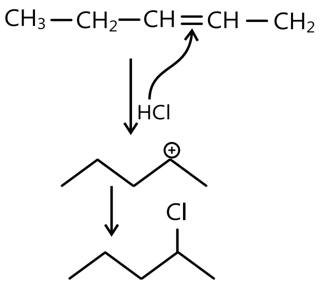
$$CF_3-(CH_2)_3-\overset{\oplus}{C}H_2-CH_3$$

$$\downarrow$$

$$CF_3-(CH_2)_3-\underset{\displaystyle Cl}{\underset{|}{CH_2}}-CH_3$$

(B)


(C)


(D)


Sol 27: (A,B,C,D)

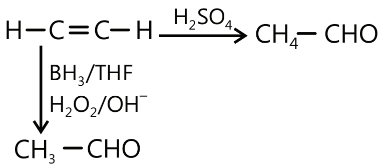
(A) $Al_4C_3 \xrightarrow{H_2O} Al(OH)_3 + 3CH_4\,4Al^{3+} + 3C^{4-}$

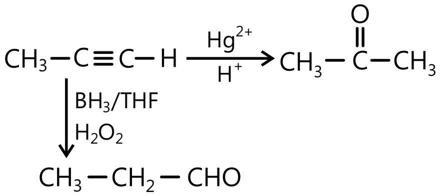
(B) $Ca^{2+}\ {}^{-}C\equiv C^{-} + H_2O \longrightarrow Ca(OH)_2 + HC\equiv CH$

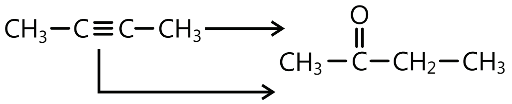
(C) $2Mg^{2+} + C_3^{4-} + H_2O \longrightarrow Mg(OH)_2 + H_3C{-}C\equiv CH$

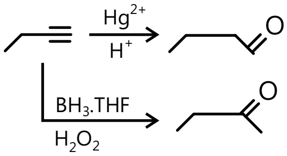
(D) $Me_3C{-}H + KMnO_4 \longrightarrow Me_3C{-}OH$

Sol 28: (A,C)

(A)


(B)


(C)


(D)


Assertion Reasoning Type

Sol 29: (B) When the C=C bond is conjugated with a C=O group, the electron withdrawing nature of carbonyl group polarizes the C=C bond so the nucleophilic attack can take place at the C=C carbon.

Sol 30: (A) Alkyl iodides are more reactive than alkyl chlorides for elimination reactions as I– is a better leaving group than Cl–

Sol 31: (A) is a stronger base than F–because the negative charge density on carbon is greater than the negative charge density of F–.

Sol 32: (A) CH3–C≡C–CH3 is more reactive than CH≡CH towards HCl because the carbocation formed is more stable in thecase of CH3C≡C–CH3 than CH≡CH.

Sol 33: (B) Alkynes are electron-rich nucleophiles with a cylindrical electron cloud formed of two bonds around a carbon-carbon bond. An electrophilic reagent can therefore easily react with the relatively weak alkyne bond.

Comprehension Type

Sol 34: (A) $CH_3-CH_2-Br \longrightarrow$

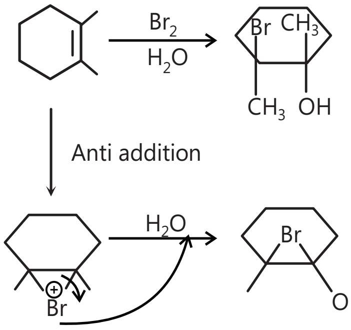
55 gm

$$\frac{m}{208} = \frac{55}{58}$$

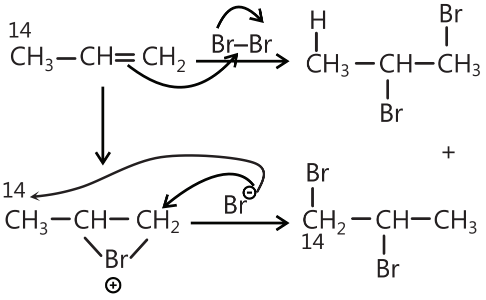
Sol 35: (A) 2.432g

Sol 36: (A) Alkenes generally forms by elimination.

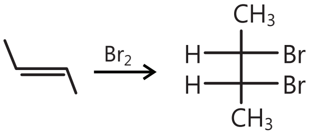
Sol 37: (D)



Sol 38: (C)



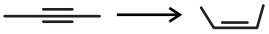
Sol 39: (B)



(B) Anti Addition

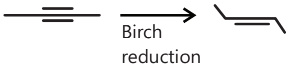
Match the Columns

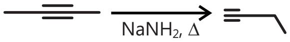
Sol 40:

(A) 

cis addition

$H_2/Pd/BaSO_4$

(B) 

(C) 

Isomerism

(D) 

Isomerism

A → q; B → p; C → s; D → r

Sol 41: (A) → (p) Markonikov

(B) → (r) Anti-markonikov

(C) → (s) Alkylic carbon get brominated

(D) → (q) Br_2 addition

Sol 42: (A) → (q) Free radical mechanism

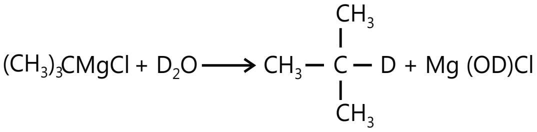
(B) → (r) Decarboxylation

(C) → (s) Free radical mechanism

(D) → (p) Same as grignard

Previous Years' Questions

Sol 1: (A)



$$(CH_3)_3CMgCl + D_2O \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{C}}-D + Mg(OD)Cl$$

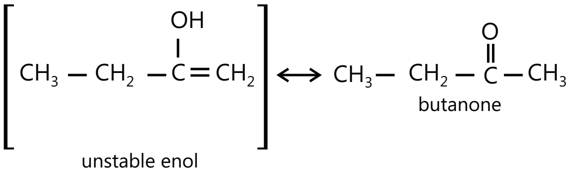
Sol 2: (D) According to the IUPAC conventions, compound can be numbered as:

$$H_2\overset{1}{C}=\overset{2}{C}H-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}\equiv\overset{6}{C}-H$$

Here, C-2 is sp^2 and C-3 is sp^3 hybridised.

Sol 3: (A) Oxymercuration - demercuration brings about Markownikoff's addition of water as

$$CH_3-CH_2-C\equiv C-H + H_2SO_4 \xrightarrow{HgSO_4}$$



$$\left[CH_3-CH_2-\overset{OH}{C}=CH_2\right] \longleftrightarrow CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

unstable enol

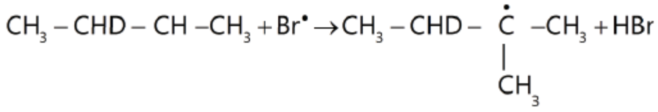
butanone

Sol 4: (B) Ammonical $CuCl_2$ forms red precipitate with terminal alkynes, can be used to distinguish terminal alkynes from internal alkynes:

$$CH_3-CH_2-C\equiv C-H+CuCl_2 \xrightarrow{NH_3(aq)}$$

$$\underset{\text{red–ppt}}{CH_3-CH_2-C\equiv C^-Cu^+}\downarrow$$

Sol 5: (B) Bromination is highly selective, occur at the carbon where the most stable free radical is formed:

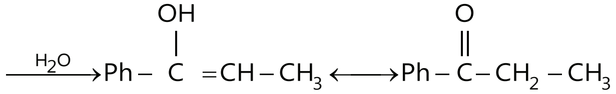


$$CH_3-CHD-CH-CH_3+Br^\bullet \rightarrow CH_3-CHD-\underset{\underset{CH_3}{|}}{\dot{C}}-CH_3+HBr$$

(a tertiary free radical)

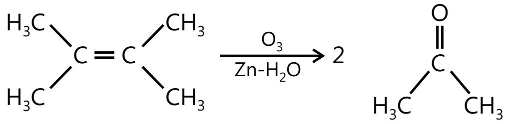
Sol 6: (A) Reaction proceeds through carbocation intermediate:

$$Ph-C\equiv C-CH_3+H^+ \longrightarrow Ph-C^+=CH-CH_3$$

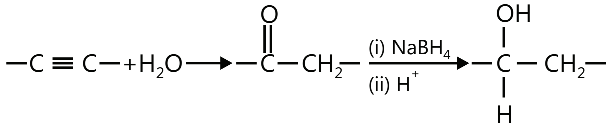


$$\xrightarrow{H_2O} Ph-\overset{\overset{OH}{|}}{C}=CH-CH_3 \longleftrightarrow Ph-\overset{\overset{O}{\|}}{C}-CH_2-CH_3$$

Sol 7, 8: (D, B) The final ozonolysis product indicates that the alkene before ozonolysis is



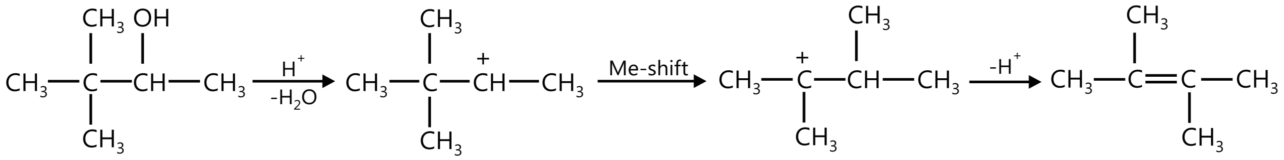
Also P(C_6H_{10}) has two degree of unsaturation and oxymercuration demercuration hydration indicates that it is an alkyne. As alkyne, on hydration, gives a carbonyl compound which on reduction with $NaBH_4$ gives a 2° alcohol.



$$-C\equiv C-+H_2O\longrightarrow -\overset{\overset{O}{\|}}{C}-CH_2- \xrightarrow[\text{(ii) }H^+]{\text{(i) }NaBH_4} -\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-$$

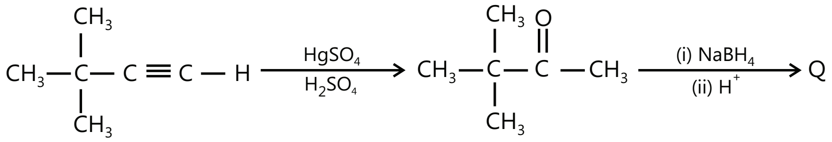
2° alcohol

The secondary alcohol that can give above shown alkene on acid catalyzed dehydration is



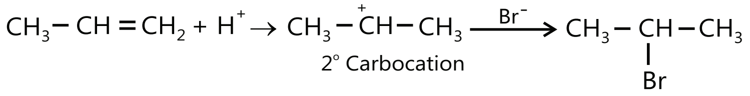
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\overset{OH}{|}}{CH}-CH_3 \xrightarrow[-H_2O]{H^+} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{+}{CH}-CH_3 \xrightarrow{\text{Me-shift}} CH_3-\underset{\underset{CH_3}{|}}{\overset{+}{C}}-\overset{\overset{CH_3}{|}}{CH}-CH_3 \xrightarrow{-H^+} CH_3-\overset{\overset{CH_3}{|}}{C}=\underset{\underset{CH_3}{|}}{C}-CH_3$$

2° carbocation



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-C\equiv C-H \xrightarrow[H_2SO_4]{HgSO_4} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow[\text{(ii) }H^+]{\text{(i) }NaBH_4} Q$$

Sol 9: (i) Free radical chorination of alkane require energy which is supplied either in the form of heat or radiation.



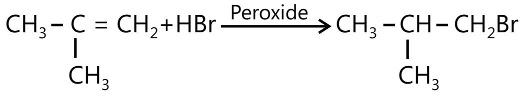
$$CH_3-CH=CH_2+H^+\rightarrow CH_3-\overset{+}{C}H-CH_3 \xrightarrow{Br^-} CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$$

2° Carbocation

Isopropyl bromide

(ii) Addition of HBr proceeds through carbocation intermediates.

Sol 10: (i)



$$\underset{\substack{|\\CH_3}}{CH_3-C}=CH_2+HBr\xrightarrow{\text{Peroxide}}CH_3-\underset{\substack{|\\CH_3}}{CH}-CH_2Br$$

2-methyl propene   Isopropyl bromide

In the absence of peroxide, HBr would be added giving tertiary butyl bromide.

(ii) Tertiary alkynes are slightly acidic, forms silver salt with ammoniacal solution of silver nitrate:

$$R-C\equiv C-H+AgNO_3\xrightarrow{NH_3(aq)}R-\underset{\text{white ppt.}}{C\equiv C}\ Ag\downarrow$$

Solution for the Q. No. 11 and 12: (A, C)