

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 one 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

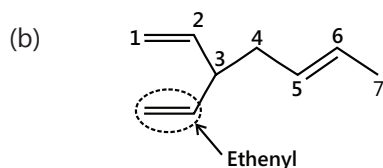
Step 1: Identify and name the longest continuous chain of C atoms which contains the double bond(s) (# C + -ene).

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.

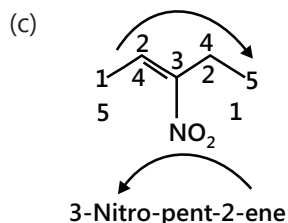
Step 3: Locate the double bond by the lower numbered C-atom joined by the double bond (e.g. 1-butene).

Step 4: Locate and name attached groups.

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



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



3. HYBRIDIZATION OF ALKENES

- 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**.
- Since only two of 2p orbitals were 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

- Free rotation is not possible around double bonds, therefore there are two different forms of 2-butene, which are **geometric isomers** of each other.
- 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.
- Geometric isomers can have drastically different chemical and physical properties.

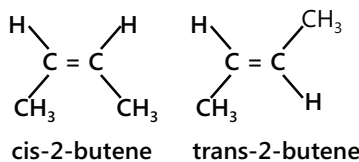
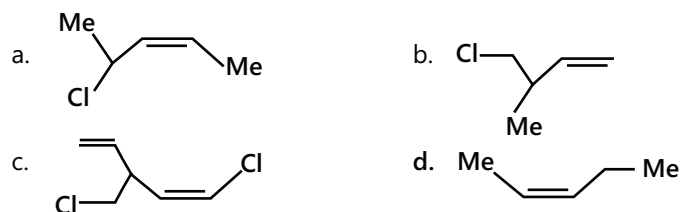
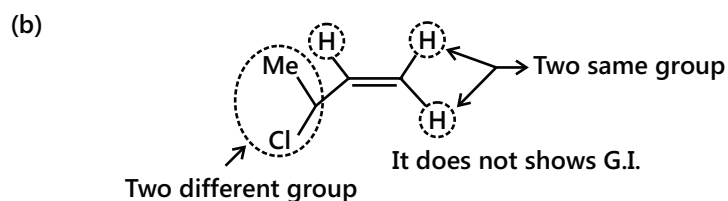
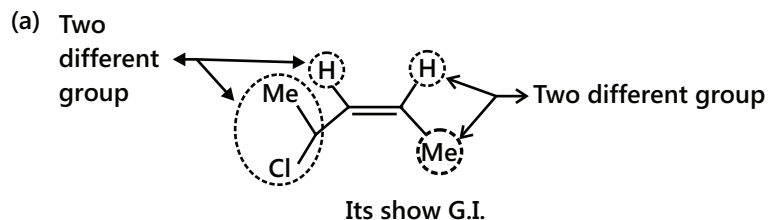


Illustration 3: Which of the following do not show G.I.?



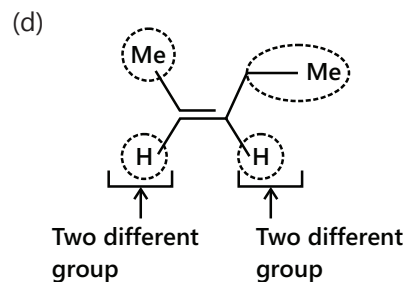
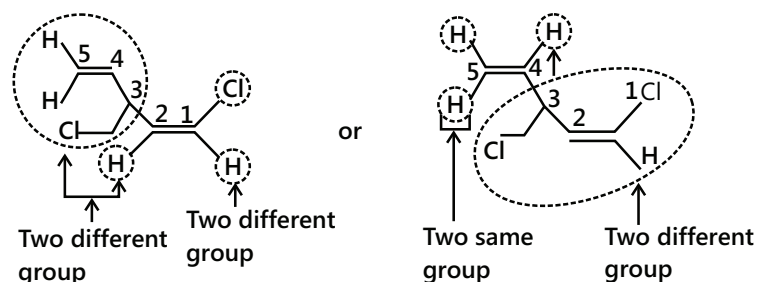
(JEE MAIN)

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



Option (b) does not show G.I

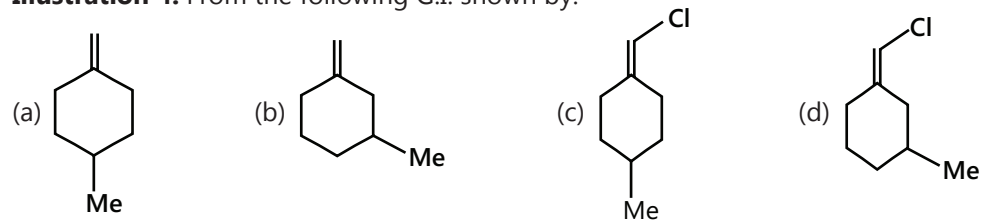
(c) Option (c) show G.I. at the double bond between $C_1 - C_2$ but does not show G.I. at the double bond between $C_4 - C_5$.



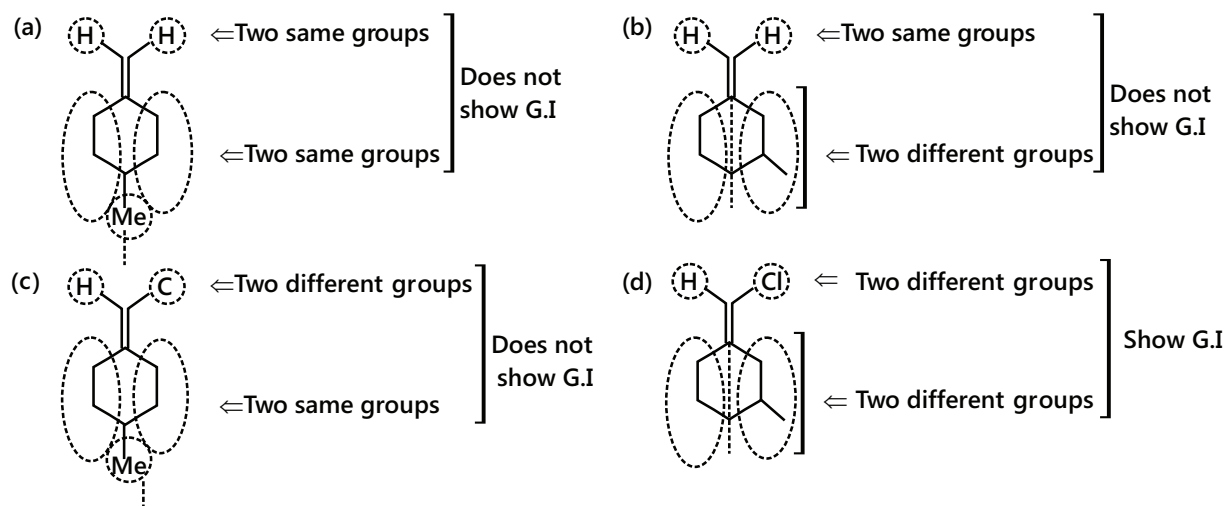
Shows G.I.

Shows G.I.

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

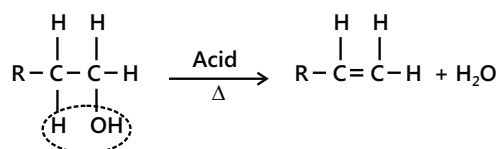


Sol: In order to show Geometrical isomerism the alkene must contain different substituents .i.e. the substituents on both the carbon bearing double bonds must have different substituents. **(JEE ADVANCED)**



5. PREPARATION OF ALKENES

5.1 Dehydration of alcohols

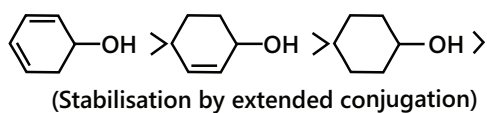
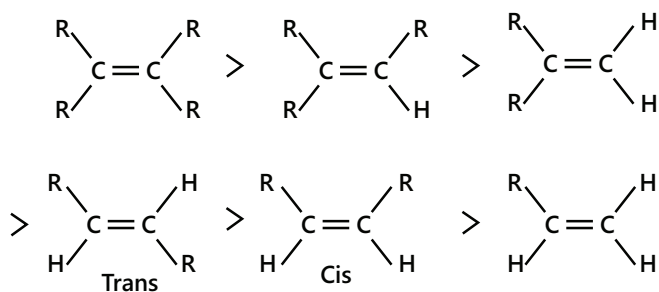


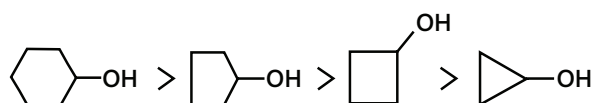
Ease of dehydration of alcohols: $3^\circ > 2^\circ > 1^\circ$, because the alkenes formed are more stable.

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

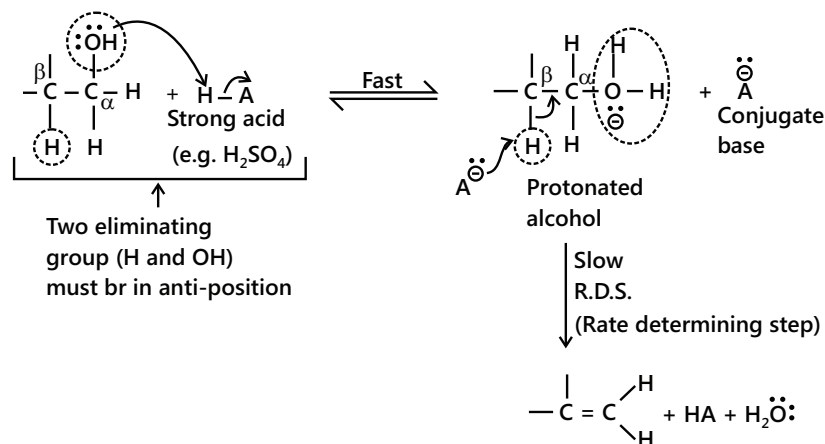
1. Conc. H_2SO_4 at 443 – 453 K (170 – 180°C) acts as Lowry Bronsted acid $\text{H}^\oplus$ donor.
2. H_3PO_4 (Phosphoric acid at 470 K).
3. Al_2O_3 at 633 K (380°C) acts as a Lewis acid.
4. Heating with P_2O_5 or P_4O_{10} (phosphorous pentoxide).
5. Heating with POCl_3 (phosphorous oxychloride) + pyridine.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

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





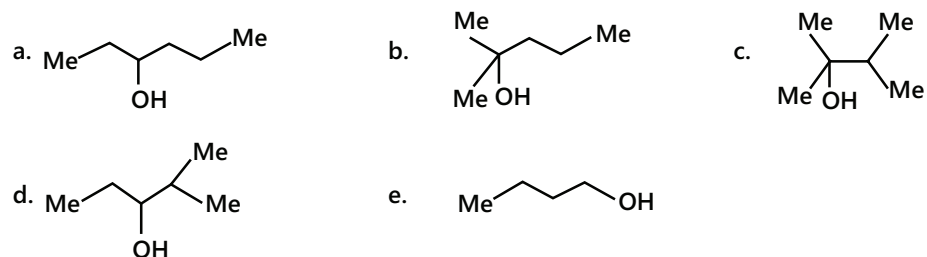
(Due to ring stability)

Mechanism of dehydration of 1° alcohols: E₂ 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(-OH₂⁺) and the elimination of protonated hydroxyl group (a good leaving group) takes place simultaneously to form double bond.

$$\text{Rate} = k [\text{A}^-] [\text{protonated alcohol}]$$

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.

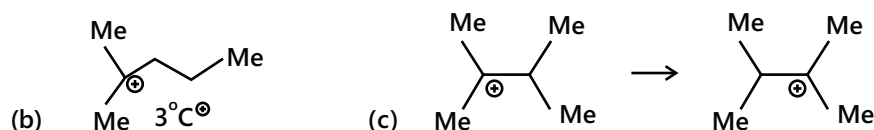
Illustration 5: Arrange the following alcohols in the decreasing order of their ease of dehydration with H₂SO₄.

(JEE MAIN)

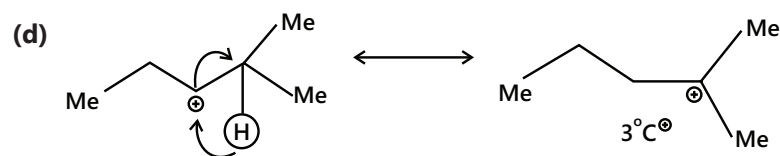
Sol: Order of stability of carbocation: 3° > 2° > 1°

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.



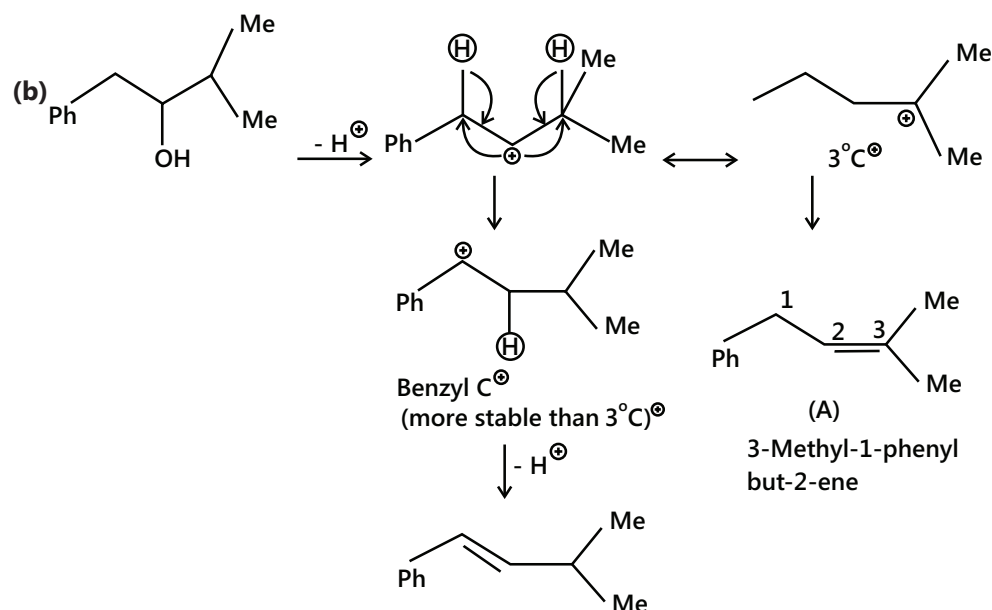
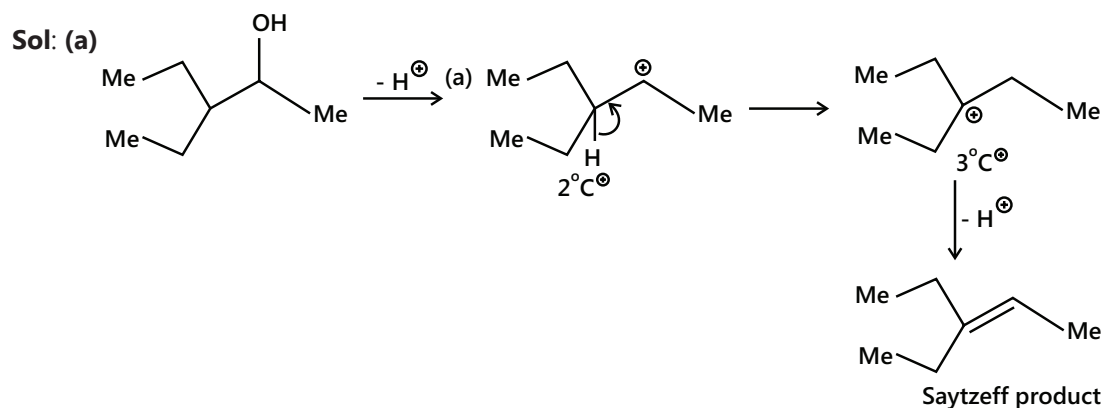
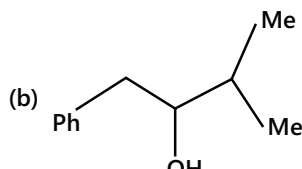
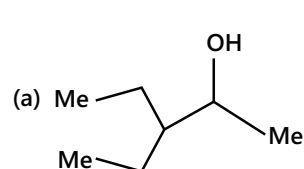
Remaining (a) and (d) both are 2° alcohols, 2° carbocation can be stabilized to 3° via 1, 2- $\text{H}^\oplus$ shift and gives a more substituted alkene



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:

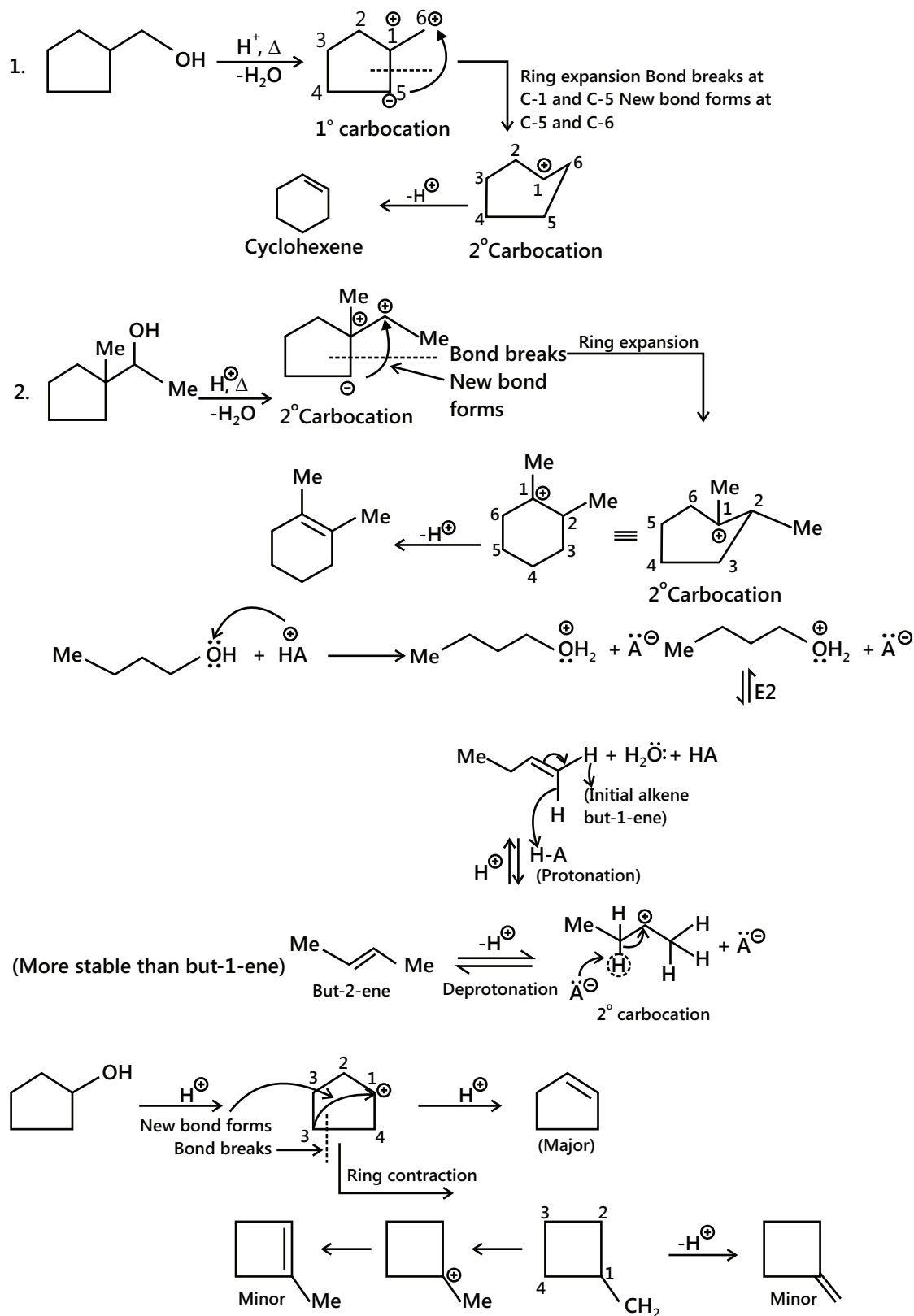
(JEE ADVANCED)



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:

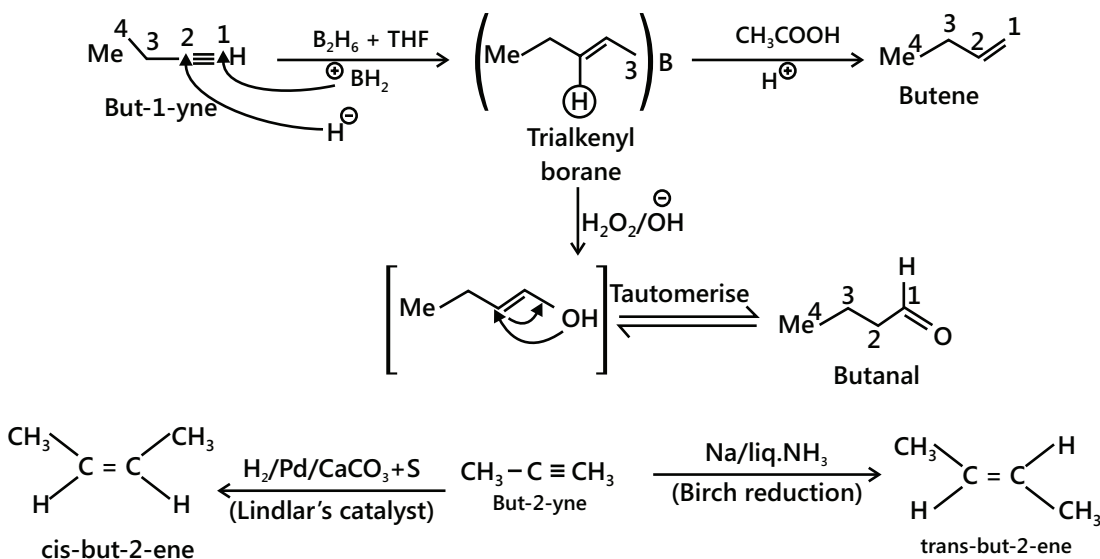


Whenever a carbocation is formed on the ring, ring contraction takes place. But in this case, ring strain is not relieved (because higher homologue cyclic ring has to change to lower one), however, the products corresponding to ring contraction are formed in smaller amounts.

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/BaSO₄ or CaCO₃ poisoned with PbCO₃ or Lindlar's catalyst(quinolone) (ii) B₂H₆ in THF/ ether+ CH₃COOH.
- (ii) Trans-alkenes are formed by hydrogenation in presence of Na+liq.NH₃(Birch reduction)
- (a) With terminal alkyne.



- (b) With internal alkynes:

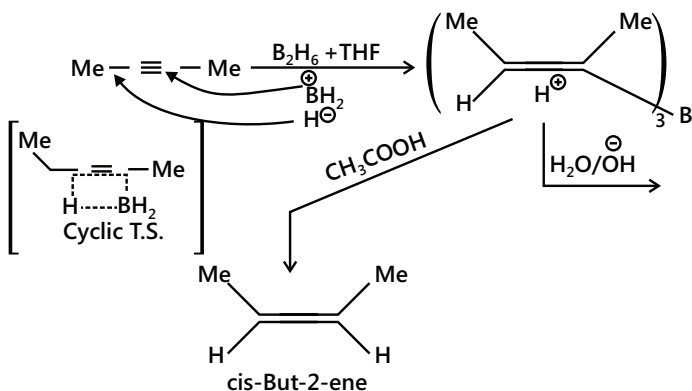
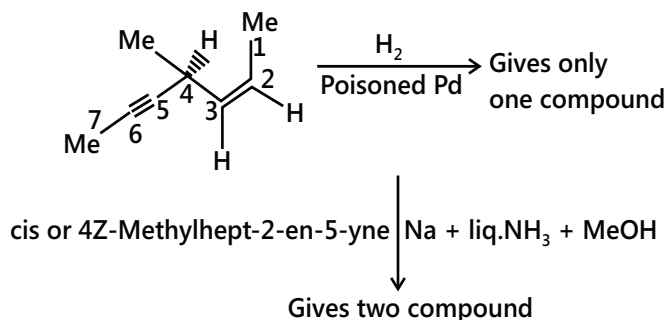


Illustration 7: Explain

(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.

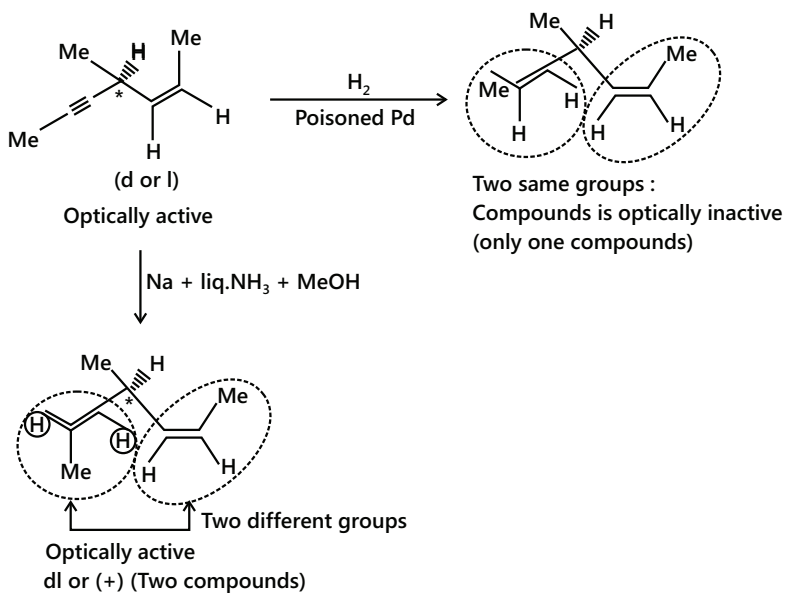
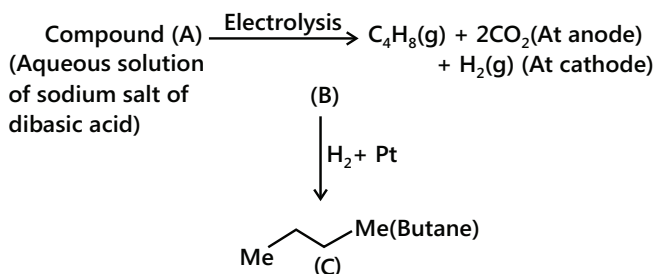


Illustration 8: Identify A and B

(JEE MAIN)



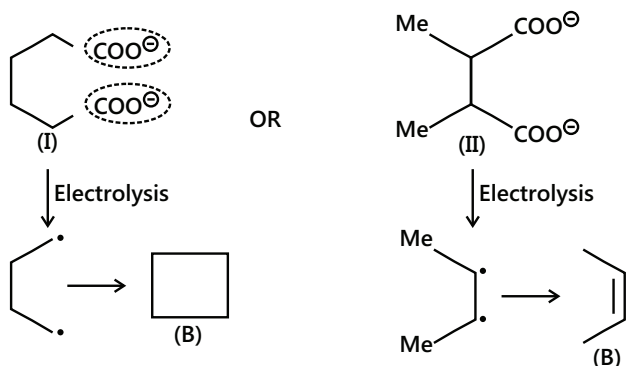
Gas (B) gives test for unsaturation, i.e. it decolourises Br_2 water and aq. KMnO_4 solution.

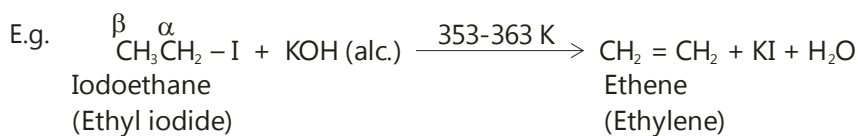
Sol: From the given data it appears that the starting compound contains 6 carbon in its backbone. (Since product formed is butene (4 carbon) and 2 molecule of CO_2 (2 carbon).

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.

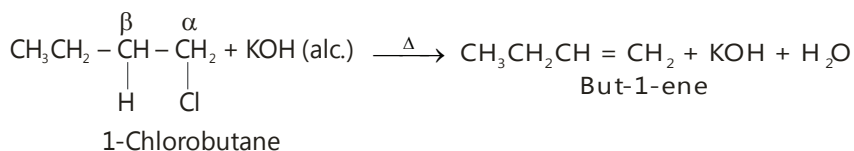
The two possible structure of the dibasic acids are as follows:



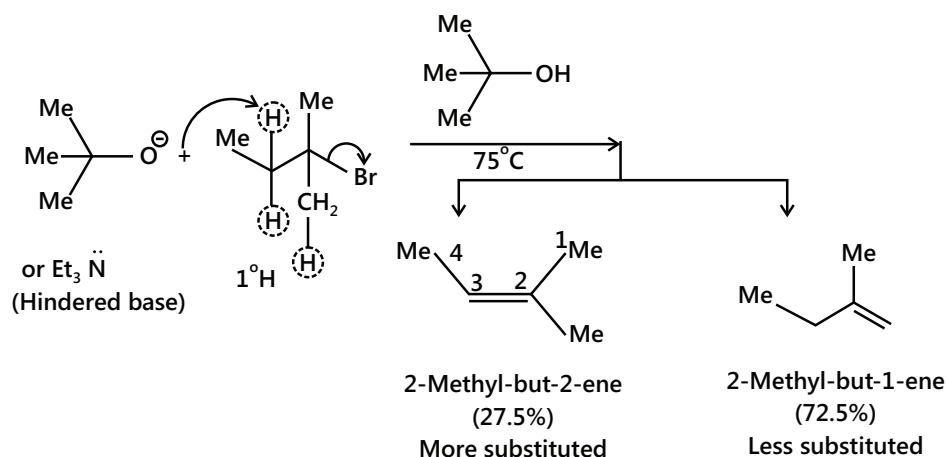


This process of the removal of a molecule of a halogen halide (HCl, HBr or HI) from a haloalkane to form an alkene is called dehydrohalogenation. Dehydrohalogenation is an example of an elimination reaction. Since, in this reaction, a hydrogen is removed from β -carbon and halogen from the α -carbon, 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.



1. When a bulky base is used, e.g. potassium tert-butoxide in tert-butyl alcohol or $\text{Et}_3\ddot{\text{N}}$, for the dehydrohalogenation of RX, the less-substituted alkene (Hofmann product) is favoured.



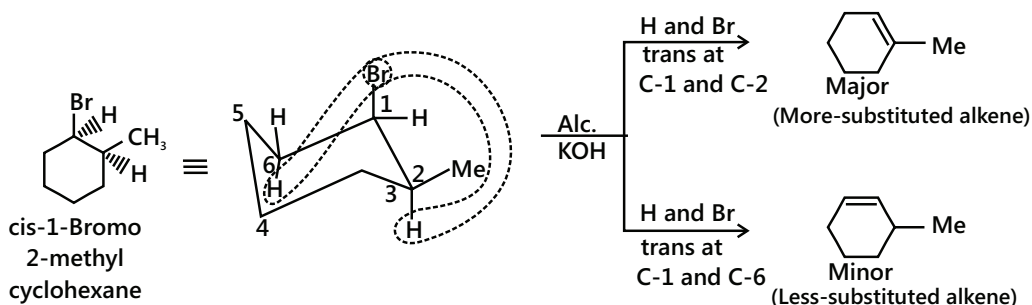
It is due to the steric hindrance of the bulky base. The large tert-butoxide ion finds difficulty in removing one of the internal 2° H atoms because of greater steric hindrance (or crowding) at that site in the transition state (T.S.). It removes one of the more exposed 1°H atoms of the methyl group 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.

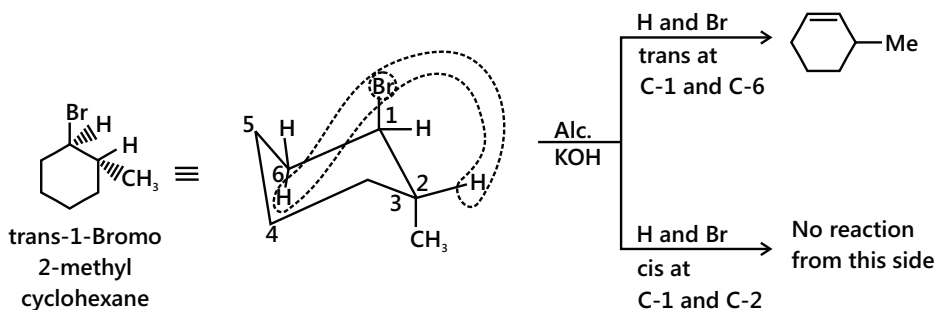
When the more substituted alkene obtained by Saytzeff rule is sterically hindered, the less-substituted alkene is formed in a major amount.

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

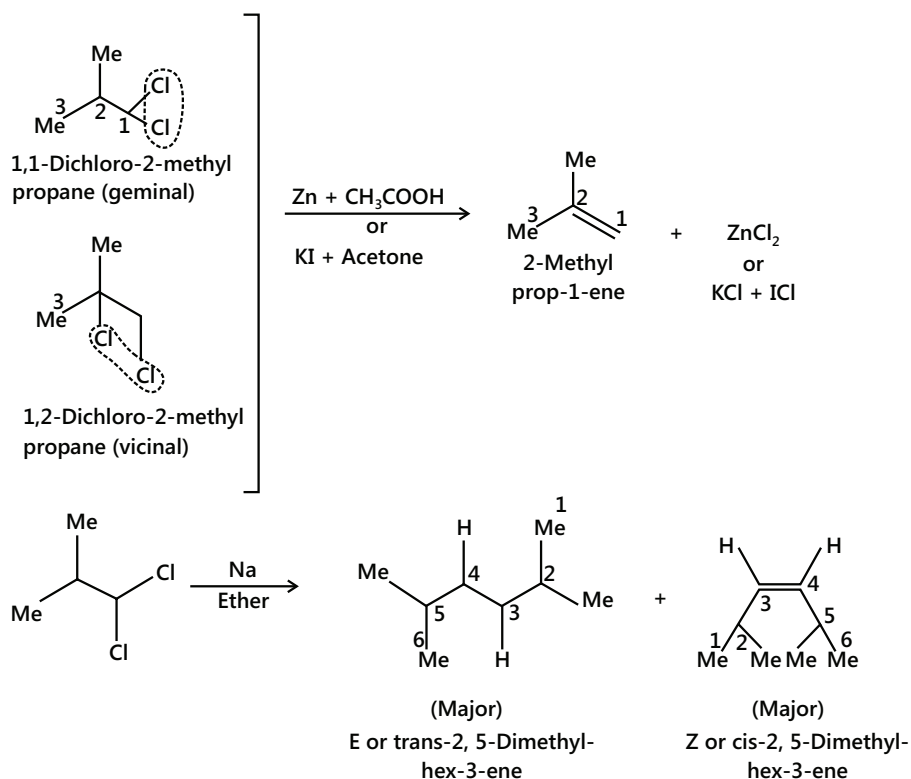
(i) Anti-elimination can occur in two ways with cis-isomer.



(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.

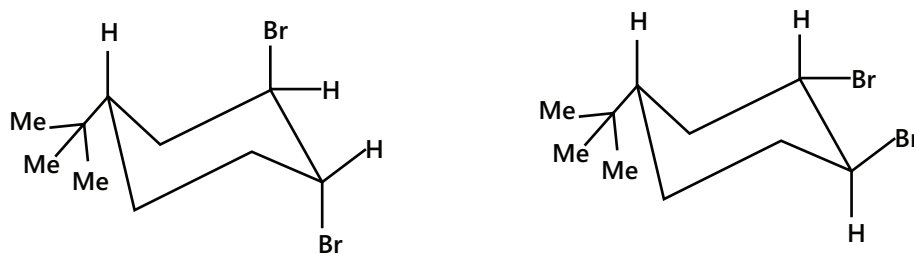


Illustration 9: Identify all the possible alkenes that would be formed on the dehydrohalogenation of the following organic halides with alcoholic KOH. Also, identify the major alkene.

- (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.

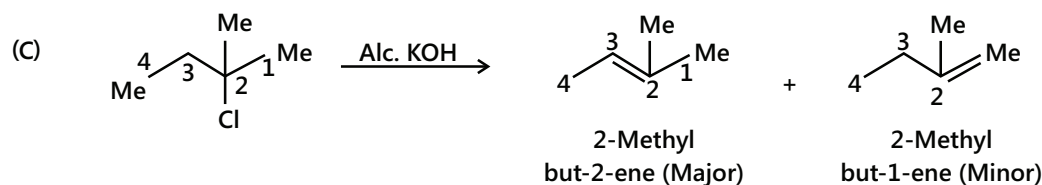
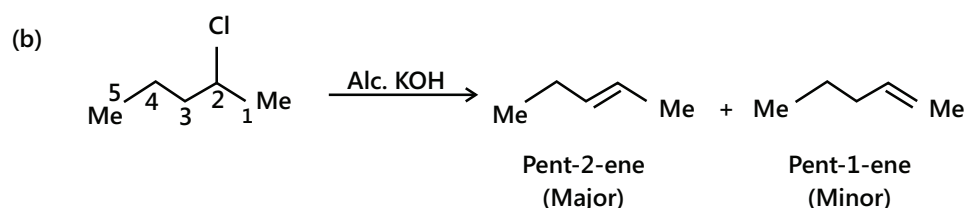
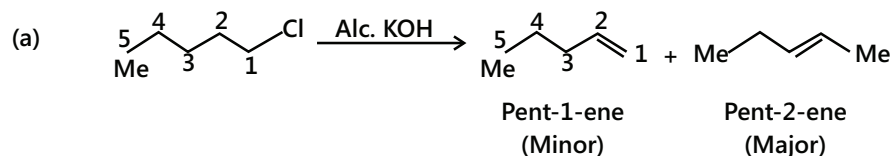
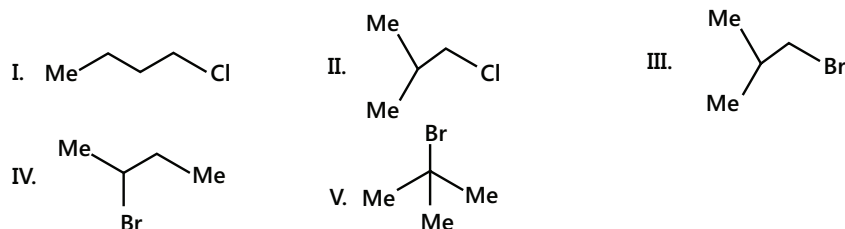
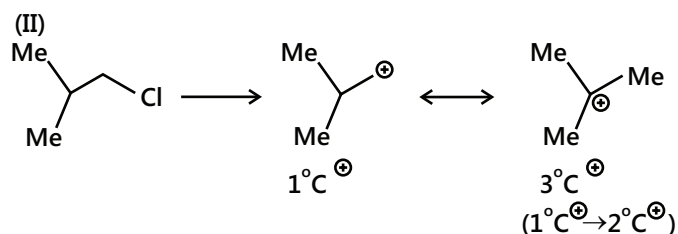
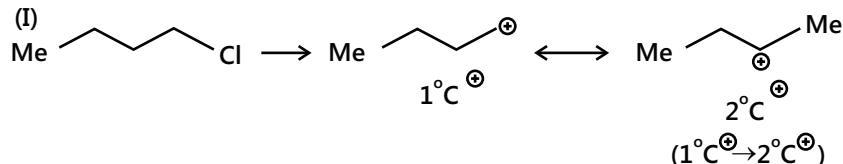


Illustration 10: Predict the order of reactivity of the following compounds in dehydrohalogenation. **(JEE MAIN)**

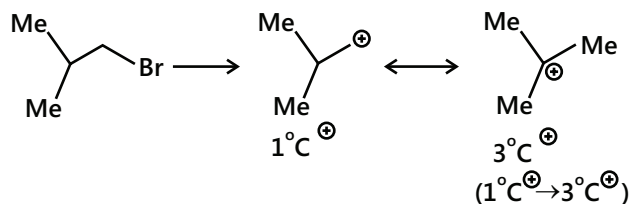


Sol: Order of formation of carbocation is $3^\circ > 2^\circ > 1^\circ$

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

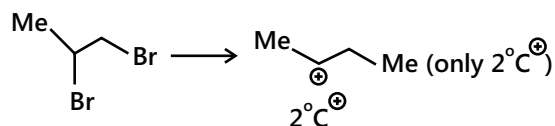


(III)



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

(IV)



(V)

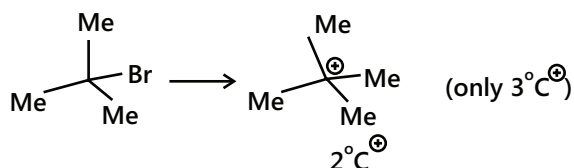
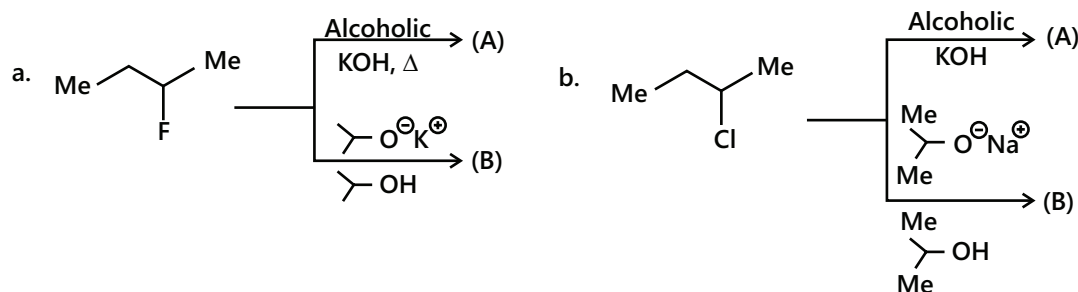


Illustration 11: Given the major and minor products of the following reactions.



(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.

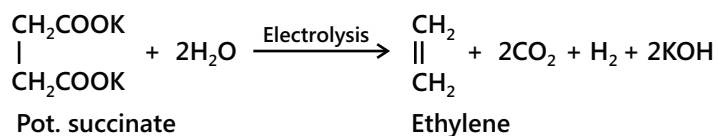
(a) Here RX is RF, thus less-substituted alkene (Hofmann elimination) is formed, irrespective of whether the base is bulky or non-bulky. Both (A) and (B) are same.

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

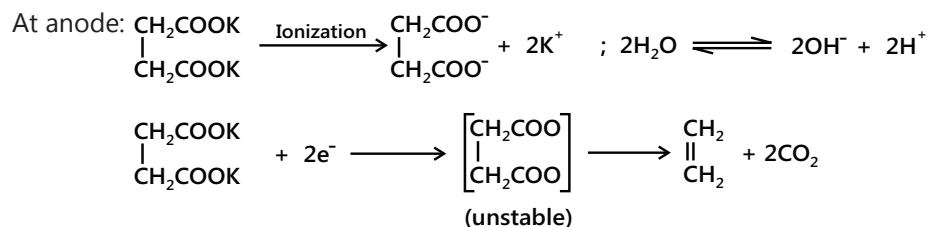
(B) Base used is bulky thus the Hofmann product is formed (Less-substituted alkene)

5.5 Kolbe's Electrolytic Method

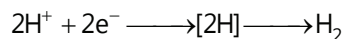
Electrolysis of sodium or potassium salts of saturated dicarboxylic acids gives alkenes. For example,



The reaction is believed to occur by the following steps:



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.



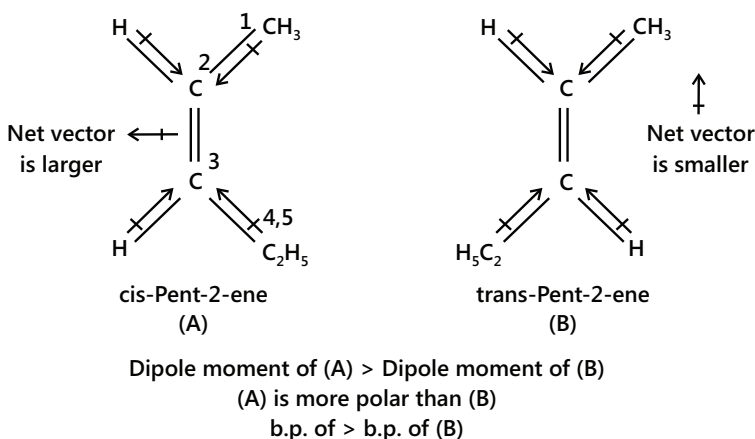
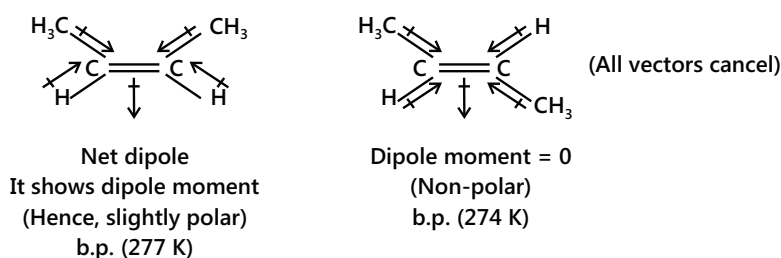
6. PHYSICAL PROPERTIES OF ALKENES

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 $\{4^\circ\text{C}\}$ than trans-2-butene $\{1^\circ\text{C}\}$ because in cis isomer, two C-C bond dipoles rain force each other yielding a small net molecular dipole.
4. Range of physical states: $\leq 4\text{C's}$ – gases, $5 - 17\text{C's}$ – liquid, $\geq 18\text{C's}$ – 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 $-\text{CH}_2-$ 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.



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°

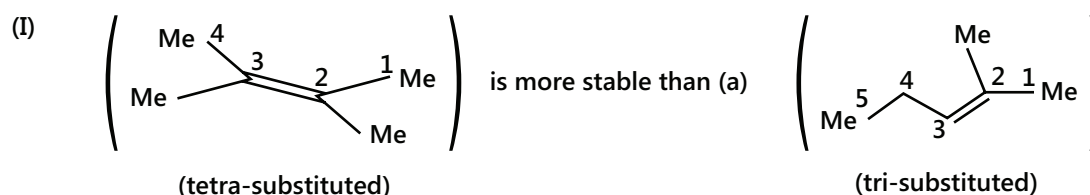
II. (c) Hexene (d) cis-Hex-3-ene

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

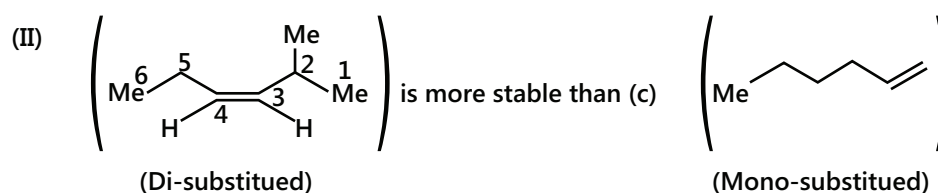
IV. (g) cis-Hex-3-ene (h) trans-Hex-3-ene

(JEE MAIN)

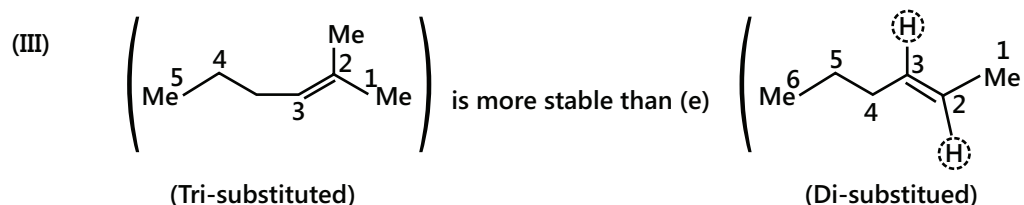
Sol:



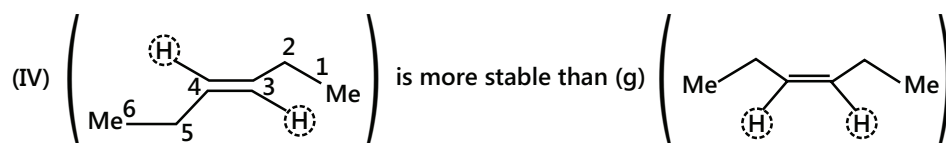
ΔH_h° cannot be used because the same alkane is not produced on hydrogenation. So, ΔH_C° is used to determine the relative stabilities of the alkene pairs because on complete combustion, the alkene requires same moles of O_2 and produces same moles of CO_2 and H_2O (same formula: C_6H_{12}).



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



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}).

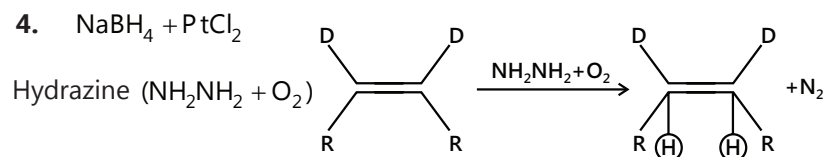


7. REACTIONS OF ALKENES

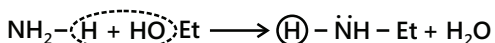
7.1 Hydrogenation of Alkenes

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

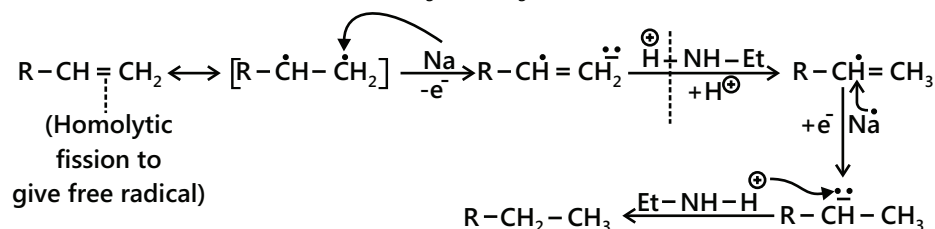
1. Pt or Pd or Ni or PtO_2
2. Pd + C or Pt + C (C $\Rightarrow$ charcoal), Wilkinson's catalyst $[\text{RhCl}(\text{Ph}_3\text{P})_3]$ Chlorotris (triphenyl phosphine) rhodium (I)
3. $\text{NaBH}_4 + \text{AlCl}_3$ in diglyme (solvent)



5. Birch Reduction: Birch reduction (alkali metals, such as Na and K in liquid $\text{NH}_3 + \text{EtOH}$ or MeOH), Mechanism of only terminal ($\text{C} = \text{C}$) bond to ($\text{C} - \text{C}$) bond:



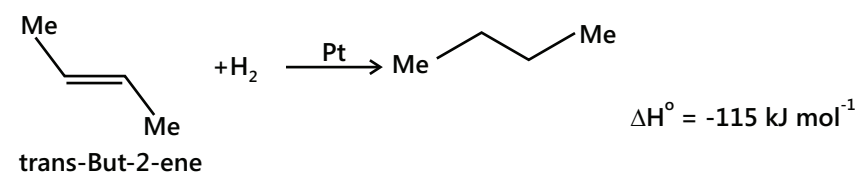
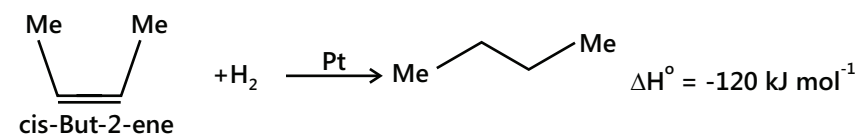
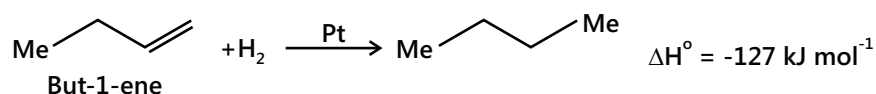
Source of H atom is from liquid NH_3 . If ND_3 is used, D atom will be added.



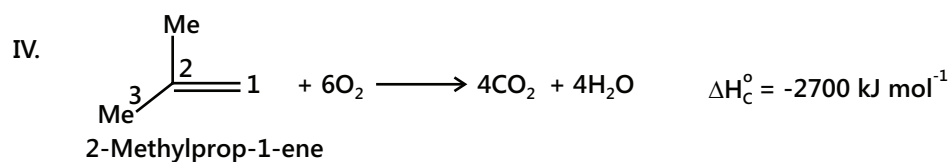
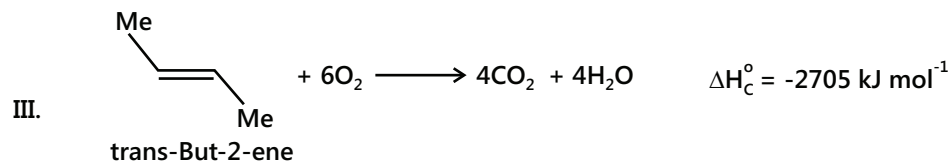
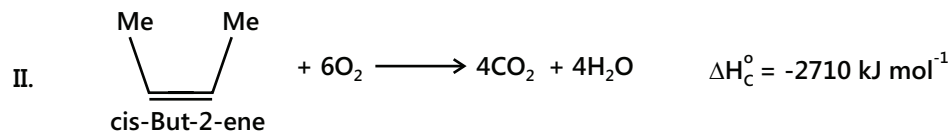
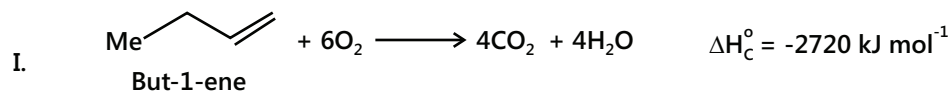
Heat of hydrogenation: The energy released when one mole of alkenes is hydrogenated with H_2 is called the heat of hydrogenation.

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



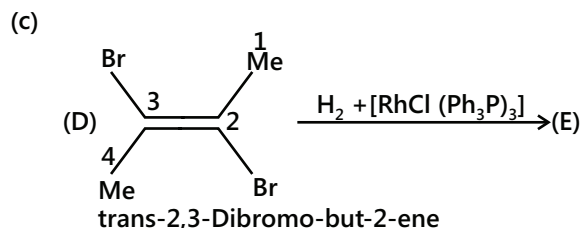
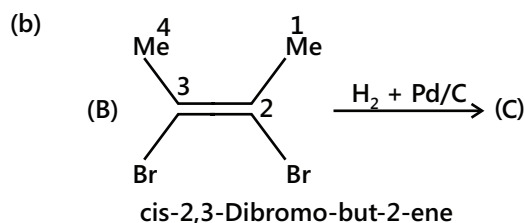
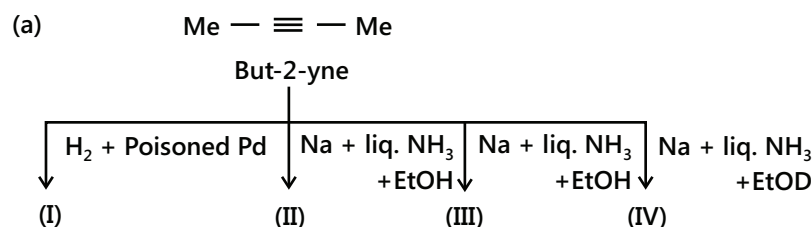
Heat of Combustion: When the hydrogenation of the alkene does not give the same alkane, the heat of combustion is used to measure their relative stabilities. More negative the value of ΔH_C° , less stable is the compound or vice versa.



Although each isomer mentioned above (I – IV) consumes 6 moles of O₂ and produces 4 moles of CO₂ and 4 moles of H₂O, 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).

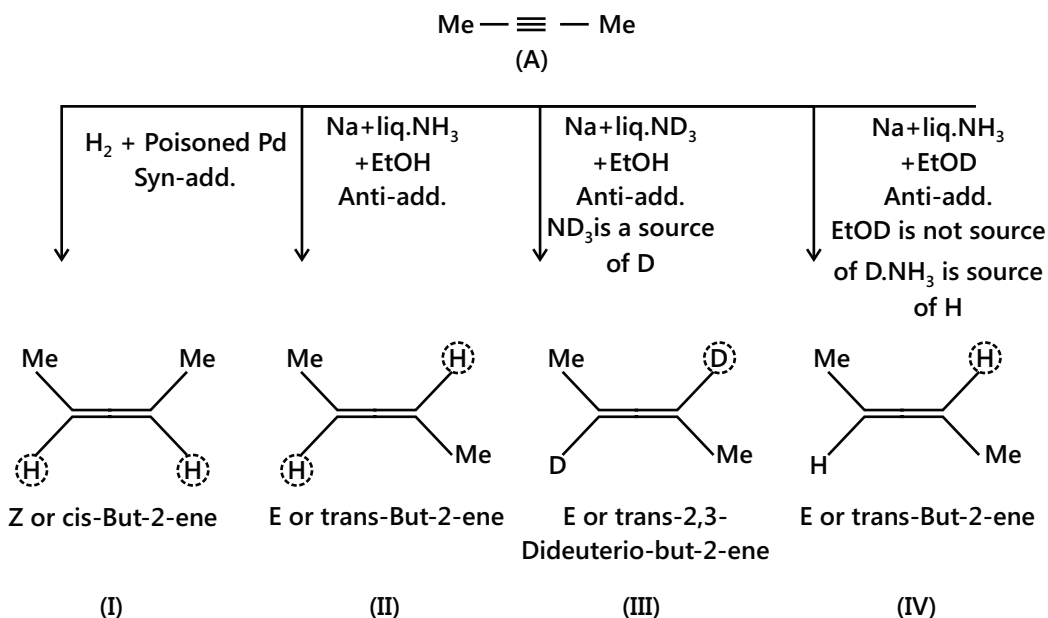
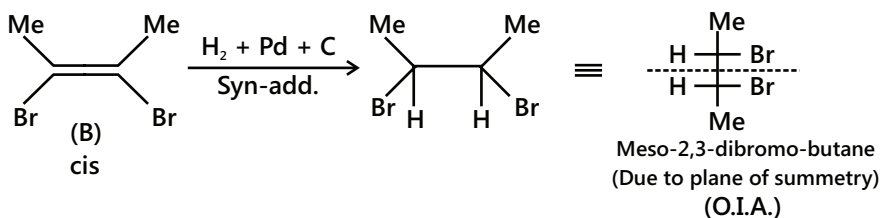
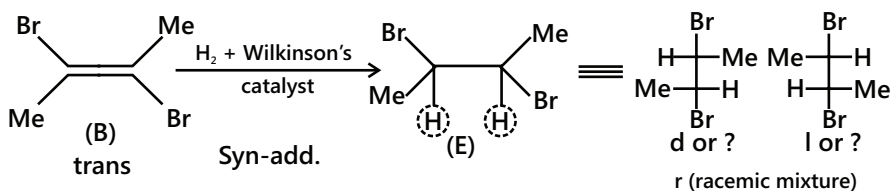
Illustration 13: Give the products with their stereoisomers, if any.

(JEE ADVANCED)



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.

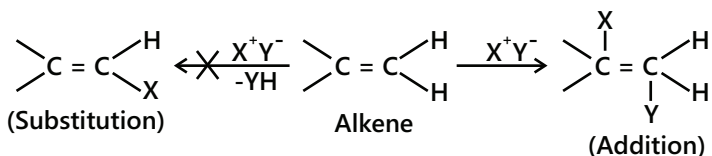
(a)

(b) **Note:** Metal + H_2 does not reduce ($\text{R}-\text{X}$) to ($\text{R}-\text{H}$) but reduced ($\text{Ar}-\text{X}$) to ($\text{Ar}-\text{H}$).Reactant is cis + mechanism of addition is syn $\rightarrow$ product is meso.(c) Reactant is trans + mechanism of addition is syn $\rightarrow$ product is dl or ($\pm$) 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 forms a covalent bond with π electrons of alkene and the positive charge is transferred to the remaining doubly bonded carbon.

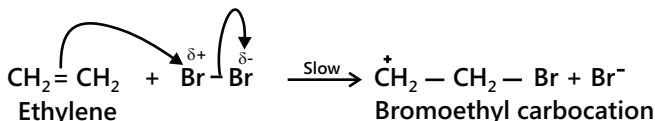
In second step of E.A.R. positively charged intermediate combines with electron rich anion to form the second covalent bond. That is one weak π bond is broken and two strong σ bonds are formed.



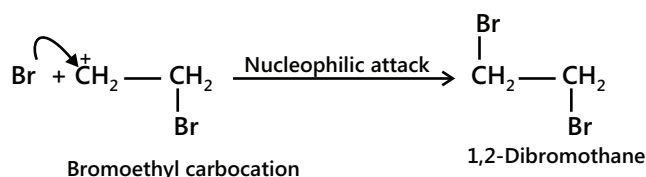
Let us illustrate the mechanism of electrophilic addition reactions by taking the example of addition of Br_2 to ethylene. The reaction occurs by a two-step ionic mechanism as discussed below:

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

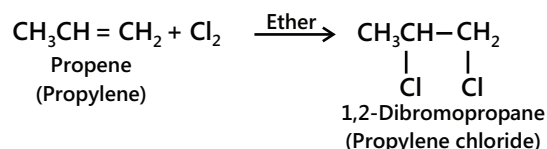
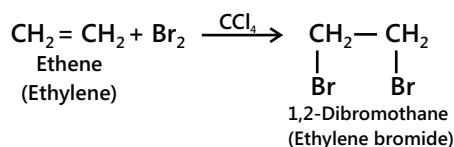


Step-2: The carbocation formed in **step-1** being a reactive chemical species immediately undergoes a nucleophilic attack by the bromide ion present in the solution forming the addition product. This step is fast and hence does not affect the rate of the reaction.



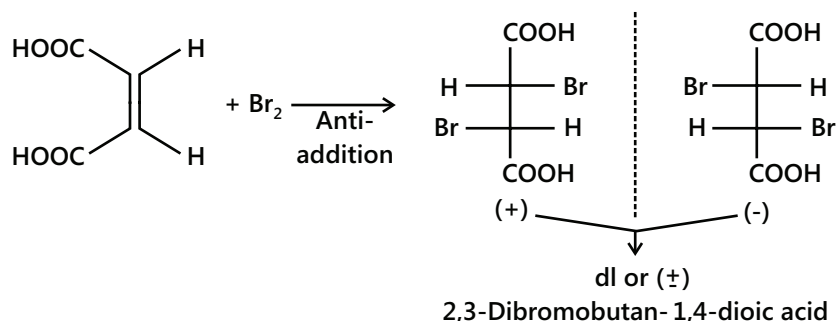
7.3 Addition of X_2

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

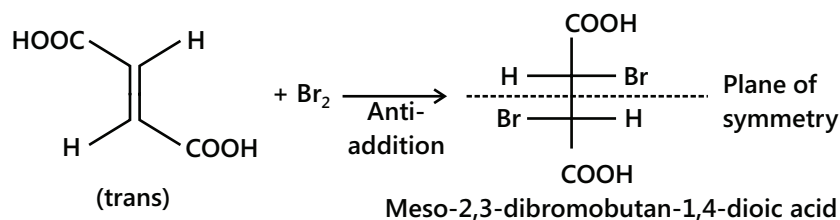


During the addition of bromine to alkenes, bromine loses its orange red colour, since the dibromide formed is colourless. This reaction is, therefore, used as a **test for unsaturation in organic compounds**. Reactivity order: $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$ (because the $E_{\text{activation}}$ order is: $\text{F}_2 < \text{Cl}_2 < \text{Br}_2 < \text{I}_2$).

Reactant cis (with two same groups) + mechanism of addition of Br_2 is anti (with two same groups) $\Rightarrow$ product is dl or ($\pm$) 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.

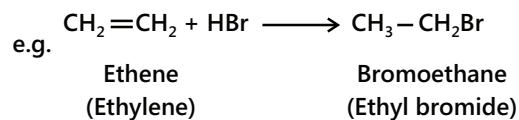
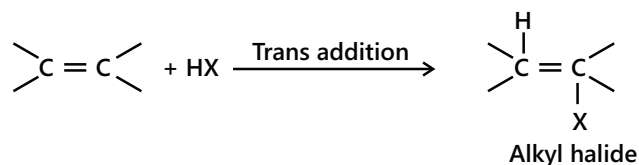


Fumaric acid (trans) + Br₂ (anti-addition) → Meso product



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),

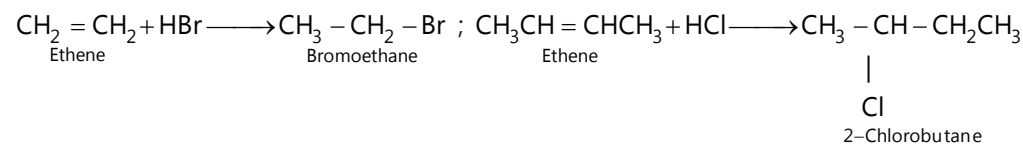


The order of reactivity of halogen halides in this reaction is: $\text{HI} > \text{HBr} > \text{HCl}$. This order of reactivity can be explained on the basis of bond dissociation energies of the halogen halides; lower the bond dissociation energy, more reactive is the halogen halide ;

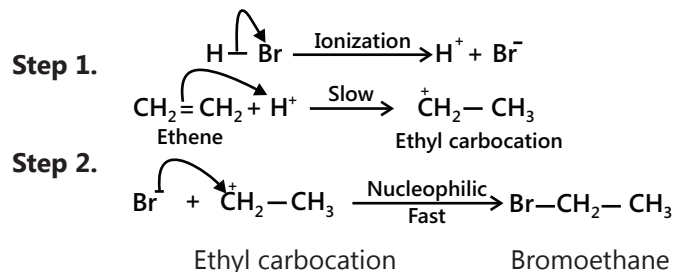


The actual product formed, however, depends upon whether the alkene is symmetrical or unsymmetrical as discussed below:

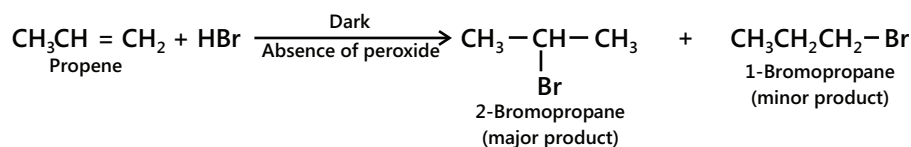
(i) Addition to symmetrical alkenes. When the alkene is symmetrical only one product is theoretically possible. For example,



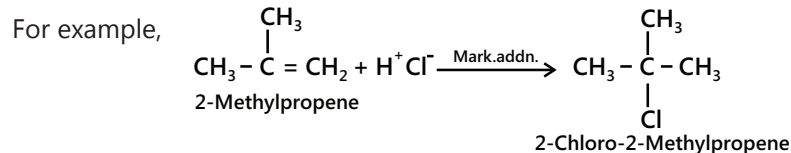
Mechanism: Like the addition of halogen, addition of halogen halides to alkenes is also an electrophilic addition reaction and occurs by the following two steps:



(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.

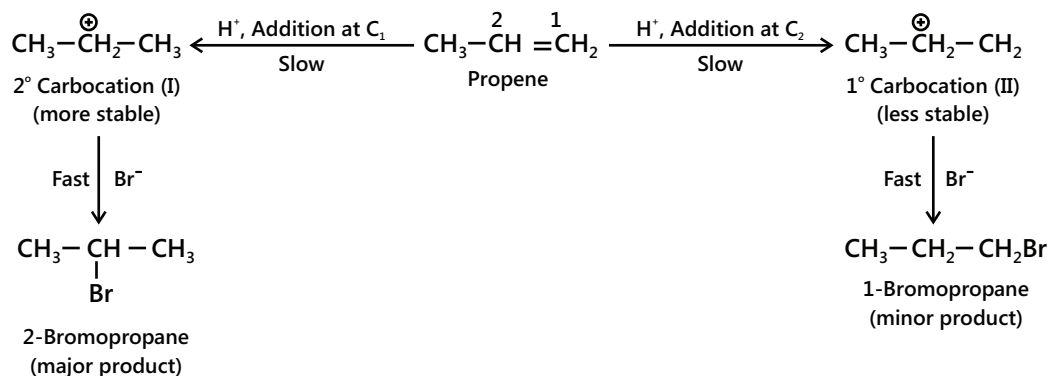


Markovnikov's rule: The rule states that: "The addition of unsymmetrical reagents such as HX, H₂O, HOX, etc. to unsymmetrical alkenes occurs in such a way that the negative part of the addendum (i.e., adding molecule) goes to that carbon atom of the double bond which carries lesser number of hydrogen atoms."

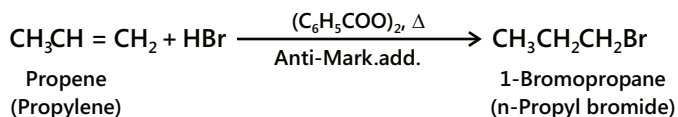


Theoretical explanation of Markovnikov's rule: The addition of hydrogen halides to alkenes is an electrophilic addition reaction. Thus, during the addition of HBr to propene, the first step involves the addition of a proton. This addition, in principle, can occur in two ways. If the proton adds on the 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.

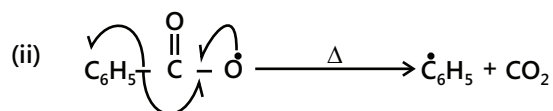
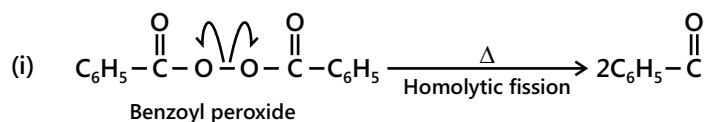


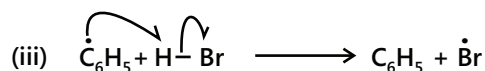
Peroxide effect: It should be noted that Markovnikov's rule is not always followed. In the presence of peroxides such as benzoyl peroxide (C₆H₅CO-O-O-COC₆H₅), the addition of HBr (but not of HCl or HI) to unsymmetrical alkenes takes place contrary to Markovnikov's rule. This is known as **Peroxide effect** or **Kharasch effect**. Thus,



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

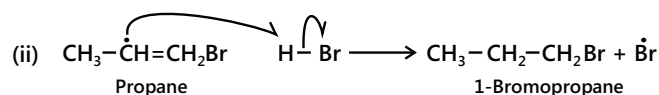
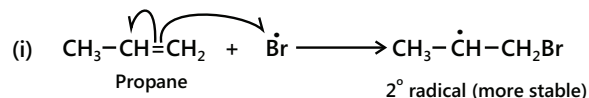
(a) **Initiation.**



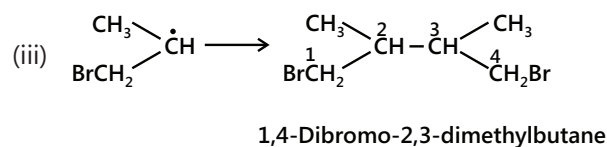
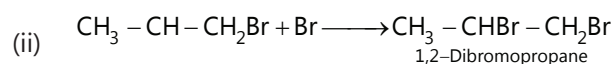
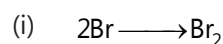


(b) Propagation: It consists of two steps.

During the first step, a $\text{Br}^\cdot$ 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.



(c) Termination:



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

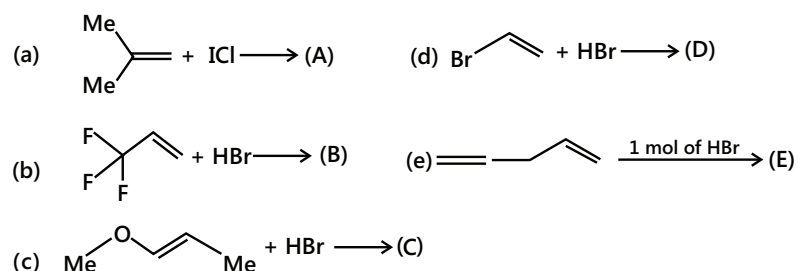
X in HX	ΔH (in kJ/mole)	
	(i) $\text{X} + \text{CH}_2 = \text{CHCH}_3 \longrightarrow \text{XCH}_2-\text{CH}-\text{CH}_3$	(ii) $\text{XCH}_2-\text{CHCH}_3 + \text{HX} \longrightarrow \text{XCH}_2-\text{CH}_2\text{CH}_3 + \text{X}$
F	-209	+159
Cl	-101	+27
Br	-42	-37
I	+12	-104

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

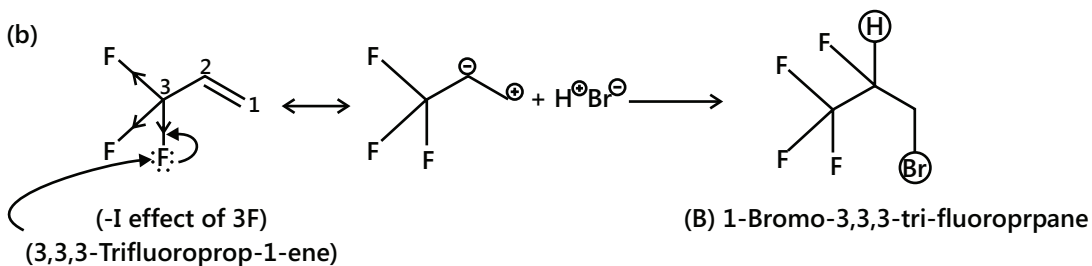
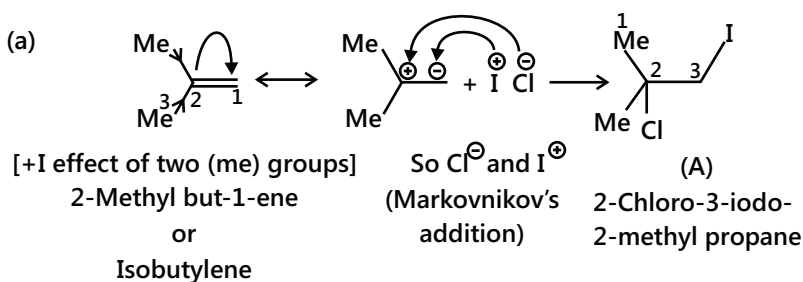
From the above data, it is clear that only with HBr, both the steps are exothermic and hence the peroxide effect is observed. With HCl or HF, the peroxide effect is not observed because the second step involving the reaction of carbon radical with HCl or HF is endothermic. Further, the peroxide effect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



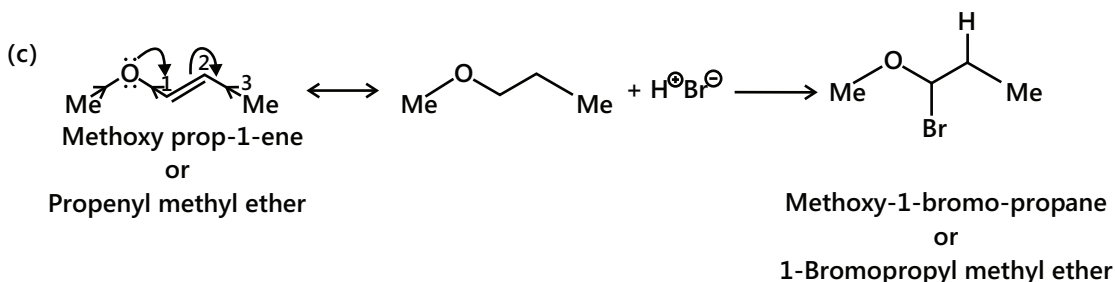
Sol:



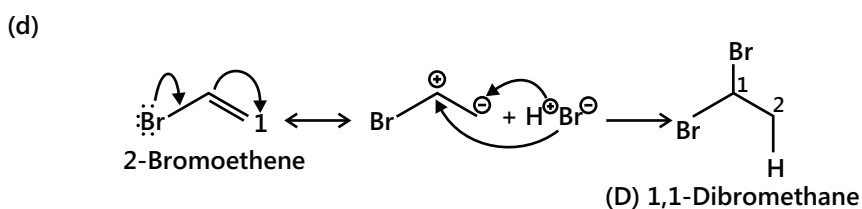
F is highly electronegative in nature. Due to the $-I$ effect of three F atoms, addition is anti-Markovnikov's (negative part of the reagent is adding to the C atom containing more number of H atoms).

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.

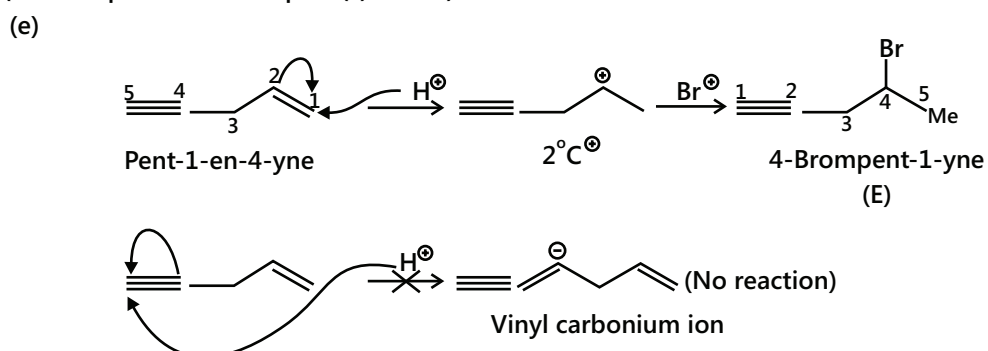
So the $-I$ effect of F atoms is operative and, hence, the electromeric effect of double bond takes place from C_1 to C_2 .



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.



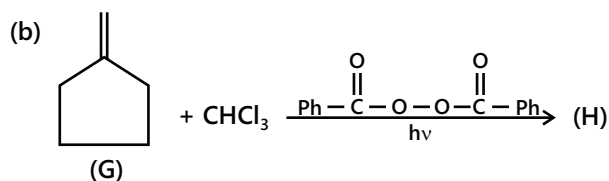
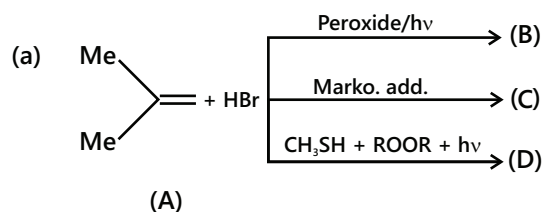
(Same explanation as in part (c) above)



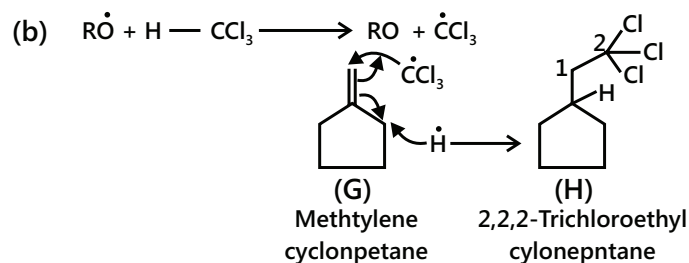
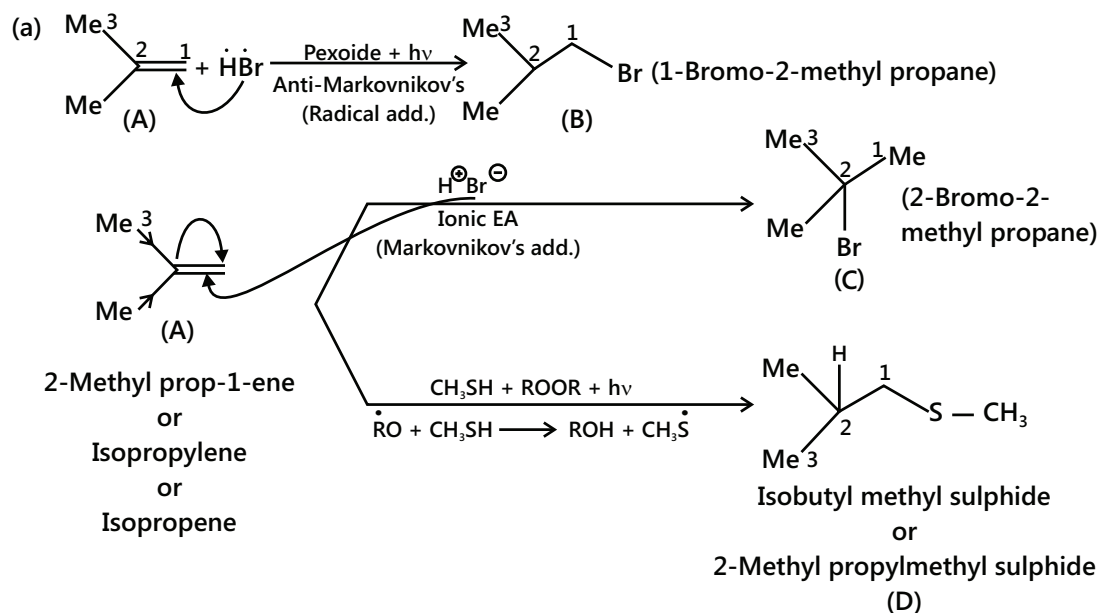
Since, alkyl carbonium ion is more stable than vinyl carbonium ion, alkene reacts at a faster rate than alkynes towards FA.

Illustration 15: Complete the following reaction:

(JEE ADVANCED)

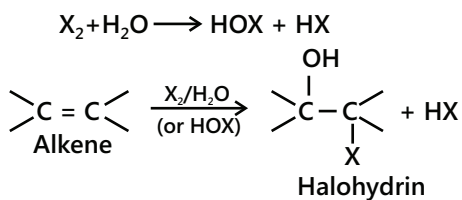


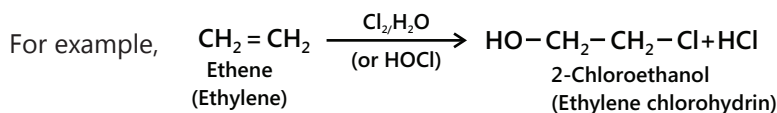
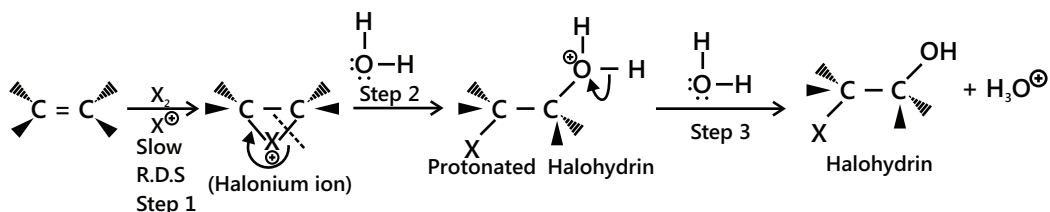
Sol: It is an example of free radical mechanism.



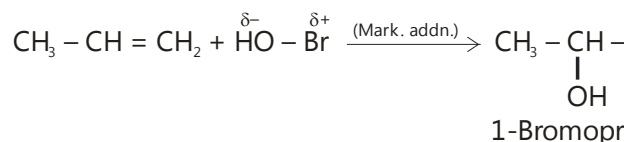
7.5 Addition of HOX

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.

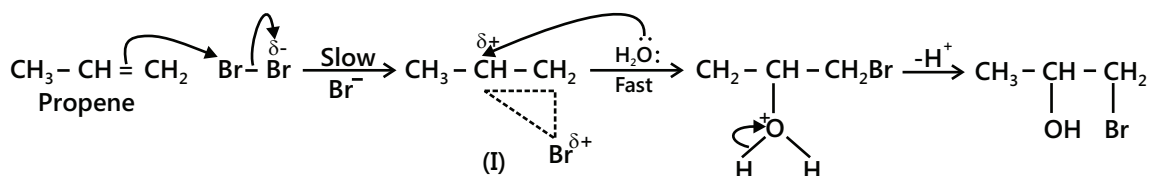
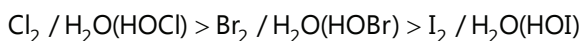


Mechanism:

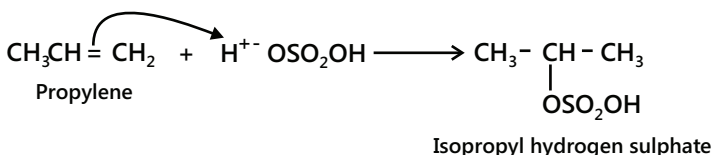
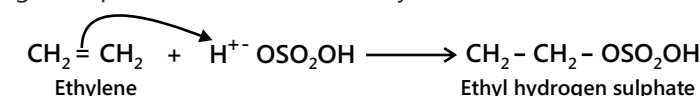
The overall reaction involves the addition of the elements of hypohalous acid ($HO-X$) in accordance with Markovnikov's rule.



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

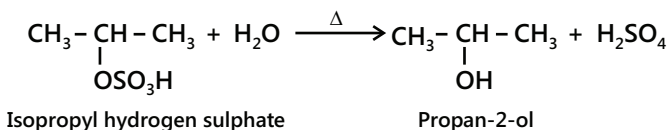
**7.6 Addition of H_2O (Indirect)**

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.

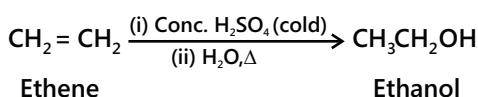


Importance. Alkyl hydrogen sulphates on boiling with water, undergoes hydrolysis to produce alcohols.

For example,



Thus, alkenes can be converted into alcohols as follows:

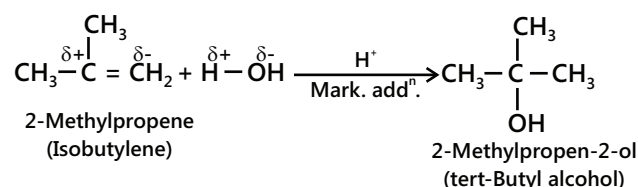


This overall two-step conversion of an alkene first into alkyl hydrogen sulphate followed by hydrolysis with boiling water to form alcohols is called the **indirect hydration of alcohols**.

7.7 Addition of H₂O (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.

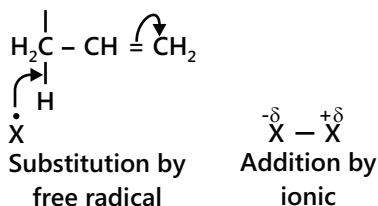
For example,



7.8 Allylic Substitution

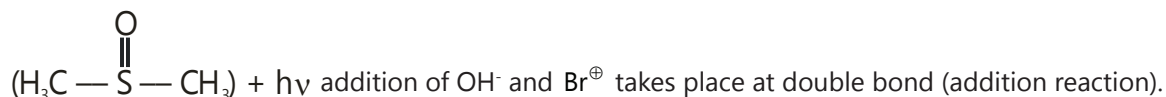
Alkenes mainly show two types of reactions:

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

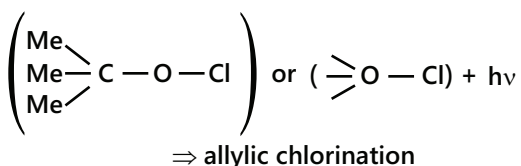


Allylic halogenations can be carried out by the following reagents:

1. Cl₂ at high temperature (773 K) or Br₂ at 400 K.
2. NBS (N-bromosuccinimide) $\left(\begin{array}{c} \text{O} \\ || \\ \text{C} \\ / \quad \backslash \\ \text{C} \quad \text{C} \\ \backslash \quad / \\ \text{O} \quad \text{NBr} \end{array} \right) + h\nu$
3. With NBS + DMSO (dimethyl sulphoxide)

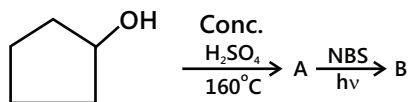
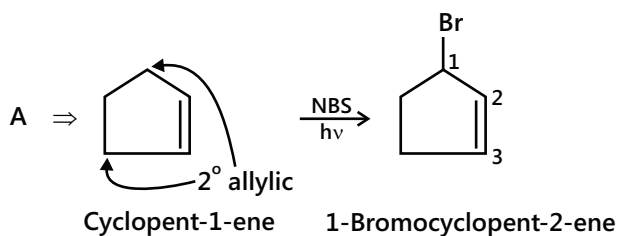
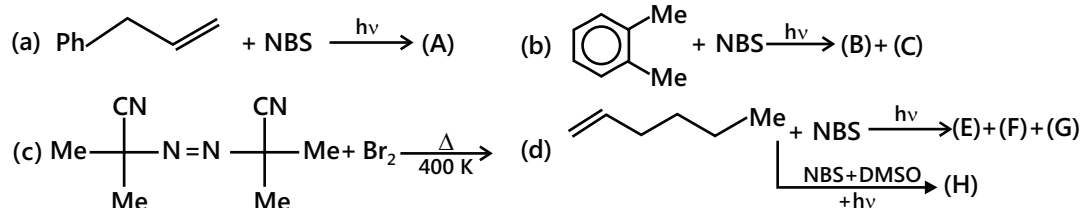
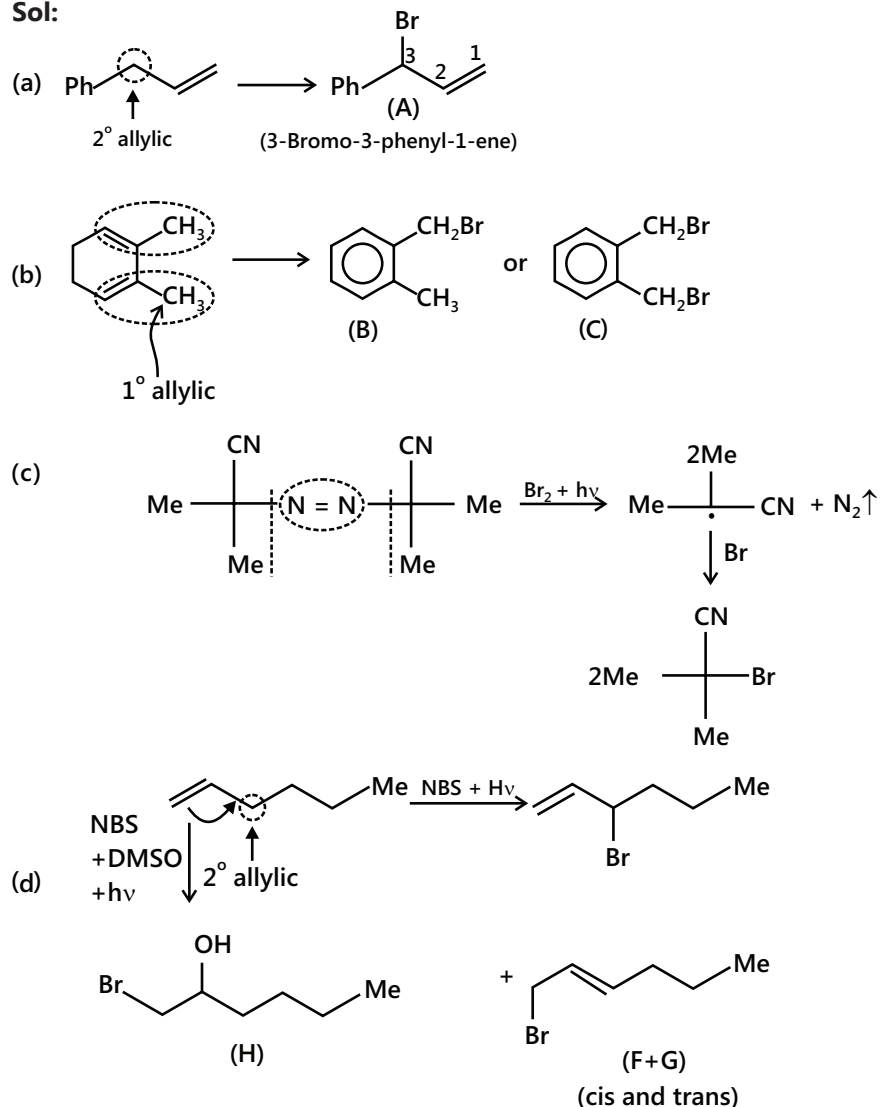


4. Cl₂SO₂ (sulfuryl chloride) $\Rightarrow$ allylic chlorination
5. t-Butyl hypochlorite



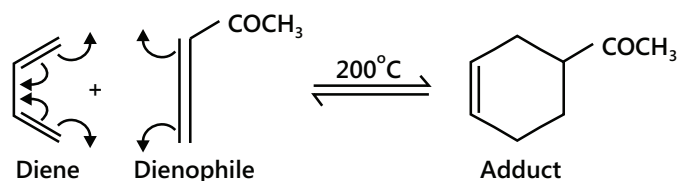
The relative rate of abstraction of hydrogen:

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

Illustration 16: Complete the following reaction:**(JEE MAIN)****Sol:****Illustration 17:** Give the products of the reactions given below**(JEE ADVANCED)****Sol:**

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 ($-\text{COOH}$), ($-\text{COOR}$), ($-\text{CHO}$), ($-\text{NO}_2$), and ($-\text{CN}$), 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 gives cis and fumaric acid gives trans isomers, both by cis-addition.

Mechanisms: cis-additions

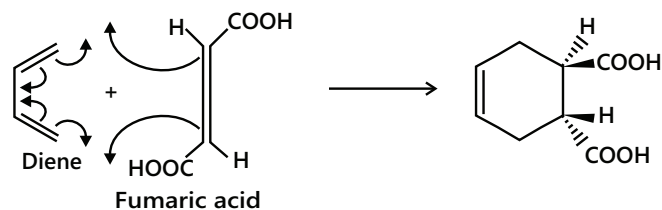
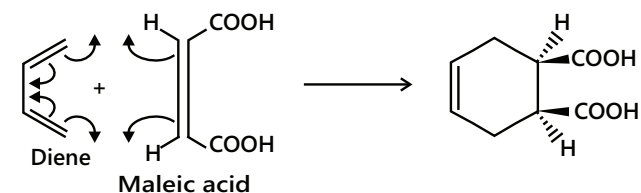
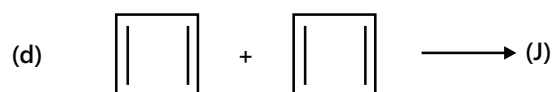
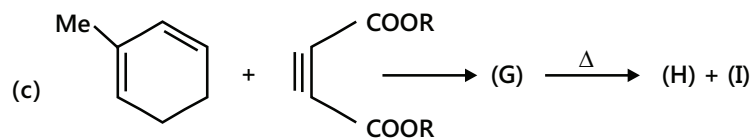
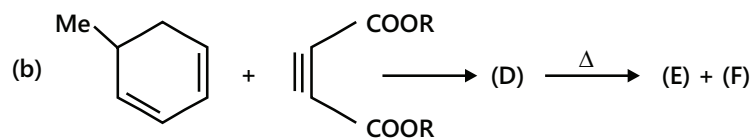
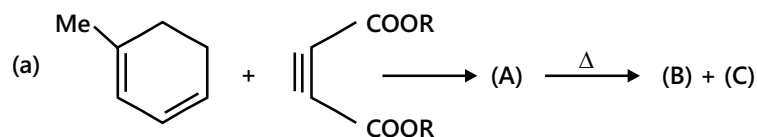
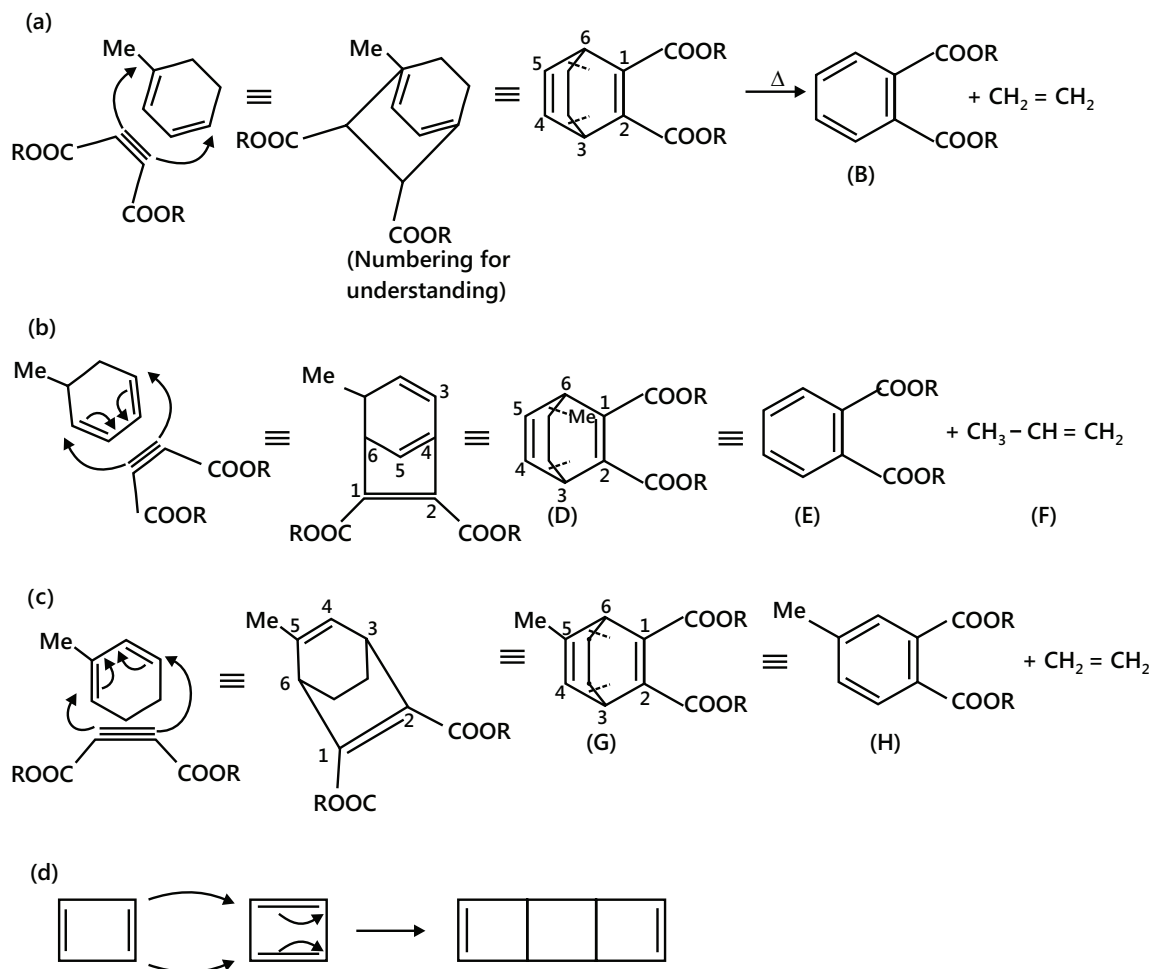


Illustration 18: Complete the following reactions:

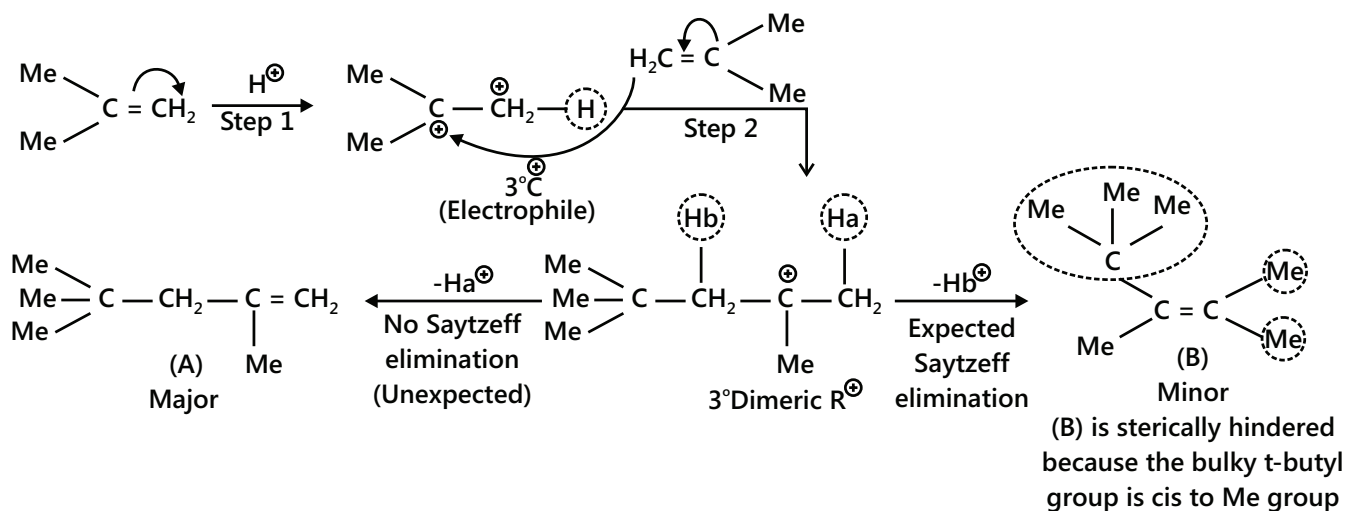


Sol: These are examples of Diels Alder reaction. Diene and dienophile combine to form new ring. The mechanism is concerted type (Bond breaking and bond making takes place simultaneously)

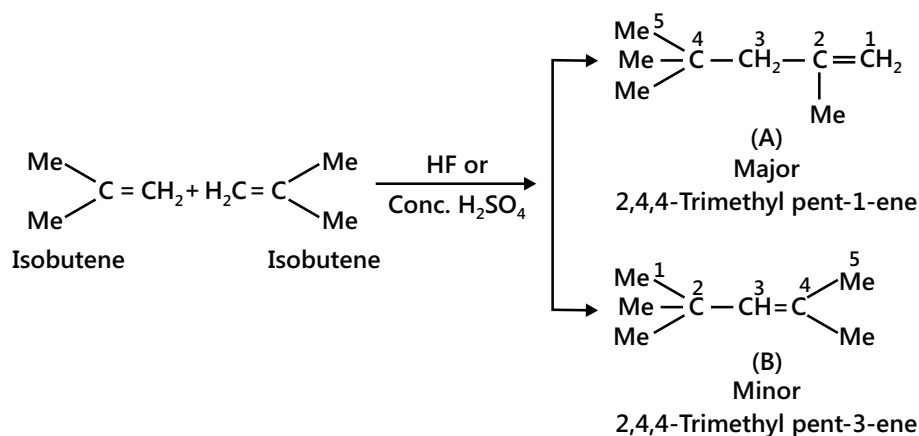


7.10 Dimerisation

Mechanism:



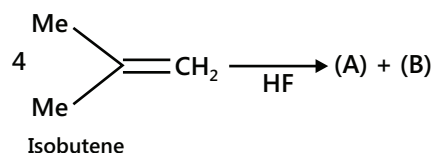
Alkene in the presence of HF or conc. H_2SO_4 or H_3PO_4 gives two alkenes (C_8H_{16}).



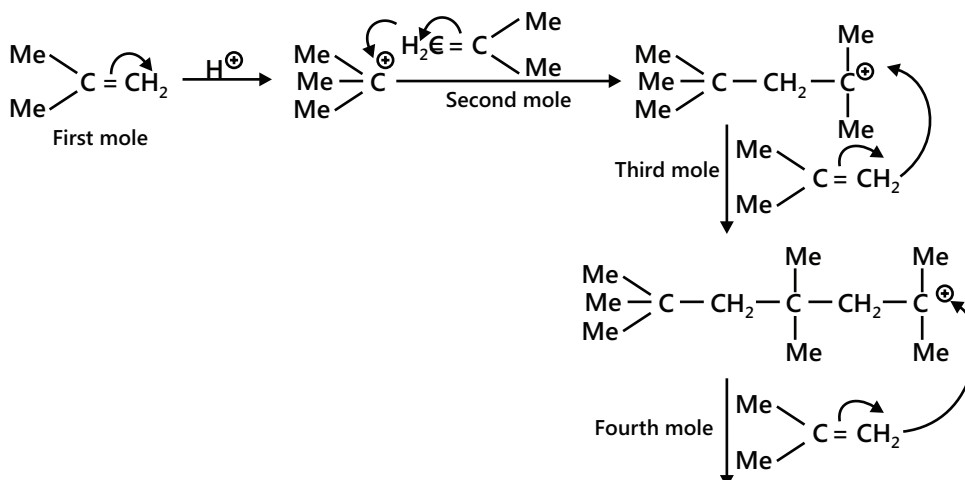
HCl, HBr, and HI cannot be used as acid catalysts. An acid catalyst must have a weak nucleophilic conjugate base to avoid addition of HX to the ($\text{C} = \text{C}$) bond. Cl^- , Br^- and I^- , the conjugate bases of HCl, HBr, and HI, respectively; are good nucleophiles that bind to alkyl carbocation;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

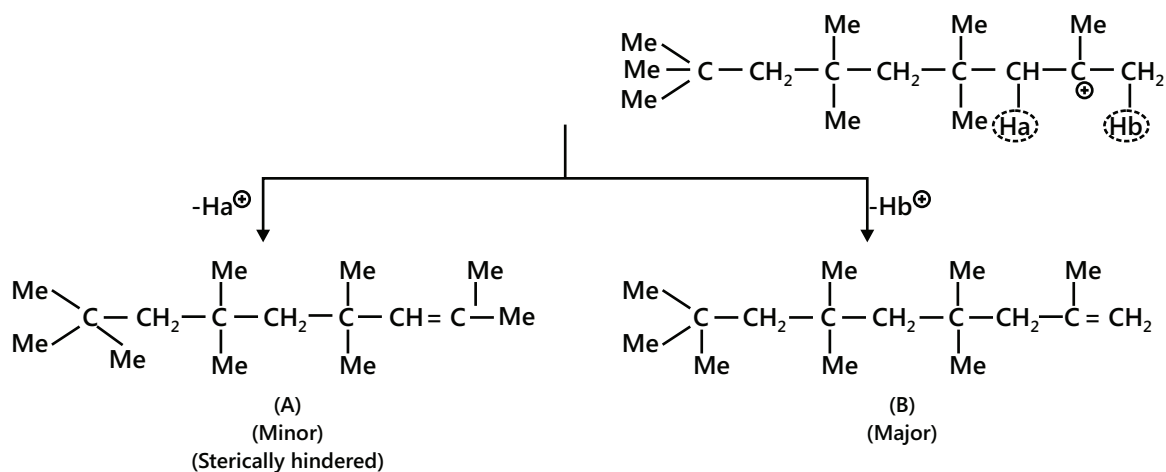
BF_3 with a little amount of H_2O can also be used to initiate the dimerisation or polymerisation of an alkene only at 73K. It is due to the formation of strong Bronsted acid ($\text{BF}_3 + \text{H}_2\text{O} \rightleftharpoons \text{HBF}_3 \cdot \text{OH}$), which provides H^+ to alkene to form the R^+ .

Illustration 19: Complete the following reaction:



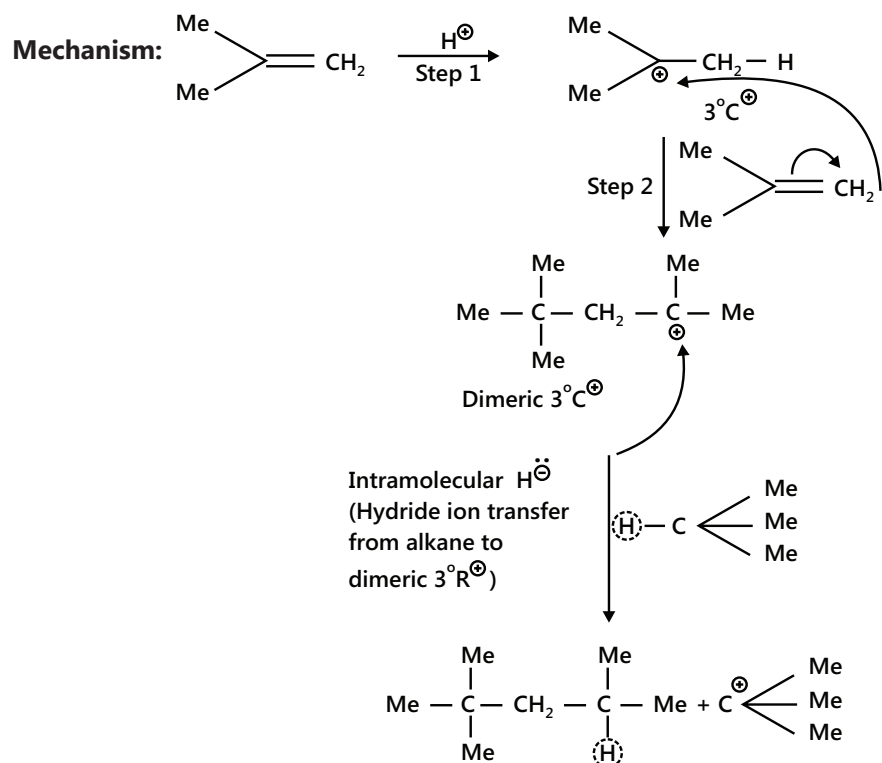
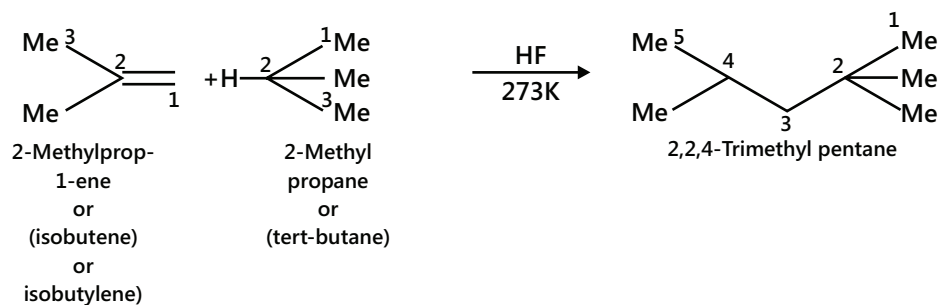
Sol:





7.11 Alkylation

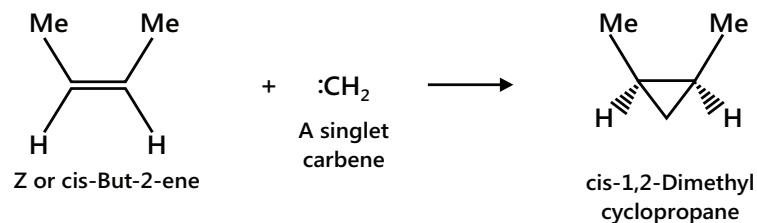
Alkylation is the addition of alkene to alkane in the presence of H_2SO_4 or HF at 273 K.



The propagation step is the chain reaction that continues when Me_3C^+ adds to a molecule of isobutene to form the same 3°R^+ , 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 π -bond to give a cyclopropane ring.

Stereochemistry of Carbene: The addition of a singlet carbene ($^1\text{CH}_2$) is both stereospecific and stereoselective and syn, while the addition of a triplet carbene ($^3\text{CH}_2$) 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.

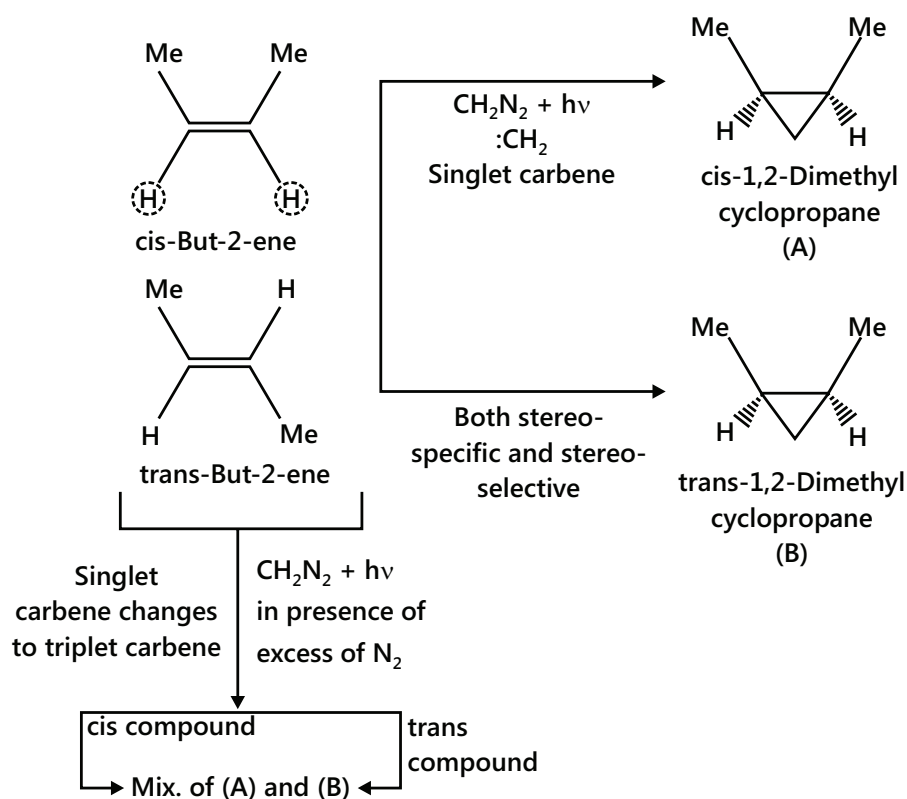
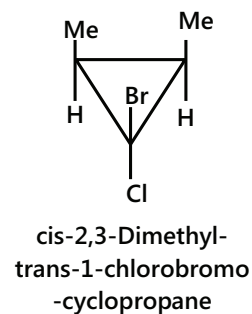
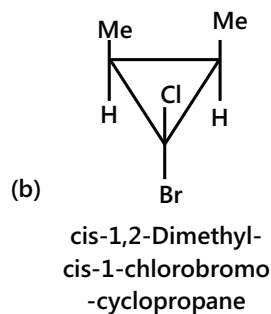
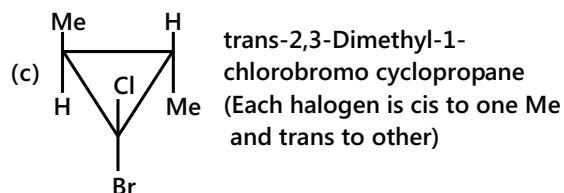
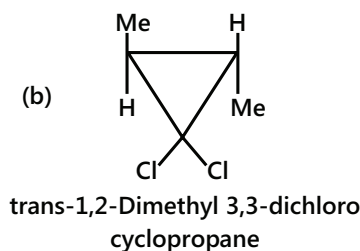
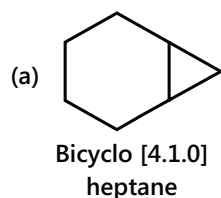
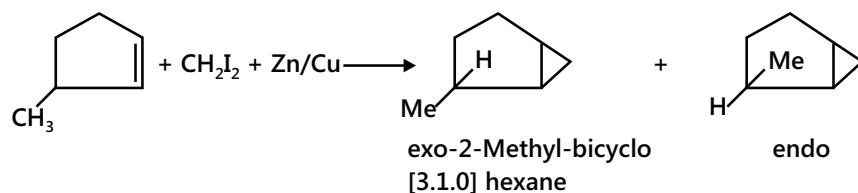


Illustration 20: Give the product of the following:

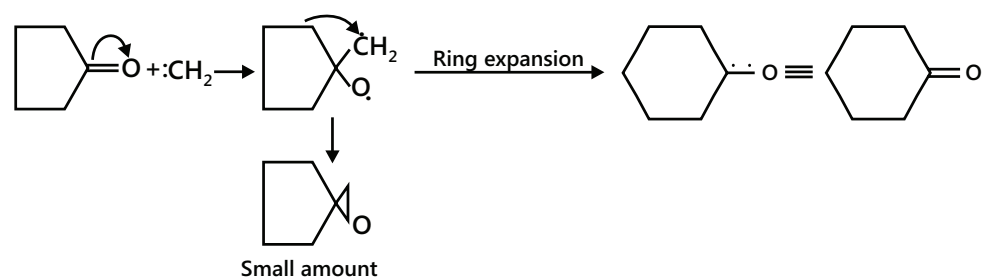
- (a) Cyclohexane + $\text{CH}_2\text{N}_2 + h\nu$ (b) Trans-2-Butene + $\text{CHCl}_3 + \text{KOH}$
 (c) Cis-2-Butene + $\text{HCBBr}_2\text{Cl} + \text{KOH}$ (d) Trans-2-Butene + $\text{HCBBr}_2\text{Cl} + \text{KOH}$
 (e) 3-Methylcyclopentene + $\text{CH}_2\text{I}_2 + \text{Zn/Cu}$ (couple) (Simmons-Smith reaction)
 (f) C1CCC(=O)C1 + $\text{CH}_2\text{N}_2 \xrightarrow{h\nu}$

Sol:

(e) Two diastereomers are obtained:

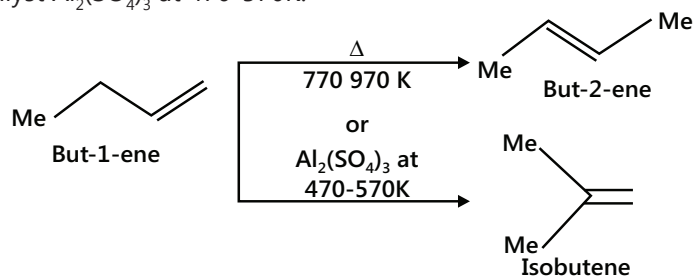


(f) By this method 7- to 10-memberd cyclic ring can be prepared.

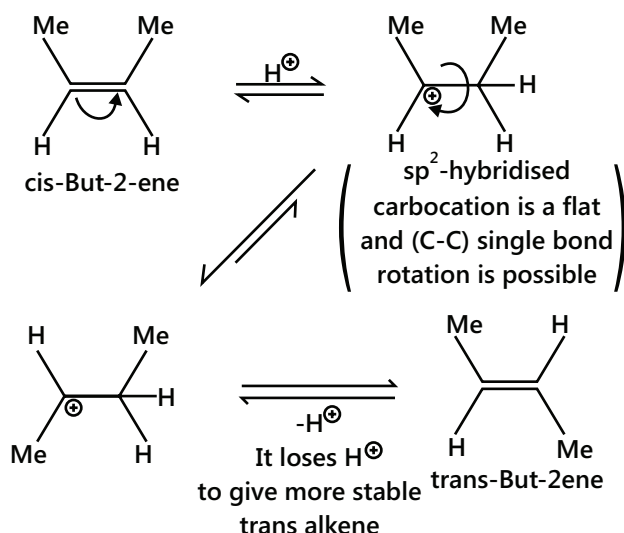


7.13 Isomerisation and the Shifting of Double Bond

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 $\text{Al}_2(\text{SO}_4)_3$ 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.

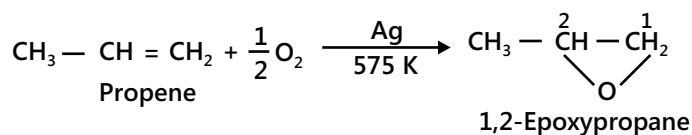
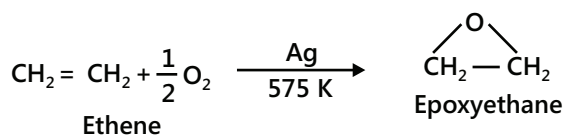


7.14 Oxidation Reactions

1. Complete oxidation with oxygen or air – Combustion: All combustion reactions are highly exothermic in nature. For example, $CH_2 = CH_2 + 3O_2 \longrightarrow 2CO_2 + 2H_2O$; $\Delta_c H = -1411 \text{ kJ mol}^{-1}$.

2. Controlled oxidation with oxidising agent gives different products:

(i) Oxidation with oxygen: Alkenes react with O₂ 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:

- Cold alkaline or aqueous KMnO₄ solution:** It is also called Baeyer's reagent. It is a test for unsaturation for both alkenes and alkynes. The pink colour of KMnO₄ is discharged and the black-brown precipitate of MnO₂ is obtained, and alkenes are converted to diols.
- OsO₄ (osmium tetroxide)** in pyridine or ether solution followed by the reaction with Na₂SO₃/H₂O or NaHSO₃/H₂O converts alkene to diols and OsO₄ to Os metal.
- With catalytic amount of OsO₄ in H₂O₂:** 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**.

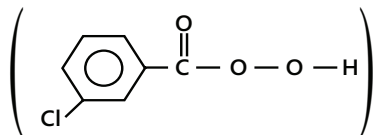
Anti Hydroxylation with the following reagents :

- Peroxy acid followed by the hydrolysis with H₂O:**

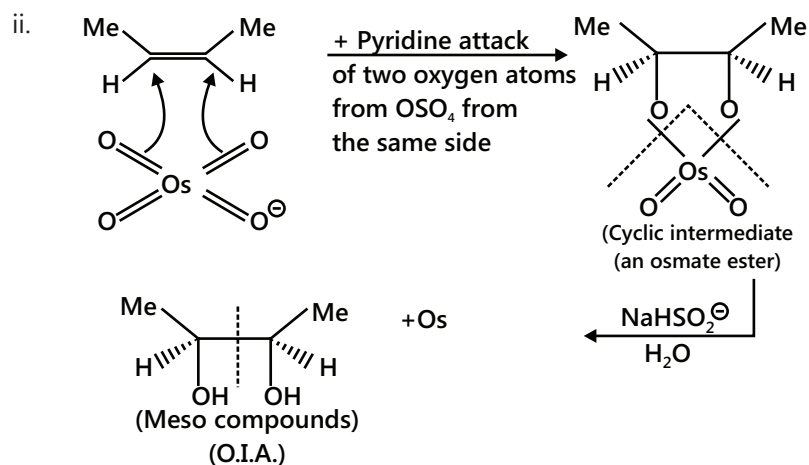
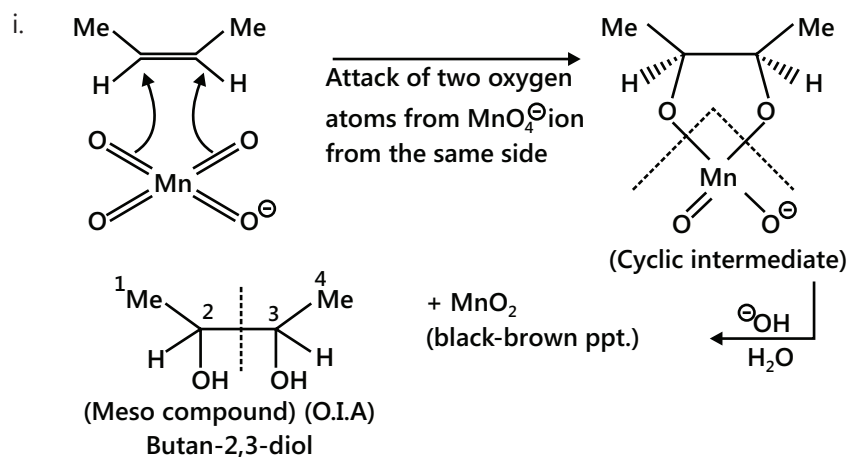
For example,

- i. $\text{Ph}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{O}-\text{H}$, ii. $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{O}-\text{H}$, peroxymethanoic acid or peroxyformic acid, and Peroxybenzoic acid

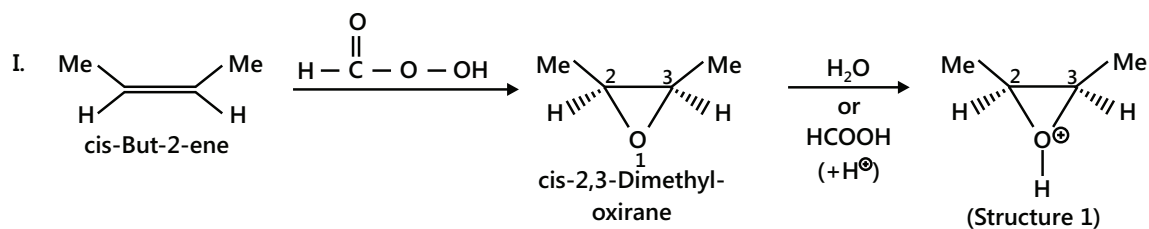
- iii. MCPBA (m-chloroperbenzoic acid)



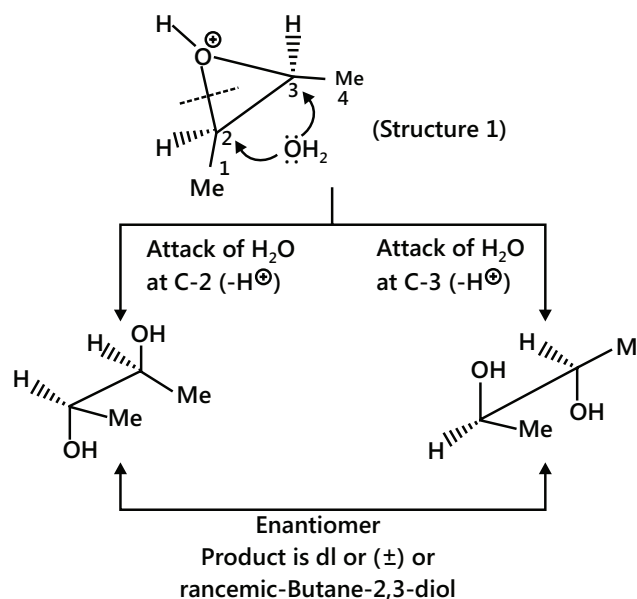
Mechanism of syn hydroxylation:



Mechanism of Anti-hydroxylation



II.

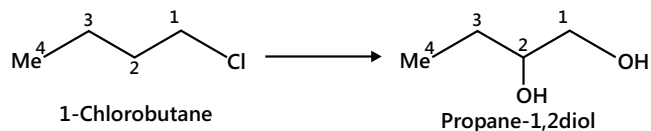


For syn hydroxylation,

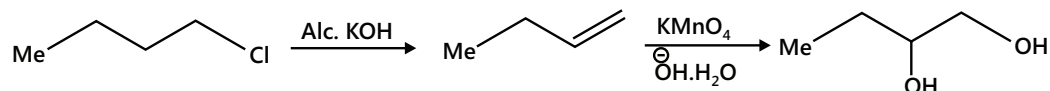
	Reactant	Reagent mechanism	Product
1.	Cis (with two same groups)	Syn (with two same ($-\text{OH}$) groups)	Meso
2.	Trans (with two same groups)	Syn (with two same ($-\text{OH}$) groups)	($\pm$) or racemate
3.	Cis or trans (with two different groups)	Syn (with two same ($-\text{OH}$) groups)	($\pm$) or racemate

For anti-Hydroxylation,

	Reactant	Reagent mechanism	Product
1.	Cis (with two same groups)	Anti (with two same ($-\text{OH}$) groups)	($\pm$) or racemate
2.	Trans (with two same groups)	Anti (with two same ($-\text{OH}$) groups)	Meso
3.	Cis or trans (with two different groups)	Anti (with two same ($-\text{OH}$) groups)	($\pm$) or racemic

Illustration 21: Convert

Sol: First the compound undergoes dehydrohalogenation reaction to form an unsaturation. This on treatment with aq. KMnO_4 gives diol.



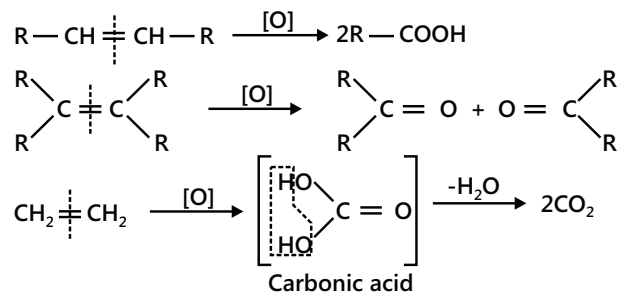
7.14.2 Cleavage

A. Oxidative cleavage

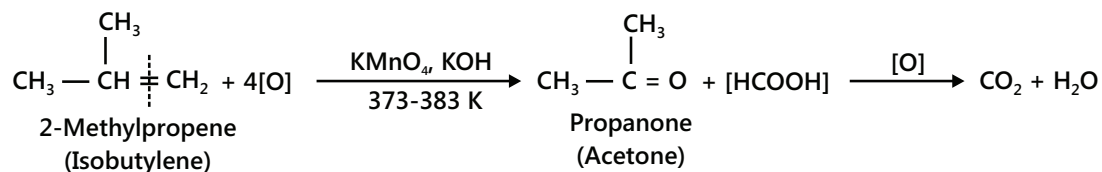
Alkenes are oxidatively cleaved by any of the following reagents:

1. Hot alkaline KMnO_4 solution followed by acidification

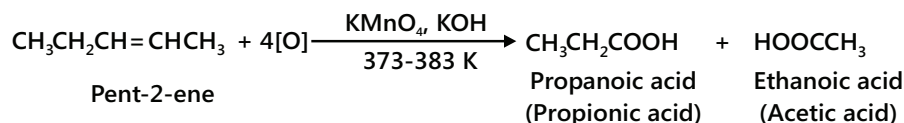
- Hot acidic KMnO_4 solution.
- Hot acidic $\text{K}_2\text{Cr}_2\text{O}_7$ solution.



With terminal alkenes, one of the products is always methanoic acid (formic acid) with on further oxidation gives $\text{CO}_2 + \text{H}_2\text{O}$. For example,



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



Rules of oxidation:

$\text{CH}_2 \Rightarrow$	CO_2
$\text{R}-\text{CH} \Rightarrow$	$\text{R}-\text{COOH}$
$\text{R}_2\text{C}=\text{CH}_2$	$ \begin{array}{ccc} \text{R} & & \text{R} \\ & \diagdown & / \\ & \text{C}=\text{C} & \\ & / & \diagdown \\ \text{R} & & \text{R} \end{array} \Rightarrow \begin{array}{ccc} \text{R} & & \text{R} \\ & \diagdown & / \\ & \text{C}=\text{O} & \\ & / & \diagdown \\ \text{R} & & \text{R} \end{array} $

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.

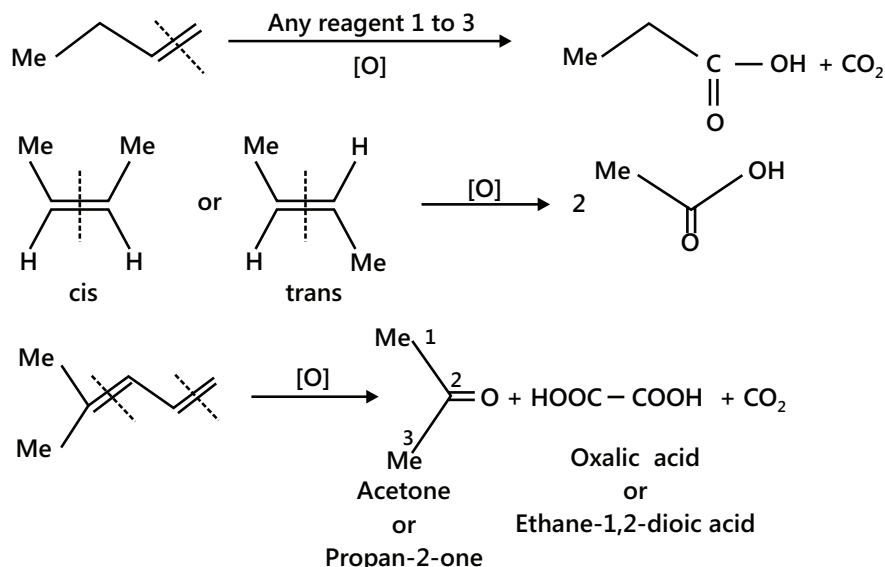
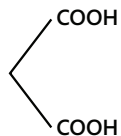


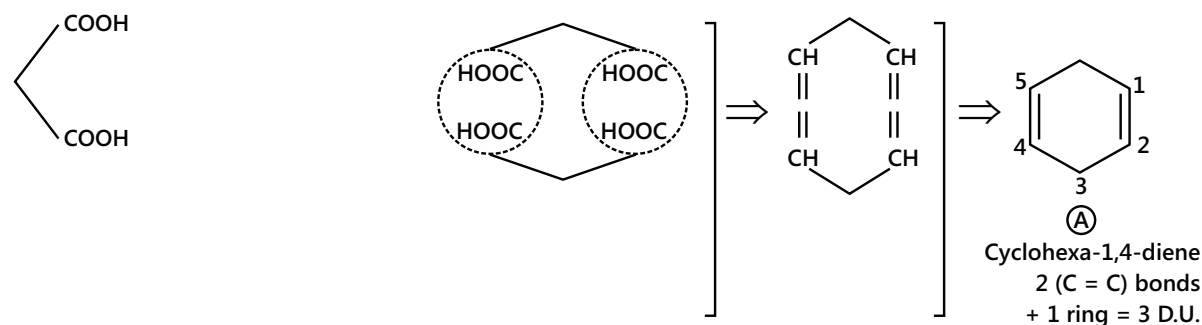
Illustration 22: Compound (A) (C_6H_8) $\xrightarrow{[O]}$ Malonic acid only. Identify compound (A).

Sol: First, calculate the degree of unsaturation.

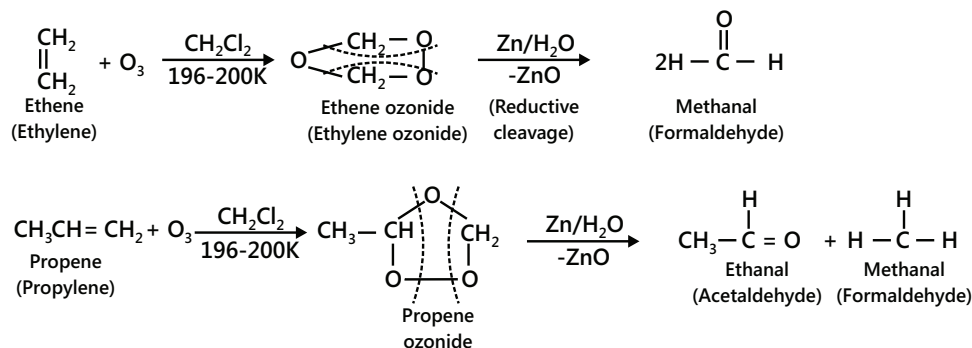
$$D.U. = \frac{(2n_C + 2) - n_H}{2} = \frac{(2 \times 6 + 2) - 8}{2} = 3^\circ$$

Structure of malonic acid is $\Rightarrow$ 

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



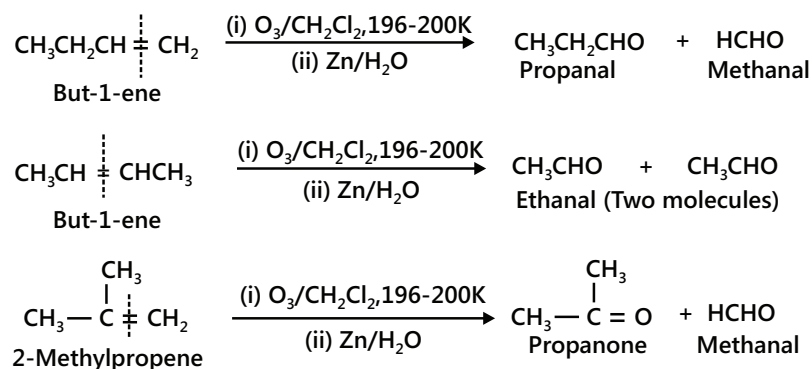
B. Ozonolysis (Oxidation with ozone): When ozone is passed through a solution of an alkene in some inert solvent such as CH_2Cl_2 , $CHCl_3$ or CCl_4 at a low temperature (196-200K), it oxidises alkenes to ozonides. Ozonides are unstable and explosive compounds. Therefore, they are not usually isolated 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.

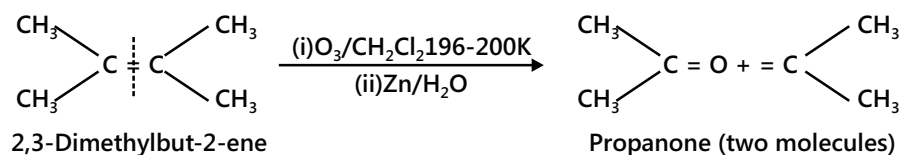


However, if the ozonide are decomposed only with water, the H_2O_2 produced during the reaction oxidises the initially formed aldehydes to the corresponding acids (oxidative cleavage).

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 reductive and oxidative ozonolysis

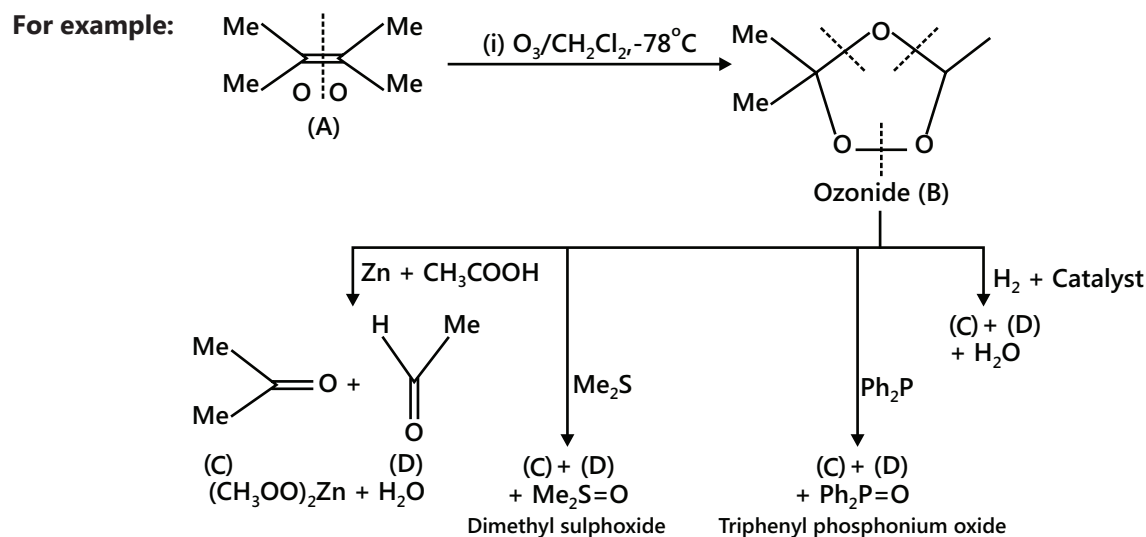
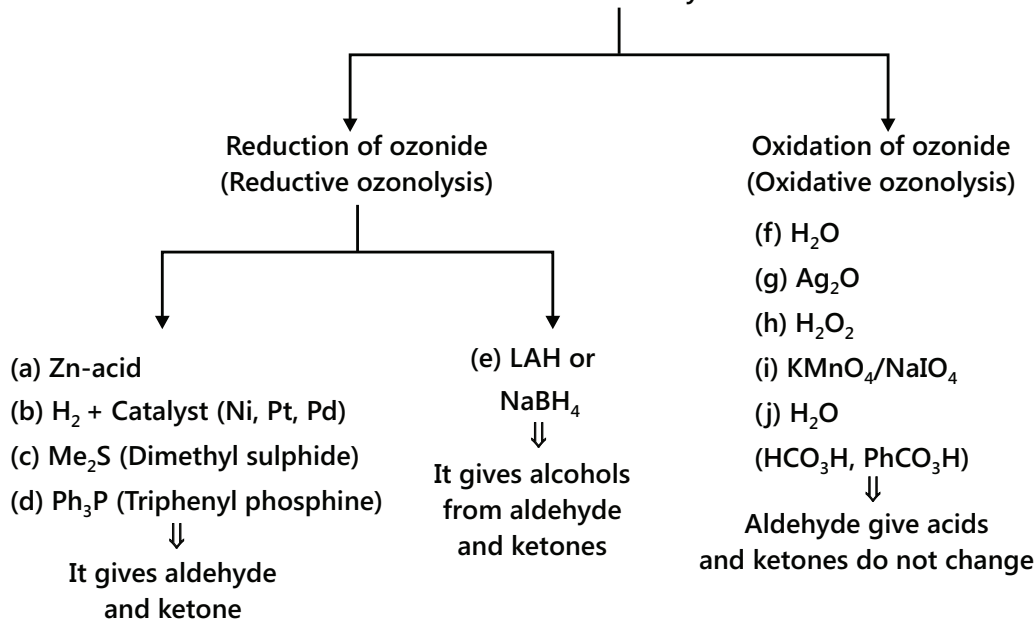
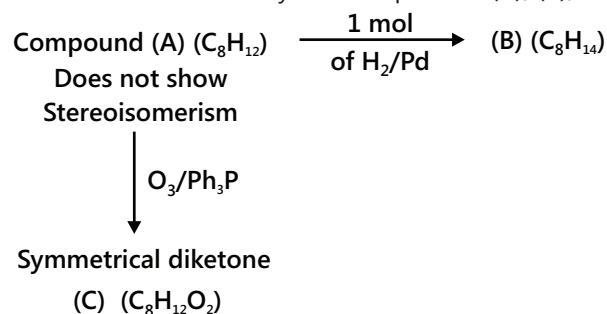


Illustration 23: Identify the compounds (A), (B), and (C).

(JEE MAIN)



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

$$\text{D.U. in (A)} = \frac{(2n_C + 2) - n_H}{2} = \frac{(2 \times 8 + 2) - 12}{2} = 3^\circ;$$

$$\text{D.U. in (B)} = \frac{(2n_C + 2) - n_H}{2} = \frac{(2 \times 8 + 2) - 14}{2} = 2^\circ$$

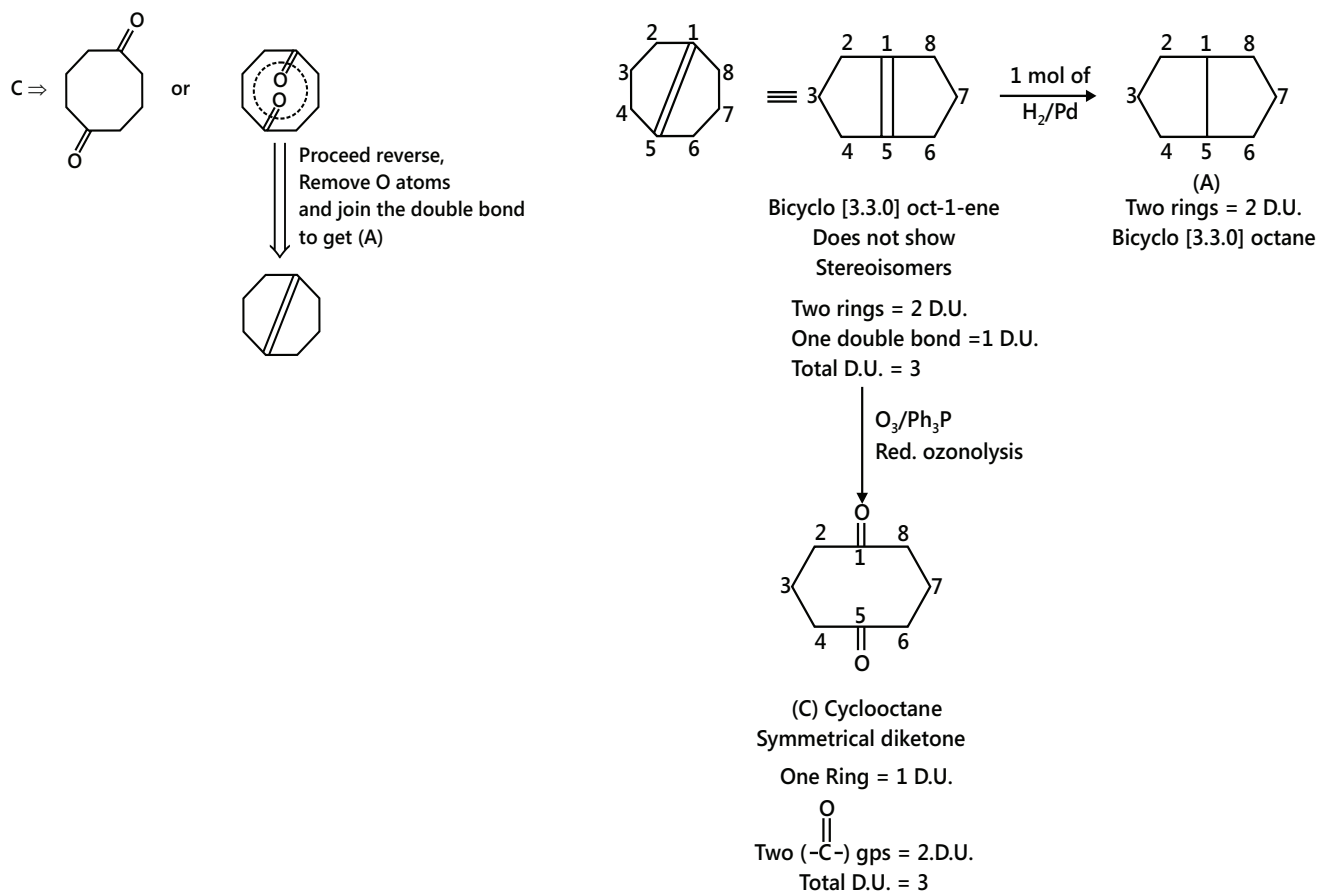
$$\text{D.U. in (C)} = \frac{(2 \times 8 + 2) - 12}{2} = 3^\circ$$

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 ($\text{C} = \text{C}$) bond or one ring of eight C atoms.

One ($\text{C} = \text{C}$) bond is not possible because after ozonolysis of (A), the double bond cannot be left behind. So (C) is

8C ring with two ($-\text{C}(=\text{O})-$) groups at the symmetric position.



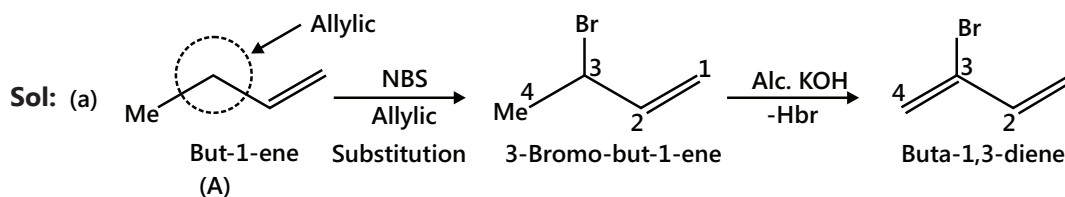
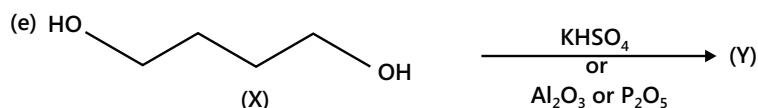
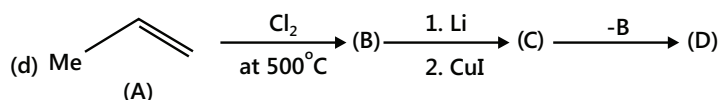
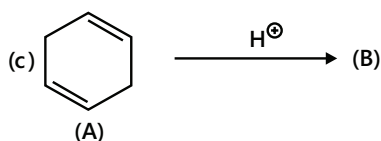
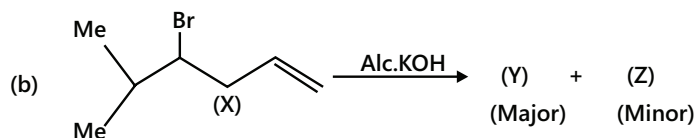
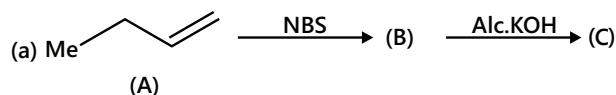
8. USES OF ALKENES

- (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.

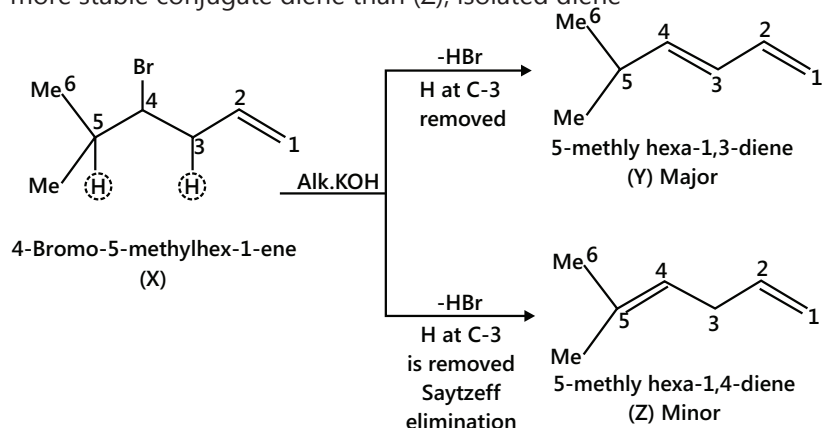
Solved Examples

JEE Main/Boards

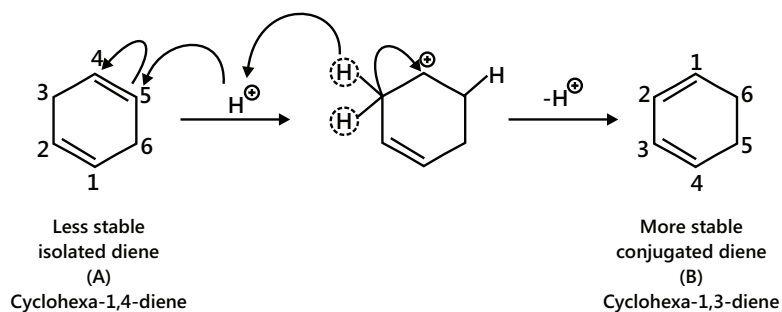
Example 1: Complete the following reactions:



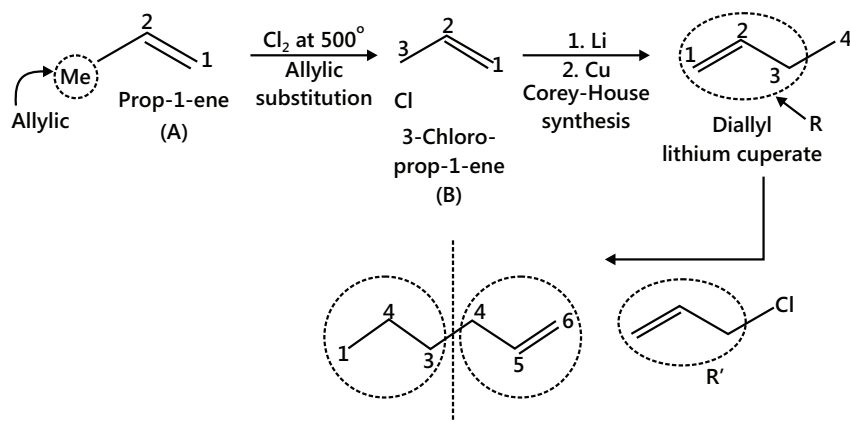
(b) (Z) is formed by Saytzeff's elimination, but the product (Y) is formed in major amount because product (Y) is a more stable conjugate diene than (Z), isolated diene



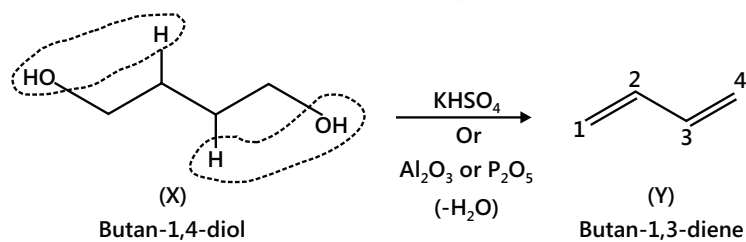
(c)



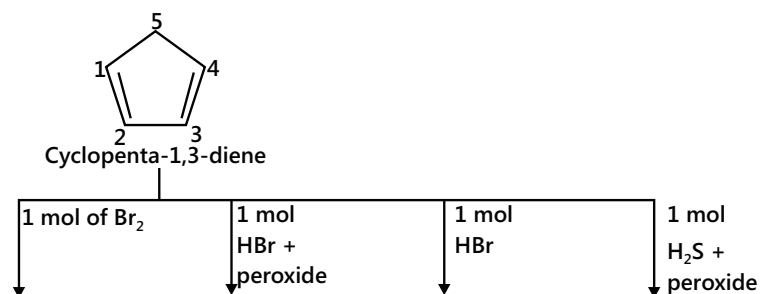
(d)



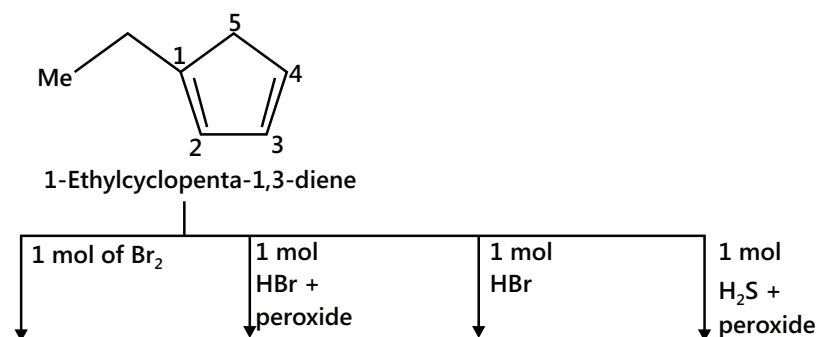
(e)

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

(a)

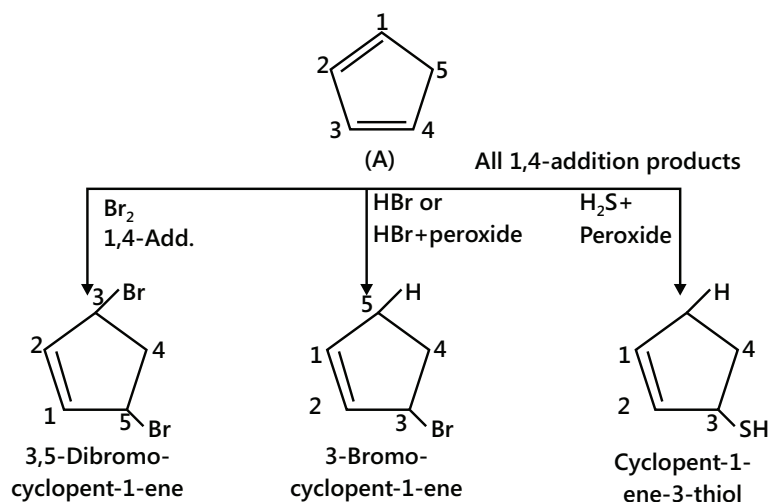


(b)

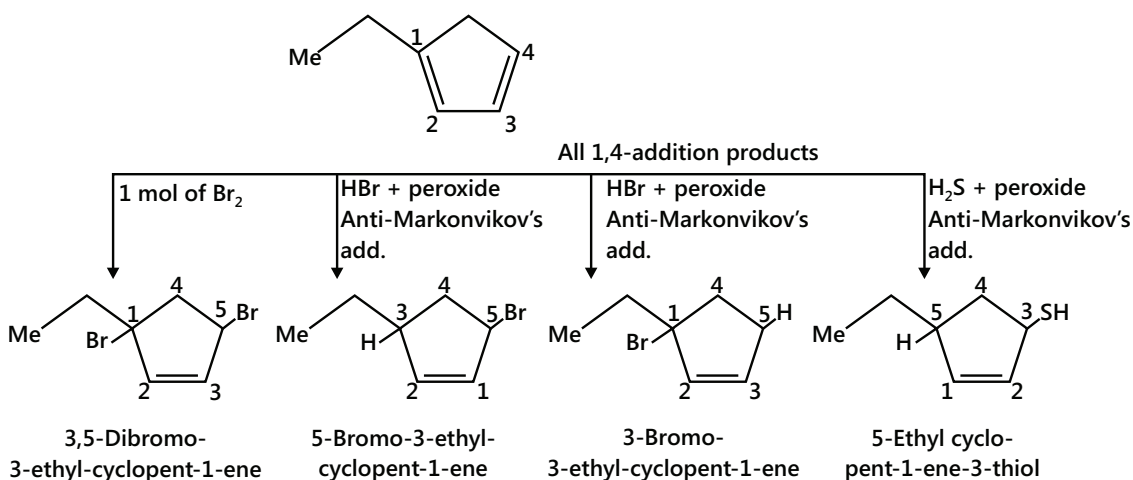


Sol:

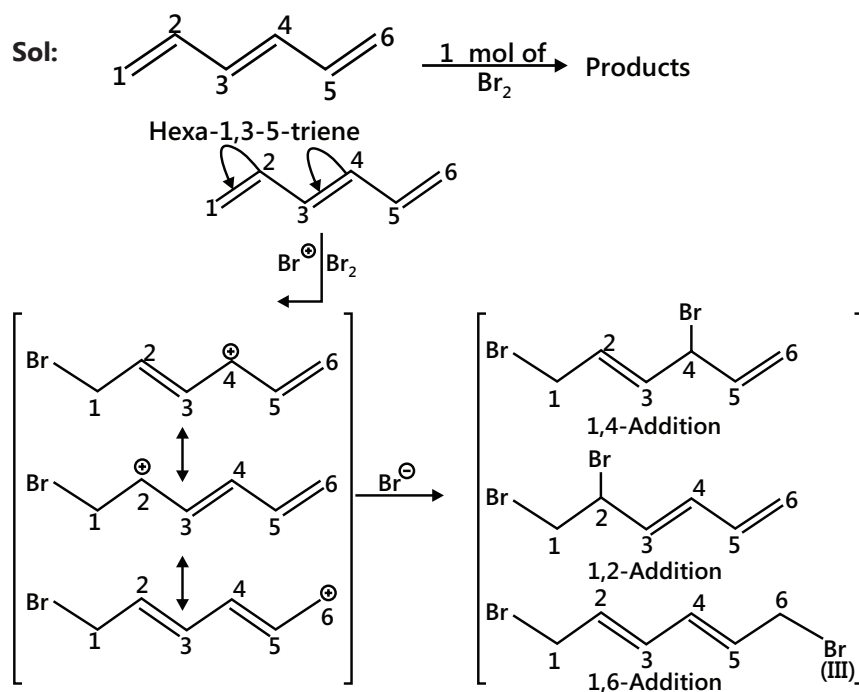
(a)

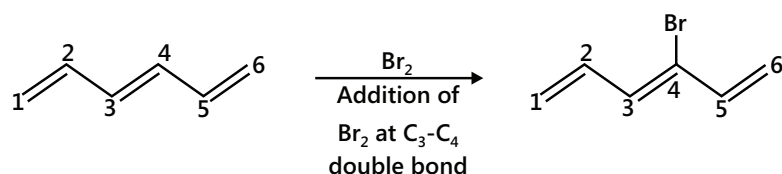


(b)



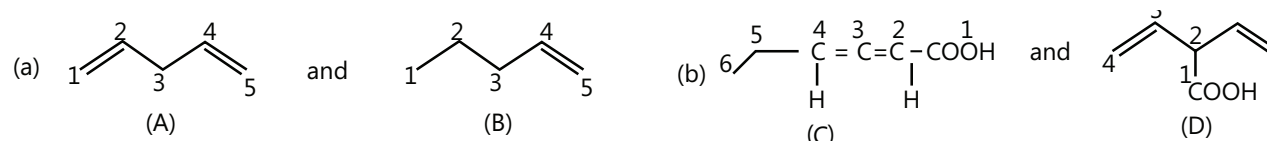
Example 3: Write all the possible structures and give the structure of the products that are thermodynamically favoured.

Sol:

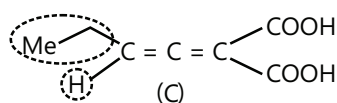


More stable Products (II and III, conjugate dienes) are thermodynamically favoured products than I and IV (isolated dienes)

Example 4: Distinguish between the given pairs.



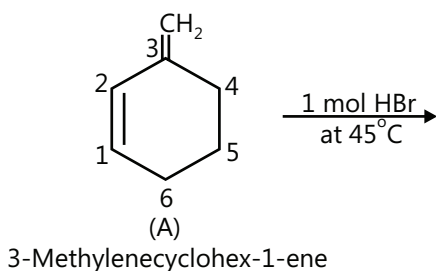
Sol: (a) Compounds (A) and (B) are distinguished chemically by quantitative catalytic hydrogenation. Since compound (A) has two double bond whereas compound (B) has only one double bond. Compound (A) will require 2 moles of H_2 for 1 mole of (A) while (B) will requires 1 mole of H_2 per mole of (B).



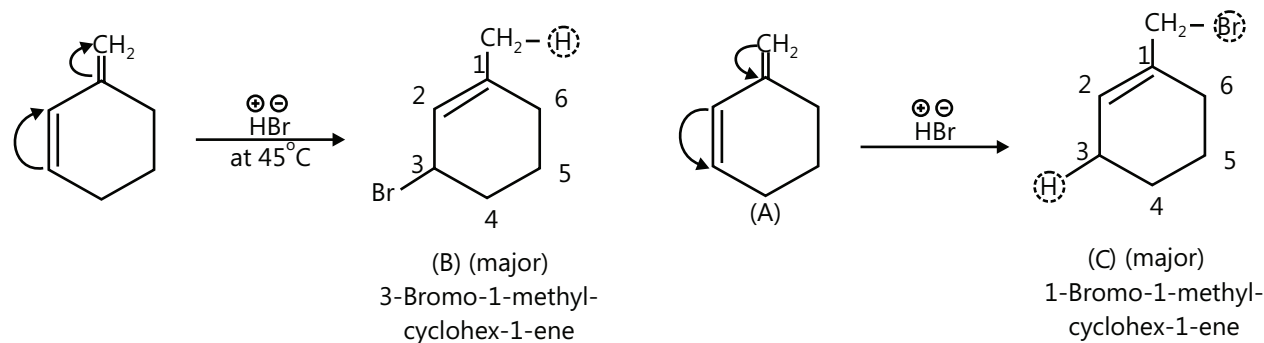
(b) Allene (C) with different groups on each of the double bonds is optically active and can be resolved into its enantiomers.

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

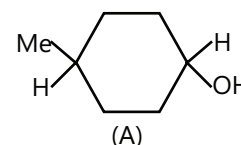
Example 5: Give the major and minor products.

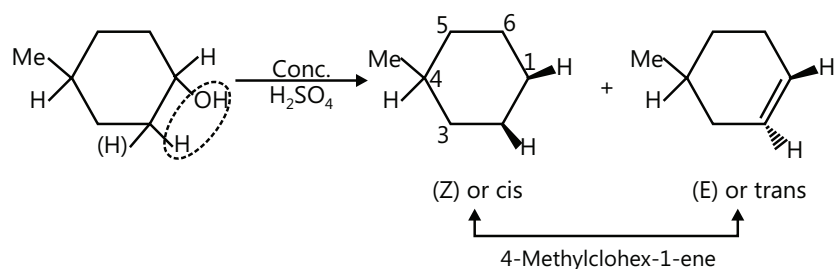
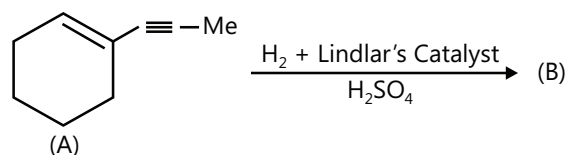


Sol: At high temperature (45°C), 1, 4-addition products is more favourable.

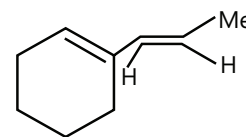
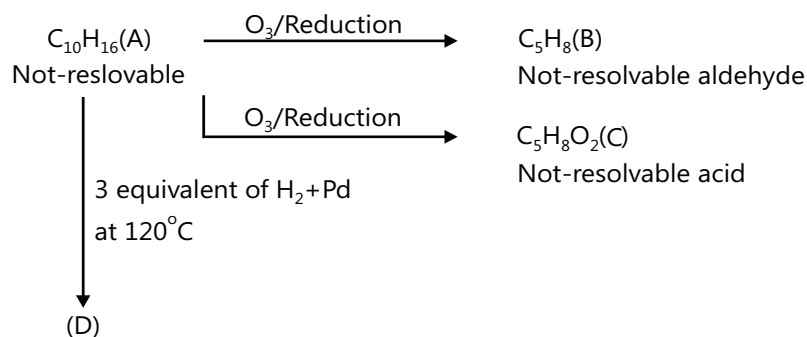


Example 6: Dehydration of (A) with conc. H_2SO_4 gives a compound that exists in two isomeric forms. Give the structures of both the isomers.



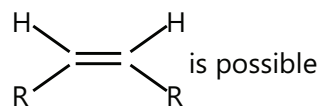
Sol:**Example 7:**

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

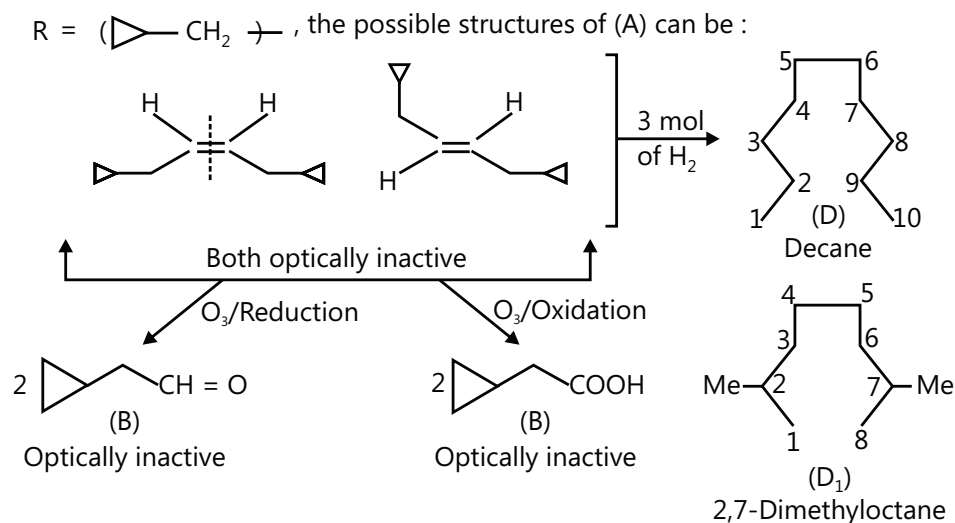
**Example 8:**

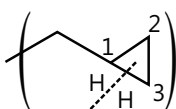
Write all the possible structures of (A), (B) and (C).

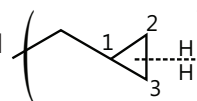
Sol: Since the reductive and oxidative ozonolysis products are different, the alkene of the type



If $R = (\triangle - \text{CH}_2 -)$, the possible structures of (A) can be:



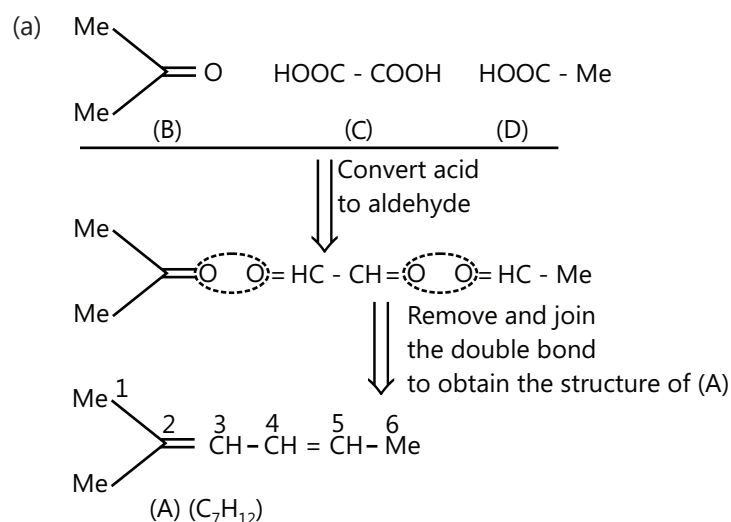
(D) is obtained when ($C_1 - C_3$) bond breaks 

(D₁) 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.

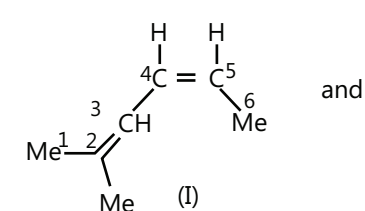


Sol:

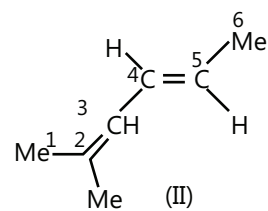


Here Compound (A) shows G.I around $C_4 - C_5$ double bond (since the two groups around C-4 and C-5 are different) but do not show G.I around $C_2 - C_3$ double bond because the two groups around C-2 are the same.

Number of stereoisomers for (A) — 2

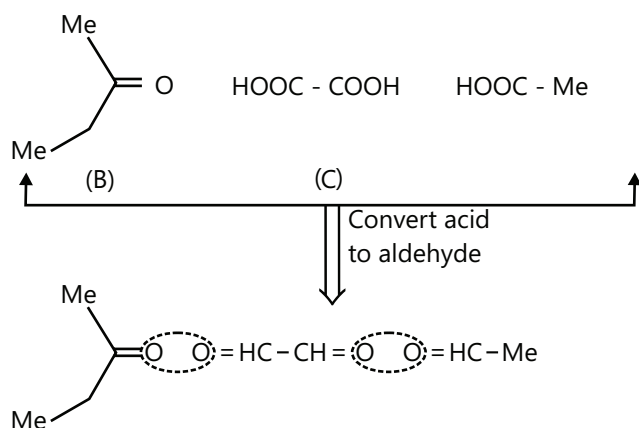


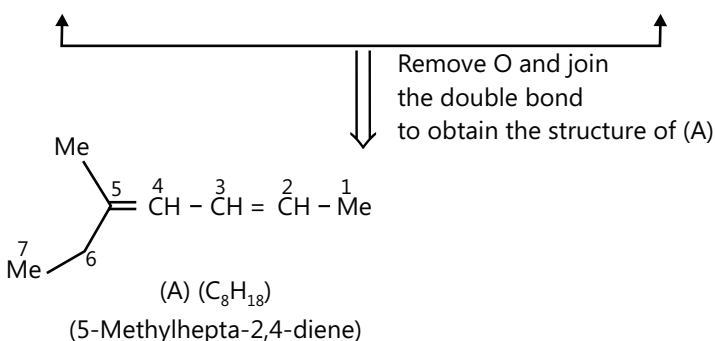
4Z-2-Methylhexa-2,4-diene



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

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





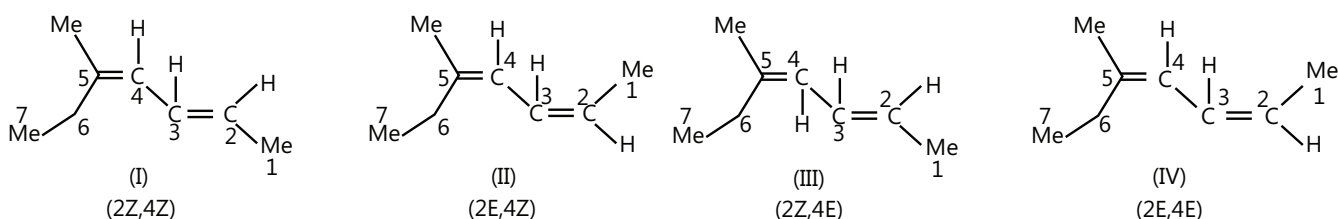
(A) shows geometrical isomers around both ($C_2 - C_3$) and ($C_4 - C_5$) double bonds (two of the groups around these double bonds are different)

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

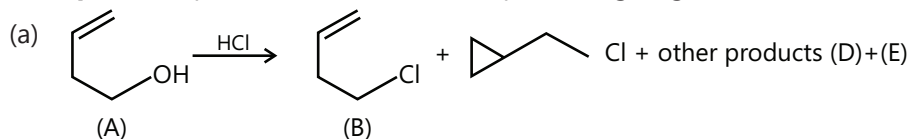
Number of G.I. when the terminal groups are different = 2^n , where n is the number of double bonds (two double bonds).

$$\text{G.I.} = 2^2 = 4$$

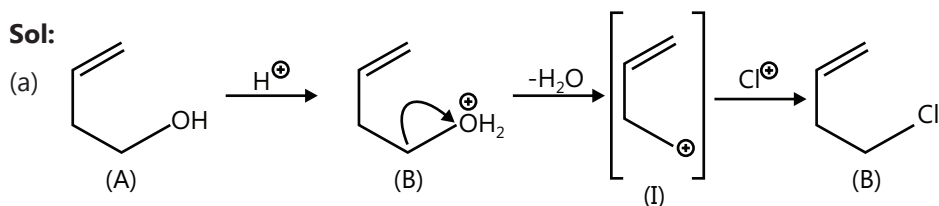
Number of stereoisomers of (A) = 4



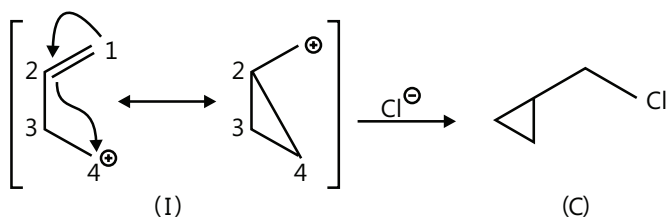
Example 10: Explain the formation of the products giving the structures of the intermediates.



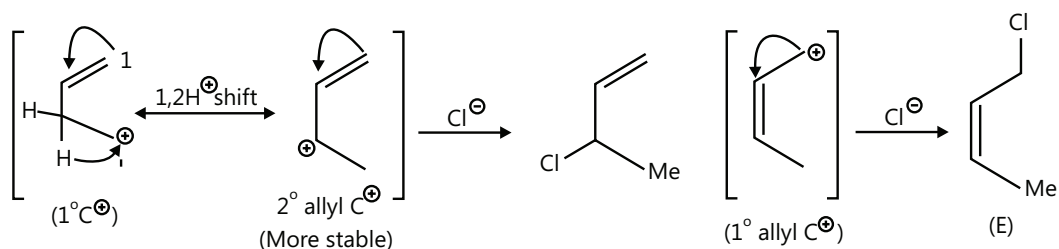
Sol:



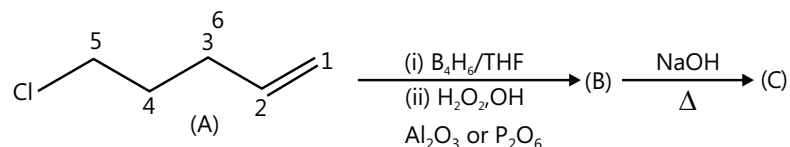
In this reaction presence of double bond influences the reaction pathway and unusual product may also be formed. Due to the presence of e^- -rich double bond, the intermediate (I) carbocation may also involve intra-molecular rearrangement to form a three membered cyclic ring as shown below:



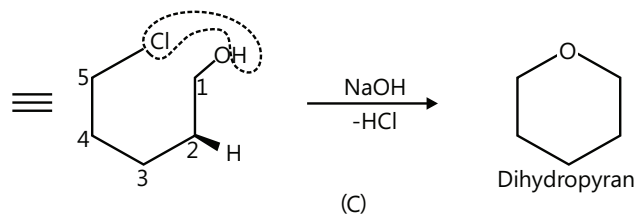
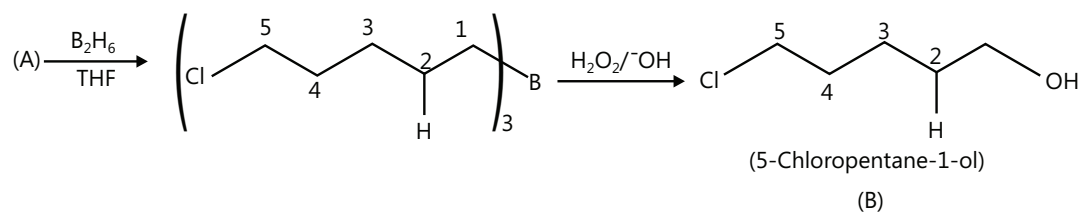
Other products can be obtained due to carbocation (I) rearrangement.



Example 11: Complete the following reaction:

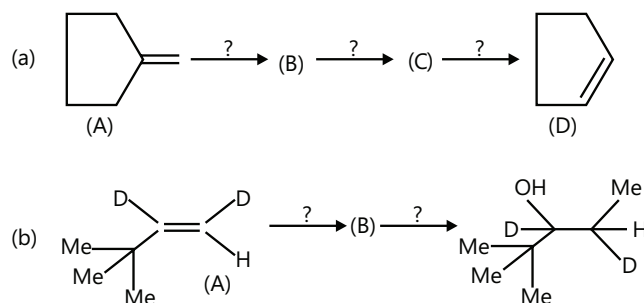


Sol: It is an example of hydroboration-oxidation reaction, it is used in the formation of alcohol from an alkene. It follows anti-Markovnikov's rule, and the addition of H and OH is syn (cis) (addition of H and BH_2 takes place from the same side)



JEE Advanced/Boards

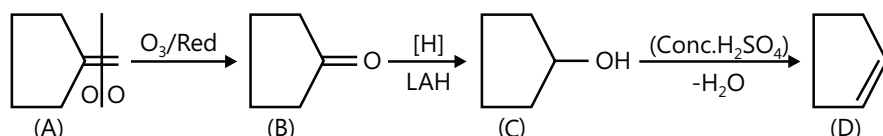
Example 1: Complete the following reaction with appropriate reagents.



Sol: (a) Compound (D) Contains a ($\text{C} = \text{C}$) 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 ($>\text{C} = \text{O}$) using reducing agent like LAH.

$\therefore$ So (B) contains a keto group ($>\text{C} = \text{O}$), ($>\text{C} = \text{O}$) group can be obtained from (A) by ozonolysis.

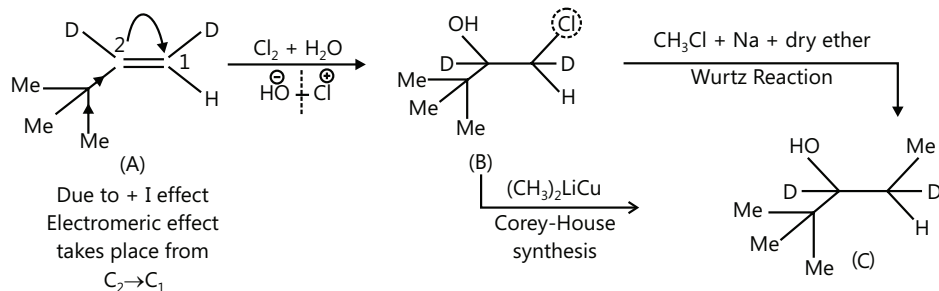
The different steps are as follows:



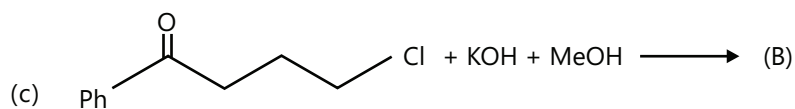
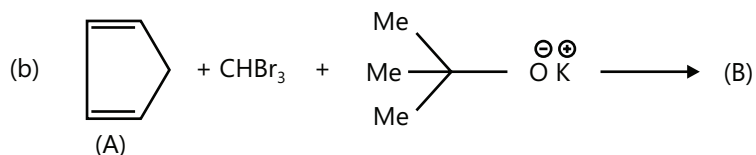
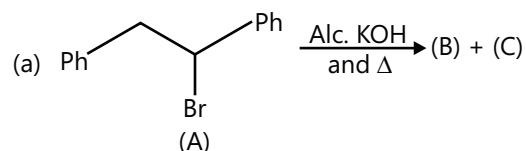
(b) **Proceeding reverse:** (Retrosynthetic approach)

Compound (D) contains one Me and one -OH group. It can be obtained by adding ($\text{Cl}_2 + \text{H}_2\text{O}$) (HOCl) to (A).

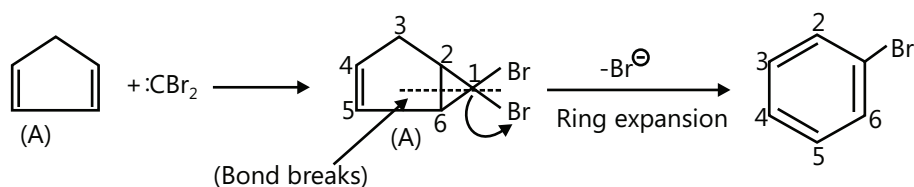
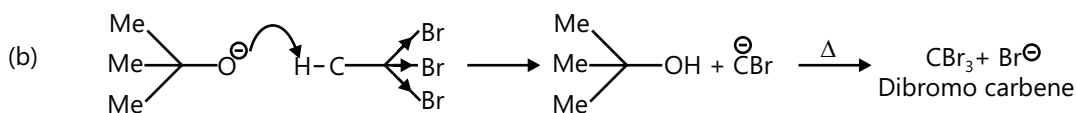
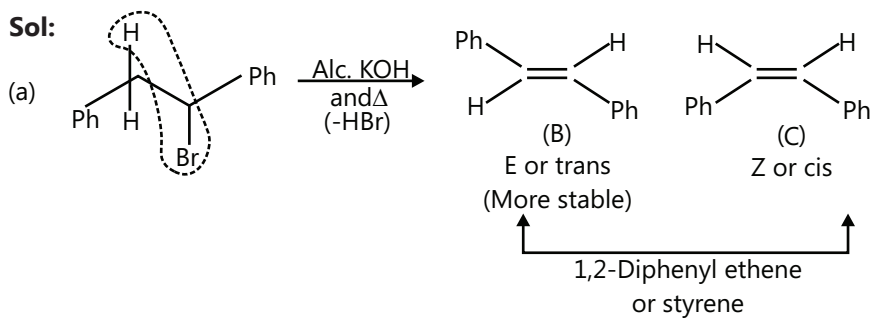
Thus compound (B) will have one OH and one Cl group; now one Me group can be added to (B) by Corey-House synthesis or Wurtz reaction of (B).



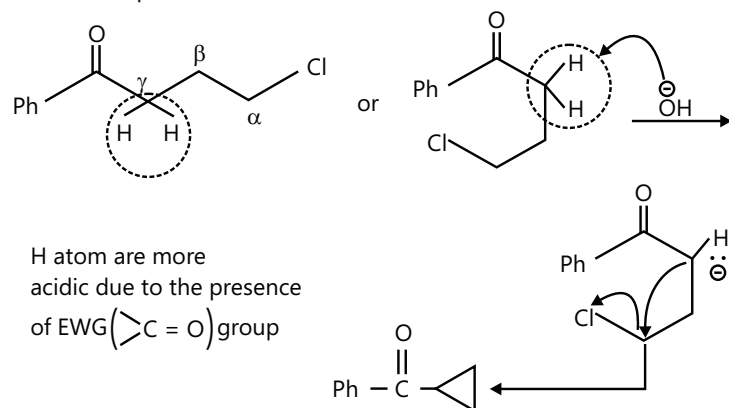
Example 2: Complete the following reactions:



Sol:



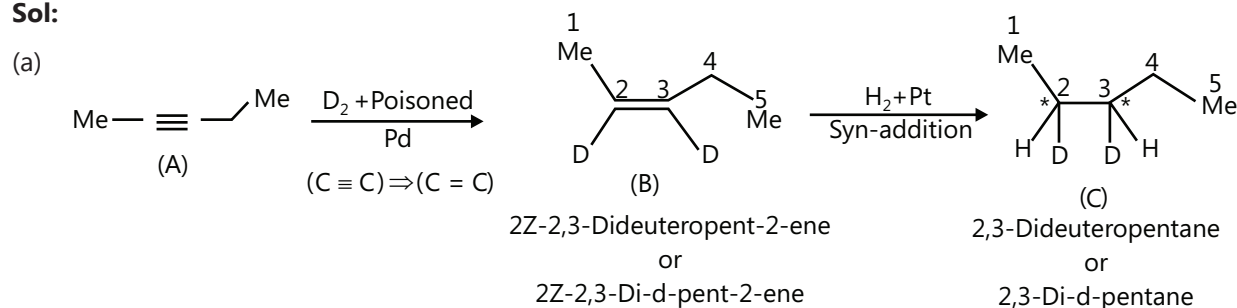
(c) It is an example of α -elimination.



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

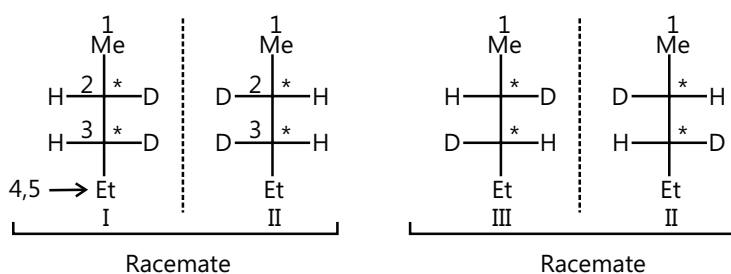
- (a) $(\text{A}) \text{Me}^1-\text{C}^2\equiv\text{C}^3-\text{C}^4\text{Me}^5 \xrightarrow{\text{D}_2 + \text{Poisoned Pd}} (\text{B}) \xrightarrow{\text{H}_2 + \text{Pt}} \text{C (No. of isomers)}$
- (b) $(\text{B}) (\text{from Problem A}) \xrightarrow{\text{Baeyer's reagent}} (\text{D}) + (\text{E}) \text{ (Colour of precipitate)}$
- (c) $(\text{B}) \xrightarrow{\text{PhCO}_3\text{H} + \text{H}_2\text{O}} (\text{D})$
- (d) $(\text{A}) \xrightarrow{\text{Na} + \text{liq. ND}_3 + \text{EtOH}} (\text{F}) \xrightarrow[\text{OSO}_4/\text{NaHSO}_3, \text{PhCO}_3\text{H}/\text{H}_2\text{O}]{\text{Alk. KMnO}_4} (\text{D})$

Sol:



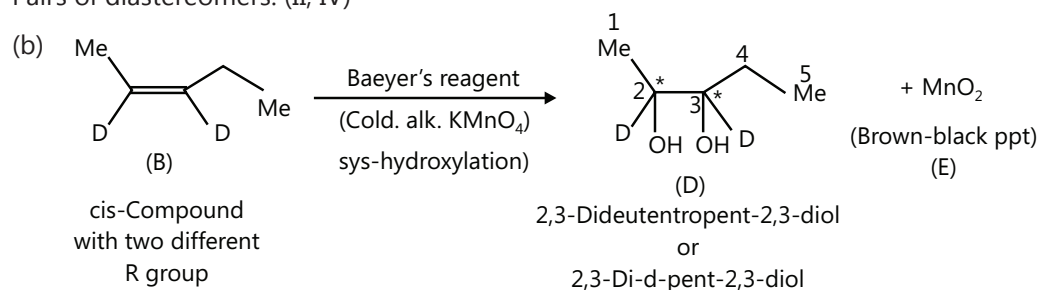
Since Addition of D_2 by $(\text{D}_2 + \text{Pd})$ is a syn addition Compound (B) is a cis compound and the addition of $\text{H}_2 + \text{Pt}$ is also syn. But (B) has two different (R) groups (Me and Et), so the product (C) will not be Meso but a racemic compound.

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

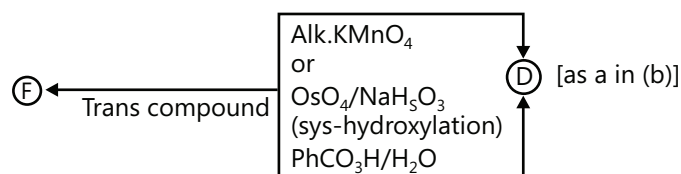
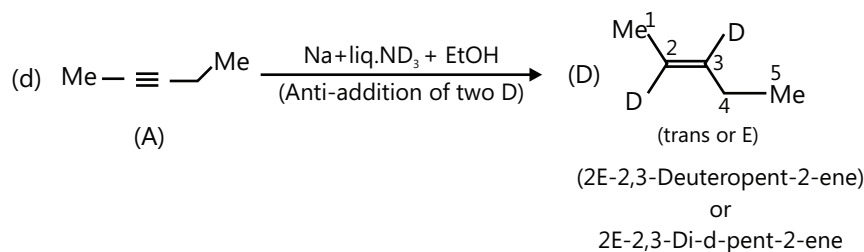
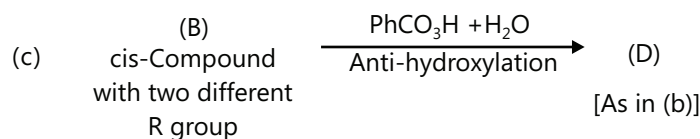


Pairs of enantiomers: I and II; III and IV (I, III); (I, IV); (II, III),

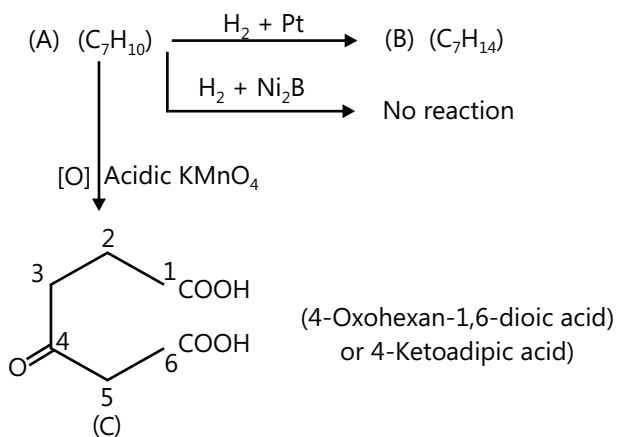
Pairs of diastereomers: (II, IV)



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



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



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

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

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

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

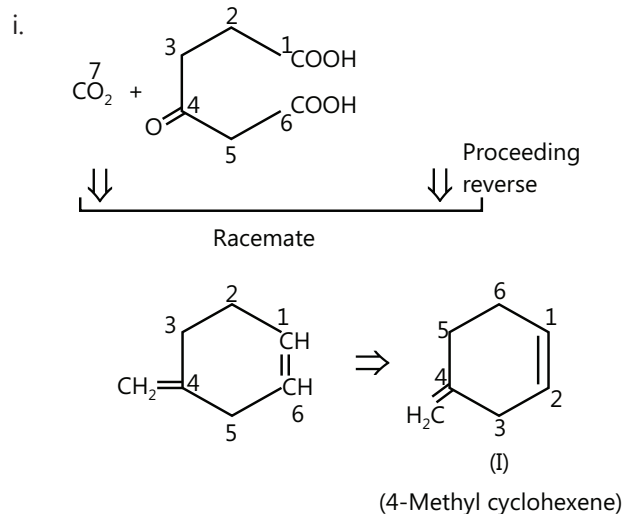
Therefore, (A) does not contain ($\text{C} \equiv \text{C}$) bond.

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 ($\text{C} = \text{C}$) bonds; hence, (A) is a diene.

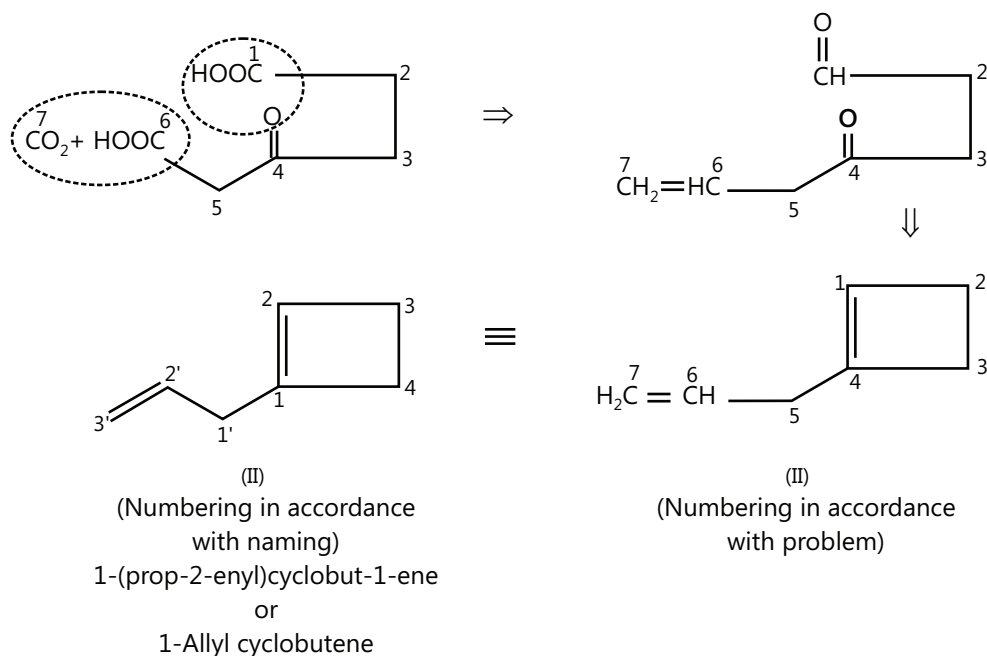
Total number of C atoms in (A)=7
 Total number of C atoms in (C)=6 $\left[\begin{array}{l} \text{one C atoms is lost as } \text{CO}_2 \end{array} \right]$

Possible structure of (A) are as follows:

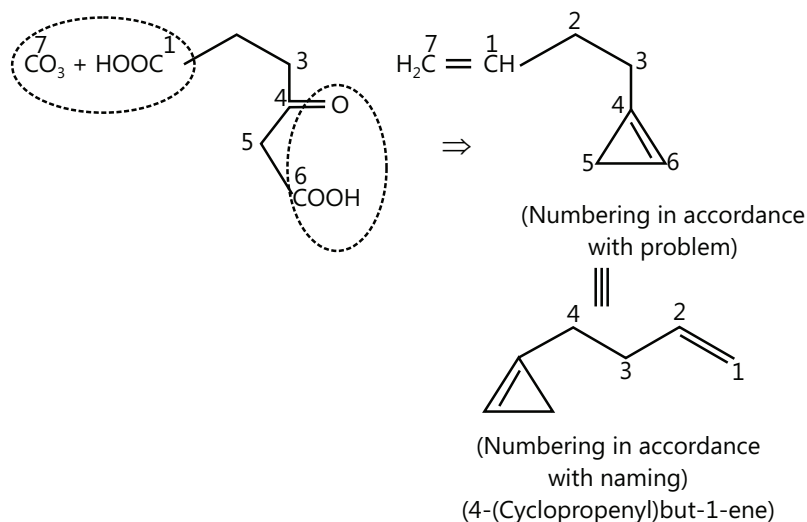


ii. Other two possibilities of the combination are as follows:

(a) ($\overset{1}{\text{COOH}}$) Groups combines with ($\overset{4}{\text{C}}=\text{H}$) group and $\overset{7}{\text{CO}_2}$ combination with ($\overset{6}{\text{COOH}}$).



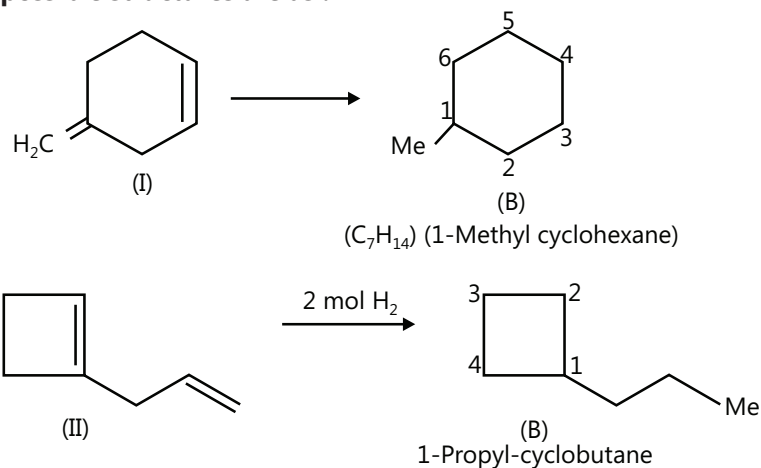
(b) $\overset{6}{\text{COOH}}$ Groups combines with (C=O) group and CO_2 is in combination with $\overset{1}{\text{COOH}}$



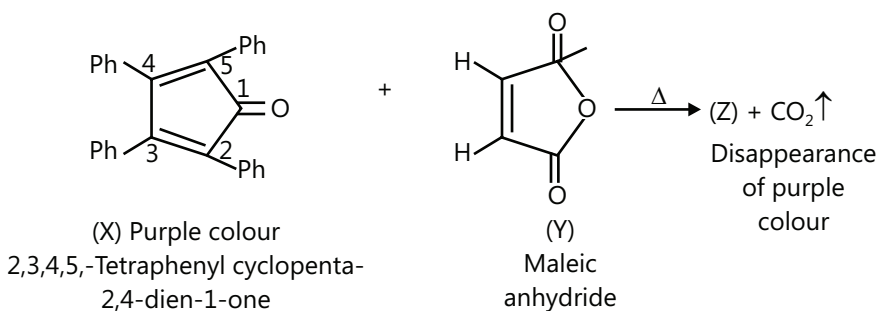
Structure III is not possible, because on hydrogenation (A) gives (B) (C_7H_{14}), i.e., it absorbs 2 mol of H_2 , whereas III will absorb 3 mol of H_2 .

Because of highly strained ring Structure III is unlikely.

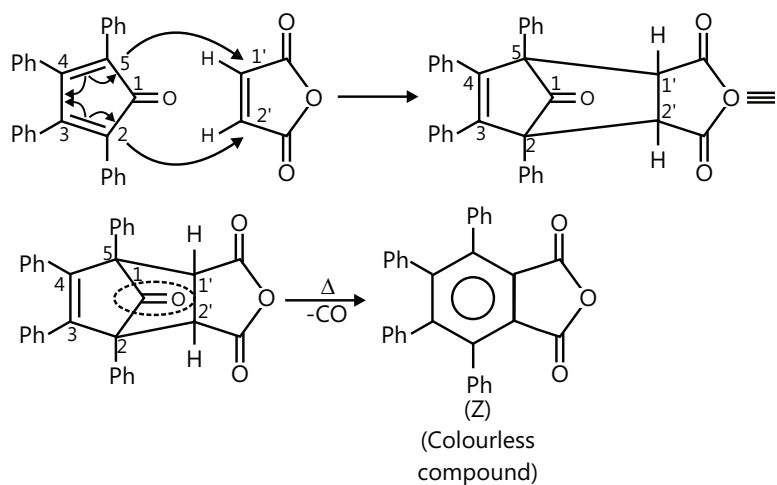
Two possible structures are as :-



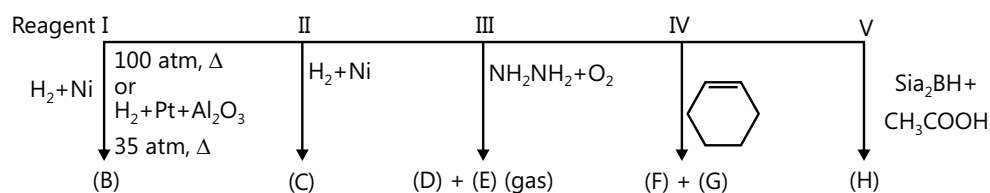
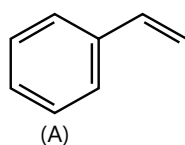
Example 5: Complete the following reactions:



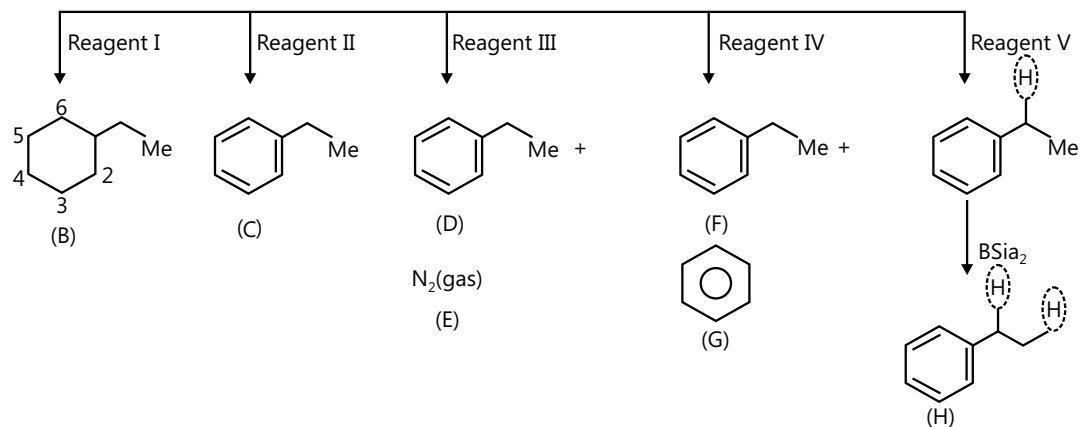
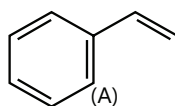
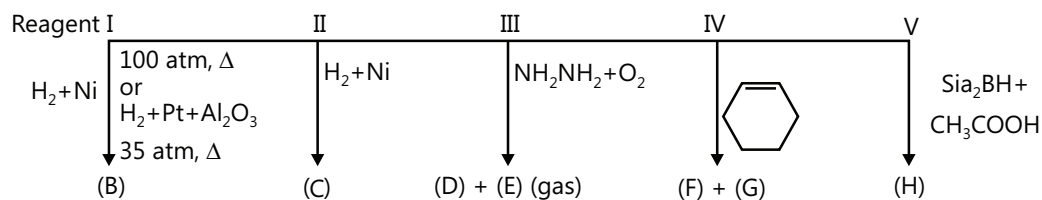
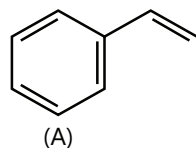
Sol: It is an example of Diels Alder reaction. The mechanism is a concerted type (bond breaking and bond making takes place simultaneously)



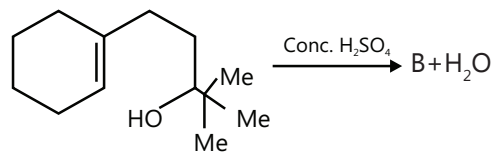
Example 6: Identify (A) to (H)



Sol:

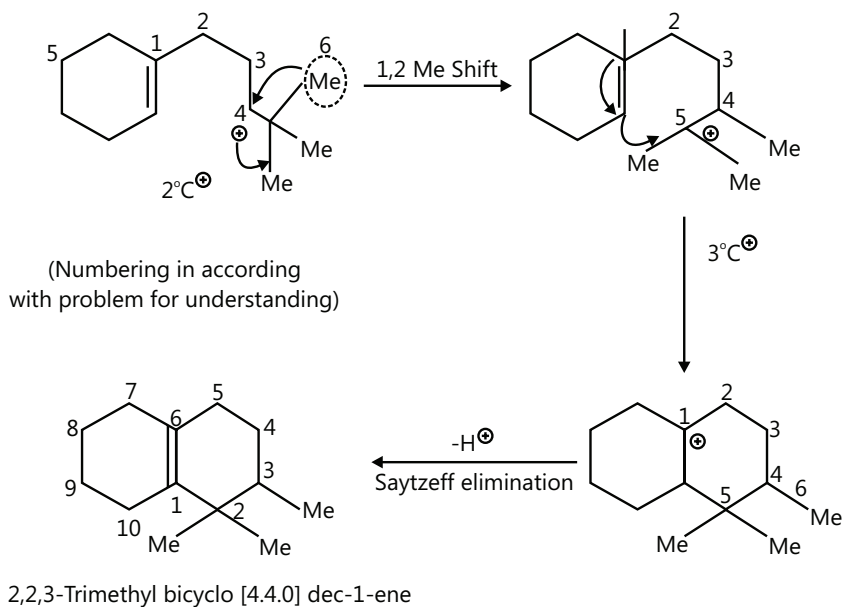


Example 7: Write the product with its mechanism.

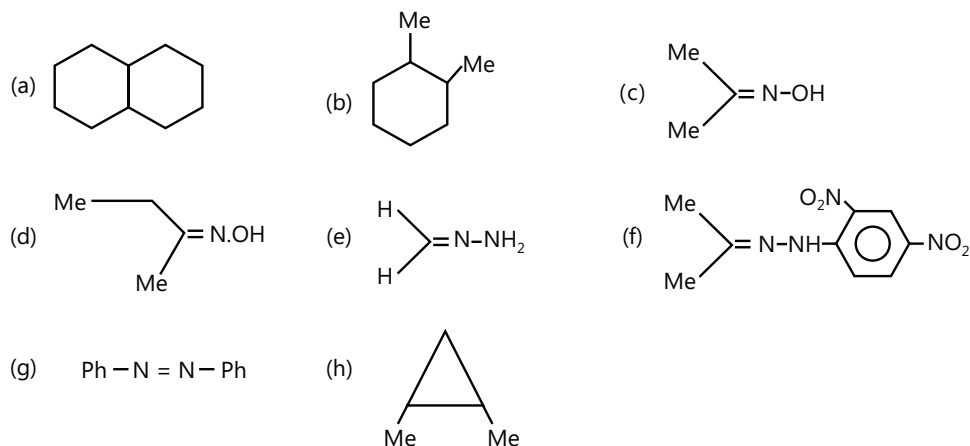


(A)

Sol:

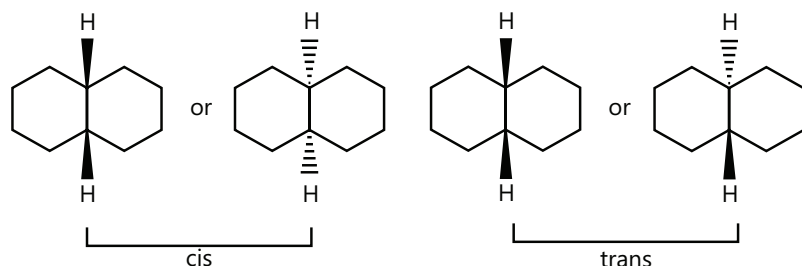


Example 8: Which of the following show G.I.?



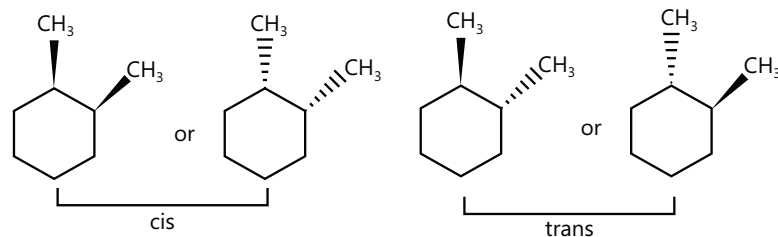
Sol: In order to show geometrical isomerism the alkene must contain different substituents i.e. the substituents on both the carbon bearing double bond must have different substituents

(a) It shows G.I.

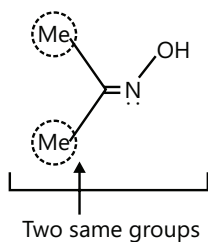


- (i) Two atoms on the dotted line (.....) means that the groups are below the plane of the ring.
- (ii) Two atoms on the bold lines (.....) means that the groups are above the plane of the ring.
- (iii) One atom on the dotted line (.....) means that one group is below and another is above the plane of the ring.

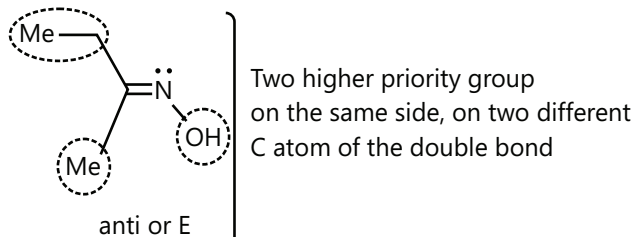
(b) It shows G.I.



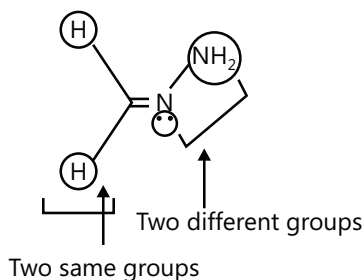
(c) It does not show G.I.



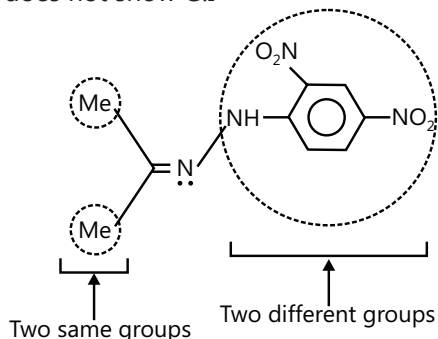
Priority of $C_2H_5 > CH_3$ and $OH > LP$ of e s



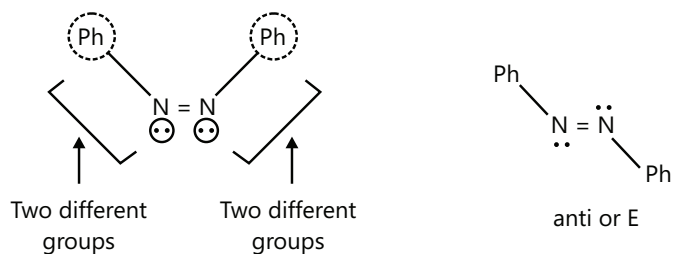
(e) It does not show G.I.



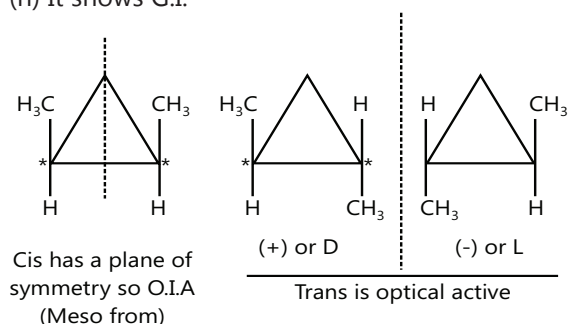
(f) It does not show G.I.



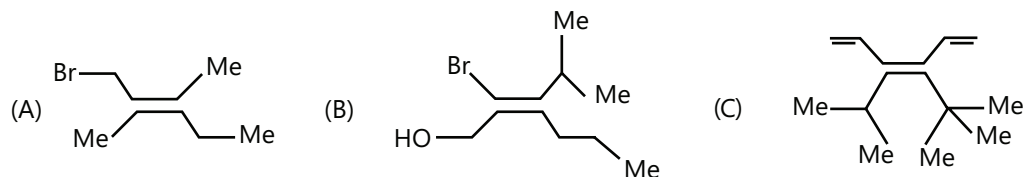
(g) It shows G.I.



(h) It shows G.I.

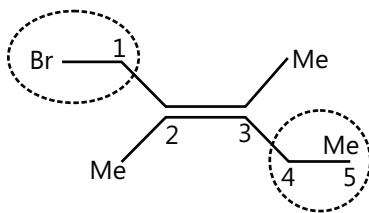


Example 9: Give IUPAC name to each of the following using E or Z designations.



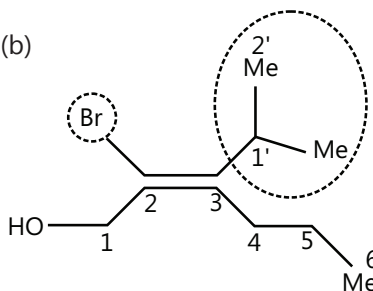
Sol:

(a)



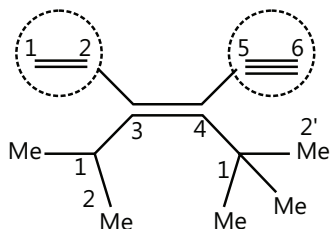
Two higher priority groups on opposite side, 1E,
1-Bromo-2,3-dimethyl pent-2-ene

(b)



Priority of $(-\text{Br}) > (-\text{CH}_2\text{OH})$ and $[(\text{CH}_3)_2\text{CH}-] > (-\text{C}_3\text{H}_7)$.
Two higher priority groups on the same side.
2Z,2-Bromo-3-(1-methyl ethyl) hex-2-en-1-ol

(c)



Priority of $\text{HC} \equiv \text{C}- > (\text{CH}_3)_3\text{C}- > \text{CH}_2=\text{CH}-\text{B} > (\text{CH}_3)_2\text{CH}-$
Two higher priority groups on the same side.
3Z,3-(1-methyl ethyl)-4-(1-1-Dimethyl ethyl)-hexa-1,3-diene-5-yne

ALKYNES

1. INTRODUCTION

1.1 Nomenclature

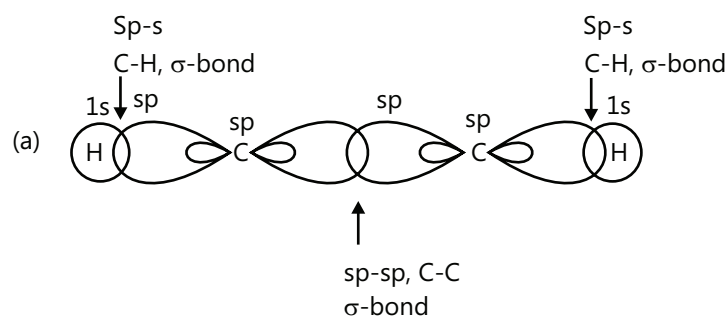
Alkynes are unsaturated hydrocarbons that contain ($\text{C}\equiv\text{C}$) bond. Their general formula is $\text{C}_n\text{H}_{2n-2}$.

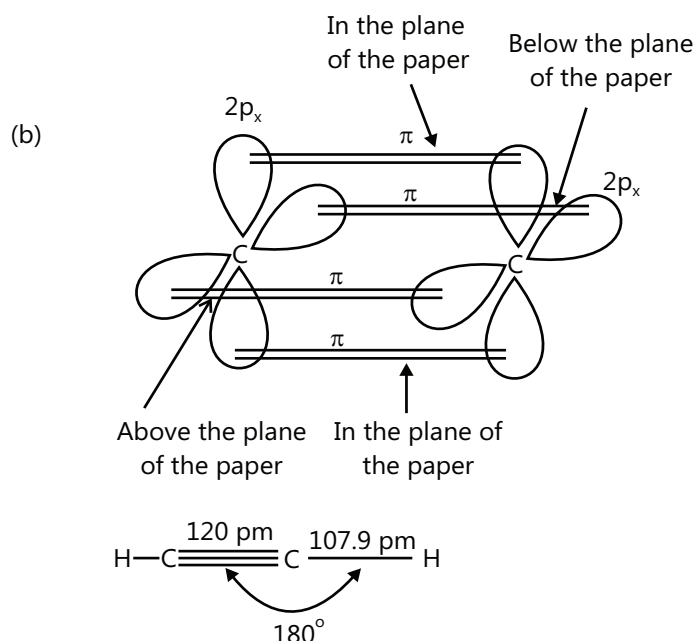
Condensed	Stick	Bond line	IUPAC name	Common or trivial name
C_2H_2	$\text{H}-\text{C}\equiv\text{C}-\text{H}$		Ethyne	Acetylene
C_3H_4	$\text{H}_3\text{C}-\text{C}\equiv\text{C}-\text{H}$		Propyne	Methylacetylene
C_4H_6	$\text{CH}_3-\text{CH}_2-\text{C}\equiv\text{CH}$ $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$		But-1-yne But-2-yne	Ethylacetylene Dimethyl acetylene
C_5H_8	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{C}-\text{H}$		3-Methyl-but-1-yne	Propylacetylene
	or 		3-Methyl-but-1-yne	Isopropyl-acetylene
	or $\text{CH}_3-\text{CH}_2-\text{C}\equiv\text{C}-\text{CH}_3$		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 -hybridized 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 1s -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.

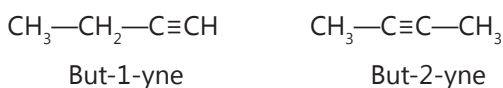




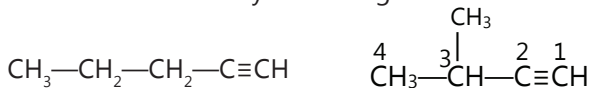
Carbon-carbon triple bond consists of one strong σ -bond and two weak π -bonds. The total strength of $\text{C}\equiv\text{C}$ bond in ethyne is 823 kJ mol^{-1} . It is stronger than the $\text{C}=\text{C}$ bond of ethene (599 kJ mol^{-1}) and $\text{C}-\text{H}$ bond of ethane (348 kJ mol^{-1}). Further, 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 $\text{C}=\text{C}$ (134 pm) and $\text{C}-\text{C}$ (154 pm).

1.3 Isomerism in Alkynes

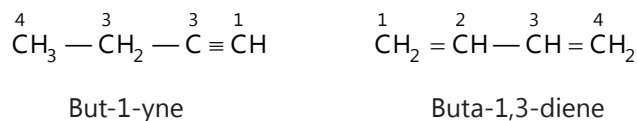
- (i) Position isomerism. The first two members, i.e., ethyne and propyne exist in one form only. However, butyne and higher alkynes exhibit position isomerism due to the different position of the triple bond on the carbon chain. For example,



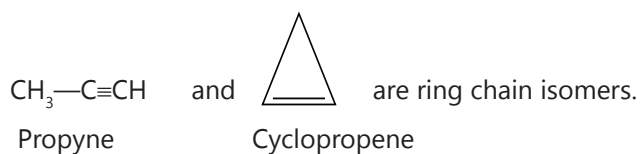
- (ii) Chain isomerism. Alkynes having five or more carbon atoms show chain isomerism.



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



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

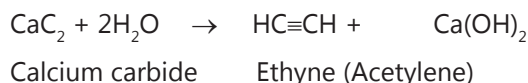


2. PREPARATION OF ALKYNES

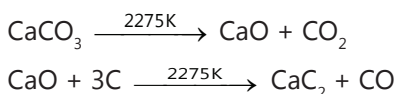
2.1 From Calcium Carbide

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.



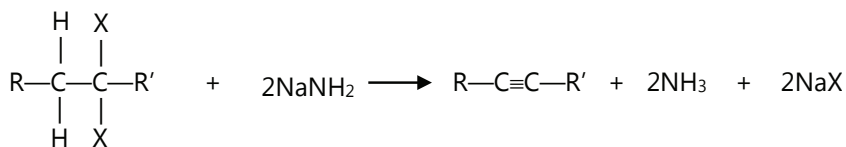
Calcium carbide needed for the purpose is manufactured by heating limestone (calcium carbonate) with coke in an electric furnace at 2275 K.



- 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.

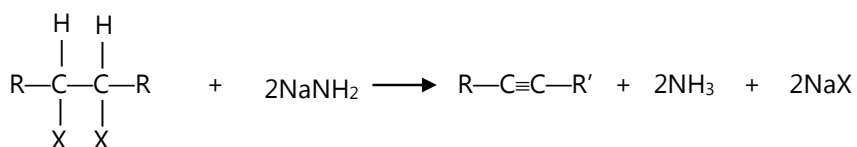
2.2 Double Dehydrohalogenation of Dihalides

Double dehydrohalogenation of a geminal dihalide



Geminal dihalide Sodium amide Alkyne Ammonia Sodium halide

Double dehydrohalogenation of a vicinal dihalide



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.

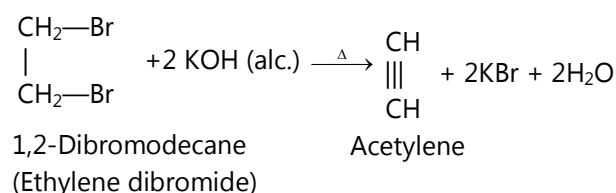
- $$(CH_3)_3CCH_2CHCl_2 \xrightarrow[NH_3]{3NaNH_2} (CH_3)_3CC\equiv CNa \xrightarrow{H_2O} (CH_3)_3CC\equiv CH$$

1,1-Dichloro-3,3-Dimethylbutane Sodium salt of alkyne product (not isolated) 3,3-Dimethyl-1-butyne (56-60%)
- $$CH_3(CH_2)_2CHCH_2Br \xrightarrow[NH_3]{3NaNH_2} CH_3(CH_2)_7C\equiv CNa \xrightarrow{H_2O} CH_3(CH_2)_7C\equiv CH$$

|
Br

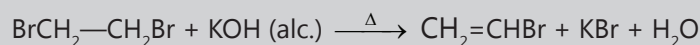
1,2-Dibromodecane Sodium salt of alkyne Product (not isolated) 1-Decyne (54%)

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 solution of KOH

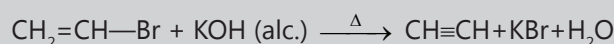


PLANCESS CONCEPTS

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



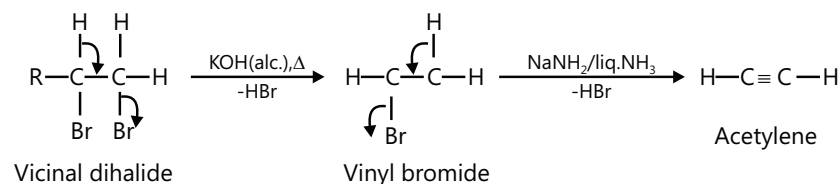
Ethylene dibromide Vinyl bromide



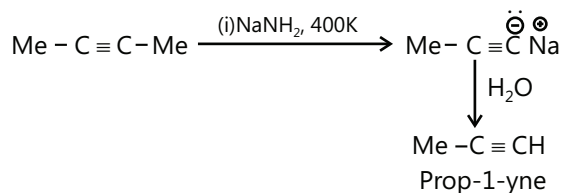
Vinyl bromide Acetylene

Aman Gour (JEE 2012, AIR 230)

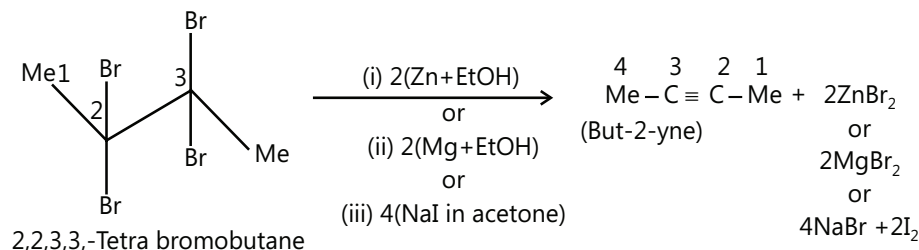
Explanation: In ethylene dibromide, Br is present on a saturated carbon atom. Therefore, Like alkyl halides, it is a reactive molecule. Consequently, on heating with alcoholic KOH, it readily eliminates a molecule of HBr to form vinyl bromide in good yield. In contrast, due to the presence of Br on a 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_3 is usually used. Thus, dehydrohalogenation of ethylene dibromide to acetylene is preferably carried out in the following two stages.



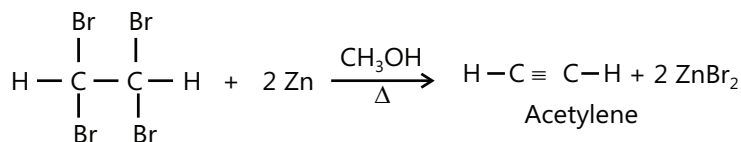
With a strong base (NH_2^-), isomerisation also takes place to give terminal alkyne.



Dehalogenation of tri/tetra halides



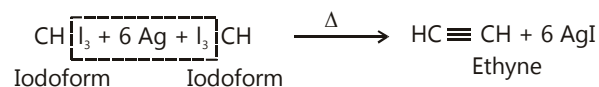
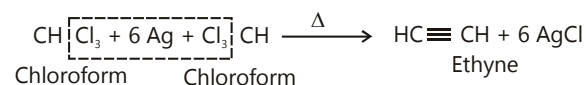
3. By dehalogenation of tetrahalides.: Tetrahaloalkanes when heated with zinc dust in methanol undergo dehalogenation to yield alkynes. For example



1,1,2,2-Tetrabromoethane

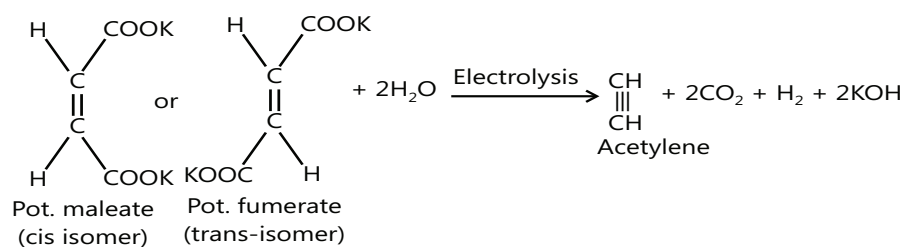
2.4 Dehalogenation of Haloforms

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

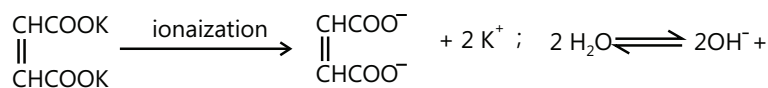


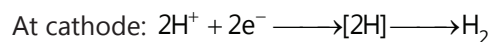
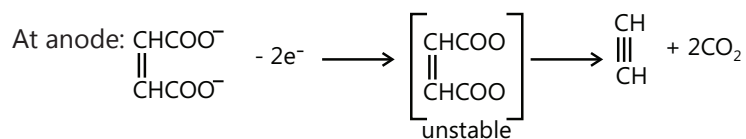
2.5 Kolbe's Electrolytic Reaction

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,



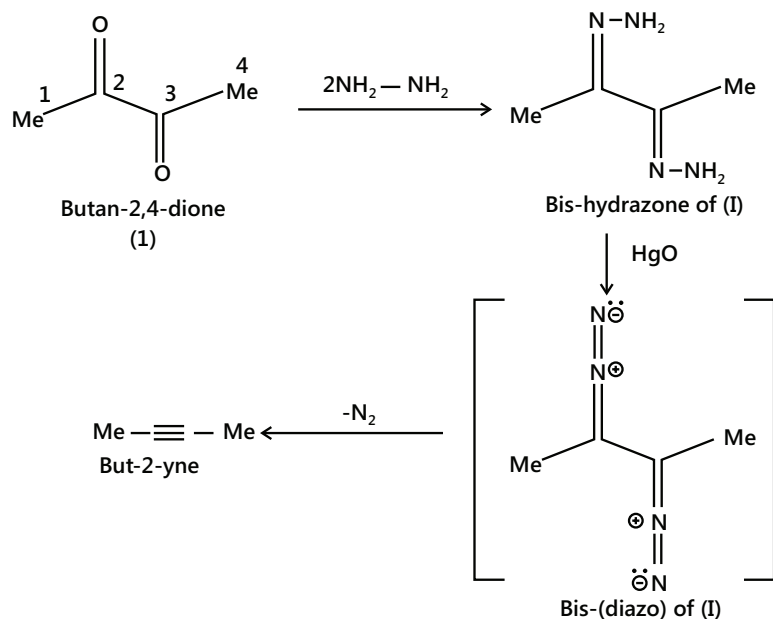
This reaction is called Kolbe's electrolytic reaction and is believed to occur by the following steps:



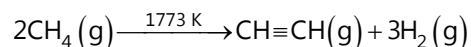


2.6 From α -diketo

α -Diketone reacts with hydrazine ($\text{NH}_2 - \text{NH}_2$) to give bis-hydrazone which on oxidation with HgO gives unstable bis(diazo) compound which decomposes to give alkyne.



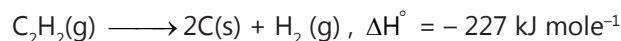
2.7 Industrial Method



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

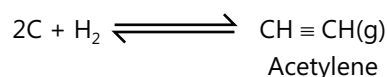
$\Delta n = n_p - n_r = 4 - 2 = 2$ mol, and this causes a significant increase in ΔS . At this high temperature, the $T\Delta S$ term in the equation $\Delta G = \Delta H - T\Delta S$ predominates, making $\Delta G = -ve$, although $\Delta H = +ve$.

But ΔH_f° for $\text{C}_2\text{H}_2 = +227 \text{ kJ mol}^{-1}$ shows that acetylene is thermodynamically unstable, explodes readily, and gets converted into its elements.



2.8 Berthelot Synthesis

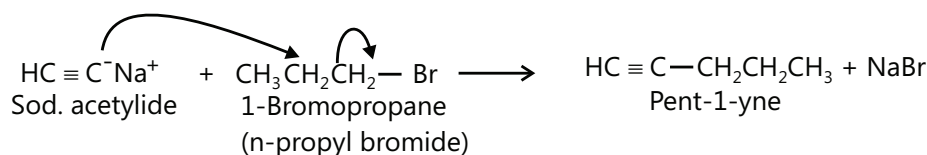
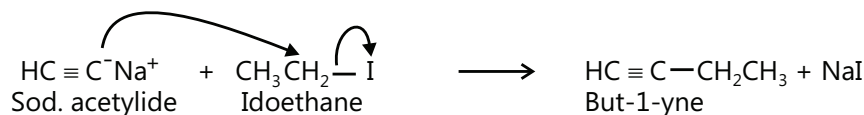
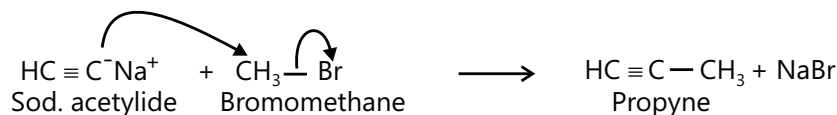
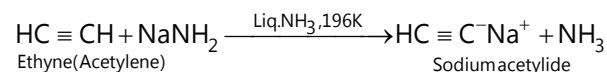
Mearcellin Berthelot synthesized acetylene from its elements (carbon and hydrogen) by striking an electric arc between two electrodes in an atmosphere of H_2 gas.



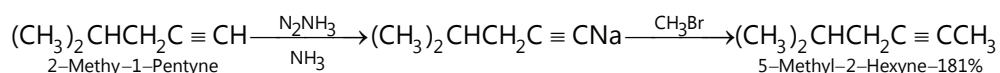
2.9 Higher Alkynes from Acetylene

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.

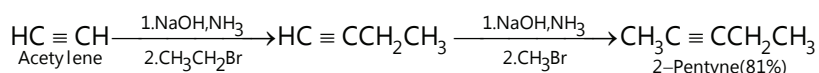
For example:



An analogous sequence usually terminal alkynes as starting material yields alkynes of the type $\text{RC} \equiv \text{CR}'$.



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



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: $\text{C}-\text{H}_{\text{sp}^3} > \text{C}-\text{H}_{\text{sp}^2} > \text{C}-\text{H}_{\text{sp}}$

Bond Strength order: $\text{C}-\text{H}_{\text{sp}} > \text{C}-\text{H}_{\text{sp}^2} > \text{C}-\text{H}_{\text{sp}^3}$

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.

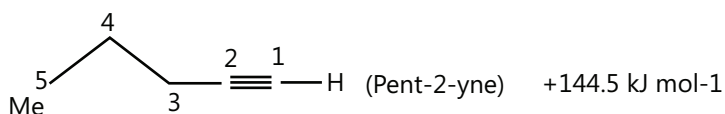
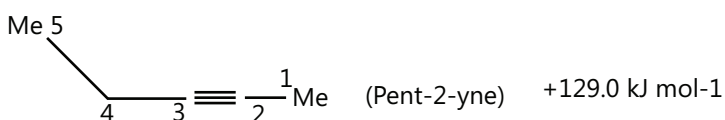
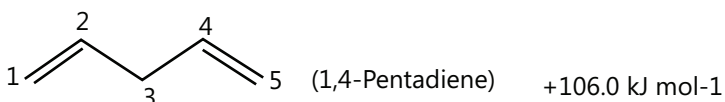
The dipole moment of alkyne is greater than those in alkene because $(\text{C} \equiv \text{C})$ sp bond is more polarized than $(\text{C} = \text{C})$ sp^2 bond: this is because C with more s character is more electronegative.

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 $0.69 - 0.77 \text{ g/cm}^3$.
- (viii) **Stability:** Alkynes are less stable than isomeric dienes as is evident from their heat of formation (ΔH_f°) values.



- (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.

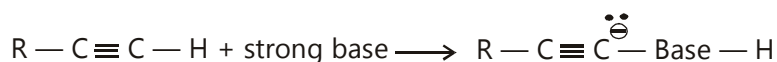
Catalytic hydrogenation, however, is an exception: Alkenes are adsorbed on the surface of catalyst only when the plane of π -bond approaches perpendicularly. In alkynes because of the cylindrical nature of π -bonds, approach by hydrogen along the axis of the cylinder is more effective and thus transition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

(x) **Acidity of alkynes:**

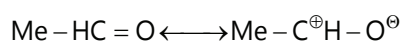
Terminal alkynes are more acidic than alkenes because alkyne C-atoms are sp hybridized and electrons in an s -orbital are more tightly held than in a p -orbital also s -electrons are closer to the nucleus.

Furthermore, since the sp orbital has more s character (50% s) than sp^2 (33% s) or sp^3 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.



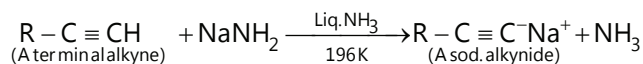
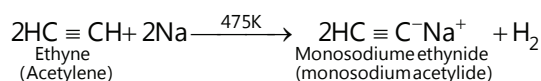
As a rule, as the s character decreases from sp to sp^2 to sp^3 hybridised C atom, the acidic character of hydrocarbons decreases in the following order.



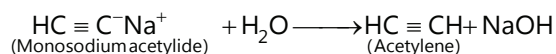
4. REACTIONS OF ALKYNES

4.1 Acidic Character

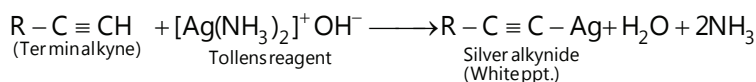
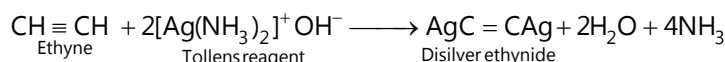
- (i) **Formation of alkali metal acetylides:** Ethyne and other terminal alkynes (Alkynes in which the triple bond is at the end of the carbon chain) or 1-alkynes react with strong bases such as sodium metal at 475 K or sodamide in liquid ammonia at 196 K to form sodium acetylides with evolution of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



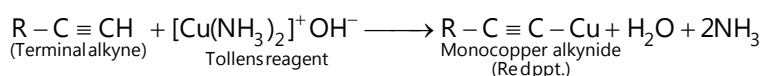
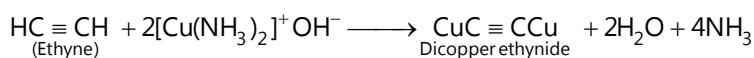
During these reactions, the acetylenic hydrogen is removed as a proton to form stable carbanions (acetylide ions). Sodium acetylide is decomposed by water regenerating acetylene. This shows that water is a stronger acid than acetylene and thus displaces acetylene from sodium acetylide.



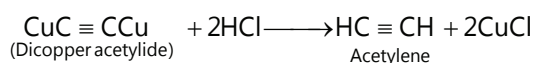
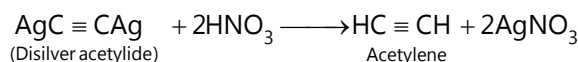
- (ii) **Formation of heavy metal acetylides:** Acetylenic hydrogens of alkynes can also be replaced by heavy metal ions such as Ag^+ and Cu^+ ions. For example, when treated with ammoniacal silver nitrate solution (Tollens's reagent), alkynes form a white precipitate of silver acetylides.



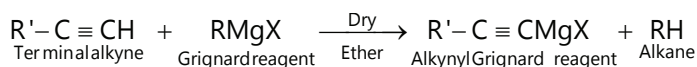
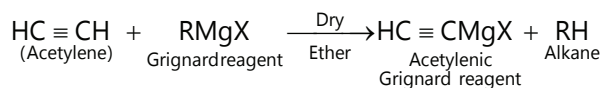
Similarly, with ammoniacal cuprous chloride solution, terminal alkynes form red ppt. of copper acetylides.



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



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

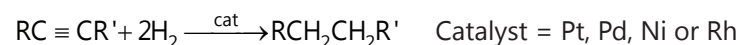


Alkynyl Grignard reagents like usual Grignard reagents can be used to prepare a variety of organic compounds.

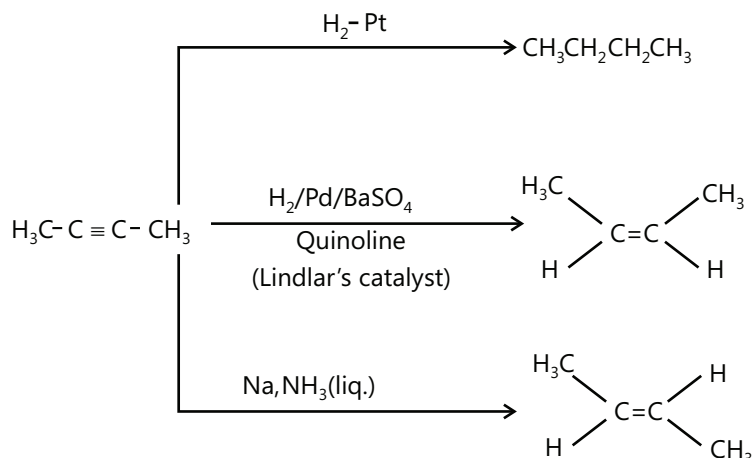
Importance: The formation of metal acetylides can be used:

- For the separation and purification of terminal alkynes from non-terminal alkynes, alkanes and alkenes.
- To distinguish terminal alkynes from non-terminal alkynes or alkenes.

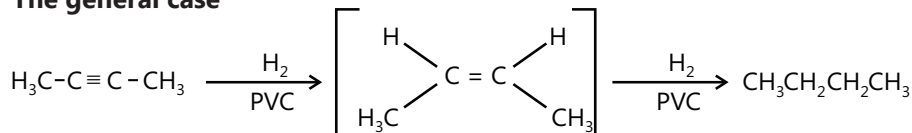
4.2 Hydrogenation / Reduction



Alkene is an intermediate



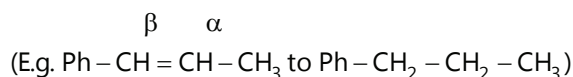
The general case



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

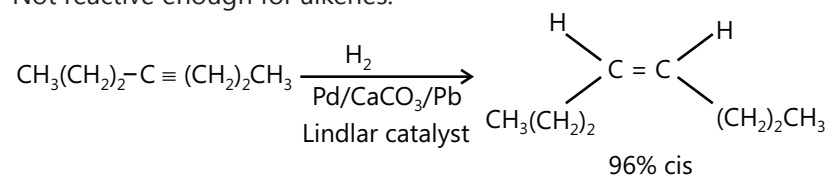
But the reaction can be stopped at the alkene stage by using the following reagents.

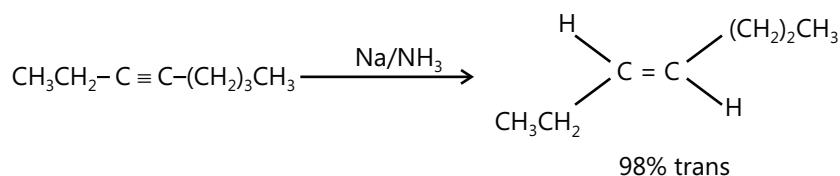
- $\text{H}_2 + \text{Pd} + \text{BaSO}_4 + \text{S}$ or quinoline in boiling xylene (called Lindlar's catalyst). In this case, reaction proceeds via syn addition of H_2 .
- $\text{H}_2 + \text{P-2}$ or Brown catalyst ($\text{H}_2 + \text{Ni} + \text{B}$) or ($\text{H}_2 + \text{Ni}_2\text{B}$). It also proceeds via syn addition of H_2 .
- Alkali metals ($\text{Na}, \text{K}, \text{Cs}$) + liq. NH_3 and $\text{C}_2\text{H}_5\text{OH}$ (It is called Birch reduction). It proceeds via anti-addition of H_2 .
- LiAlH_4 (LAH). It reduces $(\text{C} \equiv \text{C})$ to $(\text{C} = \text{C})$ via anti addition of H_2 ; does not reduce $(\text{C} = \text{C})$ to $(\text{C} - \text{C})$ bond; reduces $(\text{C} = \text{C})$ to $(\text{C} - \text{C})$ only when the phenyl group is attached to the $-\text{C}$ atom of the double bond.



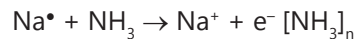
Reduction of alkynes to (Z) – alkenes

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.



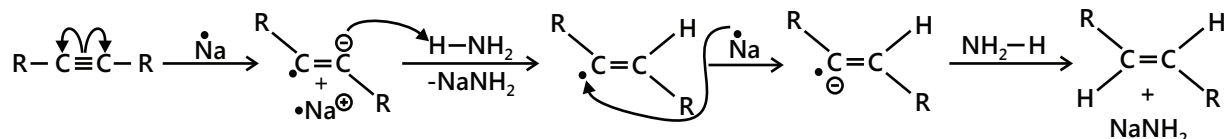


Reduction of alkynes to (E) – alkenes. Reaction via Na radical dissolved in liquid NH_3 .



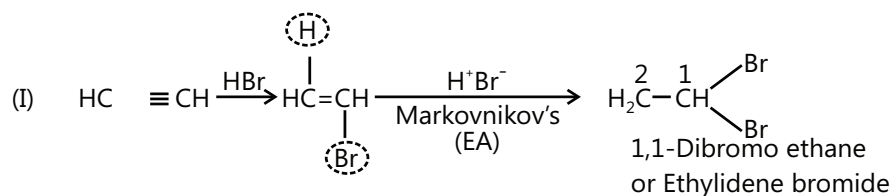
Solvated electron

Mechanism of Na/NH_3 reductions: $\text{Na}^+ \xrightarrow{-33^\circ\text{C}} \text{Na}^+ + \text{NH}_3(\text{e}^-)$



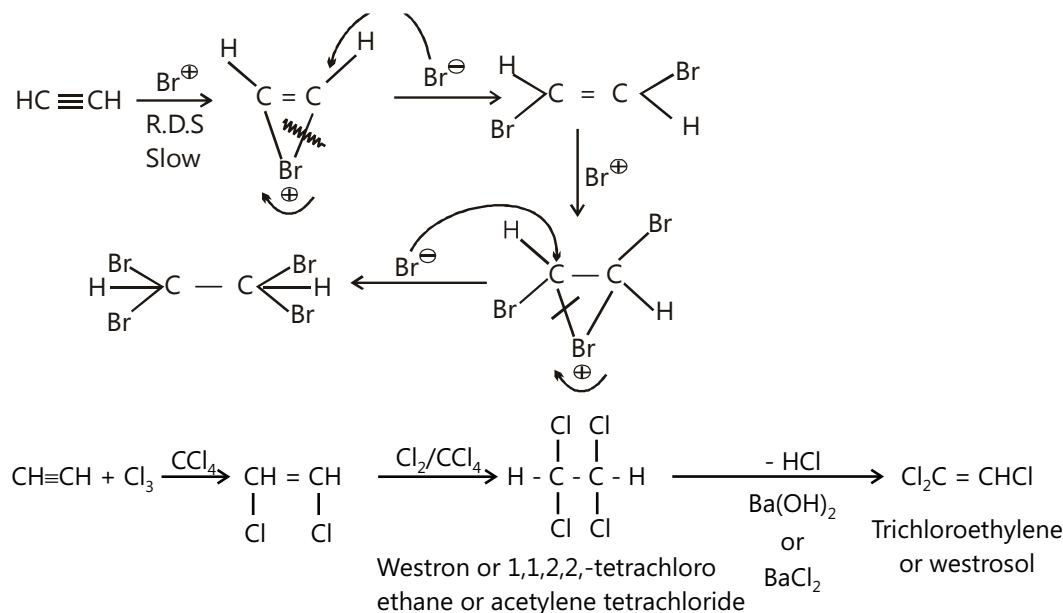
4.3 Addition of X_2

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)



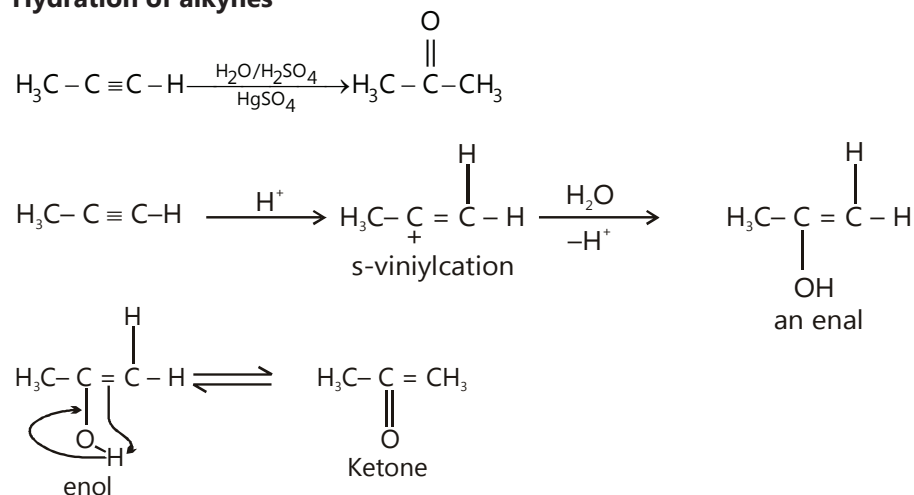
Mechanism:

Like alkenes it proceeds via the formation of intermediate cyclic bromonium ion. First, electrophile ($\text{Br}^\oplus$) adds and then the addition of nucleophile ($\text{Br}^\ominus$) from anti-position takes place. That is why this reaction is called EA (electrophilic addition) reaction. The reaction is stereospecific (attack by electrophile in a specific manner).

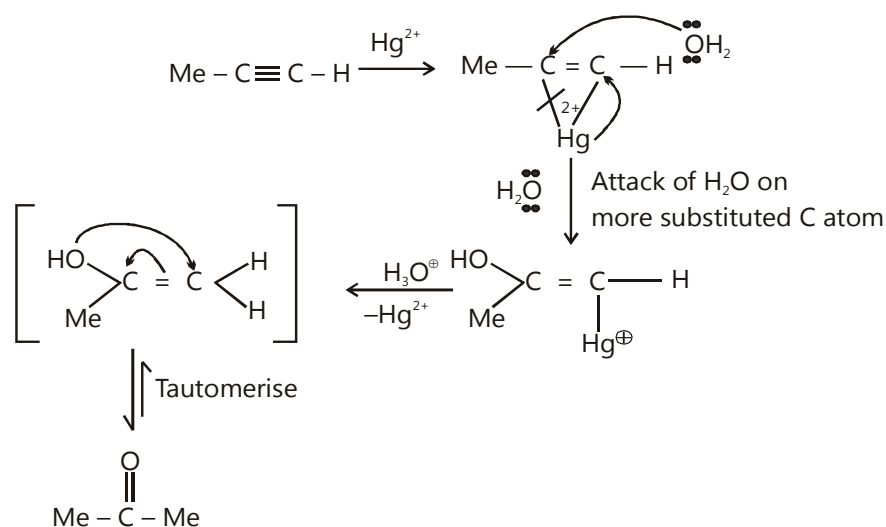


4.4 Addition of Water

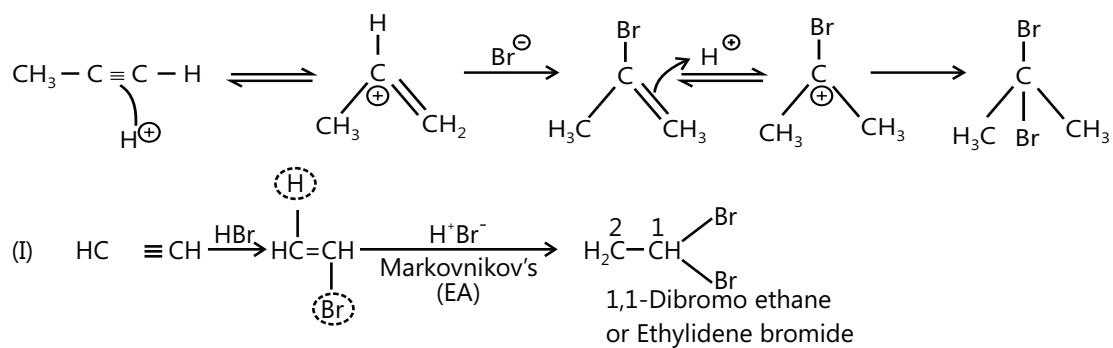
Hydration of alkynes

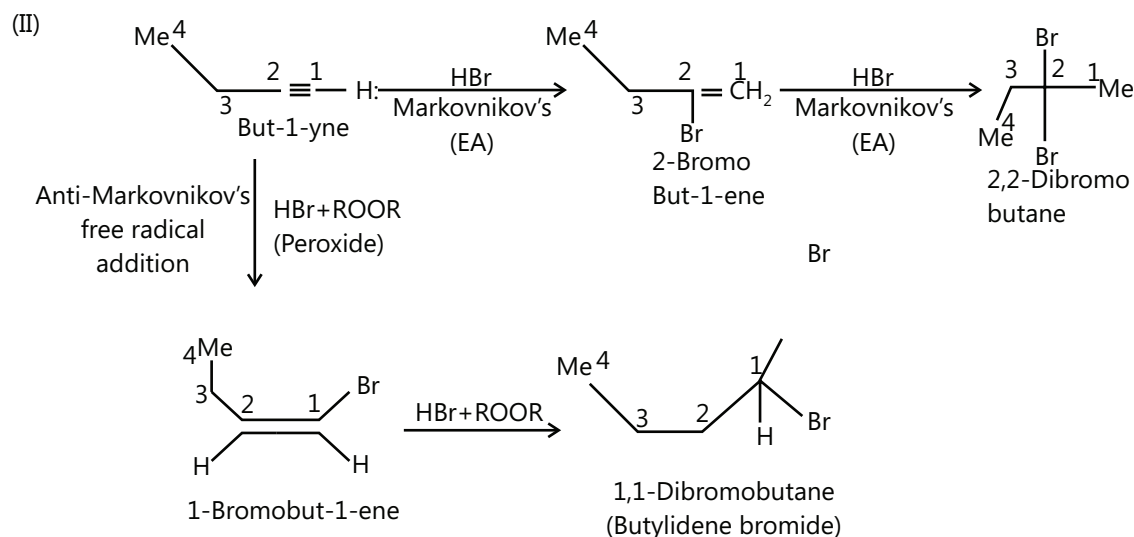


(Oxymercuration-demercuration of triple bond)



4.5 Addition of HX





PLANCESS CONCEPTS

The order of reactivity of HX is $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$

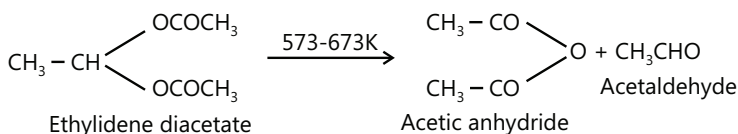
Aishwarya Karnawat (JEE 2012 AIR 839)

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.

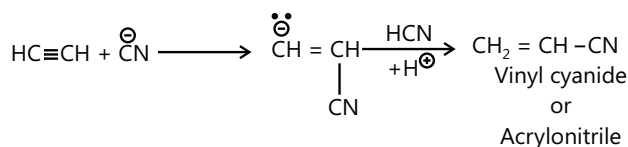


Vinyl acetate is used for the manufacture of vinyl resin. Ethylidene diacetate, when heated rapidly to 573-673K, gives acetic anhydride and acetaldehyde.

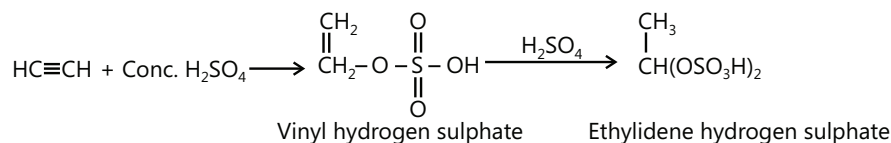


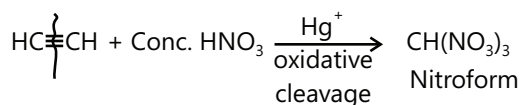
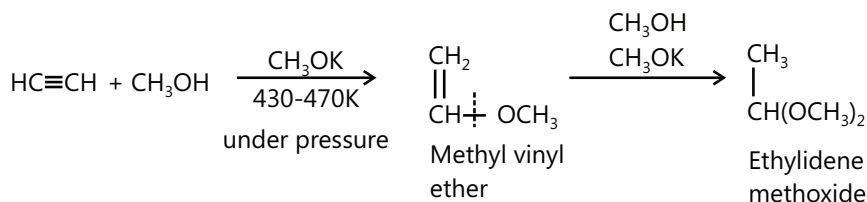
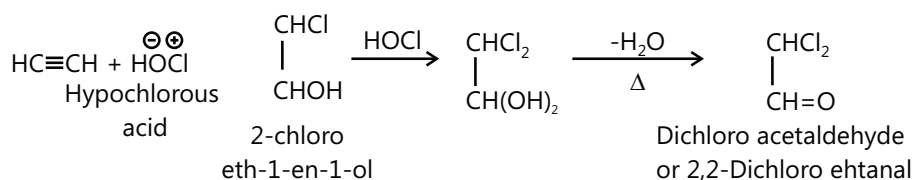
4.7 Addition of HCN

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



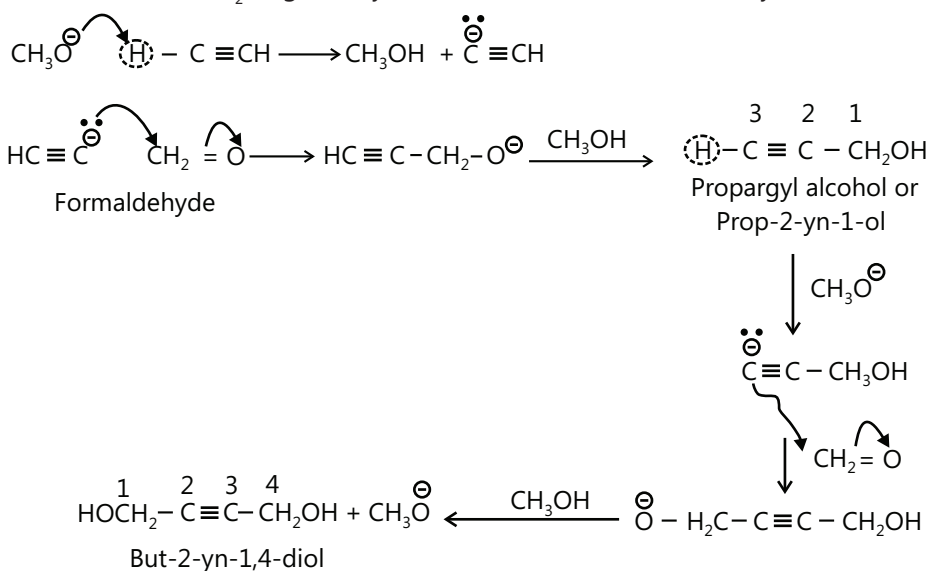
4.8 Addition to Other Compounds





4.9 Ethyne + Methanal

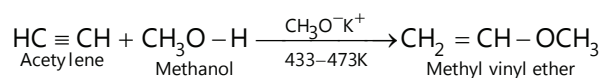
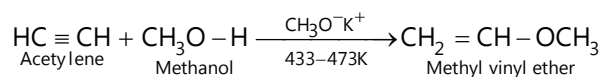
The addition of ethyne to unsaturated link like ($>\text{C}=\text{O}$) is called ethinylation. Acetylene or terminal alkyne containing $\equiv\text{CH}$ (a methine H-atom) reacts with a carbonyl group ($>\text{C}=\text{O}$) in the presence of sodium or potassium alkoxide (RONa or ROK) or NaNH_2 to give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

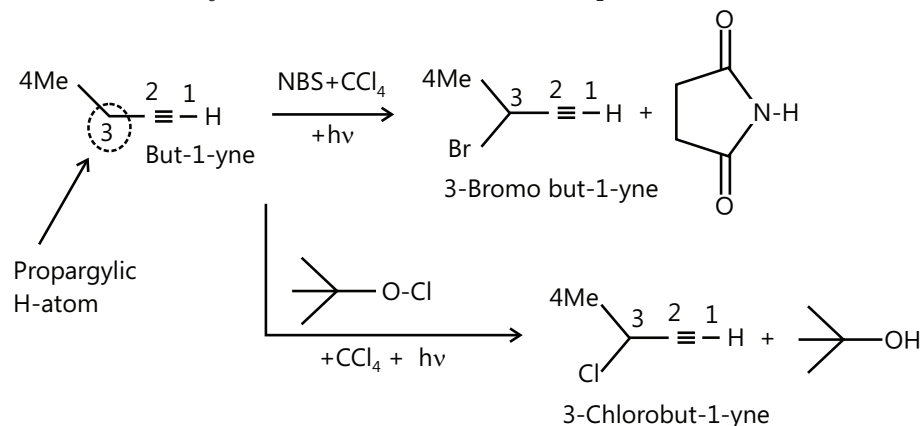
For example, when acetylene is passed into methanol at 433-473 K in presence of a small amount (1-2%) of potassium methoxide under pressure, methyl vinyl ether is formed.



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 hypochlorite), and Cl_2 at 500°C .

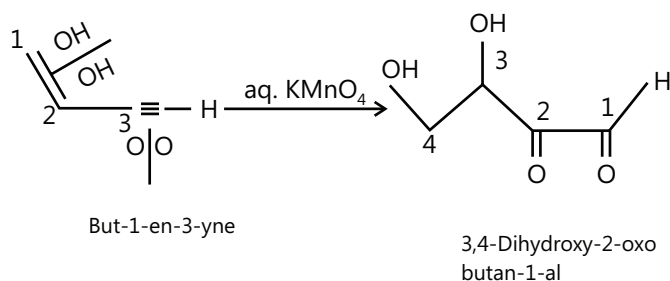
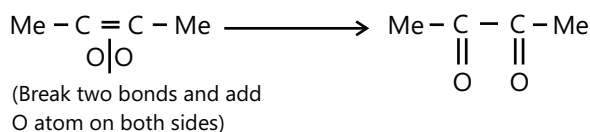
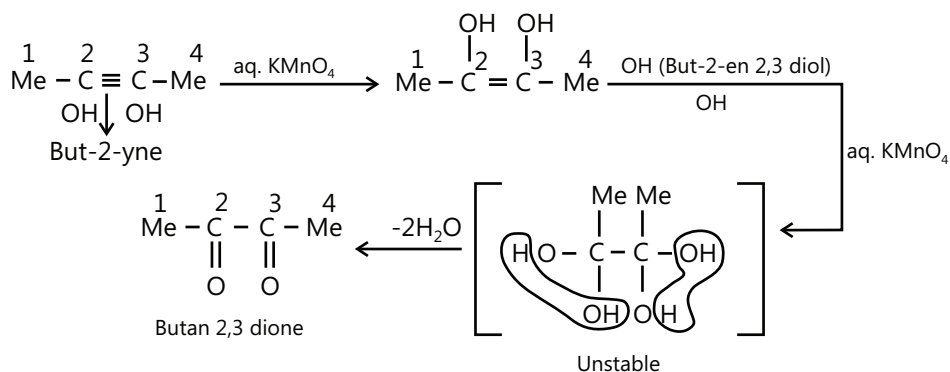


Reaction proceeds via free radical mechanism to give propargylic radical, which is stabilized by resonance via extended π -bonding.

4.12 Hydroxylation of Alkynes

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

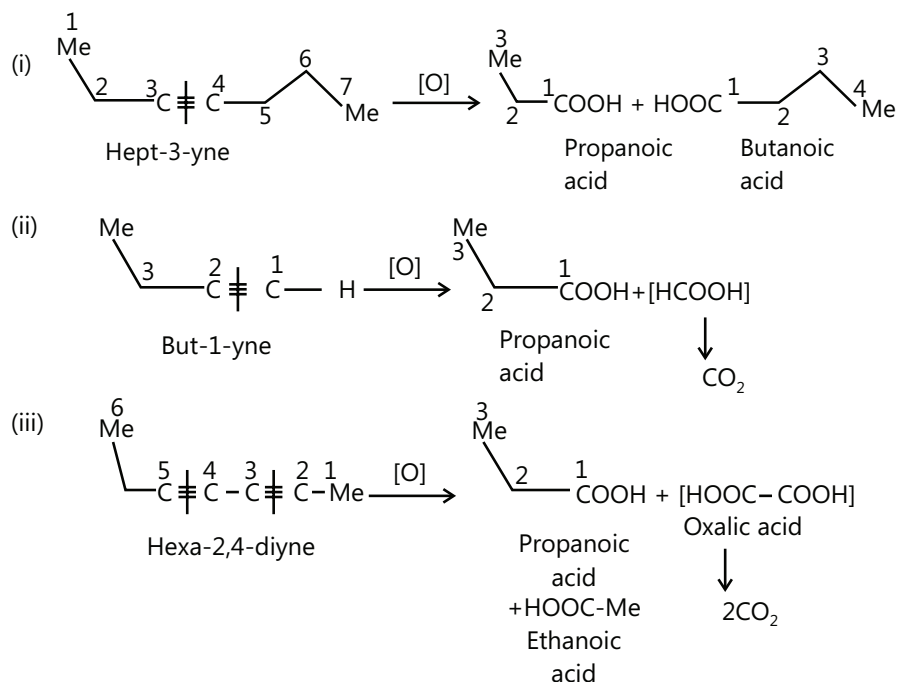
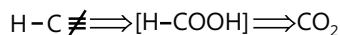
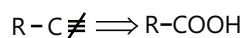
Pink colour of KMnO_4 is discharged and brown black precipitate of MnO_2 is obtained. This reaction converts alkynes first to enediols and then further gives tetraols, which being unstable lose H_2O to give diketones.



4.13 Oxidation Reactions

4.13.1 Oxidative Cleavage

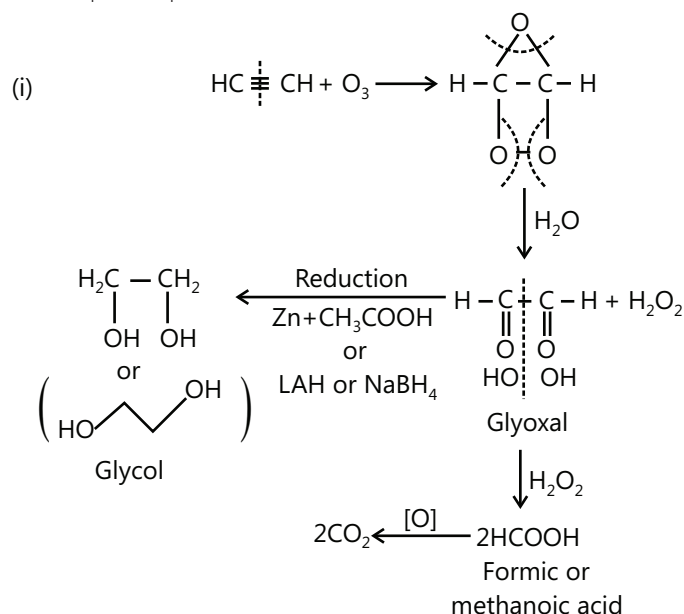
(a) Alkynes are oxidatively cleaved in alkaline or acidic conditions at higher temperature, as mentioned.



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.

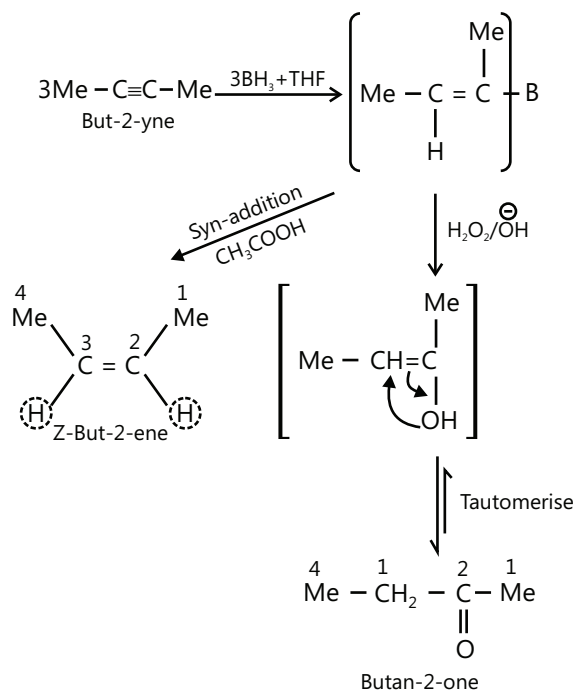


Terminal alkynes give HCOOH as one of the products which is further oxidized to CO_2

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.

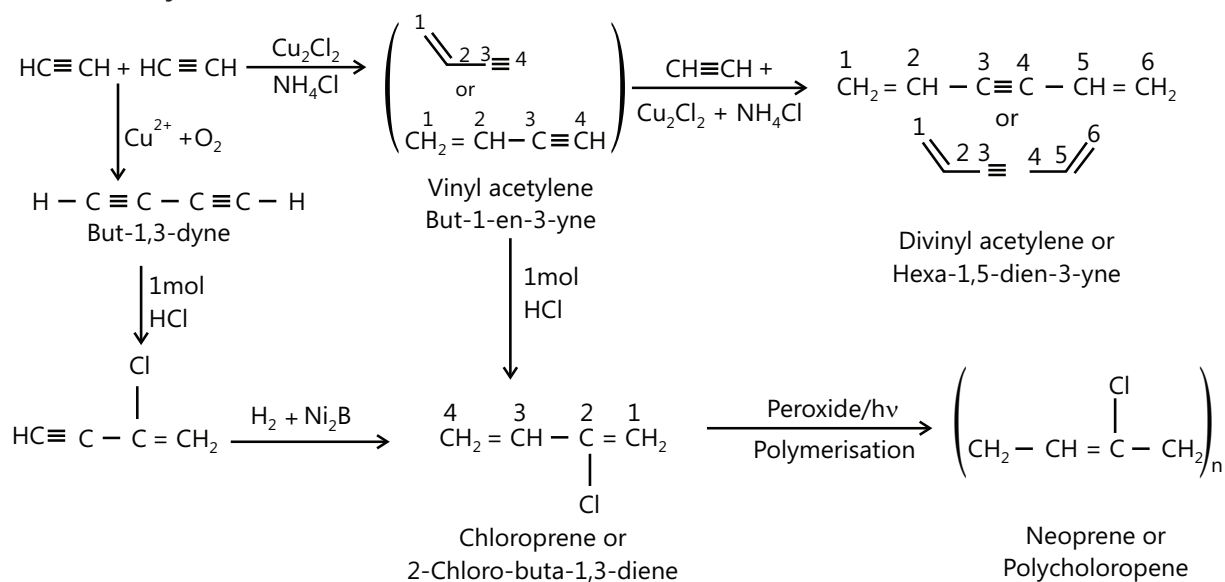
4.15 Hydroboration of Alkynes

- 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).

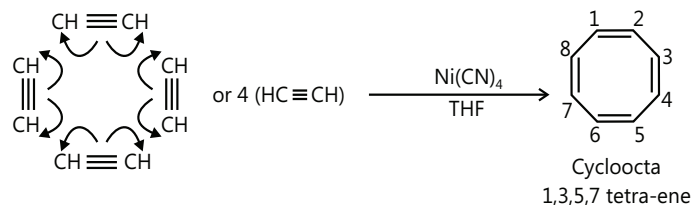
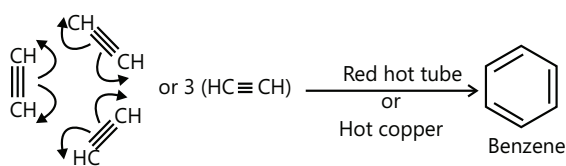


4.16 Polymerisation

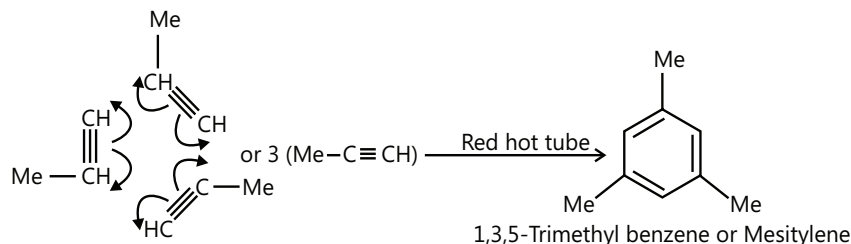
1. Linear Polymerisation



2. Cyclic Polymerisation

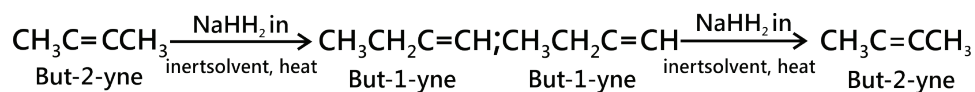


3. Propyne



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.



Uses of alkynes

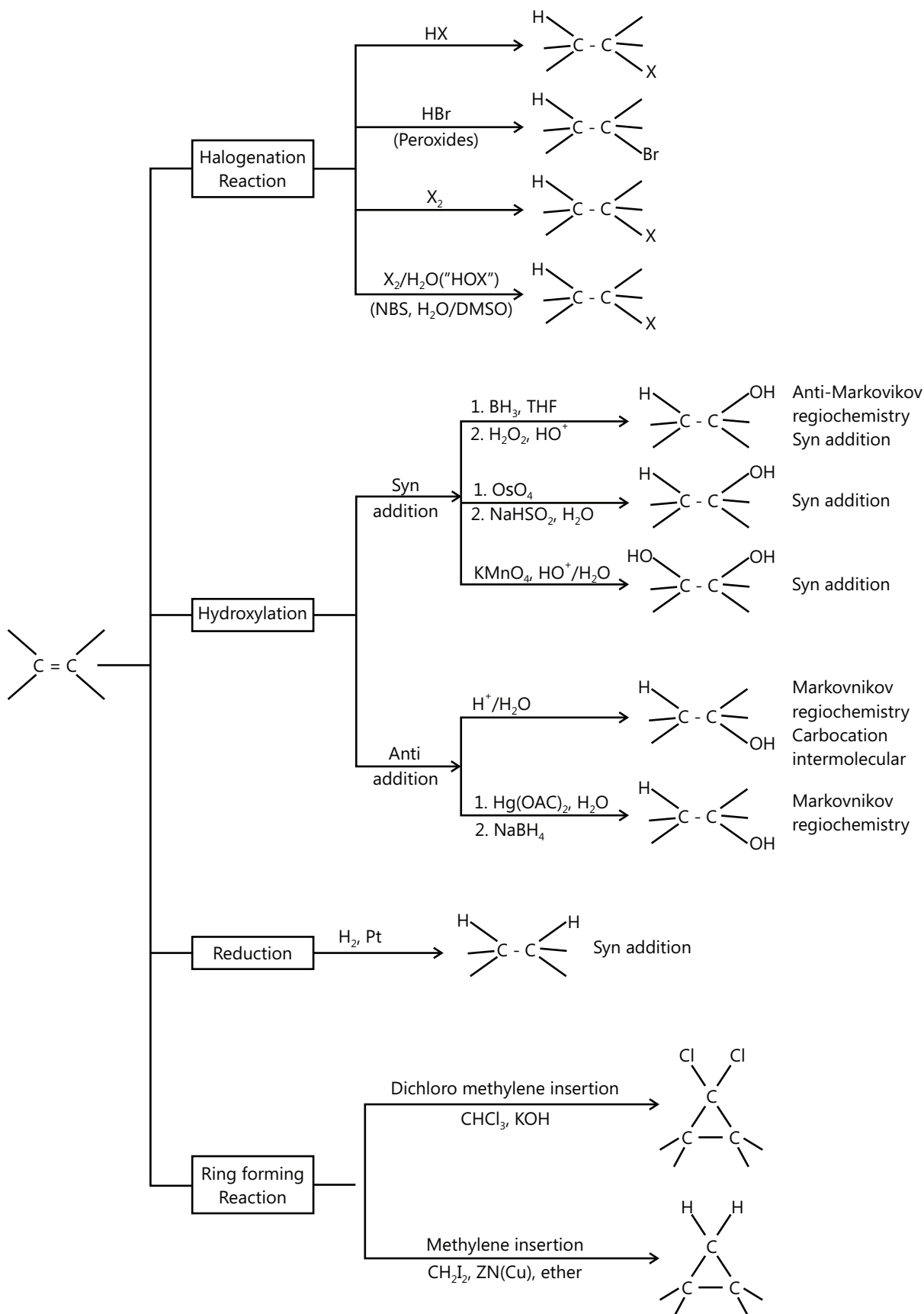
- (i) Acetylene and its derivatives are widely used in synthetic organic chemistry for synthesis of cis-and trans-alkenes, methyl ketones etc.
- (ii) Oxyacetylene flame is used for cutting and welding of metals.
- (iii) Acetylene is used as illuminant in hawker's lamp and in light houses.
- (iv) Acetylene 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.

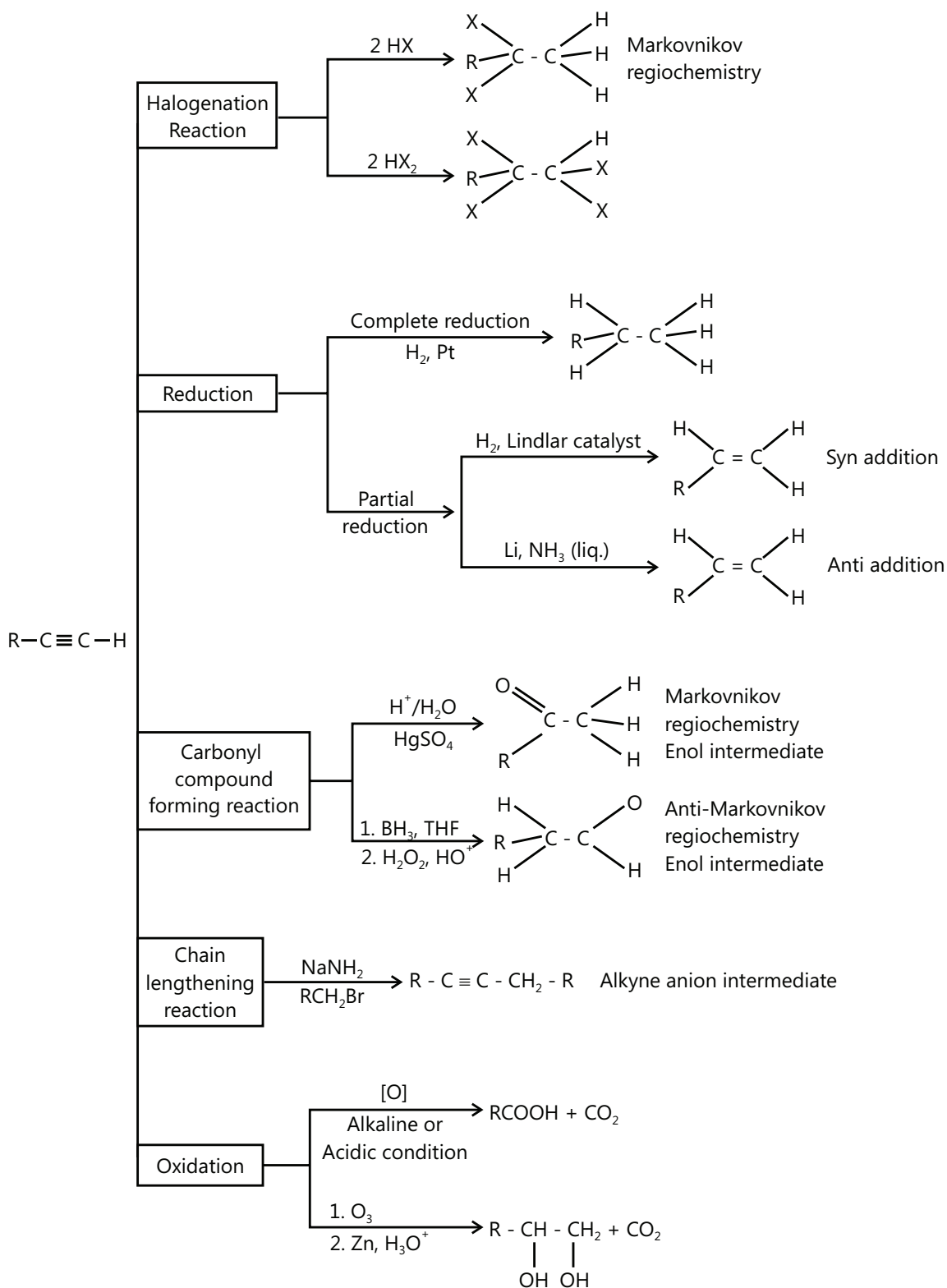
PLANCESS CONCEPTS

Difference between Alkenes and Alkynes

	Test	Alkene	Alkyne
1.	Flame observed on combustion	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 AgNO_3 solution [$\text{Ag}(\text{NH}_3)_2$] ⁺ (Tollens reagent)	No action	White 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 catalytic	Alkynes are more reactive than alkenes	
8.	Reactivity towards nucleophilic addition reaction (e.g. CN^-)	Alkynes are more reactive than alkenes	

POINTS TO REMEMBER

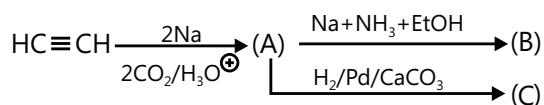




Solved Examples

JEE Main/Boards

Example 1: Identify A to C.



Sol: It is an example of ethynylation (addition of ethyne to unsaturated link like >C=C group).

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

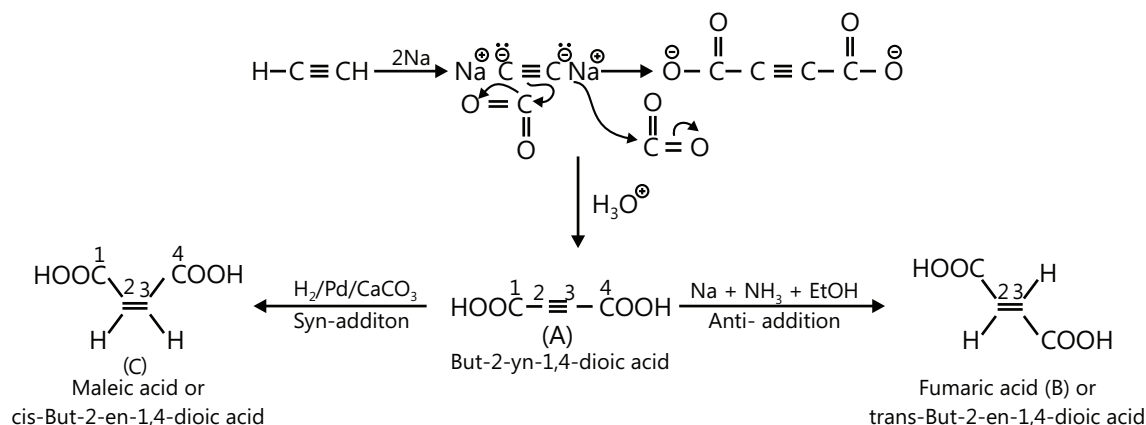
This reaction shows the acidic character of alkynes.

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

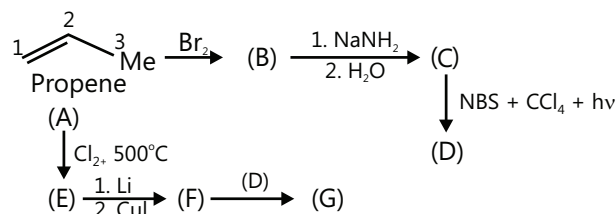
Now the carbanion reacts with two moles of carbon dioxide and forms an adduct which on treatment with acid yields acid.

Next step is reduction using Lindlar Catalyst ($\text{H}_2/\text{Pd}-\text{CaCO}_3$) the addition is syn.

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



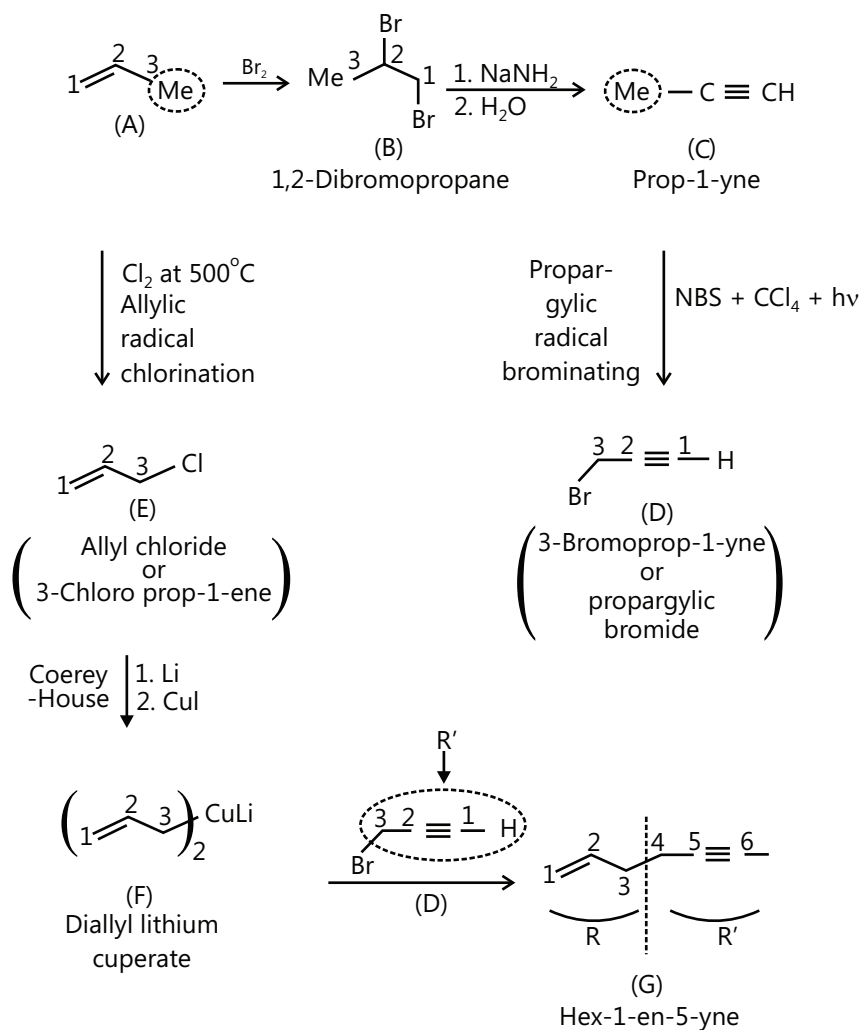
Example 2: Identify B to G.



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 .

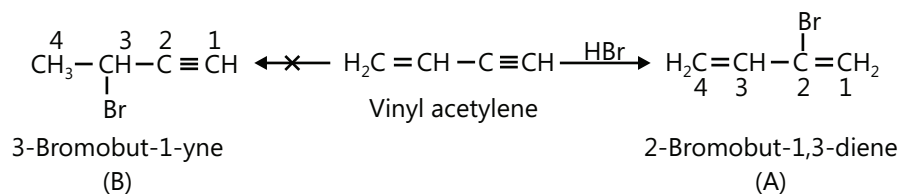
- The reaction proceeds through radical formation.
- Now Allyl chloride undergoes chain lengthening reaction to form Hex-1-en-5-yne.
- The reaction is known as Corey house synthesis



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.



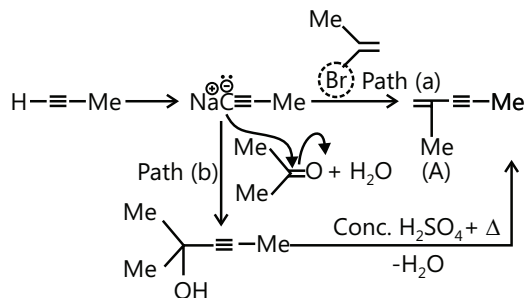
The product A (Conjugated diene) is more stable than B (an alkyne)

Example 4: There are two path (a) and (b) For the preparation of a compound (a) $\left(\begin{array}{c} 1 & 2 & 3 \\ \text{---} & \text{---} & \text{---} \\ | & & \\ \text{Me} & & \end{array} \right) = \text{---} \begin{array}{c} 4 & 5 \\ \text{---} & \text{---} \\ & \text{Me} \end{array}$

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

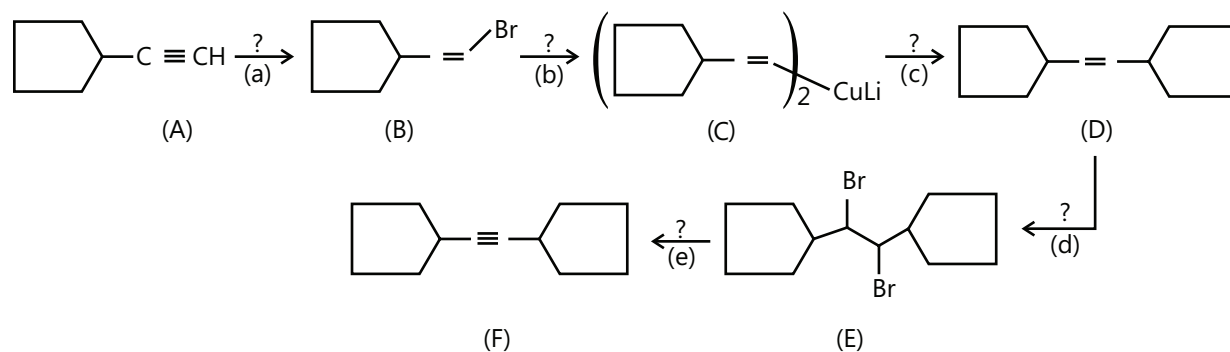
Sol: Path (b) is correct because in path (a) compound $\left(\begin{array}{c} \text{Me} \\ \text{---} \\ \text{Br} \end{array} \right)$ vinyl halide which is not reactive, so the reaction does not occur.

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



JEE Advanced/Boards

Example 1: Complete the following missing reagents



Sol: (i)

(a) $\text{HBr} + \text{Peroxide}$

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) $\text{Cyclohexyl}-\text{CH}_2\text{Br}$ Third step is the reaction with alkyl halide.

(d) Br_2/CCl_4

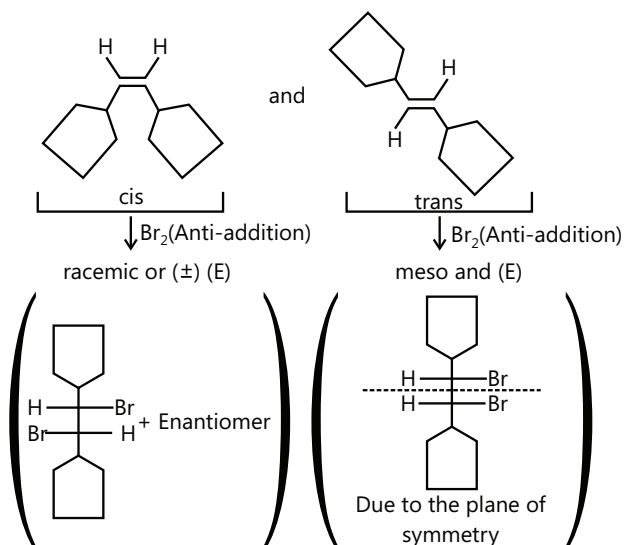
Bromination using Br_2 and CCl_4 as a solvent

(e) KOH(s) , at 473 K

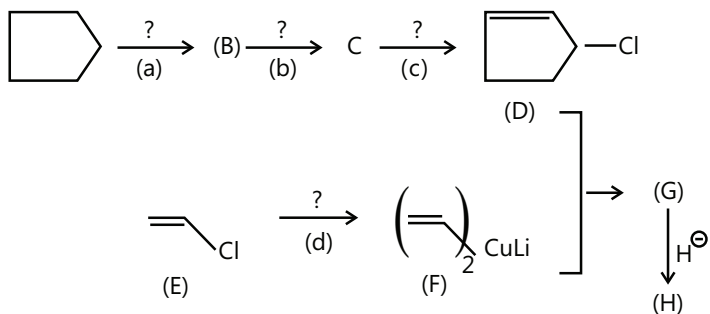
Last step is double dehalogenation using base like KOH at 473 K

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

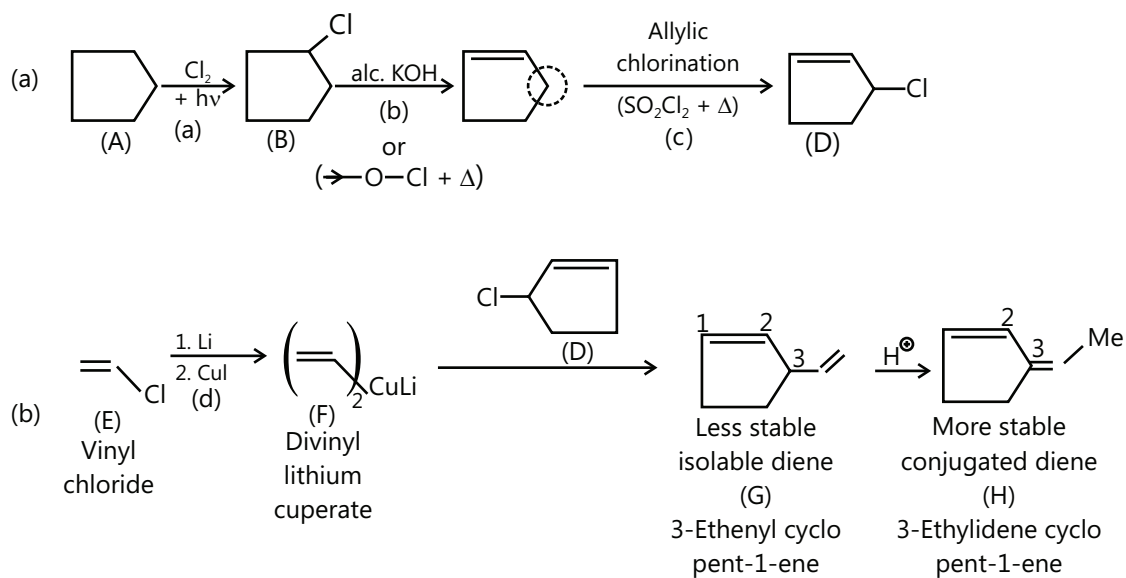
Trans compound on addition with Br_2 (Anti addition) produces Meso compound (it contains plane of symmetry)



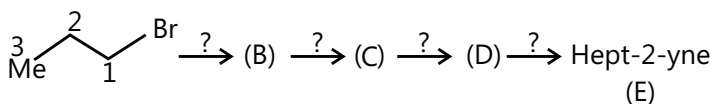
Example 2: Convert the following



Sol:

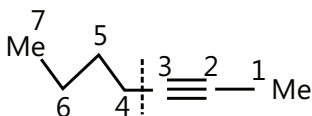


Example 3: Convert the following.



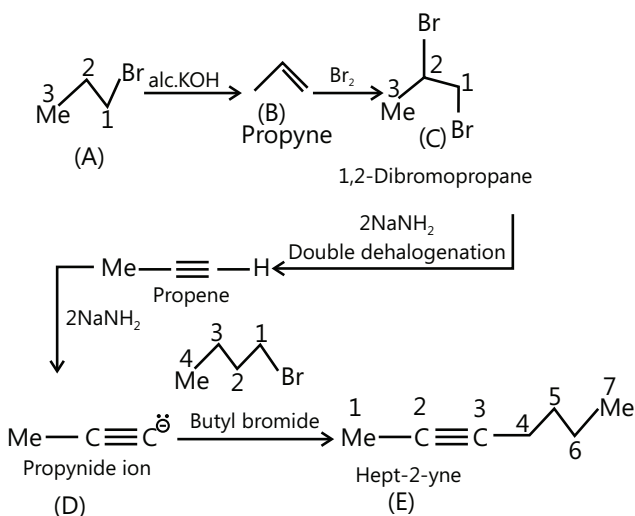
Write the structure of (E).

Sol: The structure of E is

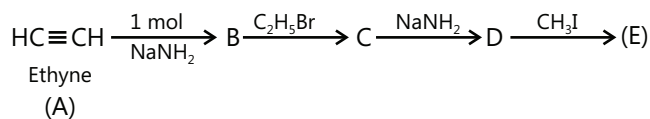


First prepare 3C – atom alkyne (Me – C $\equiv$ C – H) from (A) and then react 4C – atom RX with alkynide ion to get (E).

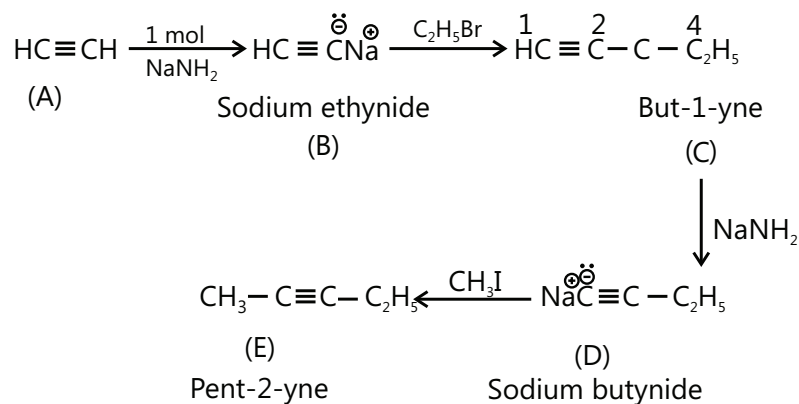
Reaction:



Example 4: Complete the following:



Sol:



JEE Main/Boards

Exercise 1

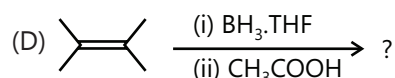
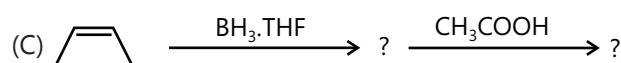
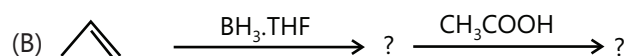
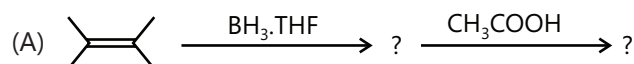
Q.1 What are alkenes? Discuss briefly the various methods used for the preparation of alkenes. Describe with a labelled diagram the laboratory preparation of ethane from ethanol.

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

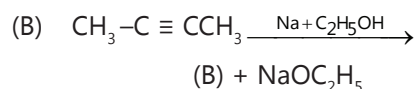
(A) 1-Ethyl cyclopentene

(B) Methylene cyclopentene

Q.3 Give the missing compounds in the following:



Q.4 Complete the following equation:



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

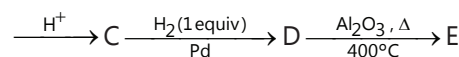
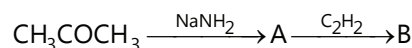
Q.6 What are alkynes? How are they prepared in the laboratory?

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

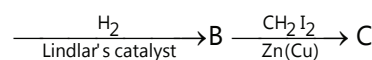
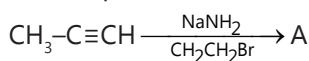
Q.8 (A) Starting with any alkyne, prepare ethyl cyclohexyl ethyne.

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

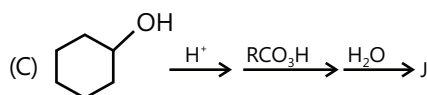
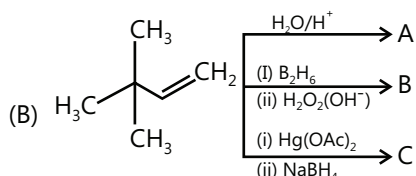
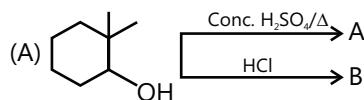
Q.9 (A) Complete the following reactions:



(B) Complete the following reactions:

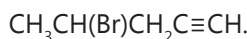


Q.10 Predict the product of the following:

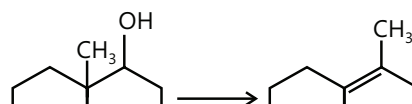


Q.11 (A) Give reasons for the following:

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



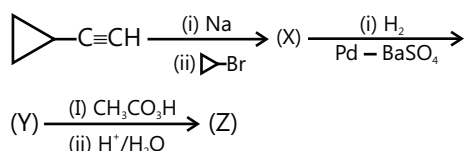
(B) Provide a suitable mechanism for the following reaction.



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

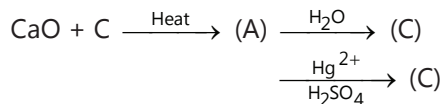
Q.4 The olefin, which on ozonolysis gives CH_3CH_2CHO and CH_3CHO

- (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:

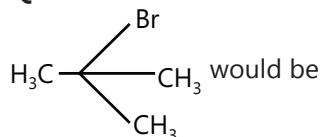


- (A) Ethanol (B) Ethyl hydrogen sulphate
(C) Ethanal (D) Ethylene glycol

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

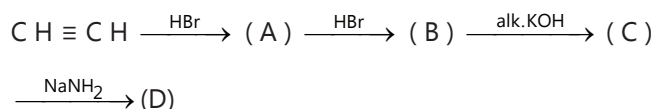


- (A) 0% (B) 83% (C) 10% (D) 100%

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)



- (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 is 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

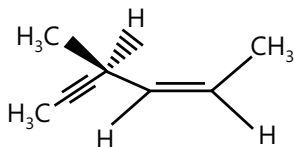
Q.5 Bayer's reagent is (1984)

- (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

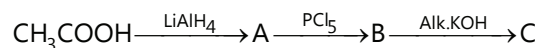
Q.11 The reaction of propene with $HOCl$ ($Cl_2 + H_2O$) proceeds through the intermediate : (2016)

- (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

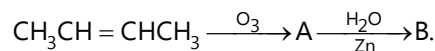
Q.13 In the reaction,



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'



The compound B is (2008)

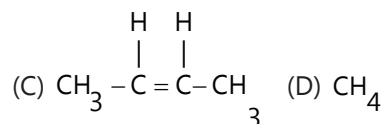
- (A) CH_3CH_2CHO
- (B) CH_3COCH_3
- (C) $CH_3CH_2COCH_3$
- (D) CH_3CHO

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 $\text{CH}_3\text{C}\equiv\text{C}-\text{H}$ produces (2008)

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



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

- (A) Propene (B) 2-methyl propene
(C) 2-butene (D) 2-methyl-2-butene

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 sulfoxide and excess of it evaporates. (2000)

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

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

JEE Advanced/Boards

Exercise 1

Q.1 Compound (X) ($\text{C}_5\text{H}_8\text{O}$) does not appreciably react with Lucas reagent at room temperature but gives a precipitate with silver nitrate (ammoniacal). With MeMgBr , 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) $\text{C}_6\text{H}_{12}\text{Cl}_2$. 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 $\text{CF}_3\text{CH}=\text{CH}_2 + \text{HBr} \xrightarrow{\text{AlBr}_3} \text{X}$

Q.6 An organic compound (A) C_9H_{12} gave (B) $\text{C}_8\text{H}_6\text{O}_4$ 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). $\text{C}_8\text{H}_5\text{BrO}_4$. What are A, B and C.

Q.7 A hydrocarbon (A) C_9H_{10} adds Cl_2 to give (B) $\text{C}_9\text{H}_{10}\text{Cl}_2$. Hydrolysis of (B) gives (C) $\text{C}_9\text{H}_{12}\text{O}_2$. Oxidation of (A) gave two acids identified as benzoic acid and acetic acids. What are A, B and C?

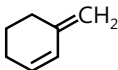
Q.8 An organic compound (A) $\text{C}_9\text{H}_{10}\text{Br}_2$ forms $\text{C}_9\text{H}_{11}\text{OBr}$ with caustic soda solution the later is resistant to further action of alkali. (B) on treating with H_2SO_4 converts into (C) with on ozonolysis gives ethanal and another compound (D). Identify (A) to (D) and give reactions.

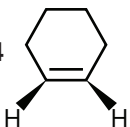
Q.9 An organic compound (A) C_6H_{10} , on reduction first gives (B) C_6H_{12} and finally (C) C_6H_{14} . (A) on ozonolysis followed by hydrolysis gives two aldehydes (D) $\text{C}_2\text{H}_4\text{O}$ and (E), $\text{C}_2\text{H}_2\text{O}_2$. Oxidation of (B) with KMnO_4 gives the acid (F) $\text{C}_4\text{H}_8\text{O}_2$. 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 $\text{C}_5\text{H}_{10}\text{O}$ when treated with dil. H_2SO_4 and HgSO_4 . (B) on oxidation with alkaline. KMnO_4 gives two isomeric acids (D) and (E) $\text{C}_4\text{H}_8\text{O}_2$. 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  + $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$

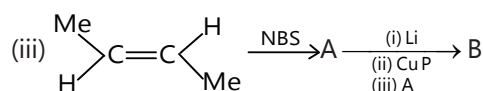
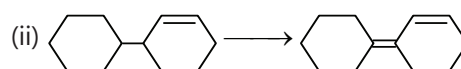
A Predict the structure of A and explain.

Q.15 A hydrocarbon (P) of the formula C_8H_{10} , on ozonolysis, gives compound Q ($\text{C}_4\text{H}_6\text{O}_2$) only. The compound (Q) can also be obtained from an alkyl bromide, R ($\text{C}_3\text{H}_5\text{Br}$) 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 $\text{C}_5\text{H}_{11}\text{Br}$. (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).

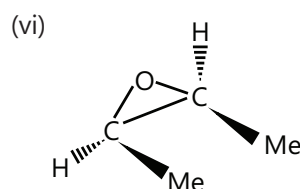
Q.17 How would you bring about the following conversion.

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



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

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



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 $\text{C}_5\text{H}_9\text{Cl}$ 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 $\text{C}_2\text{H}_4\text{O}$ (D) and $\text{C}_2\text{H}_2\text{O}_2$ (E). Oxidation of (B) with alkaline KMnO_4 gives acid (F) $\text{C}_3\text{H}_6\text{O}_2$. 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-dimethylhexane (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 90 g 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) $\text{BrCH}_2\text{-CH}_2\text{Br}$ (B) $\text{ClCH}_2\text{-CH}_2\text{Br}$
(C) Both of these (D) None of these

Q.3 The reaction conditions leading to the best yield of $\text{C}_2\text{H}_5\text{Cl}$ are

- (A) $\text{C}_2\text{H}_6(\text{excess}) + \text{Cl}_2 \xrightarrow{\text{UV light}}$
(B) $\text{C}_2\text{H}_6 + \text{Cl}_2 \xrightarrow[\text{room temp.}]{\text{dark}}$
(C) $\text{C}_2\text{H}_6 + \text{Cl}_2(\text{excess}) \xrightarrow{\text{UV light}}$
(D) $\text{C}_2\text{H}_6 + \text{Cl}_2 \xrightarrow{\text{UV light}}$

Q.4 The treatment of $\text{CH}_3\text{C}(\text{CH}_3)=\text{CHCH}_3$ with NaIO_4 or boiling KMnO_4 produces

- (A) $\text{CH}_3\text{COCH}_3 + \text{CH}_2\text{O}$ (B) $\text{CH}_3\text{CH}_2\text{CHO} + \text{CH}_3\text{CHO}$
(C) $\text{CH}_3\text{COCH}_3 + \text{CO}_2$ (D) $\text{CH}_3\text{COCH}_3 + \text{HCOOH}$

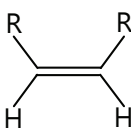
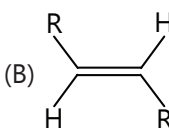
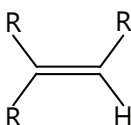
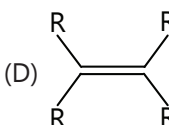
Q.5 What is the chief product obtained when n-butane is treated with bromine in the presence of light at 130°C ?

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

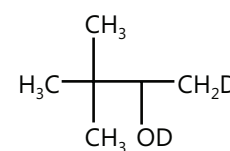
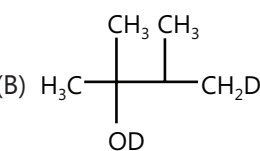
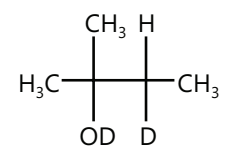
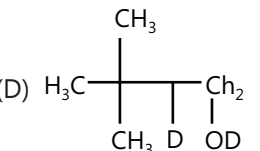
Q.6 Addition of halogen acid (HX) is least in

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

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

- (A)  (B) 
(C)  (D) 

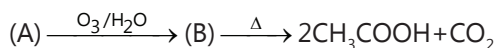
Q.8 Products of the reaction. $\text{H}_3\text{C}-\text{C}(\text{CH}_3)_2=\text{CH}_2 \xrightarrow{\text{D}_2\text{O}/\text{D}^+}$

- (A)  (B) 
(C)  (D) 

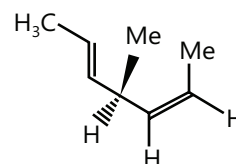
Q.9 The C-H bond length is longest in

- (A) C_2H_2 (B) C_2H_4 (C) C_2H_6 (D) $\text{C}_2\text{H}_2\text{Br}_2$

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

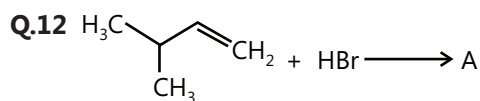


Q.11 Hydrogenation of the compound

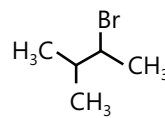
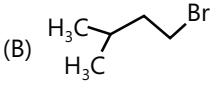
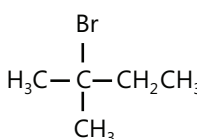


In the presence of poisoned palladium catalyst gives:

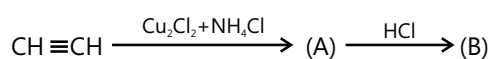
- (A) An optically active compound
(B) An optically inactive compound
(C) A racemic mixture
(D) A diastereomeric mixture

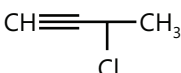
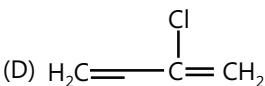


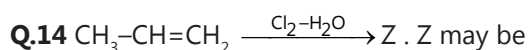
(Predominant). A is

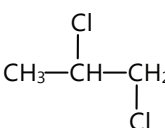
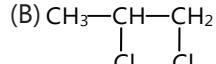
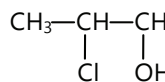
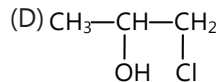
- (A)  (B) 
 (C)  (D) Non of these

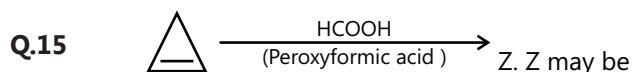
Q.13 Identify (B) in the following sequence of reactions

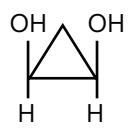
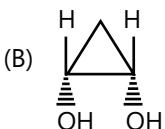
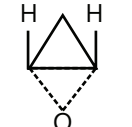


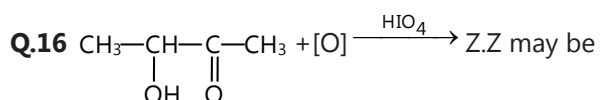
- (A) $\text{CH}_3\text{CH}_2\text{Cl}$ (B) $\text{CH}_2=\text{CH}-\text{CH}_2\text{CH}_2\text{Cl}$
 (C)  (D) 

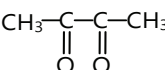


- (A)  (B) 
 (C)  (D) 



- (A)  (B) 
 (C)  (D) Non of these



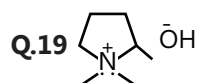
- (A) CH_3-CHO (B) CH_3-COOH
 (C)  (D) None of these

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

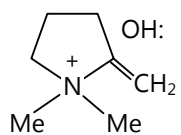
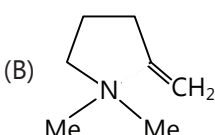
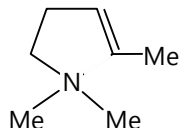
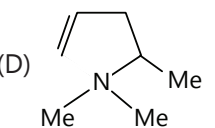
- (A) Heptan-3-ol (B) Heptan-4-ol
 (C) Heptan-2-ol (D) Heptan-1-ol

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

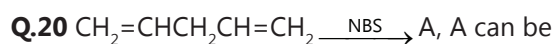
- (A) n-Butane (B) $\text{C}_2\text{H}_5\text{COOC}_2\text{H}_5$
 (C) CH_3-CH_3 (D) $\text{CH}_2=\text{CH}_2$

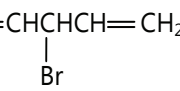
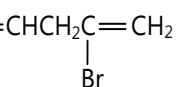


The above compound undergoes elimination on heating to yield which of the following products?

- (A)  (B) 
 (C)  (D) 

Multiple Correct Choice Type



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

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

- (A) $\text{CH}_3\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{CH}_3 + \text{KOH} \xrightarrow{\text{EtOH}}$
 (B) $\text{CH}_3\cdot\text{CH}\cdot\text{CH}_2\cdot\text{CH}_3 + \text{NaOEt} \xrightarrow[\Delta]{\text{EtOH}}$
 (C) $\text{CH}_3\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{CH}_3 + \text{Me}_3\text{CO}^-\text{K}^+ \xrightarrow{\Delta}$
 (D) $\text{CH}_3\cdot\text{CH}_2\cdot\text{CHOH}\cdot\text{CH}_3 + \text{conc. H}_2\text{SO}_4$

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.

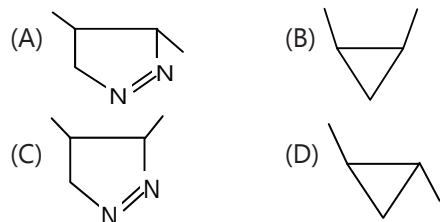
(D) Allylic chloride adds halogens faster than the corresponding vinylic chloride.

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



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

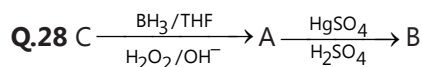
- (A) Cyclohexene
(B) 1-methylcyclohexene
(C) 1, 2-dimethylcyclohexene
(D) 1-butene

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

- (A) $CH_3(CH_2)_3CH=CH_2$ (B) $CH_3CH=CH_2$
(C) $CF_3CH=CH_2$ (D) $CF_3CH=CH_2$

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) $Mg_2C_3 + H_2O \longrightarrow CH_3C\equiv CH$
(D) $Me_3C-H + KMnO_4 \longrightarrow Me_3C-OH$



B and C are identical when A is –

- (A) $H-C\equiv C-H$ (B) $-C\equiv C-H$
(C) $-C\equiv C-$ (D) $\text{trans-}CH_3CH=CH_2$

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: $CH_3-C\equiv C-CH_3$ is more reactive than $CH\equiv CH$ towards HCl.

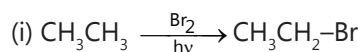
Reason: The carbocation formed is more stable in the case of $CH_3-C\equiv C-CH_3$ than $CH\equiv CH$.

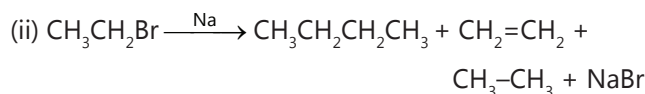
Q.33 Assertion: $CH\equiv CH$ reacts with HCl in the presence of $HgCl_2$ while $CH_2=CH_2$ does not.

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

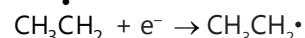
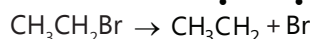
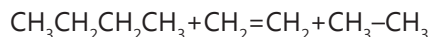
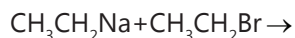
Comprehension Type (34-36)

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





Mechanism: $\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$;



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

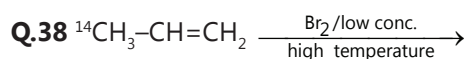
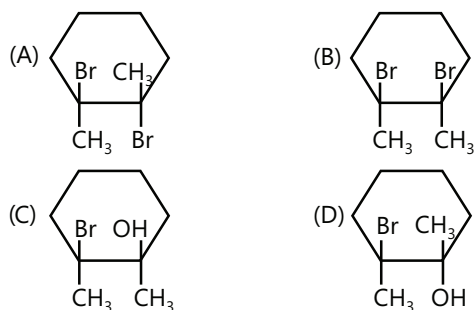
Q.36 The other products which could be formed

- (A) $\text{CH}_2=\text{CH}_2$ (B) $\text{CH}_3\text{CH}_2\text{CH}_3$
(C) CH_4 (D) $\text{CH}_3\text{CH}_2\text{CH}_2-\text{CH}_2-\text{CH}_3$

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



Product of the above reaction is

- (A) $\text{Br}-^{14}\text{CH}_2-\text{CH}=\text{CH}_2$ (B) $^{14}\text{CH}_2=\text{CH}-\text{CH}_2-\text{Br}$
(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) $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3$ cis-2-butene	(p) $\text{Na}/\text{NH}_3(\text{l})$
(B) $\text{CH}_3-\text{C}\equiv\text{C}-\text{CH}_3 \longrightarrow$ trans-2-butene	(q) $\text{H}_2/\text{Pd}/\text{BaSO}_4$
(C) $\text{CH}_3\text{C}\equiv\text{C}-\text{CH}_3 \longrightarrow$ 1-Butyne	(r) Alc. KOH, Δ
(D) $\text{CH}_3-\text{CH}_3-\text{C}\equiv\text{CH} \longrightarrow$ 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) $\text{CH}_3-\text{CH}=\text{CH}_2 \rightarrow \text{CH}_3-\text{CHBr}-\text{CH}_3$	(p) HBr
(B) $\text{CH}_3-\text{CH}=\text{CH}_2 \rightarrow \text{CH}_3-\text{CH}_2-\text{CH}_2\text{Br}$	(q) Br_2
(C) $\text{CH}_3-\text{CH}=\text{CH}_2 \rightarrow \text{BrCH}_2-\text{CH}=\text{CH}_2$	(r) HBr/Peroxide
(D) $\text{CH}_3-\text{CH}=\text{CH}_2 \rightarrow \text{CH}_3-\text{CHBr}-\text{CH}_2\text{Br}$	(s) NBS

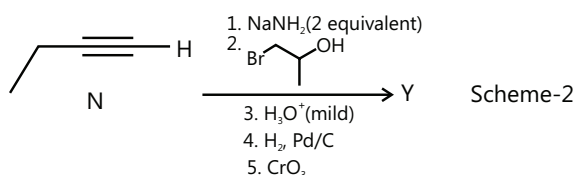
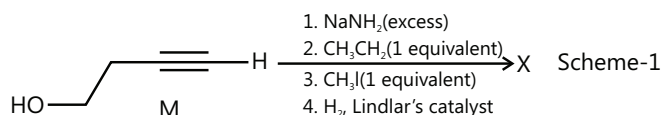
Q.42 Match the column

Column I	Column II
(A) $\text{RCOONa} \xrightarrow{\text{Electrolysis}} \text{R}-\text{R}$	(p) Corey-House reaction
(B) $\text{R}-\text{CH}_2-\text{COOH} \xrightarrow[\Delta]{\text{Soda Lime}} \text{R}-\text{CH}_3$	(q) Kolbe electrolysis
(C) $\text{RCOOH} \xrightarrow[\text{(ii) Cl}_2/\Delta]{\text{(i) AgNO}_3} \text{R}-\text{Cl}$	(r) Oakwood degradation

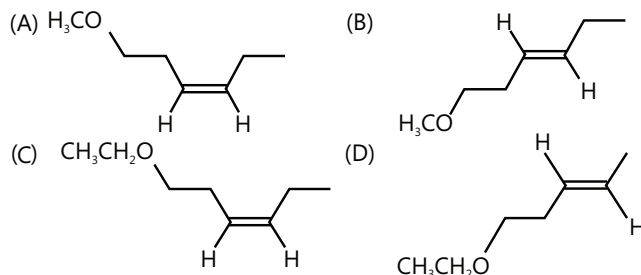
(ii) Ethyne and its derivatives will give white precipitate with ammoniacal silver nitrate solution. **(1984)**

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)**



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.

PlancEssential 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 $A \rightarrow q; B \rightarrow p; C \rightarrow s; D \rightarrow r$ Q.41 $A \rightarrow p; B \rightarrow r; C \rightarrow s; D \rightarrow q$ Q.42 $A \rightarrow q; B \rightarrow r; C \rightarrow s; D \rightarrow p$

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

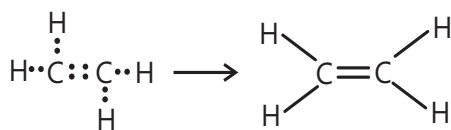
Solutions

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

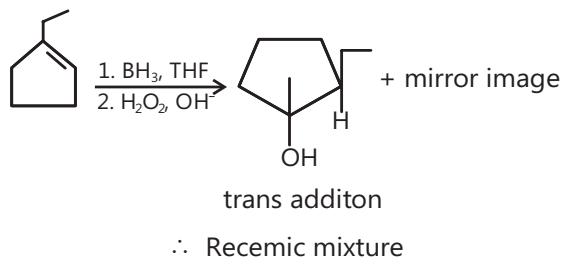
Structure:-



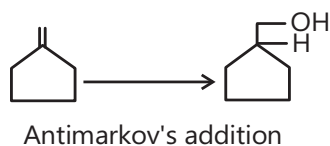
Preparation of Alkenes:-

- (1) Dehydrohalogenation of Alkyl halide
- (2) Dehydration of Alcohols
- (3) Dehalogenation of vicinal dihalides
- (4) Dehalogenation of geminal dihalide

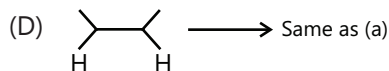
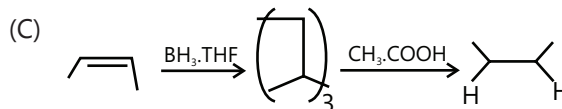
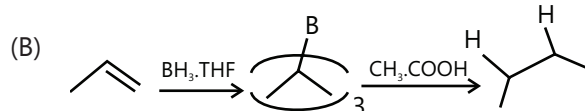
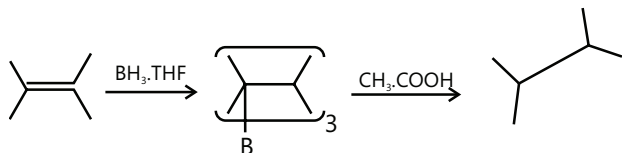
Sol 2: (A)



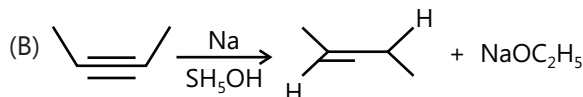
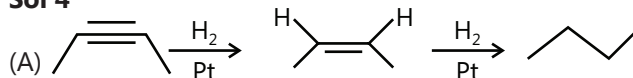
(B)



Sol 3: (A)



Sol 4



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 $\text{C}\equiv\text{C}$ bond and are highly reactive.

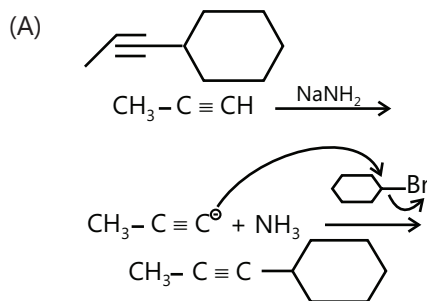
Preparation:-

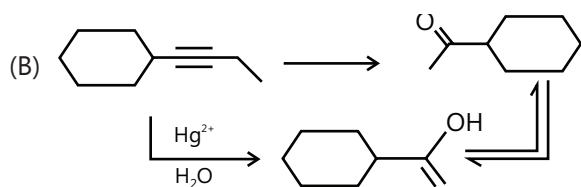
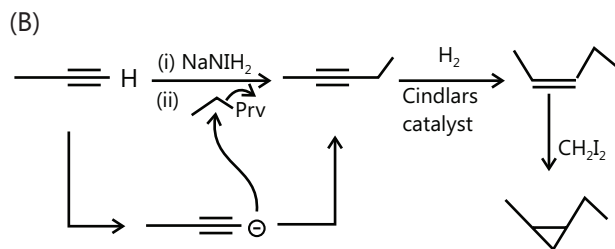
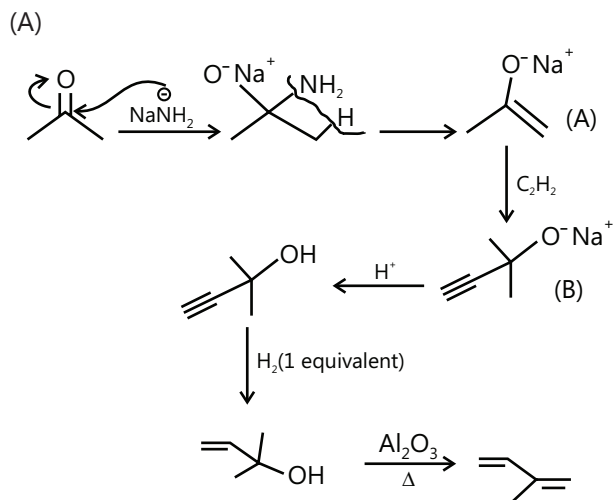
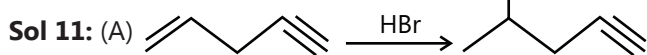
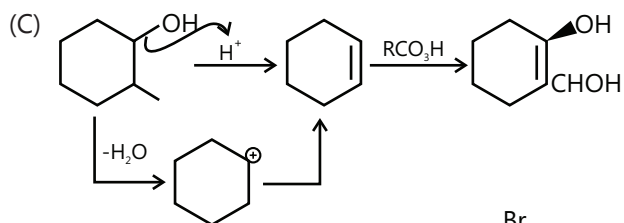
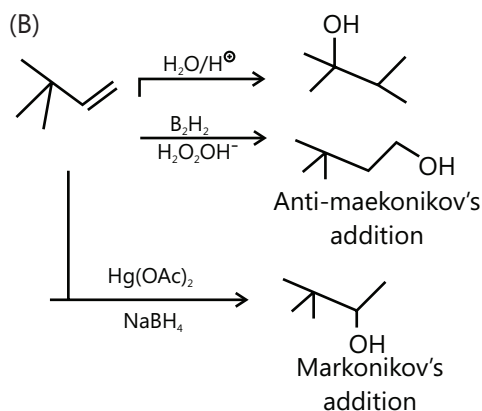
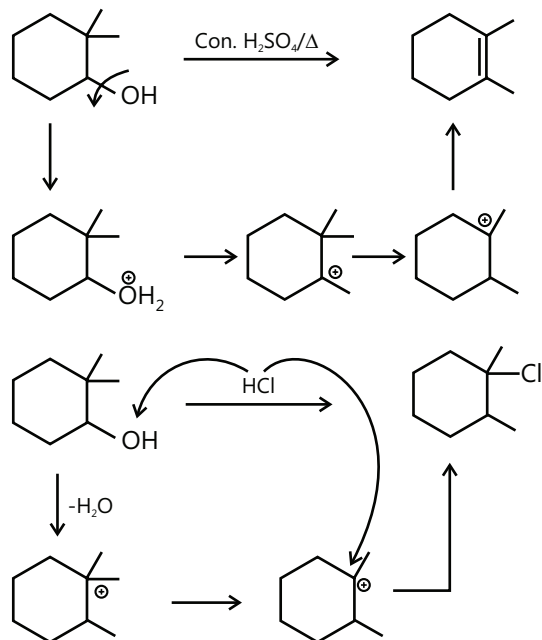
- (1) Dehydrohalogenation
- (2) From tetradehalogenation
- (3) From haloform
- (4) Kolbe's electrolytic decarboxylation
- (5) Berthlot's reaction

Sol 7: Physical properties: Refer theory pg.42

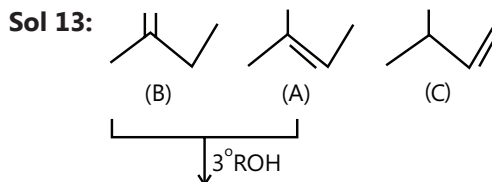
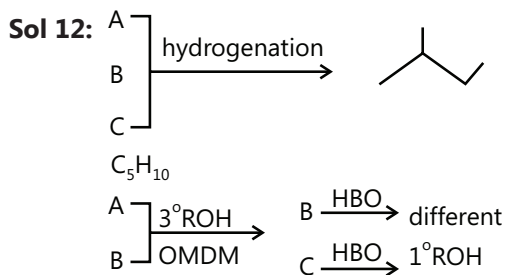
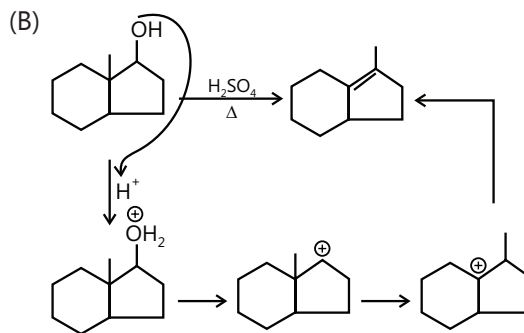
Chemical properties: Refer theory pg.44

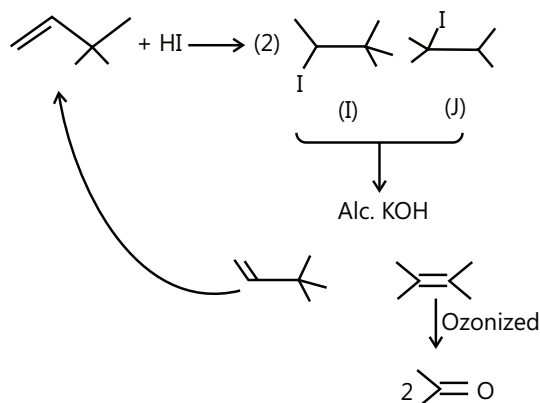
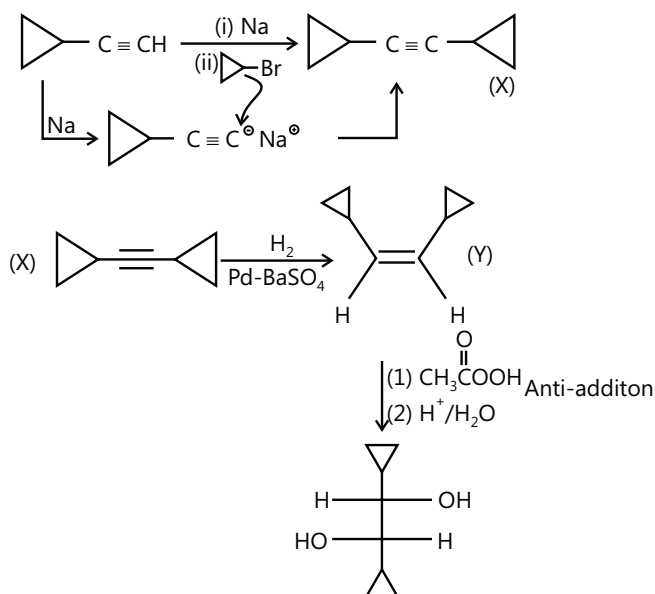
Sol 8:



**Sol 9:****Sol 10: (A)**

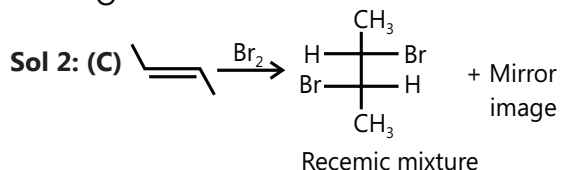
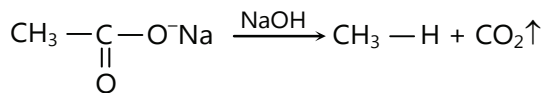
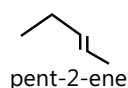
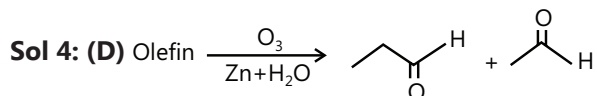
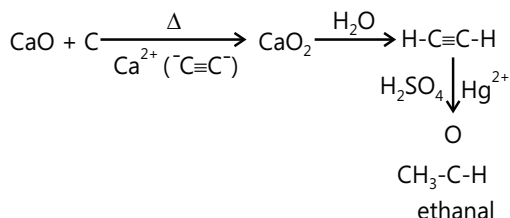
Doubled bonds are more electron donating than triple bond because of difference in electronegativity and because of which first addition will take place on double bond rather than triple bond.



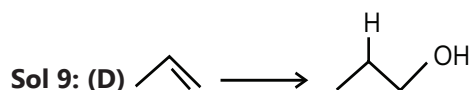
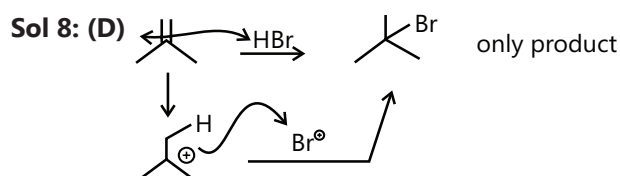
**Sol 14**

Exercise 2

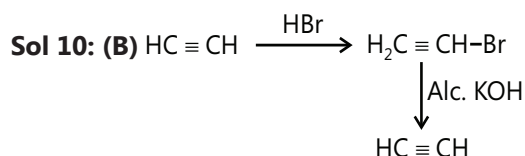
Single Correct Choice Type

Sol 1: (B) Decarboxylation of acid ion**Sol 3: (A)** Definition of conformers.**Sol 5: (C)** $\text{C} \equiv \text{C}$ is strongest because it is shortest and more orbitals are overlapping.**Sol 6: (C)****Sol 7: (B)** $\text{C}_2\text{H}_3\text{MgI} \xrightarrow{\text{H}_2\text{O}} \text{C}_2\text{H}_6$

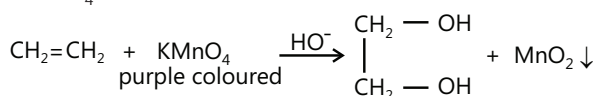
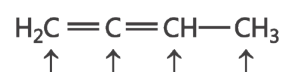
Abstracts acidic hydrogen.



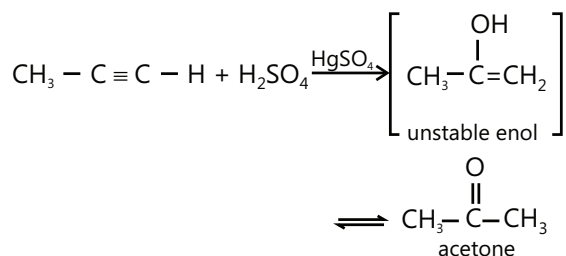
Anti Markonikov's addition

**Sol 11: (A)** Enol form is not net stable as keto is much more stable.

Previous Years' Questions

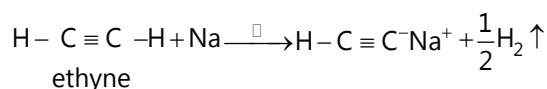
Sol 1: (B) Methane is produced due to the decay of vegetables or animal organisms present in swamps and marsh, by the action of bacteria. Due to this method of formation, methane is also known as marsh gas.**Sol 2: (D)** Unsaturated compounds which contain $\text{C}=\text{C}$ or $\text{C} \equiv \text{C}$, decolourises the purple colour of alkaline KMnO_4 solution.**Sol 3: (D)** Structural formula of 1, 2-butadiene is:

Sol 4: (C) Alkynes undergo Markownikoff's addition of water in presence of $\text{H}_2\text{SO}_4/\text{HgSO}_4$:



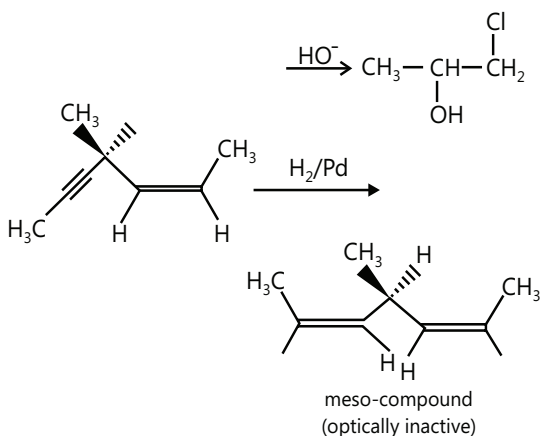
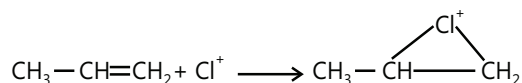
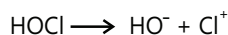
Sol 5: (A) Bayer's reagent is cold, dilute, alkaline perman-ganate solution, used to detect presence of olefinic bonds.

Sol 6: (A) Terminal alkynes are slightly acidic, forms salt with very strong base like Na, NaNH_2 etc.



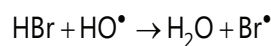
Sol 7: (B) Hydrogenation with poisoned palladium brings about cis hydrogenation of alkyne and does not affect double bonds:

Sol 8: (B)

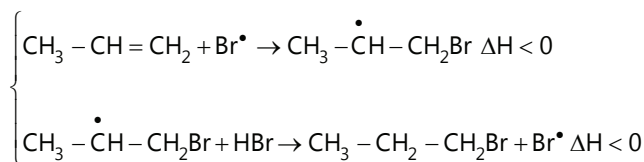


i.e. Reaction is initiated by Cl^+ (Chloronium ion electrophile).

Sol 9: (C) In addition of HBr to an alkene, in presence of peroxide, both the propagation steps are exothermic:



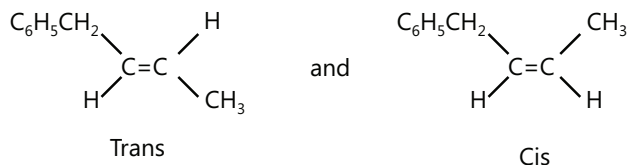
Propagation



In case of addition of HCl and HI, one of the propagation step is endothermic, reaction fail to occur.

Sol 10: (A)

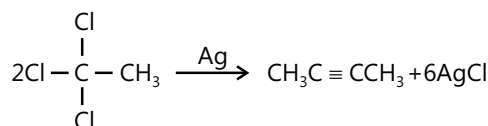
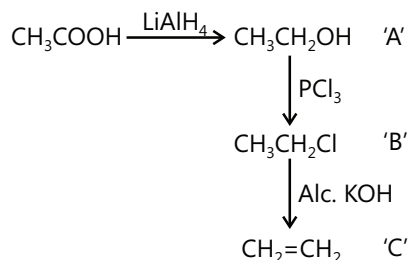
$\text{C}_6\text{H}_5\text{CH}_2 = \text{CHCH}_3$ has two geometrical isomers



So it is 1-Phenyl-2-butene

Sol.11: (D) $\text{CH}_3 - \text{CH}^+ - \text{CH}_2 - \text{Cl}$

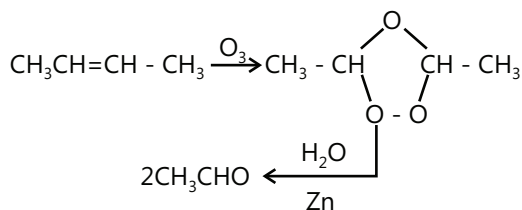
Sol 12: (A)



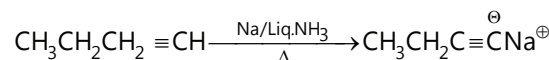
1, 1, 1- Trichloroethane

Sol 13: (C)

Sol 14: (D)



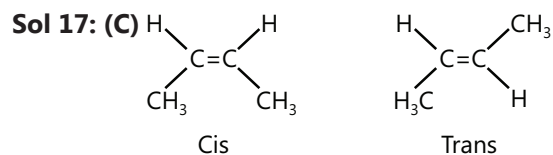
Sol 15: (B)



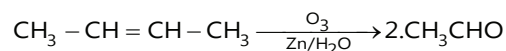
It is a terminal alkyne, having acidic hydrogen.

Note: Solve it as a case of terminal alkynes, otherwise all alkynes react with Na in liq. NH_3

Sol 16: (D) $\text{CH}_3 - \text{MgX} + \text{CH}_3 - \text{C} \equiv \text{C} - \text{H} \rightarrow \text{CH}_4$

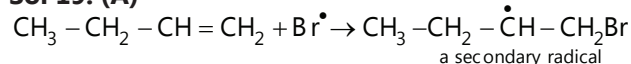


Sol 18: (C) 2-butene is symmetrical alkene



Molar mass of CH_3CHO is 44 u.

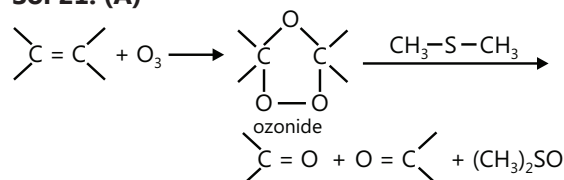
Sol 19: (A)



Therefore, Statement I is correct but Statement II is incorrect.

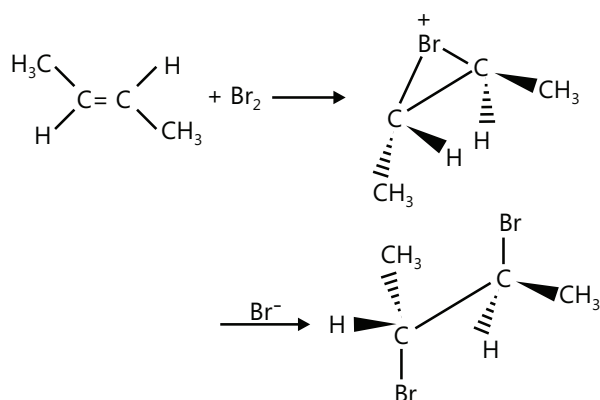
Sol 20: (B) Both Statement I and Statement II are correct and Statement II is correct explanation of Statement I.

Sol 21: (A)



Both Statement I and Statement II are correct and Statement II is correct explanation of Statement I.

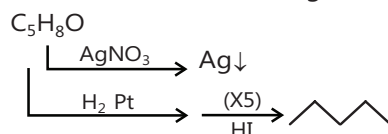
Sol 22: (B) Statement I is correct. Statement II is also correct. Meso form of the product is due to anti addition of Br on cyclic bromonium ion intermediate, hence Statement II is not correct explanation of Statement II.



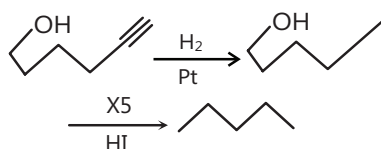
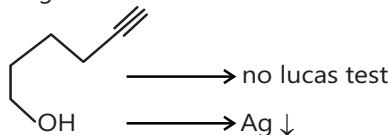
JEE Advanced/Boards

Exercise 1

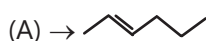
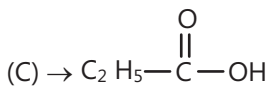
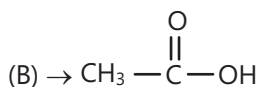
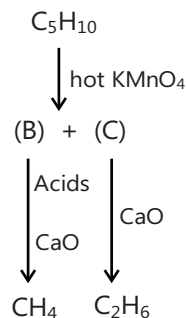
Sol 1: (X) $\not\rightarrow$ Lucas reagent



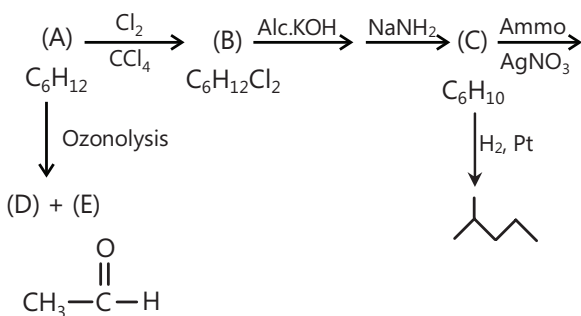
Degree of unsaturation : 2

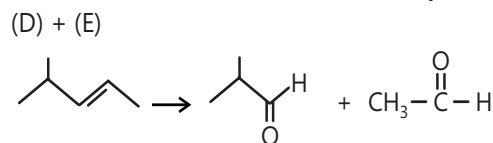
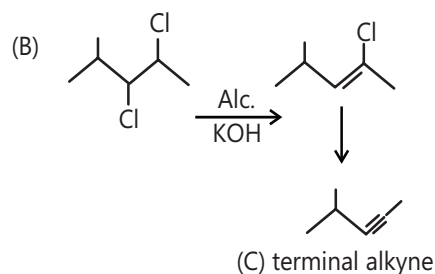


Sol 2: (A) $\xrightarrow{\text{Br}_2}$ decolourizes implies unsaturation

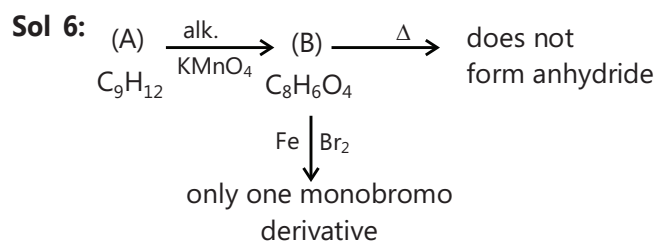
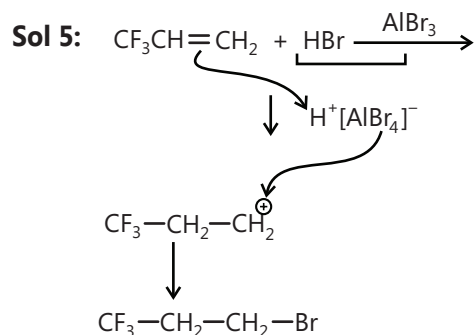
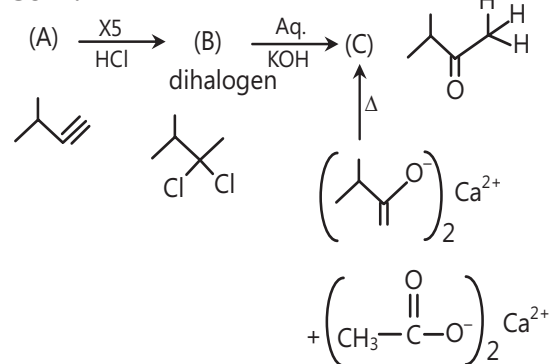


Sol 3:





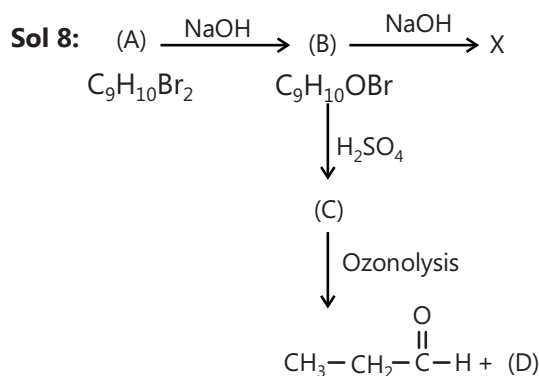
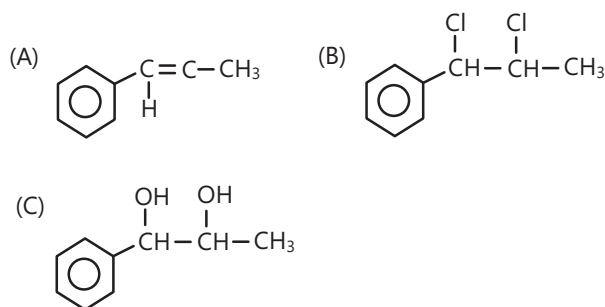
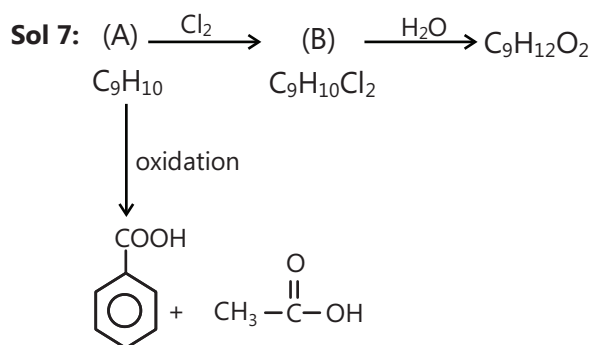
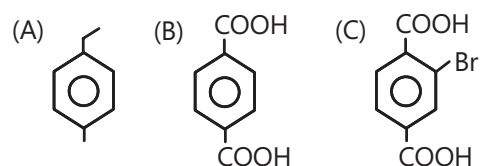
Sol 4:



Degree of unsaturation of (A) = 4

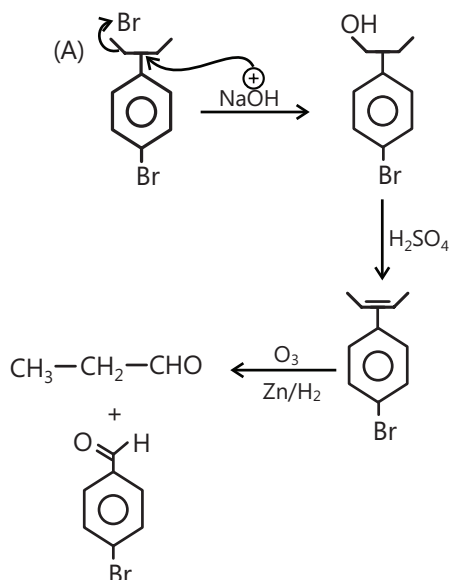
So it should contain benzene ring

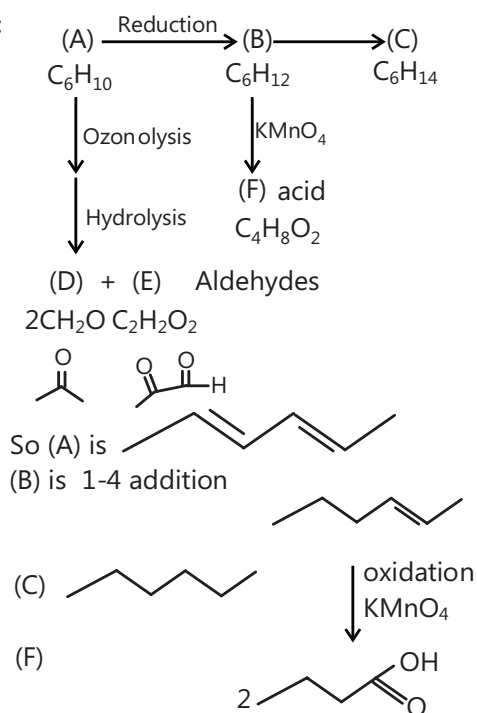
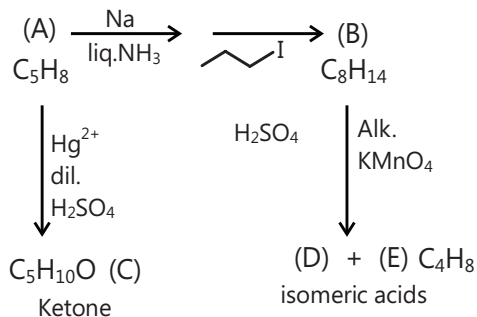
In the compound (B) both -COOH should be at para position to give only one bromination product



Since only one $-Br$ is hydrolysed

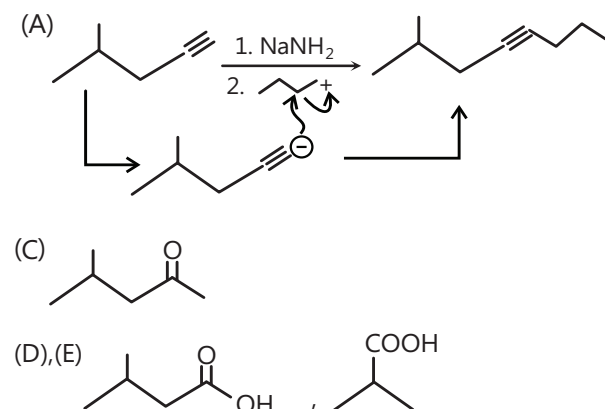
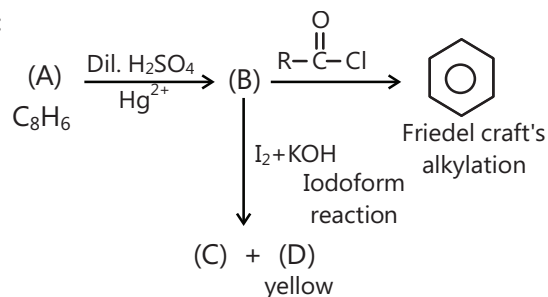
∴ One is attached to alkyl group and other one to aryl group.



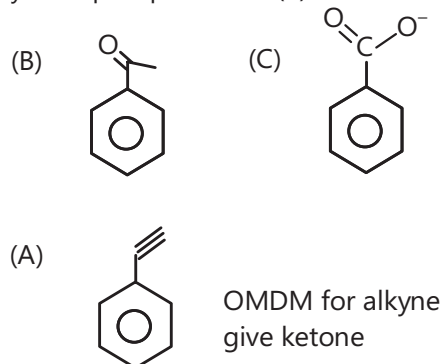
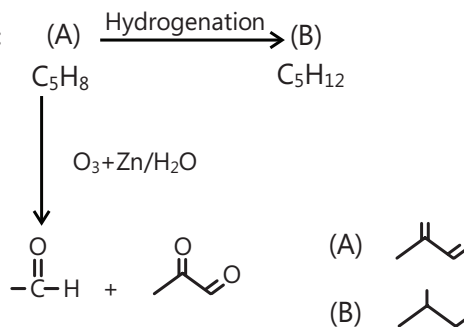
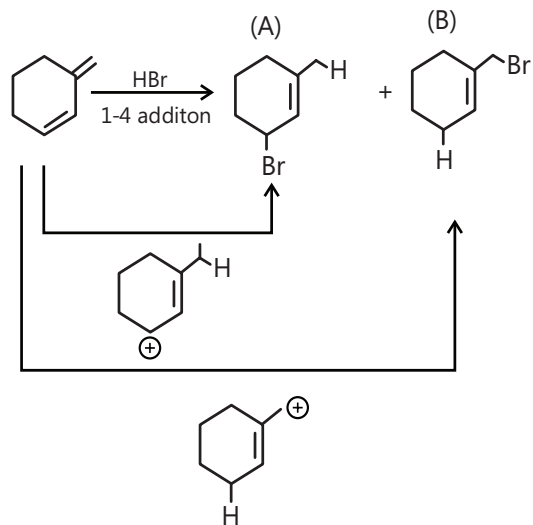
Sol 9:**Sol 10:**

Degree of unsaturation of (A) = 2

$\therefore$ Alkyne. Terminal alkyne because formation of (B) and branched because formation of ketone (C)

**Sol 11:**

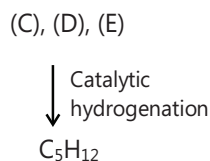
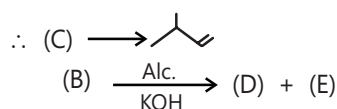
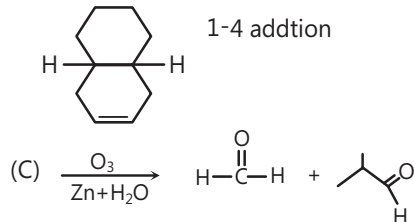
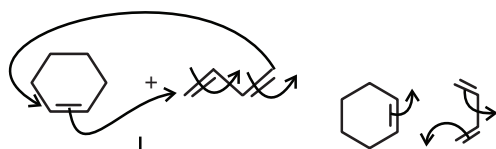
For reaction (B) $\rightarrow$ (C) it is iodoform so (D) $\rightarrow CHI_3$ yellow precipitate and (B) should have acetyl ketone.

**Sol 12:****Sol 13:**

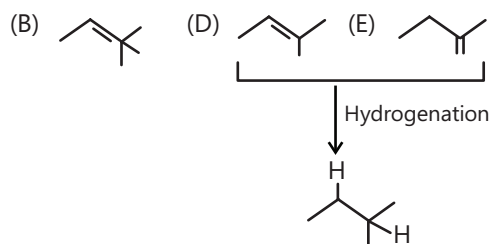
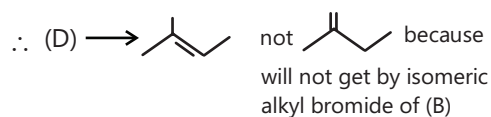
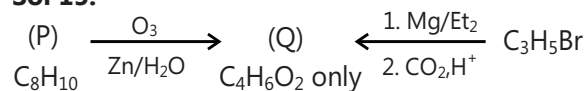
Compound (A) carbocation is more stable resonance is in both the compounds but

(A) have 3 α - H

(B) have 0 α - H

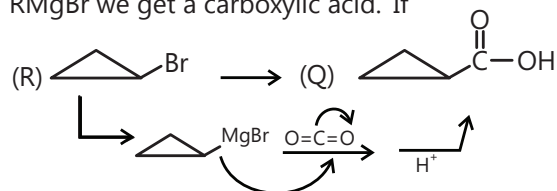
Sol 14:

$\therefore$ (D) is isomer of (C)

**Sol 15:**

$\nwarrow$ symmetric compound

Q is an acid because after reaction with CO_2 , H^+ of RMgBr we get a carboxylic acid. If



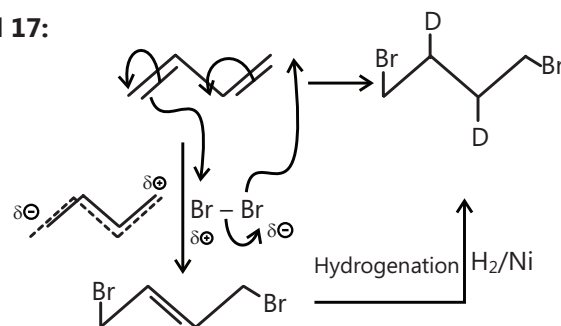
to satisfy the degree of unsaturation of (P) alkyl group must be cyclic.

Sol 16: (A), (B) $\text{C}_5\text{H}_{11}\text{Br}$

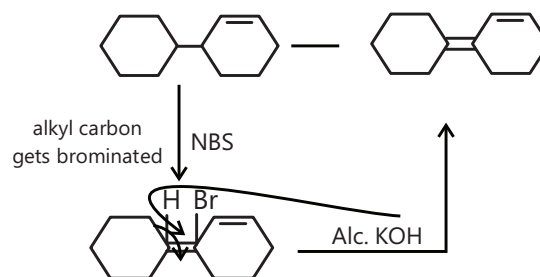
isomeric alkyl bromides (A) $\xrightarrow[\text{KOH}]{\text{alc.}}$ (C) + (D) isomers C_5H_{10}

Sol 17:

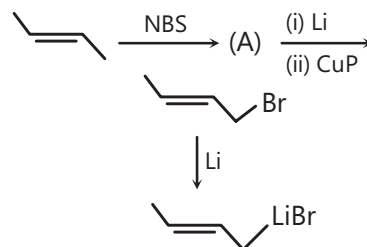
(i)



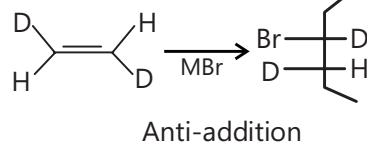
(ii)



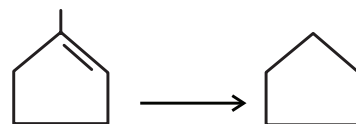
(iii)



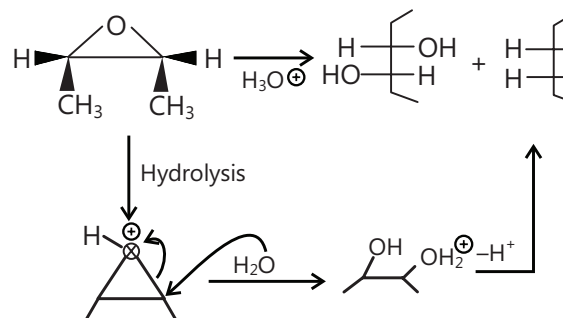
(iv)

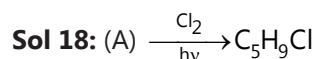


(v)



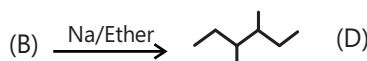
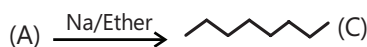
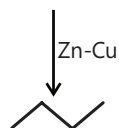
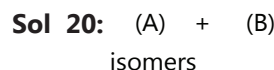
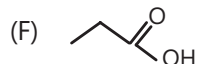
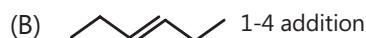
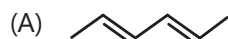
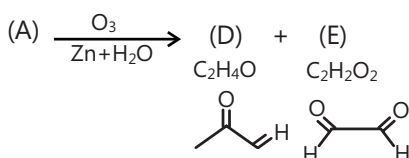
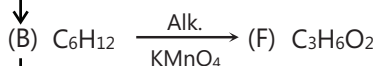
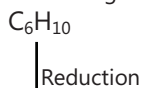
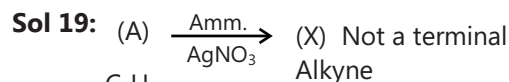
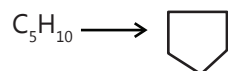
(vi)





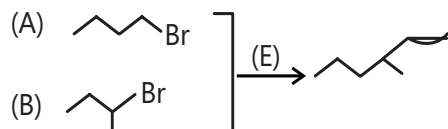
C = 85.7%; H = 14.3%

total molecular weight = 70



But mixture gives (E)

Na/Ether is Wurtz reaction and dimerise the alkyl bromide so they are symmetric.



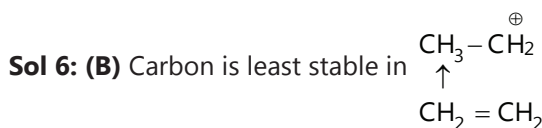
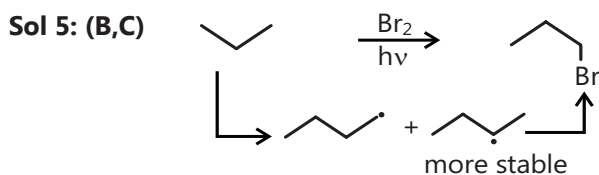
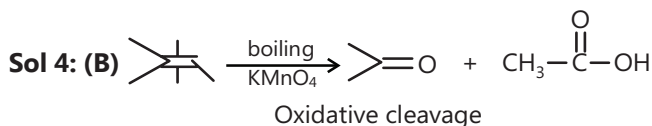
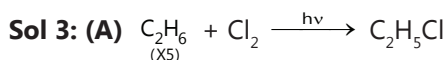
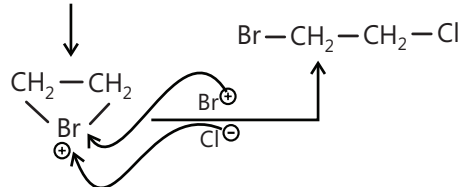
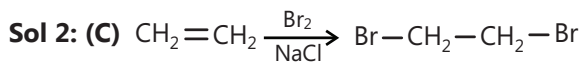
Exercise 2

Single Correct Choice Type

Sol 1: (C) Releases 1.34 mL of a gas at STP

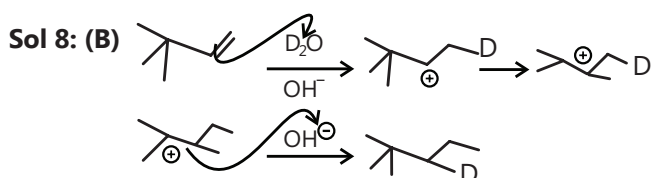
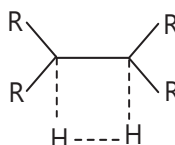
$\therefore$ 3 moles of CH_4

$\therefore$ 3 active α - H hydrogen.

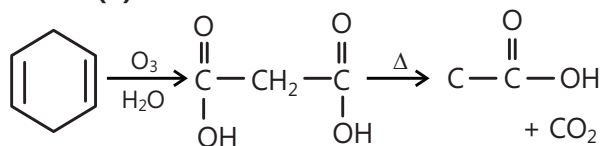
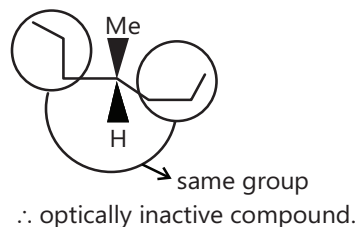
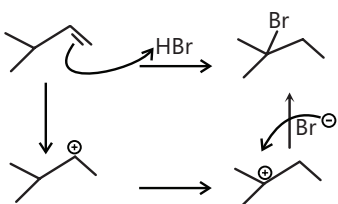
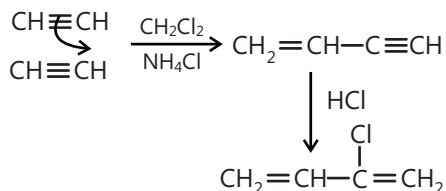
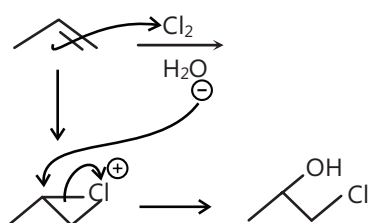
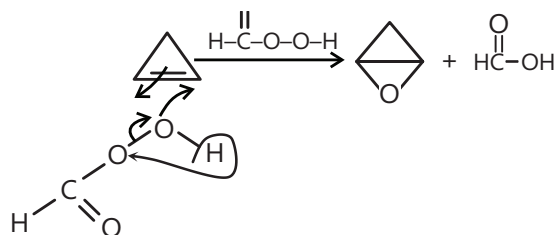
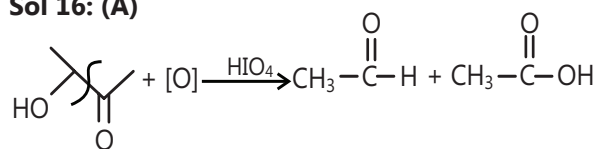
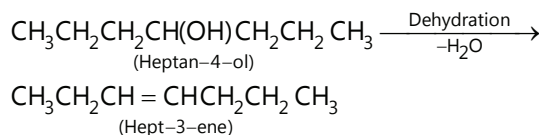
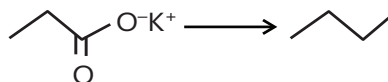
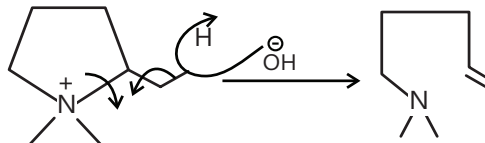
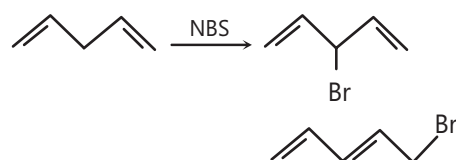
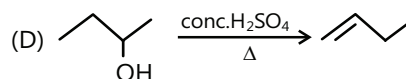
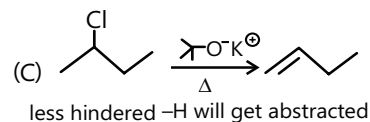
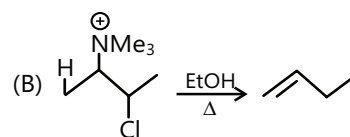
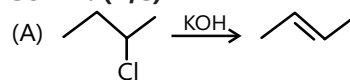


$\therefore$ Addition will be least $\text{CH}_2=\text{CH}_2$

Sol 7: (D) Stability of complex that forms during reaction with H_2

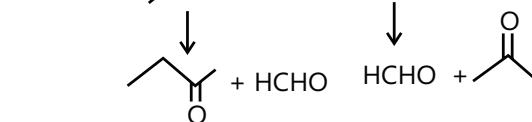
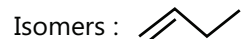
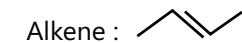
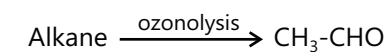


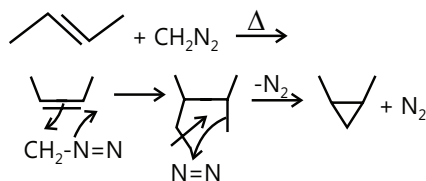
Sol 9: (C) C-C-H is sp^3 hybridised, hence 's' character is less, So bond length in C-H is longest

Sol 10: (C)**Sol 11: (B)** Hydrogenate product**Sol 12: (C)****Sol 13: (D)****Sol 14: (D)****Sol 15: (C)****Sol 16: (A)****Sol 17: (B)****Sol 18: (A)****Sol 19: (B)****Multiple Correct Choice Type****Sol 20: (A,B)****Sol 21: (B,C)**

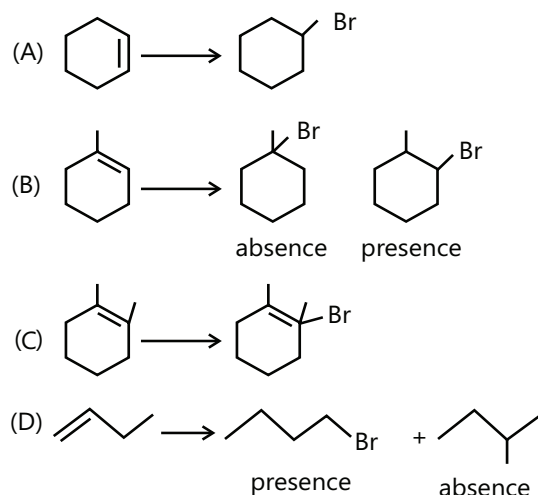
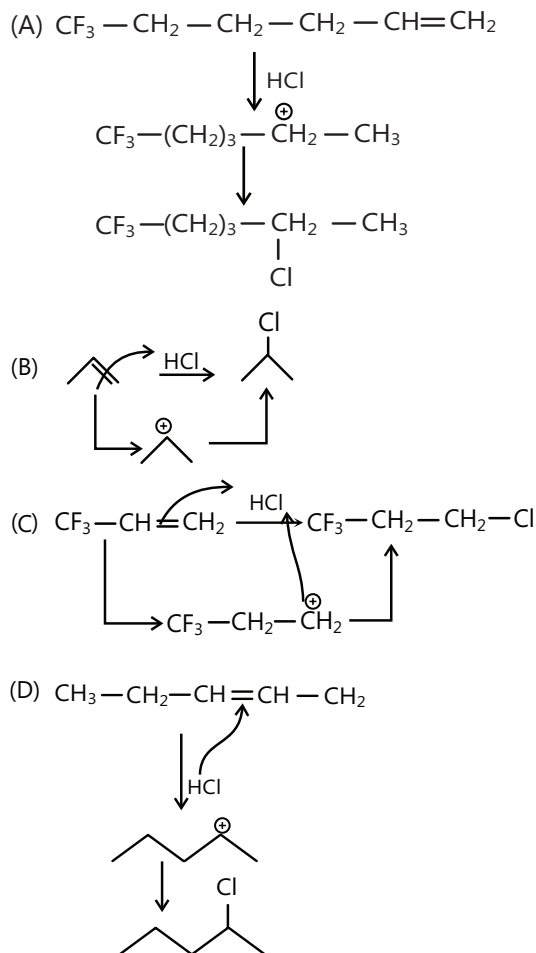
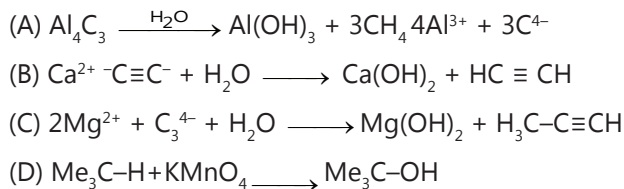
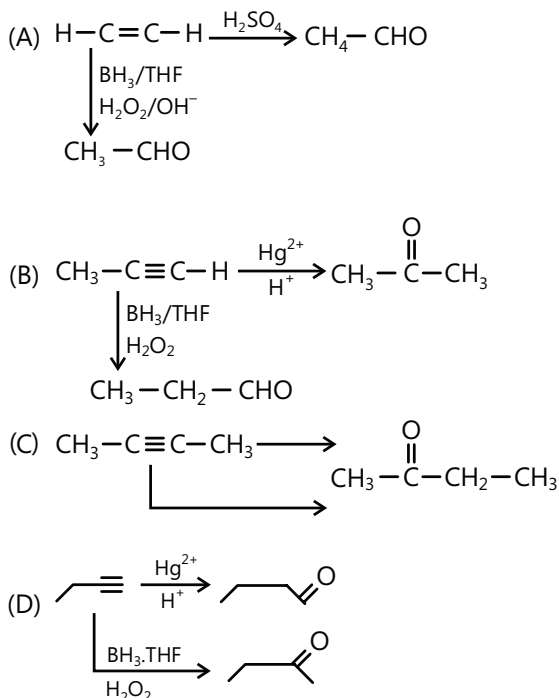
Sol 22: (A,C,D) but the reaction will be reversible since C-I is very weak.

(B) × (C) ✓ (D) more stable system

Sol 23: (A,C)

Sol 24: (A,B,C,D)

Same for trans form.

Sol 25: (A,C)**Sol 26: (A,B,D)****Sol 27: (A,B,C,D)****Sol 28: (A,C)****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.

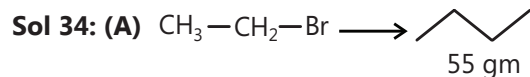
Sol 30: (A) Alkyl iodides are more reactive than alkyl chlorides for elimination reactions as I⁻ is a better leaving group than Cl⁻.

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 the case 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.

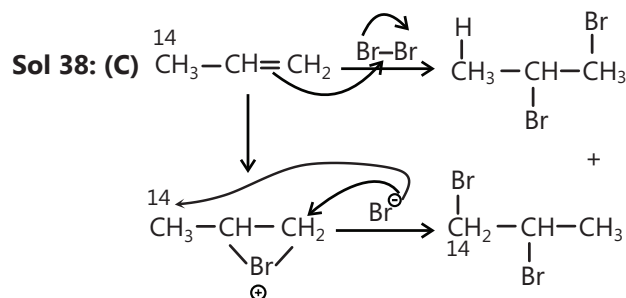
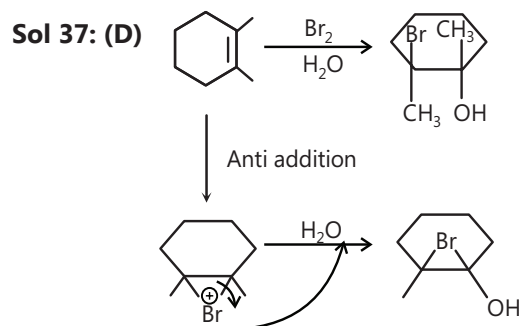
Comprehension Type



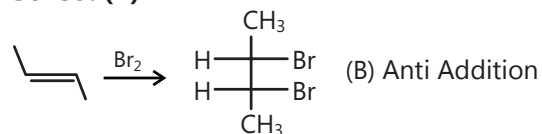
$$\frac{m}{208} = \frac{55}{58}$$



Sol 36: (A) Alkenes generally forms by elimination.

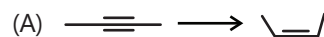


Sol 39: (B)



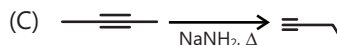
Match the Columns

Sol 40:



cis addition

$\text{H}_2/\text{Pd}/\text{BaSO}_4$



Isomerism



Isomerism

A $\rightarrow$ q; B $\rightarrow$ p; C $\rightarrow$ s; D $\rightarrow$ r

Sol 41: (A) $\rightarrow$ (p) Markonikov

(B) $\rightarrow$ (r) Anti-markonikov

(C) $\rightarrow$ (s) Alkyl carbon get brominated

(D) $\rightarrow$ (q) Br_2 addition

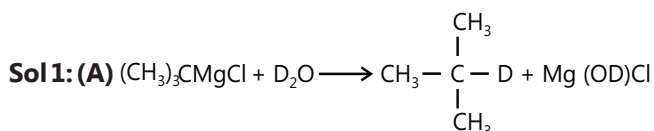
Sol 42: (A) $\rightarrow$ (q) Free radical mechanism

(B) $\rightarrow$ (r) Decarboxylation

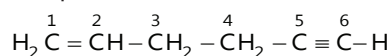
(C) $\rightarrow$ (s) Free radical mechanism

(D) $\rightarrow$ (p) Same as grignard

Previous Years' Questions

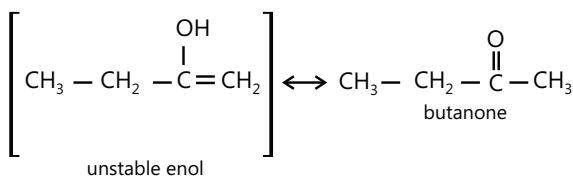
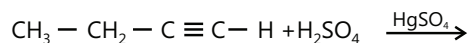


Sol 2: (D) According to the IUPAC conventions, compound can be numbered as:

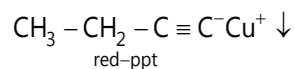
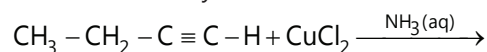


Here, C-2 is sp^2 and C-3 is sp^3 hybridised.

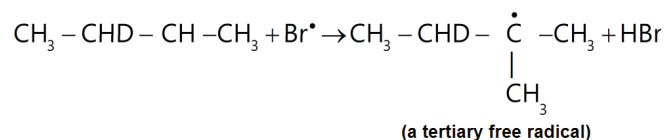
Sol 3: (A) Oxymercuration - demercuration brings about Markownikoff's addition of water as



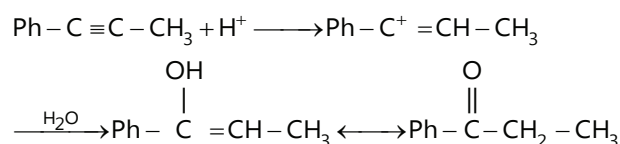
Sol 4: (B) Ammonical CuCl_2 forms red precipitate with terminal alkynes, can be used to distinguish terminal alkynes from internal alkynes:



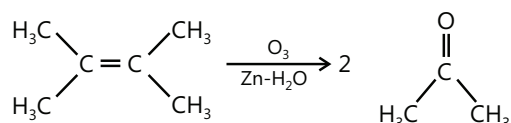
Sol 5: (B) Bromination is highly selective, occur at the carbon where the most stable free radical is formed:



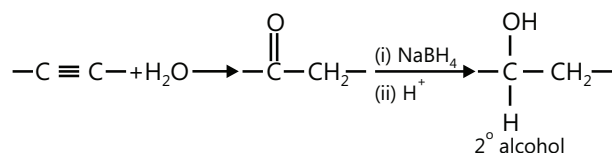
Sol 6: (A) Reaction proceeds through carbocation intermediate:



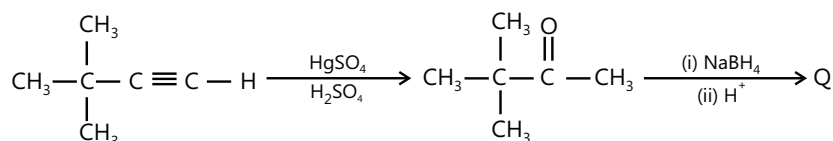
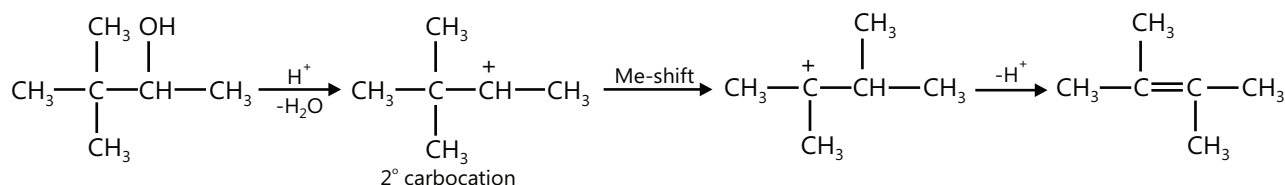
Sol 7, 8: (D, B) The final ozonolysis product indicates that the alkene before ozonolysis is



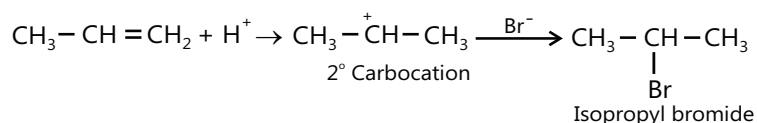
Also $\text{P}(\text{C}_6\text{H}_{10})$ has two degree of unsaturation and oxymercuration demercuration hydration indicates that it is an alkyne. As alkyne, on hydration, gives a carbonyl compound which on reduction with NaBH_4 gives a 2° alcohol.



The secondary alcohol that can give above shown alkene on acid catalyzed dehydration is

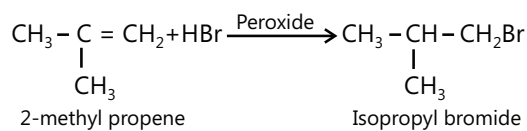


Sol 9: (i) Free radical chlorination of alkane require energy which is supplied either in the form of heat or radiation.



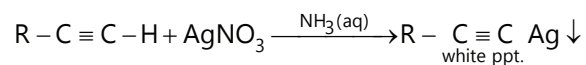
(ii) Addition of HBr proceeds through carbocation intermediates.

Sol 10: (i)



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:



Solution for the Q. No. 11 and 12: (A, C)

