11. ALKENES AND ALKYNES

UNSATURATED HYDROCARBONS

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

1. INTRODUCTION OF ALKENES

Introduction - Structure and Bonding

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

Calculating Degrees of Unsaturation

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

2. NOMENCLATURE OF ALKENES

IUPAC Nomenclature of Alkenes

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

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

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

Step 4: Locate and name attached groups.

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

If there is more than one double bond:

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

Nomenclature of Alkenes

Some alkene or alkenyl substituents have common names.

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

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

a. $CH_3 - CH = CH - CH_3$

b. $Cl_2C = CHCl$

c. $(CH_3)_2C = CH_2$

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

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

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

a. Sym-Dimethyl ethylene

b. Trichloroethylene

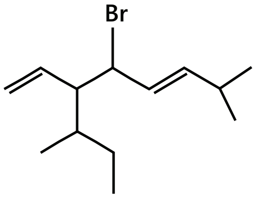
c. unsym-Dimethyl ethylene

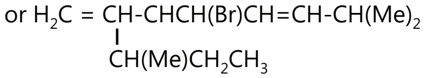
d. unsym-Divinyl ethylene

e. sym-Divinyl ethylene

Illustration 2: Write the IUPAC names of the following.

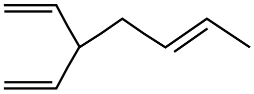
a.



or 

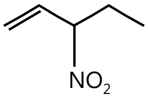
$$H_2C = \underset{\displaystyle CH(Me)CH_2CH_3}{\underset{|}{C}}H\text{-}CHCH(Br)CH{=}CH\text{-}CH(Me)_2$$

b.



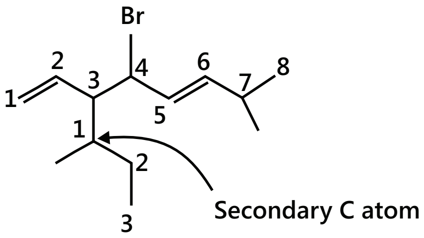
or $(H_2C = CH)_2CHCH_2CH = CHCH_3$

c.



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

Sol: (a)

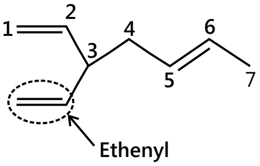


4-Bromo-3-(1-methylpropyl)-7-methyl-1, 5-octadiene

Or

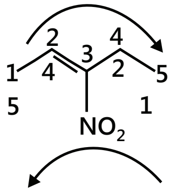
4-Bromo-3-(sec-butyl)-7-methyl-1, 5-octadiene

(b)



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

(c)



3-Nitro-pent-2-ene

3. HYBRIDIZATION OF ALKENES

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

Introduction – Structure and Bonding

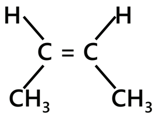
Recall that the double bond consists of a π-bond and a σ-bond.

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

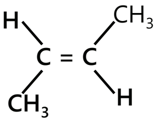
4. ISOMERIZATION

Geometric Isomers in Alkenes

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



cis-2-butene

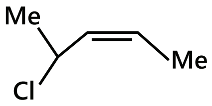


trans-2-butene

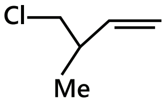
Illustration 3: Which of the following do not show G.I.?

(JEE MAIN)

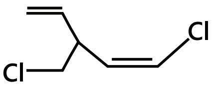
a.



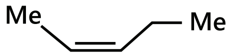
b.



c.

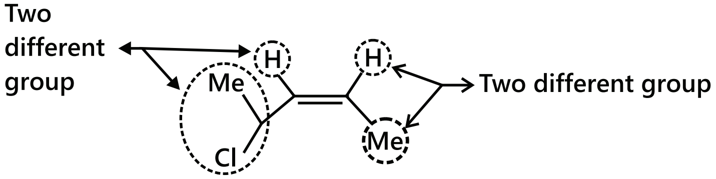


d.



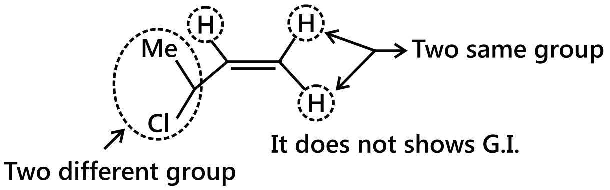
Sol: In order to show Geometrical isomerism, the alkene must contain different substituents.

(a)



Its show G.I.

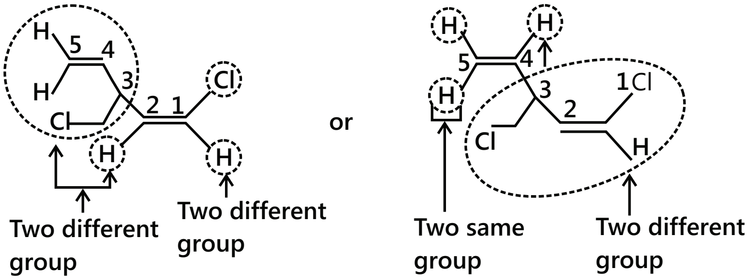
(b)



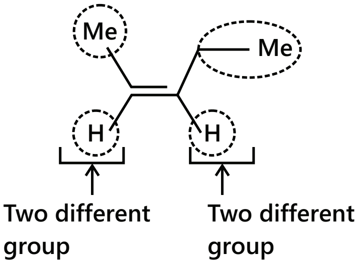
It does not shows G.I.

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 $C_4 - C_5$.



(d)

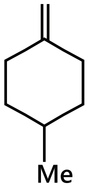


Shows G.I

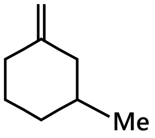
Shows G.I

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

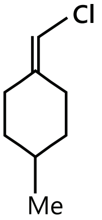
(a)



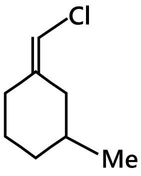
(b)



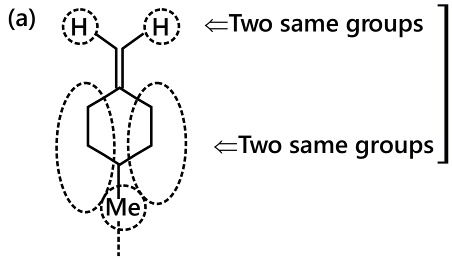
(c)

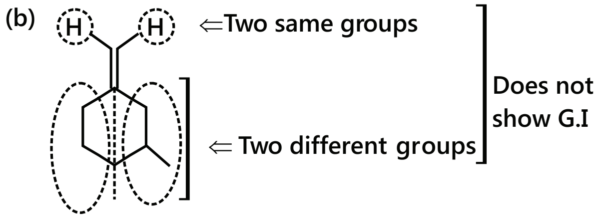


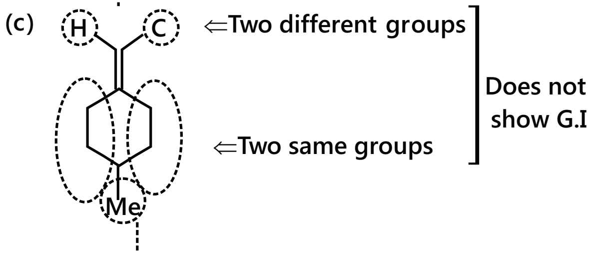
(d)

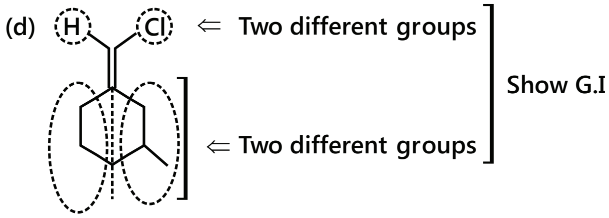


Sol: In order to show Geometrical isomerism the alkene must contain different substituents .i.e. the substituents on both the carbon bearing double bonds must have different substituents. **(JEE ADVANCED)**



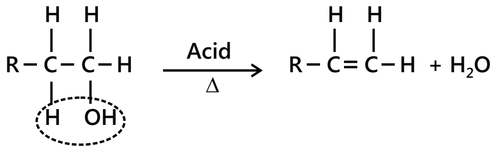






5. PREPARATION OF ALKENES

5.1 Dehydration of alcohols



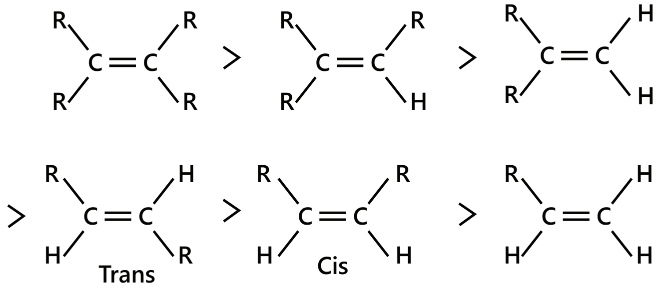
$$R-\underset{H}{\overset{H}{C}}-\underset{OH}{\overset{H}{C}}-H \xrightarrow[\Delta]{\text{Acid}} R-\overset{H}{C}=\overset{H}{C}-H + H_2O$$

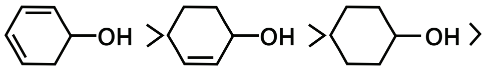
Ease of dehydration of alcohols: 3° > 2° > 1°, because the alkenes formed are more stable.

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

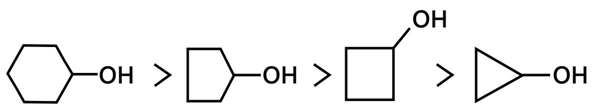
1. Conc. H_2SO_4 at 443 – 453 K (170 – 180°C) acts as Lowry Bronsted acid $H^{\oplus}$ donor.
2. H_3PO_4 (Phosphoric acid at 470 K).
3. Al_2O_3 at 633 K (380°C) acts as a Lewis acid.
4. Heating with P_2O_5 or P_4O_{10} (phosphorous pentoxide).
5. Heating with $POCl_3$ (phosphorous oxychloride) + pyridine.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

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



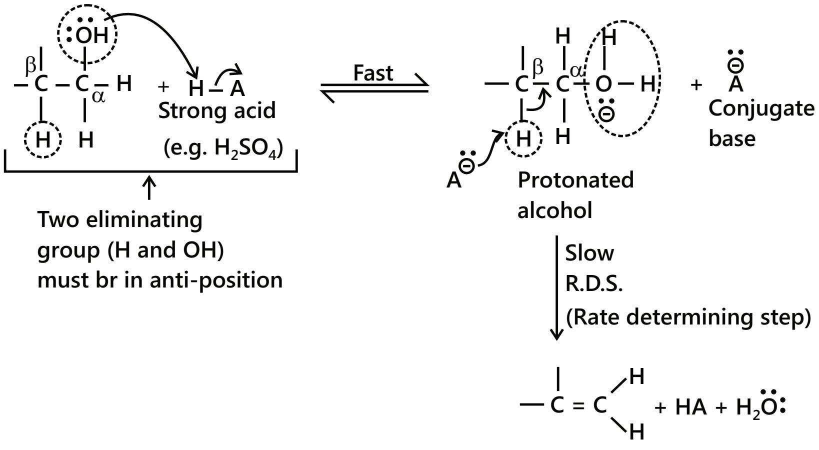


(Stabilisation by extended conjugation)



(Due to ring stability)

Mechanism of dehydration of 1° alcohols: E_2 mechanism



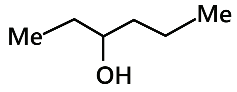
1. The first step in the dehydration of 1° alcohols is protonation.
2. The second step is the attack of C_B (conjugated base) at –proton($-OH_2^+$) and the elimination of protonated hydroxyl group (a good leaving group) takes place simultaneously to form double bond.

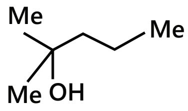
   $\text{Rate}=k\left[\overset{\ominus}{\ddot{A}}\right]$ [protonated alcohol]

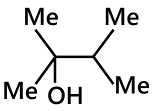
3. Kinetics of the reaction is of the second order and bimolecular.
4. Two eliminating groups (i.e., H and OH groups) must be in anti-position.
5. Reaction is stereospecific and stereo selective (or regioselective).
6. No rearrangement takes place.

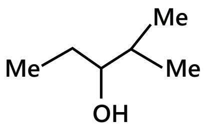
Illustration 5: Arrange the following alcohols in the decreasing order of their ease of dehydration with H_2SO_4.

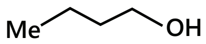
(JEE MAIN)

a.


b.


c.


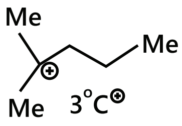
d.


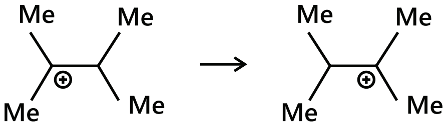
e.


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

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

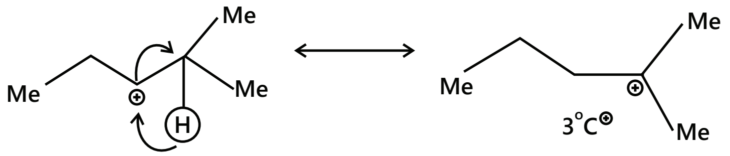
We can see that options (b) and (c) are 3° alcohols, since dehydration of alcohol proceeds through the formation of carbocation, we have to take into consideration the stability of carbocation. 3° carbocation in (c) is more stable due to resonance and gives a more substituted alkene.

(b)


(c)


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

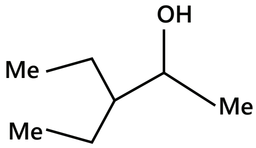
(d)



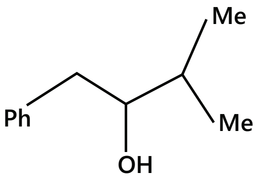
So, the order of dehydration is: (c) > (b) > (d) > (a) > (e)

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

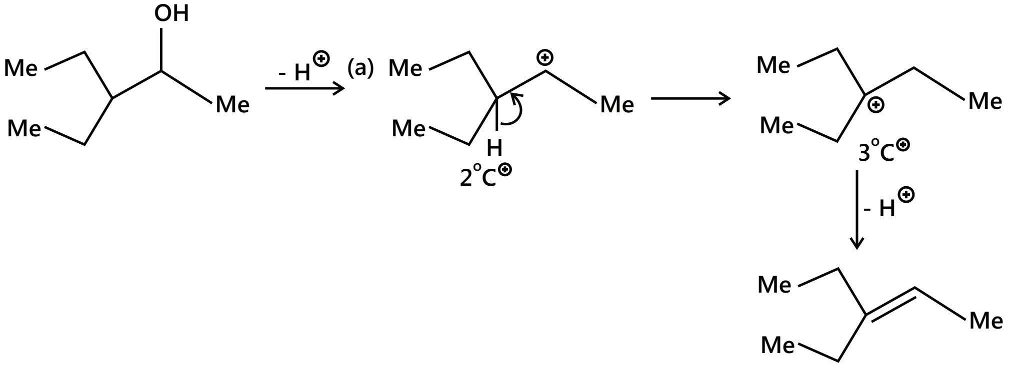
(a)



(b)

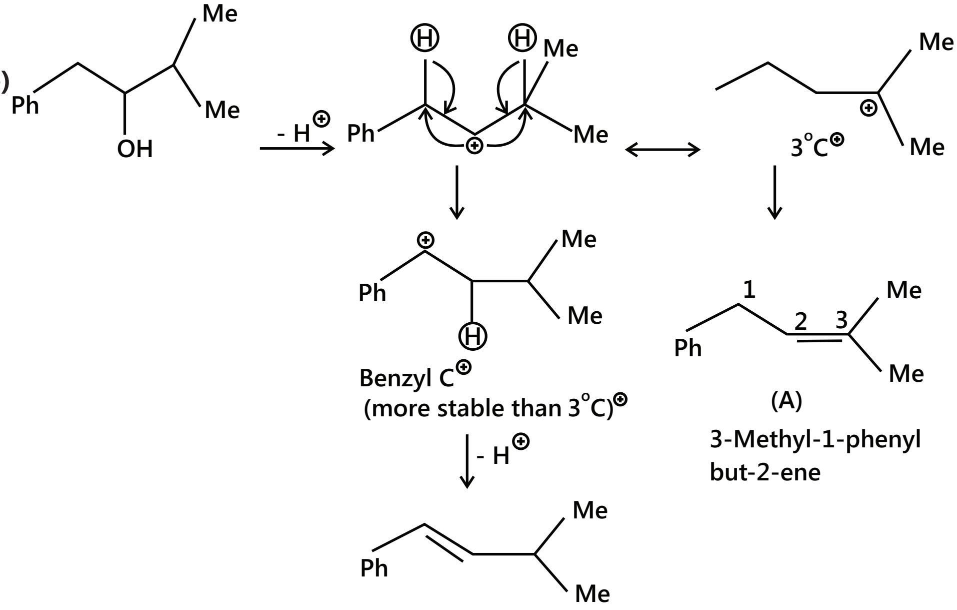


Sol: **(a)**



Saytzeff product

(b)

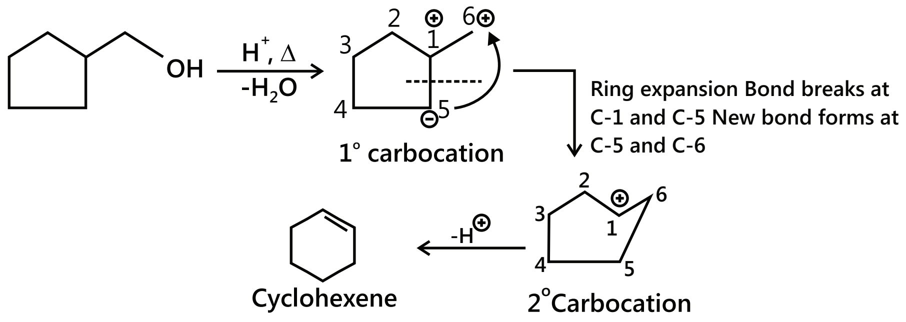


5.2 Rearrangement and Ring Expansion

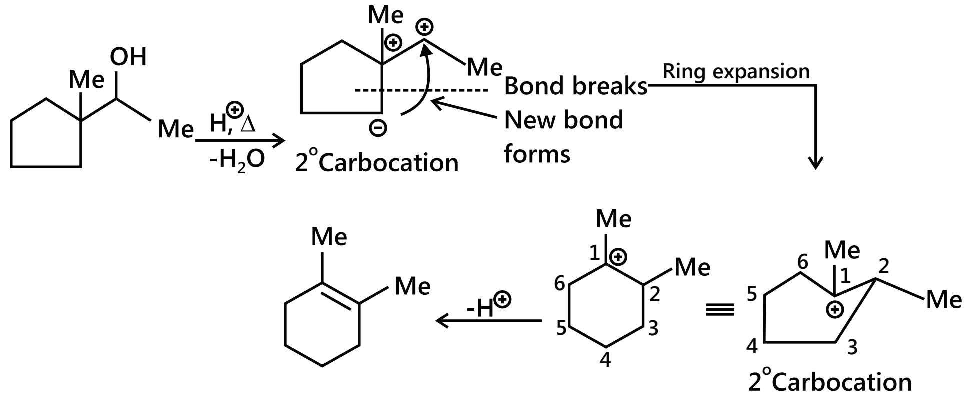
Rearrangement results in the substitution, elimination, and ring expansion or ring contraction. In case of cyclic alcohols, whenever a carbocation is formed outside, the next C atom of a ring, ring expansion may take place, if a relief in the ring strain occurs.

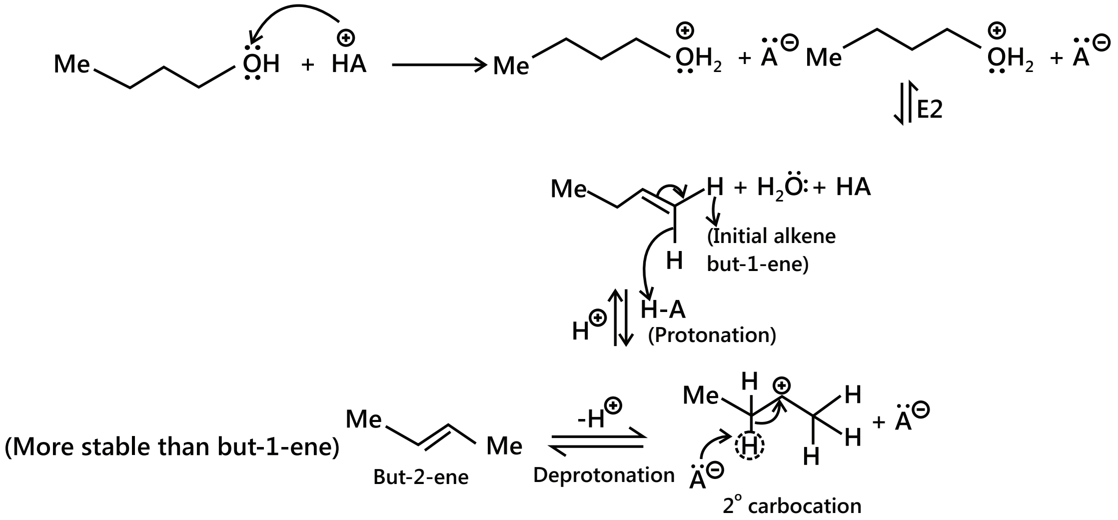
Examples of Ring Expansion:

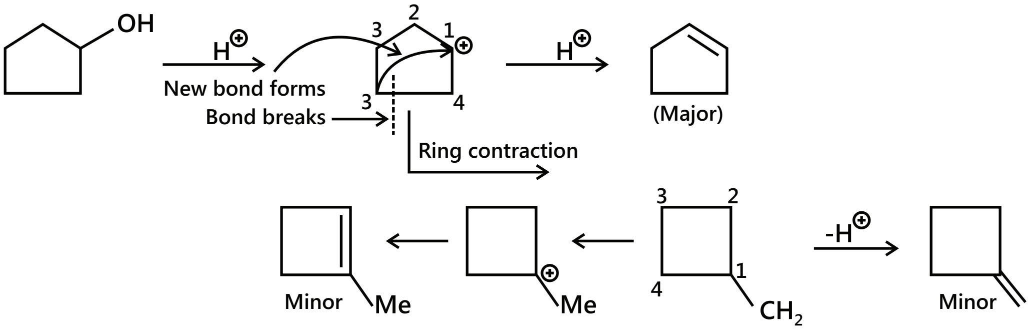
1.



2.







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

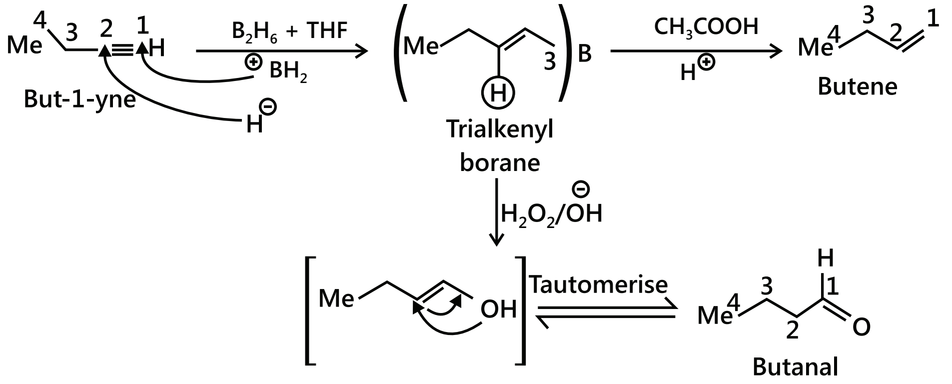
5.3 From Alkynes

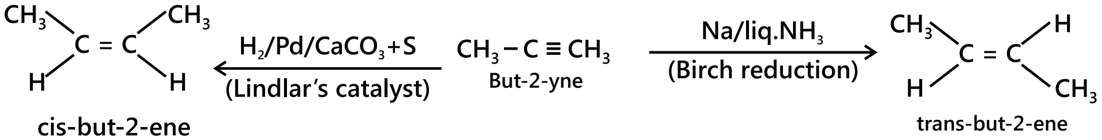
1. By partial reduction of alkynes. The catalytic hydrogenation of alkynes to alkenes occurs faster than that of alkenes to alkanes. Therefore, by using a specific catalyst, it is possible to stop the reduction to give cis-or trans-alkenes depending upon the nature of the catalyst used.

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

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

(a) With terminal alkyne.





(b) **With internal alkynes**:

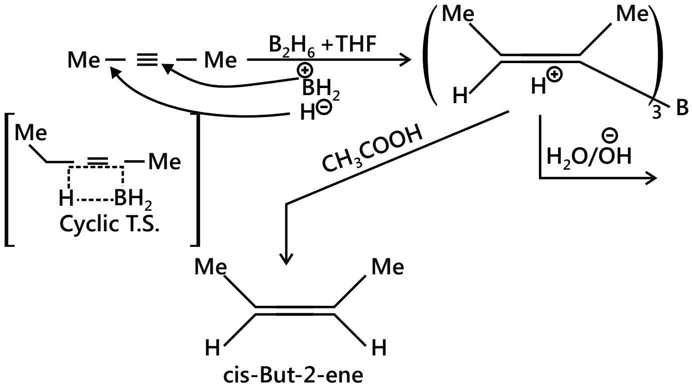
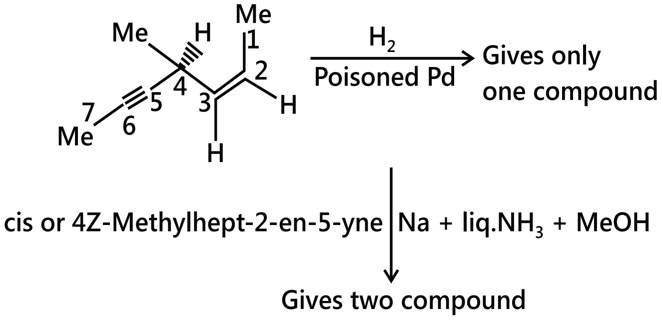
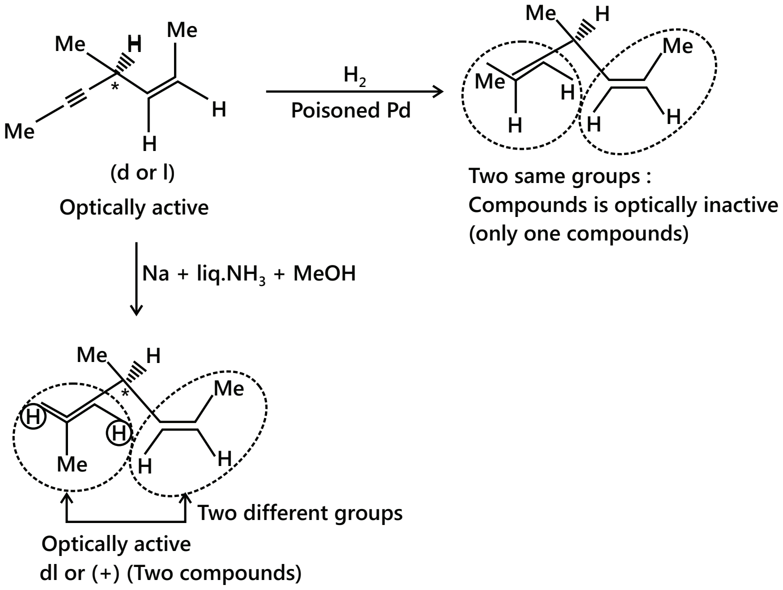


Illustration 7: Explain **(JEE ADVANCED)**



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

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



(d or l)
Optically active

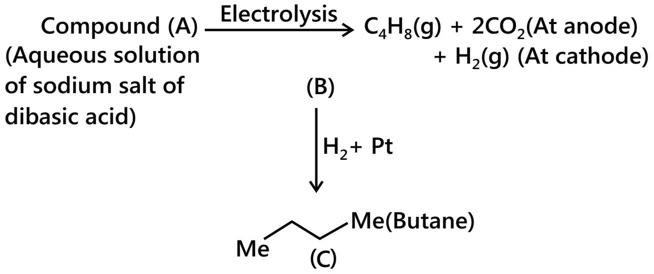
Two same groups :
Compounds is optically inactive
(only one compounds)

Two different groups

Optically active
dl or (+) (Two compounds)

Illustration 8: Identify A and B

(JEE MAIN)



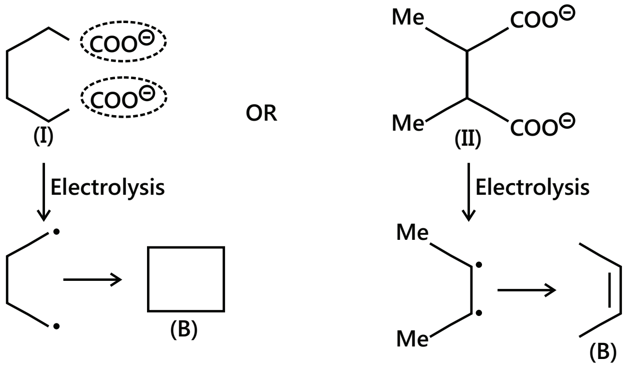
Gas (B) gives test for unsaturation, i.e. it decolourises Br_2 water and aq. $KMnO_4$ solution.

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

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

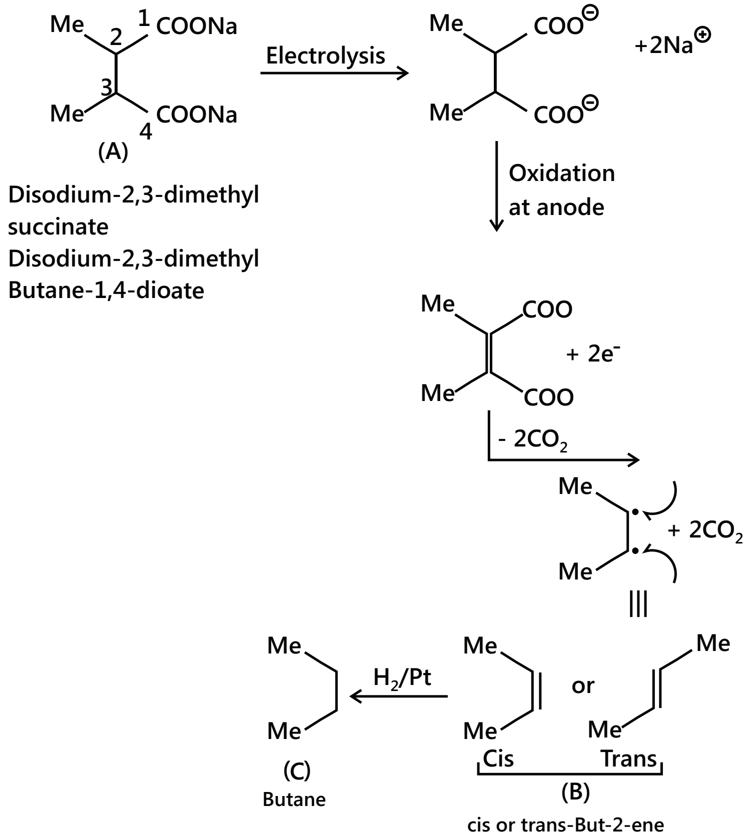
The first step is Kolbe's Electrolysis which proceeds through free radical mechanism.

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



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

Possible reaction is as follows:

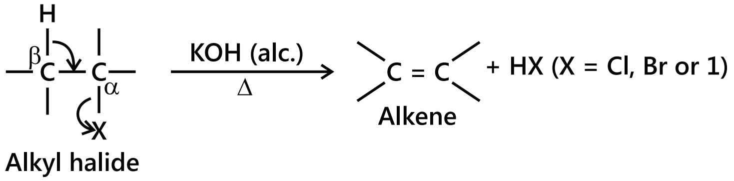


At the cathode, the reduction of H_2O takes place (since reduction potential of H_2O > reduction potential of Na^+ ion).

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

5.4 From Alkyl Halides

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



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

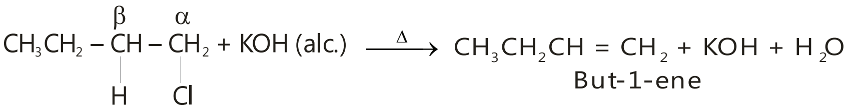
Iodoethane (Ethyl iodide) → Ethene (Ethylene)

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

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

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

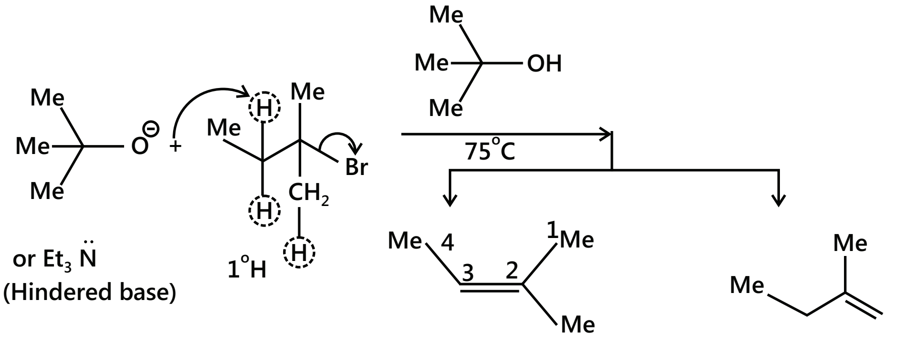
Saytzeff rule: Depending upon the structure, alkyl halides may give one or more isomeric alkenes. For example, dehydrohalogenation of 1-chlorobutane gives only one alkene, i.e., but-1-ene since only one type of β-hydrogen is available on the left side of the molecule.



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

1-Chlorobutane

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



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

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

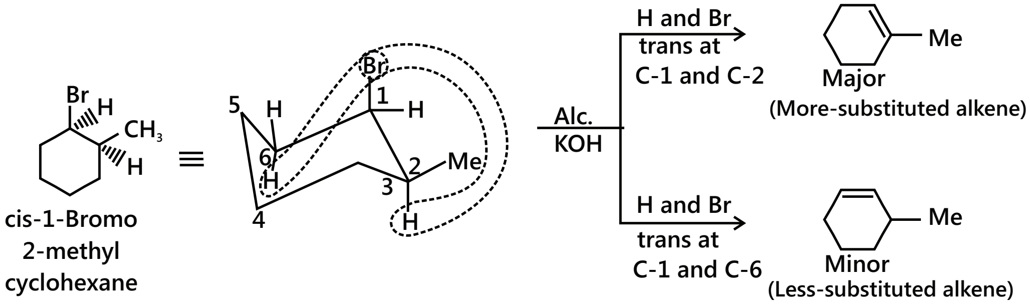
It is due to the steric hindrance of the bulky base. The large tert-butoxide ion finds difficulty in removing one of the internal 2° H atoms because of greater steric hindrance (or crowding) at that site in the transition state (T.S.). It removes one of the more exposed 1°H atoms of the methyl group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

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

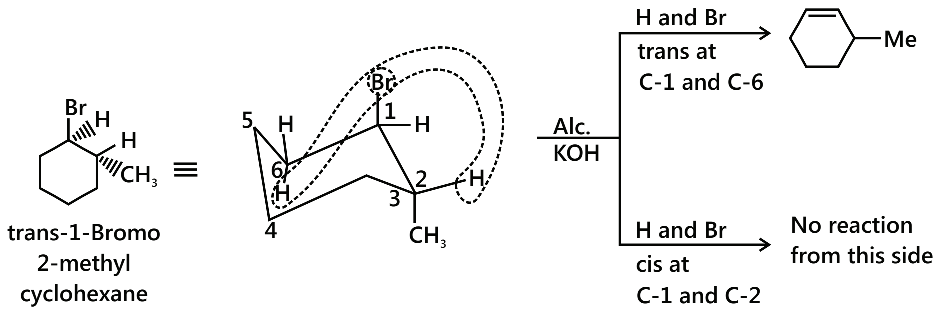
When the more substituted alkene obtained by Saytzeff rule is sterically hindered, the less-substituted alkene is formed in a major amount.

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

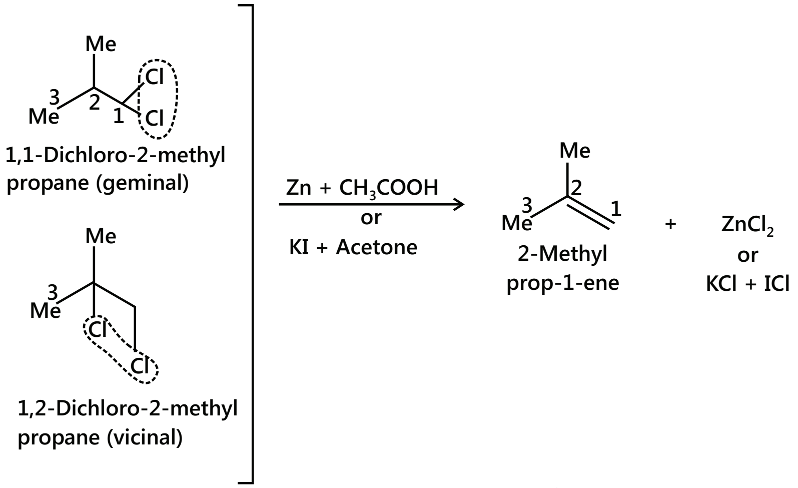
(i) Anti-elimination can occur in two ways with cis-isomer.

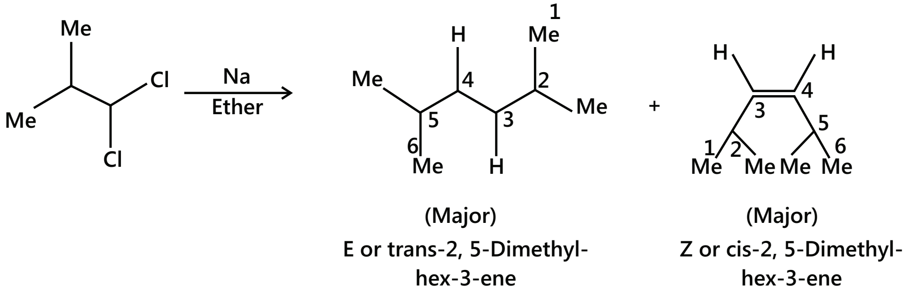


(ii) Anti-elimination can occur in one way with the trans- isomer.



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

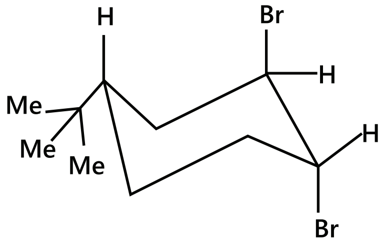


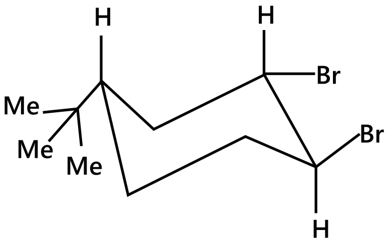


E_2 Dehalogenation is anti

Reaction is stereospecific

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





A forms alkene B does not.

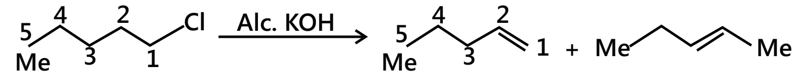
Illustration 9: Identify all the possible alkenes that would be formed on the dehydrohalogenation of the following organic halides with alcoholic KOH. Also, identify the major alkene.

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

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

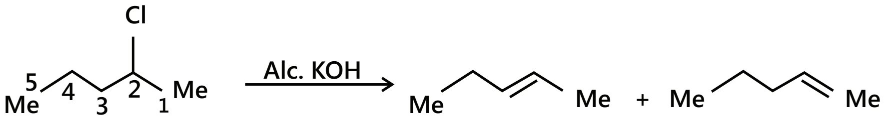
Order of stability of carbocation – tert> sec>primary.

(a)



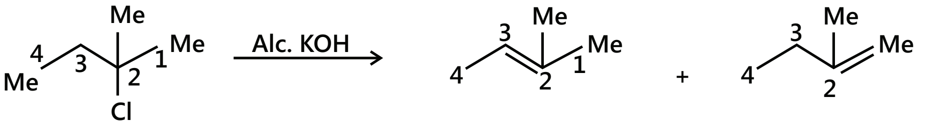
Pent-1-ene (Minor) **Pent-2-ene (Major)**

(b)



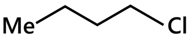
Pent-2-ene (Major) **Pent-1-ene (Minor)**

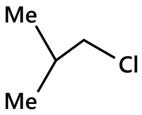
(C)

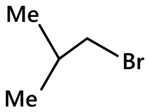


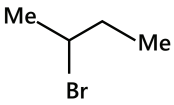
2-Methyl but-2-ene (Major) **2-Methyl but-1-ene (Minor)**

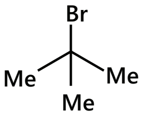
Illustration 10: Predict the order of reactivity of the following compounds in dehydrohalogenation. **(JEE MAIN)**

I.


II.


III.


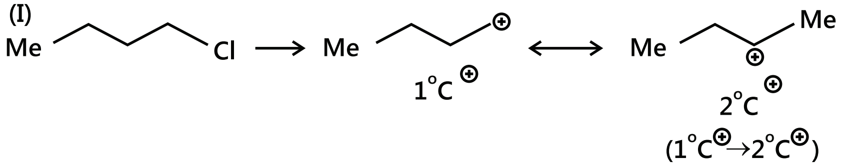
IV.


V.


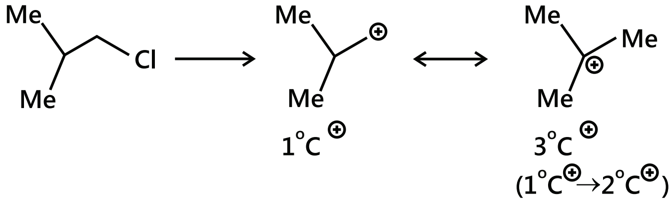
Sol: Order of formation of carbocation is 3° > 2° > 1°

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

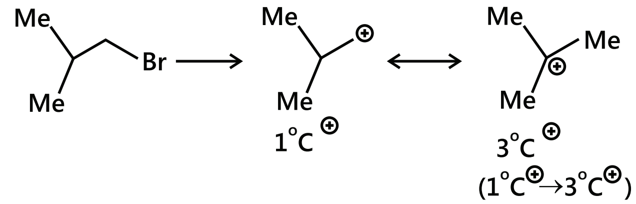
(I)



(II)

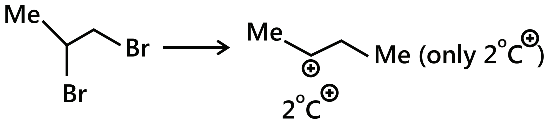


(III)



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

(IV)



(V)

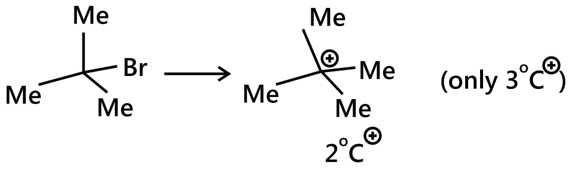
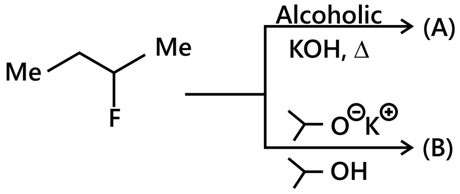
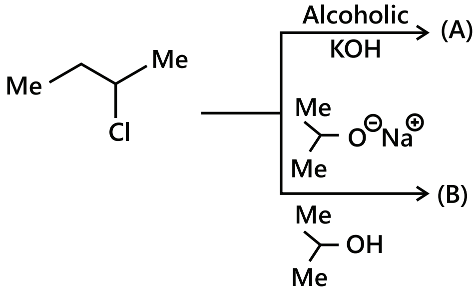


Illustration 11: Given the major and minor products of the following reactions.

a.

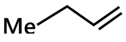


b.

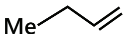


(JEE ADVANCED)

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

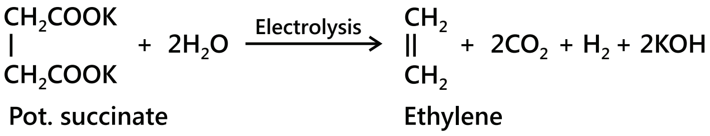
(a) Here RX is RF, thus less-substituted alkene (Hofmann elimination) is formed, irrespective of whether the base is bulky or non-bulky. Both (A) and (B) are same. 

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

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

5.5 Kolbe's Electrolytic Method

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

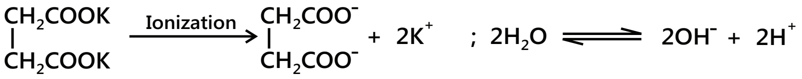


$$\begin{array}{c}CH_2COOK\\ |\\ CH_2COOK\end{array} + 2H_2O \xrightarrow{\text{Electrolysis}} \begin{array}{c}CH_2\\ ||\\ CH_2\end{array} + 2CO_2 + H_2 + 2KOH$$

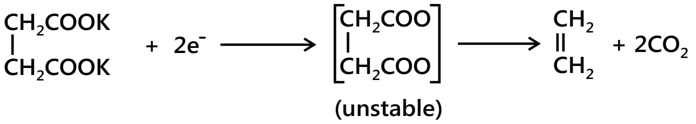
Pot. succinate   Ethylene

The reaction is believed to occur by the following steps:

At anode:



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



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

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

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

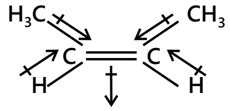
6. PHYSICAL PROPERTIES OF ALKENES

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

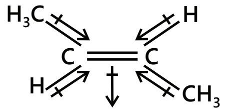
6.1 Boiling Point

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

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

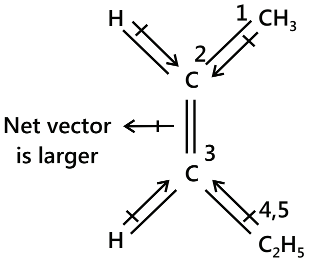


Net dipole
It shows dipole moment
(Hence, slightly polar)
b.p. (277 K)

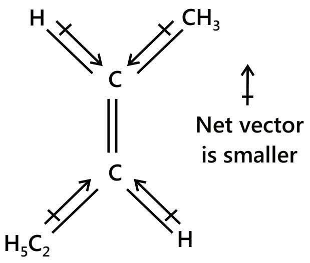


(All vectors cancel)

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



cis-Pent-2-ene
(A)



trans-Pent-2-ene
(B)

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

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

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

6.2 Solubility

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

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

ii. For which pairs could you use ΔH_h°?

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

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

(b) 2,3-Dimethyl-but-2-ene ΔH_C°

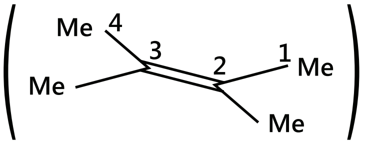
II. (c) Hexene (d) cis-Hex-3-ene

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

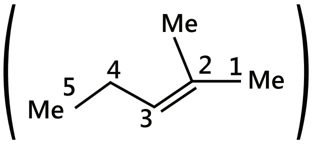
IV. (g) cis-Hex-3-ene (h) trans-Hex-3-ene **(JEE MAIN)**

Sol:

(I)



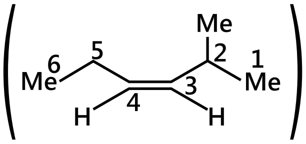
is more stable than (a)



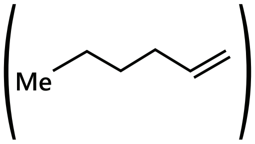
(tetra-substituted) **(tri-substituted)**

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

(II)



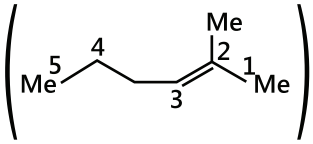
is more stable than (c)



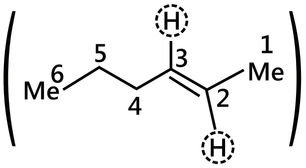
(Di-substitued) **(Mono-substitued)**

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

(III)

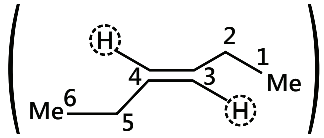


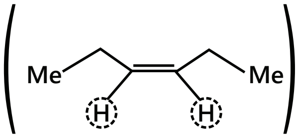
is more stable than (e)



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

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

(IV) 

is more stable than (g) 

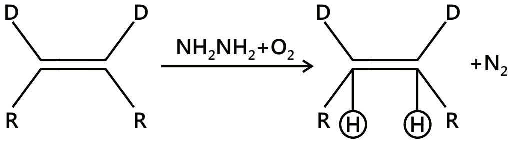
7. REACTIONS OF ALKENES

7.1 Hydrogenation of Alkenes

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

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

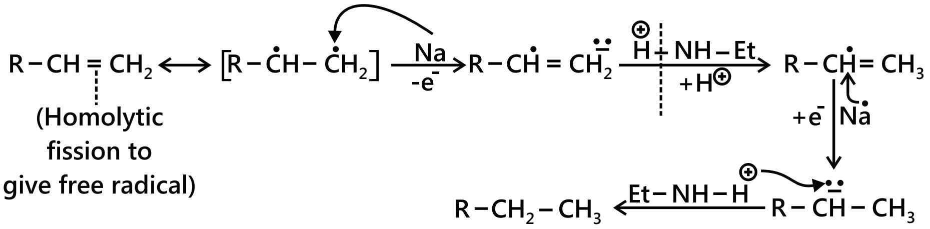
Hydrazine $(NH_2NH_2 + O_2)$



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

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

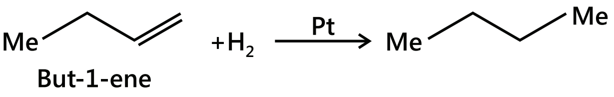
Source of H atom is from liquid NH_3. If ND_3 is used, D atom will be added.



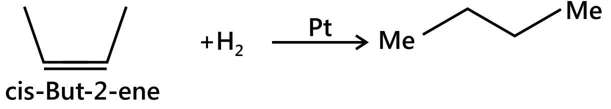
Heat of hydrogenation: The energy released when one mole of alkenes is hydrogenated with H_2 is called the heat of hydrogenation.

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

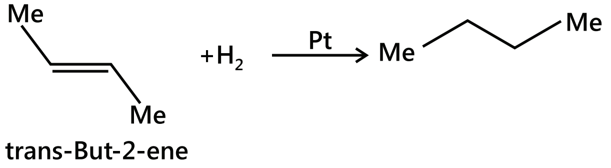
Trans-But-2-ene > cis-But-2-ene > But-1-ene



ΔH° = -127 kJ mol^{-1}



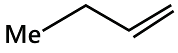
ΔH° = -120 kJ mol^{-1}



ΔH° = -115 kJ mol^{-1}

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

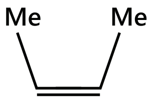
I.



But-1-ene

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

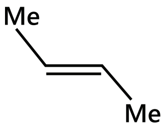
II.



cis-But-2-ene

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

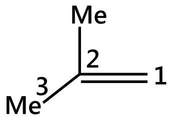
III.



trans-But-2-ene

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

IV.



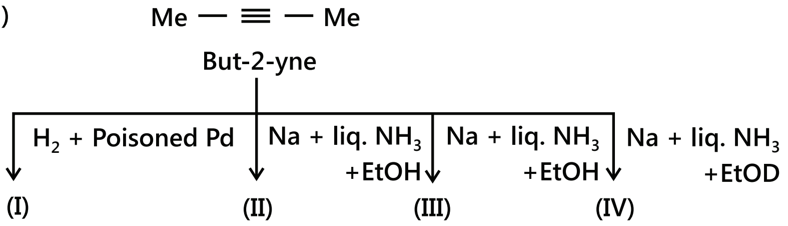
2-Methylprop-1-ene

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

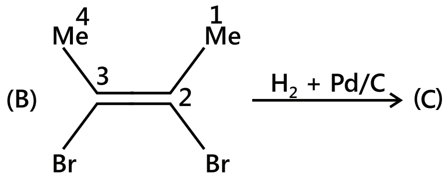
Although each isomer mentioned above (I – IV) consumes 6 moles of O_2 and produces 4 moles of CO_2 and 4 moles of H_2O, the comparison of ΔH_C° shows that (IV) is most stable among the four isomers because it evolves the least heat. Thus, the order of stability is: (IV) > (III) > (II) > (I).

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

(a)

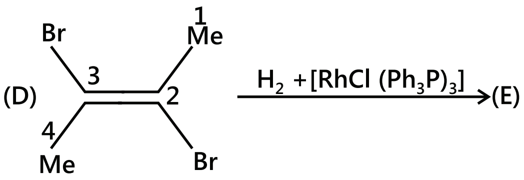


(b)



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

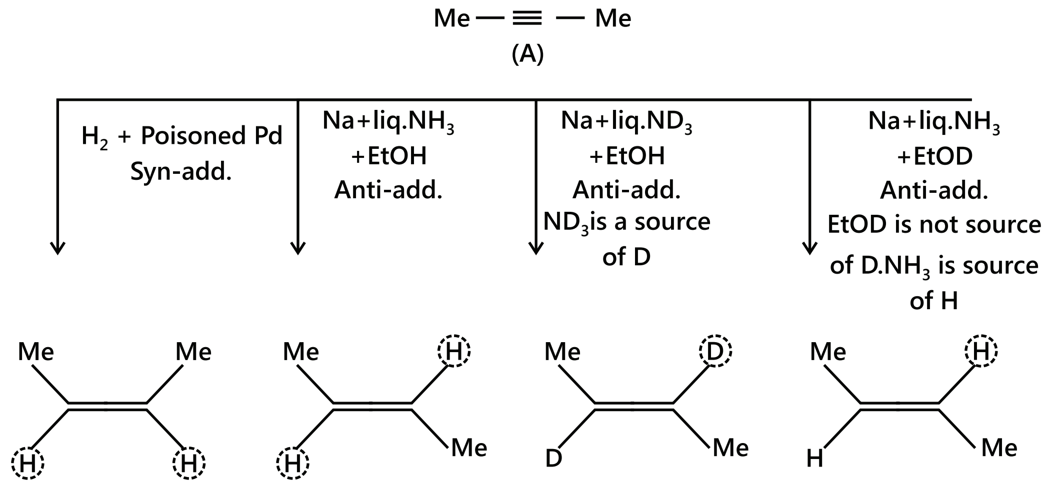
(c)



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

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

(a)



Z or cis-But-2-ene
(I)

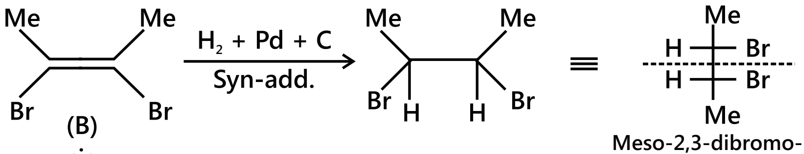
E or trans-But-2-ene
(II)

E or trans-2,3-Dideuterio-but-2-ene
(III)

E or trans-But-2-ene
(IV)

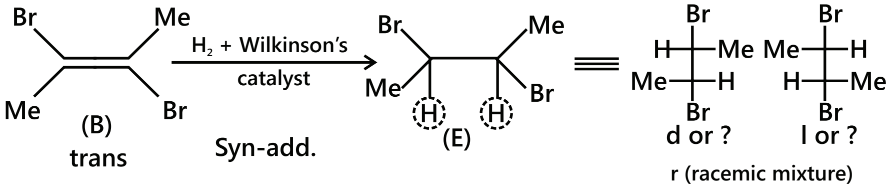
(b) **Note:** Metal + H_2 does not reduce (R – X) to (R – H) but reduced (Ar – X) to (Ar – H).

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



Meso-2,3-dibromo-butane
(Due to plane of summetry)
(O.I.A.)

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

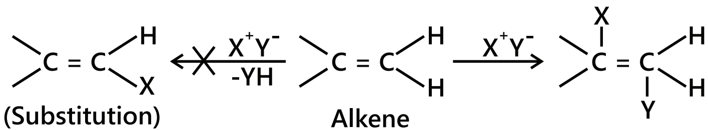


r (racemic mixture)

7.2 Electrophilic Addition Reactions

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

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



(Substitution)

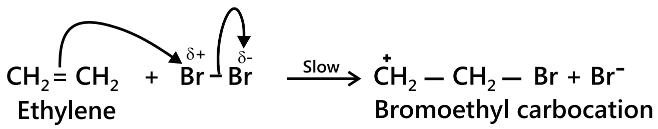
Alkene

(Addition)

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

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

This step can simply be represented as

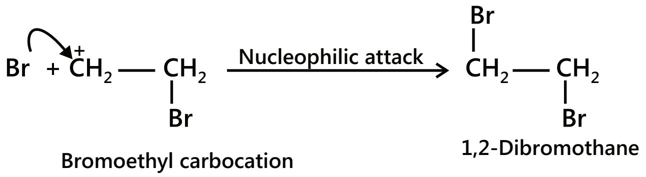


$$CH_2=CH_2 + \overset{\delta+}{Br}-\overset{\delta-}{Br} \xrightarrow{\text{Slow}} \overset{+}{C}H_2-CH_2-Br + Br^-$$

Ethylene

Bromoethyl carbocation

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



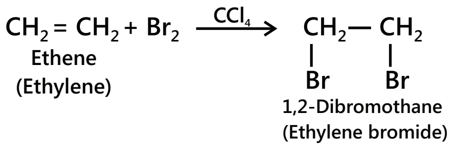
$$Br + \overset{+}{C}H_2-\underset{Br}{CH_2} \xrightarrow{\text{Nucleophilic attack}} \overset{Br}{CH_2}-\underset{Br}{CH_2}$$

Bromoethyl carbocation

1,2-Dibromothane

7.3 Addition of X_2

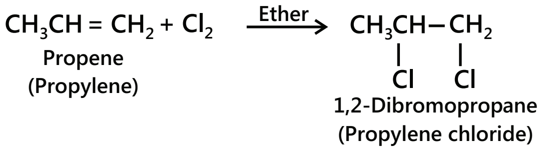
Addition of halogens: Halogens such as chlorine and bromine readily add to alkenes to form 1, 2-dihaloalkanes. For example,



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

Ethene (Ethylene)

1,2-Dibromothane (Ethylene bromide)



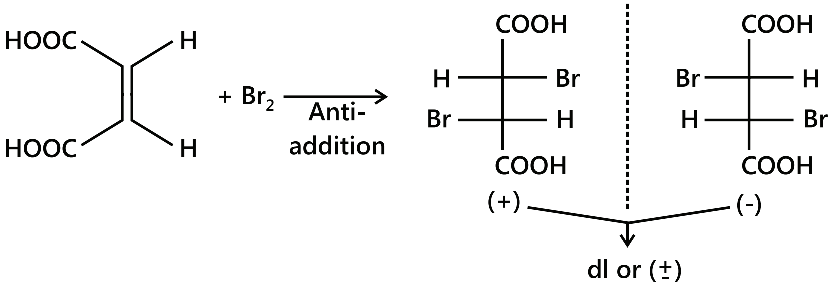
$$CH_3CH=CH_2+Cl_2 \xrightarrow{\text{Ether}} CH_3\underset{Cl}{CH}-\underset{Cl}{CH_2}$$

Propene (Propylene)

1,2-Dibromopropane (Propylene chloride)

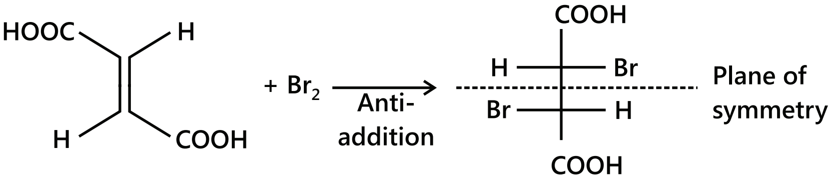
During the addition of bromine to alkenes, bromine loses its orange red colour, since the dibromide formed is colourless. This reaction is, therefore, used as a **test for unsaturation in organic compounds.** Reactivity order: $F_2 > Cl_2 > Br_2 > I_2$ (because the $E_{activation}$ order is: $F_2 < Cl_2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

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



2,3-Dibromobutan- 1,4-dioic acid

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

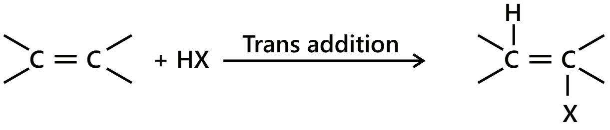


(trans)

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

7.4 Addition of HX

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



Alkyl halide

e.g.

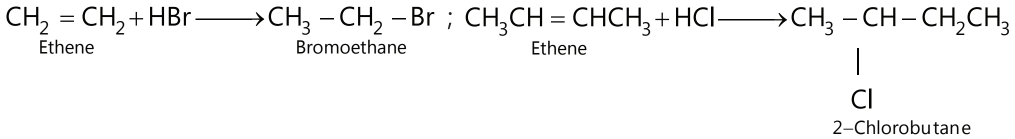
$$\underset{\text{(Ethylene)}}{\underset{\text{Ethene}}{CH_2{=}CH_2}} + HBr \longrightarrow \underset{\text{(Ethyl bromide)}}{\underset{\text{Bromoethane}}{CH_3-CH_2Br}}$$

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

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

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

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

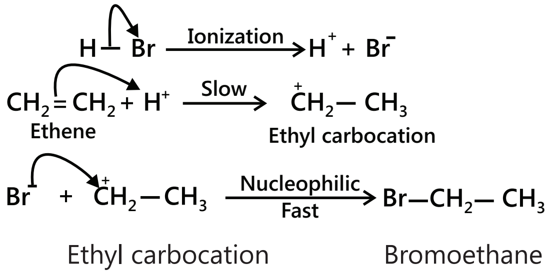


$$\underset{\text{Ethene}}{CH_2=CH_2} + HBr \longrightarrow \underset{\text{Bromoethane}}{CH_3-CH_2-Br} \;;\; \underset{\text{Ethene}}{CH_3CH=CHCH_3} + HCl \longrightarrow \underset{\text{2–Chlorobutane}}{CH_3-\underset{\displaystyle Cl}{\underset{|}{CH}}-CH_2CH_3}$$

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

Step 1.

Step 2.



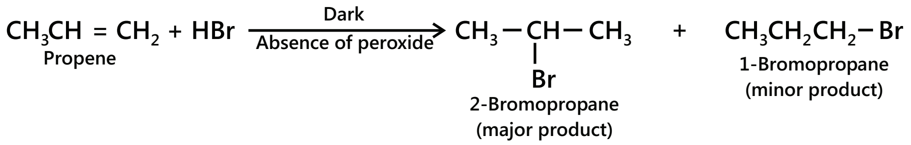
$$H-Br \xrightarrow{\text{Ionization}} H^+ + Br^-$$

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

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

Ethyl carbocation Bromoethane

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

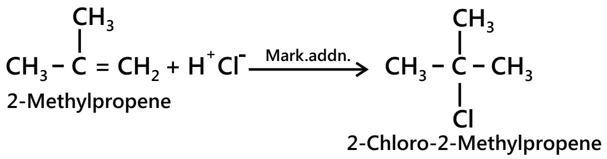


$$CH_3CH=CH_2 + HBr \xrightarrow[\text{Absence of peroxide}]{\text{Dark}} CH_3-\underset{\displaystyle Br}{\underset{|}{C}H}-CH_3 + CH_3CH_2CH_2-Br$$

Propene; 2-Bromopropane (major product); 1-Bromopropane (minor product)

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

For example,

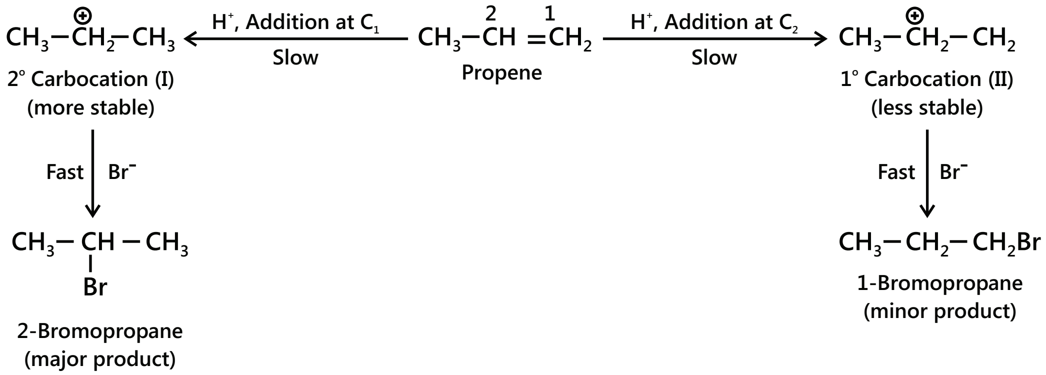


$$CH_3-\overset{\displaystyle CH_3}{\overset{|}{C}}=CH_2 + \overset{+}{H}\overset{-}{Cl} \xrightarrow{\text{Mark.addn.}} CH_3-\underset{\displaystyle Cl}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_3$$

2-Methylpropene; 2-Chloro-2-Methylpropene

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

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



$$CH_3-\overset{\oplus}{C}H_2-CH_3 \xleftarrow[\text{Slow}]{H^+,\text{ Addition at }C_1} CH_3-\overset{2}{C}H=\overset{1}{C}H_2 \xrightarrow[\text{Slow}]{H^+,\text{ Addition at }C_2} CH_3-\overset{\oplus}{C}H_2-CH_2$$

2° Carbocation (I) (more stable); Propene; 1° Carbocation (II) (less stable)

$$\downarrow \text{Fast } Br^- \qquad\qquad \downarrow \text{Fast } Br^-$$

$$CH_3-\underset{\displaystyle Br}{\underset{|}{C}H}-CH_3 \qquad\qquad CH_3-CH_2-CH_2Br$$

2-Bromopropane (major product); 1-Bromopropane (minor product)

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

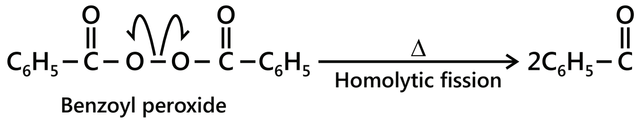
$$CH_3CH=CH_2 + HBr \xrightarrow[\text{Anti-Mark.add.}]{(C_6H_5COO)_2,\ \Delta} CH_3CH_2CH_2Br$$

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

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

(a) Initiation.

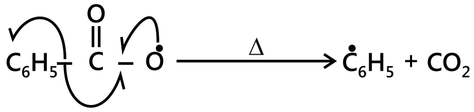
(i)



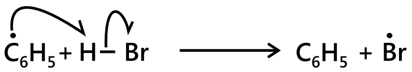
$$C_6H_5-\overset{\displaystyle O}{\overset{\|}{C}}-O-O-\overset{\displaystyle O}{\overset{\|}{C}}-C_6H_5 \xrightarrow[\text{Homolytic fission}]{\Delta} 2C_6H_5-\overset{\displaystyle O}{\overset{\|}{C}}$$

Benzoyl peroxide

(ii)

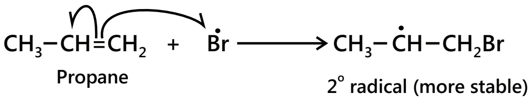


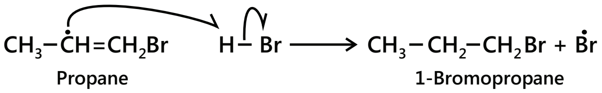
$$C_6H_5-\overset{\displaystyle O}{\overset{\|}{C}}-\dot{O} \xrightarrow{\Delta} \dot{C}_6H_5 + CO_2$$

(iii) 

(b) Propagation: It consists of two steps.

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

(i) 

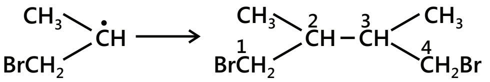
(ii) 

(c) Termination:

(i) $2Br \longrightarrow Br_2$

(ii) $CH_3-CH-CH_2Br+Br \longrightarrow CH_3-CHBr-CH_2Br$

1,2–Dibromopropane

(iii) 

1,4-Dibromo-2,3-dimethylbutane

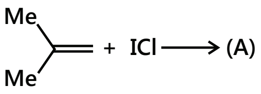
HCl, HF and HI do not obey Peroxide effect. Only HBr does WHY?

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

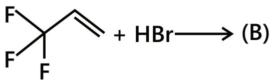
In HBr, both the steps being exothermic, it obeys the peroxide effect.

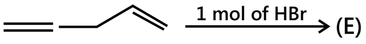
From the above data, it is clear that only with HBr, both the steps are exothermic and hence the peroxide effect is observed. With HCl or HF, the peroxide effect is not observed because the second step involving the reaction of carbon radical with HCl or HF is endothermic. Further, the peroxide effect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

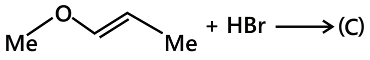
Illustration 14: Complete following reactions: **(JEE MAIN)**

(a) 

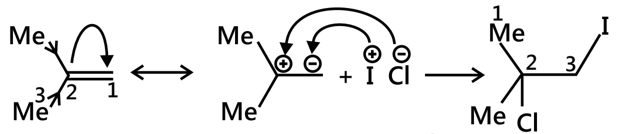
(d) 

(b) 

(e) 

(c) 

Sol: (a)

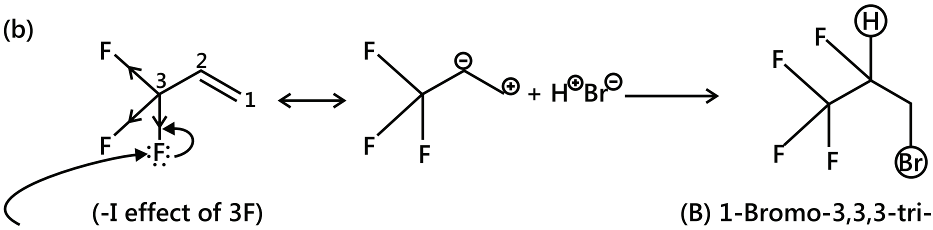


[+I effect of two (me) groups]
2-Methyl but-1-ene
or
Isobutylene

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

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

(b)



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

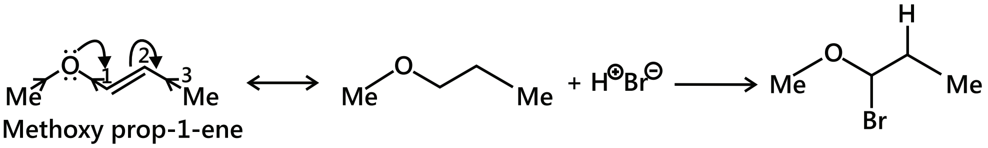
(B) 1-Bromo-3,3,3-tri-fluoroprpane

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

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

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

(c)

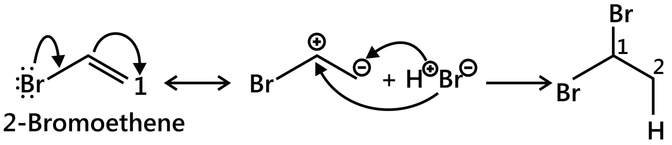


Methoxy prop-1-ene
or
Propenyl methyl ether

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

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

(d)

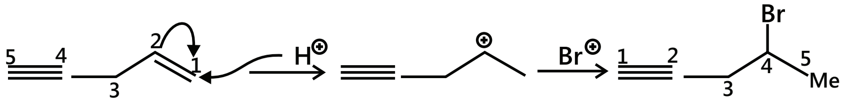


2-Bromoethene

(D) 1,1-Dibromethane

(Same explanation as in part (c) above)

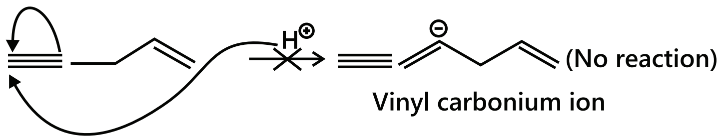
(e)



Pent-1-en-4-yne

2°C$^{\oplus}$

4-Brompent-1-yne
(E)

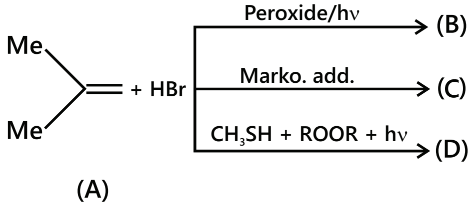


Vinyl carbonium ion

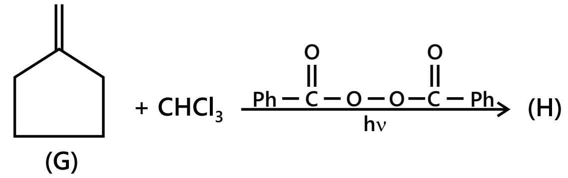
Since, alkyl carbonium ion is more stable than vinyl carbonium ion, alkene reacts at a faster rate than alkynes towards FA.

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

(a)

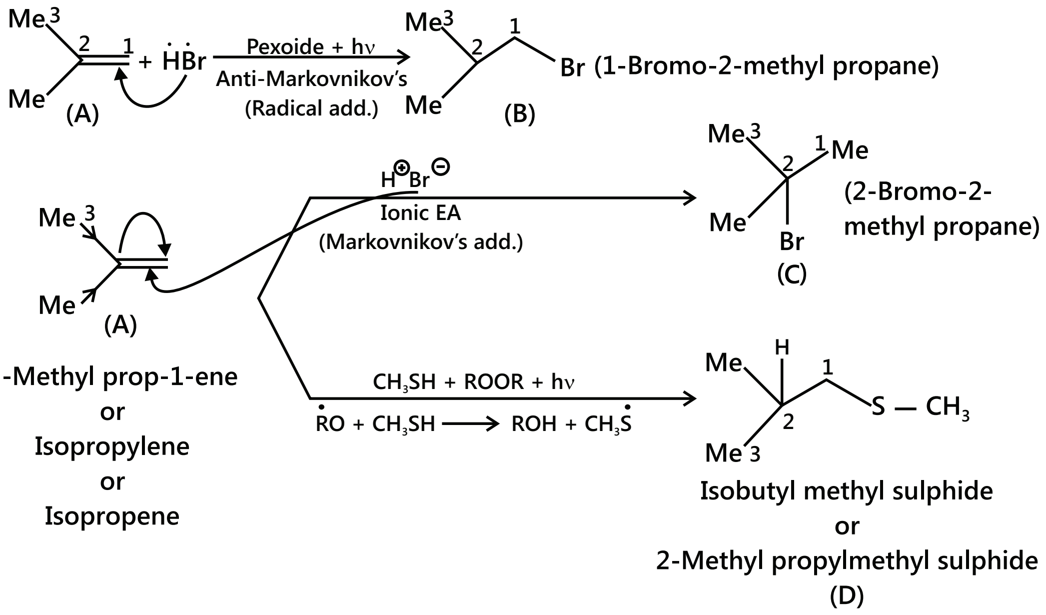


(b)

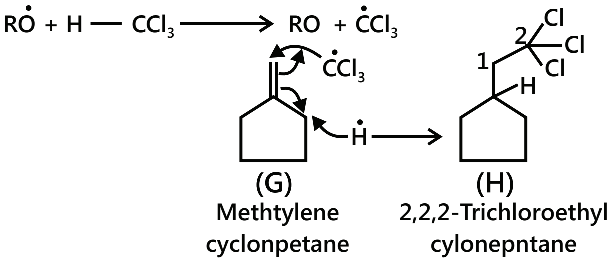


Sol: It is an example of free radical mechanism.

(a)



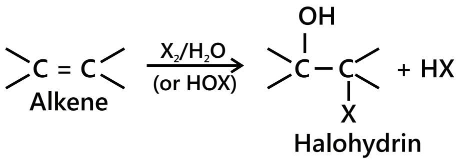
(b)



7.5 Addition of HOX

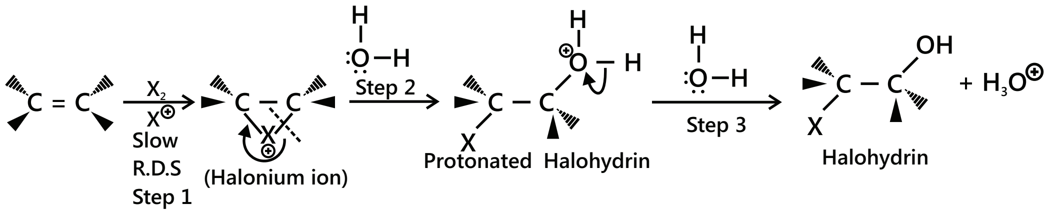
Addition of the elements of hypohalous acids (HOX where X = Cl, Br or I) – Halohydrin formation. Chlorine and bromine in the presence of water readily add to alkenes to form the corresponding halohydrins.

$$X_2 + H_2O \longrightarrow HOX + HX$$



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

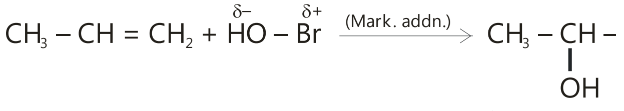
Mechanism:



For example,

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

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

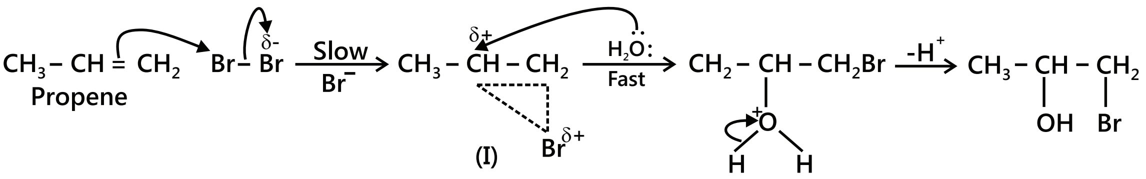


$$CH_3-CH=CH_2 + \overset{\delta-}{HO}-\overset{\delta+}{Br} \xrightarrow{\text{(Mark. addn.)}} CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-$$

1-Bromopr

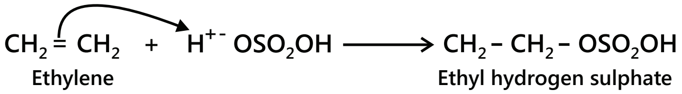
The order of reactivity of different hypohalous acids, i.e., X_2/H_2O (HOX) is:

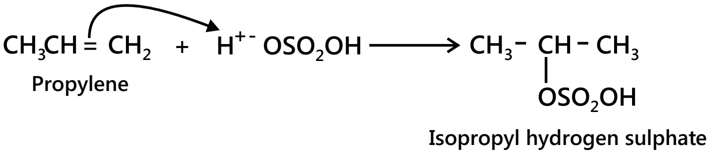
$$Cl_2/H_2O(HOCl) > Br_2/H_2O(HOBr) > I_2/H_2O(HOI)$$



7.6 Addition of H_2O (Indirect)

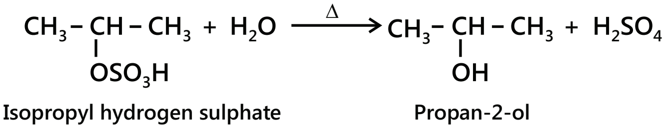
Addition of sulphuric acid – Indirect hydration of alkenes. Cold, conc. H_2SO_4 adds to alkenes to form alkyl hydrogen sulphates. In the case of unsymmetrical alkenes, addition occurs in accordance with Markovnikov's rule.





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

For example,



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

Thus, alkenes can be converted into alcohols as follows:

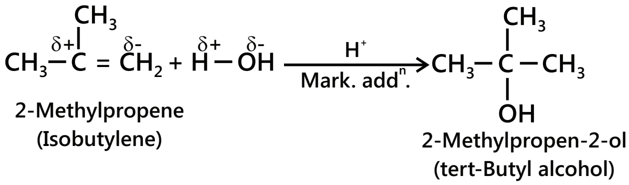
$$\underset{\text{Ethene}}{CH_2=CH_2} \xrightarrow[\text{(ii) } H_2O,\Delta]{\text{(i) Conc. } H_2SO_4\text{ (cold)}} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

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

7.7 Addition of H_2O (Direct)

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

For example,

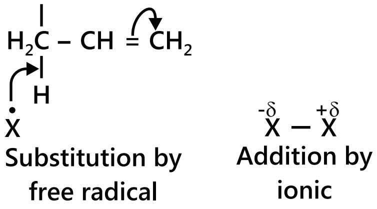


$$CH_3-\overset{\overset{CH_3}{|}}{\overset{\delta+}{C}}=\overset{\delta-}{CH_2}+\overset{\delta+}{H}-\overset{\delta-}{OH}\xrightarrow[\text{Mark. add}^n.]{H^+}CH_3-\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$$

7.8 Allylic Substitution

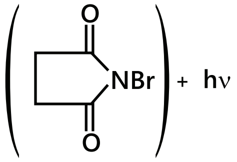
Alkenes mainly show two types of reactions:

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

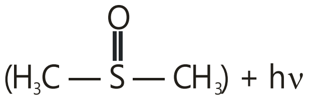


Allylic halogenations can be carried out by the following reagents:

1. Cl_2 at high temperature (773 K) or Br_2 at 400 K.
2. NBS (N-bromosuccinimide)

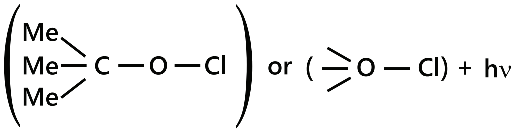


3. With NBS + DMSO (dimethyl sulphoxide)



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

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

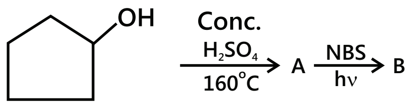


⇒ **allylic chlorination**

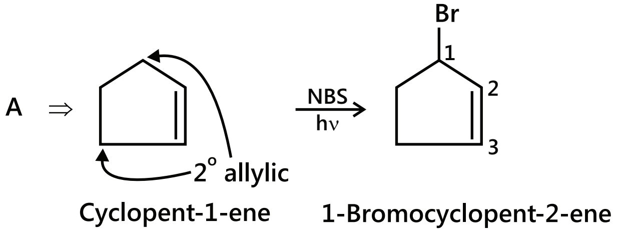
The relative rate of abstraction of hydrogen:

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

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



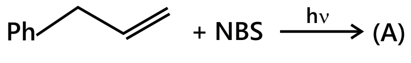
Sol:



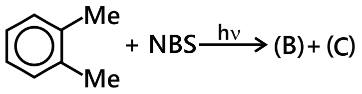
Cyclopent-1-ene 1-Bromocyclopent-2-ene

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

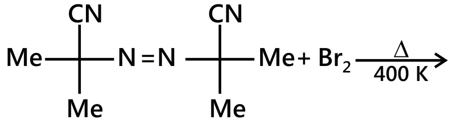
(a)



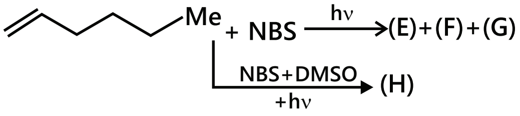
(b)



(c)

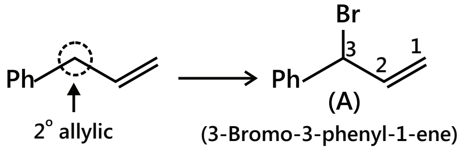


(d)



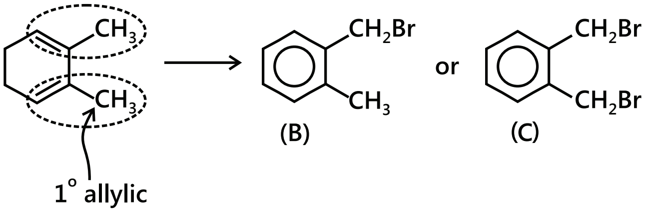
Sol:

(a)

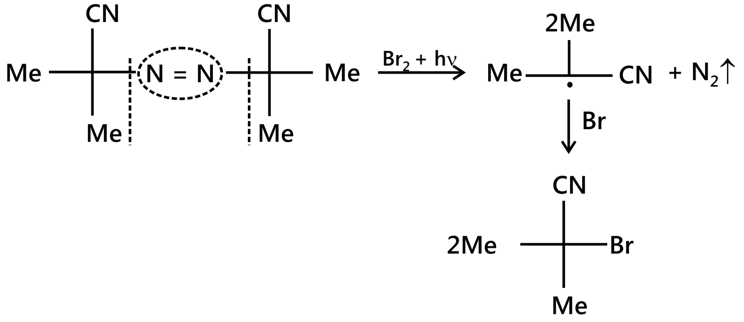


(3-Bromo-3-phenyl-1-ene)

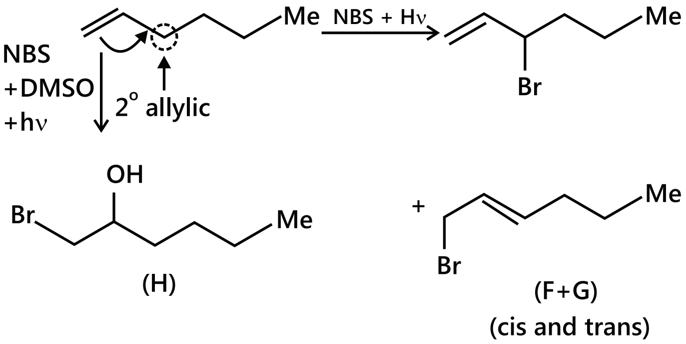
(b)



(c)

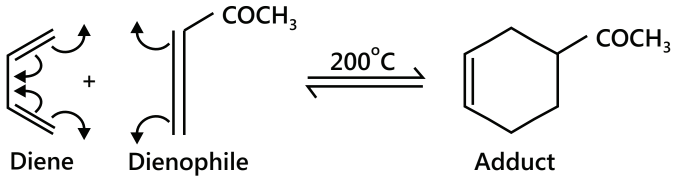


(d)



7.9 Diels Alder Reaction

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

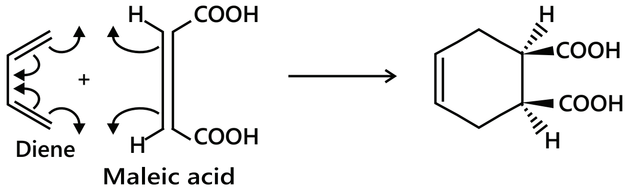


Mechanism: It takes place by concerted mechanism called pericyclic reaction. In a concerted mechanism, breaking and formation of bonds takes place simultaneously.

The reaction proceeds faster when the dienophiles have e^- withdrawing groups, such as (—COOH), (—COOR), (—CHO), (—NO$_2$), and (—CN), and dienes have e^- donating groups such as (Me), (Et), etc. So, 1, 3-butadiene is less reactive than its mono-, di-, and trimethyl derivatives.

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

Mechanisms: cis-additions



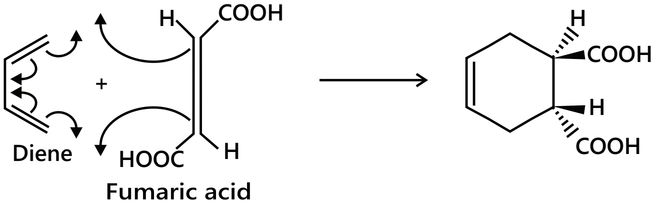
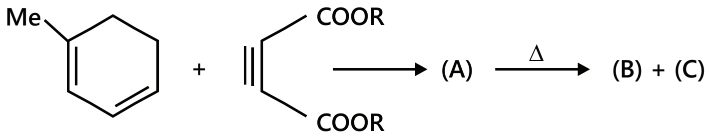
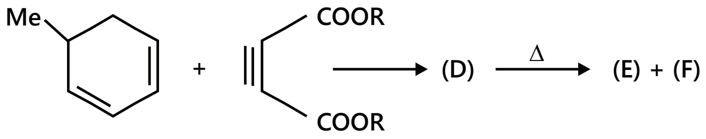


Illustration 18: Complete the following reactions:

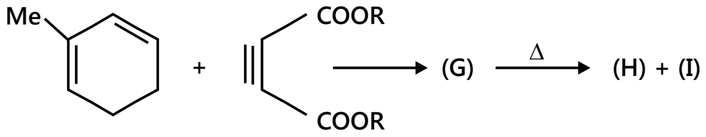
(a)



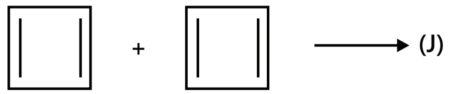
(b)



(c)

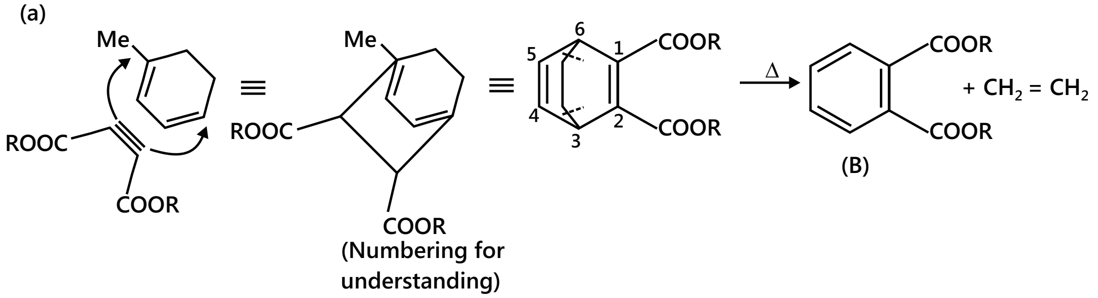


(d)

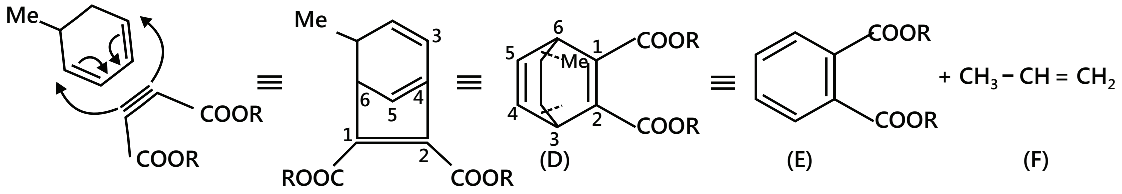


Sol: These are examples of Diels alder reaction. Diene and dienophile combine to form new ring. The mechanism is concerted type (Bond breaking and bond making takes place simultaneously)

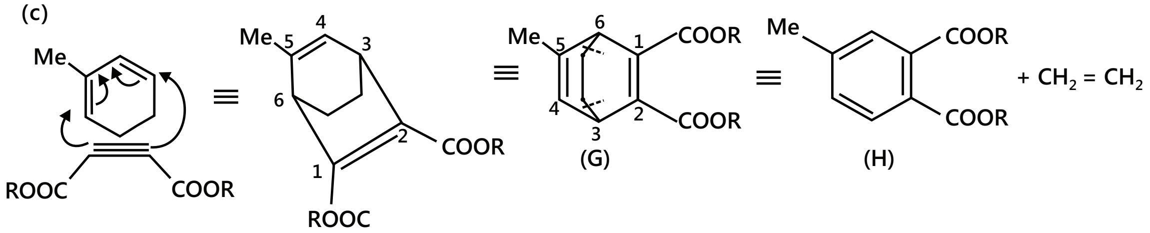
(a)



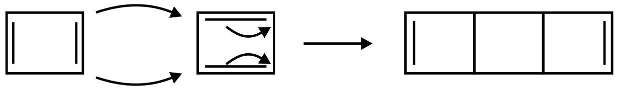
(b)



(c)

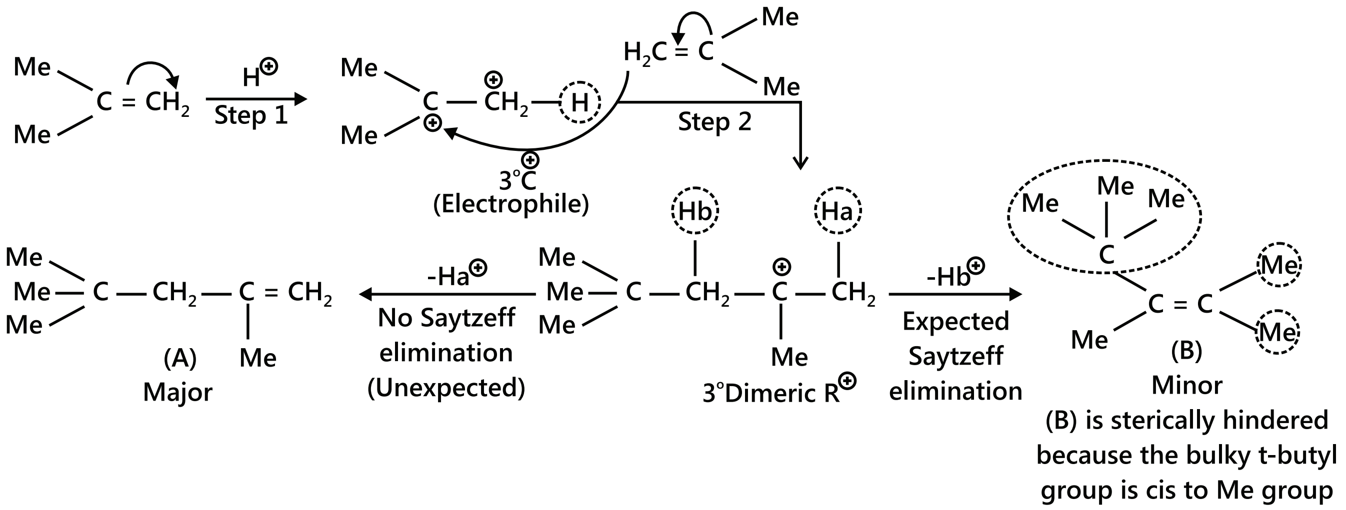


(d)

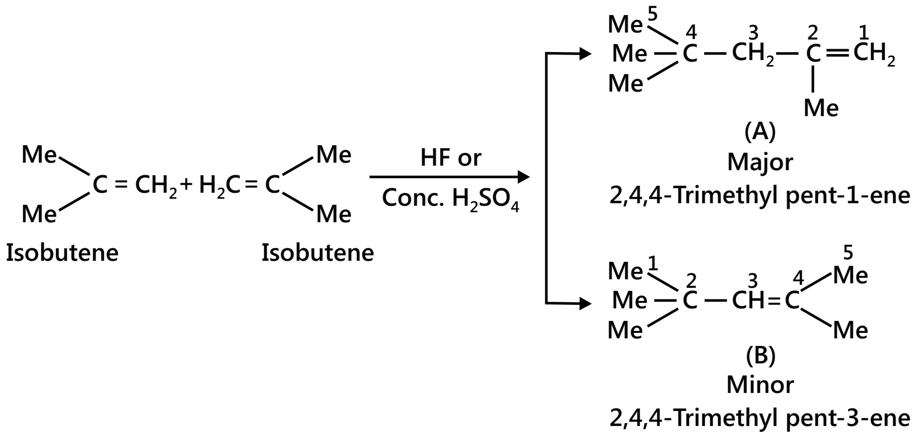


7.10 Dimerisation

Mechanism:



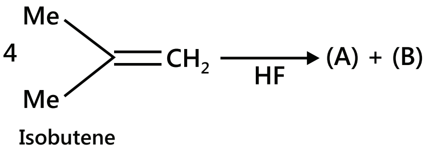
Alkene in the presence of HF or conc. H_2SO_4 or H_3PO_4 gives two alkenes (C_8H_{16}).



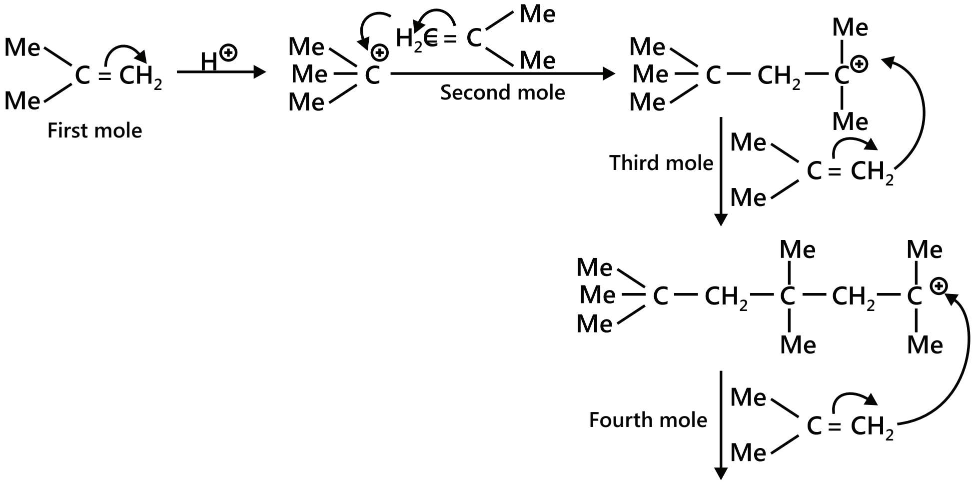
HCl, HBr, and HI cannot be used as acid catalysts. An acid catalyst must have a weak nucleophilic conjugate base to avoid addition of HX to the (C = C) bond. $Cl^{\ominus}$, $Br^{\ominus}$ and $I^{\ominus}$, the conjugate bases of HCl, HBr, and HI, respectively; are good nucleophiles that bind to alkyl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

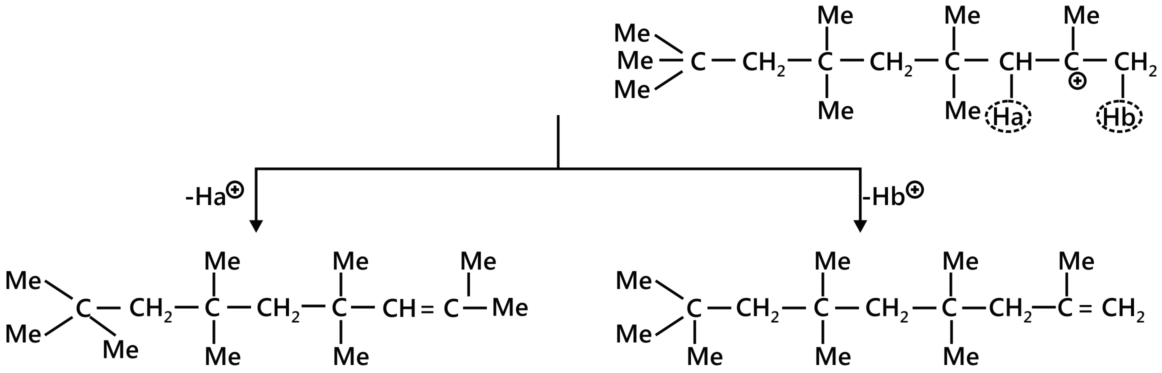
BF_3 with a little amount of H_2O can also be used to initiate the dimerisation or polymerisation of an alkene only at 73K. It is due to the information of strong Bronsted acid ($BF_3 + H_2O \rightleftharpoons HBF_3 \cdot OH$), which provides $H^{\oplus}$ to alkene to form the $R^{\ominus}$.

Illustration 19: Complete the following reaction:



Sol:



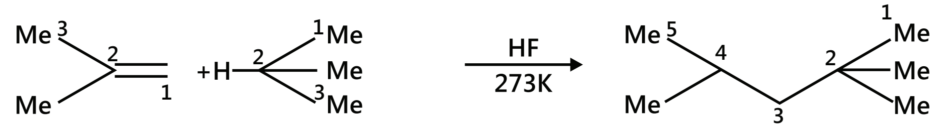


(A)
(Minor)
(Sterically hindered)

(B)
(Major)

7.11 Alkylation

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

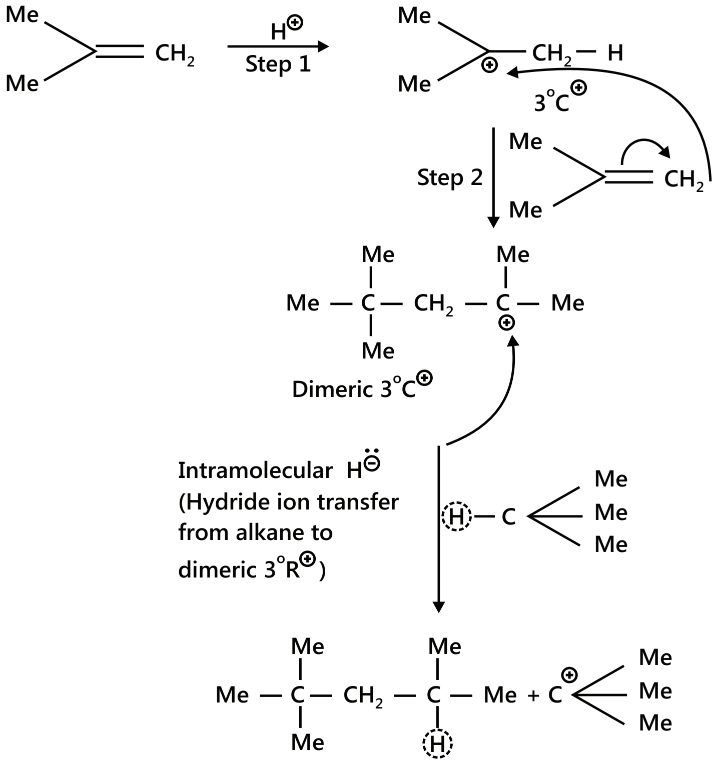


2-Methylprop-1-ene
or
(isobutene)
or
isobutylene)

2-Methyl propane
or
(tert-butane)

2,2,4-Trimethyl pentane

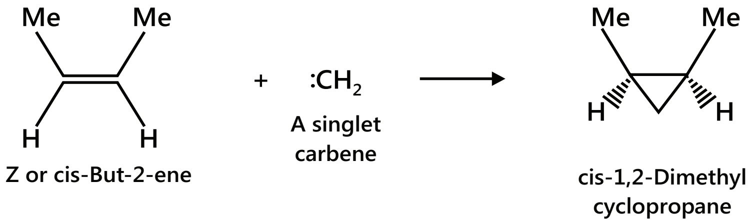
Mechanism:



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

7.12 Carbene Insertion to Alkenes

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



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

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

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

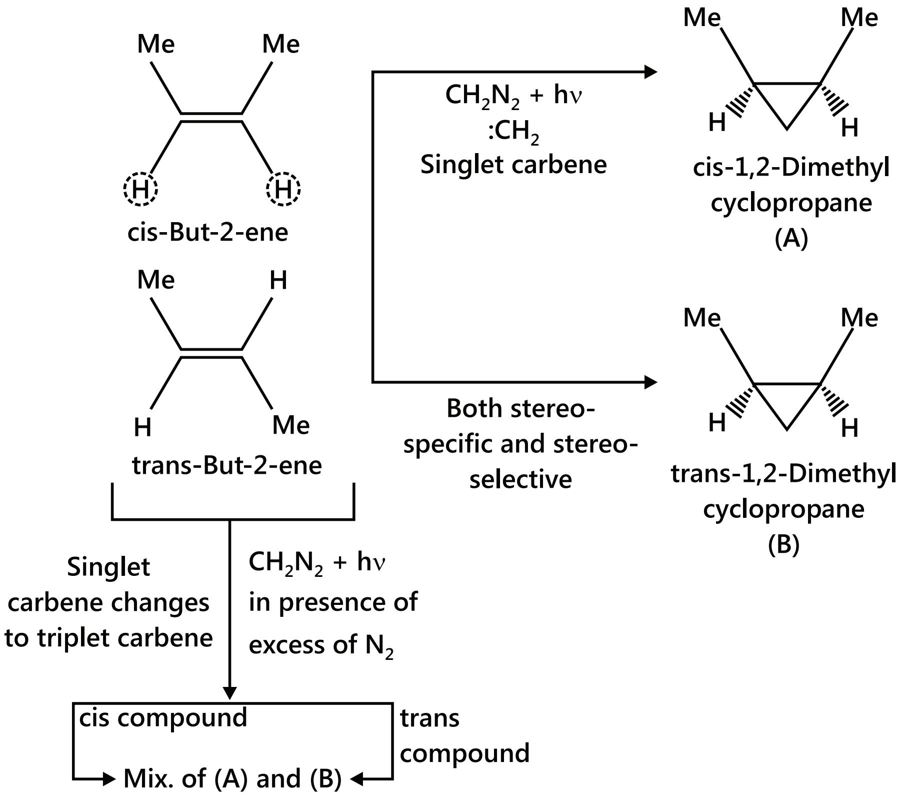


Illustration 20: Give the product of the following:

(a) Cyclohexane + CH_2N_2 + hν

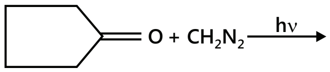
(b) Trans-2-Butene + $CHCl_3$ + KOH

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

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

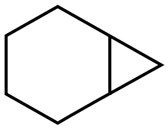
(e) 3-Methylcyclopentene + CH_2I_2 + Zn/Cu (couple) (Simmons-Smith reaction)

(f)



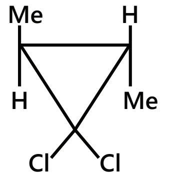
Sol:

(a)



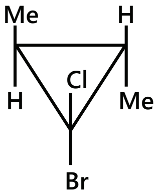
Bicyclo [4.1.0] heptane

(b)



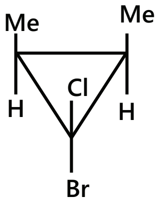
trans-1,2-Dimethyl 3,3-dichloro cyclopropane

(c)

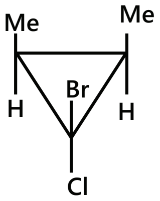


trans-2,3-Dimethyl-1-chlorobromo cyclopropane (Each halogen is cis to one Me and trans to other)

(b)

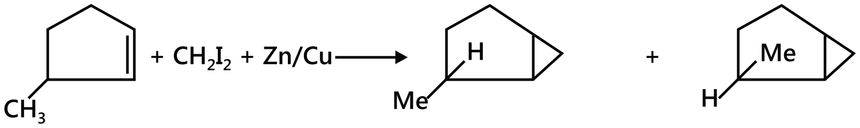


cis-1,2-Dimethyl-cis-1-chlorobromo -cyclopropane



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

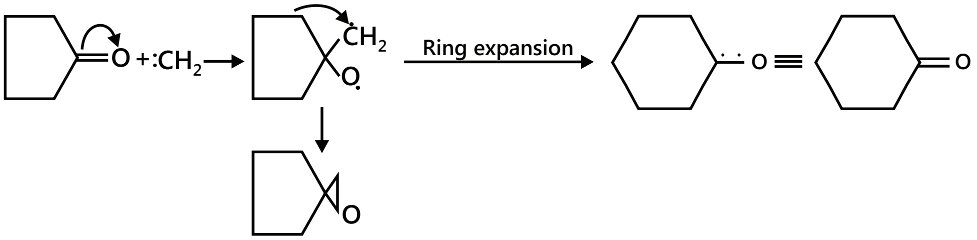
(e) Two diastereomers are obtained:



exo-2-Methyl-bicyclo [3.1.0] hexane

endo

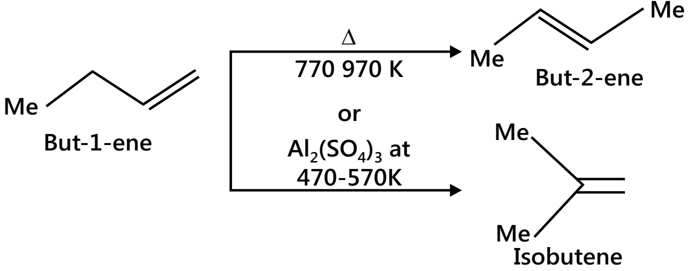
(f) By this method 7- to 10-memberd cyclic ring can be prepared.



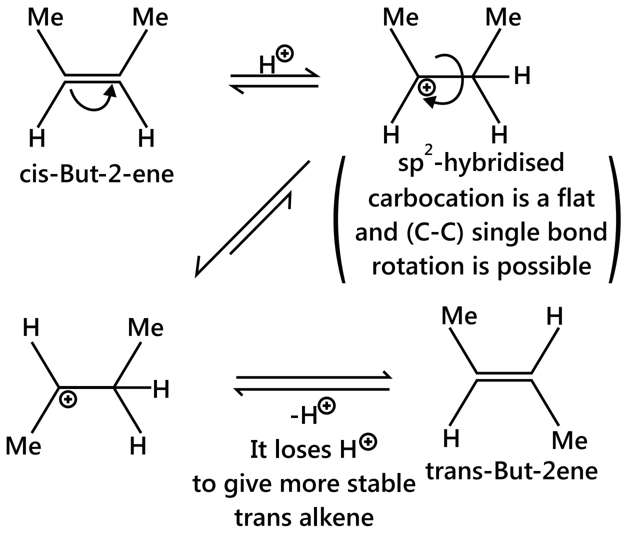
Small amount

7.13 Isomerisation and the Shifting of Double Bond

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



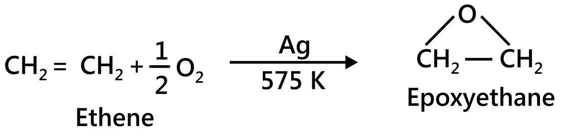
When either a cis or trans alkene is placed in a strong acid solution, each of them is converted to a mixture of 76% of trans and 24% of the cis-isomer. The ratio of isomers is thermodynamically or equilibrium controlled.



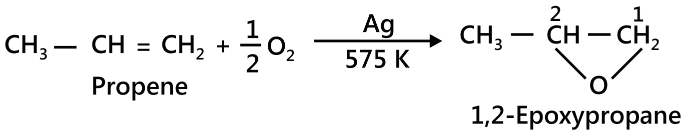
7.14 Oxidation Reactions

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

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



$$CH_2 = CH_2 + \frac{1}{2}O_2 \xrightarrow[575\ K]{Ag} \overset{O}{CH_2 - CH_2}$$



$$CH_3 - CH = CH_2 + \frac{1}{2}O_2 \xrightarrow[575\ K]{Ag} CH_3 - \underset{O}{\overset{2}{CH} - \overset{1}{CH_2}}$$

7.14.1 Hydroxylation

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

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

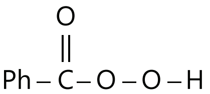
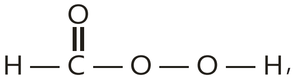
(b) **OsO_4 (osmium tetraoxide)** in pyridine or ether solution followed by the reaction with Na_2SO_3/H_2O or $NaHSO_3/H_2O$ converts alkene to diols and OsO_4 to Os metal.

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

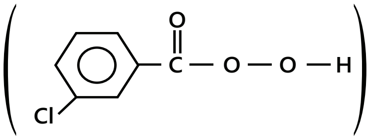
Anti Hydroxylation with the following reagents :

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

For example,

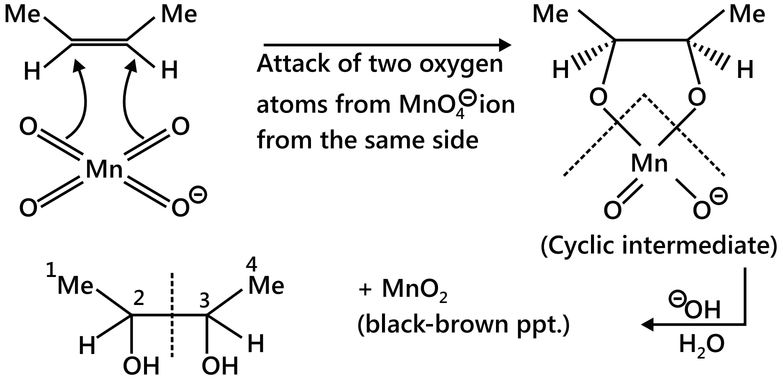
i. 
$Ph-\overset{O}{\overset{\|}{C}}-O-O-H$
Peroxybenzoic acid, ii. 
$H-\overset{O}{\overset{\|}{C}}-O-O-H$, peroxymethanoic acid or peroxyformic acid, and

iii. MCPBA (m-chloroperbenzoic acid)



Mechanism of syn hydroxylation:

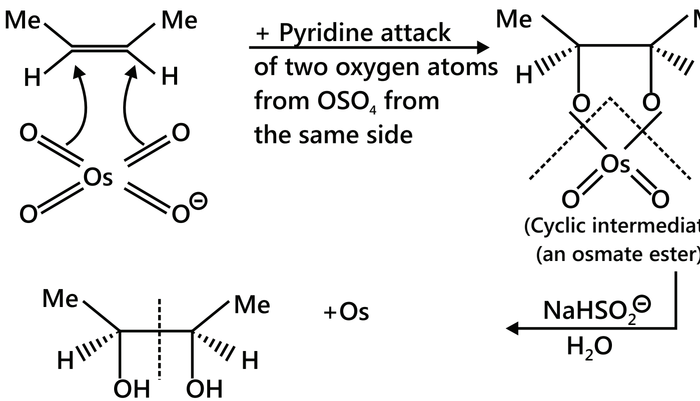
i.



(Cyclic intermediate)

(Meso compound) (O.I.A)
Butan-2,3-diol

ii.

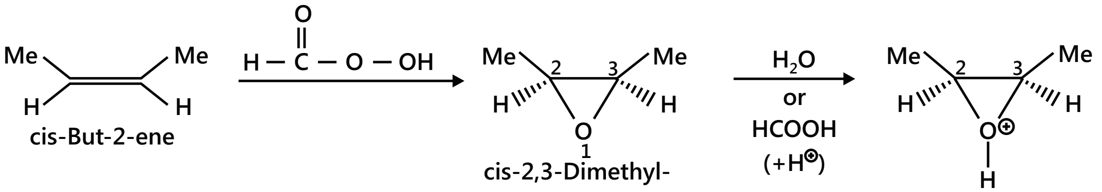


(Cyclic intermediate
(an osmate ester)

(Meso compounds)
(O.I.A.)

Mechanism of Anti-hydroxylation

I.

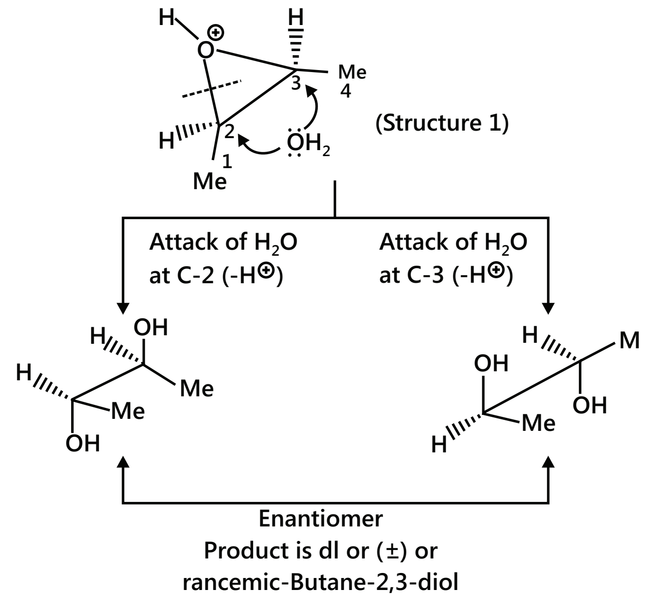


cis-But-2-ene

cis-2,3-Dimethyl-
oxirane

(Structure 1)

II.



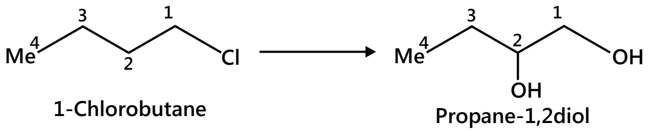
For syn hydroxylation,

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

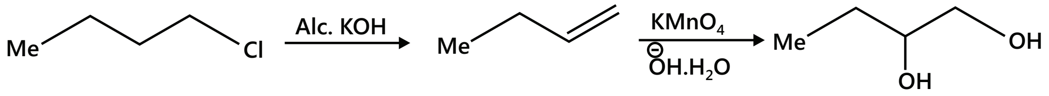
For anti-Hydroxylation,

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

Illustration 21: Convert



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



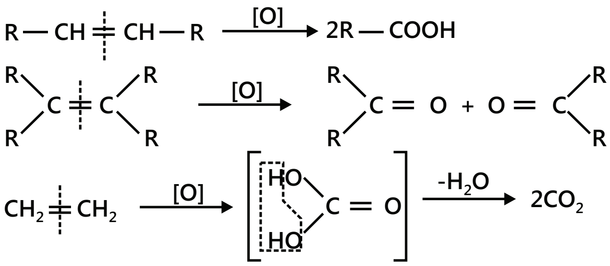
7.14.2 Cleavage

A. Oxidative cleavage

Alkenes are oxidatively cleaved by any of the following reagents:

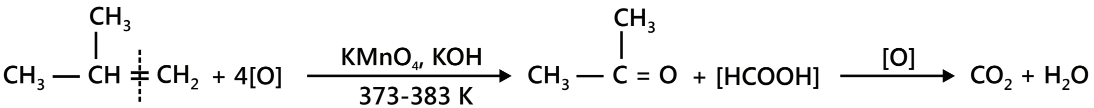
1. Hot alkaline $KMnO_4$ solution followed by acidification

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



Carbonic acid

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



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

2-Methylpropene
(Isobutylene)

Propanone
(Acetone)

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

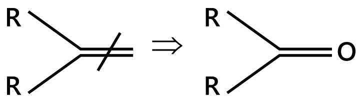
$$CH_3CH_2CH=CHCH_3 + 4[O] \xrightarrow[373\text{-}383\ K]{KMnO_4,\ KOH} CH_3CH_2COOH + HOOCCH_3$$

Pent-2-ene

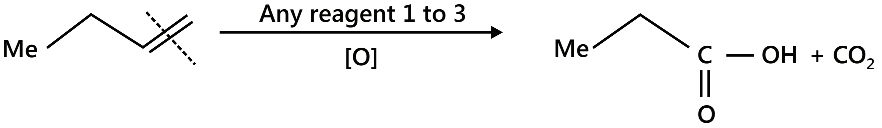
Propanoic acid
(Propionic acid)

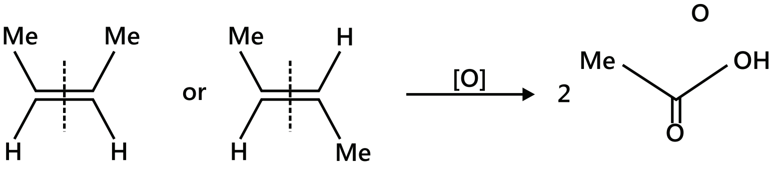
Ethanoic acid
(Acetic acid)

Rules of oxidation:

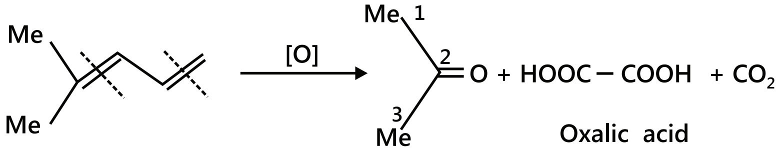
$CH_2 \neq \Rightarrow$	CO_2
$R-CH \neq \Rightarrow$	$R-COOH$
$R_2C=CH_2$	

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





cis trans



Acetone
or
Propan-2-one

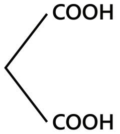
Oxalic acid
or
Ethane-1,2-dioic acid

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

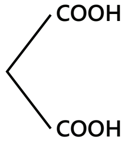
Sol: First, calculate the degree of unsaturation.

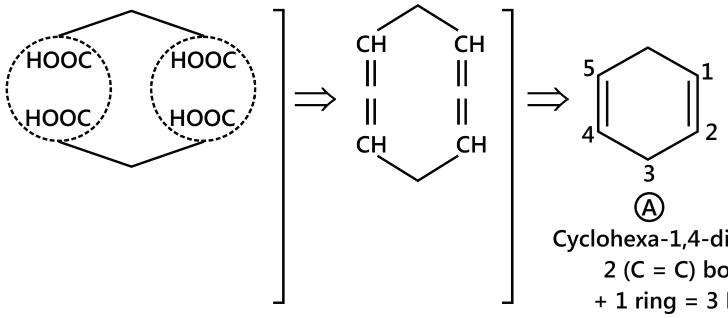
$$\text{D.U.} = \frac{(2n_C + 2) - n_H}{2} = \frac{(2 \times 6 + 2) - 8}{2} = 3^\circ$$

Structure of malonic acid is ⇒



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

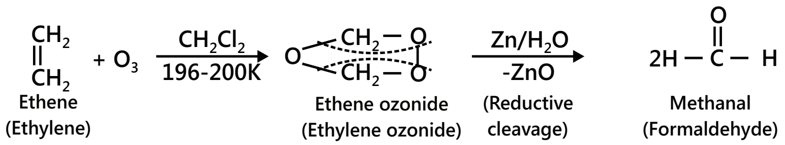


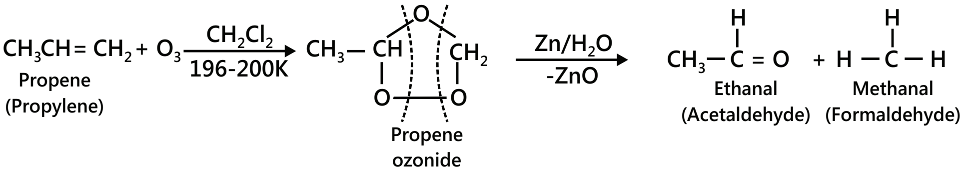


Ⓐ

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

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





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

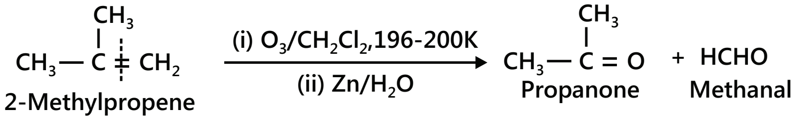
This two-step conversion of an alkene into an ozonide followed by its reductive cleavage to yield carbonyl compounds is called ozonolysis.

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

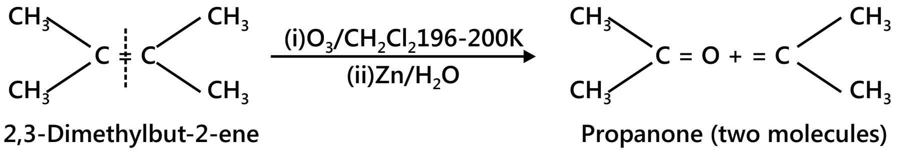
$$\underset{\text{But-1-ene}}{CH_3CH_2CH = CH_2} \xrightarrow[\text{(ii) Zn/}H_2O]{\text{(i) }O_3/CH_2Cl_2\text{,196-200K}} \underset{\text{Propanal}}{CH_3CH_2CHO} + \underset{\text{Methanal}}{HCHO}$$

$$\underset{\text{But-1-ene}}{CH_3CH = CHCH_3} \xrightarrow[\text{(ii) Zn/}H_2O]{\text{(i) }O_3/CH_2Cl_2\text{,196-200K}} CH_3CHO + CH_3CHO$$

Ethanal (Two molecules)



$$\underset{\text{2-Methylpropene}}{CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} = CH_2} \xrightarrow[\text{(ii) Zn/}H_2O]{\text{(i) }O_3/CH_2Cl_2\text{,196-200K}} \underset{\text{Propanone}}{CH_3 - \overset{\overset{\displaystyle CH_3}{|}}{C} = O} + \underset{\text{Methanal}}{HCHO}$$



Reagents used for reducive and oxidative ozonoylsis

Reduction of ozonide (Reductive ozonolysis)

- (a) Zn-acid
- (b) H_2 + Catalyst (Ni, Pt, Pd)
- (c) Me_2S (Dimethyl sulphide)
- (d) Ph_3P (Triphenyl phosphine)

⇓ It gives aldehyde and ketone

- (e) LAH or $NaBH_4$

⇓ It gives alcohols from aldehyde and ketones

Oxidation of ozonide (Oxidative ozonolysis)

- (f) H_2O
- (g) Ag_2O
- (h) H_2O_2
- (i) $KMnO_4/NaIO_4$
- (j) H_2O
- (HCO_3H, $PhCO_3H$)

⇓ Aldehyde give acids and ketones do not change

For example:

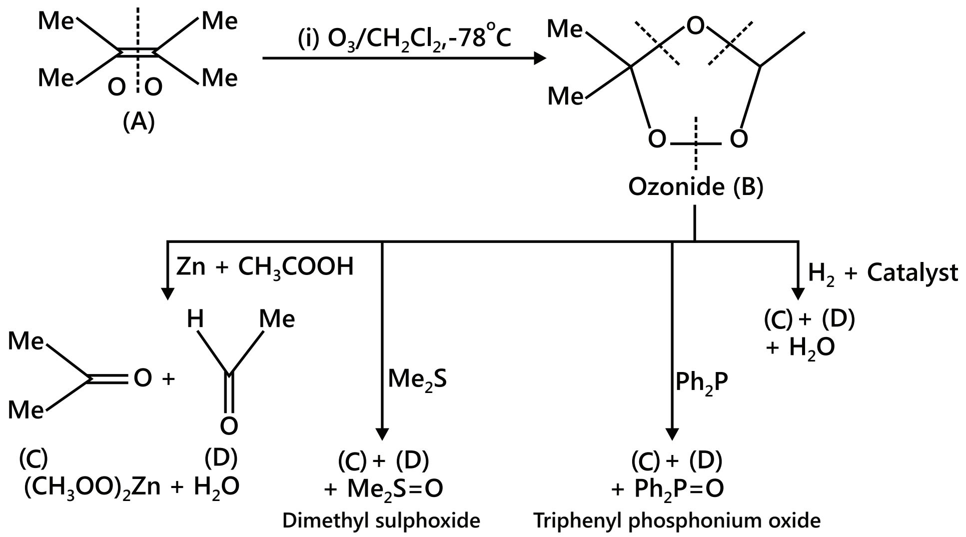


Illustration 23: Identify the compounds (A), (B), and (C). **(JEE MAIN)**

Compound (A) (C_8H_{12}) $\xrightarrow[\text{of } H_2/Pd]{\text{1 mol}}$ (B) (C_8H_{14})

Does not show Stereoisomerism

$\big\downarrow O_3/Ph_3P$

Symmetrical diketone

(C) ($C_8H_{12}O_2$)

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

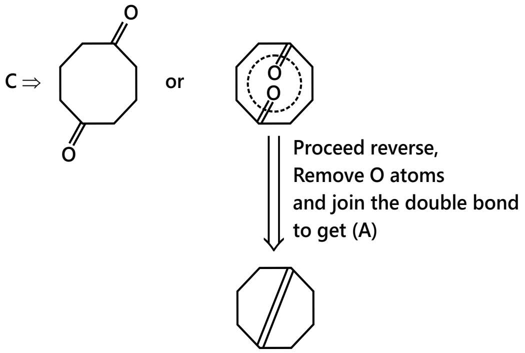
D.U. in (A) = $\frac{(2n_C+2)-n_H}{2} = \frac{(2\times8+2)-12}{2} = 3^o$; D.U. in (B) = $\frac{(2n_C+2)-n_H}{2} = \frac{(2\times8+2)-14}{2} - 2^o$

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

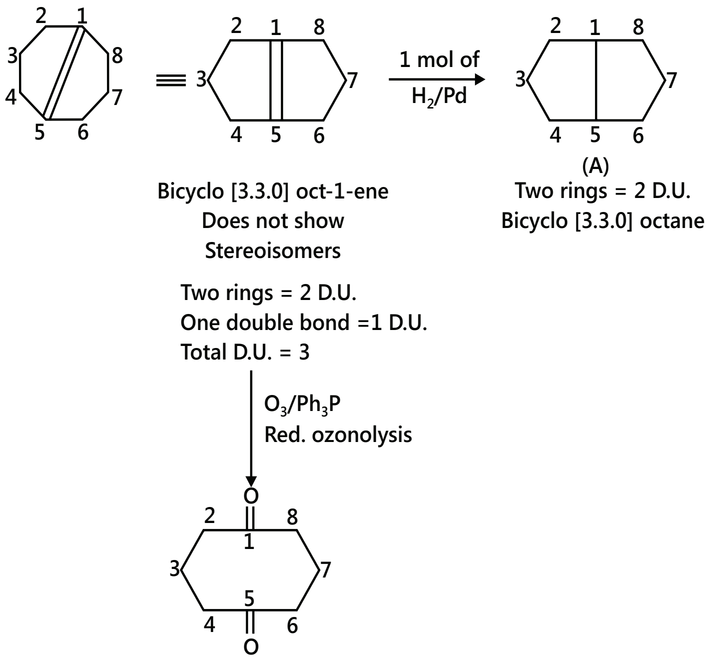
In compound (C), Degree of Unsaturation is 3°. Out of three, two are due to diketone.

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

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



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



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

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

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

(C) Cyclooctane
Symmetrical diketone

One Ring = 1 D.U.

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

8. USES OF ALKENES

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

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

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

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

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