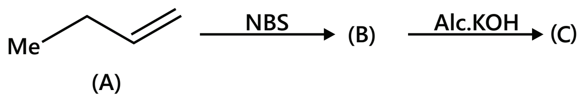
Solved Examples

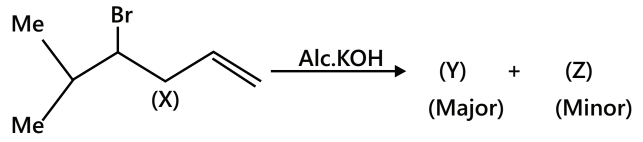
JEE Main/Boards

Example 1: Complete the following reactions:

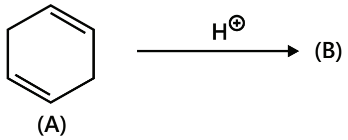
(a)



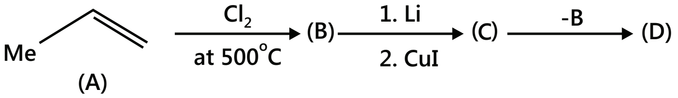
(b)



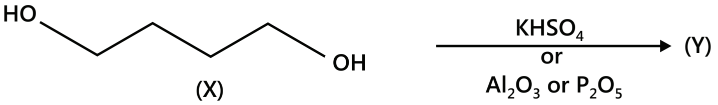
(c)



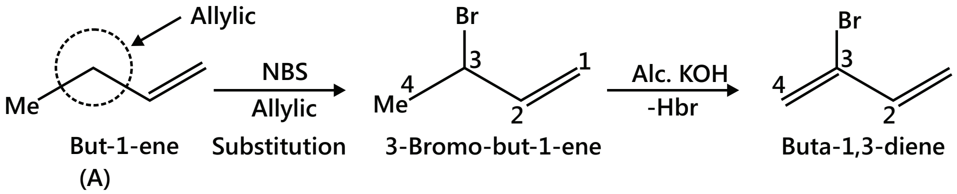
(d)



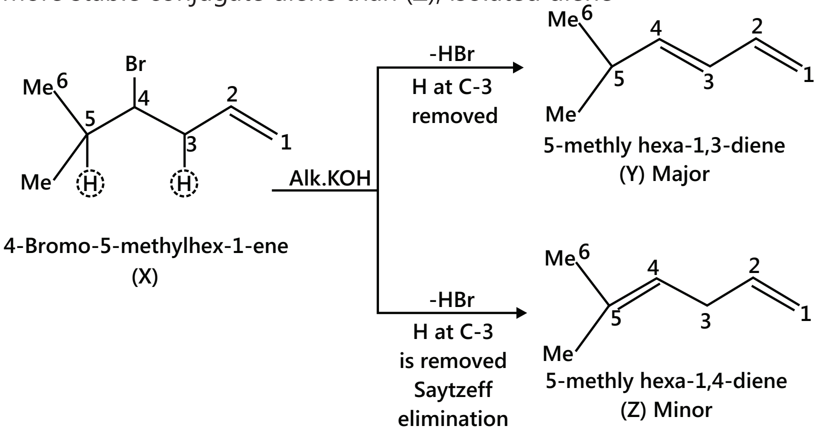
(e)



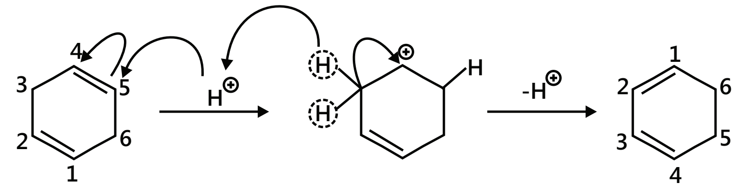
Sol: (a)



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



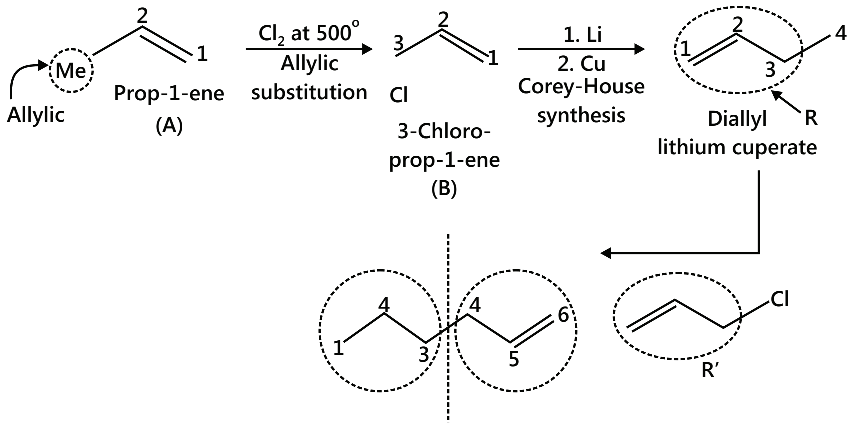
(c)



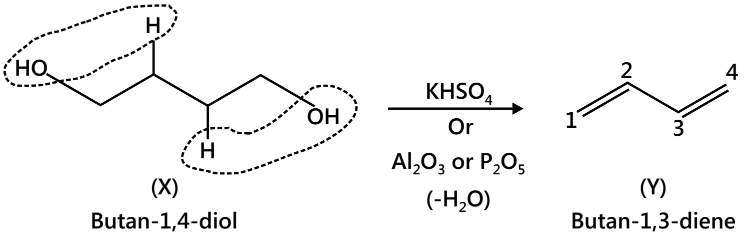
Less stable
isolated diene
(A)
Cyclohexa-1,4-diene

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

(d)

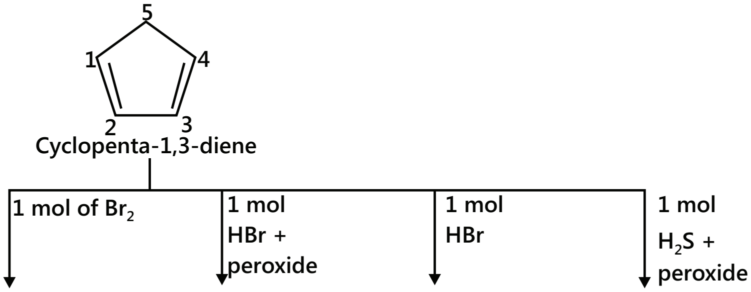


(e)

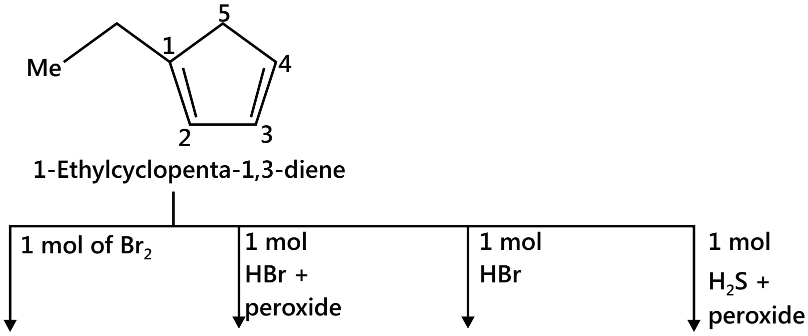


Example 2: Give the major products (not stereoisomers) of the following:

(a

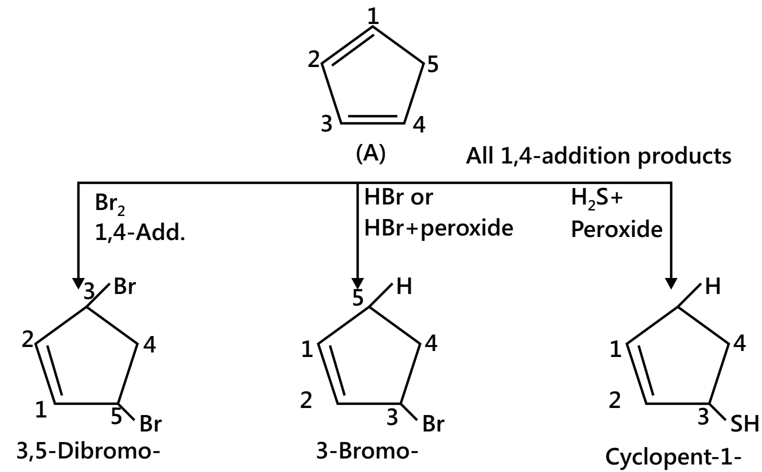


(b)



Sol:

(a)

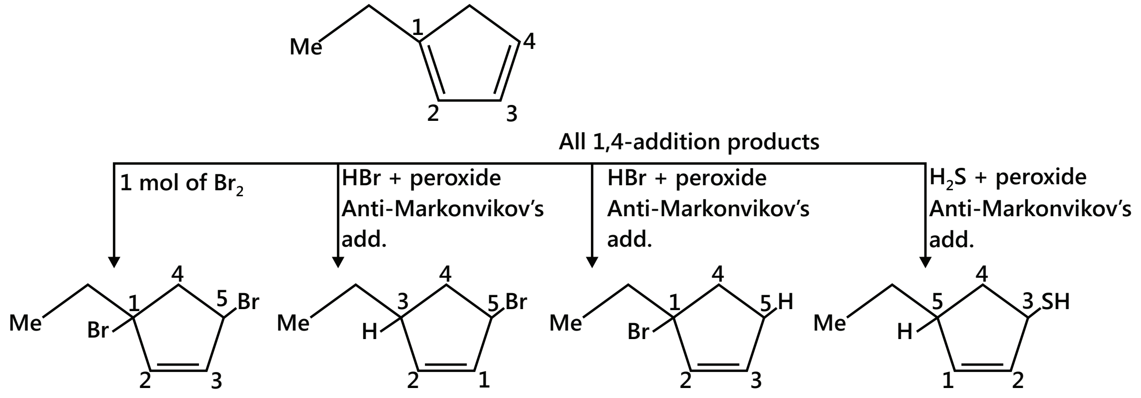


3,5-Dibromo-
cyclopent-1-ene

3-Bromo-
cyclopent-1-ene

Cyclopent-1-
ene-3-thiol

(b)



3,5-Dibromo-
3-ethyl-cyclopent-1-ene

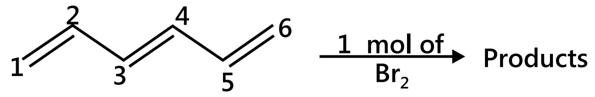
5-Bromo-3-ethyl-
cyclopent-1-ene

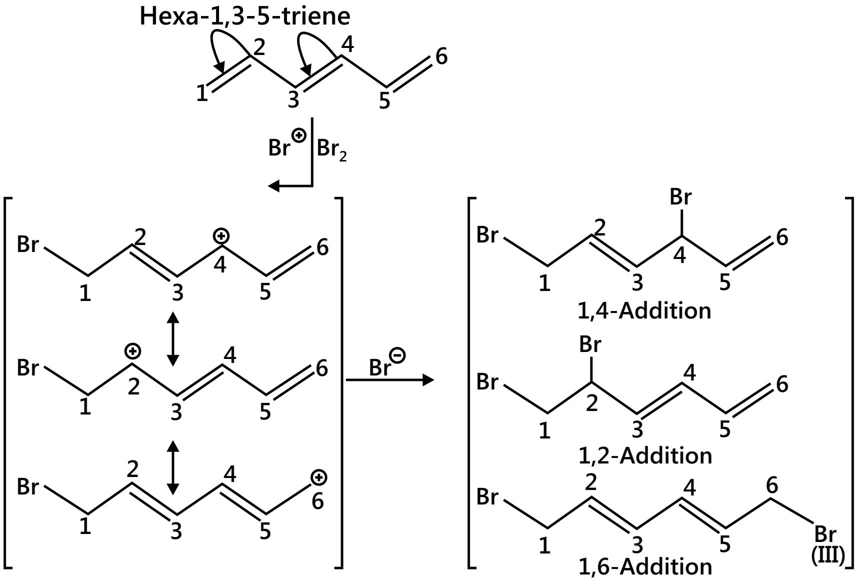
3-Bromo-
3-ethyl-cyclopent-1-ene

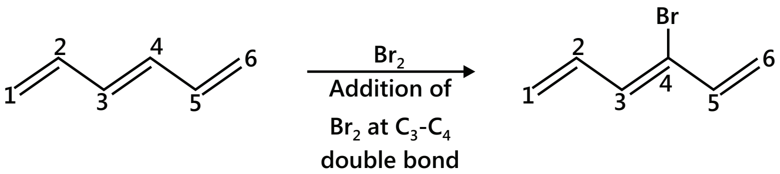
5-Ethyl cyclo-
pent-1-ene-3-thiol

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

Sol:



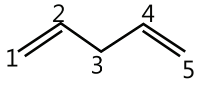




More stable Products (II and III, conjugate dienes) are thermodynamically favoured products than I and IV (isolated dienes)

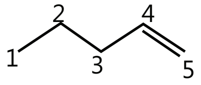
Example 4: Distinguish between the given pairs.

(a)



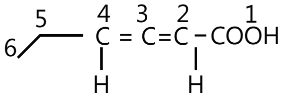
(A)

and



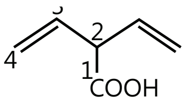
(B)

(b)



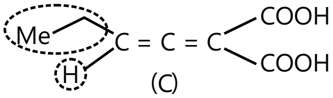
(C)

and



(D)

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

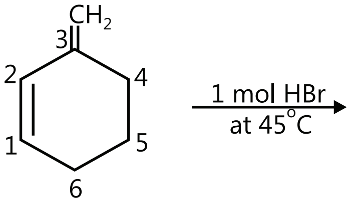


(C)

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

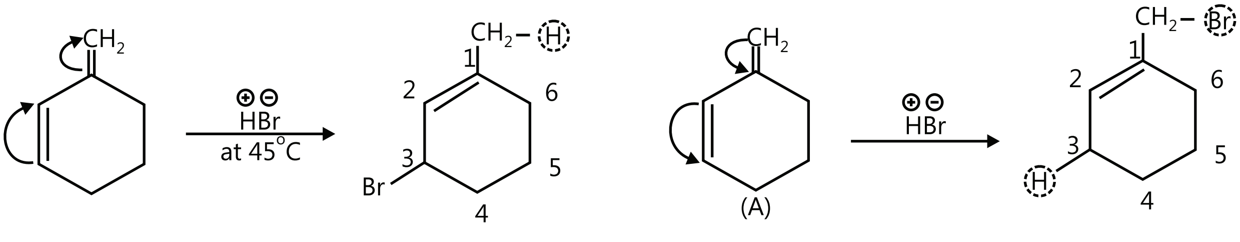
Compound (D) is conjugate diene and does not show optical isomerism.

Example 5: Give the major and minor products.



(A)
3-Methylenecyclohex-1-ene

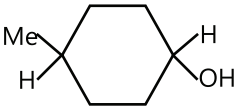
Sol: At high temperature (45°C), 1, 4-addition products is more favourable.



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

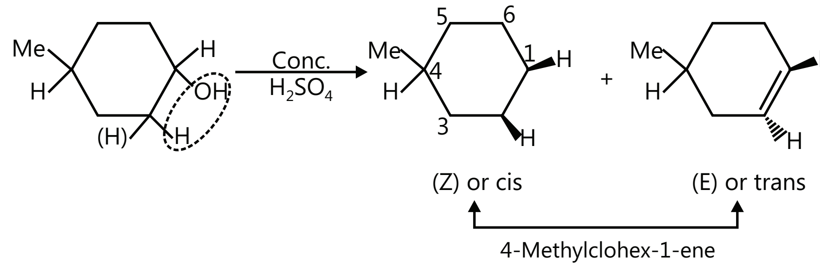
(C) (major)
1-Bromo-1-methyl-
cyclohex-1-ene

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

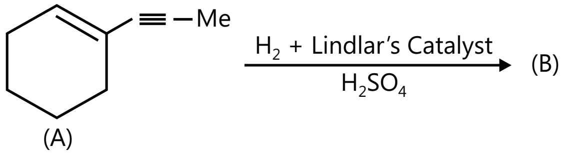


(A)

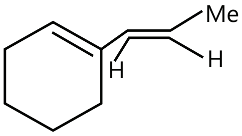
Sol:



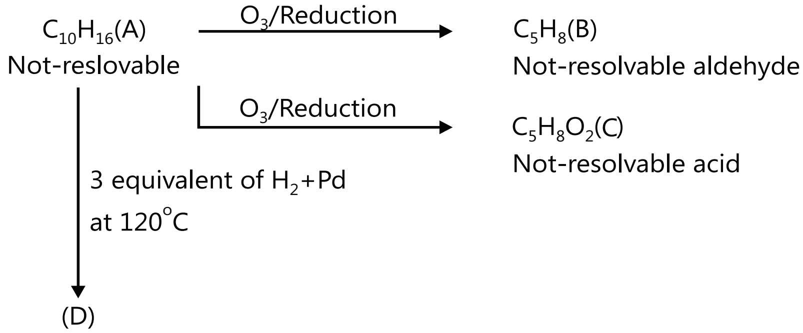
Example 7:



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

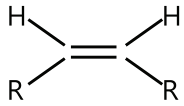


Example 8:



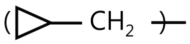
Write all the possible structures of (A), (B) and (C).

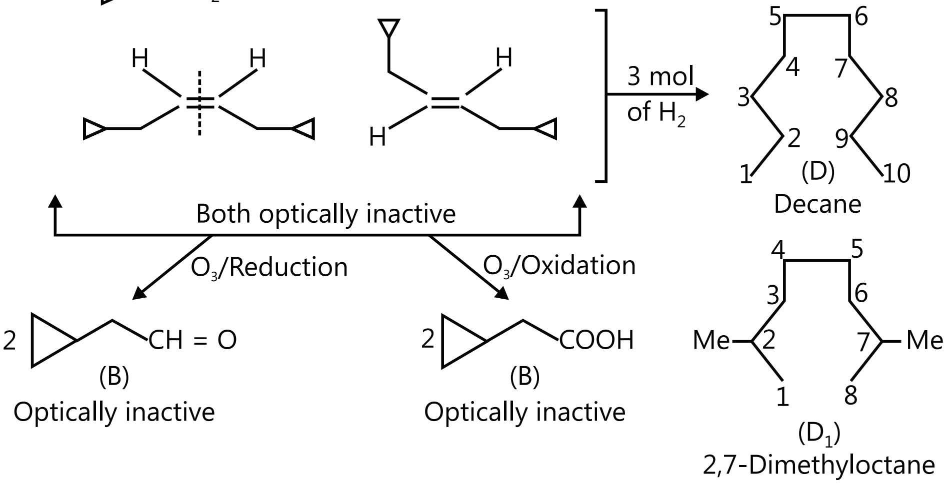
Sol: Since the reductive and oxidative ozonolysis products are different, the alkene of the type

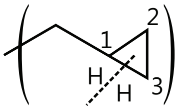


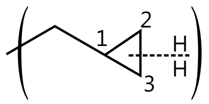
is possible

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

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



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

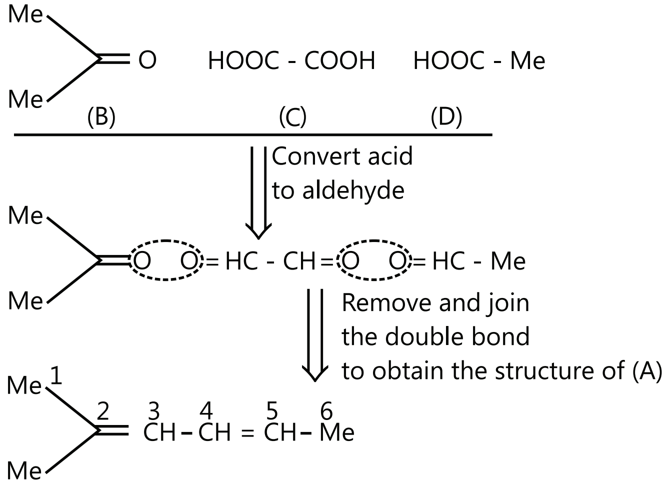
(D_1) is obtained when ($C_2 - C_3$) bond  breaks during hydrogenation of (A).

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

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

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

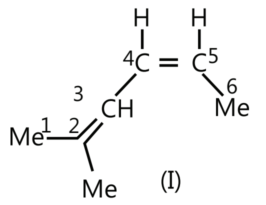
Sol:

(a) 

(A) (C_7H_{12})

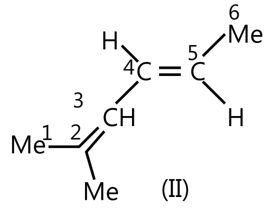
Here Compound (A) shows G.I around $C_4 — C_5$ double bond (since the two groups around C-4 and C-5 are different) but do not show G.I around $C_2 — C_3$ double bond because the two groups around C-2 are the same.

Number of stereoisomers for (A) — 2



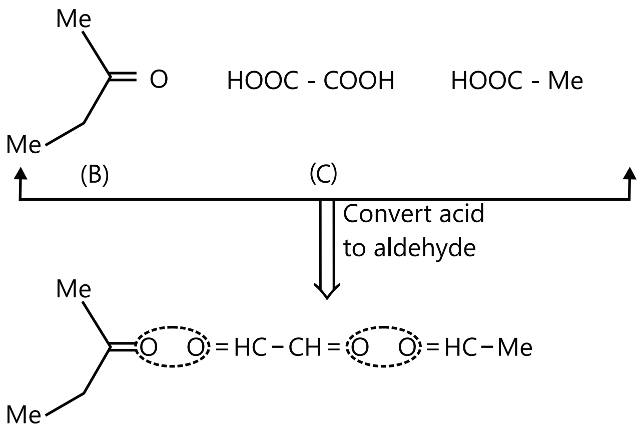
4Z-2-Methylhexa-2,4-diene

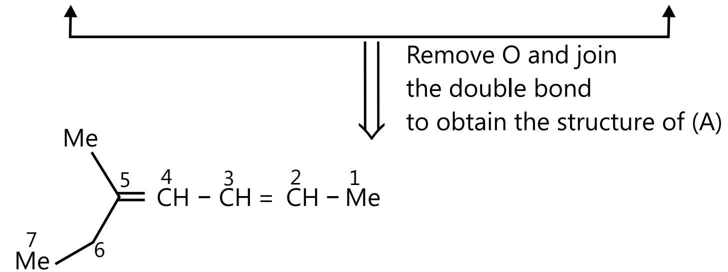
and



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

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





(A) (C_8H_{18})

(5-Methylhepta-2,4-diene)

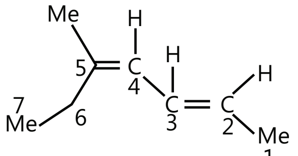
(A) shows geometrical isomers around both (C_2 — C_3) and (C_4 — C_5) double bonds (two of the groups around these double bonds are different)

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

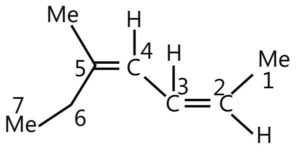
Number of G.I. when the terminal groups are different = 2^n, where n is the number of double bonds (two double bonds).

G.I. = 2^2 = 4

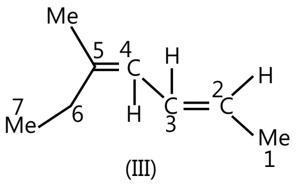
Number of stereoisomers of (A) = 4



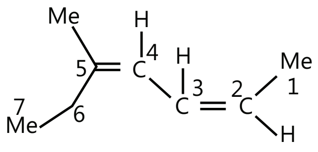
(I)
(2Z,4Z)



(II)
(2E,4Z)



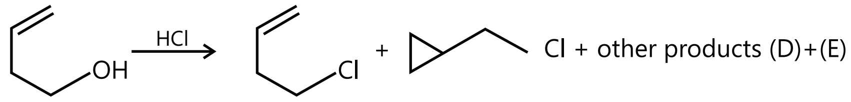
(III)
(2Z,4E)



(IV)
(2E,4E)

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

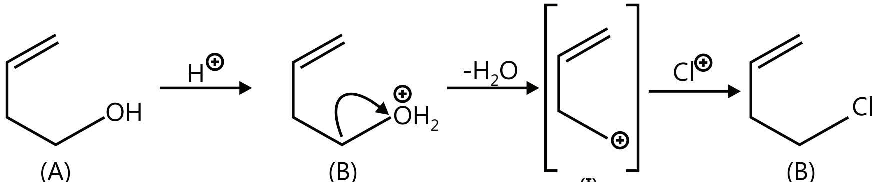
(a)



(A) (B)

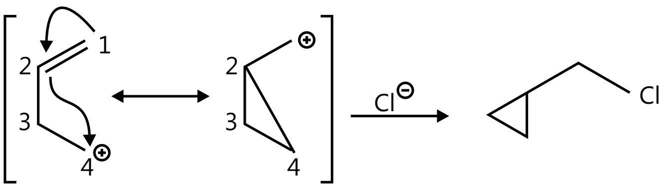
Sol:

(a)



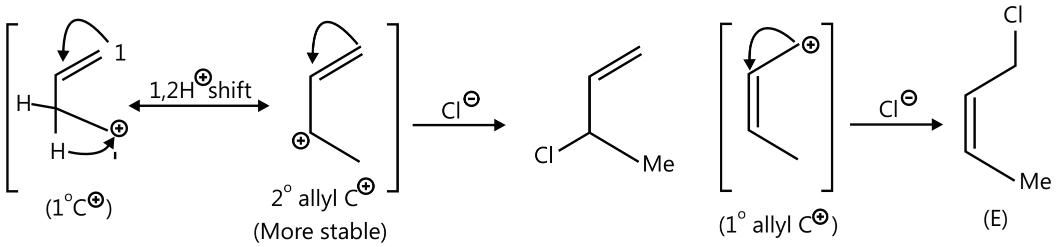
(A) (B) (I) (B)

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

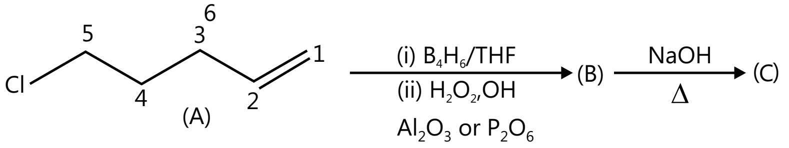


(I) (C)

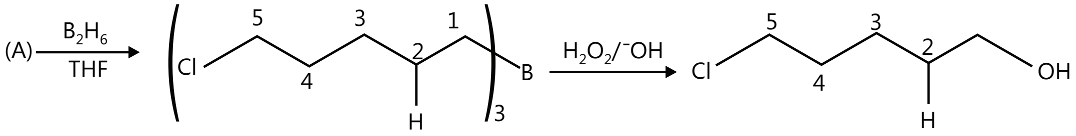
Other products can be obtained due to carbocation (I) rearrangement.



Example 11: Complete the following reaction:

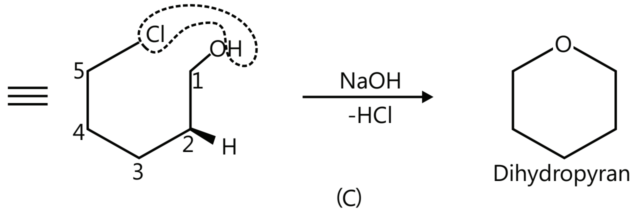


Sol: It is an example of hydroboration-oxidation reaction, it is used in the formation of alcohol from an alkene. It follows anti-Markovnikov's rule, and the addition of H and OH is syn (cis)(addition of H and BH_2 takes place from the same side)



(5-Chloropentane-1-ol)

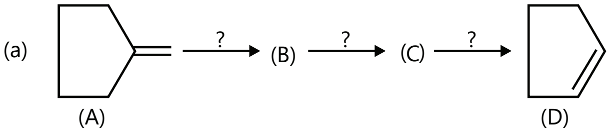
(B)

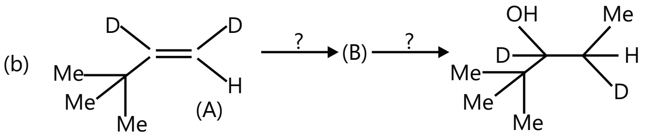


(C)

JEE Advanced/Boards

Example 1: Complete the following reaction with appropriate reagents.

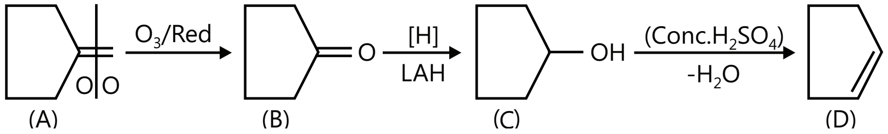




Sol: (a) Compound (D) Contains a (C = C) bond in the ring, Double bond can be obtained by the dehydration of alcohol.So, (C) is an alcohol.Alcohol (C) is obtained by the reduction of (>C = 0) using reducing agent like LAH.

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

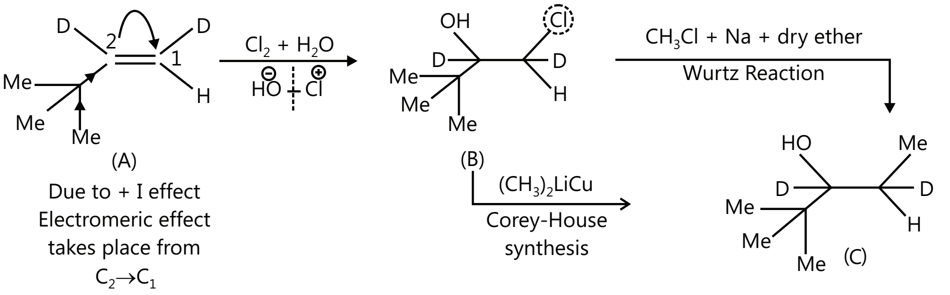
The different steps are as follows:



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

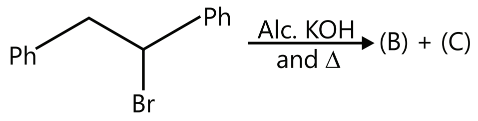
Compound (D) contains one Me and one –OH group. It can be obtained by adding (Cl_2+ H_2O) (HOCl) to (A).

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



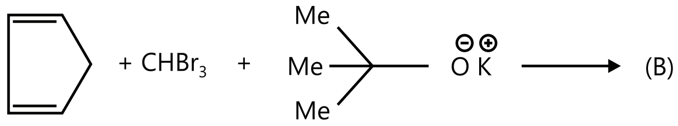
Example 2: Complete the following reactions:

(a)



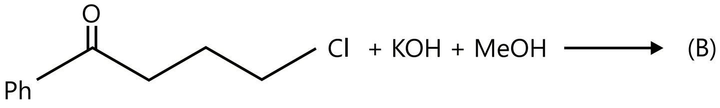
(A)

(b)



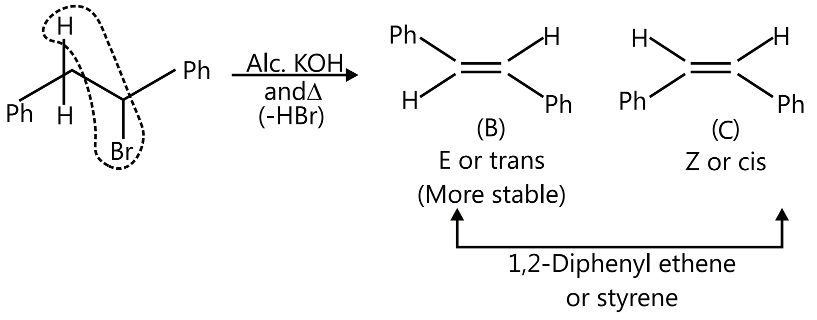
(A)

(c)

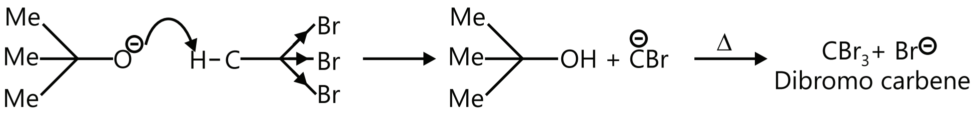


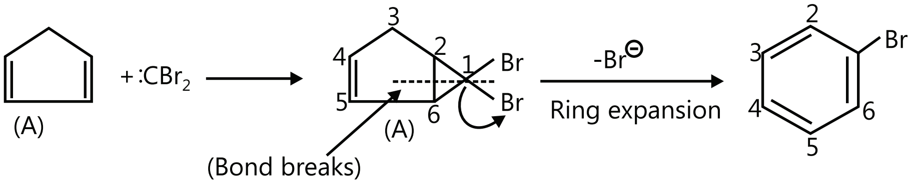
Sol:

(a)

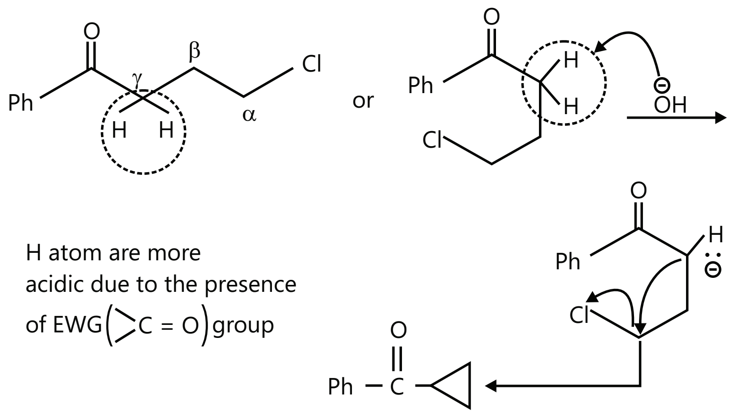


(b)



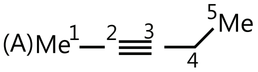


(c) It is an example of -elimination.



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

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

(a) 

$\xrightarrow{D_2\text{+ Poisoned Pd}}$ (B) $\xrightarrow{H_2\text{+Pt}}$ C (No. of isomers)

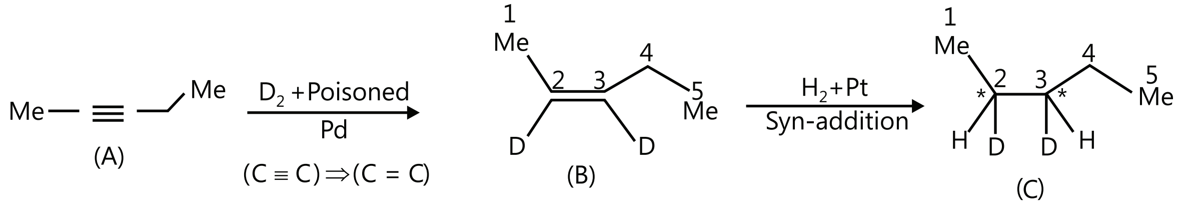
(b) (B)(from Problem A) $\xrightarrow[\text{reagent}]{\text{Baeyer's}}$ (D) + (E) (Colour of precipitate)

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

(d) (A) $\xrightarrow{Na\text{+liq. }ND_3\text{+ EtOH}}$ (F) $\xrightarrow[\substack{\text{or}\\ OSO_4/NaHSO_3\\ PhCO_3H/H_2O}]{Alk.KMnO_4}$ (D)

Sol:

(a)



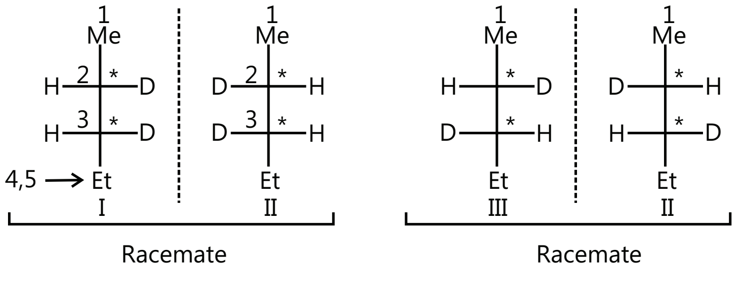
(A)

(B)
2Z-2,3-Dideuteropent-2-ene
or
2Z-2,3-Di-d-pent-2-ene

(C)
2,3-Dideuteropentane
or
2,3-Di-d-pentane

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

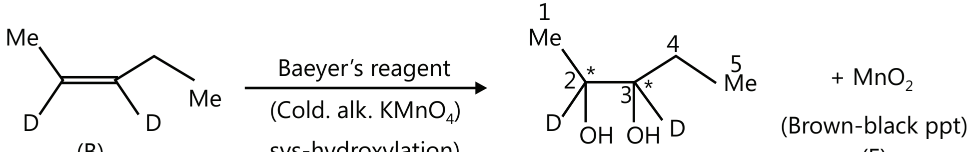
Compound (C) contains two chiral carbon, thus the number of optical isomers will be $2^2 = 4$ (two pairs of enantiomer). These are:



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

Pairs of diastereomers: (II, IV)

(b)



(B)

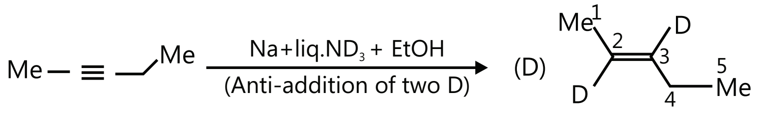
cis-Compound
with two different
R group

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

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

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

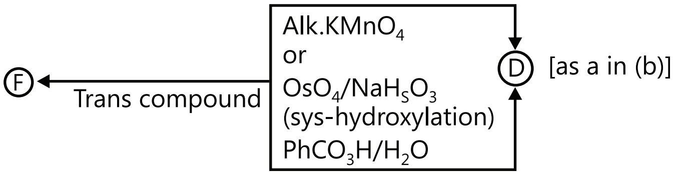
(d)



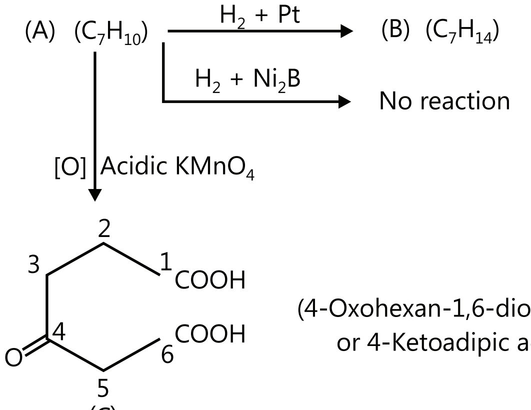
(A)

(trans or E)

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



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



(C)

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

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

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

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

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

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

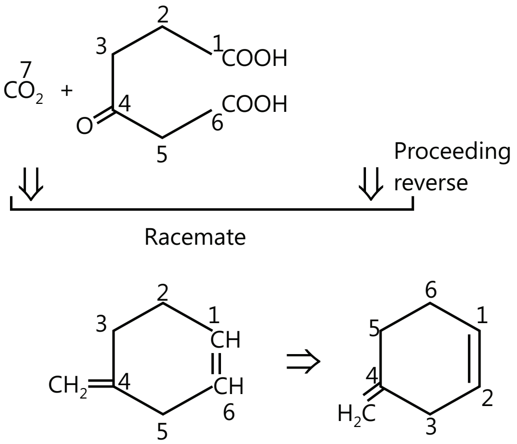
As we have calculated, (B) has 1.D.U., it must be a ring (because after hydrogenation of (A) no double bond will be left)

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

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

Possible structure of (A) are as follows:

i.

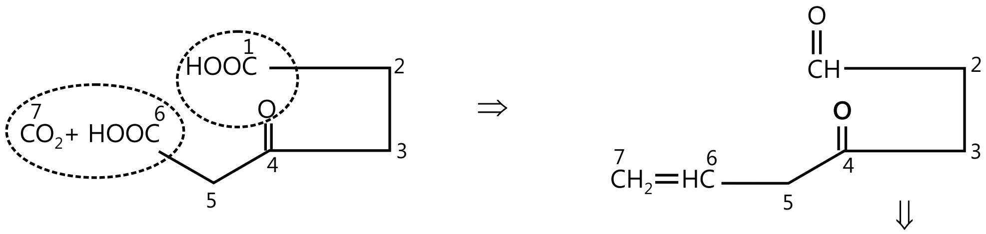


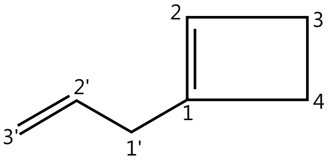
(I)

(4-Methyl cyclohexene)

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

(a) $\overset{1}{(\text{COOH})}$ Groups combines with $(\overset{4}{\text{C}}=\text{H})$ group and $\overset{7}{CO_2}$ combination with $(\overset{6}{\text{COOH}})$.





≡

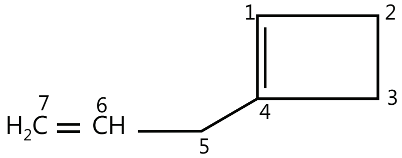
(II)

(Numbering in accordance with naming)

1-(prop-2-enyl)cyclobut-1-ene

or

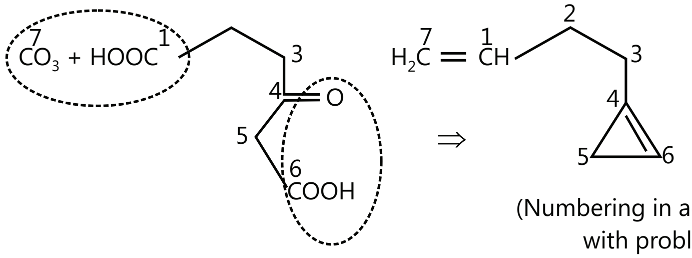
1-Allyl cyclobutene



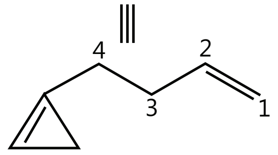
(II)

(Numbering in accordance with problem)

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



(Numbering in accordance
with problem)

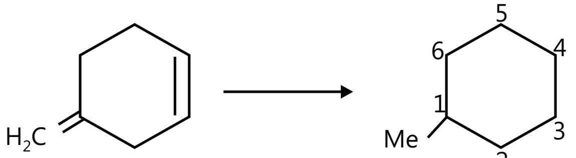


(Numbering in accordance
with naming)
(4-(Cyclopropenyl)but-1-ene)

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

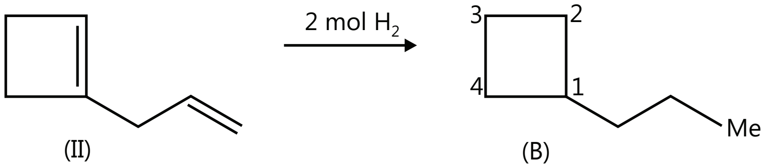
Because of highly strained ring Structure III is unlikely.

Two possible structures are as :-



(I)

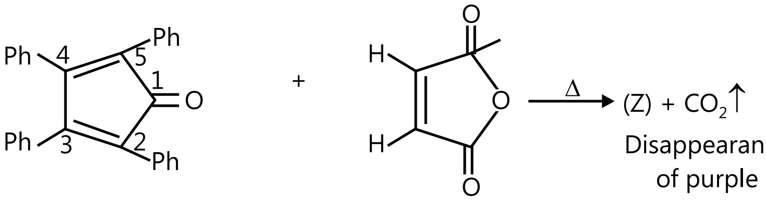
(B)
(C_7H_{14}) (1-Methyl cyclohexane)



(II)

(B)
1-Propyl-cyclobutane

Example 5: Complete the following reactions:

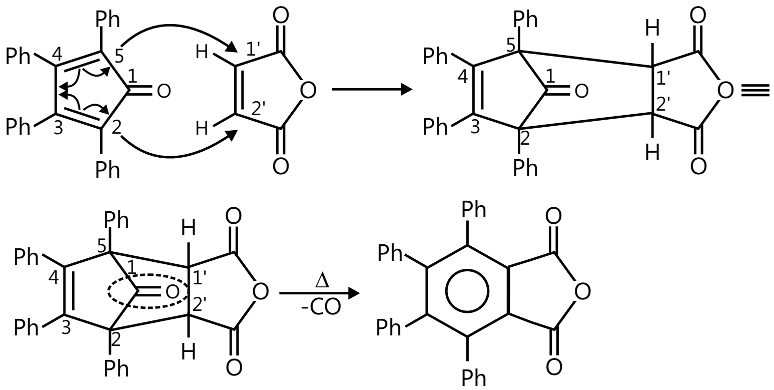


Disappearance
of purple
colour

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

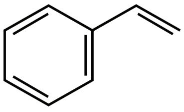
(Y)
Maleic
anhydride

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

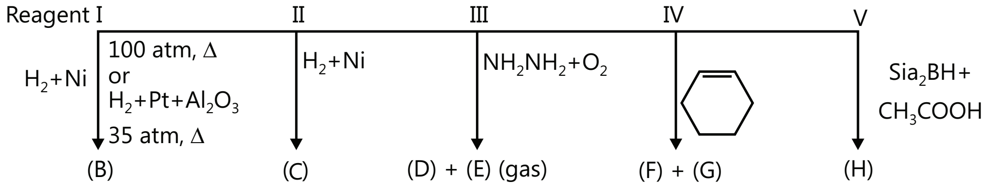


(Z)
(Colourless compound)

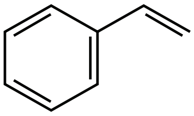
Example 6: Identify (A) to (H)



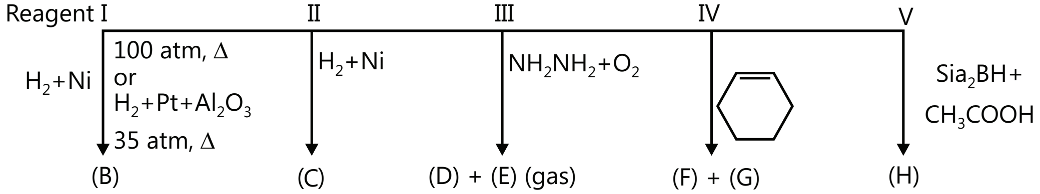
(A)

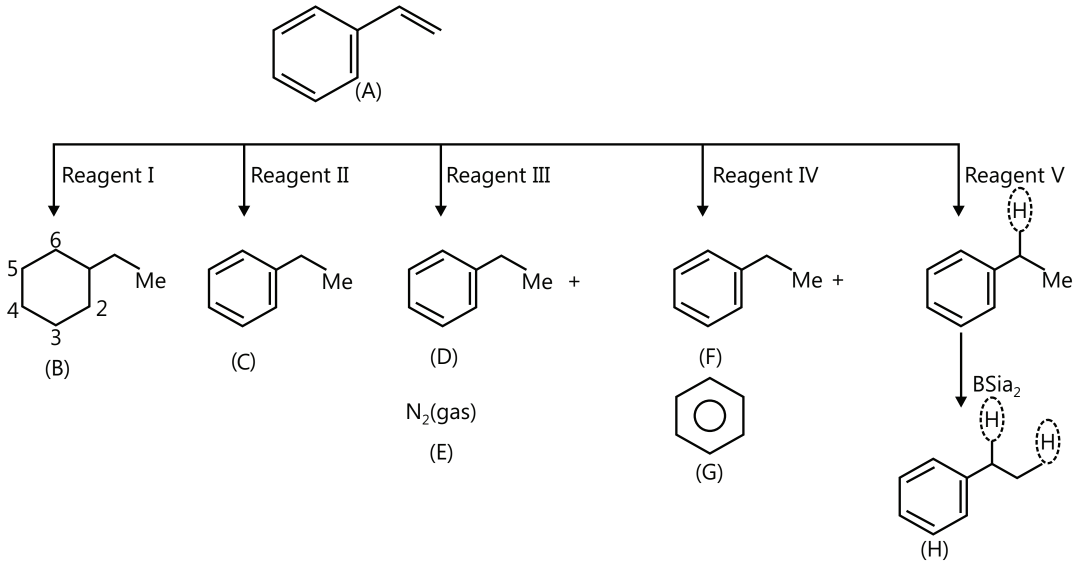


Sol:

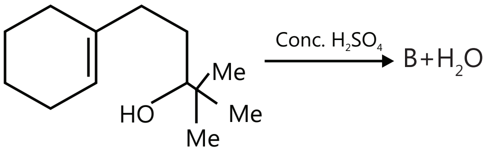


(A)



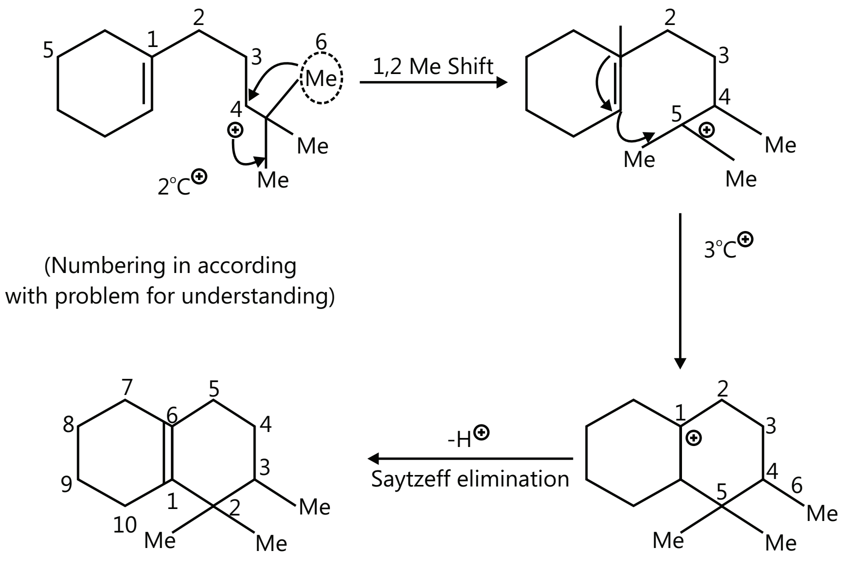


Example 7: Write the product with its mechanism.



(A)

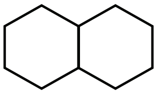
Sol:

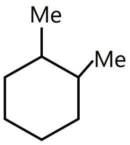


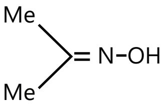
(Numbering in according with problem for understanding)

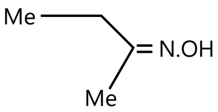
2,2,3-Trimethyl bicyclo [4.4.0] dec-1-ene

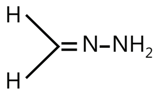
Example 8: Which of the following show G.I.?

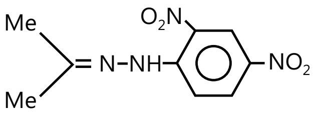
(a) 

(b) 

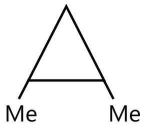
(c) 

(d) 

(e) 

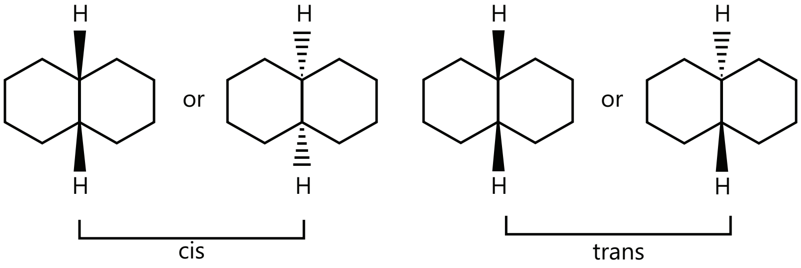
(f) 

(g) Ph − N = N − Ph

(h) 

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

(a) It shows G.I.

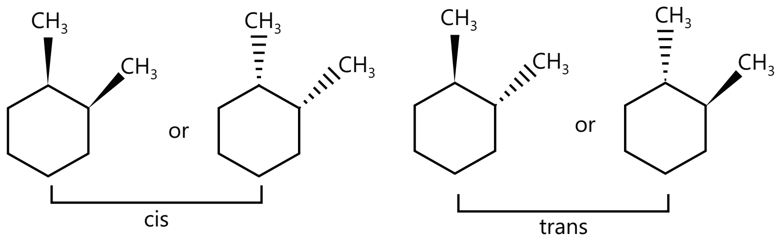


(i) Two atoms on the dotted line (..........................) means that the groups are below the plane of the ring.

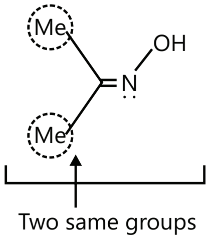
(ii) Two atoms on the bold lines (**..........................**) means that the groups are above the plane of the ring.

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

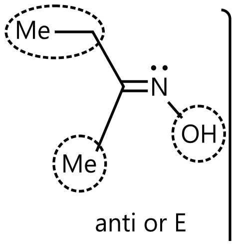
(b) It shows G.I.



(c) It does not show G.I.



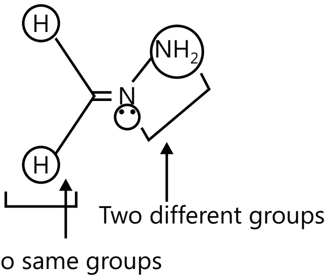
Priority of C_2H_5 > CH_3 and OH > LP of e s



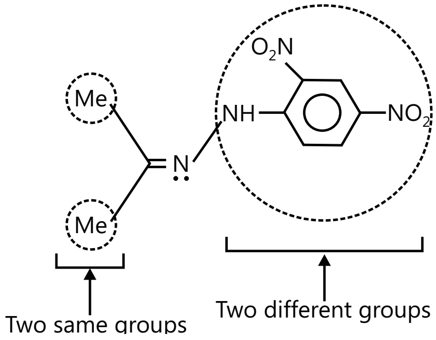
Two higher priority group on the same side, on two different C atom of the double bond

anti or E

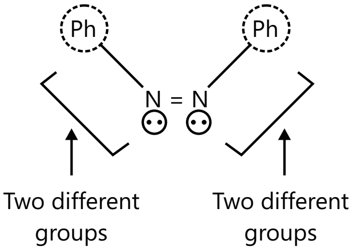
(e) It does not show G.I

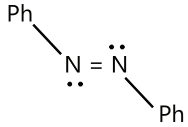


(f) It does not show G.I



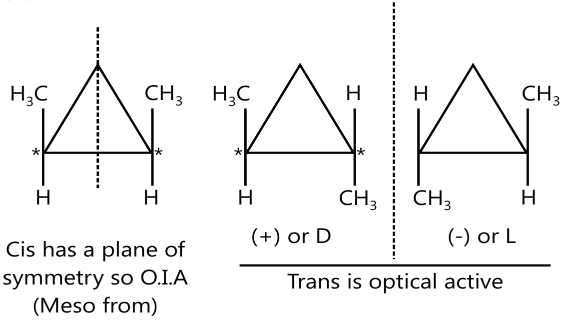
(g) It shows G.I.





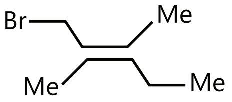
anti or E

(h) It shows G.I.

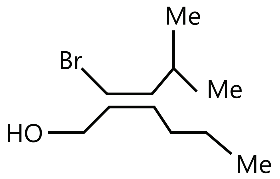


Example 9: Give IUPAC name to each of the following using E or Z designations.

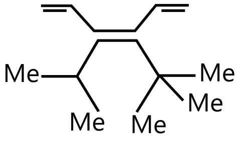
(A)



(B)

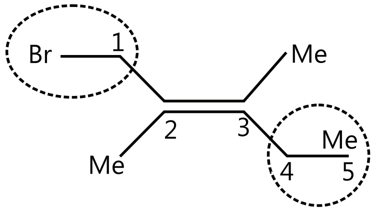


(C)



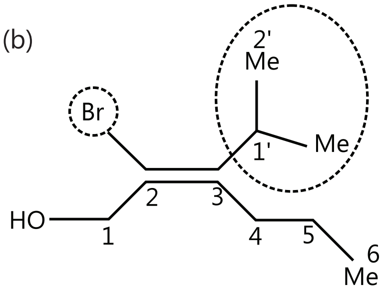
Sol:

(a)



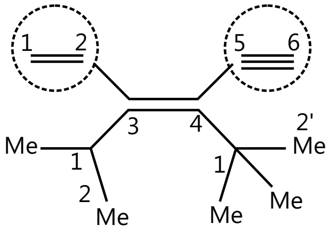
Two higher priority groups on opposite side,1E,
1-Bromo-2,3-dimethyl pent-2-ene

(b)



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

(c)



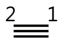
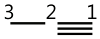
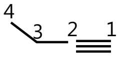
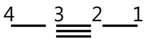
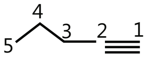
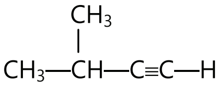
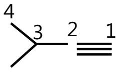
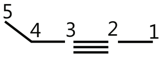
Priority of HC ≡ C- > $(CH_3)_3C$- > CH_2=CH-B> $(CH_3)_2CH$-
Two higher priority groups on the same side.
3Z,3-(1-methyl ethyl)-4-(1-1-Dimethyl ethyl)-hexa-1,3-dine-5-yne

ALKYNES

1. INTRODUCTION

1.1 Nomenclature

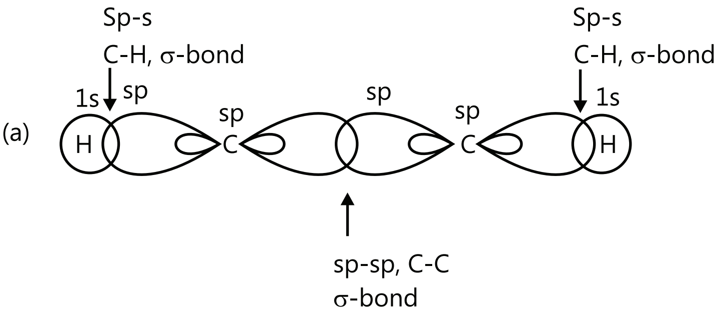
Alkynes are unsaturated hydrocarbons that contain (C≡C) bond. Their general formula is C_nH_{2n-2}.

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

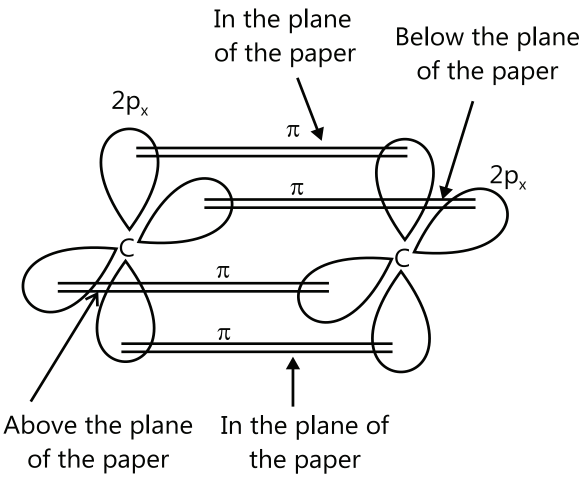
1.2 Structure

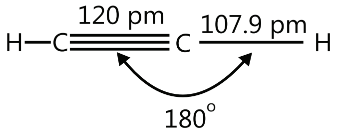
Each carbon atom of ethyne is sp-hybridized. One sp-hybridized orbital of each carbon undergoes head on overlap with sp-hybrisized orbital of another carbon to form a sp-sp, C-C, σ-bond. The second sp-hybridized orbital of each carbon overlaps along the internuclear axis with 1 s-orbital of each of the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

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



(b)





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

1.3 Isomerism in Alkynes

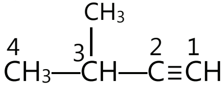
(i) Position isomerism. The first two members, i.e., ethyne and propyne exist in one form only. However, butyne and higher alkynes exhibit position isomerism due to the different position of the triple bond on the carbon chain. For example,

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

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

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

$CH_3—CH_2—CH_2—C\equiv CH$



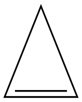
$\overset{4}{C}H_3—\overset{3}{C}H(CH_3)—\overset{2}{C}\equiv\overset{1}{C}H$

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

$\overset{4}{CH_3}—\overset{3}{CH_2}—\overset{3}{C}\equiv\overset{1}{CH}$ $\qquad$ $\overset{1}{CH_2}=\overset{2}{CH}—\overset{3}{CH}=\overset{4}{CH_2}$

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

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

$CH_3—C\equiv CH$ and  are ring chain isomers.

Propyne $\qquad$ Cyclopropene

2. PREPARATION OF ALKYNES

2.1 From Calcium Carbide

Alkynes are prepared by the following general methods.

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

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

   Calcium carbide   Ethyne (Acetylene)

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

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

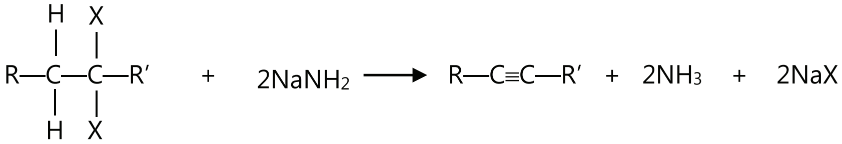
   $CaO + 3C \xrightarrow{2275K} CaC_2 + CO$

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

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

2.2 Double Dehydrohalogenation of Dihalides

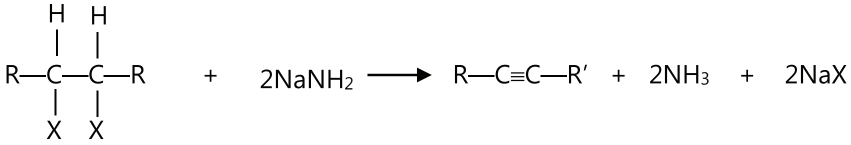
Double dehydrohalogenation of a geminal dihalide



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

Geminal dihalide   Sodium amide   Alkyne   Ammonia   Sodium halide

Double dehydrohalogenation of a vicinal dihalide



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

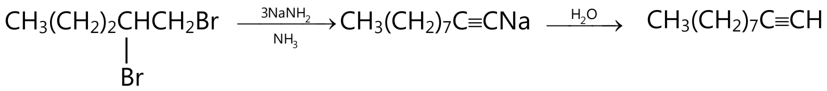
Vicinal dihalide   Sodium amide   Alkyne   Ammonia   Sodium halide

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

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

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

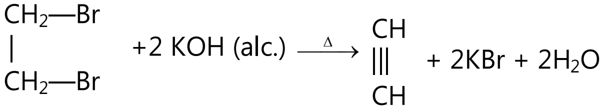
2.



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

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

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



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

1,2-Dibromodecane (Ethylene dibromide)	Acetylene

PLANCESS CONCEPTS

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

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

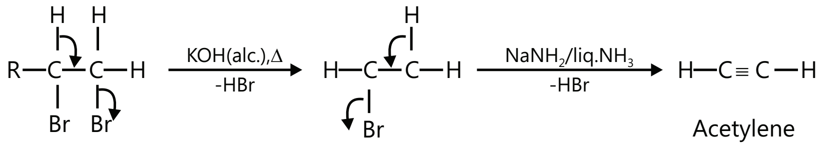
Ethylene dibromide	Vinyl bromide

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

Vinyl bromide	Acetylene

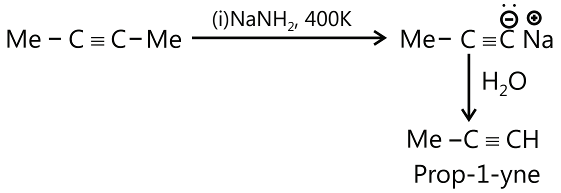
Aman Gour (JEE 2012, AIR 230)

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



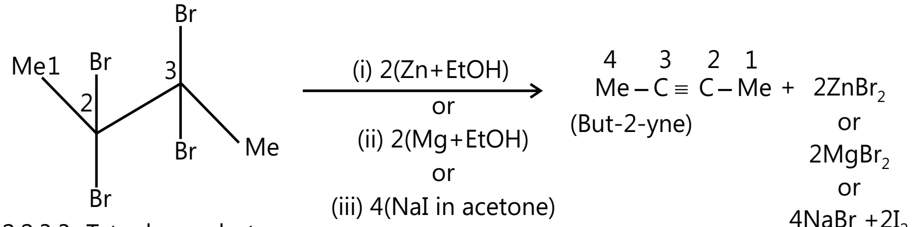
Vicinal dihalide　Vinyl bromide　Acetylene

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



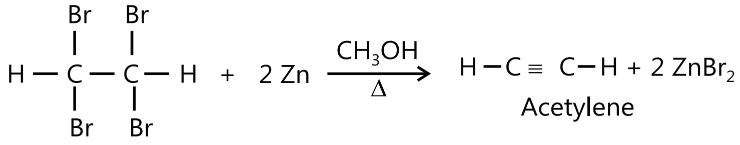
$$\mathrm{Me-C{\equiv}C-Me} \xrightarrow{\text{(i)}\mathrm{NaNH_2},\ 400\mathrm{K}} \mathrm{Me-C{\equiv}\overset{\ominus}{\ddot{C}}\ \overset{\oplus}{Na}} \xrightarrow{\mathrm{H_2O}} \underset{\text{Prop-1-yne}}{\mathrm{Me-C{\equiv}CH}}$$

Dehalogenation of tri/tetra halides



2,2,3,3,-Tetra bromobutane

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



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

1,1,2,2-Tetrabromoethane

2.4 Dehalogenation of Haloforms

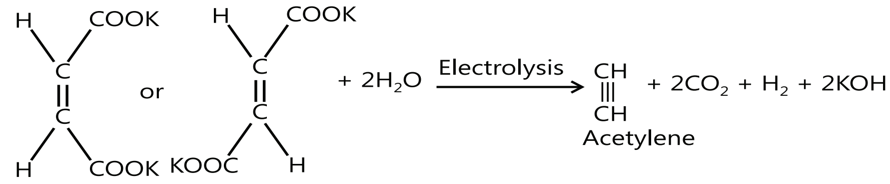
By dehalogenation of haloforms: Chloroform and iodoform on heating with silver powder undergo dehalogenation to form ethyne.

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

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

2.5 Kolbe's Electrolytic Reaction

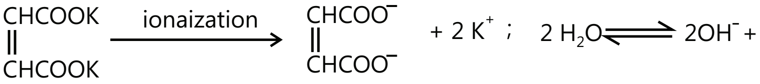
Kolbe's electrolytic reaction: Acetylene can be prepared by electrolysis of a concentrated solution of sodium or potassium salt of maleic acid or fumaric acid. Thus,



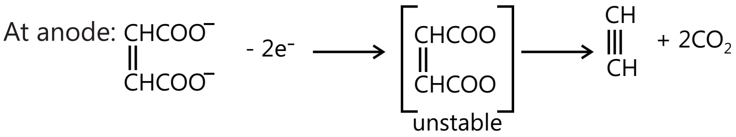
Pot. maleate (cis isomer)

Pot. fumerate (trans-isomer)

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



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

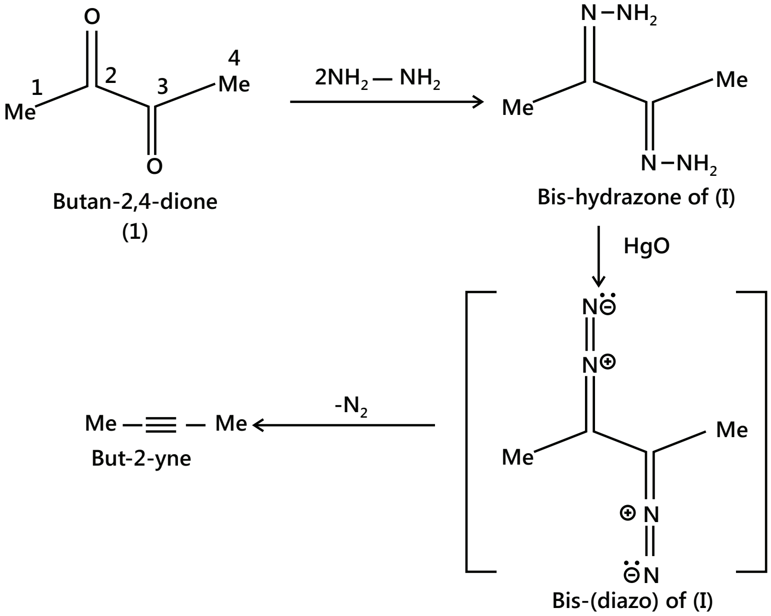
At anode: 

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

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

2.6 From α-diketo

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



2.7 Industrial Method

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

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

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

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

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

2.8 Berthelot Synthesis

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

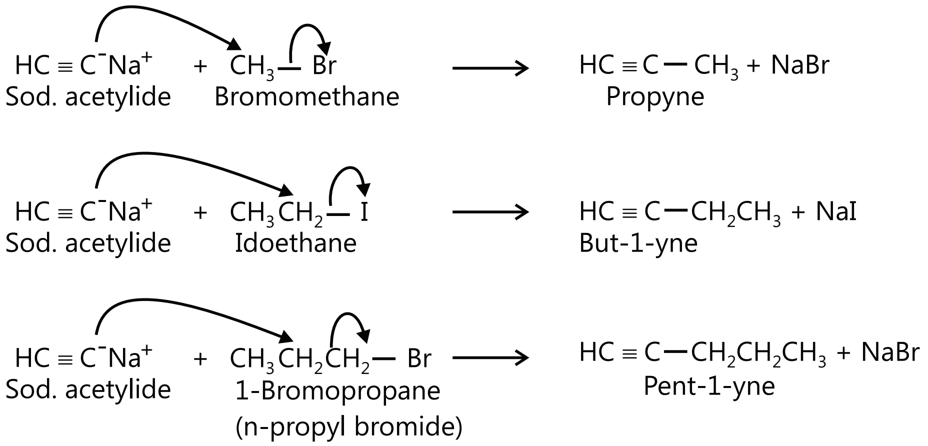
$$2C + H_2 \rightleftharpoons \underset{\text{Acetylene}}{CH \equiv CH(g)}$$

2.9 Higher Alkynes from Acetylene

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

For example:

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



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

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

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

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

3. PROPERTIES OF ALKYNES

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

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

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

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

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

(iii) Solubility and Dipole moment

Decreasing solubility in H_2O: Alkynes > Alkenes > Alkanes

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

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

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

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

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

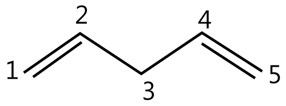
(iv) Smell: All alkynes are odourless except acetylene which has a garlic smell due to the presence of impurity, phosphine.

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

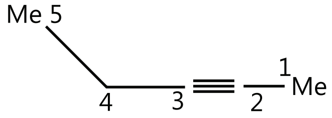
(vi) Melting and Boiling points: The m.p. and b.p. of alkynes are slightly higher than those of the corresponding alkenes and alkanes. This is probably due to the presence of a triple bond, alkynes have linear structures and hence their molecules can be more closed packed in the crystal lattice as compared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

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

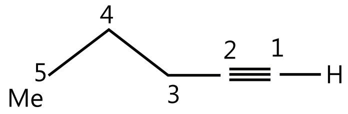
(viii) Stability: Alkynes are less stable than isomeric dienes as is evident from their heat of formation (ΔH_f°) values.



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



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



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

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

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

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

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

(x) Acidity of alkynes:

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

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

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

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

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

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

4. REACTIONS OF ALKYNES

4.1 Acidic Character

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Importance: The formation of metal acetylides can be used:

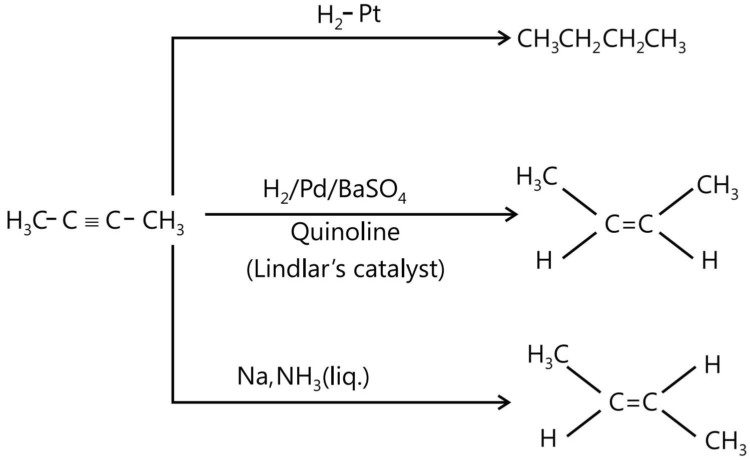
(a) For the separation and purification of terminal alkynes from non-terminal alkynes, alkanes and alkenes.

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

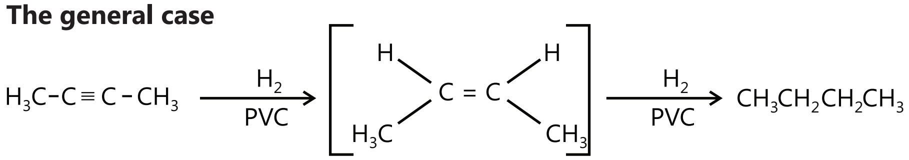
4.2 Hydrogenation / Reduction

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

Alkene is an intermediate



The general case



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

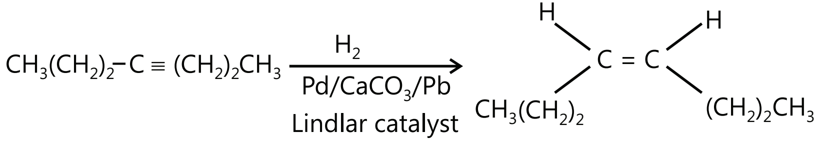
But the reaction can be stopped at the alkene stage by using the following reagents.

- **(a)** H_2 + Pd + $BasO_4$ + S or quinoline in boiling xylene (called Lindlar's catalyst). In this case, reaction proceeds via syn addition of H_2.
- **(b)** H_2 + P-2 or Brown catalyst (H_2 + Ni + B) or (H_2 + Ni_2B). It also proceeds via syn addition of H_2.
- **(c)** Alkali metals (Na, K, Cs) + liq. NH_3 and C_2H_5 OH (It is called Birch reduction). It proceeds via anti-addition of H_2.
- **(d)** $LiAlH_4$(LAH). It reduces $(C \equiv C)$ to (C = C) via anti addition of H_2; does not reduce (C = C) to (C — C) bond; reduces (C=C) to (C —C) only when the phenyl group is attached to the -C atom of the double bond.

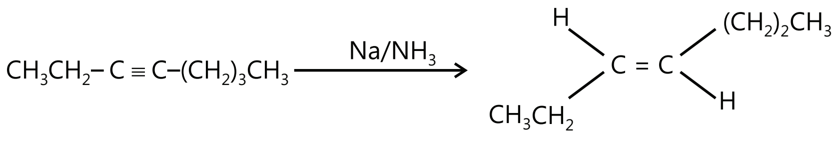
  (E.g. $Ph - \overset{\beta}{C}H = \overset{\alpha}{C}H - CH_3$ to $Ph - CH_2 - CH_2 - CH_3$)

Reduction of alkynes to (Z) – alkenes

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



96% cis



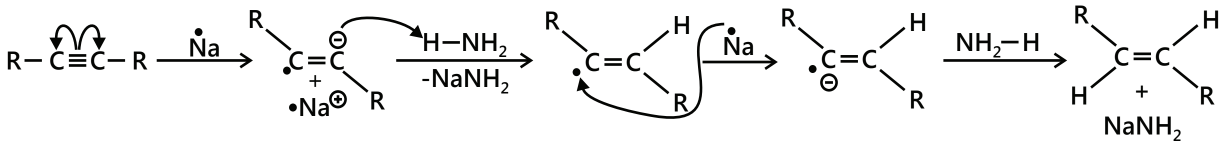
98% trans

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

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

Solvated electron

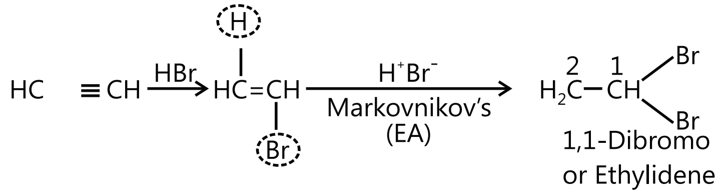
Mechanism of Na/NH_3 reductions: $Na^+ \xrightarrow{-33°C} Na^+ + NH_3(e^-)$



4.3 Addition of X_2

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

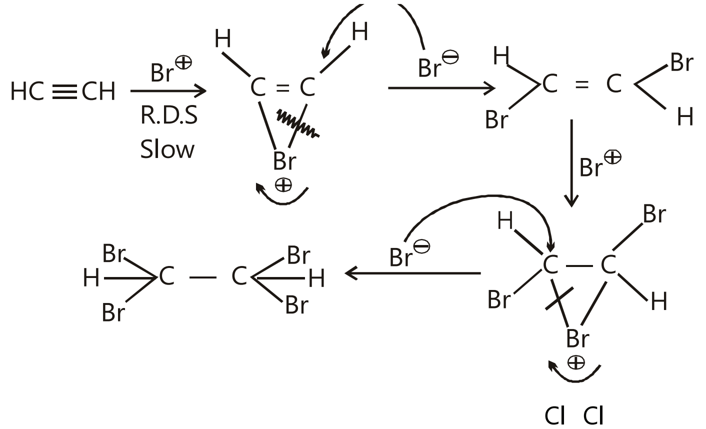
(I)

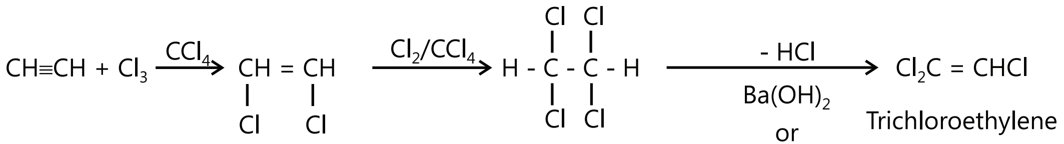


1,1-Dibromo ethane
or Ethylidene bromide

Mechanism:

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





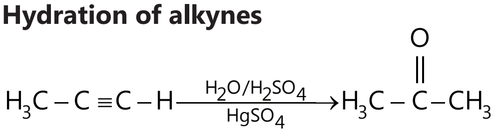
$$CH\equiv CH + Cl_3 \xrightarrow{CCl_4} \underset{Cl}{CH} = \underset{Cl}{CH} \xrightarrow{Cl_2/CCl_4} H-\overset{Cl}{\underset{Cl}{C}}-\overset{Cl}{\underset{Cl}{C}}-H \xrightarrow[Ba(OH)_2 \text{ or } BaCl_2]{-HCl} Cl_2C = CHCl$$

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

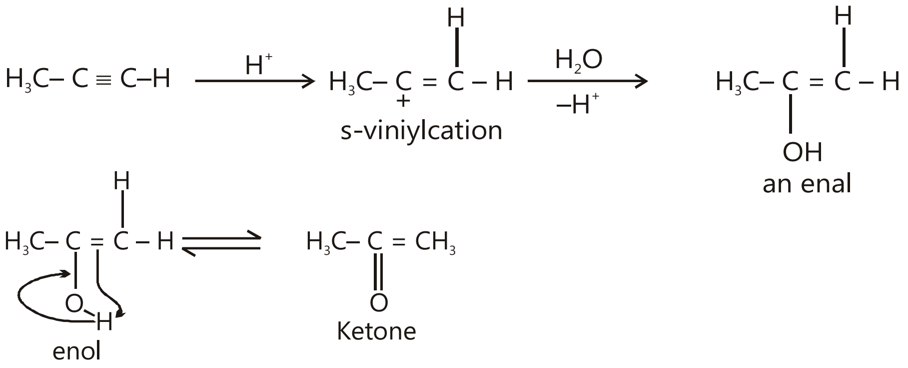
Trichloroethylene
or westrosol

4.4 Addition of Water

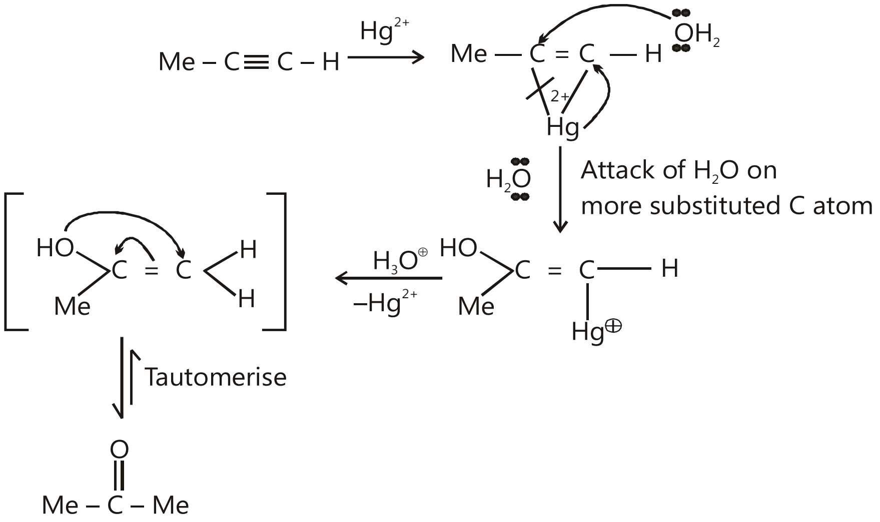
Hydration of alkynes



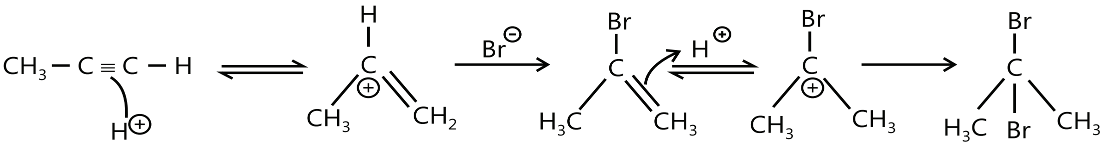
$$H_3C-C\equiv C-H \xrightarrow[HgSO_4]{H_2O/H_2SO_4} H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$



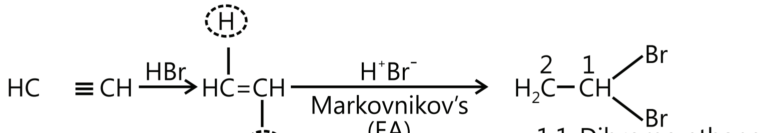
(Oxymercuration-demercuriation of triple bond)



4.5 Addition of HX

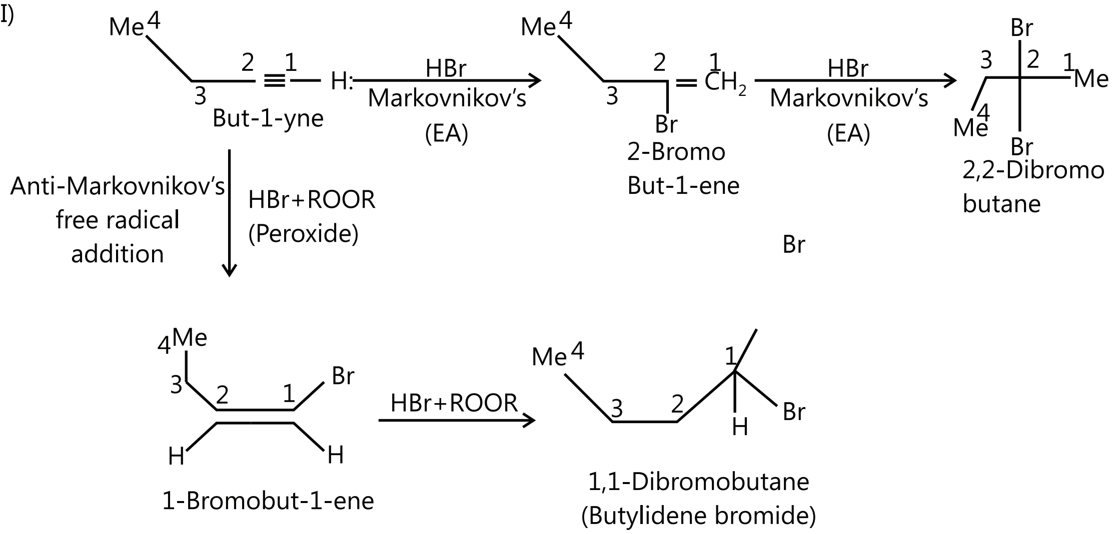


(I)



1,1-Dibromo ethane
or Ethylidene bromide

(II)



PLANCESS CONCEPTS

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

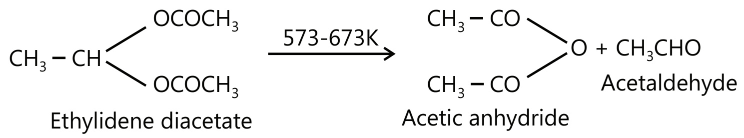
Aishwarya Karnawat (JEE 2012 AIR 839)

4.6 Addition of Acids

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

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

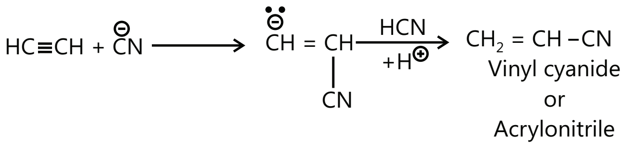
Vinyl acetate is used for the manufacture of vinyl resin. Ethylidene diacetate, when heated rapidly to 573-673K, gives acetic anhydride and acetaldehyde.



$$\underset{\text{Ethylidene diacetate}}{CH_3-CH(OCOCH_3)_2}\xrightarrow{573\text{-}673K}\underset{\text{Acetic anhydride}}{(CH_3-CO)_2O}+\underset{\text{Acetaldehyde}}{CH_3CHO}$$

4.7 Addition of HCN

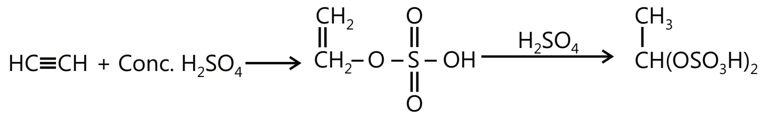
The reaction is nucleophilic addition (NA) initiated by CN$^-$ from NaCN.



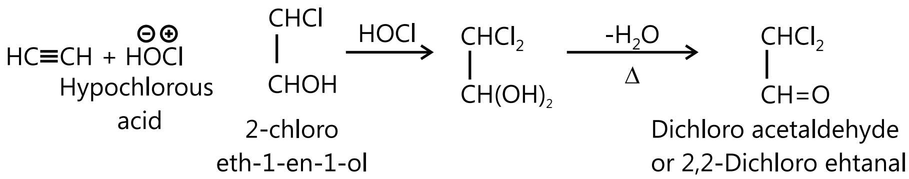
$$HC\equiv CH+\overset{\ominus}{C}N\longrightarrow \overset{\ominus}{C}H=CH-CN\xrightarrow[+H^{\oplus}]{HCN}CH_2=CH-CN$$

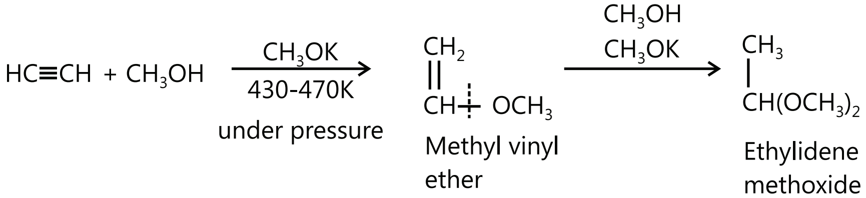
Vinyl cyanide
or
Acrylonitrile

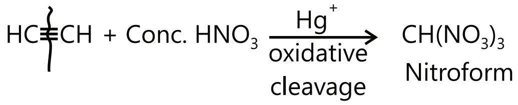
4.8 Addition to Other Compounds



$$HC\equiv CH+\text{Conc. }H_2SO_4\longrightarrow \underset{\text{Vinyl hydrogen sulphate}}{CH_2=CH-O-SO_2-OH}\xrightarrow{H_2SO_4}\underset{\text{Ethylidene hydrogen sulphate}}{CH_3-CH(OSO_3H)_2}$$



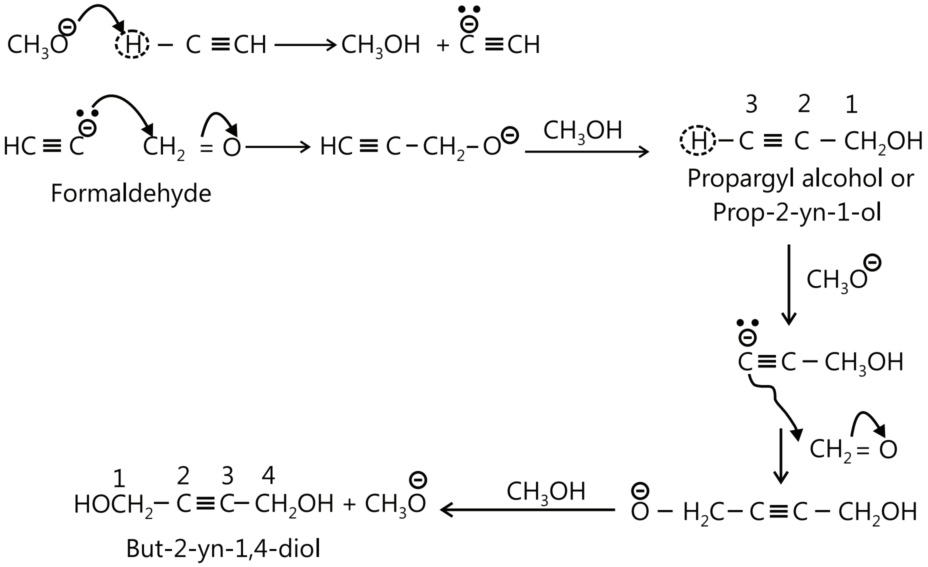




$$HC\equiv CH + \text{Conc. } HNO_3 \xrightarrow[\text{oxidative cleavage}]{Hg^+} \underset{\text{Nitroform}}{CH(NO_3)_3}$$

4.9 Ethyne + Methanal

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



4.10 Nucleophilic Addition

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

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

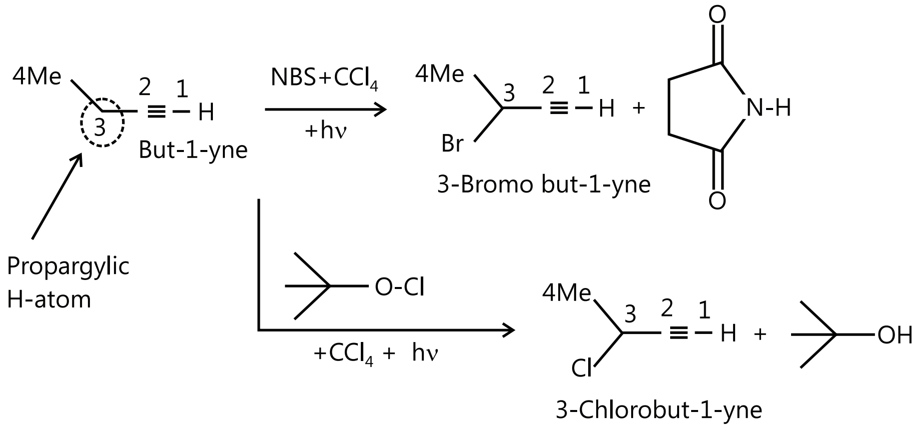
$$\underset{\text{Acetylene}}{HC\equiv CH} + \underset{\text{Methanol}}{CH_3O-H} \xrightarrow[433-473K]{CH_3O^-K^+} \underset{\text{Methyl vinyl ether}}{CH_2=CH-OCH_3}$$

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

Methyl vinyl ether is used for making polyvinyl ether plastics.

4.11 Propargylic Halogenation

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

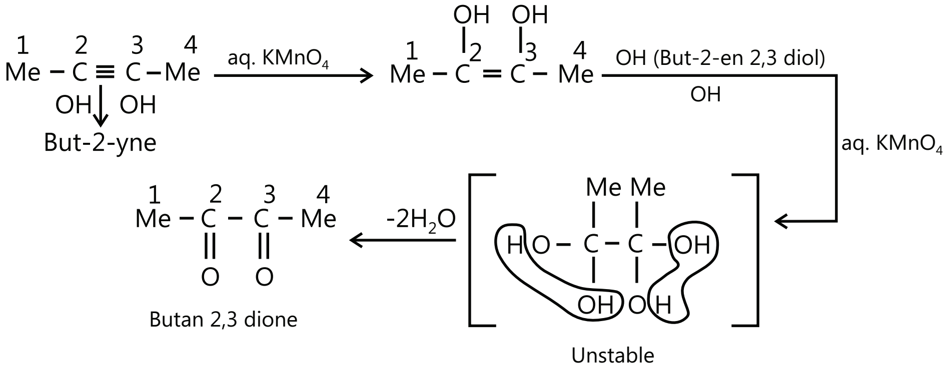


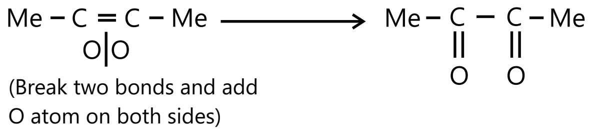
Reaction proceeds via free radical mechanism to give propargylic radical, which is stabilized by resonance via extended π-bonding.

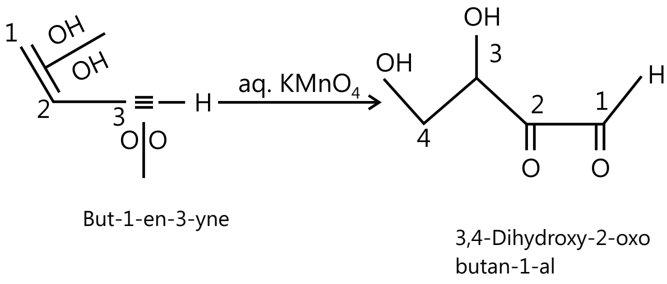
4.12 Hydroxylation of Alkynes

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

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







4.13 Oxidation Reactions

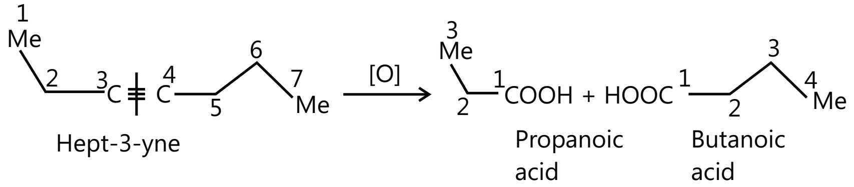
4.13.1 Oxidative Cleavage

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

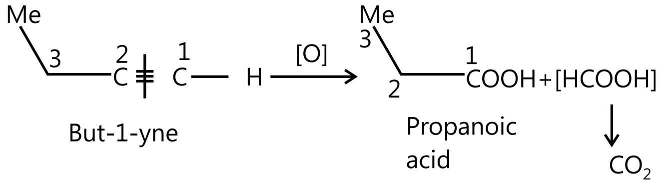
$$R-C\not\equiv \Longrightarrow R-COOH$$

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

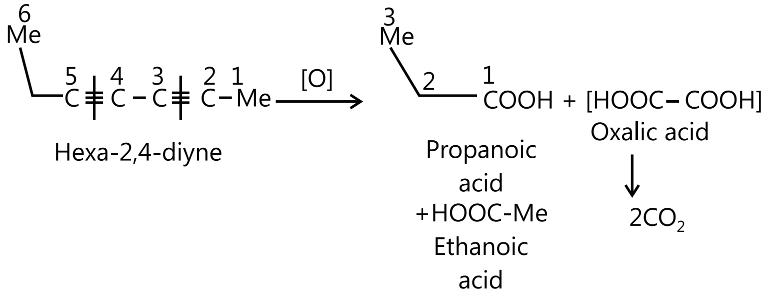
(i)



(ii)



(iii)

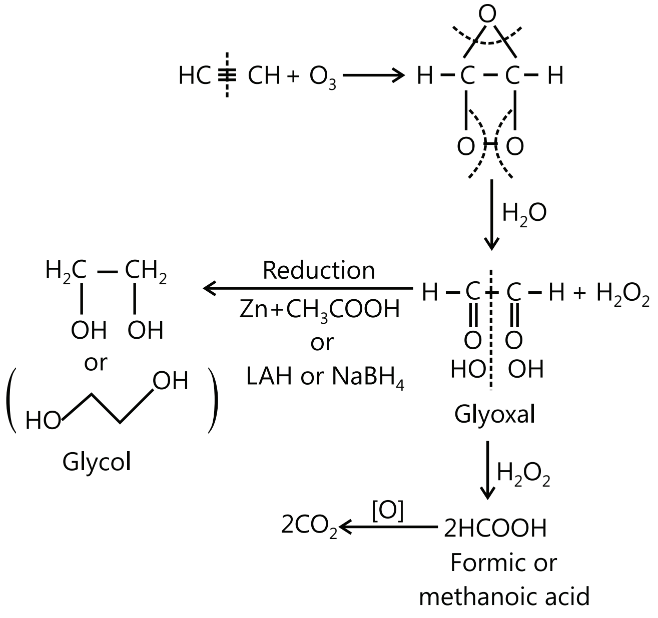


CrO_3 in CH_3COOH oxidizes alkenes but does not affect alkynes

4.14 Ozonolysis of Alkynes

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

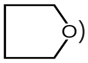
(i)

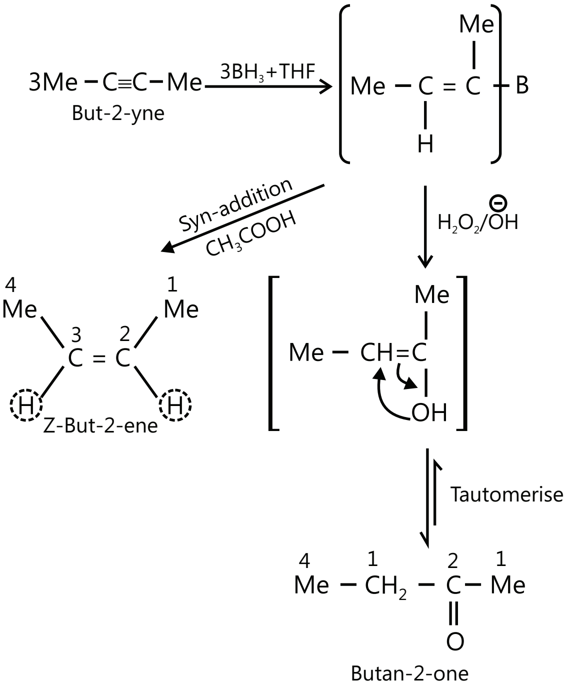


Terminal alkynes give HCOOH as one of the products which is further oxidized to CO_2

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

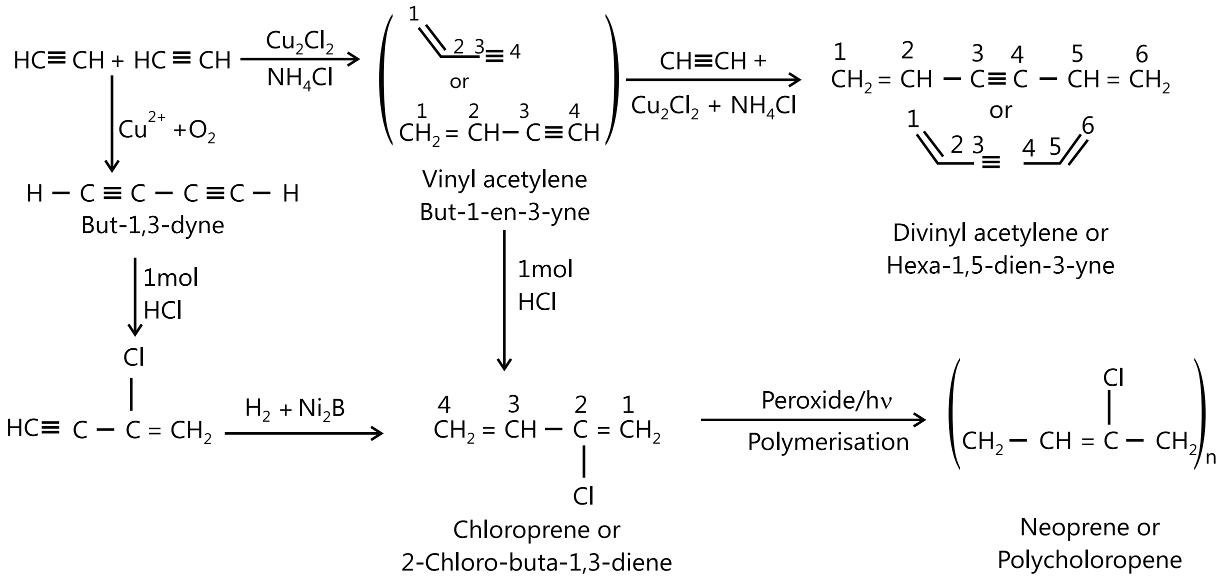
4.15 Hydroboration of Alkynes

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

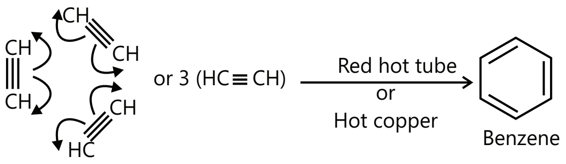


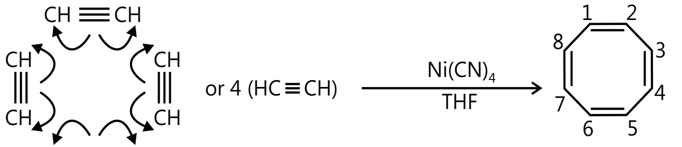
4.16 Polymerisation

1. Linear Polymerisation



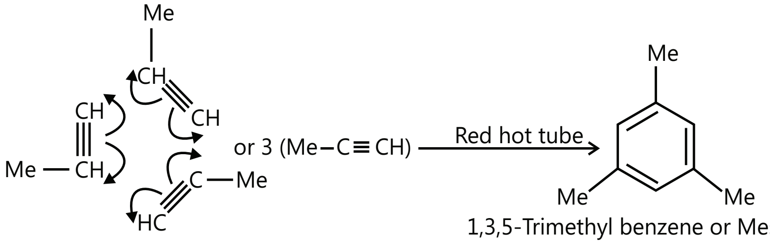
2. Cyclic Polymerisation





Cycloocta
1,3,5,7 tetra-ene

3. Propyne



1,3,5-Trimethyl benzene or Mesitylene

4.17 Isomerization

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

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

Uses of alkynes

(i) Acetylene and its derivatives are widely used in synthetic organic chemistry for synthesis of cis-and trans-alkenes, methyl ketones etc.

(ii) Oxyacetylene flame is used for cutting and welding of metals.

(iii) Acetylene is used as illuminant in hawker's lamp and in light houses.

(iv) Acetylene is used for the ripening of fruits and vegetables.

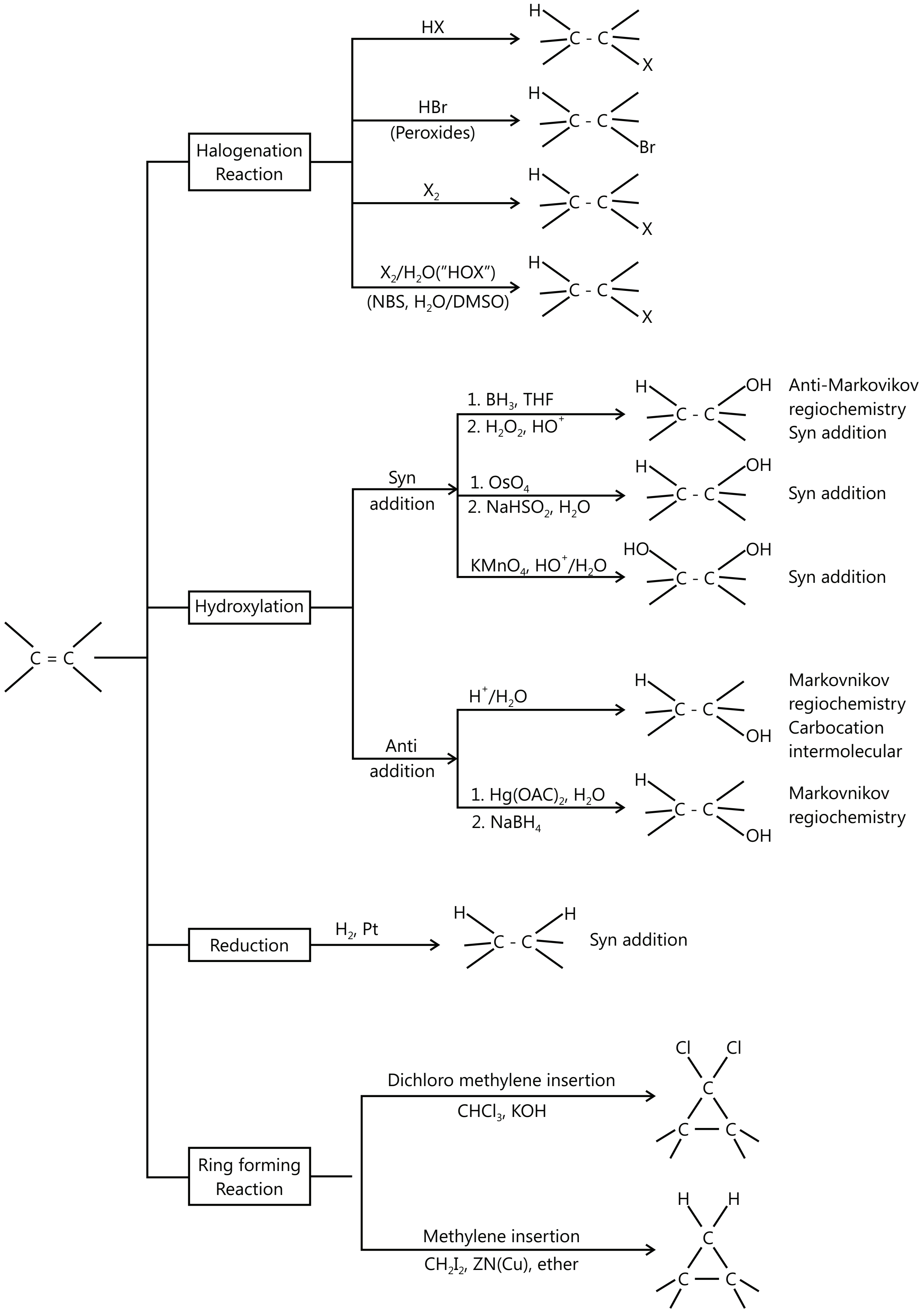
(v) Acetylene is used for manufacture of ethyl alcohol, acetaldehyde, acetic acid, vinyl plastics, synthetic rubbers such as Buna N and synthetic fibers such as Orlon.

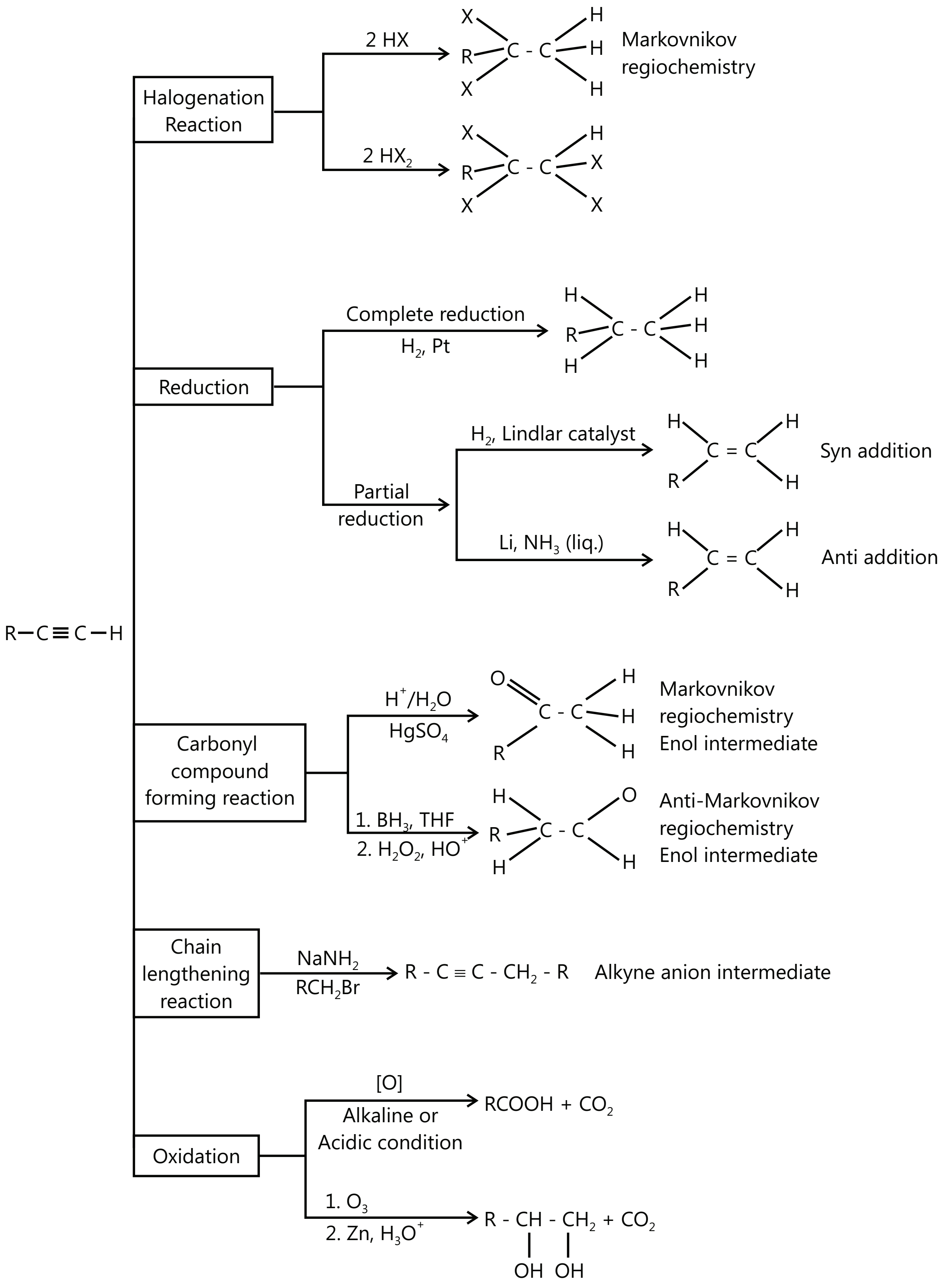
PLANCESS CONCEPTS

Difference between Alkenes and Alkynes

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

POINTS TO REMEMBER

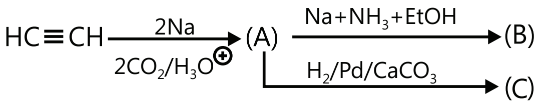


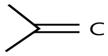

R—C≡C—H
Halogenation Reaction
2 HX
Markovnikov regiochemistry
2 HX2
Reduction
Complete reduction
H2, Pt
Partial reduction
H2, Lindlar catalyst
Syn addition
Li, NH3 (liq.)
Anti addition
Carbonyl compound forming reaction
H+/H2O
HgSO4
Markovnikov regiochemistry
Enol intermediate
1. BH3, THF
2. H2O2, HO+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

Solved Examples

JEE Main/Boards

Example 1: Identify A to C.



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

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

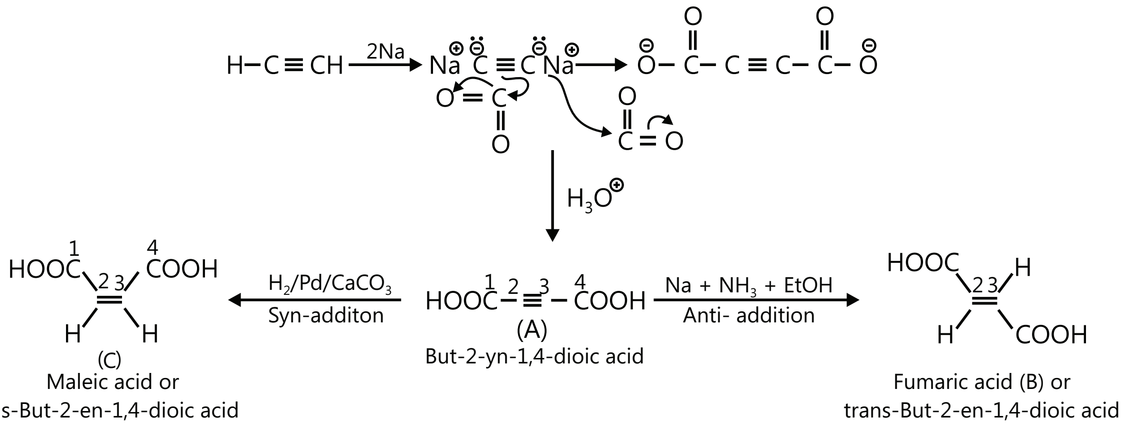
This reaction shows the acidic character of alkynes.

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

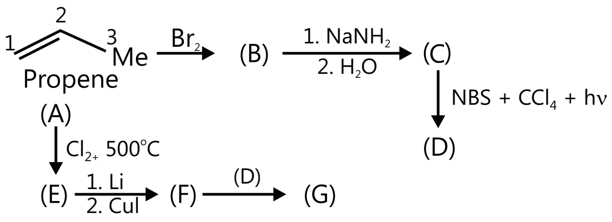
Now the carbanion reacts with two moles of carbon dioxide and forms an adduct which on treatment with acid yields acid.

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

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



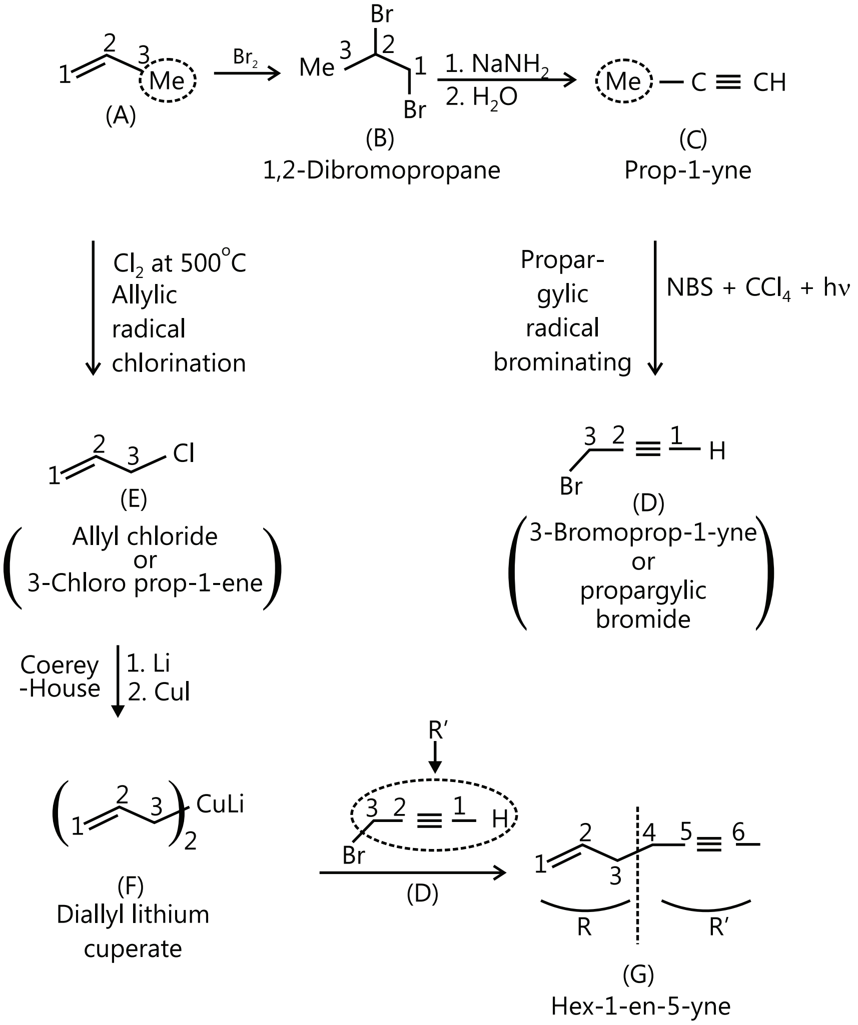
Example 2: Identify B to G.



Sol:

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

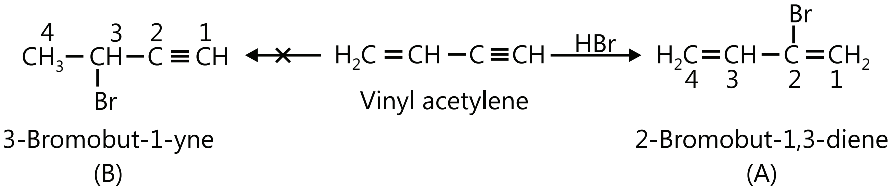
- The reaction proceeds through radical formation.
- Now Allyl chloride undergoes chain lengthening reaction to form Hex-1-en-5-yne.
- The reaction is known as Corey house synthesis



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

Sol:

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

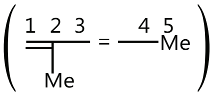


$$\underset{\text{3-Bromobut-1-yne (B)}}{\overset{4}{C}H_3-\overset{3}{C}H(Br)-\overset{2}{C}\equiv\overset{1}{C}H} \;\not\longleftarrow\; \underset{\text{Vinyl acetylene}}{H_2C=CH-C\equiv CH} \xrightarrow{HBr} \underset{\text{2-Bromobut-1,3-diene (A)}}{\underset{4}{H_2C}=\underset{3}{C}H-\underset{2}{C}(Br)=\underset{1}{C}H_2}$$

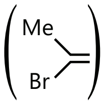
3-Bromobut-1-yne
(B)

2-Bromobut-1,3-diene
(A)

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

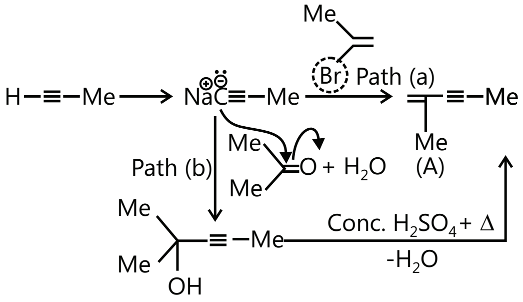
Example 4: There are two path (a) and (b) For the preparation of a compound (a) 

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

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

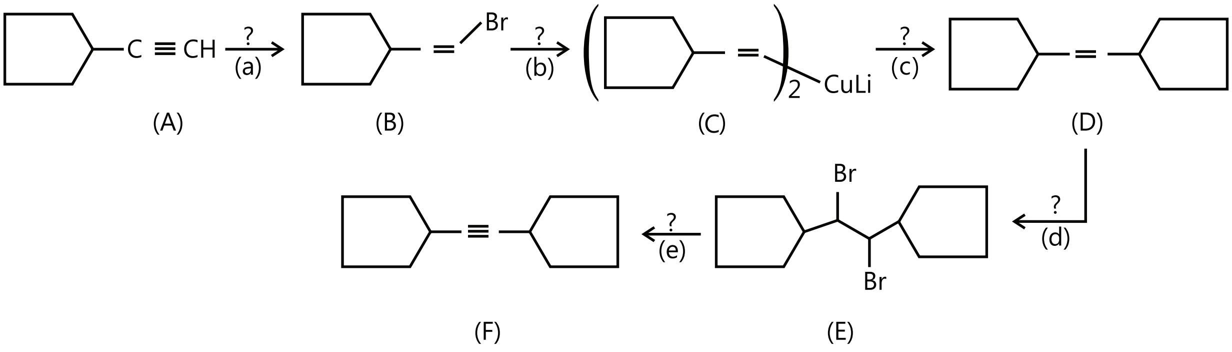
vinyl halide which is not reactive, so the reaction does not occur.

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



JEE Advanced/Boards

Example 1: Complete the following missing reagents

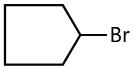


Sol: (i)

(a) HBr + Peroxide

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

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

(c) 

Third step is the reaction with alkyl halide.

(d) Br_2/CCl_4

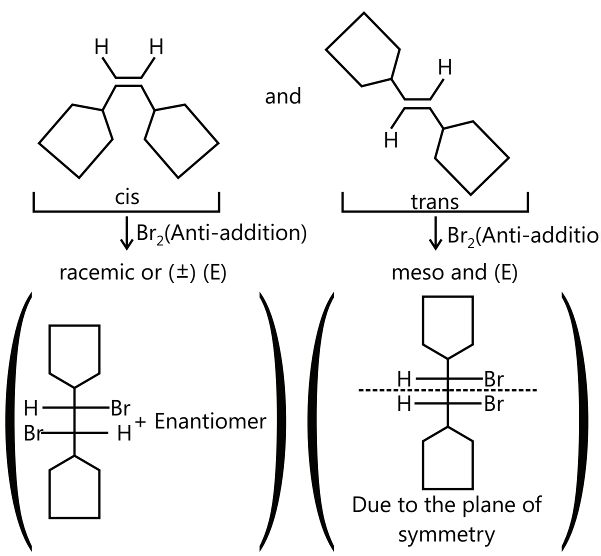
Bromination using Br_2 and CCl_4 as a solvent

(e) KOH(s), at 473 K

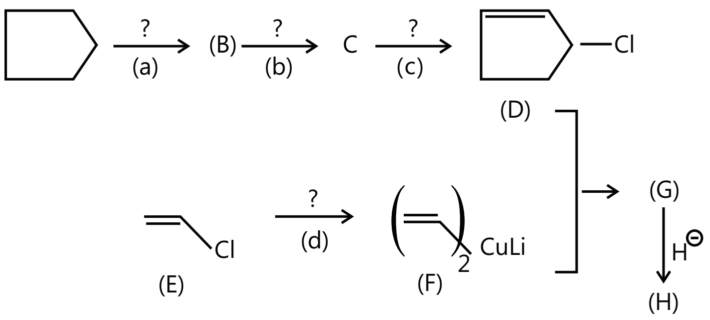
Last step is double dehalogenation using base like KOH at 473 K

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

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

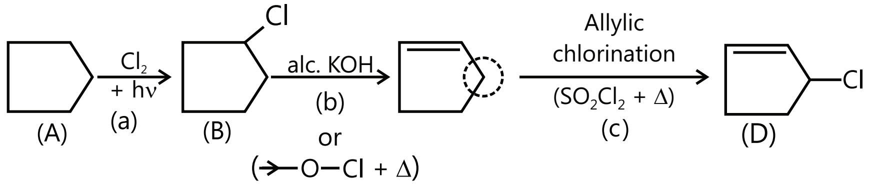


Example 2: Convert the following

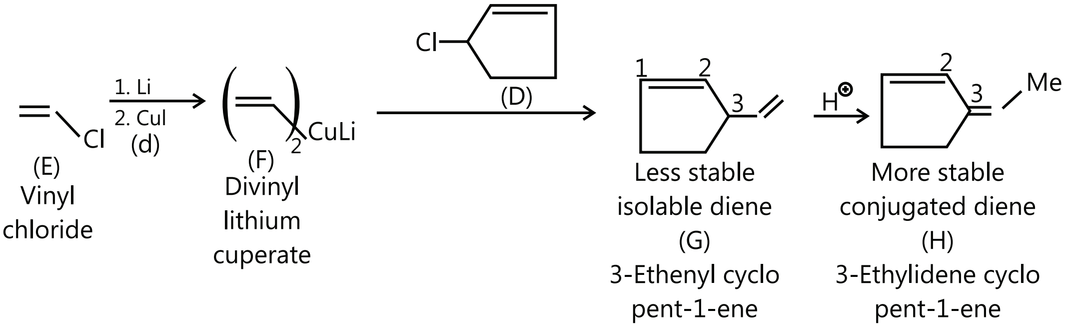


Sol:

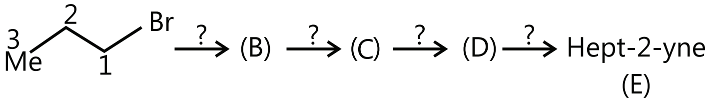
(a)



(b)

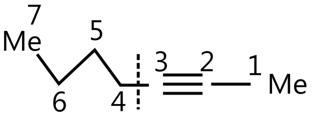


Example 3: Convert the following.



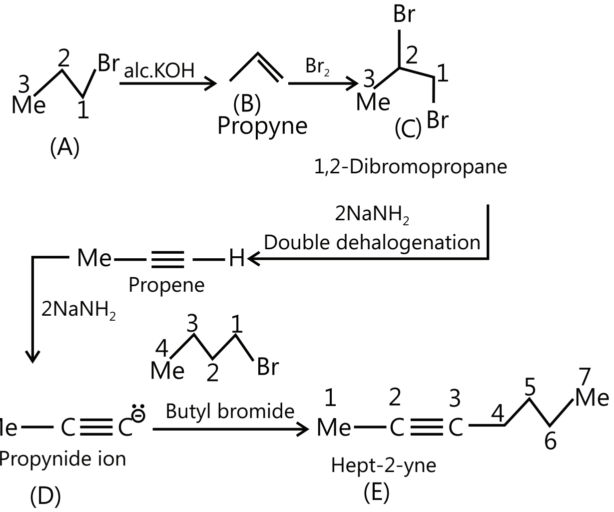
Write the structure of (E).

Sol: The structure of E is



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

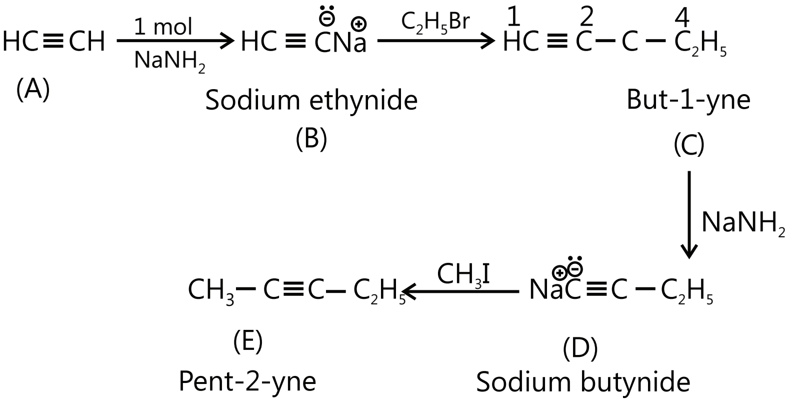
Reaction:



Example 4: Complete the following:

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

Sol:



JEE Main/Boards

Exercise 1

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

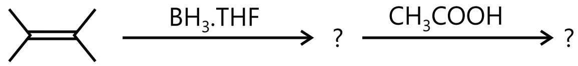
Q.2 Write the major products of the hydrocarbon and oxidation of:

(A) 1-Ethyl cyclopentene

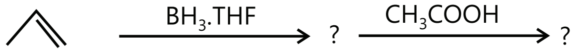
(B) Methylene cyclopentene

Q.3 Give the missing compounds in the following:

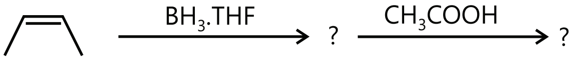
(A)



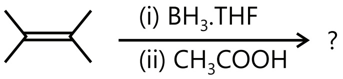
(B)



(C)



(D)



Q.4 Complete the following equation:

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

$\xrightarrow[Pt]{H_2} CH_3CH_2CH_2CH_3$

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

(B) + $NaOC_2H_5$

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

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

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

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

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

Q.9 (A) Complete the following reactions:

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

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

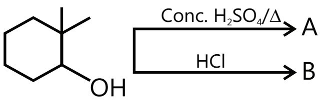
(B) Complete the following reactions:

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

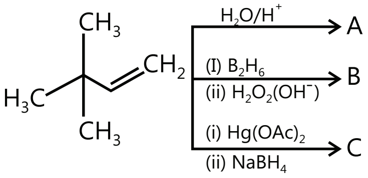
$$\xrightarrow[\text{Lindlar's catalyst}]{H_2} B \xrightarrow[Zn(Cu)]{CH_2I_2} C$$

Q.10 Predict the product of the following:

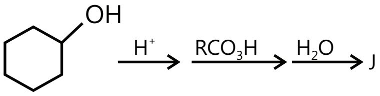
(A)



(B)



(C)

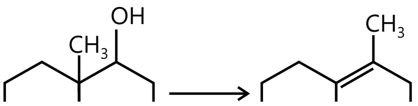


Q.11 (A) Give reasons for the following:

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

$CH_3CH(Br)CH_2C{\equiv}CH$.

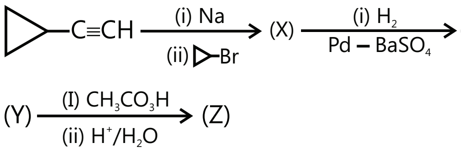
(B) Provide a suitable mechanism for the following reaction.



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

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

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



Exercise 2

Single Correct Choice Type

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

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

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

(A) (+) 2, 3-dibromobutane

(B) (–) 2, 3-dibromobutane

(C) rac -2, 3-dibromobutane

(D) meso -2,3-dibromobutane

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

(A) Conformers (B) Diastereomers

(C) Enantiomers (D) Positional isomers

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

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

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

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

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

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

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

(D) None of these

Q.6 End product of the following sequence is:

$$CaO + C \xrightarrow{\text{Heat}} (A) \xrightarrow{H_2O} (C)$$

$$\xrightarrow[H_2SO_4]{Hg^{2+}} (C)$$

(A) Ethanol (B) Ethyl hydrogen sulphate

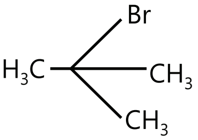
(C) Ethanal (D) Ethylene glycol

Q.7 The treatment of C_2H_5MgI with water produces

(A) Methane (B) Ethane

(C) Ethanal (D) Ethanol

Q.8 When isobutene is brominated, the percentage of



would be

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

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

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

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

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

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

(A) Ethanol (B) Ethyne

(C) Ethanal (D) Ethene

Q.11 Which one is highly unstable?

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

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

Previous Years' Questions

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

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

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

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

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

(A) Only sp-hybridised carbon atoms

(B) Only sp^2-hybridised carbon atoms

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

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

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

(A) Propanal (B) Propyl hydrogen sulphate

(C) Acetone (D) Propanol

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

(A) Alkaline permanganate solution

(B) Acidified permanganate solution

(C) Neutral permanganate solution

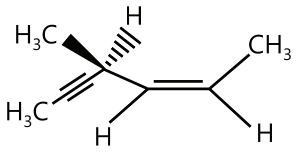
(D) Aqueous bromine solution

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

(A) Ethyne (B) Ethene

(C) Benzene (D) Ethane

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



(A) An optically active compound

(B) An optically inactive compound

(C) A racemic mixture

(D) A diastereomeric mixture

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

(A) H^+ in the first step

(B) Cl^+ in the first step

(C) OH^- in the first step

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

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

(A) Both are highly ionic

(B) One is oxidising and the other is reducing

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

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

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

(A) 1-Phenyl-2-butene

(B) 3-Phenyl-1-butene

(C) 2-Phenyl-1-butene

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

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

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

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

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

(A) Acetylene (B) Ethene

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

Q.13 In the reaction,

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

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

(A) Acetaldehyde (B) Acetylene

(C) Ethylene (D) Acetyl chloride

Q.14 In the following sequence of reactions, the alkene affords the compound 'B'

$$CH_3CH = CHCH_3 \xrightarrow{O_3} A \xrightarrow[Zn]{H_2O} B.$$

The compound B is ***(2008)***

(A) CH_3CH_2CHO (B) CH_3COCH_3

(C) $CH_3CH_2COCH_3$ (D) CH_3CHO

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

(A) $CH_3CH_2CH_2C \equiv CCH_2CH_2CH_3$

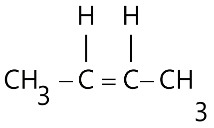
(B) $CH_3CH_2C \equiv CH$

(C) $CH_3CH \equiv CHCH_3$

(D) $CH_3CH_2C \equiv CCH_2CH_3$

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

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

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

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

(A) Propene (B) 2-methyl propene

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

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

(A) Propene (B) 1–butene

(C) 2–butene (D) Ethene

Assertion and Reason Type

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

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

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

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

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

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

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

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

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

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

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

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

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

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

JEE Advanced/Boards

Exercise 1

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

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

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

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

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

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

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

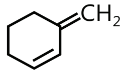
Q.8 An organic compound (A) $C_9H_{10}Br_2$ forms $C_9H_{11}OBr$ with caustic soda solution the later is resistant to further action of alkali. (B) on treating with H_2SO_4 converts into (C) with on ozonolysis gives ethanal and another compound (D). Identify (A) to (D) and give reactions.

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

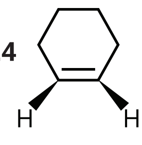
Q.10 An organic compound (A) of molecular formula C_5H_8 when treated with Na in liquid ammonia followed by reaction with n-propyl iodide yields (B) C_8H_{14}. (A) gives a ketone $C_5H_{10}O$ when treated with dil. H_2SO_4 and $HgSO_4$. (B) on oxidation with alkaline. $KMnO_4$ gives two isomeric acids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

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

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

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

Draw all possible carbocations and state which carbocation is more stable

Q.14 

$+CH_2{=}CH{-}CH{=}CH_2$

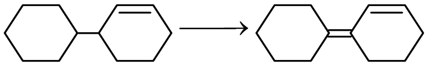
A Predict the structure of A and explain.

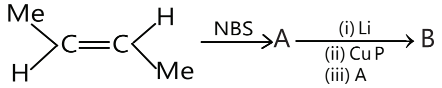
Q.15 A hydrocarbon (P) of the formula C_8H_{10}, on ozonolysis, gives compound Q ($C_4H_6O_2$) only. The compound (Q) can also be obtained from an alkyl bromide, R (C_3H_5Br) upon treatment with Mg in dry ether, followed by CO_2 and acidification. Identify (P), (Q) and (R) and give equations for the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

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

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

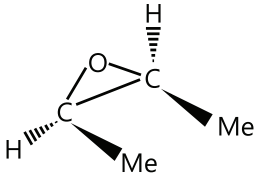
(i) 1, 3-Butadiene to racemic - 1, 4-dibromo -2, 3-dideutrobutene

(ii) 

(iii) 

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

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

(vi) 

to (S, S) – Glycol + R, S Glycol

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

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

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

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

Exercise 2

Single Correct Choice Type

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

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

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

(A) $BrCH_2\text{-}CH_2Br$ (B) $ClCH_2\text{-}CH_2Br$

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

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

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

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

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

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

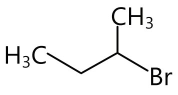
Q.4 The treatment of $CH_3C(CH_3)=CHCH_3$ with $NaIO_4$ or boiling $KMnO_4$, produces

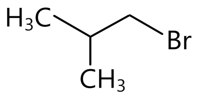
(A) $CH_3COCH_3 + CH_2O$ (B) $CH_3CH_2CHO + CH_3CHO$

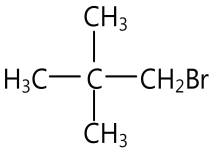
(C) $CH_3COCH_3 + CO_2$ (D) $CH_3COCH_3 + HCOOH$

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

(A) 

(B) 

(C) 

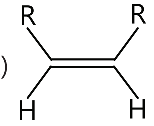
(D) 

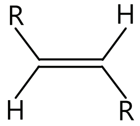
Q.6 Addition of halogen acid (HX) is least in

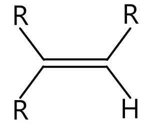
(A) $CH_2=CHCl$ (B) $CH_2=CH_2$

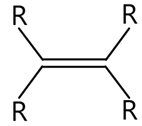
(C) $CH_3-CH=CH_2$ (D) $(CH_3)_2C=CH_2$

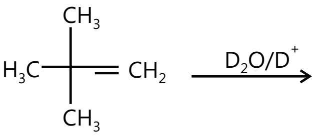
Q.7 Which of the following alkene will react fastest with H_2 under catalytic hydrogenation condition?

(A) 

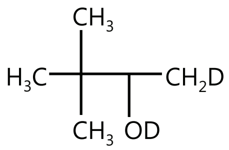
(B) 

(C) 

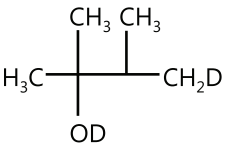
(D) 

Q.8 Products of the reaction. 

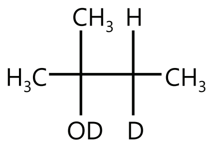
$H_3C-\overset{CH_3}{\underset{CH_3}{C}}=CH_2 \xrightarrow{D_2O/D^+}$

(A) 

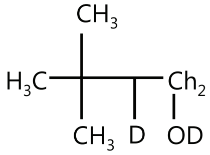
$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-\underset{OD}{CH}-CH_2D$

(B) 

$H_3C-\overset{CH_3}{\underset{OD}{C}}-\overset{CH_3}{CH}-CH_2D$

(C) 

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

(D) 

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

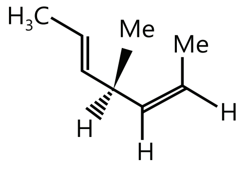
Q.9 The C–H bond length is longest in

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

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

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

Q.11 Hydrogenation of the compound



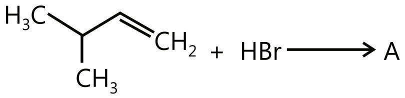
In the presence of poisoned palladium catalyst gives:

(A) An optically active compound

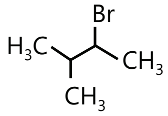
(B) An optically inactive compound

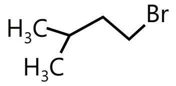
(C) A racemic mixture

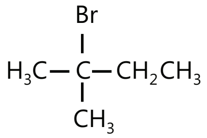
(D) A diastereomeric mixture

Q.12 

(Predominant). A is

(A) 

(B) 

(C) 

$H_3C-\underset{CH_3}{\overset{Br}{C}}-CH_2CH_3$

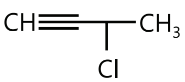
(D) Non of these

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

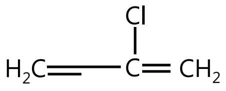
$CH\equiv CH \xrightarrow{Cu_2Cl_2+NH_4Cl} (A) \xrightarrow{HCl} (B)$

(A) CH_3CH_2Cl

(B) $CH_2=CH-CH_2CH_2Cl$

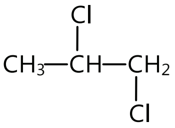
(C) 

$CH\equiv\underset{Cl}{C}-CH_3$

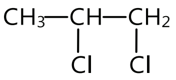
(D) 

$H_2C=\overset{Cl}{C}=CH_2$

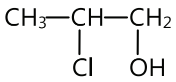
Q.14 $CH_3-CH=CH_2 \xrightarrow{Cl_2-H_2O} Z$. Z may be

(A) 

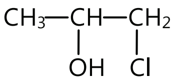
$CH_3-\overset{Cl}{CH}-\underset{Cl}{CH_2}$

(B) 

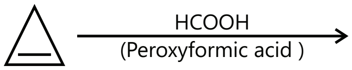
$CH_3-\underset{Cl}{CH}-\underset{Cl}{CH_2}$

(C) 

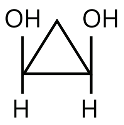
$CH_3-\underset{Cl}{CH}-\underset{OH}{CH_2}$

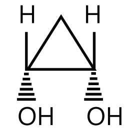
(D) 

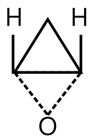
$CH_3-\underset{OH}{CH}-\underset{Cl}{CH_2}$

Q.15 

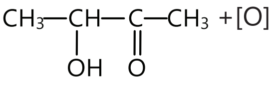
Z. Z may be

(A) 

(B) 

(C) 

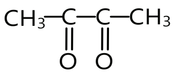
(D) Non of these

Q.16 

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

(A) CH_3-CHO

(B) CH_3-COOH

(C) 

$CH_3-\underset{O}{\underset{\|}{C}}-\underset{O}{\underset{\|}{C}}-CH_3$

(D) None of these

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

(A) Heptan-3-ol

(B) Heptan-4-ol

(C) Heptan-2-ol

(D) Heptan-1-ol

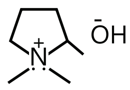
Q.18 Aqueous solution of potassium propanoate is electrolysed. Possible organic products are:

(A) n-Butane

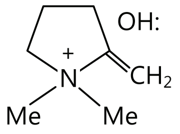
(B) $C_2H_5COOC_2H_5$

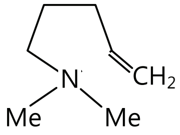
(C) CH_3-CH_3

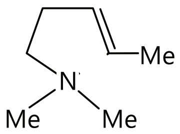
(D) $CH_2=CH_2$

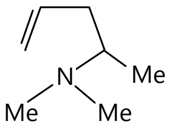
Q.19 

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

(A) 

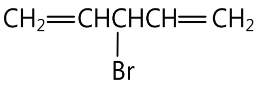
(B) 

(C) 

(D) 

Multiple Correct Choice Type

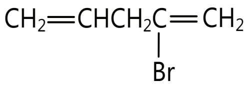
Q.20 $CH_2=CHCH_2CH=CH_2 \xrightarrow{NBS}$ A, A can be

(A) 

$CH_2=CH\underset{Br}{CH}CH=CH_2$

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

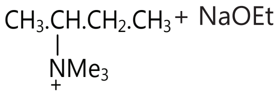
(C) $CH_2=CHCH_2CH=CHBr$

(D) 

$CH_2=CHCH_2\underset{Br}{C}=CH_2$

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

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

(B) 

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

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

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

Q.22 Select true statement(s):

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

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

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

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

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

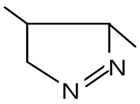
(A) Propanone (B) Ethanal

(C) Methanal (D) Only propanal

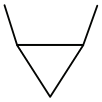
Q.24 $CH_3{-}CH{=}CH{-}CH_3 + CH_2N_2 \xrightarrow[\Delta]{} A$

A can be

(A)



(B)



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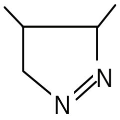

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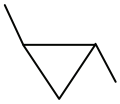


Q.25 Which of the following will give same product with HBr in presence or absence of peroxide.

(A) Cyclohexene

(B) 1-methylcyclohexene

(C) 1, 2-dimethylcyclohexene

(D) 1-butene

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

(A) $CH_3.(CH2)_3.CH{=}CH_2$ (B) $CH_3.CH{=}CH_2$

(C) $CF_3.CH{=}CH_2$ (D) $CF_3.CH{=}CH_2$

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

(A) $Al_4C_3 + H_2O \longrightarrow CH_4$

(B) $CaC_2 + H_2O \longrightarrow C_2H_2$

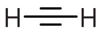
(C) $Mg2C_3 + H_2O \longrightarrow CH_3C{\equiv}CH$

(D) $Me_3C{-}H + KMnO_4 \longrightarrow Me_3C{-}OH$

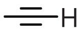
Q.28 $C \xrightarrow[H_2O_2/OH^-]{BH_3/THF} A \xrightarrow[H_2SO_4]{HgSO_4} B$

B and C are identical when A is –

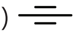
(A)



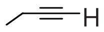
(B)



(C)



(D)



Assertion Reasoning Type

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

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

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

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

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

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

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

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

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

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

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

Q.32 Assertion: $CH_3{-}C{\equiv}C{-}CH_3$ is more reactive than $CH{\equiv}CH$ towards HCl.

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

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

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

Comprehension Type (34-36)

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

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

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

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

$CH_3CH_2Na + CH_3CH_2Br \rightarrow$

$CH_3CH_2CH_2CH_3 + CH_2=CH_2 + CH_3–CH_3$

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

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

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

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

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

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

Q.36 The other products which could be formed

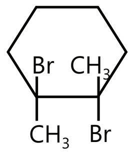
(A) $CH_2=CH_2$ (B) $CH_3CH_2CH_3$

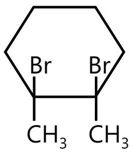
(C) CH_4 (D) $CH_3CH_2CH_2–CH_2–CH_3$

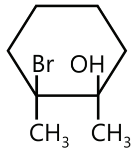
Comprehension Type (36-38)

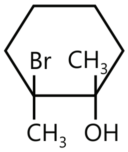
The functional group in alkenes is C–C double bond which is made of one σ-bond and one π-bond. The weaker π-bond would tend to attract the electrophile and convert itself to a stable carbonium ion which reacts with nucleophile remainder to form the addition product. The addition reaction of alkenes is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

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

(A)


(B)


(C)


(D)


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

Product of the above reaction is

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

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

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

(A) Racemic mixture (B) Meso form

(C) Optically pure (D) No specific stereochemistry

Match the Columns

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

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

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

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

Q.42 Match the column

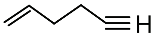
Column I	**Column II**
(A) $RCOONa \xrightarrow{\text{Electrolysis}} R–R$	(p) Corey-House reaction
(B) $R–CH_2–COOH \xrightarrow[\Delta]{\text{Soda Lime}} R–CH_3$	(q) Kolbe electrolysis
(C) $RCOOH \xrightarrow[\text{(ii) } Cl_2/\Delta]{\text{(i) } AgNO_3} R–Cl$	(r) Oakwood degradation

Previous Years' Questions

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

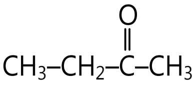
(A) $(CH_3)_3CD$ (B) $(CH_3)_3OD$

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

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

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

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

(A) 
$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-CH_3$
(B) $CH_3-CH_2-CH_2-CHO$

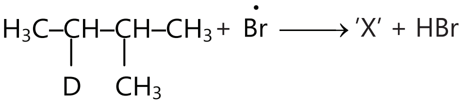
(C) $CH_3-CH_2-CHO + HCHO$

Q.4 Identify a reagent from the following list which can easily distinguish between 1-butyne and 2-butyne. ***(2002)***

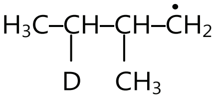
(A) Bromine, CCl_4 (B) H_2, Lindlar catalyst

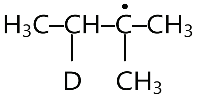
(C) Dilute H_2SO_4, $HgSO_4$ (D) Ammoniacal $CuCl_2$ solution

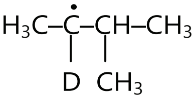
Q.5 Consider the following reaction

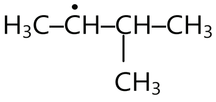

$H_3C-\underset{D}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-CH_3 + \dot{Br} \longrightarrow$ 'X' + HBr

Identify the structure of the major product X ***(2002)***

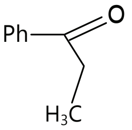
(A) 
$H_3C-\underset{D}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{CH}}-\dot{C}H_2$

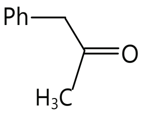
(B) 
$H_3C-\underset{D}{\underset{|}{CH}}-\underset{CH_3}{\underset{|}{\dot{C}}}-CH_3$

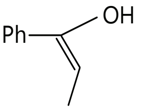
(C) 
$H_3C-\underset{D}{\underset{|}{\dot{C}}}-\underset{CH_3}{\underset{|}{CH}}-CH_3$

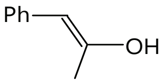
(D) 
$H_3C-\dot{C}H-\underset{CH_3}{\underset{|}{CH}}-CH_3$

Q.6 $Ph-C\equiv C-CH_3 \xrightarrow[H^+]{Hg^{2+}} A$; A is ***(2003)***

(A) 

(B) 

(C) 

(D) 

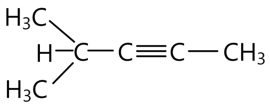
Comprehension Based Questions (Q.7 & 8)

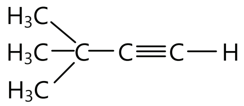
An acyclic hydrocarbon P, having molecular formula C_6H_{10}, gave acetone as the only organic product through the following sequence of reactions, in which Q is an intermediate organic compound.

Q.7 The structure of compound P is

(A) $CH_3CH_2CH_2CH_2-C\equiv C-H$

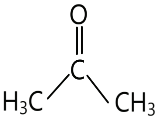
(B) $H_3CH_2C-C\equiv C-CH_2CH_3$

(C) 

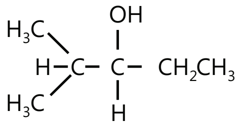
(D) 

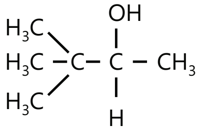
Q.8 The structure of the compound Q is

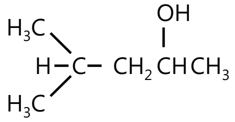
$$\underset{(C_6H_{10})}{P} \xrightarrow[\text{(ii) NaBH}_4\text{/ethanol (iii) dil. acid}]{\text{(i) dil. }H_2SO_4/HgSO_4} Q \xrightarrow[\text{(ii) }O_3\text{/ethanol (iii) Zn/}H_2O]{\text{(i) dil. }H_2SO_4\text{ (catalytic amount) }(-H_2O)} 2$$



(2011)

(A) 

(B) 

(C) 

(D) $CH_3CH_2CH_2CH(OH)CH_2CH_3$

Q.9 Give reasons for the following in one or two sentences: ***(1983)***

(i) Methane does not react with chlorine in dark.

(ii) Propene reacts with HBr to give isopropyl bromide but does not give n-propyl bromide.

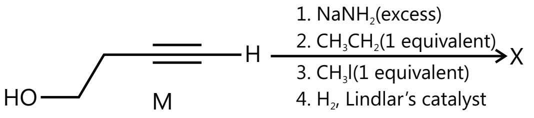
Q.10 Following statements are true, only under some specific conditions. Write the condition for each sub question in not more than two sentences:

(i) 2-methyl propene can be converted into isobutyl bromide by hydrogen bromide

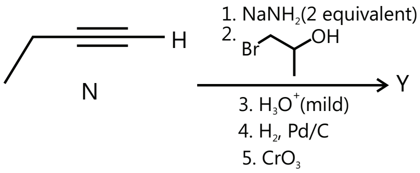
(ii) Ethyne and its derivatives will give white precipitate with ammoniacal silver nitrate solution. ***(1984)***

Paragraph for Questions 11 and 12

Schemes 1 and 2 describe sequential transformation of alkynes M and N. Consider only the major products formed in each step for both schemes.

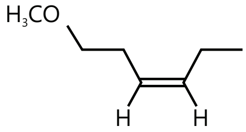


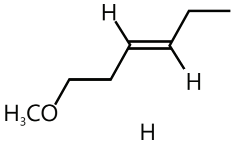
Scheme-1

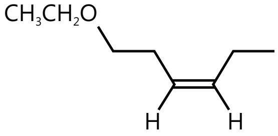


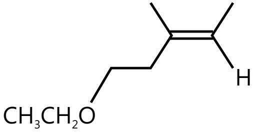
Scheme-2

Q.11 The product X is ***(2014)***

(A)


(B)


(C)


(D)


Q.12 The correct statement with respect to product Y is ***(2014)***

(A) It gives a positive Tollens test and is a functional isomer of X.

(B) It gives a positive Tollens test and is a geometrical isomer of X.

(C) It gives a positive iodoform test and is a functional isomer of X.

(D) It gives a positive iodoform test and is a geometrical isomer of X.

PlancEssential Questions

JEE Main/Boards

Exercise 1

Q.3 Q.8 Q.13 Q.15 (b) Q.20 (a)

Exercise 2

Q.1 Q.7 Q.9 Q.14 Q.28

Previous Years' Questions

Q.10 Q.13

JEE Advanced/Boards

Exercise 1

Q.1 Q.8 Q.13 Q.18 Q.21

Exercise 2

Q.5 Q.9 Q.14 Q.22 Q.26

Previous Years' Questions

Q.6 Q.8

Answer Key

JEE Main/Boards

Exercise 2

Single Correct Choice Type

Q.1 B **Q.2** C **Q.3** A **Q.4** D **Q.5** C **Q. 6** C
Q.7 B **Q.8** D **Q. 9** D **Q.10** B **Q.11** A

Previous Years' Questions

Q.1 B **Q.2**.D **Q.3** D **Q.4** C **Q.5** A **Q.6** A **Q 7** B
Q.8 B **Q.9** C **Q.10** A **Q.11** A **Q.12** D **Q.13** C **Q.14** D
Q.15 B **Q.16** D **Q.17** C **Q.18** C **Q.19** A **Q. 20** B **Q.21** A
Q.22 B

JEE Advanced/Boards

Exercise 2

Single Correct Choice Type

Q.1 C **Q.2** C **Q.3** A **Q.4** B **Q.5** B,C **Q.6** B **Q.7** D
Q.8 B **Q.9** C **Q.10** C **Q.11** B **Q.12** C **Q.13** D **Q.14** D
Q.15 C **Q.16** A **Q.17** B **Q.18** A **Q.19** B

Multiple Correct Choice Type

Q.20 A,B **Q.21** B,C **Q.22** A,C,D **Q.23** A,C **Q.24** A,B,C,D **Q.25** A,C **Q.26** A,B,D
Q.27 A,B,C,D **Q.28** A,C

Assertion Reasoning Type

Q.29 B **Q.30** A **Q.31** A **Q.32** A **Q.33** B

Comprehension Type

Q.34 A **Q.35** A **Q.36** A **Q.37** D **Q.38** C **Q.39** B

Match the Columns

Q.40 A → q; B → p; C → s; D → r **Q.41** A → p; B → r; C → s; D → q **Q.42** A → q; B → r; C → s; D → p

Previous Years Questions

Q.1 A **Q.2** D **Q.3** A **Q.4** D **Q.5** B **Q.6** A **Q.7** D
Q.8 B **Q.11** A **Q.12** C

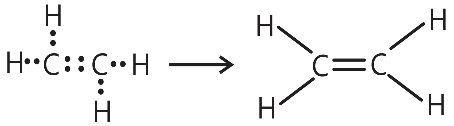
Solutions

JEE Main/Boards

Exercise 1

Sol 1: Alkenes are substances which contain less hydrogen than the maximum quantity of hydrogen which a carbon atom can have

Structure:-



Preparation of Alkenes:-

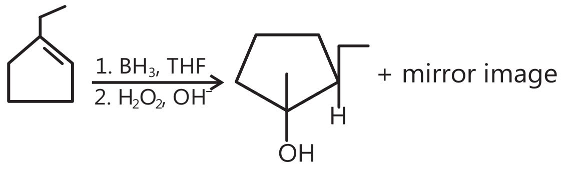
(1) Dehydrohalogenation of Alkyl halide

(2) Dehyration of Alcohols

(3) Dehalogenation of vicinal dihalides

(4) Dehalogenation of geminal dihalide

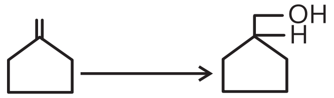
Sol 2: (A)



trans additon

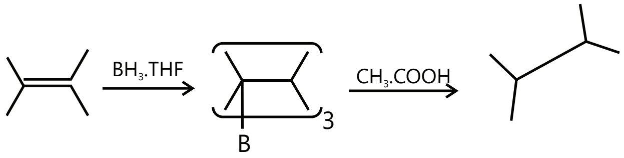
∴ Recemic mixture

(B)

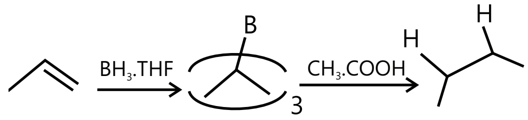


Antimarkov's addition

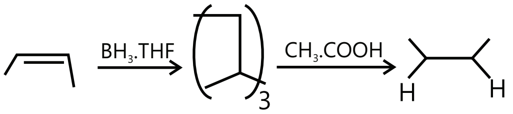
Sol 3: (A)



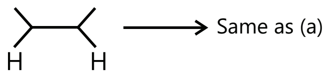
(B)



(C)

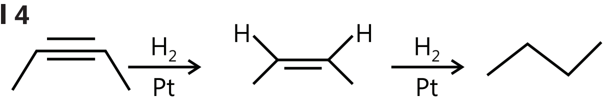


(D)

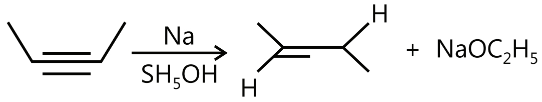


Sol 4

(A)



(B)



Sol
5: Physical properties: Refer theory pg.26

Chemical properties: Refer theory pg.29

Sol 6: Alkynes:-

In the family of hydrocarbon alkynes are the most unsaturated one with C≡C bond and are highly reactive.

Preparation:-

(1) Dehydrohalogenation

(2) From tetradehalogenation

(3) From haloform

(4) Kolbe's electrolytic decarboxylation

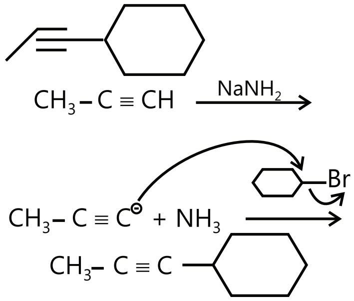
(5) Berthlot's reaction

Sol 7: Physical properties: Refer theory pg.42

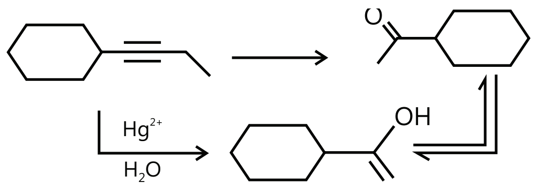
Chemical properties: Refer theory pg.44

Sol 8:

(A)

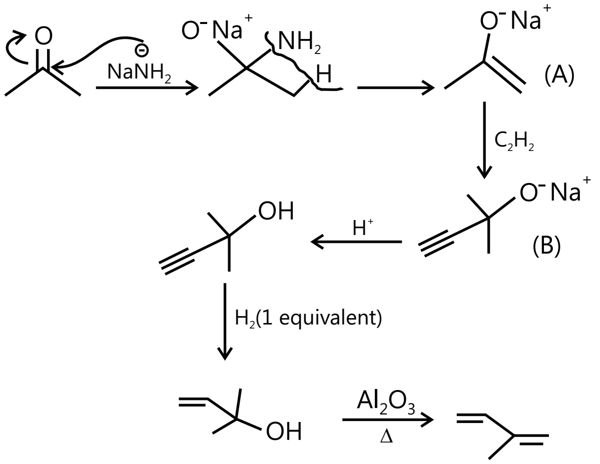


(B)

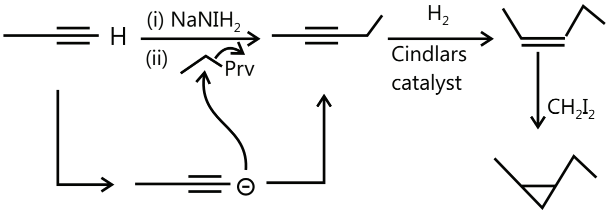


Sol 9:

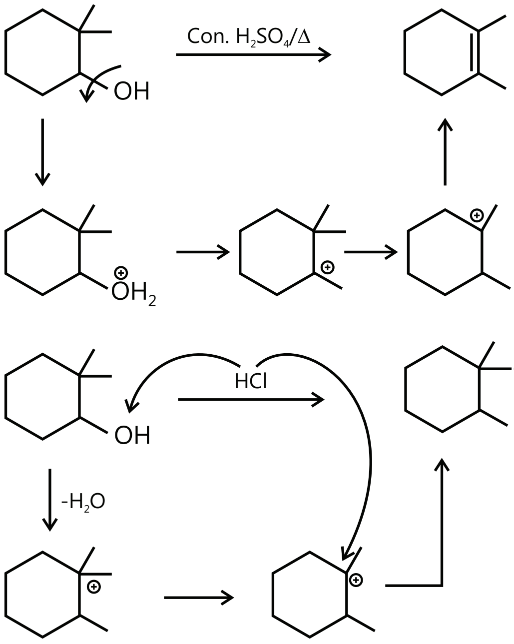
(A)



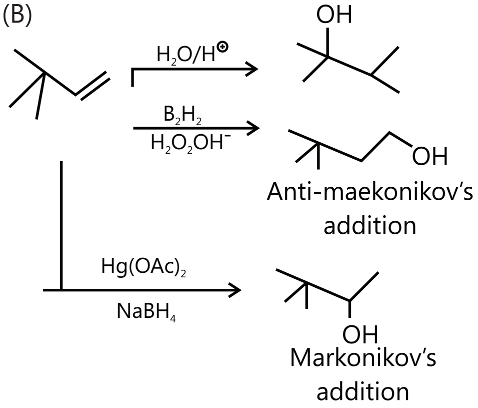
(B)



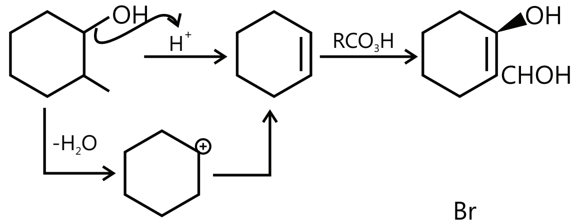
Sol 10: (A)



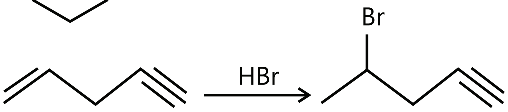
(B)



(C)

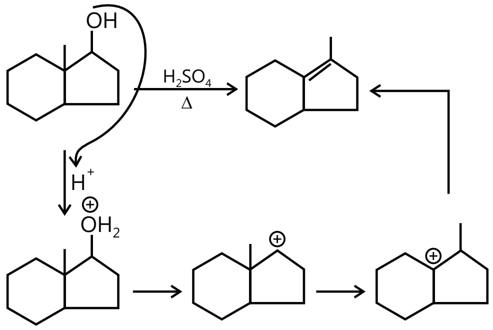


Sol 11: (A)

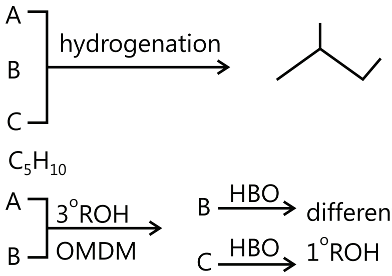


Doubled bonds are more electron donating than triple bond because of difference in electronegativity and because of which first addition will takes place on double bond rather than triple bond.

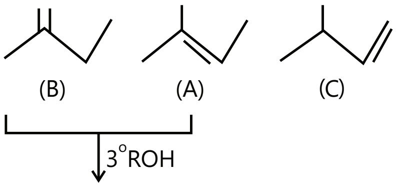
(B)

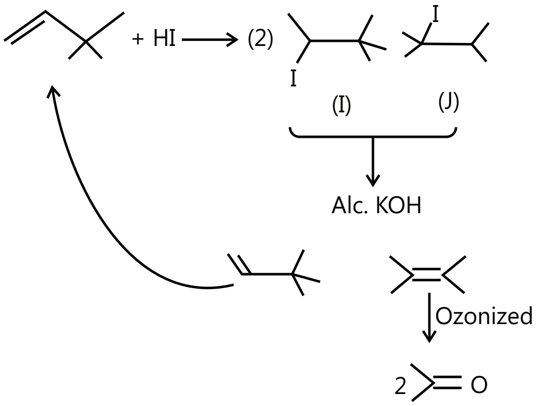


Sol 12:

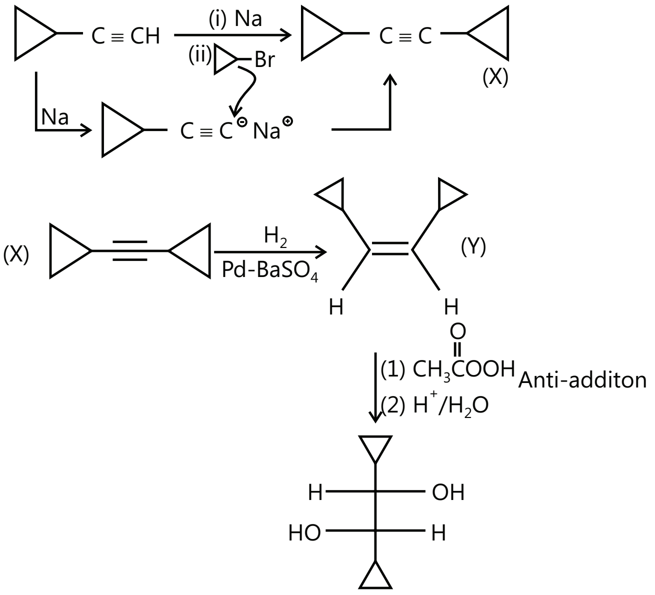


Sol 13:





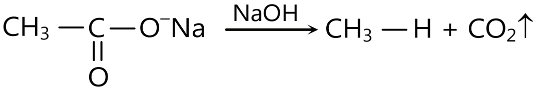
Sol 14



Exercise 2

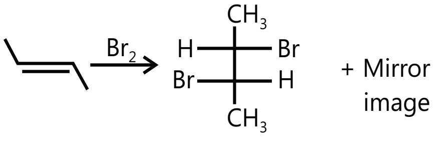
Single Correct Choice Type

Sol 1: (B) Dicarboxylation of acid ion



$$CH_3-\underset{\underset{O}{\|}}{C}-O^{-}Na \xrightarrow{NaOH} CH_3-H + CO_2\uparrow$$

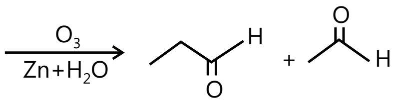
Sol 2: (C)

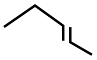


Recemic mixture

Sol 3: (A) Definition of conformers.

Sol 4: (D) Olefin

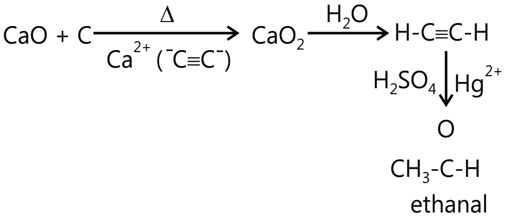




pent-2-ene

Sol 5: (C) C ≡ C is strongest because it is shortest and more orbitals are overlapping.

Sol 6: (C)



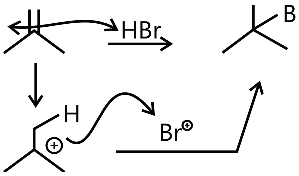
$$CaO + C \xrightarrow[Ca^{2+}\,(^{-}C\equiv C^{-})]{\Delta} CaO_2 \xrightarrow{H_2O} H\text{-}C\equiv C\text{-}H \xrightarrow{H_2SO_4,\ Hg^{2+}} CH_3\text{-}\overset{\overset{O}{}}{C}\text{-}H$$

ethanal

Sol 7: (B) $C_2H_3MgI \xrightarrow{H_2O} C_2H_6$

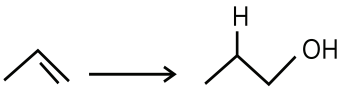
Abstracts acidic hydrogen.

Sol 8: (D)



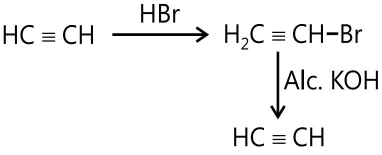
only product

Sol 9: (D)



Anti Markonikov's addition

Sol 10: (B)



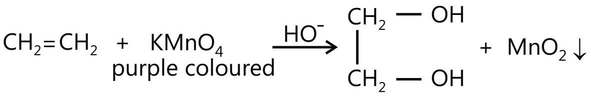
$$HC\equiv CH \xrightarrow{HBr} H_2C\equiv CH-Br \xrightarrow{Alc.\ KOH} HC\equiv CH$$

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

Previous Years' Questions

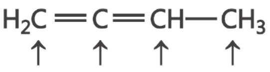
Sol 1: (B) Methane is produced due to the decay of vegetables or animal organisms present in swamps and marsh, by the action of bacteria. Due to this method of formation, methane is also known as marsh gas.

Sol 2: (D) Unsaturated compounds which contain C=C or C≡C, decolourises the purple colour of alkaline $KMnO_4$ solution.



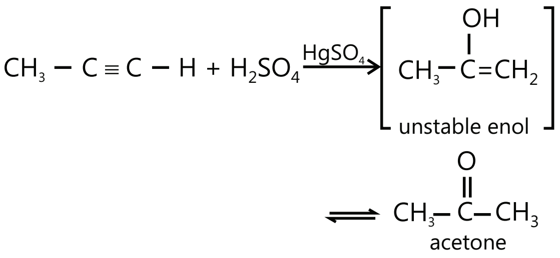
$$\underset{}{CH_2{=}CH_2} + \underset{\text{purple coloured}}{KMnO_4} \xrightarrow{HO^{-}} \begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array} + MnO_2\downarrow$$

Sol 3: (D) Structural formula of 1, 2-butadiene is:



$$\underset{\uparrow}{H_2C}=\underset{\uparrow}{C}=\underset{\uparrow}{CH}-\underset{\uparrow}{CH_3}$$

Sol 4: (C) Alkynes undergo Markownikoff's addition of water in presence of $H_2SO_4/HgSO_4$:



$$CH_3-C\equiv C-H + H_2SO_4 \xrightarrow{HgSO_4} \left[CH_3-\overset{OH}{\overset{|}{C}}=CH_2\right]_{\text{unstable enol}} \rightleftharpoons CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

acetone

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

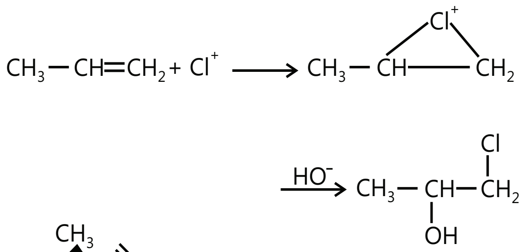
Sol 6: (A) Terminal alkynes are slightly acidic, forms salt with very strong base like Na, $NaNH_2$ etc.

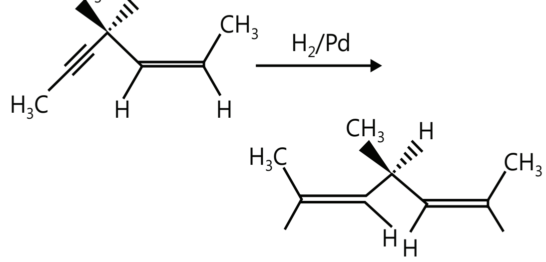
$$\underset{\text{ethyne}}{H-C\equiv C-H} + Na \longrightarrow H-C\equiv C^{-}Na^{+} + \frac{1}{2}H_2\uparrow$$

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

Sol 8: (B)

$HOCl \longrightarrow HO^{-} + Cl^{+}$





meso-compound
(optically inactive)

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

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

$HBr + HO^{\bullet} \rightarrow H_2O + Br^{\bullet}$

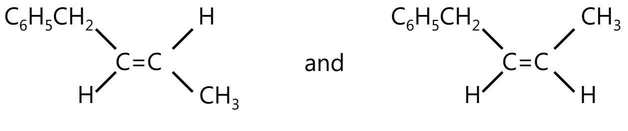
Propagation

$$\begin{cases} CH_3-CH=CH_2+Br^{\bullet} \rightarrow CH_3-\dot{C}H-CH_2Br \ \ \Delta H<0 \\ CH_3-\dot{C}H-CH_2Br+HBr \rightarrow CH_3-CH_2-CH_2Br+Br^{\bullet} \ \ \Delta H<0 \end{cases}$$

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

Sol 10: (A)

$C_6H_5CH_2$=$CHCH_3$ has two geometrical isomers



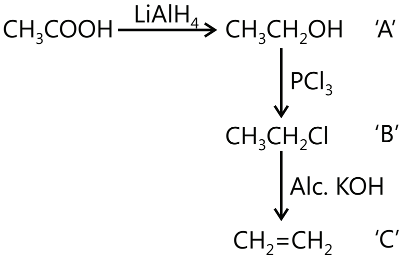
Trans

Cis

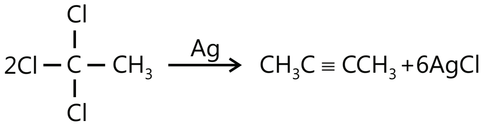
So it is 1-Phenyl-2-butene

Sol.11: (D) $CH_3-CH^{+}-CH_2-Cl$

Sol 12: (A)



$$\begin{array}{lll} CH_3COOH \xrightarrow{LiAlH_4} & CH_3CH_2OH & \text{'A'} \\ & \downarrow PCl_3 & \\ & CH_3CH_2Cl & \text{'B'} \\ & \downarrow \text{Alc. KOH} & \\ & CH_2=CH_2 & \text{'C'} \end{array}$$

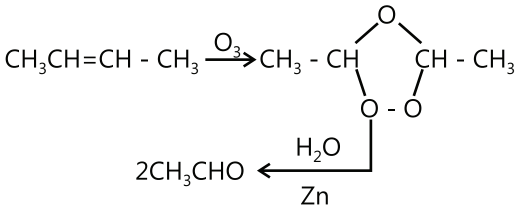


$$2Cl-\underset{Cl}{\underset{|}{\overset{Cl}{\overset{|}{C}}}}-CH_3 \xrightarrow{Ag} CH_3C\equiv CCH_3+6AgCl$$

1, 1, 1- Trichloroethane

Sol 13: (C)

Sol 14: (D)



Sol 15: (B)

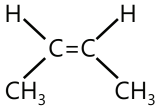
$$CH_3CH_2CH_2\equiv CH \xrightarrow[\Delta]{Na/Liq.NH_3} CH_3CH_2C\equiv \overset{\ominus}{C}Na^{\oplus}$$

It is a terminal alkyne, having acidic hydrogen.

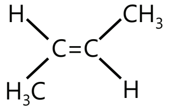
Note: Solve it as a case of terminal alkynes, otherwise all alkynes react with Na in liq. NH_3

Sol 16: (D) $CH_3-MgX+CH_3-C\equiv C-H\rightarrow CH_4$

Sol 17: (C)



Cis



Trans

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

$$CH_3-CH=CH-CH_3\xrightarrow[Zn/H_2O]{O_3}2.CH_3CHO$$

Molar mass of CH_3CHO is 44 u.

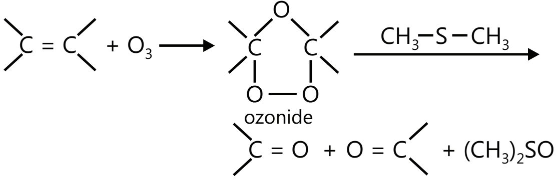
Sol 19: (A)

$$CH_3-CH_2-CH=CH_2+Br^{\bullet}\rightarrow CH_3-CH_2-\underset{\text{a secondary radical}}{\dot{C}H}-CH_2Br$$

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

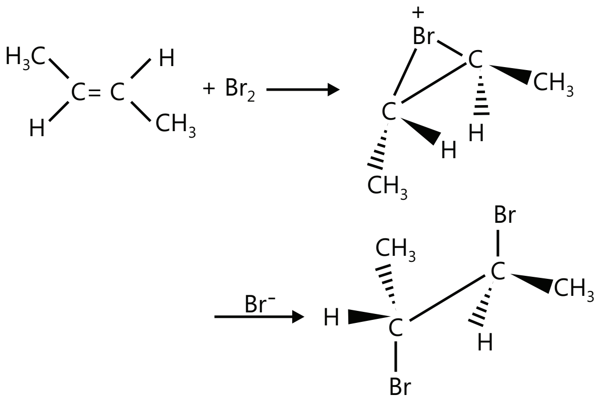
Sol 20: (B) Both Statement I and Statement II are correct and Statement II is correct explanation of Statement I.

Sol 21: (A)



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

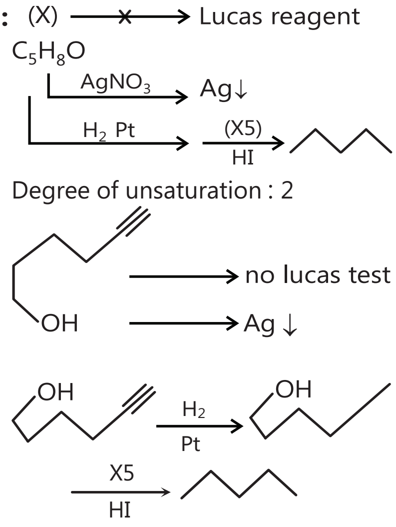
Sol 22: (B) Statement I is correct. Statement II is also correct. Meso form of the product is due to anti addition of Br on cyclic bromonium ion intermediate, hence Statement II is not correct explanation of Statement II.



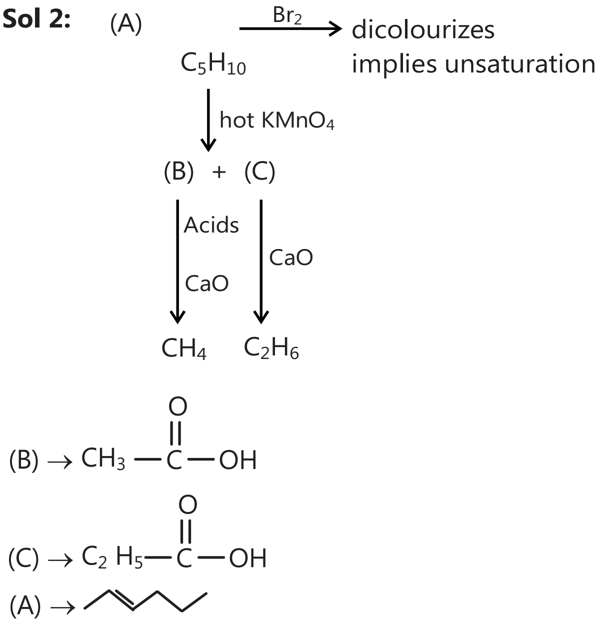
JEE Advanced/Boards

Exercise 1

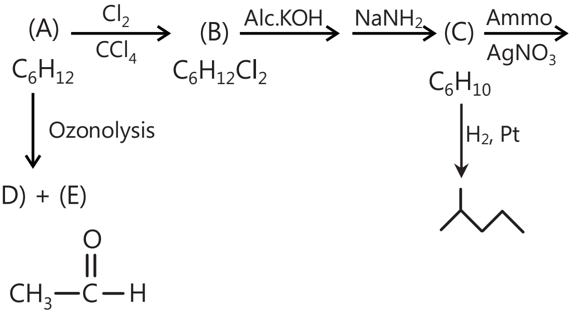
Sol 1:



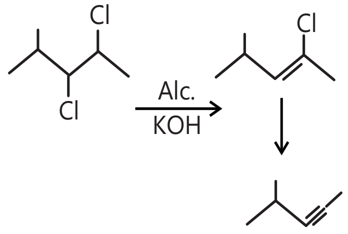
Sol 2:



Sol 3:

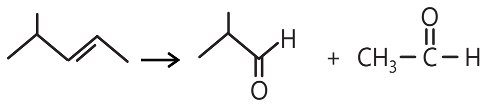


(B)

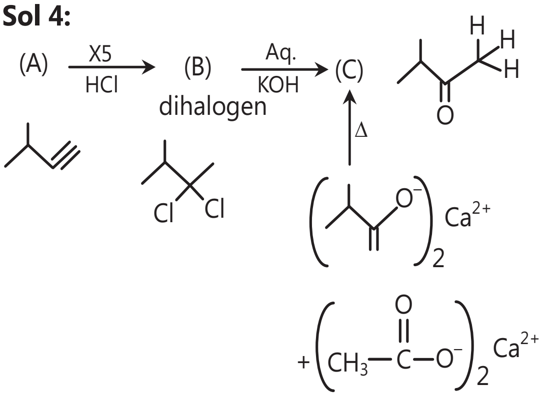


(C) terminal alkyne

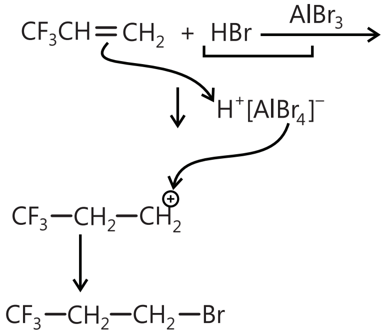
(D) + (E)



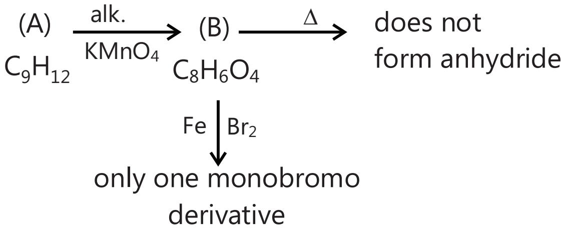
Sol 4:



Sol 5:



Sol 6:



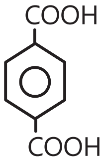
Degree of unsaturation of (A) = 4

So it should contain benzene ring

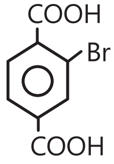
In the compound (B) both –COOH should be at para position to give only one bromination product

(A)

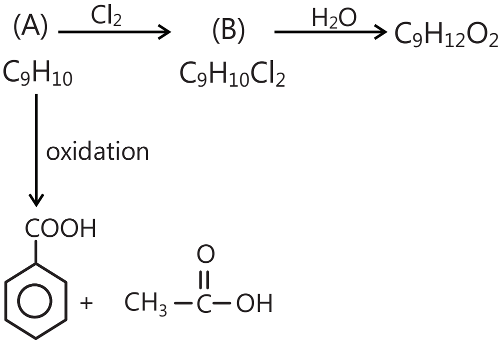
(B)



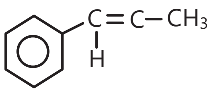
(C)



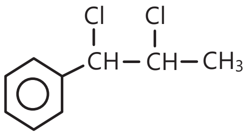
Sol 7:



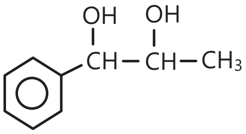
(A)



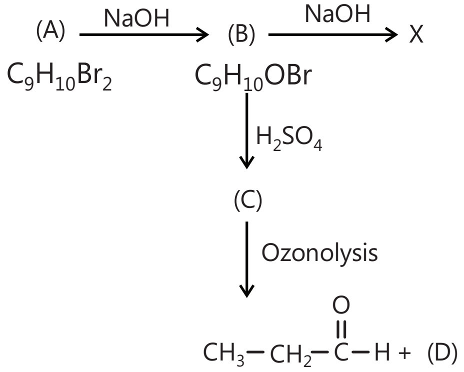
(B)



(C)

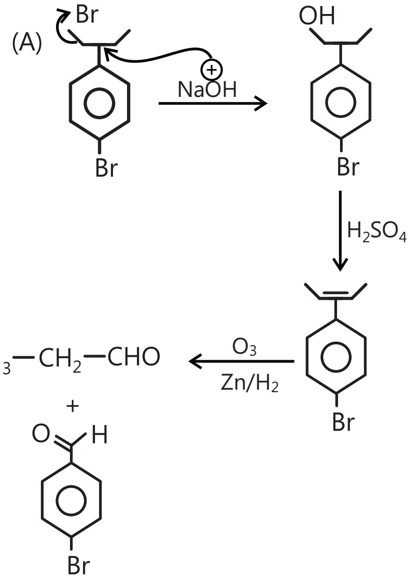


Sol 8:

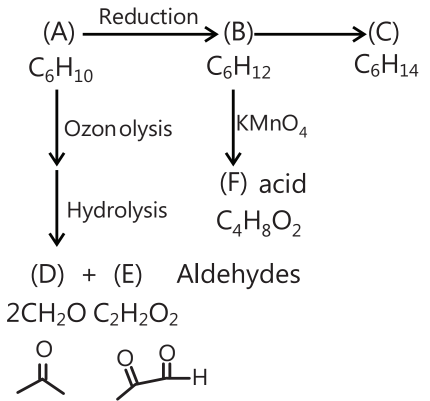


Since only one –Br is hydrolysed

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

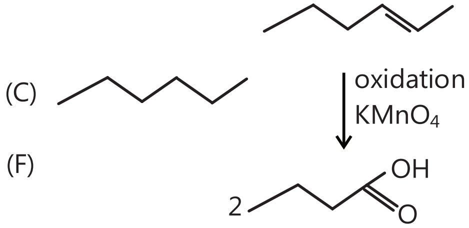


Sol 9:

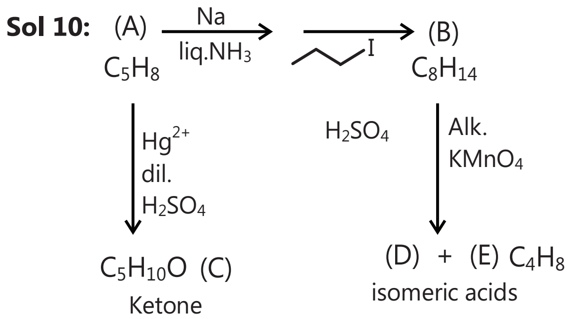


So (A) is

(B) is 1-4 addition



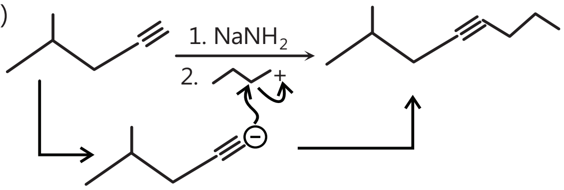
Sol 10:



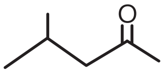
Degree of unsaturation of (A) = 2

∴ Alkyne. Terminal alkyne because formation of (B) and branched because formation of ketone (C)

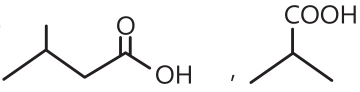
(A)



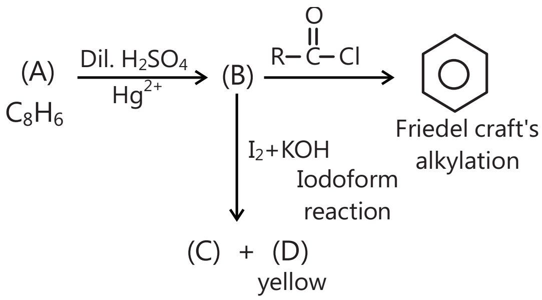
(C)



(D),(E)

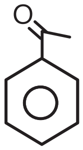


Sol 11:

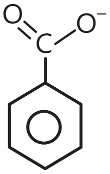


For reaction (B) → (C) it is iodoform so (D) → CHI_3 yellow precipitate and (B) should have acetyl ketone.

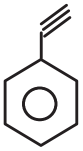
(B)



(C)

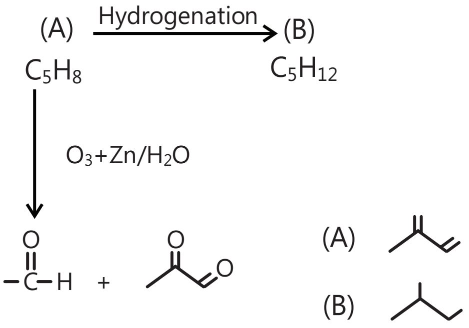


(A)

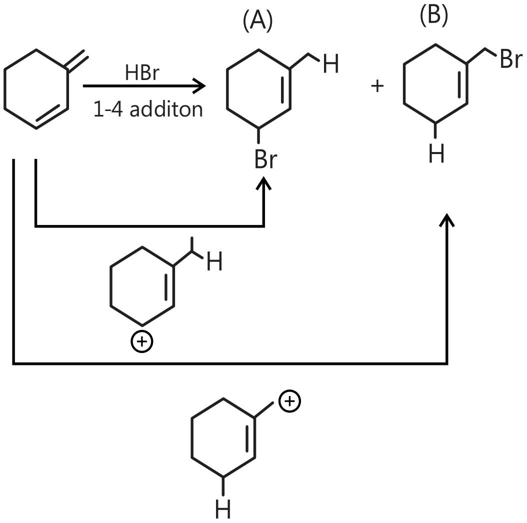


OMDM for alkyne give ketone

Sol 12:



Sol 13:

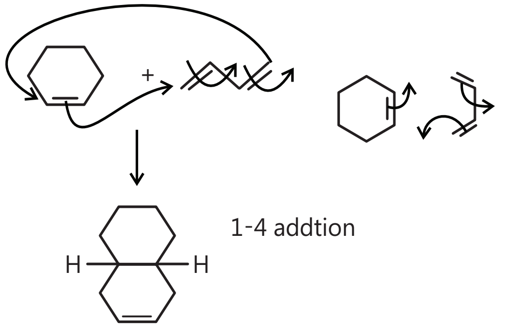


Compound (A) carbocation is more stable resonance is in both the compounds but

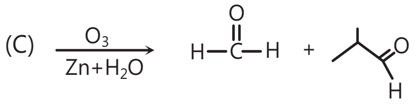
(A) have 3 α – H

(B) have 0 α – H

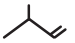
Sol 14:



1-4 addtion



∴ (C) $\longrightarrow$



$(B) \xrightarrow[KOH]{Alc.} (D) + (E)$

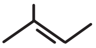
(C), (D), (E)

$\downarrow$ Catalytic hydrogenation

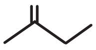
C_5H_{12}

∴ (D) is isomer of (C)

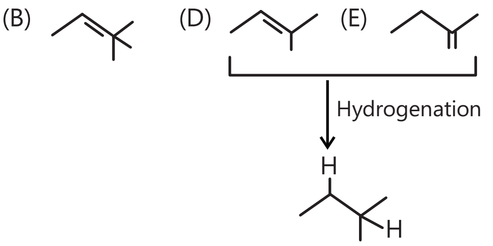
∴ (D) $\longrightarrow$



not



because will not get by isomeric alkyl bromide of (B)

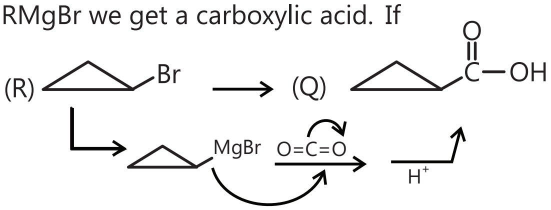


Sol 15:

$$\underset{C_8H_{10}}{(P)} \xrightarrow[Zn/H_2O]{O_3} \underset{C_4H_6O_2 \text{ only}}{(Q)} \xleftarrow[2.\ CO_2,H^+]{1.\ Mg/Et_2} C_3H_5Br$$

symmetric compound

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



∴ (P)

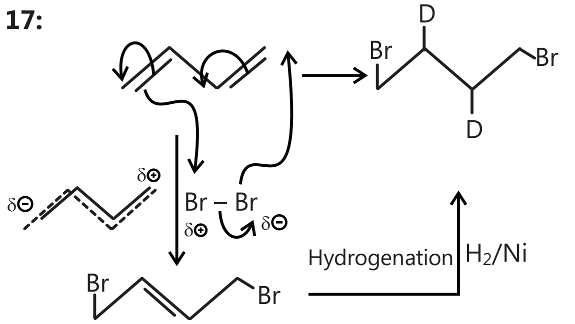
to satisfy the degree of unsaturation of (P) alkyl group must be cyclic.

Sol 16: (A), (B) $C_5H_{11}Br$

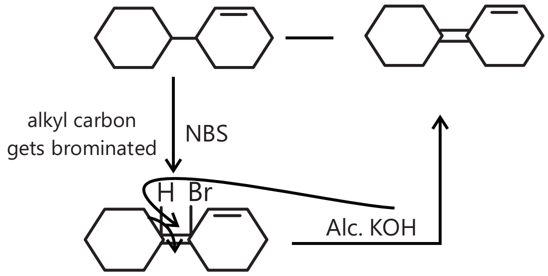
isomeric alkyl bromides (A) $\xrightarrow[KOH]{alc.}$ (C) + (D) isomers C_5H_{10}

Sol 17:

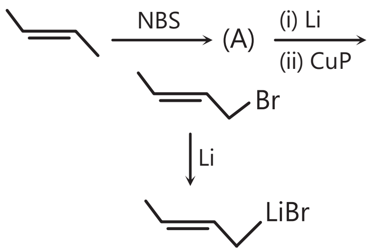
(i)



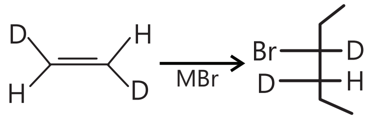
(ii)



(iii)

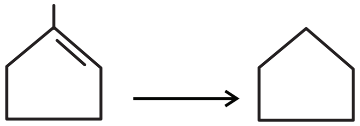


(iv)

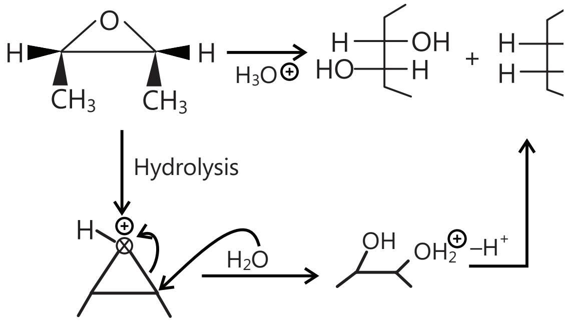


Anti-addition

(v)



(vi)



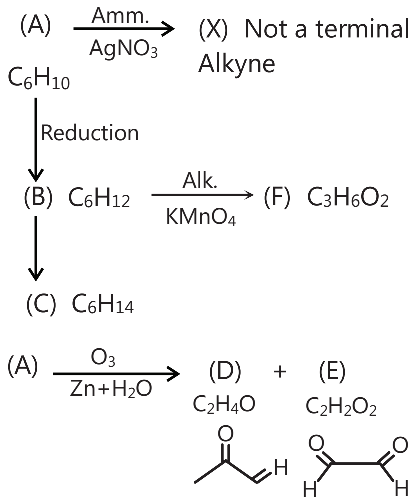
Sol 18: (A) $\xrightarrow[h\nu]{Cl_2} C_5H_9Cl$

C = 85.7%; h = 14.3%

total molecular weight = 70

$C_5H_{10} \longrightarrow$ 

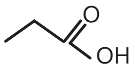
Sol 19:



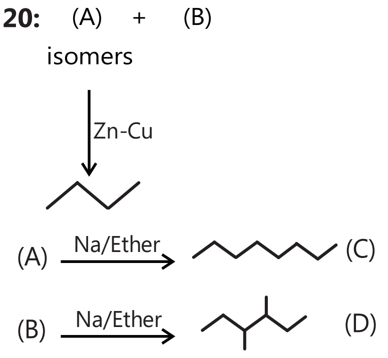
(A) 

(B)  1-4 addition

(C) 

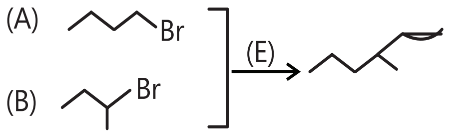
(F) 

Sol 20:



But mixture gives (E)

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



Exercise 2

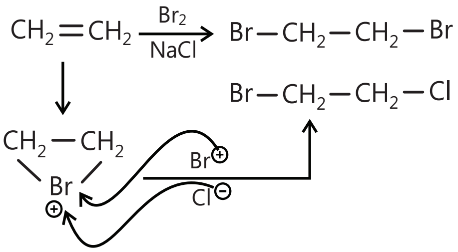
Single Correct Choice Type

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

∴ 3 moles of CH_4

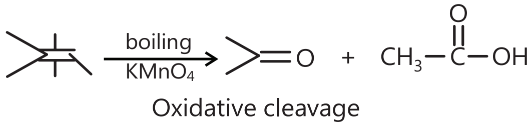
∴ 3 active α - H hydrogen.

Sol 2: (C)

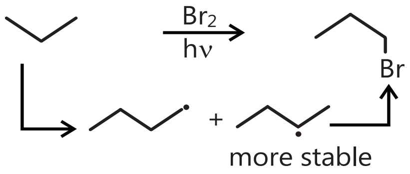


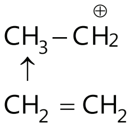
Sol 3: (A) $\underset{(X5)}{C_2H_6} + Cl_2 \xrightarrow{h\nu} C_2H_5Cl$

Sol 4: (B)



Sol 5: (B,C)

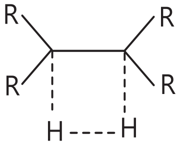


Sol 6: (B) Carbon is least stable in 

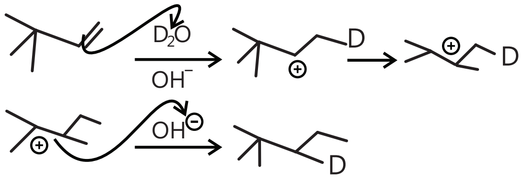
$$\begin{array}{c} CH_3-\overset{\oplus}{C}H_2 \\ \uparrow \\ CH_2=CH_2 \end{array}$$

∴ Addition will be least $CH_2=CH_2$

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

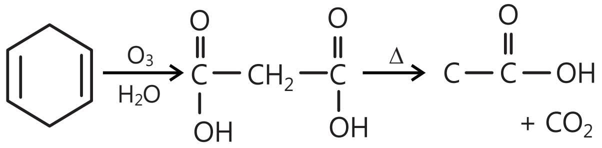


Sol 8: (B)

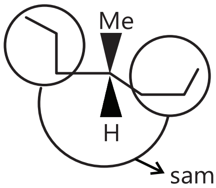


Sol 9: (C) C-C-H is sp^3 hybridised, hence 's' character is less, So bond length in C-H is longest

Sol 10: (C)

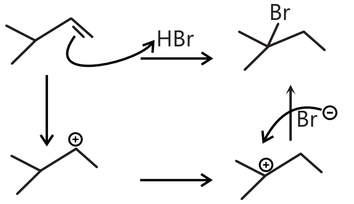


Sol 11: (B) Hydrogenate product

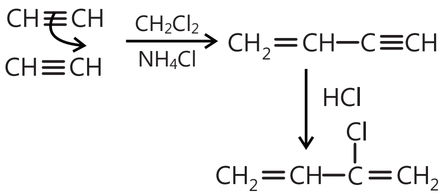


∴ optically inactive compound.

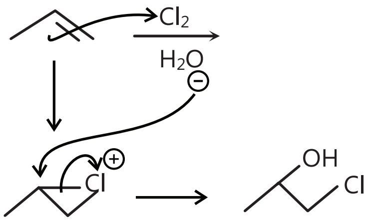
Sol 12: (C)



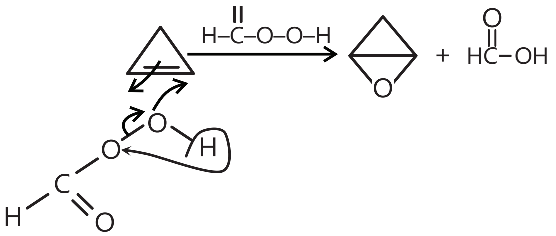
Sol 13: (D)



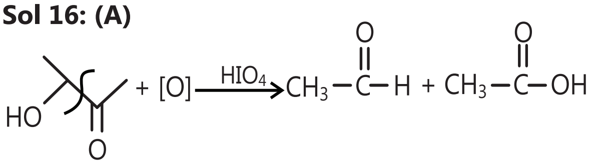
Sol 14: (D)



Sol 15: (C)



Sol 16: (A)

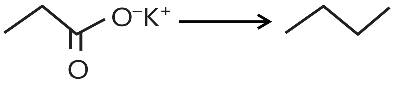


Sol 17: (B)

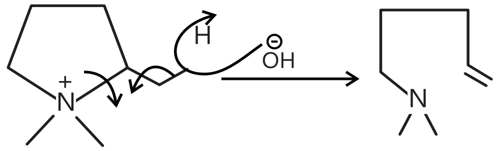
$$\underset{\text{(Heptan–4–ol)}}{CH_3CH_2CH_2CH(OH)CH_2CH_2CH_3} \xrightarrow[-H_2O]{\text{Dehydration}}$$

$$\underset{\text{(Hept–3–ene)}}{CH_3CH_2CH = CHCH_2CH_2CH_3}$$

Sol 18: (A)

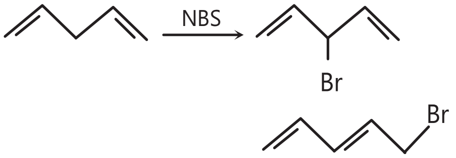


Sol 19: (B)



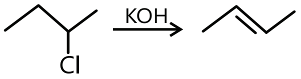
Multiple Correct Choice Type

Sol 20: (A,B)

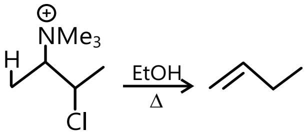


Sol 21: (B,C)

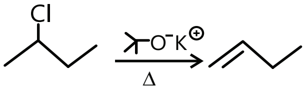
(A)



(B)

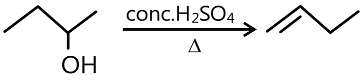


(C)



less hindered –H will get abstracted

(D)



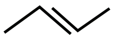
Sol 22: (A,C,D) but the reaction will be reversible since C–I is very week.

(B) × (C) ✓ (D) more stable system

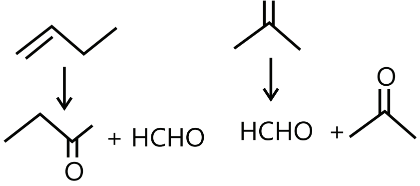
Sol 23: (A,C)

Alkane $\xrightarrow{\text{ozonolysis}}$ CH_3-CHO

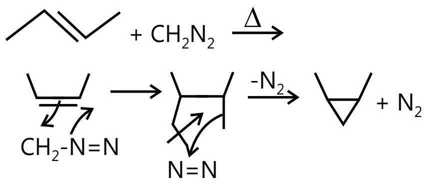
Alkene :



Isomers :

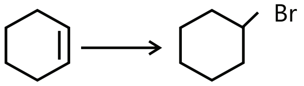


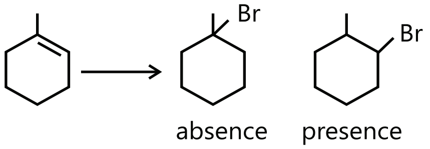
Sol 24: (A,B,C,D)

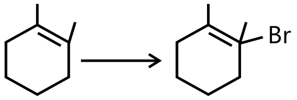


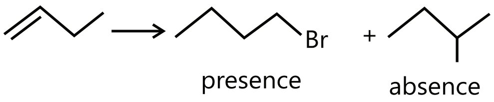
Same for trans form.

Sol 25: (A,C)

(A)


(B)


(C)


(D)


Sol 26: (A,B,D)

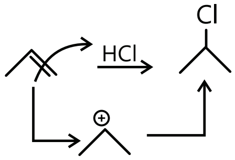
(A) $CF_3-CH_2-CH_2-CH_2-CH=CH_2$

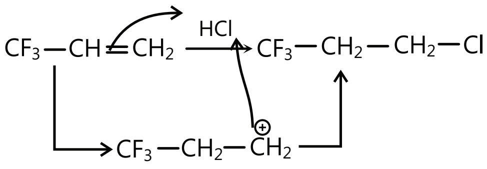
$$\downarrow HCl$$

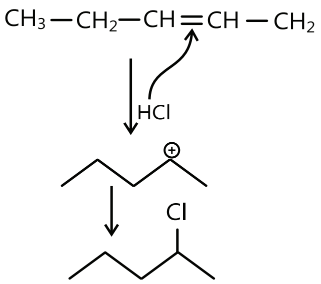
$$CF_3-(CH_2)_3-\overset{\oplus}{C}H_2-CH_3$$

$$\downarrow$$

$$CF_3-(CH_2)_3-\underset{\displaystyle Cl}{\underset{|}{CH_2}}-CH_3$$

(B)


(C)


(D)


Sol 27: (A,B,C,D)

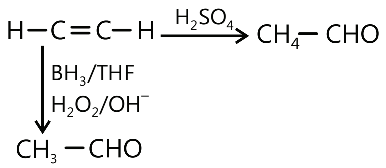
(A) $Al_4C_3 \xrightarrow{H_2O} Al(OH)_3 + 3CH_4 4Al^{3+} + 3C^{4-}$

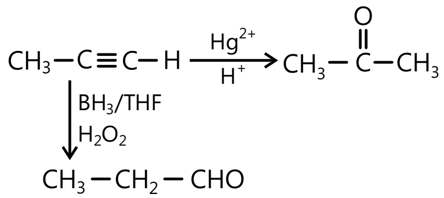
(B) $Ca^{2+}\ {}^{-}C\equiv C^{-} + H_2O \longrightarrow Ca(OH)_2 + HC\equiv CH$

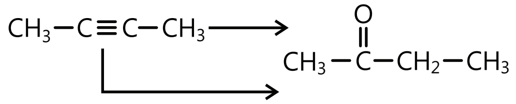
(C) $2Mg^{2+} + C_3^{4-} + H_2O \longrightarrow Mg(OH)_2 + H_3C-C\equiv CH$

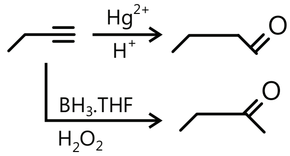
(D) $Me_3C-H+KMnO_4 \longrightarrow Me_3C-OH$

Sol 28: (A,C)

(A)


(B)


(C)


(D)


Assertion Reasoning Type

Sol 29: (B) When the C=C bond is conjugated with a C=O group, the electron withdrawing nature of carbonyl group polarizes the C=C bond so the nucleophilic attack can take place at the C=C carbon.

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

Sol 31: (A) is a stronger base than F–because the negative charge density on carbon is greater than the negative charge density of F–.

Sol 32: (A) CH3–C≡C–CH3 is more reactive than CH≡CH towards HCl because the carbocation formed is more stable in thecase of CH3C≡C–CH3 than CH≡CH.

Sol 33: (B) Alkynes are electron-rich nucleophiles with a cylindrical electron cloud formed of two bonds around a carbon-carbon bond. An electrophilic reagent can therefore easily react with the relatively weak alkyne bond.

Comprehension Type

Sol 34: (A) $CH_3-CH_2-Br \longrightarrow$ 

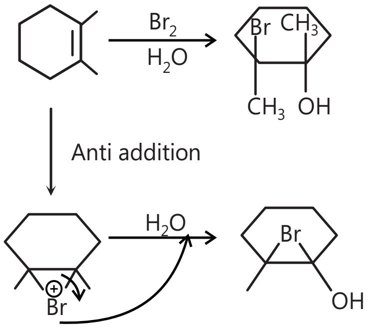
55 gm

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

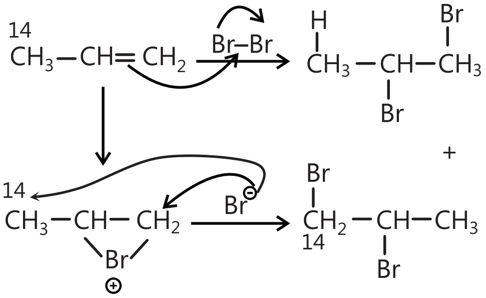
Sol 35: (A) 2.432g

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

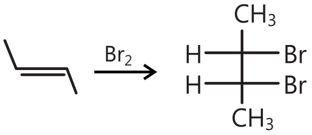
Sol 37: (D)



Sol 38: (C)



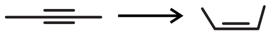
Sol 39: (B)



(B) Anti Addition

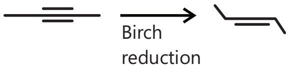
Match the Columns

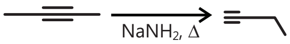
Sol 40:

(A) 

cis addition

$H_2/Pd/BaSO_4$

(B) 

(C) 

Isomerism

(D) 

Isomerism

A → q; B → p; C → s; D → r

Sol 41: (A) → (p) Markonikov

(B) → (r) Anti-markonikov

(C) → (s) Alkylic carbon get brominated

(D) → (q) Br_2 addition

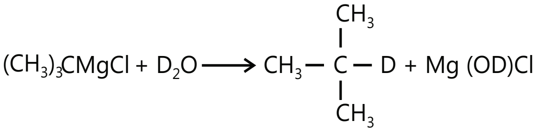
Sol 42: (A) → (q) Free radical mechanism

(B) → (r) Decarboxylation

(C) → (s) Free radical mechanism

(D) → (p) Same as grignard

Previous Years' Questions

Sol 1: (A) 

$$(CH_3)_3CMgCl + D_2O \longrightarrow CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-D + Mg(OD)Cl$$

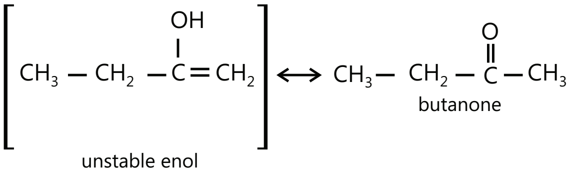
Sol 2: (D) According to the IUPAC conventions, compound can be numbered as:

$$H_2\overset{1}{C}=\overset{2}{C}H-\overset{3}{C}H_2-\overset{4}{C}H_2-\overset{5}{C}\equiv\overset{6}{C}-H$$

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

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

$$CH_3-CH_2-C\equiv C-H + H_2SO_4 \xrightarrow{HgSO_4}$$



$$\left[CH_3-CH_2-\overset{OH}{\overset{|}{C}}=CH_2\right] \longleftrightarrow CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$$

unstable enol

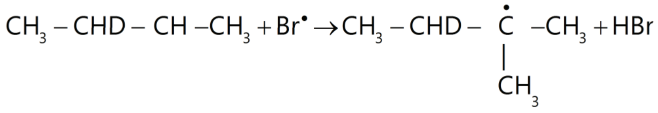
butanone

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

$$CH_3-CH_2-C\equiv C-H+CuCl_2\xrightarrow{NH_3(aq)}$$

$$\underset{\text{red–ppt}}{CH_3-CH_2-C\equiv C^{-}Cu^{+}}\downarrow$$

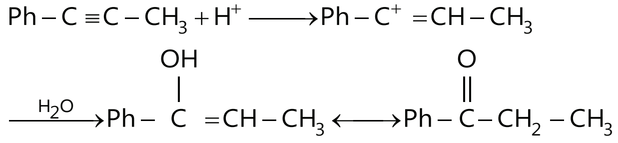
Sol 5: (B) Bromination is highly selective, occur at the carbon where the most stable free radical is formed:



$$CH_3-CHD-CH-CH_3+Br^{\bullet}\rightarrow CH_3-CHD-\underset{\underset{CH_3}{|}}{\overset{\bullet}{C}}-CH_3+HBr$$

(a tertiary free radical)

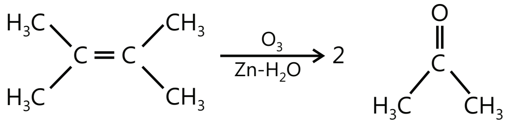
Sol 6: (A) Reaction proceeds through carbocation intermediate:



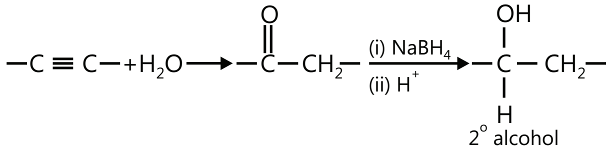
$$Ph-C\equiv C-CH_3+H^{+}\longrightarrow Ph-C^{+}=CH-CH_3$$

$$\xrightarrow{H_2O}Ph-\overset{\overset{OH}{|}}{C}=CH-CH_3\longleftrightarrow Ph-\overset{\overset{O}{||}}{C}-CH_2-CH_3$$

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



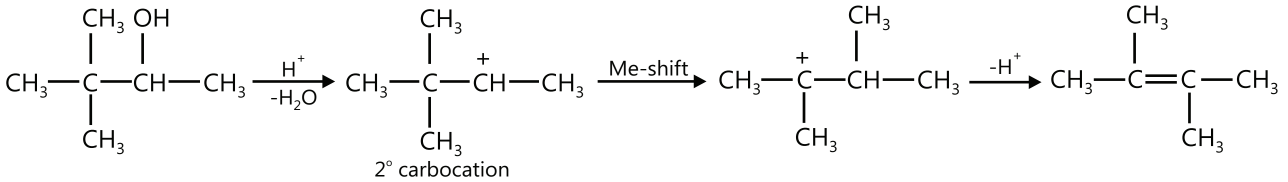
Also $P(C_6H_{10})$ has two degree of unsaturation and oxymercuration demercuration hydration indicates that it is an alkyne. As alkyne, on hydration, gives a carbonyl compound which on reduction with $NaBH_4$ gives a 2° alcohol.



$$-C\equiv C-+H_2O\longrightarrow-\overset{\overset{O}{||}}{C}-CH_2-\xrightarrow[\text{(ii) }H^{+}]{\text{(i) }NaBH_4}-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-$$

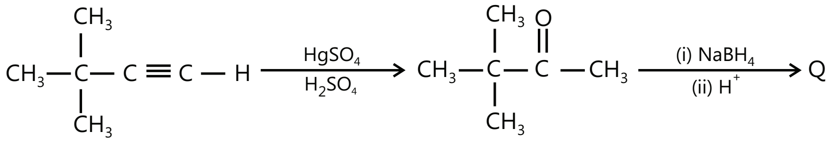
2° alcohol

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



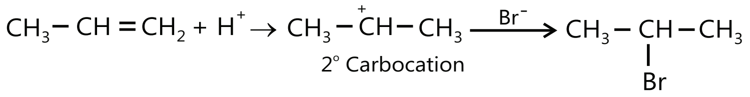
$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\overset{OH}{|}}{CH}-CH_3\xrightarrow[-H_2O]{H^{+}}CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{+}{CH}-CH_3\xrightarrow{\text{Me-shift}}CH_3-\underset{\underset{CH_3}{|}}{\overset{+}{C}}-\overset{\overset{CH_3}{|}}{CH}-CH_3\xrightarrow{-H^{+}}CH_3-\overset{\overset{CH_3}{|}}{C}=\underset{\underset{CH_3}{|}}{C}-CH_3$$

2° carbocation



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-C\equiv C-H\xrightarrow[H_2SO_4]{HgSO_4}CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\overset{O}{||}}{C}-CH_3\xrightarrow[\text{(ii) }H^{+}]{\text{(i) }NaBH_4}Q$$

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



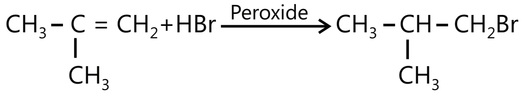
$$CH_3-CH=CH_2+H^{+}\rightarrow CH_3-\overset{+}{C}H-CH_3\xrightarrow{Br^{-}}CH_3-\underset{\underset{Br}{|}}{CH}-CH_3$$

2° Carbocation

Isopropyl bromide

(ii) Addition of HBr proceeds through carbocation intermediates.

Sol 10: (i)



$$\underset{\text{2-methyl propene}}{CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2}+HBr\xrightarrow{\text{Peroxide}}\underset{\text{Isopropyl bromide}}{CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_2Br}$$

In the absence of peroxide, HBr would be added giving tertiary butyl bromide.

(ii) Tertiary alkynes are slightly acidic, forms silver salt with ammoniacal solution of silver nitrate:

$$R-C\equiv C-H+AgNO_3\xrightarrow{NH_3(aq)}R-\underset{\text{white ppt.}}{C\equiv C}\ Ag\downarrow$$

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