CHAPTER 6

Aliphatic Hydrocarbons (Alkynes)

INTRODUCTION

- Alkynes are the acyclic hydrocarbons in which the unsaturation between carbon atoms is triple bond (C≡C)
- Hybridisation of triple bonded carbon in alkyne is sp
- Geometry of unsaturated carbon is linear in alkynes
- Bond angle in alkyne on sp carbon atom is 180°
- The general formula is C_nH_{2n-2} (n = 2, 3, 4, 5, ...)
- Nature of bonding

Bond	Bond length	Bond energy
C≡C	1.20 Å	200 kcal/mole
≡C–H	1.08 Å	121 kcal/mole

- Alkynes show the following isomerism and in the table below each isomerism is given with minimum number of carbon atoms required for the isomerism

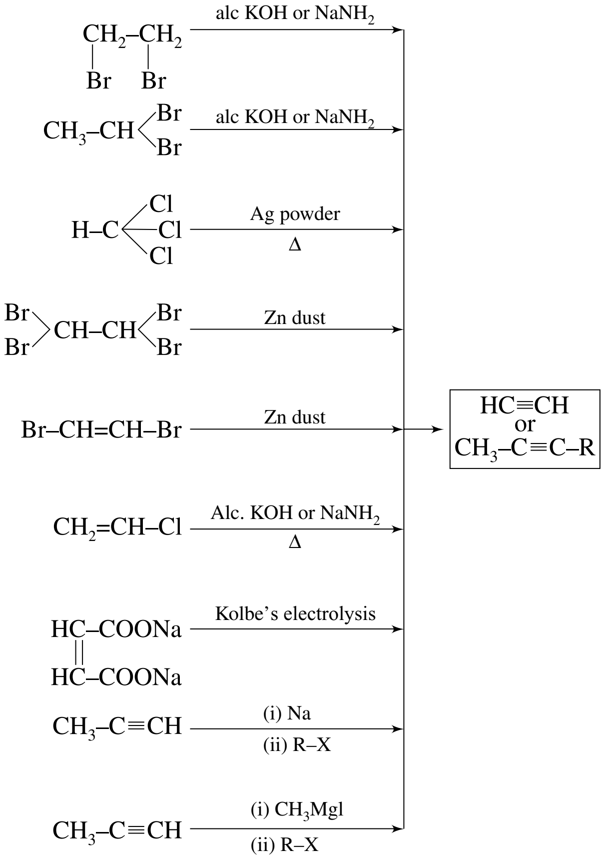
Isomerism	Minimum number carbon
Chain isomerism	5
Position isomerism	4
Functional isomerism	3
Ring chain isomerism	3
Optical isomerism	6

PHYSICAL PROPERTIES

- **Physical state:**
  C_2–C_4 → Gaseous C_5–C_{11} → Liquid C_{12} and above → Solid
- Alkynes are colourless, odourless and tasteless
- Lower alkynes are partially soluble in H_2O (It is due to its polarisability)
- Higher alkynes are insoluble in water due to more % of covalent character
- Completely soluble in organic solvents
- Melting point and Boiling point increases with molecular mass and decreases with number of branches

$$\text{Boiling point (B.P.) and Melting point (M.P.)} \propto \text{Molecular weight} \propto \frac{1}{\text{Number of branches}}$$

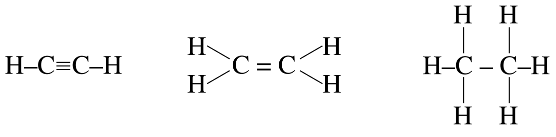
METHOD OF PREPRATION



CHEMICAL PROPERTIES OF ALKYNES

1. Acidic Nature of Terminal Alkynes

The hydrogen atoms of ethyne are considerably more acidic than those of ethane or ethene



$pK_a = 25$ $\quad pK_a = 44$ $\quad pK_a = 50$

The order of basicities of the anions is opposite the relative acidity of the hydrocarbons. The ethanide ions is the most basic and the ethynide ion is the least basic.

Relative Basicity

$$CH_3CH_2\text{:}^- > CH_2 = CH\text{:} > HC{\equiv}C\text{:}^-$$

What we have said about ethyne and ethynide ions is true of any terminal alkyne (RC≡CH) and any alkynide ion ($RC{\equiv}C\text{:}^-$).

If we include other hydrogen compounds of the first-row elements of the periodic table, we can write the following orders of relative acidities and basicities.

Relative Acidity

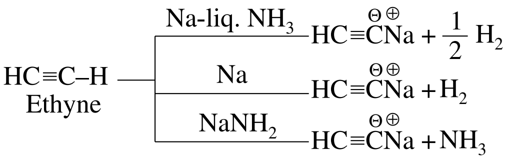
$$\begin{array}{lcccccc} & H\text{–}\ddot{\underset{..}{O}}H > & H - \ddot{\underset{..}{O}}R > & H\text{–}C{\equiv}CR > & H\text{–}\ddot{N}H_2 > & H\text{–}CH = CH_2 > & H\text{–}CH_2CH_3 \\ pK_a & 15.7 & 16\text{-}17 & 25 & 38 & 44 & 50 \end{array}$$

Relative Basicity

$$\overset{\ominus}{O}H < \overset{\ominus}{O}R < \overset{\ominus}{C} \equiv CR < \overset{\ominus}{N}H_2 < \overset{\ominus}{C}H = CH_2 < \overset{\ominus}{C}H_2CH_3$$

We see from the order just given that while terminal alkynes are more acidic than ammonia, they are less acidic than alcohols and are less acidic than water.

(I) Formation of sodium alkylide: Sodium ethynide and other sodium alkynides can be prepared as given below

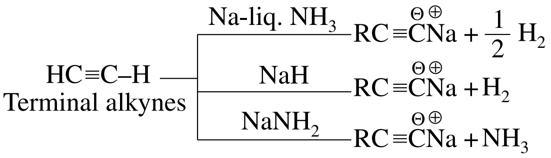


$$\underset{\text{Ethyne}}{HC\equiv C-H} \xrightarrow{\text{Na-liq. }NH_3} HC\equiv\overset{\ominus\oplus}{C}Na + \frac{1}{2}H_2$$

$$HC\equiv C-H \xrightarrow{Na} HC\equiv\overset{\ominus\oplus}{C}Na + H_2$$

$$HC\equiv C-H \xrightarrow{NaNH_2} HC\equiv\overset{\ominus\oplus}{C}Na + NH_3$$

Sodium ethynide



$$\underset{\text{Terminal alkynes}}{HC\equiv C-H} \xrightarrow{\text{Na-liq. }NH_3} RC\equiv\overset{\ominus\oplus}{C}Na + \frac{1}{2}H_2$$

$$HC\equiv C-H \xrightarrow{NaH} RC\equiv\overset{\ominus\oplus}{C}Na + H_2$$

$$HC\equiv C-H \xrightarrow{NaNH_2} RC\equiv\overset{\ominus\oplus}{C}Na + NH_3$$

Sodium Alkylide ion

Hence, ethyne and other terminal alkynes (1-alkynes) are weakly acidic in character. During these reaction, the acetylenic hydrogen is removed as a proton to form stable carbanions (acetylide ions)

Note: Ethyne and terminal alkynes do not give acid-base reaction with NaOH.

$$RC\equiv CH + NaOH \cancel{\longrightarrow} RC\equiv\overset{\ominus\oplus}{C}Na + H_2O$$

This reaction is not feasible because water (H_2O) is more acidic than ethyne and terminal alkynes

(II) Reaction with Grignard reagent: (Alkylation of acetylene and terminal alkynes).

$$HC\equiv CH + CH_3MgI \longrightarrow CH_4 + CH\equiv C\text{–}MgI$$

$$HC\equiv C\text{–}MgI + ICH_3 \longrightarrow \underset{\text{Propyne}}{CH\equiv C\text{–}CH_3} + MgI_2$$

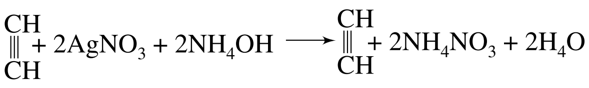
(III) Reaction with X_2 + Aqueous alkali: Electrophilic substitution reaction takes place.

$$HC\equiv CH + 2Cl_2 + 2NaOH \longrightarrow Cl\text{–}C\equiv C\text{–}Cl + 2NaCl + 2H_2O$$

$$HC\equiv CH + I_2 + 2NH_4OH \longrightarrow I\text{–}C\equiv C\text{–}I + 2NH_3 + 2H_2O$$

(IV) Test of terminal alkynes:

(i) With ammonical solution of silver nitrate (Tollens' reagent).

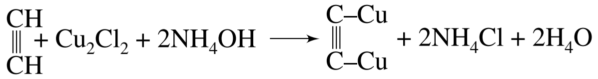


$$\begin{matrix}CH\\ \parallel\!| \\ CH\end{matrix} + 2AgNO_3 + 2NH_4OH \longrightarrow \begin{matrix}CH\\ \parallel\!| \\ CH\end{matrix} + 2NH_4NO_3 + 2H_4O$$

Silver acetylide
(White ppt.)

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

(ii) With ammonical solution of cuprous chloride



$$\begin{matrix}CH\\ |||\\ CH\end{matrix} + Cu_2Cl_2 + 2NH_4OH \longrightarrow \begin{matrix}C\text{–}Cu\\ |||\\ C\text{–}Cu\end{matrix} + 2NH_4Cl + 2H_4O$$

Acetylene — Cuprous acetylide (Red ppt.)

$$R\text{–}C\equiv CH + [Cu(NH_3)_2]^+\ \overline{O}H \longrightarrow R\text{–}C\equiv C\text{–}Cu + H_2O + 2NH_3$$

(Terminal alkyne) — Copper alkynide (Red ppt.)

Note: Copper and silver acetylides are very sensitive to shock when dry and may explode violently. However, these can be decomposed by acids to regenerate acetylene.

$$Cu\text{–}C\equiv C\text{–}Cu + 2HCl\ (dil.) \longrightarrow CH\equiv CH + 2CuCl\downarrow\ \downarrow$$

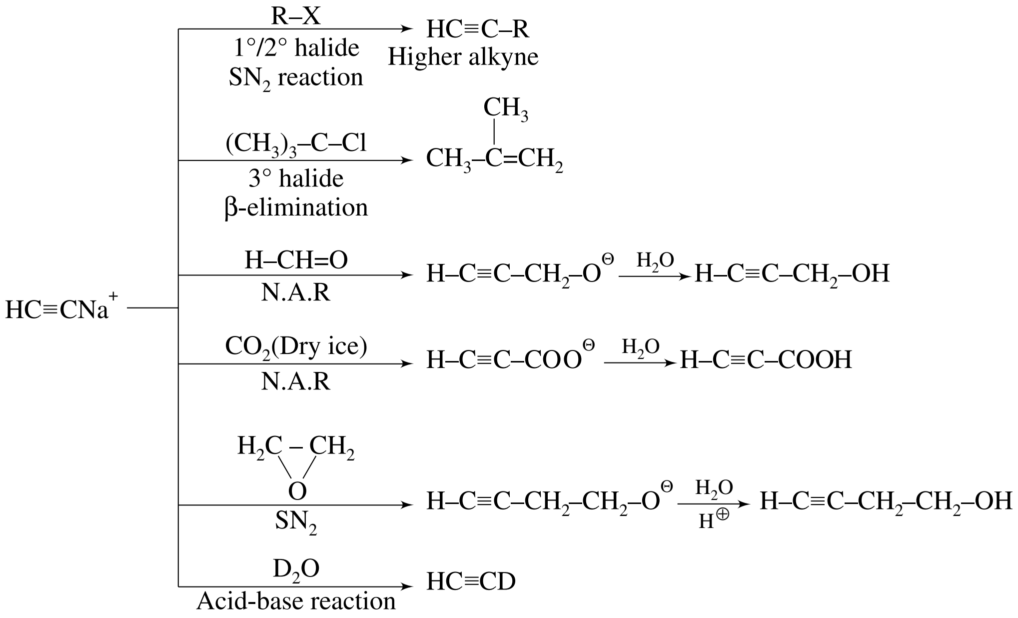
Cuprous acetylide — Acetylene

$$Ag\text{–}C\equiv C\text{–}Ag + 2HNO_3\ (dil.) \longrightarrow CH\equiv CH + 2AgNO_3$$

Silver acetylide — Acetylene

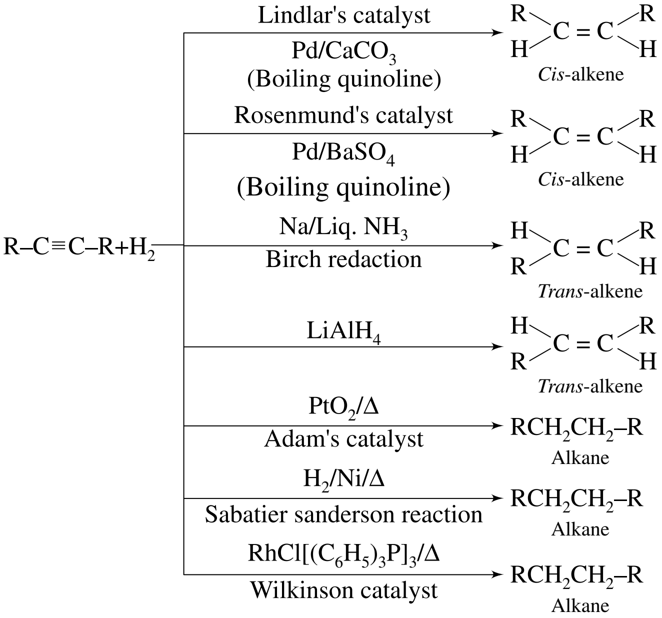
Hence, these reactions can be utilised for the separation of acetylene from a mixture containing ethane, ethylene and acetylene.

(V) Reaction of Sodium Alkynides: Sodium alkynides are useful intermediates for the synthesis of other higher alkynes and also gives many more other reaction.

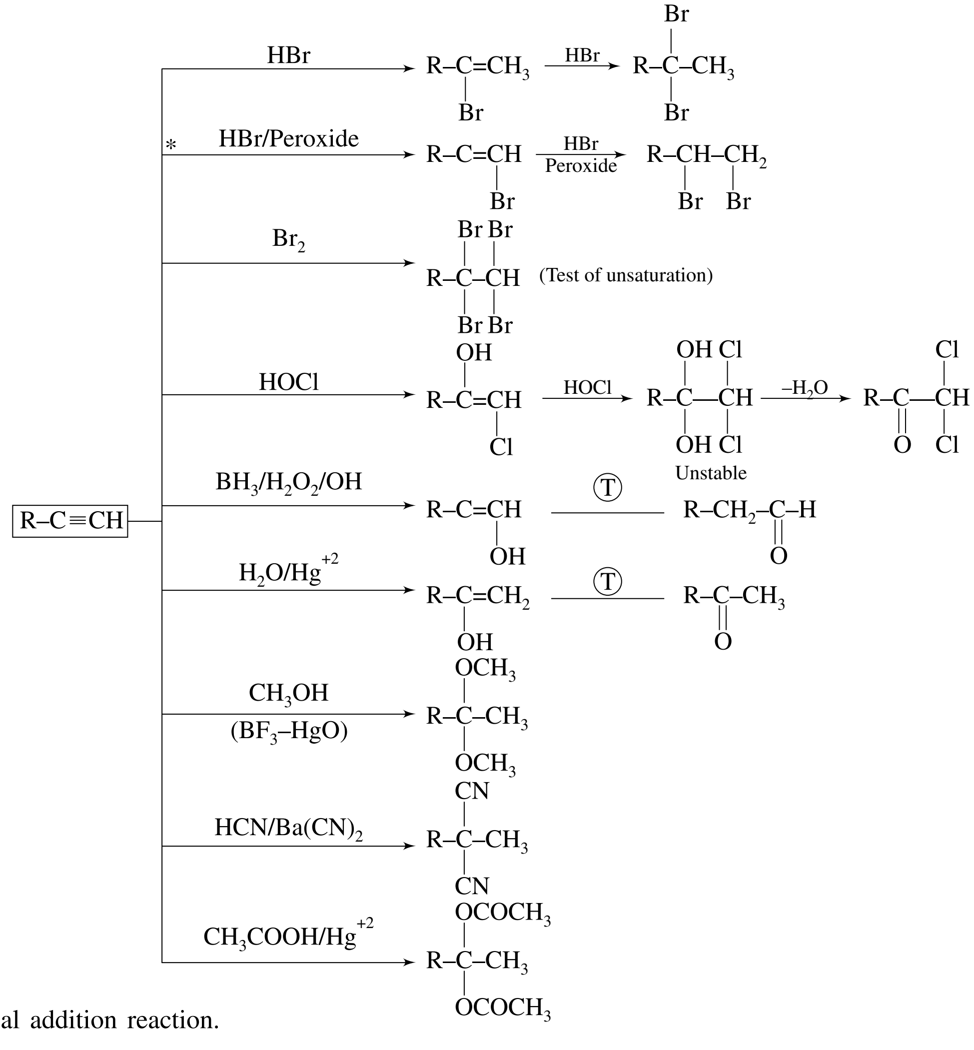


2. Addition Reactions

(i) Addition of hydrogen (Hydrogenation):

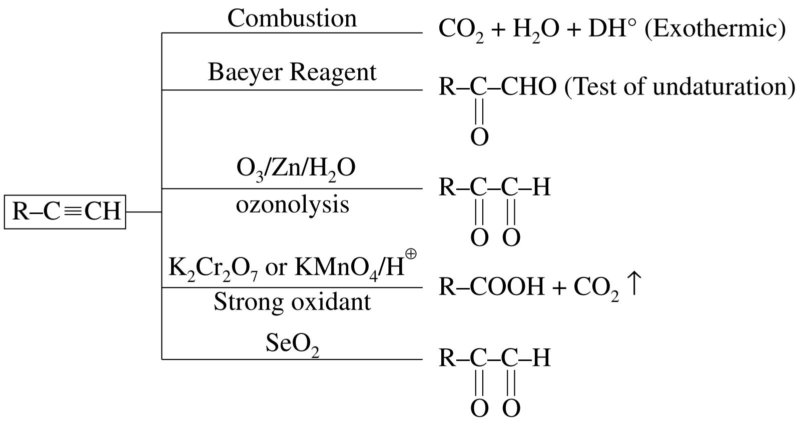


(ii) Ionic addition reaction:



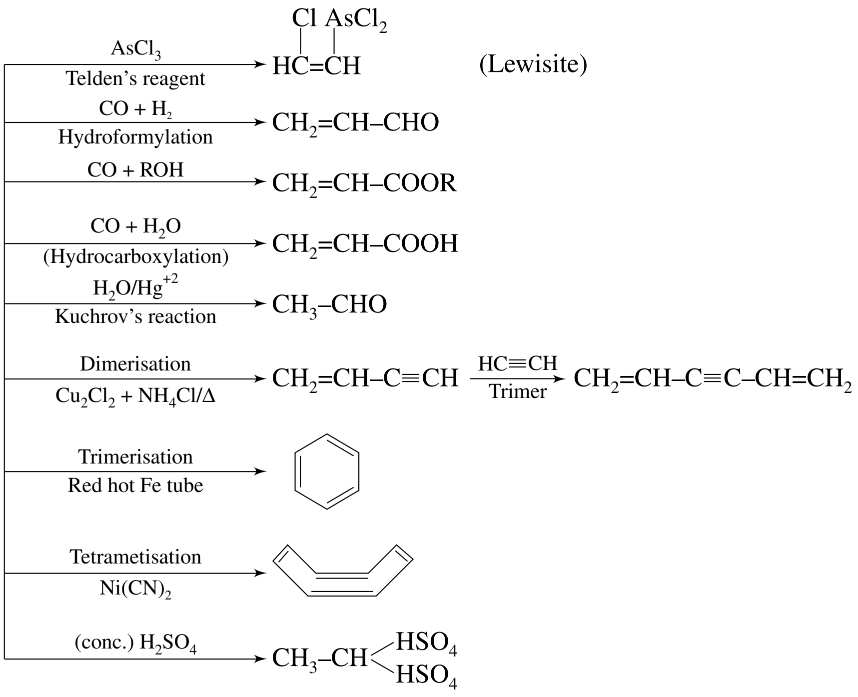
* It is free radical addition reaction.

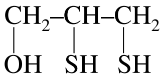
3. Oxidation Reactions:



Special Points:

- Ethyne is used in oxy-acetylene flame (2800–3200°C) which is used for cutting and welding of metals
- Ethyne is used in carbide lamps for lighting (is an illuminating agent in hawker's lamp)
- When hydrogen is passed in atmosphere of electric arc between carbon electrode, a mixture of H_2 and ethyne is formed **(Berthelot Method)**
- Mixture of ethyne and nitrogen in electric spark converts into HCN
- Ethyne burns with sooty flame due to presence of high percentage of carbon
- Acetylene is used in artificial ripening of fruits
- Pure acetylene **(NARCYLENE)** is odourless and impure acetylene has odour like garlic. It is due to impurities of arsene (AsH_3) and phosphine (PH_3)
- Acetylene and 1-alkyne are acidic in nature. It is due to greater electronegativity of sp hybridised carbon
- Acetylene has two acidic hydrogen atoms. It can neutralise two equivalents of base at the same time. So it is also called as dibasic acid. But the base should be very stronger as $\overset{\ominus}{N}H_2$ or $\overset{\ominus}{C}H_2$, etc.
- Some other reactions of acetylene are:



- **Lewisite** is highly explosive which was used in the World War II. **British anti-Lewisite (B.A.L.)** is an organic compound whose structure is 
$$\underset{OH}{\underset{|}{CH_2}}-\underset{SH}{\underset{|}{CH}}-\underset{SH}{\underset{|}{CH_2}}$$

- Hydrolysis of metal carbides gives following hydrocarbons:

$Al_4C_3 + 12\ H_2O \longrightarrow 3CH_4 + 4\ Al(OH)_3$

$Be_2C + 4H_2O \longrightarrow CH_4 + 2\ Be\ (OH)_2$

$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$

$Mg_2C_3 + 4H_2O \longrightarrow C_3H_4 + 2\ Mg(OH)_2$

SOLVED EXAMPLE

1. Acetylene and propyne are separately treated with warm aqueous H_2SO_4 (30%) in the presence of $HgSO_4$ as catalyst. The products formed in these two experiments are, respectively

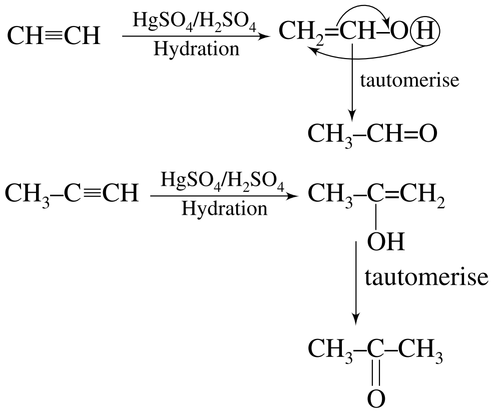
(1) acetone and acetaldehyde

(2) acetaldehyde and propionaldehyde

(3) acetone and propionaldehyde

(4) acetaldehyde and acetone

Sol. **[4]**



$$CH{\equiv}CH \xrightarrow[\text{Hydration}]{HgSO_4/H_2SO_4} CH_2{=}CH{-}OH \xrightarrow{\text{tautomerise}} CH_3{-}CH{=}O$$

$$CH_3{-}C{\equiv}CH \xrightarrow[\text{Hydration}]{HgSO_4/H_2SO_4} CH_3{-}\underset{OH}{\underset{|}{C}}{=}CH_2 \xrightarrow{\text{tautomerise}} CH_3{-}\underset{O}{\underset{||}{C}}{-}CH_3$$

2. Consider the following two reactions.

$CH_3C \equiv CCH_3 \xrightarrow[\text{quinoline}]{H_2, Pd/BaSO_4} (A);$

$CH_3C \equiv CCH_3 \xrightarrow{Na/NH_3(I)} (B)$

The products (A) and (B) are

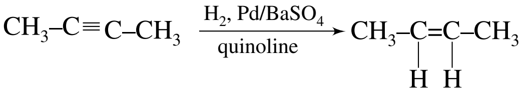
(1) *trans*-but-2-ene and *cis*-but-2-ene, respectively

(2) *cis*-but-2-ene and *trans*-but-2-ene, respectively

(3) both *cis*-but-2-ene

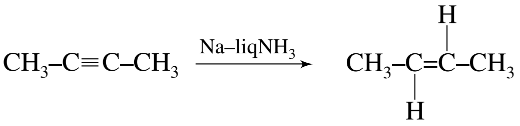
(4) both *trans*-but-2-ene

Sol. **[2]**



$$CH_3{-}C{\equiv}C{-}CH_3 \xrightarrow[\text{quinoline}]{H_2,\ Pd/BaSO_4} CH_3{-}\underset{H}{\underset{|}{C}}{=}\underset{H}{\underset{|}{C}}{-}CH_3$$

Syn addition *cis*-2-butene



$$CH_3{-}C{\equiv}C{-}CH_3 \xrightarrow{Na{-}liqNH_3} CH_3{-}\underset{H}{\underset{|}{C}}{=}\overset{H}{\overset{|}{C}}{-}CH_3$$

Anti addition *trans*-2-butene

3. Two gases P and Q both decolourise aqueous bromine but only one of them gives white ppt. with Tollens' reagent. P and Q are likely to be:

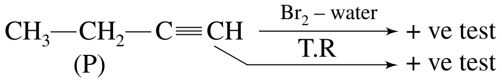
(1) $H_2C = CH_2$ and $CH_3 - C \equiv C - CH_3$

(2) $HC \equiv CH$ and $CH_3 - CH_2 - C \equiv CH$

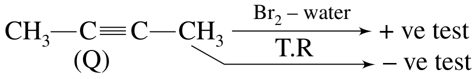
(3) $HC \equiv CH$ and $CH_3 - C \equiv CH$

(4) $CH_3{-}CH_2{-}C \equiv CH$ and $CH_3{-}C \equiv C{-}CH_3$

Sol. **[4]**



$$\underset{(P)}{CH_3{-}CH_2{-}C{\equiv}CH} \xrightarrow{Br_2 - water} +\text{ ve test};\quad \xrightarrow{T.R} +\text{ ve test}$$



$$\underset{(Q)}{CH_3{-}C{\equiv}C{-}CH_3} \xrightarrow{Br_2 - water} +\text{ ve test};\quad \xrightarrow{T.R} -\text{ ve test}$$

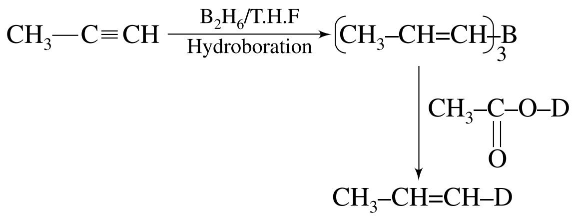
Only terminal alkynes (having acidic H) give white ppt. with Tollens' reagent

4. Propyne is allowed to react with B_2H_6 and the product is subsequently treated with CH_3COOD. The final product formed is

(1) 1-deuteriopropane (2) 2-deuteriopropane

(3) 1-deuteriopropene (4) 2-deuteriopropene

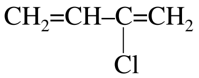
Sol. **[3]**



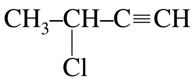
$CH_3-C\equiv CH \xrightarrow[\text{Hydroboration}]{B_2H_6/T.H.F} (CH_3-CH=CH)_3B \xrightarrow{CH_3-\underset{\underset{O}{\parallel}}{C}-O-D} CH_3-CH=CH-D$

1-Deuteropropene

5. 1-Buten-3-yne, $CH_2=CH-C\equiv CH$, reacts with HCl (one mole) at a low temperature to form mainly:

(1) 

$CH_2=CH-\underset{\underset{Cl}{|}}{C}=CH_2$

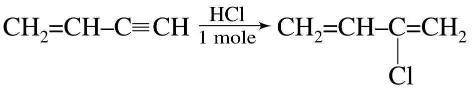
(2) 

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

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

(4) $CH_3CH=C=CHCl$

Sol. **[1]**

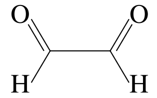


$CH_2=CH-C\equiv CH \xrightarrow[\text{1 mole}]{HCl} CH_2=CH-\underset{\underset{Cl}{|}}{C}=CH_2$

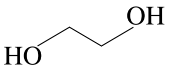
Conjugated stable alkene

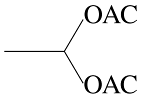
6. $\underset{(x)}{H-\equiv-H} \xrightarrow[\text{(i) } H_2O/Zn]{\text{(i) } O_3} (A) \xrightarrow{Zn/CH_3COOH} (B)$

Compound (B):

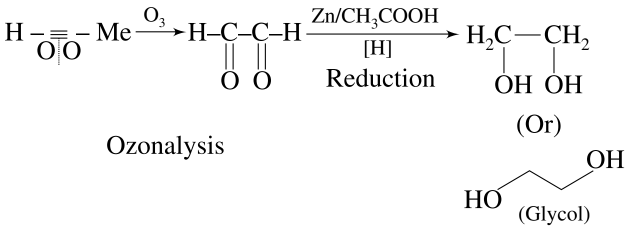
(1) 

(2) Me–COOH

(3) 

(4) 

Sol. **[3]**



7. In which of the following conditions does the reaction take place?

$CH\equiv CH + CH_3OH \longrightarrow CH_3O-CH=CH_2$

(1) $CH\equiv CH + CH_3OH \xrightarrow[160-200°C]{KOMe}$

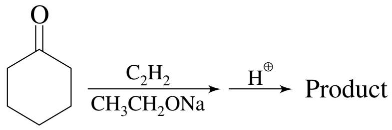
(2) $CH\equiv CH + CH_3OH \xrightarrow{Conc.H_2SO_4}$

(3) $CH\equiv CH + CH_3OH \xrightarrow{anhyd.ZnCl_2}$

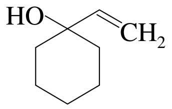
(4) $CH\equiv CH + CH_3OH \xrightarrow[ClHC=CHCl]{dil.HCl}$

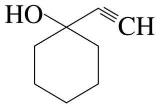
Sol. **[1]**

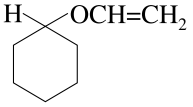
$CH\equiv CH + CH_3OH \xrightarrow[160-200°C]{KOMe} CH_3-O-CH=CH_2$

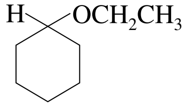
8. 

The Major product is:

(1) 

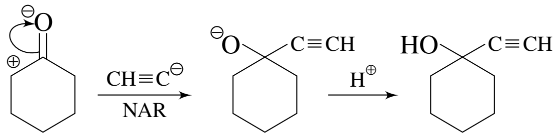
(2) 

(3) 

(4) 

Sol. **[2]**

$CH\equiv CH \xrightarrow{C_2H_5ONa} CH\equiv C^{\ominus}(nu^{\ominus})$



9. Which 2, 3-dibromobutane is treated with KOH in ethanol, 2-bromo-2-butene is formed which does not undergo further dehydrobromination to form 2-butyne under similar condition because

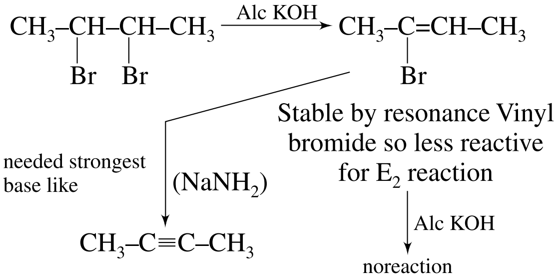
(1) H and Br are not *trans*

(2) There is no further B-H available

(3) Vinyl bromide is very less reactive in E_2 elimination reaction

(4) Reactant is more stable than product

Sol. **[3]**



$CH_3-\underset{\underset{Br}{|}}{CH}-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow{\text{Alc KOH}} CH_3-\underset{\underset{Br}{|}}{C}=CH-CH_3$

10. $X \xrightarrow{Na} \xrightarrow{CH_3Br} Y \xrightarrow{Na} \xrightarrow{C_3H_7Br}$ 2-Hexyne.

X and Y are respectively:

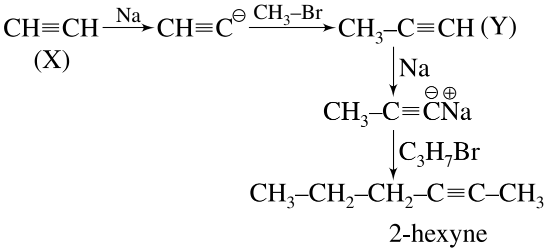
(1) $CH_2{=}CH_2$, $CH_3{-}C{\equiv}CH$

(2) $CH{\equiv}CH$, $CH_3{-}C{\equiv}CH$

(3) $CH{\equiv}CH$, $CH_3{-}CH{=}CH_2$

(4) $CH{\equiv}CH$, $HC{\equiv}C{-}CH_2Br$

Sol. **[2]**



$$\underset{(X)}{CH\equiv CH}\xrightarrow{Na}CH\equiv C^{\ominus}\xrightarrow{CH_3-Br}CH_3-C\equiv CH\ (Y)$$

$$\xrightarrow{Na} CH_3-C\equiv \overset{\ominus\oplus}{C}Na \xrightarrow{C_3H_7Br} \underset{\text{2-hexyne}}{CH_3-CH_2-CH_2-C\equiv C-CH_3}$$

EXERCISE 1

1. Consider the following reaction.

$CH_3C{\equiv}CCH_3 \xrightarrow{Na/NH_3(1)} (X)$;

$CH_3C{\equiv}CCH_3 \xrightarrow[2.CH_3COOH]{1.BH_3} (Y)$

The products (X) and (Y) are, respectively

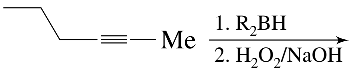
(1) (E)-but-2-ene and butan-2-one

(2) (Z)-but-2-ene and (E)-but-2-ene

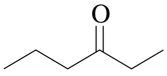
(3) (*E*)-but-2-ene and (*Z*)-but-2-ene

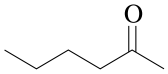
(4) Both (*E*)-but-2-ene

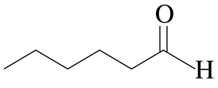
2. The product of the reaction

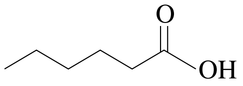


is

(1) 

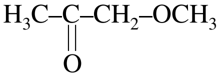
(2) 

(3) 

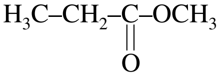
(4) 

3. $H_3C - C \equiv C{-}OCH_3 \xrightarrow{Hg^{2+}/H^+/H_2O}$ Product

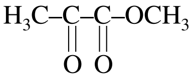
Major product of the reaction will be:

(1) 

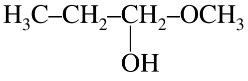
$H_3C-\underset{\underset{O}{\|}}{C}-CH_2-OCH_3$

(2) 

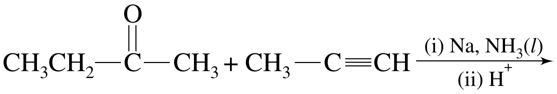
$H_3C-CH_2-\underset{\underset{O}{\|}}{C}-OCH_3$

(3) 

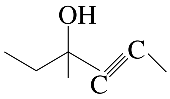
$H_3C-\underset{\underset{O}{\|}}{C}-\underset{\underset{O}{\|}}{C}-OCH_3$

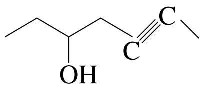
(4) 

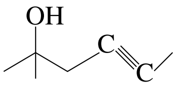
$H_3C-CH_2-\underset{\underset{OH}{|}}{CH_2}-OCH_3$

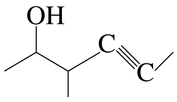
4. 

$CH_3CH_2-\overset{\overset{O}{\|}}{C}-CH_3 + CH_3-C\equiv CH \xrightarrow[(ii)\ H^+]{(i)\ Na,\ NH_3(l)}$

(1) 

(2) 

(3) 

(4) 

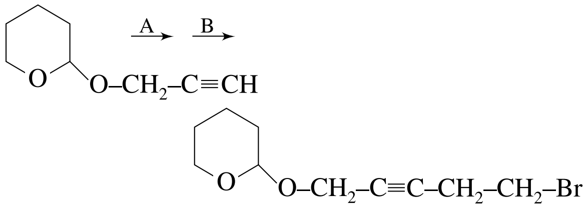
5. Which of the following statements is true for ethane, ethane and acetylene?

(1) Acetylene is the weakest acid and has the longest C–H bond distance

(2) Acetylene is the strongest acid and has the shortest C–H bond distance

(3) Ethane is the strongest acid and has the longest C–H bond distance

(4) Ethane is the strongest acid and has the shortest C–H bond distance

6. 

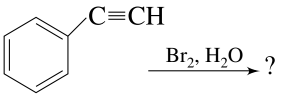
To carry out above conversion, (A) and (B) respectively, are:

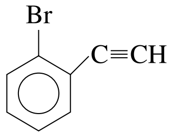
(1) $NaNH_2$, Cl – CH_2 – CH_2 – Br

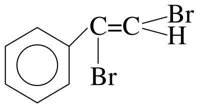
(2) $NaNH_2$, F – CH_2 – CH_2 – Br

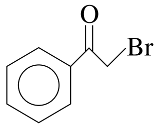
(3) $NaNH_2$, I – CH_2 – CH_2 – Br

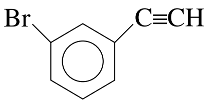
(4) $NaNH_2$, I – CH_2 – CH_2 – I

7. 

(1) 

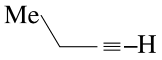
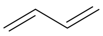
(2) 

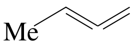
(3) 

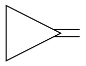
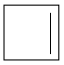
(4) 

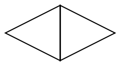
8. An organic compound (A) (C_4H_6) forms a precipitate with Tollens' and Fehling's reagents. (A) has an isomer (B). (B) reacts with 1 mol of Br_2 to form 1,4-dibromo-2-butene. (A) and (B) are:

A **B**

(1)  & 

(2) Me – ≡–H & 

(3)  & 

(4) Me – ≡–Me & 

9. Consider the following sequence of reactions:

$CH_3C \equiv CH \xrightarrow[2.\ CH_3I]{1.\ NaNH_2} (A) \xrightarrow{Na/NH_3(l)} (B) \xrightarrow[heat]{CH_2N_2} (C)$

The final product (C) is:

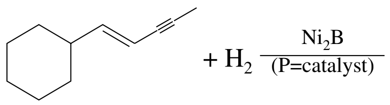
(1) but-2-yne

(2) *trans*-but-2-ene

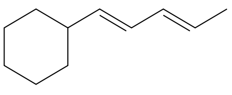
(3) *cis*-1, 2-dimethylcyclopropane

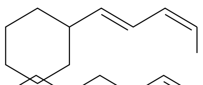
(4) (±)-*trans*-1, 2-dimethylcyclopropane

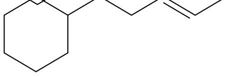
10. Which of the following products is expected in the reaction?

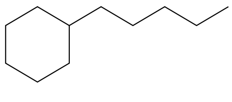


$+ H_2 \xrightarrow[(P=catalyst)]{Ni_2B}$

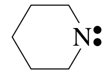
(1) 

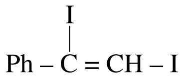
(2) 

(3) 

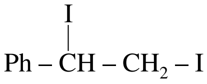
(4) 

11. $Ph-C\equiv C-H \xrightarrow{I_2}$ Major product:



(1) 

$Ph-\overset{I}{C}=CH-I$

(2) 

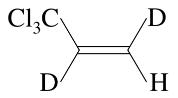
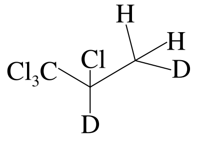
$Ph-\overset{I}{C}H-CH_2-I$

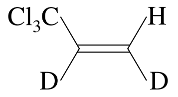
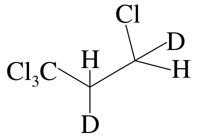
(3) $Ph - C \equiv C - I$

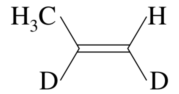
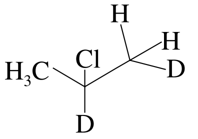
(4) $I - C \equiv C - H$

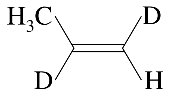
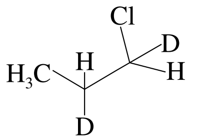
12. $\xrightarrow[D_2+P\text{-}2\text{catalyst}]{} (A) \xrightarrow{HCl} (B)$

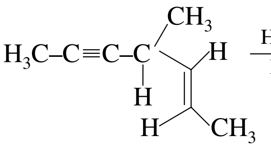
Compounds (A) and (B) are:

(1)  

(2)  

(3)  

(4)  

13. 

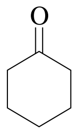
$\xrightarrow[Isoquinoline]{H_2,\ Pd-BaSO_4}$ Product:

(1) an optically active compound

(2) an optically inactive compound

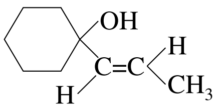
(3) a racemic mixture

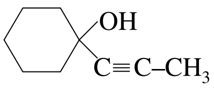
(4) a diastereomeric mixture

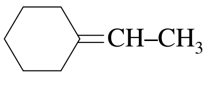
14. 

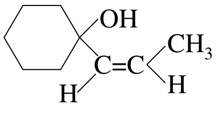
$\xrightarrow[H^+H_2O]{\overset{\oplus}{Na}\overset{\ominus}{C}\equiv C-CH_3} X \xrightarrow[isoquinoline]{H_2,\ Pd-BaSO_4} Y$

Identify the structure of Y:

(1) 

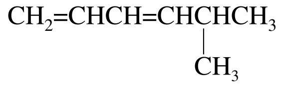
(2) 

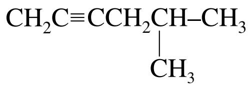
(3) 

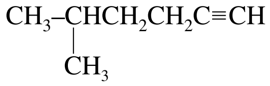
(4) 

15. On catalytic hydrogenation, a compound X (C_7H_{12}) absorbs 2 mol of hydrogen and yields 2-methylhexane. On treatment with $Ag(NH_3)_2OH$, X gives a precipitate which contains silver and which regenerates X on treatment with dilute HNO_3. The structure of X is

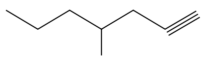
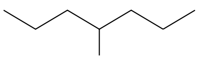
(1) $CH_3CH_2CH_2CH_2CH_2C\equiv CH$

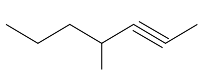
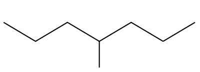
(2) 
$CH_2=CHCH=CH\underset{CH_3}{CH}CH_3$

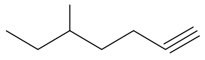
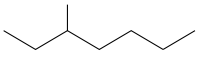
(3) 
$CH_2C\equiv CCH_2\underset{CH_3}{CH}-CH_3$

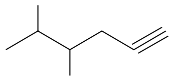
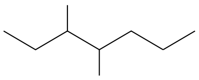
(4) 
$CH_3-\underset{CH_3}{CH}CH_2CH_2C\equiv CH$

16. An optically active compound A has the molecular formula C_8H_{14}. The Compound gives a precipitate when treated with a solution containing $Ag(NH_3)_2OH$. On catalytic hydrogenation (A) yield B (C_8H_{18}). Compound (B) is optically inactive and cannot be resolved. Propose the structure of A and B.

(1)  and 

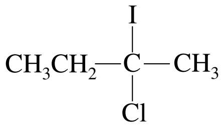
(2)  and 

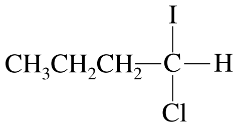
(3)  and 

(4)  and 

17. Consider the following sequence of reactions.

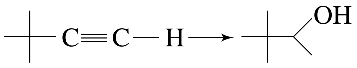
$CH_3-CH_2-C\equiv CH \xrightarrow{HCl} (A) \xrightarrow{HI} (B)$

(1) 
$CH_3CH_2-\overset{I}{\underset{Cl}{C}}-CH_3$

(2) 
$CH_3CH_2CH_2-\overset{I}{\underset{Cl}{C}}-H$

(3) $CH_3CH_2CH_2ClCH_2I$ (4) $CH_3CH_2CHICH_2Cl$

18. Select the reagent for following transformation:



(1) H_2-Pd, HCHO, H_2SO_4

(2) H_2, Pd-$BaSO_4$; $Hg(OAc)_2$, H_2O, $NaBH_4$, $\overset{\ominus}{O}H$

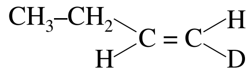
(3) BH_3, H_2O_2, $\overset{\ominus}{O}H$, Pd-C

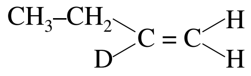
(4) Hg^{+2}, H_2SO_4, H_2, Pd-$BaSO_4$

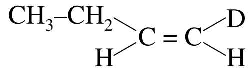
19. In the reaction

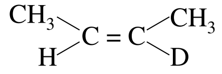
$CH_3CH_2C\equiv CH \xrightarrow[THF]{BH_3} I \xrightarrow{CH_3COOD} II$

the end product is

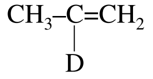
(1) 

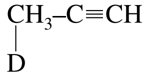
(2) 

(3) 

(4) 

20. 1,1-Dichloropropane is treated with an excess of sodium amide in liquid ammonia. The reaction product is then treated with heavy water to give

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

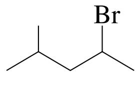
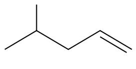
(2) 
$\underset{D}{CH_3}-C\equiv CH$

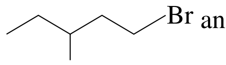
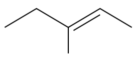
(3) $CH_3-C\equiv CH$

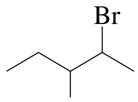
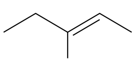
(4) $CH_3C\equiv CH-D$

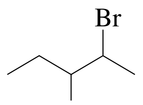
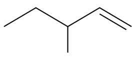
EXERCISE 2

1. An organic compound X ($C_6H_{13}Br$) is optically active. X on treatment with $(CH_3)_3COK$ in $(CH_3)_3COH$ gives Y (C_6H_{12}), a major product. Y on treatment with Br_2-CCl_4 in the presence of $FeBr_3$ gives a dibromide which on further treatment with $NaNH_2$ gives C_6H_{10} which is still optically active. Hence, X and Y. respectively, are

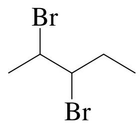
(1)  and 

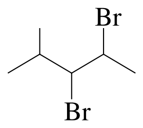
(2)  and 

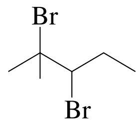
(3)  and 

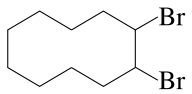
(4)  and 

2. When vicinal dibromide is heated with KOH in ethanol (~ 200°C), double dehydrohalogenation takes place giving alkyne. Which of the following fails to give alkyne according to this procedure?

(1) 

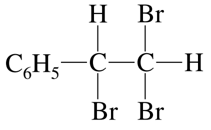
(2) 

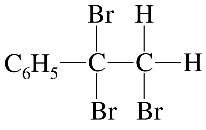
(3) 

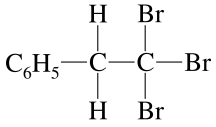
(4) 

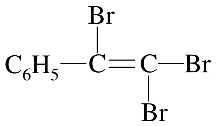
3. The major product of the following reactions is

$C_6H_5—C≡C—H + Br_2—H_2O \xrightarrow{HBr}$

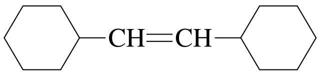
(1)

$C_6H_5-\underset{Br}{\overset{H}{C}}-\underset{Br}{\overset{Br}{C}}-H$

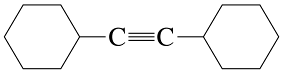
(2)

$C_6H_5-\underset{Br}{\overset{Br}{C}}-\underset{Br}{\overset{H}{C}}-H$

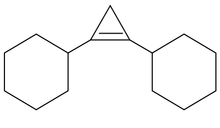
(3)

$C_6H_5-\underset{H}{\overset{H}{C}}-\underset{Br}{\overset{Br}{C}}-Br$

(4)

$C_6H_5-\overset{Br}{C}=\underset{Br}{C}-Br$

4. A hydrocarbon X ($C_{14}H_{22}$) on treatment with H_2/Pt gives $C_{14}H_{26}$. Also X on treatment with alkaline $KMnO_4$ followed by hydrolysis of products yields $C_7H_{12}O_2$ which on further heating with soda lime gives cyclohexane. Hence, X is

(1)


(2)


(3)


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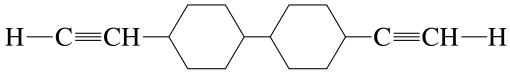
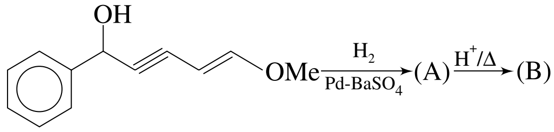
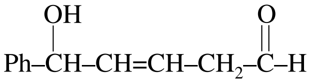


5.


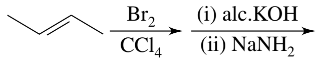
Product (B) is:

(1)

$Ph-\overset{OH}{C}H-CH=CH-CH_2-\overset{O}{\overset{\|}{C}}-H$

(2) Ph–CH=CH–CHO

(3) Ph–$(CH=CH)_2$–CHO

(4) Ph–$(CH = CH)_3$–CHO

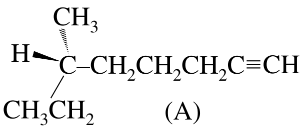
6.


(A); Product (A) is:

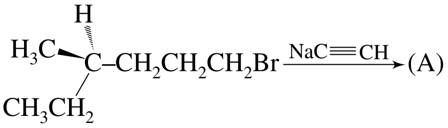
(1) $H_2C=CH–CH=CH_2$ (2) $CH_3–C≡C–CH_3$

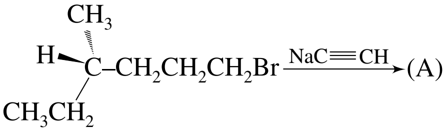
(3) $CH_3–CH_2–C≡CH$ (4) $CH_3–CH=C=CH_2$

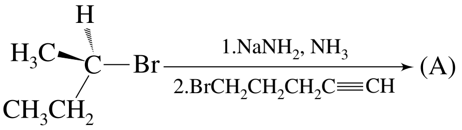
7. Which combination is best for preparation of the compound (A) shown below?

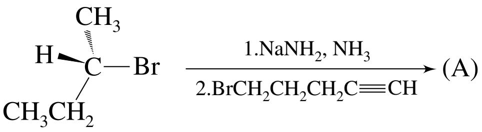


(A)

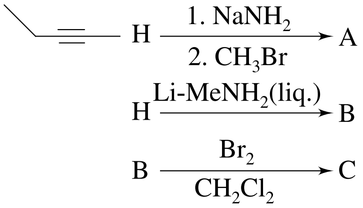
(1)


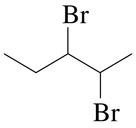
(2)


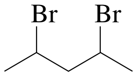
(3)


(4)


8. What is the final product, C, of the following reaction sequence?



(1)


(2)


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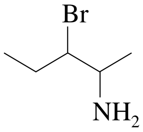
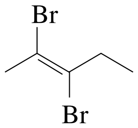


(4)


9. Predict the product of the following reaction sequence.

$$\text{ethyne} \xrightarrow[\substack{(2)\ \text{excess I—CH}_3\text{—(CH}_2)_2\text{—CH}_3 \\ (3)\ H^{\ominus}}]{(1)\ \text{excess NaNH}_2}$$

(1) 6-iodo-1-hexyne (2) 1-hexyne

(3) 5-decyne (4) 1-iodo-1-hexene

10. Choose the sequence of steps that describes the best synthesis of 1-butene from ethanol :

(1) (1) NaC ≡ CH; (2) H_2, Lindlar Pd

(2) (1) NaC ≡ CH; (2) Na, NH_3

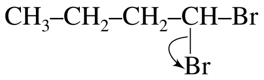
(3) (1) HBr, heat; (2) NaC ≡ CH; (3) H_2, Lindlar Pd

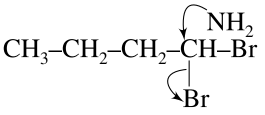
(4) (1) HBr, heat; (2) $KOC(CH_3)_3$, DMSO; (3) H_2, Lindlar catalyst

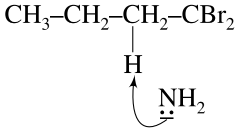
11. Which of the following best describes what happens in the first step in the mechanism of reaction shown below?

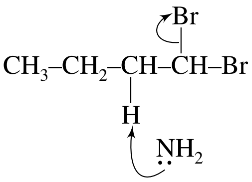
$CH_3CH_2CH_2CHBr_2 + 3NaNH_2 \longrightarrow$

$CH_3—CH_2—C\equiv CNa + 2NaBr + 3NH_3$

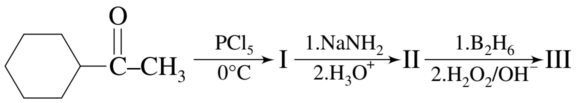
(1) 

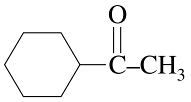
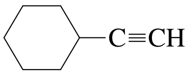
(2) 

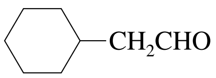
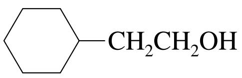
(3) 

(4) 

12. In the following sequence of reactions, what is the end product (III)?

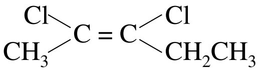


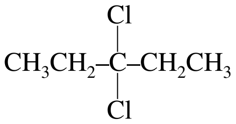
(1)  (2) 

(3)  (4) 

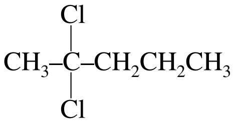
13. What is the major product of the following reaction?

$CH_3C\equiv C–CH_2–CH_3 \xrightarrow[Cl_2]{1\text{ mole of}}$

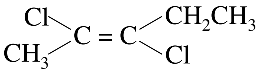
(1) 

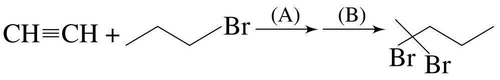
(2) 

$CH_3CH_2–\overset{Cl}{\underset{Cl}{C}}–CH_2CH_3$

(3) 

$CH_3–\overset{Cl}{\underset{Cl}{C}}–CH_2CH_2CH_3$

(4) 

14. 

Reagent A and B are, respectively,

(1) A = $NaNH_2$, B = HBr

(2) A ⇒ $NaNH_2$, B = Br_2/CCl_4

(3) A ⇒ NaOH, B = HBr

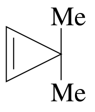
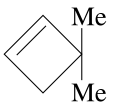
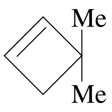
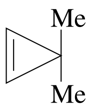
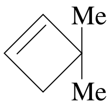
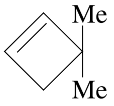
(4) A ⇒ NaOH, B = Br_2/CCl_4

15. $(A)(C_5H_8) \xrightarrow[H_2 + Pt]{1\text{ mole}} (B)(C_5H_{10})$

Resolvable Non-resolvable

$(C)(C_5H_8) \xrightarrow[H_2 + Pt]{2\text{ mole}} (D)(C_5H_{12})$

Which statement is correct about (A) and (C)?

	(A)	(C)
(1)		
(2)		
(3)		MeHC = C = CHMe
(4)	MeHC = C = CHMe	

EXERCISE 3

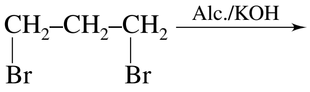
One and More Than One Option Correct Type Question

1. Which of the following reactions will give $CH_2=C=CH_2$?

(1) $CH_2Br–CBr = CH_2 \xrightarrow{Zn/CH_3OH}$

(2) $HC\equiv C - CH_2CO_2H \xrightarrow[2.\text{ electrolysis}]{1.\ K_2CO_3(aq)}$

(3) $2CH_2 = CHCH_2I \xrightarrow{2Na}$

(4) 

$\underset{Br}{CH_2}–CH_2–\underset{Br}{CH_2} \xrightarrow{Alc./KOH}$

2. Which of the following reagent(s) can be used to distinguish between 1-hexyne and 2-hexyne?

(1) Ammoniacal $AgNO_3$ solution

(2) Ammoniacal solution of Cu(II) tartarate

(3) Cold, dilute and alkaline $KMnO_4$

(4) $H_2SO_4/HgSO_4$

3. Which of the following sets of reagent when applied sequentially, on 2-butyne will produce a meso product?

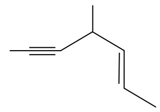
(1) CCl_4/CCl_2 then Br_2/CCl_4

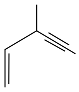
(2) $Na/NH_3(l)$ then Br_2/CCl_4

(3) $Pd/BaSO_4/H_2$ then $Br_2–CCl_4$

(4) $Pd/BaSO_4/H_2$ then $OsO_4/NaHSO_3$

4. Which would produce chiral molecule after treatment with Lindlar catalyst?

(1)


(2)


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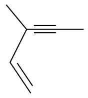
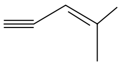


(4)


Assertion and Reason Type Question

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

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

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

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

5. **Statement I:** Sodium alkynides ($RC\equiv\overset{\ominus}{C}\ \overset{\oplus}{Na}$) cannot be alkylated with $(CH_3)_3C–Br$ to form $R–C\equiv C–C(CH_3)_3$.

Statement II: The approach of the nucleophile $RC\equiv C^-$ from the opposite side of the C–Br of $(CH_3)_3CBr$ is hindered by the three bulky methyl groups.

6. **Statement I:** Treatment of either 1,2-dibromobutane or 2,2-dibromobutane with $NaNH_2$ gives the same 1-butyne.

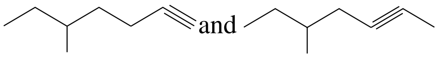
Statement II: $NaNH_2$ forms salt with terminal alkyne which makes possible the above observation

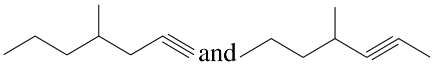
Comprehension Type Question

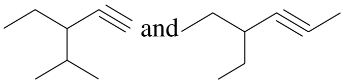
Comprehension (Q. 7–9)

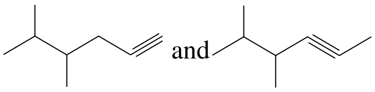
Two isomeric alkynes A and B have molecular formula C_8H_{14} A on treatment with ammoniacal $AgNO_3$ solution forms a white precipitate while B on similar treatment formed no precipitate. Also both A and B are chiral and hydrogenation of either A or B with H_2/Pt gives the same achiral hydrocarbon C (C_8H_{18}). Treatment of A with $HgSO_4/H_2SO_4$ (aq.) gives D ($C_8H_{16}O$) as major product, while on similar treatment of B, mixture of D and E in comparable amounts are formed.

7. The structures of A and B are respectively

(1)


(2)


(3)


(4)


8. The correct statement regarding A and B is

(1) A and B are chain isomers

(2) A and B are positional isomers

(3) A and B are stereoisomers

(4) Both A and B have only one methyl group

9. What is true regarding A and B?

(1) Both will evolve $H_2(g)$ on heating with Na metal

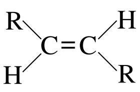
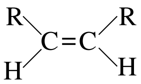
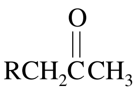
(2) A will give same product with either $HgSO_4/H_2SO_4$ or $B_2H_6/H_2O_2/NaOH$

(3) B will give same product with either $HgSO_4/H_2SO_4$ or $B_2H_6/H_2O_2/NaOH$

(4) Both will produce white ppt. with Tollens' reagent

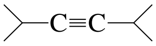
Column Matching Type Question

10. Mach the following

Column-I	***Column-II***
(A) $R–C\equiv C–R + Pd/C/H_2 \longrightarrow$	(p) 
(B) $R–C\equiv C–R + Li/NH_3 \longrightarrow$	(q) RCH_2CH_2R
(C) $R–C\equiv C–R + Pd/CaCO_3/PbO/H_2 \longrightarrow$	(r) 
(D) $R–C\equiv C–R + \dfrac{BH_3.THF}{CH_3COOH}$	(s)  $RCH_2\overset{O}{\overset{\Vert}{C}}CH_3$

(1) A → p; B → q; C → r; D → q
(2) A → q; B → p; C → r; D → q
(3) A → r; B → s; C → q; D → p
(4) A → q; B → r; C → p; D → s

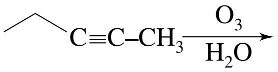
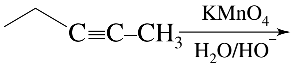
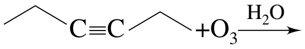
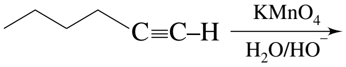
11. Column-I has some alkynes and Column-II has their corresponding reaction products. Match them appropriately.

Column-I	***Column-II***
(1) 1-pentyne	(P) Gives two carbonyls when treated with $H_2SO_4/HgSO_4$
(2) 2-pentyne	(Q) Gives a single carbonyls when treated with $H_2SO_4/HgSO_4$
(3) 	(R) Decolourises brown colour of $Br_2–H_2O$ solution
(4) $C_6H_5–C≡C–CH_3$	(S) First on reaction with $Na/NH_3(l)$ the addition of Br_2 gives racemic dibromides

Code

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

12. Column-I has some reaction and Column-II has the characteristics of reactions and products of Column-I. Match the appropriately.

Column-I	***Column-II***
(A) 	(P) Gives only one type of carboxylic acid
(B) 	(Q) Gives more than one type of carboxylic acids
(C) 	(R) Gives off CO_2
(D) 	(S) Involve an *in situ* preparation of oxidizing agent

Code

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

Single Digit Integer Type Question

13. In the reaction below:

$$\underset{X}{CH_3–C≡C–C≡C–C_2H_5} \xrightarrow{\text{Lindlar's catalyst excess}} \xrightarrow{Br_2\text{-}CCl_4}$$

how many different isomers of tetrabromides are formed?

14. One mole of 1,2-dibromopropane on treatment with X moles of $NaNH_2$ followed by treatment with ethyl bromide gave a pentyne. The value of X is

15. How many different isometric alkynes on catalytic hydrogenation can give 2, 3, 4-trimethyl heptane?

EXERCISE 4

1. Reaction **[AIEEE-2002]**

$H–C≡C–H + HOCl \longrightarrow$ Product, here product will be

(1) $CHCl_2–CHO$ (2) $CHO–CHO$
(3) $CH–Cl≡CHCl$ (4) $CHCl_2–CHCl_2$

2. Acetylene does not react with **[AIEEE-2002]**

(1) $NaNH_2$ (2) NaOH
(3) Na metal (4) Ammonical $AgNO_3$

3. Which of the following reactions will yield 2, 2-dibromopropane? **[AIEEE-2007]**

(1) $CH_3–C≡CH + 2HBr \longrightarrow$

(2) $CH_3CH = CHBr + HBr \longrightarrow$

(3) $CH≡CH + 2HBr \longrightarrow$

(4) $CH_3–CH = CH_2 + HBr \longrightarrow$

4. The hydrocarbon which can react with sodium in liquid ammonia is **[AIEEE-2008]**

(1) $CH_3CH_2C≡CH$

(2) $CH_3CH=CHCH_3$

(3) $CH_3CH_2C≡CCH_2CH_3$

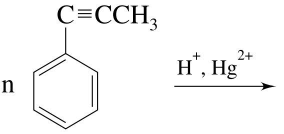
(4) $CH_3CH_2CH_2C≡CCH_2CH_2CH_3$

5. The hydration of propyne results in formation of **[JEE Main Online-2012]**

(1) Propanol-1 (2) Propanal

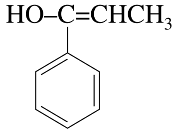
(3) Acetone (4) Propene

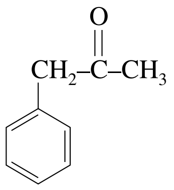
6. In the given reaction

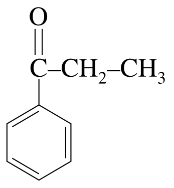


The product 'A' is

[JEE Main Online-2012]

(1)


(2)


(3)


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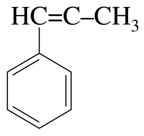
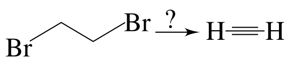


7. The major organic compound formed by the reaction of 1, 1, 1–trichloroethane with silver powder is **[JEE Main Online-2014]**

(1) Ethene (2) 2-Butyne

(3) 2-Butene (4) Acetylene

8. The reagent(s) for the following conversion,



is/are **[IIT Online-2007]**

(1) alcoholic KOH

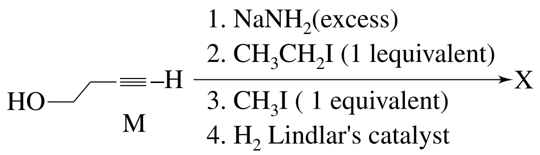
(2) alcoholic KOH followed by $NaNH_2$

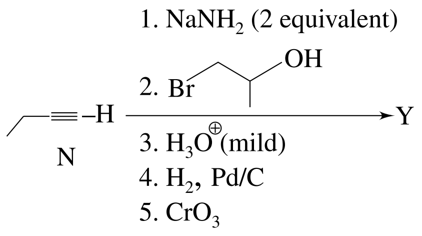
(3) aqueous KOH followed by $NaNH_2$

(4) Zn/CH_3OH

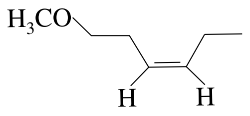
Passage: (9 and 10)

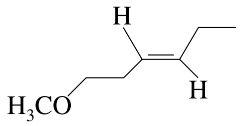
Schemes 1 and 2 describe sequential transformation of alkynes M and N. Consider only the major products formed in each step for both the schemes.

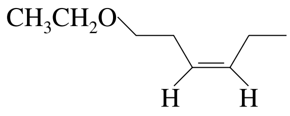


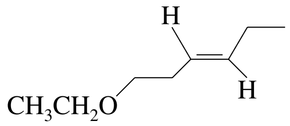


9. The product X is- **[JEE Adv.-2014]**

(1)


(2)


(3)


(4)


10. The correct statement with respect to product Y is **[JEE Adv.-2014]**

(1) It gives a positive Tollens' test and is a functional isomer of X

(2) It gives a positive Tollens' test and is a geometrical isomer of X

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

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

ANSWER KEY

EXERCISE # 1

1. (3) 2. (2) 3. (2) 4. (1) 5. (2)
6. (3) 7. (3) 8. (1) 9. (4) 10. (2)
11. (3) 12. (2) 13. (1) 14. (4) 15. (4)
16. (1) 17. (1) 18. (2) 19. (1) 20. (4)

EXERCISE # 2

1. (4) 2. (3) 3. (2) 4. (2) 5. (3)
6. (2) 7. (2) 8. (1) 9. (3) 10. (3)
11. (4) 12. (3) 13. (4) 14. (1) 15. (3)

EXERCISE # 3

1. (1,4) 2. (1,2) 3. (1,2,4) 4. (1,2,3) 5. (1)
6. (1) 7. (2) 8. (2) 9. (3) 10. (2)
11. (1) 12. (1) 13. (4) 14. (3) 15. (8)

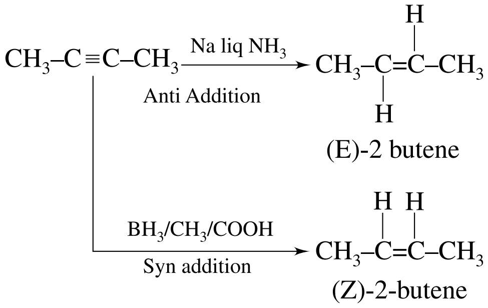
EXERCISE # 4

1. (1) 2. (2) 3. (1) 4. (1) 5. (3)
6. (3) 7. (2) 8. (2) 9. (1) 10. (3)

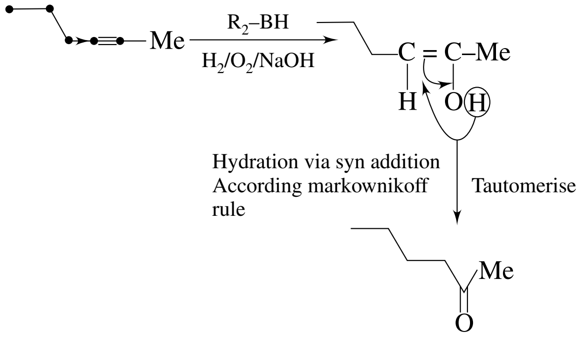
HINT AND SOLUTION

EXERCISE # 1

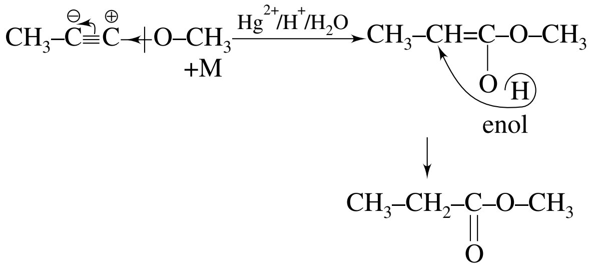
1. [3]



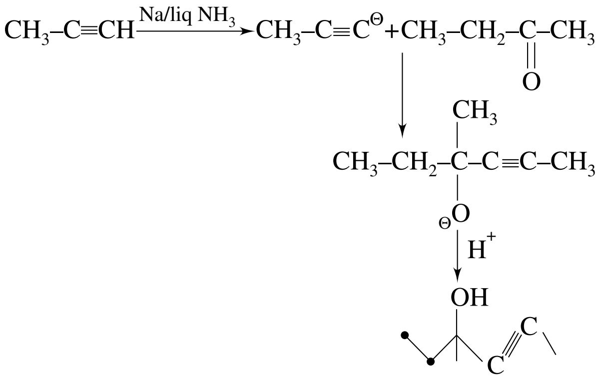
2. [2]



3. [2]

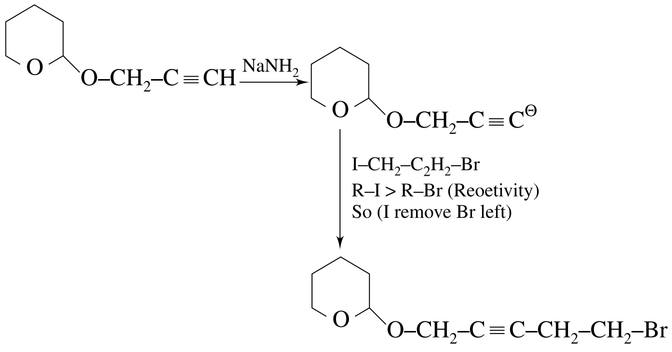


4. [1]

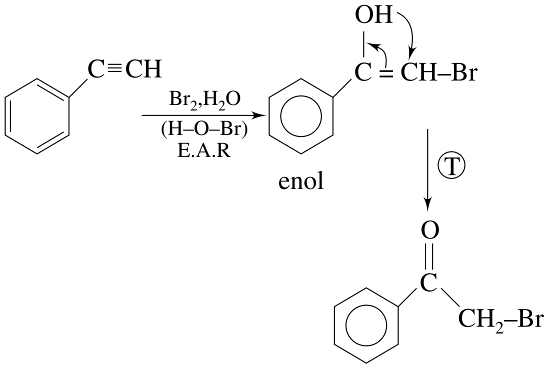


5. [2]

6. [3]

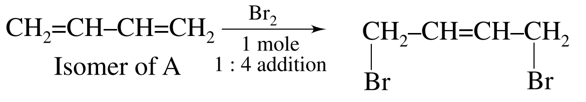


7. [3]



8. [1] A must be teminal alkyne

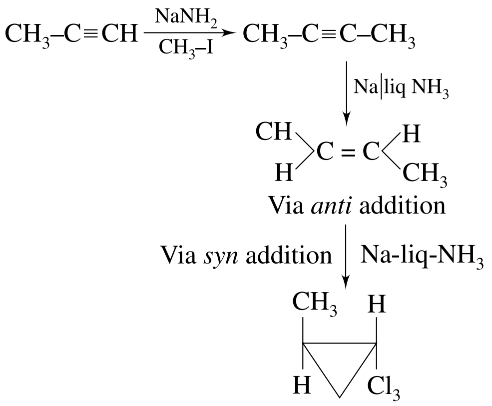
$$\underset{\substack{(A)\\(C_4H_6)}}{CH_3-CH_2-C\equiv CH} \xrightarrow[\text{reagent}]{\text{Tollen's}} \underset{\text{White ppt}}{CH_3-CH_2-C\equiv C-Ag}$$



$$\underset{\text{Isomer of A}}{CH_2=CH-CH=CH_2} \xrightarrow[\substack{1\text{ mole}\\1:4\text{ addition}}]{Br_2} \underset{Br}{CH_2}-CH=CH-\underset{Br}{CH_2}$$

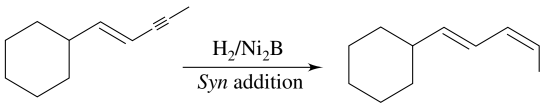
1, 4-dibromo-2-butene

9. [4]



(±)-trans-1,2-dimethylcyclopropane

10. [2]

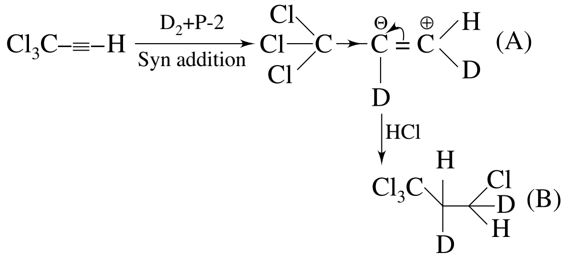


11. [3]

Electrophile substitution reaction takes place

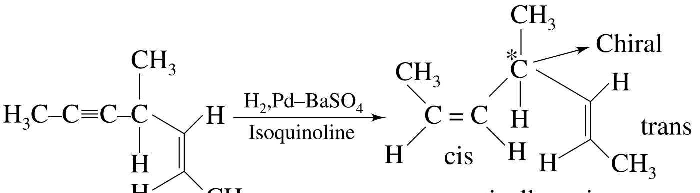
$$Ph-C\equiv C-H \xrightarrow{I_2/\text{base}} Ph-C\equiv C-I$$

12. [2]



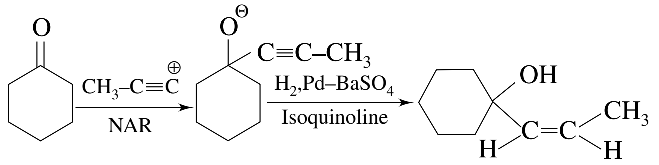
(Due to –I effect of three Cl atoms, electromeric effect takes place from C–1 to C–2)

13. [1]

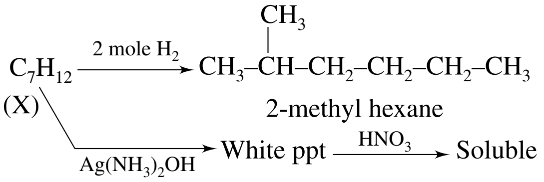


optically active

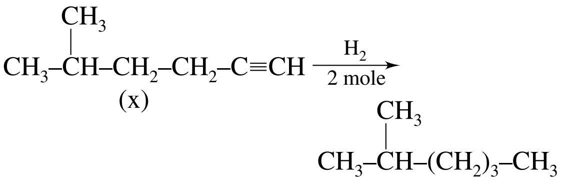
14. [4]



15. [4]

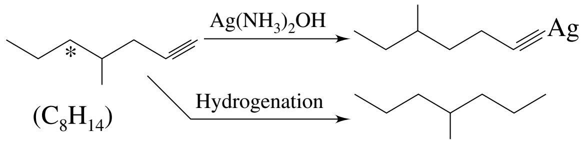


X → must be terminal alkyne having iso group



$$\underset{(x)}{CH_3-\overset{CH_3}{CH}-CH_2-CH_2-C\equiv CH} \xrightarrow[2\text{ mole}]{H_2} CH_3-\overset{CH_3}{CH}-(CH_2)_3-CH_3$$

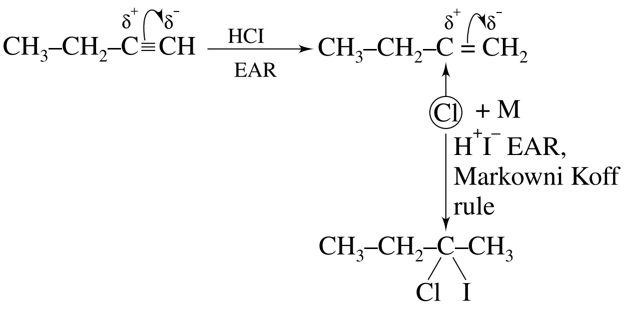
16. [1] A must be terminal alkyne



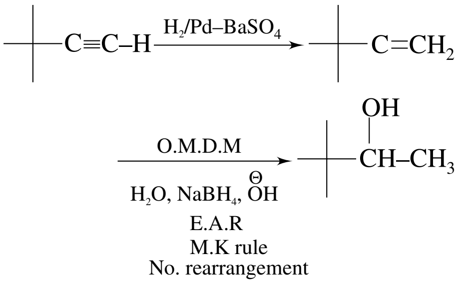
(C_8H_{14})
Optically active
(A)

(C_8H_{18})
Optically inactive
(B)

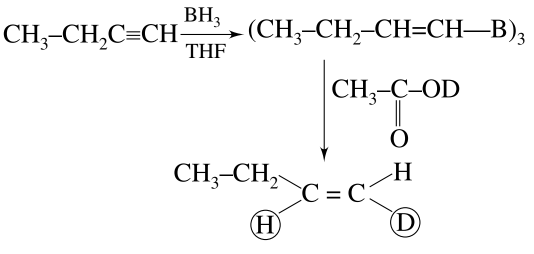
17. [1]



18. [2]

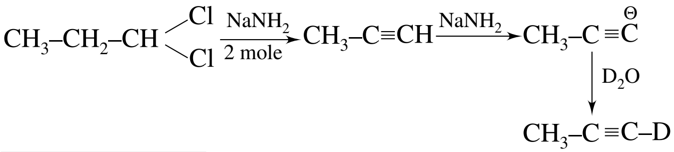


19. [1]



via syn addition

20. [4]

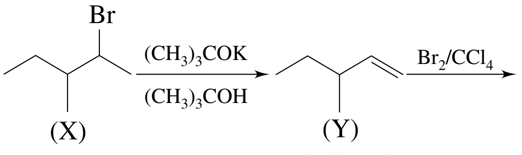


EXERCISE # 2

1. [4]

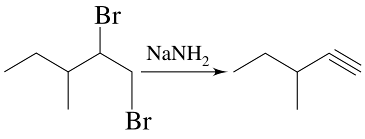
The last product formed after dehydrobromination (–2HBr) is an alkyne. The only optically active alkyne with six carbon atoms is 3-methly-1-pentene.

Hence, Y must be 3-methyl-1-pentene.



(X) Optically active

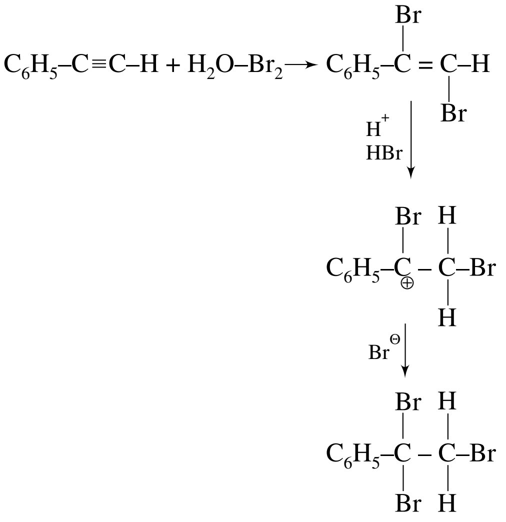
(Y) Optically active



2. [3]

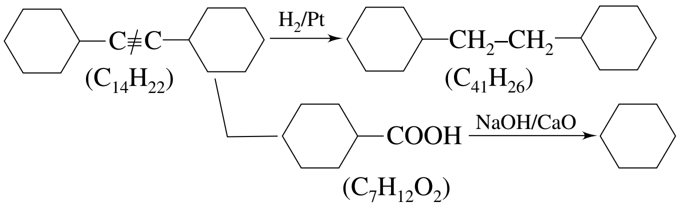
Triple bond cannot be formed in option 3 here between carbons bearing bromine atoms.

3. [2]

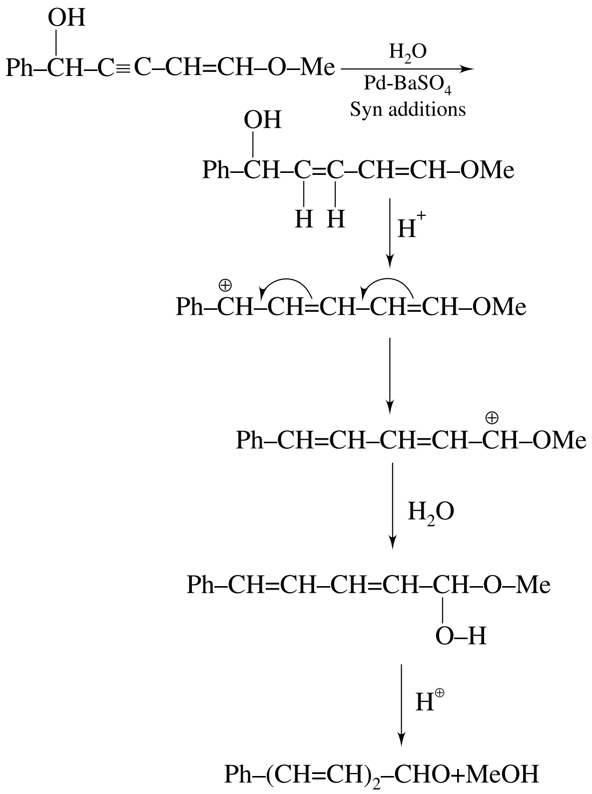


4. [2]

Decarboxylation reaction indicates that the acid is cyclohexane carboxylic acid. Hence, the alkyl must by dicyclohexyl ethyne.

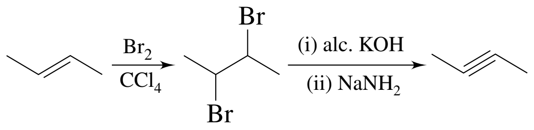


5. [3]

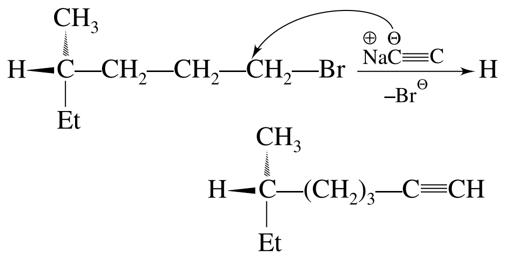


6. [2]

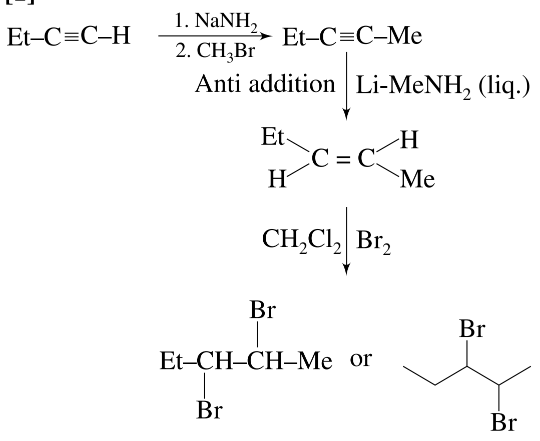
Formation of vicinal di-halide followed by two consecutive E_2 reaction.



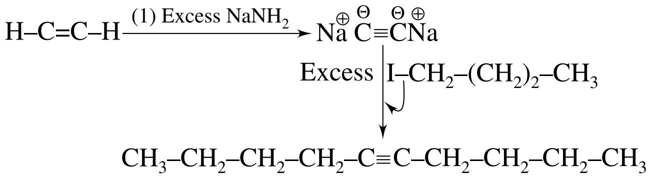
7. [2]



8. [1]

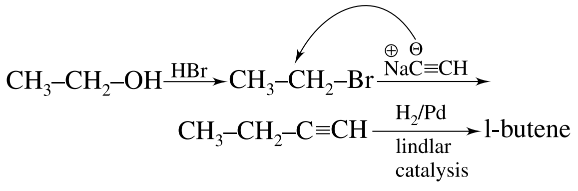


9. [3]



5-Decyne

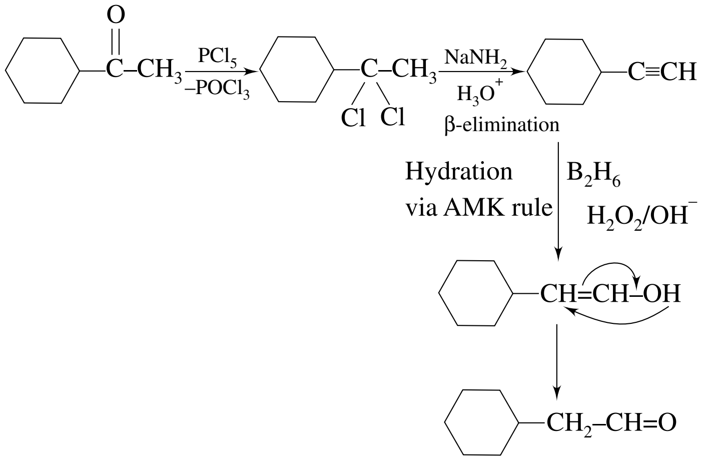
10. [3]



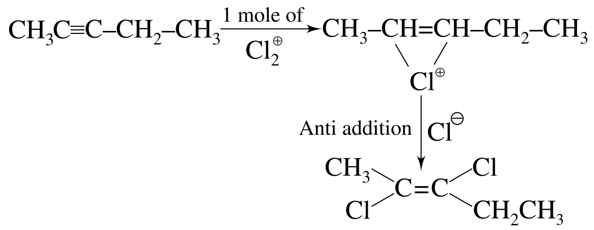
11. [4]

Strong base NH_2^- takes H from β-position.

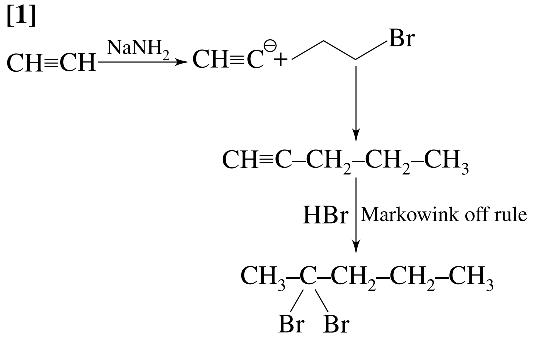
12. [3]



13. [4]



14. [1]

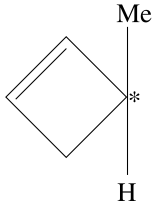


15. [3]

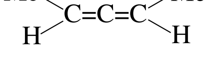
$$DU = (C + 1) - \left(\frac{H + X + N}{2}\right) = (5 + 1) - \frac{8}{2} = 2$$

D.U. of A is 2, it must have 3C, 4 C or 5C-ring, but 5C-ring alkene will not show optical isomerism

So structure of (A) ⇒

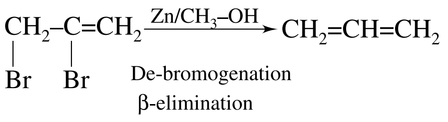


Similarly, D.U. of C is also 2, it must have two double bond, so that cannot have ring; therefore, only allenes with two different groups are resolvable. So the structure of (C) is:



EXERCISE # 3

1. [1, 4]

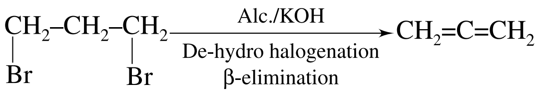


$$\underset{Br}{CH_2}-\underset{Br}{C}=CH_2 \xrightarrow{Zn/CH_3-OH} CH_2=CH=CH_2$$

De-bromogenation
β-elimination

$$HC\equiv C-CH_2CO_2H \xrightarrow[\text{2. electrolysis}]{\text{1. } K_2CO_3(aq)} CH\equiv C-CH_2-CH_2-C\equiv CH$$

$$2CH_2 = CHCH_2I \xrightarrow{2Na} CH_2=CH-CH_2-CH_2-CH=CH_2$$



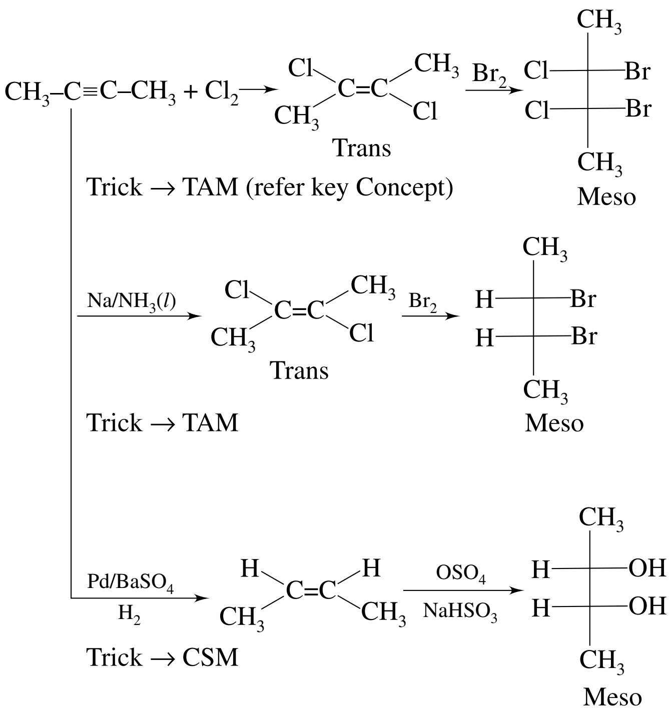
$$\underset{Br}{CH_2}-CH_2-\underset{Br}{CH_2} \xrightarrow[\text{De-hydro halogenation}]{\text{Alc./KOH}} CH_2=C=CH_2$$

β-elimination

2. [1, 2]

1-hexyne being terminal alkyne, has acidic hydrogen, forms silver and copper salt precipitate respectively while with internal alkyne, 2-hexyne, no such precipitate is formed. Cold, dilute and alkaline $KMnO_4$ (Baeyer's reagent) gives positive test with both terminal and internal alkynes, cannot be used for distinction between them.

3. [1, 2, 3]



Trans

Trick → TAM (refer key Concept)

Meso

Trans

Trick → TAM

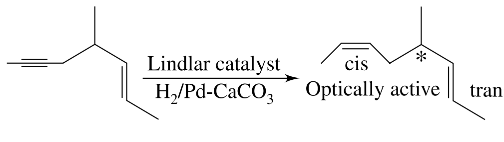
Meso

Trick → CSM

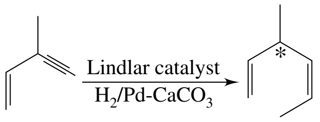
Meso

4. [1, 2, 3]

(1)

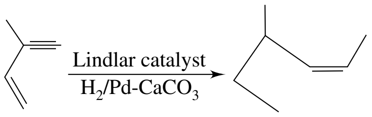


(2)



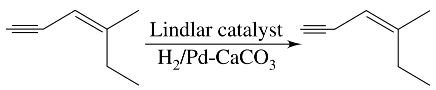
Optically active

(3)



Optically active

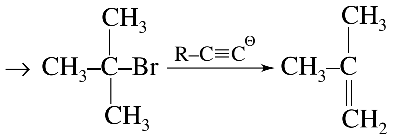
(4)



Optically inactive

5. [1]

→ 3° halide will give β-elimination reaction predominantly with $R-C\equiv C^{\ominus}$



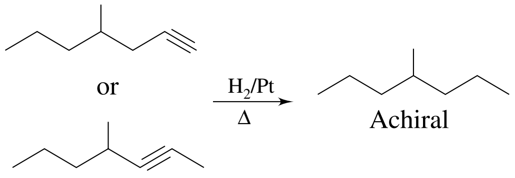
$$\rightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Br \xrightarrow{R-C\equiv C^{\ominus}} CH_3-\overset{CH_3}{\underset{CH_2}{C}}$$

i.e., $nu^{\ominus}$ do not approach from opposite site

6. [1]

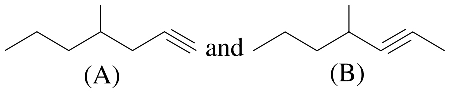
7. [9]

Since, both A and B giving achiral alkane 'C' on catalytic hydrogenation methyl group must be at the central carbon.



Both chiral

Since, A reacts with Tollens' reagent, B does not, A is terminal alkyne while B is internal alkyne Hence,



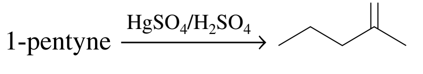
7. [2]

8. [2]

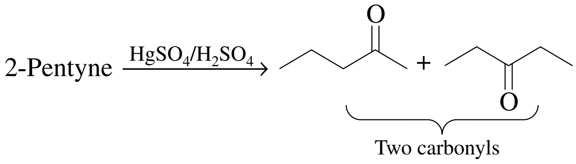
9. [3]

10. [2]

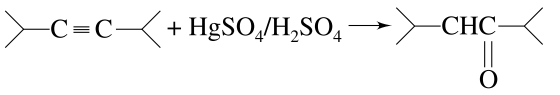
11. [1]

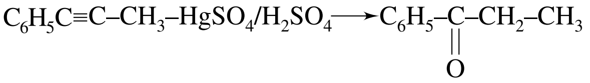


Single carbonyl



Two carbonyls





$$C_6H_5C{\equiv}C{-}CH_3{-}HgSO_4/H_2SO_4 \longrightarrow C_6H_5{-}\underset{\underset{O}{\|}}{C}{-}CH_2{-}CH_3$$

Single carbonyl (2)

All of the above decolourises brown Br_2–H_2O solution

(A) → Q, R, S; (B) → P, R, S; (C) → Q, R; (D) → Q, R, S

12. [1]

Ozonolysis of alkynes followed by hydrolysis result in formation of carboxylic acids as

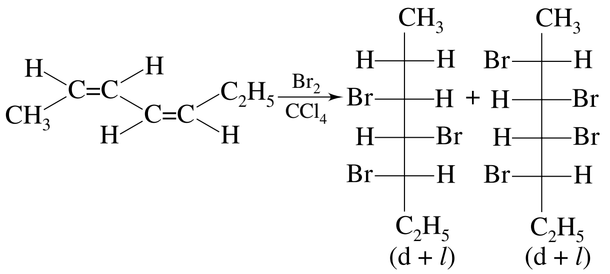
$$R{-}C{\equiv}C{-}R' + O_3 \xrightarrow{H_2O} R{-}COOH + R'{-}COOH$$

Here, hydrolysis of intermediate ozonide produces H_2O_2 which oxidizes the previously formed aldehydes into R–COOH

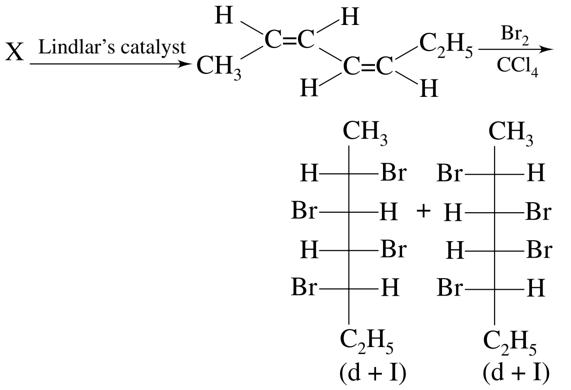
The aldehydes are oxidised further into carboxylic acid. With KMnO4, all internal or terminal alkynes are oxidised to acid

A → Q, S; B → Q; C → P, S; D → P, R

13. [4]

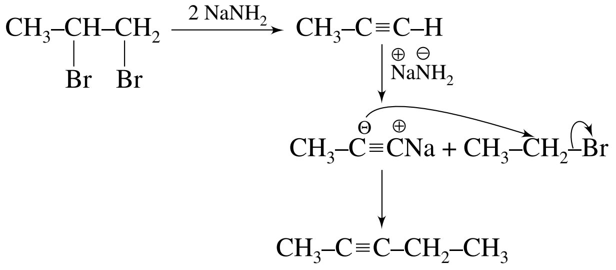


Only *anti*-dibromide at each double bond is formed.



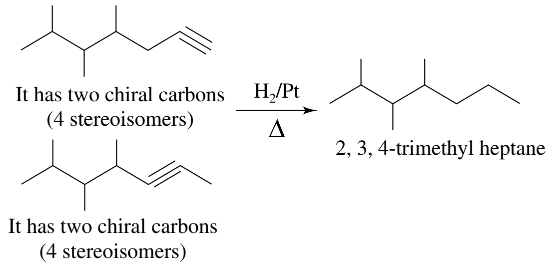
Only *anti*-dibromide at each double bond is formed.

14. [3]



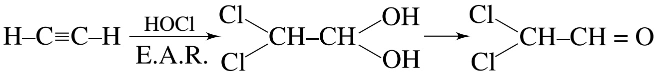
Total 3 moles of $NaNH_2$ are required.

15. [8]



EXERCISE # 4

1. [1]



$$H{-}C{\equiv}C{-}H \xrightarrow[E.A.R.]{HOCl} \begin{matrix}Cl\\Cl\end{matrix}{>}CH{-}CH{<}\begin{matrix}OH\\OH\end{matrix} \longrightarrow \begin{matrix}Cl\\Cl\end{matrix}{>}CH{-}CH=O$$

2. [2]

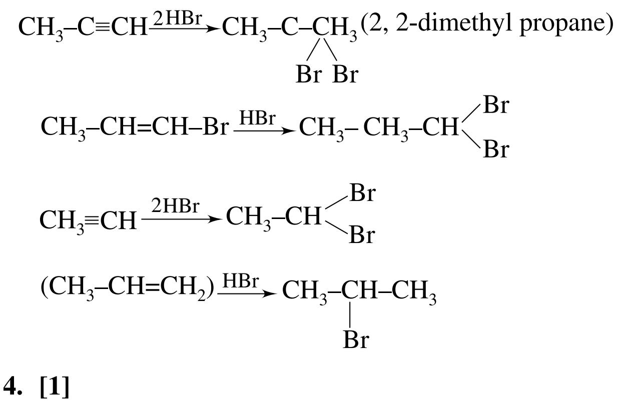
$$H{-}C{\equiv}CH \xrightarrow{NaOH} CH{\equiv}\overset{\ominus}{C}\overset{\oplus}{Na} + H_2O$$

This reaction is not possible due to SAWB Theory

Acidic strength H–C≡CH < H_2O

So that this reaction is not feasible.

3. [1]



$$CH_3{-}C{\equiv}CH \xrightarrow{2HBr} CH_3{-}\underset{Br\ Br}{C}{-}CH_3 \text{ (2, 2-dimethyl propane)}$$

$$CH_3{-}CH{=}CH{-}Br \xrightarrow{HBr} CH_3{-}CH_3{-}CH{<}\begin{matrix}Br\\Br\end{matrix}$$

$$CH_3{\equiv}CH \xrightarrow{2HBr} CH_3{-}CH{<}\begin{matrix}Br\\Br\end{matrix}$$

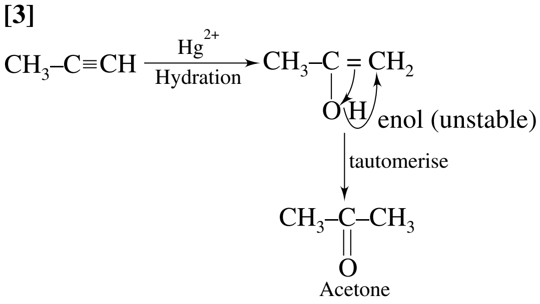
$$(CH_3{-}CH{=}CH_2) \xrightarrow{HBr} CH_3{-}\underset{Br}{CH}{-}CH_3$$

4. [1]

Only acidic H alkyne gives acid base reaction with Na/liq NH_3

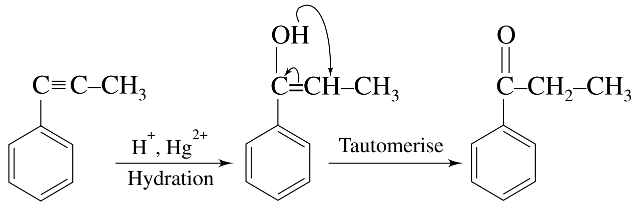
$$CH_3CH_2{\equiv}CH \xrightarrow[\Delta]{Na/liq.\ NH_3} CH_3CH_2C{\equiv}CNa + NH_3$$

5. [3]

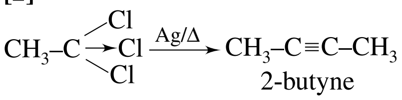

$CH_3-C\equiv CH \xrightarrow[\text{Hydration}]{Hg^{2+}} CH_3-\underset{OH}{C}=CH_2$ enol (unstable) $\xrightarrow{\text{tautomerise}} CH_3-\underset{O}{\overset{\|}{C}}-CH_3$

Acetone

6. [3]


(relatively stable enol)

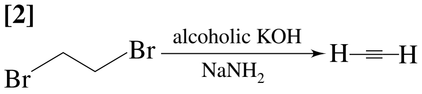
7. [2]


$CH_3-CCl_3 \xrightarrow{Ag/\Delta} CH_3-C\equiv C-CH_3$

2-butyne

This reaction completed by methyl carbyne ($CH_3-\overset{\cdots}{C}$) intermediate **

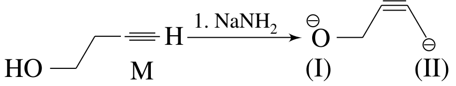
8. [2]



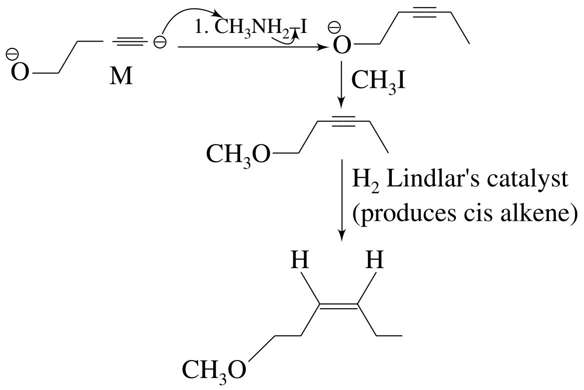
9. [1]

This problem can be solved by using the concept of nucleophilic substitution reaction, oxidation reaction and reduction reaction including strength of nucleophile and regioselectivity.

Reaction of Scheme 1 can be completed as



Among two nacked nucleophilic group I and II, II is more nucleophilic and then will react selectively as follows

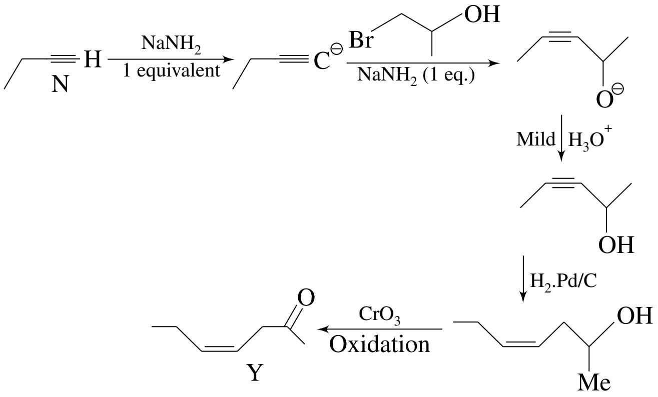


Hence, using the concept of regioselectivity we come on the conclusion that final product is correctly represented by structure (1).

10. [3]

This problem can be solved by using the concept of iodoform test and functional isomerism,

Iodoform test the compound containing $-COCH_3$ or $-CH(OH)$ group will undergo iodoform test.



Thus, X and Y are function isomers of each other and Y Gives iodoform test due to the presence of CH_3CO group as indicated Hence, correct choice is (3)