EXAM DRILL

Hydrocarbons

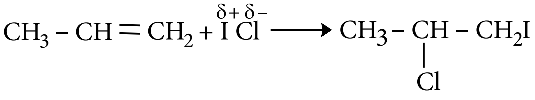
CHAPTER
13

ANSWERS

1. (b) :

$$CH_3-CH{=}CH_2+Cl_2\xrightarrow{400\text{-}600°C}\underset{\text{Allyl chloride}}{Cl-CH_2-CH{=}CH_2}$$

At high temperature, halogenation takes place at allylic position.

2. (c) : 

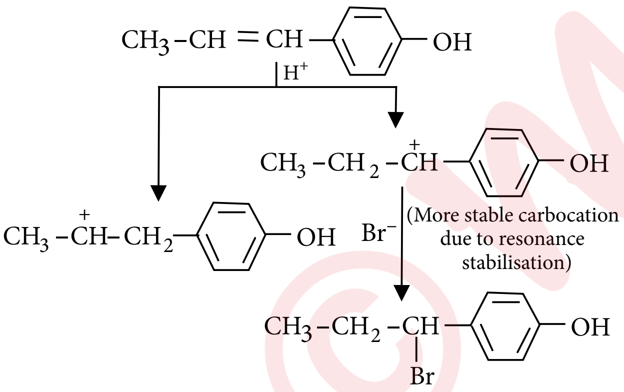
$$CH_3-CH{=}CH_2+\overset{\delta+}{I}\overset{\delta-}{Cl}\longrightarrow CH_3-\underset{\underset{Cl}{|}}{CH}-CH_2I$$

In case of addition of interhalogen compounds, the halogen atom with lower electronegativity is assigned partial positive charge whereas halogen atom with comparatively higher electronegativity is assigned partial negative charge. Order of electronegativity of various halogen atoms is

$$F > Cl > Br > I$$

3. (d)

4. (b) :



5. (d) : $(CH_3)_2C=CH_2$ is the most stable alkene among the given compounds (due to higher substitution at doubly bonded carbon atom), hence least reactive.

6. (d) : Hex-3-yne yields propanoic acid as the only product upon treatment with ozone followed by hydrolysis.

7. (c) : Lower boiling point of *trans*-isomers of alkenes is due to their less polar nature.

8. (b) : Among the given substituents, —Cl is an *ortho* and *para* director and ring deactivating.

9. Benzene

10. Biphenyl

11. Gammaxene

12. *n*-Hexane

13. Torsional strain

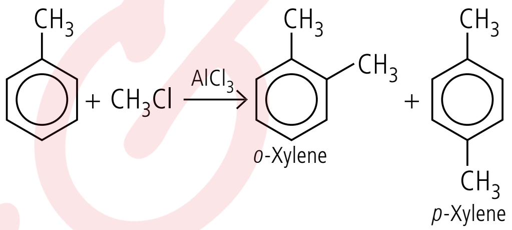
14. (a) : Isomers of pentane and their boiling points are :

Pentane ; b.pt - 309.1 K

2-Methylbutane ; b.pt-300.9 K

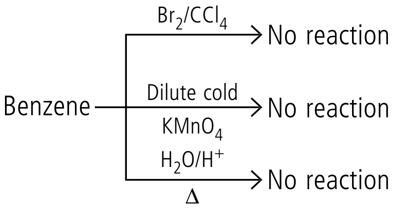
2, 2-Dimethylpropane ; bpt.-282.5 K

15. (a) :



16. (b) : In the case of aryl halides, halogens are moderately deactivating because of their strong –*I* effect. The Overall electron density on benzene ring decreases due to this-*I*- effect. It makes further substitution difficult. However, due to resonance the electron density on *o*– and *p*– positions is greater than that at the *m*-position. Hence they are also called *o*– and *p*– directing groups.

17. Benzene could be constructed as a straight chain or ring compound having double (C=C) and/or triple (C≡C) bond. But benzene did not behave like alkenes or alkynes. It did not decolourise bromine in carbon tetrachloride or cold aqueous potassium permanganate solution. It did not add water in the presence of acids.



OR

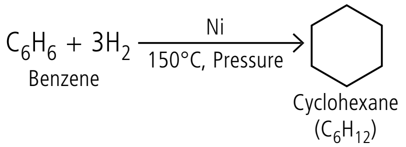
Evidences showing the cyclic structure of benzene are :

(a) Substitution of benzene : Benzene reacts with bromine in the presence of $FeBr_3$ (catalyst) to form monobromo benzene.

$$\underset{\text{Benzene}}{C_6H_6}+Br_2\xrightarrow{FeBr_3}\underset{\text{Bromobenzene}}{C_6H_5Br}+HBr$$

In this reaction one monobromobenzene and no isomeric products were obtained indicating that all six hydrogen atoms in benzene were identical. This could be possible only if benzene has a cyclic structure of six carbons and to each carbon was attached one hydrogen.

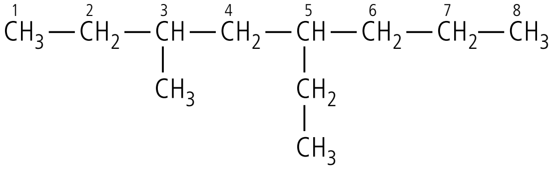
(b) Addition of hydrogen : Benzene added three moles of hydrogen in the presence of nickel catalyst to give cyclohexane.



This confirmed the cyclic structure of benzene and showed the presence of three carbon-carbon double bonds.

18.

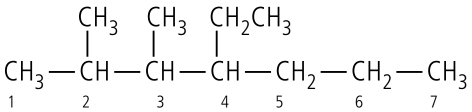
(i)



$$\overset{1}{CH_3}-\overset{2}{CH_2}-\underset{\substack{|\\ CH_3}}{\overset{3}{CH}}-\overset{4}{CH_2}-\underset{\substack{|\\ CH_2\\ |\\ CH_3}}{\overset{5}{CH}}-\overset{6}{CH_2}-\overset{7}{CH_2}-\overset{8}{CH_3}$$

5-Ethyl-3-Methyloctane

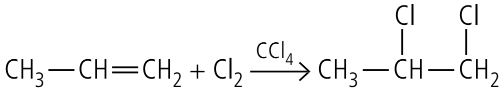
(ii)



$$\underset{1}{CH_3}-\underset{2}{\overset{\substack{CH_3\\ |}}{CH}}-\underset{3}{\overset{\substack{CH_3\\ |}}{CH}}-\underset{4}{\overset{\substack{CH_2CH_3\\ |}}{CH}}-\underset{5}{CH_2}-\underset{6}{CH_2}-\underset{7}{CH_3}$$

4-Ethyl-2, 3-dimethylheptane

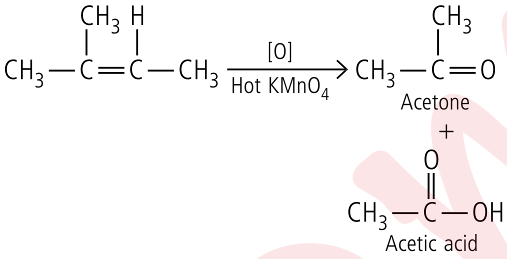
19. (i)



$$CH_3-CH=CH_2+Cl_2\xrightarrow{CCl_4}CH_3-\overset{\substack{Cl\\ |}}{CH}-\overset{\substack{Cl\\ |}}{CH_2}$$

Propene 1, 2-Dichloropropane

(ii)



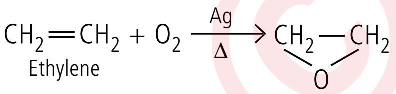
$$CH_3-\overset{\substack{CH_3\\ |}}{C}=\overset{\substack{H\\ |}}{C}-CH_3\xrightarrow[\text{Hot } KMnO_4]{[O]}CH_3-\overset{\substack{CH_3\\ |}}{C}=O+CH_3-\overset{\substack{O\\ \|}}{C}-OH$$

Acetone

Acetic acid

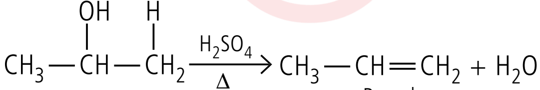
OR

(i)



Ethylene oxide

(ii)



$$CH_3-\overset{\substack{OH\\ |}}{CH}-\overset{\substack{H\\ |}}{CH_2}\xrightarrow[\Delta]{H_2SO_4}CH_3-CH=CH_2+H_2O$$

Propylene

20. To synthesise propane from methane use Corey-House synthesis instead of Wurtz reaction because Corey-House synthesis give a symmetric alkane while Wurtz reaction gives only symmetrical alkane.

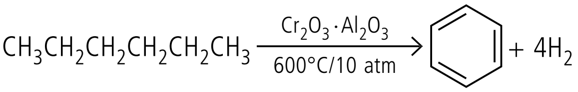
$$\underset{\text{Methane}}{CH_4}\xrightarrow[UV]{Cl_2}CH_3Cl\xrightarrow{Na}CH_3CH_3\xrightarrow[UV]{Cl_2}CH_3CH_2Cl$$

$$CH_3CH_2Cl\xrightarrow{Li}CH_3CH_2Li\xrightarrow{CuI}(CH_3CH_2)_2CuLi$$

$$\downarrow CH_3Cl$$

$$\underset{\text{Propane}}{CH_3CH_2CH_3}$$

21. When *n*-hexane is passed over Cr_2O_3 supported over alumina at 600°C, benzene is produced. Platinum supported over alumina can also be used as a catalyst. The reaction involves simultaneous cyclisation and dehydrogenation.



Benzene

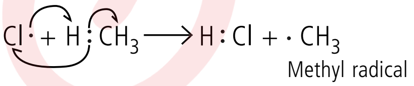
22. $CH_4 + Cl_2 \xrightarrow{UV} CH_3Cl + HCl$

Mechanism : The chlorination of alkanes takes place through the formation of free radicals.

Chain-initiation step : Chlorine molecule undergoes homolytic fission to give chlorine free radicals.

$$Cl:Cl \xrightarrow[\text{or } \Delta]{\text{UV light}} Cl\cdot + Cl\cdot$$

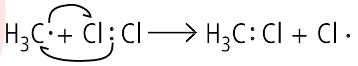
Chain-propagation step : (a) Chlorine free radical attacks methane to produce HCl and methyl free radical.



$$Cl\cdot + H:CH_3 \longrightarrow H:Cl + \cdot CH_3$$

Methyl radical

(b) Methyl free radical attacks chlorine molecule to give methyl chloride and chlorine free radical.



$$H_3C\cdot + Cl:Cl \longrightarrow H_3C:Cl + Cl\cdot$$

Steps (a) and (b) are replaced over and over again.

Chain-termination steps : The above chain reaction comes to half when any two free radicals combine.

For example,

$Cl\cdot + \cdot Cl \longrightarrow Cl-Cl$

$CH_3\cdot + \cdot Cl \longrightarrow CH_3-Cl$

$CH_3\cdot + \cdot CH_3 \longrightarrow CH_3-CH_3$

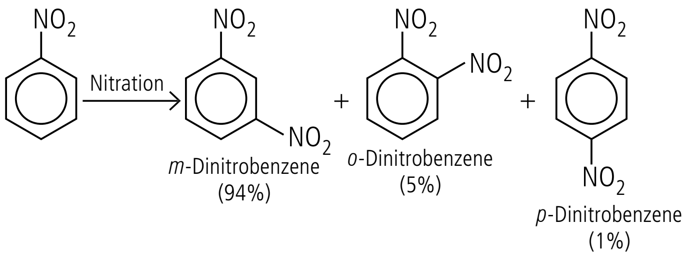
23. Wurtz synthesis : Higher alkanes are produced by heating an alkyl halide (*RX*) with sodium metal in dry ether solution. Two molecules of the alkyl halide lose their halogen atoms as Na*X*. The net result is the joining of two alkyl groups to yield a symmetrical alkane (*R*—*R*) type having an even number of carbon atom.

Examples :

$$CH_3CH_2-Cl + 2Na + Cl-CH_2CH_3 \xrightarrow{Ether} \underset{n\text{-Butane}}{CH_3CH_2-CH_2CH_3} + 2Na$$

Limitation : The use of two different alkyl halides in *Wurtz* reaction always leads to a mixture of alkanes. The separation of these alkanes is not always easy because of little difference in their boiling points.

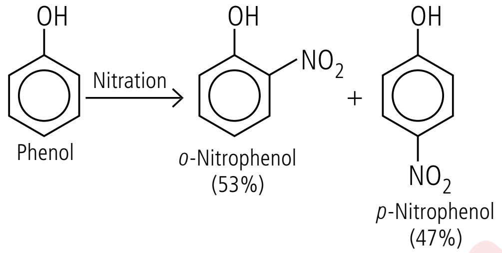
24. The substituents which direct the second incoming substituent primarily to the *meta* position are referred to as *meta*-directors. For example, nitration of nitrobenzene gives 94% of *m*-dinitrobenzene and only 5% of *ortho* and 1% of *para*-dinitrobenzene.



Thus the substituent —NO_2 group, which has directed the second —NO_2 group to the *meta* position, is designated as *meta*-director. Some common meta directing groups are : —SO_3H, —CN, —NO_2, —CHO, —COOH.

OR

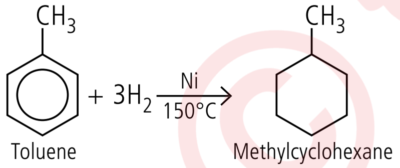
Certain substituents direct the second susbtituent to the *ortho* and *para* position simultaneously. These are called *ortho-para* director. For example, when phenol is nitrated, the only products obtained are *o*-nitrophenol (53%) and *p*-nitrophenol (47%) and no *meta* isomer is produced.



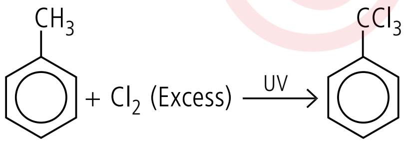
The substituent —OH is said to have directed the —NO_2 group to *ortho* and *para* positions on the ring. Hence, —OH is designated as *ortho-para* director.

Some common *ortho-para* directing groups are —Cl, —Br, —OH, —NH_2, —CH_3, —C_2H_5.

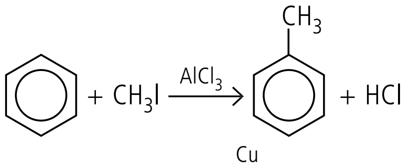
25. (i)



(ii)



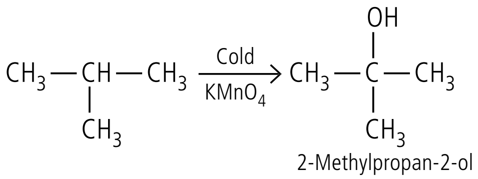
(iii)



26. (i) $$2CH_4 + O_2 \xrightarrow[573\ K/1100\ atm]{Cu} 2CH_3OH$$

Methanol

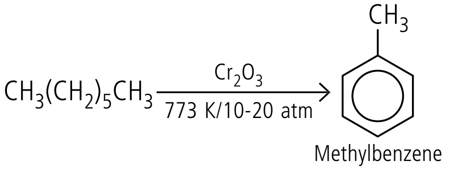
(ii)



$$CH_3-\underset{\underset{CH_3}{|}}{CH}-CH_3 \xrightarrow[KMnO_4]{Cold} CH_3-\overset{\overset{OH}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$$

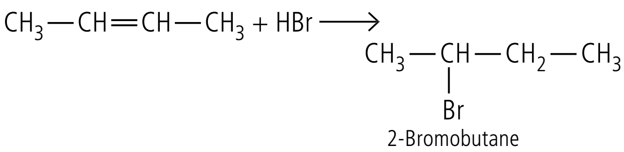
2-Methylpropan-2-ol

(iii)



OR

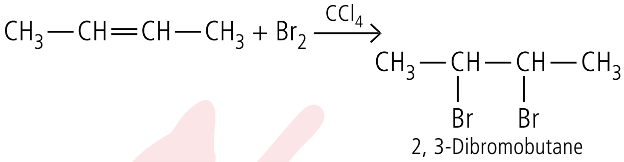
(i)



$$CH_3-CH{=}CH-CH_3 + HBr \longrightarrow CH_3-\underset{\underset{Br}{|}}{CH}-CH_2-CH_3$$

2-Bromobutane

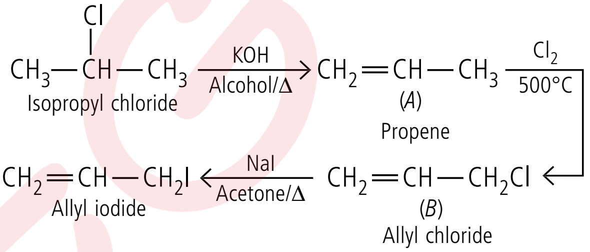
(ii)



$$CH_3-CH{=}CH-CH_3 + Br_2 \xrightarrow{CCl_4} CH_3-\underset{\underset{Br}{|}}{CH}-\underset{\underset{Br}{|}}{CH}-CH_3$$

2, 3-Dibromobutane

27.



28. **(i)** **(c)** **:** But-1-yne add in $AgNO_3$ solution of alcohol give white ppt. but, but-2-yne not give this test

$$CH_3-CH_2-CH{\equiv}CH + Ag^+ \longrightarrow CH_3-CH_2-CH{\equiv}CAg$$

White ppt.

$$CH_3-C{\equiv}C-CH_3 + Ag^+ \longrightarrow \text{No ppt.}$$

(ii) $CH{\equiv}CNa + BrCH_2-CH{=}CH_2 \longrightarrow CH{\equiv}C-CH_2-CH-CH_2$

(iii) $HC{\equiv}CH > CH_3-C{\equiv}CH > CH_3-C{\equiv}C-CH_3$

(iv) Acetylene is acidic but it does not turn blue litmus paper red because it is a weaker acid than water.

(v) $CH_3-CH_2-CH_2-CH + Ag^+ \longrightarrow CH_3CH_2CH_2C{\equiv}CAg$

White ppt.

but pent-2-yne does not give this test.

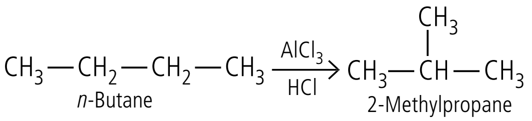
29. (i) $CH_3CH_2COONa + NaOH \xrightarrow{\Delta} CH_3-CH_3 + Na_2CO_3$

Sodium propionate Ethane

(ii) $CH_3CH_2-Cl + 2Na + Cl-CH_3 \xrightarrow[Ether]{Dry} CH_3-CH_3$

$+ CH_3CH_2CH_2CH_3 + CH_3CH_2CH_3 + 2NaCl$

(iii)



$$\underset{n\text{-Butane}}{CH_3-CH_2-CH_2-CH_3} \xrightarrow[HCl]{AlCl_3} CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_3$$

2-Methylpropane

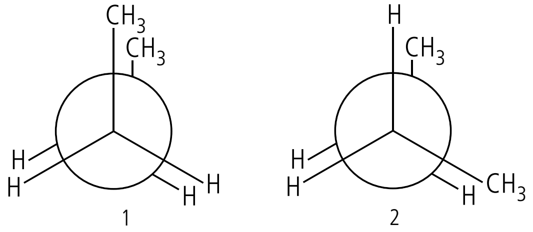
(iv) $CH_3CH_2Br + Li(CH_3)_2Cu \longrightarrow CH_3CH_2CH_3 + CH_3Cu + LiBr$

(v) $CH_3-CH{=}CH_2 + H_2 \xrightarrow[\Delta]{Pt} CH_3-CH_2-CH_3$

Propane

OR

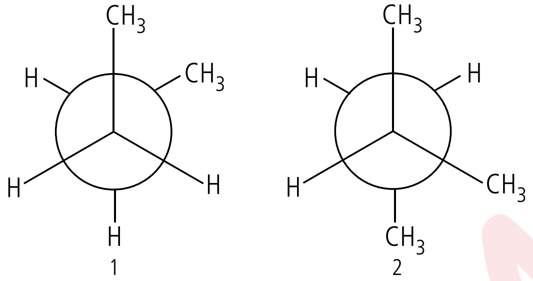
Conformation of butane : All eclipsed conformations are equivalent in case of ethane and propane. But in the case of butane, two distinct conformations are possible, one in which a methyl group is eclipsed by a methyl group and the other in which the methyl groups are eclipsed by hydrogens.



Eclipsed conformations of butane

out of these two eclipsed conformations, the one having larger methyl groups eclipsed (1), will naturally experience more repulsive forces than the one where a methyl group is faced with a hydrogen atom (2). Thus, the conformation (2) is favoured from stability stand point.

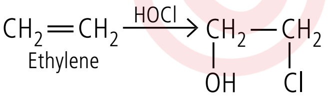
Like wise, it will be observed that for butane two different staggered conformations are possible.



Staggered conformation of butane

In (1) the methyl groups are at an angle of 60° to each other. This is called gauche conformation. In (2) the methyl groups are at an angle of 180° to each other. This is called Anti or *Trans* conformation. The repulsive forces will be greater in (1) than in (2) due to proxime of the methyl groups in the former. Consequently the conformation (2) is associated with least energy and maximum stability.

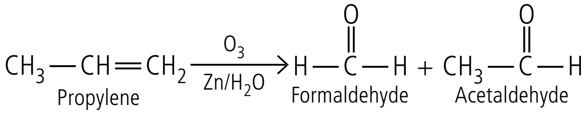
30. (a) (i)



$$\underset{\text{Ethylene}}{CH_2{=}CH_2} \xrightarrow{HOCl} \underset{OH}{CH_2}-\underset{Cl}{CH_2}$$

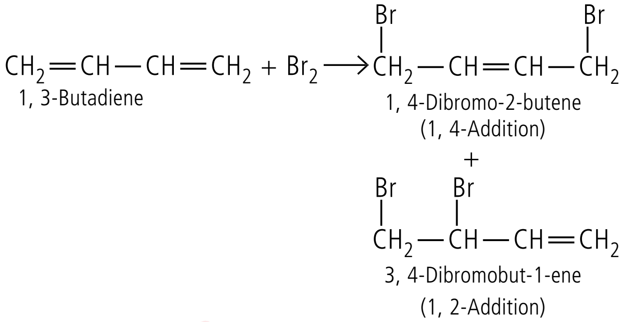
Ethylene Chlorohydrin

(ii)



$$\underset{\text{Propylene}}{CH_3-CH{=}CH_2} \xrightarrow[Zn/H_2O]{O_3} \underset{\text{Formaldehyde}}{H-\overset{\overset{O}{\|}}{C}-H} + \underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{O}{\|}}{C}-H}$$

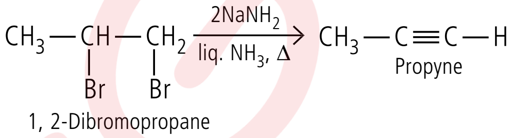
(iii)



$$\underset{\text{1, 3-Butadiene}}{CH_2{=}CH-CH{=}CH_2} + Br_2 \longrightarrow \underset{\substack{\text{1, 4-Dibromo-2-butene}\\ \text{(1, 4-Addition)}}}{\overset{Br}{CH_2}-CH{=}CH-\overset{Br}{CH_2}}$$
$$+ \underset{\substack{\text{3, 4-Dibromobut-1-ene}\\ \text{(1, 2-Addition)}}}{\overset{Br}{CH_2}-\overset{Br}{CH}-CH{=}CH_2}$$

(b) $\underset{\text{Acetylene}}{H-C\equiv C-H} + Na \xrightarrow[NH_3]{\text{Liquid}} \underset{\text{Sod. acetylide}}{H-C\equiv \bar{C}:\overset{+}{Na}} + 1/2H_2$

(c)



$$\underset{\text{1, 2-Dibromopropane}}{CH_3-\underset{Br}{CH}-\underset{Br}{CH_2}} \xrightarrow[\text{liq. }NH_3,\ \Delta]{2NaNH_2} \underset{\text{Propyne}}{CH_3-C\equiv C-H}$$

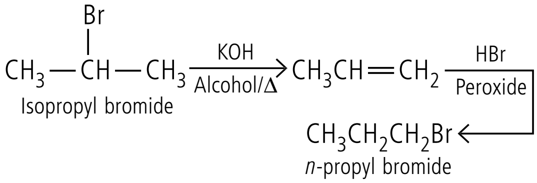
OR

(a) (i) $HC\equiv CH + Cu_2Cl_2 + 2NH_4OH \longrightarrow \underset{\text{Red ppt.}}{Cu_2C\equiv CCu} + 2NH_4Cl + 2H_2O$

(ii) $HC\equiv CH + 2AgNO_3 + 2NH_4OH \longrightarrow \underset{\text{White ppt.}}{AgC\equiv CAg} + 2NH_4NO_3 + 2H_2O$

(b) $\underset{\text{Acetylene}}{HC\equiv CH} \xrightarrow{NaNH_2} HC\equiv C^-Na^+ \xrightarrow{CH_3CH_2Br} \underset{\text{But-1-yne}}{HC\equiv CCH_2CH_3}$

(c)



$$\underset{\text{Isopropyl bromide}}{CH_3-\overset{Br}{CH}-CH_3} \xrightarrow[\text{Alcohol}/\Delta]{KOH} CH_3CH{=}CH_2 \xrightarrow[\text{Peroxide}]{HBr} \underset{n\text{-propyl bromide}}{CH_3CH_2CH_2Br}$$

(d) Both propene and propane are gases. Pass them through dilute cold, $KMnO_4$, solution (purple) or Br_2 in CCl_4 solution (red.) propene will decolourise both the solutions, propane does not react.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