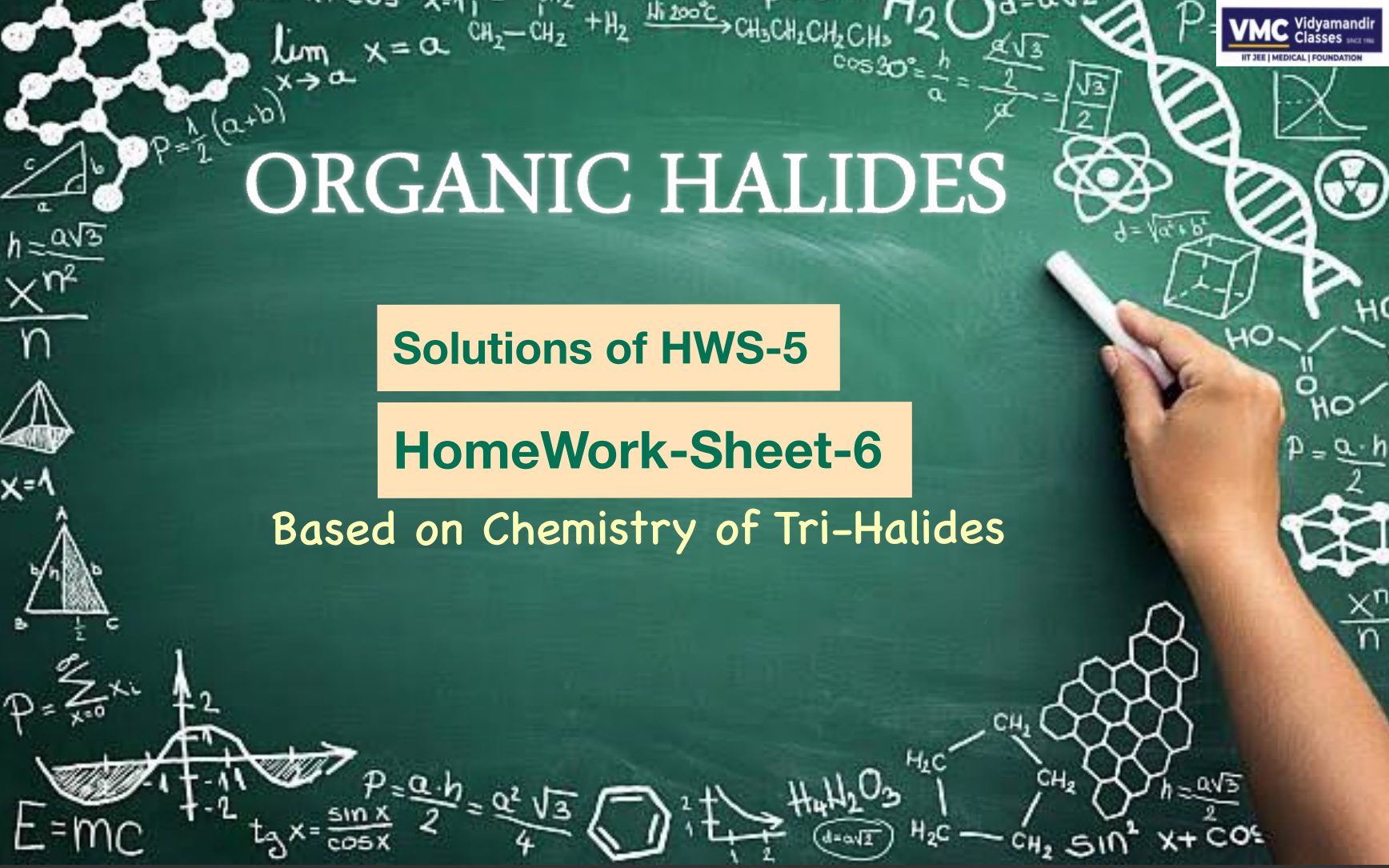

VMC Vidyamandir Classes
IIT JEE | MEDICAL | FOUNDATION
ORGANIC HALIDES
Solutions of HWS-5
HomeWork-Sheet-6
Based on Chemistry of Tri-Halides

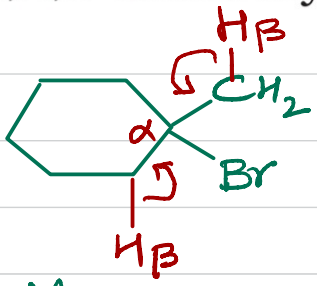
Solutions (HWS-5)

1. Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene:

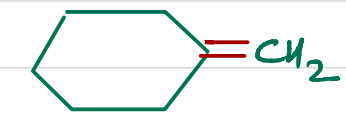
(i) 1-Bromo-1-methylcyclohexane (ii) 2-Chloro-2-methylbutane

(iii) 2,2,3-Trimethyl-3-bromopentane.

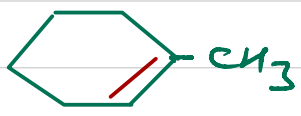
(i)



$\xrightarrow[EtOH]{EtO^{-}Na^{+}}$

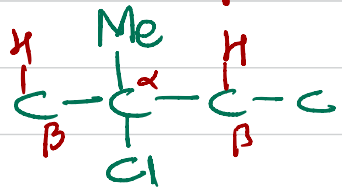


(Minor) +

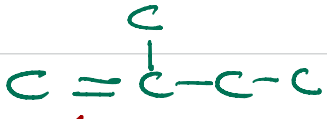


(Major)

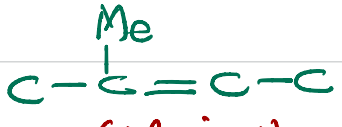
(ii)



$\xrightarrow[EtOH]{EtO^{-}Na^{+}}$



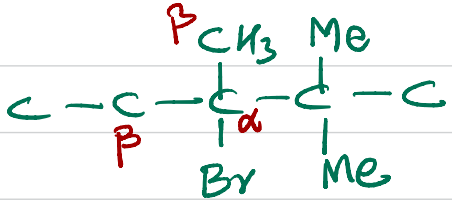
(Minor) +



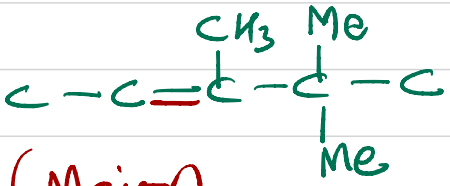
(Major)

Saytzeff (More alkylated)

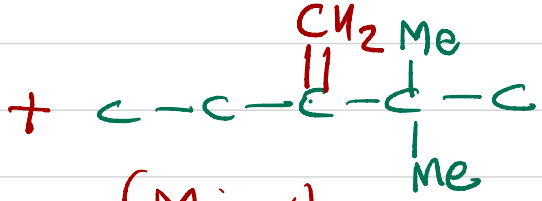
(iii)



$\xrightarrow[EtOH]{EtO^{-}Na^{+}}$



(Major) +



(Minor)

How will you bring about the following conversions?

(i) Ethanol to but-1-yne (ii) Ethane to bromoethene (iii) Propene to 1-nitropropane (iv) Toluene to benzyl alcohol (v) Propene to propyne (vi) Ethanol to ethyl fluoride (vii) Bromomethane to propanone (viii) But-1-ene to but-2-ene (ix) 1-Chlorobutane to n-octane (x) Benzene to biphenyl.

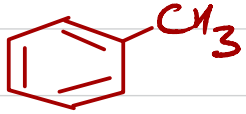
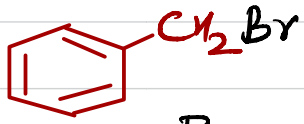
(i) $C-C-OH \xrightarrow[2.\ alc\ KOH]{1.\ PCl_5} C=C \xrightarrow[CCl_4]{Cl_2} C(Cl)-C-Cl \xrightarrow[2.0\ eq]{NaNH_2} C\equiv C \xrightarrow[1.0\ eq]{NaNH_2} H-C\equiv C^{-}\,Na^{+}$

$H-C\equiv C^{-}\,Na^{+} \xrightarrow{C-C-Br} C-C-C\equiv C$ (1-Butyne.)

(ii) $CH_3CH_3 \xrightarrow[\Delta]{Br_2} \xrightarrow[KOH]{alc} C=C \xrightarrow[CCl_4]{Br_2} C(Br)-C-Br \xrightarrow[KOH\ (1.0\ eq)]{alc} CH_2=CHBr$

(iii) $CH_3CH=CH_2 \xrightarrow[Pd-C]{H_2} C-C-C \xrightarrow[\Delta]{HNO_3} C-C-C-NO_2$ (gives mixture)

$\xrightarrow[Peroxide]{HBr} C-C-C-Br$ (anti M-addn) $\xrightarrow{AgNO_2} C-C-C-NO_2$ (better method)

(iv)  $\xrightarrow[CCl_4]{NBS}$  $\xrightarrow[H_2O]{KOH}$  (Benzyl alcohol)

(v) $C-C=C \xrightarrow[CCl_4]{Br_2} C(Br)(Br)-C(Br)-C \xrightarrow[2.0\ eq]{NaNH_2} C-C\equiv C$

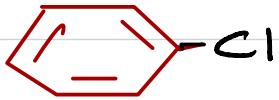
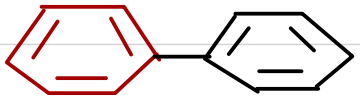
(vi) Ethanol to ethyl fluoride (vii) Bromomethane to propanone (viii) But-1-ene to but-2-ene (ix) 1-Chlorobutane to n-octane (x) Benzene to biphenyl.

(vi) $C-C-OH \xrightarrow{PCl_5} C-C-Cl \xrightarrow{AgF} C-C-F$ (Swarts Rxn)

(vii) $CH_3Br \longrightarrow C-\overset{O}{\overset{\|}{C}}-C$ It needs use of Grignard reagent. We will do it later.

(viii) $C-C-C=C \xrightarrow[M\text{-addn}]{HCl} C-C-\underset{Cl}{C}-C \xrightarrow[KOH,\,\Delta]{alc} C-C=C-C$ Major (Saytzeff)

(ix) $C-C-C-C-Cl \xrightarrow[D.E]{Na} C-C-C-C-C-C-C-C$ (n-octane)

(x)  $\xrightarrow[AlCl_3]{Cl_2}$  $\xrightarrow[D.E]{Na}$ or $\xrightarrow[\Delta]{Cu}$ 

Biphenyl

3. Explain why

(i) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?

(ii) alkyl halides, though polar, are immiscible with water?

(iii) Grignard reagents should be prepared under anhydrous conditions?

Give the uses of freon 12, DDT, carbon tetrachloride and iodoform.

(i) Dipole moment (μ) = $q \times d$.

Now C–Cl bond in Chlorobenzene is LESS POLAR than in cyclohexyl chloride because 'C' in chlorobenzene is sp^2 & thus an electron-withdrawing whereas 'C' in cyclohexyl chloride is sp^3 (electron releasing.

So it results in less polarity of C-Cl bond in chlorobenzene. Secondly, C-Cl bond in chlorobenzene is shorter due to partial double bond character because of resonance unlike in cyclohexyl chloride. So as a result of both charge (q) & distance (d), the dipole moment is less.

(ii) Alkyl halides are weakly polar due to weak dipole-dipole interactions unlike in water where due to H-bonding in water molecules. So alkyl halides are neither able to break H-bonds existing among water molecules nor they are able to form new H-bonds. Hence they are very weakly (almost insoluble) soluble in water.

(iii) $RX + Mg \xrightarrow{\text{Ether}} R\overset{\delta-}{Mg}\overset{\delta+}{X}$

Note that alkyl group in Grignard reagent acquires a carbanion character due to which they are very good bases. As a result, they abstract H-atom from water (acting as Bronsted base: proton acceptor) hence we should have aprotic solvent (not having an acidic -H atom) like ethers for Grignard reagent to be stable.

(iv) Please refer to (read) pages: 308 & 309 from NCERT book (unit-10)

4. Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$, which is more easily hydrolysed by aqueous KOH?

5. *p*-Dichlorobenzene has higher m.p. and solubility than those of *o*- and *m*-isomers. Discuss.

lesser ← correction

4. $C_6H_5CH_2Cl + KOH_{aq} \longrightarrow$ Visualise Path-II.

$\longrightarrow C_6H_5\overset{+}{C}H_2 + Cl^-$

SN

benzyl carbocation : highly stable.

$\xrightarrow{\bar{O}H_{aq}} C_6H_5CH_2OH$

* we will do proper mechanism in next chapter.

$C_6H_5\underset{Cl}{CH}-C_6H_5 + KOH_{aq} \longrightarrow C_6H_5-\overset{+}{C}H-C_6H_5 + Cl^-$

diphenyl methyl carbocation is more stable than benzyl carbocation

$\xleftarrow{\bar{O}H_{aq}}$

$C_6H_5\underset{OH}{CH}-C_6H_5$

So $C_6H_5\underset{Cl}{CH}-C_6H_5$ is more easily hydrolysed than $C_6H_5CH_2Cl$.

5. p-dichlorobenzene is most symmetric of all isomeric (o, p, m). As a result, its molecules pack very effectly in their crystal lattice resulting in higher melting point. Also observe that dipole moment; $\mu = 0$ for p-dichlorobenzene due to symmetry making it almost non-polar. So obviously it will be poorly soluble as compared to other isomers.

6. How the following conversions can be carried out?
   (i) Propene to propan-1-ol
   (ii) Ethanol to but-1-yne
   (iii) 1-Bromopropane to 2-bromopropane
   (iv) Toluene to benzyl alcohol

(i) $CH_3-CH=CH_2 \xrightarrow[\text{Peroxide}]{HBr} CH_3-CH_2-CH_2-Br \xrightarrow{\text{aq. KOH}} CH_3-CH_2-CH_2-OH$

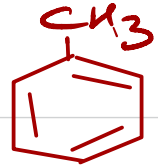
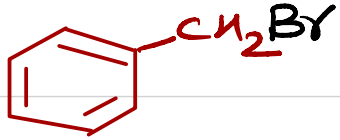
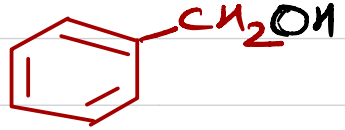
Anti-M-addn

$CH_3-CH=CH_2 \xrightarrow[2.\ H_2O_2/\bar{O}H]{1.\ BH_3/THF} CH_3-CH_2-CH_2-OH$ (Not in CBSE/NCERT)

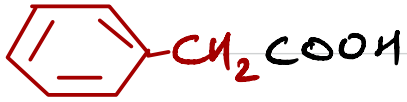
Anti-M addn.

(ii) $CH_3-CH_2-OH \longrightarrow CH_3-CH_2-C\equiv CH$ [repeated. see Q. 2(i)]

(iii) $CH_3-CH_2-CH_2-Br \xrightarrow[KOH,\ \Delta]{alc} CH_3-CH=CH_2 \xrightarrow[M\text{-addn}]{HBr} CH_3-\underset{Br}{CH}-CH_3$

(iv)  $\xrightarrow[CCl_4, \Delta]{NBS}$ or $\xrightarrow[\Delta]{Br_2}$  $\xrightarrow[KOH]{aq}$ (SN) 

(v) Benzene to 4-bromonitrobenzene

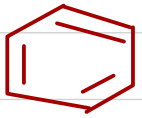
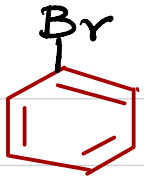
(vi) Benzyl alcohol to 2-phenylethanoic acid 

(vii) Ethanol to propanenitrile CH_3CH_2CN

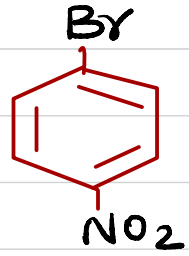
(viii) Aniline to chlorobenzene

(ix) 2-Chlorobutane to 3, 4-dimethylhexane

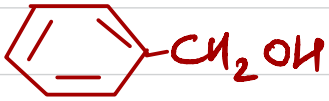
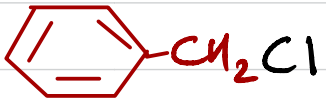
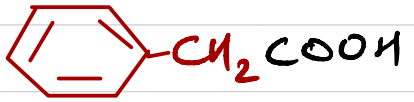
(x) 2-Methyl-1-propene to 2-chloro-2-methylpropane

(v)  $\xrightarrow[Fe]{Br_2}$ (SE Rxn)  $\xrightarrow[H_2SO_4(c)]{HNO_3(c)}$ (Nitration)

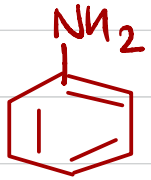
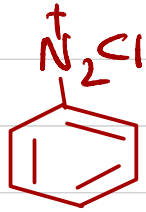
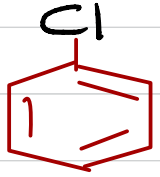
• Br is an o/p-directing group.



4-Bromonitrobenzene

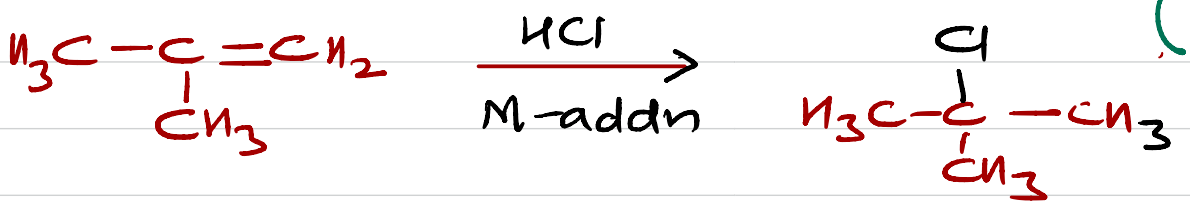
(vi)  $\xrightarrow[\text{or } SOCl_2]{PCl_5}$  $\xrightarrow[alc.]{KCN}$  $\xrightarrow{H_3O^+}$ 

(vii) $CH_3CH_2OH \xrightarrow[\text{or } SOCl_2]{PCl_5} CH_3CH_2Cl \xrightarrow[alc.]{KCN} CH_3CH_2CN$

(viii)  $\xrightarrow[HCl,\ (0\text{-}5^\circ C)]{NaNO_2}$  $\xrightarrow[HCl]{CuCl}$ 

(ix) 

(3,4-Dimethyl hexane)

(x) 

7. The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.

$RCl \xrightarrow[aq]{KOH} ROH$

In aqueous medium, $\bar{O}H$ furnished by KOH act as strong Nucleophile but weak base as $\bar{O}H$ ions are hydrated (stable) so S_N reaction is dominant to give alcohols.

$RCl \xrightarrow[KOH]{alc} \equiv \frac{ROH}{KOH}$ or $\frac{KOH}{ROH} \equiv OH^-_{alc}$ act as strong base as they are not highly solvated. Thus they are less stable & act as weak Nu^- but strong bases.

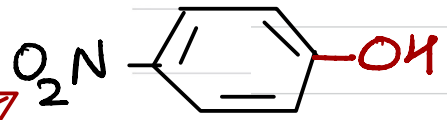
8. How the following conversions can be carried out?

(xi) Ethyl chloride to propanoic acid

(xii) But-1-ene to n-butyliodide

(xiii) 2-Chloropropane to 1-propanol

(xiv) Isopropyl alcohol to iodoform

(xv) Chlorobenzene to *p*-nitrophenol 

(xi) $CH_3-CH_2-Cl \xrightarrow{KCN} CH_3-CH_2-CN \xrightarrow{H_3O^+} CH_3-CH_2-COOH$

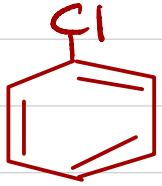
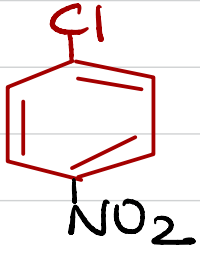
(xii) $CH_3-CH_2-CH=CH_2 \xrightarrow[\text{Peroxide}]{HBr} CH_3-CH_2-CH_2-CH_2-Br$ (Anti-M) $\xrightarrow[\text{acetone}]{NaI} CH_3-CH_2-CH_2-CH_2-I$

Finkelstein Rxn

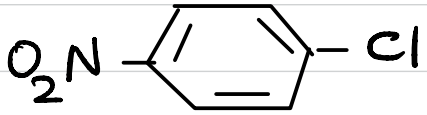
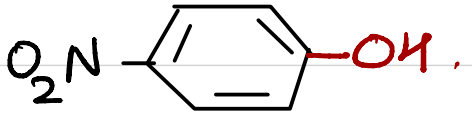
(xiii) $CH_3-\underset{Cl}{CH}-CH_3 \xrightarrow[KOH]{\text{alc.}} CH_3-CH=CH_2 \xrightarrow[2.\ aq\ KOH]{1.\ HBr/\text{Peroxide}} CH_3-CH_2-CH_2-OH$

(xiv) $CH_3-\underset{OH}{CH}-CH_3 + NaOH + I_2 \longrightarrow CHI_3 + CH_3-COONa$

*(We will do this Rxn in Tri-halides)

(xv)  $\xrightarrow[H_2SO_4(c)]{HNO_3(c)}$ 'Cl' is o/p-directing 

Now $-NO_2$ is at p-position to -Cl atom
& it is a deactivating group so there will be activated SN.

 $\xrightarrow[H_2O]{NaOH}$ 

(xvi) 2-Bromopropane to 1-bromopropane

(xvii) Chloroethane to butane

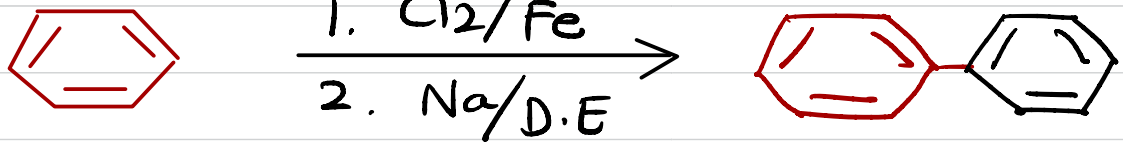
(xviii) Benzene to diphenyl

(xix) *tert*-Butyl bromide to isobutyl bromide

(xx) Aniline to phenylisocyanide

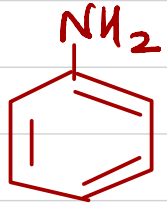
(xvi) $CH_3-CH(Br)-CH_3 \xrightarrow[KOH]{alc} CH_3-CH=CH_2 \xrightarrow[Peroxide]{HBr} CH_3-CH_2-CH_2-Br$

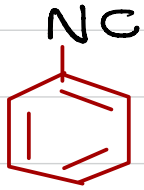
(xvii) $CH_3-CH_2-Cl \xrightarrow[D.E]{Na} CH_3-CH_2-CH_2-CH_3$

(xviii) 

(xix) $(CH_3)_3C-Br \xrightarrow[KOH, \Delta]{alc} (CH_3)_2C=CH_2 \xrightarrow[Peroxide]{HBr} (CH_3)_2CH-CH_2-Br$

Isobutyl bromide

(xx) 

$+ CHCl_3 + KOH_{alc} \xrightarrow{\Delta}$ 

$+ KCl + H_2O$

Phenyl isocyanide (carbylamine)

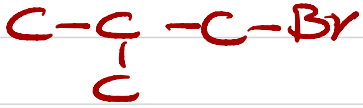
* Carbylamine Reaction (To be done in Tri-halides)

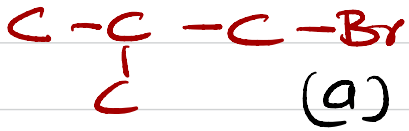
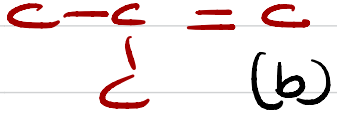
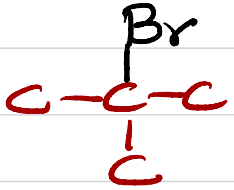
9. Primary alkyl halide C_4H_9Br (a) reacted with alcoholic KOH to give compound (b). Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d), C_8H_{18} which is different from the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.

(a) C_4H_9Br (1°) $\xrightarrow[KOH]{alc}$ (b) $\xrightarrow{HBr}$ (c) an isomer of (a)

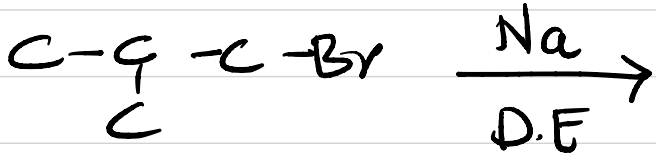
(a) can be either C-C-C-C-Br or 

(a) $\xrightarrow[D.E]{Na}$ d (C_8H_{18}) [C-C-C-C-Br $\xrightarrow[D.E]{Na}$ C-C-C-C-C-C-C-C $\neq$ d.]

$\Rightarrow$ (a) is 

-  (a) $\xrightarrow[KOH]{alc}$  (b) $\xrightarrow{HBr}$  (c)

(c) is an isomer of (a)

- 

(d).

10. What happens when

(i) n-butyl chloride is treated with alcoholic KOH,

(ii) bromobenzene is treated with Mg in the presence of dry ether,

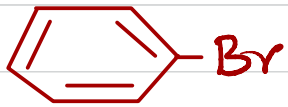
(iii) chlorobenzene is subjected to hydrolysis,

(iv) ethyl chloride is treated with aqueous KOH,

(v) methyl bromide is treated with sodium in the presence of dry ether,

(vi) methyl chloride is treated with KCN?

(i) $C-C-C-C-Br \xrightarrow[ROH]{KCN} C-C-C-C-CN$ Pentanenitrile

(ii)  $\xrightarrow[D.E]{Mg}$  $MgBr$ Phenyl mag. bromide
Aromatic Grignard reagent

(iii)  $\xrightarrow[H_2O]{KOH}$ No Reaction due to $C:::Cl$ (partial double character) bond because of resonance.

(iv) $C-C-Cl \xrightarrow[aq]{KOH} C-C-OH$ (SN Rxn)

(v) $CH_3Br \xrightarrow[D.E]{Na}$ (Wurtz) CH_3-CH_3

(vi) $CH_3Cl \xrightarrow[alc]{KCN} CH_3-CN$

Module Illustrations: (Try without referring solutions)

Illustration - 7 *Identify A, B, C, ...*

(a) $CH_3CHO \xrightarrow{PCl_5} A \xrightarrow{aq.KOH} B \xrightarrow[Cl_2]{NaOH} C(\ell) + D(aq.)$

(b) $C_3H_6Cl_2\ (A) \xrightarrow{aq.KOH} B \xrightarrow{NaOH\ /\ I_2} C\downarrow\ +\ D(aq.)$

Illustration - 8 *An organic compound (A) ; $C_4H_8Cl_2$ on hydrolysis forms another compound (B) ; C_4H_8O.*

(a) *If the compound (B) responds positively to iodoform test, then identify (A) and (B).*

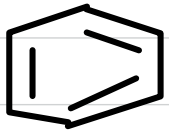
(b) *If (B) does not responds to iodo form test, then identify possible structures of (A) and (B).*

(c) *If all possible structures of (B) visualised above in (a) and (b) are treated with Zn–Hg/HCl, what are the products ?*

Illustration - 9 *An organic compound (A), C_8H_9Br reacts with aq.KOH solution to give another compound (B), $C_8H_{10}O$. The compound (B) upon treatment of alkaline solution of iodine gives a yellow precipitate. The filtrate on acidification gives a white solid (C), $C_7H_6O_2$. Give structures of A, B, C and explain the reactions involved.*

Illustration - 10 *An alkene (A) $C_{16}H_{16}$ on ozonolysis gives only one product (B) C_8H_8O. Compound (B) on reaction with $NaOH/I_2$ yields sodium benzoate. Compound (B) reacts with Zn-Hg/HCl yielding a hydrocarbon (C) C_8H_{10}. Write the structures of compounds (B) and (C). Based on this information two isometric structures can be proposed for alkene (A). Write their structures and identify the isomer which on catalytic hydrogenation ($H_2/Pd - C$) gives a racemic mixture.*

Identify the products. A, B, ... P, Q, ... S, T ...etc

1.  $\xrightarrow[AlCl_3]{CH_3Cl}$ $\xrightarrow[excess]{Cl_2/h\nu}$ $\xrightarrow[2.\ H^+]{1.\ NaOH\ aq}$ $\xrightarrow[H_2SO_4(c)]{HNO_3(c)}$ P

2. $CH_3CH_2CH_2CH_3$ $\xrightarrow[\Delta]{Br_2}$ $\xrightarrow[H_2O]{KOH}$ $\xrightarrow[Cl_2]{NaOH}$ Q↓ + R(aq)

R(aq) $\xrightarrow[2.\ RedP/HI]{1.\ H^+}$ (S)

Q↓ $\xrightarrow{CH_3COCH_3}$ (T)

3. C_2H_4 $\xrightarrow[H_2SO_4(c)]{H_2O}$ $\xrightarrow[Cl_2]{NaOH}$ $\xrightarrow[h\nu]{O_2}$ A

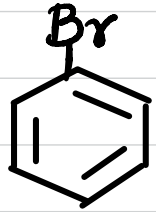
A $\xrightarrow[(excess)]{EtOH}$ B

4. C_8H_6 (X) $\xrightarrow[aq.]{AgNO_3}$ white ppt

(X) $\xrightarrow[HgSO_4]{H_2O/H^+}$ $\xrightarrow[I_2]{NaOH}$ Y(↓) + Z(aq) $\xrightarrow[CaO,\ \Delta]{NaOH}$ C

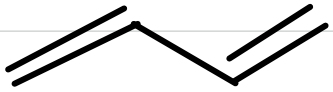
Y(↓) $\xrightarrow[\Delta]{O_2}$ products.(?)

Identify the end product in each of following.

5.  $\xrightarrow{KNH_2}$ $\xrightarrow[HCl;\ 0^\circ C]{NaNO_2}$ $\xrightarrow[\Delta]{KI}$ $\xrightarrow[Na/D.E]{PhI}$

6.  $\xrightarrow[EtOH]{KCN}$ $\xrightarrow{H_3O^+}$ $\xrightarrow{\Delta}$

7. C_3H_6 $\xrightarrow[CCl_4]{NBS}$ $\xrightarrow[alc.]{KCN}$ $\xrightarrow{H_3O^+}$ $\xrightarrow{(O)}$

8.  $\xrightarrow[40^\circ C]{Br_2}$ $\xrightarrow[H_2O]{KOH}$ $\xrightarrow[KMnO_4]{alk.}$ $\xrightarrow{(n)\ MeMgBr}$

How many moles (n) of MeMgBr are required ?

9. Identify A, B, C .... (A) : $C_4H_8O_2$ reacts with moist Ag_2O to give a compound which reacts with Br_2 in CCl_4 to form (B). Compound (B) on hydrolysis & then followed by action of $NaOH/I_2$ gives a mixture of (C) & (D).