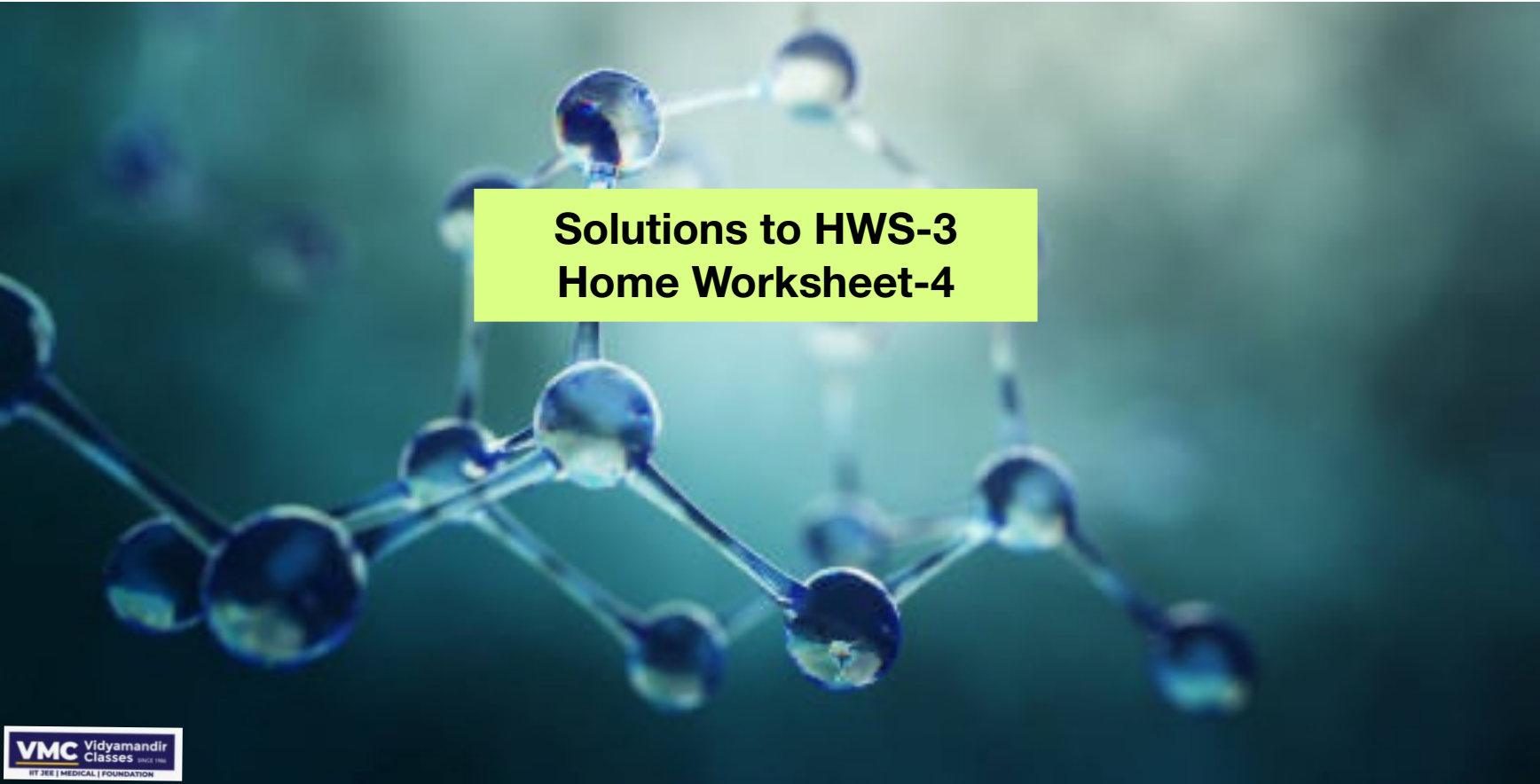


Solutions to HWS-3
Home Worksheet-4

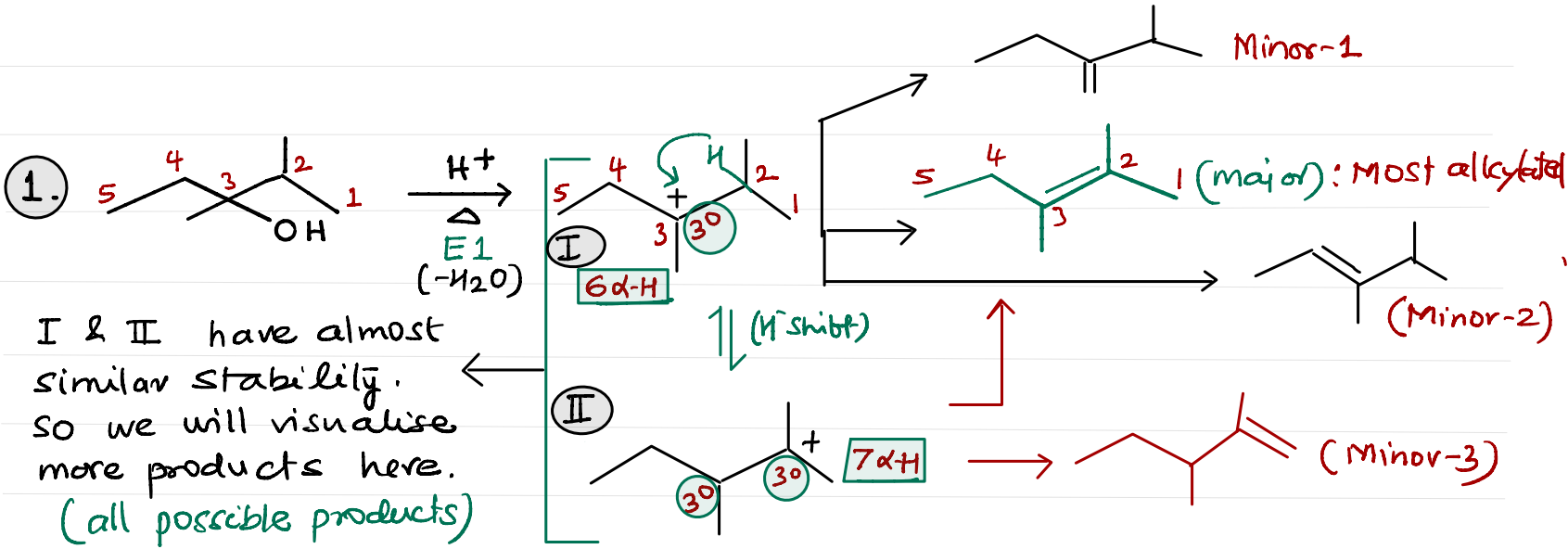
Reactions Name
Oxygen Containing Organic Compounds

Preparation of Glycols:-

1. Hydroxylation of Alkenes
2. Hydrolysis of Viccinal Dihalides
3. Hydrolysis of Viccinal Halo-hydrins
4. Hydrolysis of Oxiranes
5. Reduction of Glyoxal(s)
6. Reductive Hydrolysis of Carbonyl Compounds
   (Bimolecular Reduction)

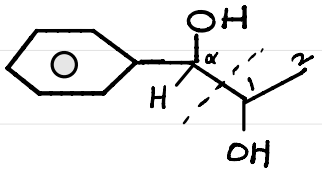
Chemical Properties (Reactions):-

1. Reaction with Phosphorus Trichloride & Thionyl chloride
2. Reaction with Organic & Inorganic Acids
3. Polymerisation
4. Condensation
5. Acetal Formation
6. Oxidation
   (A) Simple Oxidation (B) Oxidative Cleavage
7. Pinnacol-Pinnacolone Rearrangement



Typical shift: $1^\circ \rightarrow 2^\circ \rightarrow 3^\circ$

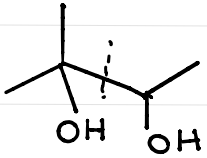
$3^\circ \rightarrow 3^\circ$ based upon H-effect (α-H Number)

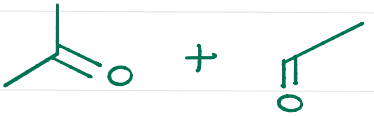
1. 

(O) →  + $\overset{2}{C}H_3\overset{1}{C}OOH$

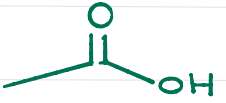
due to α-H, it will give benzoic acid & 2nd product will be acid as (O) ≡ strong OA.

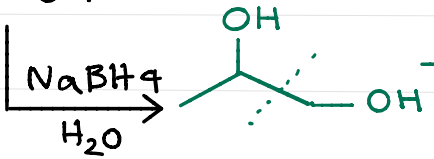
HIO_4 →  + $\overset{2}{C}H_3\overset{1}{C}HO$

2. 

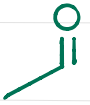
HIO_4 → 

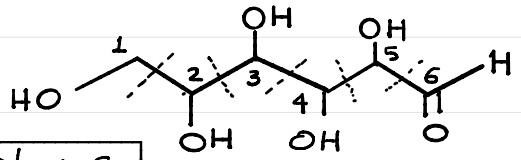
3. 

HIO_4 →  + HCHO



$NaBH_4$, H_2O

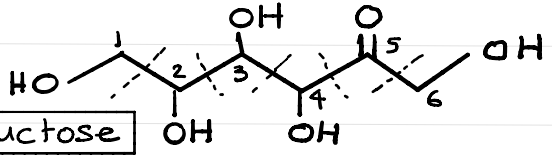
HIO_4 →  + HCHO

4. 

Glucose

$x HIO_4$ → ($x = ?$) $x = 5$

$HCHO + 5HCOOH$ (C-2, 3, 4, 5, 6 form HCOOH)

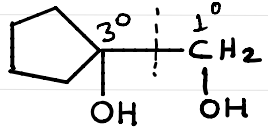
5. 

fructose

$x HIO_4$ → ($x = ?$) $x = 5$

$2HCHO + 3HCOOH + 5CO_2 / H_2O$

(C-1, 6) (C-2, 3, 4)

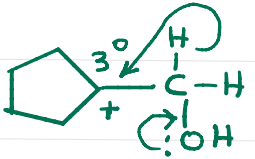
6. 

HIO_4 →

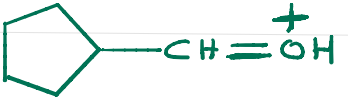
$+ HCHO$

1. H_2SO_4 conc.

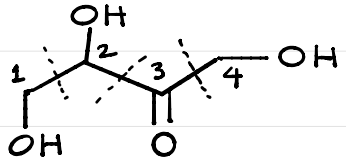
2. $(-H_2O)$



H^- Shift

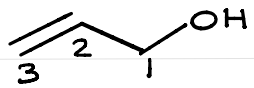


$-H^+$

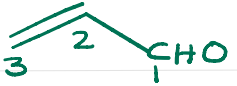
7. 

$\xrightarrow[x = 3]{x\ HIO_4}$ $2HCHO + HCOOH + CO_2 / H_2O$

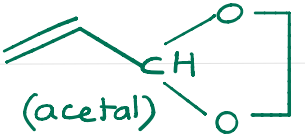
(1,4) (2) (3)

8. 

allyl alcohol

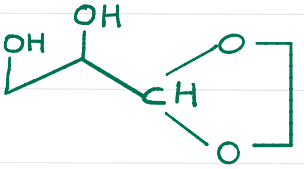
$\xrightarrow[Py]{CrO_3}$ 

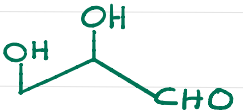
($\approx$ PCC = collin's reagent)

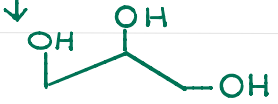
$\xrightarrow[HCl(g)]{CH_2-CH_2\ (OH\ OH)}$ 

(acetal)

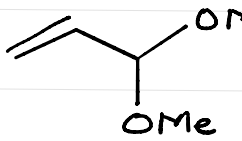
$\xleftarrow[KMnO_4]{alk.}$ Syn hydroxylation

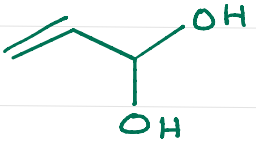


$\xleftarrow{H_3O^+}$ 

$\xrightarrow{NaBH_4}$ 

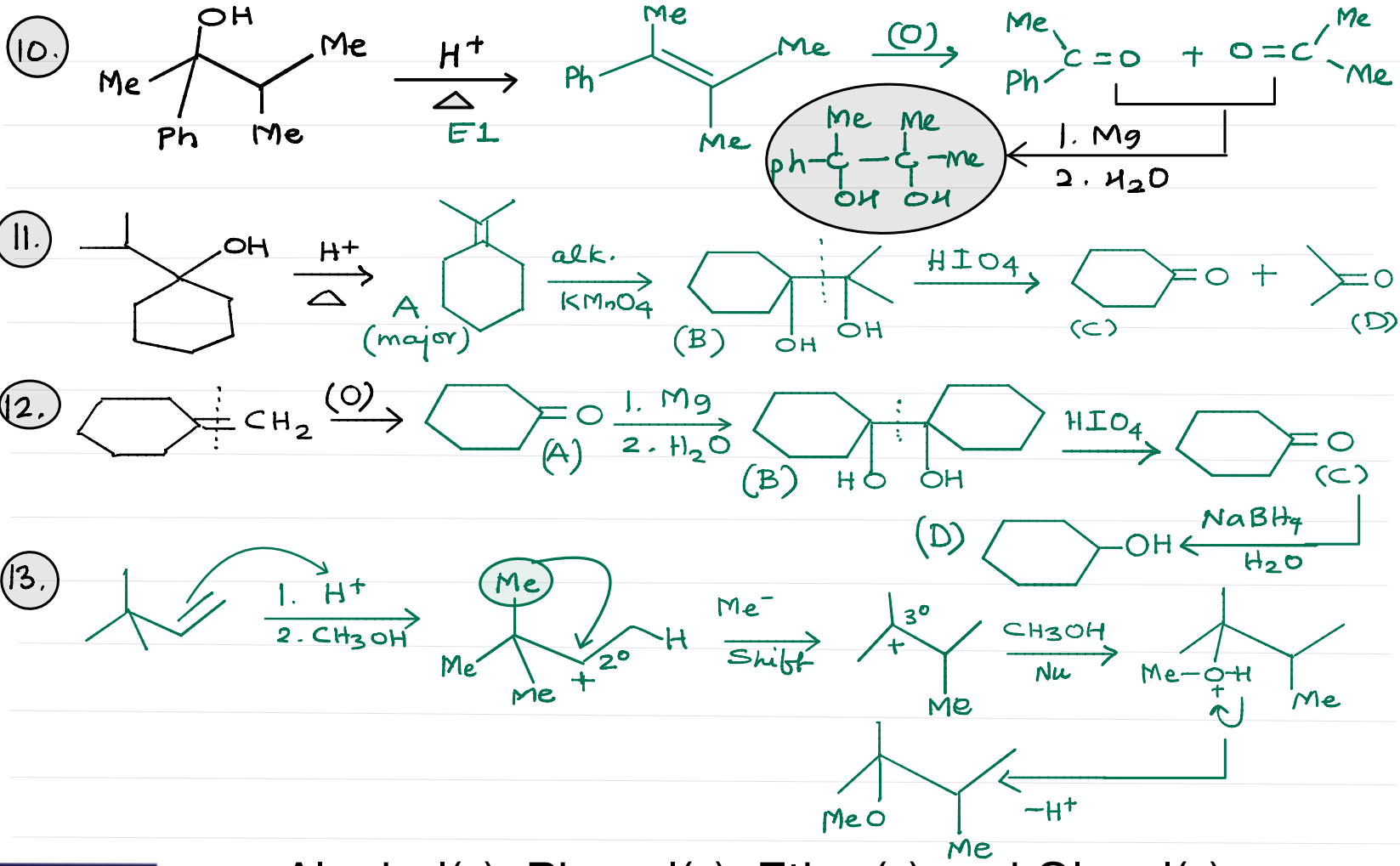
(Glycerol)

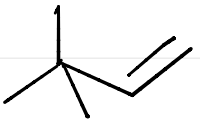
9. 

$\xrightarrow{H_3O^+}$ 

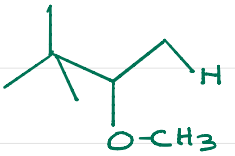
(gem-diol)

$\xrightarrow{-H_2O}$ 

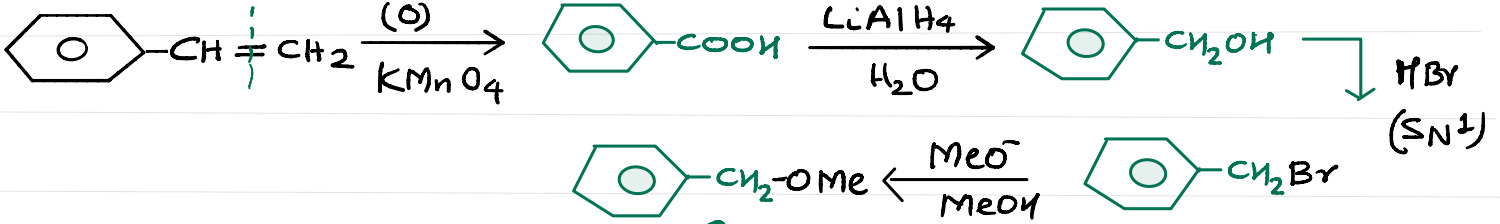

10.
OH
Me
Me
Ph
Me
H+
E1
Me
Ph
Me
Me
(O)
Me
Ph
C=O
+
O=C
Me
Me
1. Mg
2. H2O
Me Me
ph–C–C–Me
OH OH
11.
OH
H+
A
(major)
alk.
KMnO4
(B)
OH
OH
HIO4
(C)
+
O
(D)
12.
CH2
(O)
O
(A)
1. Mg
2. H2O
(B)
HO
OH
HIO4
O
(C)
(D)
OH
NaBH4
H2O
13.
1. H+
2. CH3OH
Me
Me
Me
+
2°
H
Me−
Shift
3°
+
Me
CH3OH
Nu
Me–O–H
+
Me
MeO
Me
−H+

13. 

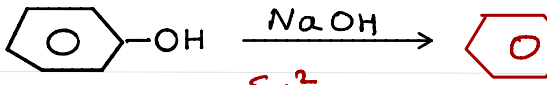
$\xrightarrow[2.\ NaBH_4]{1.\ Hg(OAc)_2/THF/CH_3OH}$



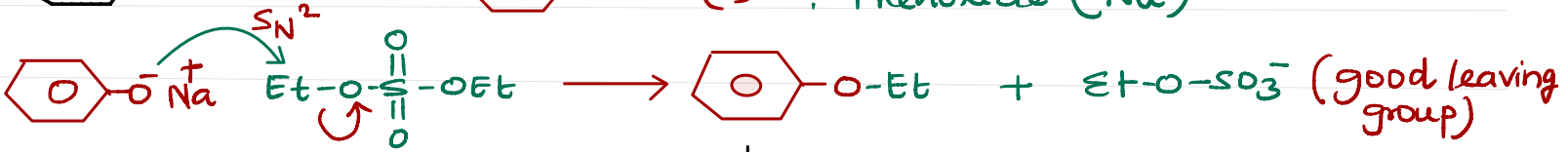
- This does not involve Carbocation so no rearrangement

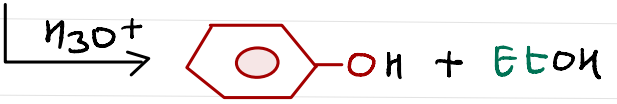
14. 

15. $2\ EtOH + H_2SO_4 \longrightarrow Et\text{-}O\text{-}SO_2\text{-}OEt$ (A) diethyl sulphate

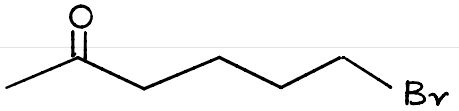


(B) : Phenoxide (Nu^-)

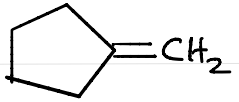




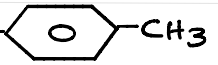
.Hydrolysis of ethers

1. 

$\xrightarrow[Et_2O]{Mg}$ $\xrightarrow{H_2O}$ $\xrightarrow[\Delta]{H^+}$ A $\xrightarrow{alk.\ KMnO_4}$ B $\xrightarrow{H_2SO_4}$ C

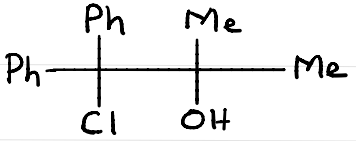
2. 

$\xrightarrow{alk.\ KMnO_4}$ A $\xrightarrow{HIO_4}$ [B + C] $\xrightarrow[H_2O]{NaBH_4}$ [C + D] $\xrightarrow[140^\circ C]{H_2SO_4}$ E

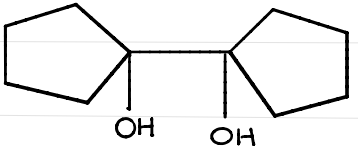
3. Ph–OH $\xrightarrow{NaOH}$ (A) + Et–O–SO_2– 

$\longrightarrow$ (B) anion + A

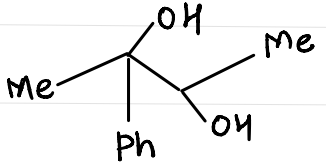
A $\xrightarrow{H_3O^+}$ C + D

4. 

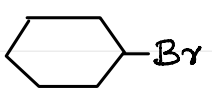
$\xrightarrow{Ag^+}$ A

5. 

$\xrightarrow{H_2SO_4}$ A $\xrightarrow[H_2O]{LiAlH_4}$ B $\xrightarrow[\Delta]{H^+}$ C (Major)

6. 

$\xrightarrow[Conc.]{H_2SO_4}$ A $\xrightarrow[H_2O]{NaBH_4}$ $\xrightarrow[T=160^\circ C]{H_2SO_4(C)}$ B (major)

7. 

1. KOH(aq)
2. NaH

A

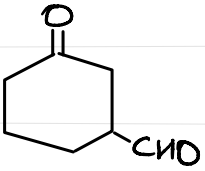
EtO^- / EtOH, Δ

NBS / CCl_4

B

$A + B \longrightarrow C + D$

• Explain formation of C & D and identify major & minor.

8. 

$(CH_2OH)_2$ / H+

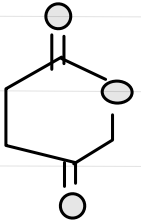
MeMgBr / THF

H_3O^+

A

H_2CrO_4

B

9. 

$LiAlH_4$ / H_2O

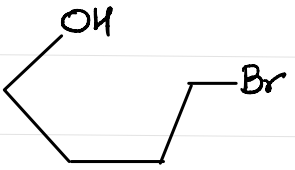
A

HIO_4

(B + C)

(O)

Products

10. 

$\bar{O}H$ / base

A (Major) + B (Minor)

A $\xrightarrow[\Delta]{HI}$ C

B $\xrightarrow[\Delta]{H^+}$ D