ALKYNES:-

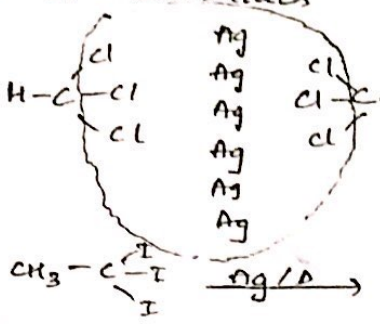
Preparations:

1) $CH_4 + O_2 \xrightarrow[1500^\circ C]{\text{Electric arc}} H-C\equiv C-H$

2) Hydrolysis of Carbides

3) Kolbe's Electrolysis.

4) 1,1,1-trihalides



$\xrightarrow{-6AgCl}$ $H-C\equiv C-H$

$\xrightarrow{Mg/\Delta}$ $CH_3-C\equiv C-CH_3$

5)

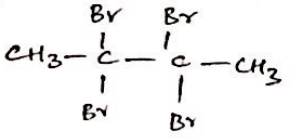
(i) $Br-CH_2-CH_2-Br \longrightarrow H-C\equiv C-H$ (2007 JEE)

A) Alc. KOH (2 Eq) ✗

B) alc. KOH (1 eq) ; fuming KOH (150-200°C)
80°C (1 eq)

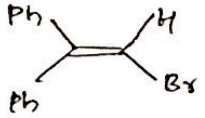
C) alc. KOH (1 eq), $NaNH_2$ (1 eq)

(ii)



$\xrightarrow{Zn/\Delta}$ $C-C\equiv C-C$

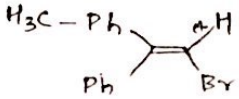
(iii)



$\xrightarrow[\Delta]{NaNH_2}$ $Ph-C\equiv C-Ph$ (2004-JEE)

Mech:-?

(iv)



$\xrightarrow[\Delta]{NaNH_2}$ $Ph-C\equiv C-Ph-CH_3$

major

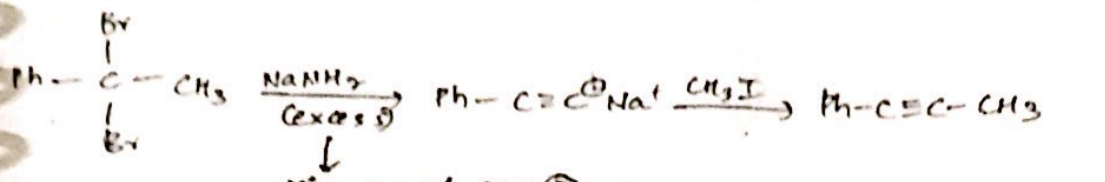
Hint:-

(25)

$CH_3-C\equiv C-H \xrightarrow{NaOH}$ No Reaction.

$\downarrow NaNH_2$

(26) NH_3 + $CH_3-C\equiv C^{\ominus}$ $Na^{\oplus}$



Min no-of eq: (3)

for 2 Eq;

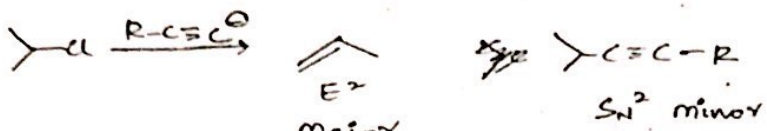
NOTE:

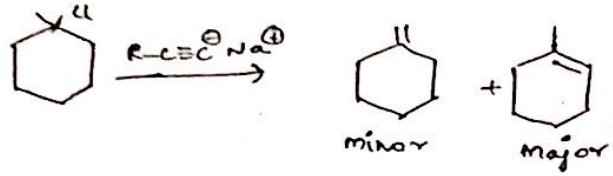
(i) $R-C\equiv C^{\ominus}Na^{\oplus}$ obtained from weak acid; Hence, its mindset preferrebaly acts as base rather than Nucleophile.

∴ With primary halides, S_N2 path is pre-dominant

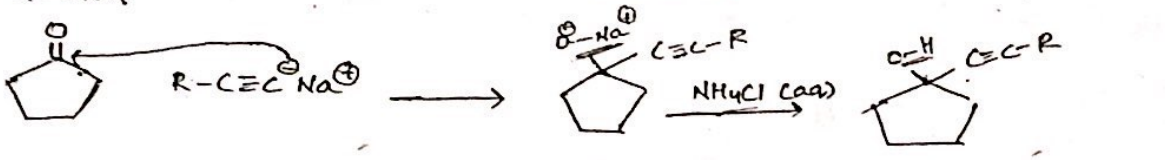
With secondary & 3° halides, E2 path is pre-dominant.

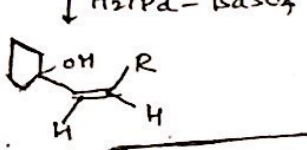
Eg:

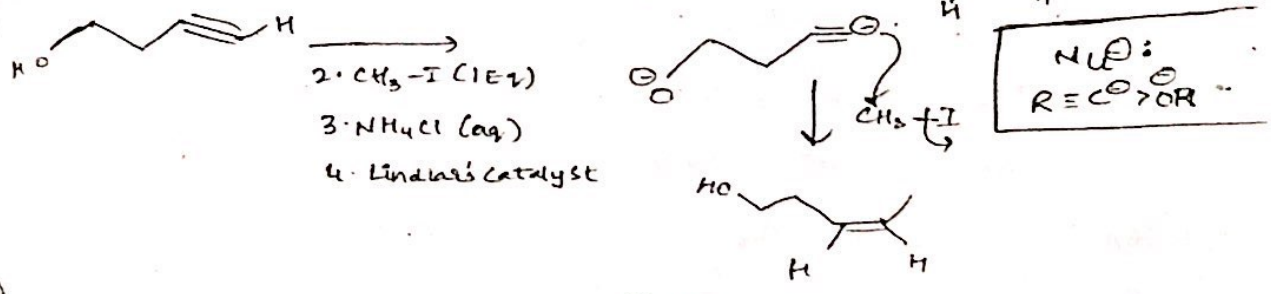
1) 

2) 

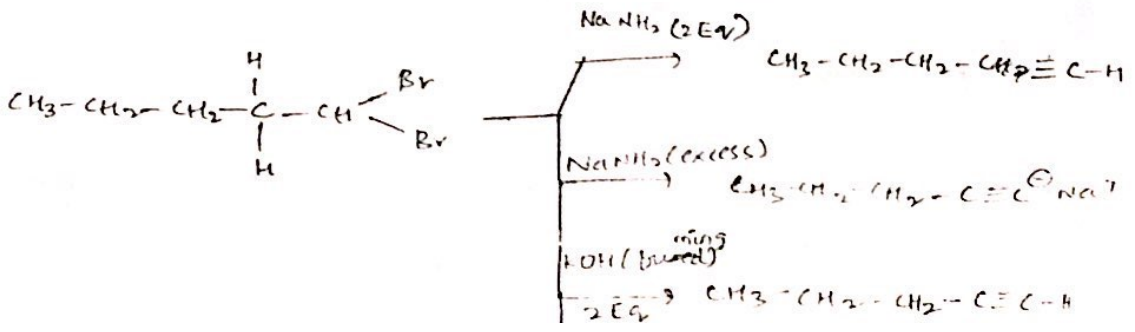
(ii) It gives nucleophilic addition ~~compounds~~ Reactions with Carbonyl compounds





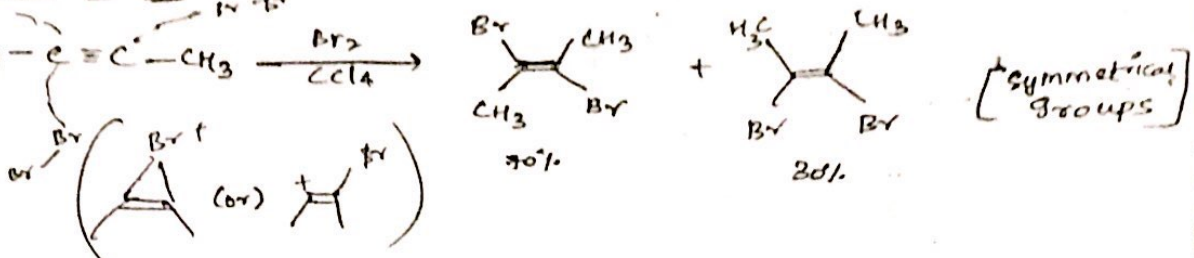
8) 

(v)



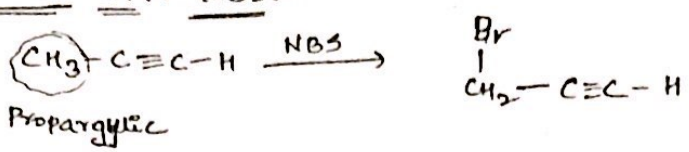
nd anti addition takes place.

Addition of X_2 :-



→ Not stereo specific but stereo selective

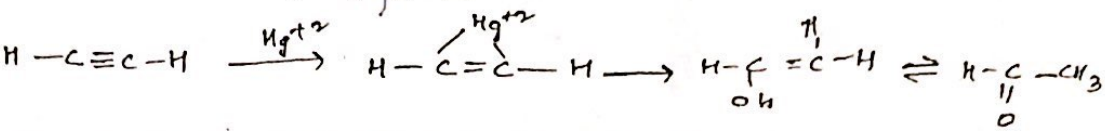
) Reaction with NBS:-

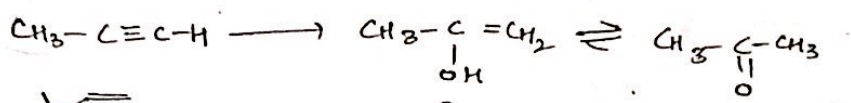


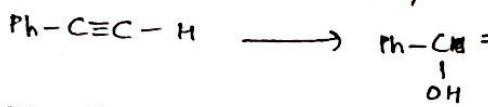
NBS forms also in propargylic

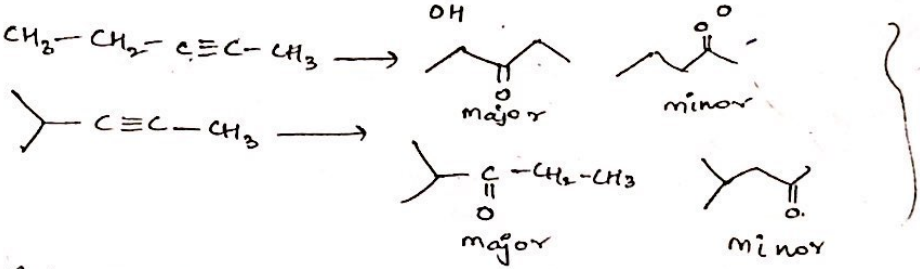
) Reaction - OMD: $CHgSO_4/H_2SO_4$(dil.))

Eg-1:





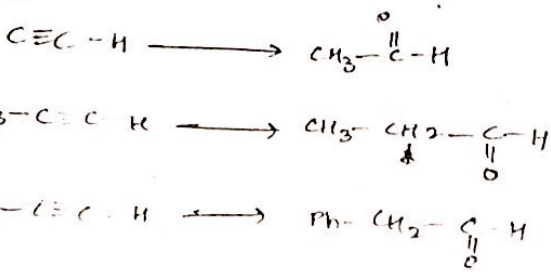




→ Partial +ve does not stabilised by hyper conjugation, stabilised by Inductive effect & Resonance.

5) HBO :-

Eg.

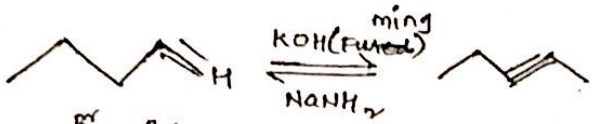


$CH_3-CH_2-C\equiv C-CH_3$ ← KOH (buried) excess ming

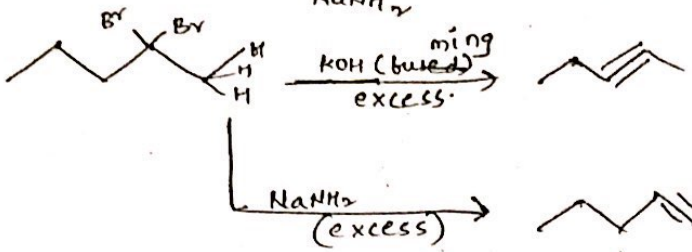
Reason: Since, the stability of alkene is as follows:

$$H-C\equiv C-H < CH_3-CH_2-C\equiv C-H < CH_3-C\equiv C-CH_3$$

Fact:



B)



PROPERTIES OF ALKYNES:

1) **Addition of HX:**

i) $CH_3-C\equiv C-H \xrightarrow{H-Cl} A \xrightarrow{H-Cl} B$ (A: $CH_3-CH=CH_2$, Cl; DA (-M); B: $CH_3-\overset{Cl}{\underset{Cl}{C}}-CH_3$)

*

ii) $CH_3-C\equiv C-H \xrightarrow[ROOR]{H-Br} P \xrightarrow[ROOR]{H-Br} Q$ (P: $CH_3-CH=CH-Br$; Q: $CH_3-CH_2-CHBr_2$)

B) $CH_3-CH_2-C\equiv C-CH_3 \xrightarrow{H-Cl\ (1\,eq)}$ No of products (4)

B) $Ph-C\equiv C-CH_3 \xrightarrow{H-Cl}$ major ?

(*JEE)

(To avoid rep. from methyl group)

REACTIVITY TOWARDS ELECTRO-PHILIC ADDITION:

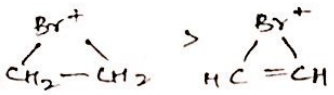
$C=C > C\equiv C$ (Reactivity)

↑

→ Due to High s-character, its difficult to donate π-e^-

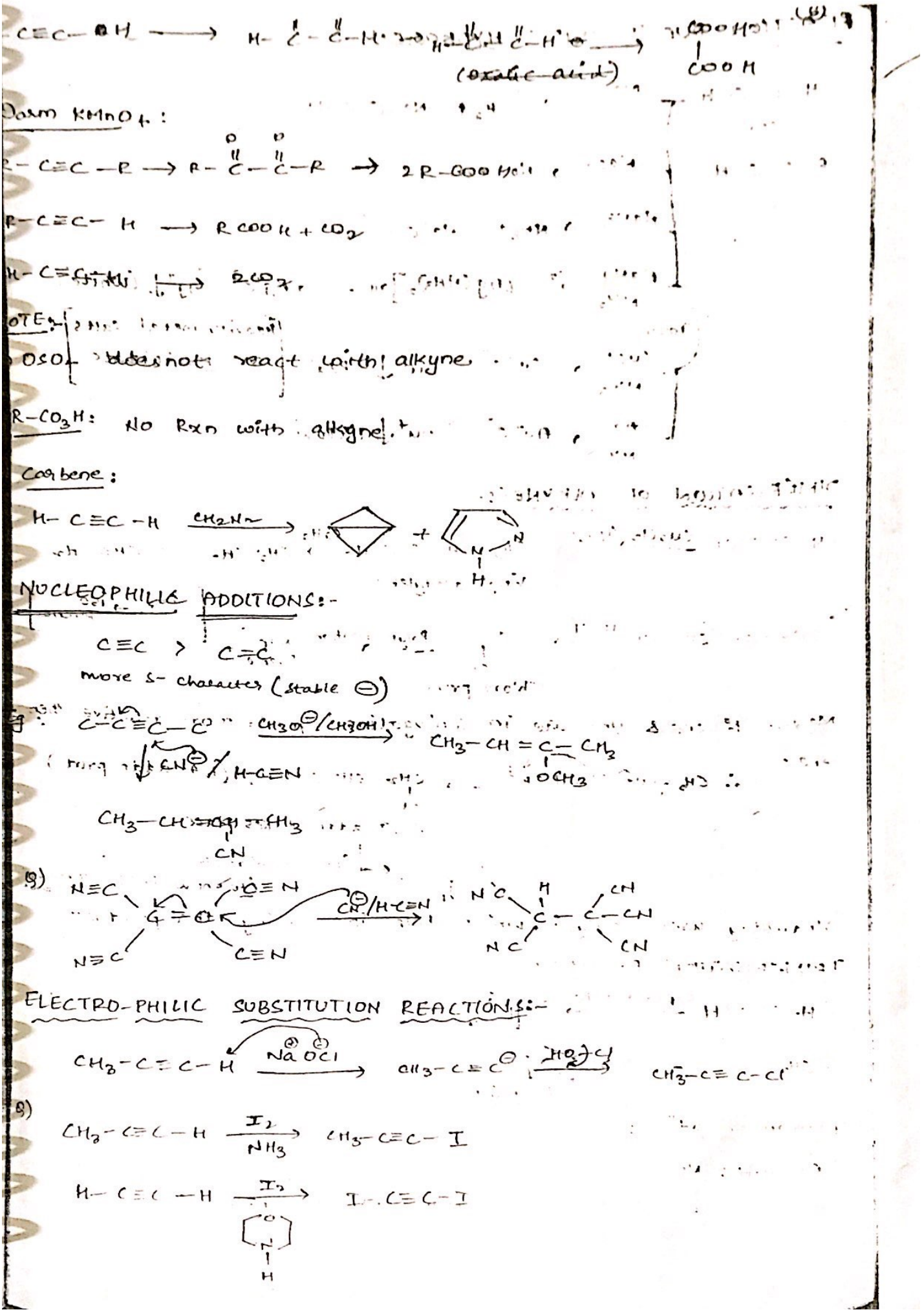
→ Forms Unstable intermediates.

Stability: $CH_3-\overset{\oplus}{C}H_2 > H_2C=\overset{\oplus}{C}H$



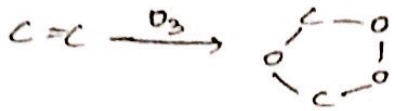
NOTE:-

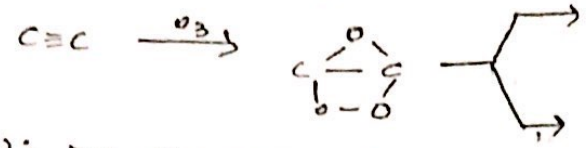
→ Due to Unstable intermediates, ion-pair mechanisms are more preferable. Therefore, Stereo specifity looses, both syn



→ No rearrangement & anti-markonikov product

b) OZONOLYSIS:-



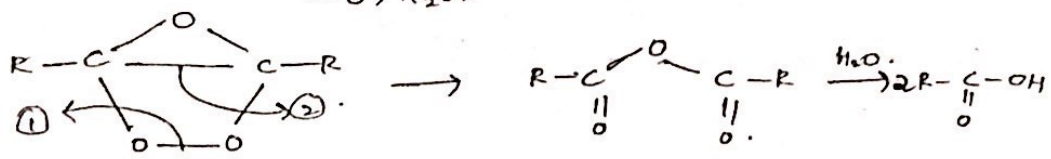


Case (i): Reductive ozonolysis

→ Zn/Me$_2$S/Ph$_3$O ; H$_2$O

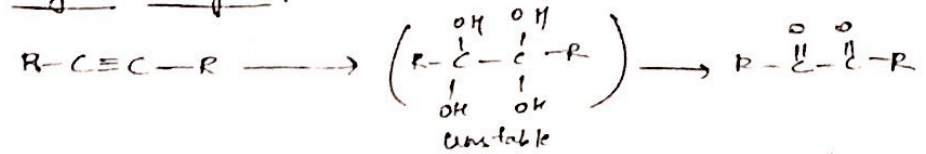
Case (ii): Oxidative Ozonolysis.

H$_2$O ; H$_2$O$_2$

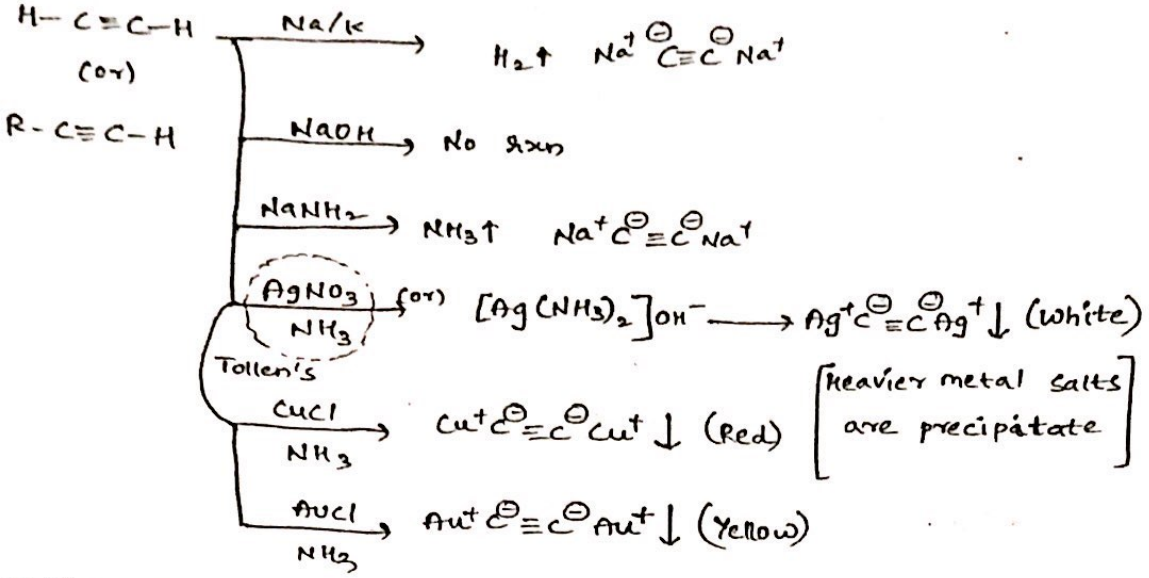


(anhydrides are intermediates)

7) Bayer's Reagent:



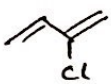
REACTION DUE TO ACIDIC HYDROGEN:-



DIMERISATION OF ALKYNES:-

$H-C\equiv C-H \xrightarrow{CH_2Cl_2/NH_4Cl} CH_2=CH-C\equiv C-H \xrightarrow{C_2H_2} CH_2=CH-C\equiv C-CH=CH_2$

Vinyl acetylene

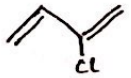
*Q) $CH_2=CH-C\equiv C-H \xrightarrow{H-Cl}$  (Cl) Chloro prene $\xrightarrow{\text{Polymerisation}}$ (Neo Prene) [ → iso prene]

Mech:- If ene & yne are in conjugation; yne is more reactive than ene.

∴ $CH_2=CH-C\equiv CH \xrightarrow{H^{\oplus}} CH_2-CH=C=CH_2$ (1,4-addn prod.)

Cl

∴ 1,4 addn takes place.

 ← (Due to miracle)

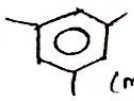
(Cl)

(to know, Refer 11 Phenol book)

→ Industry uses catalyst which helps in forming the product.

TRIMERISATION REACTION:-

$H-C\equiv C-H \xrightarrow{\text{Red hot Fe/Cu}}$ 

$CH_3-C\equiv CH \longrightarrow$  (major)

Tetramerisation:-

Reagent: $Ni(CN)_4$

$H-C\equiv C-H \longrightarrow$ COT (cyclo octa Tetraene)

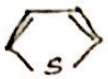
MISCELLENEOUS REACTIONS :-

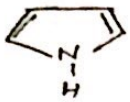
1) $CH_2=CH_2 \xrightarrow{S_2Cl_2}$  (used in WW-I)

Mustard gas

2) $H-C\equiv C-H \xrightarrow[AlCl_3]{AsCl_3}$ $CH-Cl$ ‖ $CH-AsCl_2$ (WW-2)

Lewisite

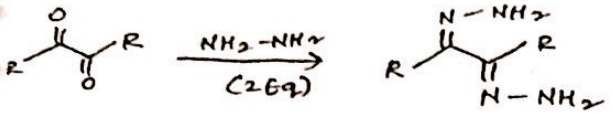
3) $H-C\equiv C-H \xrightarrow[\Delta]{S}$ 

4) $H-C\equiv C-H \xrightarrow[\Delta]{NH_3}$ 

5) $H-C\equiv C-H \not\rightarrow$ 

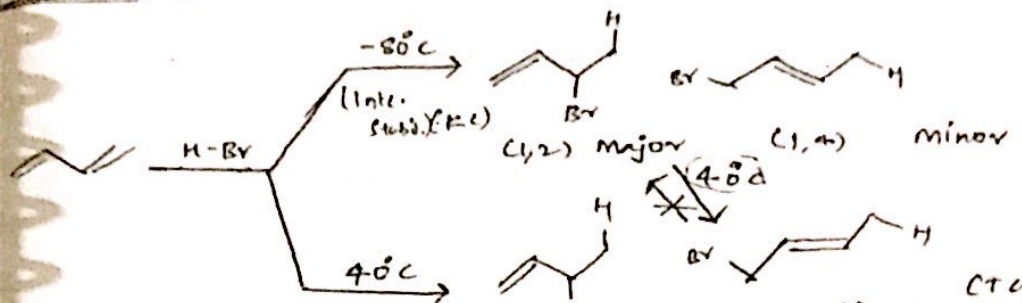
6) $H-C\equiv C-H \xrightarrow[H_2CrO_4]{\text{chromic acid}} CH_3-COOH$

(addition of water followed by oxidation)

7) 

Reagent used to distinguish	C-C-C-C	C-C=C-C	C-C-C≡CH	C-C≡C-C
Na/K	-ve	-ve	+ve	-ve
$NaNH_2$	–	–	+	–
NaOH	–	–	–	–
$AgNO_3/NH_3$	–	–	+	–
Br_2/CCl_4	–	+	+	+
Bayer's reagent	–	+	+	+

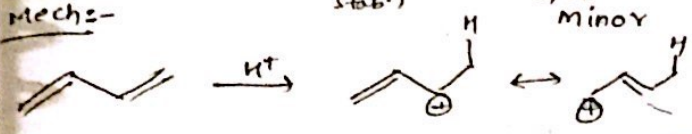
Addition of H-X :

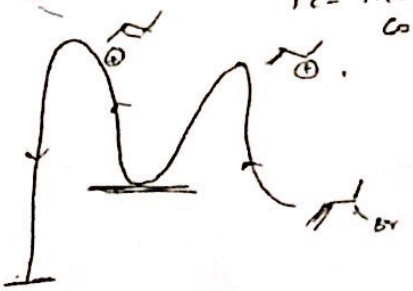


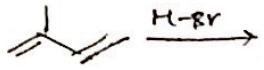
KC - Kinetically controlled.

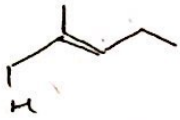
TC - Thermodically controlled.

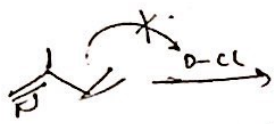
Mech:-



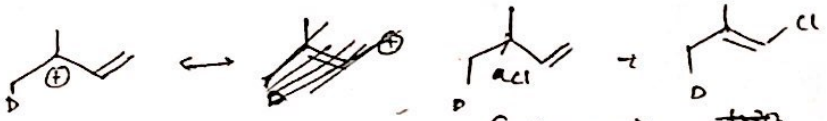


Q)  H-Br → Major is?

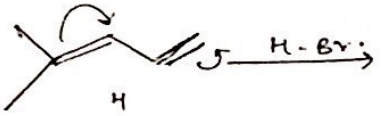


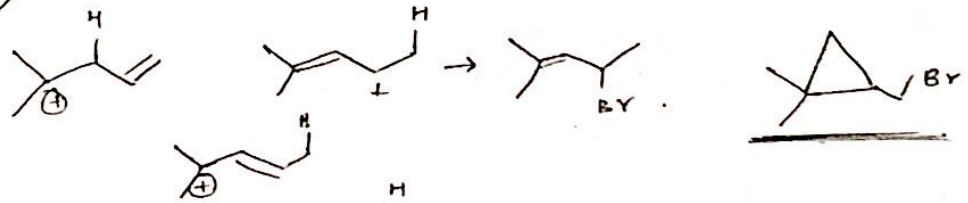
Q)  D-Cl → No-of products (structural isomers)

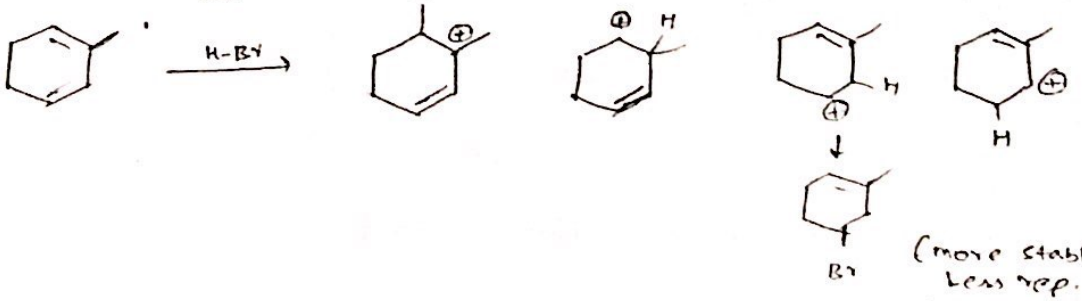
→ two



(only two).

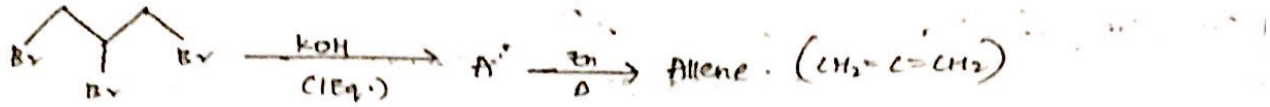
Q) 

Sol: 

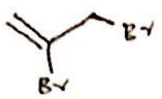
Q) 

(more stable) Less rep. (major)

DIENES:-

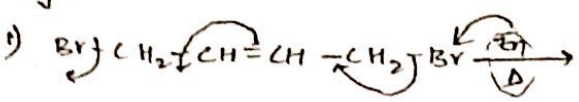


Iupac name of A is: ?



(2,3-dibromo prop-1-ene)

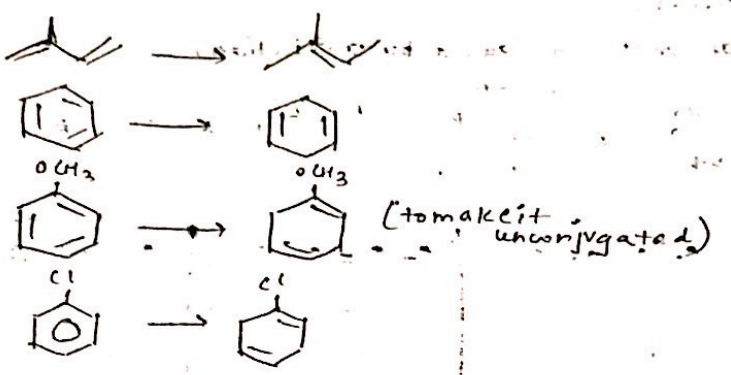
Eg:

1) 

(1,4-elemination)

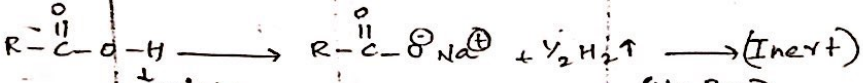
2) $Br-CH_2-C\equiv C-CH_2-Br \xrightarrow[\Delta]{Zn} CH_2=C=C=CH_2$ (1,4 elimination).

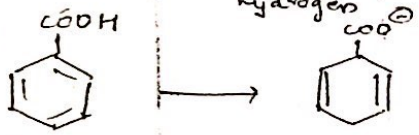
3) Na/liq. NH_3 :- Conjugated systems are reduced to unconjugated (π-bonds).



(tomakeit unconjugated)

Hint:-

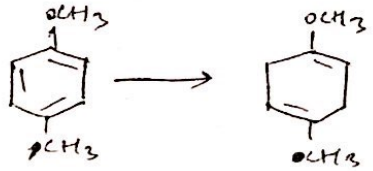


4) 

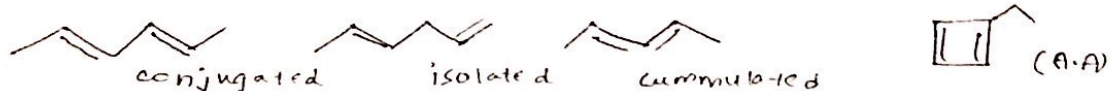
(Birch observation)

Note: +M groups ⇒ product obtained with ipso unsaturation

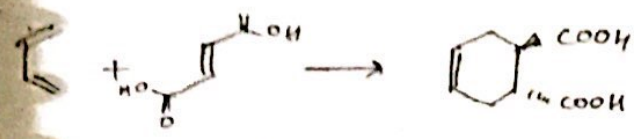
-M groups ⇒ product obtained with ipso saturation.

5) 

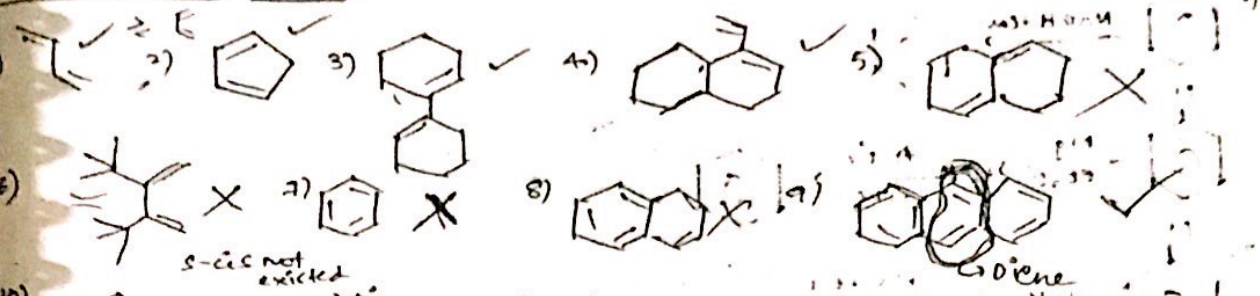
PROPERTIES OF DIENES:-



Stability: ① > ② > ③ > ④.



Examples for Dienes:

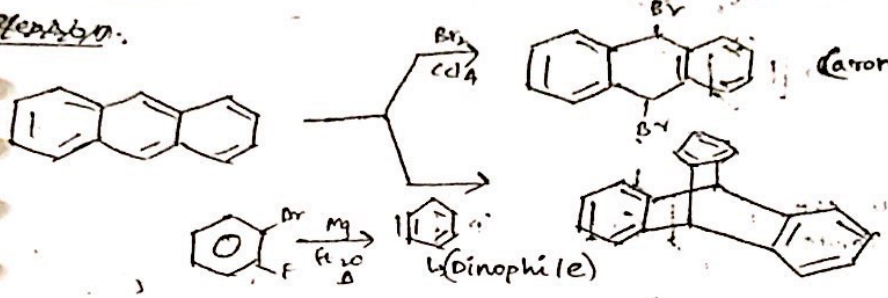


→ Dienes should possess 'σ-cis (s-cis) configuration.

LEWIRE → cyclic are better than acyclic dienes.

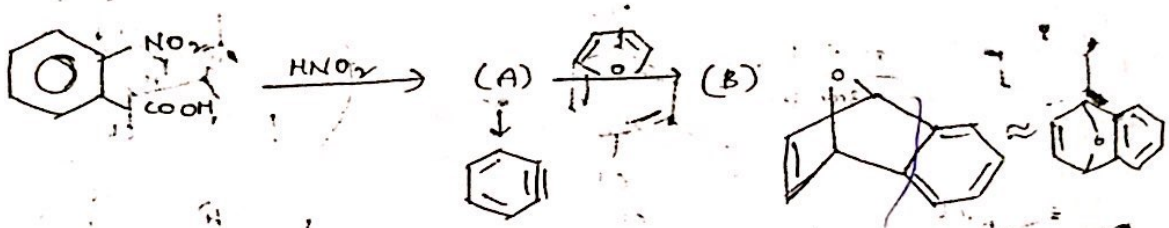
Reaction:

8)

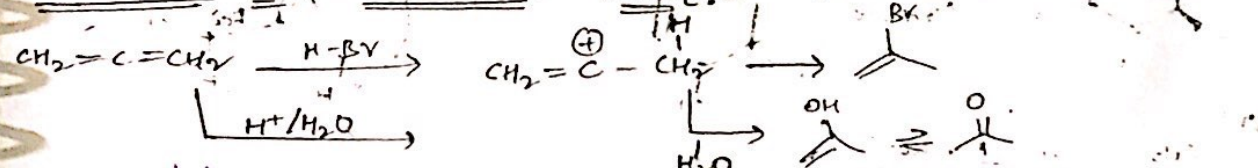


(aromaticity !)

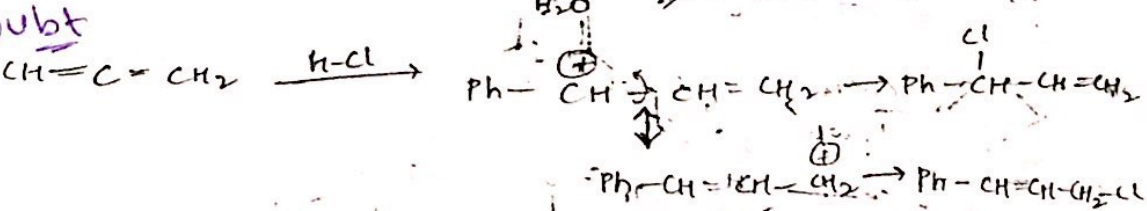
9)



PROPERTIES OF ACCUMULATED DIENE:-



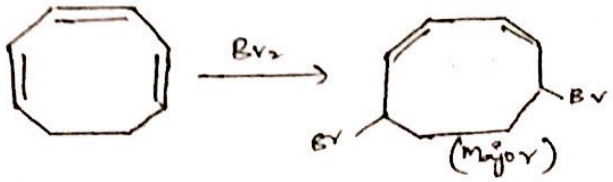
Doubt

10) 

major

ADDITION OF ALKENES :-

a)



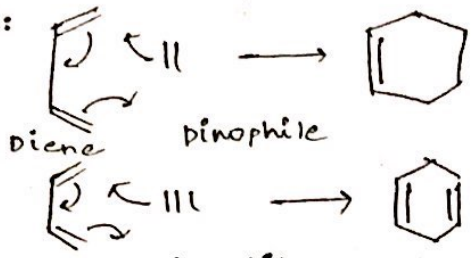
DIELS-ALDER REACTION :-

→ Peri-cyclic reaction (4π + 2π cyclic addition)

→ Occurs either by means of Δ (or) hν

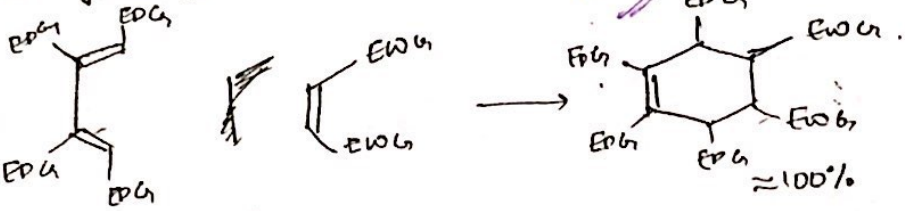
→ Also catalysed by Lewis acids.

Eg:

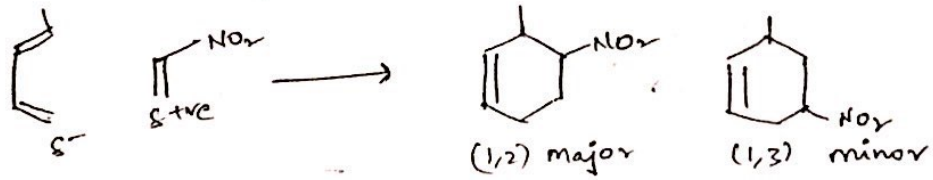


[Concerted GTS#]
[Product - 6 membered ring]

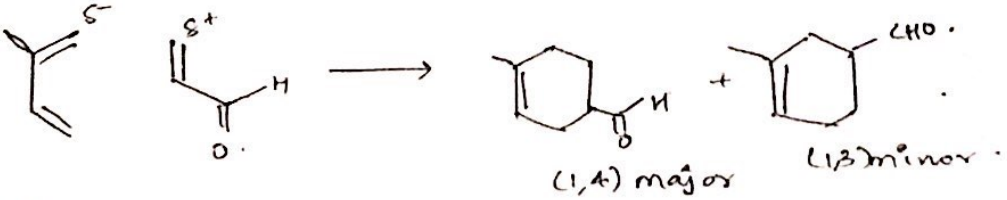
→ Poor yield's.



a)

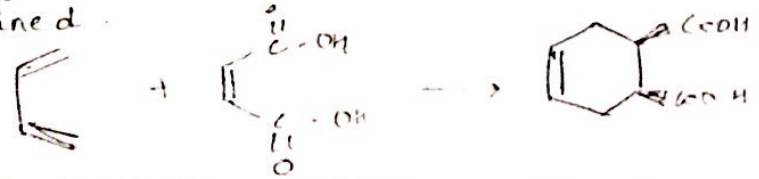


a)

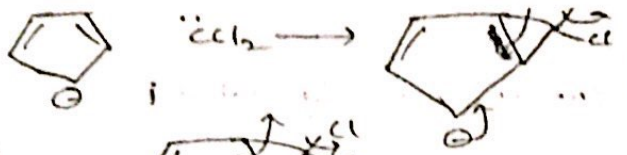


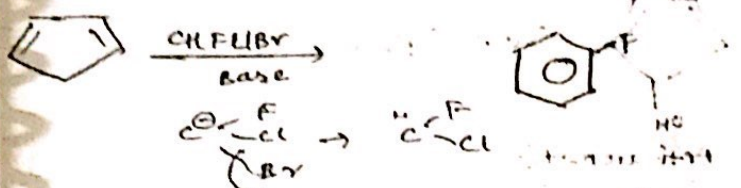
NOTE :

→ During Reaction dinophile stereo-chemistry will be retained

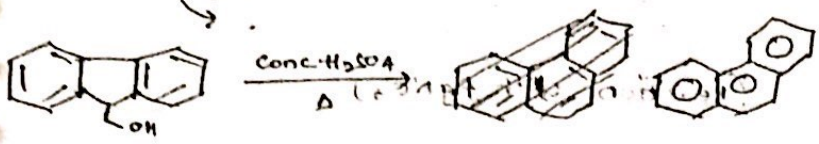


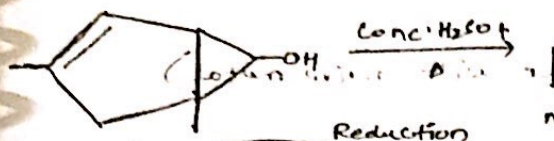
Mech i)



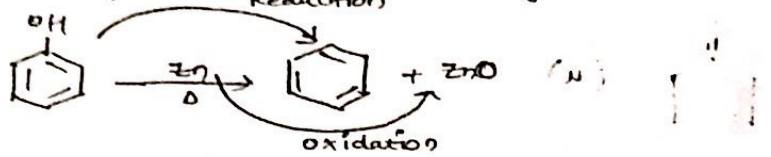


v)

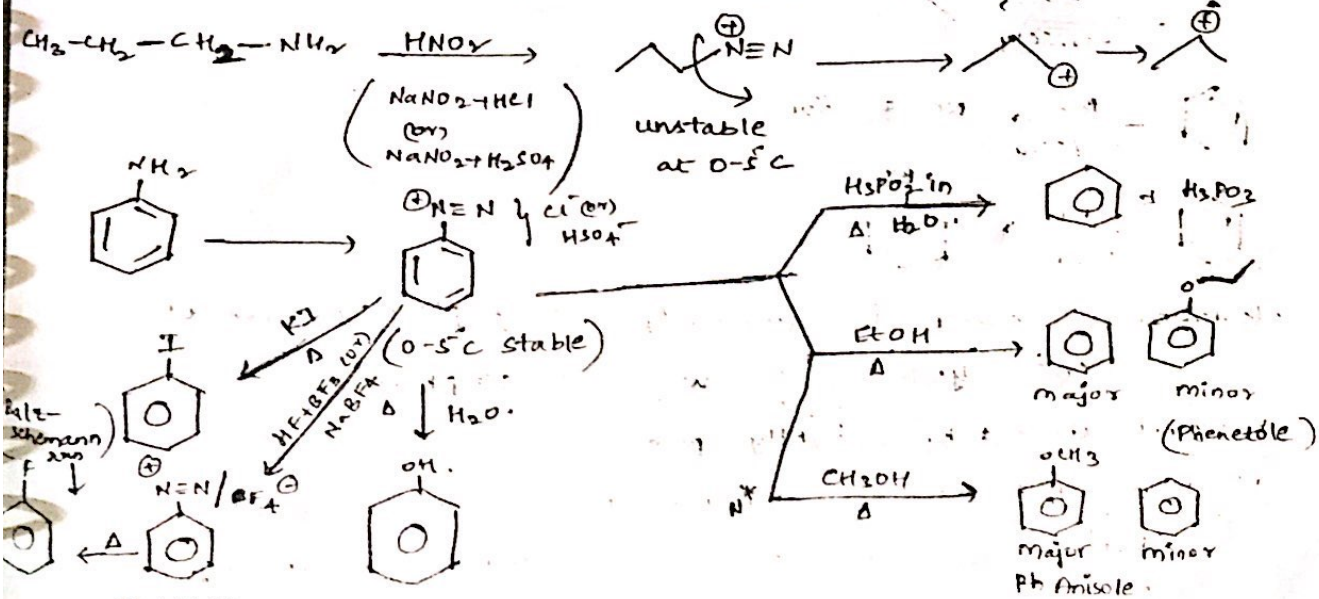




vi)



vii) BY USING BENZENE DIAZONIUM SALT:-



Stable at Room temperature.