ETHER

SN1 SN2

$\overset{\delta+}{R}-\overset{\delta-}{X} \xrightarrow{OH^-} R-OH$

OH^- → SN1 → 2 step मा हुन्छ

X^- → SN2 → 1 step मा हुन्छ

(i) $R-X \rightarrow R^+ + X^-$ (Carbocation)

(ii) $OH^- + R^+ \rightarrow R-OH + X^-$

Rxn of SN1 ∝ stability of C^+

$CH_3-\overset{\oplus}{CH_2}\ \overset{\ominus}{Cl}$ → 3° α-H

$CH_3-\overset{\oplus}{CH}(CH_3)-Cl$ → 6 α-H

$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl$ → 9 α-H

(rate of SN1 → 3° > 2° > 1°)

S_N2 (single step)

$$R-X + OH^- \longrightarrow R-OH + X^-$$

rate of S_N2 → $CH_3-Cl > 1^\circ > 2^\circ > 3^\circ$

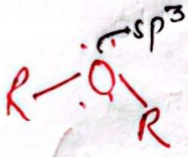
→ $CH_3-\underset{H}{\overset{C_2H_5}{\underset{|}{\overset{|}{C}}}}-Cl$ > $C_2H_5-\underset{H}{\overset{C_2H_5}{\underset{|}{\overset{|}{C}}}}-Cl$

S_N2 fast — S_N2 slow

→ $CH_3-\underset{H}{\overset{C_2H_5}{\underset{|}{\overset{|}{C}}}}-Cl$ ✗ $H-\underset{H}{\overset{C_2H_5}{\underset{|}{\overset{|}{C}}}}-Cl$

S_N2 slow — S_N2 fast

→ Ether – $R-O-R$



sp^3

– $\frac{2}{3}$ alkyl group same → simple ether.

– alkyl grp dif → mixed ether.

bond angle → 110°

CCl_4 — sp^3 : 109.8°

$R-O-H$ 108.5° — $H-O-H$ 104.5°

General Method of Preparation

① Rxn of alkyl halide with dry Ag_2O

$$R-X + Ag_2O \xrightarrow{(dry)} R-O-R + 2AgX$$

but moist Ag_2O → Alcohol

P.9.

$$CH_3-Cl + Ag_2O \longrightarrow CH_3-O-CH_3 + 2AgCl$$

CH_3-Cl

ether

$$\begin{matrix} C_2H_5-Cl \\ C_2H_5-Cl \end{matrix} + \underset{dry}{Ag_2O} \longrightarrow CH_2CH_3-O-C_2H_5 + 2AgCl$$

(2) $CH_3-CH_2-OH + \text{conc. } H_2SO_4 \xrightarrow{110^\circ C} C_2H_5HSO_4$

$\xrightarrow{140^\circ} C_2H_5-O-C_2H_5$ (ether) (413K) का हुन्छ

$\xrightarrow{170^\circ C} CH_2=CH_2$

(3) $R-O-H \xrightarrow{CH_2N_2 / O} R-O-CH_3$ (ether)

Diazomethane

(4) Williamson synthesis [NSR]

$$RO^-Na^+ + \overset{\delta+}{R}-\overset{\delta-}{X} \xrightarrow[\text{[NSR]} \to SN_2]{} R-O-R + NaX$$

ether

$$CH_3O^-Na^+ + CH_3-Cl \xrightarrow[SN_2]{NSR} CH_3-O-CH_3 + NaCl$$

Abhishek

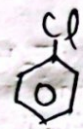
$(CH_2=CH-Cl)$ No SN_1, SN_2 due to double bond.

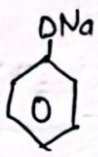
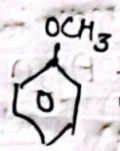


(double Bond wala C. संग Cl छ भने SN_1 / SN_2 हुँदैन।)

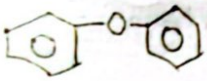
e.g. $CH_3-CH_2-CH=CH-Cl$.

$= CH_3-\overset{CH_3}{\underset{CH_3}{C}}-Cl$ 3° – (SN_1 हुन्छ, SN_2 हुँदैन)

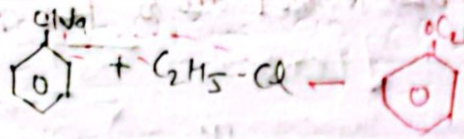
$\rightarrow CH_3O^-Na^+ +$  $\longrightarrow X$ (no ether)

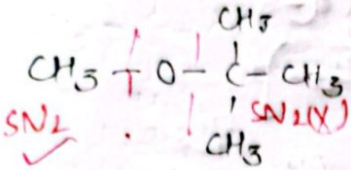
$\rightarrow$  $+ CH_3-Cl \rightarrow$  $=$

Anisole

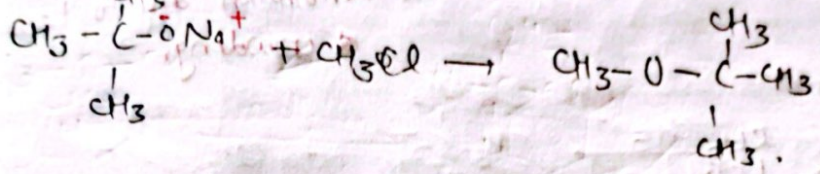
 – can't be prepared from williamson synthesis

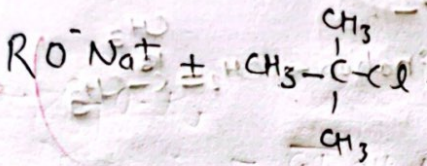
 – it can be prepared.

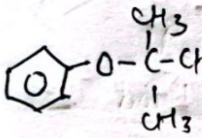


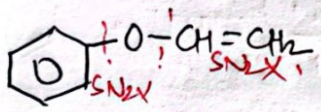
 → it can be prepared

SN2 ✓ SN2(X)



but, 

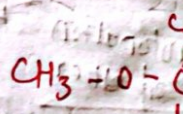
 (X) not prepared.

 – not prepared

– Both sym. & unsym ethers are prepared by S_N2 method.

Q. Methyl tert-butyl ether is prepared by:–

(a) $(C_2H_5)_3CONa + CH_3Cl$

(b) $(CH_3)_3CONa + C_2H_5-Cl$ → 

(c) $(CH_3)_3CONa + CH_3-Cl$

(d) $CH_3ONa + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl$

① $CH_3-O-CH_2-CH_3$

ⓐ $CH_3O^-Na^+ + CH_3-CH_2-Cl$

ⓑ $CH_3-CH_2-O^-Na^+ + CH_3-Cl$ → best method due to less crowding.

② $CH_3-CH_2-O-CH(CH_3)-CH_3$

ⓐ $CH_3-CH_2-O-Na + CH_3-CH(CH_3)-Cl$

ⓑ $CH_3-CH(CH_3)-ONa + CH_3-CH_2-Cl$ → best combination due to less crowding.

→ $RONa + CH_3-C(CH_3)_2-Cl \longrightarrow NoSN_2$.

(elimination → $CH_2=C(CH_3)-CH_3$) বন্ধ

Chemical properties

(A) Cleavage of ether by HX

$R-O-R \xrightarrow[\text{cold}]{HI\ (anhy)} SN_2$.

$\xrightarrow[\text{cold}]{\text{conc HI}} SN_1/SN_2$.

$\xrightarrow[\text{Hot/excess}]{\text{conc HI}} SN_1/SN_2$

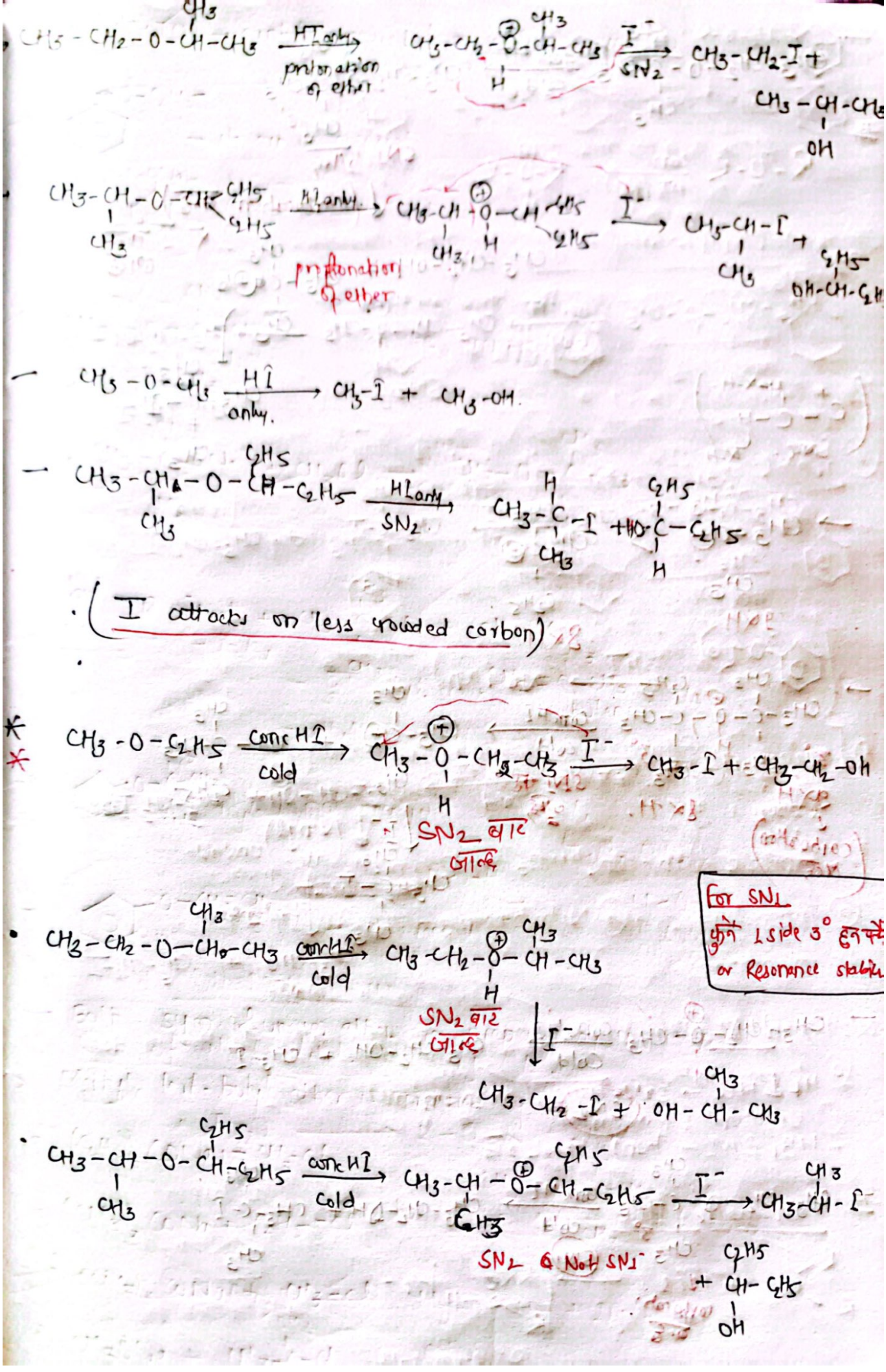
• $R-\ddot{O}-R + H-I \xrightarrow[\text{anhydrous}]{} R-\overset{\oplus}{O}(H)-R \xrightarrow{I^-} R-I + R-OH$.

H^+/I

protonation of ether

e.g. $CH_3-O-CH_2-CH_3 \xrightarrow[SN_2]{HI\ anhy} CH_3-\overset{\oplus}{O}(H)-CH_2-CH_3 \xrightarrow[SN_2]{I^-} CH_3-I + CH_3-CH_2-OH$.

less crowded



$CH_3-CH_2-O-CH(CH_3)-CH_3 \xrightarrow[\text{protonation of ether}]{HI\ only} CH_3-CH_2-\overset{\oplus}{O}(H)-CH(CH_3)-CH_3 \xrightarrow[SN_2]{I^-} CH_3-CH_2-I + CH_3-CH(OH)-CH_3$

$CH_3-CH(CH_3)-O-CH(C_2H_5)_2 \xrightarrow[\text{protonation of ether}]{HI\ only} CH_3-CH(CH_3)-\overset{\oplus}{O}(H)-CH(C_2H_5)_2 \xrightarrow{I^-} CH_3-CH(CH_3)-I + OH-CH(C_2H_5)-C_2H_5$

- $CH_3-O-CH_3 \xrightarrow[\text{only}]{HI} CH_3-I + CH_3-OH$

- $CH_3-CH(CH_3)-O-CH(C_2H_5)-C_2H_5 \xrightarrow[SN_2]{HI\ only} CH_3-C(H)(CH_3)-I + HO-C(C_2H_5)(H)-C_2H_5$

(I attacks on less crowded carbon)

* $CH_3-O-C_2H_5 \xrightarrow[\text{cold}]{conc\ HI} CH_3-\overset{\oplus}{O}(H)-CH_2-CH_3 \xrightarrow{I^-} CH_3-I + CH_3-CH_2-OH$

SN_2 बाट जान्छ

For SN_1
फुने 1 side 3° हुन पर्दै
or Resonance stability

- $CH_3-CH_2-O-CH(CH_3)-CH_3 \xrightarrow[\text{cold}]{conc\ HI} CH_3-CH_2-\overset{\oplus}{O}(H)-CH(CH_3)-CH_3 \xrightarrow{I^-} CH_3-CH_2-I + OH-CH(CH_3)-CH_3$

SN_2 बाट जान्छ

- $CH_3-CH(CH_3)-O-CH(C_2H_5)-C_2H_5 \xrightarrow[\text{cold}]{conc\ HI} CH_3-CH(CH_3)-\overset{\oplus}{O}-CH(C_2H_5)-C_2H_5 \xrightarrow{I^-} CH_3-CH(CH_3)-I + CH(C_2H_5)(OH)-C_2H_5$

SN_2 Not SN_1

→ $CH_3-CH_2-O-C(CH_3)_3 \xrightarrow[\text{cold}]{\text{conc HI}} CH_3-CH_2-\overset{\oplus}{O}(H)-C(CH_3)_3$ 3°

SN1 जाल्द

↓ (carbocation बन्द) र I तेहि जाल्द

$CH_3-CH_2-OH + CH_3-C(CH_3)_3\oplus$

$CH_3-C(CH_3)_3-I$

$\left(C^+-C(H-\alpha-H)-H\right)$ α-C, α-H

→ $CH_3-C(CH_3)_3\oplus$ > $CH_3-C(CH_3)_2\oplus$

9αH 8αH

→ $CH_3-C(CH_3)_3-\overset{\oplus}{O}(H)-C(CH_3)_2-CH_3$ 3° 3°

9αH (carbocation बन्द) 8αH

$\xrightarrow[\text{cold}]{\text{conc HI}}$ SN1 पट जुड़ि

$CH_3-C(CH_3)_3\oplus + OH-C(CH_3)_2-CH_3$

↓ I^-

$CH_3-C(CH_3)_3-I$

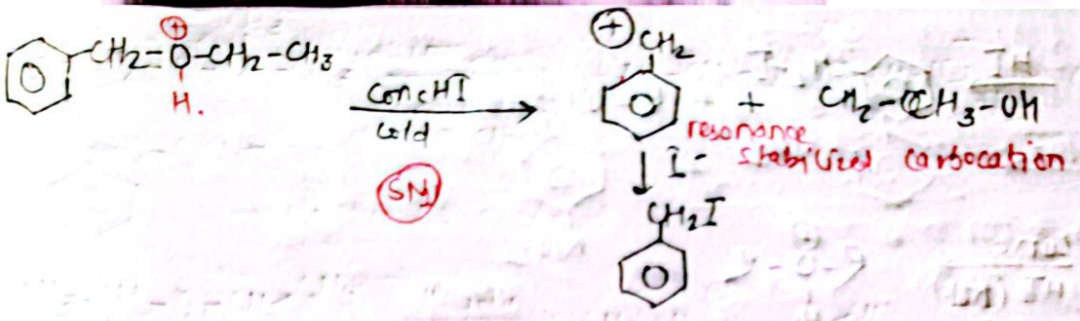
→ $CH_3-CH_2-\overset{\oplus}{O}(H)-CH_3 \xrightarrow[\text{cold}]{\text{conc HI}} CH_3-CH_2-OH + CH_3-I$

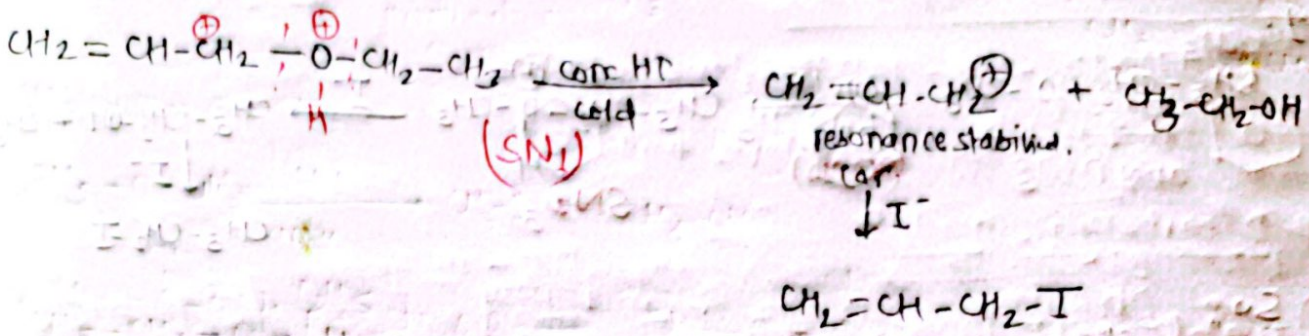
SN2

→ $CH_3-CH_2-O-C(CH_3)_3$ 3° $\xrightarrow[\text{cold}]{\text{conc HI}}$ $CH_3-CH_2-OH + CH_3-C(CH_3)_3-I$

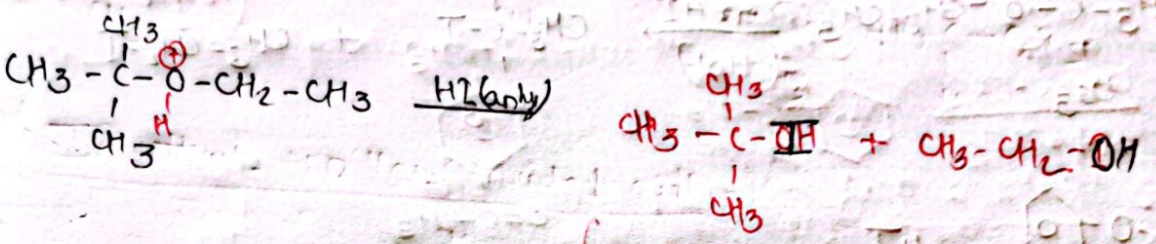
SN1

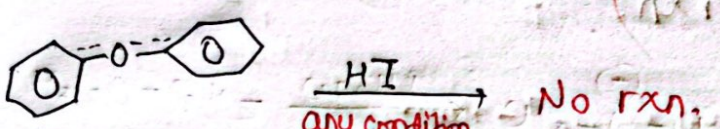
↓ carbocation बन्द



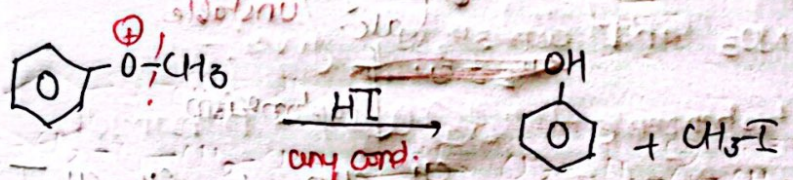


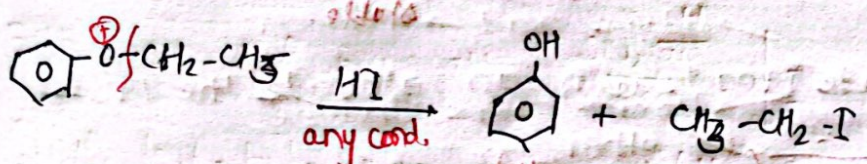
Q.





due to resonce
partial double-bond ocu





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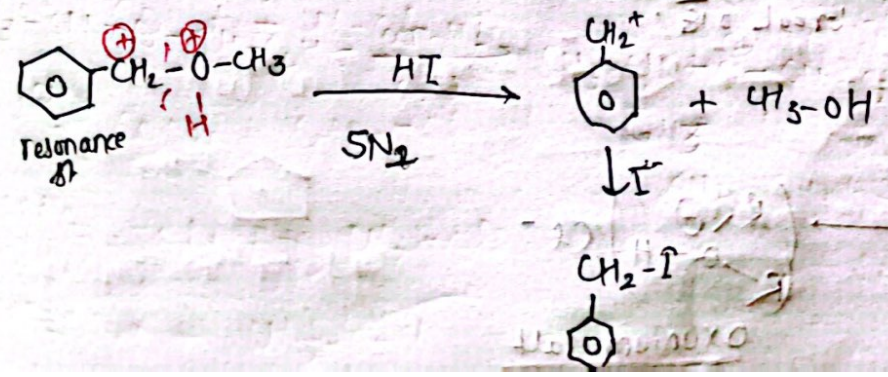

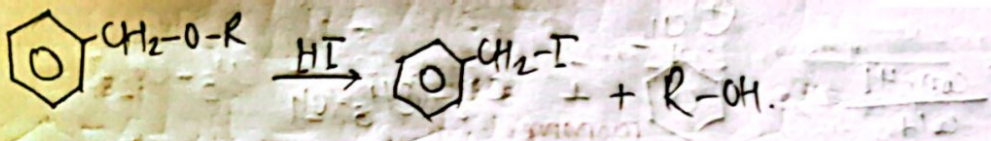

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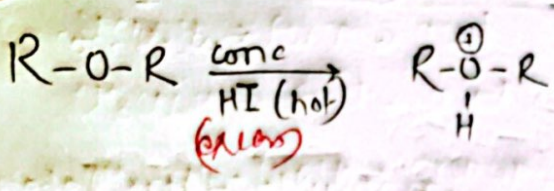
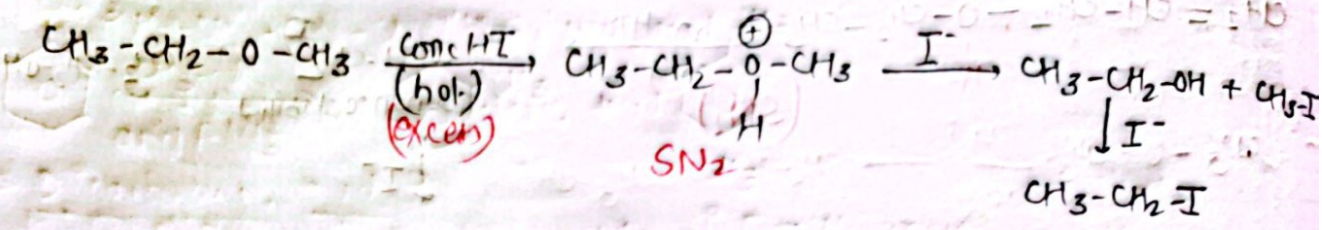
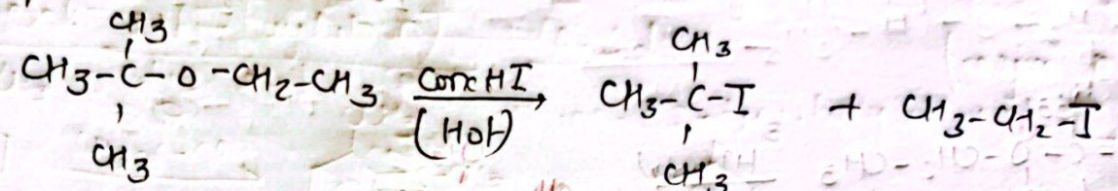


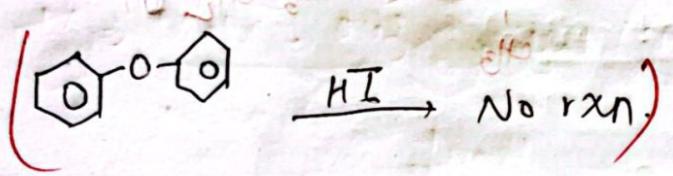
(excess)

e.g.

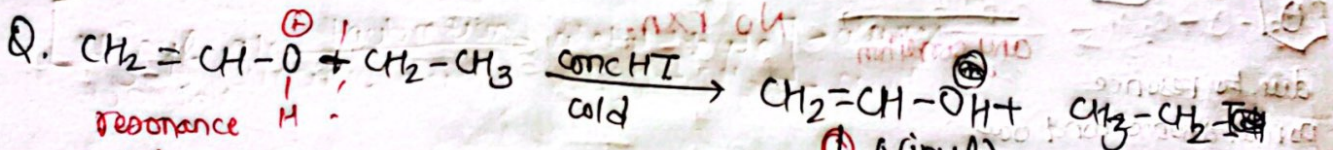


So,



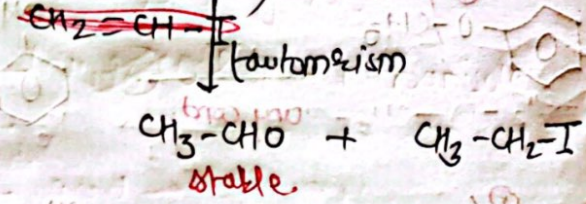


Q.



Resonance stable.

(Vinyl ale.) unstable

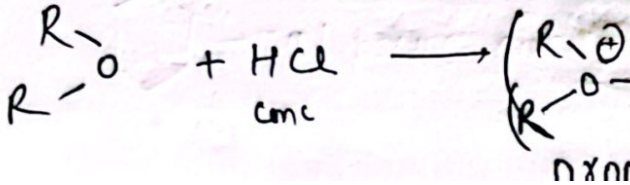


stable.

HX

- HF & HCl → salt बनाते (oxonium salt)
- HBr & HI → bond break हो जाते।

Rxn with HCl



Oxonium salt

Rxn with PCl_5

$$R-O-R \xrightarrow[PCl_5]{\Delta} 2R-Cl + POCl_3$$

eg.

$$C_2H_5-O-C_2H_5 \xrightarrow[PCl_5]{\Delta} 2C_2H_5-Cl + POCl_3$$

Acetylation

$$C_2H_5-O-C_2H_5 + CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{AlCl_3} C_2H_5-O-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3CH_2Cl$$

Hydrolysis of ether (imp)

$C_2H_5-O-C_2H_5$

- dil H_2SO_4 → No rxn
- dil H_2SO_4, Δ → $2C_2H_5OH + H_2O$
- conc H_2SO_4 → $(C_2H_5-\overset{+}{O}(H)-C_2H_5)\,HSO_4^-$
- conc H_2SO_4, Δ → $2C_2H_5HSO_4 + H_2O$ (salt)

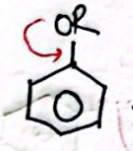
ethyl H-sulphate.

Chlorination of ether

$CH_3-CH_2-O-CH_2-CH_3$

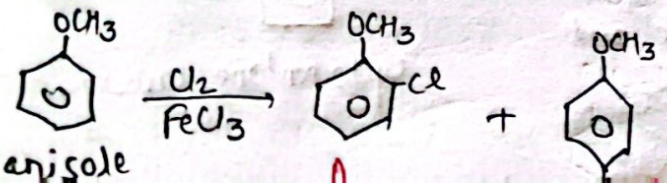
- Cl_2, sunlight → $CCl_3CCl_2-O-CCl_2-CCl_3$ perchloro ether
- Cl_2, dark → $CH_3-\underset{Cl}{CH}-O-\underset{Cl}{CH}-CH_3$

#



(aromatic ether) ESR ↑, o,p-directing, +R group

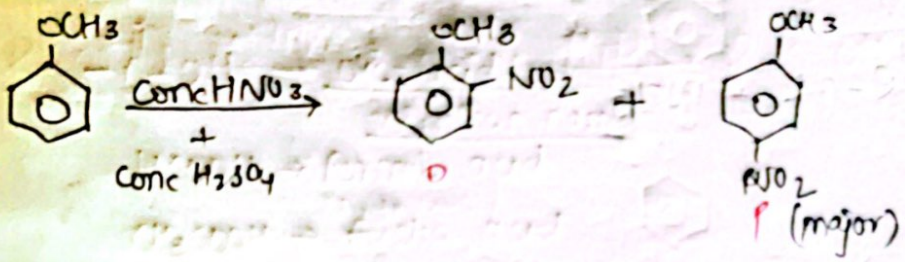
(1) Halogenation



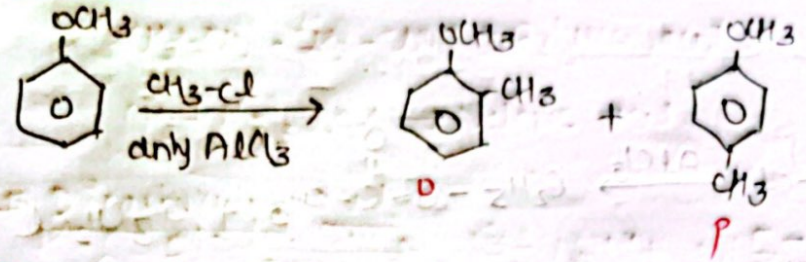
anisole

A

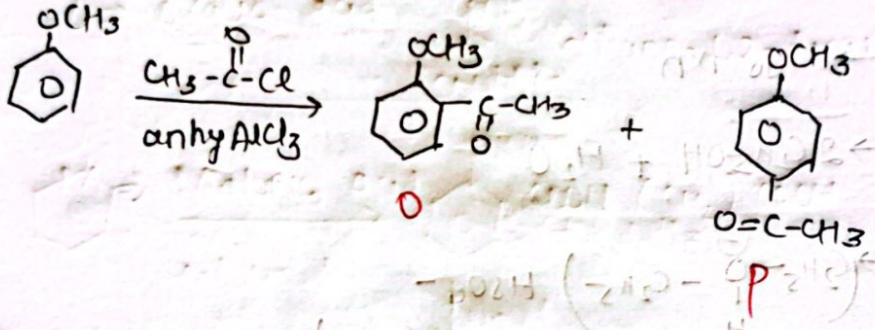
(2) Nitration



(3) friedel craft (alkylation)



(4) friedel craft (acylation)



(major p-) wala always.

[vinyl alc $\xrightarrow{\text{tautomerism}}$ acetaldehyde] - always.
Unstable Stable.

Q. Anisole with conc HNO_3 and conc. H_2SO_4 gives:-

(a) phenol (b) Nitrobenzene (c) o & p - nitroanisole
(d) m-nitroanisole

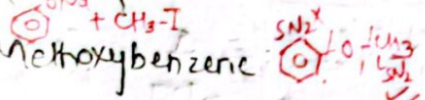
Q. When 1° alkyl halide reacts with an alkoxide the product is:-

(a) hydrocarbon (b) ether
(c) unsaturated hydrocarbon (d) alcohol

$R-X + RO^-Na^+ \longrightarrow R-O-R + NaX$ (Williamson)

Q. Which of the Following cannot be prepared by using williamson synthesis?

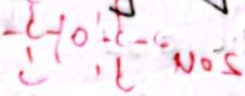
(a) Methoxybenzene



(b) Benzyl-p-nitrophenyl ether

(c) Methyl ter-butyl ether

(d) Di-tertiary butyl ether



Q. When diethyl ether is treated with excess of Cl_2 in presence of sunlight, the product formed is:-

(a) $CH_3CHCl-O-CH_2CH_3$

(b) $CH_3CHCl-O-CHClCH_3$

(c) $CCl_3CCl_2-O-CCl_2CCl_3$

(d) $CH_3CCl_2-O-CHClCH_3$

$C_2H_5-O-C_2H_5$

Q. In williamson synthesis, ethoxyethane is prepared by:-

(a) passing ethanol over alumina

(b) heating ethanol with dry Ag_2O

(c) heating sod. ethoxide with ethyl bromide

(d) treating ethyl alc. with excess of H_2SO_4 at 443K.

Q. An aromatic ether is not cleaved by HI even at 525K. The compound is:-

(a) $C_6H_5OCH_3$

(b) $C_6H_5O-C_6H_4(CH_3)$



(c) $C_6H_5OC_3H_7$

(d) Tetrahydrofuran

Q. Ether is obtained from ethyl alc:-

(a) In presence of H_2SO_4 at 413K

(b) at 478K

(c) at 303K

(d) at 273K.