Q. No. 2 Part (i)

REACTIONS OF NITRATES

$LiNO_3$: The $LiNO_3$ is least stable to heat among all alkali metals. When heated its dissociations take place as:-

$$4LiNO_3 \xrightarrow{Heat} 2Li_2O + 4NO_2 + O_2$$

It's instability leads to its different behaviour from others.

$NaNO_3$: It is more stable to heat then $LiNO_3$. On heating it is dissociated as

$$2NaNO_3 \xrightarrow{Heat} 2NaNO_2 + O_2$$

$Mg(NO_3)_2$: It will decompose on strong heat to produce:

$$2Mg(NO_3)_2 \xrightarrow{Heat} 2MgO + 4NO_2 + O_2$$

Q. No. 2 Part (ii) The electronic configurations of Cu and Cr are

^{29}Copper Cu → $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^{10}$

^{24}Chromium Cr → $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$

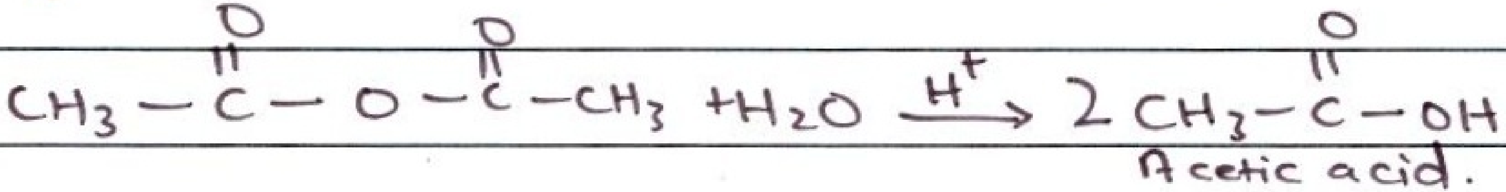
According to Auf Bau's principle electrons occupy separate orbitals if available and lower energy orbitals are filled first. The lower n+L value orbitals should be filled first. So according to this n+1 value of 4s is 4 and 3d is 5 so 4s should have been filled first but this is not the case in Cr or Cu because of stability half filled and completely filled d-orbital these elements show this configuration like Mn and Zn respectively.

$Cr \rightarrow \overset{4s}{\boxed{\uparrow}}\quad \overset{3d}{\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}\boxed{\uparrow}}\qquad Cu \rightarrow \overset{4s}{\boxed{\uparrow}}\quad \overset{3d}{\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}}$

Q. No. 2 Part (iii) Acetic anhydride →

$$CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3$$

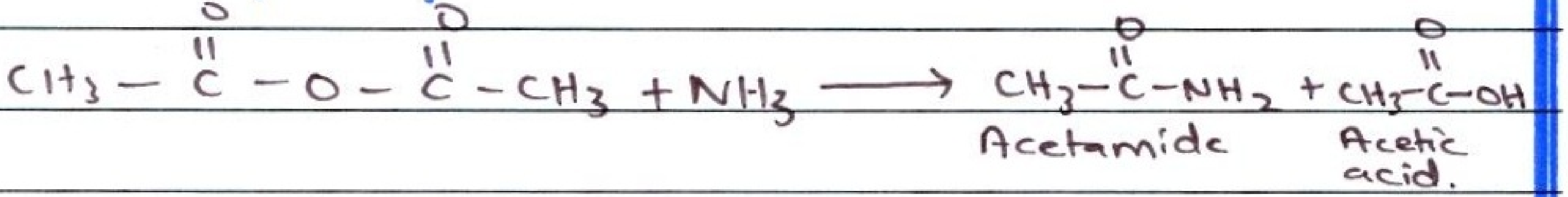
H_2O → They react with water in presence of strong acid or base to form acid from which it derived.



$$CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + H_2O \xrightarrow{H^+} 2\,CH_3-\overset{\overset{O}{\|}}{C}-OH$$

Acetic acid.

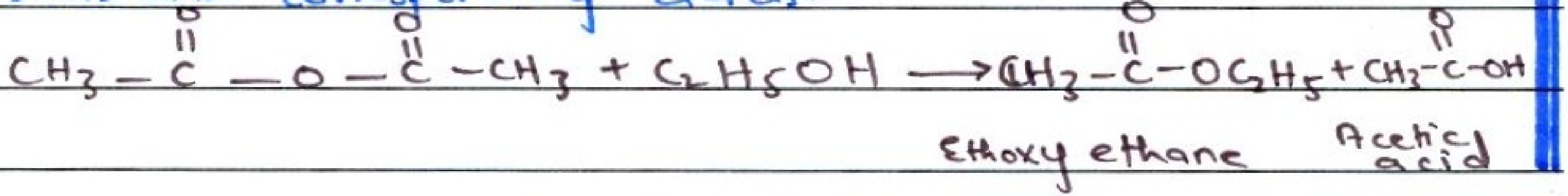
NH_3 → They react with NH_3 to form amides. and corresponding acids.



$$CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + NH_3 \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-NH_2 + CH_3-\overset{\overset{O}{\|}}{C}-OH$$

Acetamide — Acetic acid.

C_2H_5OH → They react with alcohols to form esters and corresponding acids.

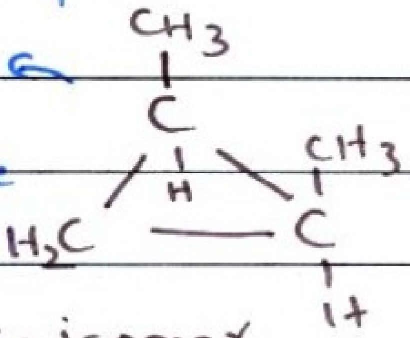


$$CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + C_2H_5OH \longrightarrow CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5 + CH_3-\overset{\overset{O}{\|}}{C}-OH$$

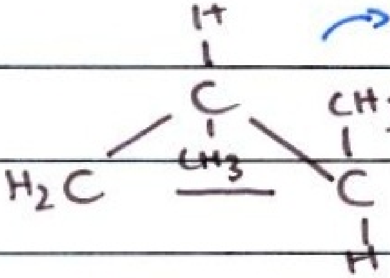
Ethoxy ethane — Acetic acid

Q. No. 2 Part (iv) We see the structure of 1,2-dimethyl cyclopropane.

bulky groups on same side



cis-isomer



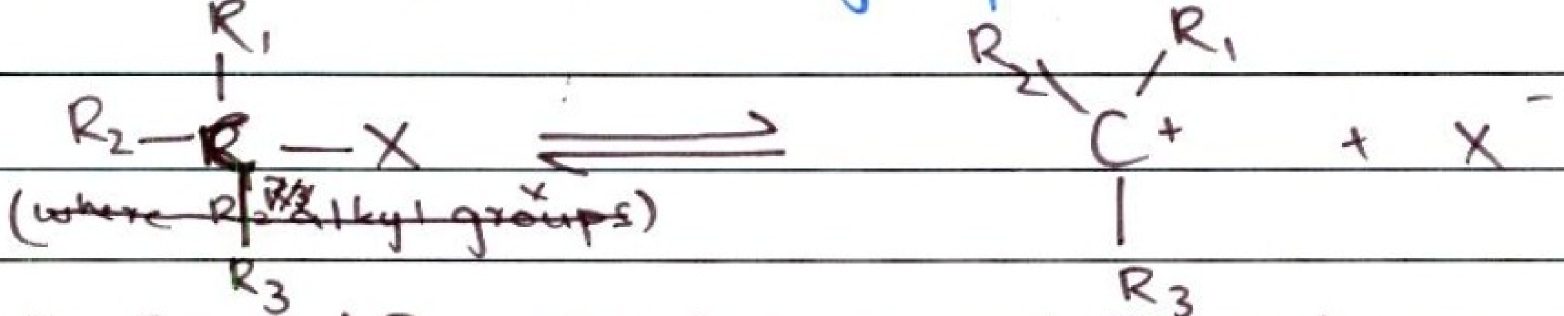
→ bulky groups on opposite side.

trans-isomer

we know cyclic compounds containing two different groups other than H are able to exibit geometric isomerism because restriction between the C–C bond is restricted as it will break the closed chain and compound will not remain cyclic. In 1,2-dimethy cyclopropane the presence of two methyl groups on different carbon atom either on similar side or opposite side exhibit isomerism

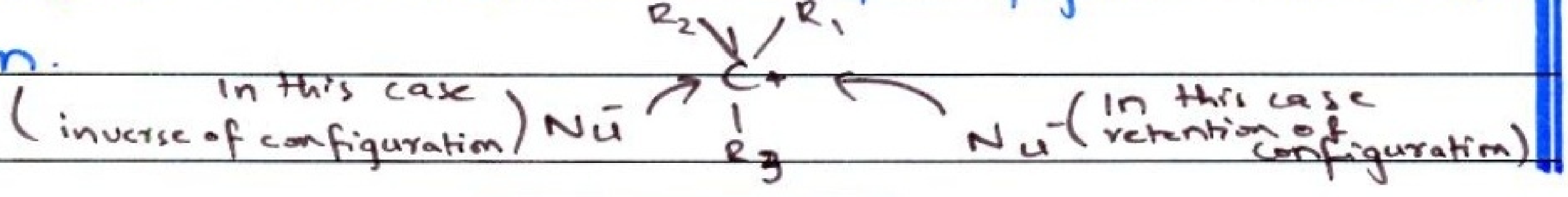
Q. No. 2 Part (v) **SN$_1$ reaction:** It is a unimolecular nucleophilic substitution reaction.

Mechanism: In this reaction the substrate i.e. Alkyl halide dissociates reversibly in carbocation and X^- ion where $X = Cl, Br, I$. This step is slow and rate determing step.



The R_1, R_2 and R_3 may be same or different.

In this step the attacking nucleophile attacks on carbocation with 50% inversion of configuration and 50% retion.



Q. No. 2 Part (vi) CrO_4^{2-} is soluble in water and gives a bright yellow solution. when an acid is added to this solution it is converted into $Cr_2O_7^{2-}$ reversibly. at equilibrium. The orange colour appears inplace of yellow colour

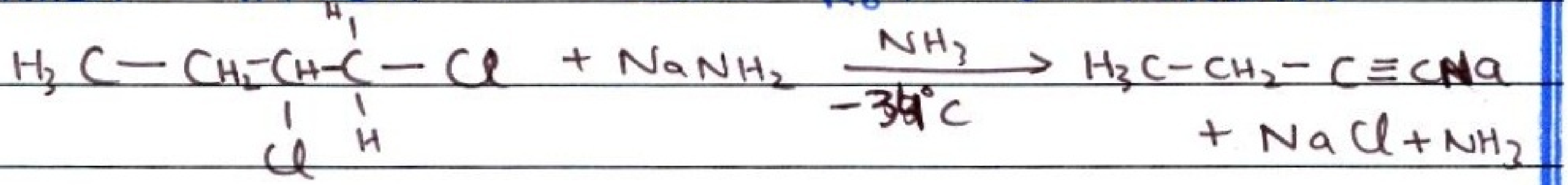
$$2CrO_4^{2-} + 2H^+ \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

But if an alkali is added to above equilibrium mixture concentration of H^+ ions decreases and reaction shifts in backward direction.

$$Cr_2O_7^{2-} + 2OH^- \rightleftharpoons 2CrO_4^{2-} + H_2O$$

so in presence of acid reaction proceeds in foward direction and in alkali backward direction.

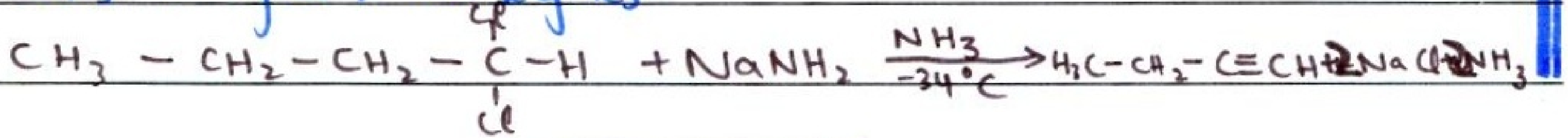
Q. No. 2 Part (vii) **Vicinal dihalide:-** A vicinal dihalide is a specie which have halogens on adjacent carbon atoms. Dehydrohalogen of vicinal dihalide to remov 2 HX molecules from it produces Alkyne. To produce terminal alkynes we use $NaNH_2$ in liquid Ammonia. In KOH it would not be terminal.



$$H_3C-CH_2-\underset{\underset{Cl}{|}}{CH}-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{C}}-Cl + NaNH_2 \xrightarrow[-34^\circ C]{NH_3} H_3C-CH_2-C\equiv CNa + NaCl + NH_3$$

$$H_3C-CH_2-C\equiv CNa + H_2O \longrightarrow H_3C-CH_2-C\equiv CH + NaOH$$

Geminal dihalide: Specie which has halogens on same carbon atom. Upon reaction with $NaNH_2$ in liquid NH_3 it gives Alkynes.

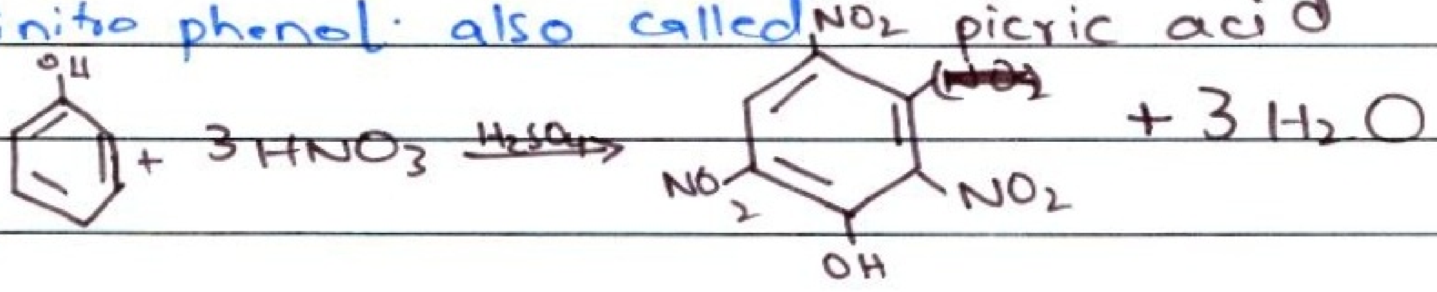


$$CH_3-CH_2-CH_2-\underset{\underset{Cl}{|}}{\overset{Cl}{C}}-H + NaNH_2 \xrightarrow[-34^\circ C]{NH_3} H_3C-CH_2-C\equiv CH + 2NaCl + 2NH_3$$

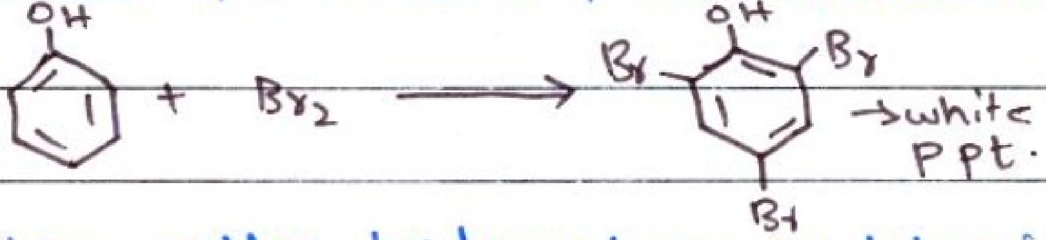
Q. No. 2 Part (viii) REACTIONS OF PHENOL

Phenols react with following as

HNO_3 → It reacts conc. HNO_3 to produce 2,4,6 Trinitro phenol. also called picric acid

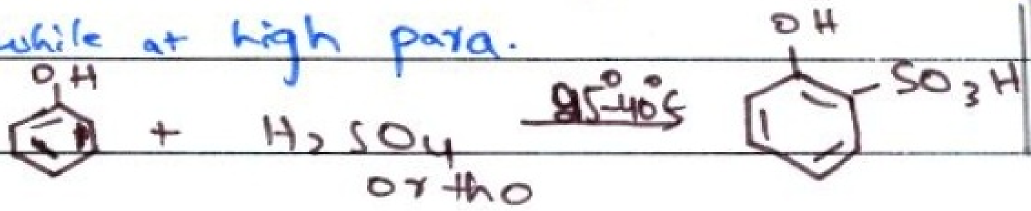


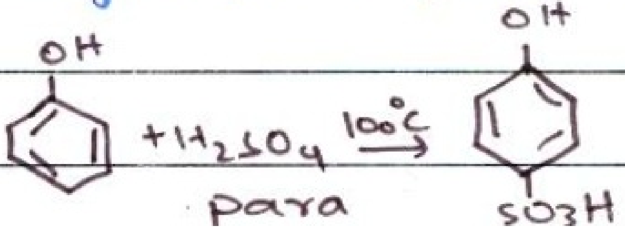
aq. Br_2 → It reach with aq. Br_2 to give white white precipitate of 2,4,6 Tribomo phenol which is also test for phenol.



Conc. H_2SO_4 →

At low temperature it gives ortho hydroxy benzene sulphonic acid while at high para.



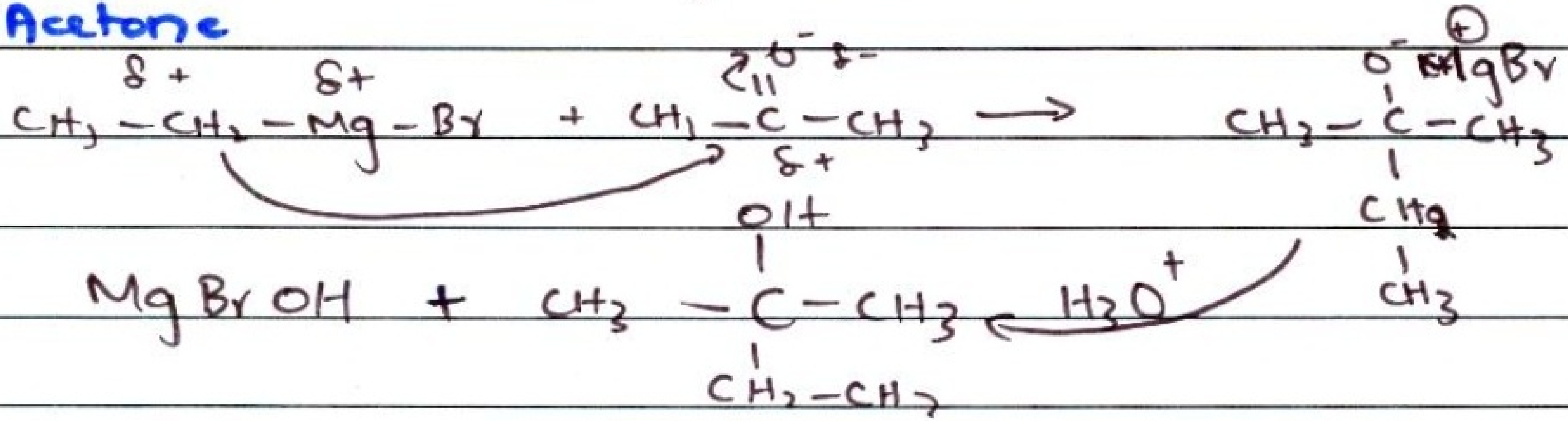


Q. No. 2 Part (ix) Both are elimination reactions of alkyhalides.

E_1 Reaction	E_2 Reaction
i) It is unimolecular elimination reaction.	(i) It is bimolecular elimination reaction.
ii) Alkyl halides dissociates in carbocation before forming of new bond. Reaction takes place in two steps.	(ii) No carbocation is formed. Bond breaking and formation takes place in single step.
(iii) It's rate is affected by concentration of Alkyl halide. first order reaction $= k[R-X]$	(iii) It's rate is affected by both alkyhalide and nucleophile. second order $= k[R-X][Nu^-]$
iv) favoured by tertiary alkyl halides.	iv) favoured by secondary alkyl halide.
v) favoured in polar solvents.	v) favoured in non polar solvents

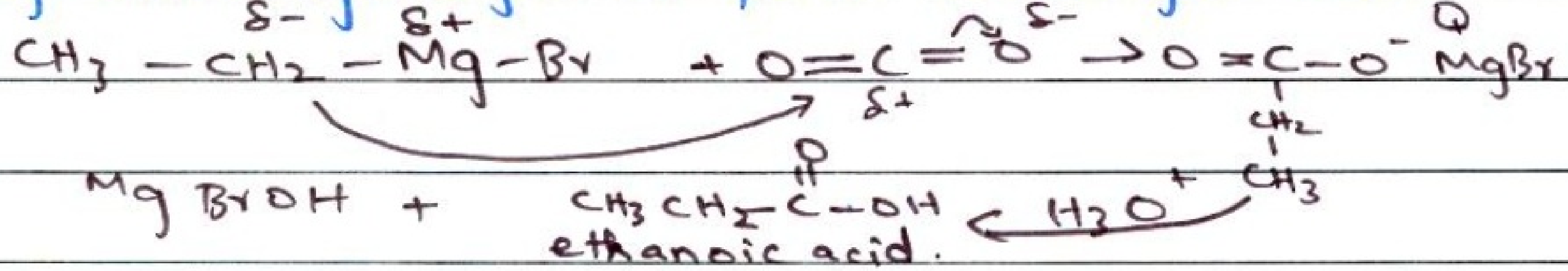
Q. No. 2 Part (x) $CH_3-CH_2-Mg-Br$

a) Acetone

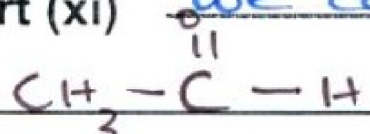


It reacts with grignard's reagent to form tertiary alcohol after hydrolysis in presence mineral acid. In this case it forms 1- ethyl-1,1-dimethyl alcohol

b) CO_2 → Grignard's reagent react with CO_2 followed by acid hydrolysis to form carboxylic acid.

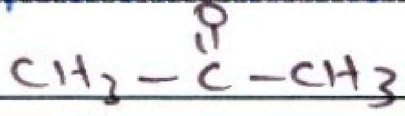


Q. No. 2 Part (xi) we can see from their structures as



$CH_3-\overset{O}{\overset{\|}{C}}-H$

Acetaldehyde



$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$

Acetone

i) As acetone is surrounded by 2 bulky groups of CH_3 so approach of nucleophile to electrophilic Carbonyl carbon will face greater stearic repulsion of greater bulky groups. while in acetaldehyde there is only 1 bulky group so stearic repulsions are less.

ii) As we know methyl groups have a weakly electron donating inductive effect so in case of acetone two methyl groups make the electrophilic carbonyl carbonyl carbon less electrophilic and lesser affinity for nucleophile while 1 methy group in the other.

Q. No. 2 Part (xii) Chloro-fluoro carbons like Freon-1 ($CFCl_3$) or Freon-2 (CF_2Cl_2) used in refrigerators as refrigerants, in Air conditioners, fire extinguishers and cleaners of electric components. They upon leakage enters the atmosphere but remain inert within the troposphere. As they reach the stratosphere absorption of UV-light of sun breaks the C–Cl bond to generate $\dot{C}l$ free radical which is a major contributor in ozone depletion.

$$CFCl_3 \xrightarrow{h.v} \dot{C}F\dot{C}l_2 + \dot{C}l$$

$$\dot{C}l + O_3 \longrightarrow \dot{O}Cl + O_2$$

$$\dot{O}Cl + \dot{O} \longrightarrow O_2 + \dot{C}l$$

This single $\dot{C}l$ can destroy thousands or lacs of ozone molecules.

Q. No. 2 Part (xiii) **Data**

Mg-24 mass = m_1 = 24 amu % age abundance = 78.70 % = R_1

Mg-25 mass = m_2 = 25 amu % age abundance = 10.13 = R_2

Mg-26 mass = m_3 = 26 amu % age abundance = 11.17 = R_3

Required

relative atomic mass = ?

formula

$$M = \frac{R_1 m_1 + R_2 m_2 + R_3 m_3}{100}$$

Solution:-

$$M = 24 \times 78.70 + 25 \times 10.13 + 26 \times 11.17 / 100$$

= (~~24.1735) amu~~) 24.3247 amu

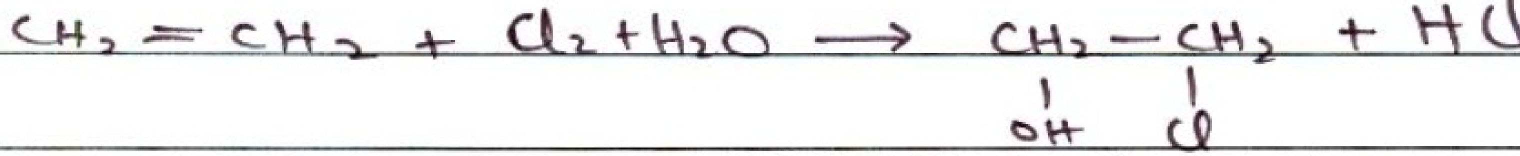
Result: So relative atomic mass is 24.3247 amu.

Q. No. 2 Part (xiv) **Ehanol:** ethene can be converted into ethanol by addition of water in presence of strong acid. Ethene reacts with ~~(Alkyl hydrogen sulphate)~~ conc. H_2SO_4 to from alkyl hydrogen sulphate which upon heating with boiled water at 100°C produces ethanol.

$$CH_2=CH_2 + H_2SO_4 \longrightarrow CH_3-CH_2-OSO_3H$$

$$CH_3-CH_2-OSO_3H + H_2O \xrightarrow{100^\circ C} CH_3-CH_2-OH + H_2SO_4$$

Ethylene chlorohydrin: Ethene upon reaction with hypochlorous acid reach to form Ethylene chloro hydrin. In this reaction molecules of solvent becomes reactants too.



$$CH_2=CH_2 + Cl_2 + H_2O \longrightarrow \underset{OH}{\underset{|}{CH_2}}-\underset{Cl}{\underset{|}{CH_2}} + HCl$$

Ethylen chlorohydrin

CARBON DIOXIDE;-

Carbon dioxide is a simple triatomic covalent molecule. As we know elements at top of group IV A (for) are nonmetals and form acidic oxides so CO_2 is an acidic oxide having reacts with water and bases as;-

Reaction with water; Carbon dioxide reacts and dissolves slightly in water to produce H^+ ions(strictly hydroxonium ions) and Hydrogen Carbonate ions.

$$CO_{2(g)} + H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + HCO_{3(aq)}^{-1}$$

Reaction with base; CO_2 reacts with hot and concentrated NaOH to either form sodium carbonate or sodium hydrogen Carbonate depending upon concentration of reactants.

$$CO_{2(g)} + 2NaOH_{(aq)} \longrightarrow Na_2CO_{3(aq)} + H_2O_{(l)}$$

Oxides of Ge, Sn and Pb:-

Monoxides; They are form monoxides with formula XO where X = (Ge, Sn, and Pb) These oxides are amphoteric in nature

Reaction with acids:

Monoxides reacts with dilute cold HCl to form salt and water as;

$$XO_{(g)} + 2HCl_{(aq)} \longrightarrow XCl_{2(aq)} + H_2O_{(l)}$$

when PbO reacts with dilute HCl it forms insoluble layer of $PbCl_2$ on PbO and stops further reaction.

$$PbO_{(g)} + 2HCl_{(aq)} \longrightarrow PbCl_{2(s)} + H_2O_{(l)}$$

But in concentrated ~~(H_2SO_4)~~ HCl insolubility disappears and $PbCl_2$ reacts with excess of Cl^{-1} ions to form complex $PbCl_4^{2-}$ soluble in water.

$$PbCl_2 + 2Cl^{-1} \longrightarrow PbCl_4^{2-}$$

Reaction with bases;-

Monoxides reacts with hot concentrated NaOH as

$$XO + 2NaOH \longrightarrow Na_2XO_2 + H_2O$$

where X = Sn, Ge, Pb

Dioxides;-

They also form dioxide with formula XO_2 where X = (Ge, Sn and Pb) They are also amphoteric in nature.

Reaction with acids:

They react with cold concentrated HCl to form ~~(PbT)~~ XCl_4 as

$$XO_2 + 4HCl \longrightarrow XCl_4 + 2H_2O$$

The compound XCl_4 reacts with excess of Cl^{-1} ions to form XCl_6^{2-} complex ion.

$$XCl_4 + 2Cl^{-1} \longrightarrow XCl_6^{2-}$$

where X = Ge, Sn, Pb

The reaction has to be done with ice cold HCl in case of $PbCl_4$ or else it will dissociate in $PbCl_2$ and Cl_2 due to preferred oxidation state of +2 to that of +4 (Inert pair effect)

$$PbCl_4 \longrightarrow PbCl_2 + Cl_2$$

Reaction with bases

They react with hot concentrated NaOH to form soluble ion $X(OH)_6^{2-}$ as:-

$$XO_2 + 2NaOH + 2H_2O \longrightarrow Na_2X(OH)_6$$

where X = Ge, Sn, Pb

OXIDATION STATES OF GROUP IV A ELEMENTS

The first two members of group IVA are C and Si which show only +4 oxidation states. While rest show +2 and +4 oxidation states. The reason for this and increase in stability of lower oxidation states down the group can be explained by inert pair effect.

INERT PAIR EFFECT

The valence shell configuration of these elements is ns^2np^2. When all four valence electrons are lost the element shows +4 oxidation state. But when np^2 electrons are lost only the element shows +2 oxidation states.

"These ns^2 electrons which donot react and remain inert are called as inert electrons and effect is called as inert pair effect."

Reason;-

We know Carbon and silicon lack d or f orbitals being members of period 2 and 3 respectively. But as we move down the group d and f subshells are introduced in Ge, Sn, Pb. These subshells have poor shielding power and donot cause so much shielding of outer electrons from nucleus. But with electrons protons are added which have a nuclear charge and attract the ns^2 electrons towards them making them inert. So they donot excite and remain as it is.

STABILITY OF OXIDATION STATES: The stability of +2 oxidation state increases down the group while that of +4 decreases down the group. So we come to know.

$Ge^{4+} > Sn^{+4} > Pb^{+4}$ → stability order

and

$Pb^{+2} > Sn^{+2} > Ge^{+2}$ → stability order.

Germanium;

In germanium +4 oxidation state is more stable than +2 so compounds having germanium in +2 oxidation states act as powerful reducing agents and oxidize themselves to +4 in Ge. While that of Ge^{+4} compounds are (~~reducing~~) oxidizing agents. which are very weak.

$$Ge^{+2} \xrightarrow[\text{oxidizes into}]{} Ge^{+4} + 2e^-$$

Q. No. 4 (Page 3)

Tin:

In tin → Sn +4 oxidation state is more stable than +2 so compounds having tin in +2 oxidation states act as powerful reducing agents and oxidize themselves to +4 in Ti - while that of Sn^{+4} compounds are oxidizing agents which are very weak.

$$Sn^{+2} \longrightarrow Ge^{+4} + 2e^-$$

↳ oxidize into

Lead

In Pb → lead +2 oxidation state is more stable than +4 so compounds having lead in +4 oxidation states act as powerful oxidizing agents and reduceds themselve to +2 in Pb. while that of Pb^{+2} compounds are reducing agents which are very weak.

$$Pb^{+4} + 2e^- \longrightarrow Pb^{+2}$$

↳ reduce to

FAJAN'S RULE: The fajan's rule states

> "Small sized cations with higher charge density makes the bond more covalent"

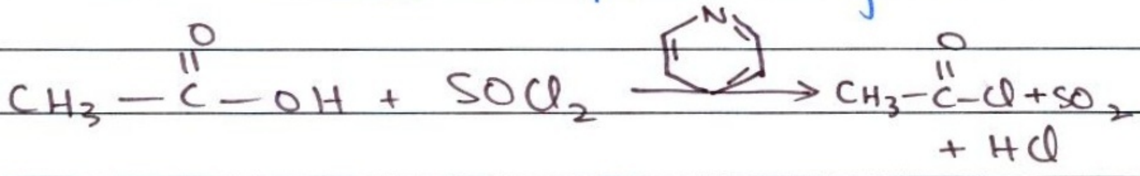
Example: So $SnCl_4$ will be covalent due to small sized Sn^{+4} ions while that of Sn^{+2} ions will form ionic compounds as $SnCl_2$.

REACTIONS OF ACYL CHLORIDES

We know carboxylic acid derivative of $-\overset{O}{\overset{\|}{C}}-X$ where X may be Cl or Br. These are formed by replacement of OH by halogen in carboxylic acids.

Reaction of Carboxylic acid to form Acety Chloride ;- ($CH_3-\overset{O}{\overset{\|}{C}}-Cl$)

Carboxylic acids are reacted with thionyl Chloride in the presence of pyridine as solvent to form corresponding acyl chloride. In this case Acetic acid will react with $SOCl_2$ to form Acetyl chloride.

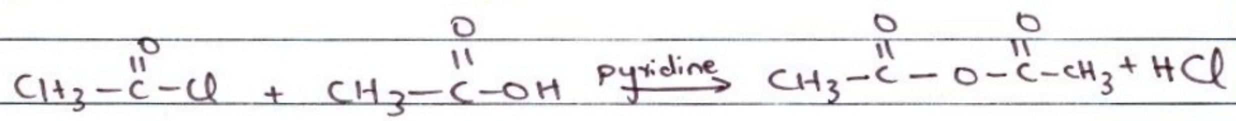


$$CH_3-\overset{O}{\overset{\|}{C}}-OH + SOCl_2 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-Cl + SO_2 + HCl$$

In this acetyl chloride is prepared from carboxylic acid.

Reactions of Acetyl chloride;

i) Acetic Acid; It reacts with acetic acid in the presence of pyridine to form Acetic Anhydride as:

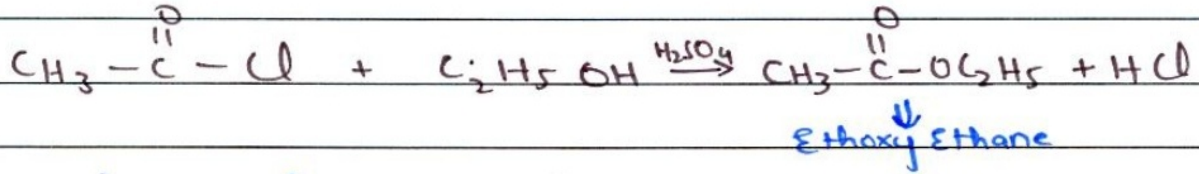


$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + CH_3-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{\text{Pyridine}} CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + HCl$$

In this way acetic anhydride with formula $CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$ are formed from acetyl chloride.

ii) **Ethanol;**

The Acyl chlorides react with alcohols in the presence of concentrated H_2SO_4 to produce ester with water. In this EthoxyEthane will be produced.

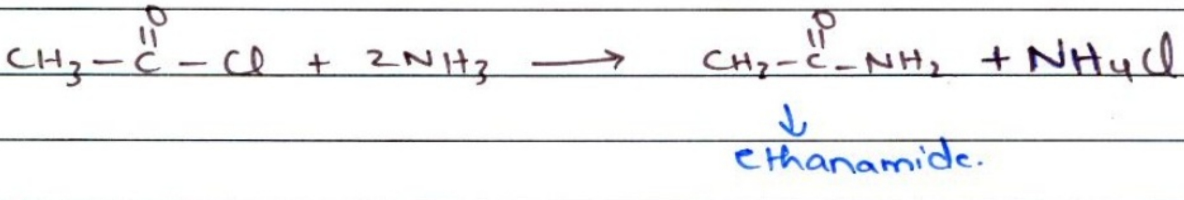


$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + C_2H_5OH \xrightarrow{H_2SO_4} \underset{\overset{\Downarrow}{\text{Ethoxy Ethane}}}{CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5} + HCl$$

This is called as estirification.

iii) **NH_3**

They react with NH_3 to form amides. In this case ethanamide will be produced.



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl + 2NH_3 \longrightarrow \underset{\overset{\downarrow}{\text{ethanamide.}}}{CH_3-\overset{O}{\overset{\|}{C}}-NH_2} + NH_4Cl$$

Q. No. 5 (Page 3)

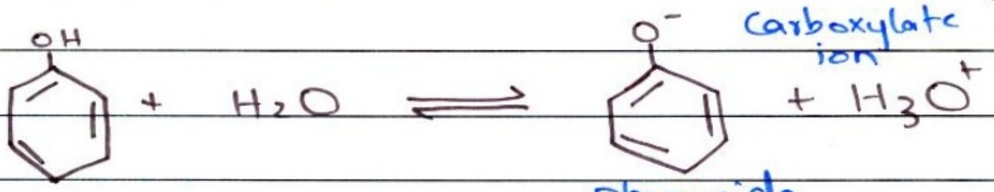
Q. No. 6 (Page 1)

STABILITY OF CONJUGATE BASES AND ACIDIC STRENGTHS OF ACIDS, PHENOLS AND ALCOHOLS

The carboxylic acids are strongest acids of them all. They have a pka value 5 while phenols have a pka value 10 while alcohols have a pka value of 16-20. The greater the pka value the weaker the acids. But all of them are very weak when compared with mineral acids. Their acidic strengths depend on the stability of their conjugate bases of carboxylate ion, phenoxide ion and Alkoxide ion.

$$CH_3-\overset{\overset{O}{||}}{C}-OH + H_2O \rightleftharpoons CH_3\overset{\overset{O}{||}}{C}-O^- + H_3O^+$$

Carboxylate ion



phenoxide ion

$$C_2H_5OH + H_2O \rightleftharpoons C_2H_5O^- + H_3O^+$$

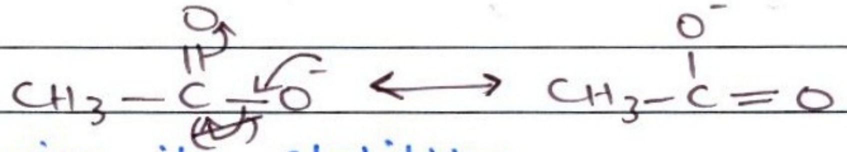
Alkoxide ion.

⇓ Hydroxonium ion

Carboxylate ion:-

The carboxylate ion is stabilized due to spreading of negative charge on the oxygen atom of carbonyl group.

Q. No. 6 (Page 2)

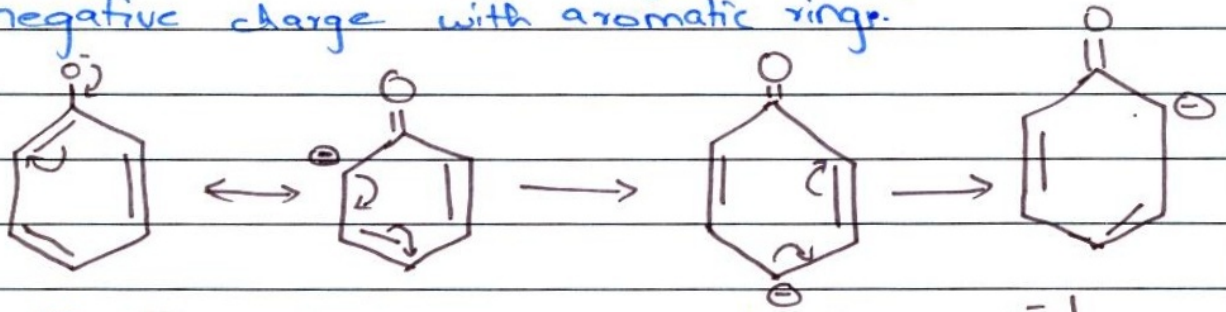


$CH_3-\overset{O}{\overset{\|}{C}}-O^- \longleftrightarrow CH_3-\overset{O^-}{\overset{|}{C}}=O$

increasing its stability.

Phenoxide ion;

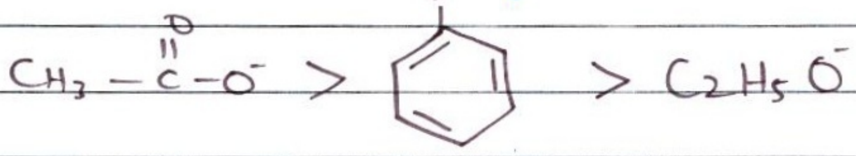
In case of phenoxide ion the negative charge is dispersed and conjugate base is stabilized by delocatization of negative charge with aromatic ring.



The following resonating structures enhance its stability.

Alkoxide ion;

The negative charge on alkoxide ion is localized and its the strongest base. Due to - resonance in this case it is weakest base so in terms of stability.

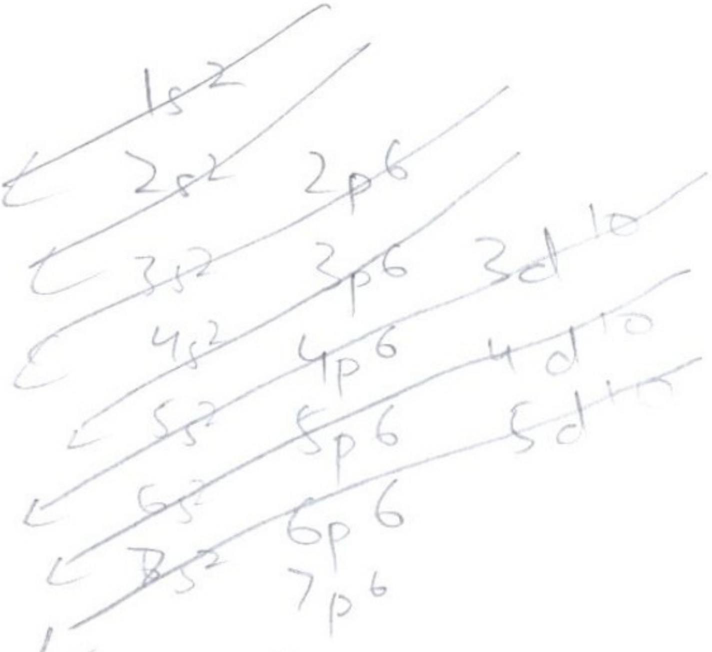


Q. No. 6 (Page 3)

^{29}Cu

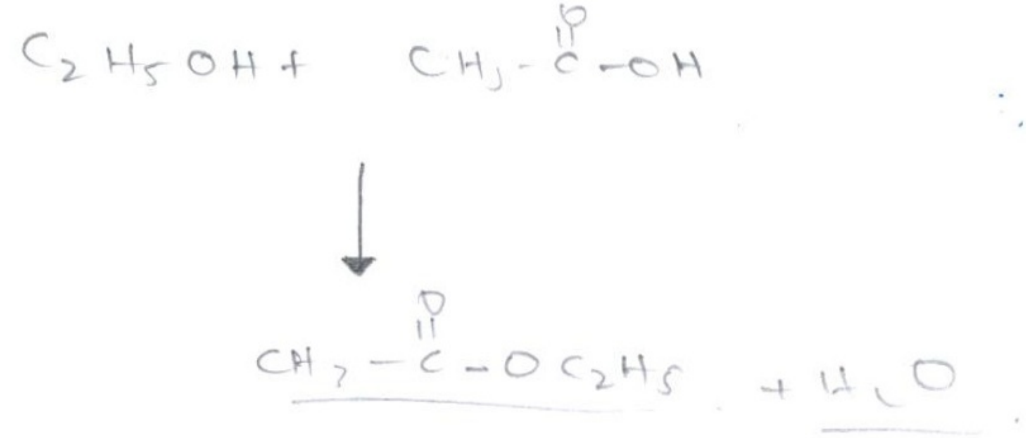
21	22	23	24	
Sc	Ti	V	Cr	M

Cr

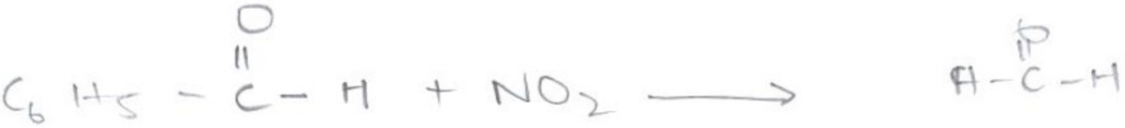


$^{29}Cu = 1s^2 \cdot 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$

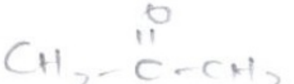
$^{24}Cr = 1s^2 2s^2 2p^6 3s^2 \cdot 3p^6 4s^1 3d^5$



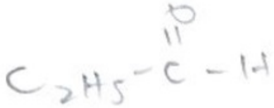
$$C_2H_5OH + CH_3-\overset{O}{\overset{\|}{C}}-OH \longrightarrow \underline{CH_3-\overset{O}{\overset{\|}{C}}-OC_2H_5} + \underline{H_2O}$$



$$C_6H_5-\overset{O}{\overset{\|}{C}}-H + NO_2 \longrightarrow H-\overset{O}{\overset{\|}{C}}-H$$

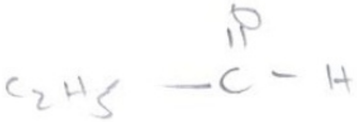


$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$



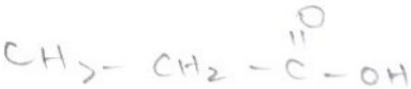
$$C_2H_5-\overset{O}{\overset{\|}{C}}-H$$

CH_4



$$C_2H_5-\overset{O}{\overset{\|}{C}}-H$$

$CH_2=CH_2$

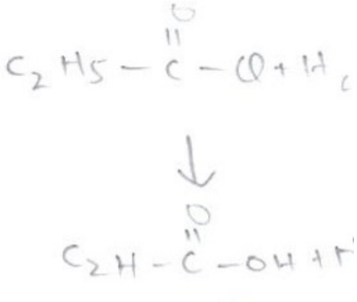


$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-OH$$

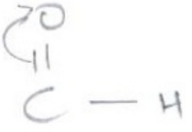
$C_2H\ddot{O}H$

CH_3CH_2OH

H_2



$$C_2H_5-\overset{O}{\overset{\|}{C}}-O + H_2$$
$$\downarrow$$
$$C_2H-\overset{O}{\overset{\|}{C}}-OH + H$$



$$\overset{O}{\overset{\|}{C}}-H$$

$$\overset{\ominus}{R}-OH$$