Carboxylic Acid & its derivatives

$-\overset{O}{\overset{\|}{C}}-OH$ → oic acid.

common names

$HCOOH$ → Formic acid

CH_3COOH → Acetic acid

CH_3-CH_2-COOH → propionic acid (propanoic acid) ← IUPAC

$CH_3-CH_2-CH_2-COOH$ → Butyric acid

$CH_3-(CH_3)_3COOH$ → Valeric acid.

* Dicarboxylic acid

@ Oh my son go and play (A.S ↓es.) 5 – CH_2 group. (C ↑ A.S ↓)

O ⇒ oxalic acid $\begin{matrix} COOH \\ | \\ COOH \end{matrix}$ ethane-1,2-dicarboxylic acid.

M ⇒ Malonic acid. $COOH(CH_2)COOH$ $\begin{matrix} COOH \\ | \\ CH_2 \\ | \\ COOH \end{matrix}$

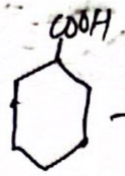
S ⇒ Succinic acid $COOH-(CH_2)_2-COOH$

G ⇒ Gultaric acid $COOH-(CH_2)_3-COOH$

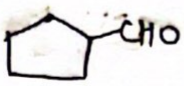
A ⇒ Adipic acid $COOH-(CH_2)_4-COOH$

• Nylon-6,6 (polymer) → Adipic acid (6C) → monomers
→ Hexamethylene diamine (6C) $NH_2(CH_2)_6NH_2$

Pimelic acid → $COOH-(CH_2)_5-COOH$



→ cyclohexane carboxylic acid



cyclopentane carboxylic acid

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CH_2-COOH
$|$
$CH-COOH$
$|$
CH_2-COOH

propane-1,2,3-tricarboxylic acid.

CH_2-COOH
$|$
CH_2-COOH

→ Butane-1,4-dioic acid.

3 वटा or 3 भन्दा वढी
COOH group attach हुन direct carbon sangs then not dioic acid
put carboxylic acid in suffix

General Method of preparation

① From Grignard reagent — with solid CO_2 : Dry ice

$$R\text{-}MgX + O=\overset{\delta+}{C}=\overset{\delta-}{O} \longrightarrow O=\underset{R}{C}-O^-\overset{+}{Mg}X \xrightarrow{H_2O/H^+} R-\overset{O}{\overset{\|}{C}}-OH + Mg\text{-}$$

R^- --

Carb. acid

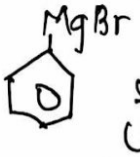
Trick

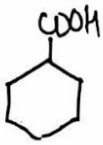
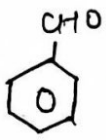
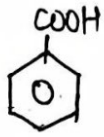
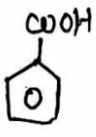
$$R-\underset{X}{MgX}\ (+COOH) \xrightarrow[(ii)\ H_2O/H^+]{(i)\ CO_2} R-COOH$$

carboxylic acid.

Q. $C_2H_5-MgBr \xrightarrow[(ii)\ H_3O^+]{(i)\ CO_2}$?

→ C_2H_5-COOH.

Q.  $\xrightarrow[(ii)\ H_3O^+]{(i)\ CO_2}$?

(a)  (b)  (c)  (d) 

② By complete hydrolysis of cyanide / nitrile

$$R-C\equiv N \xrightarrow[\text{or } H^+/HCl \text{ or comp. hydrol}]{\text{dil } HCl} R-COOH + NH_3$$

Nitrile

$$NH_3 \xrightarrow{H^+} R-COOH + NH_4^+$$

C. acid.

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Mechanism

$R-C\equiv N \xrightarrow{H^+/H_2O} R-\underset{\text{amide}}{\underset{\text{(partial Hydrolysis)}}{C(=O)-NH_2}} \xrightarrow{H_2O} R-\underset{\text{acid.}}{C(=O)-OH} + NH_3 \xrightarrow{H^+} NH_4^+$

e.g.

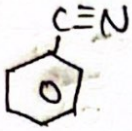
$CH_3-CN \xrightarrow{H^+/H_2O} CH_3-COOH + NH_4^+$

#Alkaline hydrolysis

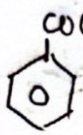
$R-C\equiv N \xrightarrow[\text{or } OH^-/H_2O]{\text{dil NaOH}} R-COOH + NH_3$

$R-COOH \xrightarrow{NaOH} RCOONa$ (salt.)

ammonia.



$\xrightarrow[\text{or dil NaOH}]{OH^-/H_2O}$



$+ NH_3$

$\xrightarrow{NaOH}$



sod. benzoate

salt.

but;

$R-N\overset{\ominus}{=}\overset{\oplus}{C} \xrightarrow{H^+/H_2O} R-NH_2 + HCOOH$

isocyanide — 1° amine.

e.g. $CH_3-N\overset{\ominus}{=}\overset{\oplus}{C} \xrightarrow{H^+/H_2O} CH_3-NH_2 + HCOOH$

Formic acid. (always)

(3) Oxidation of Alkene

$CH_3-\underset{O}{CH}=\underset{O}{CH}-CH_2-CH_3 \xrightarrow[\text{or } K_2Cr_2O_7/H^+]{KMnO_4/H^+} CH_3-COOH + CH_3-CH_2-COOH$

or

O_3/H_2O (oxidative)

$CH_3-CH_2-CH_2-CH=CH-CH_2-CH_3 \xrightarrow{KMnO_4/H^+} CH_3-CH_2-CH_2-COOH + CH_3-CH_2-COOH$

→ $CH_3-C(CH_3)=CH-CH_3 \xrightarrow{KMnO_4/H^+} CH_3-C(=O)-CH_3 + CH_3COOH$

(Ketone)

Not further oxidation. Cut add. can.

→ $CH_3-CH=CH_2 \xrightarrow{KMnO_4/H^+} CH_3-COOH + HCOOH$

$HCOOH \xrightarrow{[O]} CO_2 + H_2O$

(4) Oxidation of Alkyne

$CH_3-C(OH)=C(OH)-CH_3 \xrightarrow[\text{or } K_2Cr_2O_7/H^+ \text{ or } O_3/H_2O]{KMnO_4/H^+} CH_3-C(=O)-OH + CH_3-C(=O)-OH$

- $CH_3-CH_2-C\equiv C-CH_2-CH_3 \xrightarrow{KMnO_4/H^+} 2\,CH_3-CH_2-COOH$

→ $CH_3-CH_2-C\equiv C-H \xrightarrow{KMnO_4/H^+} CH_3-CH_2-COOH + H-COOH$

$HCOOH \xrightarrow{[O]} CO_2 + H_2O$

∴ $R-CH=CH-R \xrightarrow{[O]} 2\,R-COOH.$

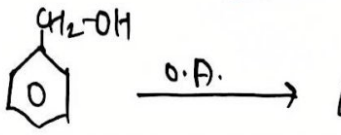
$R-C\equiv C-R \xrightarrow{[O]} 2\,R-COOH$

(5) By oxidation of primary alcohol

O.A ⇒ $KMnO_4$ / $K_2Cr_2O_7$ / conc HNO_3, CrO_3 in H_2SO_4 → Johns reagent

$R-CH_2-OH \xrightarrow{O.A} R-COOH.$

e.g. $CH_3-CH_2-CH_2-OH \xrightarrow{O.A} CH_3-CH_2-COOH.$



Benzoic ...

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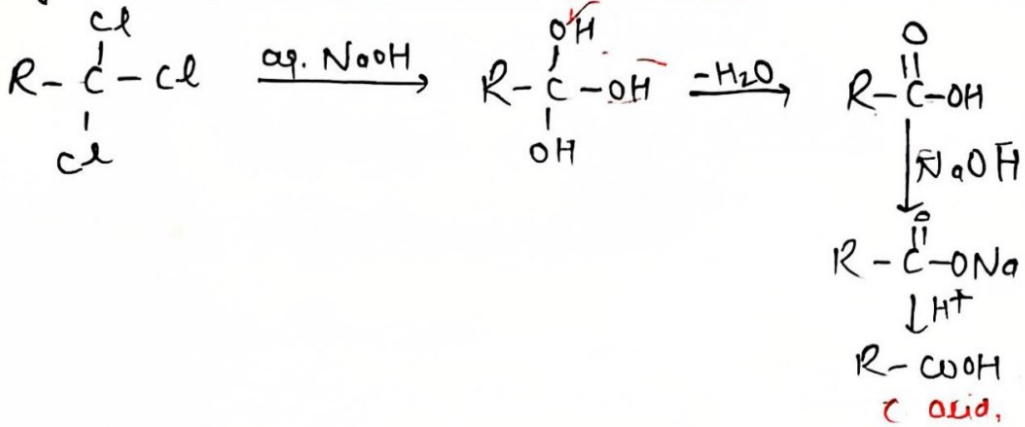
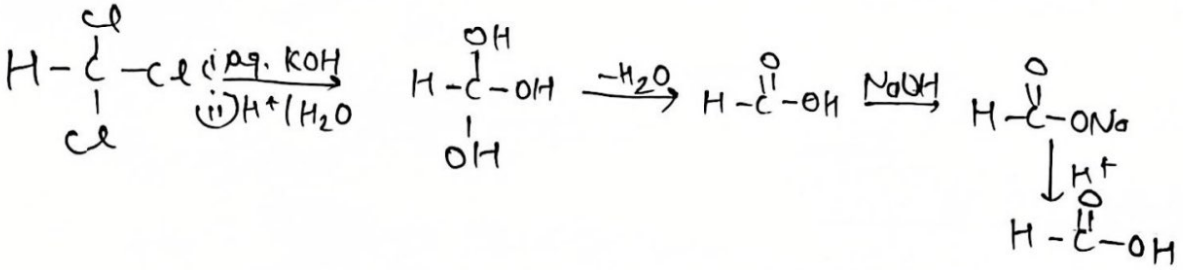
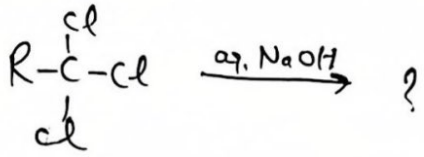
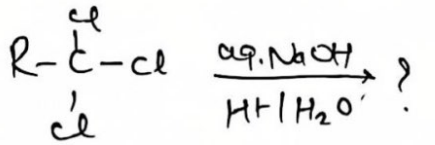
(6) By hydrolysis of trihalo compound





Q.  ?

(a) R-COOH (b) R-COONa

Q.  ?

(a) R-COOH (b) R-COONa

(7) By oxidation of Aldehyde

$R-CHO \xrightarrow{[O]} R-COOH$

- $KMnO_4$
- $K_2Cr_2O_7$
- Tollen reagent.
- Fehling soln
- Benedict soln.

(8) By hydrolysis of acid derivative

$R-C(=O)-Z + H-OH \longrightarrow R-C(=O)-OH + H-X$

Z = Cl, OR, NH_2, $O-C(=O)-R$

ester, amide, anhydride

e.g. $R-\overset{O}{\overset{\|}{C}}-Cl + H-O-H \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH + HCl$

$R-\overset{O}{\overset{\|}{C}}-OR + H-O-H \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH + ROH$ (alc.)

$R-\overset{O}{\overset{\|}{C}}-NH_2 + H-O-H \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH + NH_3 \xrightarrow{H^+} NH_4^+$

Imp:

$\rightarrow R-\overset{O}{\overset{\|}{C}}-NH_2 + HNO_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH + N_2 + H_2O$ (C. acid)

$\rightarrow R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R \xrightarrow{H_2O} 2R-\overset{O}{\overset{\|}{C}}-OH$

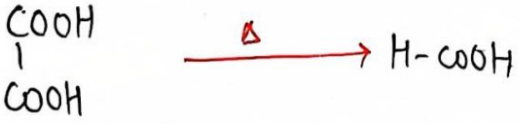
(9) From sodium alkoxide

$RONa + CO \xrightarrow[\text{pressure}]{\Delta} RCOONa \xrightarrow{H_2O/H^+} RCOOH$

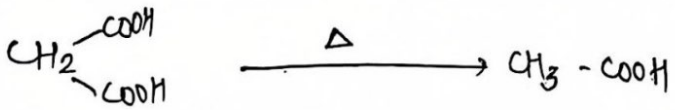
e.g. $CH_3ONa + CO \xrightarrow[P]{\Delta} CH_3COONa \xrightarrow{H_2O/H^+} CH_3COOH$

(10) By heating dicarboxylic acid

Blaise's Rxn



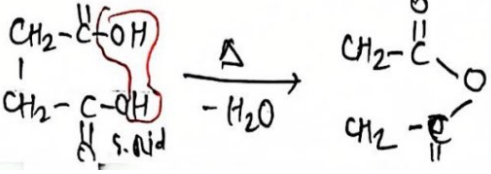
1,2-dicarboxylic acid (Oxalic acid)



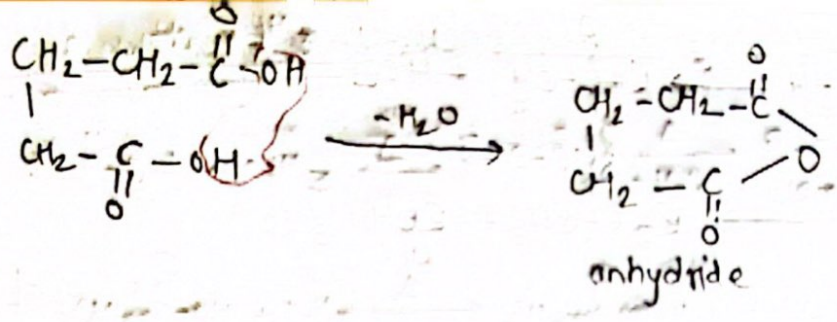
1,3-dicarboxylic acid (Malonic acid)

1,4 > carboxy. acid $\xrightarrow{\Delta}$ anhydride

1,5

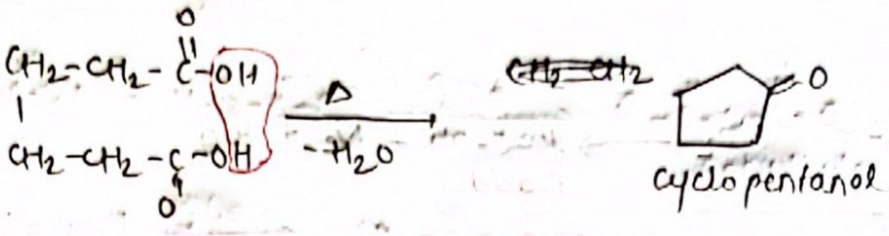


Succinic anhydride.

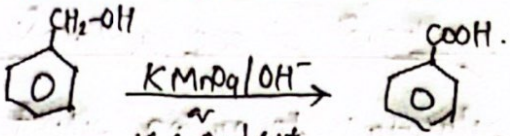


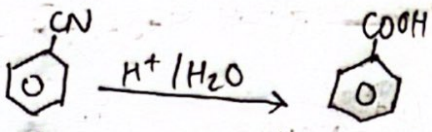
1,6
1,7 car. acid. $\xrightarrow[-H_2O \& CO_2]{\Delta}$ cyclic ketone.

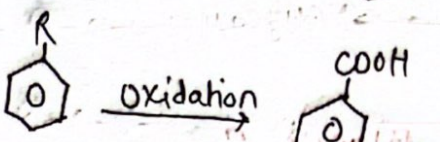
e.g.



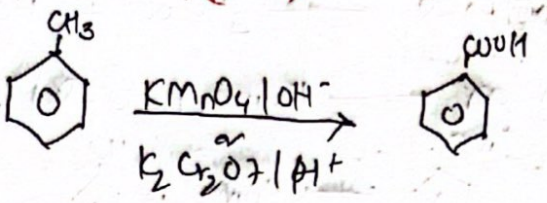
* Preparation of Benzoic acid

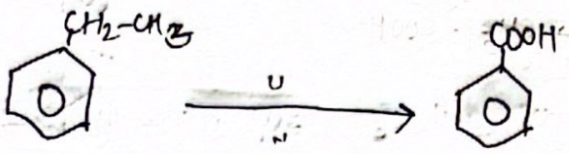
① 

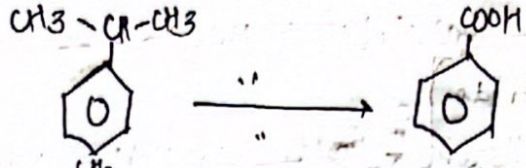
② 

③ 

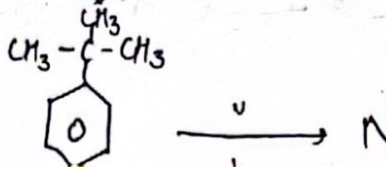
& doesn't depend on C no.

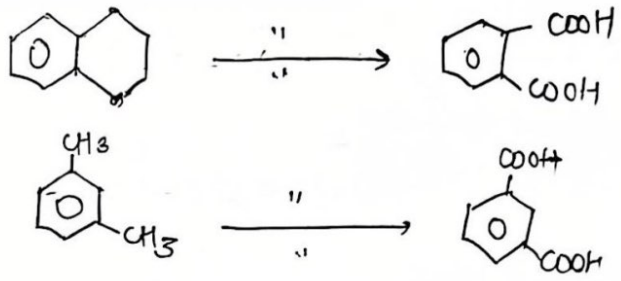






but.





(4) Koch Rxn

$HCOOH$ X, CH_3COOH X.

$$CH_2=CH_2 + CO + H_2O \xrightarrow[\text{High temp}^r,\ \text{High Pre.}]{H_3PO_4} CH_3-CH_2-COOH$$

Chemical properties

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

A. Rxn involving cleavage of C-OH group

(1) Rxn with PCl_5

$$R-\overset{O}{\overset{\|}{C}}-O-H \xrightarrow{PCl_5} R-\overset{O}{\overset{\|}{C}}-Cl + POCl_3 + HCl$$

(2) Rxn with PCl_3

$$R-COOH + PCl_3 \longrightarrow R-\overset{O}{\overset{\|}{C}}-Cl + H_3PO_3$$

(3) $SOCl_2$ rxn

$$R-\overset{O}{\overset{\|}{C}}-O-H + SOCl_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-Cl + SO_2 + HCl$$

↳ Thionyl chl

(4) $R-COOH + \left.\begin{matrix} PCl_5 \\ PCl_3 \\ SOCl_2 \end{matrix}\right\} \longrightarrow R-COCl.$

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(4) Rxn with NH_3

$$R-\overset{O}{\overset{\|}{C}}-OH + NH_3 \xrightarrow{\Delta} R-\overset{O}{\overset{\|}{C}}-O^-Na^+ \xrightarrow[-H_2O]{\Delta} R-\overset{O}{\overset{\|}{C}}-NH_2$$

amide

eg. $CH_3-\overset{O}{\overset{\|}{C}}-OH + NH_3 \xrightarrow{\Delta} CH_3-\overset{O}{\overset{\|}{C}}-NH_2 + H_2O$

(5) Esterification : Esters studied.

(6) P_2O_5 / conc H_2SO_4

$$R-\overset{O}{\overset{\|}{C}}-OH + H-O-\overset{O}{\overset{\|}{C}}-R \xrightarrow[\text{conc. } H_2SO_4]{P_2O_5} R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$$

anhydride.

$$2CH_3COOH \xrightarrow[\text{or conc } H_2SO_4]{P_2O_5} CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3$$

(B) Reaction due to Breaking of $R-\overset{O}{\overset{\|}{C}}-O/H$ bond

(1) Acidic nature of carboxylic acid

$$-R-\overset{O}{\overset{\|}{C}}-OH + Na \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^-Na^+ + \tfrac{1}{2}H_2\uparrow$$

$$-R-\overset{O}{\overset{\|}{C}}-OH + NaH \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^-Na^+ + H_2\uparrow$$

$$-R-\overset{O}{\overset{\|}{C}}-OH + NaOH \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^-Na^+ + H_2O$$

$$\rightarrow R-\overset{O}{\overset{\|}{C}}-OH + NaNH_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^-Na^+ + NH_3$$

but, ($R-OH + NaOH \longrightarrow$ no rxn)

$$-\text{C}_6\text{H}_5-OH + NaOH \longrightarrow \text{C}_6\text{H}_5-O^-Na^+$$

$$\rightarrow \text{C}_6\text{H}_5-OH + NaHCO_3 \longrightarrow \text{No rxn.}$$

$$-R-COOH + NaHCO_3 \longrightarrow$$

$$R-\overset{O}{\overset{\|}{C}}-OH + NaHCO_3 \longrightarrow R-\overset{O}{\overset{\|}{C}}-ONa + H_2CO_3$$

$\downarrow$

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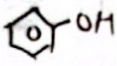
C. acid

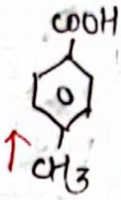
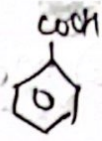
Continues

Q. Which acid gives effervescence ~~wit~~ of CO_2 with $NaHCO_3$?

(a) RCOOH (b) R–OH (c)  (d) All

* Acidic strength $\propto \frac{E.W.G}{E.D.G}$ (E.W.G → लिनि, E.D.G → Donating)

Q. Acidic strength :-

(a)  (b)  (c) 

(a > c > b)

* $\boxed{A.S \propto K_a \propto \frac{1}{pK_a}}$

Q. Acidic strength :-

(a) $CH_3-CH_2-CH_2-\overset{Cl}{CH}-COOH$ (b) $CH_3-CH_2-\overset{Cl(-I)}{CH}-CH_2-COOH$

(c) $CH_3-\overset{Cl}{CH}-CH_2-CH_2-COOH$ (d) $\overset{Cl}{CH_2}-CH_2-CH_2-CH_2-COOH$. $I \propto \frac{1}{dist}$

a > b > c > d.

Q. Acidic strength :-

(a) $CH_3-CH_2-\overset{F}{CH}-COOH$ (b) $CH_3-CH_2-\overset{Cl}{CH}-COOH$

(c) $CH_3-CH_2-\overset{Br}{CH}-COOH$ (d) $CH_3-CH_2-\overset{I}{CH}-COOH$

$-I \rightarrow F > Cl > Br > I$

A.S → a > b > c > d.

Q. $Cl-\overset{Cl}{\underset{Cl}{C}}-COOH > Cl-\overset{Cl}{CH}-COOH > Cl-CH_2-COOH$

Q. $CH\equiv\overset{sp}{C}-COOH > CH_2=\overset{sp^2}{CH}-COOH > CH_3-\overset{sp^3}{CH_2}-COOH$

$-I \rightarrow sp > sp^2 > sp^3$

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Q. Weakest acid among the following is:-

(a) acetic acid (b) phenol (c) water (d) Acetylene

Q. Which of the following is least acidic?

(a) C_2H_5OH (b) CH_3COOH (c) C_6H_5OH (d) $ClCH_2COOH$

Q. The acid produced (A) in the sequence given below is:-

$$C_2H_5I \xrightarrow[KOH]{\text{Alcoholic}} X \xrightarrow[CCl_4]{Br_2} Y \xrightarrow{KCN} Z \xrightarrow{H_3O^+} A$$

(a) Succinic acid (b) Malonic acid (c) Oxalic acid.

(d) Maleic acid.

X = ethene ($CH_2 = CH_2$)

Y = $CH_2(Br)-CH_2(Br)$

A = $CH_2(COOH)-CH_2(COOH)$

Q. Acyl halide is formed by reacting PCl_5 with:-

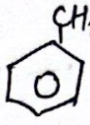
(a) alcohol (b) ester (c) Amide (d) Both Ca. acid & ester

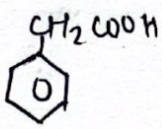
$R-\overset{O}{\overset{\|}{C}}-Cl$

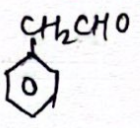
Q. From the following values of dissociation constants (K_a) of 4 acids which value represents the strongest acid?

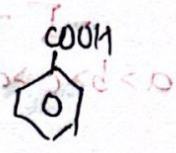
(a) 2×10^{-2} (b) 2×10^{-1} (c) 3×10^{-4} (d) 2×10^{-4}

acidity $\propto K_a$

Q.  $\xrightarrow[(ii)\ H^+/H_2O]{(i)\ KMnO_4/OH^-}$?

(a) 

(b) 

(c) 

(d) 

(2) Insertion of carbene ($:CH_2$)

Diazomethane

$$R-\overset{O}{\overset{\|}{C}}-O-H \xrightarrow[\Delta]{CH_2N_2} R-\overset{O}{\overset{\|}{C}}-O-CH_3$$

methyl ester

$$CH_3-\overset{O}{\overset{\|}{C}}-O-H \xrightarrow[\Delta]{CH_2N_2} CH_3-\overset{O}{\overset{\|}{C}}-O-CH_3$$

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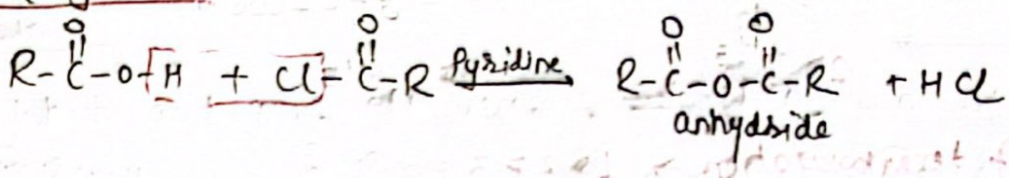
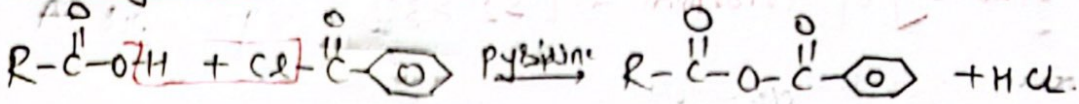
③ Acetylation



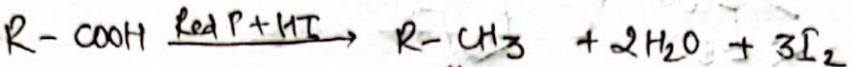
④ Benzoylation



© Rxn involving COOH group as a whole

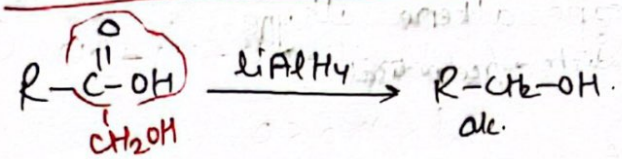
* Redⁿ rxn

① Reduction to alkane



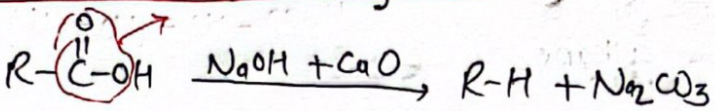
e.g. $CH_3-COOH \xrightarrow{Red\ P + HI} CH_3-CH_3$ (ethane)

② Reduction to Alcohol

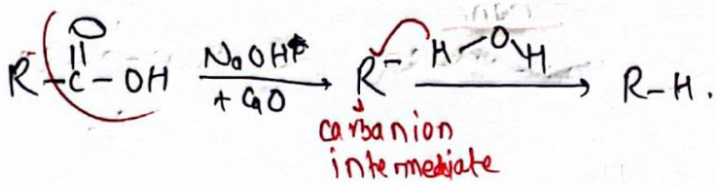


* Decarboxylation

① Soda-lime decarboxylation



* Intermediate :- carbanion (C^-)



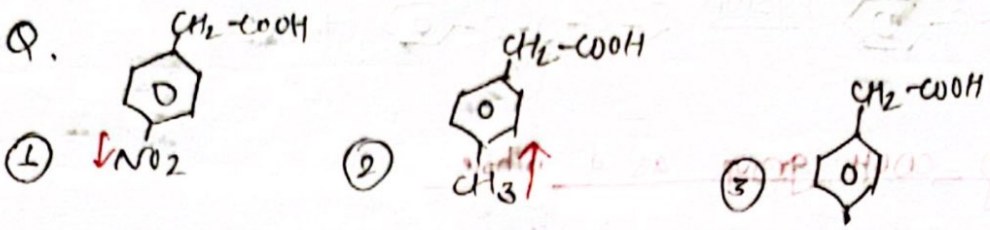
Rate of rxn ∝ stability of intermediate.

Q. CH_3-CH_2-COOH (1) $CH_3-CH(CH_3)-COOH$ (2) $CH_3-C(CH_3)_2-COOH$ (3)

rate of decarboxylation → 1 > 2 > 3

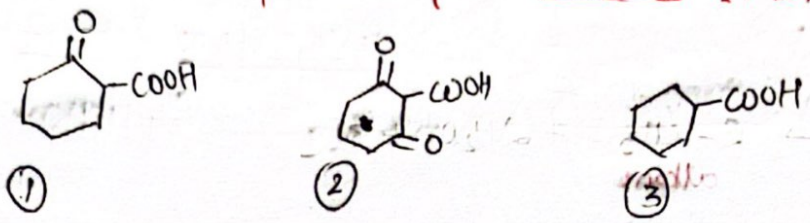
Stability of carbamion → 1° > 2° > 3°

Q.



rate of decarboxyl → ~~1>2>3~~ 1 > 3 > 2.

Q.



rate of decarboxylation → 2 > 1 > 3

② Electrolytic decarboxylation

Kolbe's electrolysis :- Alkane, alkene, alkyne.
└ intermediate → free radical.

→ $R-\overset{O}{\overset{\|}{C}}-O-Na \xrightarrow{electrolysis}$ Alkane

Sod. salt of monoc. acid.

$R-COONa$
$R-COONa$ → $R-R$ alkane

e.g. $2\ CH_3-COONa \xrightarrow{electrolysis} CH_3-CH_3$ ethane

→ $CH_2-COONa$ ‖ $CH_2-COONa$ → $CH_2=CH_2$ ethene

Sod. salt of saturated dicarboxylic acid

Sod. sukeinate

→ $CH-COONa$
$|||$
$CH-COONa$ ⟶ $CH \equiv CH$
ethyne

Sod. salt of unsaturated dicarboxylic acid

Sod. maleate (cis)

→ $H-C(COONa)$
$|||$
$C-H$ ⟶ $CH \equiv CH$
ethyne

$COONa$

sod. fumrate (trans)

Anode	Cathode	Soln
Hydrocarbon + CO_2	H_2	NaOH ↑ pH ↑

] in Kolbe's synthesis

D. Rxn due to alkyl groups (R-COOH)

① HVZ rxn (Hell Volhard Zelinsky)

→ α-H must be present

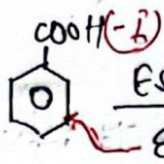
– It is halogenation in the +nce of phosphorus

→ $CH_3-COOH + Br_2$ or $Cl_2 \xrightarrow[\Delta]{Red\ P} Br(Cl)-CH_2-COOH$.

→ $CH_3-COOH + Br_2$ excess $\xrightarrow[\Delta]{Red\ P} Br-C(Br)(Br)-COOH$

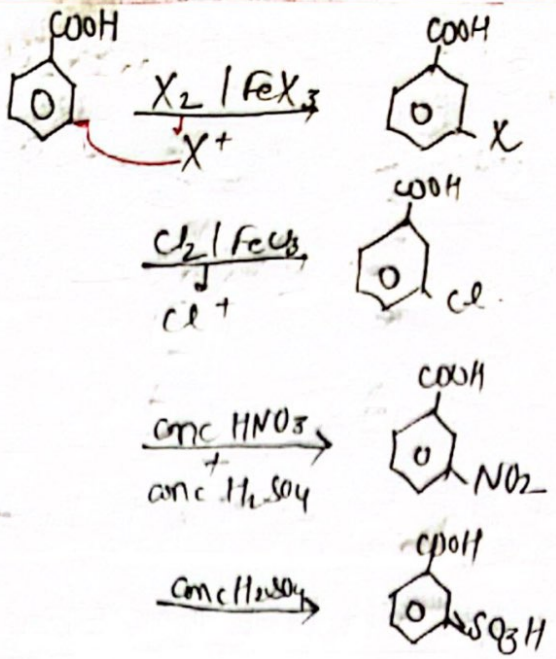
* $CH_3-CH_2-COOH \xrightarrow[Red\ P]{Br_2} CH_3-CH(Br)-COOH$

* $CH_3-CH(CH_3)-CH_2-COOH \xrightarrow[Red\ P]{Cl_2} CH_3-CH(CH_3)-CH(Cl)-COOH$

\# 

$\xrightarrow{ESR}$ Meta directing group.

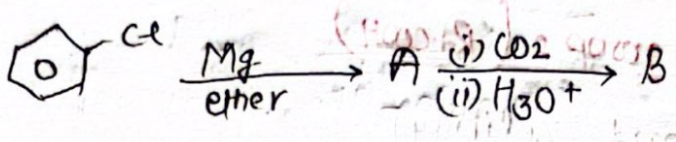
(1)

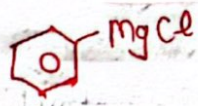


Friedel craft rxn

Alkylation — Acylation — No rxn

Q.

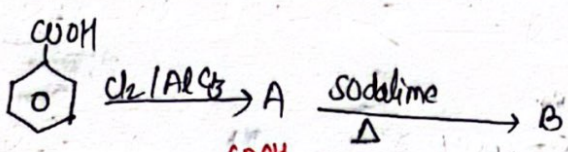


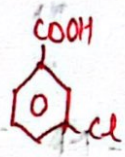
A = 

B = 

(benzoic acid)

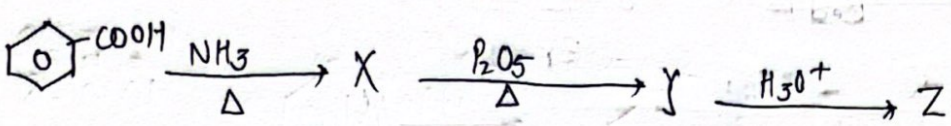
Q.

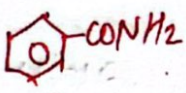


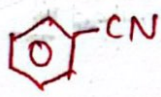
A = 

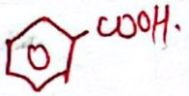
B = 

Q.



X = 

Y = 

Z = 

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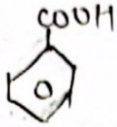
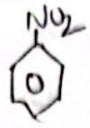
Q. $CH_3-CH_2-CH_2-COOH \xrightarrow[\text{Red P } \Delta]{} P \xrightarrow[\Delta]{\text{alc. KOH}} Q$..

$P = CH_3-\underset{\beta}{CH_2}-\underset{\alpha}{\overset{Br}{CH}}-COOH$

$Q = CH_3-CH=CH-COOH$ } α-β elimination. ↳ alc. KOH.

crotonic acid.

Q. Doesnot give Friedel craft rxn.

(a)  (b)  (c)  ~~(d)~~ All

Acid Derivatives

$R-\overset{O}{\overset{\|}{C}}-OH$ —
- $\xrightarrow{+Cl} R-\overset{O}{\overset{\|}{C}}-Cl$ (acid chloride)
- $\xrightarrow{+OR} R-\overset{O}{\overset{\|}{C}}-OR$ (ester)
- $\xrightarrow{+O-\overset{O}{\overset{\|}{C}}-R} R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$ (anhydride)
- $\xrightarrow{+NH_2} R-\overset{O}{\overset{\|}{C}}-NH_2$ (amide)

$R-\overset{O}{\overset{\|}{C}}-Z$ ↳ acid derivatives (leaving group)

* Nucleophilic substitution through addition elimination - show ↻ 1 ↺.

$R-\overset{O}{\overset{\|}{C}}-Z \xrightarrow{E-Nu} R-\underset{Nu}{\overset{O^-}{C}}-Z \longrightarrow R-\overset{O}{\overset{\|}{C}}-Nu + E-Z$ ↳ also nucleophilic

elim. of L.G.

e.g. $R-\overset{O}{\overset{\|}{C}}-Cl$ (a. chl) $\xrightarrow{R-\overset{-}{O}H^{+}} R-\underset{OR}{\overset{O^-}{C}}-Cl \longrightarrow R-\overset{O}{\overset{\|}{C}}-OR$ ester $+ HCl$

$R-\overset{\delta-}{\overset{O}{\overset{\|}{C}}}-Z$ ($\delta+$)

* Rate of rxn or reactivity

Rate of rxn ∝ +ve charge on sp^2 C.

∝ leaving tendency of leaving group

leaving tendency of leaving group ∝ acidic strength.

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① $R-\overset{O}{\overset{\|}{C}}-Cl$ HCl ③ $R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$ RCOOH

② $R-\overset{O}{\overset{\|}{C}}-OR$ ROH ④ $R-\overset{O}{\overset{\|}{C}}-NH_2$ NH_3

reactivity → $RCOCl > RCOOCOR > RCOOR > RCONH_2$
(1) (3) (2) (4)
@ A An E Am

Acid chloride :- oyl chloride

General method of prep.

$R-\overset{O}{\overset{\|}{C}}-OH$ —
- PCl_5 → $R-\overset{O}{\overset{\|}{C}}-Cl + POCl_3 + HCl$
- PCl_3 → $R-\overset{O}{\overset{\|}{C}}-Cl + H_3PO_3$
- $SOCl_2$, pyridine → $R-\overset{O}{\overset{\|}{C}}-Cl + SO_2\uparrow + HCl\uparrow$

Rxn NSR through add^n–elimination.

① $R-\overset{O}{\overset{\|}{C}}-Cl + H-OH \longrightarrow R-\overset{O}{\overset{\|}{C}}-OH + HCl$ (Hydrolysis)

② $R-\overset{O}{\overset{\|}{C}}-Cl + H-O-R \longrightarrow R-\overset{O}{\overset{\|}{C}}-OR + HCl$

③ $R-\overset{O}{\overset{\|}{C}}-Cl + H-O-\overset{O}{\overset{\|}{C}}-R \longrightarrow R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R + HCl$

④ $R-\overset{O}{\overset{\|}{C}}-Cl + H-NH_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-NH_2 + HCl$

⑤ $R-\overset{O}{\overset{\|}{C}}-Cl$ + benzene $\xrightarrow[AlCl_3]{anhy.}$ benzene-$C(=O)-R$ [ESR]

⑥ $R-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{H_2/Pd\,BaSO_4} R-\overset{O}{\overset{\|}{C}}-H$

$R-\overset{O}{\overset{\|}{C}}-Cl + H-H$

(7) $R-\overset{O}{\overset{\|}{C}}-Cl$ + $R-\underset{O}{\underset{\|}{C}}-Cl$ + $Cd(R)_2$ (dialkyl cadmium) $\longrightarrow$ $2R-\overset{O}{\overset{\|}{C}}-R$ (Ketone) + $CdCl_2$

(8) $R-\overset{O}{\overset{\|}{C}}-Cl$ + $\xrightarrow{RONa}$ $R-\overset{O}{\overset{\|}{C}}-OR$ + NaCl.

(9) $R-\overset{O}{\overset{\|}{C}}-Cl$ + $H-\overset{H}{N}-R$ $\longrightarrow$ $R-\overset{O}{\overset{\|}{C}}-N(H)(R)$ + HCl.

(10) $R-\overset{O}{\overset{\|}{C}}-Cl$ + $H-N(R)(R)$ $\longrightarrow$ $R-\overset{O}{\overset{\|}{C}}-N(R)(R)$

(11) $R-\overset{O}{\overset{\|}{C}}-Cl$ $\xrightarrow{\overset{\oplus}{K}\overset{\ominus}{CN}}$ $R-\overset{O}{\overset{\|}{C}}-CN$

Acid anhydride

General method of preparation

$R-\overset{O}{\overset{\|}{C}}-OH$, $R-\underset{O}{\underset{\|}{C}}-OH$ $\xrightarrow[\Delta \text{ or conc } H_2SO_4/\Delta]{P_2O_5}$ $R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$ (anhydride) + H_2O

Rxn

(1) Hydrolysis

$R-\overset{O}{\overset{\|}{C}}-\overset{H}{O}-\overset{O}{\overset{\|}{C}}-R$ (OH) $\xrightarrow{H_2O}$ $2R-\overset{O}{\overset{\|}{C}}-OH$

(2) $R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$ (H, OR) $\xrightarrow{R-OH}$ $R-\overset{O}{\overset{\|}{C}}-OH$ + $R-\overset{O}{\overset{\|}{C}}-OR$

(3) $R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$ (H, NH_2) $\xrightarrow{NH_3}$ $R-\overset{O}{\overset{\|}{C}}-OH$ + $R-\overset{O}{\overset{\|}{C}}-NH_2$

(4) $R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$ (CH_2OH, CH_2OH) $\xrightarrow{LiAlH_4}$ $R-CH_2OH$ + $R-CH_2OH$.

(5) $R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R$ (H, Cl) $\xrightarrow{HCl}$ $R-\overset{O}{\overset{\|}{C}}-OH$ + $R-\overset{O}{\overset{\|}{C}}-Cl$

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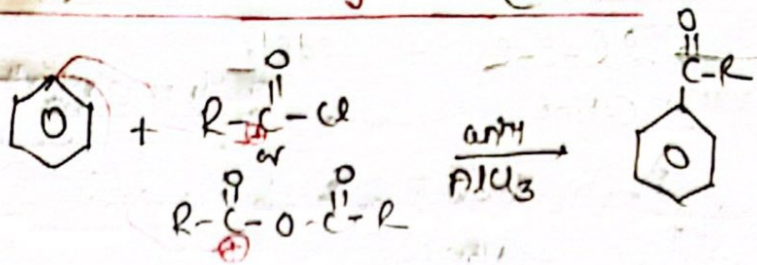
Friedel craft acylation (E.S.R)

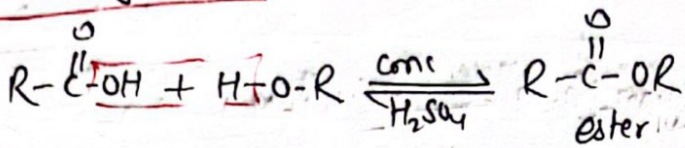


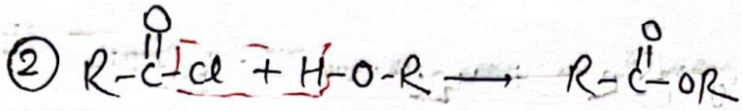
Ester → fruity smell.

- Functional isomer → carboxylic acid.
- General formula → $C_nH_{2n}O_2$.

* General method of preparation

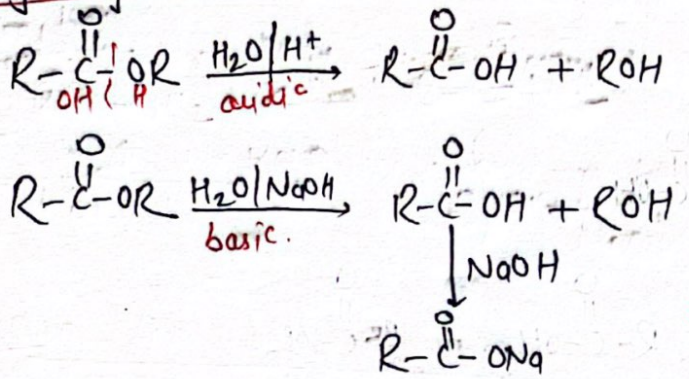
① Esterification



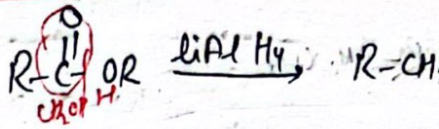


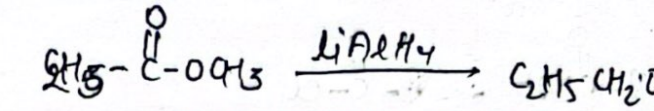
* Rxn

① Hydrolysis



② Reduction



e.g. 

- $C_2H_5-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-CH_3 \xrightarrow{LiAlH_4} C_2H_5-CH_2OH + CH_3-CH_2-CH_2-OH.$

CH_2OH

- $R-\overset{O}{\overset{\|}{C}}-OR \xrightarrow{Na + C_2H_5OH} R-CH_2OH + ROH$ – Bouveault blanc rxn.

$\xrightarrow{LiAlH_4/H^+} R-CH_2OH + ROH$

$\xrightarrow{NaBH_4/H^+}$ No rxn.

Q. $C_2H_5-\overset{O}{\overset{\|}{C}}-O-CH_3 \xrightarrow[Na + C_2H_5OH]{LiAlH_4/H^+} C_2H_5-CH_2OH + CH_3OH.$

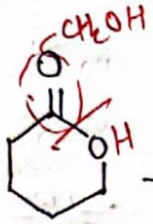
$\xrightarrow{NaBH_4/H^+}$ No rxn.

Q. $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-O-C_2H_5 \xrightarrow{LiAlH_4} CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-CH_2OH + C_2H_5-OH.$

$CH-OH$ CH_2OH

aceto acetic ester. (AAE)

$\xrightarrow[\text{Ketone संग मात्र Rxn. गई}]{NaBH_4} CH_3-\overset{OH}{\overset{|}{C}H}-CH_2-\overset{O}{\overset{\|}{C}}-O-C_2H_5$

Q.  $\xrightarrow{LiAlH_4} \overset{OH}{\overset{|}{C}H_2}-CH_2-CH_2-CH_2-CH_2-OH.$

③ Trans-esterification: exchange of alkyl group of ester & alc.

$R-\overset{O}{\overset{\|}{C}}-O-R' + R''-OH \rightleftharpoons R-\overset{O}{\overset{\|}{C}}-O-R'' + R'-OH$

④ PCl_5

$R-\overset{O}{\overset{\|}{C}}-O-R \xrightarrow{PCl_5} R-\overset{O}{\overset{\|}{C}}-Cl + POCl_3 + RCl$

Cl PCl_3 Cl

⑤ $SOCl_2$

$R-\overset{O}{\overset{\|}{C}}-O-R \xrightarrow{SOCl_2} R-\overset{O}{\overset{\|}{C}}-Cl + SO_2\uparrow + RCl\uparrow.$

Cl SO H

⑥ HI

$R-\overset{O}{\overset{\|}{C}}-O-R \xrightarrow{HI} R-\overset{O}{\overset{\|}{C}}-OH + RI$

H I

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Amide ($CONH_2$)

* Preparation

① $R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{NH_3} R-\overset{O}{\overset{\|}{C}}-O^- NH_4^+ \xrightarrow[-H_2O]{\Delta} R-\overset{O}{\overset{\|}{C}}-NH_2$

ammonium carboxylate — amide

$\therefore R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[\Delta]{NH_3} R-\overset{O}{\overset{\|}{C}}-NH_2$

② $R-C\equiv N \xrightarrow[\text{p. hydrolysis}]{H^+/H_2O} R-\overset{O}{\overset{\|}{C}}-NH_2$

conc HCl

③ Acid derivative

- $R-\overset{O}{\overset{\|}{C}}-Cl + H-NH_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-NH_2 + HCl$
- $R-\overset{O}{\overset{\|}{C}}-OR + H-NH_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-NH_2 + ROH$
- $R-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-R + H-NH_2 \longrightarrow R-\overset{O}{\overset{\|}{C}}-NH_2 + R-\overset{O}{\overset{\|}{C}}-OH$

properties

$R-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2 \longleftrightarrow R-\overset{O^-}{C}=\overset{+}{N}H_2$

(I) (basic) — Resonating str. — (II) (Acidic)

so, amide → amphoteric in nature.

Rxn

① $R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{acidic Hyd.}]{H^+/H_2O} R-\overset{O}{\overset{\|}{C}}-OH + NH_3 \xrightarrow{H^+} NH_4^+$

② $R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{basic hyd.}]{NaOH/H_2O} R-\overset{O}{\overset{\|}{C}}-OH + NH_3$

$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{NaOH} R-\overset{O}{\overset{\|}{C}}-O^- Na^+ + NH_3$

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(3) $R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{or } PCl_5 \text{ or } SOCl_2]{P_2O_5/\Delta} R-C\equiv N + H_2O$

cyanide.

(4) $R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[\text{or } LiAlH_4]{H_2/Pt} R-CH_2-NH_2$

CH_2

$\xrightarrow{NaBH_4}$ No rxn

(5) $R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{HNO_2} R-\overset{O}{\overset{\|}{C}}-OH + N_2 + H_2O$

OH / N / O

e.g. $CH_3-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{HONO} CH_3-\overset{O}{\overset{\|}{C}}-OH + N_2 + H_2O$

OH / N / O

(6) $R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow{Br_2 + 4KOH} R-NH_2 + K_2CO_3 + 2KBr + H_2O$

XX

→ Hoffmann Bromamide dehydration rxn.

→ Decarboxylation rxn.

- Nitrene → intermediate.

$\square\ddot{N}-$ 6e⁻

↑

└ electrophile

(7) $R-\overset{O}{\overset{\|}{C}}-N\begin{matrix}(H)\\H\end{matrix} + R-MgX \longrightarrow R-H + R-\overset{O}{\overset{\|}{C}}-N\begin{matrix}MgX\\H\end{matrix}$

alkane