Polymers

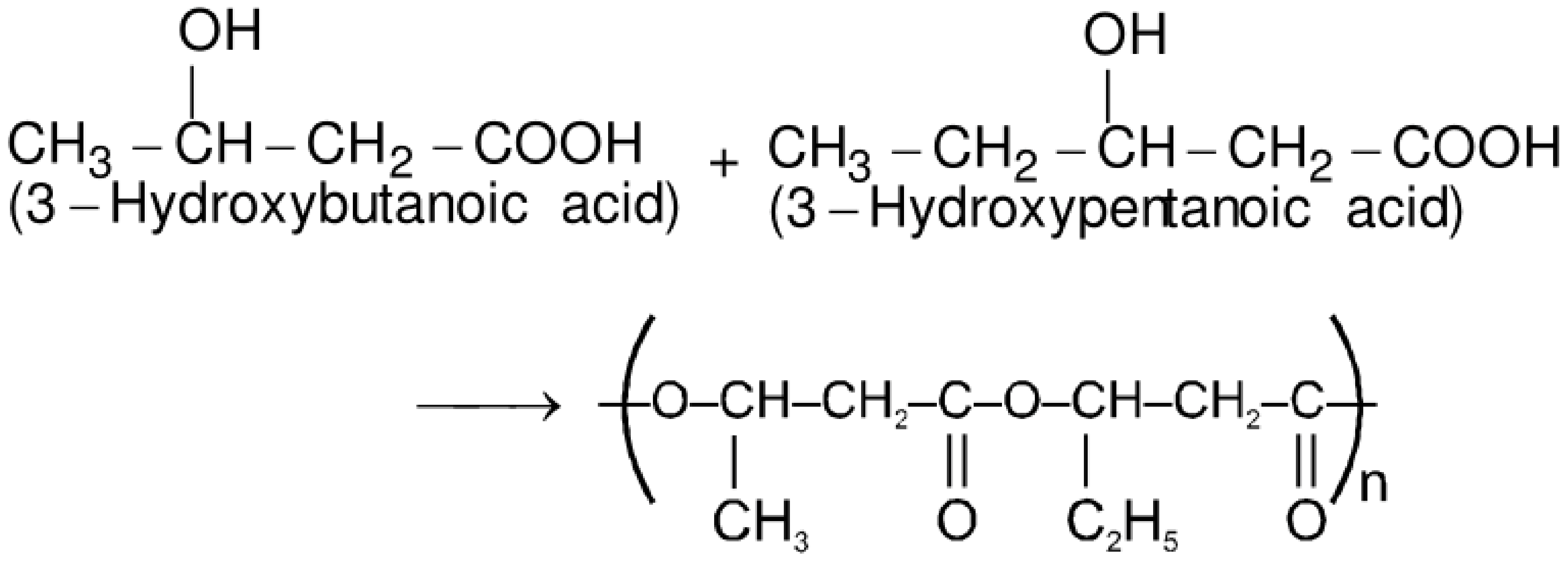
Biodegradable Polymers :

A large number of polymers are quite resistant to the environmental degradation processes and are thus responsible for the accumulation of polymeric soild waste materials. These soild wastes cause acute environmental problems and remain undegraded for quite a long time. In view of the general awareness and concern for the problems created by the polymeric soild wastes, certain new biodegradable synthetic polymers have been designed and developed. These polymers contain functional groups similar to the functional groups present in biopolymers.

Aliphatic polyesters are one of the important classes of biodegradable poylmers. Some examples are given below :

(a) Poly β-hydroxybutyrate – co–β-hydroxy valerate (PHBV) :

It is obtained by the copolymerisation of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid.



$$\underset{\text{(3 – Hydroxybutanoic acid)}}{CH_3-\overset{\overset{OH}{|}}{C}H-CH_2-COOH} + \underset{\text{(3 – Hydroxypentanoic acid)}}{CH_3-CH_2-\overset{\overset{OH}{|}}{C}H-CH_2-COOH}$$

$$\longrightarrow \left(O-\underset{\underset{CH_3}{|}}{CH}-CH_2-\underset{\underset{O}{||}}{C}-O-\underset{\underset{C_2H_5}{|}}{CH}-CH_2-\underset{\underset{O}{||}}{C} \right)_n$$

PHBV

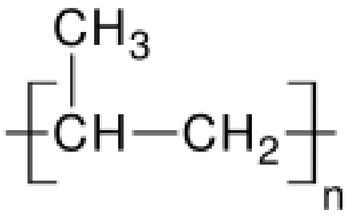
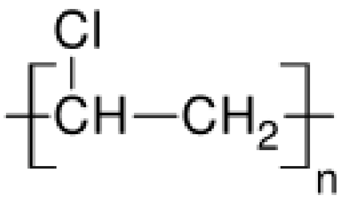
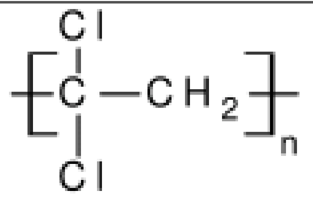
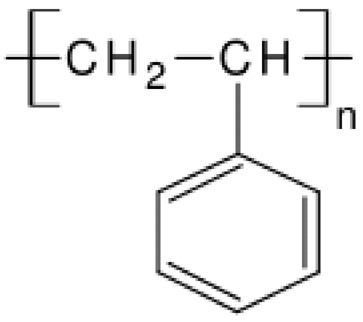
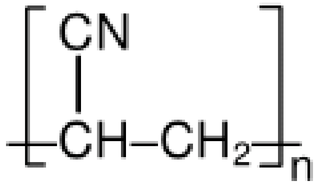
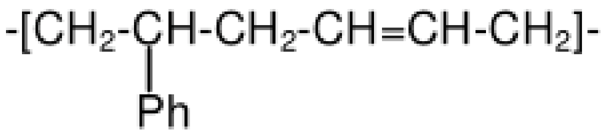
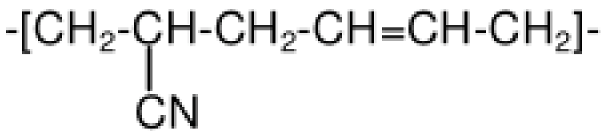
PHBV is used in speciality packaging, orthopaedic devices and in controlled release of drugs. PHBV undergoes bacterial degradation in the environment.

(b) Nylon–2–nylon–6 :

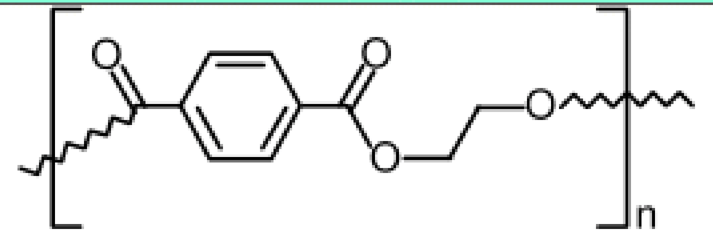
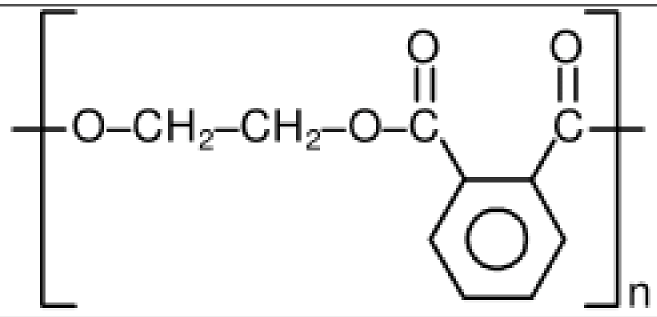
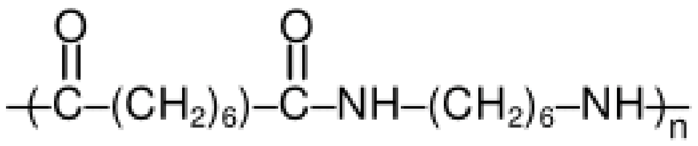
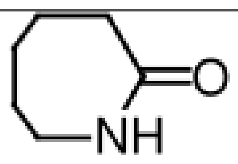
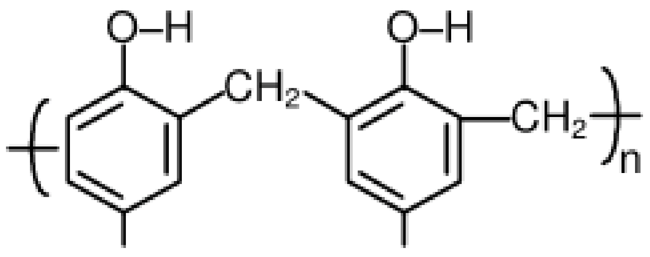
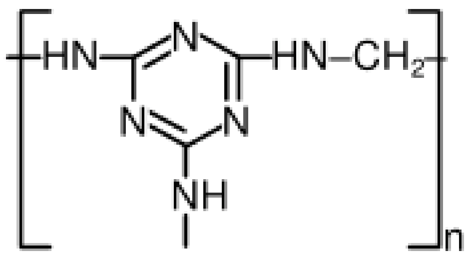
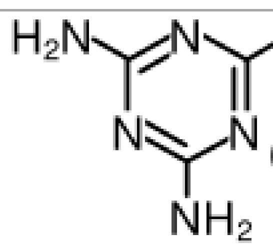
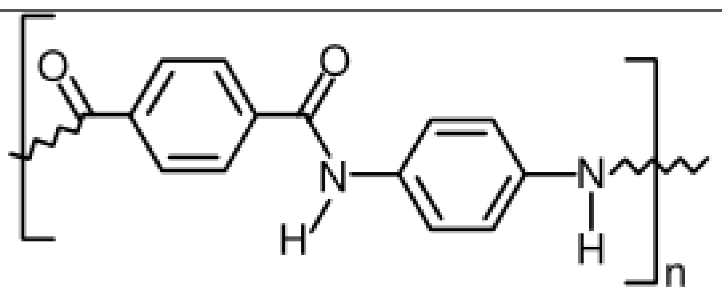
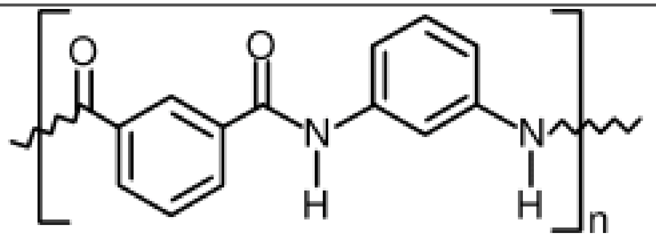
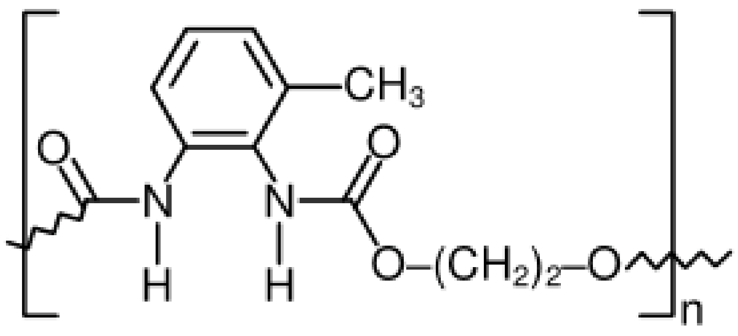
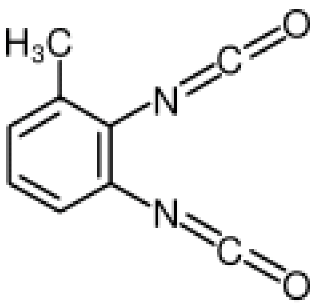
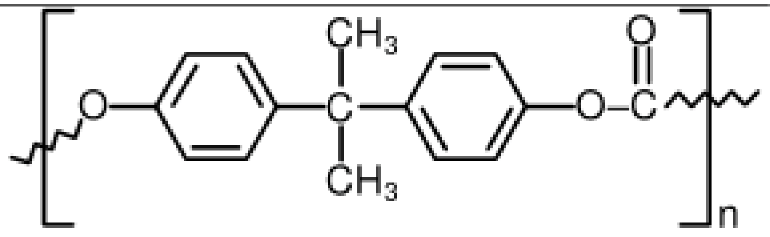
It is an alternating polyamide copolymer of glycine ($H_2N–CH_2–COOH$) and amino caproic acid ($H_2N(CH_2)_5COOH$) and it is also biodegradable polymer.

$$nH_2N-CH_2-COOH + nH_2N-(CH_2)_5-COOH \longrightarrow \left[NH-CH_2-CO-NH-(CH_2)_5-CO \right]_n$$

Some common addition polymers/chain growth polymer

S. No.	Name(s)	Formula	Monomer	Uses
1.	Polyethylene (low density (LDPE))	$-(CH_2\text{-}CH_2)_n-$	$CH_2{=}CH_2$ (ethylene)	Film wrap, Plastic Bags
2.	Polyethylene (high density (HDPE))	$-(CH_2\text{-}CH_2)_n-$	$CH_2{=}CH_2$ (ethylene)	Electrical insulation bottles, toys
3.	Polypropylene (PP) different grades	 $\left[\overset{CH_3}{\overset{\vert}{CH}}-CH_2\right]_n$	$CH_2{=}CHCH_3$ (propylene)	Manufacture of ropes, toys, pipes, fibres etc.
4.	Poly vinyl chloride (PVC)	 $\left[\overset{Cl}{\overset{\vert}{CH}}-CH_2\right]_n$	$CH_2{=}CHCl$ (vinyl chloride)	Manufacture of rain coats, hand bags, vinyl flooring, water Pipes etc.
5.	Poly vinylidene chloride (Saran A)	 $\left[\underset{\underset{Cl}{\vert}}{\overset{\overset{Cl}{\vert}}{C}}-CH_2\right]_n$	$CH_2{=}CCl_2$ (vinylidene chloride)	Seat covers, films & fibers
6.	Polystyrene (Styron)		$CH_2{=}CHC_6H_5$ (styrene)	As insulator, wrapping material, manufactures of toys, radio and Television cabinets
7.	Polyacrylonitrile (PAN, Orlon, Acrilan)	 $\left[\overset{CN}{\overset{\vert}{CH}}\text{–}CH_2\right]_n$	$CH_2{=}CHCN$ (acrylonitrile)	Rugs, Blankets clothing
8.	Polytetrafluoroethylene (PTFE, Teflon)	$-(CF_2\text{-}CF_2)_n-$	$CF_2{=}CF_2$ (tetrafluoroethylene)	Non-stick surfaces electrical insulation
9.	Poly methyl methacrylate (PMMA, Lucite, Plexiglas, perspex)	$-[CH_2C(CH_3)CO_2CH_3]_n-$	$CH_2{=}C(CH_3)CO_2CH_3$ (methylmethacrylate)	Lighting covers, signs skylights
10.	Poly vinyl acetate (PVAc)	$-(CH_2\text{-}CHOCOCH_3)_n-$	$CH_2{=}CHOCOCH_3$ (vinyl acetate)	Latex paints, Adhesives
11.	Natural Rubber	$-[CH_2\text{-}CH{=}C(CH_3)\text{-}CH_2]_n-$ (cis)	$CH_2{=}CH\text{–}C(CH_3){=}CH_2$ (isoprene)	Requires vulcanization for practical use
12.	Neoprene	$-[CH_2\text{-}CH{=}CCl\text{-}CH_2]_n-$	$CH_2{=}CH\text{-}CCl{=}CH_2$ (chloroprene)	Synthetic rubber, oil resistant seal, gaskets, hoses & conveyor belts
13.	SBR styrene butadiene rubber (Buna-S)	 $\text{-}[CH_2\text{-}\underset{\underset{Ph}{\vert}}{CH}\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2]\text{-}$	$H_2C{=}CHC_6H_5$ and $H_2C{=}CH\text{-}CH{=}CH_2$	Tyres, floortiles, foot wear & cable insulation
14.	Nitrile Rubber (Buna-N)	 $\text{-}[CH_2\text{-}\underset{\underset{CN}{\vert}}{CH}\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2]\text{-}$	$H_2C{=}CHCN$ and $H_2C{=}CH\text{-}CH{=}CH_2$	Making oil seals, tank lining and hoses

Some condensation polymers/step growth polymers

S.	Name(s)	Formula	Monomer	Uses
1.	Polyester/Dacron/ Terylene/Mylar		$HO_2C\ C_6H_4\ CO_2H$ (Terephthalic acid) $HO-CH_2CH_2-OH$ Ethylene glycol	Fabric, Tyrecord
2.	Glyptal or Alkyds resin		$HO_2C-C_6H_4-CO_2H$ (Phthalic acid) $HO-CH_2CH_2-OH$	Paints and Lacquers
3.	Polyamide (Nylon 6,6)	$\sim[CO(CH_2)_4CO-NH(CH_2)_6NH]_n\sim$	$HO_2C-(CH_2)_4-CO_2H$ $H_2N-(CH_2)_6-NH_2$	Parachutes & Clothing
4.	Nylon 6,10	 $\left[\overset{\overset{O}{\Vert}}{C}-(CH_2)_6-\overset{\overset{O}{\Vert}}{C}-NH-(CH_2)_6-NH\right]_n$	$HOOC-(CH_2)_8-COOH$ $H_2N-(CH_2)_6-NH_2$	
5.	Polyamide Nylon 6, Perlon-L	$\sim[CO(CH_2)_5NH]_n\sim$		Rope & Tyrecord
6.	Bakelite		PhOH + HCHO in (excess)	Electrical Switch, combs, Handle of Utensils, computer discs and Bowling Balls
7.	Urea-formaldehyde resin	$(-NH-CO-NH-CH_2-)_n$	$H_2N-CO-NH_2$ (Urea) HCHO (Formaldehyde)	Making unbreakable cups and laminated sheets.
8.	Melamine formaldehyde resin		 (melamine) +HCHO (formaldehyde)	Unbreakable crockery
9.	Polyamide Kevlar		Para $HO_2C-C_6H_4-CO_2H$	Tyre
10.	Polyamide Nomex		Meta $HO_2C-C_6H_4-CO_2H$ Meta $H_2N-C_6H_4-NH_2$	
11.	Polyurethane Spandex		$HOCH_2CH_2OH$ 	Foams, Shoes, Automobile seats and components
12.	Polycarbonate Lexan		$(HO-C_6H_4-)_2C(CH_3)_2$ (Bisphenol A) $X_2C=O$ (X = OCH_3 or Cl)	Bike helmet, goggles, bullet proof glass

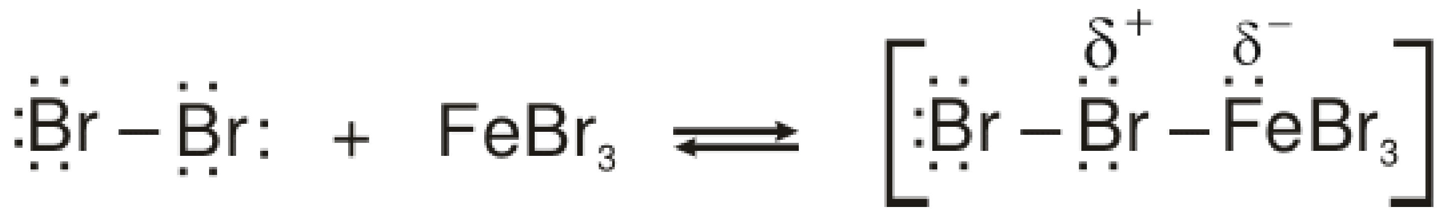
Aromatic Compounds

Electrophilic aromatic substitution :

(a) Bromination of Benzene :

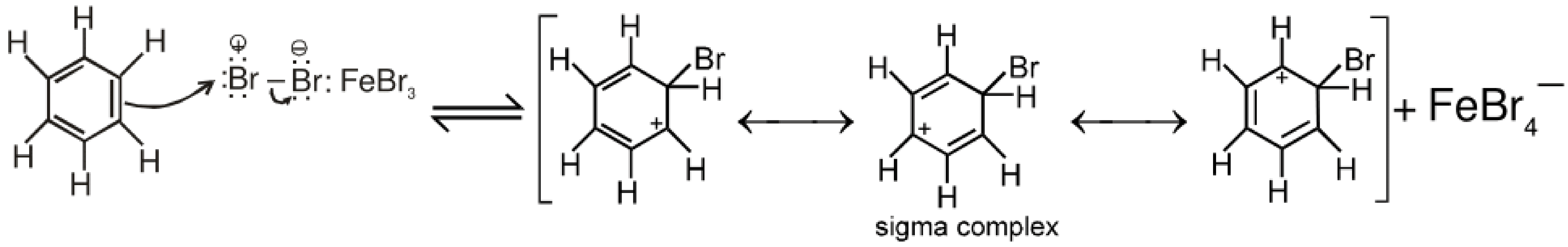
Bromination follows the general mechanism for electrophilic aromatic substitution. Bromine itself is not sufficiently electrophilic to react with benzene, but a strong Lewis acid such as $FeBr_3$ catalyzes the reaction.

Step 1 : Formation of a stronger electrophile.

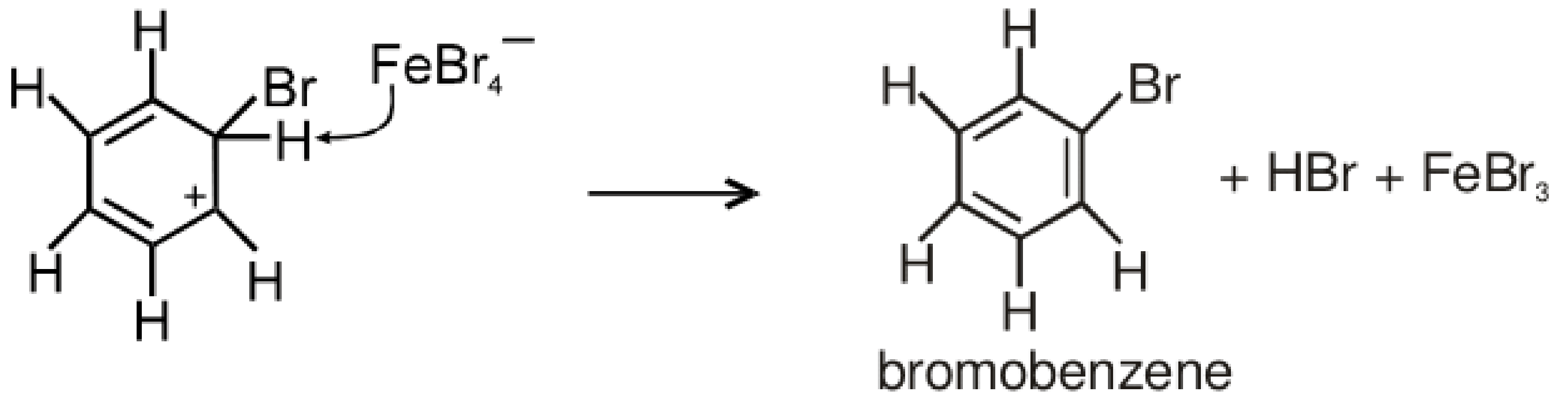


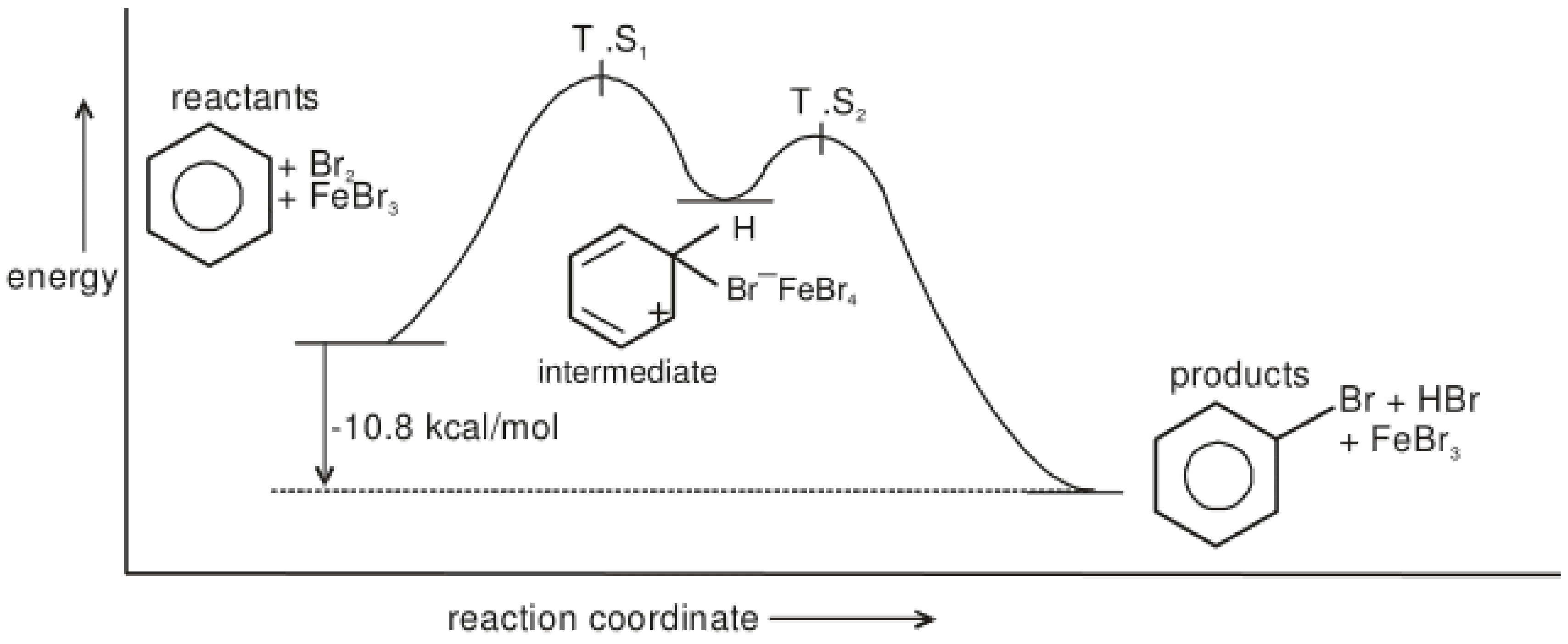
$$\mathrm{:\ddot{B}r - \ddot{B}r: + FeBr_3 \rightleftharpoons \left[:\ddot{B}r - \overset{\delta^+}{\ddot{B}r} - \overset{\delta^-}{Fe}Br_3\right]}$$

Step 2 : Electrophilic attack and formation of the sigma complex.

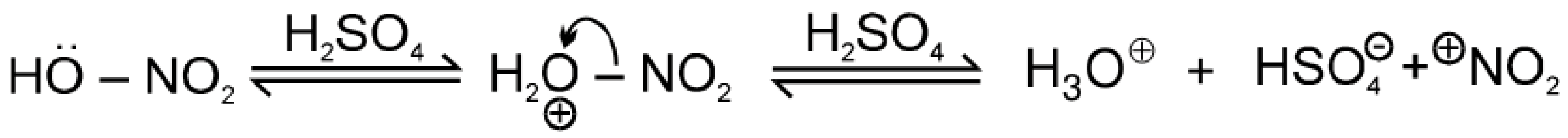


Step 3 : Loss of a proton gives the products.

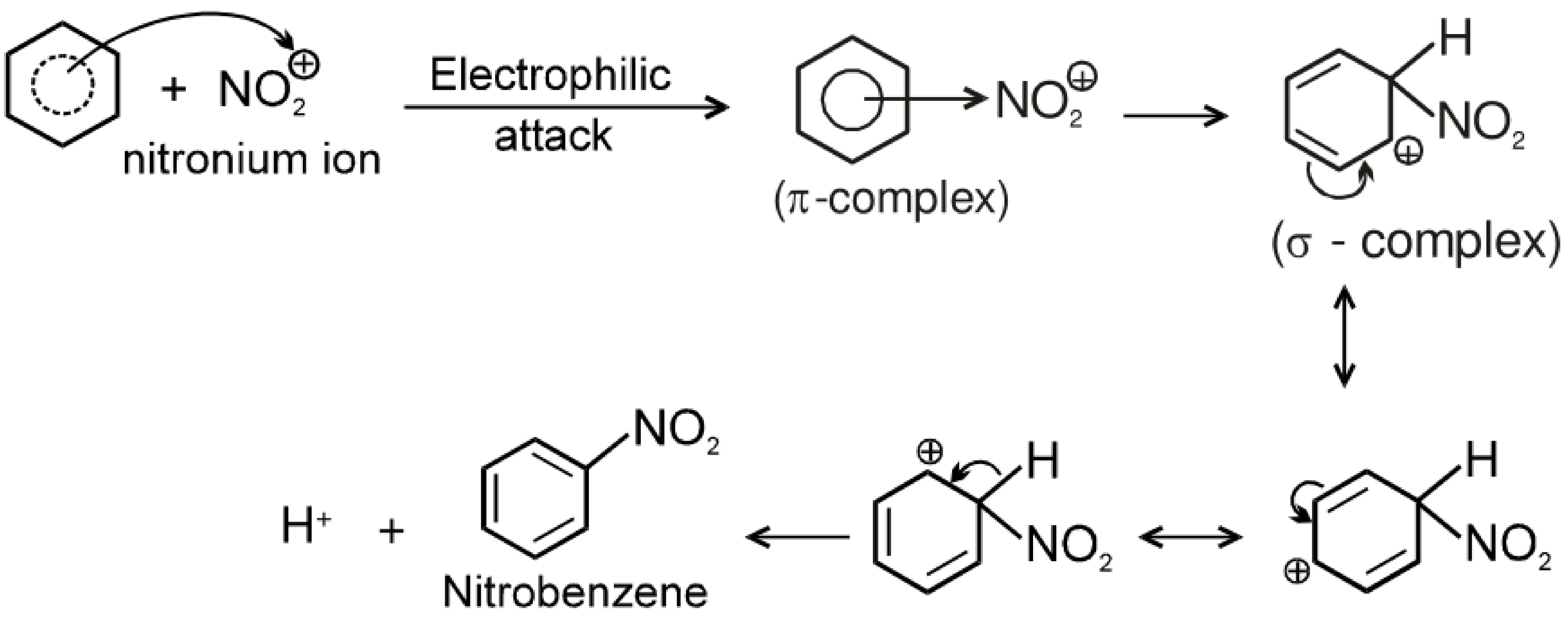




(b) Nitration :



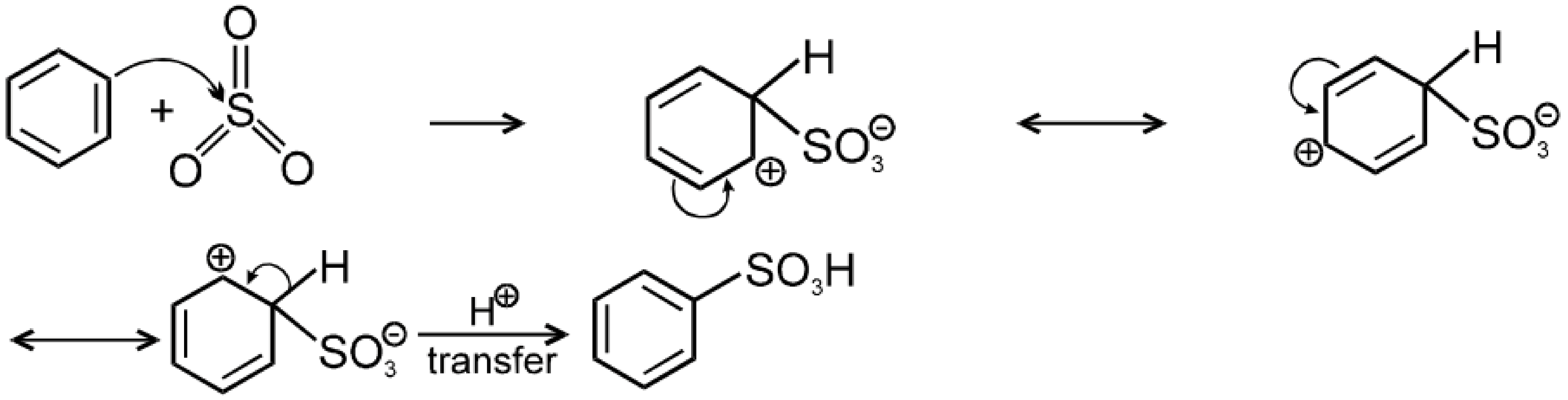
$$\mathrm{H\ddot{O} - NO_2 \overset{H_2SO_4}{\rightleftharpoons} H_2\underset{\oplus}{O} - NO_2 \overset{H_2SO_4}{\rightleftharpoons} H_3O^{\oplus} + HSO_4^{\ominus} + {}^{\oplus}NO_2}$$



(c) Sulphonation :

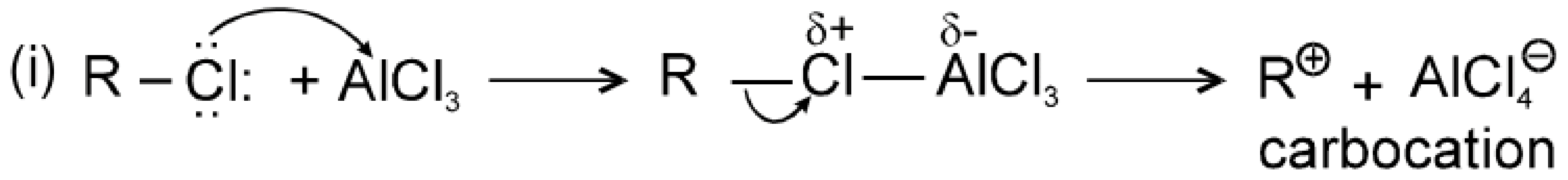
The electrophilic reagent, SO_3, attacks the benzene ring to form the intermediate carbocation.

$$2H_2SO_4 \rightleftharpoons SO_3 + H_3O^{\oplus} + SO_4^{\ominus}$$



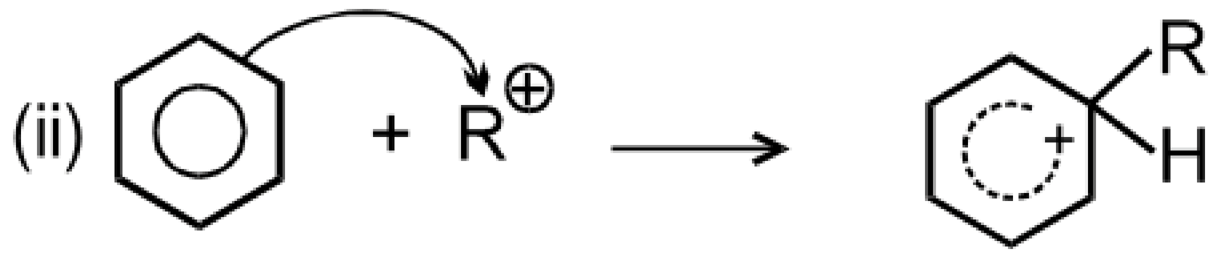
(d) Friedel Craft reaction :

Alkylation mechanism :

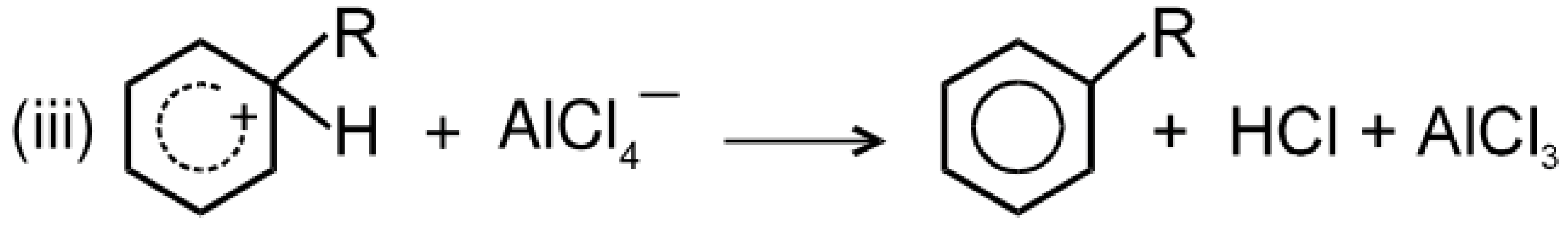


(i) $R-\ddot{\underset{..}{Cl}}: + AlCl_3 \longrightarrow R - \overset{\delta+}{Cl} - \overset{\delta-}{AlCl_3} \longrightarrow R^{\oplus} + AlCl_4^{\ominus}$

carbocation



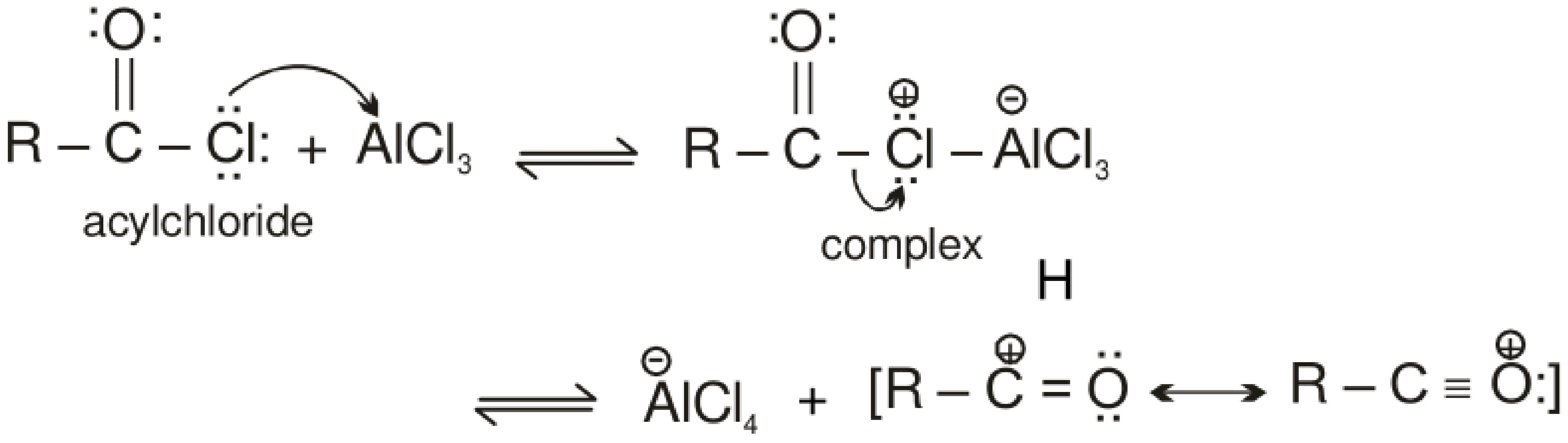
σ-complex



Acylation mechanism :

Acylation of benzene may be brought about with acid chlorides or anhydrides in presence of Lewis acids.

Step 1 : Formation of an acylium ion.



$$R-\overset{\overset{:O:}{\|}}{C}-\ddot{\underset{..}{Cl}}: + AlCl_3 \rightleftharpoons R-\overset{\overset{:O:}{\|}}{C}-\overset{\oplus}{\ddot{\underset{..}{Cl}}}-\overset{\ominus}{AlCl_3}$$

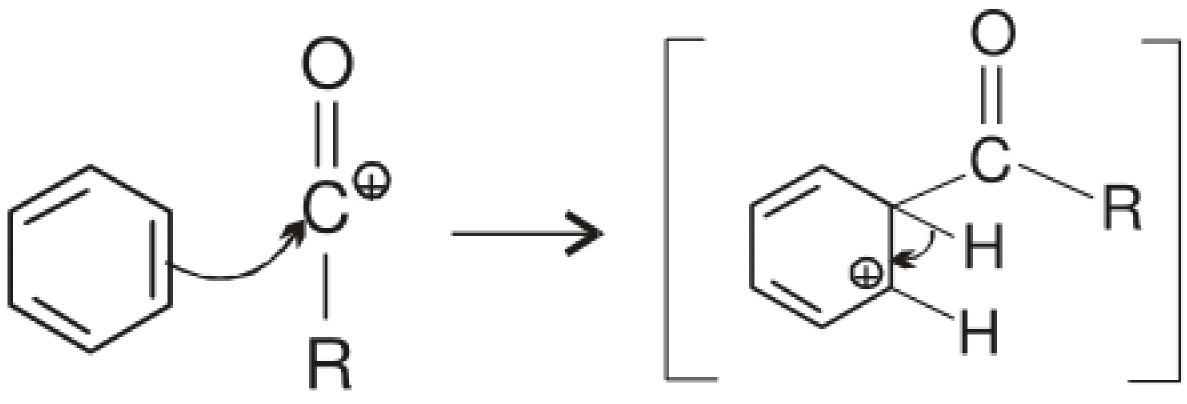
acylchloride

complex

$$\rightleftharpoons \overset{\ominus}{AlCl_4} + [R-\overset{\oplus}{C}=\ddot{\underset{..}{O}} \longleftrightarrow R-C\equiv\overset{\oplus}{O}:]$$

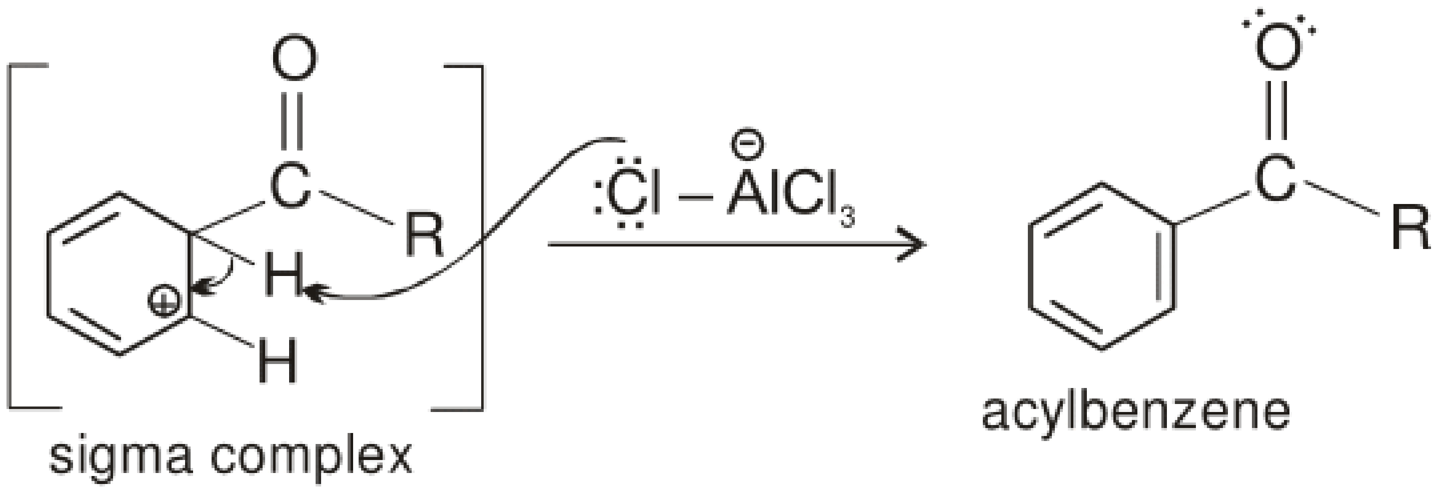
acylium ion

Step 2 : Electrophilic attack.

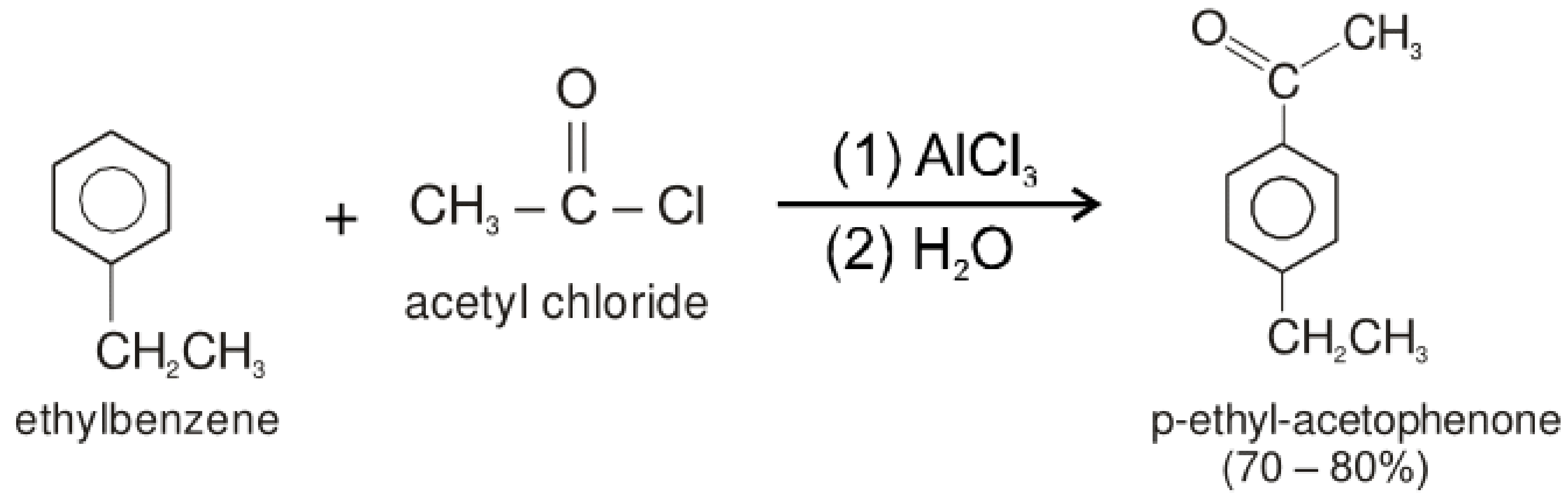


sigma complex

Step 3 : Loss of a proton. Complexation of the product.

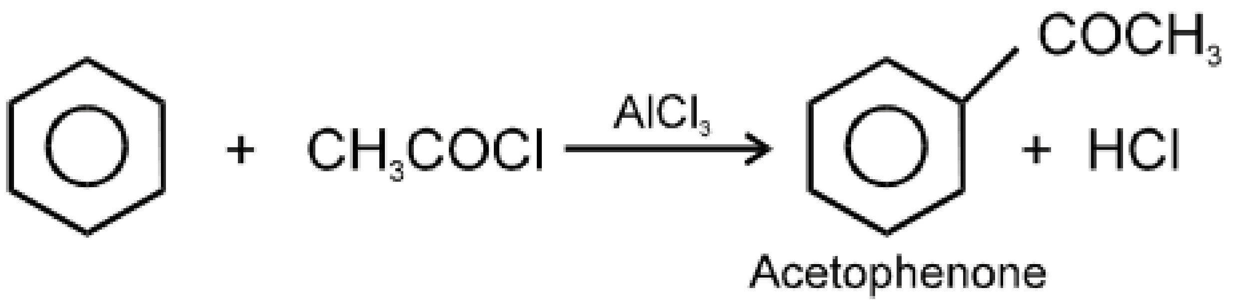


e.g.

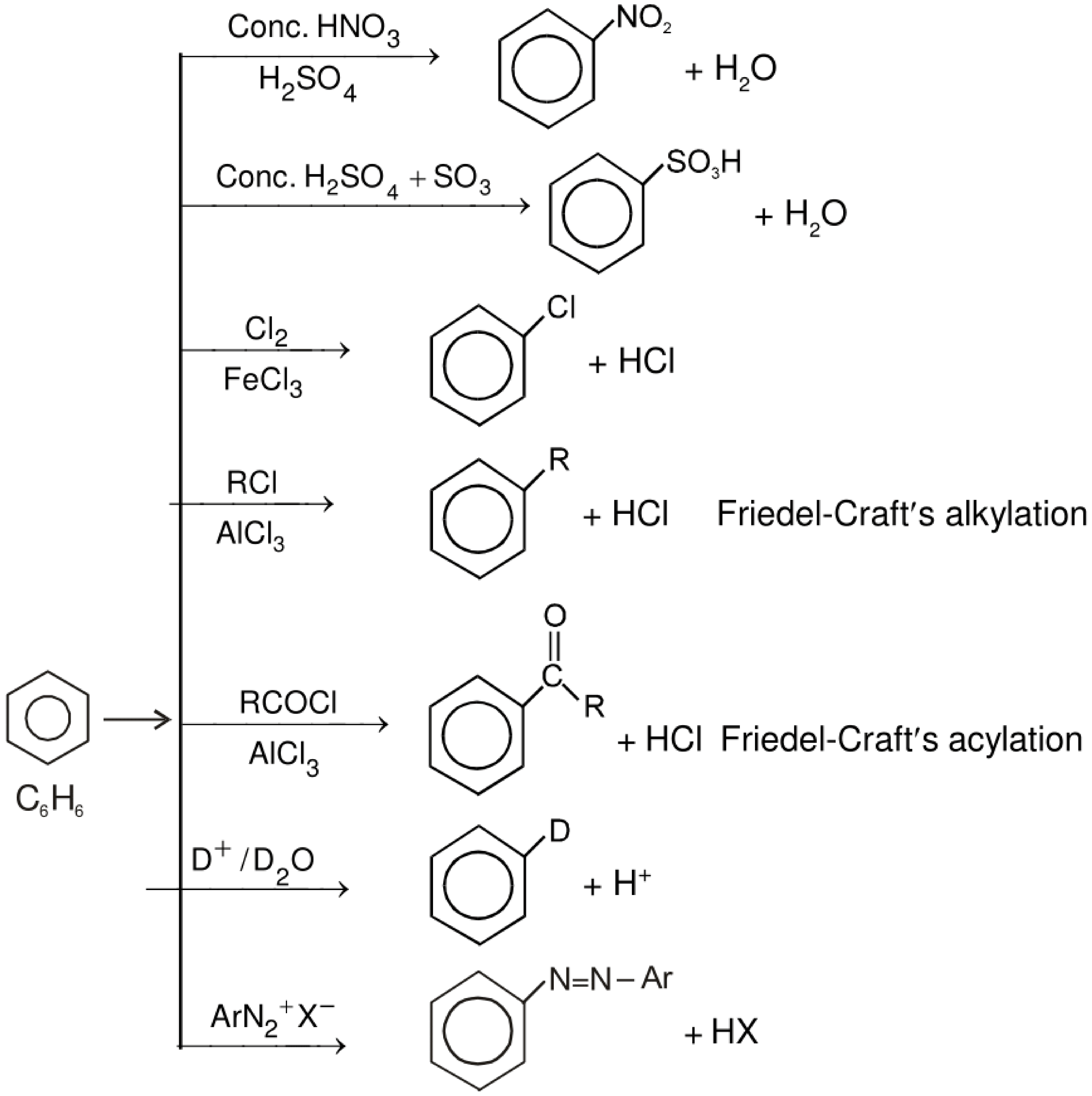


Note : Friedel-Crafts acylations are generally free from rearrangements and multiple substitution. They do not go on strongly deactivated rings.

e.g.

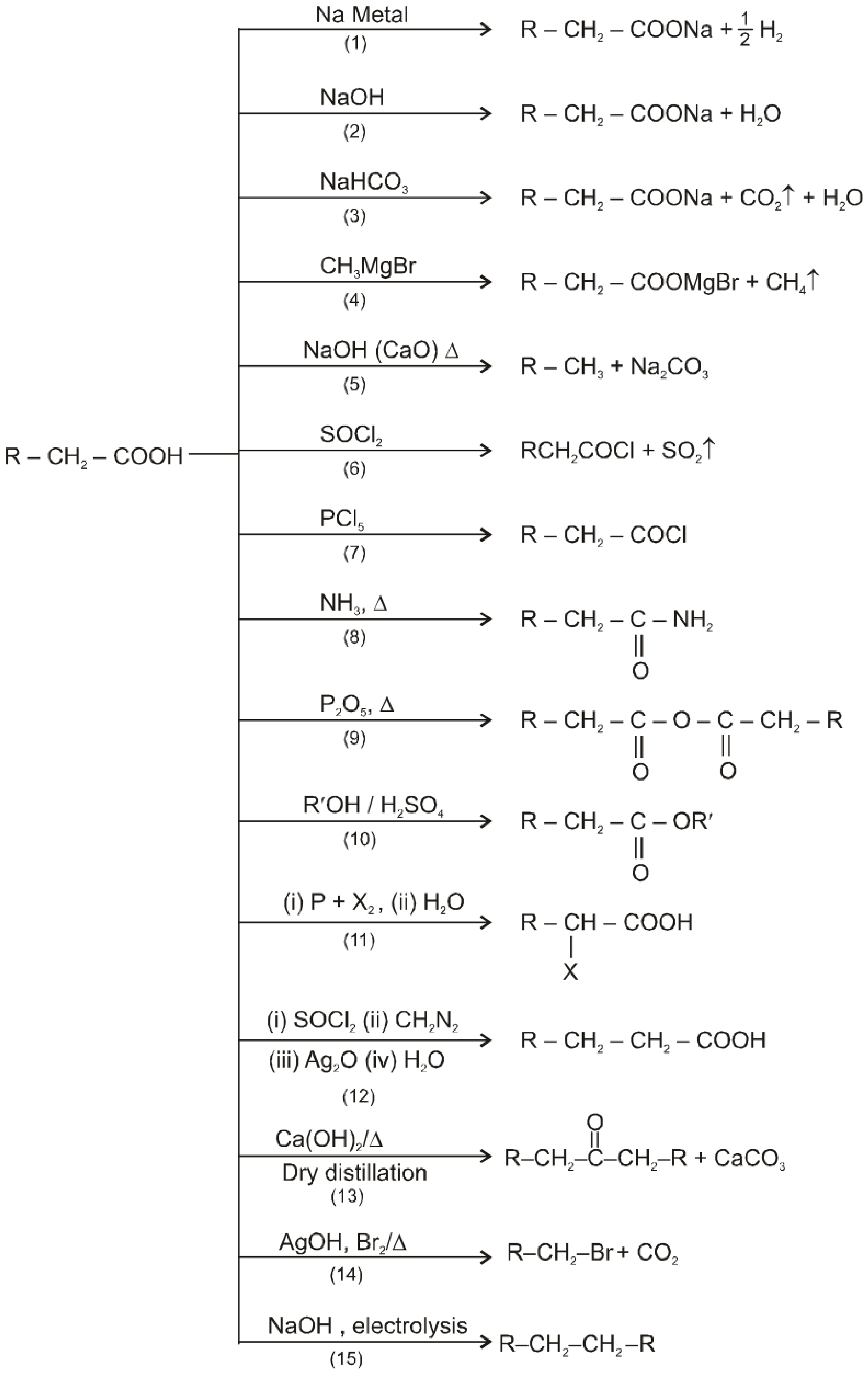


Chemical Reactions of Benzene :



Carboxylic Acid & Derivatives

Summary of reactions of carboxylic acids :



$$R-CH_2-COOH \xrightarrow[(1)]{\text{Na Metal}} R-CH_2-COONa + \tfrac{1}{2}H_2$$

$$\xrightarrow[(2)]{NaOH} R-CH_2-COONa + H_2O$$

$$\xrightarrow[(3)]{NaHCO_3} R-CH_2-COONa + CO_2\uparrow + H_2O$$

$$\xrightarrow[(4)]{CH_3MgBr} R-CH_2-COOMgBr + CH_4\uparrow$$

$$\xrightarrow[(5)]{NaOH\ (CaO)\ \Delta} R-CH_3 + Na_2CO_3$$

$$\xrightarrow[(6)]{SOCl_2} RCH_2COCl + SO_2\uparrow$$

$$\xrightarrow[(7)]{PCl_5} R-CH_2-COCl$$

$$\xrightarrow[(8)]{NH_3,\ \Delta} R-CH_2-\underset{\underset{O}{\|}}{C}-NH_2$$

$$\xrightarrow[(9)]{P_2O_5,\ \Delta} R-CH_2-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-CH_2-R$$

$$\xrightarrow[(10)]{R'OH\ /\ H_2SO_4} R-CH_2-\underset{\underset{O}{\|}}{C}-OR'$$

$$\xrightarrow[(11)]{(i)\ P + X_2,\ (ii)\ H_2O} R-\underset{\underset{X}{|}}{CH}-COOH$$

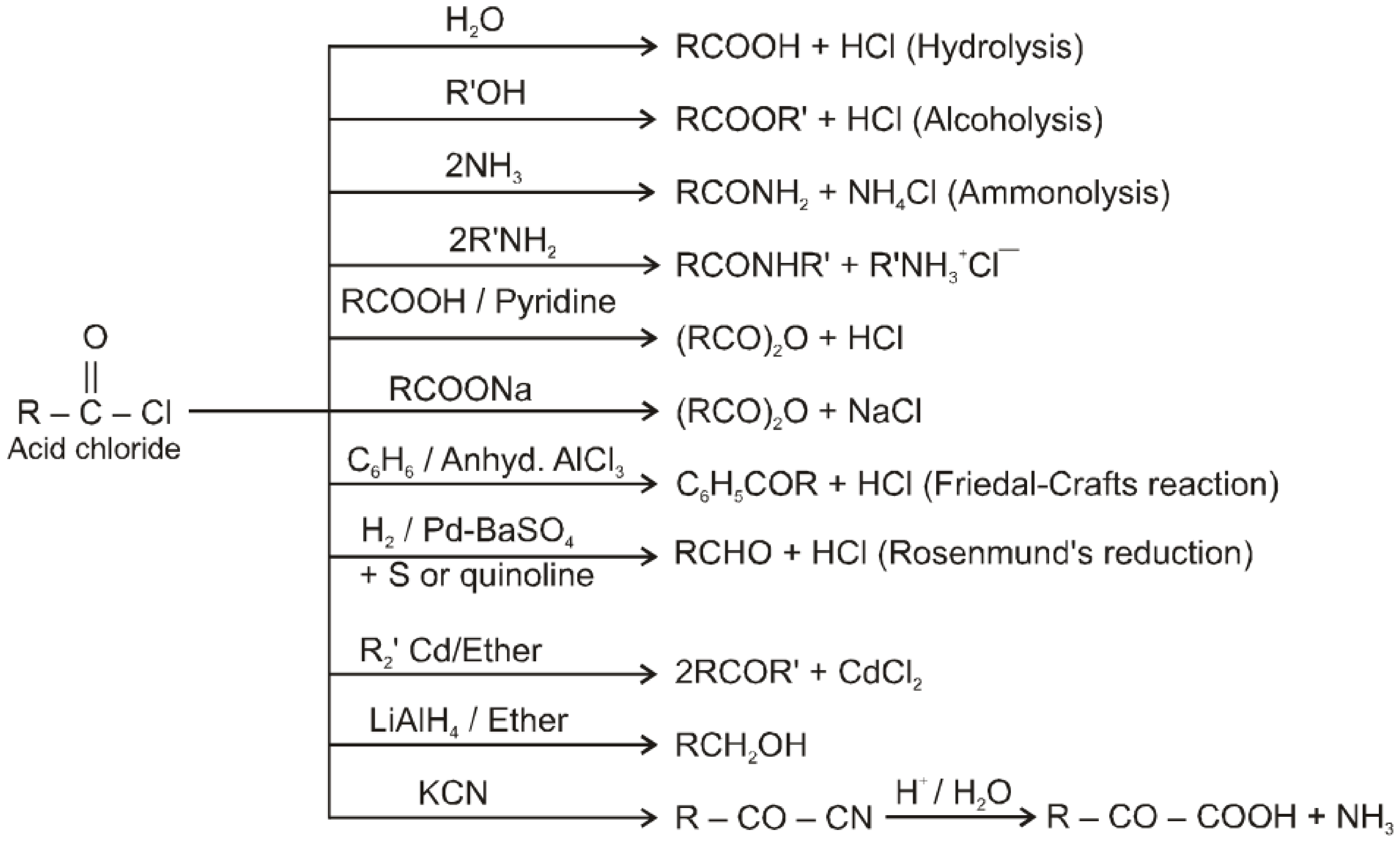
$$\xrightarrow[\text{(iii) } Ag_2O \text{ (iv) } H_2O \quad (12)]{\text{(i) } SOCl_2 \text{ (ii) } CH_2N_2} R-CH_2-CH_2-COOH$$

$$\xrightarrow[\text{Dry distillation} \quad (13)]{Ca(OH)_2/\Delta} R-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-R + CaCO_3$$

$$\xrightarrow[(14)]{AgOH,\ Br_2/\Delta} R-CH_2-Br + CO_2$$

$$\xrightarrow[(15)]{NaOH\ ,\ \text{electrolysis}} R-CH_2-CH_2-R$$

Summary of reactions of acid halide



$$\underset{\text{Acid chloride}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl}$$

$$\xrightarrow{H_2O} RCOOH + HCl \text{ (Hydrolysis)}$$

$$\xrightarrow{R'OH} RCOOR' + HCl \text{ (Alcoholysis)}$$

$$\xrightarrow{2NH_3} RCONH_2 + NH_4Cl \text{ (Ammonolysis)}$$

$$\xrightarrow{2R'NH_2} RCONHR' + R'NH_3^+Cl^-$$

$$\xrightarrow{RCOOH\ /\ Pyridine} (RCO)_2O + HCl$$

$$\xrightarrow{RCOONa} (RCO)_2O + NaCl$$

$$\xrightarrow{C_6H_6\ /\ Anhyd.\ AlCl_3} C_6H_5COR + HCl \text{ (Friedal-Crafts reaction)}$$

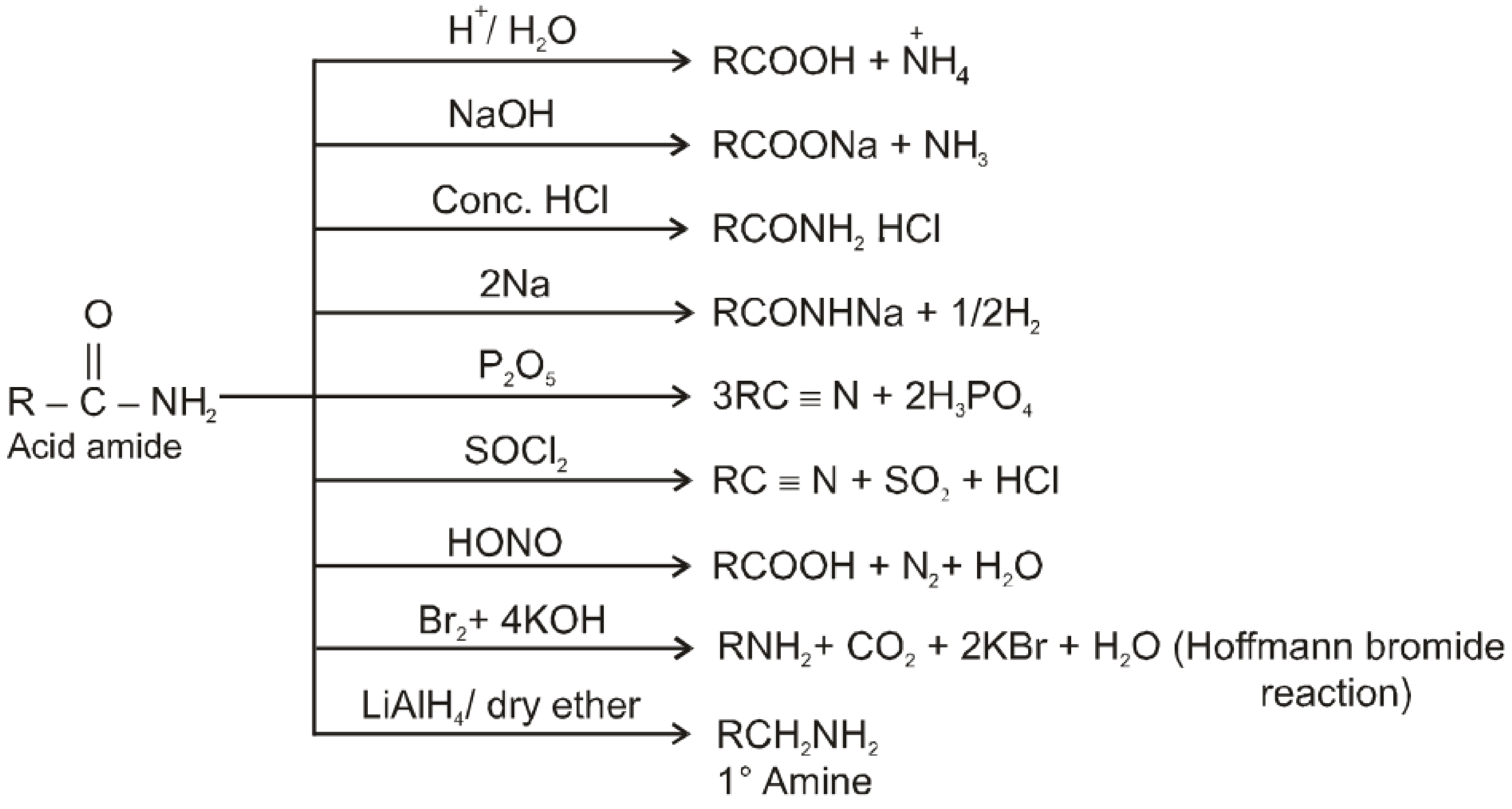
$$\xrightarrow[+\ S\ or\ quinoline]{H_2\ /\ Pd\text{-}BaSO_4} RCHO + HCl \text{ (Rosenmund's reduction)}$$

$$\xrightarrow{R_2'\ Cd/Ether} 2RCOR' + CdCl_2$$

$$\xrightarrow{LiAlH_4\ /\ Ether} RCH_2OH$$

$$\xrightarrow{KCN} R-CO-CN \xrightarrow{H^+\ /\ H_2O} R-CO-COOH + NH_3$$

Summary of reaction of amide:



$$\underset{\text{Acid amide}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2}$$

$$\xrightarrow{H^+/\ H_2O} RCOOH + \overset{+}{N}H_4$$

$$\xrightarrow{NaOH} RCOONa + NH_3$$

$$\xrightarrow{Conc.\ HCl} RCONH_2\ HCl$$

$$\xrightarrow{2Na} RCONHNa + 1/2H_2$$

$$\xrightarrow{P_2O_5} 3RC \equiv N + 2H_3PO_4$$

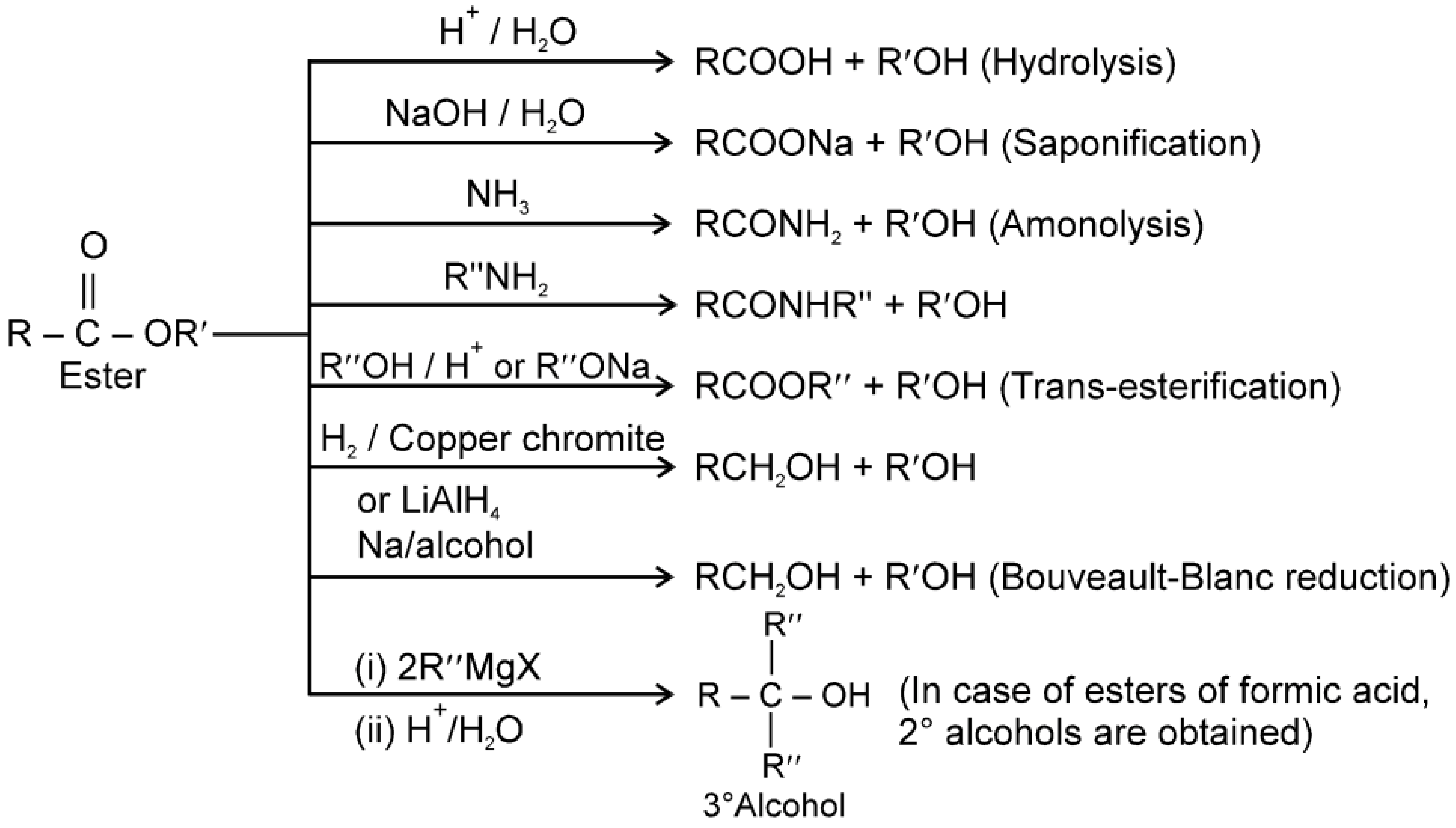
$$\xrightarrow{SOCl_2} RC \equiv N + SO_2 + HCl$$

$$\xrightarrow{HONO} RCOOH + N_2 + H_2O$$

$$\xrightarrow{Br_2 + 4KOH} RNH_2 + CO_2 + 2KBr + H_2O \text{ (Hoffmann bromide reaction)}$$

$$\xrightarrow{LiAlH_4/\ dry\ ether} \underset{1°\ \text{Amine}}{RCH_2NH_2}$$

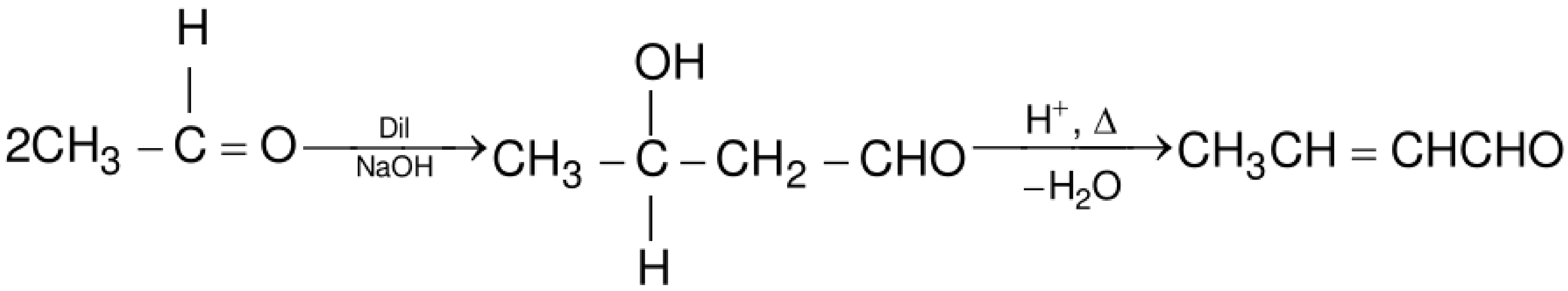
Summary of reaction of esters :



Aldehydes & Ketones

Aldol condensation :

Carbonyl compounds having acidic sp^3 α-H shows this reaction in presence of dil. NaOH or dil. acid.



$$2CH_3-\overset{\overset{H}{|}}{C}=O \xrightarrow[NaOH]{Dil} CH_3-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2-CHO \xrightarrow[-H_2O]{H^+,\ \Delta} CH_3CH=CHCHO$$

Crossed aldol condensation

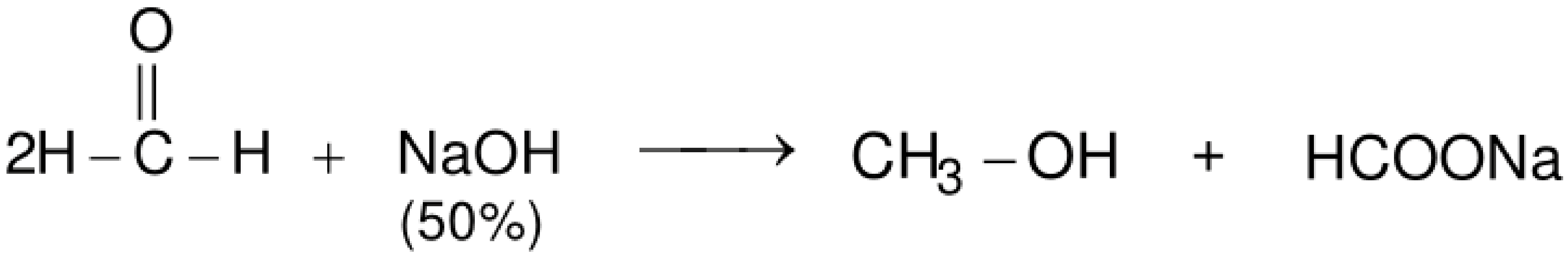
(i) $CH_3CHO + HCHO \xrightarrow{Dil.\ NaOH} HOCH_2–CH_2–CHO \xrightarrow[\Delta]{H^+\ /\ H_2O} CH_2=CH–CHO$

(ii) $CH_3COCH_3 + HCHO \xrightarrow{Dil.\ NaOH} CH_3CO–CH_2CH_2OH \xrightarrow[\Delta]{H^+\ /\ H_2O}$

$CH_3CO–CH=CH_2$

Cannizzaro reaction :

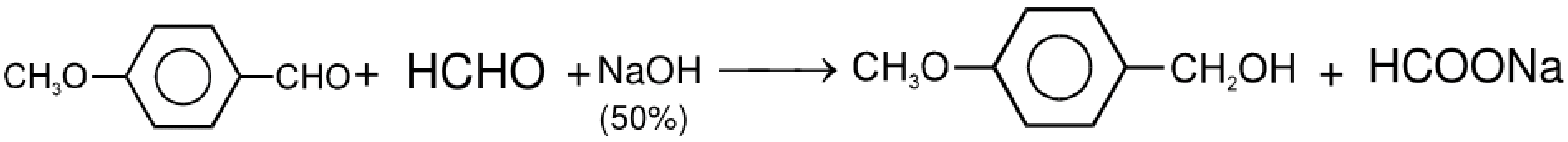
Carbonyl compounds not having $sp^3\alpha$-H shows following disproportion reaction



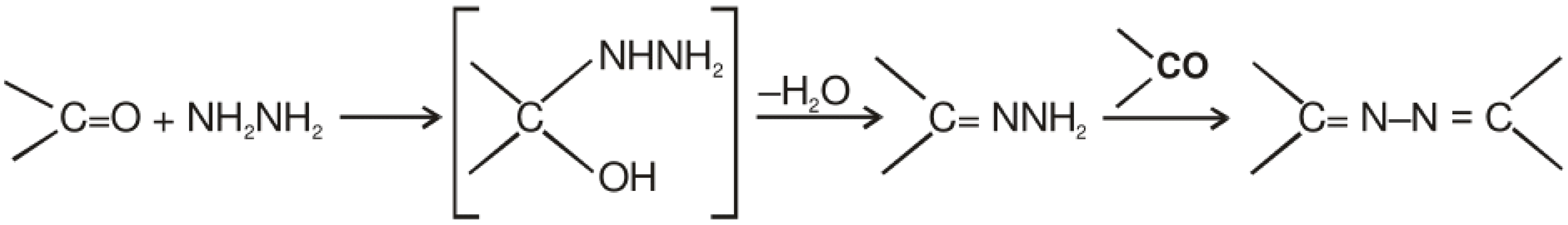
$$2H-\overset{\overset{O}{||}}{C}-H + \underset{(50\%)}{NaOH} \longrightarrow CH_3-OH + HCOONa$$

$$2C_6H_5CHO + \underset{(50\%)}{NaOH} \longrightarrow C_6H_5CH_2OH + C_6H_5COONa$$

Crossed Cannizzaro reaction :



Formation of hydrzones and azines



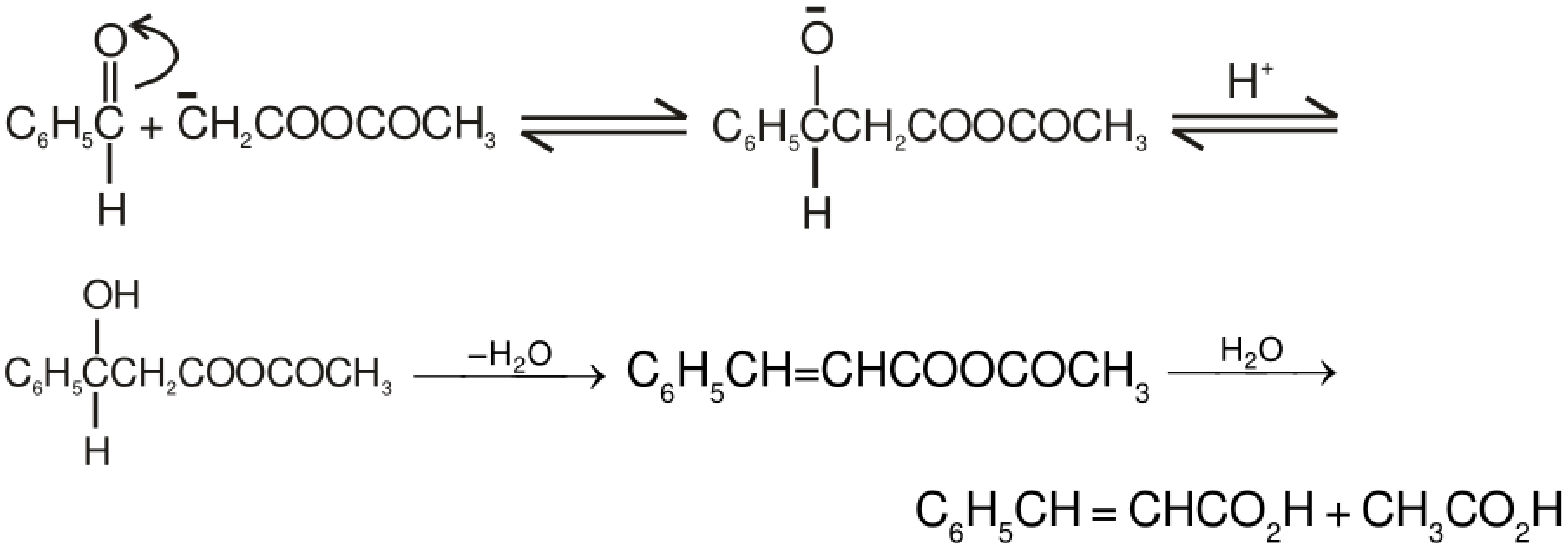
Perkin reaction :

When benzaldehyde (or any other aromatic aldehyde) is heated with the anhydride of an aliphatic acid (containing two α-hydrogen atoms) in the presence of its sodium salt, condensation takes place to form a β-arylacrylic acid ; e.g., with acetic anhydride and sodium acetate, cinnamic acid is formed.

$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3CO_2Na} C_6H_5CH = CHCO_2H$$

Mechanism :

$$CH_3COOCOCH_3 + CH_3CO_2^- \rightleftharpoons \bar{C}H_2COOCOCH_3 + CH_3CO_2H$$



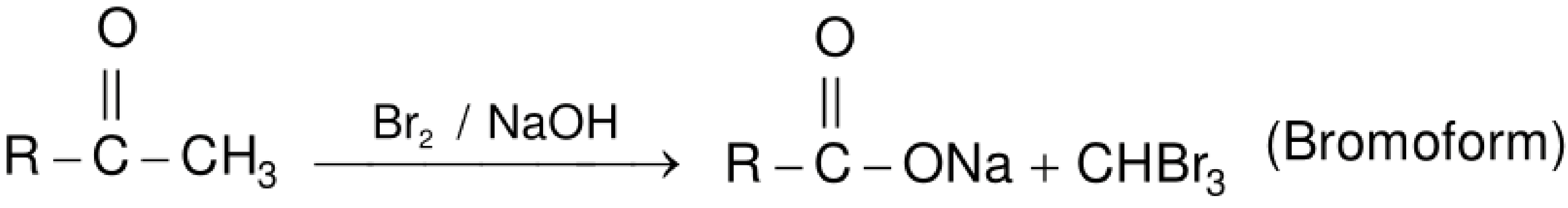
$$C_6H_5\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{C}} + \bar{C}H_2COOCOCH_3 \rightleftharpoons C_6H_5\underset{\underset{H}{|}}{\overset{\overset{\bar{O}}{|}}{C}}CH_2COOCOCH_3 \overset{H^+}{\rightleftharpoons}$$

$$C_6H_5\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{C}}CH_2COOCOCH_3 \xrightarrow{-H_2O} C_6H_5CH{=}CHCOOCOCH_3 \xrightarrow{H_2O}$$

$$C_6H_5CH = CHCO_2H + CH_3CO_2H$$

Haloform reaction :

Acetaldehyde and methylalkyl ketones react rapidly with halogen (Cl_2, Br_2 or I_2) in the presence of alkali to give haloform and acid salt.

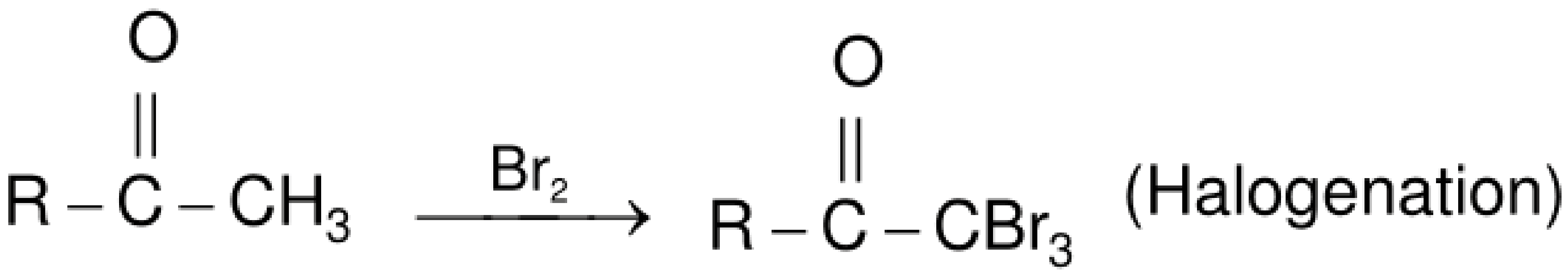


$$R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{Br_2\ /\ NaOH} R-\overset{\overset{O}{\|}}{C}-ONa + CHBr_3 \text{ (Bromoform)}$$

In this reaction $-CH_3$ of $CH_3-\overset{\overset{O}{\|}}{C}-$ group is converted into haloform as it contains acidic hydrogen atom and rest-part of alkyl methyl ketone give acid salt having carbon atom corresponding to alkyl ketone.

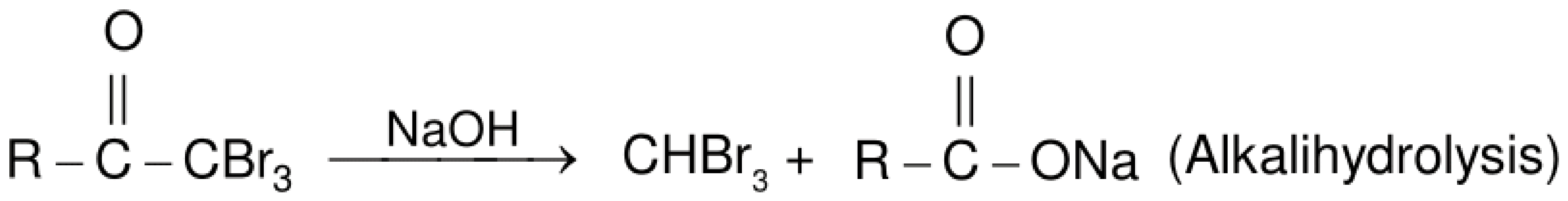
Preparation of haloform from methylketone involves two steps.

(a) Halogenation



$$R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{Br_2} R-\overset{\overset{O}{\|}}{C}-CBr_3 \text{ (Halogenation)}$$

(b) Alkalihydrolysis

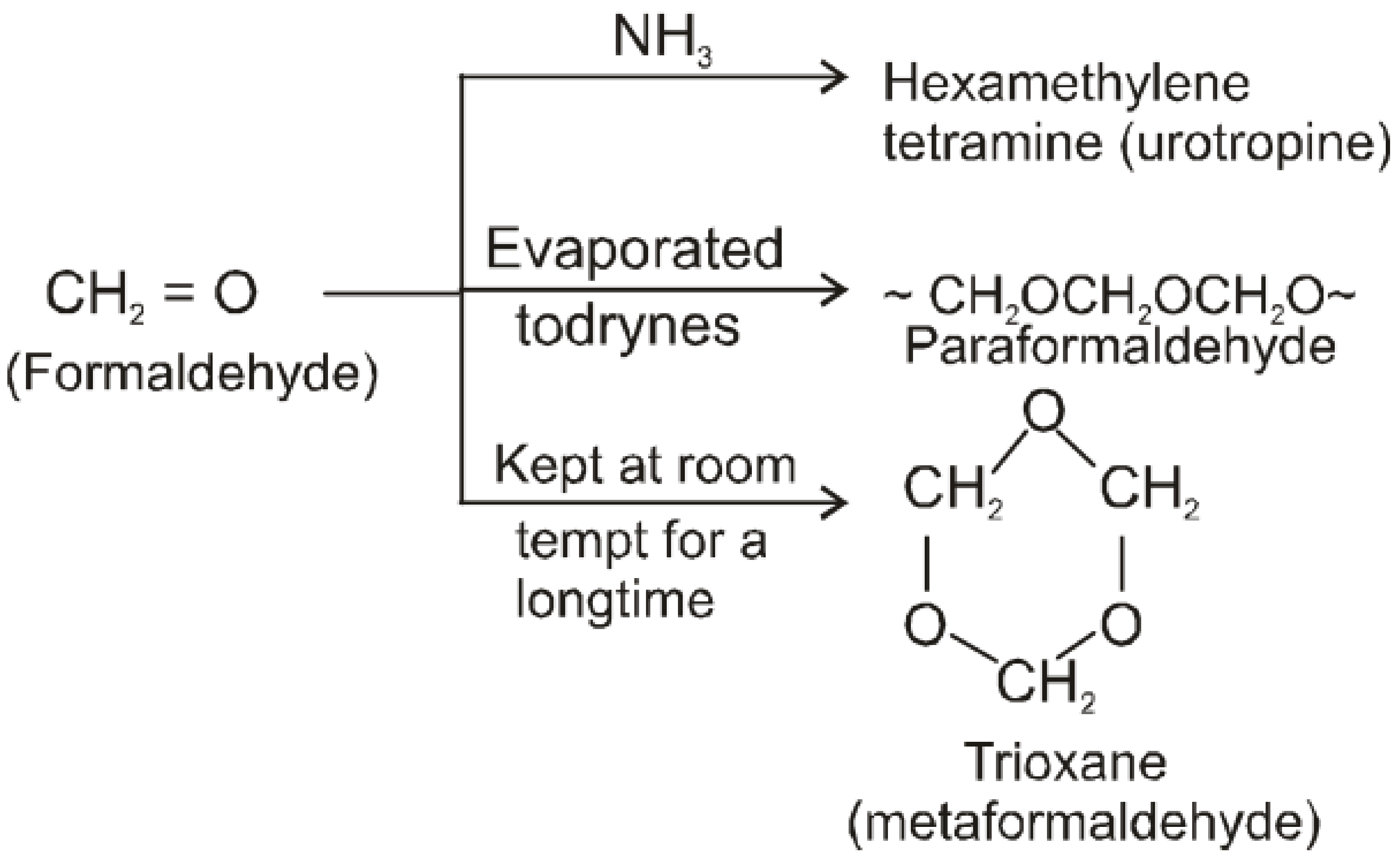


$$R-\overset{\overset{\large O}{||}}{C}-CBr_3 \xrightarrow{NaOH} CHBr_3 + R-\overset{\overset{\large O}{||}}{C}-ONa \text{ (Alkalihydrolysis)}$$

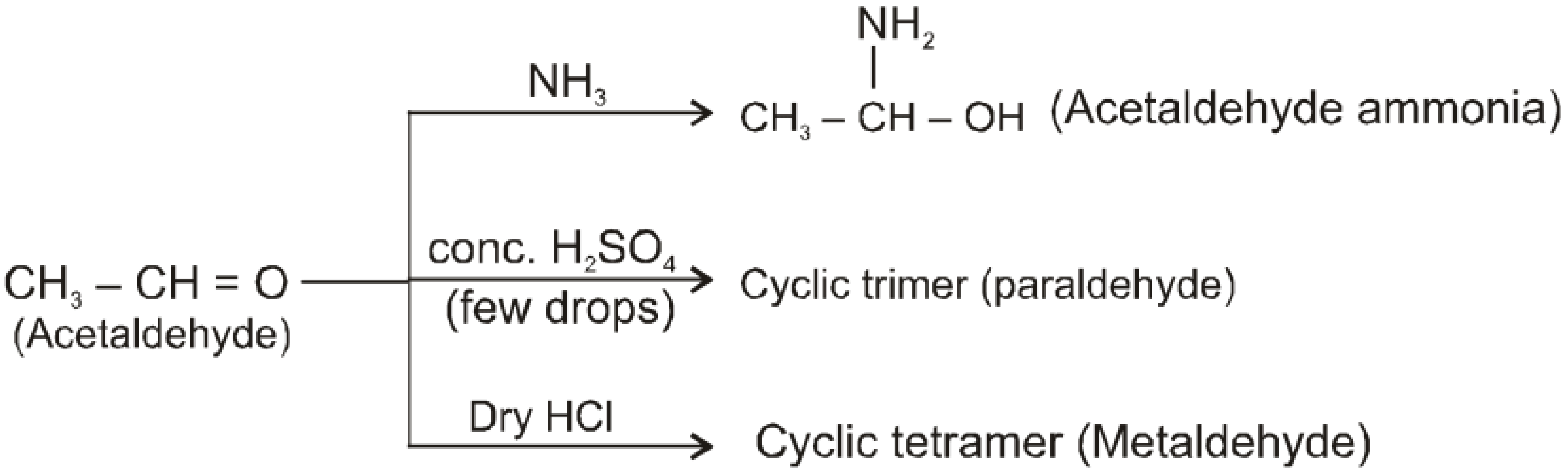
Note : This reaction is used to distinguish the presence of $CH_3-\overset{\overset{O}{||}}{C}-$ group.

Other reactions :

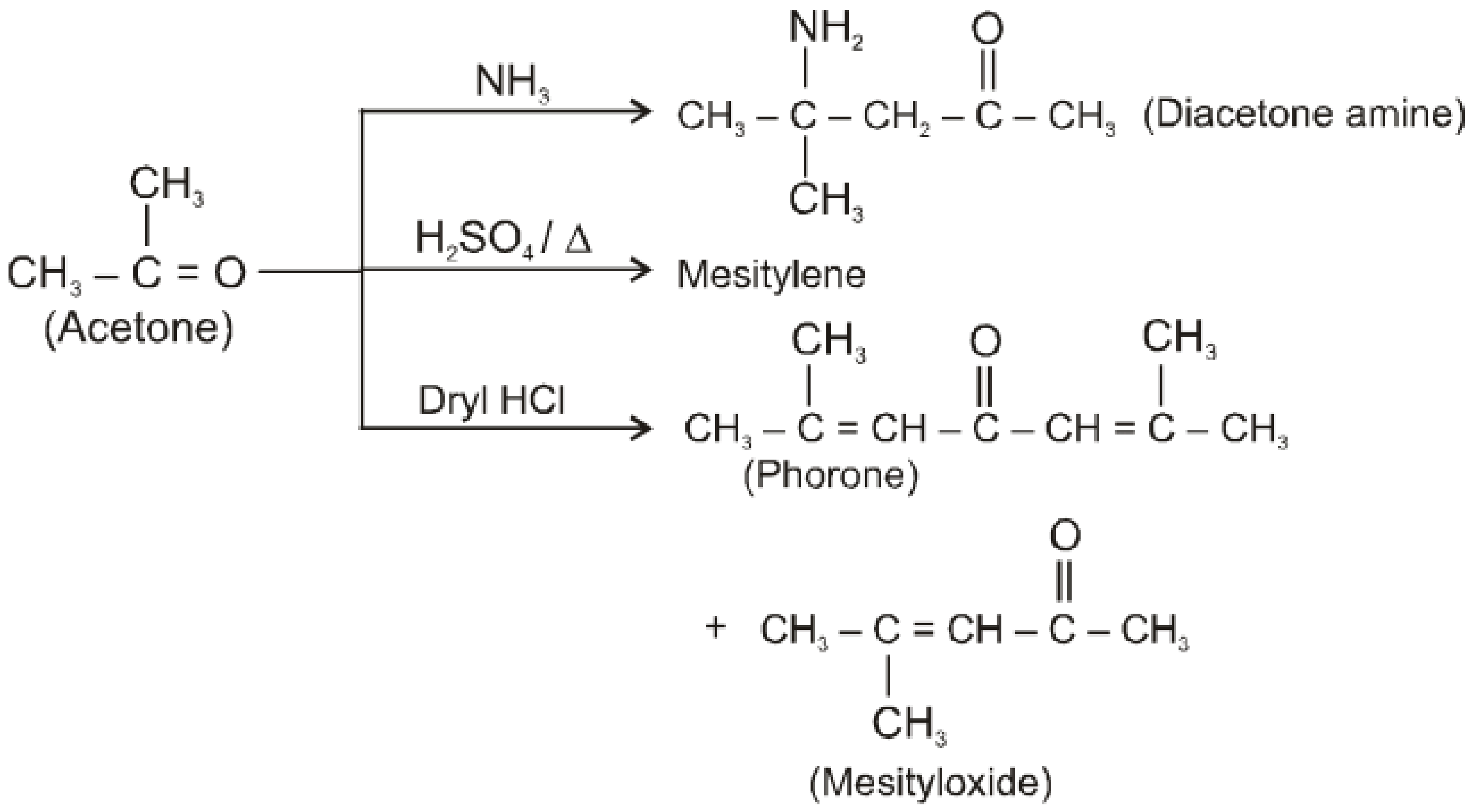
(1)



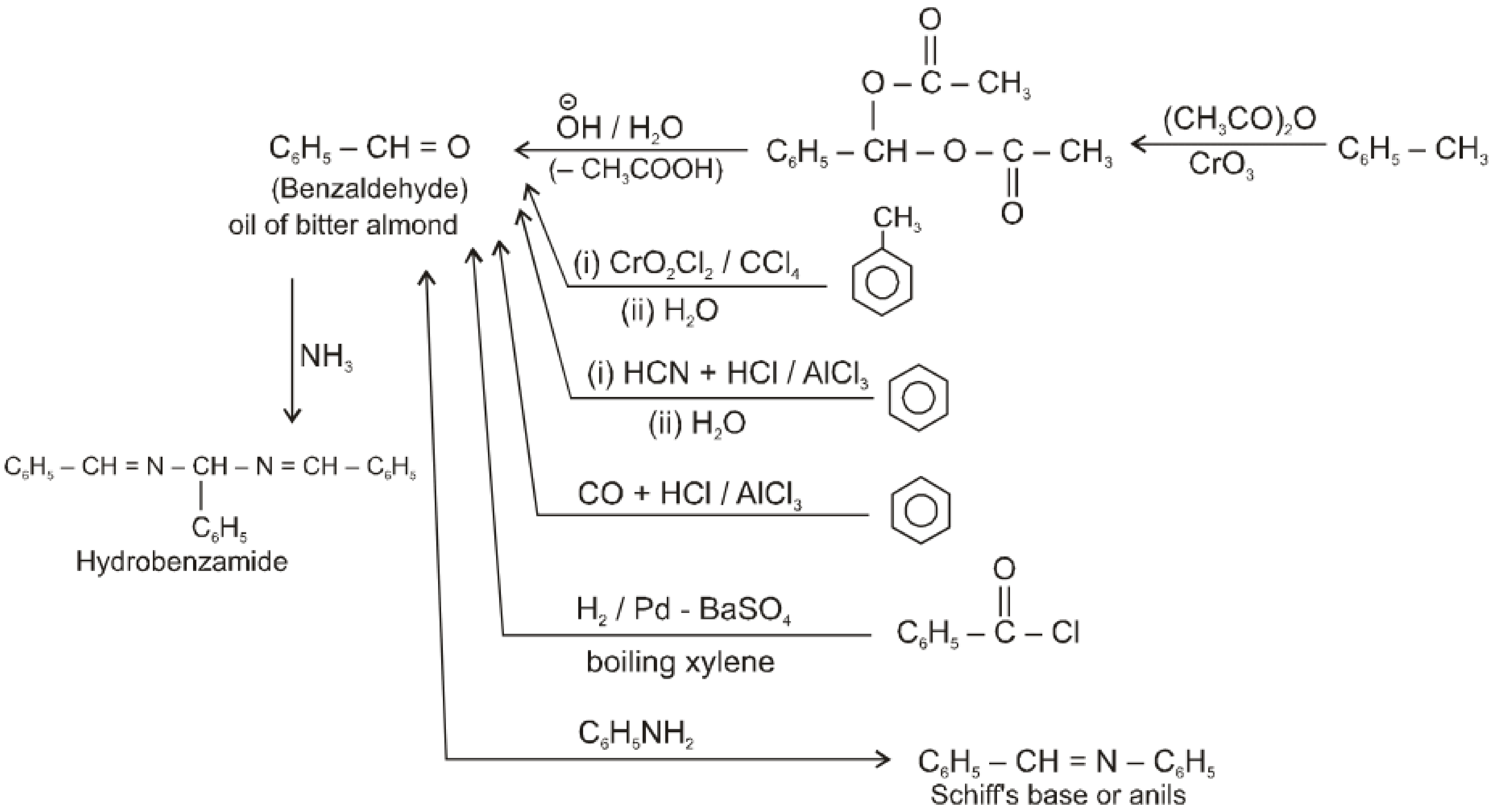
(2)



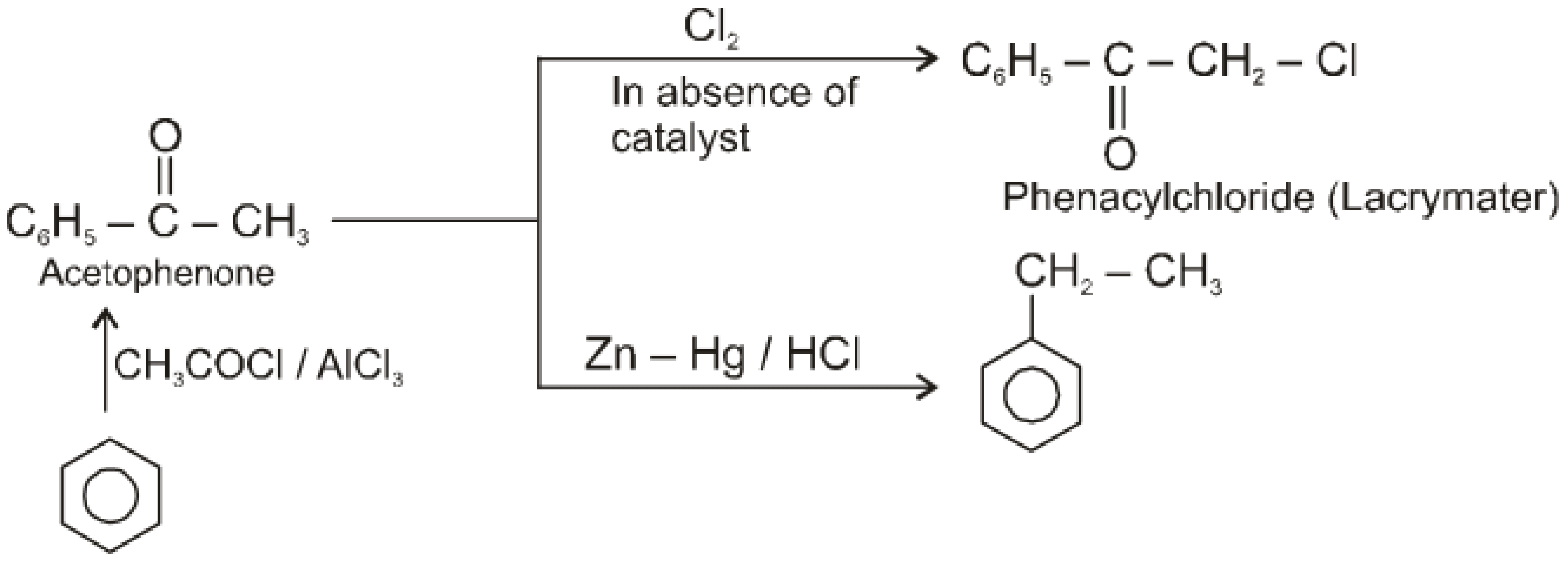
(3)



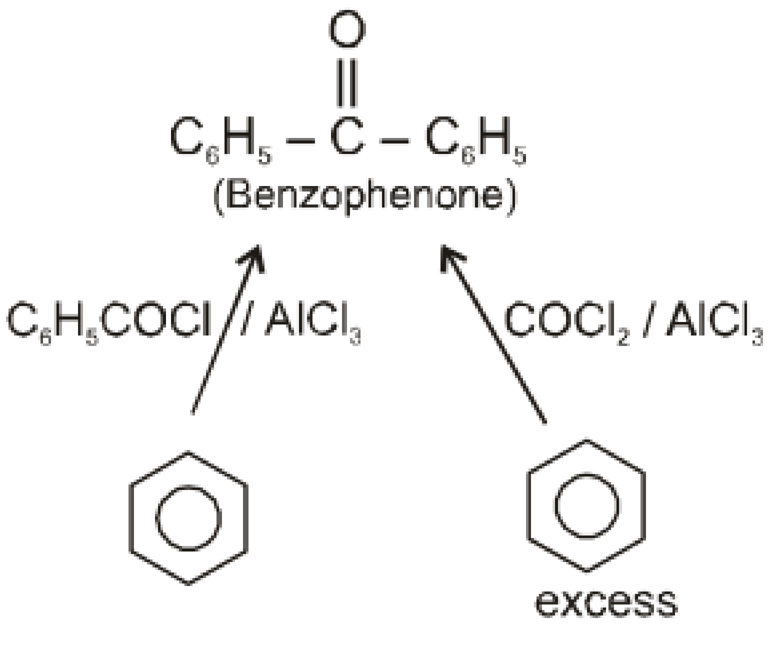
(4)


$C_6H_5-CH=O$
(Benzaldehyde)
oil of bitter almond
$\overset{\ominus}{O}H / H_2O$
$(-CH_3COOH)$
$O-C(=O)-CH_3$
$C_6H_5-CH-O-C(=O)-CH_3$
$(CH_3CO)_2O$
CrO_3
$C_6H_5-CH_3$
(i) CrO_2Cl_2 / CCl_4
(ii) H_2O
CH_3
(i) HCN + HCl / $AlCl_3$
(ii) H_2O
CO + HCl / $AlCl_3$
H_2 / Pd - $BaSO_4$
boiling xylene
$C_6H_5-C(=O)-Cl$
NH_3
$C_6H_5-CH=N-CH(C_6H_5)-N=CH-C_6H_5$
Hydrobenzamide
$C_6H_5NH_2$
$C_6H_5-CH=N-C_6H_5$
Schiff's base or anils

(5)


$C_6H_5-C(=O)-CH_3$
Acetophenone
$CH_3COCl / AlCl_3$
Cl_2
In absence of catalyst
$C_6H_5-C(=O)-CH_2-Cl$
Phenacylchloride (Lacrymater)
Zn – Hg / HCl
CH_2-CH_3

(6)


$C_6H_5-C(=O)-C_6H_5$
(Benzophenone)
C_6H_5COCl / $AlCl_3$
$COCl_2 / AlCl_3$
excess

Oxidation Reaction

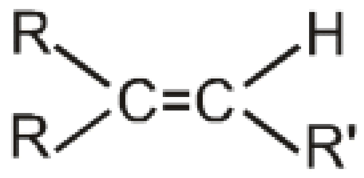
(1) $KMnO_4$ (in both medium) or
$K_2Cr_2O_7$ (in acidic medium)

Aldehyde $\longrightarrow$ Acid

1° Alcohol $\longrightarrow$ Acid

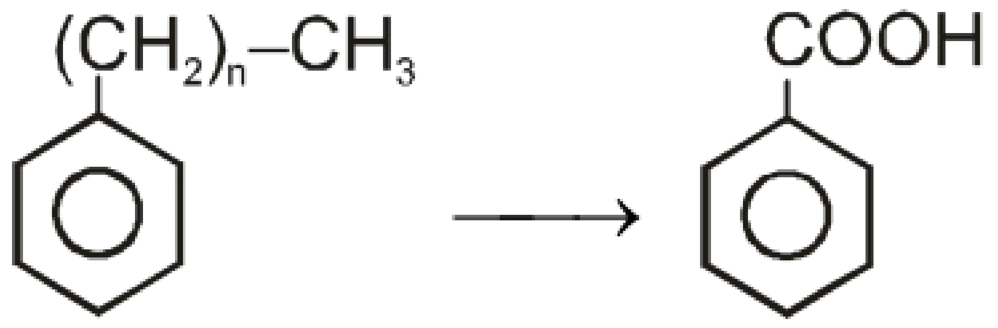
2° Alcohol $\longrightarrow$ Ketone

3° Alcohol $\longrightarrow$ No reaction

Alkene :  $\longrightarrow$ $R_2C{=}O + R'COOH$

Alkyne : $R{-}C{\equiv}C{-}R'$ $\longrightarrow$ $RCOOH + R'COOH$

Oxidation of aromatic side chain :



(2) PCC (Pyridinium chloro chromate)
CrO_3/HCl/Pyridine

1° ROH $\longrightarrow$ Aldehyde

2° ROH $\longrightarrow$ Ketone

3° ROH $\longrightarrow$ No reaction

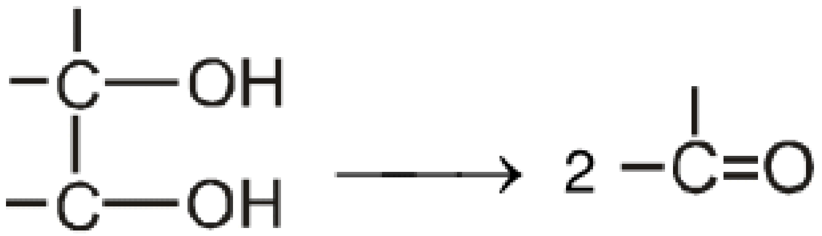
(3) Cu/573 K

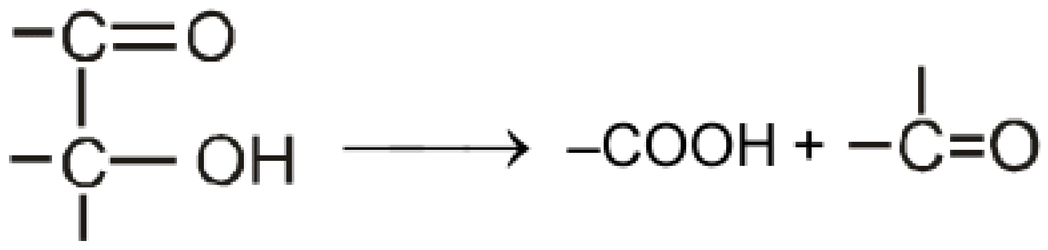
1°Alcohol $\longrightarrow$ Aldehyde

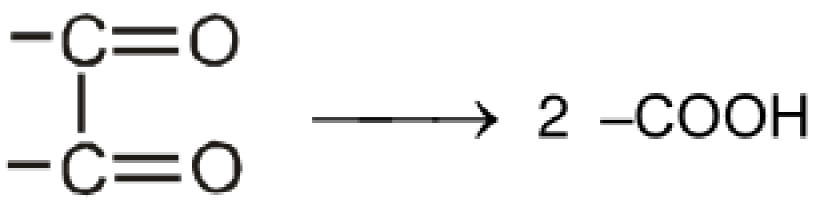
2° Alcohol $\longrightarrow$ Ketone

3° Alcohol $\longrightarrow$ Alkene

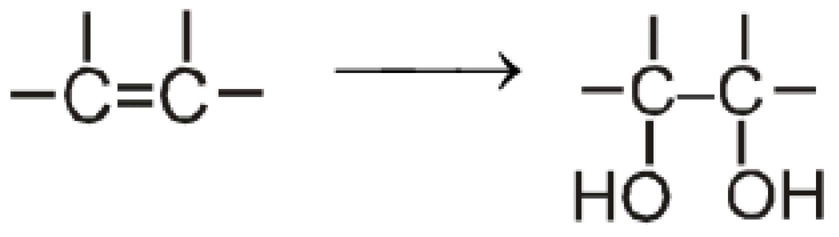
(4) HIO_4 (Periodic Acid)
Condition : Vicinal diol, α- Hydroxy ketone & α-diketone can oxidise by HIO_4







(5) Baeyer's reagent and OsO_4 + $NaHSO_3$

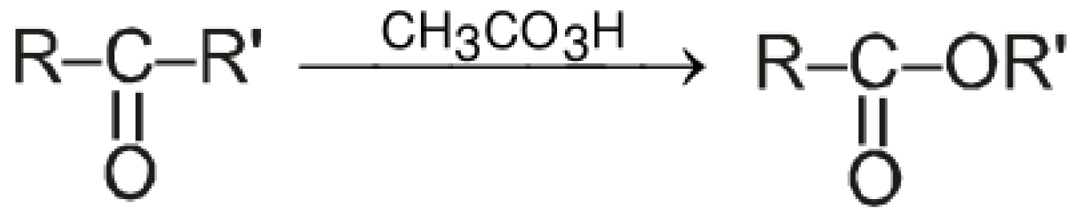


$$-\overset{|}{C}=\overset{|}{C}- \longrightarrow -\underset{HO}{\overset{|}{\underset{|}{C}}}-\underset{OH}{\overset{|}{\underset{|}{C}}}-$$

stereospecific syn addition

$$-C\equiv C- \longrightarrow -\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-$$

(6) Baeyer–Villiger oxidation (m-CPBA or CH_3CO_3H)

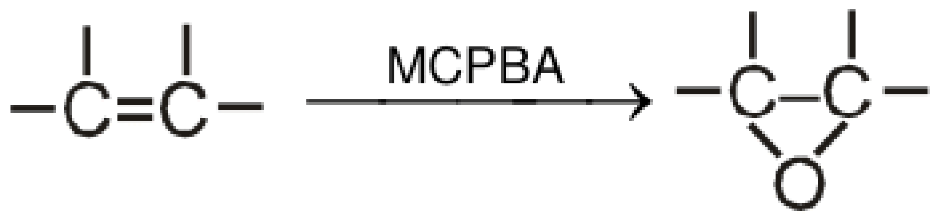


$$R-\underset{\underset{O}{\|}}{C}-R' \xrightarrow{CH_3CO_3H} R-\underset{\underset{O}{\|}}{C}-OR'$$

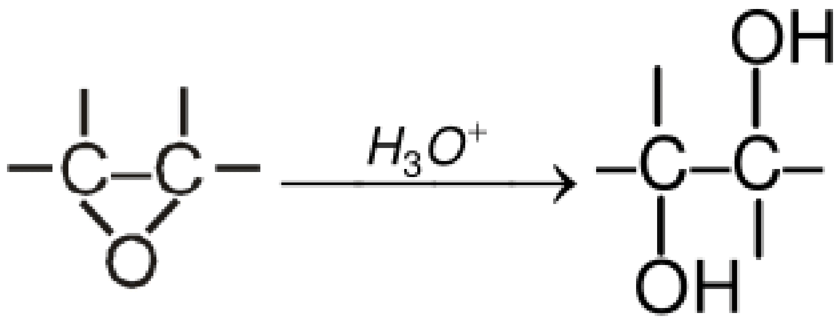
Priority of shift (O accepting aptitude)

R' = Ph > Ethyl > Methyl

(7) Prilezhaev reaction



Anti hydroxylation :



(8) oxidation by HNO_3

Aldehyde ⟶ Acid

1° Alcohol ⟶ Acid

2° Alcohol ⟶ no recation

3° Alcohol ⟶ No reaction

(9) oxidation by MnO_2

1° Alcohol ⟶ Aldehyde

2° Alcohol ⟶ Ketone

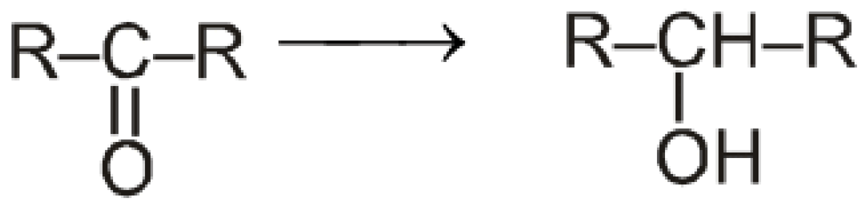
3° Alcohol ⟶ No reaction

Note : Only allylic and benzylic alcohols are oxidised by MnO_2.

Reduction

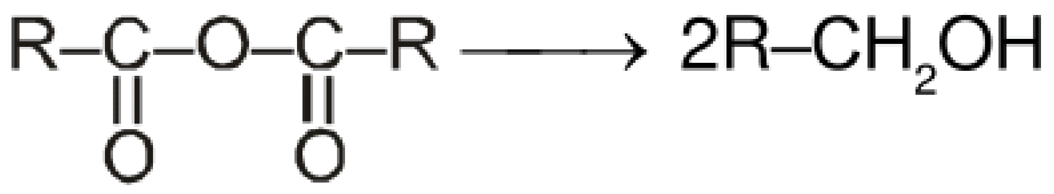
(1) $LiAlH_4$

$R\text{–}CHO \longrightarrow RCH_2OH$

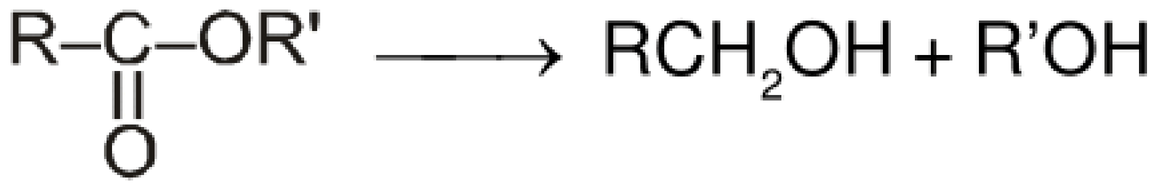


$R\text{–}\overset{\displaystyle O}{\overset{\|}{C}}\text{–}R \longrightarrow R\text{–}\underset{\displaystyle OH}{\underset{|}{CH}}\text{–}R$

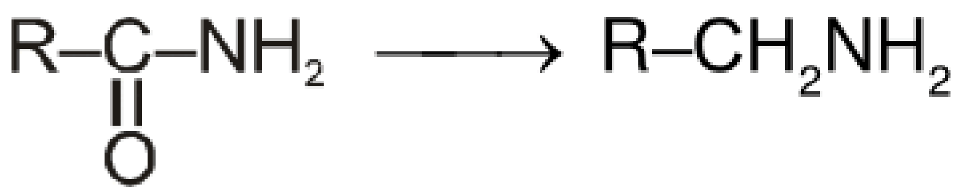
$RCOOH \longrightarrow R\text{–}CH_2OH$



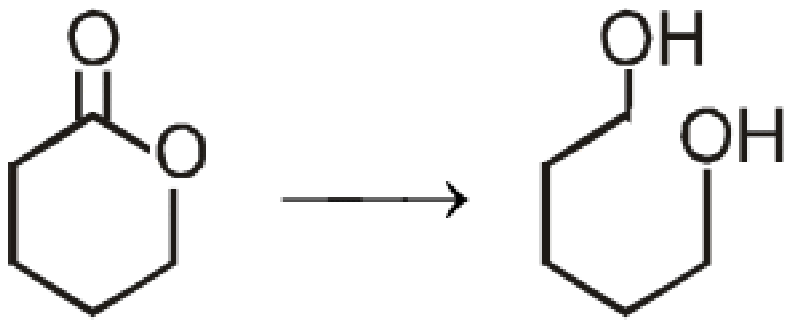
$R\text{–}\underset{\displaystyle O}{\underset{\|}{C}}\text{–}O\text{–}\underset{\displaystyle O}{\underset{\|}{C}}\text{–}R \longrightarrow 2R\text{–}CH_2OH$

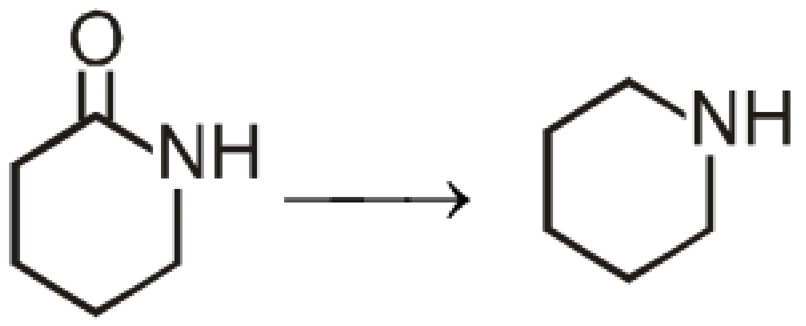


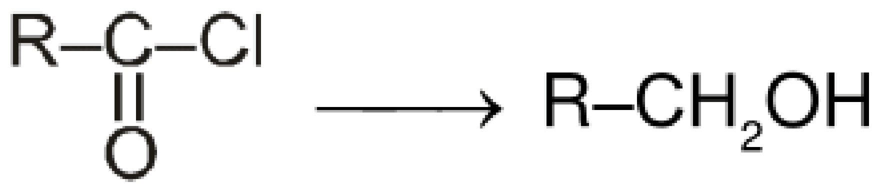
$R\text{–}\underset{\displaystyle O}{\underset{\|}{C}}\text{–}OR' \longrightarrow RCH_2OH + R'OH$



$R\text{–}\underset{\displaystyle O}{\underset{\|}{C}}\text{–}NH_2 \longrightarrow R\text{–}CH_2NH_2$







$R\text{–}\underset{\displaystyle O}{\underset{\|}{C}}\text{–}Cl \longrightarrow R\text{–}CH_2OH$

$R\text{–}CN \longrightarrow R\text{–}CH_2\text{–}NH_2$

$C = C / C\equiv C \longrightarrow$ No reaction

Exception : **$Ph\text{–}CH\text{=}CH\text{–}COOH \longrightarrow Ph\text{–}CH_2\text{–}CH_2\text{–}CH_2OH$**

(2) $NaBH_4$, EtOH

Aldehyde ⟶ 1° Alcohol

Ketone ⟶ 2 °Alcohol

Acid halide ⟶ 1° Alcohol

(3) Na/EtOH (Bouvealt Blanc reduction)

Aldehyde ⟶ 1° Alcohol

Ketone ⟶ 2º Alcohol

Acid halide ⟶ 1° Alcohol

Ester ⟶ Alcohol + Alcohol

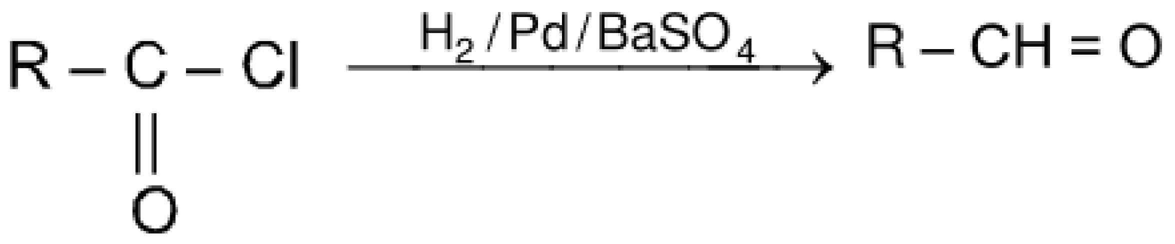
$RCN \longrightarrow RCH_2NH_2$

(4) Na–Hg/HCl or $Al[OCHMe_2]_3$ (MPV Reduction)

Aldehyde ⟶ 1° Alcohol

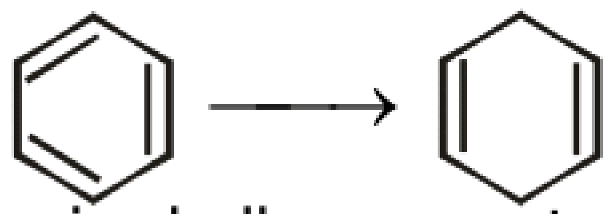
Ketone ⟶ 2° Alcohol

(5) Rossenmund's Reduction

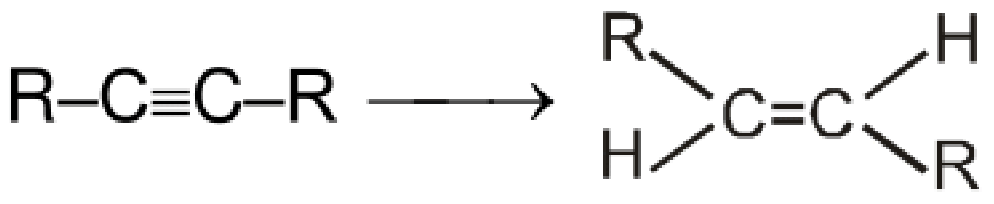


$R - \underset{\displaystyle O}{\underset{\|}{C}} - Cl \xrightarrow{H_2/Pd/BaSO_4} R - CH = O$

(6) Birch reduction (Li/Na/K + Liquid NH_3)



Note : Terminal alkynes not reduced



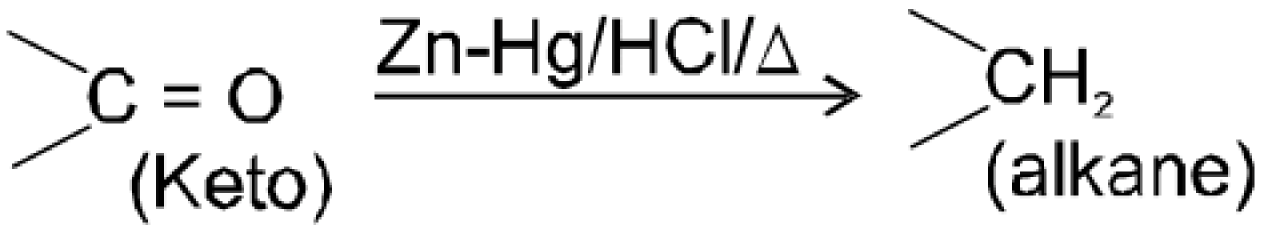
(trans alkene)

(7) Stephen's Reduction

$$R - C \equiv N \xrightarrow[\text{(2) } H_2O]{\text{(1) } SnCl_2/HCl} R - CH = O$$

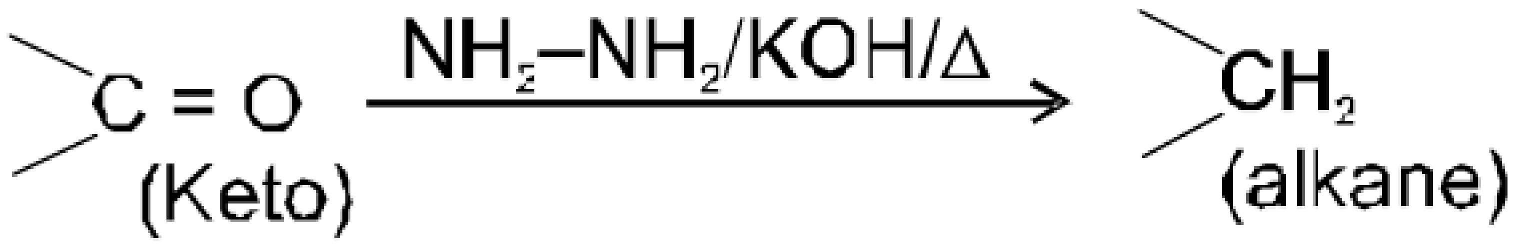
Note : DIBAL-H is also used for same conversion.

(8) Clemmensen Reduction



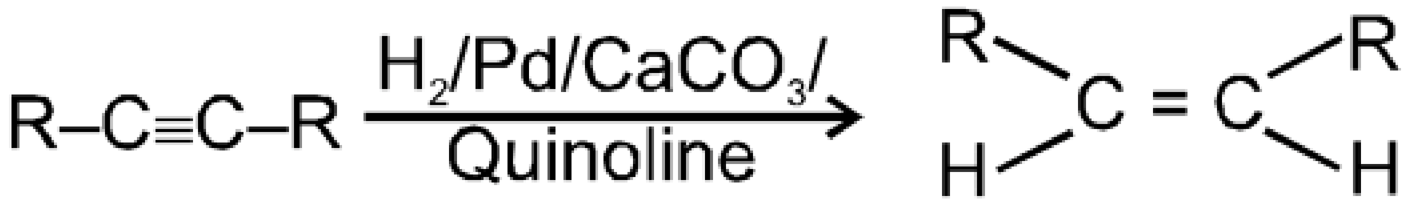
Avoid if acid sensitive
groups are present in molecule.
e.g. C=C,C≡C,OH, OR,

(9) Wolff-Kishner Reduction



Avoid if base sensitive
groups are present in molecule.
e.g.COOR,COX,CONH$_2$,
–CO–O–CO–, R-X

(10) Lindlar Catalyst



Syn addition
(Cis alkene)

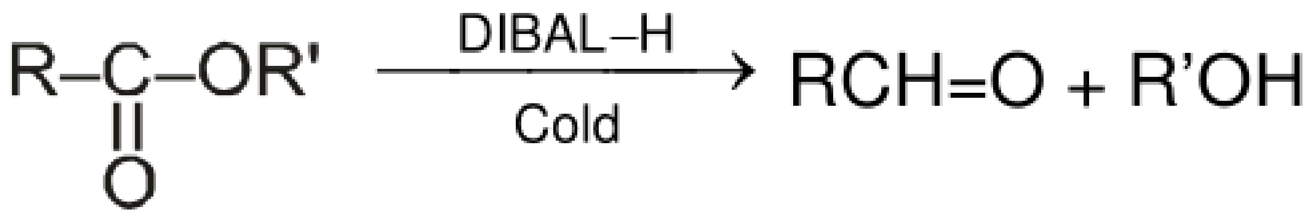
Note : H_2, Pd, $BaSO_4$ is also used for same conversion.

(11) Red Phosphorus and HI

Almost all functional groups contaning compounds converts into corresponding alkane by red P + HI.

- $R–CH_2OH \longrightarrow R - CH_3$
- $R–CHO \longrightarrow R - CH_3$
- $R_2CO \longrightarrow R_2CH_2$ (Alkane)

(12) DIABAL-H reduction



$$R–\underset{\underset{O}{\parallel}}{C}–OR' \xrightarrow[\text{Cold}]{\text{DIBAL–H}} RCH=O + R'OH$$

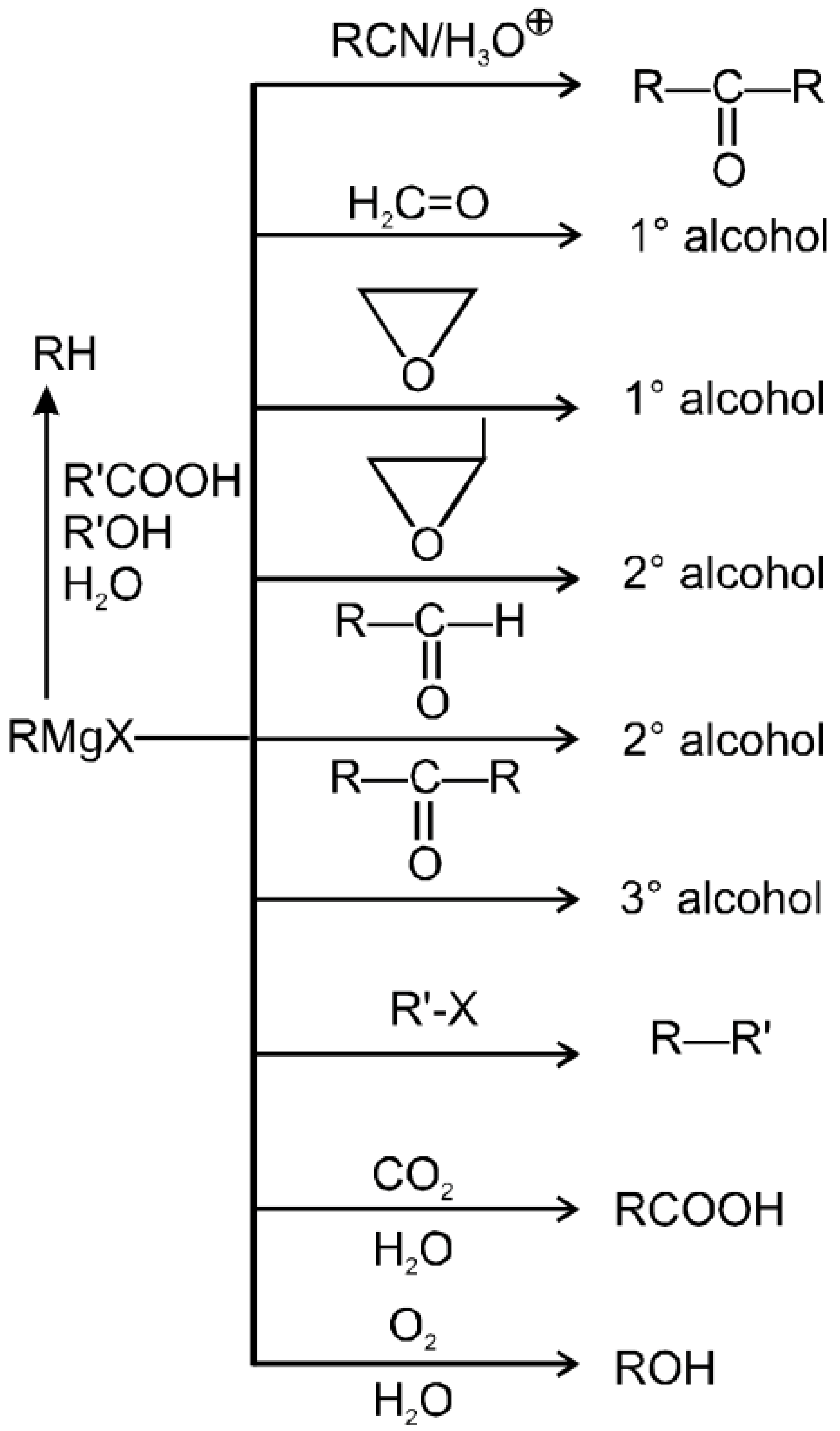
$$R–C \equiv N \xrightarrow{\text{DIBAL–H}} R–CH=O$$

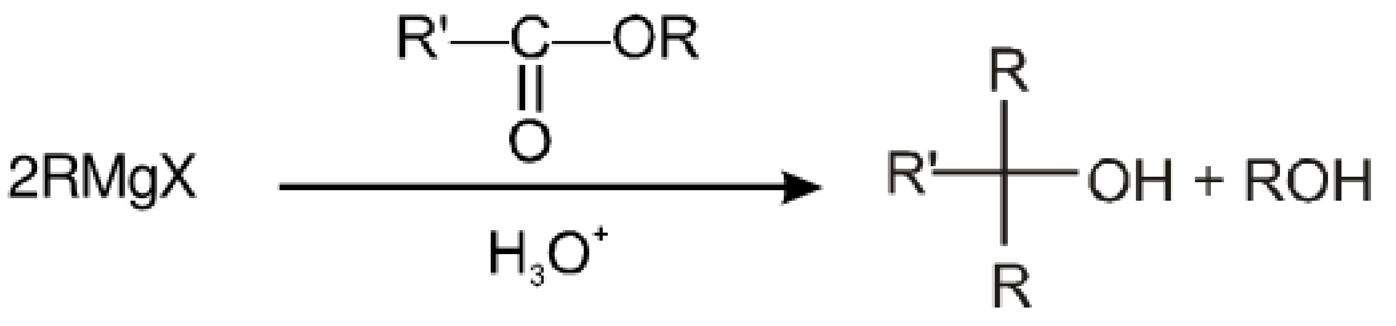
At ordinary temperature esters reduced to alcohols but at low temperature esters reduced to aldehyde.

Grignard reagents

Grignard's Reagent : RMgX (alkyl magnesium halide)

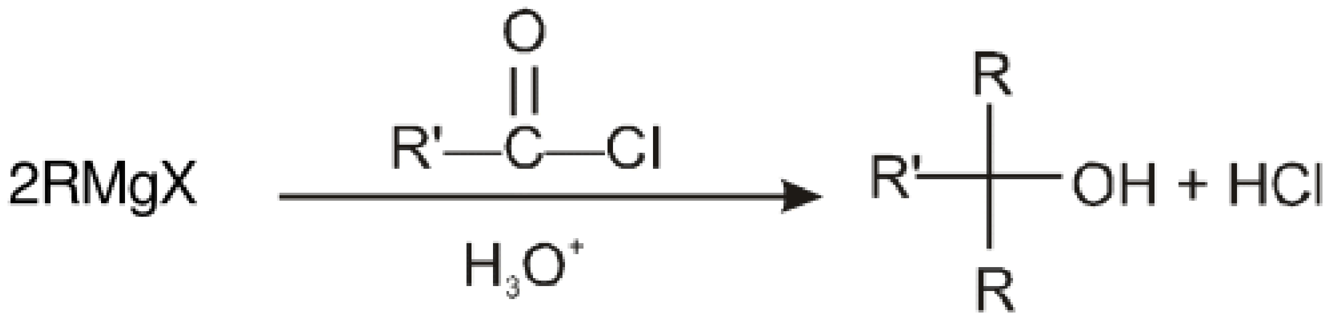
* Active – H Containing compounds $\xrightarrow{RMgX}$ R – H





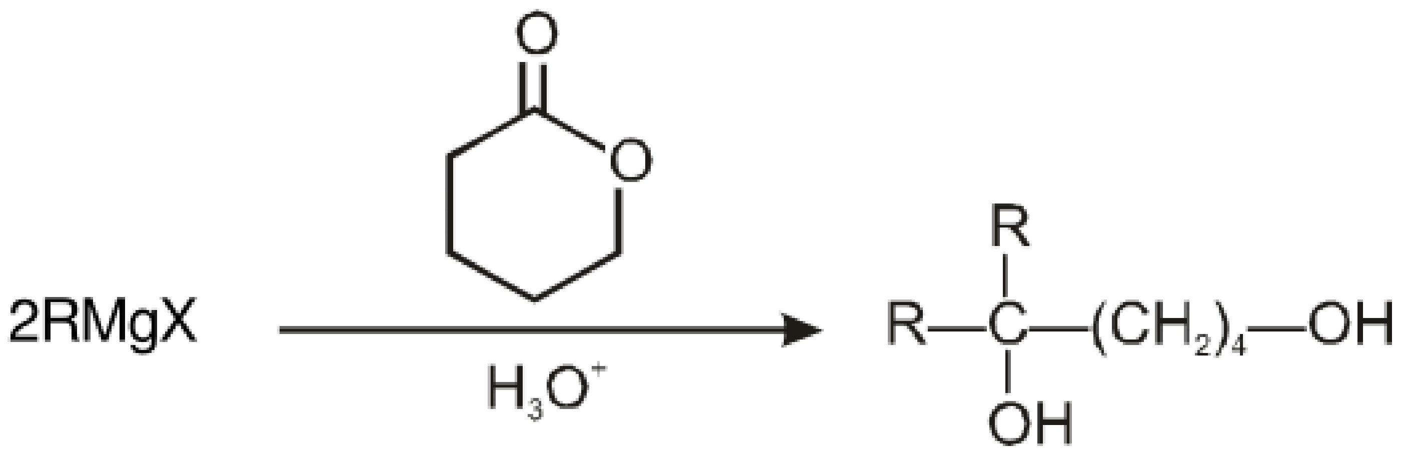
$$2RMgX \xrightarrow[H_3O^+]{R'-\underset{\underset{\displaystyle O}{\|}}{C}-OR} R'-\underset{R}{\overset{R}{C}}-OH + ROH$$

(two alkyl groups come from Grignard Reagent)



$$2RMgX \xrightarrow[H_3O^+]{R'-\overset{\overset{\displaystyle O}{\|}}{C}-Cl} R'-\underset{R}{\overset{R}{C}}-OH + HCl$$

(two alkyl groups come from Grignard Reagent)

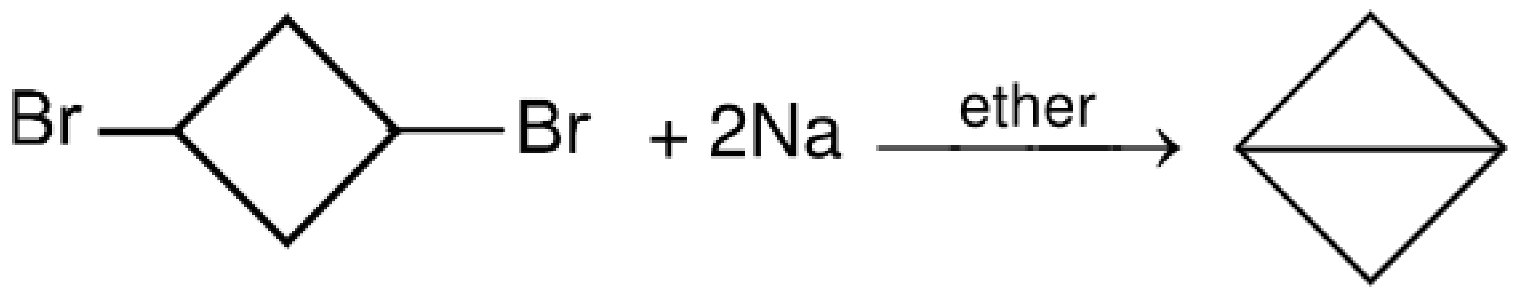


(two alkyl groups come from Grignard Reagent)

Alkane

Wurtz reaction (Reagent : Na, ether) 1° & 2° alkyl halides give this reaction.

$R-X + 2Na \xrightarrow{\text{ether}} R-R$; $R-X + R'-X + 2Na \xrightarrow{\text{ether}} R-R' + R-R + R'-R'$

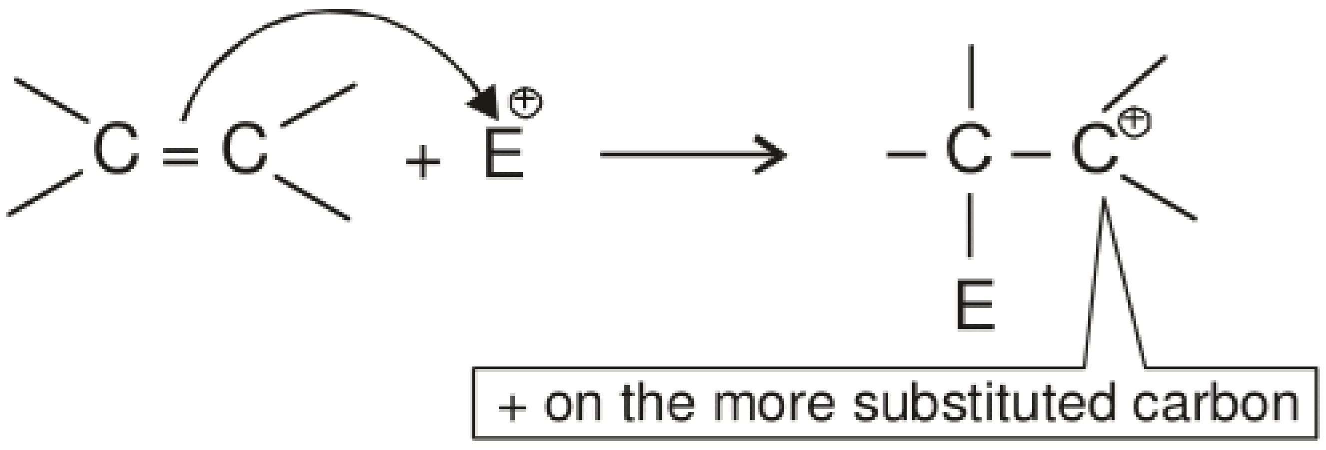


Alkene & Alkyne

Characteristic reaction of Alkene & Alkyne is Electrophilic addition reaction.

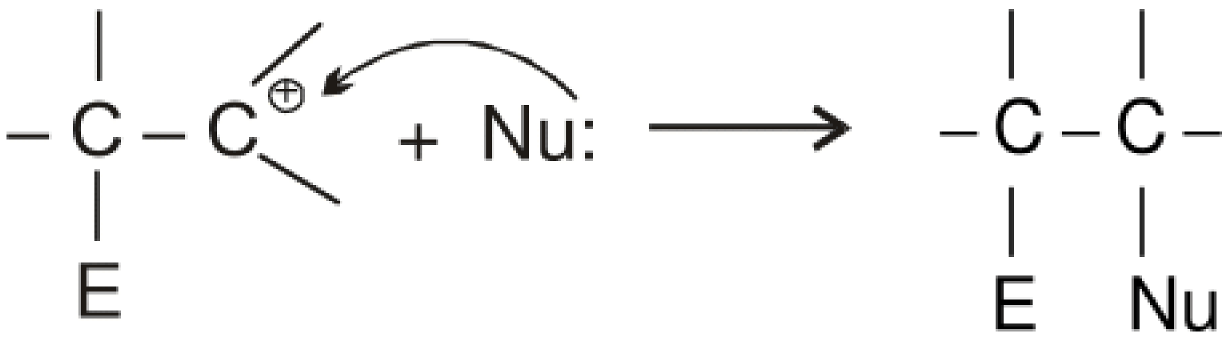
Mechanism

Step 1 : Attack of the electrophile on π bond forms a carbocation.

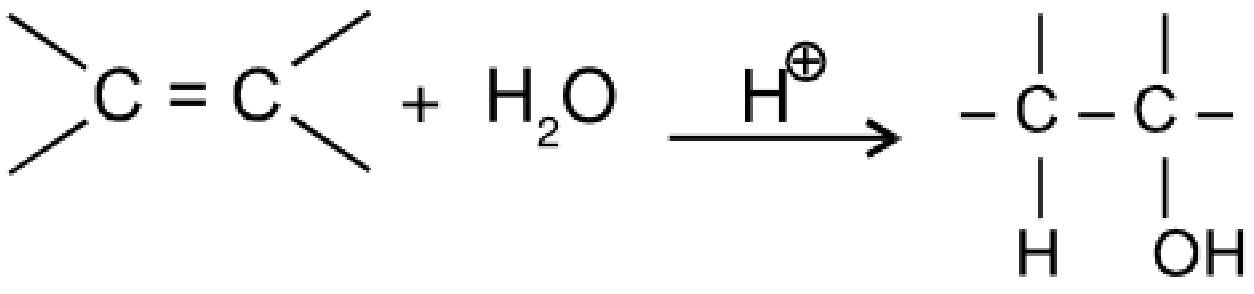


+ on the more substituted carbon

Step 2 : Attack by a nucleophile gives the product of addition.

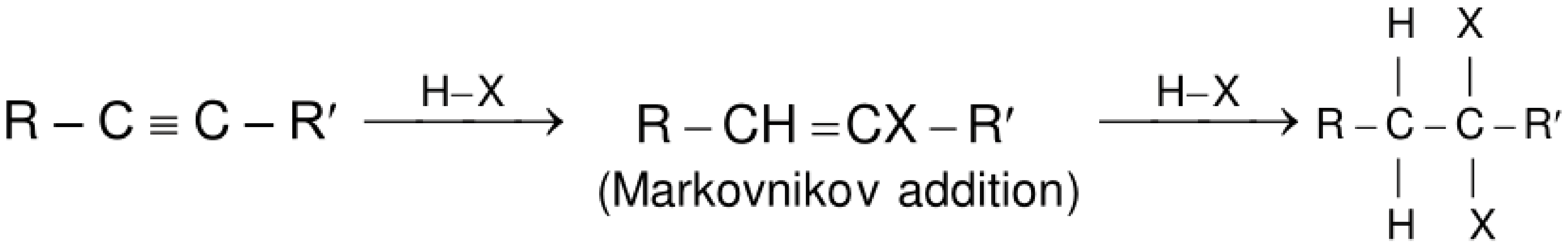


e.g. (a) Addition of water



(Markovnikov orientation)

(b) Addition of hydrogen halides (where HX = HCl, HBr, HI)



$$R-C\equiv C-R' \xrightarrow{H-X} \underset{\text{(Markovnikov addition)}}{R-CH=CX-R'} \xrightarrow{H-X} R-\overset{H}{\underset{H}{C}}-\overset{X}{\underset{X}{C}}-R'$$

Note: When electrophiles are: Cl^+, Br^+, I^+, NO_2^+ or Hg^{2+} then stereochemistry is important and major product is formed by anti addition.

Alkyl halide

Nucleophilic substitution Reaction (S_N1, S_N2)

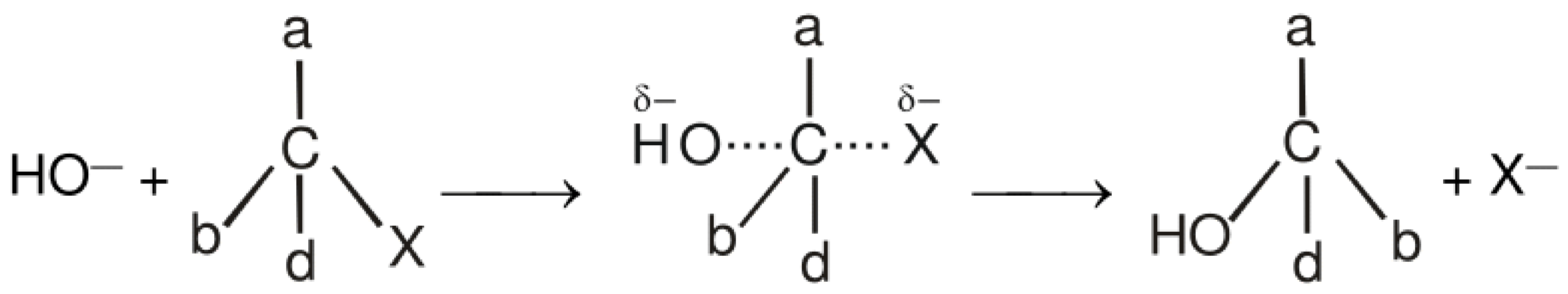
S_N1 reaction :

$R{-}X + H_2O \xrightarrow{AgNO_3} R^+ + AgX\downarrow \longrightarrow ROH$ (R may rearrange)

Alkylhalide are hydrolysed to alcohol very slowly by water, but rapidly by silver oxide suspended in boiling water.

S_N2 reaction :

Mechanism : $HO^- \;\; R-X \longrightarrow \overset{\delta-}{H}O\cdots R\cdots \overset{\delta-}{X} \longrightarrow HO-R+X^-$



Alcohol

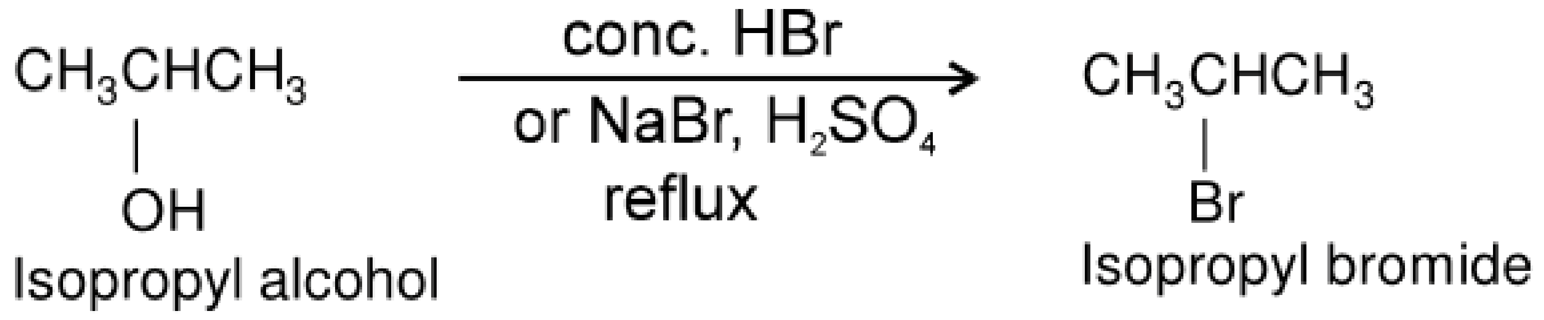
S_N1 reaction :

$R{-}OH \xrightarrow{H^\oplus} R-\overset{\oplus}{O}H_2 \xrightarrow{-H_2O} \overset{\oplus}{R} \xrightarrow{X^\ominus} R-X$(R may rearrange)

Reactivity of HX : HI > HBr > HCl

Reactivity of ROH : allyl, benzyl > 3° > 2° > 1° (Carboocation)

e.g.



$$\underset{\text{OH}}{CH_3\overset{}{C}HCH_3} \xrightarrow[\text{or NaBr, }H_2SO_4\text{ reflux}]{\text{conc. HBr}} \underset{\text{Br}}{CH_3CHCH_3}$$

Isopropyl alcohol → Isopropyl bromide

S_N2 reaction :

$ROH + PCl_5 \longrightarrow RCl + POCl_3$

$ROH + PCl_3 \longrightarrow RCl + H_3PO_3$

$ROH + SOCl_2 \xrightarrow{\text{Pyridine}} RCl + SO_2 + HCl$

Williamson's synthesis :

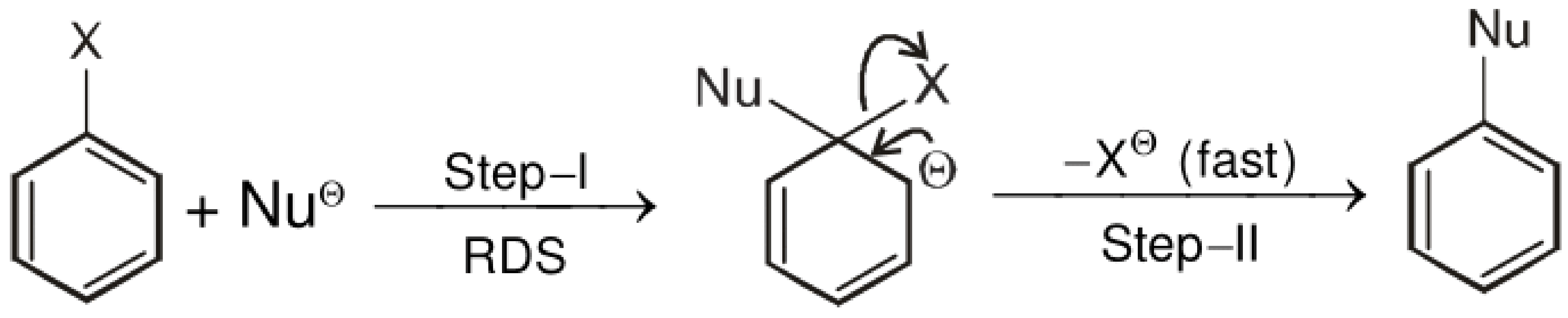
It is the reaction in which sodium or potassium alkoxide is heated with an alkyl halide (S_N2).

$$R_1O^- + R^2{-}X \rightleftharpoons R\,^1\overset{\delta-}{O}\ldots\ldots R^2\ldots\ldots\overset{\delta-}{X} \longrightarrow R^1OR^2 + X^-\text{(g)}$$

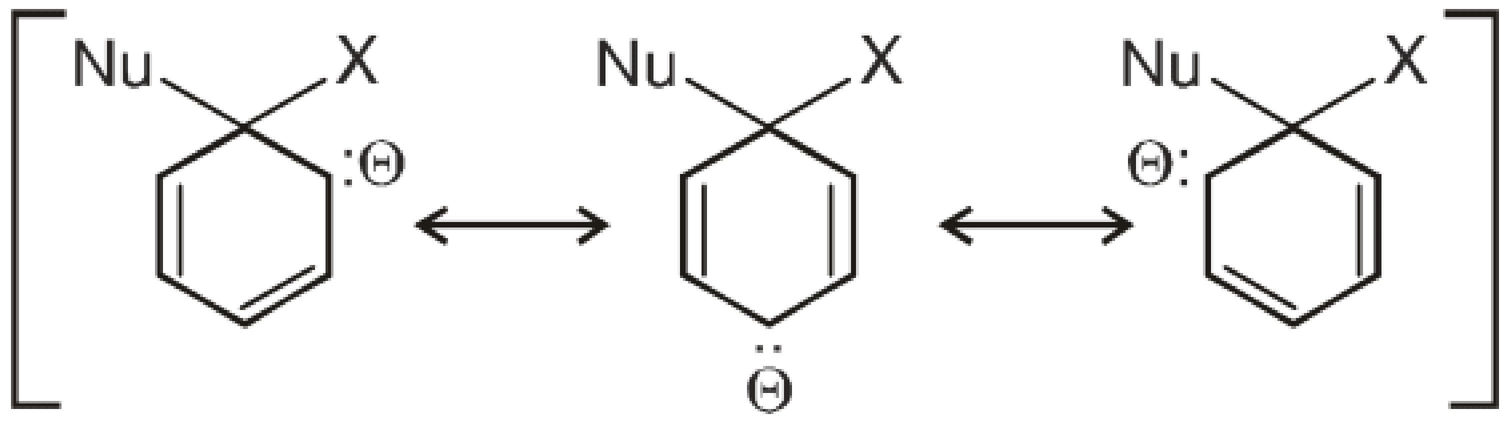
This method is particularly useful for preparing mixed ethers.

Nucleophilic Aromatic Substitution of aryl halides(S_N2Ar):

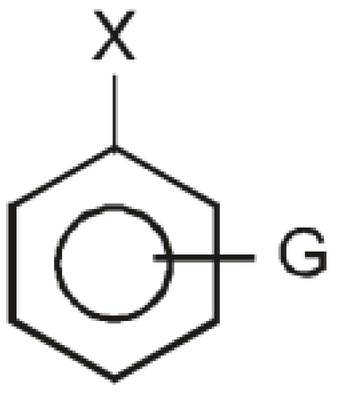
- An electron withdrawing group at ortho or para positions with respect to a good leaving groups are necessary conditions for S_N2 Ar.



Intermediate ion is stabilized by resonance. and are stable salts called Meisenheimer salts.



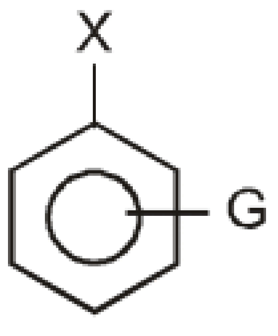
- A group that withdraws electrons tends to neutralize the negative charge of the ring and this dispersal of the charge stabilizes the carbanion.



G withdraws electrons : stabilizes carbanion, activates the Ar-S_N2 reaction.

($-\overset{+}{N}(CH_3)_3$, $-NO_2$, –CN, $-SO_3H$, –COOH, –CHO, –COR, –X)

- A group that releases electrons tends to intensify the negative charge, destabilizes the carbanion, and thus slows down reaction.



G ($-NH_2$, –OH, –OR, –R)releases electrons : destabilizes carbanion, deactivates the Ar-S_N2 reaction.

Element effect :

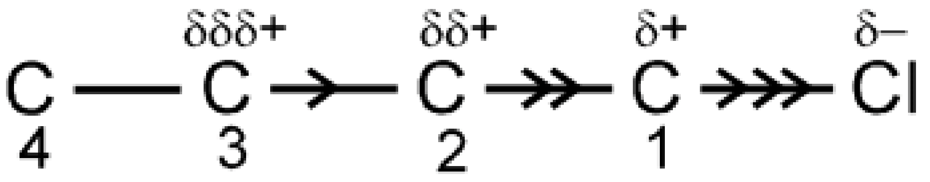
Reactivity order towards S_N2Ar with different halogens
Ar-F > Ar-Cl > Ar-Br > Ar-I

1. Inductive effect

The normal C–C bond has no polarity as two atoms of same electronegativity (EN) value are connected to each other. Hence the bond is nonpolar. Consider a carbon chain in 1-Chloro butane, here due to more EN of Cl atom C–Cl bond pair is slightly displaced towards Cl atom hence creating partial negative ($\delta -$) charge over Cl atom and partial positive ($\delta +$) charge over C_1 atom.

Now since C_1 is slightly positive, it will also cause shifting of C_1–C_2 bond pair electrons towards itself causing C_2 to acquire small positive charge. Similarly C_3 acquires slightly positive charge creating an induction of charge in carbon chain. Such an effect is called inductive effect.

Diagram showing I effect



$$\underset{4}{C} - \overset{\delta\delta\delta+}{\underset{3}{C}} \rightarrow \overset{\delta\delta+}{\underset{2}{C}} \twoheadrightarrow \overset{\delta+}{\underset{1}{C}} \ggg \overset{\delta-}{Cl}$$

The arrow shows electron withdrawing nature of – Cl group.

Thus inductive effect may be defined as a permanent displacement of σ bond pair electrons due to a dipole. (Polar bond)

Some important points are:

(a) It can also be defined as polarisation of one bond caused by polarisation of adjacent bond.

(b) It is also called transmission effect.

(c) It causes permanent polarisation in molecule, hence it is a permanent effect.

(d) The displacement of electrons takes place due to difference in electronegativity of the two atoms involved in the covalent bond.

(e) The electrons never leave their original atomic orbital.

(f) Its magnitude decreases with distance and it is almost negligible after 3rd carbon atom.

(g) The inductive effect is always operative through σ bond, does not involve π bond electron.

Types of inductive effects :

(a) – I Effect : The group which withdraws electron cloud is known as – I group and its effect is called – I effect. Various groups are listed in their decreasing – I strength as follows.

$$-\overset{\oplus}{N}R_3 > -\overset{\oplus}{S}R_2 > -\overset{\oplus}{N}H_3 > -NO_2 > -SO_2R > -CN > -CHO > -COOH > -F >$$
$$-Cl > -Br > -I > -OR > -OH > -C{\equiv}CH > -NH_2 > -C_6H_5 > -CH{=}CH_2 > -H.$$

(b) + I effect : The group which release electron cloud is known as + I group and effect is + I effect.

$-\overset{\ominus}{O} > -CO\overset{\ominus}{O} > -C(CH_3)_3 > -CH(CH_3)_2 > -CH_2-CH_3 > -CH_3 > -D > -H$

The hydrogen atom is reference for + I and – I series. The inductive effect of hydrogen is assumed to be zero.

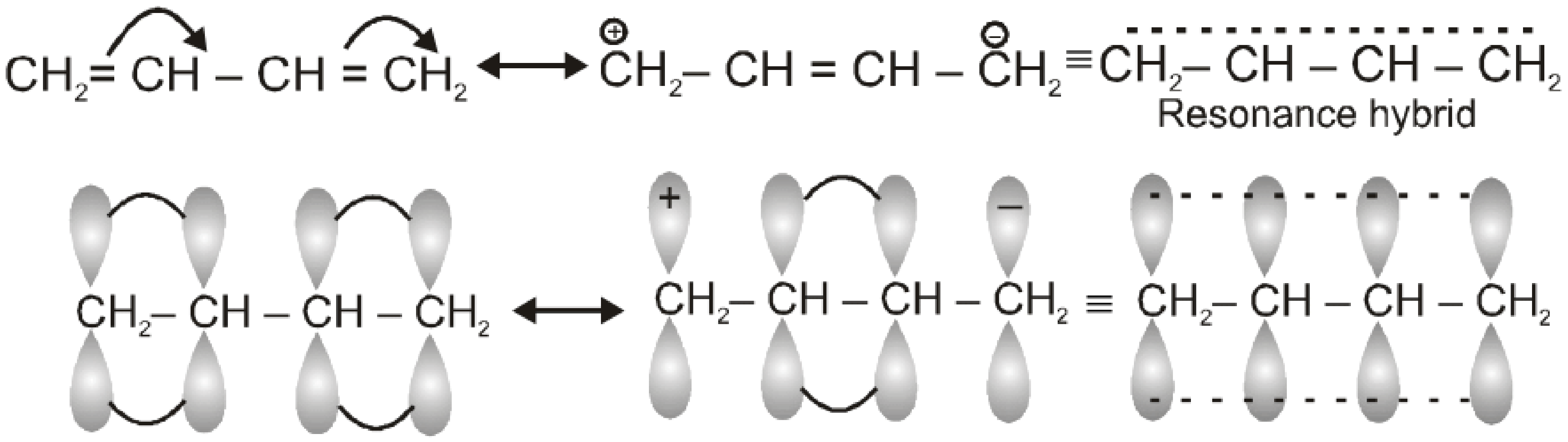
Ex. Let us consider effect of COOH & – COO⁻ in carbon chain

(a) $^{\ominus}OOC \rightarrow \overset{\delta-}{C}H_2 \rightarrow \overset{\delta\delta-}{C}H_2 \rightarrow CH_3$ (b) $HOOC \leftarrow \overset{\delta+}{C}H_2 \leftarrow \overset{\delta\delta+}{C}H_3$

Due to e^- donating nature of $-CO\overset{\ominus}{O}$ carbon chain has become partially negative but – COOH is – I group therefore carbon chain has become partially positive.

2. Resonance

Resonance is the phenomenon in which two or more structures involving in identical position of atom, can be written for a particular species, all those possible structures are known as resonating structures or canonical structures. Resonating structures are only hypothetical but they all contribute to a real structure which is called resonance hybrid. The resonance hybrid is more stable than any resonating structure.



Resonance hybrid :

The most stable resonating structure contribute maximum to the resonance hybrid and less stable resonating structure contribute minimum to resonance hybrid.

Conjugation:

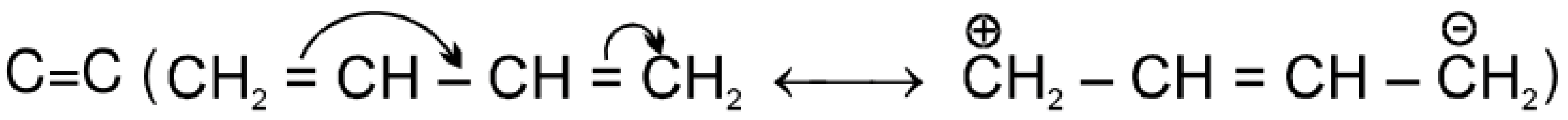
A given atom or group is said to be in conjugation with an unsaturated system if:-

(i) It is directly linked to one of the atoms of the multiple bond through a single bond.

(ii) It has π bond, positive charge, negative charge, odd electron or lone pair electron.

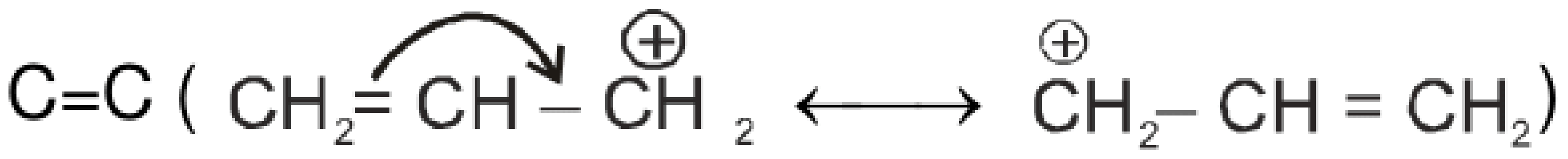
Types of Conjugation :

1. Conjugation between C = C and



$C{=}C\ (CH_2 = CH - CH = CH_2 \longleftrightarrow \overset{\oplus}{C}H_2 - CH = CH - \overset{\ominus}{C}H_2)$

2. Conjugation between +ve charge and

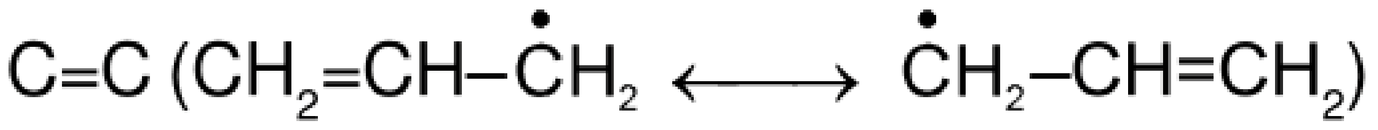


$C{=}C\ (CH_2 = CH - \overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2 - CH = CH_2)$

3. Conjugation between lone pair and

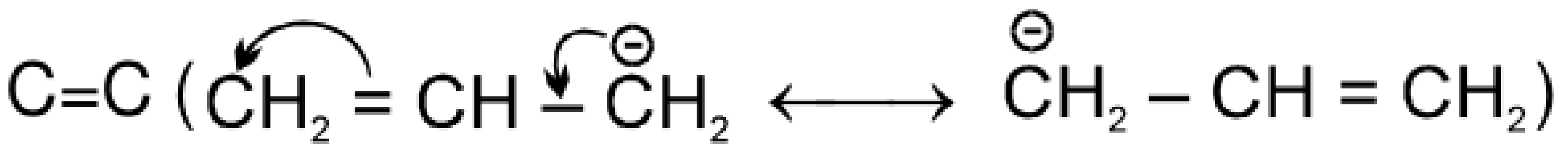
$C{=}C\ (:\ddot{Cl} - CH = CH_2 \longleftrightarrow \overset{\oplus}{Cl} = CH - \overset{\ominus}{C}H_2)$

4. Conjugation between odd electron and



$C{=}C\ (CH_2{=}CH{-}\dot{C}H_2 \longleftrightarrow \dot{C}H_2{-}CH{=}CH_2)$

5. Conjugation between negative charge and

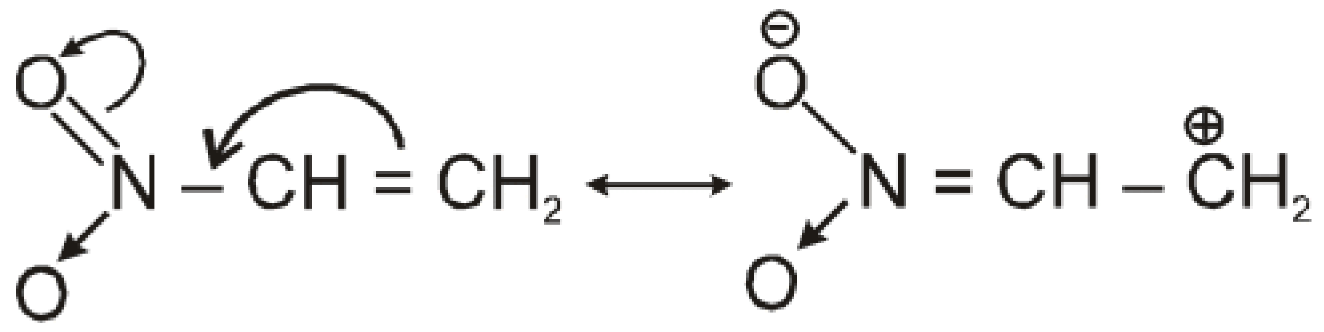


$C{=}C\ (CH_2 = CH - \overset{\ominus}{C}H_2 \longleftrightarrow \overset{\ominus}{C}H_2 - CH = CH_2)$

3. Mesomeric effect (or Resonance effect)

Mesomeric effect is defined as permanent effect of π electron shifting from multiple bond to atom or from multiple bond to single bond or from lone pair to single bond. This effect mainly operates in conjugated system of double bond. So that this effect is also known as conjugate effect.

Ex.



Types of Mesomeric effects :

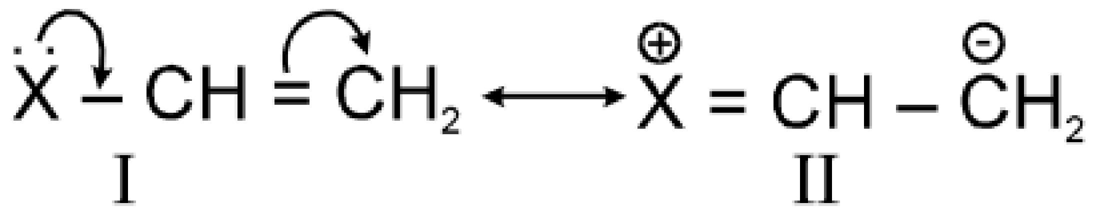
(a) Positive Mesomeric effect (+M effect) :

When the group donates electron to the conjugated system it shows + M effect.

Relative order of +M groups (usually followed) :

$-\overset{\ominus}{O} > -NH_2 > -NHR > -NR_2 > -OH > -OR > -NHCOR > -OCOR > -Ph > -F > -Cl > -Br > -I > -NO$

Ex. (I)



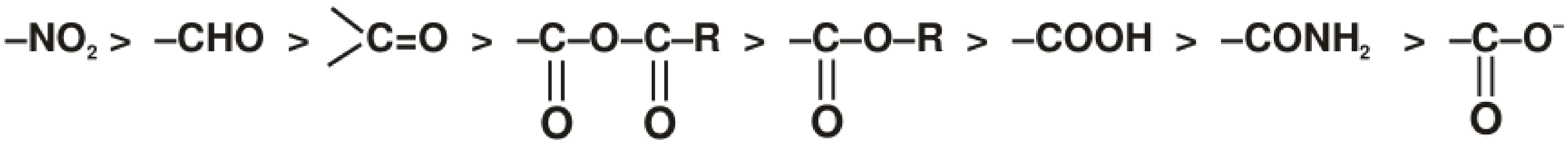
$\ddot{X} - CH = CH_2 \longleftrightarrow \overset{\oplus}{X} = CH - \overset{\ominus}{C}H_2$

I II

(b) Negative Mesomeric effect (–M effect) :

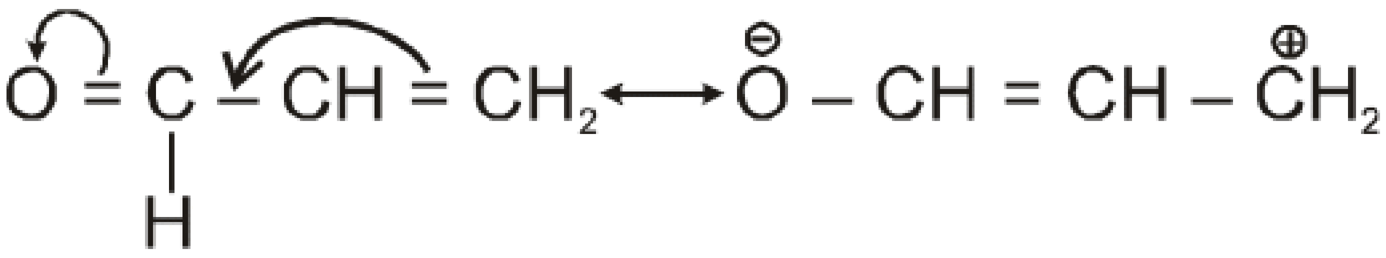
When the group withdraws electron from the conjugated system, it shows – M effect

Relative order of –M groups (usually followed) :



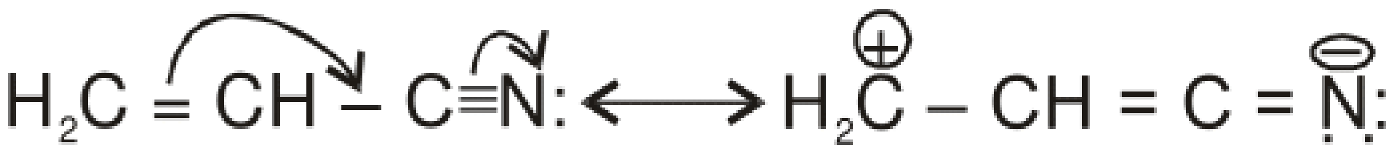
$$-NO_2 > -CHO > \;>C{=}O > -\underset{\|\atop O}{C}-O-\underset{\|\atop O}{C}-R > -\underset{\|\atop O}{C}-O-R > -COOH > -CONH_2 > -\underset{\|\atop O}{C}-O^-$$

Ex. (I)



$$O=\underset{|\atop H}{C}-CH=CH_2 \longleftrightarrow \overset{\ominus}{O}-CH=CH-\overset{\oplus}{C}H_2$$

(II)



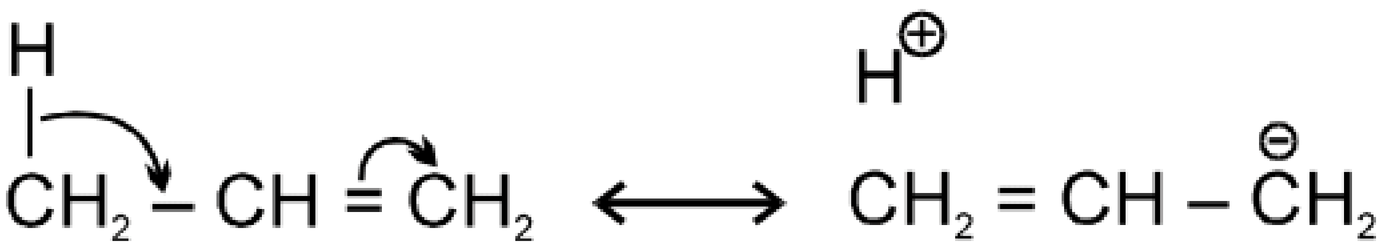
$$H_2C=CH-C\equiv N: \longleftrightarrow H_2\overset{\oplus}{C}-CH=C=\overset{\ominus}{\ddot{N}}:$$

4. Hyperconjugation

It is delocalisation of sigma electron with p-orbital. Also known as σ π-conjugation or no bond resonance. It may takes place in alkene, alkynes, carbocation, free radical, benzene nucleus.

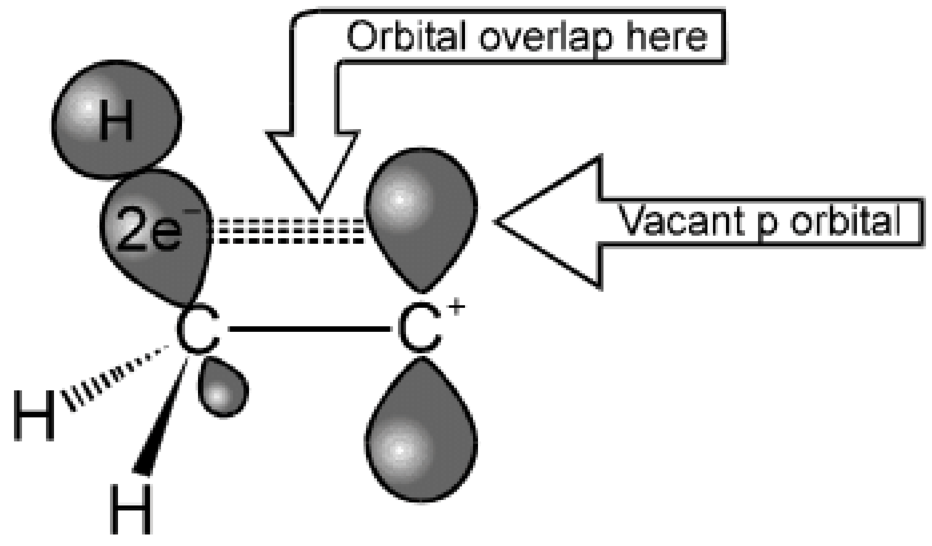
Necessary Condition : Presence of at least one hydrogen at saturated carbon which is α with respect to alkene, alkynes, carbocation, free radical, benzene nucleus.

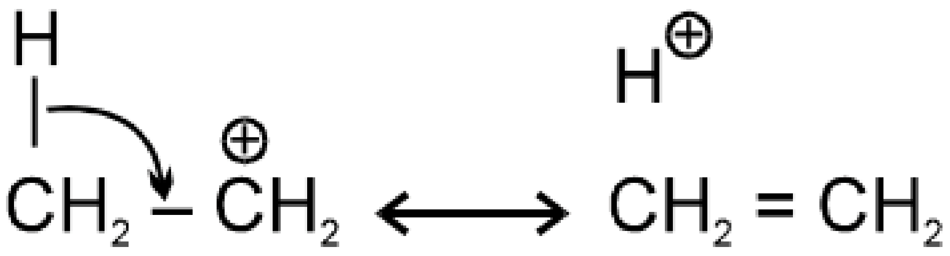
(i) Hyperconjugation in alkene



$$\overset{H\atop |}{C}H_2-CH=CH_2 \longleftrightarrow \overset{H^{\oplus}}{CH_2}=CH-\overset{\ominus}{C}H_2$$

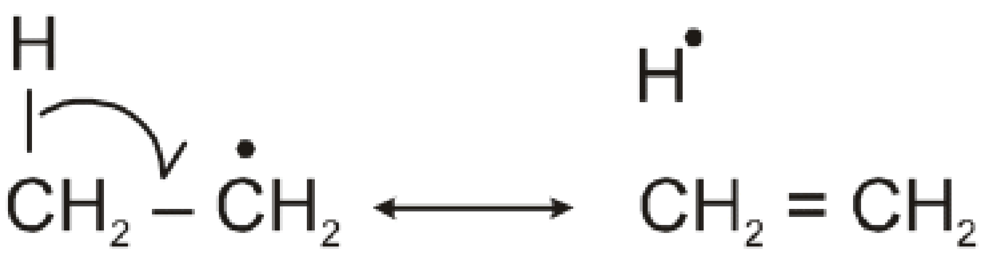
(ii) Hyperconjugation in carbocation





$$\overset{H\atop |}{C}H_2-\overset{\oplus}{C}H_2 \longleftrightarrow \overset{H^{\oplus}}{CH_2}=CH_2$$

(iii) Hyperconjugation in radical



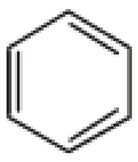
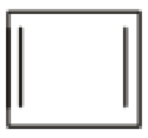
$$\overset{H\atop |}{C}H_2-\dot{C}H_2 \longleftrightarrow \overset{H^{\bullet}}{CH_2}=CH_2$$

5. Aromatic character [The Huckel 4n + 2 rule]

The following rules are useful in predicting whether a particular compound is aromatic or non–aromatic. Aromatic compounds are cyclic and planar. Each atom in an aromatic ring is sp^2 hybridised. The cyclic π molecular orbital (formed by overlap of p-orbitals) must contain $(4n + 2)$ π electrons, i.e., 2, 6, 10, 14 .... π electrons. Where n = an integer 0, 1, 2, 3,..............

Aromatic compounds have characteristic smell, have extra stability and burn with sooty flame.

Comparision between aromatic, anti aromatic and non-aromatic compounds.

Characteristics	Aromatic compounds (A)	Anti Aromatic compounds (B)	Non-Aromatic compounds (C)
Example			
1. Structure	Cyclic, planar all atoms of ring sp^2 hybridised	Cyclic, planar all atoms of ring sp^2 hybridised	Cyclic or acyclic planar,or non planar sp or sp^2 or sp^3
2. No. of π e^-s in the ring	$(4n+2)\pi e^-$ (Huckle's rule)	$(4n)\pi e^-$	Any no. of πe^-s
3. MOT	Unpaired e^-s in B.M.O.	Some πe^-s in non-bonding M.O.	B.M.O. / Non-bonding M.O.
4. Overlapping	Favourable over lapping of p orbital	Unfavourable over lapping of p orbital	Simple overlaping like alkenes
5. Resonance energy (R.E.)	Very high R.E. > 20-25 kcal/mol	Zero	4-8 kcal/mol like alkenes
6. Stability	Have extra stability due to close conjugation of π e^-s	Unstable not-exist at room temperature	Normal stability like a conjugated system
7. Characteristic Reactions	Electrophilic substitution Reaction	Dimerisation reaction to attain stability	Electrophilic addtion reaction like alkenes

Stability of compounds : Aromatic > Non-Aromatic > Anti-Aromatic

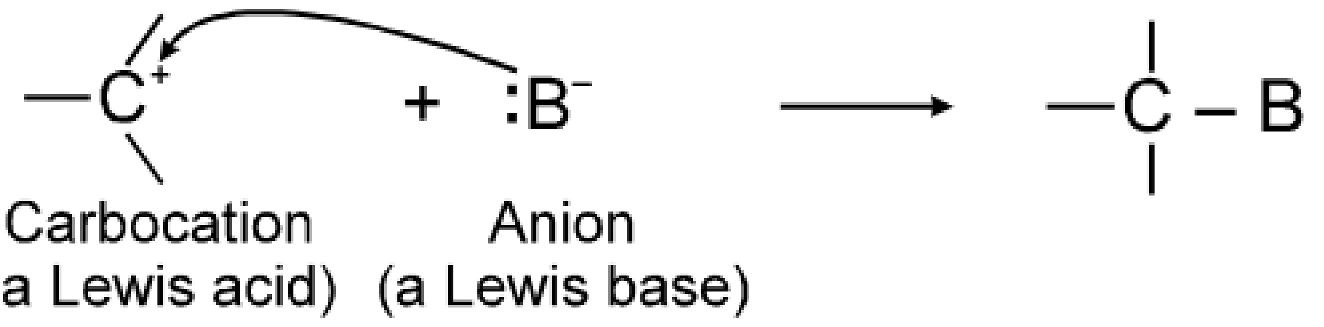
(A) Carbocation :

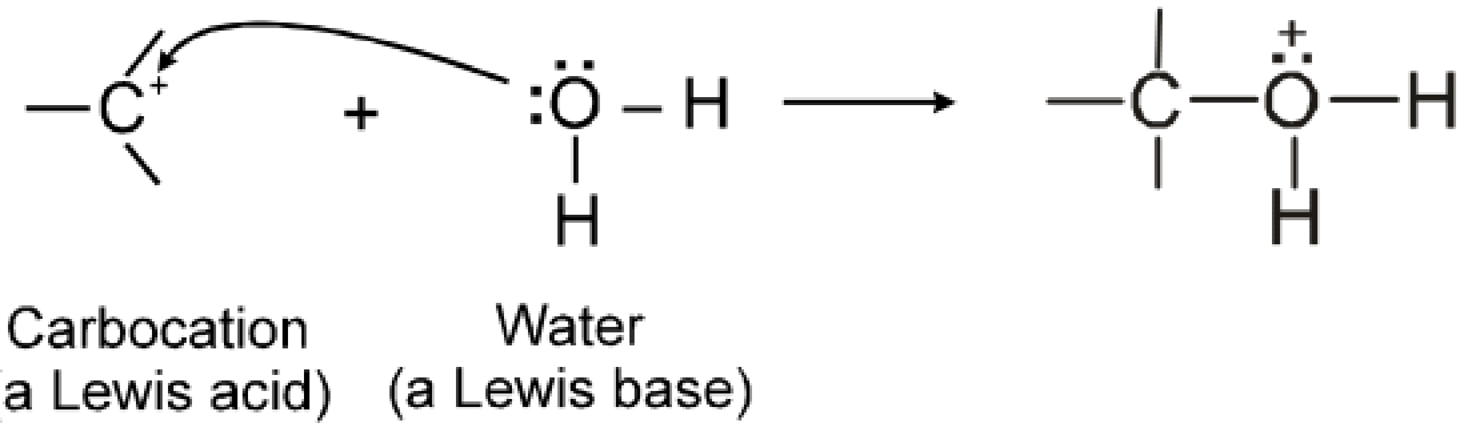
Definition : A carbon intermediate which contain three bond pair & a positive charge on it is called carbocation.

Hybridisation : Carbocation may be sp^2 & sp hybridised

Hybridisation	Example
sp^2	$\overset{\oplus}{C}H_3,\ CH_3\overset{\oplus}{C}H_2,\ CH_3\overset{\oplus}{C}HCH_3,\ (CH_3)_3\overset{\oplus}{C}$
sp	$H_2C = \overset{\oplus}{C}H\ ,\ HC \equiv \overset{\oplus}{C}$

Carbocations are electron deficient. They have only six electrons in their valence shell, and because of this, carbocations act as Lewis acids. Most of the carbocations are short-lived and highly reactive, they occur as intermediates in some organic reactions. Carbocations react with Lewis bases or ions that can donate the electron pair, that they need to achieve a stable octet of electrons (i.e., the electronic configuration of a noble gas):





Because carbocations are electron seeking reagents, chemists call them electrophiles. All Lewis acids, including protons, are electrophiles. By accepting an electron pair, a proton achieves the valence shell configuration of helium; carbocations achieve the valence shell configuration of neon.

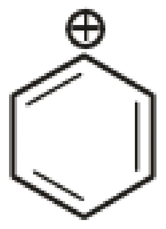
Stability : Carbocations are stabilised by

(i) + I effect (ii) + M effect

(iii) Hyperconjugation (iv) delocalisation of charge

General stability order :

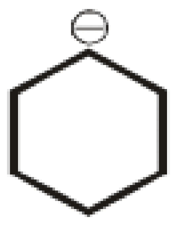
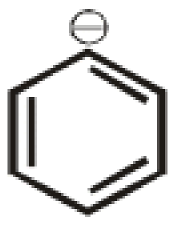
$$Ph_3\overset{\oplus}{C} > Ph_2\overset{\oplus}{C}H > Ph-\overset{\oplus}{C}H-R > CH_2=CH-\overset{\oplus}{C}H-R \gtrsim (CH_3)_3\overset{\oplus}{C} \gtrsim$$

$$Ph\overset{\oplus}{C}H_2 > CH_2=CH-\overset{\oplus}{C}H_2 \geq (CH_3)_2\overset{\oplus}{C}H > CH_3-\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3 > CH_2=\overset{\oplus}{C}H \simeq$$ 

(B) Carbanion :

Definition : A carbon intermediate which contain three bond pair and a negative charge on it, is called carbanion.

Hybridisation : Hybridisation of carbanion may be sp^3, sp^2 & sp.

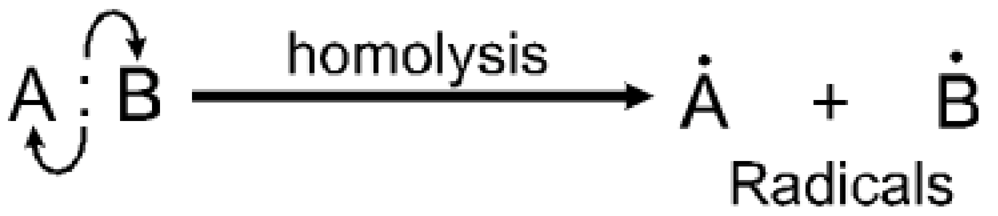
Hybridisation	Example
sp^3	$\overset{\ominus}{C}H_3$, $CH_3-\overset{\ominus}{C}H_2$, $CH_3\overset{\ominus}{C}HCH_3$, $(CH_3)_3\overset{\ominus}{C}$, 
sp^2	$H_2C=\overset{\ominus}{C}H$, $CH_2=CH-\overset{\ominus}{C}H_2$, 
sp	$HC\equiv\overset{\ominus}{C}$

Stability of carbanion : Carbanions are stabilised by electron withdrawing effect as

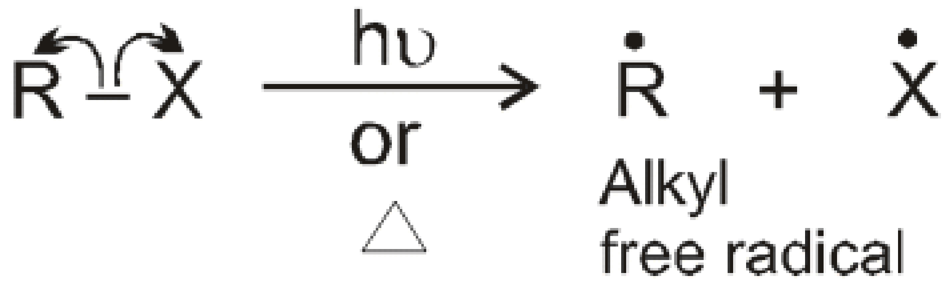
(i) – I effect (ii) – m effect (iii) Delocalisation of charge

(C) Free Radicals :

Homolysis of covalent bond results into free radical intermediates possess the unpaired electrons.



It is generated in presence of Sun light, Peroxides or High temperature



Free Radical : An uncharged intermediate which has three bond pair and an unpaired electron on carbon.

Note : (i) It is Neutral species with odd e^-

(ii) It is paramagnetic in nature due to odd e^-

(iii) No rearrangement is observed generally.

(iv) Carbon atom having odd electron is in sp^2 hybridised state

(v) Any reaction if it is carried out in the presence of sunlight, peroxide or high temperature it generally proceeds via free radical intermediate.

☞ **Stability of free radical :** It is stabilised by resonance, hyperconjugation and + I groups.

Ex. $(H_3C)_3C^{\bullet} > H_3C-\dot{C}H-CH_3 > H_3C-\dot{C}H_2 > \dot{C}H_3$

(Stability order)

(D) Carbenes (Divalent Carbon intermediates) :

Definition : There is a group of intermediates in which carbon forms only two bonds. These neutral divalent carbon species are called carbenes. Most carbenes are highly unstable that are capable of only fleeting existence. Soon after carbenes are formed, they usually react with another molecules.

Methods of preparation of carbene :

$CHCl_3 + HO^{\ominus} \xrightarrow{-HCl} :CCl_2$; $CH_2I_2 + Zn \xrightarrow[\Delta]{-ZnI_2} :CH_2$

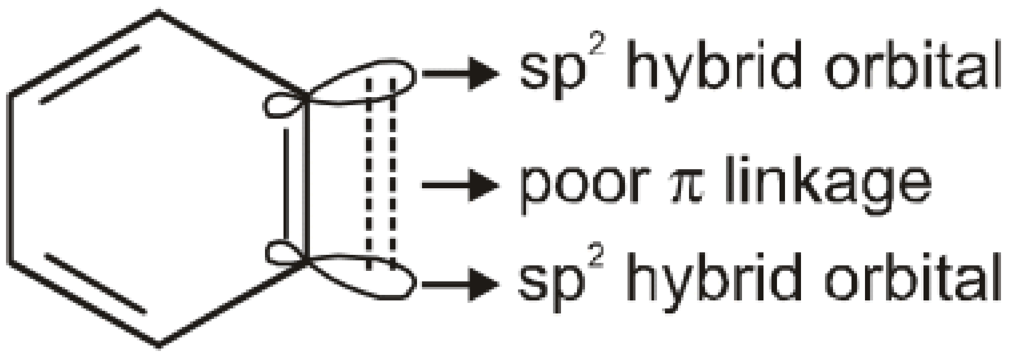
(E) Nitrenes :

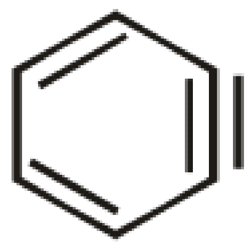
The nitrogen analog of carbenes are nitrenes. They are very much reactive since in them octet of N is incomplete. In nitrenes only one valencies of N are satisfied.

$R-\underset{\cdot\cdot}{\ddot{N}}$ $H-\underset{\cdot\cdot}{\ddot{N}}$

(F) Benzyne :

The benzene ring has one extra C – C π bond in benzyne





Clearly, we can see that the newly formed π bond cannot enter in resonance with other π orbitals of ring. since it is in perpendicular plane.

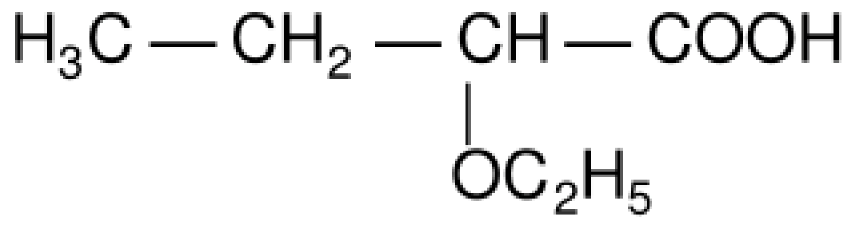
It is also important to note that hybridisation of each carbon involved in 'Benzynic bond' is sp^2 since the overlap between these sp^2 hybrid orbitals is not so much effective.

Structure Isomerism

Isomers	Characteristics	Conditions
(1) Chain Isomers	They have different size of main chain or side chain	They have same nature of locants
(2) Positional Isomers	They have different position of locants	They should have same size of main chain and side chain and same nature of locant
(3) Functional Isomers	Different nature of locant	Chain and positional isomerism is not considered
(4) Metamerism	Different nature of alkyl group along a polyvalent functional group	They should have same nature of functional groups chain & positional isomer is ignored
(5) Tautomerism	Different position of hydrogen atoms	The two functional isomers remains in dynamic equilibrium to each other

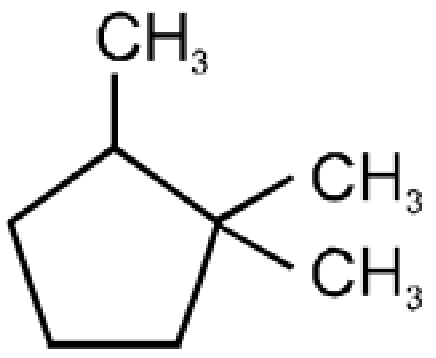
MISCELLANEOUS SOLVED PROBLEMS

1. Write the IUPAC name of following compounds.

(i) 

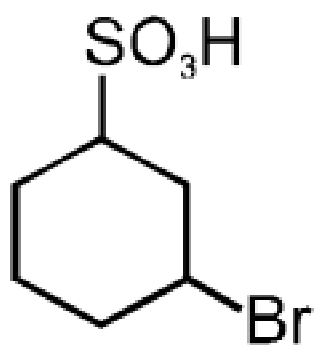
$H_3C-CH_2-\underset{OC_2H_5}{\underset{|}{CH}}-COOH$

(ii) 3-Bromocyclohexane-1-sulphonic acid

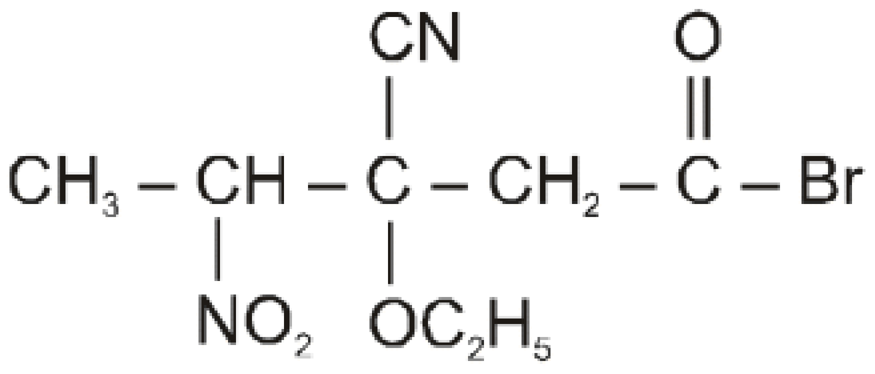
(iii) 

(iv) 3-Cyano-3-ethoxy-4-nitropentanoyl bromide

Sol. (i) 2-Ethoxybutanoic acid

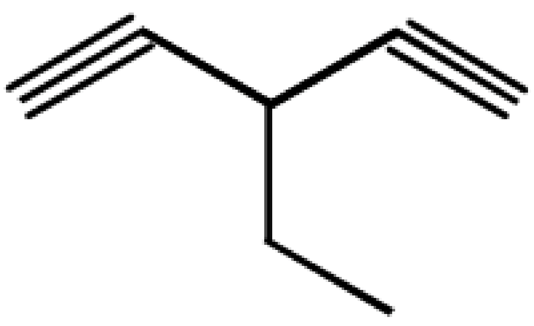
(ii) 

(iii) 1,1, 2-Trimethylcyclopentane

(iv) 

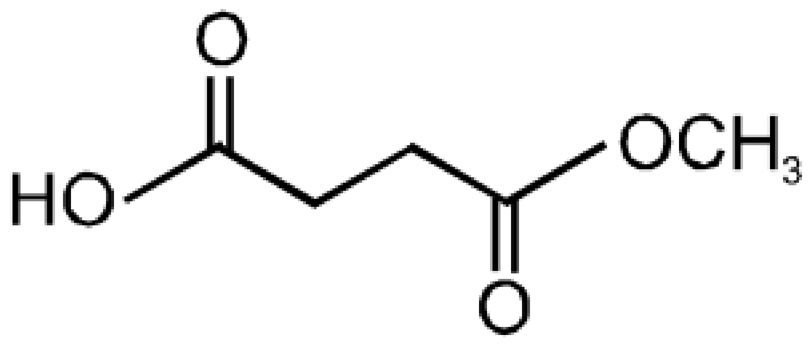
$CH_3-\underset{NO_2}{\underset{|}{CH}}-\overset{CN}{\overset{|}{\underset{OC_2H_5}{\underset{|}{C}}}}-CH_2-\overset{O}{\overset{||}{C}}-Br$

2. Draw the structure of following IUPAC name.

(i) 

(ii) 3-Methoxycarbonylpropanoic acid

Sol. (i) 3-Ethylpenta-1,4-diyne **(ii)**

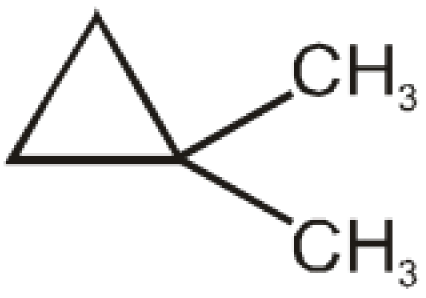


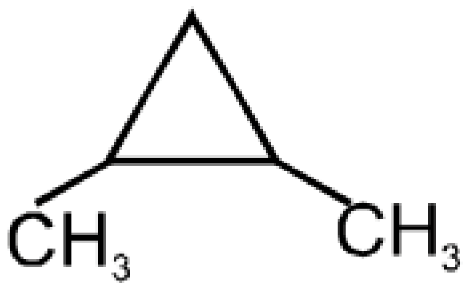
3. Find total number of structure isomers of dimethyl cyclopropane and dimethyl cyclobutane are respectively.

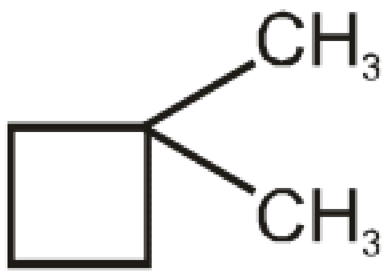
(A) 4, 6 (B) 3, 4 (C) 4, 5 (D) 2, 3

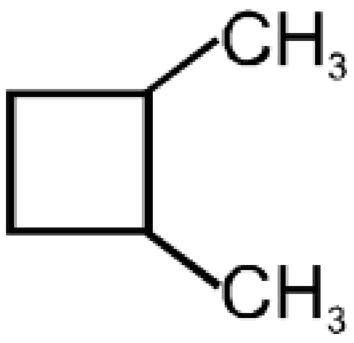
Ans. (D)

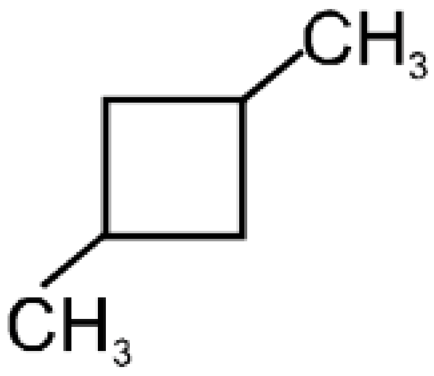
Sol.







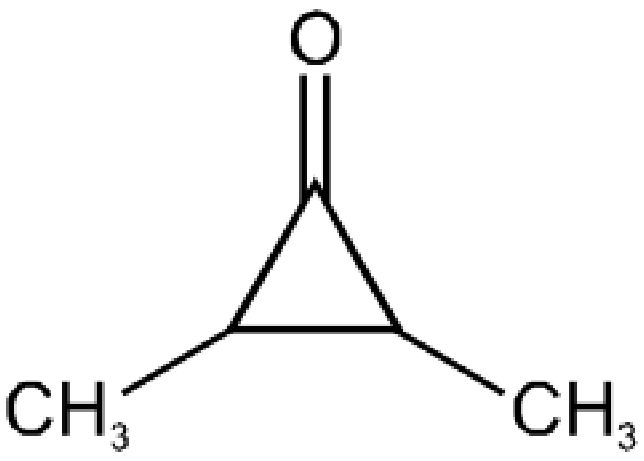


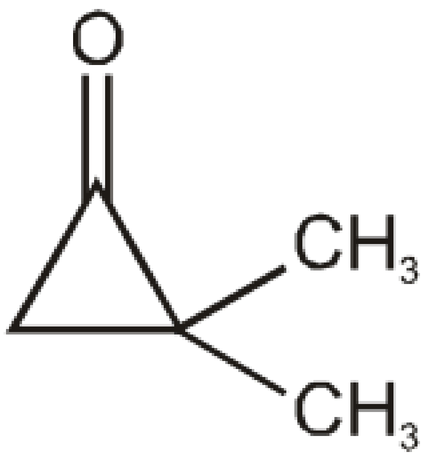


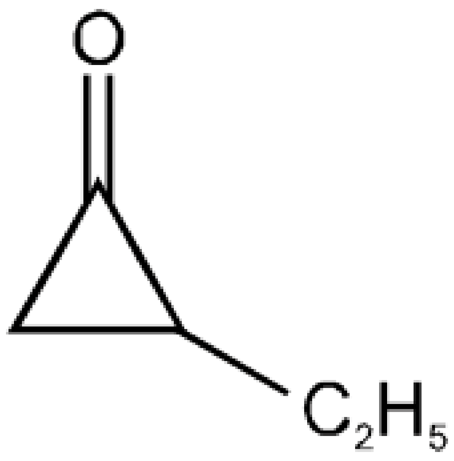
4. How many structures of cycloalkanone are possible with molecular formula C_5H_8O.

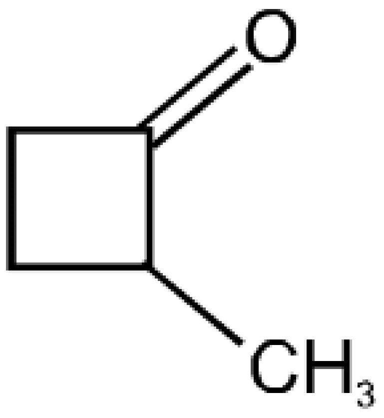
Ans. 6

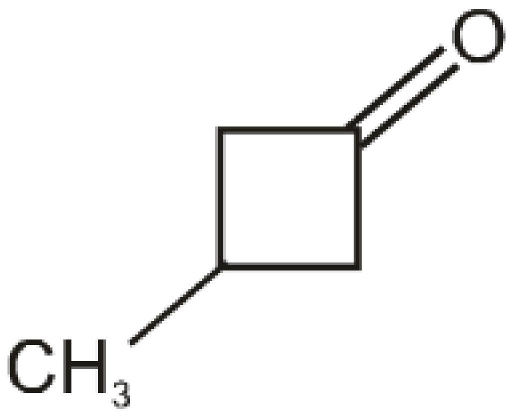
Sol.

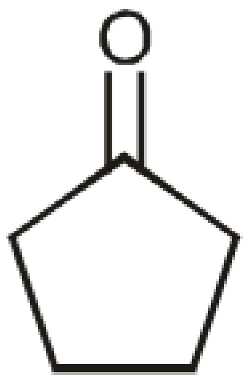








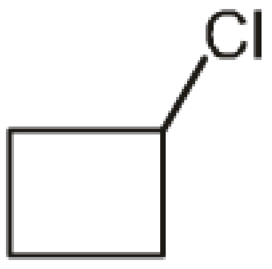


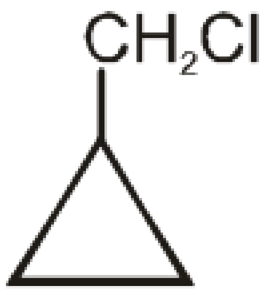


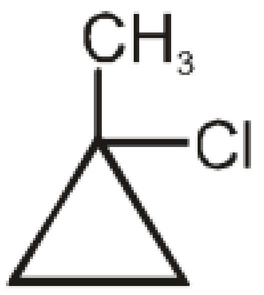
5. Find out the total number of cyclic isomers of the compound (X) C_4H_7Cl.

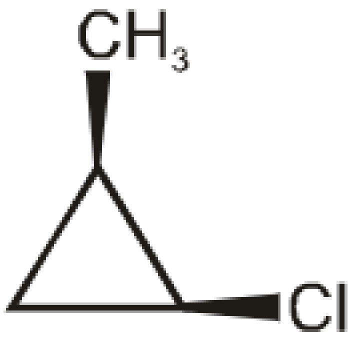
Ans. 4.

Sol. $X = C_4H_7Cl$ $DU = 5 - \frac{8}{2} = 1$





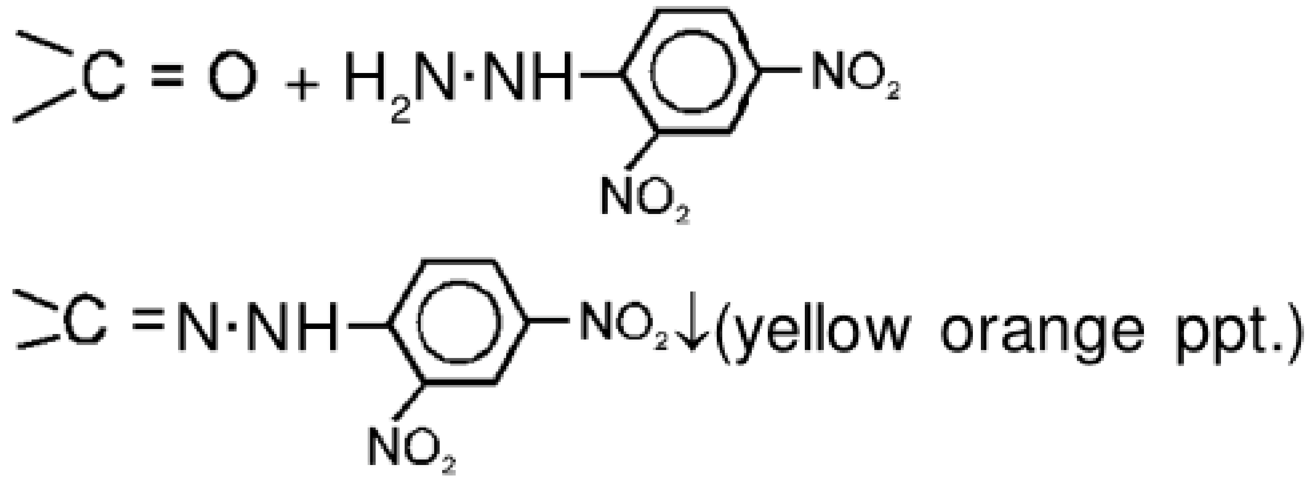
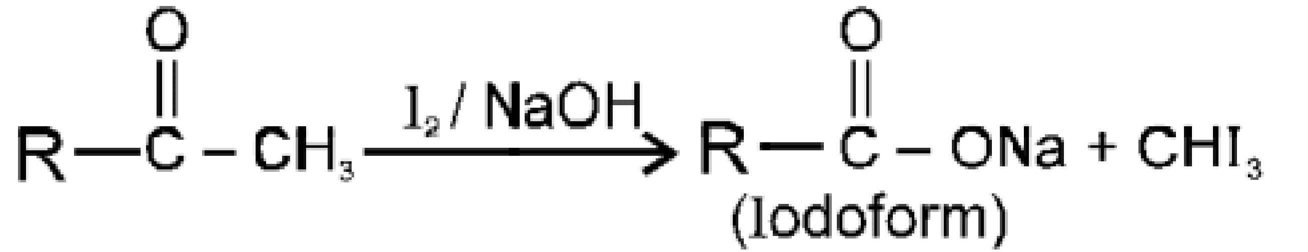
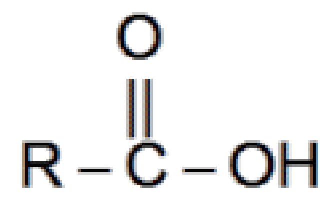




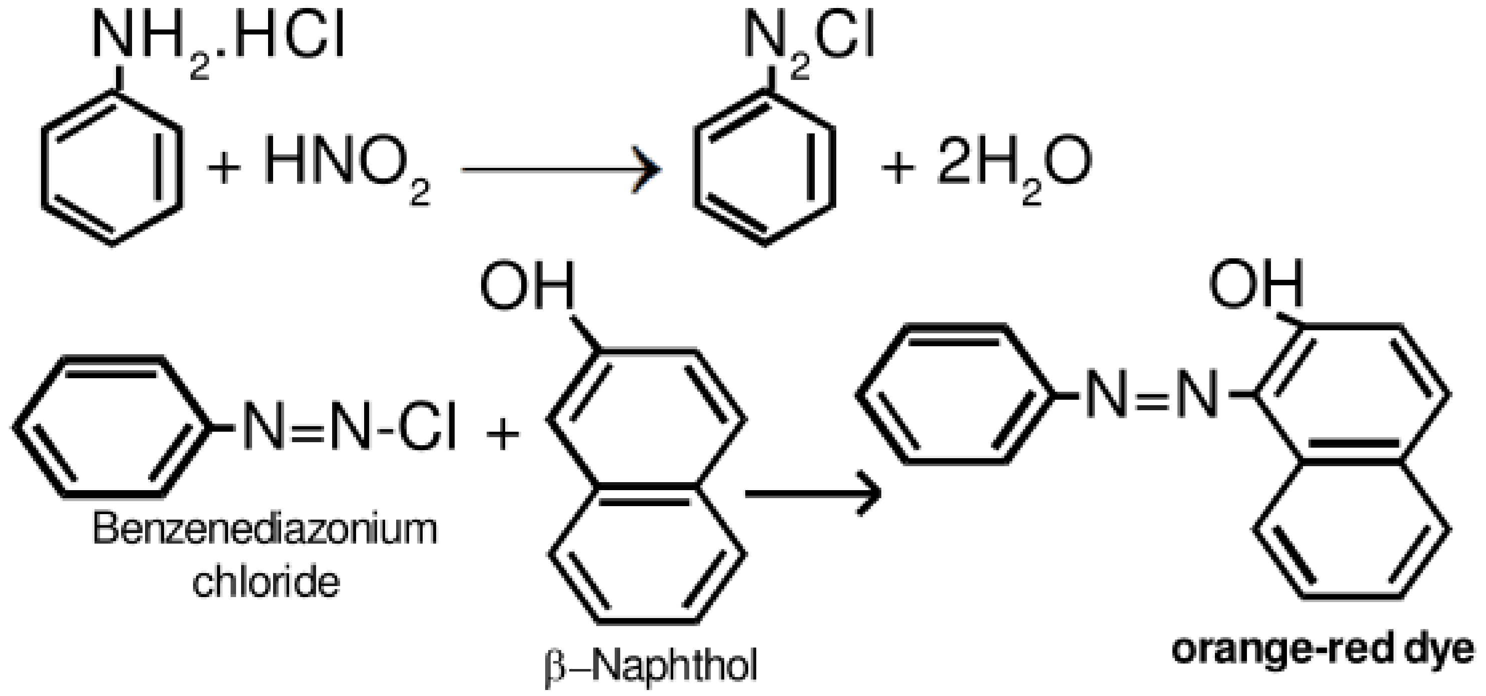
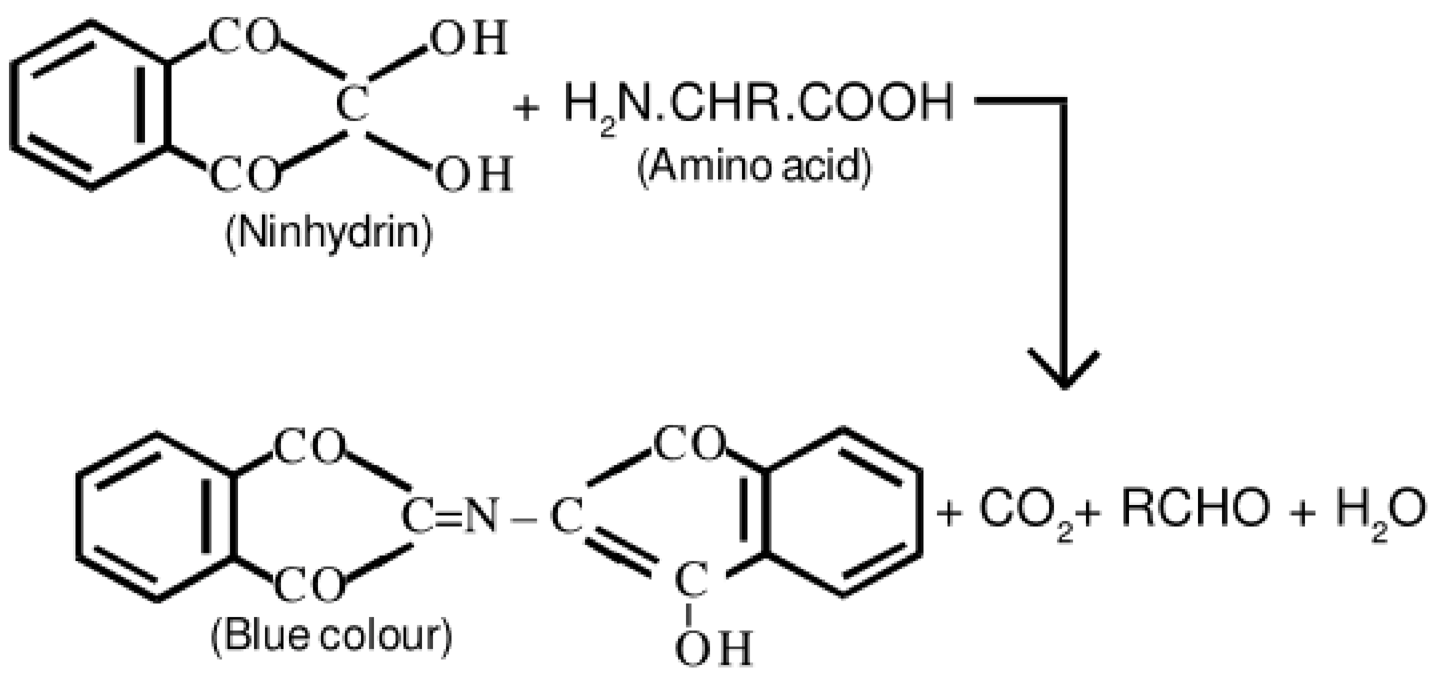
Total = 4

Identification of Functional Groups by Laboratory Tests

Functional Groups	Reagent	Observation	Reaction	Remarks
C–C (Alkane)	conc. H_2SO_4 conc. NaOH $KMnO_4$ $LiAlH_4$	NR NR NR NR	--------------	Inert paraffins
C=C / C≡C	[Bayer's reagent] alk. dil. cold $KMNO_4$	Pink colour disappears	$CH_2{=}CH_2+H_2O+O \xrightarrow{alk.KMnO_4} \underset{\underset{OH}{\vert}}{CH_2}-\underset{\underset{OH}{\vert}}{CH_2}$	Hydroxylation
C=C / C≡C	Br_2 / H_2O	Red colour decolourises	$Br_2+CH_2{=}CH_2 \longrightarrow$ white ppt	Bromination
C=C	O_3(ozone)	$>$C=O Compounds	$H_2C{=}CH_2 + O_3 \xrightarrow{Zn/H_2O} 2HCHO$	Ozonolysis
C≡C	O_3	Acid formed.	$R{-}C{\equiv}C{-}R' \xrightarrow{O_3} RCOOH + R'COOH$	Ozonolysis
R–C≡CH (Terminal alkyne)	(a) Cuprous chloride+NH_4OH	Red ppt.	$R{-}C{\equiv}CH + CuCl \xrightarrow{NH_4OH} R{-}C{\equiv}C\ Cu\downarrow$ (red)	
	(b) $AgNO_3$+NH_4OH	White ppt.	$R{-}C{\equiv}CH + Ag^+ \longrightarrow R{-}C{\equiv}C\ Ag\downarrow$ (white)	
(R–OH)	Na	Bubbles of H_2 come out	$2ROH + Na \rightarrow 2RONa + H_2\uparrow$	Presence of active 'H'
ROH 3° 2° 1°	Lucas Reagent [Conc. HCl + anhyd. $ZnCl_2$]	(3)° Cloudiness appears immidiately (2°) Cloudiness appears within 5 min. (1°) Cloudiness appear after 30 min.	$R{-}OH + HCl \xrightarrow{anhydrous\ ZnCl_2} \underbrace{R-Cl}_{cloudiness} + H_2O$	Lucas Test I. ter.alcohol II. sec. alcohol III. pri.alcohol

Functional Groups	Reagent	Observation	Reaction	Remarks
Ar–OH Enols	$FeCl_3$ (Neutral)	Coloured ppt. (violet, blue, green buff)	$6C_6H_5OH + FeCl_3 \longrightarrow [Fe(PhO)_6]^{-3}$	Test of enols/phenols
$>C=O$	2, 4-Dinitrophenyl hydrazine (2, 4-DNP) solution	Yellow orange ppt.		DNP-test
R–CHO	Fehling solution A & B	Red ppt.	$RCHO + Cu^{+2} \rightarrow RCOOH + Cu_2O\downarrow + 2H_2O$ Fehling sol^n. Red	Fehling's test
	Tollen's reagent	Black ppt. or silver mirror	$RCHO + Ag^+ \rightarrow RCOOH + 2Ag$ (Silver mirror)	Tollen's test
	Schiff's Reagent *	Pink colour resume		
$R–COCH_3$ or $ArCOCH_3$ or CH_3CHO	I_2 / NaOH	Yellow ppt of CHI_3 (iodoform)	 $R-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{I_2/NaOH} R-\overset{O}{\overset{\|}{C}}-ONa + CHI_3$ (Iodoform)	Iodoform reaction
 $R-\overset{O}{\overset{\|}{C}}-OH$	Blue litmus	Litmus change to red.		Litmus test.
	Conc. $NaHCO_3$ solution	Effervescence evolve.	$R-COOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2\uparrow$	Sodium bicarbonate test
Ester	NaOH, phenophthalein	Pink colour ↓ disappear on heating.	RCOOR' + NaOH + Phenophthalein $\downarrow\Delta$ (pink) RCOOH + R' OH (Colourless solution)	
Amides	Conc. NaOH, Δ	Smell of NH_3	$RCONH_2 + NaOH \xrightarrow{\Delta} RCOONa + NH_3\uparrow$	

★ Schiff's reagent : p-Rosiniline hydrochloride saturated with SO_2 so it is colourless. The pink colour is resumed by RCHO.

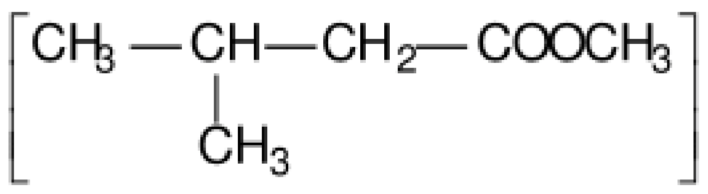
Functional Groups	Reagent	Observation	Reaction	Remarks
Nitro Compounds (RCH_2NO_2) or $ArNO_2$	Mulliken's test	black ppt	$\underset{(R-NO_2)}{Ar-NO_2} \xrightarrow[(1)]{Zn / NH_4Cl, \Delta} ArNHOH \xrightarrow[(2)]{\overset{\text{Tollen's reagent}}{AgNO_3 + NH_4OH}} Ag\downarrow$	
Amines(pri.) RNH_2	$CHCl_3$, KOH	Nauseating odour (Offensive smell) (Carbylamine)	$RNH_2 + CHCl_3 + 3KOH \rightarrow RNC + 3KCl + 3H_2O$	Carbylamine Reaction
	HNO_2 ($NaNO_2$+HCl)	Effervescence of N_2	$RNH_2 + HONO \rightarrow ROH + N_2 + H_2O$	
Ar. amines. $ArNH_2$	HNO_2 ($NaNO_2$+HCl) + β-Naphthol	Orange red dye is formed	$NaNO_2 + HCl \rightarrow NaCl + HNO_2$  	Azo dye test
R_2NH Sec. Amines	(i) $NaNO_2 + H_2SO_4$ (ii) Phenol	red colouration Liebermann test	 	Ninhydrin test
Carbohydrate	Molisch's reagent (10% α-naphthol in alcohol).	Violet colour		
Amino acids	Ninhydrin reagent (0.2 % sol.^{n})	Blue colour		

ORGANIC CHEMISTRY

Nomenclature

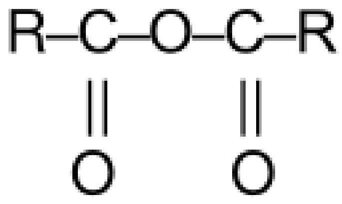
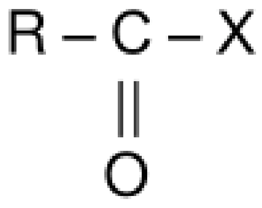
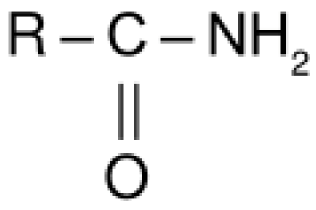
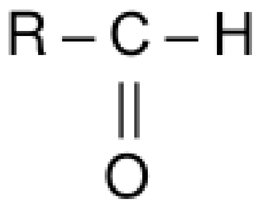
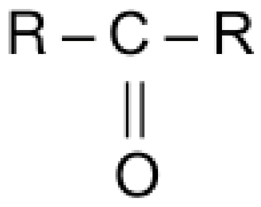
Examples of Compound containing different functional groups with common / trival names.

No. of carbon atoms	Prefix	–CHO (Aldehyde)	–COOH(–ic acid)	–COCl.(–yl chloride)	$–CONH_2$ (Amide)
1	Form	$HCHO$ Formaldehyde	$HCOOH$ Formic acid	$HCOCl$ Formyl chloride	$HCONH_2$ Formamide
2	Acet	CH_3CHO Acetaldehyde	CH_3COOH Acetic acid	CH_3COCl Acetyl chloride	CH_3CONH_2 Acetamide
3	Propion	CH_3CH_2CHO Propion aldehyde	CH_3CH_2COOH Propionic acid	CH_3CH_2COCl Propionyl chloride	$CH_3CH_2CONH_2$ Propionamide
4	Butyr	$CH_3CH_2CH_2CHO$ n–Butyraldehyde	$CH_3CH_2CH_2COOH$ n–Butyric acid	$CH_3CH_2CH_2COCl$ n–Butyryl chloride	$CH_3CH_2CH_2CONH_2$ n–Butyramide
5	Valer	$CH_3CH_2CH_2CH_2CHO$ n–Valeraldehyde	$CH_3CH_2CH_2CH_2COOH$ n–Valeric acid	$CH_3CH_2CH_2CH_2COCl$ n–Valeryl chloride	$CH_3CH_2CH_2CH_2CONH_2$ n–Valeramide
3C+1 Double bond	Acryl	$CH_2=CH–CHO$ Acrylaldehyde	$CH_2 = CH–COOH$ Acrylic acid	$CH_2 = CH–COCl$ Acryl chloride	$CH_2=CH–CONH_2$ Acrylamide
4C + 1 Double bond (at 2nd Carbon. atom)	Croton	$CH_3–CH=CH–CHO$ Crotonaldehyde	$CH_3CH_2 = CH–COOH$ Crotonic acid	$CH_3CH_2 = CH–COCl$ Crotonyl chloride	$CH_3CH_2 = CH–CONH_2$ Crotonamide

No. of carbon atoms	Prefix	–CN(–O nitrile)	$-N \overset{\rightarrow}{=} C$(Oisonitrile) If Suffix isocyanide is used than. Carbon atom of – NC not counted. If suffix carbyl amine is used. Carbon atom of – NC not counted. If O-isonitrile is used → Carbon atom of – NC counted	—COOR Ester
1	Form	$H-C \equiv N$ Formonitrile	$H-N \overset{\rightarrow}{=} C$ Formoisonitrile	$HCOOCH_3$ Methyl formate
2	Acet	$CH_3C \equiv N$ Acetonitrile	$CH_3-N \overset{\rightarrow}{=} C$ Acetoisonitrile	CH_3COOCH_3 Methyl acetate
3	Propion	$CH_3CH_3\ C \equiv N$ Propionitrile	$CH_3CH_2N \overset{\rightarrow}{=} C$ Propionisonitrile	$CH_3CH_2COOCH_3$ Methyl propionate
4	Butyr	$CH_3CH_2CH_2\ C \equiv N$ n–Butyronitrile	$CH_3CH_2CH_2N \overset{\rightarrow}{=} C$ n–Butyroisonitrile	$CH_3CH_2CH_2COOCH_3$ Methyl n–butyrate
5	Valer	$CH_3CH_2CH_2CH_2\ C \equiv N$ n–Valeronitrile	$CH_3CH_2CH_2CH_2N \overset{\rightarrow}{=} C$ n–Valeroisonitrile	 $\left[CH_3-\underset{\displaystyle CH_3}{\underset{\vert}{CH}}-CH_2-COOCH_3\right]$ Methyl isovalerate
3 C +1 Double bond	Acryl	$CH_2 = CH - C \equiv N$ Acrylonitrile	$CH_2 = CH-NC$ Acrylisonitrile	$CH_2=CHCOOCH_3$ Methyl acrylate
4C + 1 Double bond (at 2nd Carbon. atom)	Croton	$CH_3CH = CH - C \equiv N$ Crotononitrile	$CH_3-CH=CH-NC$ Crotonoisonitrile	$CH_3CH=CHCOOCH_3$ Methyl crotonate

Secondary suffix of some common functional groups (IUPAC)

A secondary suffix is added to the primary suffix to indicate the nature of the functional group present in the organic compounds. Secondary suffix of important functional groups are given below in their decreasing order of seniority.

	Class	**Name**	**Suffix**	**Prefix**
1.	R–COOH	Alkanoic Acid	– oic acid (carboxylic acid)	carboxy
2.	$R-SO_3H$	Alkane sulhonic Acid	– sulphonic acid	sulpho
3.	 $R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R$	Alkanonic Anhydride	– oic anhydride (carboxylic anhydride)	------------
4.	R–COOR	Alkyl alkanoate	– oate (carboxylate)	alkoxy carbonyl or alkanoyl oxy
5.	 $R-\underset{\underset{O}{\|}}{C}-X$	Alkanoyl halide	–oyl halide (carbonyl halide)	halo carbonyl
6.	 $R-\underset{\underset{O}{\|}}{C}-NH_2$	Alkanamide	– amide (carboxamide)	carbamoyl
7.	$R-C\equiv N$	Alkanenitrile	– nitrile (carbonitrile)	cyano
8.	 $R-\underset{\underset{O}{\|}}{C}-H$	Alkanal	– al (carbaldehyde)	formyl / oxo
9.	 $R-\underset{\underset{O}{\|}}{C}-R$	Alkanone	– one	oxo
10.	R–OH	Alkanol	– ol	hydroxy
11.	R–SH	Alkanethiol	– thiol	mercapto
12.	$R-NH_2$	Alkanamine	– amine	amino

IUPAC system of nomenclature

The IUPAC name of any organic compound consists of maximum five parts in the following sequence.

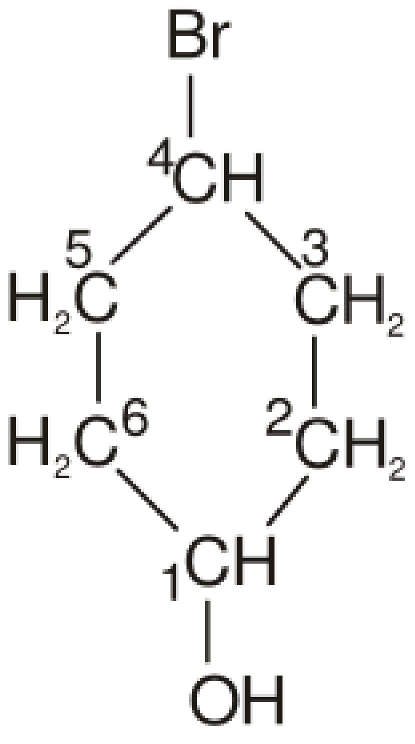
Secondary prefix + Primary prefix + Word root + Primary suffix + Secondary suffix

The following examples illustrate the use of word root, primary suffix and secondary suffix in naming of organic compounds.

Organic compounds	Word root	Primary suffix	Secondary suffix	IUPAC name
CH_3CH_2OH	Eth	an(e)	ol	Ethanol
$CH_3CH_2CH_2NH_2$	Prop	an(e)	amine	Propanamine
$CH_3CH_2CH_2COOH$	But	an(e)	oic acid	Butanoic acid
CH_3CH_2CN	Prop	an(e)	nitrile	Propanenitrile
$CH_2=CHCHO$	Prop	en(e)	al	Propenal
$HC\equiv CCOOH$	Prop	yn(e)	oic acid	Propynoic acid

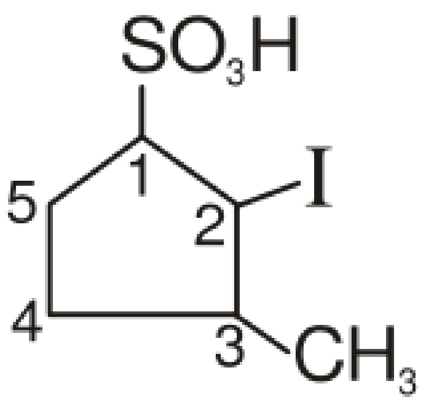
The following examples illustrate the use of word root , primary prefix and secondary prefix in naming of organic compounds.

Ex.(i)



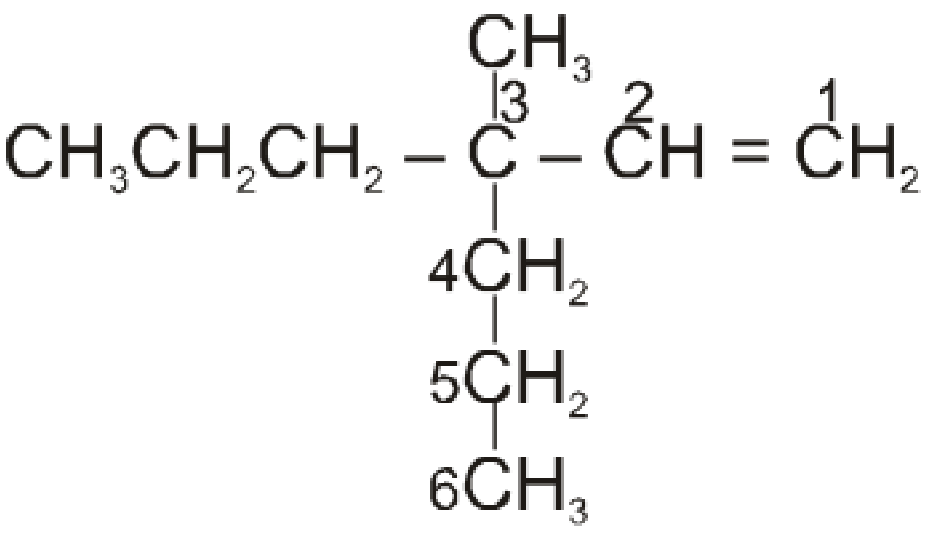
4-Bromo	+	cyclo	+	hex	+	an (e)	+	1-ol
Secondary prefix		Primary prefix		Word root		Primary suffix		Secondary suffix

(ii)



2-Iodo-3-methyl	+	cyclo	+	pent	+	ane	+	1-sulphonic acid
Secondary prefix		Primary prefix		Word root		Primary suffix		Secondary suffix

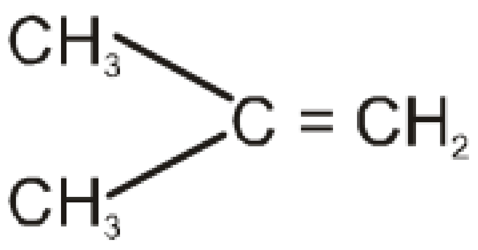
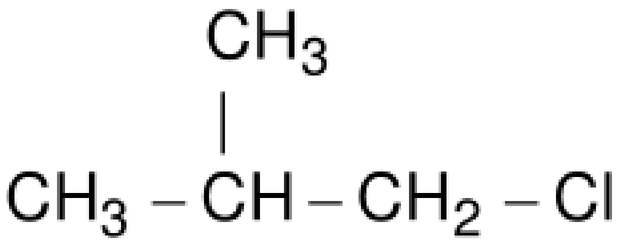
(iii)

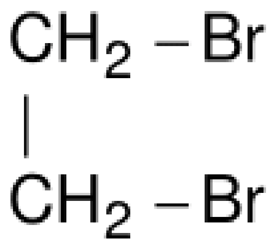
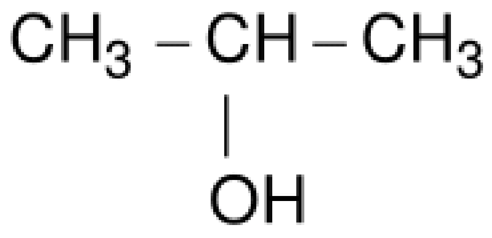
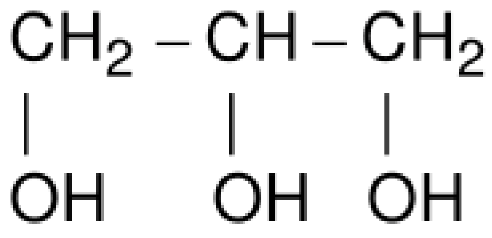
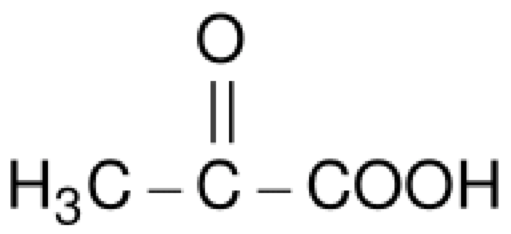
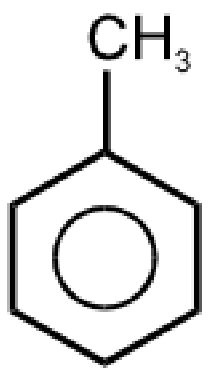


$$\mathrm{CH_3CH_2CH_2-\underset{\begin{array}{c}|\\ {}^{4}CH_2\\ |\\ {}^{5}CH_2\\ |\\ {}^{6}CH_3\end{array}}{\overset{\begin{array}{c}CH_3\\ |3\end{array}}{C}}-\overset{2}{C}H=\overset{1}{C}H_2}$$

Position of double bond will be indicated as no. 1, Hence name will be 3–Methyl–3–propylhex–1–ene

Common and IUPAC Names of Some Organic Compounds

S.No.	Compound	Common names	IUPAC name
1.	$CH_3CH=CH_2$	Propylene	Propene
2.		Isobu ene	2-Methylpropene
3.	$H_3C–C\equiv CH$	Methyl acetylene	Propyne
4.	 $CH_3-\overset{\overset{CH_3}{\vert}}{CH}-CH_2-Cl$	Isobutyl chloride	1-Chloro-2-methylpropane

5.	 $\begin{array}{l}CH_2-Br\\ \vert\\ CH_2-Br\end{array}$	Ethylene dibromide	1, 2-Dibromoethane
6.	$CH_2=CH-Cl$	Vinyl chloride	Chloroethene
7.	 $CH_3-\underset{\substack{\vert\\ OH}}{CH}-CH_3$	Isopropyl alcohol	Propan-2-ol
8.	$CH_2=CH-CH_2-OH$	Allyl alcohol	Prop-2-en-1-ol
9.	 $\underset{\substack{\vert\\ OH}}{CH_2}-\underset{\substack{\vert\\ OH}}{CH}-\underset{\substack{\vert\\ OH}}{CH_2}$	Glycerol or Glycerine	Propane-1, 2, 3-triol
10.	CH_3-CHO	Acetaldehyde	Ethanal
11.	$CH_3-CO-CH_2CH_3$	Ethyl methyl ketone	Butanone
12.	CH_3-COOH	Acetic acid	Ethanoic acid
13.	 $\begin{array}{l}COOH\\ \vert\\ COOH\end{array}$	Oxalic acid	Ethanedioic acid
14.	 $H_3C-\overset{\substack{O\\ \Vert}}{C}-COOH$	Pyruvic acid	2-Oxopropanoic acid
15.	CH_3-COCl	Acetyl chloride	Ethanoyl chloride
16.	CH_3-CONH_2	Acetamide	Ethanamide
17.	CH_3-NH_2	Methylamine	Methanamine
18.	CH_3-CN	Methyl cyanide or Acetonitril	Ethanenitrile
19.	$CH_3-N^{+}\equiv C^{-}$	Methyl isocyanide or Methyl carbylamine	Methane isocyanide
20.		Toluene	Methylbenzene or Toluene

Polymers

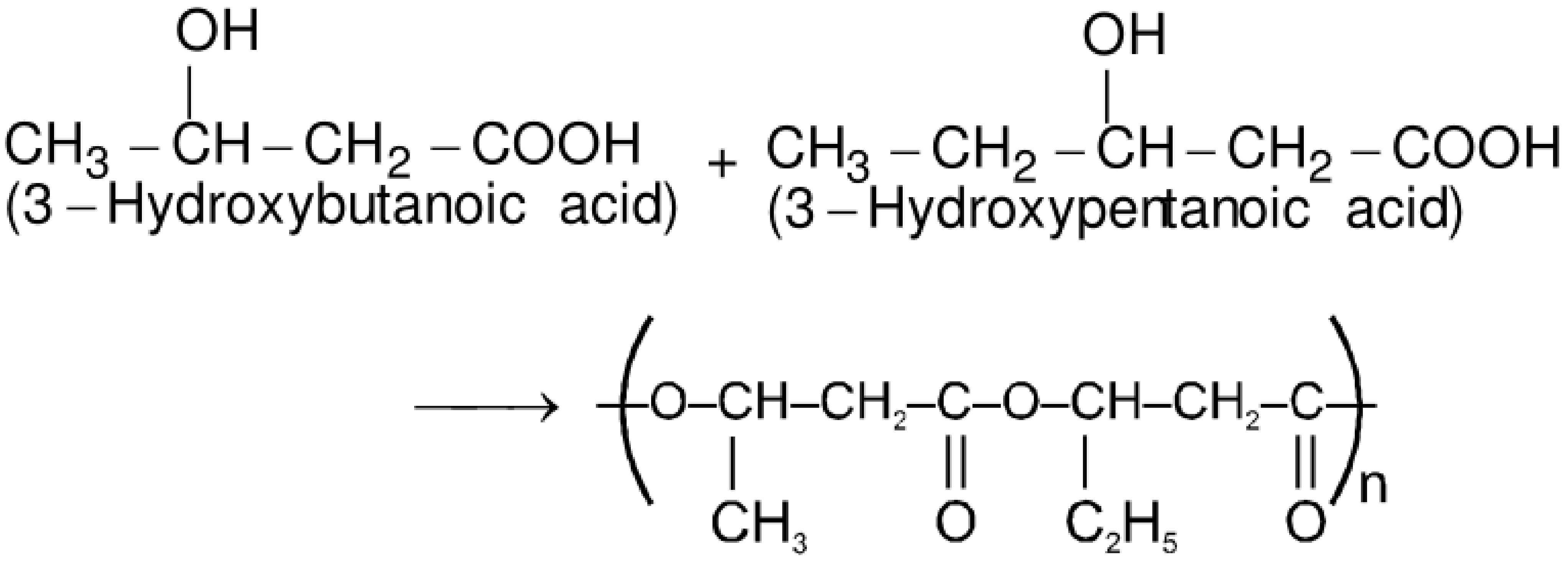
Biodegradable Polymers :

A large number of polymers are quite resistant to the environmental degradation processes and are thus responsible for the accumulation of polymeric soild waste materials. These soild wastes cause acute environmental problems and remain undegraded for quite a long time. In view of the general awareness and concern for the problems created by the polymeric soild wastes, certain new biodegradable synthetic polymers have been designed and developed. These polymers contain functional groups similar to the functional groups present in biopolymers.

Aliphatic polyesters are one of the important classes of biodegradable poylmers. Some examples are given below :

(a) Poly β-hydroxybutyrate – co–β-hydroxy valerate (PHBV) :

It is obtained by the copolymerisation of 3-hydroxybutanoic acid and 3-hydroxypentanoic acid.



$$\underset{\text{(3 – Hydroxybutanoic acid)}}{CH_3-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_2-COOH} + \underset{\text{(3 – Hydroxypentanoic acid)}}{CH_3-CH_2-\overset{\overset{\displaystyle OH}{|}}{C}H-CH_2-COOH}$$

$$\longrightarrow \left(O-\underset{\underset{\displaystyle CH_3}{|}}{CH}-CH_2-\underset{\underset{\displaystyle O}{||}}{C}-O-\underset{\underset{\displaystyle C_2H_5}{|}}{CH}-CH_2-\underset{\underset{\displaystyle O}{||}}{C} \right)_n$$

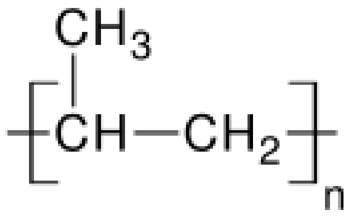
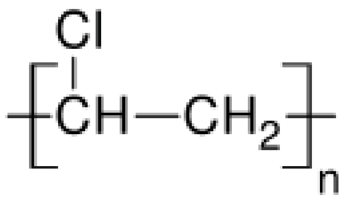
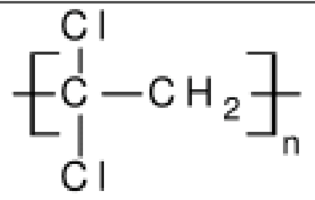
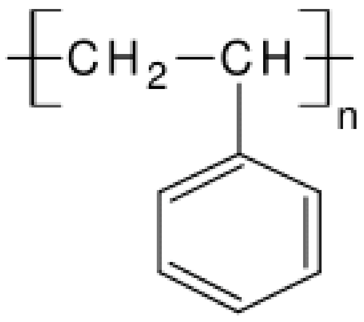
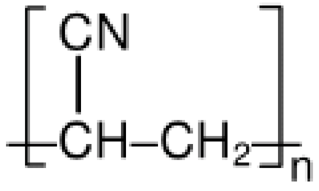
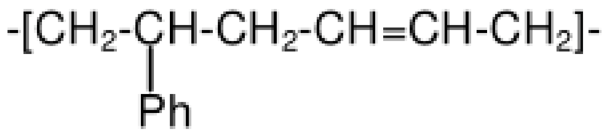
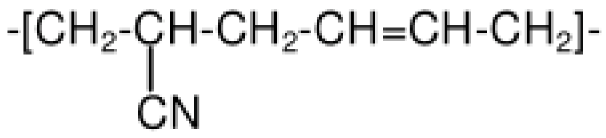
PHBV

PHBV is used in speciality packaging, orthopaedic devices and in controlled release of drugs. PHBV undergoes bacterial degradation in the environment.

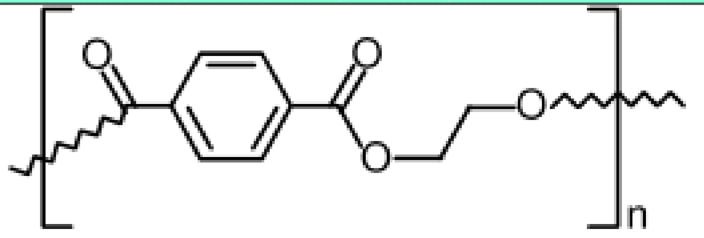
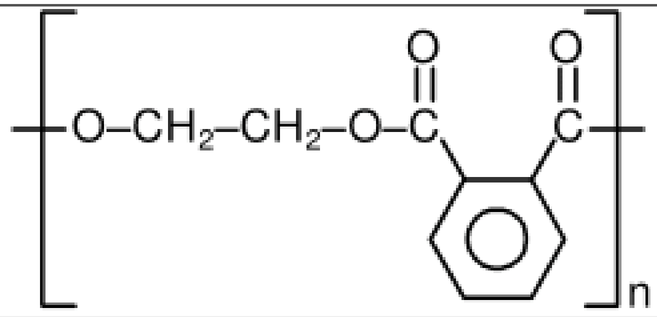
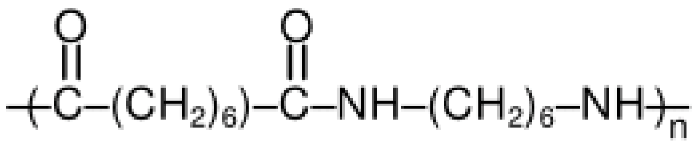
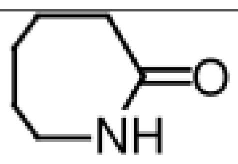
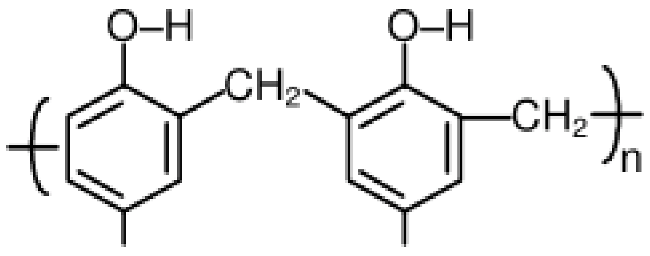
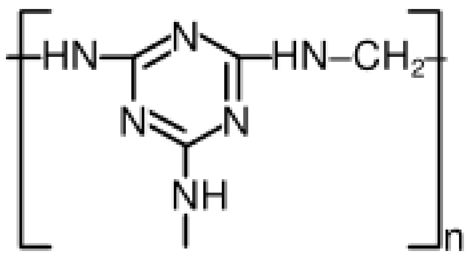
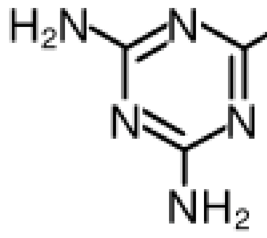
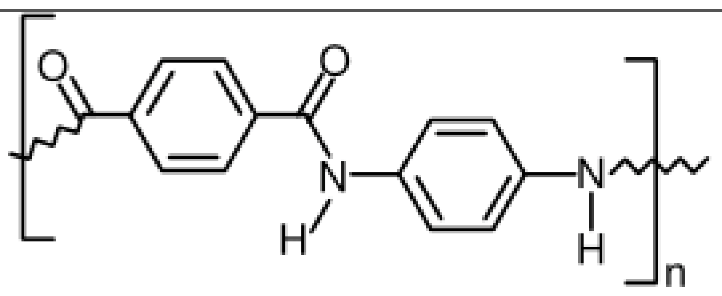
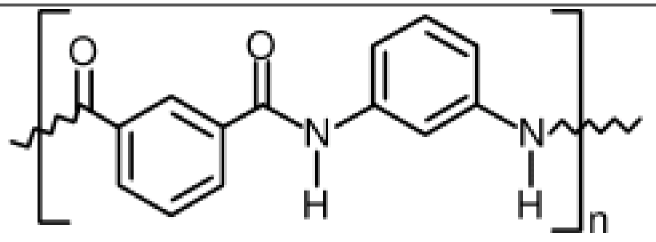
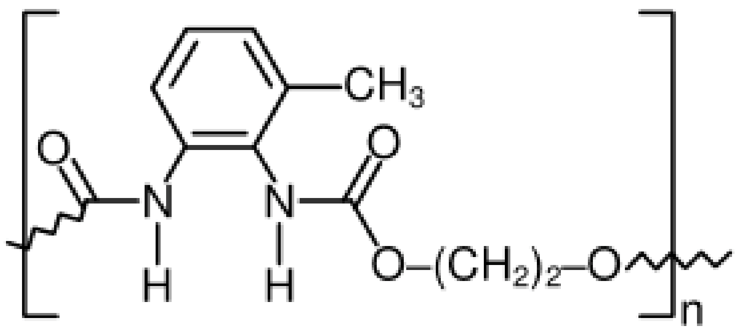
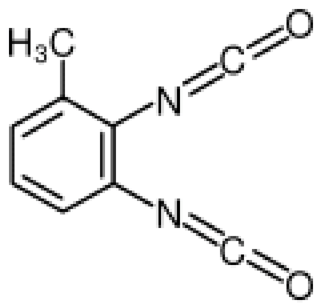
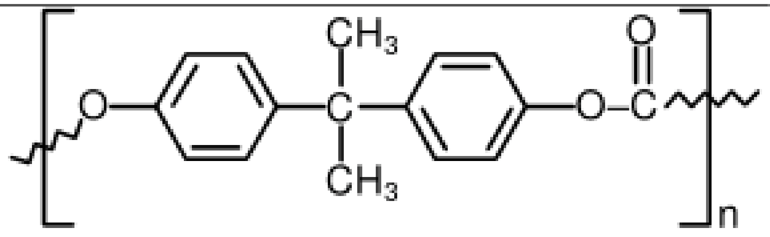
(b) Nylon–2–nylon–6 :

It is an alternating polyamide copolymer of glycine (H_2N-CH_2-COOH) and amino caproic acid ($H_2N(CH_2)_5COOH$) and it is also biodegradable polymer.

$$nH_2N-CH_2-COOH + nH_2N-(CH_2)_5-COOH \longrightarrow \left[NH-CH_2-CO-NH-(CH_2)_5-CO \right]_n$$

Some common addition polymers/chain growth polymer				
S. No.	**Name(s)**	**Formula**	**Monomer**	**Uses**
1.	Polyethylene (low density (LDPE))	$-(CH_2\text{-}CH_2)_n-$	$CH_2{=}CH_2$ (ethylene)	Film wrap, Plastic Bags
2.	Polyethylene (high density (HDPE))	$-(CH_2\text{-}CH_2)_n-$	$CH_2{=}CH_2$ (ethylene)	Electrical insulation bottles, toys
3.	Polypropylene (PP) different grades	 $\left[\overset{CH_3}{\overset{\mid}{C}H}-CH_2\right]_n$	$CH_2{=}CHCH_3$ (propylene)	Manufacture of ropes, toys, pipes, fibres etc.
4.	Poly vinyl chloride (PVC)	 $\left[\overset{Cl}{\overset{\mid}{C}H}-CH_2\right]_n$	$CH_2{=}CHCl$ (vinyl chloride)	Manufacture of rain coats, hand bags, vinyl flooring, water Pipes etc.
5.	Poly vinylidene chloride (Saran A)	 $\left[\underset{Cl}{\overset{Cl}{C}}-CH_2\right]_n$	$CH_2{=}CCl_2$ (vinylidene chloride)	Seat covers, films & fibers
6.	Polystyrene (Styron)		$CH_2{=}CHC_6H_5$ (styrene)	As insulator, wrapping material, manufactures of toys, radio and Television cabinets
7.	Polyacrylonitrile (PAN, Orlon, Acrilan)	 $\left[\overset{CN}{\overset{\mid}{C}H}-CH_2\right]_n$	$CH_2{=}CHCN$ (acrylonitrile)	Rugs, Blankets clothing
8.	Polytetrafluoroethylene (PTFE, Teflon)	$-(CF_2\text{-}CF_2)_n-$	$CF_2{=}CF_2$ (tetrafluoroethylene)	Non-stick surfaces electrical insulation
9.	Poly methyl methacrylate (PMMA, Lucite, Plexiglas, perspex)	$-[CH_2C(CH_3)CO_2CH_3]_n-$	$CH_2{=}C(CH_3)CO_2CH_3$ (methylmethacrylate)	Lighting covers, signs skylights
10.	Poly vinyl acetate (PVAc)	$-(CH_2\text{-}CHOCOCH_3)_n-$	$CH_2{=}CHOCOCH_3$ (vinyl acetate)	Latex paints, Adhesives
11.	Natural Rubber	$-[CH_2\text{-}CH{=}C(CH_3)\text{-}CH_2]_n-$ (cis)	$CH_2{=}CH{-}C(CH_3){=}CH_2$ (isoprene)	Requires vulcanization for practical use
12.	Neoprene	$-[CH_2\text{-}CH{=}CCl\text{-}CH_2]_n-$	$CH_2{=}CH\text{-}CCl{=}CH_2$ (chloroprene)	Synthetic rubber, oil resistant seal, gaskets, hoses & conveyor belts
13.	SBR styrene butadiene rubber (Buna-S)	 $\text{-}[CH_2\text{-}\underset{Ph}{\underset{\mid}{C}H}\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2]\text{-}$	$H_2C{=}CHC_6H_5$ and $H_2C{=}CH\text{-}CH{=}CH_2$	Tyres, floortiles, foot wear & cable insulation
14.	Nitrile Rubber (Buna-N)	 $\text{-}[CH_2\text{-}\underset{CN}{\underset{\mid}{C}H}\text{-}CH_2\text{-}CH{=}CH\text{-}CH_2]\text{-}$	$H_2C{=}CHCN$ and $H_2C{=}CH\text{-}CH{=}CH_2$	Making oil seals, tank lining and hoses

Some condensation polymers/step growth polymers

S.	Name(s)	Formula	Monomer	Uses
1.	Polyester/Dacron/ Terylene/Mylar		$HO_2C\ C_6H_4\ CO_2H$ (Terephthalic acid) $HO–CH_2CH_2–OH$ Ethylene glycol	Fabric, Tyrecord
2.	Glyptal or Alkyds resin		$HO_2C–C_6H_4–CO_2H$ (Phthalic acid) $HO–CH_2CH_2–OH$	Paints and Lacquers
3.	Polyamide (Nylon 6,6)	$\sim[CO(CH_2)_4CO–NH(CH_2)_6NH]_n\sim$	$HO_2C–(CH_2)_4–CO_2H$ $H_2N–(CH_2)_6–NH_2$	Parachutes & Clothing
4.	Nylon 6,10	 $\left(\overset{O}{\overset{\|}{C}}–(CH_2)_6)–\overset{O}{\overset{\|}{C}}–NH–(CH_2)_6–NH\right)_n$	$HOOC–(CH_2)_8–COOH$ $H_2N–(CH_2)_6–NH_2$	
5.	Polyamide Nylon 6, Perlon-L	$\sim[CO(CH_2)_5NH]_n\sim$		Rope & Tyrecord
6.	Bakelite		PhOH + HCHO in (excess)	Electrical Switch, combs, Handle of Utensils, computer discs and Bowling Balls
7.	Urea-formaldehyle resin	$(–NH–CO–NH–CH_2–)_n$	$H_2N–CO–NH_2$ (Urea) HCHO (Formaldehyde)	Making unbreakable cups and laminated sheets.
8.	Melamine formaldehyde resin		 (melamine) +HCHO (formaldehyde)	Unbreakabl e crockery
9.	Polyamide Kevlar		Para $HO_2C–C_6H_4–CO_2H$	Tyre
10.	Polyamide Nomex		Meta $HO_2C–C_6H_4–CO_2H$ Meta $H_2N–C_6H_4–NH_2$	
11.	Polyurethane Spandex		$HOCH_2CH_2OH$ 	Foams, Shoes, Automobile seats and components
12.	Polycarbonate Lexan		$(HO–C_6H_4–)_2C(CH_3)_2$ (Bisphenol A) $X_2C=O$ (X = OCH_3 or Cl)	Bike helmet, goggles, bullet proof glass

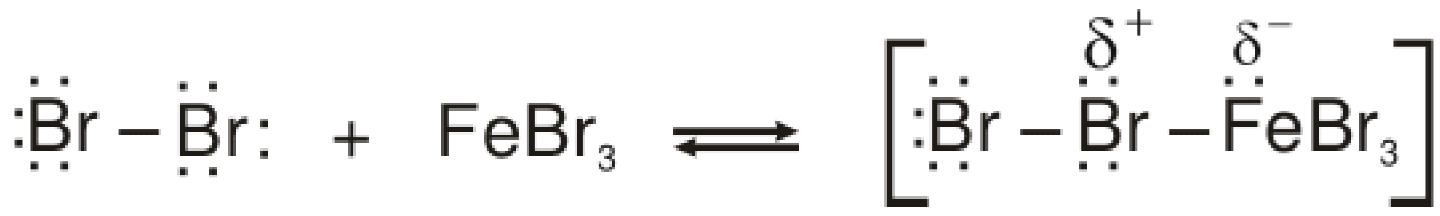
Aromatic Compounds

Electrophilic aromatic substitution :

(a) Bromination of Benzene :

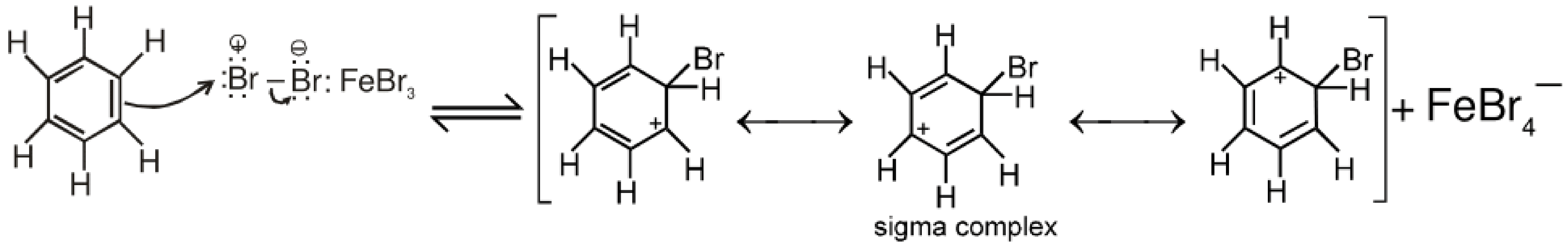
Bromination follows the general mechanism for electrophilic aromatic substitution. Bromine itself is not sufficiently electrophilic to react with benzene, but a strong Lewis acid such as $FeBr_3$ catalyzes the reaction.

Step 1 : Formation of a stronger electrophile.

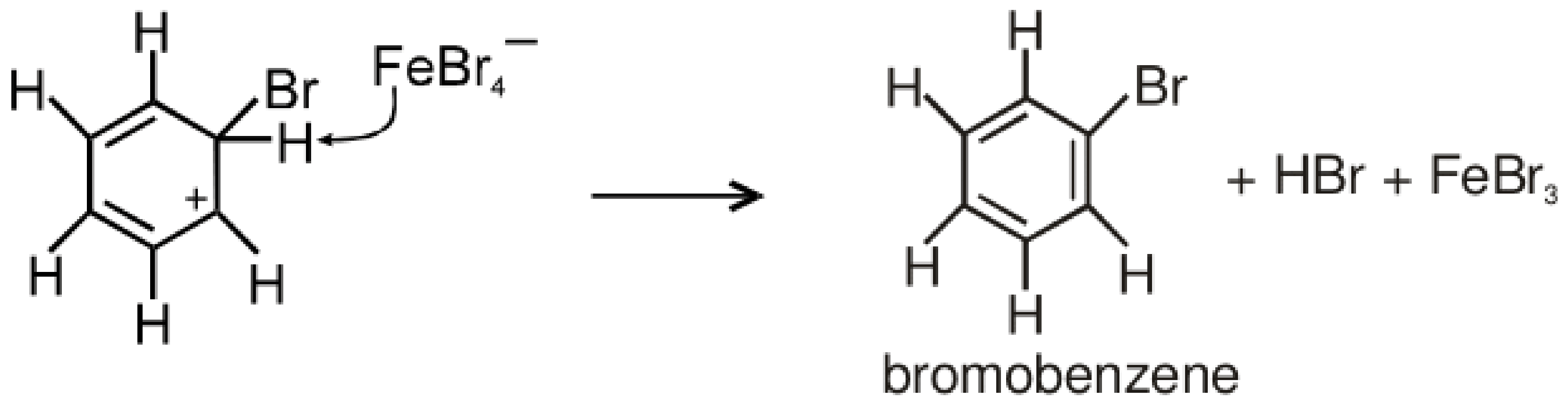


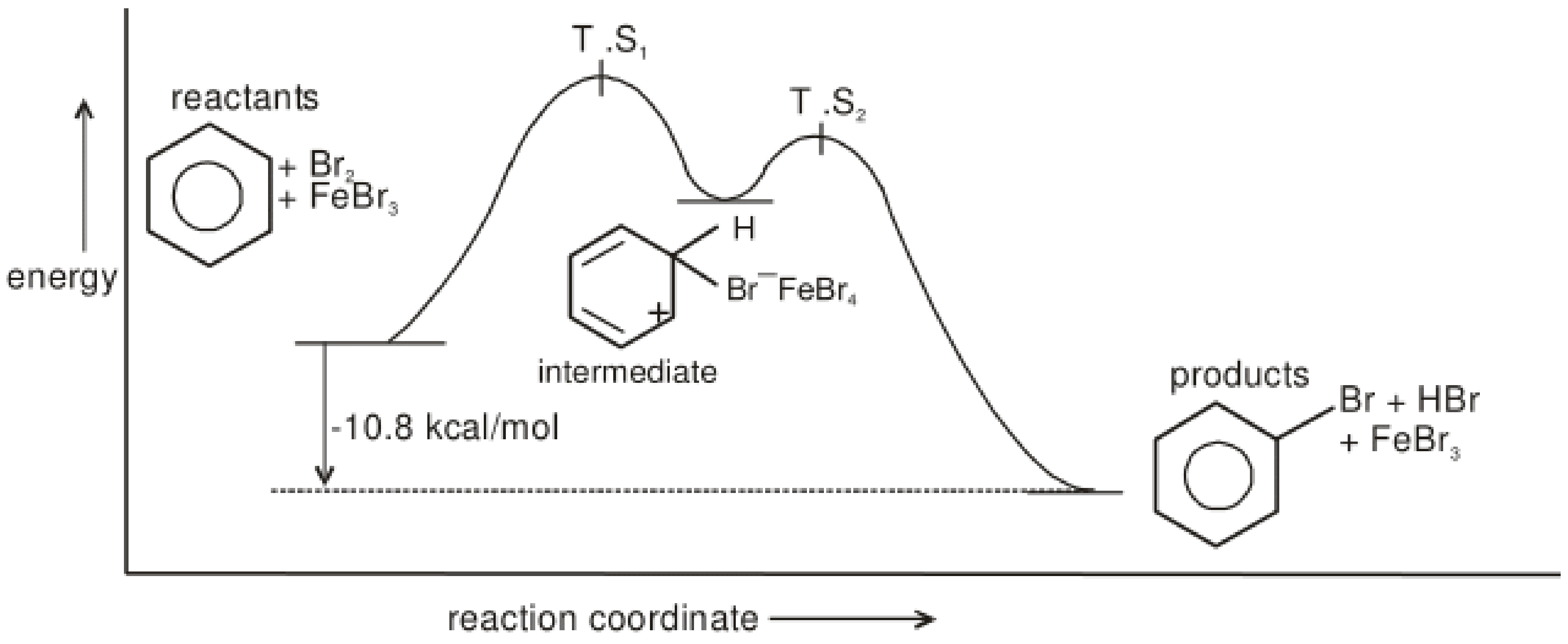
$$:\ddot{\underset{..}{Br}}-\ddot{\underset{..}{Br}}: + FeBr_3 \rightleftharpoons \left[:\ddot{\underset{..}{Br}}-\overset{\delta^+}{\ddot{\underset{..}{Br}}}-\overset{\delta^-}{FeBr_3}\right]$$

Step 2 : Electrophilic attack and formation of the sigma complex.

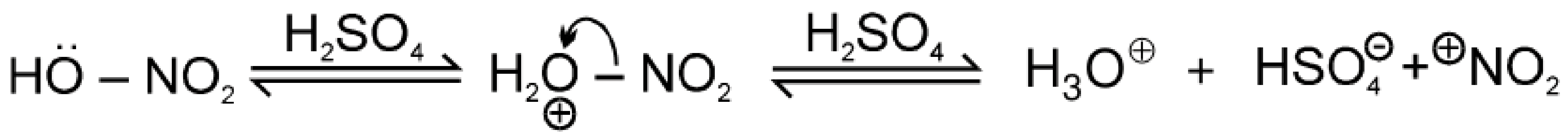


Step 3 : Loss of a proton gives the products.

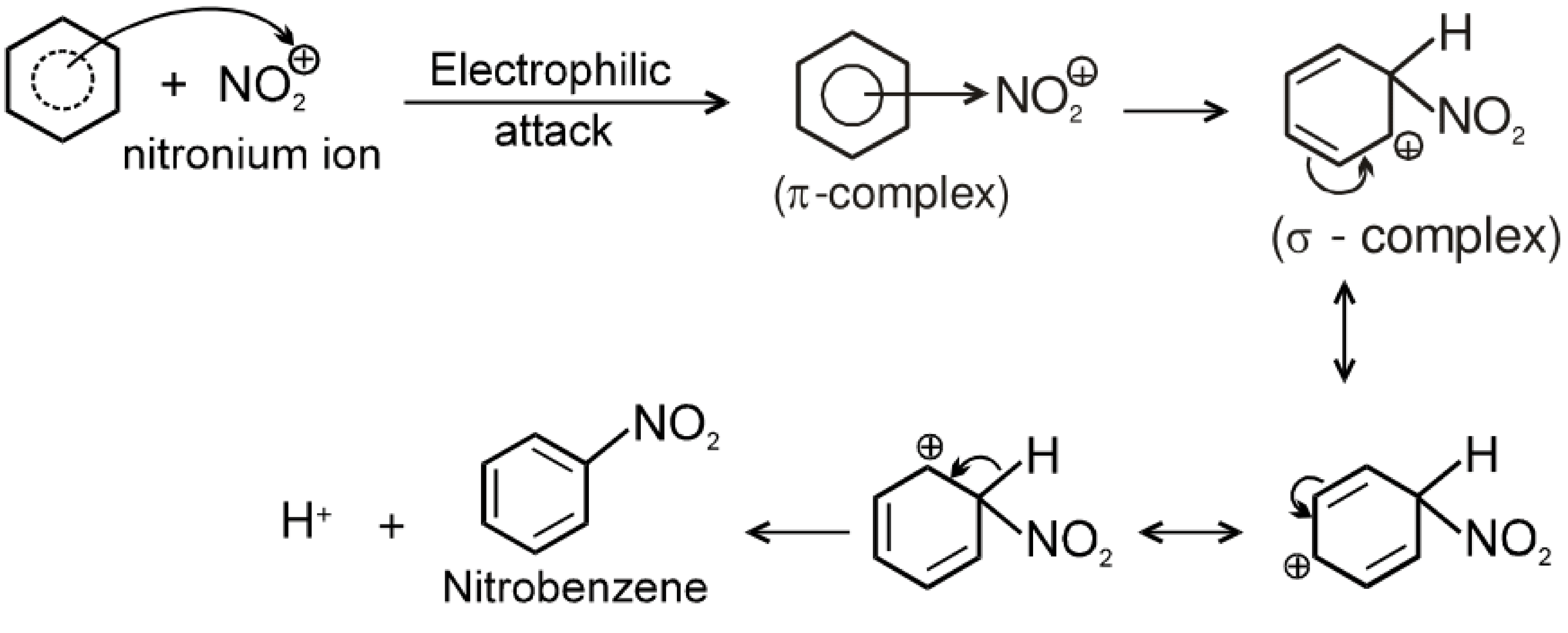




(b) Nitration :



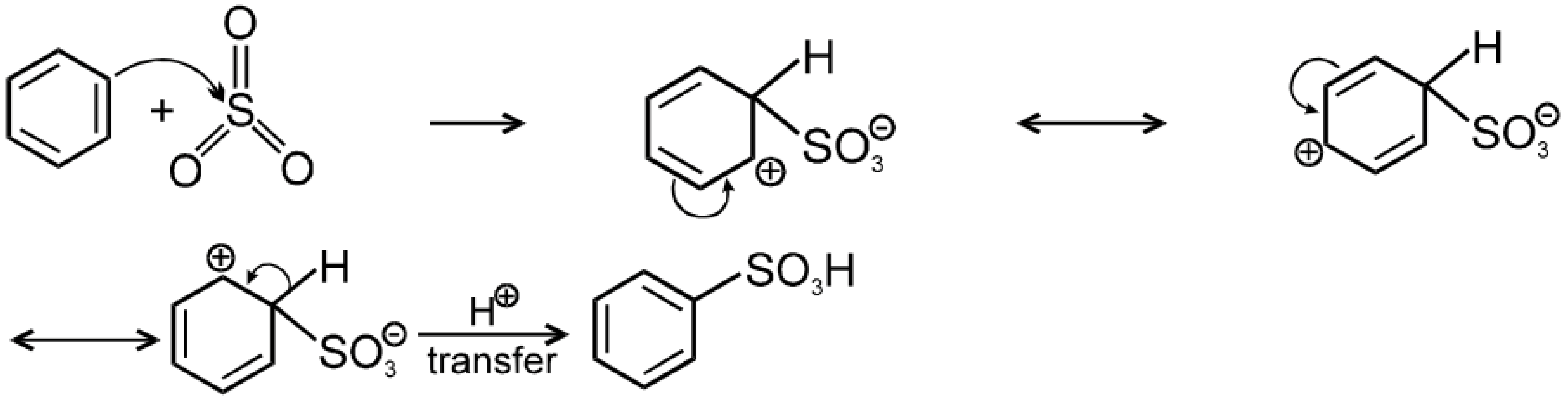
$$H\ddot{O}-NO_2 \underset{}{\overset{H_2SO_4}{\rightleftharpoons}} H_2\underset{\oplus}{O}-NO_2 \overset{H_2SO_4}{\rightleftharpoons} H_3O^{\oplus} + HSO_4^{\ominus} + {}^{\oplus}NO_2$$



(c) Sulphonation :

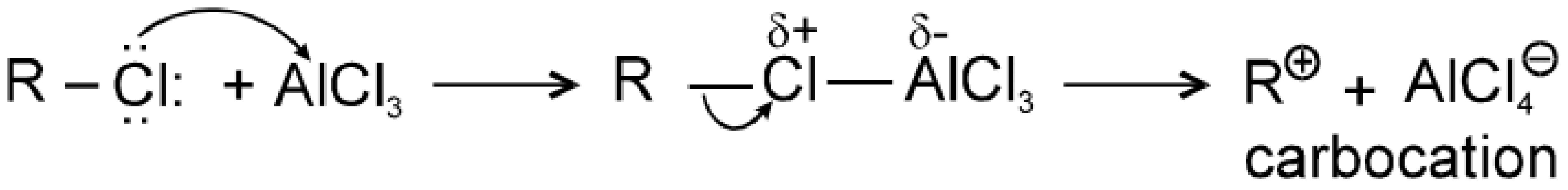
The electrophilic reagent, SO_3, attacks the benzene ring to form the intermediate carbocation.

$$2H_2SO_4 \rightleftharpoons SO_3 + H_3O^{\oplus} + SO_4^{\ominus}$$

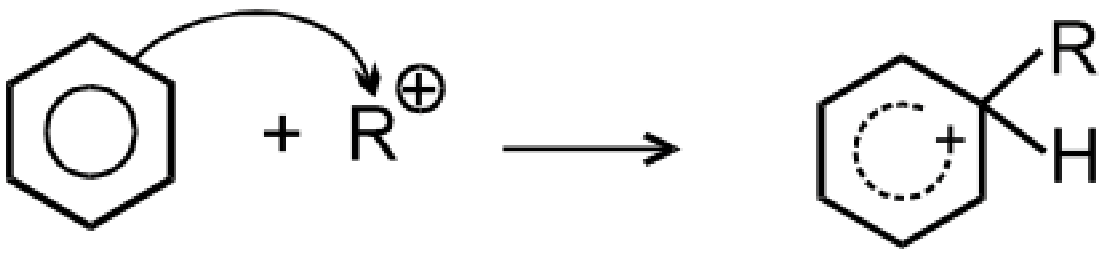


(d) Friedel Craft reaction :

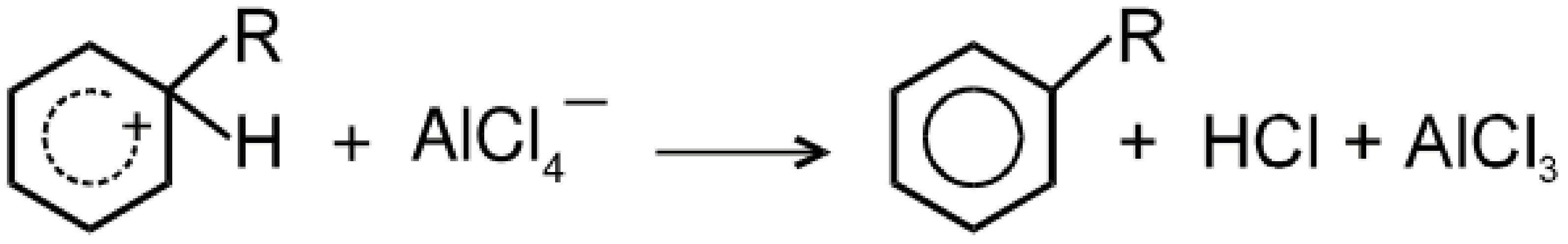
Alkylation mechanism :

(i) 

$$R-\ddot{\underset{\cdot\cdot}{Cl}}: + AlCl_3 \longrightarrow R-\overset{\delta+}{Cl}-\overset{\delta-}{AlCl_3} \longrightarrow R^{\oplus} + AlCl_4^{\ominus}$$

(ii) 

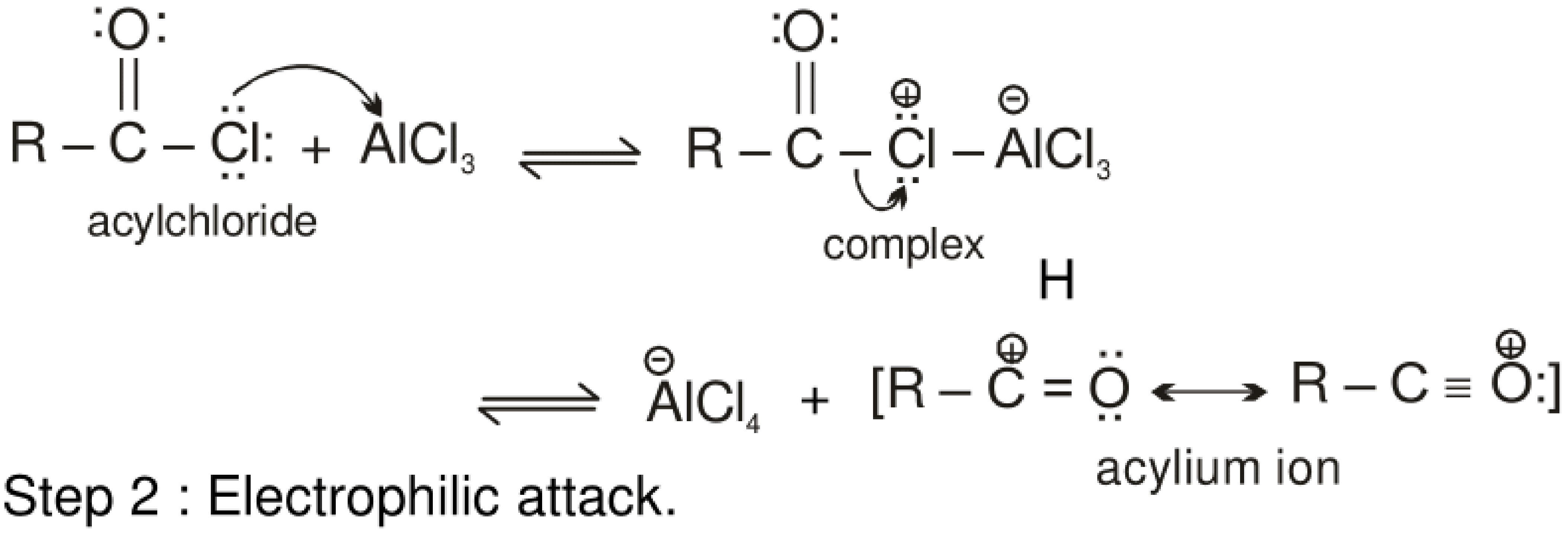
σ-complex

(iii) 

Acylation mechanism :

Acylation of benzene may be brought about with acid chlorides or anhydrides in presence of Lewis acids.

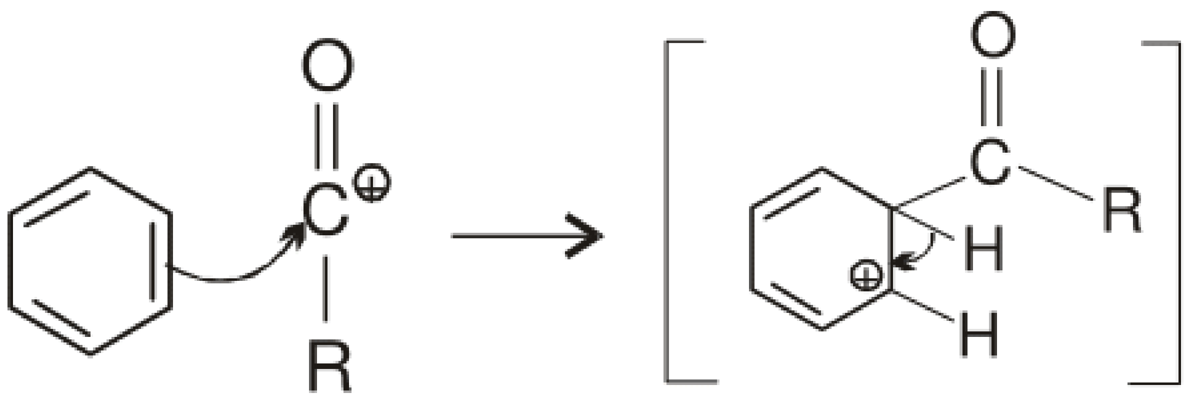
Step 1 : Formation of an acylium ion.



$$R-\overset{\overset{:O:}{||}}{C}-\ddot{\underset{\cdot\cdot}{Cl}}: + AlCl_3 \rightleftharpoons R-\overset{\overset{:O:}{||}}{C}-\overset{\oplus}{\ddot{Cl}}-\overset{\ominus}{AlCl_3}$$

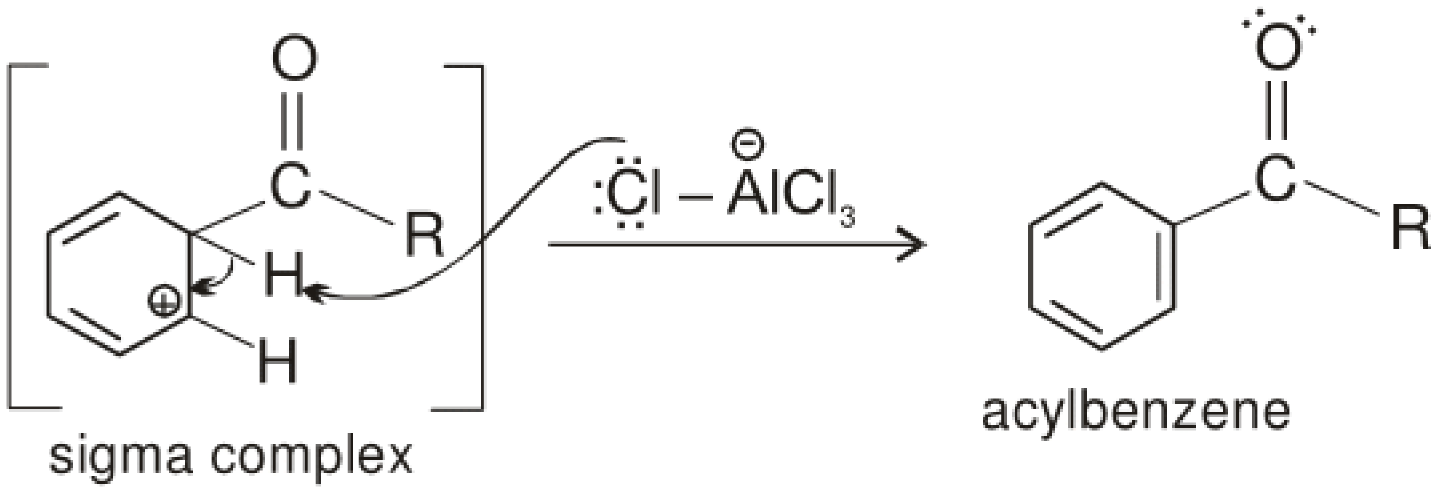
$$\rightleftharpoons \overset{\ominus}{AlCl_4} + [R-\overset{\oplus}{C}=\ddot{\underset{\cdot\cdot}{O}} \longleftrightarrow R-C\equiv\overset{\oplus}{O}:]$$

Step 2 : Electrophilic attack.

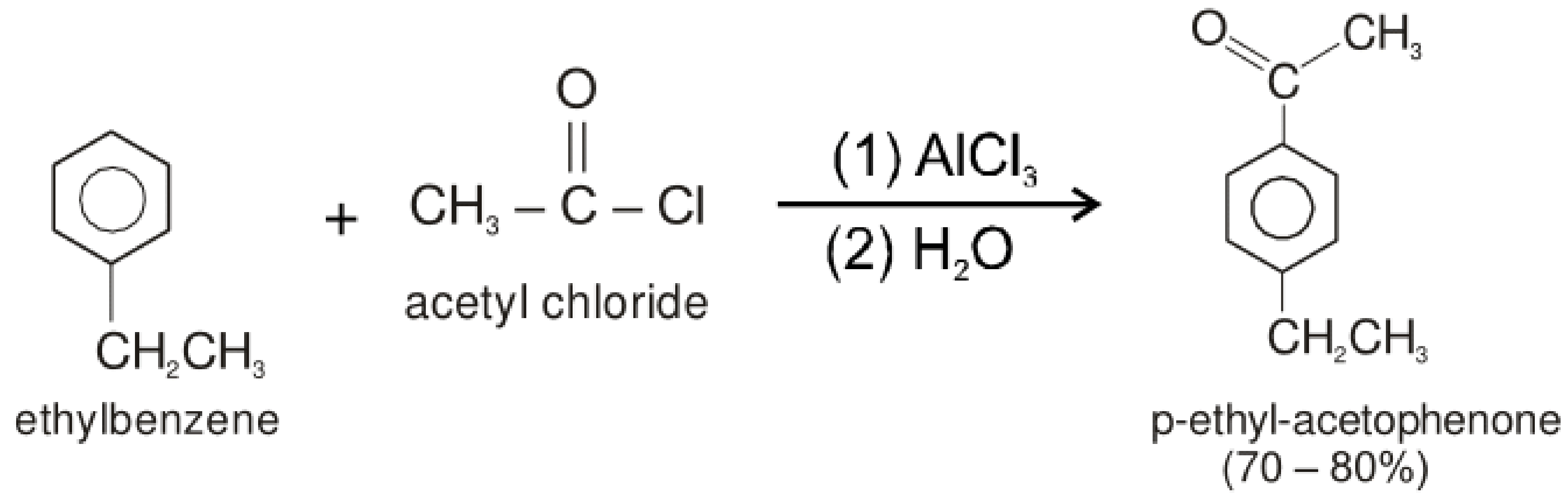


sigma complex

Step 3 : Loss of a proton. Complexation of the product.

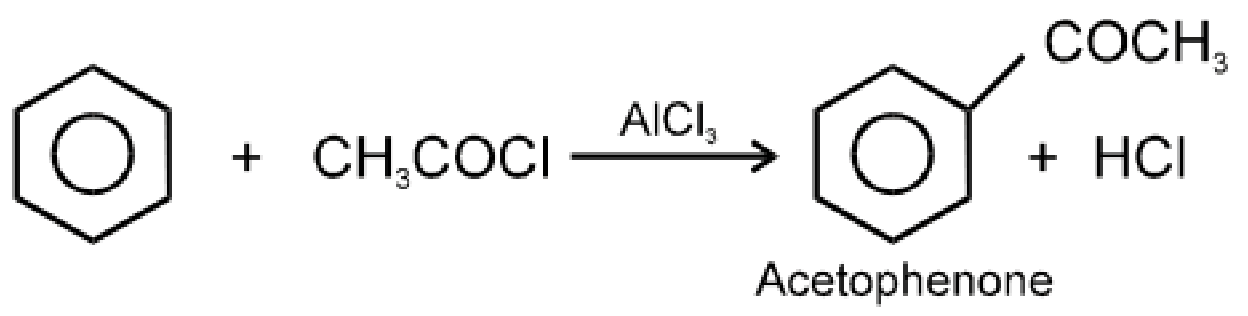


e.g.

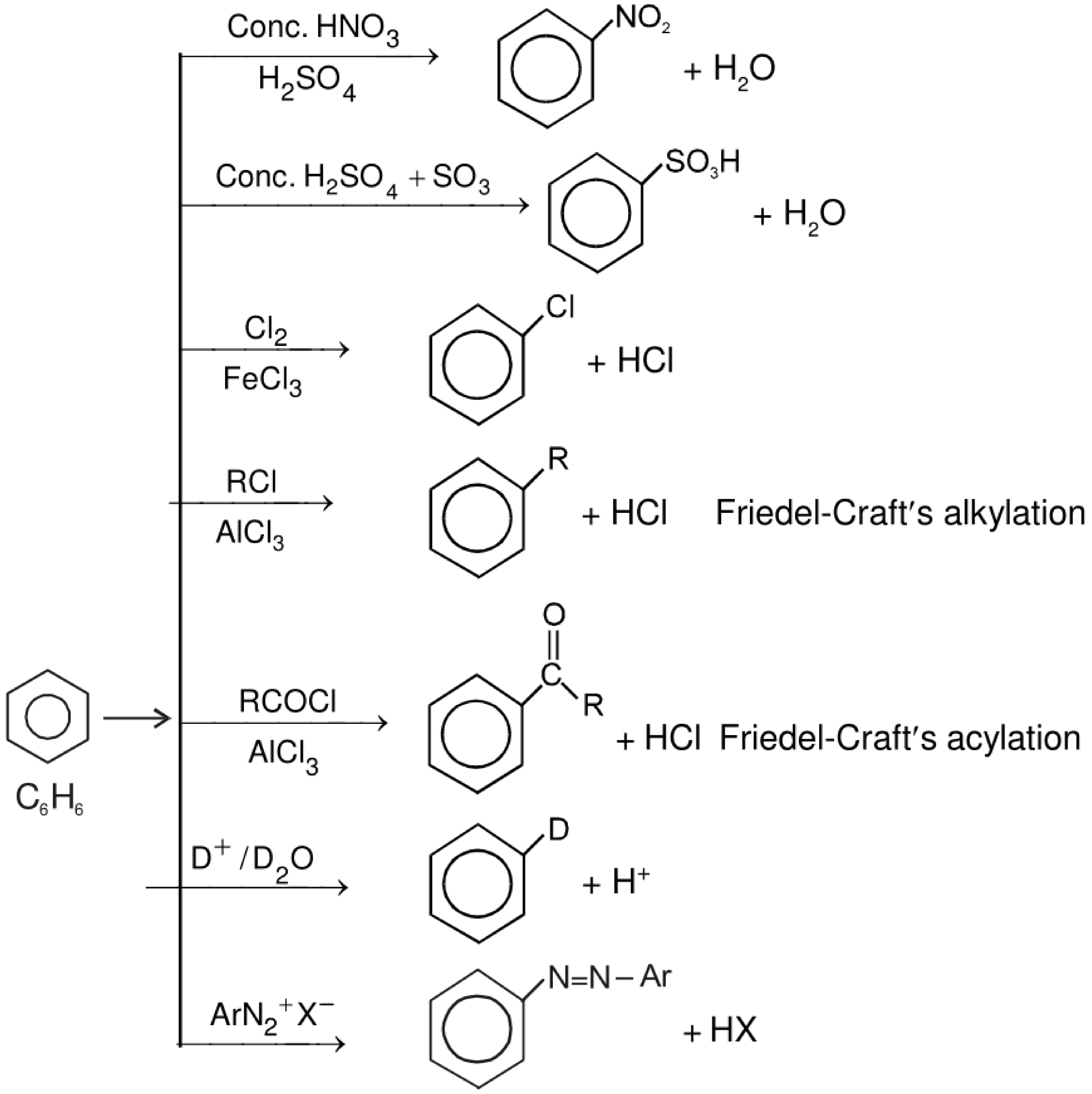


Note : Friedel-Crafts acylations are generally free from rearrangements and multiple substitution. They do not go on strongly deactivated rings.

e.g.

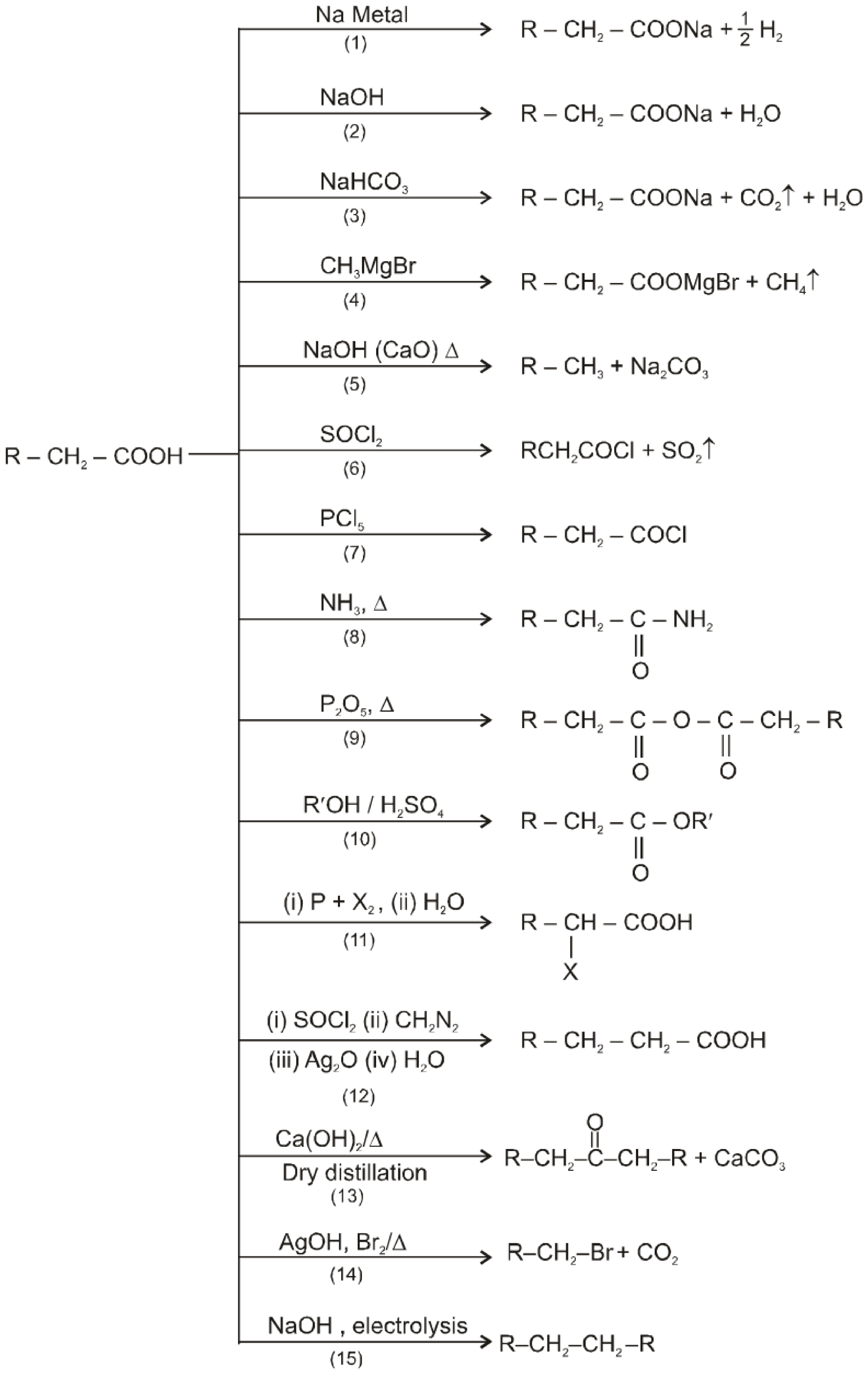


Chemical Reactions of Benzene :



Carboxylic Acid & Derivatives

Summary of reactions of carboxylic acids :



$$R-CH_2-COOH \xrightarrow[(1)]{\text{Na Metal}} R-CH_2-COONa + \tfrac{1}{2}H_2$$

$$\xrightarrow[(2)]{NaOH} R-CH_2-COONa + H_2O$$

$$\xrightarrow[(3)]{NaHCO_3} R-CH_2-COONa + CO_2\uparrow + H_2O$$

$$\xrightarrow[(4)]{CH_3MgBr} R-CH_2-COOMgBr + CH_4\uparrow$$

$$\xrightarrow[(5)]{NaOH\ (CaO)\ \Delta} R-CH_3 + Na_2CO_3$$

$$\xrightarrow[(6)]{SOCl_2} RCH_2COCl + SO_2\uparrow$$

$$\xrightarrow[(7)]{PCl_5} R-CH_2-COCl$$

$$\xrightarrow[(8)]{NH_3,\ \Delta} R-CH_2-\underset{\underset{O}{\|}}{C}-NH_2$$

$$\xrightarrow[(9)]{P_2O_5,\ \Delta} R-CH_2-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-CH_2-R$$

$$\xrightarrow[(10)]{R'OH\ /\ H_2SO_4} R-CH_2-\underset{\underset{O}{\|}}{C}-OR'$$

$$\xrightarrow[(11)]{(i)\ P + X_2,\ (ii)\ H_2O} R-\underset{\underset{X}{|}}{CH}-COOH$$

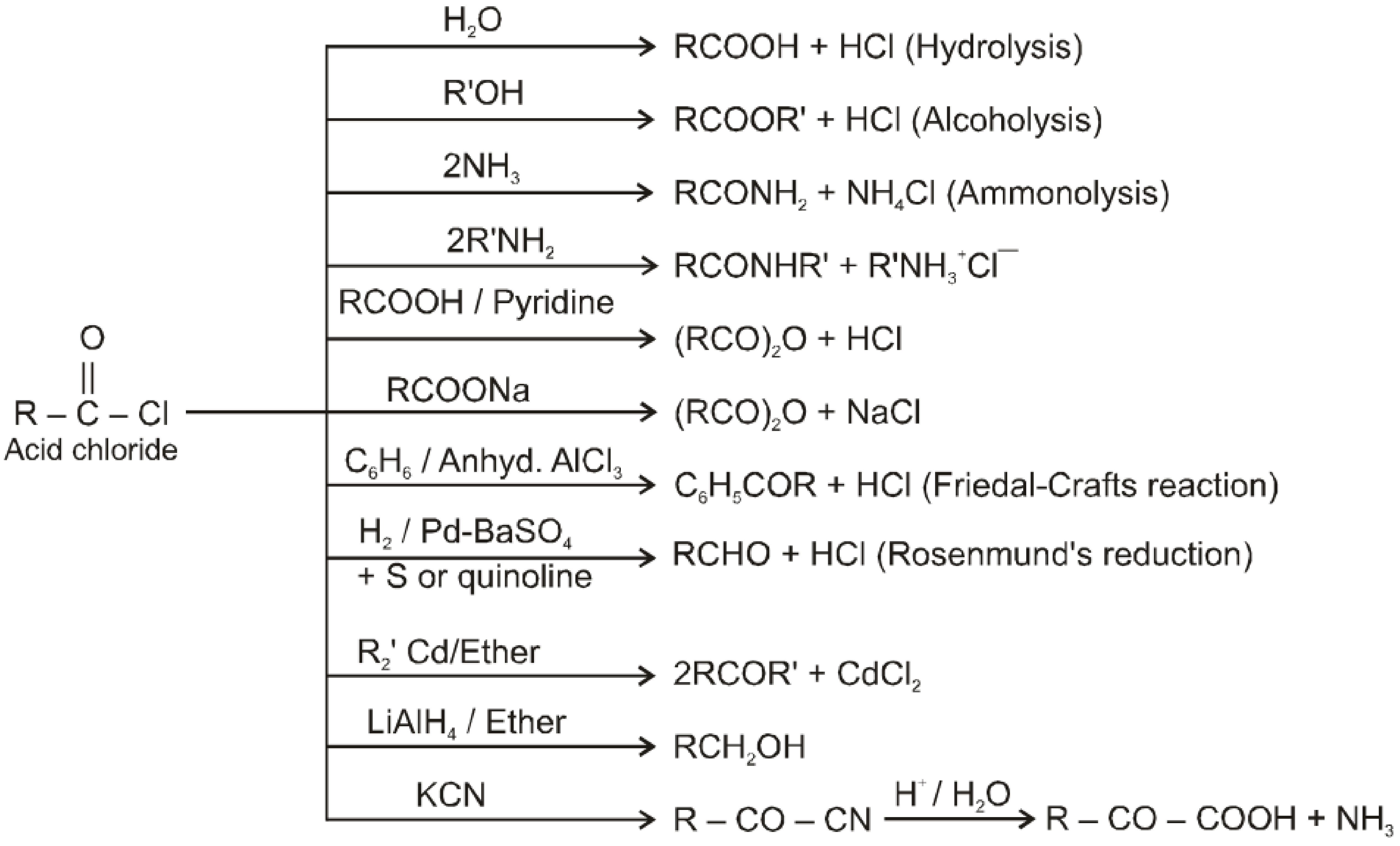
$$\xrightarrow[\text{(iii) }Ag_2O\text{ (iv) }H_2O\ (12)]{\text{(i) }SOCl_2\text{ (ii) }CH_2N_2} R-CH_2-CH_2-COOH$$

$$\xrightarrow[\text{Dry distillation (13)}]{Ca(OH)_2/\Delta} R-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-R + CaCO_3$$

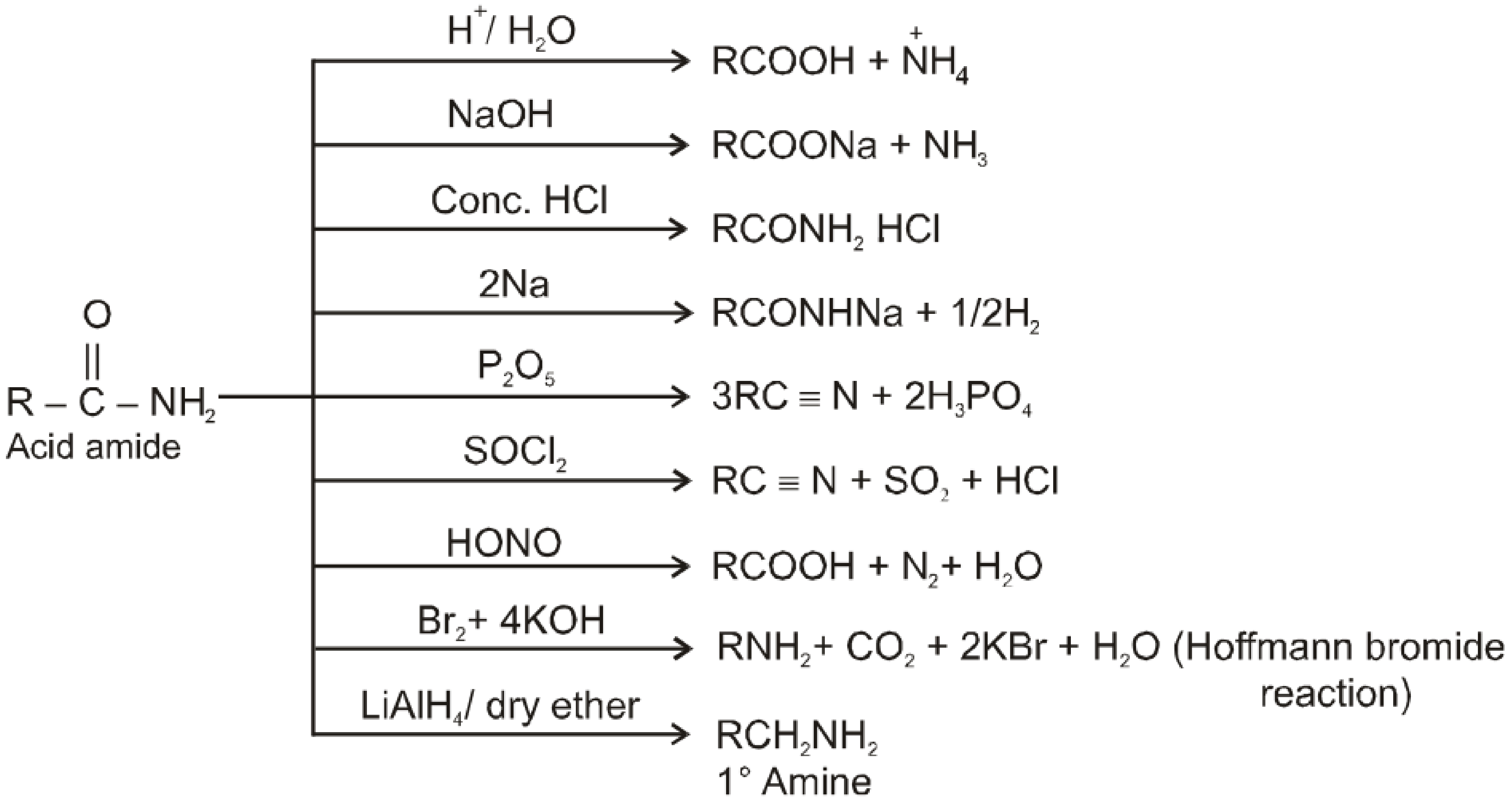
$$\xrightarrow[(14)]{AgOH,\ Br_2/\Delta} R-CH_2-Br + CO_2$$

$$\xrightarrow[(15)]{NaOH\ ,\ \text{electrolysis}} R-CH_2-CH_2-R$$

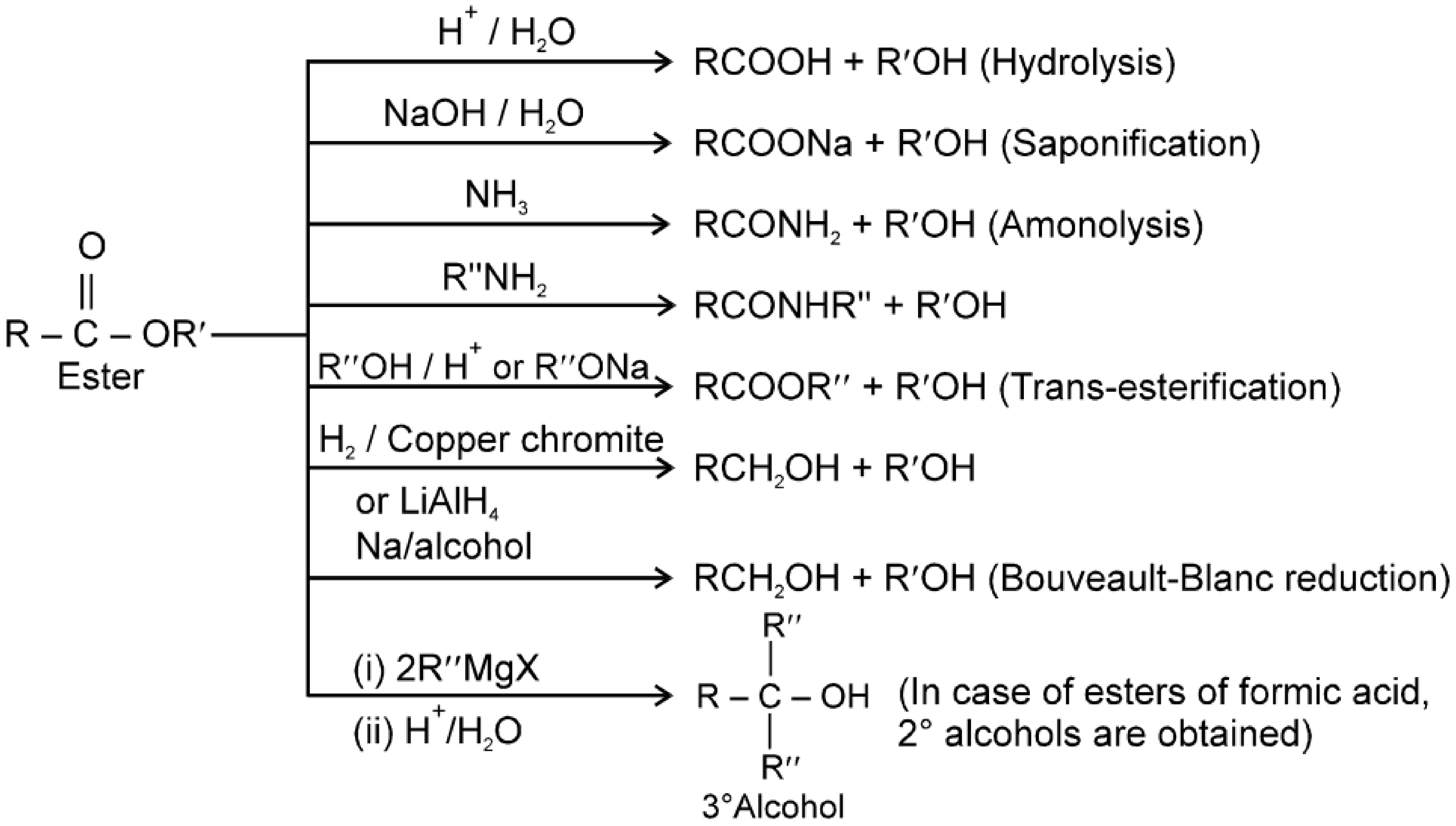
Summary of reactions of acid halide



Summary of reaction of amide:



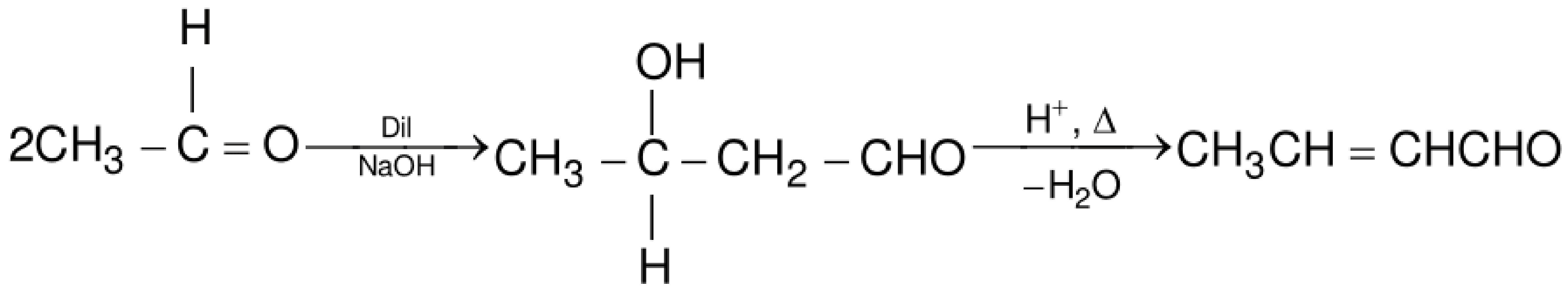
Summary of reaction of esters :



Aldehydes & Ketones

Aldol condensation :

Carbonyl compounds having acidic sp^3 α-H shows this reaction in presence of dil. NaOH or dil. acid.



$$2CH_3-\overset{\overset{\large H}{|}}{C}=O \xrightarrow[NaOH]{Dil} CH_3-\underset{\underset{\large H}{|}}{\overset{\overset{\large OH}{|}}{C}}-CH_2-CHO \xrightarrow[-H_2O]{H^+,\ \Delta} CH_3CH=CHCHO$$

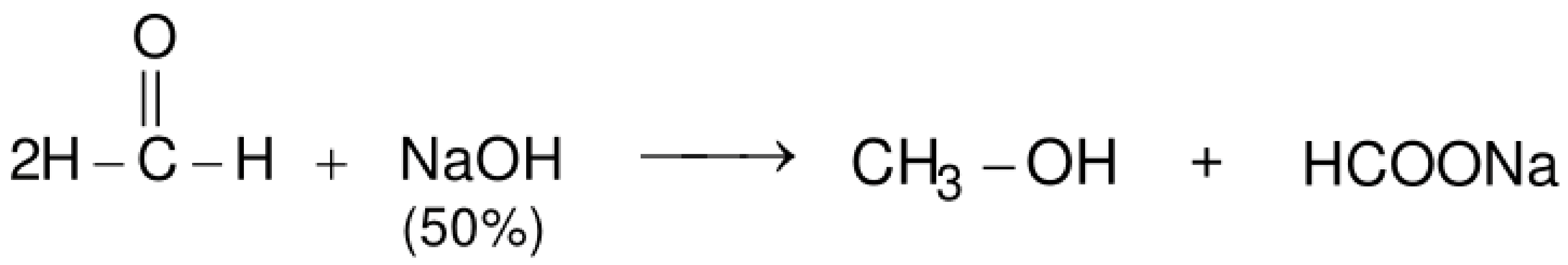
Crossed aldol condensation

(i) $CH_3CHO + HCHO \xrightarrow{\text{Dil. NaOH}} HOCH_2\text{–}CH_2\text{–}CHO \xrightarrow[\Delta]{H^+\ /\ H_2O} CH_2\text{=}CH\text{–}CHO$

(ii) $CH_3COCH_3 + HCHO \xrightarrow{\text{Dil. NaOH}} CH_3CO\text{–}CH_2CH_2OH \xrightarrow[\Delta]{H^+\ /\ H_2O}$ $CH_3CO\text{–}CH\text{=}CH_2$

Cannizzaro reaction :

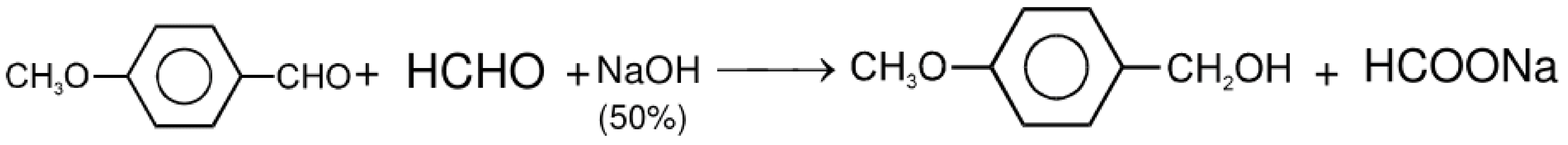
Carbonyl compounds not having sp^3α-H shows following disproportion reaction



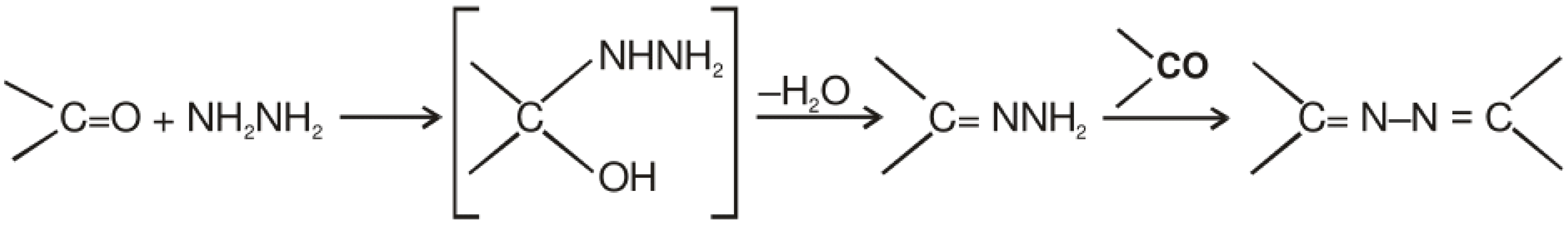
$$2H-\overset{\overset{\large O}{||}}{C}-H + \underset{(50\%)}{NaOH} \longrightarrow CH_3-OH + HCOONa$$

$$2C_6H_5CHO + \underset{(50\%)}{NaOH} \longrightarrow C_6H_5CH_2OH + C_6H_5COONa$$

Crossed Cannizzaro reaction :



Formation of hydrzones and azines



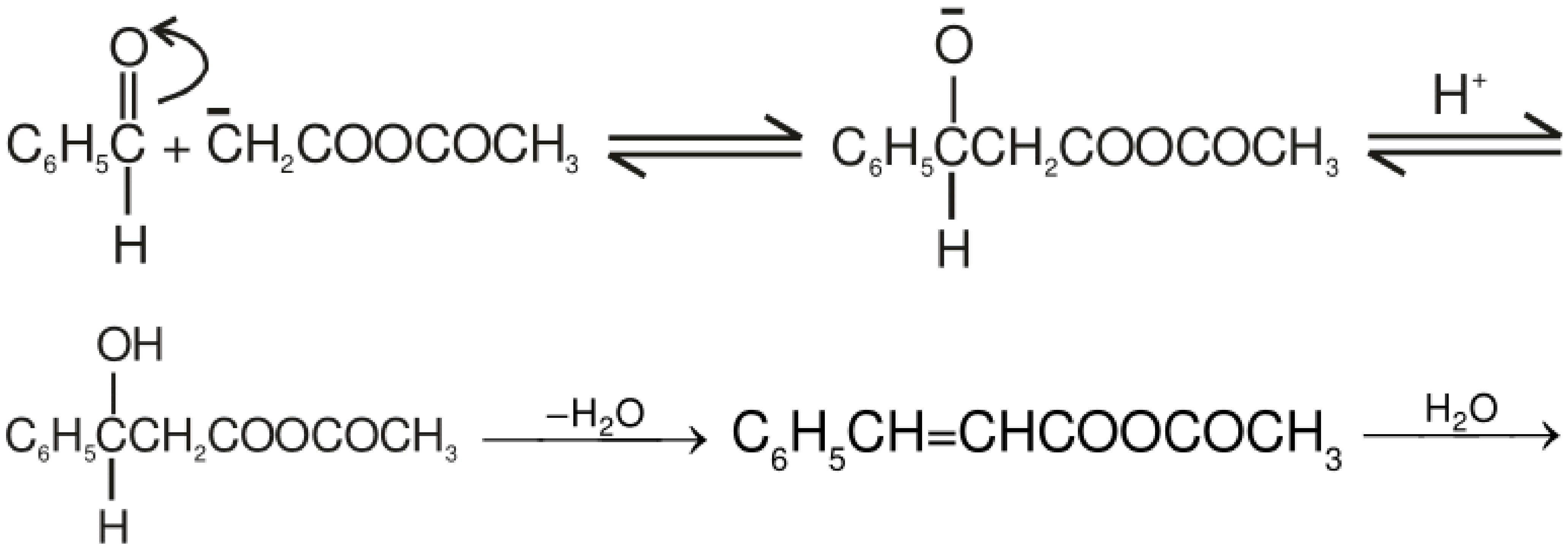
Perkin reaction :

When benzaldehyde (or any other aromatic aldehyde) is heated with the anhydride of an aliphatic acid (containing two α-hydrogen atoms) in the presence of its sodium salt, condensation takes place to form a β-arylacrylic acid ; e.g., with acetic anhydride and sodium acetate, cinnamic acid is formed.

$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3CO_2Na} C_6H_5CH = CHCO_2H$$

Mechanism :

$$CH_3COOCOCH_3 + CH_3CO_2^- \rightleftharpoons \bar{C}H_2COOCOCH_3 + CH_3CO_2H$$



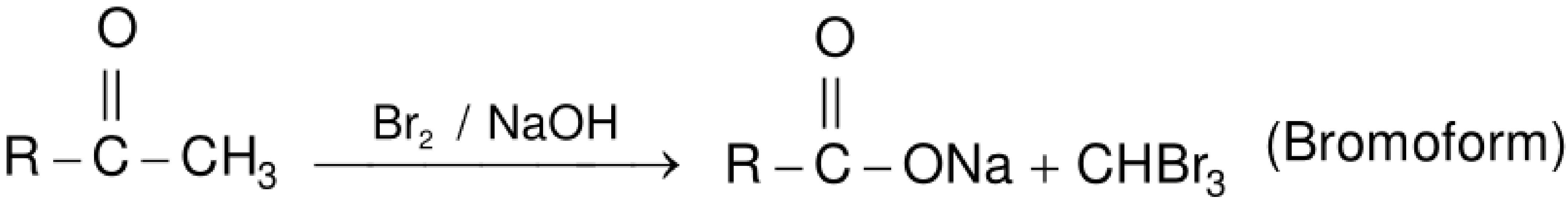
$$C_6H_5\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{C}} + \bar{C}H_2COOCOCH_3 \rightleftharpoons C_6H_5\overset{\overset{\bar{O}}{|}}{\underset{\underset{H}{|}}{C}}CH_2COOCOCH_3 \xrightleftharpoons{H^+}$$

$$C_6H_5\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}CH_2COOCOCH_3 \xrightarrow{-H_2O} C_6H_5CH{=}CHCOOCOCH_3 \xrightarrow{H_2O}$$

$$C_6H_5CH = CHCO_2H + CH_3CO_2H$$

Haloform reaction :

Acetaldehyde and methylalkyl ketones react rapidly with halogen (Cl_2, Br_2 or I_2) in the presence of alkali to give haloform and acid salt.

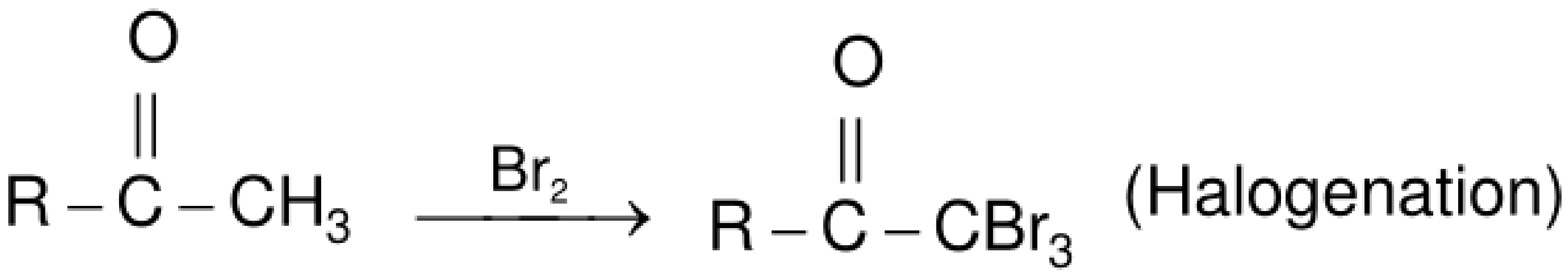


$$R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{Br_2\ /\ NaOH} R-\overset{\overset{O}{\|}}{C}-ONa + CHBr_3 \quad \text{(Bromoform)}$$

In this reaction $-CH_3$ of $CH_3-\overset{\overset{O}{\|}}{C}-$ group is converted into haloform as it contains acidic hydrogen atom and rest-part of alkyl methyl ketone give acid salt having carbon atom corresponding to alkyl ketone.

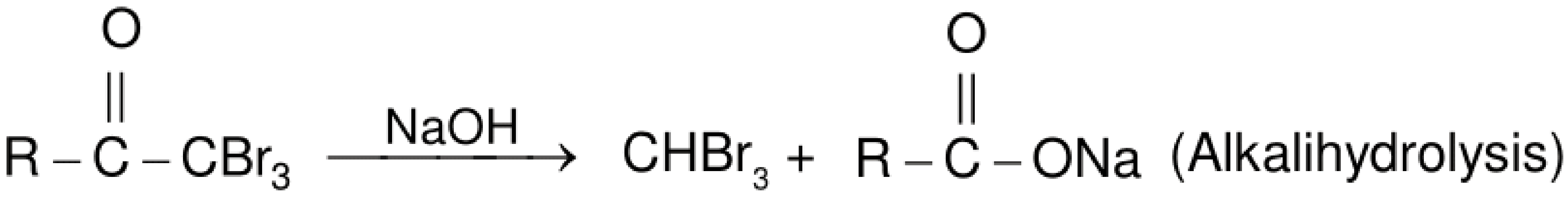
Preparation of haloform from methylketone involves two steps.

(a) Halogenation



$$R-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{Br_2} R-\overset{\overset{O}{\|}}{C}-CBr_3 \quad \text{(Halogenation)}$$

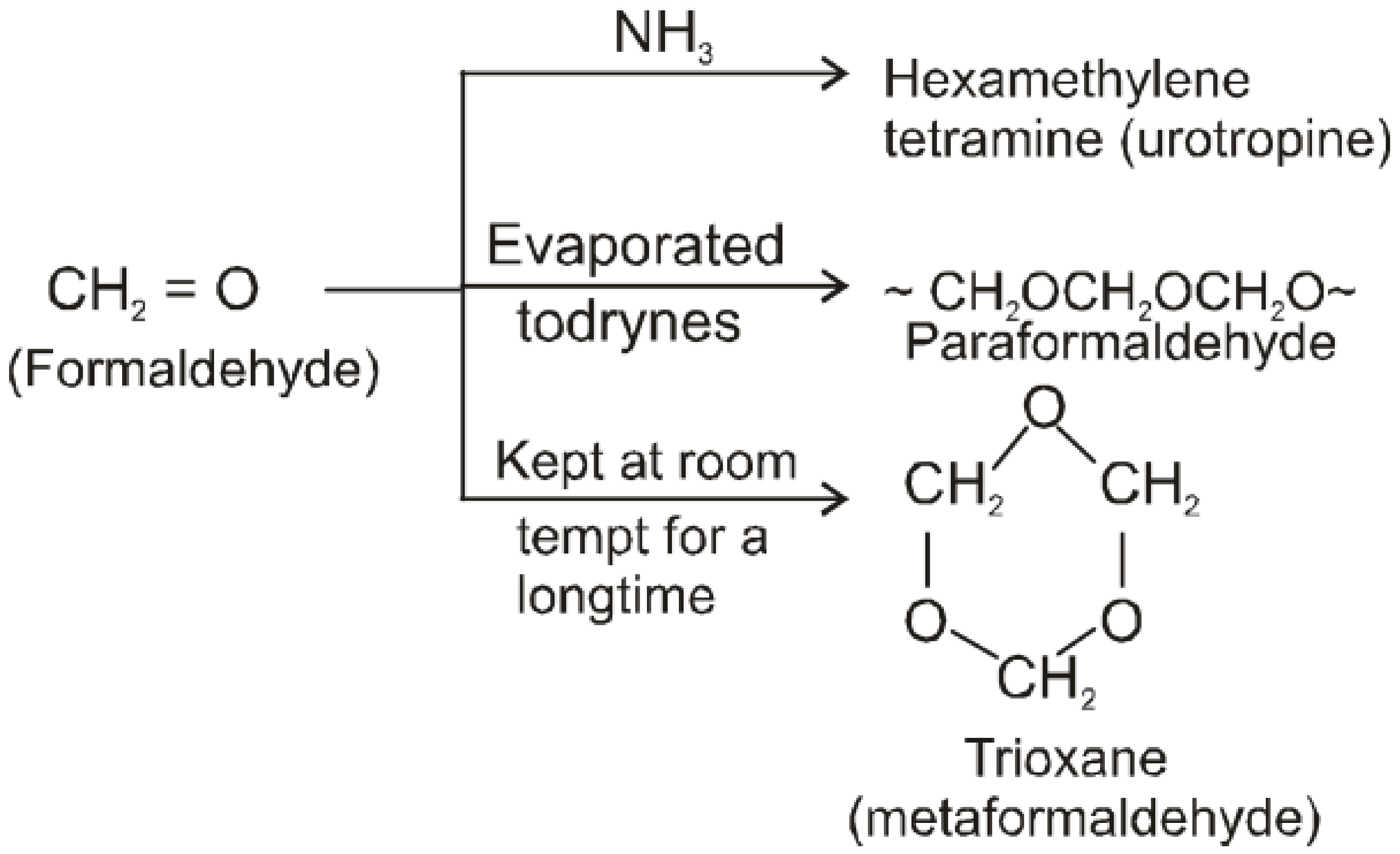
(b) Alkalihydrolysis

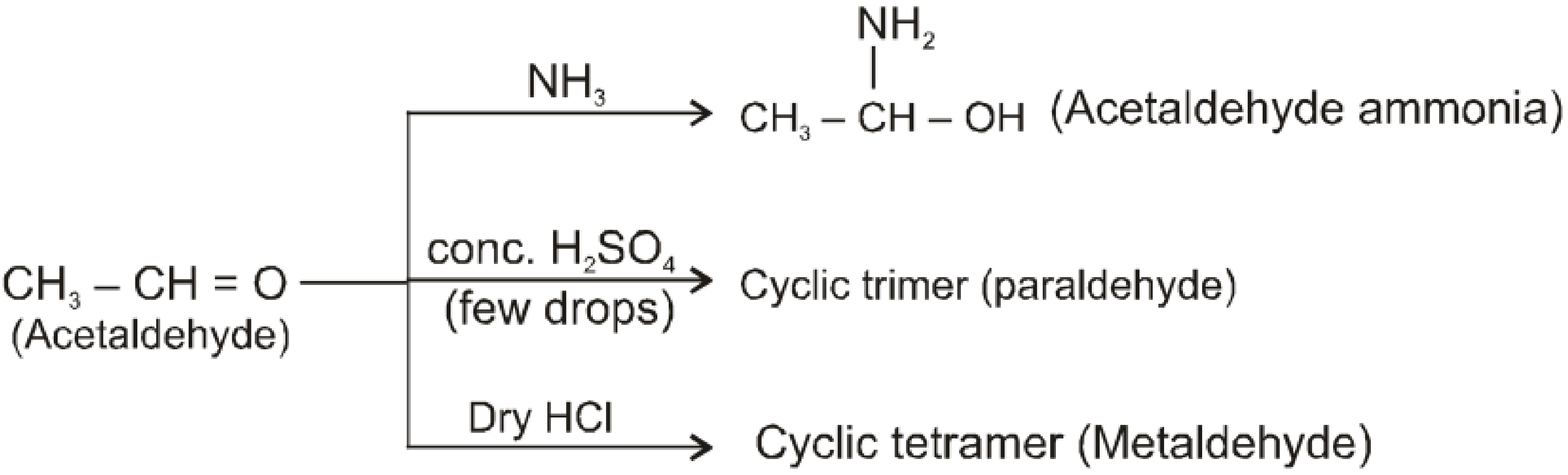


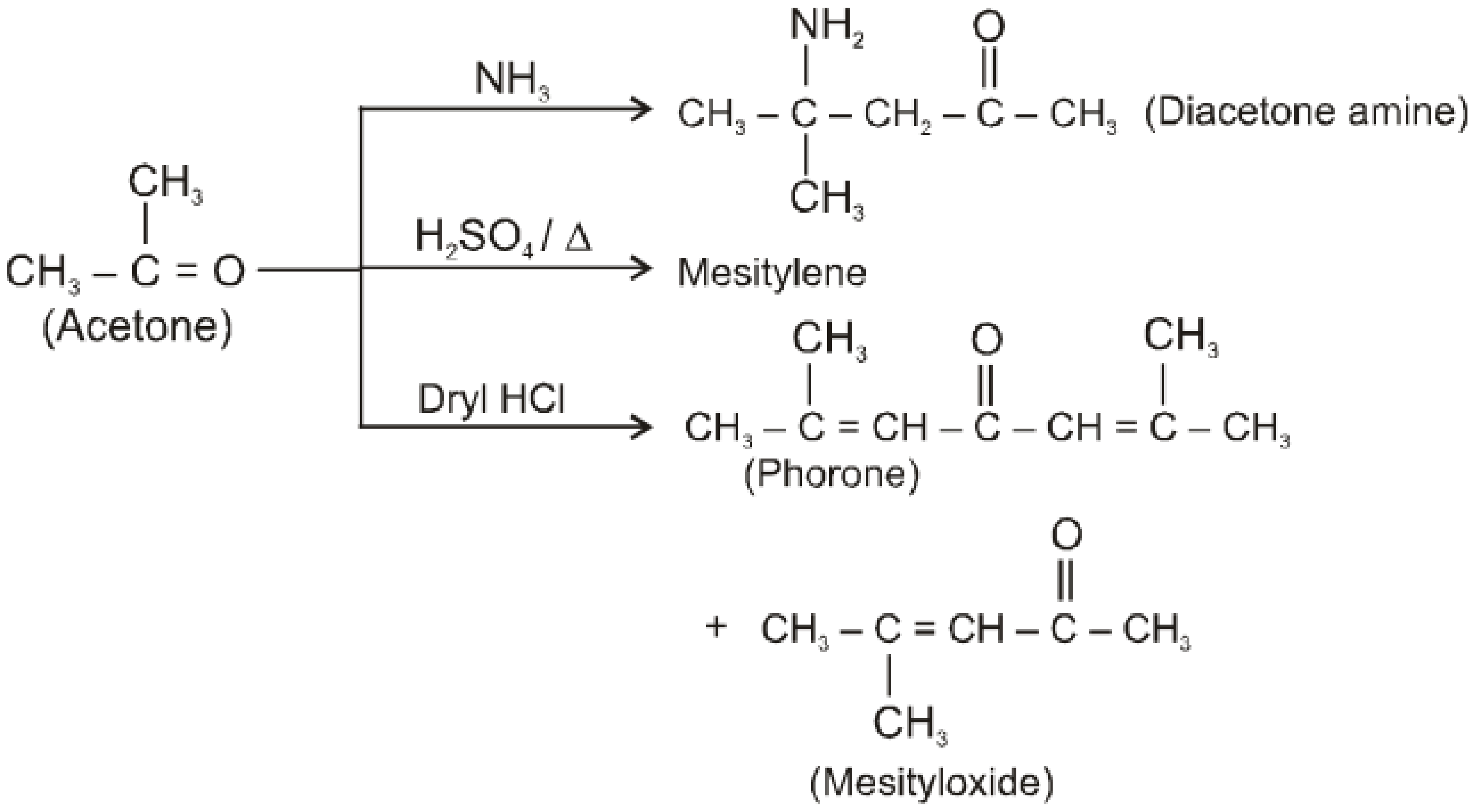
$$R-\overset{\overset{\displaystyle O}{||}}{C}-CBr_3 \xrightarrow{NaOH} CHBr_3 + R-\overset{\overset{\displaystyle O}{||}}{C}-ONa \text{ (Alkalihydrolysis)}$$

Note : This reaction is used to distinguish the presence of $CH_3-\overset{\overset{\displaystyle O}{||}}{C}-$ group.

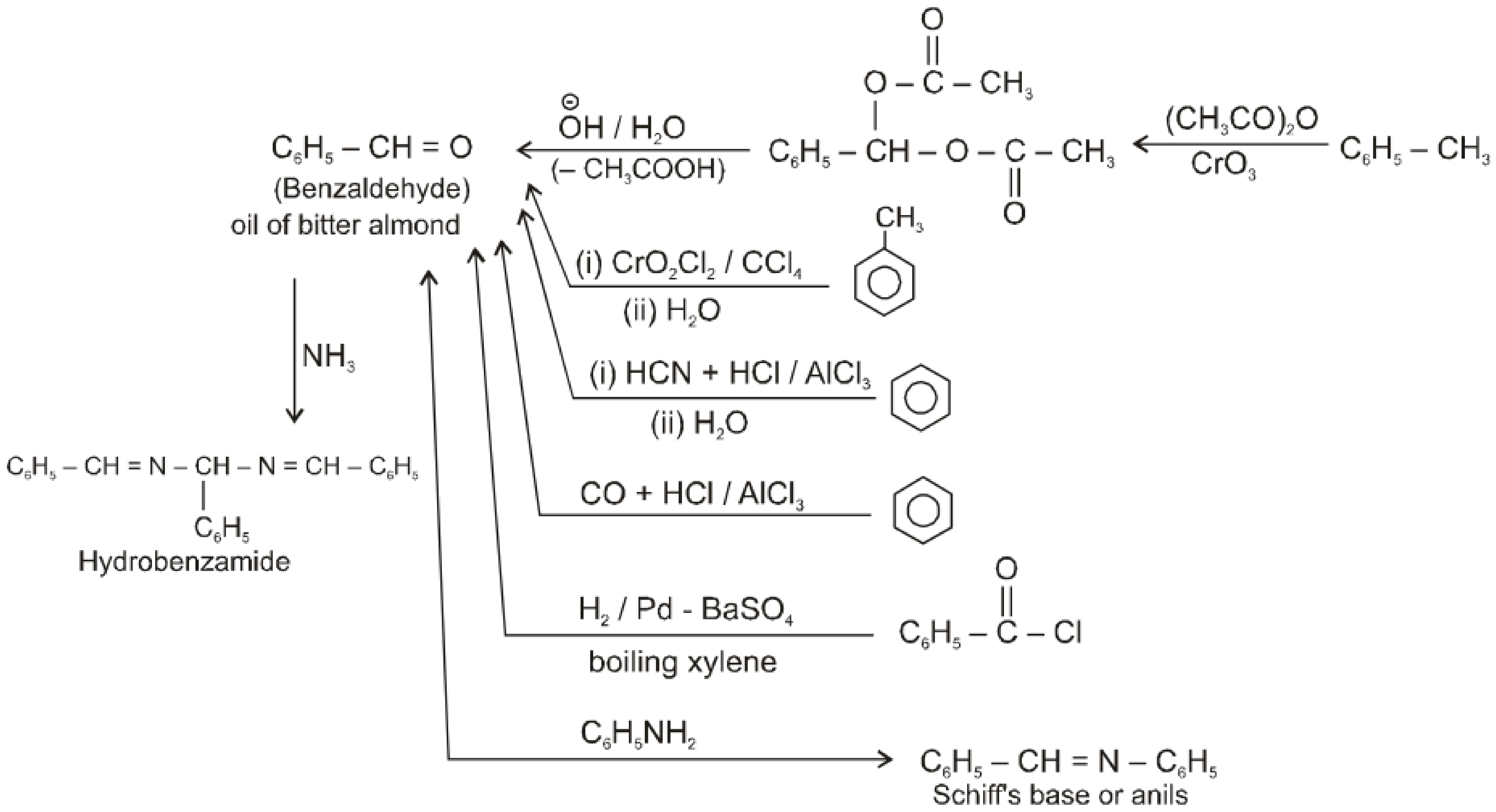
Other reactions :

(1) 

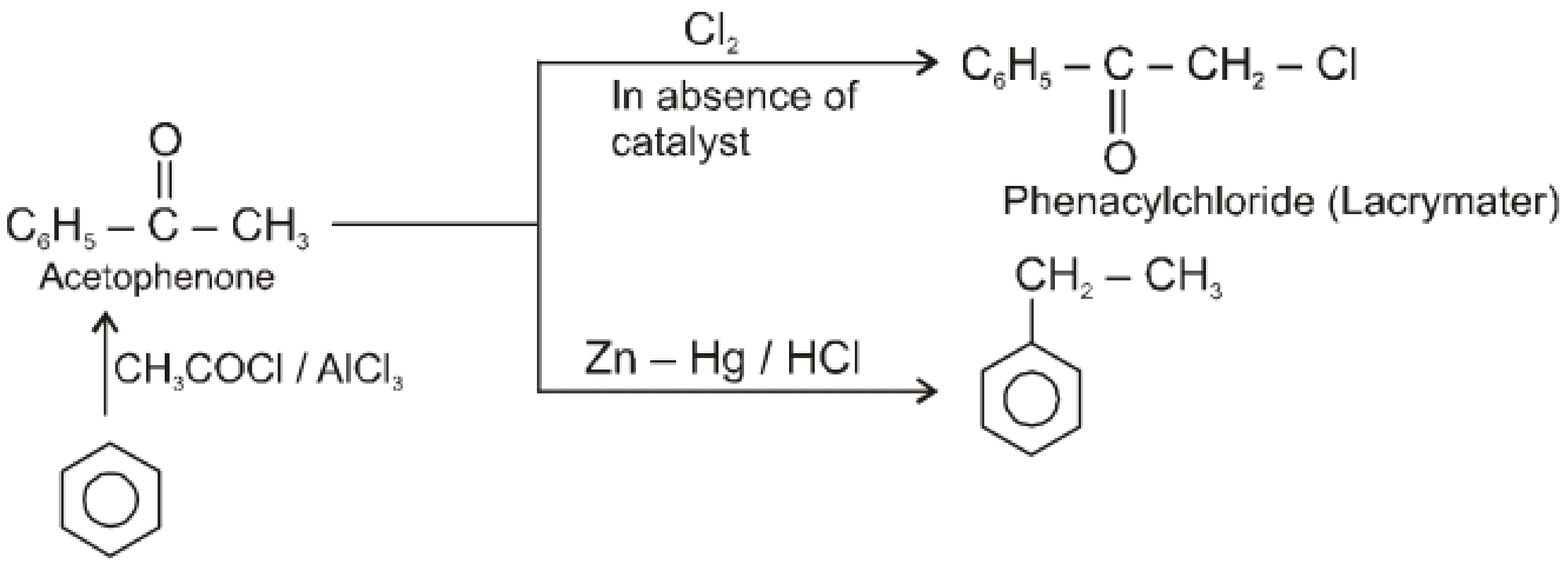
(2) 

(3) 

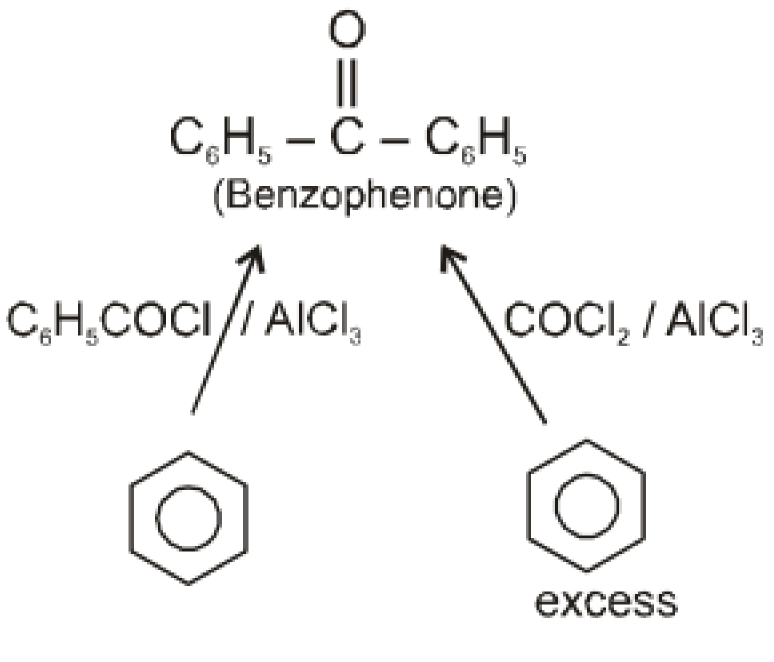
(4)


$C_6H_5-CH=O$
(Benzaldehyde)
oil of bitter almond
$\overset{\ominus}{O}H / H_2O$
$(-CH_3COOH)$
$C_6H_5-CH(O-CO-CH_3)-O-CO-CH_3$
$(CH_3CO)_2O$
CrO_3
$C_6H_5-CH_3$
(i) CrO_2Cl_2 / CCl_4
(ii) H_2O
CH_3
(i) HCN + HCl / $AlCl_3$
(ii) H_2O
CO + HCl / $AlCl_3$
H_2 / Pd - $BaSO_4$
boiling xylene
$C_6H_5-CO-Cl$
NH_3
$C_6H_5-CH=N-CH(C_6H_5)-N=CH-C_6H_5$
Hydrobenzamide
$C_6H_5NH_2$
$C_6H_5-CH=N-C_6H_5$
Schiff's base or anils

(5)


$C_6H_5-CO-CH_3$
Acetophenone
$CH_3COCl / AlCl_3$
Cl_2
In absence of
catalyst
$C_6H_5-CO-CH_2-Cl$
Phenacylchloride (Lacrymater)
Zn – Hg / HCl
CH_2-CH_3

(6)


$C_6H_5-CO-C_6H_5$
(Benzophenone)
C_6H_5COCl / $AlCl_3$
$COCl_2 / AlCl_3$
excess

Oxidation Reaction

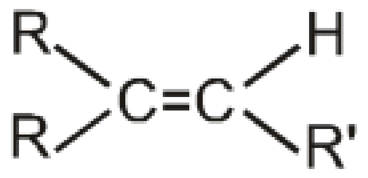
(1) $KMnO_4$ (in both medium) or
$K_2Cr_2O_7$ (in acidic medium)

Aldehyde ⟶ Acid

1° Alcohol ⟶ Acid

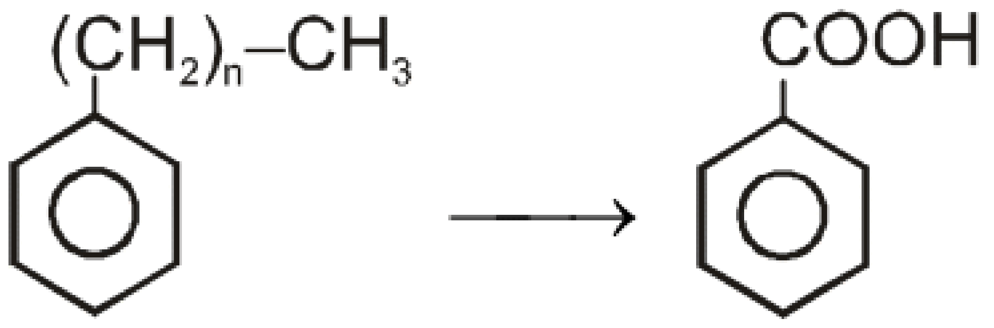
2° Alcohol ⟶ Ketone

3° Alcohol ⟶ No reaction

Alkene :  ⟶ $R_2C=O + R'COOH$

Alkyne : $R{-}C{\equiv}C{-}R'$ ⟶ $RCOOH + R'COOH$

Oxidation of aromatic side chain :



(2) PCC (Pyridinium chloro chromate)
CrO_3/HCl/Pyridine

1° ROH ⟶ Aldehyde

2° ROH ⟶ Ketone

3° ROH ⟶ No reaction

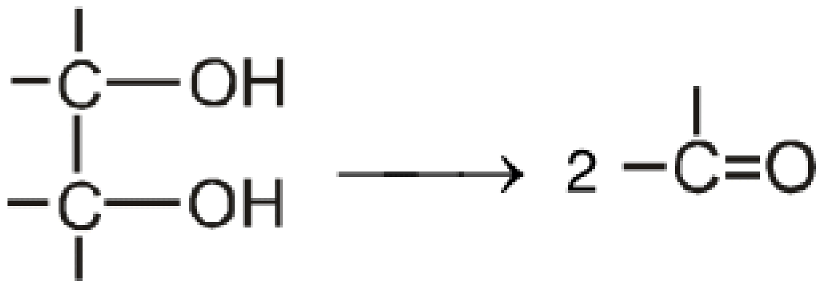
(3) Cu/573 K

1°Alcohol ⟶ Aldehyde

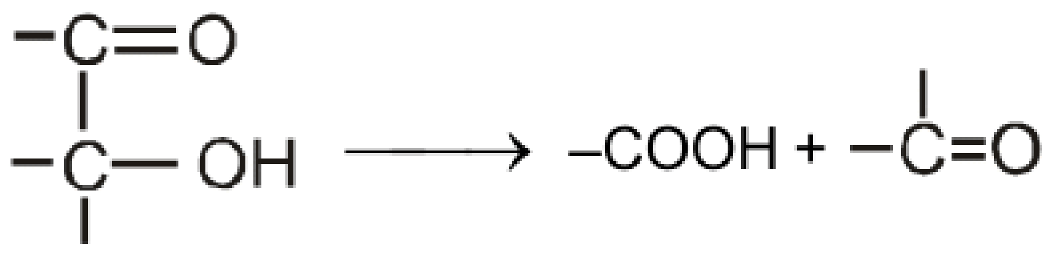
2° Alcohol ⟶ Ketone

3° Alcohol ⟶ Alkene

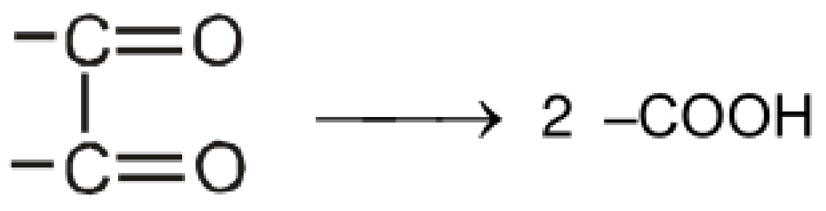
(4) HIO_4 (Periodic Acid)
Condition : Vicinal diol, α- Hydroxy ketone & α-diketone can oxidise by HIO_4



$$-\overset{|}{\underset{|}{C}}{-}OH,\ -\overset{|}{\underset{|}{C}}{-}OH \longrightarrow 2\ -\overset{|}{C}{=}O$$

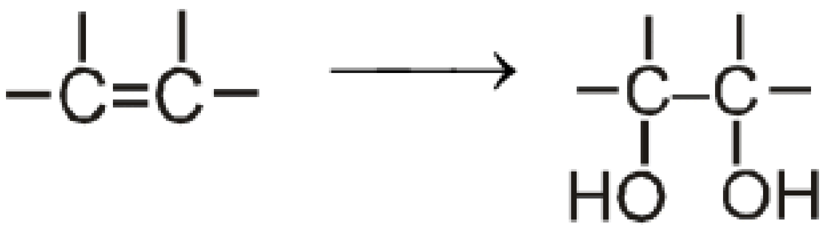


$$-C{=}O,\ -\overset{|}{\underset{|}{C}}{-}OH \longrightarrow -COOH + -\overset{|}{C}{=}O$$



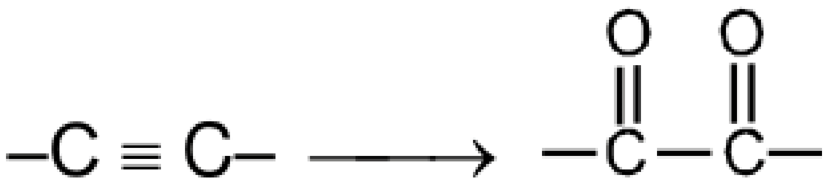
$$-C{=}O,\ -C{=}O \longrightarrow 2\ -COOH$$

(5) Baeyer's reagent and $OsO_4 + NaHSO_3$



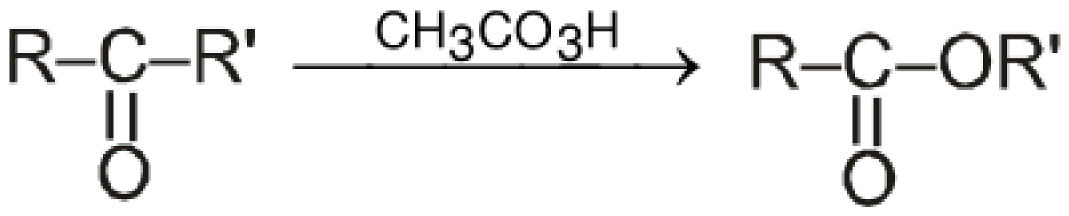
$$-\overset{|}{C}=\overset{|}{C}- \longrightarrow -\underset{HO}{\overset{|}{\underset{|}{C}}}-\underset{OH}{\overset{|}{\underset{|}{C}}}-$$

stereospecific syn addition



$$-C\equiv C- \longrightarrow -\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-$$

(6) Baeyer–Villiger oxidation (m-CPBA or CH_3CO_3H)

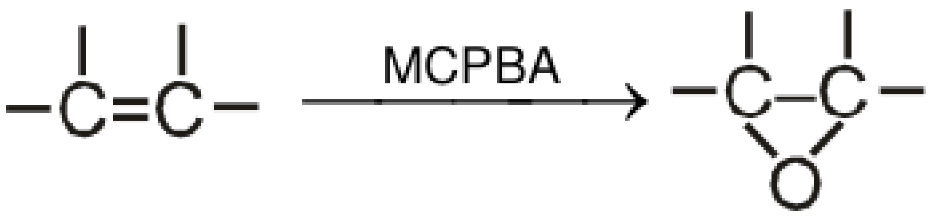


$$R-\underset{O}{\underset{\|}{C}}-R' \xrightarrow{CH_3CO_3H} R-\underset{O}{\underset{\|}{C}}-OR'$$

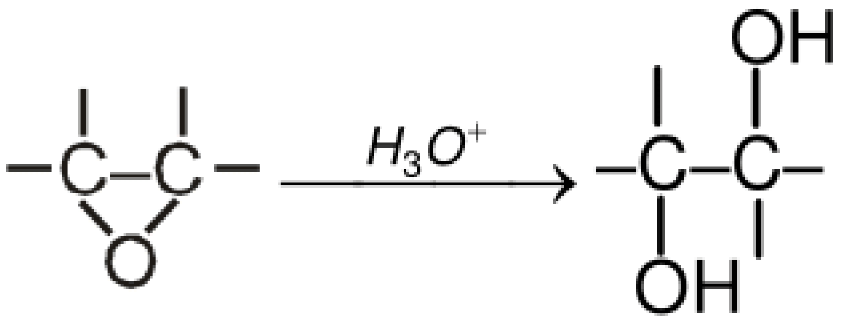
Priority of shift (O accepting aptitude)

R' = Ph > Ethyl > Methyl

(7) Prilezhaev reaction



Anti hydroxylation :



(8) oxidation by HNO_3

Aldehyde → Acid

1° Alcohol → Acid

2° Alcohol → no recation

3° Alcohol → No reaction

(9) oxidation by MnO_2

1° Alcohol → Aldehyde

2° Alcohol → Ketone

3° Alcohol → No reaction

Note : Only allylic and benzylic alcohols are oxidised by MnO_2.

Reduction

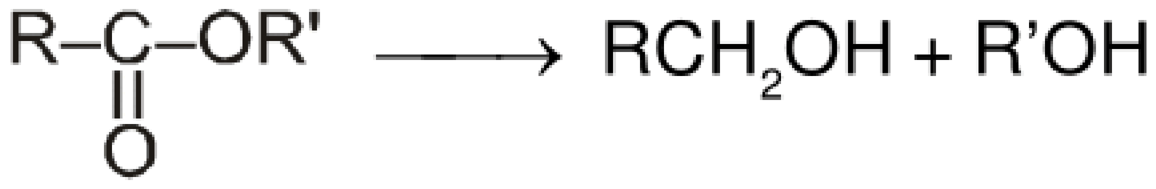
(1) $LiAlH_4$

$R–CHO \longrightarrow RCH_2OH$

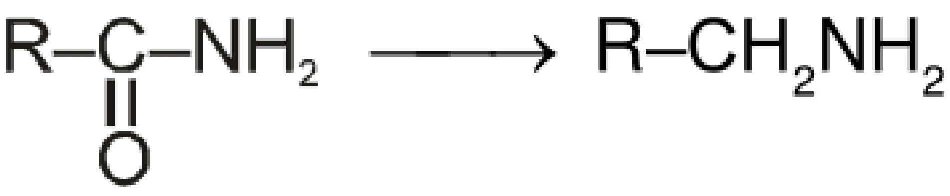
$R–\overset{O}{\overset{\|}{C}}–R \longrightarrow R–\underset{OH}{\underset{|}{C}H}–R$

$RCOOH \longrightarrow R–CH_2OH$

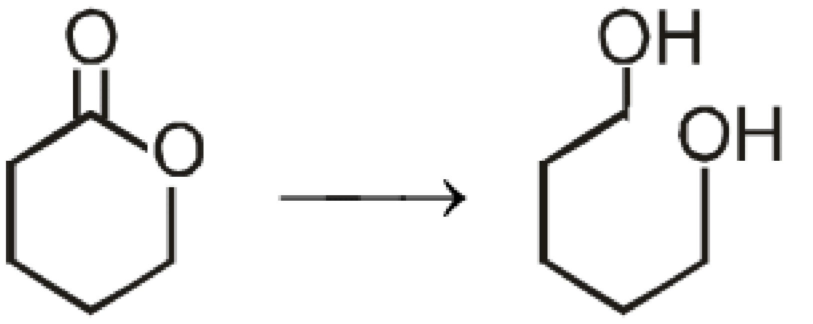
$R–\underset{O}{\underset{\|}{C}}–O–\underset{O}{\underset{\|}{C}}–R \longrightarrow 2R–CH_2OH$

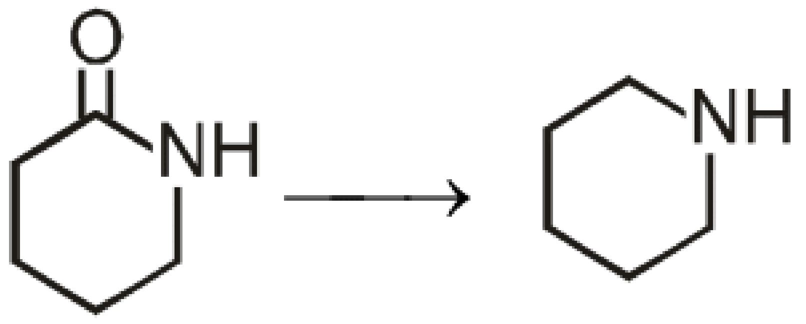


$R–\underset{O}{\underset{\|}{C}}–OR' \longrightarrow RCH_2OH + R'OH$



$R–\underset{O}{\underset{\|}{C}}–NH_2 \longrightarrow R–CH_2NH_2$





$R–\underset{O}{\underset{\|}{C}}–Cl \longrightarrow R–CH_2OH$

$R–CN \longrightarrow R–CH_2–NH_2$

$C = C / C≡C \longrightarrow$ No reaction

Exception : **$Ph–CH=CH–COOH \longrightarrow Ph–CH_2–CH_2–CH_2OH$**

(2) $NaBH_4$, EtOH

Aldehyde ⟶ 1° Alcohol

Ketone ⟶ 2 °Alcohol

Acid halide ⟶ 1° Alcohol

(3) Na/EtOH (Bouvealt Blanc reduction)

Aldehyde ⟶ 1° Alcohol

Ketone ⟶ 2º Alcohol

Acid halide ⟶ 1° Alcohol

Ester ⟶ Alcohol + Alcohol

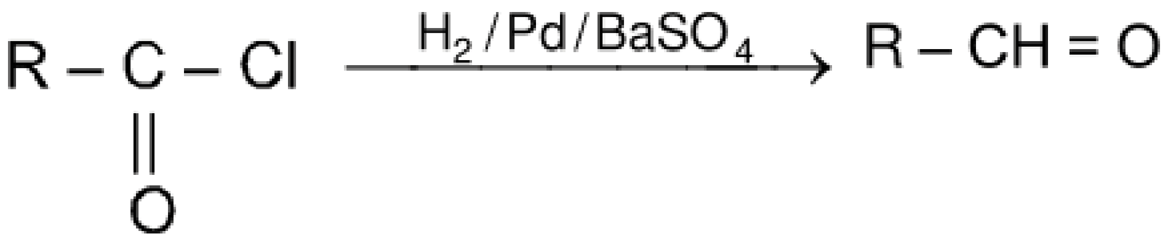
$RCN \longrightarrow RCH_2NH_2$

(4) Na–Hg/HCl or $Al[OCHMe_2]_3$ (MPV Reduction)

Aldehyde ⟶ 1° Alcohol

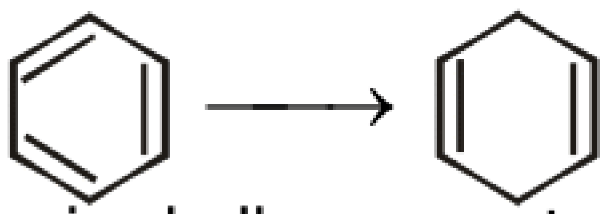
Ketone ⟶ 2° Alcohol

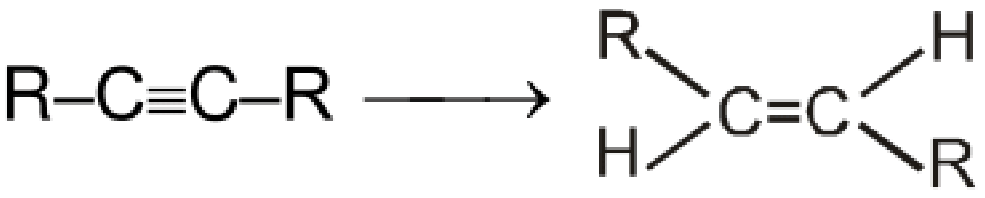
(5) Rossenmund's Reduction



$R–\underset{O}{\underset{\|}{C}}–Cl \xrightarrow{H_2/Pd/BaSO_4} R–CH=O$

(6) Birch reduction (Li/Na/K + Liquid NH_3)





$R–C≡C–R \longrightarrow$ (trans alkene)

Note : Terminal alkynes not reduced

(7) Stephen's Reduction

$$R-C\equiv N \xrightarrow[\text{(2) } H_2O]{\text{(1) } SnCl_2/HCl} R-CH=O$$

Note : DIBAL-H is also used for same conversion.

(8) Clemmensen Reduction

$$>C=O \xrightarrow{Zn\text{-}Hg/HCl/\Delta} >CH_2$$

(Keto) (alkane)

Avoid if acid sensitive
groups are present in molecule.
e.g. C=C,C≡C,OH, OR,

(9) Wolff-Kishner Reduction

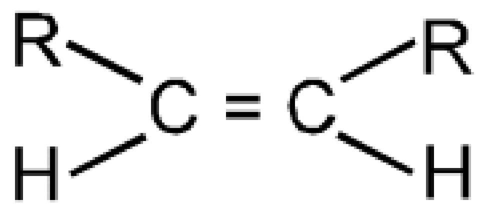
$$>C=O \xrightarrow{NH_2-NH_2/KOH/\Delta} >CH_2$$

(Keto) (alkane)

Avoid if base sensitive
groups are present in molecule.
e.g.COOR,COX,CONH$_2$,
–CO–O–CO–, R-X

(10) Lindlar Catalyst

$$R-C\equiv C-R \xrightarrow[\text{Quinoline}]{H_2/Pd/CaCO_3/}$$



Syn addition
(Cis alkene)

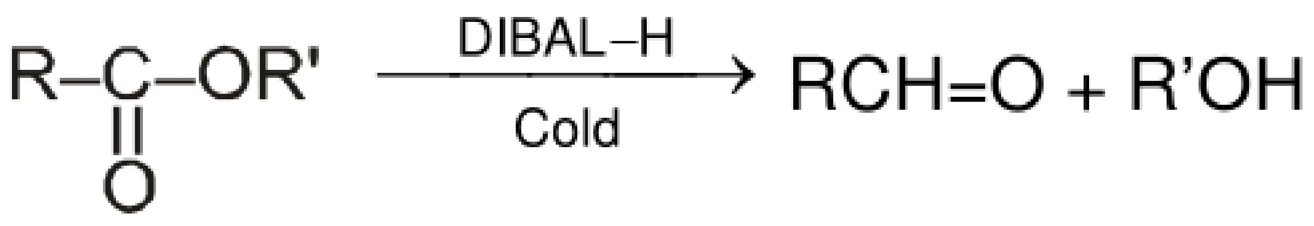
Note : H_2, Pd, $BaSO_4$ is also used for same conversion.

(11) Red Phosphorus and HI

Almost all functional groups contaning compounds converts into corresponding alkane by red P + HI.

- $R-CH_2OH \longrightarrow R-CH_3$
- $R-CHO \longrightarrow R-CH_3$
- $R_2CO \longrightarrow R_2CH_2$ (Alkane)

(12) DIABAL-H reduction



$$R-\underset{\underset{O}{\|}}{C}-OR' \xrightarrow[\text{Cold}]{\text{DIBAL-H}} RCH=O + R'OH$$

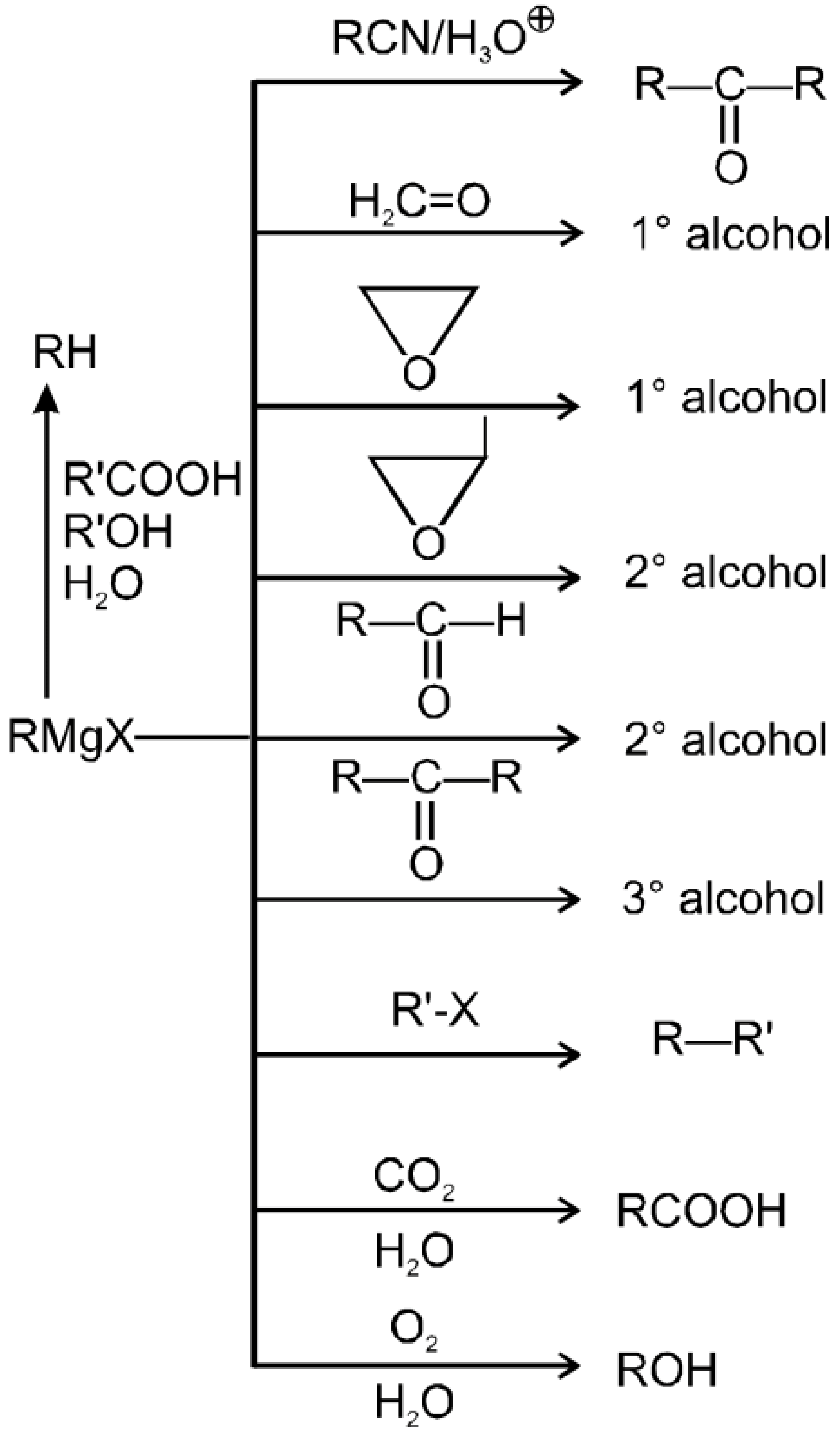
$$R-C\equiv N \xrightarrow{\text{DIBAL-H}} R-CH=O$$

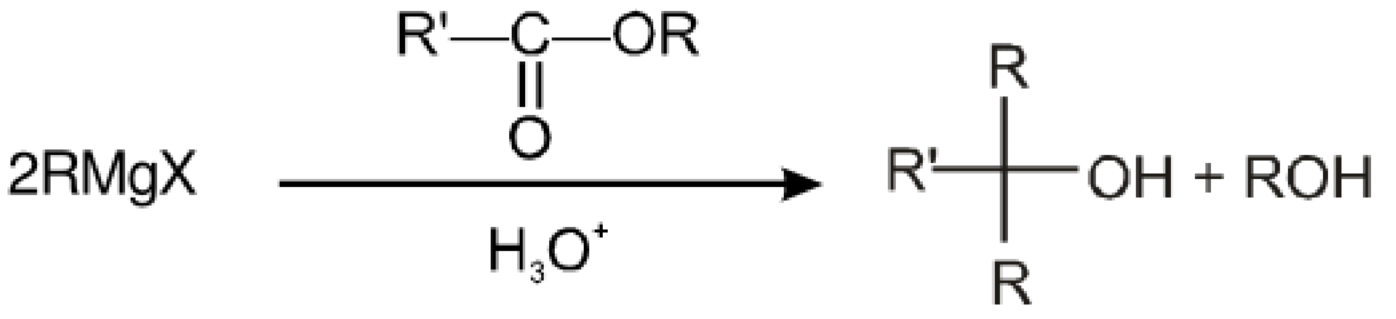
At ordinary temperature esters reduced to alcohols but at low temperature esters reduced to aldehyde.

Grignard reagents

Grignard's Reagent : RMgX (alkyl magnesium halide)

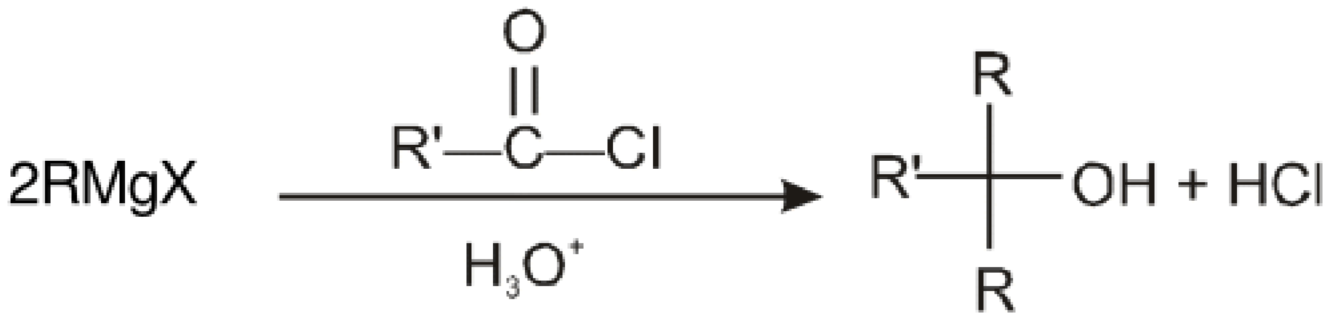
* Active – H Containing compounds $\xrightarrow{RMgX}$ R – H





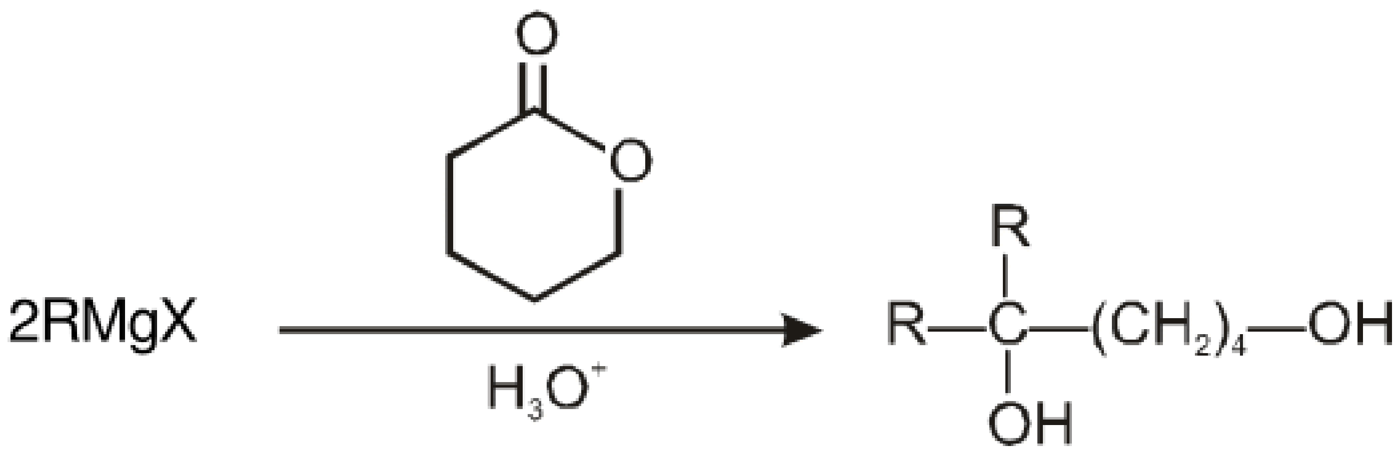
$$2RMgX \xrightarrow[H_3O^+]{R'-\overset{O}{\overset{\|}{C}}-OR} R'-\underset{R}{\overset{R}{C}}-OH + ROH$$

(two alkyl groups come from Grignard Reagent)



$$2RMgX \xrightarrow[H_3O^+]{R'-\overset{O}{\overset{\|}{C}}-Cl} R'-\underset{R}{\overset{R}{C}}-OH + HCl$$

(two alkyl groups come from Grignard Reagent)

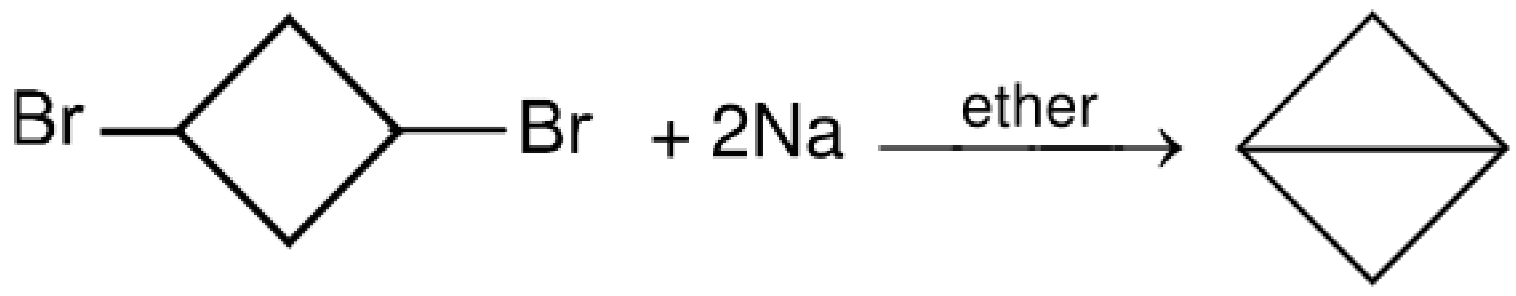


(two alkyl groups come from Grignard Reagent)

Alkane

Wurtz reaction (Reagent : Na, ether) 1° & 2° alkyl halides give this reaction.

$R-X + 2Na \xrightarrow{\text{ether}} R-R$; $R-X + R'-X + 2Na \xrightarrow{\text{ether}} R-R' + R-R + R'-R'$

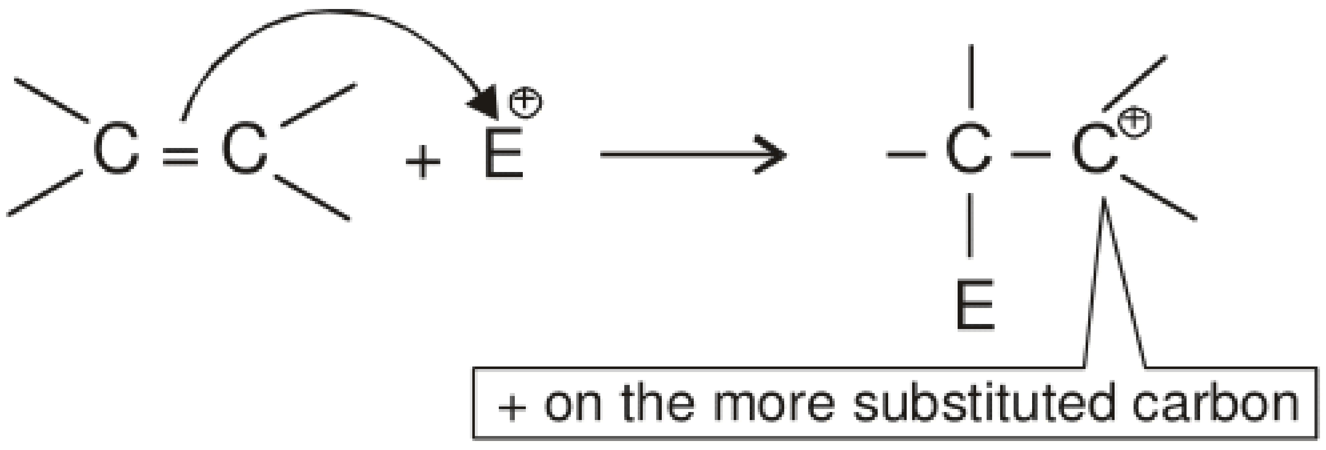


Alkene & Alkyne

Characteristic reaction of Alkene & Alkyne is Electrophilic addition reaction.

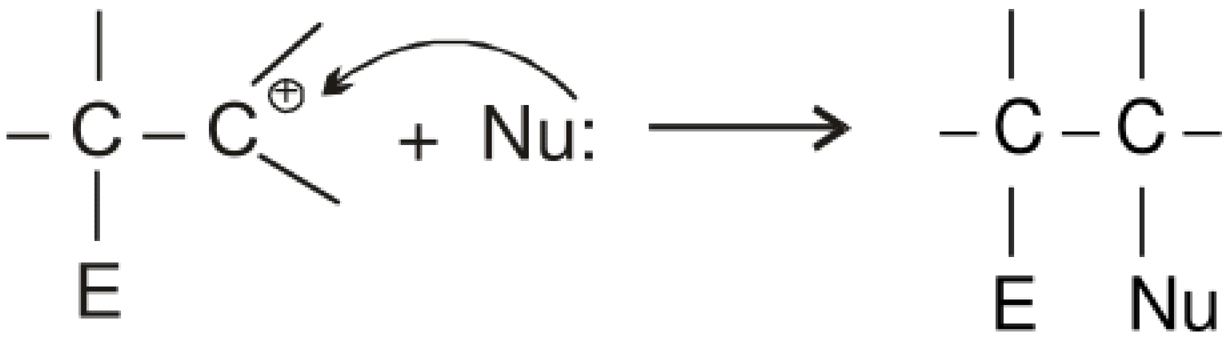
Mechanism

Step 1 : Attack of the electrophile on π bond forms a carbocation.

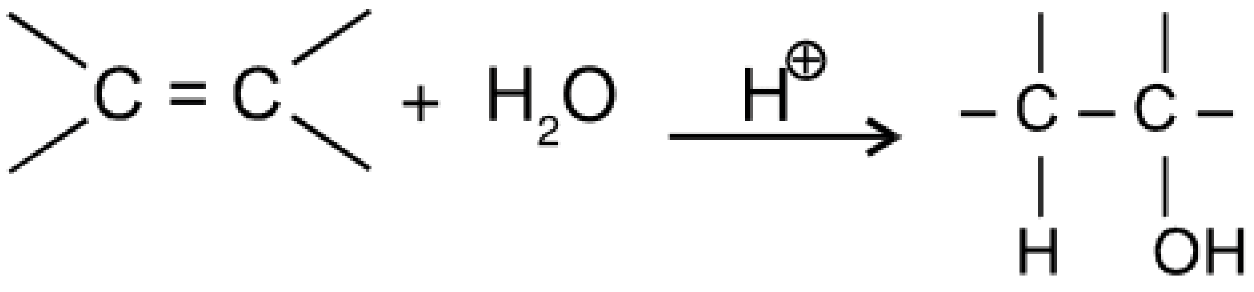


+ on the more substituted carbon

Step 2 : Attack by a nucleophile gives the product of addition.

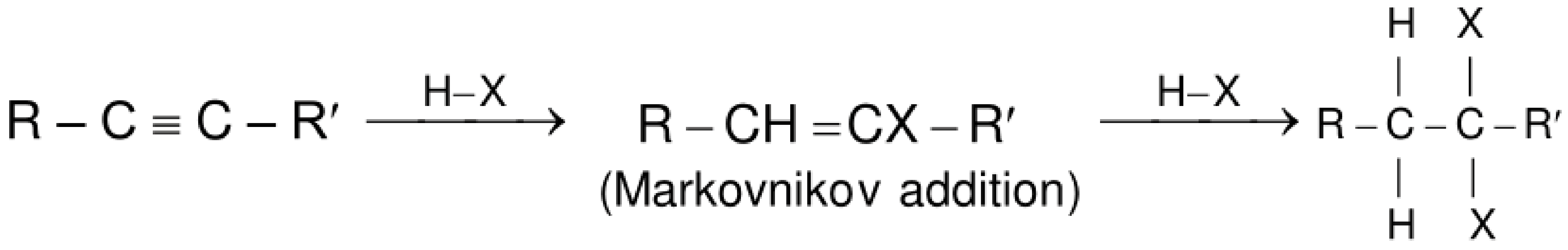


e.g. (a) Addition of water



(Markovnikov orientation)

(b) Addition of hydrogen halides (where HX = HCl, HBr, HI)



$$R-C\equiv C-R' \xrightarrow{H-X} R-CH=CX-R' \xrightarrow{H-X} R-\underset{H}{\overset{H}{C}}-\underset{X}{\overset{X}{C}}-R'$$

(Markovnikov addition)

Note: When electrophiles are: Cl^+, Br^+, I^+, NO_2^+ or Hg^{2+} then stereochemistry is important and major product is formed by anti addition.

Alkyl halide

Nucleophilic substitution Reaction (S_N1, S_N2)

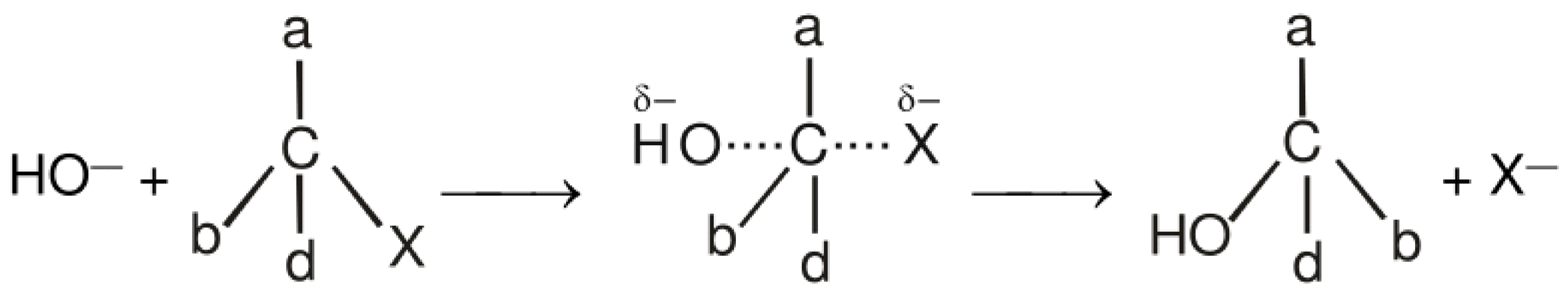
S_N1 reaction :

$R{-}X + H_2O \xrightarrow{AgNO_3} R^{+} + AgX\downarrow \longrightarrow ROH$ (R may rearrange)

Alkylhalide are hydrolysed to alcohol very slowly by water, but rapidly by silver oxide suspended in boiling water.

S_N2 reaction :

Mechanism : $HO^{-} \;\; R-X \longrightarrow \overset{\delta-}{H}O\cdots R\cdots\overset{\delta-}{X} \longrightarrow HO-R+X^{-}$



Alcohol

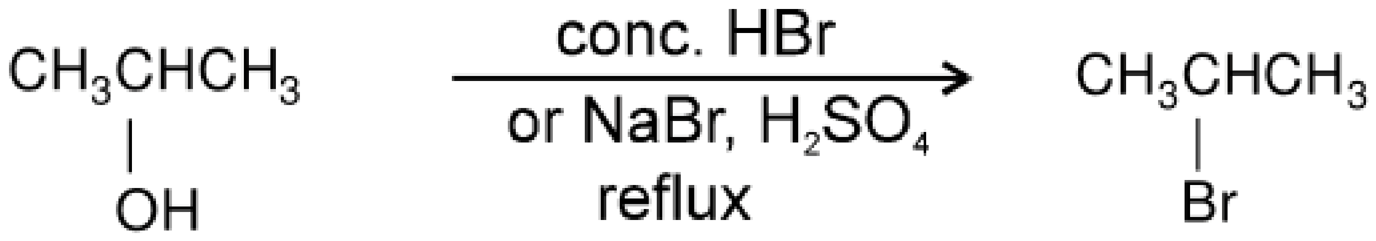
S_N1 reaction :

$R{-}OH \xrightarrow{H^{\oplus}} R-\overset{\oplus}{O}H_2 \xrightarrow{-H_2O} \overset{\oplus}{R} \xrightarrow{X^{\ominus}} R-X$(R may rearrange)

Reactivity of HX : HI > HBr > HCl

Reactivity of ROH : allyl, benzyl > 3° > 2° > 1° (Carboocation)

e.g.



$$\underset{\displaystyle\text{OH}}{CH_3\underset{|}{C}HCH_3} \xrightarrow[\text{or NaBr, } H_2SO_4 \text{ reflux}]{\text{conc. HBr}} \underset{\displaystyle\text{Br}}{CH_3\underset{|}{C}HCH_3}$$

Isopropyl alcohol Isopropyl bromide

S_N2 reaction :

$ROH + PCl_5 \longrightarrow RCl + POCl_3$

$ROH + PCl_3 \longrightarrow RCl + H_3PO_3$

$ROH + SOCl_2 \xrightarrow{\text{Pyridine}} RCl + SO_2 + HCl$

Williamson's synthesis :

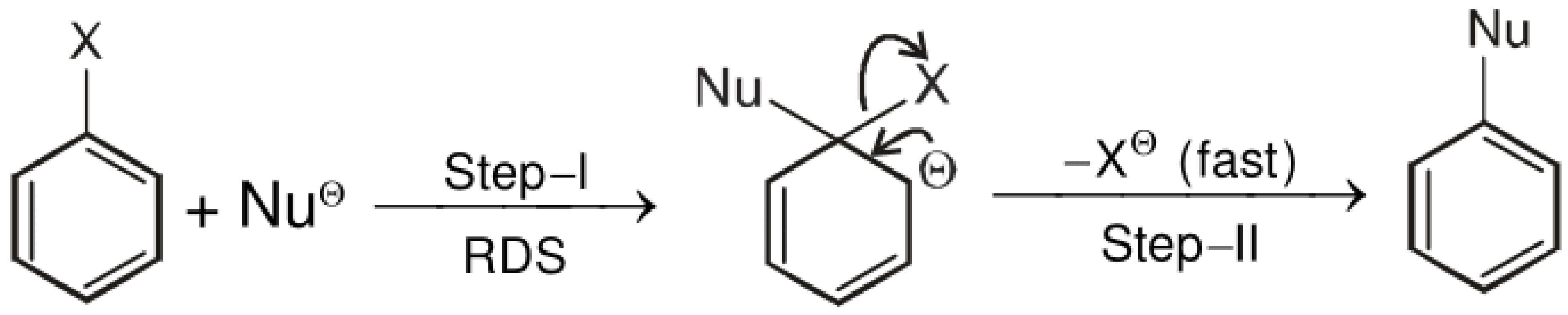
It is the reaction in which sodium or potassium alkoxide is heated with an alkyl halide (S_N2).

$R_1O^{-} + R^2{-}X \rightleftharpoons R^{1}\overset{\delta-}{O}\ldots\ldots R^2\ldots\ldots\overset{\delta-}{X} \longrightarrow R^1OR^2 + X^{-}\,(g)$

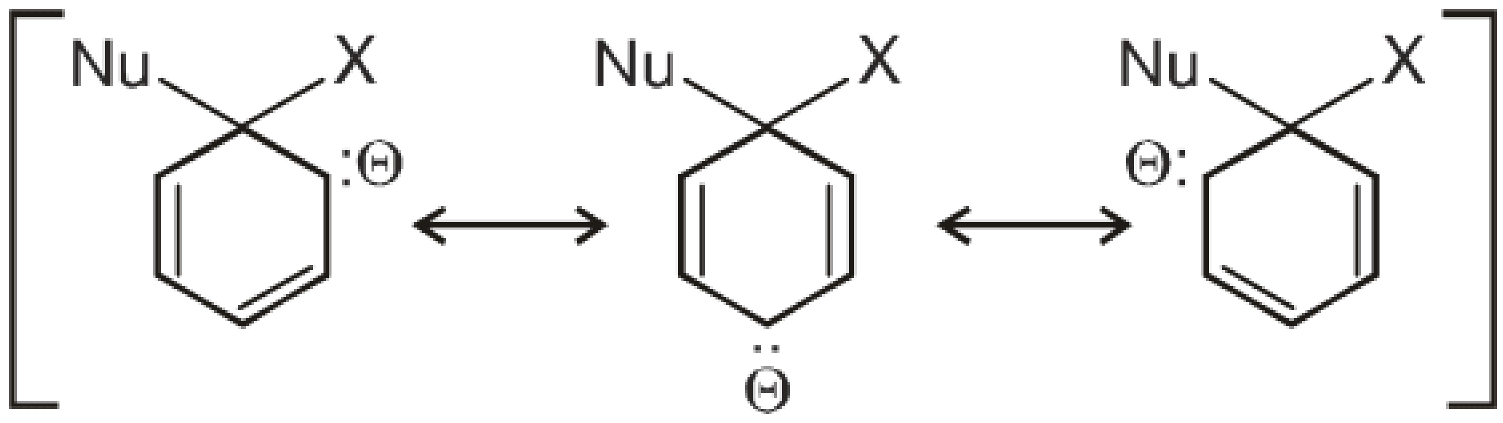
This method is particularly useful for preparing mixed ethers.

Nucleophilic Aromatic Substitution of aryl halides(S_N2Ar):

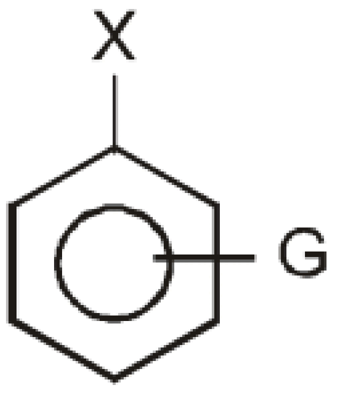
- An electron withdrawing group at ortho or para positions with respect to a good leaving groups are necessary conditions for S_N2 Ar.



Intermediate ion is stabilized by resonance. and are stable salts called Meisenheimer salts.



- A group that withdraws electrons tends to neutralize the negative charge of the ring and this dispersal of the charge stabilizes the carbanion.

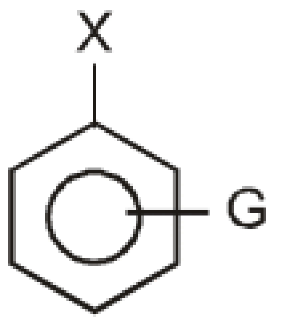


G withdraws electrons : stabilizes carbanion, activates the

Ar-S_N2 reaction.

($-\overset{+}{N}(CH_3)_3$, $-NO_2$, $-CN$, $-SO_3H$, $-COOH$, $-CHO$, $-COR$, $-X$)

- A group that releases electrons tends to intensify the negative charge, destabilizes the carbanion, and thus slows down reaction.



G ($-NH_2$, $-OH$, $-OR$, $-R$)releases electrons : destabilizes carbanion, deactivates the Ar-S_N2 reaction.

Element effect :

Reactivity order towards S_N2Ar with different halogens
Ar-F > Ar-Cl > Ar-Br > Ar-I

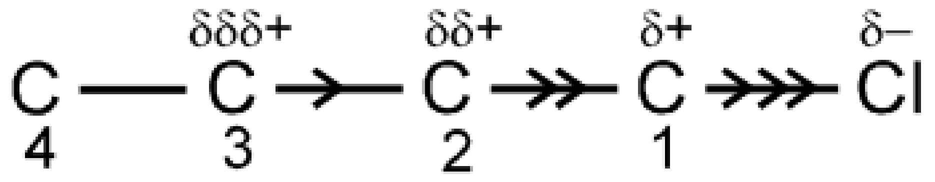
General Organic Chemistry

1. Inductive effect

The normal C–C bond has no polarity as two atoms of same electronegativity (EN) value are connected to each other. Hence the bond is nonpolar. Consider a carbon chain in 1-Chloro butane, here due to more EN of Cl atom C–Cl bond pair is slightly displaced towards Cl atom hence creating partial negative ($\delta -$) charge over Cl atom and partial positive ($\delta+$) charge over C_1 atom.

Now since C_1 is slightly positive, it will also cause shifting of C_1–C_2 bond pair electrons towards itself causing C_2 to acquire small positive charge. Similarly C_3 acquires slightly positive charge creating an induction of charge in carbon chain. Such an effect is called inductive effect.

Diagram showing I effect



$$\underset{4}{C} - \overset{\delta\delta\delta+}{\underset{3}{C}} \rightarrow \overset{\delta\delta+}{\underset{2}{C}} \twoheadrightarrow \overset{\delta+}{\underset{1}{C}} \twoheadrightarrow\!\!\!\rightarrow \overset{\delta-}{Cl}$$

The arrow shows electron withdrawing nature of – Cl group.

Thus inductive effect may be defined as a permanent displacement of σ bond pair electrons due to a dipole. (Polar bond)

Some important points are:

(a) It can also be defined as polarisation of one bond caused by polarisation of adjacent bond.

(b) It is also called transmission effect.

(c) It causes permanent polarisation in molecule, hence it is a permanent effect.

(d) The displacement of electrons takes place due to difference in electronegativity of the two atoms involved in the covalent bond.

(e) The electrons never leave their original atomic orbital.

(f) Its magnitude decreases with distance and it is almost negligible after 3rd carbon atom.

(g) The inductive effect is always operative through σ bond, does not involve π bond electron.

Types of inductive effects :

(a) – I Effect : The group which withdraws electron cloud is known as – I group and its effect is called – I effect. Various groups are listed in their decreasing – I strength as follows.

$$-\overset{\oplus}{N}R_3 > -\overset{\oplus}{S}R_2 > -\overset{\oplus}{N}H_3 > -NO_2 > -SO_2R > -CN > -CHO > -COOH > -F >$$
$$-Cl > -Br > -I > -OR > -OH > -C{\equiv}CH > -NH_2 > -C_6H_5 > -CH{=}CH_2 > -H.$$

(b) + I effect : The group which release electron cloud is known as + I group and effect is + I effect.

$-\overset{\ominus}{O} > -CO\overset{\ominus}{O} > -C(CH_3)_3 > -CH(CH_3)_2 > -CH_2-CH_3 > -CH_3 > -D > -H$
The hydrogen atom is reference for + I and – I series. The inductive effect of hydrogen is assumed to be zero.

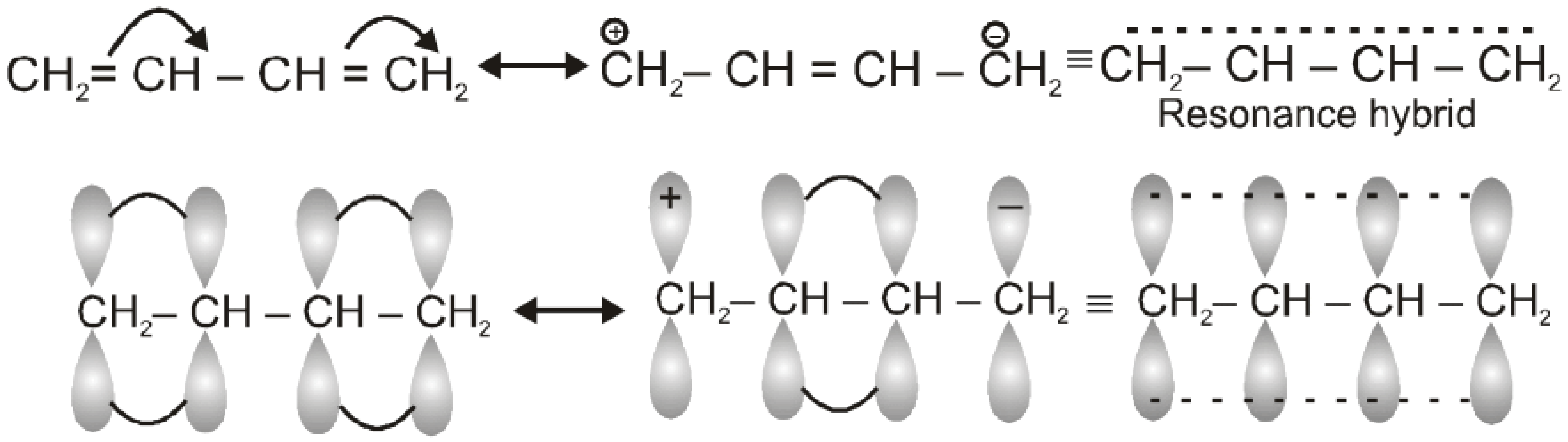
Ex. Let us consider effect of COOH & – COO⁻ in carbon chain

(a) $^{\ominus}OOC \rightarrow \overset{\delta-}{C}H_2 \rightarrow \overset{\delta\delta-}{C}H_2 \rightarrow CH_3$ (b) $HOOC \leftarrow \overset{\delta+}{C}H_2 \leftarrow \overset{\delta\delta+}{C}H_3$

Due to e^- donating nature of $-CO\overset{\ominus}{O}$ carbon chain has become partially negative but – COOH is – I group therefore carbon chain has become partially positive.

2. Resonance

Resonance is the phenomenon in which two or more structures involving in identical position of atom, can be written for a particular species, all those possible structures are known as resonating structures or canonical structures. Resonating structures are only hypothetical but they all contribute to a real structure which is called resonance hybrid. The resonance hybrid is more stable than any resonating structure.



Resonance hybrid :

The most stable resonating structure contribute maximum to the resonance hybrid and less stable resonating structure contribute minimum to resonance hybrid.

Conjugation:

A given atom or group is said to be in conjugation with an unsaturated system if:-

(i) It is directly linked to one of the atoms of the multiple bond through a single bond.

(ii) It has π bond, positive charge, negative charge, odd electron or lone pair electron.

Types of Conjugation :

1. Conjugation between C = C and

$$C{=}C\ (CH_2 = CH - CH = CH_2 \longleftrightarrow \overset{\oplus}{C}H_2 - CH = CH - \overset{\ominus}{C}H_2)$$

2. Conjugation between +ve charge and

$$C{=}C\ (CH_2 = CH - \overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2 - CH = CH_2)$$

3. Conjugation between lone pair and

$$C{=}C\ (:\ddot{C}l - CH = CH_2 \longleftrightarrow \overset{\oplus}{C}l = CH - \overset{\ominus}{C}H_2)$$

4. Conjugation between odd electron and

$$C{=}C\ (CH_2{=}CH{-}\dot{C}H_2 \longleftrightarrow \dot{C}H_2{-}CH{=}CH_2)$$

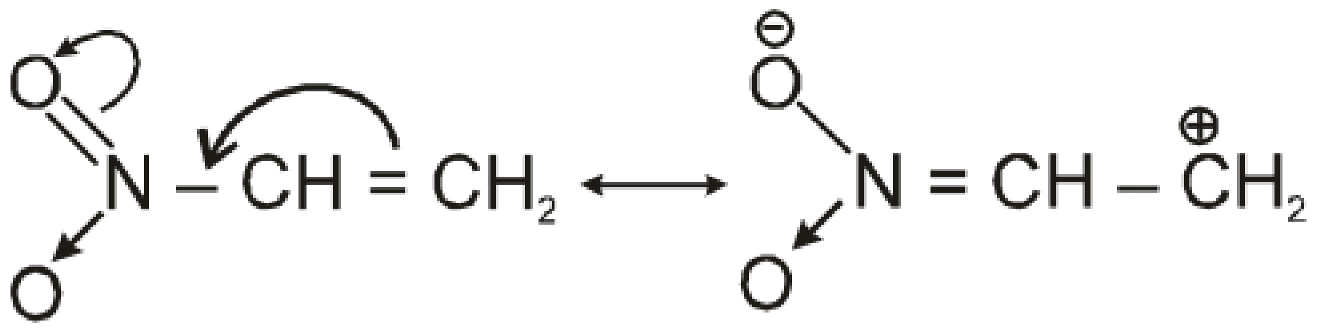
5. Conjugation between negative charge and

$$C{=}C\ (CH_2 = CH - \overset{\ominus}{C}H_2 \longleftrightarrow \overset{\ominus}{C}H_2 - CH = CH_2)$$

3. Mesomeric effect (or Resonance effect)

Mesomeric effect is defined as permanent effect of π electron shifting from multiple bond to atom or from multiple bond to single bond or from lone pair to single bond. This effect mainly operates in conjugated system of double bond. So that this effect is also known as conjugate effect.

Ex.



Types of Mesomeric effects :

(a) Positive Mesomeric effect (+M effect) :

When the group donates electron to the conjugated system it shows + M effect.

Relative order of +M groups (usually followed) :

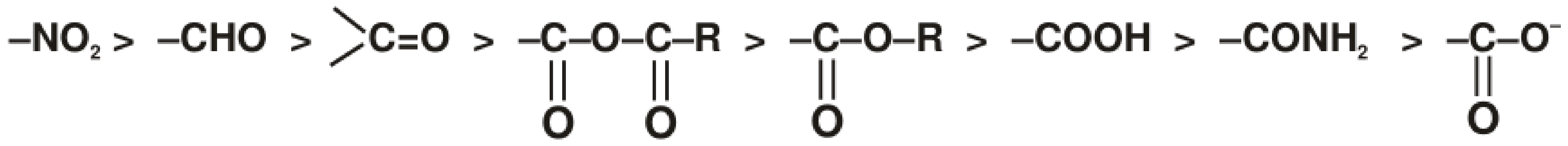
$-\overset{\ominus}{O} > -NH_2 > -NHR > -NR_2 > -OH > -OR > -NHCOR > -OCOR > -Ph >$
$-F > -Cl > -Br > -I > -NO$

Ex. (I) $\underset{\text{I}}{\ddot{X} - CH = CH_2} \longleftrightarrow \underset{\text{II}}{\overset{\oplus}{X} = CH - \overset{\ominus}{C}H_2}$

(b) Negative Mesomeric effect (–M effect) :

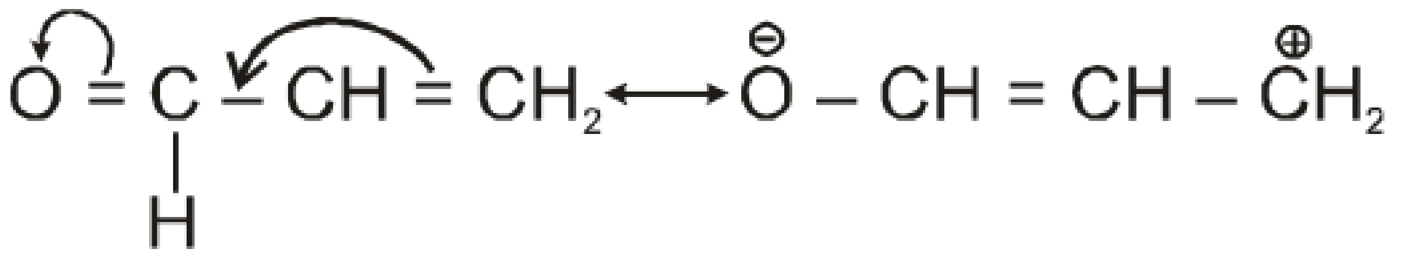
When the group withdraws electron from the conjugated system, it shows – M effect

Relative order of –M groups (usually followed) :

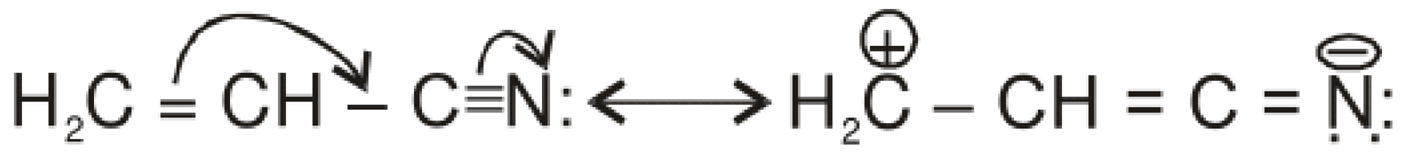


$$-NO_2 > -CHO > \rangle C{=}O > -\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R > -\underset{\underset{O}{\|}}{C}-O-R > -COOH > -CONH_2 > -\underset{\underset{O}{\|}}{C}-O^-$$

Ex. (I)



(II)

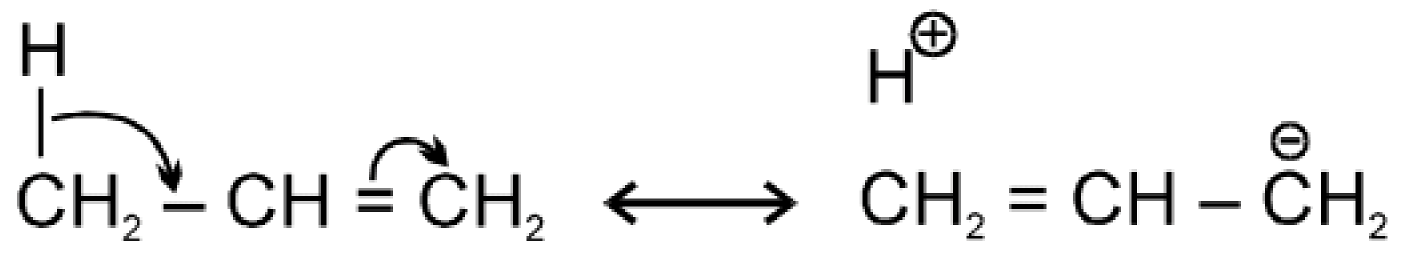


4. Hyperconjugation

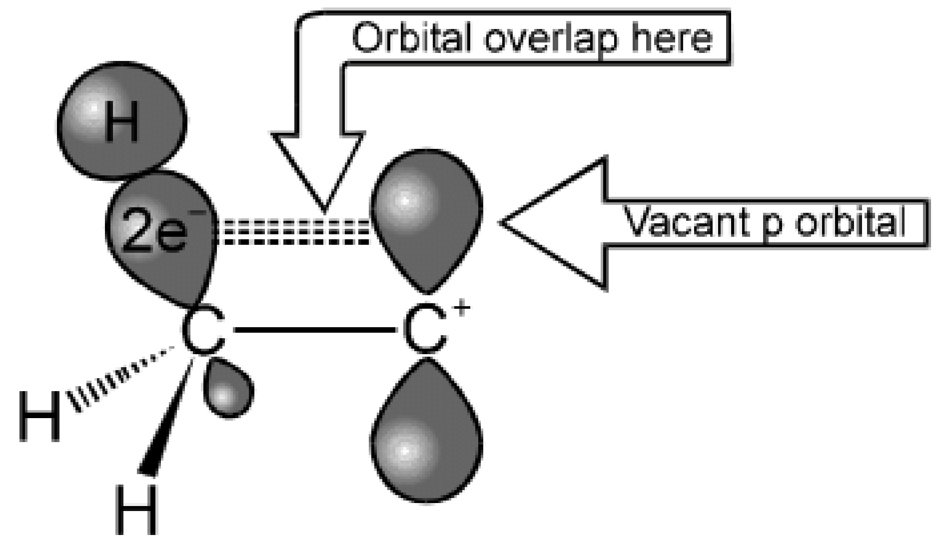
It is delocalisation of sigma electron with p-orbital. Also known as σ π-conjugation or no bond resonance. It may takes place in alkene, alkynes, carbocation, free radical, benzene nucleus.

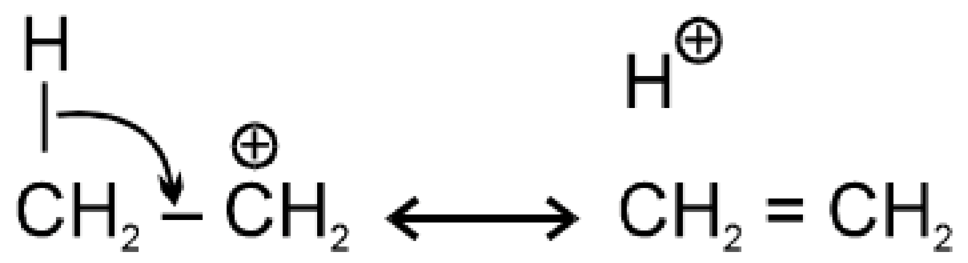
Necessary Condition : Presence of at least one hydrogen at saturated carbon which is α with respect to alkene, alkynes, carbocation, free radical, benzene nucleus.

(i) Hyperconjugation in alkene

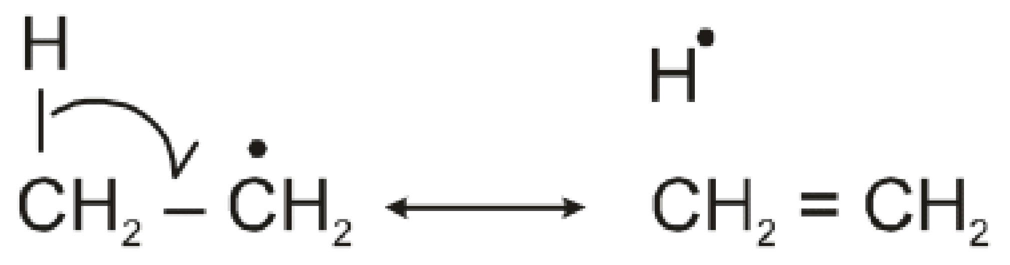


(ii) Hyperconjugation in carbocation





(iii) Hyperconjugation in radical

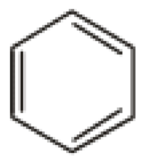
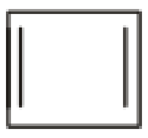


5. Aromatic character [The Huckel 4n + 2 rule]

The following rules are useful in predicting whether a particular compound is aromatic or non–aromatic. Aromatic compounds are cyclic and planar. Each atom in an aromatic ring is sp^2 hybridised. The cyclic π molecular orbital (formed by overlap of p-orbitals) must contain $(4n + 2)$ π electrons, i.e., 2, 6, 10, 14 .... π electrons. Where n = an integer 0, 1, 2, 3,..............

Aromatic compounds have characteristic smell, have extra stability and burn with sooty flame.

Comparision between aromatic, anti aromatic and non-aromatic compounds.

Characteristics	Aromatic compounds (A)	Anti Aromatic compounds (B)	Non-Aromatic compounds (C)
Example			
1. Structure	Cyclic, planar all atoms of ring sp^2 hybridised	Cyclic, planar all atoms of ring sp^2 hybridised	Cyclic or acyclic planar,or non planar sp or sp^2 or sp^3
2. No. of π e^-s in the ring	$(4n+2)\pi e^-$ (Huckle's rule)	$(4n)\pi e^-$	Any no. of πe^-s
3. MOT	Unpaired e^-s in B.M.O.	Some πe^-s in non-bonding M.O.	B.M.O. / Non-bonding M.O.
4. Overlapping	Favourable over lapping of p orbital	Unfavourable over lapping of p orbital	Simple overlaping like alkenes
5. Resonance energy (R.E.)	Very high R.E. > 20-25 kcal/mol	Zero	4-8 kcal/mol like alkenes
6. Stability	Have extra stability due to close conjugation of π e^-s	Unstable not-exist at room temperature	Normal stability like a conjugated system
7. Characteristic Reactions	Electrophilic substitution Reaction	Dimerisation reaction to attain stability	Electrophilic addtion reaction like alkenes

Stability of compounds : Aromatic > Non-Aromatic > Anti-Aromatic

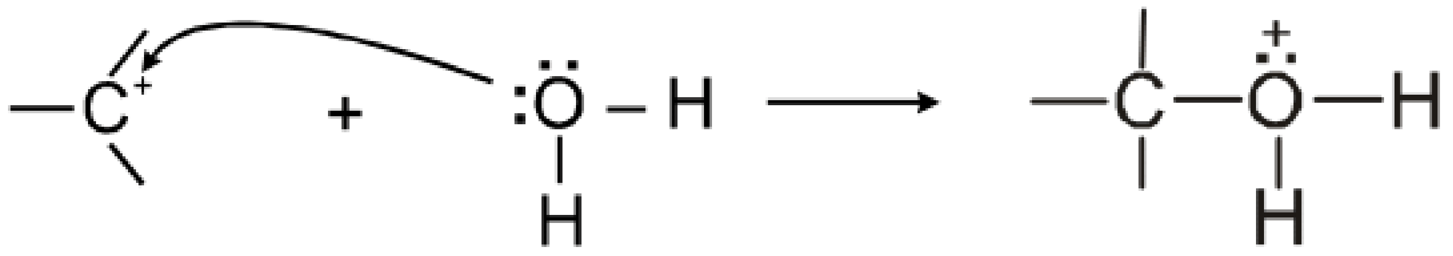
(A) Carbocation :

Definition : A carbon intermediate which contain three bond pair & a positive charge on it is called carbocation.

Hybridisation : Carbocation may be sp^2 & sp hybridised

Hybridisation	Example
sp^2	$\overset{\oplus}{C}H_3,\ CH_3\overset{\oplus}{C}H_2,\ CH_3\overset{\oplus}{C}HCH_3,\ (CH_3)_3\overset{\oplus}{C}$
sp	$H_2C=\overset{\oplus}{C}H\ ,\ HC\equiv\overset{\oplus}{C}$

Carbocations are electron deficient. They have only six electrons in their valence shell, and because of this, carbocations act as Lewis acids. Most of the carbocations are short-lived and highly reactive, they occur as intermediates in some organic reactions. Carbocations react with Lewis bases or ions that can donate the electron pair, that they need to achieve a stable octet of electrons (i.e., the electronic configuration of a noble gas):



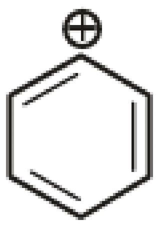
Because carbocations are electron seeking reagents, chemists call them electrophiles. All Lewis acids, including protons, are electrophiles. By accepting an electron pair, a proton achieves the valence shell configuration of helium; carbocations achieve the valence shell configuration of neon.

Stability : Carbocations are stabilised by

(i) + I effect
(ii) + M effect
(iii) Hyperconjugation
(iv) delocalisation of charge

General stability order :

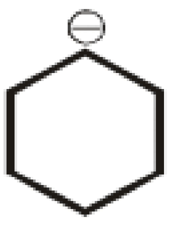
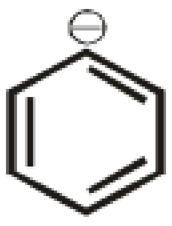
$$Ph_3\overset{\oplus}{C} > Ph_2\overset{\oplus}{C}H > Ph-\overset{\oplus}{C}H-R > CH_2=CH-\overset{\oplus}{C}H-R \gtrsim (CH_3)_3\overset{\oplus}{C} \gtrsim$$

$$Ph\overset{\oplus}{C}H_2 > CH_2=CH-\overset{\oplus}{C}H_2 \geq (CH_3)_2\overset{\oplus}{C}H > CH_3-\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3 > CH_2=\overset{\oplus}{C}H \simeq$$ 

(B) Carbanion :

Definition : A carbon intermediate which contain three bond pair and a negative charge on it, is called carbanion.

Hybridisation : Hybridisation of carbanion may be sp^3, sp^2 & sp.

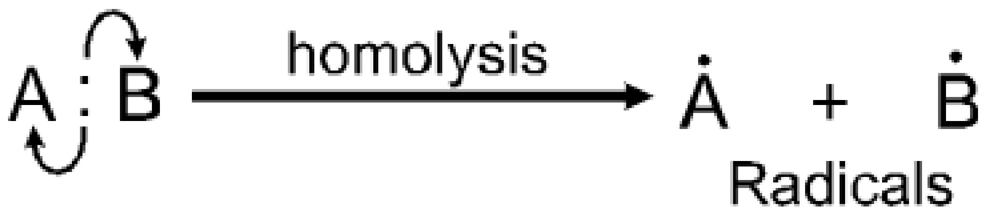
Hybridisation	Example
sp^3	$\overset{\ominus}{C}H_3$, $CH_3-\overset{\ominus}{C}H_2$, $CH_3\overset{\ominus}{C}HCH_3$, $(CH_3)_3\overset{\ominus}{C}$, 
sp^2	$H_2C=\overset{\ominus}{C}H$, $CH_2=CH-\overset{\ominus}{C}H_2$, 
sp	$HC\equiv\overset{\ominus}{C}$

Stability of carbanion : Carbanions are stabilised by electron withdrawing effect as

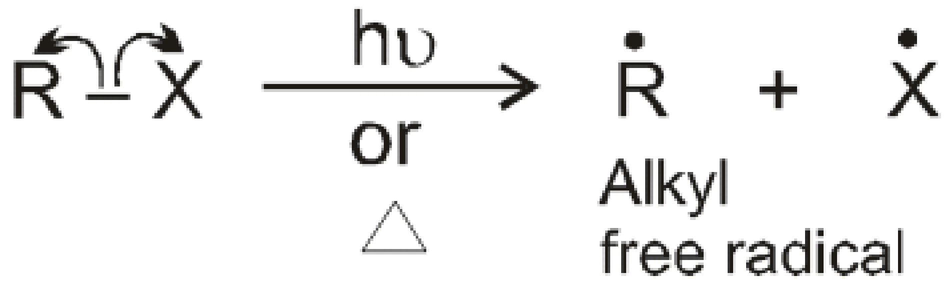
(i) – I effect (ii) – m effect (iii) Delocalisation of charge

(C) Free Radicals :

Homolysis of covalent bond results into free radical intermediates possess the unpaired electrons.



It is generated in presence of Sun light, Peroxides or High temperature



Free Radical : An uncharged intermediate which has three bond pair and an unpaired electron on carbon.

Note : (i) It is Neutral species with odd e^-

(ii) It is paramagnetic in nature due to odd e^-

(iii) No rearrangement is observed generally.

(iv) Carbon atom having odd electron is in sp^2 hybridised state

(v) Any reaction if it is carried out in the presence of sunlight, peroxide or high temperature it generally proceeds via free radical intermediate.

☞ **Stability of free radical :** It is stabilised by resonance, hyperconjugation and + I groups.

Ex. $(H_3C)_3C^{\bullet} > H_3C-\dot{C}H-CH_3 > H_3C-\dot{C}H_2 > \dot{C}H_3$

(Stability order)

(D) Carbenes (Divalent Carbon intermediates) :

Definition : There is a group of intermediates in which carbon forms only two bonds. These neutral divalent carbon species are called carbenes. Most carbenes are highly unstable that are capable of only fleeting existence. Soon after carbenes are formed, they usually react with another molecules.

Methods of preparation of carbene :

$CHCl_3 + HO^{\ominus} \xrightarrow{-HCl} :CCl_2$; $CH_2I_2 + Zn \xrightarrow[\Delta]{-ZnI_2} :CH_2$

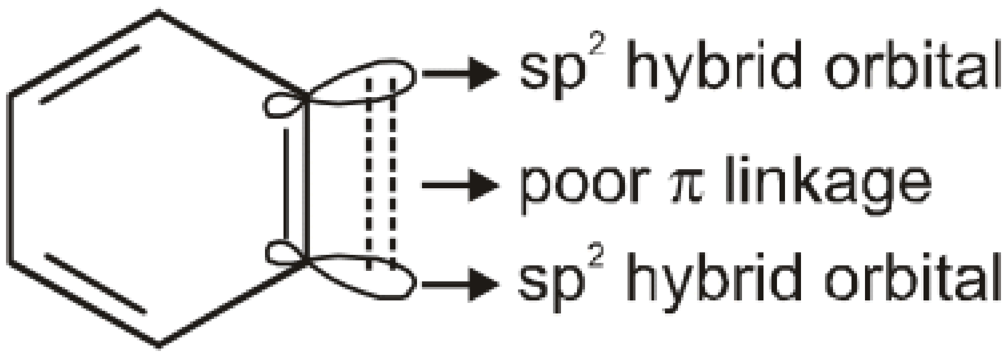
(E) Nitrenes :

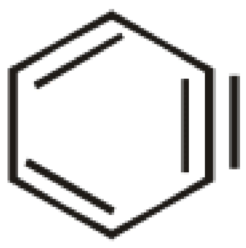
The nitrogen analog of carbenes are nitrenes. They are very much reactive since in them octet of N is incomplete. In nitrenes only one valencies of N are satisfied.

$R-\underset{\cdot\cdot}{\ddot{N}}$ $H-\underset{\cdot\cdot}{\ddot{N}}$

(F) Benzyne :

The benzene ring has one extra C – C π bond in benzyne





Clearly, we can see that the newly formed π bond cannot enter in resonance with other π orbitals of ring. since it is in perpendicular plane.

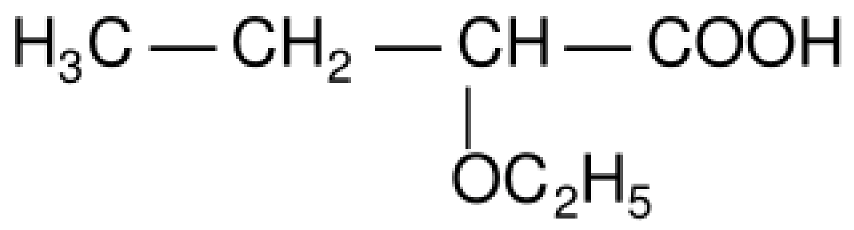
It is also important to note that hybridisation of each carbon involved in 'Benzynic bond' is sp^2 since the overlap between these sp^2 hybrid orbitals is not so much effective.

Structure Isomerism

Isomers	Characteristics	Conditions
(1) Chain Isomers	They have different size of main chain or side chain	They have same nature of locants
(2) Positional Isomers	They have different position of locants	They should have same size of main chain and side chain and same nature of locant
(3) Functional Isomers	Different nature of locant	Chain and positional isomerism is not considered
(4) Metamerism	Different nature of alkyl group along a polyvalent functional group	They should have same nature of functional groups chain & positional isomer is ignored
(5) Tautomerism	Different position of hydrogen atoms	The two functional isomers remains in dynamic equilibrium to each other

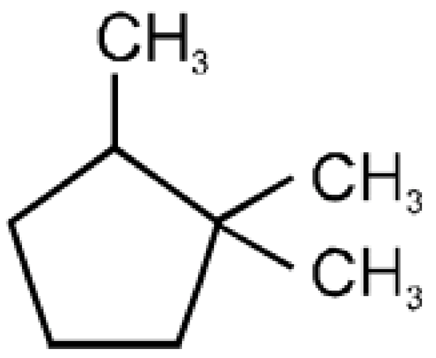
MISCELLANEOUS SOLVED PROBLEMS

1. Write the IUPAC name of following compounds.

(i) 

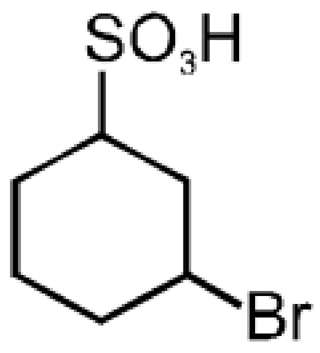
$H_3C-CH_2-\underset{\underset{OC_2H_5}{|}}{CH}-COOH$

(ii) 3-Bromocyclohexane-1-sulphonic acid

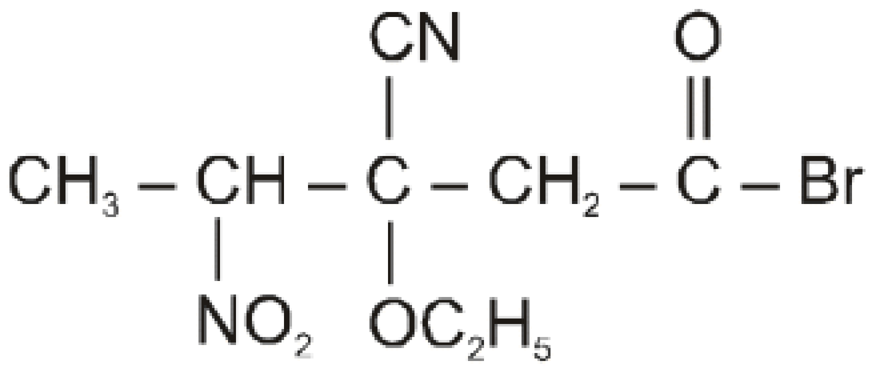
(iii) 

(iv) 3-Cyano-3-ethoxy-4-nitropentanoyl bromide

Sol. (i) 2-Ethoxybutanoic acid

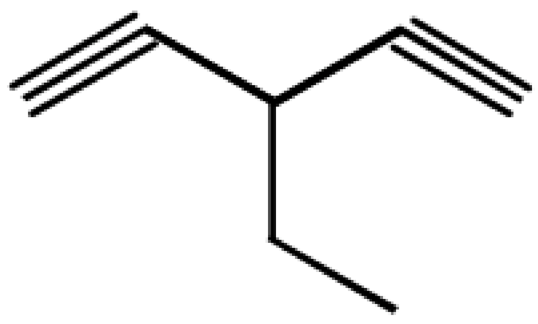
(ii) 

(iii) 1,1, 2-Trimethylcyclopentane

(iv) 

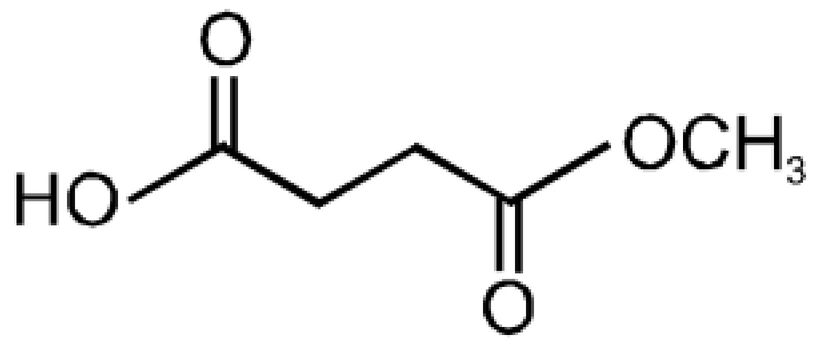
$CH_3-\underset{\underset{NO_2}{|}}{CH}-\overset{\overset{CN}{|}}{\underset{\underset{OC_2H_5}{|}}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-Br$

2. Draw the structure of following IUPAC name.

(i) 

(ii) 3-Methoxycarbonylpropanoic acid

Sol. (i) 3-Ethylpenta-1,4-diyne **(ii)**

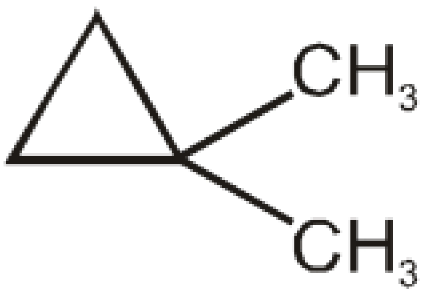


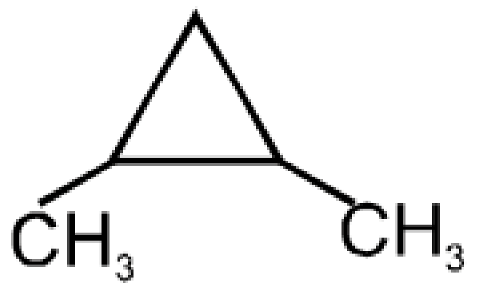
3. Find total number of structure isomers of dimethyl cyclopropane and dimethyl cyclobutane are respectively.

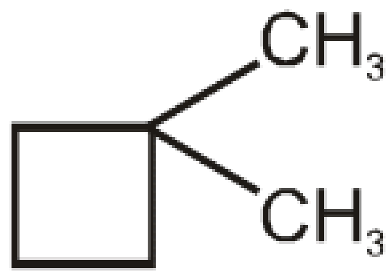
(A) 4, 6 (B) 3, 4 (C) 4, 5 (D) 2, 3

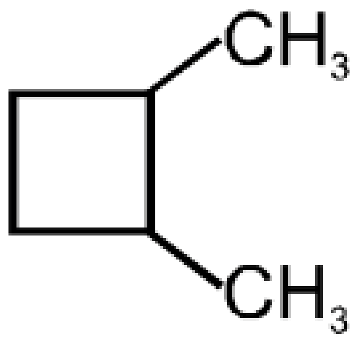
Ans. (D)

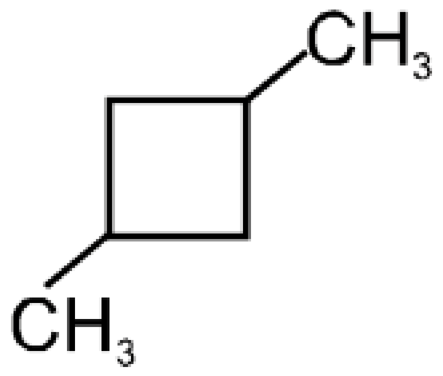
Sol.







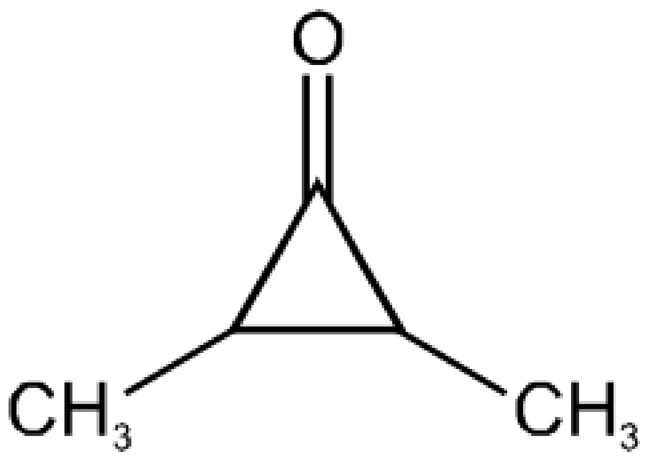


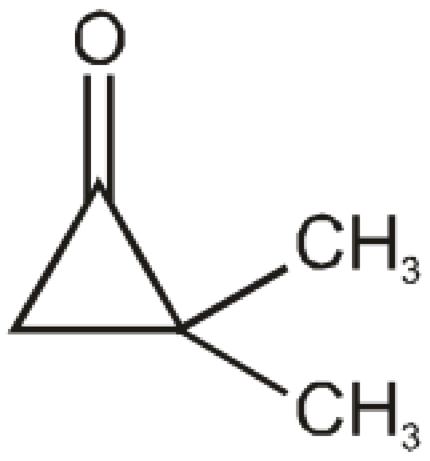


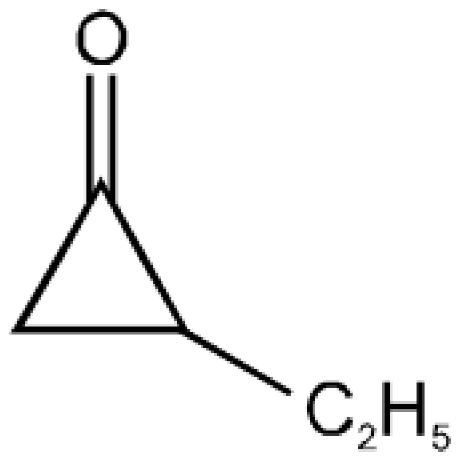
4. How many structures of cycloalkanone are possible with molecular formula C_5H_8O.

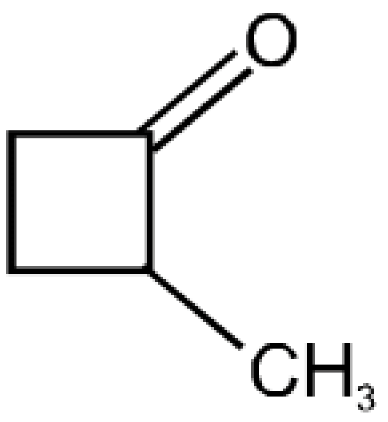
Ans. 6

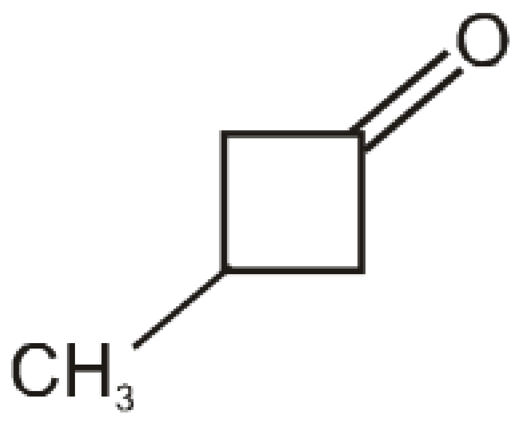
Sol.

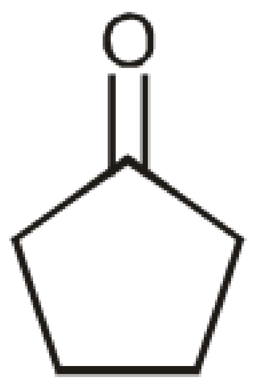








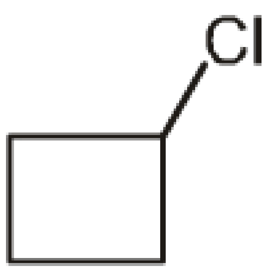


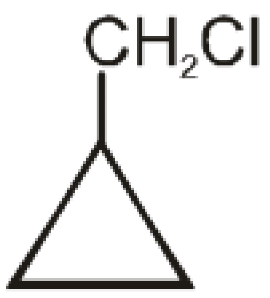


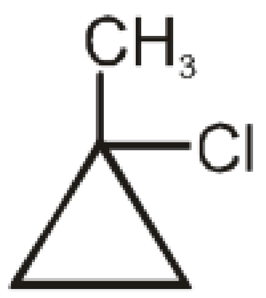
5. Find out the total number of cyclic isomers of the compound (X) C_4H_7Cl.

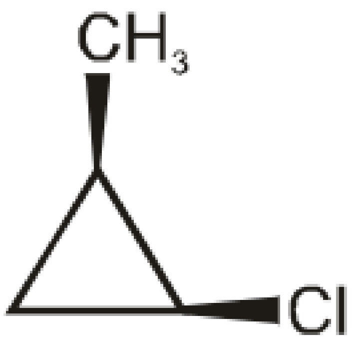
Ans. 4.

Sol. $X = C_4H_7Cl$ $DU = 5 - \frac{8}{2} = 1$





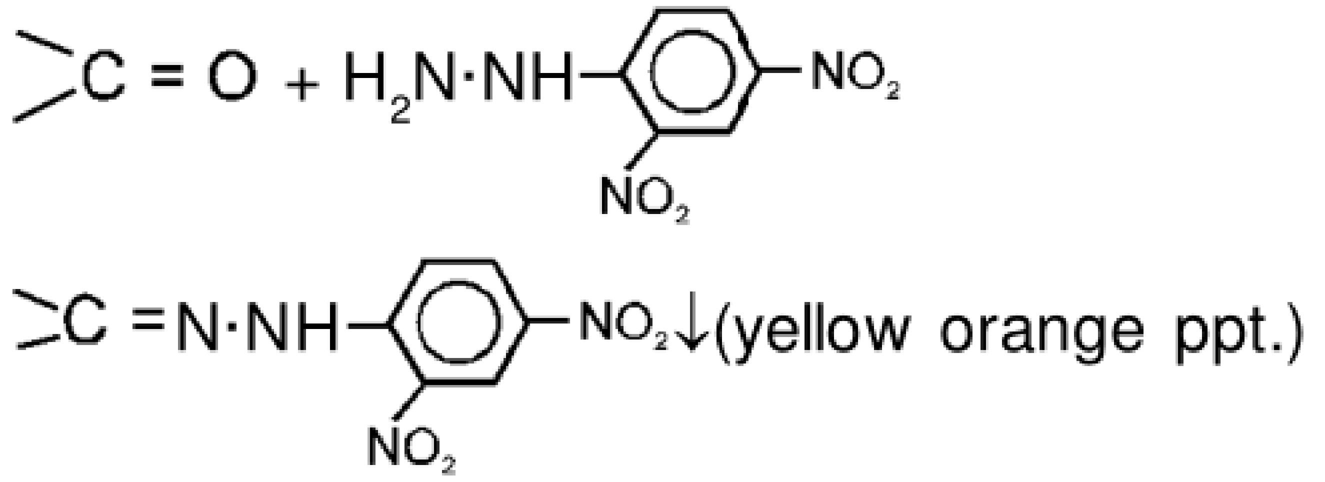
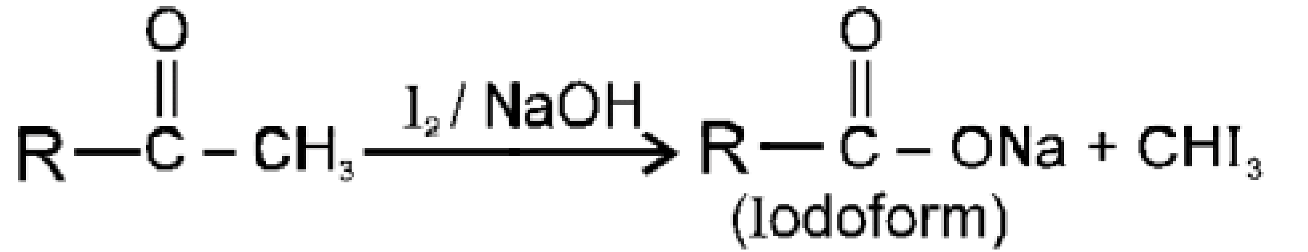
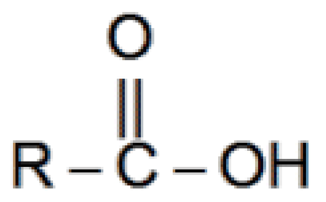




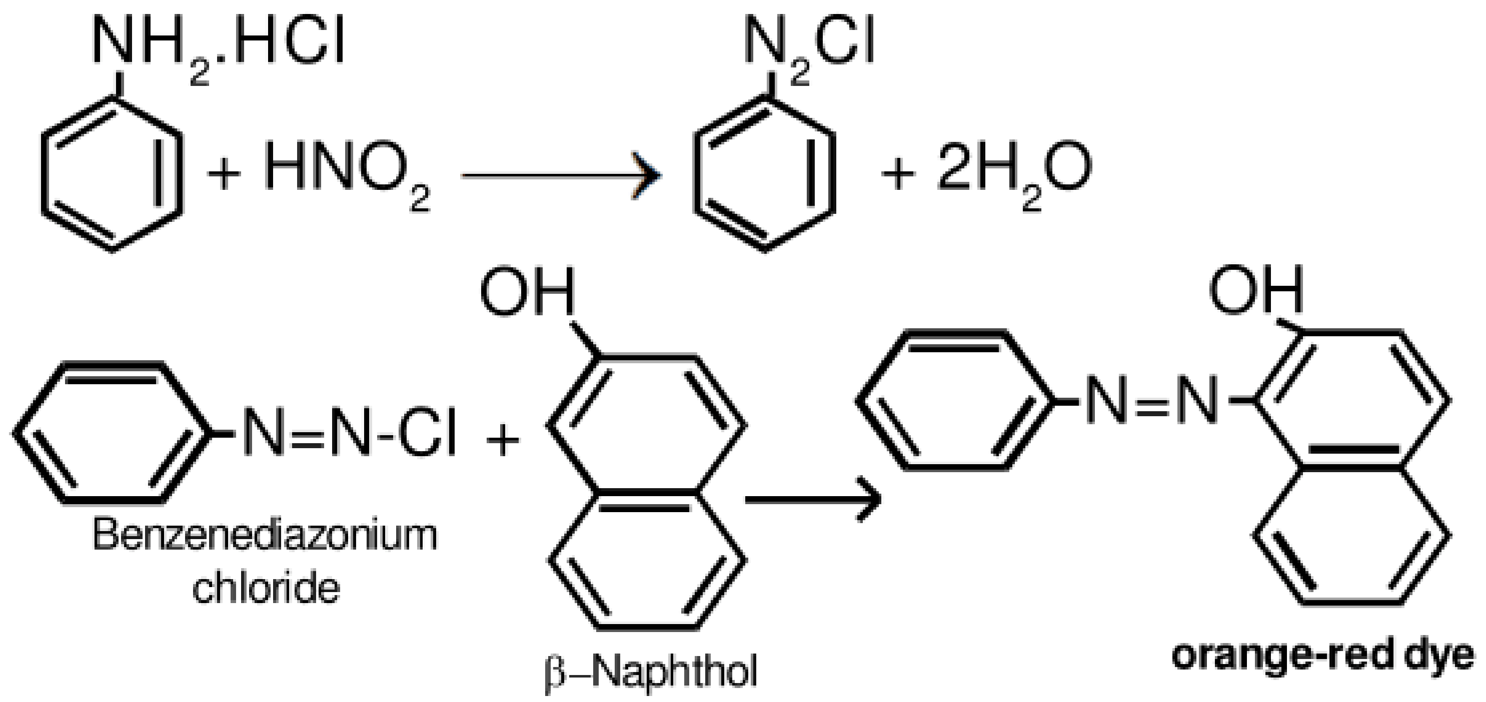
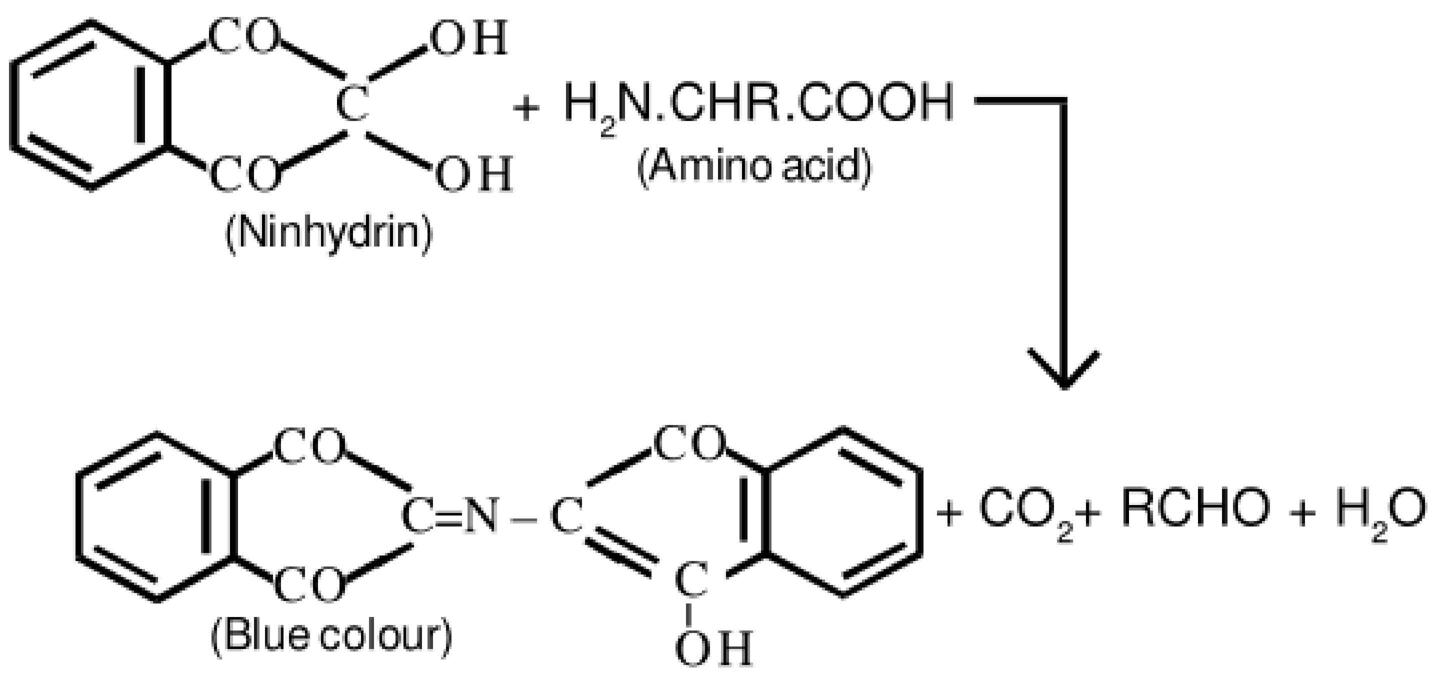
Total = 4

Identification of Functional Groups by Laboratory Tests

Functional Groups	Reagent	Observation	Reaction	Remarks
C–C (Alkane)	conc. H_2SO_4 conc. NaOH $KMnO_4$ $LiAlH_4$	NR NR NR NR	--------------	Inert paraffins
C=C / C≡C	[Bayer's reagent] alk. dil. cold $KMNO_4$	Pink colour disappears	$CH_2=CH_2+H_2O+O \xrightarrow{alk.KMnO_4} \underset{OH}{\underset{\vert}{CH_2}}-\underset{OH}{\underset{\vert}{CH_2}}$	Hydroxylation
C=C / C≡C	Br_2 / H_2O	Red colour decolourises	$Br_2+CH_2=CH_2 \longrightarrow$ white ppt	Bromination
C=C	O_3(ozone)	$>C=O$ Compounds	$H_2C=CH_2 + O_3 \xrightarrow{Zn/H_2O} 2HCHO$	Ozonolysis
C≡C	O_3	Acid formed.	$R-C\equiv C-R' \xrightarrow{O_3} RCOOH + R'COOH$	Ozonolysis
R–C≡CH (Terminal alkyne)	(a) Cuprous chloride+NH_4OH (b) $AgNO_3+NH_4OH$	Red ppt. White ppt.	$R-C\equiv CH + CuCl \xrightarrow{NH_4OH} R-C\equiv C\ Cu\downarrow$ (red) $R-C\equiv CH + Ag^+ \longrightarrow R-C\equiv C\ Ag\downarrow$ (white)	
(R–OH)	Na	Bubbles of H_2 come out	$2ROH + Na \rightarrow 2RONa + H_2\uparrow$	Presence of active 'H'
ROH 3° 2° 1°	Lucas Reagent [Conc. HCl + anhyd. $ZnCl_2$]	(3)° Cloudiness appears immidiately (2°) Cloudiness appears within 5 min. (1°) Cloudiness appear after 30 min.	$R-OH + HCl \xrightarrow{anhydrous\ ZnCl_2} \underbrace{R-Cl}_{cloudiness} + H_2O$	Lucas Test I. ter.alcohol II. sec. alcohol III. pri.alcohol

Functional Groups	Reagent	Observation	Reaction	Remarks
Ar–OH Enols	$FeCl_3$ (Neutral)	Coloured ppt. (violet, blue, green buff)	$6C_6H_5OH + FeCl_3 \longrightarrow [Fe(PhO)_6]^{-3}$	Test of enols/phenols
$>C=O$	2, 4-Dinitrophenyl hydrazine (2, 4-DNP) solution	Yellow orange ppt.		DNP-test
R–CHO	Fehling solution A & B	Red ppt.	$\underset{\text{Fehling sol}^n.}{RCHO + Cu^{+2}} \rightarrow RCOOH + \underset{\text{Red}}{Cu_2O\downarrow} + 2H_2O$	Fehling's test
	Tollen's reagent	Black ppt. or silver mirror	$RCHO + Ag^+ \rightarrow RCOOH + 2Ag$ (Silver mirror)	Tollen's test
	Schiff's Reagent *	Pink colour resume		
R–$COCH_3$ or $ArCOCH_3$ or CH_3CHO	I_2 / NaOH	Yellow ppt of CHI_3 (iodoform)	 $R-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{I_2/NaOH} R-\overset{O}{\overset{\|}{C}}-ONa + \underset{\text{(Iodoform)}}{CHI_3}$	Iodoform reaction
 $R-\overset{O}{\overset{\|}{C}}-OH$	Blue litmus	Litmus change to red.		Litmus test.
	Conc. $NaHCO_3$ solution	Effervescence evolve.	$R-COOH + NaHCO_3 \longrightarrow RCOONa + H_2O + CO_2\uparrow$	Sodium bicarbonate test
Ester	NaOH, phenophthalein	Pink colour ↓ disappear on heating.	RCOOR' + NaOH + Phenophthalein (pink) $\downarrow\Delta$ RCOOH + R' OH (Colourless solution)	
Amides	Conc. NaOH, Δ	Smell of NH_3	$RCONH_2 + NaOH \xrightarrow{\Delta} RCOONa + NH_3\uparrow$	

★ Schiff's reagent : p-Rosiniline hydrochloride saturated with SO_2 so it is colourless. The pink colour is resumed by RCHO.

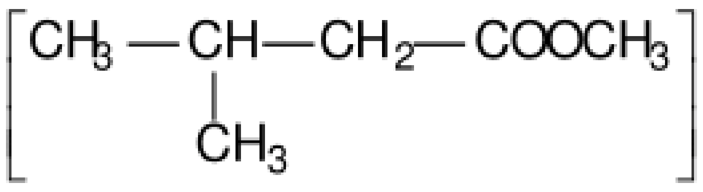
Functional Groups	**Reagent**	**Observation**	**Reaction**	**Remarks**
Nitro Compounds (RCH_2NO_2) or $ArNO_2$	Mulliken's test	black ppt	$\begin{matrix} Ar-NO_2 \\ (R-NO_2) \end{matrix} \xrightarrow[(1)]{Zn / NH_4Cl, \Delta} ArNHOH \xrightarrow[(2)]{\substack{\text{Tollen's reagent} \\ AgNO_3 + NH_4OH}} Ag\downarrow$	
Amines(pri.) RNH_2	$CHCl_3$, KOH	Nauseating odour (Offensive smell) (Carbylamine)	$RNH_2 + CHCl_3 + 3KOH \rightarrow RNC + 3KCl + 3H_2O$	Carbylamine Reaction
	HNO_2 ($NaNO_2$+HCl)	Effervescence of N_2	$RNH_2 + HONO \rightarrow ROH + N_2 + H_2O$	
Ar. amines. $ArNH_2$	HNO_2 ($NaNO_2$+HCl) + β-Naphthol	Orange red dye is formed	$NaNO_2 + HCl \rightarrow NaCl + HNO_2$  $NH_2.HCl$ + HNO_2 → N_2Cl + $2H_2O$ N=N-Cl + OH → N=N- OH Benzenediazonium chloride β–Naphthol orange-red dye	Azo dye test
R_2NH Sec. Amines	(i) $NaNO_2 + H_2SO_4$ (ii) Phenol	red colouration Liebermann test	 CO C OH OH CO + $H_2N.CHR.COOH$ (Ninhydrin) (Amino acid) CO C=N – C CO C OH + CO_2+ RCHO + H_2O (Blue colour)	Ninhydrin test
Carbohydrate	Molisch's reagent (10% α-naphthol in alcohol).	Violet colour		
Amino acids	Ninhydrin reagent (0.2 % sol.^{n})	Blue colour		

ORGANIC CHEMISTRY

Nomenclature

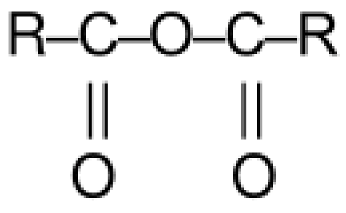
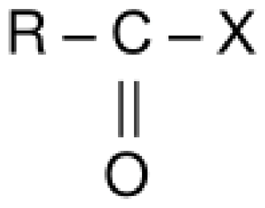
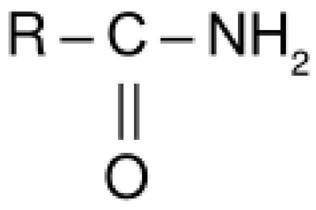
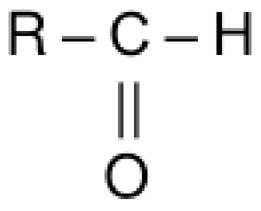
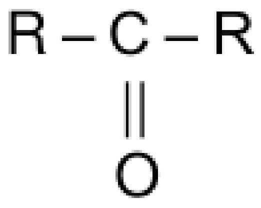
Examples of Compound containing different functional groups with common / trival names.

No. of carbon atoms	Prefix	–CHO (Aldehyde)	–COOH(–ic acid)	–COCl.(–yl chloride)	$-CONH_2$ (Amide)
1	Form	HCHO Formaldehyde	HCOOH Formic acid	HCOCl Formyl chloride	$HCONH_2$ Formamide
2	Acet	CH_3CHO Acetaldehyde	CH_3COOH Acetic acid	CH_3COCl Acetyl chloride	CH_3CONH_2 Acetamide
3	Propion	CH_3CH_2CHO Propion aldehyde	CH_3CH_2COOH Propionic acid	CH_3CH_2COCl Propionyl chloride	$CH_3CH_2CONH_2$ Propionamide
4	Butyr	$CH_3CH_2CH_2CHO$ n–Butyraldehyde	$CH_3CH_2CH_2COOH$ n–Butyric acid	$CH_3CH_2CH_2COCl$ n–Butyryl chloride	$CH_3CH_2CH_2CONH_2$ n–Butyramide
5	Valer	$CH_3CH_2CH_2CH_2CHO$ n–Valeraldehyde	$CH_3CH_2CH_2CH_2COOH$ n–Valeric acid	$CH_3CH_2CH_2CH_2COCl$ n–Valeryl chloride	$CH_3CH_2CH_2CH_2CONH_2$ n–Valeramide
3C+1 Double bond	Acryl	$CH_2=CH-CHO$ Acrylaldehyde	$CH_2 = CH-COOH$ Acrylic acid	$CH_2 = CH-COCl$ Acryl chloride	$CH_2=CH-CONH_2$ Acrylamide
4C + 1 Double bond (at 2nd Carbon. atom)	Croton	$CH_3-CH=CH-CHO$ Crotonaldehyde	$CH_3CH_2 = CH-COOH$ Crotonic acid	$CH_3CH_2 = CH-COCl$ Crotonyl chloride	$CH_3CH_2 = CH-CONH_2$ Crotonamide

No. of carbon atoms	Prefix	$-CN$(–O nitrile)	$-N \overset{\rightarrow}{=} C$(Oisonitrile) If Suffix isocyanide is used than. Carbon atom of – NC not counted. If suffix carbyl amine is used. Carbon atom of – NC not counted. If O-isonitrile is used → Carbon atom of – NC counted	$-COOR$ Ester
1	Form	$H-C \equiv N$ Formonitrile	$H-N \overset{\rightarrow}{=} C$ Formoisonitrile	$HCOOCH_3$ Methyl formate
2	Acet	$CH_3C \equiv N$ Acetonitrile	$CH_3-N \overset{\rightarrow}{=} C$ Acetoisonitrile	CH_3COOCH_3 Methyl acetate
3	Propion	$CH_3CH_3\ C \equiv N$ Propionitrile	$CH_3CH_2N \overset{\rightarrow}{=} C$ Propionisonitrile	$CH_3CH_2COOCH_3$ Methyl propionate
4	Butyr	$CH_3CH_2CH_2\ C \equiv N$ n–Butyronitrile	$CH_3CH_2CH_2N \overset{\rightarrow}{=} C$ n–Butyroisonitrile	$CH_3CH_2CH_2COOCH_3$ Methyl n–butyrate
5	Valer	$CH_3CH_2CH_2CH_2\ C \equiv N$ n–Valeronitrile	$CH_3CH_2CH_2CH_2N \overset{\rightarrow}{=} C$ n–Valeroisonitrile	 $\left[CH_3-\underset{\displaystyle CH_3}{\underset{\mid}{CH}}-CH_2-COOCH_3\right]$ Methyl isovalerate
3 C +1 Double bond	Acryl	$CH_2 = CH - C \equiv N$ Acrylonitrile	$CH_2 = CH-NC$ Acrylisonitrile	$CH_2=CHCOOCH_3$ Methyl acrylate
4C + 1 Double bond (at 2nd Carbon. atom)	Croton	$CH_3CH = CH - C \equiv N$ Crotononitrile	$CH_3-CH=CH-NC$ Crotonoisonitrile	$CH_3CH=CHCOOCH_3$ Methyl crotonate

Secondary suffix of some common functional groups (IUPAC)

A secondary suffix is added to the primary suffix to indicate the nature of the functional group present in the organic compounds. Secondary suffix of important functional groups are given below in their decreasing order of seniority.

	Class	Name	Suffix	Prefix
1.	$R{-}COOH$	Alkanoic Acid	– oic acid (carboxylic acid)	carboxy
2.	$R{-}SO_3H$	Alkane sulhonic Acid	– sulphonic acid	sulpho
3.	 $R-\underset{\underset{O}{\|}}{C}-O-\underset{\underset{O}{\|}}{C}-R$	Alkanonic Anhydride	– oic anhydride (carboxylic anhydride)	------------
4.	$R{-}COOR$	Alkyl alkanoate	– oate (carboxylate)	alkoxy carbonyl or alkanoyl oxy
5.	 $R-\underset{\underset{O}{\|}}{C}-X$	Alkanoyl halide	–oyl halide (carbonyl halide)	halo carbonyl
6.	 $R-\underset{\underset{O}{\|}}{C}-NH_2$	Alkanamide	– amide (carboxamide)	carbamoyl
7.	$R-C\equiv N$	Alkanenitrile	– nitrile (carbonitrile)	cyano
8.	 $R-\underset{\underset{O}{\|}}{C}-H$	Alkanal	– al (carbaldehyde)	formyl / oxo
9.	 $R-\underset{\underset{O}{\|}}{C}-R$	Alkanone	– one	oxo
10.	$R{-}OH$	Alkanol	– ol	hydroxy
11.	$R{-}SH$	Alkanethiol	– thiol	mercapto
12.	$R{-}NH_2$	Alkanamine	– amine	amino

IUPAC system of nomenclature

The IUPAC name of any organic compound consists of maximum five parts in the following sequence.

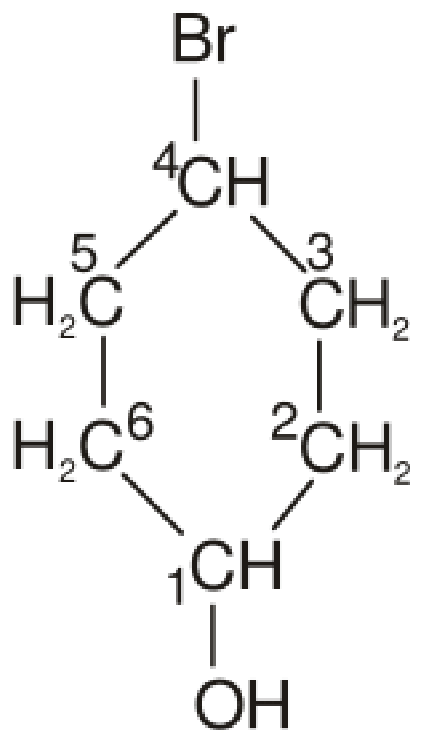
Secondary prefix + Primary prefix + Word root + Primary suffix + Secondary suffix

The following examples illustrate the use of word root, primary suffix and secondary suffix in naming of organic compounds.

Organic compounds	Word root	Primary suffix	Secondary suffix	IUPAC name
CH_3CH_2OH	Eth	an(e)	ol	Ethanol
$CH_3CH_2CH_2NH_2$	Prop	an(e)	amine	Propanamine
$CH_3CH_2CH_2COOH$	But	an(e)	oic acid	Butanoic acid
CH_3CH_2CN	Prop	an(e)	nitrile	Propanenitrile
$CH_2 = CHCHO$	Prop	en(e)	al	Propenal
$HC \equiv CCOOH$	Prop	yn(e)	oic acid	Propynoic acid

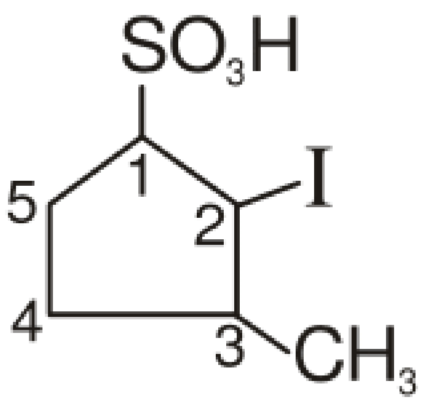
The following examples illustrate the use of word root , primary prefix and secondary prefix in naming of organic compounds.

Ex.(i)



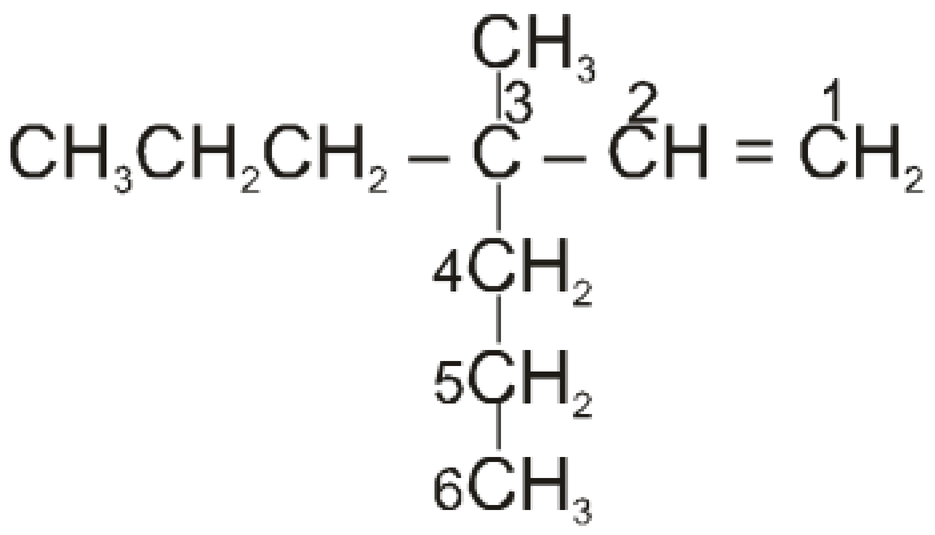
4-Bromo	+	cyclo	+	hex	+	an (e)	+	1-ol
Secondary prefix		Primary prefix		Word root		Primary suffix		Secondary suffix

(ii)



2-Iodo-3-methyl	+	cyclo	+	pent	+	ane	+	1-sulphonic acid
Secondary prefix		Primary prefix		Word root		Primary suffix		Secondary suffix

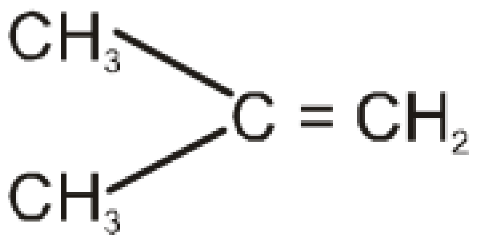
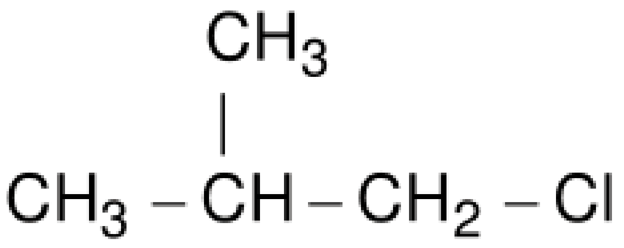
(iii)

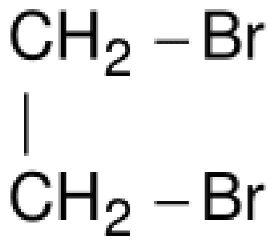
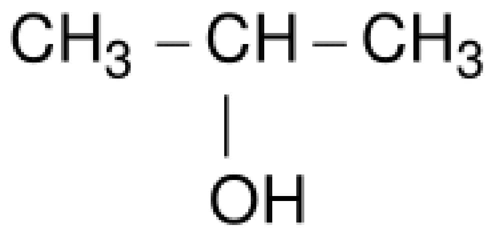
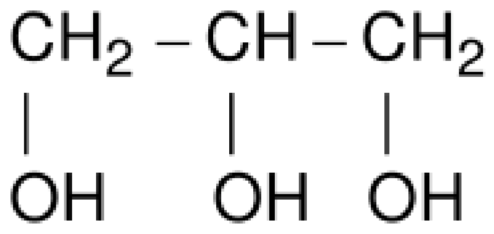
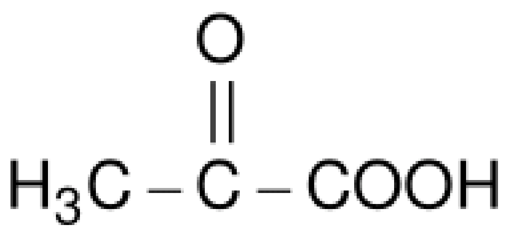
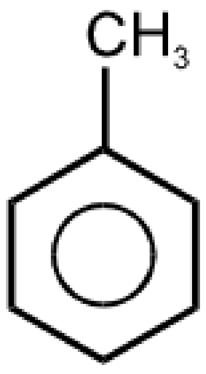


$$CH_3CH_2CH_2-\overset{CH_3}{\underset{CH_2CH_2CH_3}{\overset{|}{\underset{|}{C}}}}-CH=CH_2$$

Position of double bond will be indicated as no. 1, Hence name will be 3–Methyl–3–propylhex–1–ene

Common and IUPAC Names of Some Organic Compounds

S.No.	Compound	Common names	IUPAC name
1.	$CH_3CH{=}CH_2$	Propylene	Propene
2.	 $(CH_3)_2C=CH_2$	Isobutylene	2-Methylpropene
3.	$H_3C{-}C{\equiv}CH$	Methyl acetylene	Propyne
4.	 $CH_3-\overset{CH_3}{\overset{\mid}{C}H}-CH_2-Cl$	Isobutyl chloride	1-Chloro-2-methylpropane

5.	 $\begin{array}{l}CH_2-Br\\ \vert\\ CH_2-Br\end{array}$	Ethylene dibromide	1, 2-Dibromoethane
6.	$CH_2=CH-Cl$	Vinyl chloride	Chloroethene
7.	 $CH_3-\underset{OH}{\underset{\vert}{CH}}-CH_3$	Isopropyl alcohol	Propan-2-ol
8.	$CH_2=CH-CH_2-OH$	Allyl alcohol	Prop-2-en-1-ol
9.	 $\underset{OH}{\underset{\vert}{CH_2}}-\underset{OH}{\underset{\vert}{CH}}-\underset{OH}{\underset{\vert}{CH_2}}$	Glycerol or Glycerine	Propane-1, 2, 3-triol
10.	CH_3-CHO	Acetaldehyde	Ethanal
11.	$CH_3-CO-CH_2CH_3$	Ethyl methyl ketone	Butanone
12.	CH_3-COOH	Acetic acid	Ethanoic acid
13.	 $\begin{array}{l}COOH\\ \vert\\ COOH\end{array}$	Oxalic acid	Ethanedioic acid
14.	 $H_3C-\overset{O}{\overset{\Vert}{C}}-COOH$	Pyruvic acid	2-Oxopropanoic acid
15.	CH_3-COCl	Acetyl chloride	Ethanoyl chloride
16.	CH_3-CONH_2	Acetamide	Ethanamide
17.	CH_3-NH_2	Methylamine	Methanamine
18.	CH_3-CN	Methyl cyanide or Acetonitril	Ethanenitrile
19.	$CH_3-N^+\equiv C^-$	Methyl isocyanide or Methyl carbylamine	Methane isocyanide
20.		Toluene	Methylbenzene or Toluene