IUPAC system I IUPAC name of aldehyde ix Obtained by replacing 'e' (terminal) of parent alkane by al'. The carrengl carron of aldered is numbered as 1' while counting the carbon atoms.

Alkane-e+al = Alkanal. 5 4 3 2 1 C-C-C-C-CHO

Aliphatic aldehydes:

Acetaldehyde propionaldehyde Budysuldehyde c· N => Formaldehyde propanal Ethanal I-N=1 Methanail

CH-CH-CH2-1-H (H3CH2CH2-CH2-C-H ∠-Chlorobutyraldehyde 13-Bromobutyruldehy.

de CIVE valeraldehyde 3-Brosonbutana 2-chlorobutana pentanal

CH3 CH-CH-CH2-CH2-1-H CH2-CH-CH2-H 23 3 2-Hydroxybutgraldehyde 3-Hydroxybutamal C·IV-3 y-mettyfvaleraldehyde I·N=) 4-mettyfpentanal

Aromatic aldehydes

(·N·=) Benzaldehyde

I.N.=) Benzaldehyde

salicylaldehyde (otydroxy-benzouldehyde)

2-Hydroxybenzaldehyde

m-Hitrobenzuldehyde m-meltyllen-3-Nitrobenzaldehyde

3-reltyfsen zalachypice

Ketone:>

Common system /2 common name of ketone is written by Writing the namer of alkyl or anyl groups attached to the carbonyl carbon atom in the alphabetical order before the word 'ketone'.

IUPAC system; I IUPAC name of ketone is obtained by replacing 'e' (terminal) of parent alkane by 'one'.

Alkane-etone -> Alkanone.

Aliphatic ketones 🤧 ethylpropylketone Hexan-3-one [·IV=] Dimetujketone Diettyketone (Aceture) pentan-3 one [H3 0 3-pentanone 2-Bromodietay/ketone 2-Bromopentarr3-one (·N·→ Methylisopropylketone IND 3-Melty/butan-2-one

Arumatic Ketones -CH3

(.N=) Acetophenone (Methylphenylketone)

I'N: > Acetophenone (phenylettanone)

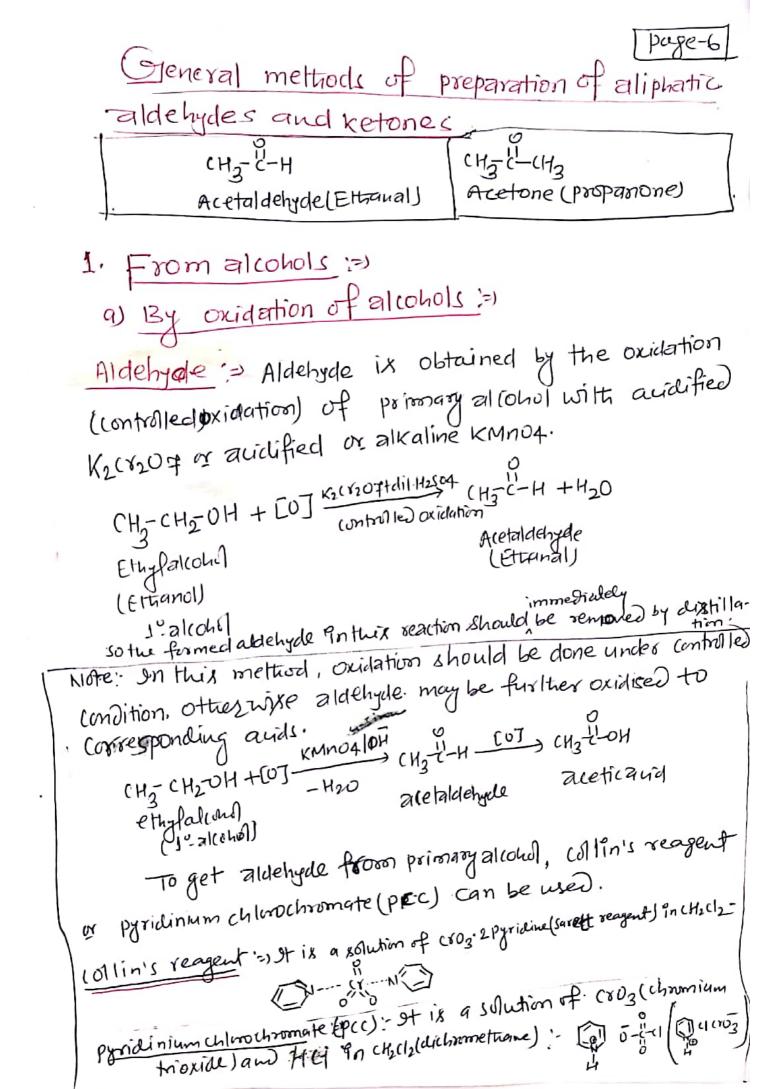
Benzophenone (Diphenylketone) Benzophenone (Dipheny mettanone)

consumply group is attached to a senzene A ketone in which the

Aliphatic aldehydes and ketones I somerism in aldehydes and ketoner: they (aldehydes and ketones) show the following ng types of structural ixornerisons. 1 chain isomerism; Aldehydes containing four or more c-atoms and ketones containing five or more c-atoms show chain isomerism. C4H80 Aldehyde CH3 (H3-(H2-CH0 CH3-CH0 CH3-CH0) Butanal 2-Metty/propanal (H3 CH2CH2CH2CH3 (H3 CH-CH-CH3 53432213 433 pentan-2-one 3-Methylbutan-2-one CSHIDD 2) Position isomerism > Aldehydes generally donot

show position isomerism because - tho group in ald-ehyde is present at the end of the chain. Ketones containing five or more c-attorns show(exhibit) position isomerismo

3 Functional isomerism;> Aldehydes and ketones having some no. of c-atoms (at least three re-atoms Show functional isomerism. (H3-CH2-CHD (H3-{1-(H3) C3460



Pagat

Ketone: ketone is obtained by the oxidation of secondary alcord with acidified K2(1207 or acidified or alkaline KMno4.

b. By catalytic dehydrogenation of alcohols :>

Aldehyde: Aldehyde is obtained by passing vapours of primary alcohol over heated copper at 300c.

<u>Ketone</u>; Ketone is obtained by passing vapours of secondary alcohol over heated copper at 300°c.

any always on
$$\frac{cu}{(H_3-cH-cH_3)} - \frac{cu}{300°c} > cH_3-cH-cH_3 + H_2\uparrow$$

Tropropyl alcolul (propan-2-01)

 $\frac{(h_3-cH-cH_3)}{(h_3-cH-cH_3)} - \frac{(h_3-cH-cH_3)}{(h_3-cH-cH_3)} + \frac{(h_3-cH-cH_3)}{(h_3-cH-cH_3)}$

2. From alkenes: By ozonolysx of alkenex:

Alkene reacts with ozone (03) in presence of cc14 to form ozonide (Unstable) which on hydrolysiz with H20 (water) in presence of zinc gives cashonyl compound (aldebyde or land Ketone).

=> In this reaction, if the doubly bunded carbon has a Hatum, then aldehydes are formed on the other hand, if these is no H-atom on doubly bonded carbon atom, then ketone

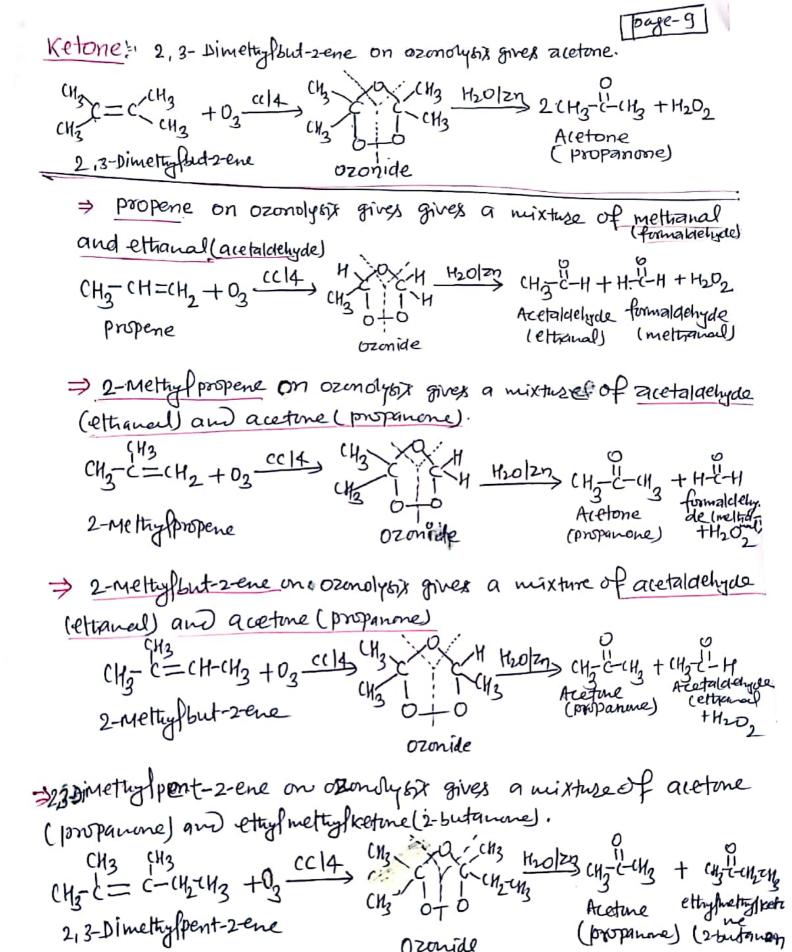
> In case of symmetrical alkene, two same molecules of carronyl compounds (aldelyde or ketone) are formed but In case of unsymmetrical alkene, mixture of carronyl Compounds (aldelydeand and sidelyde or aldelyde and kotone or ketone and ketone) is formed

(i.e. Nature of products formed depend upon the nature of alkenes)

Ethene on Ozonolysix gives formaldehyde Aldehyde: CH2= (H2+03 cc/4, H) CH H20/20 2H-E-H + H20/20 forsmaldehade o-io formaldehyde ozonide (Methanal) ethylene (ethene)

. But-2-ene on ozonolysis gives atetaldelyde CH3 CH= CH-CH3 +03 CC14 H2012n 2CH3-C-H+H202

CH3 CH3 CH3 Acetaldehide (Ethanal) But-2-ene ozonide 2-Butene



Ozonide

+ 1120s

(propanne) (2 butones

3. From acid chloride (acyl chloride);=)

Aldehede; By Rosenmund's reduction):
Aldehede; Aldehyde is prepared by the reduction of
Auid Chloride with H2 (hydrogen) in the presence of palladium catalyst suspended in Baso4 (barium sulphate). Twis
reaction is known as posenmund's reduction reaction.

Note: Dindles's catalyst: pol/Baso4 is poisoned by sulphur or quinoline (ETT) to prevent the reduction of aldelyde to introhol. Ketunes can not be prepared by this method. Furmal dehyde cannot be prepared because furnyl chloride (McOC) is unstable at room temperature.

Ketone; => ketone ix prepared by treating acid chloride with dialog cadmium [cd(CH3)] in the presence of dry-ether;

2 CH3 C-CI + Cd(CH3)2 (H3-C-CH3 + Cd Cl2)

dimelty cadmium Acetone

Acetyl chloride (Proparone)

(tilianoyf chloride)

4. from gen-dihaloalkane (gen dihalide): By the hydrolysix of gen dihalides:

Aldehyde: Aldehyde is prepared by the hydrolysis of gen dinalide (two halogen atoms attached to terminal

(35600 atom) with agraliali like KOH, NAOH, CaloH) pr B4(01)

R-(H2-GH + Ca(DH)2
$$\xrightarrow{\triangle}$$
 R-(H2-GH) $\xrightarrow{\bigcirc}$ R-(H2-GH) $\xrightarrow{\bigcirc}$ R-(H2-GH) $\xrightarrow{\bigcirc}$ R-(H2-GH) $\xrightarrow{\bigcirc}$ R-(H2-GH)2 $\xrightarrow{\bigcirc}$ Aldehyde.

Teominal generalized in a literature of the contraction of t

Ketone: Ketone is prepared by the hydrolysis (Loiling) of gem dihalide (two halogen atoms attached to Carbon atom other than terminal carbon atom) with carbon atom other than terminal carbon atom) with agrakali Kott, Naon, Ca(OH)2, 139(OH)2.

R-C-R+
$$(a[OH]_2 \xrightarrow{A} R-C-R \xrightarrow{OTH} R-C-R + H_2O$$

Non-terminal generalisation Alkanechial

(Unstable)

(H₂-C-CH₃+(a(OH)₂-CaCl₂

(2)2-bichlim propane)

(Unstable)

(Unstable)

(Unstable)

5. From alkgores & By catalytic hydration of alkgressia

Aldehyde: Acetaldehyde is obtained by the catalytic hydration of acetyfene (eltyne) with 20-40%. H2504 and 1% Hg504 as catalyst at 60°C.

H-C=C-H+H₂0 20-40%. H₂504, 60°C H-C=C-H Regrangement (y₃-t'-H)

Acetylene (ethenol) (Hand)

Unstable)

Telegrande

Note: Besides. acetylene (ettyne) all alkgnes give ketones in presence of 2040 % H2SUR and LX. Hysol at 60°C.

etone: Ketone is prepared by the catalytic hydratics, of alkyne [except: acetylene (ethyne)] with 2040%.

H2SO4 and 1%. H9SO4 at 60°C. It follows prosikovnikov's

CH3 C=CH+ H2O 20-40%. H2SO4, (H3 C=CH2 Rearrangements (H3 C-CH3 Methy) acetylene

(Propyne)

Propen-20)

(mytuble)

Acetone

(propanone

Physical properties:

1. Physical State > Formaldelyde ix agos and acetaldehyde ix volatile liquid. Lower addenydes and ketone s (upto (11) are colourless liquids. but higher members are solids.

(40%, aqueous solution of formalidelyde is called forma-I'm, which it used as preservative of anatomic specimens).

- 2-smells Lower aldehyder have unpleasant irritating odours while higher aldehydes and ketones poesess pleaxant odours.
- 3. Solubility: Aldehydes and Ketones containing four carson atoms are soluble due to the formation, of intermolecular hydrogen binding between Carbonyl group and water moreculex

But higher aldehydes and ketones are insoluble due the increase in the size of alkylgroups and their hydrophobic nature.

4. Boiling points and ketones have higher boiling points than those of alkanes butter luver boiling points than those of comparable weights

of alcohols and carsoxylicavids. Their higher boiling points the an the alkaner are due to intermoleular dipole-dipole interaction between opposite ends of dipoles.

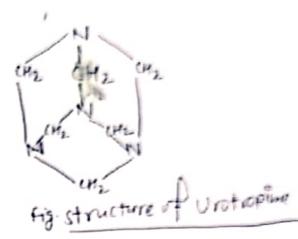
5-0----cst St | 11 St C-----OS-Fig- Dipule-dipule zinteraction.

However, these dipole-dipole interactions are weaker than the intermolecular hydrogen sindings in alcohols and cassoxylicacids.

Isomeric aldehodes possess less boiling point than 2 someric ketones.

propanal propanal soc

Dipôle-dipôle interaction ix weaker in aldehyde tran



b) With NH20H (hydroxylamine) to form oxime aldehyde or ketone reacts with hydroxylamine to form aldoxime or ketoxime.

H $(H_3 - C \pm O + H_2 N - O H) \longrightarrow (H_3 - C = N - O H) + H_2 O$ Acetaldehyde hydroxylamine (ethanaloxime) $(H_3 - C \pm O + H_2 N - O H) \longrightarrow (H_3 - C = N - O H) + H_2 O$ Acetone hydroxylamine Acetoxime (ketoxime)

(propanone)

(propanoneoxime)

C) With NH2-NH2 (hydrazine); => to form hydrazone Aldehyde or ketone reacts with hydrazone (N2H4) to form aldehyde or ketone hydrazone.

e) With 2,4-DNP or 2,4-DNPH (2,4-dinitrophenylhydrazine);

(H2N-NH= 10/2); =) to form yellow crystalline

PPt. of 2,4-dinitrophenylhydrazone.

(H3-C+0+ H2NI-NH-(O) ---> (H3-C=N-NH-(O) + H2O

Acetone Phenylhydrazone

(propanone phenyl hydrazone)

phenyl hydrazine

Acetone

(propanone)

Aldehyde or ketone reacts with 2,4- DNP to form yellow crystalline precipitate of aldelyder ketone-2,4dinitrophenylhydrazone. This reaction is used to identify the carbonyl group (aldehyde and ketone) from Other categories of organic compounds in the laboratory. CH3-C+0+ H2N-NH-(0)-NO2-+(H2-C=N-NH-(0)-NO2+160 2,4-DNP Acetaldelyde Ethanal-214-director phenylhyd (Ethanal) (Yellow crystalline ppt) orange red ppt CH_2 1402 CH2-C = 0 + H3N-NH-(0)-NO2-> (H2-c=10-NH-O)-N102 +H20 Acetone 2,4-NNP Propanone-2,4-clinitrophonylhydra-(propanone) (Yellow copstalline ppt) orange red ppt. An aqueous solution of 21-4-DNP (dinitrophenyl hydraz fre) is called f) with KN-NH-E-NH2 (semicarbazide) = to form semicarbazone Aldehyde or ketone reacts with semicorbazide to form aldehyde or ketone semi arobazone. CH3-C-D+ H2N-NH-C-NH2-> CH3-C=N-NH-E-NH2+H2D Acetaldelicle semicarbazone Semicabazide (Ethanal Semicarbane) Acetaldehyde (Ethanal) CH3-C+0+H2N-NH-C-NH2-> CH3-C=N-NH-C-NH2+H20 Acetone Lemicassazone Semicarbazide Acetone

(propanone)

(Propanone semicars azone)

Bistinction between oldehyder and ketone.

a) With Tollen's reagent (Ammonical silvernitrate solution):

Ammonical silvernitrate (AgNO3) solution is call

ad Tollen's reagent.

Tollen's reasent ix prepared by adding ammonium hydr Oxide (NH40H) to Aginoz solution till the grey pot of Agon (formed by adding few drops of dil NaOH with Agrio3) just formed first gets dissolved.

Agnio3+ MH40H-> AgoH +NH4NO3 2 AgoH = Ag20 + H20 gregippt

Ag20 +4NH40H ->2[Ag(NH3)2]04 +3H20

Tollen's reagent
[Biammine Sivery hydroxide]

AgoH +2N1H4OH -> Ag(NH2)3 OH

when an aldehyde is warmed with Tollen's reagent, it (aldehyde) gets oxidized to ammonium carboxylate and silver ions get reduced to metallic silver. This metallic silver gets deposited on the inner wall of the test tube to form a silvernirror. Therefore, this reaction is also known as Silver mirror text.

R-C-H +2[Ag(NH3)2] OH WATM R-C-ONTH4 + 2Ag V +3NH3+ H2D Ammonium carboxylate Tollen's reagent

Aldehyde

CH3-C-H +2 [Ag (NH3)2] OH warm CH3-C-ONH4 +2 Ag + +3NH3 + H2D Acetaldehyde jollen's reagent Ammonium acetate sine mirror (Ethanal)

()-C-H + 2 [Ag(NH3)2]OH WARM ()-C-ONTH4 +2Ag + +3NH3+ H2O Tollen's ocapeul genzaldehyde

But Ketone does not give Tollen's reagent.

b) With Fehling's solution (Fehling text)

Fehling solution ix a mixture of Fehling-A and Fehling B. Fehling-A=> cuso4 solution.

Fehling-B= sodium potassium tartarate (Rochelle Salt) in NGOH solution.

(CHOH)2 COOK sod. Put. tartarate.

When an aldehyde is warmed with fehlings solution, it aldehyde) oxidises to ansoxylic acid and a red ppt of cuzo (cuprous oxide) ix obtained.

R-C-H + C42+ 40H Warm> R-E-OH+ C4201 +2H20 Aldehyde from Felling solution (2004)

CHg-1-11 + (42+ +4 OH - Warm > CH3-1-0H + C4201, +2420 Acetaldehyde from fehling solution (Red PPt)
(Ethanal)

But ketone doesnot give this test.

Benzaldehyde also doesend give this test.

Reason: o due to lack of a- hydrogen in benzaldehyde it cannot form an enolate and true donor give a positive text with felling s solution which is comparatively a weaker oridizing agent trans Men's reagent, under usual anditions.

This test is used to identity aliphatic aldehyde from anomal aldehyde and ketone:

a) With H2 in presence of Ni, polar pt or LiAlH4 or NaBHA) reduction of ;c=0 group

Aldehyde and ketone can be reduced to primary and secondary alcohols respectively by using reducing agents like H2/Niorpdorpt or LiAIH4 or NaBH4(sodium borohydride).

CH₃-C-CH₃+H₂
$$\xrightarrow{Ni}$$
 CH₃-CH-CH₃

ixopropytalcohol

Acetone

(propanone)

 2° -alcohol

Mechanism: LiAIH4
$$\Longrightarrow$$
 Li $^{\circ}$ + AIH4: $^{\circ}$ LiAIH4 \Longrightarrow CH3-C-H \Longrightarrow CH3-C-H \Longrightarrow CH3-C-H \Longrightarrow CH3-C-H \Longrightarrow CH3-G-H \Longrightarrow CH3-G-H

b) With zn-Hg (zinc amalgam) /cmc:Hc1 ((lemmensen's reduction):>

carbonyl compound (aldehyde or ketone) reacts with zinc.amolg-and znity) in presence of conc. Hel to form an alkane. This

page-26 reaction is known as clemmensen's reduction; This reaction converts the carbonyl group (; c=0) into methylene group ()CH2). [) (=0 + 4 [H] = ZM-Hg, (MEHL)) CH2 + H20 CH2-C-H + 4[H] Zn-Hg, CH3CH3:1+ H2O eltane

(Ettanal) CH3-C-(H3+4 CH] Zn-Hg, CH3 CH2-CH3+ H20 propane Acetone (propanone)

c) With N244 (hydrazine) in presence of ettylene glycol (wolff-kishner reduction)

Carbonyl compound (aldehyde or ketone) reacts with alkaline hydrazine (N2H44 NHZNIZ and WasHACKOH) Pr presence of ethyleneglycol (40-c4z-c4zoH) at 200°c to form an alkane. This reaction is known as wolft-kishner reduction. This reaction converts carrongly group (70=0) 2nto methylene group (>CH2).

Acetaldehyde

Acetaldehyde

Aldehyde or ketone reacts with puls to form gerndichloride (gem-dichloroalkane).

5. Reactions due to alkyl group

Acetone (propanone) Two morecules

=> With dil. alkali (dil. NaoH) >> Aldol condensation >>

Two molecules of aldehyde or ketone containing X-hydrogen undergoe self condensation in the presence of dil. alkali like dil. NaoH to give B-hydroxyaldehyde (called aldol) or 13-hydroxyketone. This reaction is known as aldol condensa-Acetaldehyde (eltranal)

Two morecules

(H3-C-C-CH3 + H-CH2-C-CH3 dil·NaoH (H3-C-CH2-C-CH3

Acetane I parrognamia) 4-Hydroxy-4-Meltylpentan-2one

50 Itie formed 13-hydroxyaldelyde or 13-hydroxyketene [Page-78]

on heating [warming] windergoes delydsation to form unsaturated

Eldelyde or ketone.

(H3-CH-CH-H) (H3-CH-CH-H+H2O)

B-Hydroxybutgraldelyde But-2-enal (crotonaldelyde)

(3-Hydroxybutanal)

TOH

(H3-C-CH-CH2) (H3-C-CH3 +H2O)

CH3-C-CH3 + CH3 + CH

6. Miscellaneous reactions;

9) With concinant or 50% NaOH (Cannizzaro's reaction):

Aldehydes having no x-hydrogen (eg. HCHO, GHSCHO, R3CCHO etc) undergo selt oxidation and reduction on the presence of conc. NaoH & 50%. NaoH to form sodium salt of presence of conc. NaoH & 50%. NaoH to form sodium salt of Corsovylic and alcohol respectively. This reaction is consizerous reaction. This reaction is also known as cannizerous reaction. This reaction is also known as clisproportionation reaction.

page-29

b) Reaction methanal (formal dehyde) with phenol:

Formaldehyde (Methanal) (ondenses with phenol in the presence of acid or bake as cartalyst to bakelite (phenolformaldehyde resin). This reaction is known as Lader-Manase's reaction.

9) Furmation of intermediates i.e. O-hydroxybenzylakohol and P-hydro xy benzyl alcohol.

b) Formation of linear polymer:

i) fromation of cruss-linked polymer;

O-Hydroxybenzyfalcohol p-hydroxybenzyfalcohol

OR n 0 + 7 + 2=0 H+ or OH - n H20 formaldehyde (Mettanal)

Aromatic aldehyder and ketones.

page-30

Aromatic aldehyde:



Benzaldehide

General methodof preparation of benzaldelyde

1. From toluene (methylbenzene);

Benzaldehyde is prepared by the oxidation of Holuene (Methylbenzene) with chromic anhydride rie chromium trioxide ((103) in acetic anhydride for audified ceriumoxide (CeO2/H+) T followed by hydrolysis in the presence alkali.

The function of aletic anhydride is to prevent the further oxidation of aldehole into the corresponding and

(methy benzene)

$$\frac{\text{CH2}}{\text{CH3}} + 2\text{COJ} \xrightarrow{\text{CeO2/H}} 0 + \text{H2O}$$

Toluene (Methylbenzene)

2. From benzoyl chloride; (Rosenmund's reduction);

Benzoyl chloride reacts with H2 in presence of pa/Baso4 to form benzaldelyde. This reaction is known as Rosenmund's reduction: E-cl pd/Baso4 OJ + HC/ Clindles 15 Catalyst) Bo Calcoling

BenzoxIchloride

properties of benzaldehyde:

I reportant reactions of benzaldehyde different from aliphatic

1. perkin condensation (perkin reaction)

Benzaldehyde (aromaticaldehyde) reacts with acetic anhydride (aliphatic anhydride having at least two x-hydrogenations) in the presence of sodium acetate (sodium salt of aliphatic aux) to give - Cinnamic aud (x, B-unxaturated acid). This reaction is known as perkin condensation.

Ch is known as perkin condensation.

CH=CH-COOH

CON 18 KNOWN OF PERKIN CONDENSATION BY CH=CH-COOH

C-H

C-H

CH3-C-O-C-CH3

Acetic anhydride

Benzaldehyde (Ettranoic anhydride)

Cinnamicaud

Cinnamicaud

Carbon Acetic acid

2. Benzoin condensation; Benzaldehyde (assorbatic aldehyde) is heated (refluxed) with an alcoholic solution of KCNL potassium (yanide) to form benzoin (x-hydroxyketone). This reaction is known

as benzoin condensation. In this reaction, two motecules of benzaldelyde undergo condensation to form a molecule of benzoin.

Benzaldehyde (two morecules)

Benzoin (a-hydroxyketone

3. Cannizzarois reaction : Benzaldehyde (having no d-hydrogen) undergoes oxidation and reduction in presence of concillator or So! Navy to form sodium benzoate and wenzylalcone respectively. This reaction is known as cannizzaro's reaction.

Benzyfalcoho) sodiumbenzoute Benzaldehyde (two molecules) (reduces product) (ourdizes product

4. Electrophilic substitution reactions (Reactions due to benzere ring)

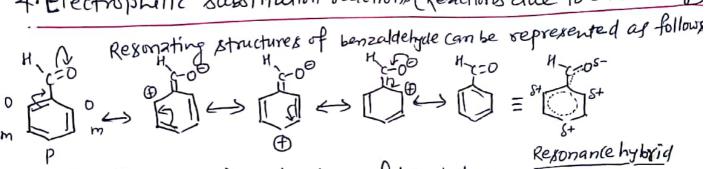
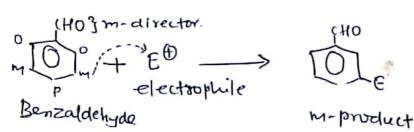


Fig-Resonating structures of benzaldehyde

Resonance hybrid

Here, - (HO group &n benzaldehyde is electron withdrawing group (Elsb). It decreases electron density at 0- and p- positions in the benzene ring of benzaldelyde. Because of this, the electron density is relatively higher at meta position than at ortho and para positions. Therefore, electrophile can attack at metapositions Hehre, electrophilic substitution reaction in benzaldehyde takes place at meta-position i.e - cho group In benzaldelyde is m-directing.





Some electrophilic substitution reactions on benzaldehyde are given below:

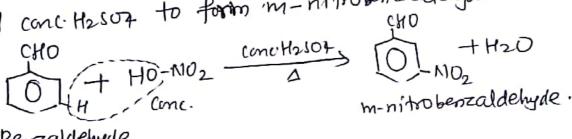
I. Chlorination (Halogenation):

Benzaldehyde reacts with chlorine in presence of feets

m-chloro benzaldelywe Benzaldehyde

II Nitration: Berzaldehyde is heated (at 140°C) with conc. HNO3

and conc. H2507 to form m-nitrobenzaldehyde.



Benzaldehyde

(III) <u>Sulphonation</u>: 3 Berzaldehyde reacts with funning H2504

to form on-benzaldehyde sulphonic aud' CHO

CHO

SO3H

Funity Come.

Benzaldehyde

Sulphenic Aug

Aromatic Ketones;

preparation of Acetophenone from benzene by friedet craft's augia-

When benzene is heated with acetylchloride in the presence of anh. Alclz, Acetophenone is obtained. This reaction is known as friedel-craft's acylation.

Benzene

Mechanism;

$$CH_{3} = \frac{1}{C} - CI + AICI_{3} \Rightarrow CH_{3} = \frac{1}{C} + AICI_{4}$$

$$electropule$$

$$+ \frac{1}{C} - CH_{3} \Rightarrow CH_{3} = \frac{1}{C} - CH_{3}$$

$$+ \frac{1}{C} - CH_{3} \Rightarrow CH_{3} = \frac{1}{C} - CH_{3}$$

$$+ \frac{1}{C} - CH_{3} \Rightarrow CH_{3} = \frac{1}{C} - CH_{3}$$

$$+ \frac{1}{C} - CH_{3} \Rightarrow CH_{3} = \frac{1}{C} - CH_{3} \Rightarrow CH_{3} \Rightarrow CH_{3} = \frac{1}{C} - CH_{3} \Rightarrow CH$$