ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

'Preparation of Aldehydes and Ketones

(51 By midi:don of alcohols

Aldehydes anid ketones aregenerally prepared by oxidation .of primary and secondary alcohols., respectively_

RCI-$1_2$01-1 RCHO

R -CH -C-R'

011 0

ay delhydiffligEflati4211 of alcohols

Primary and secondary alcohols give aldehydes and ketones, cespectlwely.

R - CH_2 – H a R1HI

R - CH -RI R - C -R'

OH 0

(111) By ozonolysis *of* alkenes

R CH CH-R 00. (lilark,o Hn.c) 2RCHO

O– CH Roi gfiaii? HNC! Cfle 4-1 0 °

bffualcloh,plia

(hi By hydration of Ames

CH CH+ H_2O GH -OHIO

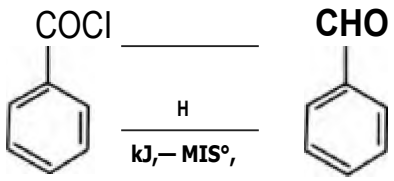
Keltklehrit.

R -C z.C1-1+1-1$_2$0 CO

Wow

Preparation of Aldehydes

{l} Rosen mild reduction



be ruoyi chloride **be nza Iclehyde**

Fornaidlehlede cannot be prepared by this method as INCOCI is highly unstable.

(ii) From nitries

RCN +5rbC1, + NI-I RCHO

This reaction Is called Stephen ruction.

Alternatildely, nitriles are selectively reduced tre diisolautylalurninium hydride, IlDiBAL ·l·1] Lo i mines which on hydrolysis give aldehydes.

RCN)RCl-10

Similarly, asters can also be reduced to 211dlehyrdes. with EkAL•H.

CI-I (CI⁻₁ ρ₃ ⁻ COCIC2Hs (ρ) COAL 41 0 ¹¹20 **CH ; (Cl·l – Cli0**

ON) Etard rcaction

toluene benzaidehyde

Using chromium oxide iCrOR) Toluene or substituted toluene i5 Wroderted to ti.erizalciehycle in presence of chromic oxide in acetic anhydride_


+CrO,

273-183K


CH{DCOCE10$_2$

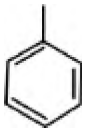
A

CHO

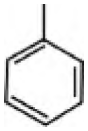
Benzaldehyde

{liv) Side chair! halogenatiOn Is followed by hyclrolvsls of toluene

CH_3

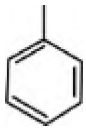

Cl, /hu

CFICl$_2$


h,o

373K

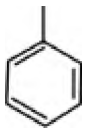
CHO



{v} Gatterrnann-Hoch synthesis


Anhy.AICI,ICua

CHO



Preparation of Ketones

Fron acyl chlorides

X

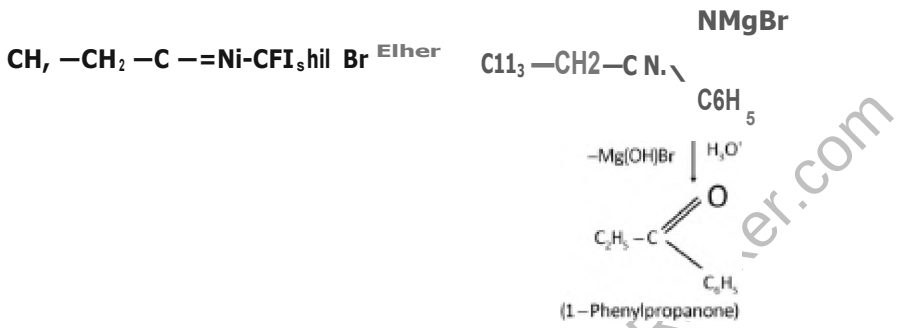
2R– riol g – X + $CdC1_2$——— R_2 Cd + 2M g

Cl

2R' – C – Cl— R_2Cd • 2R' — C — R + $CdCl_z$

O O

(il) Frain ritrihn.

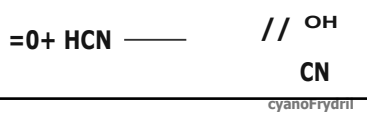


{ili] Friedel-Cratt% acvlation

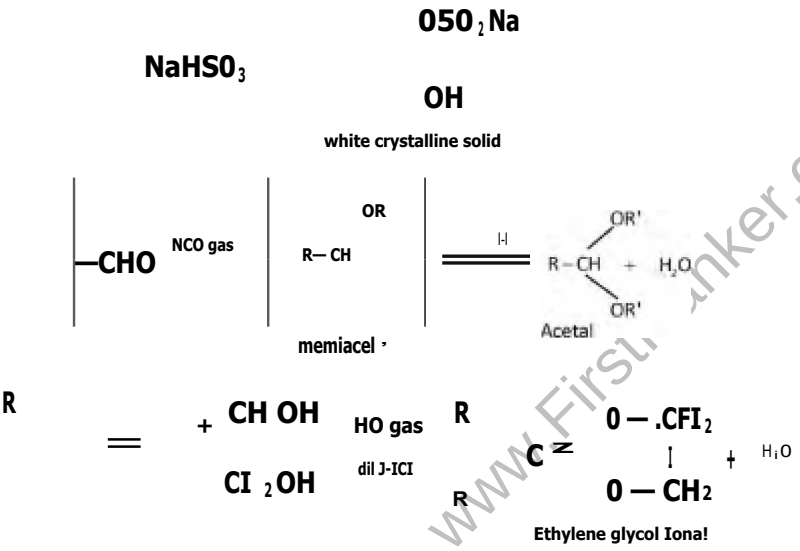
{iv) Oppenauer oxidation

Chernkal Reactions of Alclehydes and Ketones

M Addition .0.f hyd rogen cyanide

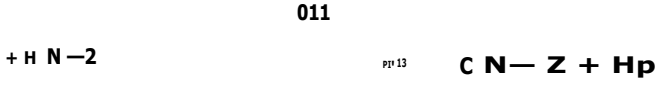


Addition of sodium hydrogen sulphite



ii) Addition of Grigriard reagerrt (RPoigx) to form alcohol

OA Addition of ammonia and its d.eriliativm



= aryl!, 0P-I, NH_S. C_6H_5NH, NH NI-j, etc

	rent name	Carbonyl derivative	roduct Name
It	Amine	_c - NR	Substituted 'mine (5chifts base)
-0H	Hydroxyl amine	-C = N _ OH	Oxi me
-NH,	Hydrazine	-C .N-141-1,	Hydrazone
— NH —)	Men* hydrazine	>C = N _NH	Pherrylnydrazone
NO — NH NO2	2, 4- di nitrouhenYI hydrazine-	NO,	2, 4-di nitropnenyl hyd razone
O — NH— C— NH.	emi. carbazide	O >C=N-NH-C-NH,	Semi_carbazone

Reduction

(1). Clernrnensen reduction

$$\text{Fe}\ C = O \xrightarrow{Zn-HR} \quad + H_2O$$

(1). Wo111-16shner reduction

$$C = O \xrightarrow{\text{-14}} C = N - NH_2 \xrightarrow[A]{\text{KOH ethyleneglycol}} CH_2 + N_2$$

(34. Oxidation

ti) Aldehydes are oxidized to acids in presence of mild oxidizing agents $AgNO_3$, K_2CrO_7.

FL C.iHO CCCIA

(ii) Ketones are oxidized under drastic conditions i.e. with powerful oxidizing agents like HNO_3, $K_2Cr_2O_7$/H-I_2SO_4, KMnO$_4$ /Ham, at hkgher temperature,

$R\text{-}\overset{1}{C}H_2\text{-}\overset{2}{C}O\text{-}\overset{3}{}$ - COOH tR'-C1-1,COOHI R -CH_2COOH tR'-0001

,Er•icrt Cr c2 koftzli 0_3, tk rgror-{$_2$ -C_l l2crdi

Hallpform reaction

$$R-\overset{O}{\overset{\|}{C}}H_3 \xrightarrow{NeDX} \underset{O}{\overset{\|}{C}}-0N2 + CH; = Cl_i Br_i$$

Cid) Aldol condensation

$$2.01_3-CHO \xrightarrow[Lmb.i]{ill\ \cdot\cdot\ MH} CH, CFI\ CH\ CHO \xrightarrow{1^\circ} CH\ \_\ CH{=}CHCHO$$

bui 2' • a•ol

OH

3 Ldri JI

;a1r1n11

$$2C11_3COCH, \xrightarrow{FLa101•11,} CH_a-\underset{OH}{\overset{CH,}{C}}-CH2COCH \xrightarrow{A} CH_3-\underset{}{\overset{CH}{C}}=CH=COCH_3$$

piroparione

4 - metFrylperrt - 3 arh-2 —cone

I rnesityl oxide)

Cross al de I conclensati on

Base catalysed crossed aldol condensation between an aromatic aldehyde and an aliphatic aldehyde or ketone is ca Iled Claisen-Schirrkidt condensation or Claisen reaction.

$CH, CH{=}CH{-}CH0 + CH,CI\text{-}1_2CH = C-CHO$

bkd - -t.eqd

C

2methyipcnt 2 mai

$CH, -CHO + CH_3C1\text{-}1,CEIC$

Iselfackg produces)

C $-CH, -CH{=}CH{-}CH0 + CH_3-CH\ CCHO$

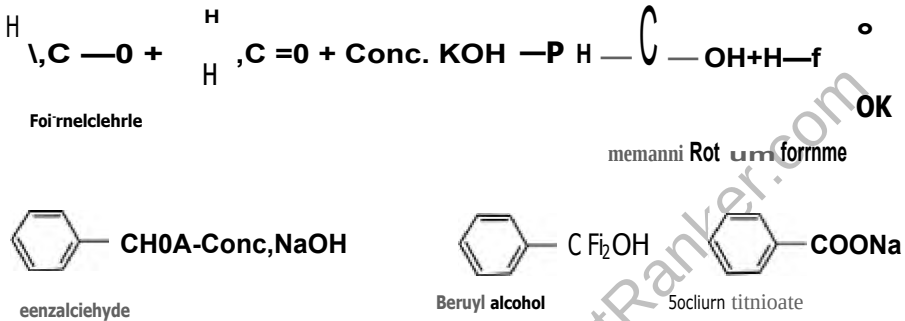
pant-2 -anal

CI_{-L}

2 rnethylbut - 2 - cm!

(crDss aldDI product!

C.annizzaro reaction



Test to distinguish aldehydes and ketones ;

(I} Tolleres test When an aldehyde is heated with Tollen's reagent it forms salter mirror_

Tollenrs reagent Is arnmonlacall solution of Ag1103

$RCHO + 2(4041\text{-}1)_2 + 30\text{-}1 \text{ —*RC00 } +24 + 211_20 = 4NH_1$

Ketones do nit form silver mirror and Fiance do not give this test_

{2 FehlIng's test When an aldehyde is heated with Fehilingrs reagent it forms reddish. brown precipitates Of cuprous oxide.

Fehlints reagent Fehling solution A (aoueous solurtion of $CuSO_3$) + Fehling solution B alka II ne solution of sodi urn potassium tartarate)

$R.\text{-}CHO + 2Cli^{t} + 50H^{-} \text{–P. } RCCIO^{-} + Cu_20 +$
Red Brown poi

Ketones do not give this test.

Carboxylic Acids

Methods of Preparation Di. carboxylic Adds

From primary alcohols and aldehydes

{a) RC $H_201\text{-}I$ 11 ·· in ·· mna4 ·· u· **)R,COCPH**

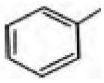
0311 $R01\cdot l_2OH$ .C11: 4129:34 AC01011

From aldehydes.

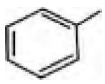
IRC1401⁻1+21ACJIN N_2 r +301-1 -RCS +2Ag + 214_20 +4N

R -CH.0 $2Cu^2t$ -$50H^-$ -0. RCOO + Cup+ $3H_2O$

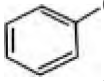
From alkyl benzenes



KM.NO, KOH
Heat



COOK Fi o



COOFI

Benzoic 'Cid

Frorn acid derharthres

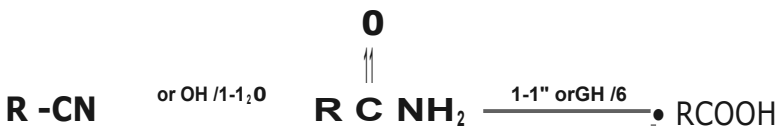
All acid derivatives likE amides RCON Hi), acid halides (RCOCIII. ti.AbEn (RC00111), acid anhydrides {ROD-O-WN on hydrolysis 13ive carboxylic acids. All acid derivatives break from RCO^+.

RCOZ ail. HarCH-1 RODOid

Z - x(x = a Br, OR'. RCCO - etc •

Em ^4Yr $^{10}11.^{111}0^1$Y5FS FOCI IIRCO40"· RCOCI4R·

From nitriles and amides



From allgenes

Suite* substituted alkenes are oxidized to carboxylic acids an oxidation with acidic potassium permanganate or acidic potassItim dichromate.

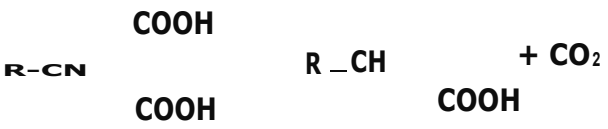
{al R -CH = CH -R "".31111-1+) 2R COOH

R -CH - CH _ IR, KI-"41+ R C001-1+R, -COOH

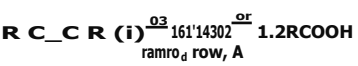
From Grlgrvard reagents

R-Mg-X • 0.C.0 ^{bff} R — RCOOkl
Cr MIX

Sy heating; germinal &carboxylic acid5

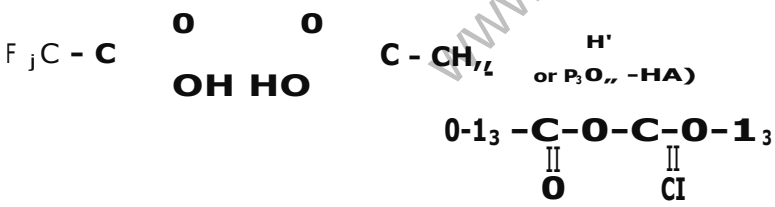


From alkynes



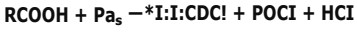
Reactions cif Carboxylic adds

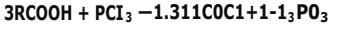
Formation of anhydride

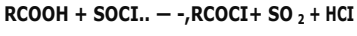


Esterification

Reactions with pa$_s$, pa and sod,





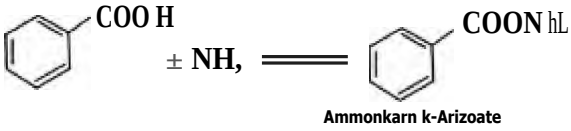


Rea ction with ammonia NH3}

Carboxylic acids react with ammonia to give ammonium salt which on further heating at high temperature gives amides_

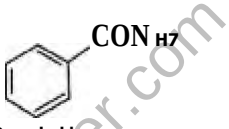
{a) C1⁻]0:01⁻1.F NI⁻1 CI⁻]3C OCI NH1 Aj-F12° ,f1tCCIN H2
Ammonium winal:4;' gi.courni d

{14



Ammonkarn k-Arizoate

It



Benzairnide

Chemical reactions involving — 01301-1 group

(a) Reduction

ReDOH 1.91.04.1 1etlmr cH2 — 04.1
11 H,s 011 H

(b) Di carboxyletion

RECION21 HaaH Ca" 1741:Fc 3:11 FR I-1 .4. N.9 2 CO,

SubStitutian reattiOnS in the hydrocarbOn part

Hell-Vollriard-Zelinsicy reaction

P. —CH 2 – CCIOH X2Iked ,R CH —COON

X

X = Cl. er
ce-HalocarbarFlicacid

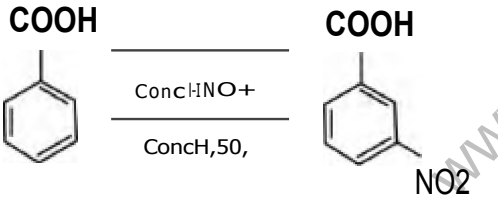
Arndt-E istert reartigpi

RCOOH PCL RCOC1 cH242 RCOCHN2 H° RCH2COOH
dam. kegone

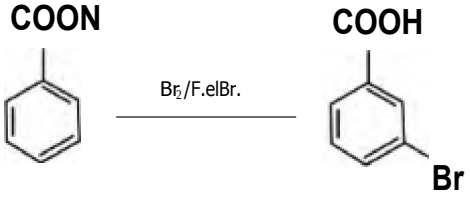
Reducing property

HgCi, Jr Hg 2HCI + Ca 2

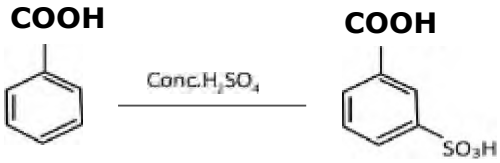
Electrophilic 5101:Wi1hitiori reildiEmS. Of amniotic acicil5



rri. -Nitiroberaoic acid



rn IBrorriObeilZOiC acrd



3-SUlphOnie benzoic acid