AMINES

Mei hip&ri **Preparation a Arniirtes**

(i) By reduction of nitro compounds

Nitro compounds Carl be catalytically reduced by passing [1'MR:igen. gas irk presence of Raney Ni, finely .divideci Pt or PO a5. catalym at room temperature_

la) IR **—NO,** + 31⁻¹z R 21-Ip

{io Ar - NO_2 +3H2 $\xrightarrow{HL}$ Ix Ix Ar NH_2 - 2-1 0

Nitro compounds can also be reduced with active. rriatak such as Fe. sn,, Zn etc. with conc. HCII.

(a) R _ NO2 3.H2 $\xrightarrow{srifFici\ Dr\ WIG\ ,R\ Nit}$ +21-l20

(10 Ar-h10$_2$ +3H$_2$ $\xrightarrow{5fir\ HCl\ or}$ NH_2 - ^2H_2O

(ii) By Hoffmann's method {Arnrn000lysis of alkyl hal idesic

RNH E$_i$NH 13'i R N X
ua.hymary
trrIP771.11'1 salL

- The free amine can be obtained frorn the aromonpurn salt by treatment with a strong base :

IA Ni-I$_i$ - RX RNI-r$_3$ X $\xrightarrow{ti}$ RNI$_2$ 4. H_2O I No' X
41° arriiitl

(b) RNH_2 Fri(—I.- Rill-11X' $\xrightarrow{ri;2\ 41}$ r FE_2 111-1 +Na$^-$X$^-$
LP•mino

R_2N11-I +PY —> R_3NH' X $\xrightarrow[Napri]{}$ R_3N +H_2O+ Na' X
0"soirpo

- Order of reactivity of halides Is: RI s RBr > I CI

{Ili) By reduction of nitvi l•s ;

Nitrites ca n be reduced to amines IJsirkg H_of IJi, $LiAlIF_4$ Dr Kla{HE)/(.$_7H_2OH$

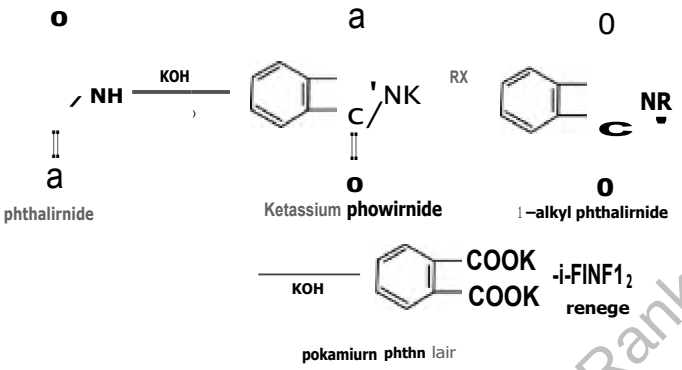
fhl i
Nal)49)1 C21-15 C4-I
Or
R-C=.14 $\xrightarrow{LiIJH4}$ R CH_2 -NH,

{iv) By reduction of amides :

Amides are reduced to corresponding amines byr LI AI H.,

O
R _ C _ Lave$_{ij}$ 11-a R CIL -

(v) Gabriel's phth Iimide reaction

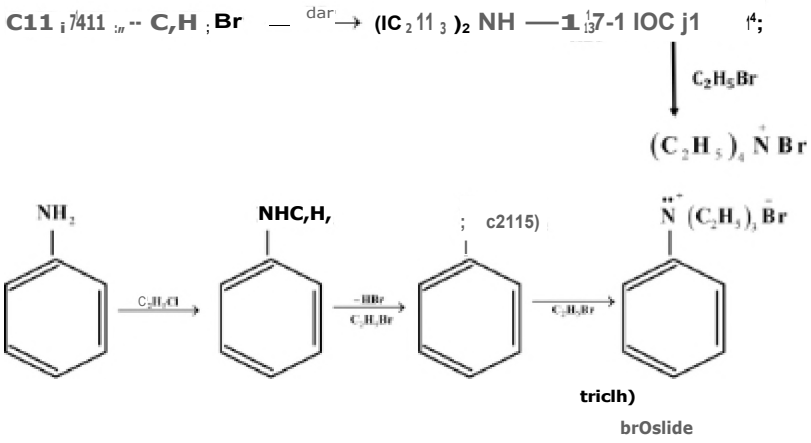


(vi) Hofmann'brornamicle degradation reaction'

R $\cdot f131_2$ + 4NaOH—)RN I^-_2 +14a_2CO_3 + Maar + $2H_2O$

Reactions of Amines

(i) Akialion



{ii) Arylation

C11-N1-1 2-F CHXOCI-B "=> C 2 11 1 - -C -h HCl
| ||
H

0 0 I II
H o

(Ii1)13enzovlation

NI'IH2+q1-15cDo ire CI 3NHC00 5 1-15 .1 I-ICI

Biarooylation of andlInt is 1010Wro as Schotitan Baurnariri peactlork.

(iv) Ca rbylarn irla reaction, [orilv by 1' a mirras]

R CHC13 +31(.01-1 114114 R —N=C t 3K1+)2O
(P. IAKI 5 1 :EIIVriPArei

Methyl iso•cye nate gas (0-1 _No= r 0) was responsible fir Bhopal gas tragedy in December 1984_

(v) FrAacItion with r iti duS acid

RNI-12 +1-1NO2 432-1-c

Quantitatiwe evolution of nitrogen i5 1.1 d in animation of amine acids and prOteins.

Cd-I, 2 7 2+21 C,1-115N CI + + 2H-0

Reaction with aryl. Sulpheiclylthleiride [Iiinsberg reagent]

CI
5—C1 R — N— 1:1 + KC]
0 11
t a mine N - k.y Denzer su Ipicnarni de
(soluble in a kal)

UOISSIUIPV MOSUOV

— O
‖
0 R

2 amine

LN—Ft
II I
O R

N1,71- alk ly benzene die
(insoluble in elk&li)

O
R R.
O

No rs,2ction

3[6] a min

Reaction with aldehydes

Sthiff bag e-i d t i med.

c~ H NH_S + 014CCH —)$C_{is}H_5N$ = CH-C_6H_5
tweakkihoe tipkirlioere
ad'A

El eci ra phi! Ic sulOstItution reactions

NH, + Br_2/H_2O → NH, Br Eh- + 3.1-1111-
Milk= Hr

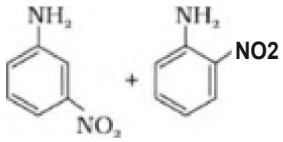
2,4 ,6-TrihrirrEiminilktic
light yellow ppt

Nitration

{a) Under stoongly acidic medium aniline gets protonated to fond anillni urn lon, which Is deactivating group and is meta directing. Hence rn-nitroaniline is also. farmed in 47 % along with prtho and para products.

NH,

.11,50._ 2E181(3,



NO,

(5]'44 (4796)

Aromatic amines cannot be nitrated directly because 4101 being a strong oxidizing agent oxidizes it forming black mass.

{b) Nitration by protecting the —NH2 group by at'etylation reaction with acetic anhydride ;

NH, NHCOCH,, NHCCICH, NIL

{Cii,C0)39 1H:a0,. 1-1,S0,.. 2.118K≥ OH Cor

Pyrirline

NO1 NO1

Acelandide p-Nilroaccitordlide

[cli Sul phonation On sul phonation, aniline giwes sulphanilic acid, as the major pro hint.

rFL1 4 NIl,E iSO, NH, N3'1

4 9.3r 473

SO,F SO,

by li Rai nulph.ate sulplu ad 13 &Miff 11311

Oxidation

001101g agant	Pr dun
Acidified KMnQ. (or 14a2cr2o, +cusci,,, + ail add)	Aniline back (a dye)
Chromic acid rNa2cr2o, + conic H2SO4)	p•benEaquinone
Cares acid (H2so5)	Nitrobenzene and nitrosobenzene
Conc. Nitric acid	decomposes

Benzene Diazdnium Chloride (C_6H_5N; ;, Cl

Preparation tDiazotisaticin reaction

CE1-15N1-1 +1\1 0102 21.1C1 273_2711 K C_6 = N— CI + NaCi +2F1$_2$O

Chemical reactions

C,H,+N,1 +11,P0 $_1$ -HCI

C,1-1,+N $_1$ FICI+CH,CHO E).eariniirkaiinel)

C $_h$B „Br

i brr.irri 064,Ln7ene)

(o)Recctions involving di5placenient 0f nitrogen

ettelifici ≥ ArC!.

Ctorntur ArDr 1. Ns

CUM /KM ArC74 +

CufFICI) ArCl + 1, + CUM

cuIHBr Arflr + Oliva

Kr An + KCI N,

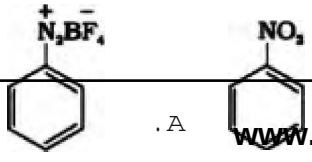
Atka

1'1:13F, Ar kEsi, Ar—r' BP.+ N$_s$

HIPC^{1}1^{+} Arli + iv% 4- Ha

ArOH + 1½ + He]

CH,,CI'40H) + N, CHCHO

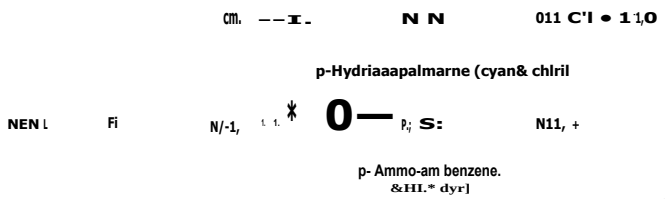


HB

. A

+ N w,

Azo coupling reactions



Alkyl Cya nides

Methods of Preparation

(0 From alkyl halides

$RX + KCN \rightarrow$ (11:CPC, Dell OL'', moor)

(ii) From acid amides

$RCONH_2 \xrightarrow{P_2O_5}$ RC N (Ita)

Reactions of Alkyl Cyanides

(i) Hydrolysis

$RCN \xrightarrow[Alk]{ter-} RCONH_2 \xrightarrow[Fe]{} RCOOH + NH_3$ (trYchlY5·0, erri, carbOxyk Mid)

(II) Reduction

$RCN + 4[H] \xrightarrow{Na\ cCL_5/H} RCH_2NH_2$

$RCN + 4[H] \xrightarrow{Li^{\circ}1F./} RCH_2NH_2$ (Mendkis reduction)

$RCN \xrightarrow{SnCl_2\ 11\text{-}10} R\ CH = NH.\ HCl \xrightarrow{H_2O} RCHO + NH_4Cl$ (mine hp:hid-ion&, Idsluid0)

010 Reaction with Grignard reagent

$$RCN + R'MgX \rightarrow R-C=N-MgX \xrightarrow{2H_2O} R-C=O$$

Alkyl iscyanIdle.

Methods of Preparatiae

(a) From alkyl halides

R + AgN a RNC +RCN (ma}*

[13) Carbylamlne reoction

RN -I2 +CHC1.3 + YOH kirj RhIC +31:C1+ 1-1 2O

(r) From fornamidle

Poong N_ C+E1 2O

Reactions of Alkyl isocya n ides

Hydrolvsls

R -N - 2H2O 1- >R1%.11-1 2 +HCOOH

RN C + 4(l-1) 11411C2'15CH or Nior Pi ?RNI-ICH3 amine

AthiltIon reaction

Due to the presence of unshaved pair of electnons on C atom, alkyl isocya ni des give addition reaction_

RNC ı 5 - oRNCS

RNC+1-40.-->RNCO + Fig

HNC+ 0 1 RNCO

(iv) rsomerisatIon At 25CPC, It Isornerizes to &rile.

RNC RCN

Nitro Compounds

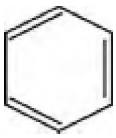
Methods of Preparation

From alkyl halides

RX + $AgNO_2$ I.P.1[1]**10_2 + MX**

(11) Nitration: Narking mixture is corm H NO1 corm H19134

NO,



+Conc.II $NO_{\%}$ —ide— | ||

Reactions of Nitro Compounds

Reduction

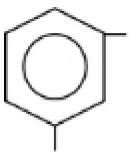
Witham/HO or catalytic hydros.enation.. nitroalka nes are reduced to amines_

RNO_2 6111 5foci R NI-1_2 • Zip

If neutral reducing agent like Zn dut+ is used, lwtlroxylarninas are obtained as major product.

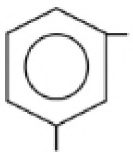
RNO, I 41H] —2nINH4C1— **– INHOI-i+Hp**
IlwiNcirmlarnine

In the pr sent▮ ofNH)aorNk5, selective reduction take-A place_



NO_2

+311%:■,),S



NO,

4•64/41., -211,0+3S

(Boils redu.Ti4O)

Nitrobenzene giwe$ different procluck5 with different raagent5 and in different med 9.

Medium	Fteagint	Product
Acid	Sn/I-ICI	Aniline
Neutral	?n,INItiCI NaAs03,1NaOH	N -phenyl nycl rexylam bis AMXbeilEend ($C_{,6}H_5N$ = NC_6H_5)

Alkaline	2n/Na01-1, CH 30H ZniNa0H, C2F150H	Azobeinzene hydra benzene
rotetaillit hydride	LiAh1	an.ilirie.
Elect...01'01e	tlil H604	p-anrilnophenol

Action of 14401

nitroalkane gives nitrolic acid which giyes red colour with Na(111.

R.C1-1 2 N111, —9→ RC(NO2 — NON "CM RCN°, NON.
- H2 O LVD!IC acid !red)

2 ritrolk.anes give pseudenitrol with I-1402

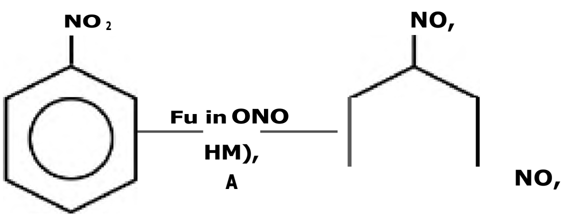
RCIANO2 —HrKI2 / -H2°→ R2C – Ha OH Blue
|
NO2
Pseudonitrol

Nei rarborrirl synthesis

R - CH,NO, NiaOH CHI — N-O-Ne scroki R — = o
aideForde

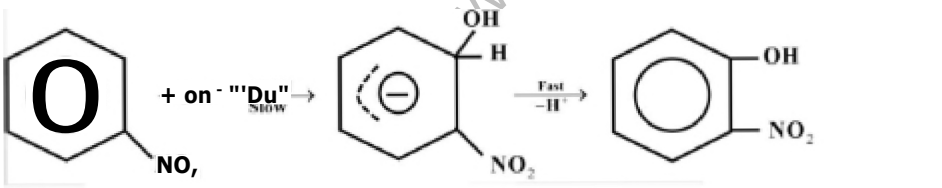
a

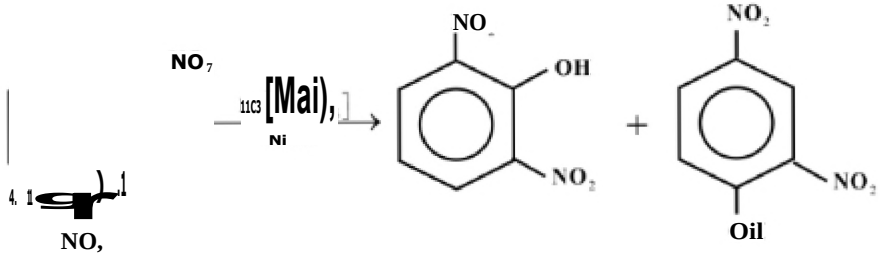
Electrophilic substitution On nitration

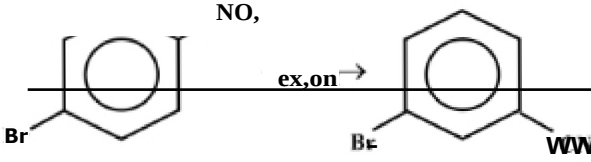


Tn- din krill enzen

Nucleophilic sulniltvtiork reactiOn -NO2 IgrOtip artheate5 the ring towards nucleophilic 5LrIntitution,







{.von Richter reaction)