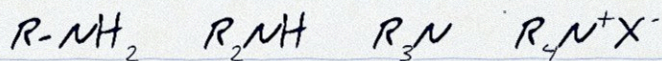


Amines

Amines = derivatives of ammonia obtained by replacing one, two or all three H of NH_3 by alkyl / aryl group(s). N is trivalent + has a lone pair \Rightarrow acts as Lewis base / nucleophile.



\leftarrow 1, 2, 3
 \leftarrow + salt

Structure of Amines

N is sp^3 hybridised \Rightarrow pyramidal.

Three sp^3 orbitals \rightarrow N-H or N-C bonds;
fourth sp^3 holds the lone pair.

C-N-E angle $<$ 109.5° (lone pair pushes).

Trimethylamine : C-N-C = 108° .

Classification (1, 2, 3 deg)

1° : R-NH_2 one H of NH_3 replaced

2° : R-NH-R' two ~~H atom~~ H replaced

3° : R_3N all three H replaced

'Simple' : all R groups same. 'Mixed' :

different R / Ar groups on N.

Ex. CH_3NH_2 (1°) ; $\text{CH}_3\text{-NH-CH}_3$ (2°)

$(\text{CH}_3)_3\text{N}$ (3°) ; $\text{C}_6\text{H}_5\text{NH}_2$ = aniline (1° , aryl)

Aryl amine \Rightarrow -NH₂ directly on benzene ring.

Nomenclature

Common System

Prefix the alkyl group to the word 'amine' as ONE word (e.g. methylamine, ethylamine).

2 or 3 same groups \rightarrow use di- or tri- prefix.

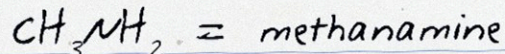
Mixed $2^\circ/3^\circ$: list groups alphabetically.

IUPAC System

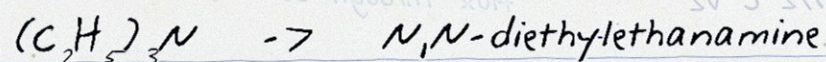
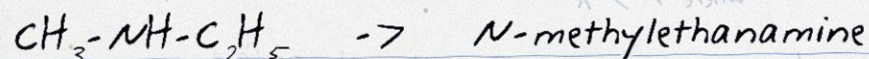
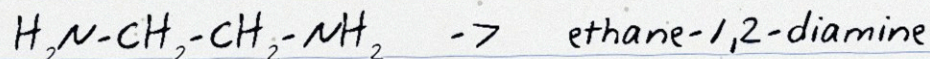
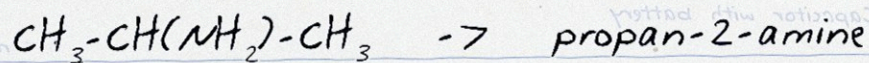
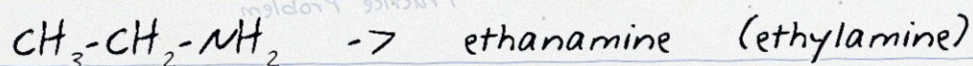
Replace 'e' of parent alkane by suffix 'amine'.

(= alkanamine). Number from end nearest $-NH_2$.

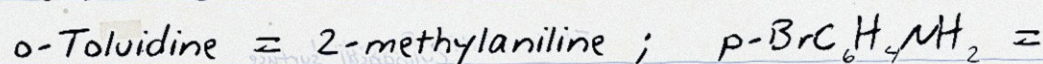
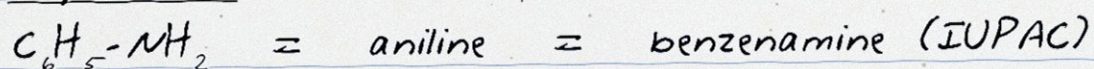
For $2/3$ deg amines, locant 'N' marks substituent on the nitrogen atom.



\leftarrow IUPAC
 \leftarrow name



Arylamines



4-bromobenzenamine. Aryl = on aromatic ring.

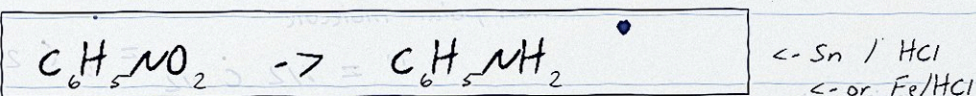
Preparation : Reductions

1. Reduction of Nitro Compounds



in ethanol ; also nitroalkanes \rightarrow alkanamines.

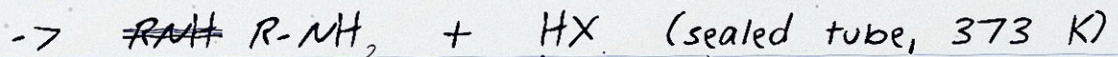
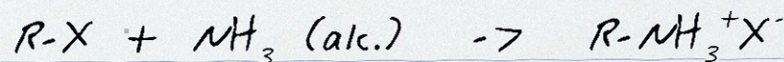
Also : $\text{Sn} + \text{HCl}$ or $\text{Fe} + \text{HCl}$ (acidic medium).



$\text{Fe} + \text{HCl}$ preferred industrially - FeCl_2

hydrolyses to give back $\text{HCl} \Rightarrow$ catalytic only.

2. Ammonolysis of Alkyl Halides

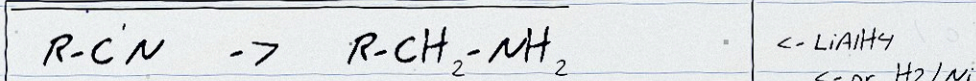


* Further reaction \Rightarrow 2 deg, 3 deg, 4 deg amm. salt.

Reactivity of RX : $\text{R-I} > \text{R-Br} > \text{R-Cl}$

Use large excess of NH_3 to favour 1 deg amine.

3. Reduction of Nitriles

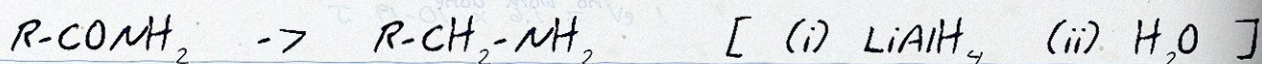


Adds ONE carbon \Rightarrow 'ascent of amine series'.

$\text{Na(Hg)} / \text{C}_2\text{H}_5\text{OH}$ also works (Mendius rxn).

4. Reduction of Amides

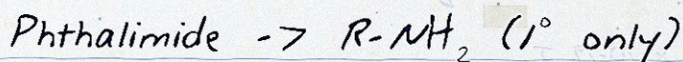
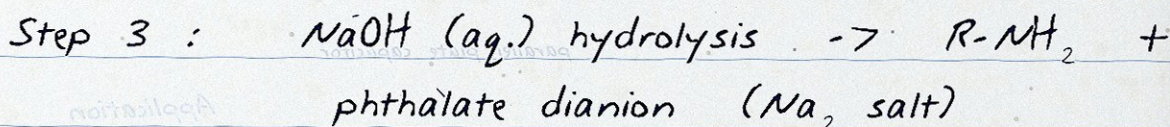
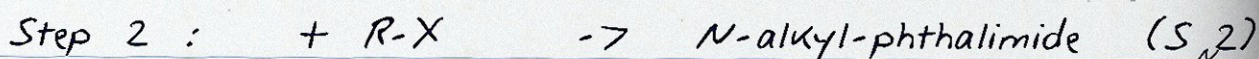
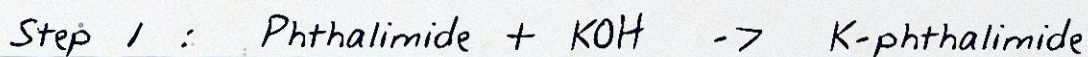
Preparation (contd.)



Gives 1 deg amine with same C count as amide.

5. Gabriel Phthalimide Synthesis

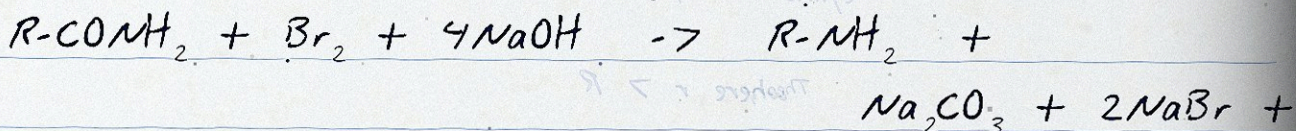
Pure 1 deg amine route (no 2/3 deg side product).



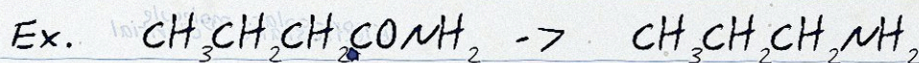
* \leftarrow no
* \leftarrow ArNH₂ ?

Aryl amines CANNOT be made by Gabriel : aryl halides do NOT undergo SN with phthalimide ion.

6. Hoffmann Bromamide Degradation



Amine has ONE LESS carbon than amide (R group migrates from C=O carbon to N atom).



(butanamide \rightarrow propan-1-amine).

Physical Properties

Physical State & Smell

Lower aliphatic amines : gases :- fishy smell.

C₃ - C₁₁ : liquids ; higher : solids.

Aniline & arylamines : colourless \rightarrow brown on storage (~~redn~~ oxidation by air).

Solubility

Lower amines miscible with water - H-bond via

N-H ... O with H₂O. Higher R \rightarrow insoluble

(hydrophobic chain dominates).

All amines soluble in EtOH, ether, benzene.

Alcohols more polar than amines (O more EN).

Boiling Point

1, 2 deg amines form intermolecular N-H...N

H-bonds. 3° amine has NO N-H \Rightarrow no H-bond.

B.P. : 1° > 2° > 3° (same M.Wt.)

\leftarrow N-H = more H-bond

Compare (M = 73 g/mol) :

n-BuNH₂ = 350.8 K > (Et)₂NH = 329.3 K >

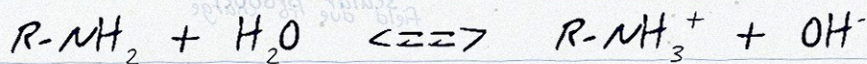
Et₂NMe ~~327~~ = 310.5 K > iso-pentane = 300.8 K

n-BuOH (M = 74) = 390.3 K (alcohol ALWAYS >

amine of same mass : O more EN, stronger H-bond).

Basic Character of Amines

Lone pair on N accepts H⁺ ⇒ amine = base.

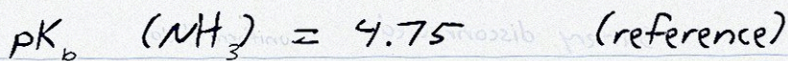


$$K_b = \frac{[RNH_3^+][OH^-]}{[RNH_2]}$$

← pK_b

← = -log K_b

Larger K_b / smaller pK_b ⇒ stronger base.

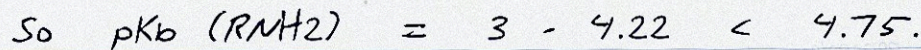


Alkanamines > NH₃

(i) +I effect of R : pushes e⁻ toward N ⇒

lone pair more available for protonation.

(ii) RNH₃⁺ stabilised by +I of R group.



Order in Aqueous Phase (subtle !)

Three factors compete :

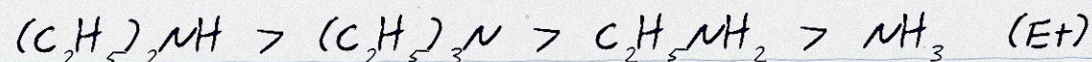
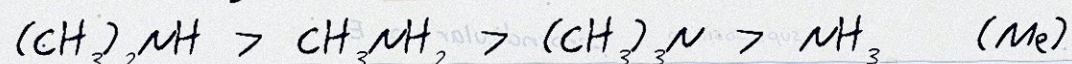
(1) +I effect - favours 3° > 2° > 1°

(2) Solvation of amine RNH₃⁺ - more H = more H-bond

so 1° > 2° > 3° (opposite to +I)

(3) Steric hindrance of bulky R → blocks H-bond.

Observed (aqueous) :



Arylamines vs NH_3

Aniline - weak base ($\text{pK}_b = 9.38$) \ll NH_3 .

Reason: lone pair on N is in conjugation with the ring (5 resonance structures) - it delocalises into ring, less available for H^+ .

Anilinium ion PhNH_3^+ : only 2 Kekule forms (no lone pair to feed ring) \Rightarrow aniline more stable than anilinium \Rightarrow weak base.

EDG \rightarrow pK_b drops; EWG \rightarrow pK_b rises

Order: $(\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3 > \text{PhNH}_2$

R1. Salt Formation (basic char.)

$\text{R-NH}_2 + \text{HCl} \rightarrow \text{R-NH}_3^+\text{Cl}^-$ (alkyl-amm. salt)

$\text{PhNH}_2 + \text{HCl} \rightarrow \text{PhNH}_3^+\text{Cl}^-$ (anilinium chloride)

Salt + $\text{NaOH} \rightarrow$ free amine + H_2O + NaX

Basis to separate amines from non-basic neutrals.

R2. Alkylation (with R-X)

$\text{RNH}_2 \rightarrow [\text{RX}] \text{R}_2\text{NH} \rightarrow [\text{RX}] \text{R}_3\text{N} \rightarrow [\text{RX}] \text{R}_4\text{N}^+\text{X}^-$

Stepwise S

$\text{S}_{\text{N}}2$; excess $\text{RX} \Rightarrow$ quaternary salt.

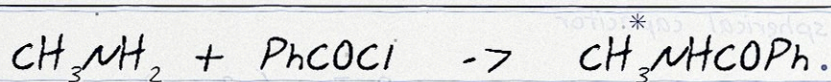
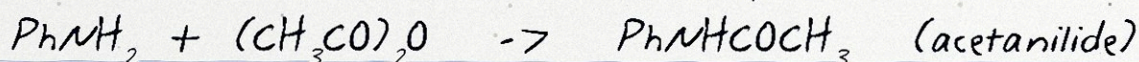
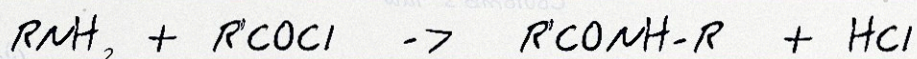
Side reaction in ammonolysis (mixture problem).

Reactions (contd.)

R3. Acylation

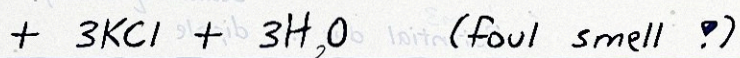
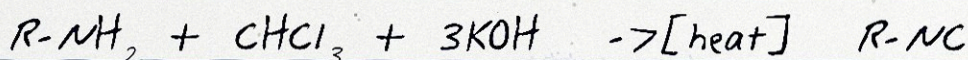
1, 2 deg amines react with acid chloride /

anhydride / ester \rightarrow amides. Base = pyridine.



\leftarrow benzoyl-
 \leftarrow ation

R4. Carbylamine (Isocyanide) Test



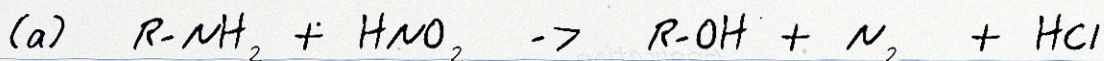
Given ONLY by 1 deg amines (alip. & arom.) \rightarrow

definitive test for primary amines.

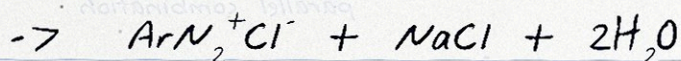
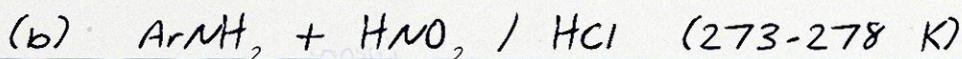
2°, 3° amines \Rightarrow no reaction.

R5. Reaction with HNO₂

HNO₂ made in situ from NaNO₂ + HCl.



(1 deg aliphatic ; N₂ evolved - used in protein / amino-acid estimation.)



(stable diazonium salt - versatile !)

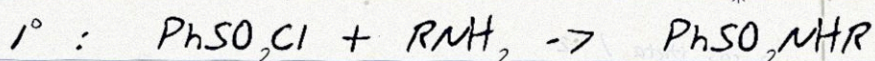
(c) 2 deg / 3 deg amines : different products.

Hinsberg Test & EAS

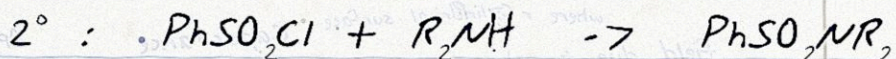
R6. Hinsberg's Test (PhSO_2Cl)

Benzenesulphonyl chloride distinguishes 1, 2, 3

amines :



acidic N-H \Rightarrow SOLUBLE in NaOH.



no N-H \Rightarrow INSOLUBLE in NaOH.

3^o : no reaction with PhSO_2Cl .

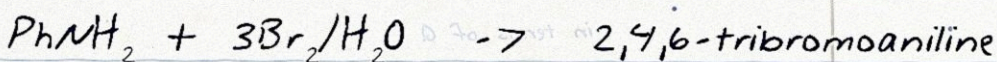
Often p-TolSO₂Cl used today (less hazardous).

R7. EAS on Aniline

-NH₂ is STRONG ring activator + o/p-director

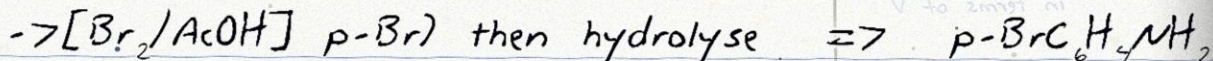
(+M \gg -I).

(a) Bromination :



(white ppt - trisubstituted at once !)

For mono-bromo \Rightarrow acetylate first (acetanilide)



(b) Nitration ($\text{HNO}_3 + \text{H}_2\text{SO}_4, 288 \text{ K}$) :

gives p (51%) + m (47%) + o (2%) !

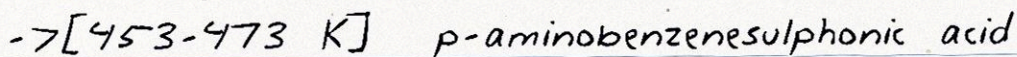
m-NO₂ appears because in acid, PhNH_3^+ forms

(meta-directing due to +M₃). Protection by

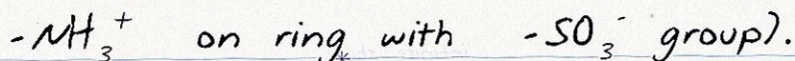
acetylation gives p-nitroaniline as major.

Sulphonation & Diazonium

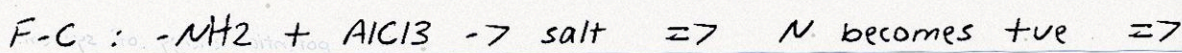
(c) Sulphonation :



= sulphanilic acid (exists as Zwitter ion :

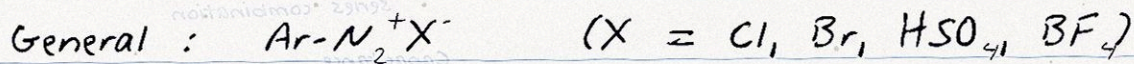


(d) Friedel-Crafts ? aniline does NOT undergo



strongly deactivating \rightarrow no F-C product.

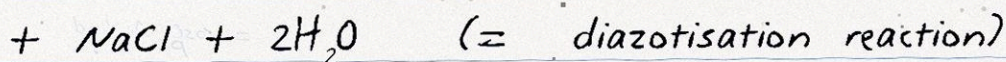
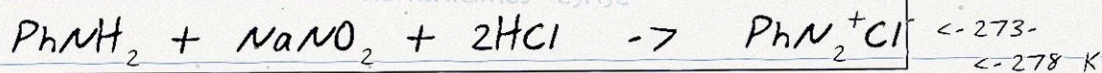
II. Diazonium Salts



Aryl diazonium salts - stable for short time

at 273-278 K (resonance stabilised by ring).

Alkyl RN_2^+ = very unstable (decomposes fast).



Physical Properties

$\text{PhN}_2^+\text{Cl}^-$: colourless crystalline, soluble in water, decomposes when dry \rightarrow used in situ.

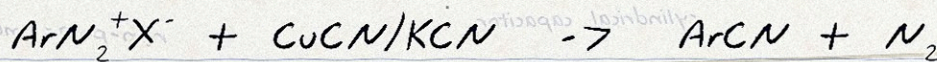
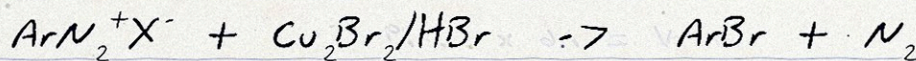
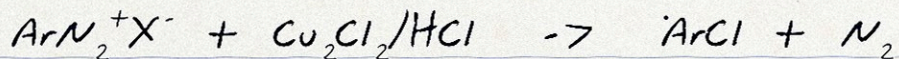
$\text{PhN}_2^+\text{BF}_4^-$ - more stable (used for ArF synth.).

Diazonium Reactions (A)

A. Reactions displacing N_2 (gas evolved)

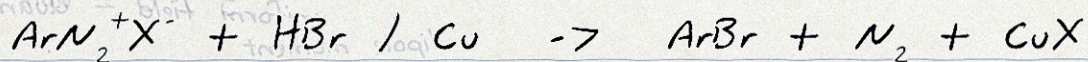
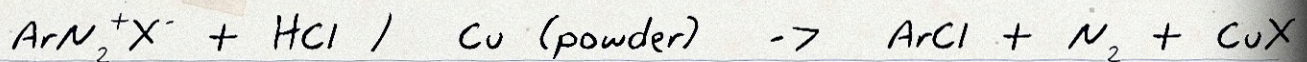
B. Reactions retaining diazo group \Rightarrow azo dyes.

A1. * Sandmeyer Reaction

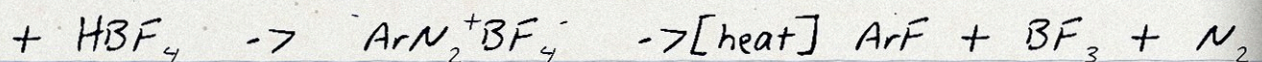
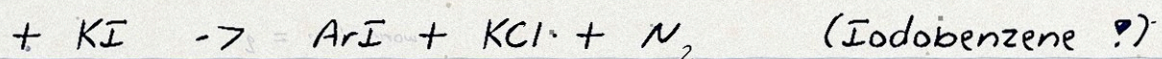


Yields better than Gattermann.

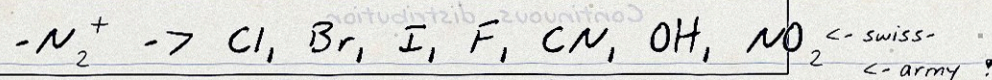
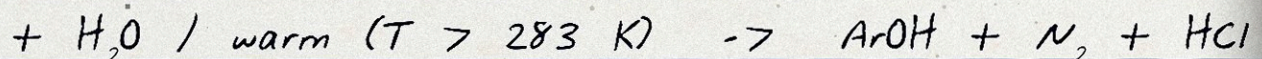
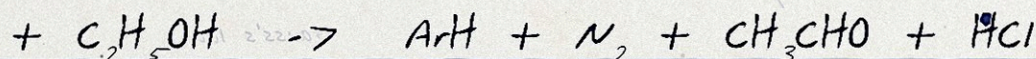
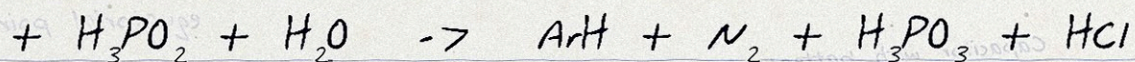
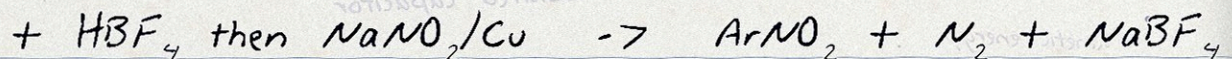
A2. Gattermann Reaction



A3. Replacement by I, F, OH, H, NO₂



(Baltz-Schiemann reaction)



Coupling & Importance

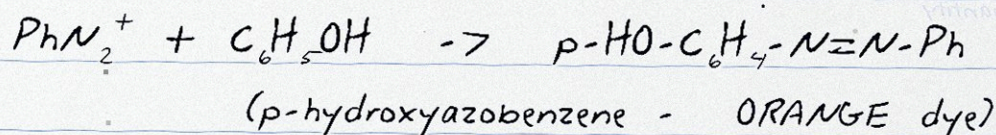
B. Coupling Reactions (retain $-N=N-$)

Diazonium ion = weak electrophile - attacks

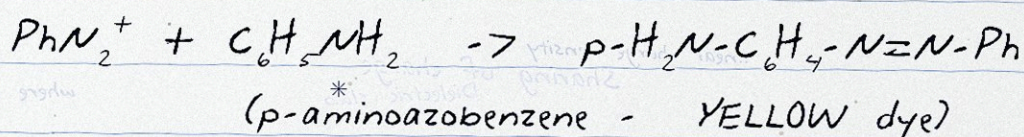
STRONGLY activated arenes (phenol, aniline).

Para-coupling preferred \Rightarrow AZO dye ($-N=N-$).

With phenol (OH^- , cold) :



With aniline (H^+ , cold) :



Why are Diazonium Salts useful ?

- * Introduce $-F$, $-I$, $-CN$ groups - cannot be done by direct halogenation of benzene !
- * Make m-Br phenol, p-Br aniline, p-nitroaniline via protect / deprotect.
- * AZO dyes = textile, food colours.
- * Make ArH (deamination) via H_3PO_2 .

Amine \rightarrow diazonium \rightarrow Ar-X

← key
← tool ?

Tertiary amines e.g. $(CH_3)_3N$ - insect attractants.