Chapter 20: Amines

Amines: derivatives of ammonia with one or more alkyl or aryl groups bonded to the nitrogen

1°	2°	3°
$R-\ddot{N}H_2$	$R-\ddot{N}(-H)-R$	$R-\ddot{N}(-R)-R$

- Hydrogen bonding can occur with amines much like alcohols

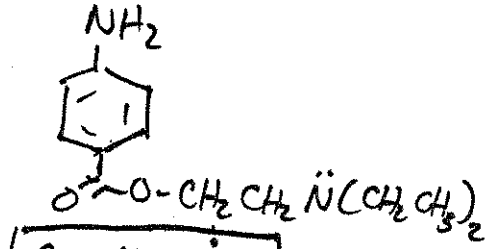
$$R-O-H^{\delta+}\cdots{}^{\delta-}O-R \quad > \quad R-\ddot{N}(-H)-H^{\delta+}\cdots:\ddot{N}(-H)-R$$

stronger H-bond — weaker H-bond

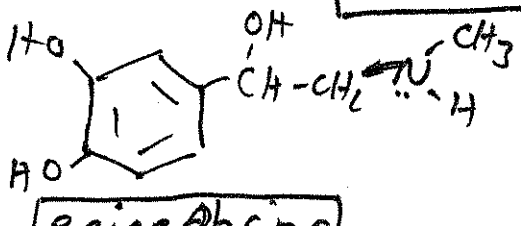
- Hydrogen bonding effects boiling point and solubility of amines (boiling pt higher because of stronger intermolecular interactions & soluble in H_2O) ↑ more

→ Many amines have potent biological activity (found in many different natural products and man-made drugs)

- See pg 805 in text for representative structures



novocaine (anaesthetic)



epinephrine (adrenal hormone)

Nomenclature

1° Amines

- Common name
  → name the alkyl group bonded to the N atom followed by suffix name "amine"
- IUPAC name
  → find longest continuous carbon chain bonded to the amine N and change "e" ending of parent alkane to "amine" suffix. (Use usual rules of nomenclature to # chain & name substituents)

ex 

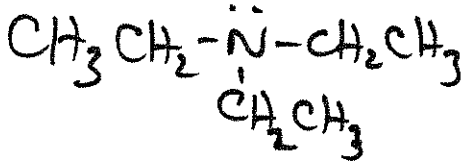
common _____ _____

IUPAC _____ _____

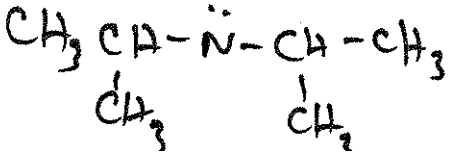
2° and 3° Amines

→ 2° and 3° amines with identical alkyl groups are named by using the prefix di or tri with the name of the primary amine

ex.



triethylamine



_____

→ 2° and 3° amines with more than one kind of alkyl group are named as N-substituted primary amines, as described in the example below.

Ex: Give the common + IUPAC name of $CH_3-\underset{\underset{CH_3}{|}}{CH}-\ddot{N}H-CH_3$

1. Find the longest alkyl chain (or largest ring) bonded to the N-atom and name it as the parent amine (assign a common or IUPAC name)

$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{H}{|}}{\ddot{N}}-CH_3$ Common: isopropylamine

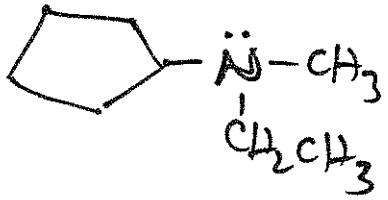
IUPAC: 2-propanamine

2. Name the other groups on the N atom as alkyl groups, alphabetize names, and put the prefix "N-" before the name.

$CH_3-\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{H}{|}}{\ddot{N}}-CH_3$ Common: N-methylisopropylamine

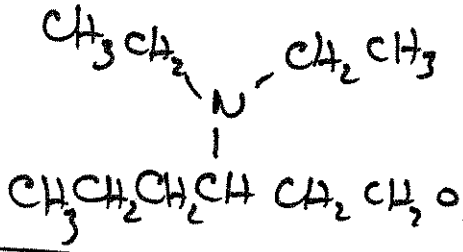
IUPAC: N-methyl-2-propanamine

Give the common + IUPAC names of the following amines:

	Common	IUPAC
		
$CH_3CH_2\underset{\underset{CH_3}{|}}{CH}-\underset{\underset{H}{|}}{\ddot{N}}H$		

- Aldehydes, ketones, carboxylic acids, alcohols, etc. (See table in Ch. 14 → Table 14.1 p 539 in text) Take priority over amines in nomenclature. The amine is named as a substituent group → "amino"

ex: IUPAC

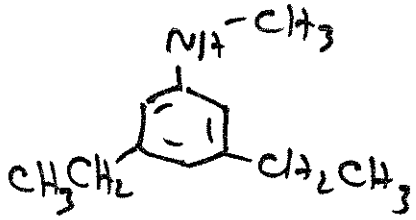


3-(N,N-diethylamino)-1-hexanol

Aromatic Amines

- derivatives of aniline

aniline



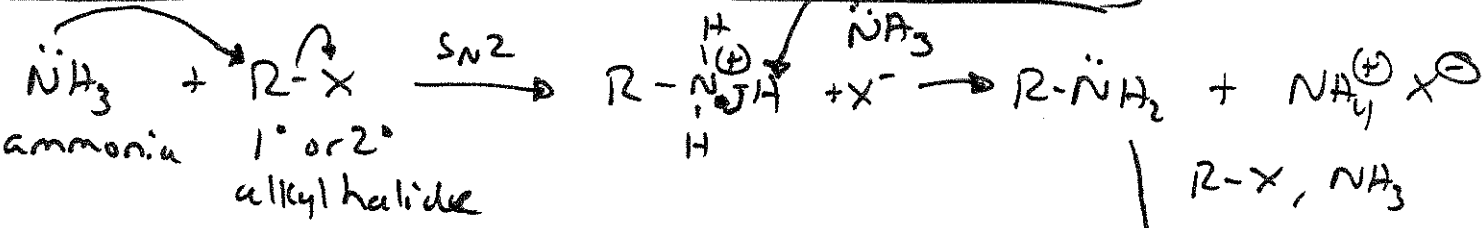
→ Common heterocyclic amines

Pyridine

piperidine

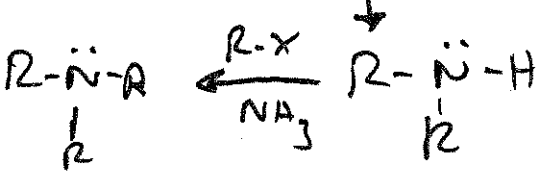
Pyrrolidine

Reactions of Amines w/ Alkyl Halides



ammonia; 1° or 2° alkyl halide

- hard to make ONLY 1° amine with this rxn (but if we add excess NH_3 can favor formation of 1° amine)



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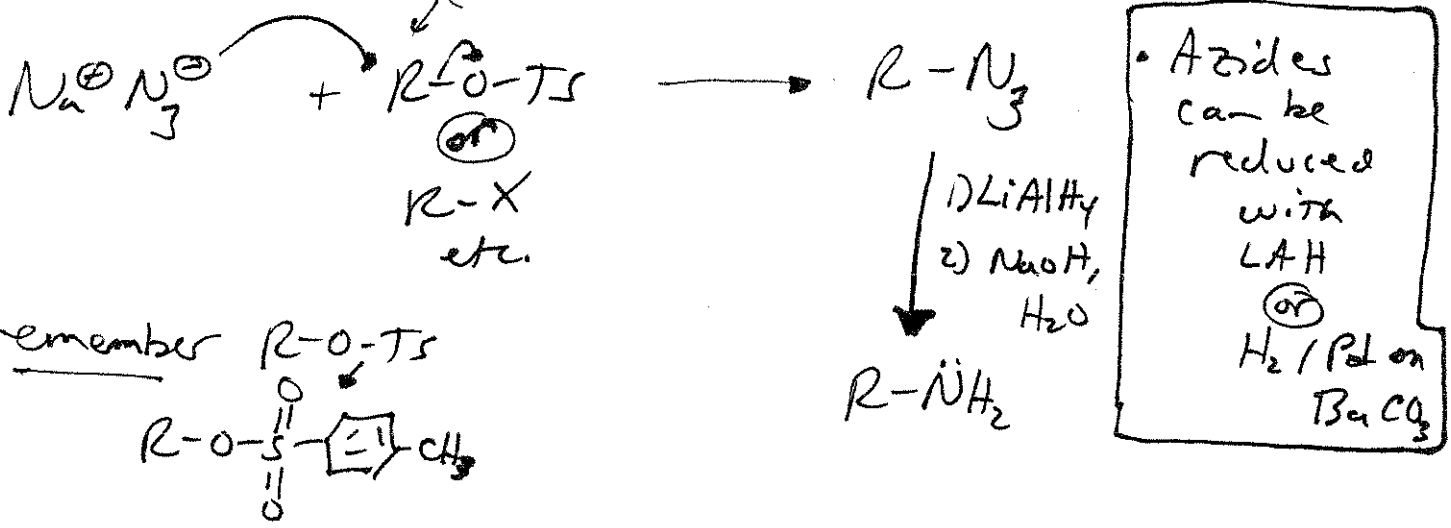
Reduction of Azides ($R-N_3$)

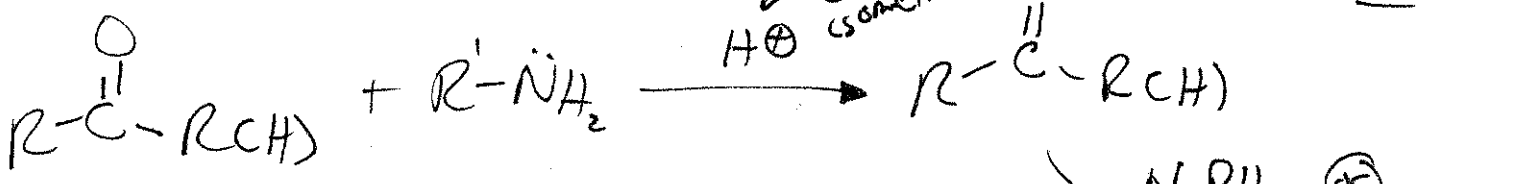
→ azide anions are good nucleophiles; can displace a good leaving group by an S_N2 rxn



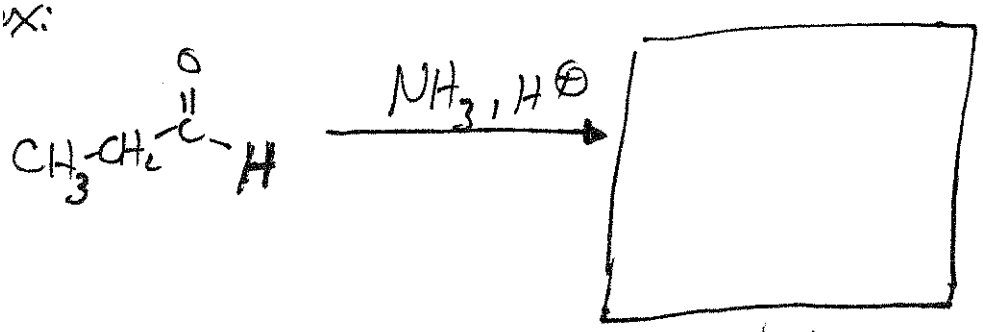
remember R-O-Ts

Reduction of Imines

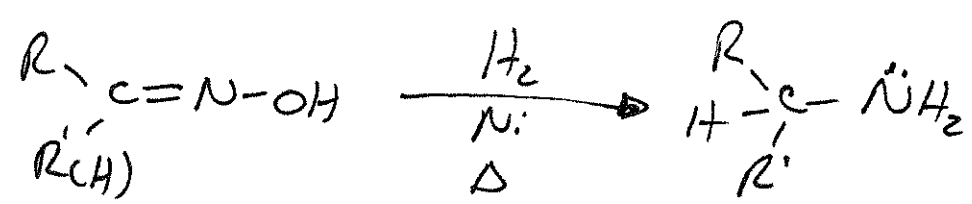
Schiff Base or imine



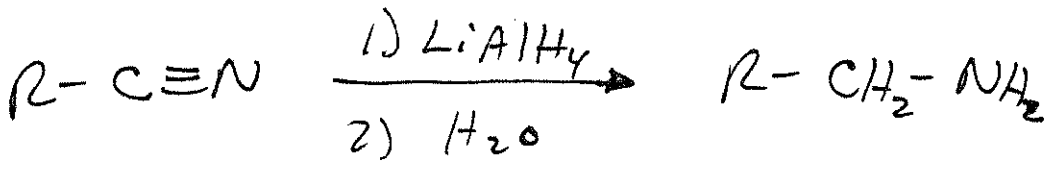
ex:



- Can also reduce nitriles + oximes to 1° amines



→ oximes reduced by H_2

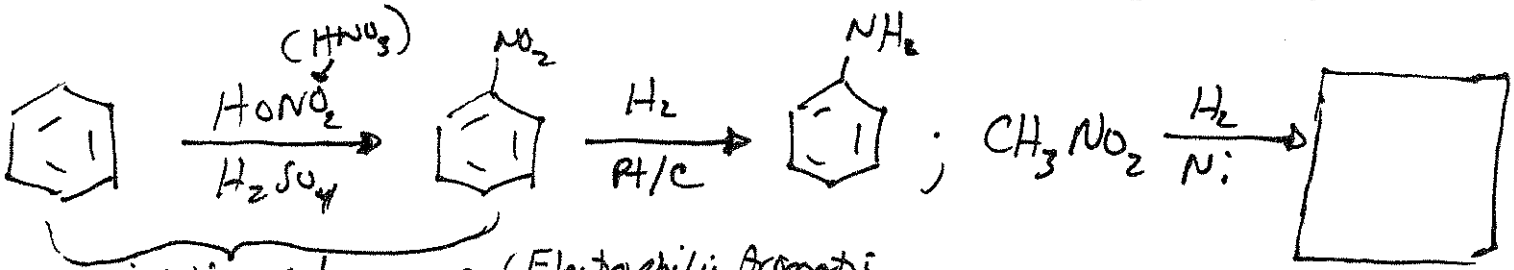


→ nitriles reduced by $LiAlH_4$

→ Can also make amines from amides (by reduction)
↳ (will discuss in Ch. 21)

- **Aromatic and alkyl Nitro Compounds**

→ can be reduced to amines by hydrogenation

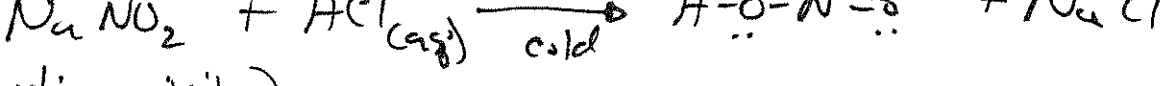


Nitration of benzene (Electrophilic Aromatic substitution (Ch. 10)

- We will skip sections **20.4 a, b + d** but you should read 20.4 © → The Art of Solving Problems

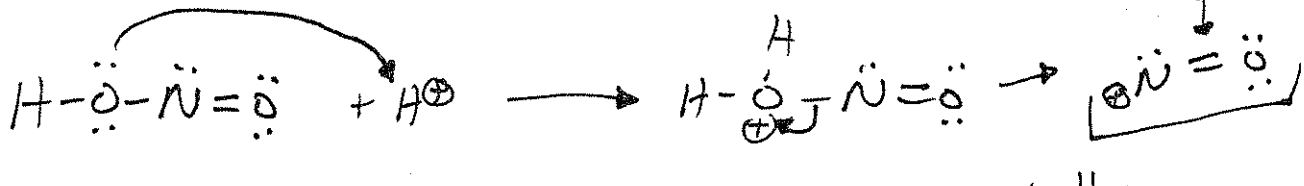
Reactions of Amines with Nitrous Acid

- Production of Nitrous Acid



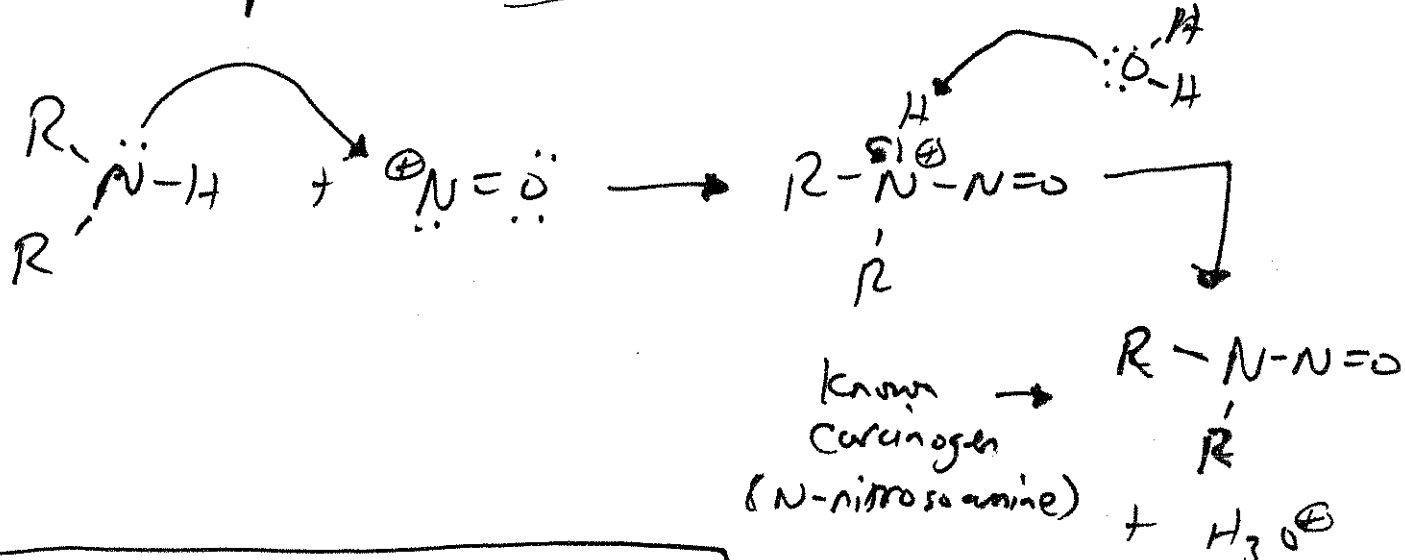
(sodium nitrite)

- In acidic solution nitrous acid is protonated + loses H_2O to form the nitrosonium ion



Reactions of $^{+}N{=}O$ with 2° amines

→ produces stable N-nitrosoamines



Diazotization Reaction

$^{+}N{=}O$ + 1° amines → formation of diazonium salts

nitrosonium ion

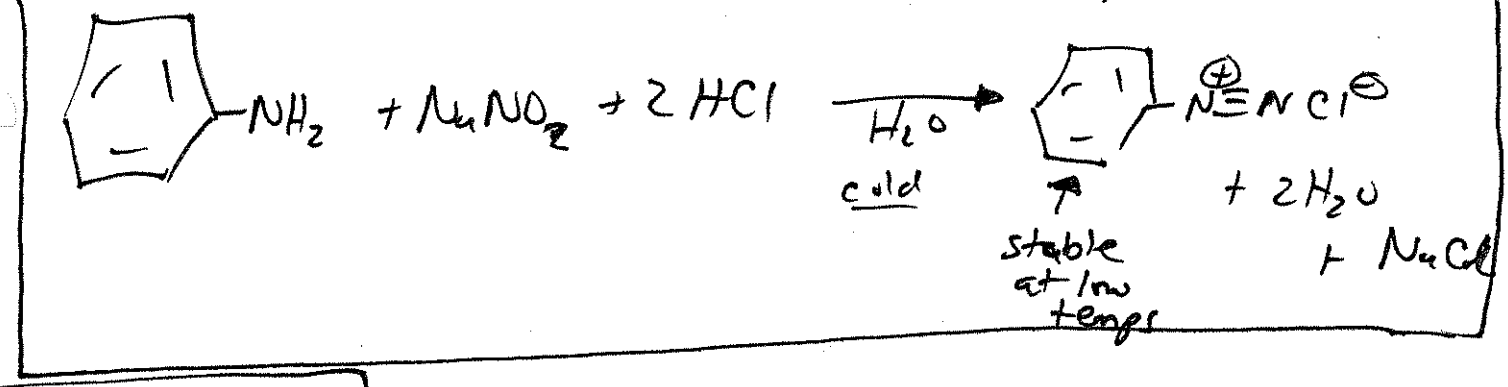
$$R\text{-}NH_2 + NaNO_2 + 2HCl \xrightarrow[H_2O]{} R\text{-}N{\equiv}N\ Cl^{\ominus} + 2H_2O + NaCl$$

alkyl group

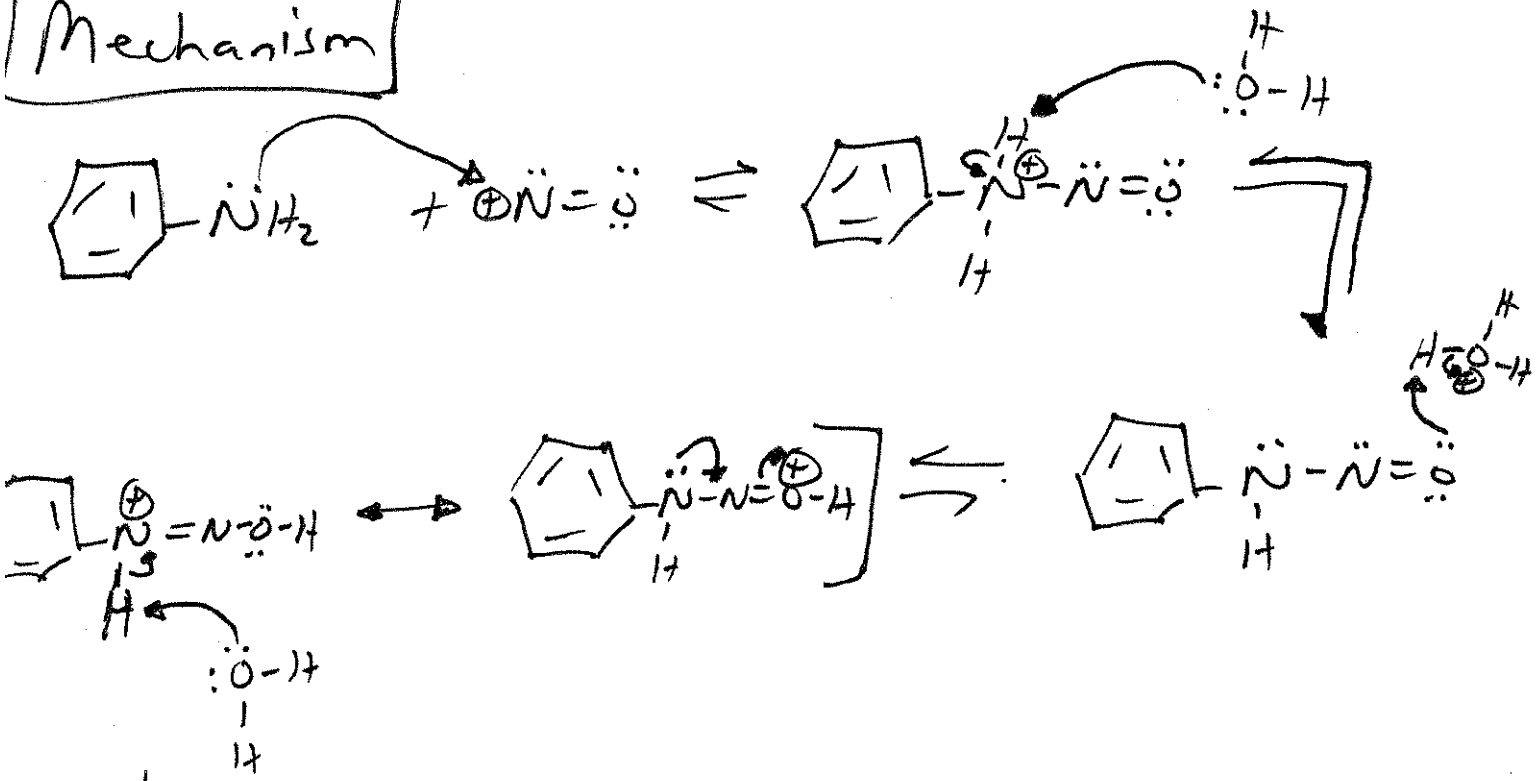
very unstable

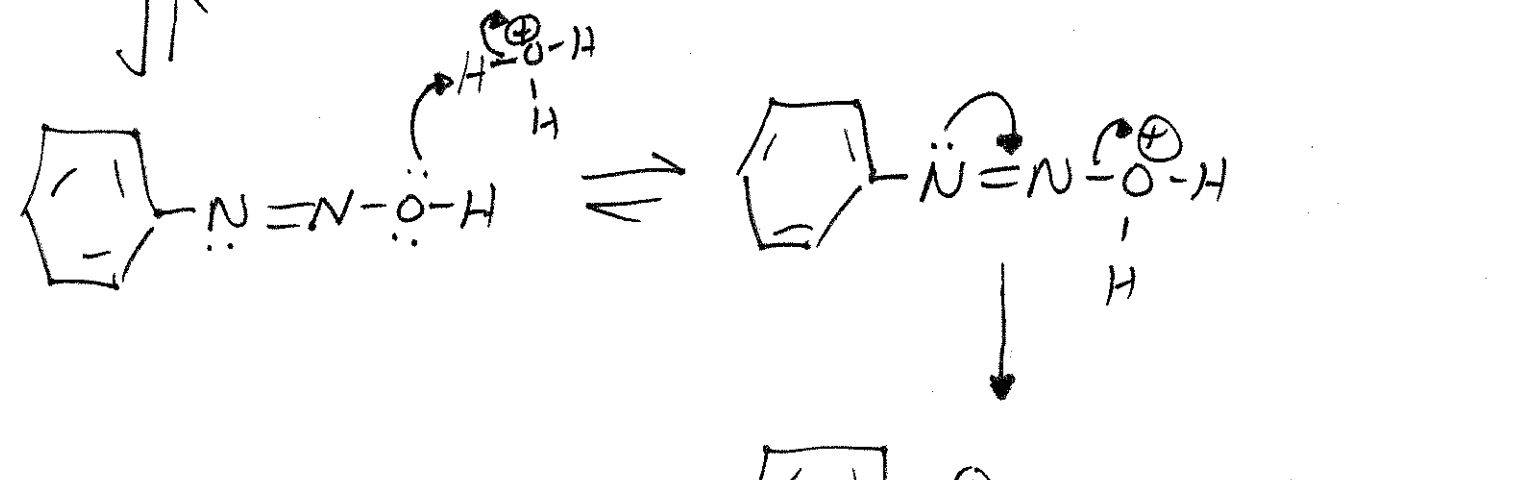
→ but if we use an aryl amine, can get a more stable diazonium salt that can be used in a number of reactions

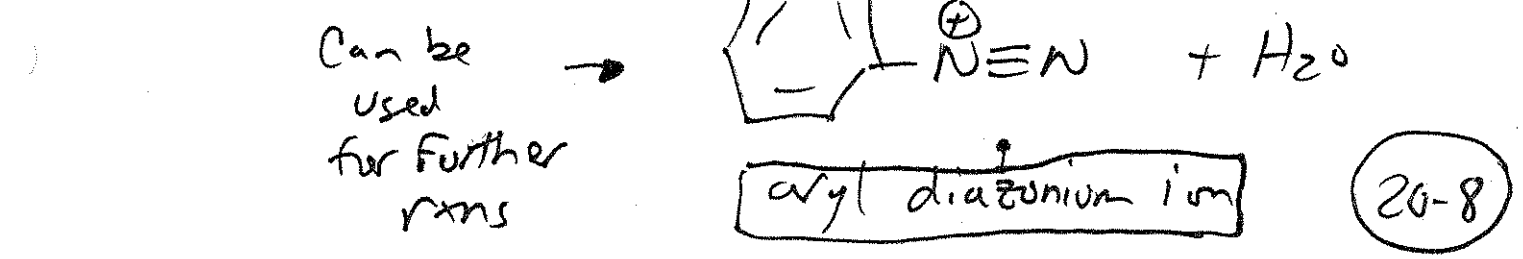
aryl diazonium chloride



Mechanism

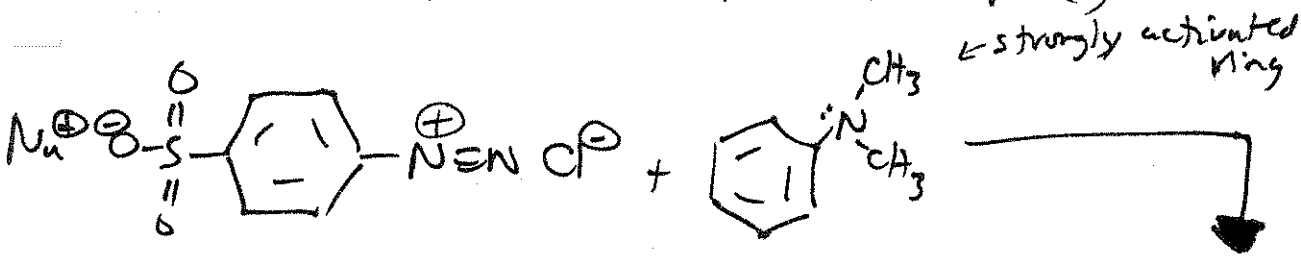




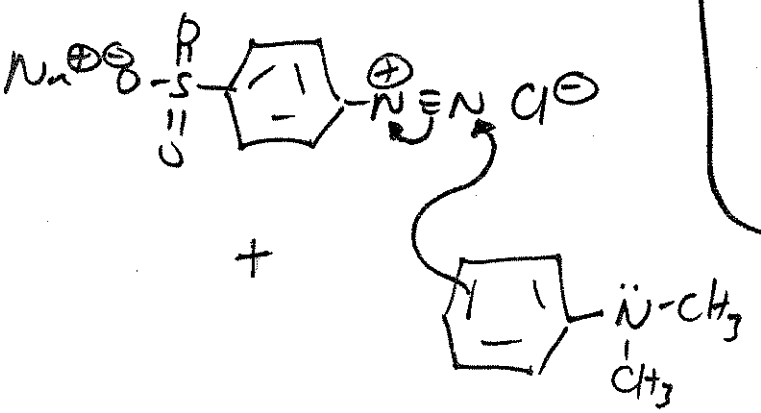


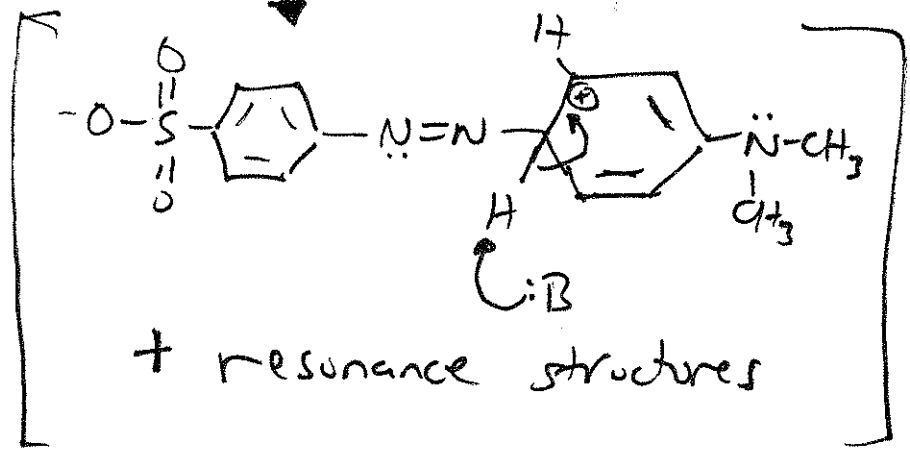
Synthesis of Azo Compounds (Azo Coupling)

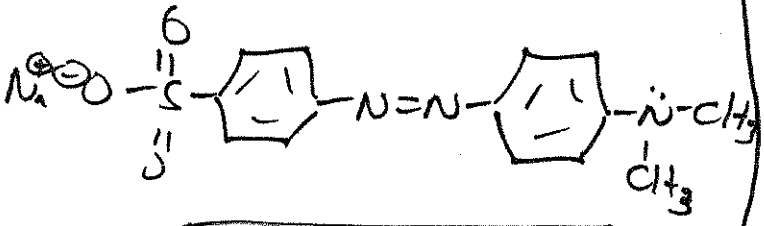
(Diazonium salt as electrophile)



Mechanism



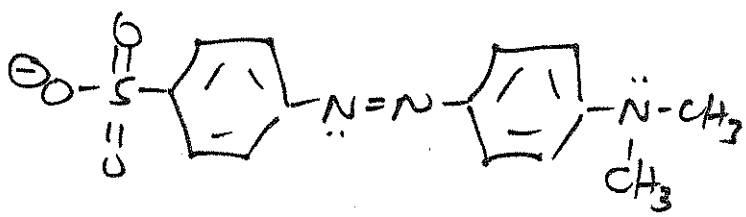




AZO COMPOUND

specifically → methyl orange → as indicator

20.8 Nitrogen-Derivative of Carbonic Acid (SKIP)



Azo compounds - highly conjugated & therefore highly colored → used for dying fabrics & as acid-base indicators