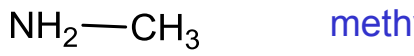
Amino compounds

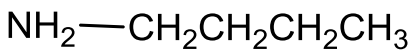
Nomenclature

alkylamine dialkylamine trialkylamine

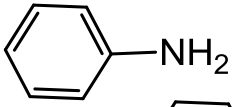
primry secondary tertiary



methylamine

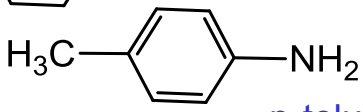


ethylamine

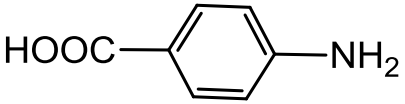


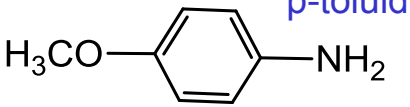
aniline

p-aminobenzoic acid.

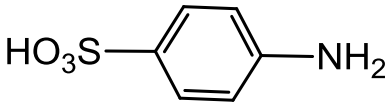


p-toluidine

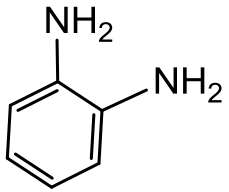




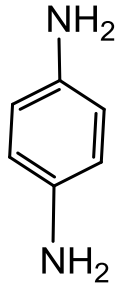
p-anisidine



kys. sulfanilic acid

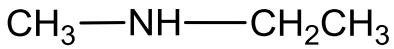


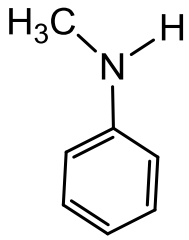
o-phenylenediamine



p-phenylenediamine

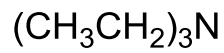
ethylmethylamine

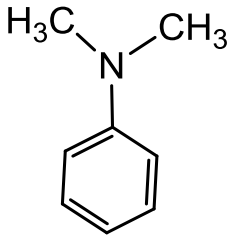




N-methylaniline

triethylamine

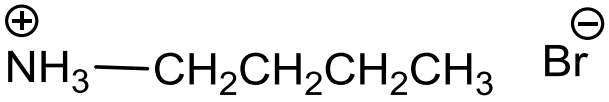




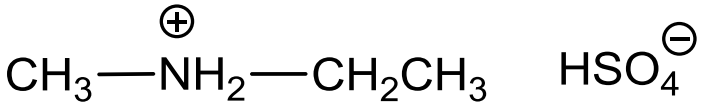
N,N-dimethylaniline

Amino compounds

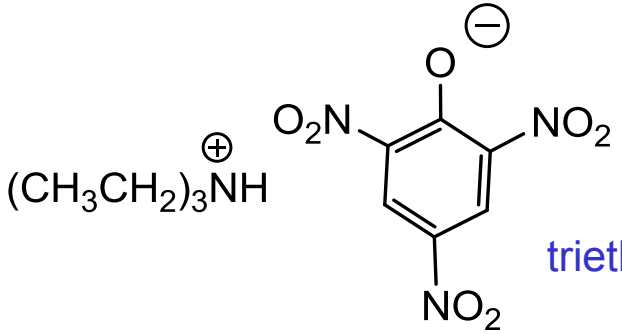
amonium salts



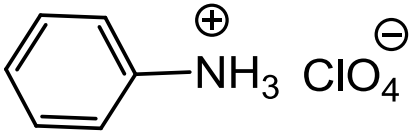
butylamonium bromide



ethylmethylamonium hydrogensulfate

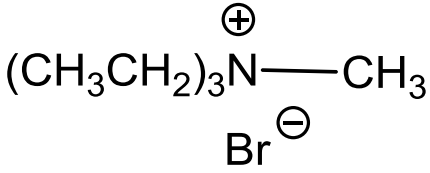


triethylamonium pikrate

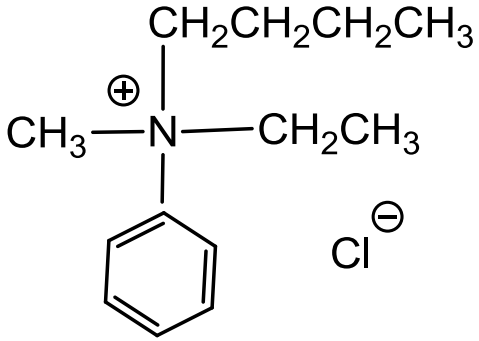


anilinium perchlorate

quarternary amonium salts

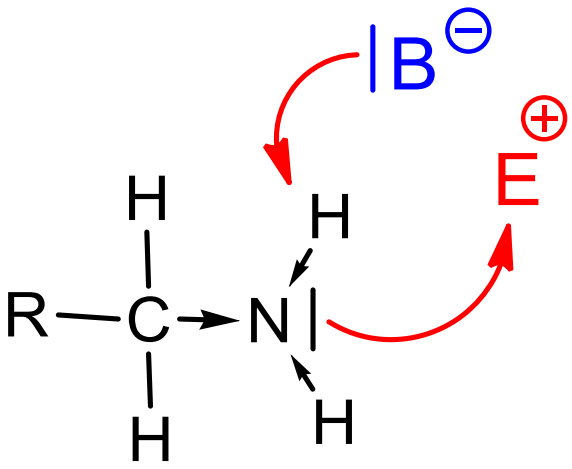


triethylmethylamonium bromid



butylethylphenylmethylamonium chloride

Amino compound



Reactivity

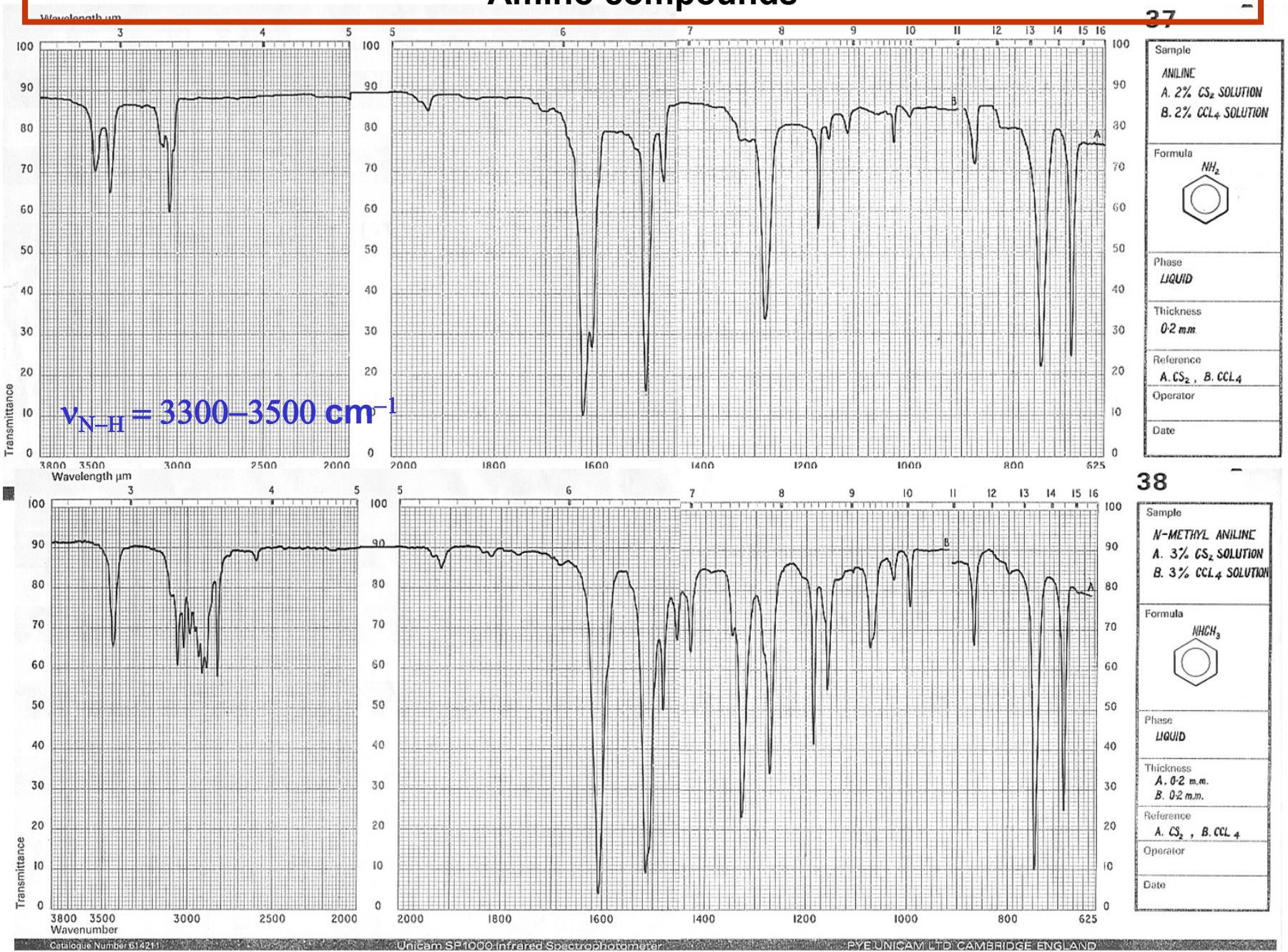
1. basic and nucleophilic properties – reactions with proton and elektrophiles
2. exceptional reaction with nitrous acid
3. hydrogen atoms at nitrogen are acidic
4. hydrogen bonds with nitrogen atom (weaker than at alcoholes)

characteristic vibration in infrared spectrum:

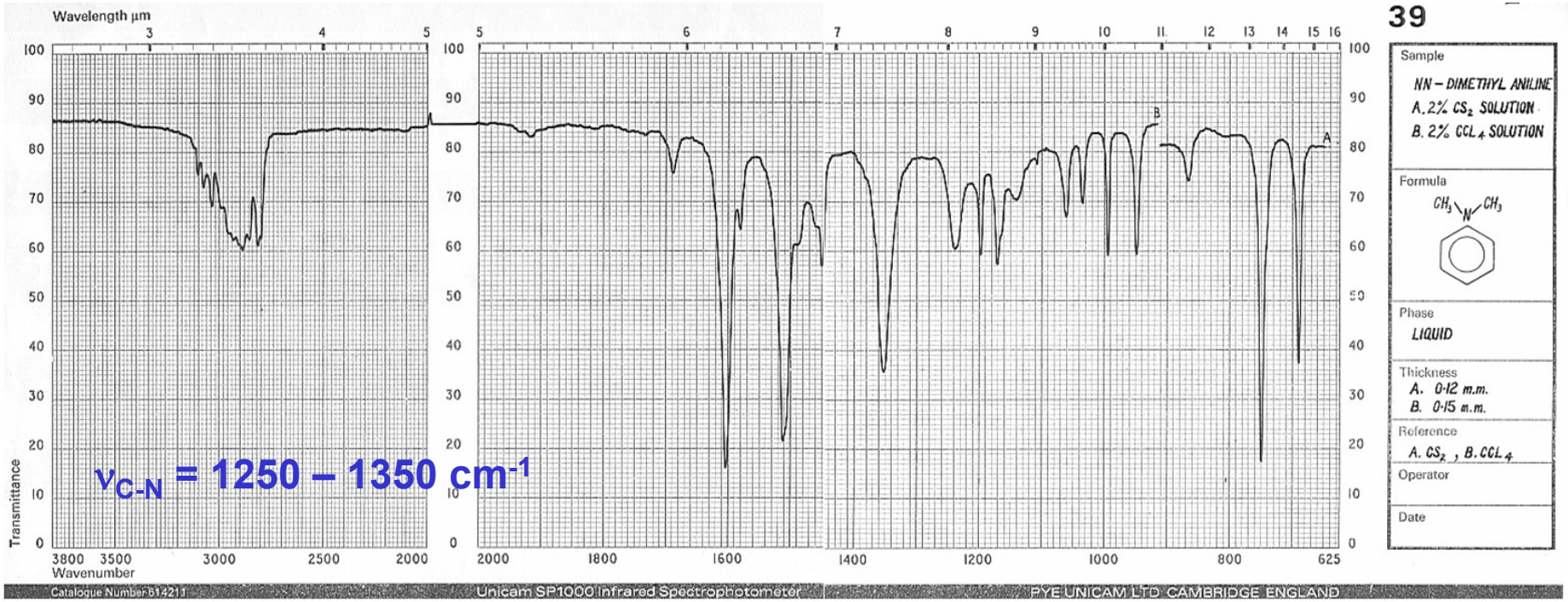
valence vibration **N-H** prim. amine – two bands (region 3300 – 3500 cm^{-1})
sek. amine - only one band
tert. amine - without any band

vibration **C-N** alifatic amines 1020 – 1220 cm^{-1}
aromatic 1250 – 1350 cm^{-1}

Amino compounds

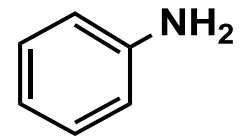


Amino compounds

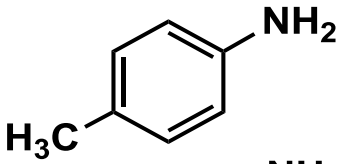


BASICITY OF AMINES

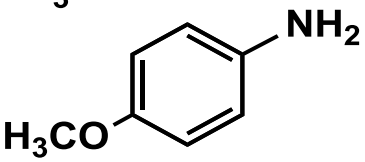
	pK_b
NH_3	4,75
$CH_3 - NH_2$	3,35
$CH_3 - NH - CH_3$	3,28
$(CH_3)_3 N$	4,25



9,33



8,94



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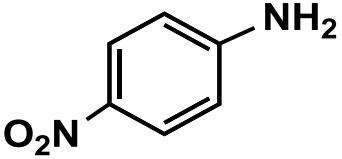
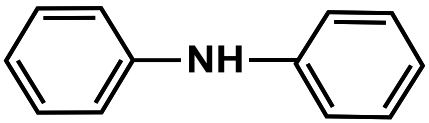
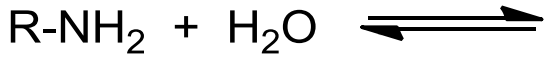


13,00

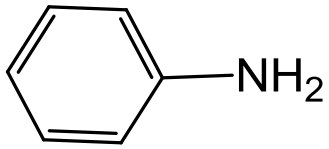


13,15

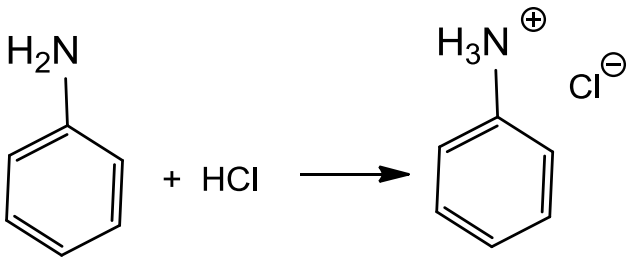


$$K_b = \frac{[RNH_3]^+ \ [HO]^-}{[RNH_2]}$$

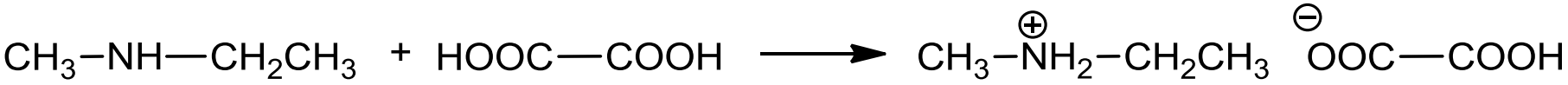
$$pK_b = - \log K_b$$



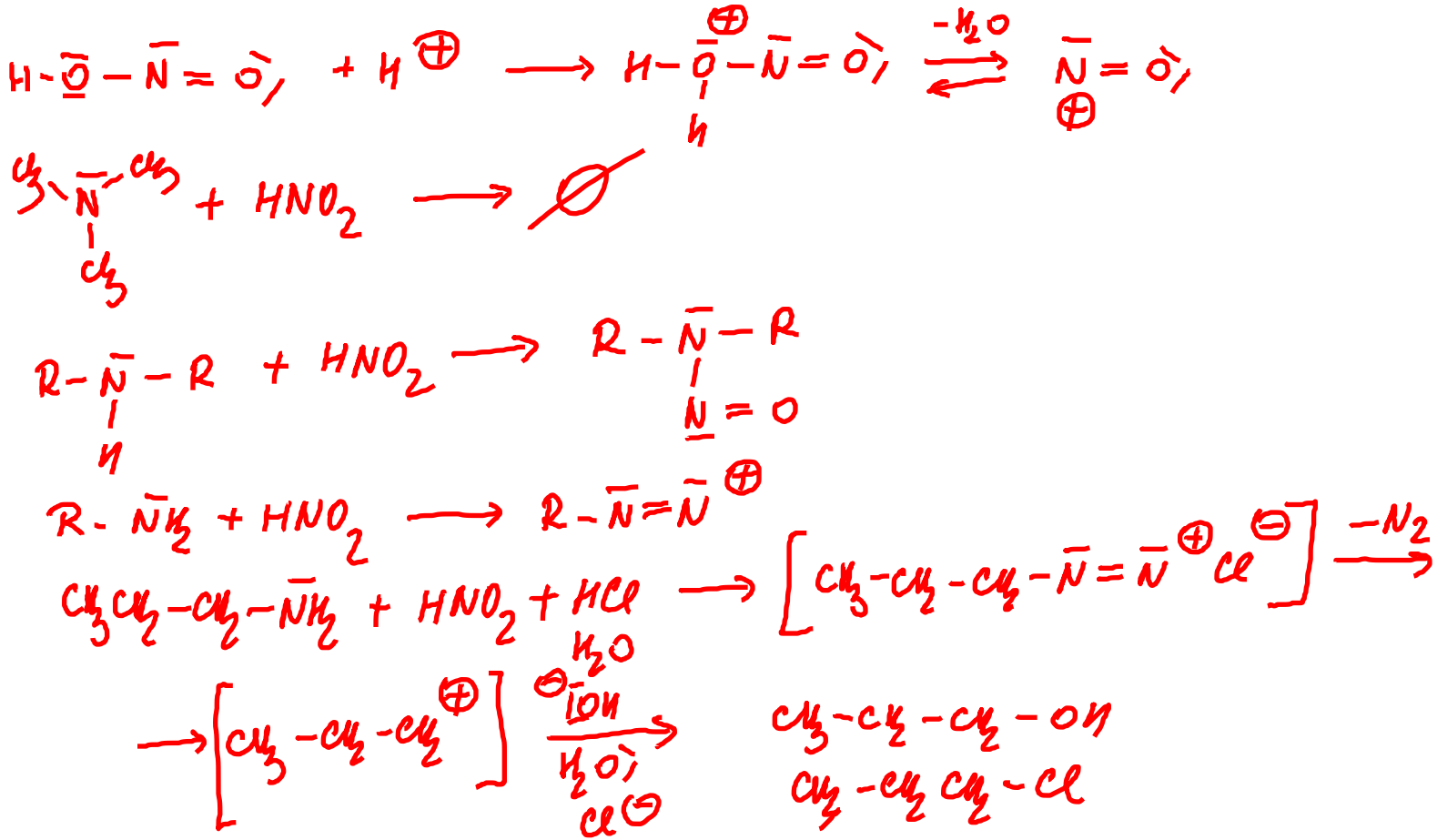
Amino compounds



1. **basic and nucleophilic properties – reactions with proton and elektrophiles**
2. exceptional reaction with nitrous acid
3. hydrogen atoms at nitrogen are acidic
4. hydrogen bonds with nitrogen atom (weaker than at alcoholes)



Amino compounds



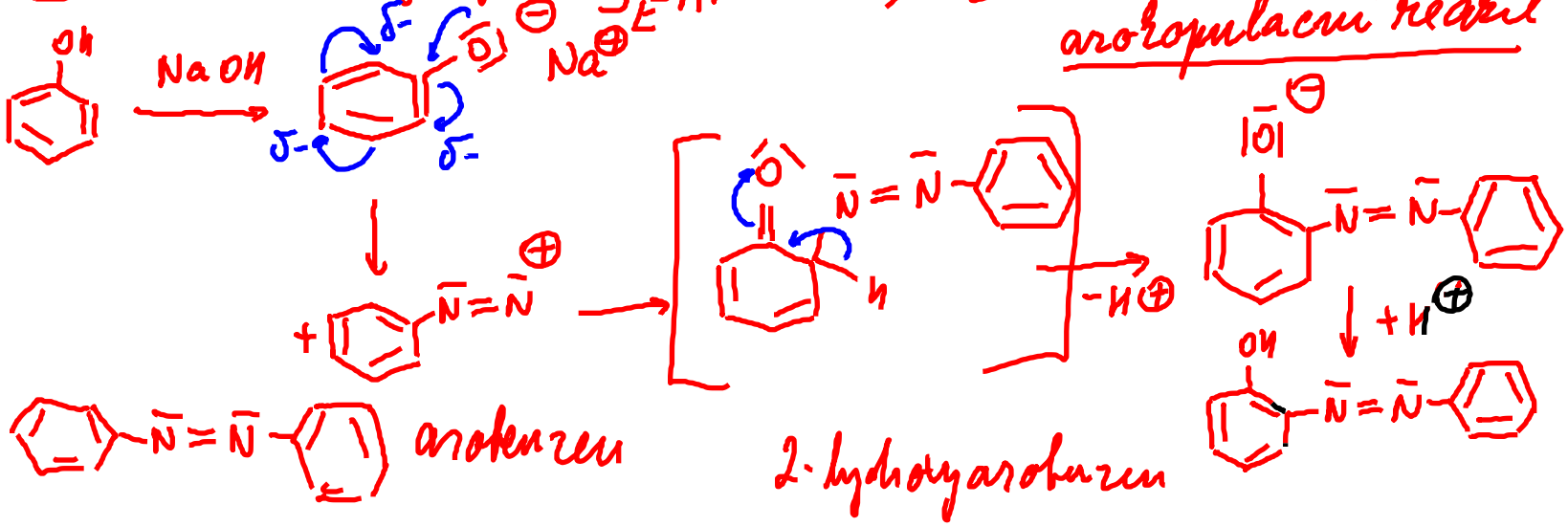
Amino compounds

stabilní do 10 °C

na 10 °C se rozkládá

slabé elektrofily s aktivovanými aromáty poskytují azobarviva

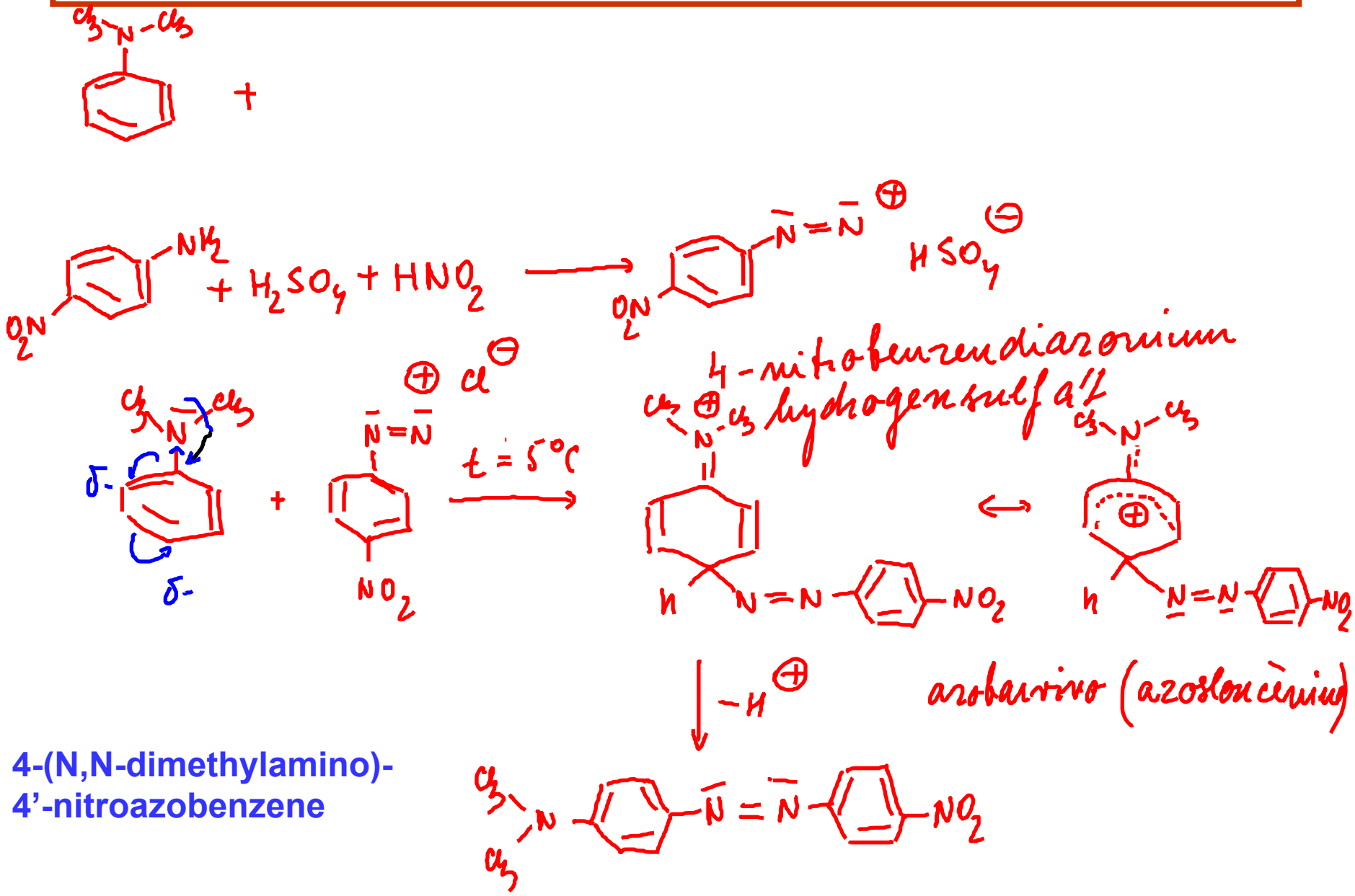
S_E-Ar ⟹ azokopulační reakce



azobenzen

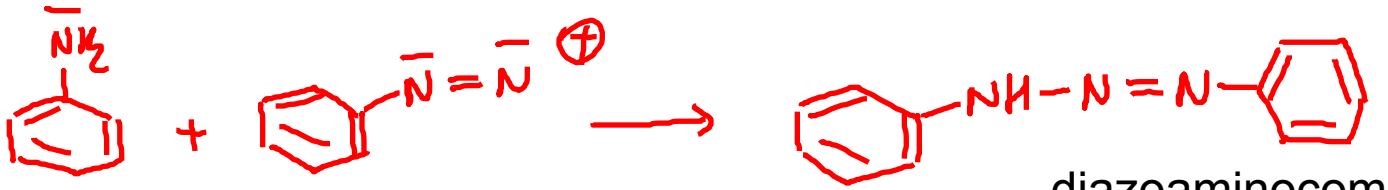
2-hydroxyazobenzen

Amino compounds



4-(N,N-dimethylamino)-4'-nitroazobenzene

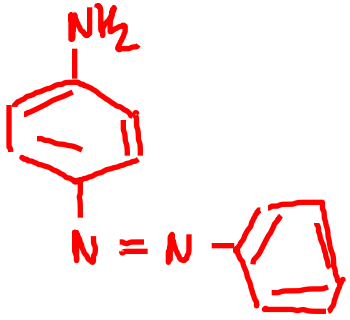
Amino compounds

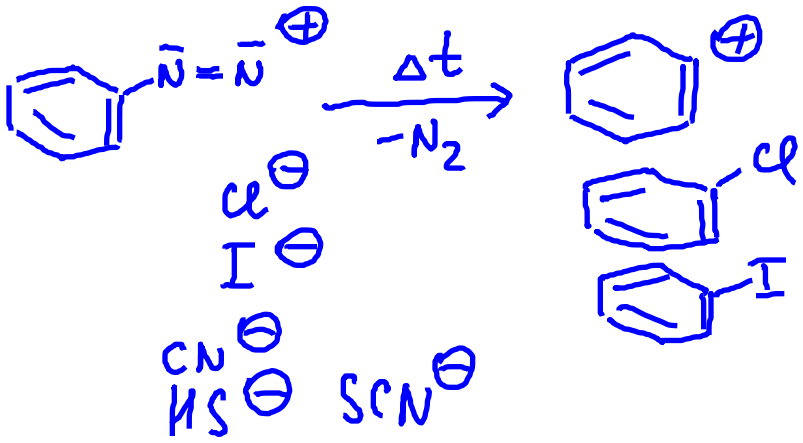


diazoaminocompounds

diazoaminobenzene

CH_3COOH





Sandmeyer Cu^+, Cu

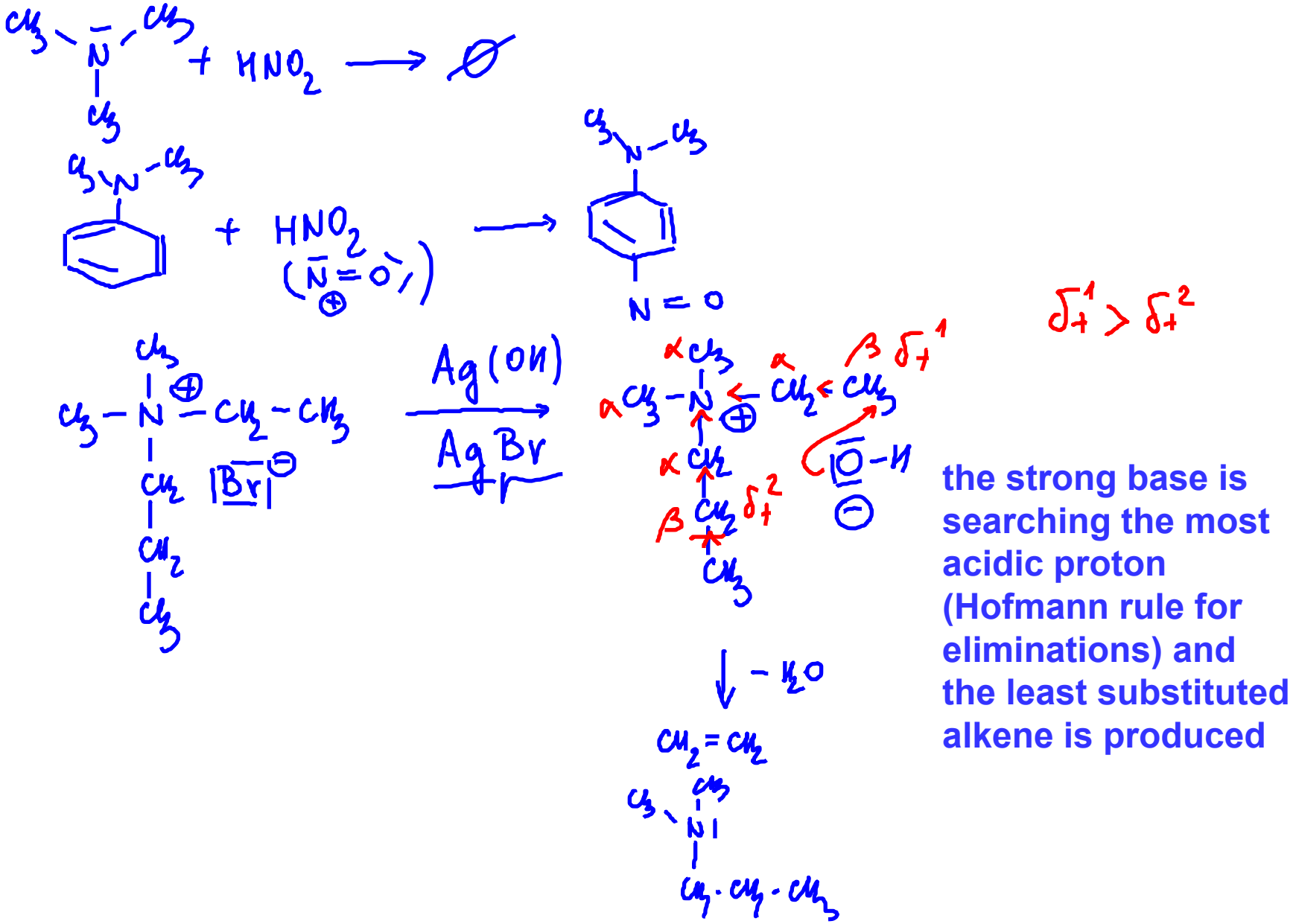
$Cu \rightarrow e^{\ominus} + Cu^+$

$Cu^+ \rightarrow e^{\ominus} + Cu^{2+}$

$Cu^{2+} + e \rightarrow Cu^+$

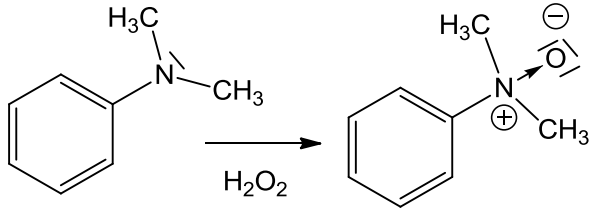
returning back

Aminosloučeniny



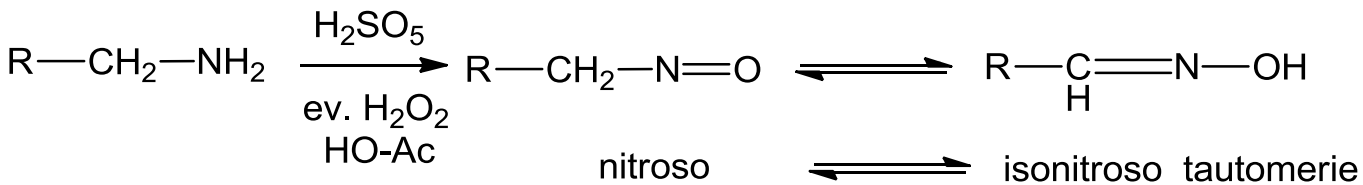
Amino compounds

OXIDATION



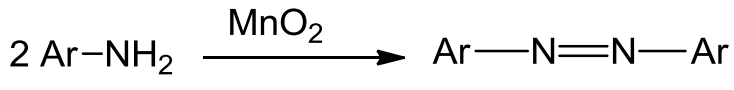
tert -amine aminoxide

primary amines alifatic + aromatic

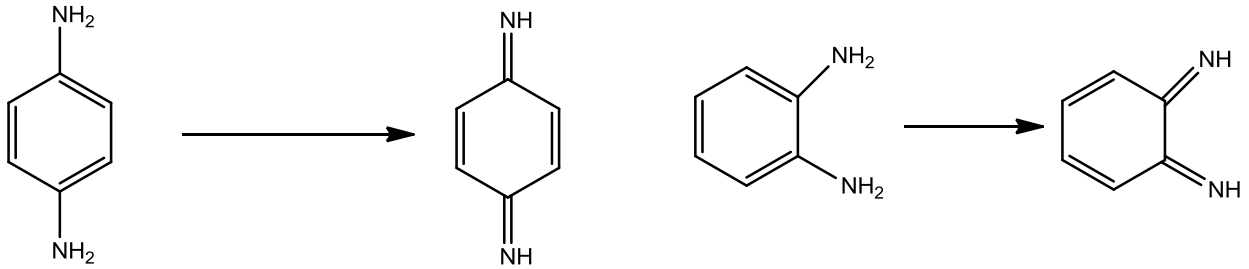


intermediate is hydroxylamine

primary amines aromatic



event. $Pb(OCOAc)_4$
O_2
sodium perboritane



diamines might be even substituted, event. one NH_2substituted by OH

quinonediimines

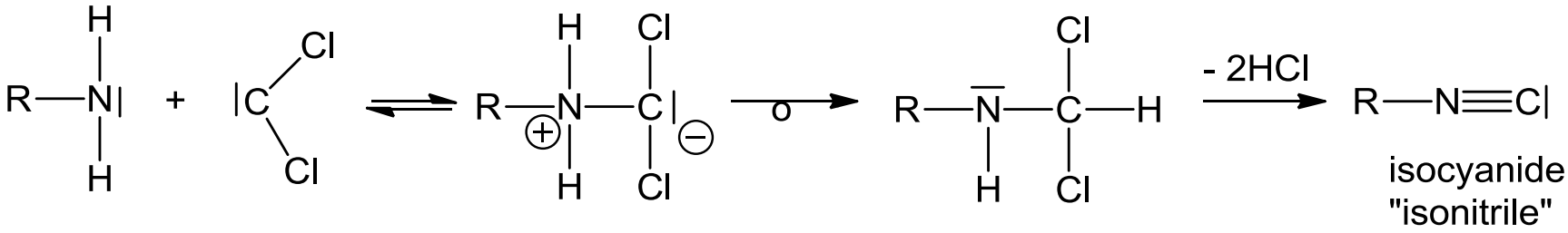
oxidation by $K_2Cr_2O_7$, Ag_2O, Ag_2CO_3, $Pb(OCOAc)_4$, HIO_4

Amino compounds

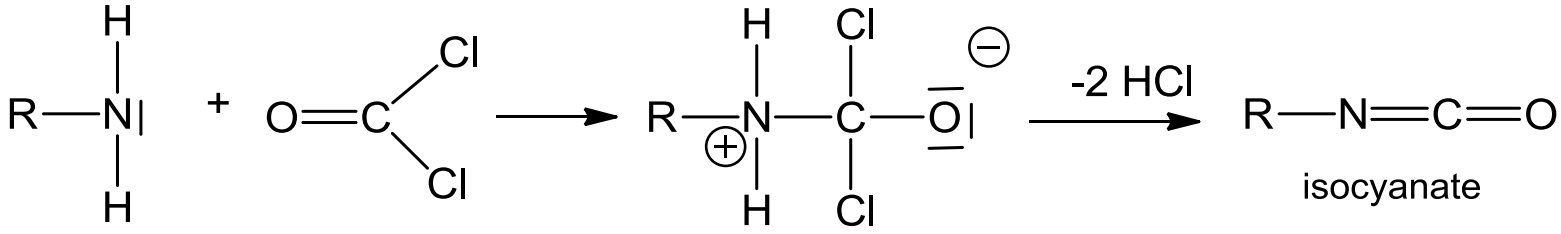
Amines as nucleophiles

Amino compounds

„isonitril test“

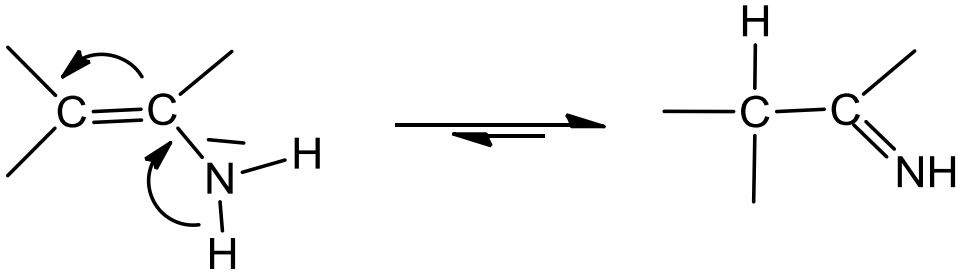


a proof of amino group in biological material



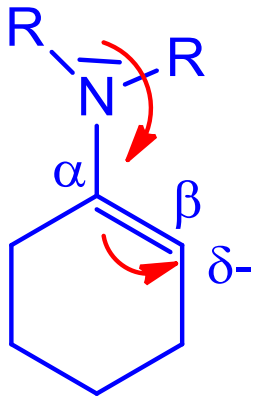
Amino compounds

ENAMINES



enamine imine

tautomerism



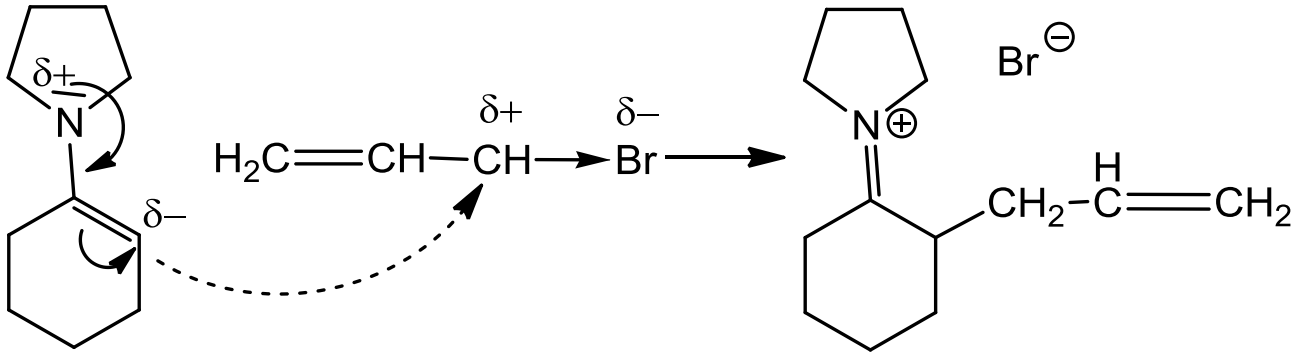
tautomerization is impossible at *t*-derivatives

application in synthesis: they are used as propriate reagents with electrophiles

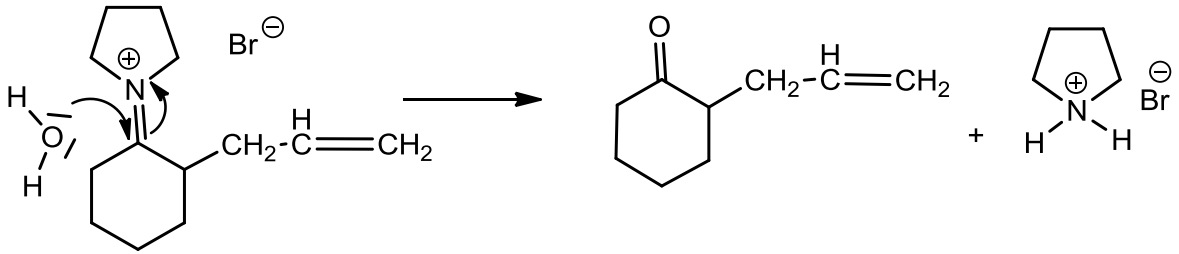
β-carbon has nucleophilic character (but not the nitrogen atom)

Amino compounds

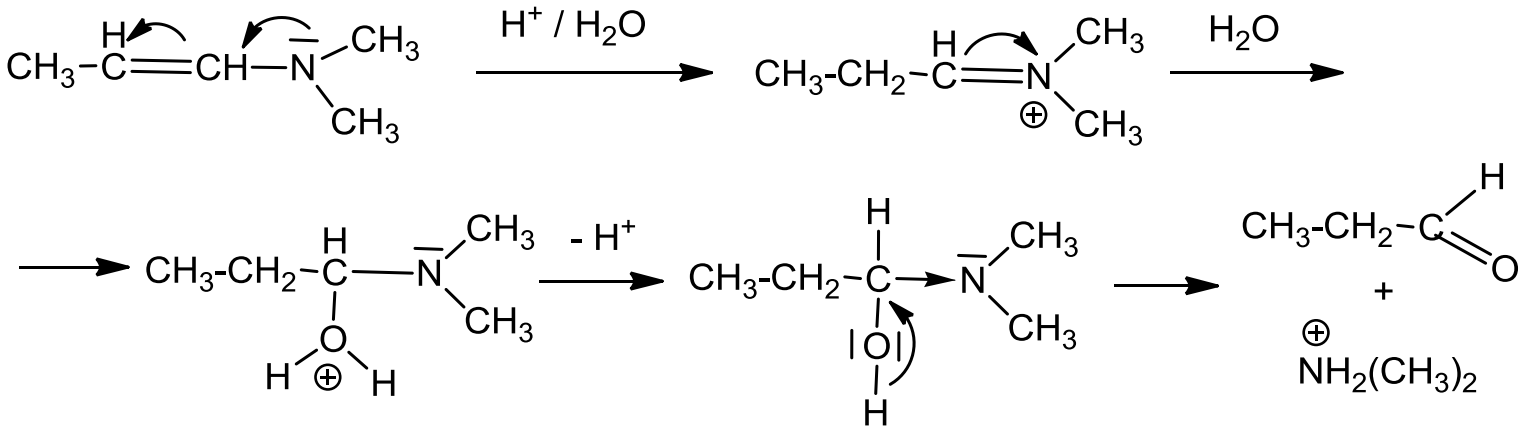
S_N



iminium salts can be easily hydrolysed



Ad_E

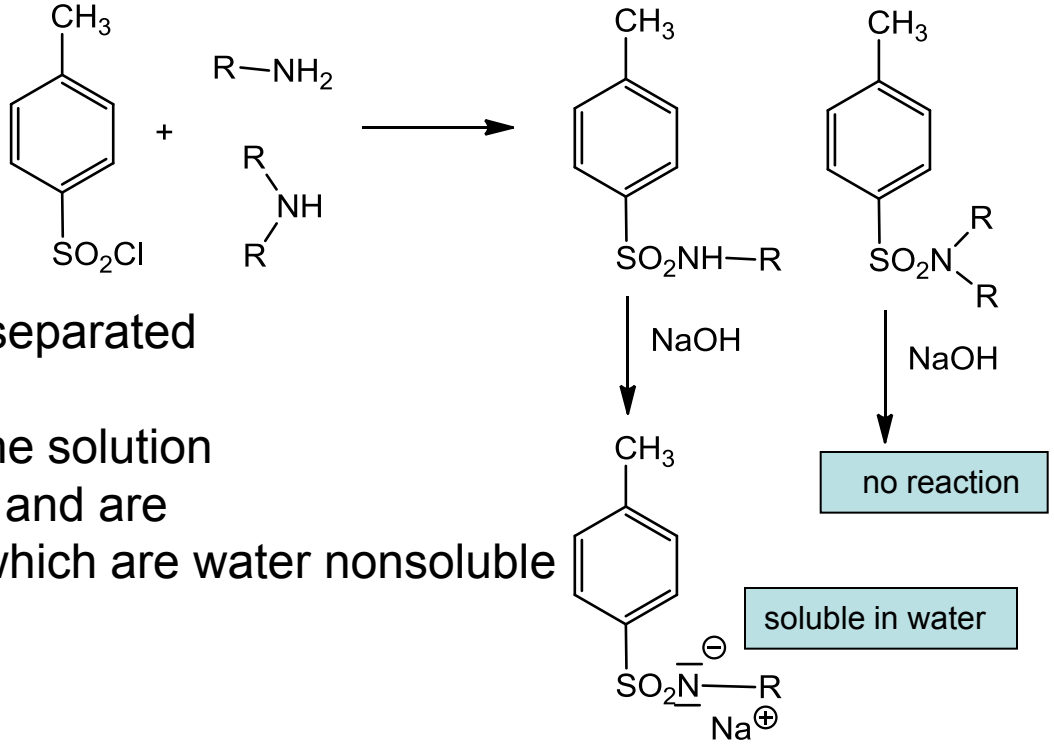


Amino compounds

PREPARATION

1. **Alkylation of ammonia** by the reaction of ammonia with alkyl halogenides is formed a mixture of primary, secondary and tertiary amino derivatives, which must be resolved:

Hinsberg method:
prim. a sec. react with
p-toluene sulfochloride

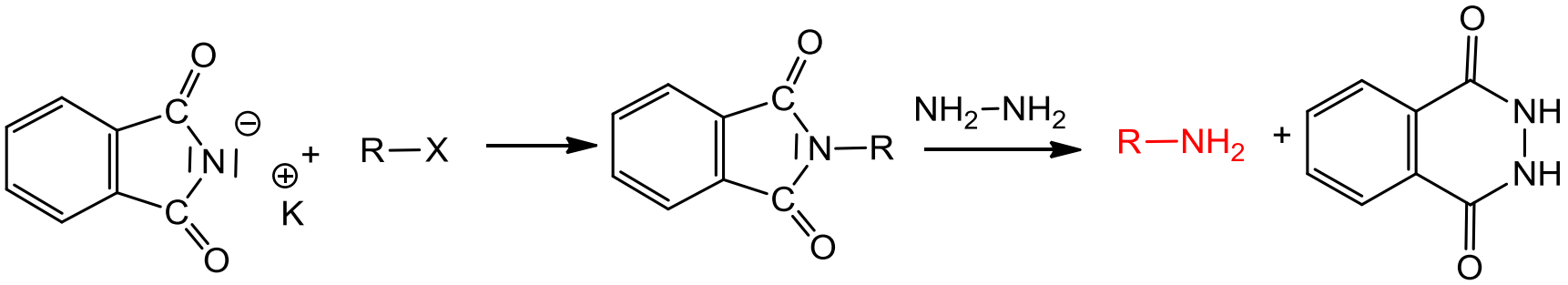


(tert. do not react) and are separated

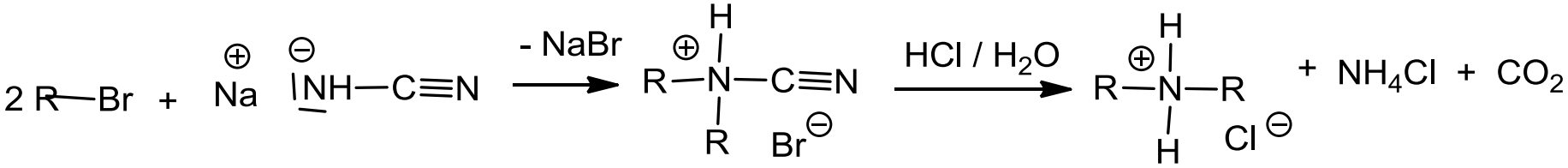
primary are soluble in alkaline solution
- they are dissolved in water and are separated from secondary, which are water nonsoluble

Amino compounds

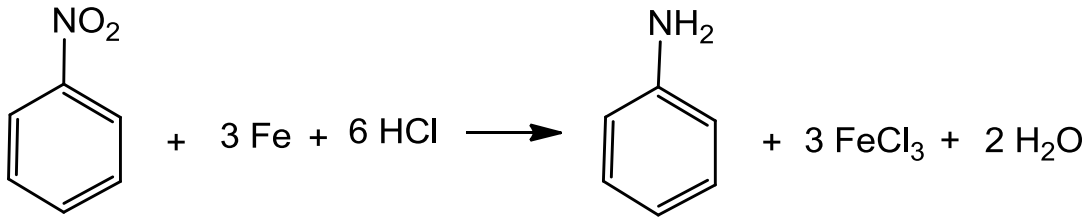
2. Gabriel method



3. Alkylation of cyanamide (sec.amines)



4. Reduction of nitro compounds (mainly aromatic)

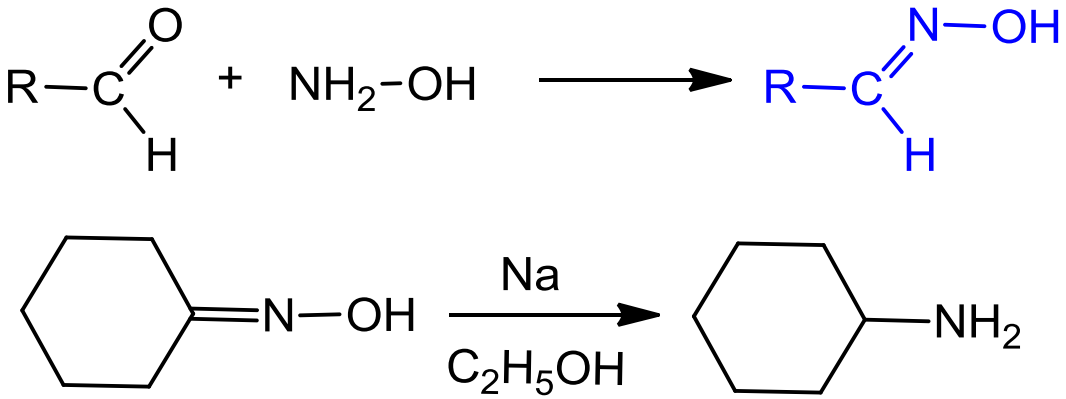


reduction agents:

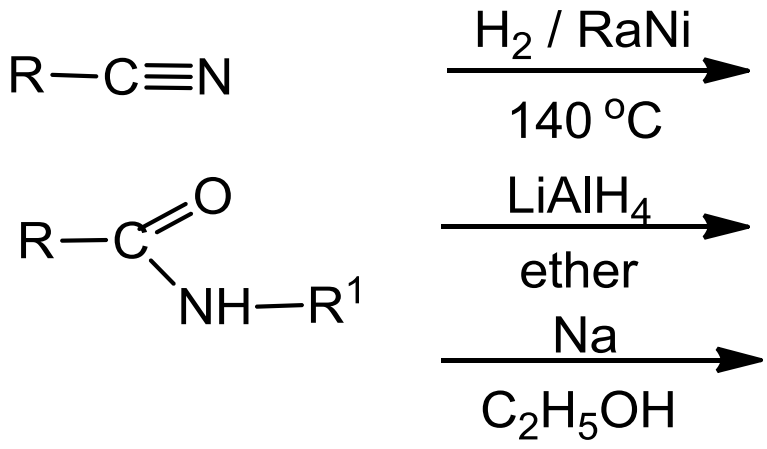
Zn, Sn, $SnCl_2$, $TiCl_3$, $CrCl_2$, Pd/ H_2

Amino compounds

5. Reduction of oximes



6. Reduction of nitriles and amides



Amino compounds

7. Hofmann's amides decomposition