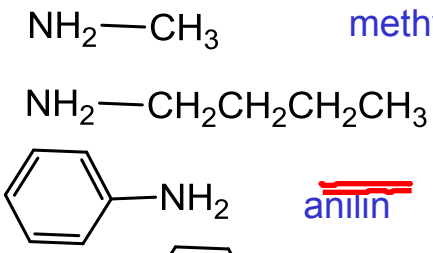
Aminosloučeniny

Názvosloví

alkylamin dialkylamin trialkylamin

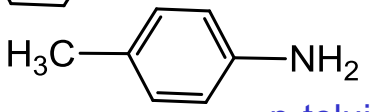
primární sekundární terciární



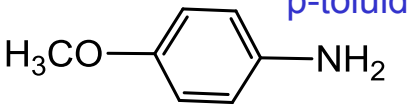
methylamin

ethylamin

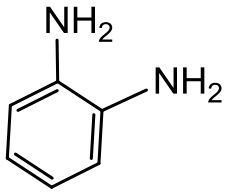
anilin



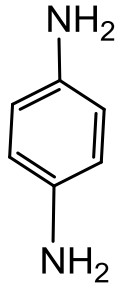
p-toluidin

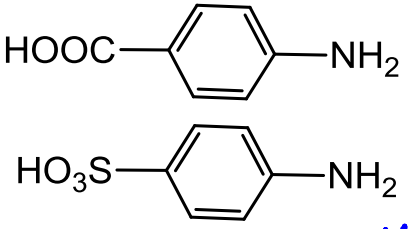


p-anisidin



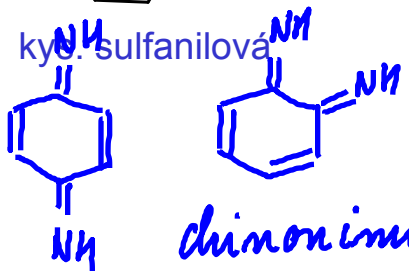
o-fenylendiamin



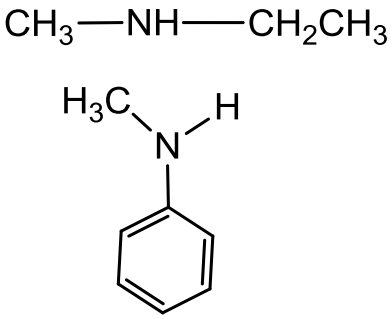


p-aminobenzoová kys.

kys. sulfanilová

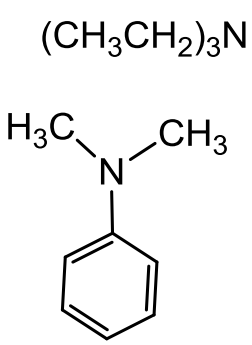


p-fenylendiamin



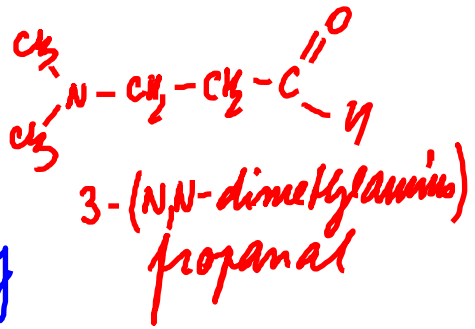
ethylmethylamin

N-methylanilin



triethylamin

N,N-dimethylanilin

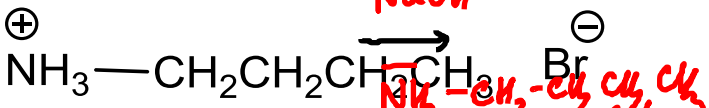


chinoniminy

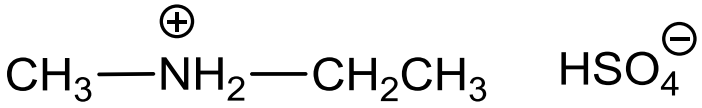
3-(N,N-dimethylamino)propanal

Aminosloučeniny

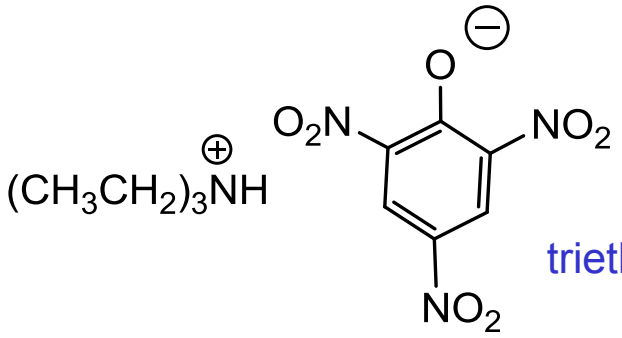
amoniové soli



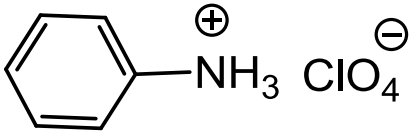
butylamonium bromid



ethylmethylamonium hydrogensulfát

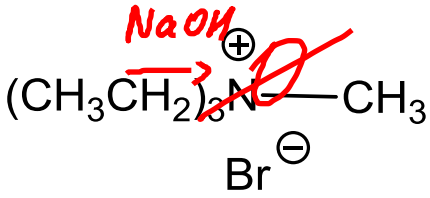


triethylamonium pikrát

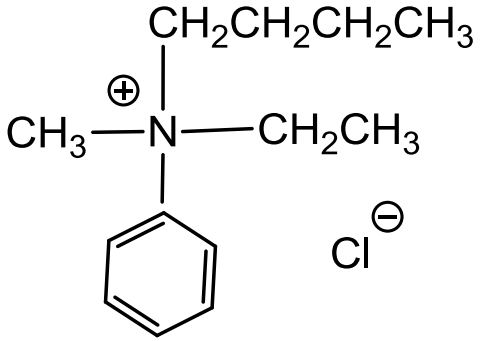


anilinium chloristan

kvarterní amoniové soli

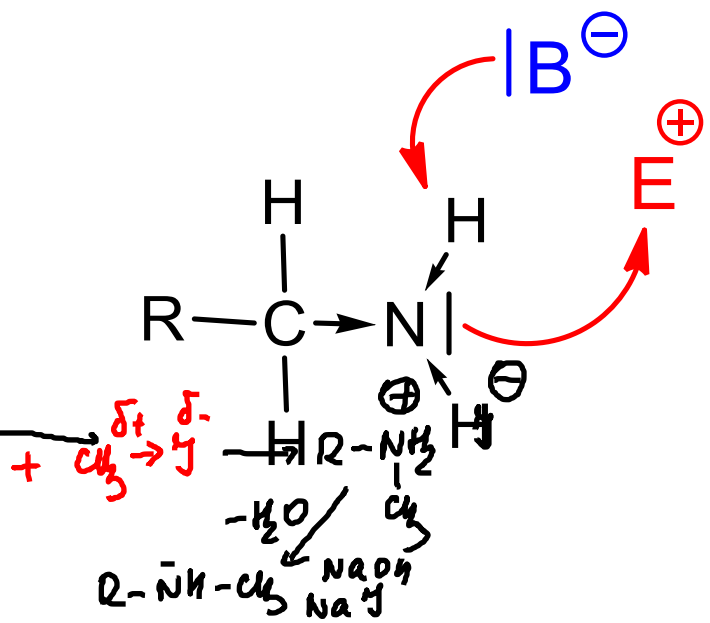


triethylmethylamonium bromid



butylethylfenylmethylamonium chlorid

Aminosloučeniny



Reaktivita

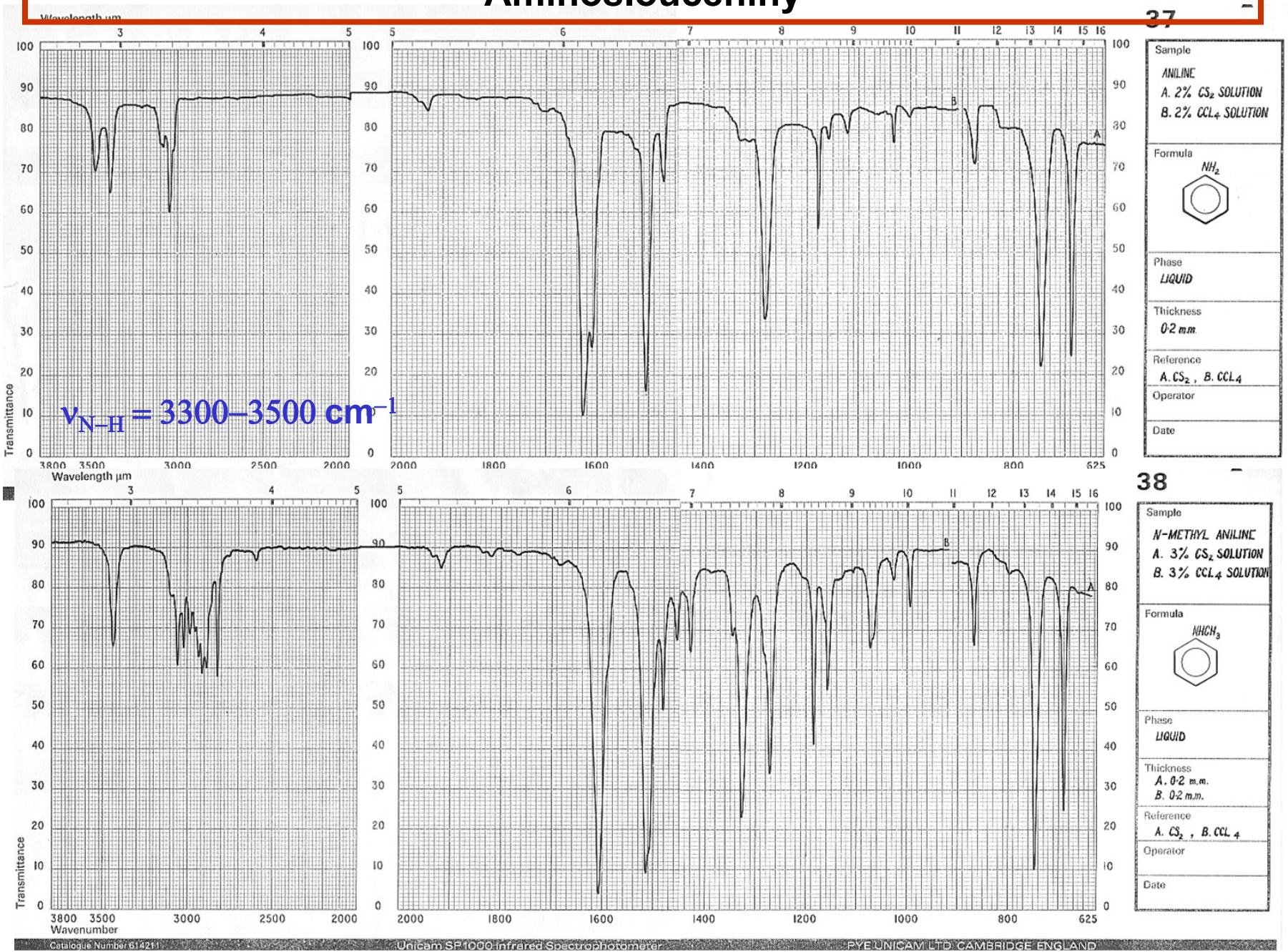
1. bazické a nukleofilní vlastnosti – reakce s protonem a elektrofily
2. zvláštní reakce s kyselinou dusitou
3. kyselé vodíkové atomy vázané na dusíku
4. vodíkové vazby mezi dusíkem a vodíkem (slabší než u alkoholů)

charakteristické vibrace v infračervených spektrech:

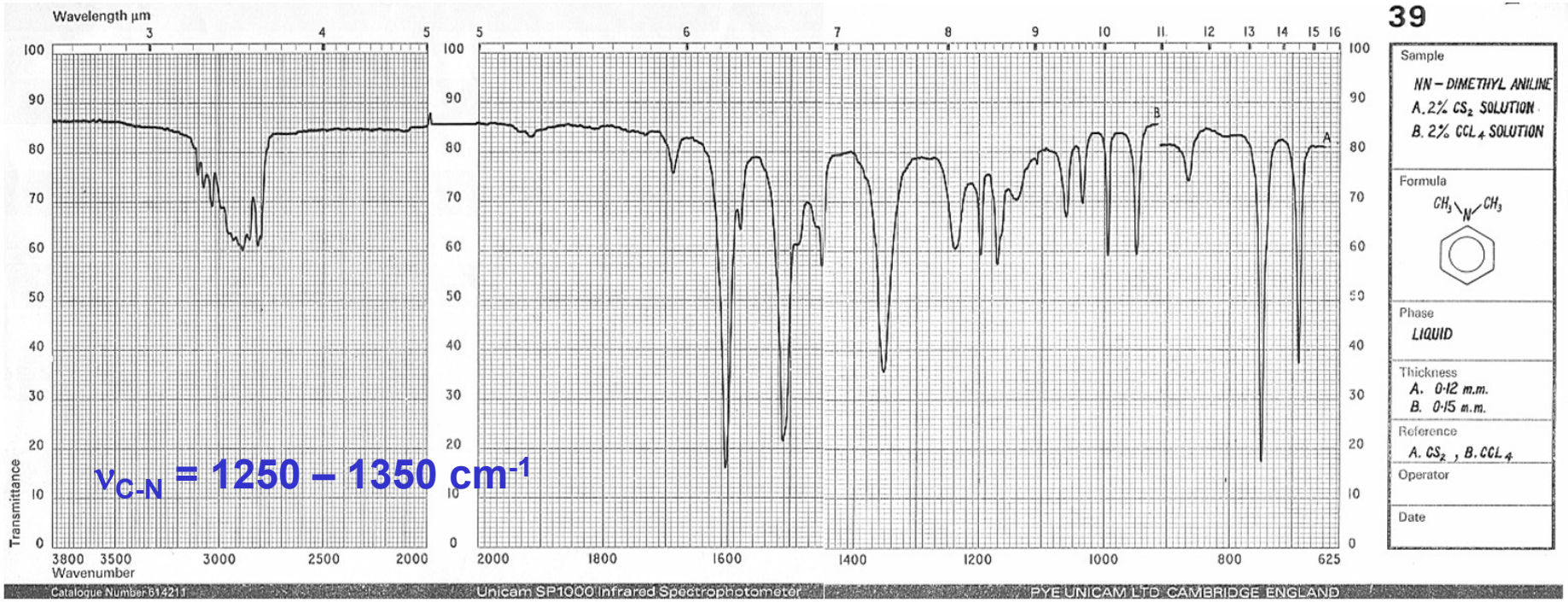
valenční vibrace **N-H** prim. amin. dva pásy v oblasti 3300 – 3500 cm^{-1}
sek. amin jen jeden pás
terc. amin bez pásu

vibrace **C-N** alifatické aminy 1020 – 1220 cm^{-1}
aromatické 1250 – 1350 cm^{-1}

Aminosloučeniny

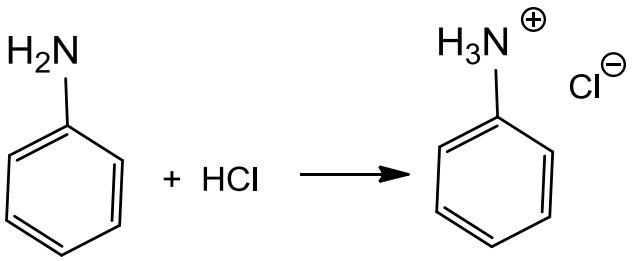


Aminosloučeniny



$\nu_{C\text{-}N}$ = 1250 – 1350 cm^{-1}

Aminosloučeniny



1. **bazické a nukleofilní vlastnosti – reakce s protonem a elektrofily**
2. zvláštní reakce s kyselinou dusitou
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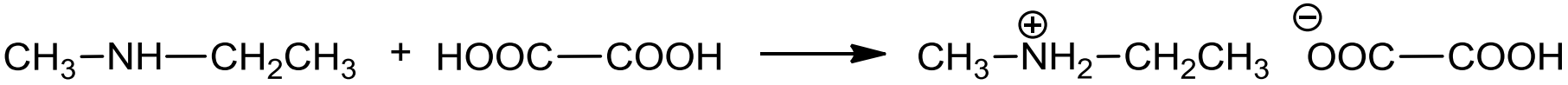
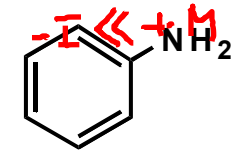
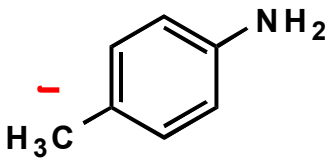
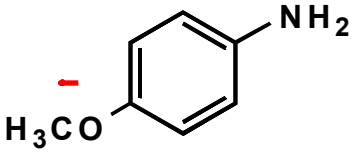
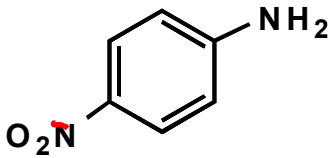
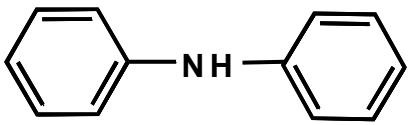
4. vodíkové vazby mezi dusíkem a vodíkem (slabší než u alkoholů)



Aminosloučeniny

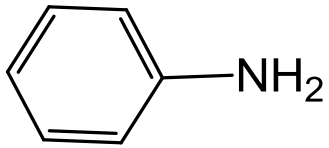
BAZICITA AMINOSLOUČENIN

	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
	8,83
	13,00
	13,15

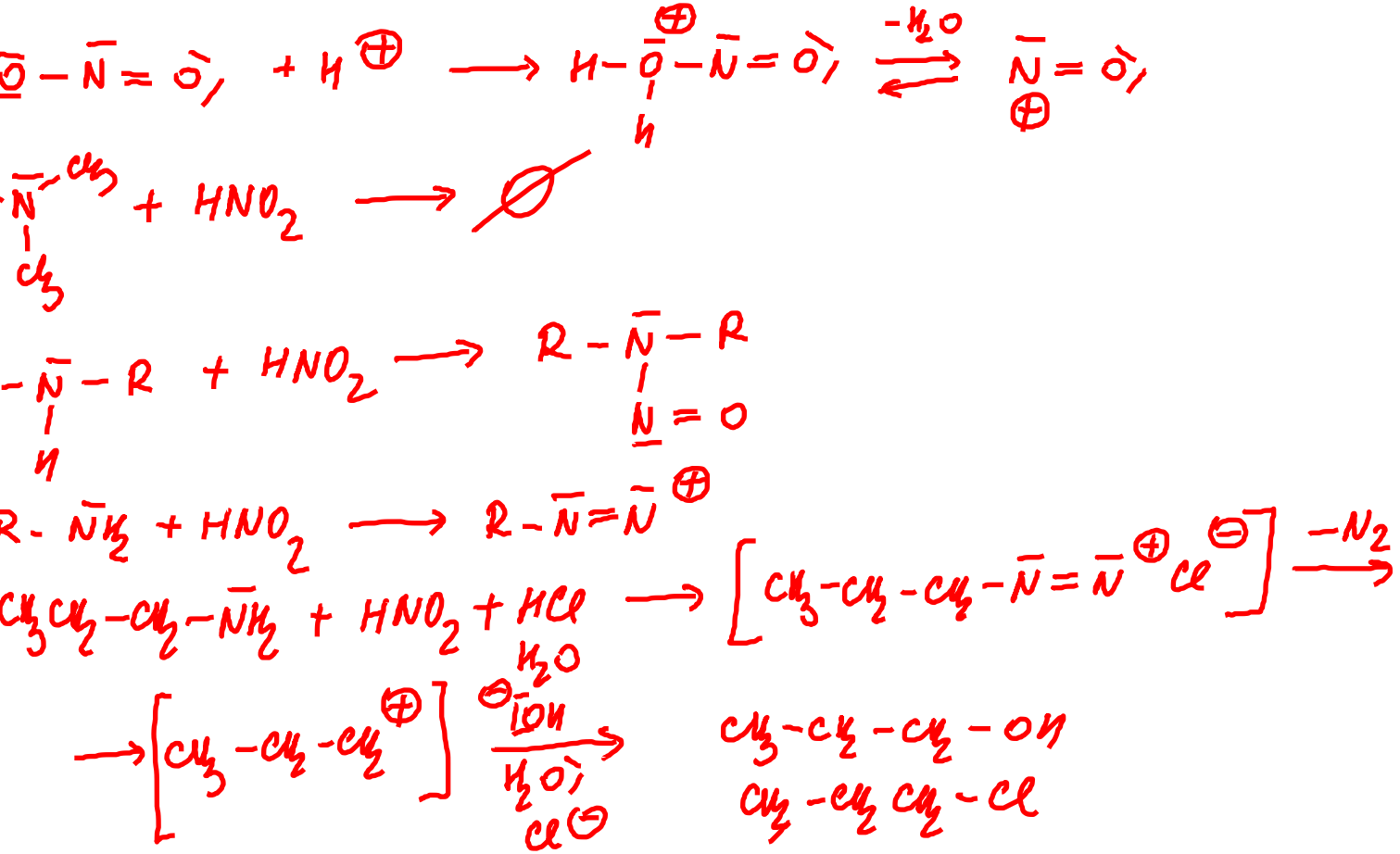
$$R\text{-}NH_2 + H_2O \rightleftharpoons RNH_3^+ + {}^-OH$$

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

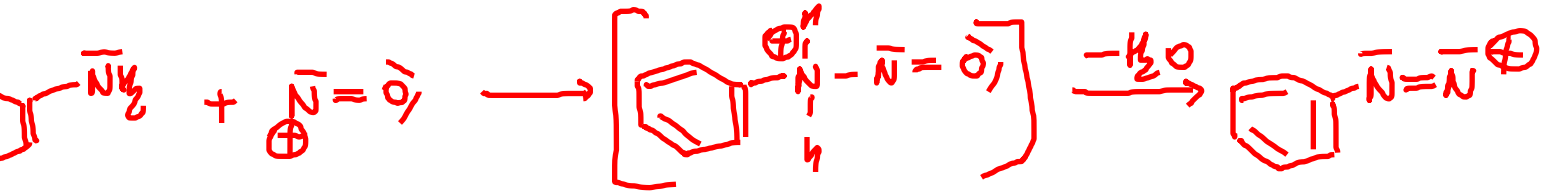
$$pK_b = -\log K_b$$



Aminosloučeniny

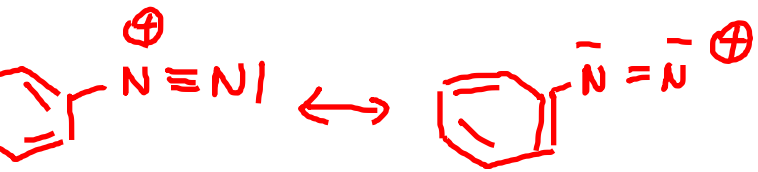


Aminosloučeniny

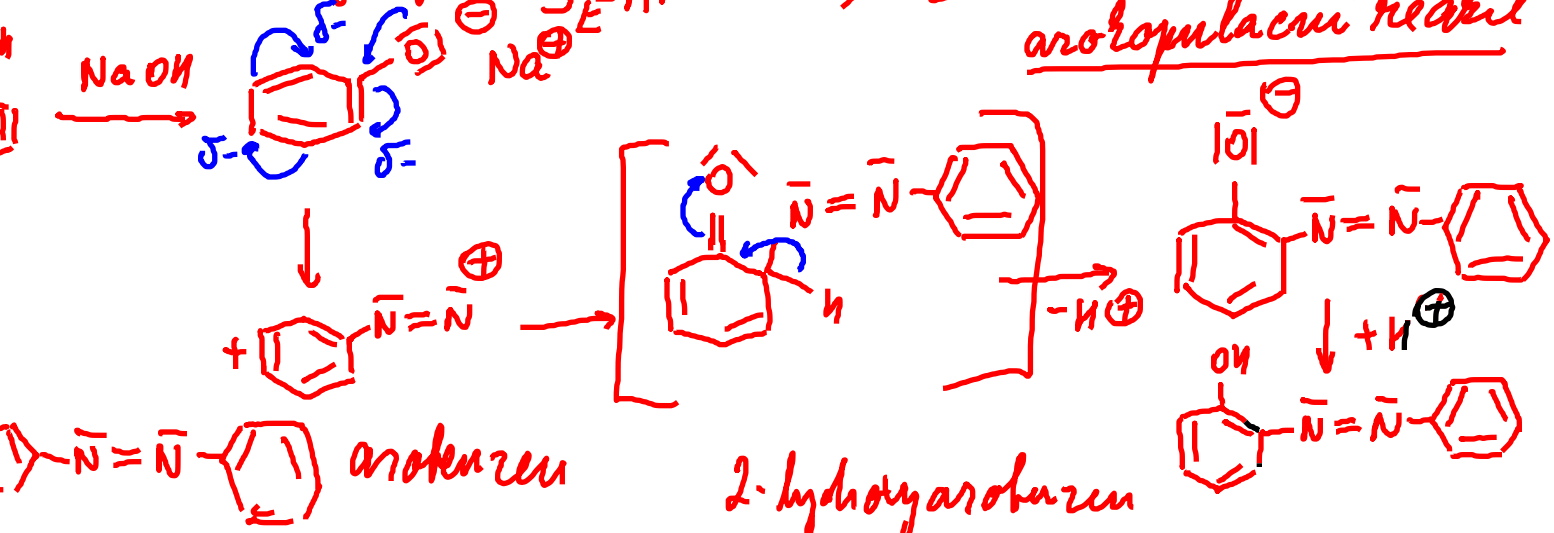


stabilní do 10 °C

na 10 °C se rozkládá



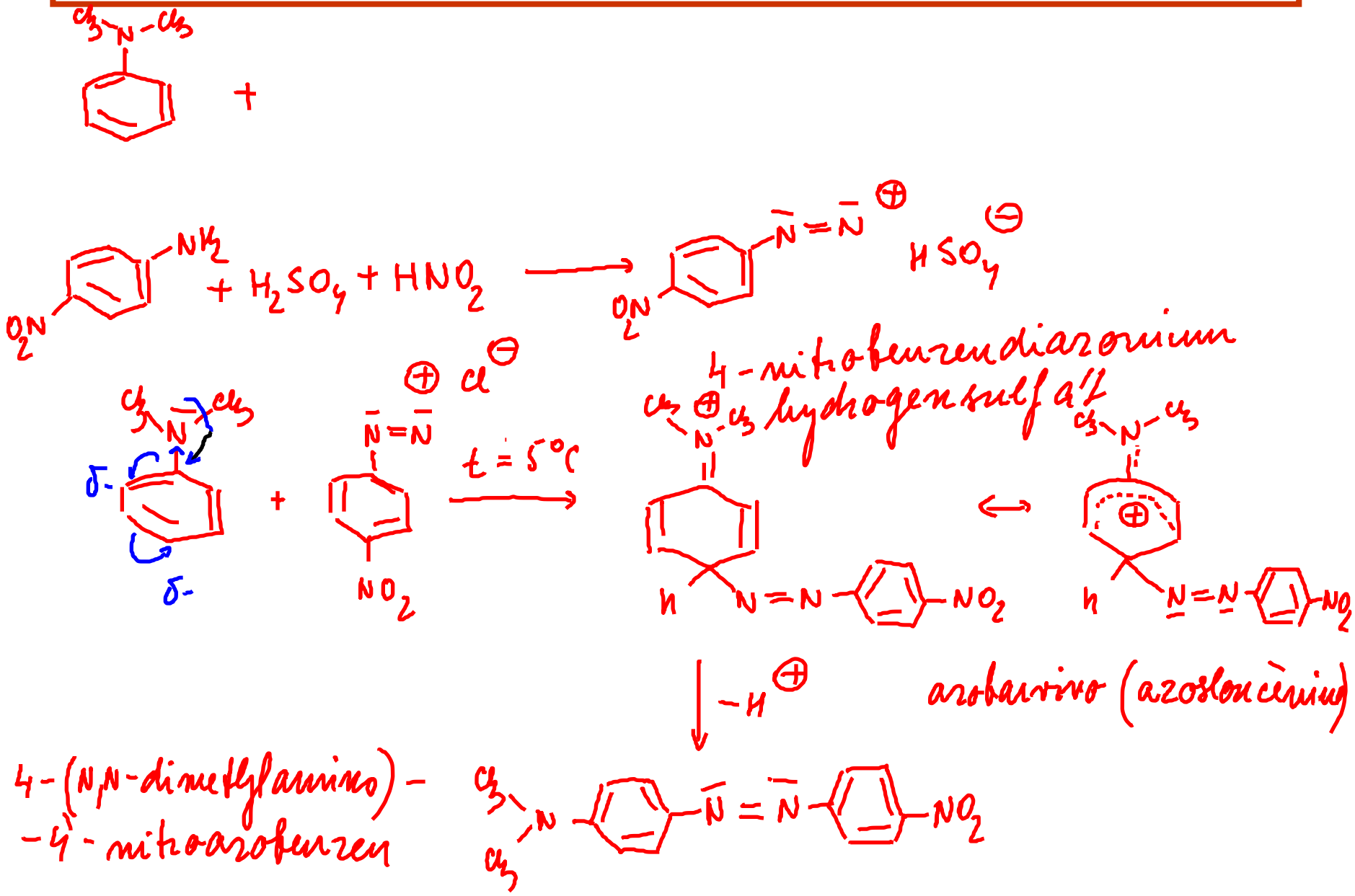
slabé elektrofily s aktivovanými aromáty poskytují S_E-Ar ⟹ azotarvivá azokopulační reakce



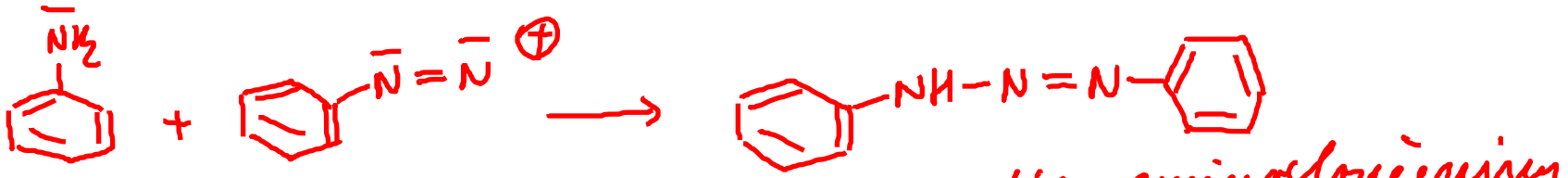
azobenzen

2-hydroxyazobenzen

Aminosloučeniny



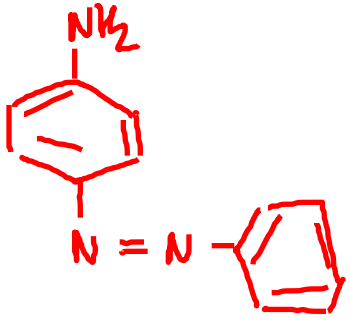
Aminosloučeniny



diazoaminosloučeniny

diazoaminobenzen

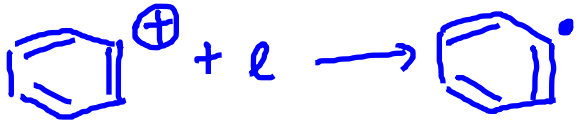
CH_3COOH

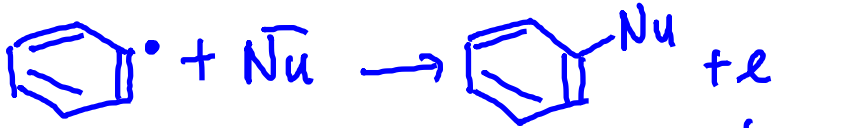


Sandmeyer Cu^+, Cu

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

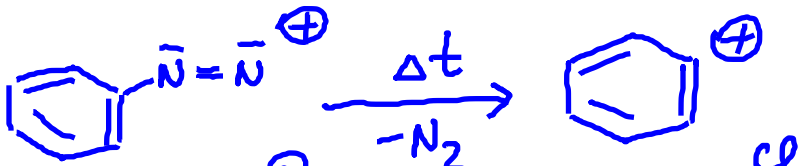
$Cu^+ \rightarrow e^\ominus + Cu^{2+}$





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

navrací k regeneraci

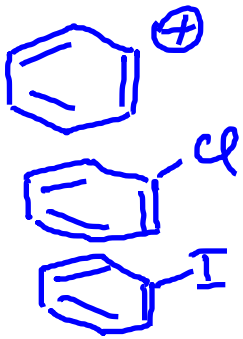


$Cl^\ominus$

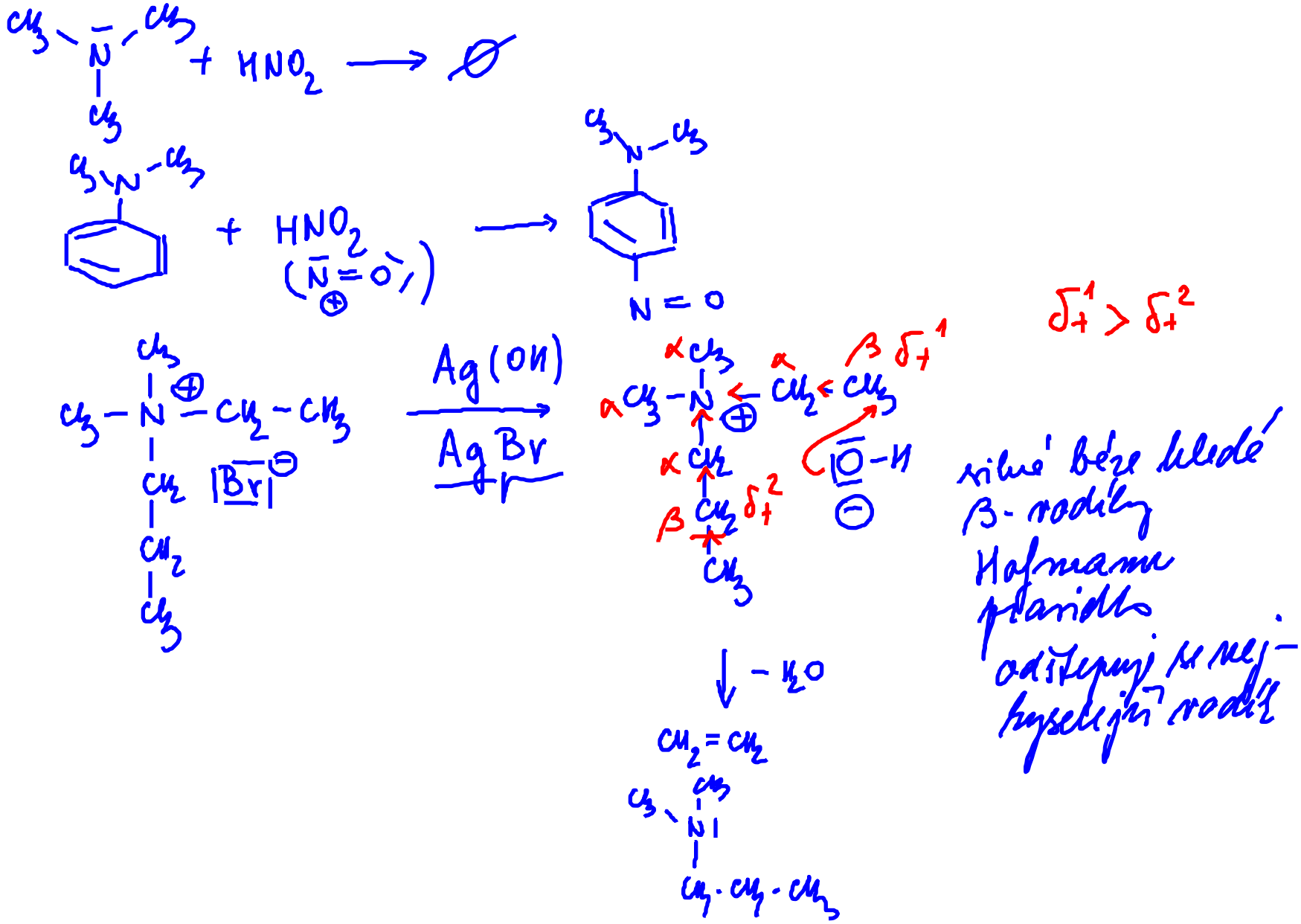
$I^\ominus$

$CN^\ominus$

$HS^\ominus$ $SCN^\ominus$

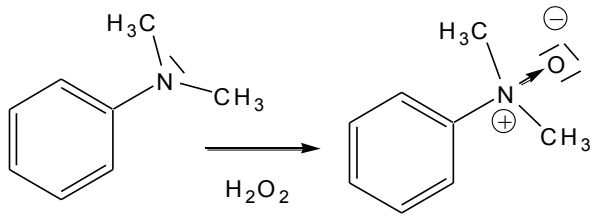


Aminosloučeniny



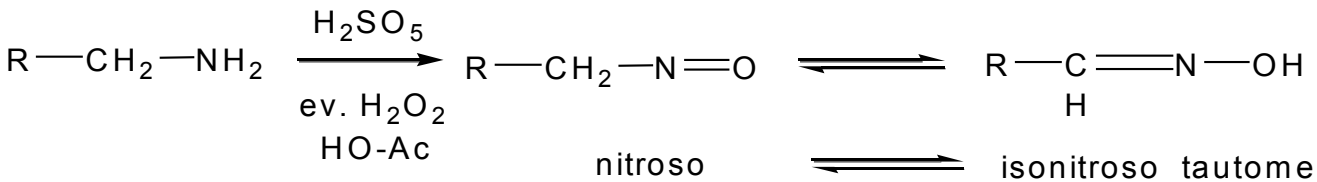
Aminosloučeniny

OXIDACE



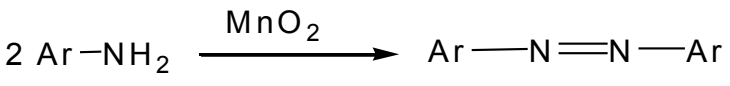
*t*erc -amin aminoxid

primární aminy alifatické + aromatické

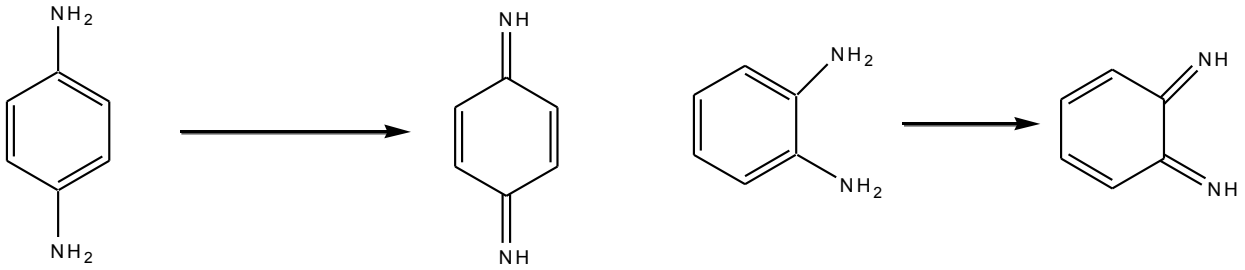


meziproduktem bývá hydroxylamin

primární aminy aromatické



event. $Pb(OCOAc)_4$
O_2
perboritan sodný



diaminy mohou být i substituované, event. jedna NH_2 nahrazena OH

vznikají chinondiiminy

oxidace $K_2Cr_2O_7$, Ag_2O, Ag_2CO_3, $Pb(OCOAc)_4$, HIO_4

Aminosloučeniny

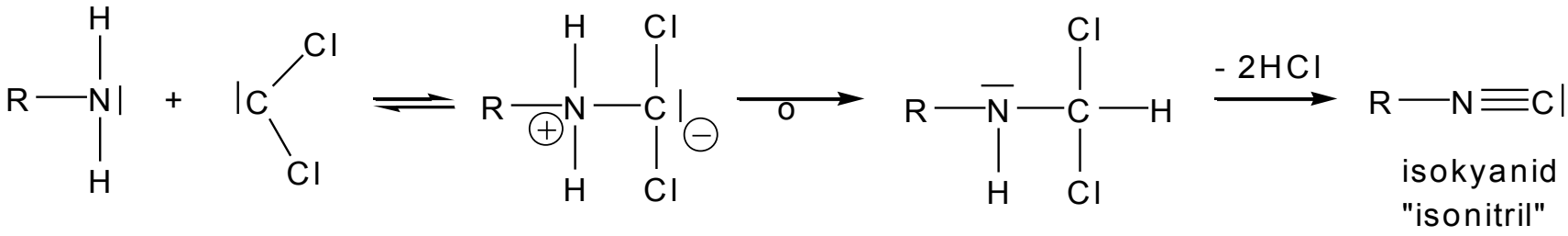
Aminy jako nukleofily

Aminosloučeniny

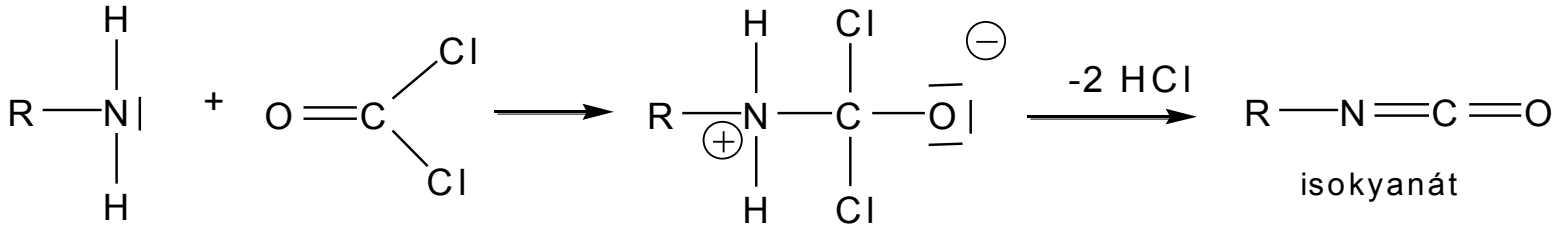
Aminy jako nukleofily

Aminosloučeniny

„isonitrilová zkouška“

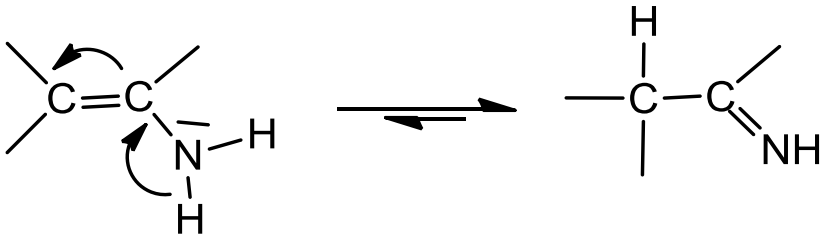


důkaz primární aminové skupiny a to i v biologickém materiálu



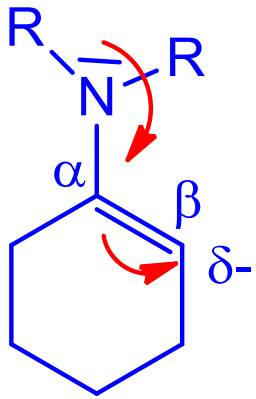
Aminosloučeniny

ENAMINY



enamin imin

tautomerie



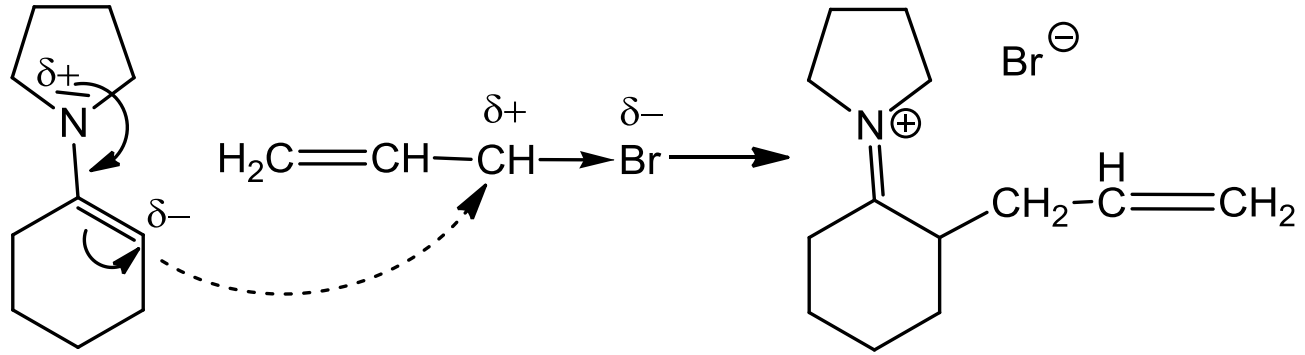
terciární aminy nemohou tautomerizovat

využití v syntéze: využívají se jako vhodné intermediáty pro reakce s elektrofily

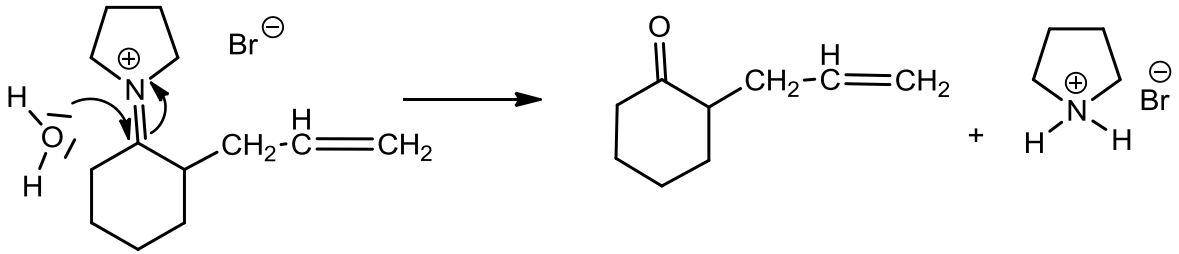
nukleofilní charakter má β-uhlík (ne dusíkový atom)

Aminosloučeniny

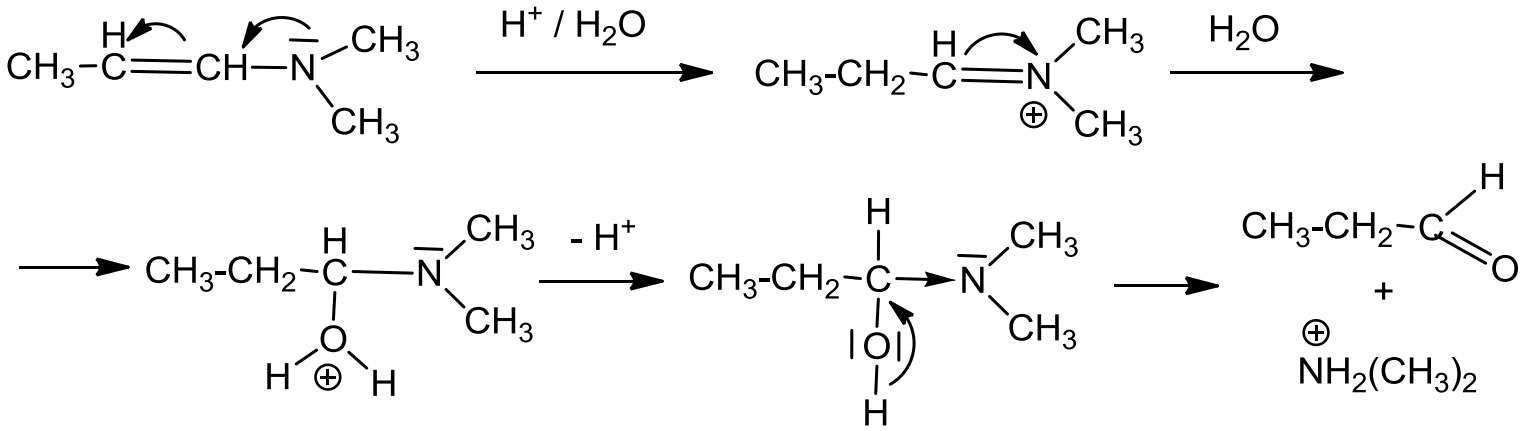
S_N



iminiové soli snadno hydrolyzují



Ad_E

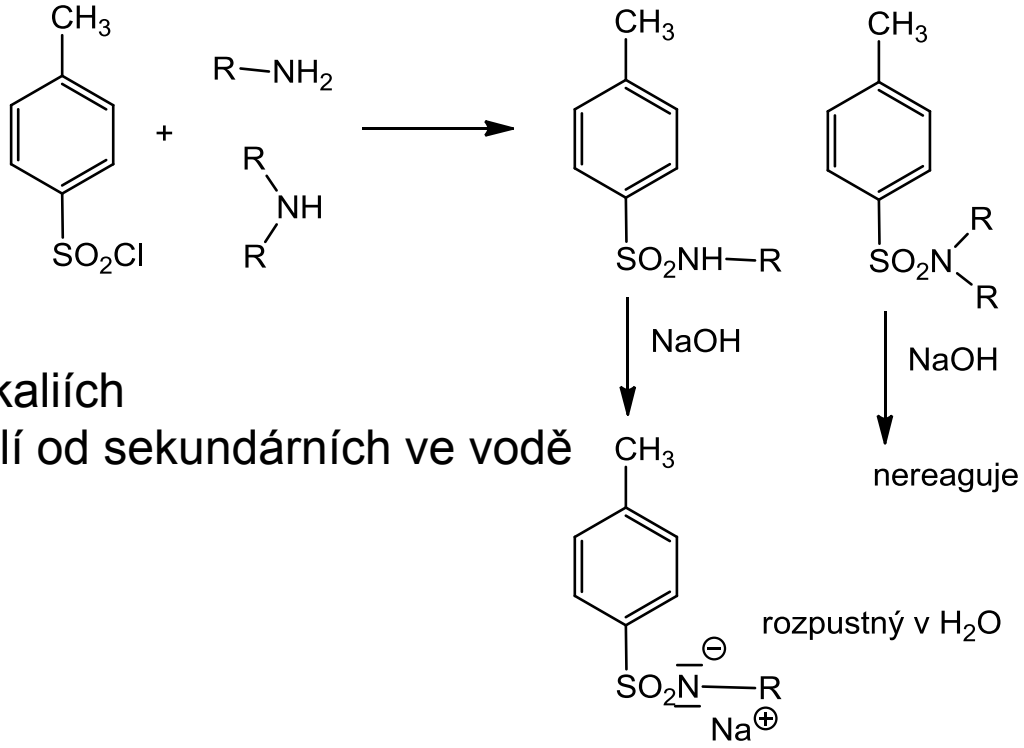


Aminosloučeniny

PŘÍPRAVA

1. **Alkylace amoniaku** reakcí amoniaku s alkylhalogenidy vzniká směs primárních, sekundárních a terciárních halogenderivátů a ty je třeba rozdělit:

Hinsbergova metoda dělení:
prim. a sek. reagují
s p-toluensulfochloridem

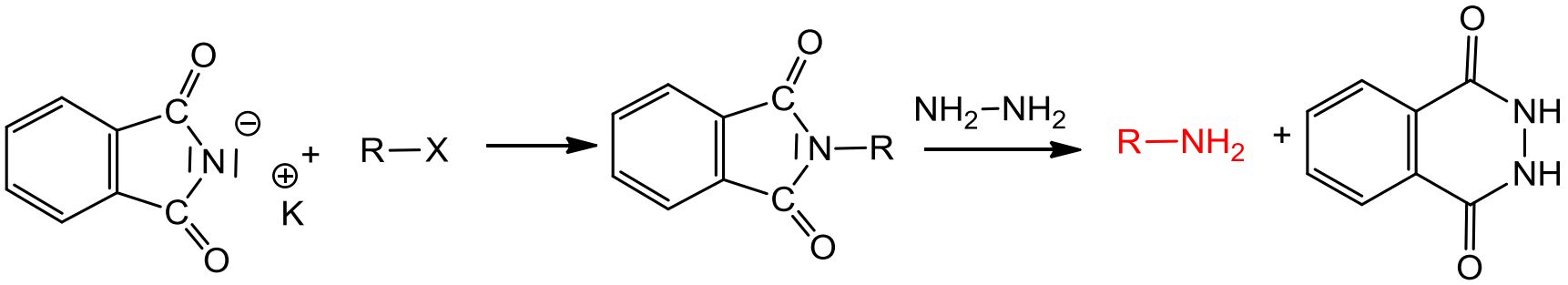


(terc. nereagují) a oddělí se

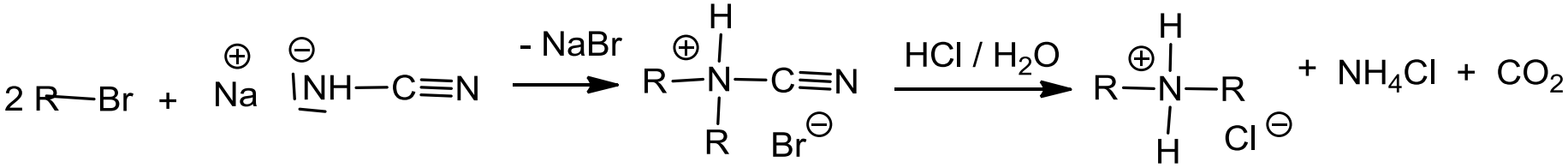
primární jsou rozpustné v alkaliích
- rozpustí se ve vodě a oddělí od sekundárních ve vodě nerozpustných

Aminosloučeniny

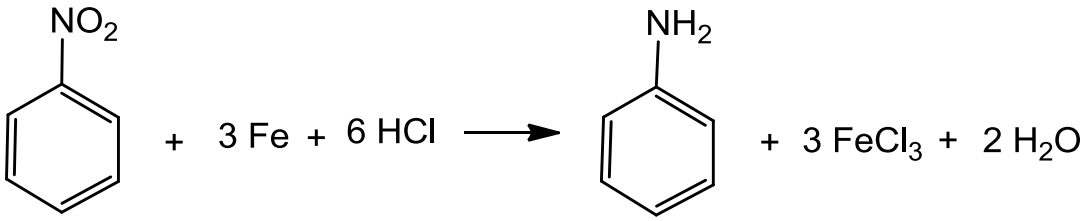
2. Gabrielova metoda



3. Alkylací kyanamidu **(sek aminy)**



4. Redukce nitrolátek (zejména aromatických)

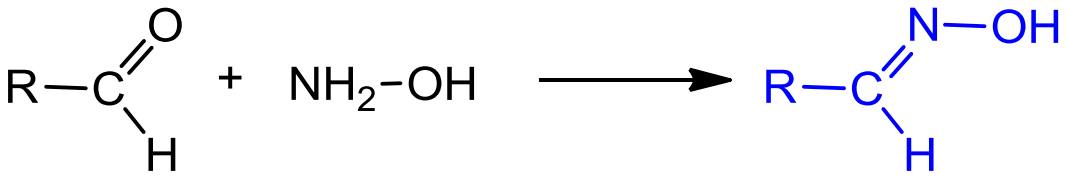


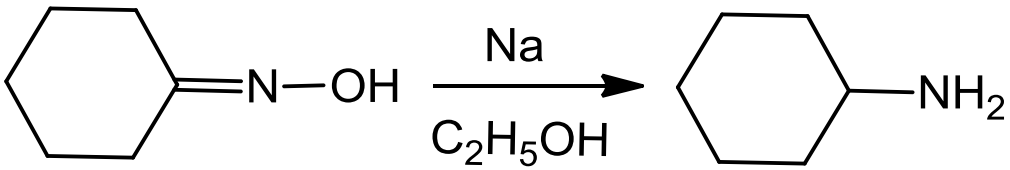
redukční činidla:

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

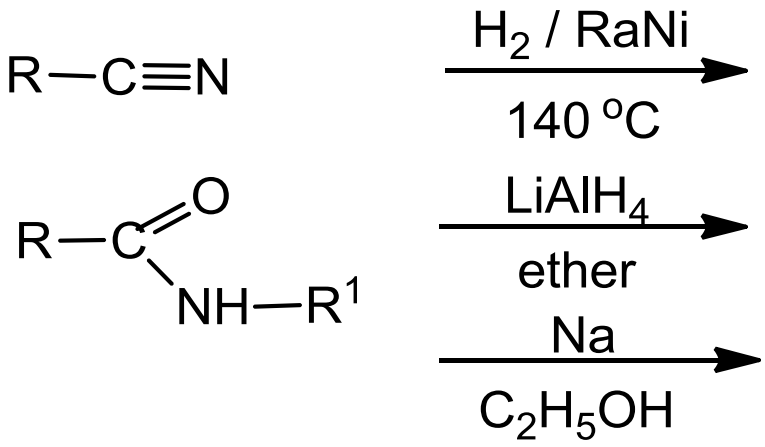
Aminosloučeniny

5. Redukce oximů





6. Redukce nitrilů a amidů



Aminosloučeniny

7. Hofmannovo odbourání amidů