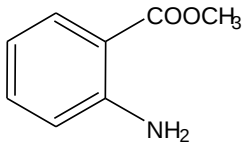
8. Előadás

Nitrogéntartalmú vegyületek

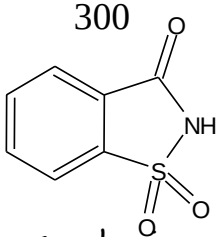
26. NITROGÉNTARTALMÚ VEGYÜLETEK

„Népszerű" származékok

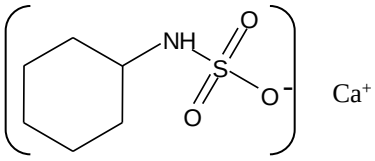


metil-antranilát
(szőlő)

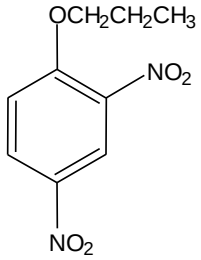
300



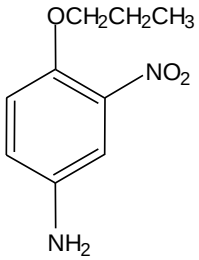
szacharin
(1977)



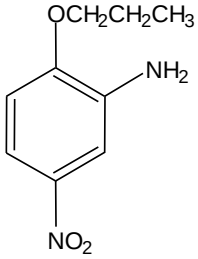
kalcium-ciklamát
(1970: rák)



keserű

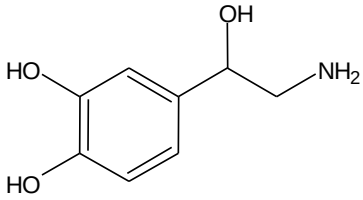


ízteln

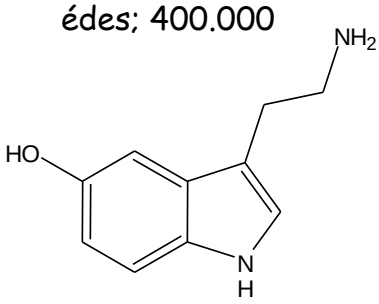


édes; 400.000

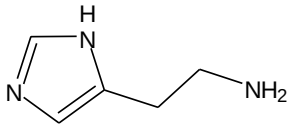
glükóz: 74



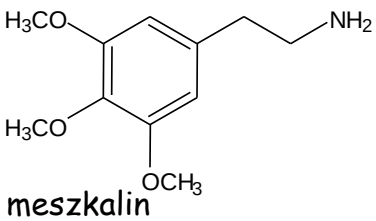
noradrenalin
-NH-CH_3: adrenalin



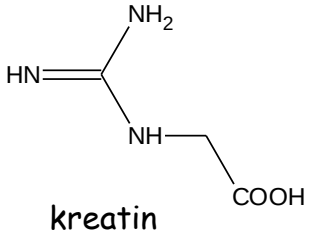
szerotonin



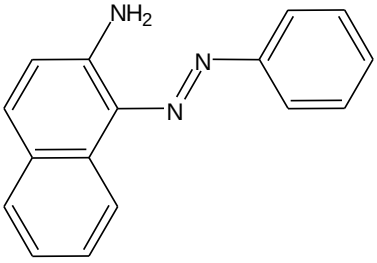
hisztamin



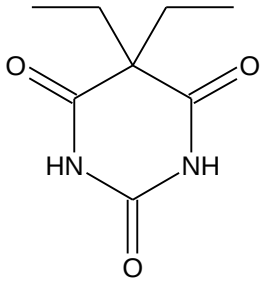
meszkalin



kreatin

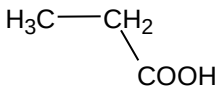


1-fenildiazenil-2-naftilamin
(ételszinezék)

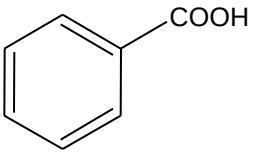


veronál

Tartósítószerek



propánsav



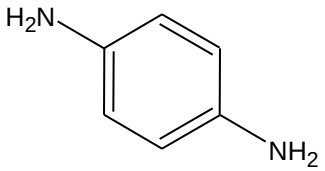
benzoesav

$NaNO_2$

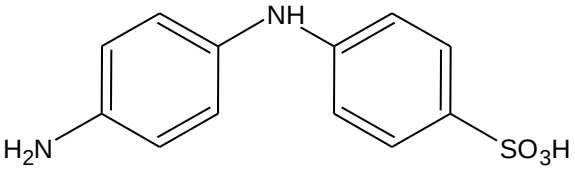
$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$ (gyomor)

H-O-N-O + RR'NH $\longrightarrow$ RR'N-N=O + H_2O

Hajfestőszerek



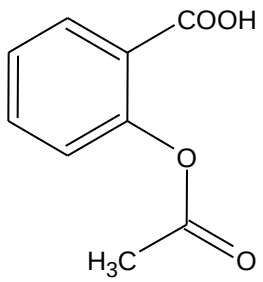
para-feniléndiamin
(fekete)



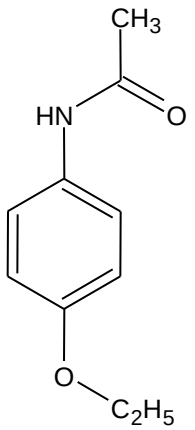
para-amino-difenilamin-szulfonsav
(„fehér", szőke)

Lázcsillapítók

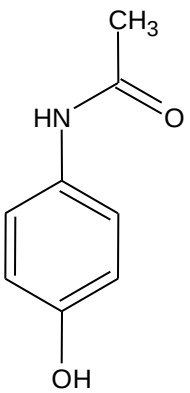
acetil-szalicilsav
(aszpirin)



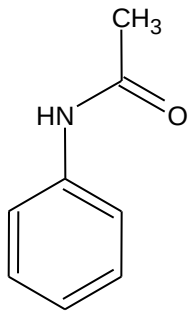
fenacetin



acetamidofén

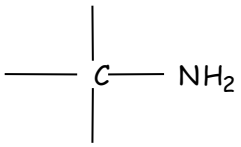


acetanilid

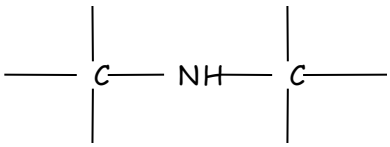


Áttekintés

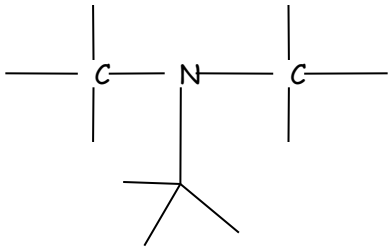
Vegyületek egy N atommal



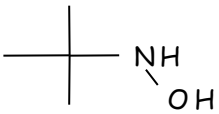
primer amin



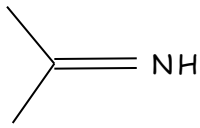
szekunder amin



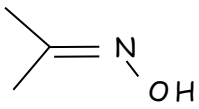
tercier amin



hidroxilamin

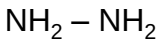


imin

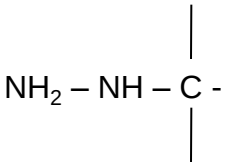


oxim

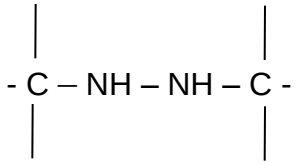
Vegyületek két N atommal



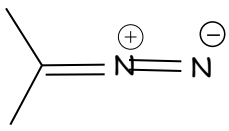
hidrazin



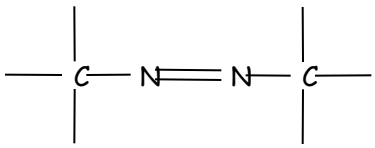
alkil - hidrazin



N,N'-dialkil hidrazin

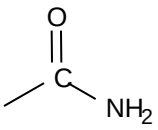


diazovegyületek

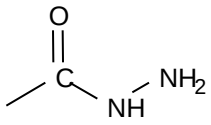


azovegyületek

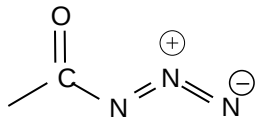
Karbonsav-származékok



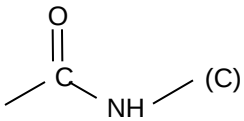
karbonsavamid
(primer)



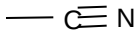
karbonsavhidrazid



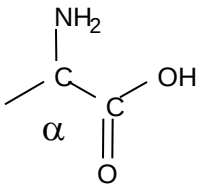
karbonsavazid



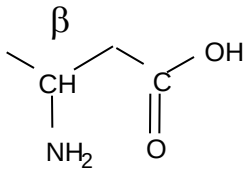
karbonsavamid
(szekunder)



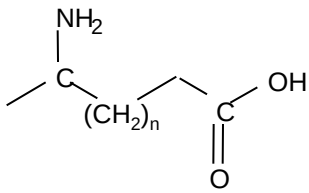
karbonsavnitril



α-amino(karbon)sav

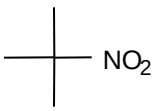


β-amino(karbon)sav

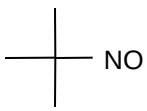


ω-amino(karbon)sav

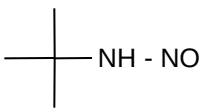
Nitro- és nitrozó vegyületek



nitrovegyületek



nitrozovegyületek



N - nitrozovegyületek

Nomenklatúra, példák

A. AMINOK

telített, telítetlen

gyűrűs, egyenes láncú

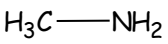
csoportok száma: egy, két... értékű

Ammónia/ammonium ion: NH_3 $\oplus NH_4$

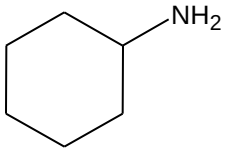
(primer, szekunder, tercier amin) (kvaterner amin)

Alkil-amin:

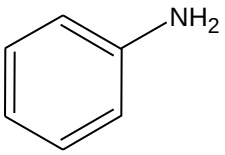
CSOPORTNÉV: amino



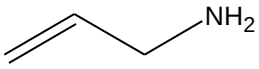
metil-amin



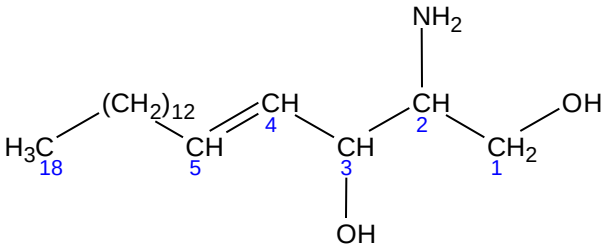
ciklohexil-amin



anilin* (aminobenzol)

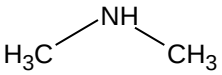


allil-amin

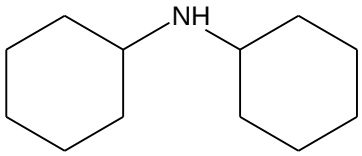


2-amino-4-oktadecén-1,3-diol

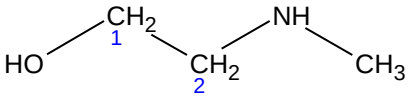
CSOPORTNÉV: alkilamino



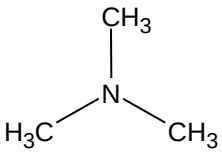
N,N-dimetil-amin



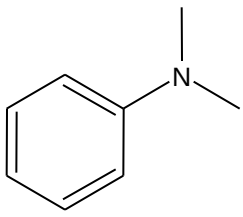
N,N-diciklohexil-amin



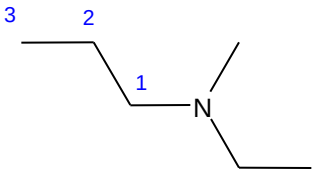
2-metilamino-1-etanol



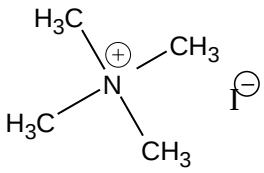
N,N,N-trimetil-amin



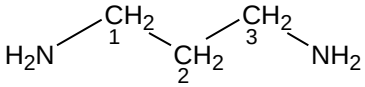
N,N-dimetil anilin



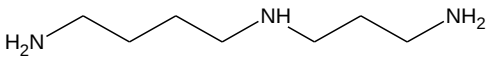
N-metil-N-etil-propilamin



tetrametil-ammónium-jodid

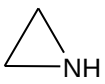


1,3-propán diamin
(trimetiléndiamin)

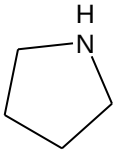


N-propilamino-N-butilamin
(spermidin*)

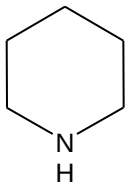
Ciklusos aminok



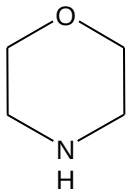
etilénimin



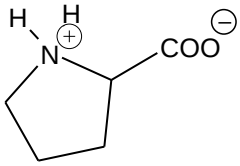
pirrolidin



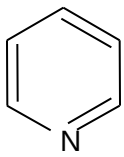
piperidin



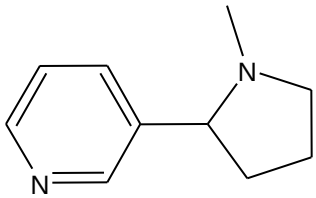
morfolin*



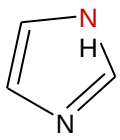
prolin



piridin



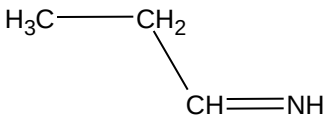
nikotin *



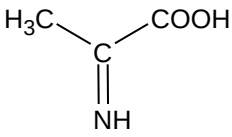
imidazol

B. IMINEK

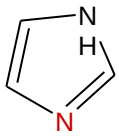
CSOPORTNÉV: imino, alkilimino



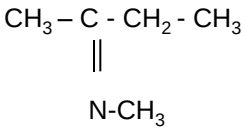
propán-1-imin



α-imino-propánsav



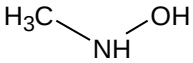
imidazol



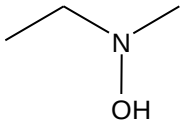
N-metilbután-2-imin
(Schiff-bázis)

C. HIDROXILAMINOK

CSOPORTNÉV: hidroxiamino

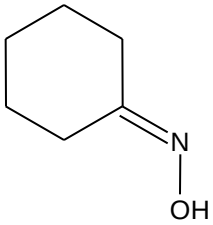


N-metil-hidroxilamin



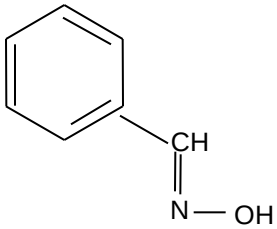
N-etil-N-metil-hidroxilamin

D. OXIMOK



ciklohexanon-oxim

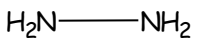
(ketoxim)



benzaldehid-oxim

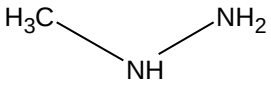
(aldoxim)

E. HIDRAZINOK

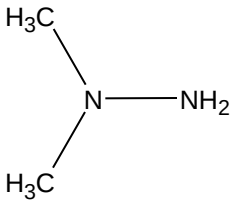


hidrazin

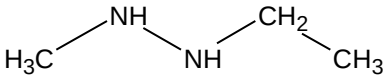
CSOPORTNÉV: hidrazino



metil-hidrazin

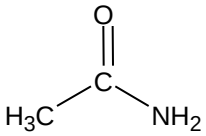


N,N-dimetil-hidrazin

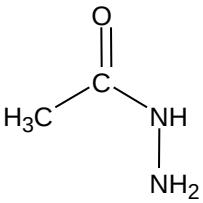


N-etil-N'-metil-hidrazin

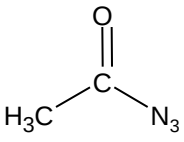
F. KARBONSAVSZÁRMAZÉK



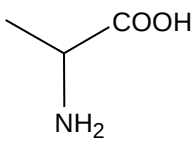
ecetsavamid



ecetsavhidrazid



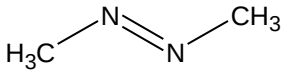
ecetsavazid



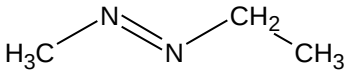
α-amino propánsav,
alanin*

G. AZO- ÉS DIAZOVEGYÜLETEK (pl. azo-alkánok)

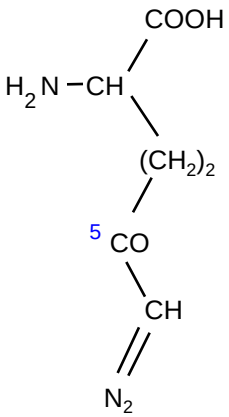
CSOPORTNÉV: alkilazo



azometán



metilazo-etán



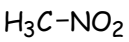
CH_2N_2
diazometán

N_2-CH-COOH
diazoecetsav

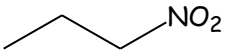
6-diazo-5-oxo-norleucin
(DON)

H. NITRO- ÉS NITROZOVEGYÜLETEK

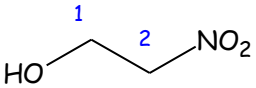
CSOPORTNÉV: nitro, nitrozo



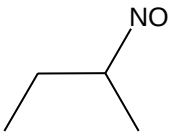
nitro-metán



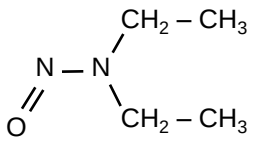
1-nitro-propán



2-nitro-1-etanol



2-nitrozo-bután

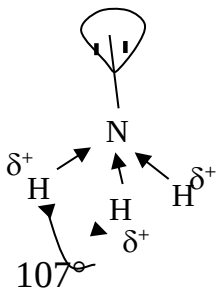


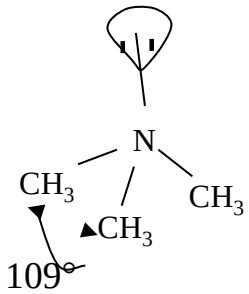
N - nitrozo – N',N' - dietilamin
(whisky)

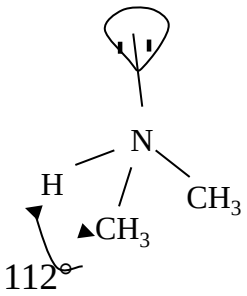
Kémiai szerkezet

A. AMINOK (HIDRAZINOK)

N^7: $1s^2$, $2s^2$, $2p_x^1$, p_y^1, p_z^1 EN:3,0 $N(sp^3)$







- 3 kötő sp^3 pálya
- 1 nemkötő sp^3 pálya
- nemkötő > kötő (térigény)
- piramisos térszerkezet

⇩

ha a három szubsztituens különböző, az amin királis

nagy csoportoknál

μ=1,44 D μ=0,61 D

Kiralitás: tercier amin (I), kvaterner amin (II)

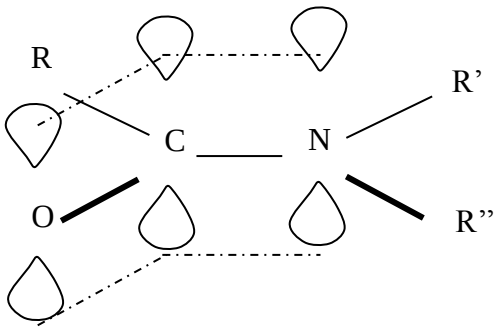
(I)

gyors racemizáció

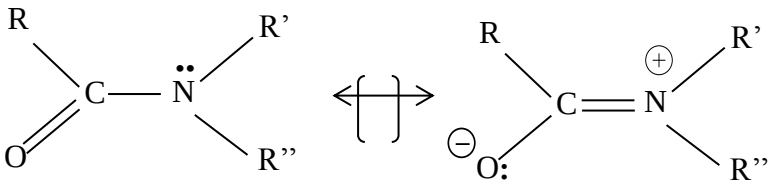
(II)

rezolválható

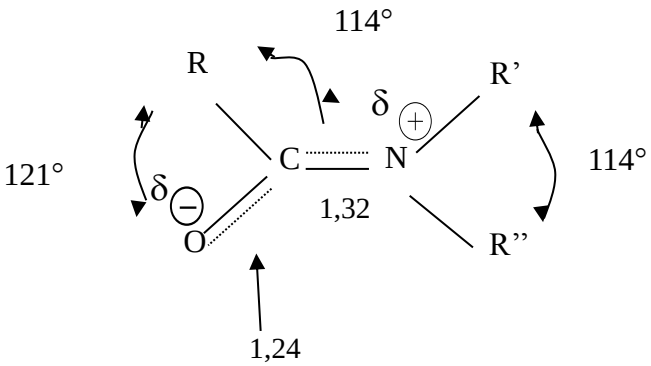
B. KARBONSAVAMIDOK C(sp²), O(sp²), N(sp²)



- 3 kötő sp² pálya
- 1 nemkötő p pálya
- planáris konfiguráció



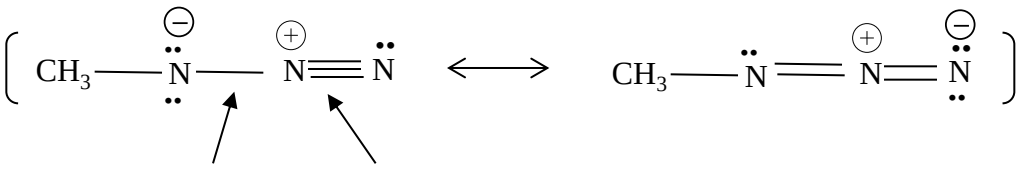
határszerkezetek



gátolt rotáció
cisz-transz izoméria

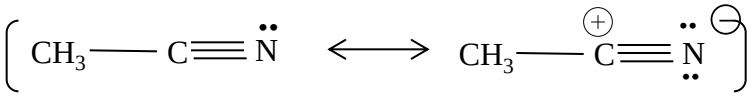
B. KARBONSAVAZIDOK C(sp³), N(sp)

metilazid



126 pm 112 pm

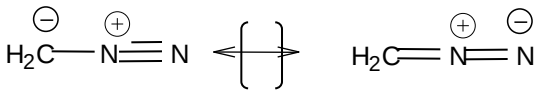
C. KARBONSAVNITRILEK C(sp), N(sp)



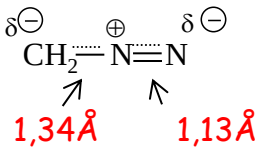
acetonitril

C. DIAZOVEGYÜLETEK C(sp²), N(sp)

Példa: CH_2N_2, diazometán, fp.: - 23°C, sárga gáz

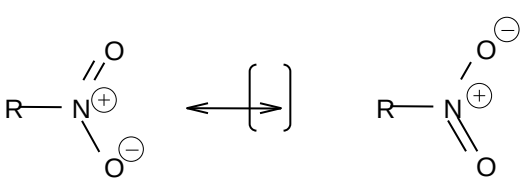


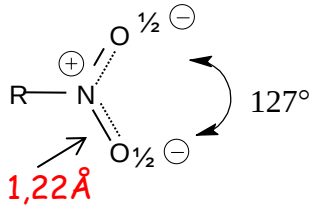
C-N	1,47Å
N=N	1,24Å
C=N	1,34Å
N≡N	1,09Å



lineáris konfiguráció konjugált rendszer

D. NITROVEGYÜLETEK C(sp³), O(sp²), N(sp²)

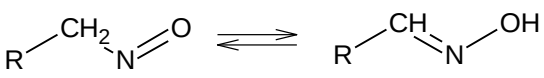


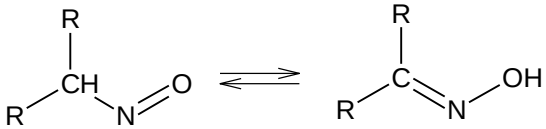


planáris konfiguráció szimmetrikus konjugált rendszer

r(N-O) 1,36Å > r(N═O) 1,22Å > r(N=O) 1,15Å

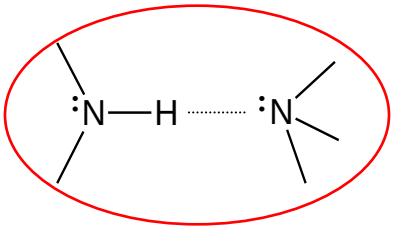
E. NITROZOVEGYÜLETEK C(sp³)/C(sp²), O(sp²), N(sp²)





nitrozo – oxim tautomeria

Fizikai sajátságok



A. AMINOK H-híd: donor és akceptor

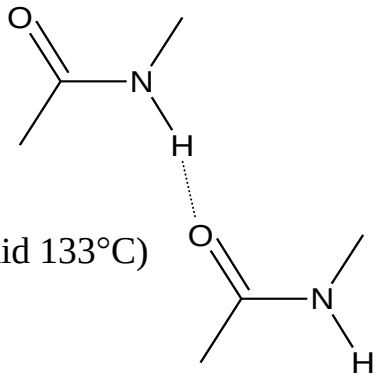
1. Oldékonyság: vízben jobb, mint az alkoholok

oldószerek: dietil-amin, trietil-amin (89,5°C), piperidin (106°C), morfolin (129°C)

2. Forráspont

	Mt	Fp
CH_3-CH_2-CH_2-CH_2-NH_2	73	78°C
CH_3-CH_2-CH_2-CH_2-CH_3	72	36°C
CH_3-CH_2-NH-CH_2-CH_3	73	55,5°C
CH_3-CH_2-N$(CH_3)_2$-CH_2-CH_3	73	37,5°C
CH_3-CH_2-$CH(CH_3)$-CH_3	72	28°C

B. KARBONSAVAMIDOK H-híd: donor és akceptor



1. Halmazállapot: kis mt amidok kristályosak

(pl. acetamid op.: 81°C, karbamid 133°C)

2. Oldékonyság: magas

3. Térszerkezet stabilizálása: α-hélix, β-réteg, β-kanyar

C. NITROVEGYÜLETEK dipólus-dipólus

1. Forráspont: magas

	Mt	Fp
CH_3NO_2	61	101°C
CH_3COCH_3	58	56°C

2. Oldékonyság: vízben rossz

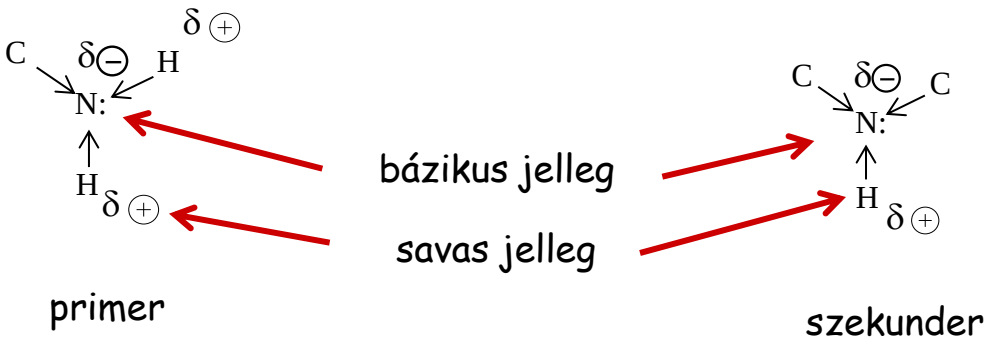
Aminok kémiai reakciói

1. Sav-bázis sajátságok
2. Redukció, oxidáció
3. Elimináció
4. Szubsztitúció (alkilezés, acilezés)
5. Reakció salétromossavval

1. Sav-bázis sajátságok

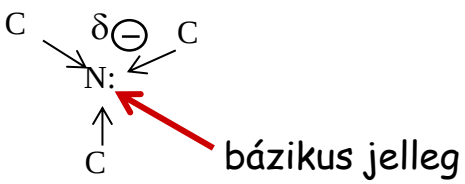
EN(N)=3,0 EN(C)=2,5

$$K_b = \frac{[R\text{-}NH_3^+]\,[OH^-]}{[R\text{-}NH_2]} \qquad pK_b = -\lg K_b$$



primer

szekunder



tercier

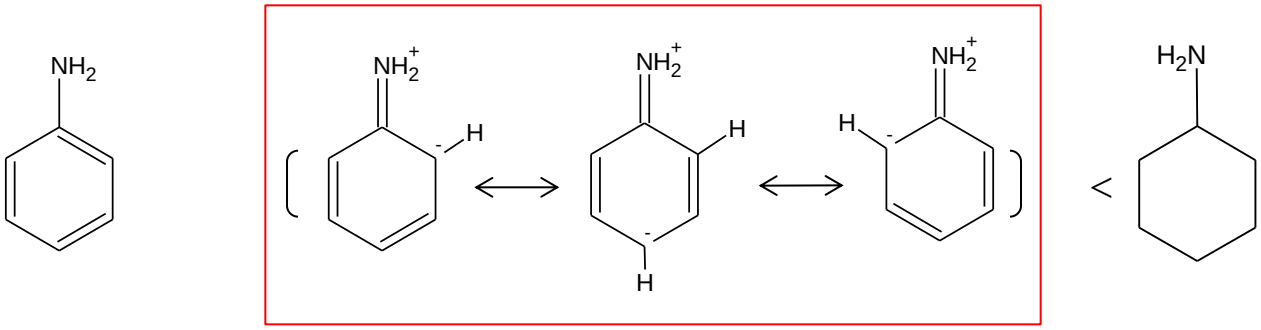
A. Telített aminok

$R\text{-}NH_2$, $RR'\text{-}NH$: igen gyenge savak

$R\text{-}NH_2$, $RR'\text{-}NH$, R_3N: gyenge bázisok

	pK_a	pK_b
NH_3	9,25	4,75
CH_3NH_2	10,64	3,36
$(CH_3)_2NH$	10,75	3,25
$(CH_3)_3N$	9,72	4,28

B. Aromás aminok



anilin

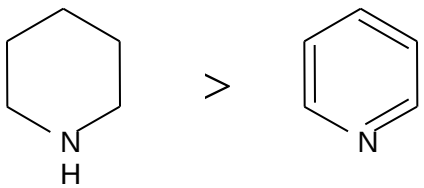
$pK_b = 9,42$

protonált anilin

ciklohexil-amin

$pK_b = 3,35$

C. Heterociklusos aminok



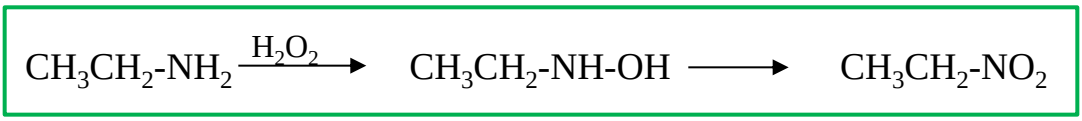
piperidin piridin

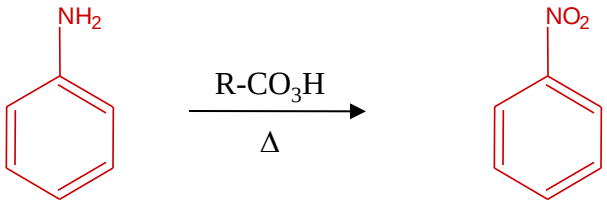
$N(sp^3)$ > $N(sp^2)$

$pK_b = 2,8$ 8,8

2. Oxidáció, redukció

Aminok oxidációja



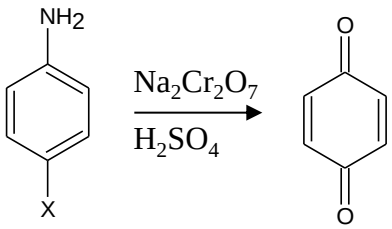


nitrobenzol

$R_3C\text{-}NH_2 \xrightarrow{KMnO_4} R_3C\text{-}NO_2$

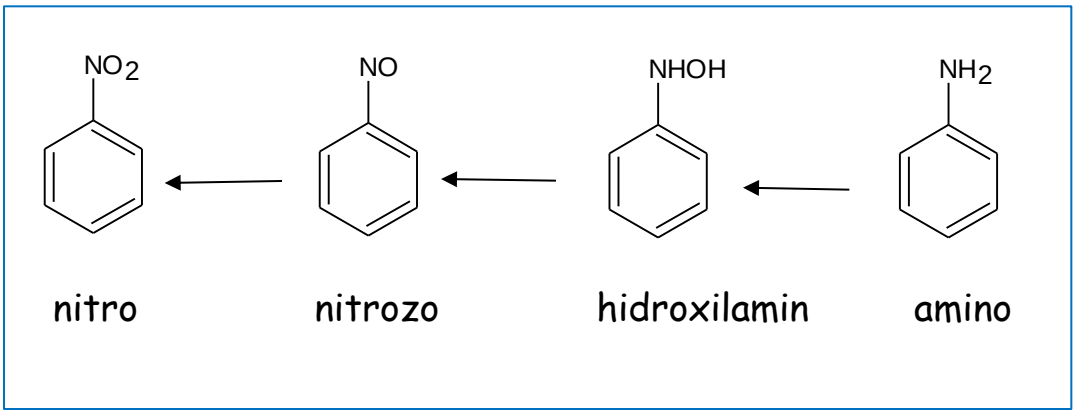
$(CH_3)_2\text{-}NH \xrightarrow[R\text{-}CO_3H]{H_2O_2\ vagy} (CH_3)_2N\text{-}OH$ hidroxilamin

$(CH_3)_3N \xrightarrow[R\text{-}CO_3H]{H_2O_2\ vagy} (CH_3)_3N^+\text{-}O^-$ aminoxid (N-oxid)



X=H, OH, NH_2
(csak para)

Aromás aminovegyületek oxidációja



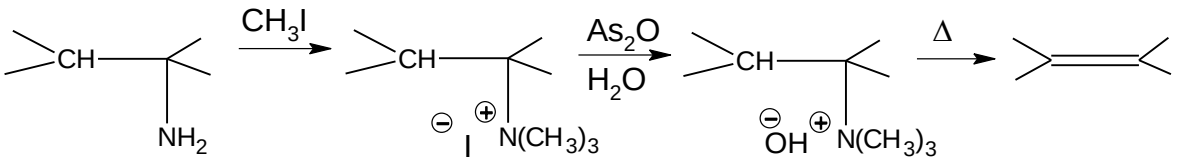
Összehasonlítás: N tartalmú vegyületek redukciója

kiindulási vegyület	Pt	Pd/csontszén	Raney Ni	H_2/kat	termék
R-NO_2				X	R-NH_2 amin
Ar-NO_2		X	X		Ar-NH_2 amin
R-CH=N-OH oxim				X	-CH_2-NH_2 amin
RQC=N-OH				X	
R-CH=N-Q Schiff-bázis				X	-CH_2-NH-Q szek. amin
anilin			X		ciklohexil-amin
pirrol	X				pirrolidin

Lásd még: -CO-NH_2, -CO-NHR, -CO-NR_2, -CN

3. Eliminációk

Hofmann-elimináció - aminok

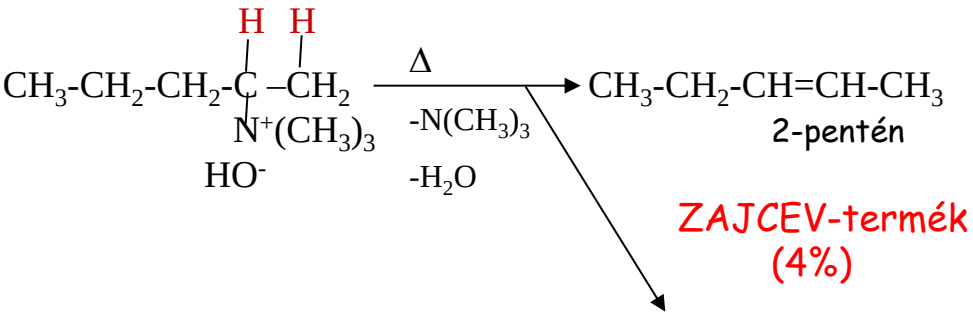


primer amin

olefin

Q-NHR, Q-NRR' ⟶ Me_2RN, MeRR'N + Q olefin

Példa



2-pentil-trimetil-ammónium hidroxid

4. Szubsztitúció

ALKILEZÉS

A. alkil – halogenid (R-X)

B. alkohol

C. oxovegyület (reduktív)

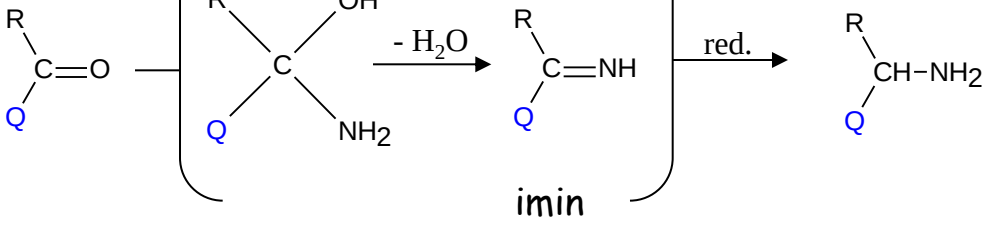
A. $NH_3 + CH_3I \longrightarrow CH_3\overset{+}{N}H_3\bar{I} \xrightarrow{+ NaOH} CH_3\text{-}NH_2 + NaI + H_2O$

$CH_3\text{-}NH_2 + CH_3I \longrightarrow (CH_3)_2\overset{+}{N}H\bar{I}$ .....

keverék

B. $NH_3 + CH_3CH_2OH \xrightarrow[\text{hev.}]{Al_2O_3} CH_3CH_2NH_2 + H_2O$

$CH_3CH_2NH_2 + CH_3CH_2OH \longrightarrow CH_3CH_2\text{-}NH\text{-}CH_2CH_3 + H_2O$ ....

C. $NH_3 +$ 

redukálószer: H_2/kat, HCOOH

analógia: biológiai aminálás

ACILEZÉS karbonsavszármazékok

CH_3-NH_2 + R-CO-Cl ⟶ CH_3-NH-CO-R + HCl

R-CO-O-CO-R R-COOH

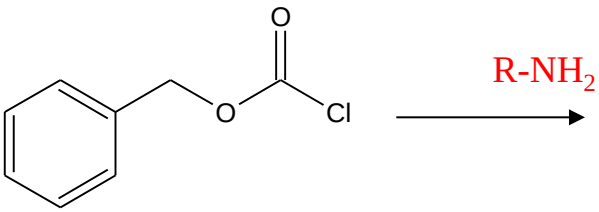
R-CO-OEt acil-amin EtOH

R-CO-N_3 HN_3

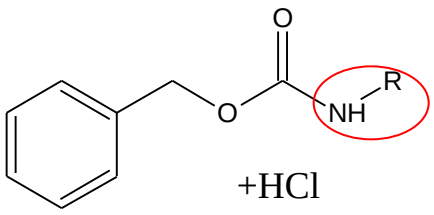
karbonsavszármazék

Példák

a) sav-halogenid



$R\text{-}NH_2$



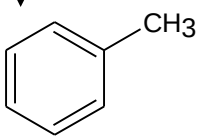
+HCl

benziloxi-karbonil-klorid (Z-Cl)

ZERVAS

benziloxi-karbonil-amin

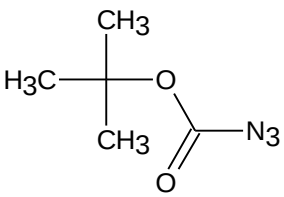
HBr/CH_3COOH



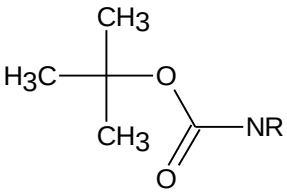
+ CO_2

b) sav -azid

+ $R\text{-}NH_2$



$R\text{-}NH_2$



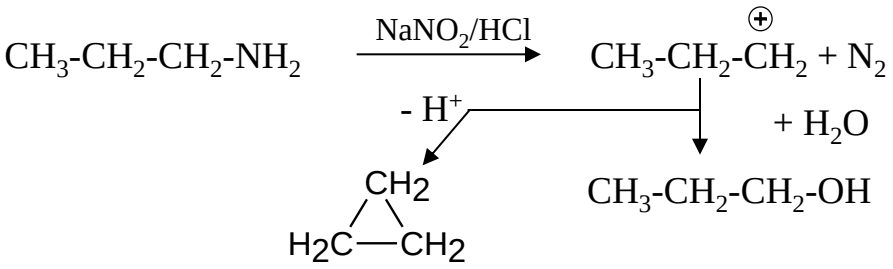
+ HN_3

^{t}butiloxi-karbonil-azid

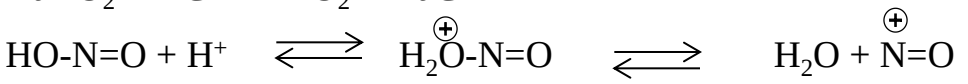
BOC-amin(osav)

5. Reakció salétromossavval

Alkil-amin primer amin: N meghatározás (van Slyke)

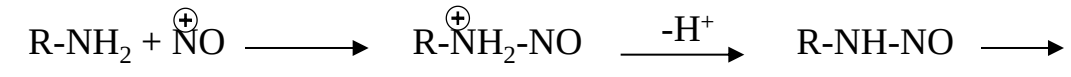


Reagens: $NaNO_2 + HCl = HNO_2 + NaCl$

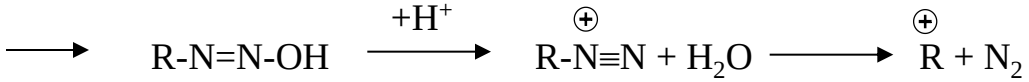


nitrozil kation

Mechanizmus



N-nitrozo-amin



„diazo”-sav

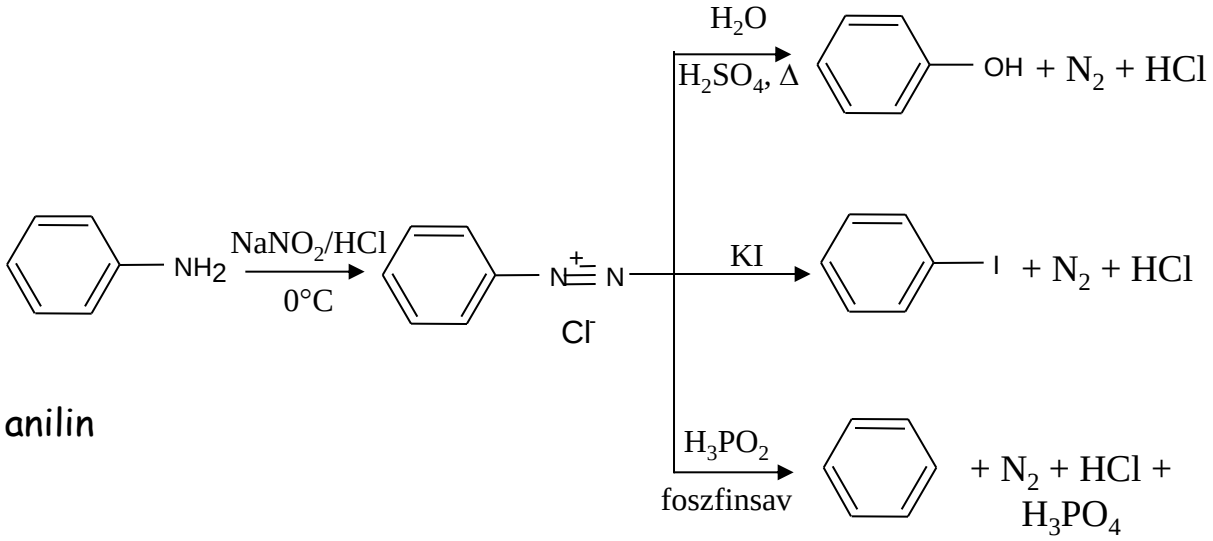
diazónium ion

karbénium ion

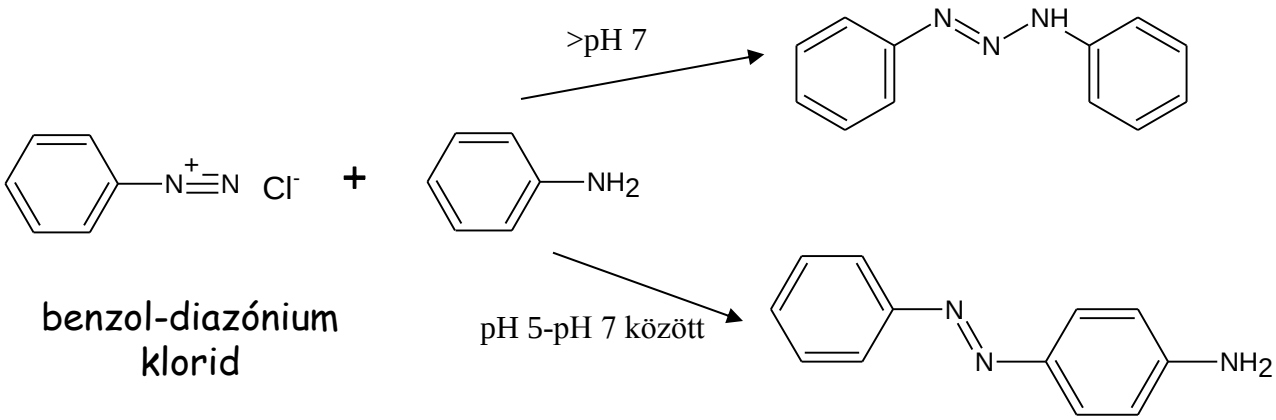
Felhasználás:

primer amin:	N_2
szekunder amin:	sárga olaj vagy csapadék
tercier amin:	nincs N_2, nincs csapadék

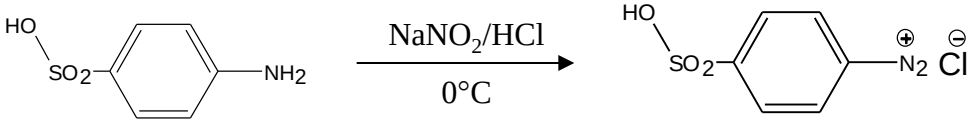
Aromás amin (diazotálás)



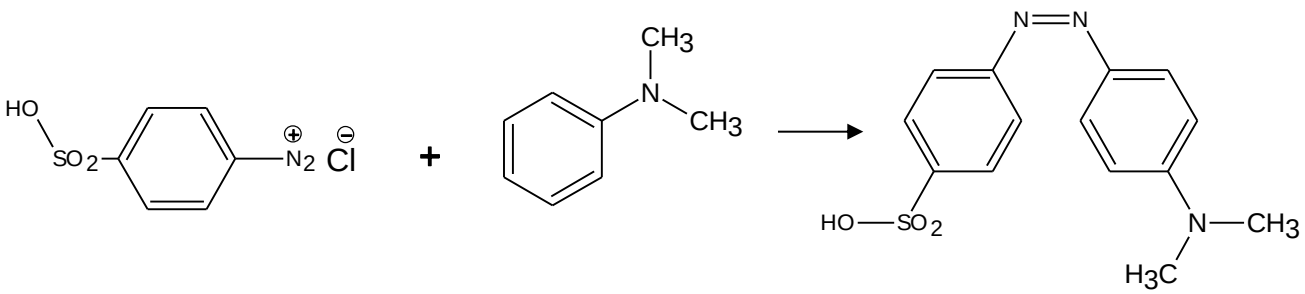
Kapcsolási reakciók



színezékipar



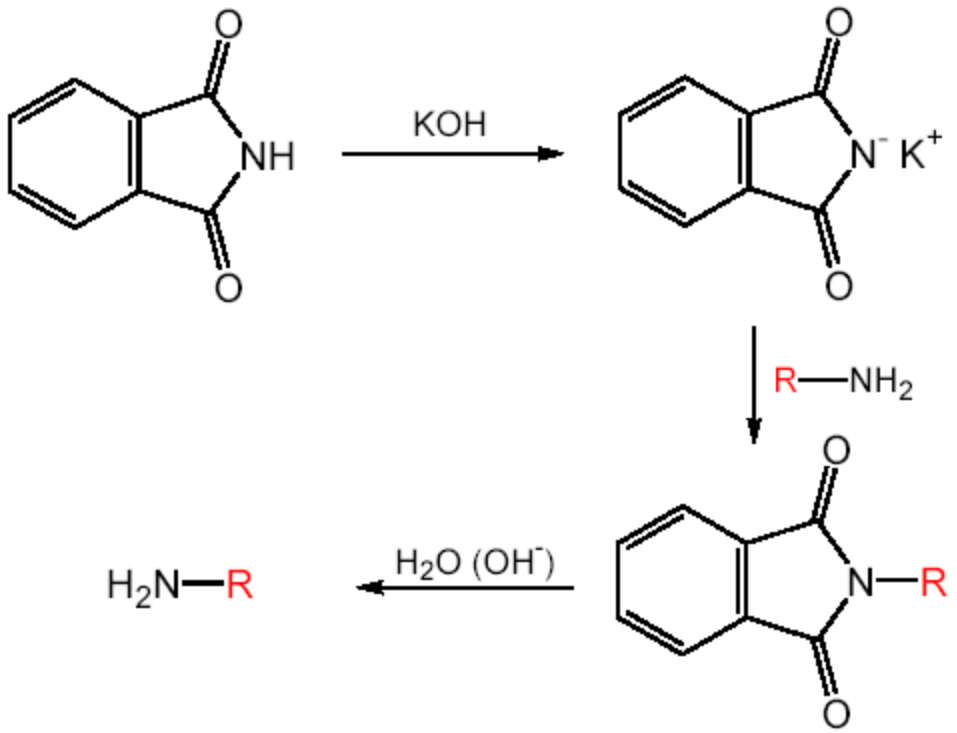
szulfanilsav



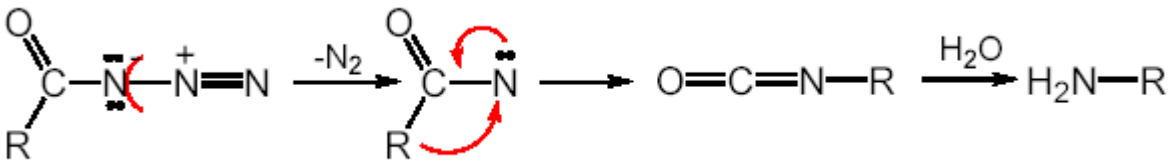
Aminok előállítása

1. Ammónia alkilezése

2. Gabriel szintézis



3. Curtius lebontással karbonsavazidból

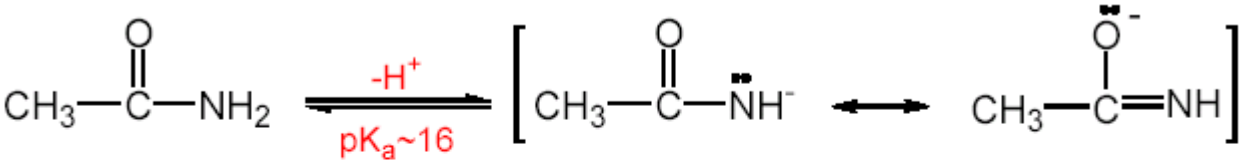


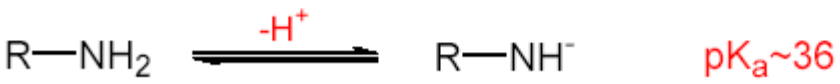
Karbonsavamidok reakciói

1. Sav-bázis sajátságok
2. Redukció, oxidáció
3. Hofmann lebontás

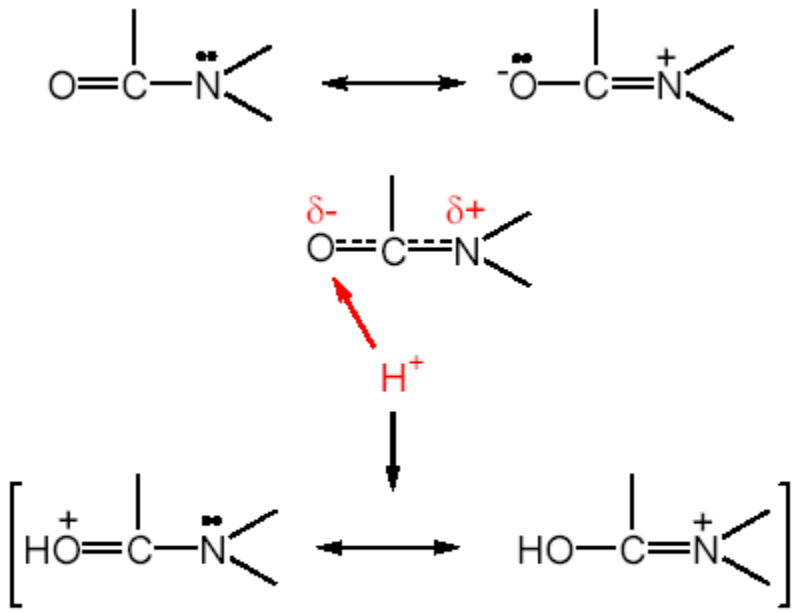
1. Sav-bázis sajátság

Savasság (N-H savak)





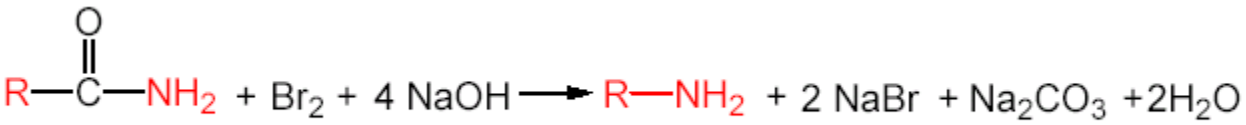
Bázicitás



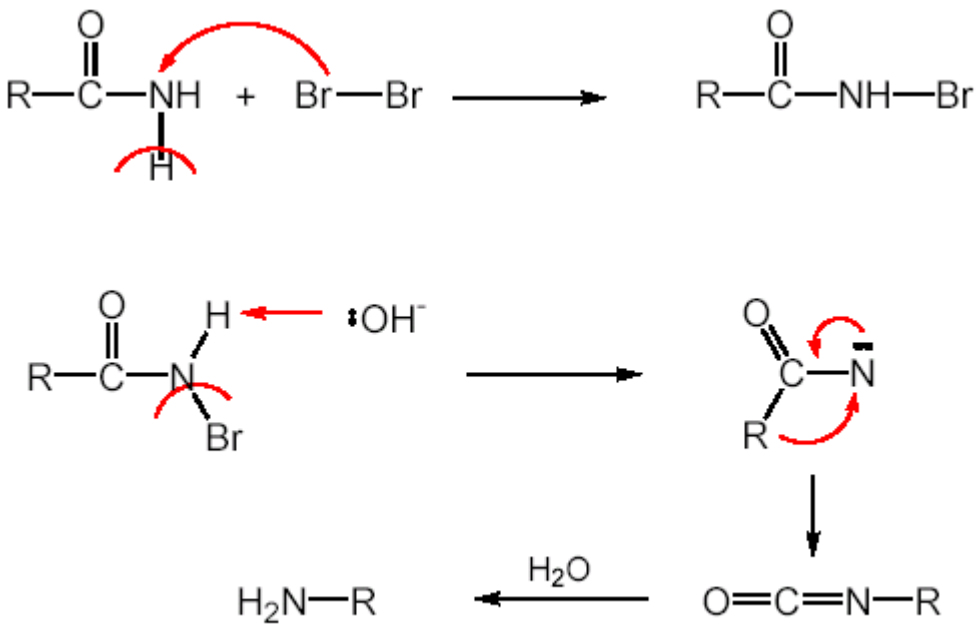
CH_3-CO-NH_2: pK_b = 13.7

2. Redukció, oxidáció (lásd: karbonsavszármazékok)

3. Hofmann lebontás



Mechanizmus

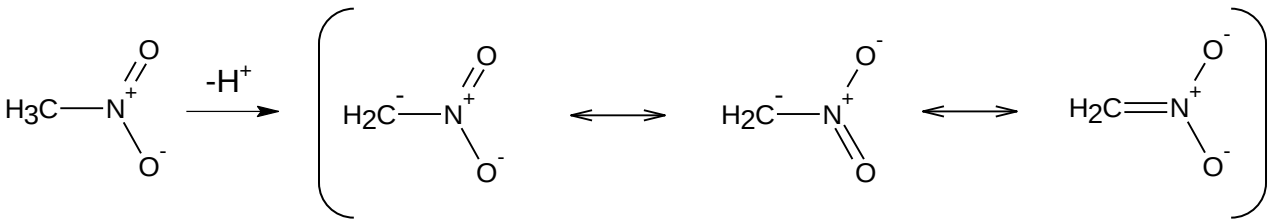


Nitrovegyületek reakciói

1. Sav-bázis sajátságok
2. Redukció, oxidáció

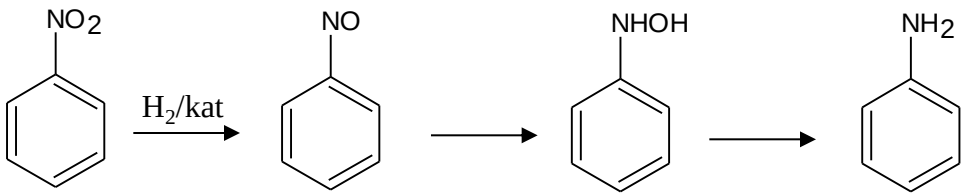
1. Nitrovegyületek C-H savak

CH_3NO_2, primer és szekunder nitrovegyületek lúgban oldódnak



4 atom, 4 elektron konjugáció

2. Nitrovegyületek redukciója



nitro nitrozó hidroxilamin amino