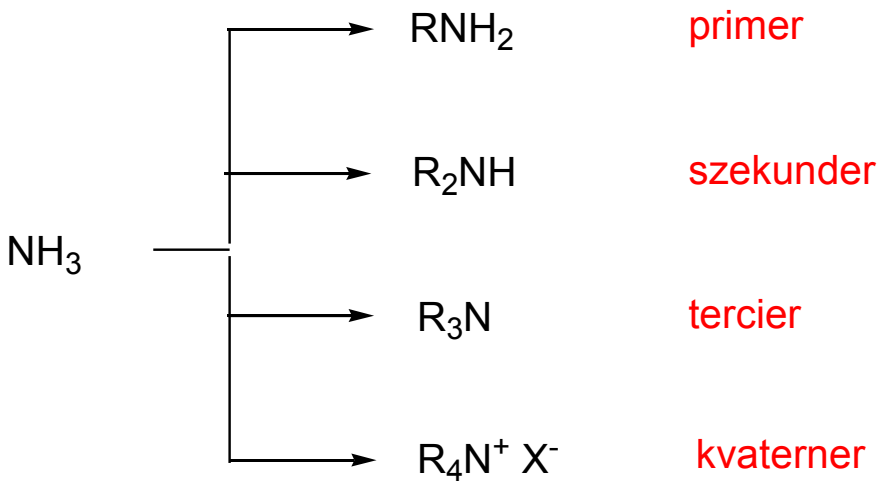
NITROGÉNTARTALMÚ SZÉNVEGYÜLETEK

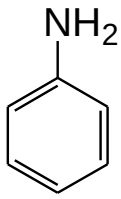
Aminok



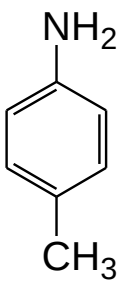
Elnevezés

általános név: alkil-amin (dialkil-amin, trialkil-amin)
előtagként: aminocsoport (NH_2)

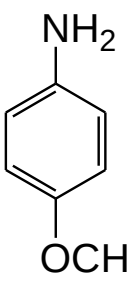
CH_3NH_2 metil-amin	$CH_3CH_2NH_2$ etil-amin	$CH_3CH_2CH_2NH_2$ propil-amin
$(CH_3)_2NH$ dimetil-amin	$(C_2H_5)_3N$ trietil-amin	$CH_3\text{-}NH\text{-}C_2H_5$ etil-metil-amin
$NH_2CH_2CH_2OH$ 2-aminoetanol	$CH_3CH(NH_2)CH_2OH$ 2-aminopropán-1-ol	$NH_2CH_2CH_2COOH$ 3-aminopropionsav



anilin
(aminobenzol)

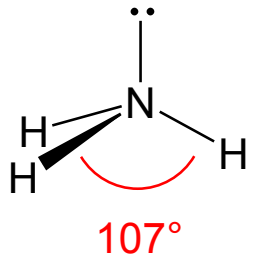


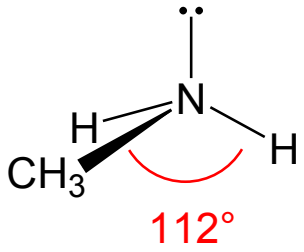
p-toluidin

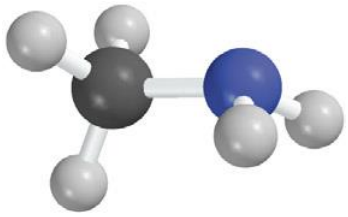


p-anizidin

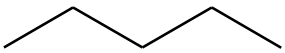
Elektron- és térszerkezet



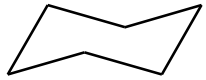




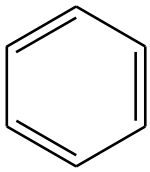
analóg szerkezetek



pentán

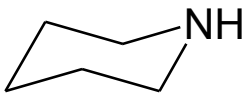


ciklohexán

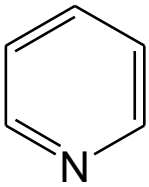


benzol

dietil-amin



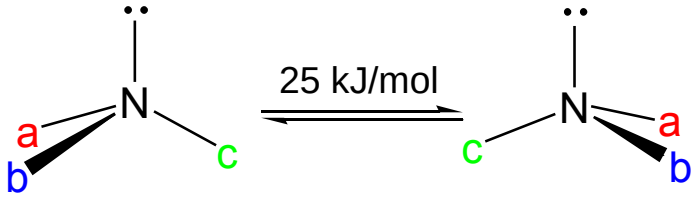
piperidin



piridin

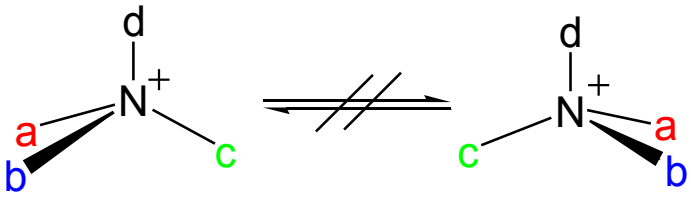
királis nitrogénatom

tercier amin



gyors racemizáció

kvaterner ammóniumsó

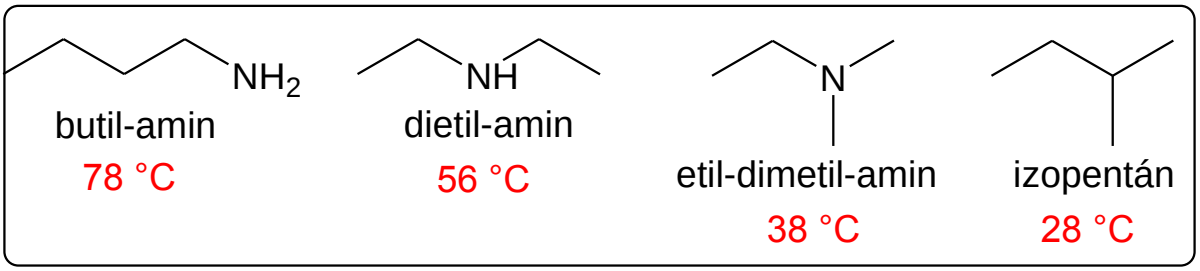


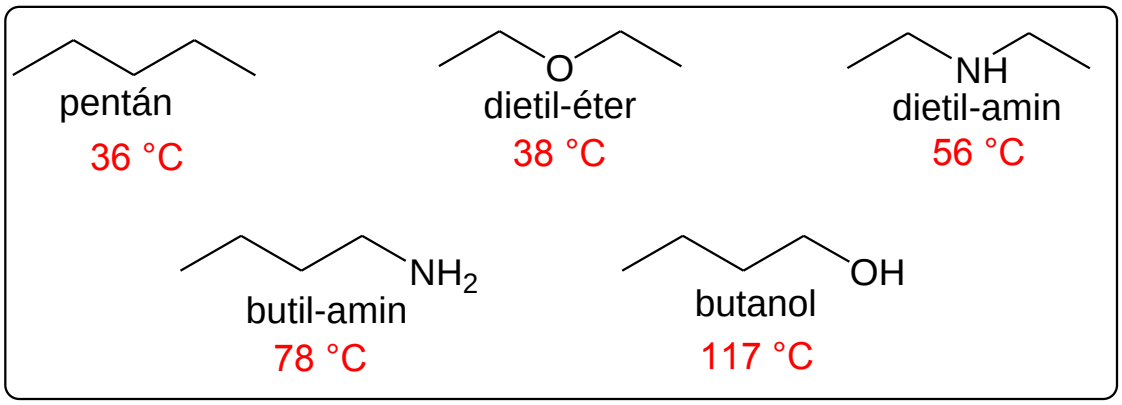
rezolválható

Fizikai tulajdonságok

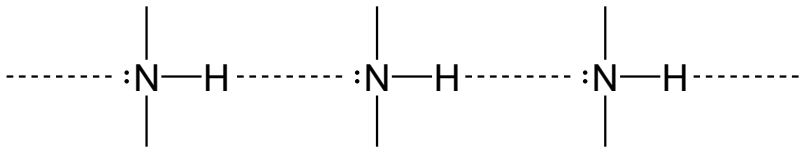
Forráspont

CH_3CH_3	CH_3NH_2	CH_3OH
etán	metil-amin	metanol
-89 °C	-6 °C	65 °C





Hidrogénkötés



Az aminok bázicitása

$$R{-}NH_2 + H_2O \underset{}{\overset{K_b}{\rightleftharpoons}} R{-}\overset{+}{N}H_3 + OH^-$$

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

	K_b	pK_b
NH_3	$1{,}8 \times 10^{-5}$	4.70
$MeNH_2$	$4{,}4 \times 10^{-4}$	3.36
Me_2NH	$5{,}1 \times 10^{-4}$	3.25
Me_3N	$5{,}3 \times 10^{-5}$	4.28

Báziserősség (vizes közegben)

R-csoport +I effektusa $\longrightarrow$

$NH_3 < R\text{-}NH_2 < \mathbf{R_2NH} > R_3N$

kationok szolvatációs készsége $\longleftarrow$

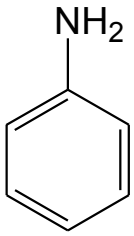
$$CH_3NH_2 + CH_3COOH \longrightarrow CH_3NH_3^+ + CH_3COO^-$$

pK_s=4,7 $\qquad$ pK_s=10.7

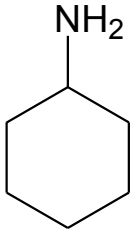
$$CH_3NH_3^+ + OH^- \longrightarrow CH_3NH_2 + H_2O$$

pK_s=10.7 $\qquad$ pK_s=15.7

Aromás aminok bázicitása



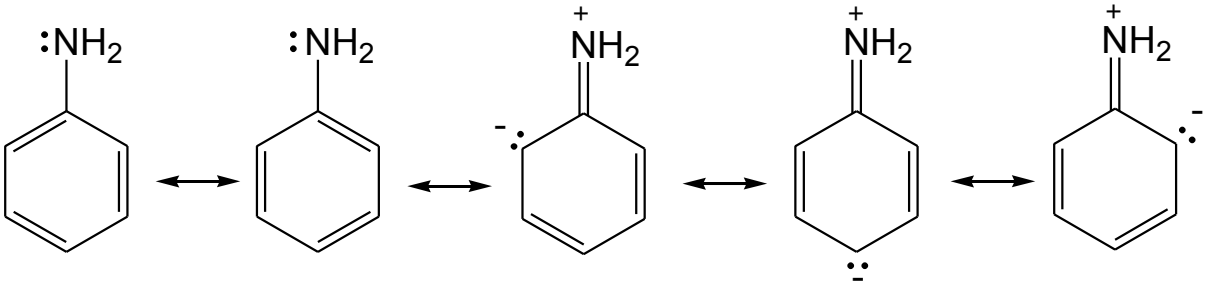
anilin



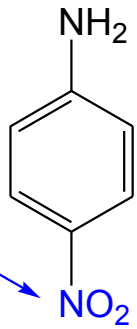
ciklohexil-amin

K_b	$3{,}8 \times 10^{-10}$	$4{,}4 \times 10^{-4}$
pK_b	9.4	3.3
	aromás (gyengébb bázis)	alifás (erősebb bázis)

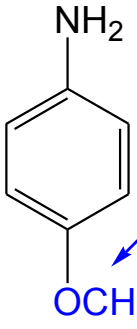
delokalizált π-elektronrendszer



	$C_6H_5NH_2$	$(C_6H_5)_2NH$	$(C_6H_5)_3N$
	anilin	difenil-amin	trifenil-amin
K_b	$3{,}8 \times 10^{-10}$	6×10^{-14}	10^{-19}
pK_b	9,4	13,2	19



p-nitroanilin



p-anizidin

elektronszívó csoport

csökkenő bázicitás

elektronküldő csoport

növekvő bázicitás

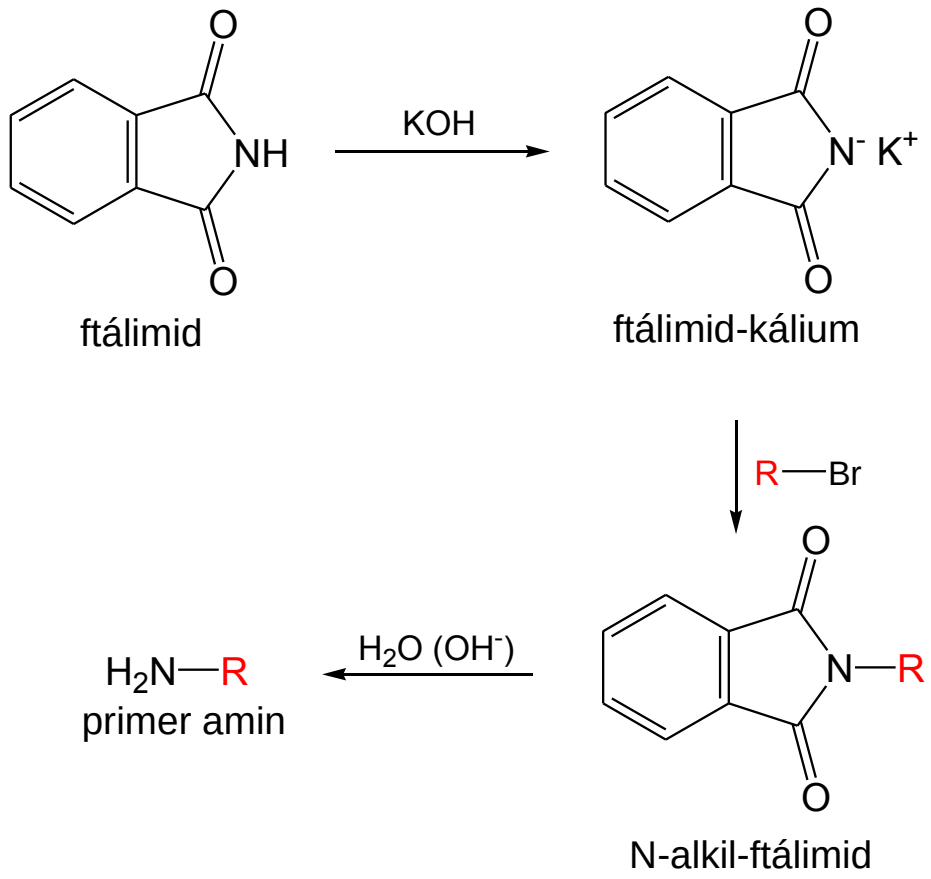
K_b	10^{-13}	2×10^{-9}
pK_b	13	8.7

Az aminok előállítása

Az ammónia alkilezése (S_N reakció) ⟶ keveréktermék

$$NH_3 \xrightarrow[-HX]{R\text{-}X} R\text{-}NH_2 \xrightarrow[-HX]{R\text{-}X} R_2NH \xrightarrow[-HX]{R\text{-}X} R_3N \xrightarrow{R\text{-}X} RN_4^+\ X^-$$

Primer aminok előállítása (Gabriel szintézis)



Aminok előállítása redukciós módszerekkel

karbonsavszármazékok redukciója

$$\underset{\text{karbonsavnitril}}{R{-}C{\equiv}N} \xrightarrow[H_2/\text{kat.}]{LiAlH_4\ \text{v.}} R{-}CH_2{-}NH_2$$

$$\left[\, R{-}Br \xrightarrow{NaCN} R{-}C{\equiv}N \,\right]$$

$$\underset{\text{karbonsavamid}}{R{-}CO{-}NH_2} \xrightarrow{LiAlH_4} R{-}CH_2{-}NH_2$$

$$\left[\, R{-}CO{-}Cl \xrightarrow{NH_3} R{-}CO{-}NH_2 \,\right]$$

azidok redukciója

$$\underset{\text{alkil-azid}}{R{-}CH_2{-}N_3} \xrightarrow[H_2/\text{kat.}]{LiAlH_4\ \text{v.}} R{-}CH_2{-}NH_2$$

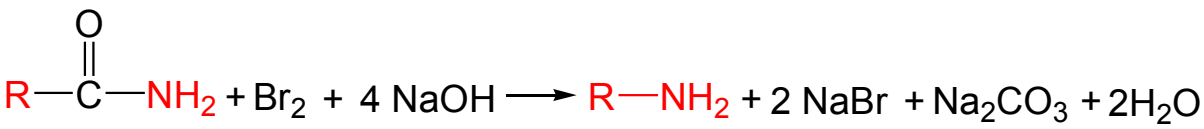
$$\left[\, R{-}CH_2Br \xrightarrow{NaN_3} R{-}CH_2N_3 \,\right]$$

oxovegyületek reduktív aminálása

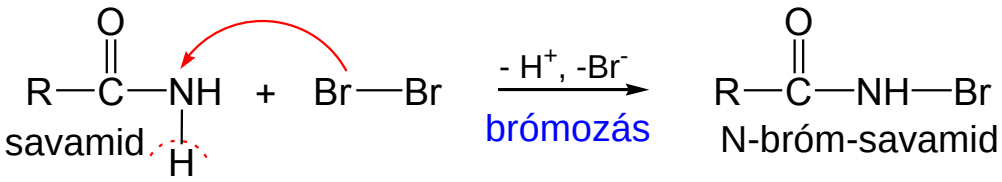
$$R{-}CHO + NH_3 \longrightarrow \underset{\text{imin köztitermék}}{\left[\, R{-}CH{=}NH \,\right]} \xrightarrow{H_2/\text{kat.}} \underset{\text{primer amin}}{R{-}CH_2{-}NH_2}$$

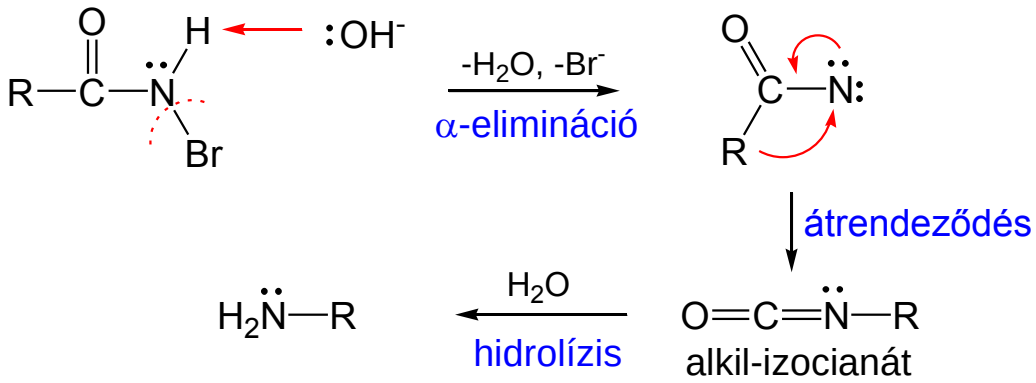
$$R{-}CHO + QNH_2 \longrightarrow \underset{\text{Schiff-bázis köztitermék}}{\left[\, R{-}CH{=}NQ \,\right]} \xrightarrow{H_2/\text{kat.}} \underset{\text{szekunder amin}}{R{-}CH_2{-}NHQ}$$

Hofmann lebontás

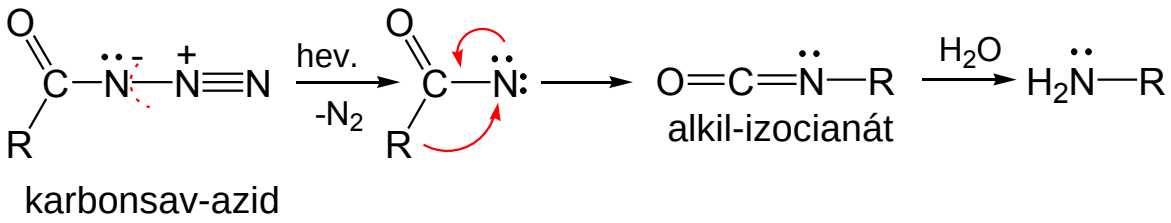


Mechanizmus





Curtius lebontás

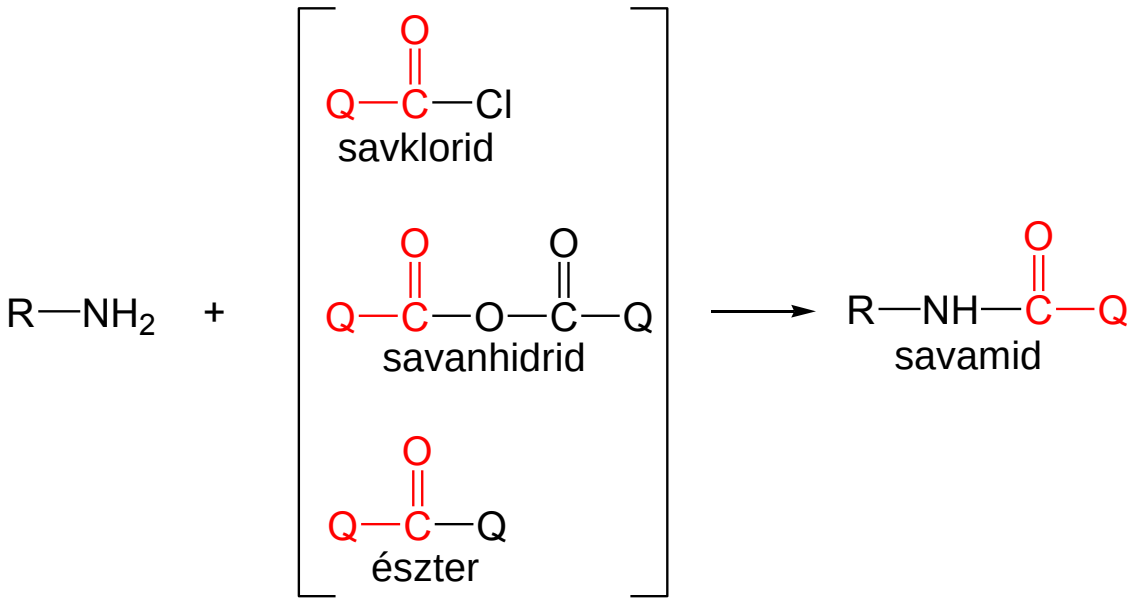


AZ AMINOK KÉMIAI TULAJDONSÁGAI

Az aminok alkilezése (ld. korábban)

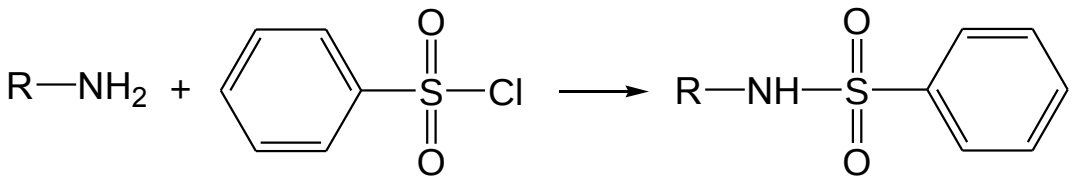
$$R\text{-}NH_2 \xrightarrow[-HX]{R\text{-}X} R_2NH \xrightarrow[-HX]{R\text{-}X} R_3N \xrightarrow{R\text{-}X} RN_4^+\ X^-$$

Az aminok acilezése (ld. karbonsavszármazékok ammonolízise)



Az aminok acilezése szulfonil-kloridokkal

$$\underset{\text{amin}}{R{-}NH_2} + \underset{\text{szulfonil-klorid}}{Q{-}SO_2Cl} \longrightarrow \underset{\text{szulfonamid}}{R{-}NH{-}SO_2Q}$$



benzolszulfonil-klorid N-alkil-benzolszulfonamid

Hinsberg-próba (aminok rendűségének megállapítása)

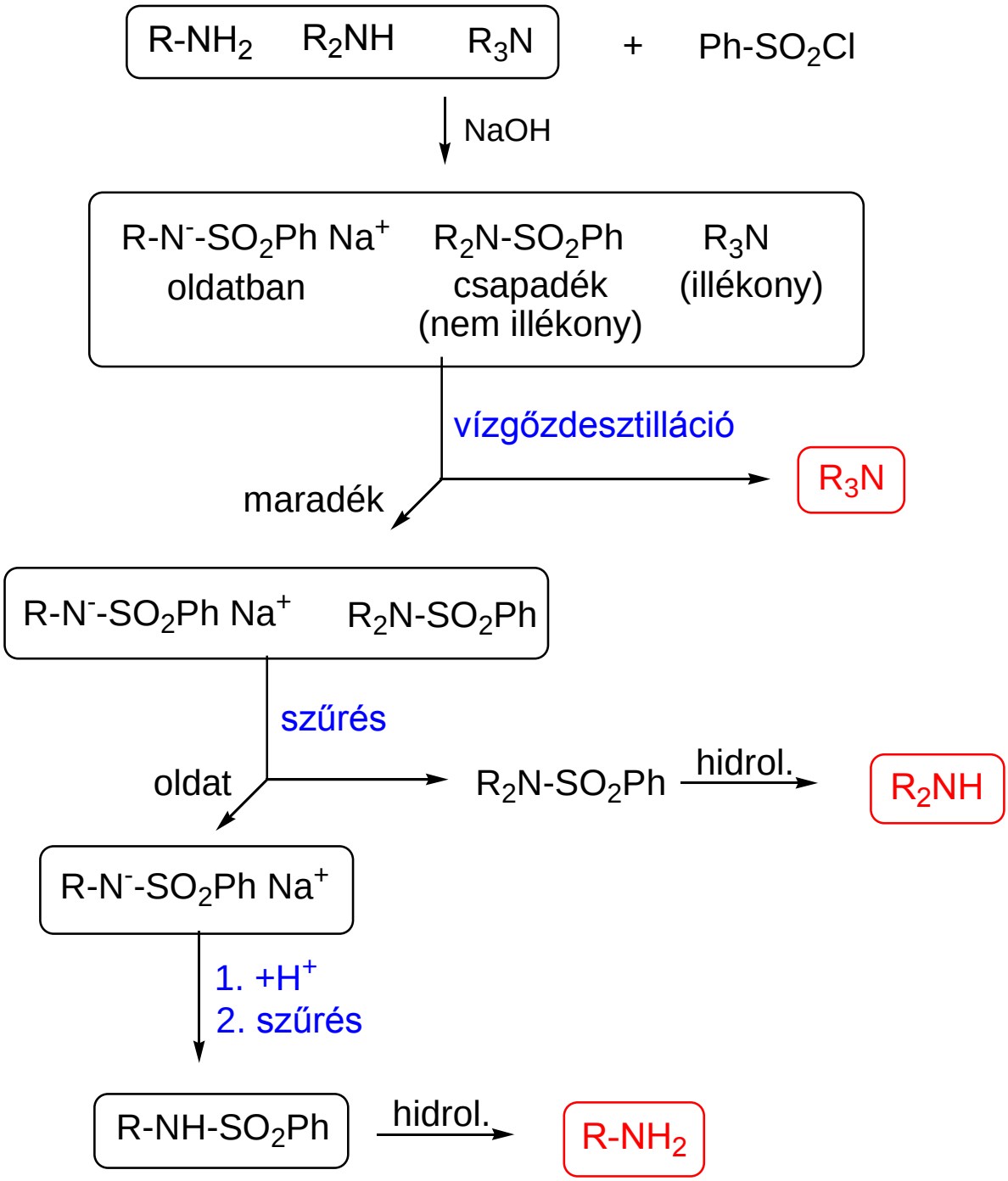
$$\underset{\text{primer amin}}{R\text{-}NH_2} + Ph\text{-}SO_2Cl \xrightarrow[H_2O]{NaOH} R\text{-}NH\text{-}SO_2Ph \xrightarrow{NaOH} \boxed{R\text{-}N^-\text{-}SO_2Ph\ Na^+ \text{ oldódik}}$$

savas jelleg

$$\underset{\text{szekunder amin}}{R_2NH} + Ph\text{-}SO_2Cl \xrightarrow{NaOH} \boxed{R_2N\text{-}SO_2Ph \text{ csapadék}}$$

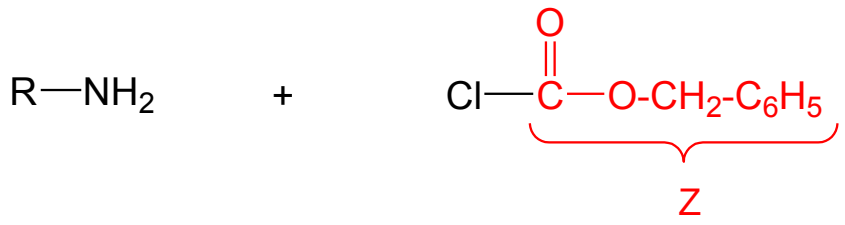
$$R_3N + Ph\text{-}SO_2Cl \not\longrightarrow \boxed{\text{nincs reakció}}$$

Különböző rendűségű aminok elválasztása

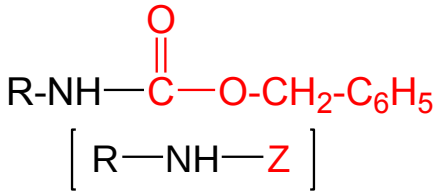


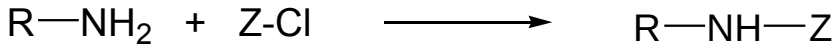
Az aminocsoport védése

1.

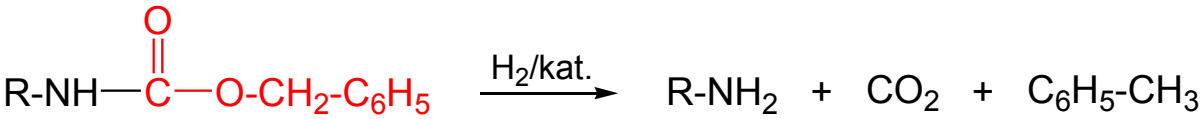


benziloxi-karbonil-klorid (Z-Cl)
(klórhangyasav-benzilészter)





Védőcsoport eltávolítás



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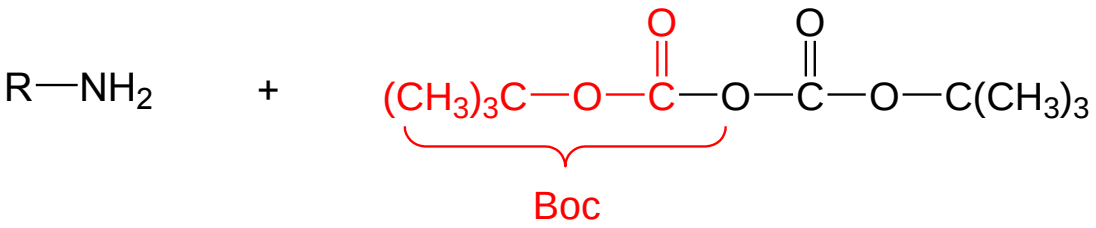
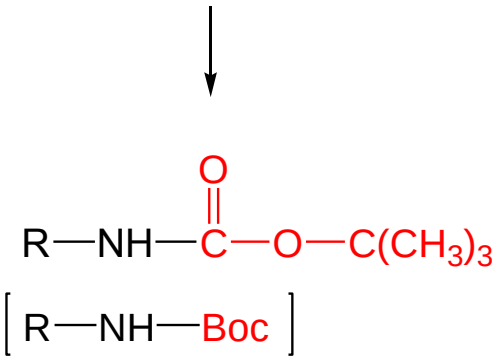
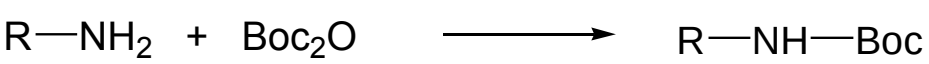
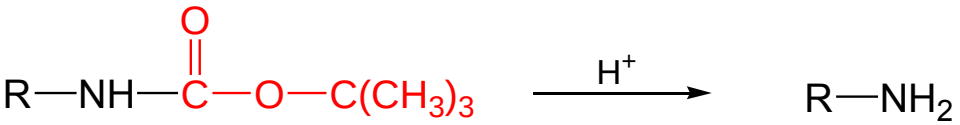


di-terc-butil-dikarbonát (Boc-anhidrid, Boc_2O)



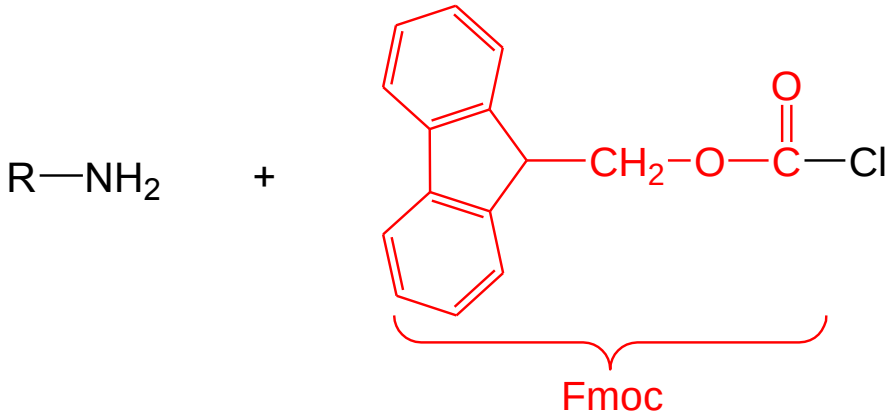


Védőcsoport eltávolítás

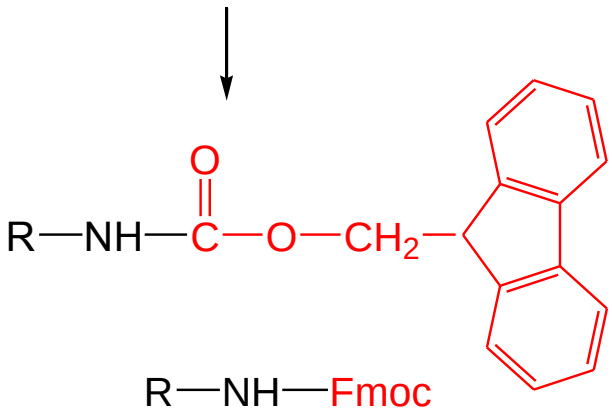


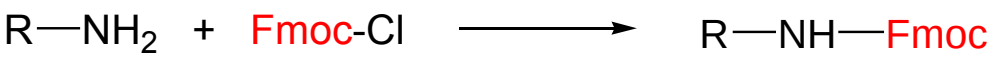
sav pl. HCl-MeOH, CF_3COOH

3.

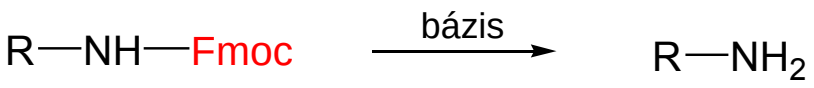


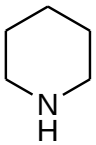
9-fluorenil-metil-oxi-karbonil-klorid (Fmoc-klorid, Fmoc-Cl)





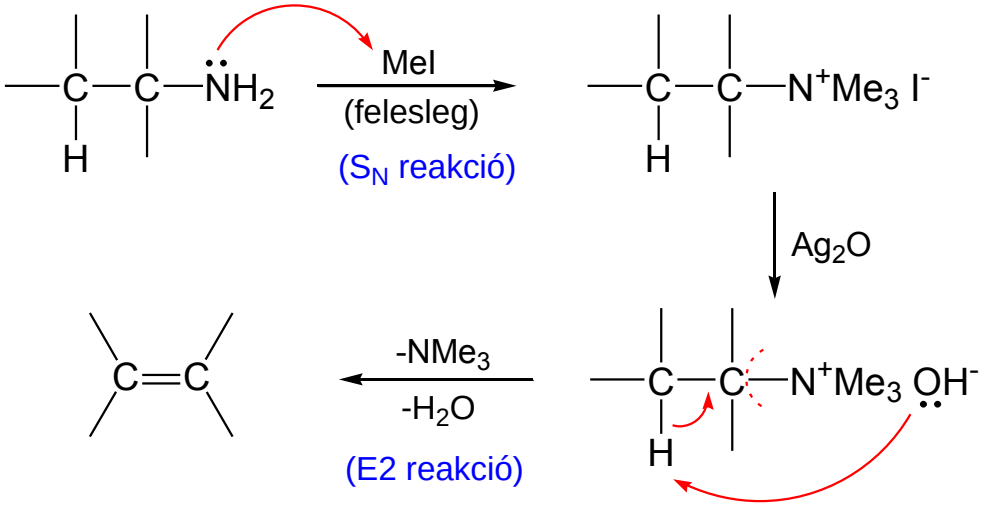
Védőcsoport eltávolítás

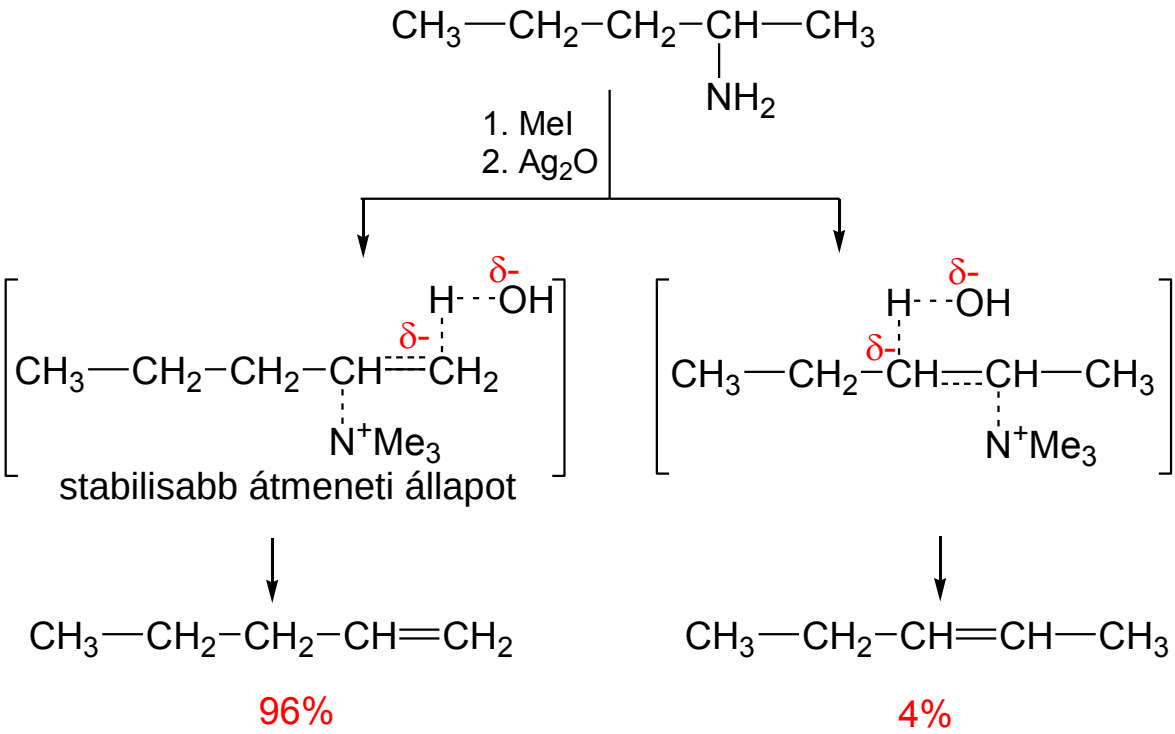


bázis pl. piperidin 

Hofmann-eliminációó (aminból alkén)

August Wilhelm von Hofmann (1818–1892) was born in Germany. He first studied law and then changed to chemistry. He founded the German Chemical Society. Hofmann taught at the Royal College of Chemistry in London for 20 years and then returned to Germany to teach at the University of Berlin. He was one of the founders of the German dye industry. Married four times—he was left a widower three times—he had 11 children.





Hofmann-szabály (a Zajcev-szabállyal ellentétes termék)

Fázistranszfer katalízis ammóniumsókkal

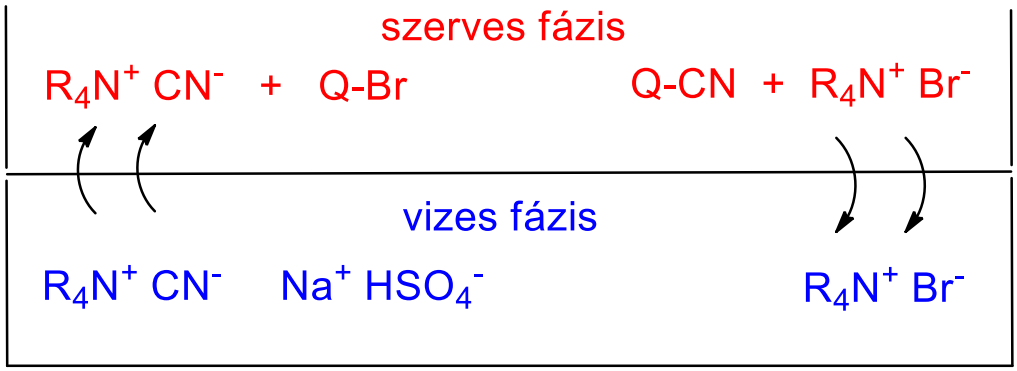
$$CH_3(CH_2)_5Br + NaCN \xrightarrow{R_4N^+\ HSO_4^-} CH_3(CH_2)_5CN + NaBr$$

szerves oldószerben oldódik

vízben oldódik

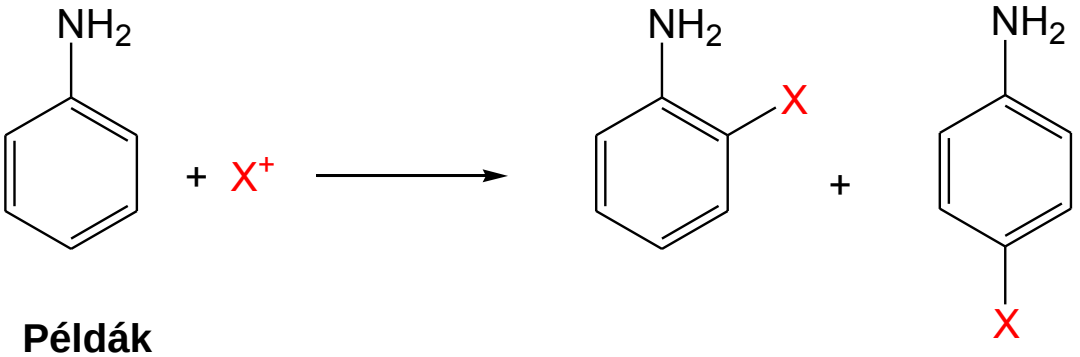
$R_4N^+\ HSO_4^-$: fázistranszfer katalizátor

pl.: $Bu_4N^+\ HSO_4^-$; $C_6H_5CH_2(CH_2CH_3)_3N^+\ HSO_4^-$

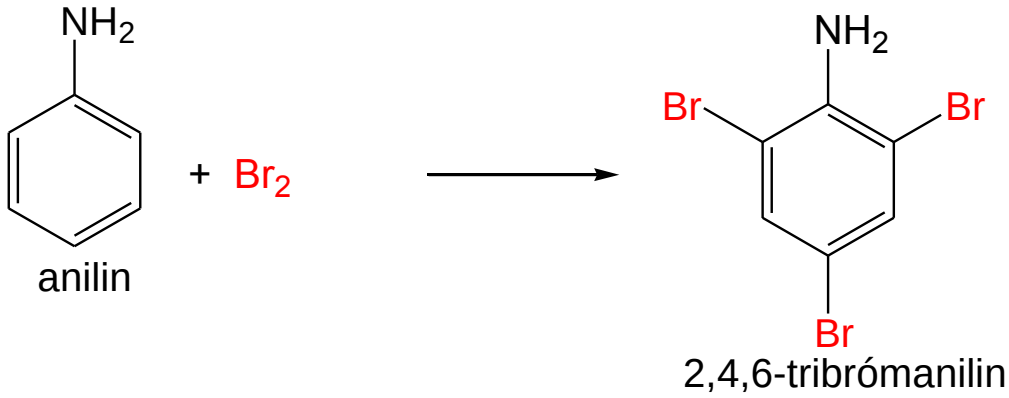


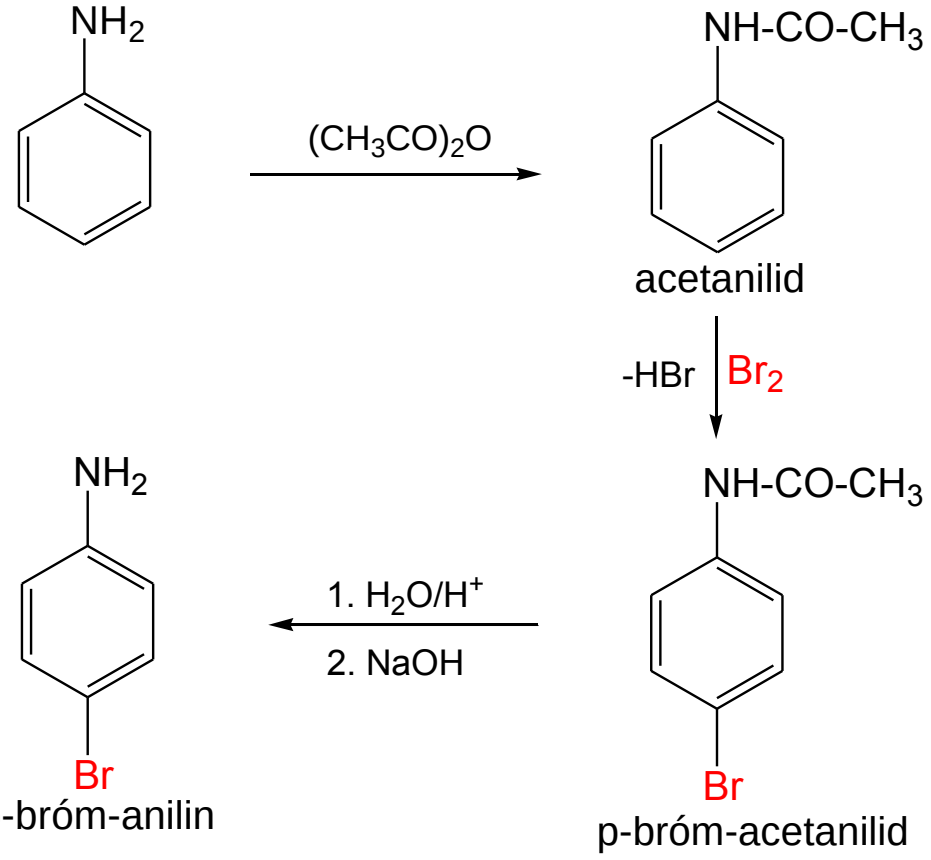
Aromás aminok kémiai tulajdonságai

Elektrofil szubsztitúciós reakciók (o-, p-irányítás, aktiválás)



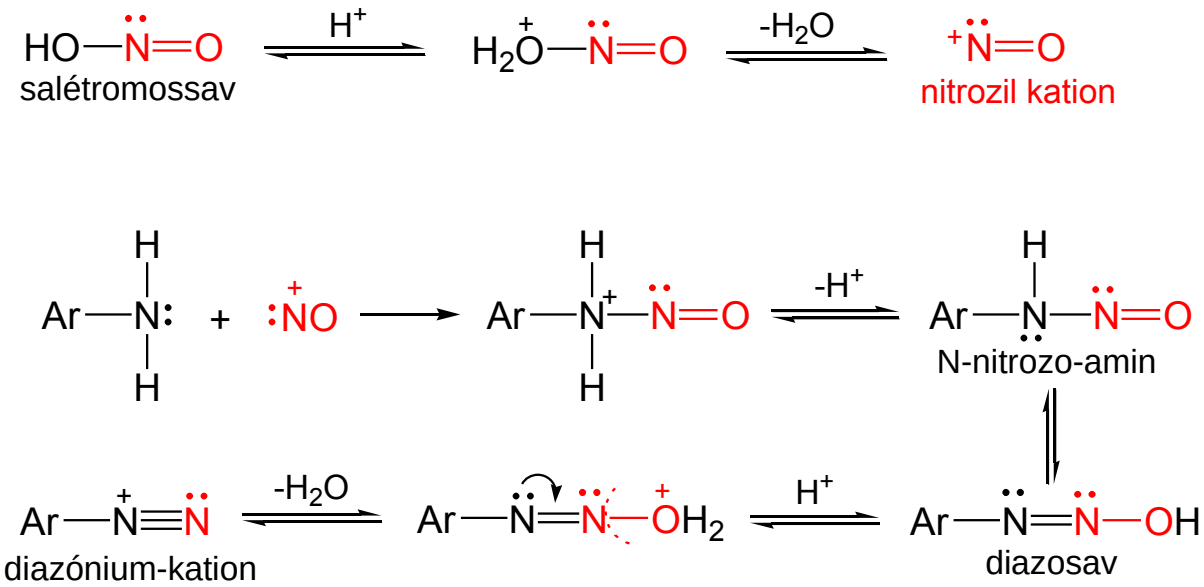
Példák





Diazotálás

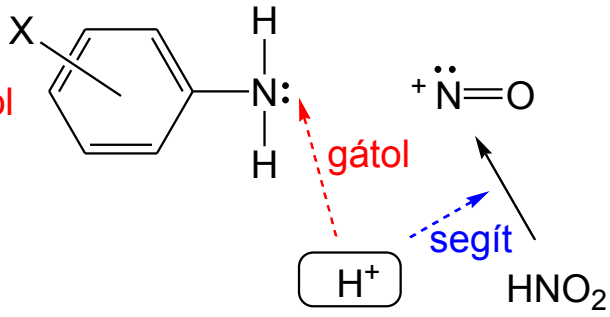
$$\underset{\text{aril-amin}}{Ar\text{-}NH_2} + NaNO_2 + 2\,HCl \xrightarrow{0\,^\circ C} \underset{\text{aril-diazóniumsó}}{Ar\text{-}N_2^+\,Cl^-} + NaCl + 2\,H_2O$$



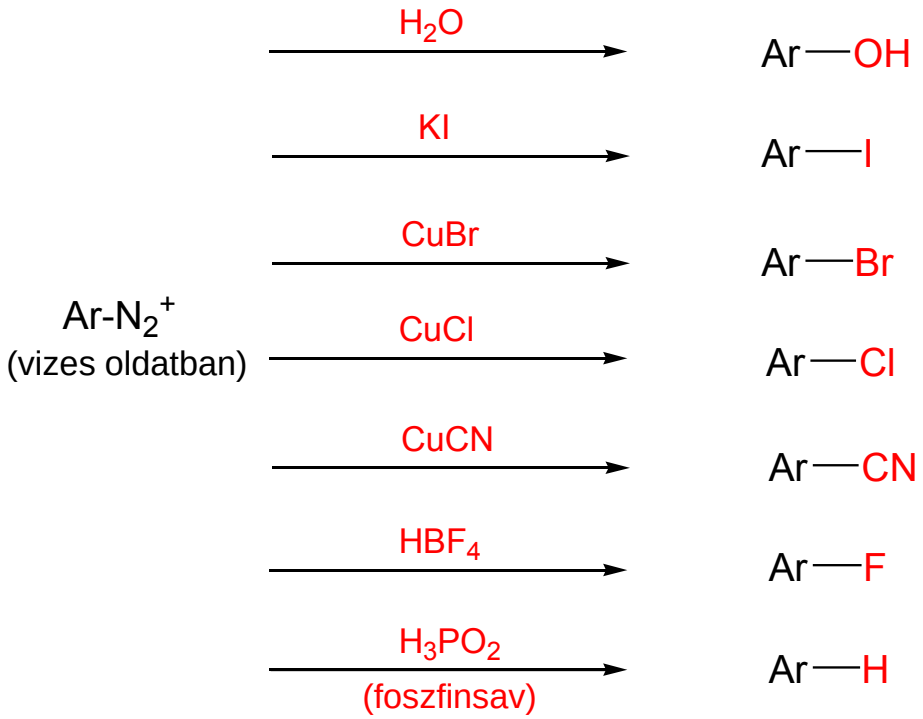
szubsztituált anilinszármazék

elektronküldő X: segít

elektronvonzó X: gátol

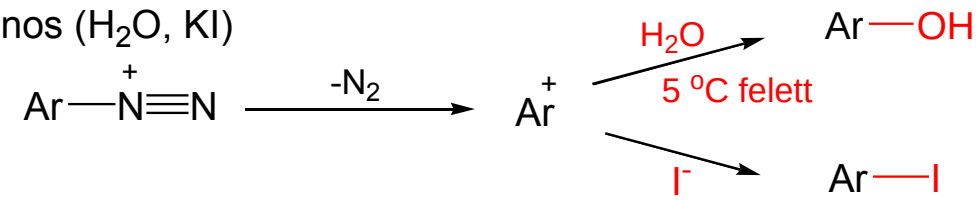


Diazóniumsók szubsztitúciós reakciói

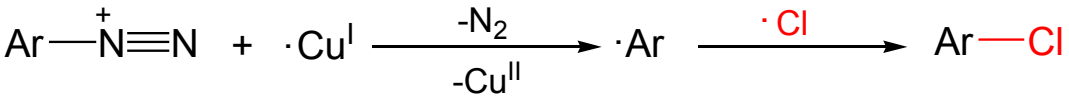


Mechanizmus

ionos (H_2O, KI)

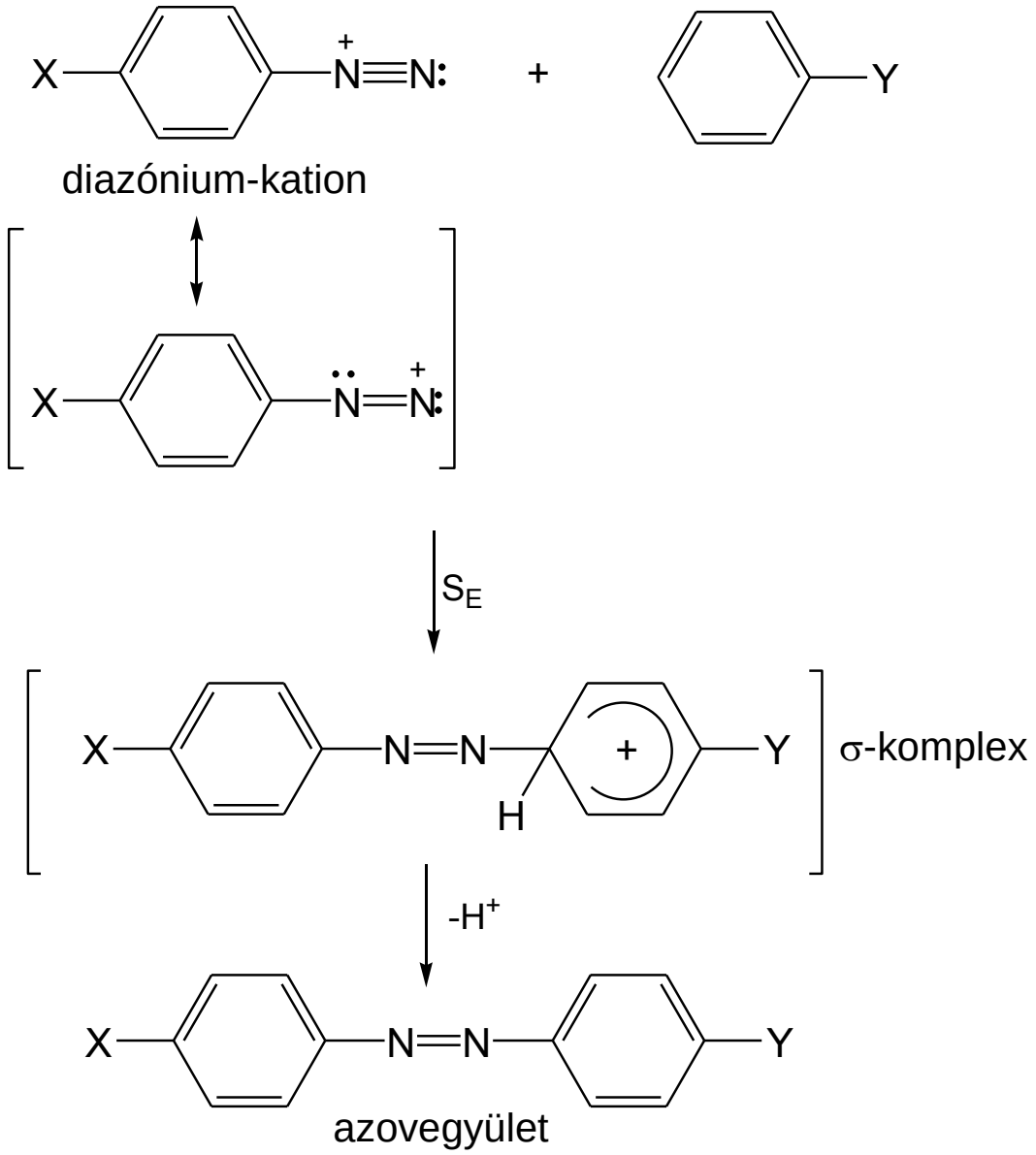


gyökös (Sandmeyer reakció, CuBr, CuCl, CuCN)



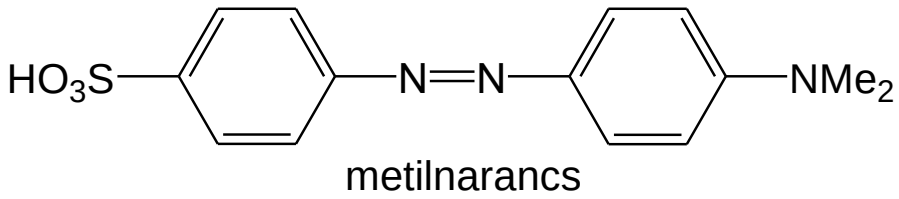
Traugott Sandmeyer (1854–1922) was born in Switzerland. He received a Ph.D. from the University of Heidelberg and discovered the reaction that bears his name in 1884. He was a scientist at Geigy Co. in Basel, Switzerland.

A diazóniumsók kapcsolási reakciói (azokapcsolás)



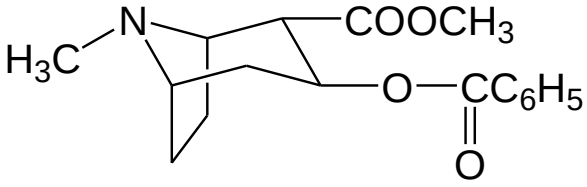
elektronvonzó X (pl. SO_3H)
elektronküldő Y (pl. OH, NMe_2) } segít

Példa

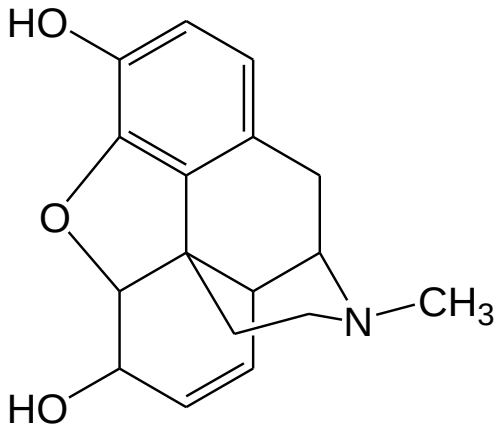


metilnarancs

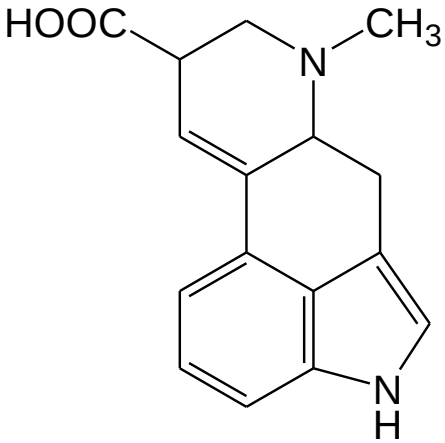
Alkaloidok



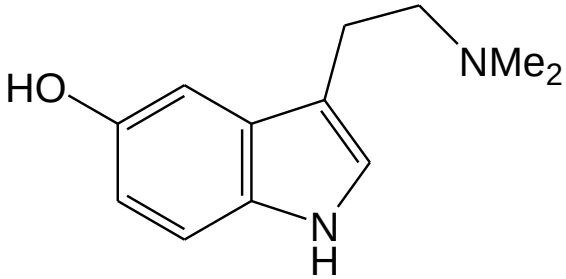
kokain



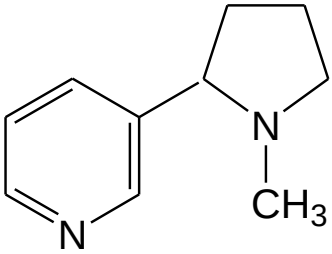
morfin



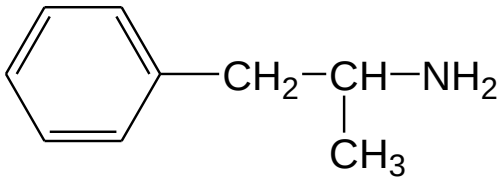
lizergsav



bufotenin



nikotin

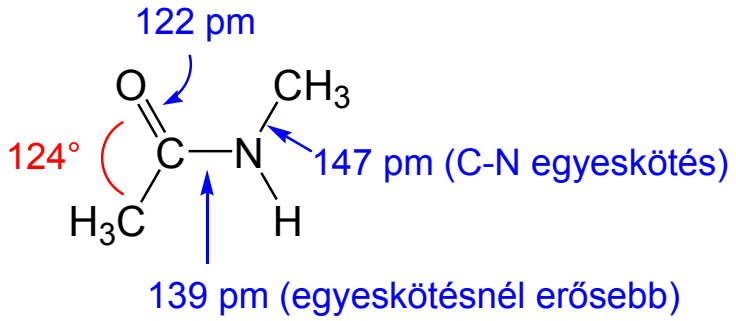


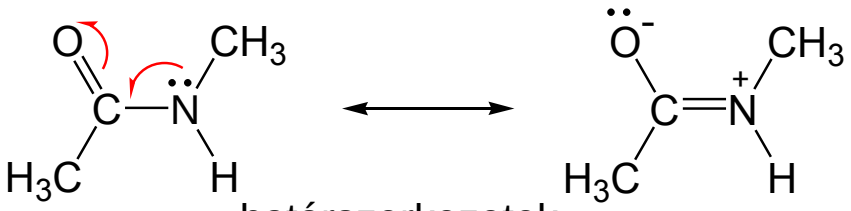
amfetamin

Karbonsavamidok

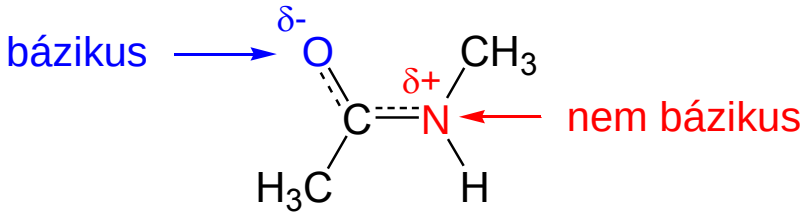
Az amidok szerkezete

N-metil-acetamid

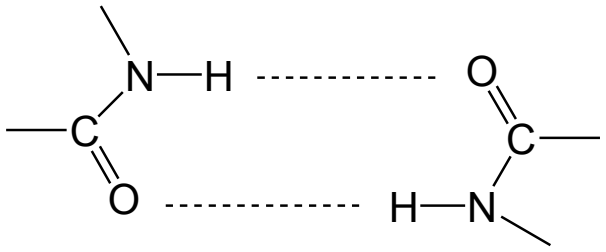




határszerkezetek

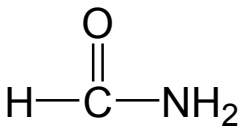


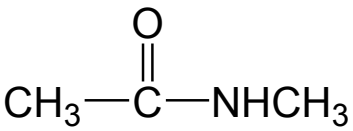
6 atom egy síkban



dimer szerkezet → magas fp, op

Példák

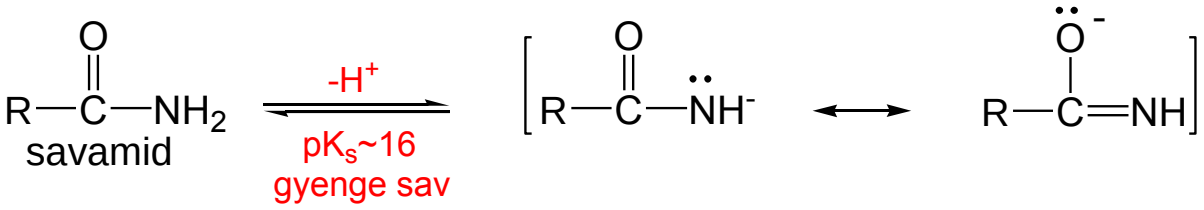


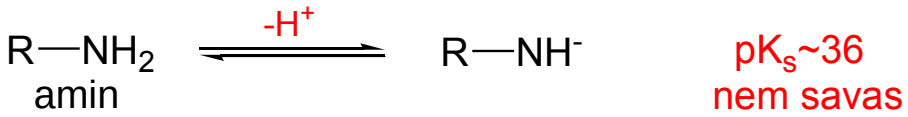


forráspont 193 °C 206 °C

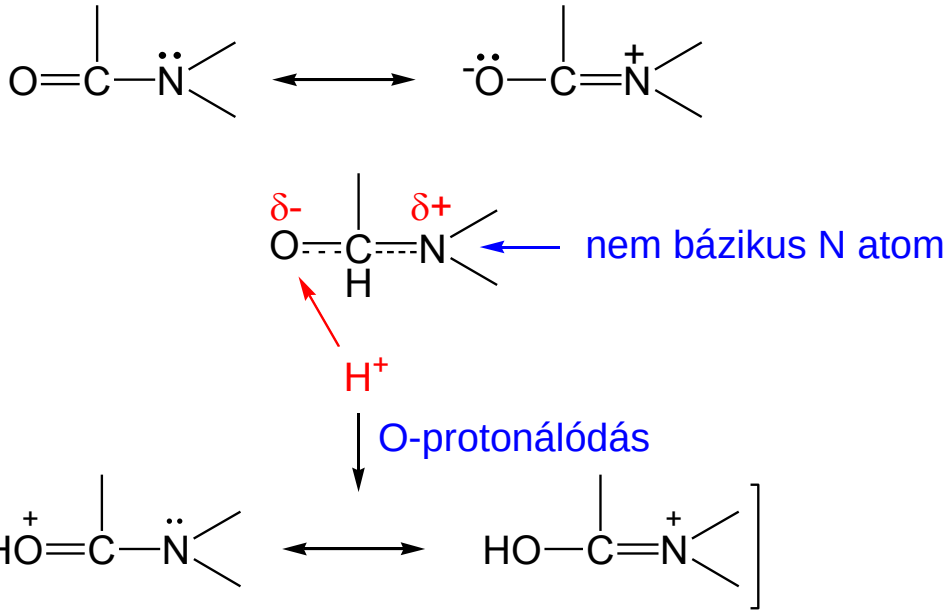
Az amidok sav-bázis tulajdonságai

Savasság



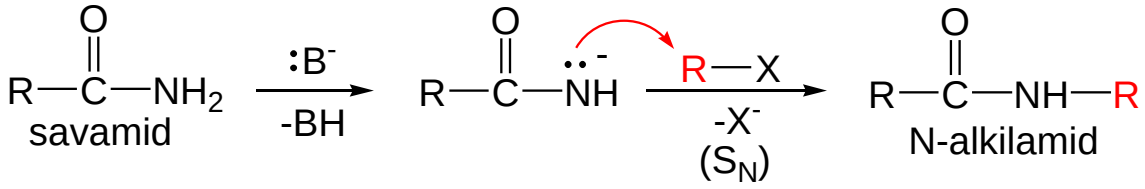


Bázicitás

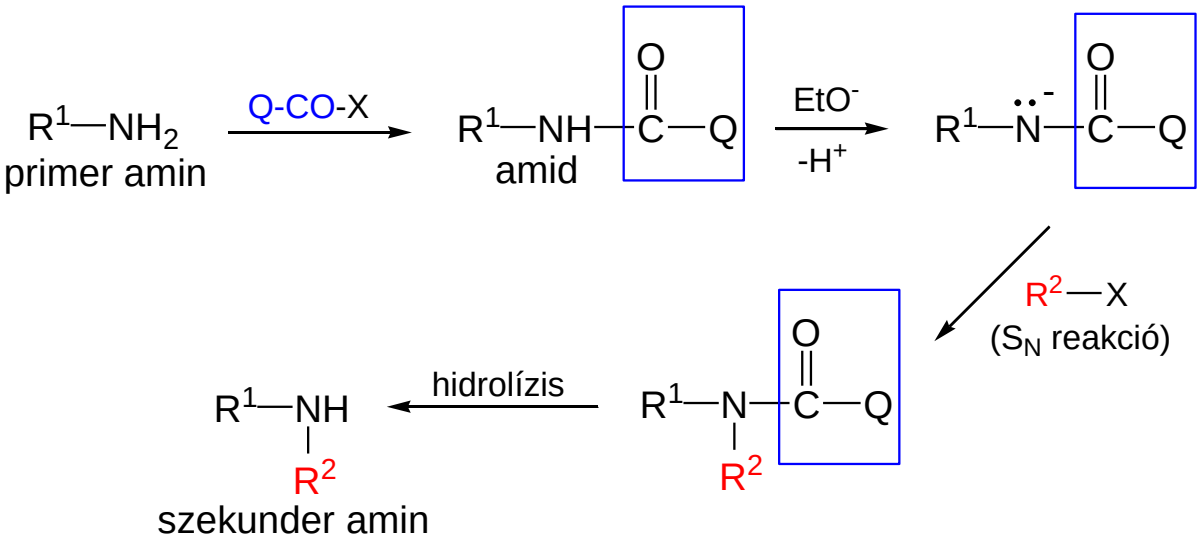


CH_3-CO-NH_2: pK_b = 13.7

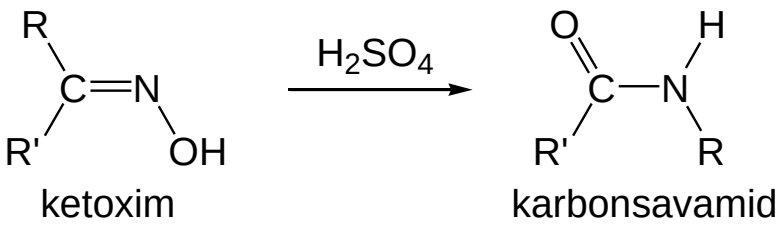
Az amidok alkilezése

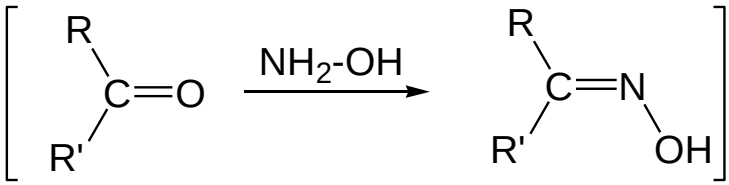


Szekunder aminok előállítása

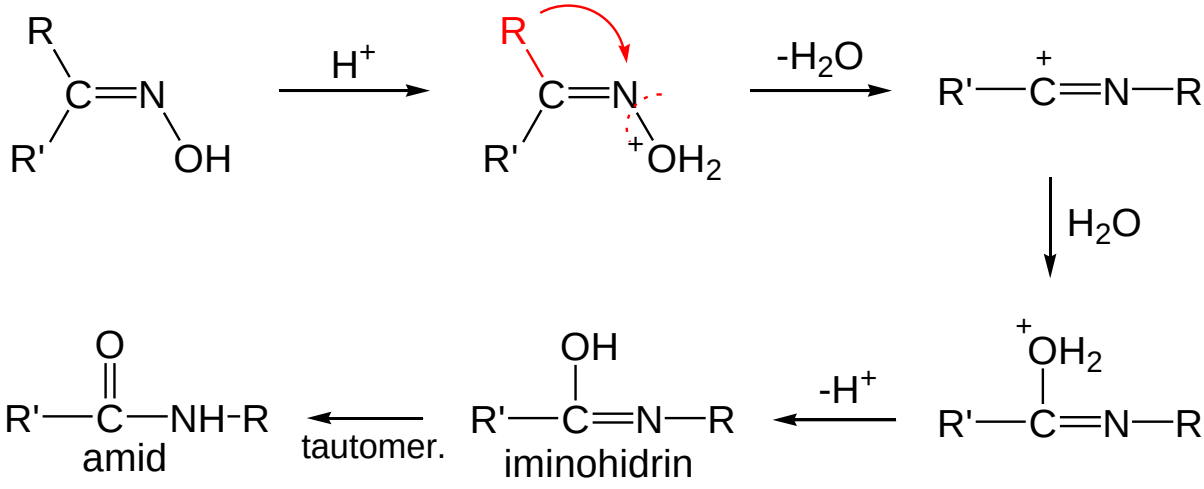


Beckmann-átrendeződés

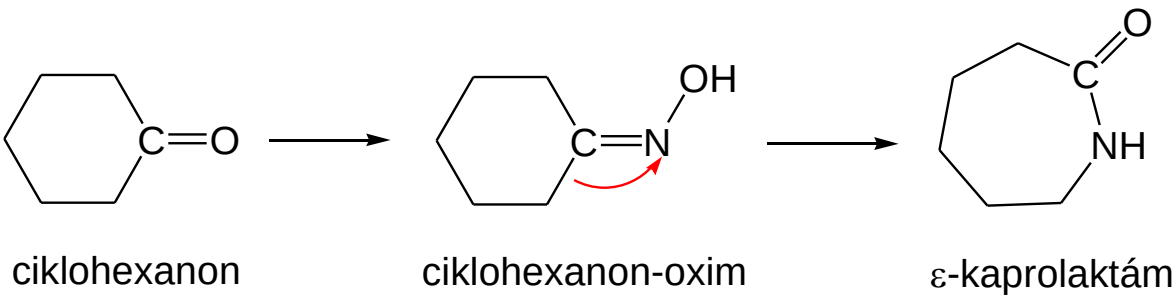




Mechanizmus

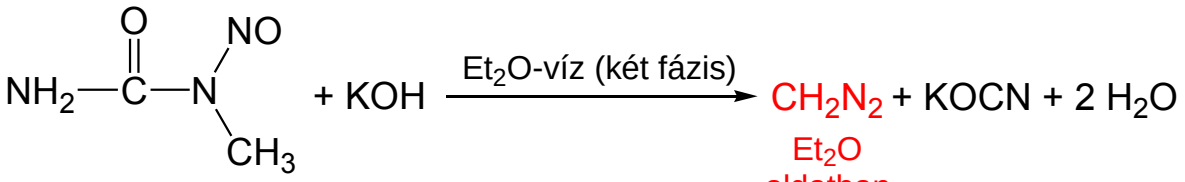


Példa



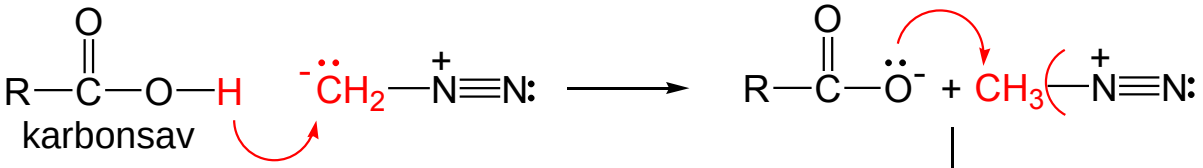
Diazometán (CH_2N_2)

Előállítás



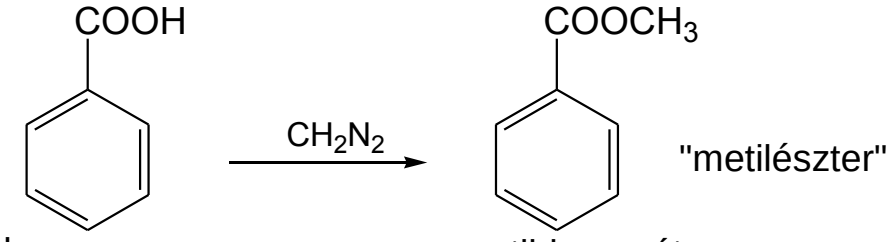
N-nitrozo-N-metilkarbamid

Felhasználás (karbonsavak és fenolok metilezése)

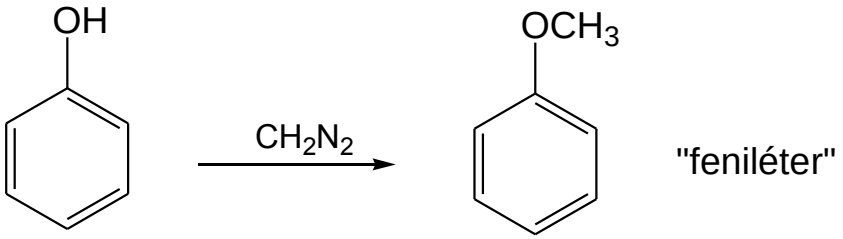


karbonsav-metilészter

Példák



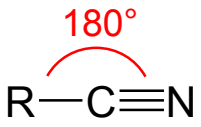
benzoesav metil-benzoát

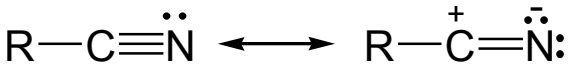


fenol anizol

További nitrogéntartalmú szénvegyületek szerkezete

Nitrilek (R-CN)

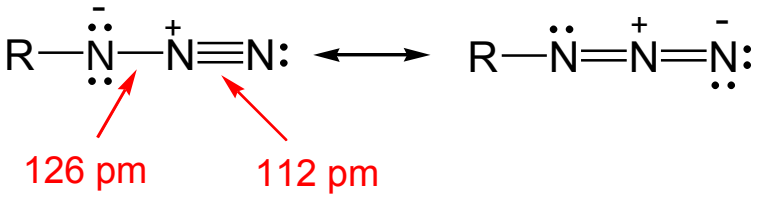




CH_3CN
acetonitril

$CH_3CH_2CH_2CN$
butánnitril

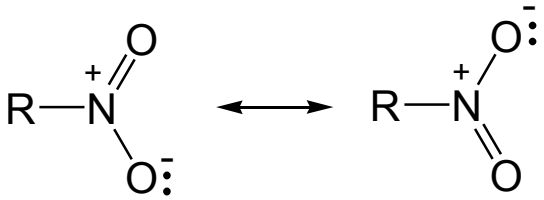
Azidok (R-N_3)



CH_3N_3
metil-azid

$CH_3CH_2CH_2N_3$
propil-azid

Nitrovegyületek (R-NO_2)

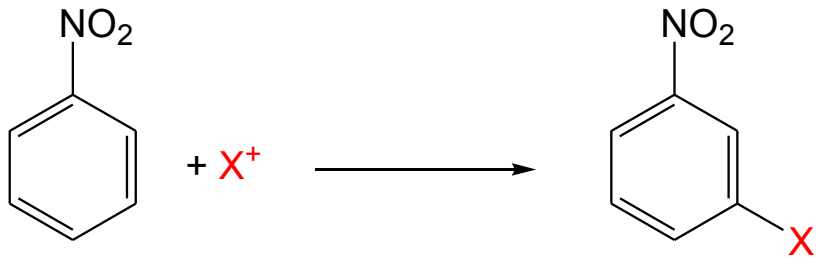


CH_3NO_2
nitrometán

$CH_3CH_2CH_2NO_2$
1-nitropropán

Aromás nitrovegyületek

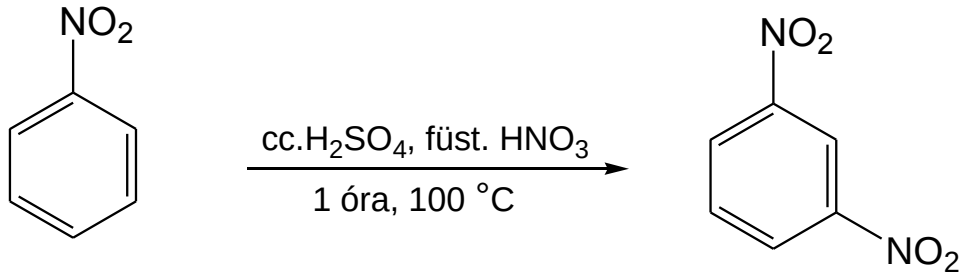
Elektrofil szubsztitúciós reakciók



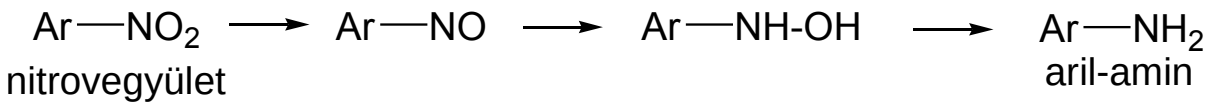
NO_2-csoport: irányítás *meta* helyzetbe

dezaktiválás

Példa



Redukció aminná



redukálószerek: H_2/kat.

fém + sav (Sn, Zn, Fe)

Vegyülettípus	Funkciós csoport	Példa

Amin	R–NH_2	CH_3NH_2
Ammóniumion	R_4N^+ (R = H vagy alkil)	$(CH_3)_4N^+$ Br^-
Imin	RR'C=NH	CH_3–CH=NH
Schiff-bázis	RR'C=NR''	CH_3–CH=NCH_3
Oxim	RR'C=N–OH	CH_3CH=NOH
Hidrazon	RR'C=N–NH_2	$(CH_3)_2$C=NNH_2
Azovegyület	R–N=N–R'	C_6H_5N=N–C_6H_5
Nitril	R–C≡N	CH_3CN
Diazóniumion	R–N^+≡N	$C_6H_5N_2^+$
Diazovegyület	RR'C^-–N^+≡N	CH_2N_2
Azid	R–N=N^+=N^-	CH_3N_3
Nitrovegyület	R–NO_2	CH_3NO_2
Savamid	R–CO–NH_2	CH_3CONH_2
Savhidrazid	R–CO–$NHNH_2$	$CH_3CONHNH_2$
Savazid	R–CO–N=N^+=N^-	CH_3CON_3