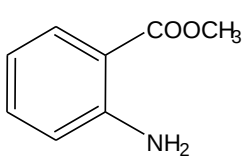
8. Előadás

Nitrogéntartalmú vegyületek.
N-tartalmú zsírsav származékok.
Aminosavak.

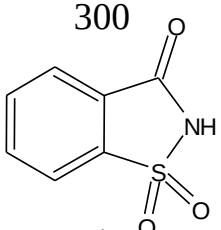
NITROGÉNTARTALMÚ VEGYÜLETEK

„Népszerű" származékok

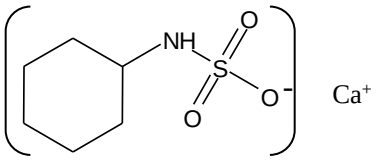


metil-antranilát
(szőlő)

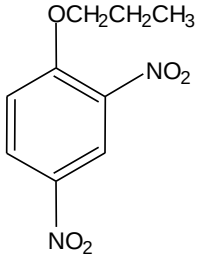
300



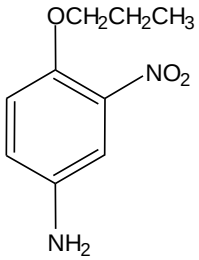
szacharin
(1977)



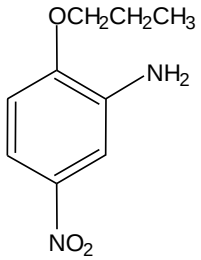
kalcium-ciklamát
(1970: rák)



keserű

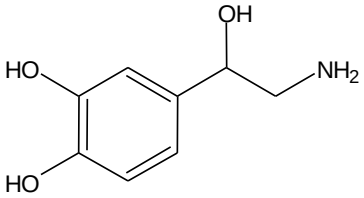


ízletlen

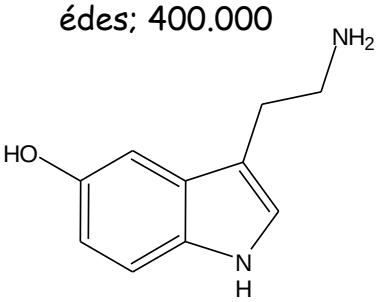


édes; 400.000

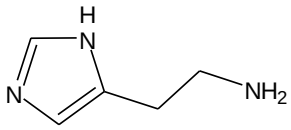
glükóz: 74



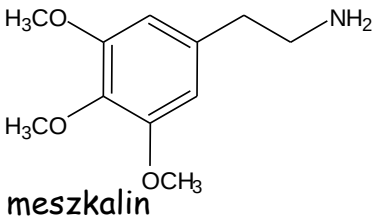
noradrenalin
-NH-CH_3: adrenalin



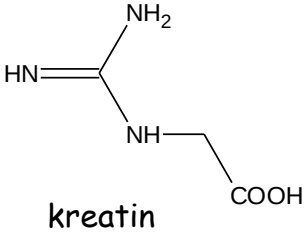
szerotonin



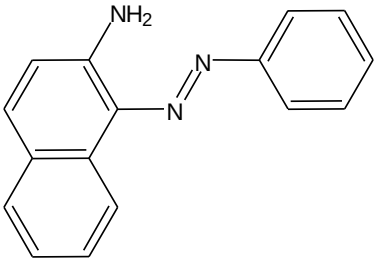
hisztamin



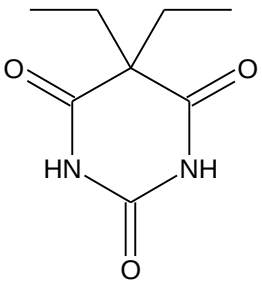
meszkalin



kreatin

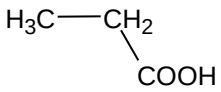


1-fenildiazenil-2-naftilamin
(ételszinezék)

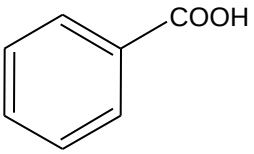


veronál

Tartósítószerek



propánsav



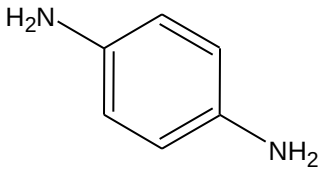
benzoesav

$NaNO_2$

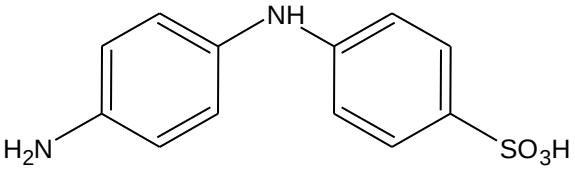
$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$ (gyomor)

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

Hajfestőszerek



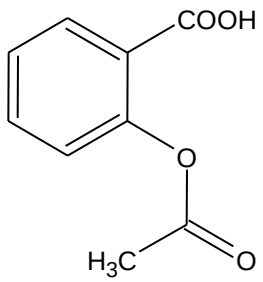
para-feniléndiamin
(fekete)



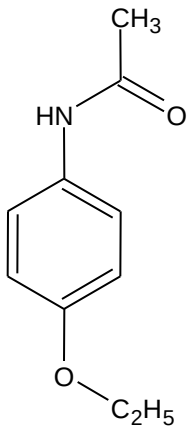
para-amino-difenilamin-szulfonsav
(„fehér", szőke)

Lázcsillapítók

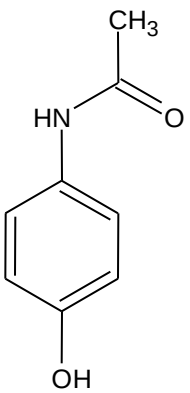
acetil-szalicilsav
(aszpirin)



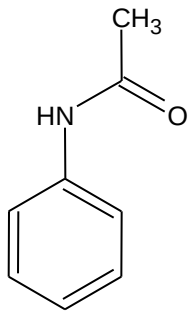
fenacetin



acetamidofén

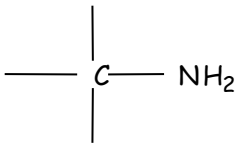


acetanilid

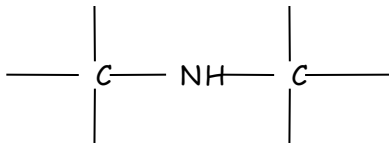


Áttekintés

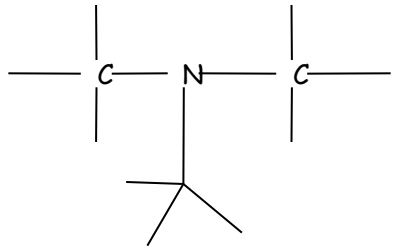
Vegyületek egy N atommal



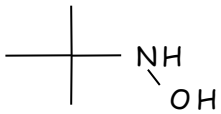
primer amin



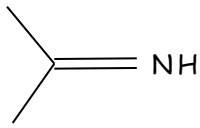
szekunder amin



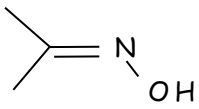
tercier amin



hidroxilamin



imin

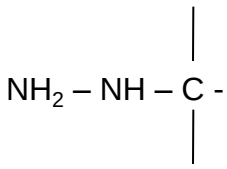


oxim

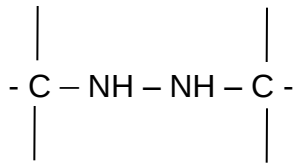
Vegyületek két N atommal

$NH_2 - NH_2$

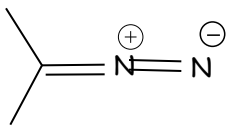
hidrazin



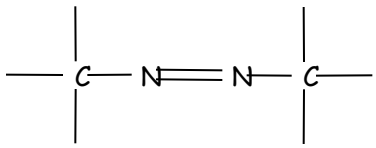
alkil - hidrazin



N,N'-dialkil hidrazin

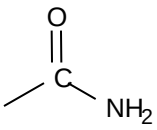


diazovegyületek

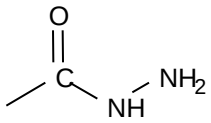


azovegyületek

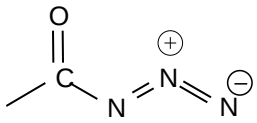
Karbonsav-származékok



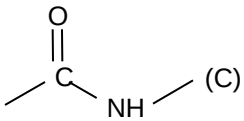
karbonsavamid
(primer)



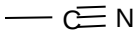
karbonsavhidrazid



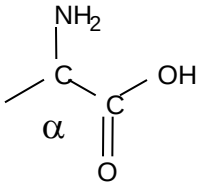
karbonsavazid



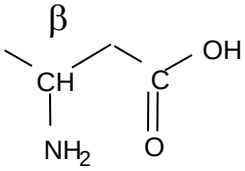
karbonsavamid
(szekunder)



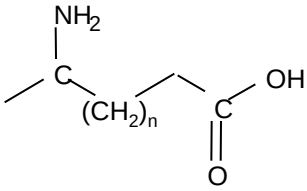
karbonsavnitril



α-amino(karbon)sav

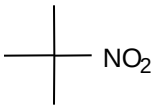


β-amino(karbon)sav

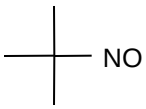


ω-amino(karbon)sav

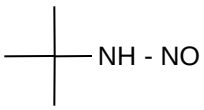
Nitro- és nitrozó vegyületek



nitrovegyületek



nitrozovegyületek



N - nitrozovegyületek

Nomenklatúra, példák

A. AMINOK

telített, telítetlen

gyűrűs, egyenes láncú

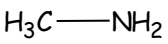
csoportok száma: egy, két... értékű

Ammónia/ammonium ion: NH_3 $\oplus NH_4$

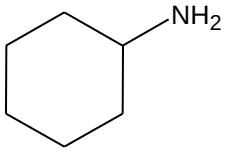
(primer, szekunder, tercier amin) (kvaterner amin)

Alkil-amin:

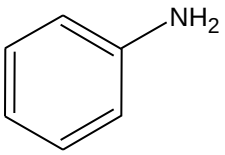
CSOPORTNÉV: amino



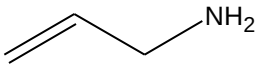
metil-amin



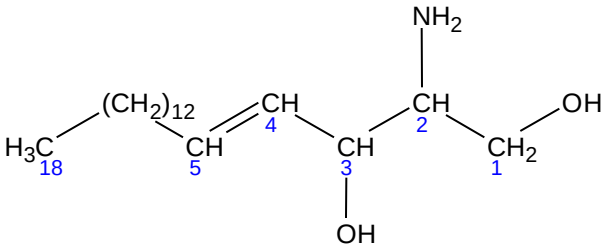
ciklohexil-amin



anilin* (aminobenzol)

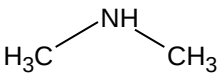


allil-amin

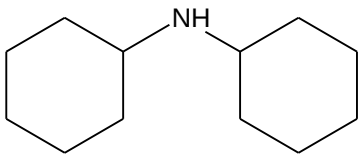


2-amino-4-oktadecén-1,3-diol

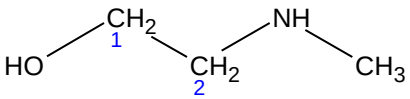
CSOPORTNÉV: alkilamino



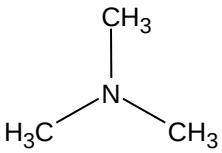
N,N-dimetil-amin



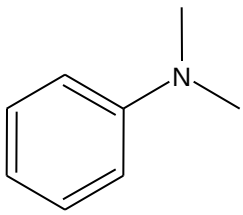
N,N-diciklohexil-amin



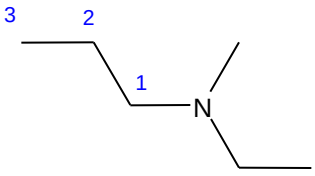
2-metilamino-1-etanol



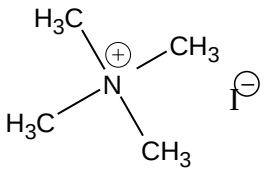
N,N,N-trimetil-amin



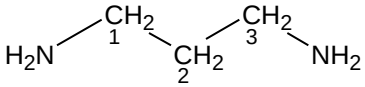
N,N-dimetil anilin



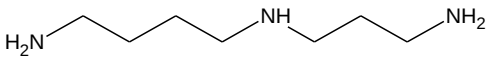
N-metil-N-etil-propilamin



tetrametil-ammónium-jodid

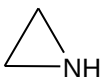


1,3-propán diamin
(trimetiléndiamin)

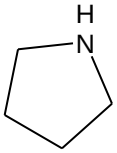


N-propilamino-N-butilamin
(spermidin*)

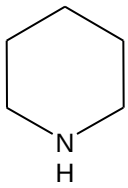
Ciklusos aminok



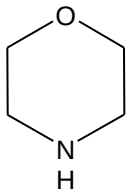
etilénimin



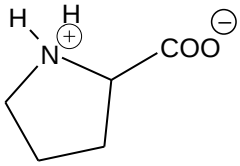
pirrolidin



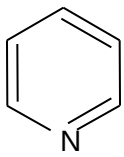
piperidin



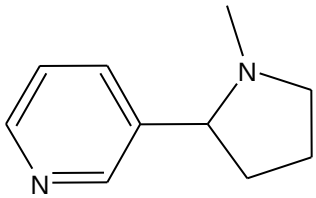
morfolin*



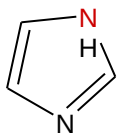
prolin



piridin



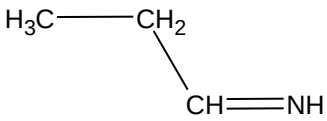
nikotin *



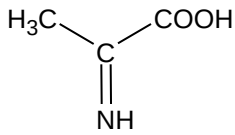
imidazol

B. IMINEK

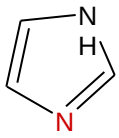
CSOPORTNÉV: imino, alkilimino



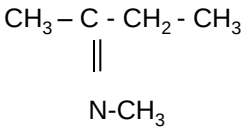
propán-1-imin



α-imino-propánsav



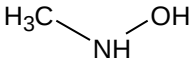
imidazol



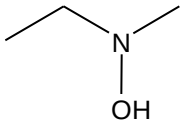
N-metilbután-2-imin
(Schiff-bázis)

C. HIDROXILAMINOK

CSOPORTNÉV: hidroxiamino

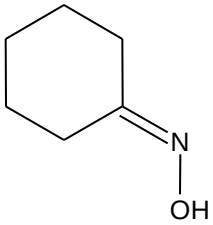


N-metil-hidroxilamin



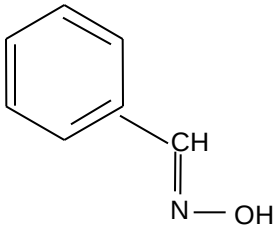
N-etil-N-metil-hidroxilamin

D. OXIMOK



ciklohexanon-oxim

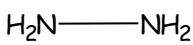
(ketoxim)



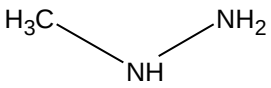
benzaldehid-oxim

(aldoxim)

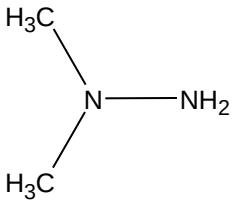
E. HIDRAZINOK



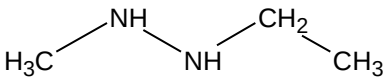
hidrazin



metil-hidrazin

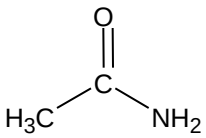


N,N-dimetil-hidrazin

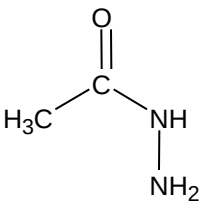


N-etil-N'-metil-hidrazin

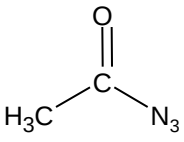
F. KARBONSAVSZÁRMAZÉK



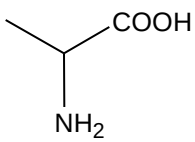
ecetsavamid



ecetsavhidrazid



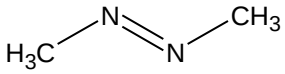
ecetsavazid



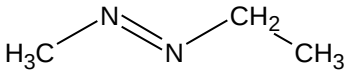
α-amino propánsav, alanin*

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

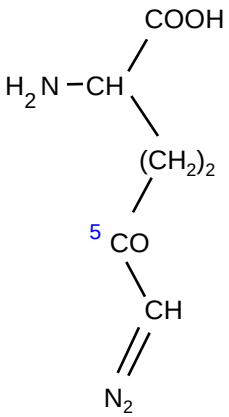
CSOPORTNÉV: alkilazo



azometán



metilazo-etán



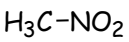
CH_2N_2
diazometán

N_2-CH-COOH
diazoecetsav

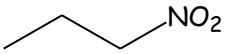
6-diazo-5-oxo-norleucin
(DON)

H. NITRO- ÉS NITROZOVEGYÜLETEK

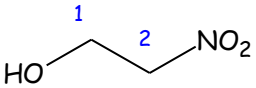
CSOPORTNÉV: nitro, nitrozo



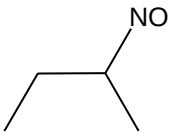
nitro-metán



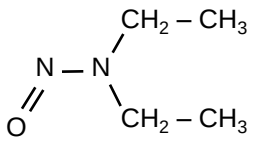
1-nitro-propán



2-nitro-1-etanol



2-nitrozo-bután

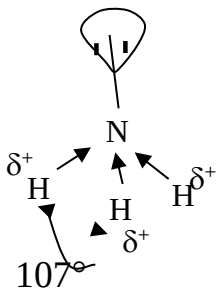


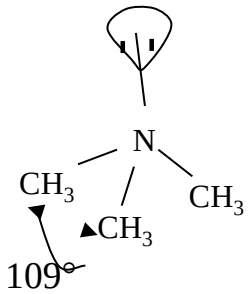
N - nitrozo – N',N' - dietilamin
(whisky)

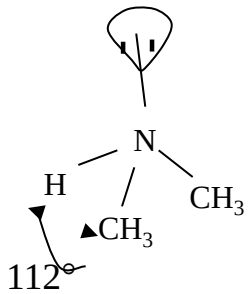
Kémiai szerkezet

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)

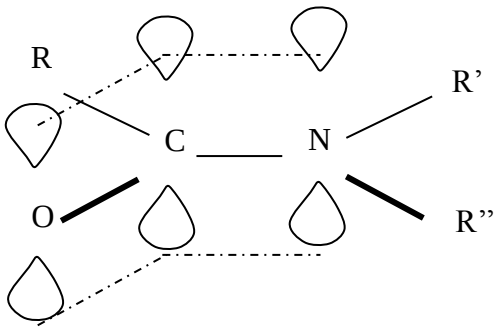
(I)

gyors racemizáció

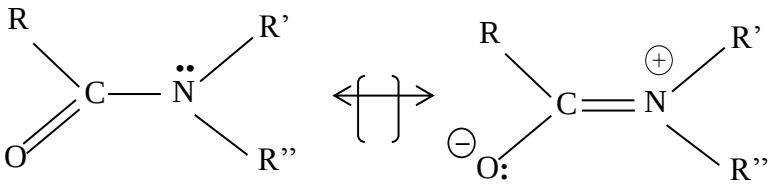
(II)

rezolválható

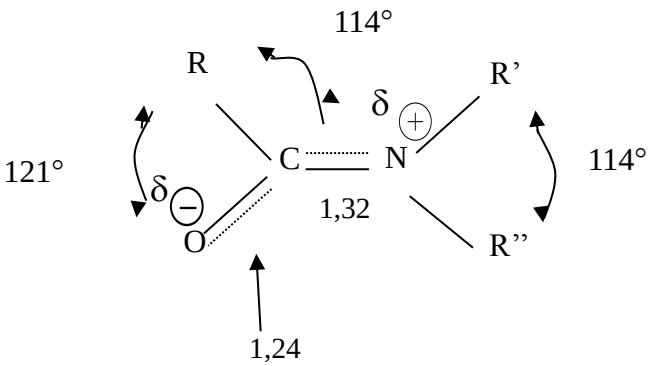
B. KARBONSAVAMIDOK $C(sp^2)$, $O(sp^2)$, $N(sp^2)$



- 3 kötő sp^2 pálya
- 1 nemkötő p pálya
- planáris konfiguráció



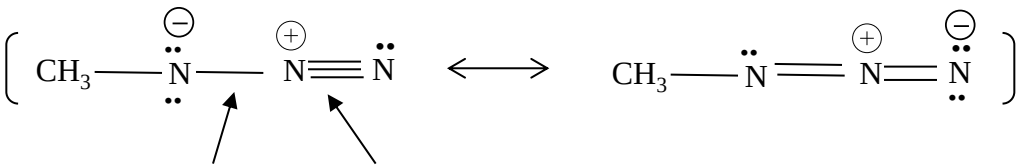
határszerkezetek



gátolt rotáció
cisz-transz izoméria

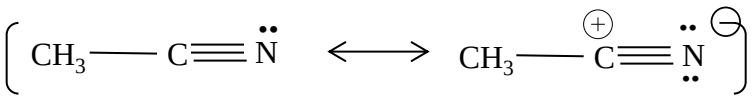
C. KARBONSAVAZIDOK $C(sp^3)$, $N(sp)$

metilazid



126 pm 112 pm

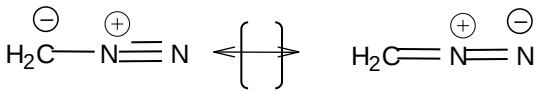
D. KARBONSAVNITRILEK $C(sp)$, $N(sp)$



acetonitril

E. DIAZOVEGYÜLETEK $C(sp^2)$, N(sp)

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

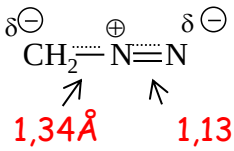


C-N 1,47Å

N=N 1,24Å

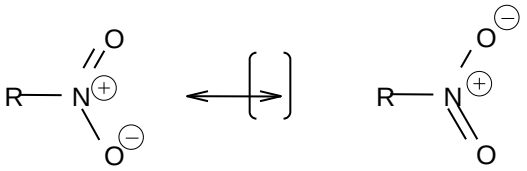
C=N 1,34Å

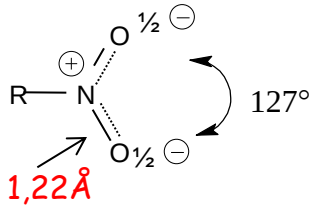
N≡N 1,09Å



lineáris konfiguráció konjugált rendszer

F. NITROVEGYÜLETEK $C(sp^3)$, $O(sp^2)$, N(sp²)

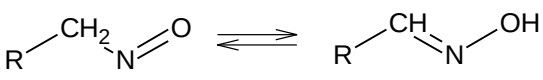


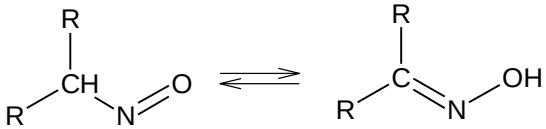


planáris konfiguráció szimmetrikus konjugált rendszer

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

G. NITROZOVEGYÜLETEK $C(sp^3)/C(sp^2)$, $O(sp^2)$, N(sp²)



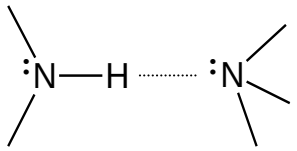


nitrozo – oxim tautomeria

Fizikai sajátságok

A. AMINOK

H-híd: donor és akceptor



1. Oldékonyság: vízben jobb, mint az alkoholok

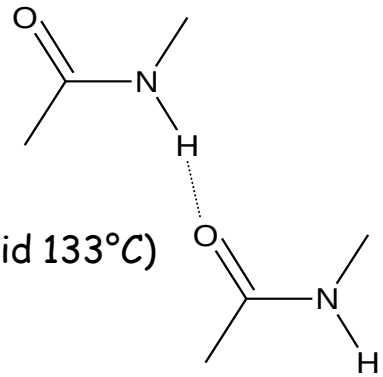
oldószerek: dietil-amin, trietil-amin (89,5°C), piperidin (106°C), morfolin (129°C)

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

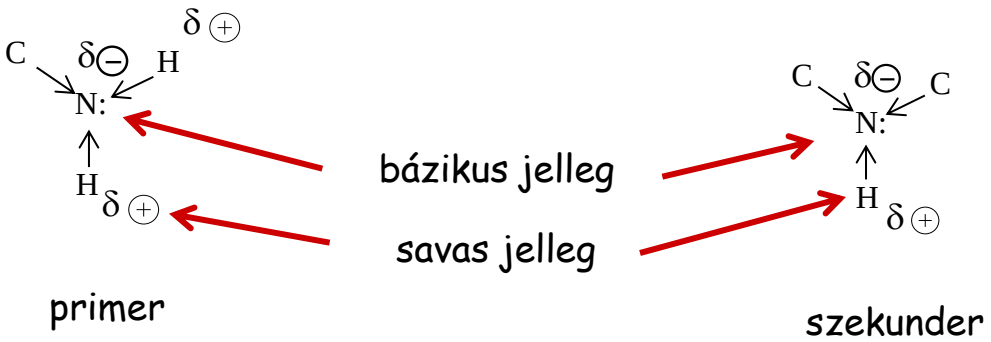
Aminok kémiai reakciói

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

1. Sav-bázis sajátságok

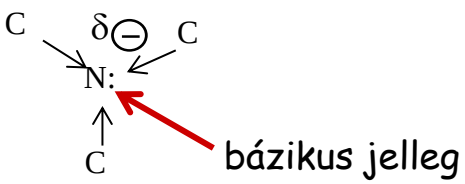
EN(N)=3,0 EN(C)=2,5

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



primer

szekunder



tercier

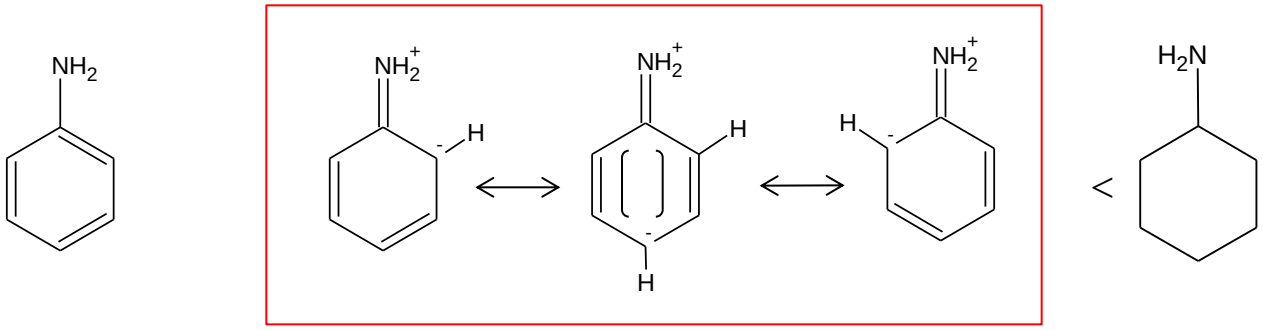
A. Telített aminok

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

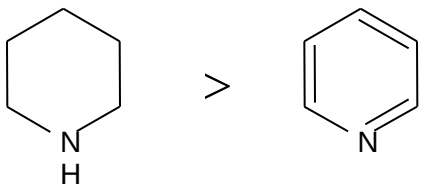
$pK_b = 9,42$

protonált anilin

ciklohexil-amin

$pK_b = 3,35$

C. Heterociklusos aminok



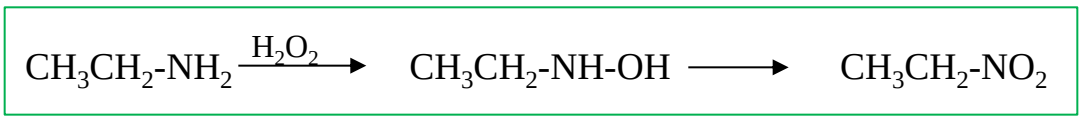
piperidin piridin

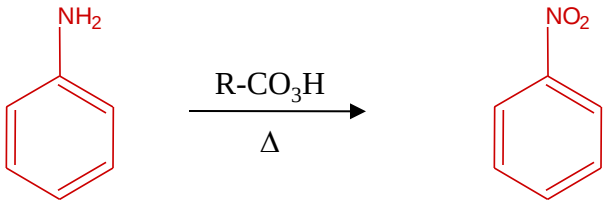
$N(sp^3)$ > $N(sp^2)$

$pK_b = 2,8$ 8,8

2. Oxidáció, redukció

Aminok oxidációja



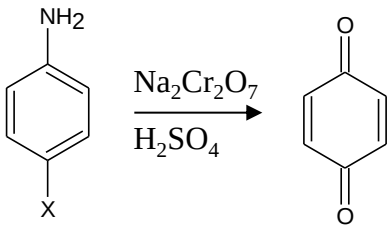


nitrobenzol

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

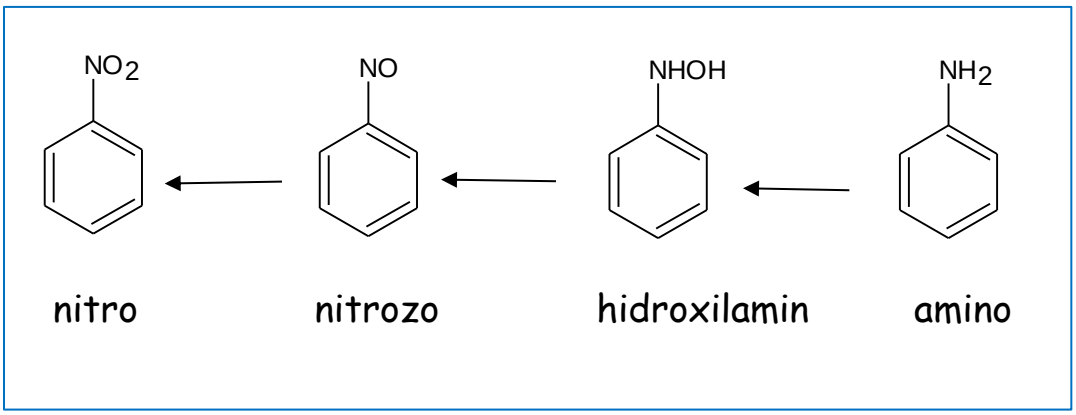
$(CH_3)_2\text{-}NH \xrightarrow[R\text{-}CO_3H]{H_2O_2 \text{ vagy}} (CH_3)_2N\text{-}OH$ hidroxilamin

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



X=H, OH, NH_2
(csak para)

Aromás aminovegyületek oxidációja



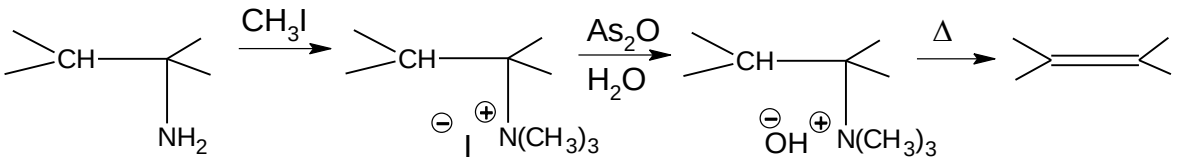
Összehasonlítás: N tartalmú vegyületek redukciója

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

Lásd még: $-CO\text{-}NH_2$, $-CO\text{-}NHR$, $-CO\text{-}NR_2$, $-CN$

3. Eliminációk

Hofmann-elimináció - aminok

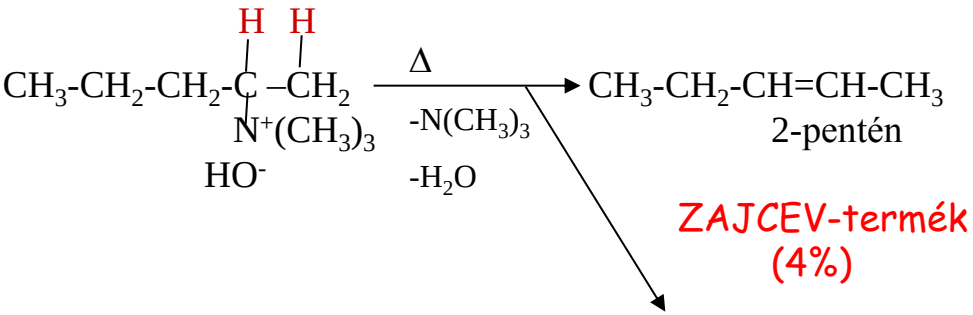


primer amin

olefin

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

Példa



2-pentil-trimetil-ammónium hidroxid

CH_3-CH_2-CH_2-CH=CH_2
1-pentén

HOFMANN-termék
(96%)

4. Szubsztitúció

ALKILEZÉS

A. alkil – halogenid (R-X)

B. alkohol

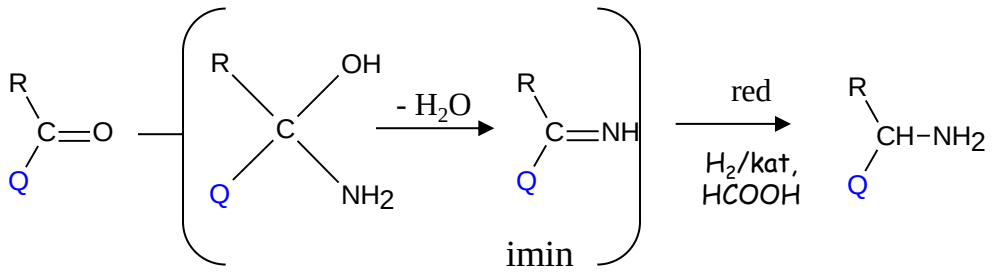
C. oxovegyület (reduktív)

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

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

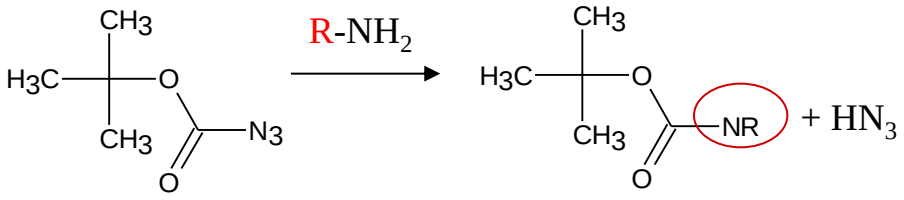
C. $NH_3 +$ 

ACILEZÉS

karbonsavszármazékok

$CH_3\text{-}NH_2$ +	R-CO-Cl	$CH_3\text{-}NH\text{-}CO\text{-}R$ +	HCl
	R-CO-O-CO-R	acil-amin	R-COOH
	R-CO-OEt		EtOH
	R-CO-N_3		HN_3

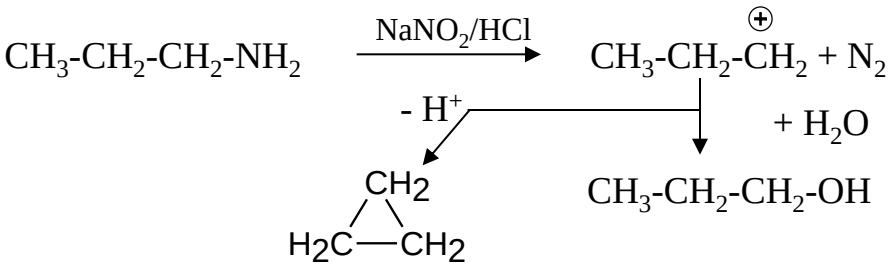
Példa: sav -azid + $R\text{-}NH_2$



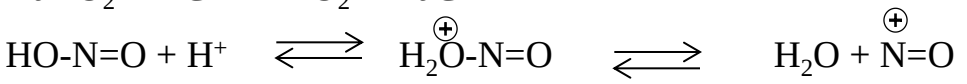
tbutiloxi-karbonil-azid BOC-amin(osav)

5. Reakció salétromossavval

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

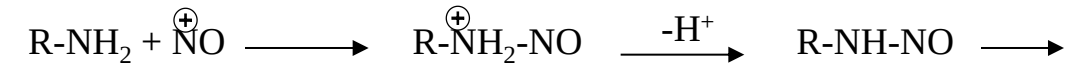


Reagens: $NaNO_2 + HCl = HNO_2 + NaCl$

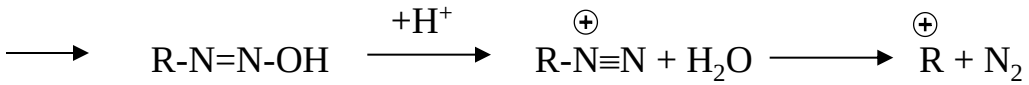


nitrozil kation

Mechanizmus



N-nitrozo-amin



„diazo”-sav

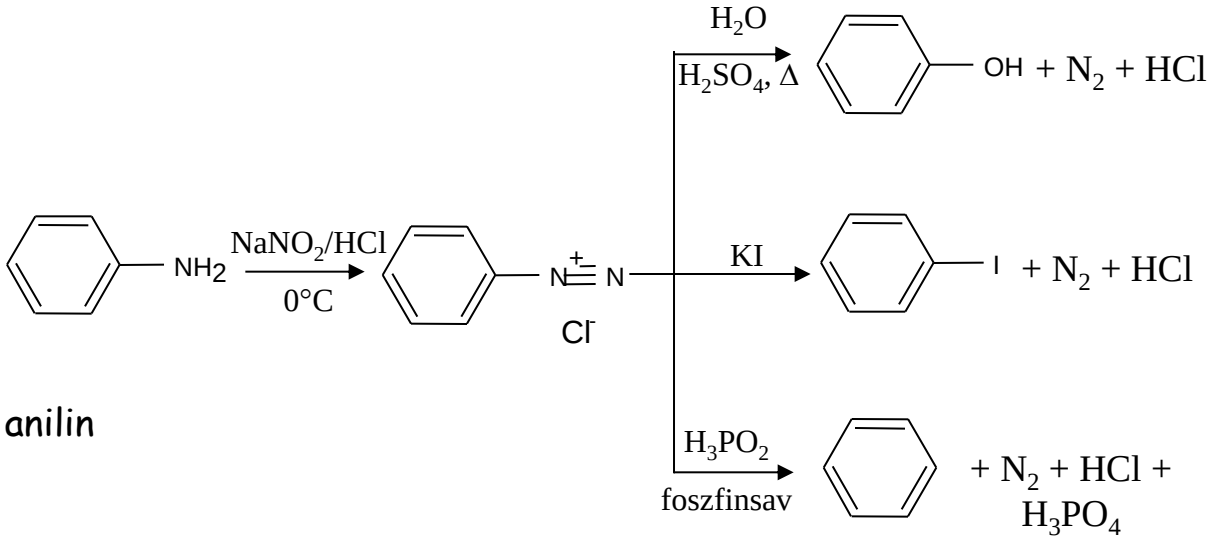
diazónium ion

karbénium ion

Felhasználás:

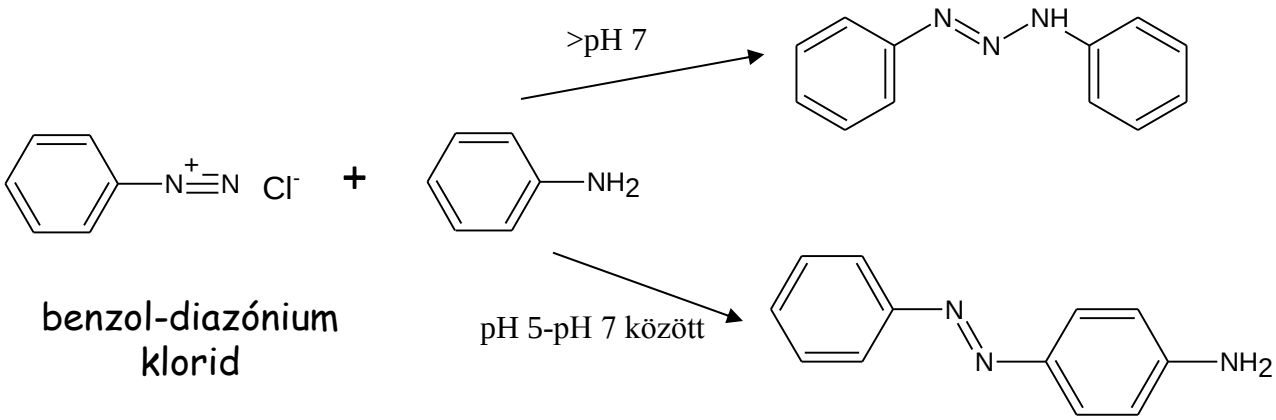
primer amin:	N_2
szekunder amin:	sárga olaj vagy csapadék
tercier amin:	nincs N_2, nincs csapadék

Aromás amin (diazotálás)



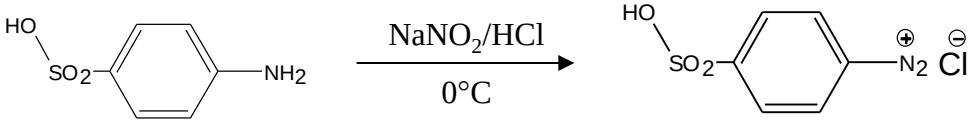
anilin

Kapcsolási reakciók

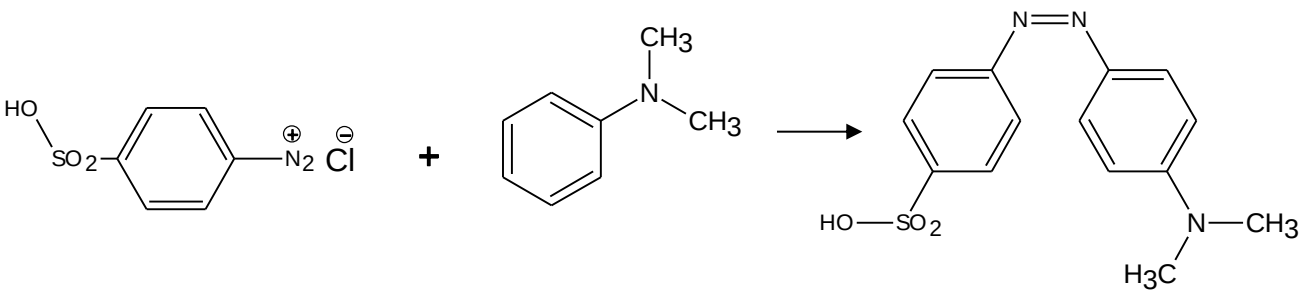


benzol-diazónium klorid

színezékipar



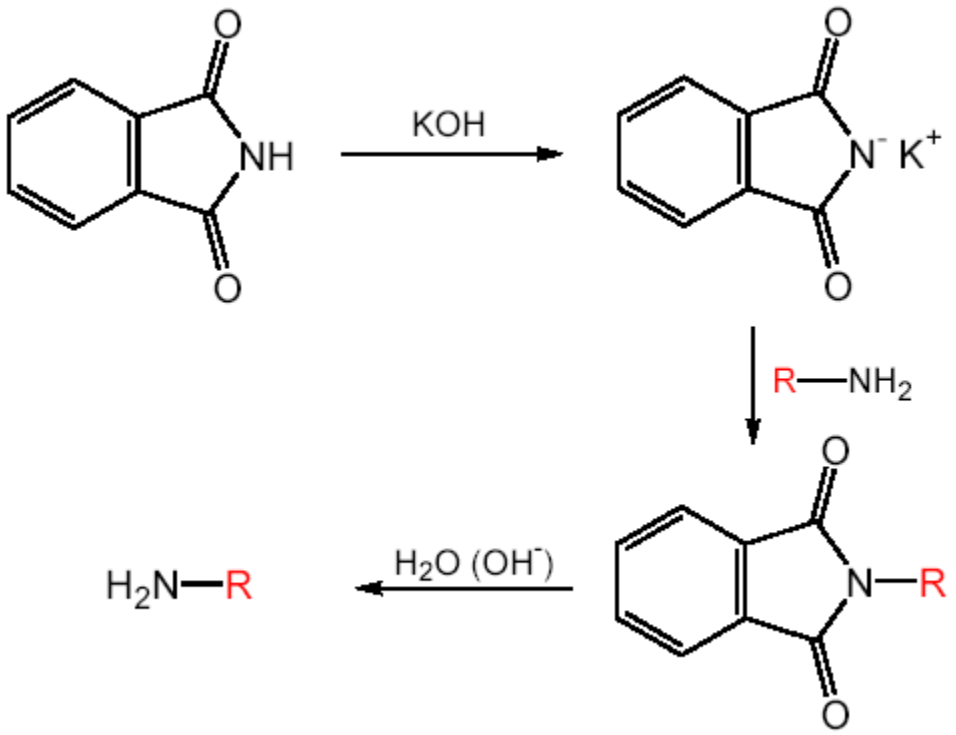
szulfanilsav



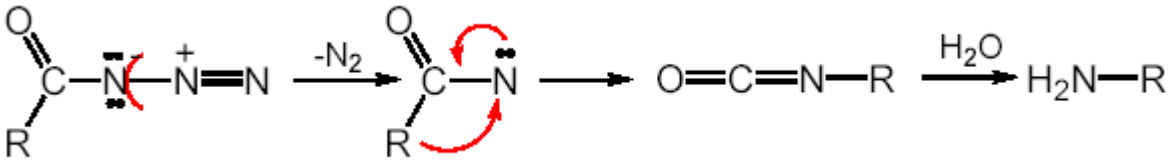
Aminok előállítása

1. Ammónia alkilezése

2. Gabriel szintézis



3. Curtius lebontással karbonsavazidból

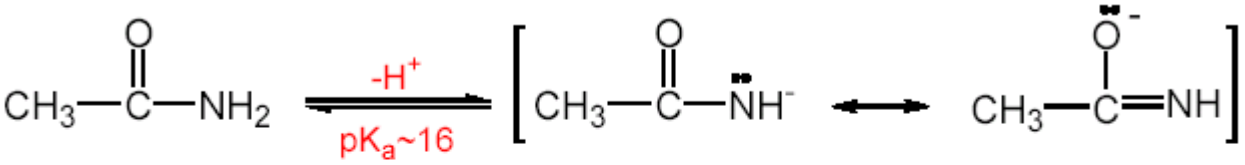


Karbonsavamidok reakciói

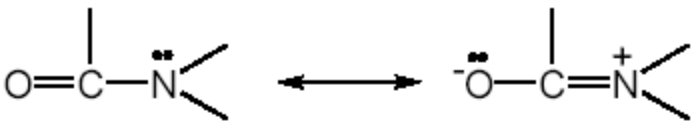
1. Sav-bázis sajátságok
2. Redukció, oxidáció

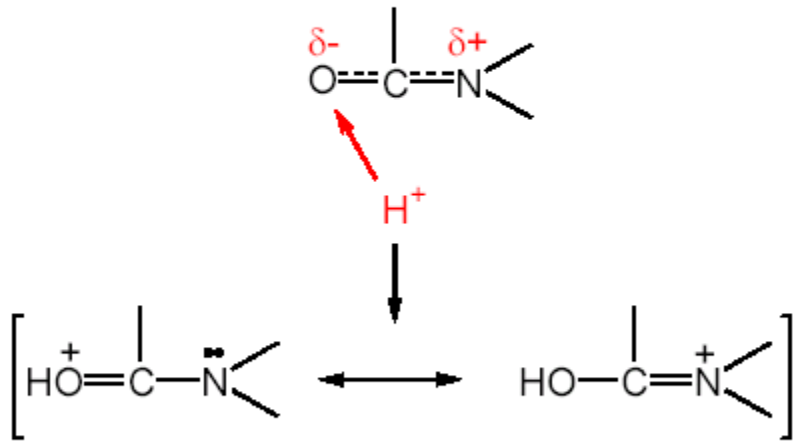
1. Sav-bázis sajátság

Savasság (N-H savak)



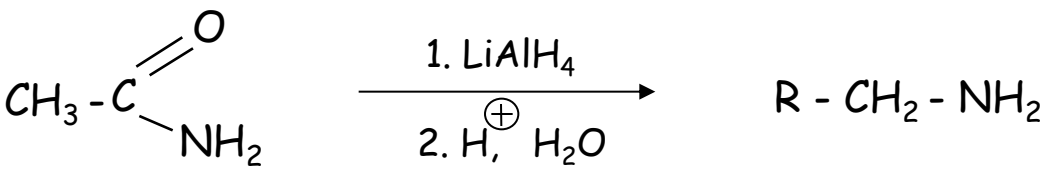
Bázicitás





CH_3-CO-NH_2: pK_b = 13.7

2. Redukció (lásd: karbonsavszármazékok)



primer amid

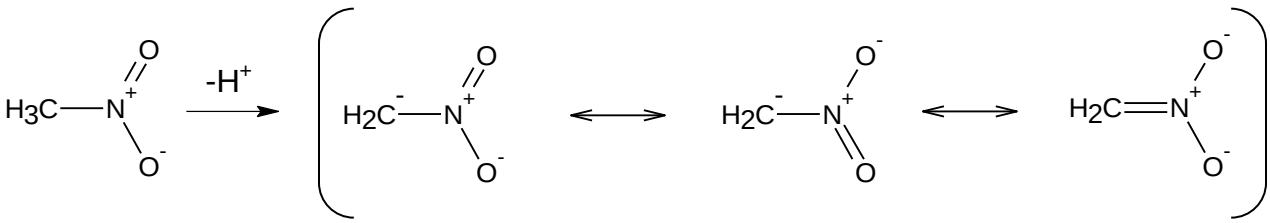
primer amin

Nitrovegyületek reakciói

1. Sav-bázis sajátságok
2. Redukció, oxidáció

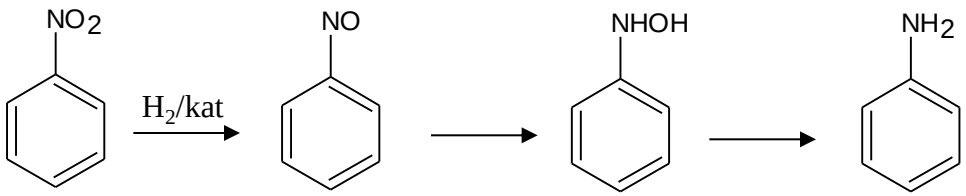
1. Nitrovegyületek *C-H savak*

CH_3NO_2, primer és szekunder nitrovegyületek lúgban oldódnak



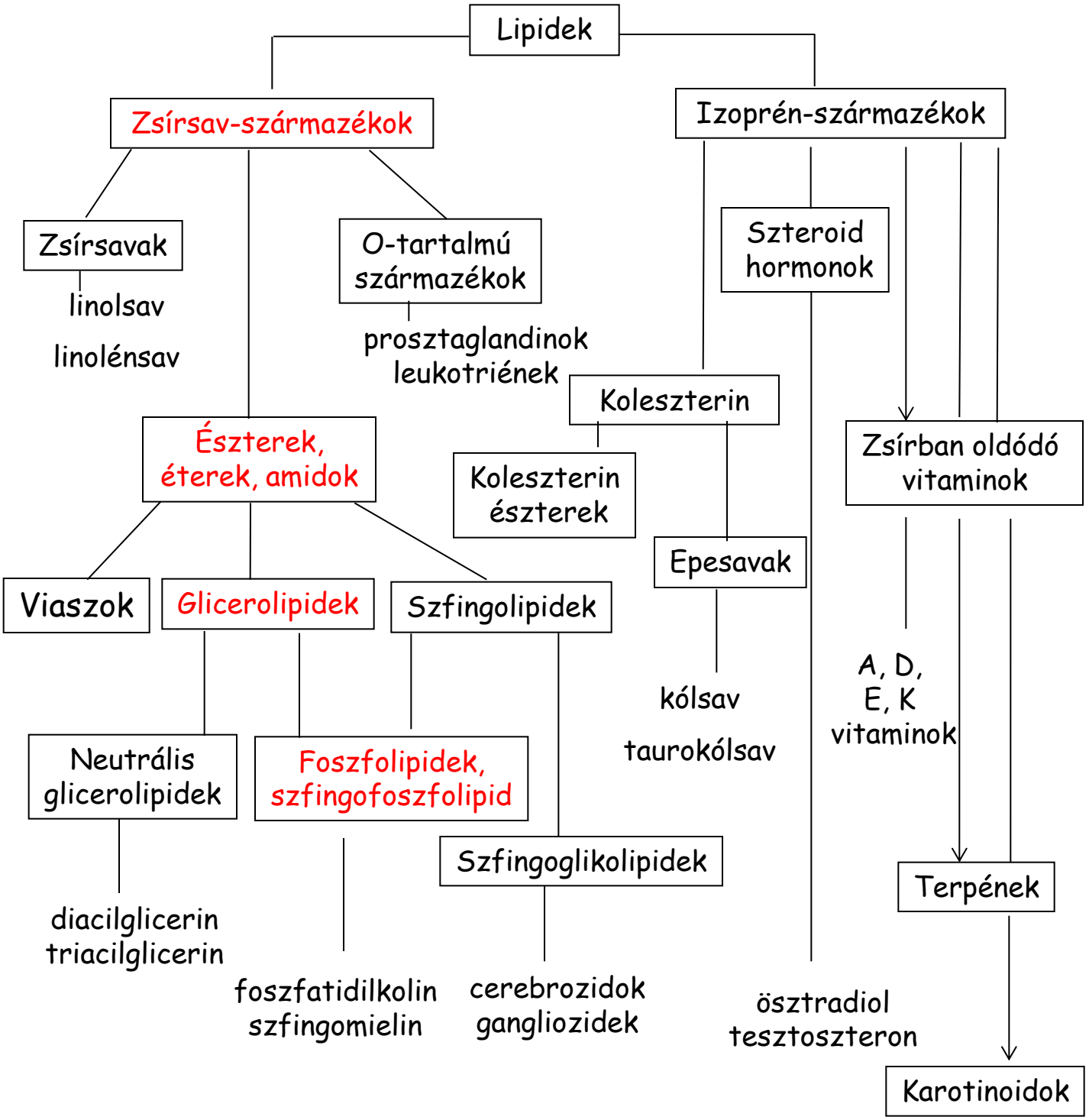
4 atom, 4 elektron konjugáció

2. Nitrovegyületek redukciója



nitro nitrozó hidroxilamin amino

Egyszerű lipidek



Glicerofoszfolipidek

Definíció: növényi vagy állati szövetből apoláros oldószerrel (éter, kloroform, benzol stb.) kioldható anyag

Egyszerű lipidek

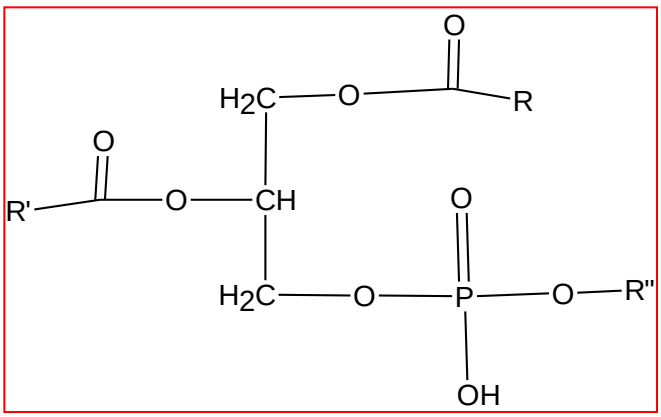
Néhány biológiai membrán lipid összetétele[a]

lipid	Százalékos összetétel			
	humán vvt plazma membrán	humán mielin	marhaszív mitokondrium	*E. coli* sejtmembrán
foszfatidsav	1,5	0,5	0	0
foszfatidilkolin	19	10	**39**	0
foszfatidiletanolamin	18	20	27	**65**
foszfatidilglicerin	0	0	0	**18**
foszfatidilinozitol	1	1	7	0
foszfatidilszerin	8,0	8,0	0,5	0
szfingomielin	**17,5**	8,5	0	0
glikolipidek	10	26	0	0
koleszterin	25	26	3	0
egyéb	0	0	23,5	17

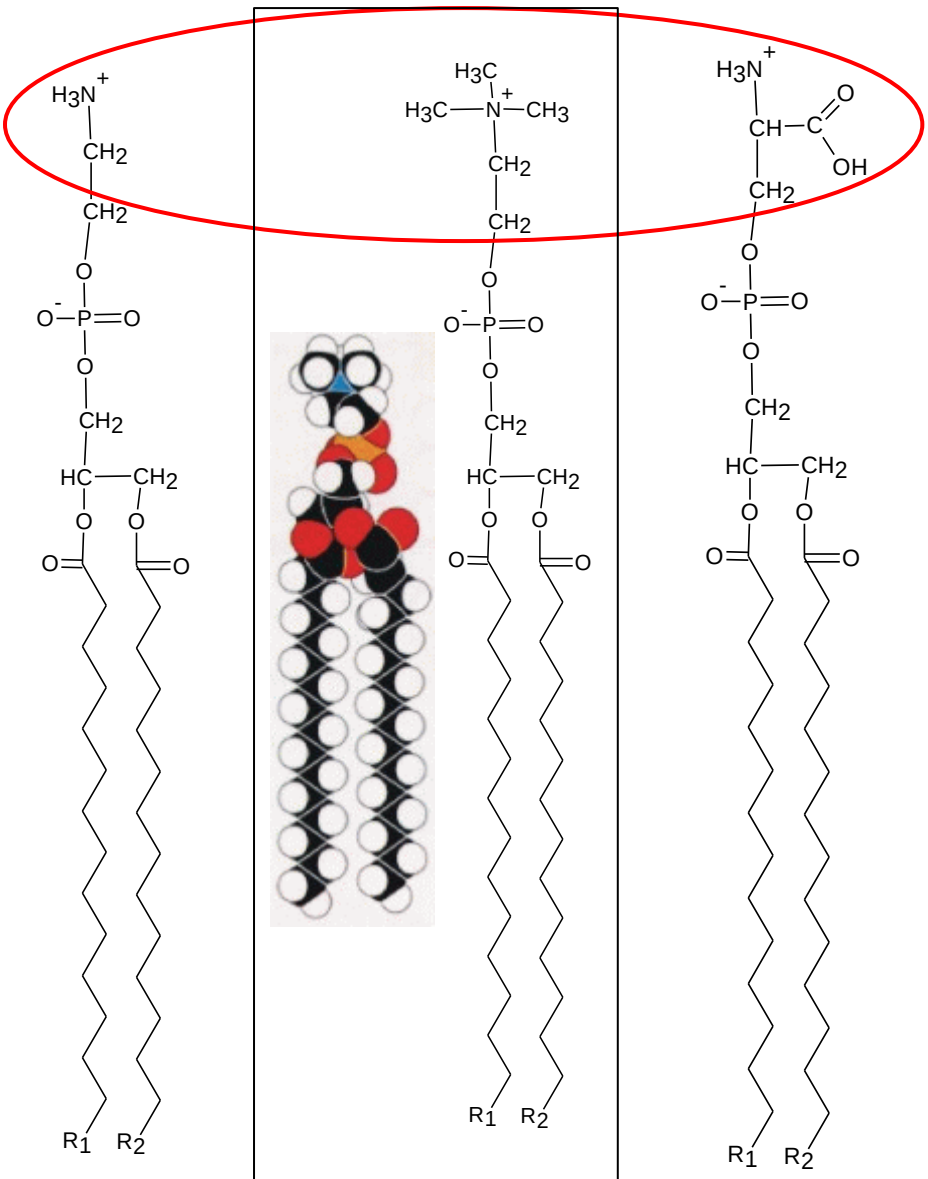
[a]Adatok forrása: C. Tanford, *The Hydrophobic Effect* (New York: Wiley, 1973)

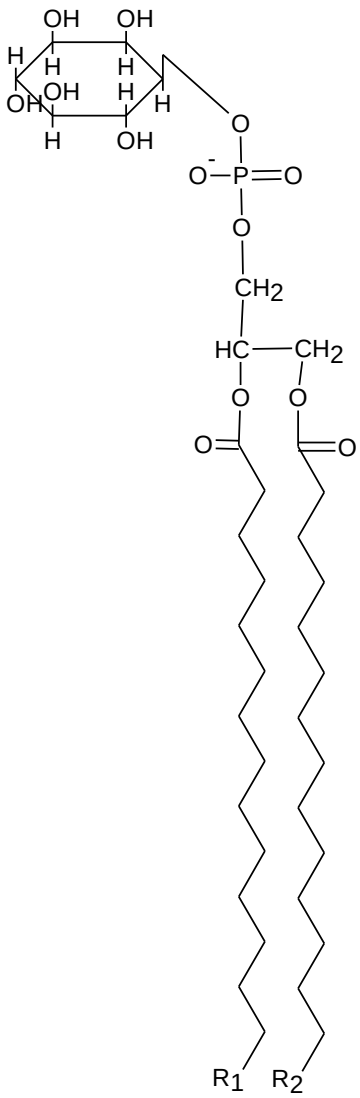
Összetett lipidek

- lipoproteinek
- proteolipidek
- foszfatido/foszfolipopeptidek
- lipoaminosavak, lipopeptidek
- lipopoliszacharidok



R" = etanolamin
kolin
szerin
inozitol





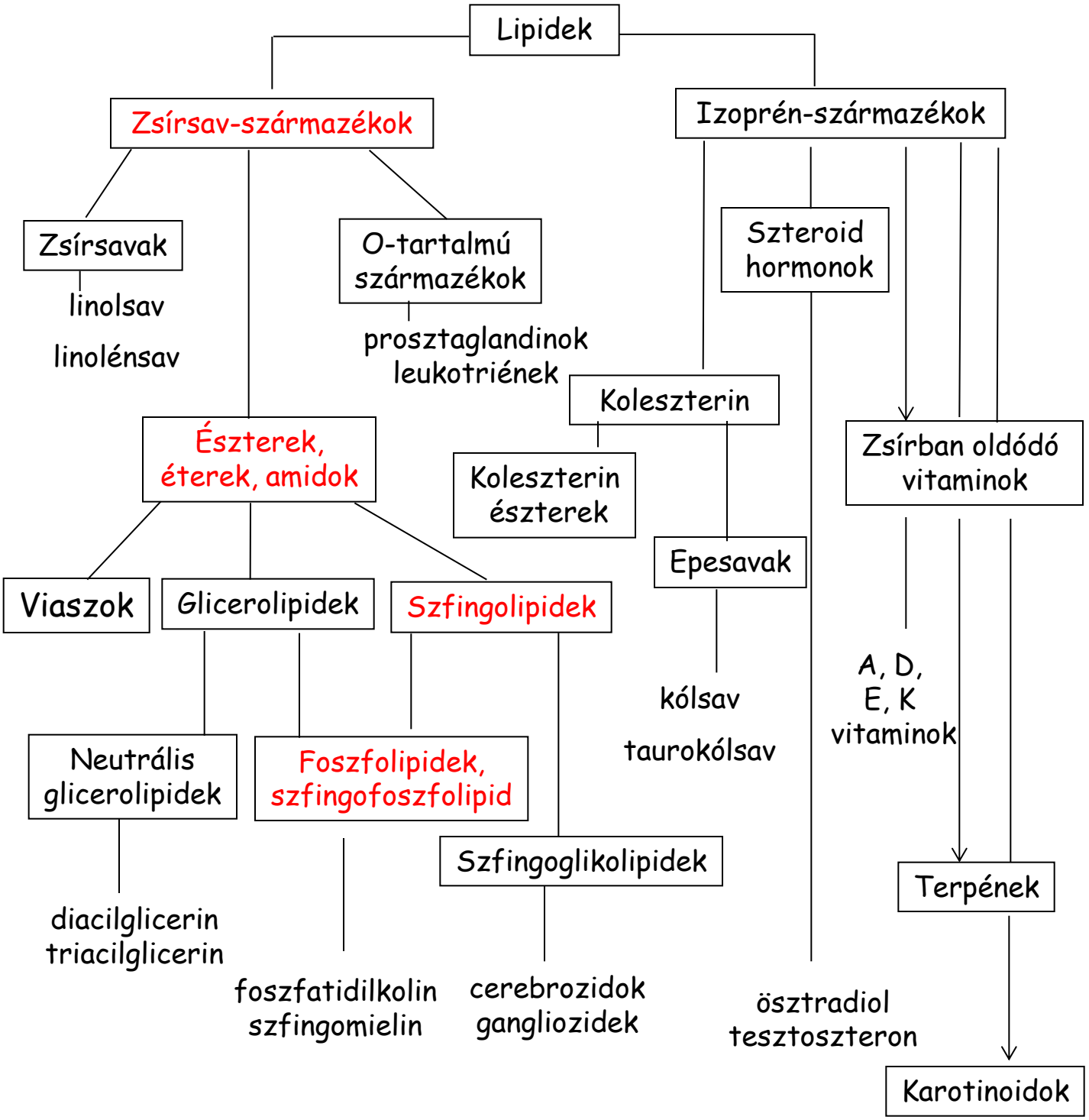
foszfatidil-
-etanolamin
(kefalin)

foszfatidil-
-kolin
(lecitin)

foszfatidil-
-szerin

foszfatidil-
-inozitol

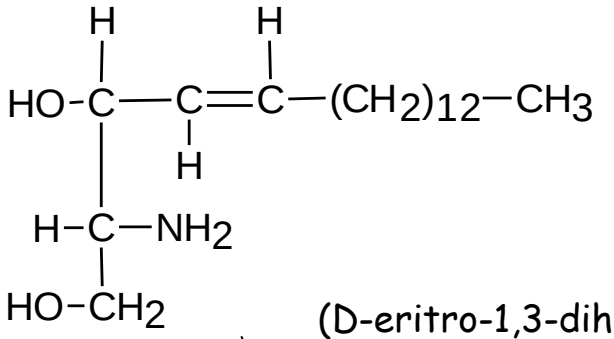
Egyszerű lipidek



Szfingolipidek

Mielinalkotók, axonvédők („szigetelők")

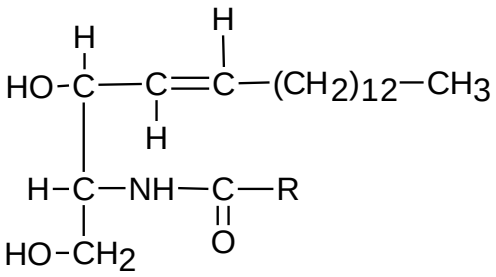
Alkohol komponens: <u>nem</u> glicerin, hanem a szfingozin, kb. 60 féle



Szfingozin

(D-eritro-1,3-dihidroxi-2-amino-transz-4-oktadecén)

acilezés



R = szénhidrogén

ceramid

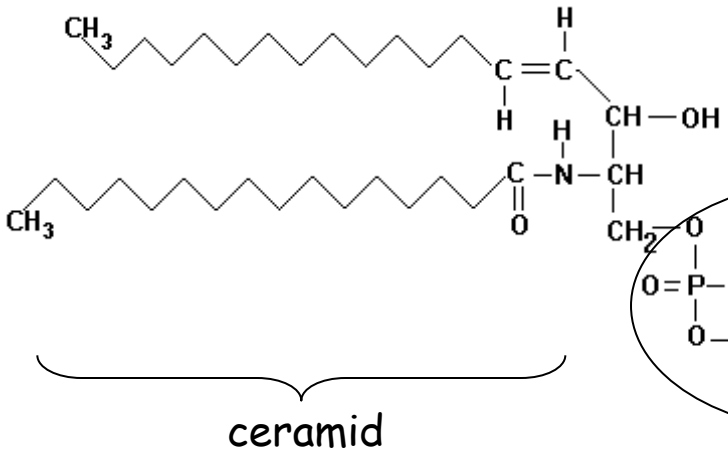
B

éterkötés

A

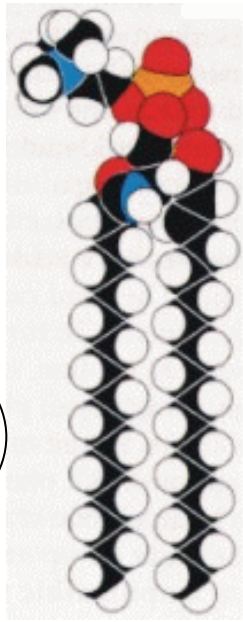
észterképzés

A észterképzés



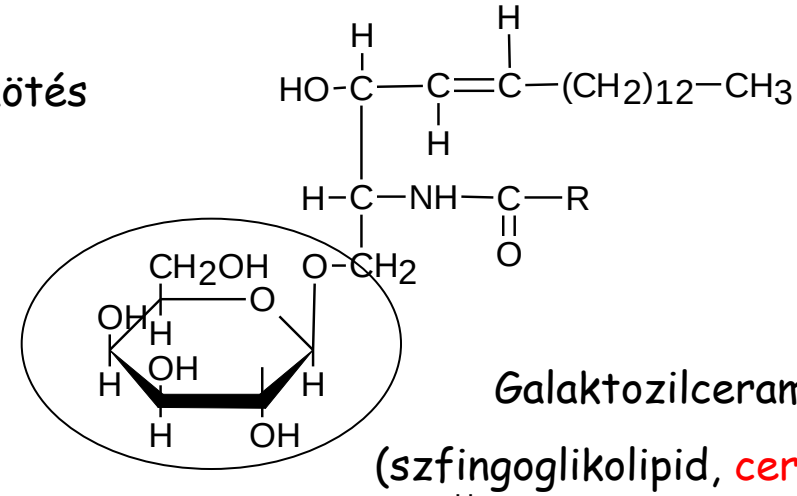
ceramid

foszfokolin



Szfingomielin (szfingofoszfolipid)

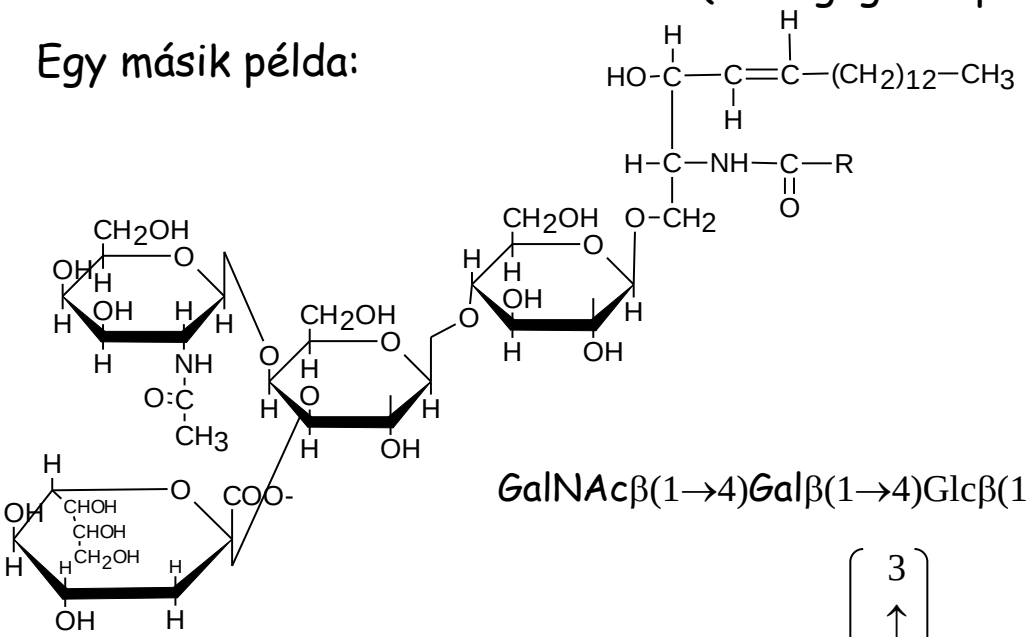
B éterkötés



Galaktozilceramid

(szfingoglikolipid, cerebrozid)

Egy másik példa:



GalNAcβ(1→4)Galβ(1→4)Glcβ(1→1)ceramid

(szfingoglikolipid, gangliozid)

$\left(\begin{array}{c} 3 \\ \uparrow \\ \alpha 2 \end{array}\right)$

Sia

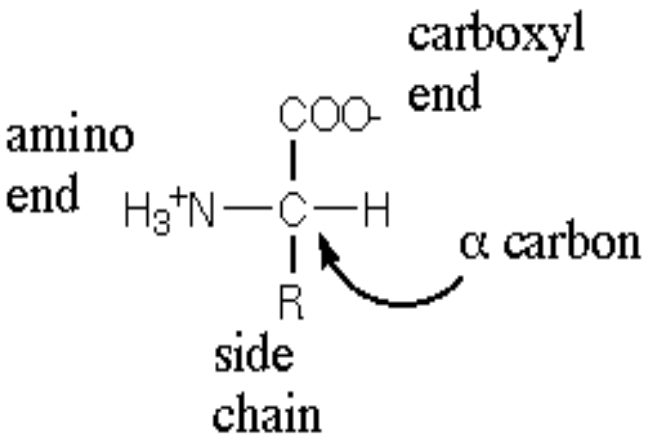
Aminosavak

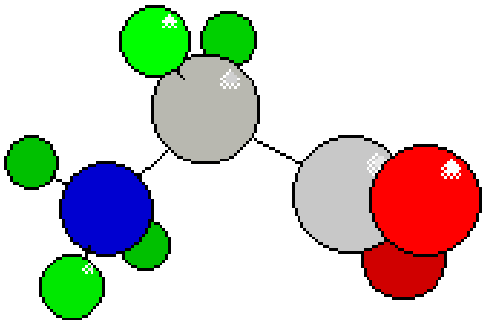
Peptid hatóanyagok

Peptide	Length	Method[a]
Oxytocin	9	C
Vasopressin analogues		
Pitressin	9	C
Lypressin	9	C
Desmopressin	9	C, SP
Terlipressin	12	C, SP
Atosiban	9	C
Adrenocorticotropic hormone (ACTH) (1–24)	24	C
Insulin	51	E, S, R
Glucagon	29	E, SP, R
Secretin	27	E
Calcitonins		
Human	32	C
Salmon	32	C, SP
Eel	32	C, SP
Dicarba-Eel (Elcatonin)	31	C, SP
Luteinizing hormone–releasing hormone (LH-RH) and analogues	10	C, SP
Leuprolide	9	C
Deslorelin	9	SP
Triptorelin	10	SP
Goserelin	10	SP
Buserelin	9	SP
Parathyroid hormone (PTH) (1–34)	34	SP
Corticotropin releasing factors		
Human	41	SP
Ovine	41	SP
Growth hormone releasing factor (1–29)	29	SP
Somatostatin and analogues	14	C, SP
Lanreotide	8	SP
Octreotide	8	C
Thyrotropin releasing hormone (TRH)	3	C
Thymosin α-1	28	SP
Thymopentin (TP-5)	5	C
Cyclosporin	11	E
Integrilin	7	C

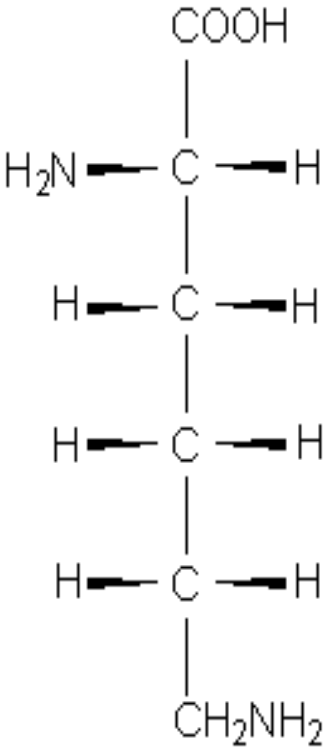
[a] Manufacturing methods: C = classical (solution-phase) chemical synthesis; E = extraction from natural sources; R = recombinant; S = semisynthesis; SP = solid-phase chemical synthesis.

Aminosavak: alaptulajdonságok



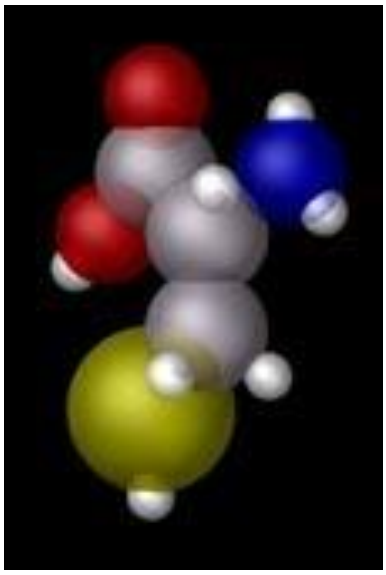


glicin



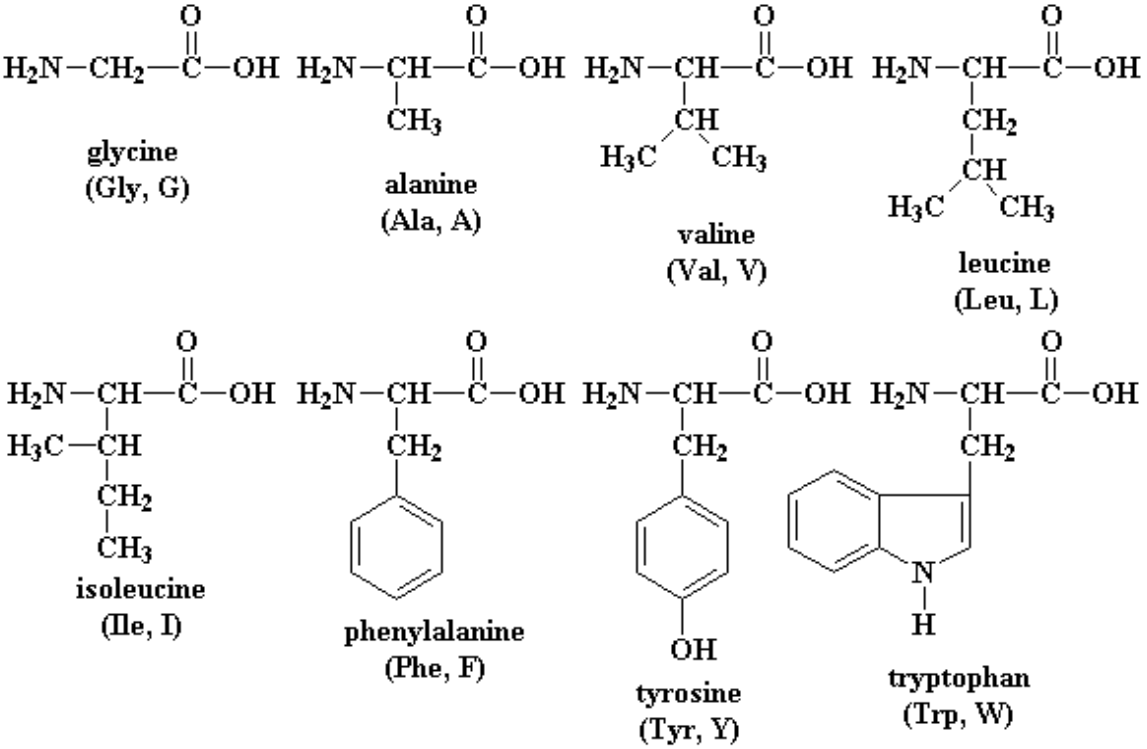
lizin

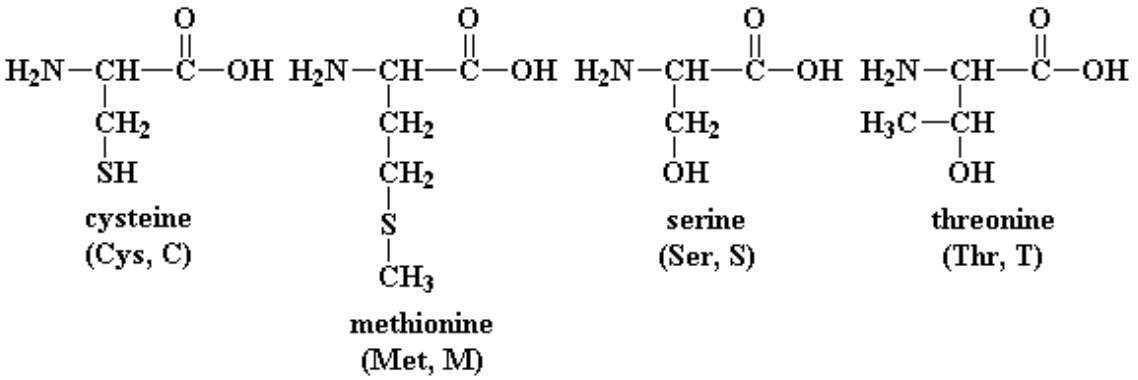
(Fischer projekció)

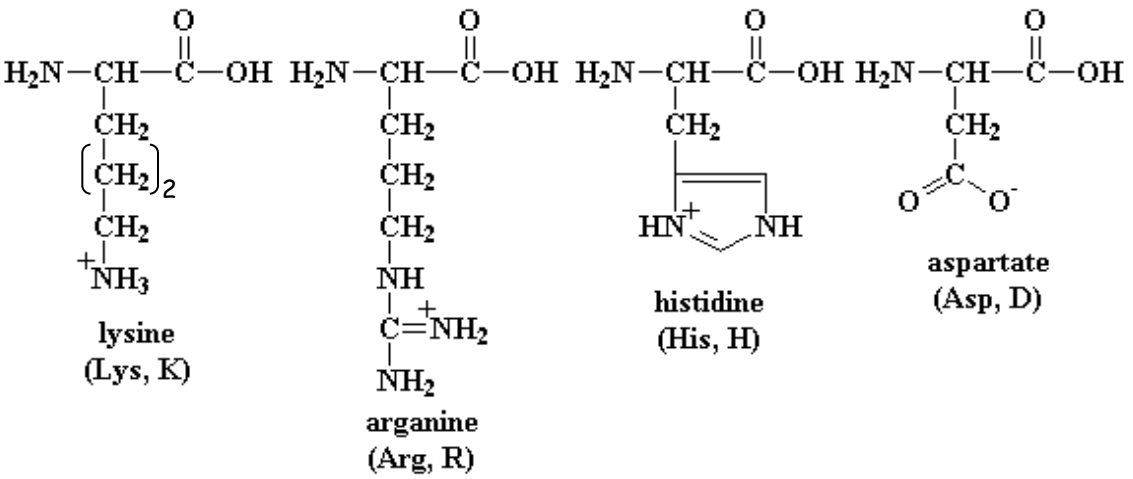


cisztein (space filling model)

Proteinalkotó aminosavak: osztályozás

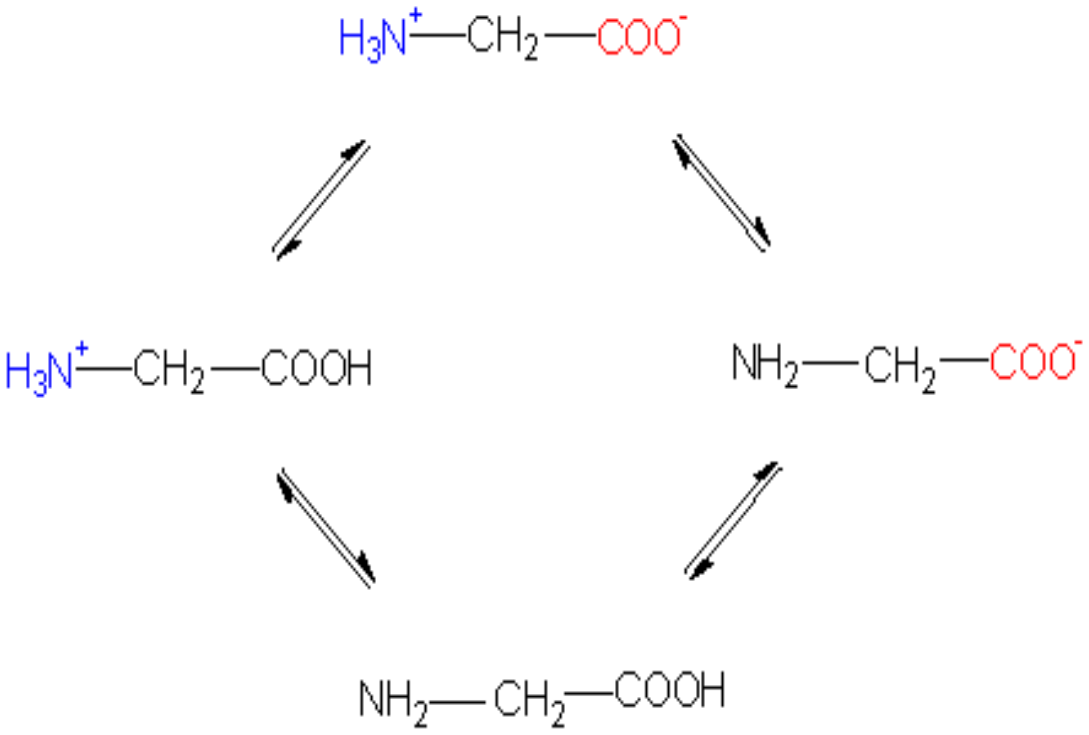


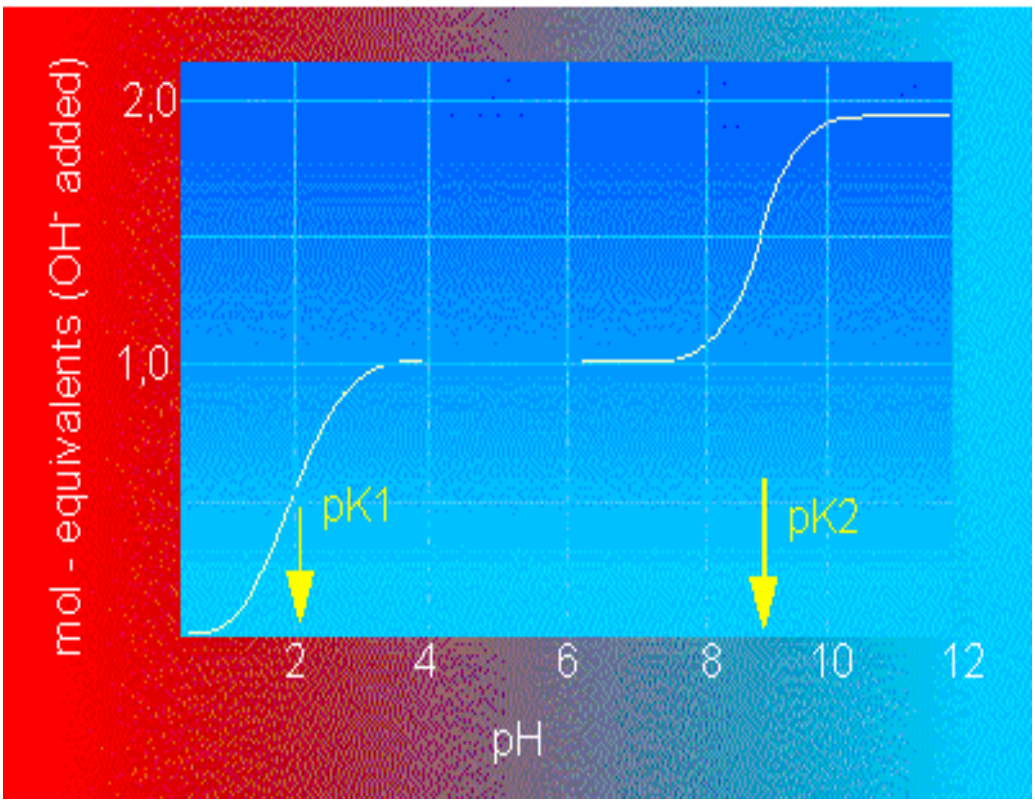


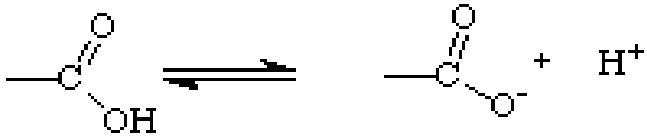
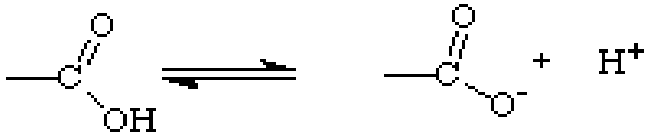
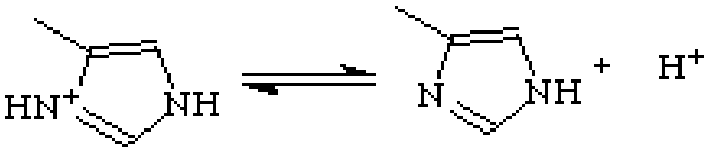
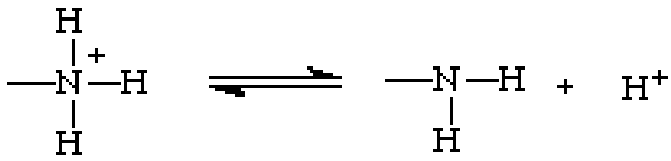
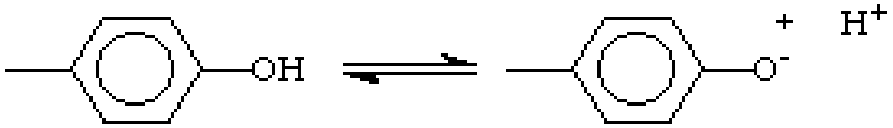
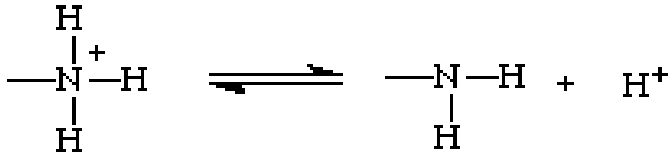
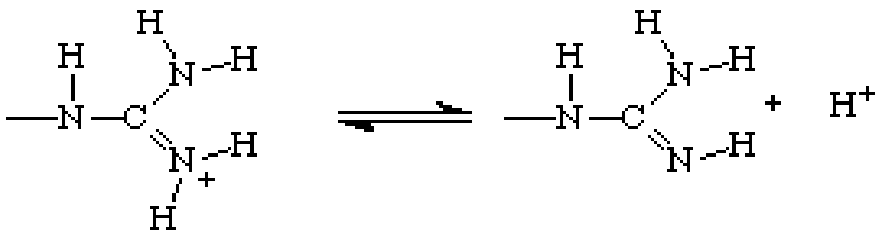


!

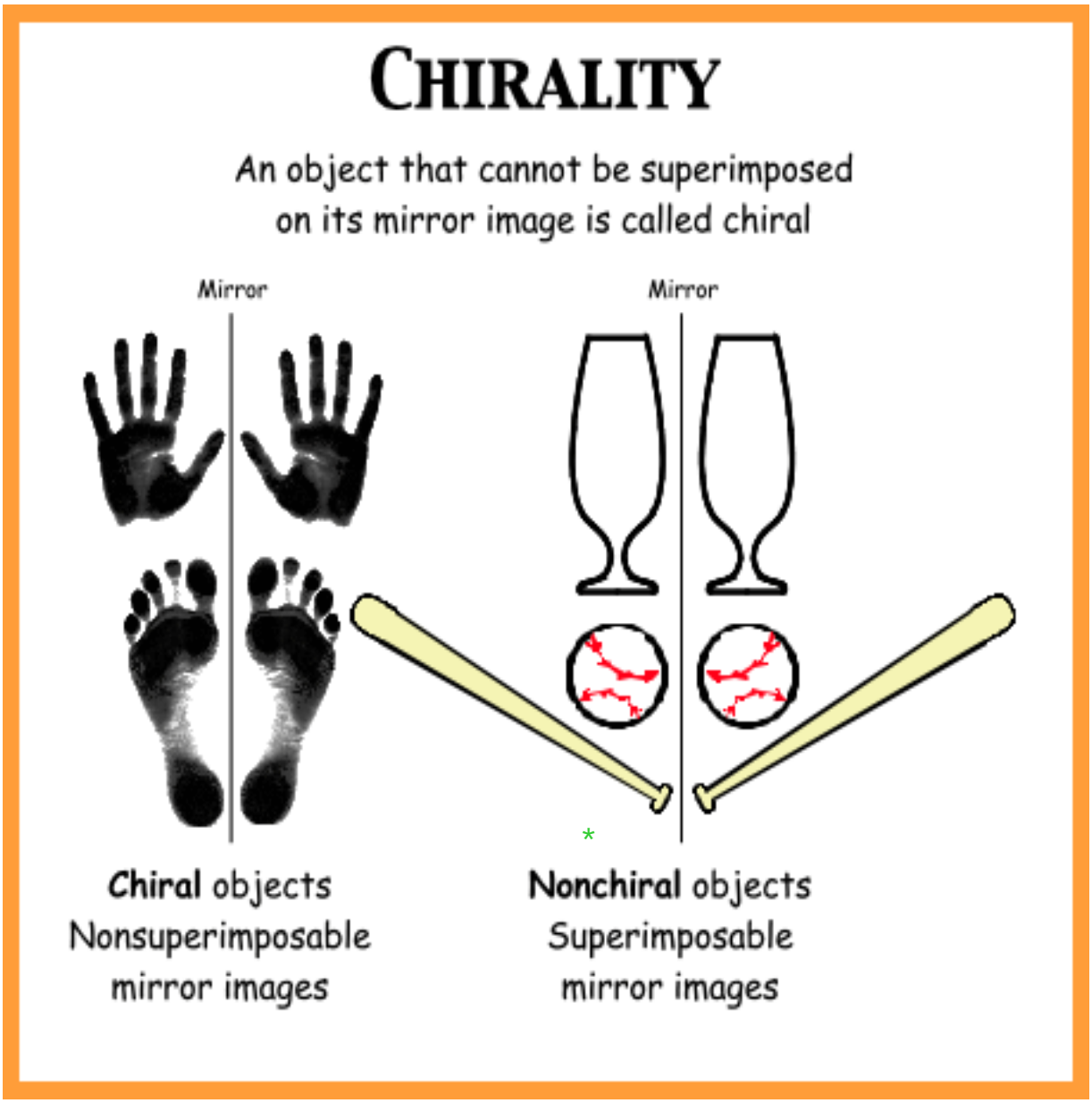
Aminosavak: α-zwitter ion és ω oldallánc

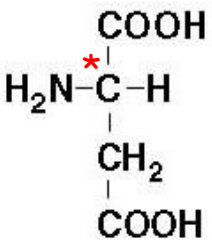




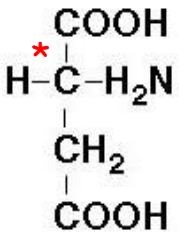
Group	Acid ⇌ Base + H^+	pK_a
Terminal carboxyl		3.1
aspartic acid or glutamic acid		4.4
Histidine		6.5
Terminal Amino		8.0
Cysteine		8.5
Tyrosine		10.0
Lysine		10.0
Arginine		12.0

Aminosavak: kiralitás



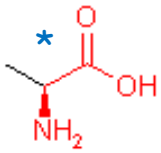


L - aszparaginsav

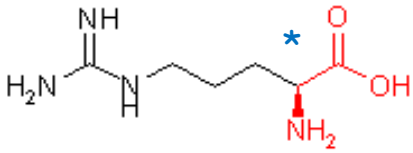


D - aszparaginsav

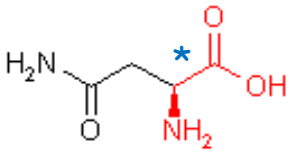
Aminosavak: kiralitás



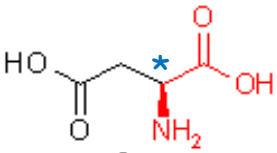
Ala



Arg



Asn



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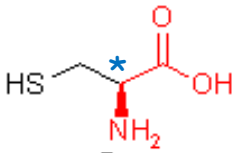
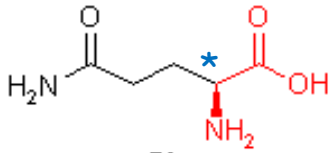
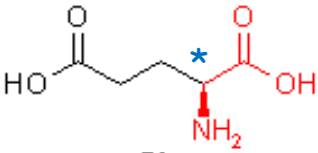


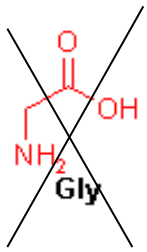
Cys



Gln



Glu



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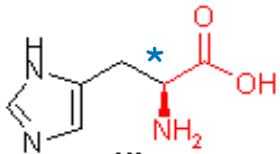
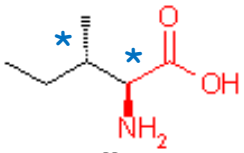
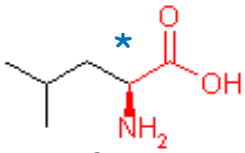


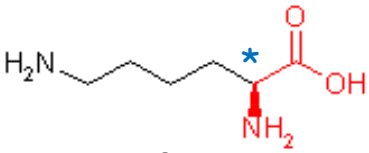
His



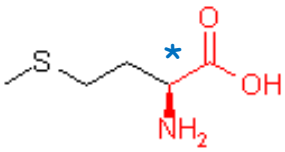
Ile



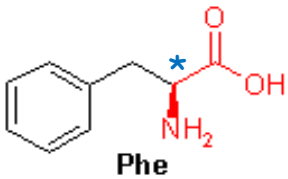
Leu



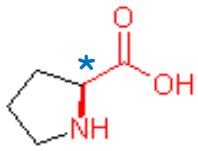
Lys



Met



Phe



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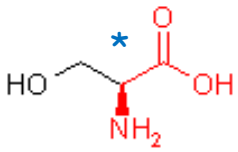
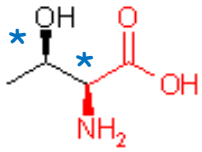
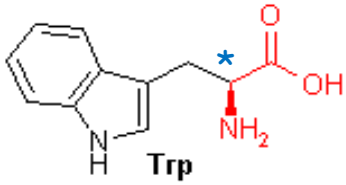


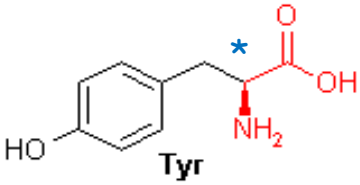
Ser



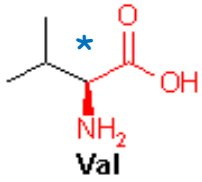
Thr



Trp

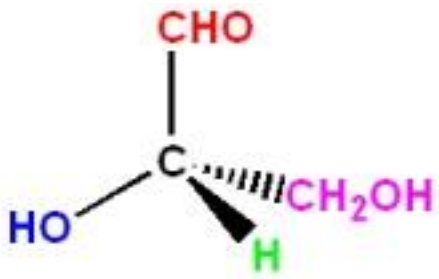


Tyr

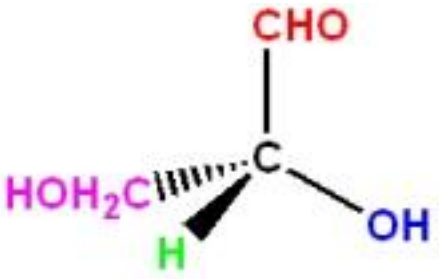


Val

Aminosavak: D/L nomenklatura



L(-) glicerinaldehid



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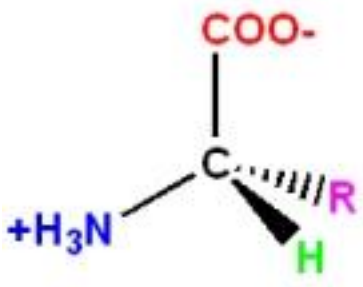
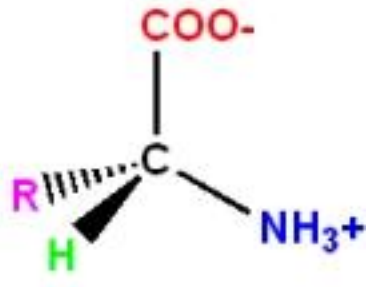
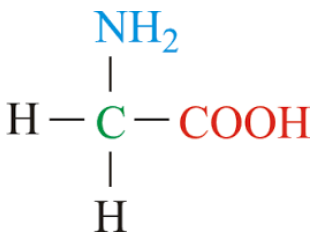


L - aminosav



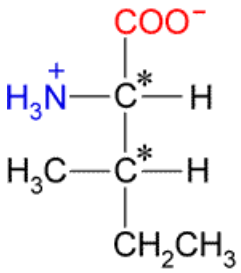
D - aminosav

Nincs királis centrum

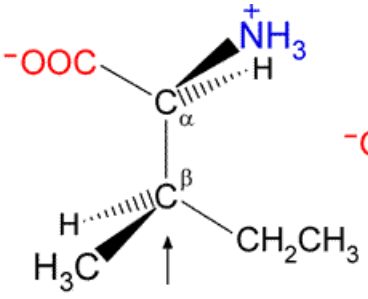


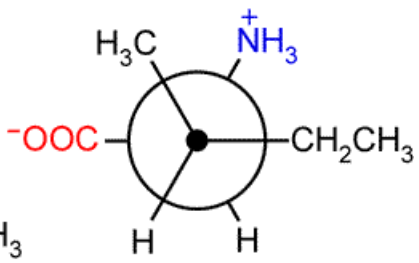
glicin

Két királis centrum



L – izoleucin (Ile)





(2S,3S)-D – izoleucin (D-Ile, i)

Aminosavak előállítása

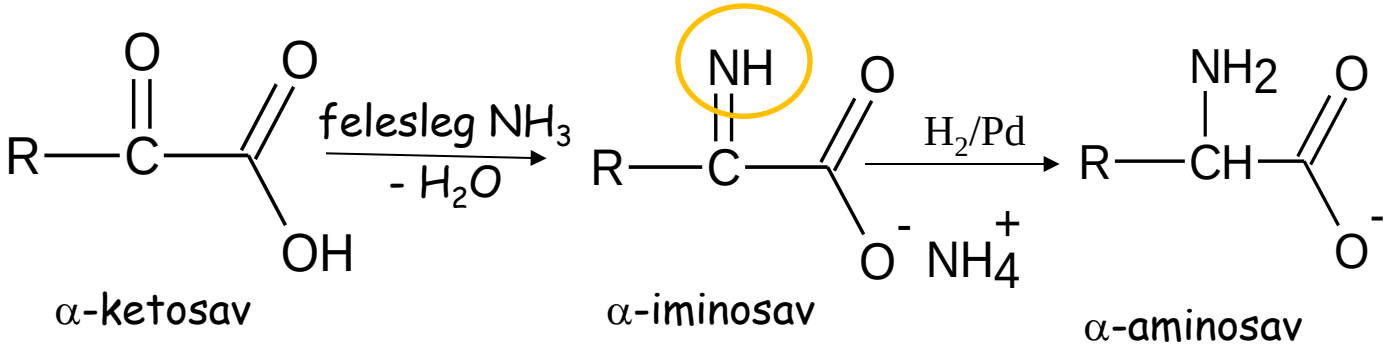
1. Fehérjék hidrolízise
2. Kémiai szintézis
3. Bioszintézis
4. Rezolválás

2. Kémiai szintézis

2. 1. Miller-kisérlet

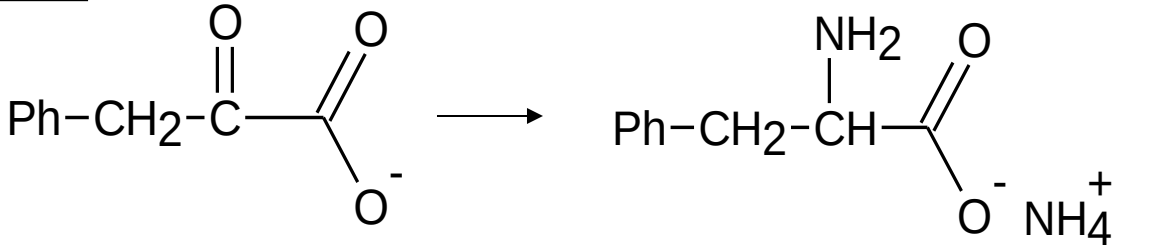
$H_2, H_2O, NH_3, CH_4 \xrightarrow[\text{kisülés}]{\text{elektromos}}$ aminosavak

2. 2. Reduktív aminálás



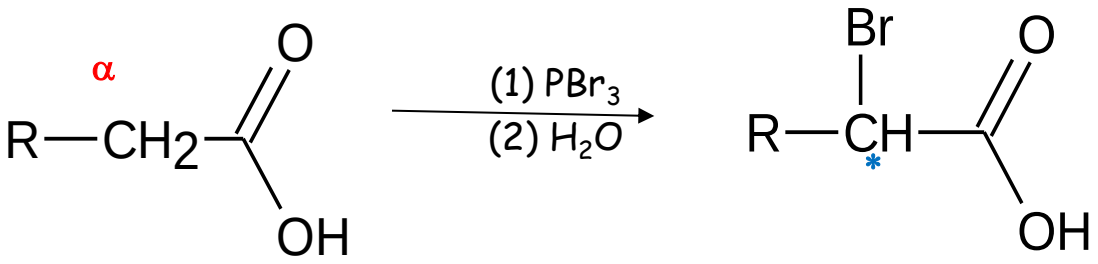
α-ketosav — α-iminosav — α-aminosav

Példa:

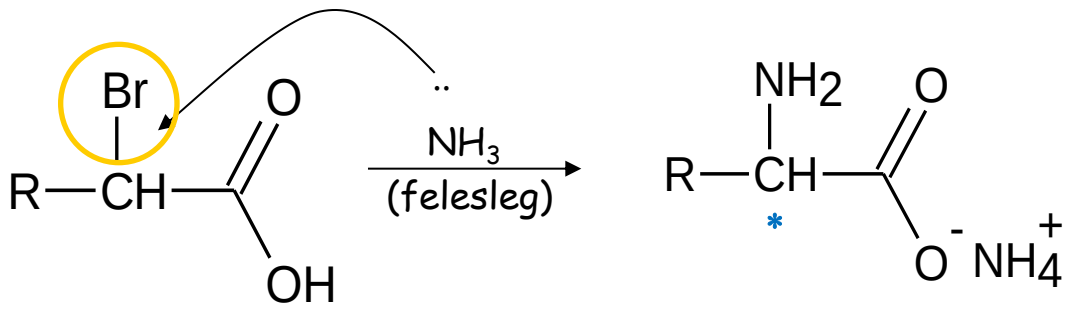


3-fenil-2-oxopropánsav — (D,L)-Phe NH_4^+ só (30 %)

2.3. Aminálás (S_N)



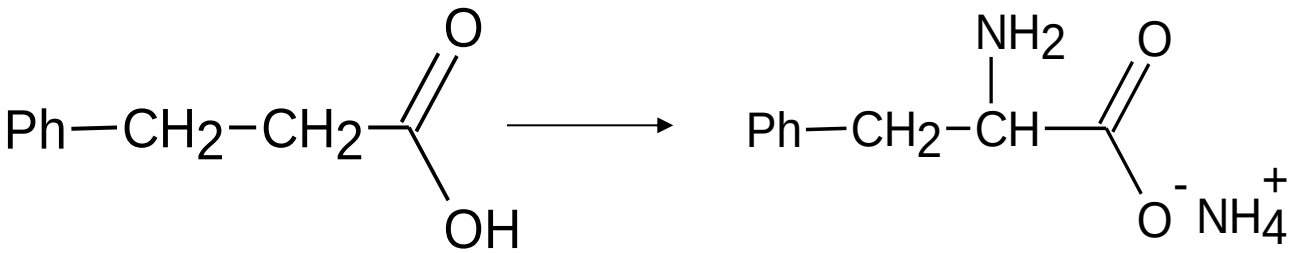
α-bróm-karbonsav



α-bróm-karbonsav

α-aminosav (racém)

Példa:

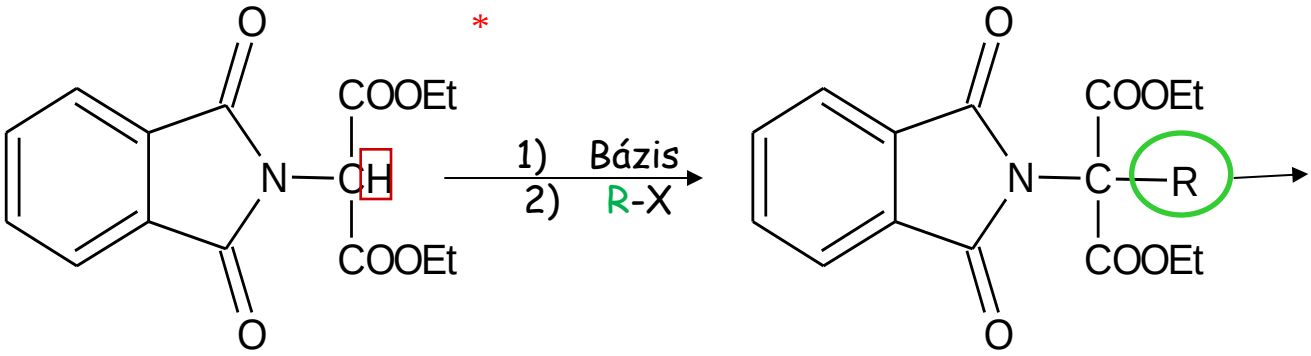


3-fenilpropánsav

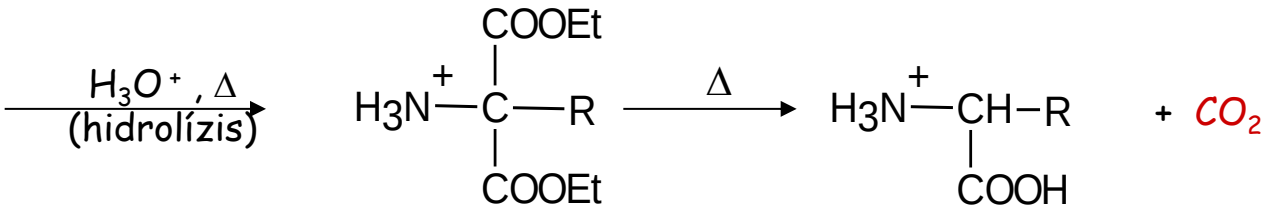
(D,L)-Phe NH_4^+ só

(30 - 50 %)

2.4. Gabriel-féle malonészter szintézis (Met, Asp)

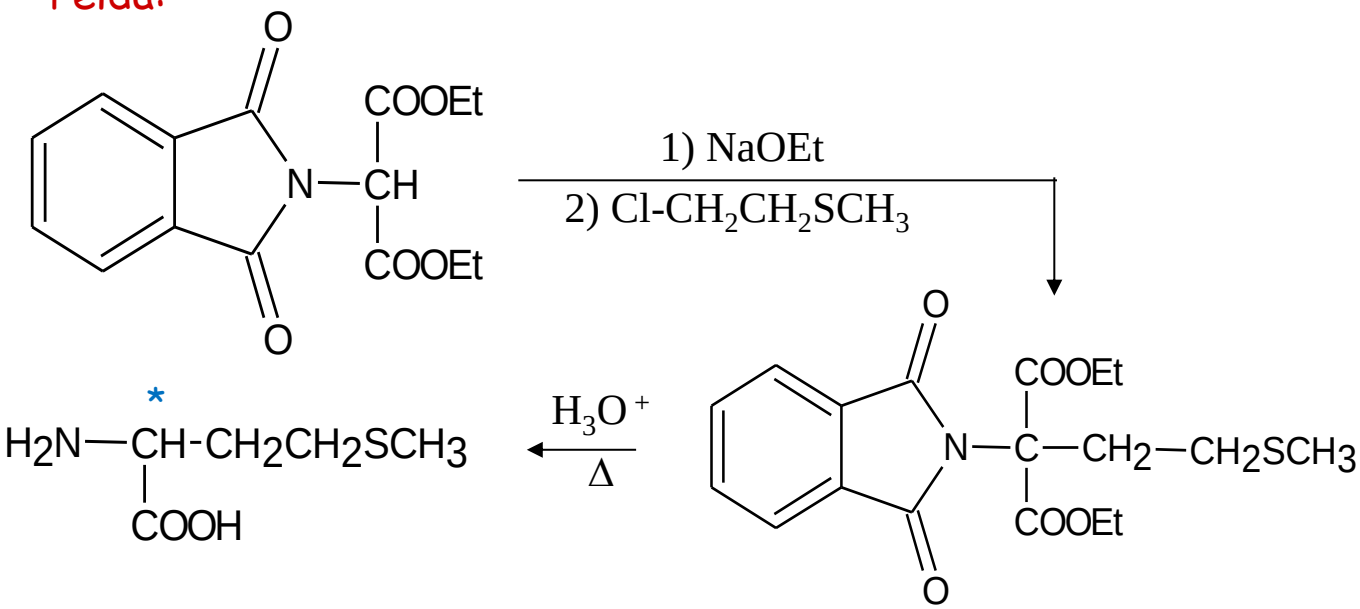


N-ftálimido malonsav dietilészter



α-aminosav

Példa:



(D,L)-metionin (racém, (DL-Met))

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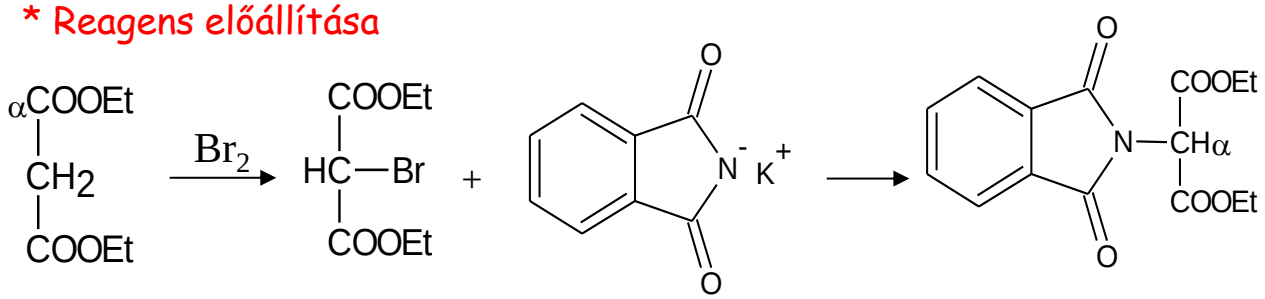
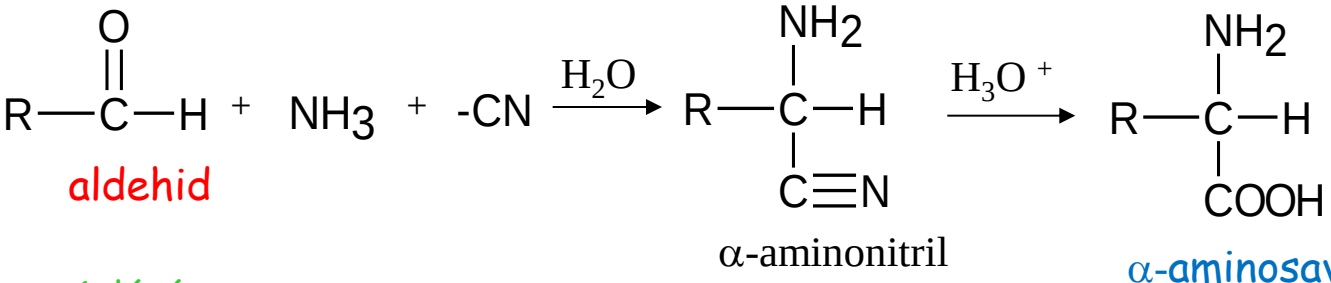
* Reagens előállítása

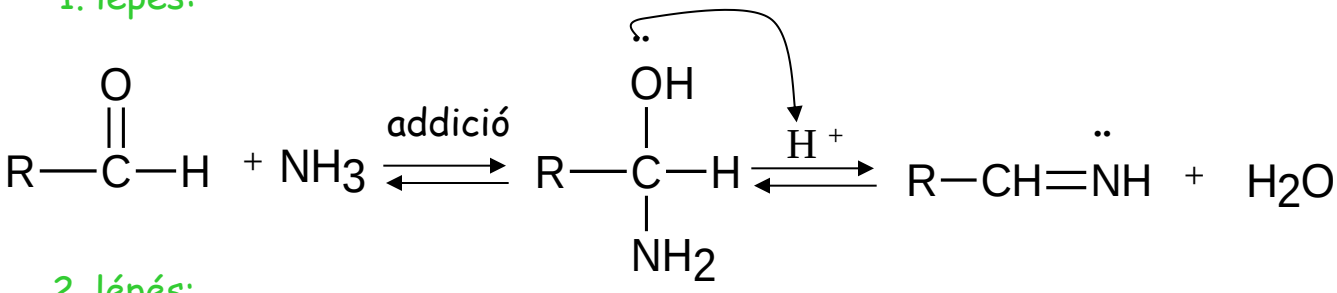


ftálimid kálium

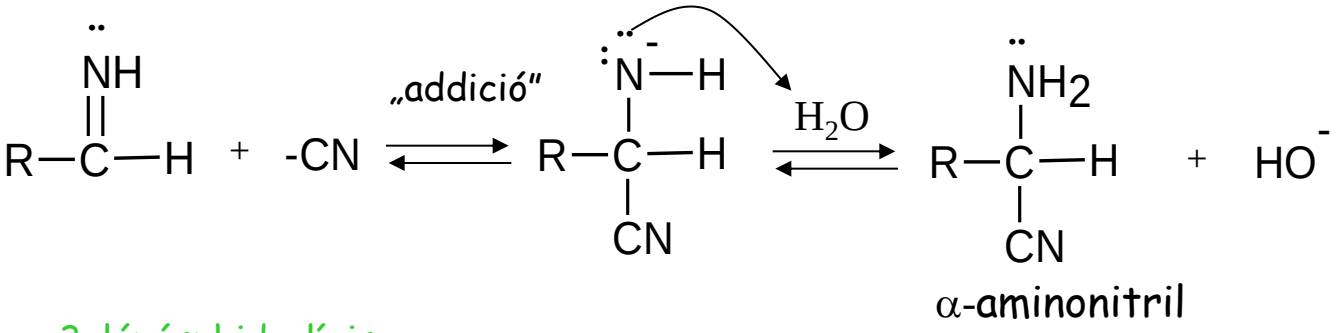
2.5. Strecker-szintézis (Ala, Phe)



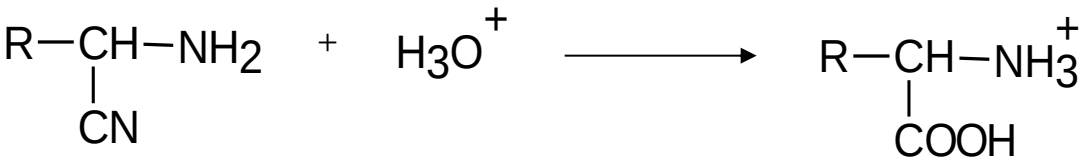
1. lépés:



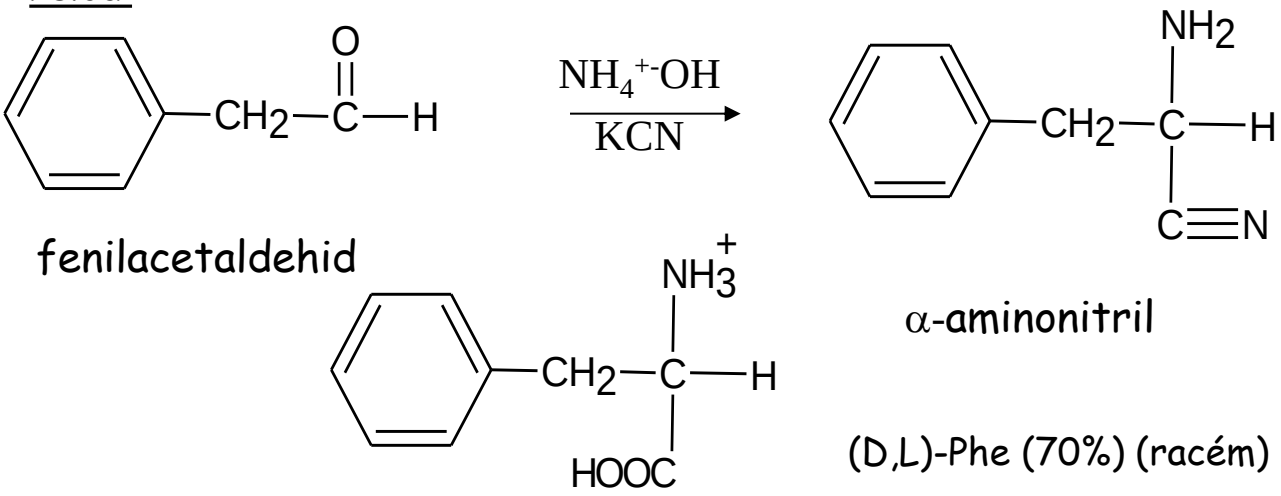
2. lépés:



3. lépés: hidrolízis

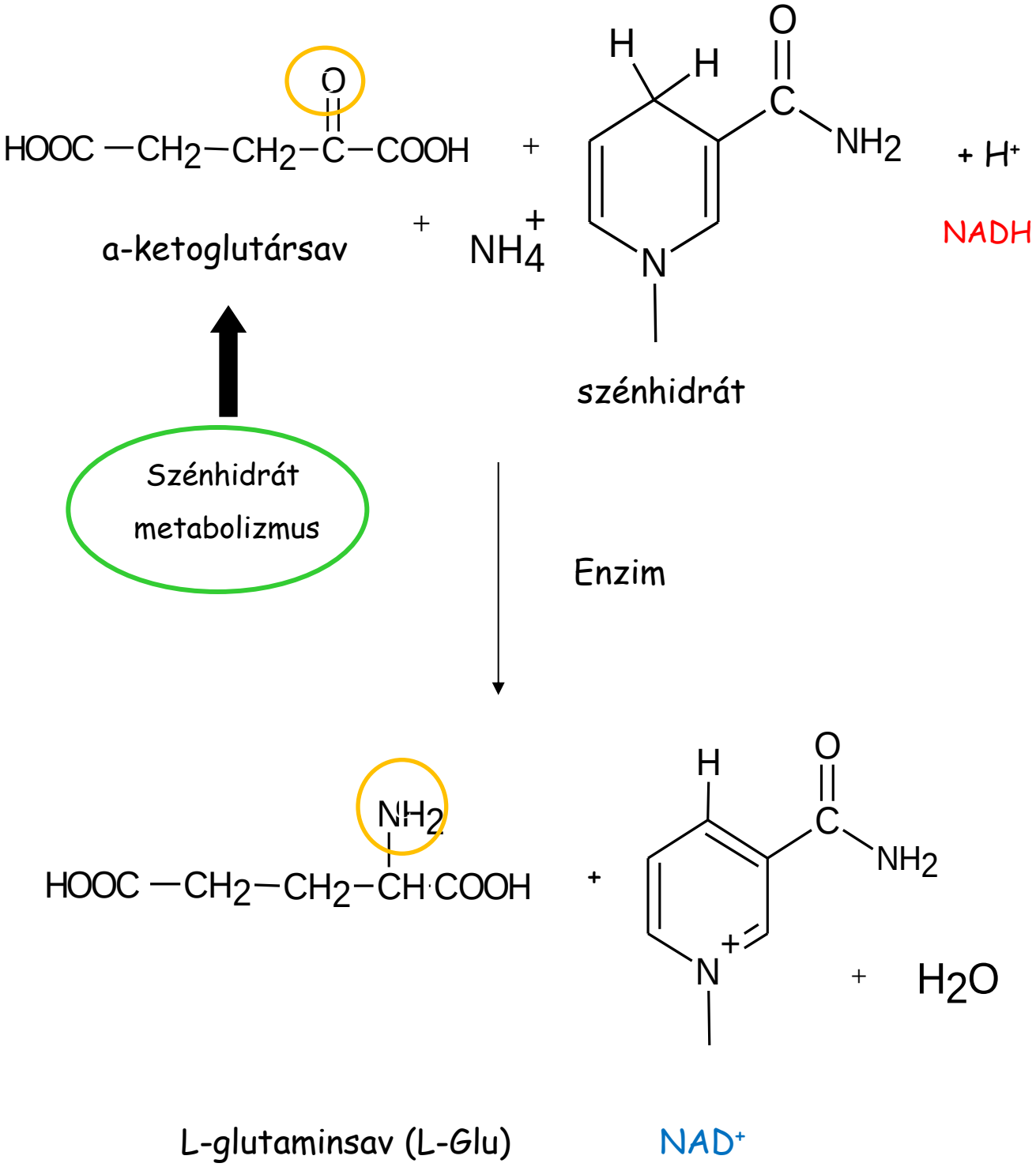


Példa:

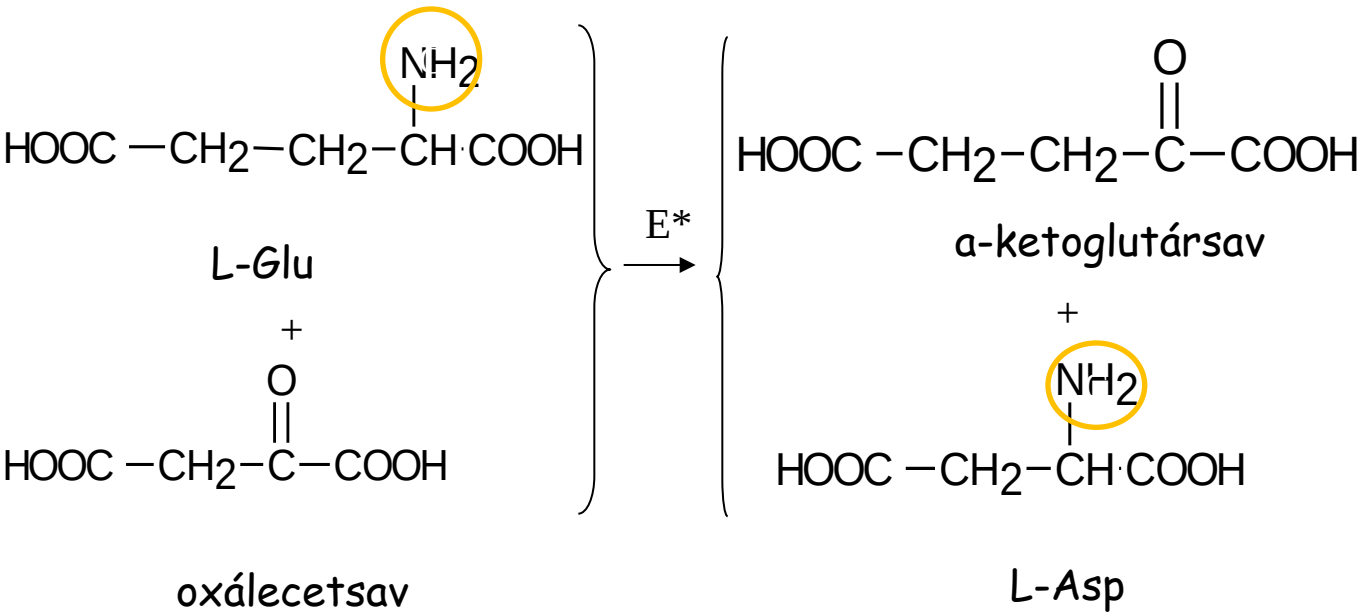


3. Bioszintézis

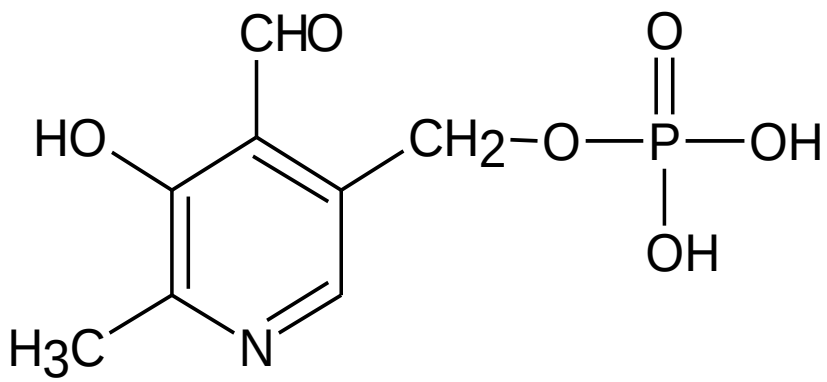
3.1. Reduktív aminálás



3.2. Transzaminálás

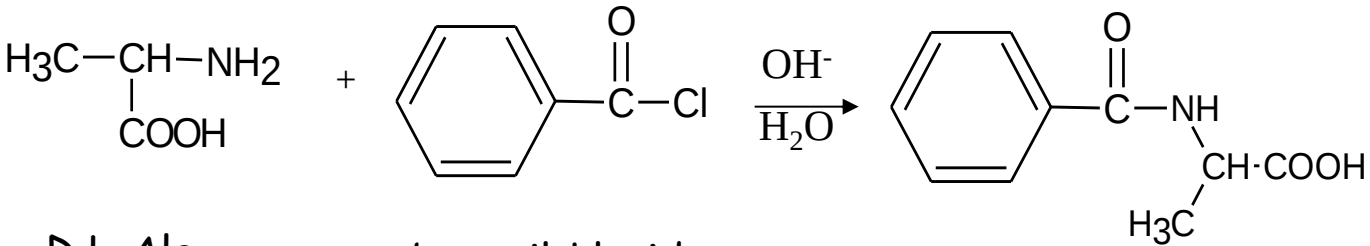


E* = Transzamináz, koenzim = piridoxál-5-foszfát



4. Rezolválás

4.1. Diasztereomer vegyületpár képzés



D,L-Ala benzoil-klorid N-benzoil-alanin + HCl

D,L-Ala

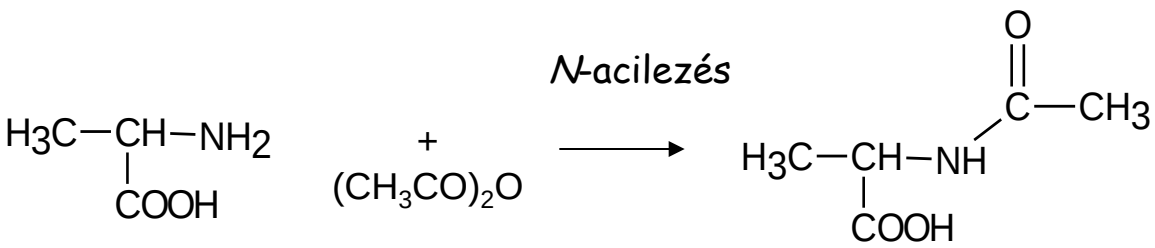
↓

N-benzoil-alanin

↓ Brucin/stcrichnin

N-benzoil-D-Ala brucin sója „oldhatatlan"	N-benzoil-L-Ala brucin sója „oldható"
↓ H^+/H_2O	↓ H^+/H_2O
N-benzoil-D-Ala	N-benzoil-L-Ala
↓ 1.) OH^-/H_2O, D 2.) H^+/H_2O	↓ 1.) OH^-/H_2O, D 2.) H^+/H_2O
D-Ala	L-Ala

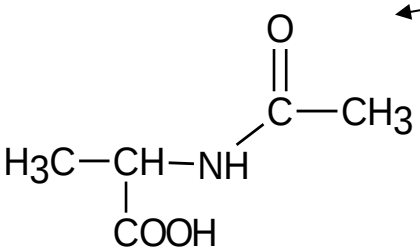
2. Enzimatikus módszer



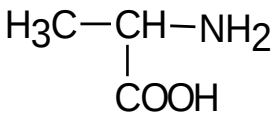
D,L-Ala

dezacetiláz

enzim

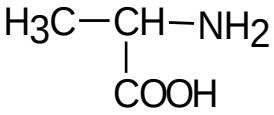


N-acetil-D-Ala



L-Ala

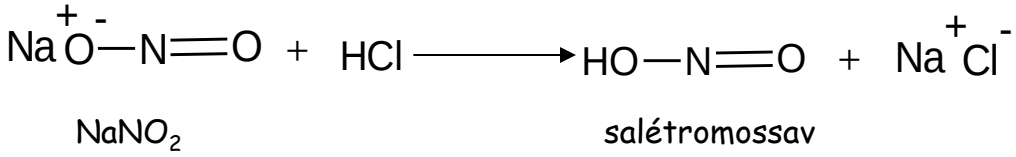
hidrolizis



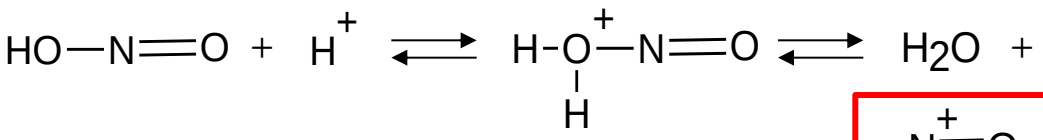
D-Ala

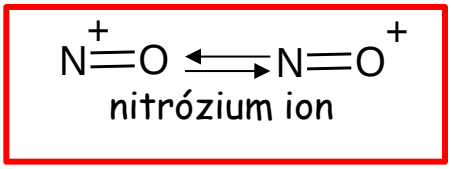
Aminosavak kimutatása

1. Reakció salétromos savval

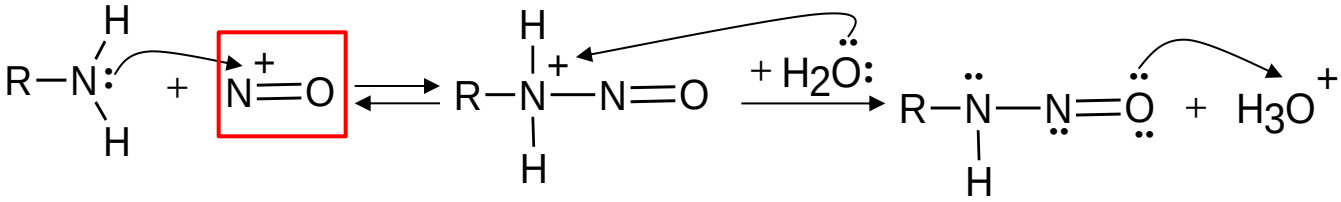


$NaNO_2$ salétromossav

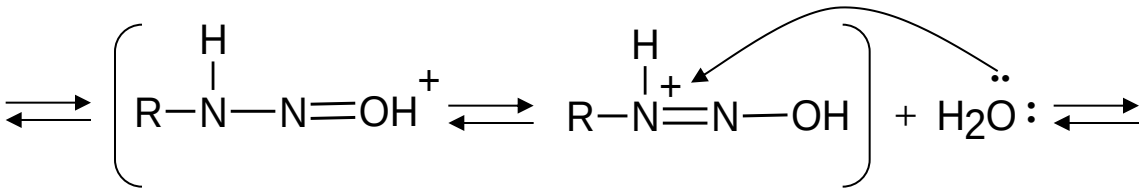


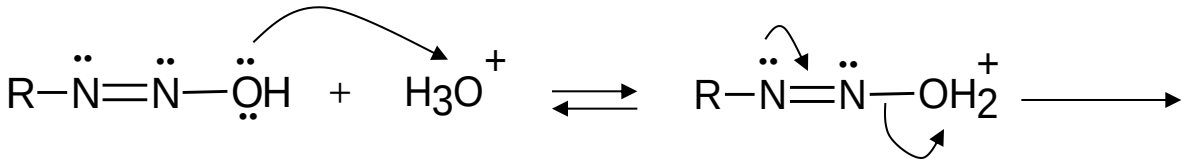


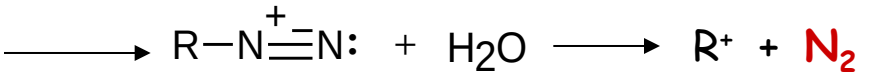
Primer amin



N-nitrozo amin

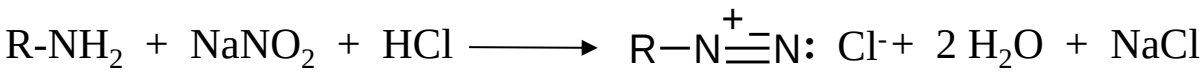




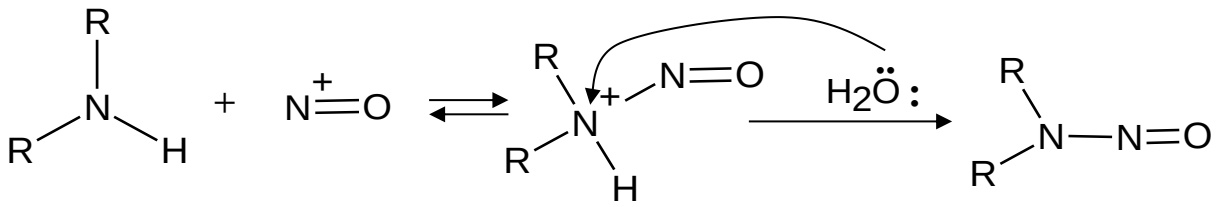


diazónium kation

Összegzés

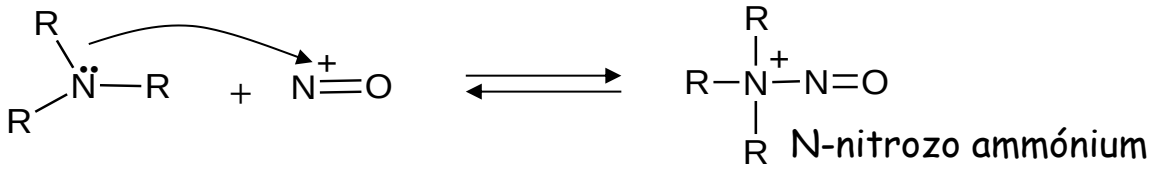


Szekunder amin



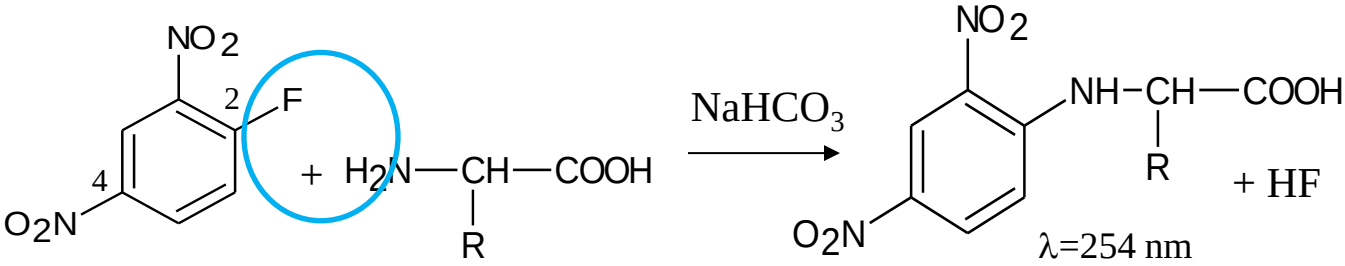
N-nitrozo amin

Tercier amin



N-nitrozo ammónium ion

2. Sanger reakció

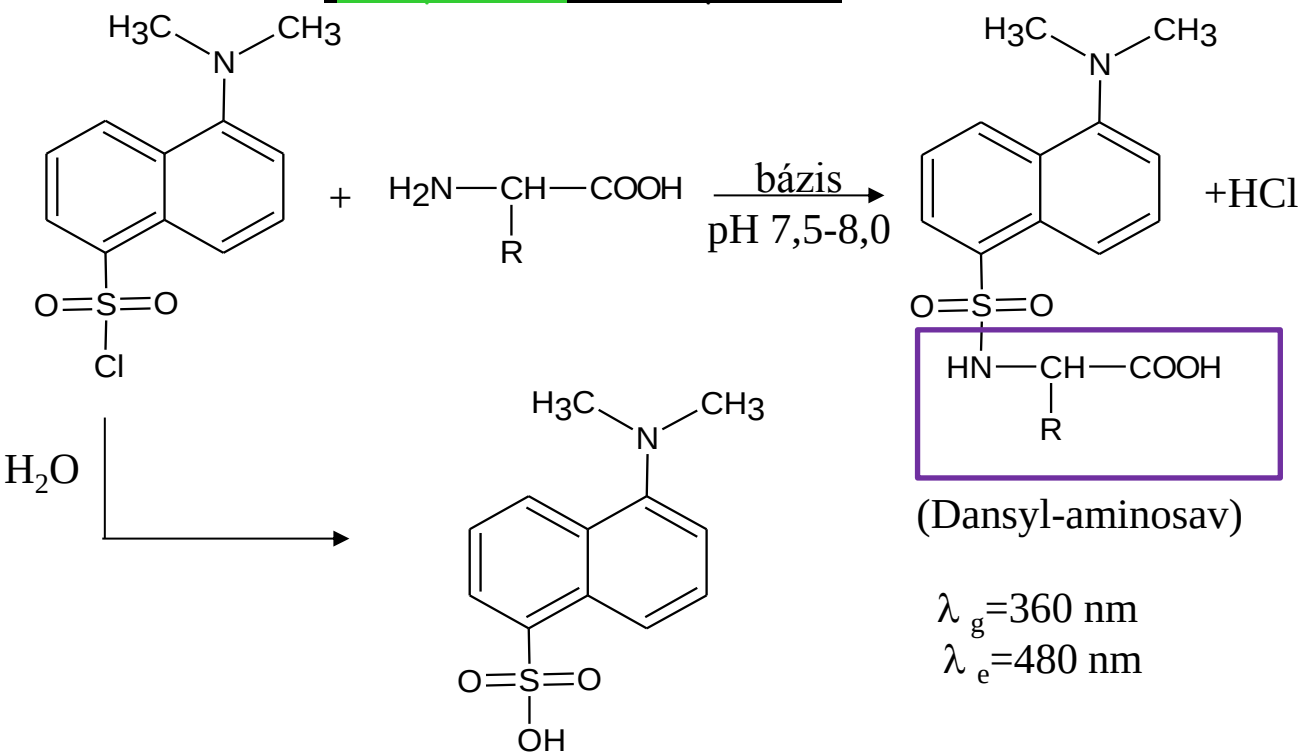


1-fluor-2,4-dinitro benzol
(Sanger, F. 1954)

2,4-dinitrofenil aminosav
(Dnp-aminosav)

3. Reakció 1-dimetilamino-naftalin-5-szulfonil kloriddal

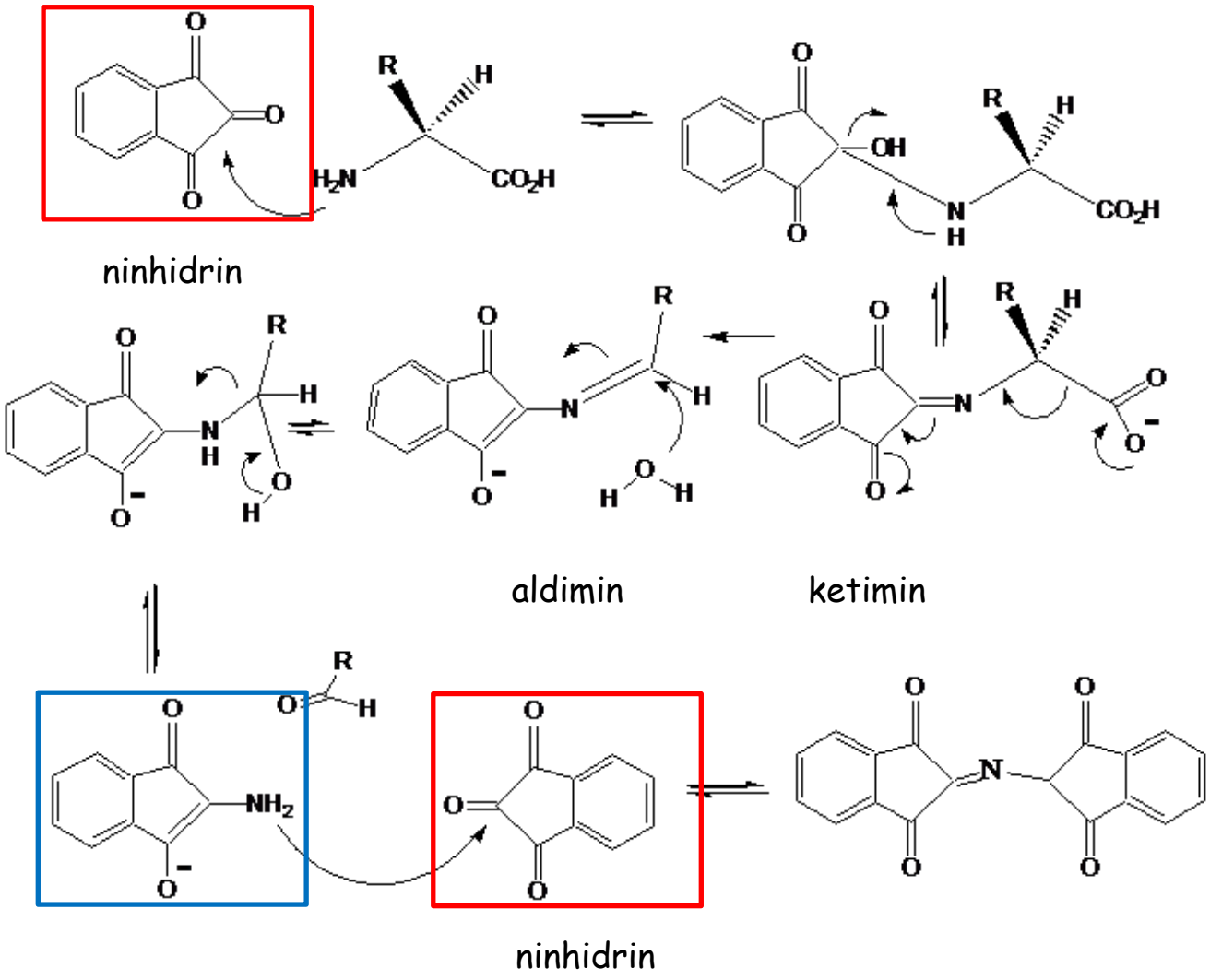
(Dansyl-klorid, Hartley, 1963)



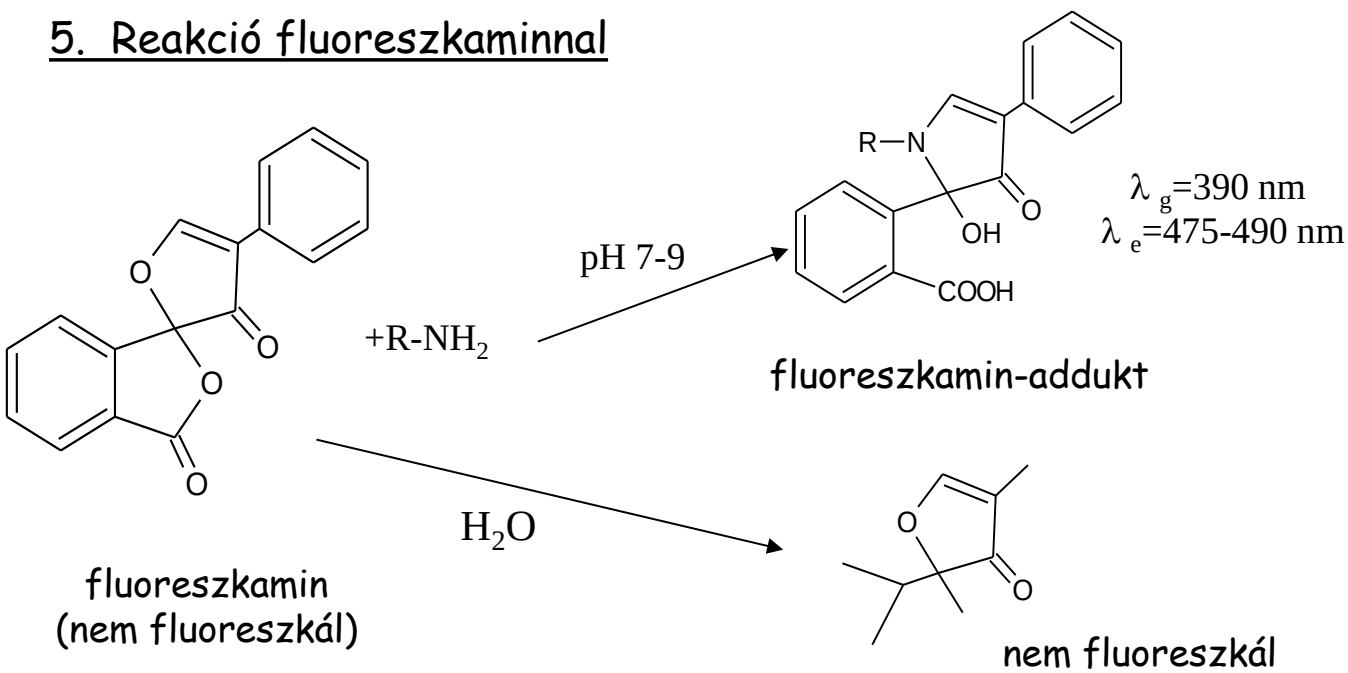
(Dansyl-aminosav)

λ_g=360 nm
λ_e=480 nm

4. Ninhidrin reakció (Ruheman, 1909)



5. Reakció fluoreszkaminnal

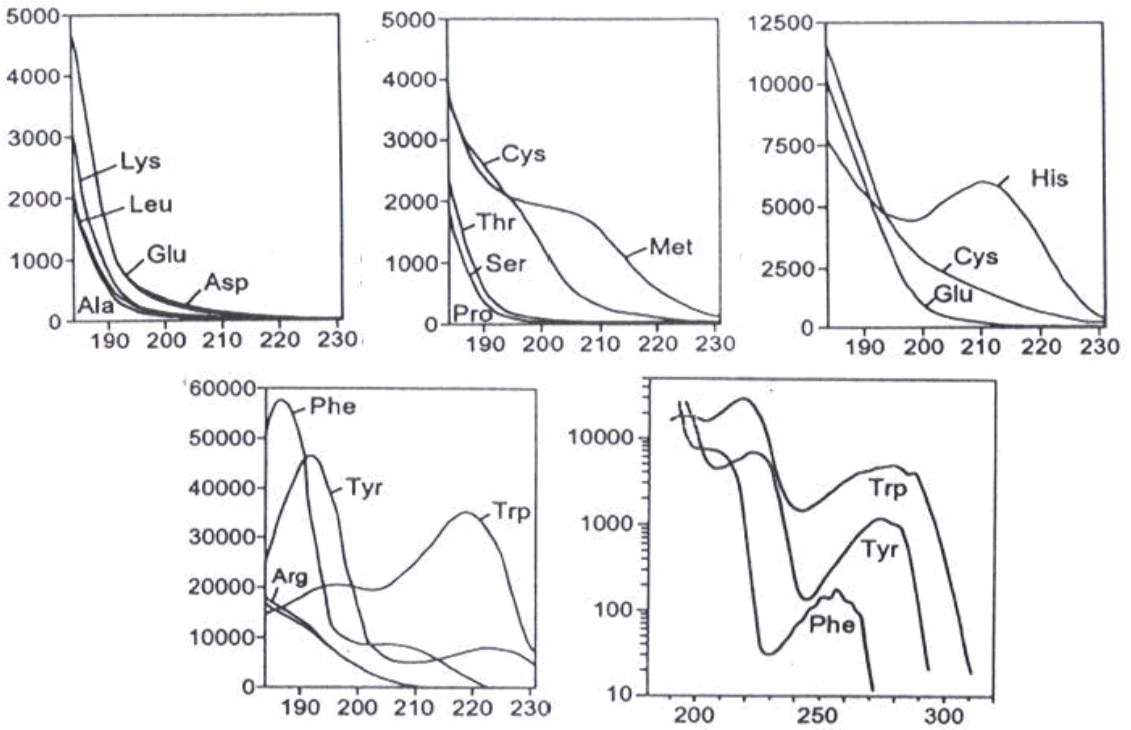


5. Spektroszkópia (UV)

	λ_{max} (nm)	ε ($M^{-1}cm^{-1}$	λ_{max} (nm)	kvantum hatásfok
Phe	257.4	197	282	0.04
Tyr	274.6	1420	303	0.21
Trp	279.8	5600	348	0.20

Módszer	kromofór	Érzékenység (mg/ml	szerkezeti hatás
A_{280}	Trp/Tyr	200-3000	erős
A_{220}	peptid kötés	1-100	nincs
fluoreszcencia	Trp	5-50	erős

Aminosavak UV-spektrumai



vizes oldat
(pH 5-6, ill. pH 3 (Cys))

Hullámhossz (nm)