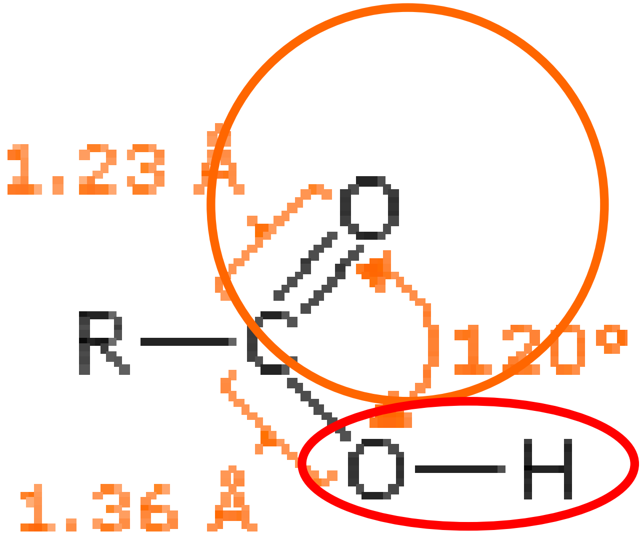
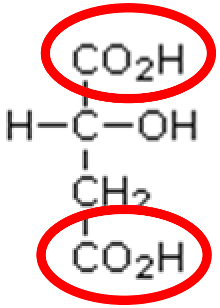
Karbonsavak



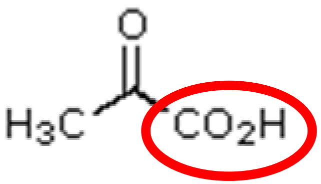
Összetett
funkciós
csoport

-COOH, azaz karboxil-csoportot tartalmazó vegyületek

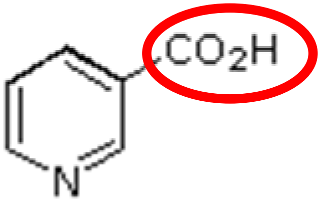
Természetes karbonsavak



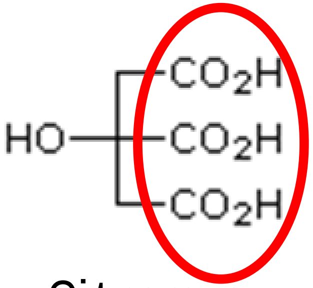
Almasav
(gyümölcsök)



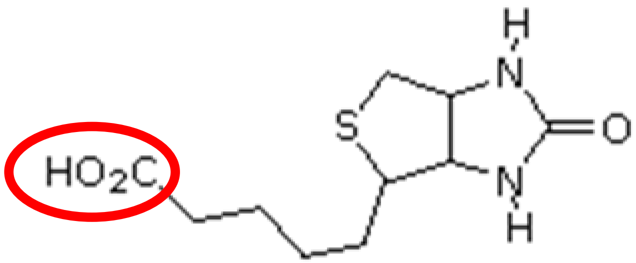
Piroszőlősav
(intermedier)



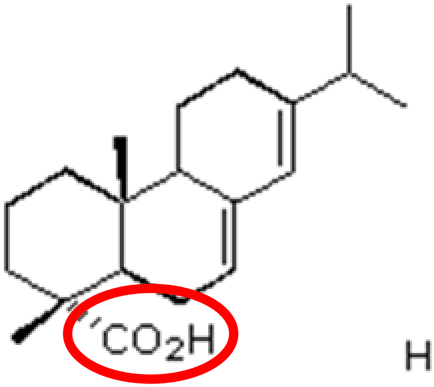
Niacin



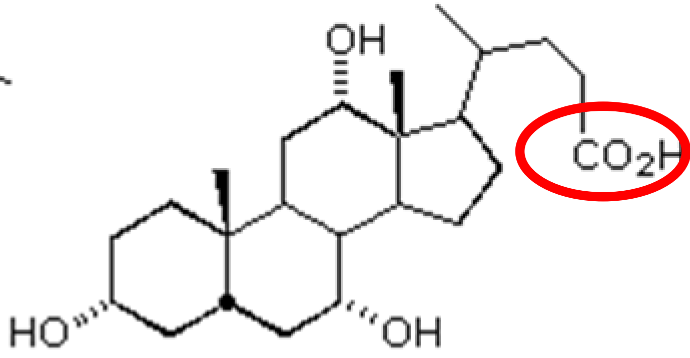
Citromsav
(citrusfélék)



Biotin
(CO_2 transzfer)



abietinsav
(gyanta)



Kolsav
(epe)

Természetes karbonsavak

$CH_3-(CH_2)_{14}-COOH$

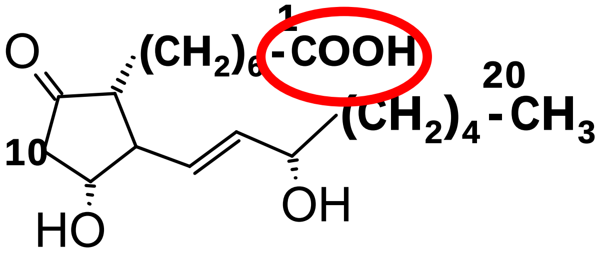
palmitinsav

$CH_3-(CH_2)_7-CH=CH-(CH_2)_7-COOH$

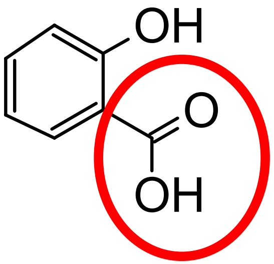
cisz: olajsav
transz: elaidinsav

$CH_3-(CH_2)_{16}-COOH$

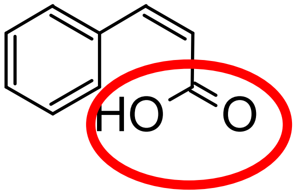
sztearinsav



Prostaglandin E
(PGE_1) 1935
1963: szintézis



szalicilsav



fahéjsav

Alkánsav (homológ sor)

Hangyasav	$HCOOH$
Etánsav, ecetsav	CH_3COOH
Propionsav	CH_3CH_2COOH
Butánsav, vajsav	$CH_3CH_2CH_2COOH$
Valeriánsav	$CH_3(CH_2)_3COOH$
Kapronsav	$CH_3(CH_2)_4COOH$
....	
Palmitinsav	$CH_3(CH_2)_{14}COOH$
Sztearinsav	$CH_3(CH_2)_{16}COOH$
....	

Alkándisav (homológ sor)

Oxálsav	$HOOC - COOH$
Malonsav	$HOOC\text{-}CH_2\text{-}COOH$
Borostyánkősav	$HOOC\text{-}(CH_2)_2\text{-}COOH$
Glutársav	$HOOC\text{-}(CH_2)_3\text{-}COOH$
Adipinsav	$HOOC\text{-}(CH_2)_4\text{-}COOH$
....	

Almasav		Elõször éretlen almából állították elõ.
Benzoesav		Egy Indonéziában honos fa gyantájából, a benzoegyantából állították elõ.
Borkõsav		Borkészítéskor "borkõ" alakjában válik ki (a borkõ, latinul *tartarus,* kálium-hidrogén-tartarát).
Borostyánkõsav (C4)		**A borostyán desztillációs bontásakor képzõdõ desztillátumban fedezték fel.**
Ecetsav (C2)		**Az ecetben található.**
Fumársav (C4)	**L, *fumus,* füst**	**A *Fumaria* nevû növényben található; a növényt régen azért égették, hogy a füstjével elûzzék a gonosz szellemeket.**
Hangyasav (C1)		**Hangyák desztillációs bontásával állították elõ.**
Glutársav (C5)		**Elõször a glutaminsavból állították elõ.**
Kapronsav	L, *caper,* kecske	Kecsketejben található vegyület, szaga a kecskére emlékeztet.
Linolsav, lenolajsav	G, *linon,* len + olaj	Glicerin-észter formájában megtalálható a lenolajban.
Maleinsav (C4)	L, *malum*, alma	Az almasav dehidratációs terméke.
Malonsav (C3)	**L, *malum*, alma**	**Elõször az almasav oxidációjával állították elõ.**
Oxálsav (C4)	**G, *oxisz*, savanyú**	**Savanyú ízû vegyület, az *Oxalis* nemzetséghez tartozó növényekbõl vonható ki.**
Palmintisav (C16)	**L, *palma,* pálma**	**Megtalálható a pálmaolaj gilcerin-észterében.**
Piroszõlõsav (C3)	**G, *piro,* tûz**	**A (szõlõbõl kiváló) borkõsav pirolízisével állítható elõ.**
Propionsav (C3)	**G, *proto,* elsõ és *pion,* zsír**	**A legrövidebb szénláncú sav, amely a hosszabb zsírsavak tulajdonságait mutatja.**
Sztearinsav	G, *sztear,* faggyú	Növényi és állati zsírok glicerin-észtereiben fordul elõ.
Tejsav (C3)		**Aludttejben fedezték fel.**
Vajsav (C4)		**Avas vajban található.**
Valeriánsav, macsakgyökérolaj		A *Valeriana officialis* (macskagyökér) gyökerébõl nyerik ki. (A macskákra ingerlõen hat a növény fõ alkaloidja.)

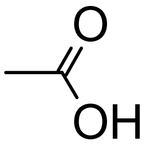
A triviális nevű karbonsavak szótövei és acilcsoportjaik nevei

név	***szótő***	***acilcsoport***	***név***	***szótő***	***acilcsoport***
akrilsav	akril	akriloil	**acetecetsav**	acetoacet	acetoacetil
benzoesav	benz	benzoil	**borostyánkősav**	szukcin	szukcinil
borkősav	tartar	tartaroil	**ecetsav**	acet	**acetil**
citromsav	citr	citroil	**hangyasav**	form	formil
glicerinsav	glicer	glicеroil	**malonsav**	malon	malonil
glikolsav	glikol	glikoloil	**oxálsav**	oxal	oxalil
fahéjsav	cinnam	cinnamoil	**propionsav**	propion	propionil
ftálsav	ftal	ftaloil	**vajsav**	butir	butiril
fumársav	fumar	fumaroil			
maleinsav	male	maleoil			
nikotinsav	nikotin	nikotinoil			
olajsav	ole	oleoil			
palmitinsav	palmit	palmitoil			
piroszőlősav	piruv	piruvoil			
sztearinsav	sztear	sztearoil			
tejsav	lakt	laktoil			

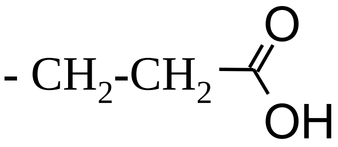
Szintézis oxidációval:

alkohol	→	**aldehid**	→	**karbonsav**
R-C-OH		**R-C=O**		**R-COOH**

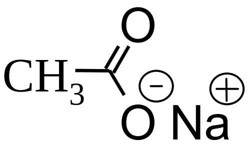
Csoportok



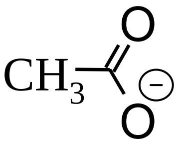
karboxi



propanoil

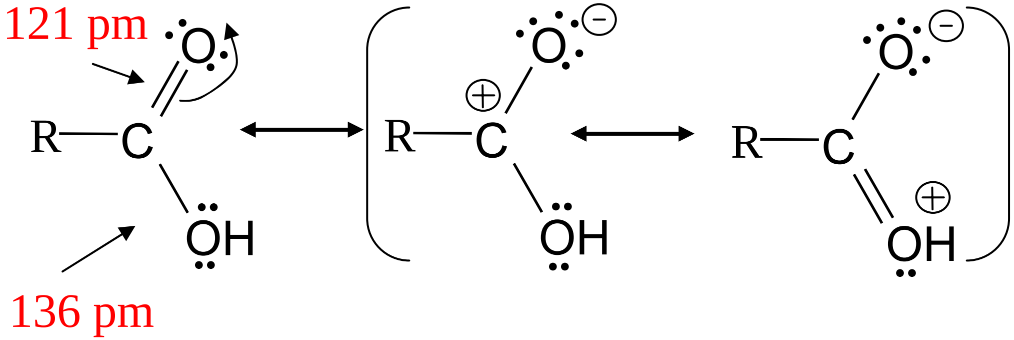


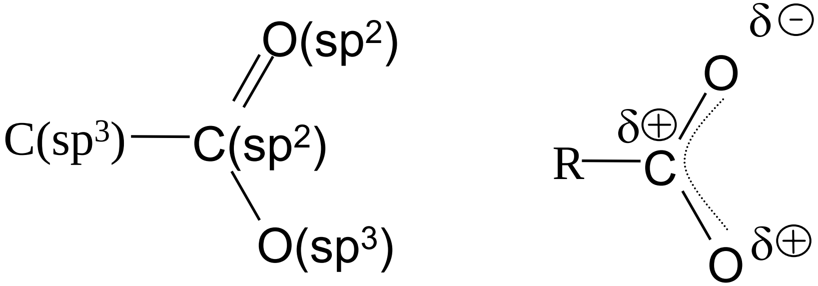
karboxilát
Na acetát



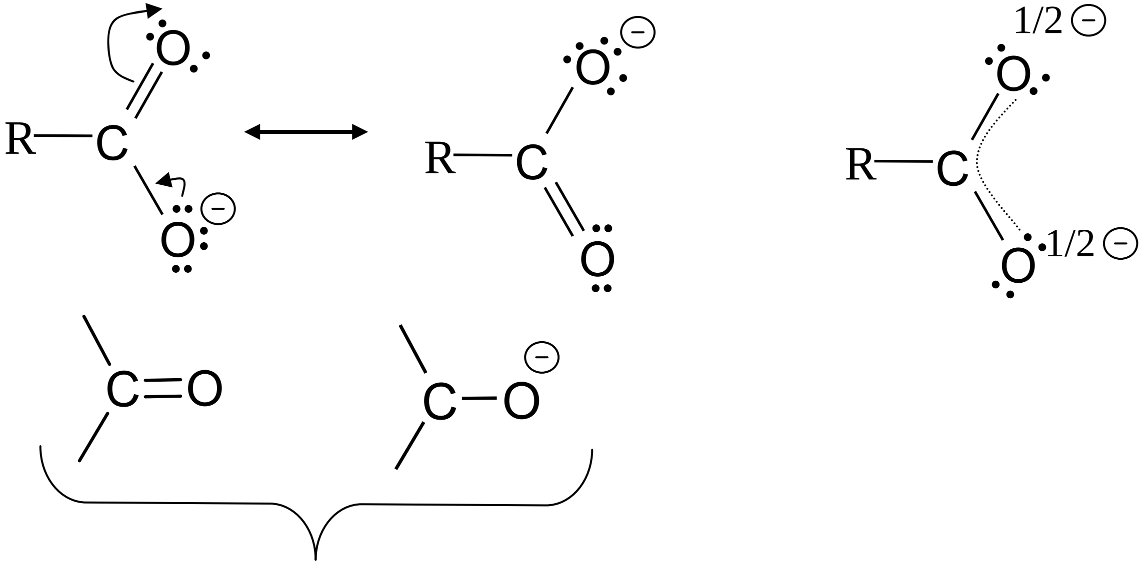
acetil-

Karboxil csoport





Karboxil csoport protonjának disszociációja után:

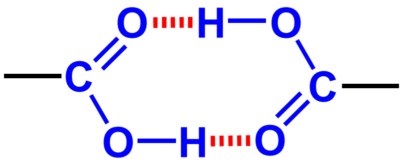


127 pm

Karboxilát csoport – szimmetrikus töltéseloszlás
(mezoméria)

Szerkezet, tulajdonságok

- Alkoholoknál magasabb olvadás és forráspont
- H-hidak erős asszociációja
- oldatban és gázfázisban dimerekké asszociálnak
- a karboxilcsoport száma alapján **egy-**, **két-**, ill. **többértékűek**
- a szénlánc jellege szerint telítettek, telítetlenek, ill. aromás karbonsavak
- a telített egyértékű, kis szénatomszámú karbonsavak folyékonyak
- a nagyobb szénatomszámúak szilárdak
- C1 – C4 még vízoldékony, C4 felett nehezen

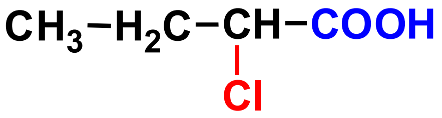
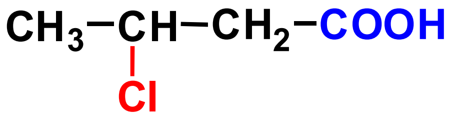
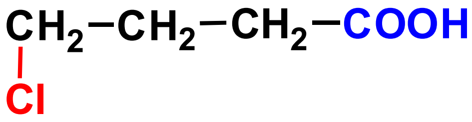
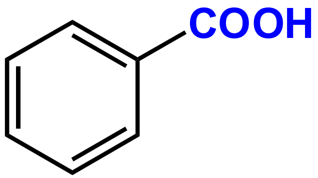


Szerkezet, tulajdonságok

- Savi jelleg
- közepesen erős szerves savak
- protonátadó készségük az ásványi savakénál kisebb
- savas jellegük a szénatomszám növekedésével csökken
- → bázisokkal vízoldékony sókat képeznek

$$\mathrm{R{-}COOH} + \mathrm{H_2O} \rightleftharpoons \mathrm{R{-}COO^{\ominus}} + \mathrm{H_3O^{\oplus}}$$

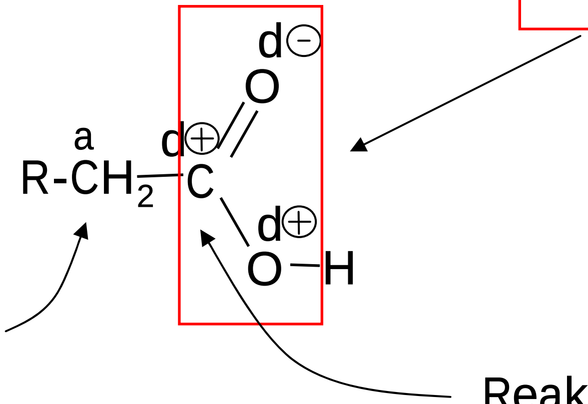
$$\mathrm{R{-}COOH} + \mathrm{NaOH} \rightleftharpoons \mathrm{R{-}COO^{\ominus}\,Na^{\oplus}} + \mathrm{H_2O}$$

	$pK_S =$		$pK_S =$
$H-COOH$	3.8	$CH_3-CH_2-CH_2-COOH$	4.9
CH_3-COOH	4.76		
CH_3-CH_2-COOH	4.9	 $CH_3-H_2C-\underset{\underset{Cl}{\vert}}{CH}-COOH$	2.81
$F-CH_2-COOH$	2.58		
$Cl-CH_2-COOH$	2.81	 $CH_3-\underset{\underset{Cl}{\vert}}{CH}-CH_2-COOH$	4.06
$Br-CH_2-COOH$	2.90		
$I-CH_2-COOH$	3.17	 $\underset{\underset{Cl}{\vert}}{CH_2}-CH_2-CH_2-COOH$	4.52
CH_3-COOH	4.76		
$ClCH_2-COOH$	2.81		4.22
$Cl_2CH-COOH$	1.29		
$Cl_3C-COOH$	0.89		

Savi jelleg: karbonsavak > fenolok > víz > alkoholok

pK_S (5) (9) (14) (16)

Kémiai reakciók



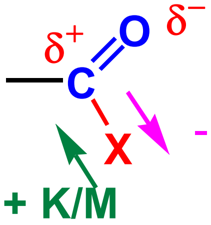
Dekarboxilálás

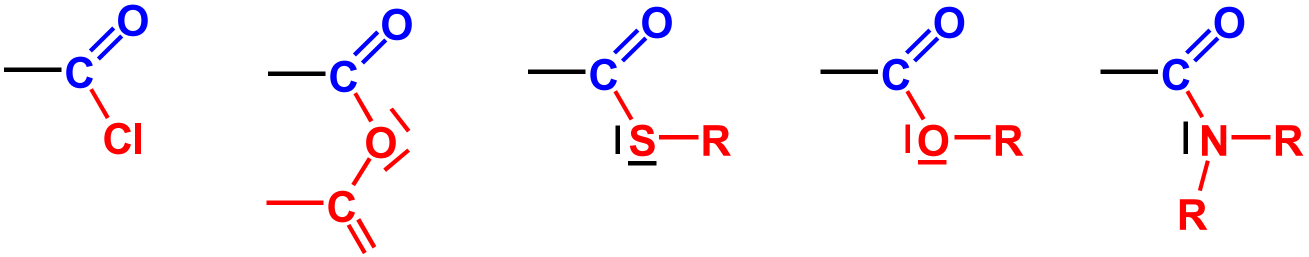
Reakció az α C-atomon
szubsztitúció

Reakció a karbonil
C-atomon

1. sav-bázis sajátság
2. redukció
3. szubsztitúció

Karbonsavszármazékok reaktivitása

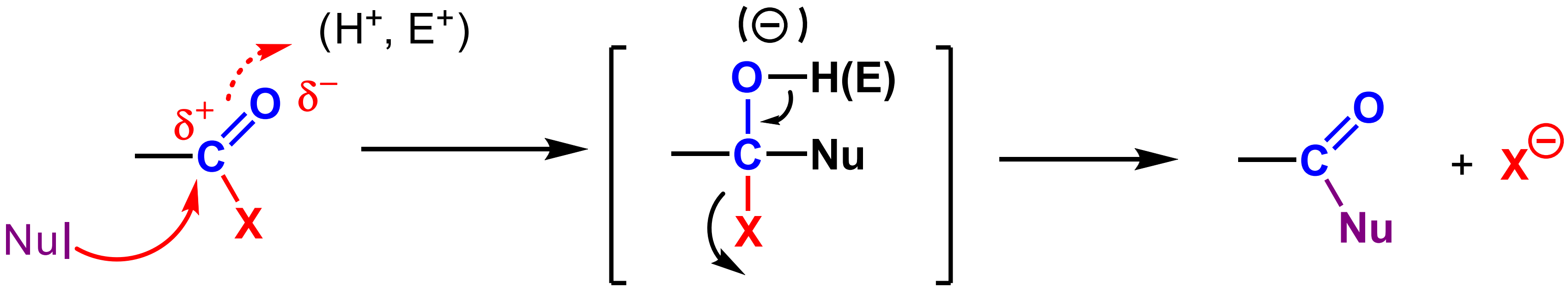




Sav- klorid anhidrid tioészter észter amid

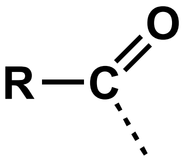
C=O kötés polarizáltsága növekedik

reaktivitás fokozódik

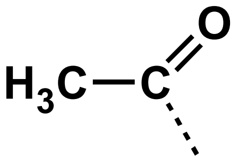


A C=O csoportnál: $\underline{\mathbf{S}_\mathbf{N}}$

A nukleofil csoportnál: **Acilálás**



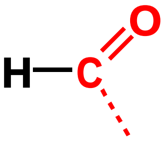
Acil -



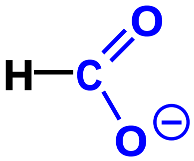
Acetil -

Karboni(y)l vs. karboxilát

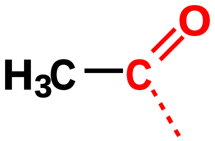
Formyl-



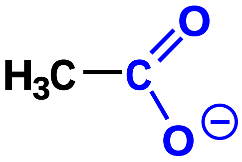
Formiát



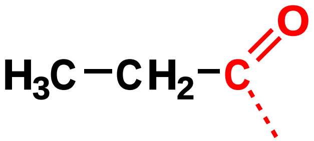
Acetyl-



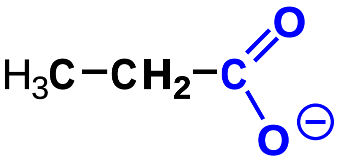
Acetát



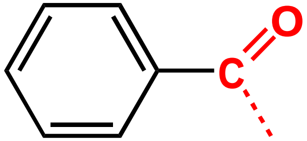
Propionyl-



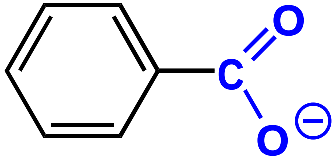
Propionát

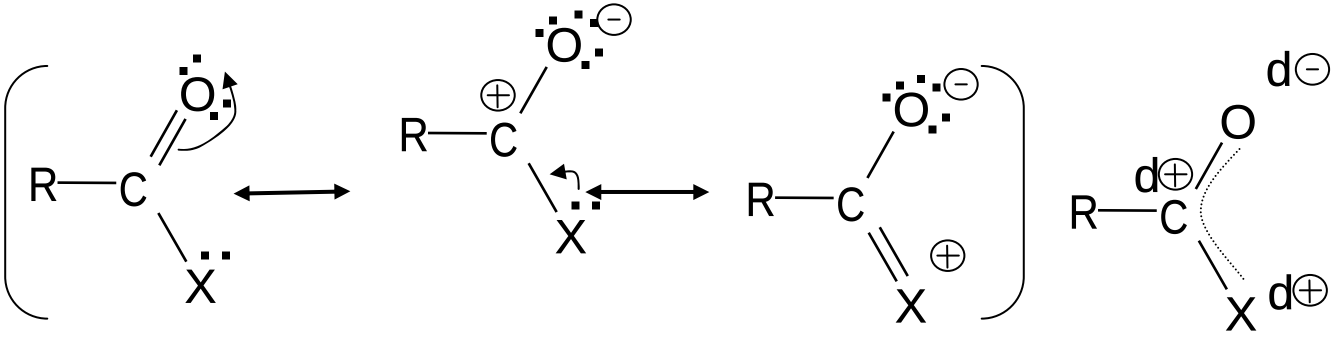


Benzoyl-



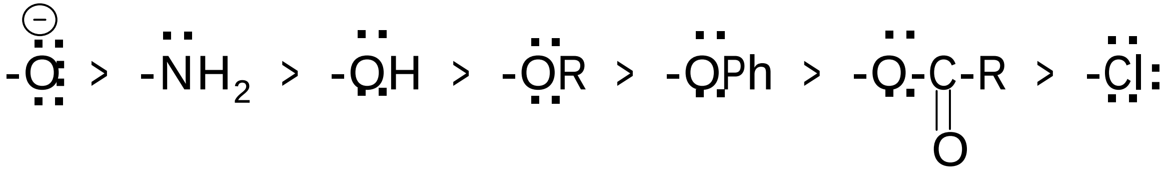
Benzoát





Konjugációs kölcsönhatás X és a karbonil C között

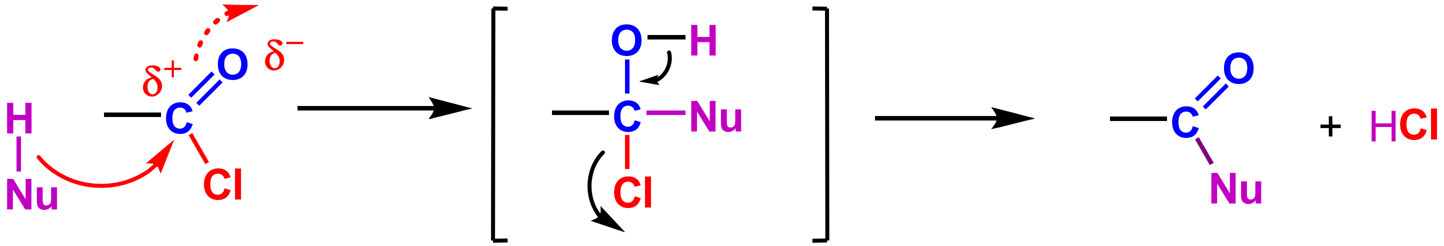
Reaktivitási sorrend a C-atomon lejátszódó reakciókra nézve:

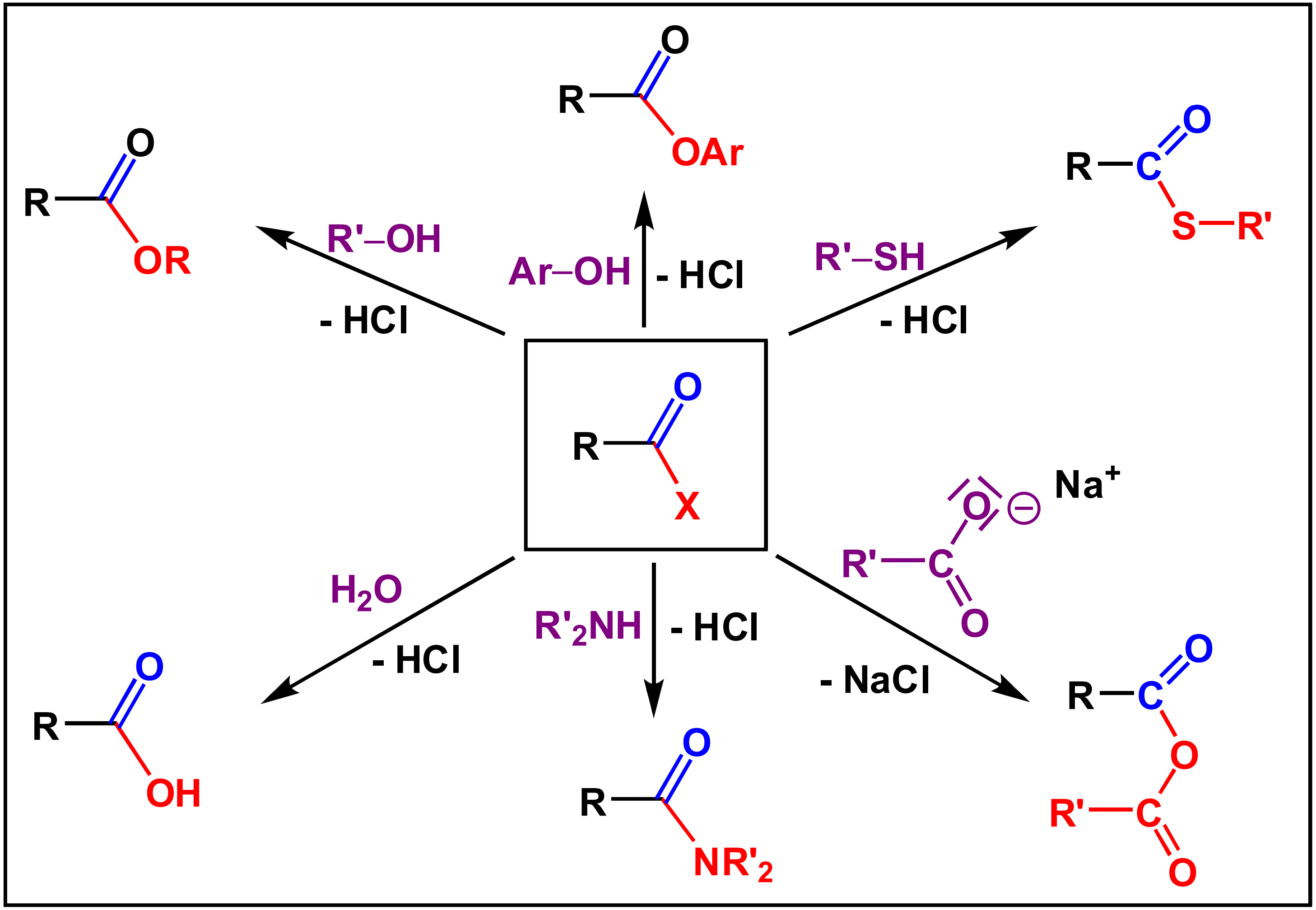


$$-O^{-} > -NH_2 > -OH > -OR > -OPh > -O-\underset{\underset{O}{\parallel}}{C}-R > -Cl$$

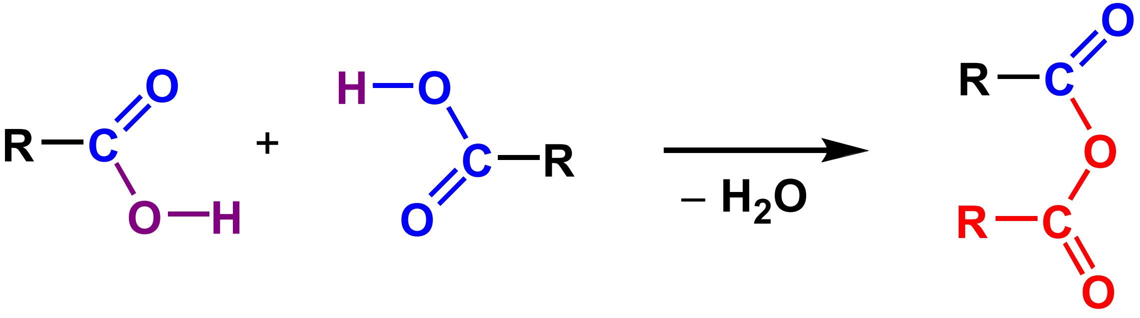
karboxilát sav észter savklorid

savamid észter anhidrid

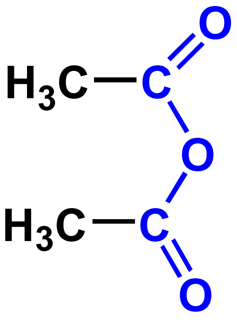

H
Nu
δ+
δ−
C
O
Cl
O—H
C—Nu
Cl
C
O
Nu
+ HCl


R
O
X
R'–OH
- HCl
R
O
OR
Ar–OH
- HCl
R
O
OAr
R'–SH
- HCl
R—C
O
S—R'
H₂O
- HCl
R
O
OH
R'₂NH
- HCl
R
O
NR'₂
R'—C
O
O
⊖
Na+
- NaCl
R—C
O
O
R'—C
O

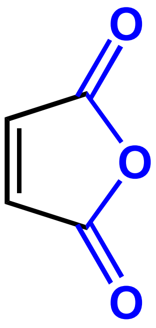
Savanhidrid



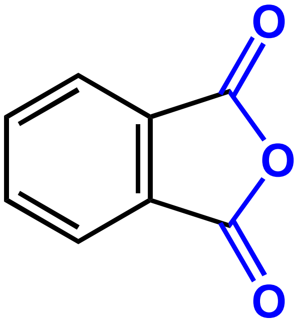
Pl.: savklorid + só



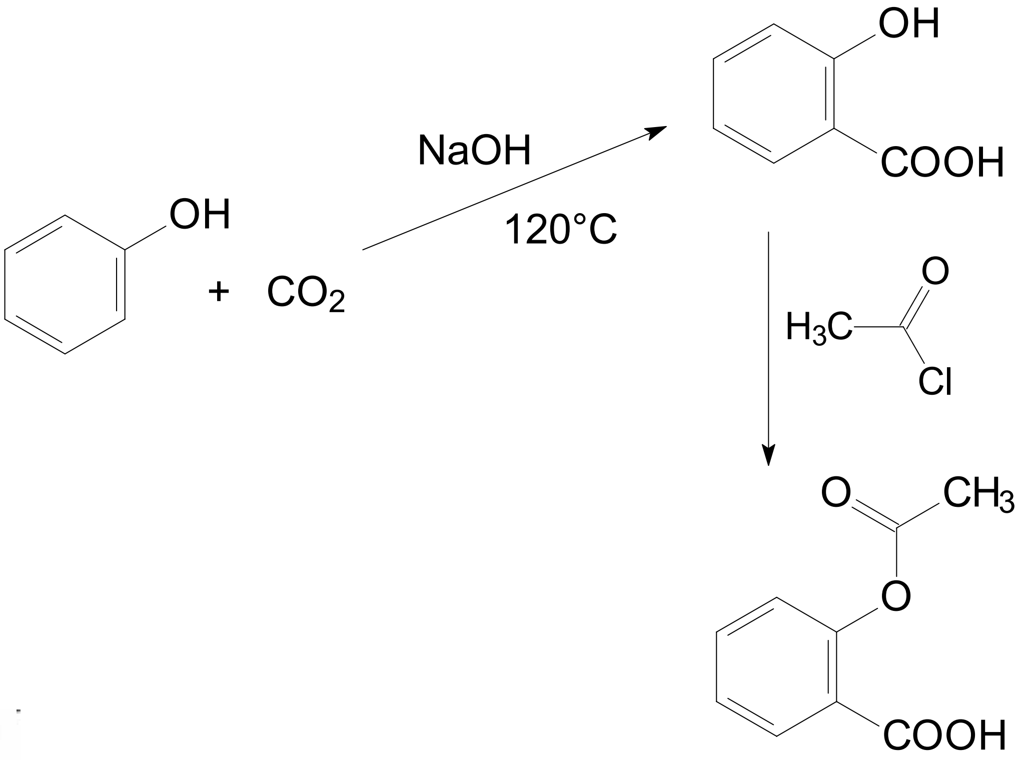
Ecetsavanhidrid
(Acetanhidrid)



Maleinsavanhidrid



Ftálsavanhidrid

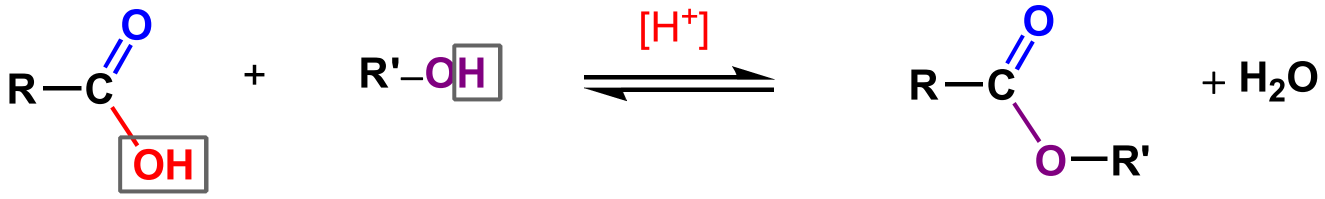


szalicilsav

1897 Hoffmann

acetilszalicilsav

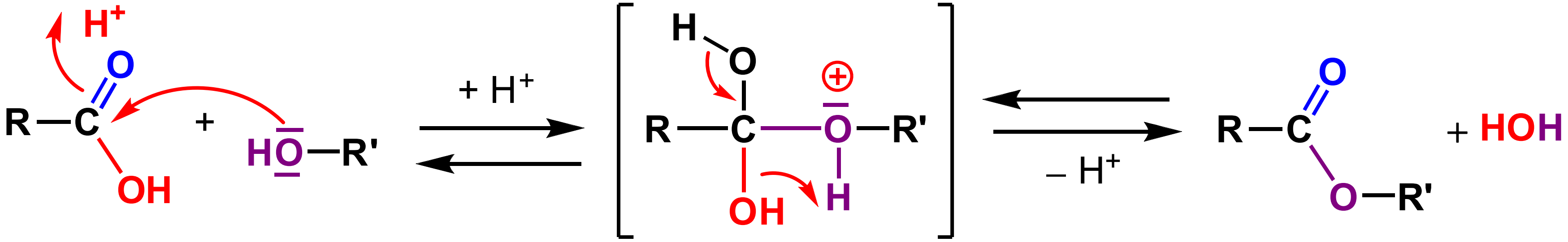
Karbonsavészter



Sav

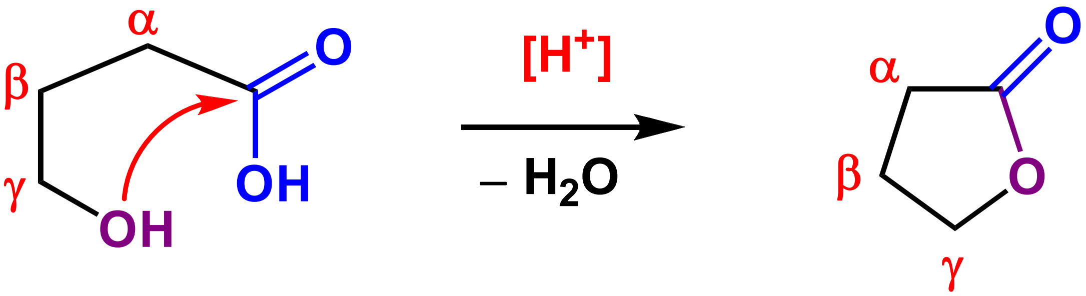
Alkohol

Észter

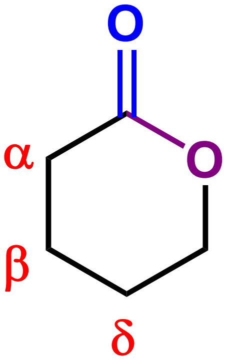


REVERZIBILIS

Laktonképzés

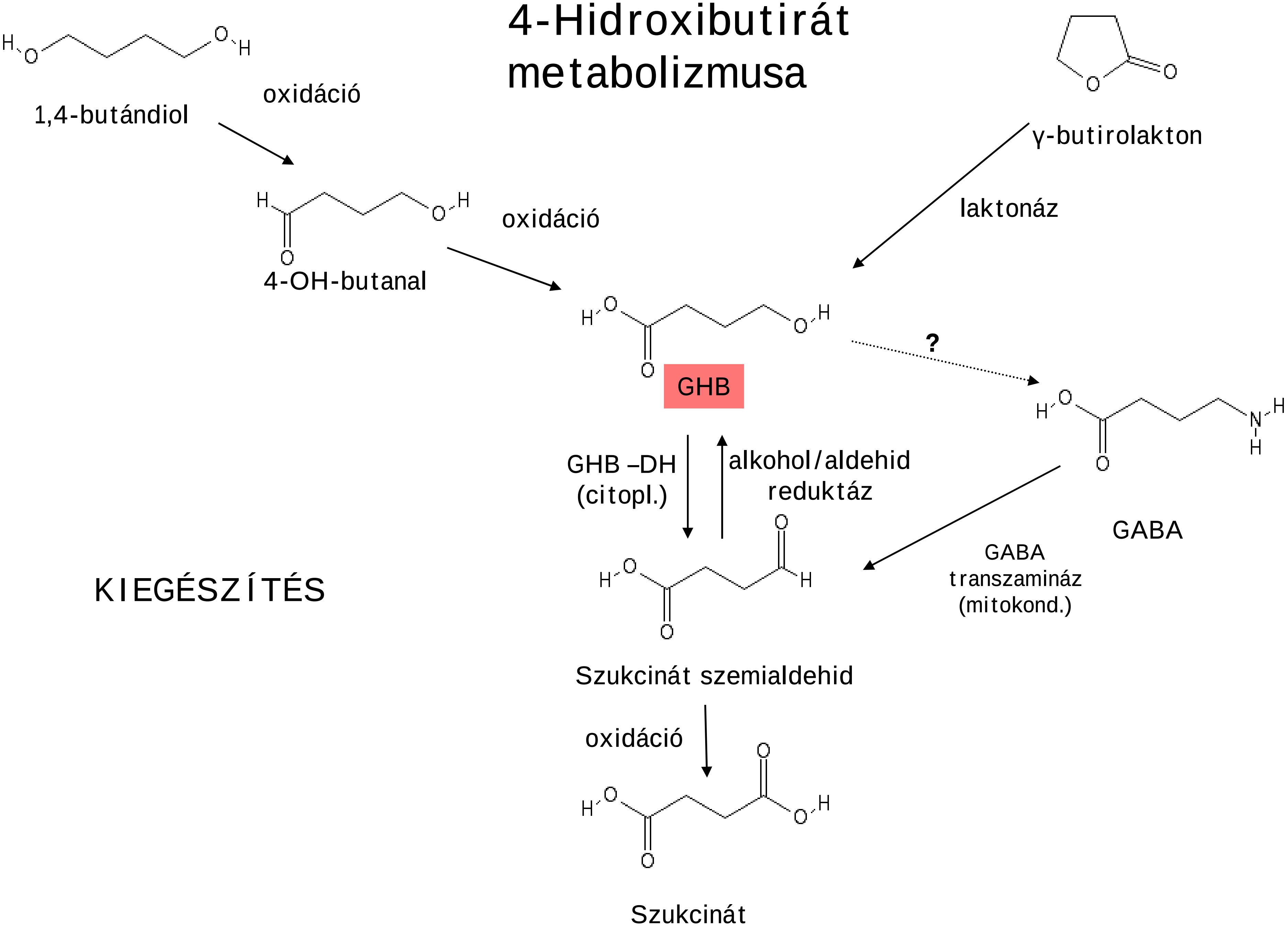


γ–Lacton



δ–Lacton

4-Hidroxibutirát metabolizmusa



1,4-butándiol

oxidáció

4-OH-butanal

oxidáció

γ-butirolakton

laktonáz

GHB

?

GABA

GHB –DH (citopl.)

alkohol/aldehid reduktáz

GABA transzamináz (mitokond.)

Szukcinát szemialdehid

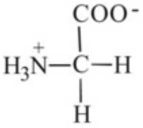
oxidáció

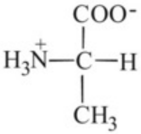
Szukcinát

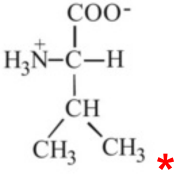
KIEGÉSZÍTÉS

Aminokarbonsavak

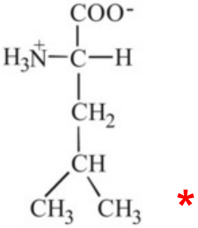
Nempoláros, alifás R-csoport (apoláros aminosavak)


glicin (Gly)

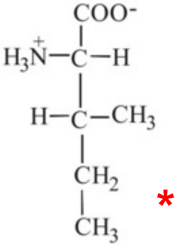

alanin (Ala)



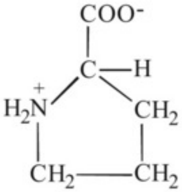
valin (Val)



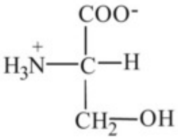
leucin (Leu)

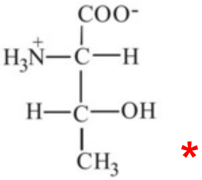


izoleucin (Ile)

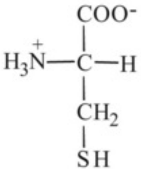

prolin (Pro)

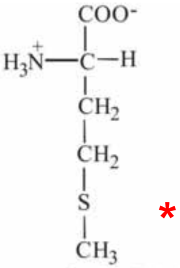
Poláros, neutrális R-csoport


szerin (Ser)

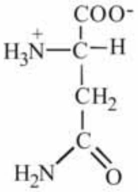


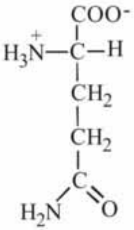
treonin (Thr)


cisztein (Cys)

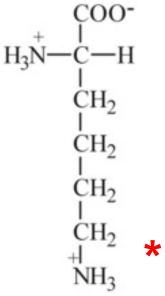


metionin (Met)

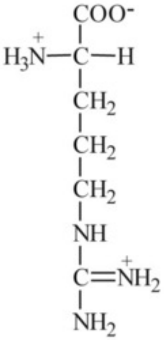

aszparagin (Asn)

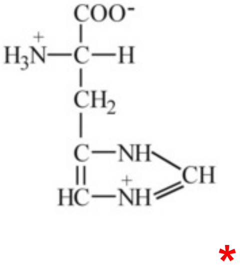

glutamin (Gln)

Pozitív töltésű R-csoport (bázikus aminosavak)



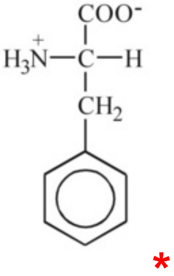
lizin (Lys)


arginin (Arg)

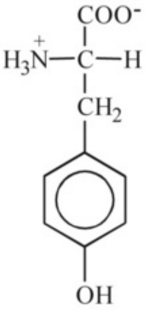


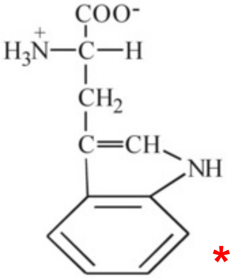
hisztidin (His)

Aromás R-csoport



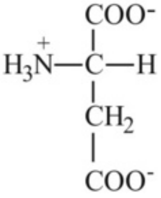
fenilalanin (Phe)

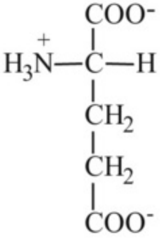

tirozin (Tyr)

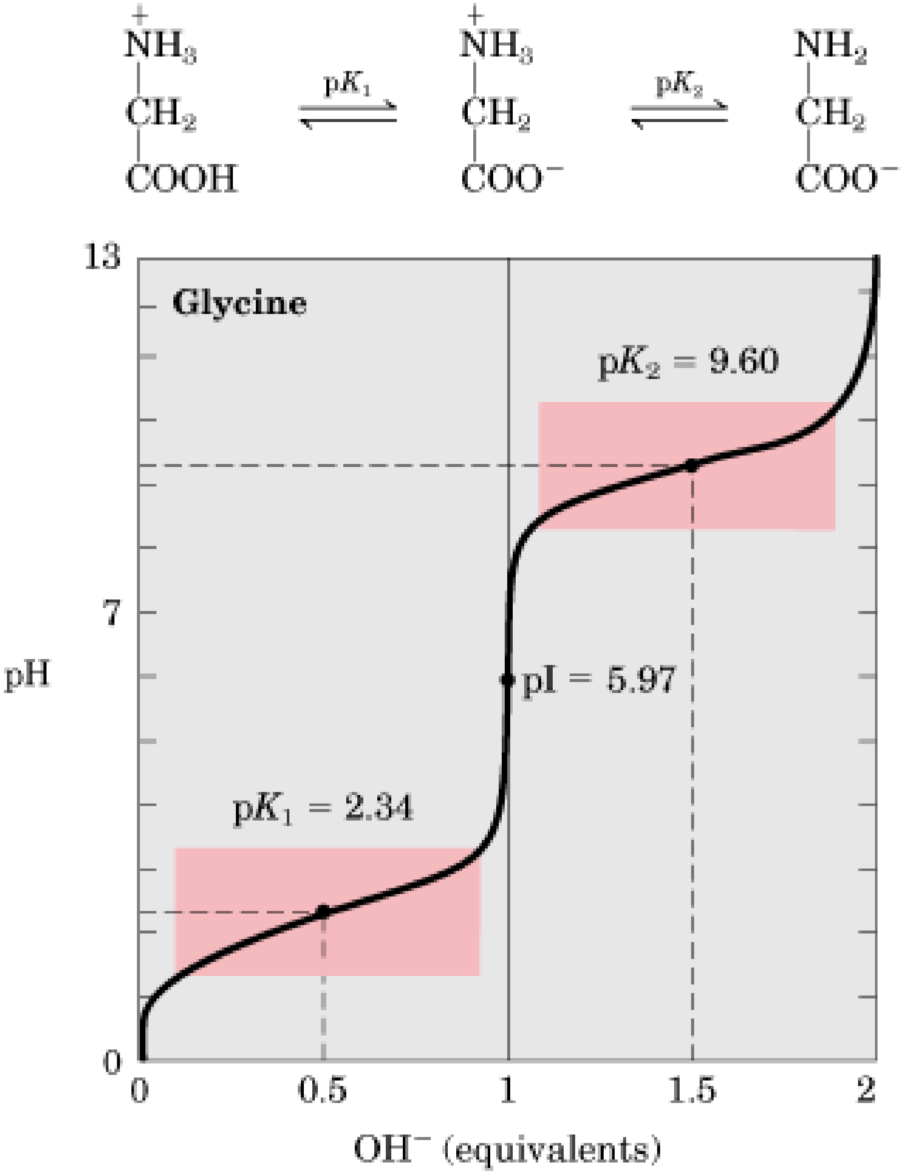


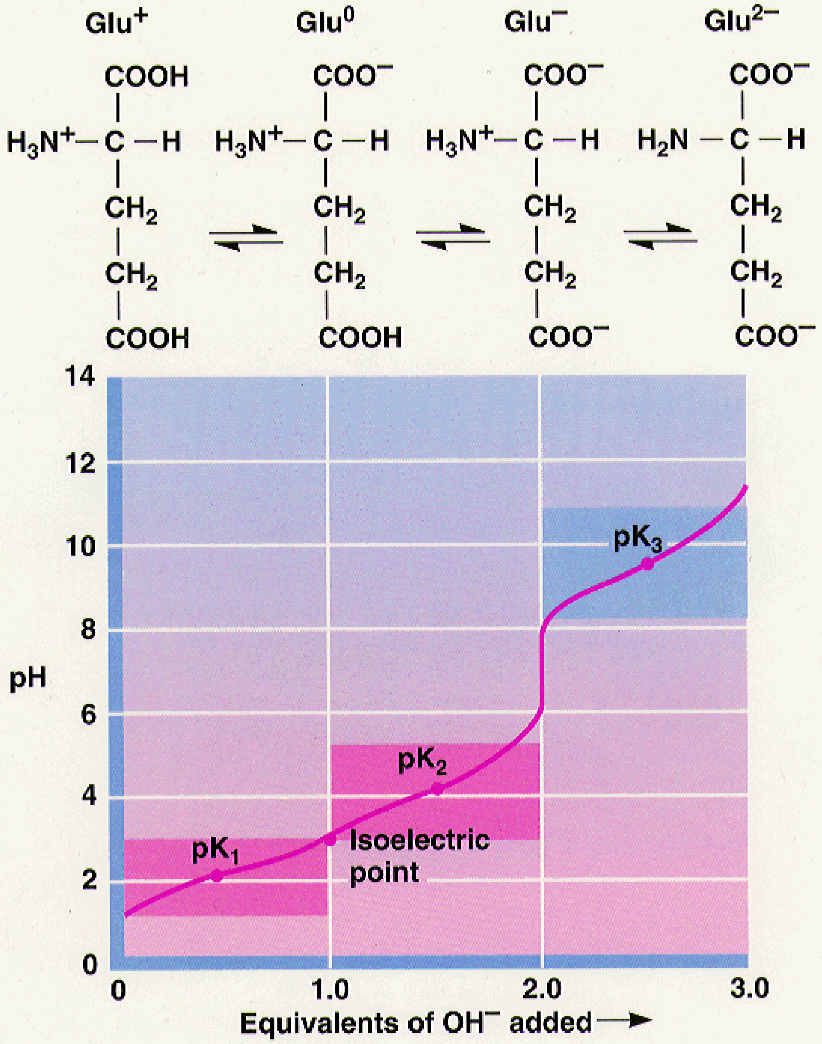
triptofán (Trp)

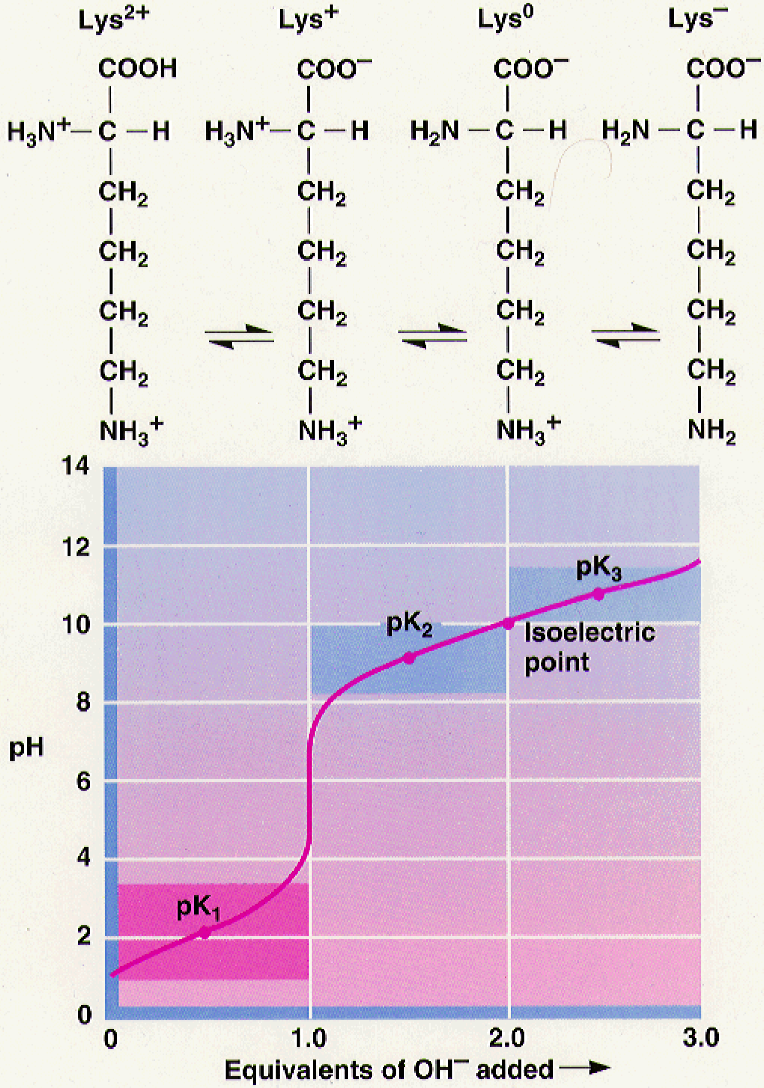
Negatív töltésű R-csoport (savas aminosavak)


aszparaginsav (Asp)


glutaminsav (Glu)

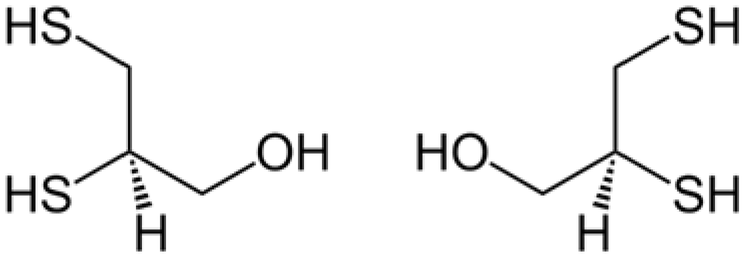

$\overset{+}{N}H_3$
CH_2
COOH
pK_1
$\overset{+}{N}H_3$
CH_2
COO^-
pK_2
NH_2
CH_2
COO^-
Glycine
pK_2 = 9.60
pI = 5.97
pK_1 = 2.34
13
7
0
pH
0
0.5
1
1.5
2
OH^- (equivalents)


Glu⁺
Glu⁰
Glu⁻
Glu²⁻
COOH
COO⁻
H₃N⁺— C — H
H₂N — C — H
CH₂
COOH
COO⁻
14
12
10
8
6
4
2
0
pH
pK₁
pK₂
pK₃
Isoelectric point
0
1.0
2.0
3.0
Equivalents of OH⁻ added


Lys²⁺
Lys⁺
Lys⁰
Lys⁻
COOH
COO⁻
H₃N⁺— C — H
H₂N — C — H
CH₂
NH₃⁺
NH₂
14
12
10
8
6
4
2
0
pH
pK₁
pK₂
pK₃
Isoelectric point
0
1.0
2.0
3.0
Equivalents of OH⁻ added

Kéntartalmú vegyületek

Merkaptánok – *mercurium captans* – BAL (dimercaprol)



alkohol – tiol

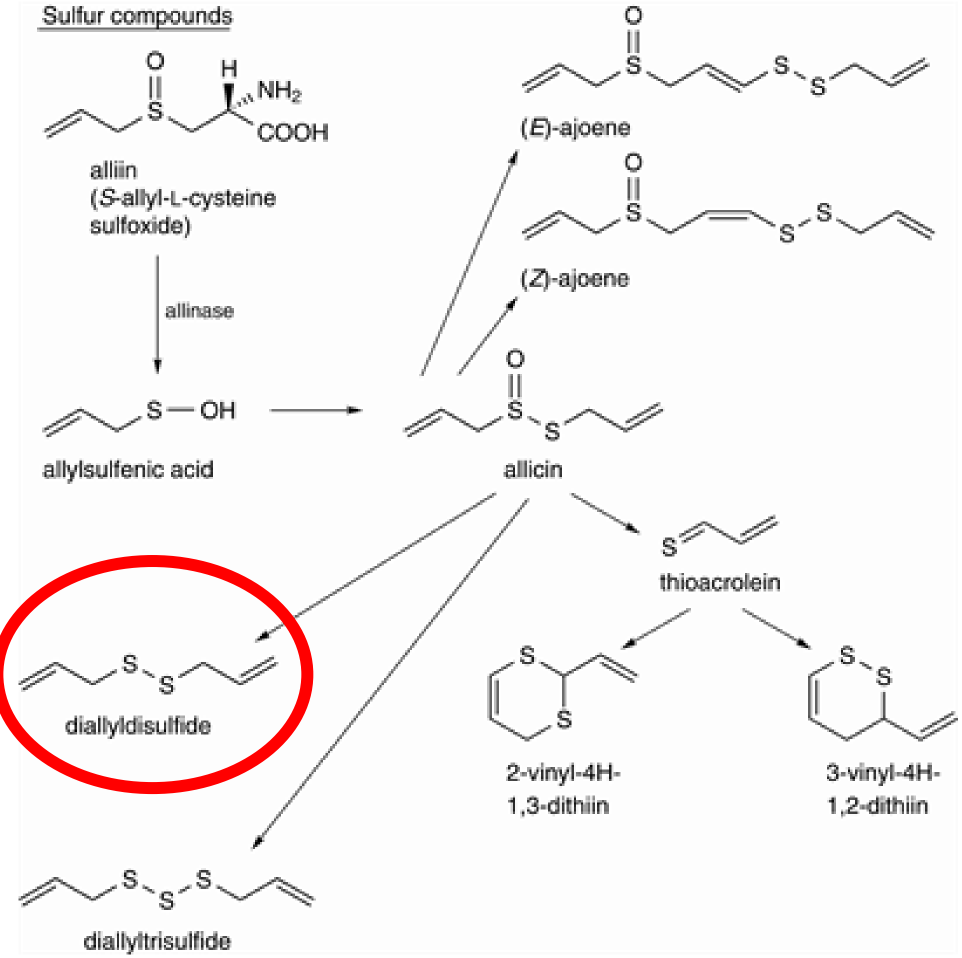
fenol - tiofenol

etanol – etántiol / merkaptoetán

propanol – propántiol / propil-merkaptán

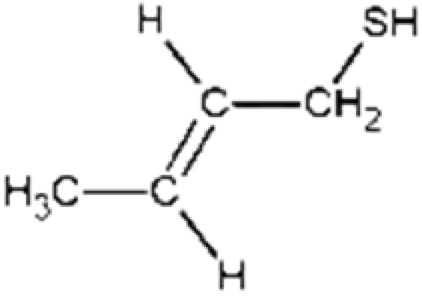
2-propénol – 2-propén-tiol / allil-merkaptán

Kéntartalmú vegyületek

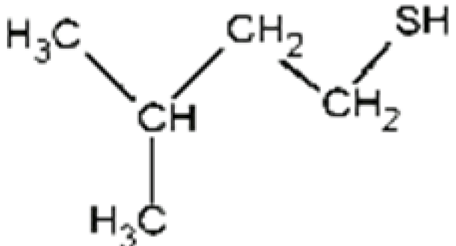


Úgy értesültem, hogy még mindig használja a házi készítésű fokhagymás szájvizét.

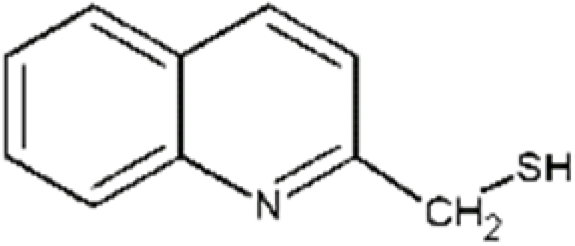
Kéntartalmú vegyületek



(E) 2-butene-1-thiol

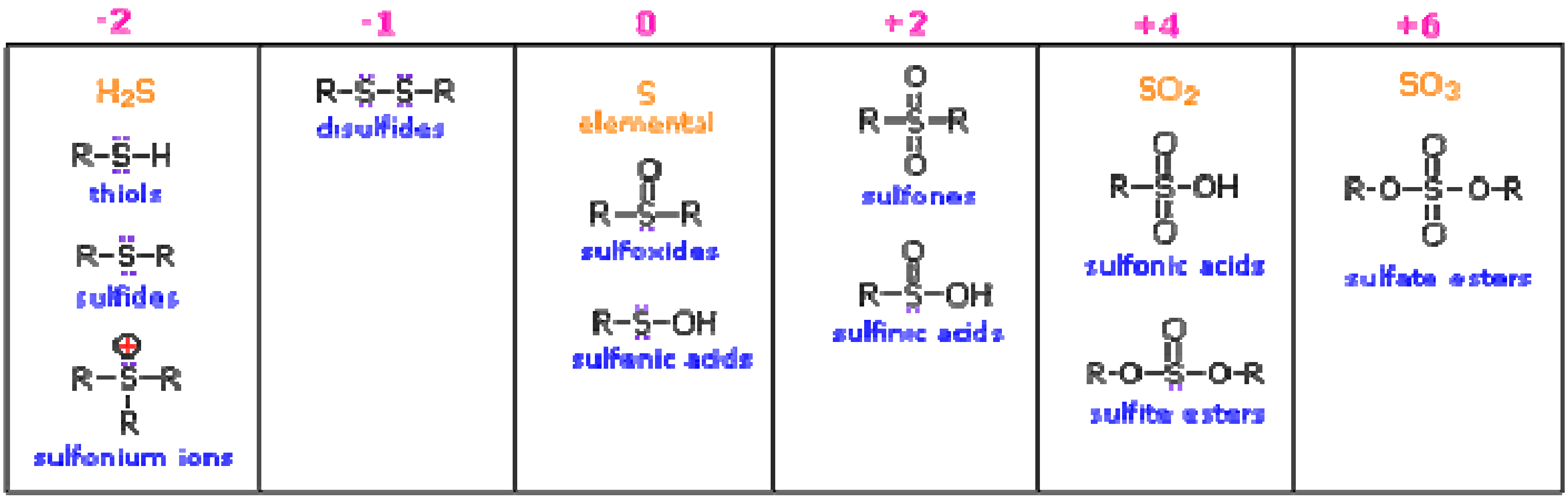


3-methyl-1-butanethiol



2-quinolinemethanthiol

Kén oxidációs állapota szerves vegyületekben



-2	-1	0	+2	+4	+6
H_2S R–S–H thiols R–S–R sulfides sulfonium ions	R–S–S–R disulfides	S elemental sulfoxides R–S–OH sulfenic acids	sulfones sulfinic acids	SO_2 sulfonic acids sulfite esters	SO_3 sulfate esters

Kéntartalmú vegyületek

Méret

S > O

polarizálhatóság

SH > OH

savasság

SH > OH → lúgokkal: sóképzés

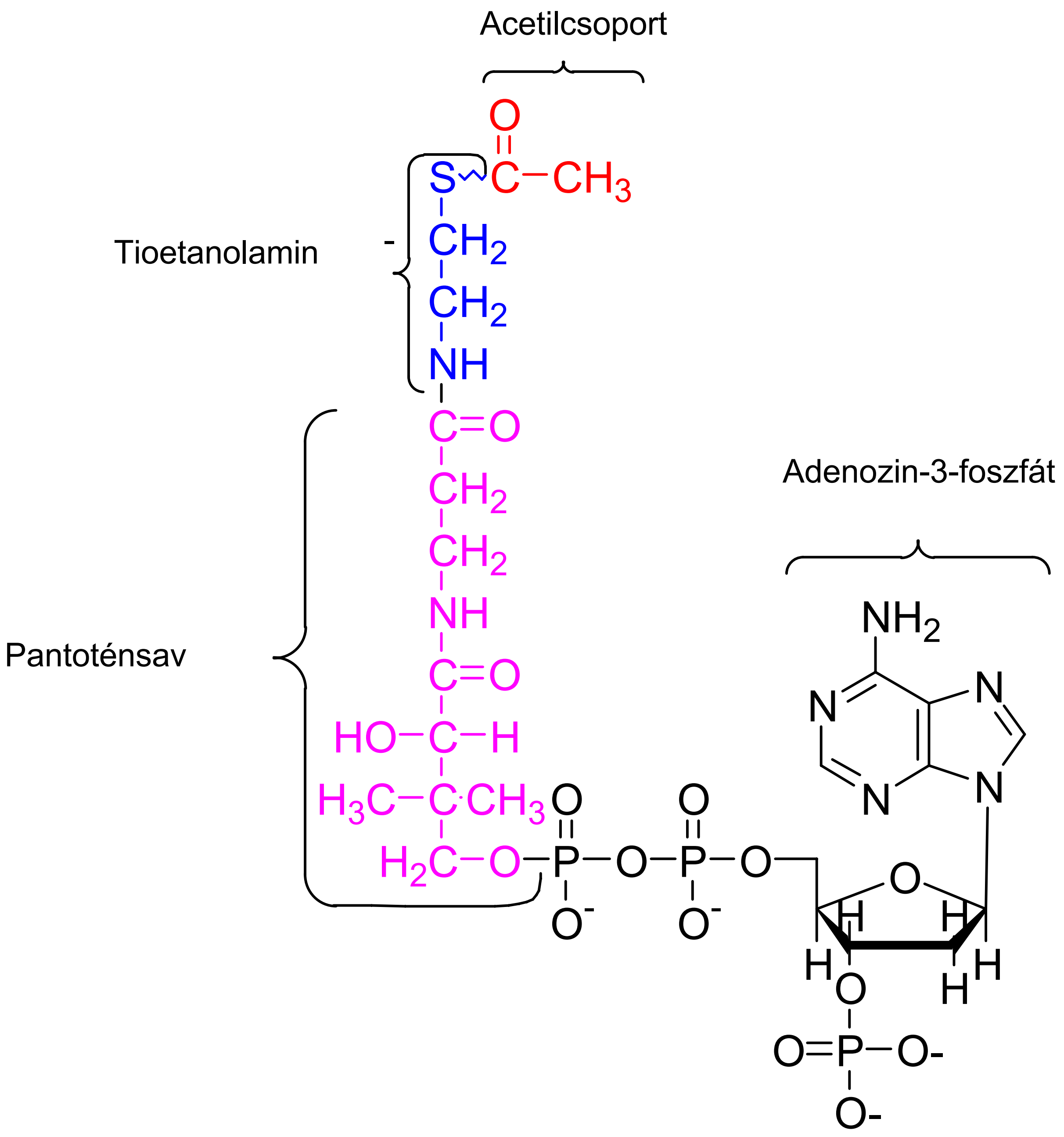
karbonsavakkal : tioészterképzés

- tioészterek nagy energiájú makroerg kötés (-30-40 kJ/mol) vö:ATP

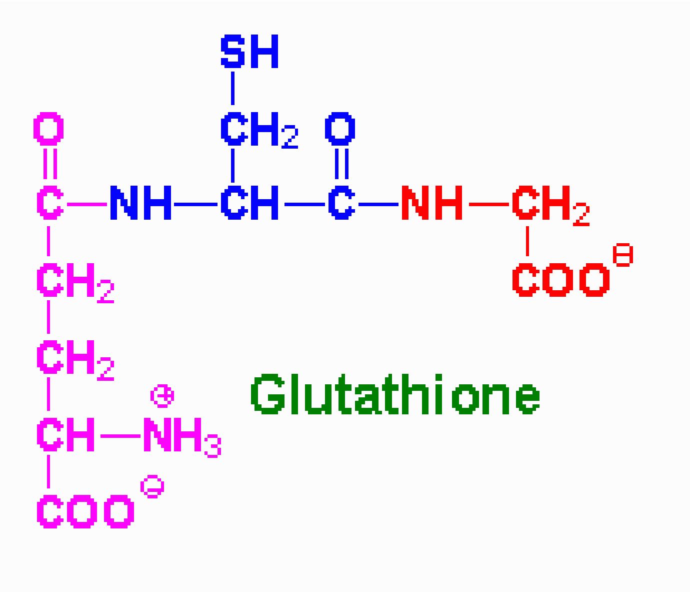
könnyen oxidálhatóak – antioxidáns (?)

- diszulfid

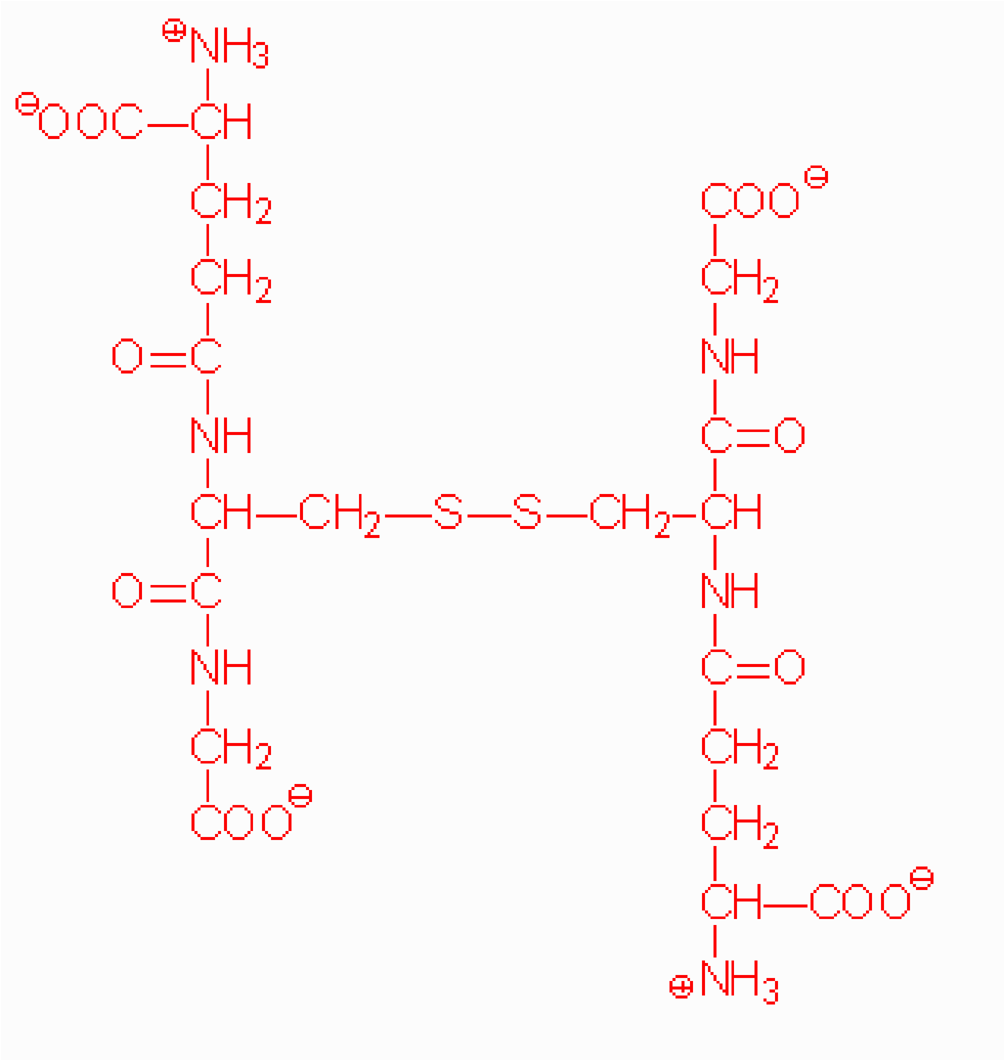
tioalkoholok aldehidekkel tiofélacetált képeznek



Acetil-koenzimA

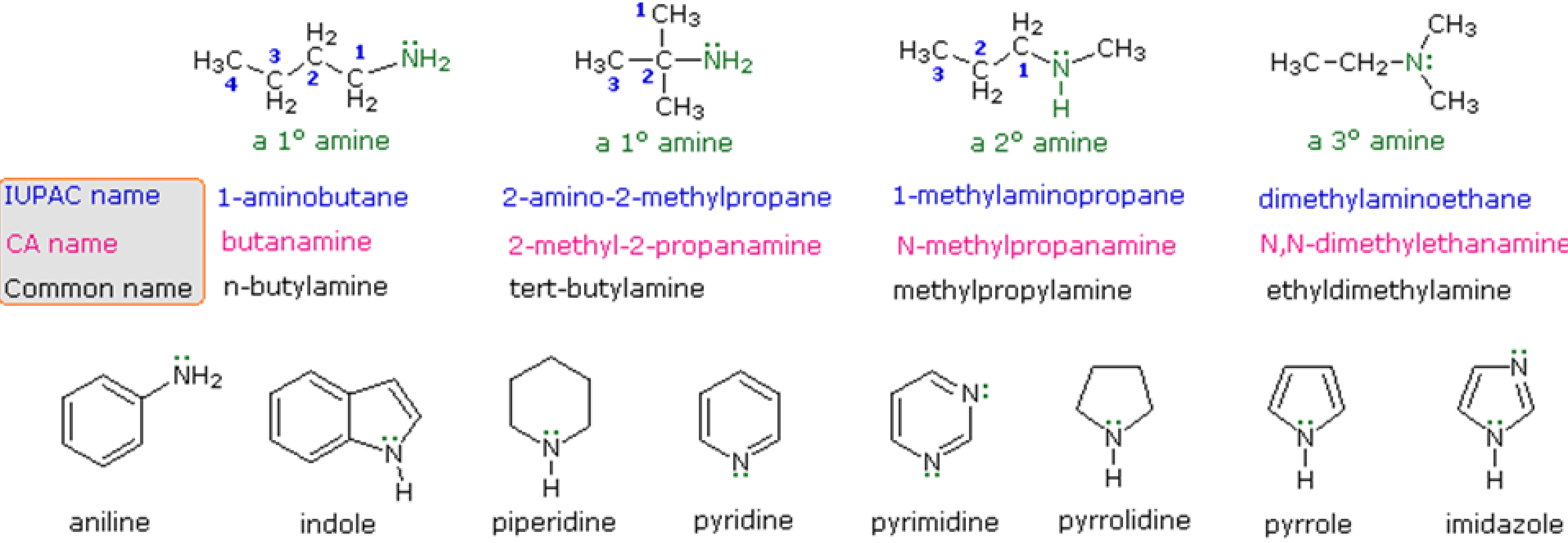


Glutathione



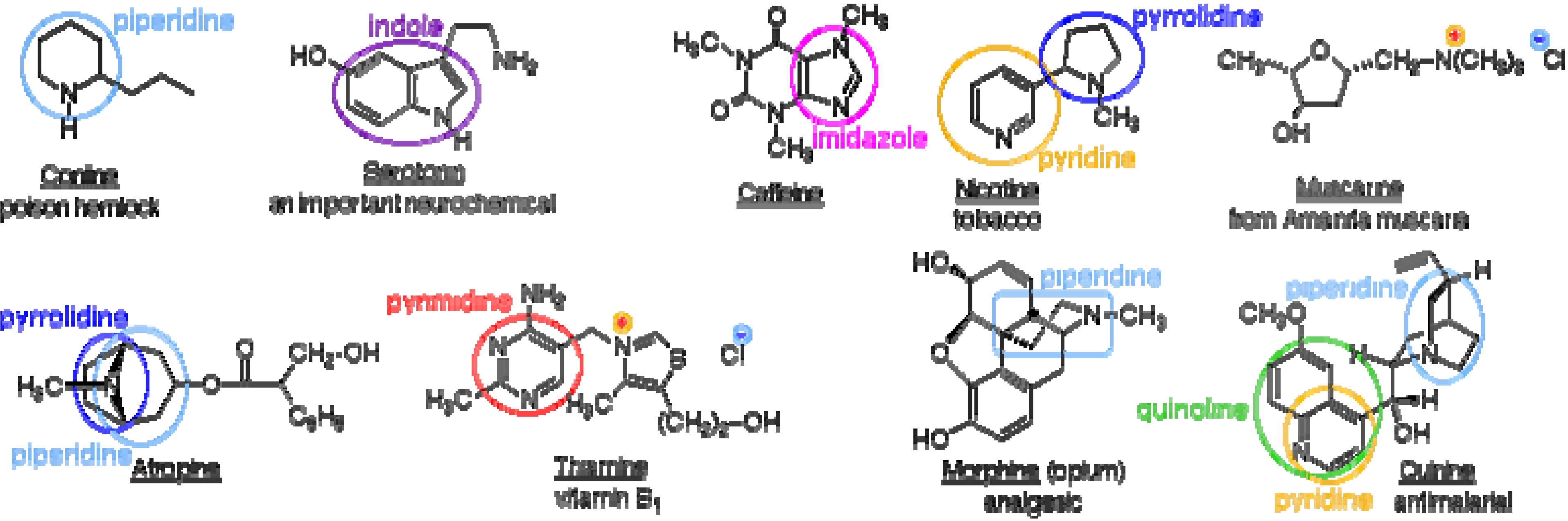
GSSG

Nitrogéntartalmú szerves vegyületek



	a 1° amine	a 1° amine	a 2° amine	a 3° amine
IUPAC name	1-aminobutane	2-amino-2-methylpropane	1-methylaminopropane	dimethylaminoethane
CA name	butanamine	2-methyl-2-propanamine	N-methylpropanamine	N,N-dimethylethanamine
Common name	n-butylamine	tert-butylamine	methylpropylamine	ethyldimethylamine

Természetes aminok



Nitrogén oxidációs állapota szerves vegyületekben

Oxidation State	**–3**	**–2**	**–1**	**0**	**+1**	**+3**
Formulas (names)	R_3N (amines) $R_4N^{(+)}$ (ammonium) C=N–R (imines) C≡N (nitriles)	$R_2N{-}NR_2$ (hydrazines) $C{=}N{-}NR_2$ (hydrazones)	RN=NR (azo cpd.) R_2NOH (hydroxyl amine) R_3NO (amine oxide)	N_2 (nitrogen) $R{-}N_2^{(+)}$ (diazonium)	R–N=O (nitroso)	$R\text{-}NO_2$ (nitro) RO–N=O (nitrite ester)

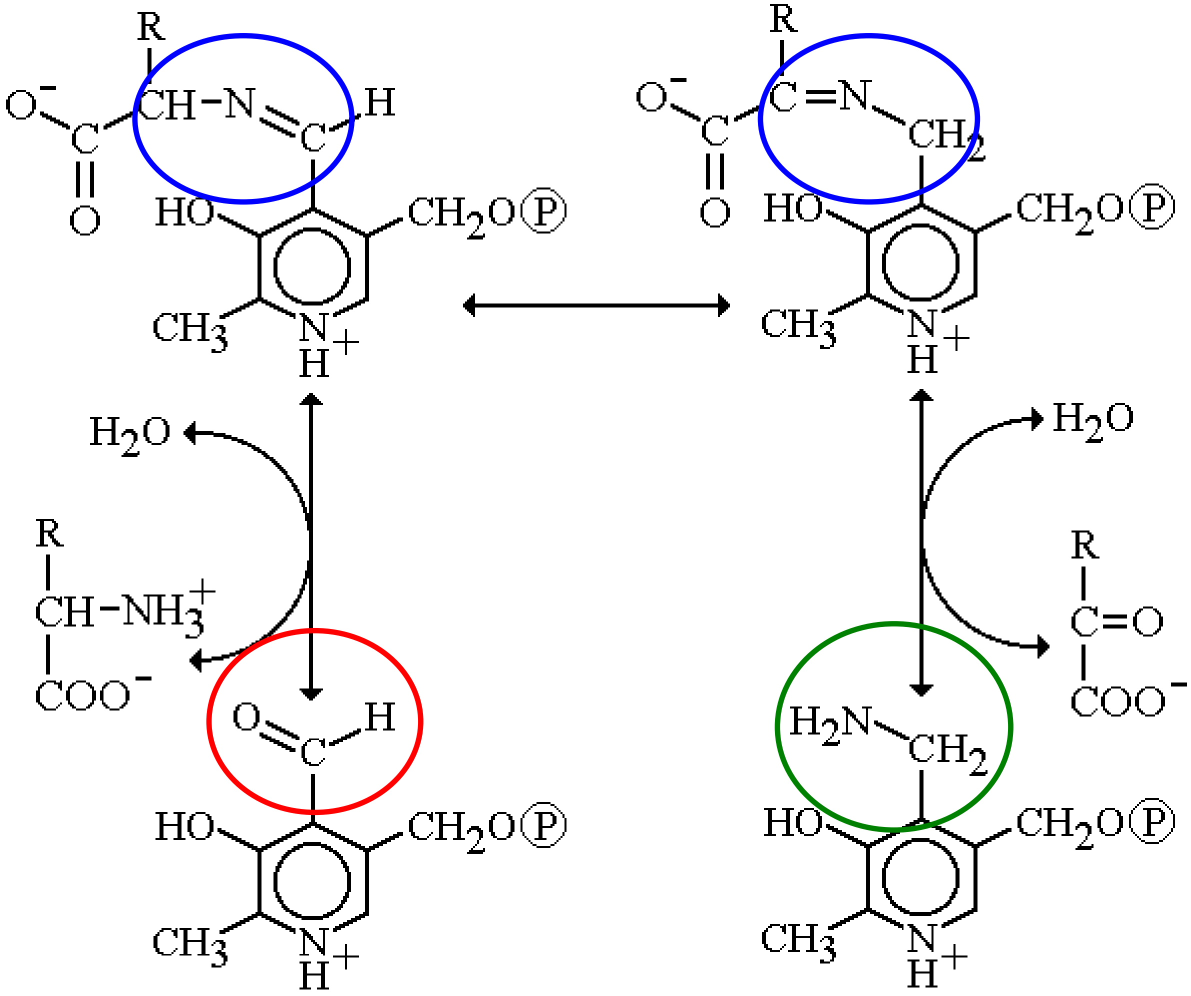
Nitrogéntartalmú szerves vegyületek

a nitrocsoport elektronszívó hatású

oxovegyületekkel a primer aminok schiff bázisokat képeznek
- transzaminálás

Transzaminálás

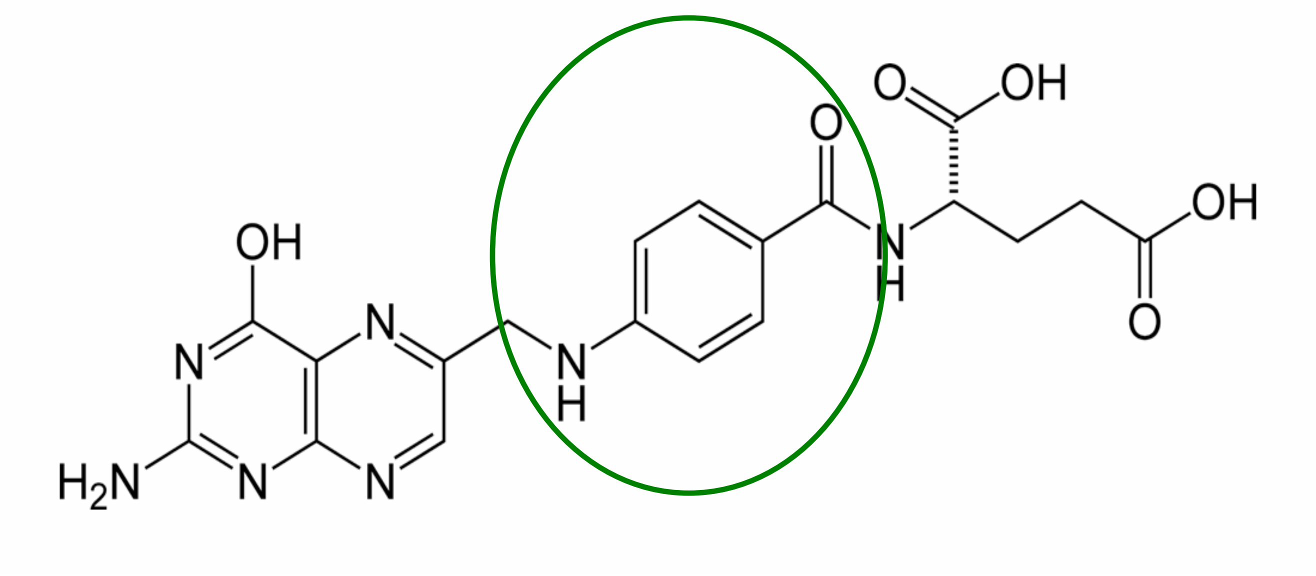
Schiff bázis

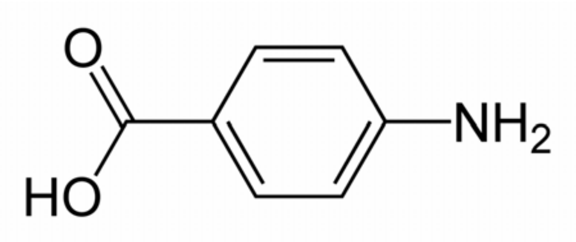


Piridoxál

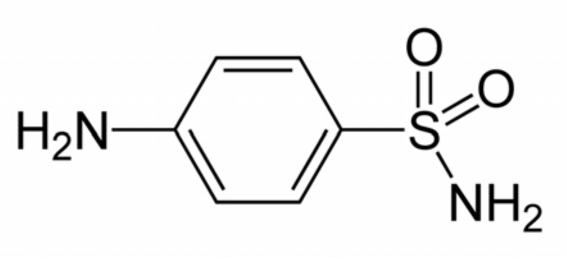
Piridoxamin

Folsav



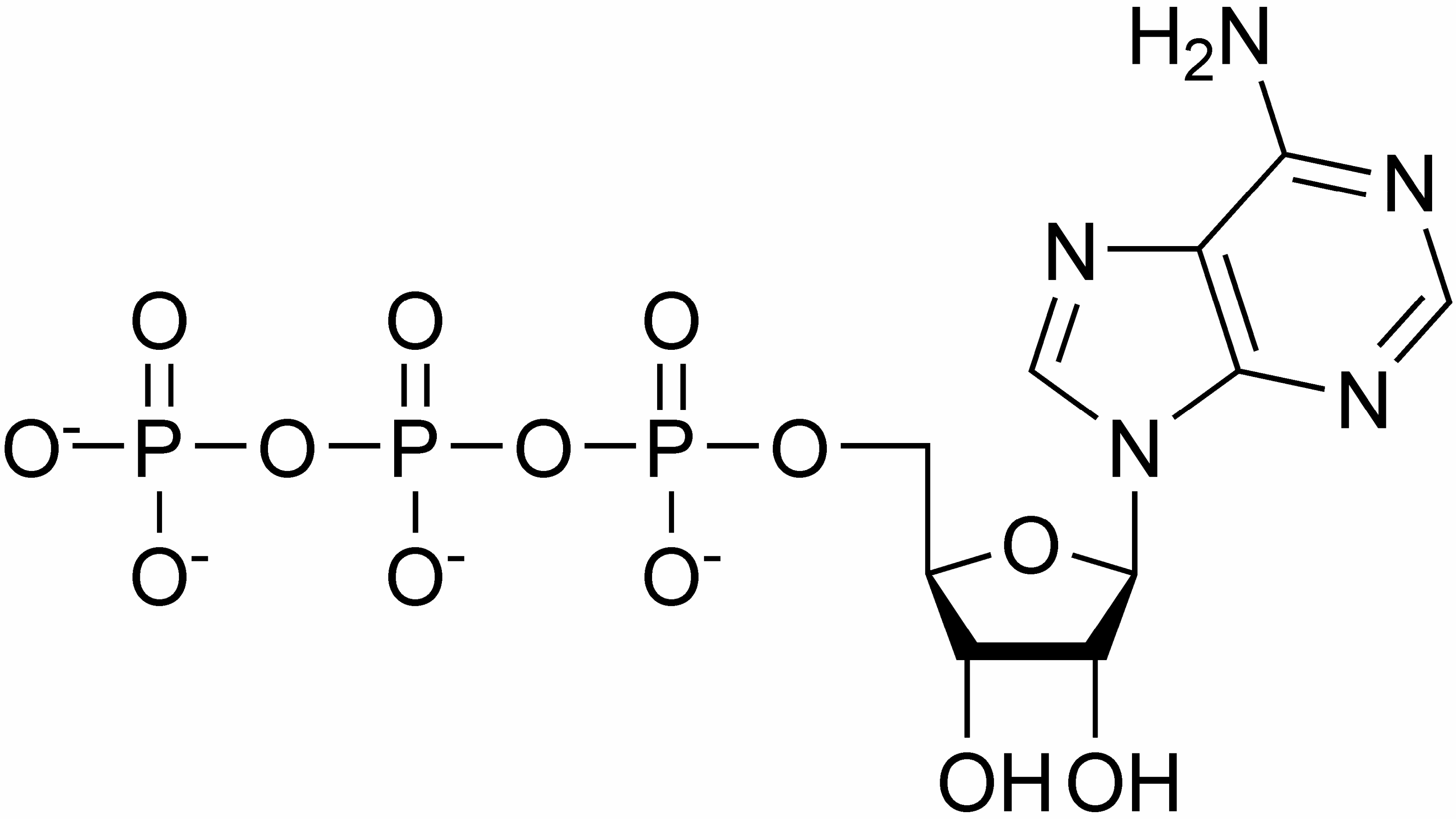


PABA

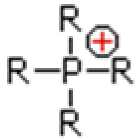
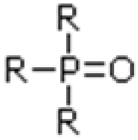
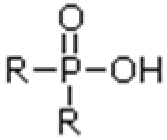
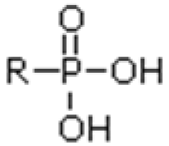
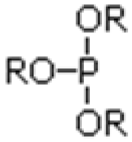
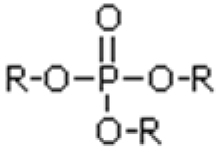


Szulfonamid - antimetabolit

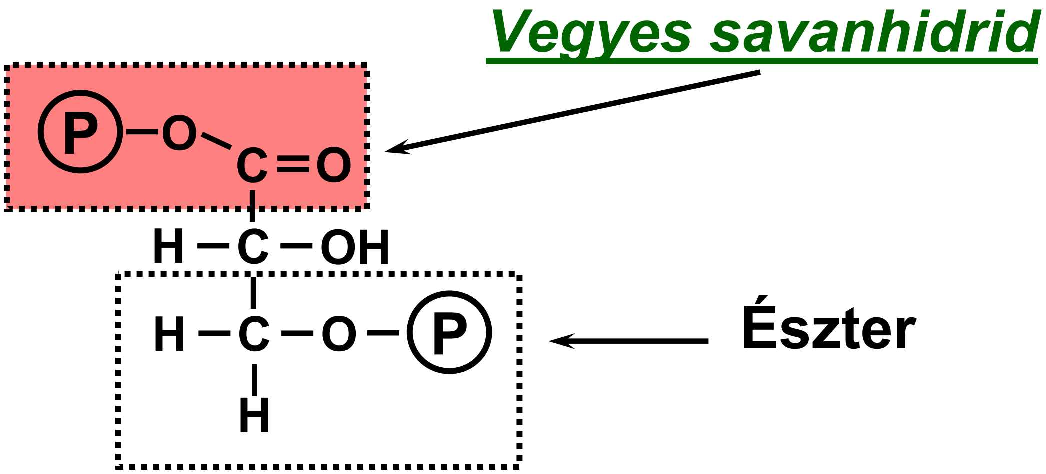
Foszfortartalmú szerves vegyületek



Foszfor oxidációs állapota szerves vegyületekben

-3	-1	0	+1	+3	+5
PH_3 phosphine R_3P trialkyl phosphines  $\mathrm{R{-}\overset{R}{\underset{R}{P}}{-}R}^{\oplus}$ tetraalkyl phosphonium	 $\mathrm{R{-}\overset{R}{\underset{R}{P}}{=}O}$ phosphine oxides	P elemental	 $\mathrm{R{-}\overset{O}{\overset{\Vert}{\underset{R}{P}}}{-}OH}$ phosphenic acids	 $\mathrm{R{-}\overset{O}{\overset{\Vert}{\underset{OH}{P}}}{-}OH}$ phosphonic acids  $\mathrm{RO{-}\overset{OR}{\underset{OR}{P}}}$ phosphite esters	P_2O_5  $\mathrm{R{-}O{-}\overset{O}{\overset{\Vert}{\underset{O{-}R}{P}}}{-}O{-}R}$ phosphate esters

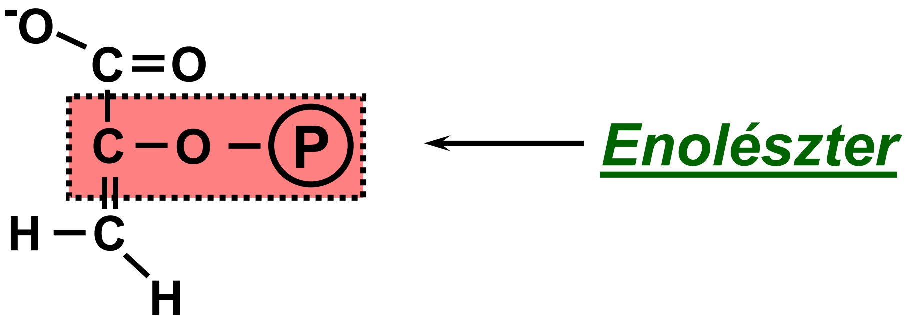
1) 1,3 Biszfoszfoglicerát



Vegyes savanhidrid

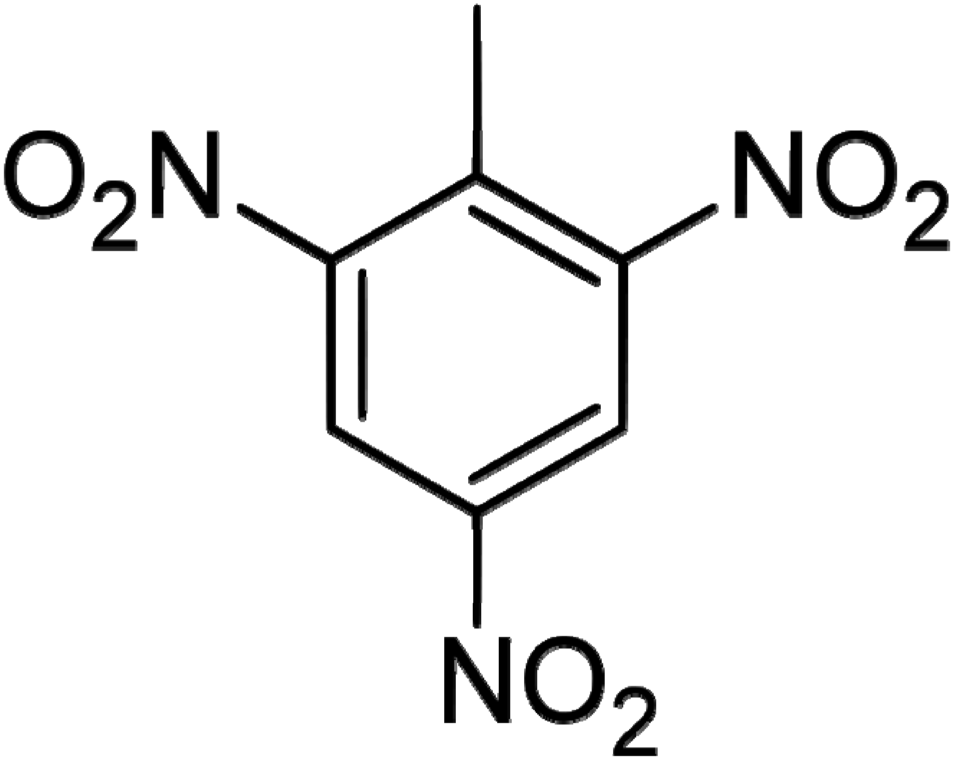
Észter

2) Foszfoenolpiruvát

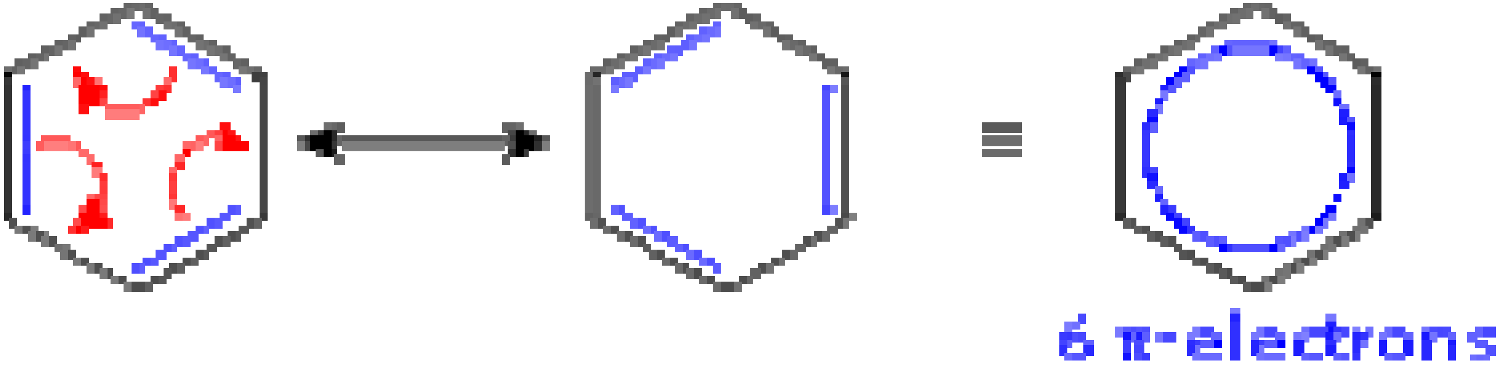


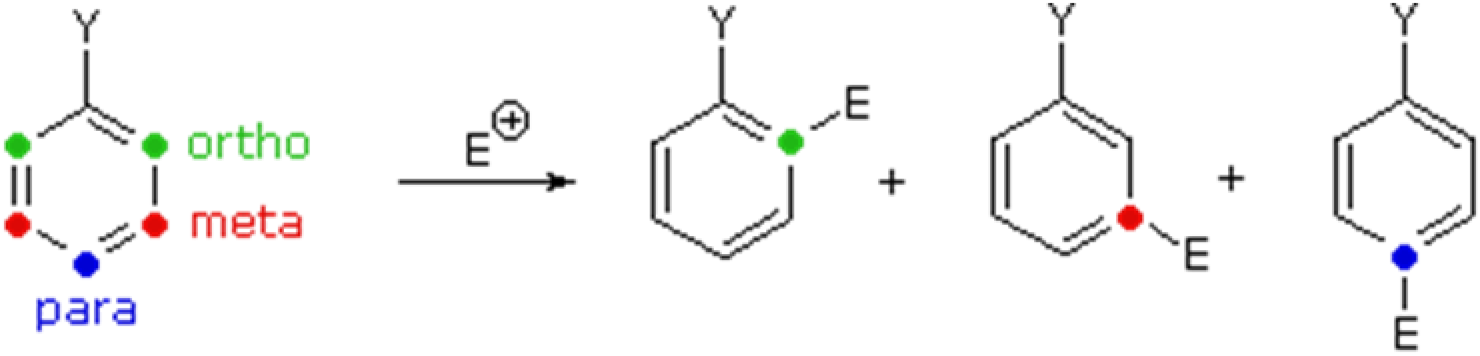
Enolészter

Aromás vegyületek



Benzol





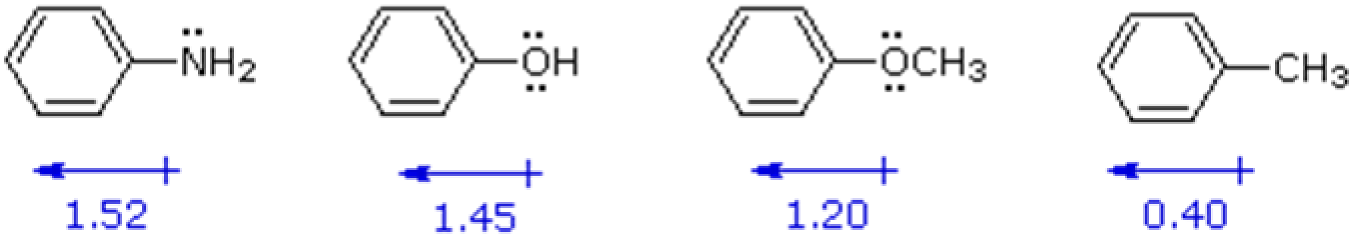
A monosubstituted benzene compound

ortho isomer

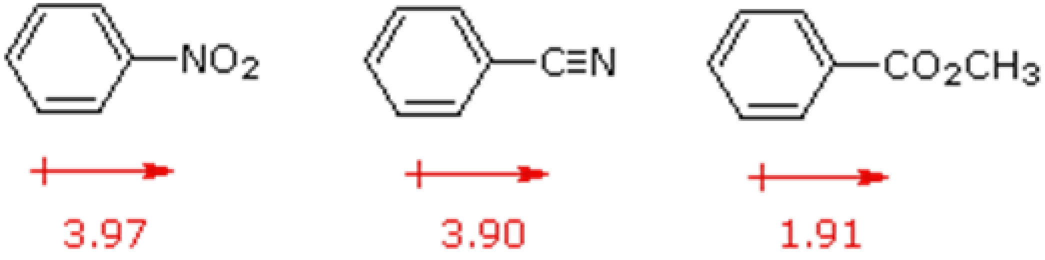
meta isomer

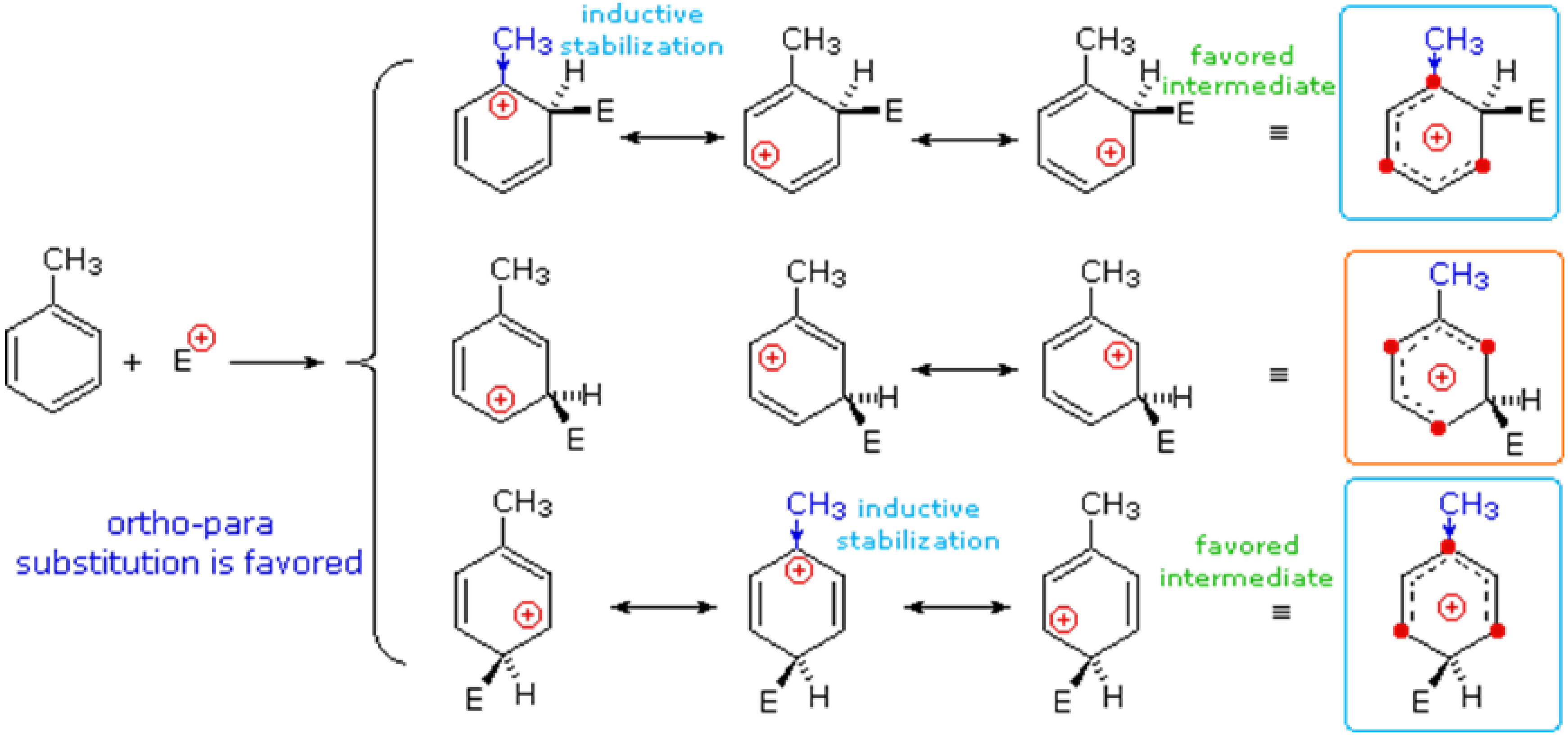
para isomer

Activating Substituents

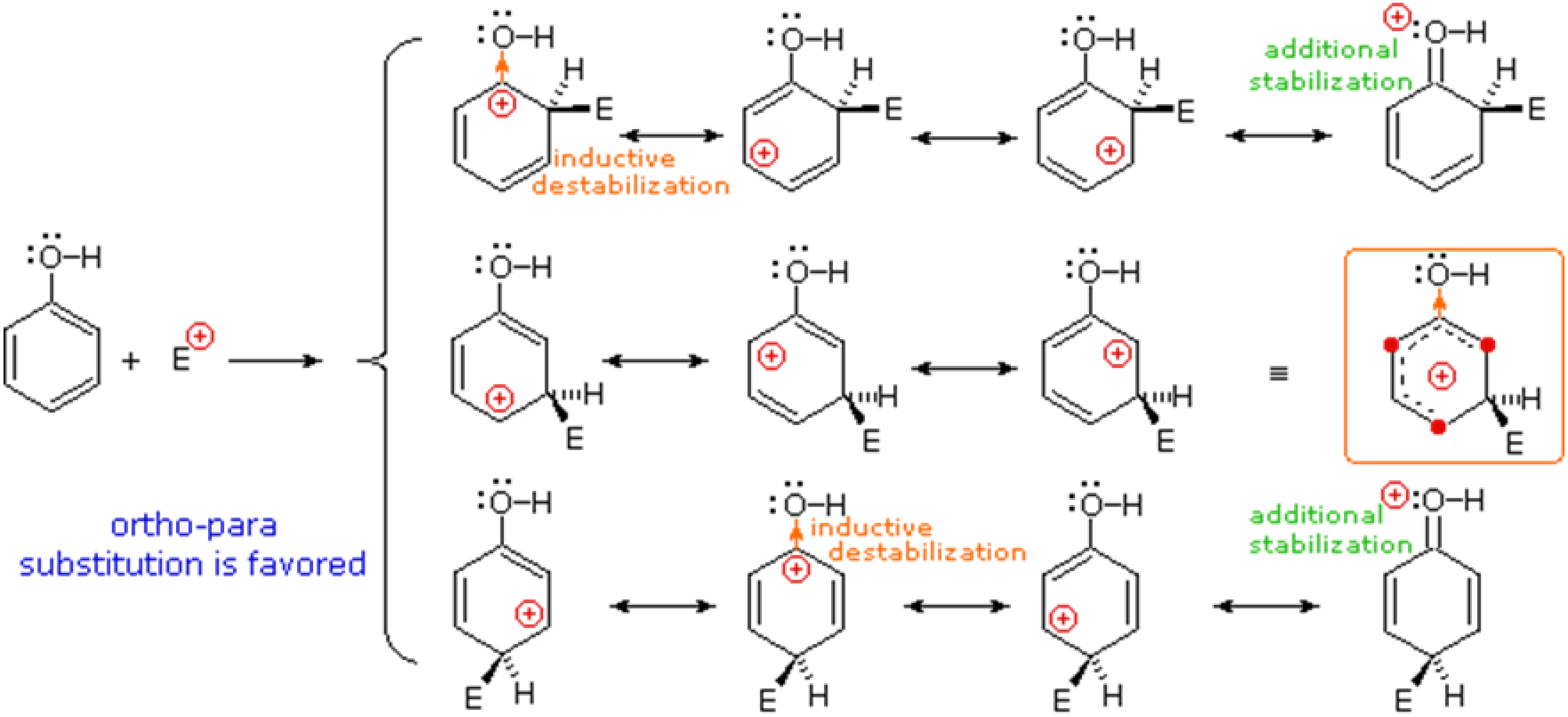


Deactivating Substituents

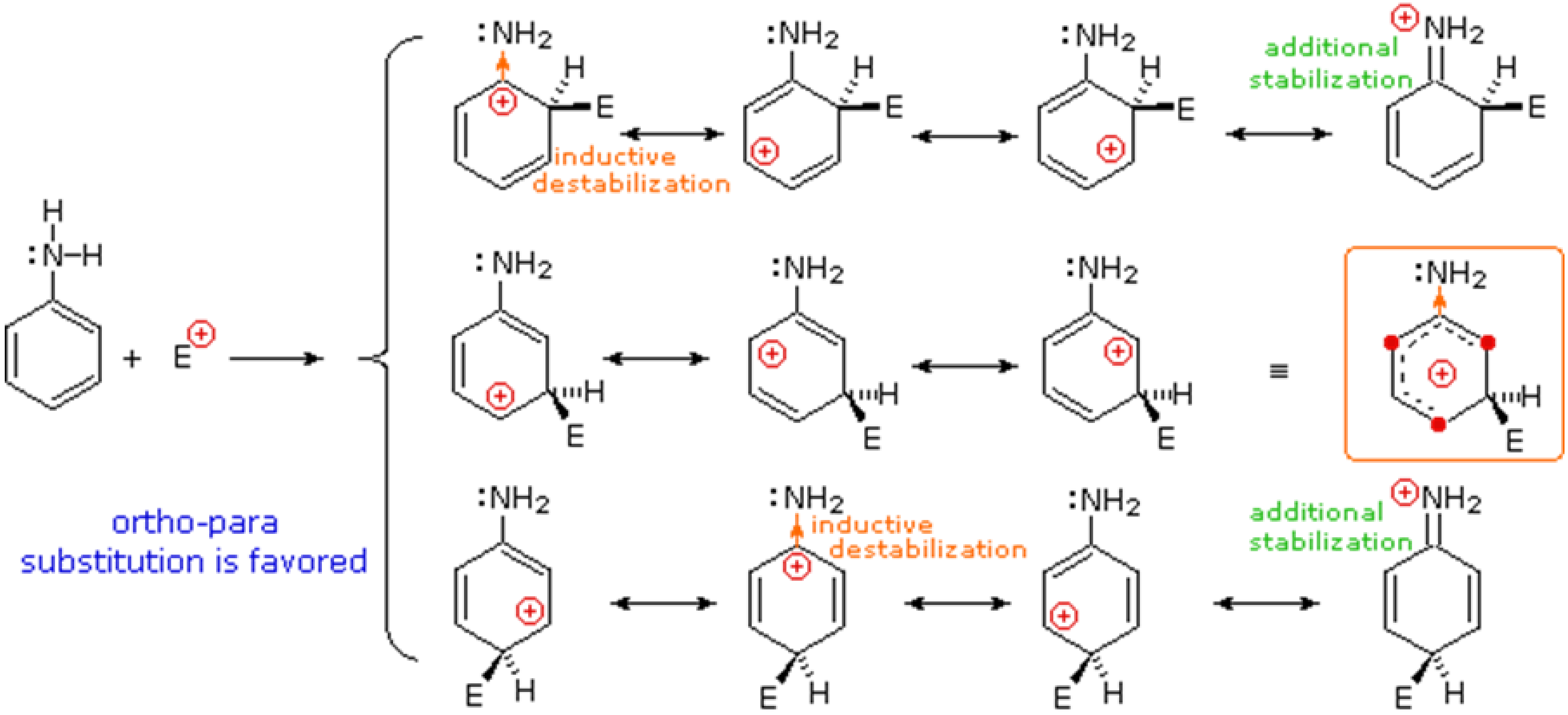




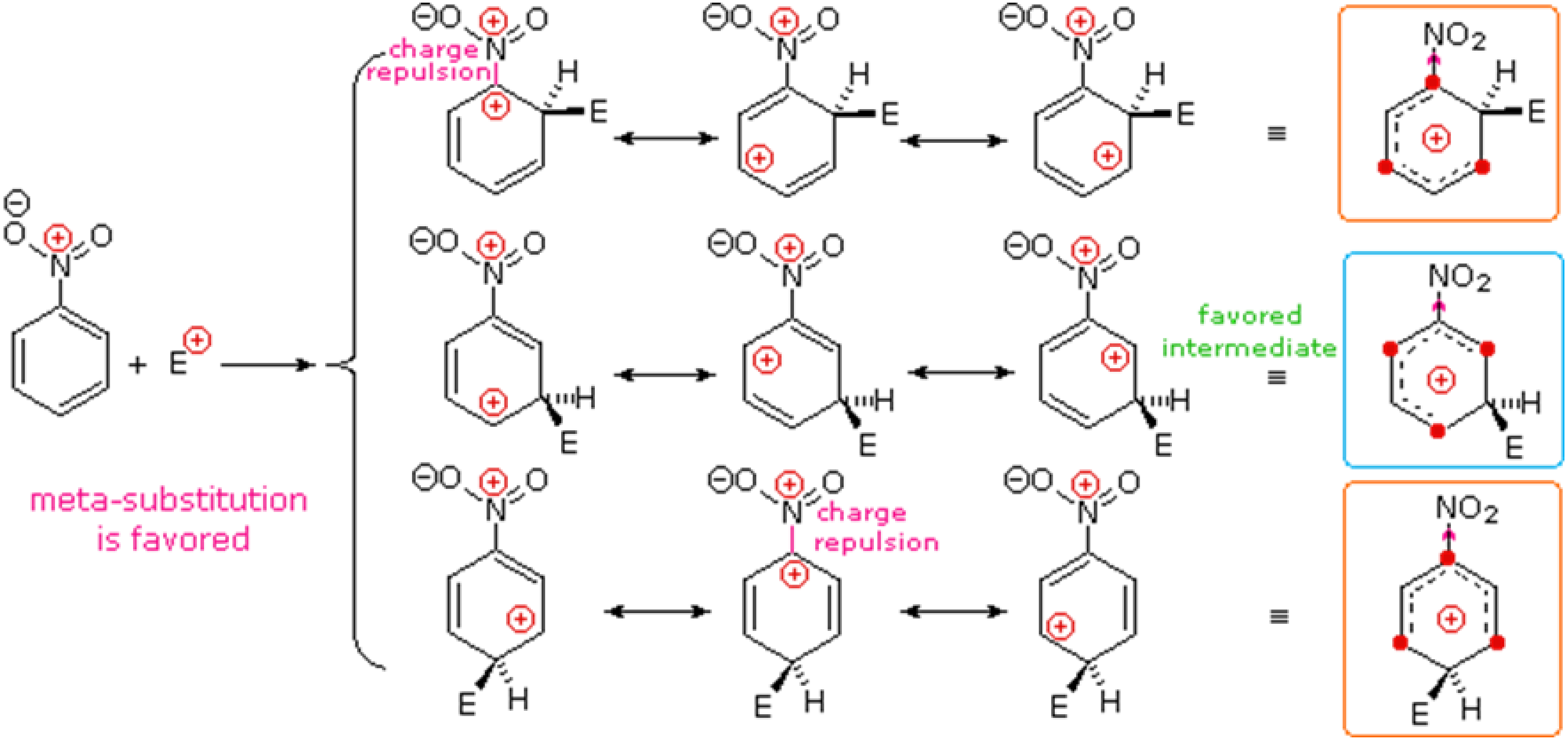
ortho-para
substitution is favored



ortho-para substitution is favored



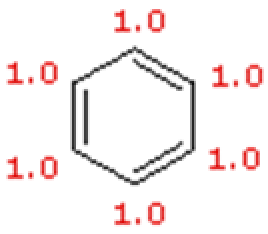
ortho-para substitution is favored

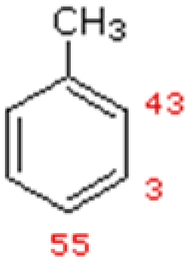


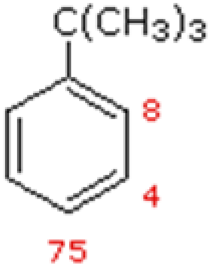
meta-substitution is favored

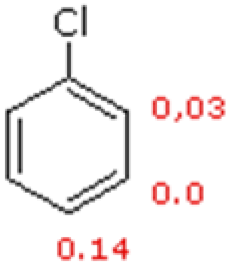
Y in C_6H_5–Y	**Reaction**	**% Ortho-Product**	**% Meta-Product**	**% Para-Product**
$–O–CH_3$	Nitration	30–40	0–2	60–70
$–O–CH_3$	F-C Acylation	5–10	0–5	90–95
$–NO_2$	Nitration	5–8	90–95	0–5
$–CH_3$	Nitration	55–65	1–5	35–45
$–CH_3$	Sulfonation	30–35	5–10	60–65
$–CH_3$	F-C Acylation	10–15	2–8	85–90
–Br	Nitration	35–45	0–4	55–65
–Br	Chlorination	40–45	5–10	50–60

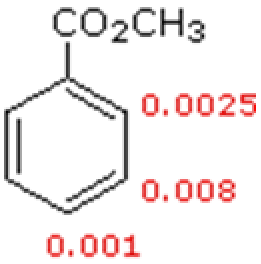
Rates of Nitration at Sites on the Benzene Ring











Total Rate	6.0	147	99	0.20	0.022
Relative Rate	1.0	24.5	16.5	0.033	0.004