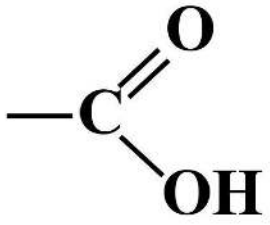
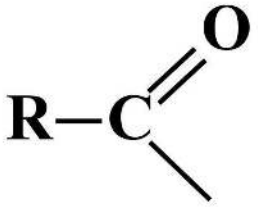
Karbonsavak és karbonsavszármazékok

Karbonsavak

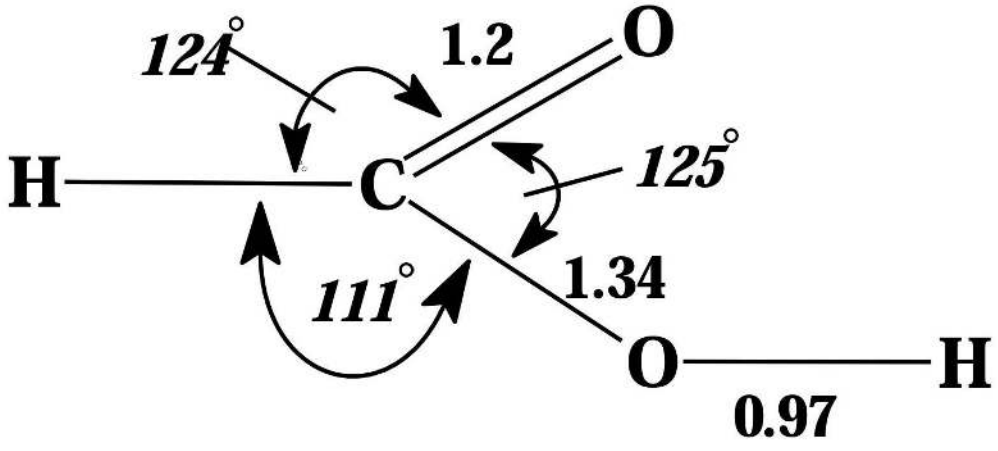
Szerkezet



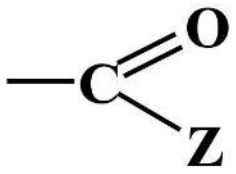
csoportot tartalmazó vegyületek



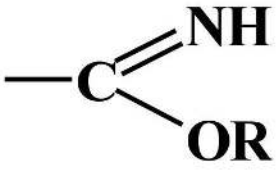
acilcsoport



Karbonsavszármazékok

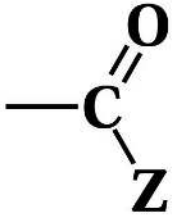


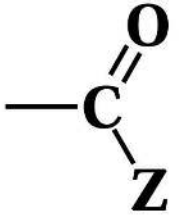
csoportot tartalmazó vegyületek,

továbbá —CN,  csoportot

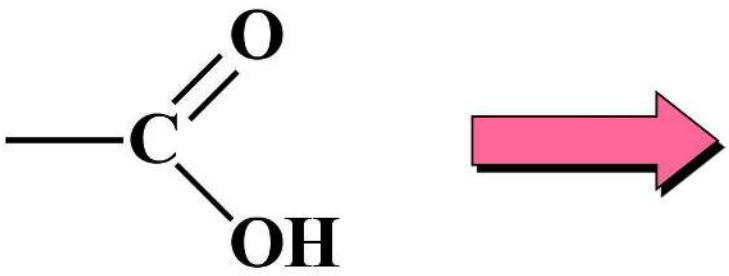
Z: heteroatom, vagy csoport

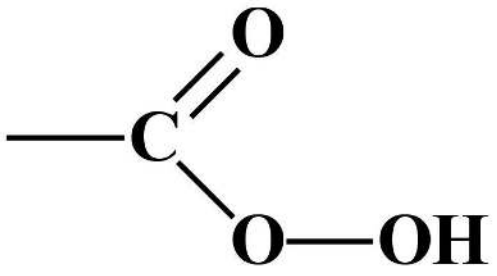
Z:	**halogén**	⟶	**savhalogenid**
	aciloxi	⟶	**savanhidrid**
	alkil/ariloxi	⟶	**észter**
	NR^1R^2	⟶	**savamid**

 **jelentése** —C≡N ⟶ **savnitril**

 **jelentése** ⟶ **imidsavészter**

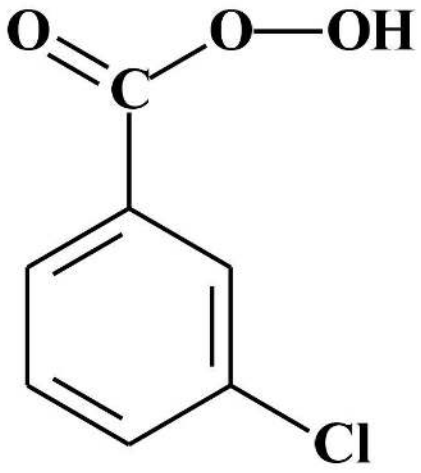
imidsav, R=H

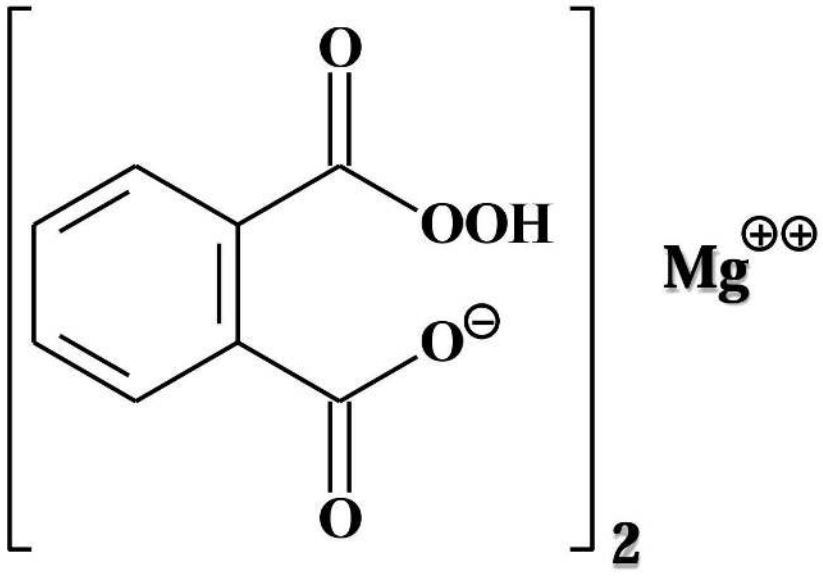




karbonsav

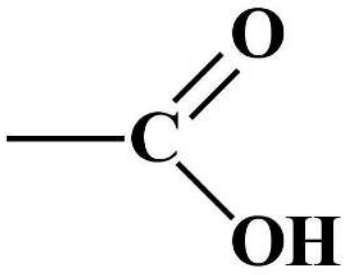
peroxikarbonsav



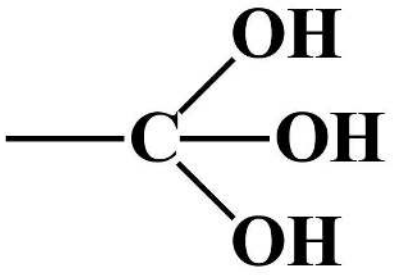


***m*-klórperbenzoesav**

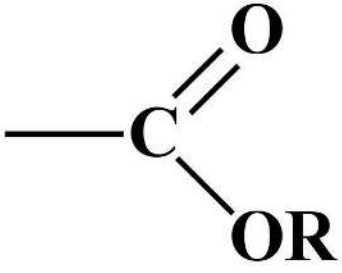
magnézium-monoperoxiftalát



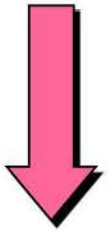
karbonsav

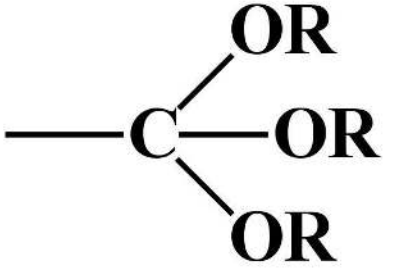


ortokarbonsav



karbonsav észter





ortokarbonsav észter

Karbonsavak

Csoportosítás

Karboxilcsoportok száma és helyzete szerint

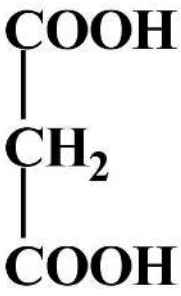
monokarbonsav

$CH_3—COOH$

dikarbonsav

$HOOC—COOH$

1,2



1,3

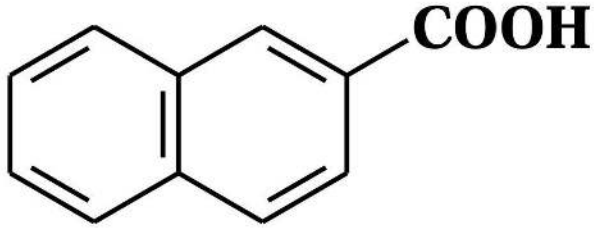
Karboxilcsoporthoz kapcsolódó szénhidrogéncsoport szerint

$H_3C—CH_2–COOH$

telített

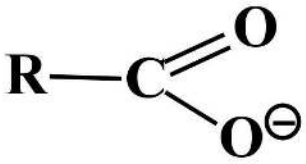
$H_2C=CH–COOH$

telítetlen



aromás

Savmaradék



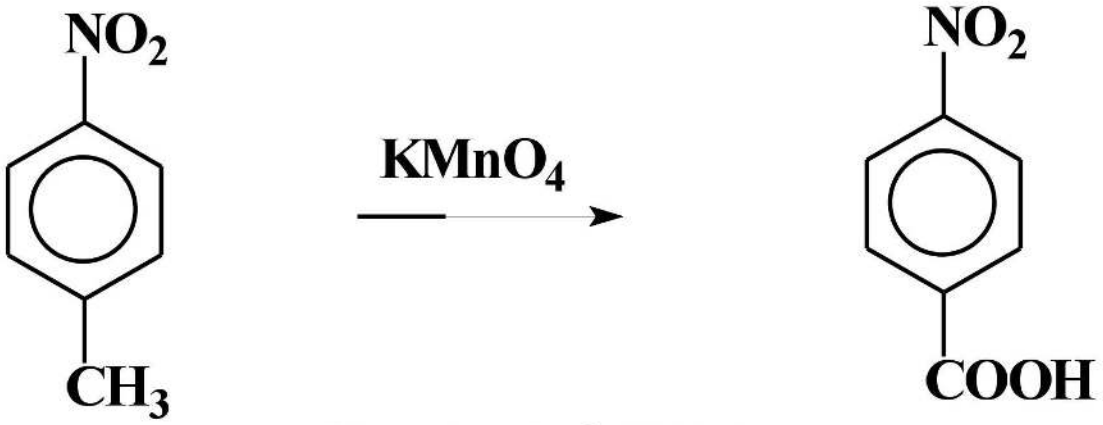
sav → oát

karbonsav → karboxilát

Előállítások

I. Preparatív módszerek

a) Oxidáció



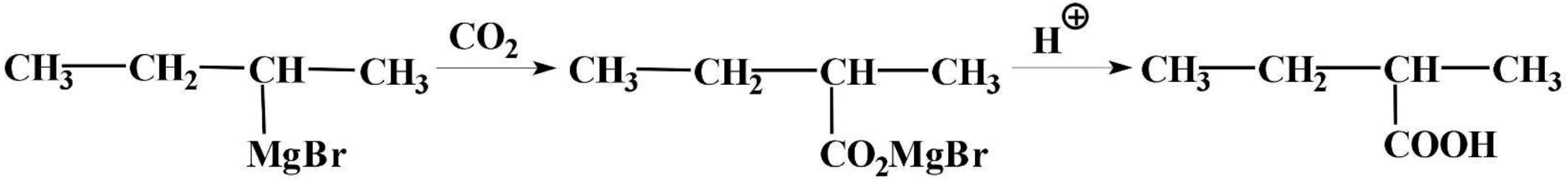
v. $Na_2Cr_2O_7$ / H_2SO_4

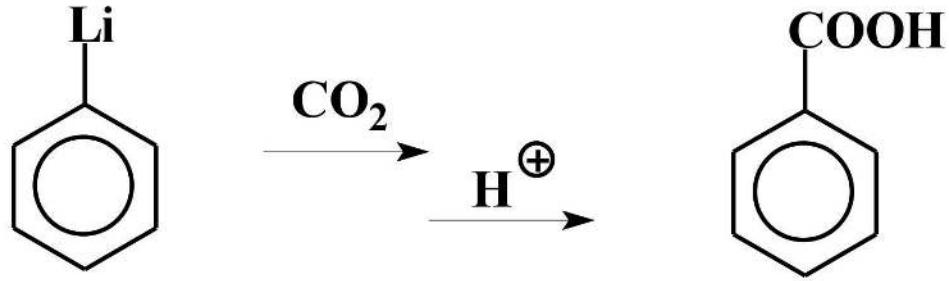
alkoholokból

aldehidekből

ketonokból

b) Fémorganikus vegyületekből

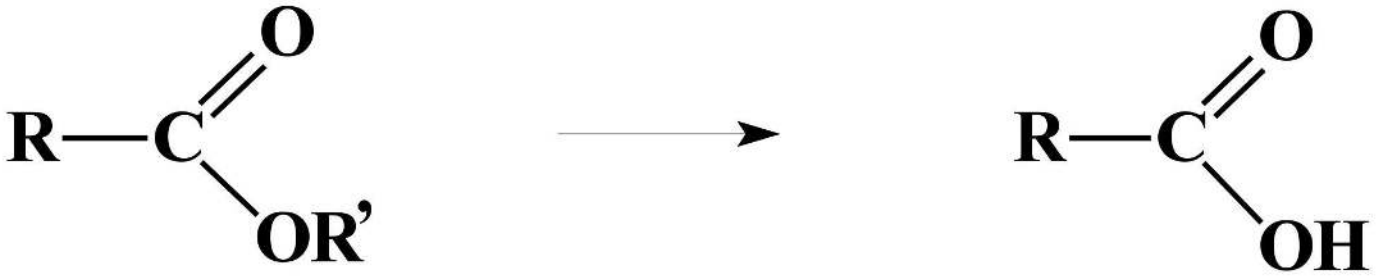




c) Nitrilekből

II. Kinyerés természetben előforduló észterekből

- **Zsírok: nagyobb szénatomszámú karbonsavak glicerinnel képzett észterei**
- **Viaszok: nagyobb szénatomszámú karbonsavak nagyobb szénatomszámú egyértékű alkoholokkal képzett észterei**

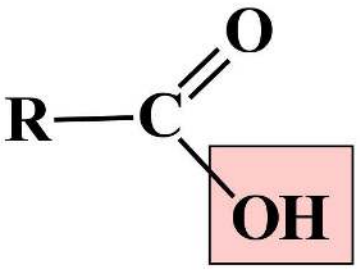


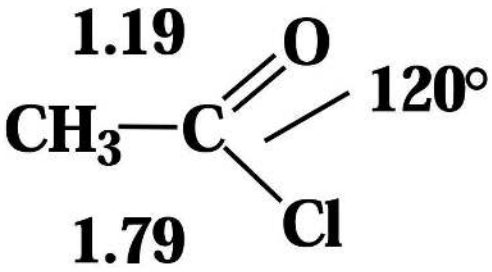
Hidrolízis körülményei:

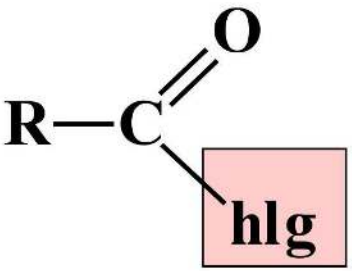
- **savval**
- **lúggal**
- **enzimmel**

Karbonsavhalogenidek

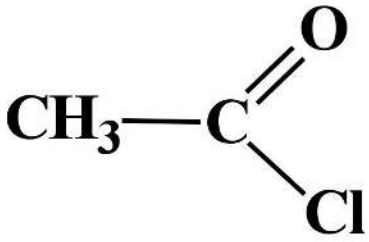
Szerkezet



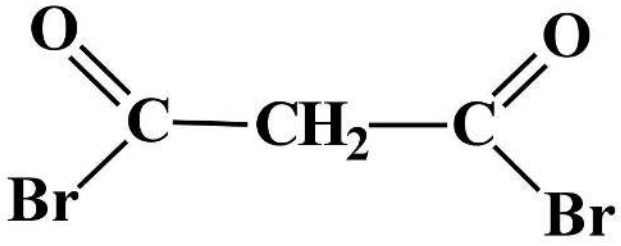




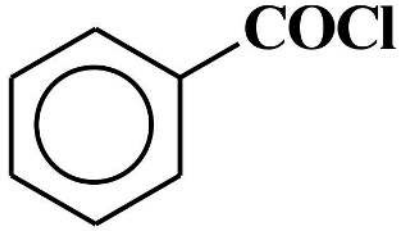
Nevezéktan



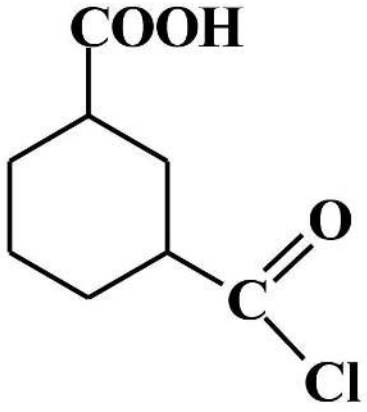
acetil-klorid



malonil-dibromid



benzoil-klorid

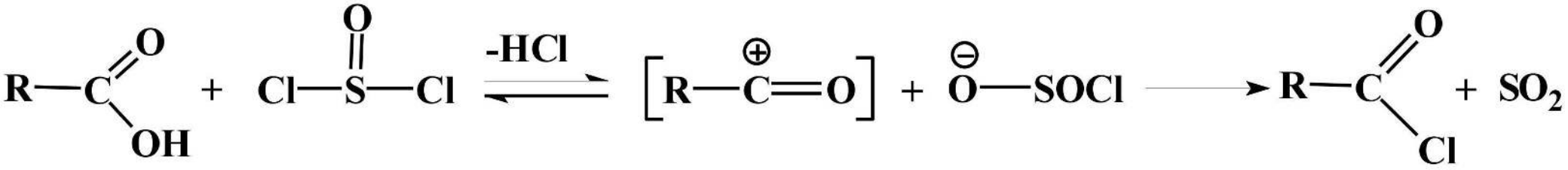


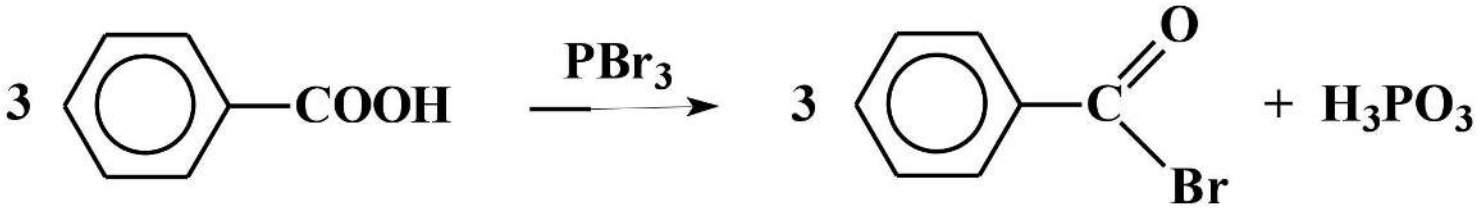
acilcsoport + halogenid

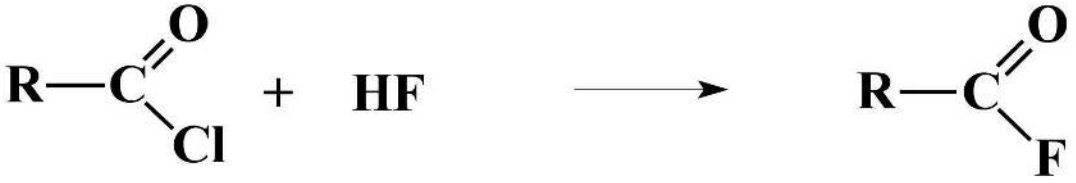
3-(klórformil)-ciklohexánkarbonsav

Előállítások

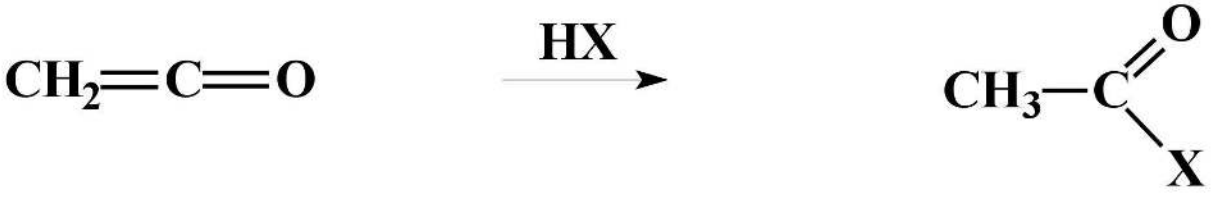
sav + foszfor-halogenid (PCl_3, PCl_5), v. szulfinil(IV)-klorid ($SOCl_2$)





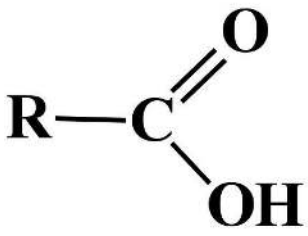


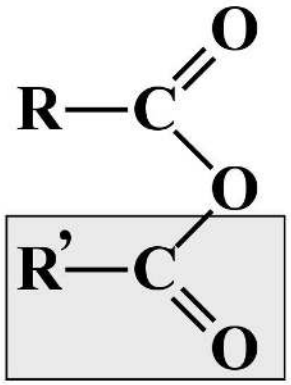
(vagy CH_3COOH/KF)



Savanhidridek

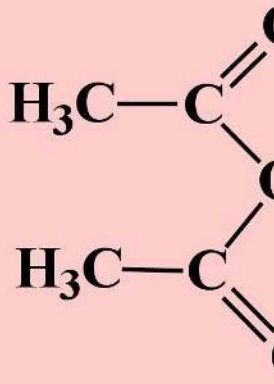
Szerkezet



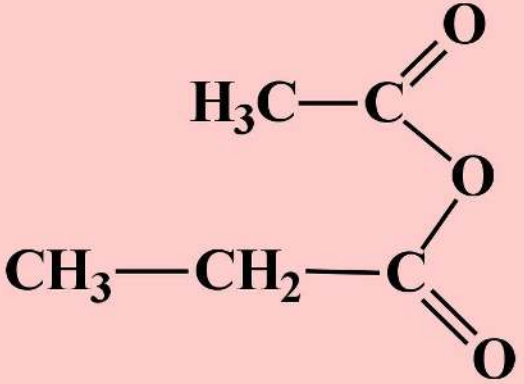


Nevezéktan

sav ⟶ **savanhidrid**



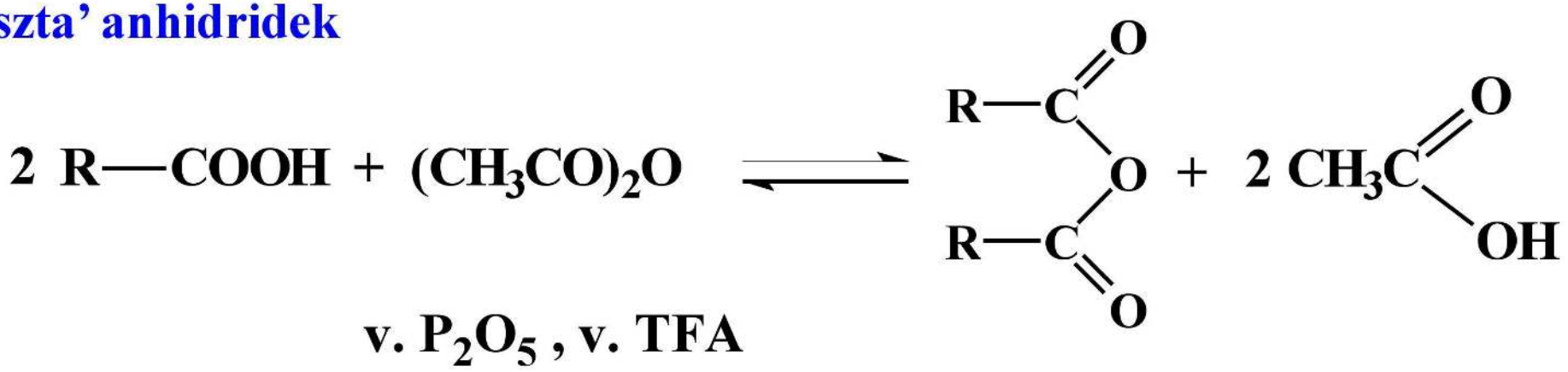
ecetsavanhidrid



ecetsav-propionsav-anhidrid

Előállítások

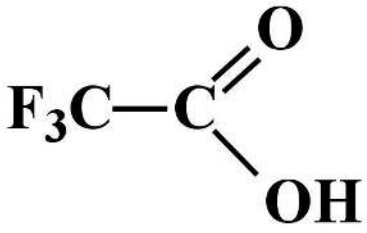
‚Tiszta' anhidridek



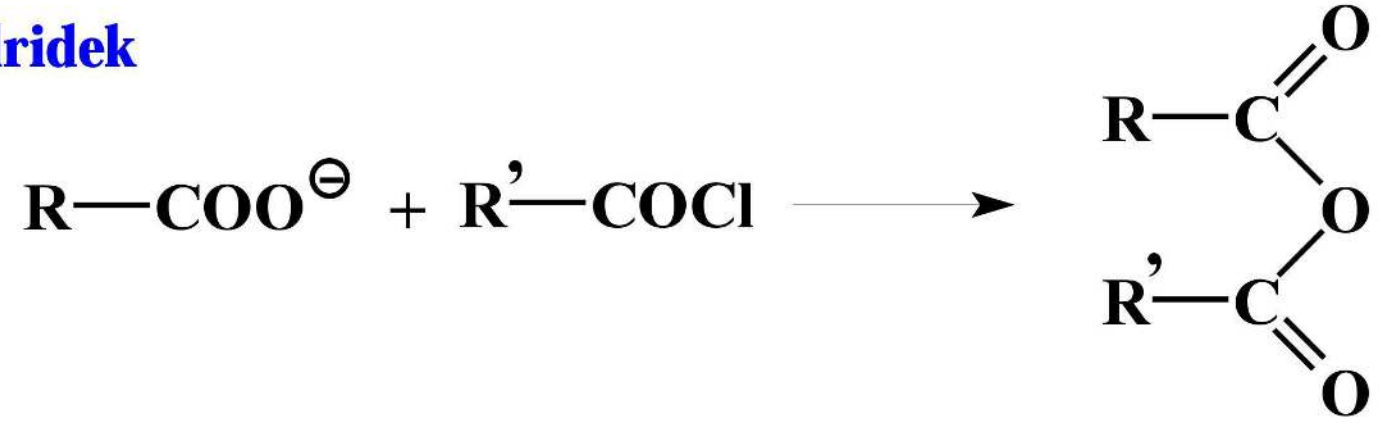
v. P_2O_5 , v. TFA

vízelvonó szerek

TFA: trifluorecetsav

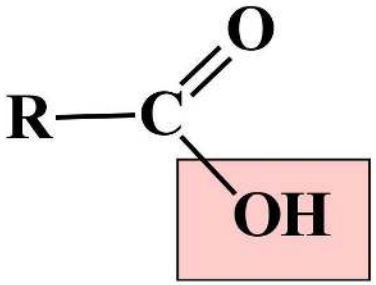


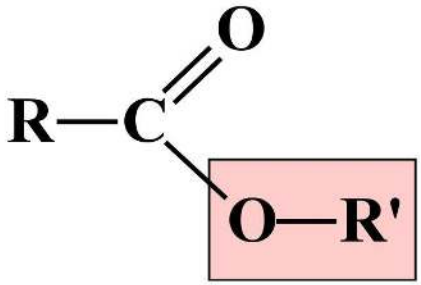
Vegyes anhidridek

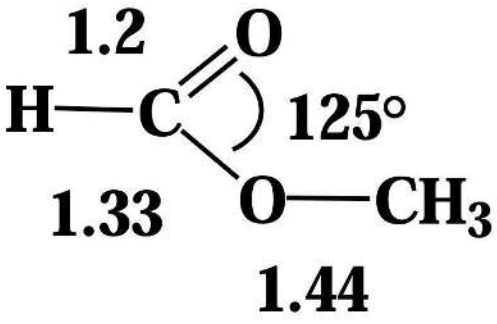


Észterek

Szerkezet

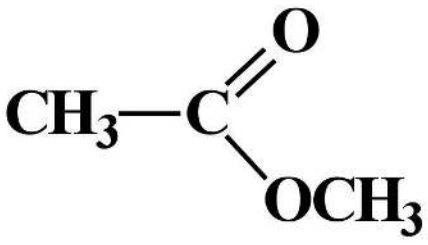




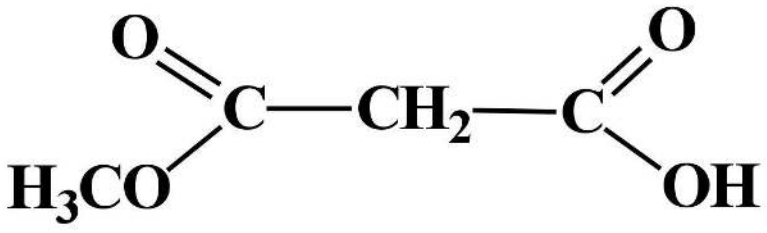


Nevezéktan

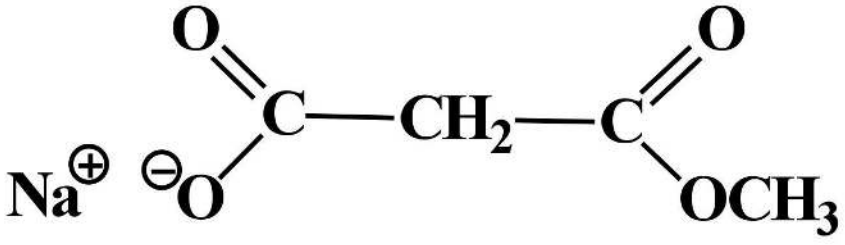
Szubsztitúciós névvel



metil-acetát

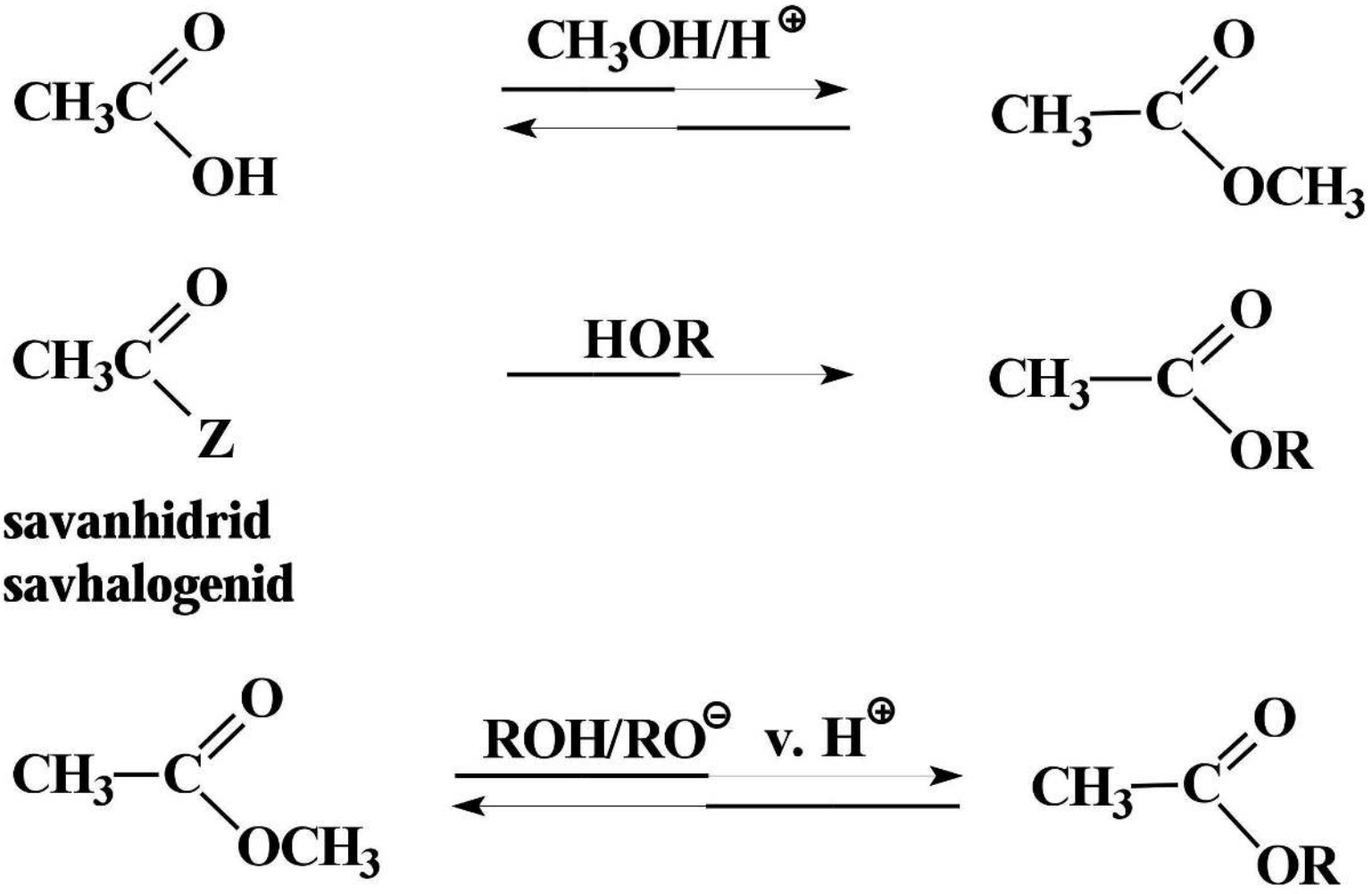


metil-hidrogén-malonát



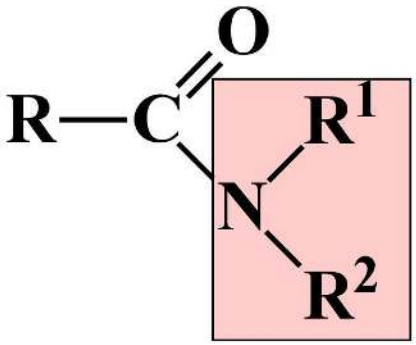
nátrium-metil-malonát

Előállítások

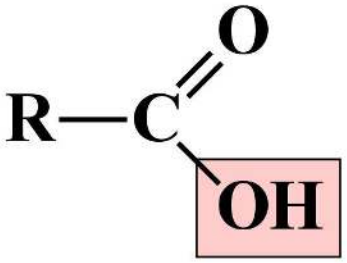


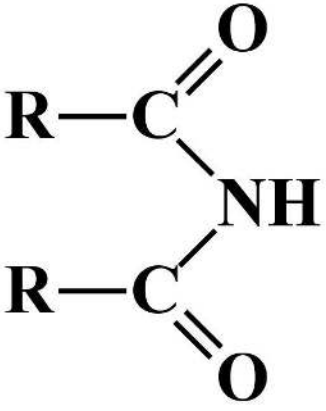
Savamidok

Szerkezet

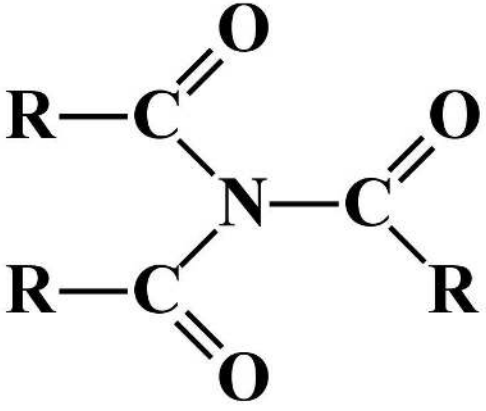


I. r





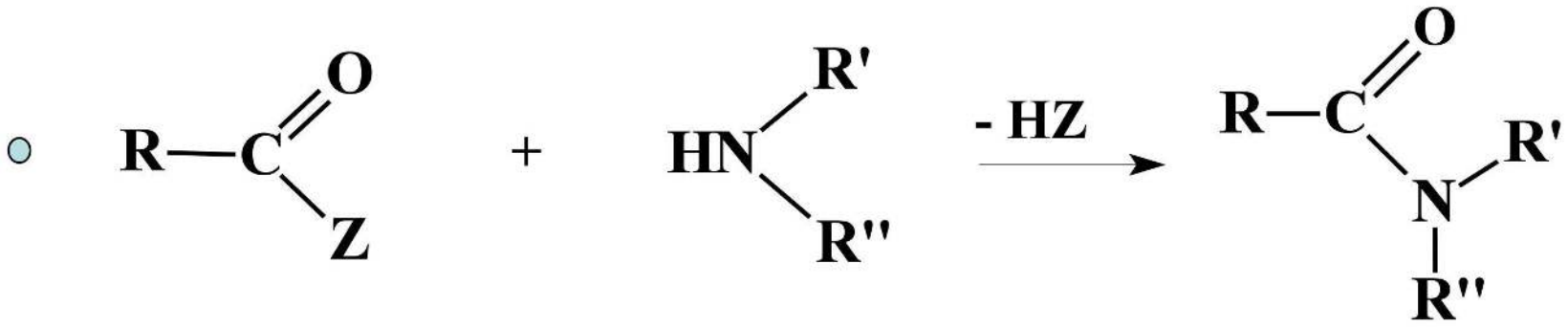
II. r



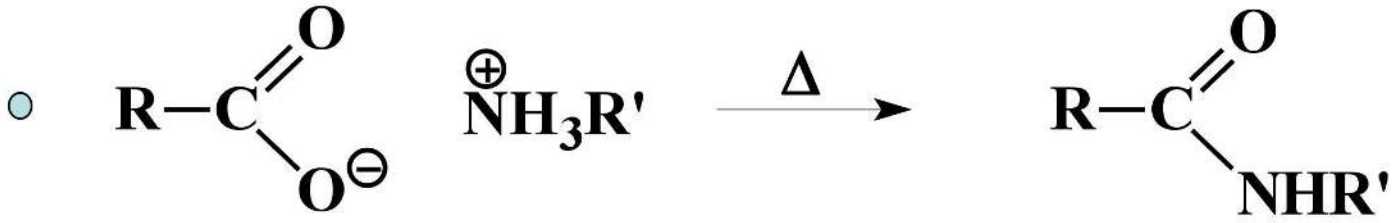
III. r

Előállítások

a) Aminek acilezésével

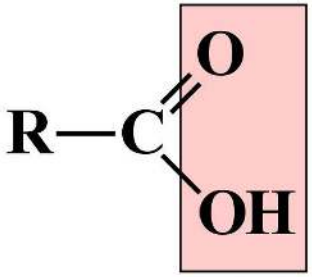


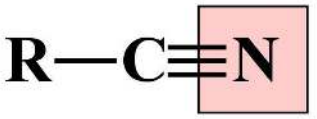
b) Ammónium-karboxilátok hevítésével



Nitrilek

Szerkezet





Nevezéktan

- szénhidrogén + nitril

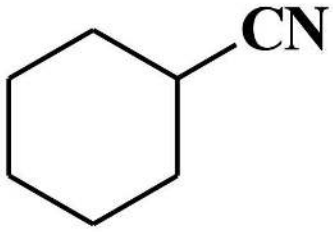
$CH_3—(CH_2)_4—C\equiv N$

hexánnitril

$N\equiv C—(CH_2)_4—C\equiv N$

hexándinitril

- karbonsav → karbonitril



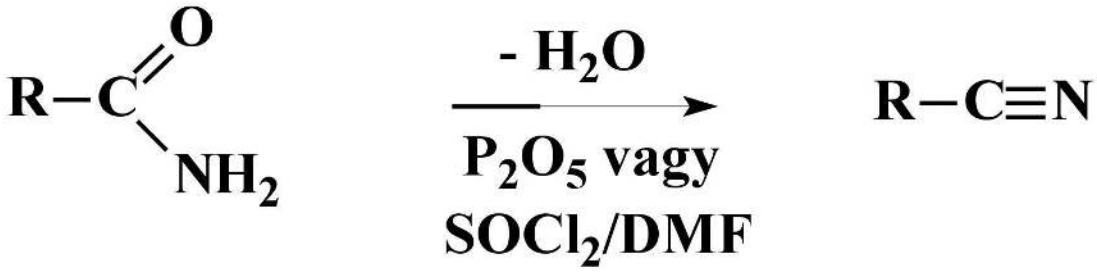
ciklohexánkarbonitril

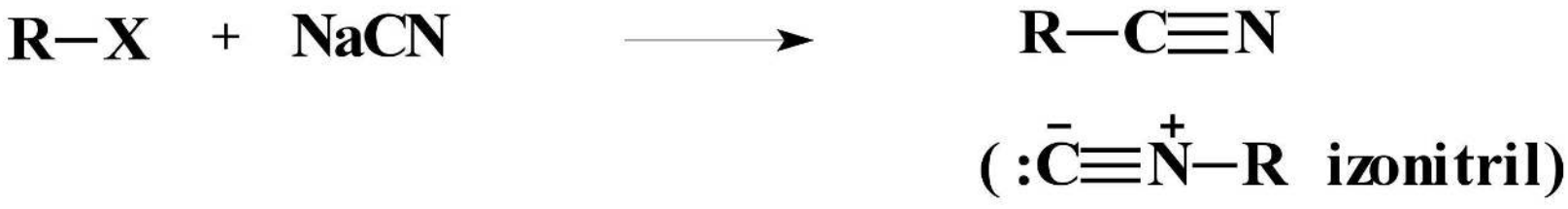
- triviális: -*sav* → *onitril*

de: acetonitril

- előtagként: ciano-

Előállítások





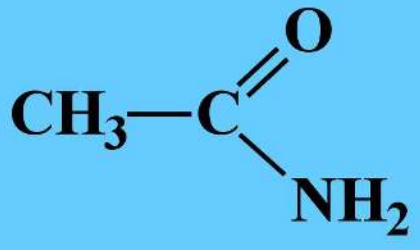
Kémiai tulajdonságok

Aciditás

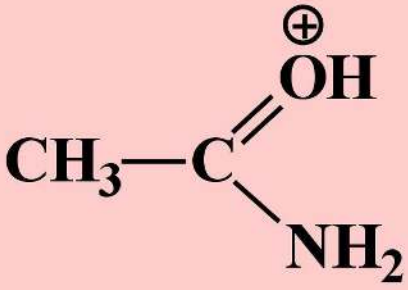
Alkoholok << Karbonsavak << Ásványi savak

	pK_a		pK_a
HCl	-7	HOOC—COOH	1,27 és 4,27
CH_3COOH	4,76	$HOOC—CH_2—COOH$	2,85 és 5,70
CH_3CH_2OH	16		

Karbonsavamidok pK_a >> savak



pK_a ~ 15



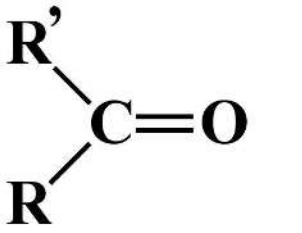
pK_a ~ 0

NH_4^+ pK_a ~ 9

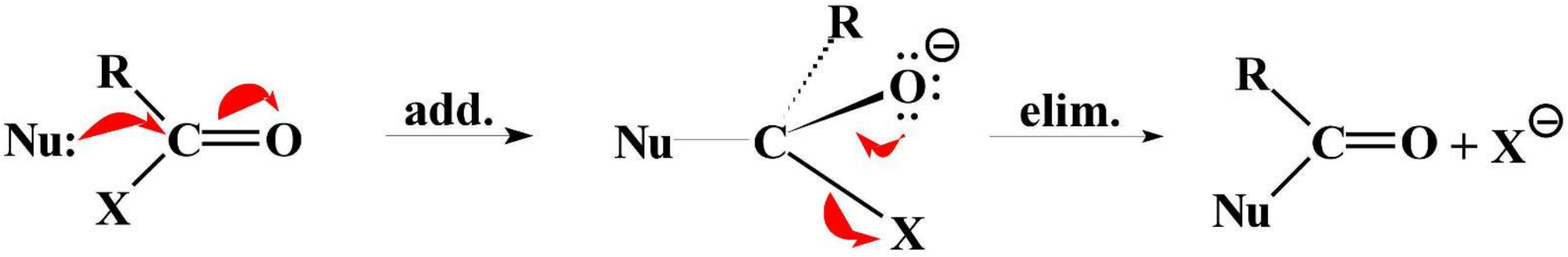
bázicitásuk << NH_3

Reaktivitás nukleofilekkel szemben - acilezési reakciók

Oxovegyületekkel összehasonlítva

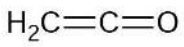


R' = H / alkil / aril, vagyis **nem jó távozó csoport**

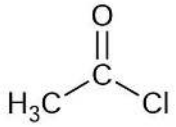


S_NAc reakciók áttekintése

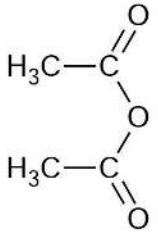
Acilezőszerek



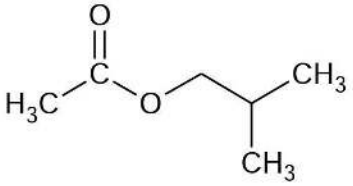
ketén



savklorid



savanhidrid

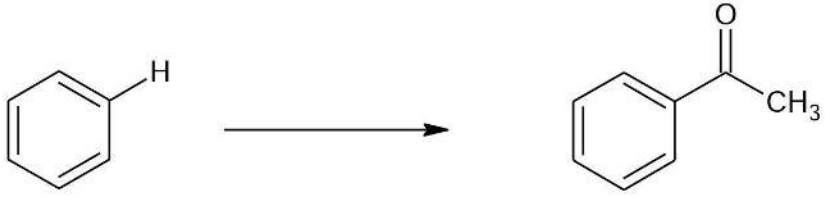


észter

S_EAr acilezési reakció

Friedl-Crafts acilezés

(savklorid, savanhidrid, $AlCl_3$)



a) Savhalogenidek

A halogénatom -I effektusa dominál

b) Savak, észterek és amidok

Delokalizáció csökkenti a reaktivitásukat

Acilezési reakciók

H-atomot acilcsoportra cserélünk ki

O, S, N, C acilezés

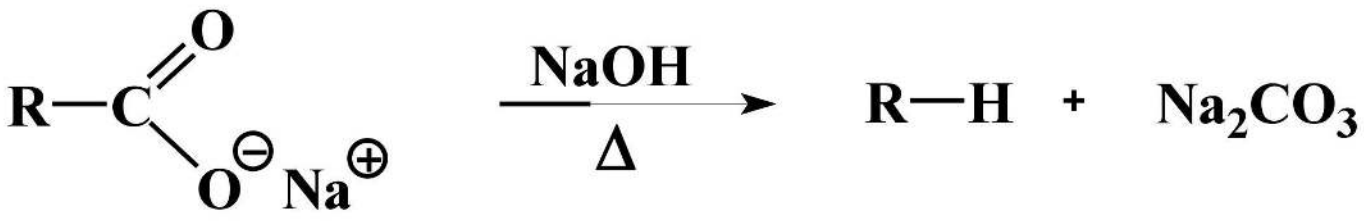
Acilezőszerek reaktivitási sora

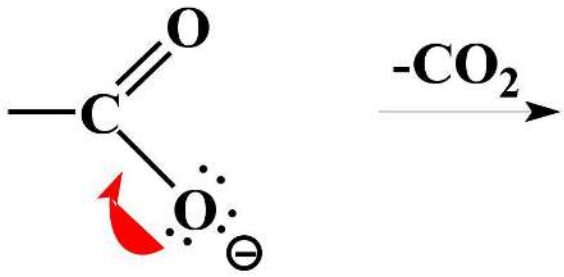
ketén > savhalogenid > savanhidrid > észter > nitril > amid, sav

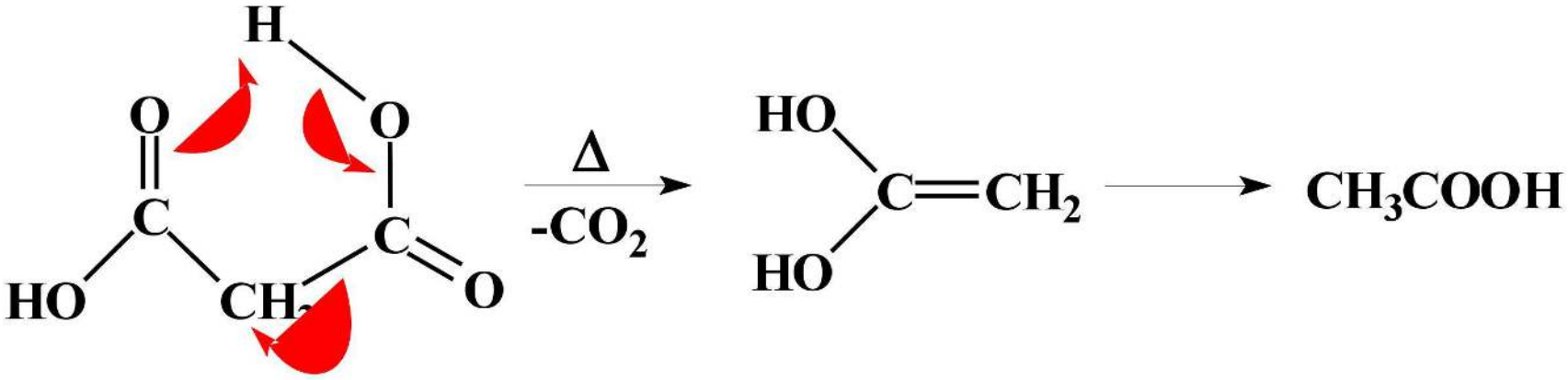
Karbonsavak és származékaik néhány fontosabb speciális reakciója

a) Karbonsavak

- **Dekarboxileződés**

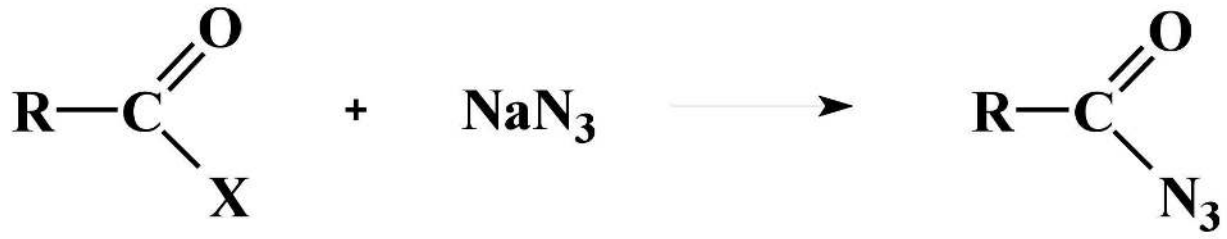




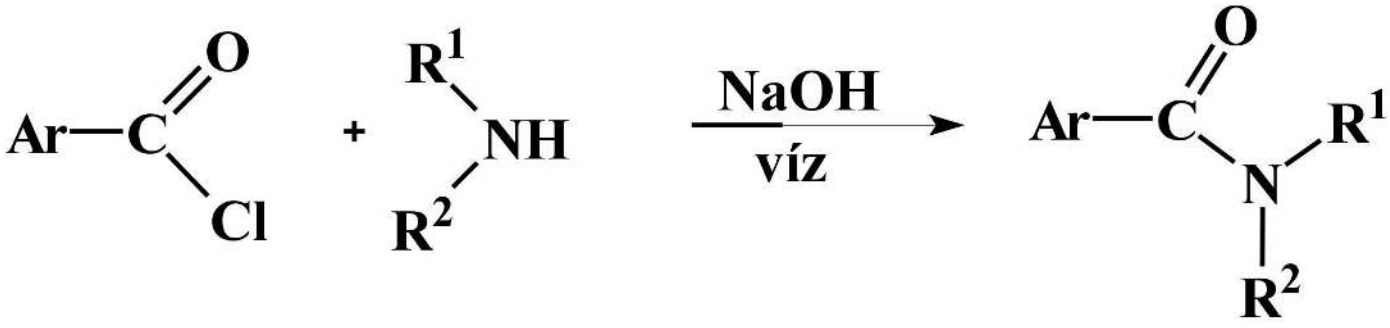


b) Savhalogenidek

- **Savazid előállítására**



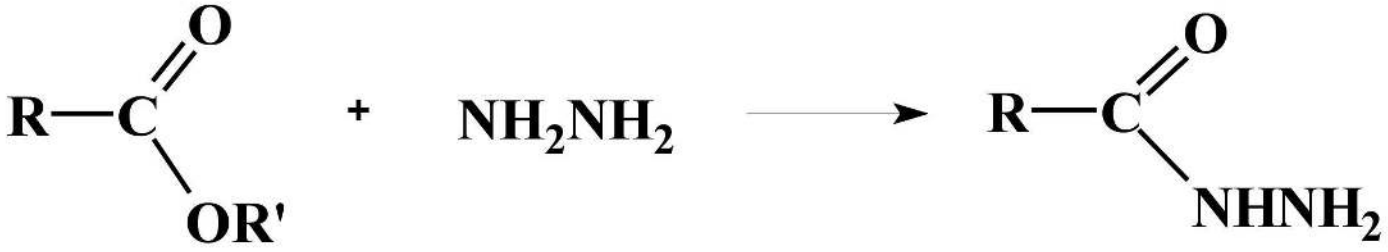
- **Schotten - Baumann acilezési módszerrel reagáltathatók a kevésbé reaktív acil-kloridok**



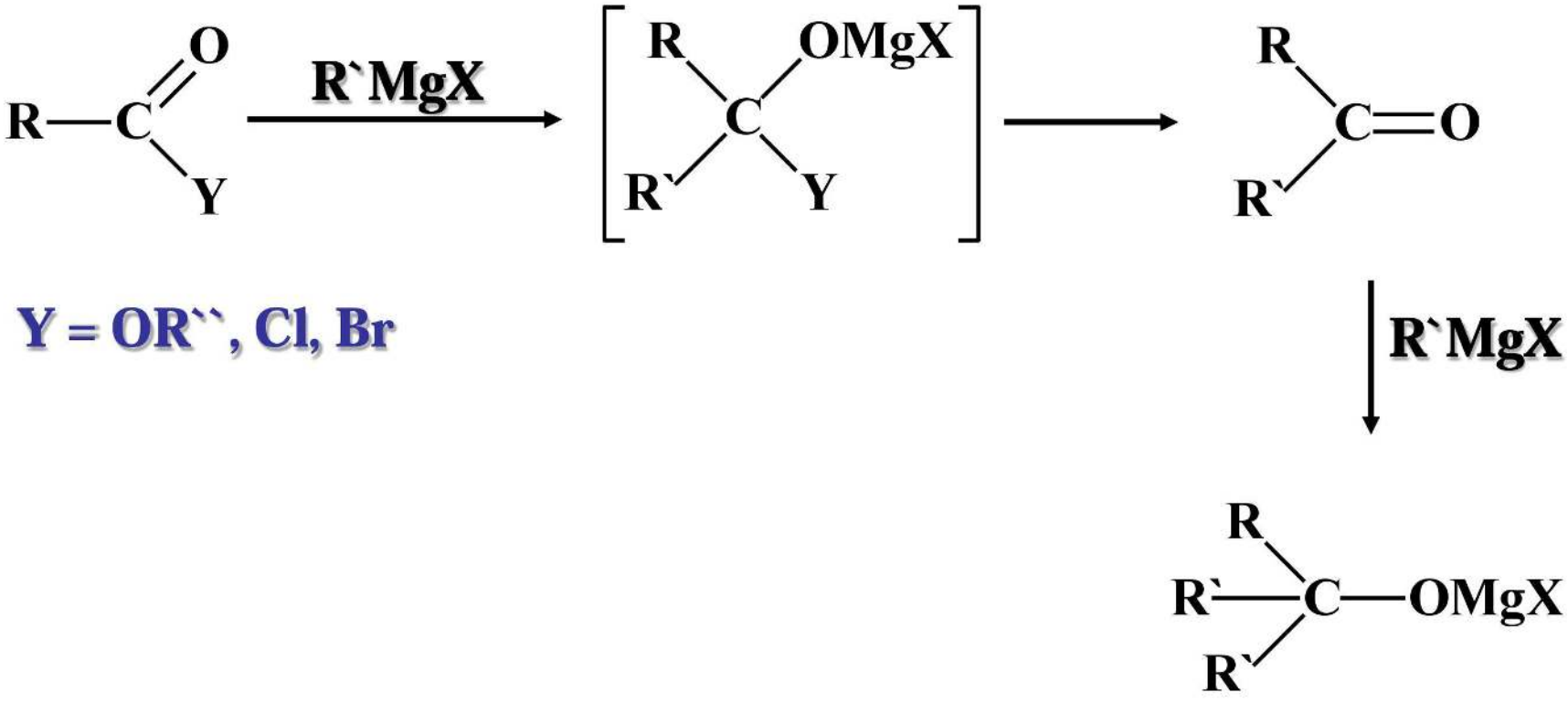
c) Észterek

- **Hidroxámsav előállítására**

- **Savhidrazid előállítására**



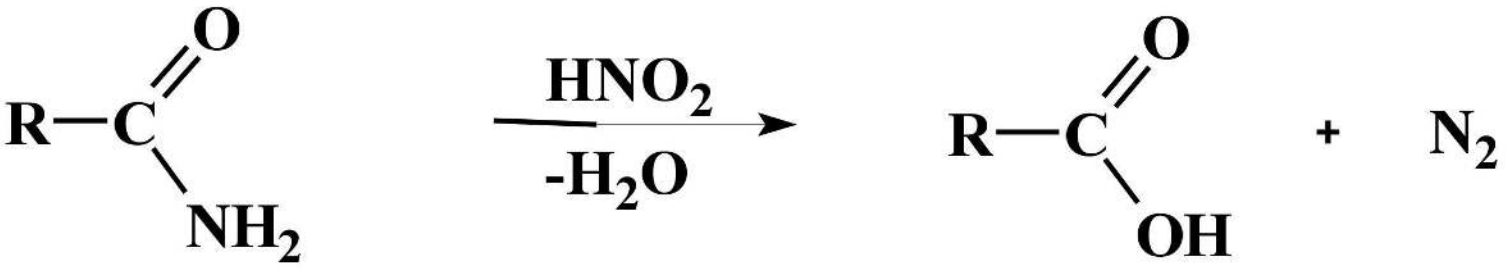
- ***terc*-Alkohol előállítása: észterből, savhalogenidből**

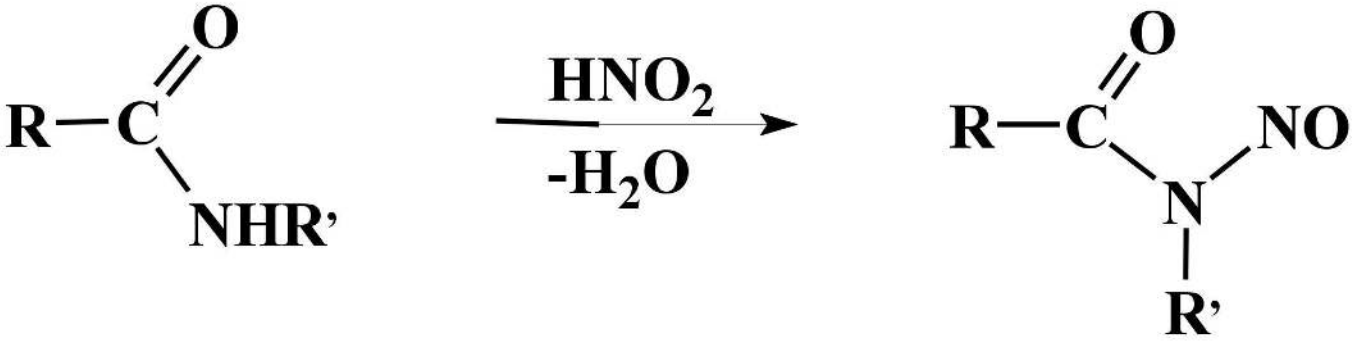


Y = OR``, Cl, Br

d) Savamidok

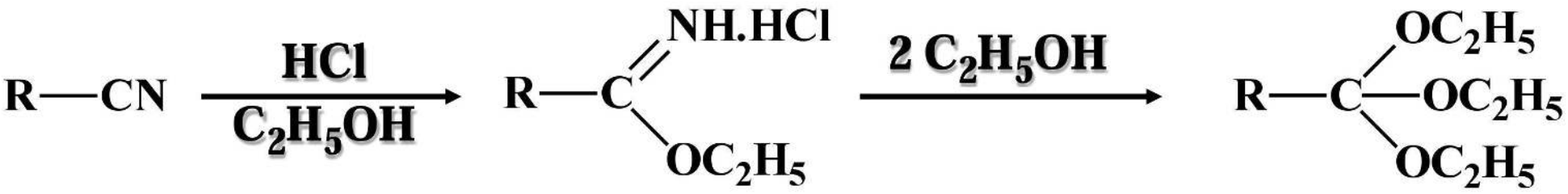
- **Reakció salétromossavval**





e) Nitrilek

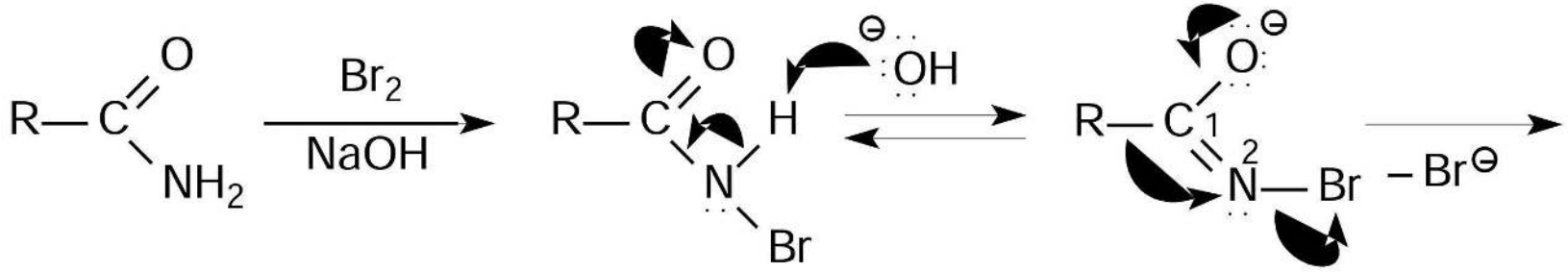
- **Ortoészterek előállítására**



imidsavészter hidroklorid

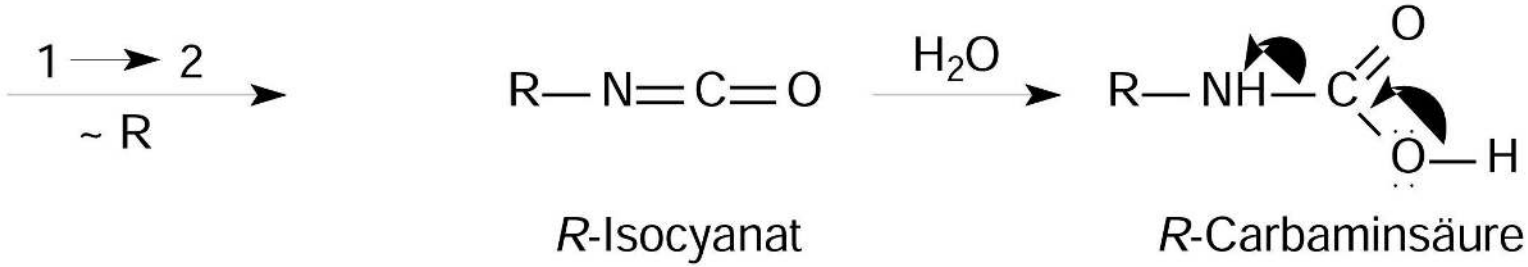
Karbonsavak és származékaik lebontási reakciói

***Hofmann*-Abbau** (und Umlagerung)



Säureamid
R = Alkyl, Aryl

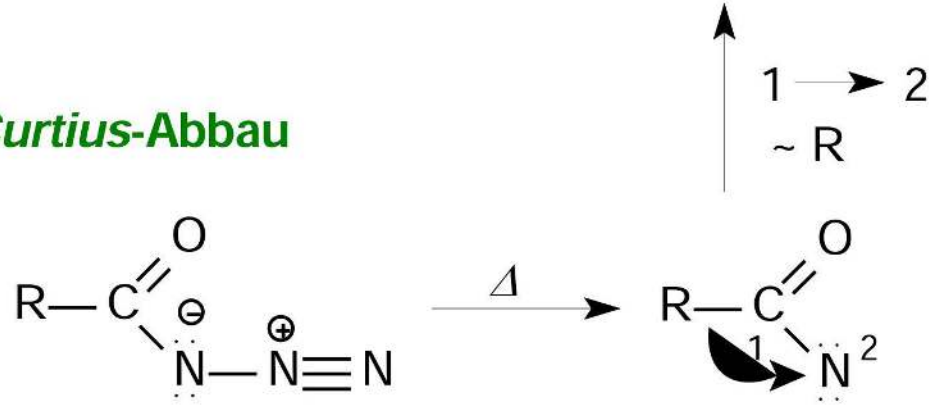
N-Bromsäureamid
(Halogenamidat)



R-Isocyanat

R-Carbaminsäure

***Curtius*-Abbau**



Säureazid

Acylnitren

Primäres Amin

Helyettesített savak

Aminosavak (és fehérjék, l. Természetes szerves vegyületek)

Halogénezett karbonsavak

Hidroxikarbonsavak

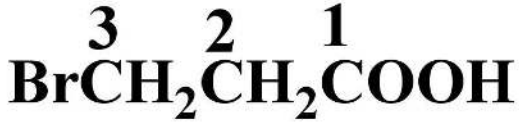
Oxokarbonsavak

Halogénezett karbonsavak

Szerkezet

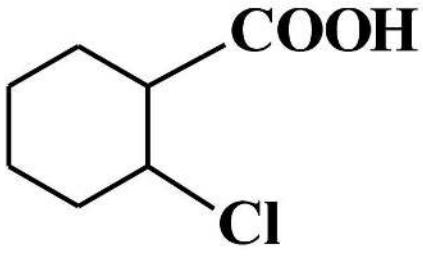
R—COOH az R halogént tartalmaz

Nevezéktan



3-brómpropionsav

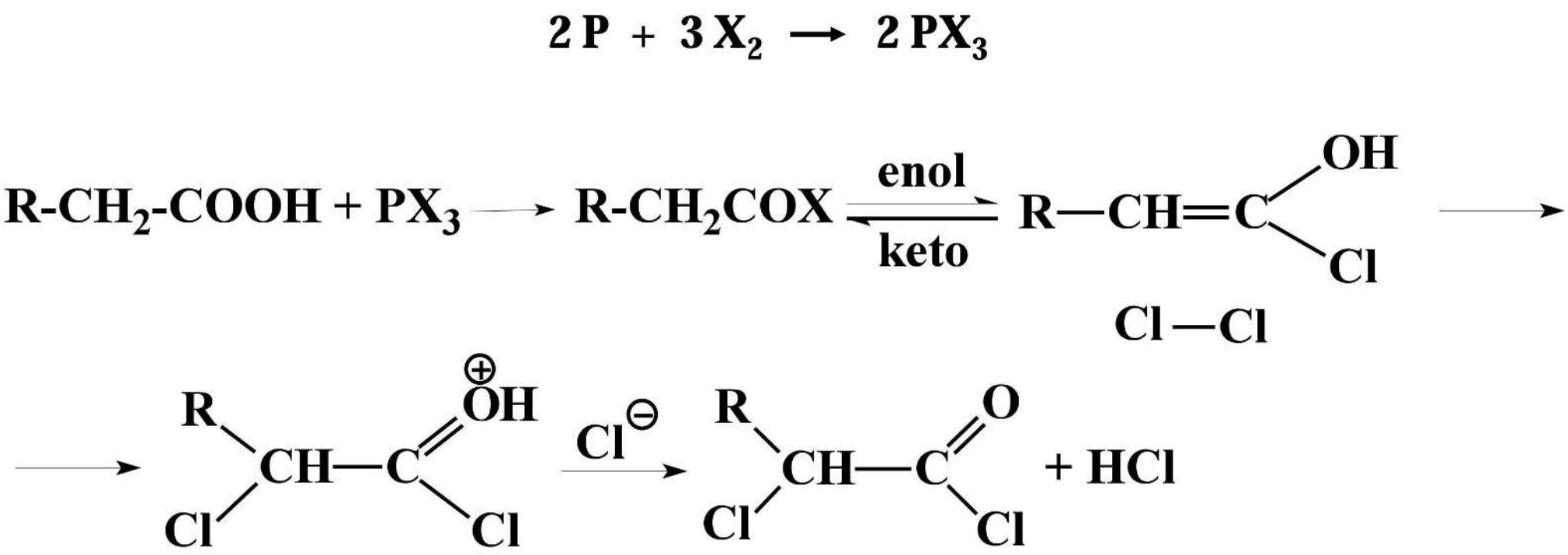
a halogén csak előtag lehet



2-klórciklohexánkarbonsav

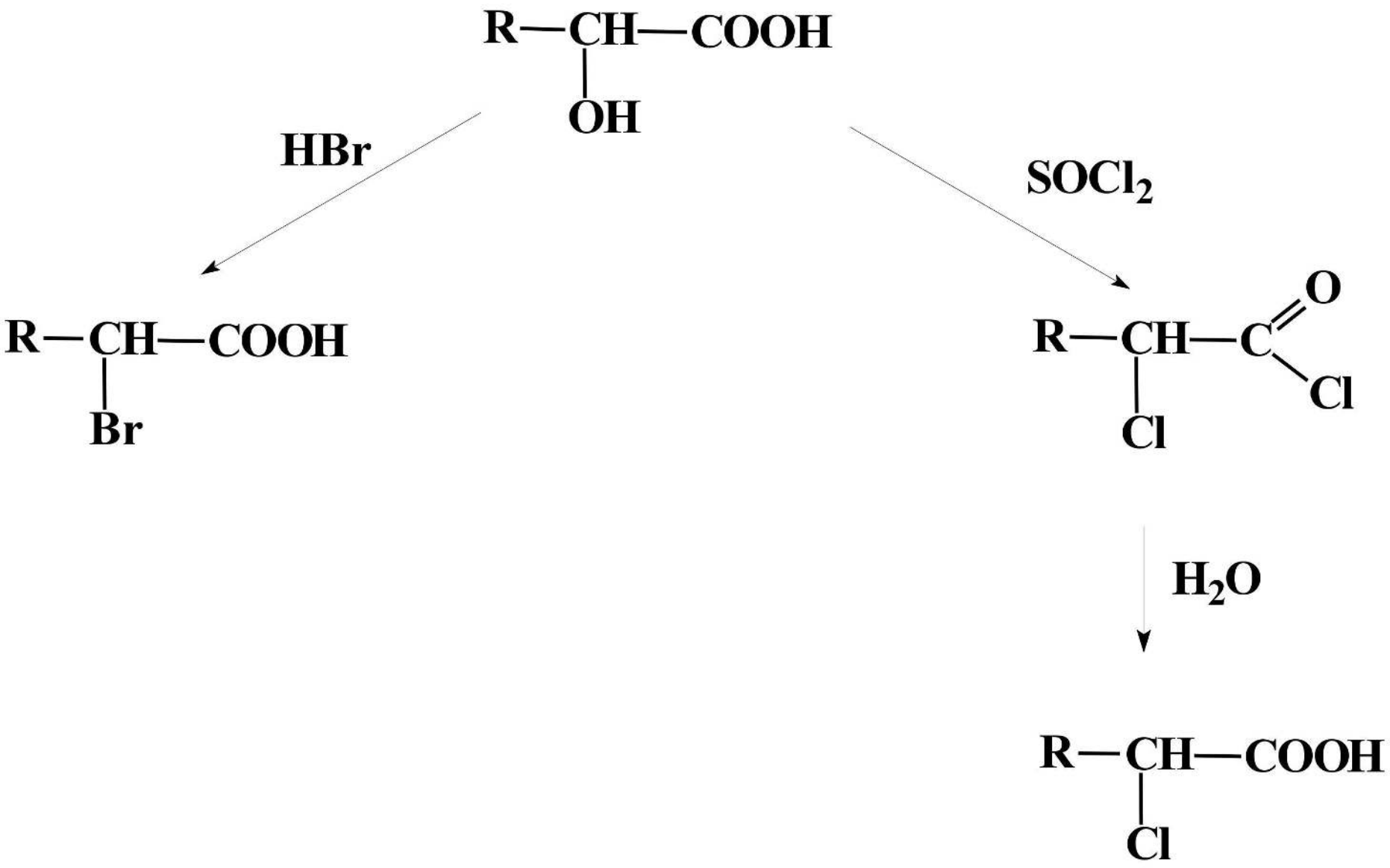
Előállítások

1. Hell-Vollhardt-Zelinszkij reakció



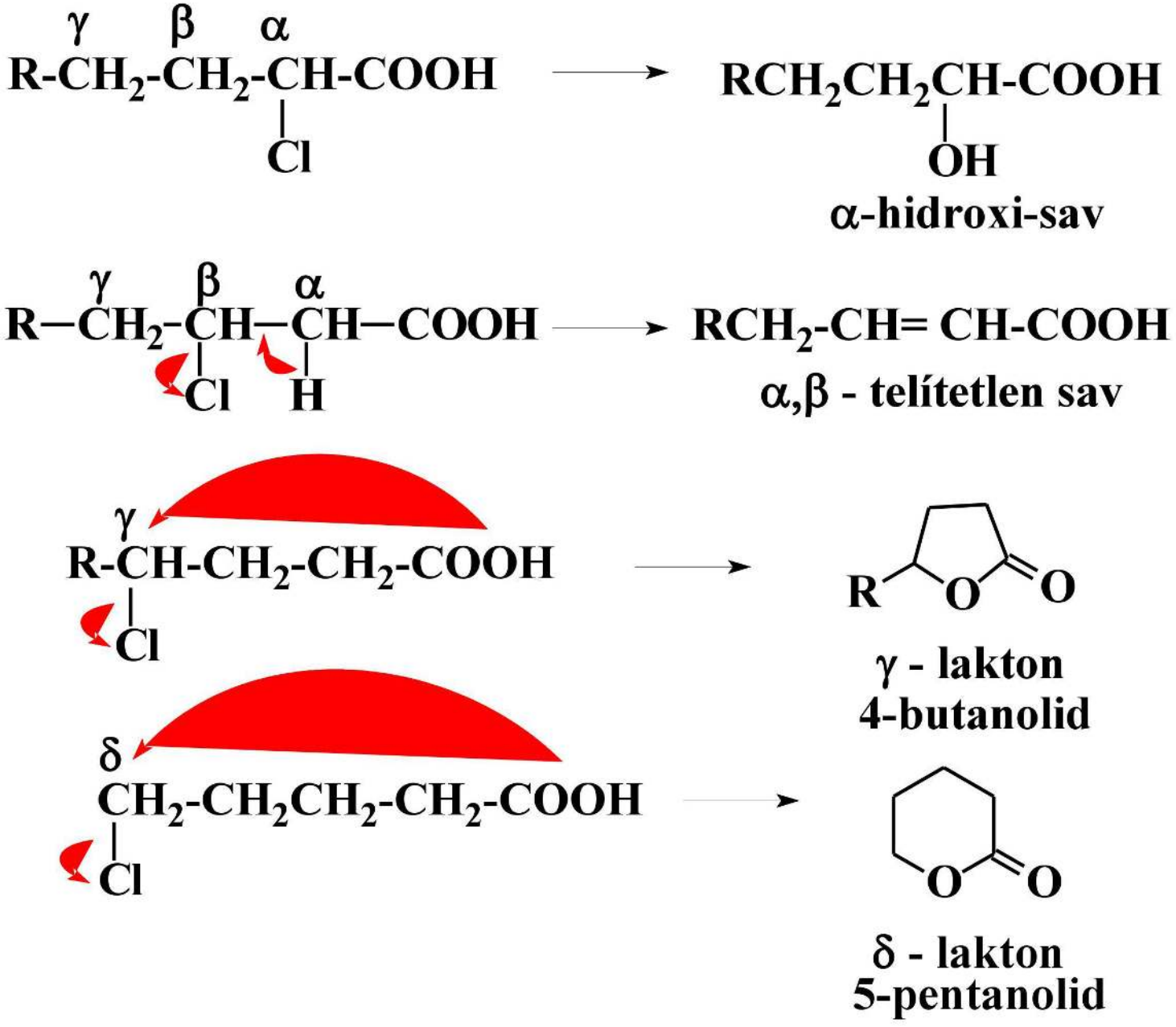
α-Halogénezett karbonsav

2. Hidroxisavakból



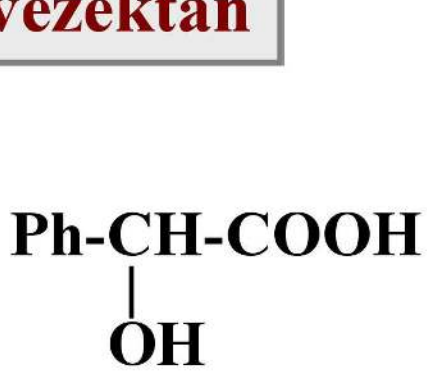
Kémiai tulajdonságok

1. Reakció lúggal (NaOH)

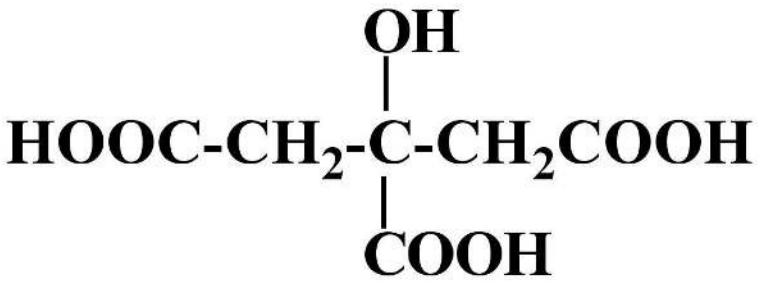


Hidroxikarbonsavak

Nevezéktan



Mandulasav
2-Fenil-2-hidroxipropionsav*



Citromsav
2-Hidroxipropán-1,2,3-trikarbonsav

Glikolsav
2-Hidroxiecetsav

Tejsav
2-Hidroxipropionsav*

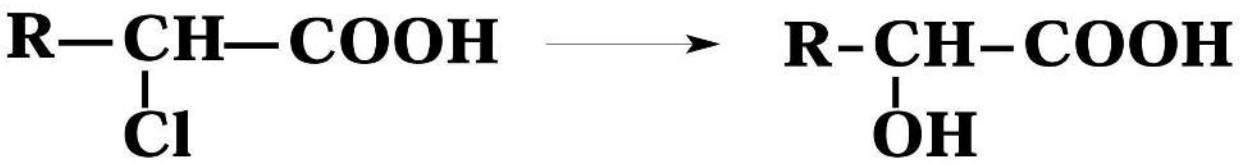
Almasav
2-Hidroxibutándisav

Borkősav
2,3-Dihidroxibutándisav

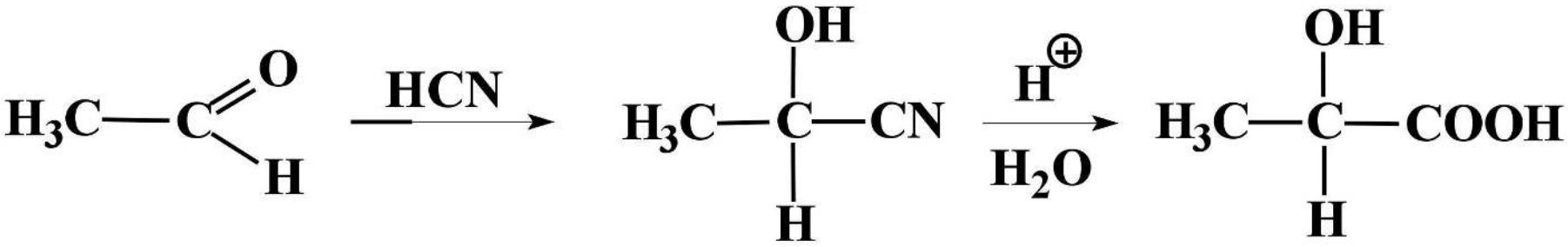
* **Propionsav (triviális név) / propánsav (szisztematikus név)**

Előállítás

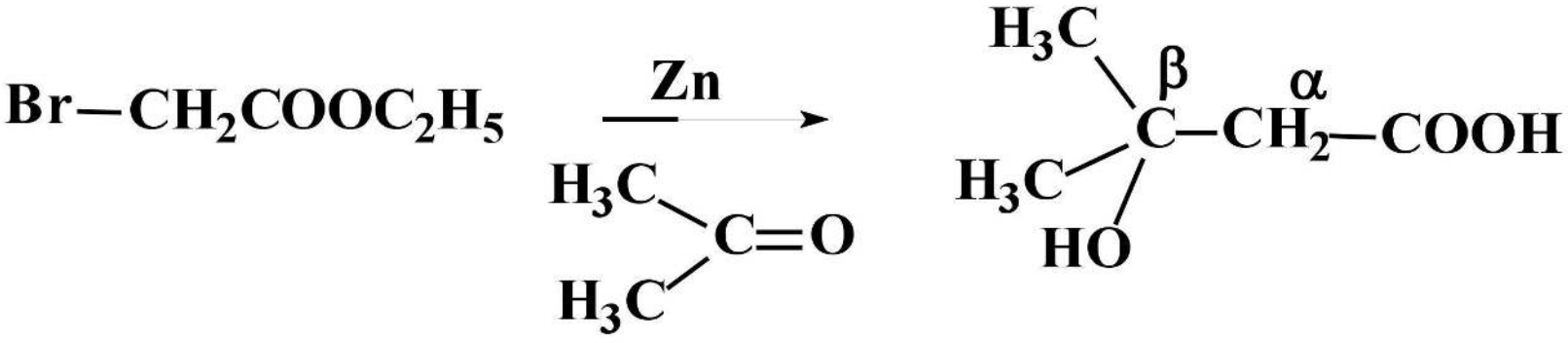
1. α-Halogénezett karbonsavakból



2. Ciánhidrinek hidrolízisével

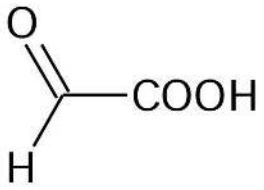


3. β-Hidroxikarbonsavak: Reformatszkij-szintézissel

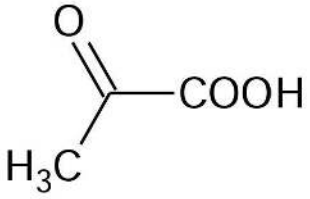


Oxokarbonsavak

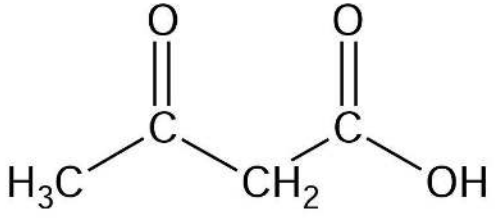
1. **α-Oxosavak: glioxilsav, piroszőlősav**
2. **β-Oxosavak: acetecetsav (észter)**
   malonsav (észter) - *dikarbonsav*



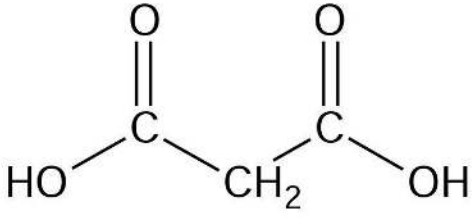
glioxilsav



piroszőlősav

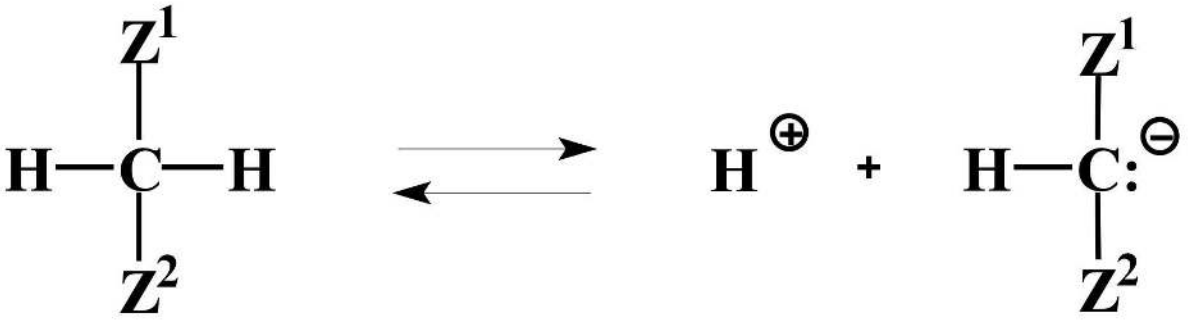


acetecetsav

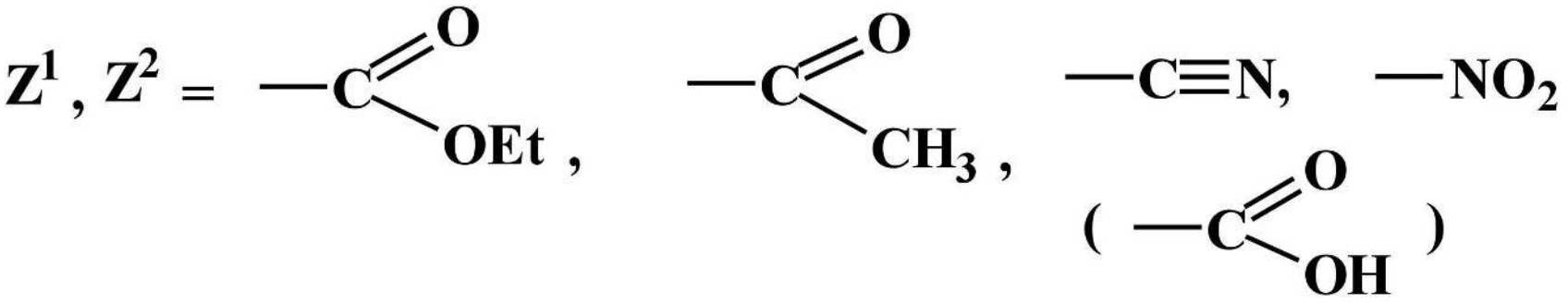


malonsav

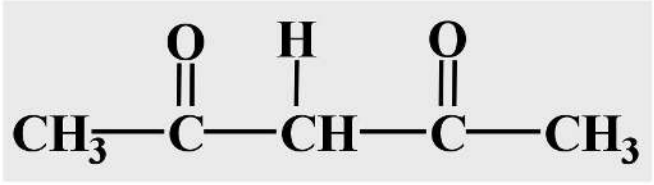
CH-sav típusú vegyületek reakciói



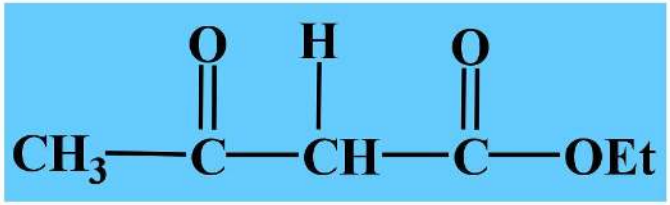
A kellő aktivitást erősen elektronvonzó csoportok biztosítják



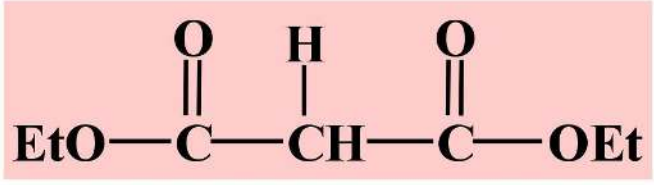
pK_a értékek:



acetil-aceton
9

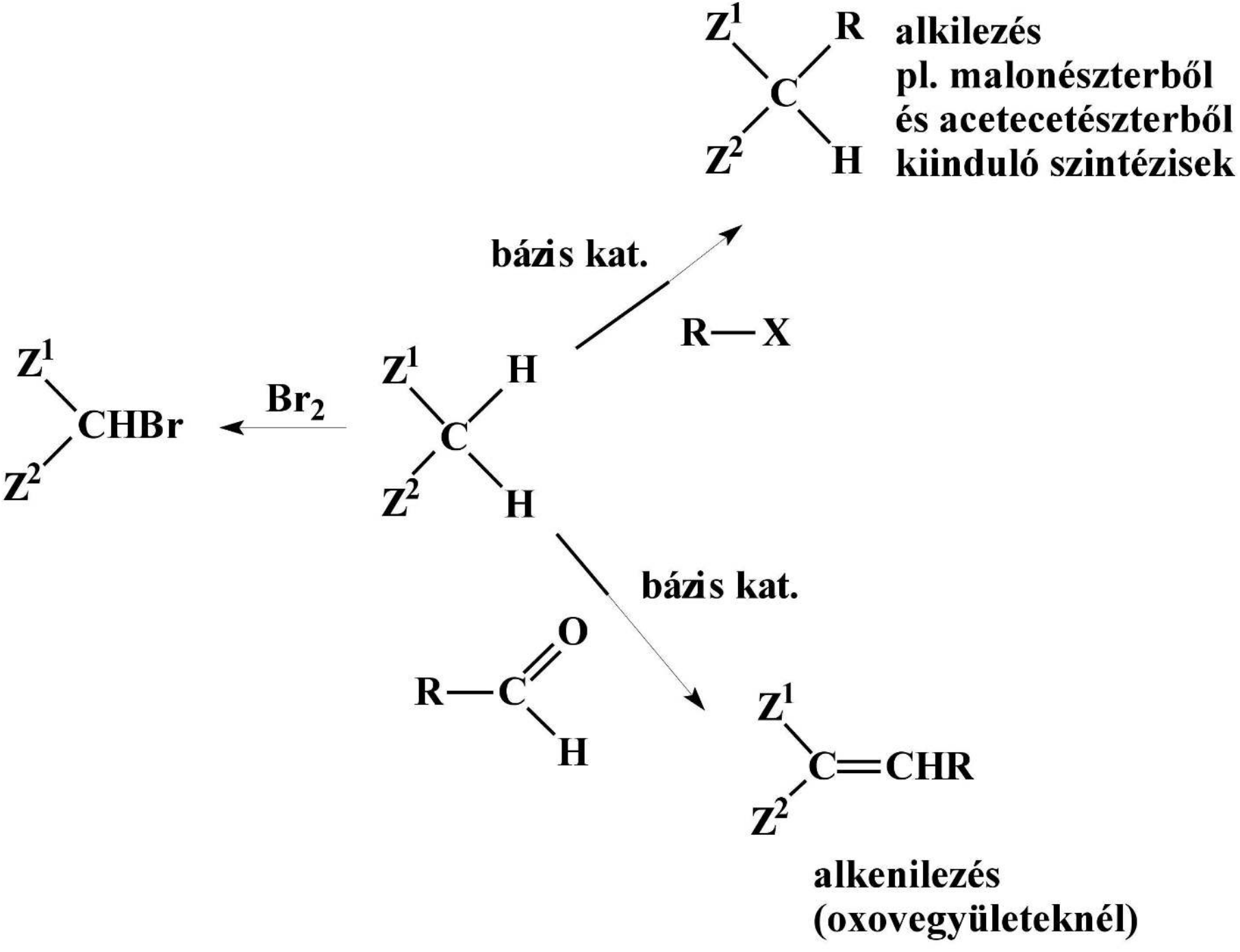


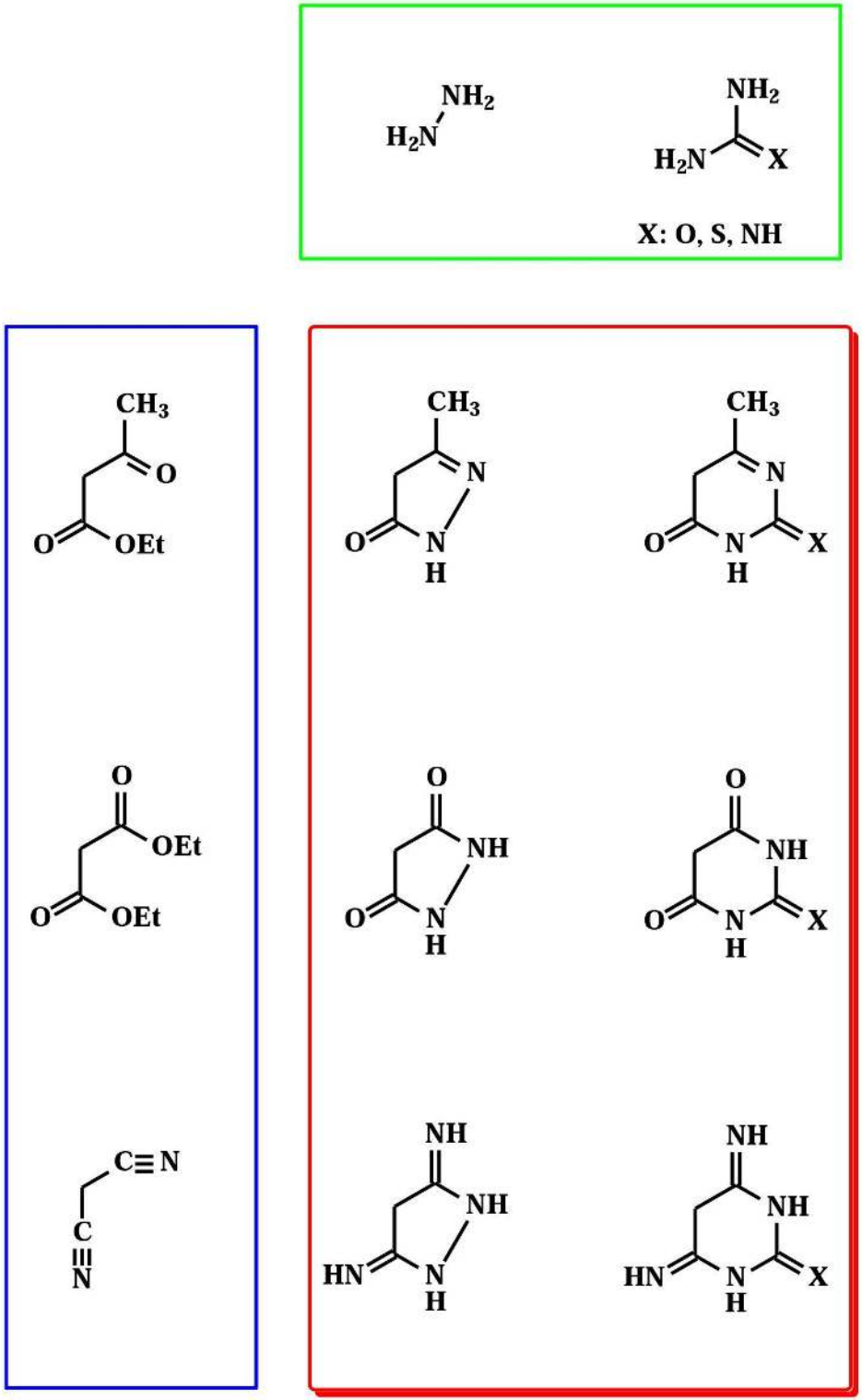
etil-acetoacetát
11



dietil-malonát
13

CH-sav típusú vegyületek reakciói




NH2
H2N
NH2
H2N
X
X: O, S, NH
CH3
O
O
OEt
CH3
N
O
N
H
CH3
N
O
N
X
H
O
OEt
O
OEt
O
NH
O
N
H
O
NH
O
N
X
H
C≡N
C
≡
N
NH
NH
HN
N
H
NH
NH
HN
N
X
H

Aminosavak

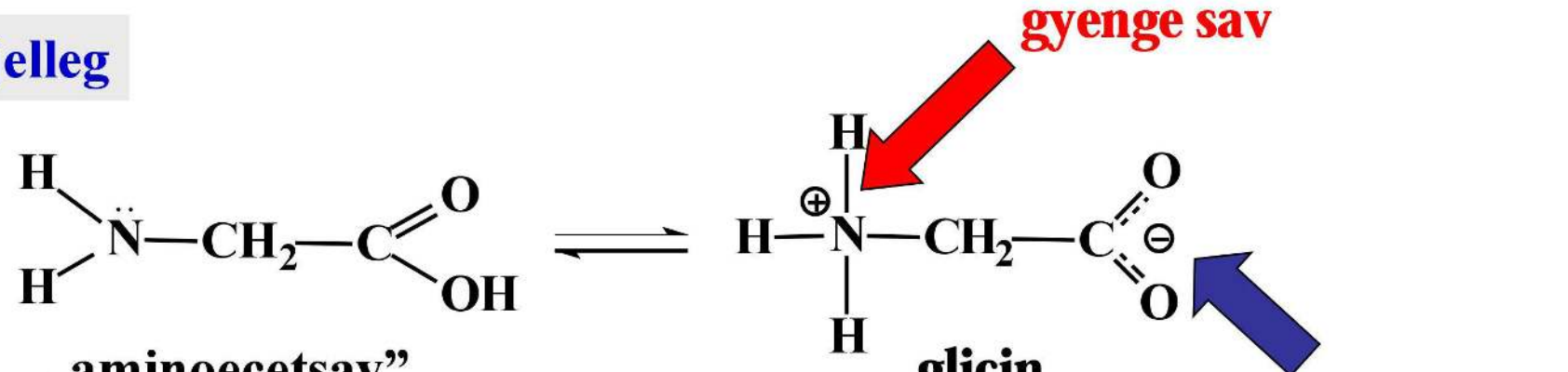
Amino- és karboxilcsoport egy molekulában.

Csoportosítás

- az amin rendűsége szerint
  (első, másod, harmad, negyedrendű)
- az amino- és karboxil-csoportok száma szerint
  monoamino-monokarbonsav
  diamino-monokarbonsav
  monoamino-dikarbonsav, stb
- a szénlánc szerkezete szerint
  nyíltláncú, gyűrűs, alifás, aromás

Kémiai tulajdonságok

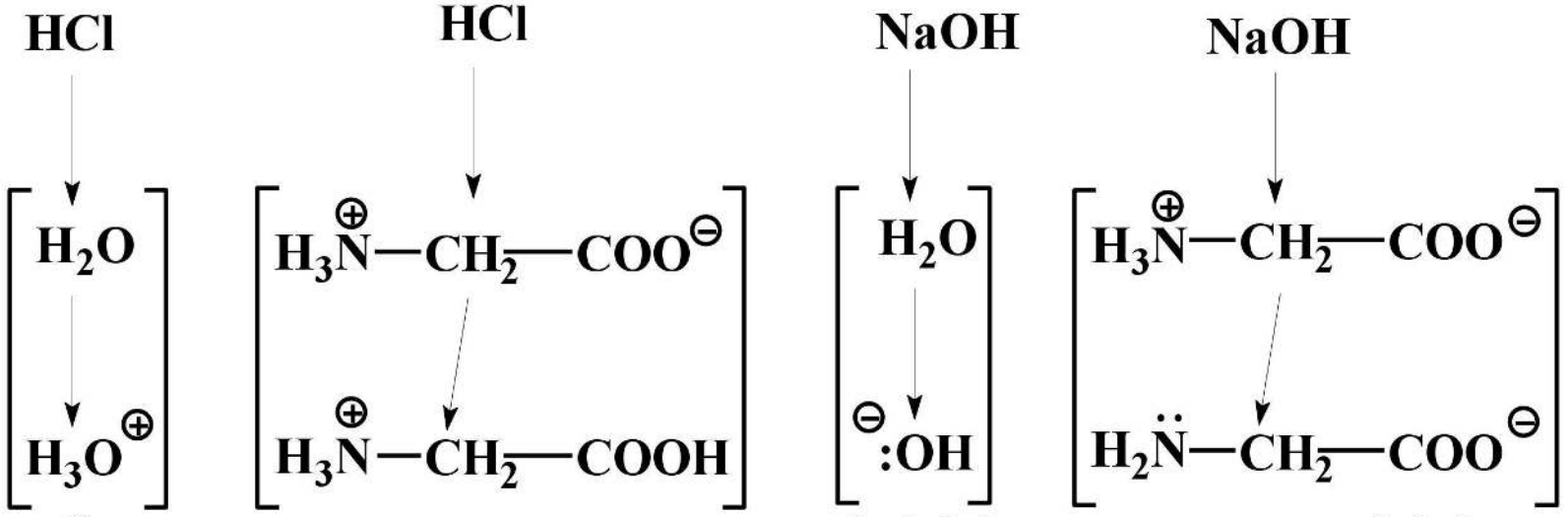
1. Sav-bázis jelleg



„aminoecetsav”
gyakorlatilag nem létezik

glicin
„ikerion”

Glicin pufferhatása



erős sav
tiszta víz

gyenge sav
puffer oldat

erős bázis
tiszta víz

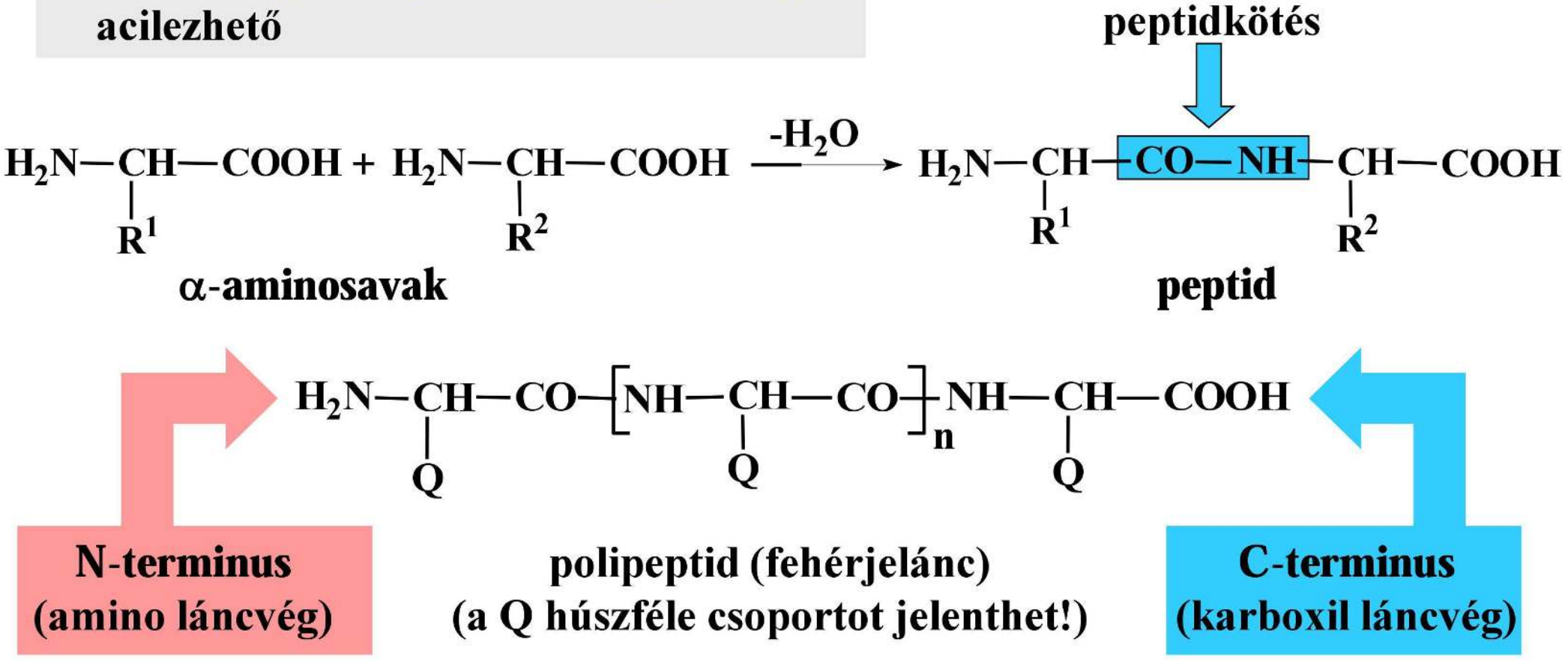
gyenge bázis
puffer oldat

2. Karboxilcsoportra jellemző tulajdonságok

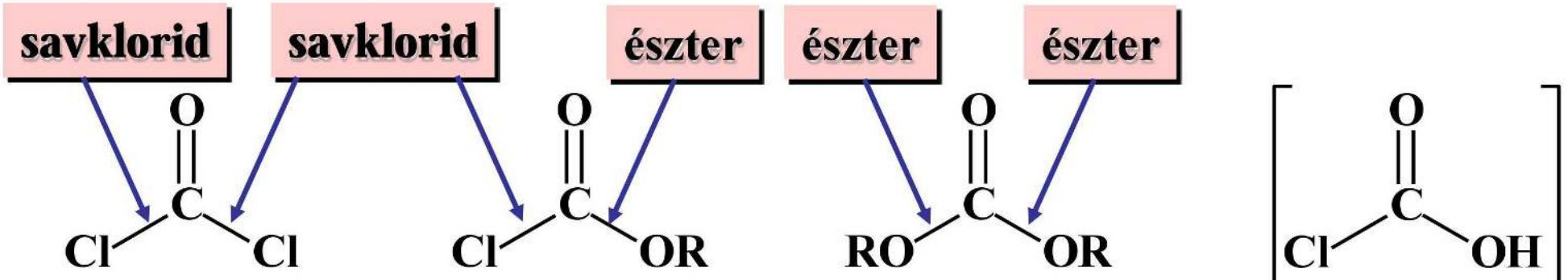
savszármazékok ➡ amidok

3. Aminocsoportra jellemző tulajdonságok

acilezhető



Szénsavszármazékok

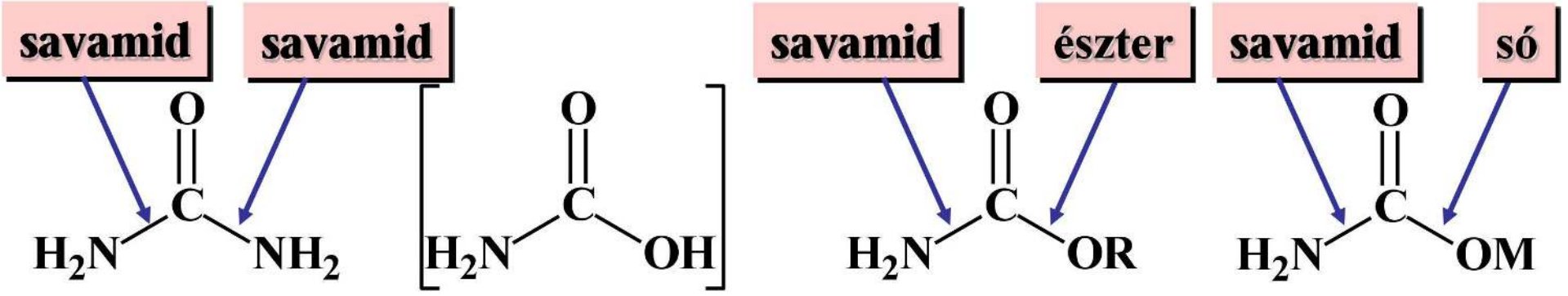


foszgén (metaszénsav-diklorid)

alkil(aril)karbono-kloridát

dialkil-karbonát

(nem létképes)



karbamid

karbamidsav (bomlékony)

alkil-karbamát (uretán)

fém-karbamát