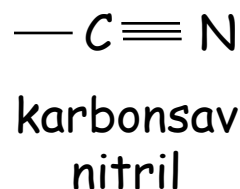
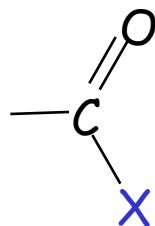
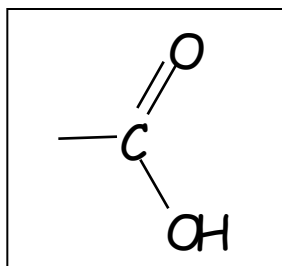
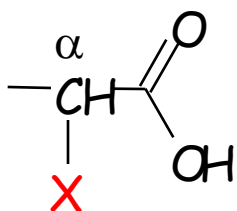


8. Előadás

Karbonsavak.
Karbonsav származékok.

24. Karbonsavak



X	Név	X	Név
F, Br, Cl	halogénsav	F, Br, Cl	savhaloid
OH	hidroxisav	OR	észter
=O	oxosav	OCOR	anhidrid
NH ₂	aminosav	NH ₂	amid

Csoportosítás

1. Nyílt láncú - gyűrűs
2. Telített - telítetlen
3. Mono-, di-....karbonsavak

Karbonsavak és savszármazékok elnevezéséhez szolgáló utótagok és végzések

$-(C)OOH^a$	-sav	$-COOH$	-karbonsav
$-(C)OOR^{a,b}$	(R)-...oát ^b	$-COOR^b$	(R)-...karboxilát ^b
gyűrűben: $-(C)O-O-^a$	-olakton	gyűrűben: $-CO-O-$	-karbolakton
$-(C)O-X^{a,c}$	-oil-halogenid	$-CO-X^c$	-karbonil-halogenid
$[-(C)O]_2O^a$	-sav-anhidrid	$(-CO)_2O$	-karbonsav-anhidrid
$-(C)O-NH_2^a$	-amid	$-CO-NH_2$	-karboxamid
$-(C)O-NH-NH_2^a$	-hidrazid	$-CO-NH-NH_2$	-karbohidrazid
$-(C)\equiv N^a$	-nitril	$-C\equiv N$	-karbonitril

(b) Dikarbonsavak, savszármazékok és szubsztituált származékok

$HOO(C)...(C)OOH^a$	-disav	$HOOC...COOH$	-dikarbonsav
gyűrűben: $-(C)O-NH-(C)O-^a$	-imid ^d	gyűrűben: $-CO-NH-CO-$	-dikarboximid
$HOO(C)...(C)O-NH_2^a$	-amidsav ^d		
$HOO(C)...(C)O-NH-C_6H_5$	-anilidsav ^d		
$HOO(C)...(C)HO^a$	-aldehidsav ^d		

Nyitrai J., Nagy J.:

**Útmutató a szerves vegyületek IUPAC-nevezéktanához.
(Magyar Kémikusok Egyesülete, 1998) 115.oldal**

Alkánsav (homológ sor)

Metánsav, hangyasav*	HCOOH
Etánsav, ecetsav*	CH ₃ COOH
Propionsav	CH ₃ CH ₂ COOH
Butánsav, vajsav*	CH ₃ (CH ₂) ₂ COOH
Pentánsav, valeriánsav*	CH ₃ (CH ₂) ₃ COOH
Hexán, kapronsav*	CH ₃ (CH ₂) ₄ COOH
....	
Palmitinsav*	CH ₃ (CH ₂) ₁₄ COOH
Sztearinsav	CH ₃ (CH ₂) ₁₆ COOH
....	

Alkándisav (homológ sor)

Etándisav, oxálsav*	HOOC - COOH
Propándisav, malonsav*	HOOC-CH ₂ -COOH
Borostyánkősav*	HOOC-(CH ₂) ₂ -COOH
Glutársav*	HOOC-(CH ₂) ₃ -COOH
Adipinsav*	HOOC-(CH ₂) ₄ -COOH
....	

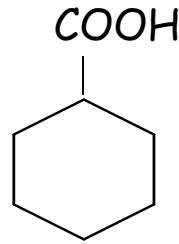
Alkénsav (homológ sor)

Propénsav, akrilsav*	CH ₂ = CH -COOH
2-Buténsav	CH ₃ -CH = CH -COOH
3-Buténsav	CH ₂ = CH -CH ₂ -COOH
2-metilpropénsav, metakrilsav*	CH ₂ = C(CH ₃) -COOH
....	

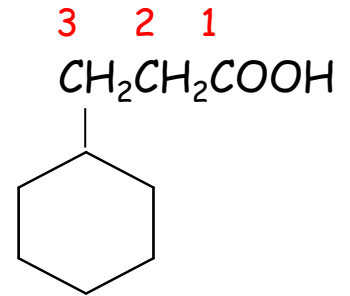
Nomenklatura

H-COOH
metánsav
hangyasav*

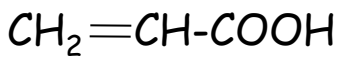
$\text{CH}_3\text{-CH}_2\text{-COOH}$
propánsav
propionsav*



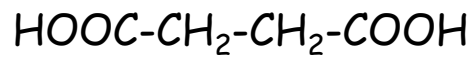
ciklohexán
karbonsav



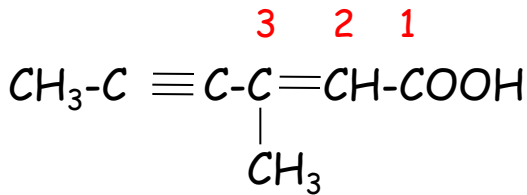
3-ciklohexil
propionsav



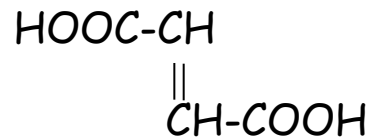
akrilsav*



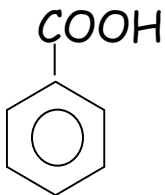
butándisav



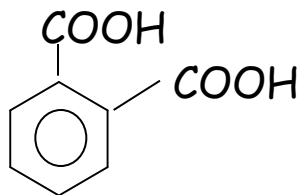
3-metil-2-hexén-4-insav



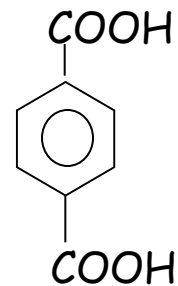
maleinsav* (cisz)
fumársav* (transz)



benzoesav*

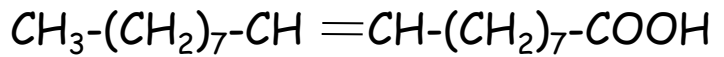
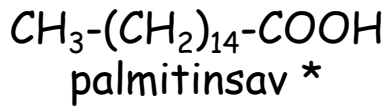


ftálsav*



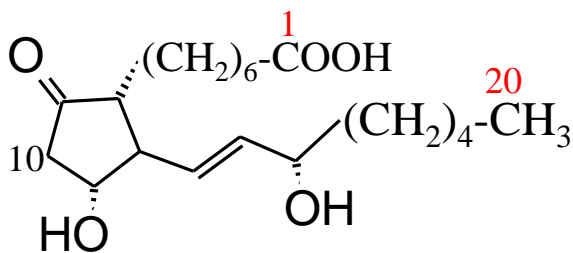
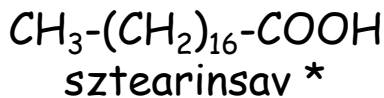
tele-ftálsav*

Természetes karbonsavak

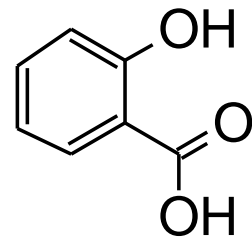


cisz: olajsav *

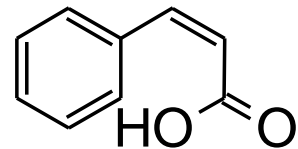
transz: elaidinsav *



Prostaglandin E
(PGE₁) 1935
1963: szintézis

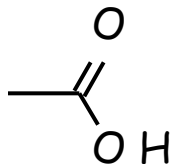


szalicilsav *

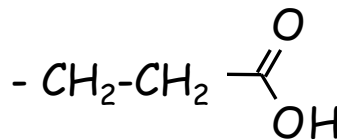


fahéjsav *

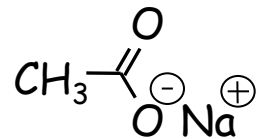
Csoportok



karboxi
(előtag)



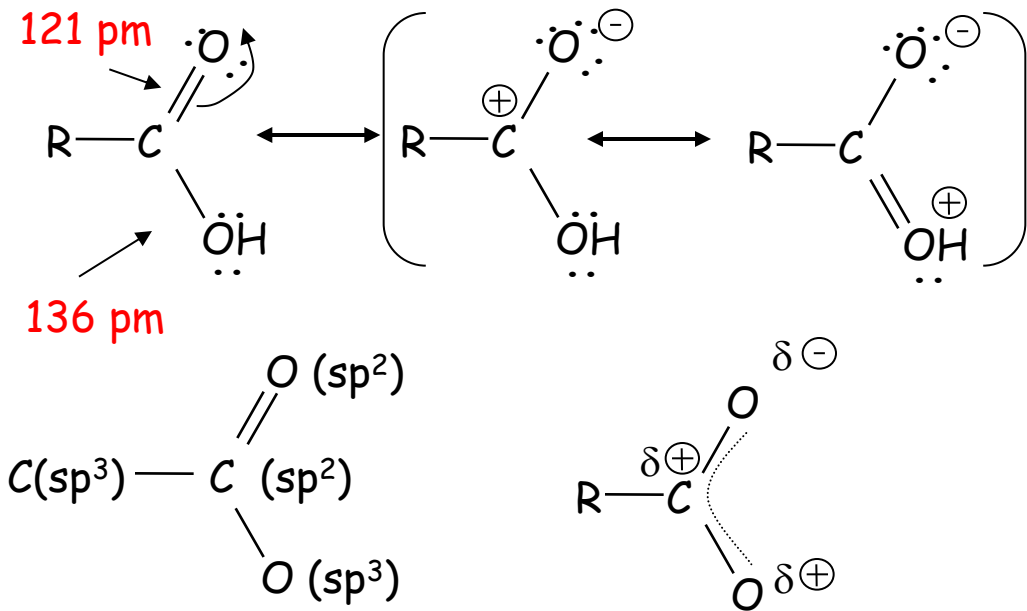
propanoil
(alkanoil)



karboxilát
(pl. Na acetát)

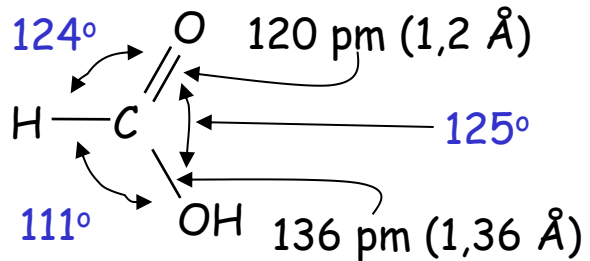
Szerkezet

1. Karboxil csoport

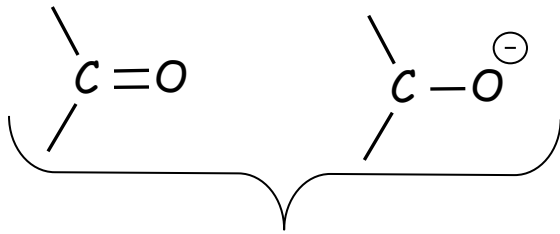
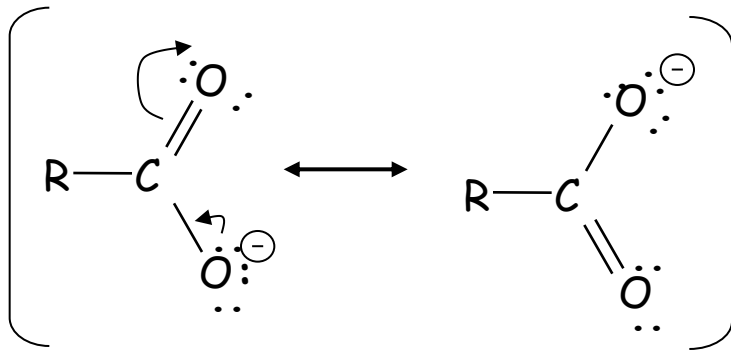


Egy példa:

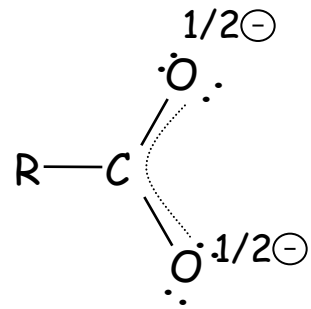
hangyasav



2. Karboxilát csoport

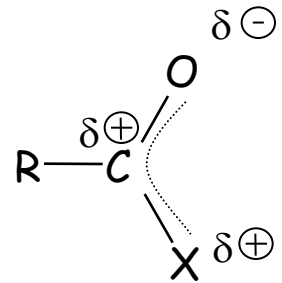
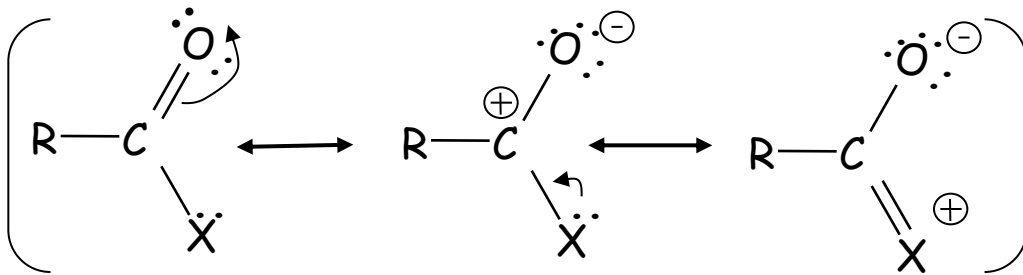


127 pm

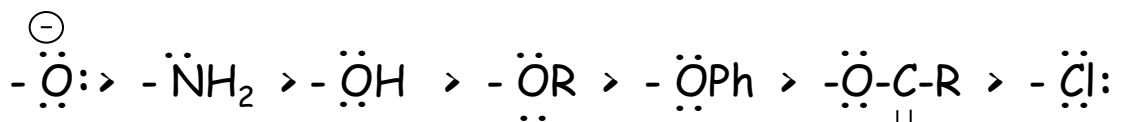


Szimmetrikus
mezoméria

3. Szubsztituált karboxil csoport



Konjugációs kölcsönhatás az X és a karbonil C között



karboxilát

savamid

sav

észter

észter

anhidrid

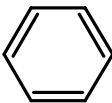
savklorid

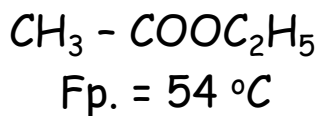
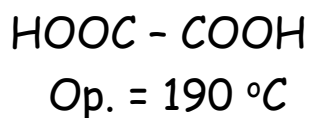
Megjegyzés:

Reaktivitási sorrend a C-atomon lejátszódó reakciókra nézve.

Fizikai tulajdonságok

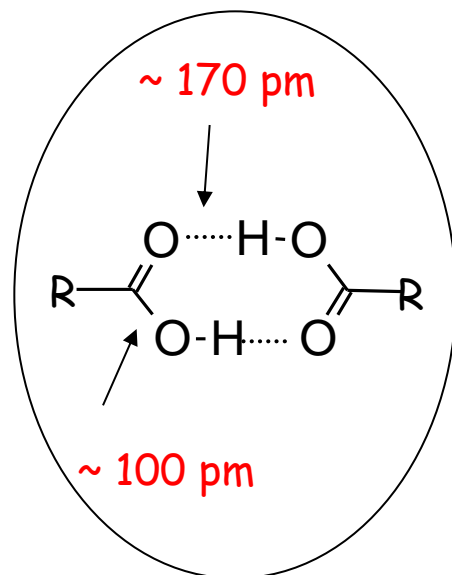
1. Forráspont, olvadáspont, oldékonyság

	Op. (°C)	Fp. (°C)	mg/ml H ₂ O	
HCOOH	8,4	101	∞	} H-kötés*
CH ₃ COOH	16,6	118	∞	
CH ₃ -(CH ₂) ₂ -CH ₃		0,5	-	
CH ₃ -O-CH ₂ -CH ₃		7,6	oldható	
CH ₃ -CO-CH ₃	-94,8	56,2	∞	} H-kötés
CH ₃ -(CH ₂) ₂ -OH	-127	97,2	∞	
CH ₃ -(CH ₂) ₂ -COOH	-5,5	164	∞	
 -COOH	122,4	250	0,21	} H-kötés*



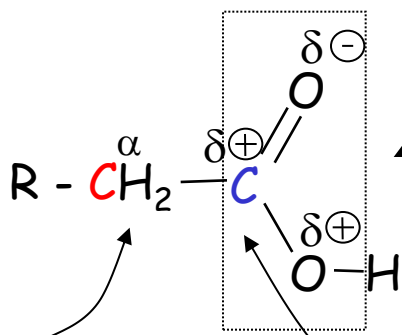
2. Halmazállapot

C 1-9 folyadék
> C 9 szilárd



Kémiai reakciók

Dekarboxileződés



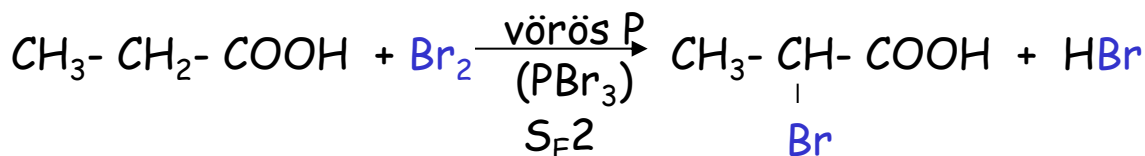
Reakció az α C-atomon
szubsztitúció

Reakció a karbonil
C-atomon

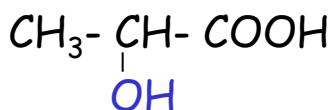
1. sav-bázis sajátság
2. redukció
3. szubsztitúció

Reakció az α -C-atomon

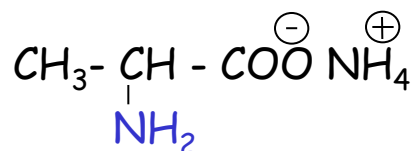
1. Brómozás



α -bróm-propionsav

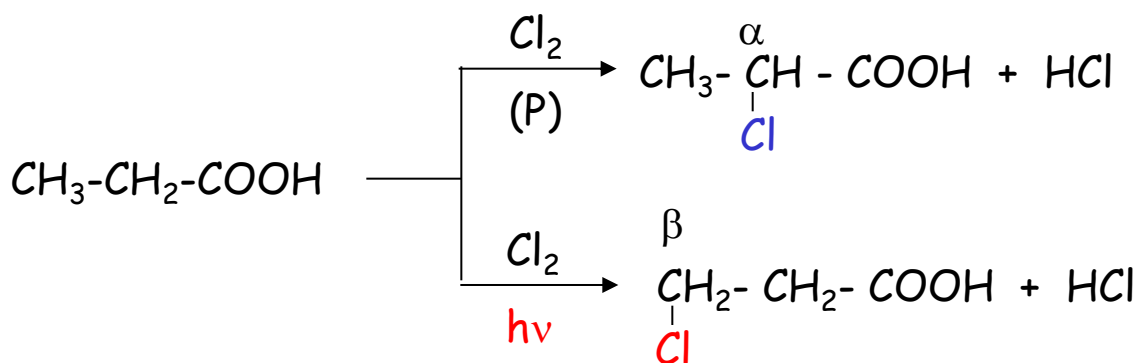


α -hidroxi-propionsav
tejsav*



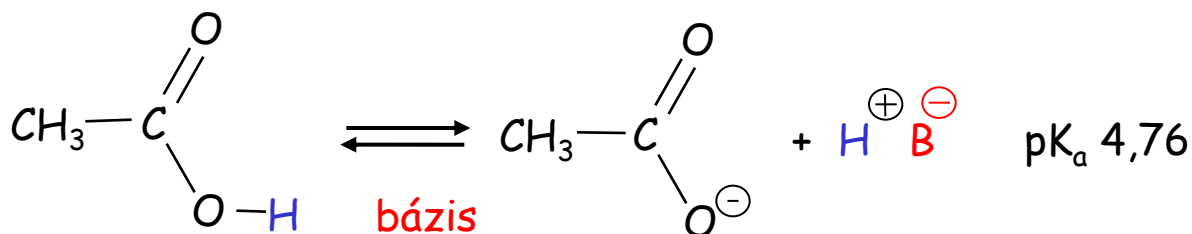
α -amino-propionsav
ammonium sója

2. Klórozás - irányított halogénezés

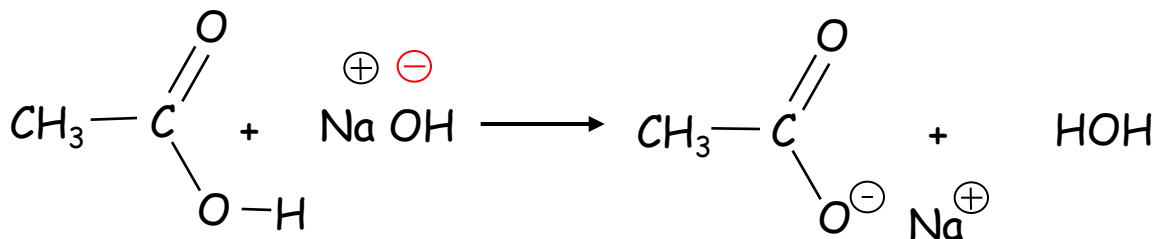


Reakció a karbonil C-atomon

1. Savi jelleg (O-H sav)



Példa: sóképzés



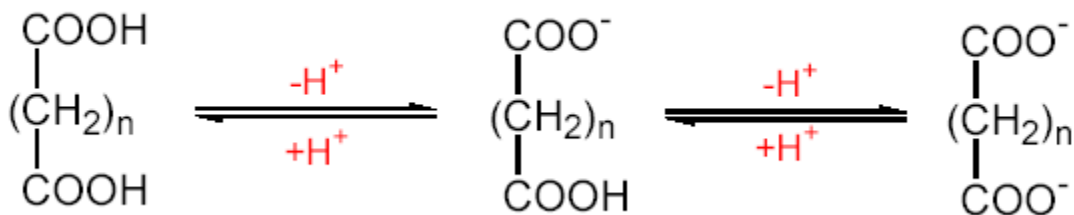
Az α -szubsztituens hatása:

	pK _a		pK _a
H-CH ₂ -COOH	4,76	CH ₃ -CH ₂ -COOH	4,87
Cl-CH ₂ -COOH	2,86	CH ₃ \CH-COOH	4,89
HO-CH ₂ -COOH	3,82	CH ₃ \CH-COOH	
H ₂ N-CH ₂ -COOH	2,34	CH ₃ \C-COOH	5,05
O=CH-COOH	3,33	CH ₃ \C-COOH	

- I effektus

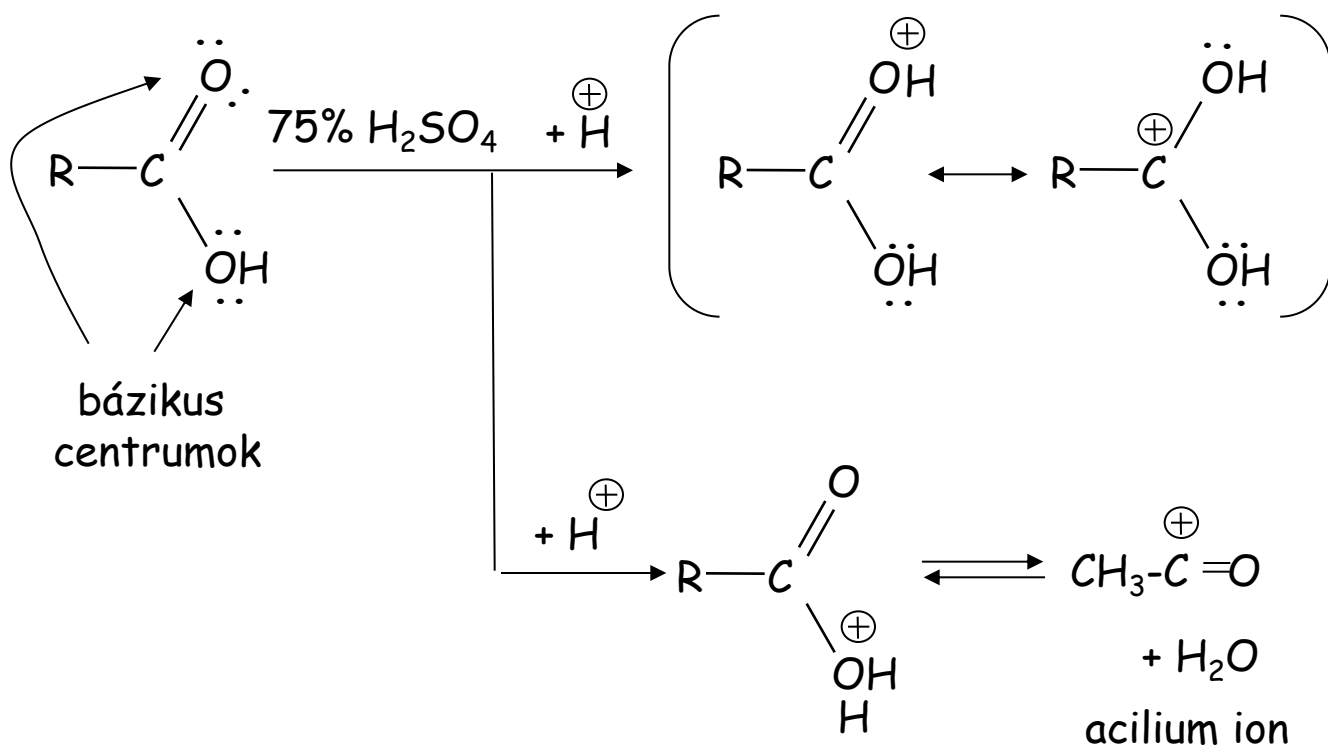
Ezen a megfigyelésen alapul az alkil csoportok + I effektusa

Dikarbonsav: szubsztituált karbonsav



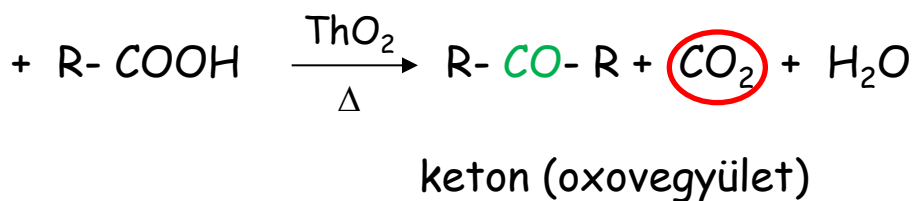
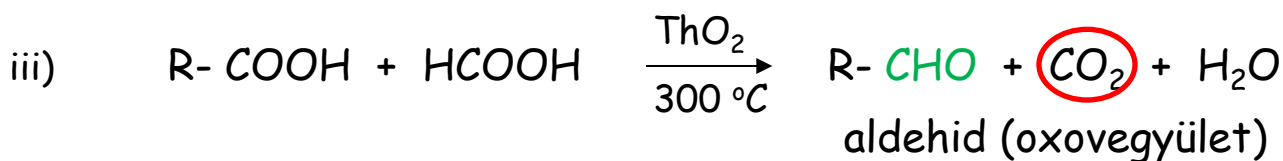
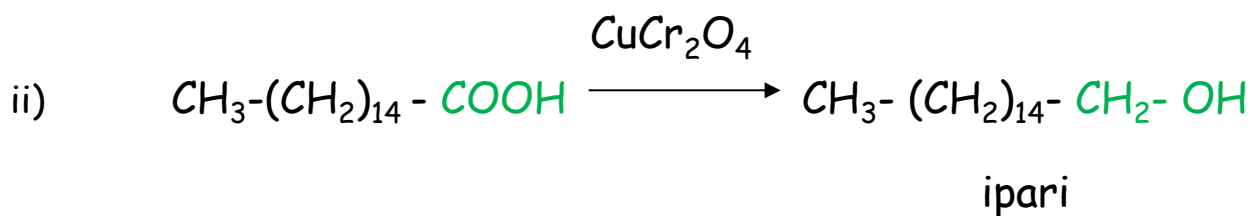
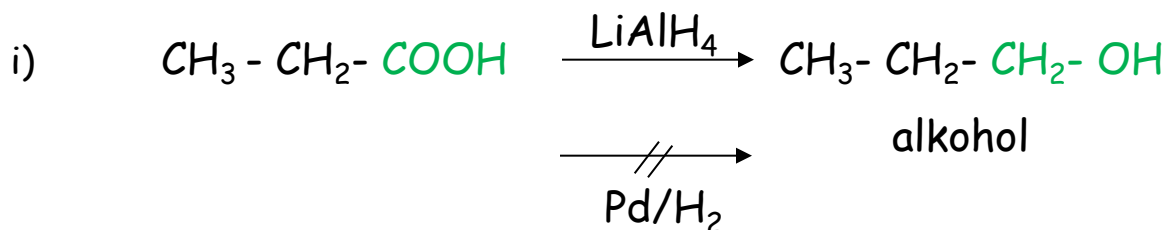
n	pK ₁	pK ₂	
0	1,27	4,28	etándisav (oxálsav*)
1	2,85	5,70	propándisav (malonsav*)
2	4,19	5,64	butándisav (borostyánkősav*)

Bázicitás: gyenge bázisok



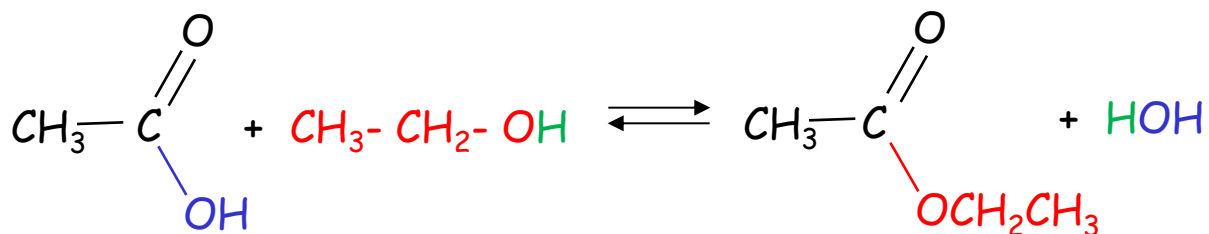
2. Redukció

Nehezebben redukálhatóak, mint az oxo vegyületek

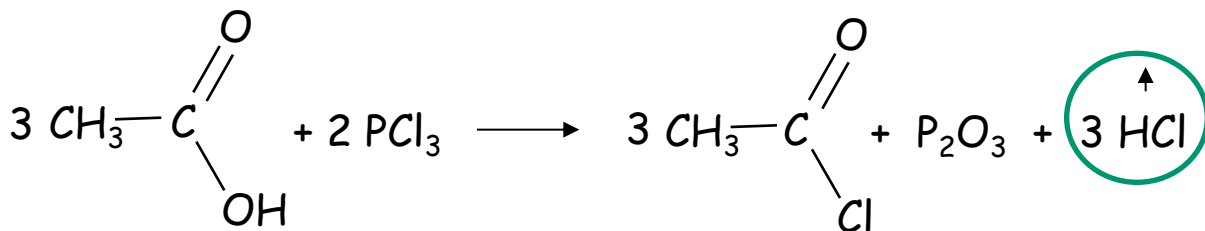
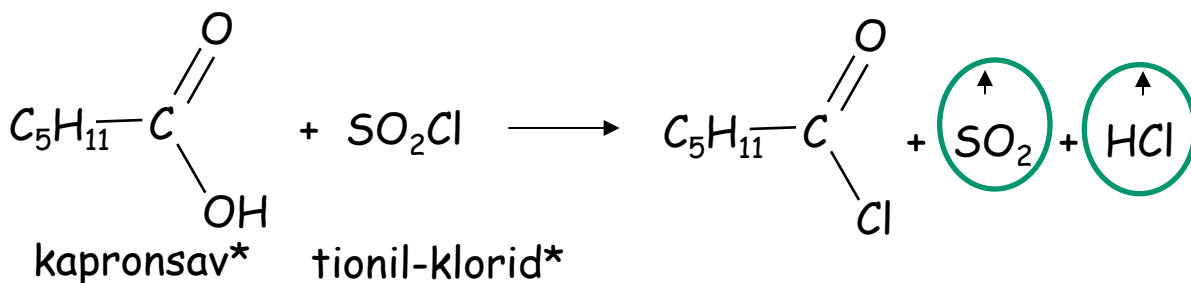


3. Szubsztitúció

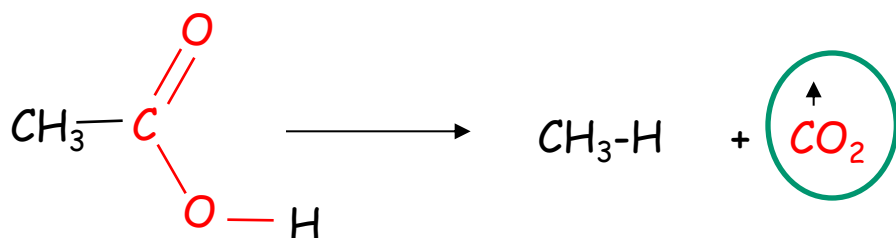
i) Reakció alkohollal



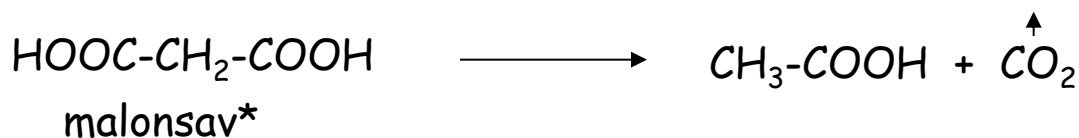
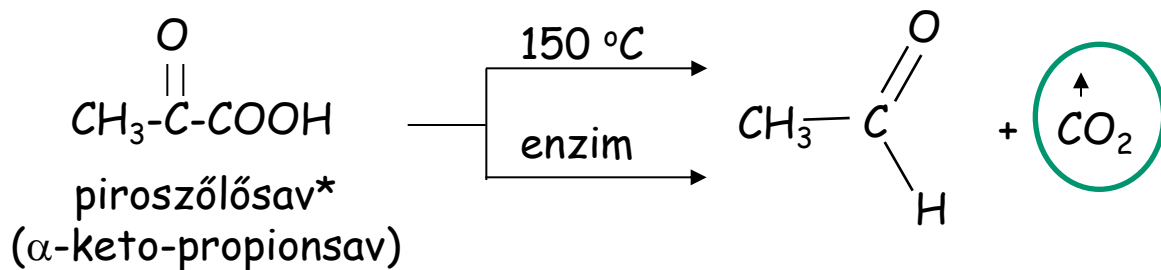
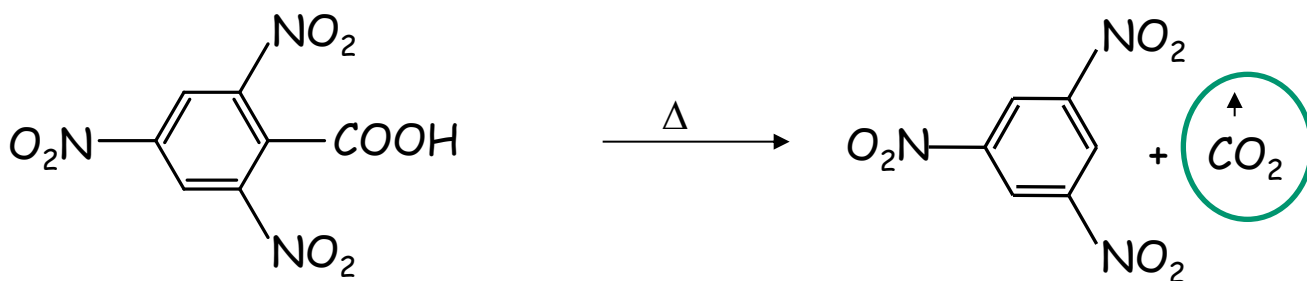
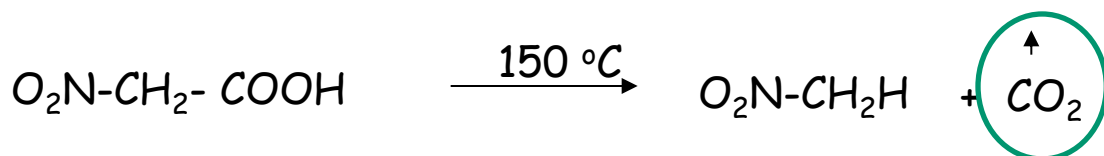
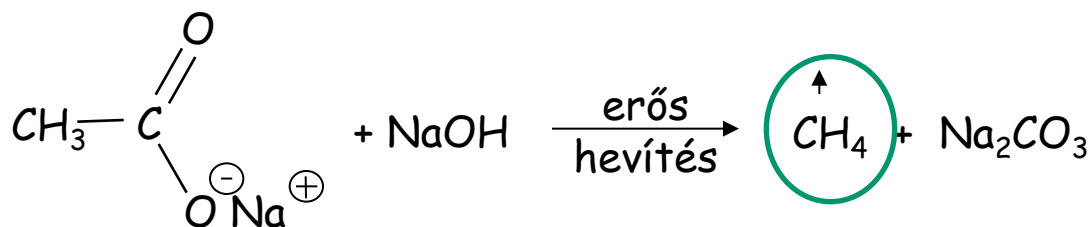
ii) Átalakítás savkloriddá



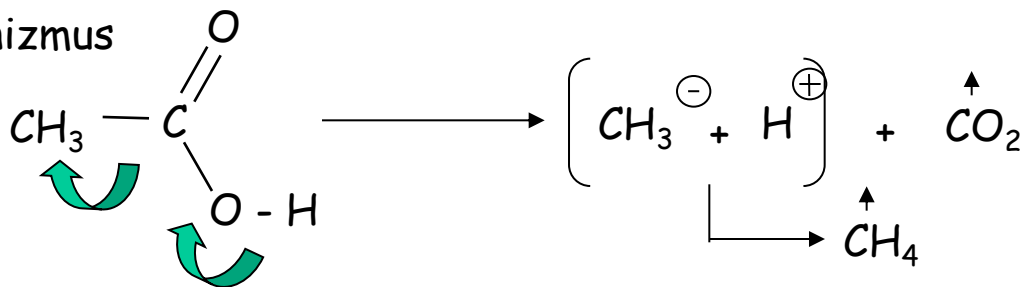
4. Dekarboxilezés



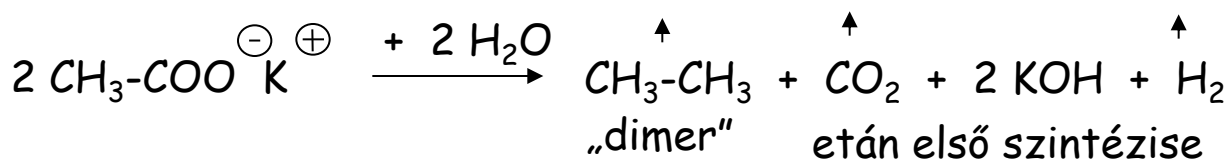
i) Termikus dekarboxilezés



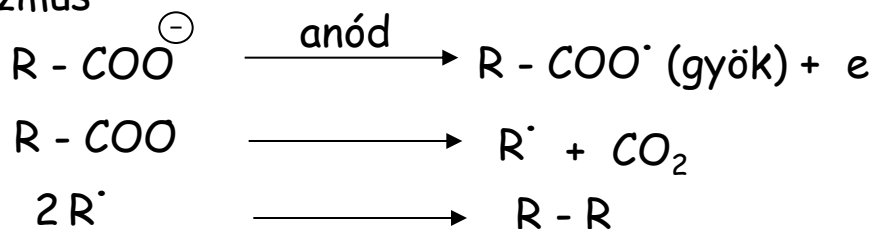
Mechanizmus



ii) Kolbe elektrolízis: szimmetrikus alkánok szintézise

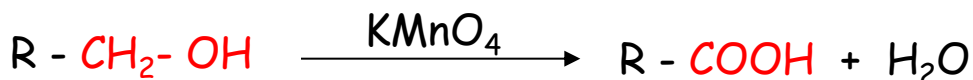


Mechanizmus

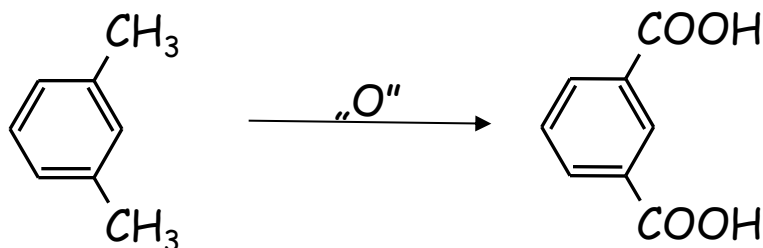


Karbonsavak előállítása

1. Primer alkoholok oxidációja / aldehidek oxidációja



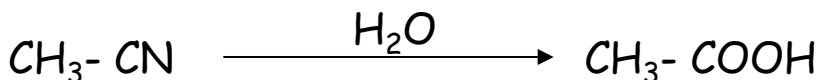
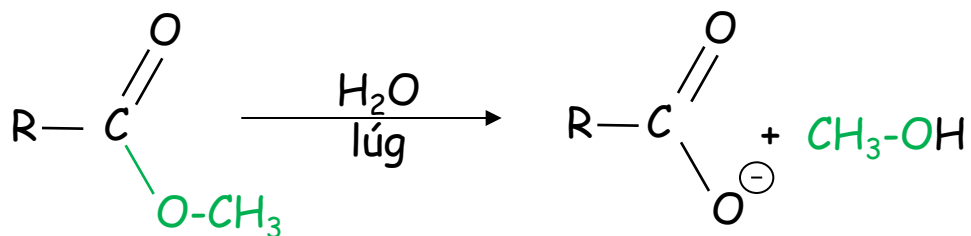
2. Aromás CH oldalláncának oxidációja



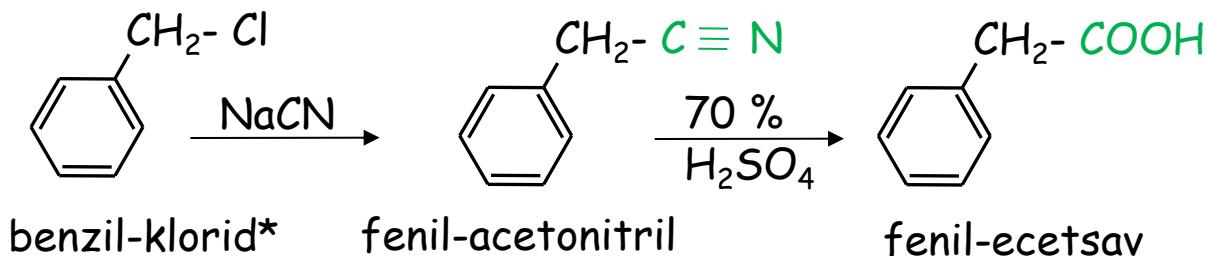
m-xilol*

izo vagy m-ftálsav*

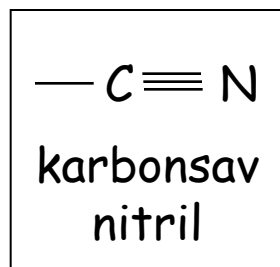
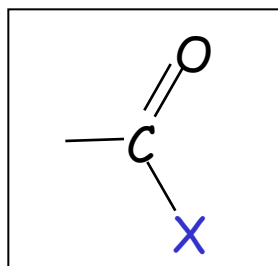
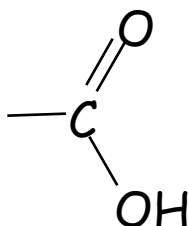
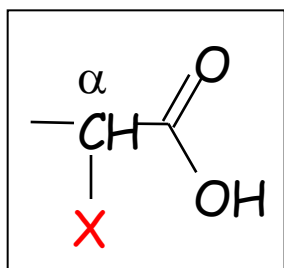
3. Észterek, nitrilek hidrolízise



4. Halogénezett CH-ből, nitrilen át hidrolízissel



25. Karbonsav származékok



X	Név	X	Név
F, Br, Cl	halogénsav	F, Br, Cl	savhaloid
OH	hidroxisav	OR	észter
=O	oxosav	OCOR	anhidrid
NH ₂	aminosav	NH ₂	amid

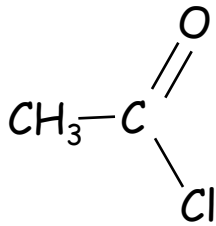
Csoportosítás

1. Nyílt láncú - gyűrűs
2. Telített - telítetlen
3. Mono-, di-....karbonsavszármazékok

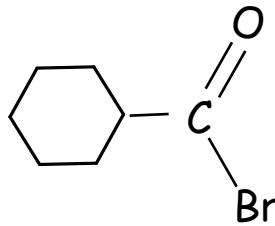
25.1. Karboxil csoportban szubsztituált származékok

Nomenklatura

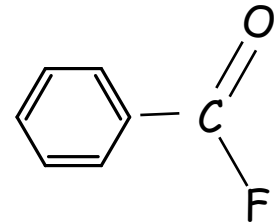
Savhalogenid



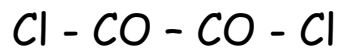
acetil-klorid



ciklohexánkarbonil-
bromid

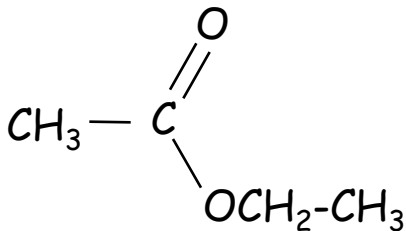


benzoil-fluorid

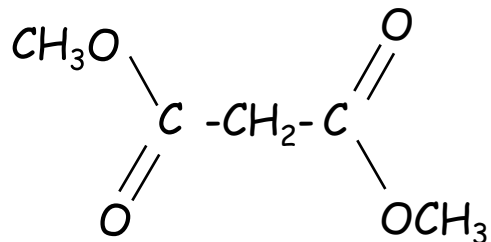


oxalil-klorid

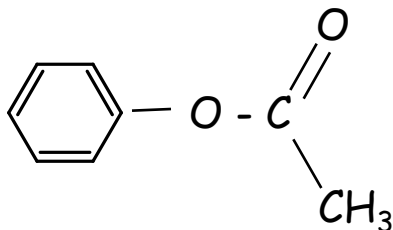
Karbonsav észter



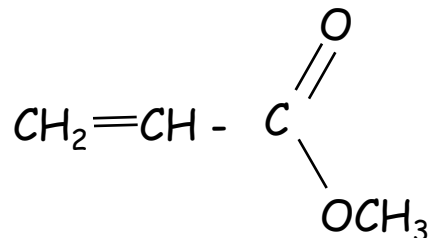
etil-acetát



dimetil-malonát

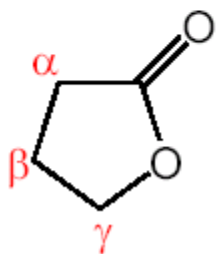
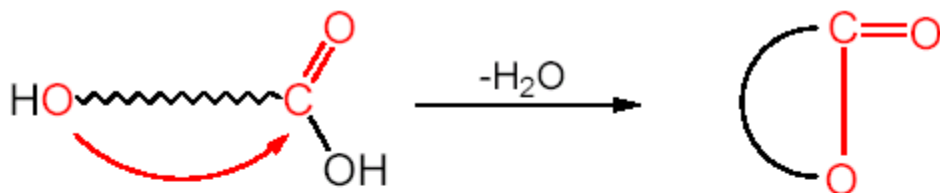


fenil-acetát

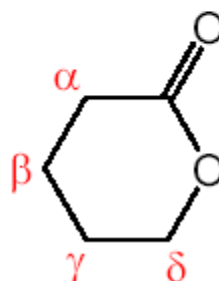


metil-akrilát

Gyűrűs észter (lakton)

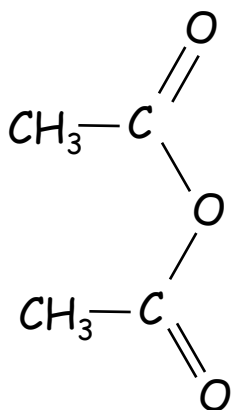


γ - butirolakton

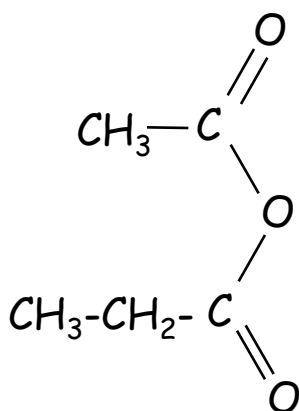


δ - valerolakton

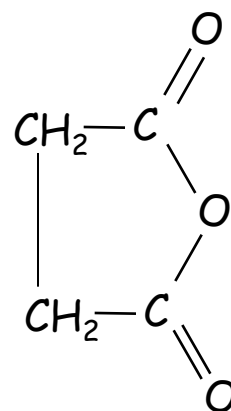
Karbonsav-anhidrid



ecetsavanhidrid,
szimmetrikus

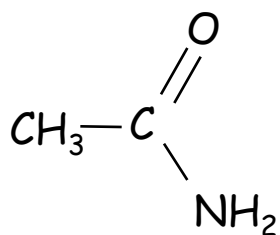


ecetsav-propionsav
anhidrid, vegyes

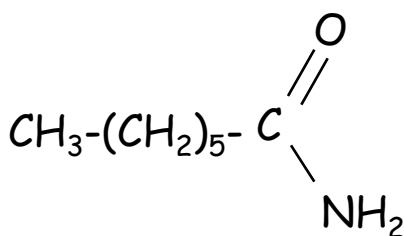


borostyánkősav
anhidrid, gyűrűs

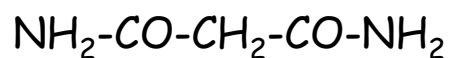
Karbonsav amid



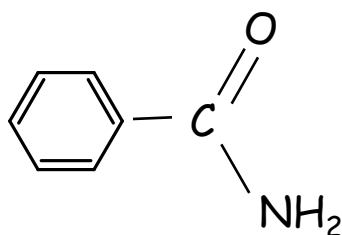
acetamid



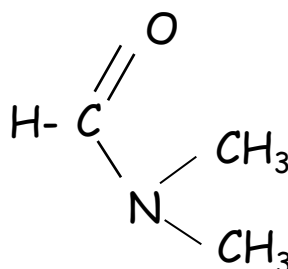
heptánsavamid



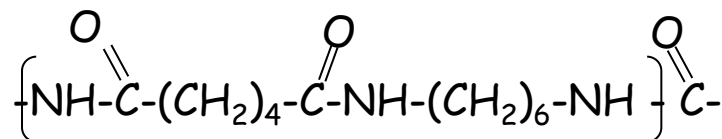
malonsavdiamid



benzamid

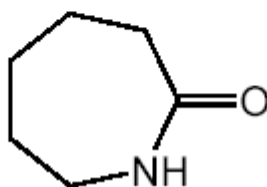
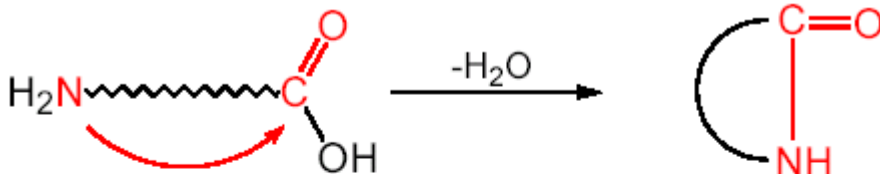


N,N-dimetil formamid



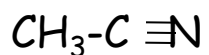
adipinsav + hexametiléndiamin „nylon-66”

Gyűrűs amid (laktám)

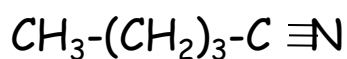


ϵ - kaprolaktám

Karbonsav nitril alkán + nitril
alkil-cianid



acetonitril
(metil cianid)



pentánnitril
(butil cianid)

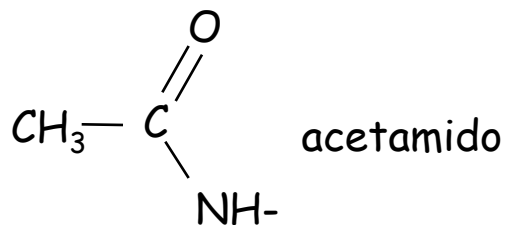


pentándinitril

Csoportok:

$\text{-C}\equiv\text{N}$ karbonitril (cianid)

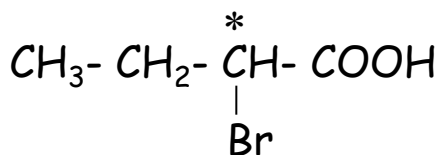
$\equiv\text{N}$ nitril



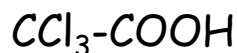
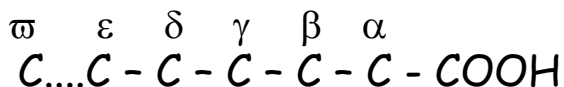
25.2. Az oldalláncban szubsztituált származékok

Nomenklatura

Halogén karbonsavak

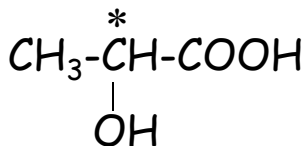


2-bróm-butánsav
2-bróm-vajsav

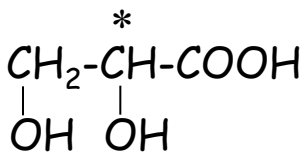


triklór-ecetsav

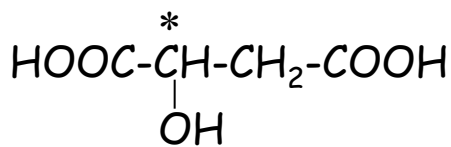
Hidroxi karbonsavak



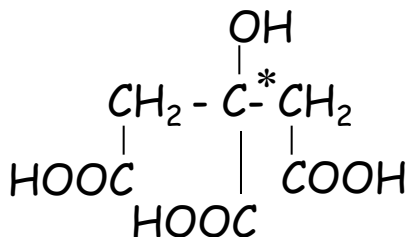
1-hidroxi-propionsav
(tejsav*)



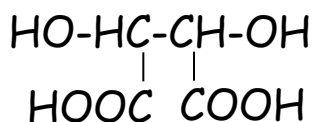
2,3-dihidroxi-propionsav
(glicerinsav*)



hidroxi-borostyánkősav
(almasav*)



2-hidroxi-1,2,3-propán trikarbonsav
(citromsav*)

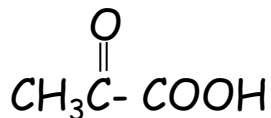


2,3-hidroxi-borostyánkősav
(borkősav*)

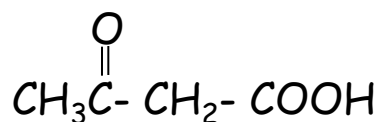
Oxo karbonsavak



oxo-ecetsav
(glioxálsav*)

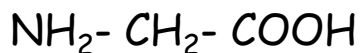


2-oxo-propionsav
(piroszőlősav*)

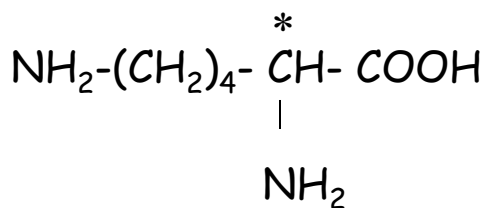


3-oxo-butánsav
(acetecetsav*)

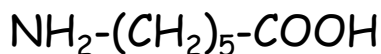
Amino karbonsavak



amino-ecetsav
(Glicin, Gly, G*)

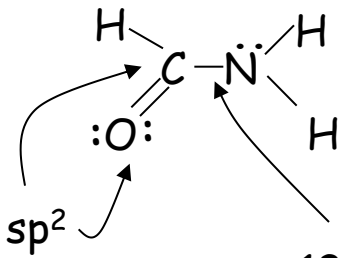


Lizin (Lys, K)*



6-amino-kaprónsav*

Kémiai szerkezet



135 pm
(v. ö. C-N, 147 pm)

példa: karbonsavamid

NHH \sphericalangle 121,5° NCH \sphericalangle 118,5°

NHC \sphericalangle 120°

Kettős kötés jelleg:

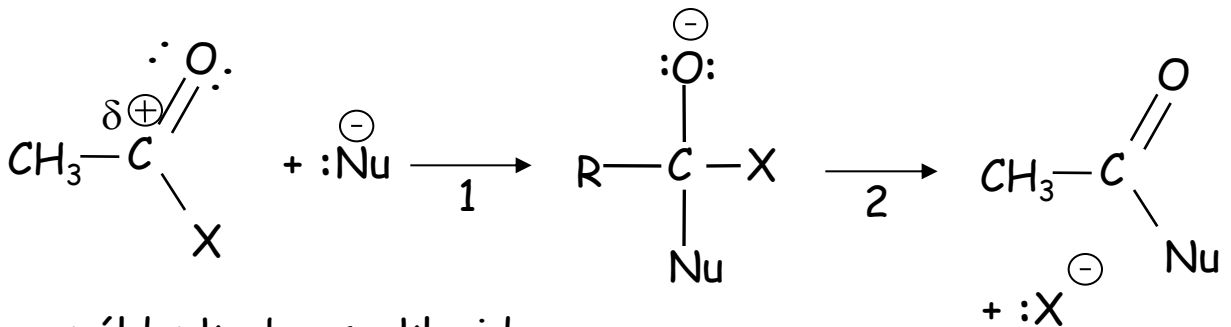
koplanáris



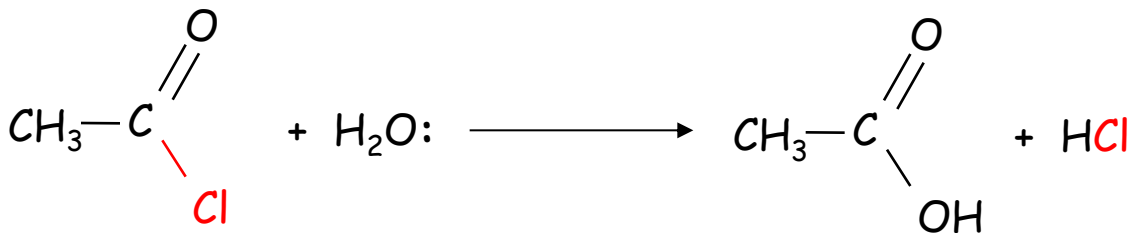
Kémiai reaktivitás

Jellemző reakciótipusok:

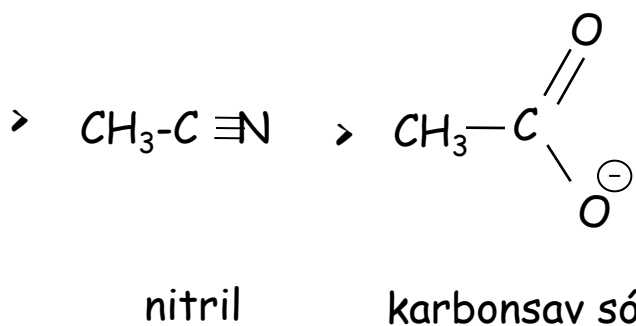
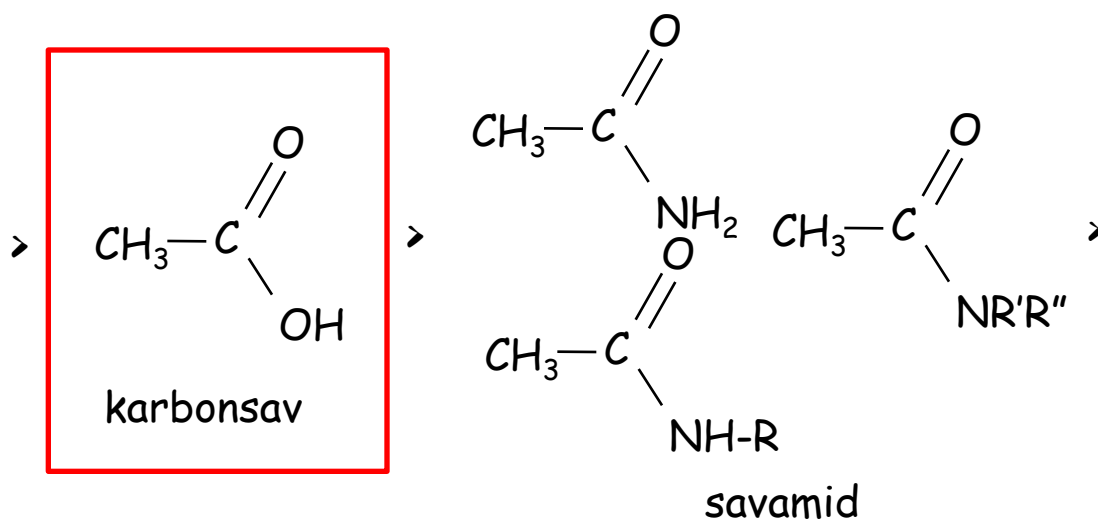
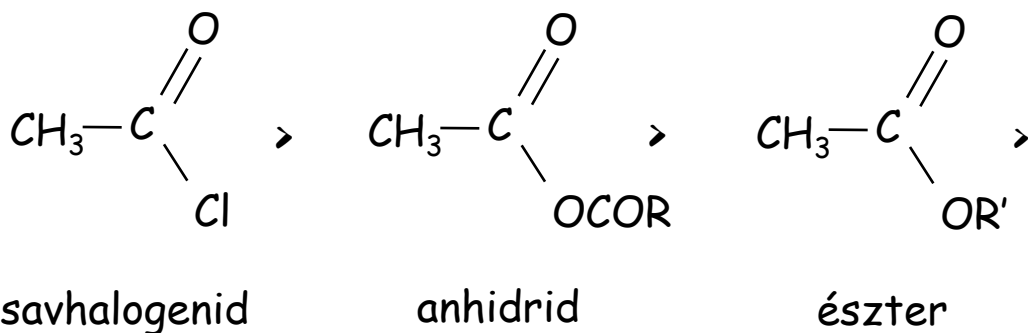
szubsztitúció = addíció + elimináció



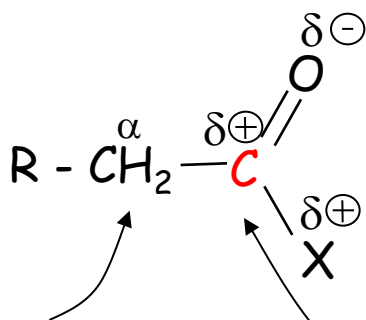
példa: karbonsavklorid



Átalakíthatóság - reaktivitási sorrend



Kémiai reakciók



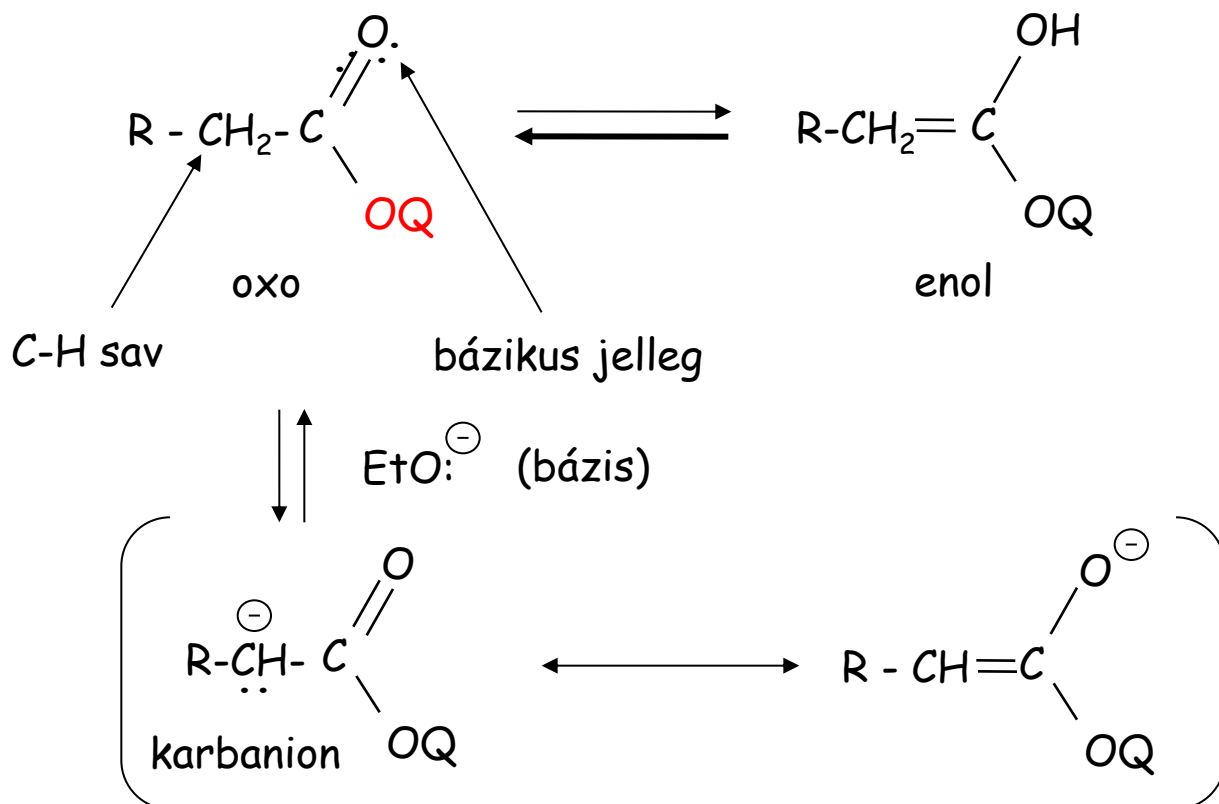
Reakció az α C-atomon

1. sav-bázis sajátság
2. Claisen kondenzáció

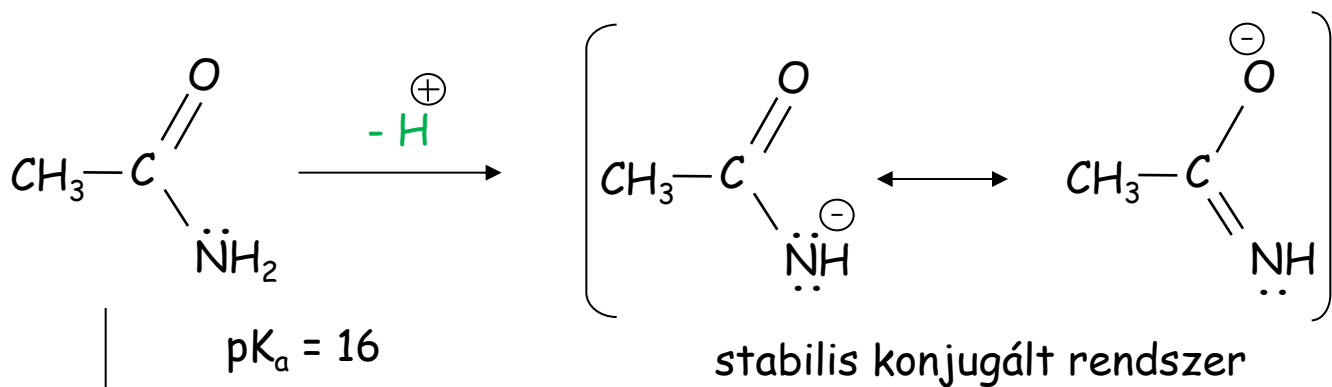
Reakció a karbonil C-atomon

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

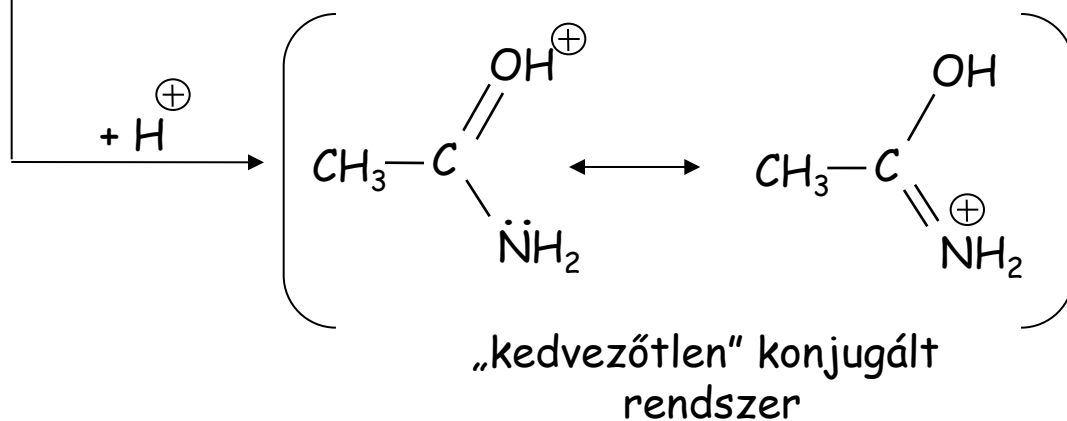
1A. Karbonsav **észterek** sav-bázis sajátság



1B. Karbonsavamidok sav - bázis sajátsága (N-H sav)



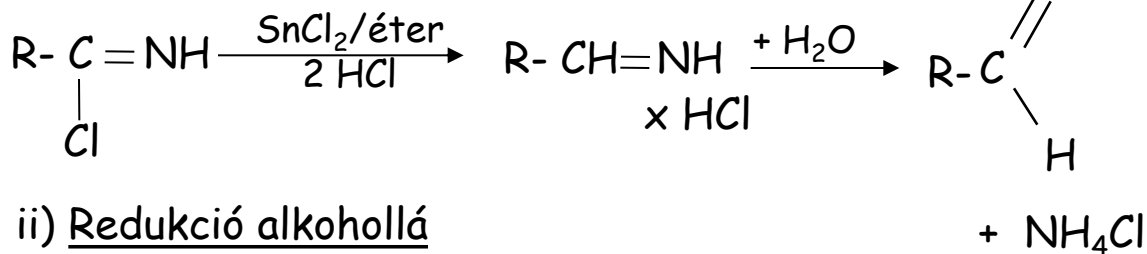
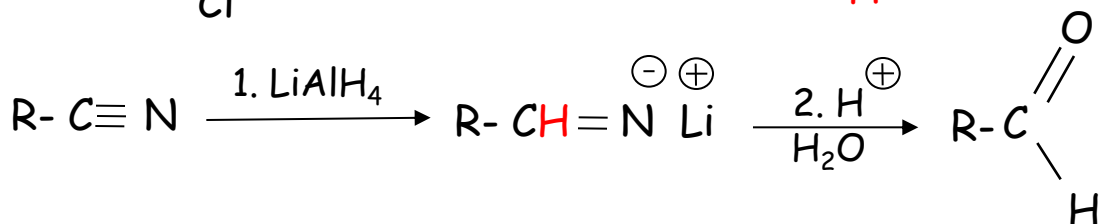
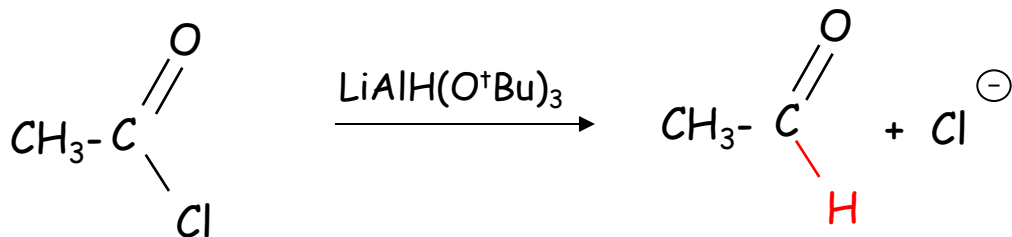
De:
primer amin $\text{pK}_a = 36$



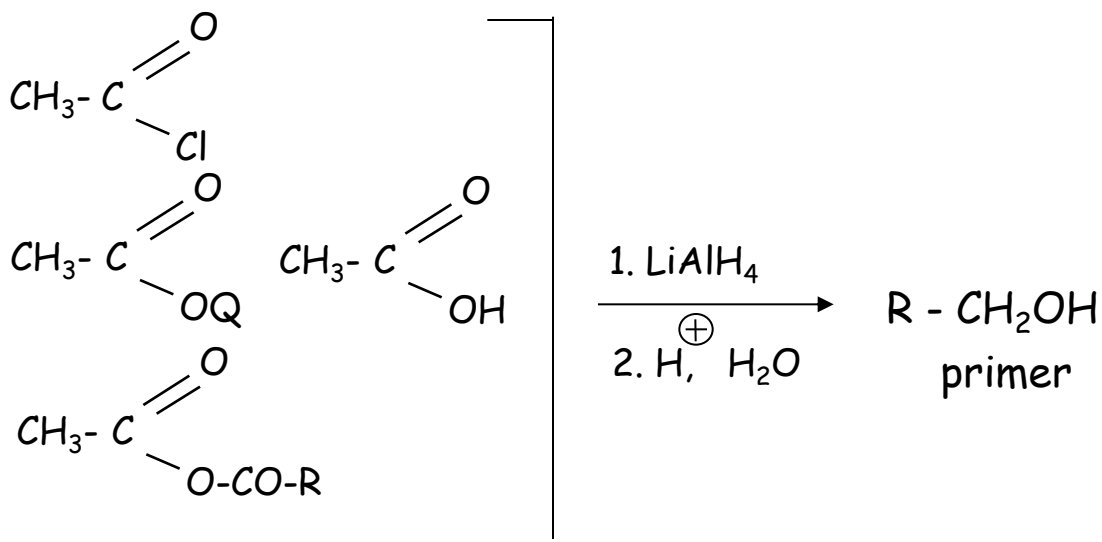
2. Redukció reakciótárs: :H^-

A karbonsavaknál könnyebben redukálhatók.

i) Redukció aldehiddé sav \rightarrow klorid \rightarrow alkohol \rightarrow nitril

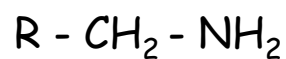
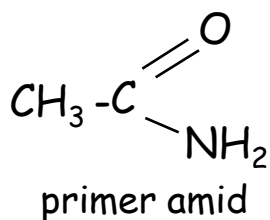


ii) Redukció alkohollá

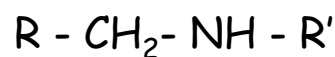
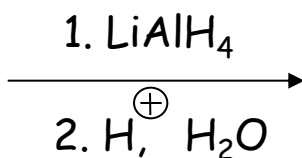
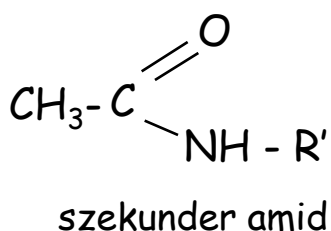


iii) Redukció aminná

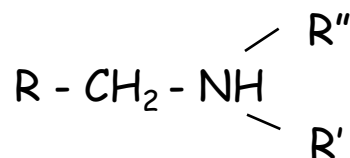
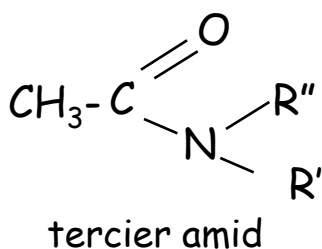
azonos C atomszám



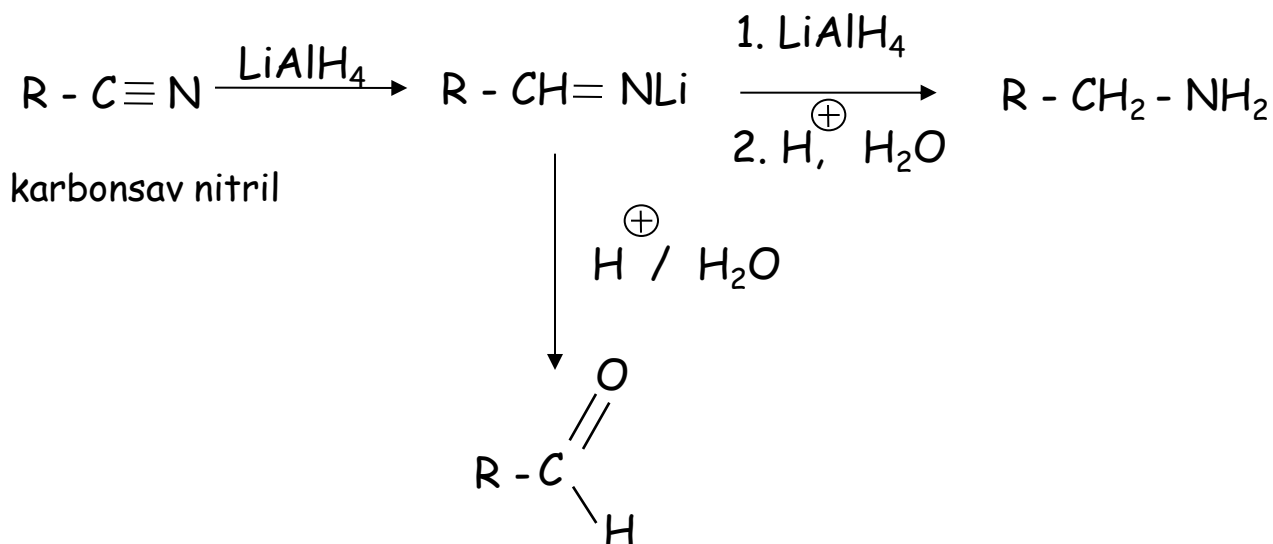
primer amin



szekunder amin



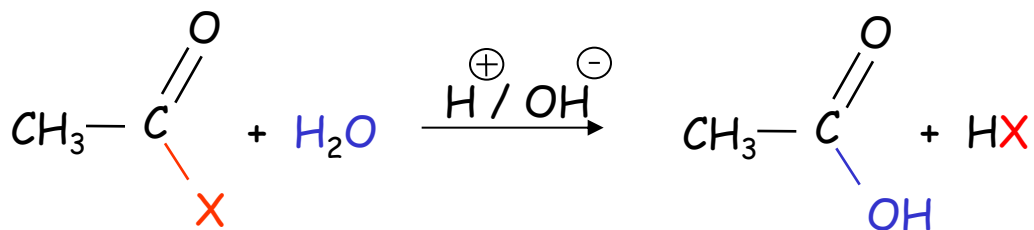
tercier amin



3. Szubsztitúciós reakciók

i) Hidrolízis

reakciótárs: H₂O

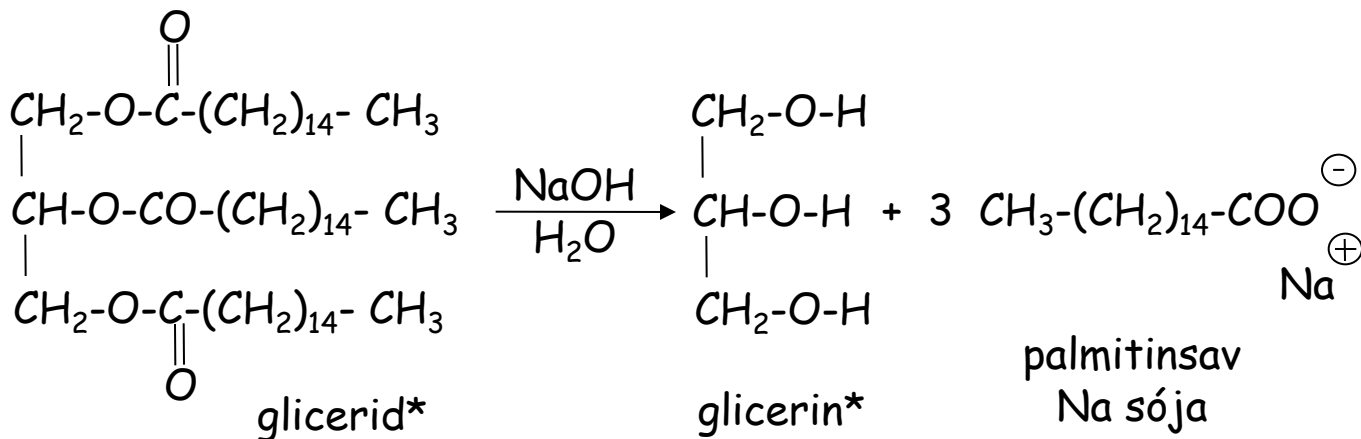


X =	Cl	gyors, heves	10 ¹¹
	$\begin{array}{c} \text{OCR} \\ \parallel \\ \text{O} \end{array}$	lassú, Δ	10 ⁷
	OR	lúg	1
	NH ₂	lúg, Δ	< 10 ⁻²
	≡N	erős lúg, Δ	n.a.
	O ⁻	-	-

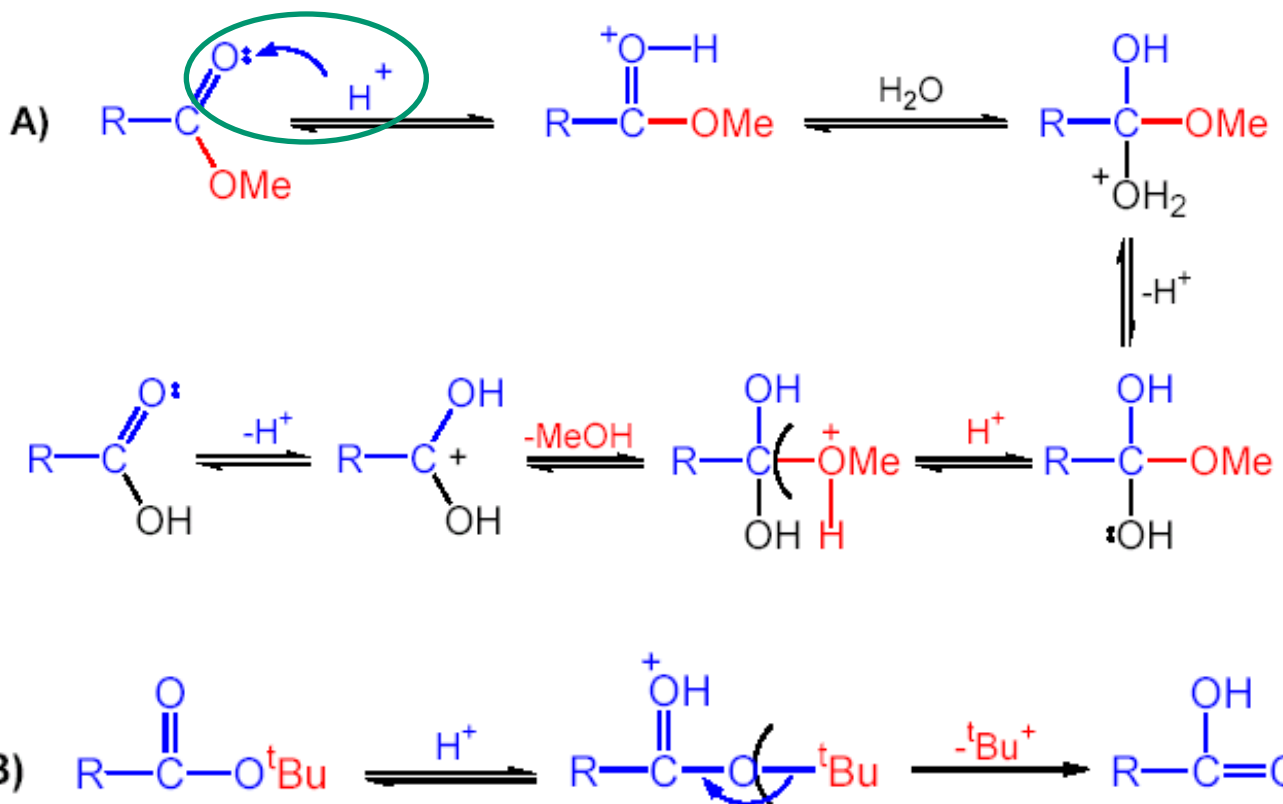
} hidrolízis
relatív sebessége
pH 7

Példa:

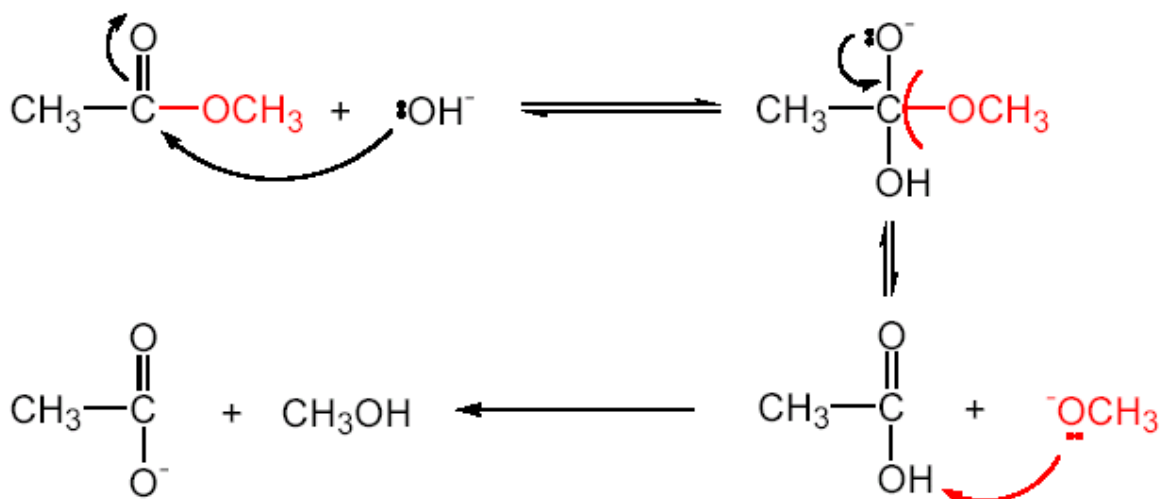
Szappanfőzés



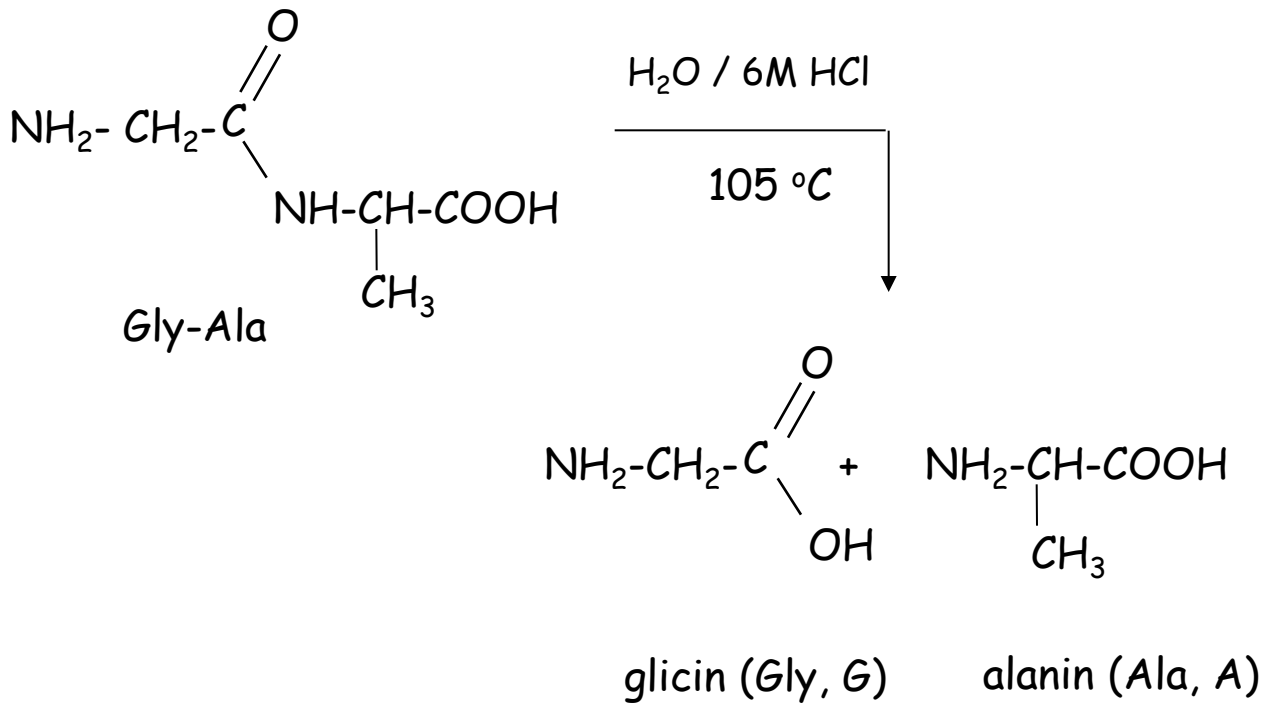
Észterek savas hidrolizise - mechanizmus



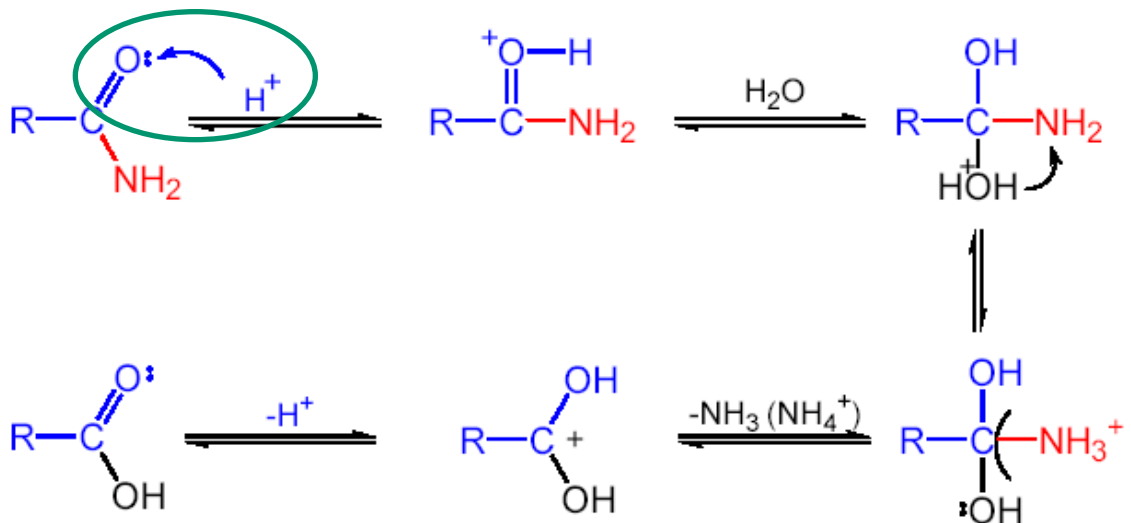
Észterek lúgos hidrolizise - mechanizmus



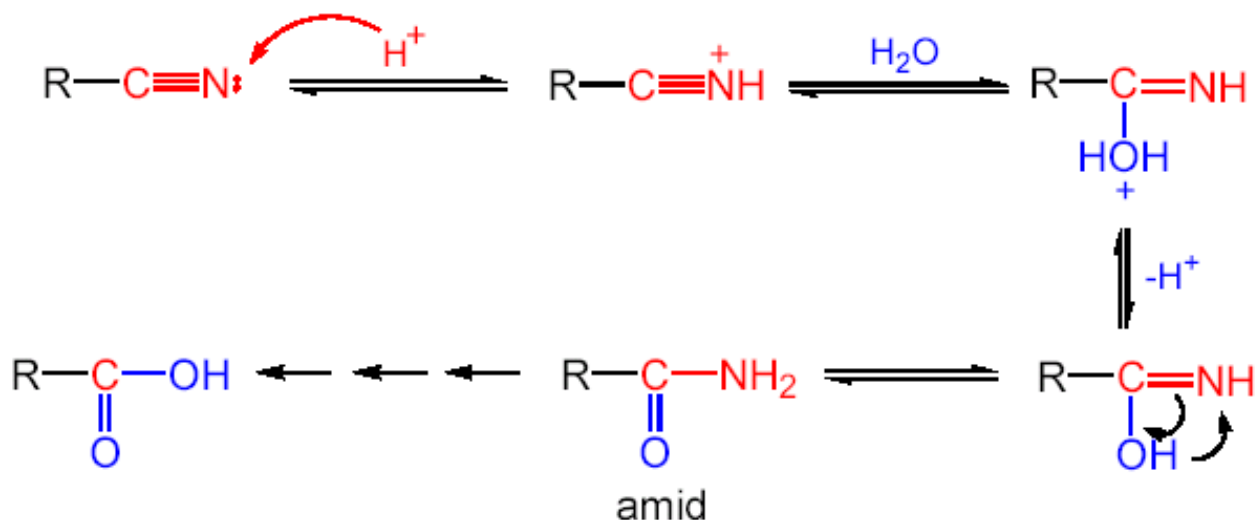
Peptid, fehérje hidrolízis, lebomlás



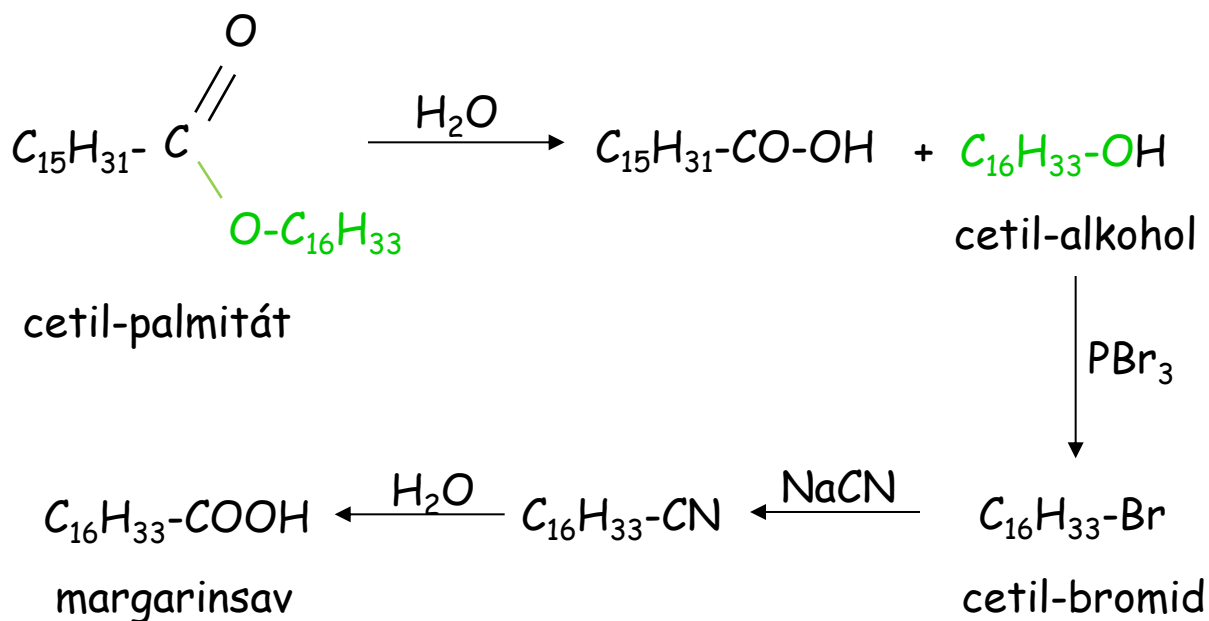
Mechanizmus



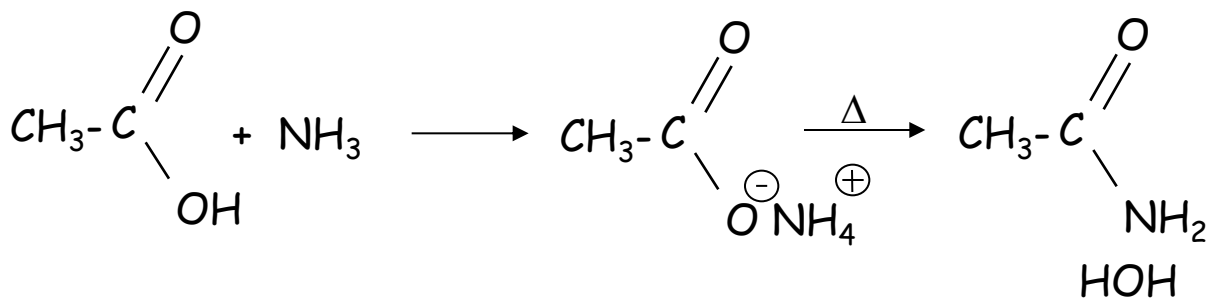
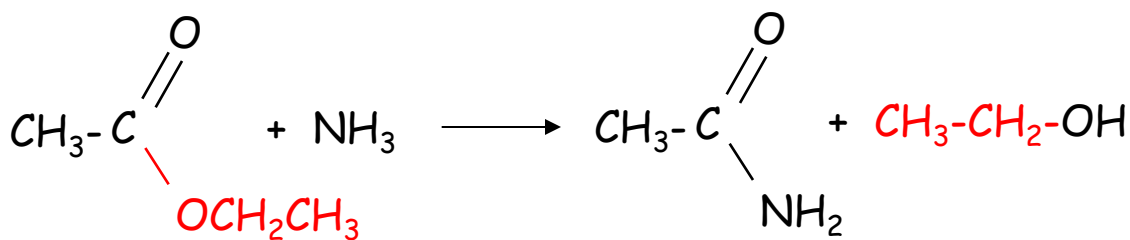
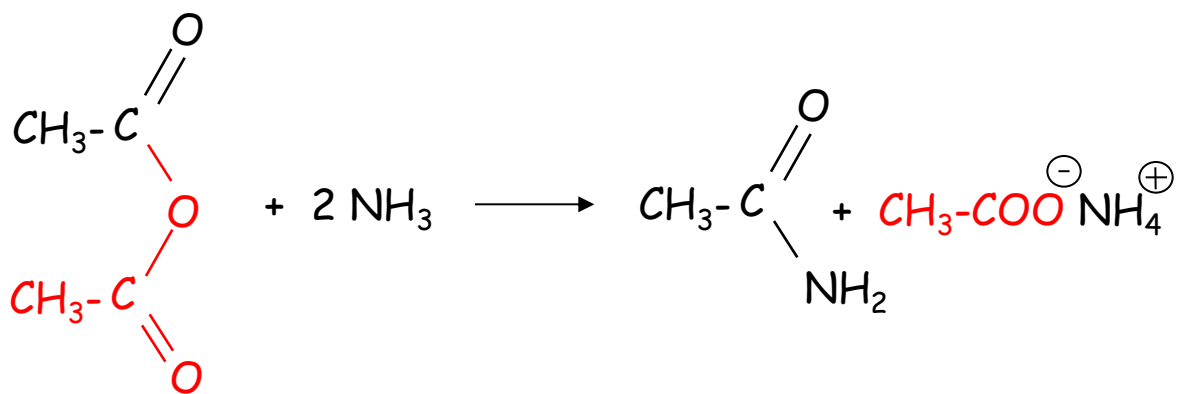
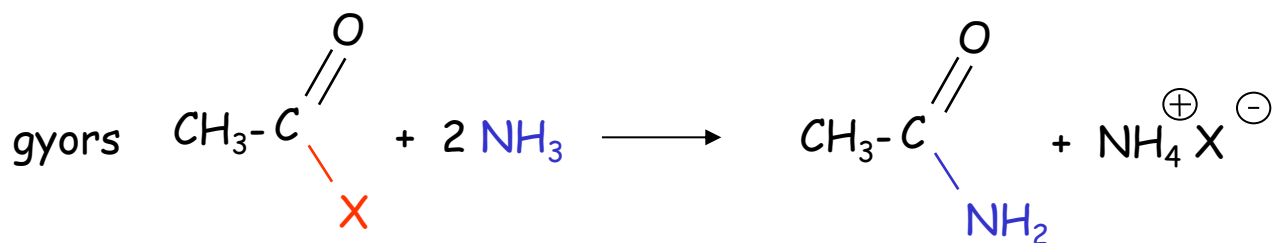
Nitrilek savas hidrolizise - mechanizmus



Összegzés: margarinsav előállítása

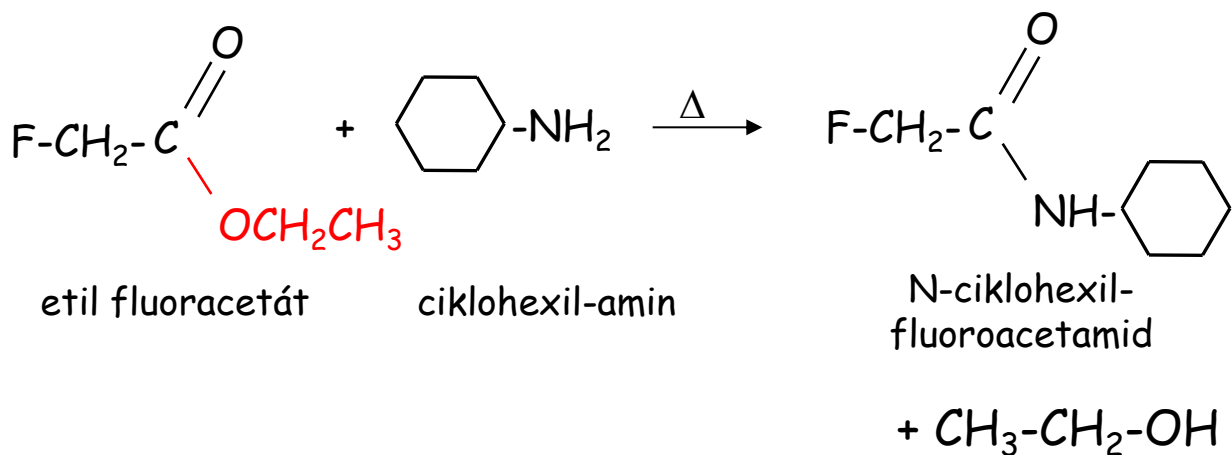


ii) Ammonolízis reakciótárs: NH_3

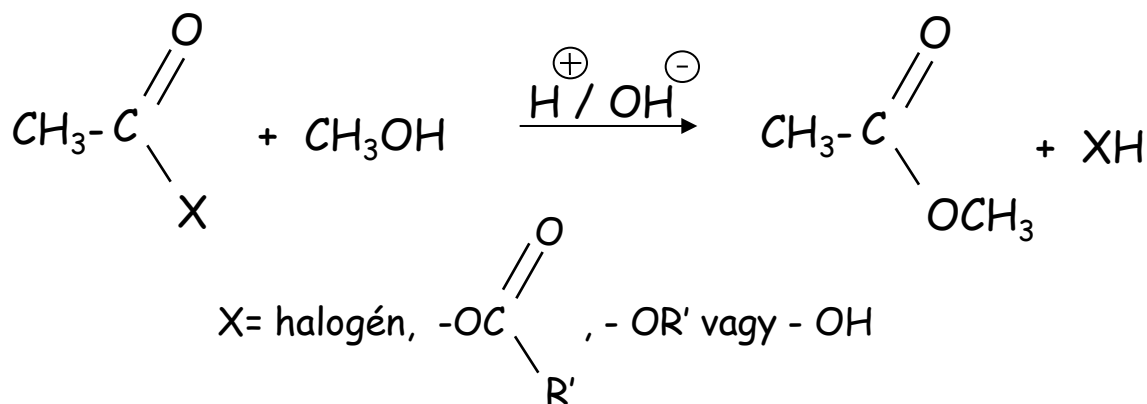


lassú

iii) Aminolízis reakciótárs: amin

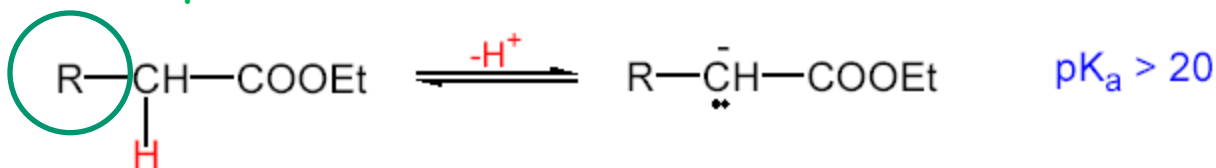


iv) Alkoholízis reakciótárs: R-OH

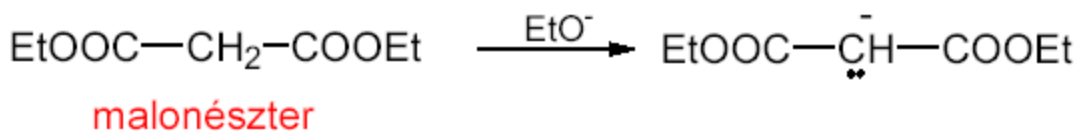
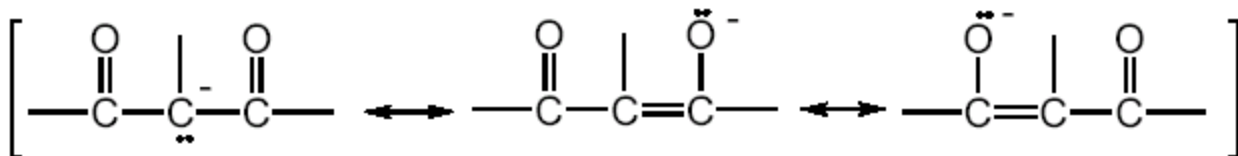
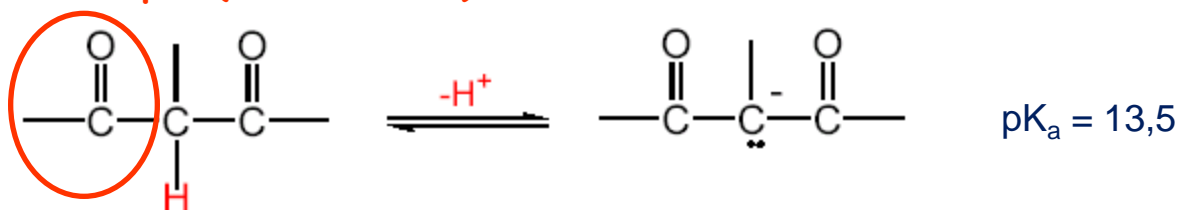


v) Claisen kondenzáció - bevezetés észterek savassága
(C-H)

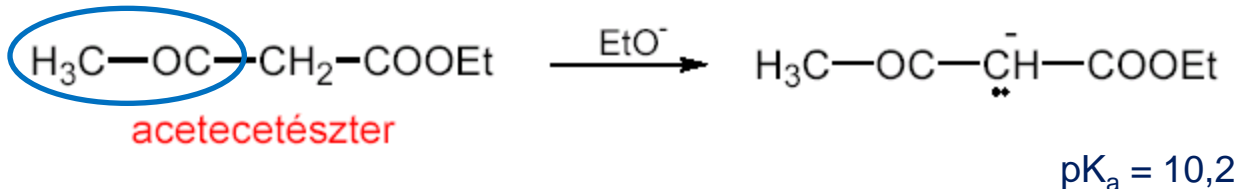
A. Típus



B. Típus (szimmetrikus)



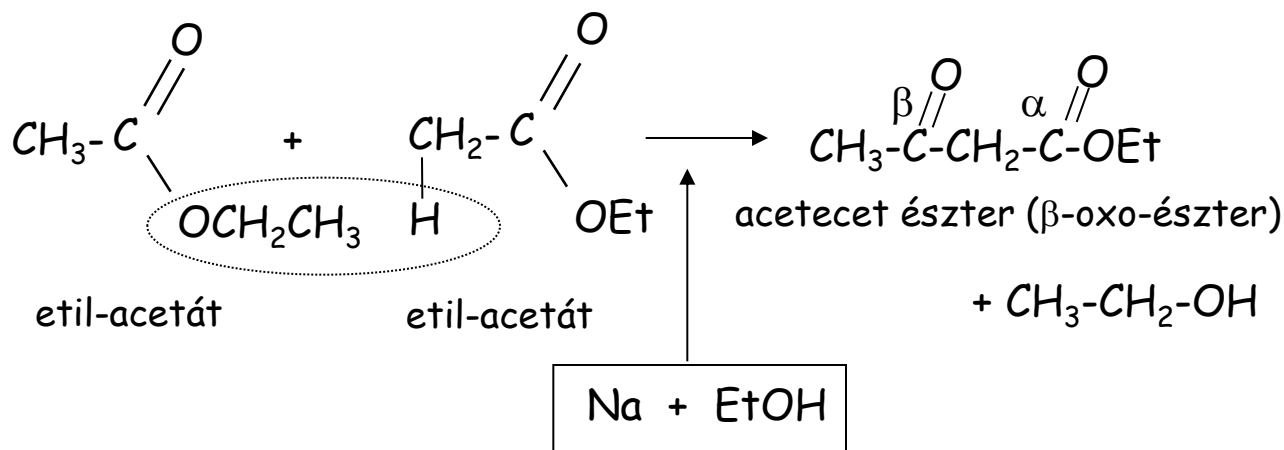
C. Típus (aszimmetrikus)



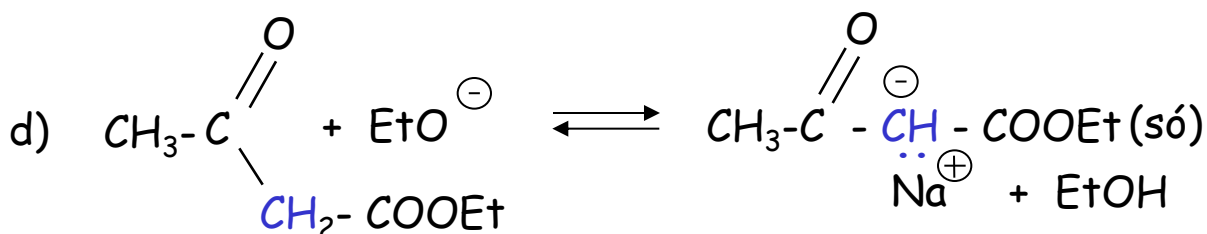
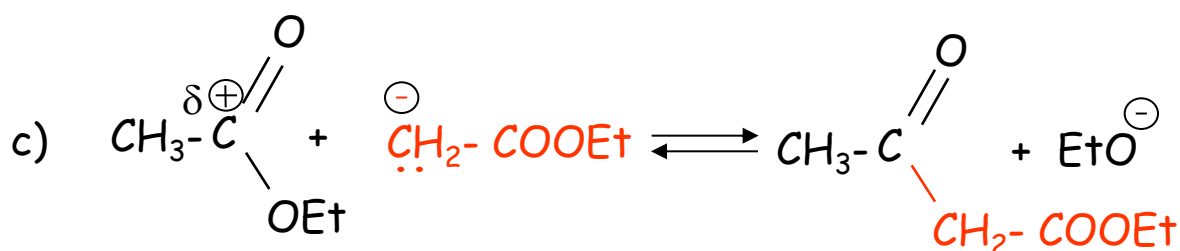
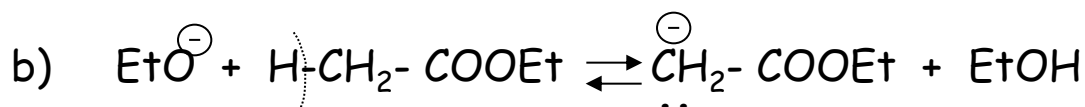
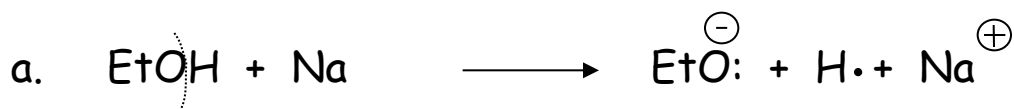
név	képlet	pK _a	delokalizáció
etilacetát	A $\text{CH}_3\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-OEt}$	>20	3 centrum
dietil malonát (malonészter)	B $\text{EtO-}\overset{\text{O}}{\parallel}\text{C}\text{-}\text{CH}_2\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-OEt}$	13,5	5 centrum
etil-acetoacetát (acetecet észter)	C $\text{CH}_3\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-}\text{CH}_2\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-OEt}$	10,2	5 centrum
etil(ciano-acetát) (ciánecet észter)	C $\text{N}\equiv\text{C}\text{-}\text{CH}_2\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-OEt}$	~12	5 centrum
etil(nitro-acetát)	C $\text{NO}_2\text{-}\text{CH}_2\text{-}\overset{\text{O}}{\parallel}\text{C}\text{-OEt}$	5,8	5 centrum

Claisen kondenzáció

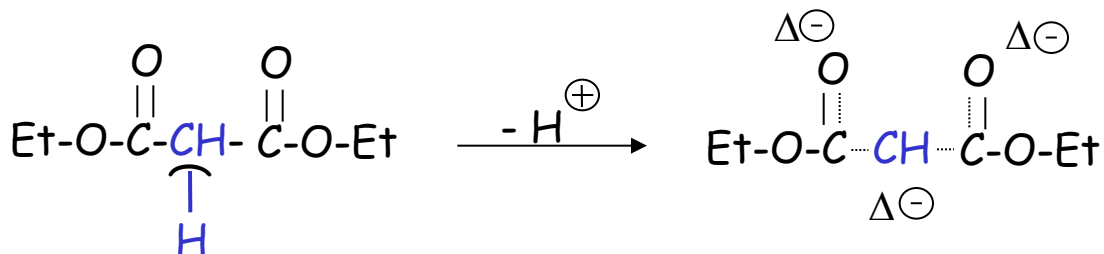
Ludwig Claisen, német (XIX-XX sz.)



Mechanizmus

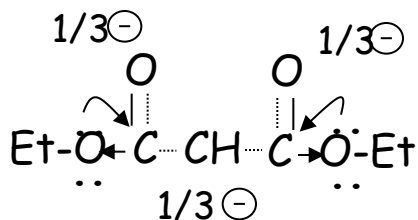
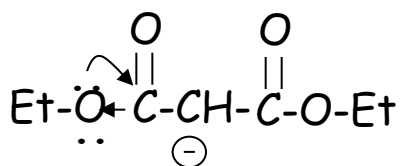


Dietil malonát, malonsavdiészter (pK = 13,5)



Mi a különbség oka?

$$\Delta^{\ominus} > 1/3^{\ominus}$$



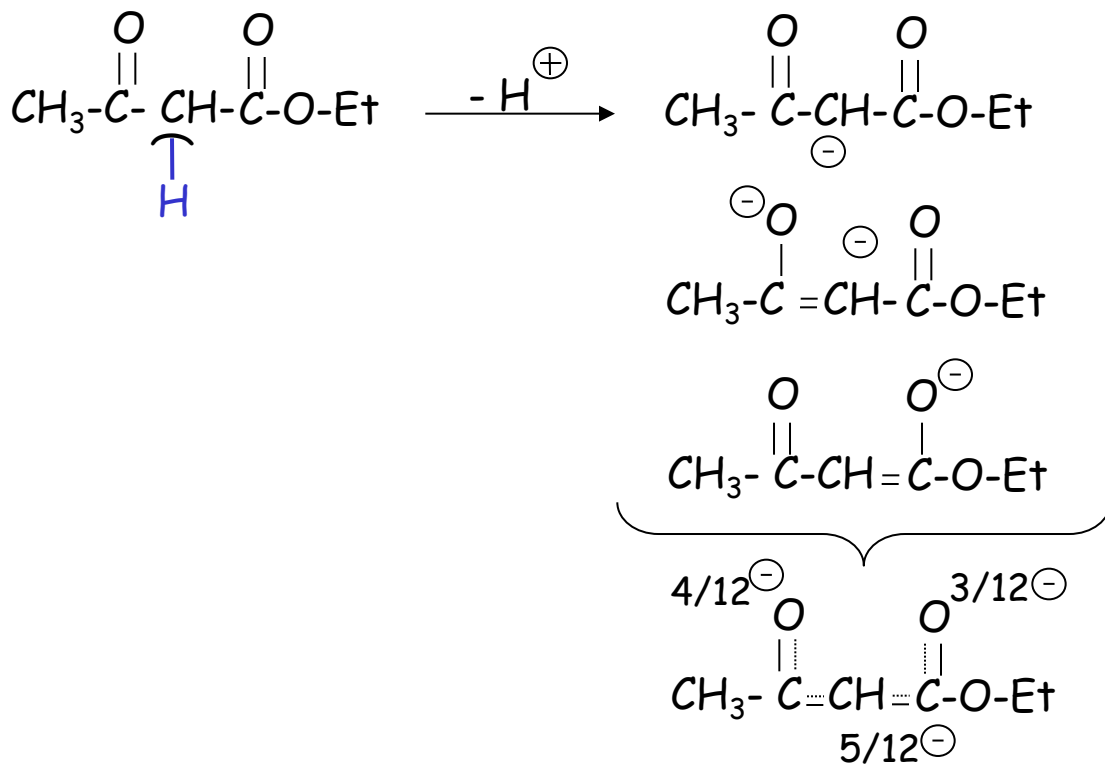
-I effektus

+ K effektus

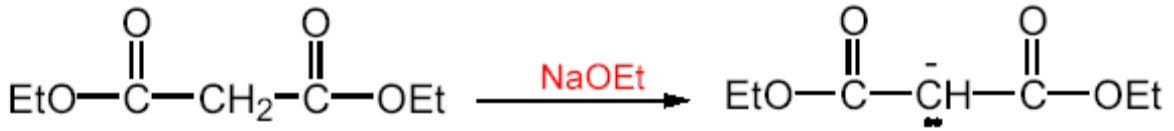
+ K > -I

1. Kevésbé delokalizálódik
2. Az α -C atom elektronmegtartó képessége csökkent

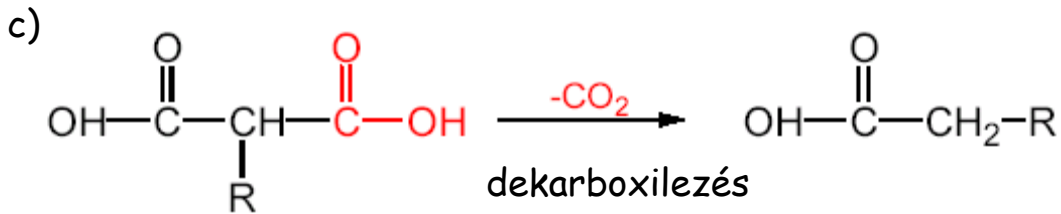
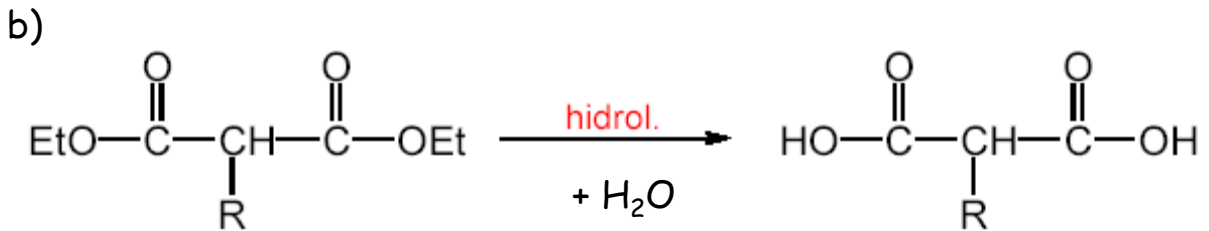
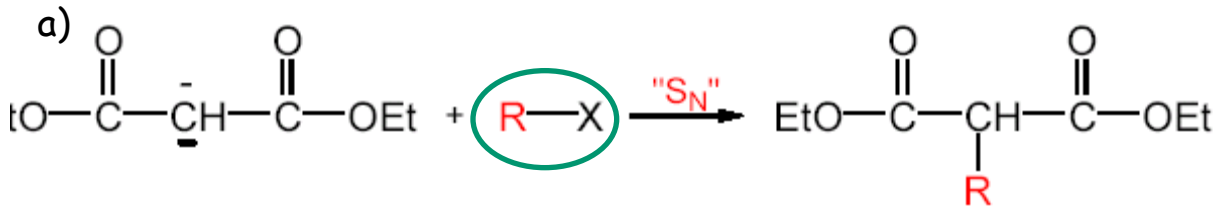
Acetecet észter (pK = 10,2)



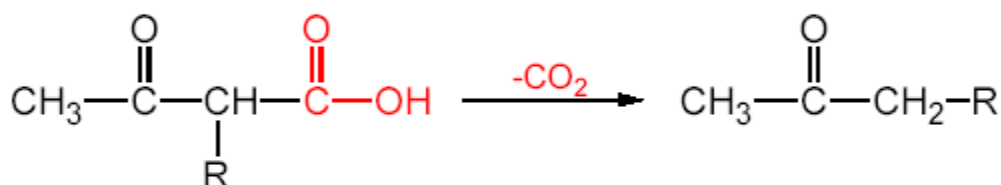
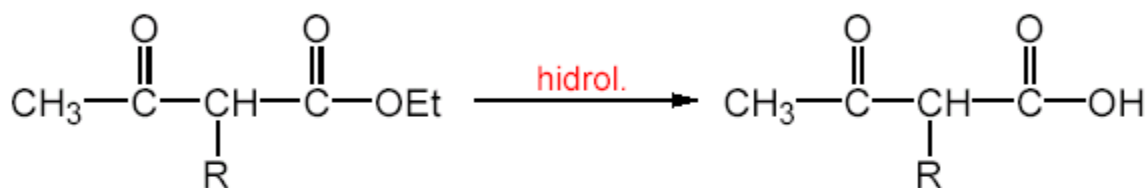
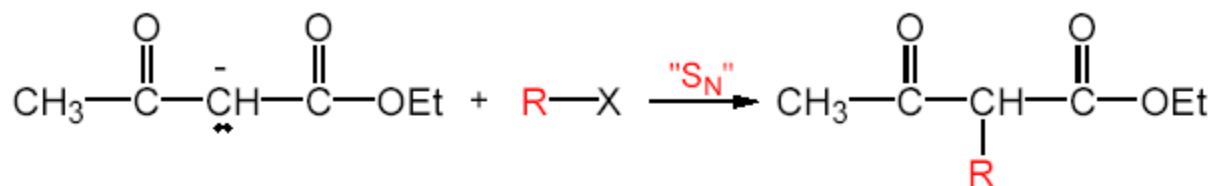
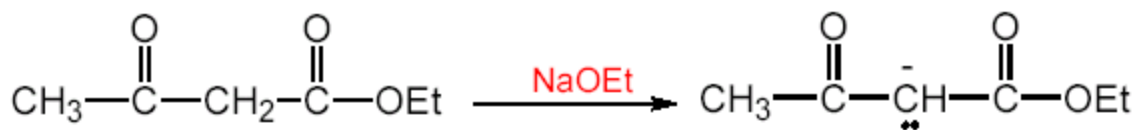
Malonészter szintézisek



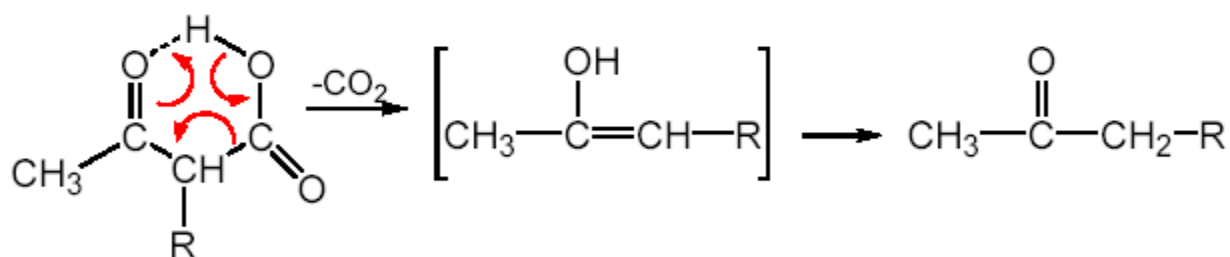
Reakció alkil halogeniddel



Acetecetészter szintézisek (lásd előző levezetés)



Dekarboxilezés



Áttekintés - összegzés

