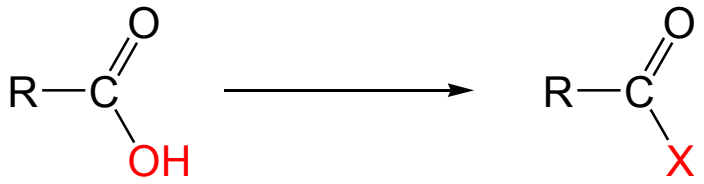
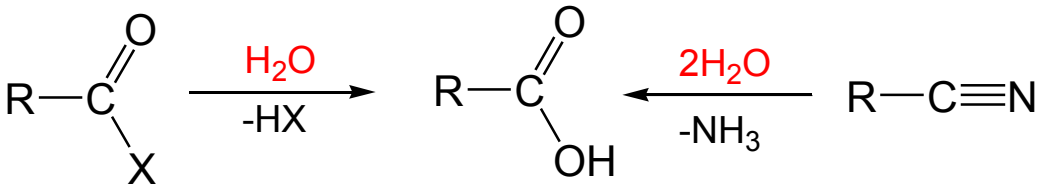
KARBONSAVSZÁRMAZÉKOK

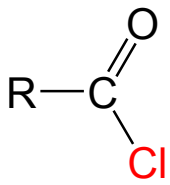
Levezetés



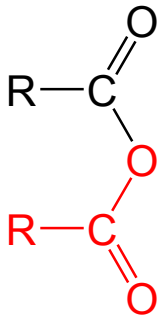
Kémiai rokonság



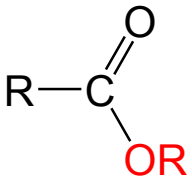
A karbonsavszármazékok típusai



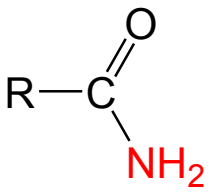
karbonsavklorid



karbonsavanhidrid



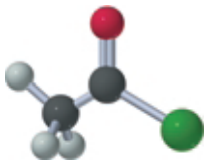
karbonsavészter



karbonsavamid

karbonsavnitril

Karbonsavkloridok



általános név: acil-klorid (karbonsav-klorid)

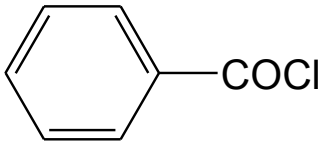
acilcsoportok

$H—CO^-$	$CH_3—CO^-$	$CH_3CH_2—CO^-$	$CH_3CH_2CH_2—CO^-$
formil	acetil	propionil	butiril

Példák

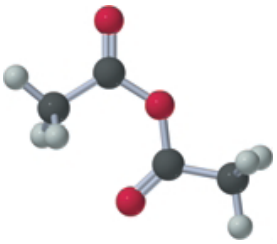
CH_3COCl
acetil-klorid
(ecetsav-klorid)

Cl-CO-CO-Cl
oxalil-klorid
(oxálsav-klorid)



benzoil-klorid
(benzoesav-klorid)

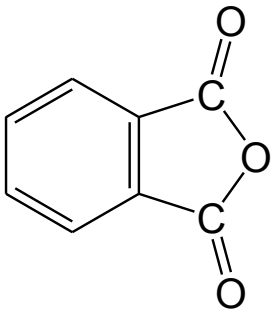
Karbonsavanhidridek



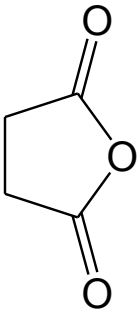
CH_3-CO-O-CO-CH_3
ecetsav-anhidrid

CH_3-CO-O-CO-C_2H_5
ecetsav-propionsav-anhidrid

gyűrűs anhidridek

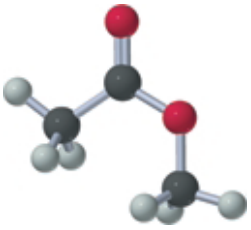


ftálsav-anhidrid



borostyánkősav-anhidrid

Karbonsavészterek

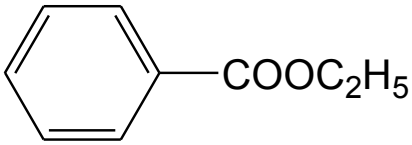


általános név: alkil-alkanoát

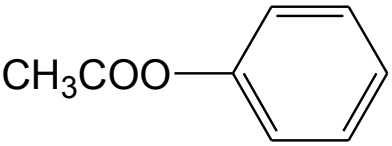
savmaradékok:	H-COO-	formiát
	CH_3-COO-	acetát
	CH_3CH_2COO-	propionát
	$CH_3CH_2CH_2COO$-	butirát

$HCOOC_2H_5$
etil-formiát

CH_3COOCH_3
metil-acetát

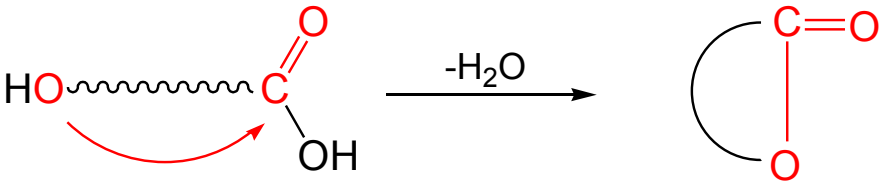


etil-benzoát



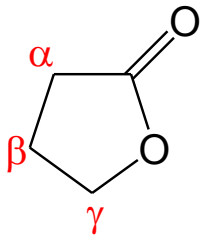
fenil-acetát

laktonok (gyűrűs észterek)

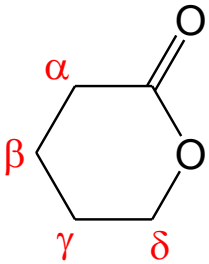


hidroxi-karbonsav

lakton

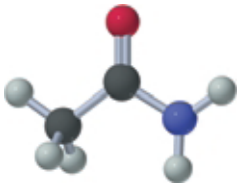


γ-butirolakton



δ-valerolakton

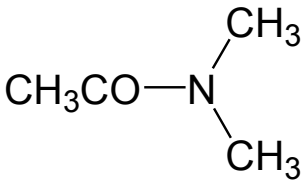
Karbonsavamidok



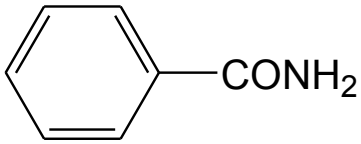
$HCONH_2$
formamid
(hangyasav-amid)

CH_3CONH_2
acetamid
(ecetsav-amid)

$CH_3CH_2CONH_2$
propionamid
(propionsav-amid)

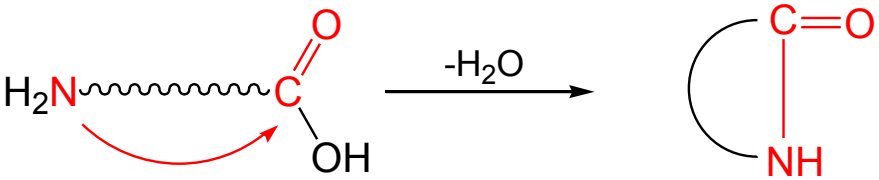


N,N-dimetilacetamid



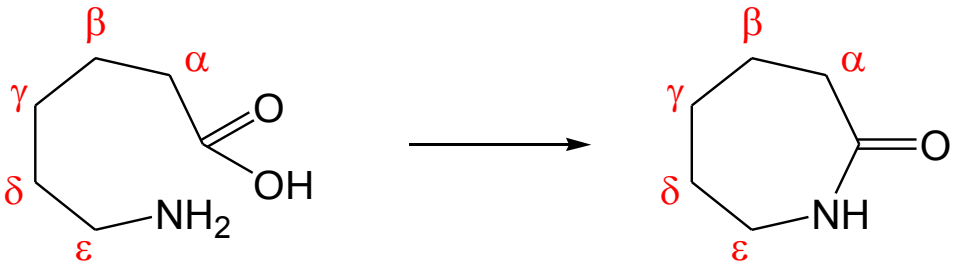
benzamid

laktámok (gyűrűs amidok)



amino-karbonsav

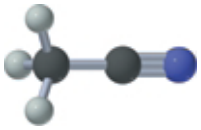
laktám



ε-amino-kapronsav

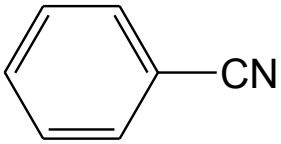
ε-kaprolaktám

Karbonsavnitrilek



CH_3CN
acetonitril
(ecetsav-nitril)

CH_3CH_2CN
propionitril
(propionsav-nitril)

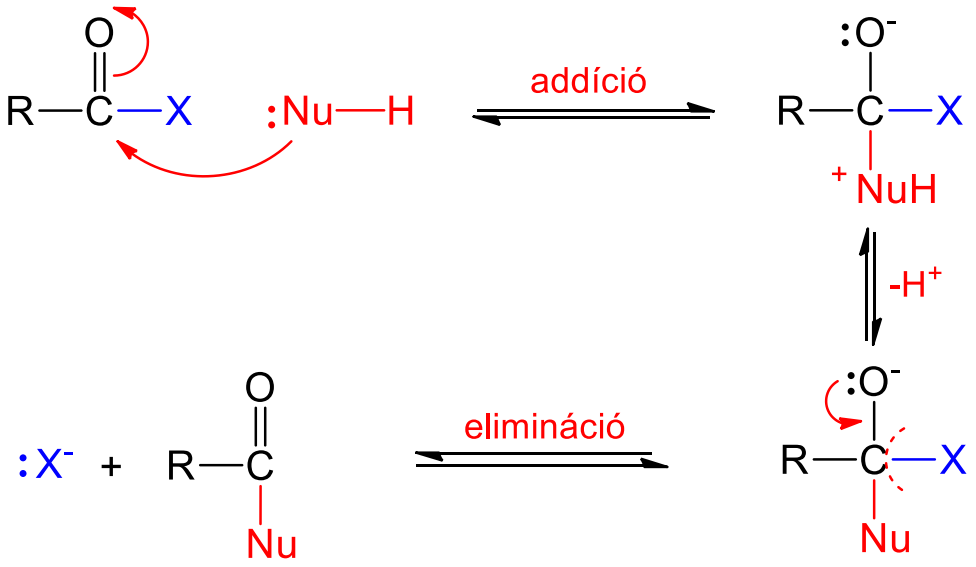


benzonitril
(benzoesav-nitril)

A KARBONSAVSZÁRMAZÉKOK REAKTIVITÁSA

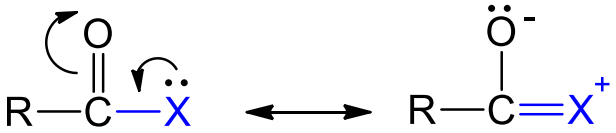
Szubsztitúció a karbonil-szénatomon

Mechanizmus



Reaktivitás

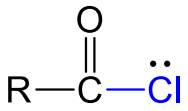
a) konjugáció (a reaktivitást csökkenti)



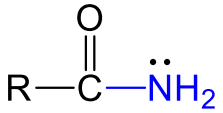
b) X^- távozó csoport (bázicitás) savi erősség

$Cl^- > Q\text{-}COO^- > QO^- > NH_2^-$ $HCl > Q\text{-}COOH > QOH > NH_3$

pK_s	-7	5	16	35



karbonsav-klorid



karbonsav-amid

gyenge elektron delokalizáció

Cl^--ion jó távozó csoport

⇓

reaktív savszármazék

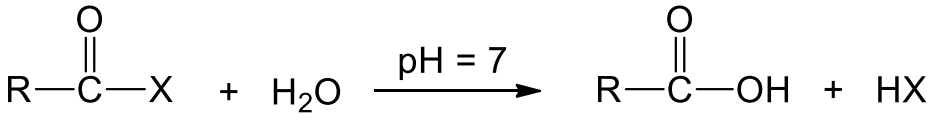
hatékony elektron delokalizáció

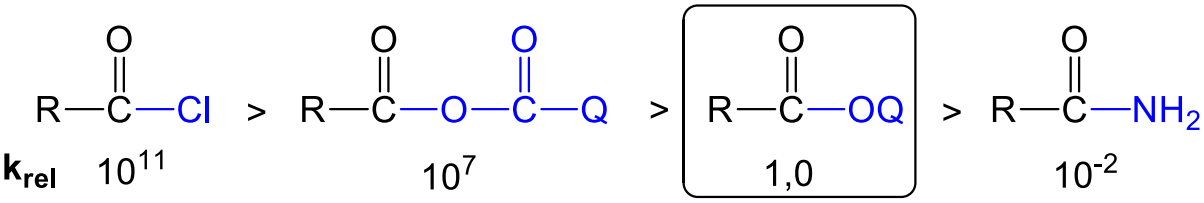
NH_2^--ion rossz távozó csoport

⇓

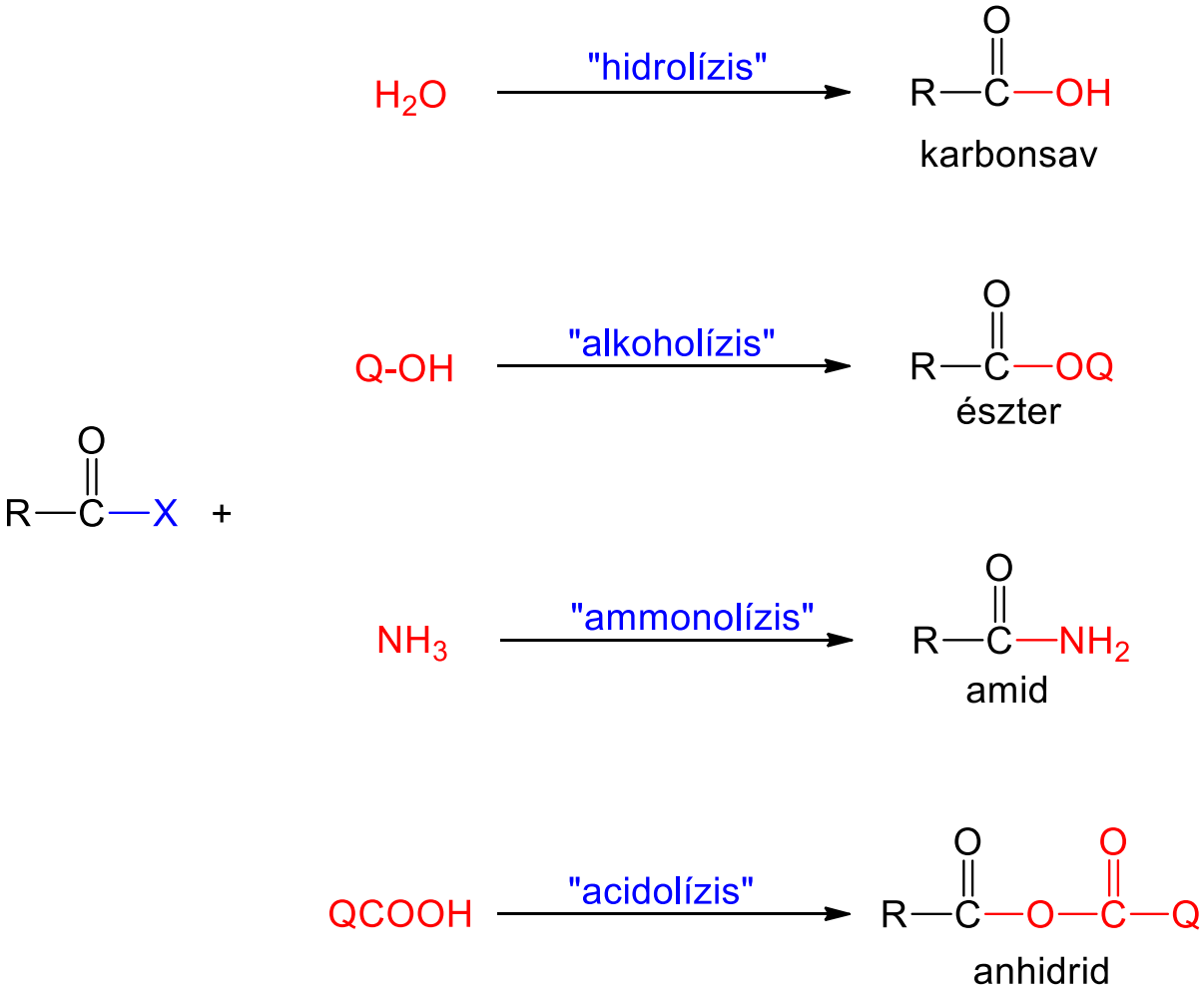
nem reaktív savszármazék

A hidrolízis reaktivitási sorrendje



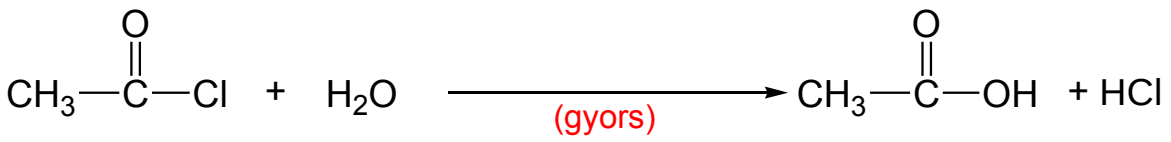


Reakciótípusok

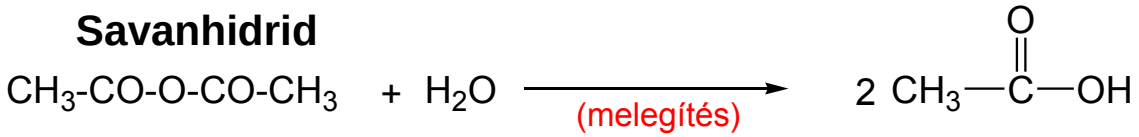


A karbonsavszármazékok hidrolízise

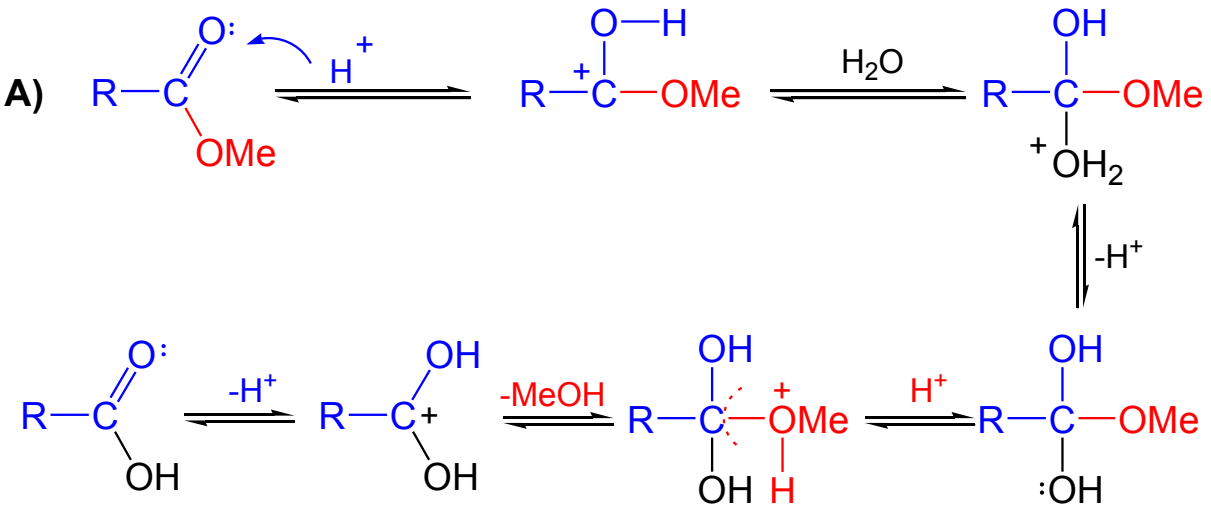
Savklorid



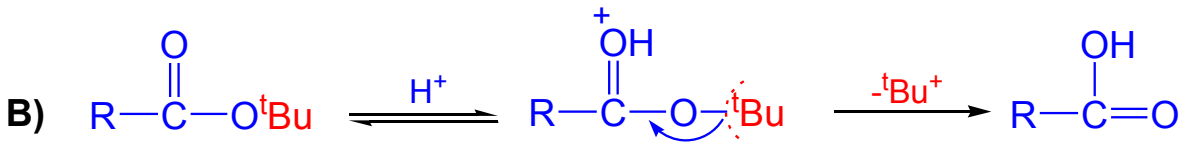
Savanhidrid



Az észterek savas hidrolízise

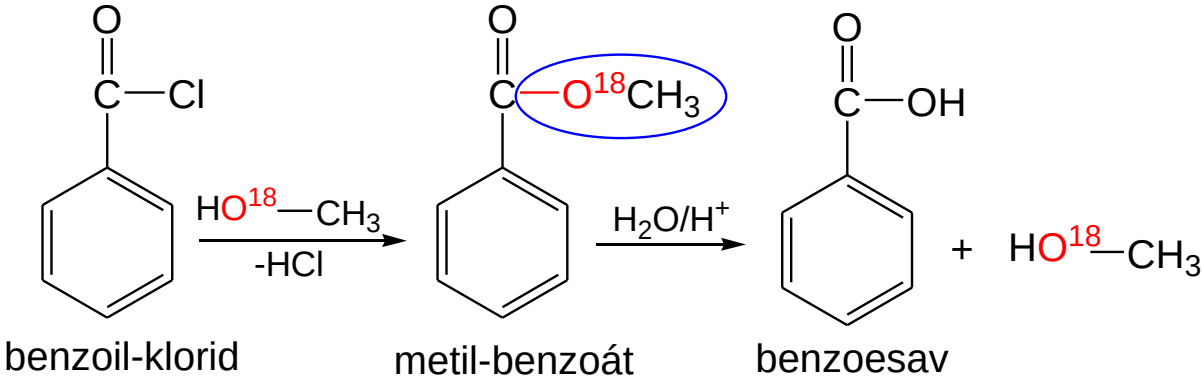


primer észteresítő alkohol ⟶ acil-O hasadás

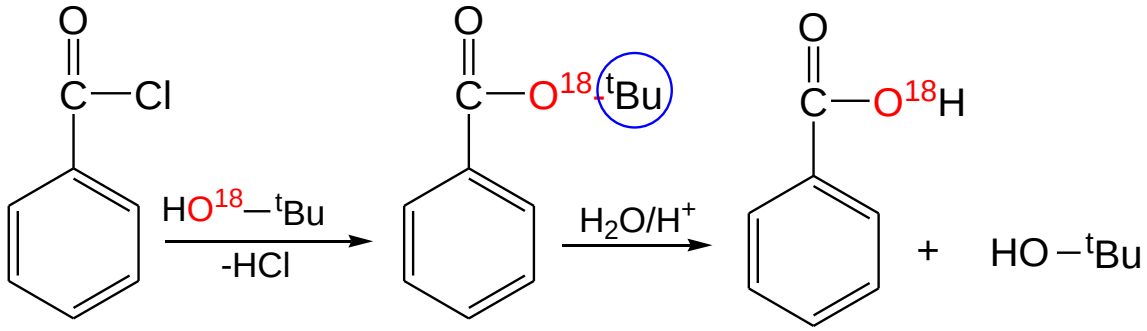


tercier észteresítő alkohol ⟶ alkil-O hasadás

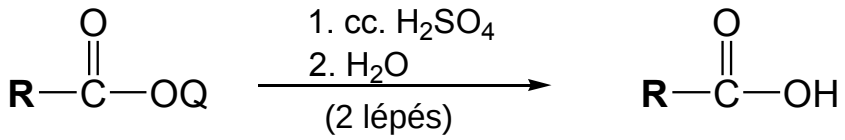
acil-O hasadás



alkil-O hasadás

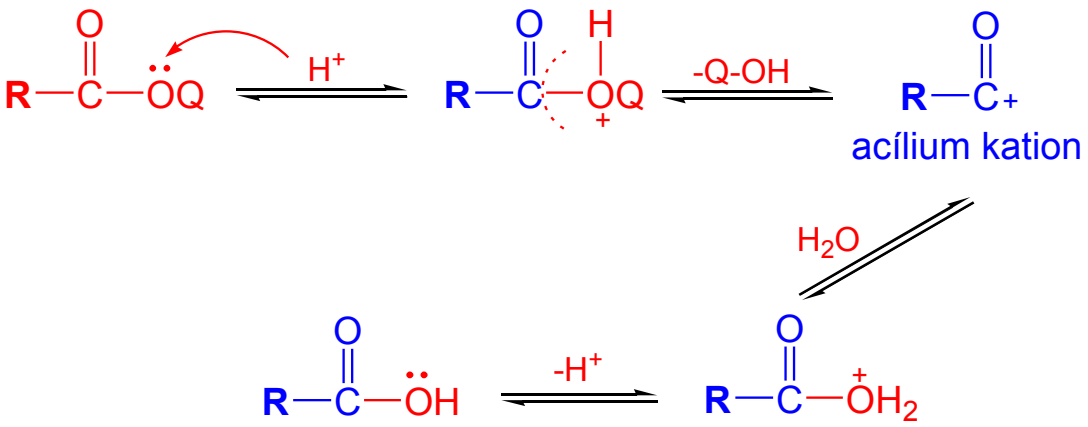


Árnyékolt karbonilcsoportot tartalmazó észterek hidrolízise

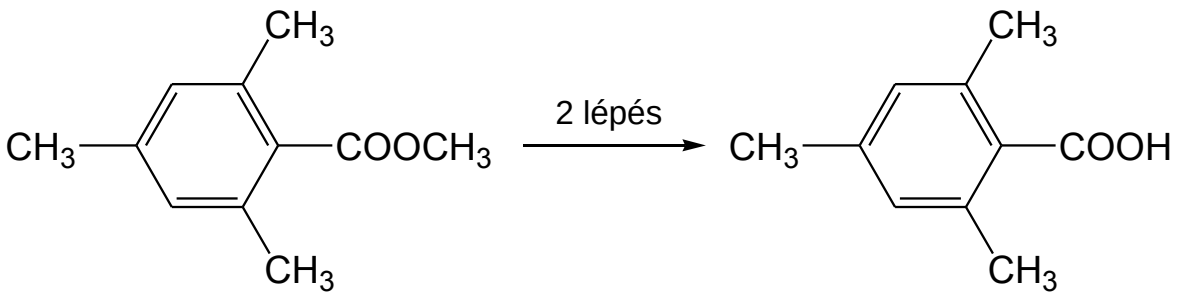


(**R**: nagy térigényű csoport)

Mechanizmus

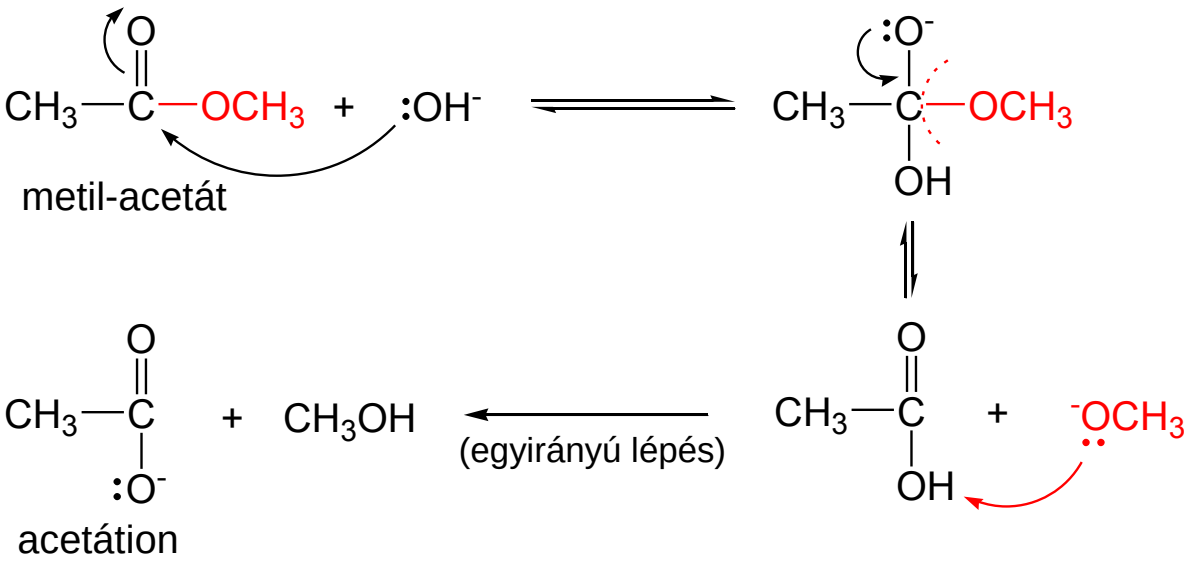


Példa

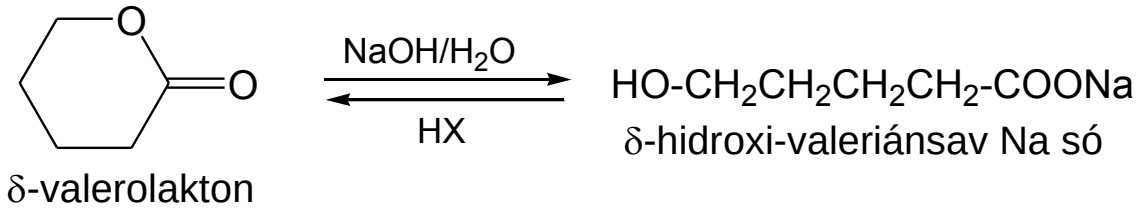


metil-(2,4,6-trimetil-benzoát) 2,4,6-trimetilbenzoesav

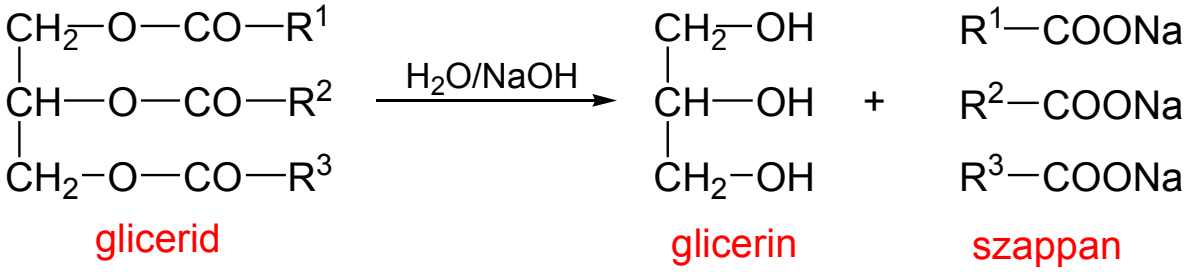
Az észterek lúgos hidrolízise (elszappanosítás)



Laktonok hidrolízise

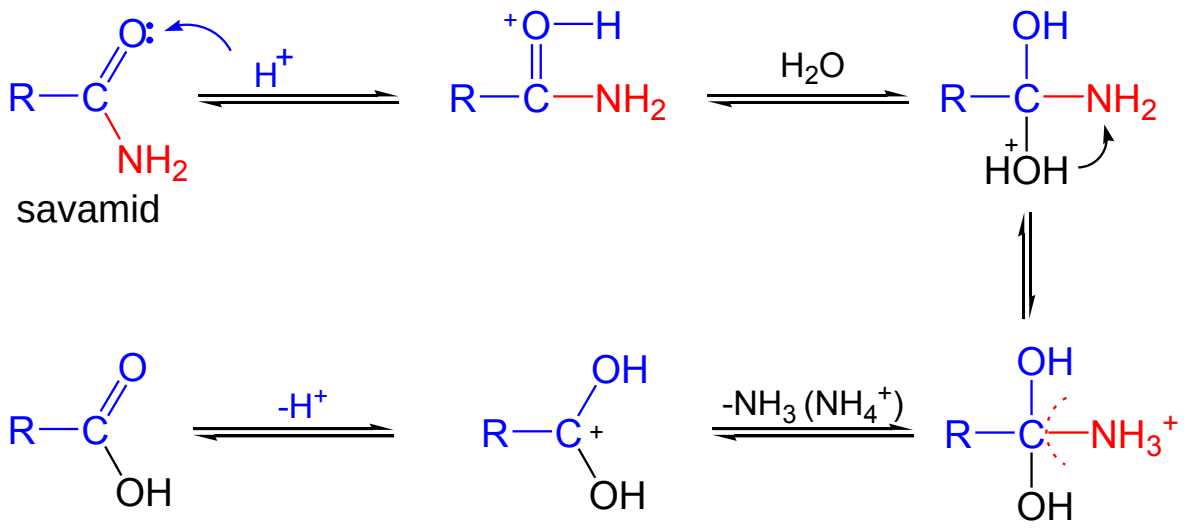


Gliceridek hidrolízise

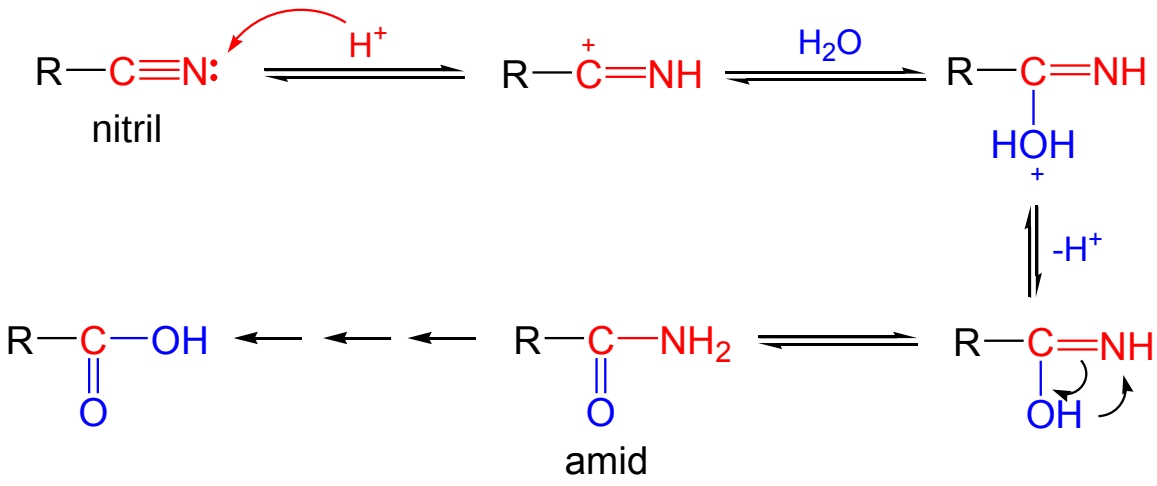


$C_{13}H_{27}COOH$	mirisztinsav
$C_{15}H_{31}COOH$	palmitinsav
$C_{17}H_{35}COOH$	sztearinsav
C_8H_{17}-CH=CH-$C_7H_{15}COOH$	olajsav

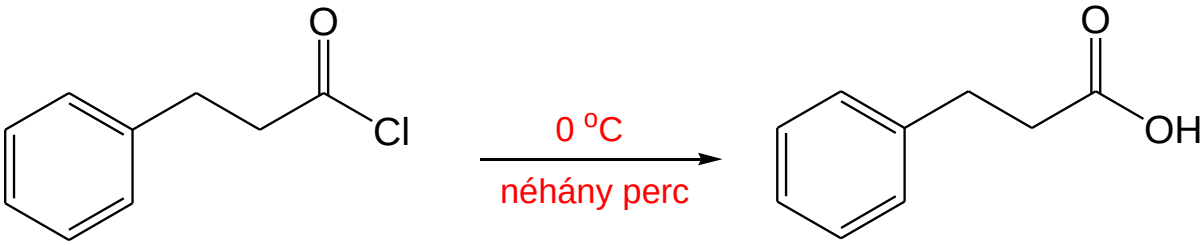
Az amidok savas hidrolízise



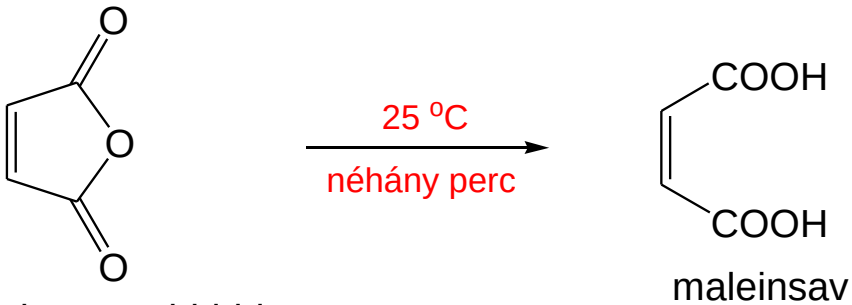
A nitrilek savas hidrolízise



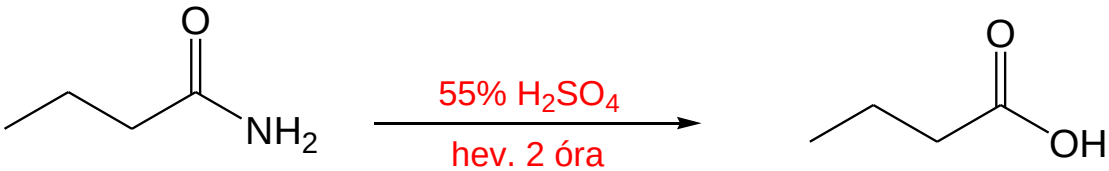
Példák karbonsavszármazékok hidrolízisére



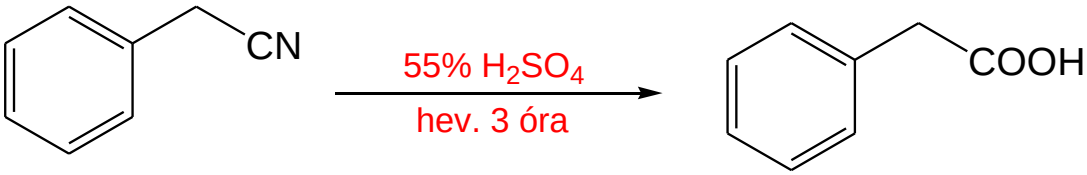
3-fenil-propionil-klorid 3-fenilpropionsav



maleinsav-anhidrid maleinsav

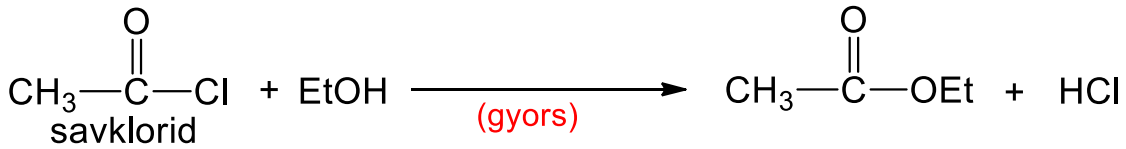


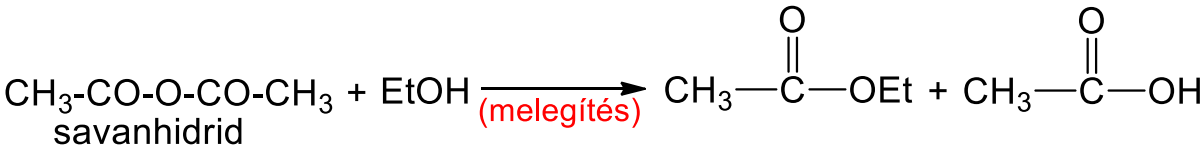
butánsav-amid vajsav (butánsav)

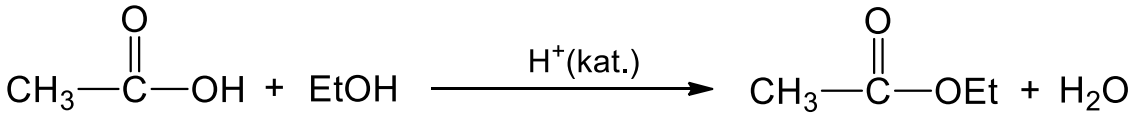


fenil-acetonitril fenilecetsav

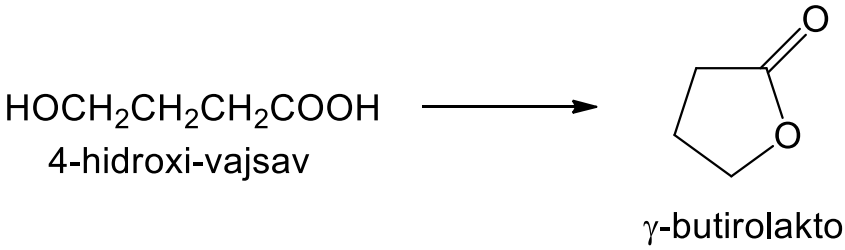
A karbonsavszármazékok alkoholízise (észterek előállítása)

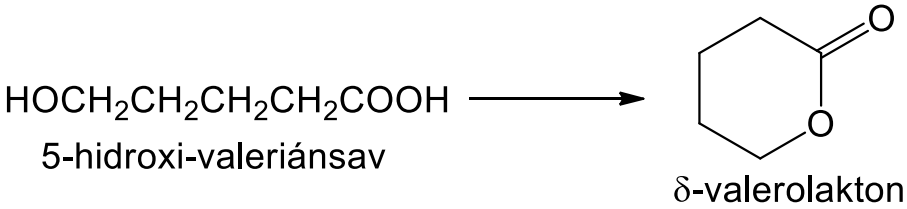




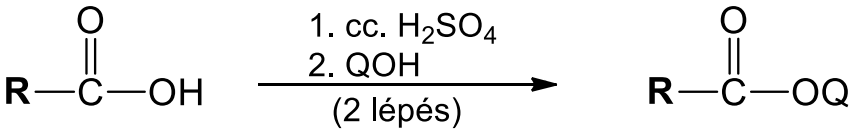


karbonsav (ld. alkoholok acilezése, közvetlen észteresítés)



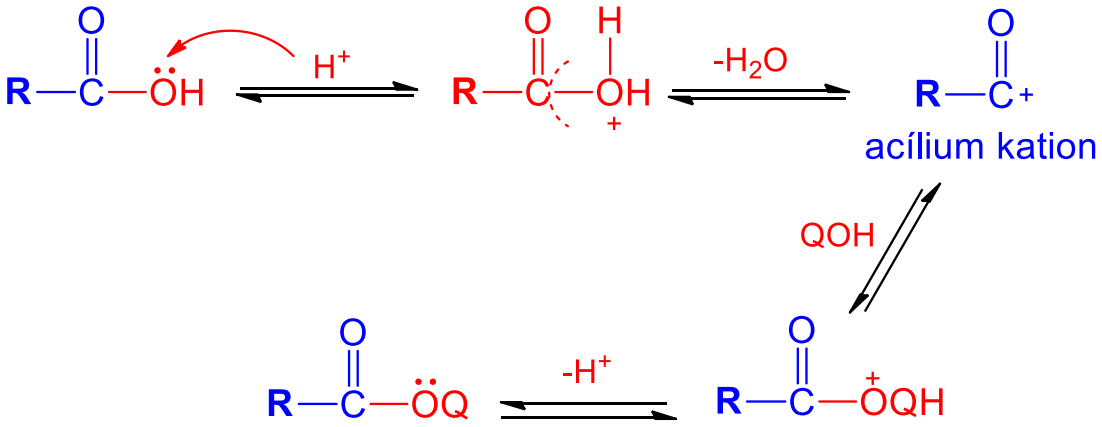


Árnyékolt karbonilcsoportot tartalmazó karbonsavak alkoholízise

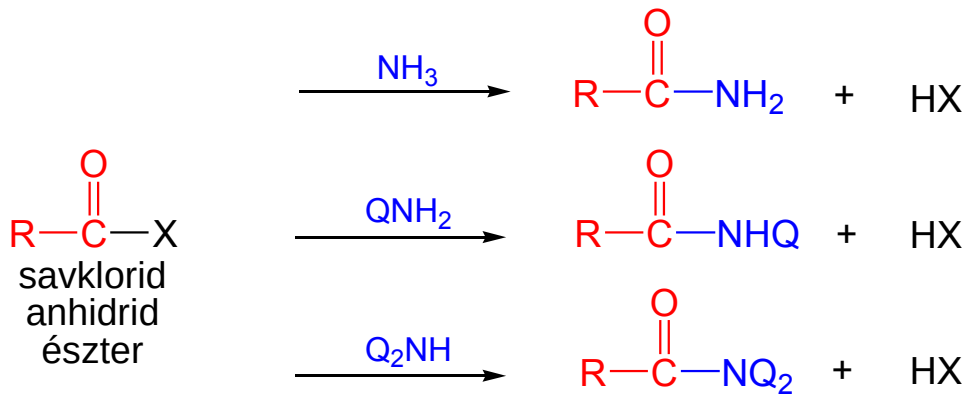


(**R**: nagy térigényű csoport)

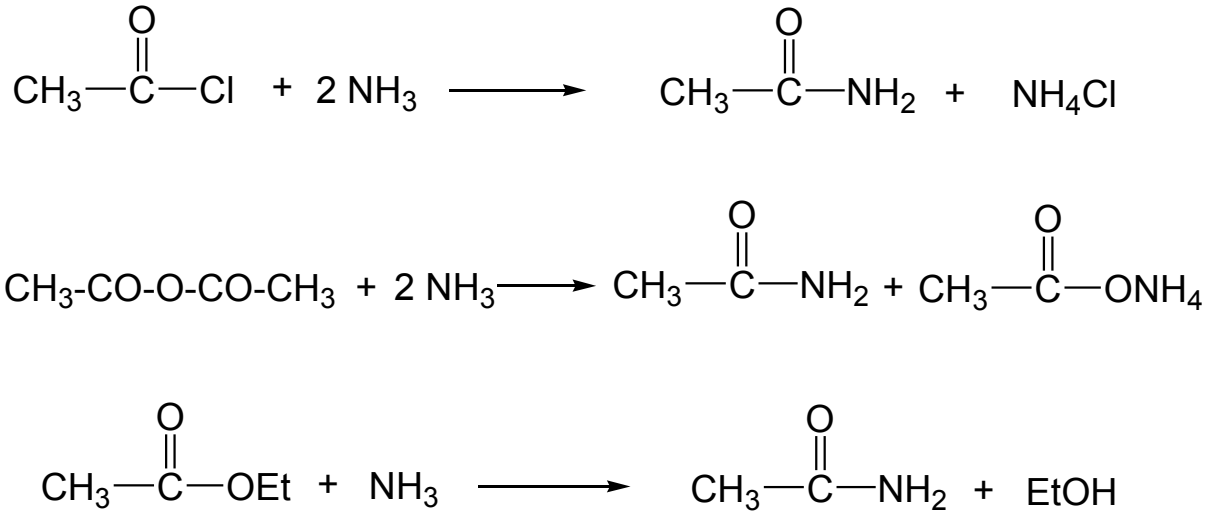
Mechanizmus



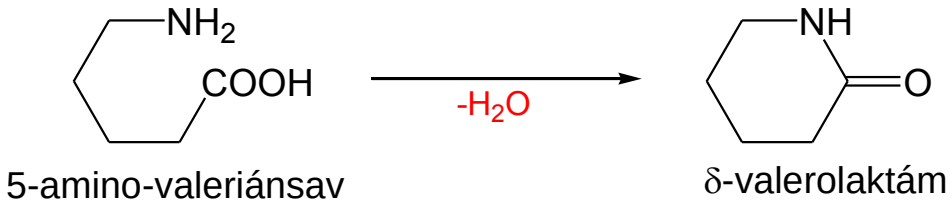
A karbonsavszármazékok ammonolízise (savamidok előállítása)



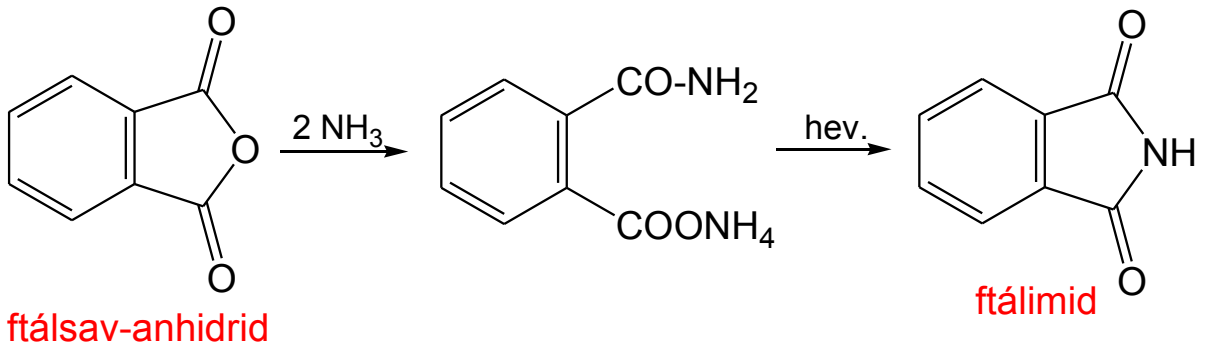
Példák



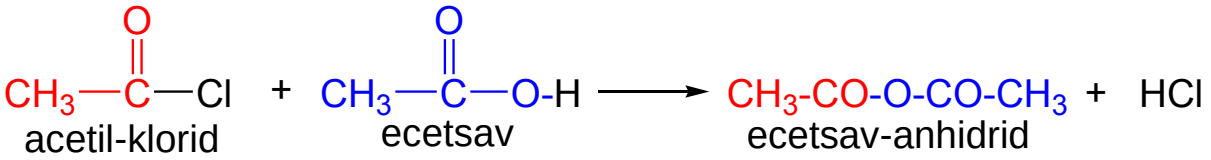
Laktámok



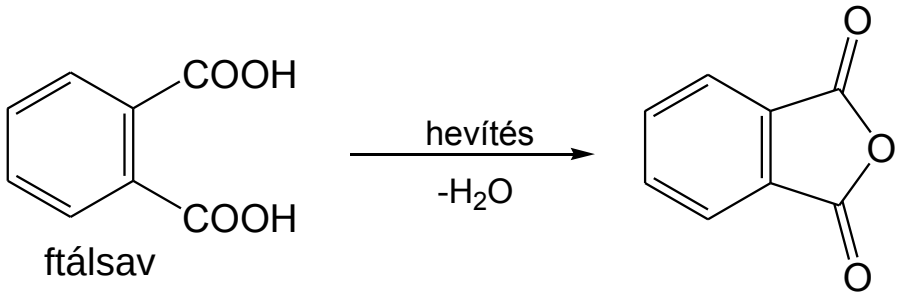
Gyűrűs anhidridek reakciója ammóniával

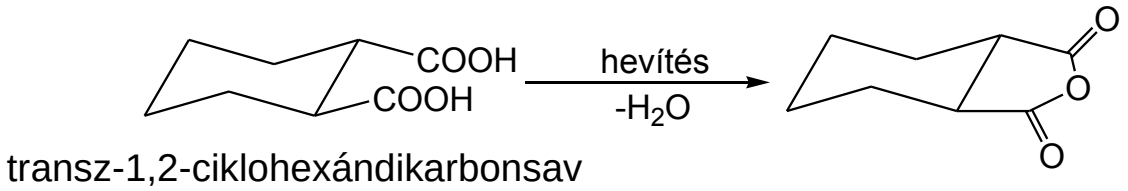


Savkloridok reakciója karbonsavakkal (acidolízis; savanhidridek előállítása)



Dikarbonsavak átalakítása gyűrűs anhidridekké





transz-1,2-ciklohexándikarbonsav

A karbonsavszármazékok redukciója

Katalitikus hidrogénezés

$$R{-}CO{-}Cl \xrightarrow{H_2/kat.} R{-}CH_2OH$$

primer alkohol

$$R{-}C{\equiv}N \xrightarrow{H_2/kat.} R{-}CH_2NH_2$$

primer amin

Redukció $LiAlH_4$-del

$$\left.\begin{array}{l} R{-}CO{-}Cl \\ R{-}CO{-}O{-}CO{-}R \\ R{-}CO{-}OQ \\ R{-}CO{-}OH \end{array}\right\} \xrightarrow[2.\ H_2O/H^+]{1.\ LiAlH_4\ (Et_2O)} R{-}CH_2OH$$

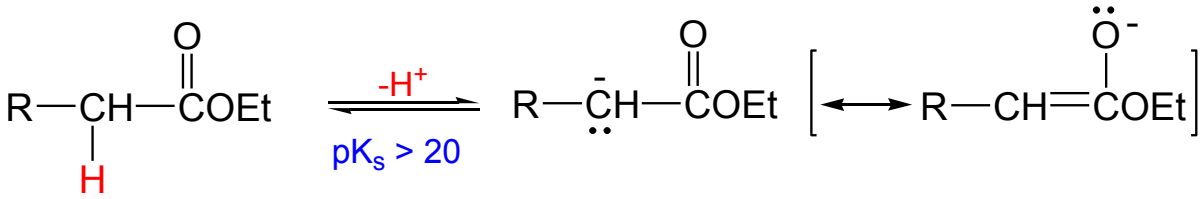
primer alkohol

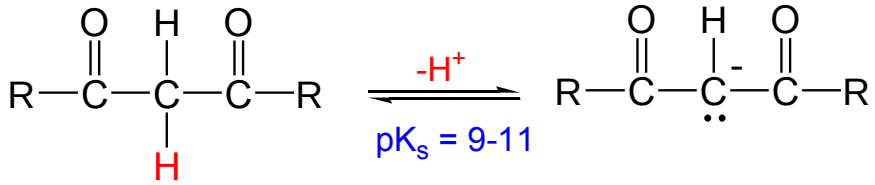
$$\left.\begin{array}{l} R{-}CO{-}NH_2 \\ R{-}C{\equiv}N \end{array}\right\} \xrightarrow[2.\ H_2O/H^+\ \ 3.\ OH^-]{1.\ LiAlH_4} R{-}CH_2NH_2$$

primer amin

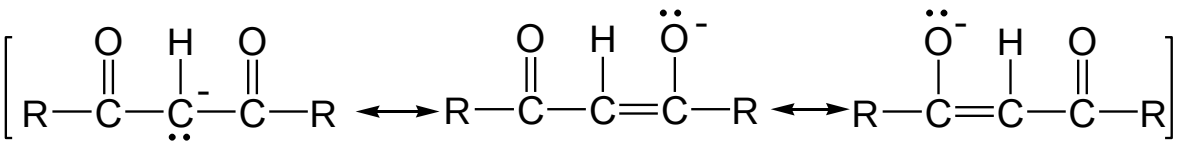
Észterek α-szénatomján lejátszódó reakciók

Az észterek C-H savi erőssége

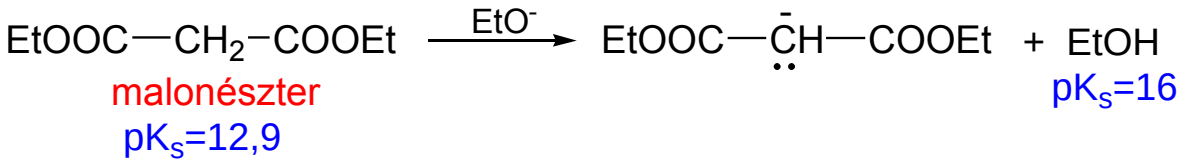


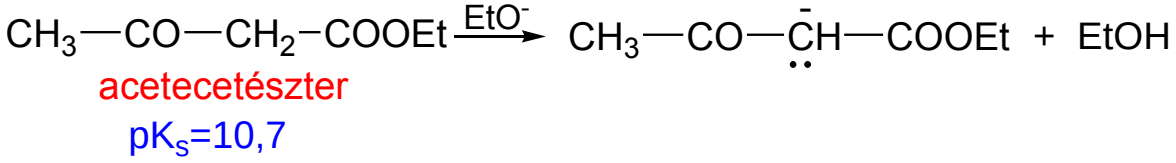


1,3-dioxovegyület

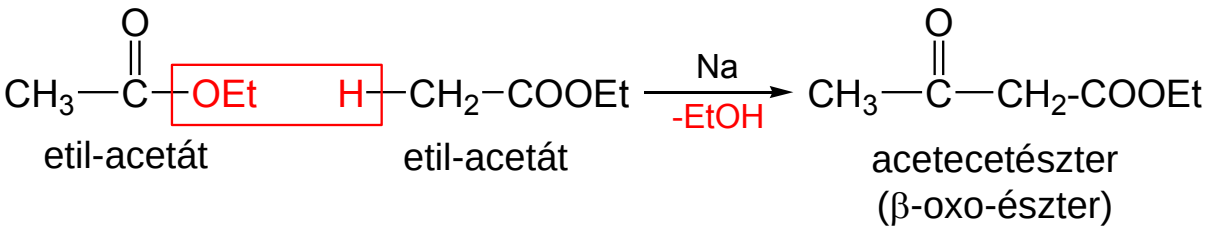


határszerkezetek

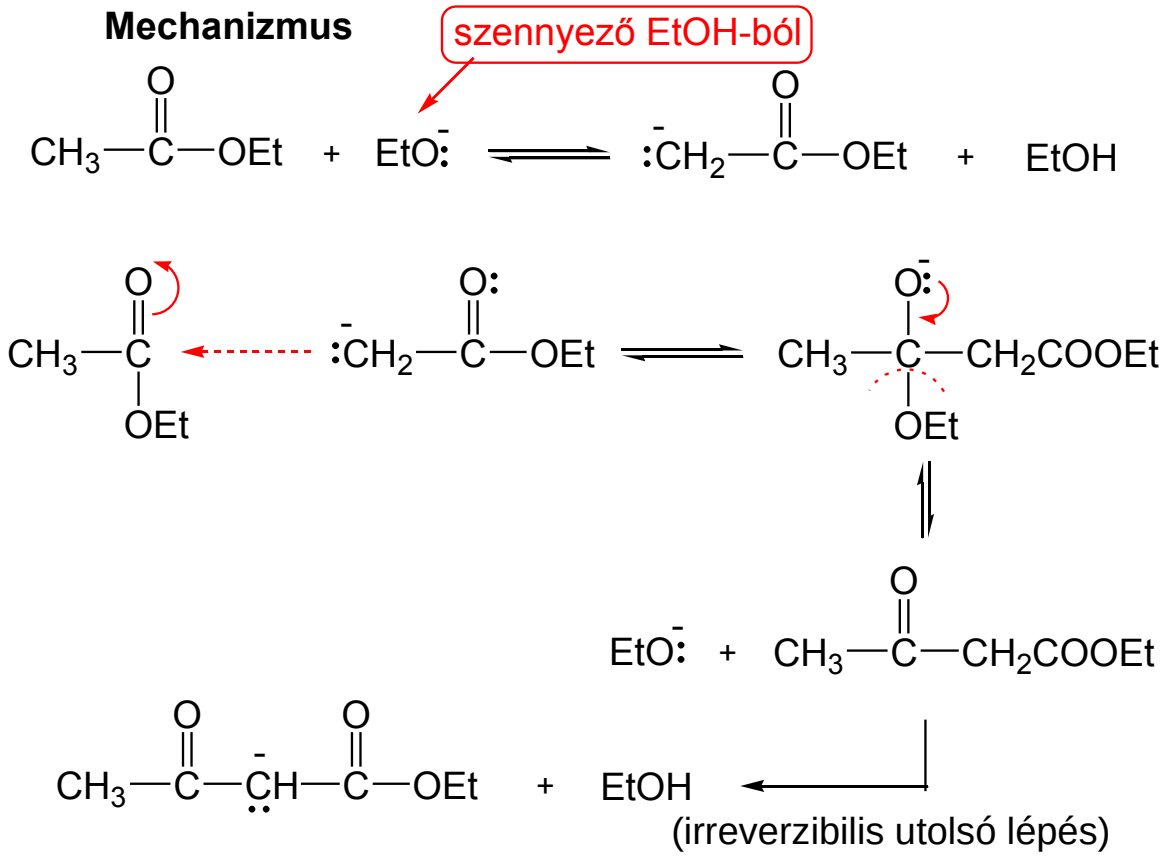




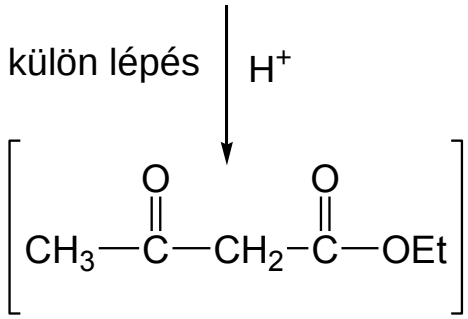
Claisen-kondenzáció



Mechanizmus

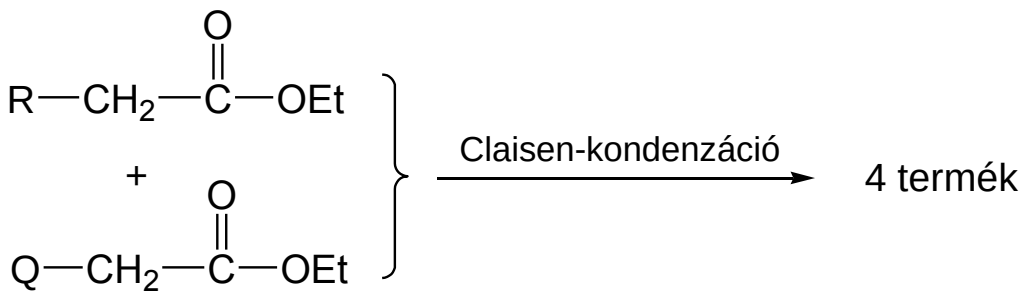


(irreverzibilis utolsó lépés)

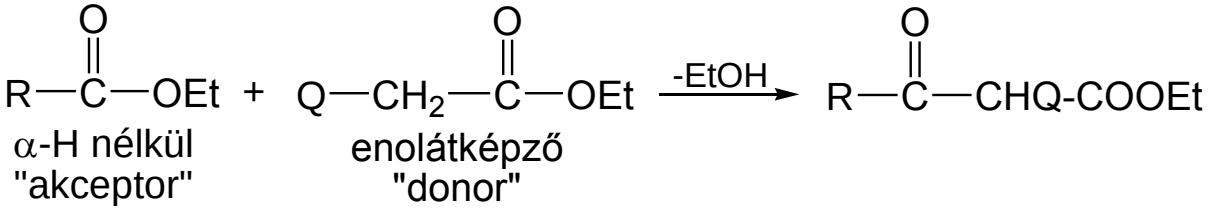


Ludwig Claisen (1851–1930) was born in Germany and received a Ph.D. from the University of Bonn, studying under Kekulé. He was a professor of chemistry at the University of Bonn, Owens College (Manchester, England), the University of Munich, the University of Aachen, the University of Kiel, and the University of Berlin.

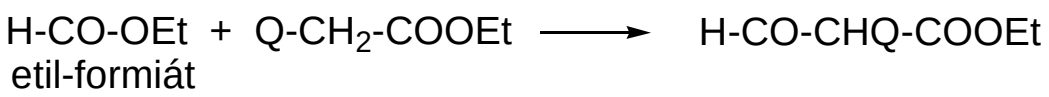
Vegyes Claisen-kondenzációk

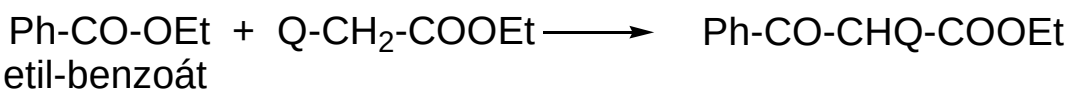


Szintetikus alkalmazás

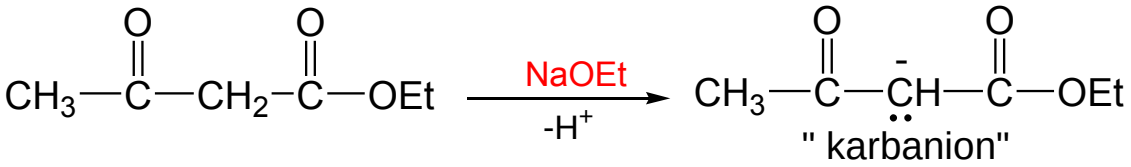


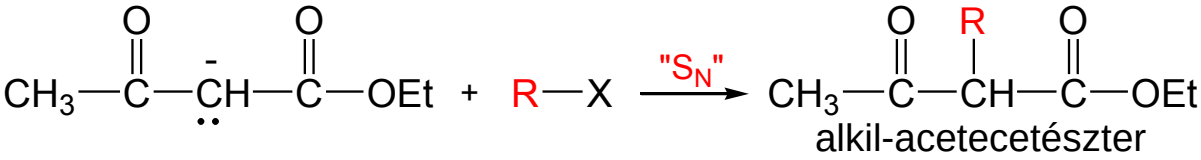
Példák

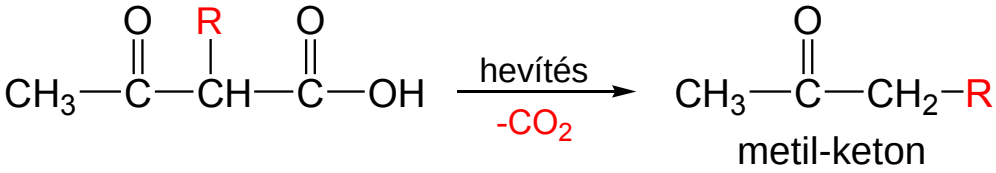




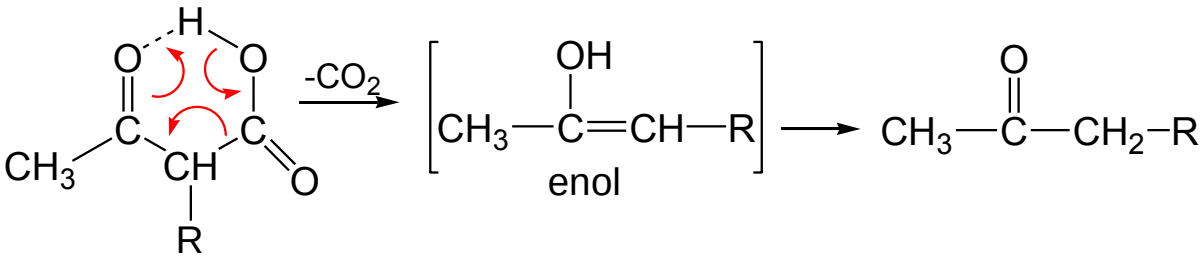
Acetecetészter szintézisek



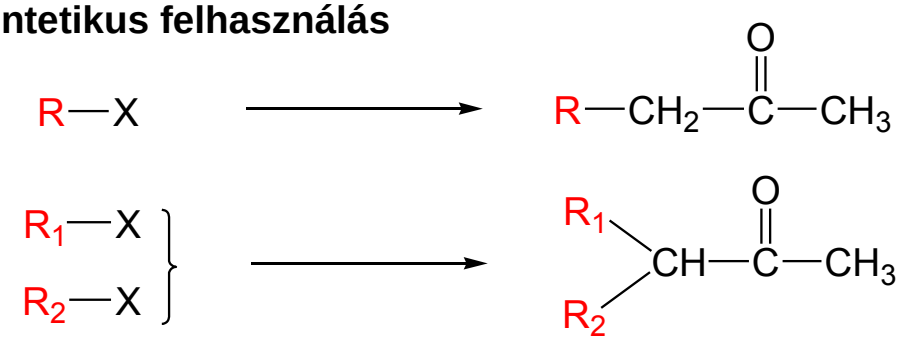




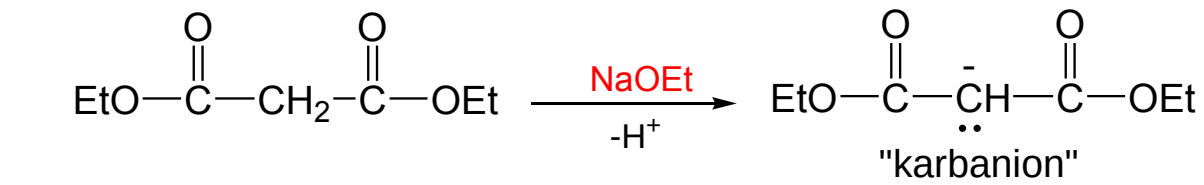
Dekarboxilezés (miért megy könnyen?)

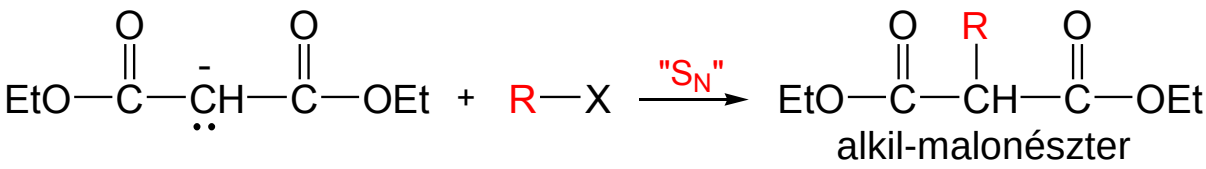


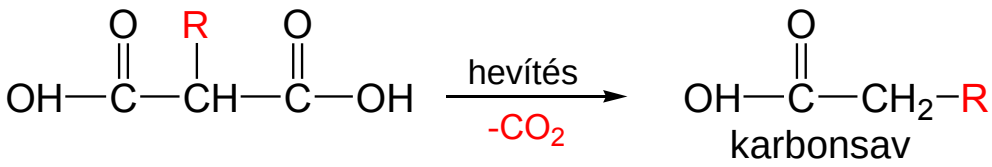
Szintetikus felhasználás



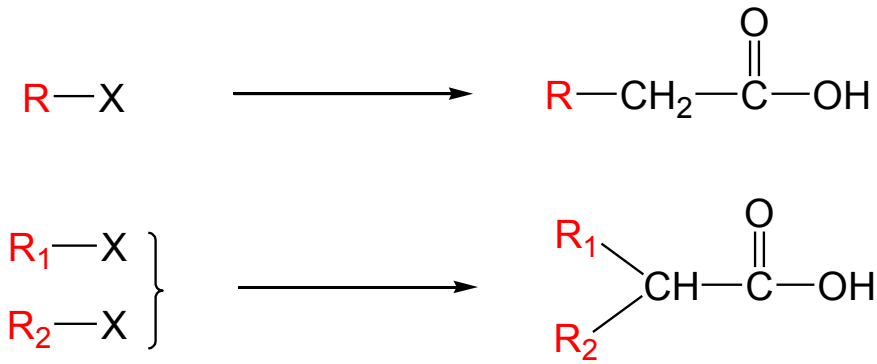
Malonészter szintézisek







Szintetikus felhasználás



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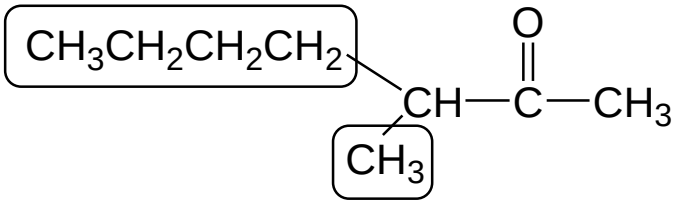
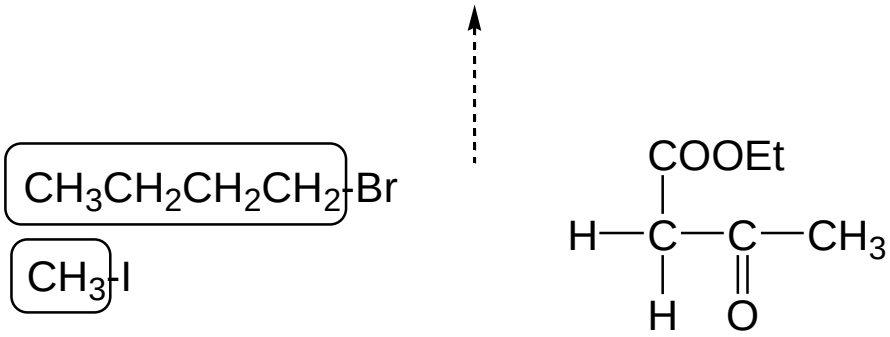


3-metilheptán-2-on



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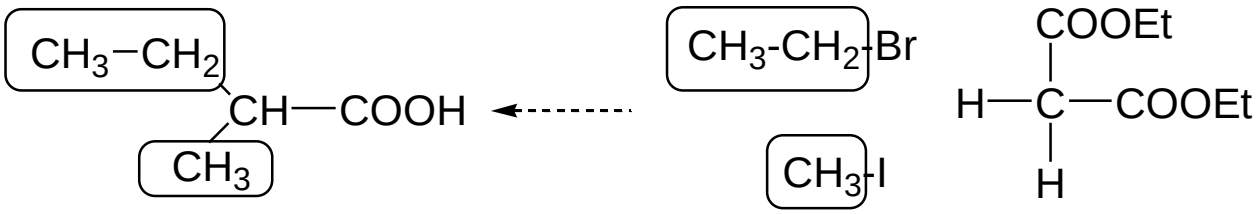
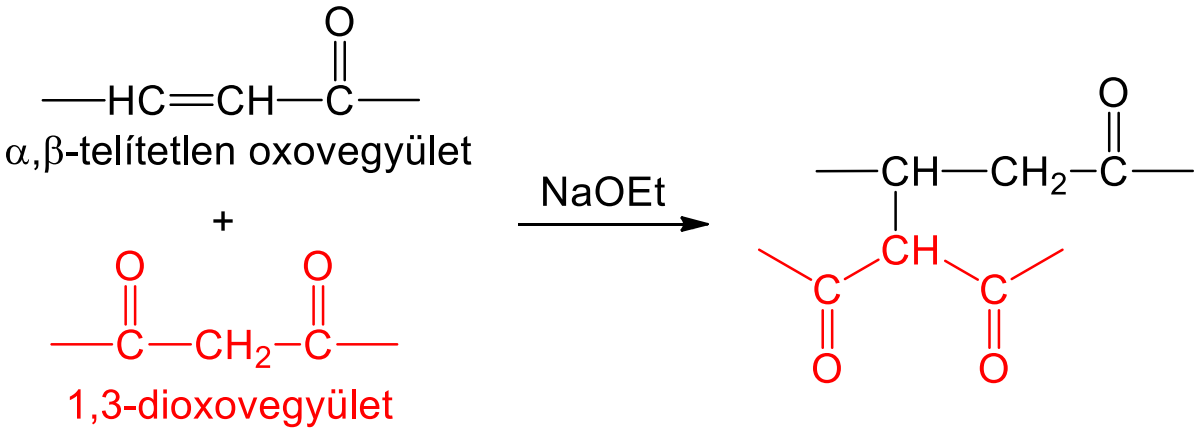
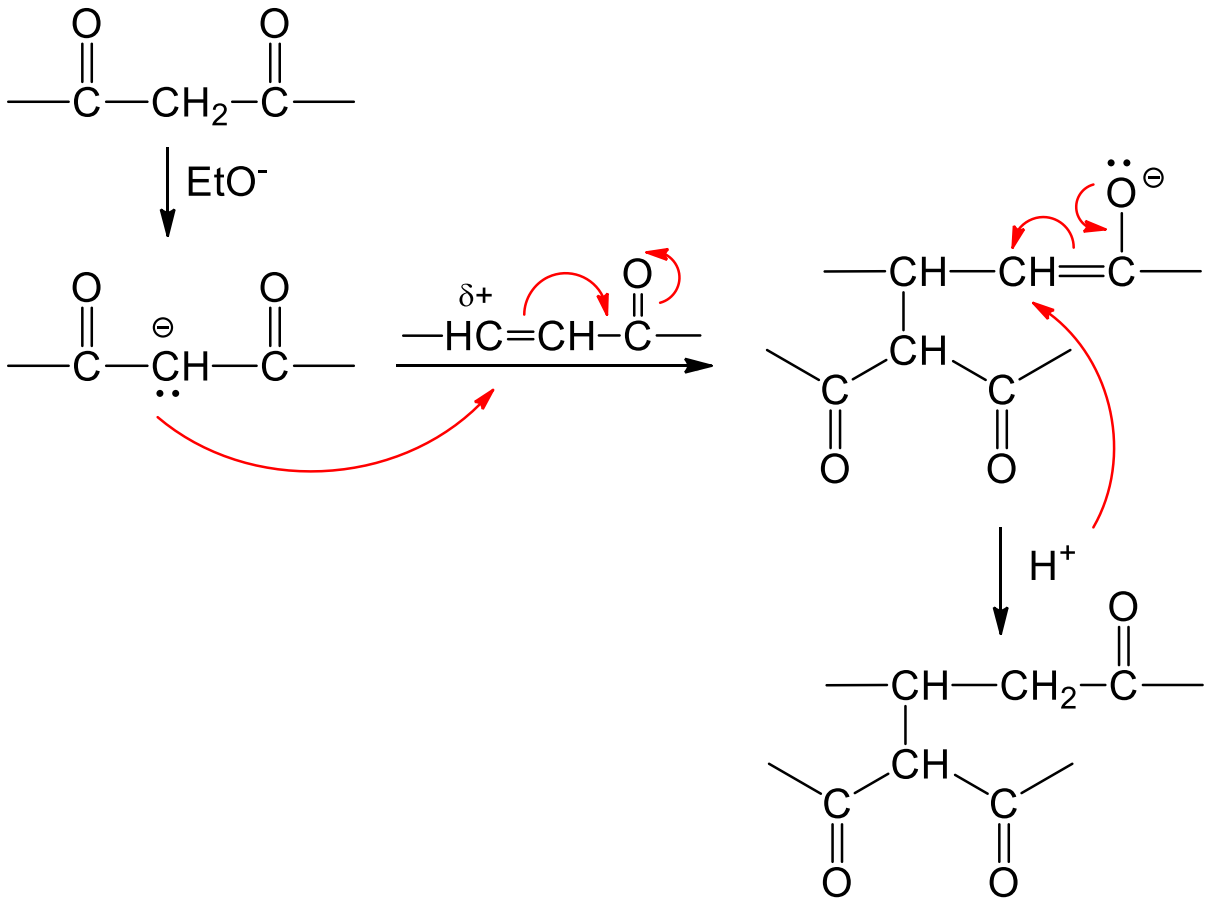


2-metil-vajsav

Michael-addíció



Mechanizmus



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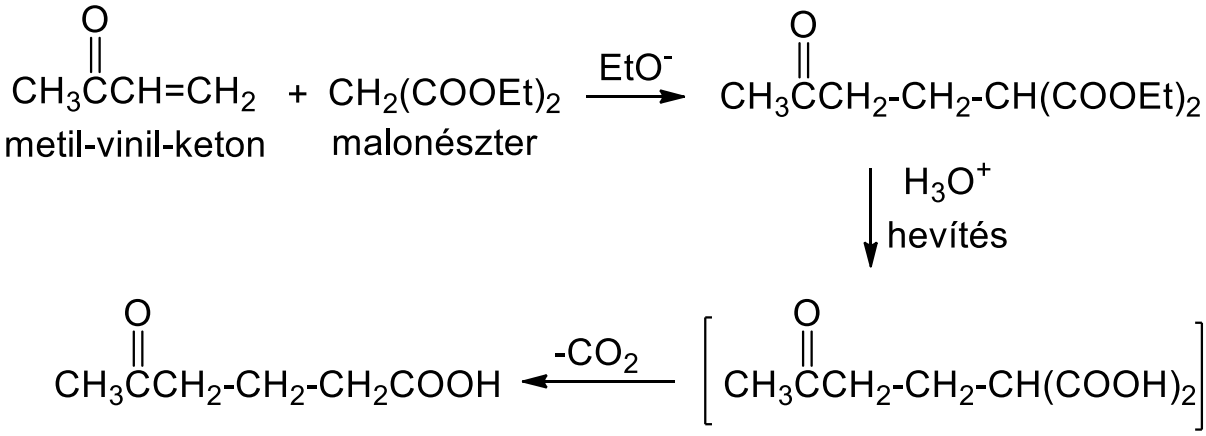
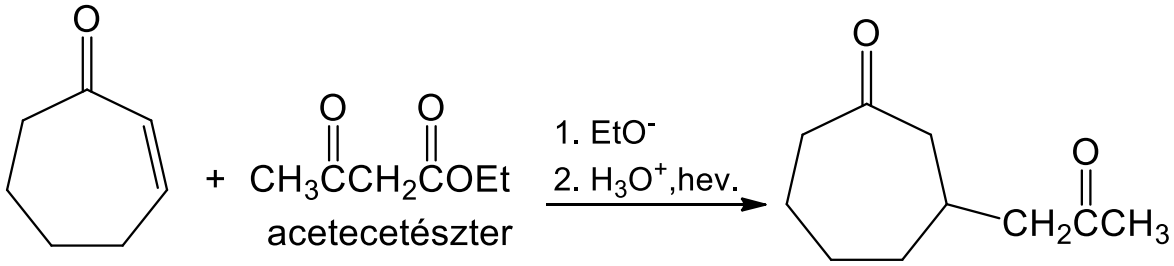

O
CH3CCH=CH2 + CH2(COOEt)2
metil-vinil-keton
malonészter
EtO-
O
CH3CCH2-CH2-CH(COOEt)2
H3O+
hevítés
O
CH3CCH2-CH2-CH2COOH
-CO2
O
CH3CCH2-CH2-CH(COOH)2


O
+
O O
CH3CCH2COEt
acetecetészter
1. EtO-
2. H3O+,hev.
O
O
CH2CCH3

Szénsavszármazékok

Levezetés