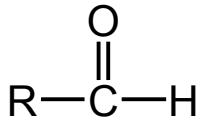
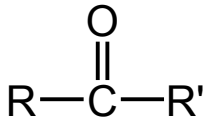
OXOVEGYÜLETEK

Levezetés

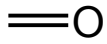


aldehid

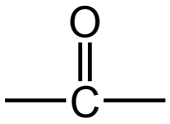


keton

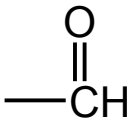
funkciós csoportok



oxocsoport



karbonilcsoport

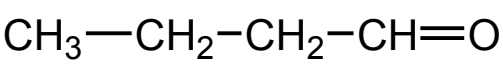


formilcsoport

Elnevezés

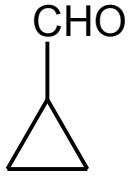
Aldehidek

nyíltláncú
(racionális név: alkánal)



butánal
butiraldehid

gyűrűs
(cikloalkánkarbaldehid)



ciklopropán-
karbaldehid

Példák (aldehidek)

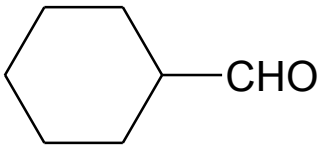
telített nyíltláncú

$HCHO$
formaldehid
(metánal)

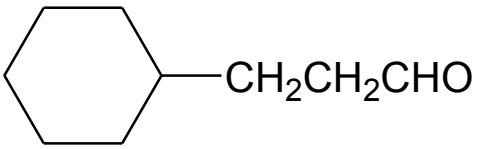
CH_3CHO
acetaldehid
(etánal)

CH_3CH_2CHO
propionaldehid
(propánal)

gyűrűs



ciklohexánkarbaldehid



3-ciklohexil-propionaldehid

telítetlen

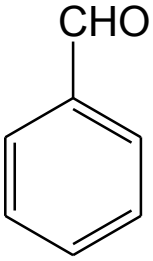
$CH_2{=}CH{-}CHO$

akrilaldehid
(prop-2-énal)

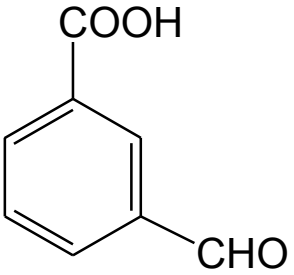
$CH_2{=}CH{-}CH_2{-}CHO$

but-3-énal

aromás



benzaldehid



3-formil-benzoesav

többértékű

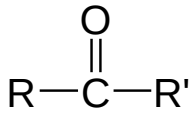
$OHC{-}CHO$

glioxál
(etándial)

$OHC{-}CH_2{-}CHO$

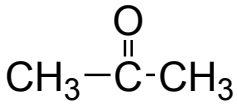
malondialdehid
(propándial)

Ketonok

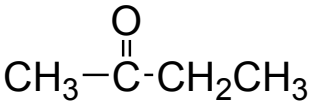


alkanon
dialkil-keton vagy alkil-alkil'-keton

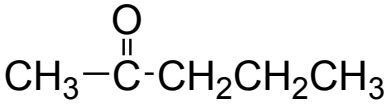
Példák (ketonok)



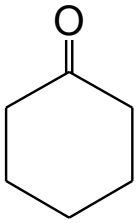
propanon
dimetil-keton
aceton



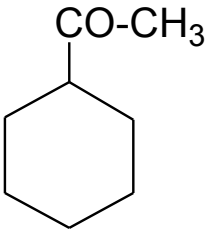
butanon
etil-metil-keton



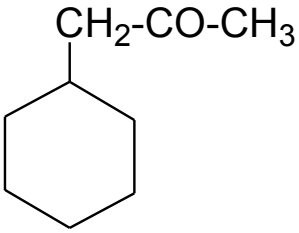
pentán-2-on
metil-propil-keton



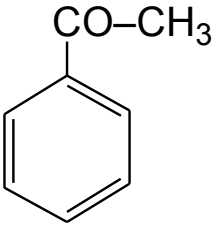
ciklohexanon



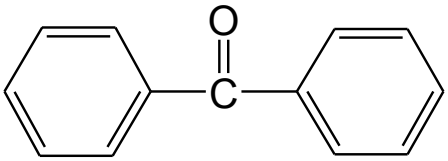
ciklohexil-metil-keton



ciklohexil-aceton



fenil-metil-keton
acetofenon

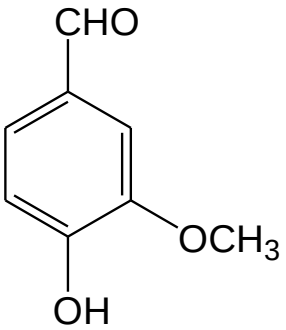


difenil-keton
benzofenon

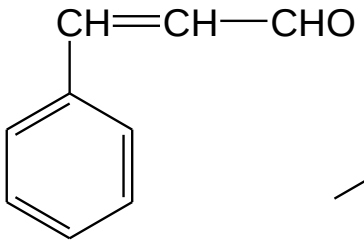
$CH_2=C=O$

ketén

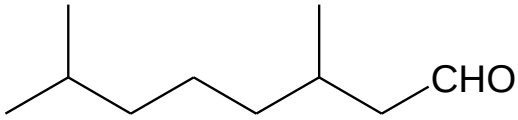
Természetben előforduló oxovegyületek



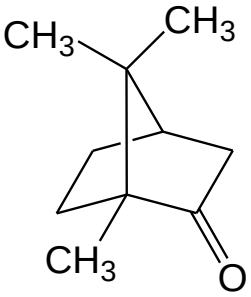
vanillin



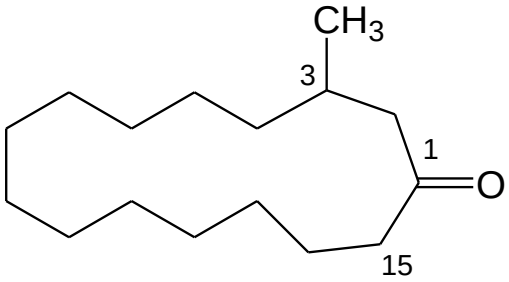
fahéjaldehid



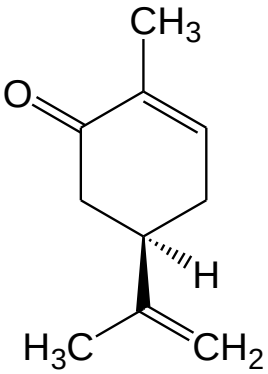
citrál



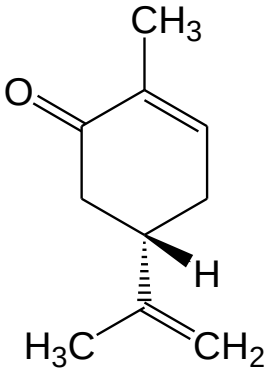
kámfor



muszkon
(3-metil-ciklopentadekanon)

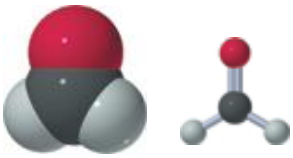


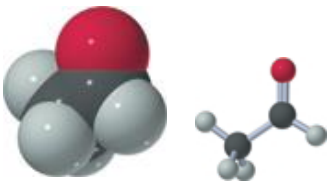
R-(-)-carvone
(fodormenta)

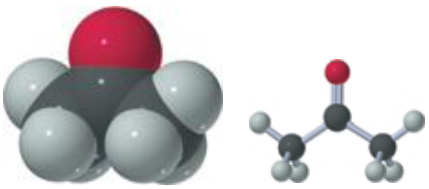


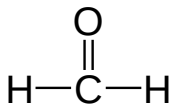
S-(+)-carvone
(kömény)

AZ OXOVEGYÜLETEK SZERKEZETE

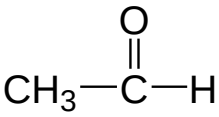




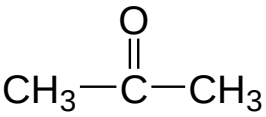




formaldehid

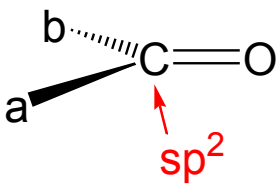


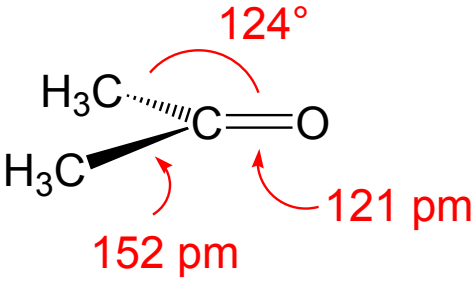
acetaldehid



aceton

Térszerkezet





(C-O kötés: 143 pm)

Kötési energia

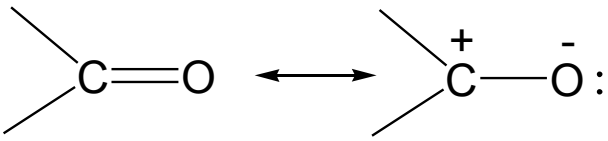
C—O

357 kJ/ mol

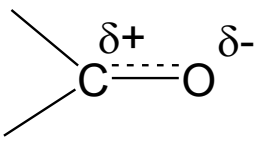
C=O

748 kJ/mol

Polaritás



40-50%



$\mu \sim 9 \times 10^{-30}$ Cm

FIZIKAI TULAJDONSÁGOK

Forráspont

	molekulatömeg	forráspont (°C)
C_2H_6 (etán)	30	–89
HCHO (formaldehid)	30	–21
CH_3OH (metanol)	32	65
C_4H_{10} (bután)	58	–1
C_2H_5CHO (propionaldehid)	58	49
$CH_3–CO–CH_3$ (aceton)	58	56
n-C_3H_7OH (propanol)	60	97

Vízoldhatóság

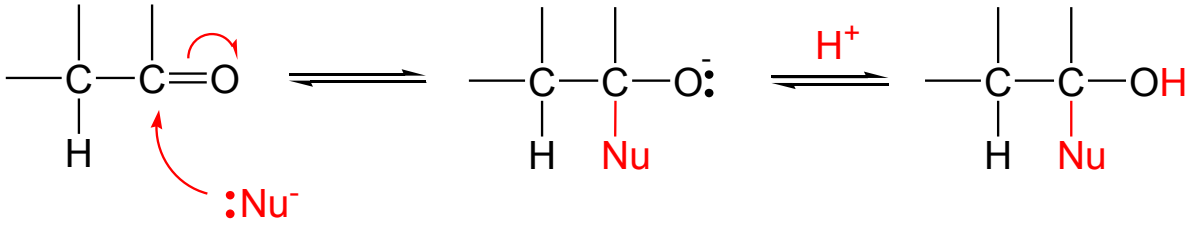
$$>C{=}O\cdots H{-}O{-}H$$

	$C_1{-}C_4$ (CHO)	korlátlan
aceton	$CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$	
butanon	$CH_3CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3$	25%
pentán-3-on	$CH_3CH_2{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_2{-}CH_3$	5%

KÉMIAI TULAJDONSÁGOK

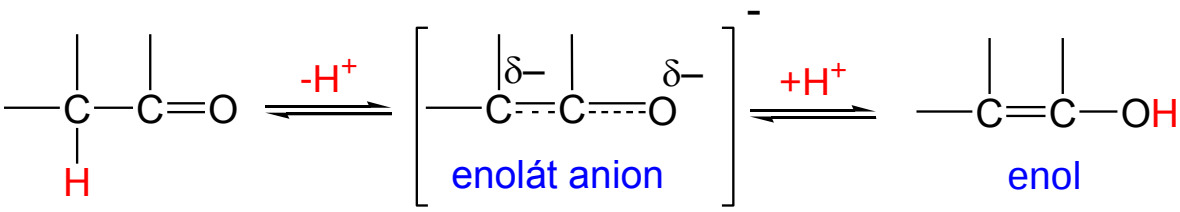
Reakciótípusok

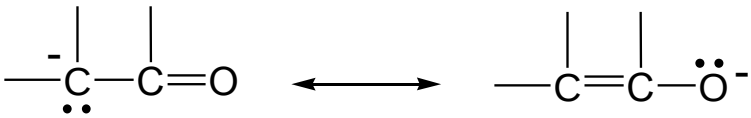
1. Reakció a karbonil-szénatomon



nukleofil addíció (Ad_N)

2. Reakció az α-helyzetű szénatomon



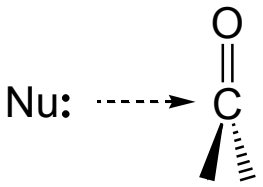


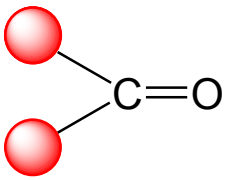
az enolát anion határszerkezetei

NUKLEOFIL ADDÍCIÓ

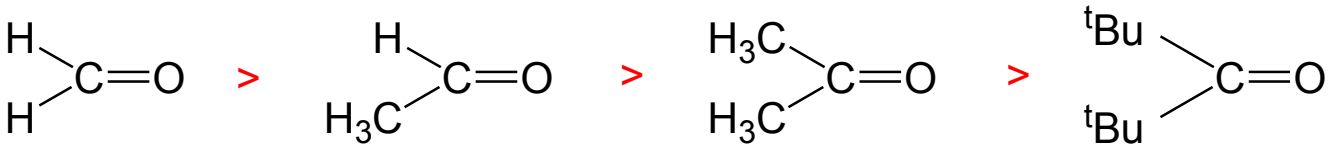
Reaktivitást befolyásoló tényezők

Térszerkezet



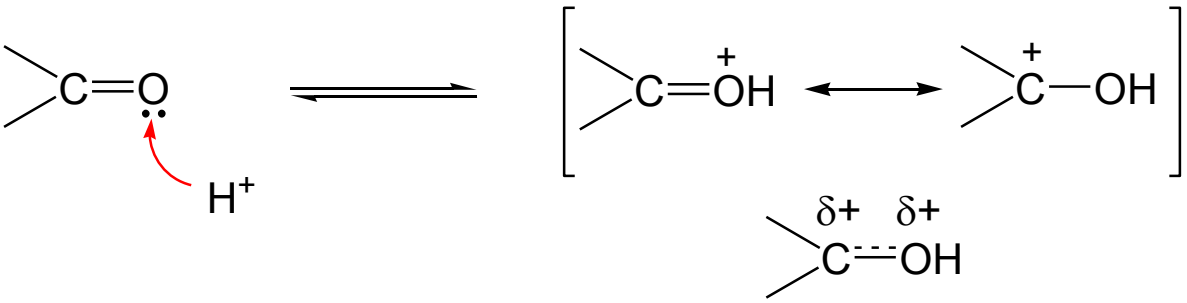


karbonil szénatom árnyékoltsága nő →



reakciókészség csökken →

Sav-katalízis



kedvező (pozitívabban polározott szénatom)

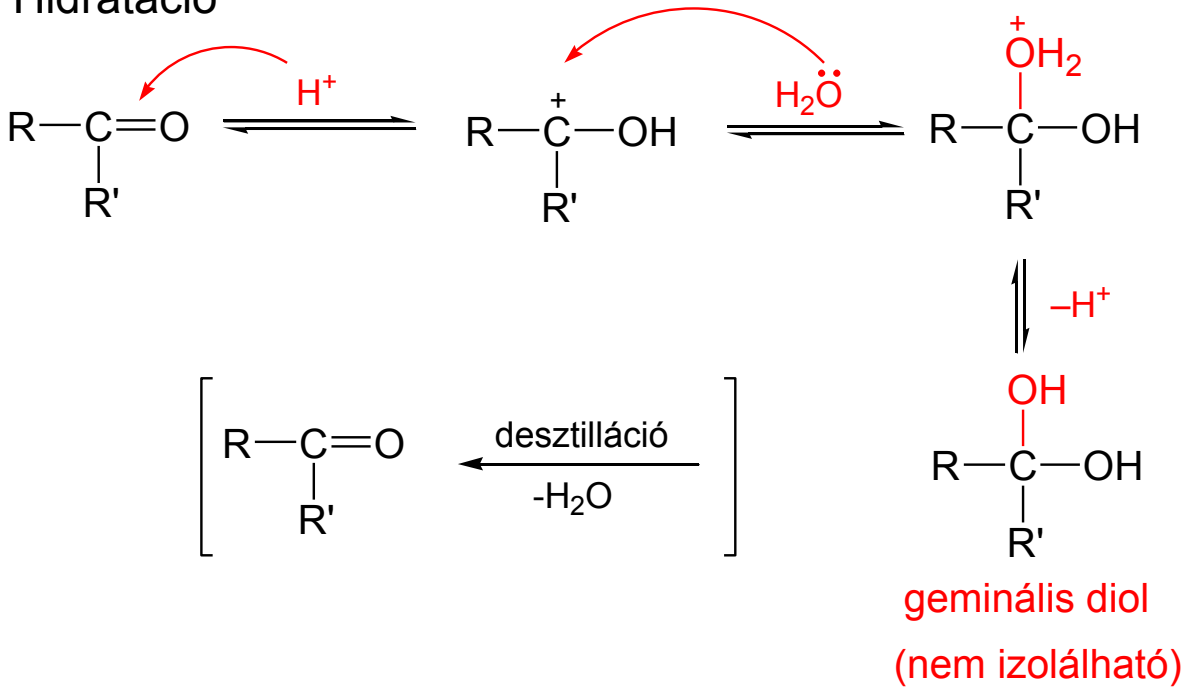
kedvezőtlen (nukleofil jelleg megszűnik)

optimális kémhatás: gyengén savas (pH~3)

NUKLEOFIL ADDÍCIÓS REAKCIÓK

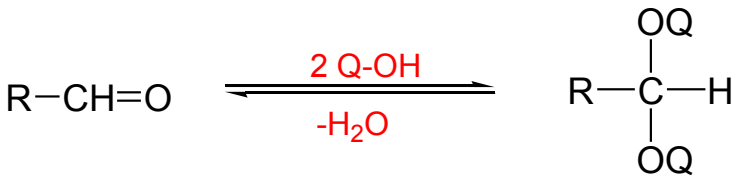
Reakció oxigén-nukleofilekkel (H_2O, R-OH)

Hidratáció



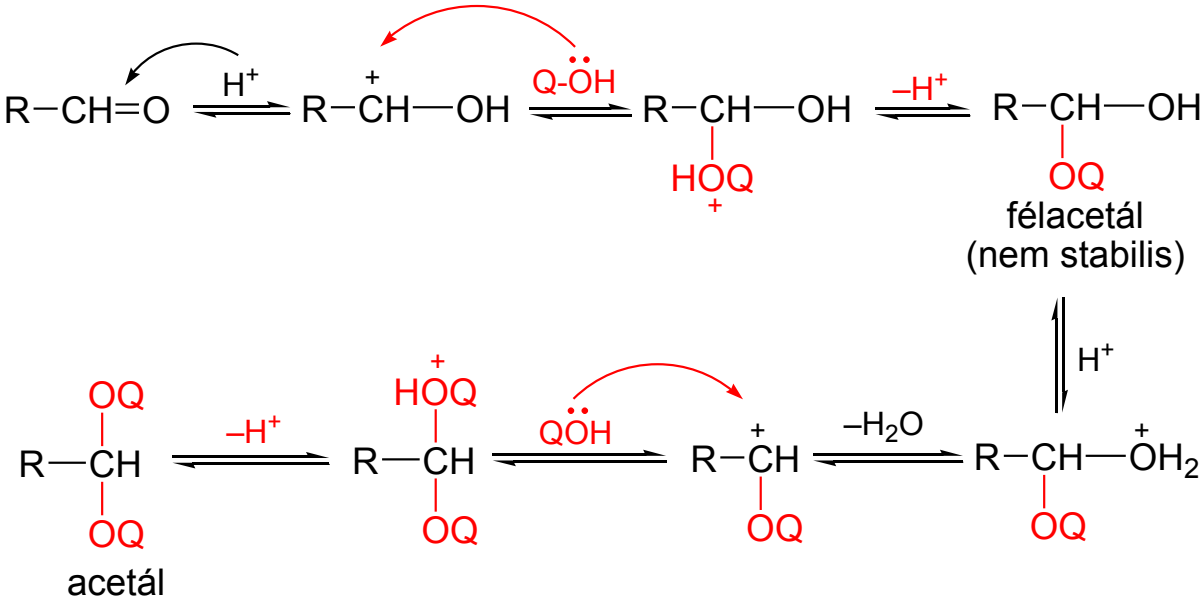
oxovegyület (1M vizes oldat)	egyensúlyi áll. (K)	hidrát (diol) forma (%)
H—CHO	41	99,96
CH_3—CHO	$1{,}8 \times 10^{-2}$	50
$(CH_3)_3C$—CHO	$4{,}1 \times 10^{-3}$	19
CH_3COCH_3	$2{,}5 \times 10^{-5}$	0,14

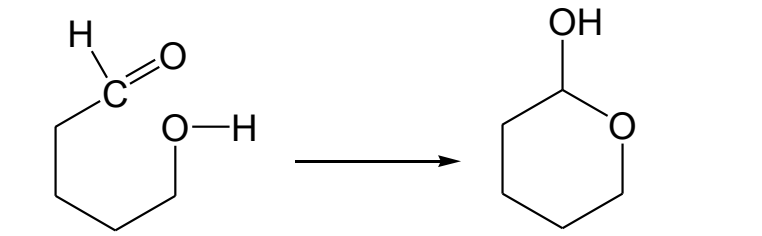
Acetálképzés (aldehidekből)



acetál

Mechanizmus

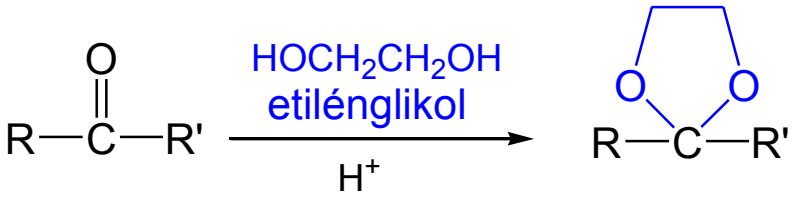




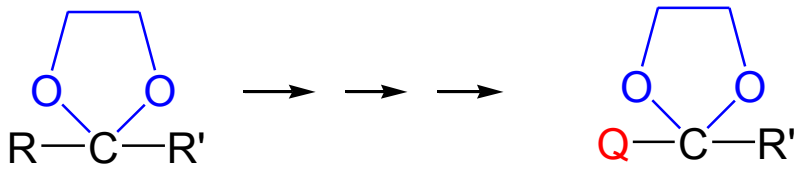
"hidroxi-aldehid" ciklofélacetál (laktol) (stabilis)

Acetál védőcsoport alkalmazása

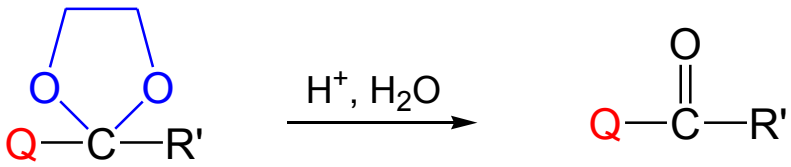
1. oxocsoport védése



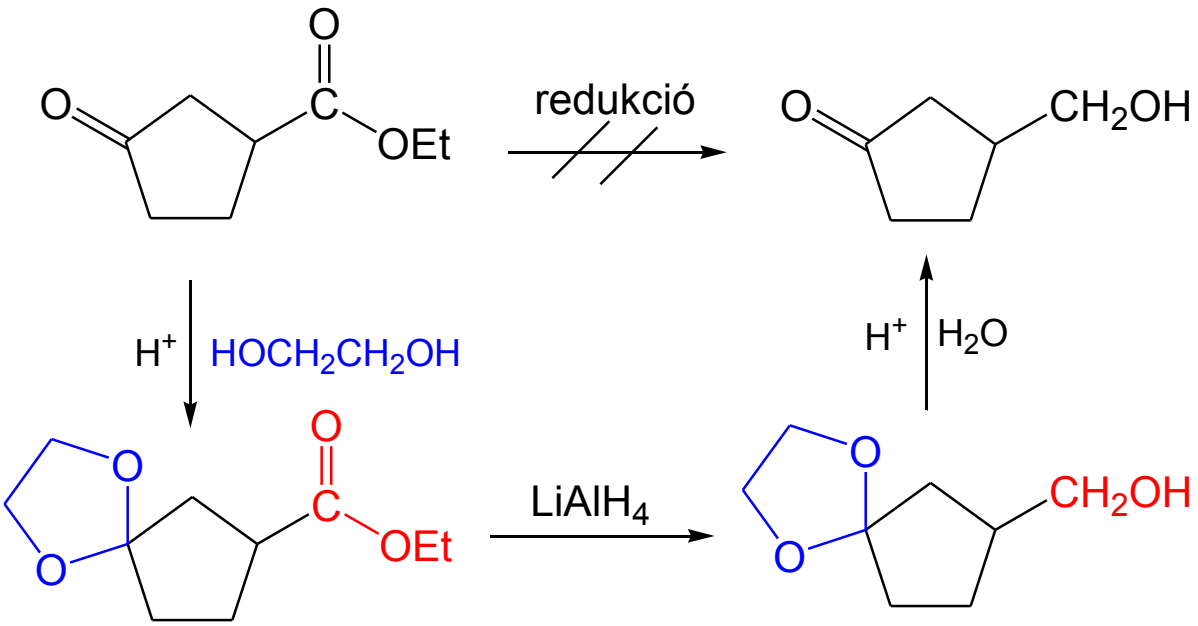
2. kémiai átalakítás



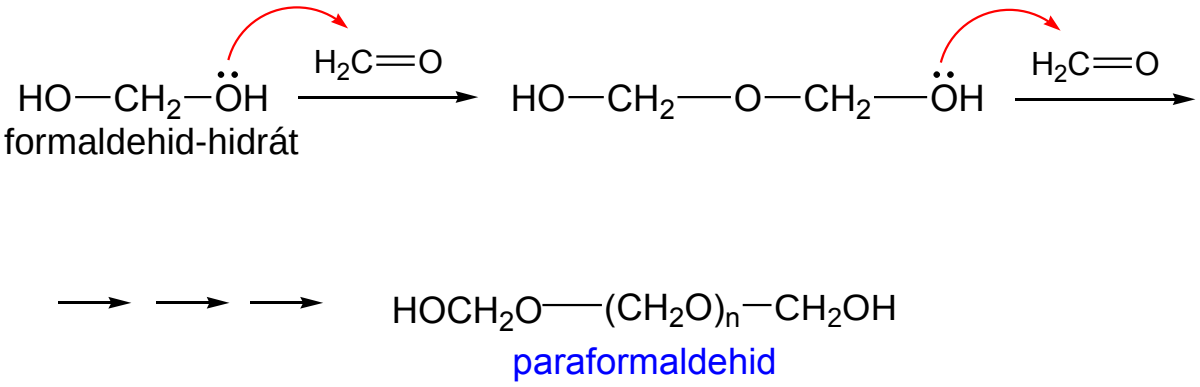
3. védőcsoport eltávolítás

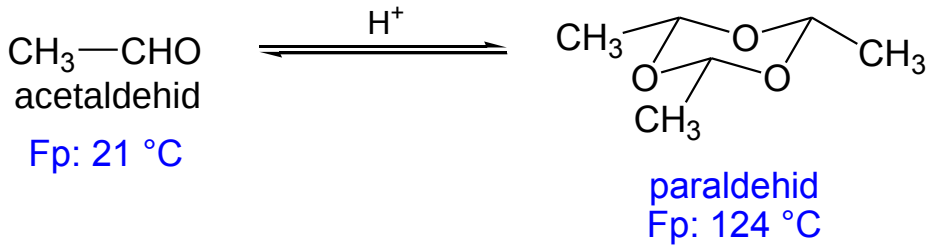


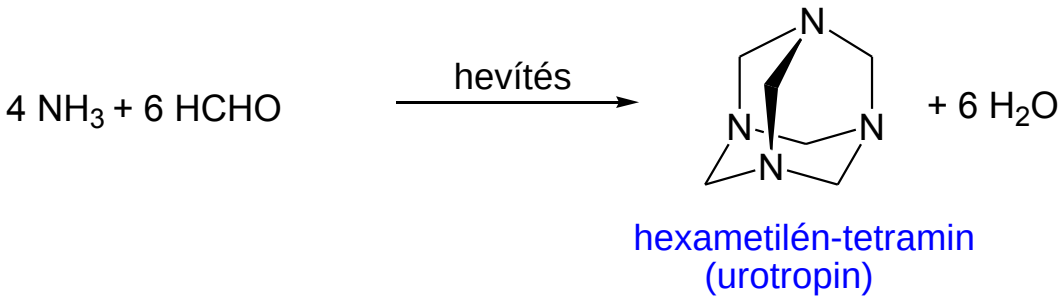
Példa



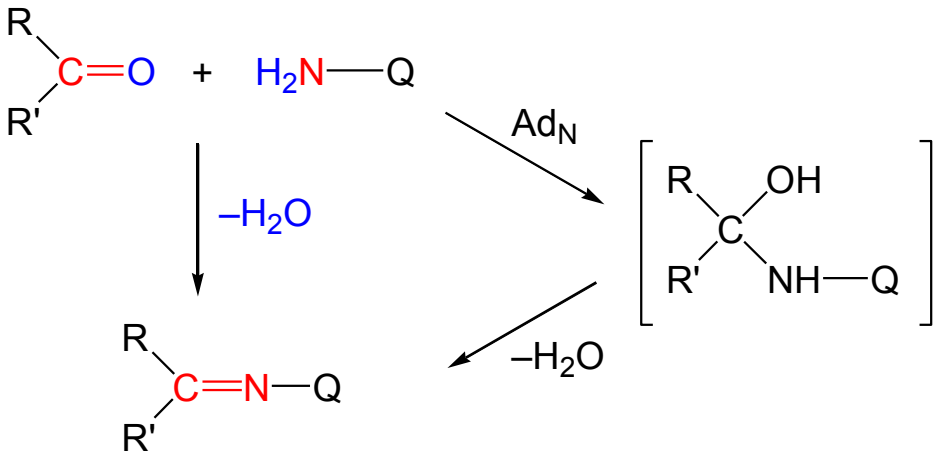
Polimerizációs reakciók



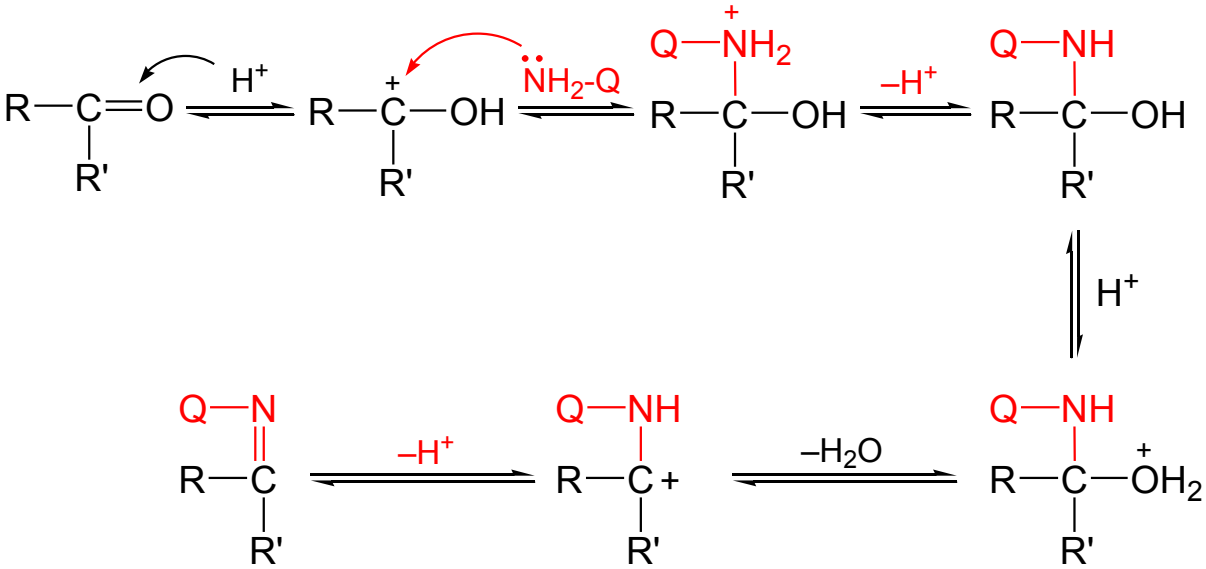


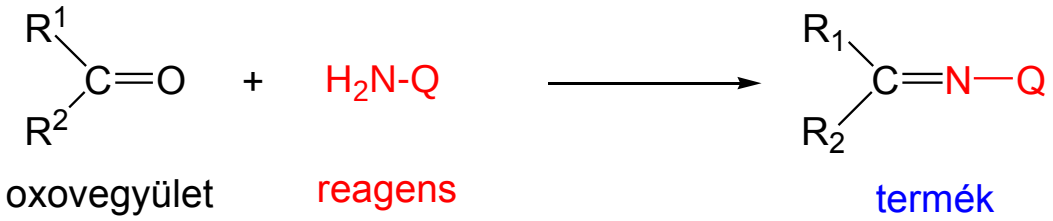


Reakció nitrogén-nukleofilekkel (NH_2-Q)

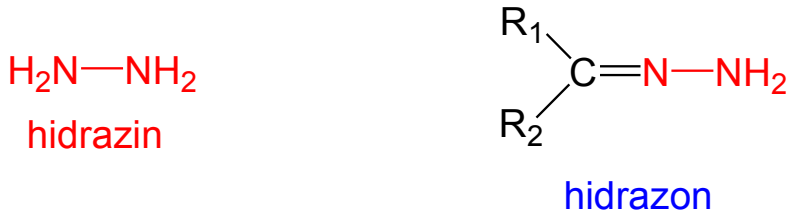


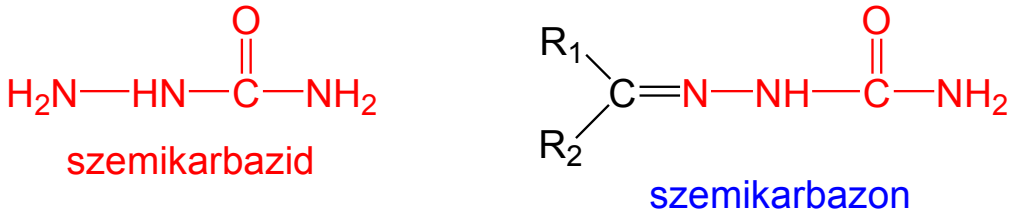
Mechanizmus




R1
C=O
R2
+
H2N-Q
R1
C=N—Q
R2
oxovegyület
reagens
termék

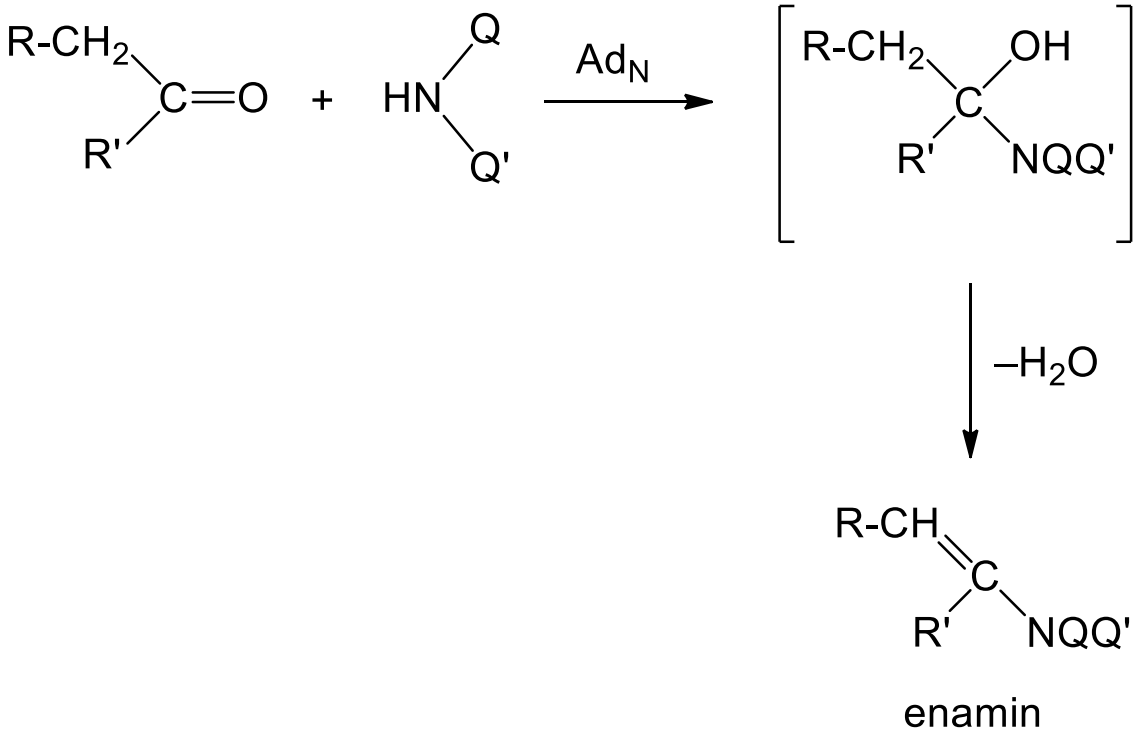
R3—NH2
amin
R1
C=N—R3
R2
Schiff-bázis


H2N—NH2
hidrazin
R1
C=N—NH2
R2
hidrazon

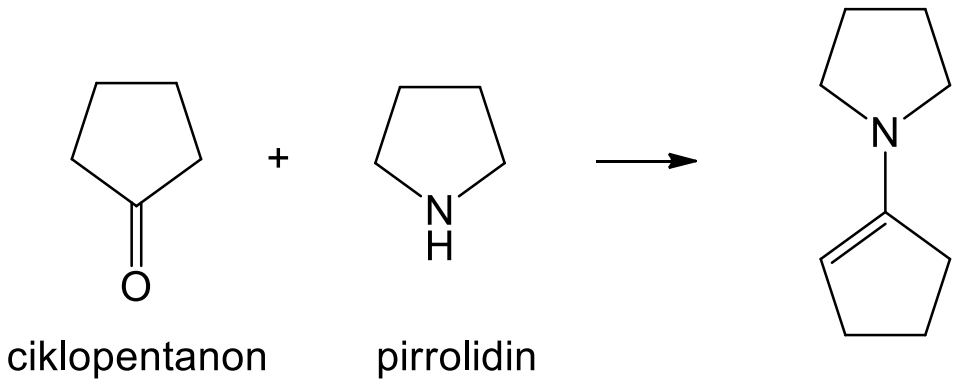

O
H2N—HN—C—NH2
szemikarbazid
R1
C=N—NH—C—NH2
R2
szemikarbazon

HO—NH2
hidroxil-amin
R1
C=N—OH
R2
oxim

Reakció szekunder aminokkal

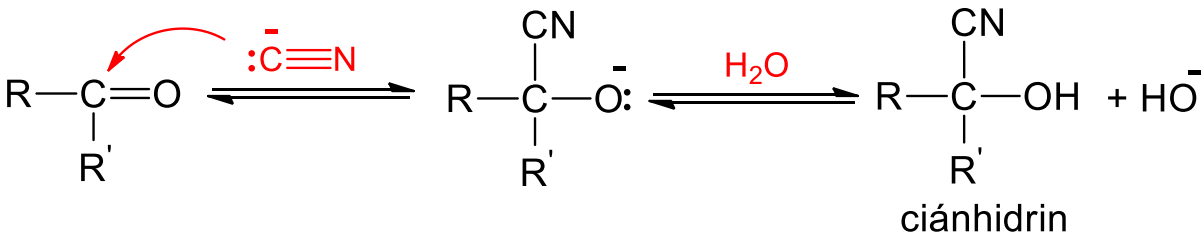


Példa

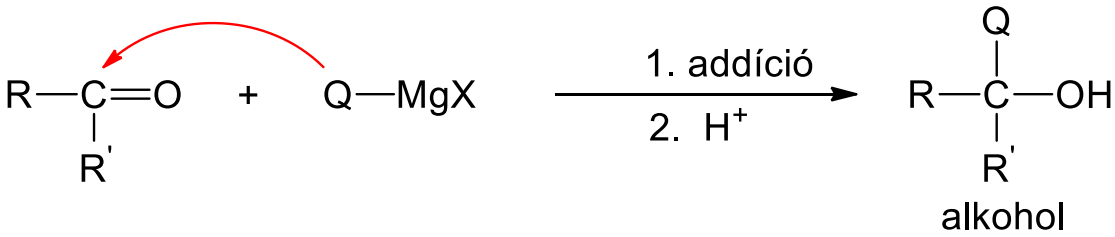


Reakció szén-nukleofilekkel

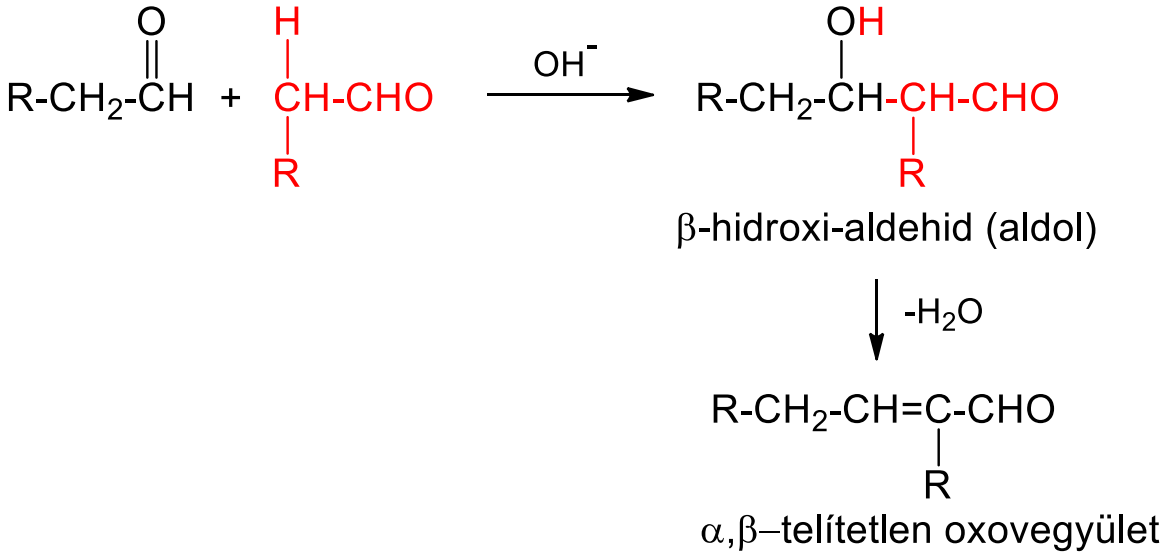
a) HCN addíció



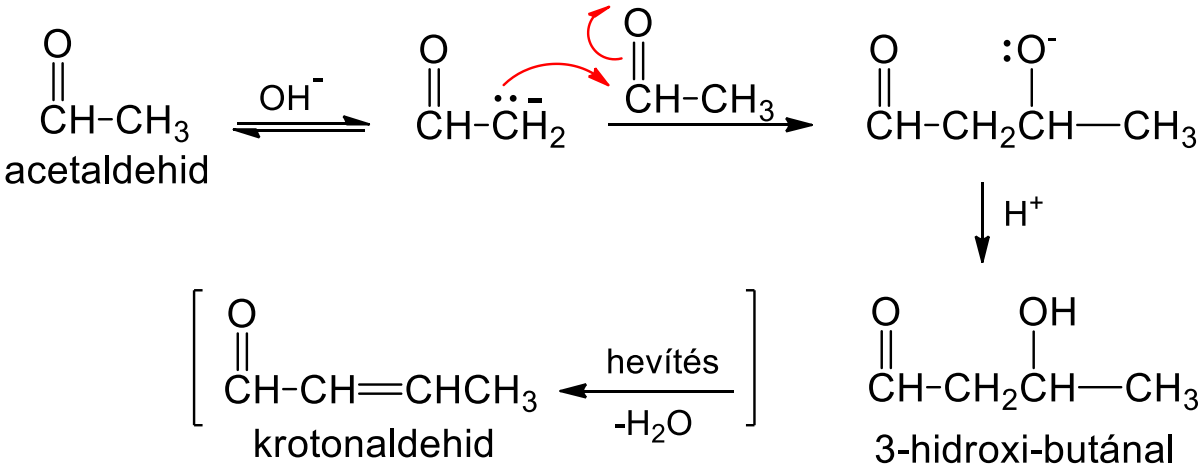
b) Grignard-reagens addíciója



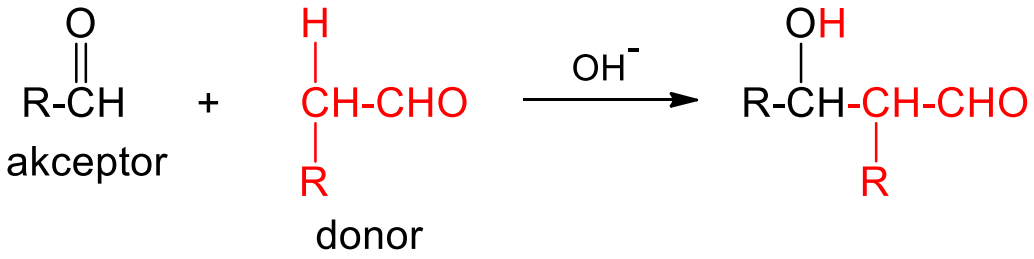
c) Aldol-addíció (aldol dimerizáció)



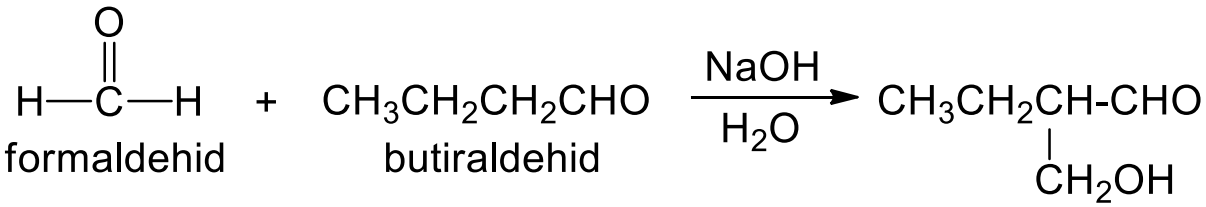
Mechanizmus

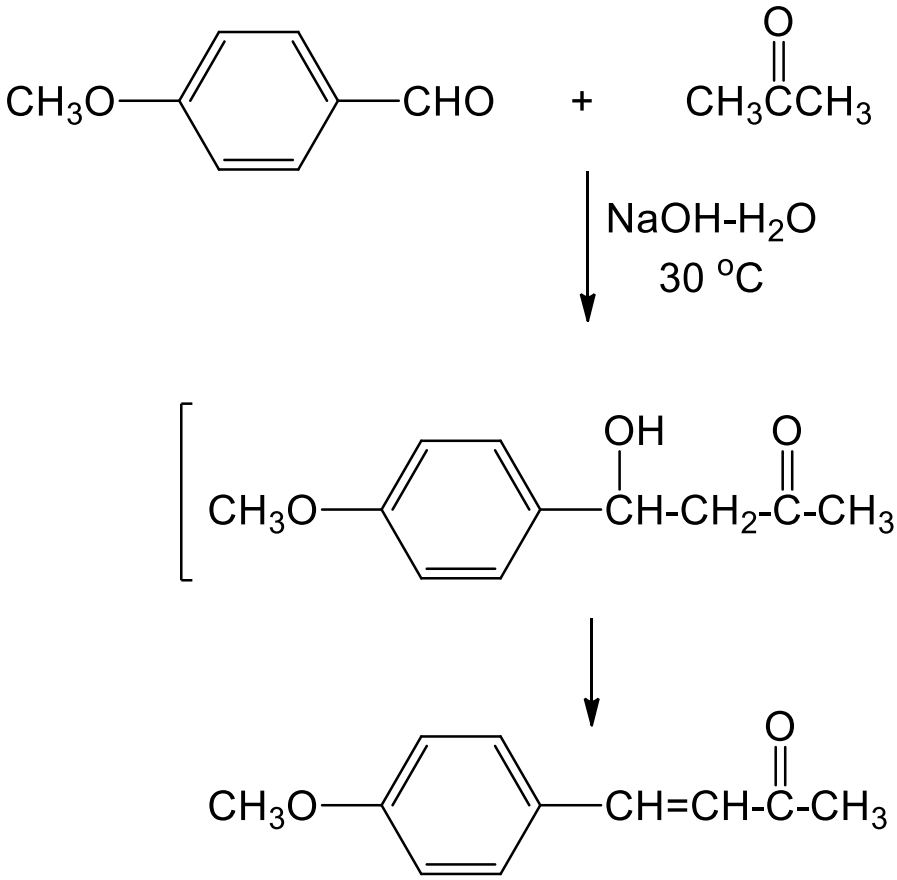


Vegyes aldol-addíció

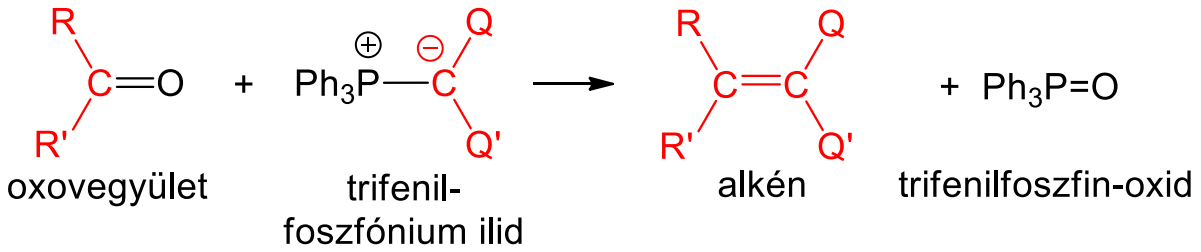


Példák

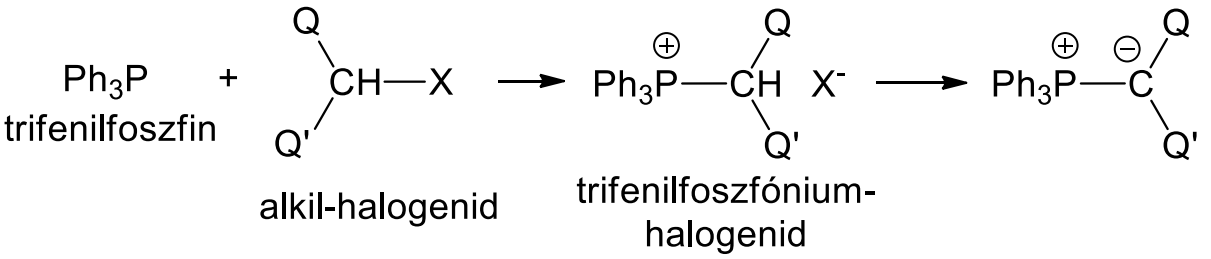




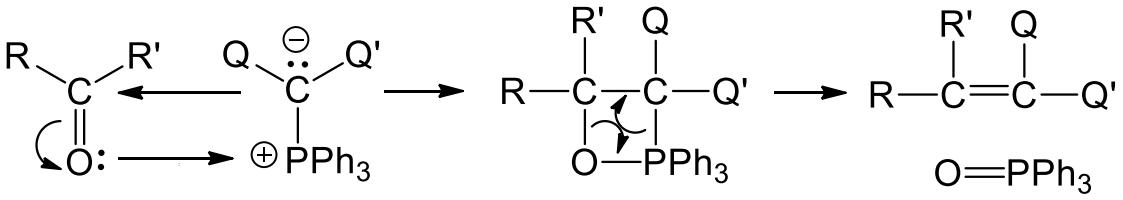
d) Wittig-reakció (alkének szintézise)



Trifenilfoszfónium ilid szintézise

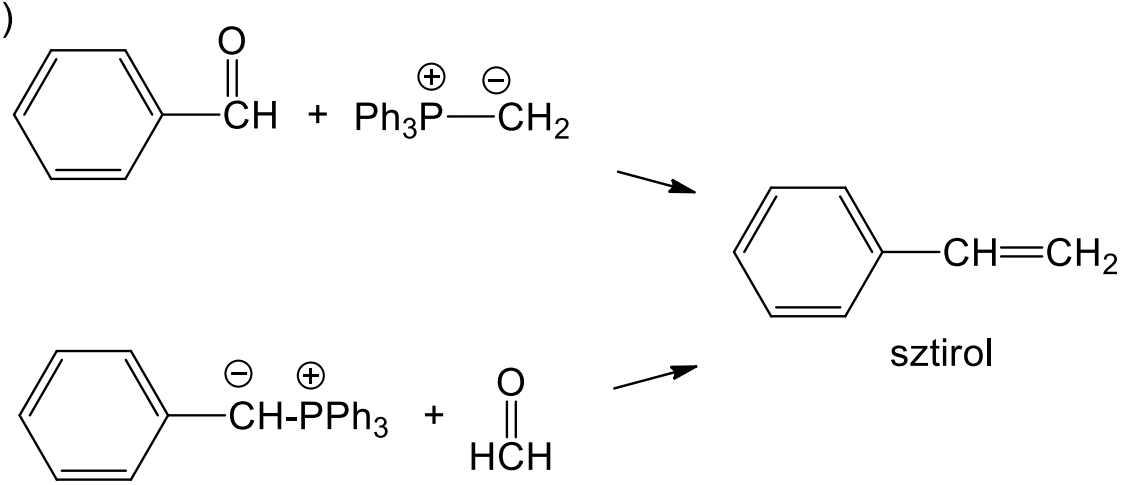


Mechanizmus

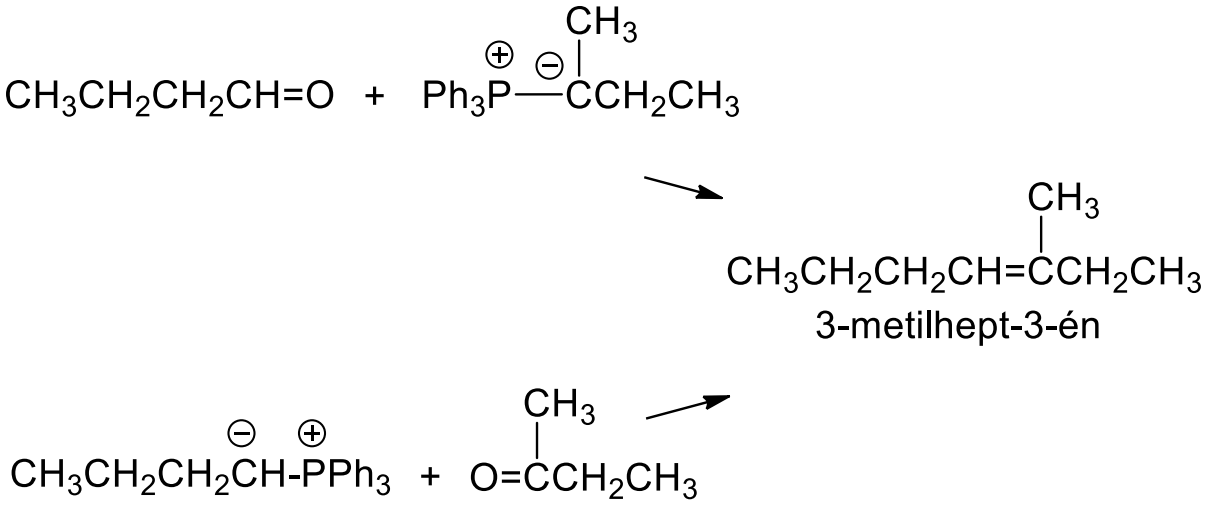


Példák Wittig-szintézisre

a)

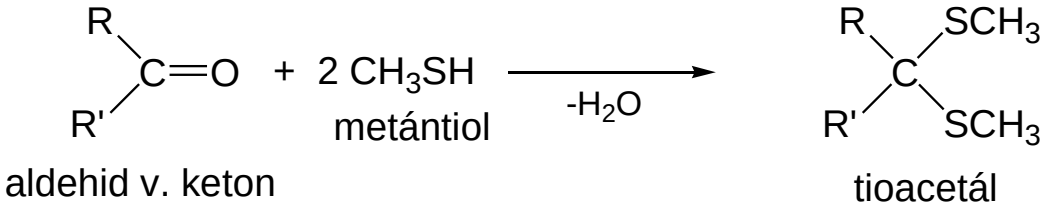


b)

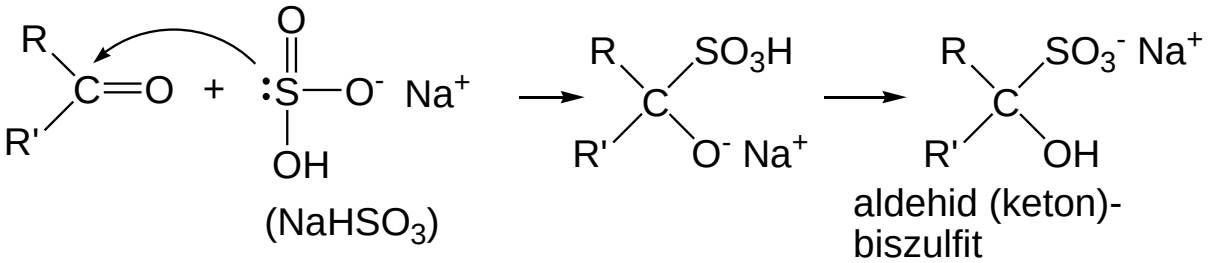


Reakció kén-nukleofilekkel

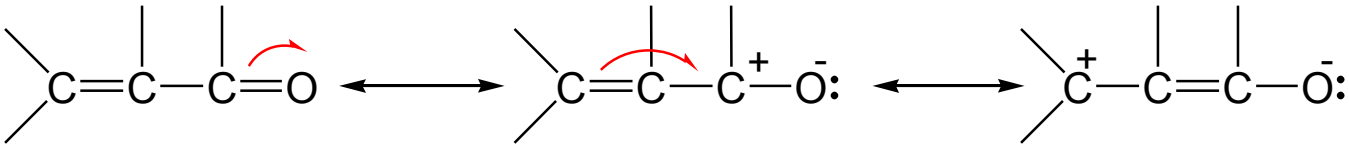
A) Tiolok reakciója



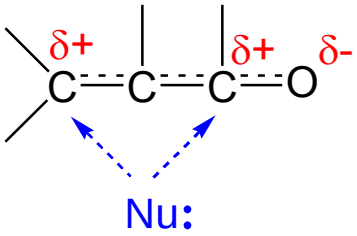
B) Nátrium-biszulfit (nátrium-hidrogénszulfit) reakciója



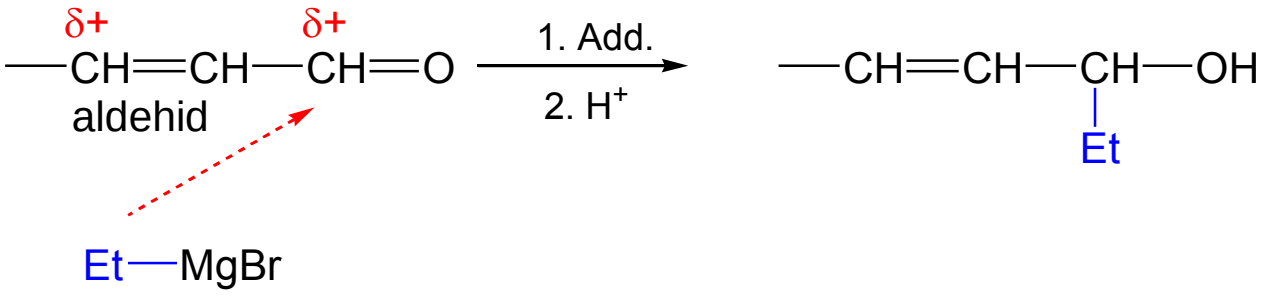
ADDÍCIÓ α,β-TELÍTETLEN OXOVEGYÜLETEKEN

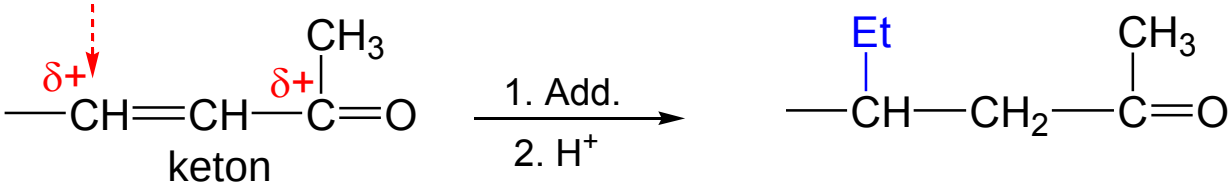


heterokonjugált kötésrendszer

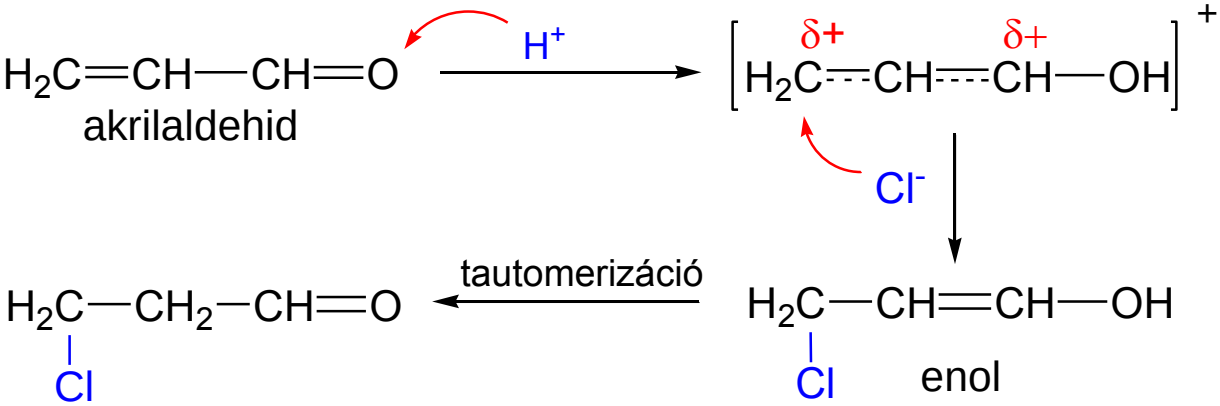


a) Reakció Grignard-reagenssel

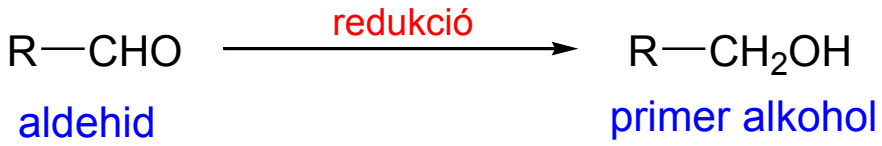


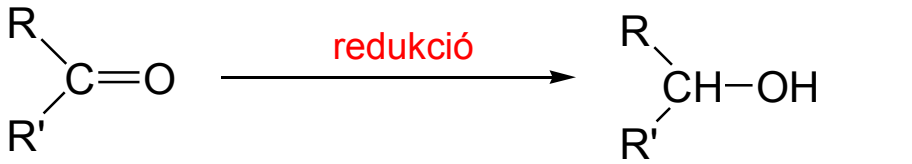


b) HCl addíció

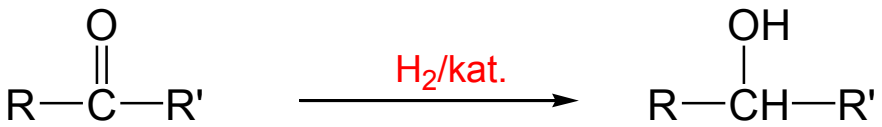


AZ OXOVEGYÜLETEK REDUKCIÓJA





Katalitikus hidrogénezés



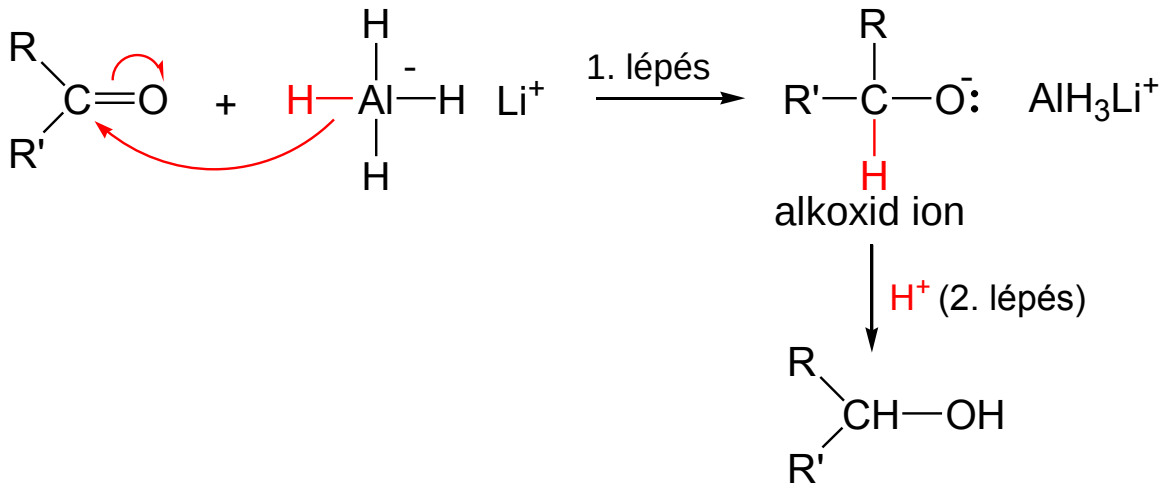
katalizátor: Pt, Pd/C, Raney-Ni

Redukció komplex fém-hidridekkel

Litium-aluminium-hidrid; $LiAlH_4$

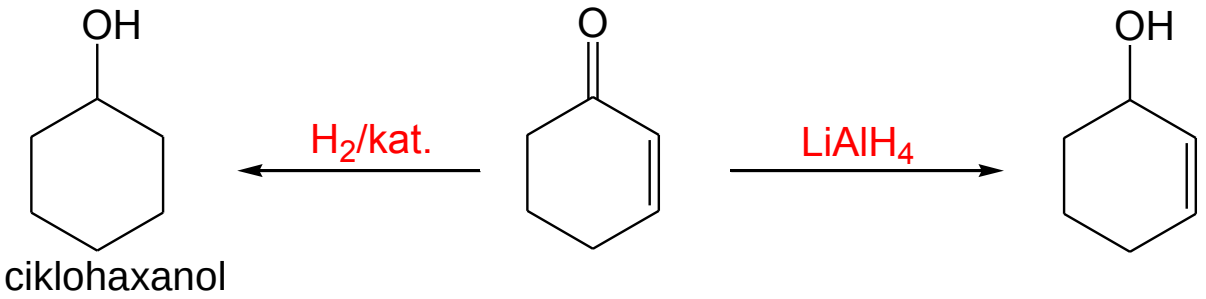
Nátrium-borohidrid; $NaBH_4$

Mechanizmus

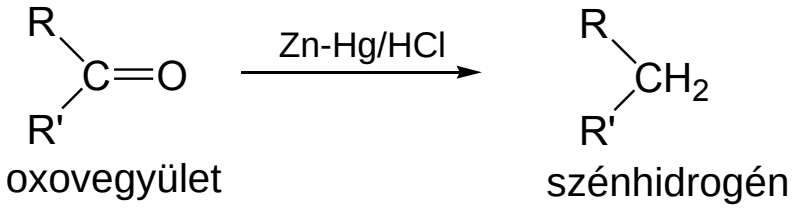


$$4\ R_2CO + LiAlH_4 \xrightarrow[2.\ H^+]{1.\ red.} 4\ R_2CH{-}OH$$

Szelektivitás



Clemmensen-redukció



AZ OXOVEGYÜLETEK OXIDÁCIÓJA

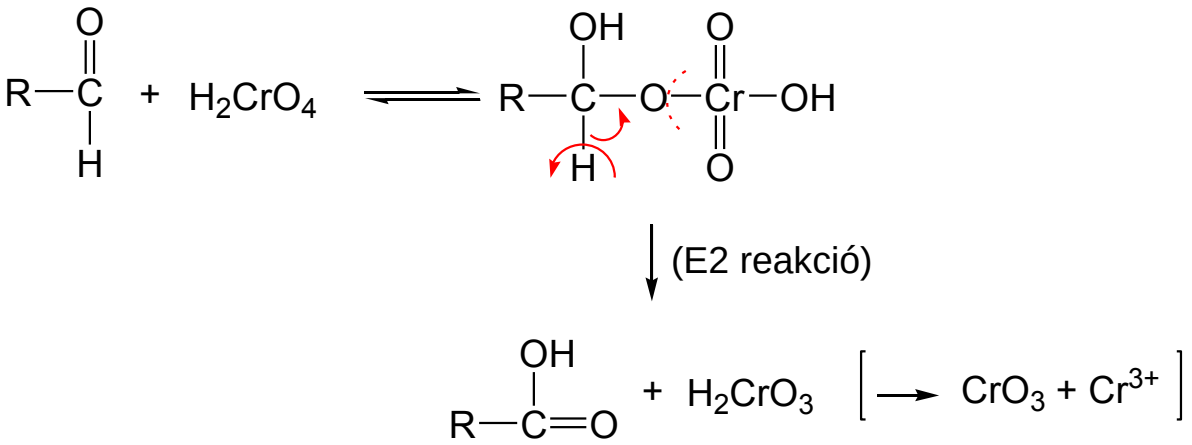
Aldehidek

$$R{-}CHO \xrightarrow{\text{oxidáció}} R{-}COOH$$

karbonsav

oxidálószerek: pl. $KMnO_4$, H_2CrO_4

Mechanizmus



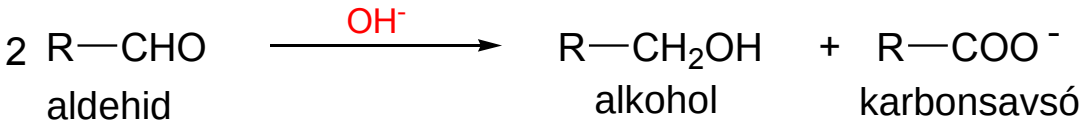
Tollens próba (ezüsttükör próba)

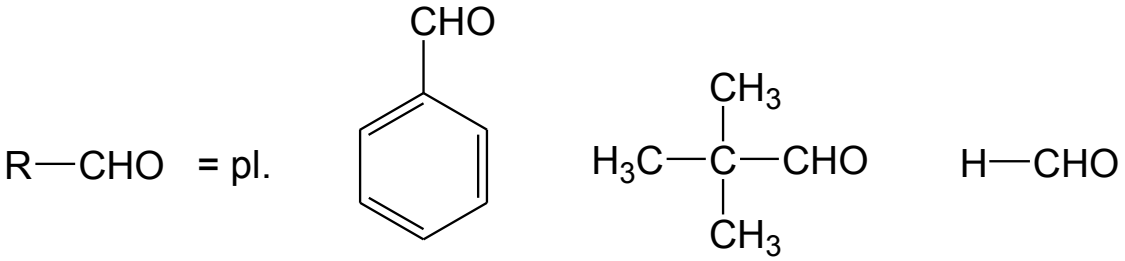
$$R{-}CHO + [Ag(NH_3)_2]OH \longrightarrow RCOOH + Ag$$

Fehling próba

$$R\text{-}CHO + Cu^{2+} \longrightarrow R\text{-}COOH + Cu_2O$$

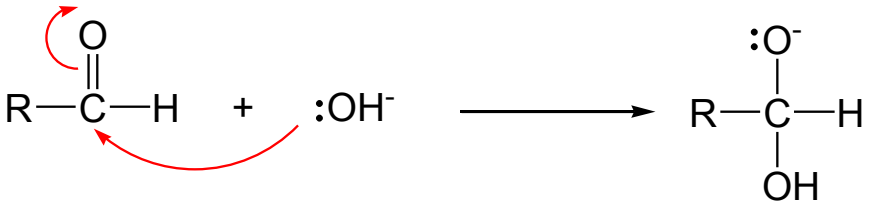
Cannizzaro-reakció

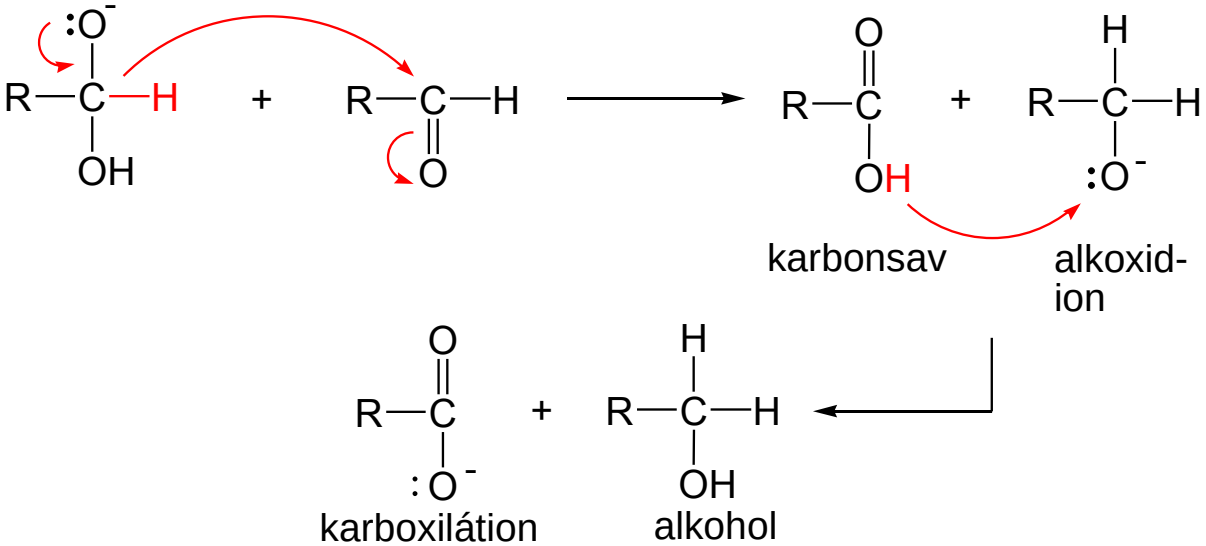




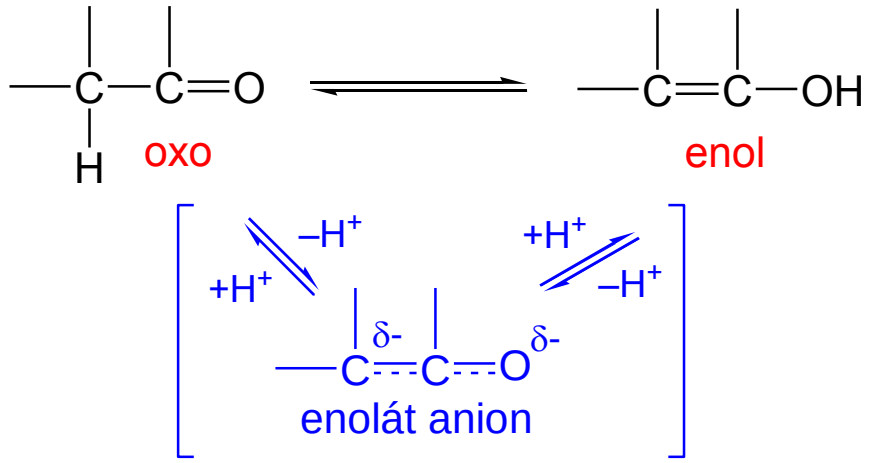
szerkezeti feltétel: α-szénatomon nincs H-atom
(ha α-szénatomon van H-atom ⟶ aldol-addíció)

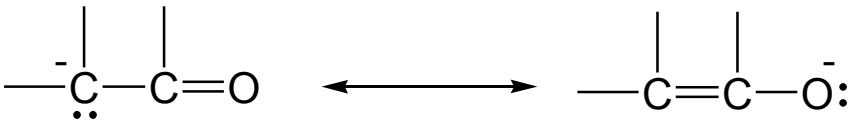
Mechanizmus





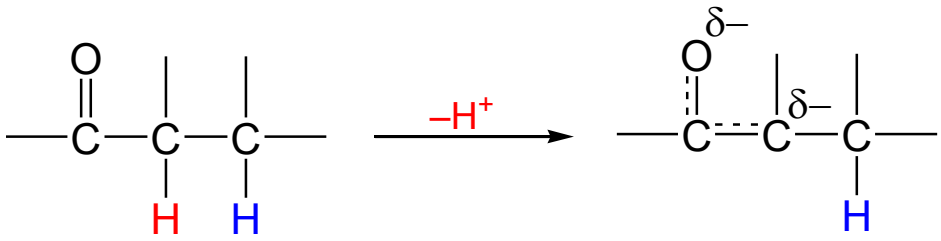
ENOL-OXO TAUTOMÉRIA





az enolát anion határszerkezetei

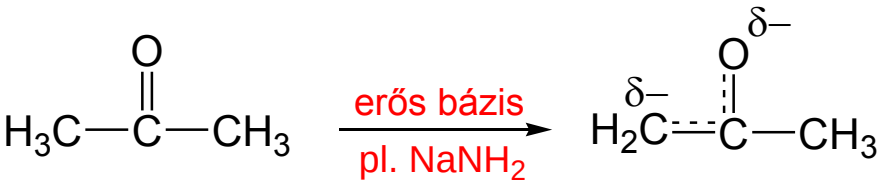
Az α-hidrogén savassága



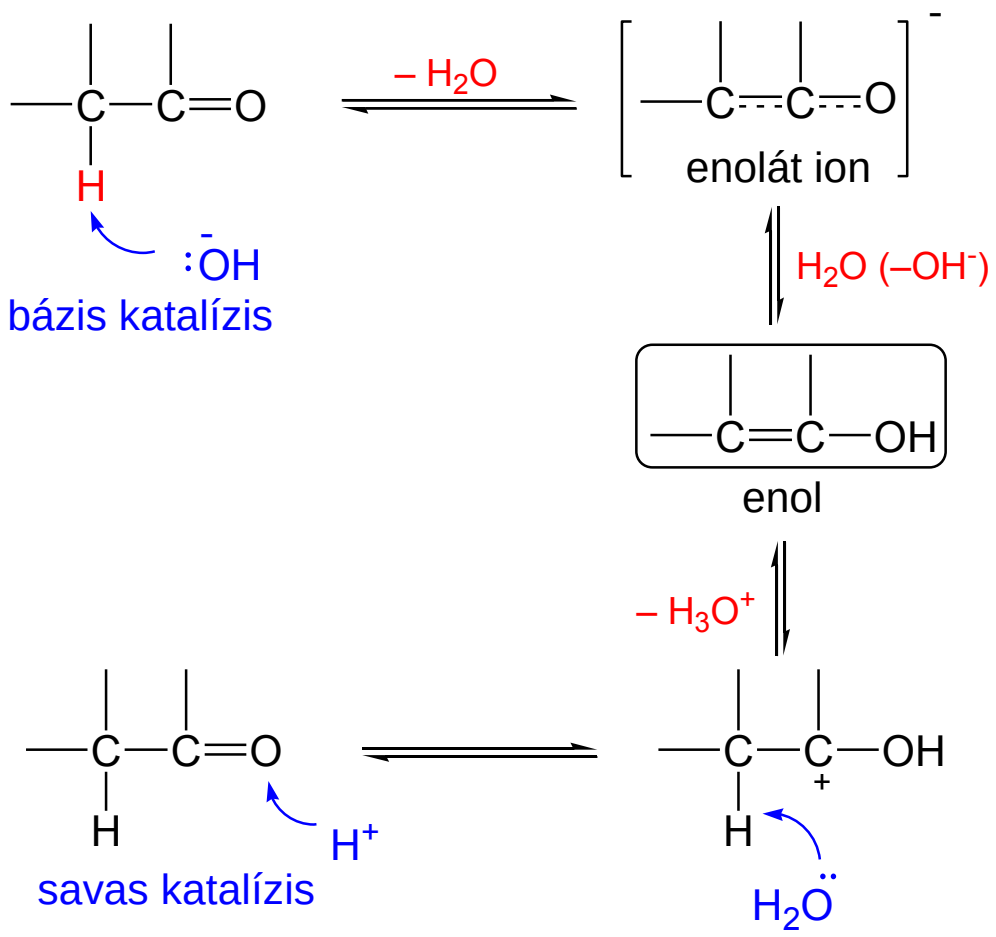
α-H
pK_s = 19-20

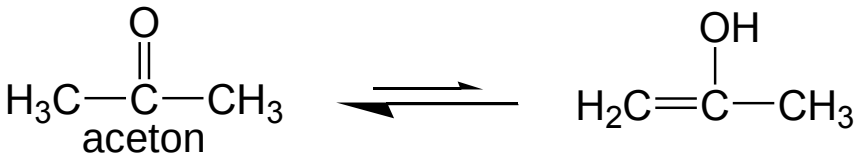
β-H
pK_s = 40-50

Sóképzés erős bázissal



Sav-bázis katalízis



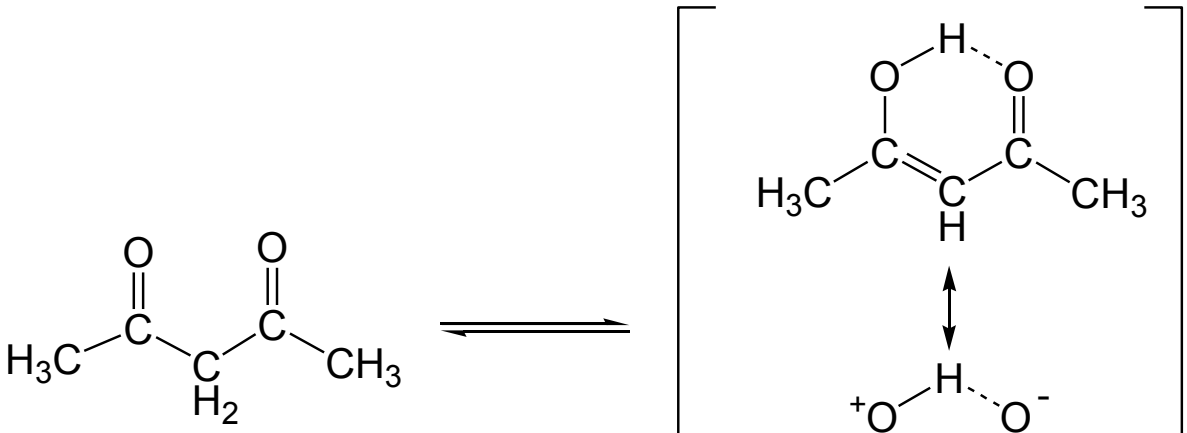


aceton

>99,99%

<0,01%

1,3-dioxovegyületek enolizációja



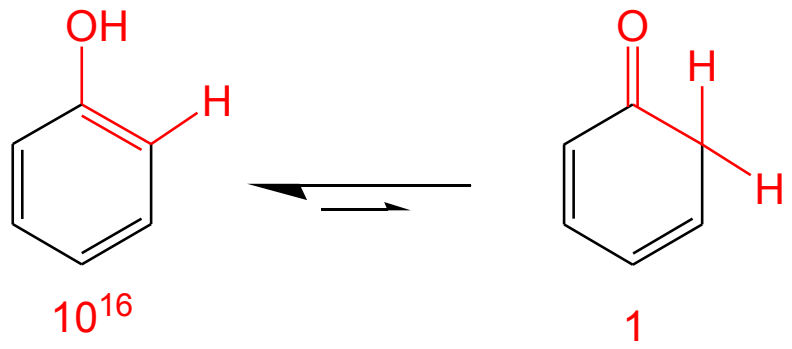
acetil-aceton
2,4-pentándion

24% (dioxo alak)

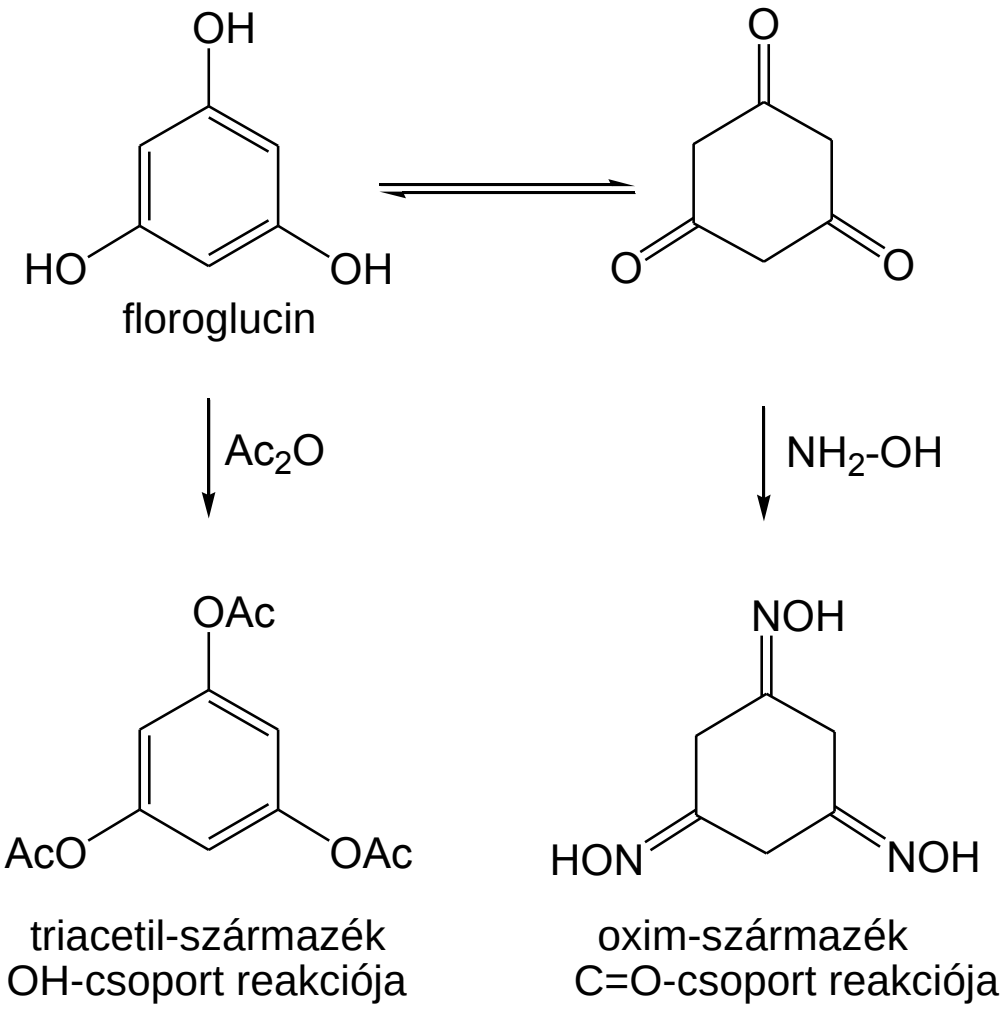
76% (enol alak)

-hidrogén-kötés
-konjugált kötésrendszer

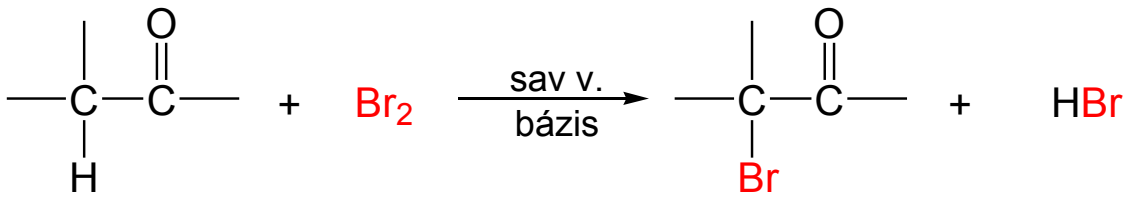
A fenolok tautomériája



Többértékű fenolok

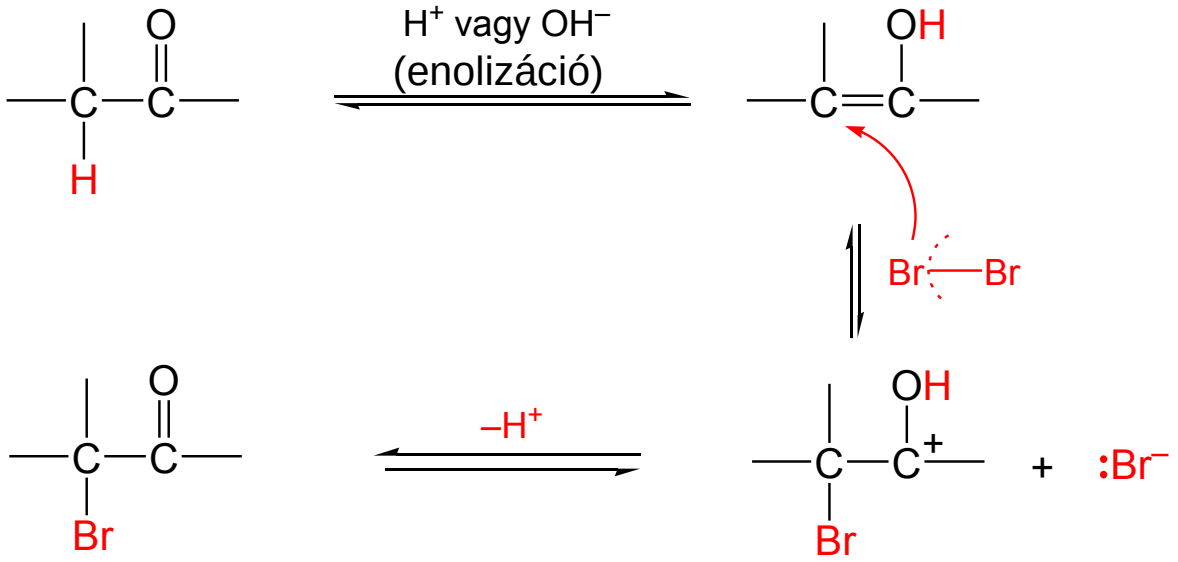


AZ OXOVEGYÜLETEK α-HELYZETŰ HALOGÉNEZÉSE

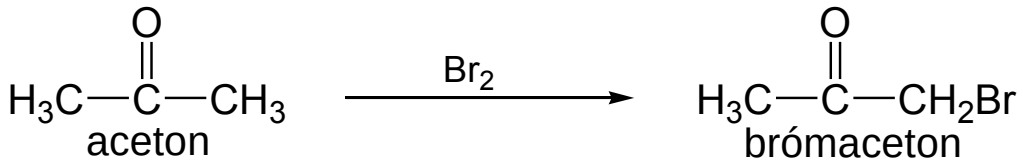


α-bróm-oxovegyület

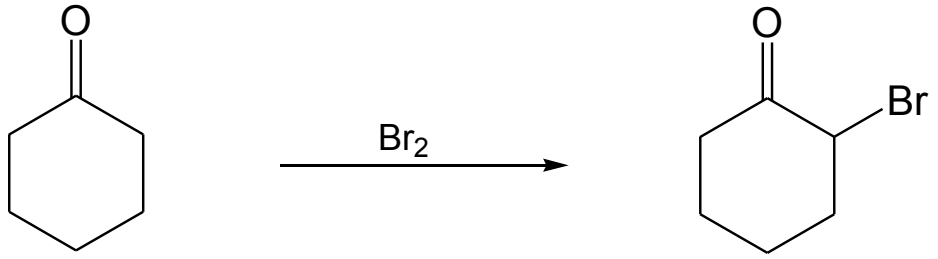
Mechanizmus



Példák

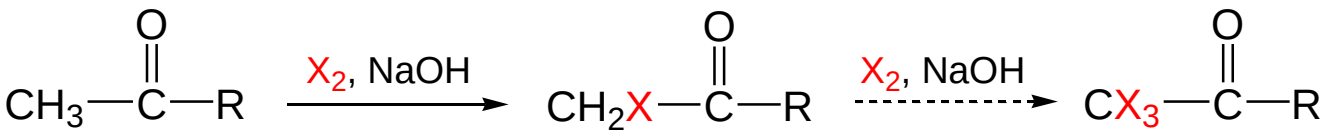


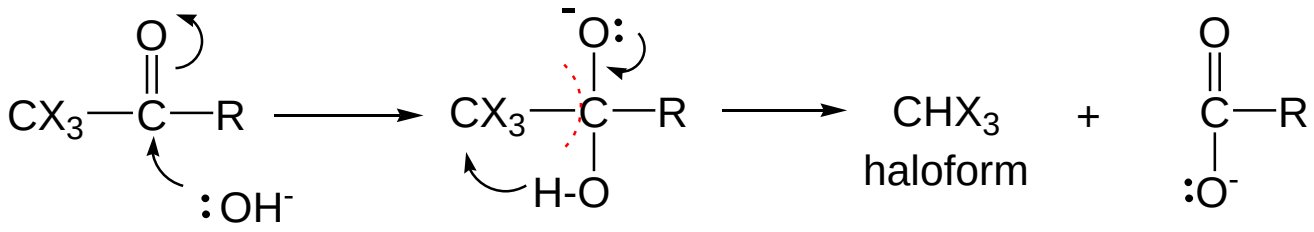
aceton brómaceton



ciklohexanon 2-brómciklohexanon

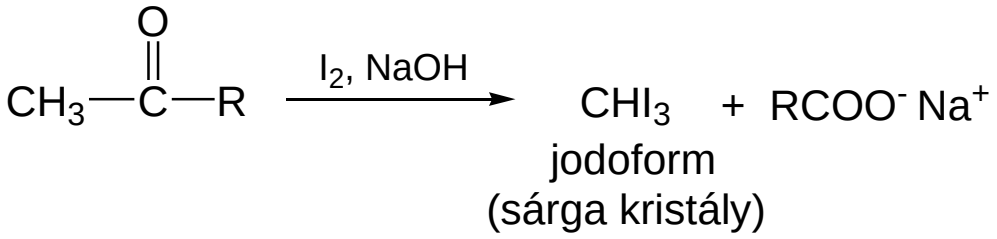
Metil-ketonok halogénezése (haloform-reakció)



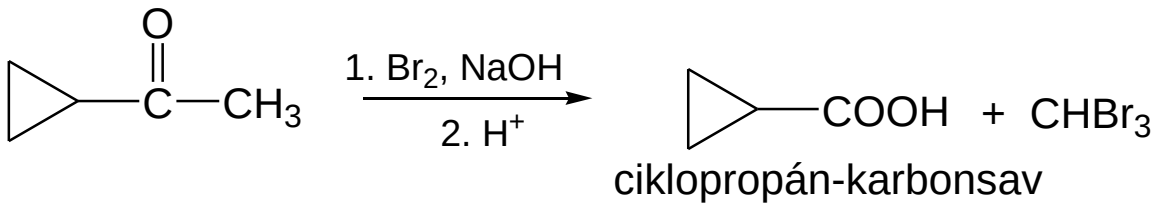


Alkalmazás

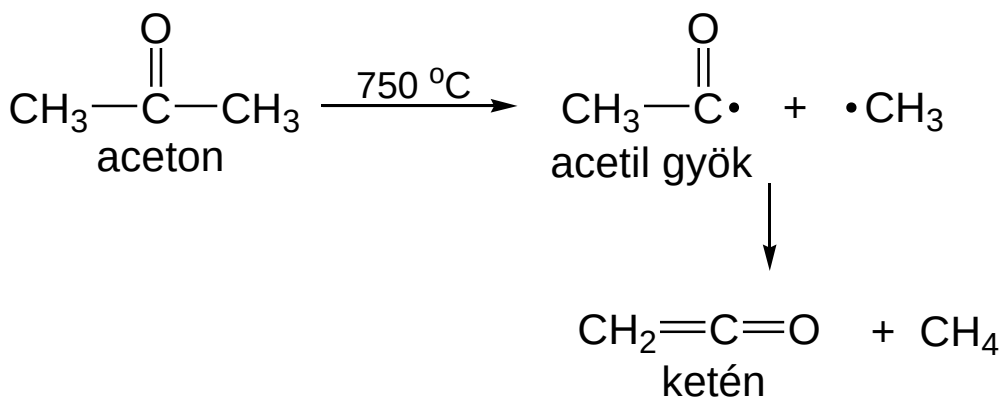
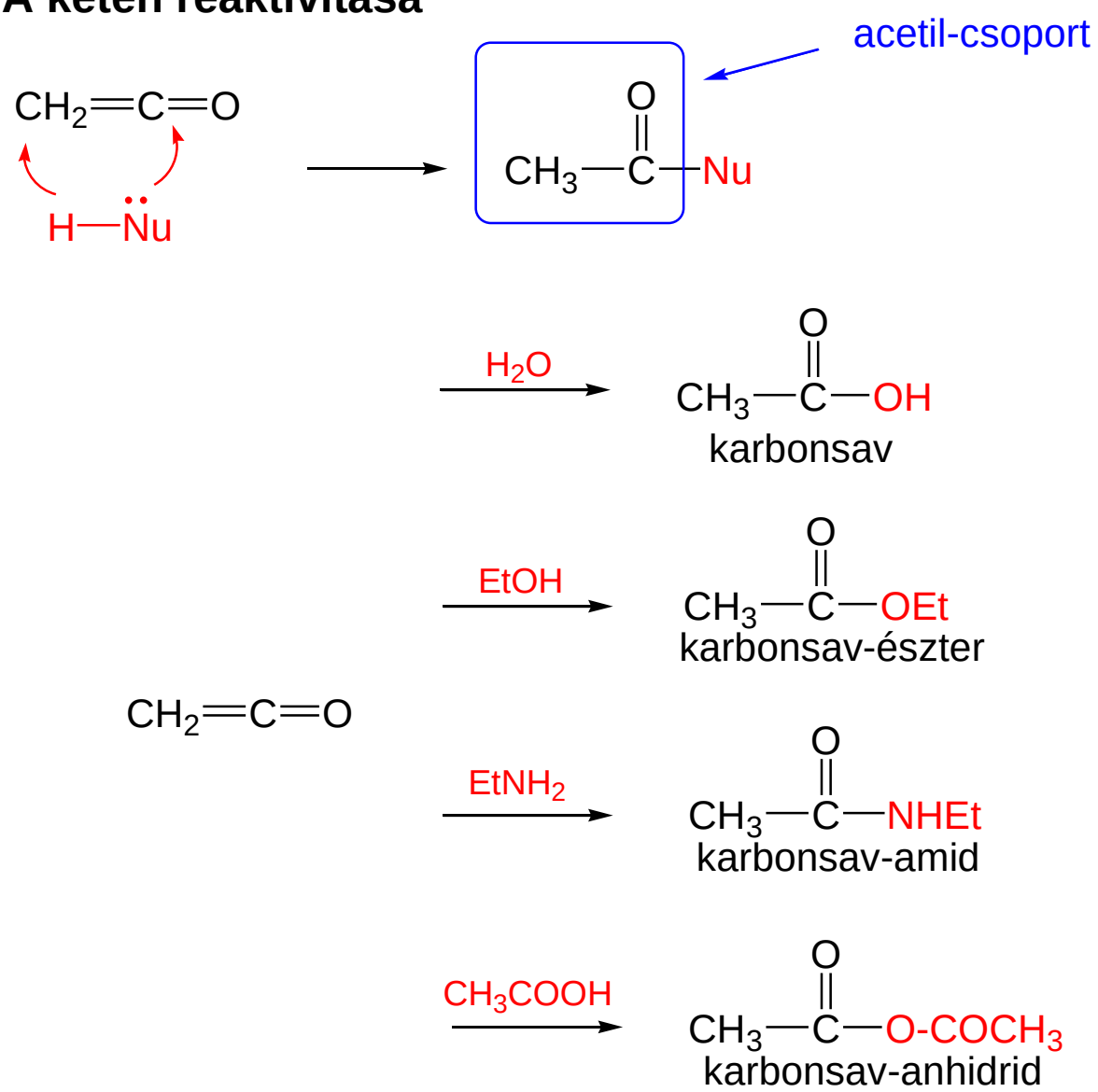
A) metil-ketonok kimutatása



B) karbonsavak előállítása



A ketén előállítása



A ketén reaktivitása