ALKOHOLOK ÉS SZÁRMAZÉKAIK

Levezetés

$$R{-}H \longrightarrow \underset{\text{alkohol}}{R{-}OH} \longleftarrow H{-}OH$$

$$R{-}O{-}H \longrightarrow \underset{\text{éter}}{R{-}O{-}R} \longleftarrow H{-}O{-}H$$

Elnevezés

Nyíltláncú, telített alkoholok

általános név: alkanol
alkil-alkohol

CH_3OH
metanol
metil-alkohol

CH_3CH_2OH
etanol
etil-alkohol

$CH_3CH_2CH_2OH$
propán-1-ol
propil-alkohol

$CH_3CH(OH)CH_3$
propán-2-ol
izopropil-alkohol

$CH_3CH_2CH_2CH_2OH$
bután-1-ol
butil-alkohol

$CH_3CH_2CH(OH)CH_3$
bután-2-ol
szek-butil-alkohol

$CH_3CH(CH_3)CH_2OH$
izobutil-alkohol

$(CH_3)_3C{-}OH$
terc-butil-alkohol

Telítetlen alkoholok

$C_nH_{2n-1}OH$ "alkenol"

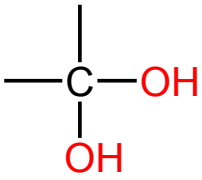
$C_nH_{2n-3}OH$ "alkinol"

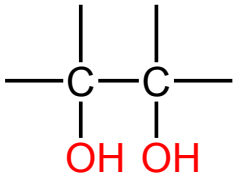
$CH_2{=}CHOH$
vinil-alkohol
(nem létképes)

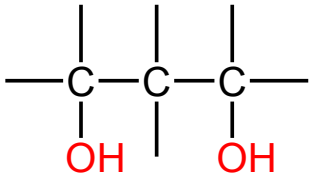
$CH_2{=}CHCH_2OH$
allil-alkohol

$CH{\equiv}CCH_2OH$
propargil-alkohol

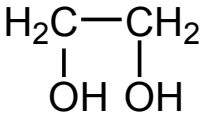
Többértékű alkoholok (diol, triol...)

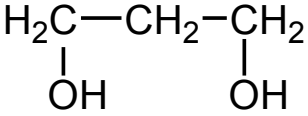

geminális

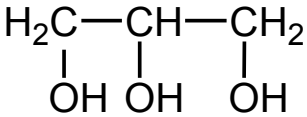

vicinális


diszjunkt

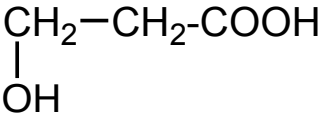
$HO{-}CH_2{-}OH$
metándiol
(nem létképes)

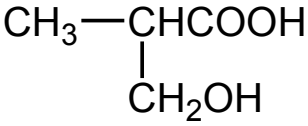

etilénglikol
(etán-1,2-diol)


propán-1,3-diol


glicerin
(propán-1,2,3-triol)

Származékok


3-hidroxi-propionsav


2-hidroximetil-propionsav

Csoportnevek

$R—O-H$ alkoxicsoport

pl. CH_3O- metoxicsoport

C_2H_5O- etoxicsoport

Sók

$R—O-H \xrightarrow{-H^+} R—\ddot{O}^-$ alkoxid ion

pl. $CH_3O^-\ Na^+$ nátrium-metoxid

Éterek

szimmetrikus éterek: dialkil-éter

vegyes éterek: alkil-alkil'-éter

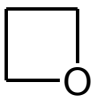
$CH_3—O—CH_3$ dimetil-éter

$C_2H_5—O—C_2H_5$ dietil-éter

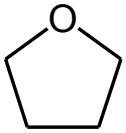
$CH_3—O—C_2H_5$ etil-metil-éter

Gyűrűs éterek

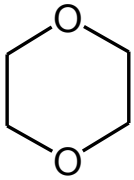
etilén-oxid



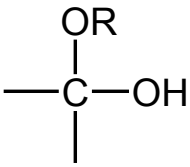
trimetilén-oxid



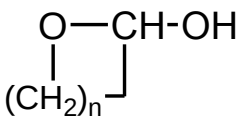
tetrahidrofurán (THF)



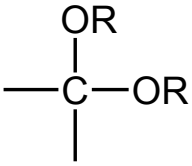
dioxán



félacetál (geminális diol féléter)



ciklofélacetál (laktol)

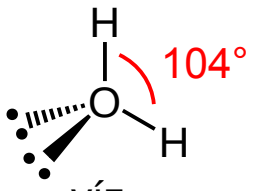


acetál (geminális diol diéter)

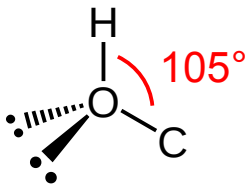
$R—O—O—H$ hidroperoxid

$R—O—O—R$ peroxid

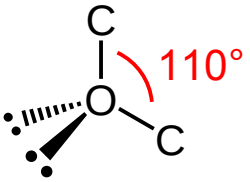
AZ ALKOHOLOK ÉS ÉTEREK SZERKEZETE



víz

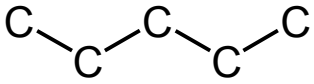


alkohol

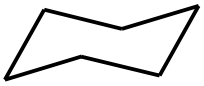


éter

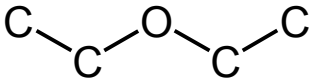
analóg szerkezetek



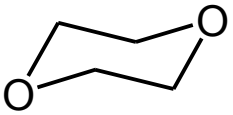
pentán



ciklohexán

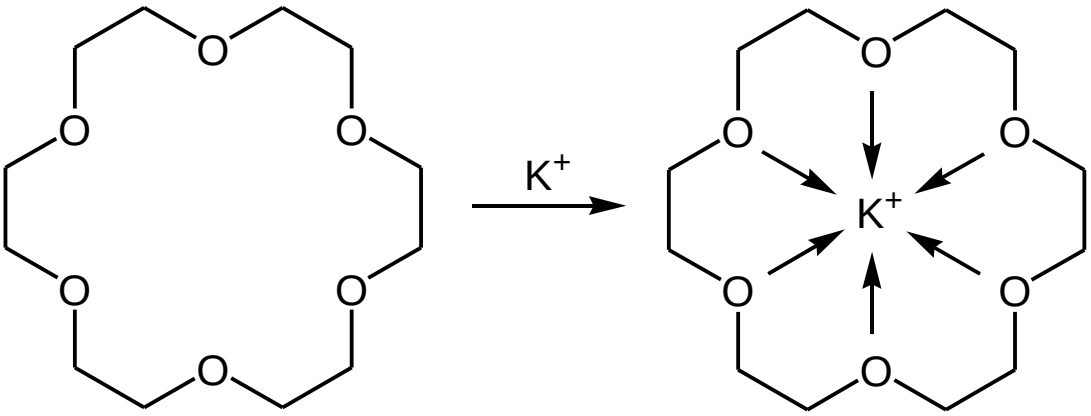


dietil-éter



dioxán

Koronaéterek



18-korona-6

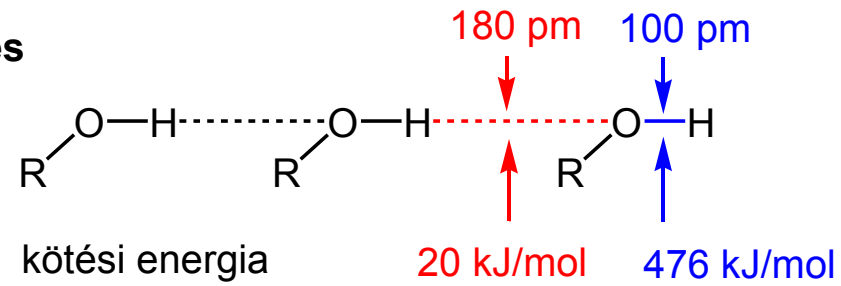
AZ ALKOHOLOK FIZIKAI TULAJDONSÁGAI

	Molekulatömeg	Forráspont (C°)
CH_3OH	32	65
CH_3CH_3	30	-89
CH_3CH_2OH	46	78
CH_3OCH_3	46	-24
$CH_3CH_2CH_3$	44	-42
$HOCH_2\text{-}CH_2OH$	62	200
$CH_3CH_2CH_2CH_3$	58	-1
$HOCH_2\text{-}CHOH\text{-}CH_2OH$	92	290
$CH_3(CH_2)_4CH_3$	86	69

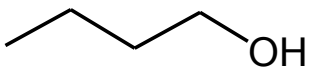
Vízoldhatóság

MeOH, EtOH, PrOH	$n\text{-}C_6H_{13}OH$	$HO\text{-}C_6H_{12}\text{-}OH$
korlátlan	0,6%	korlátlan

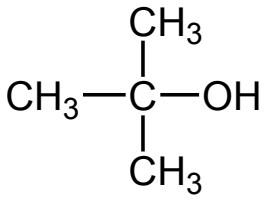
Hidrogénkötés



Olvadáspont



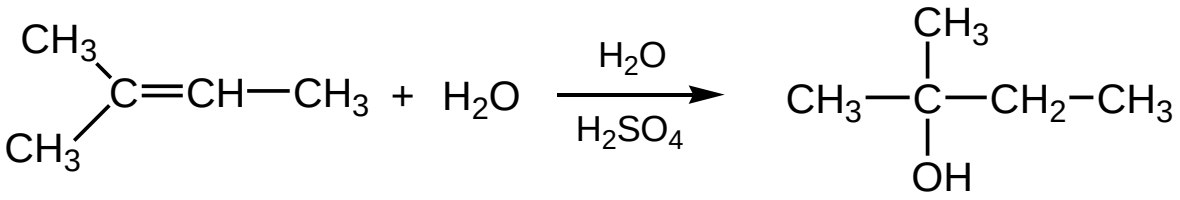
-90 °C



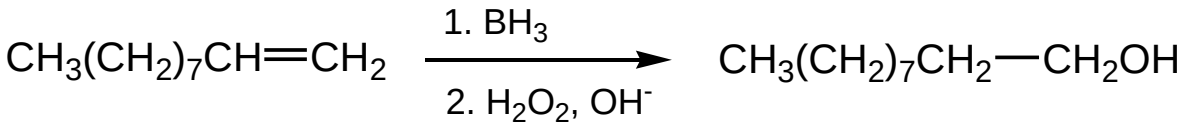
26 °C

AZ ALKOHOLOK ELŐÁLLÍTÁSA

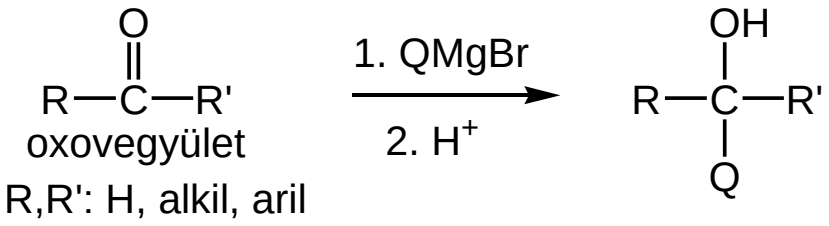
Alkének savkatalizált vízaddíciója (Markovnyikov termék)

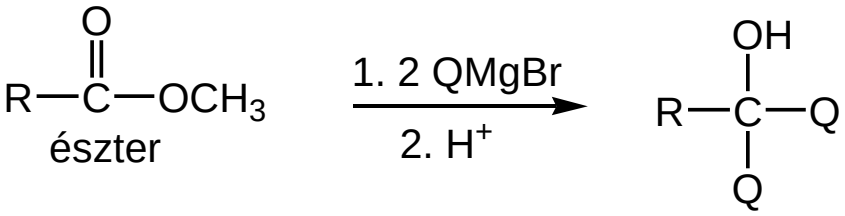


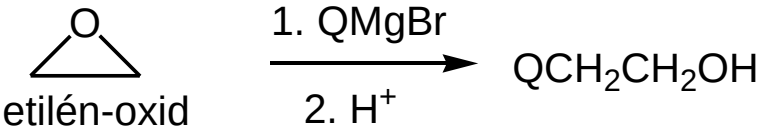
Alkének hidroborálása, oxidáció (anti-Markovnyikov termék)



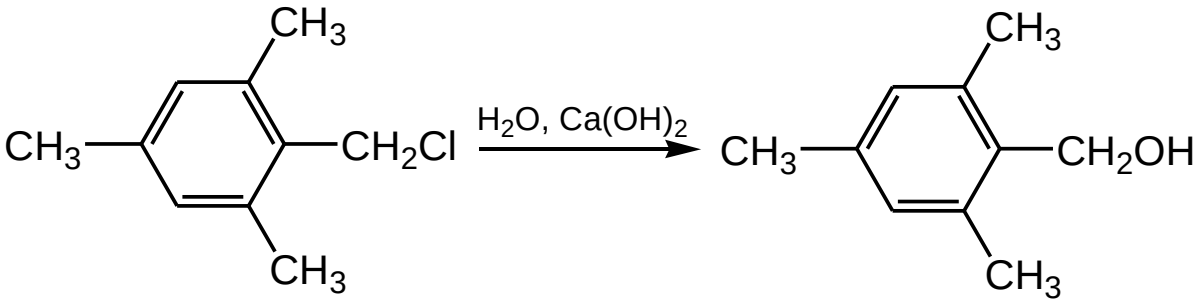
Reakciók Grignard-reagenssel





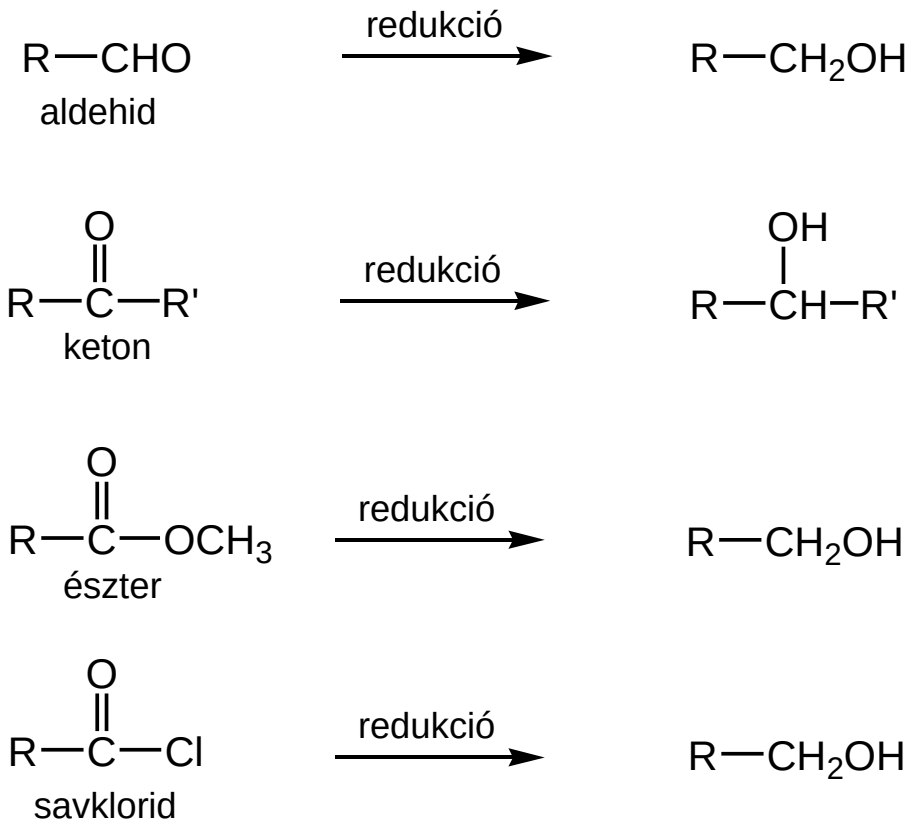


Alkil-halogenidek hidrolízise



2,4,6-trimetil-benzil-klorid 2,4,6-trimetil-benzil-alkohol

Oxovegyületek és karbonsavszármazékok redukciója
(ld. később)



AZ ALKOHOLOK REAKTIVITÁSA (ÖSSZEFOGLALÁS)

$CH_3CH_2—OH$

$\xrightarrow{NaH\ (bázis)}$ $CH_3CH_2—O^{\ominus}$ alkoxid ion

$\xrightarrow{R\text{-}X}$ $CH_3CH_2—OR$ éter

$\xrightarrow{R\text{-}CO\text{-}X}$ $CH_3CH_2—O\text{-}CO\text{-}R$ karbonsav észter

$\xrightarrow{R\text{-}SO_2\text{-}X}$ $CH_3CH_2—O\text{-}SO_2\text{-}R$ szulfonsav észter

$\xrightarrow{H\text{-}X}$ $CH_3CH_2—X$ alkil-halogenid

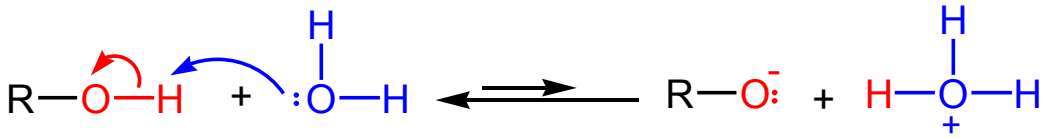
$\xrightarrow{CrO_3\ (oxid.)}$ $CH_3CH{=}O$ aldehid (CH_3COOH) (karbonsav)

$\xrightarrow{H_3O^+}$ $CH_2{=}CH_2$ alkén

$CH_3CH_2OCH_2CH_3$ éter

AZ ALKOHOLOK SAV-BÁZIS TULAJDONSÁGAI

Savi jelleg



H—A	MeOH	H_2O	EtOH	Me_3COH
K_s	$3{,}2 \times 10^{-16}$	$1{,}8 \times 10^{-16}$	$1{,}3 \times 10^{-16}$	$1{,}0 \times 10^{-19}$
pK_s	15.5	15.7	15.9	19

	CH_3CH_2OH	$ClCH_2\text{-}CH_2\text{-}OH$	$CF_3\text{-}CH_2\text{-}OH$
K_s	$1{,}3 \times 10^{-16}$	$5{,}0 \times 10^{-15}$	$4{,}0 \times 10^{-13}$
pK_s	15.9	14,3	12,4

Sóképzés

$$C_2H_5OH + HO^- \rightleftharpoons C_2H_5O^- + H_2O$$

$$C_2H_5OH + \underset{\text{amidion}}{NH_2^-} \longrightarrow C_2H_5O^- + NH_3$$

$$C_2H_5OH + Na \longrightarrow C_2H_5O^-\,Na^+ + 1/2\,H_2$$

Bázicitás

$$R\text{—}\ddot{O}H + HA \rightleftharpoons R\text{—}\overset{+}{O}H_2 + :A^-$$

$$R\text{—}\ddot{O}R + HA \rightleftharpoons R\text{—}\overset{+}{O}H\text{—}R + :A^-$$

AZ ALKOHOLOK KÉMIAI TULAJDONSÁGAI

Az alkoholok alkilezése; Williamson éterszintézis

$$R{-}O{-}H + Q{-}X \longrightarrow R{-}O{-}Q + HX$$

Alexander William Williamson (1824–1904) was born in London to Scottish parents. As a child, he lost an arm and the use of an eye. He was midway through his medical education when he changed his mind and decided to study chemistry. He received a Ph.D. from the University of Geissen in 1846. In 1849, he became a professor of chemistry at University College, London.

1. Primer alkil-halogenid (Q-X) $\longrightarrow$ S_N2

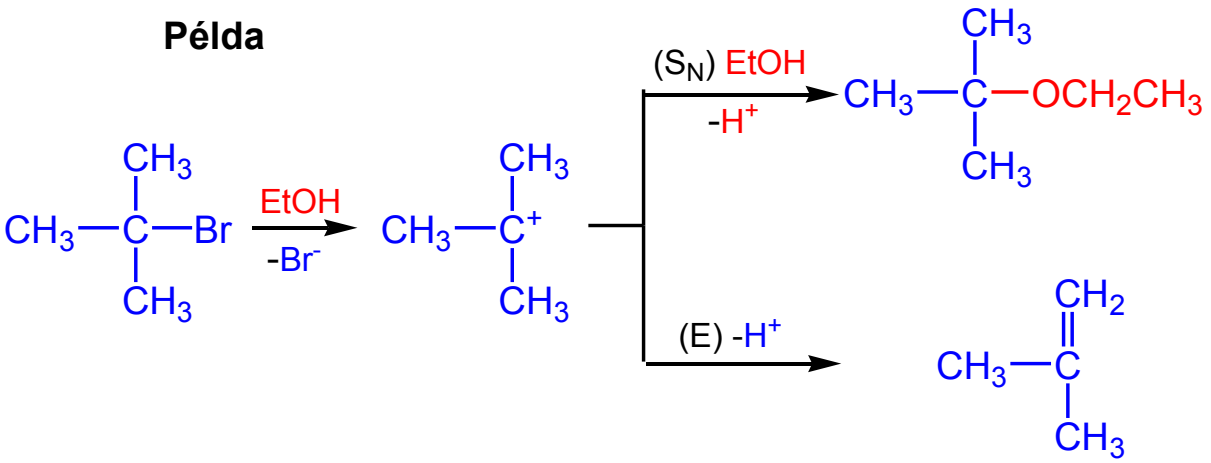
Példa

$$CH_3CH_2CH_2OH + NaH \longrightarrow CH_3CH_2CH_2O^-Na^+ + H\text{-}H$$

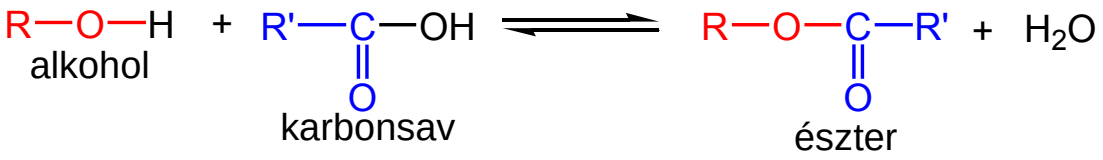
$$CH_3CH_2CH_2O^-Na^+ + CH_3CH_2I \xrightarrow{S_N2} CH_3CH_2CH_2OCH_2CH_3 + NaI$$

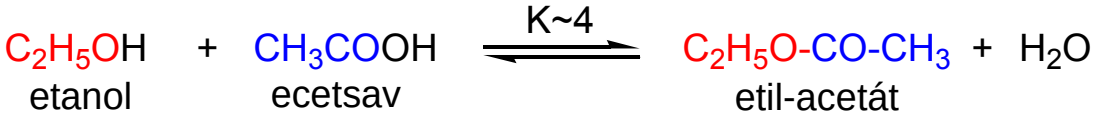
2. Tercier alkil-halogenid (Q-X) $\rightarrow$ S_N1 (éter); $\rightarrow$ E_1 (alkén)

Példa



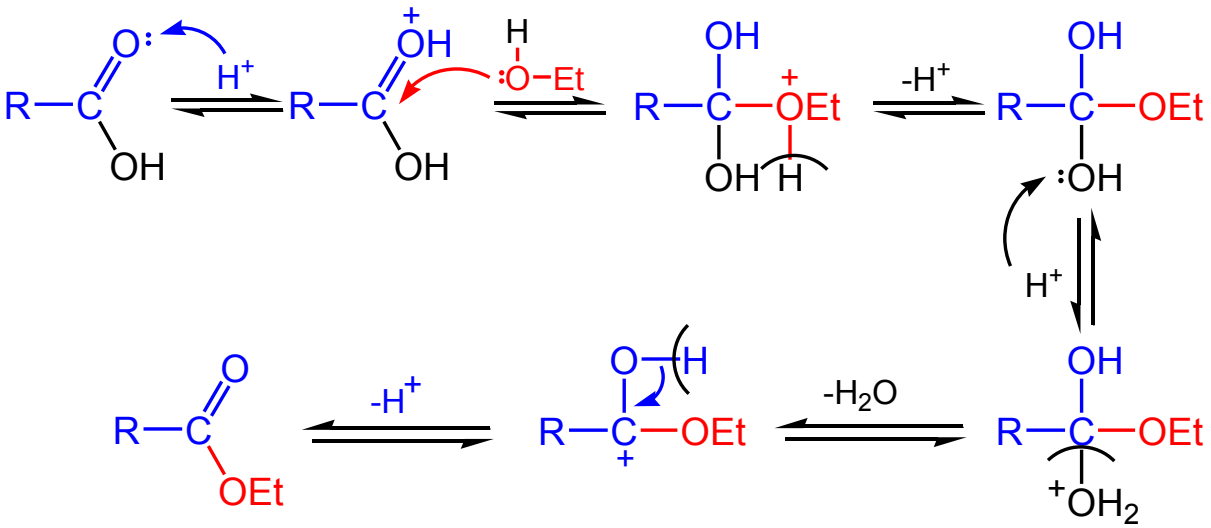
Az alkoholok acilezése. Közvetlen észteresítés.



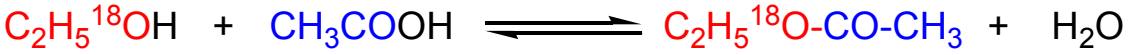


Savkatalizált észteresítés

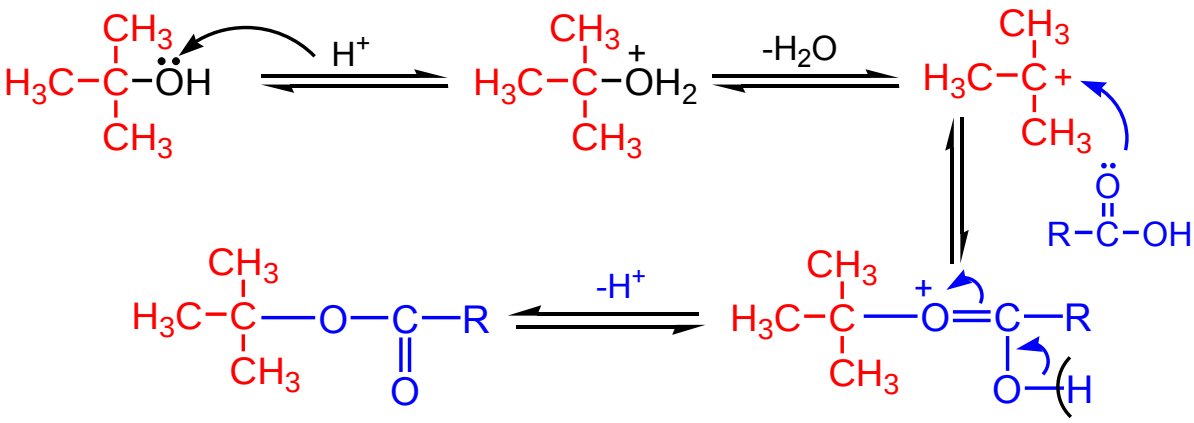
a) Primer alkoholok reakciója (pl. EtOH)



acil-O kapcsolat



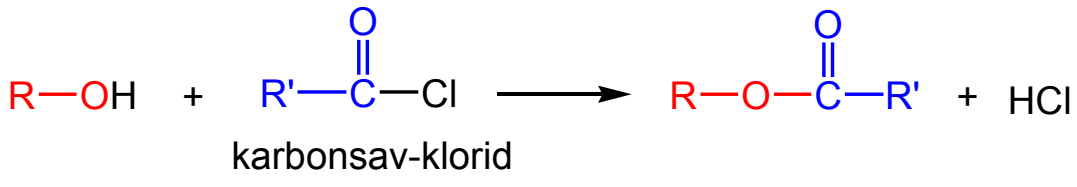
b) Tercier alkoholok reakciója (pl. terc-butil-alkohol)



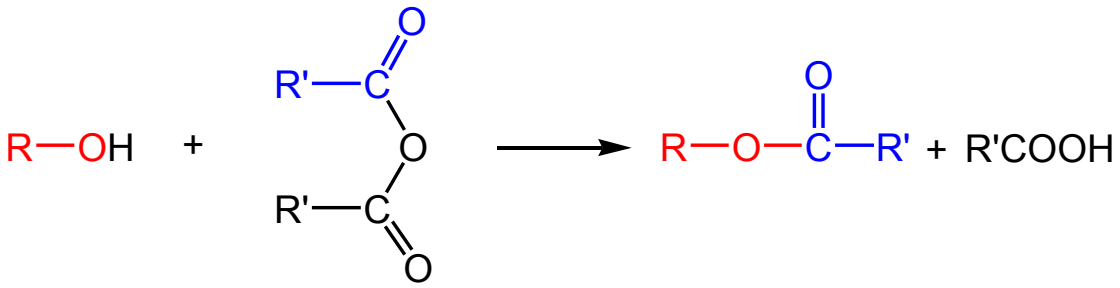
alkil-O kapcsolat

$(CH_3)_3C\text{-}^{18}OH + CH_3COOH \rightleftharpoons (CH_3)_3C\text{-}O\text{-}CO\text{-}CH_3 + H_2{}^{18}O$

Egyéb acilező reagensek (ld. karbonsavszármazékok reakciói)

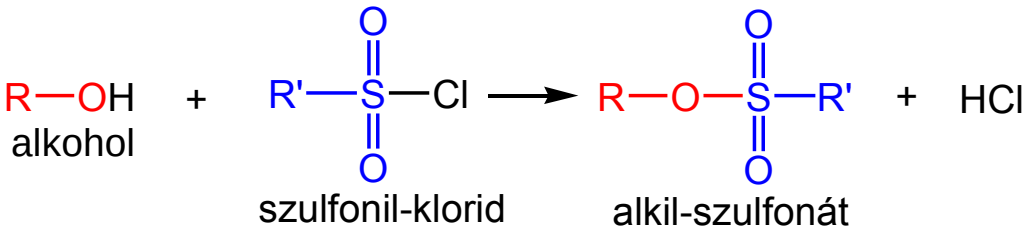


karbonsav-klorid

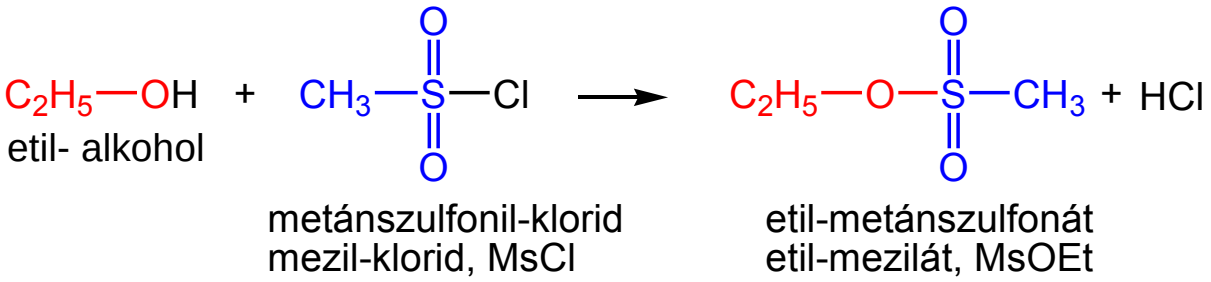


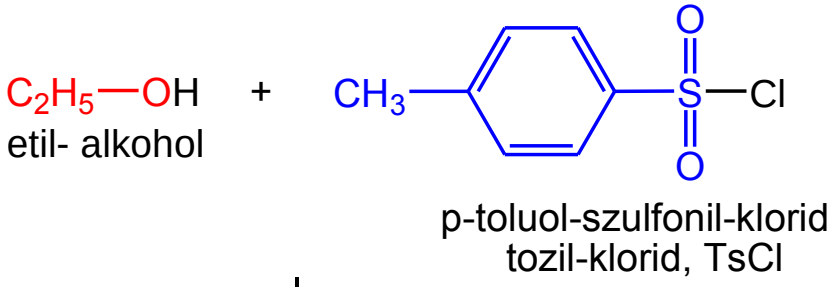
karbonsav-anhidrid

Szulfonsavak észterei

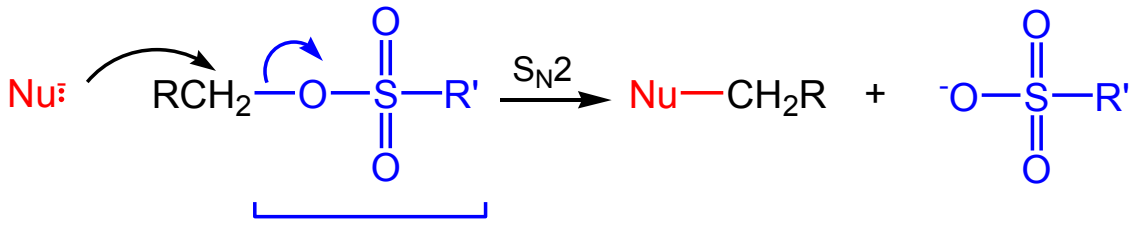


Példák



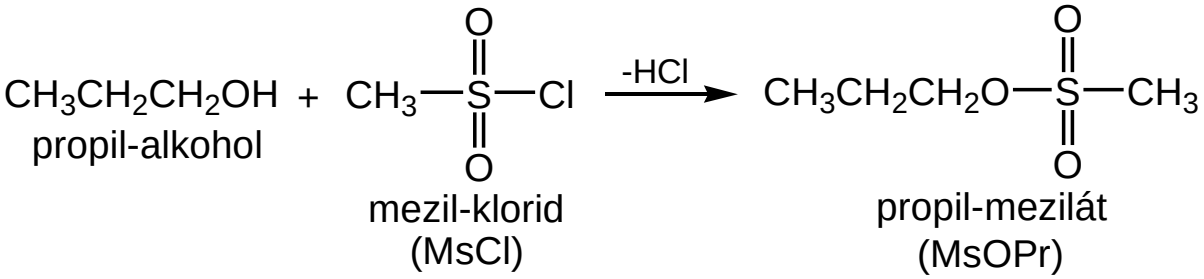


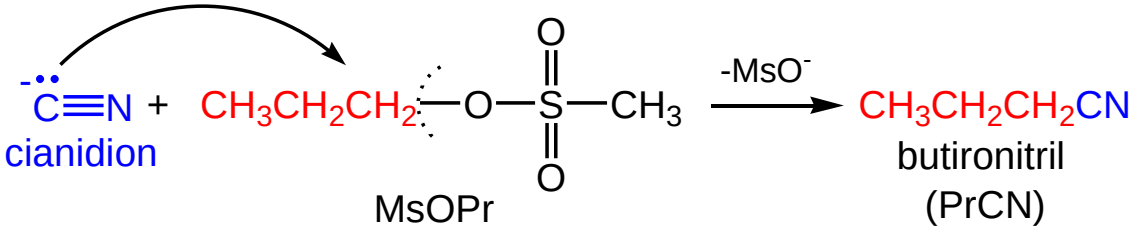
Szulfonátok felhasználása S_N2 reakciókban

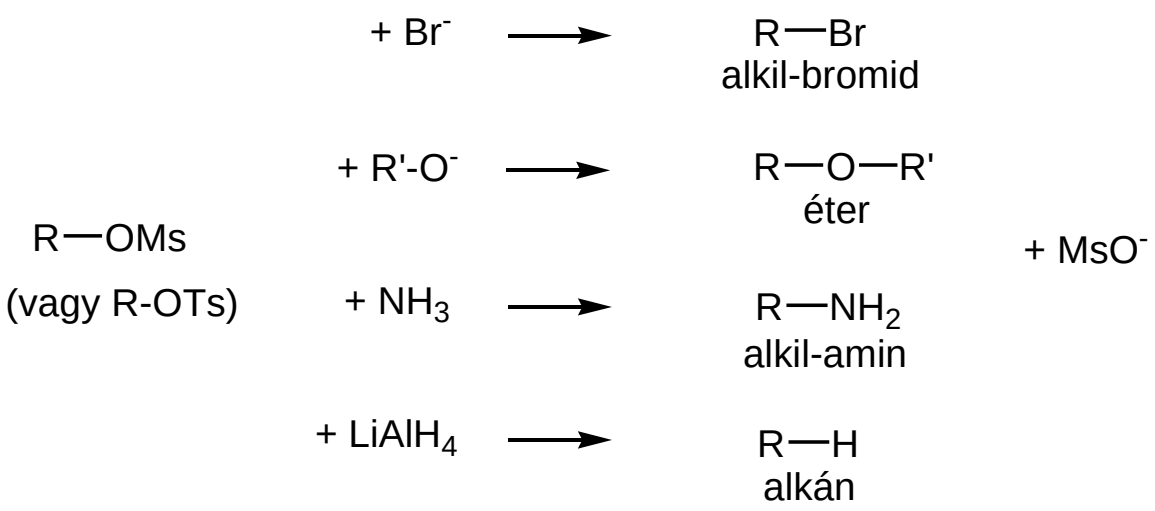


jó távozó csoport ($R'SO_2O^-$ gyenge bázis)

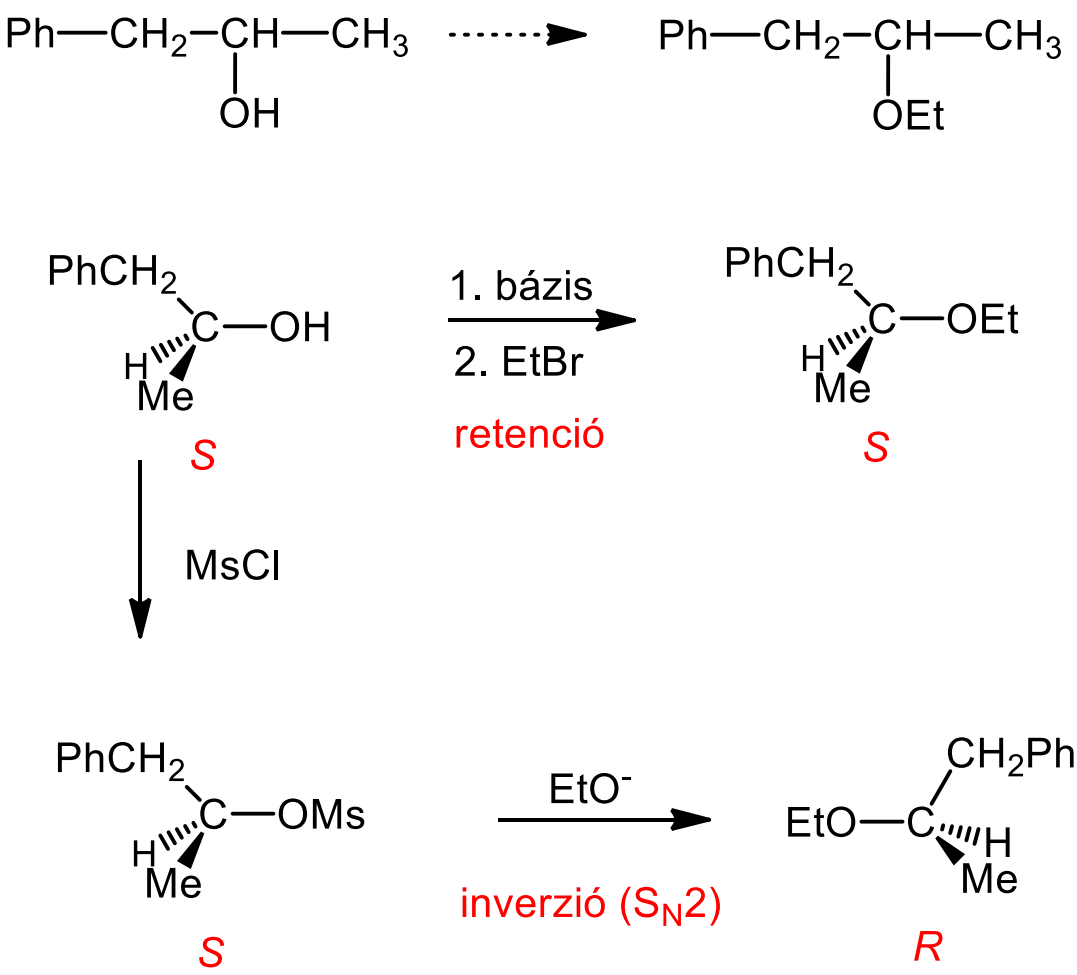
Példák







Sztereomechanizmus



Alkoholok szervetlen savakkal képzett észterei

Salétromossav észterek

$$R{-}OH + HONO \longrightarrow R{-}O{-}N{=}O$$

alkil-nitrit

Salétromsav észterek

$$R{-}OH + HONO_2 \longrightarrow R{-}O{-}NO_2$$

alkil-nitrát

$$\begin{array}{l} CH_2{-}OH \\ | \\ CH{-}OH \\ | \\ CH_2{-}OH \end{array} + HONO_2 \longrightarrow \begin{array}{l} CH_2{-}ONO_2 \\ | \\ CH{-}ONO_2 \\ | \\ CH_2{-}ONO_2 \end{array}$$

glicerin

glicerin-trinitrát

Kénsav észterek

$$R{-}OH + OH{-}SO_2{-}OH \longrightarrow RO{-}SO_2{-}OH$$

alkil-hidrogén-szulfát

$$CH_3OH \xrightarrow{H_2SO_4} CH_3O{-}SO_2{-}OH \xrightarrow{\text{deszt.}} CH_3O{-}SO_2{-}OCH_3$$

metil-hidrogén-szulfát

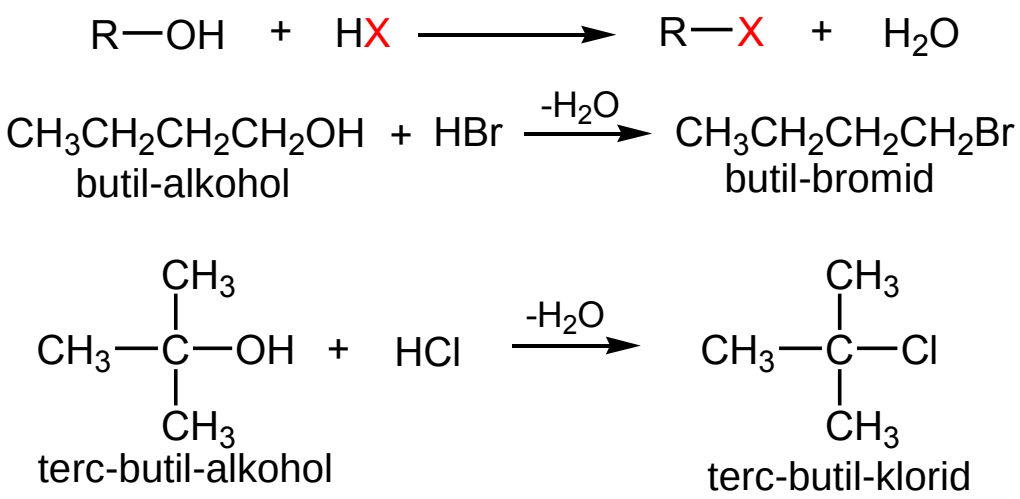
dimetil-szulfát

Foszforsav észterek

$$3\,R{-}OH + POCl_3 \longrightarrow RO{-}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle OR}{|}}{P}}{-}OR$$

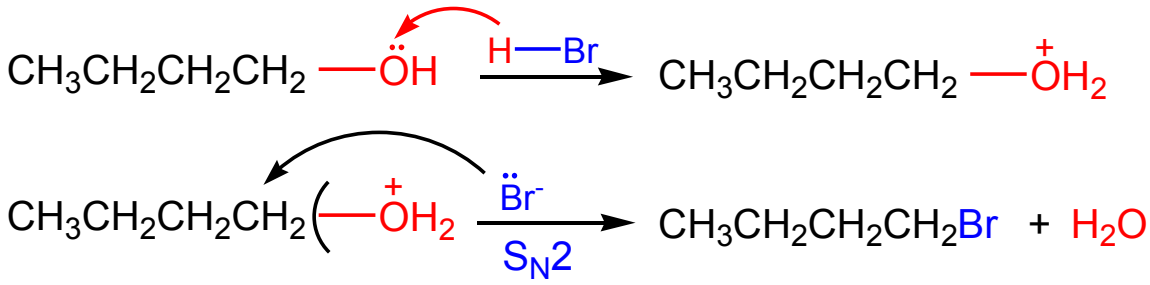
trialkil-foszfát

Alkil-halogenidek előállítása alkoholokból

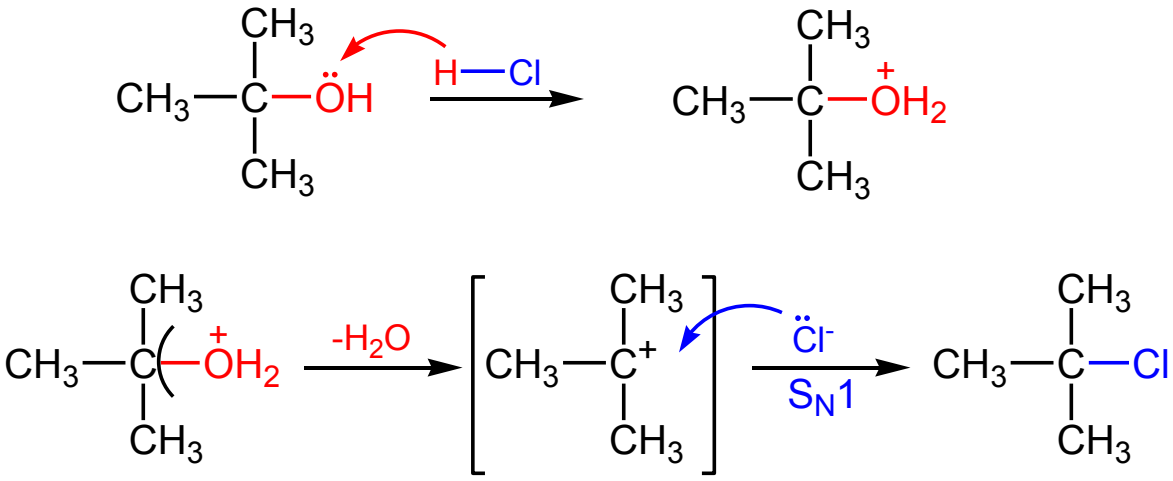


Mechanizmus

a) primer alkohol: S_N2



b) tercier alkohol: S_N1



Egyéb halogénező reagensek

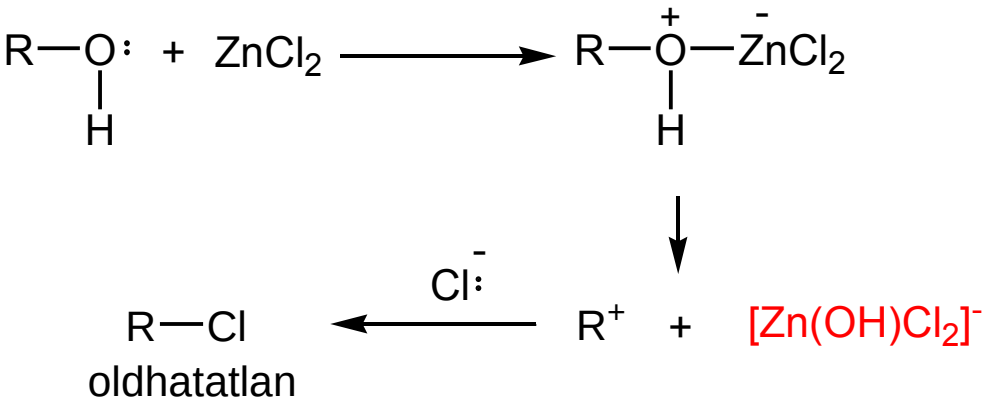
$$R{-}OH + PBr_3 \longrightarrow R{-}Br + H_3PO_3$$

foszfor-tribromid

$$R{-}OH + SOCl_2 \longrightarrow R{-}Cl + SO_2 + HCl$$

tionil-klorid

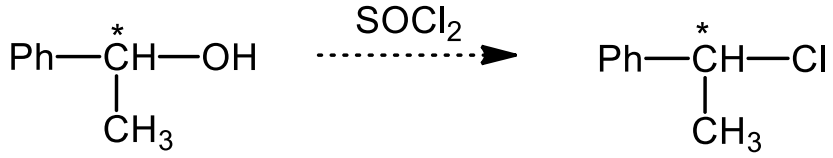
Lucas teszt (reakció cc. HCl + $ZnCl_2$ elegyével); alkoholok rendűségének meghatározása



alkohol	reakcióidő (perc)
primer	>10
szekunder	1-5
tercier	<1

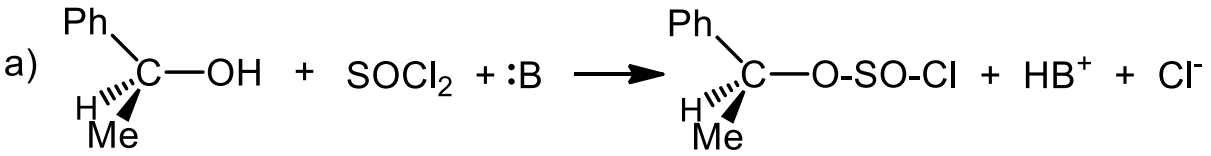
Howard J. Lucas (1885–1963) was born in Ohio and earned B.S. and M.S. degrees from Ohio State University. He published a description of the Lucas test in 1930. He was a professor of chemistry at the California Institute of Technology.

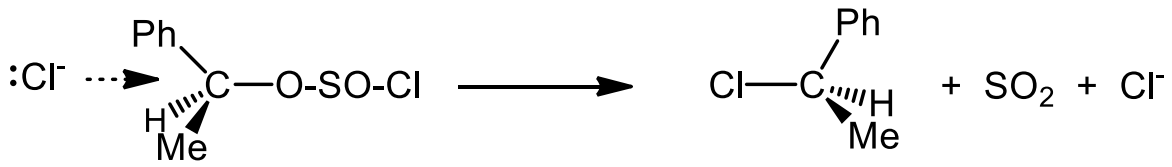
A halogénezés sztereomechanizmusa

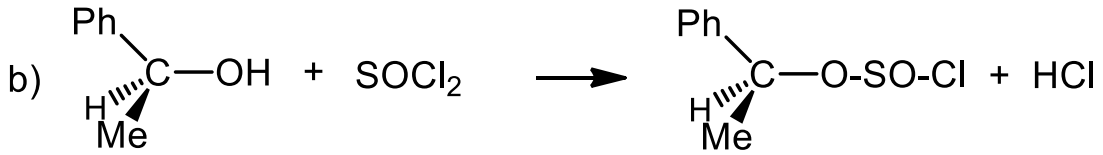


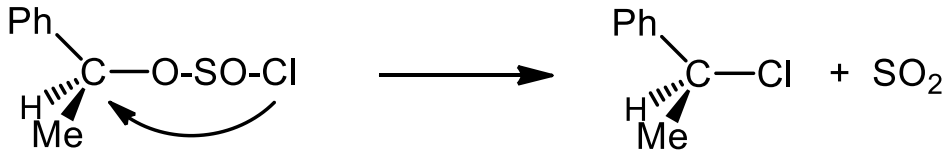
a) bázis jelenlétében ⟶ inverzió

b) bázis nélkül ⟶ retenció



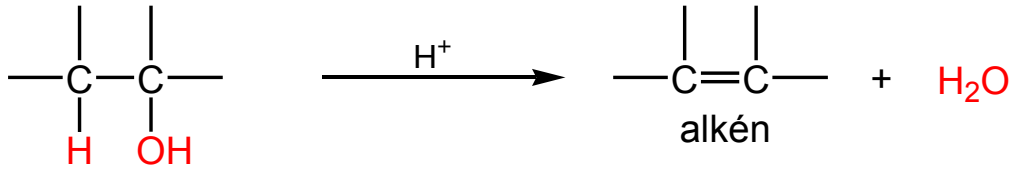




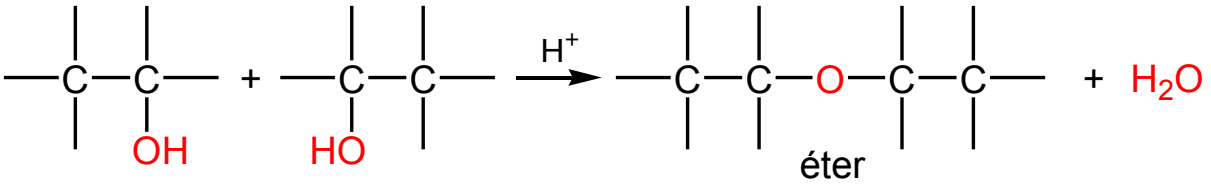


Az alkoholok dehidratálása

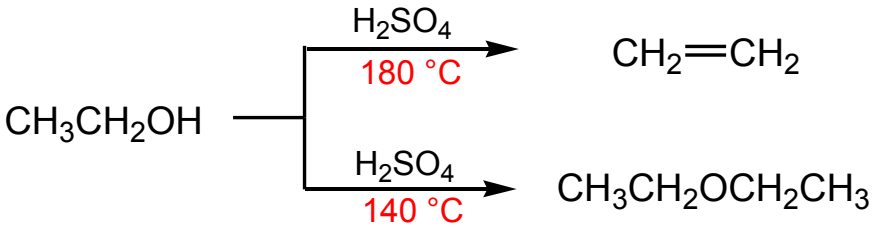
a) elimináció

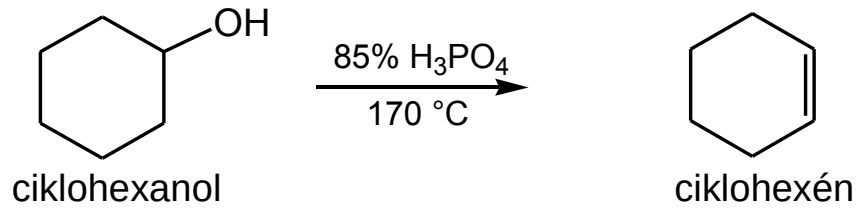


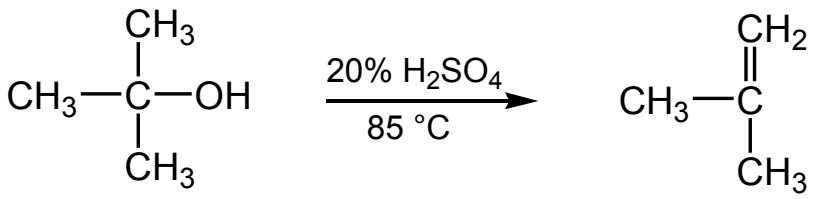
b) szubsztitúció



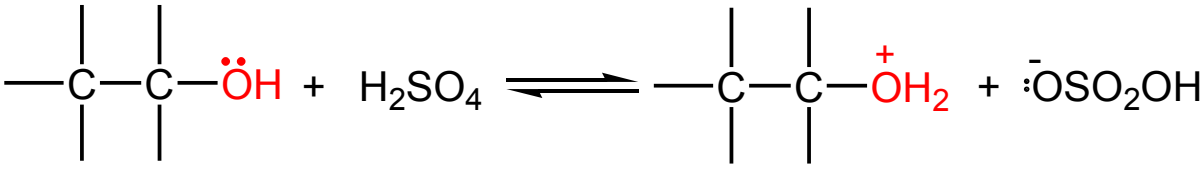
Példák





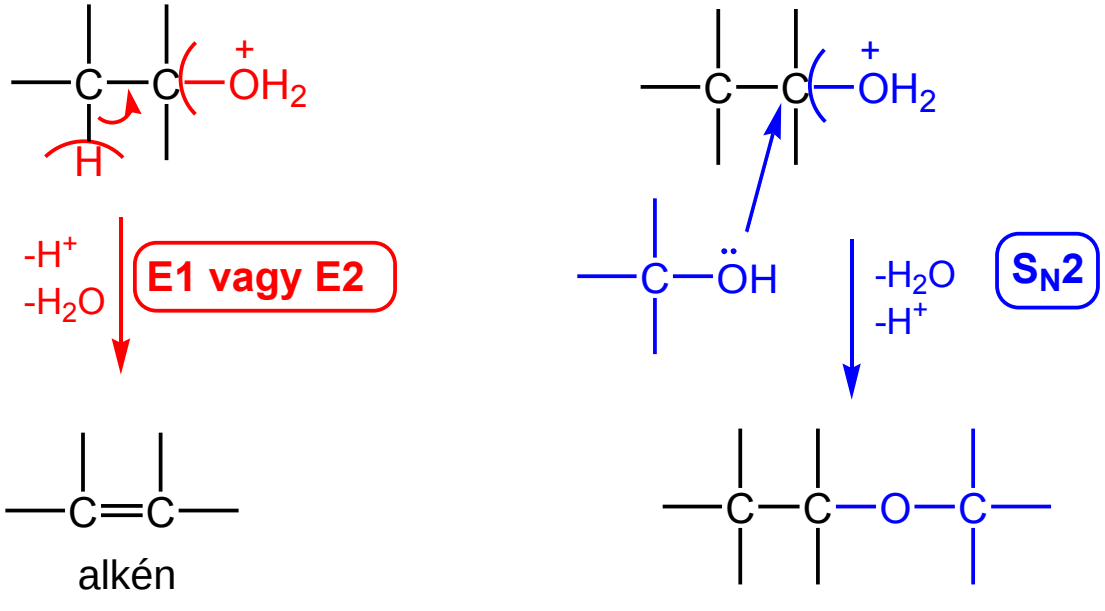


Mechanizmus



a) elimináció

b) szubsztitúció

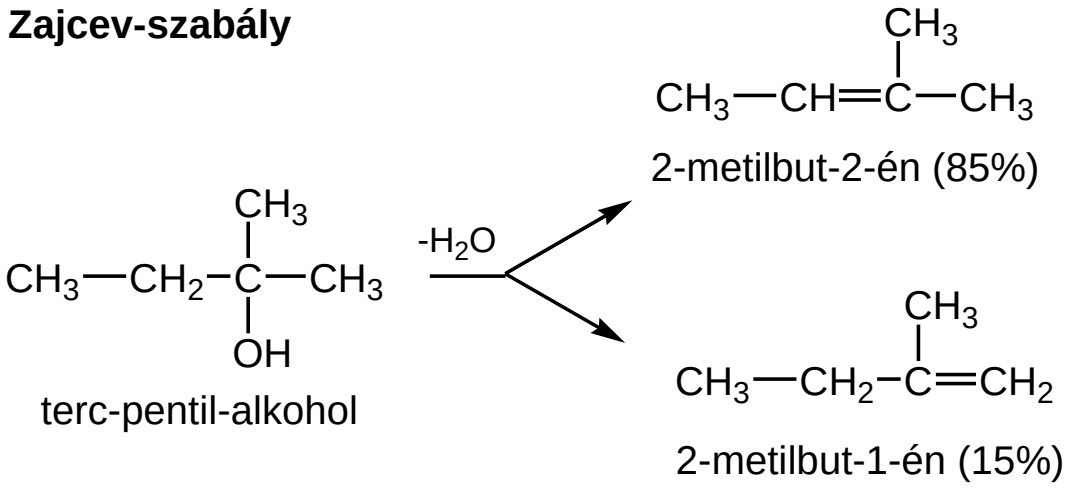


1. Primer alkohol ⟶ éter (S_N2), alkén (E2) (hőmérsékletfüggés)

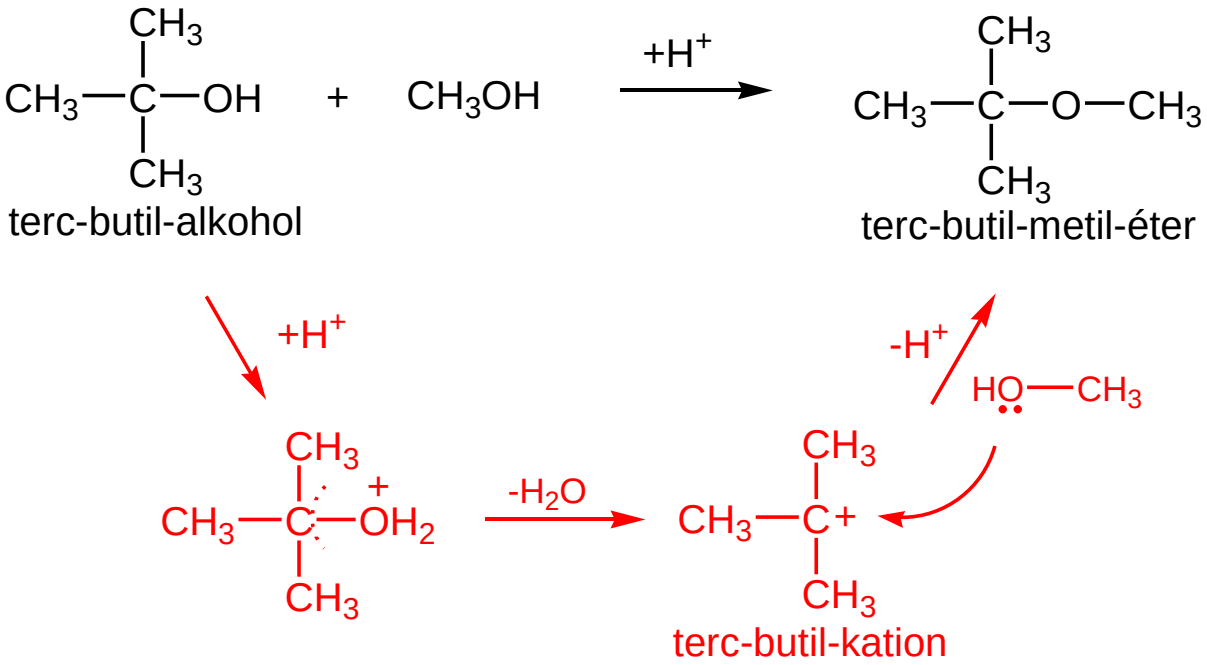
2. Szekunder alkohol ⟶ **alkén**, éter

3. Tercier alkohol ⟶ alkén (E_1)

Zajcev-szabály

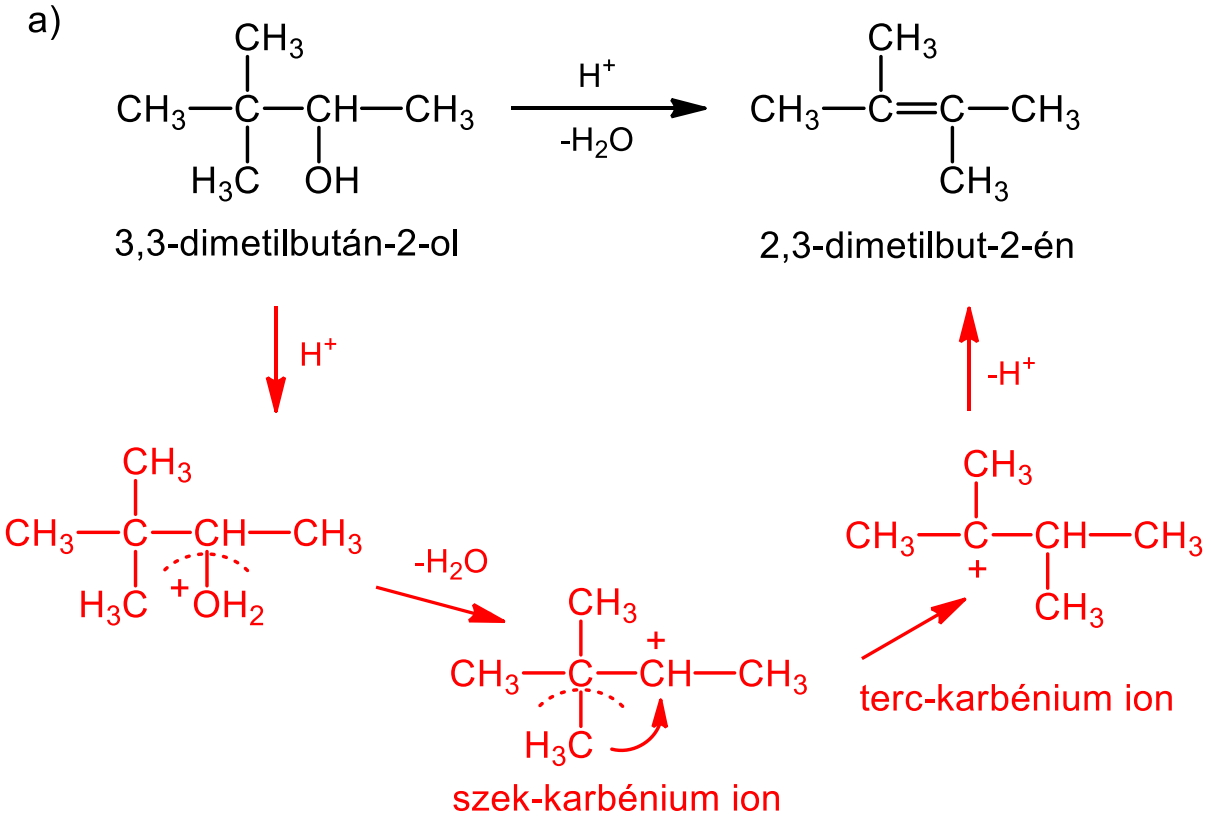


Vegyes éter előállítása

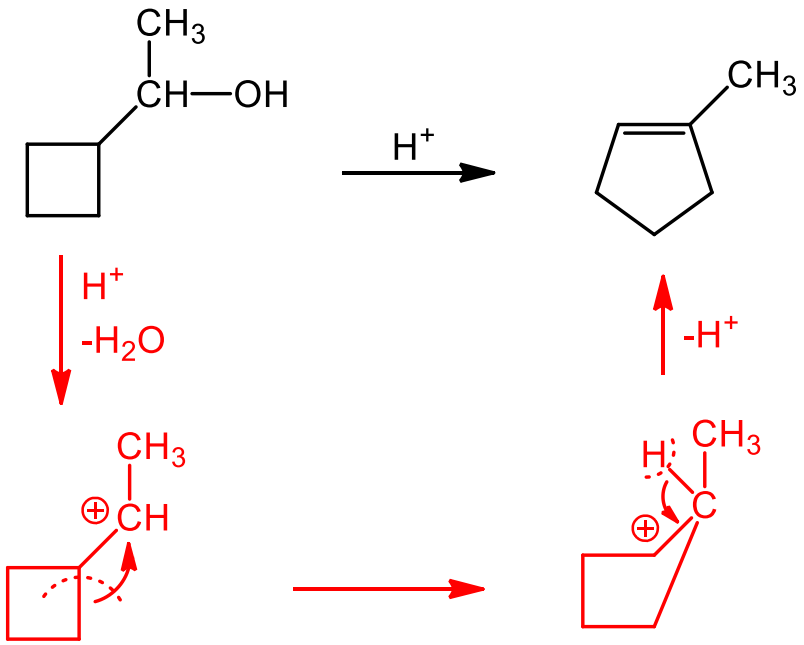


Dehidratálás átrendeződéssel (Wagner-Meerwein)

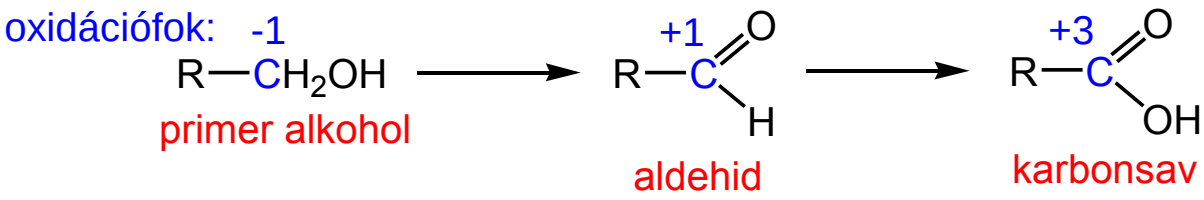
a)

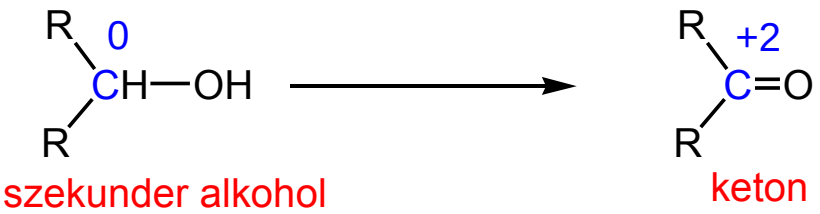


b)



Az alkoholok oxidációja





oxidálószerek: CrO_3, $Na_2Cr_2O_7$, $KMnO_4$

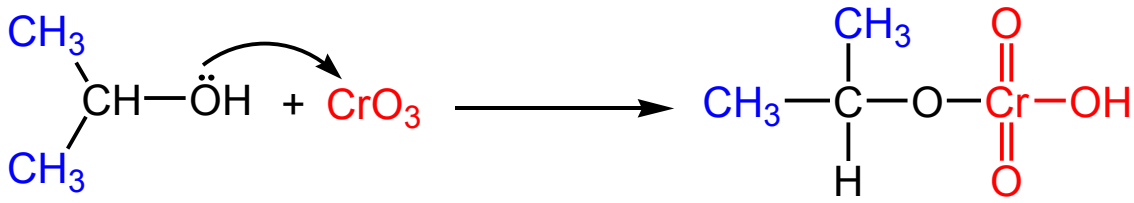
Példa

$$3\ (CH_3)_2CH\text{-}OH + 2CrO_3 + 6H^+ = 3(CH_3)_2CO + 2Cr^{3+} + 6H_2O$$

izopropil-alkohol aceton

A króm-trioxidos oxidáció mechanizmusa

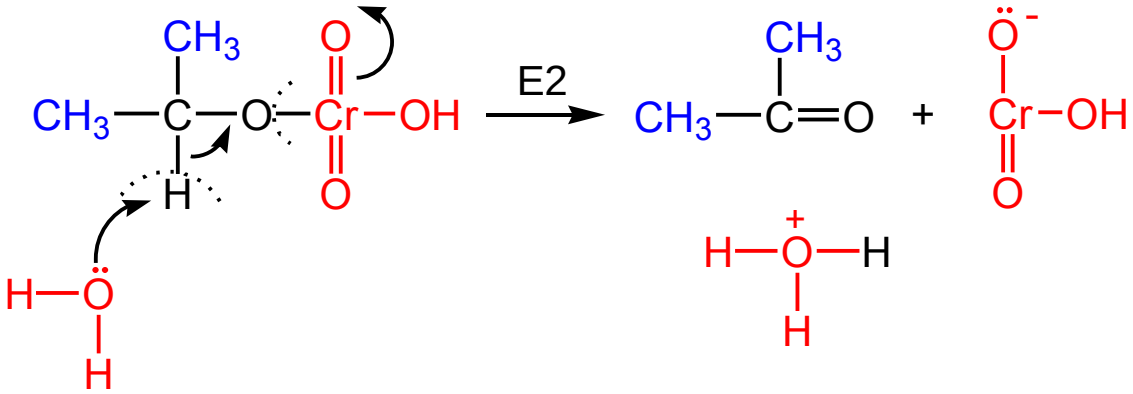
1. addíció



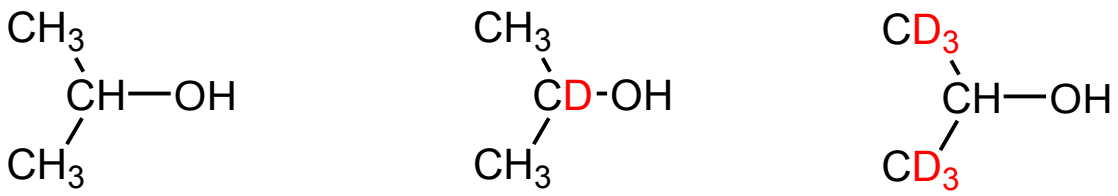
krómsav-észter

2. elimináció (E2)

sebességmeghatározó lépés

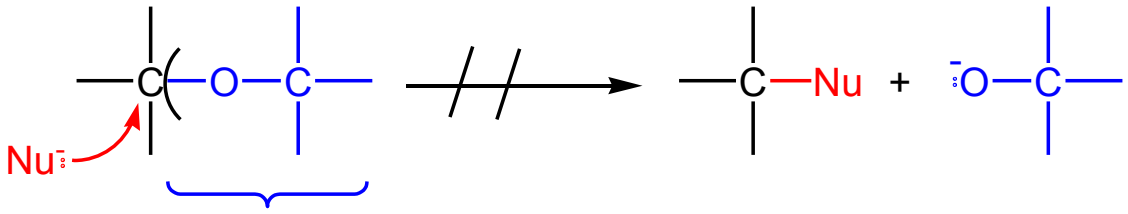


Bizonyíték (kinetikai izotópeffektus; C-D kötés nehezebben hasad, mint a C-H kötés)



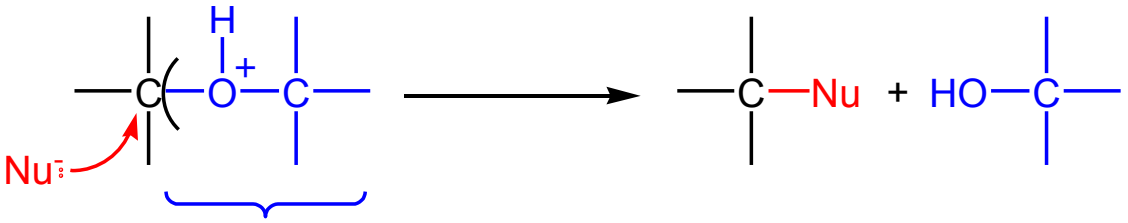
k_{rel}	1	0.16	1

Az éterkötés hasítása



R-O$^-$ rossz távozó csoport ⟶ nem hasítható

savas közegben



R-OH jó távozó csoport ⟶ hasítható

Példa

$CH_3CH_2OCH_2CH_3$ + 2 HBr ⟶ 2 CH_3CH_2Br + H_2O

dietil-éter — etil-bromid

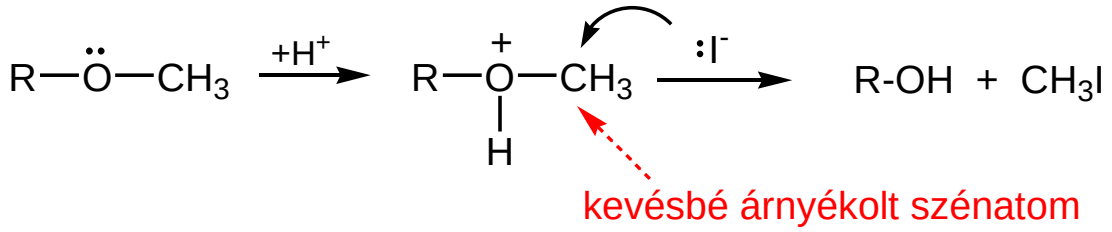
Mechanizmus

1. $CH_3CH_2\ddot{O}CH_2CH_3$ + HBr ⟶ $CH_3CH_2\overset{+}{O}(H)-CH_2CH_3$ + $\ddot{Br}^-$

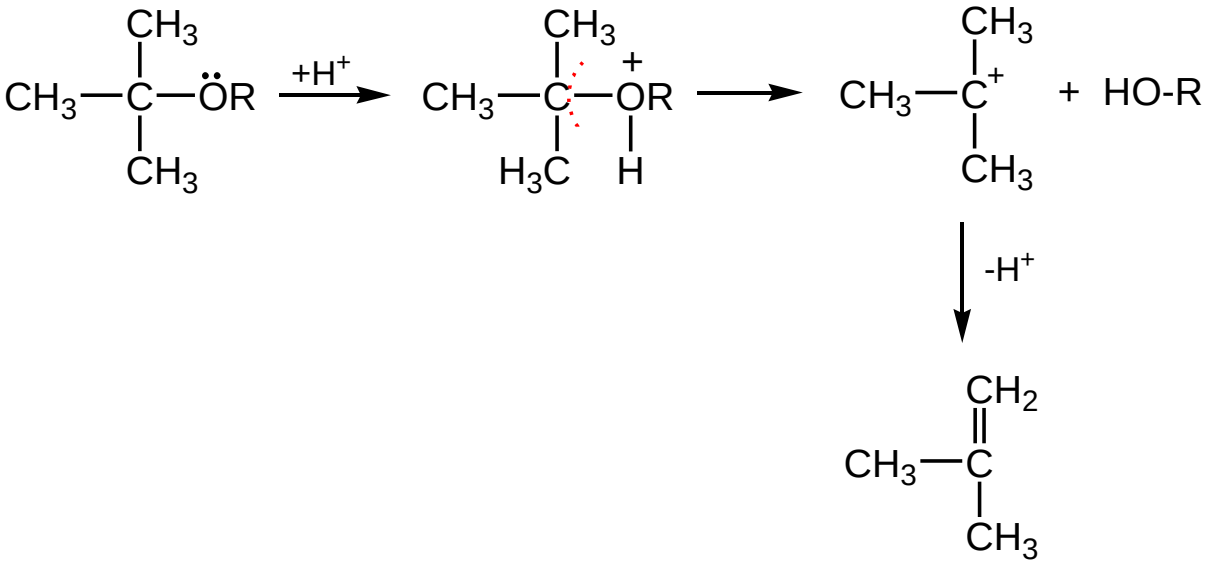
2. $CH_3CH_2\overset{+}{O}(H)-CH_2CH_3$ + $\ddot{Br}^-$ ⟶ CH_3CH_2OH + CH_3CH_2Br

3. CH_3CH_2OH + HBr ⟶ CH_3CH_2Br + H_2O

Metil-éterek hasítása

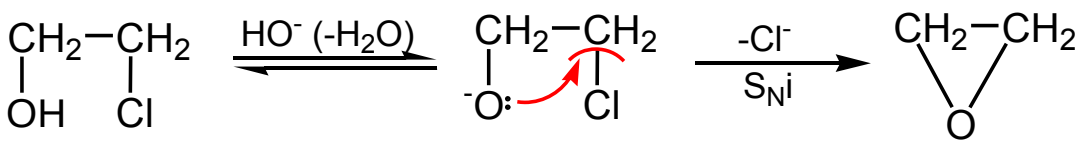


Terc-alkil-éterek hasítása



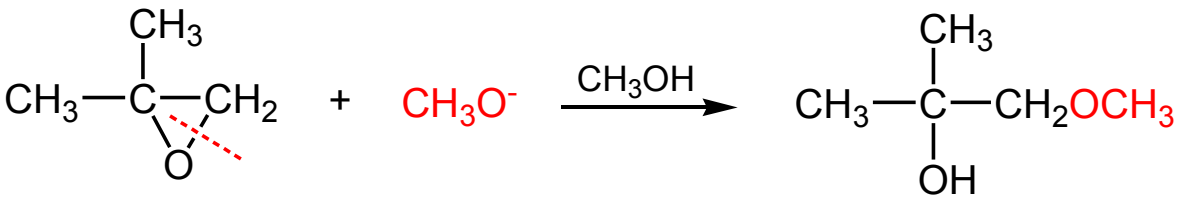
Epoxidok (oxiránok)

Előállítás

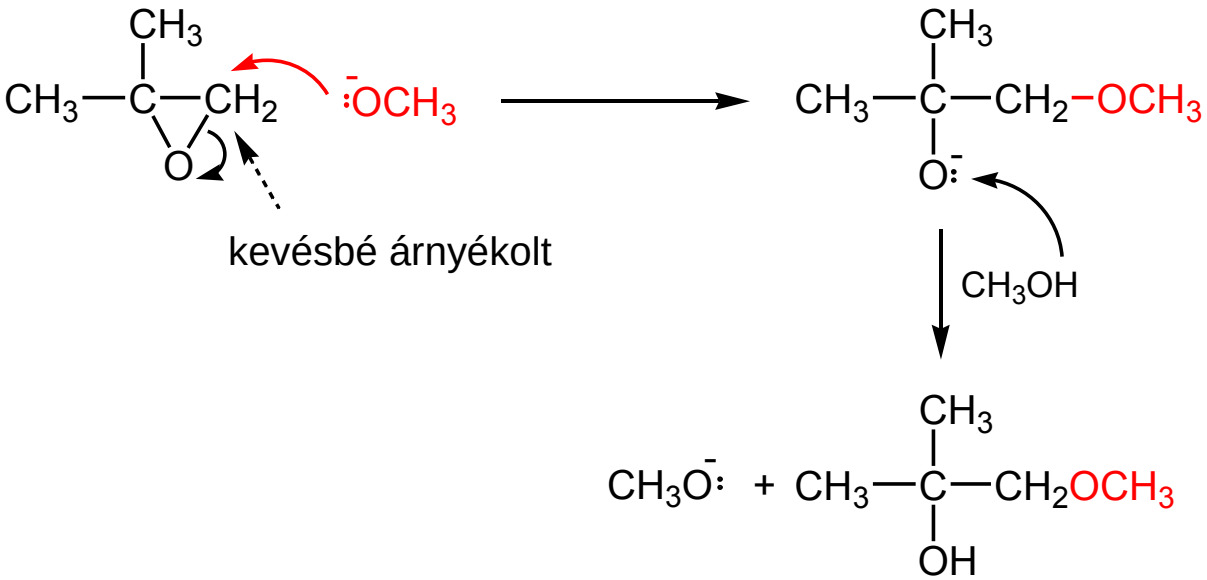


Az epoxidok hasítása

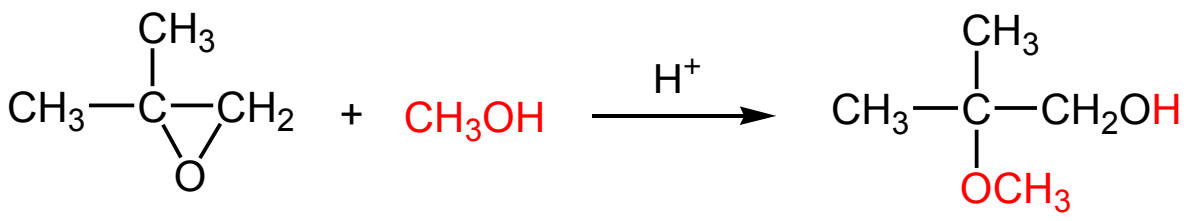
A) Bázikus közeg



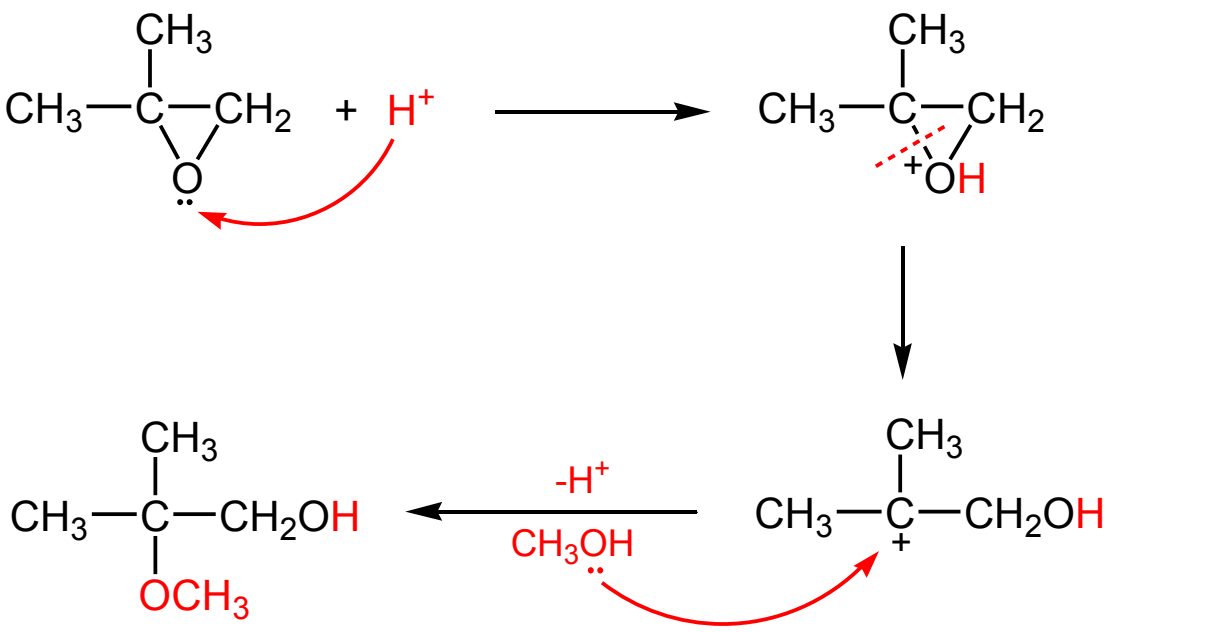
Mechanizmus (S_N2)



A) Savas közeg



Mechanizmus (S_N1)



stabilisabb karbénium ion

Az etilén-oxid reakciói