

5. Előadás

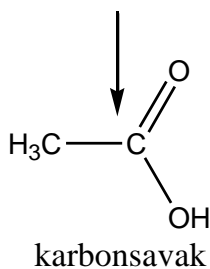
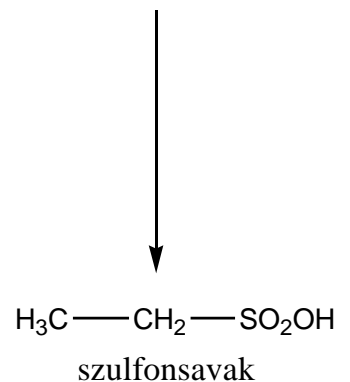
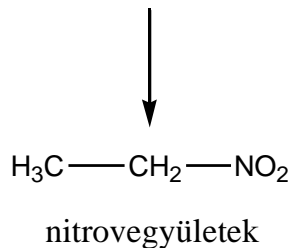
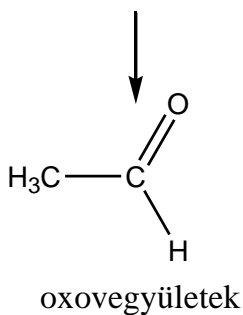
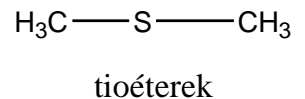
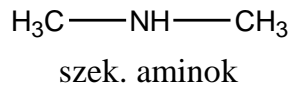
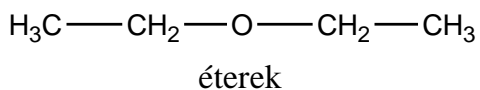
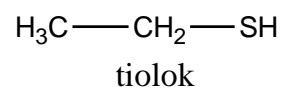
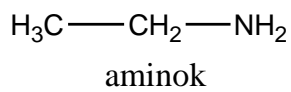
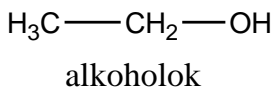
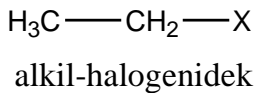
Halogénezett szénhidrogének.

Fémorganikus vegyületek.

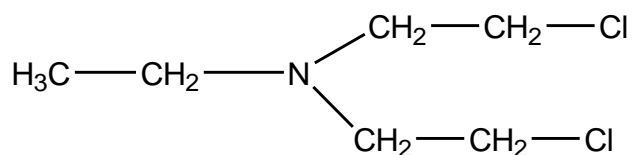
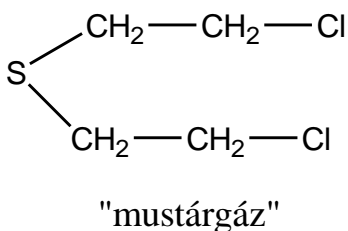
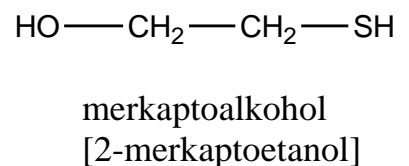
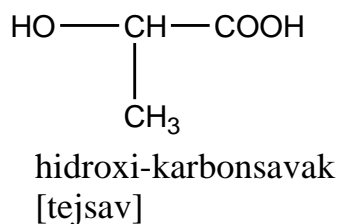
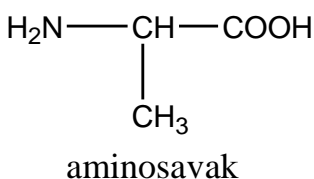
Alkoholok, éterek. Szteroidok.

SZÉNVEGYÜLETEK HETEROATOM(OK)KAL: ÁTTEKINTÉS

Egy heterofunkciós csoport (X, O, N, S, P tartalom)

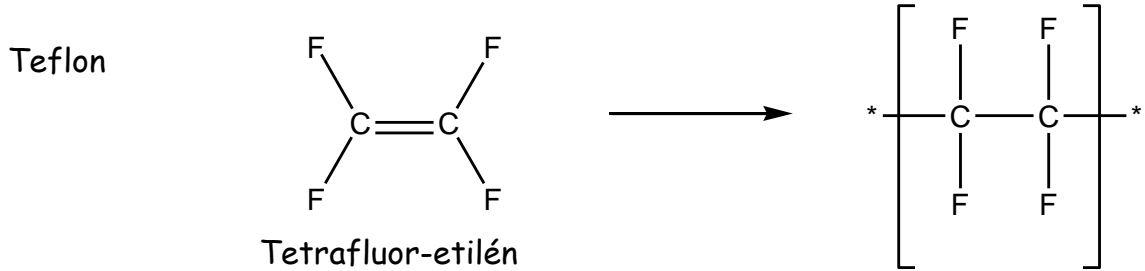
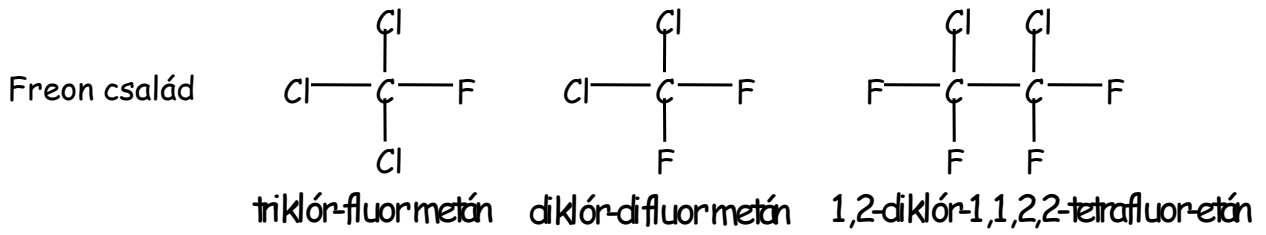


Két heterofunkciós csoport (O és N, O és S stb.)

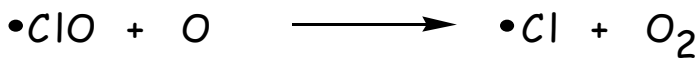
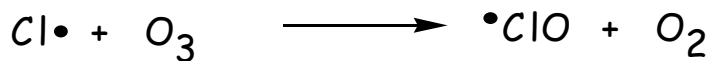
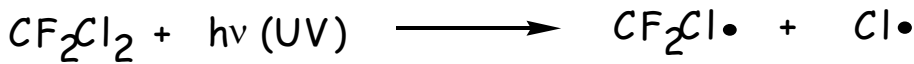


"nitrogén mustár" (1935) (1971)

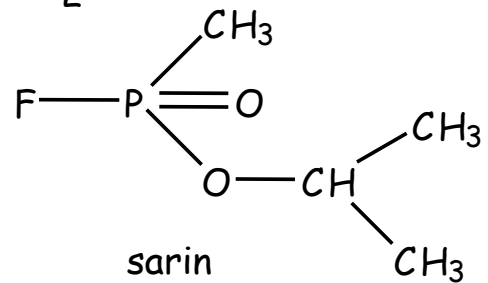
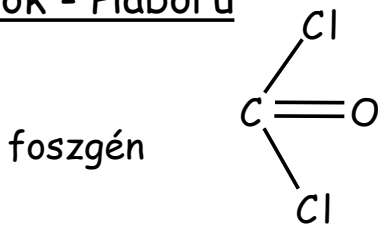
Példák: Aerosol - Hűtőszekrény



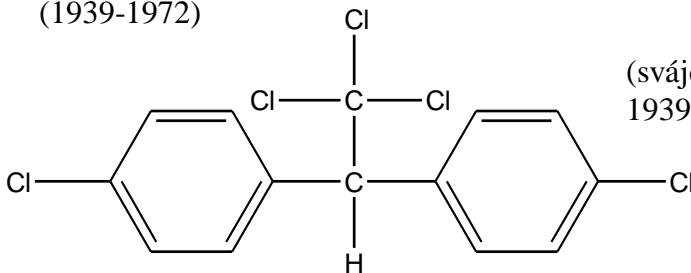
„Ózon-lyuk” (1974, F. S. Rowland)



Ideggázok - Háború



(1939-1972)



DDT

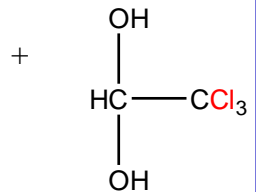
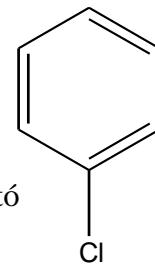
1,1-diklór-difenil-2,2,2,-triklór-etán

500 millió kg került a bioszférába

IDEGMÉREG

(svájc, P. H. Müller)
1939 szőlő, burgonya

könnyen
szintetizálható



klorál-hidrát

1939-45 25 millió életet
mentett (WHO)

1968-tól betiltott

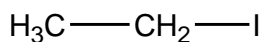
20. Halogénezett szénhidrogének

Felosztás, nomenklatura

1. Szénváz

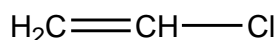
Nyílt

Alkil-
halogenid



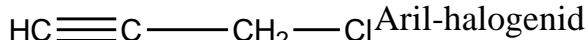
etil-jodid
jód-etán*

Alkenil-
halogenid



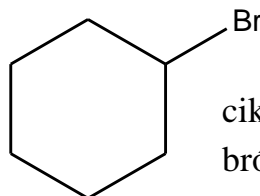
vinil-klorid
klór-etilén*

Alkinil-
halogenid



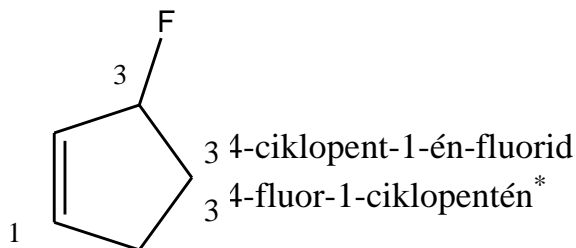
3-klór-propin*

Cikloalkil-
halogenid

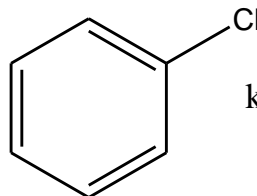


ciklohexil-bromid
bróm-ciklohexán*

Cikloalkenil-
halogenid

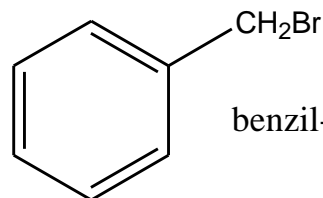


Aril-
halogenid



klór-benzol*

Aralkil-
halogenid



benzil-bromid

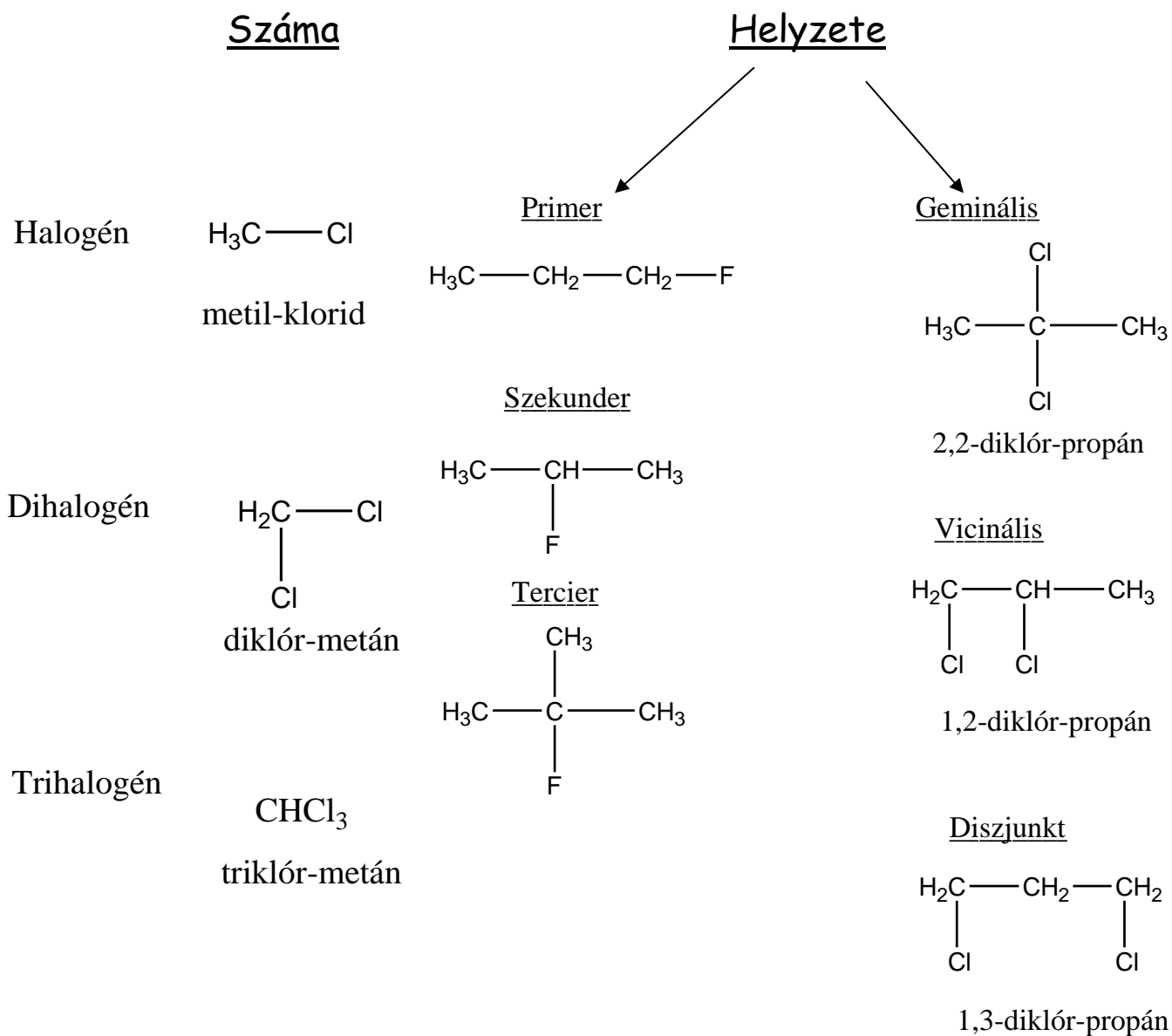
Szubsztitúciós elnevezés:*

Előtag + CH alapnév

Csoportfunkciós elnevezés:

CH csoportnév + utótag

2. Halogénatomok



Izoméria

- A. Szerkezeti izoméria: X helyzete
- B. Geometriai izoméria (kettős kötés) pl.: 1-klór-1-propén
- C. Optikai izoméria pl.: 2-klór-bután

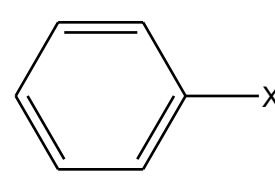
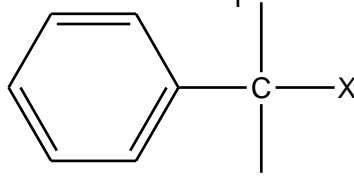
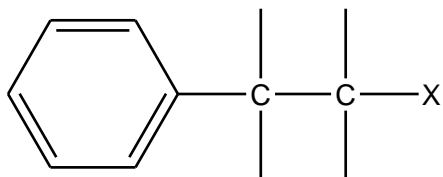
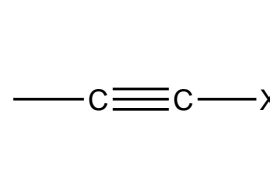
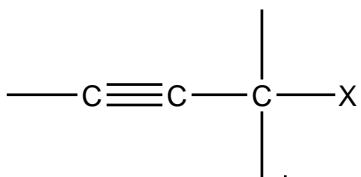
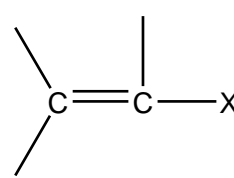
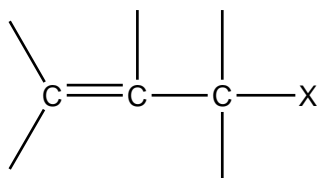
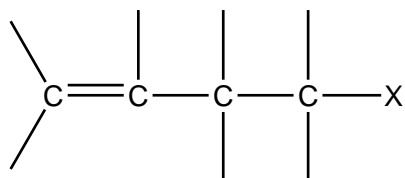
A szerkezet

Kötésmód

Alkil/Aralkil

Allil/Benzil

Vinil/Aril



$C(sp^2)-C(sp^3)-C(sp^3)-X(sp^3)$

-I effektus

$C(sp^2)-C(sp^3)-X(sp^3)$

-I effektus

+K effektus

$C(sp^2)-X(sp^3)$

-I effektus

+I effektus

EN: a.) $C(sp^2) > C(sp^3)$ b.) $F > Cl > Br > I$

Kötéshossz

F

Cl

Br

I

CH_3-CH_2-

1,40

1,79

1,97

2,16 [Å]

EN:

4,0

3,0

2,8

2,5

Kötési energia

476

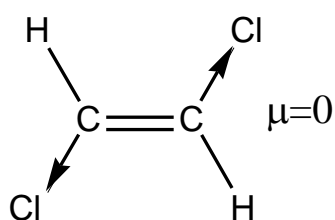
332

280

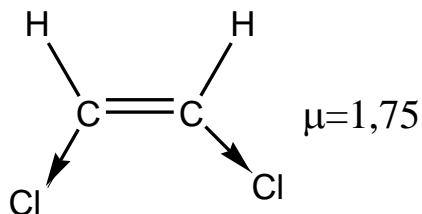
209 [kJ/mol]

Fizikai tulajdonságok

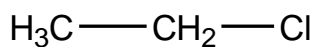
Dipólus momentum



transz-1,2-diklór-etilén

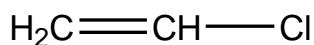


cisz-1,2-diklór-etilén

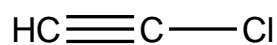


etil-klorid

$$\mu > 2,04$$

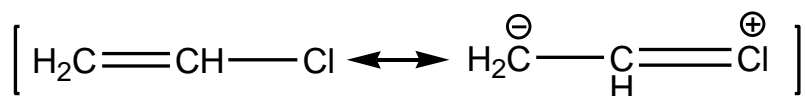


$$\mu=1,44$$



klór-acetilén

$$\mu=0,44$$



- 1.) -I effektus
- 2.) konjugáció

Forráspont, halmazállapot

	F	Cl	Br	I
Me	-78°	-24°	-3°	42°
Et	-32°	12°	38°	72°

Et-Cl: Gyorsan párolog, helyi érzéstelenítés

Halogénezett szénhidrogének reakciói

- A. Szubsztitúciós reakciók [S_N1 , S_N2]
- B. Eliminációs reakciók [E1, E2, α -, β - és γ - típus]
- C. Vinil/aril vs allil/benzil reaktivitás

A körülmények szerepe

a) Az oldószer minősége

Protikus oldószer:

Tartalmaz H^+ -t egy erősen elektronegatív atomhoz kapcsolva

(pl. H_2O , R-OH)

Aprotikus oldószer:

Nem tartalmaz H^+ -t egy erősen elektronegatív atomhoz kapcsolva

(pl. poláris DMF, DMSO; apoláris benzol, alkán)

S_N2 Gyorsabb poláris aprotikus oldószerben

S_N1 Gyorsabb poláris protikus oldószerben (ionizáló képesség!)

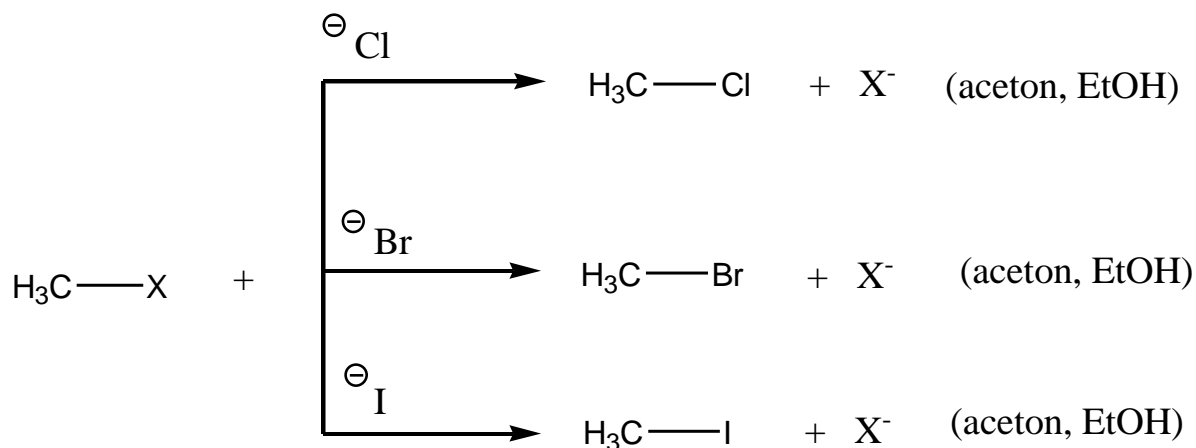
b) A reagens milyensége

c) A távozó csoport

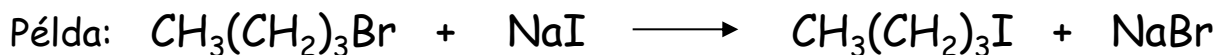
d) A szubsztrátum milyensége

A. Szubsztitúciós reakciók

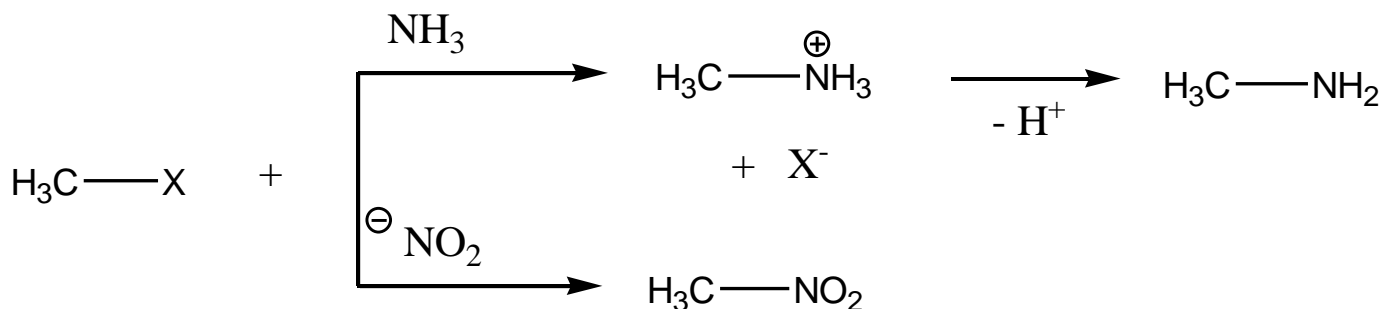
1.1. Reakció halogén nukleofilekkel (halogén csere)



Termék: alkil-halogenid



1.2. Reakció N-nukleofilekkel



Reakciótípus:

ammonolízis
„nitrálás”

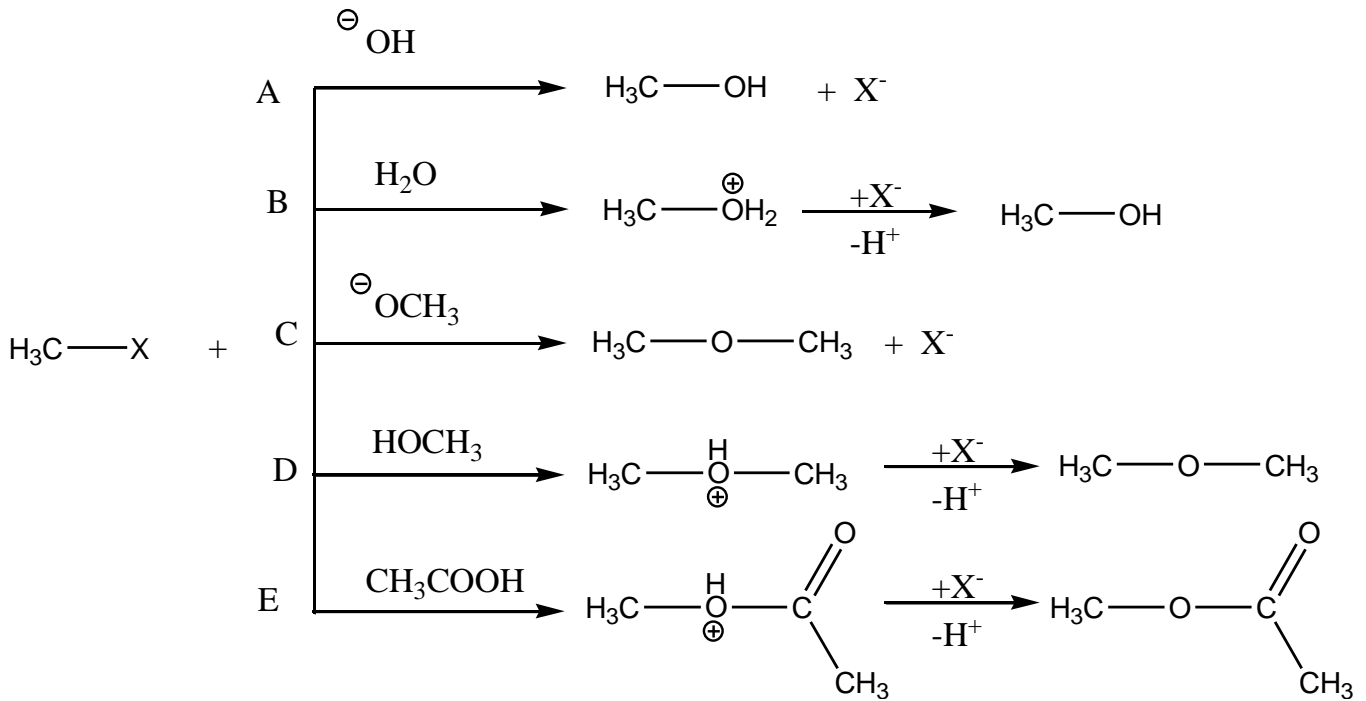
Termék:

primer amin
nitrovegyület

Jelentősége

C-N kötés kiépítése

1.3. Reakció O - nukleofilekkel



Reakciótípus

Hidrolízis

Alkoholízis

Acidolízis

Termék

Alkohol A, B

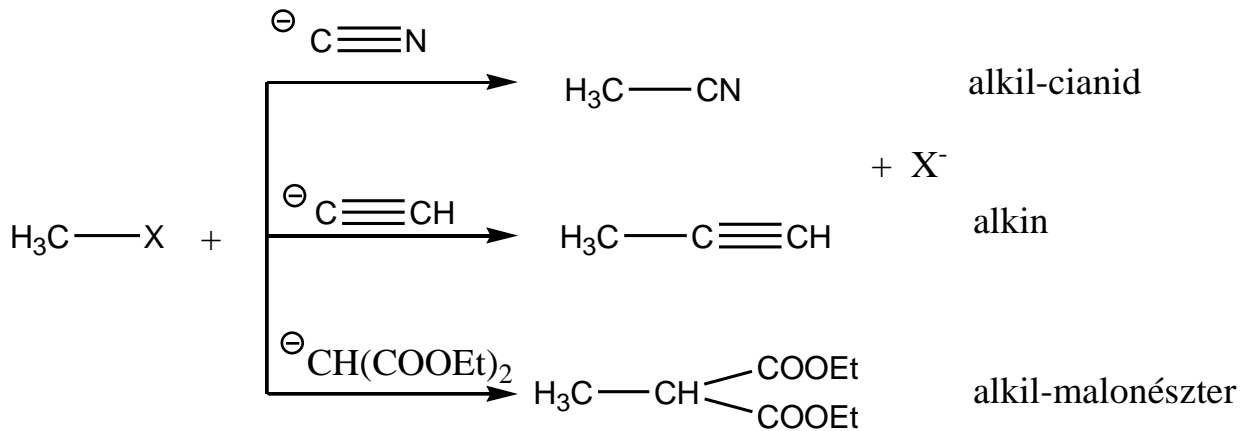
Éter C, D

Észter E

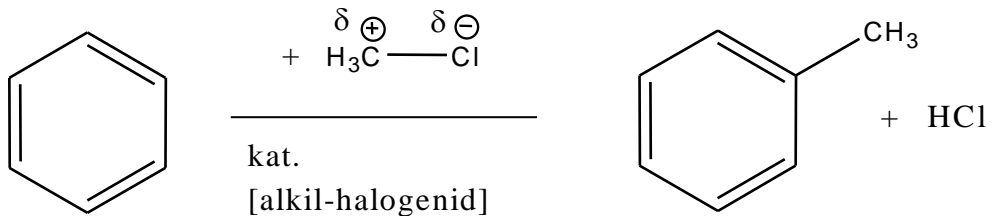
Jelentősége

C-O kötés kiépítése

1.4. Reakció C- nukleofilekkel

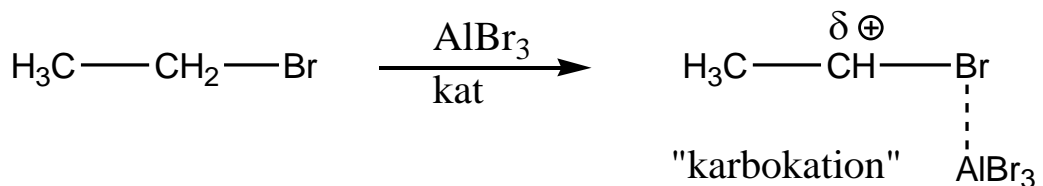


Friedel-Crafts alkilezés



Alkil-halogenid: kat. AlCl_3 , AlBr_3 , SbCl_5 , BF_3

Reagens:



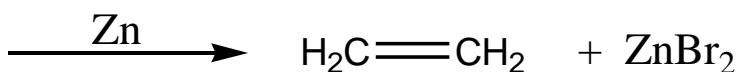
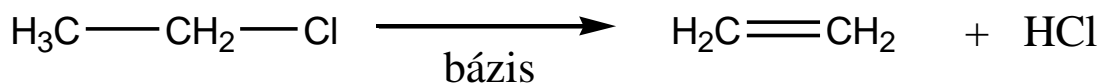
Reaktivitás: terciér > szekunder > primer

$\text{R-F} > \text{R-Cl} > \text{R-Br} > \text{R-I}$

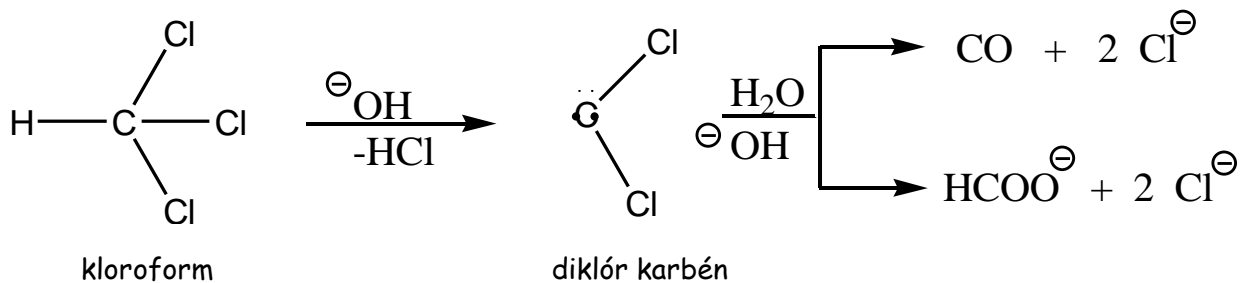
Jelentősége: C - C kötés kiépítése

B. Eliminációs reakciók

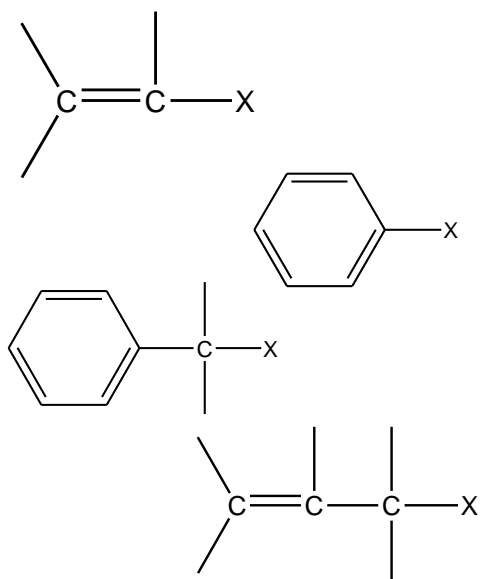
1,2 elimináció



1,1 elimináció



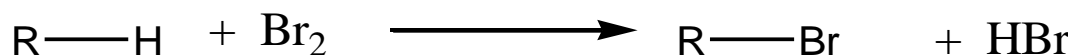
C. Vinil/aril vs allil/benzil rendszerek reaktivitása



	S_N2	S_N1		E	S_E
	-	-		lassú	-
	-	-		lassú	+
	+	+		+	-
	++	++		++	-

A HALOGÉNEZETT SZÉNHYDROGÉNEK ELŐÁLLÍTÁSA

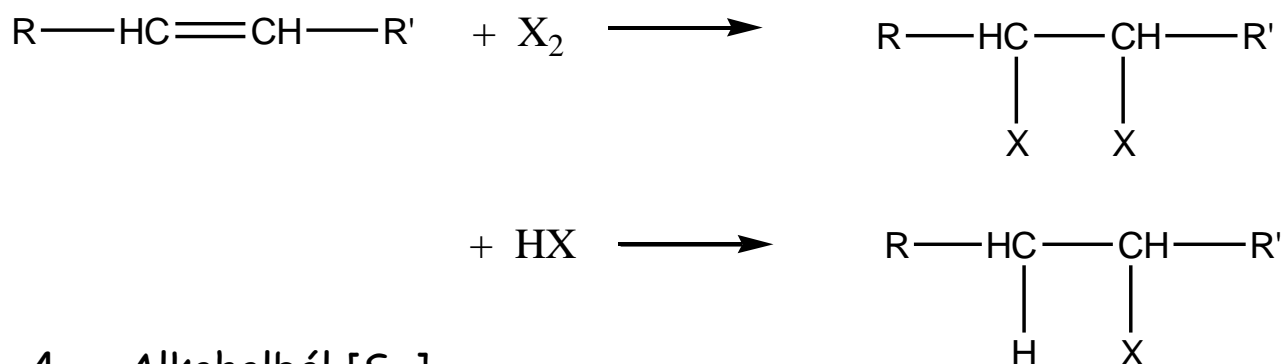
1. Alkánokból [S_R]



2. Arénekből [S_E]



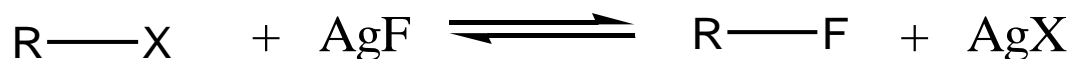
3. Telítetlen szénhidrogénből (alkén, alkin) [A_E]



4. Alkoholból [S_N]



5. Halogéncsere [S_N]

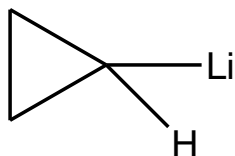


21. Fémorganikus vegyületek

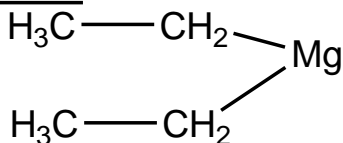
Definíció: Szén-fématom kötést tartalmazó vegyületek
(C-nukleofil forrás)



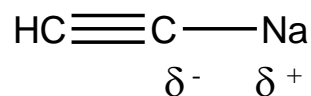
Nomenklatura, csoportosítás:



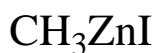
ciklopropil-litium



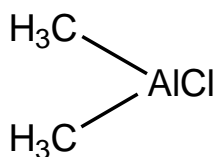
dietil-magnézium



nátrium-acetilid

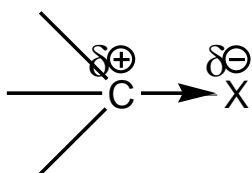


metilcink jodid



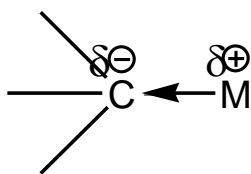
dimetilaluminium klorid

Kötésrendszer:



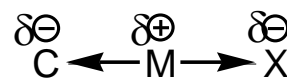
halogénezett CH-k

(C-elektrofil)



fémorganikus
A

(C-nukleofil)



fémorganikus
B

M (fém): Li, Na, K, Mg, Ca, Al, Sn, Pb, Zn, Cd, Hg

EN: 1,0; 0,9; 0,8; 1,2; 1,6; 1,9

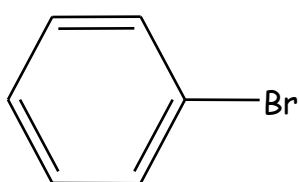
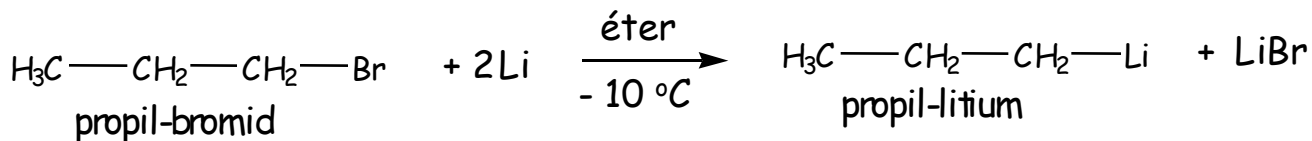
A kötés ionos jellege [%]

43; 51; 35; 22; 18; 9

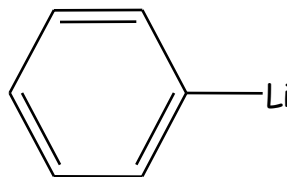
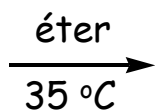
Előállítás:

$C(sp^3)$ vagy $C(sp^2)$

A. Csoport



brómbenzol

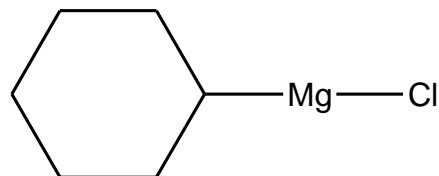
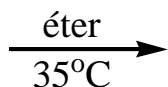
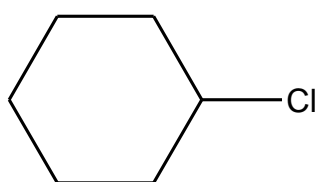
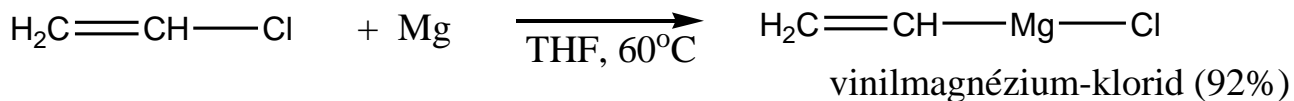
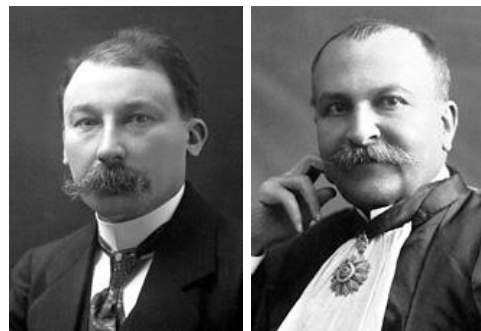


fenil litium

B. Csoport: GRIGNARD reagens

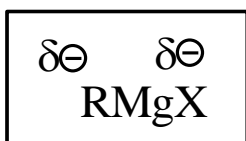
(Victor GRIGNARD + Paul SABATIER;

1912 kémiai Nobel-díj)



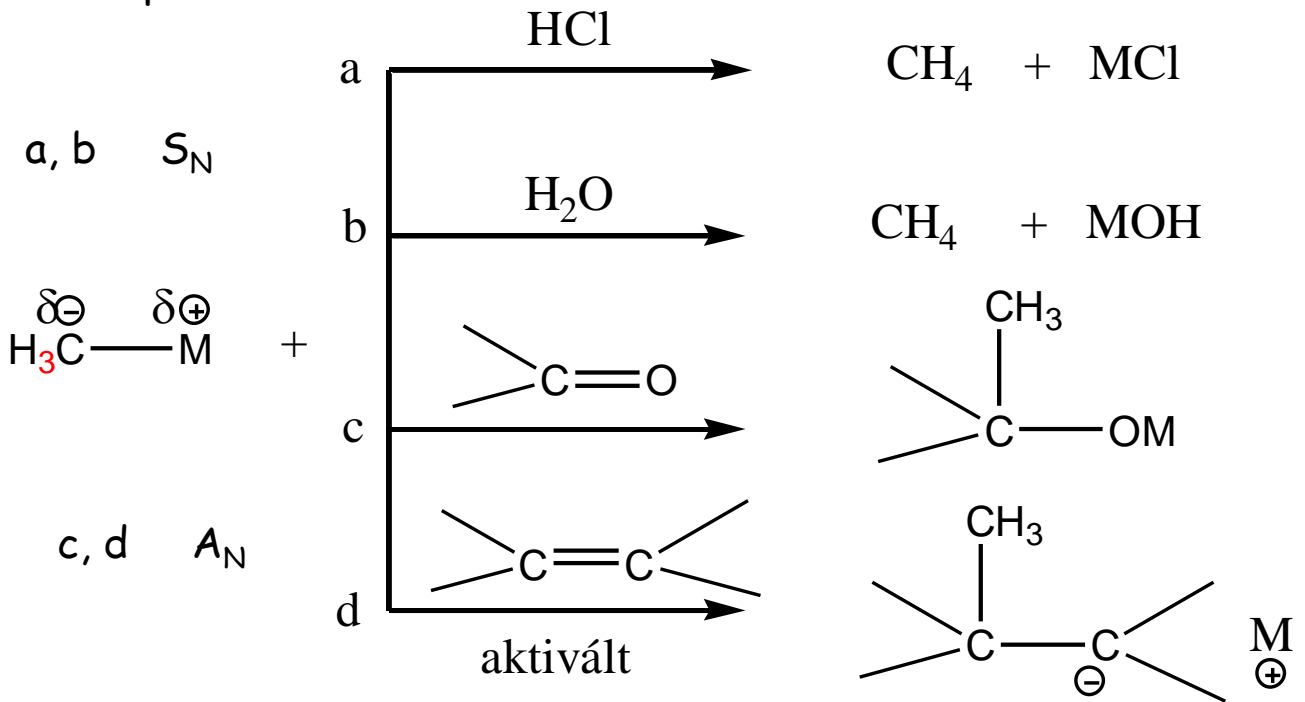
ciklohexilmagnézium klorid

R = alkil, cikloalkil, alkenil vagy aril

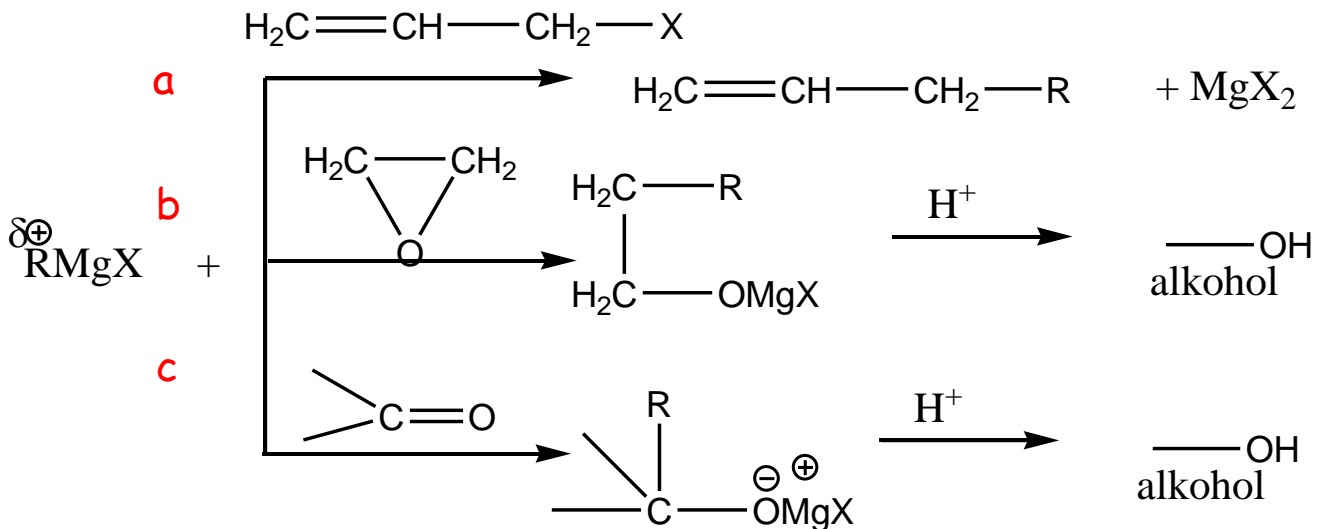


Reakciók fémorganikus vegyületek

A. Csoport

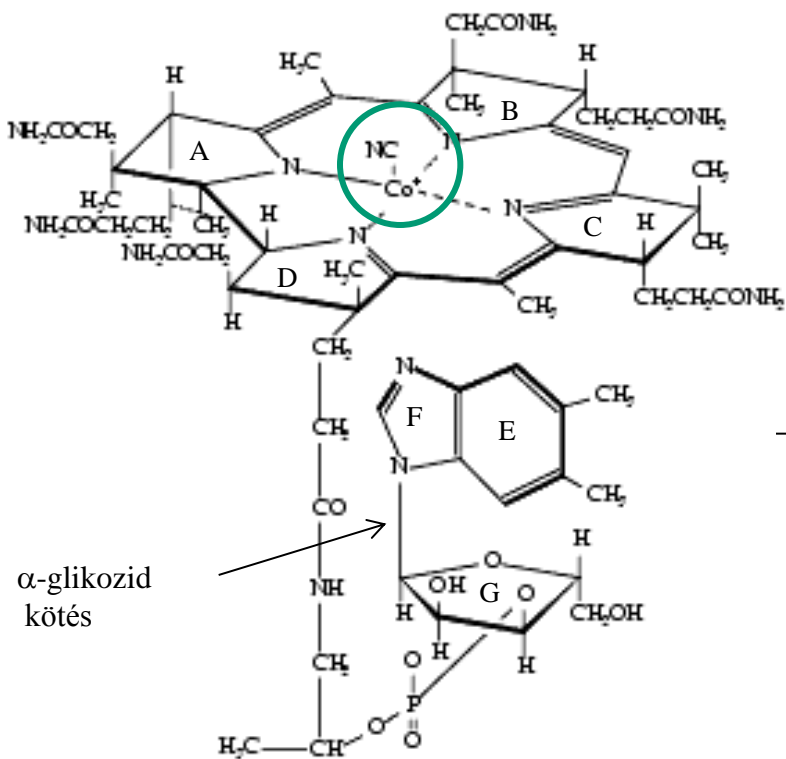


B. Csoport - Grignard-reagens



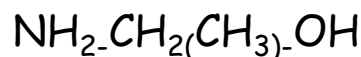
Mechanizmus: a, b S_N c A_N

B12-vitamin (kobalamin)



α -glikozid
kötés

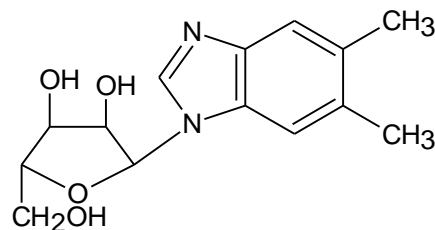
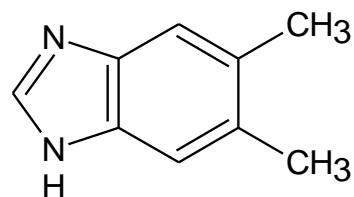
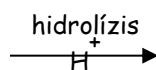
korrin-váz
(nem aromás!)



(2-hidroxi-propilamin)

+H₃PO₄ + 6 NH₃ +

+ D-ribóz +



1-(α -D-ribofuranozil)-5,6-
-dimetil-benzimidazol



1926: máj kivonat - vészes vérszegénység (Minot, Murphy)

1947: mikrobák növekedési faktora (Shoriz)

1948: izolálás tengeri algákból (Folkers, Smith)

1954-56: térszerkezet (Hodgkin)

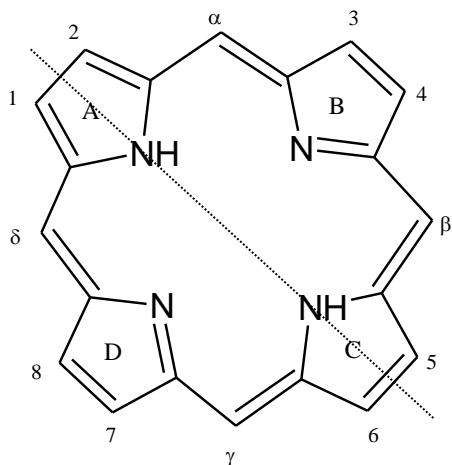
Szerkezet: D. Hodgkin, Oxford

Variációk:

- CN	B12
- OH	B12a
- NO ₂	B12c

Porfinvázak vegyületek - csoportosítás

1. Kromoproteidek (protein + prosztetikus csoport)

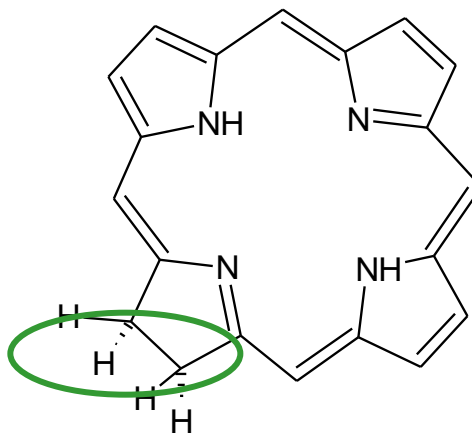


porfin - váz
(hem-proteinek)

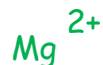


- 1.1 Hemoglobin (gerincesek)
- 1.2 Mioglobin
(izomsejtek, gerincesek/gerinctelenek)
- 1.3 Eritrokrurin
(gerinctelenek, 150 hem)
- 1.4 Kataláz, peroxidáz
(protoporfirin, Fe^{3+})
- 1.5 Citokrómok
(terminális oxidáció, $Fe^{2+} \rightarrow Fe^{3+}$)

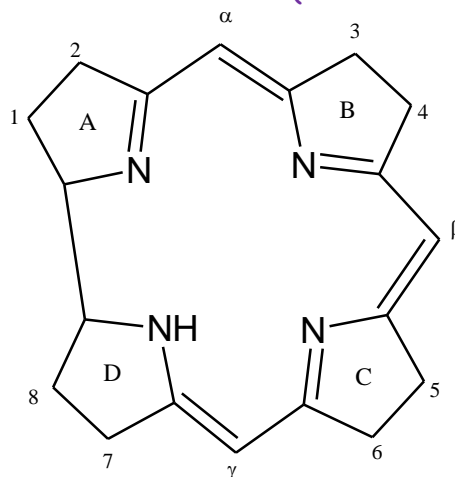
2. Klorofill (zöld növények)



klorin (7,8-dihidro-porfin) - váz



3. Cianokobalamin (B12 vitamin)



korrin



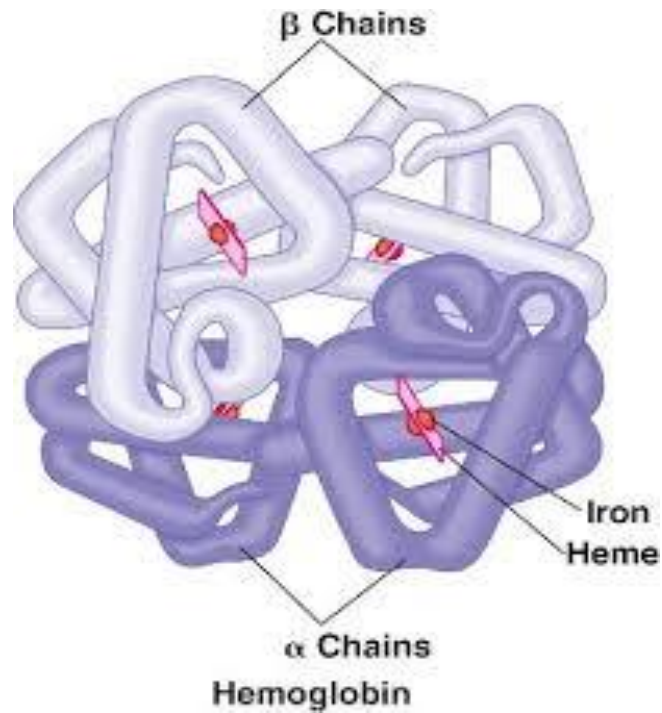
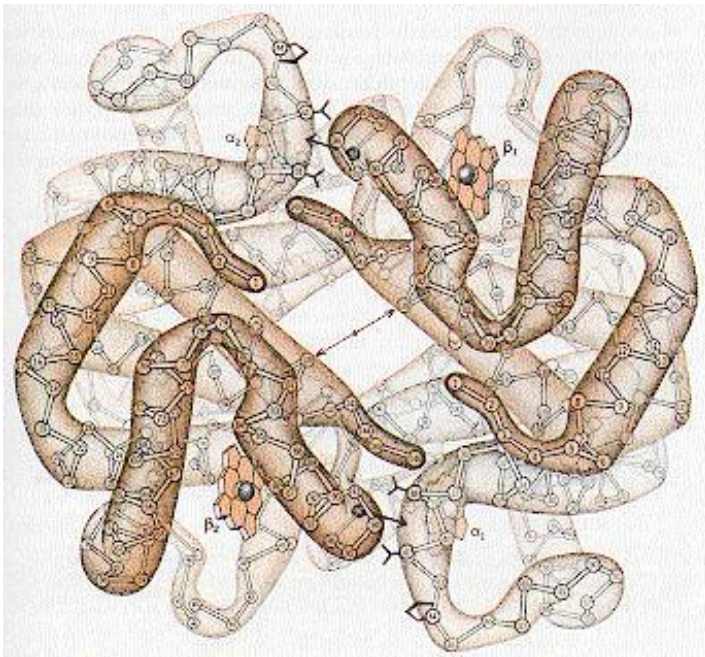
1.1 Hemoglobin (1862, kristályos)

Prosztetikus csoport (vörös) +
globin (4 polipeptid lánc, Mt: 17 000)



Max F. Perutz, 1960
Nobel díj, (J. Kendrew) 1962

www.mfpl.ac.at



phm.utoronto.ca

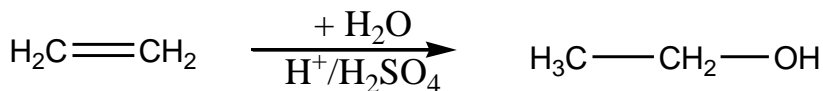
22. Alkoholok, fenolok, éterek

Faszesz (CH₃OH) Toxikus: 30ml vakság

LD₅₀ érték patkányokban

LD₅₀ = A populáció 50%-ának elhullásához szükséges dózis [g/kg]

		LD ₅₀	
metanol	CH ₃ OH		
formaldehid	HCHO	0,07	
etanol	H ₃ C—CH ₂ —OH	13,7	
1-propanol	H ₃ C—CH ₂ —CH ₂ —OH	1,87	
etilénglikol	HO—CH ₂ —CH ₂ —OH	8,54	édes
glicerol	$\begin{array}{c} \text{HO—CH}_2\text{—} \\ \\ \text{H} \\ \\ \text{C—CH}_2\text{—OH} \\ \\ \text{OH} \end{array}$	31,5	édes



(szintetikus alkohol)

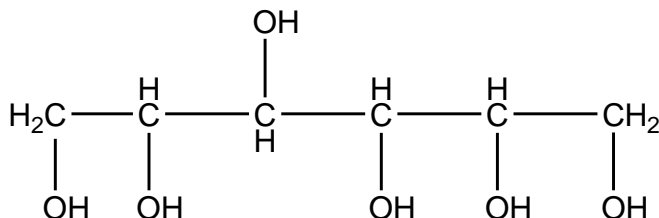
Deanturálás:

pl. metil-etil-keton (2%), metil-izobutil-keton (3%) és denatónium benzoát (0,001%)

+
metanol vagy benzin

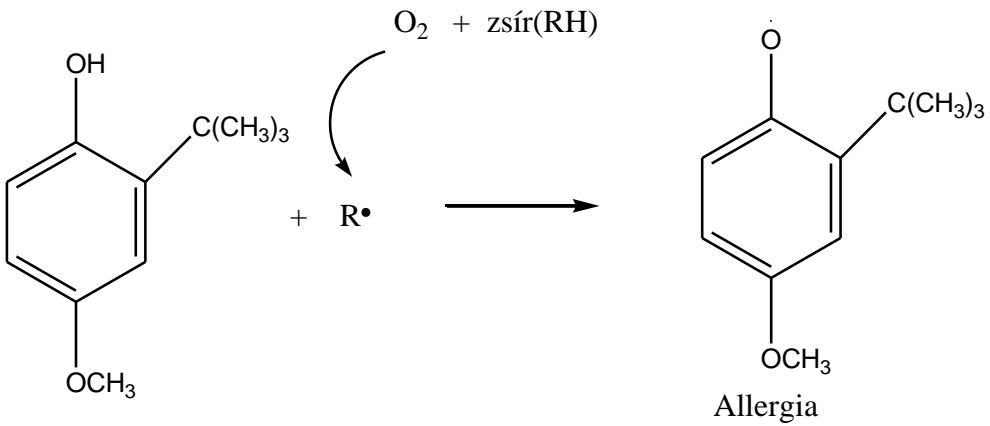
↓
Denaturált szesz

szorbit

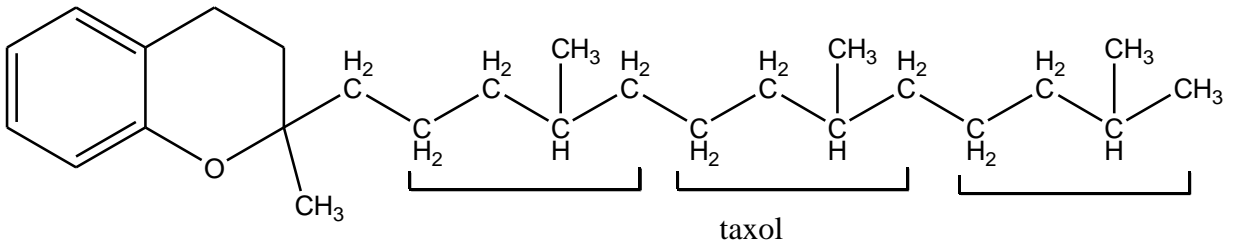


Édesítőszer
(rágógumi)

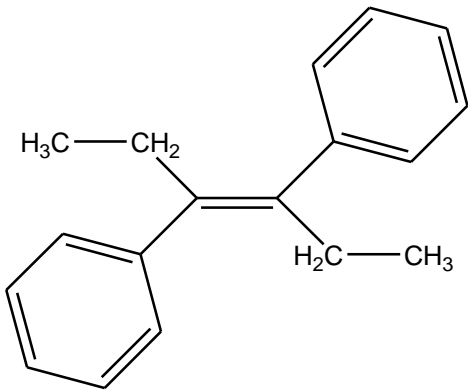
Élelmiszer"adalékok"



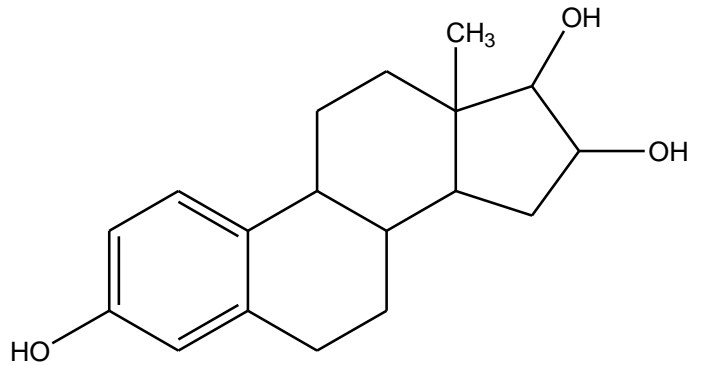
4-hidroxi-3-terc.butil anizol
(antioxidáns)



E-vitamin (taxoferol)
(természetes antioxidáns)



dietil-szilbösztrol
a. takarmány súlynövekedés -1973
b. abortusz kiváltó szer 1973-



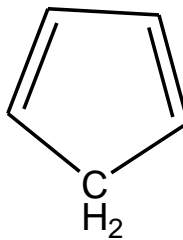
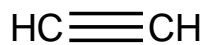
ösztriol (ösztradiol)

Felosztás:

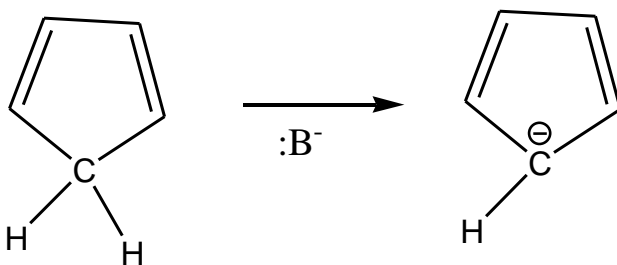
XH savak:	F-H < Cl-H < Br-H < I-H
OH savak:	CH ₃ -OH < CH ₃ COOH
CH savak:	R-CH ₂ -CN
NH savak:	R-NH ₂

Aciditás értelmezése

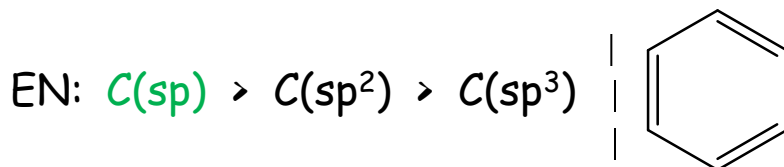
α. ΔEN alapján:



b. Anion stabilitása alapján:

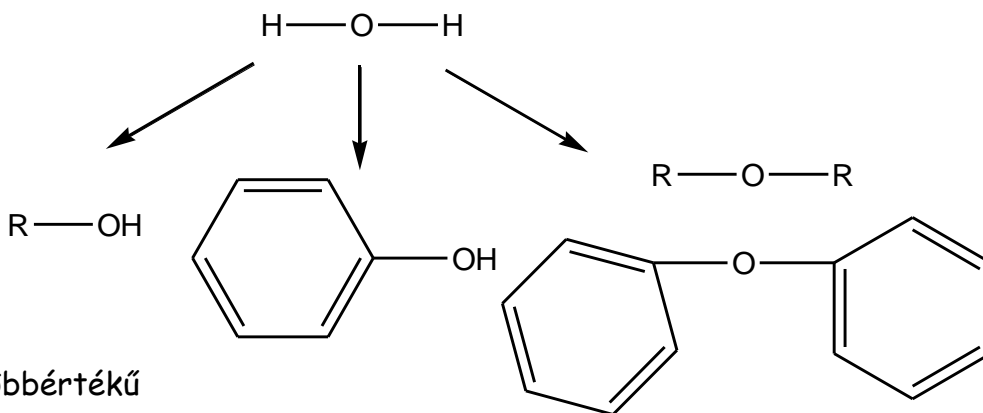


delokalizáció



pK_a 25 45 62 43

ALKOHOL, FENOL, ÉTER - származtatás

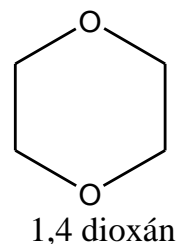
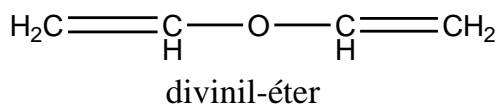
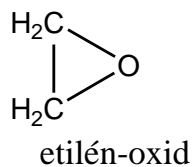
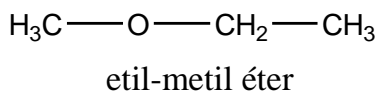
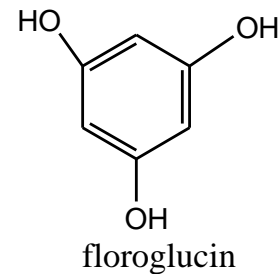
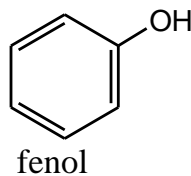
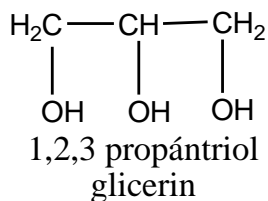
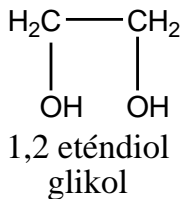
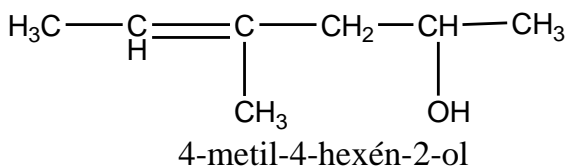
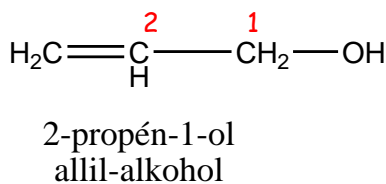
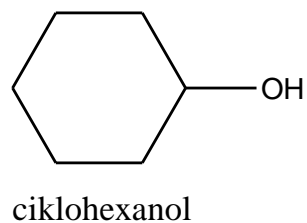
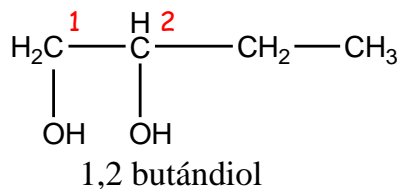
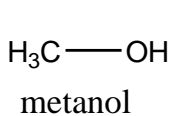


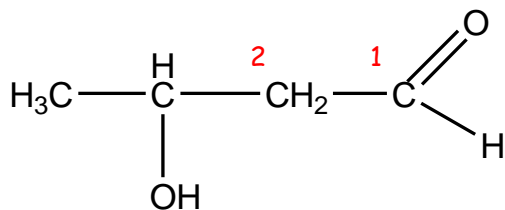
Egy-, többértékű

Primer, szekunder, terciér

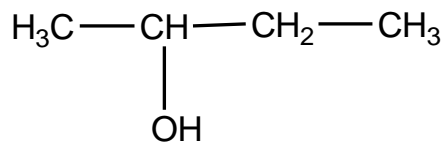
Telített, telítetlen

Nomenklatúra:





3-hidroxi-butanal
ELÓTAG



2-butanol
UTÓTAG

Csoportnevek:

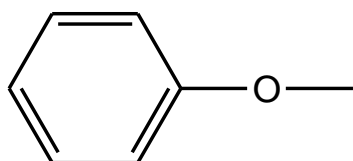
HO— hidroxi

HO—CH₂—

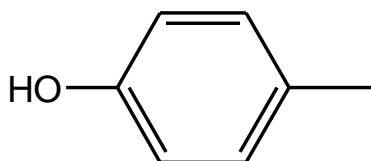
Na⁺ O[⊖]CH₃

hidroximetil

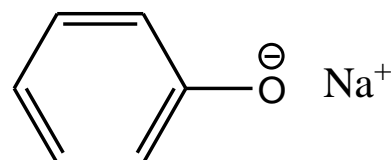
Na-metoxid



fenil-oxi



hidroxi-fenil



Na-fenolát

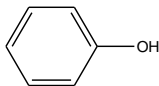
Szerkezet:

O: 2s², 2p_x²p_y¹p_z¹

alkohol	éter	fenol
O(sp ³):2,2,1,1		
COH \sphericalangle 108,5°	COC \sphericalangle 110°	COH \sphericalangle 109°
C-O 1,43Å		C-O 1,36Å
O-H 0,96Å		O-H 0,96Å
μ = 1,7 D	μ = 1,2 D	μ = 1,6 D

Fizikai tulajdonságok

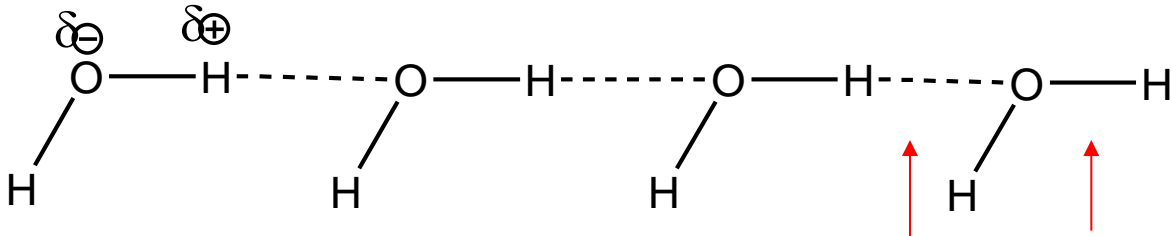
1. Olvadáspont, forráspont

	Op [°C]	Fp[°C]	oldékonyság [g/100ml víz]
CH ₃ OH	- 98	65	∞
CH ₃ CH ₃	-172	-89	-
	43	182	8,2
CH ₃ CH ₂ OH	-117	78	∞
CH ₃ -O-CH ₃	-138	-24	~∞
CH ₃ -CH ₂ -CH ₃	-190	-42	-
H ₃ C-(CH ₂) ₃ OH	-90	118	0,6
C ₂ H ₅ -O-C ₂ H ₅	-116	35	7,5
H ₃ C—CH ₂ —CH ₃	-129	36	-
HOCH ₂ -CH ₂ OH		200	∞
HOCH ₂ -CH(OH)-CH ₂ OH		290	∞

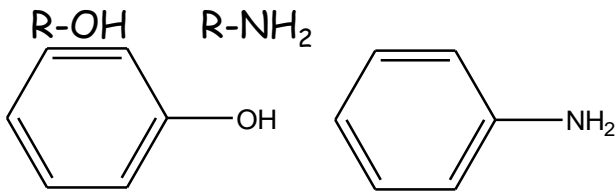
2. Oldékonyság

C ₁ - C ₃	∞
C ₄	10%
C ₅	nincs
glicerín, etilén glikol	∞

Hidrogén híd kötés



Fellép: O-H, N-H, X-H
 H₂O NH₃ F-H



R-COOH

nukleinsavak, fehérjék

476 kJ/mol

100 pm

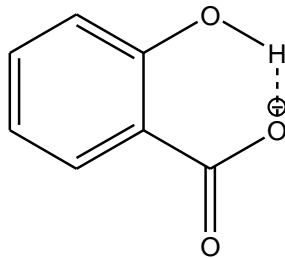
20 kJ/mol

180 pm

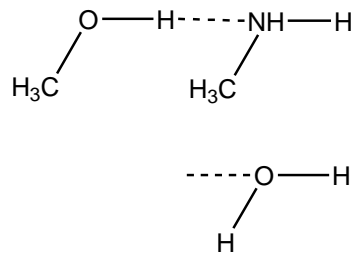
Típusai:

intramolekuláris

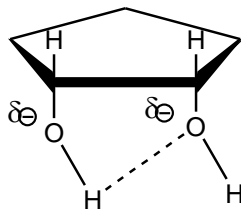
intermolekuláris



szalicilsav



DNS

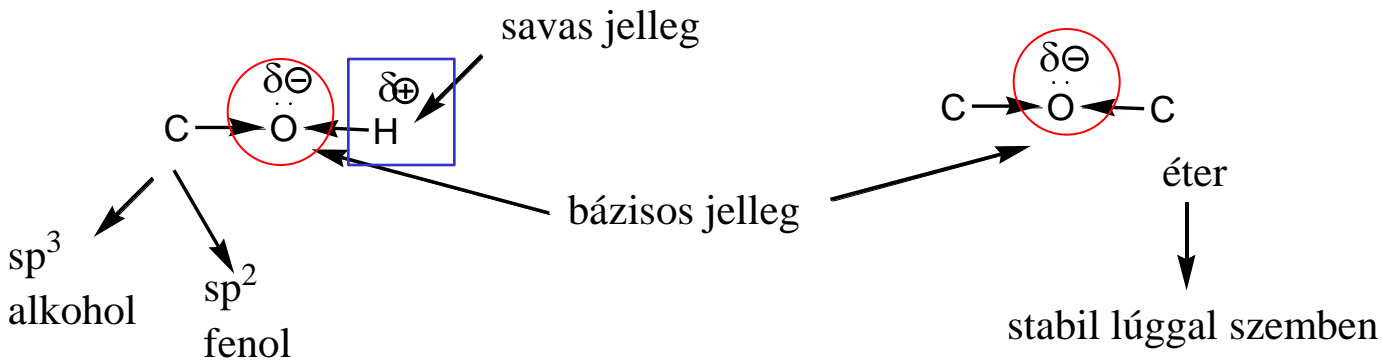


cisz-1,2-ciklopentándiol

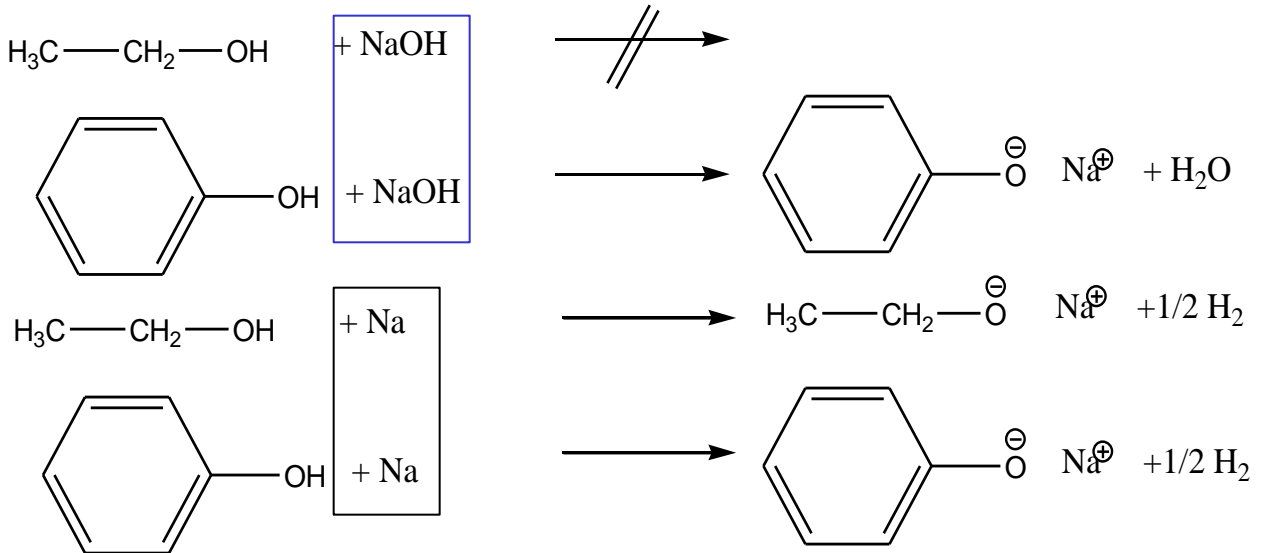
Kémiai reakciók

1. Sav-bázis reakciók
2. Oxidáció
3. Szubsztitúciós reakciók
4. Eliminációs reakciók
5. Addíciós reakciók

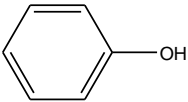
1. Sav-bázis reakciók



Savi jelleg:



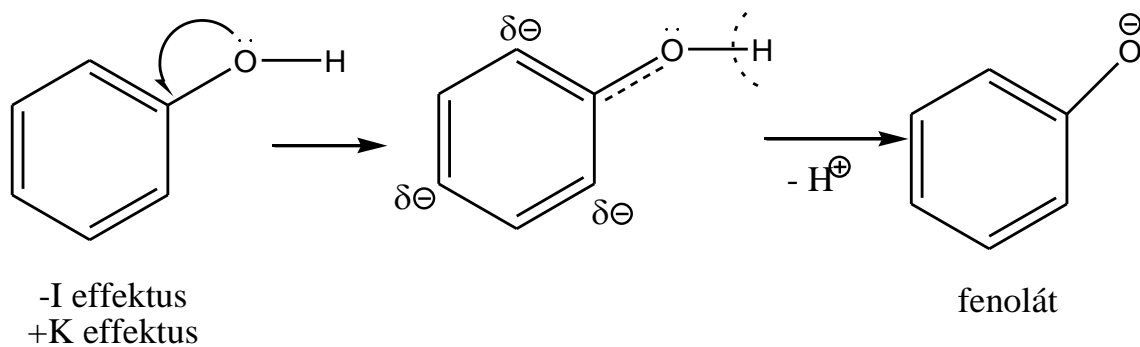
Alkohol - relatív savi erősség

	pK_s
CH_3-CH_3	40
CH_3-OH	16
$H-OH$	15,7
	10
H_2SO_4	-3

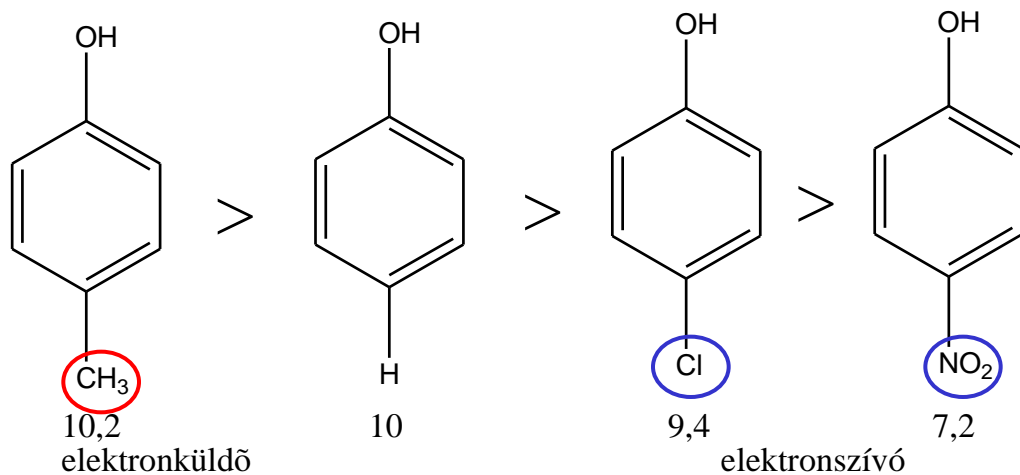
Alkohokok - rendűség

	pK_s
CH_3-OH	16
CH_3CH_2OH	17
$(CH_3)_2CH-OH$	~18
$(CH_3)_3C-OH$	19

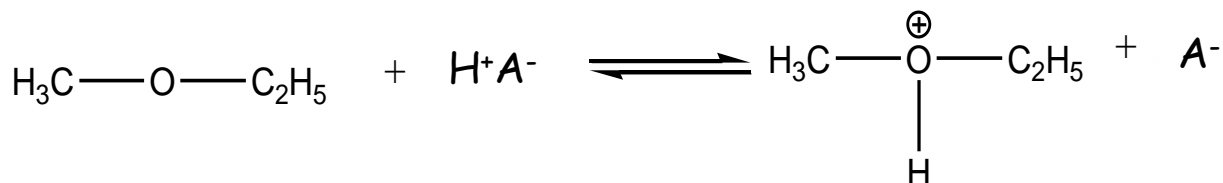
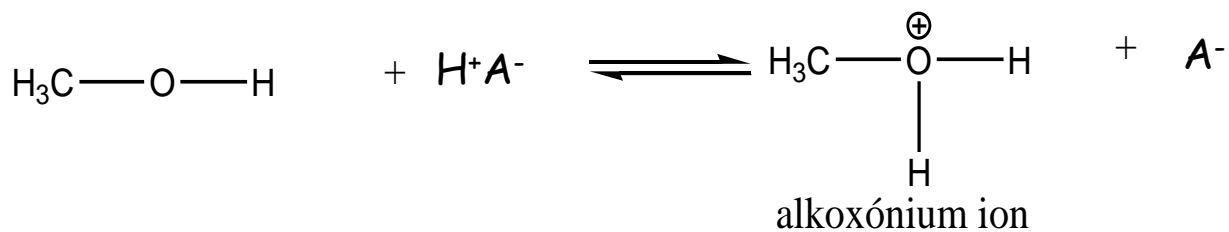
Fenokok savi jellege



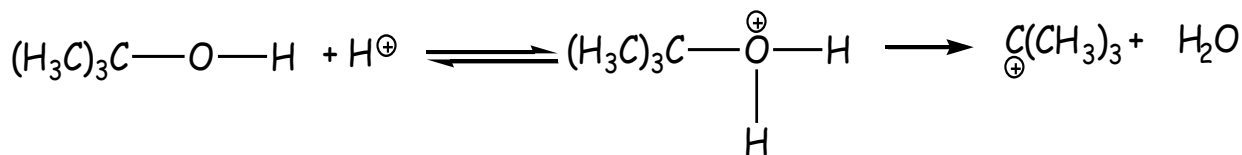
Szubsztituens hatás



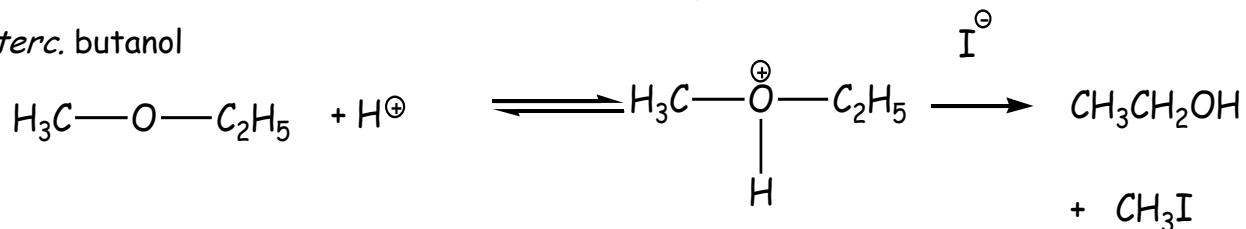
Bázikus sajátság:



Példa:

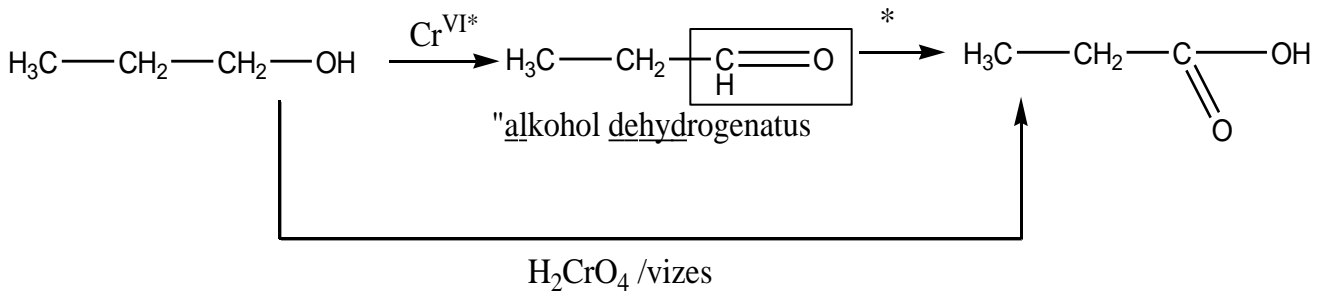


terc. butanol



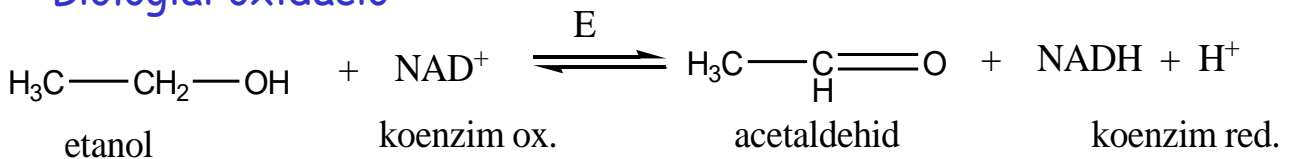
2. Oxidáció

2.1. Primer alkohol

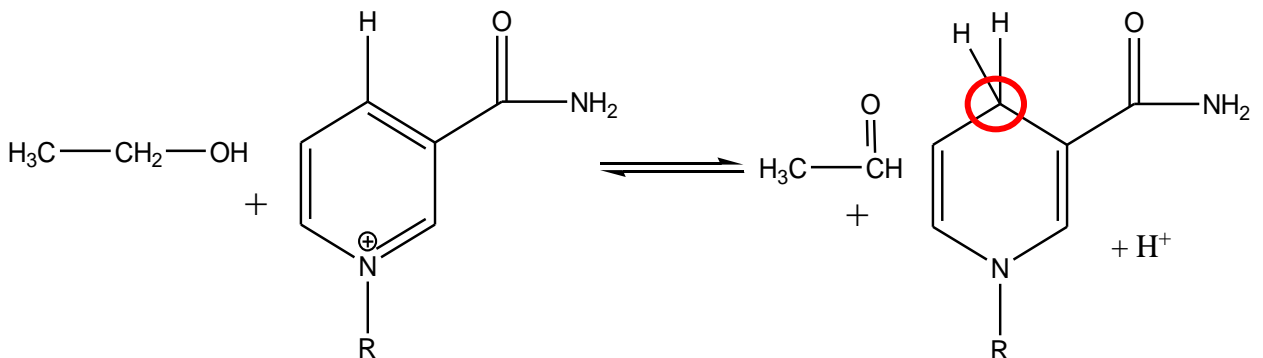


* Collins reagens: $\text{CrO}_3(\text{C}_5\text{H}_5\text{N})_2$ [piridin] / CH_2Cl_2 vízmentes

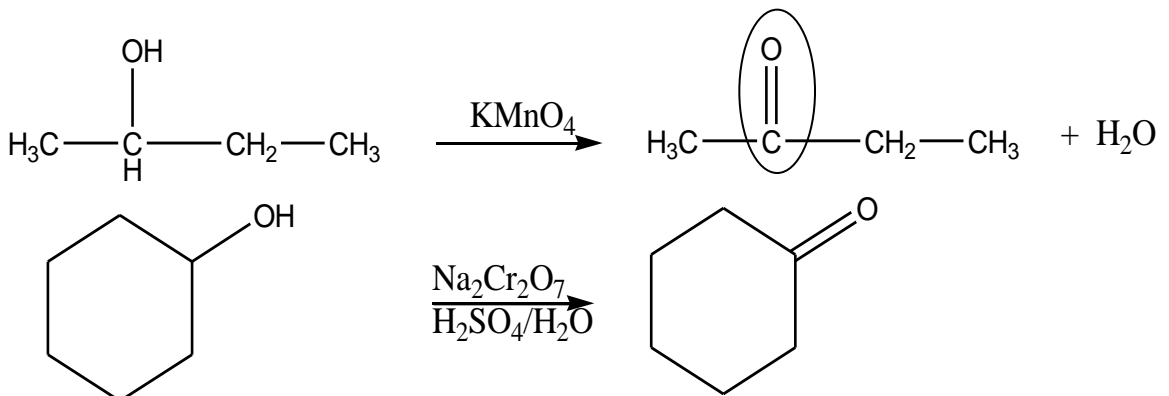
Biológiai oxidáció



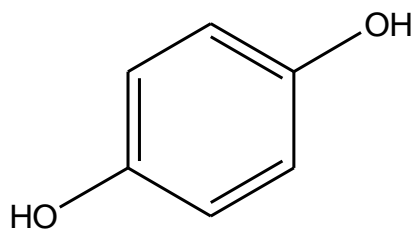
E: alkohol dehidrogenáz NAD: nikotinamid adenin dinukleotid



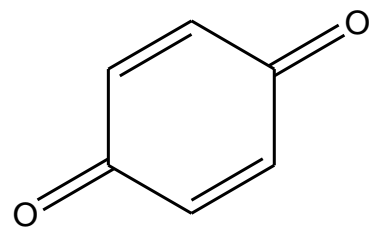
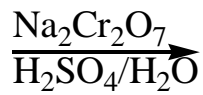
2.2. Szekunder alkohol



2.3. Fenolok

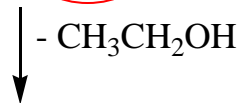
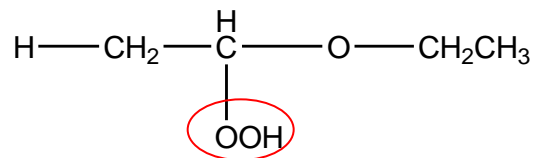
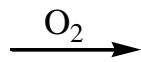
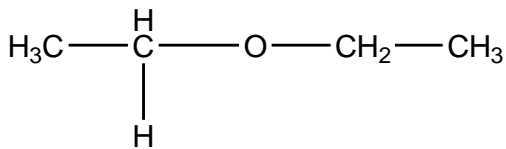


hidrokinon

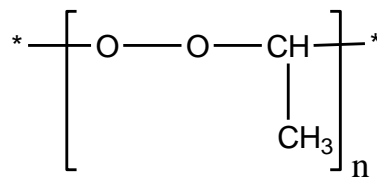


p-benzokinon

2.3. Éterek

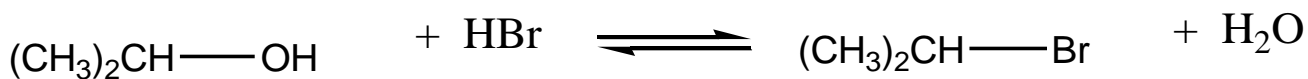


polimer
peroxid

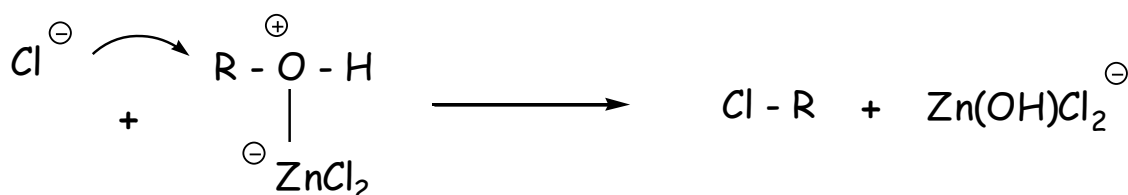
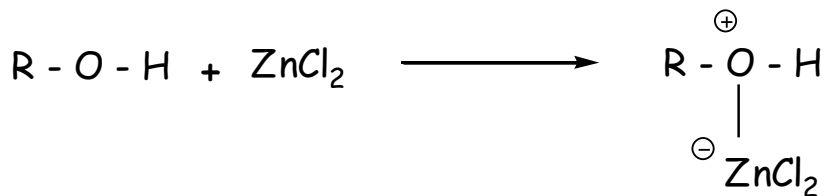


3. Szubsztitúció

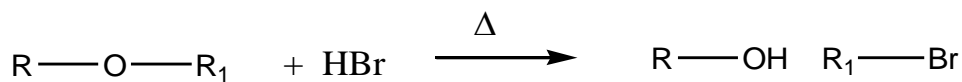
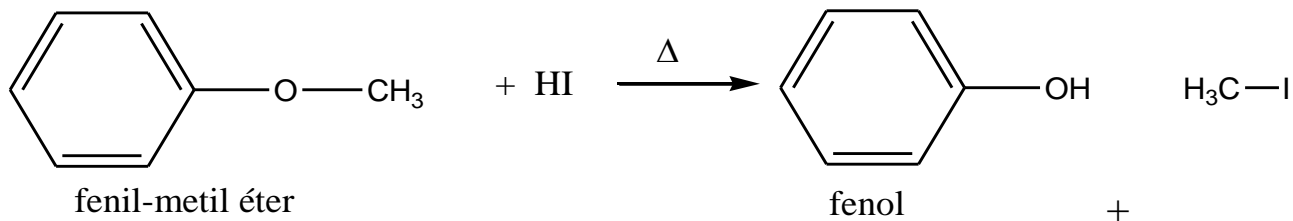
3.1. Reakció HX savval:



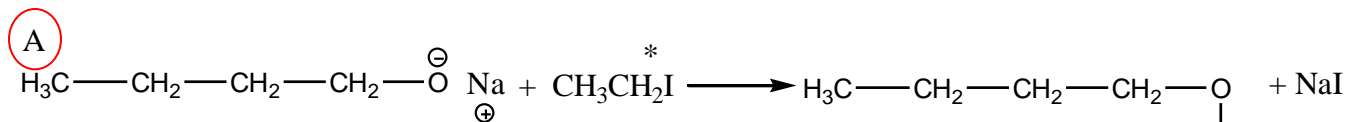
Alkalmazás: Lucas-reagens (cc. HCl + ZnCl₂)



Alkohol		Alkil-halogenid	
Tercier	+	20 °C	azonnal
Szekunder	+	20 °C	néhány perc
Primer	+	Δ	azonnal
Fenol	-	Δ	



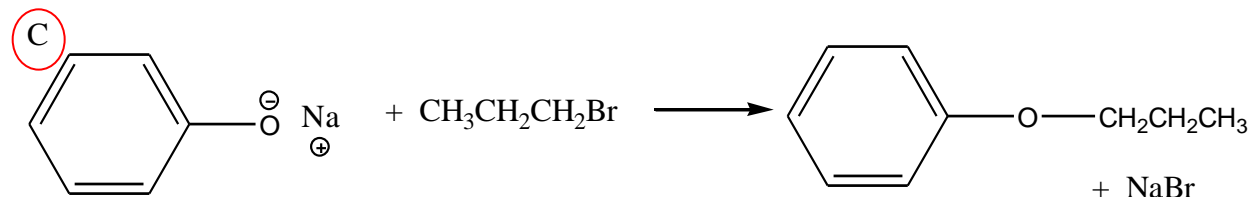
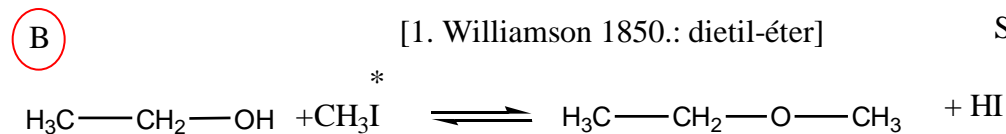
3.2. Reakció halogénezett CH-nel



[1. Williamson 1850.: dietil-éter]

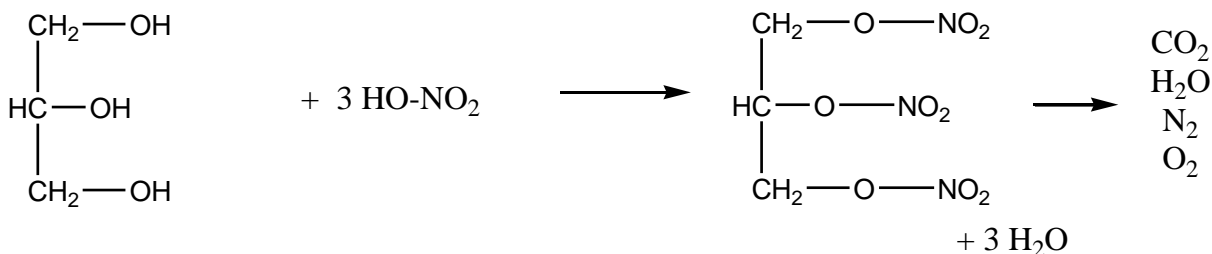
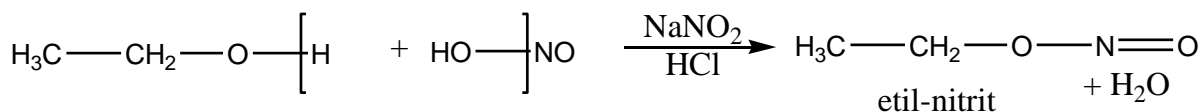
$\text{S}_{\text{N}2}$

CH_2CH_3

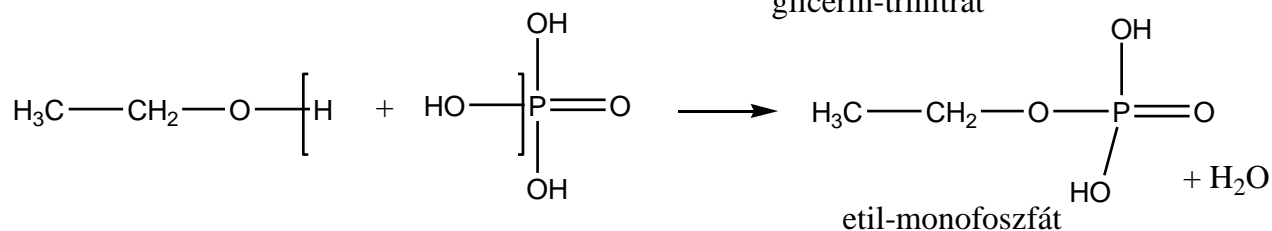


•szekunder, tercier inkább E2 reakció szerint megy

3.3. Reakció anorganikus savakkal:

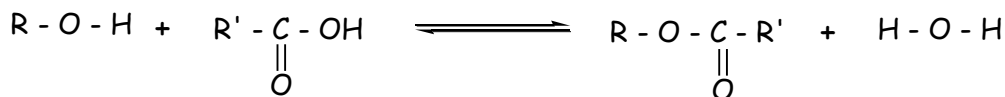


glicerín-trinitrát

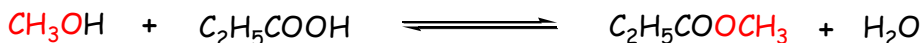


3.4. Reakció karbonsavval (alkoholok acilezése)

3.4.1. Közvetlen észterezés

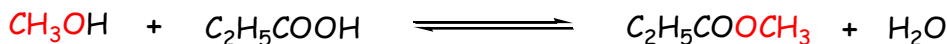
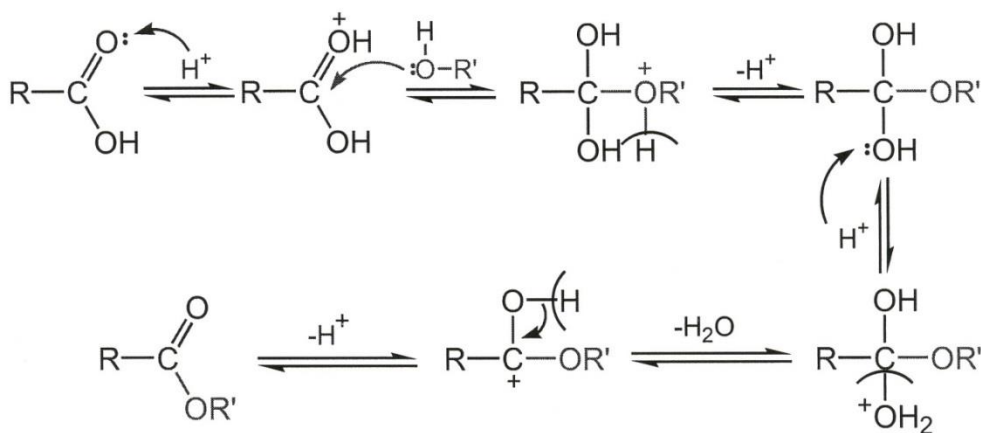


példa

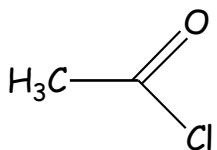


3.4.2. Savkatalizált észterezés

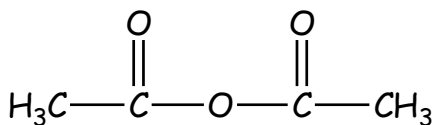
Primer alkohol reakciója (acil csoport „beépülés”)



3.5. Reakció karbonsavszármazékkal

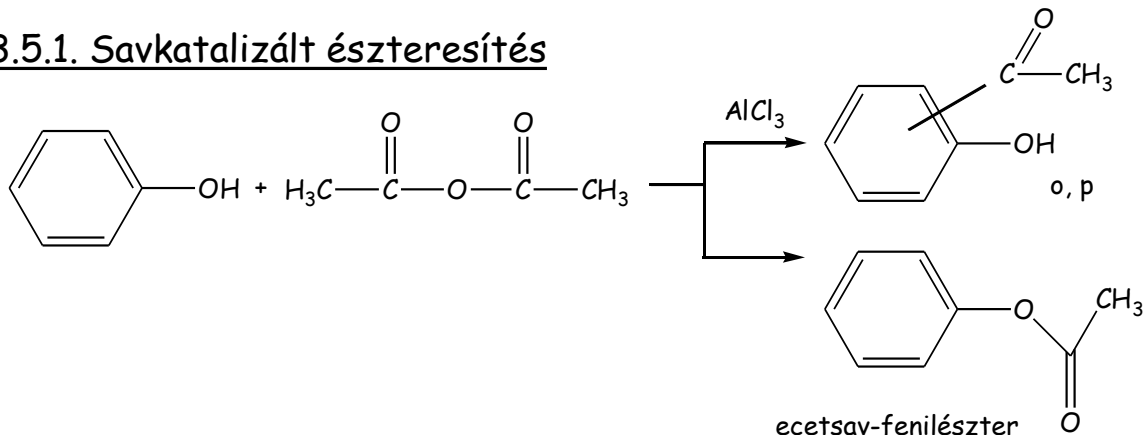


karbonsav halogenid



karbonsav anhidrid

3.5.1. Savkatalizált észterezés

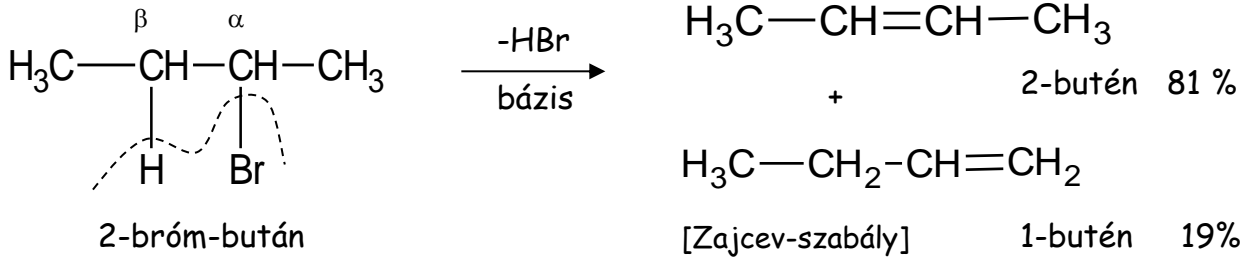


4. Elimináció

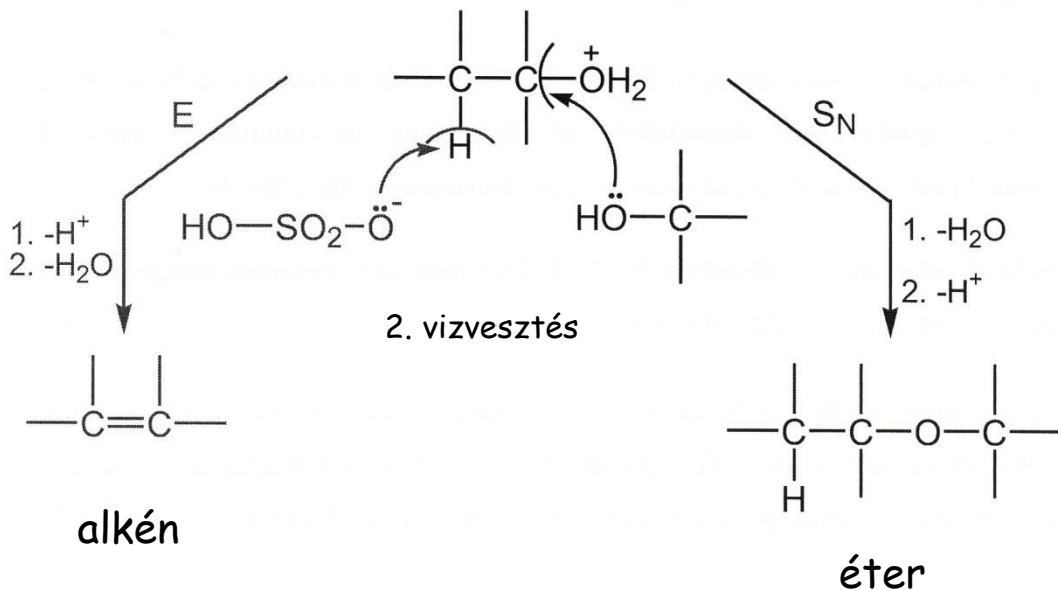
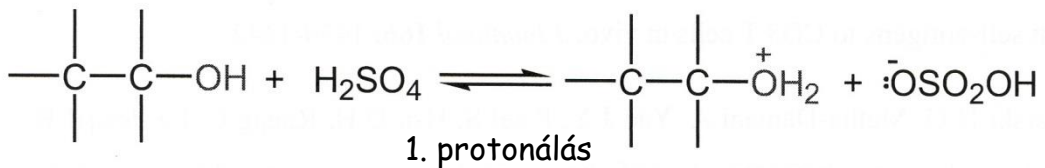
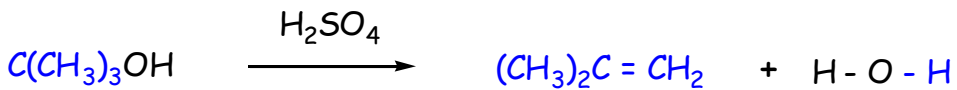
4.1. Primer alkohol



4.2. Szekunder alkohol

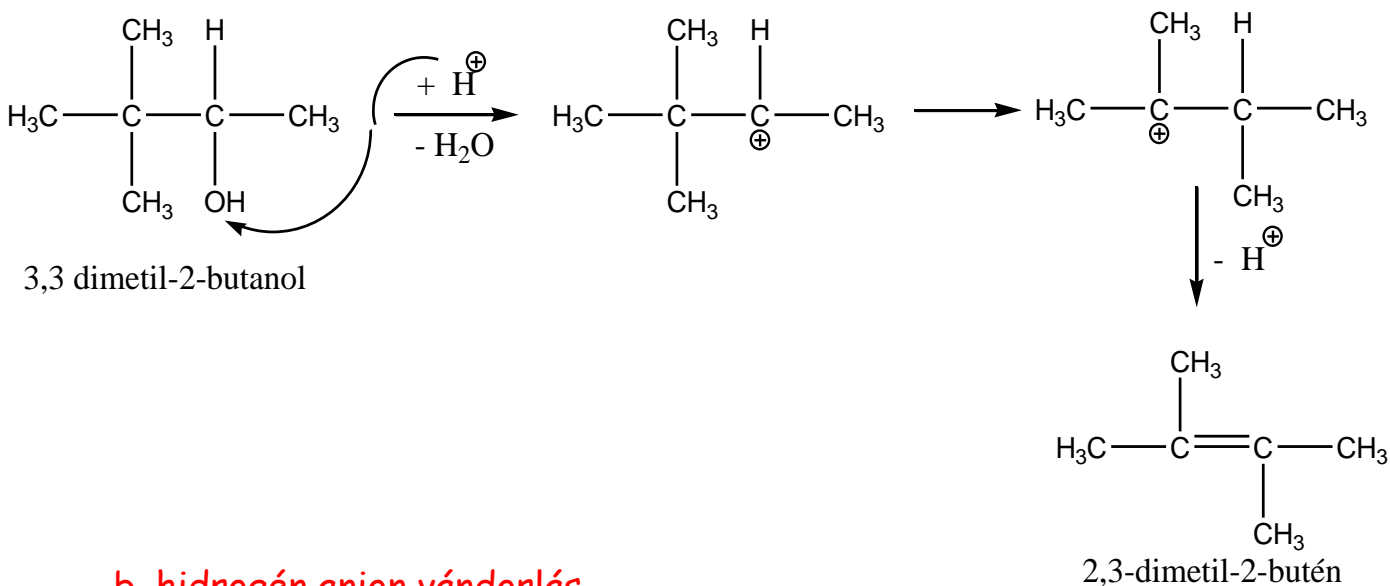


4.3. Tercier alkohol (csak alkén!)

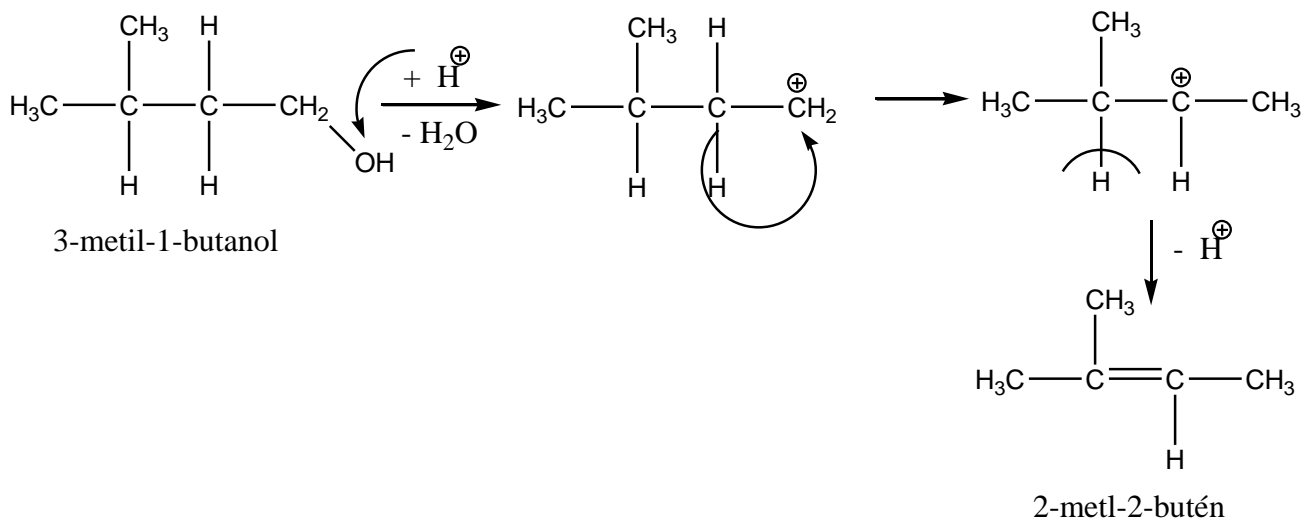


4.4. Wagner-Meerwein átrendeződés [savkatalízis]

a. metil-csoport vándorlás



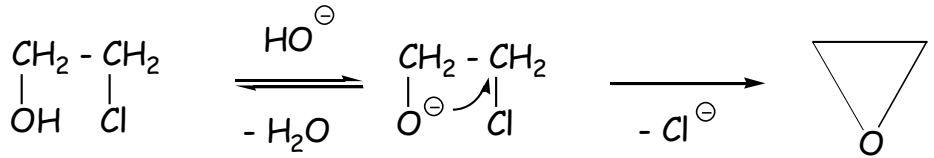
b. hidrogén anion vándorlás



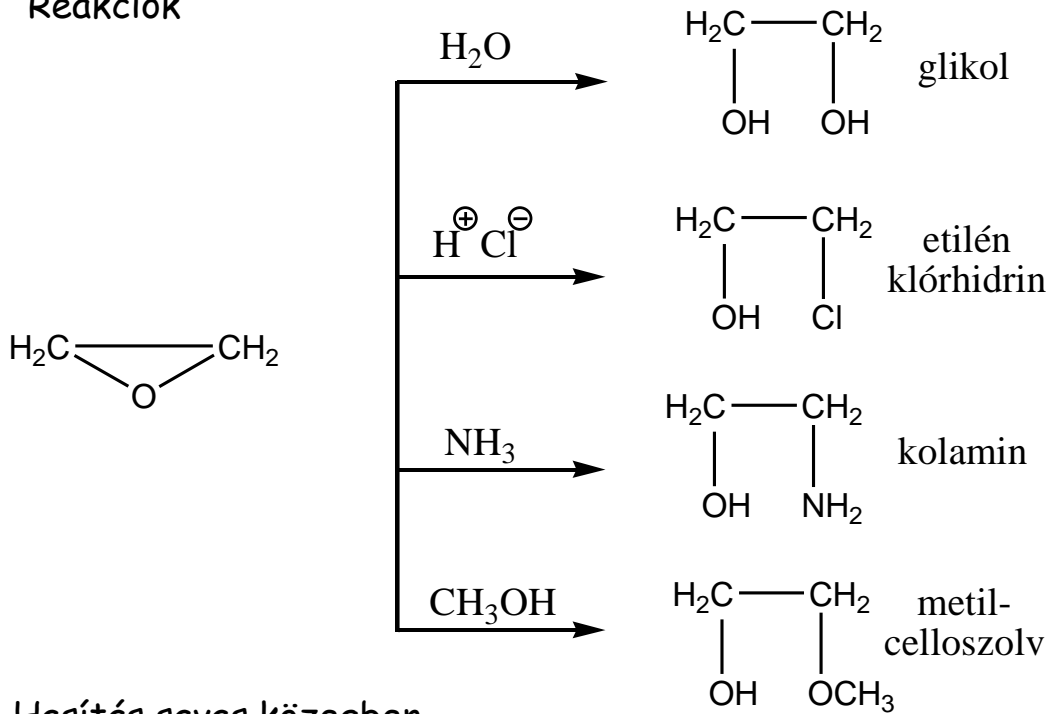
5. Addíció

[gyűrűs éterek: epoxidok (etilénoxid, oxirén) reakciói]

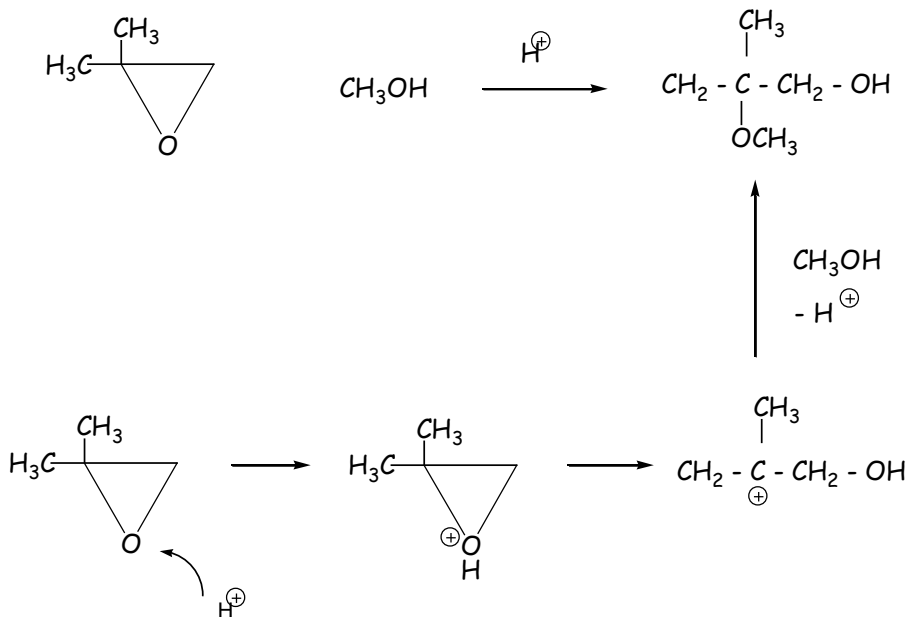
Előállítás

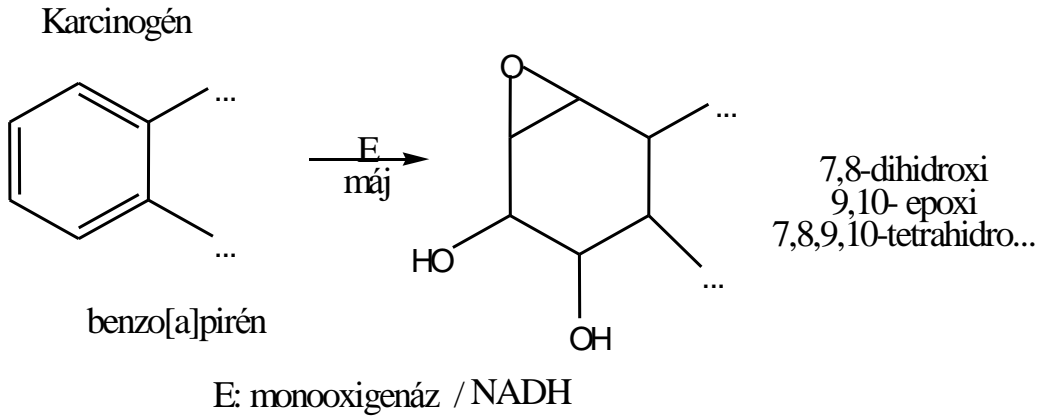
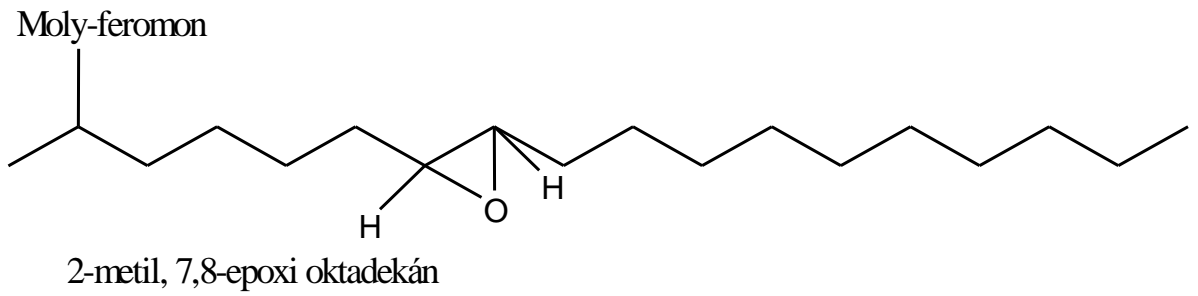


Reakciók



Hasítás savas közegben

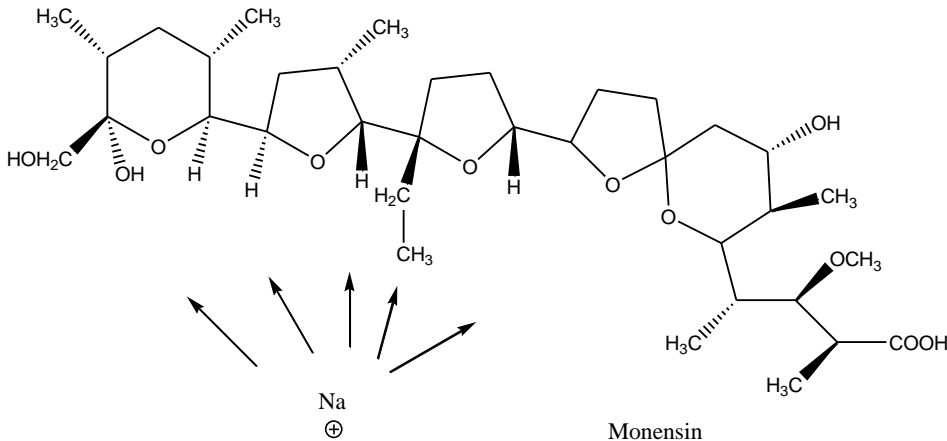




Poliéterek

Lineáris (1950)

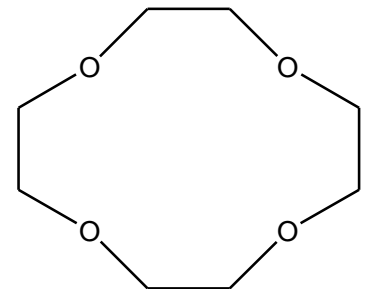
Antibiotikum - ionofór (fém-ion transzport)



Ciklusos „korona” éter

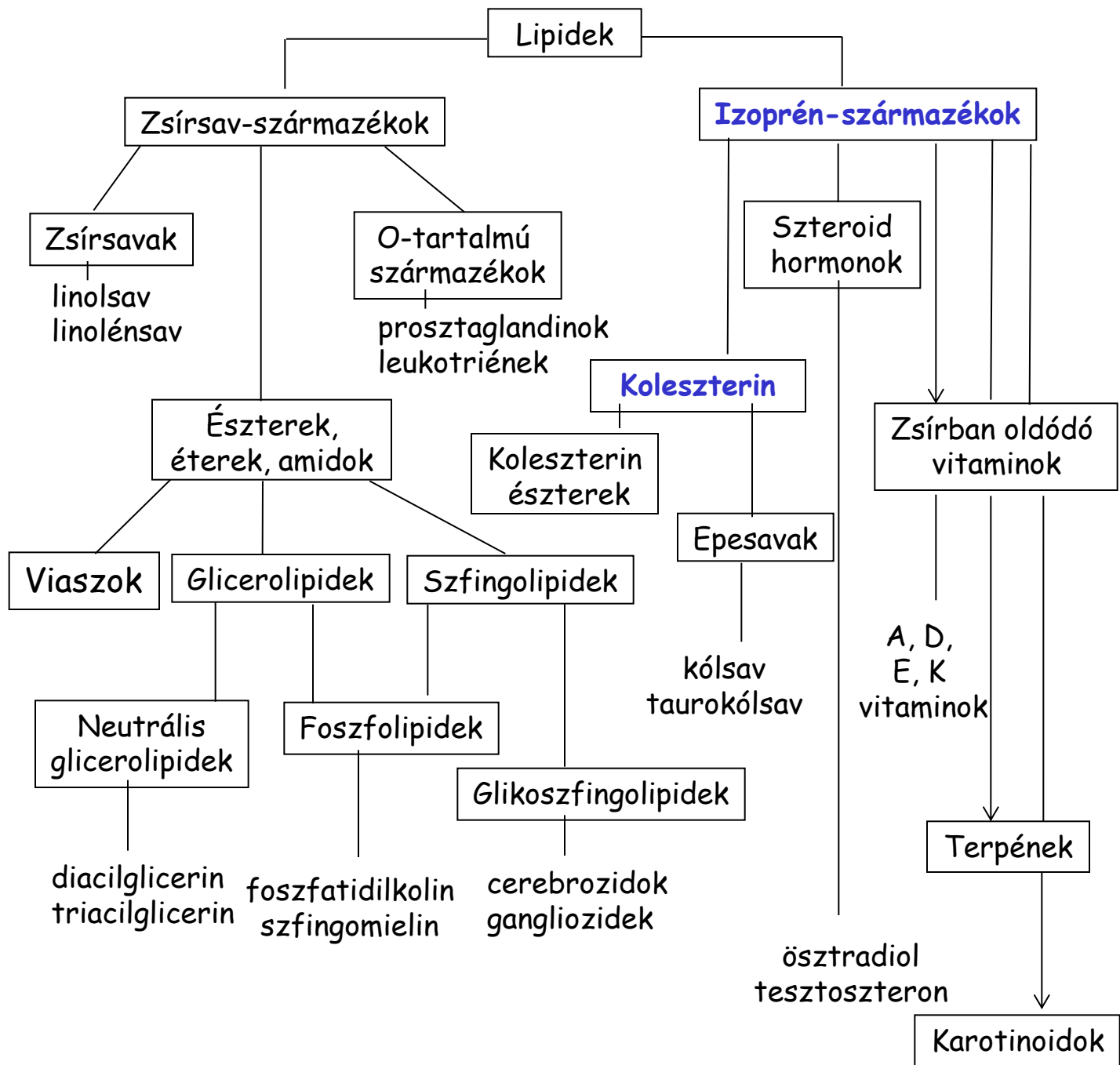
[C. J. Pedersen (1967,
Nobel díj 1987)]

Legkisebb: 4O, 8C



12-korona-4

Egyszerű lipidek



Koleszterinek

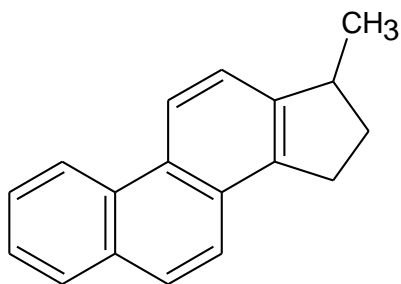
Koleszterin = kholé (epe) sztereosz (szilárd, kemény)

Napi „forgalom” 250 mg étkezés, 850 mg bioszintézis

Felnőtt: 200 g koleszterin

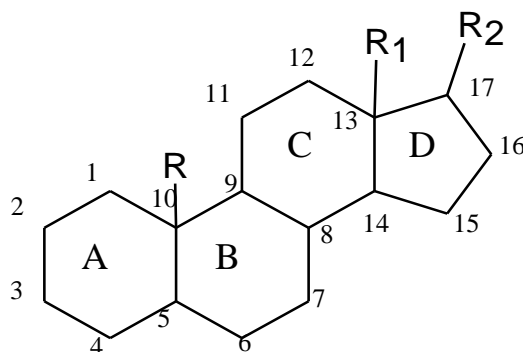
1770 Chevreul (epékő), 1928-32 Windaus, Wieland

Alapváz: Nobel-díj, 1950



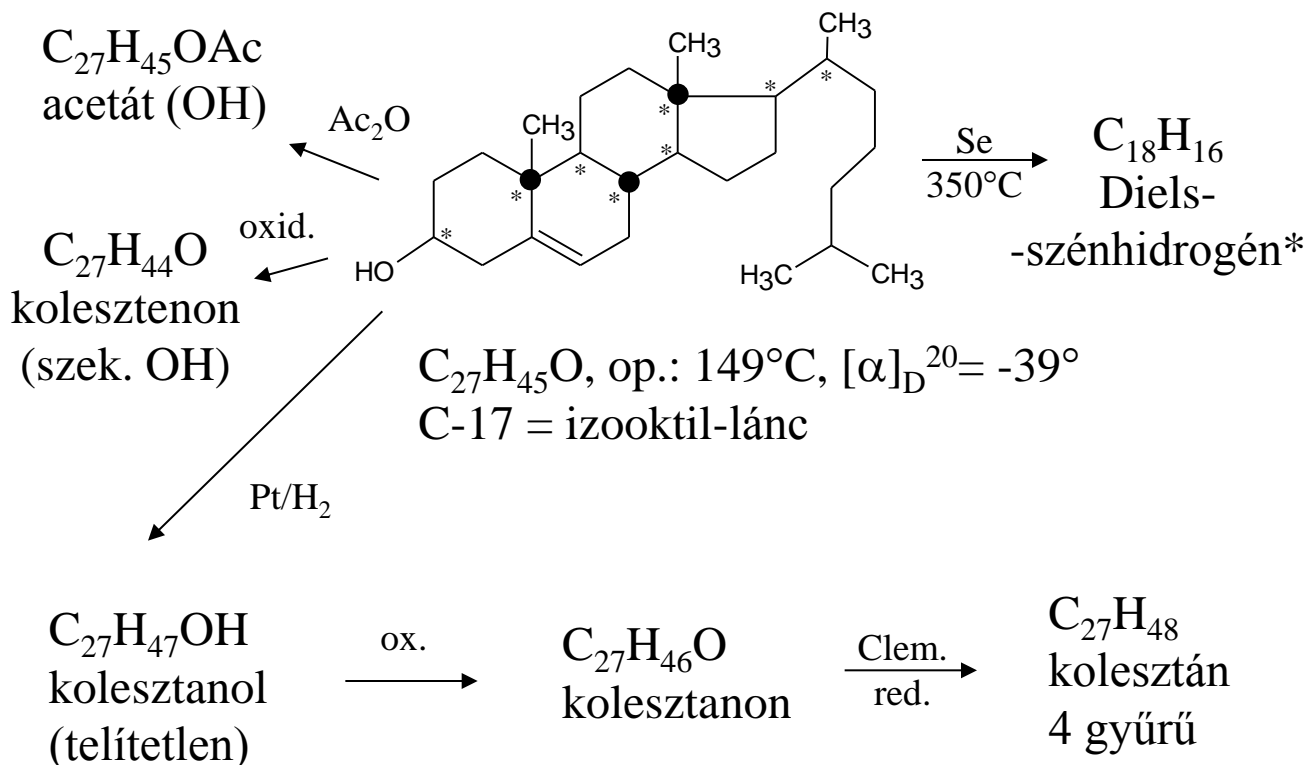
γ

γ -metil-1,2-ciklopenteno-fenantrén
(Diels-szénhidrogén, $C_{18}H_{16}$)



R és R_1 általában CH_3

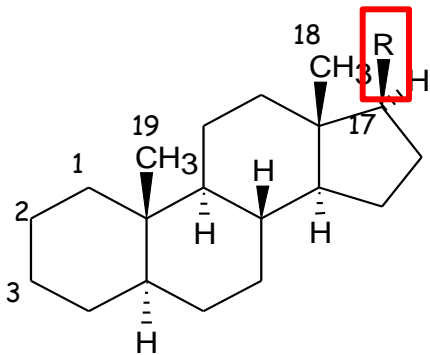
Szerkezetigazolás:



Alapvázak

R

Elnevezés



-H

androsztán

-CH₂-CH₃

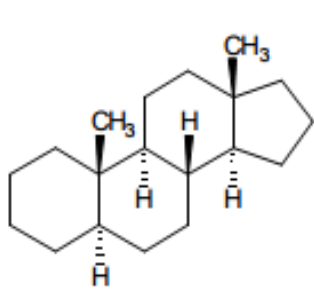
pregnán

-CH-(CH₂)₂-CH₃
|
CH₃

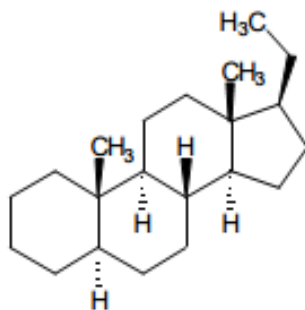
kolán

-CH-(CH₂)₃-CH-CH₃
| |
CH₃ CH₃

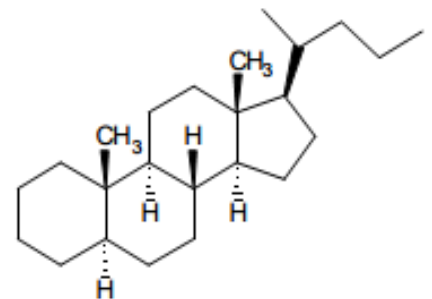
kolesztán



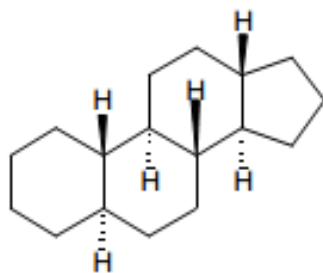
5 α -androsztán



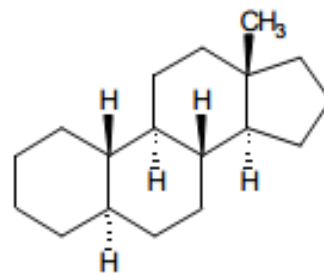
5 α -pregnán



5 α -kolán

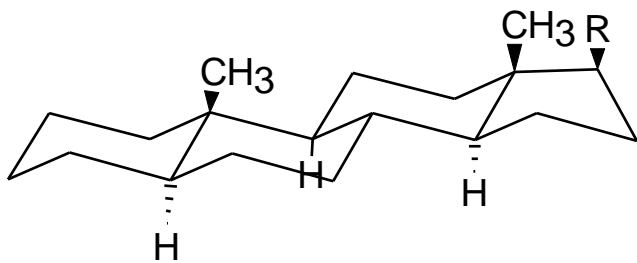


5 α -gonán



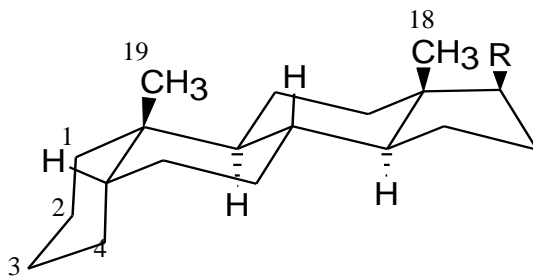
5 α -ösztrán

Koleszterinek, vázak - térszerkezet



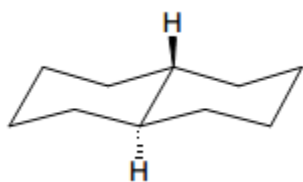
5- α szteroid (all-transz)

kolesztán

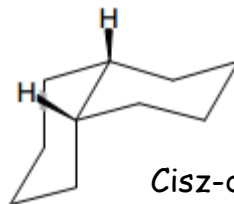


5- β szteroid
(A-B cisz, B-C, C-D transz)

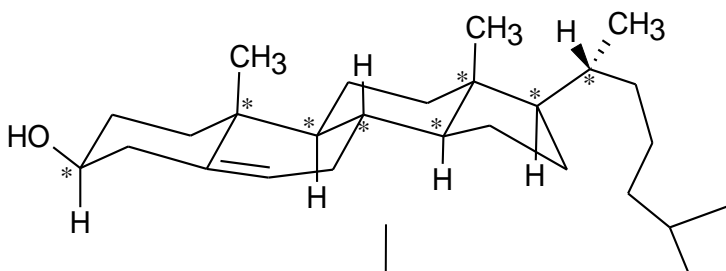
koprosztán



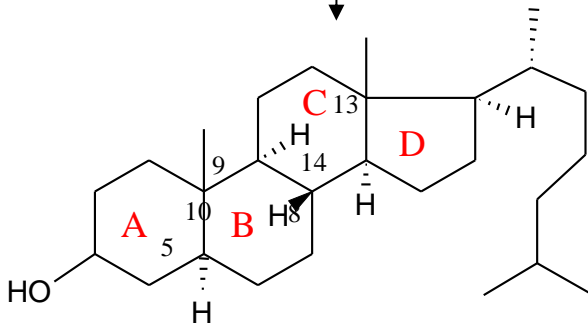
Transz-dekalin



Cisz-dekalin



redukció



kolesztanol

[5 α -kolesztán-3 β -ol]

A/B transz
B/C transz
C/D transz

9/10 anti
8/14 anti

koleszterin

•8 aszimmetria centrum
[3, 8, 9, 10, 13, 14, 17, és 20]

•sztereoizomerek száma:
 $2^8=256$

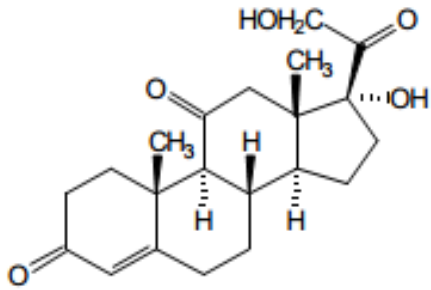
•all-transz
10,13-CH₃
17-izooktil } 3-OH
b

Jelölés

● v. | v. ▲ $\Rightarrow \beta$
„sík felett”

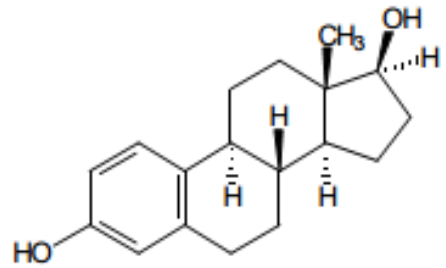
▲ $\Rightarrow \alpha$
„sík alatt”

Nomenklatura



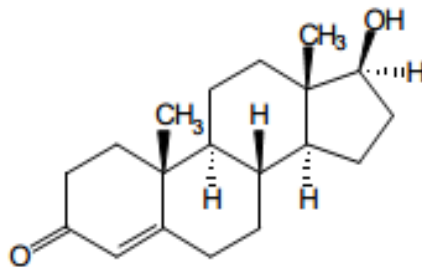
Kortizon

(17 α ,21-dihidroxi**preg**-4-en-3,11,21-trion)



17 β -ösztadiol

Ösztra-1,3,5(10)-tien-3,17 β -diol



Tesztoszteron

17 β -hidroxi**androst**-4-en-3-on

Szterinek csoportosítás

Szterinek (angol: sterol)

alkoholok

Epesavak

hidroxi-karbonsavak

Szívre ható glikozidok

Szteroid szaponinok

Szteroid alkaloidok

glikozid

Szteroid hormonok

hidroxi-oxovegyületek

Szterinek felosztása

- OH

Fitoszterinek (növényi)

Alacsonyabb rendű növények (pl. gomba)

Zooszterinek (állati, emberi) - koleszterin

Sejtmembrán felépítése

Érelmeszesedés

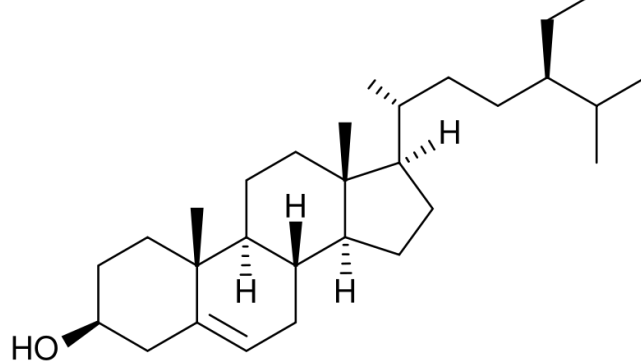
(az agy 10%-a)

Fitoszterinek (növények)



Serenoa repens

(pl. avocado, pekan-dió, sütőtök mag, kesudió, szójabab)



β -Szitosterin (op. 136-140 °C)

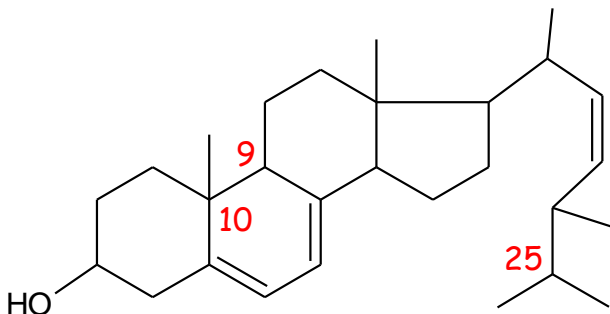
Mikoszterinek (gombák)

ergoszterin: legfontosabb gomba szterin

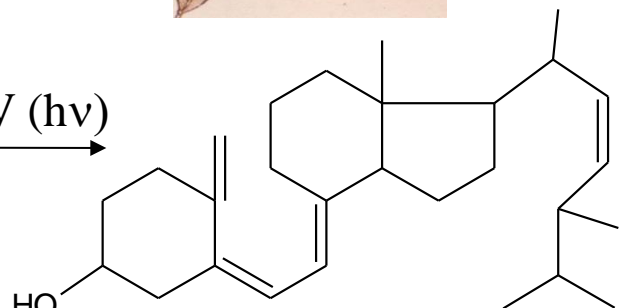
anyarozsból: Ch. J. Tanret, 1889

élesztőből: A. O. R. Windaus, 1925

(Nobel díj, 1928)

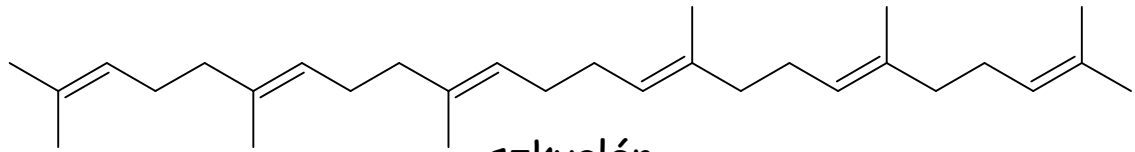


UV (hv)



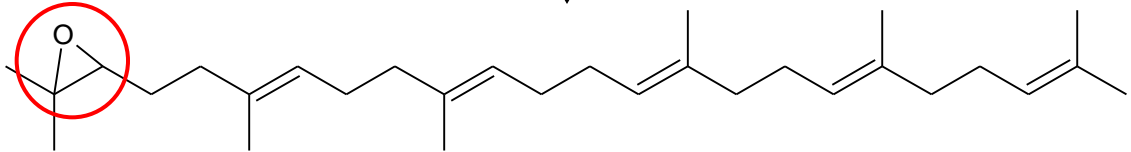
D2 vitamin

Koleszterin bioszintézise



oxidáció

O_2 , NADH, enzim

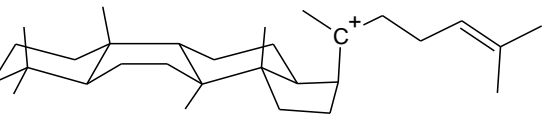


Gyűrűfelnyílás

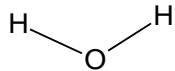
H^+
ciklizáció



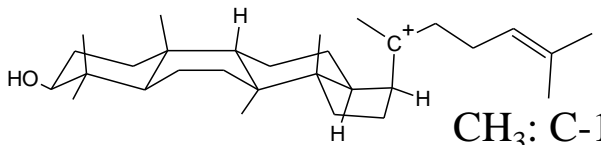
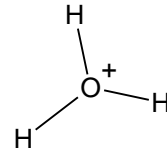
squalén-2,3-epoxid



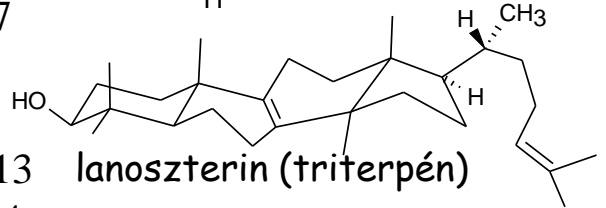
tetraciklusos karbokation



H^+ : C-17 \rightarrow C-20
C-13 \rightarrow C-17

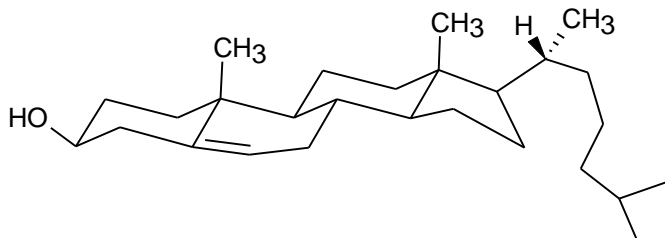


CH_3 : C-14 \rightarrow C-13
C-8 \rightarrow C-14



lanoszterin (triterpén)

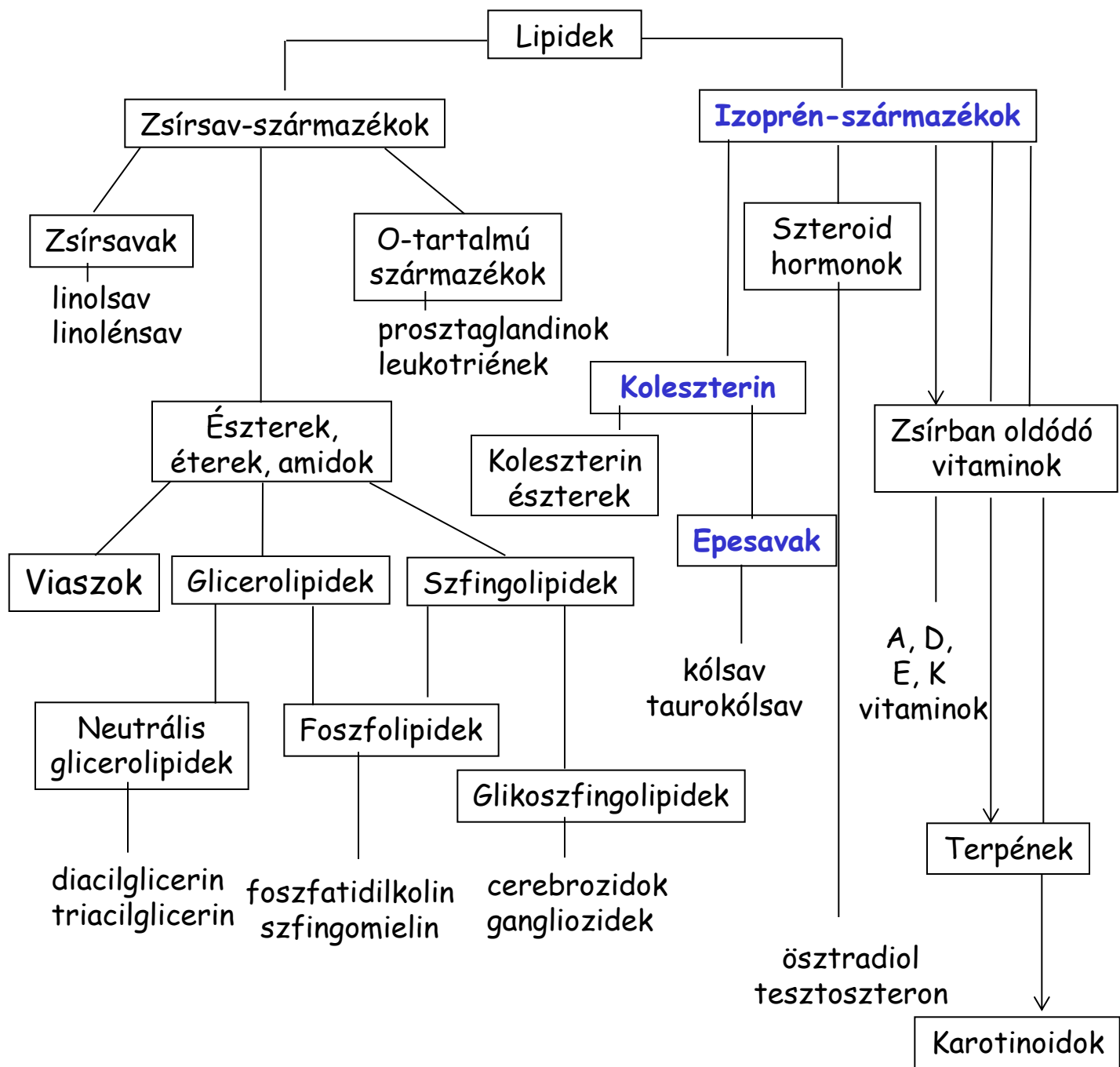
enzimek



koleszterin

N.B. lanoszterin a lanolin egyik komponense

Egyszerű lipidek

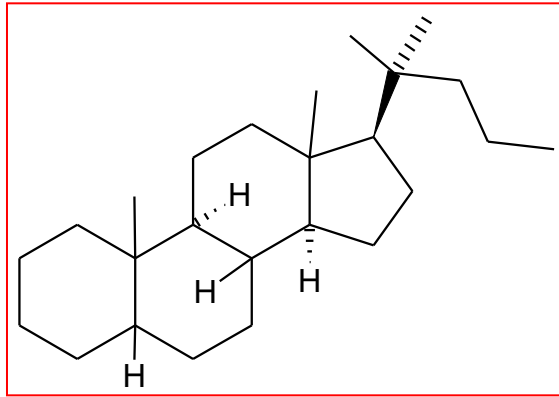


Epesavak

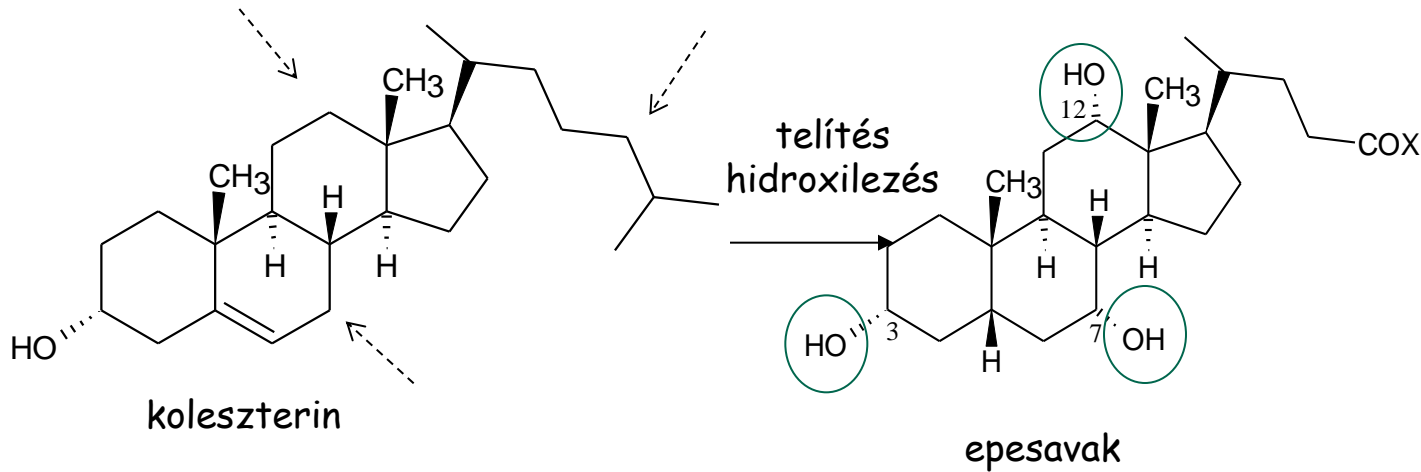
Alapváz: 5 β -kolán

hidroxi-karbonsavak

-OH
-COOH



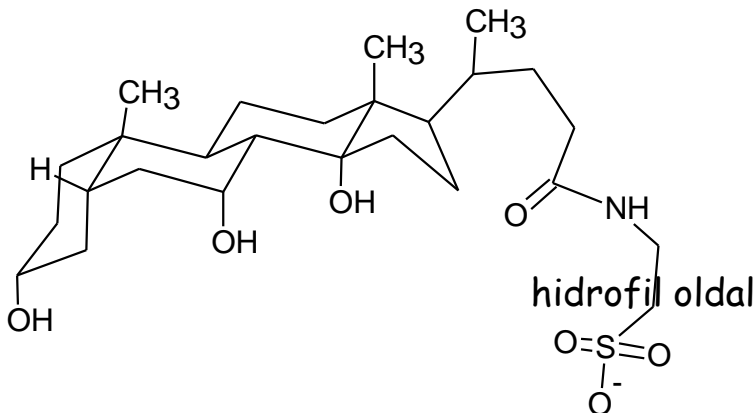
Keletkezés: máj



Funkció: zsír emésztése
lipid-transzport
(detergens)

X = OH kólsav
X = NH-CH₂-COO-Na⁺, glicin-amid
X = NH-(CH₂)₂-SO₂O-Na⁺, taurin-amid

hidrofób oldal



Emberi epe összetétele

- | | | |
|----|-------------------|-------------|
| 1. | Epesavak (sók) | 1,2-18 g/l |
| 2. | Foszfatidil-kolin | 1,4-8,0 g/l |
| 3. | Bilirubin | 0,1-0,7 g/l |
| 4. | Protein | 0,3-3,0 g/l |
| 5. | Koleszterin | 1,0-3,2 g/l |

Szteroid hormonok

Alapváz: **pregnán**

hidroxi-oxo vegyületek

-OH

-CHO

1. Mellékvesekéreg-hormonok

Reichenstein, Kendall (Nobel-díj, 1950)

40 kristályos szteroidhormon

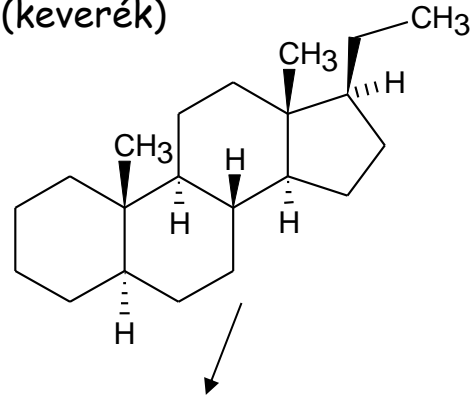
1 kg marha mellékvese → 50 mg (keverék)

Jellemzők:

- 4-es helyzetben telítetlen

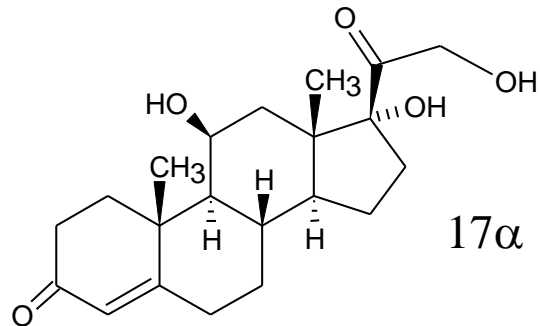
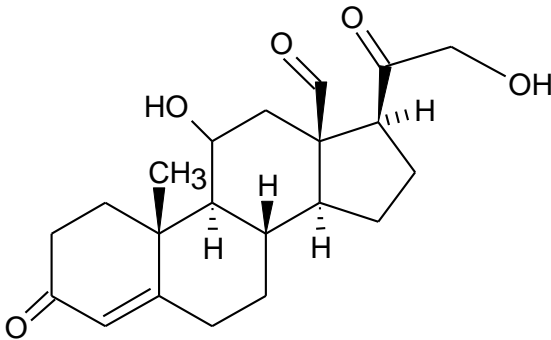
- 3,20 diketo

- 21 OH



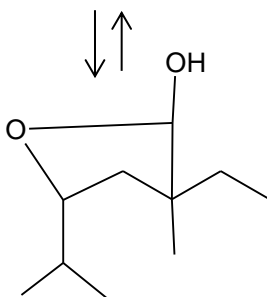
Mineralokortikoidok
(só- és vízháztartás)

Glükokortikoidok
(szénhidrátanyagcsere)



17 α

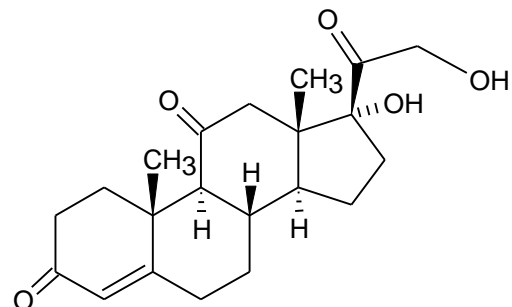
Kortizol (hidrokortizon)



aldoszteron

op.: 112-116°C,

$[\alpha]_D = +152^\circ$



17 α

Kortizon (gyulladásgátló)

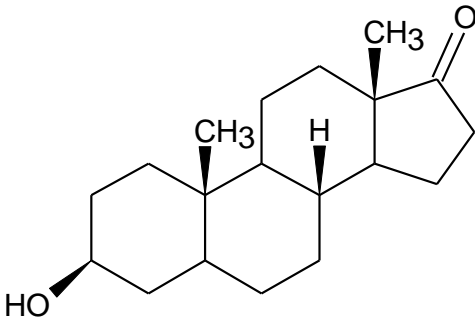
N.B. 1-2 dehidro = prednizon
prednizolon

2. Nemi hormonok

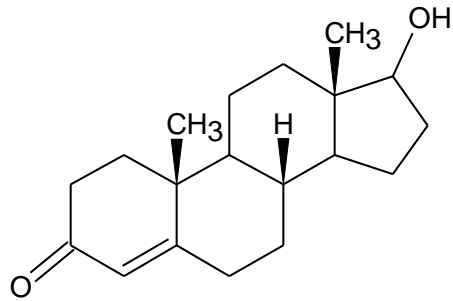
- Funkció alapján:
- A. hímvári hormonok (androgének)
 - B. tüszőhormonok (ösztrogének)
 - C. sárgatest hormonok (gesztrogének)

A. Hímivarhormonok

C19 5 α v. 5 β androsztán váz előállítás koleszterinből



androsteron (1931)
vizeletből izolált,
15000 liter \rightarrow 15 mg



tesztoszteron (1935)
ökörhérből izolált

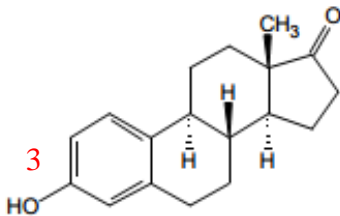
B. Folliculus (tüsző) hormonok

funkció: terhesség alatt gátolja a méh összehúzódását

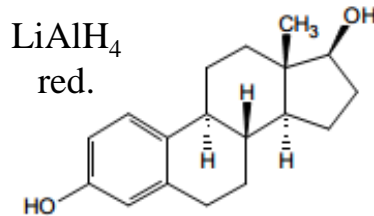
Jellemzők:

- a) aromás A gyűrű
- b) 3-as OH, fenolos!
- c) 17 β OH vagy ketocsoport

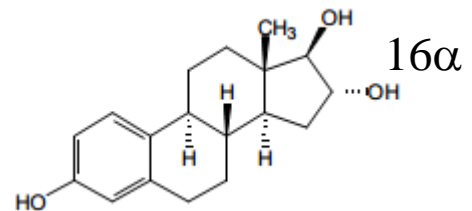
eá: koleszterinből



ösztron
(az első izolált, 1929)

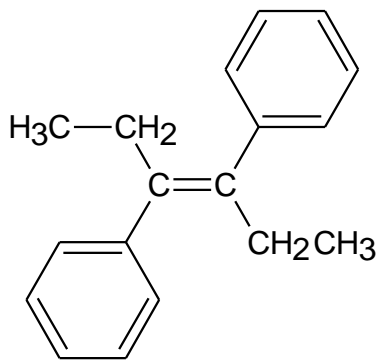


17 β -ösztradiol
4 t koca ovárium - 12 mg

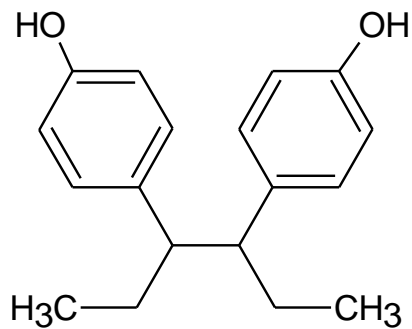


ösztriol

De: van **nem szteránváz**as, hormonhatású vegyület is



sztilbösztrol



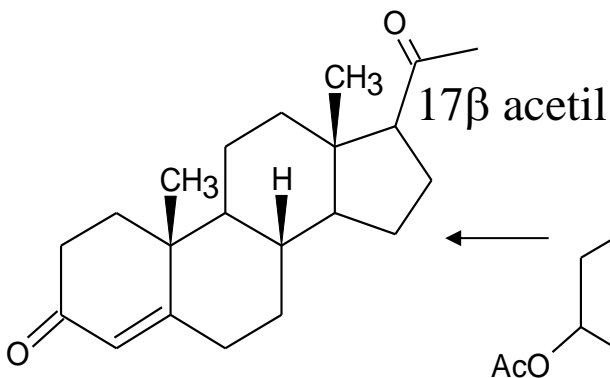
hexösztol

C. Sárgatest (corpus luteum) hormonok

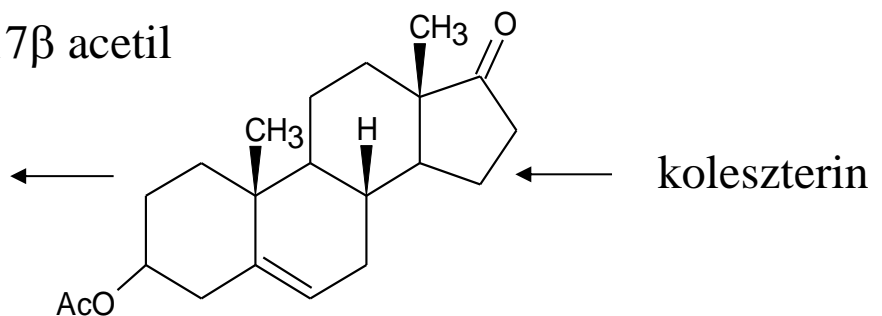
Funkció: pete felvételére, megkötésére
alkalmassá tegye a méhfalat

Alapváz: pregnán

(gesztagén hatás)



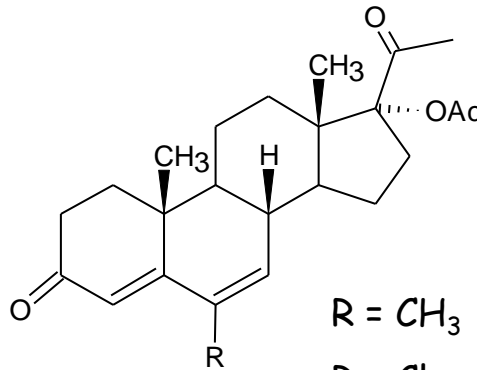
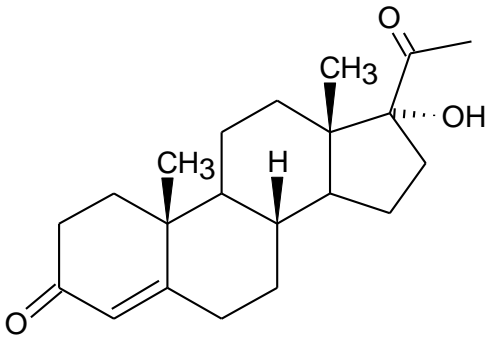
progeszteron
(egyetlen természetes!)



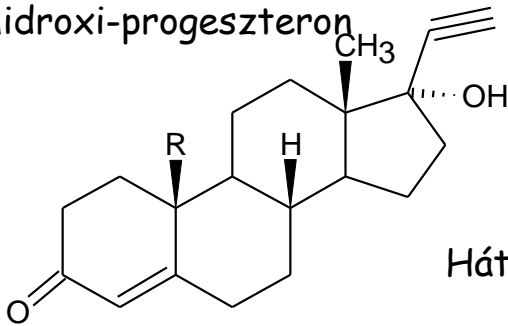
dehidroepiandroszteron-acetát

Fogamzásgátlók (1938, H. Inhoffen)

ovulációgátló: progeszteron (csak injekcióban!)



17 α -hidroxi-progeszteron



R = CH₃ etiszteron (1938)
R = H nor-etiszteron (~1960)

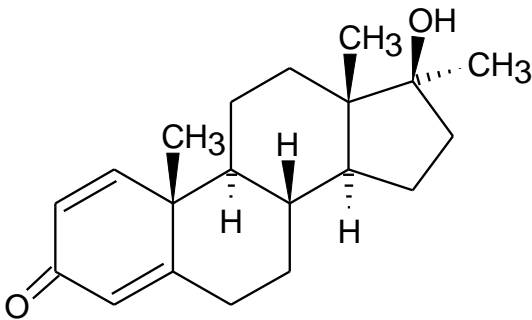
Hátrány: magas vérnyomás (3/100000)
trombózis veszély (30/100000)

Anabolikus szteroidok

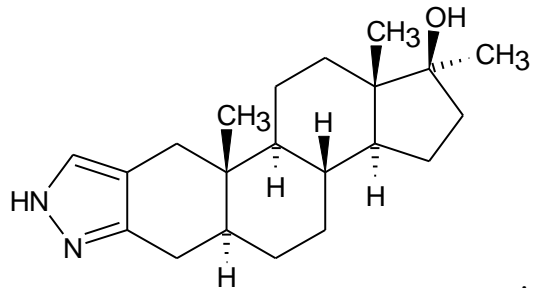
Metabolizmus

„katabolizmus”
lebontó folyamatok
nagy \rightarrow kicsi

„anabolizmus”
felépítő folyamatok
kicsi \rightarrow nagy
(tesztoszteron - izom)



dianabol



stanozolol

Ben Johnson, 1988, vizeletben