

## 6. Előadás

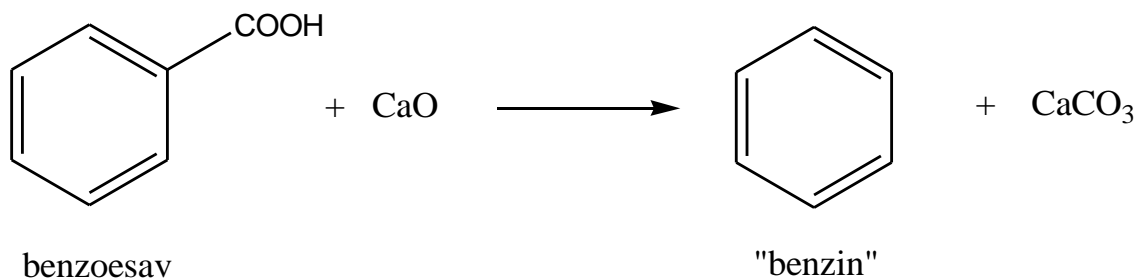
Szénhidrogének: arének.

Halogénezett szénhidrogének.

Fémorganikus vegyületek.

## 17.4. Arének

Benzol, felfedezés, 1825 Michael Faraday ;  
előállítás, 1934 Eilhard Mitscherlich (benzin)



Benzoe gyanta (Gummi benzoë) - szagtalan

Styrax - fák kérge  $\longrightarrow$  balzsam

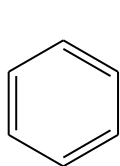
Szumatra - benzoe „in lacirmis” (könnyek)

(fahéjsav, vanillin) „in massa”

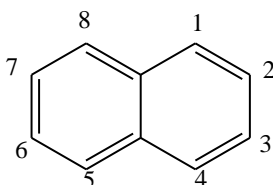
1845. A. W. Hofmann, szénkátrányból

1950. petroleumból

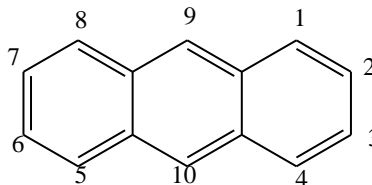
Példák:



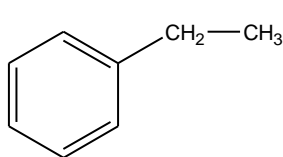
benzol



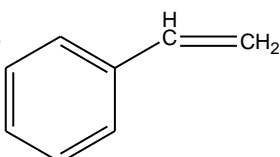
naftalin



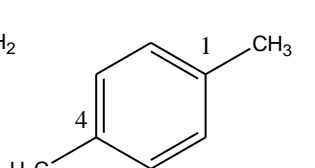
antracén



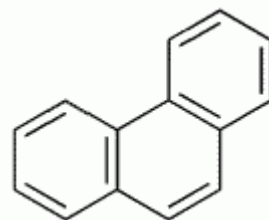
etil-benzol



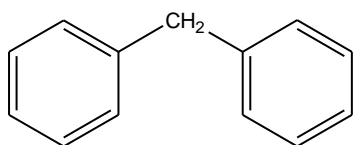
sztirol



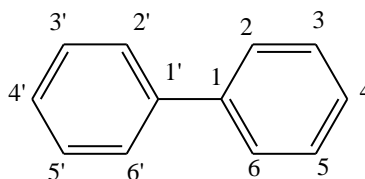
1,4-dimetil-benzol



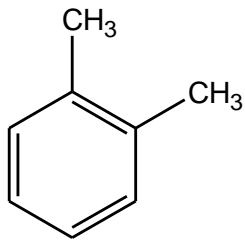
fenantrén



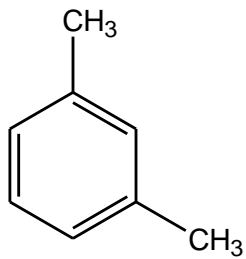
difenil-metán



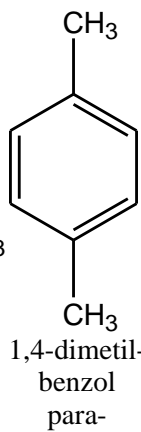
bifenil



1,2-dimetil-  
benzol  
orto-

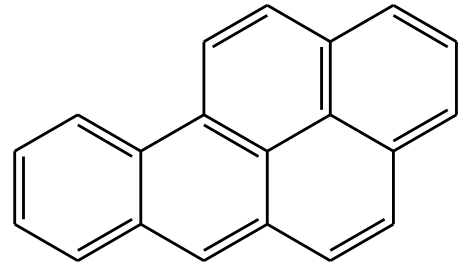


1,3-dimetil-  
benzol  
meta-



1,4-dimetil-  
benzol  
para-

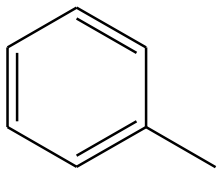
xilol



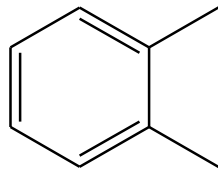
benzo[a]pirén

1775: Sir Percival Pott

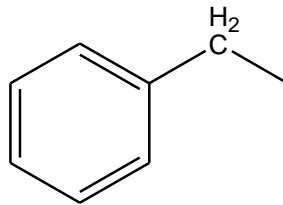
### Csoportnevek



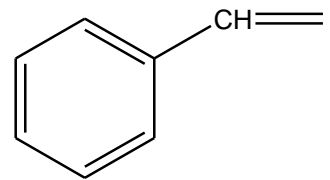
fenil



1,2-fenilén



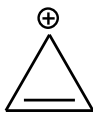
benzil



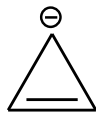
benzál

Homológ sor  $[4n+2]$

De nem tartozik ide



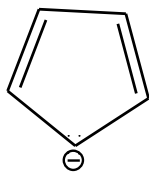
ciklopropenilium kation



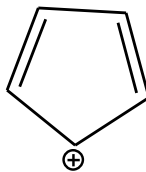
4



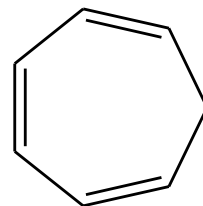
4



ciklopentadienát anion

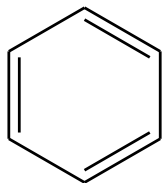


4

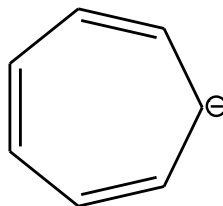


6

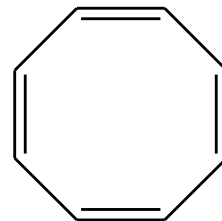
\*



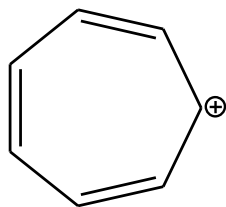
benzol



8



8



cikloheptatrienilium kation

HÜCKEL-SZABÁLY

\* Nem planáris

## Az arének szerkezete

Kötésmód  $C(sp^2) - C(sp^2)$  }  $C(p) - C(p) \pi$   
 $C(sp^2) - H(s)$  }  $\sigma$

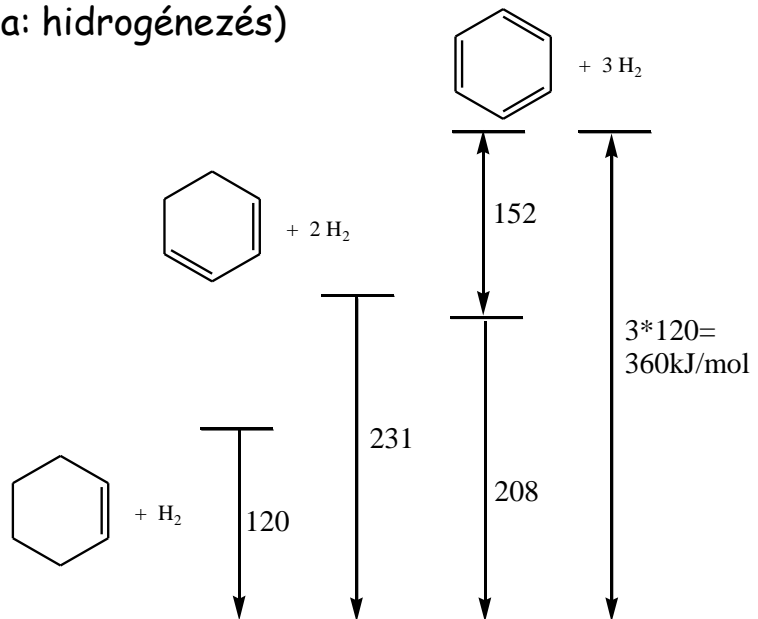
ciklusosan konjugált rendszer

Kötéshossz  $r[C(sp^2) - C(sp^2)] = 1,39 \text{ \AA}$

Kötésszög  $CCC \neq 120^\circ$  }  
 $HCC \neq 120^\circ$  } Nincs szögfeszültség

Konfiguráció planáris gyűrű

Kötési energia (példa: hidrogénezés)



## Fizikai tulajdonságok

### Halmazállapot

	op [°C]	fp [°C]		op [°C]	fp [°C]
Benzol	5,5	80	Toluol	-95	111
Naftalin	80	218	o-Xilol	-25	144
Antracén	217	340	m-xilol	-48	139
Fenantrén	99	340	p-xilol	13	138

(Bonyolultsággal nő az fp.)

Oldékonyság: Hasonló hasonlót old.

## Arének reakciói

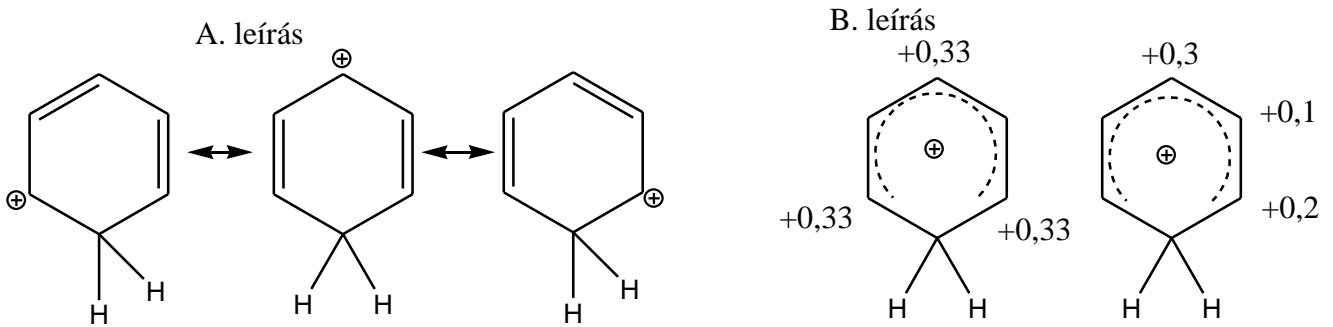
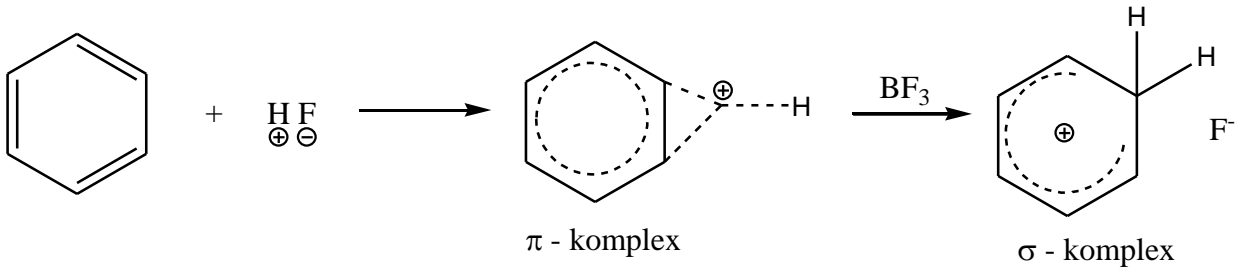
### Aromás magon

1. Sav-bázis reakció
2. Oxidáció
3. Redukció-hidrogénezés
4. Addíció
5. Elektrofil szubsztitúció

### Oldalláncon

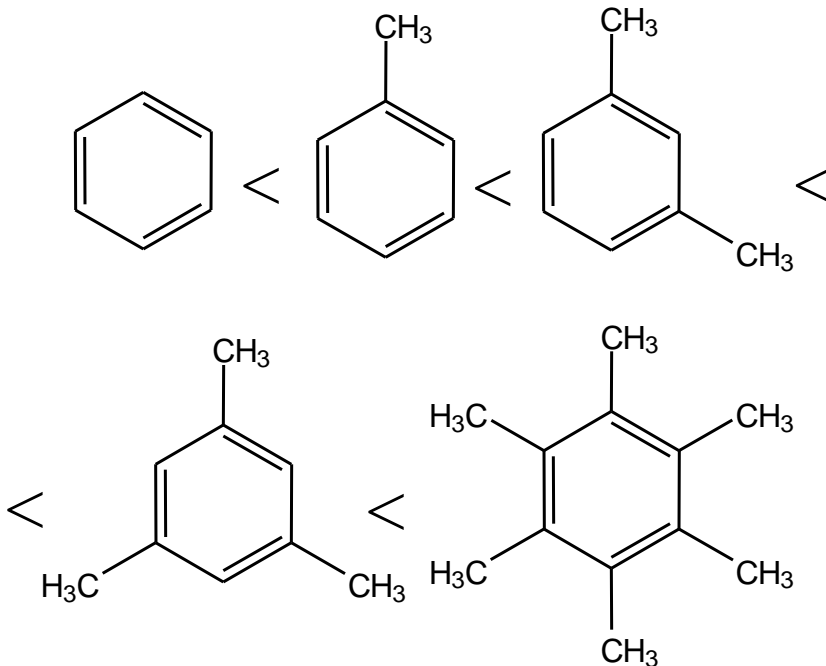
Oxidáció

# 1. Sav-bázis reakció

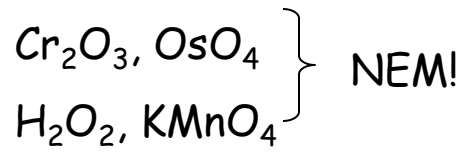


„Aktív” helyek: para > orto > meta

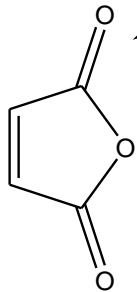
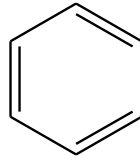
Relatív bázikusság: (+ I effektus - alkil csoport)



## 2. Oxidáció



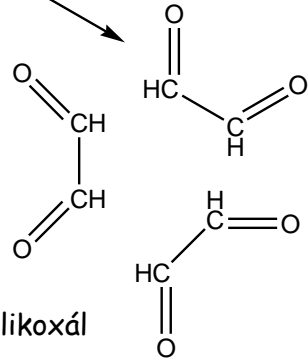
### Aromás magon



maleinsavanhidrid

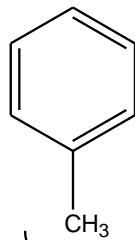
levegő,  $\text{V}_2\text{O}_5$   
 $450^\circ\text{C}$

1.  $\text{O}_3$   
2.  $\text{Zn}, \text{H}_2\text{O}$

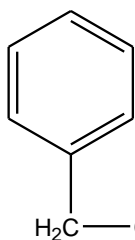


glikoxál

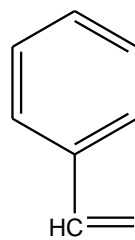
### Oldalláncon



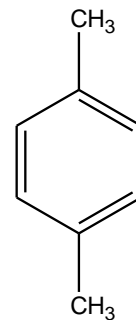
$\text{CH}_3$



$\text{H}_2\text{C}-\text{CH}_3$

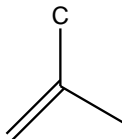


$\text{HC}=\text{CH}_2$

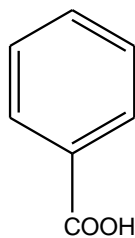


$\text{CH}_3$

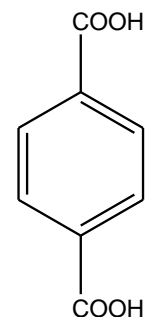
Feltétel:



$\text{KMnO}_4 (\text{OH}^-)$



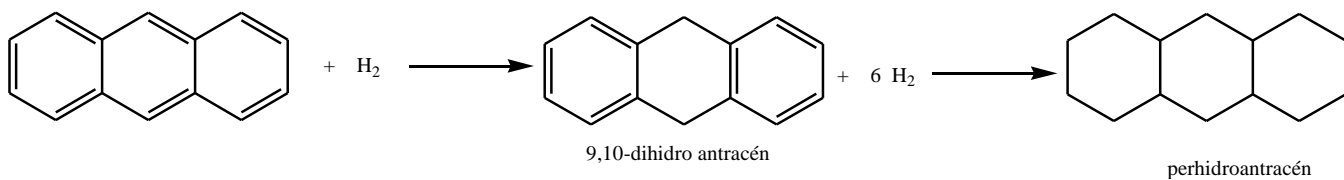
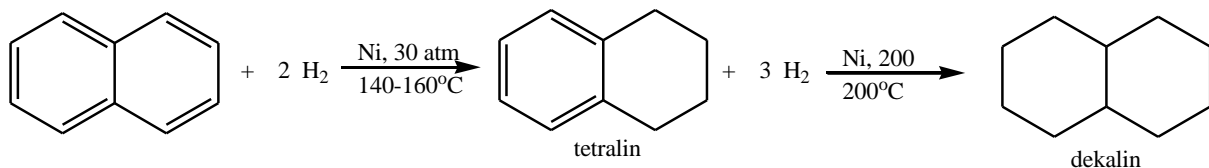
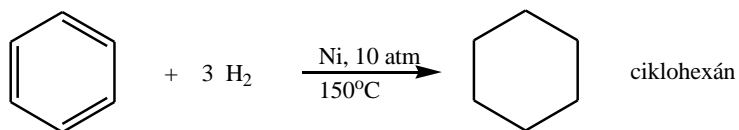
$\text{COOH}$



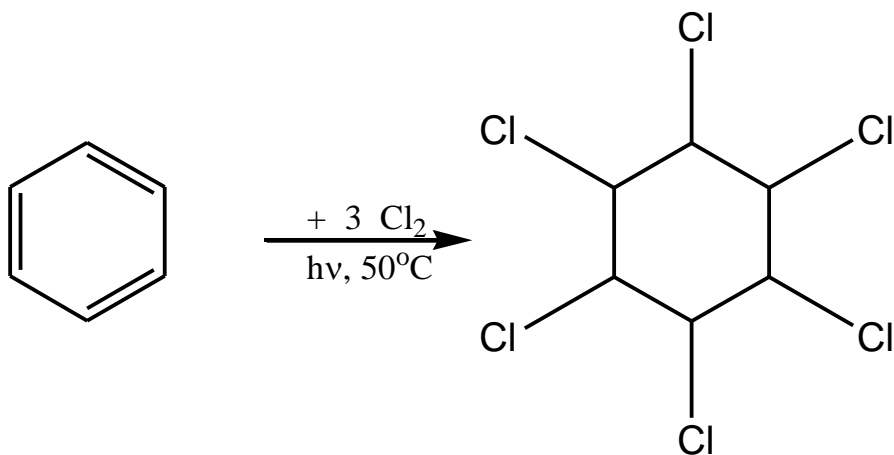
tereftálsav



### 3. Hidrogénezés [Addíció] $Ad_E$



### 4. Addíció $Ad_R$



1,2,3,4,5,6-hexaklór ciklohexán

## 5. Elektrophil szubsztitúció, $S_E$

I. Halogénezés



II. Nitrálás



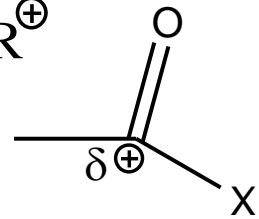
III. Szulfonálás



IV. Friedel-Crafts alkilezés



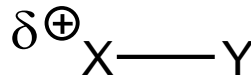
V. Friedel-Crafts acilezés



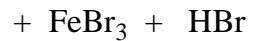
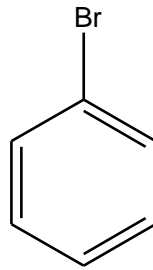
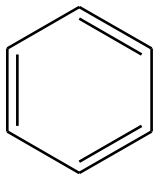
Elektrofilek



vagy

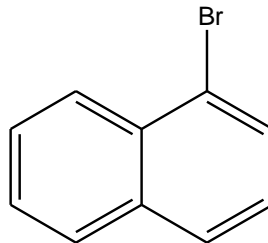
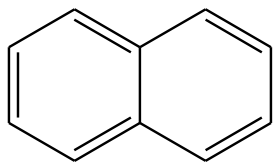
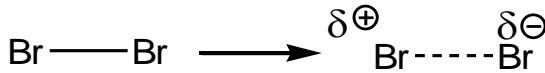


### 5.1. Halogénezés

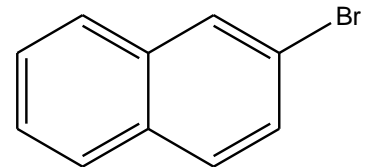


Katalizátor:  $FeCl_3, AlCl_3, ZnCl_2$

szerepe:

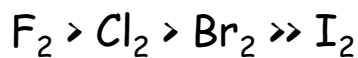


1-bróm-naftalin  
99%



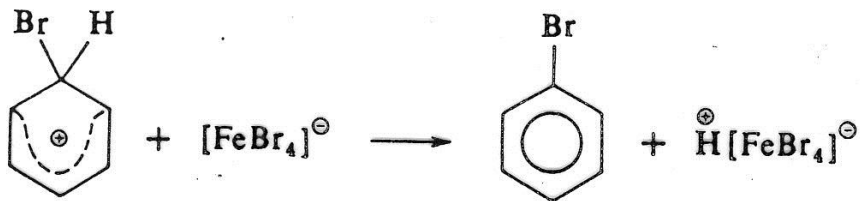
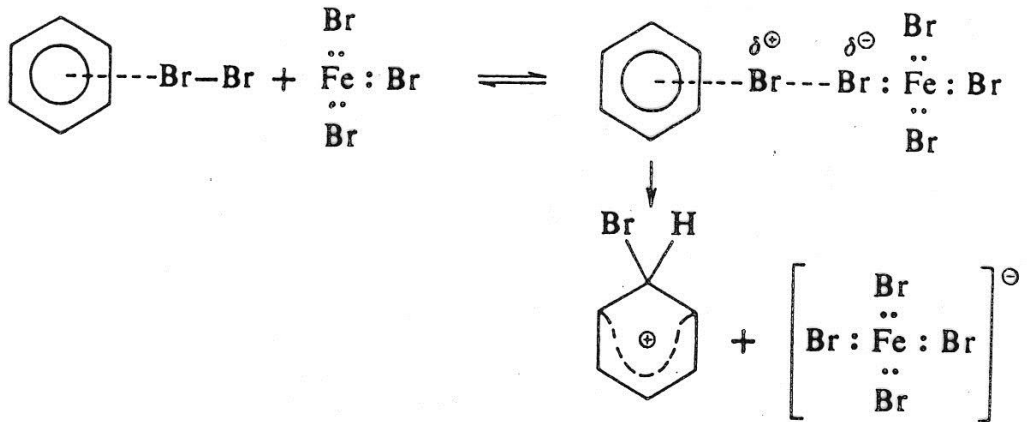
2-bróm-naftalin  
1%

Megjegyzés:

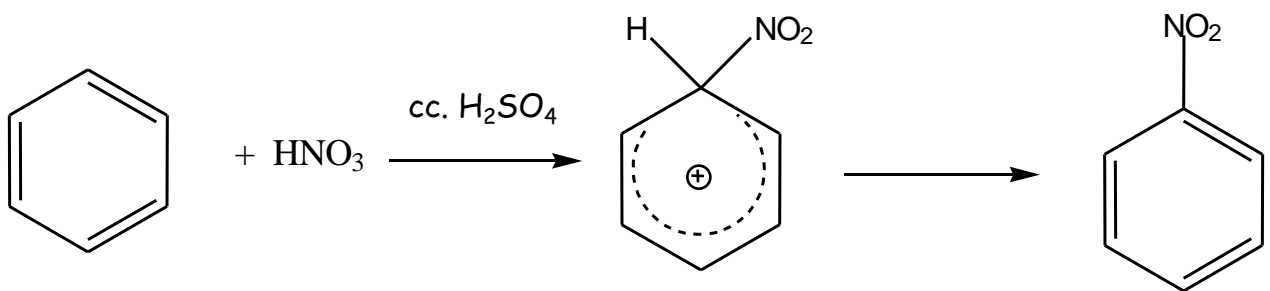


$I_2$  közvetlenül nem reagál

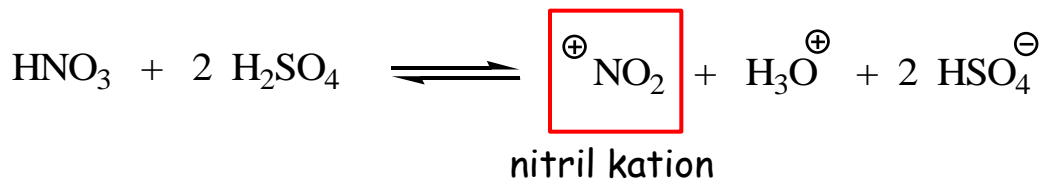
## Mechanizmus



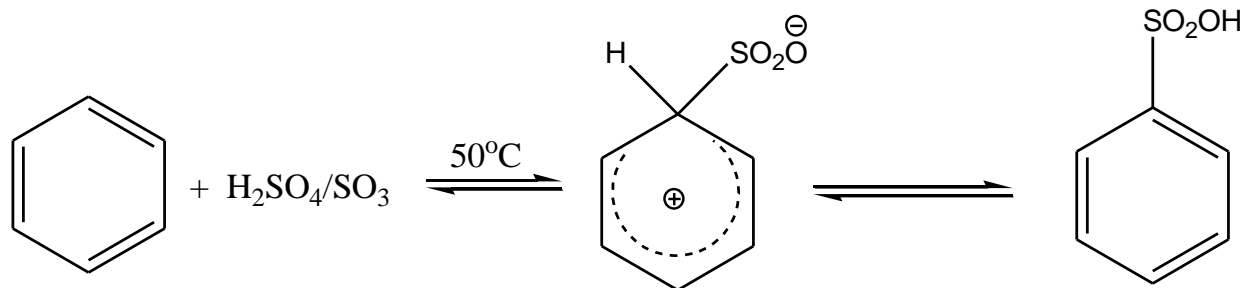
## 5.2. Nitrálás



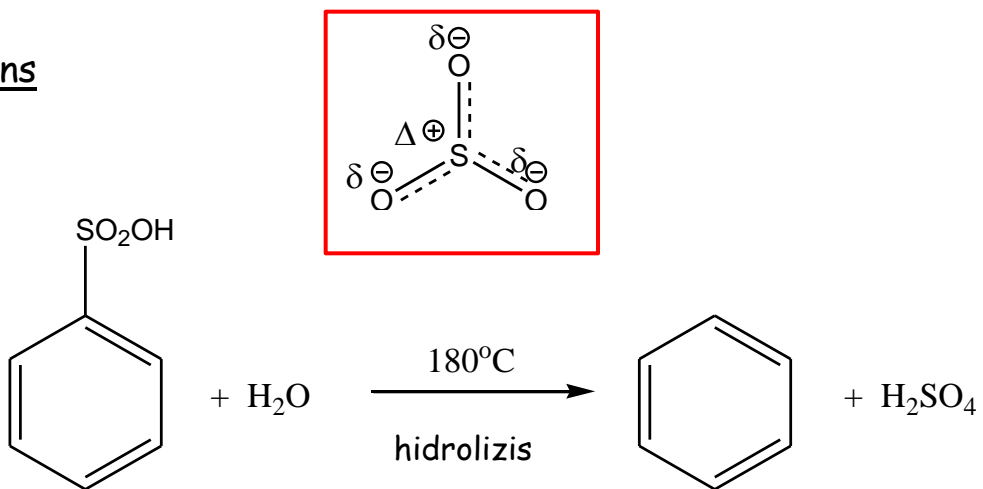
Reagens:



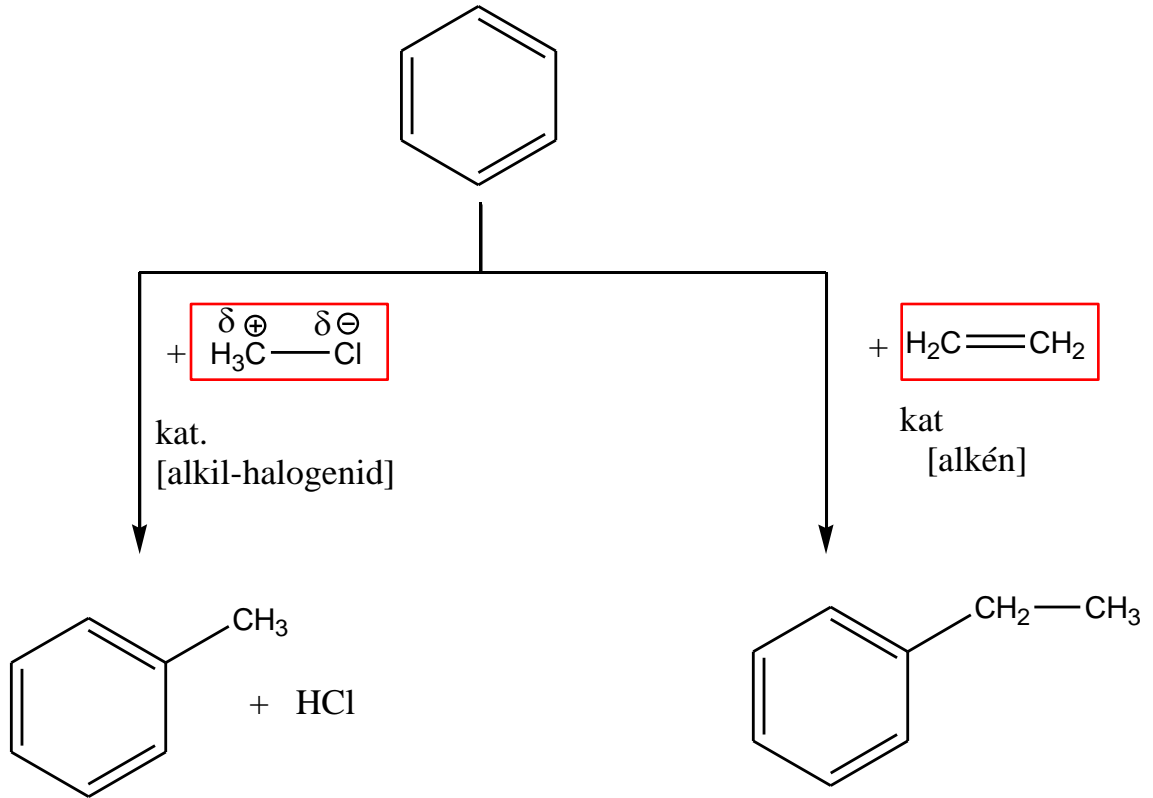
### 5.3. Szulfonálás



Reagens

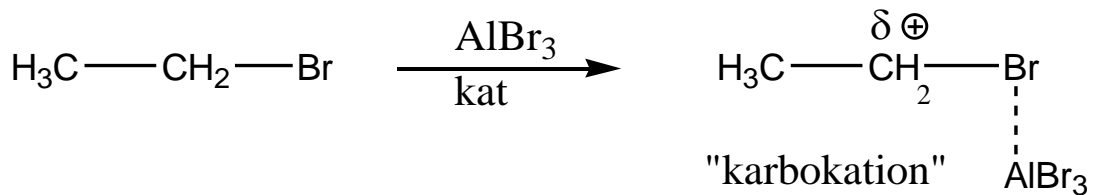


## 5.4. Friedel-Crafts alkilezés



A. Alkil-halogenid: kat.  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ ,  $\text{SbCl}_5$ ,  $\text{BF}_3$

Reagens:



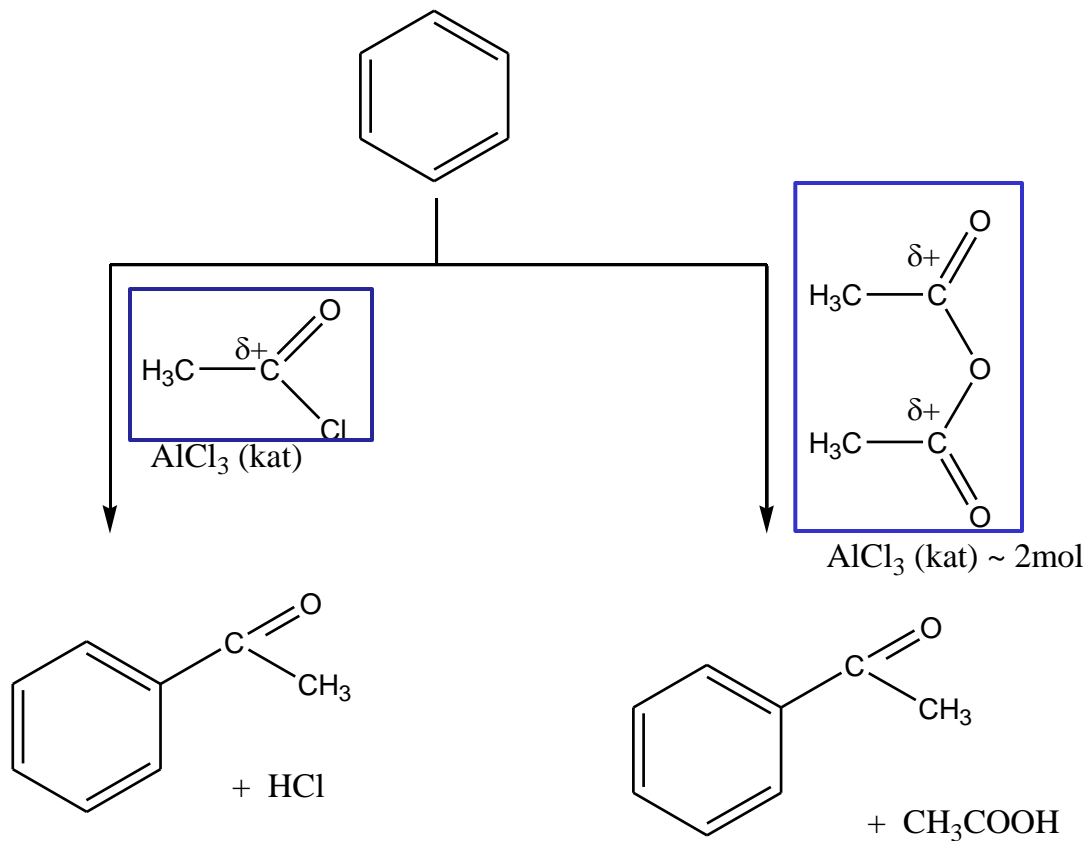
Reaktivitás: terciér > szekunder > primer

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

B. Alkén: kat. sav (pl.  $\text{H}_3\text{PO}_4$ )

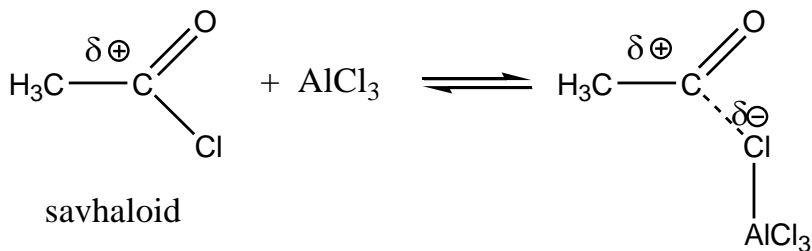
Reagens: karbokation ( $\text{CH}_2 = \text{CH}_2 + \text{H}^+ \rightarrow \text{CH}_3 - \text{CH}_2^+$ )

## 5.5. Friedel-Crafts acilezés

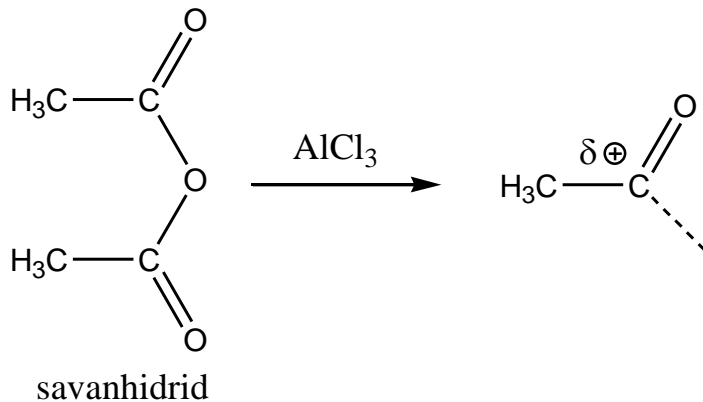


### ACETOFENON

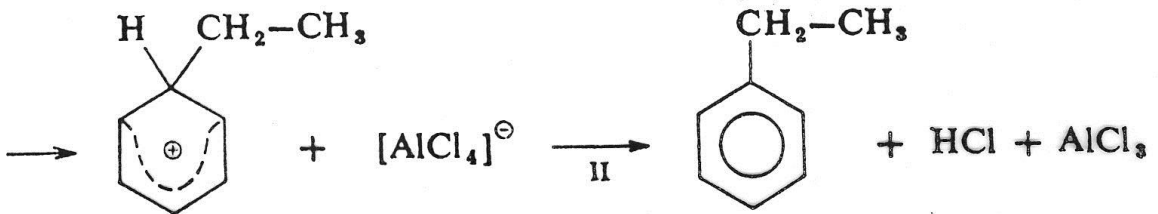
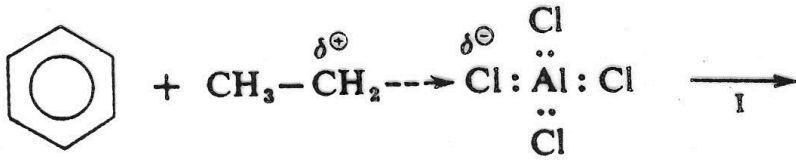
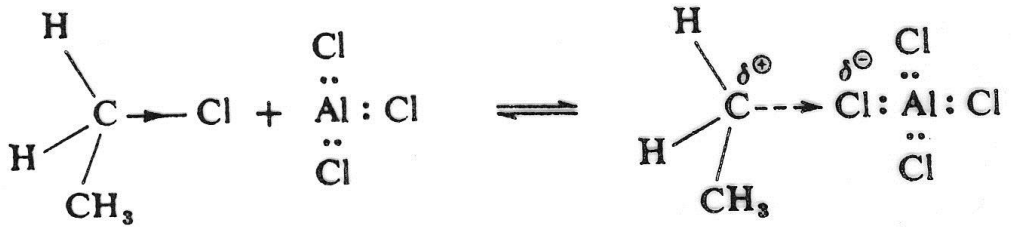
#### Reagens



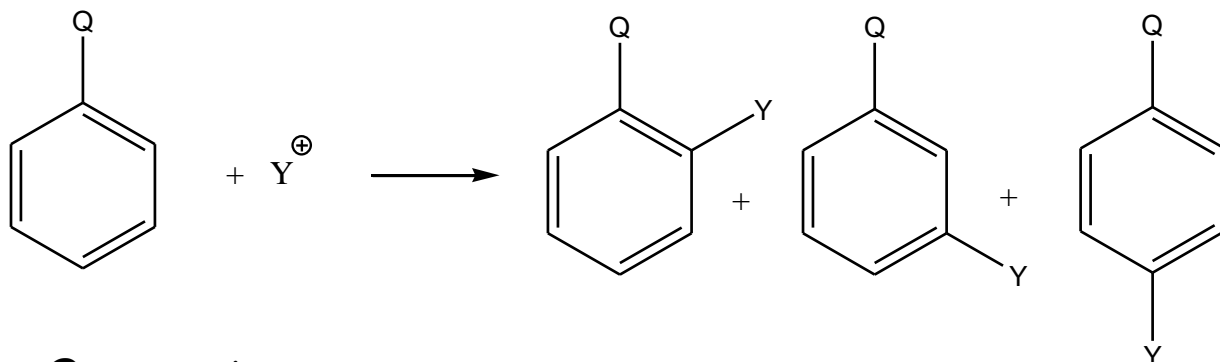
#### Reagens



# Mechanismus



## OLDALLÁNC HATÁSA AZ S<sub>E</sub> REAKCIÓRA



a Q csoport szerepe:

1. Fokozhatja/csökkentheti **a mag reakcióját** a benzolhoz viszonyítva.
2. Befolyásolhatja Y beépülésének **helyét** → irányít.

Q lehet: 1. Aktiváló - dezaktiváló

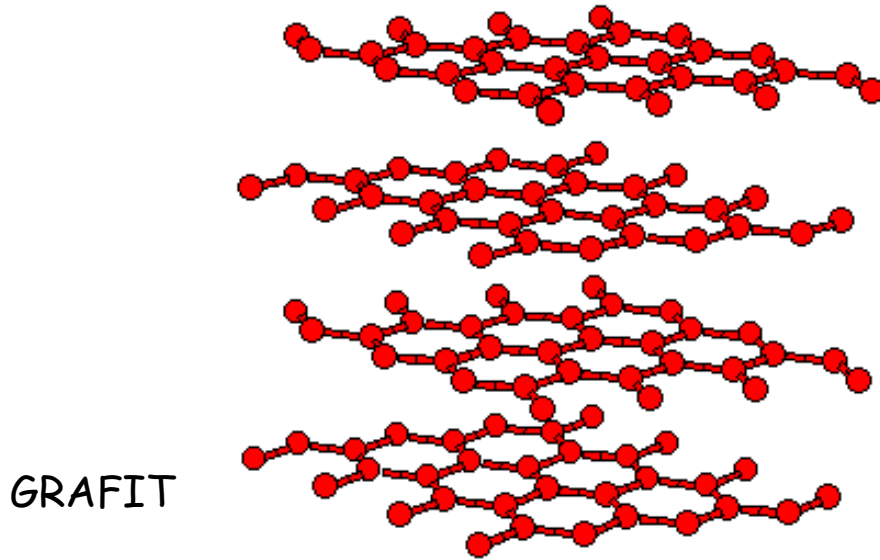
2. Irányító pozíció: orto, para, meta

Aktiváló	Dezaktiváló	
orto, para	orto, para	meta
-OH	-F, Cl, Br, I	-NO <sub>2</sub> , -NH <sup>+</sup> (CH <sub>3</sub> ) <sub>2</sub>
-OR, OAr	-CH <sub>2</sub> Cl	-COOH
-NH <sub>2</sub> , NHR		-COOR, -CN
-R, -Ar, -CHCH <sub>2</sub>		-CHO, -CRO
Növelik a gyűrű reaktivitását, legjobban az o,p pozícióban	Csökkentik a gyűrű reaktivitását, legkevésbé az o, p pozícióban	Csökkentik, de legkevésbé a m pozícióban



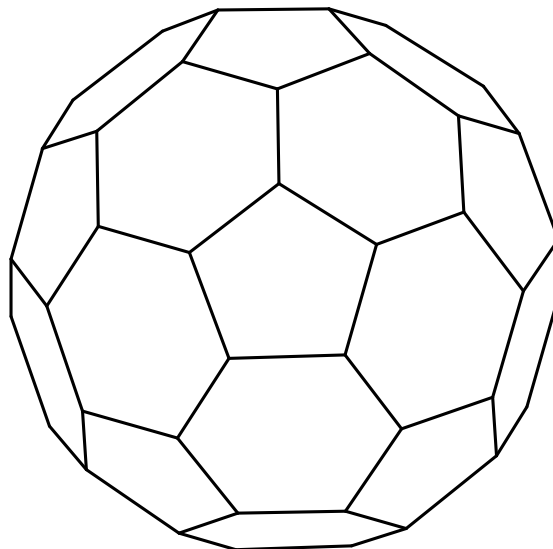
# C<sub>60</sub> KLASZTER

H. W. Kroto, R. E. Smalley (1984, Nobel díj 1996, R.F. Curl)



Lézer

C<sub>60</sub>



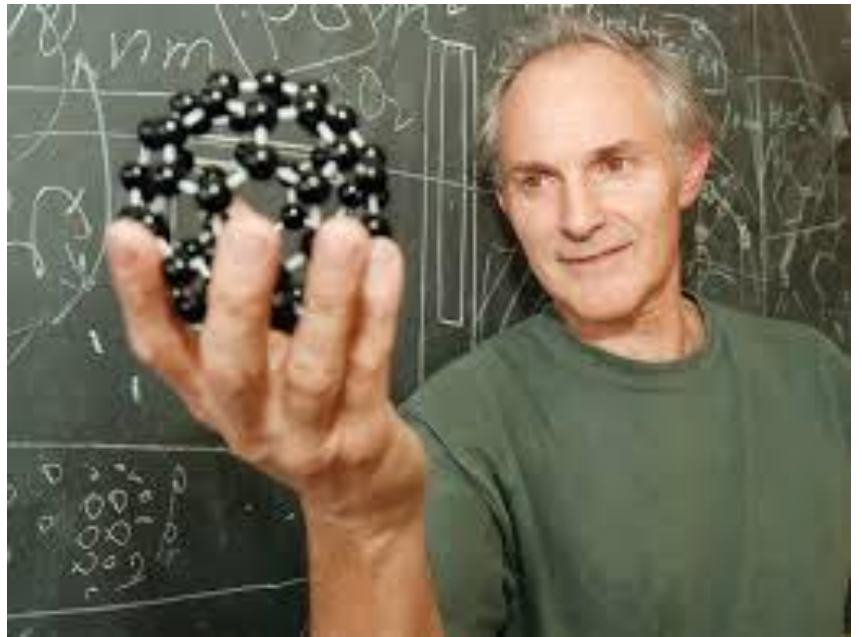
R. Buckminster

Buckminster

Fullerén

Soccerballen

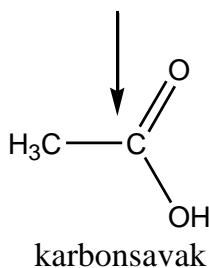
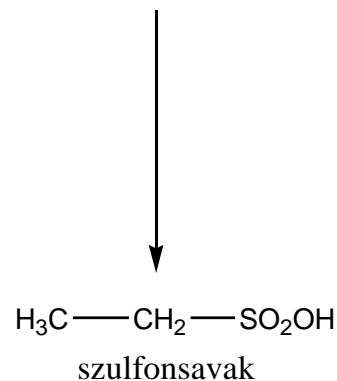
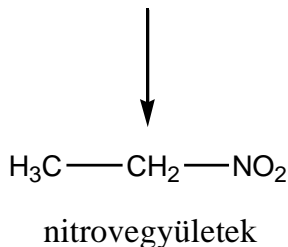
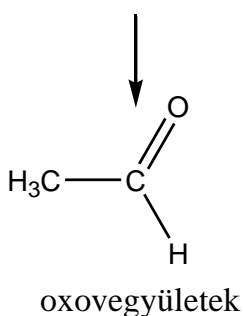
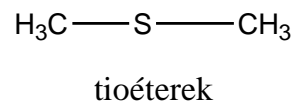
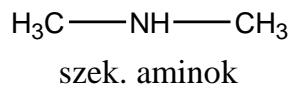
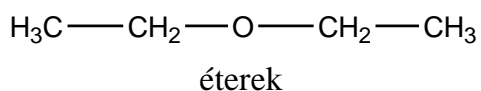
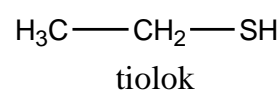
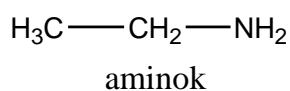
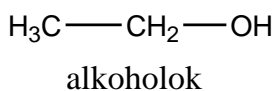
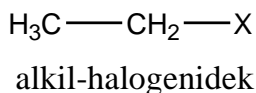
Footballen



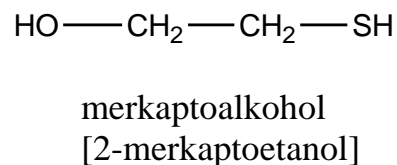
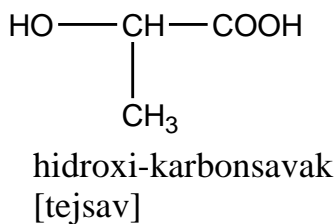
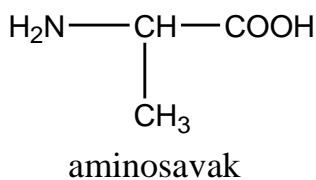
Sir Harold Walter Kroto (Budapest, 2001)

# SZÉNVEGYÜLETEK HETEROATOM(OK)KAL: ÁTTEKINTÉS

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

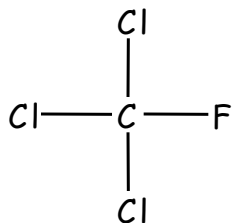


## Két heterofunkciós csoport (O és N, O és S stb.)



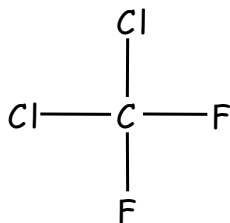
Példák:

### Aerosol - Hűtőszekrény



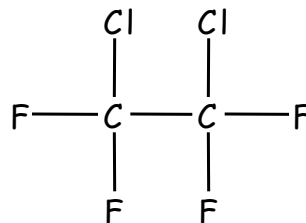
triklór-fluor metán

FREON 11



diklór-difluor metán

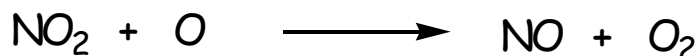
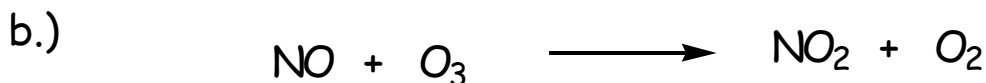
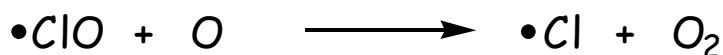
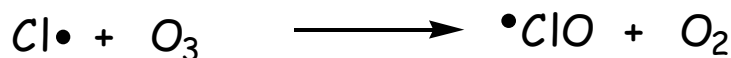
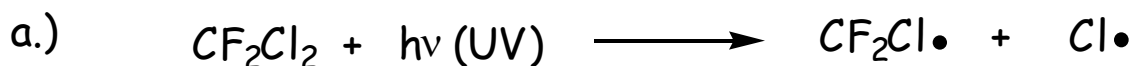
FREON 12



1,2-diklór-1,1,2,2-tetrafluor-etán

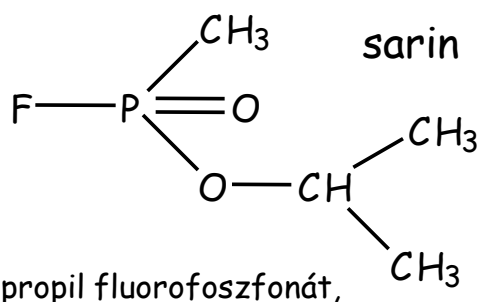
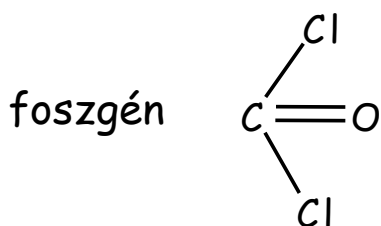
FREON 114

### „Ózon-lyuk” (1974, F. S. Rowland)



Szuperszonikus szállítás (SST)

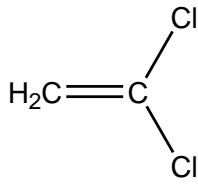
### Ideggázok - Háború



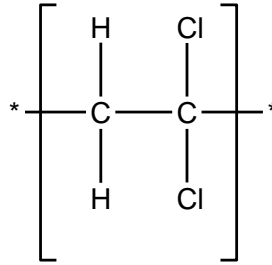
metil-O-izopropil fluorofoszfónát,

(1995, Tokyo)

## Még néhány alkalmazás:

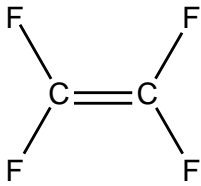


vinilidén-klorid

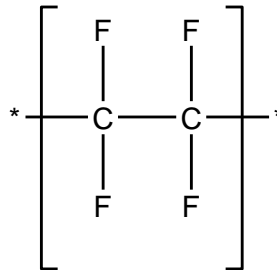


polivinilidén-klorid

"fólia"

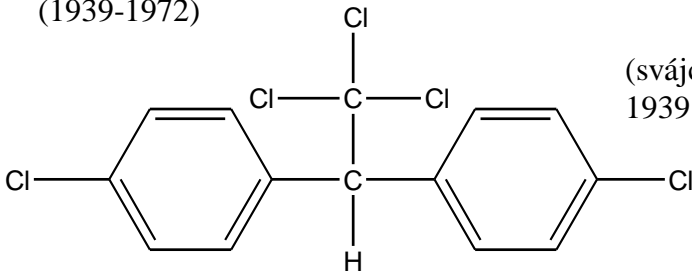


tetrafluor-etilén



"teflon"

(1939-1972)



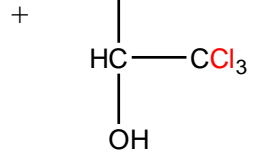
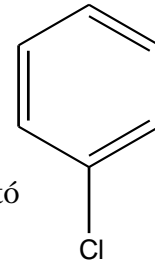
DDT

1,1-dikloro-2,2-bis(4-klorofenil)etán

500 millió kg került a bioszférába  
IDEGMÉREG

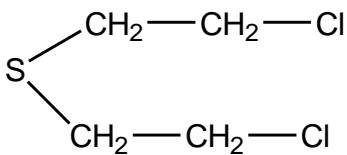
(svájc, P. H. Müller)  
1939 szőlő, burgonya

könnyen  
szintetizálható

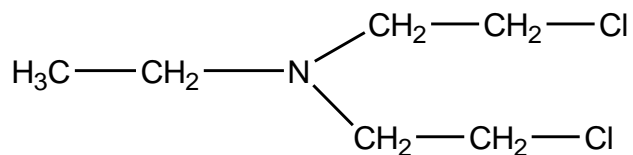


klorál-hidrát

1939-45 25 millió életet  
mentett (WHO)  
1968-tól betiltott



"mustárgáz"



"nitrogén mustár" (1935) (1971)

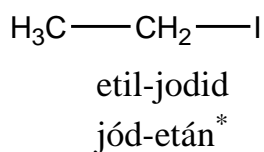
# 18. Halogénezett szénhidrogének

## Felosztás, nomenklatura

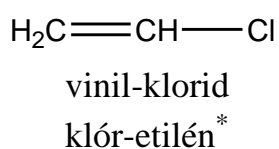
### 1. Szénváz

#### Nyílt

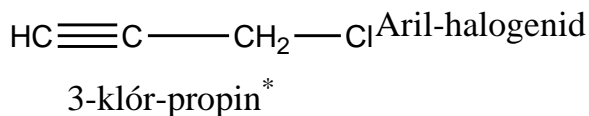
Alkil-  
halogenid



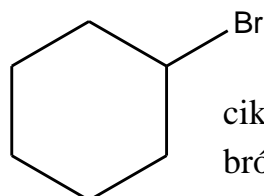
Alkenil-  
halogenid



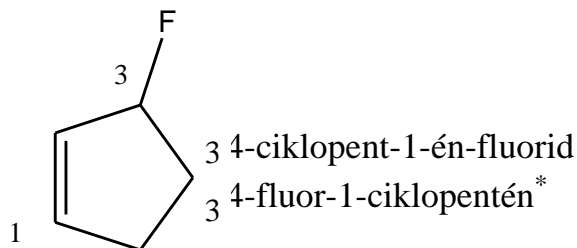
Alkinil-  
halogenid



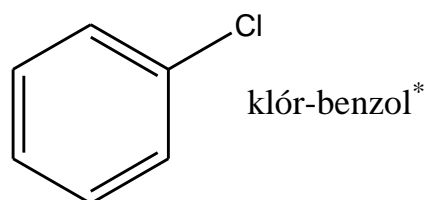
Cikloalkil-  
halogenid



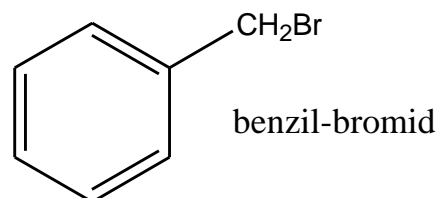
Cikloalkenil-  
halogenid



Aril-  
halogenid



Aralkil-  
halogenid



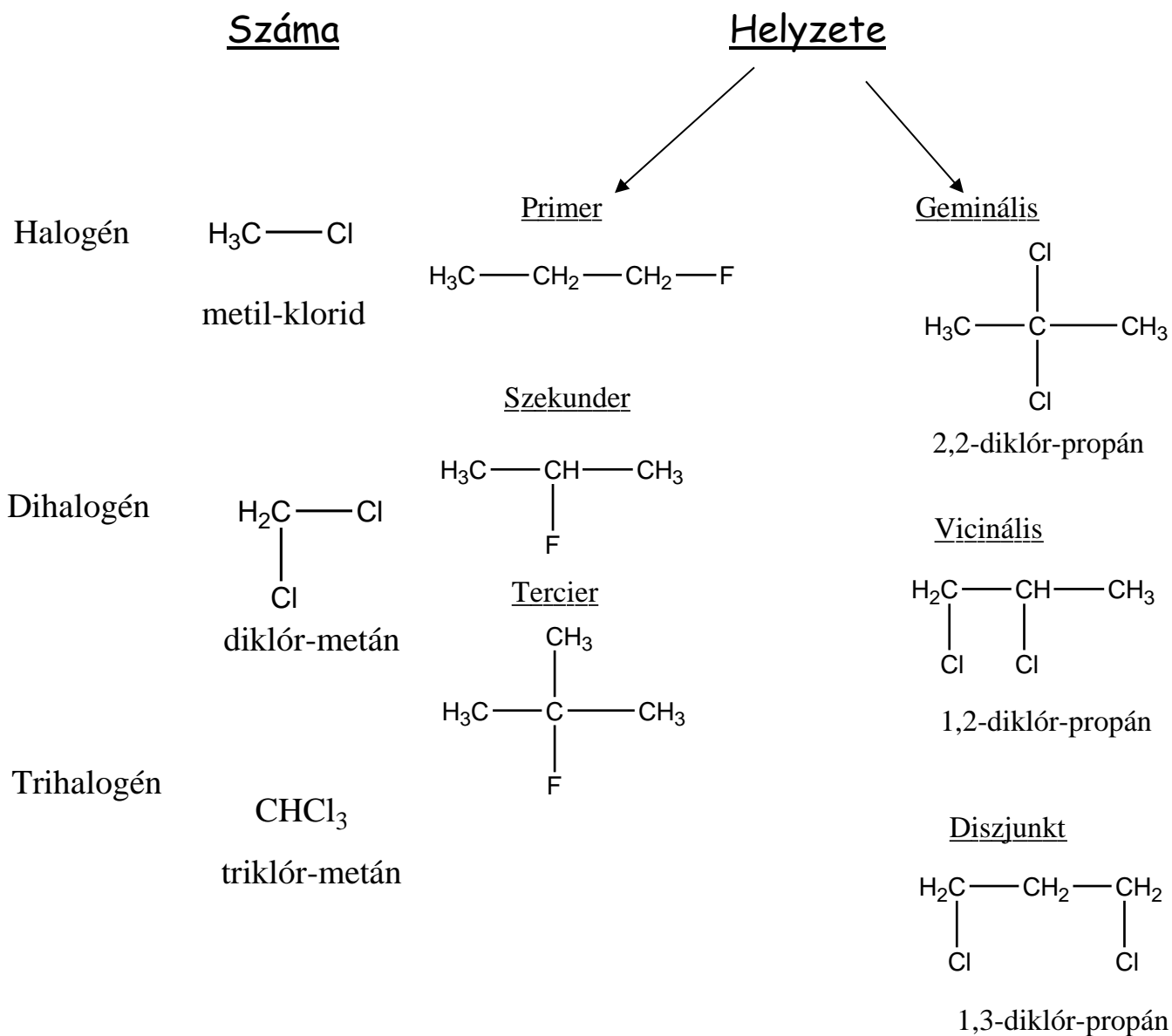
Szubsztitúciós elnevezés:\*

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

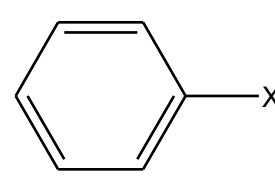
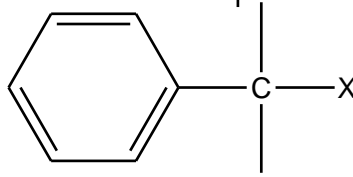
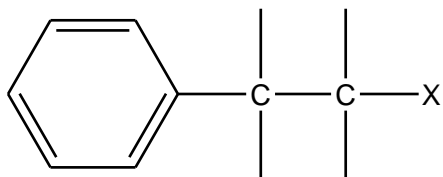
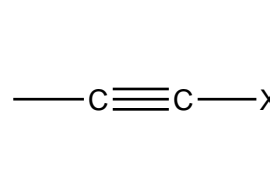
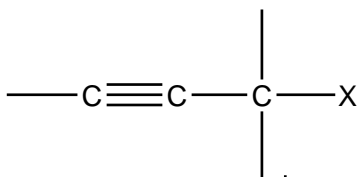
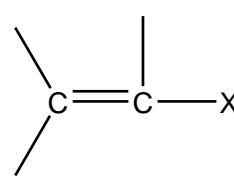
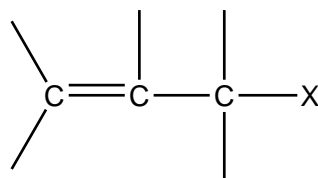
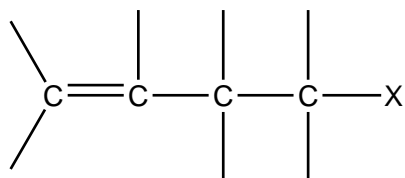
## A szerkezet

### 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

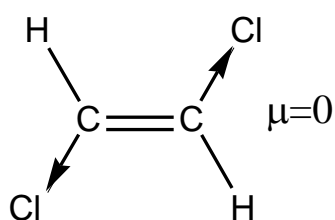
280

209 [kJ/mol]

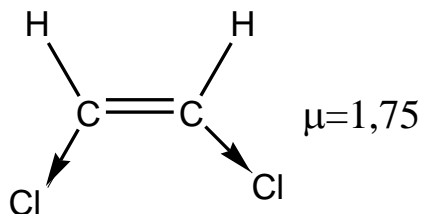


# Fizikai tulajdonságok

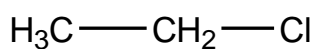
## Dipólus momentum



transz-1,2-diklór-etilén

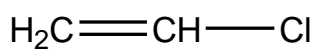


cisz-1,2-diklór-etilén

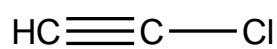


etil-klorid

$$\mu > 2,04$$

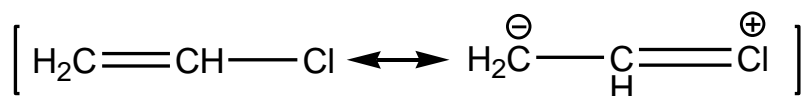


$$\mu=1,44$$



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,  $\alpha$ -,  $\beta$ - és  $\gamma$ - 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!)

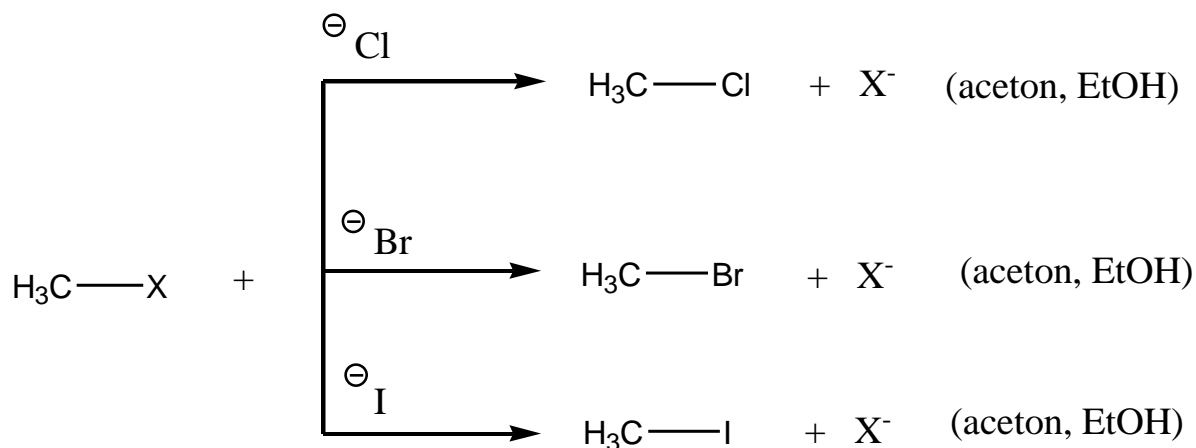
### b) A reagens milyensége

### c) A távozó csoport

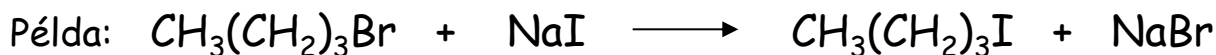
### d) A szubsztrátum milyensége

# A. Szubsztitúciós reakciók

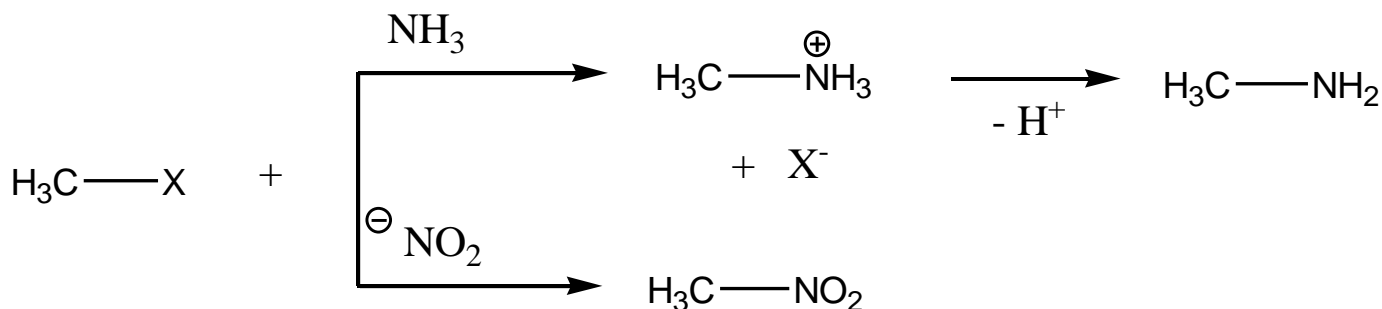
## 1.1. Reakció halogén nukleofilekkel (halogén csere)



Termék: alkil-halogenid



## 1.2. Reakció N-nukleofilekkel



Reakciótípus:

ammonolízis  
„nitrálás”

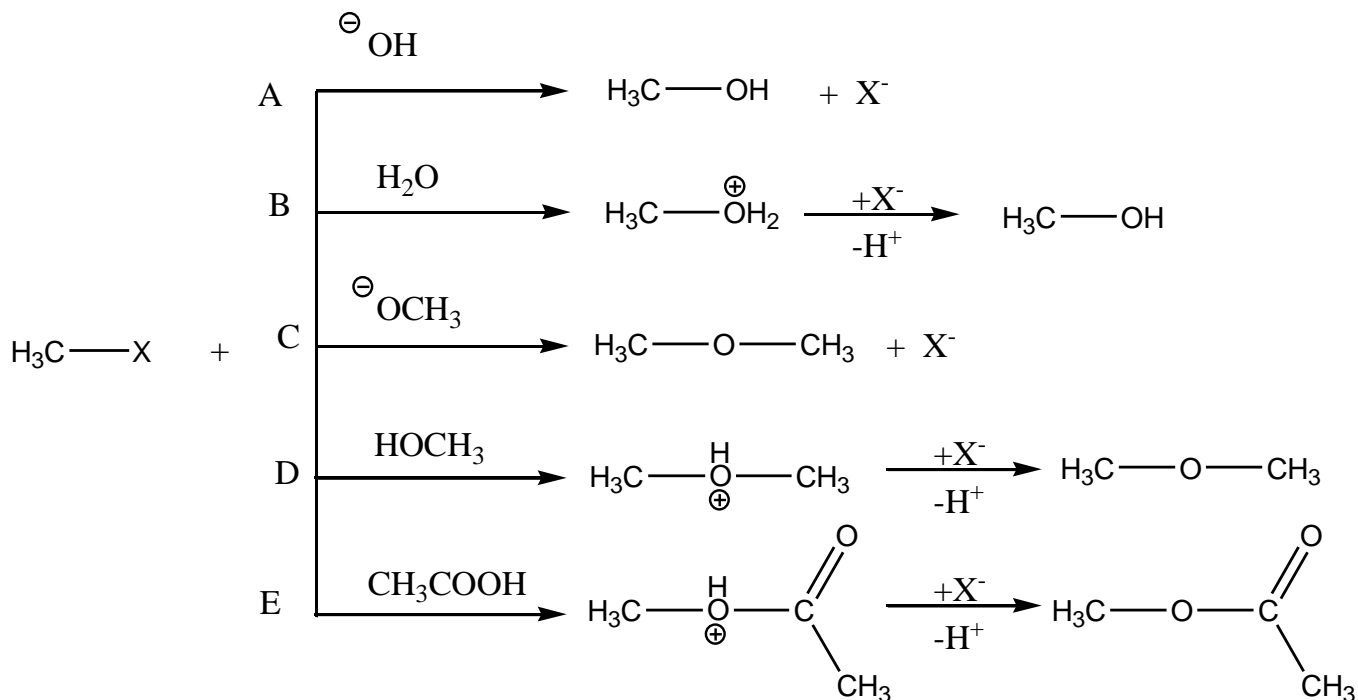
Termék:

primer amin  
nitrovegyület

Jelentősége

C-N kötés kiépítése

### 1.3. Reakció O - nukleofilekkel



#### Reakciótípus

Hidrolízis

Alkoholízis

Acidolízis

#### Termék

Alkohol      A, B

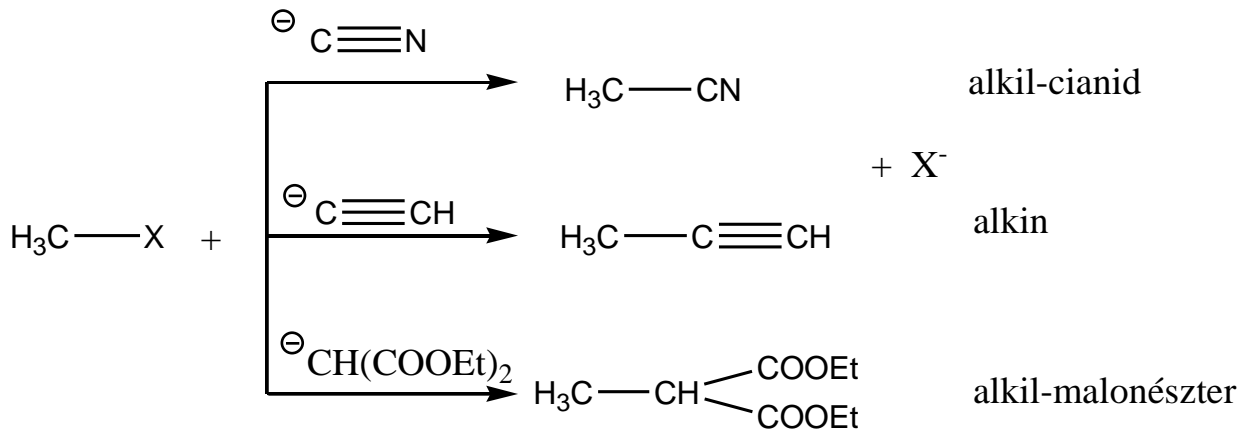
Éter            C, D

Észter         E

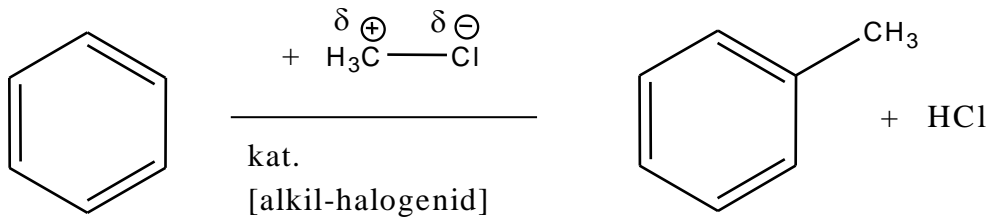
#### Jelentősége

C-O kötés kiépítése

## 1.4. Reakció C- nukleofilekkel

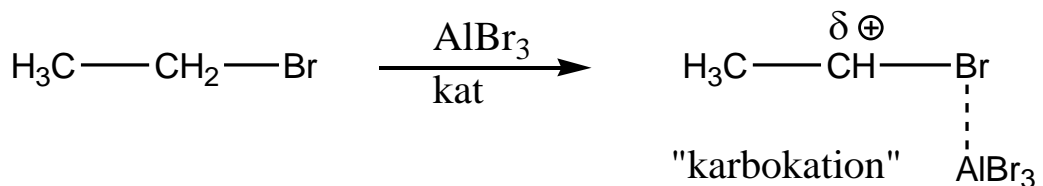


## Friedel-Crafts alkilezés



Alkil-halogenid: kat.  $\text{AlCl}_3$ ,  $\text{AlBr}_3$ ,  $\text{SbCl}_5$ ,  $\text{BF}_3$

Reagens:



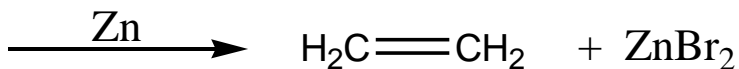
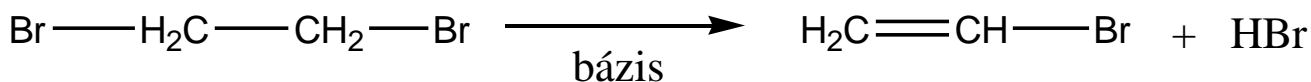
Reaktivitás: terciér > szekunder > primer

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

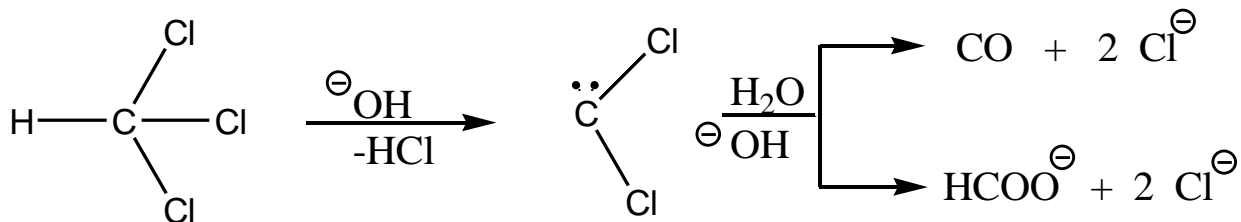
Jelentősége: C - C kötés kiépítése

## B. Eliminációs reakciók

### 1,2 elimináció



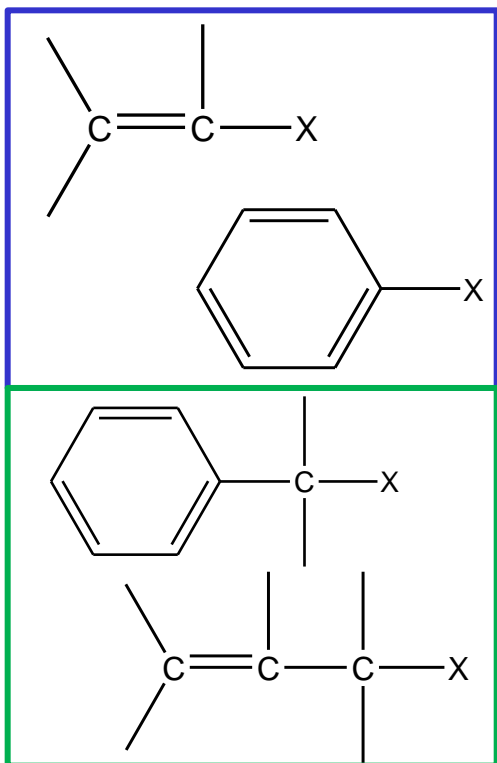
### 1,1 elimináció



kloroform

diklór karbén

C. Vinil/aryl és allyl/benzil rendszerek reaktivitásának összevetése



$\text{S}_{\text{N}}2$	$\text{S}_{\text{N}}1$	E	$\text{S}_{\text{E}}$
-	-	lassú	-
-	-	lassú	+
+	+	+	-
++	++	++	-

# A HALOGÉNEZETT SZÉNHYDROGÉNEK ELŐÁLLÍTÁSA

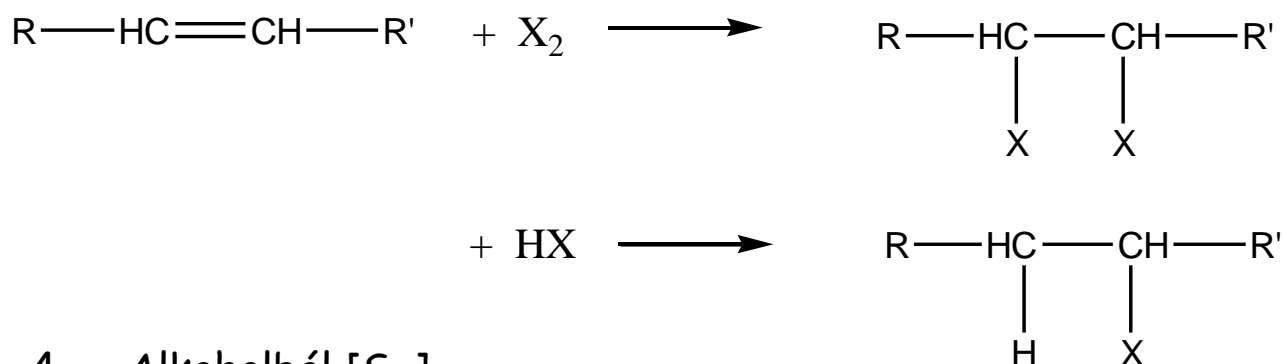
## 1. Alkánokból [ $S_R$ ]



## 2. Arénekből [ $S_E$ ]



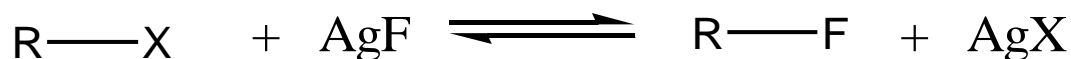
## 3. Telítetlen szénhidrogénből (alkén, alkin) [ $A_E$ ]



## 4. Alkoholból [ $S_N$ ]



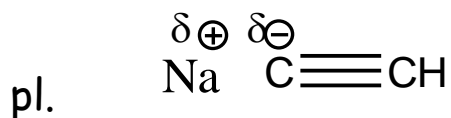
## 5. Halogéncsere [ $S_N$ ]



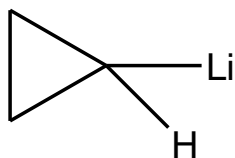


# 19. Fémorganikus vegyületek

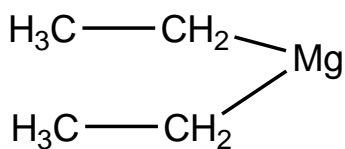
Definíció: Szén-fématom kötést tartalmazó vegyületek  
(C-nukleofil forrás)



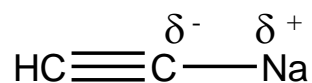
Nomenklatura, csoportosítás:



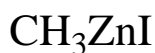
ciklopropil-litium



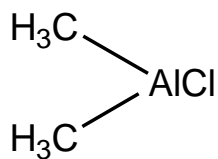
dietil-magnézium



nátrium-acetilid



metilcink jodid



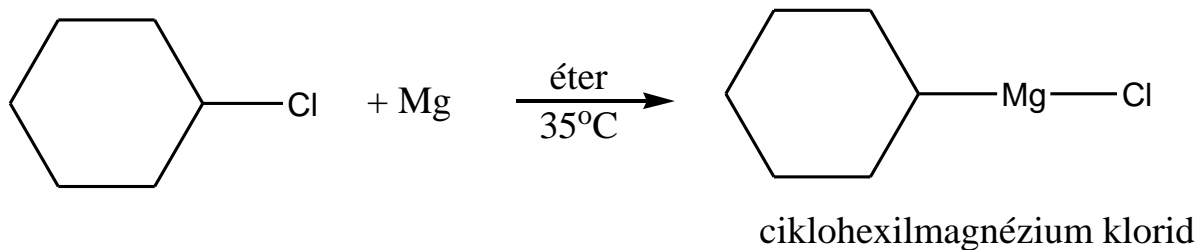
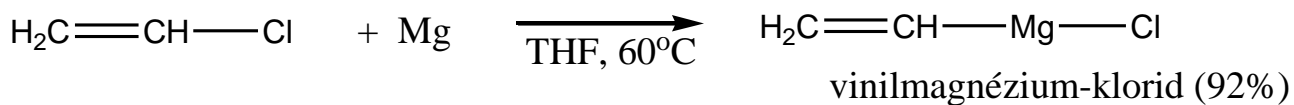
dimetilaluminium klorid



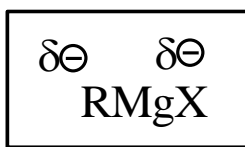
## B. Csoport: GRIGNARD reagens

(Victor GRIGNARD + Paul SABATIER;

1912 kémiai Nobel-díj)



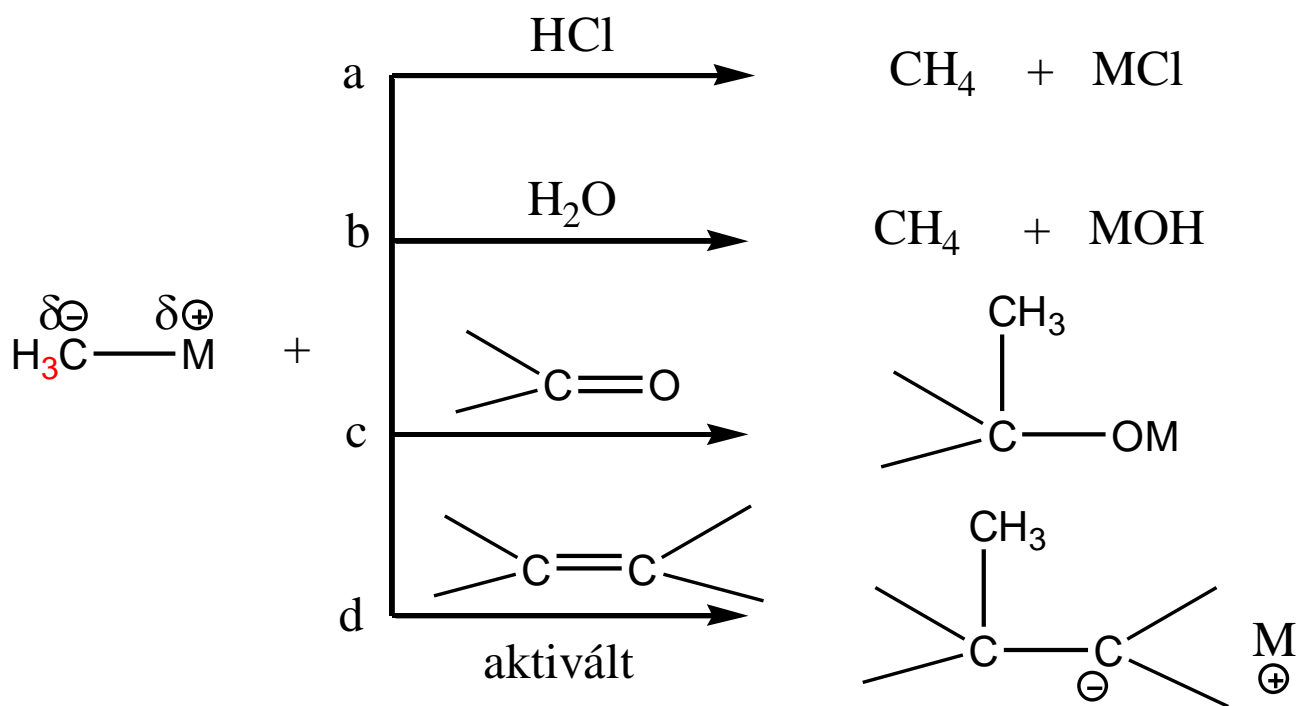
R = alkil, cikloalkil, alkenil vagy aril



RX: RI > RBr > RCl >> RF

# Reakciók fémorganikus vegyületek

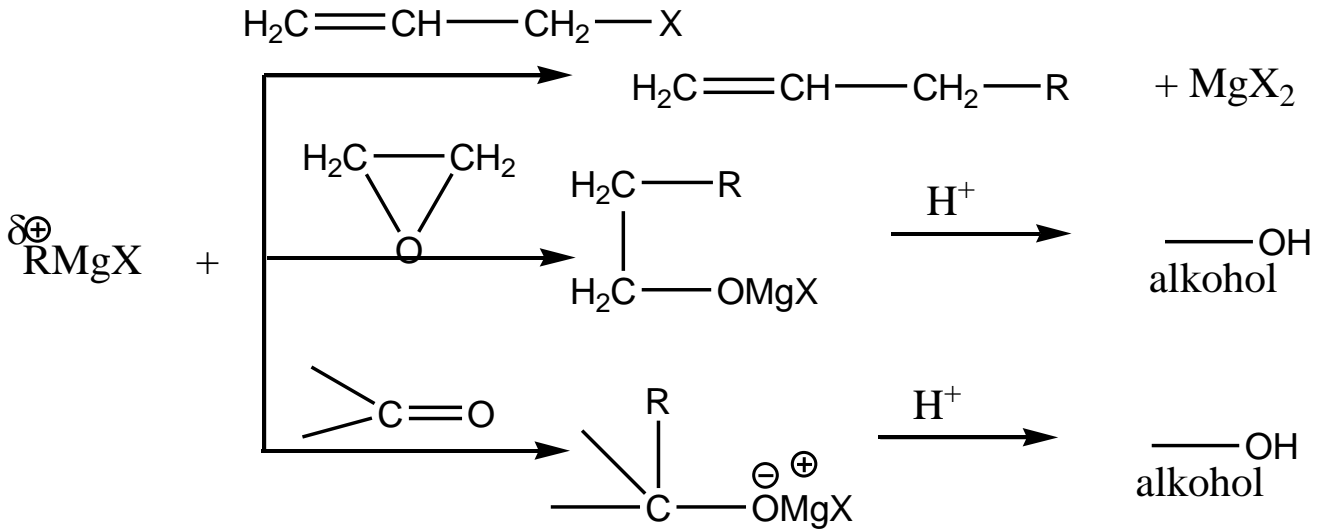
## A. Csoport



a, b  $S_N$

c, d  $A_N$

## B. Csoport - Grignard-reagens



Mechanizmus: a, b  $S_N$  c  $A_N$

