5. Előadás

Szénhidrogének:
alkánok, alkének, alkinek

17. Szénhidrogének

17.1.Alkánok (paraffinok), cikloalkánok

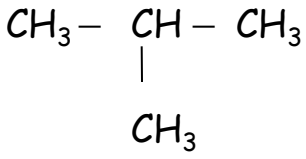
Homológ sor: eltérés egyetlen metilén (CH_2) csoportban

metán	CH_4	1
etán	C_2H_6	1
propán	C_3H_8	1
bután	C_4H_{10}	2
pentán	C_5H_{12}	
heptán	C_7H_{16}	9
...		
dekán	$C_{10}H_{22}$	75
....		

ciklopropán	C_3H_6
ciklobután	C_4H_8
ciklopentán	C_5H_{10}
ciklohexán	C_6H_{12}
.....	

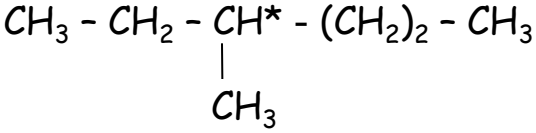
Strukturális izoméria

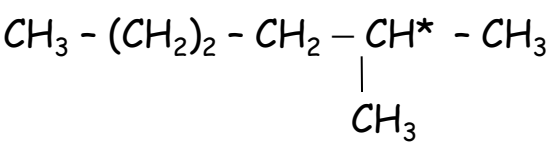
$CH_3 - CH_2 - CH_2 - CH_3$



Strukturális + optikai izoméria

$CH_3 - (CH_2)_5 - CH_3$



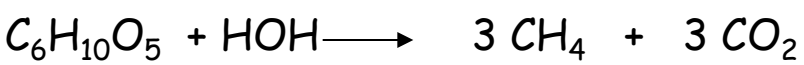


Előfordulás : metán,

Jupiter, Saturnusz, Uranusz, Neptun (redukáló atmoszféra)

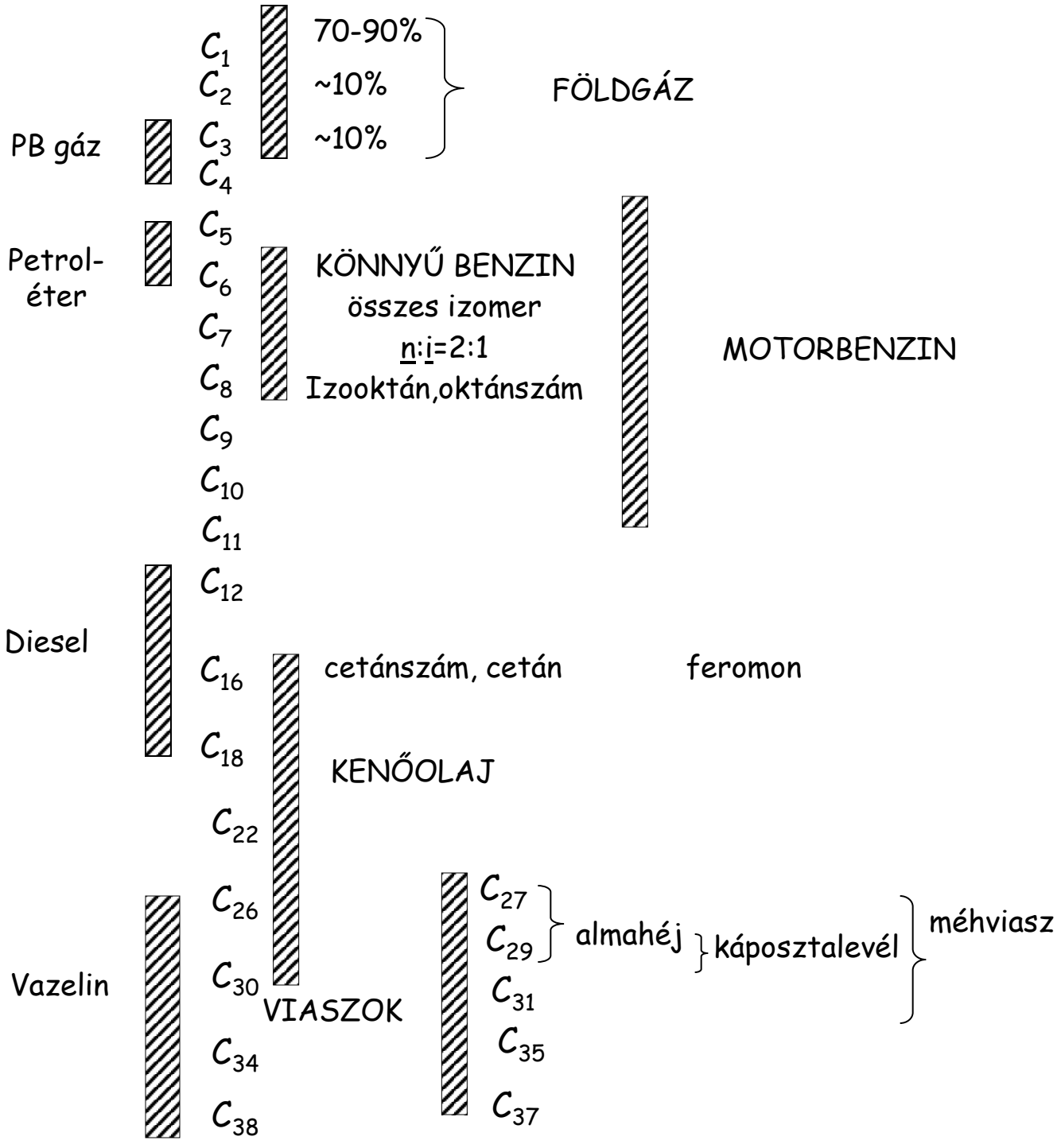
Föld (oxidáló atmoszféra)

- Anaerob baktériumok (Archeobacterium, metanogén)



- Tehén 20 liter/nap

Előfordulás



Az alkánok szerkezete

KÖTÉS MÓD

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

$C(sp^3)$ - H(s)

KÖTÉSHOSSZ

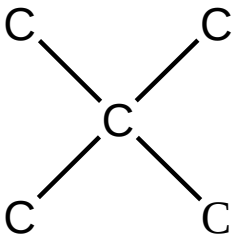
r (C – C)=1.54 Å

r (C – H)=1.09Å

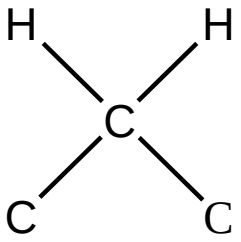
KÖTÉSSZÖG

HCH $\sphericalangle$ 109^o (CH_4)

CCC $\sphericalangle$ 109^o

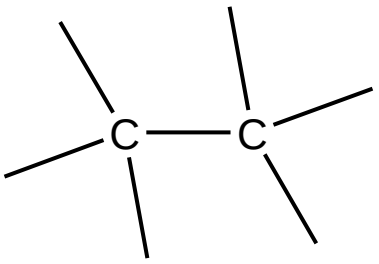


112^o



SZÖGFESZÜLTSÉG: 10^o TORZULÁS ~7.1 kJ/mol

KÖTÉSI ENERGIA



360 kJ/mol

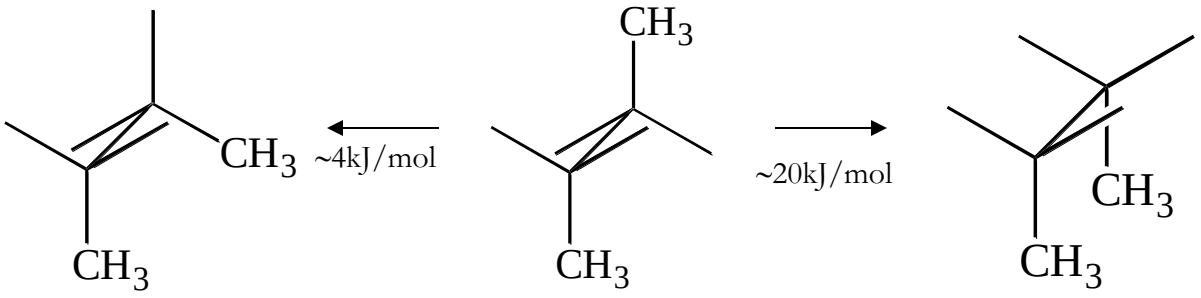
KONFIGURÁCIÓ TETRAÉDERES

KONFORMÁCIÓ ZEG-ZUGOS

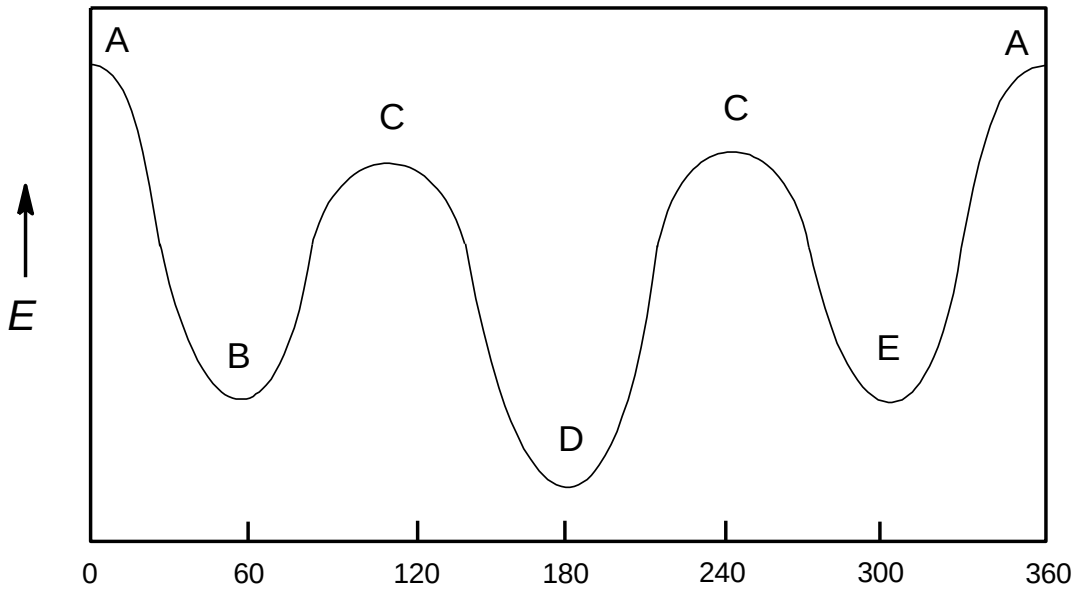
lásd: bután konformáció analízise

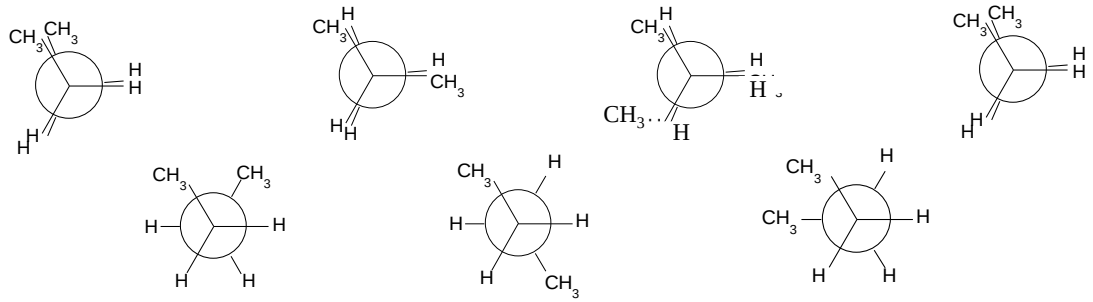
A bután konformációi

$H_3C—CH_2—CH_2—CH_3$



KJ/mol





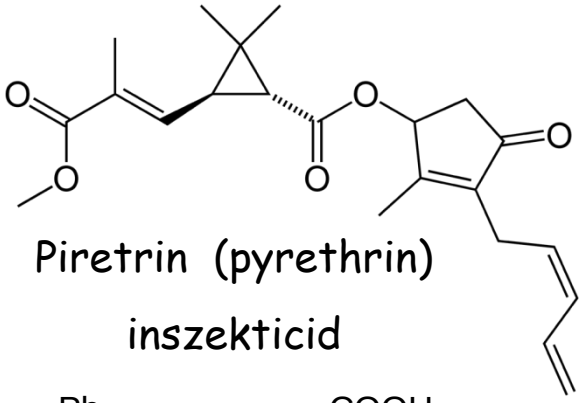
sp sk ak ap ak sk sp

G G

s szin p periplanáris

a anti k klinális

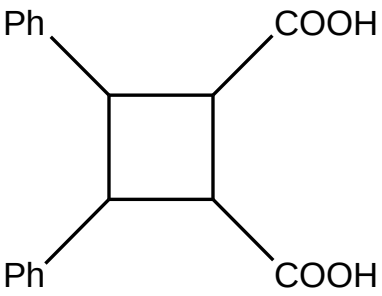
Cikloparaffinok előfordulása



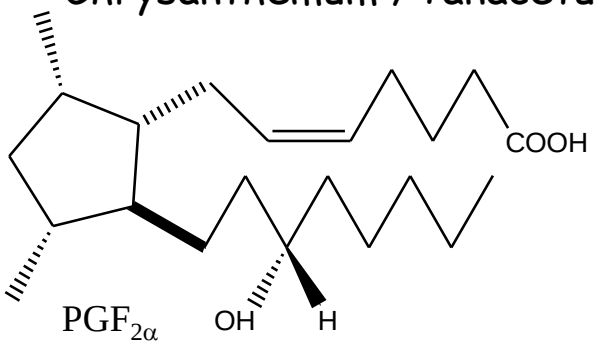
Piretrin (pyrethrin)

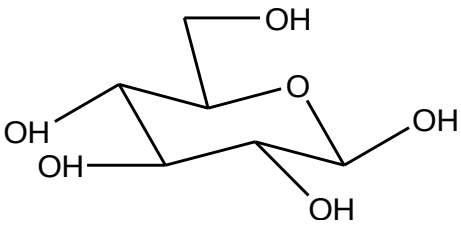
inszekticid

Chrysanthemum /Tanacetum

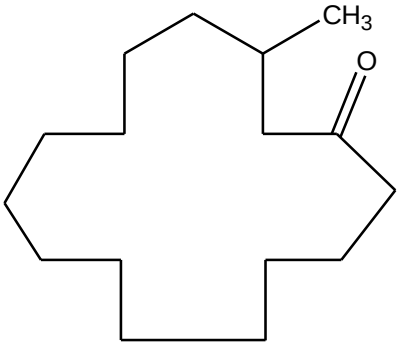


truxinsav



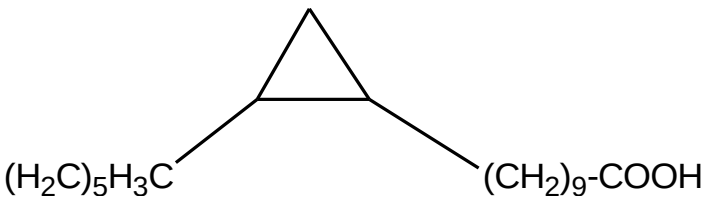


D-glükóz



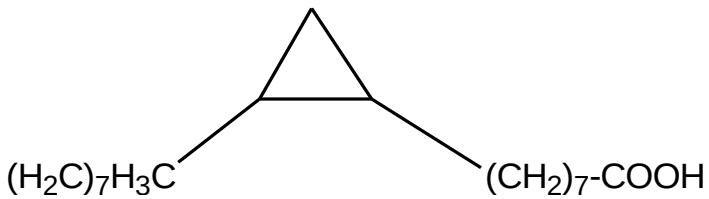
muszkon

pézsmapatkány



laktobacillinsav

SZTEROIDOK



szterkullinsav

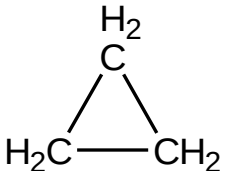
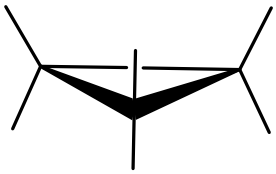
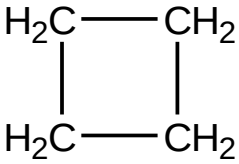
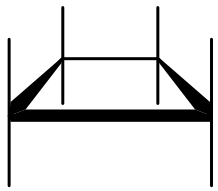
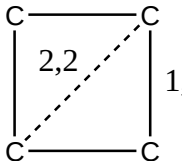
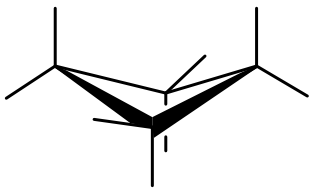
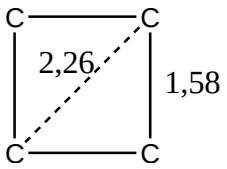
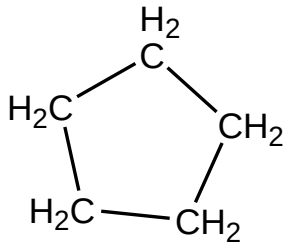
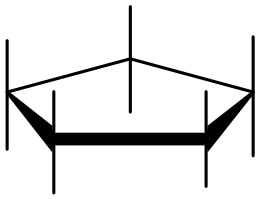
Sterculia foelida – fa magvában

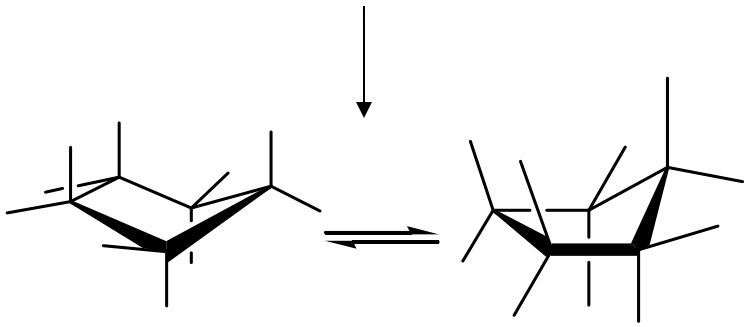
A cikloalkánok szerkezete

KÖTÉSMÓD: $C(sp^3) - C(sp^3)$

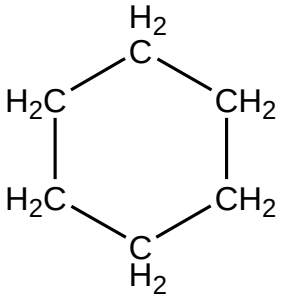
$C(sp^3) - H(s)$

KÖTÉSRENDSZER:

	SZÖGFESZÜLTSÉG	TORZIÓS	KÖTÉSI	Σ [kJ/mol]
	109,5° - 60° = 49,5°		nincs	115,1
	109,5°-90° = 19,5°	 		109,1
		 		
	109,5°-108° =1,5°			25,8

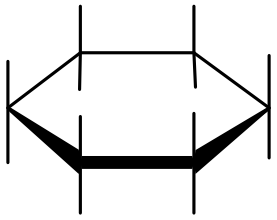


Csavart kád Boríték



109,5°-120° =

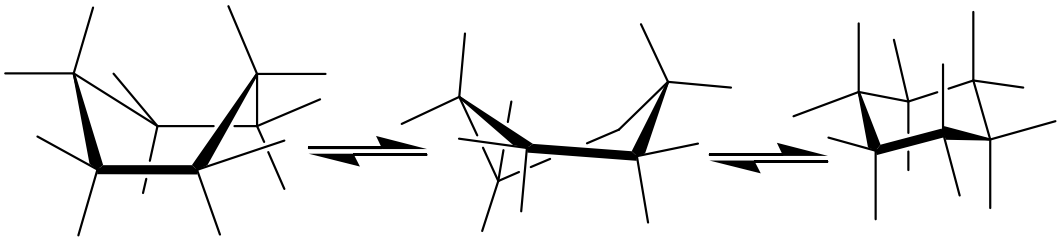
-10,5°



0,5

Baeyer-modell

SACHE – MOHR - MODELL

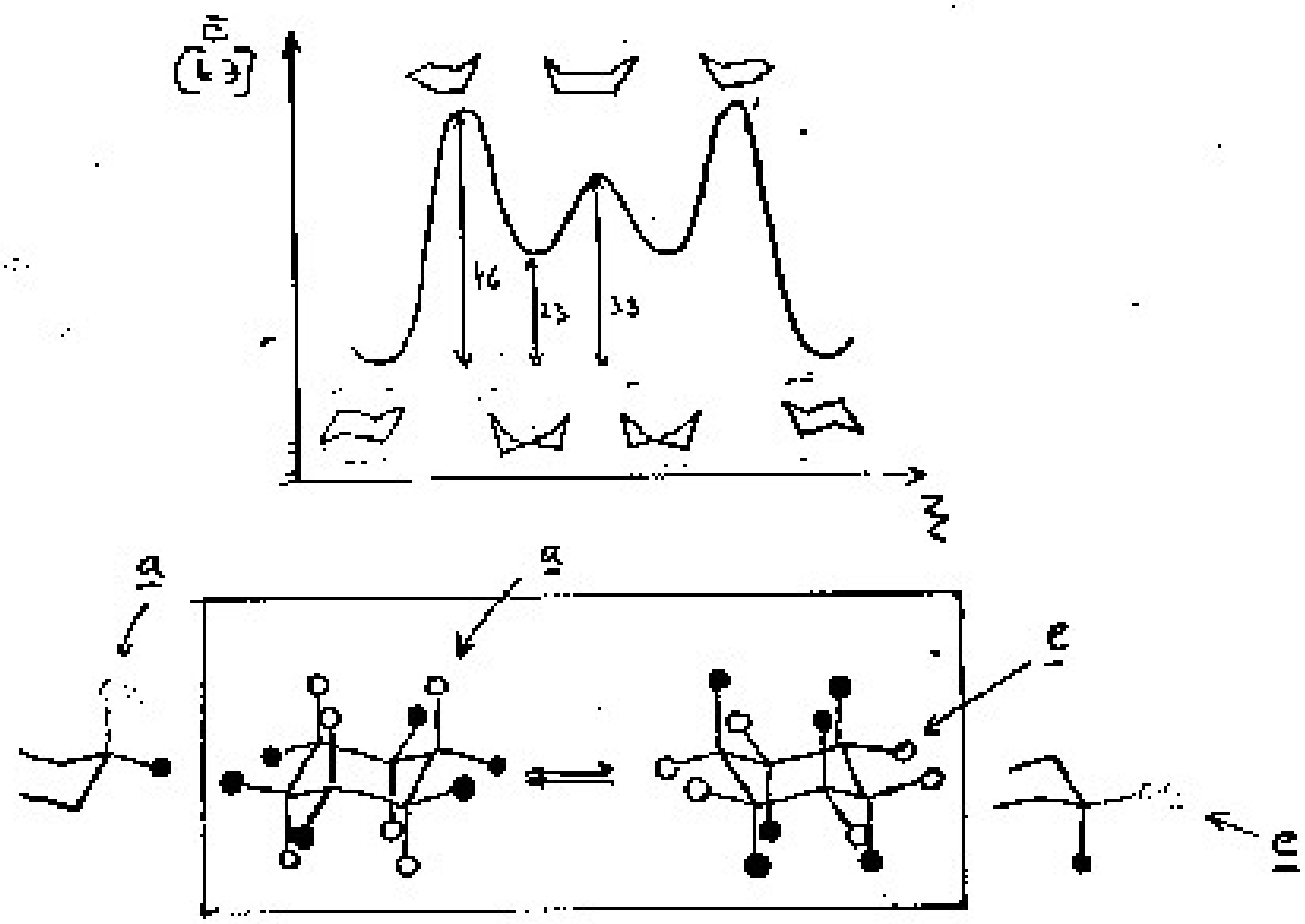


0

KÁD CSAVART KÁD SZÉK

Szögfeszültség	nincs	nincs	nincs
Torziós feszültség	van	nincs	nincs
Non-bonded feszültség	van	nincs	nincs

Szobahőmérsékleten dinamikus egyensúly



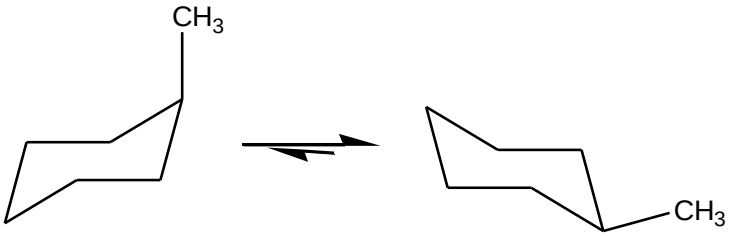
Ekvatoriális (egyenlítői) helyzet: Jele: e

a gyűrű síkjában

Axiális helyzet: Jele: a

a gyűrű síkjára merőleges

Példa:



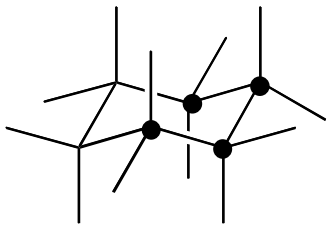
Arány 6: 94

ΔE: 7 kJ/mol

a-metil cikohexán

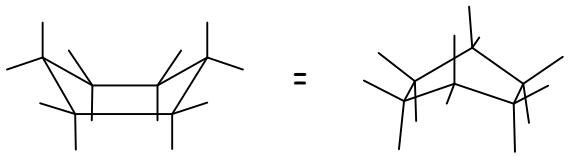
Ciklohexán

SZÉK

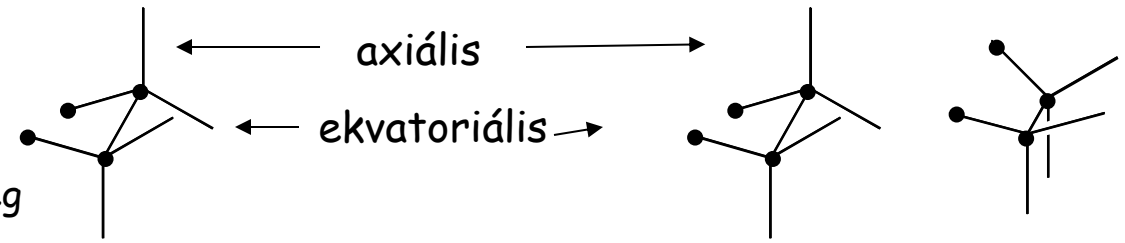


Szögfeszültség V(Θ)=0

KÁD



Szögfeszültség V(Θ)=0

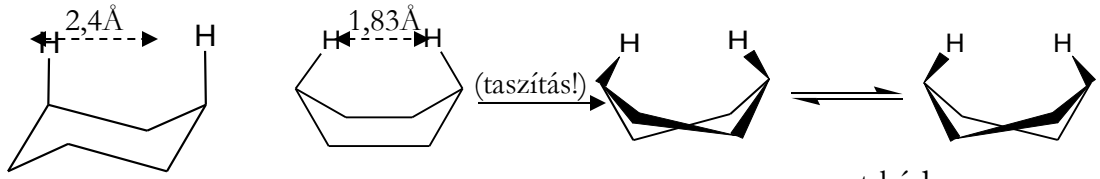


hat

négy

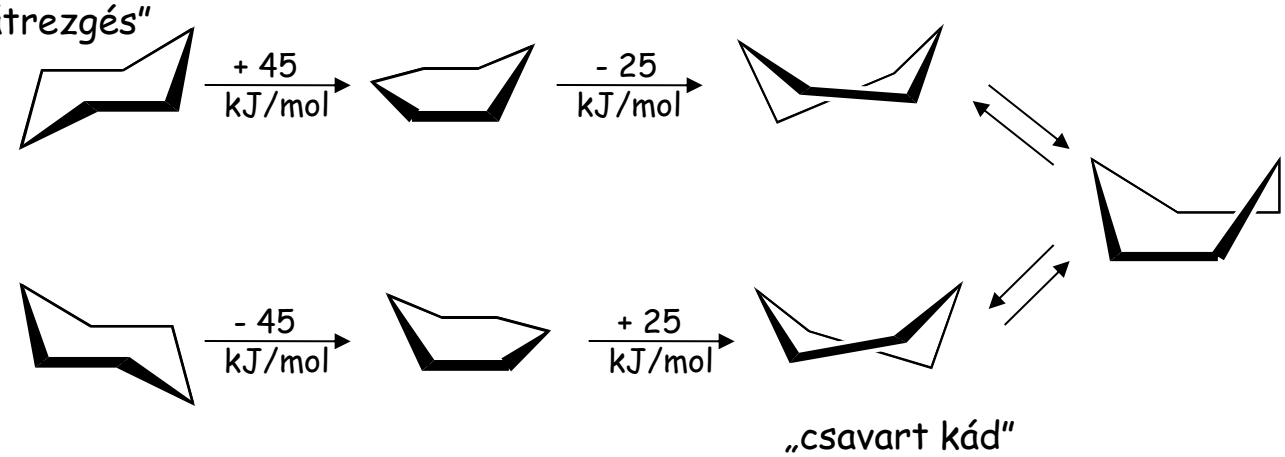
kettő

„kölcsönhatási feszültség" (nonbonded interaction)



csavart kád

„átrezgés"



„csavart kád"

10^6/sec

> 99% szék

Fizikai tulajdonságok

1. Halmazállapot [jellemzői: olvadáspont, forráspont]
2. Kölcsönhatás fénnyel (de: nem kötésfelbontás)
   - szín
   - forgatás [α]
   - törésmutató n
3. Szag
4. Oldékonyság [oldószer, hőmérséklet, nyomás]
5. Sűrűség [hőmérséklet]

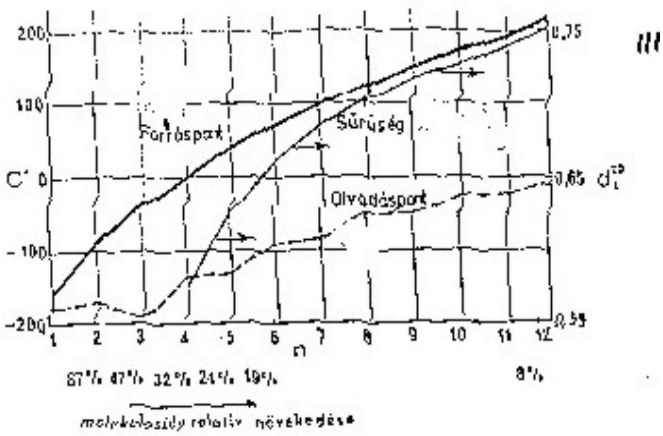
HALMAZÁLLAPOT

Kohéziós erők

$C_{1\text{-}4}$ gáz

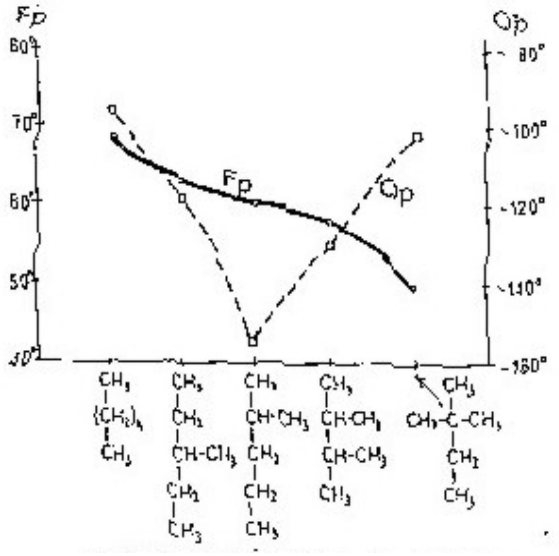
$C_{5\text{-}16}$ folyadék,
van der Waals erők

C_{17} szilárd kristályrács:
semleges molekulák



OLDÉKONYSÁG

Hasonló hasonlót old
Pl: Apoláros (pl. benzol)
v. kevéssé poláros oldószerben



Alkánok és cikloalkánok reakciói

1. Oxidáció – redukció
2. Halogénezés
3. Nitrálás

} Szobahőmérsékleten nincs kötéshasadás

A kémiai reakció körülményei:

Hőmérséklet (Δ)

Nyomás

Reakcióidő (t)

Katalizátor (kat)

Koncentráció - abszolút

- relativ (mol arány)

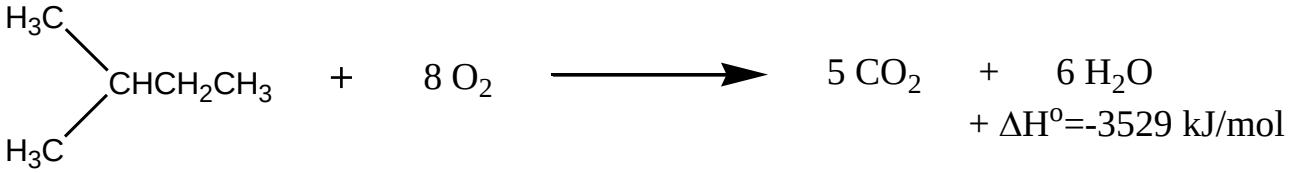
Fény ($h\nu$)

1. Oxidáció

$$C_nH_{2n+2} + (3n+1)/2\ O_2 \xrightarrow{\Delta} n\ CO_2 + (n+1)\ H_2O$$

+"égéshő"

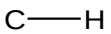
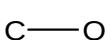
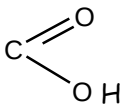
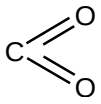
Példa



Oxidácó szám

Tegyük fel, hogy az O oxidációs száma –2 és a H oxidációs száma +1

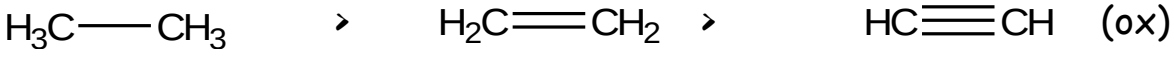
Ekkor a C oxidációs száma:

Metán	CH_4	-4	
Metanol	CH_3OH	-2	
Formaldehid	CH_2O	0	
Hangyasav	$HCOOH$	+2	
Széndioxid	CO_2	+4	

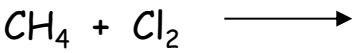
Redukált forma: CH_4

Oxidált forma: CO_2

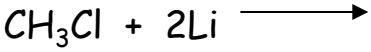
Alkalmazás:

a. 

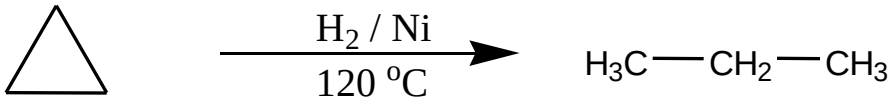
b. $EN_x > EN_c$ Oxidációs szám növelő

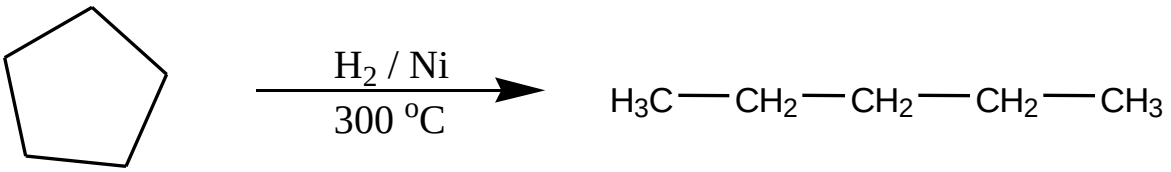


$EN_x < EN_c$ Oxidációs szám csökkentő



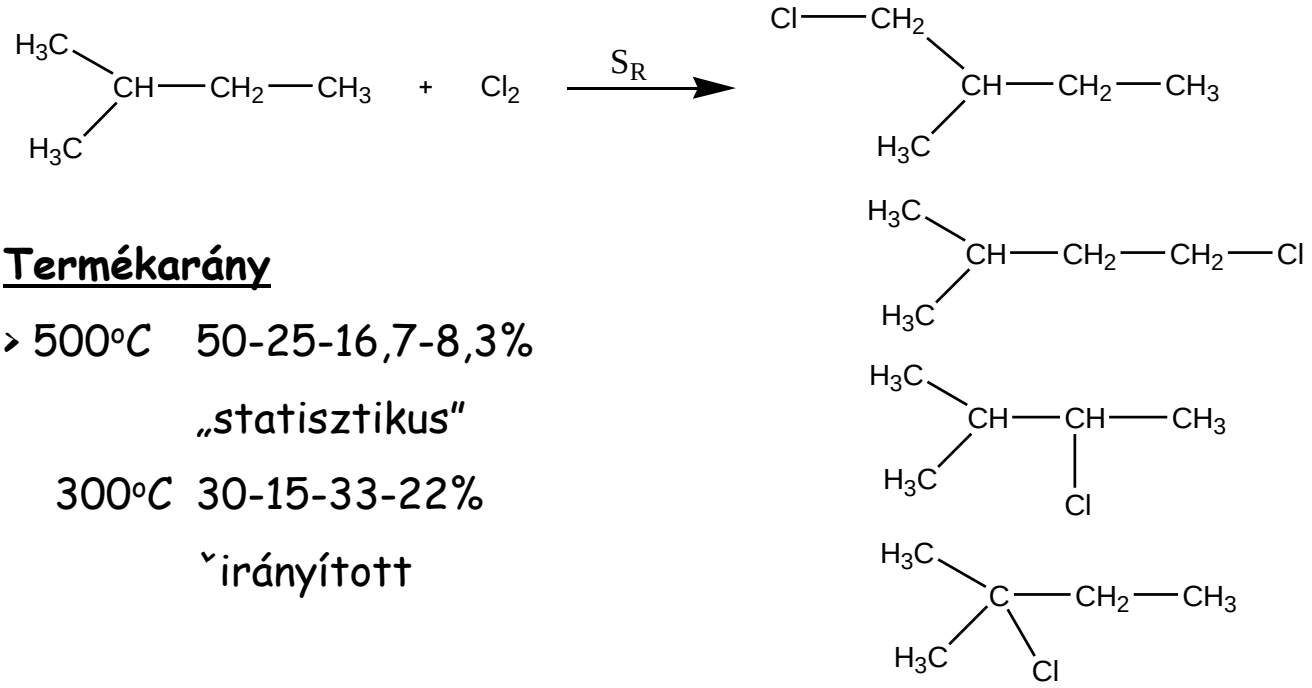
2. Redukció – hidrogénezés





3. Halogénezés

a



Termékarány

> 500°C 50-25-16,7-8,3%

„statisztikus"

300°C 30-15-33-22%

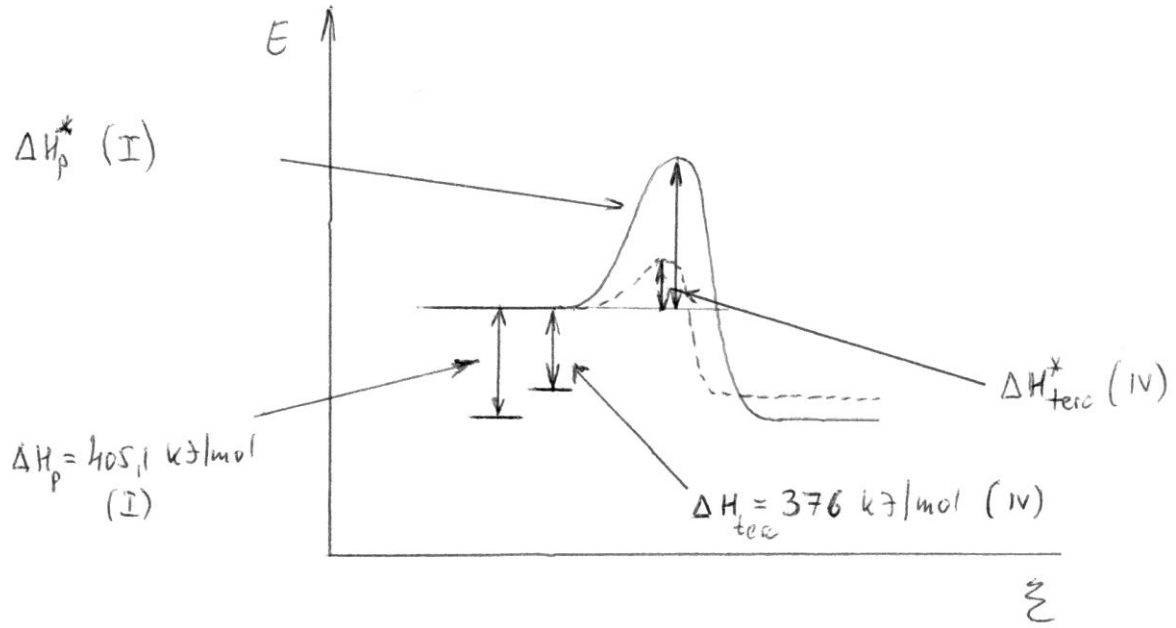
ˇirányított

Disszociációs energia:

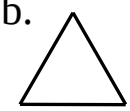
$\Delta H > \Delta H > \Delta H > \Delta H$,

(metil) (primer) (szek) (terc)

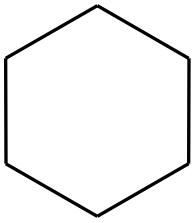
$\Delta H^* > \Delta H^* > \Delta H^* > \Delta H^*$

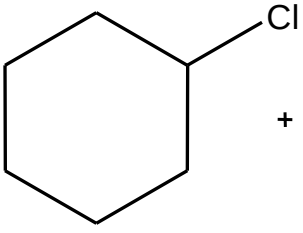


b.



+ Br_2 $\xrightarrow{20^oC}$ $CH_2Br-CH_2-CH_2Br$ A_R



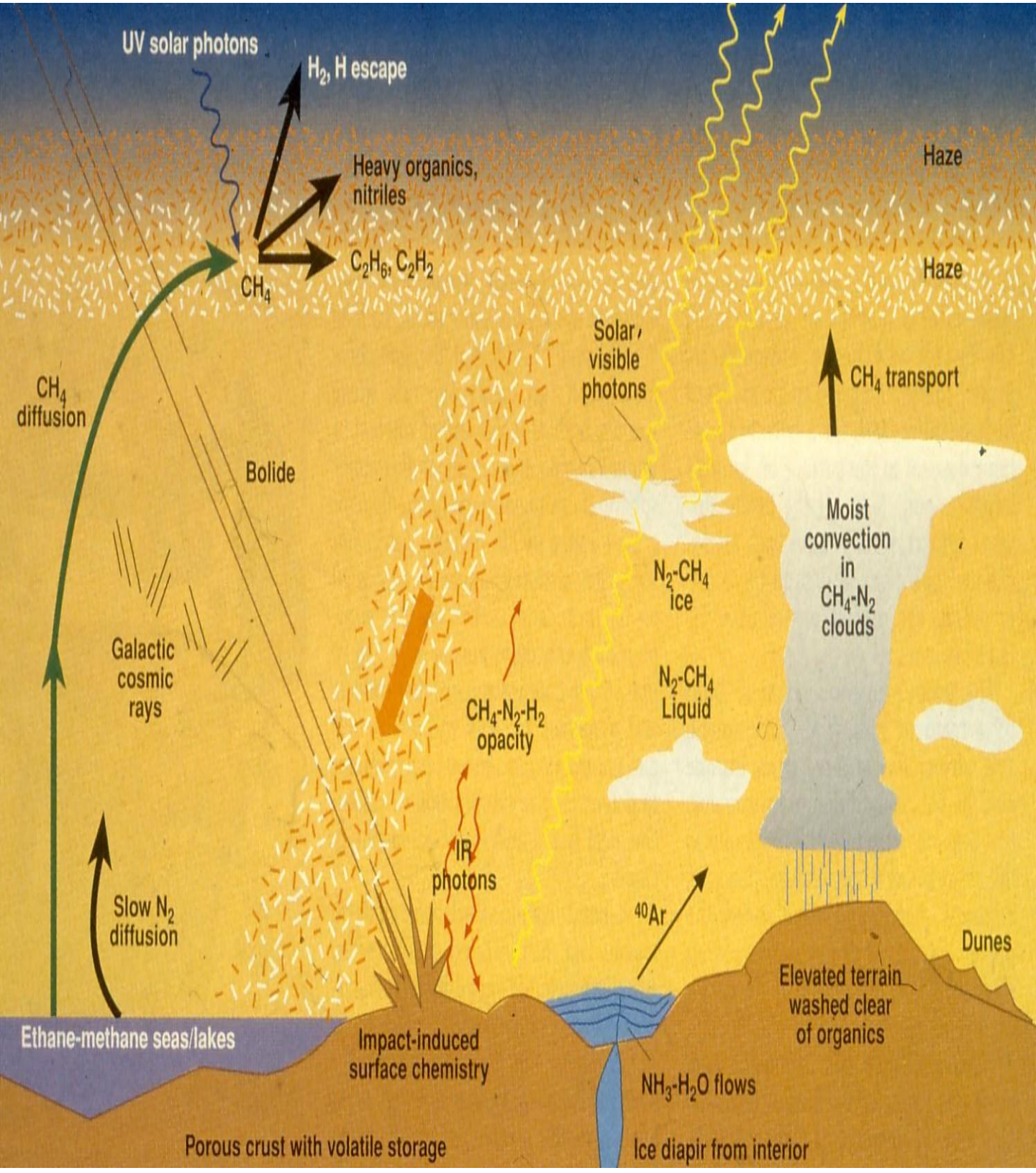
+ Cl_2 $\xrightarrow[v.\ \Delta]{h\nu}$  + HCl S_R

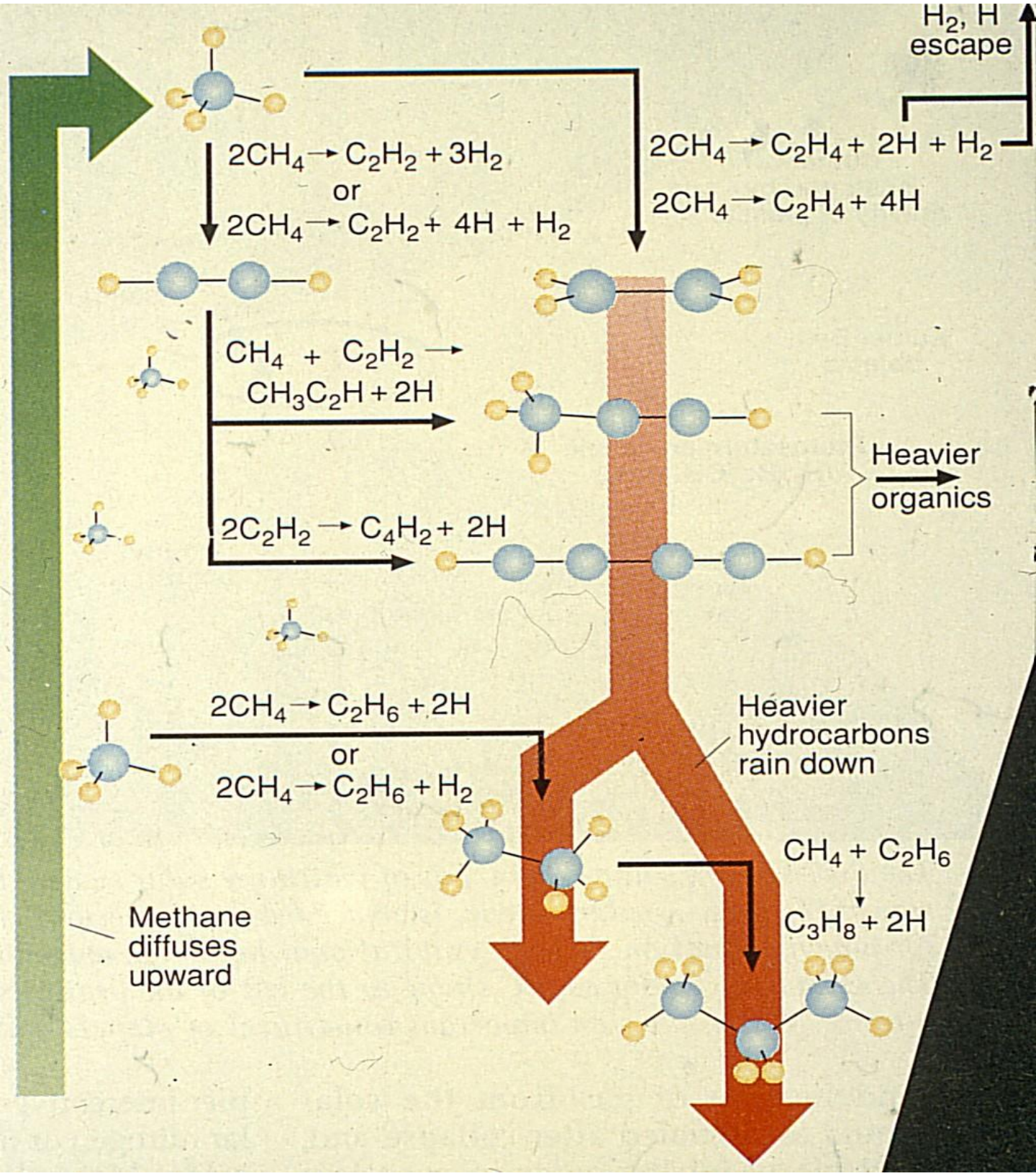
3. Nitrálás

$CH_4 + HNO_3 \xrightarrow[(450^oC)]{\Delta} CH_3NO_2 + H_2O$

nitrometán (szintelen)

$H_3C-CH_3 + HNO_3 \xrightarrow[(450^oC)]{\Delta} CH_3CH_2NO_2 + H_2O$

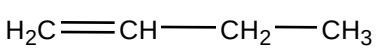

UV solar photons
H_2, H escape
Heavy organics, nitriles
C_2H_6, C_2H_2
CH_4
Haze
Haze
Solar, visible photons
CH_4 transport
CH_4 diffusion
Bolide
Moist convection in CH_4-N_2 clouds
N_2-CH_4 ice
Galactic cosmic rays
N_2-CH_4 Liquid
CH_4-N_2-H_2 opacity
IR photons
Slow N_2 diffusion
^{40}Ar
Dunes
Elevated terrain washed clear of organics
Ethane-methane seas/lakes
Impact-induced surface chemistry
NH_3-H_2O flows
Porous crust with volatile storage
Ice diapir from interior


H_2, H escape
$2CH_4 \rightarrow C_2H_2 + 3H_2$
or
$2CH_4 \rightarrow C_2H_2 + 4H + H_2$
$2CH_4 \rightarrow C_2H_4 + 2H + H_2$
$2CH_4 \rightarrow C_2H_4 + 4H$
$CH_4 + C_2H_2 \rightarrow CH_3C_2H + 2H$
Heavier organics
$2C_2H_2 \rightarrow C_4H_2 + 2H$
$2CH_4 \rightarrow C_2H_6 + 2H$
or
$2CH_4 \rightarrow C_2H_6 + H_2$
Heavier hydrocarbons rain down
$CH_4 + C_2H_6$
$C_3H_8 + 2H$
Methane diffuses upward

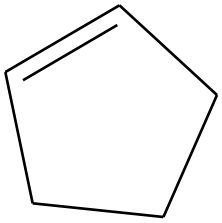
17.2. ALKÉNEK, CIKLOALKÉNEK
(gaz oléfiant, olefin, olajképző gáz 1795)

fp:-104°C fp:-34°C 1,2 diklór etán fp:83°C

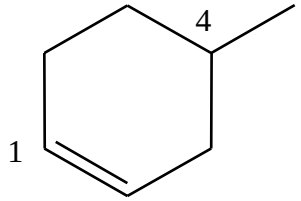
PÉLDÁK:



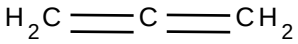
1-butén



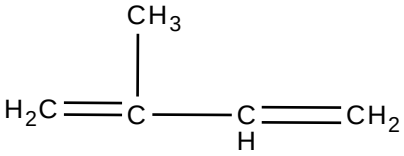
ciklopentén



4-metil – 1 -ciklohexén

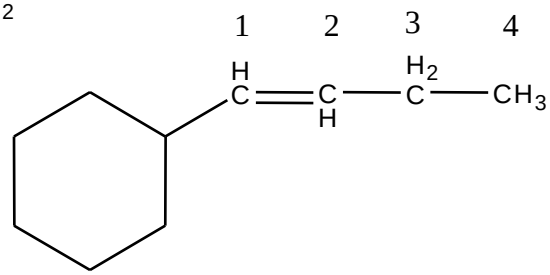


1,2-propadién (allén)

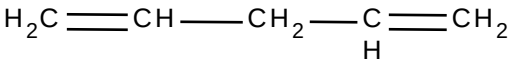


2-metil-1,3-butadién

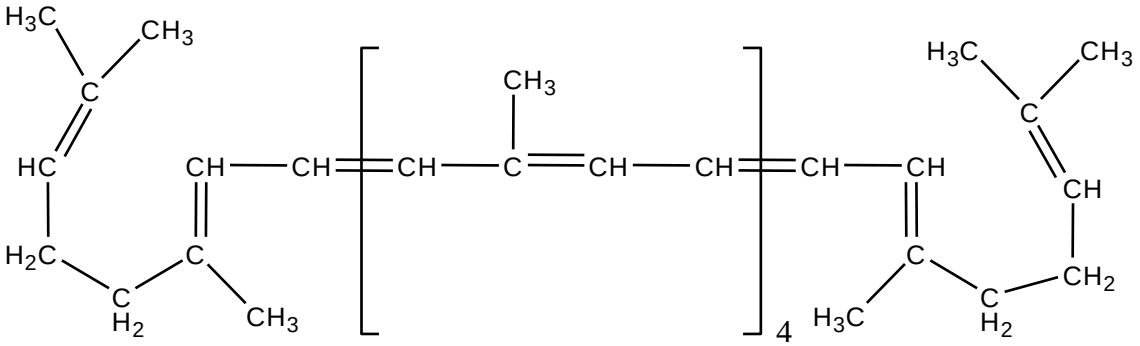
(izoprén*)



1-ciklohexil-1-butén



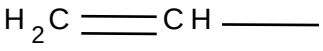
1,4-pentadién



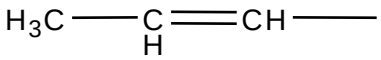
Likopin* (paradicsom pigment)

CSOPORTNEVEK

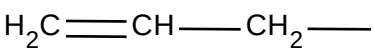
alkenil (cikloalkenil)



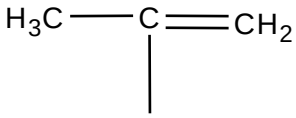
„etenil" vinil*



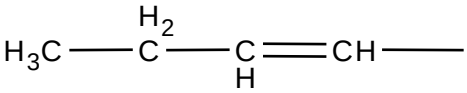
allil*



propenil*



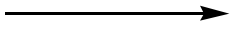
izopropenil*



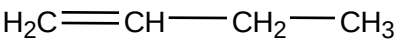
1-butenil *triviális nevek

HOMOLÓG SOR

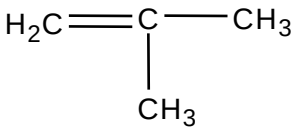
etén (etilén) C_2H_4
propén (propilén) C_3H_6
butén C_4H_8
:



strukturális izoméria

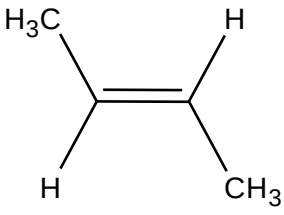


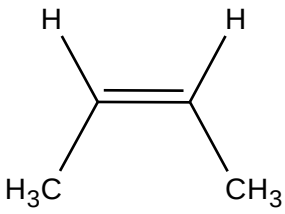
1-butén



2-metil-propén

geometriai izoméria





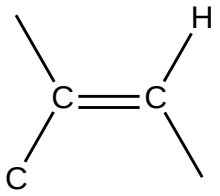
transz-2-butén cisz-2-butén

Az alkének szerkezete

Kötésmód

$C\,(sp^2) - C(sp^2)$
$C(sp^2) - H(s)$
$C(sp^2) - C(sp^3)$
} σ

$C(p) - C(p)\ \pi$



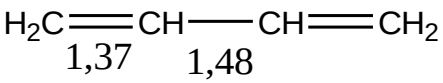
Kötéshossz

$r[C(sp^2) - C(sp^2)] = 1{,}34$ Å

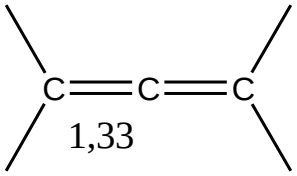
$r[C(sp^2) - H(s)] = 1{,}10$ Å

$r[C(sp^2) - C(sp^3)] = 1{,}54$ Å

De: a $r[C(sp^2) - C(sp^2)]$ [konjugált]

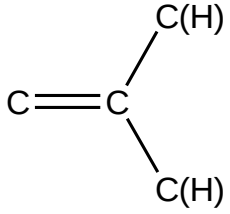


b $r[C(sp^2) - C(sp^2)]$ [kumulált dién]

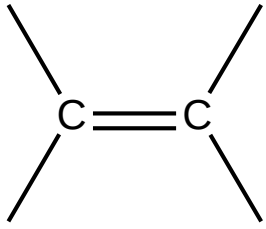


Kötésszög

CCC $\sphericalangle$ 120°
HCH $\sphericalangle$ 116,7°
HCC $\sphericalangle$ 121,6°
} szögfeszültség



Kötési energia

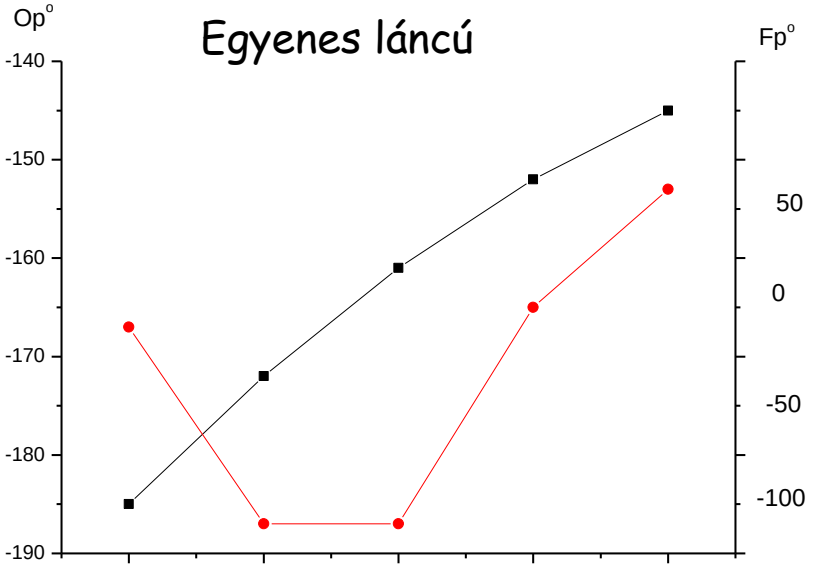


540 kJ/mol

Fizikai tulajdonságok

Halmazállapot

$C_{2\text{-}4}$	gáz
$C_{5\text{-}7}$	folyadék
$C_{8\text{-}}$	szilárd



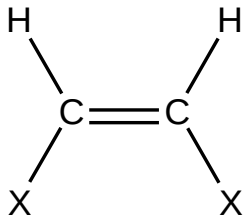
Cisz-transz izomerek

* Jobb illeszkedés, ** Jobb illeszkedés

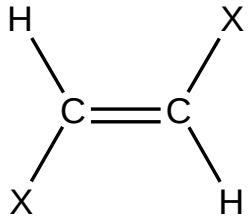
op	cisz		transz*	cisz		transz**	fp
2-butén	-139		-106	3,7		0,9	
2-pentén	-151	<	-140	37,9	>	36,4	
2-hexén	-141		-133	68,8		67,9	

Dipólusmomentum

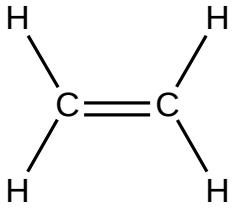
AZONOSITÁS



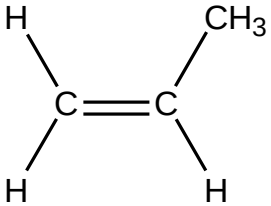
$\mu > 0$ [cisz]



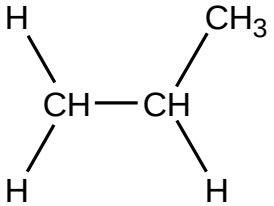
$\mu = 0$ [transz]



$\mu = 0$



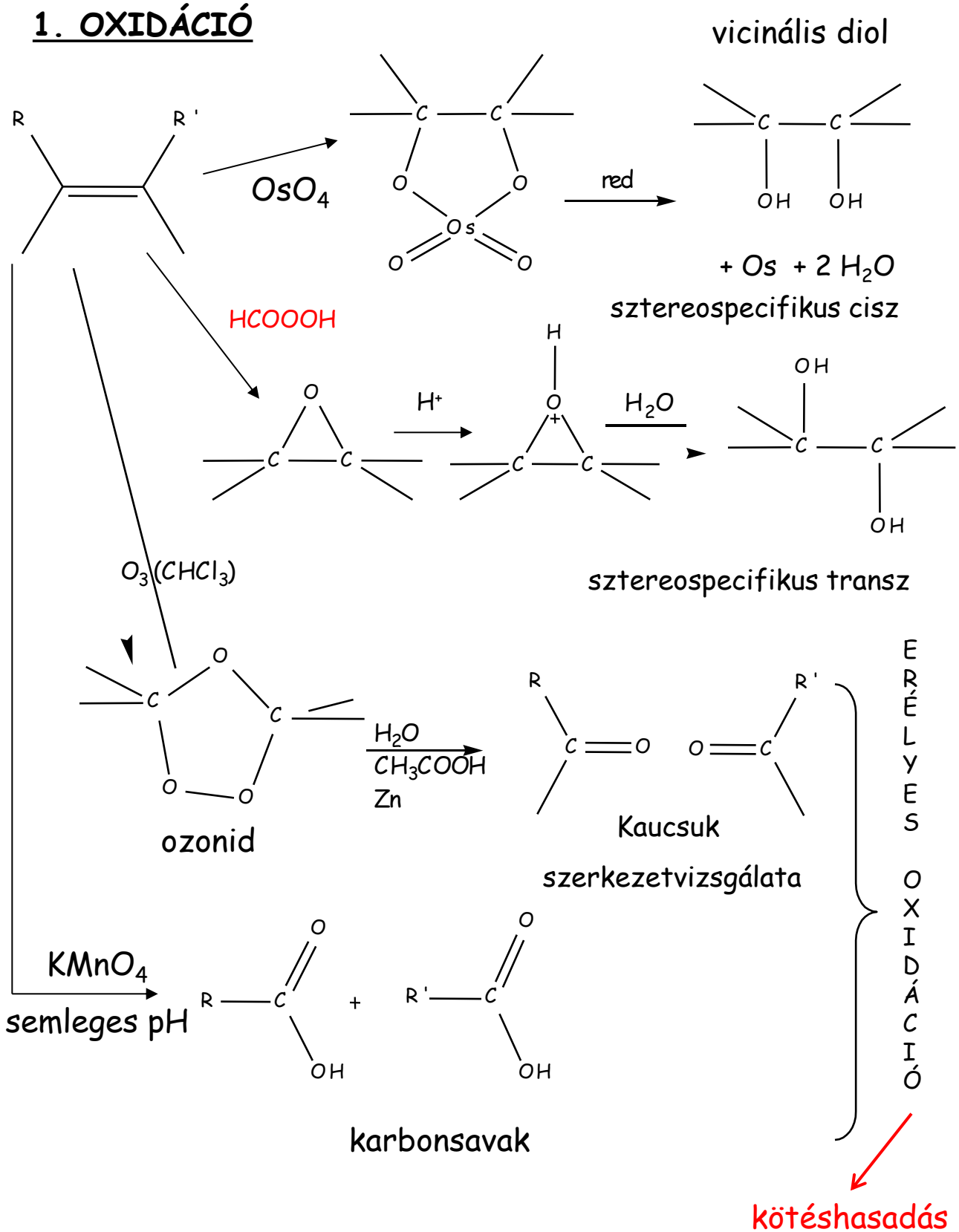
$\mu = 0,4$



$\mu = 0$

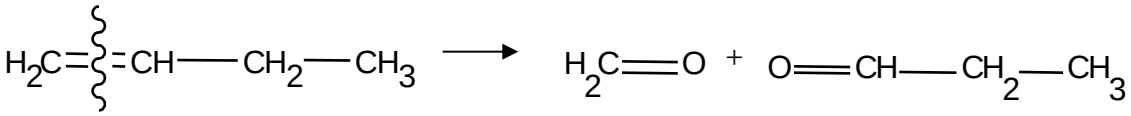
OKA: $C(sp^2)$ > $C(sp^3)$ EN

1. OXIDÁCIÓ

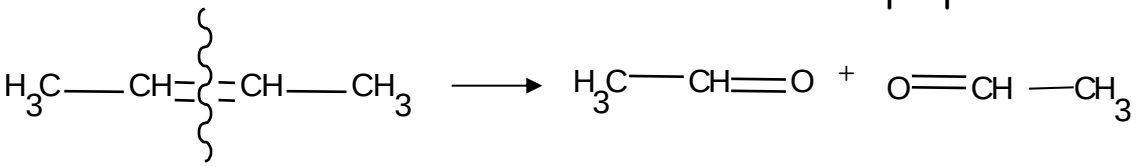

vicinális diol
R
R '
OsO_4
red
+ Os + 2 H_2O
sztereospecifikus cisz
HCOOOH
H^+
H_2O
sztereospecifikus transz
O_3 ($CHCl_3$)
ozonid
H_2O
CH_3COOH
Zn
Kaucsuk
szerkezetvizsgálata
$KMnO_4$
semleges pH
karbonsavak
ERÉLYES OXIDÁCIÓ
kötéshasadás

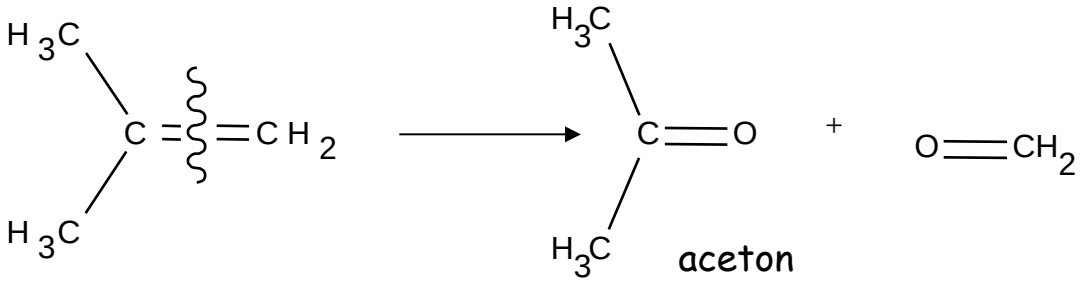
ALKALMAZÁS:

Szerkezetvizsgálat ozonidos lebontással (pl. kaucsuk)



propánal





aceton

Kiterjesztés: poliének

Szerves kémiában használt oxidáló/redukáló szerek

Oxidáló szerek

O_2	R – O – N = O	Ag_2O	MnO_2
O_3	$(CH_3)_2S = O$	HgO	$KMnO_4$
H_2O_2	halogének	CrO_3	OsO_4
R-COOOH	$FeCl_3$		$NaIO_4$
HNO_3			

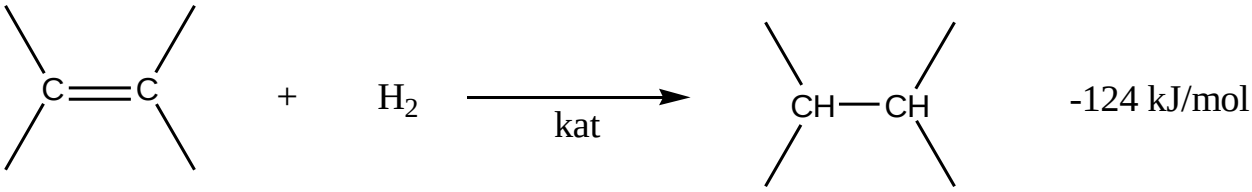
Dehidrogénező szerek Pt, Pd, S, Se

Redukáló szerek

H_2/Pt	Mg	$LiAlH_4$	$SnCl_2$	$Na_2S_2O_3$
H_2 /Pd	Zn	$NaBH_4$	$FeCl_2$	NH_2NH_2
H_2 /Ni	alkáli fémek			

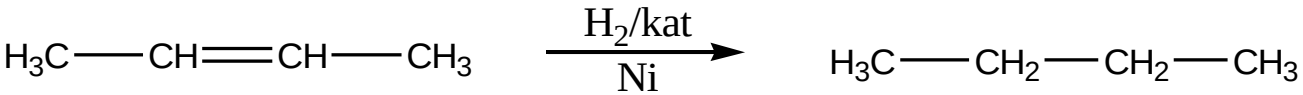
2. REDUKCIÓ – HIDROGÉNEZÉS

SZTEREOSPECIFIKUS CISZ ADDICIÓ (Ad_E)

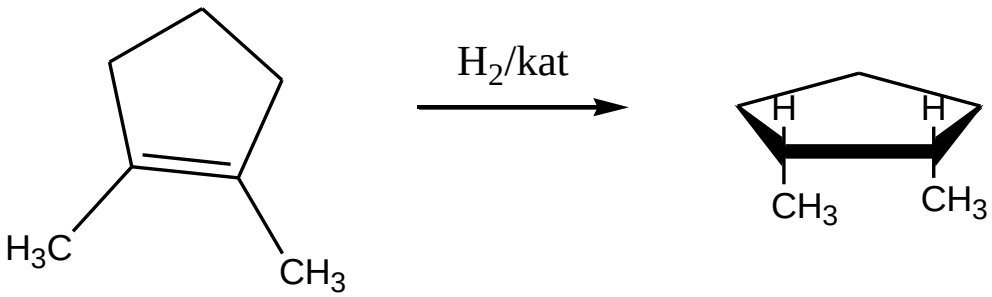


Példa:

cisz/transz



poliénre is!



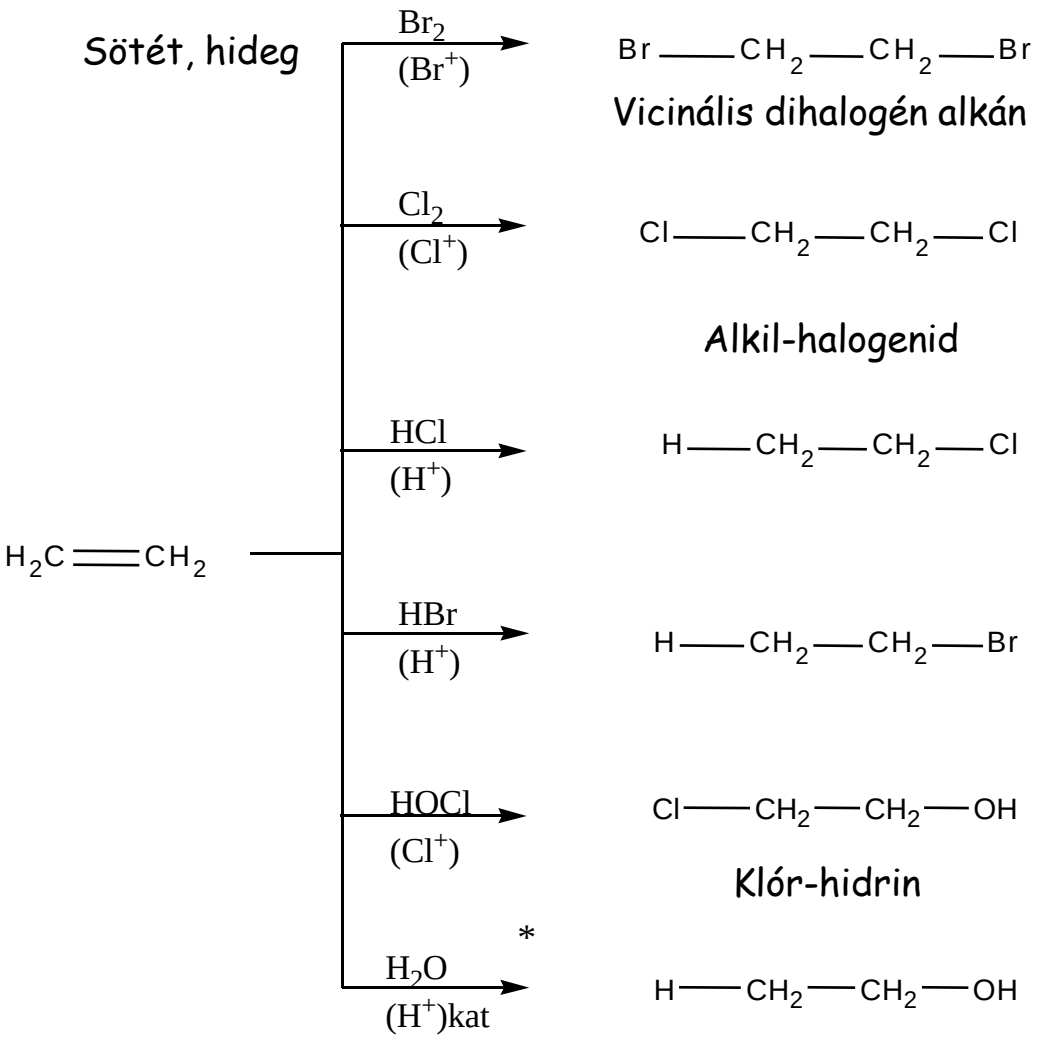
1,2-dimetil-1-ciklopentén

mezo-1,2-dimetil-ciklopentán

Alkalmazás: Telítetlen kötések számának meghatározása

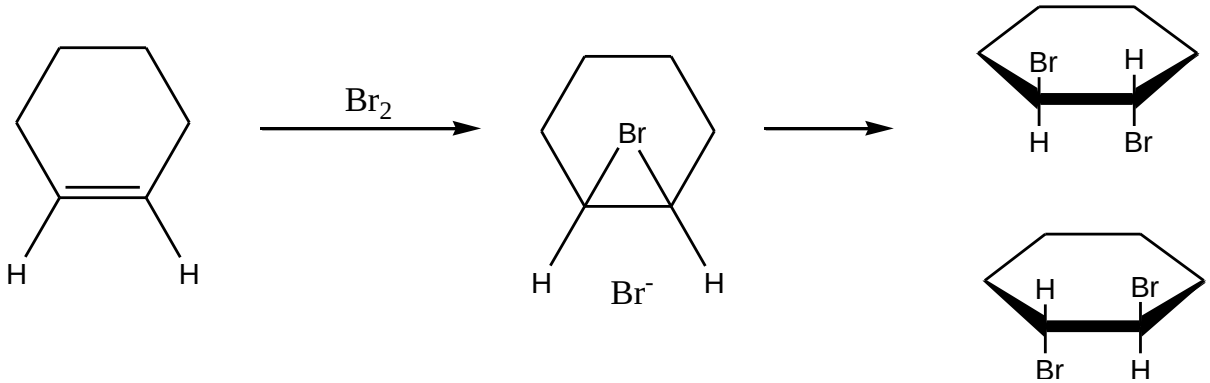
1 mmol olefinkötés 22,4ml normál H_2 gázt fejleszt

3. ELEKTROFIL ADDICIÓ (Ad_E)



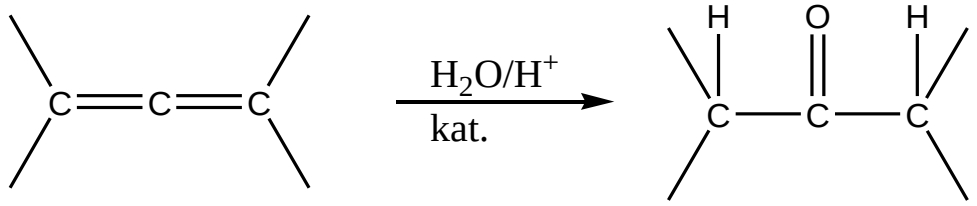
*Markovnyikov szabály

Példa: Transz-addició ⟶ enantiomerek racemátja

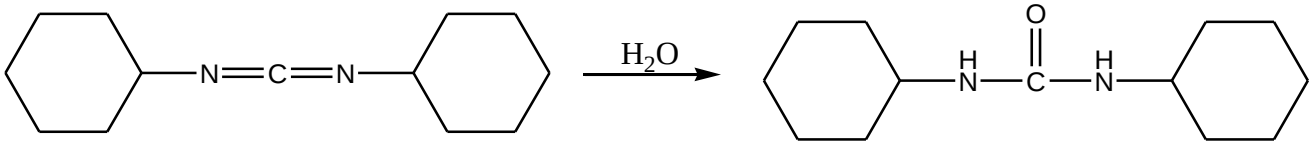


H_2O ADDICIÓ KUMULÁLT DIÉNRE

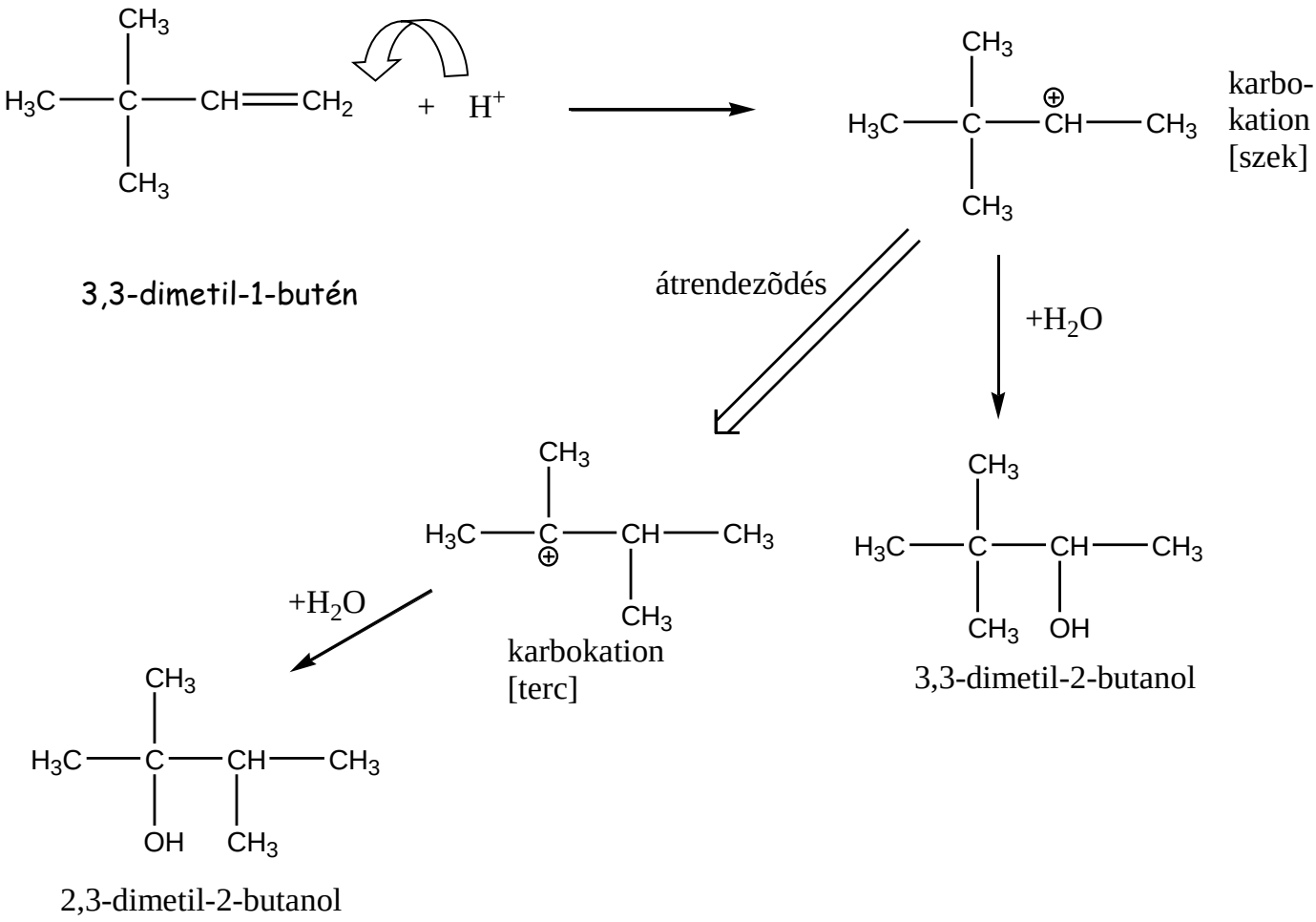
a.



b.

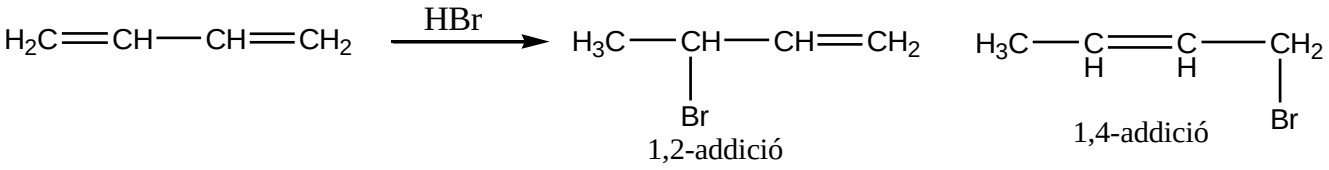


ADDICIÓ ÁTRENDEZŐDÉSSEL



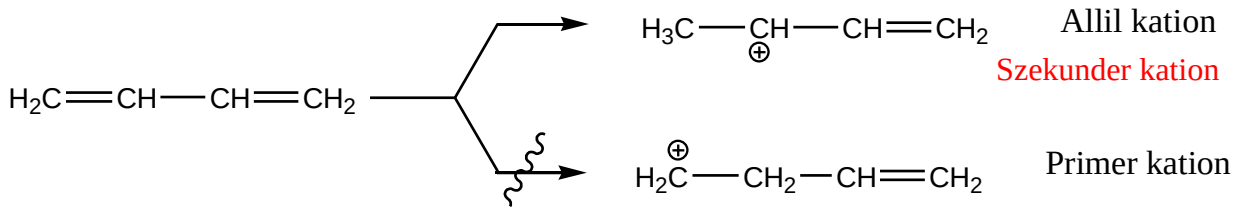
2,3-dimetil-2-butanol

RÉSZLEGES ELEKTROFIL ADDICIÓ

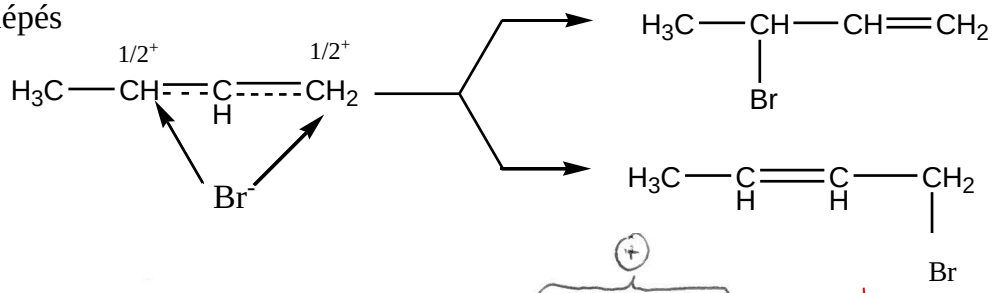


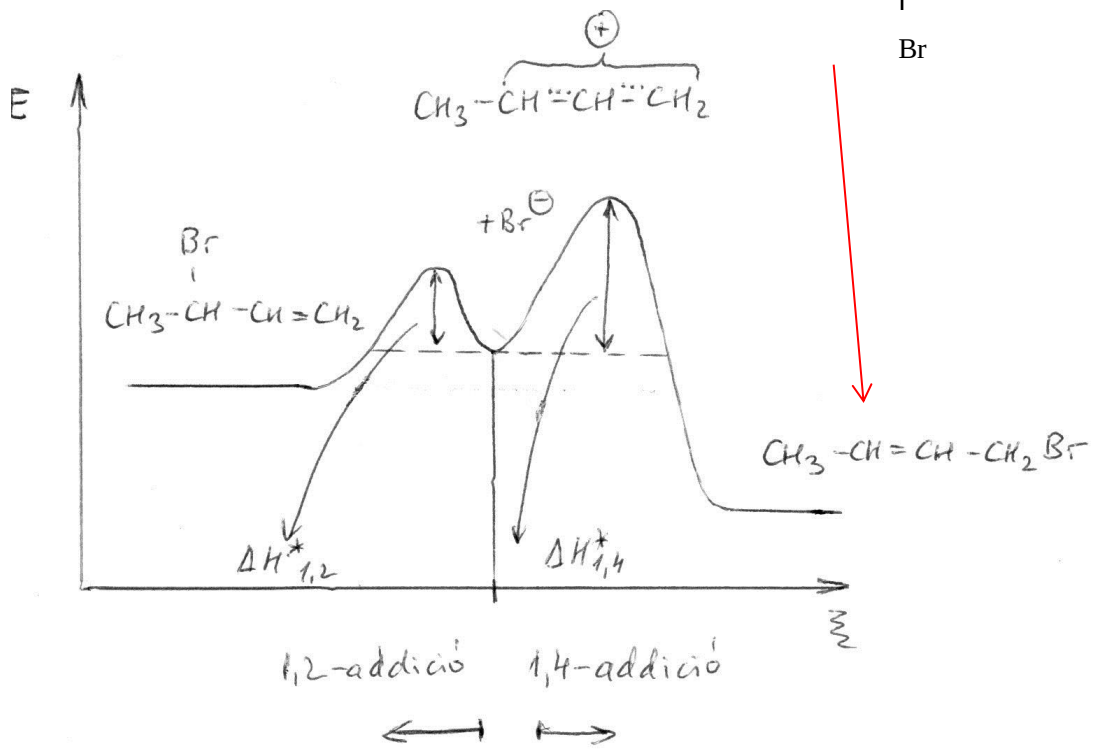
Mechanizmus:

1. lépés



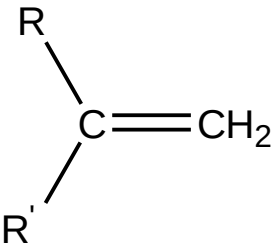
2. lépés





POLIMERIZÁCIÓ

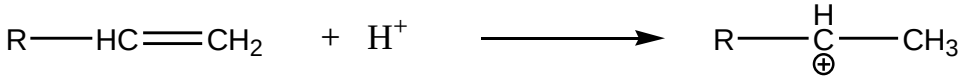
Poliaddició



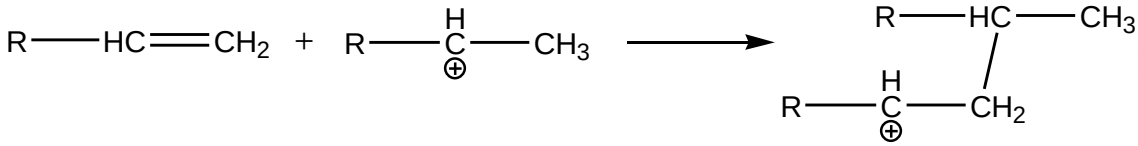
R	R′	Alapvegyület	Polimer
H	H	Etilén	Polietilén
H	CH_3	Propilén	Polipropilén
H	Cl	Vinil-klorid	PVC
H	C_6H_5	Sztirol	Polisztirol
H	$OCOCH_3$	Vinil-acetát	Poli(vinil-acetát)

Mechanizmus:

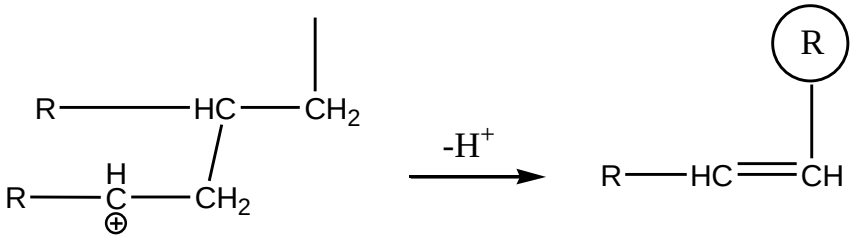
A. Kationos [savkatalizált - HF, H_2SO_4]



Kezdõ lépés



Láncnövés

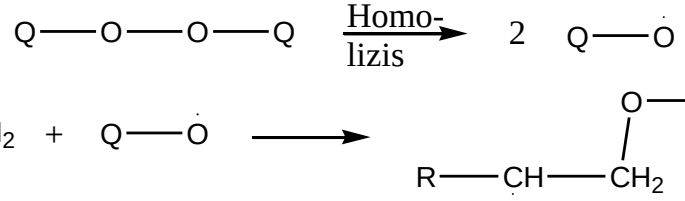


Záró lépés

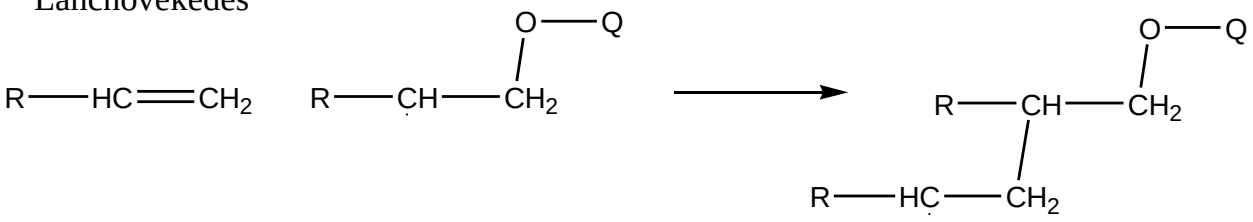
Pl.: Poliizobutilén

B. Gyökös (iniciátor)

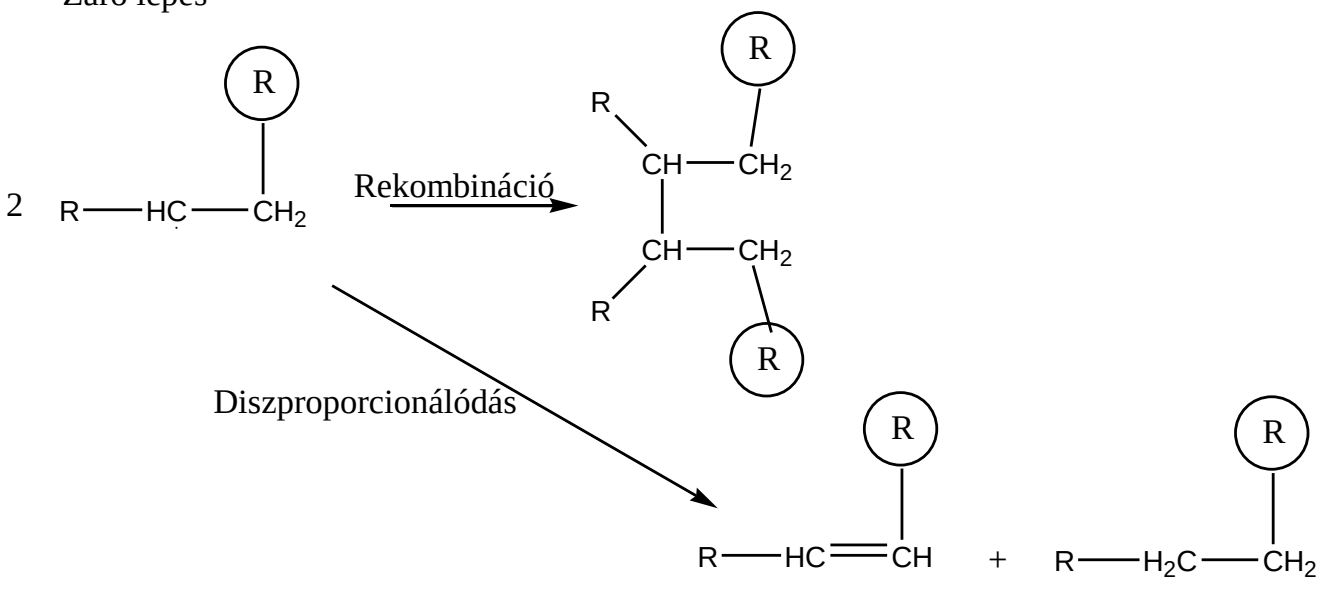
Kezdõ lépés



Láncnövekedés

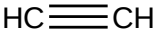


Záró lépés

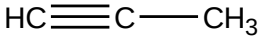


Példa: polivinilalkohol
polisztirol

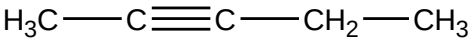
17.3 ALKINEK, CIKLOALKINEK



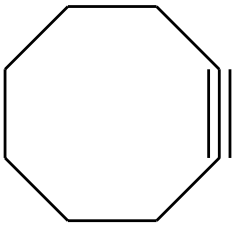
acetilén (etin)



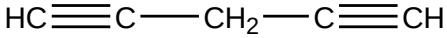
propin
(metil-acetilén)



2-pentin



ciklooktin



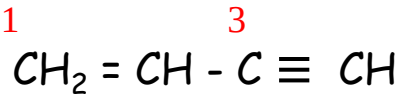
1,4-pentadiin

Nomenklatura:

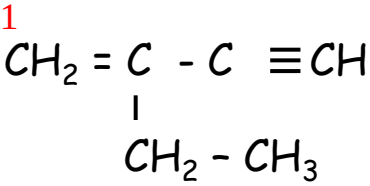
Elnevezés:

a) kettős kötés „erősebb", mint a hármas

b) leghosszabb szén lánc, amelyben az összes telitetlen kötés jelen var



1-butén-3-in



2-etil - 1-butén-3-in

Nem: „pent-1-in"

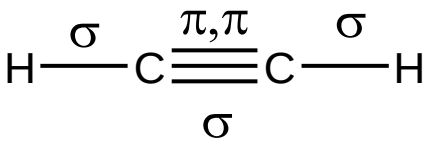
Az alkinek szerkezete

Kötésmód

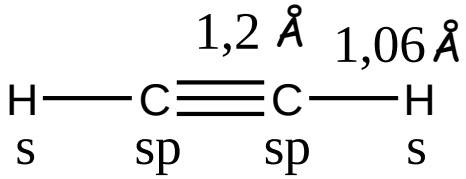
C (sp) – C(sp) σ

C(p) – C(p) π

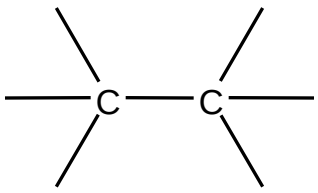
C(p) – C(p) π



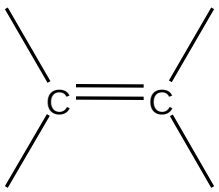
Kötéshossz



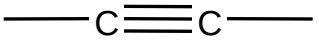
Kötési energia



360 kJ/mol

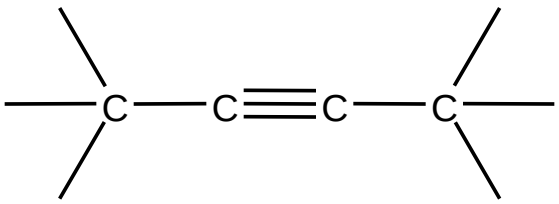


540 kJ/mol



670 kJ/mol

Konfiguráció

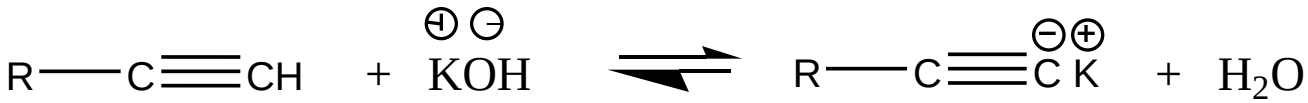


lineáris

Kötésszög CCC $\sphericalangle$ 180°

ALKINEK REAKCIÓI

1. Sav-bázis reakció

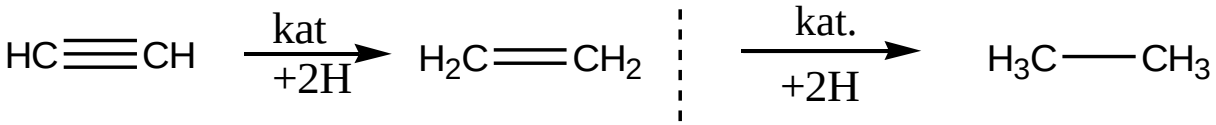


Disszociációs állandók

		pK_a
CH_3COOH	O-H sav	4,76
H_2O	O-H sav	15,7
$HC\equiv CH$	C-H sav	25,0
NH_3	N-H sav	35,0
$H_2C=CH_2$	C-H sav	36,0
H_3C-CH_3	C-H sav	42,0

Savi jelleg ↑

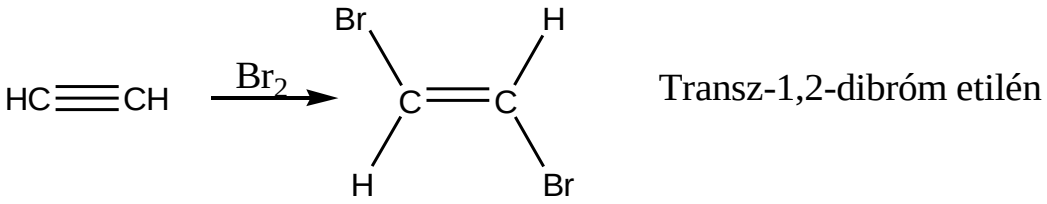
2. Redukció – hidrogénezés



Katalizátor: a) fém Zn/NaOH nascens H

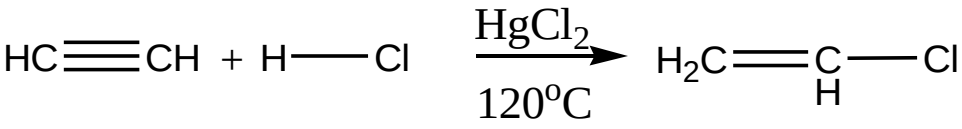
b) fém Na/NH_3 transz, részleges

3. Halogénezés

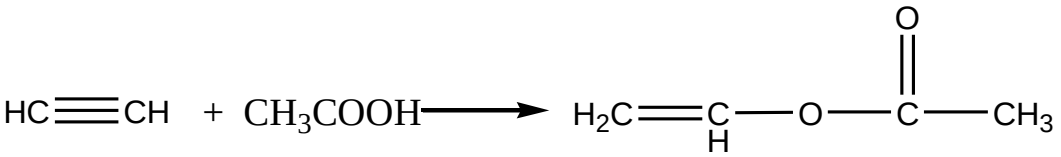


Transz-1,2-dibróm etilén

4. Savaddició (A_E) : (pl. X-H, O-H sav)

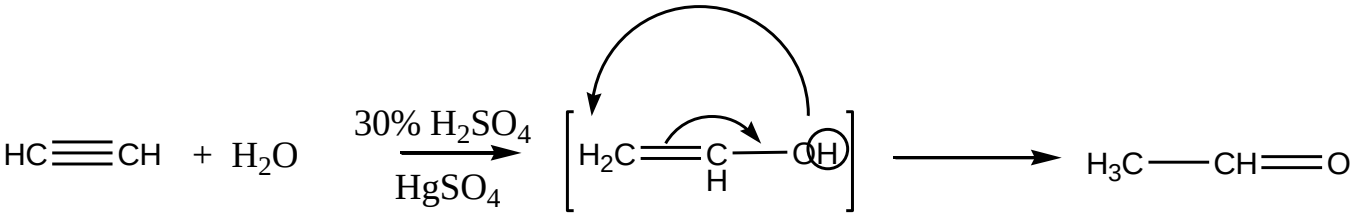


Vinil-klorid



Vinil-acetát

5. Vízaddició (A_N) és átrendeződés



Vinil-alkohol

Acetaldehid

enol - keto