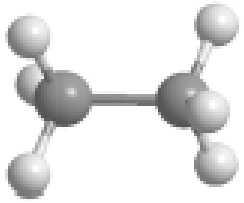
3. Alkany

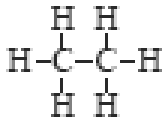
3.1. Úvod

Alkany a cykloalkany jsou hlavní složky zemního plynu a ropy, které jsou převážným zdrojem energie

Nasycené alkany a cykloalkany mají pouze **jednoduché vazby** uhlík-vodík (C-H) a uhlík-uhlík (C-C).

3.2. Struktura cykloalkanů

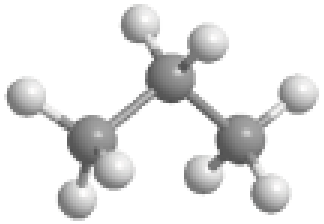


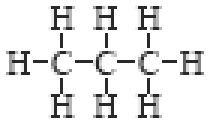


ethan

Alkany mají obecný molekularní vzorec:

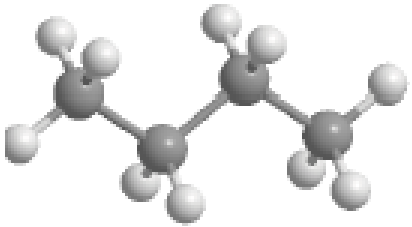
C_nH_{2n+2},

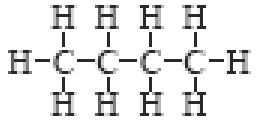




propan

kde n je počet atomů uhlíku.



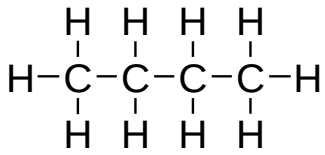


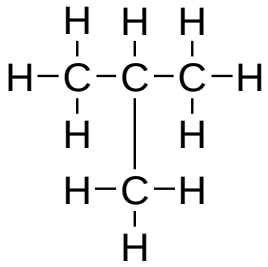
butan

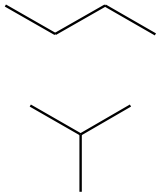
Tab. 3.1. Názvy a vzorce prvních deseti uhlovodíků

Název	Počet atomů uhlíku	Molekulární vzorec	Strukturní vzorec	Počet možných izomerů
methan	1	CH_4	CH_4	1
ethan	2	C_2H_6	CH_3CH_3	1
propan	3	C_3H_8	$CH_3CH_2CH_3$	1
butan	4	C_4H_{10}	$CH_3(CH_2)_2CH_3$	2
pentan	5	C_5H_{12}	$CH_3(CH_2)_3CH_3$	3
hexan	6	C_6H_{14}	$CH_3(CH_2)_4CH_3$	5
heptan	7	C_7H_{16}	$CH_3(CH_2)_5CH_3$	9
octan	8	C_8H_{18}	$CH_3(CH_2)_6CH_3$	18
nonan	9	C_9H_{20}	$CH_3(CH_2)_7CH_3$	35
dekan	10	$C_{10}H_{22}$	$CH_3(CH_2)_8CH_3$	75

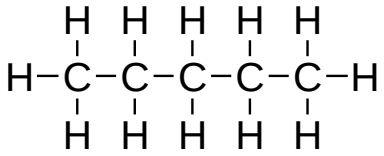
butan

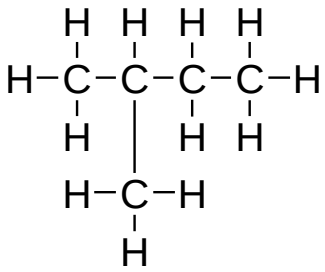


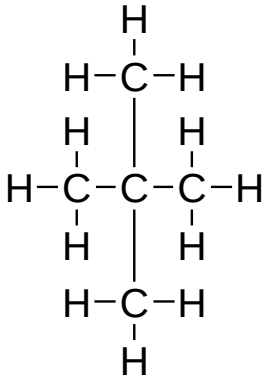


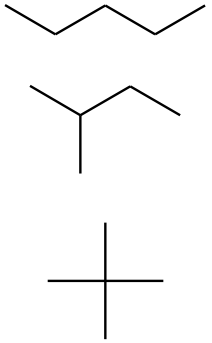


pentan









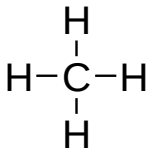
3.3. Názvosloví alkanů

1. Obecný název acyklických uhlovodíků je alkany. Přípona –*an* se používá pro všechny nasycené alkany

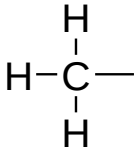
2. Názvy nerozvětvených alkanů, kromě prvních čtyř, vycházejí z počtu atomů uhlíku v molekule a jsou odvozeny od řeckých číslovek (pent-, hex-, atd.) a určují délku řetězce

3. Pro rozvětvené alkany platí, že název je odvozen od nejdelšího souvislého uhlíkatého řetězce.

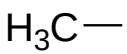
4. Funkční skupiny, které jsou navázané na hlavní řetězec se nazývají substituenty. Substituenty, které jsou složeny z atomů uhlíku a vodíku a mají pouze jednoduché vazby se nazývají alkyly. Typickým příkladem je methyl. U vyšších alkylů se postupuje podobně: ethyl, propyl, butyl atd.

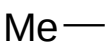


methan

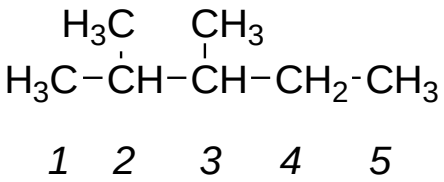


methyl





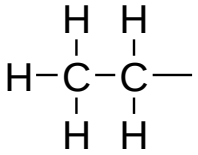
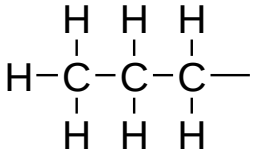
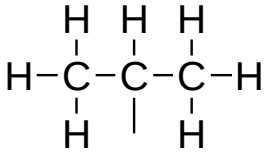
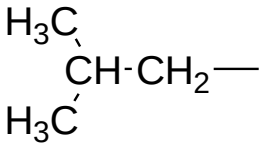
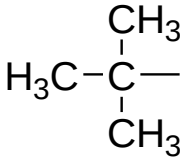
5. Hlavní řetězec je očíslován tak, aby první substituent měl co nejmenší možné číslo.



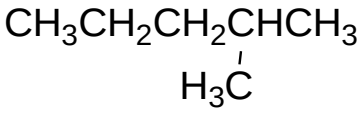
6. Jestliže molekula obsahuje dva různé substituenty tak se řadí podle abecedního pořádku, zde nutné vzít v patrnost, že předpony di-, tri- atd. nemají na abecední pořadí vliv.

3.4. Názvosloví alkylových a halogenových sustituentů

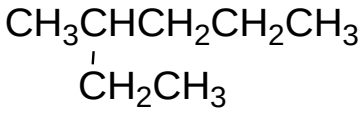
Názvosloví alkylových substituentů se tvoří nahrazením přípony *–an* příponou *–yl*.

ethyl		CH_3CH_2—	Et—
propyl		$CH_3CH_2CH_2$—	Pr—
2-propyl (isopropyl)		CH_3CHCH_3 |	*i*-Pr—
$CH_3CH_2CH_2CH_2$—	$CH_3CHCH_2CH_3$ |		
butyl	1-methylpropyl (*sec*-butyl)	2-methylpropyl (isobutyl)	1,1-dimethylethyl (*tert*-butyl)

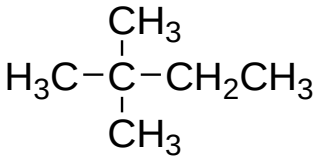
F—	Cl—	Br—	I—
fluor	chlor	brom	jod



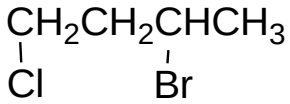
2-methylpentan



3-methylhexan



2,2-dimethylbutan

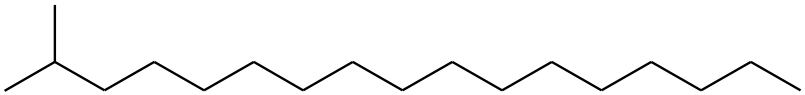


3-brom-1-chlorbutan

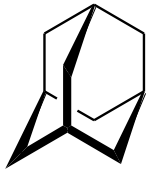
3.5. Výskyt alkanů v přírodě a jejich vlastnosti

Ropa je složitá směs organických sloučenin, z nichž větší část je tvořena alkany a cykloalkany. Složení ropy j závislé na místě původu.

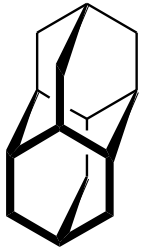
Alkany se nacházejí i přírodě a jsou produkovány některými rostlinami: cykloalkany a heptan tvoří hlavní složku terpenických silic.



2-methylheptadekan



adamantan
tricyklo[3,3,1,$1^{3,7}$]dekan

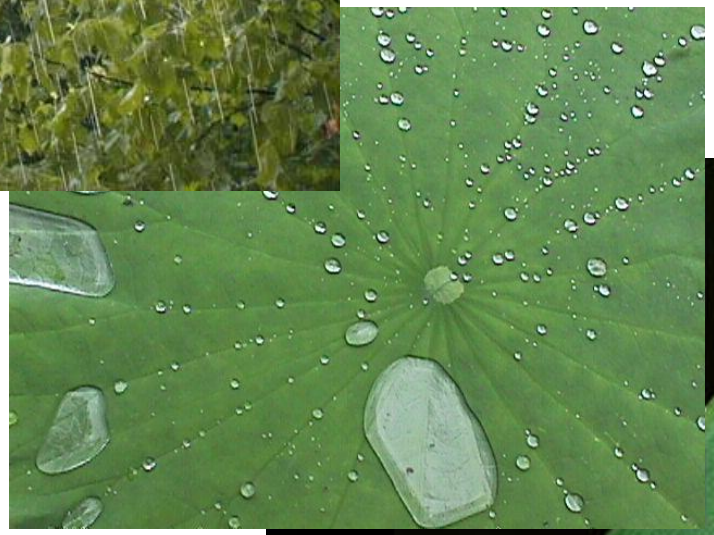


diamantan

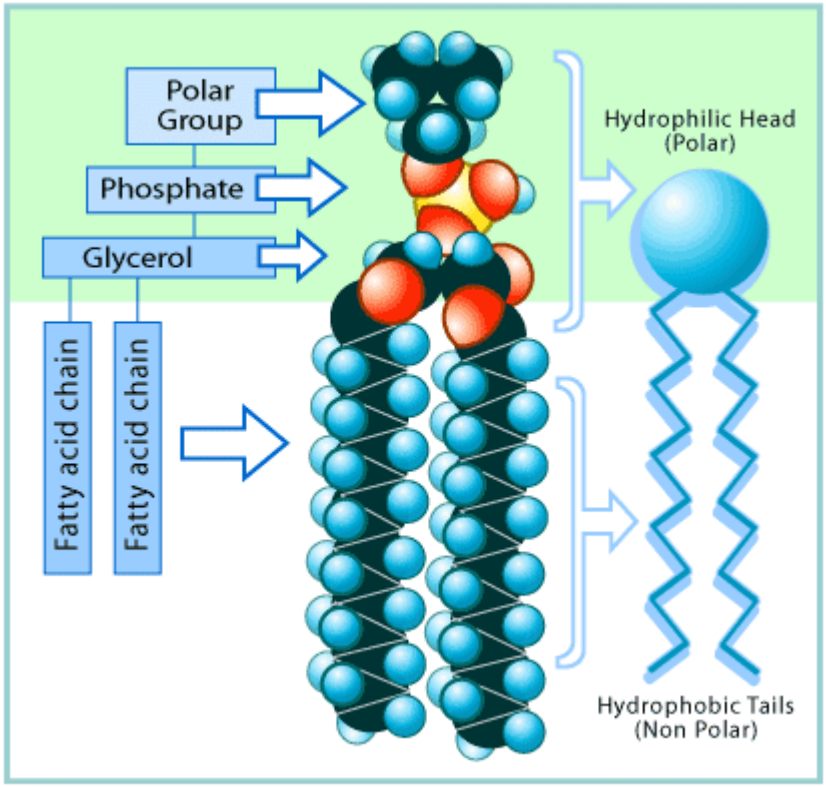
Izoloval Landa z Hodonínské ropy v roce 1932.

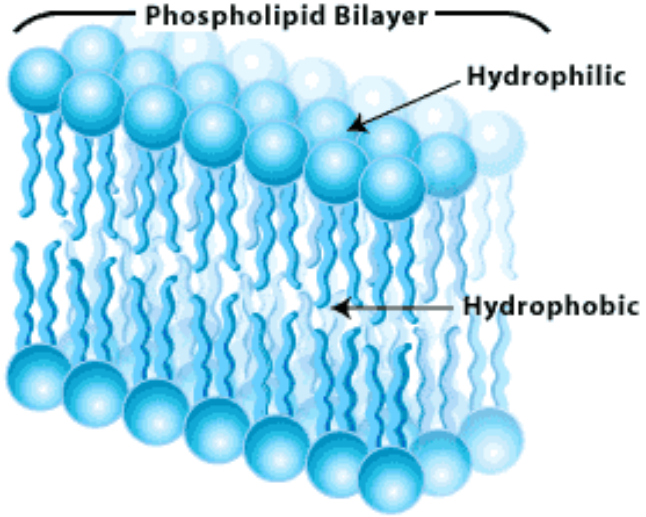
Vosky

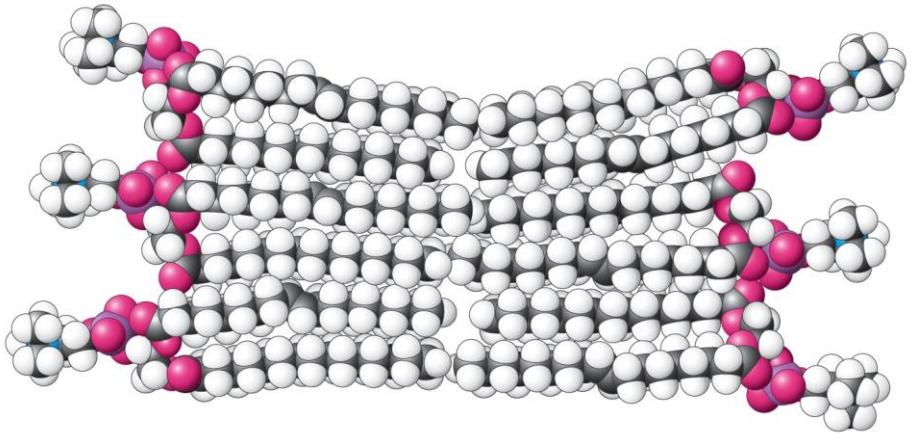
Vyšší *n*-alkany jsou součástí nebo výhradní složkou přírodních vosků a tvoří ochrannou vrstvu na rostlinách: $C_{27}H_{56}$ a $C_{29}H_{60}$ (jablka), $C_{29}H_{60}$ (zelí, brokolice) a $C_{31}H_{64}$ (tabákové listy).



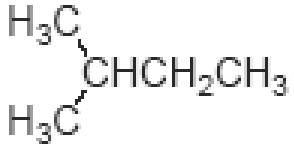
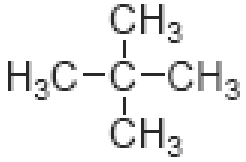
Hydrofobicita alkylových řetězců - membrány

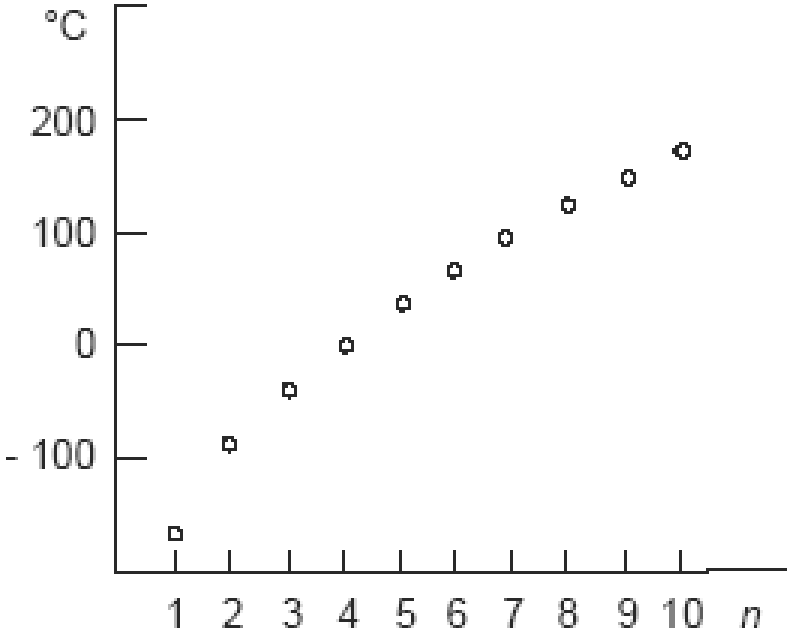






Tabulka 3.2.

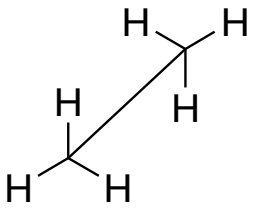
Název	Vzorec	Teplota varu (°C)
pentan	$CH_3CH_2CH_2CH_2CH_3$	36
2-methylbutan		28
2,2-dimethylpropan		10

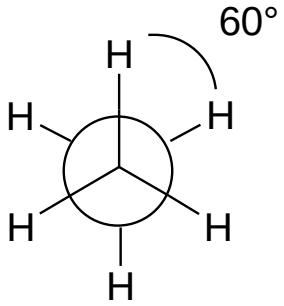


	n	bod varu (°C)
methan	1	-161
ethan	2	-88
propan	3	-42
butan	4	-0.5
pentan	5	36
hexan	6	69
heptan	7	98
oktan	8	126
nonan	9	151
dekan	10	174

3.6. Konformace alkanů

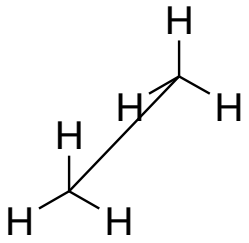
nezákrytová (střídavá) poloha

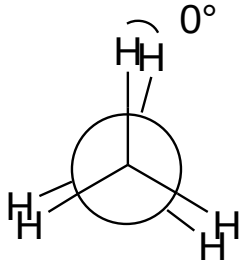




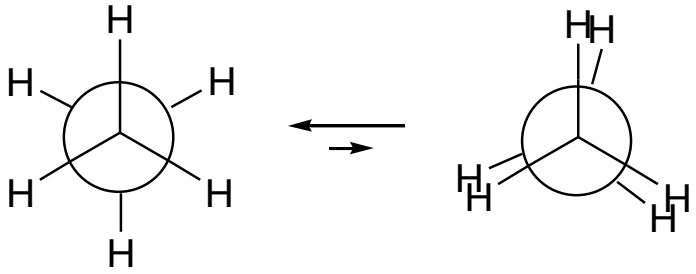
Newmanova projekce

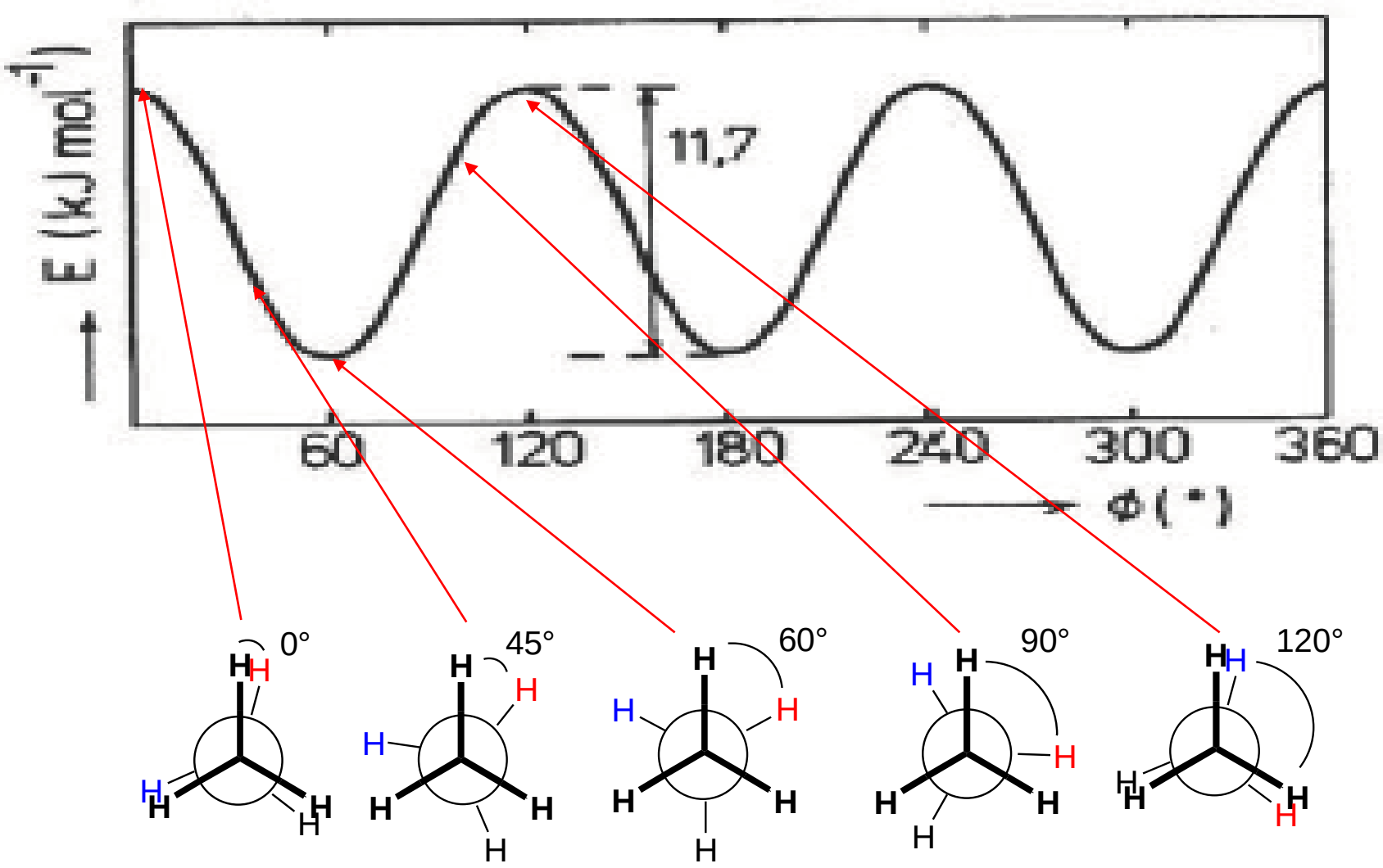
zákrytová poloha

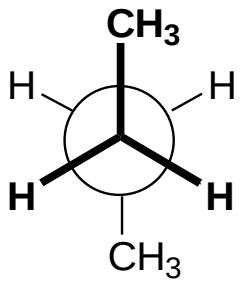




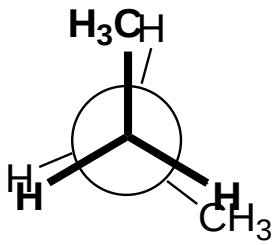
Newmanova projekce



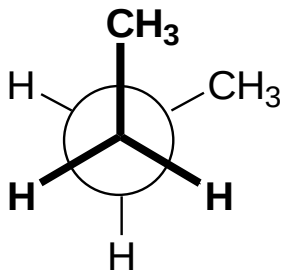

E (kJ mol⁻¹)
11.7
60
120
180
240
300
360
φ (°)
0°
45°
60°
90°
120°



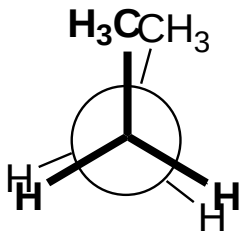
antiperiplanární



antiklinální

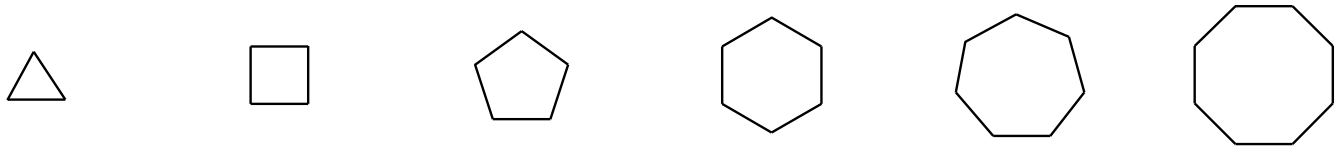


synperiplanární

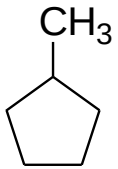


synklinální

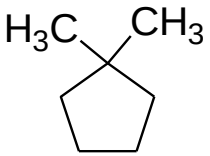
3.7. Cykloalkany



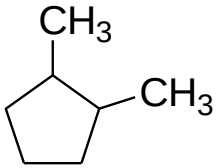
cyklopropan t.v. -37.7°C | cyklobutan t.v. 12°C | cyklopentan t.v. 49.3°C | cyklohexan t.v. 80.7°C | cykloheptan t.v. 118.5°C | cyklooctan t.v. 149°C



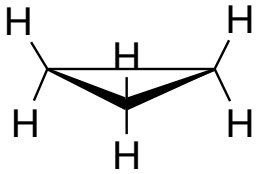
methylcyklopentan



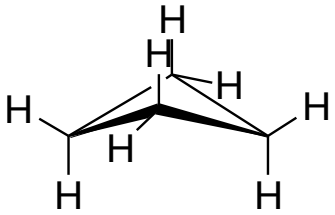
1,1-dimethylcyklopentan



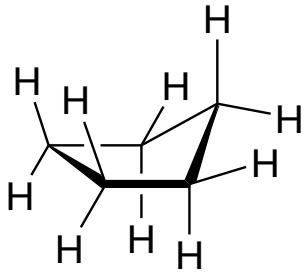
1,2-dimethylcyklopentan



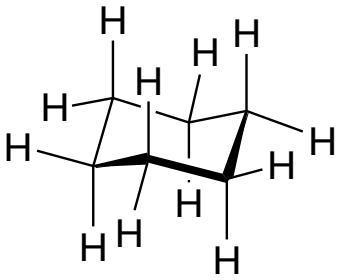
cyklopropan



cyklobutan



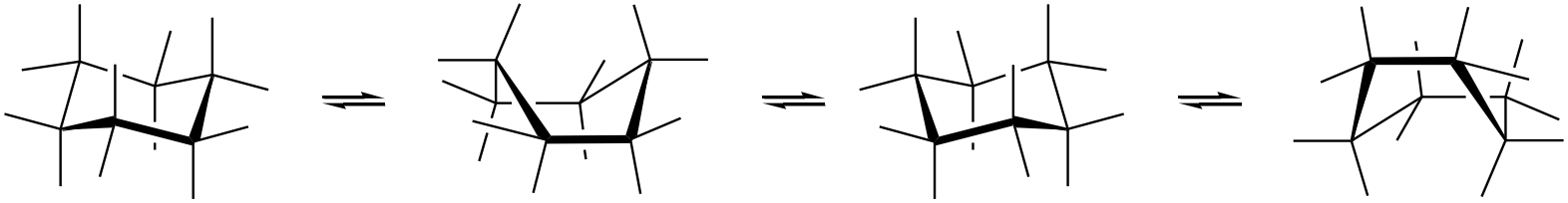
cyklopentan



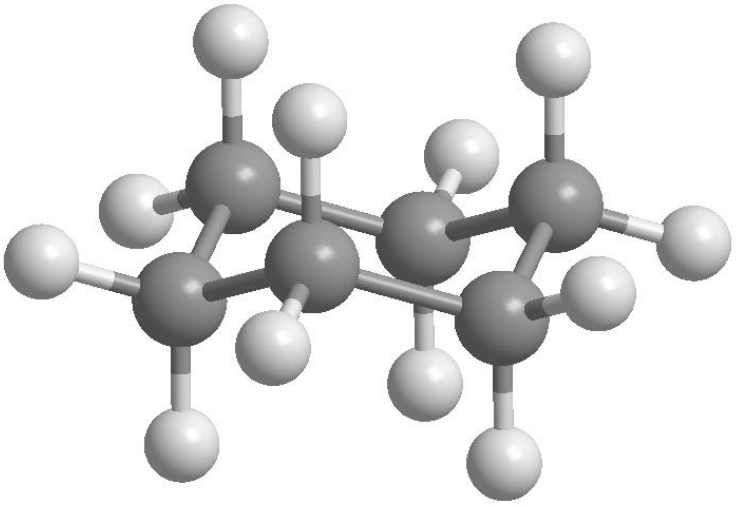
cyklohexan

Počet atomů uhlíku kruhu n	ΔH (kJ·mol^{-1})	ΔH/n (kJ·mol^{-1})	ΔH – n×659 (kJ·mol^{-1})
1 [a]	659	659	
2 [b]	1411	705	92
3	2093	697	115
4	2747	686	111
5	3322	664	27
6	3954	659	0
7	4639	662	26
8	5312	664	40

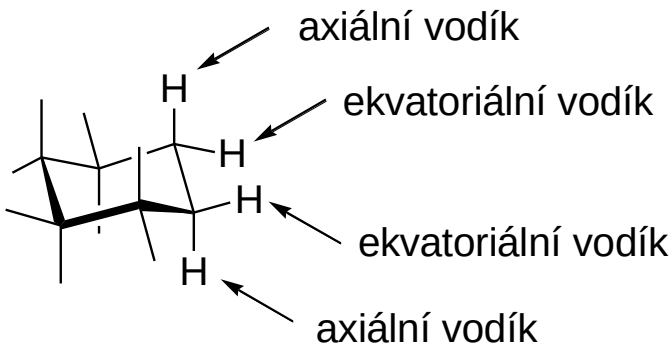
[a] (hodnota získaná ze spalných tepel alkanů. [b] Pro ethen jako nejmenší kruh.

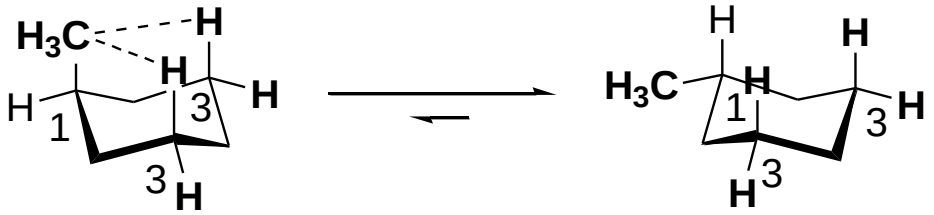


židličková konformace | vaničková konformace | židličková konformace | vaničková konformace



židličková konformace

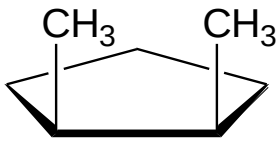




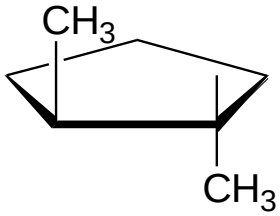
Me v axiálnípoloze 5%

Me ekvatoriální poloze 95%

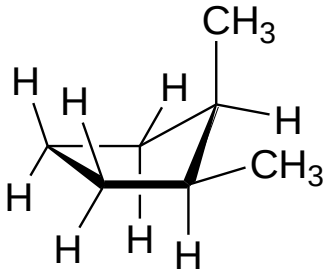
3.8. Cis a trans izomerie u cykloalkanů



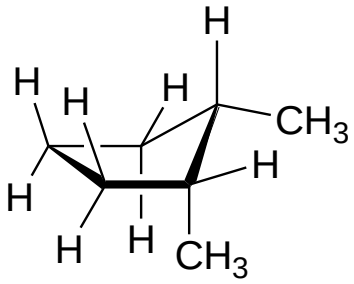
cis-1,2-dimethylcyklopentan
t.v. 99°C



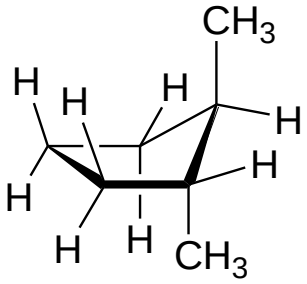
trans-1,2-dimethylcyklopentan
t.v. 92°C



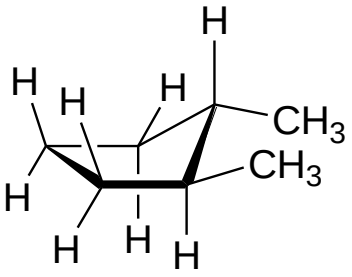
e,a



a,e



a,a



e,e
stabilnì jší

3.9. Reakce alkanů

Oxidace (spalování)

$$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O \quad 892\ kJ/mol$$

$$C_4H_{10} + 6.5O_2 \longrightarrow 4CO_2 + 5H_2O \quad 2883\ kJ/mol$$

$$2CH_4 + 3O_2 \longrightarrow 2CO + 4H_2O$$

$$CH_4 + O_2 \longrightarrow C + 2H_2O$$

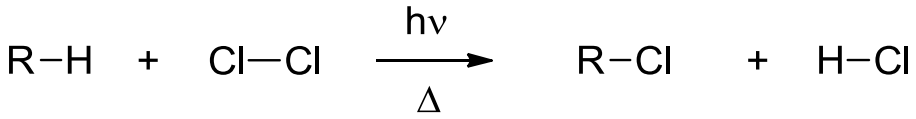
$$CH_4 + 3O_2 \longrightarrow CH_2O + H_2O$$

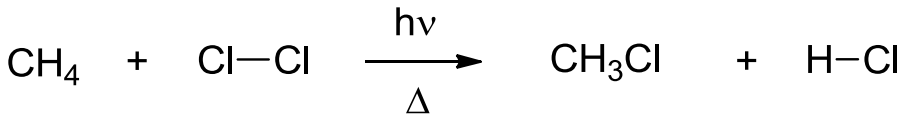
formaldehyd

$$2C_2H_6 + 3O_2 \longrightarrow 2CH_3COOH + H_2O$$

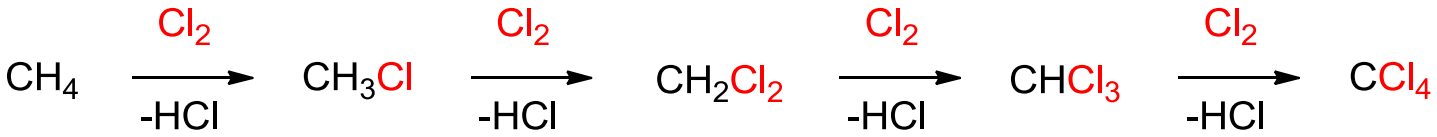
kyselina octová

Halogenace alkanů





chlormethan

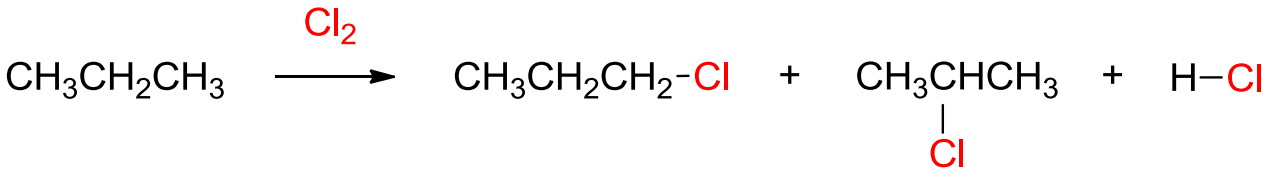


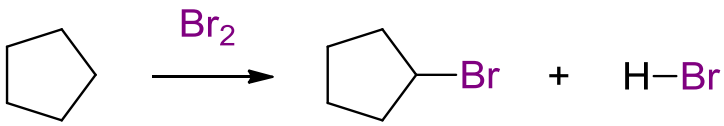
chlormethan
t.v. -24.5°C

dichlormethan
t.v. 40°C

trichlormethan
t.v. 61.7°C
(chloroform)

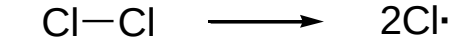
tetrachlormethan
t.v. 75.6°C



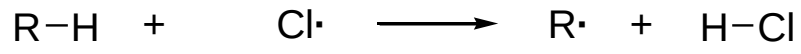


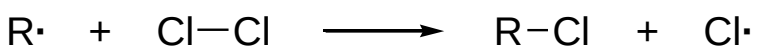
Mechanismus halogenace

Iniciace

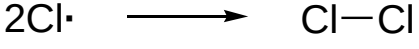


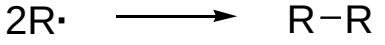
Propagace



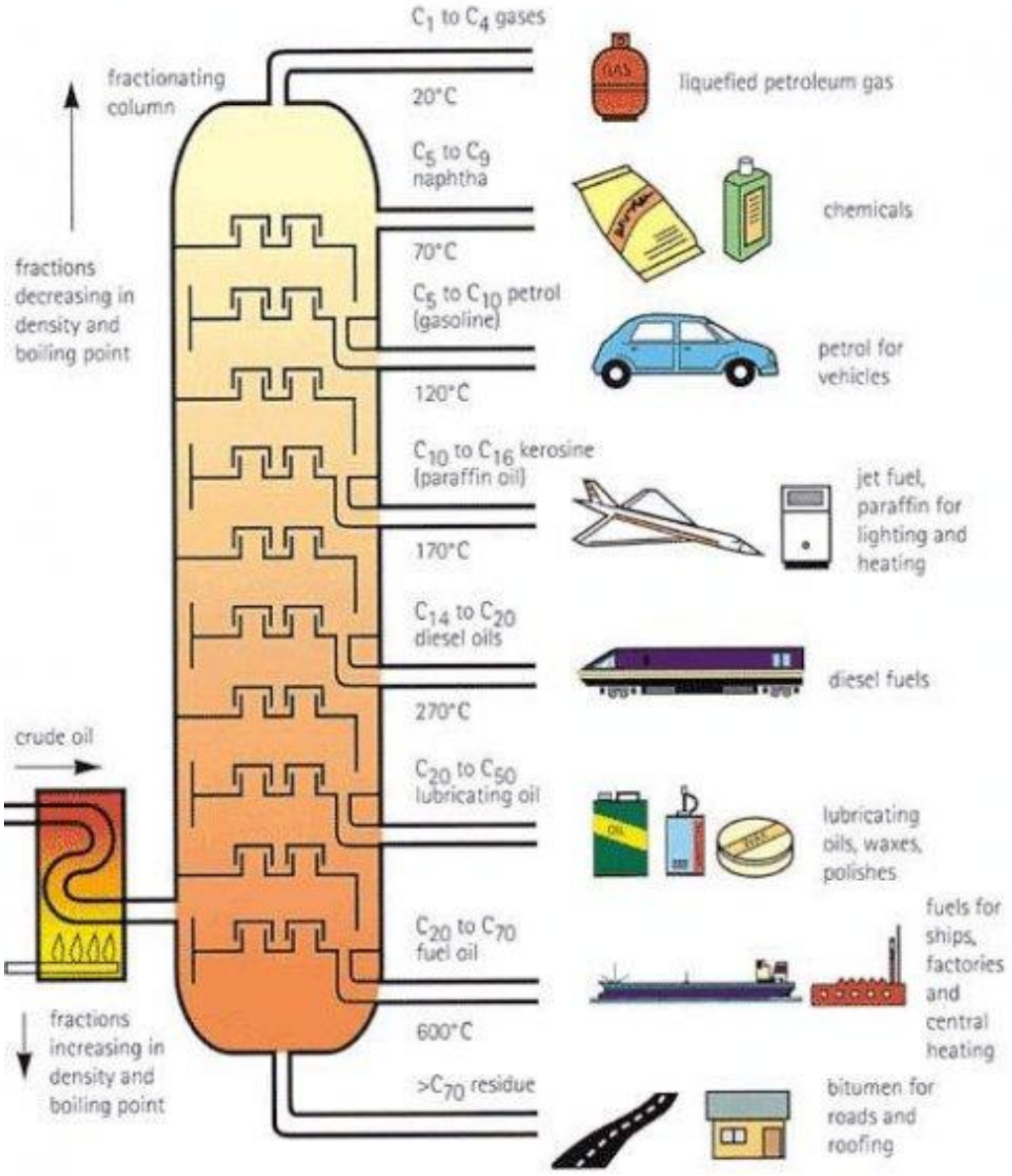


Terminace

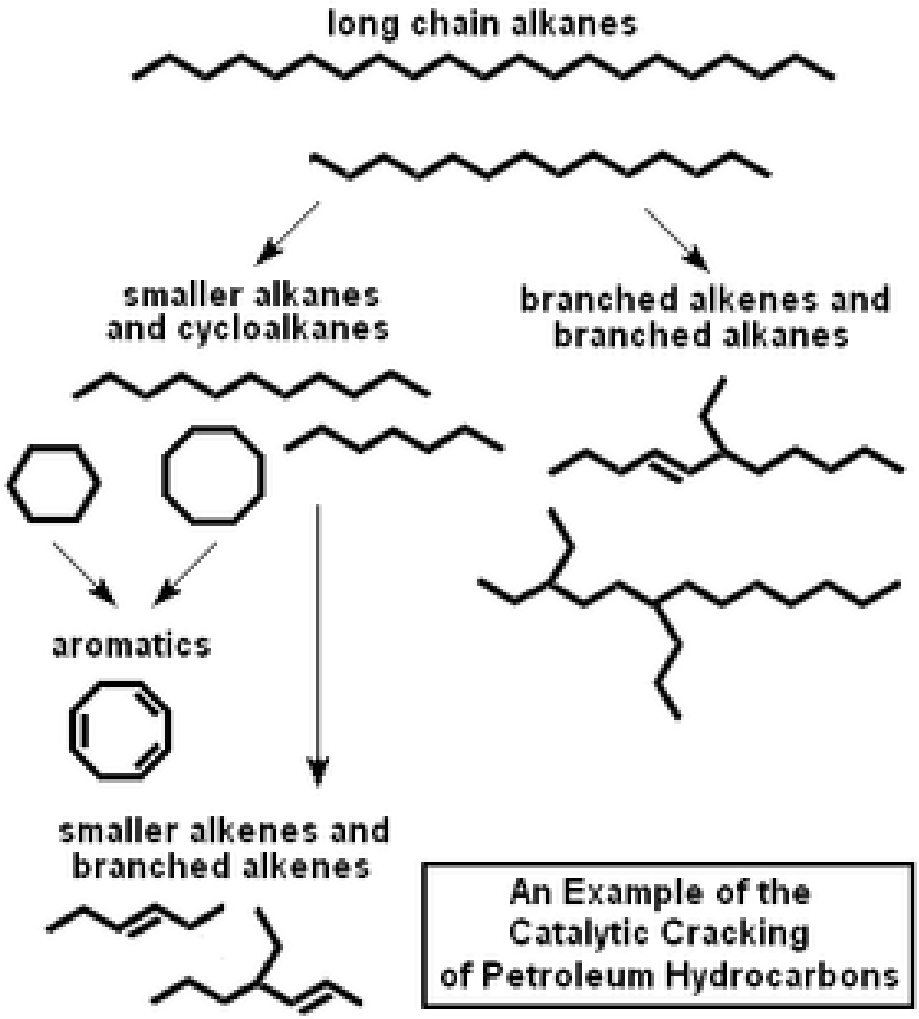




Ropa - destilace



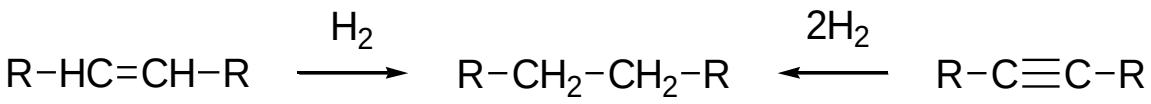
Krakování ropy - výroba benzínu



4. Alkeny a alkyny

4.1. Úvod

C_nH_{2n}		C_nH_{2n-2}
alkeny		akyny



4.2. Názvosloví alkenů a alkynů

kumulované	konjugované	izolované
C=C=C	C=C−C=C	C=C−C−C=C
C=C=C=C	C=C−C=C−C=C	C≡C−C−C−C≡C
	C≡C−C≡C	

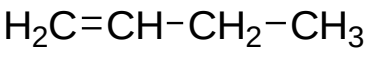
1. Dvojné vazby uhlík-uhlík se v molekule označují příponou –*en*. Když je přítomno více než jedna dvojná vazba používají se přípony jako –dien, -trien, atd. Trojné vazby se označují příponou –*yn*. V případě většího počtu těchto vazeb se používá stejný systém jako v předešlém případě. Jsou-li přítomny dvojné a trojné vazby použijí se obě přípony.

2. Číslování uhlíkového řetězce se provádí tak, aby uhlíkové atomy násobné vazby měly co nejmenší číslo

3. Pozice násobné vazby se označuje nižším číslem z obou čísel příslušejících uhlíkovým atomům násobné vazby.

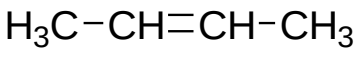
H_3C-CH_3	$H_2C=CH_2$	$HC\equiv CH$
ethan	ethen	ethyn
$H_3C-CH_2-CH_3$	$H_3C-CH=CH_2$	$H_3C-C\equiv CH$
propan	propen	propyn

Názvoslovný kmen jména (eth-, prop-, atd) vždy určuje počet uhlíkových atomů a přípona druh násobné vazby. V případě látek s počtem uhlíků 4 a více je nutné zavedení číslování k určení polohy násobné vazby.



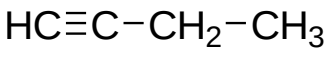
1 2 3 4

but-1-en



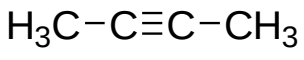
1 2 3 4

but-2-en



1 2 3 4

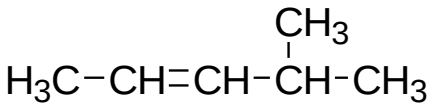
but-1-yn



1 2 3 4

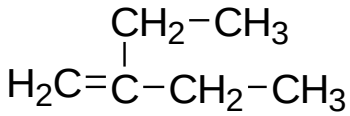
but-2-yn

V případe rozvětvených uhlovodíku má násobná vazba při číslování prioritu.



1 2 3 4 5

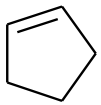
4-methylpent-2-en
(ne 2-methylpent-3-en)



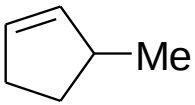
1 2 3 4

2-ethylbut-1-en

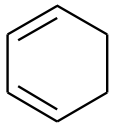
U cyklických uhlovodíků začíná číslování na dvojné vazbě.



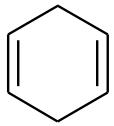
cyklopenten



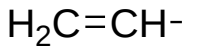
3-methylcyklopenten



1,3-cyklohexadien

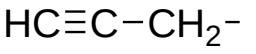


1,4-cyklohexadien

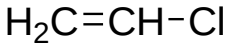


vinyl
(ethenyl)

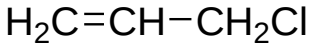
allyl
(3-propenyl)



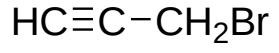
propagyl
(3-propynyl)



vinylchlorid



allylchlorid

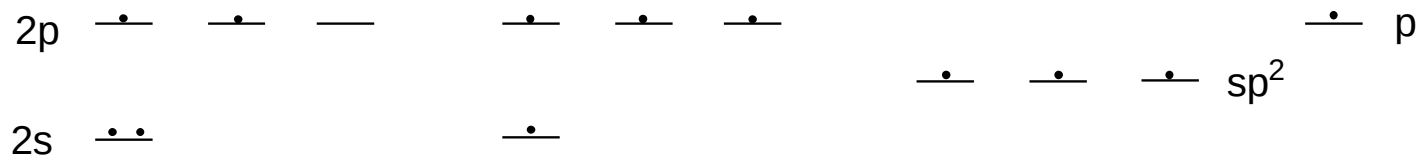


propagylbromid

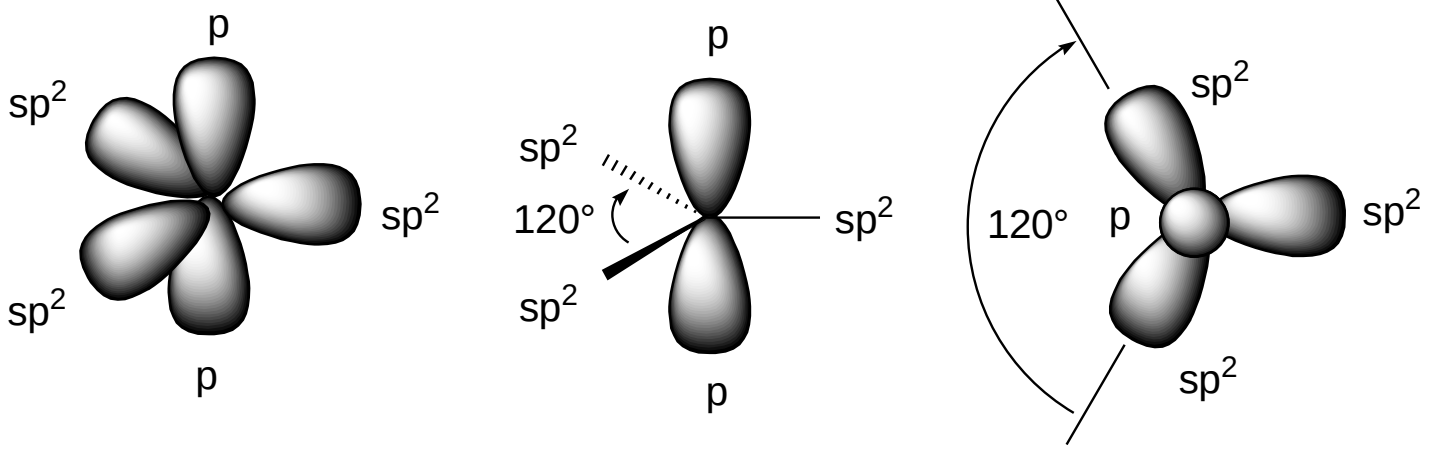
4.3 Alkeny. Vlastnosti dvojné vazby

Vlastnosti	C-C	C=C
1. Počet připojených atomu	4	3
2. Rotace	ano	ne
3. Geometrie vazby	mnoho konformací	planární
4. Úhel mezi vazbami	109.5°	120°
5. Délka vazby (Å)	1.54	1.34

4.4. Orbitalový model dvojné vazby

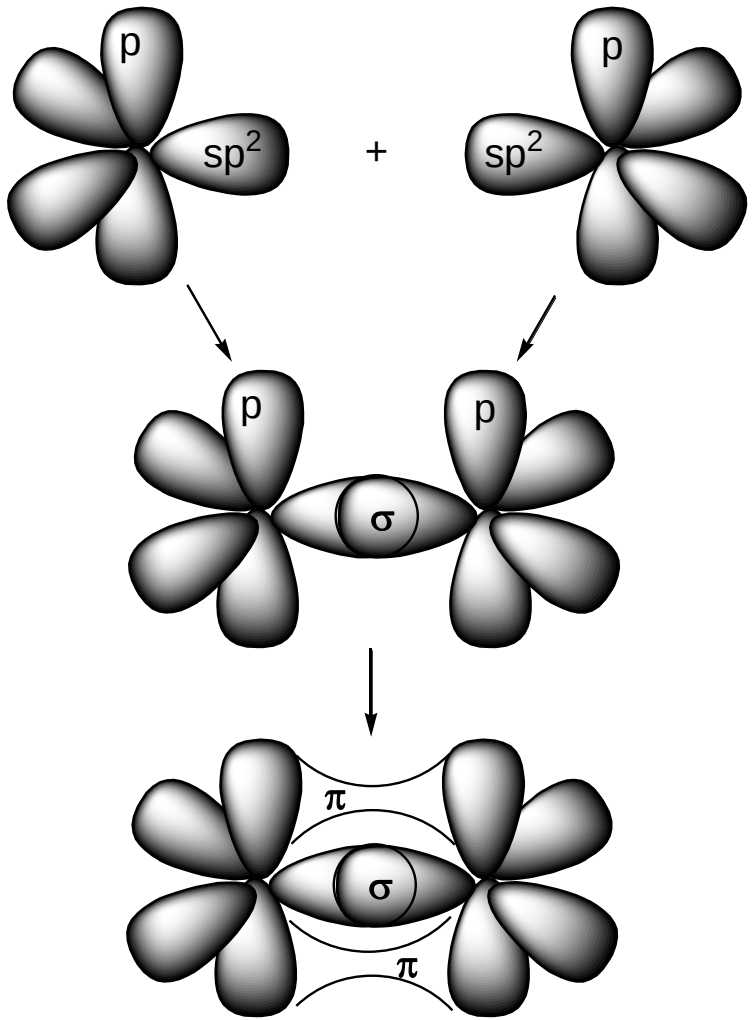


Trigonální uhlík



pohled z boku

pohled ze zhora

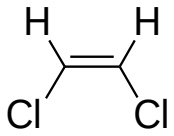


2 sp^2 hybridizované orbitaly

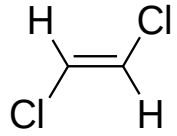
σ vazba se vytvoří dvěma elektrony překryvajících se sp^2 orbitalů

π vazba je tvořena dvěma elektrony z paralelních *p* orbitalů

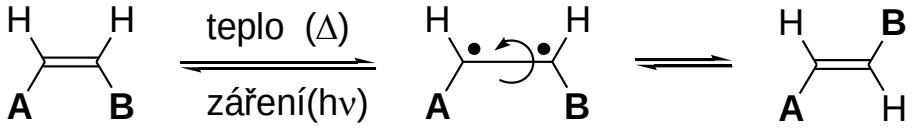
4.5. *Cis* a *trans* izomerie v alkenech

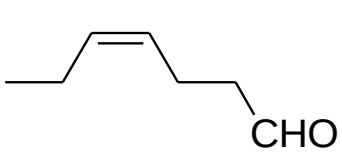


cis-1,2-dichloroethen
t.v. 60°C, t.t. -80°C

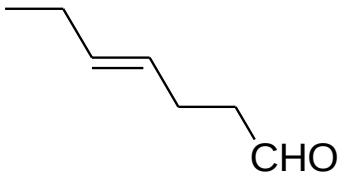


trans-1,2-dichloroethen
t.v. 47°C, t.t. -50°C





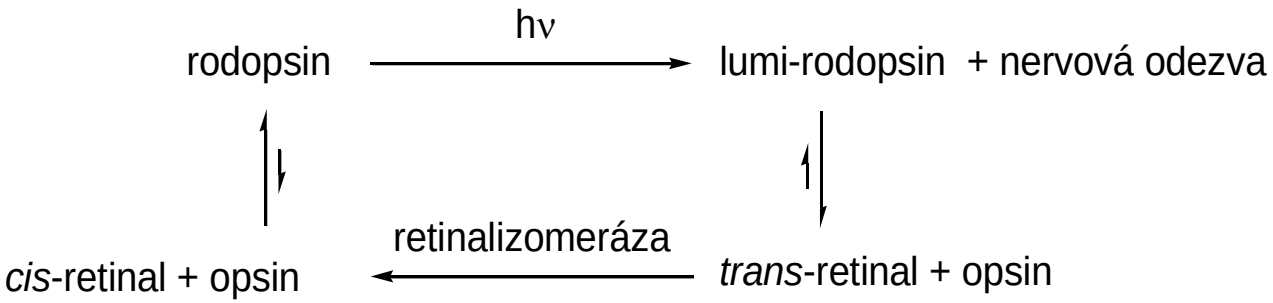
cis-4-heptenal

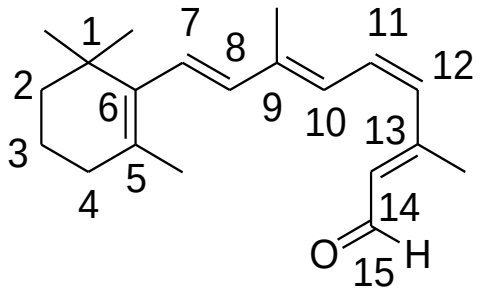


trans-4-heptenal

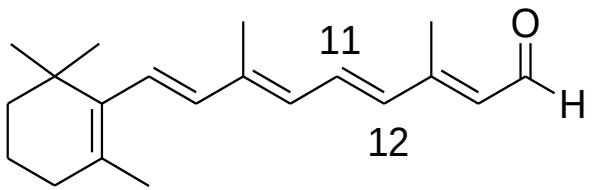
Například *cis*-4-heptenal má krémovou či máslovou vůni, kdežto *trans*-izomer ostrou vůni tmelu.

4.6. Chemie zraku

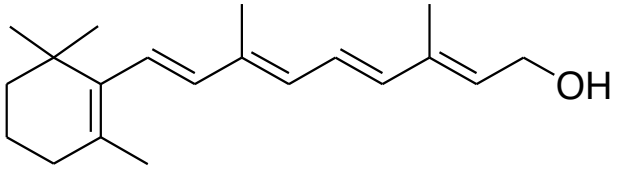




11-*cis*-retinal

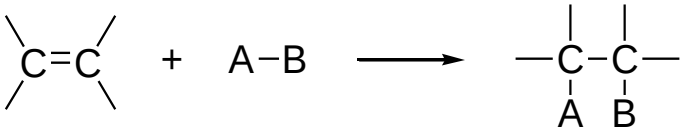


11-*trans*-retinal

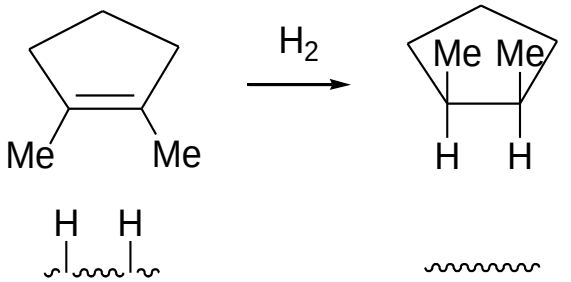


vitamin A

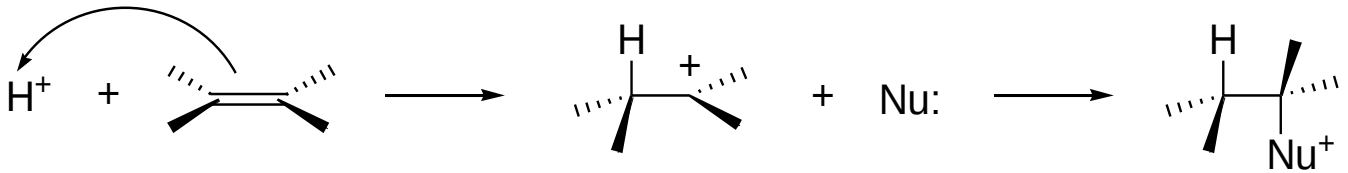
4.7. Adiční a substituční reakce alkenů



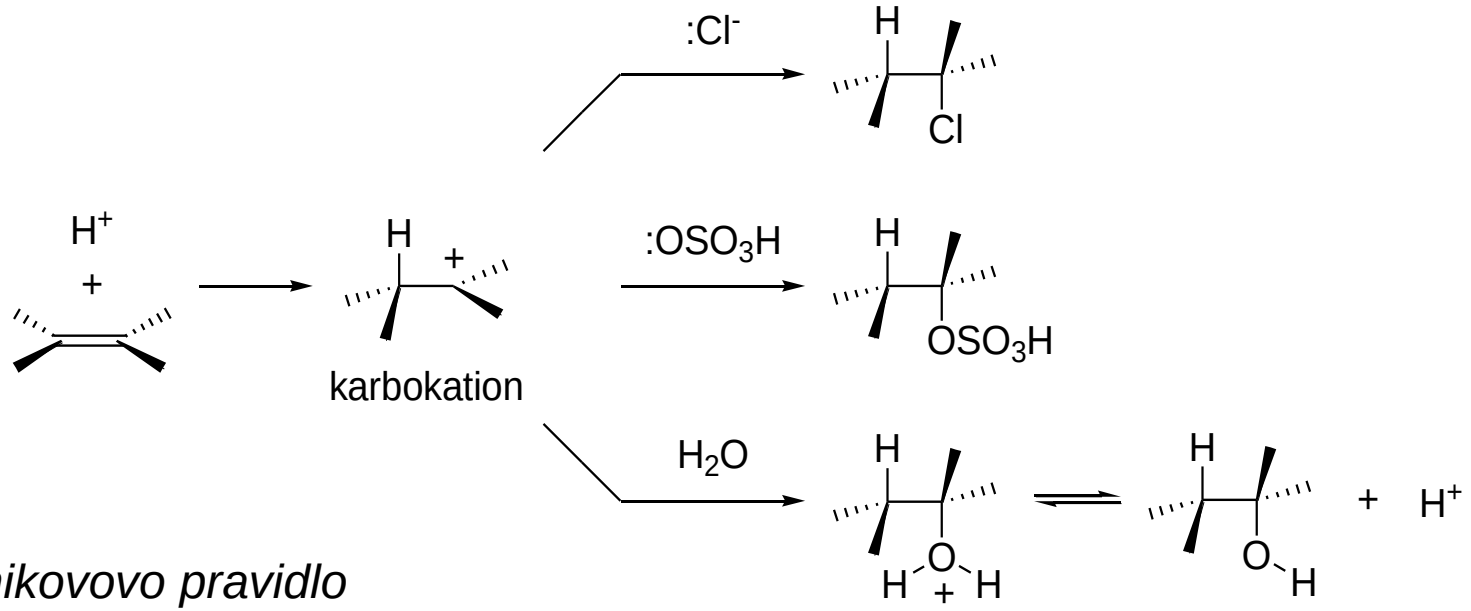
Adice vodíku



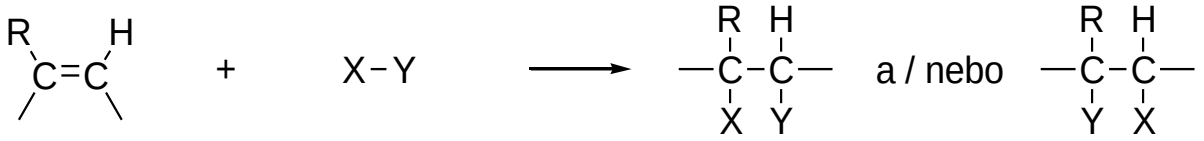
Elektrofilní adice



karbokation



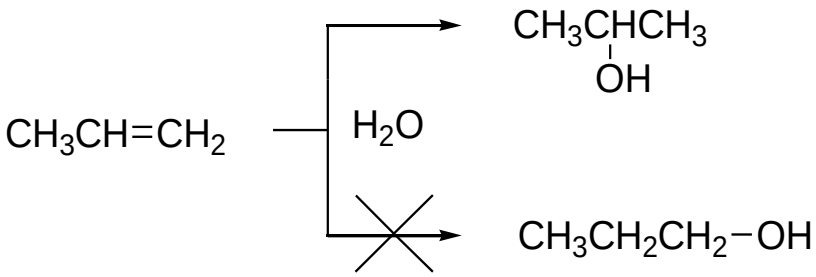
Markovnikovovo pravidlo



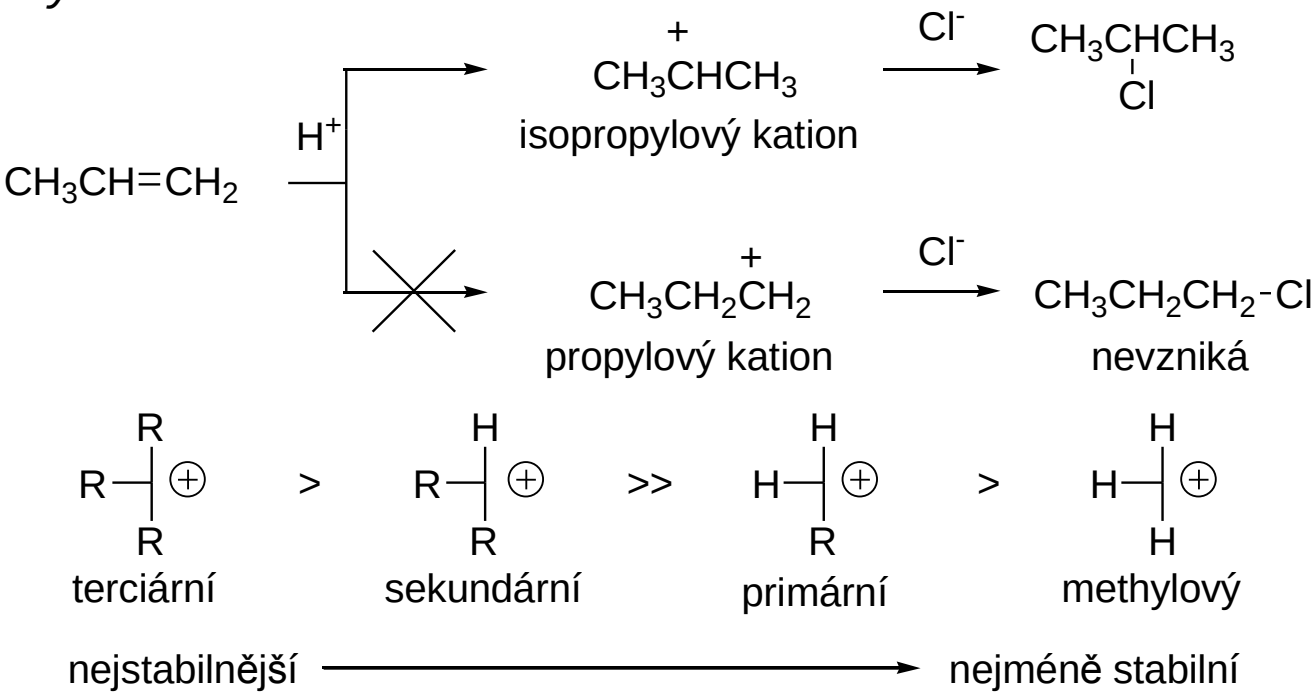
nesymetricky substituovaný alken

nesymetrické činidlo

Symetrická činidla	Nesymetrická činidla
Br-Br	H-Cl
Cl-Cl	H-OH
H-H	H-OSO_3H
$CH_2=CH_2$	$CH_3CH=CH_2$
$CH_3CH=CHCH_3$	$CH_3CH_2CH=CHCH_3$

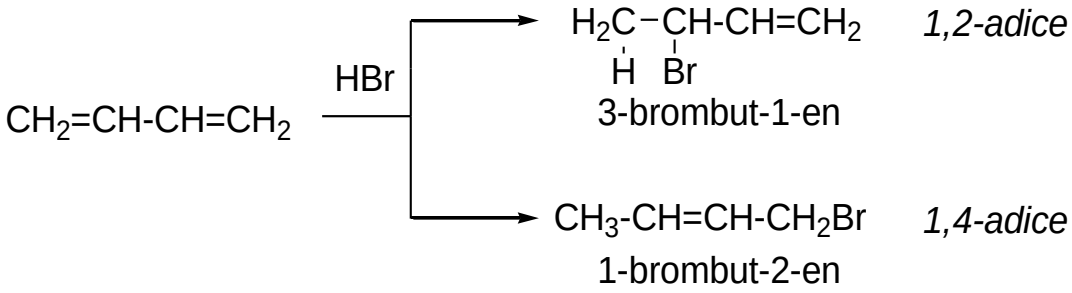


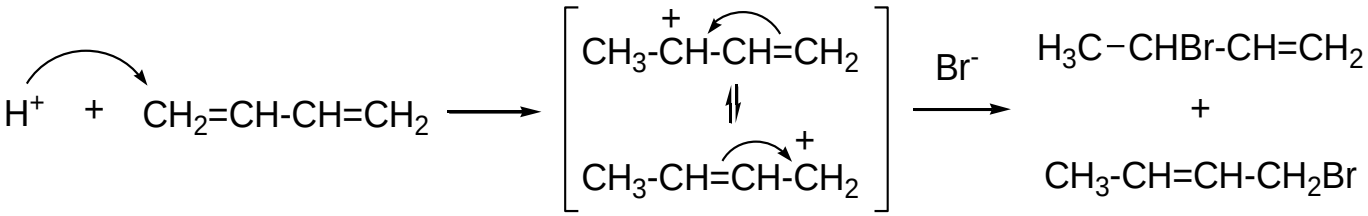
Adice nesymetrického činidla na nesymetrický alken probíhá tak, že elektropozitivní částice činidla se aduje na uhlíkový atom dvojné vazby, na který je navázán větší počet vodíkových atomů.



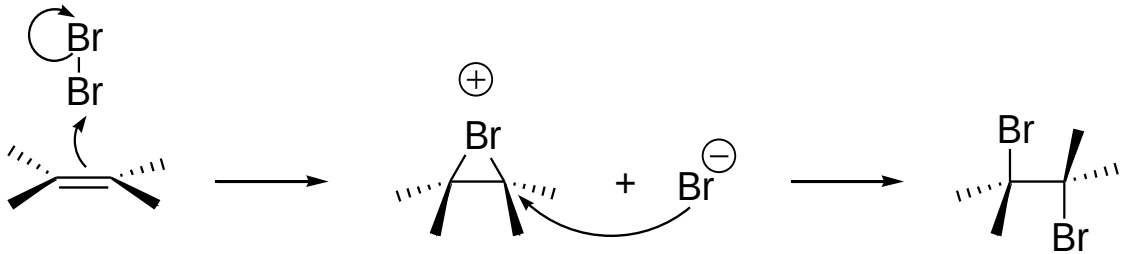
Markovnikovo pravidlo: *adice nesymetrických činidel na nesymetrickou dvojnou vazbu probíhá tak, aby vzniknul co nejstabilnější karbokation jako meziprodukt*

Adice na konjugované dieny



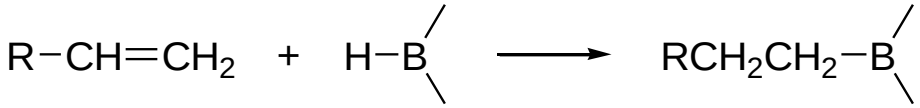


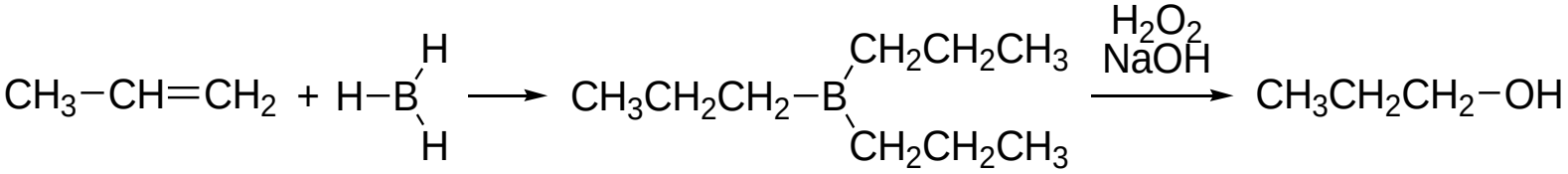
Adice halogenů

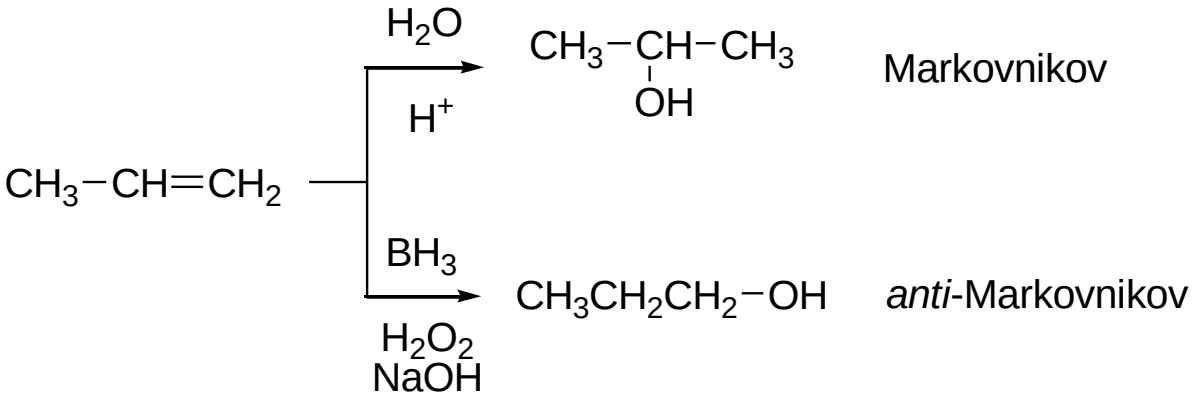


bromoniový ion

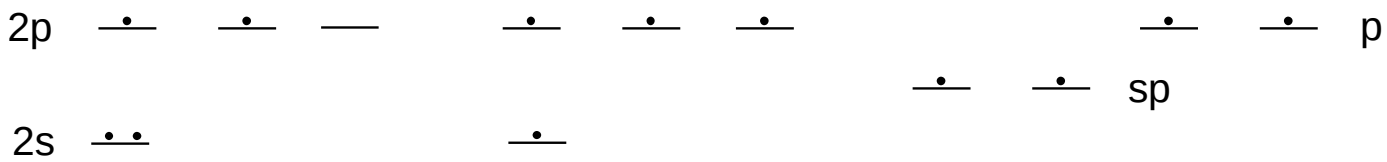
Hydroborace alkenů



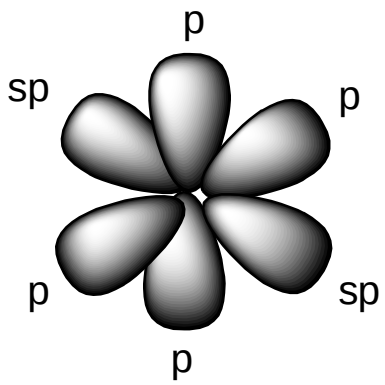


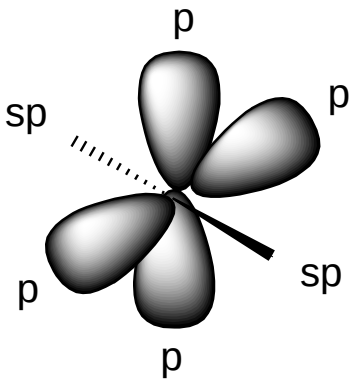


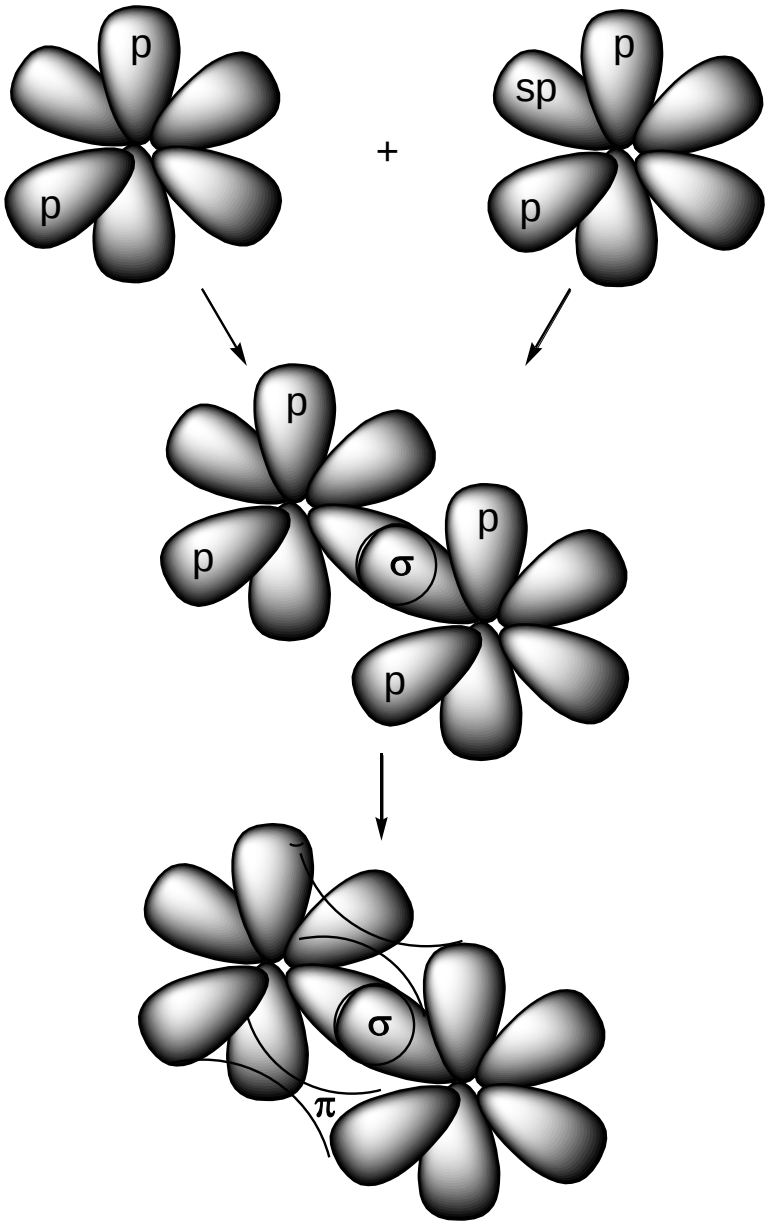
4.8. Alkyny. Vlastnosti trojné vazby



pohled z boku







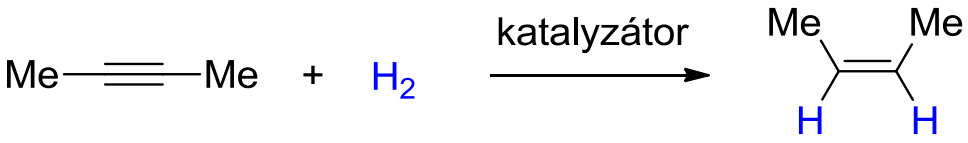
2 *sp* hybridizované orbitaly

σ vazba se vytvoří dvěma elektrony překrývajících se *sp* orbitalů

2π vazby jsou tvořeny dvěna elektrony z překrývajících se paralelních *p* orbitalu

4.9. Adiční reakce alkynů

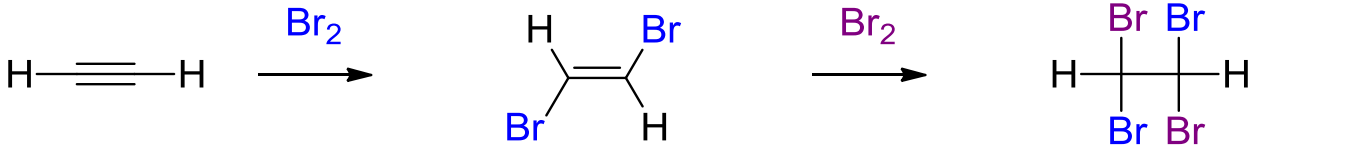
Adice vodíku



2-butyn
t.v. 27 °C

2-buten
t.v. 3.7 °C

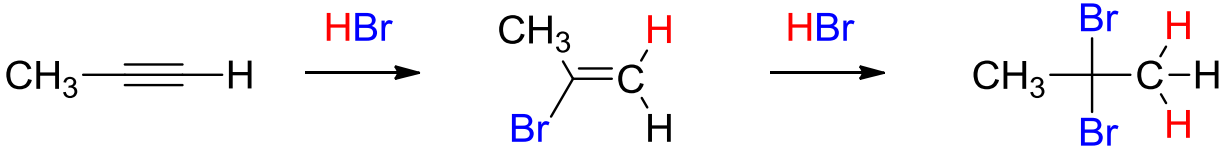
Halogenace



trans-1,2-dibromethen

1,1,2,2-tetrabromethan

Adice halogenovodíku

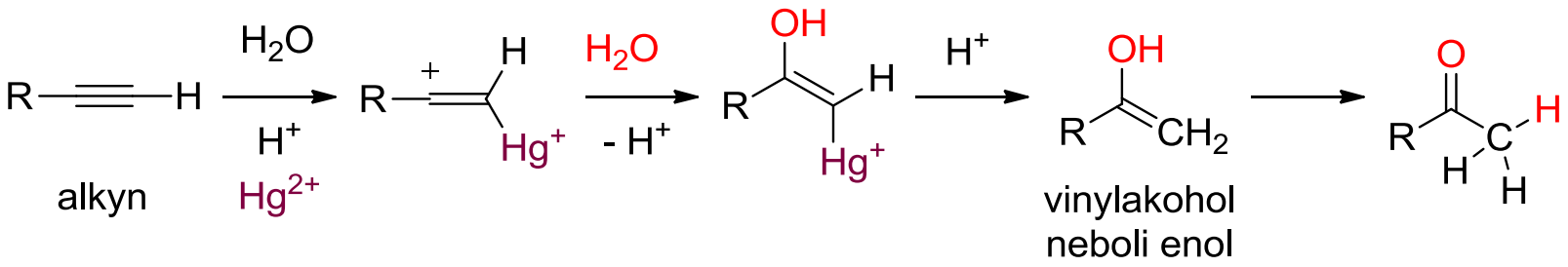


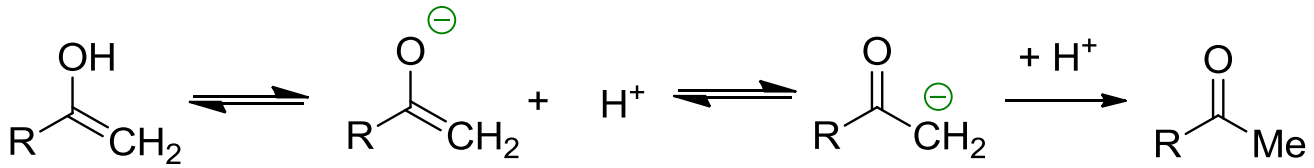
propyn

2-brompropen

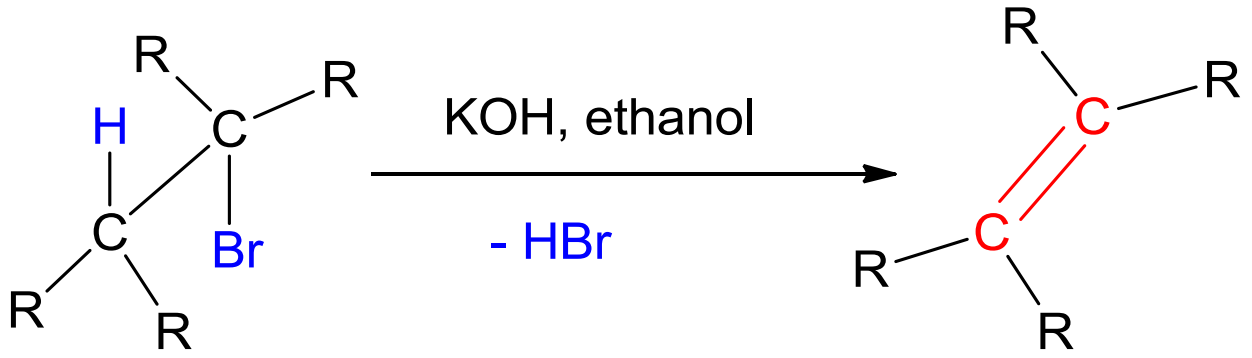
2,2-dibrompropan

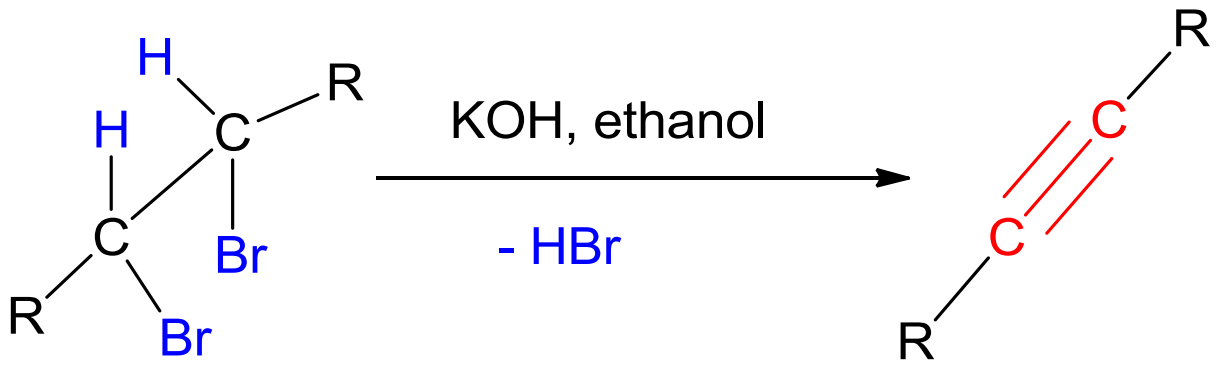
Adice vody


R
H
H_2O
H^+
Hg^{2+}
alkyn
+
Hg^+
H_2O
- H^+
OH
Hg^+
H^+
OH
CH_2
vinylakohol
neboli enol
O
H
C
H
H

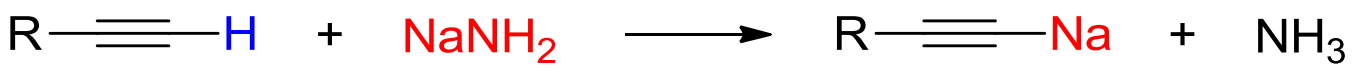

OH
CH_2
O
+
H^+
O
CH_2
+ H^+
O
Me

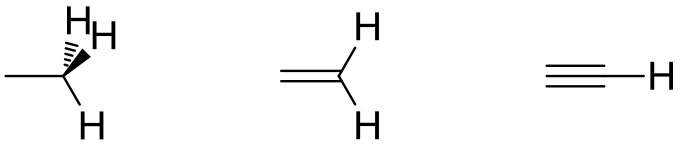
4.10. Eliminace – příprava alkenů a alkynů





4.11. Kyselost alkynů



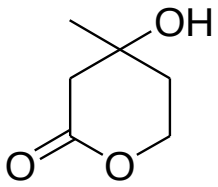


sp^3	sp^2	sp
25% s	33.3% s	50% s
75% p	66.6% p	50% p

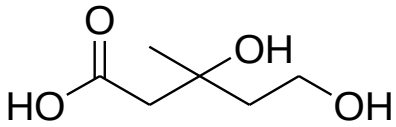
vzrůstající kyselost

4.12. Alkany a alkeny v přírodních látkách

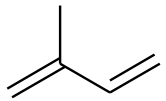
monoterpeny	(2 isoprenové jednotky, 10 atomů uhlíku)
seskviterpeny	(3 isoprenové jednotky, 15 atomů uhlíku)
diterpeny	(4 isoprenové jednotky, 20 atomů uhlíku)
sesterterpeny	(5 isoprenových jednotek, 25 atomů uhlíku),
triterpeny	(6 isoprenových jednotek, 30 atomů uhlíku),
tetraterpeny	(8 isoprenových jednotek, 40 atomů uhlíku), atd.



lakton
kyseliny mevalové

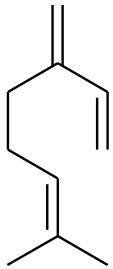


kyselina mevalová

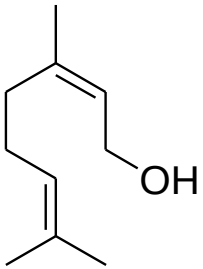


isopren
2-methylbuta-1,3-dien

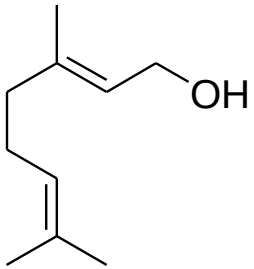
Monoterpeny



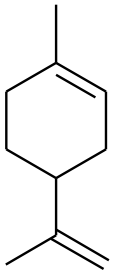
myrcen
silice vavřínová



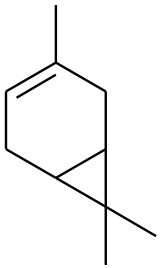
nerol
silice pomerančová



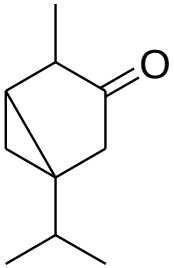
geraniol
silice růžová



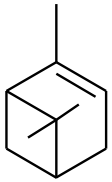
limonen
silice citrusová



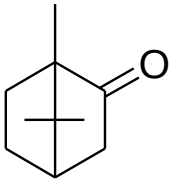
Δ^3-karen
silice terpentýnová



thujon
silice pelyňková

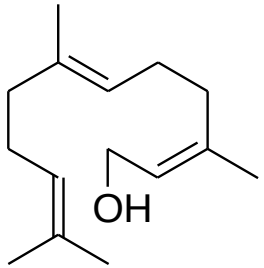


α-pinen
silice terpentýnová

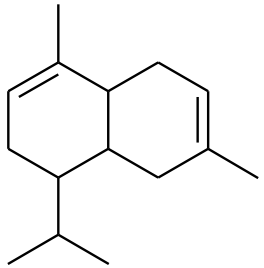


kafr
silice kafrovníková

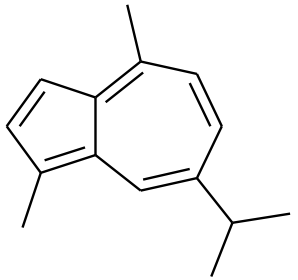
Seskviterpeny



farnesol
v různých silicích

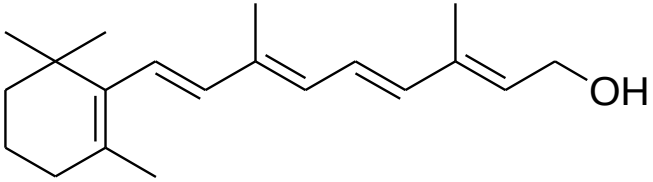


kadinen
silice jalovcová

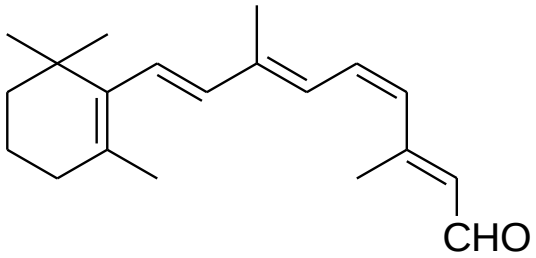


guajazulen
silice heřmánková

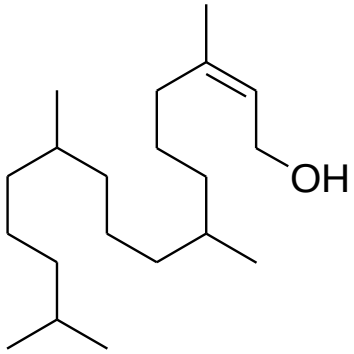
Diterpeny



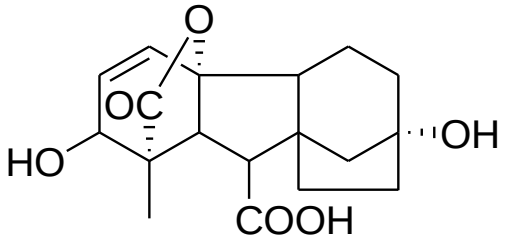
vitamin A



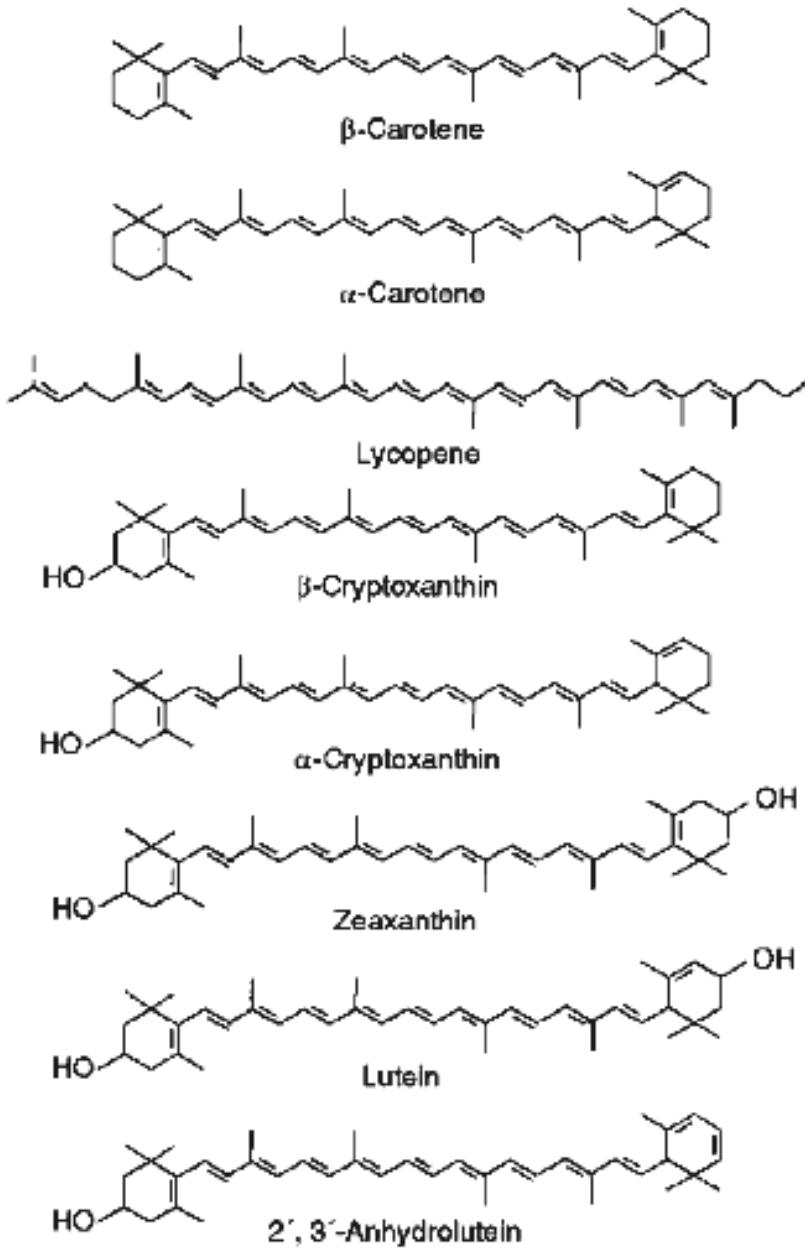
cis-retinal



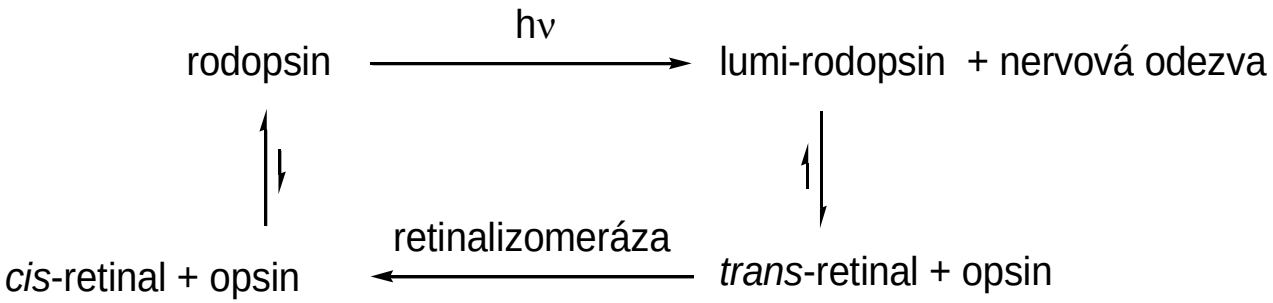
fytol
esterově vázaný v chlorofylu

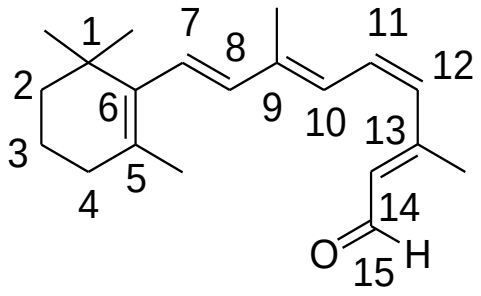


kyselina gibberelová
růstový hormon kvetoucích rostlin

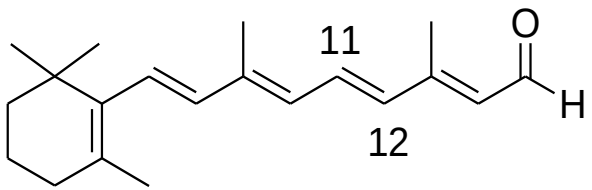

β-Carotene
α-Carotene
Lycopene
HO
β-Cryptoxanthin
HO
α-Cryptoxanthin
OH
HO
Zeaxanthin
OH
HO
Lutein
HO
2′, 3′-Anhydrolutein

4.6. Chemie zraku

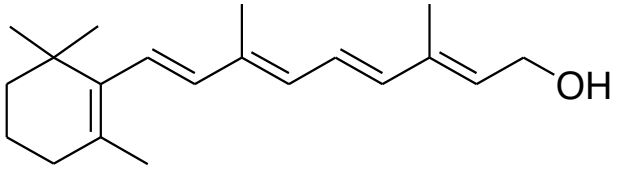




11-*cis*-retinal

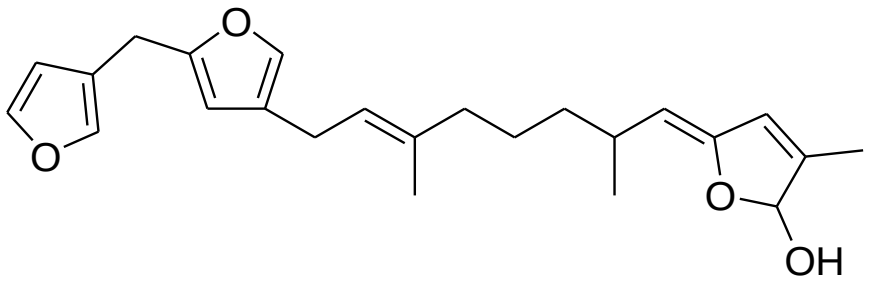


11-*trans*-retinal



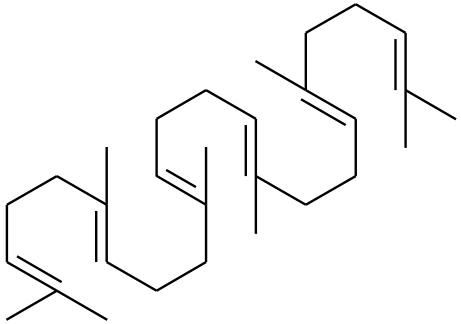
vitamin A

Sesterterpeny

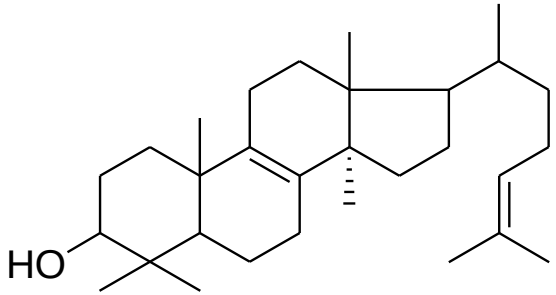


ircin
izolován z mořských živočichů

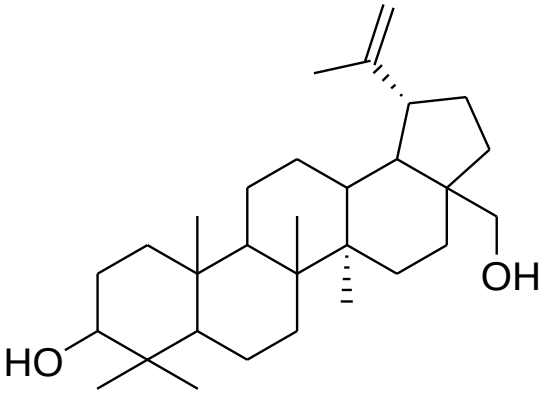
Triterpeny



skvalen
žraločí játra

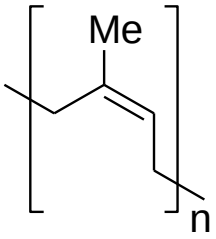


lanosterol
ovčí vlna

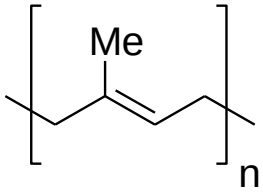


betulin
březová kůra

Polyterpeny



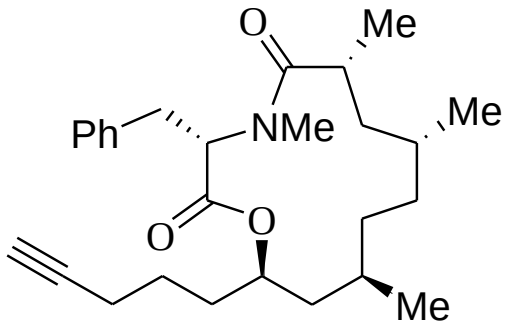
kaučuk (kaučukovník)



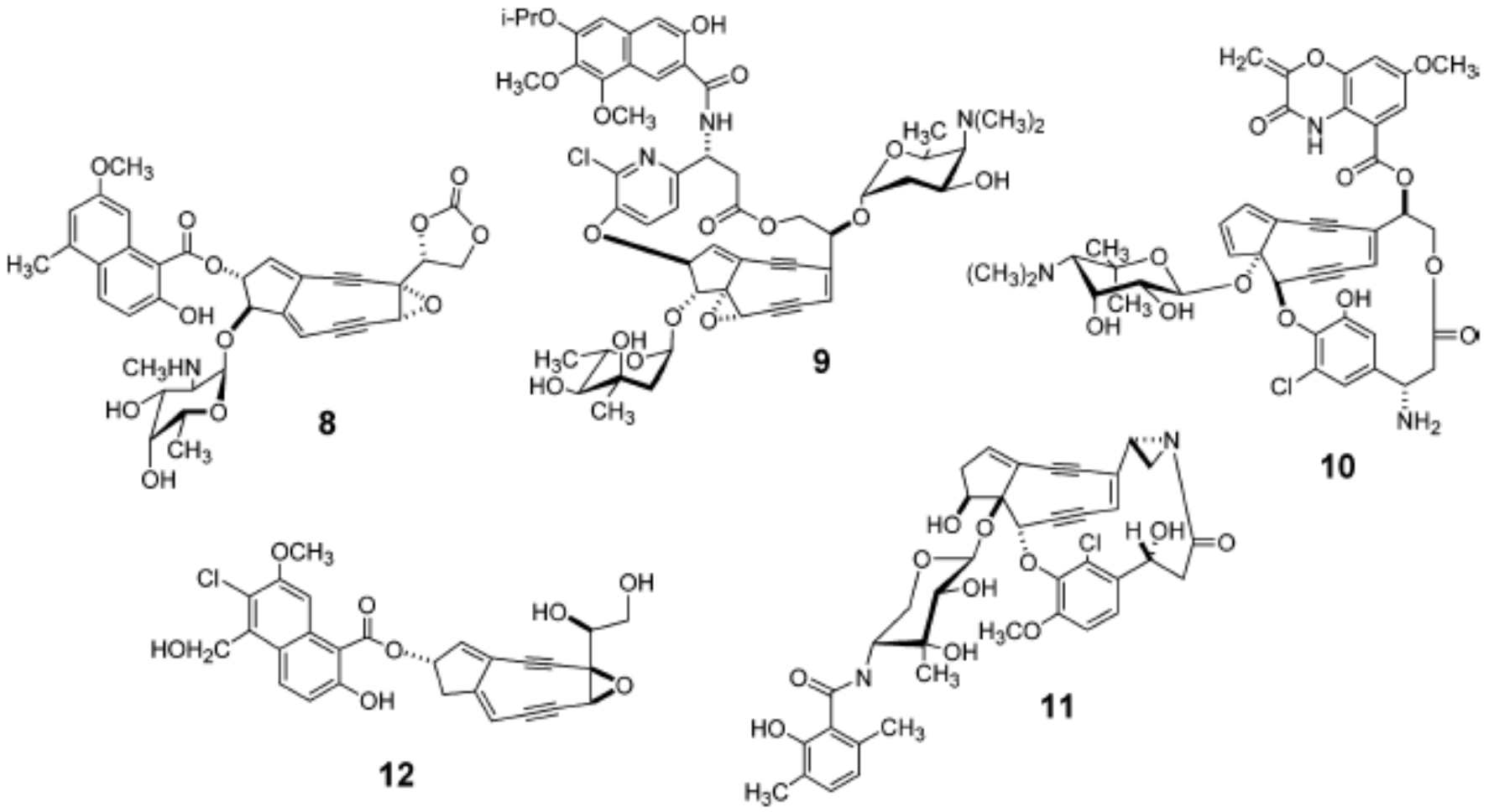
gutaperča (z tropických rostlin)

(-)-spongidepsin

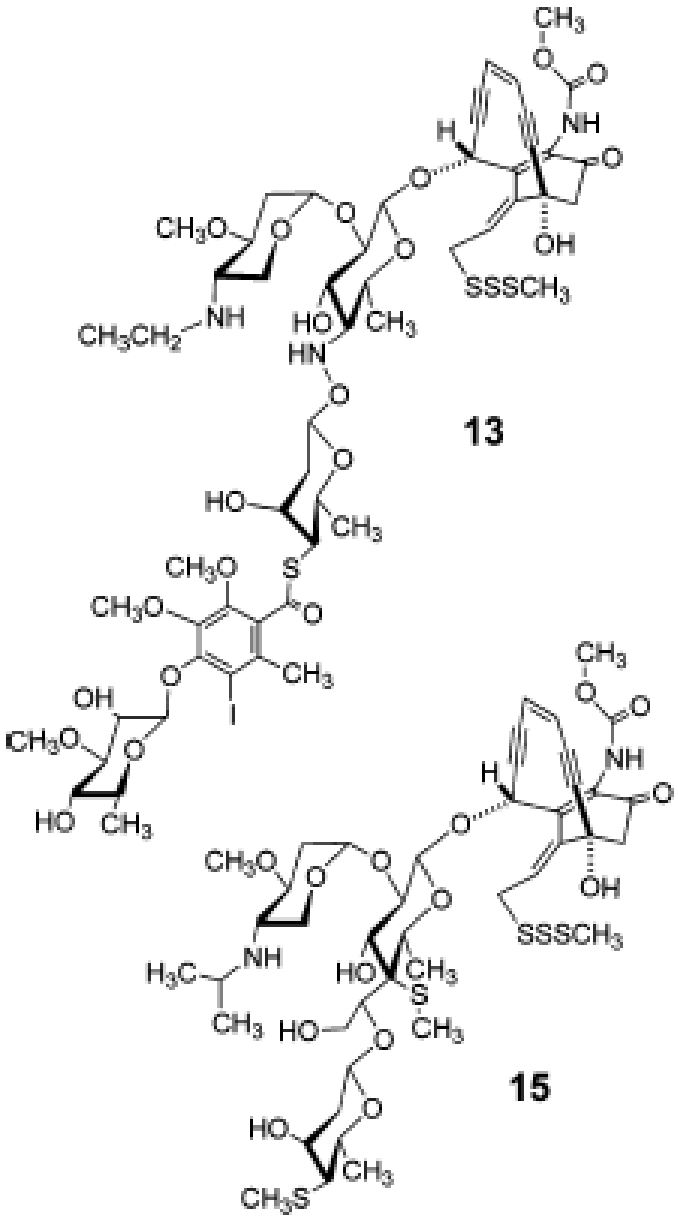
cyclodepsipeptid izolovaný z houby Spongia sp (Vanuatu). Aktivní cytostatikum pro některé linie nádorových buněk.



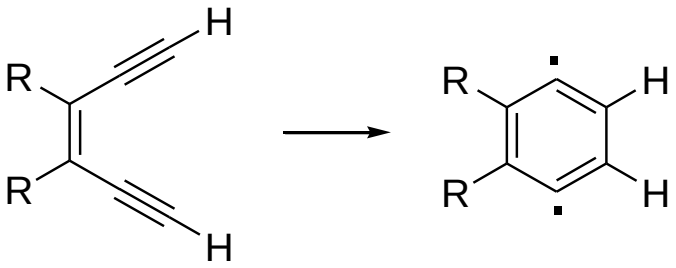
4.12. Endiynová antibiotika



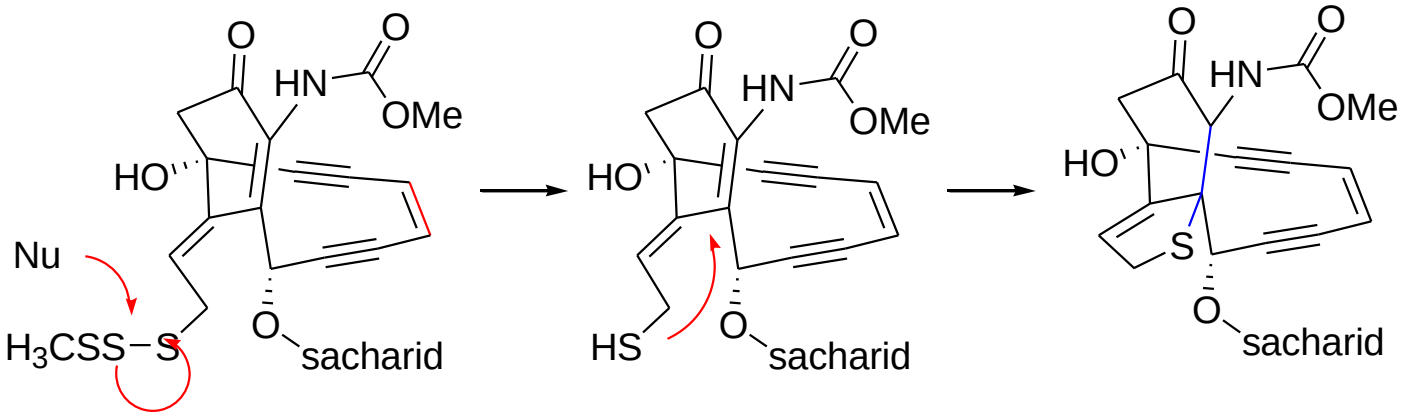
neocarzinostatin (**8**), kedarcidin, (**9**), C-1027 (**10**), maduropeptin (**11**), a N1999A2 (**12**)

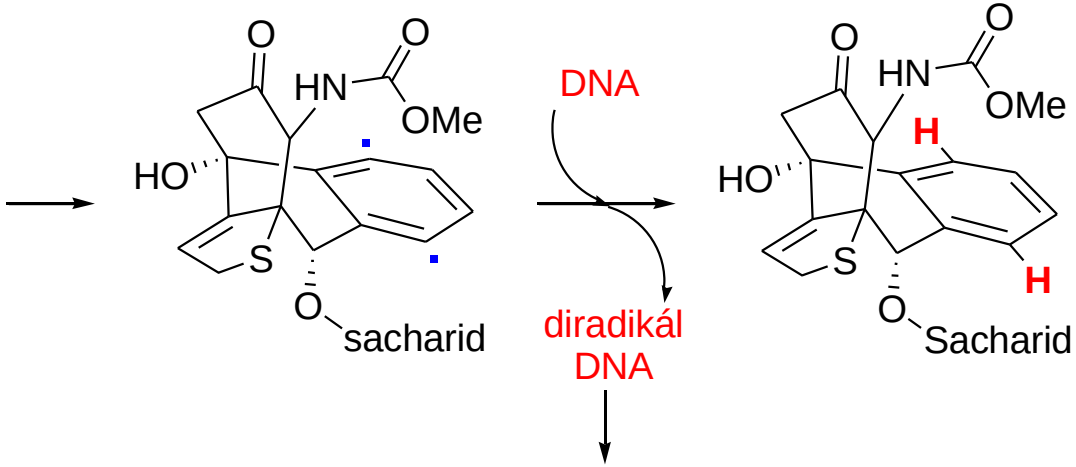


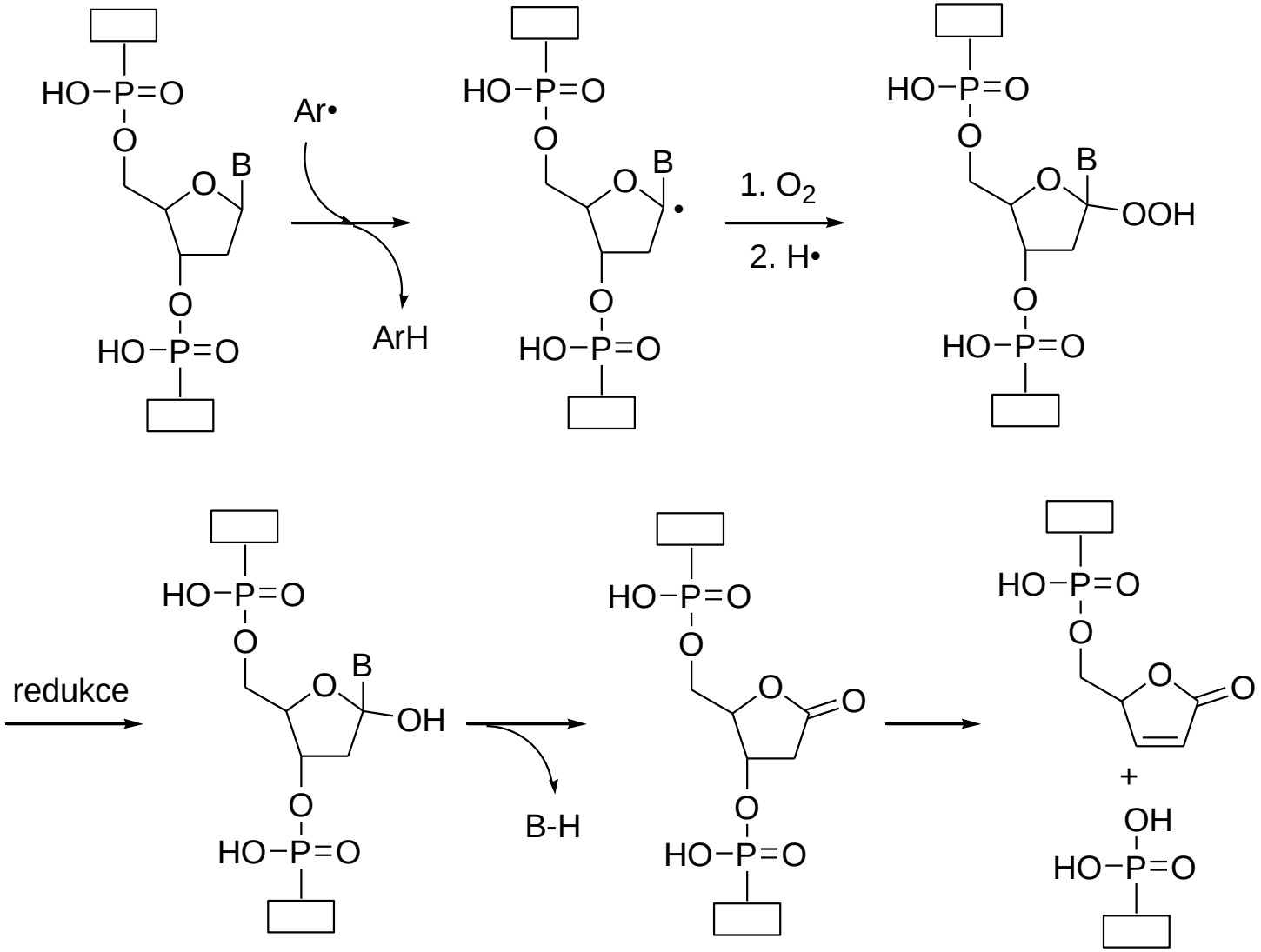
calicheamicin (**13**), esperamicin (**14**), namenamicin (**15**), shishijimicin (**16**), a dynemicin (**17**)



Bergmanův přesmyk






HO−P=O
O
B
O
O
HO−P=O
Ar•
ArH
1. O_2
2. H•
OOH
redukce
OH
B-H
+