

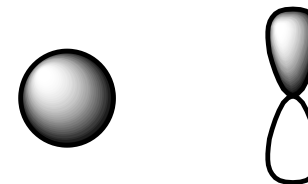
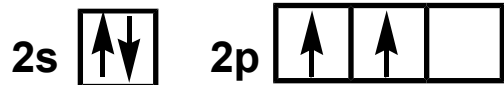
Nenasycené uhlovodíky

ALKENY A DIENY

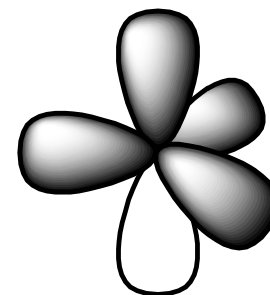
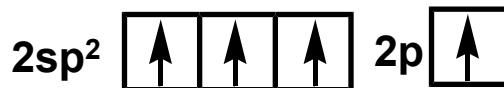
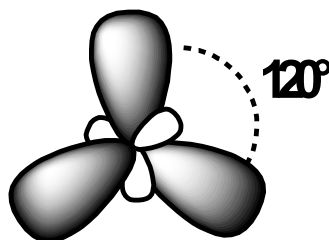
Složené pouze z atomů uhlíku a vodíku, které jsou navzájem spojené jednoduchými vazbami typu sigma (σ) a dvojnými vazbami ($\sigma + \pi$)
Obecný vzorec: C_xH_y . Pro n -alkeny $y = 2x$, pro dieny $y = 2x - 2$.

Elektronová konfigurace uhlíku:

${}_6C: 1s^2, 2s^2p^2$



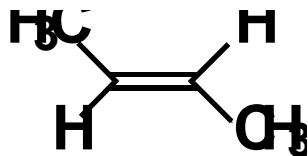
orbital p podílející se na vzniku π vazby nehybridizuje



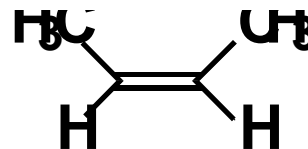
ALKENY

Struktura alkenů – geometrická izomerie

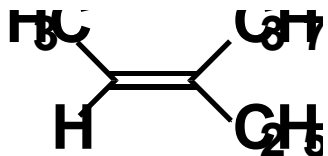
Přítomnost dvojné vazby vyjadřuje zakončení –en (předchází případně násobná částice, např. -dien, -trien), kterou předchází lokant(y).



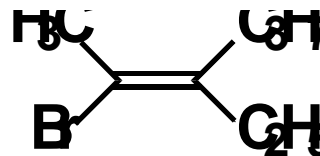
trans-but-2-en
(*E*)-but-2-en



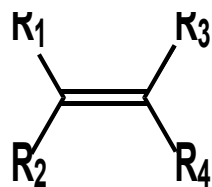
cis-but-2-en
(*Z*)-but-2-en



(*Z*)-3-ethylhex-2-en

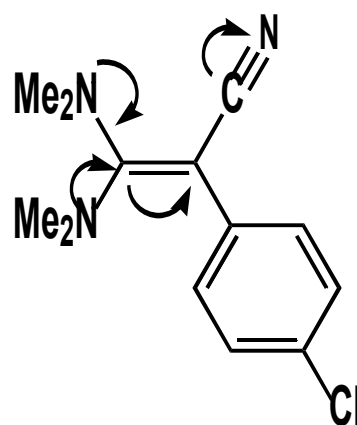


(*E*)-2-brom-3-ethylhex-2-en

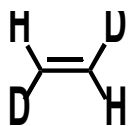


Bariera rotace 250-270 kJ/mol

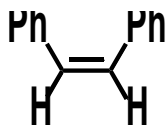
Push-pull snižuje energii bariery



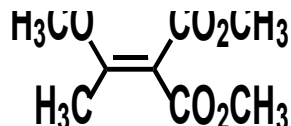
~34 kJ/mol



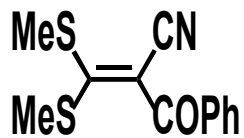
272



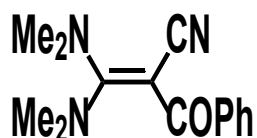
180



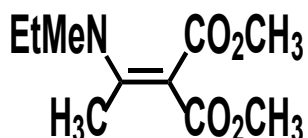
107,6



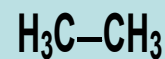
86,2



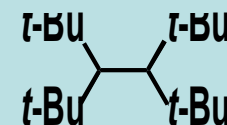
64,0



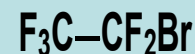
41,9



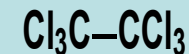
12.3



22.9



26.8



~45

Dipolový moment, teplota varu, index lomu, hustota

Compound		$\mu(\text{D})^b$	bp ($^{\circ}\text{C}$; 760 mm)	n^{20}	$D^{20}(\text{g mL}^{-1})$
CHCl=CHCl	cis	1.84	60.3	1.4486	1.2835
	trans	0	47.4	1.4454	1.2583
CHCl=CHI	cis	1.27 ^{c,d}	116–117	1.5829	2.2080 (15 $^{\circ}\text{C}$)
	trans	0.55 ^c	113–114	1.5715	2.1048 (15 $^{\circ}\text{C}$)
CH ₃ CH=CHCl	cis	1.64 ^e	32.8	1.4060	0.9347
	trans	1.97 ^e	37.4	1.4058	0.935
CH ₃ CCl=CHCl	cis	2.20 ^f	93	1.4549	1.1870 (25 $^{\circ}\text{C}$)
	trans	0.84 ^f	76	1.4498	1.1704 (25 $^{\circ}\text{C}$)
CH ₃ CH=CHCH ₃	cis	0.25 ^e	3.7	1.3931 (–25 $^{\circ}\text{C}$)	0.6213
	trans	0	0.9	1.3848 (–25 $^{\circ}\text{C}$)	0.6044
(CH ₃) ₃ CCH=CHC(CH ₃) ₃	cis	nr ^g	143	1.4266	0.7439
	trans	nr ^g	125.0	1.4115	0.7167
CH ₃ CH=CHCN	cis	4.08 ^e	108	1.4182	0.8244
	trans	4.53 ^e	122	1.4216	0.8239
EtO ₂ CCH=CHCO ₂ Et	cis	2.59 ^h	223	1.4413	1.067
	trans	2.40 ^h	218	1.4411	1.052
Cyclooctene	cis	0.43 ⁱ	74–75 ^j	1.4682 (25 $^{\circ}\text{C}$)	0.8443
	trans	0.82 ⁱ	75 ^k	1.4741 (25 $^{\circ}\text{C}$)	0.8483
Cyclodecene	cis	0.44 ⁱ	194–195 ^l	1.4858	0.8770
	trans	0.15 ⁱ	194 ^l	1.4821	0.8672

^aData from ref. 43, Beilstein, 3rd and 4th supplement, and McClellan⁶³ unless otherwise indicated.

^bIn benzene at 25 $^{\circ}\text{C}$ unless otherwise indicated.

^cData of Errera⁶⁴ as corrected (see footnote *d*).

^dReference 65.

^eIn the gas phase.⁶⁶

^fAt 30 $^{\circ}\text{C}$.

^gNot reported.

^hIn carbon tetrachloride.

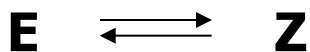
ⁱIn heptane.

^jAt 84 mm.

^kAt 78 mm.

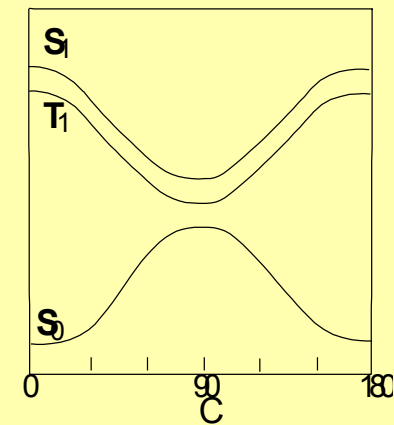
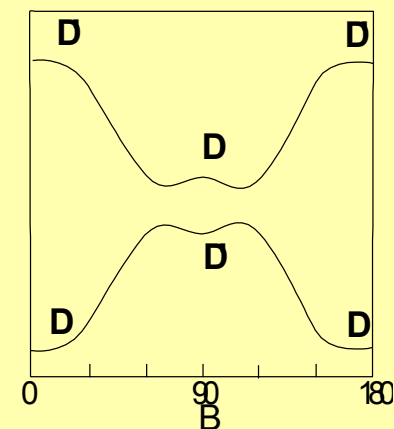
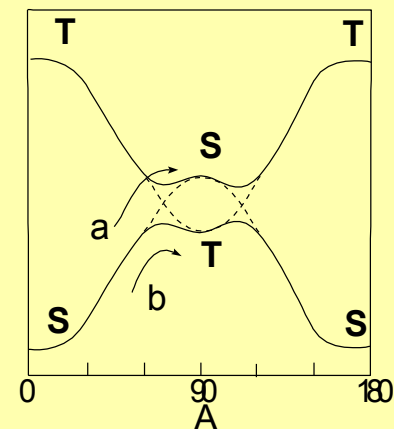
^lAt 740 mm.

Vzájemné přeměny izomerů



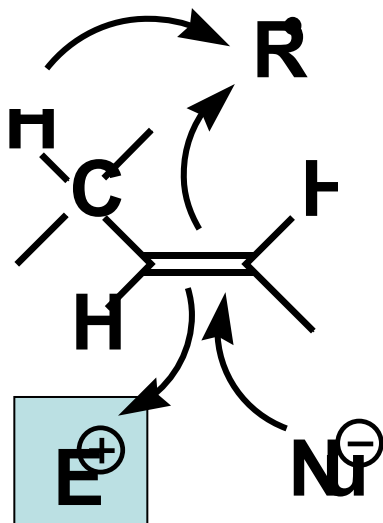
$$\Delta G^0 = -RT \ln K$$

- Teplota
- Katalýza (radikály, halogeny, Si, Sn, O₂, kyselá katalýza)
- Push-pull systémy
- Adičně-elimináčn  mechanismus
- Fotochemick  izomerace



ALKENY

Chemická reaktivita:



π – vazba zvyšuje reaktivitu nenasycených uhlovodíků. Snadný je útok elektrofilem, ale lze atakovat také radikálově i nukleofilně.

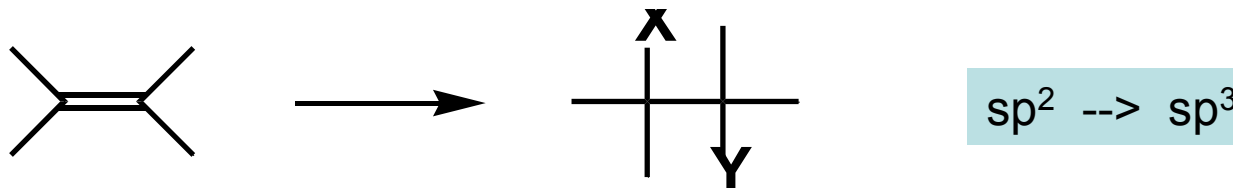
σ – vazby reagují obdobně jako v alkanech radikálovou substitucí.

Typy chemických reakcí:

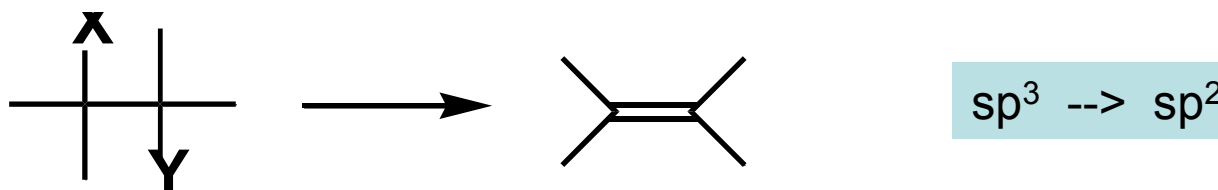
Substituce (S): náhrada jednoho substituentu druhým (např. H za Cl), hybridizace reakčního centra se nemění.



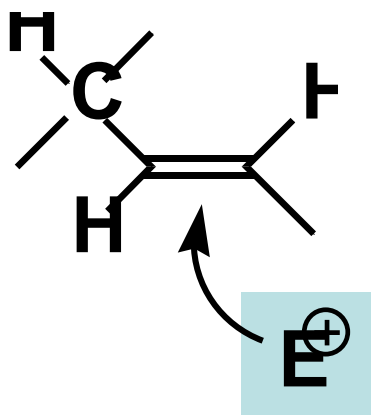
Adice (A): vznik nových vazeb mezi substrátem a reagentem na úkor násobných vazeb substrátu. Zvyšuje se hybridizace reakčního centra.



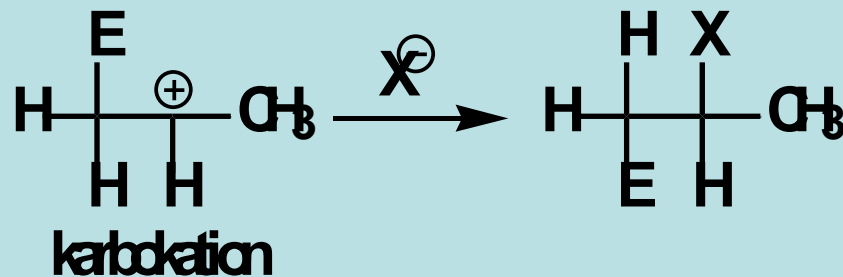
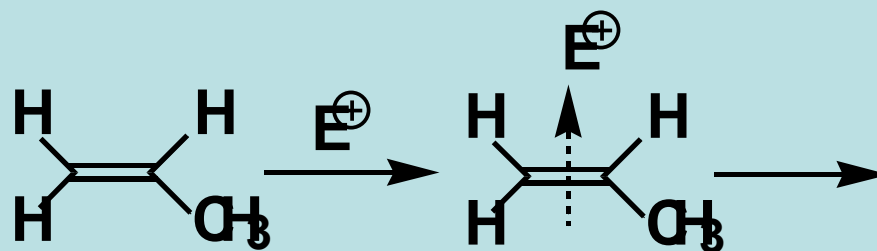
Eliminace (E): odstoupení částí molekuly substrátu za vzniku násobných vazeb, snižování hybridizace reakčního centra.



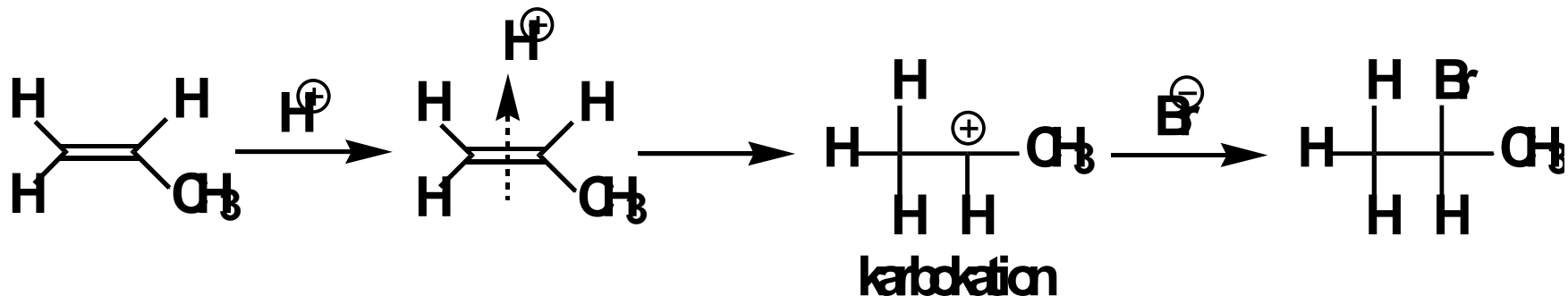
ALKENY



Adice elektrofilní (A_E)

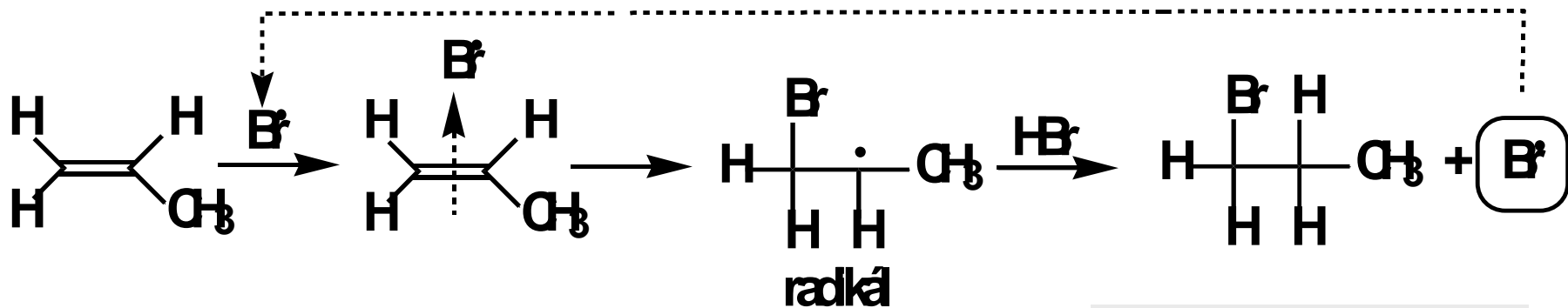


Adice elektrofilní (A_E)



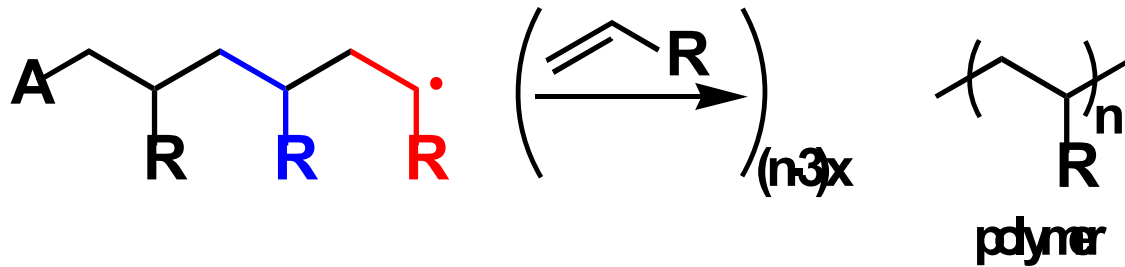
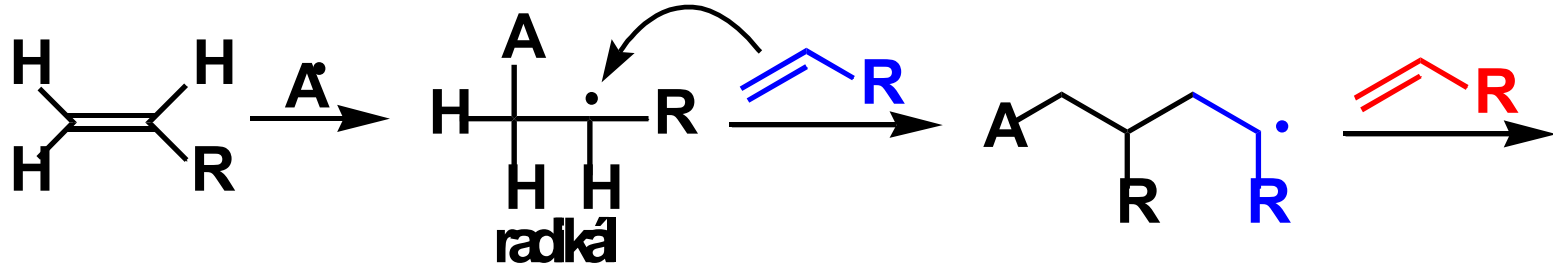
Markovnikovo pravidlo: Elektrofilní část činidla se aduje na ten uhlík dvojné vazby, který nese větší počet vodíků.
(vysvětlení: reakce preferuje vznik stabilnějšího karbokationtu).

Adice radikálová (A_R)



Antimarkovnikovský produkt
(přes stabilnější radikál)

Polymerace olefinů (alkenů)

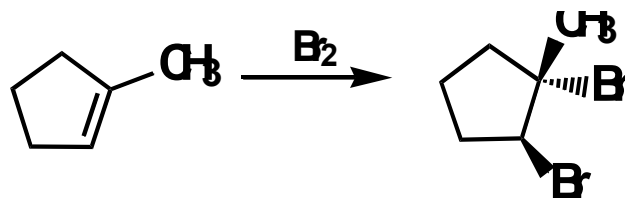


R	Monomer	Polymer
H	ethylen	polyethylen
CH ₃	propylen	polypropylen
Ph	styren	polystyren
Cl	vinylchlorid	polyvinylchlorid (PVC)
COOR	ester k. akrylové	polyakrylát
CN	akrylonitril	polyakrylonitril
OCOCH ₃	vinylacetát	polyvinylacetát

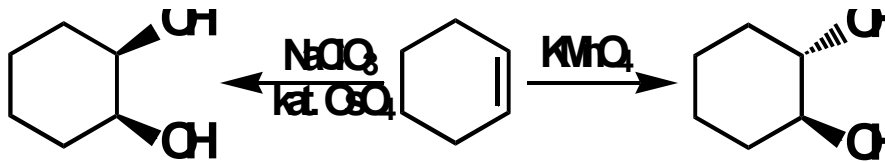
Reakce alkenů

(halogenace, hydrogenace, hydroxylace, epoxidace, ozonizace, allylová substituce)

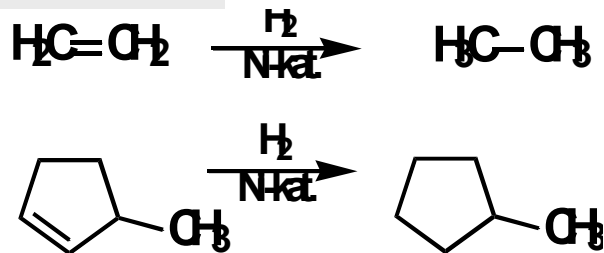
Halogenace:



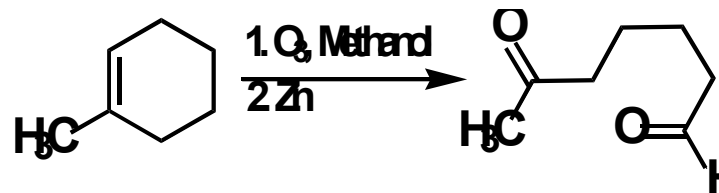
Hydroxylace



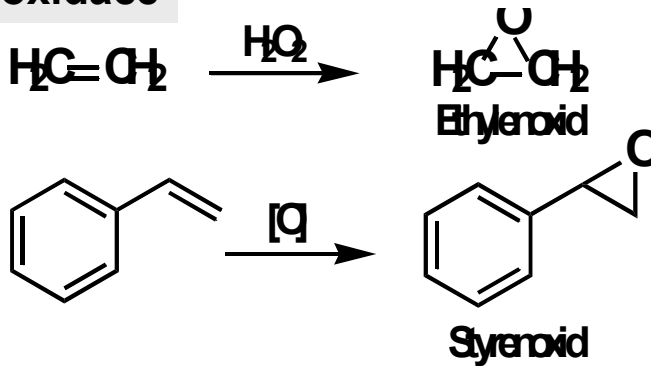
Hydrogenace:



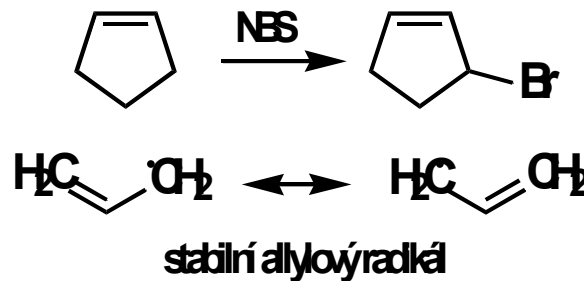
Ozonizace



Epoxidace

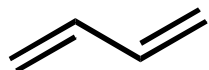


Allylová substituce



DIENY

(konjugované, kumulované, izolované)



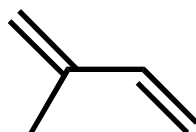
Buta-1,3-dien



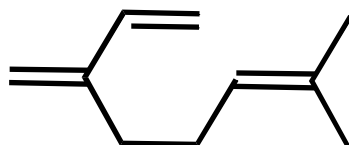
Cyklopentadien



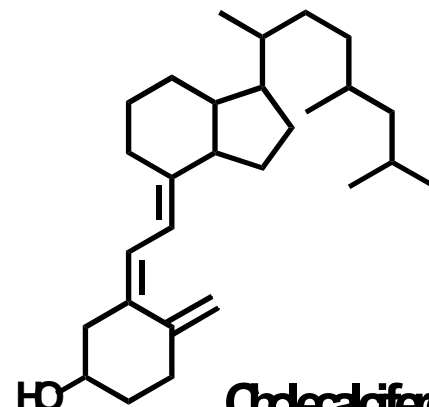
Allen



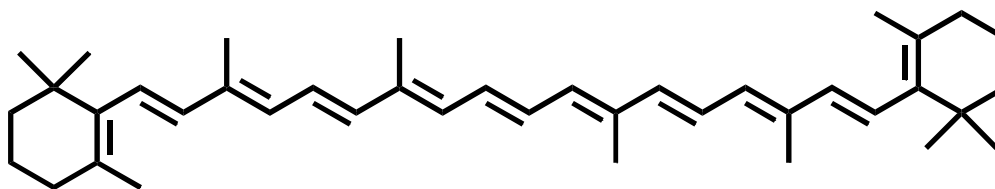
Isopren



Myrcen



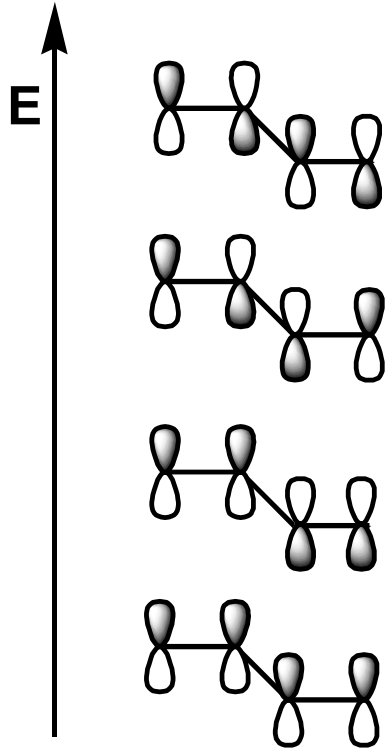
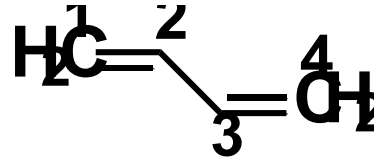
Cholecalciferol



β-Karoten

KONJUGOVANÉ DIENY

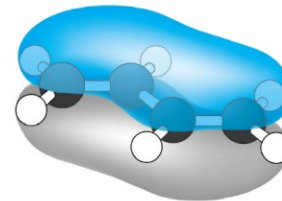
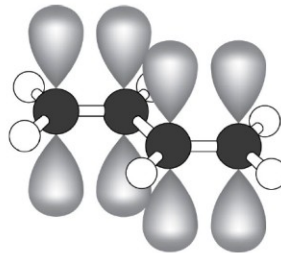
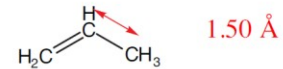
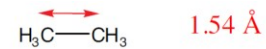
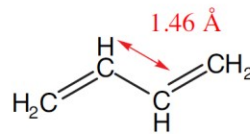
Buta-1,3-dien



$$D_{\text{C1-C2}} = D_{\text{C1-C2}} = 134 \text{ pm}$$

$$D_{\text{C2-C3}} = 148 \text{ pm}$$

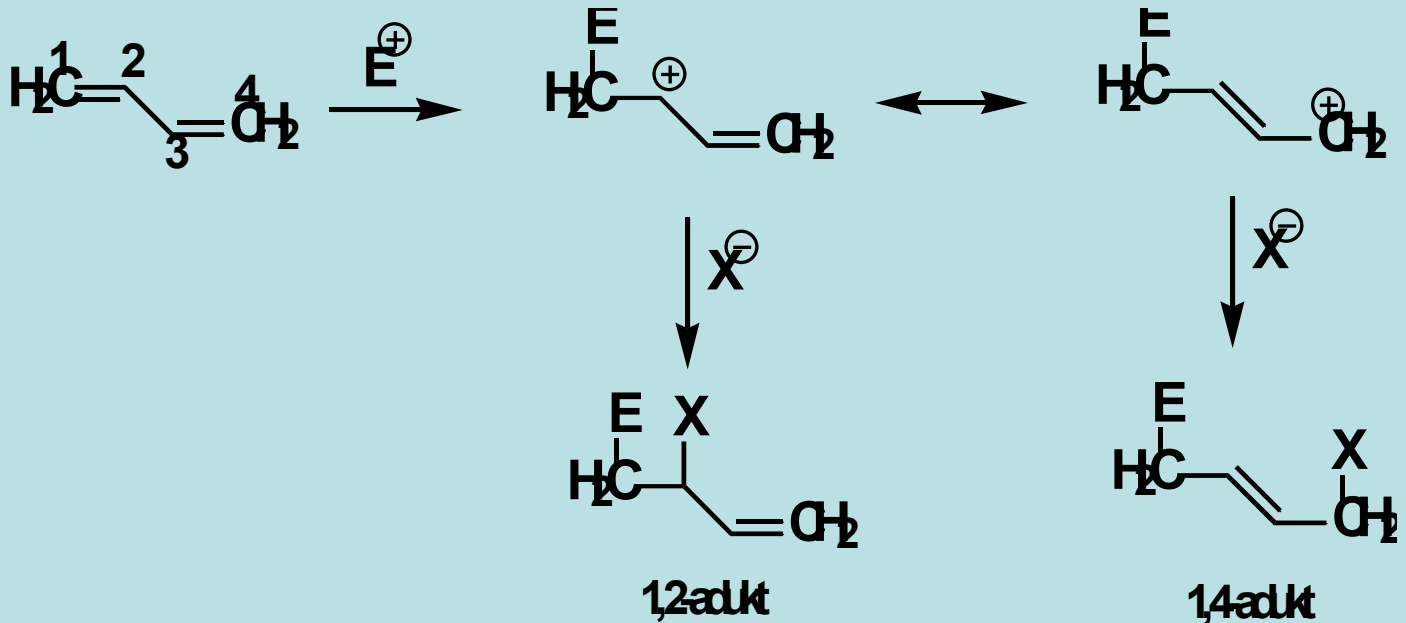
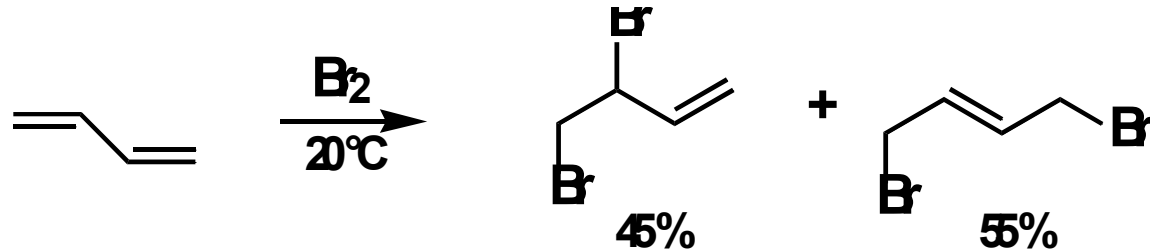
Standardní C-C vazba 154 pm



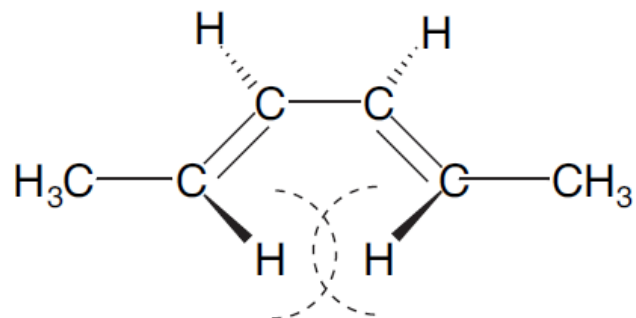
KONJUGOVANÉ DIENY

Reaktivita

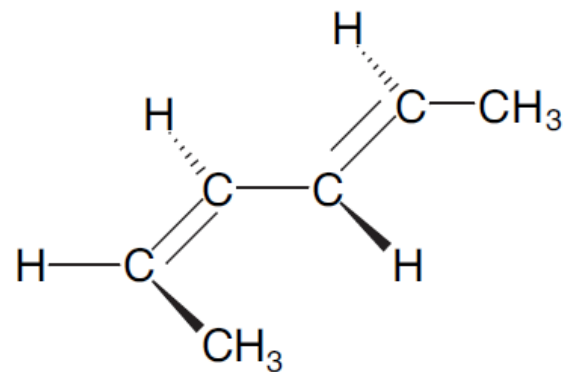
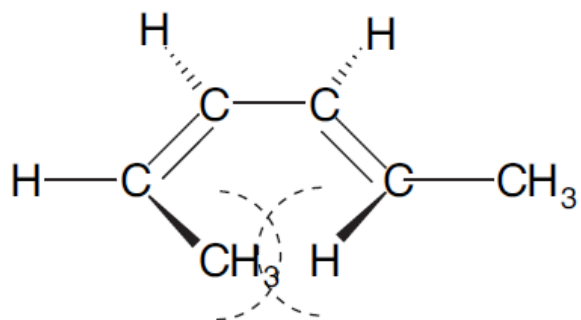
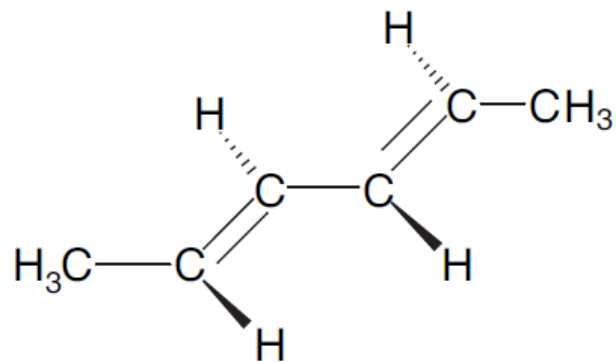
1,2- vs. 1,4-adice:



s-cis



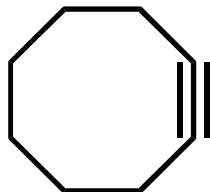
s-trans



ALKYNY



acetylen
(ethyn)

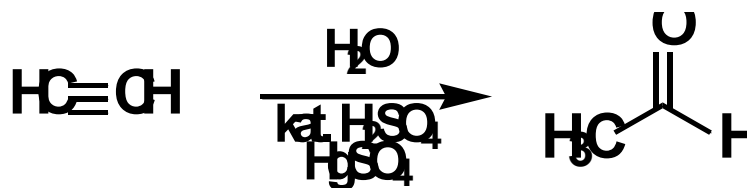


cyklooktyn

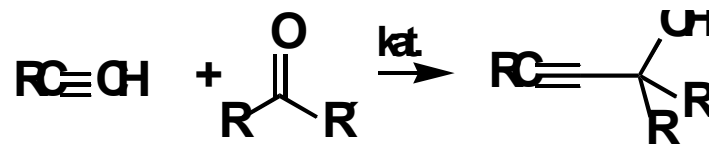
Příprava acetylenu



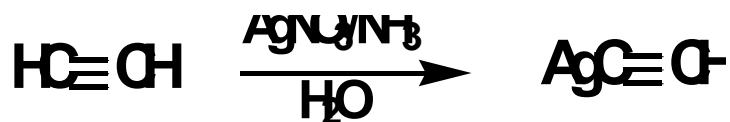
Adice vody (Kučerovova reakce)



„Kyselý“ charakter koncových acetylenů



Acetylidy



$\text{pK}_a \sim 25$