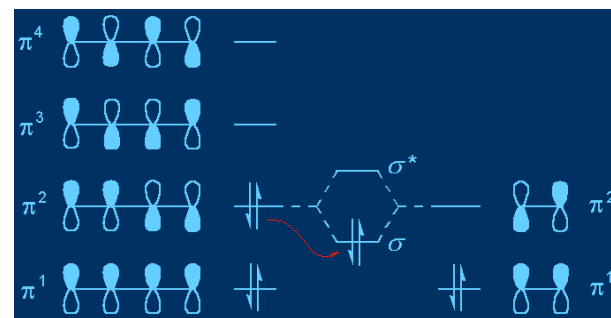
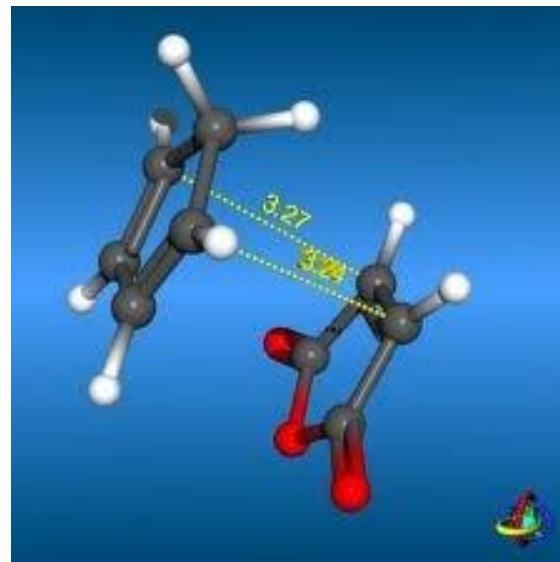
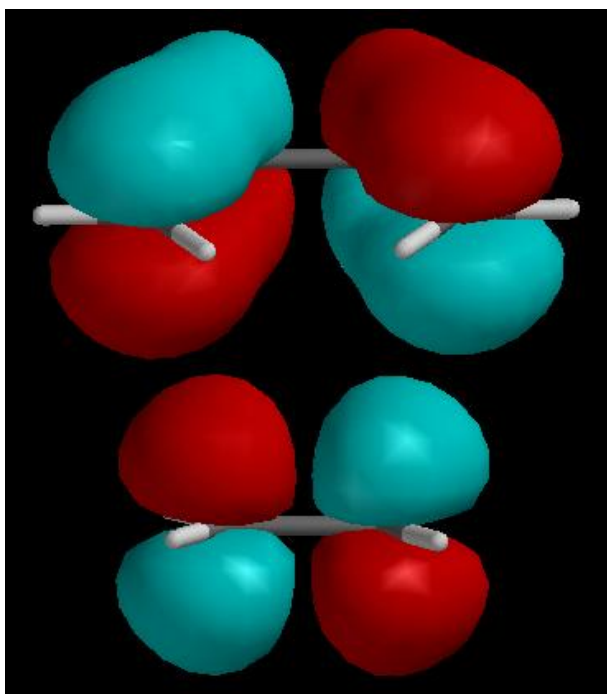
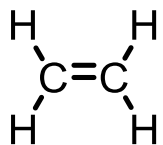


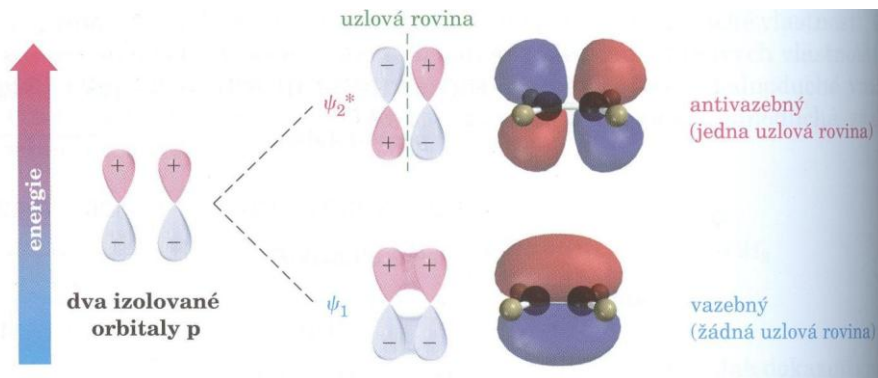
Pericyklické reakce a přesmyky



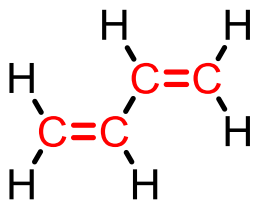
Konjugované π -systémy a delokalizace elektronů



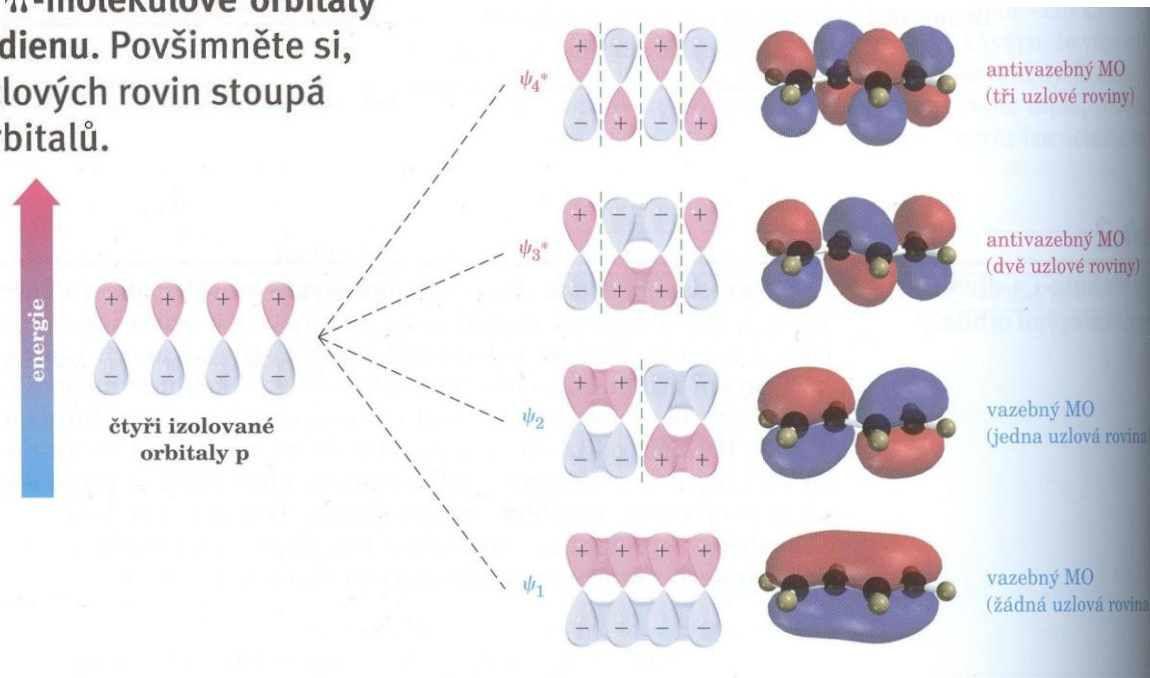
Ethen - izolovaná dvojná vazba



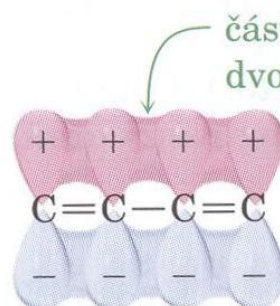
Ctyři π -molekulové orbitály v buta-1,3-dienu. Povšimněte si, že počet uzlových rovin stoupá s energií orbitalů.



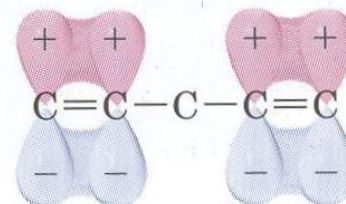
Butadien - konjugované dvojně vazby



Konjugované π -systémy a delokalizace elektronů



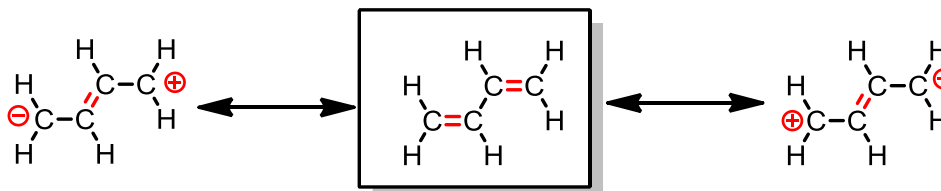
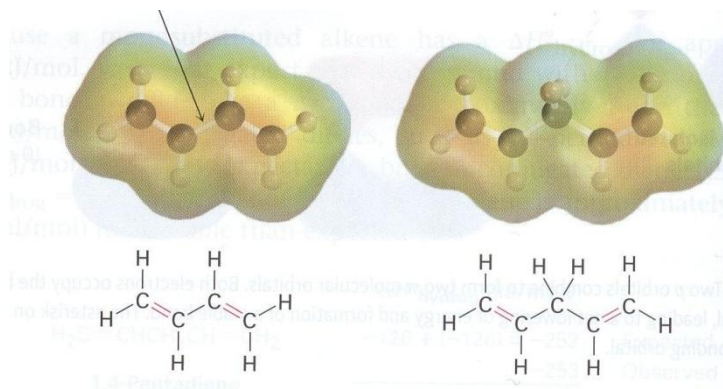
buta-1,3-dien
konjugovaný dien

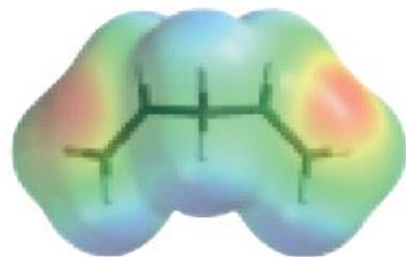
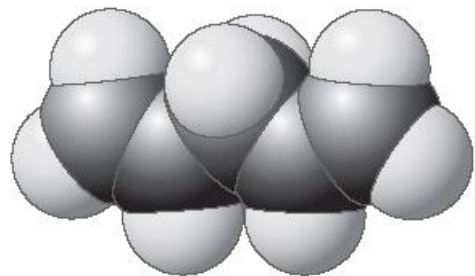
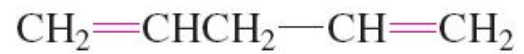


penta-1,4 dien
nekonjugovaný dien

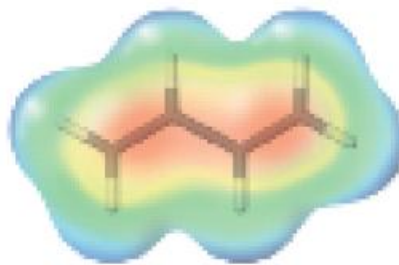
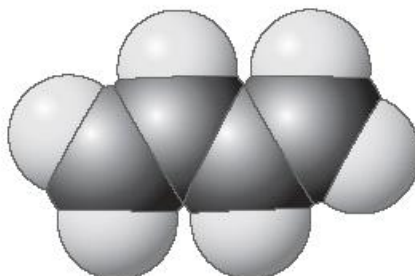
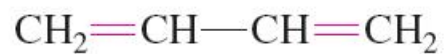
Dochází k částečné delokalizaci elektronů v rámci celého konjugovaného π -systému

částečný charakter dvojné vazby

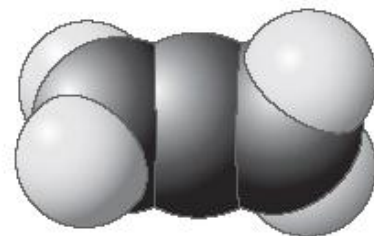




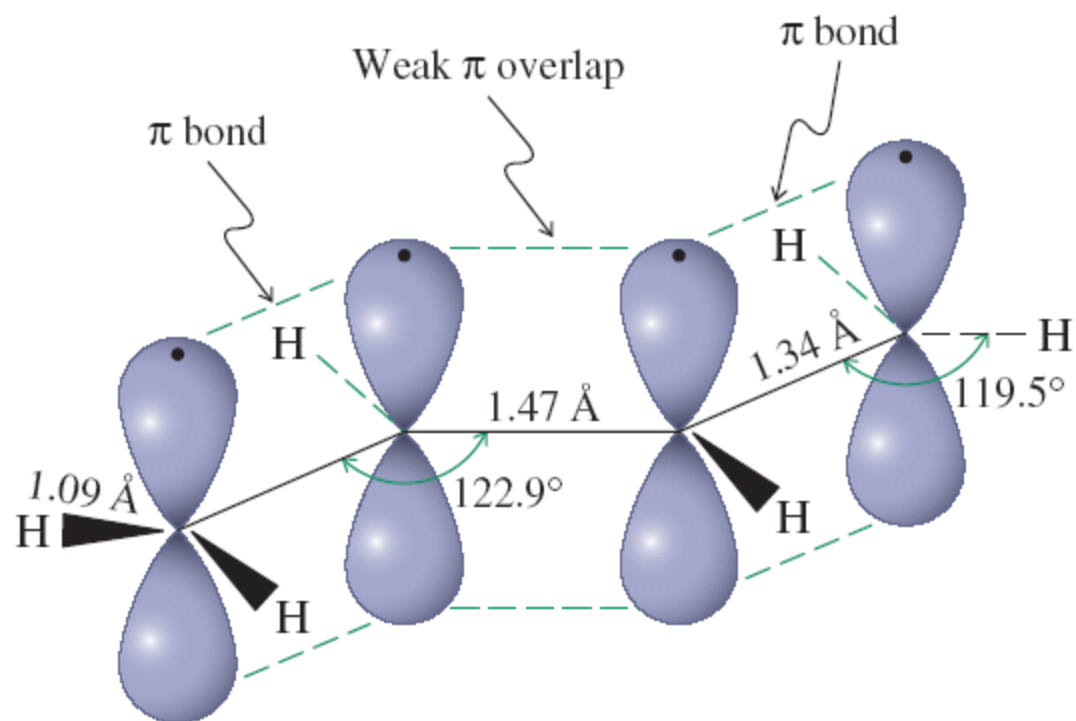
1,4-Pentadiene
(Nonconjugated)

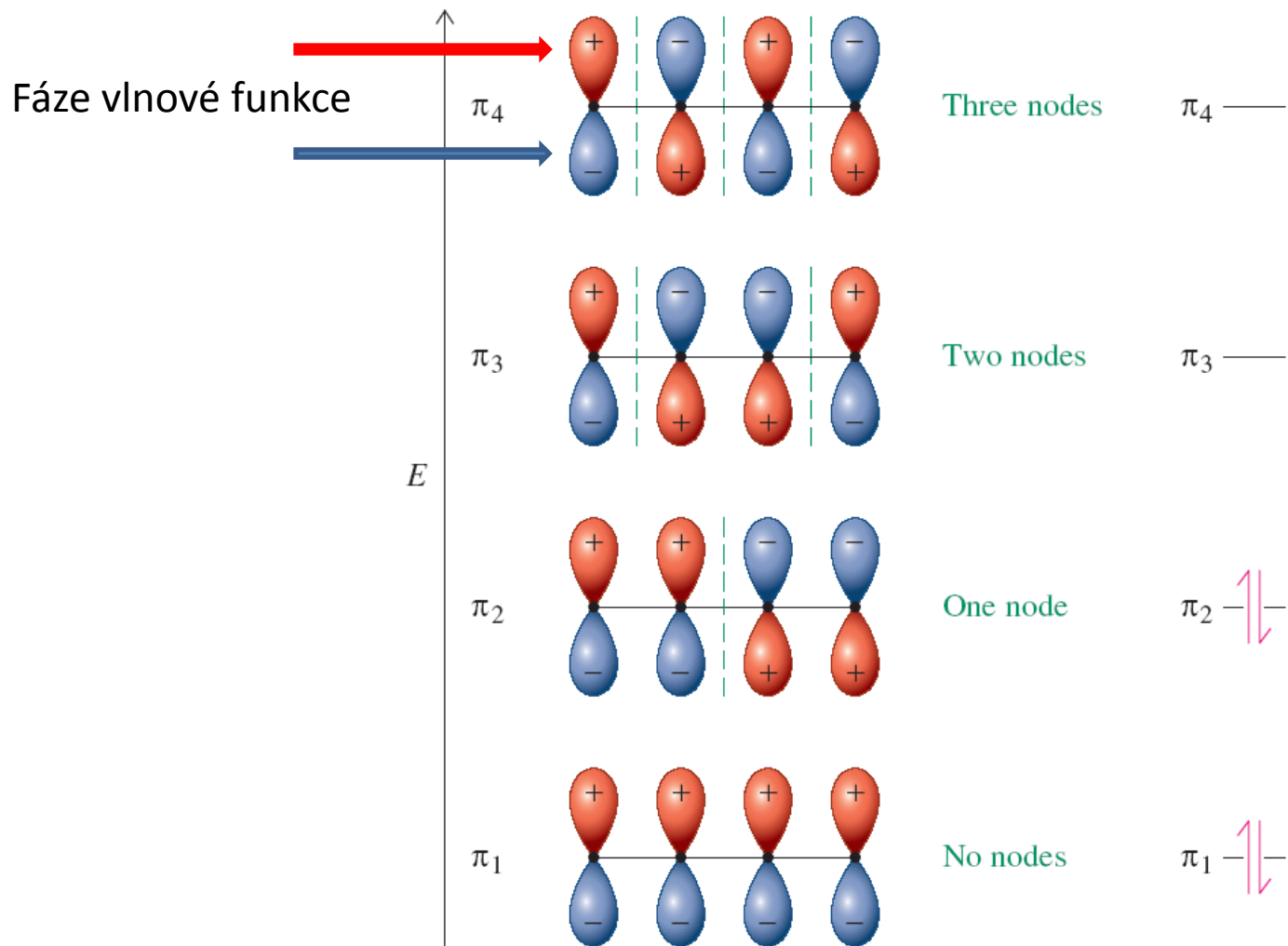


1,3-Butadiene
(Conjugated)



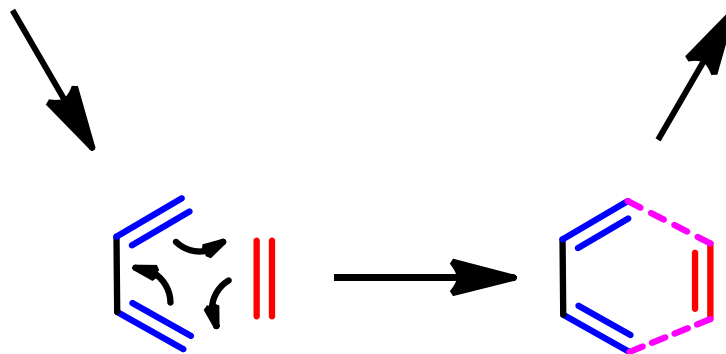
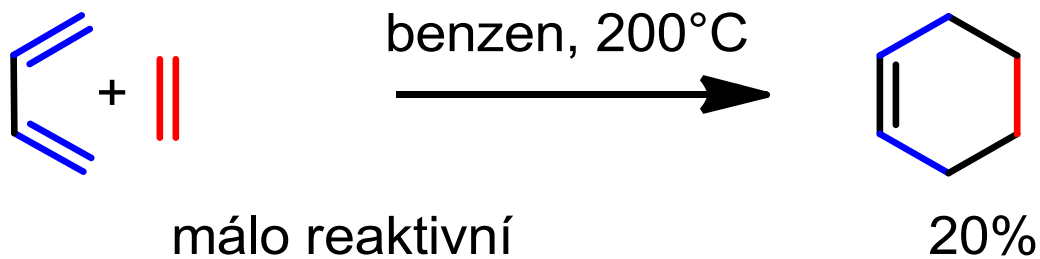
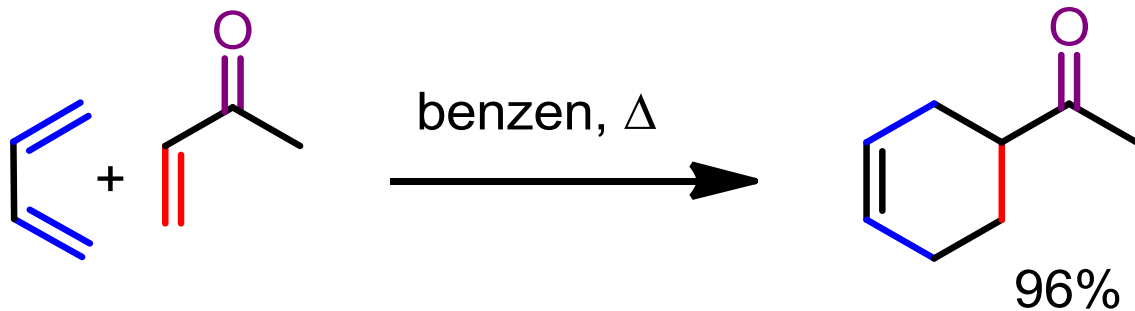
1,2-Propadiene
(Allene, nonconjugated)



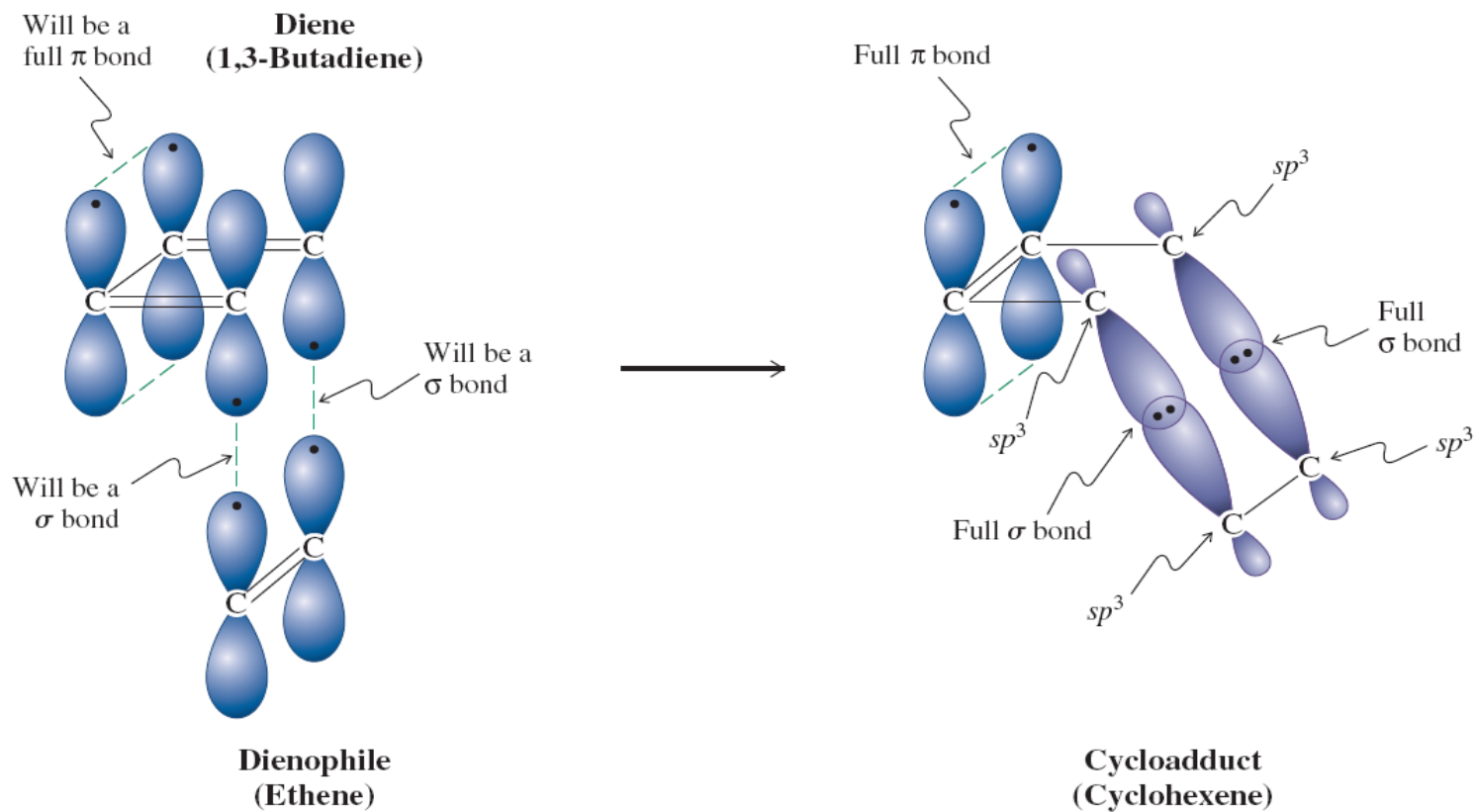
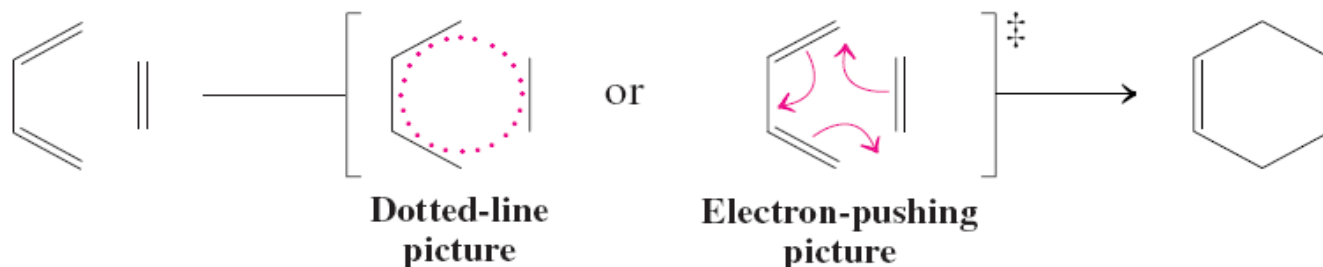


Při reakci dochází k překryvu orbitalů se **stejnou** fází vlnové funkce - reaguje prázdný orbital s nejnižší energií (**LUMO**) s plným orbitalem s nejvyšší energií (**HOMO**)

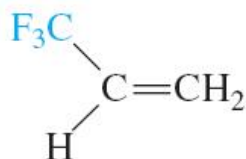
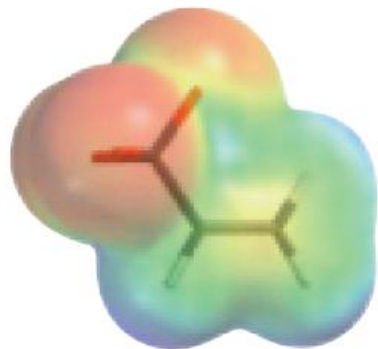
[4+2]-Cykloadiční reakce – Diels-Alderova reakce



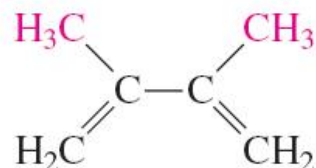
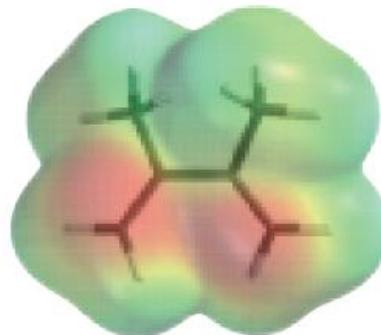
Two Pictures of the Transition State of the Diels-Alder Reaction



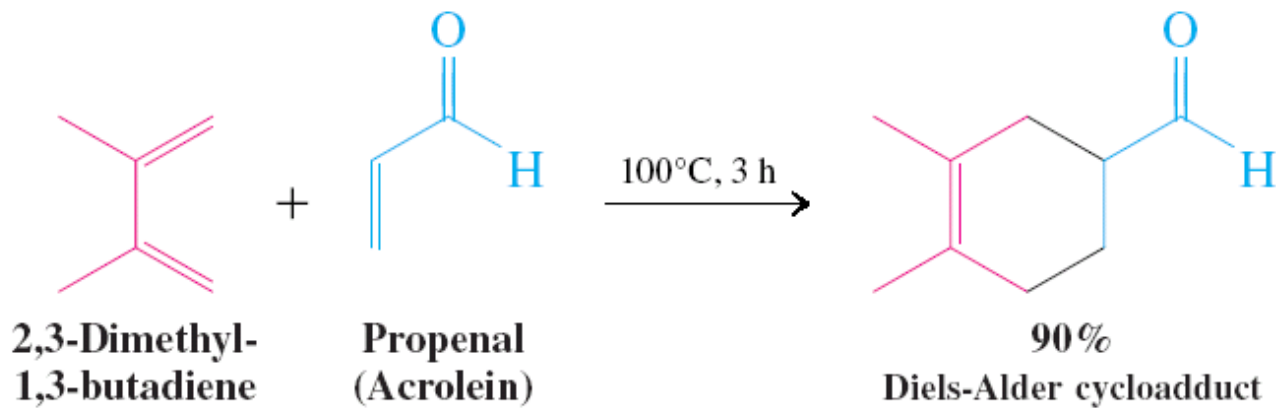
Nejvyšší výtěžky dávají reakce elektronově chudých alkenů s elektronově bohatými dieny



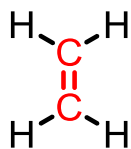
3,3,3-Trifluoro-1-propene
(An electron-poor alkene)



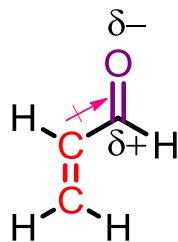
2,3-Dimethyl-1,3-butadiene
(An electron-rich diene)



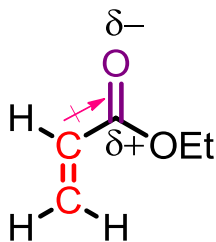
Dienofily



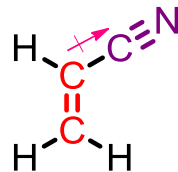
nereaktivní



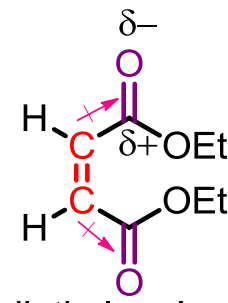
akrolein



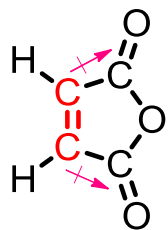
ethyl-akrylat



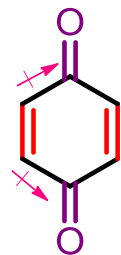
akrylonitril



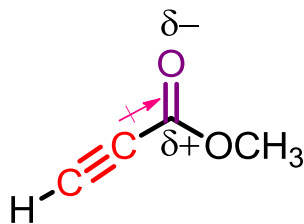
diethyl-maleat



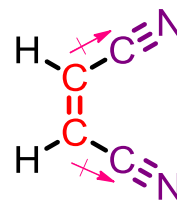
maleinanhydrid



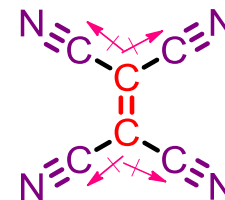
p-benzochinon



methyl-propiolat



1,2-dikyanoethen

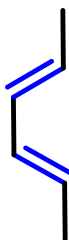
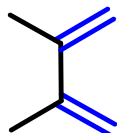


tetrakynoethen

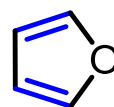
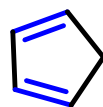
Diény



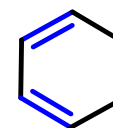
1,4-butadien



cyklopentadien

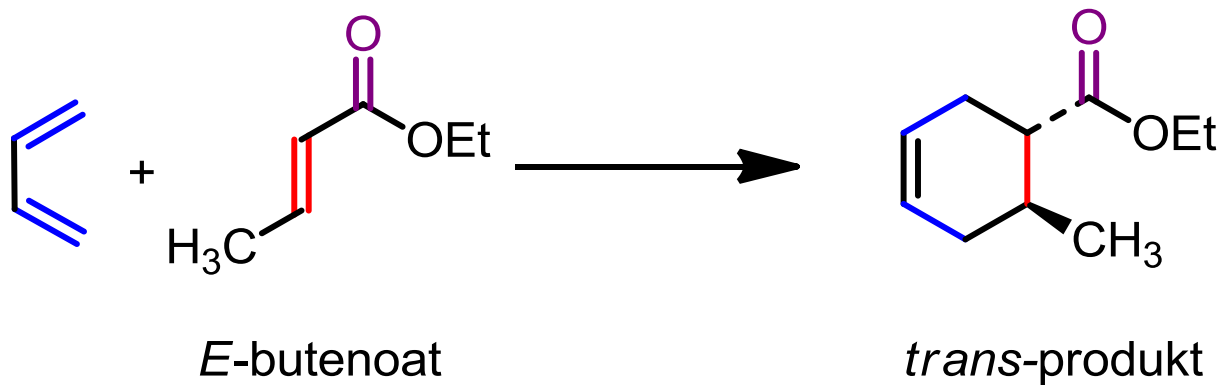
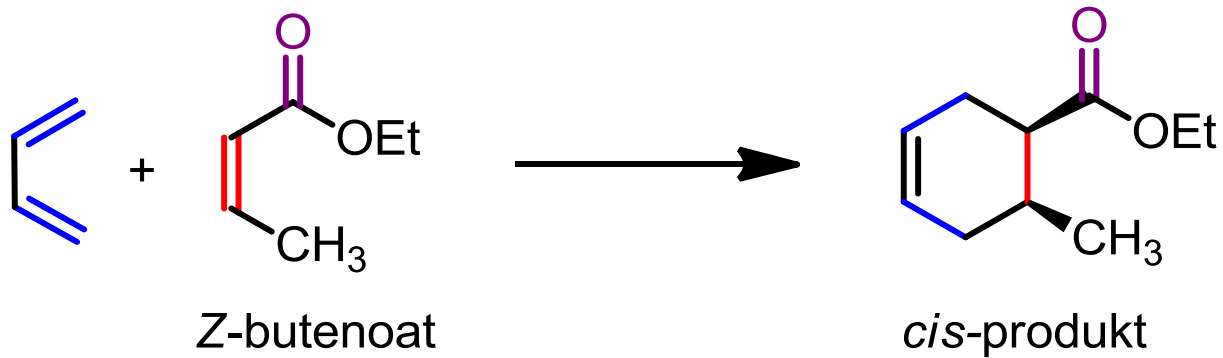


furan

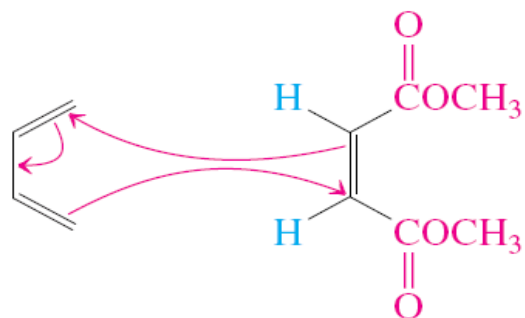


1,3-cyklohexadien

Diels-Alderova reakce je stereoselektivní

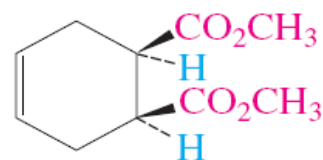


**In the Diels-Alder Reaction,
the Stereochemistry of the Dienophile Is Retained**



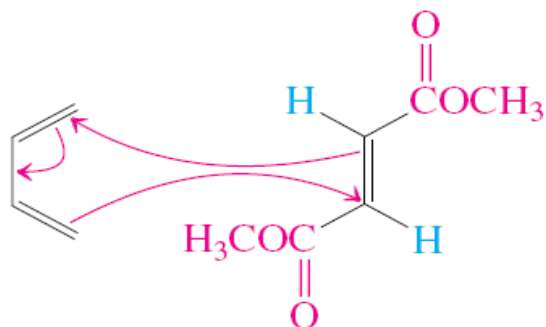
**Dimethyl *cis*-2-butenedioate
(Dimethyl maleate)
(Cis starting material)**

150–160°C, 20 h



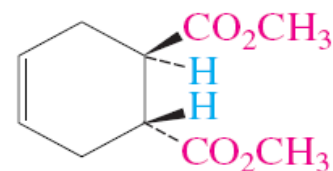
68%

**Dimethyl *cis*-4-cyclohexene-1,2-dicarboxylate
(Cis product)**



**Dimethyl *trans*-2-butenedioate
(Dimethyl fumarate)
(Trans starting material)**

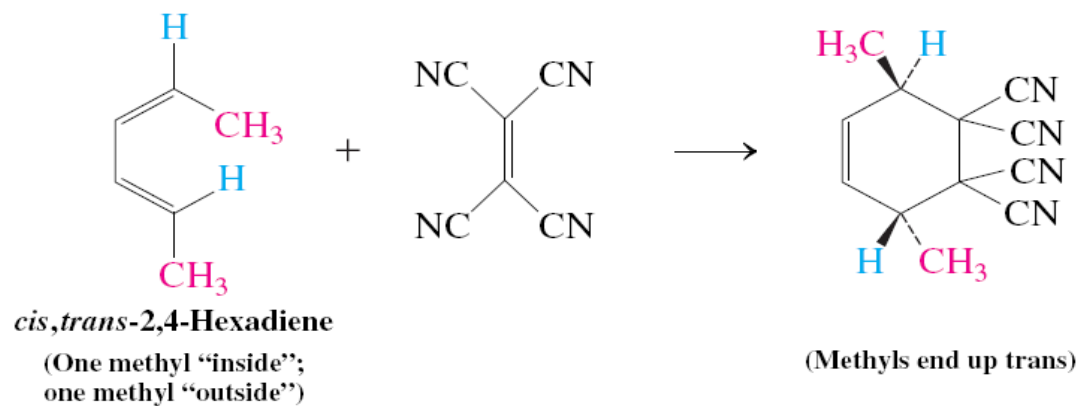
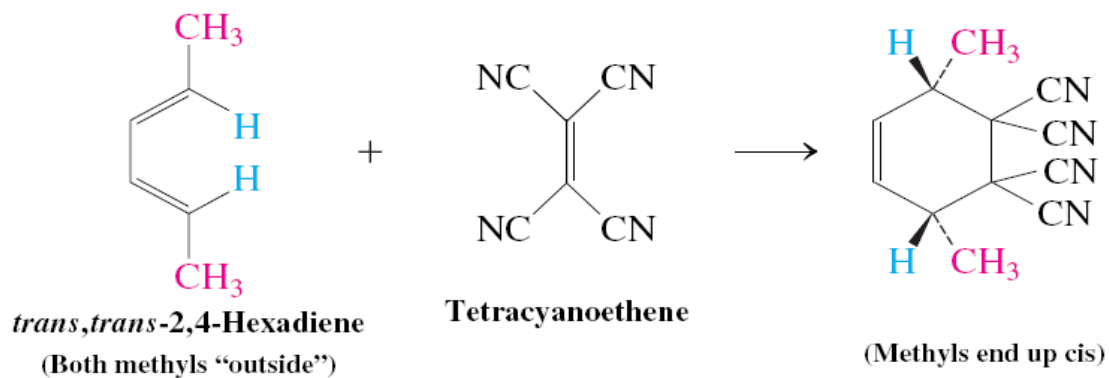
200–205°C, 3.5 h



95%

**Dimethyl *trans*-4-cyclohexene-1,2-dicarboxylate
(Trans product)**

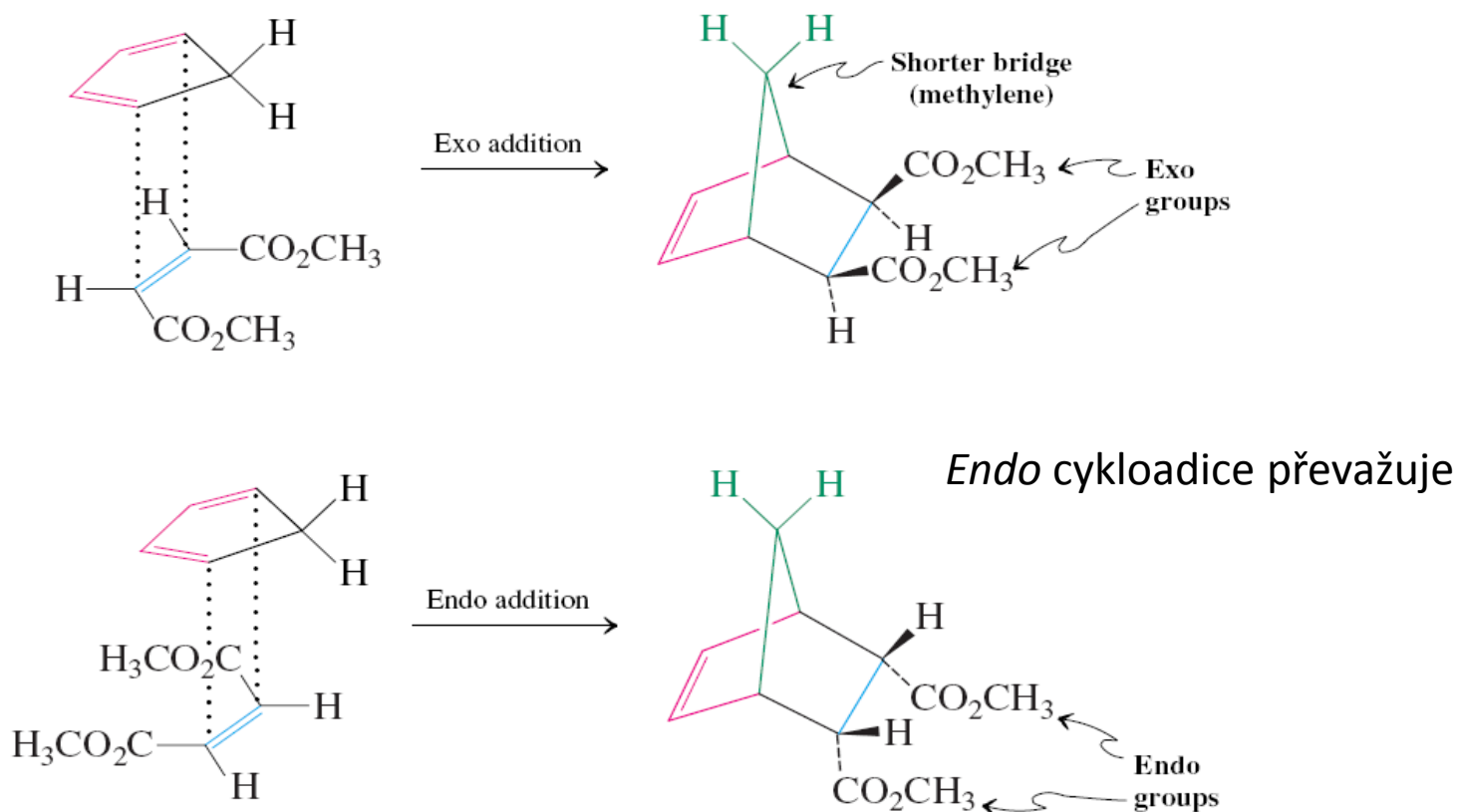
**In the Diels-Alder Reaction,
the Stereochemistry of the Diene Is Retained**



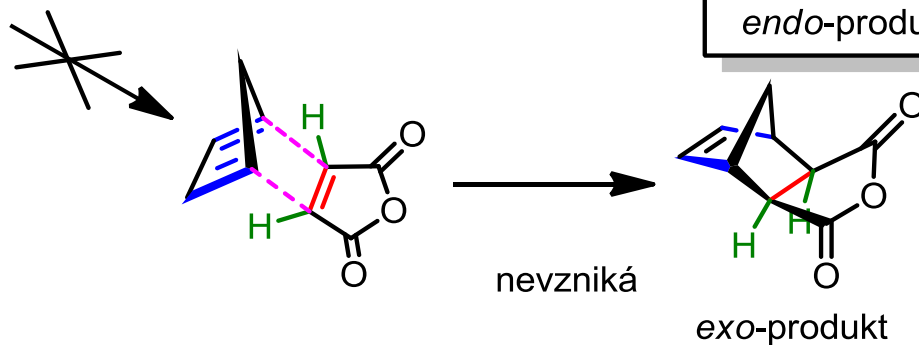
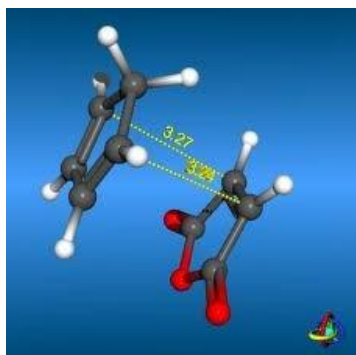
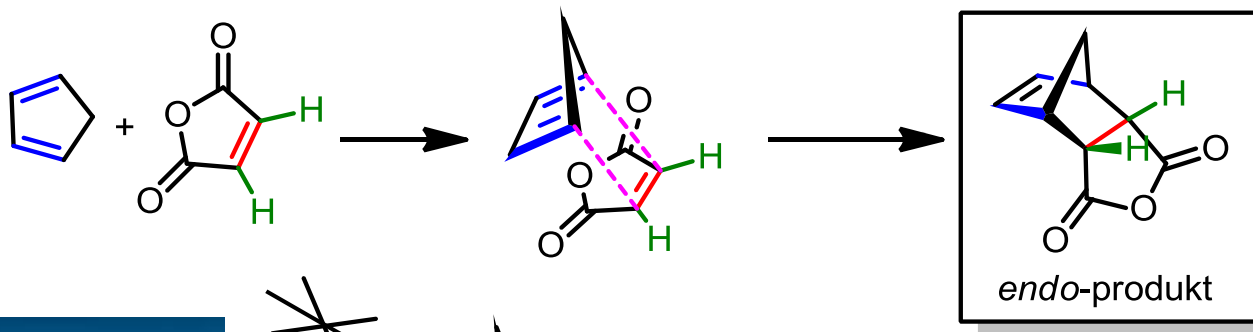
Diels-Alderovy cykloadice probíhají podle endo pravidla

Při reakci 1,3-cyclopentadienu s dimethyl cis-2-butenedioátem mohou vznikat 2 produkty: *exo* adukt a *endo* adukt:

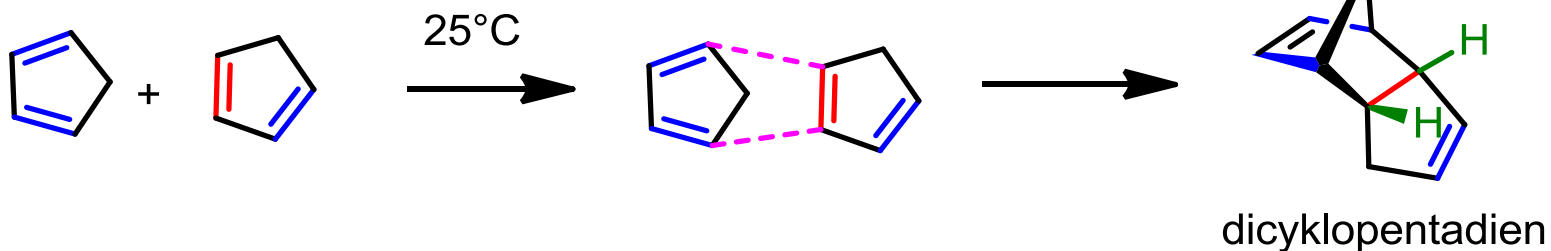
Exo and Endo Cycloadditions to Cyclopentadiene



Diels-Alderovy cykloadice probíhají podle endo pravidla

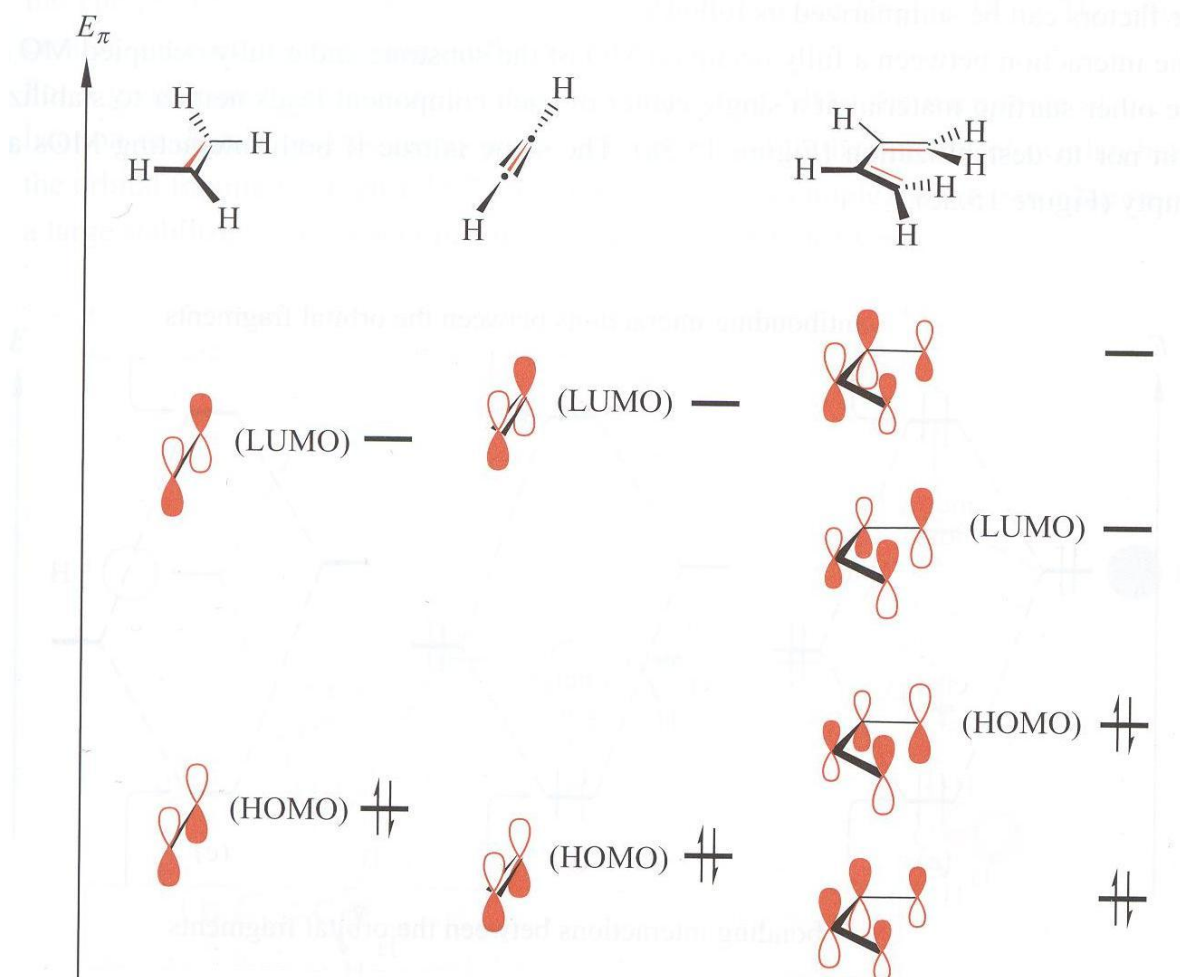


exo-produkt

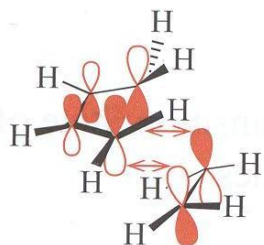


dicyklopentadien

Proč termicky probíhá [4+2]-cykloadice ?

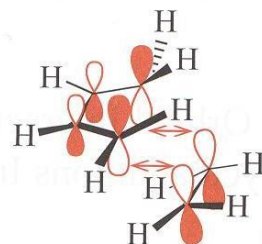


Proč termicky probíhá [4+2]-cykloadice ?



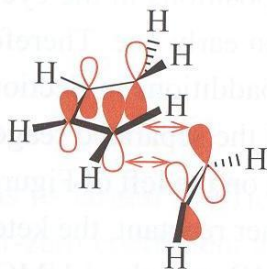
HOMO_{butadiene}/LUMO_{ethene}

$$E(\text{HOMO}_{\text{butadiene}}) - E(\text{LUMO}_{\text{ethene}}) \\ = -312 \text{ kcal/mol}$$



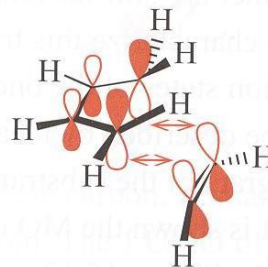
LUMO_{butadiene}/HOMO_{ethene}

$$E(\text{HOMO}_{\text{ethene}}) - E(\text{LUMO}_{\text{butadiene}}) \\ = -317 \text{ kcal/mol}$$



HOMO_{butadiene}/LUMO_{acetylene}

$$E(\text{HOMO}_{\text{butadiene}}) - E(\text{LUMO}_{\text{acetylene}}) \\ = -331 \text{ kcal/mol}$$

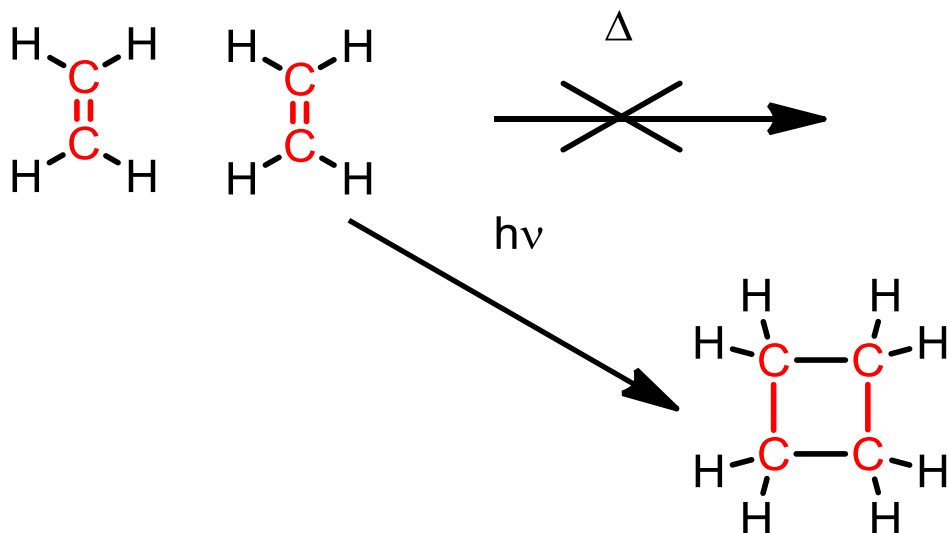


LUMO_{butadiene}/HOMO_{acetylene}

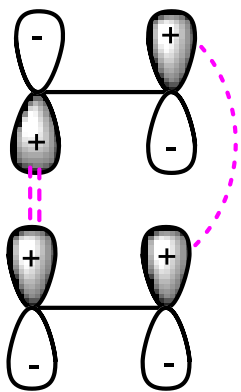
$$E(\text{HOMO}_{\text{acetylene}}) - E(\text{LUMO}_{\text{butadiene}}) \\ = -341 \text{ kcal/mol}$$

Reaguje HOMO dienofilu s LUMO dienu !

Fotochemické [2+2]-cykloadice



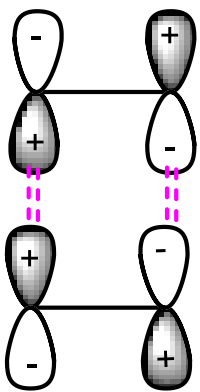
LUMO základního stavu alkenu 2



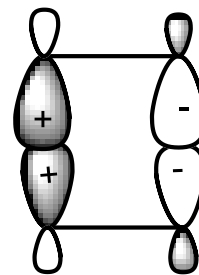
HOMO základního stavu alkenu 1

nereaguje

LUMO základního stavu alkenu 2

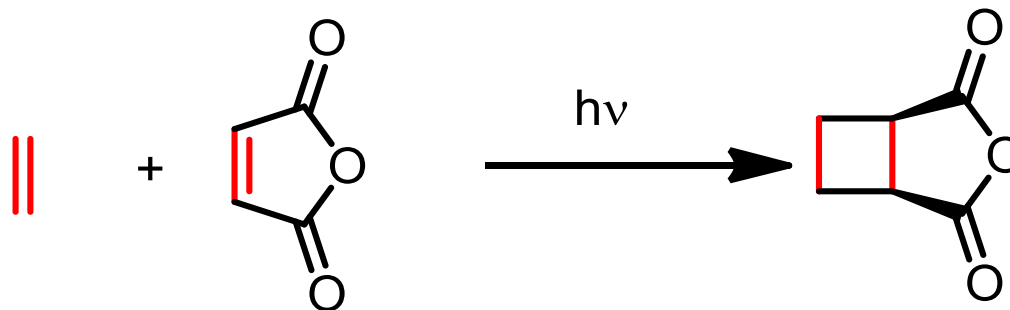
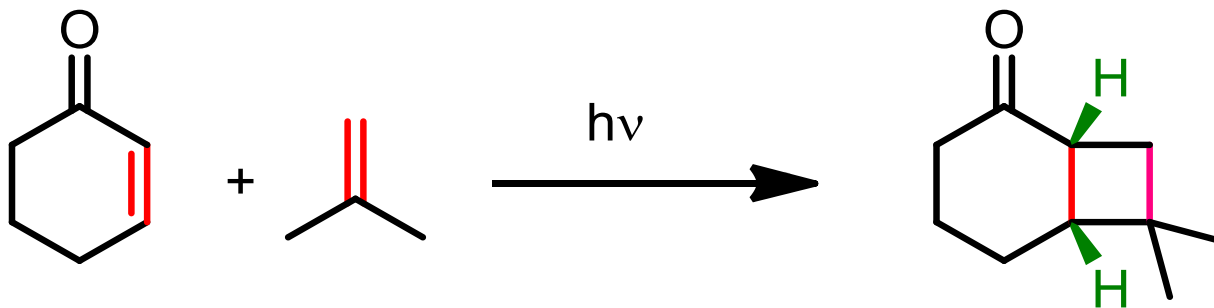


HOMO excitovaného stavu alkenu 1

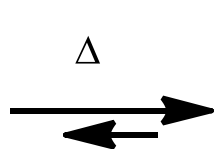
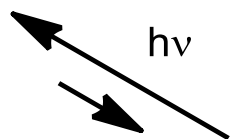
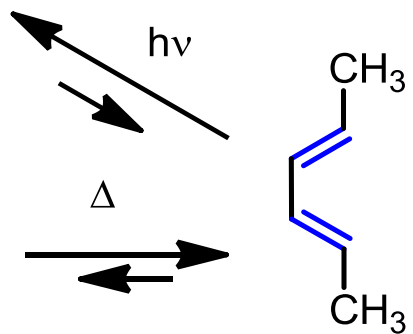
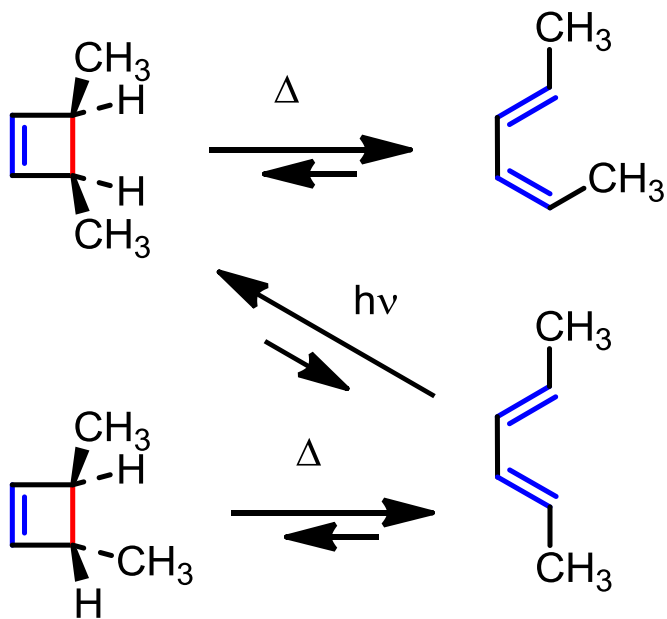
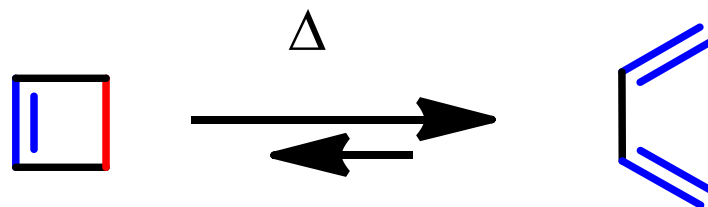
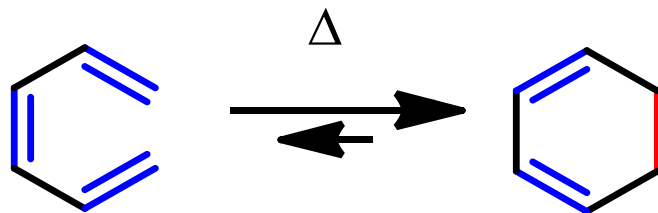


cyklobutan

Fotochemické [2+2]-cykloadice

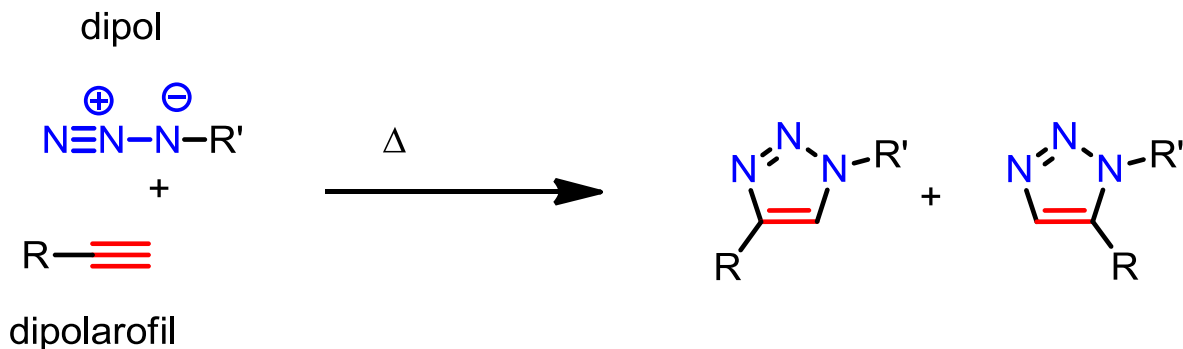


Elektrocyclické reakce

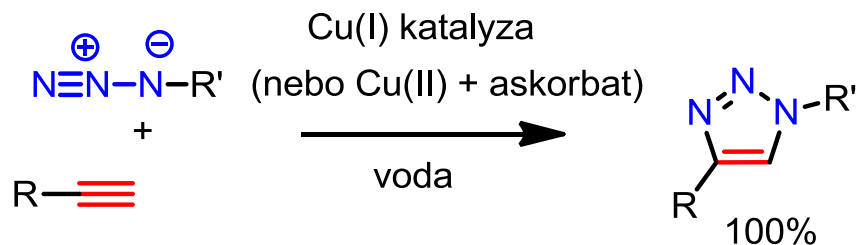


1,3-Dipolární cykloadice ([3+2]-cykloadice)

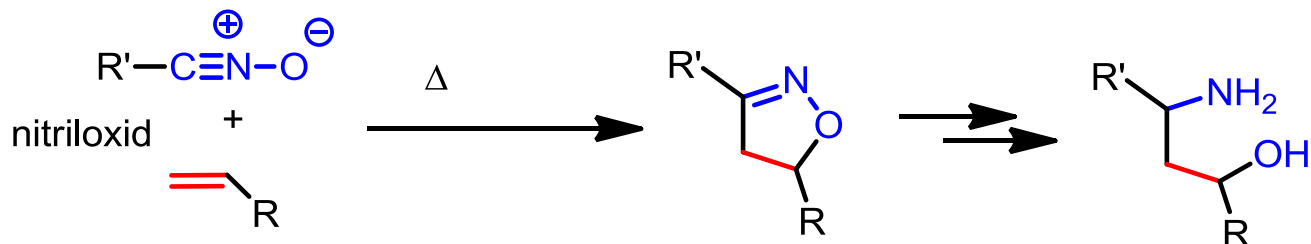
Huisgenova cykloadice



Sharpless-Meldalova “click reakce”

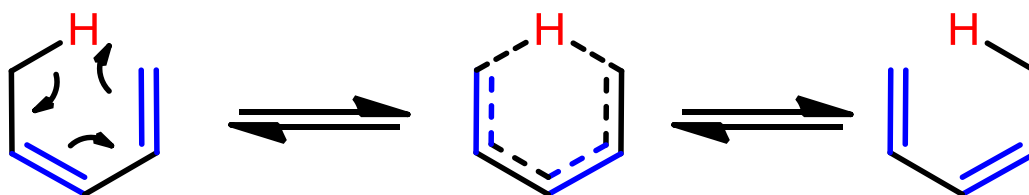


Cykloadice nitriloxidů

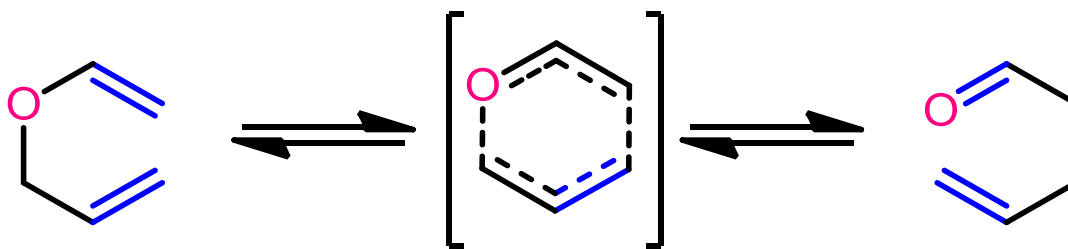


Přesmyky

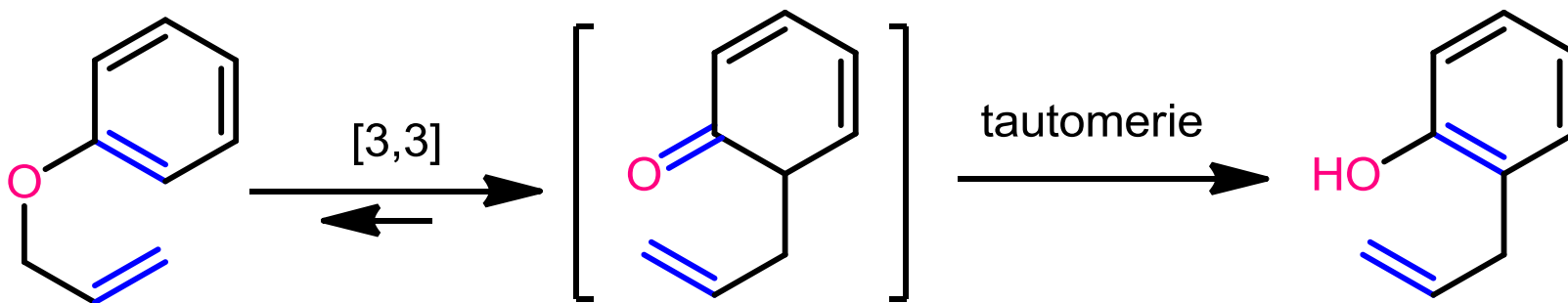
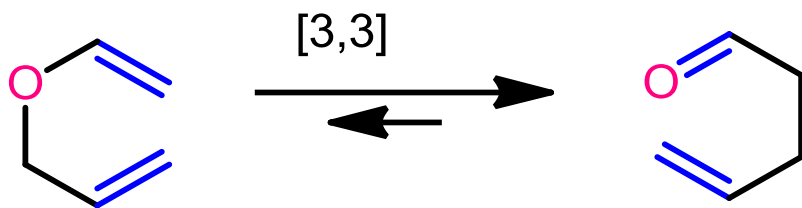
[1,5]- sigmatropní přesmyky



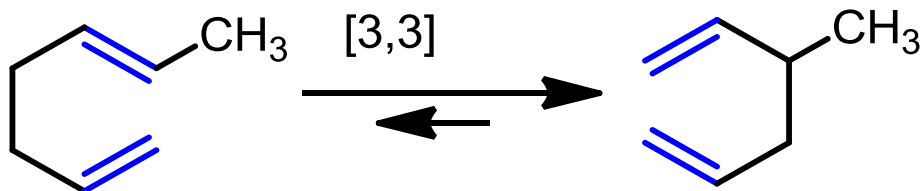
[3,3]- sigmatropní přesmyky



Claisenův přesmyk

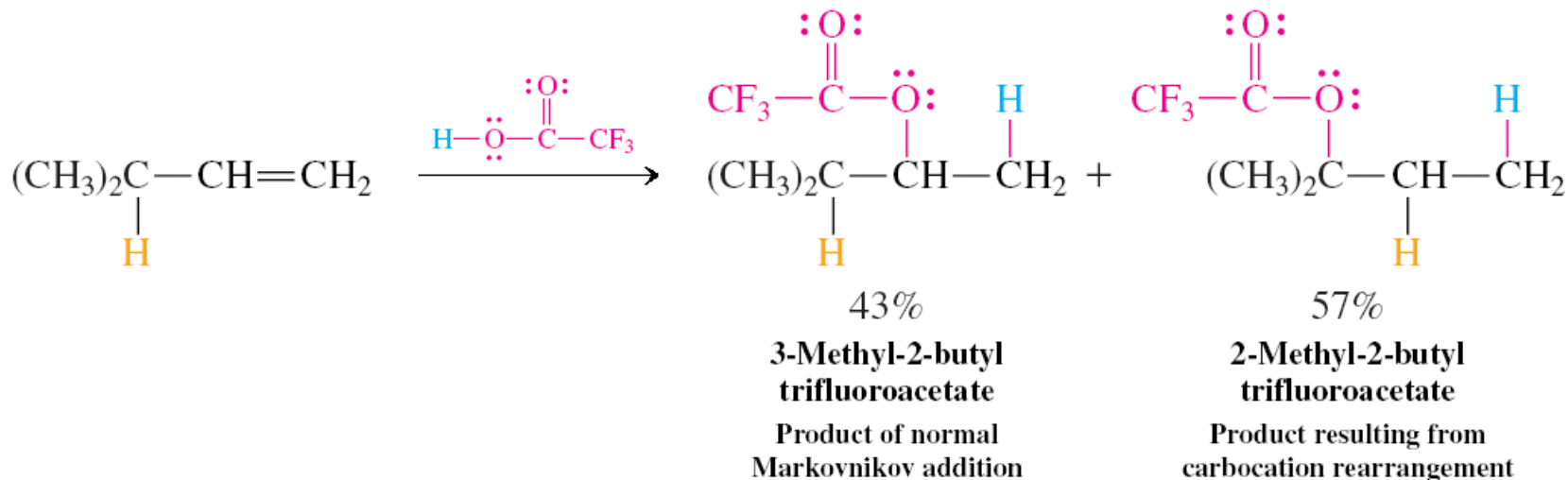


Copeho přesmyk

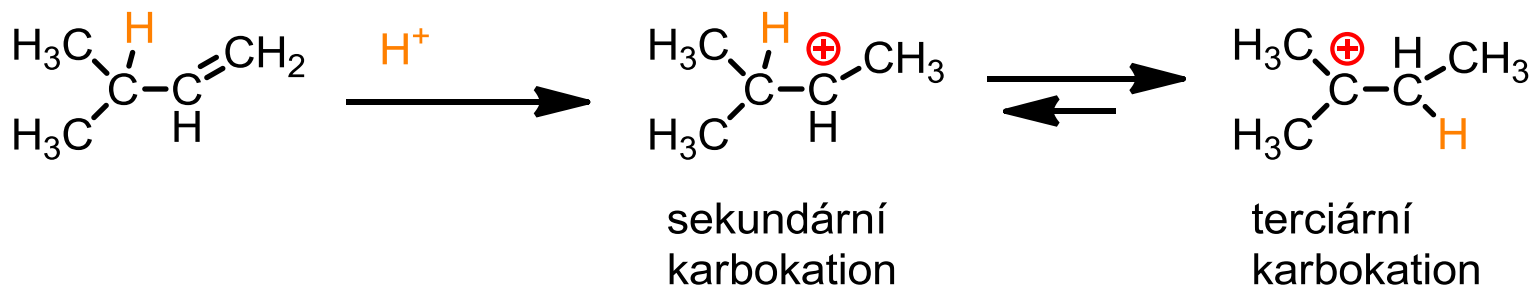


Další přesmyky (již zmiňované) – [1,2]-přesuny

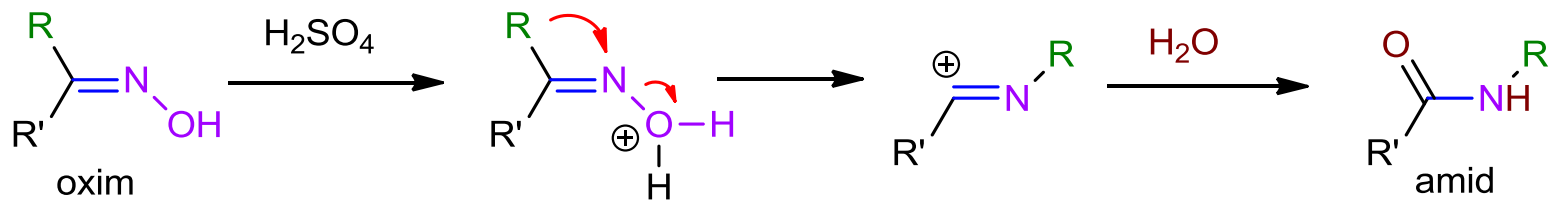
Addition of Trifluoroacetic Acid to 3-Methyl-1-butene



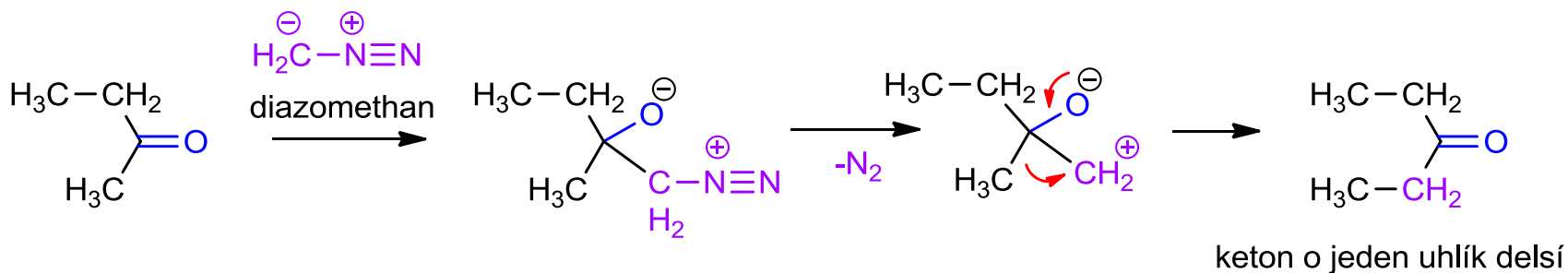
Přesmyk karbokationtu (Wagner-Meerweinův přesmyk)



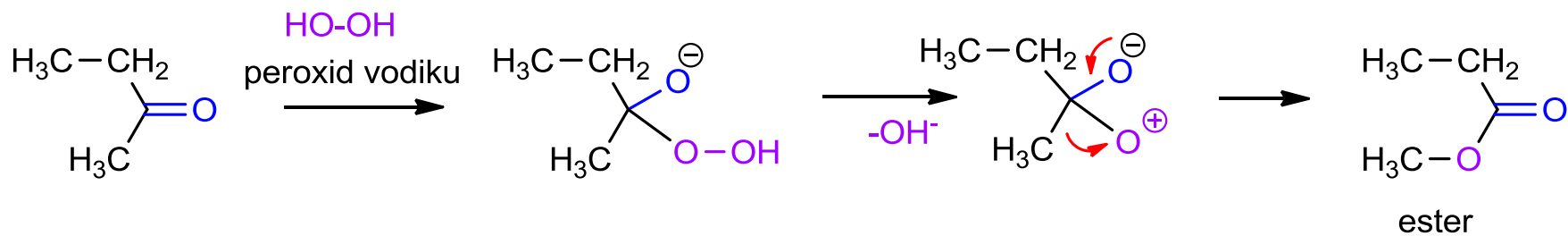
Beckmannův přesmyk oximů



Reakce ketonů s diazomethanem - homologace



Baeyer-Villigerova reakce



Pinakolový přesmyk

