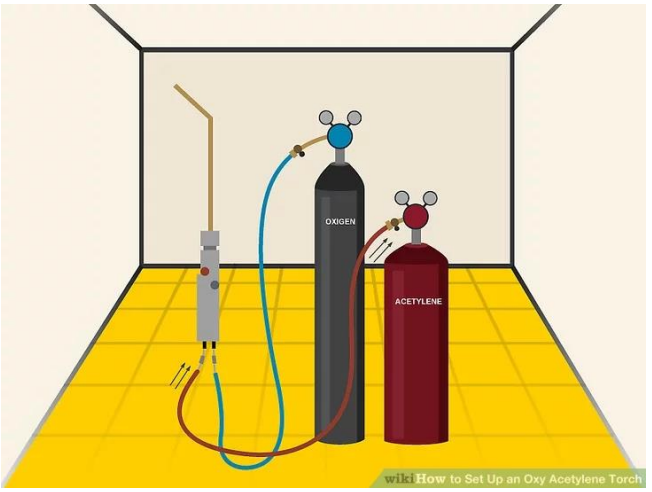
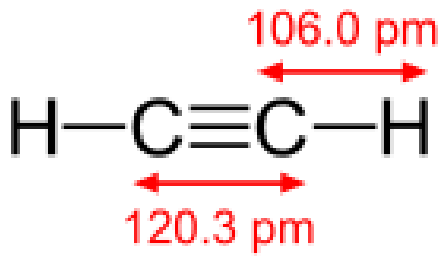

# Alkyny




https://www.wikihow.com/Set-Up-an-Oxy-Acetylene-Torch


https://jtcylinderracks.com/common-uses-for-acetylene-cylinders/




https://en.wikipedia.org/wiki/Acetylene

https://fractory.com/gas-welding-explained/

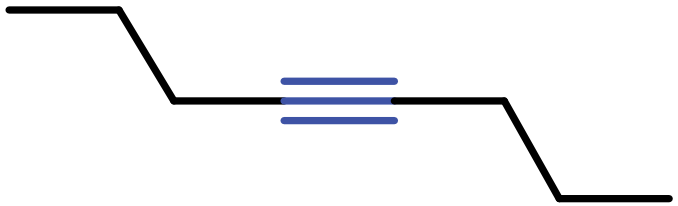
# Alkyny - klasifikace


**ethyn (acetylen)**


**terminální alkyn**


**interní alkyn**

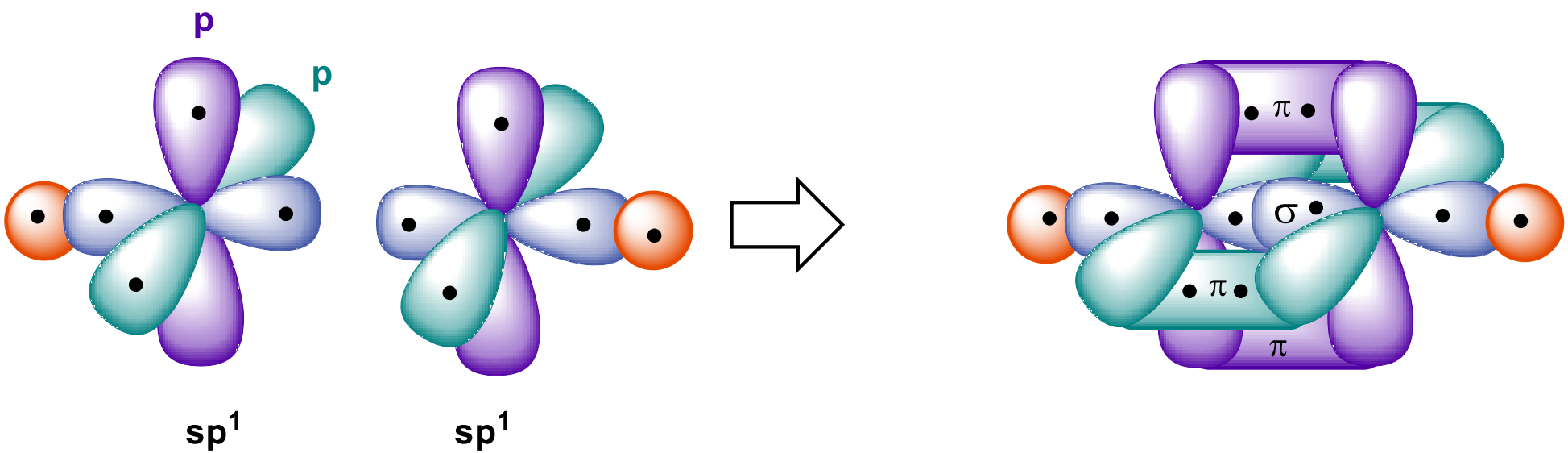
Alkyny – názvosloví (přípona –yn)

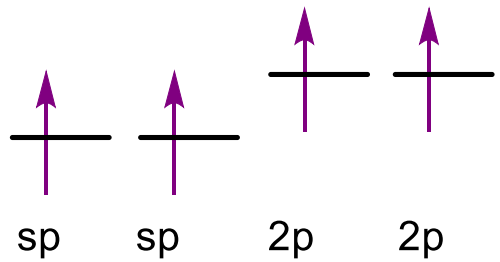


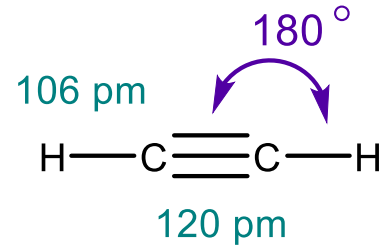
**okt-4-yn**

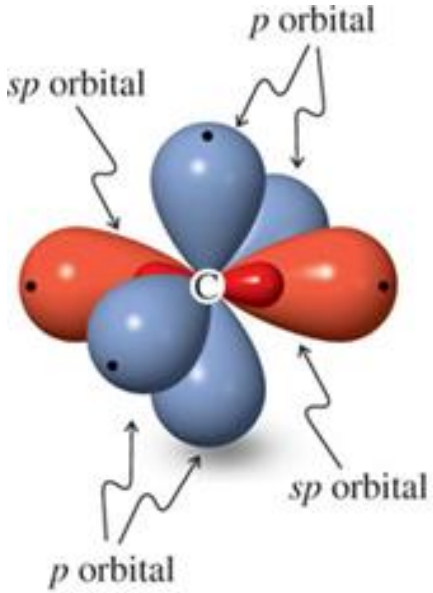
**hexa-2,4-diyn**

# Molekulové orbitaly – vznik trojné vazby C≡C

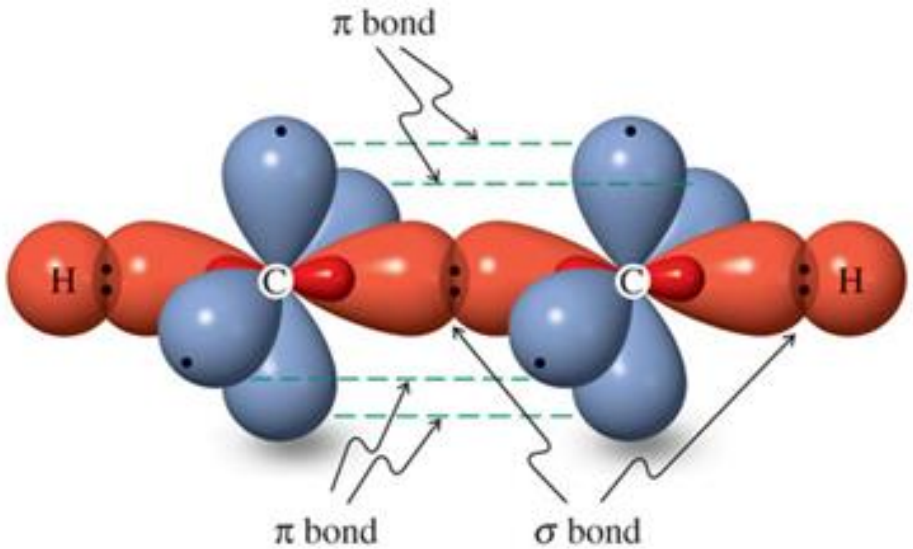


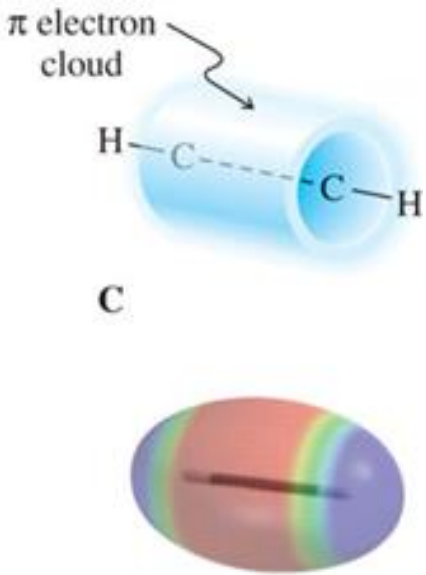






A



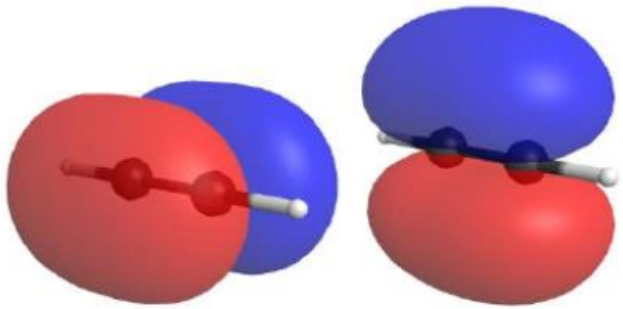

B



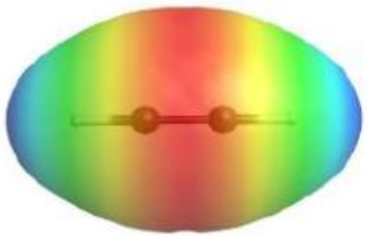

C

D

*Example of the π bonds in ethyne*

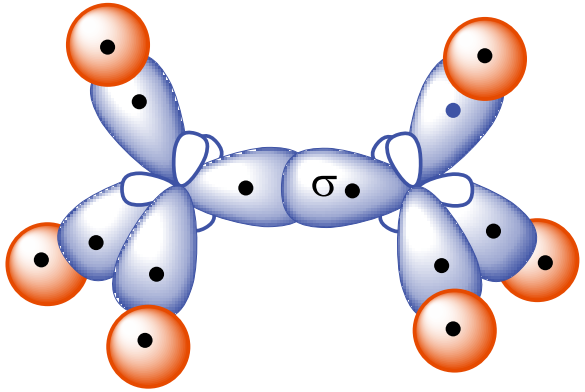


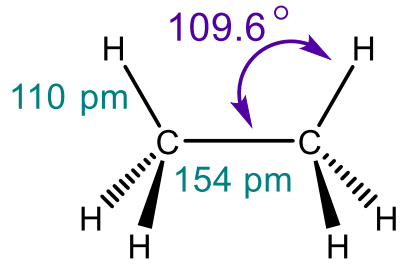
*Electrostatic potential map of ethyne (red = high electron density and blue = low electron density)*



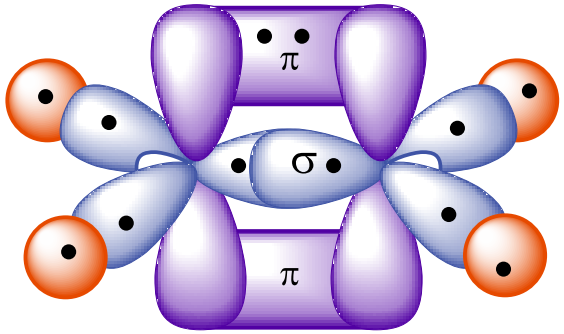
https://www.studocu.com/en-us/document/boston-university/organic-chemistry-1/reactions-of-alkynes-key/1680216

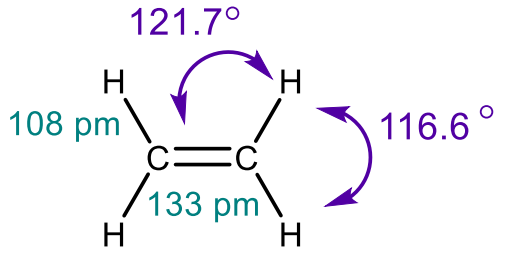
**$sp^3$**


σ

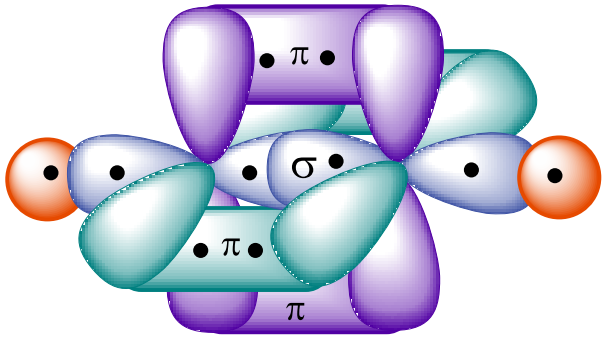

109.6°
H
H
110 pm
C
C
154 pm
H
H
H
H

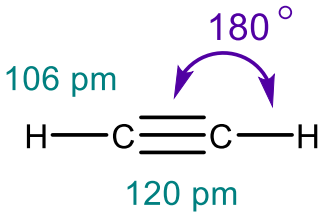
**$sp^2$**


π
σ
π

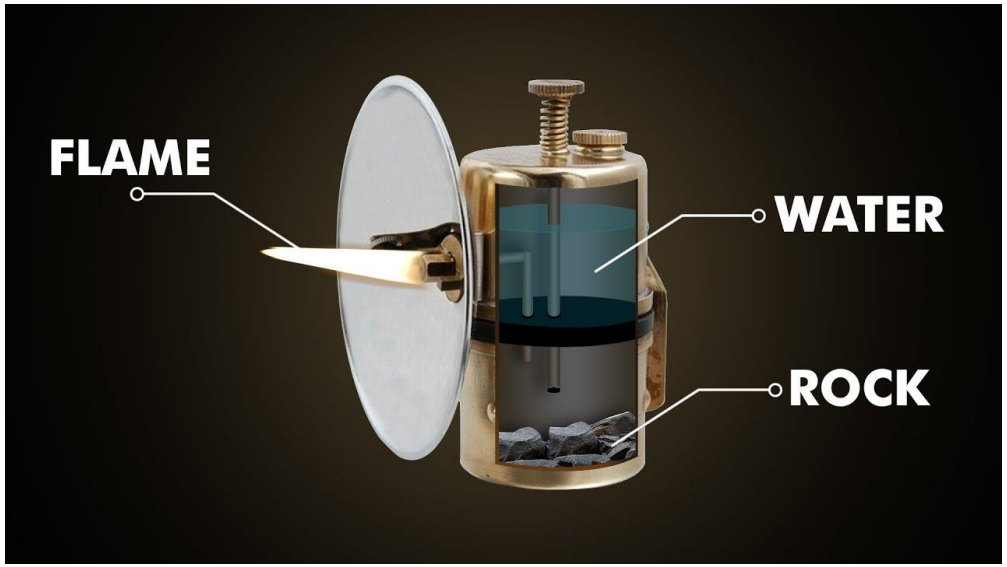

121.7°
H
H
108 pm
C
C
116.6°
133 pm
H
H

**sp**


π
σ
π
π


180°
106 pm
H—C≡C—H
120 pm

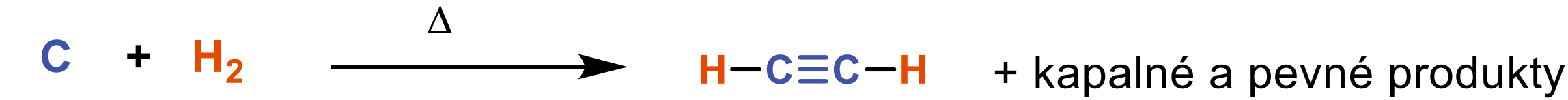
# Karbid vápenatý – karbidová lampa

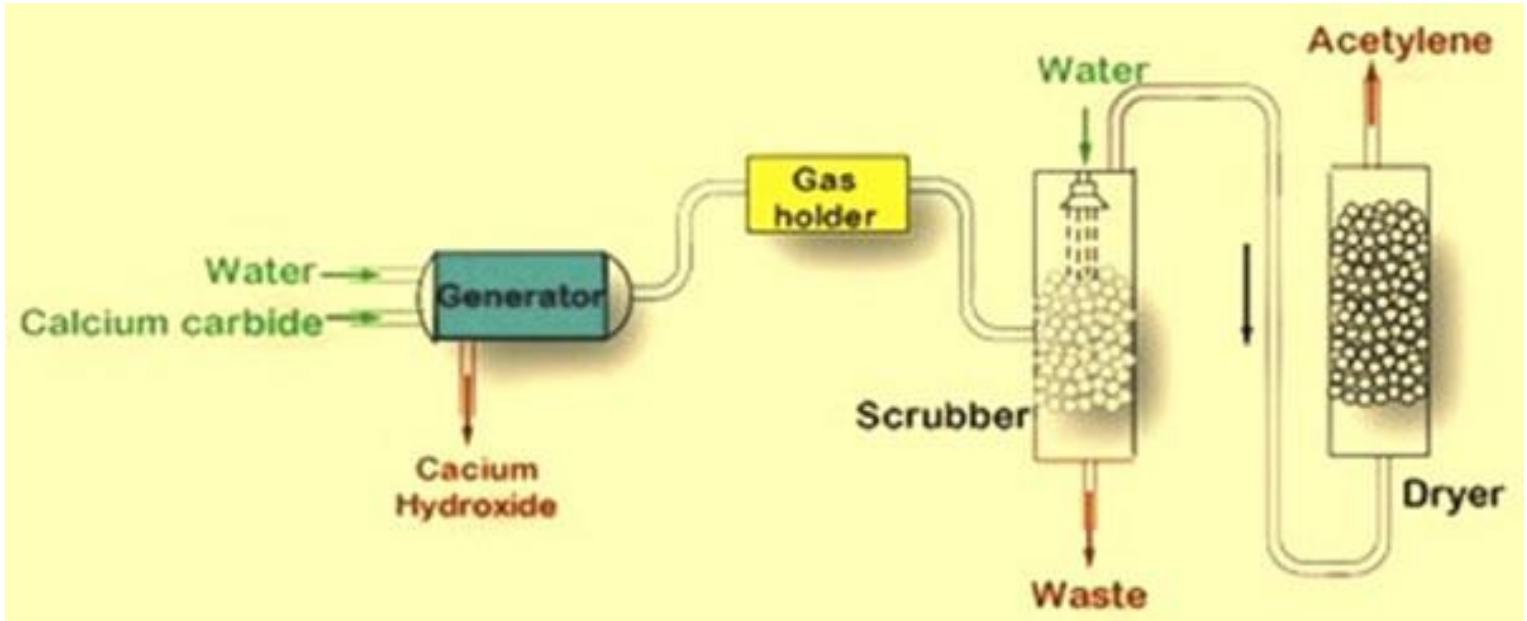



https://www.google.com/search?sca_esv=577421072&q=carbide+lamp&tbm=isch&source=lnms&sa=X&sqi=2&ved=2ahUKEwiAh5zPw5iCAxWUgf0HHaVlADIQ0pQJegQIDRAB&biw=1280&bih=563&dpr=1.5#imgrc=HbqlB_RsgffMJM

https://camachem.com/en/calcium-carbide.html

# Průmyslová výroba acetylenu

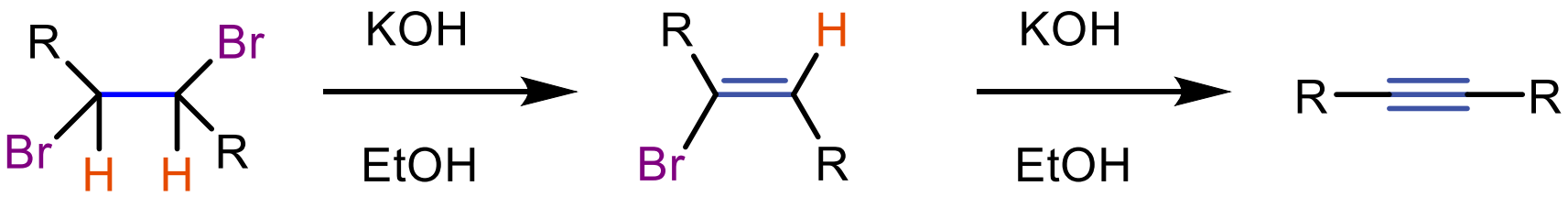


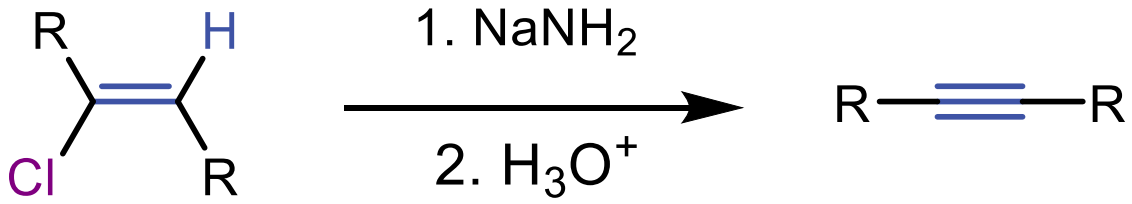




https://www.acetyleneplant.net/technology/about-acetylene-gas/

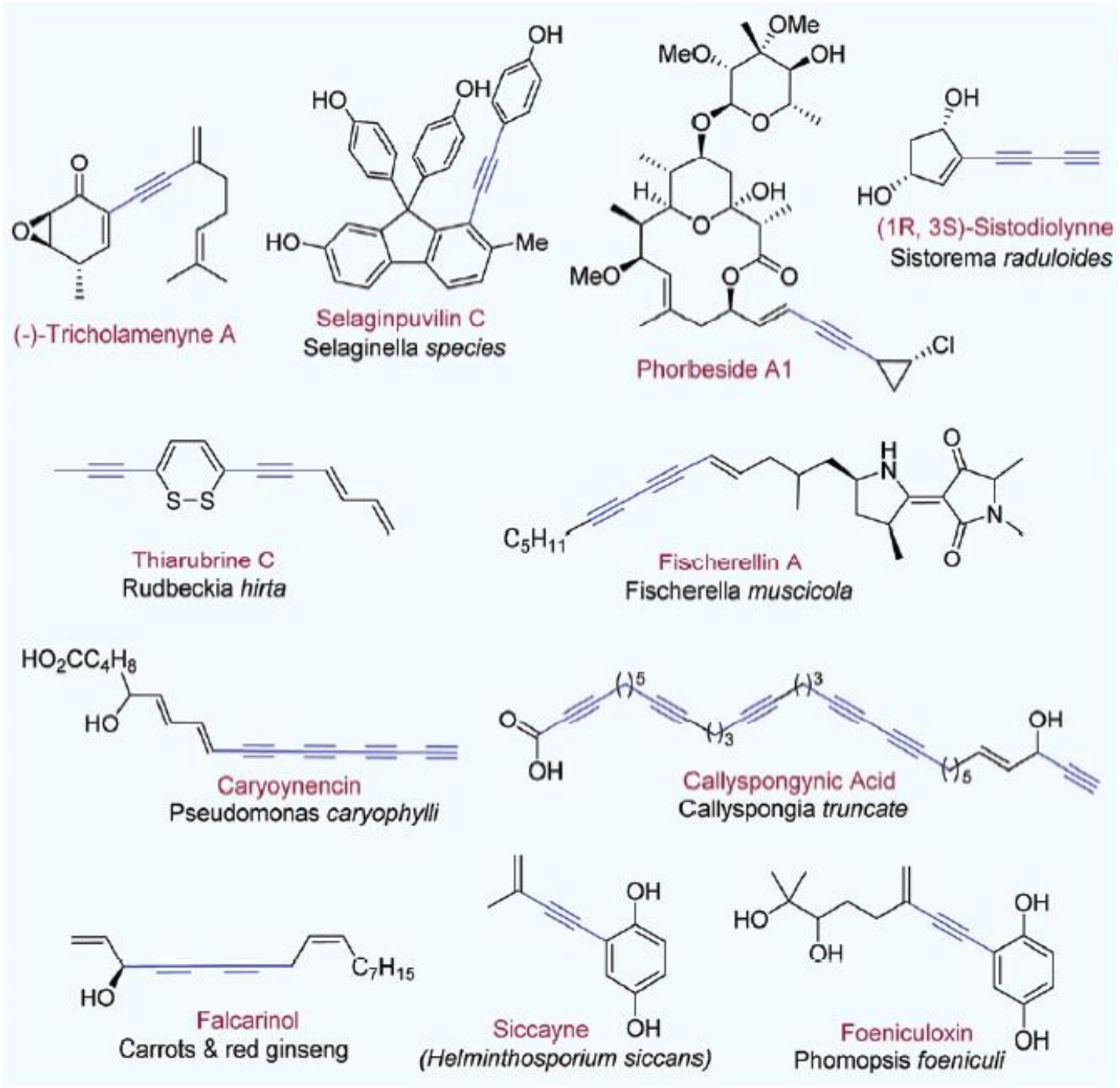
# Příprava alkynů – eliminační reakce

Eliminace halogenvodíků s alkylhalogenidů a alkenylhalogenidů - silnou bází



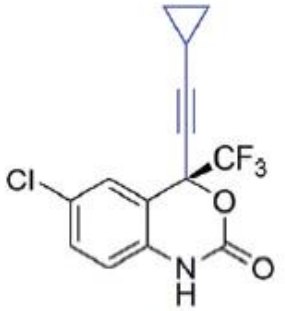



# Motivy alkynů v přírodních látkách

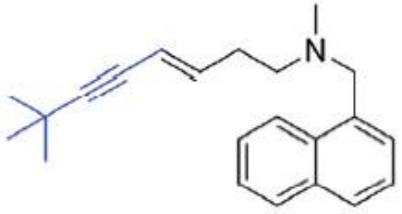



*Org. Biomol. Chem.*, **2021**, *19*, 10259–10287.

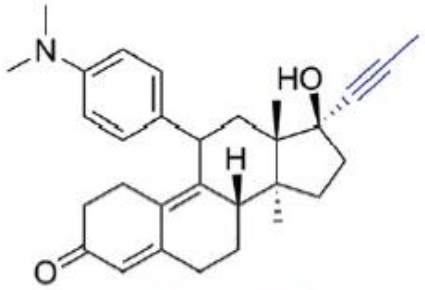
# Motivy alkynů v léčivech



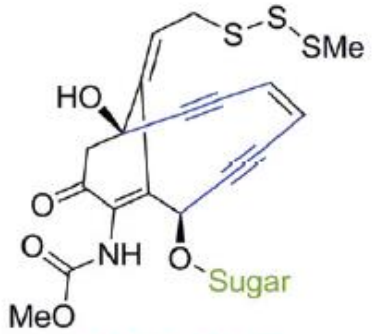

Efavirenz
Treats HIV/AIDS




Terbinafine
*Antifungal drug*

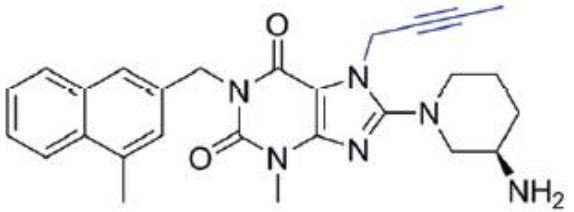



Mifepristone
For abortion



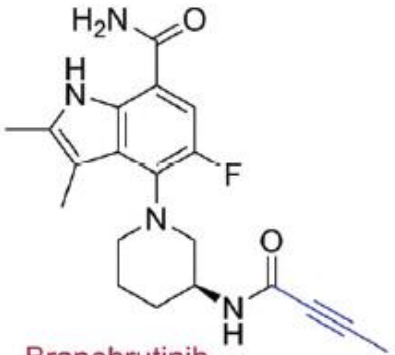

Calicheamicin
Anticancer


Mavoglurant
(MGluR5) Antagonist




Linagliptin
Anti-diabetic


Tazarotene
treats Acne vulgaris
and Psoriasis

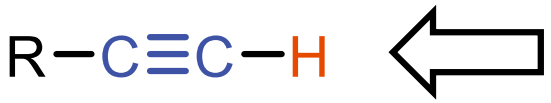



Branebrutinib
BTK inhibitor

*Org. Biomol. Chem.*, **2021**, *19*, 10259–10287.

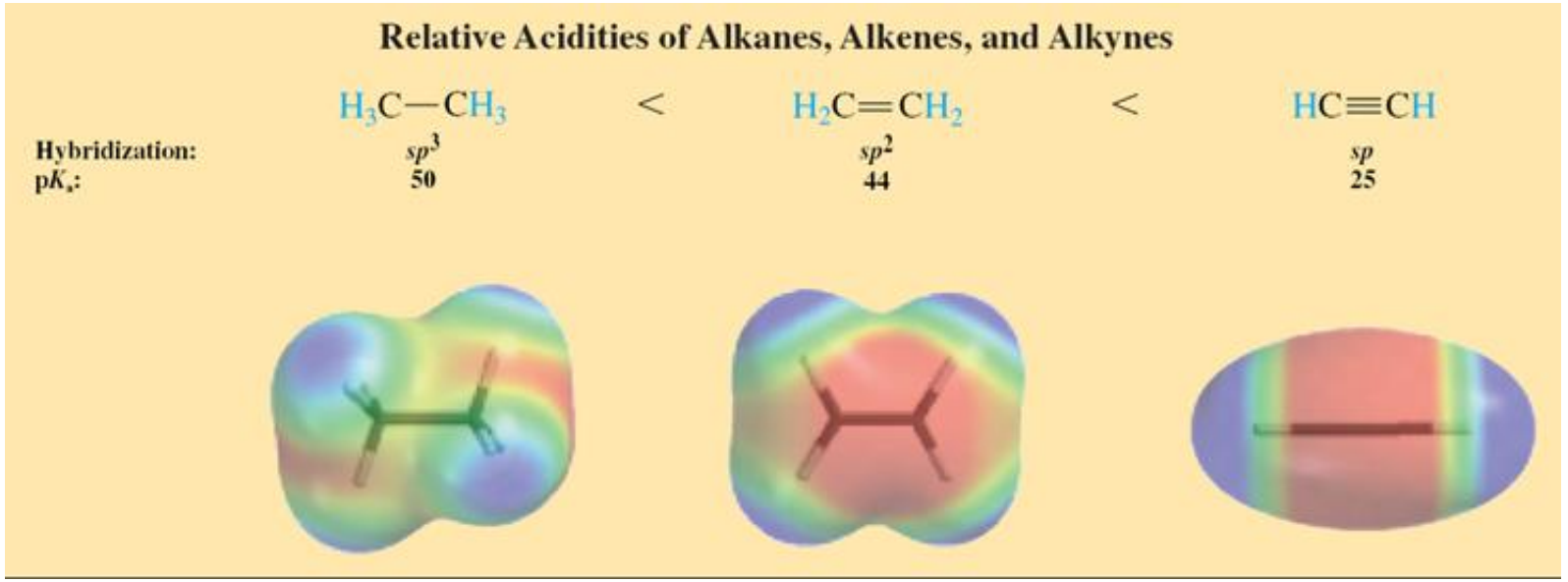
# Reaktivita alkynů

Reakce trojné vazby
(adice)




Reakce koncové C-H
(deprotonace, alkylace.....)

# Terminální alkyny: Acidita

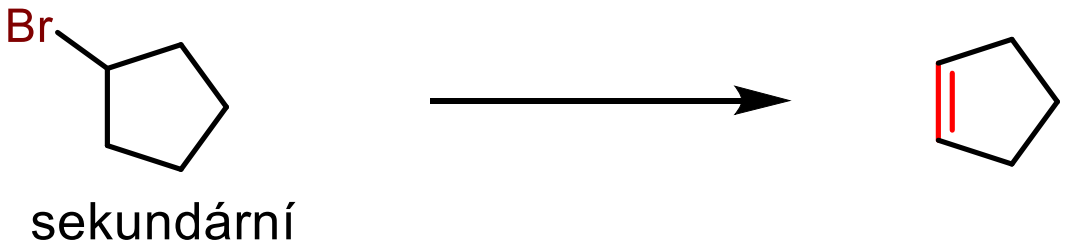


# Deprotonace terminálních alkynů (a jejich reakce)

## Deprotonace:

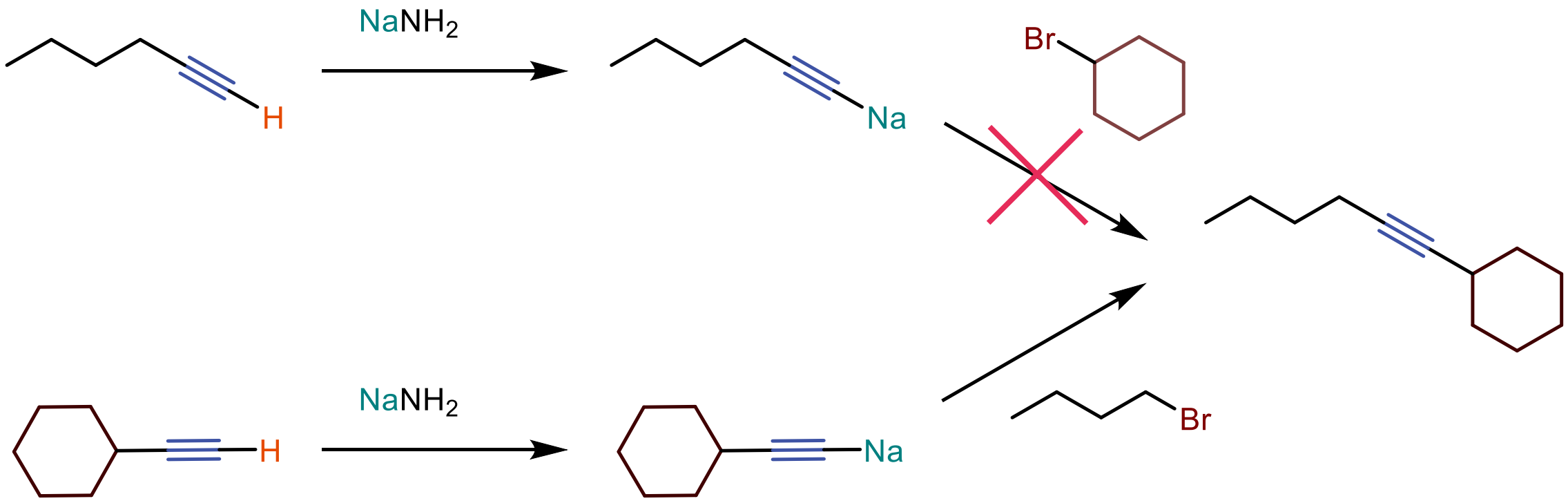


## Alkylace:

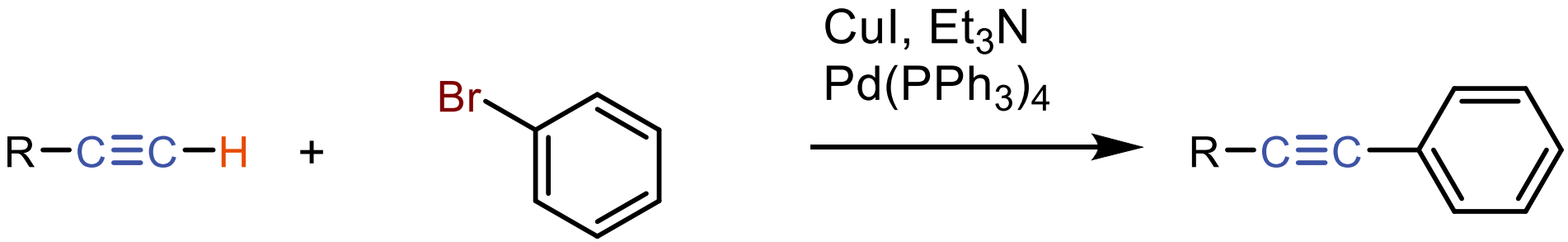

**sekundární**
**a terciární alkylhalogenidy**
**podléhají eliminaci**

# Deprotonace + alkylace - organická syntéza

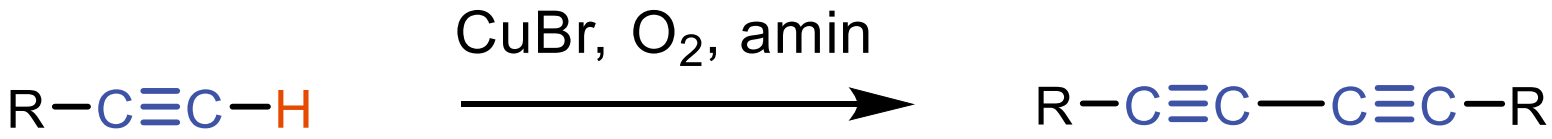


# Další reakce terminálních alkynů

Sonogashirova reakce (coupling) – příprava aryl-alkynů

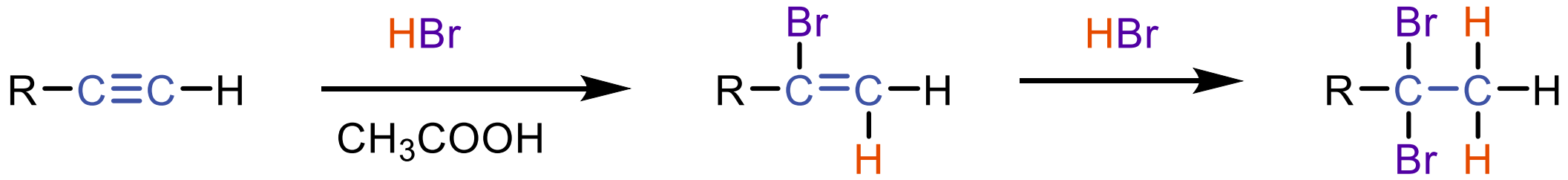


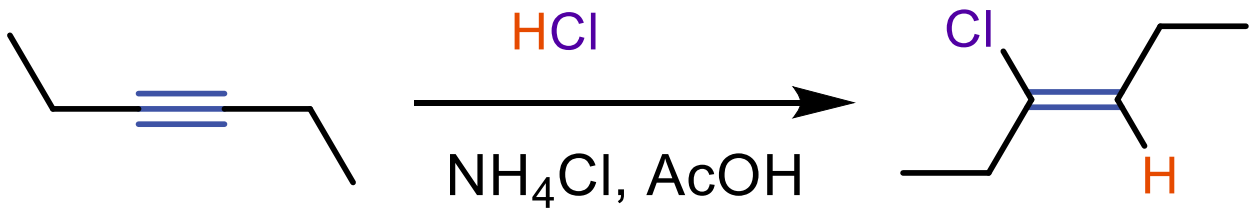

Glaserův coupling – příprava diacetylenů



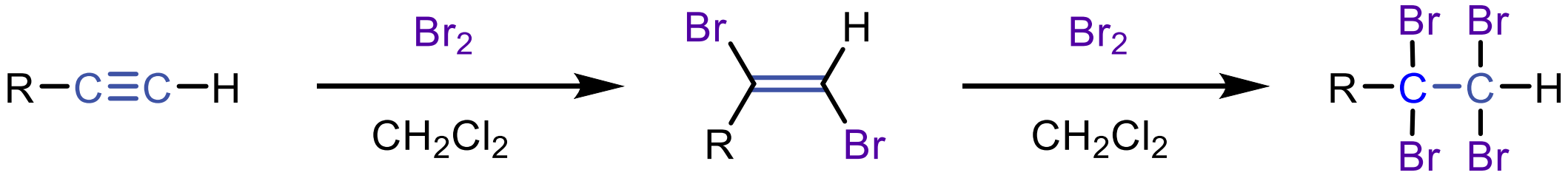
# Adiční reakce na alkyny

Adice halogenovodíků

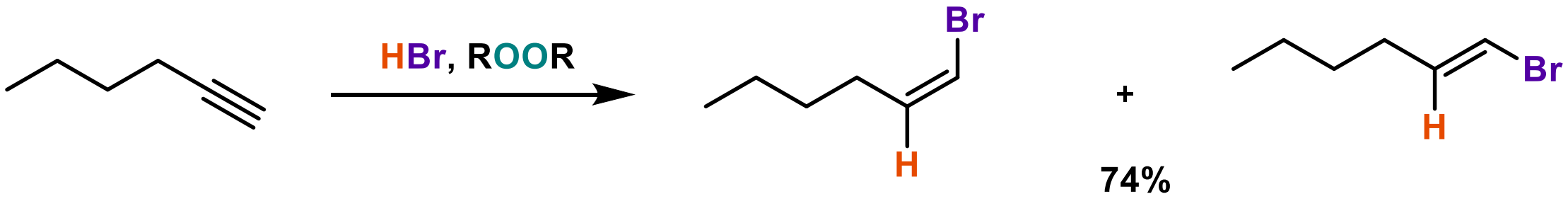



Adice halogenů



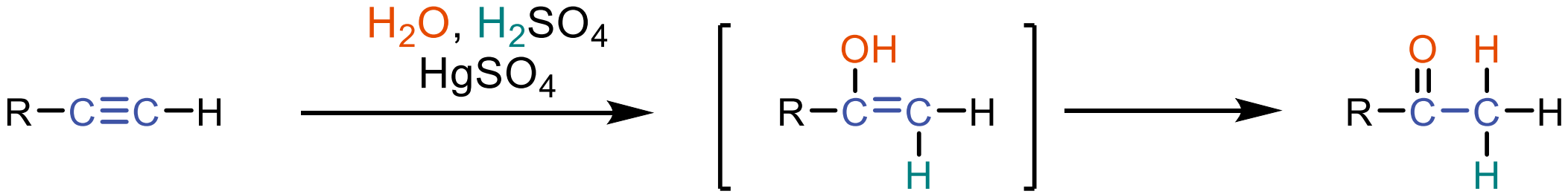
# Radikálová adice HBr na alkyny – neprobíhá podle Markovnikova pravidla



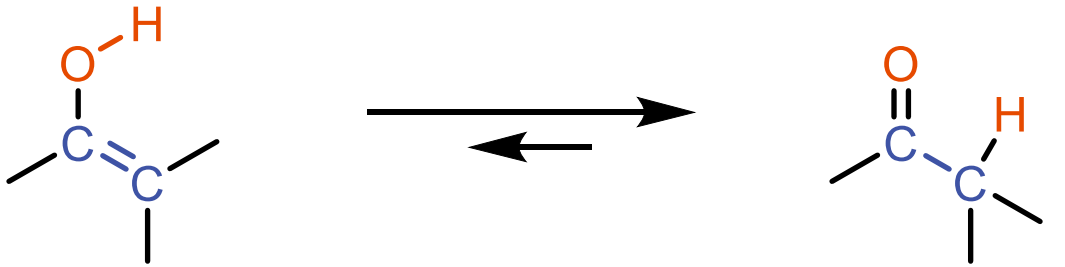

1-hexyn

*cis* a *trans*-1-brom-1-hexen

## Hydratace alkynů katalyzovaná $Hg^{2+}$



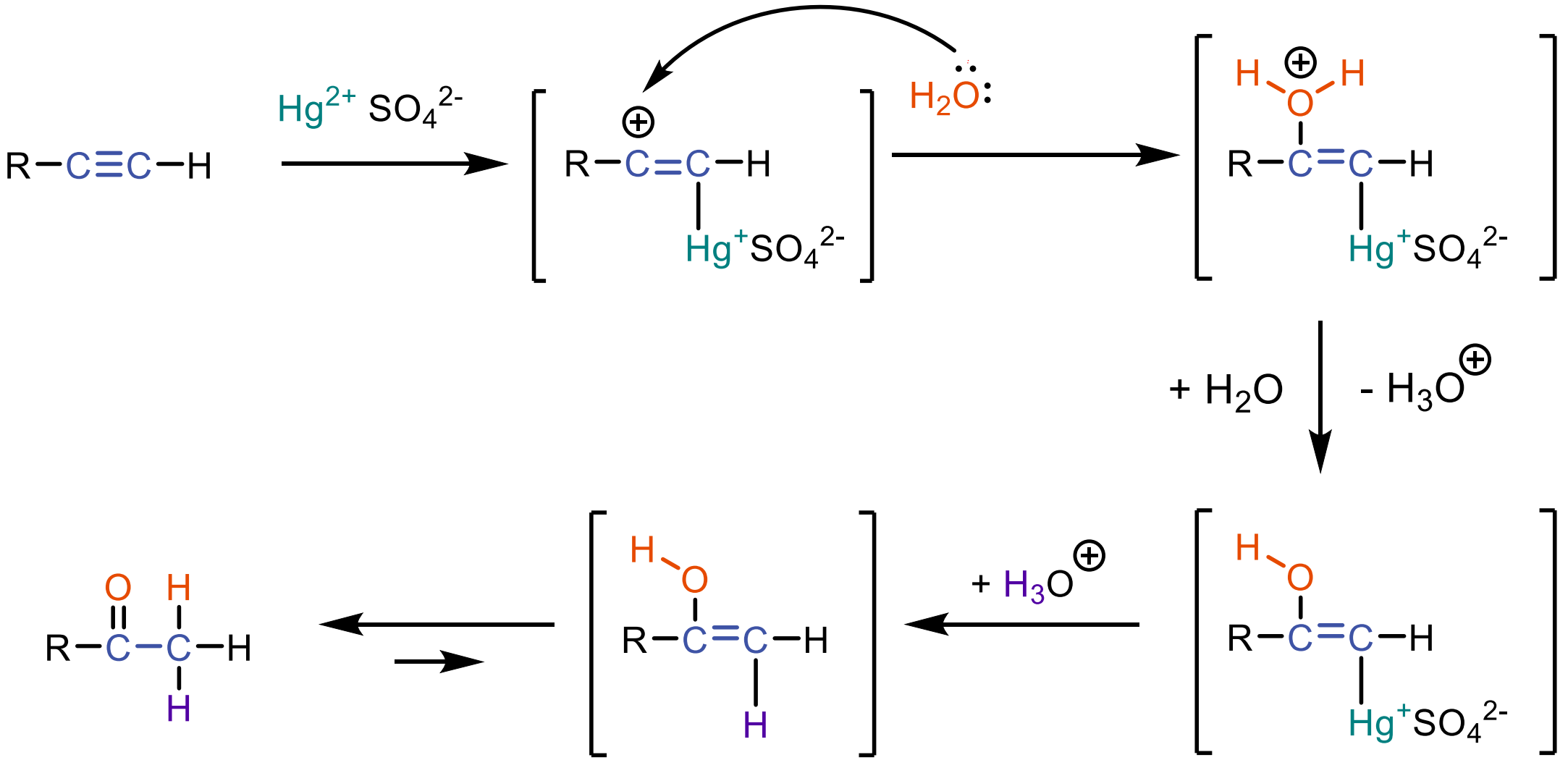

### Keto-enol tautomerie



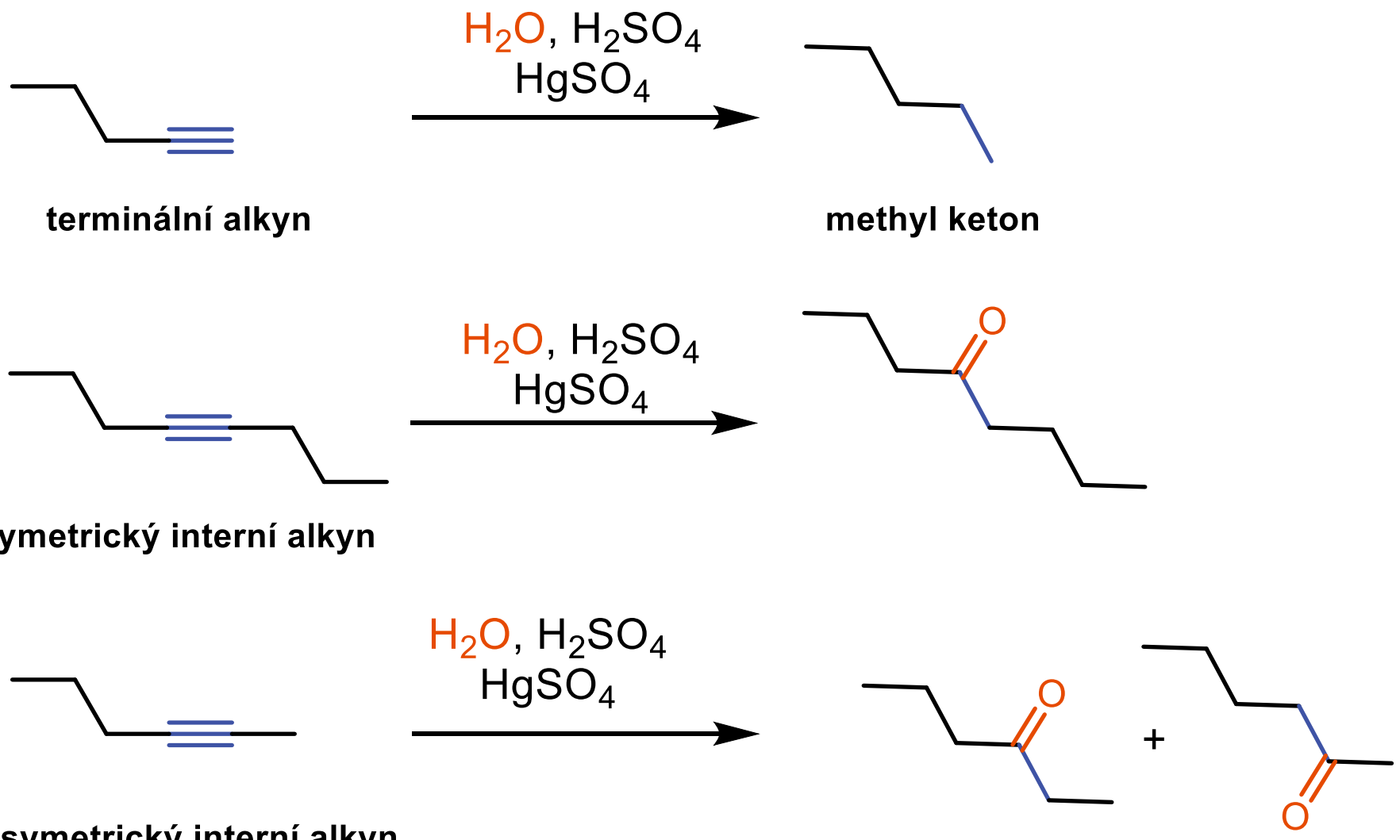

**enol** forma

**keto** forma

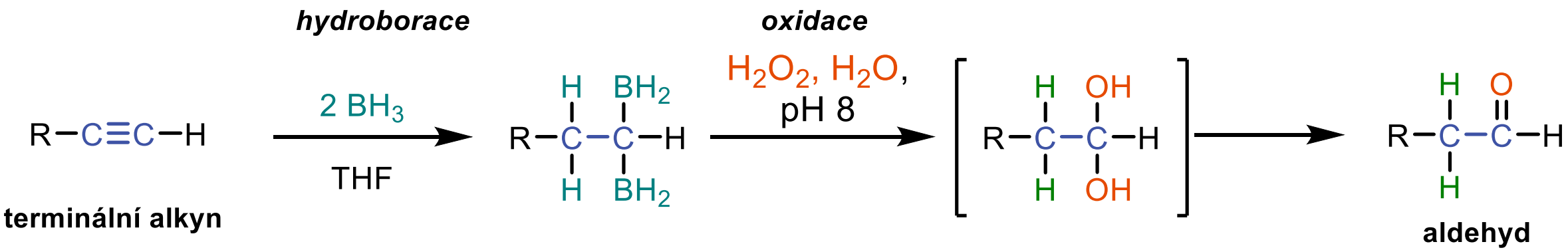
*Mechanismus hydratace alkynů*

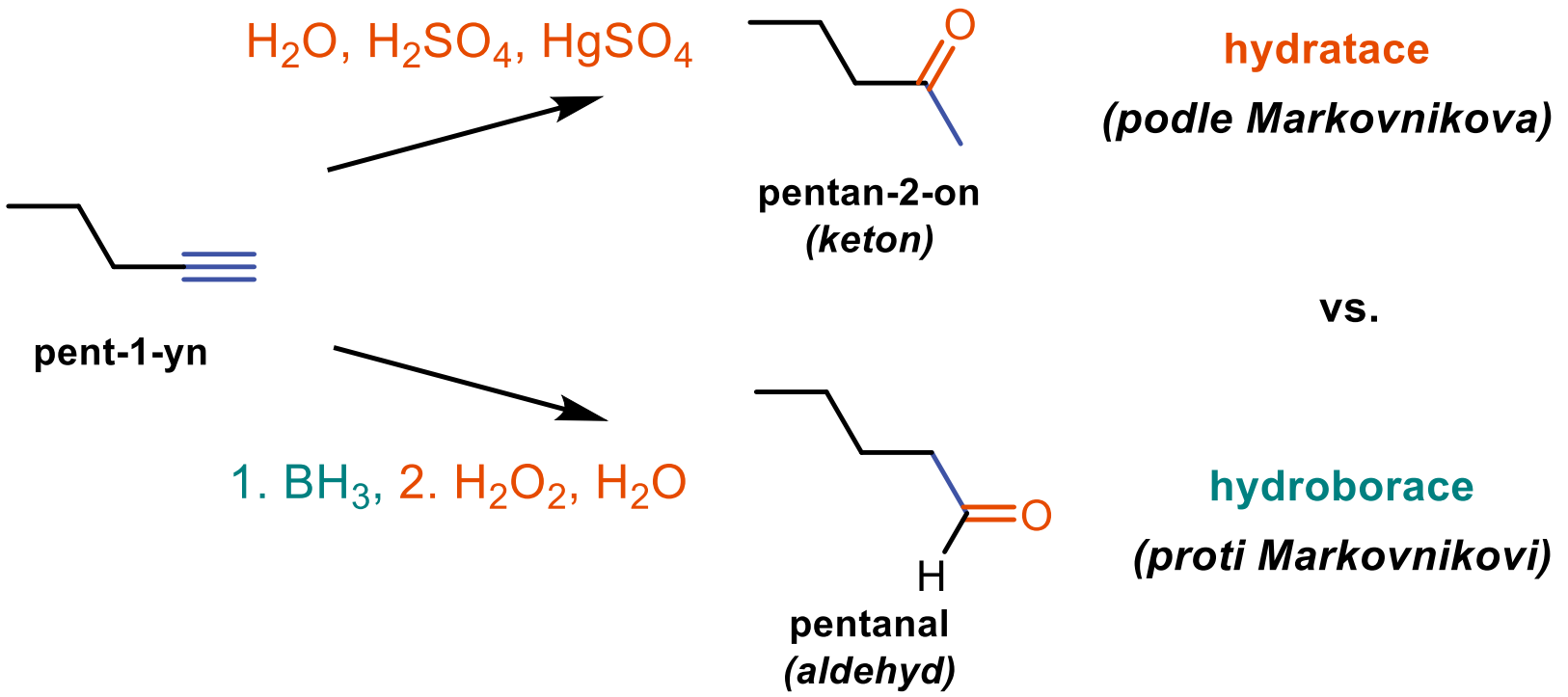


# Hydratace alkynů – syntetické využití

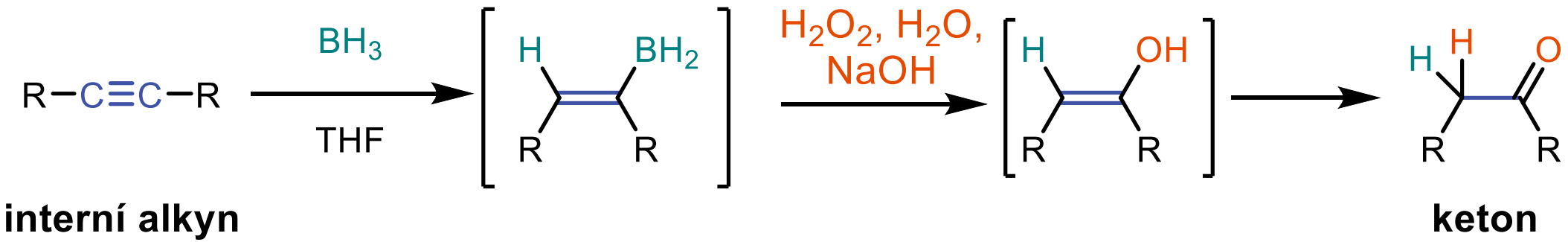


# Hydroborace alkynů

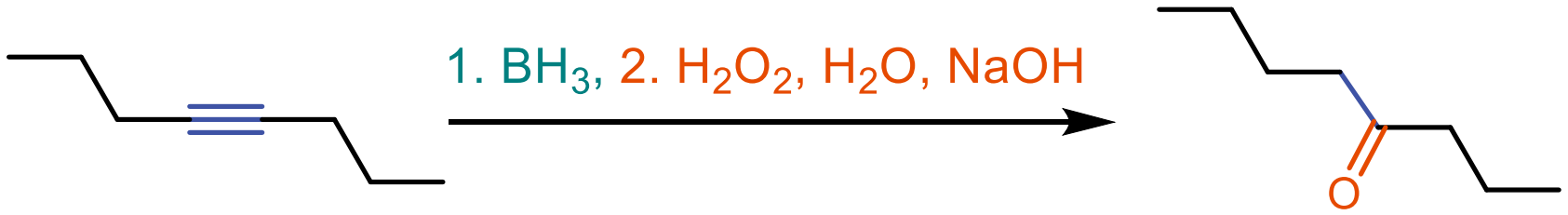


# Hydroborace alkynů

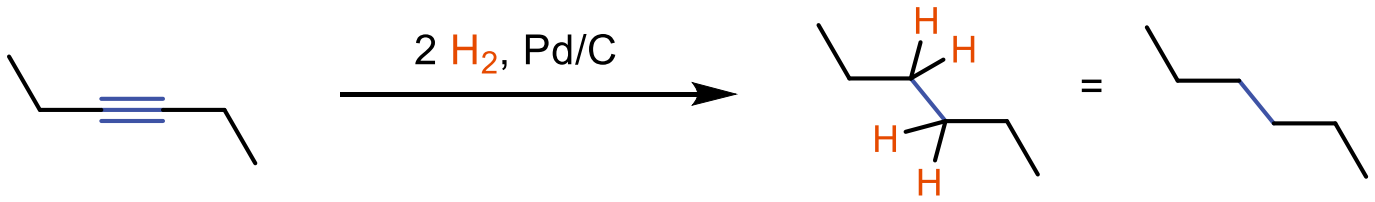



**interní alkyn** **keton**

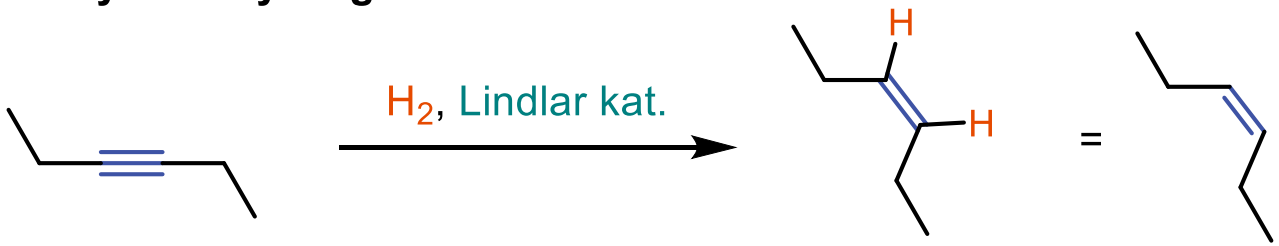


# Redukce alkynů

## Katalytická hydrogenace



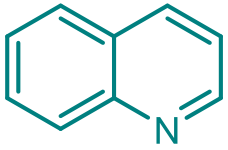

## Katalytická hydrogenace - Lindlar



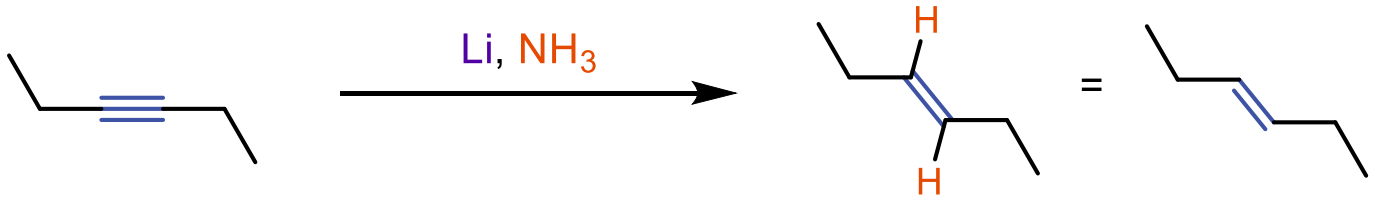

*cis*-alken
*Z*-alken

**Lindlarův katalyzátor**

5% $Pd/CaCO_3$, $Pb(OAc)_4$, chinolin

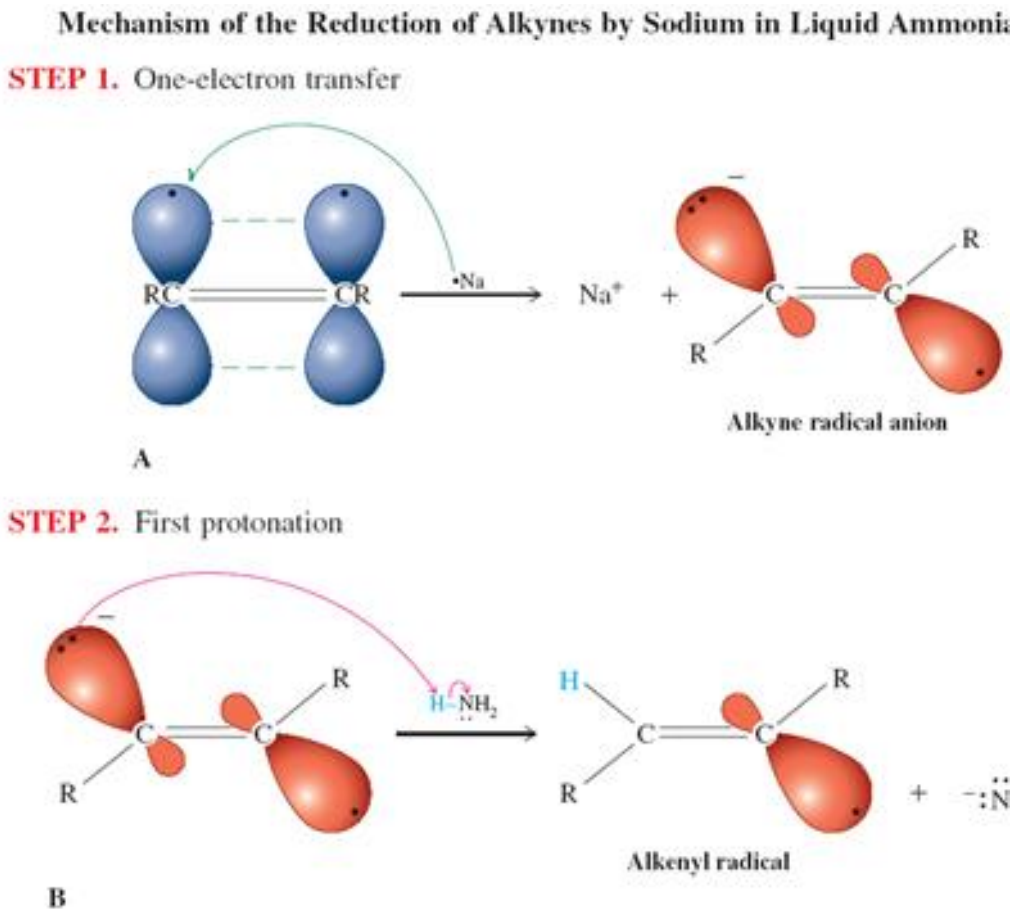


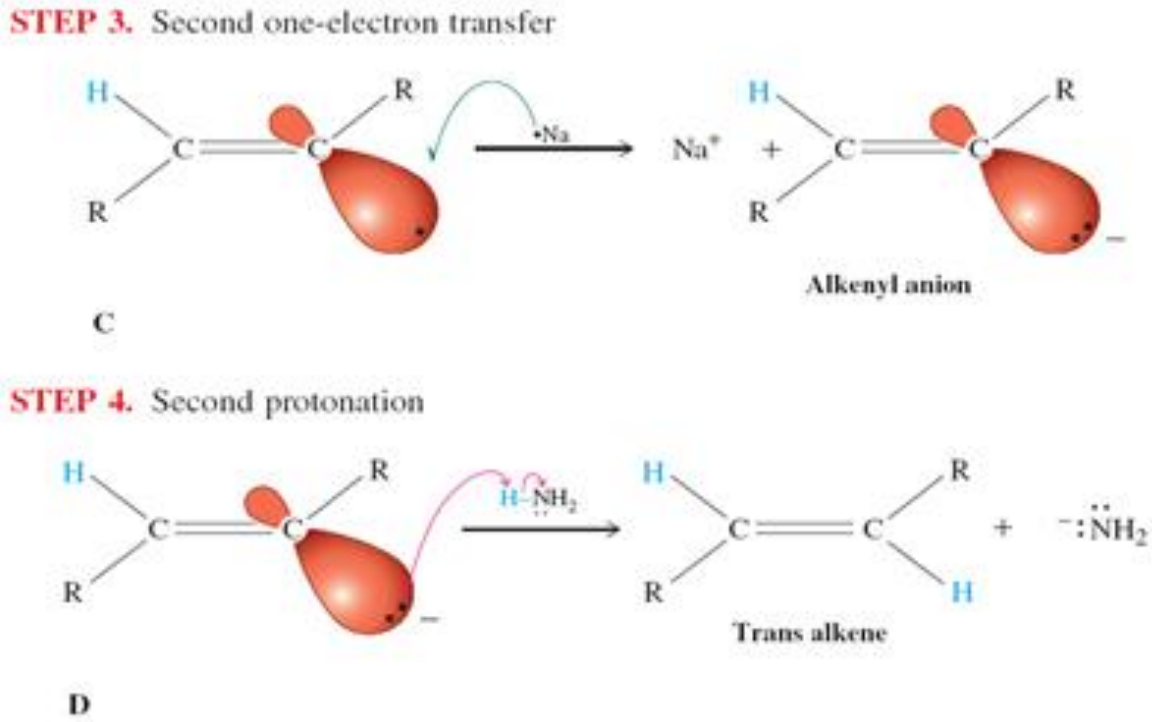

## Redukce alkalickým kovem v kapalném amoniaku (Birchova redukce)




*trans*-alken
*E*-alken

# Birchova redukce - mechanismus




Druhý transfer elektronu je rychlejší než *cis*/*trans* izomerizace alkenylového radikálu.

Finální alken je stabilní vůči redukci.

# Oxidativní štěpení alkynů