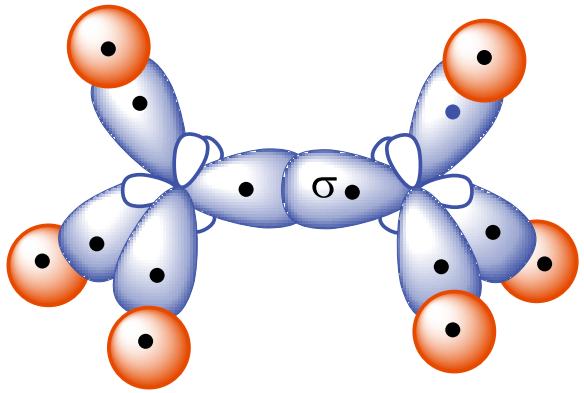
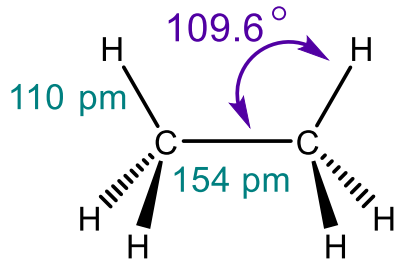
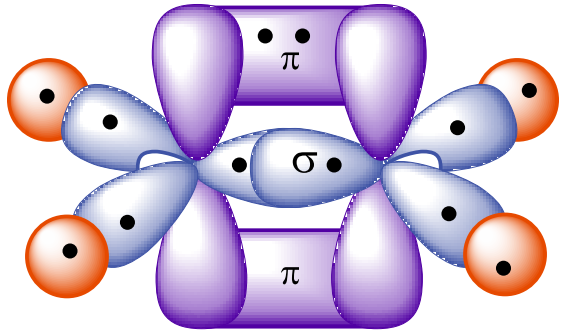
12_Souhrn a Opakování

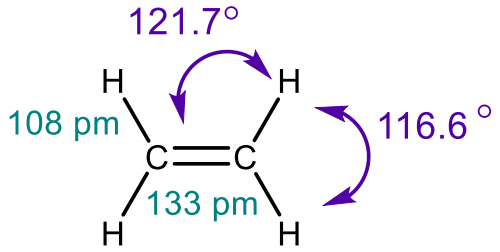
sp^3


σ

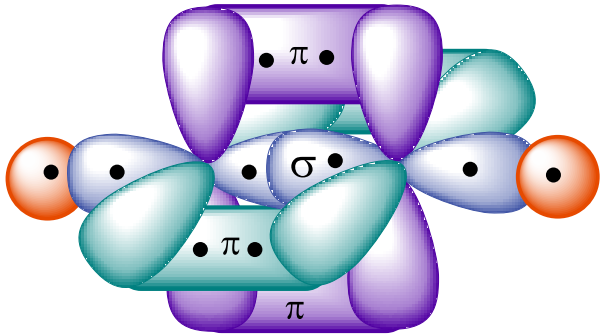

109.6°
H
H
110 pm
C
C
154 pm
H
H
H
H

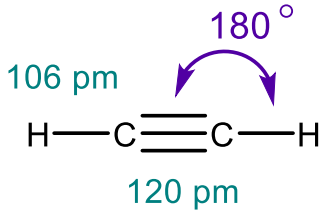
sp^2


π
σ
π


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

sp

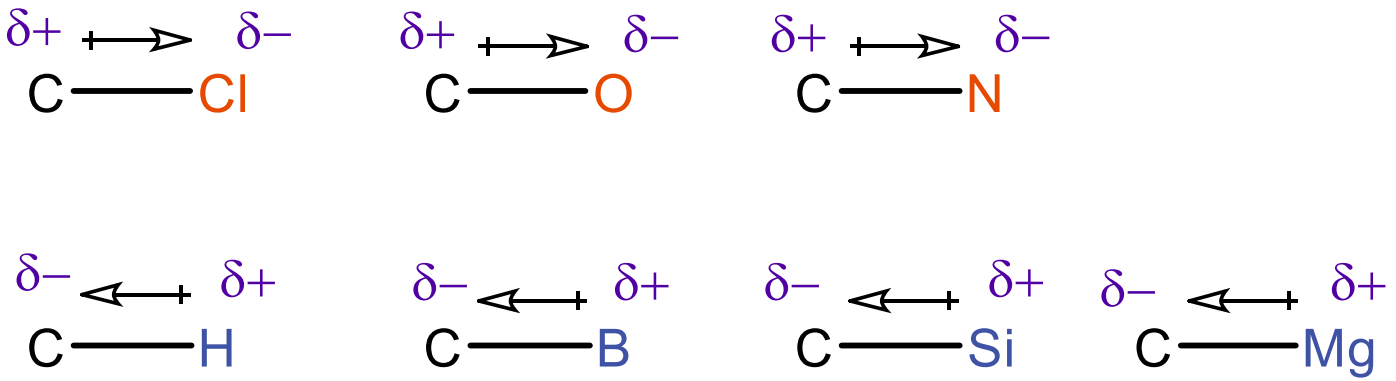

π
σ
π
π


180 °
106 pm
H—C≡C—H
120 pm

Polarita vazby

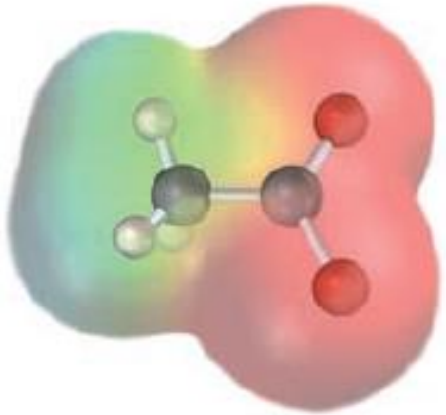
Induktivní (indukční) efekt *I*

kovalentní vazba mezi rozdílnými atomy: elektronový pár není oběma atomy sdílen stejně. (Jeden atom přitahuje elektrony více a jeden méně) – tvorba tzv. **parciálního náboje** na jednotlivých atomech → **polární kovalentní vazba**.

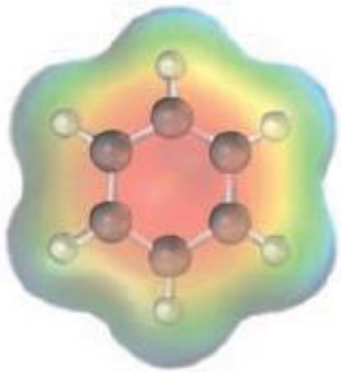


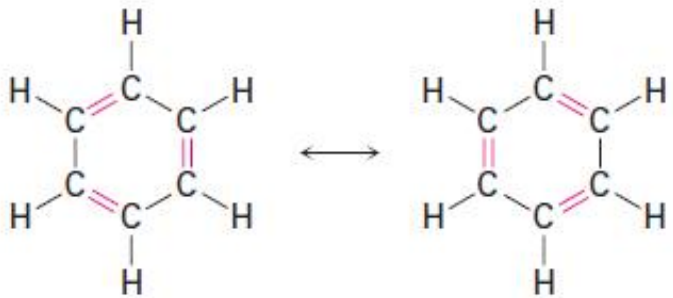
Posun valenčních elektronů označujeme u **polárních kovalentních vazeb** jako **induktivní efekt**.
Atomy nebo funkční skupiny, které přitahují elektrony silněji než vodík vykazují ***-I efekt***.
Atomy nebo funkční skupiny, které přitahují elektrony slaběji než vodík vykazují ***+I efekt***.

Rezonance

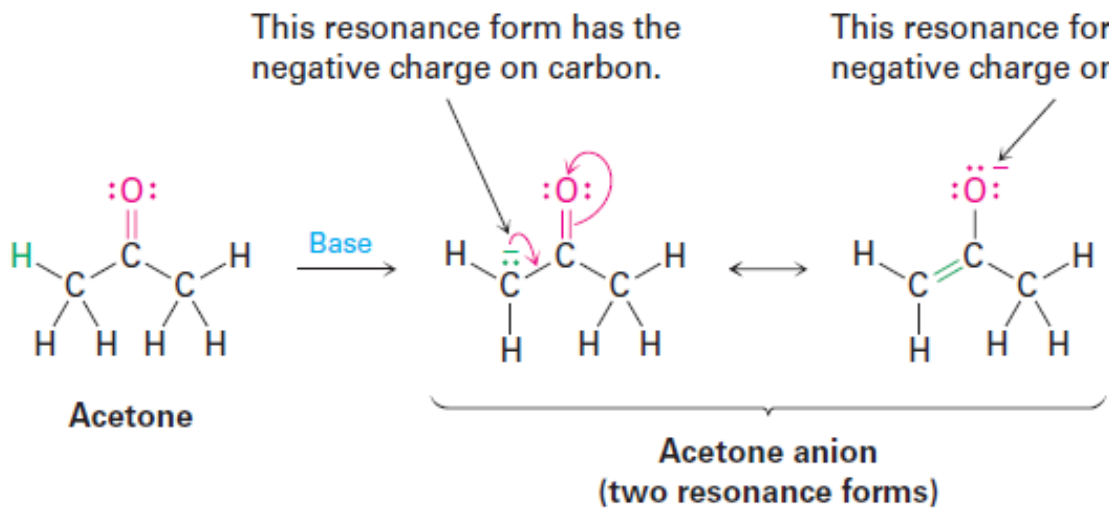


Acetate ion—two resonance forms





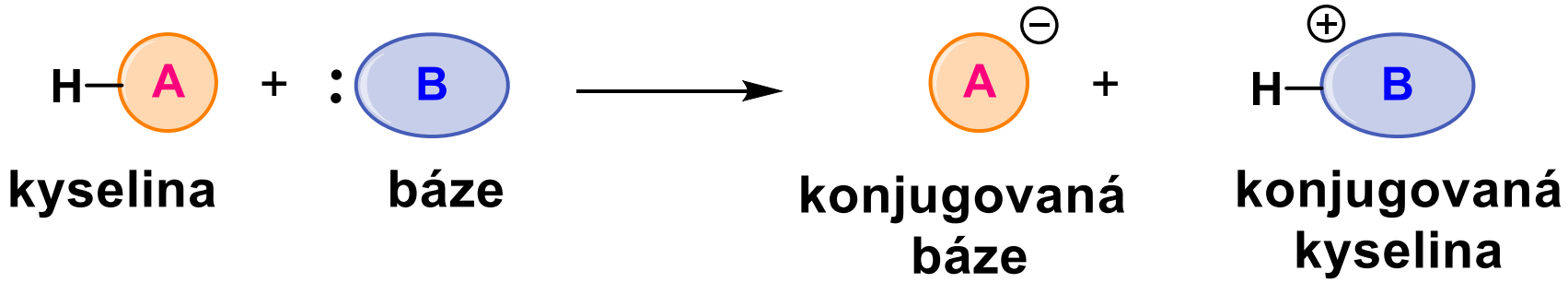
Benzene (two resonance forms)



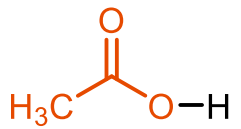
Acetone

Acetone anion
(two resonance forms)

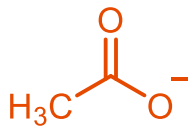
Kyseliny a Báze: **Brønstedova teorie**



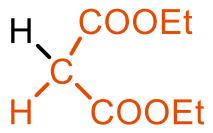
HCl	+	NaOH	→	NaCl	+	HOH
silná kyselina		silná báze		sůl		
HCl	+	H_2O	→	Cl^-	+	H_3O^+
silná kyselina		slabá báze				
H_2O	+	NH_3	→	OH^-	+	NH_4^+
slabá kyselina		slabá báze				



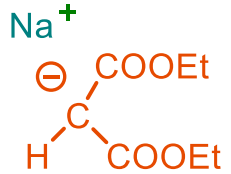
+ H_2O →



+ H_3O^+



+ $CH_3O^-Na^+$ →



+ $HOCH_3$

Kyseliny a Báze: **Brønstedova teorie**

$$HA + H_2O \rightleftharpoons A^- + H_3O^+$$

Rovnovážná konstanta $K = \dfrac{[H_3O^+]\,[A^-]}{[HA]\;[H_2O]}$

Konstanta kyselosti $K_a = K\,[H_2O] = \dfrac{[H_3O^+]\,[A^-]}{[HA]}$

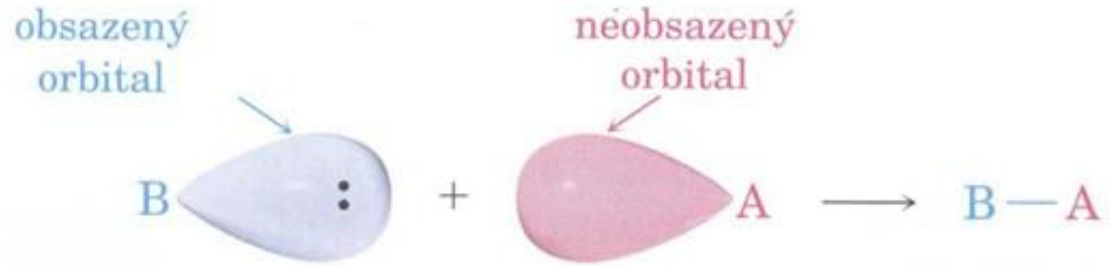
Síla kyseliny se uvává v $pK_a = -\log K_a$

TABULKA 2.3 Relativní síla některých běžných kyselin a jejich konjugovaných bází

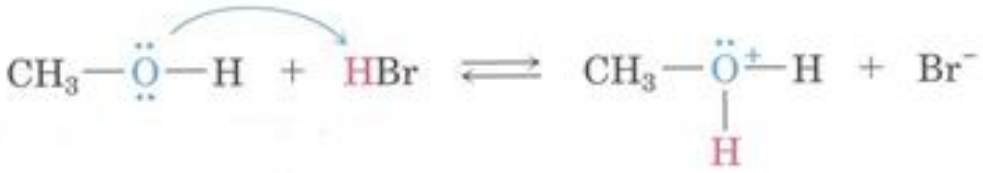
	Kyselina Název	pK_a	Konjugovaná báze Název		
slabší kyselina	CH_3CH_2OH	ethanol	16,00	$CH_3CH_2O^-$	ethoxidový ion
	H_2O	voda	15,74	HO^-	hydroxidový ion
	HCN	kyanovodíková kyselina	9,31	CN^-	kyanidový ion
	CH_3COOH	octová kyselina	4,76	CH_3COO^-	acetátový ion
	HF	kyselina fluorovodíková	3,45	F^-	fluoridový ionn
	HNO_3	kyselina dusičná	–1,3	NO_3^-	dusičnanový ion
silnější kyselina	HCl	kyselina chlorovodíková	–7,0	Cl^-	chloridový ion

silnější báze ↑ slabší báze

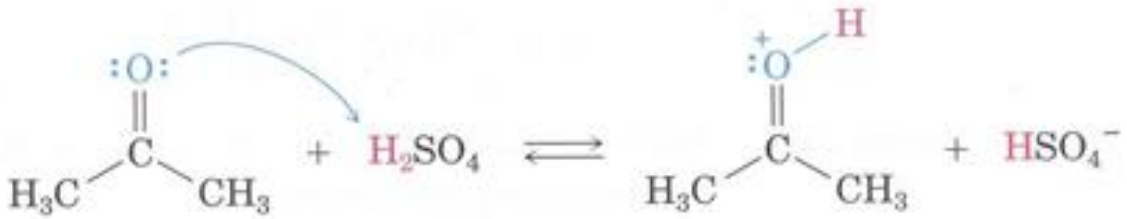
Kyseliny a Báze: **Lewisova teorie**



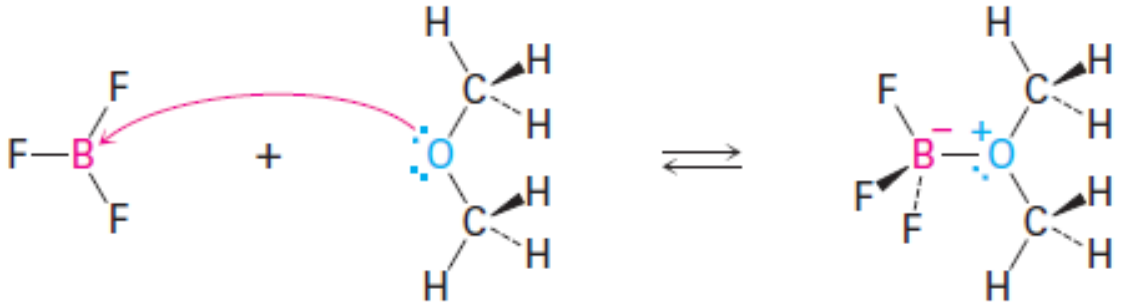
Lewisova báze **Lewisova kyselina**



methanol (báze) **bromovodík** (kyselina) **methyloxonium-bromid**



aceton (báze) **kyselina sírová**

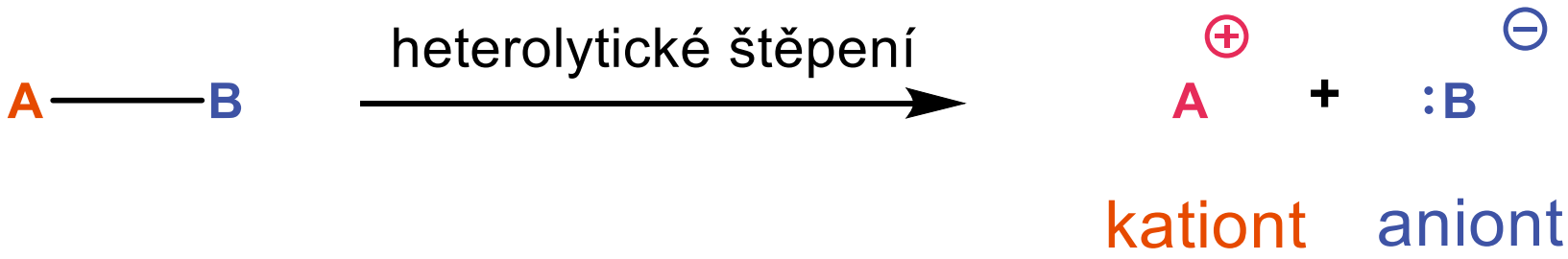


Boron trifluoride (Lewis acid) **Dimethyl ether** (Lewis base) **Acid–base complex**

Štěpení vazeb

Radikálové reakce

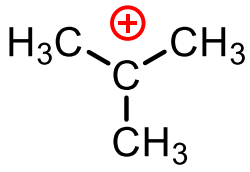
Polární reakce

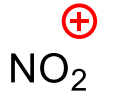


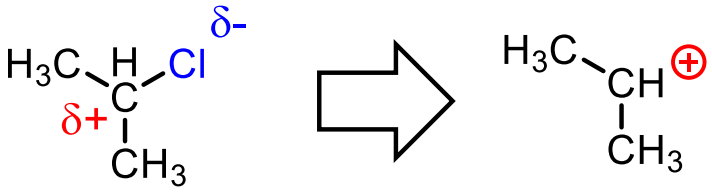
Elektrofil vs. nukleofil (reagenty)

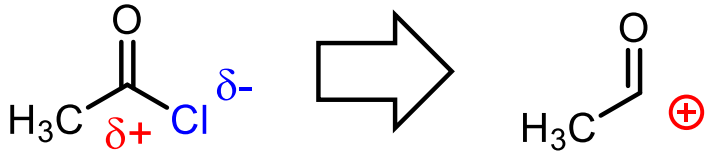
Elektrofilní reagent:

- má afinitu k záporně nabitým částicím
- Jde o kation nebo elektronově chudou neutrální molekulu



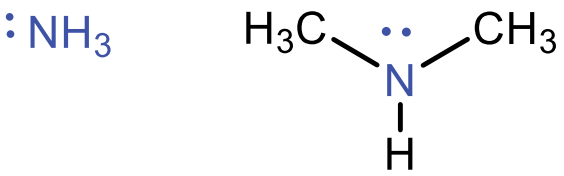


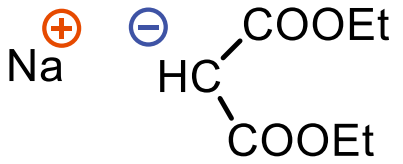


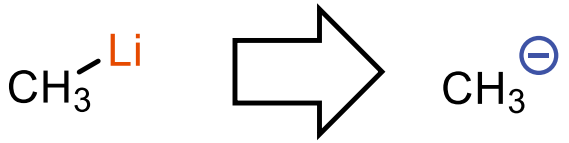


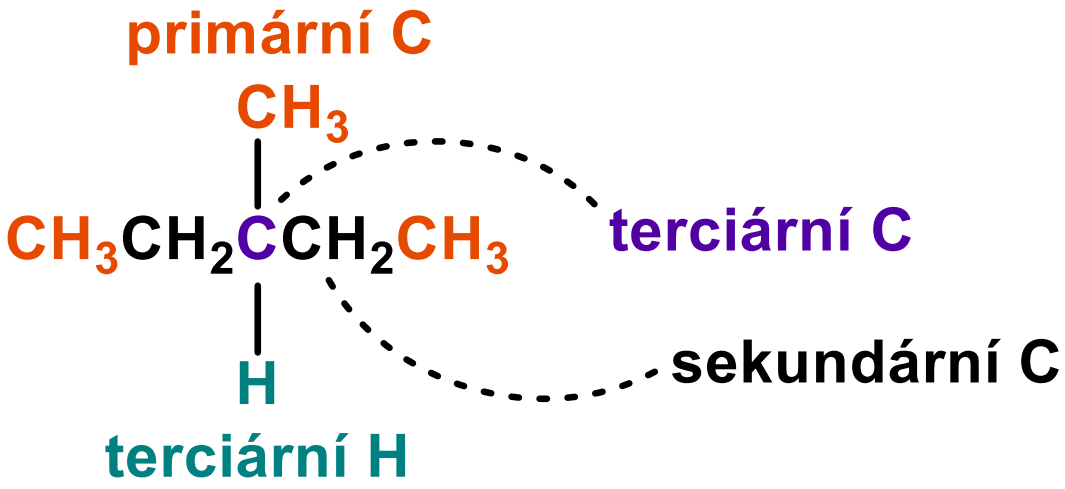
Nukleofilní reagent:

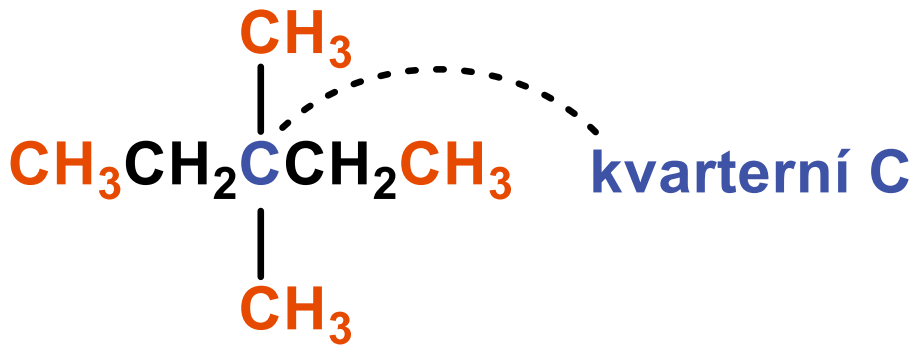
- má afinitu ke kladně nabitým částicím
- Jde o anion nebo elektronově bohatou neutrální molekulu



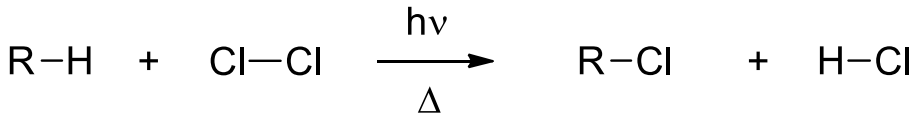




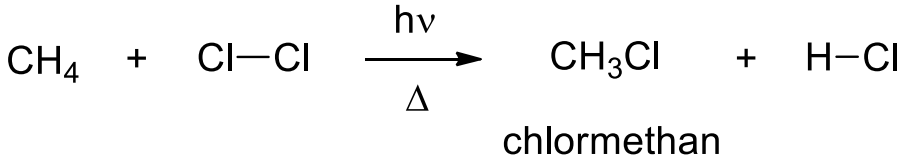

primární C
CH3
CH3CH2CCH2CH3
terciární C
sekundární C
H
terciární H

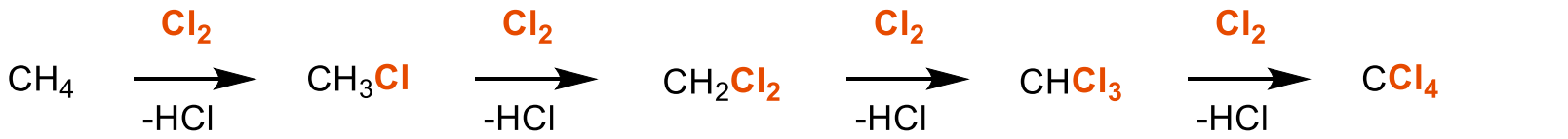

CH3
CH3CH2CCH2CH3
kvarterní C
CH3

Alkany



Halogenace alkanů:



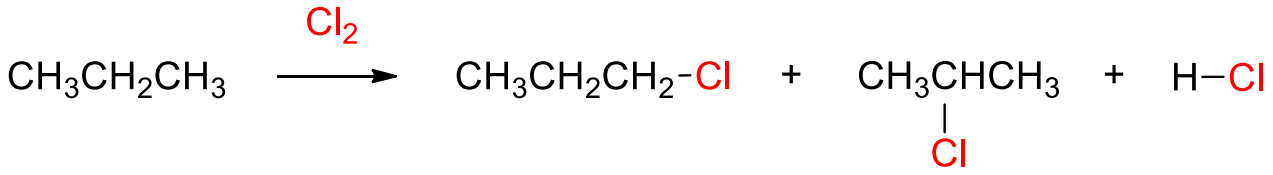


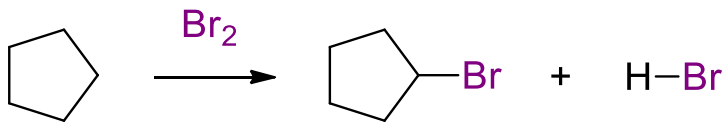
chlormethan
b.v. -24.5°C

dichlormethan
b.v. 40°C

trichlormethan
b.v. 61.7°C
(chloroform)

tetrachlormethan
b.v. 75.6°C



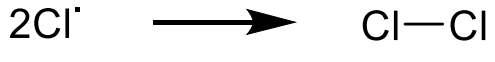


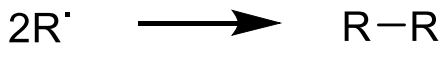
Mechanismus halogenace:

Iniciace

Propagace

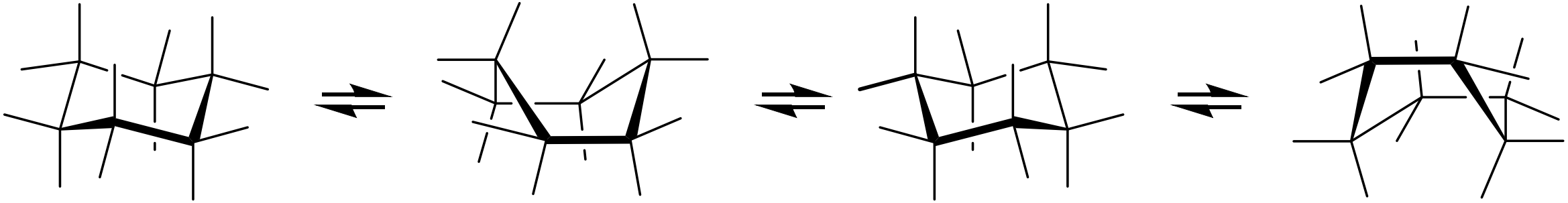
Terminace





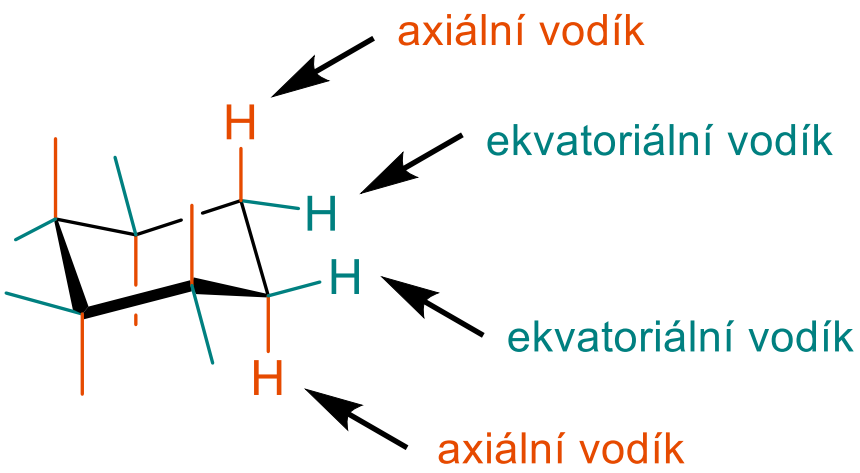
Stereochemie:

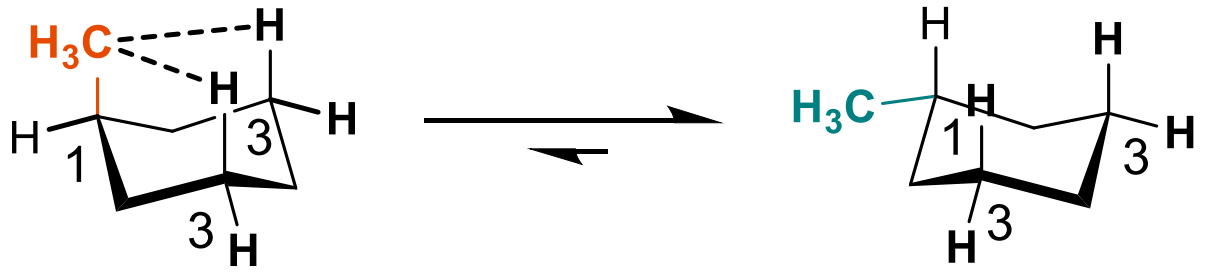
Konformace cyklohexanu



židličková konformace | **vaničková konformace** | **židličková konformace** | **vaničková konformace**

židličková konformace





Me v axiálnípoloze
5%

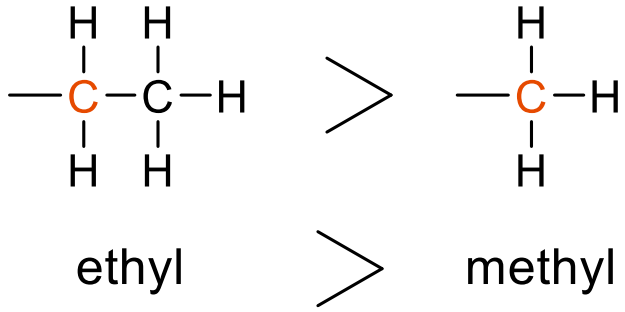
Me ekvatoriální poloze
95%

Pravidla: *Cahn-Ingold-Prelog*

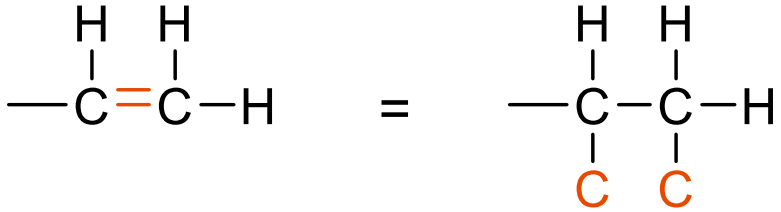
1. Priorita atomů se řídí atomovým číslem. Čím vyšší atomové číslo tím vyšší priorita.

I > Br > Cl > F > O > N > C > D > H

2. Pokud není možné určit prioritu podle pravidla 1 (např. dva atomy jsou stejné). Postupuje se podle stejného pravidla směrem od chirálního centra.

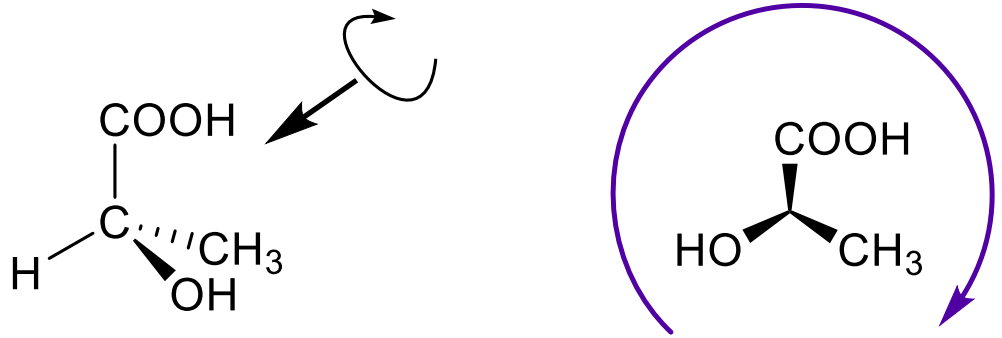


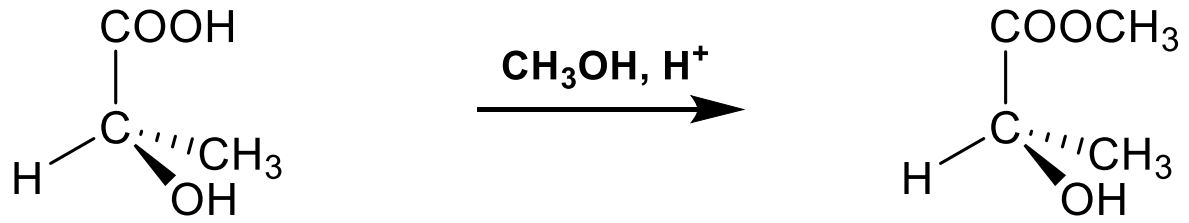
3. Násobné vazby se považují rovné násobkům jednoduchým vazeb.



Pořadí důležitosti (priority) jednotlivých atomů a funkčních skupin:

I >Br > Cl > SO_2R > SOR > SR > SH > F > OCOR > OR > OH > NO_2 > NHCOR > NR_2 > NHR > NH_2 > CCl_3 > COCl > COOR > COOH > $CONH_2$ > COR > CHO > CR_2OH > CHROH > CH_2OH > CR_3 > C_6H_5 > CHR_2 > CH_2R > CH_3 > D> H



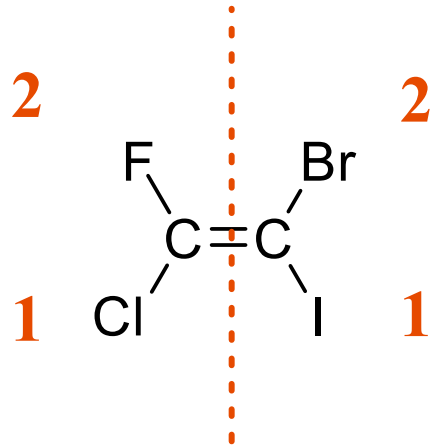


kyselina (*R*)-(-)-mléčná **methyl (*R*)-(+)-laktát**

R/S – stereodeskriptory nesouvisí se specifickou rotací!!!

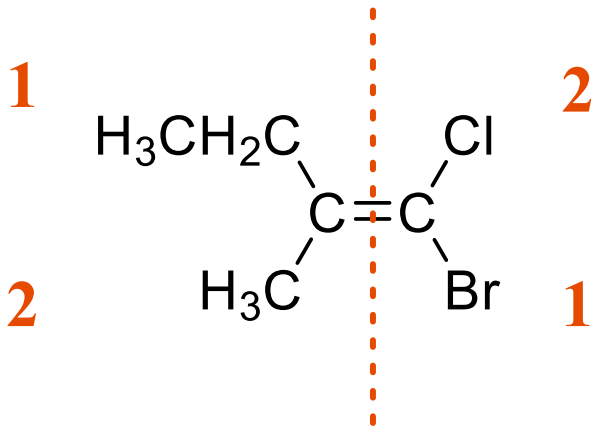
E-Z pravidla pro *cis-trans* izomerii na dvojné vazbě

Cahn-Ingold-Prelogův systém je vhodný pro popis izomerie na dvojné vazbě



Z (z německého ***zusammen***, spolu)

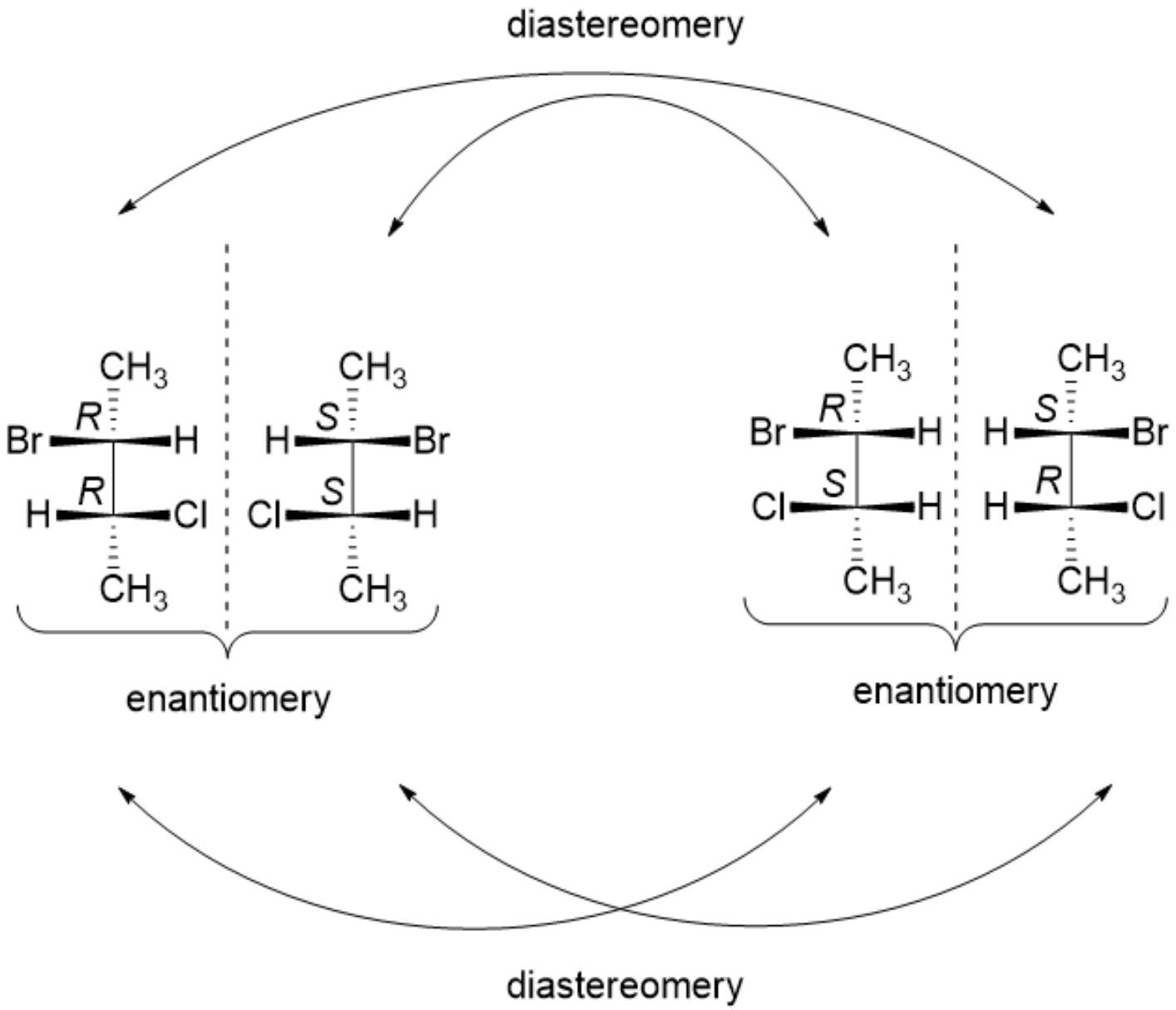
(*Z*)-1-brom-2-chlor-2-fluor-1-jodethen



E (z německého ***entgegen***, proti)

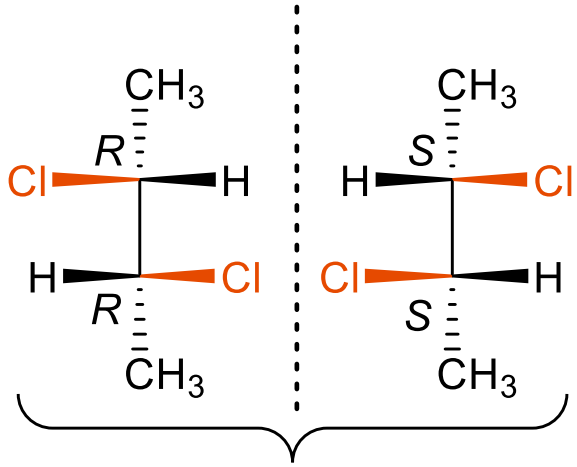
(*E*)-1-brom-1-chlor-2-methylbut-1-en

Sloučeniny s více než jedním stereogenním centrem – 2-brom-3-chlorbutan

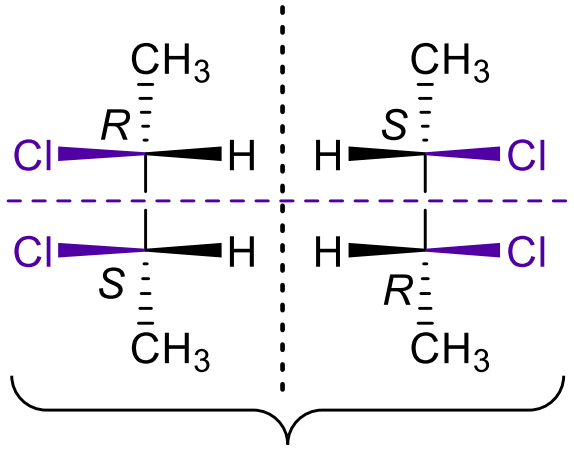


meso sloučeniny

2,3-dichlorbutan



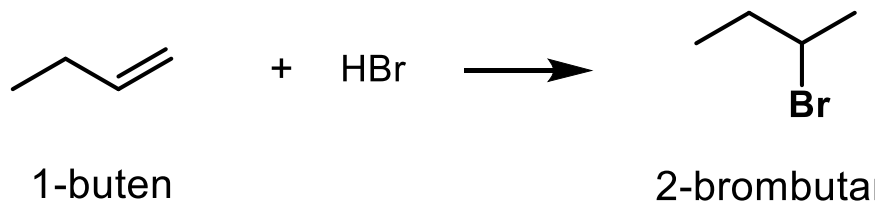
enantiomery



rovina symetrie

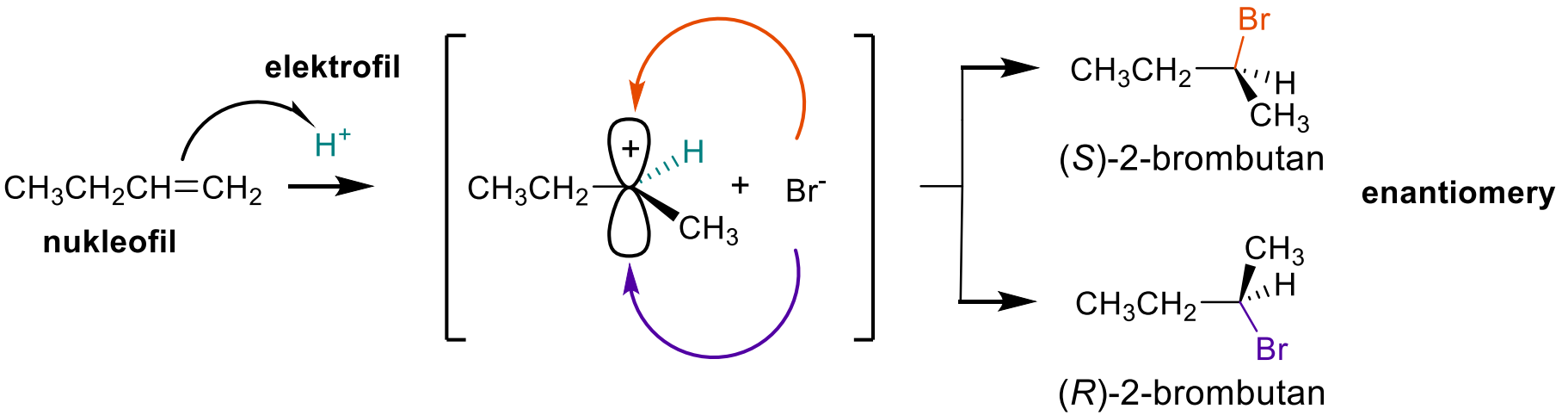
stejná sloučenina
achirální *meso* forma

Vznik a dělení enantiomerů



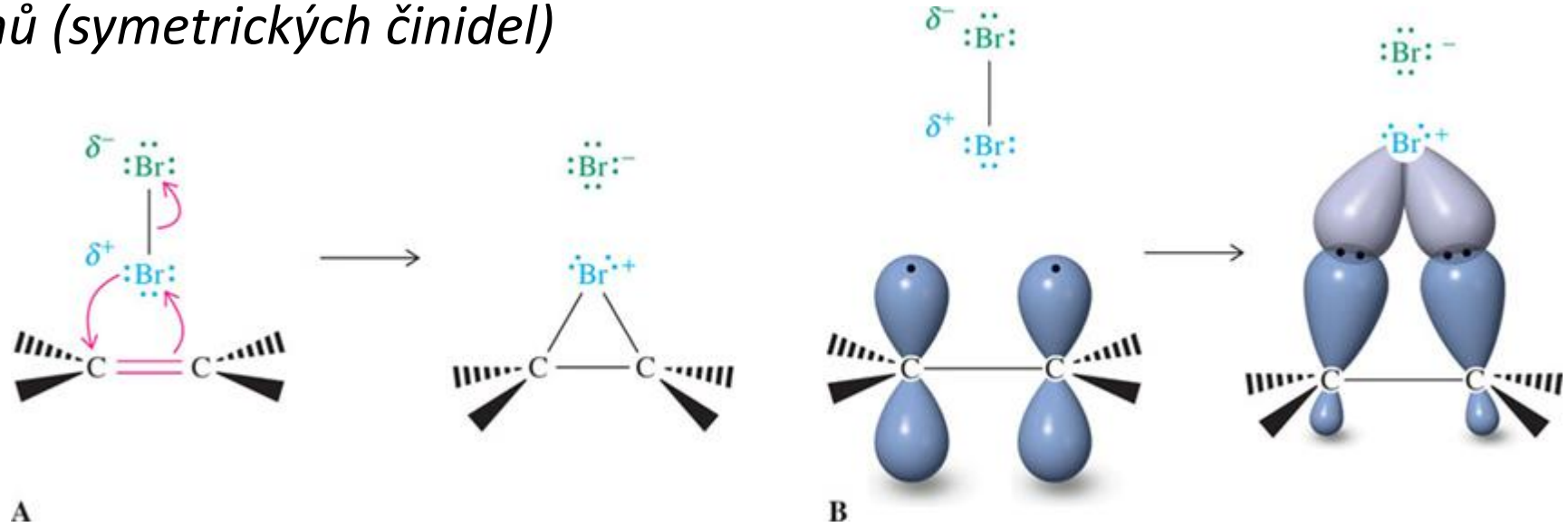
1-buten

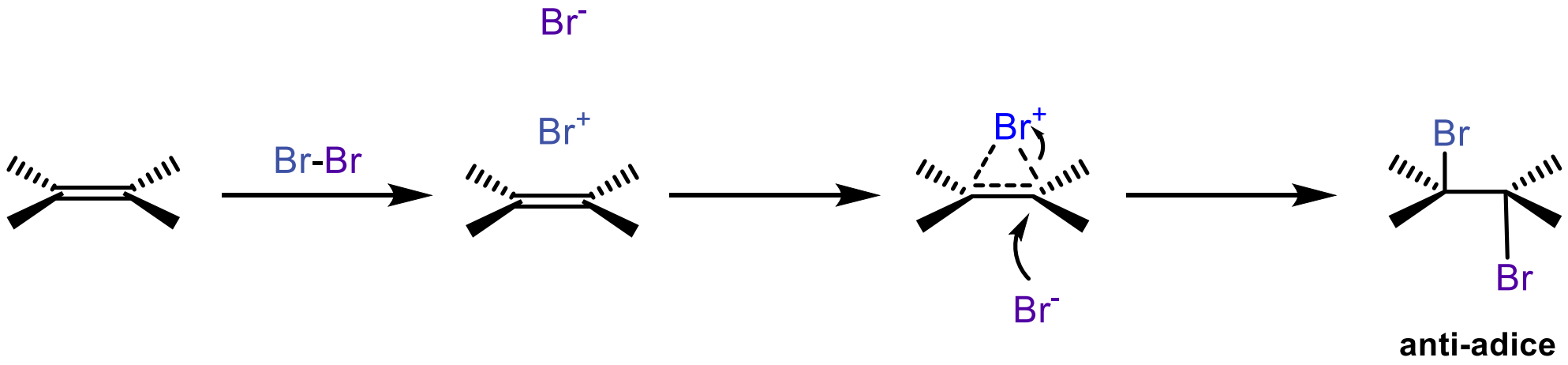
2-brombutan



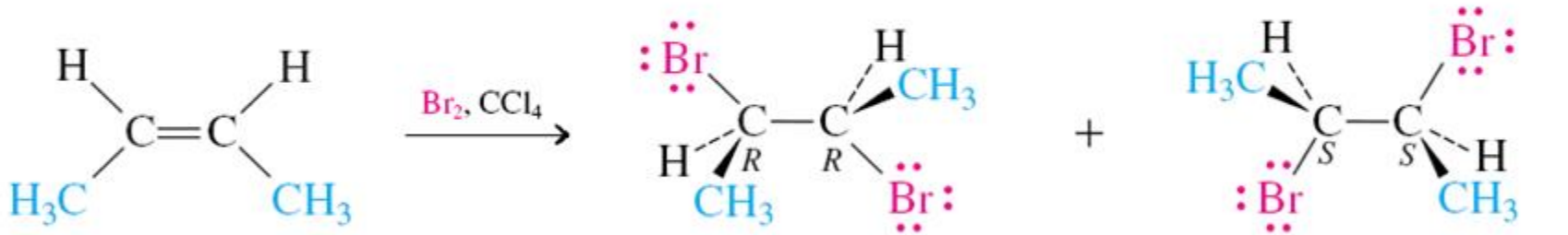
Alkeny: Elektrofilní adice

Adice halogenů (symetrických činidel)





Stereospecific 2-Butene Bromination



cis-2-Butene

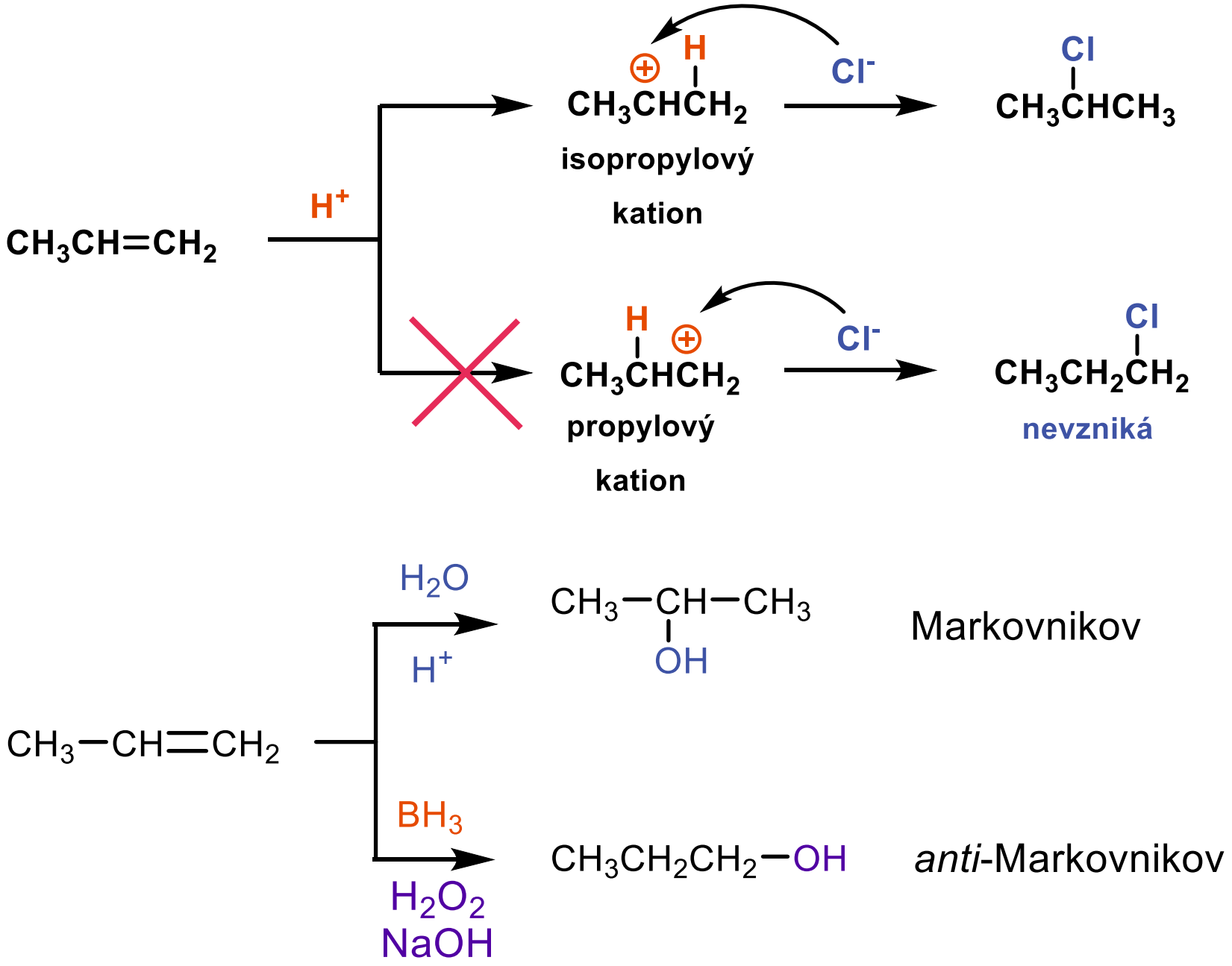
(2*R*,3*R*)-2,3-Dibromobutane

(2*S*,3*S*)-2,3-Dibromobutane

trans-2-Butene

Identical

meso-2,3-Dibromobutane

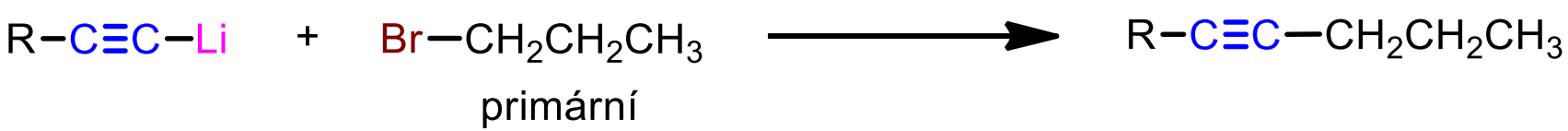

CH3CH=CH2
H+
CH3CHCH2
H
Cl-
isopropylový
kation
CH3CHCH3
Cl
CH3CHCH2
H
Cl-
propylový
kation
CH3CH2CH2
Cl
nevzniká
CH3–CH=CH2
H2O
H+
CH3–CH–CH3
OH
Markovnikov
BH3
H2O2
NaOH
CH3CH2CH2–OH
anti-Markovnikov

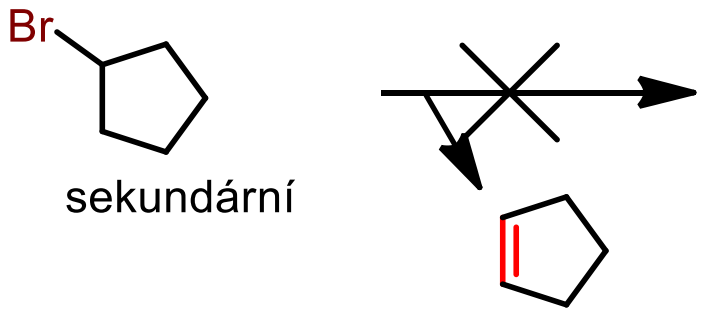
Alkyny:

Deprotonace terminálních alkynů a následné reakce

Reakce se silnými bázemi - deprotonace

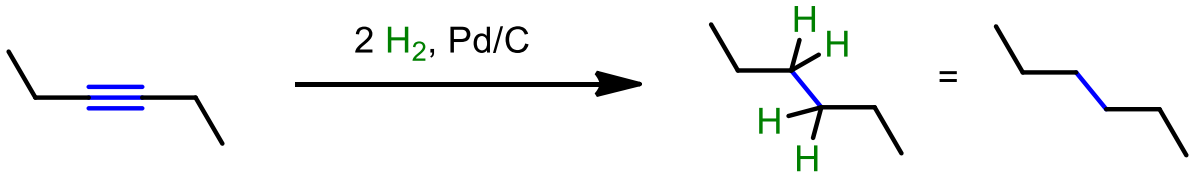
Deprotonace + alkylace



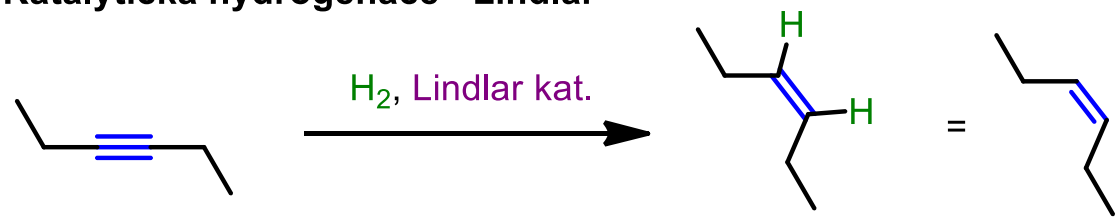


Redukce alkynů

Katalytická hydrogenace



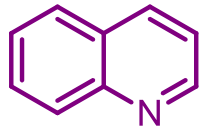
Katalytická hydrogenace - Lindlar



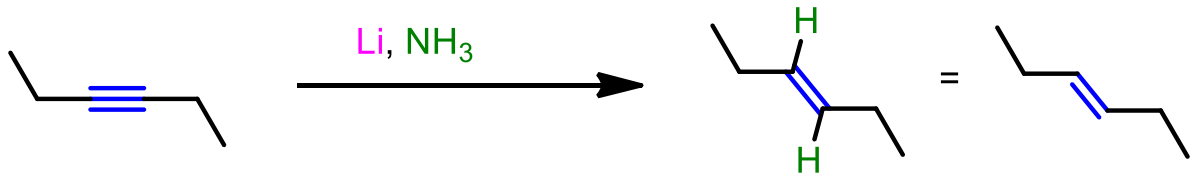
cis-alken
Z-alken

Lindlarův katalyzátor

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



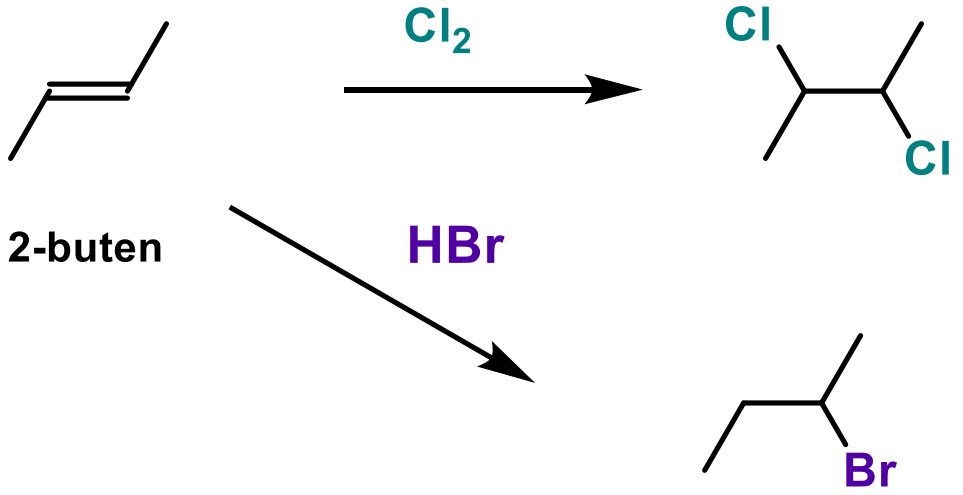
Redukce alkalickým kovem v kapalném amoniaku (Birchova redukce)



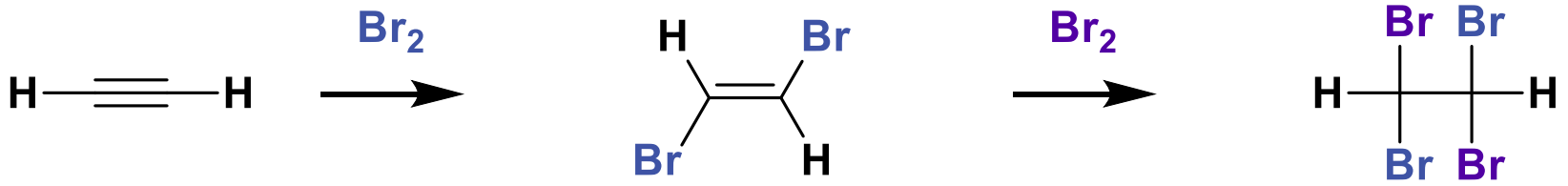
trans-alken
E-alken

Halogenderiváty

Adice na alkeny

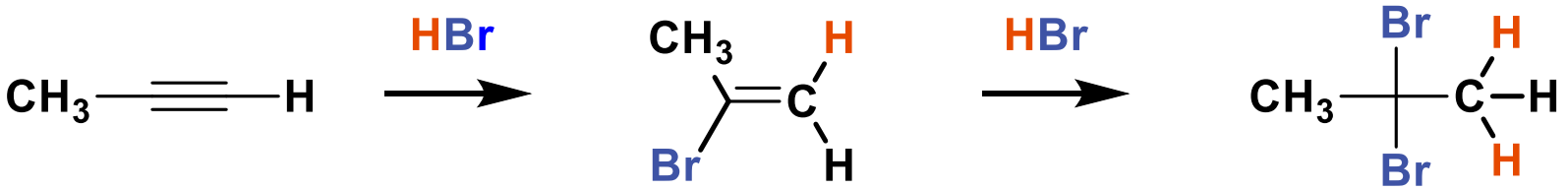


Adice na alkyny



trans-1,2-dibromethen

1,1,2,2-tetrabromethan

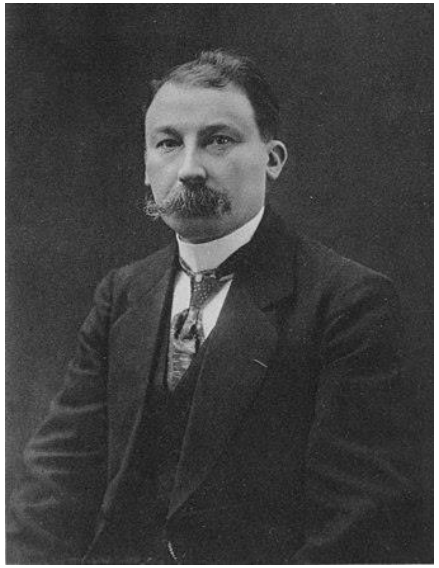


propyn

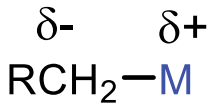
2-brompropen

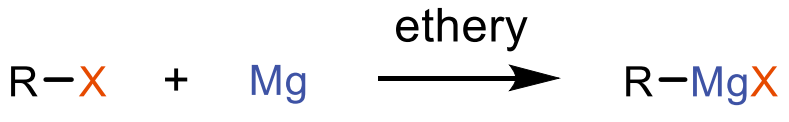
2,2-dibrompropan

Reakce alkylhalogenidů s kovy



Victor Grignard 1871
(wiki)



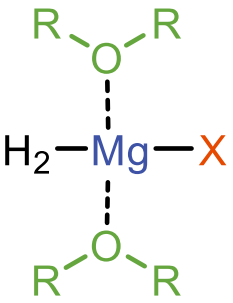


R = alkyl, aryl, alkenyl
X = Cl, Br, I

diethylether tetrahydrofuran

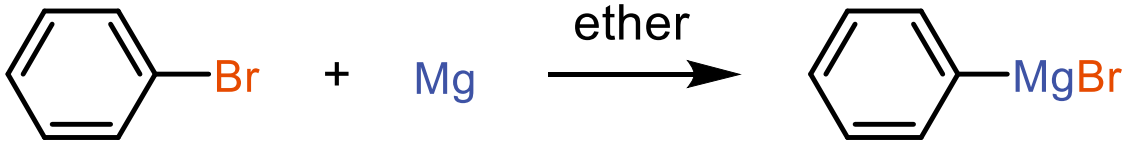
Lewisova zásada

Lewisova kyselina



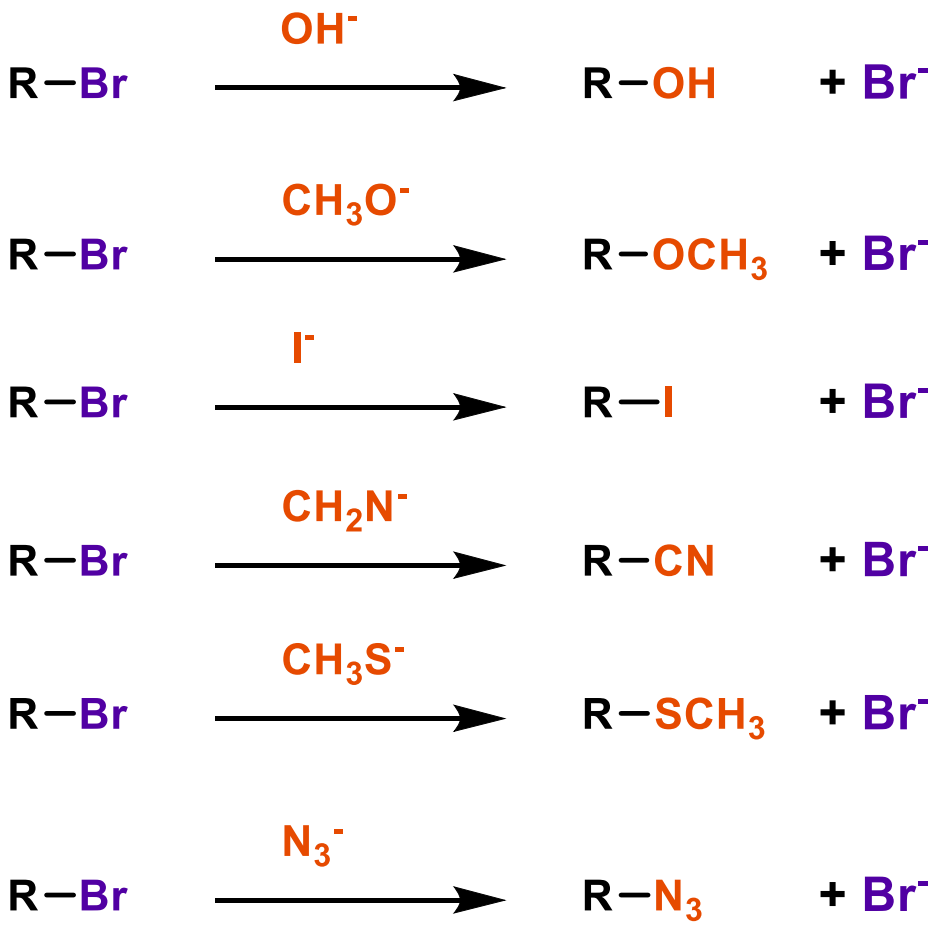
Grignardova činidla

methylmagnesiumjodid

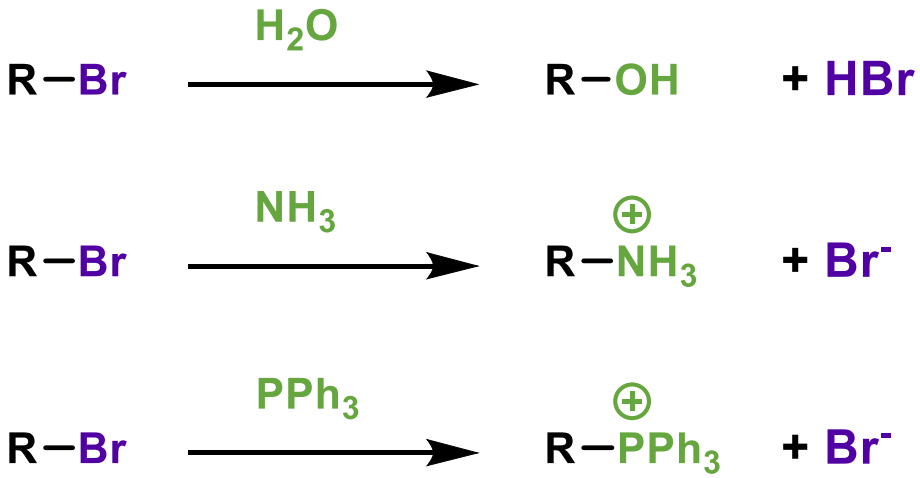


fenylmagnesiumbromid

Aniontový nukleofil

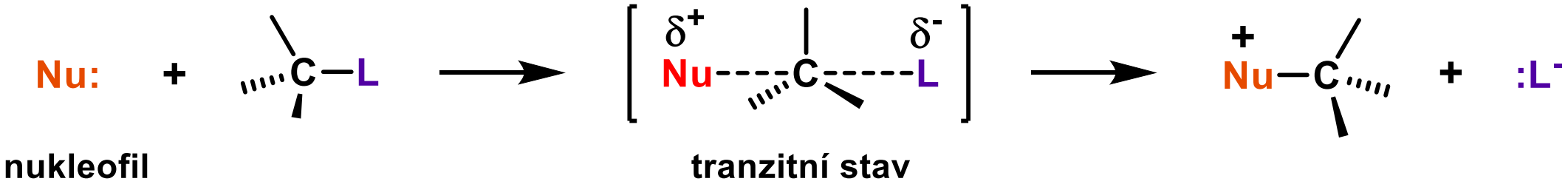


Neutrální nukleofil



Mechanismus nukleofilní substituce

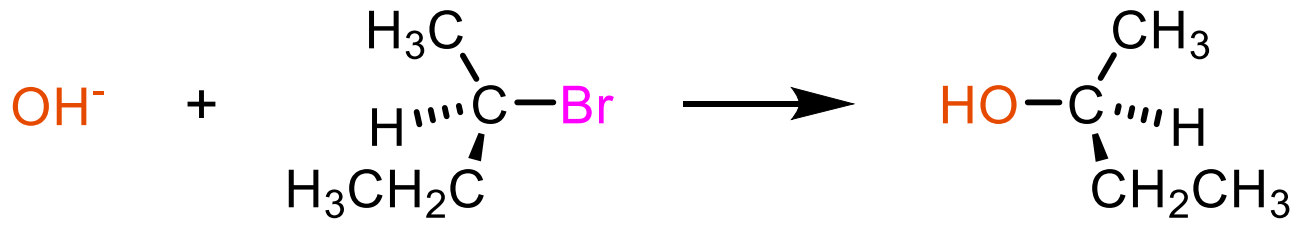
S_N2 mechanismus



S_N2 mechanismus má několik charakteristických průvodních jevů:

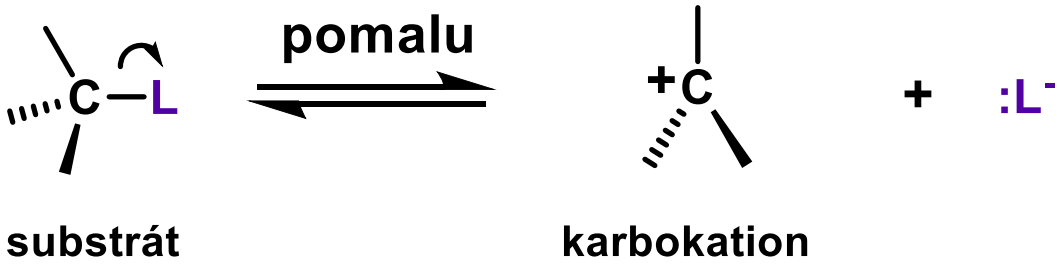
1. **Jelikož se reakce účastní nukleofil a substrát závisí reakční rychlost na koncentraci obou reaktantů.**

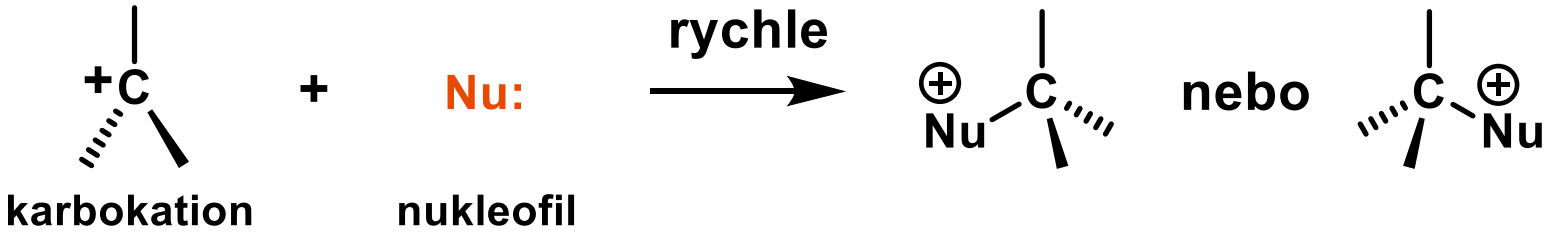
S_N2 substituce probíhá s inverzí konfigurace.



(*R*)-2-brombutan (*S*)-2-butanol

S_N1 mechanismus

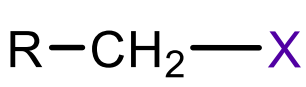
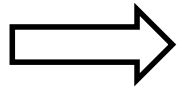


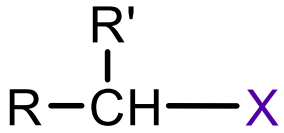
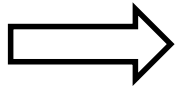


Srovnání S_N1 a S_N2 mechanismus

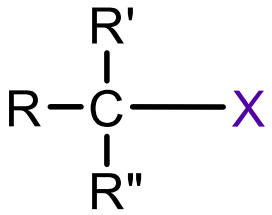
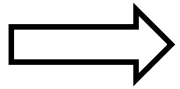
	S_N2 substituce	S_N1 substituce
Struktura halogenidu		
primární	běžná	vzácná*
sekundární	občas	občas
terciární	vzácná	běžná
Stereochemie	inverze	racemizace
Nukleofil	reakční rychlost závisí na koncentraci nukleofilu, mechanismus je upřednostňován pokud je nukleofil anion	reakční rychlost nezávisí na koncentraci nukleofilu, mechanismus je pravděpodobnější s neutrálními nukleofily
Rozpouštědlo	reakční rychlost je málo ovlivněná polaritou rozpouštědla (protická zpomalují)	Vzhledem k tomu, že meziprodukty jsou ionty, reakční rychlost závisí na polaritě rozpouštědla (polární protická urychlují)

* allylové a benzylové substráty tvoří výjimku

primární   S_N2

sekundární   S_N2 s nebazickými nukleofily

E2 se silnými bázemi

terciární   obvykle **E2**

S_N1 nebo **E1** s nebazickými nukleofily

Hückelovo pravidlo a aromaticita

Hückelovo pravidlo

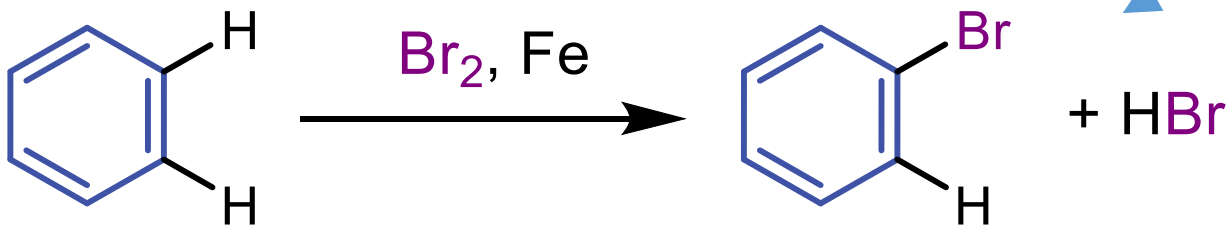
Planární cyklické systémy s **(4n+2) konjugovanými p elektrony** (n = 0, 1, 2 atd.), tj. systémy s 2, 6, 10, 14, atd. konjugovanými **p** elektrony, jsou **aromatické.**
Delokalizace p elektronů systém stabilizuje.

Planární cyklické systémy s **4n konjugovanými p elektrony**, tj. systémy s 4, 8, 12, 16, atd. konjugovanými **p** elektrony, jsou **antiaromatické.**
Delokalizace p elektronů by systém destabilizovala (nejsou delokalizovány).

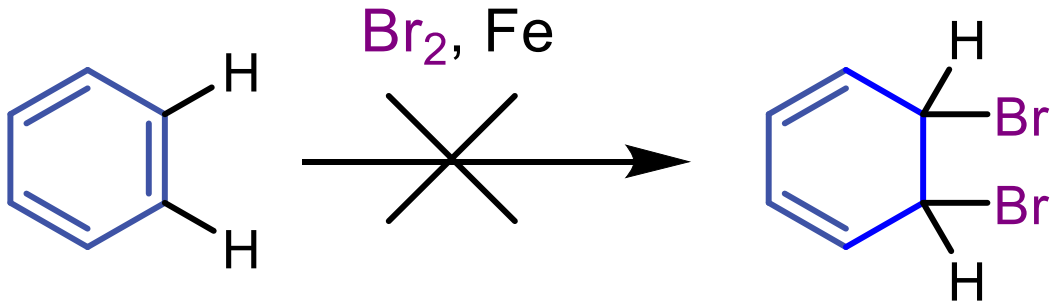
Neplanární nebo acyklické systémy s **nekonjugovanými p elektrony**, jsou **nearomatické.**
Delokalizace p elektronů v těchto systémech není možná,.

Reaktivita benzenu – elektrofilní substituce vs. adice

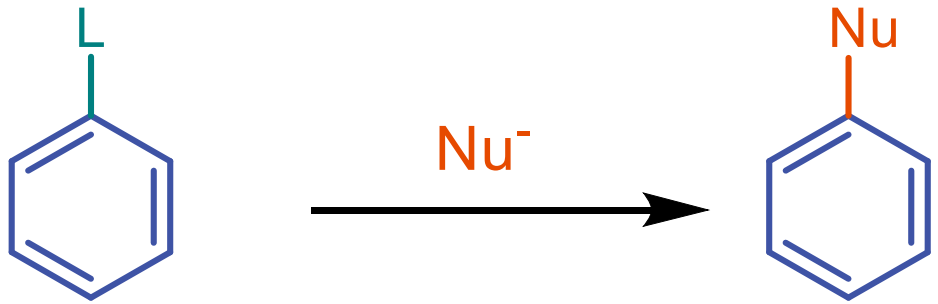
Elektrofilní substituce probíhají snadno



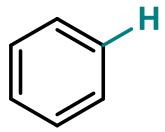
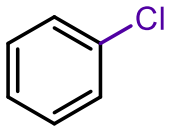
Adiční reakce neprobíhají

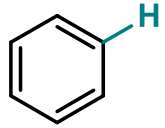
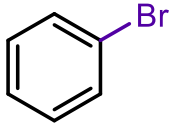


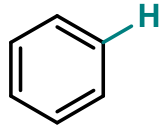
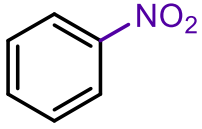
Nukleofilní substituce probíhají obtížně – pouze pro elektronově chudší systémy

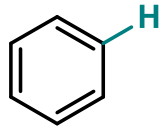
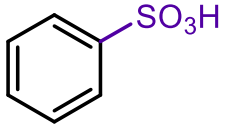


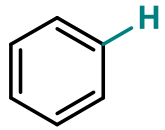
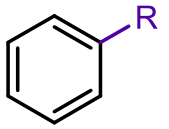
S_EAr

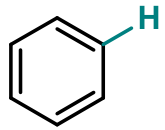
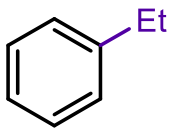
chlorace  + Cl_2 $\xrightarrow{FeCl_3}$  + HCl

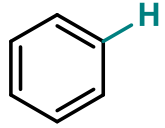
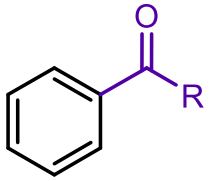
bromace  + Br_2 $\xrightarrow{FeBr_3}$  + HBr

nitrace  + HNO_3 $\xrightarrow{H_2SO_4}$  + H_2O

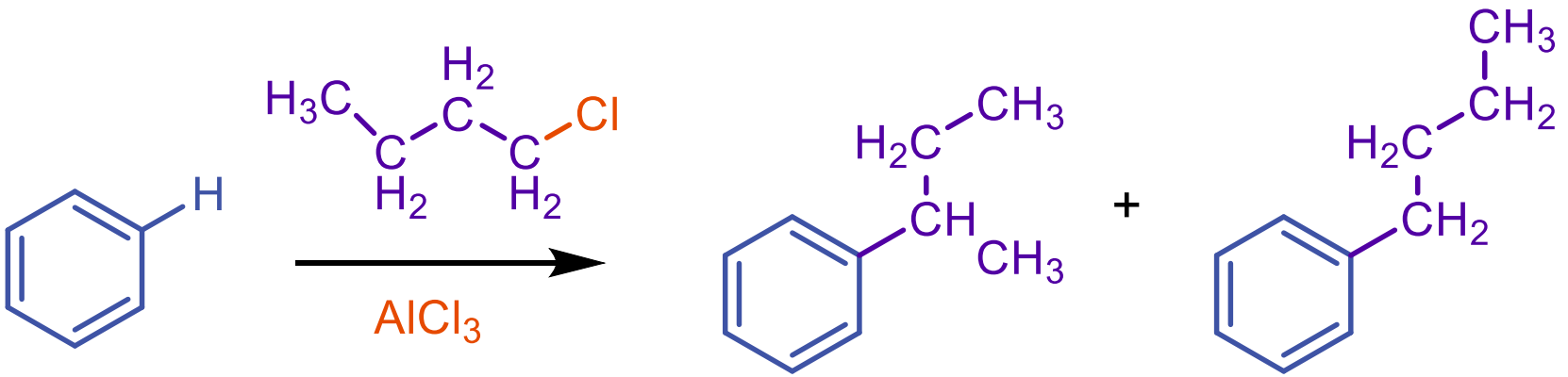
sulfonace  + H_2SO_4 $\longrightarrow$  + H_2O

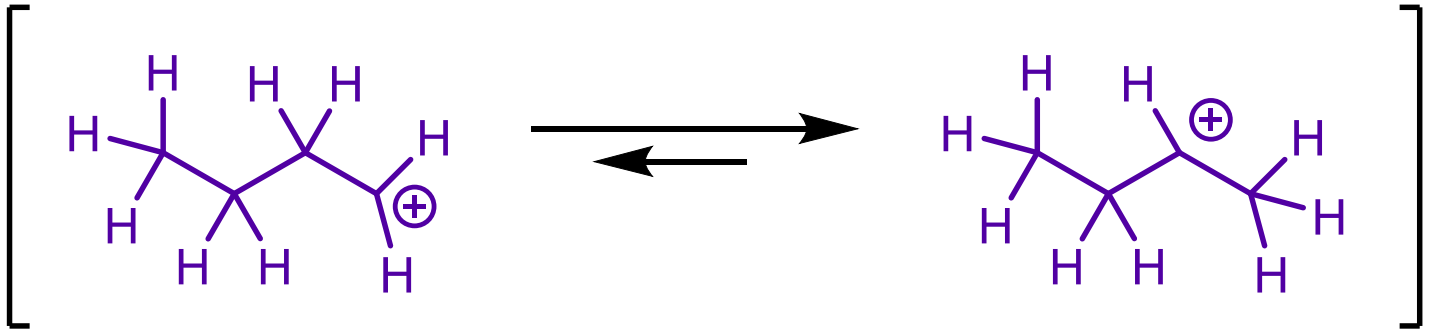
alkylace  + R-Cl $\xrightarrow{AlCl_3}$  + HCl R = Me, Et

alkylace  +  $\xrightarrow{H_2SO_4}$ 

acylace  + R-COCl $\xrightarrow{AlCl_3}$  + HCl

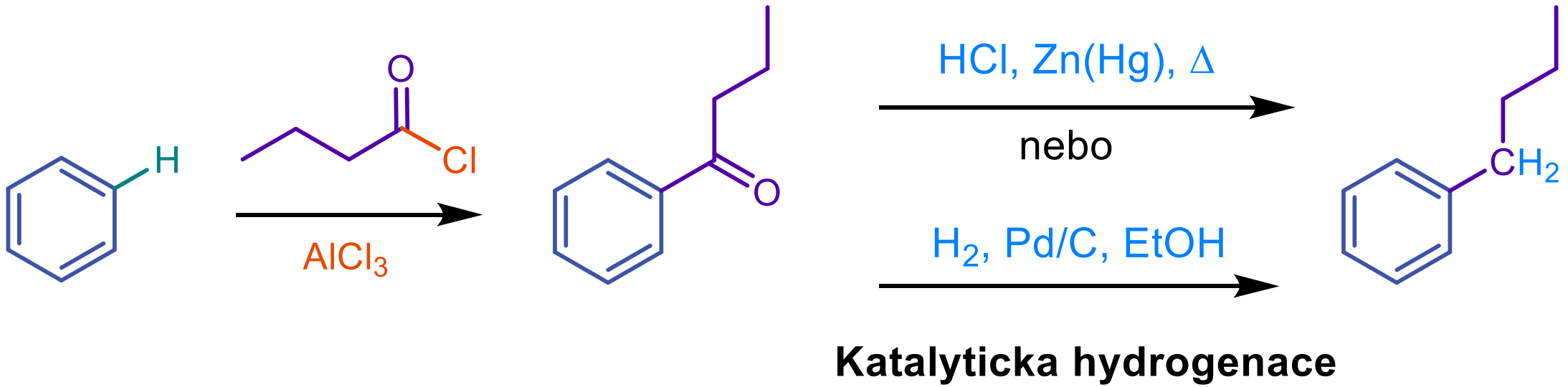
Elektrofilní alkylace (Friedel-Craftsova alkylace)





Přesmyk přesunem protonu

Příprava alkylaromátů (benzenů) — acylace + redukce

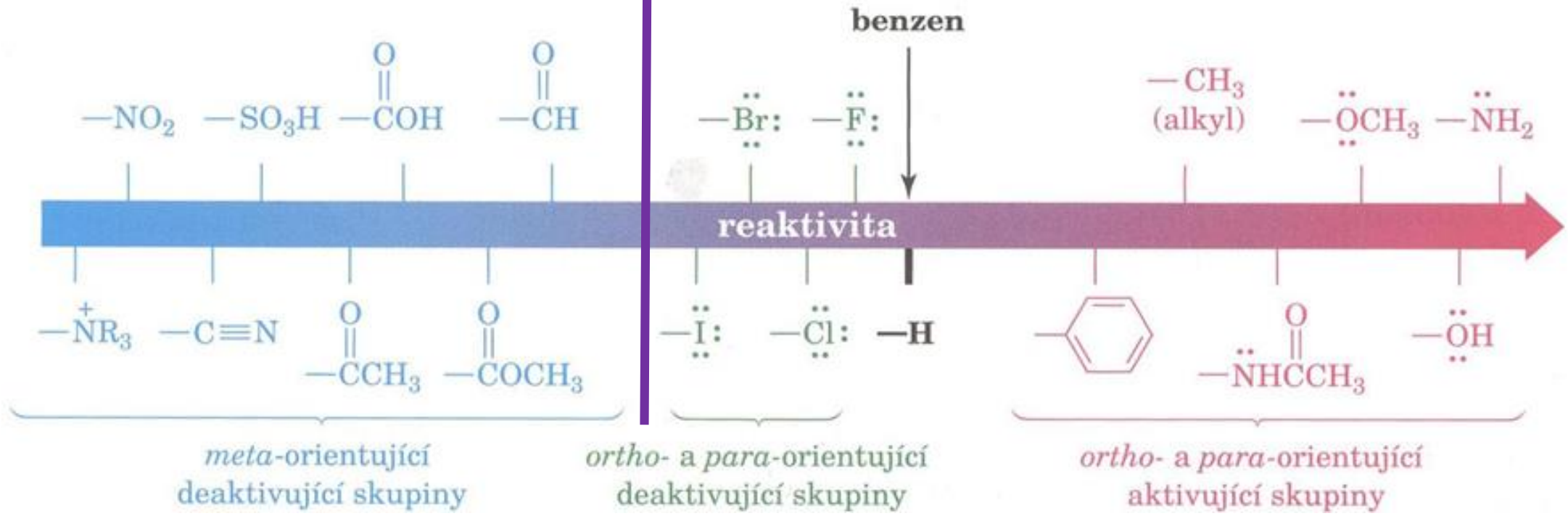


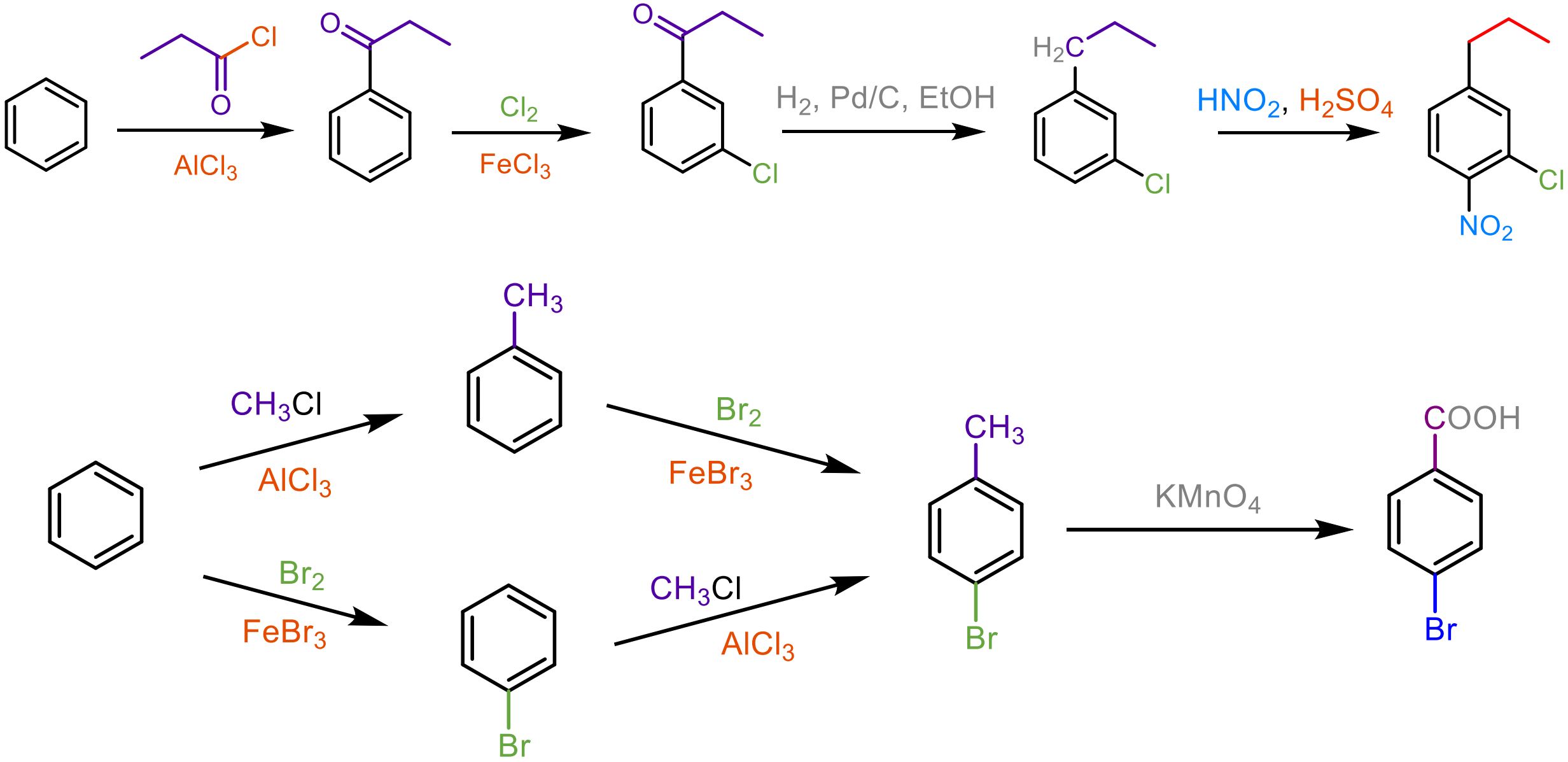
Clemmensenova redukce

Katalyticka hydrogenace

***meta* — orientující (substituenty II. třídy)**

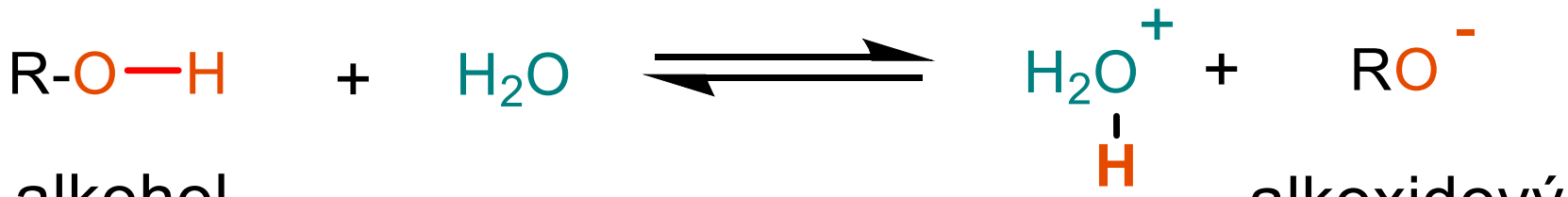
***ortho*, *para* — orientující (substituenty I. třídy)**




Cl
O
O
AlCl3
Cl2
FeCl3
O
Cl
H2, Pd/C, EtOH
H2C
Cl
HNO2, H2SO4
Cl
NO2
CH3Cl
AlCl3
CH3
Br2
FeBr3
CH3
Br
Br2
FeBr3
Br
CH3Cl
AlCl3
KMnO4
COOH
Br

Alkoholy

Acidita alkoholů a fenolů



alkohol

alkoxidový ion

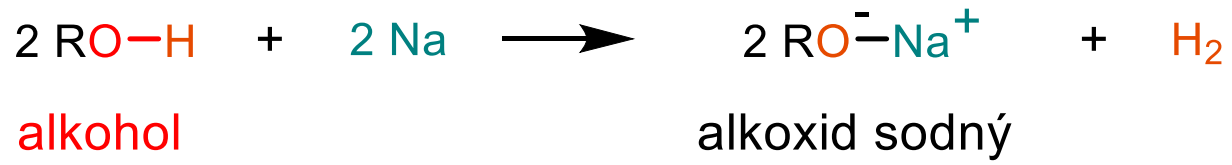
$$K_a = K[H_2O] = \frac{[H_3O^+][RO^-]}{[ROH]}\ \text{mol/l}$$

$$pK_a = -\log K_a$$

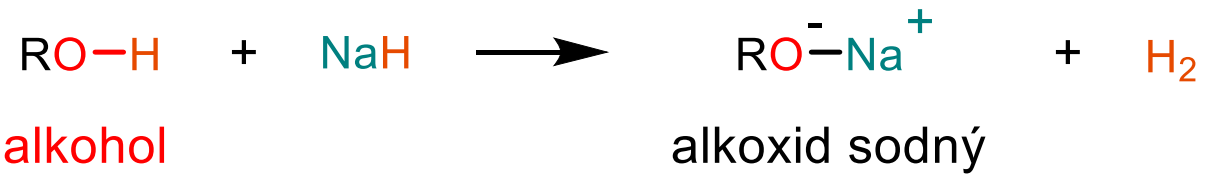
TABLE 8-2 pK_a Values of Alcohols and Related Compounds in Water

Compound	pK_a	Compound	pK_a
H_2O	15.7	$ClCH_2CH_2OH$	14.3
CH_3OH	15.5	CF_3CH_2OH	12.4
CH_3CH_2OH	15.9	$CF_3CH_2CH_2OH$	14.6
$(CH_3)_2CHOH$	17.1	$CF_3CH_2CH_2CH_2OH$	15.4
$(CH_3)_3COH$	18		

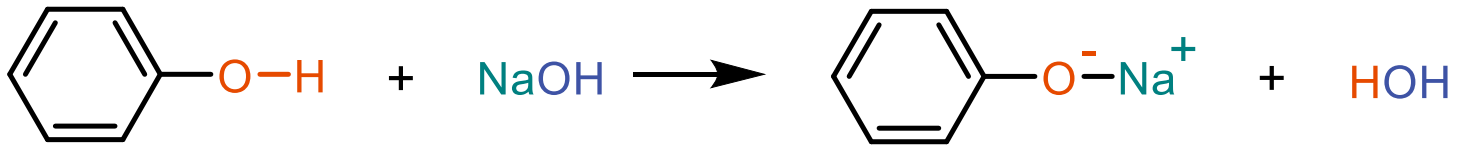
Tvorba alkoxidů/alkoholátů



alkohol — alkoxid sodný

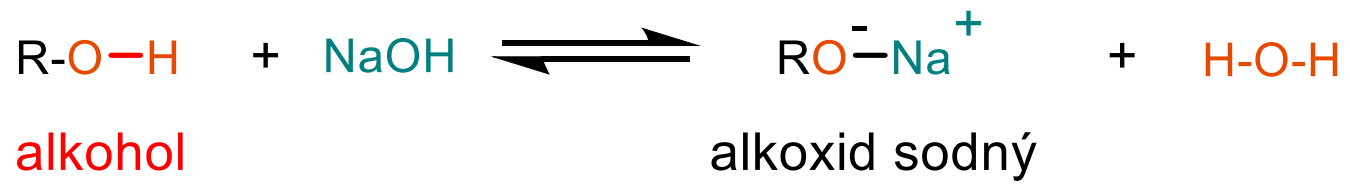


alkohol — alkoxid sodný



fenol — fenoxid sodný

Pozor: hydroxidy nestačí na deprotonaci většiny alkoholů!!!!



alkohol — alkoxid sodný

methanol *p*Ka 15.5

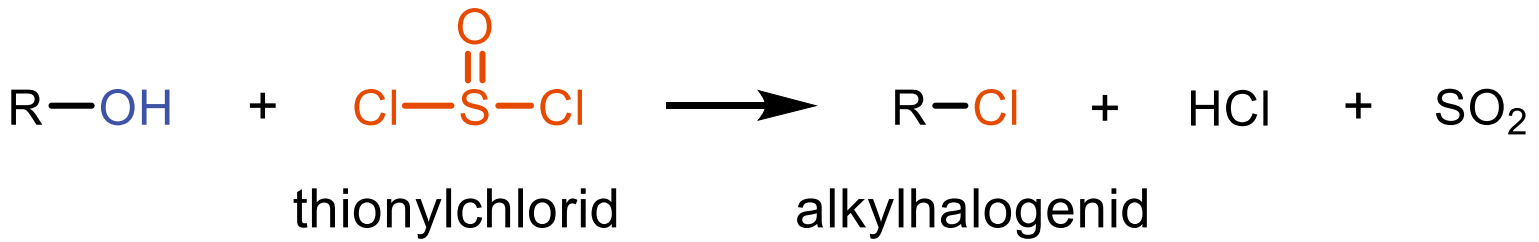
jiné alkohohy *p*Ka > 15.9

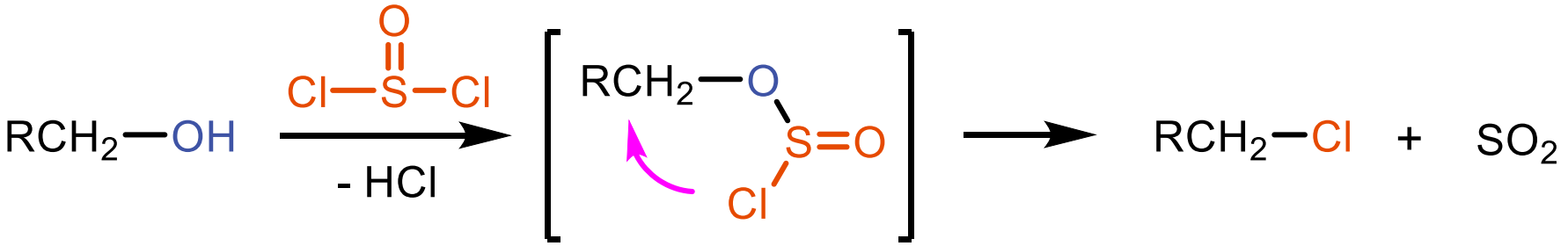
***p*Ka 15.7**

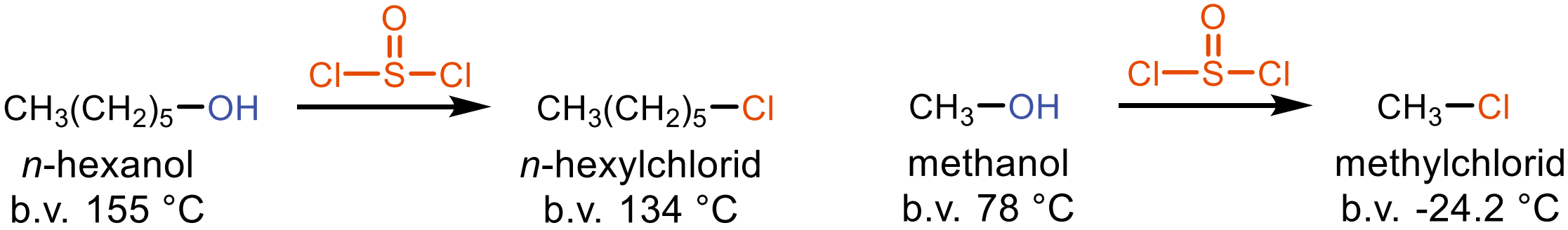
Kromě MeOH, **Voda je silnější Kyselina!**

Adice Grignardova cinidla na aldehyd, keton nebo ester

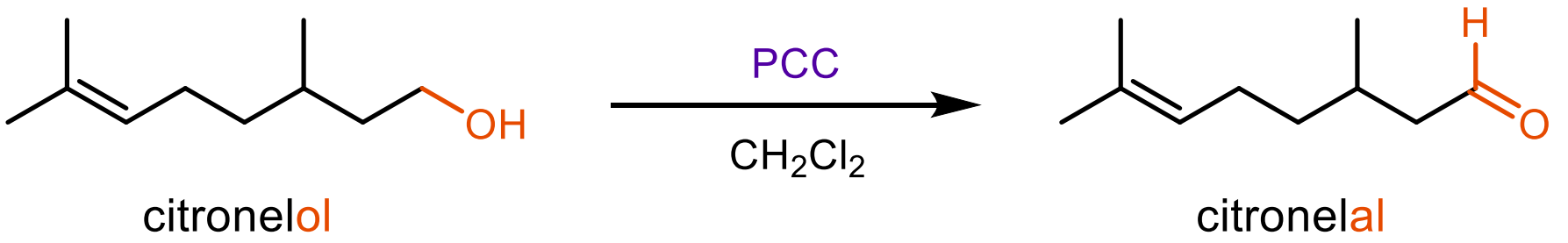
- Reakce alkoholů s thionylchloridem – příprava chloralkanů



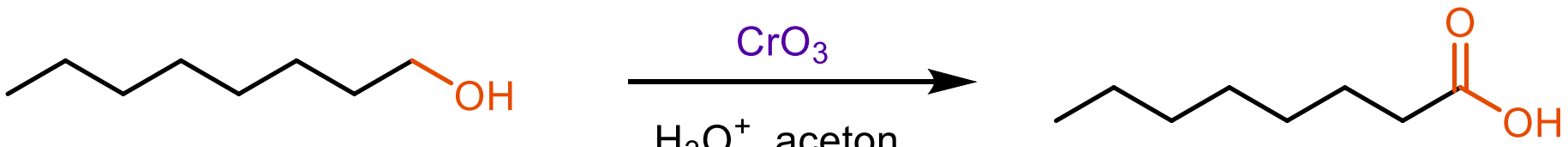




Oxidace primárních alkoholů

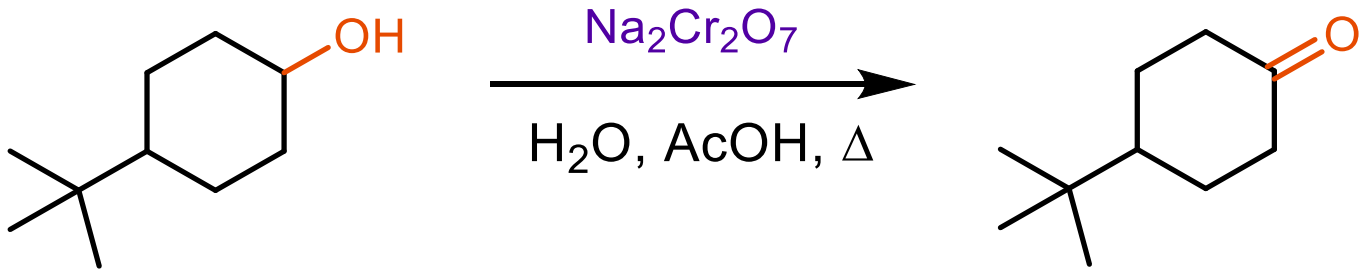


citronelol → citronelal

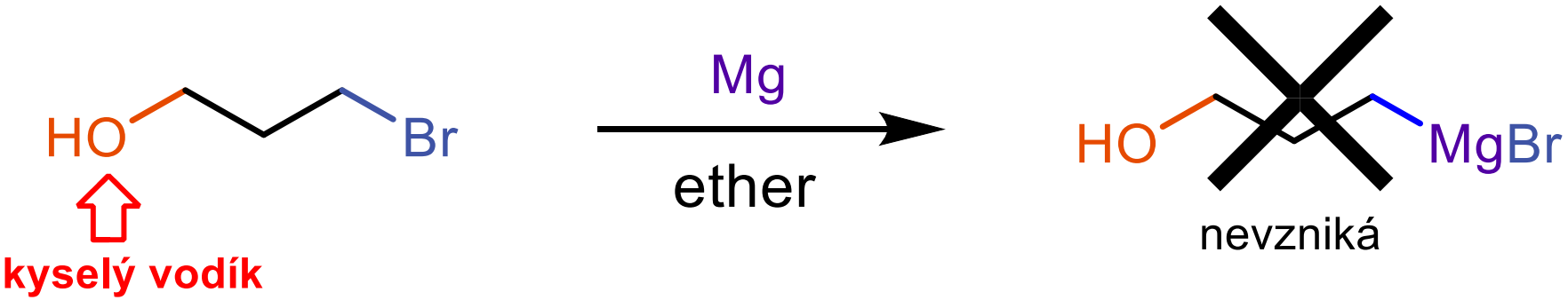


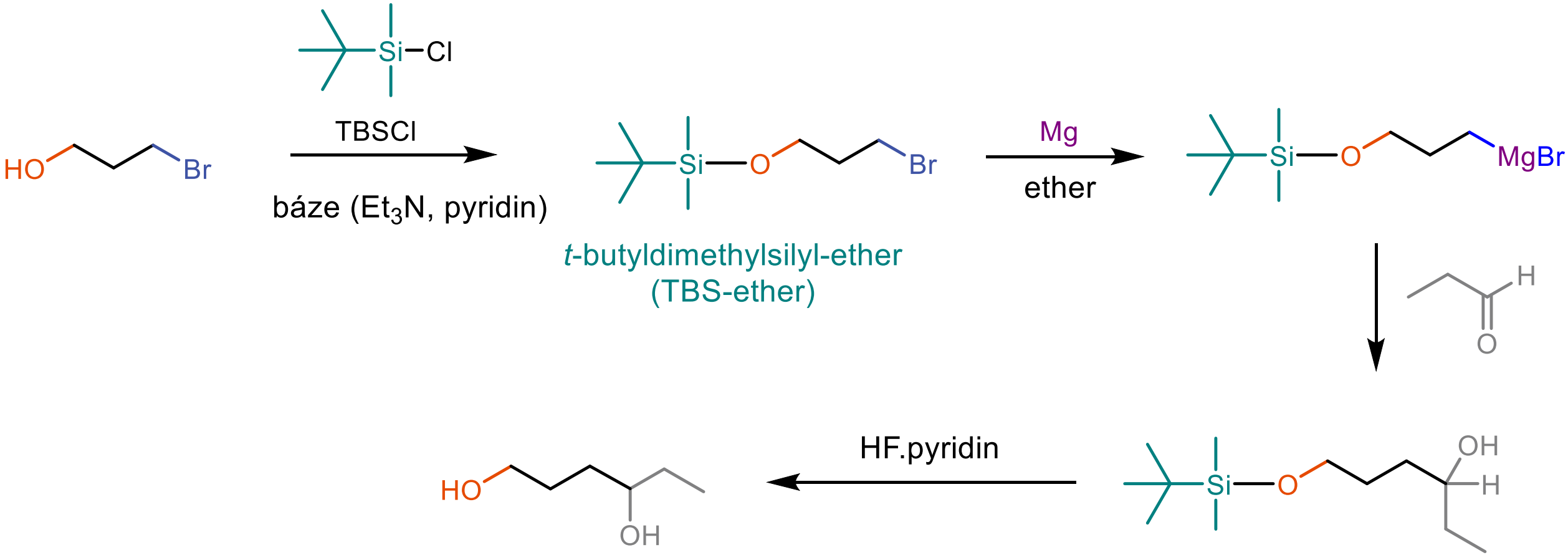
oktan-1-ol → oktanová kyselina

Oxidace sekundárních alkoholů



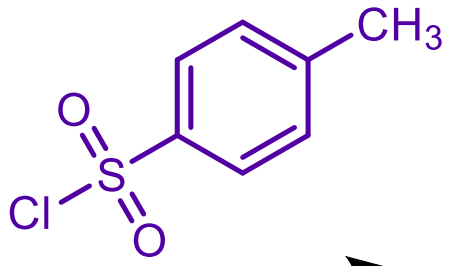
- **Chránění alkoholů**

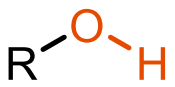




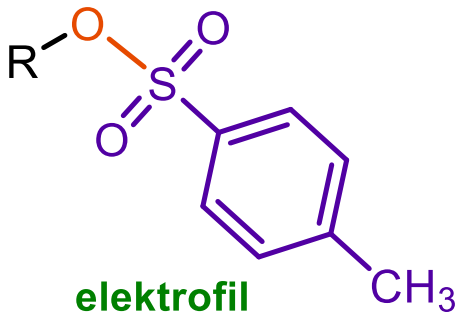
Přeměny alkoholů na reaktivní estery sulfonových kyselin

_p_-toluensulfonyl chlorid
tosyl chlorid, Ts-Cl



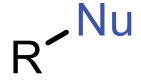


pyridin

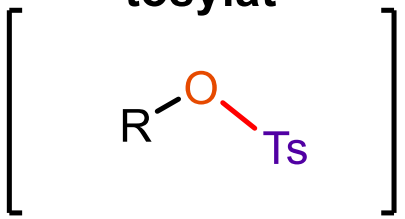


elektrofil

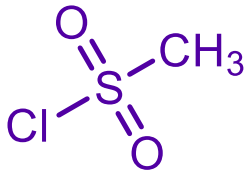
Nu^-

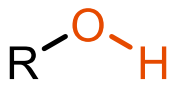


tosylát

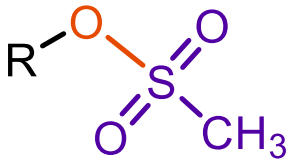


methansulfonyl chlorid
mesyl chlorid, Ms-Cl

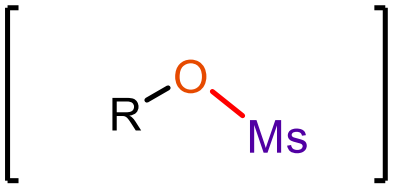




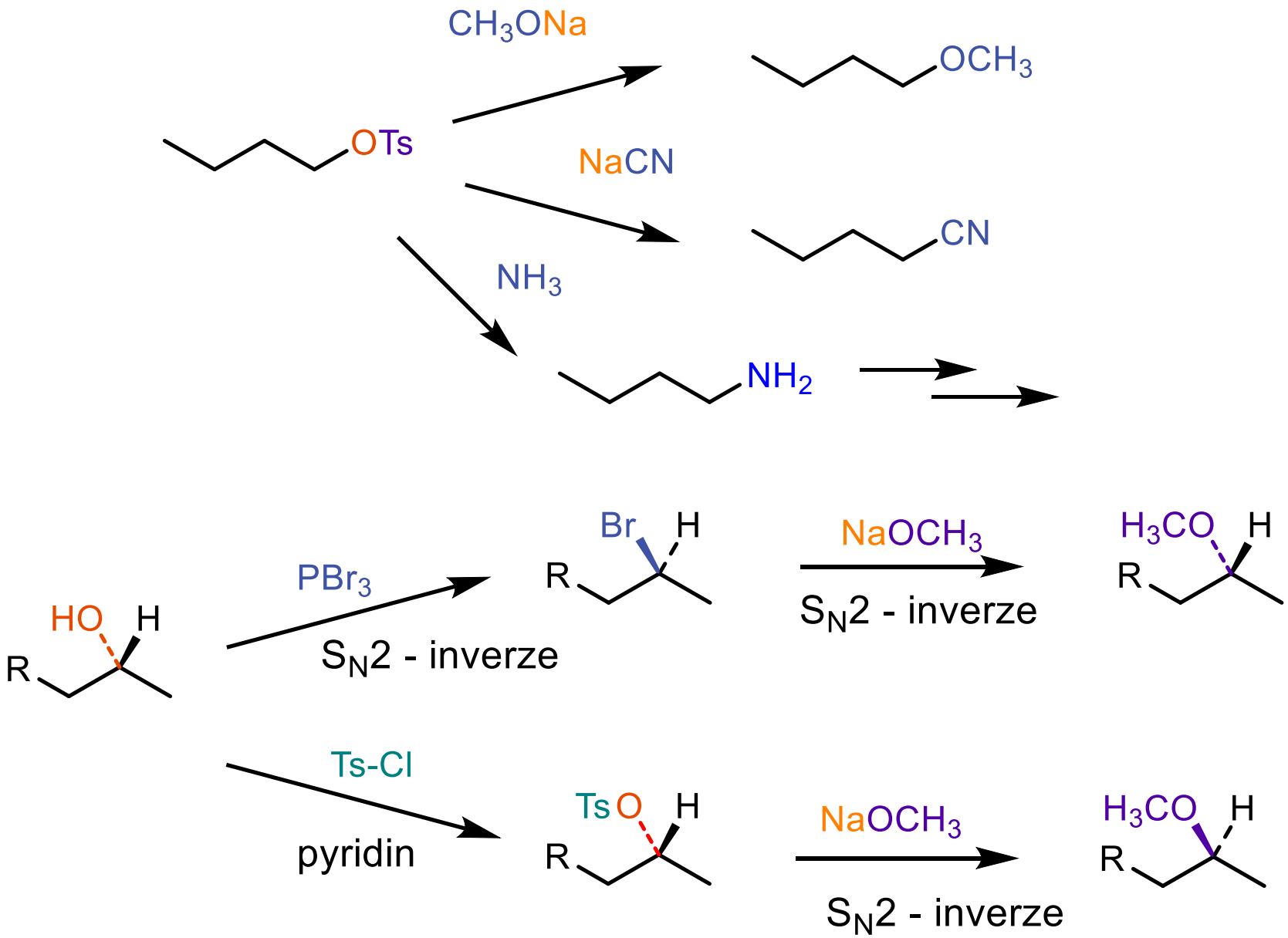
pyridin



mesylát



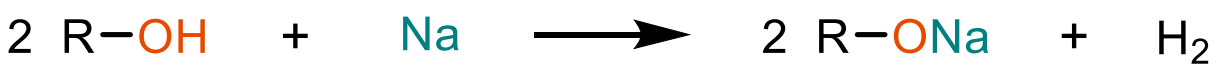
Syntetické využití reaktivních esterů sulfonových kyselin

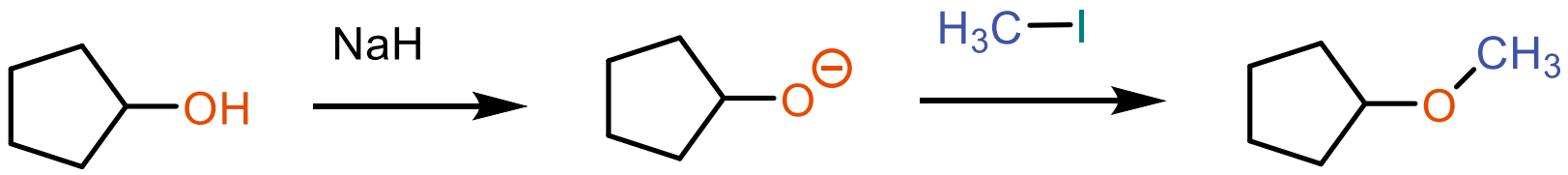


Ethery

Williamsonova syntéza.

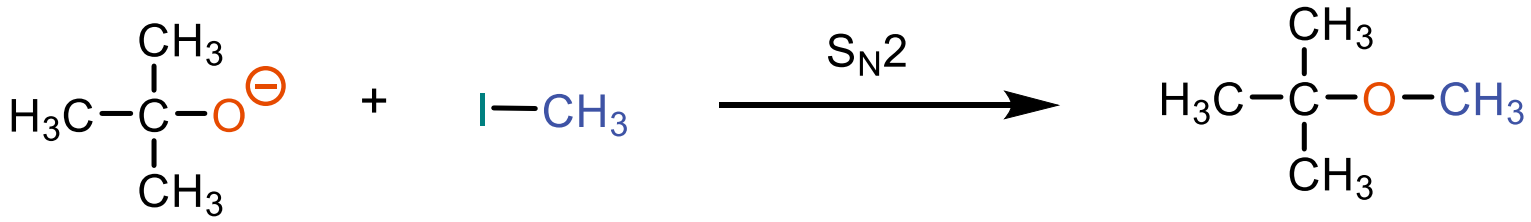
Tento proces se skládá ze dvou kroků.



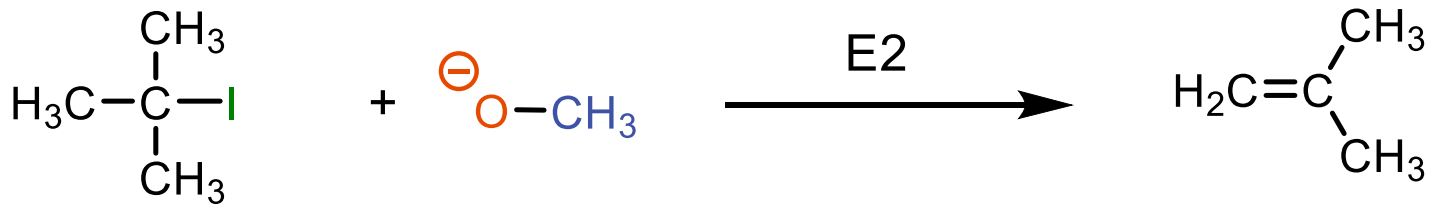


74%

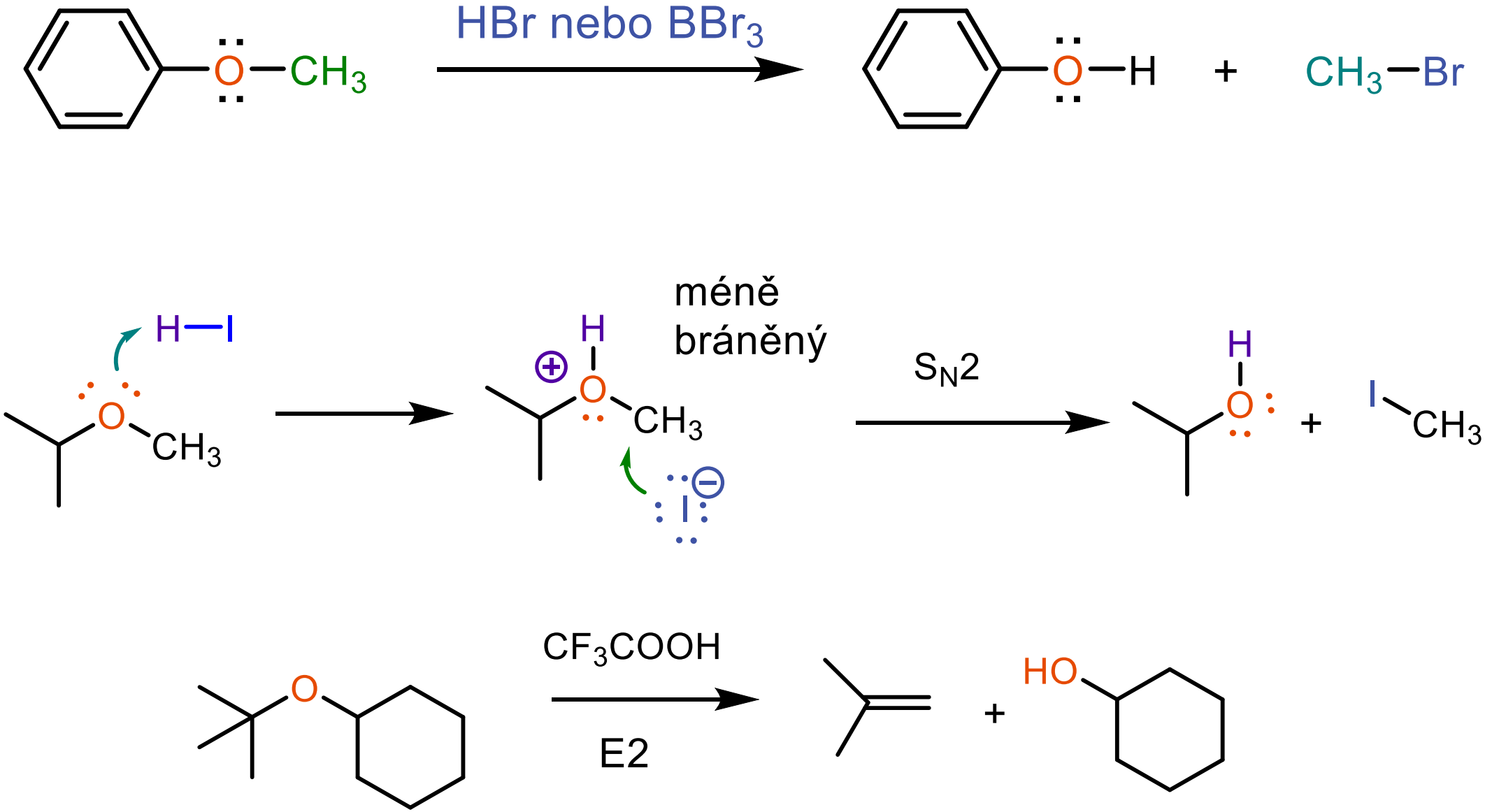
Mechanismus je S_N2:



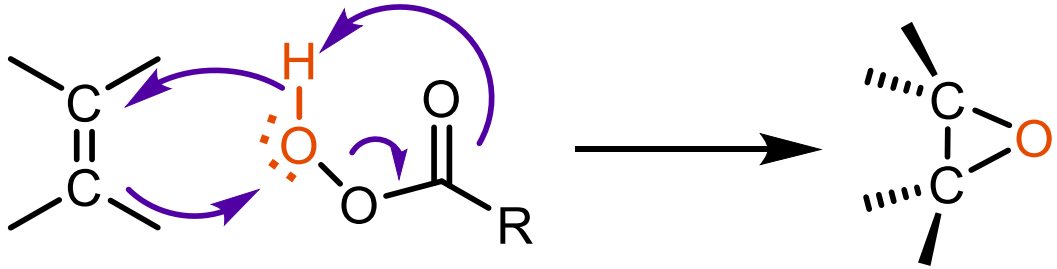
pozor: u terciálních alkylhalogenidů Dochází k eliminaci

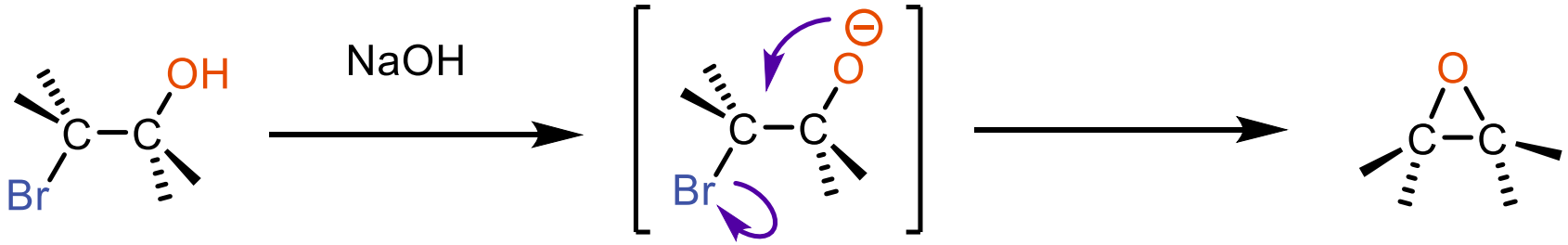


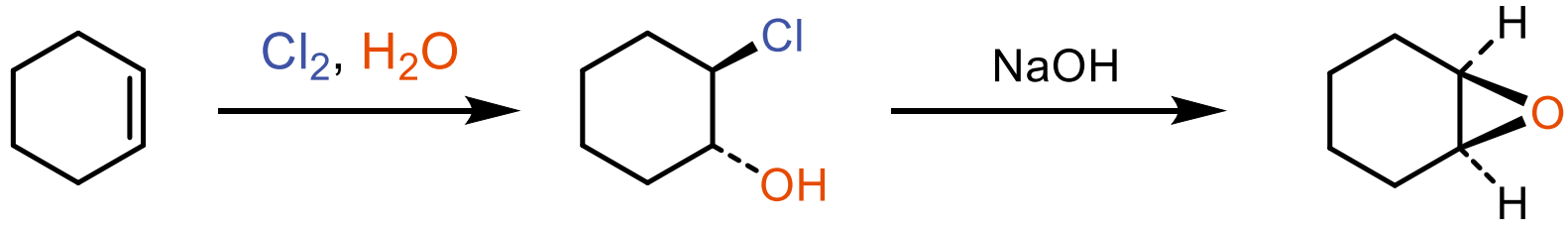
Štěpení etherů



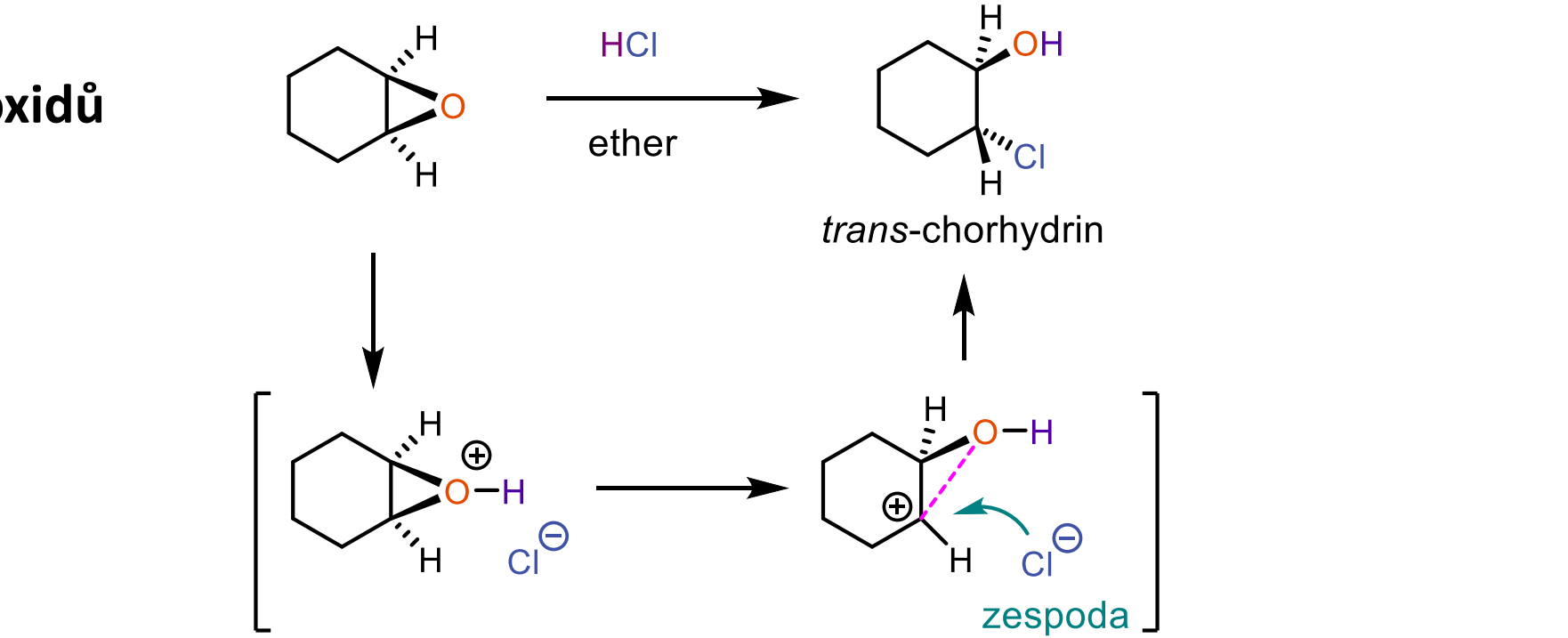
Epoxidy

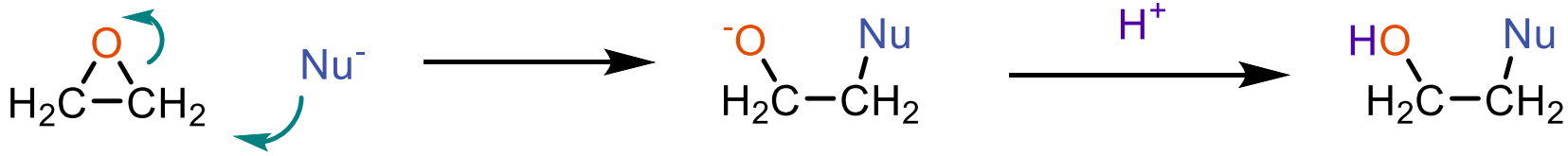


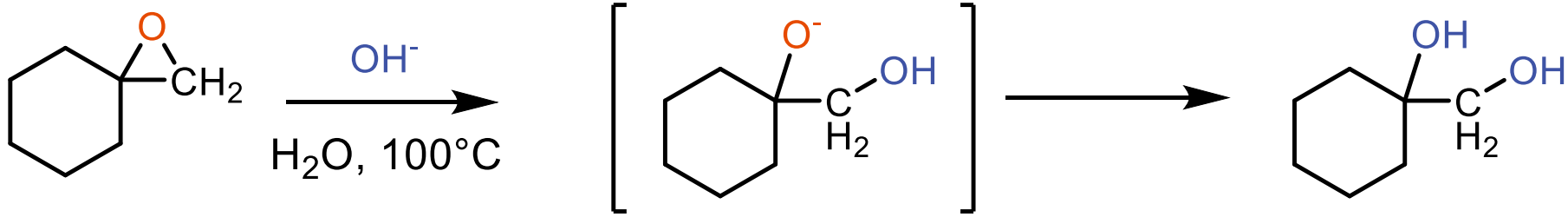




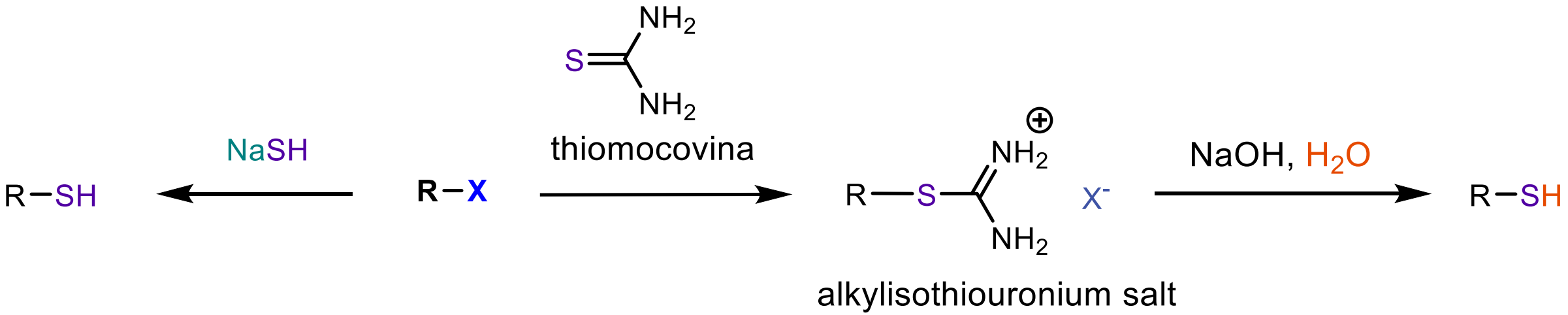
Otevírání epoxidů

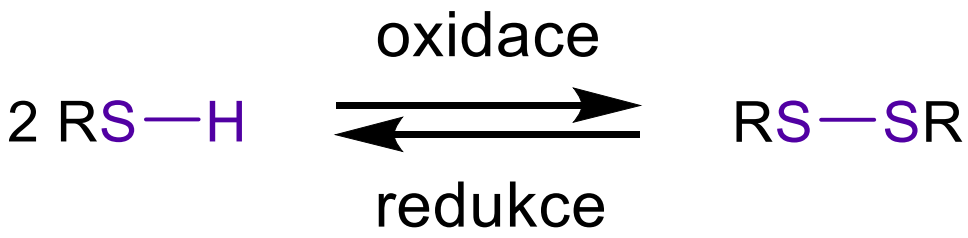






Thioly


NH2
S
NH2
thiomocovina
NaSH
R–SH
R–X
R—S
NH2
NH2
X-
alkylisothiouronium salt
NaOH, H2O
R–SH


oxidace
2 RS—H
RS—SR
redukce