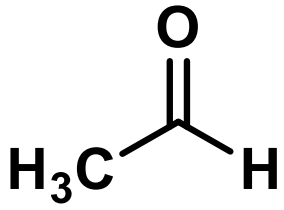
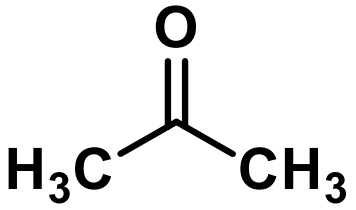
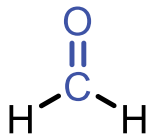
Aldehydy a Ketony



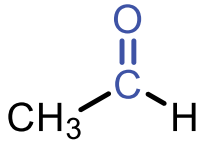


Názvosloví aldehydů a ketonů

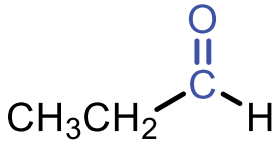
Podle názvosloví IUPAC je přítomnost aldehydové skupiny vyjádřena příponou –*al* .



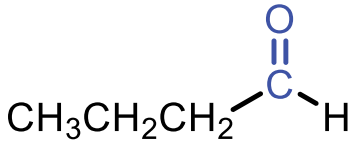
methanal
formaldehyd



ethanal
acetaldehyd

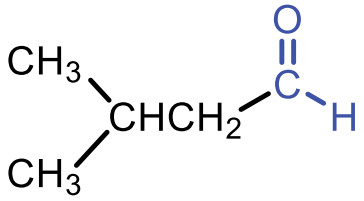


propanal
propionaldehyd

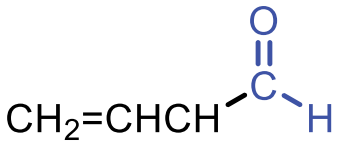


butanal
n-butyraldehyd

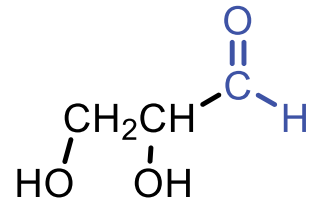
V případě substituovaných aldehydů začíná číslování uhlíkatého řetězce na aldehydovém atomu uhlíku.



3-methylbutanal

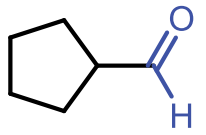


but-3-enal

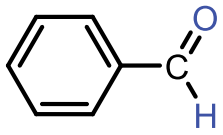


2,3-dihydroxypropanal
glyceraldehyd

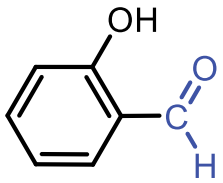
Pro cyklické aldehydy - přípona karbaldehyd, a u aromatických aldehydů často triviální názvy.
Předpona je formyl-.



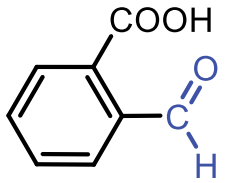
cyklopentankarbaldehyd
formylcyklopentan



benzaldehyd



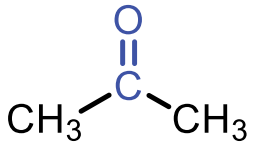
salicylaldehyd
2-hydroxybenzenkarbaldehyd



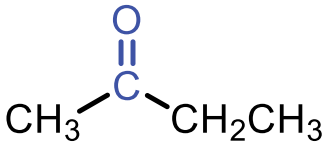
2-formylbenzoová
kyselina

Pro ketony se používá přípona –*on* .

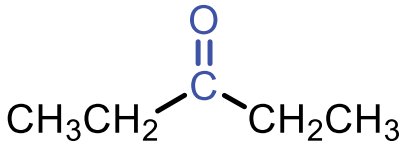
Stejně jako u aldehydů je uhlíkatý řetězec číslován tak, aby tato skupina měla co nejnižší číslo.



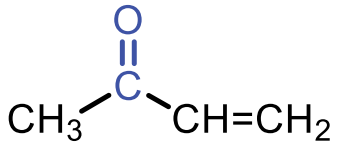
propanon
(aceton)



butan-2-on

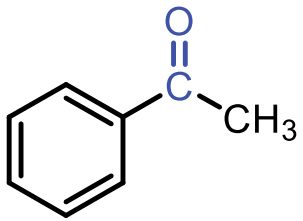


pentan-3-on
(diethylketon)

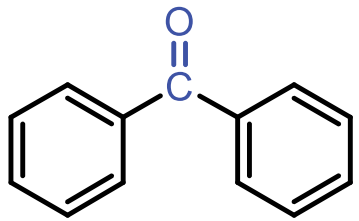


but-3-en-2-on
(methylvinylketon)

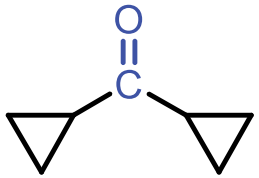
Funkční skupinové názvy se často tvoří tak, že ke slovu keton se připojí názvy připojených alkylových či arylových skupin.



acetofenon
fenylmethylketon

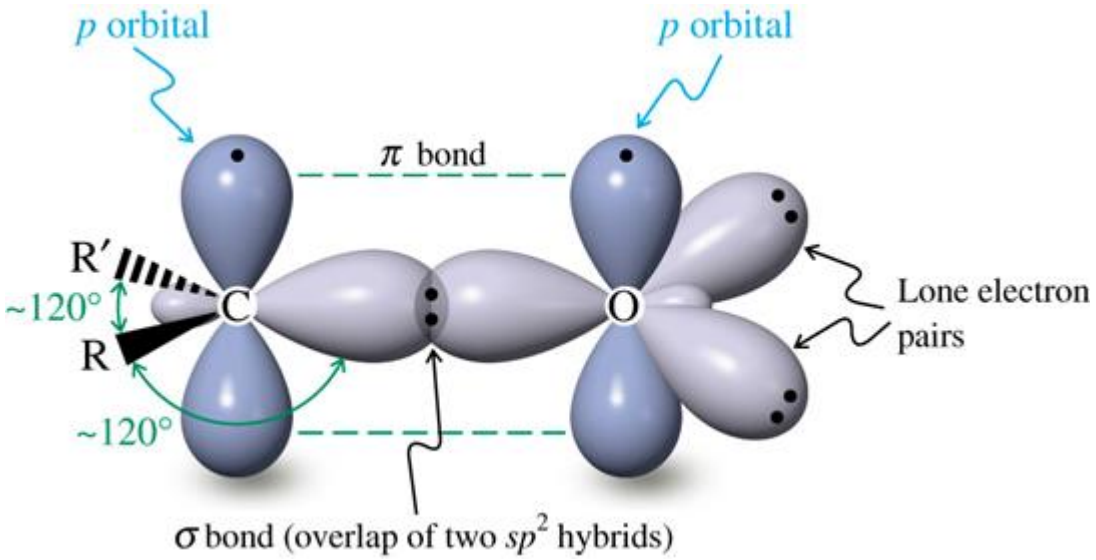


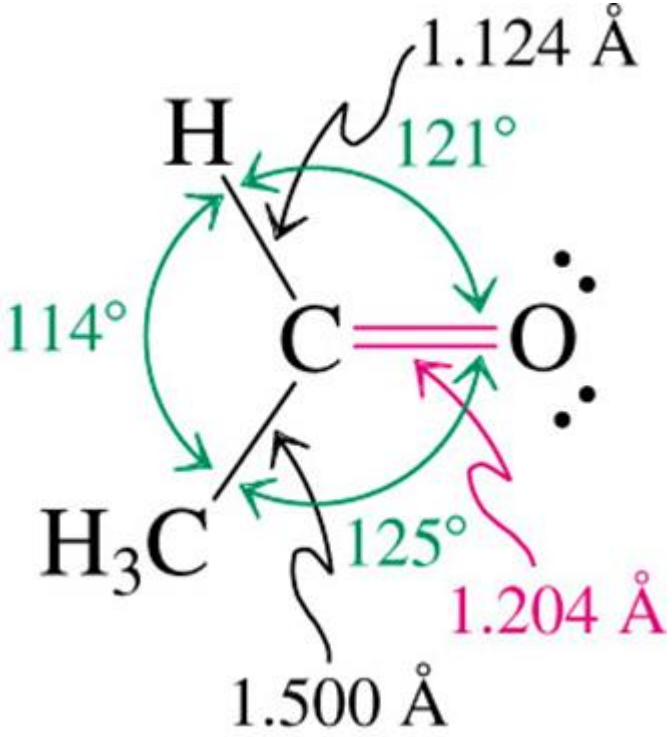
benzofenon
(difenylketon)



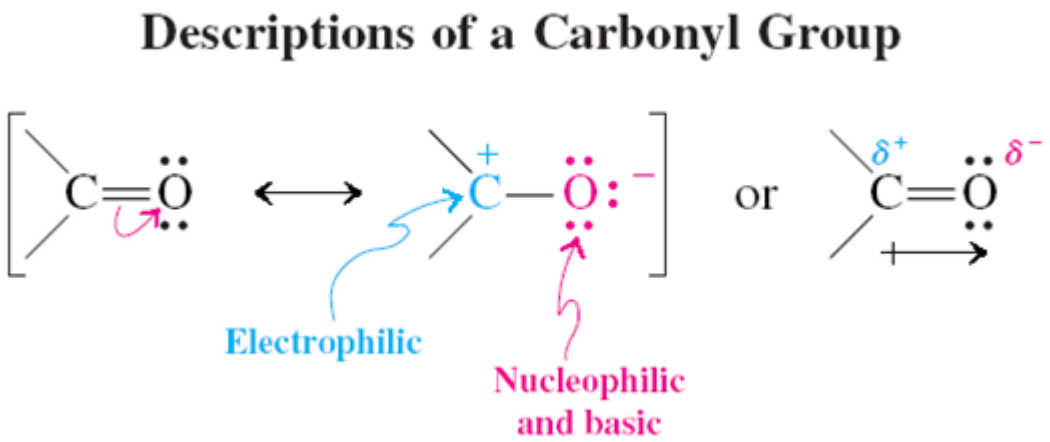
dicyklopropylketon

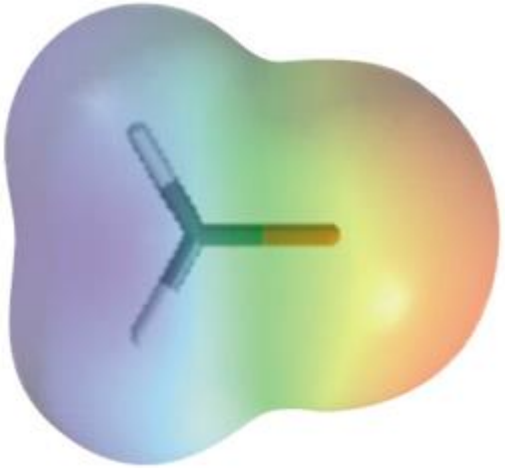
Struktura karbonylové skupiny





Struktura karbonylové skupiny – elektronová hustota



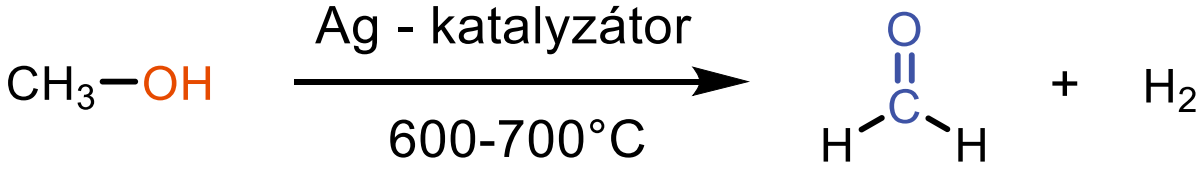


Formaldehyde

Některé důležitější aldehydy a ketony

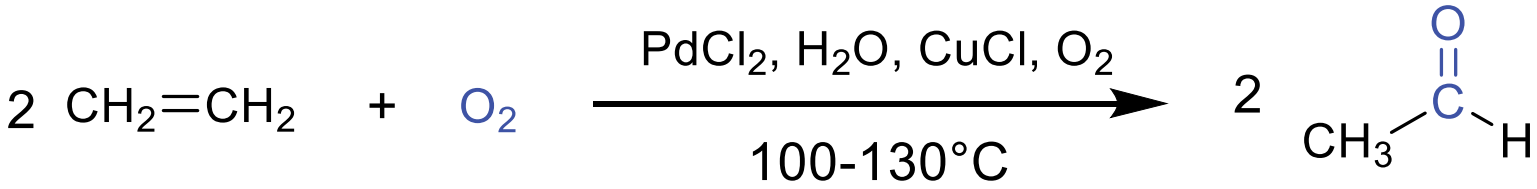
Formaldehyd (methanal), plyn (t.v. –21˚C).

Velice dobře se rozpouští ve vodě a dodává se jako 37% roztok.
Průmyslově se vyrábí oxidací methanolu na stříbrných katalyzátorech.
Konzervační činidlo, uplatňuje při výrobě plastických hmot (tzv. fenolformaldehydové pryskyřice).

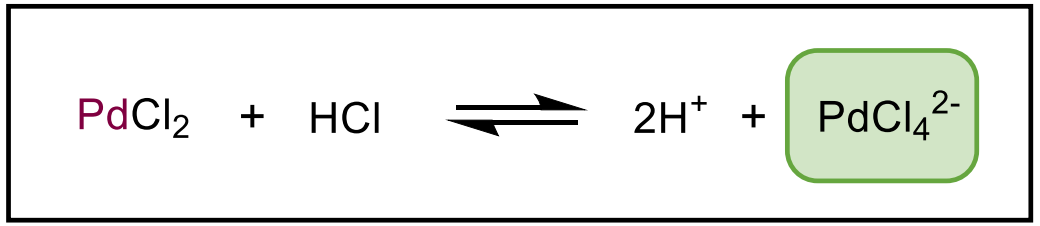


Acetaldehyd (ethanal) (t.v. 20˚C).

Vyrábí selektivní katalytickou oxidací ethylenu v přítomnosti složeným z Pd^{2+} a Cu^{1+} , tzv. Wackerova oxidace. Acetaldehyd se oxiduje buď na CH_3COOH nebo se používá na výrobu 1-butanolu atd.

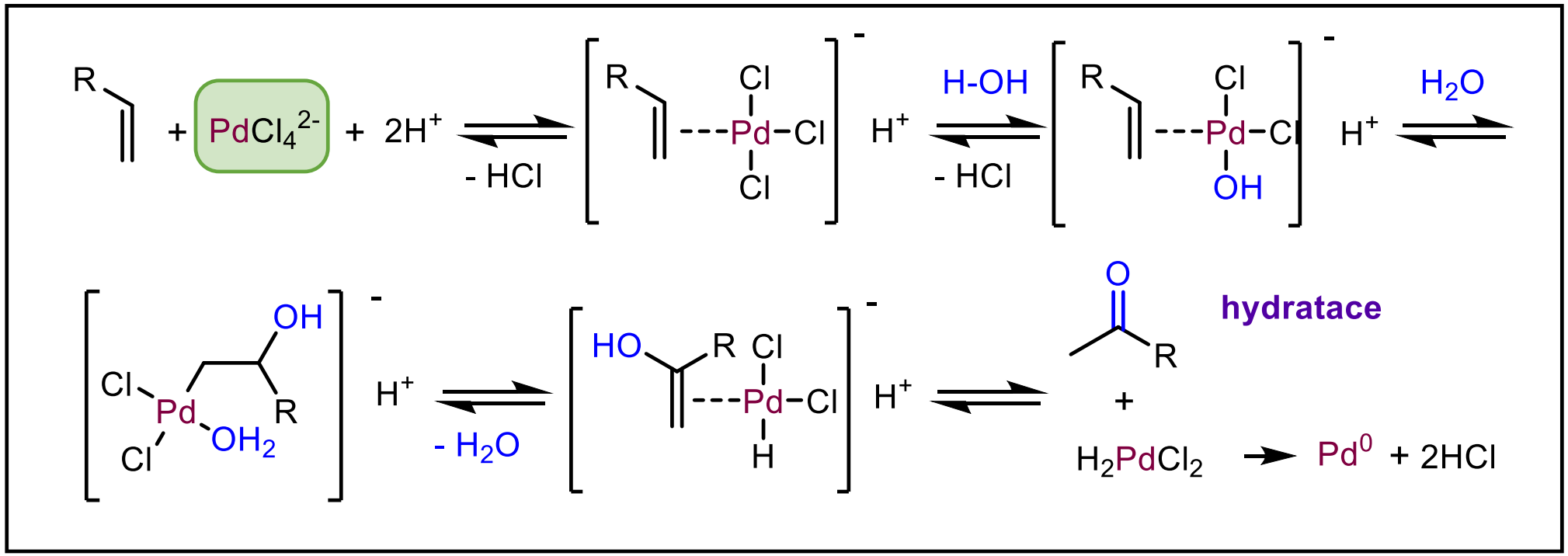


1.



Vznik katalyticky aktivní částice

2.



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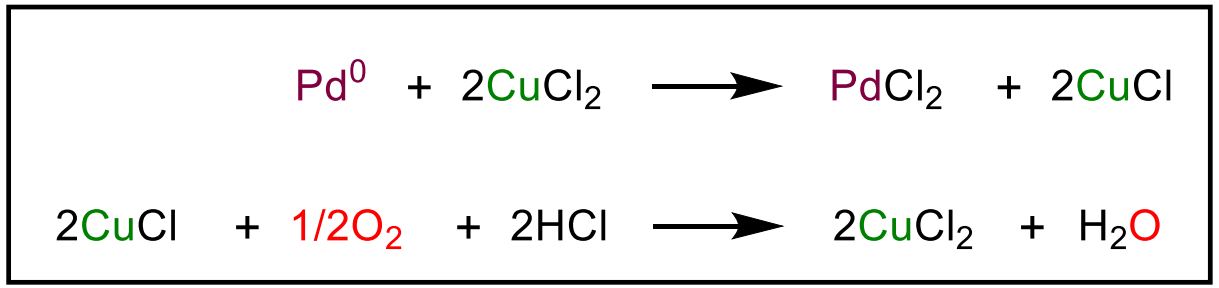
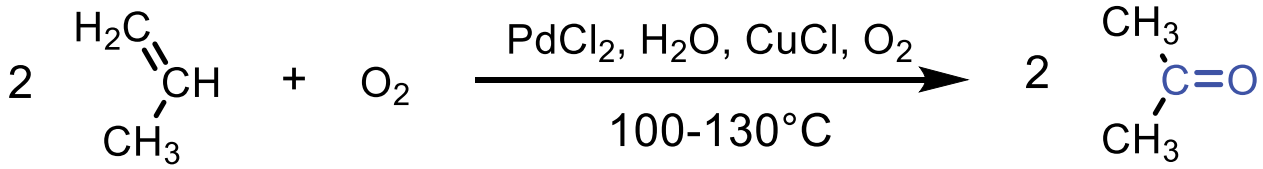
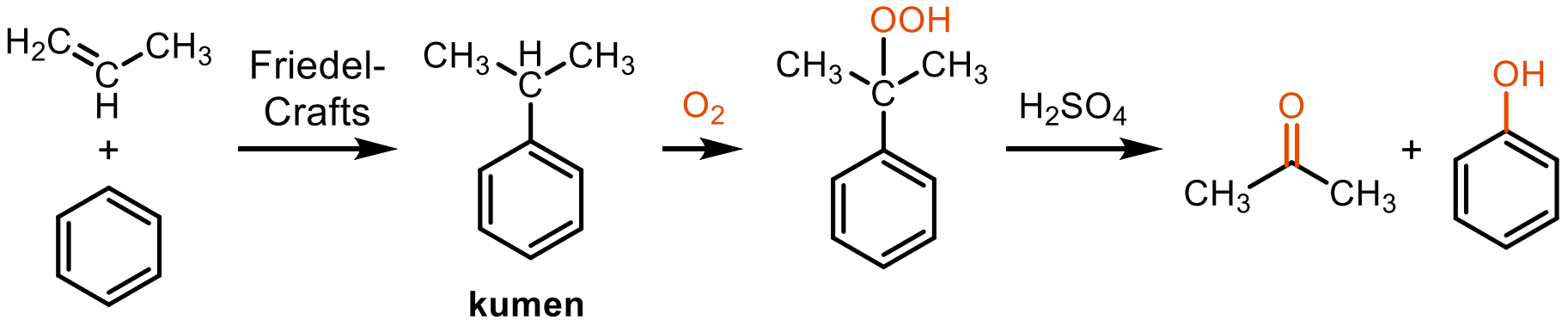


regenerace katalyzátoru

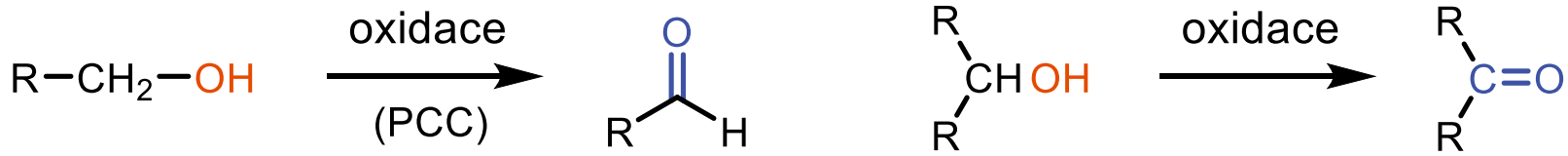
Nejjednodušším členem ketonů je aceton (t.v. 56˚C)
Průmyslově se vyrábí v milionech tun buď Wackerovou oxidací propenu,
oxidací isopropylalkoholu a nebo oxidací isopropylbenzenu. Používá přímo jako rozpouštědlo, je mísitelný jak s vodou, tak s celou řadou ostatních organických rozpouštědel.



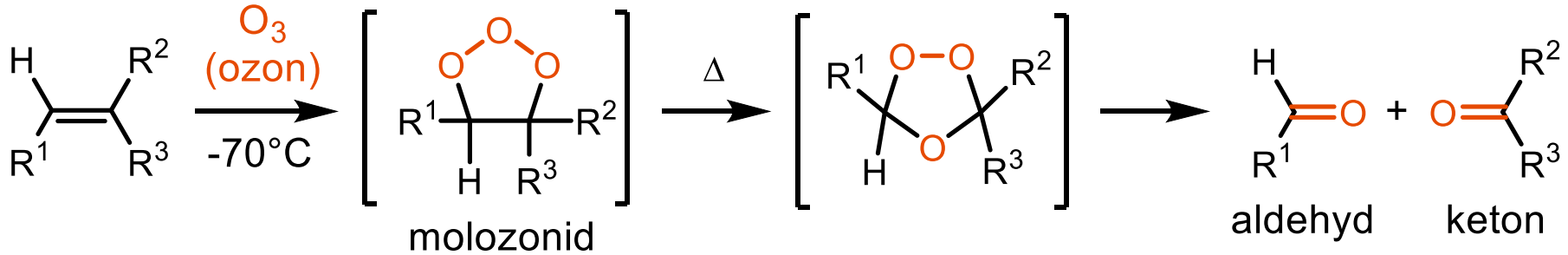


Syntéza aldehydů a ketonů

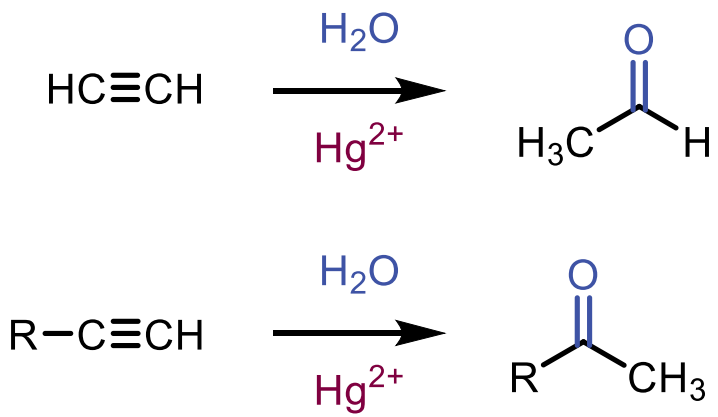
oxidace alkoholů



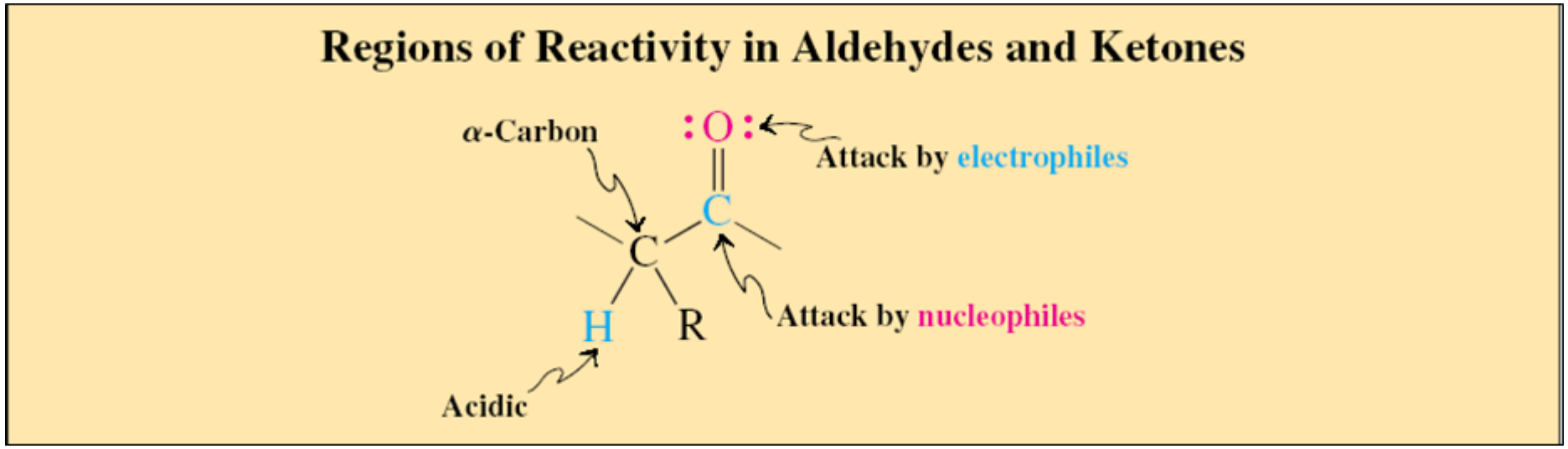
ozonolýza alkenů

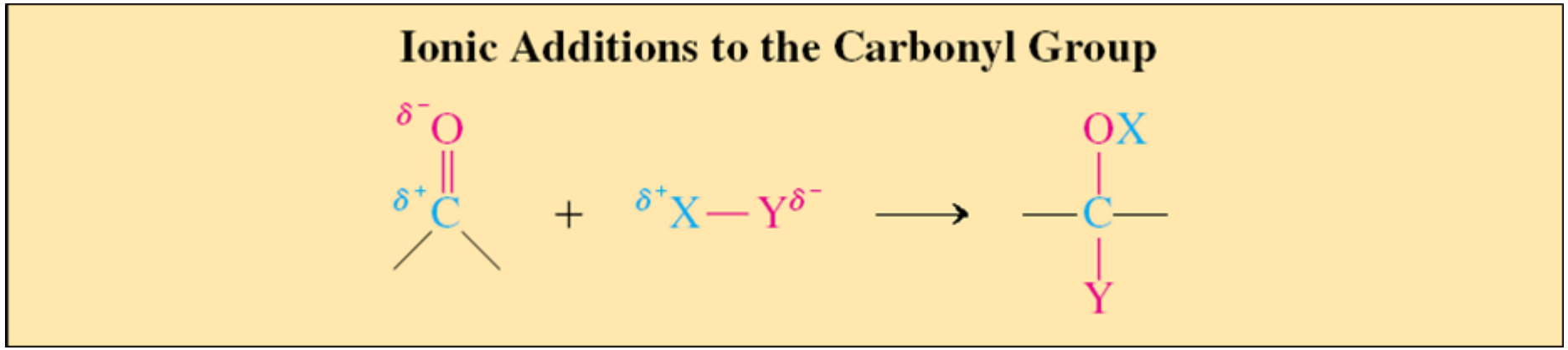


hydratace alkynů

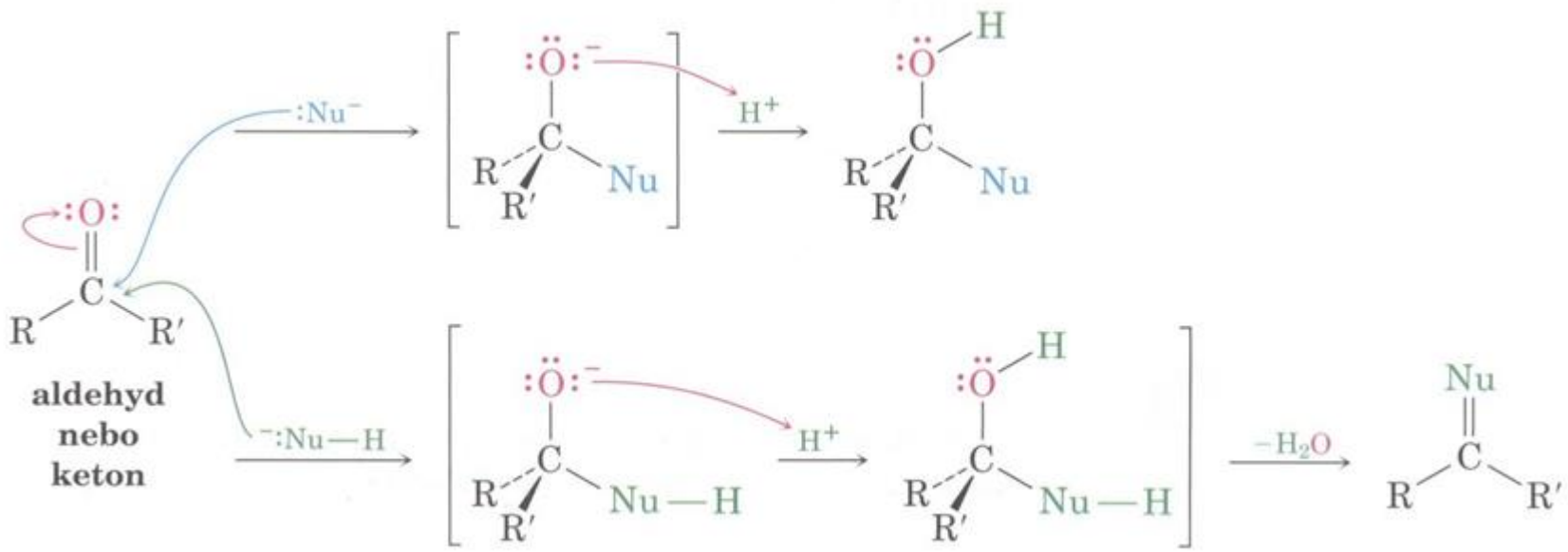


Reaktivita aldehydů a ketonů

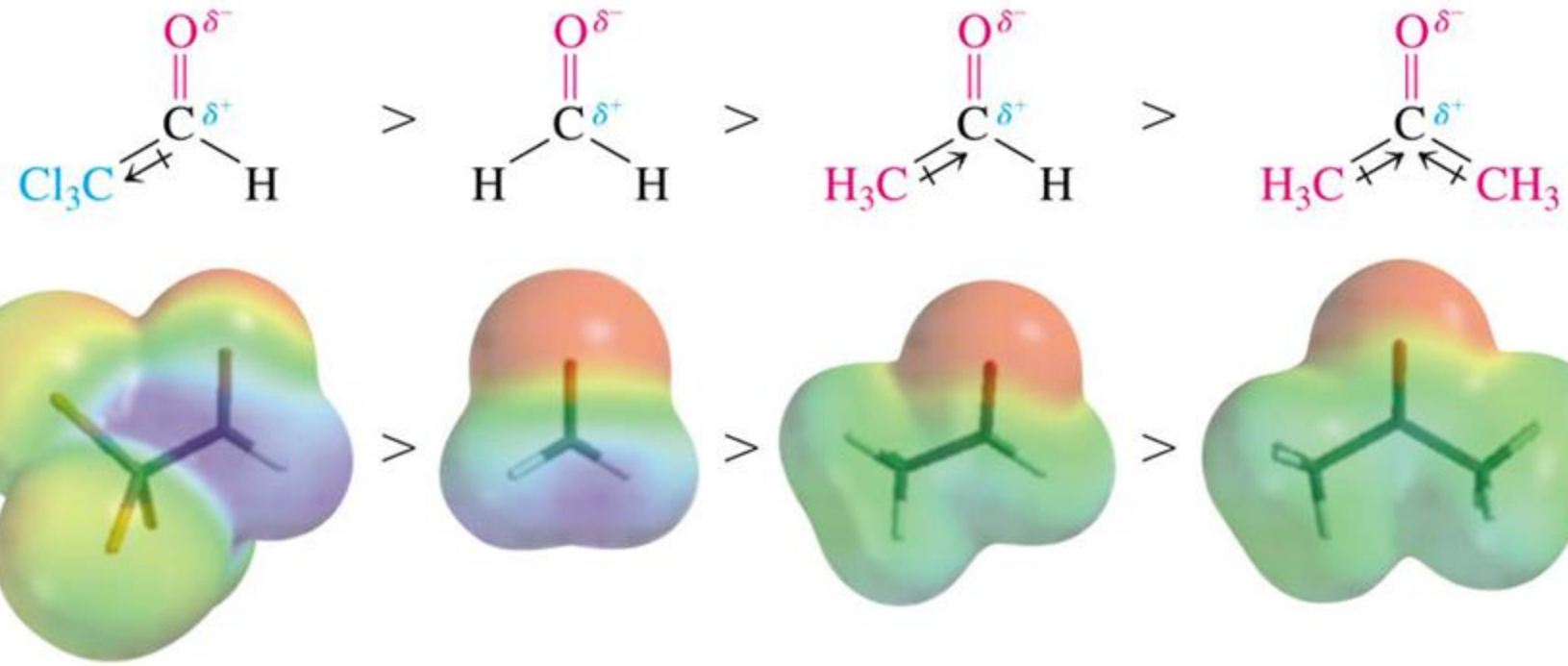




Reaktivita aldehydů a ketonů – nukleofilní adice



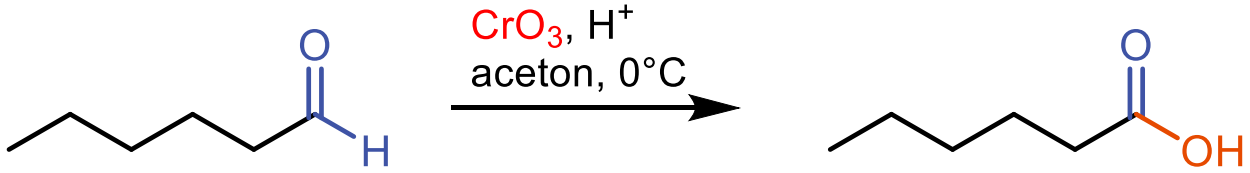
Relative Reactivities of Carbonyl Groups: Aldehydes Are More Reactive than Ketones

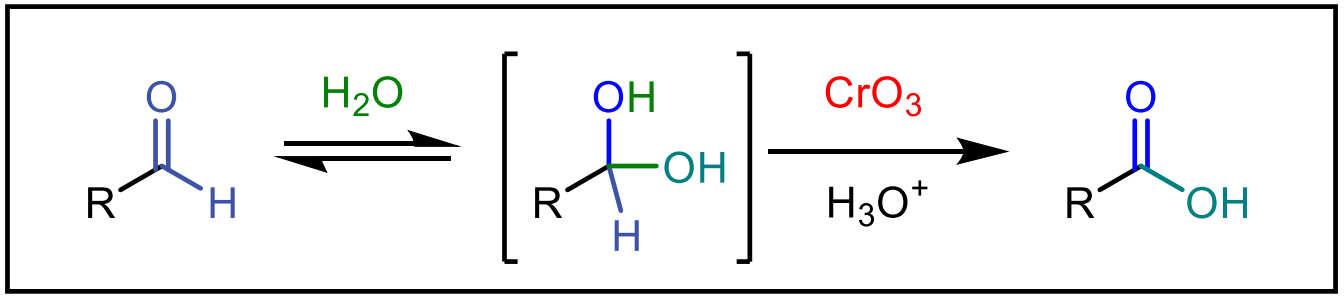


Electron-withdrawing CCl_3 group generates additional positive charge at carbonyl carbon

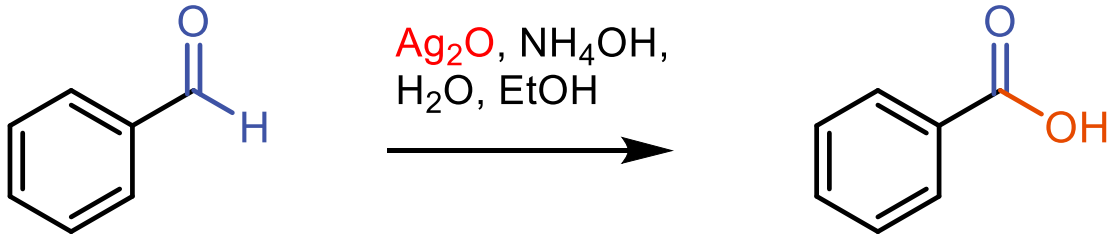
Electron-donating CH_3 groups reduce positive charge at carbonyl carbon

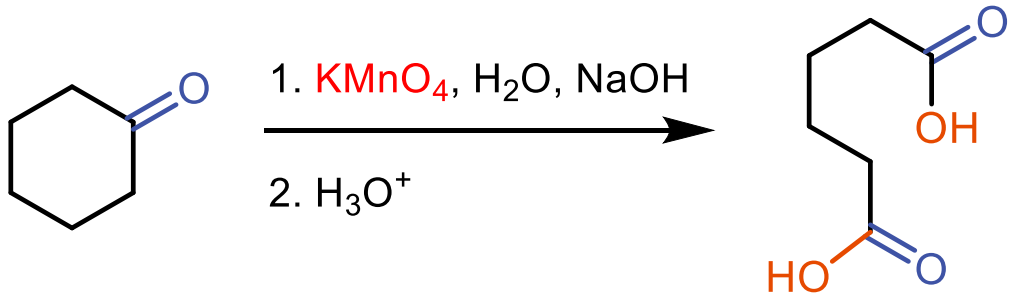
Reaktivita aldehydů a ketonů – oxidace





Tollensova reakce

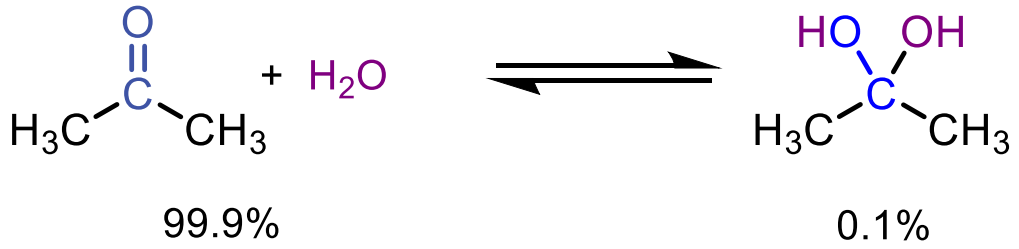


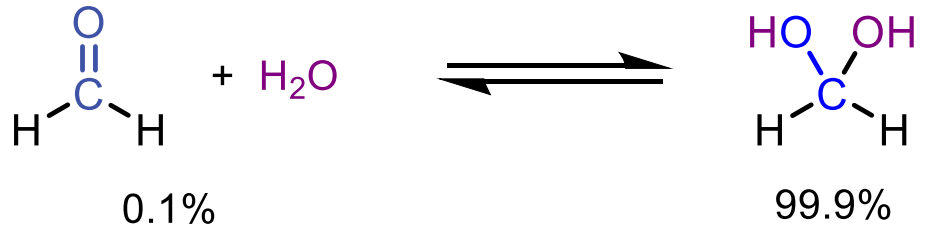


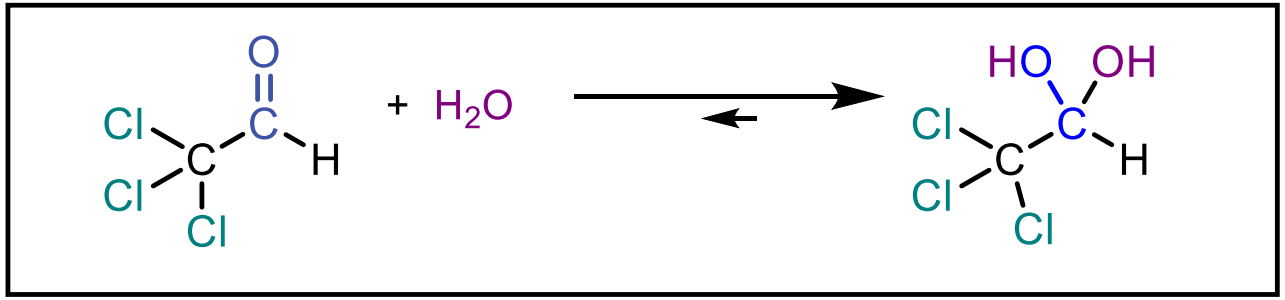
silná oxidační činidla

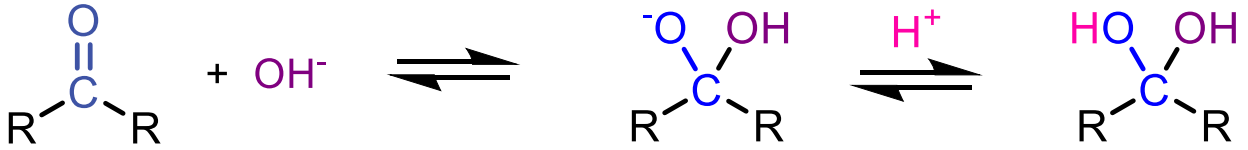
vedou k dikyselinám

Adice vody

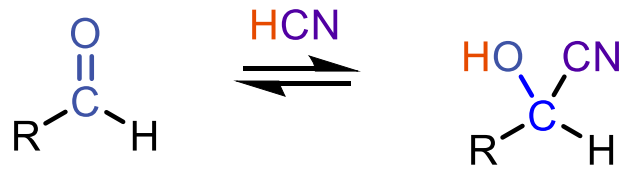

O
C
H3C
CH3
+ H2O
HO
OH
99.9%
0.1%

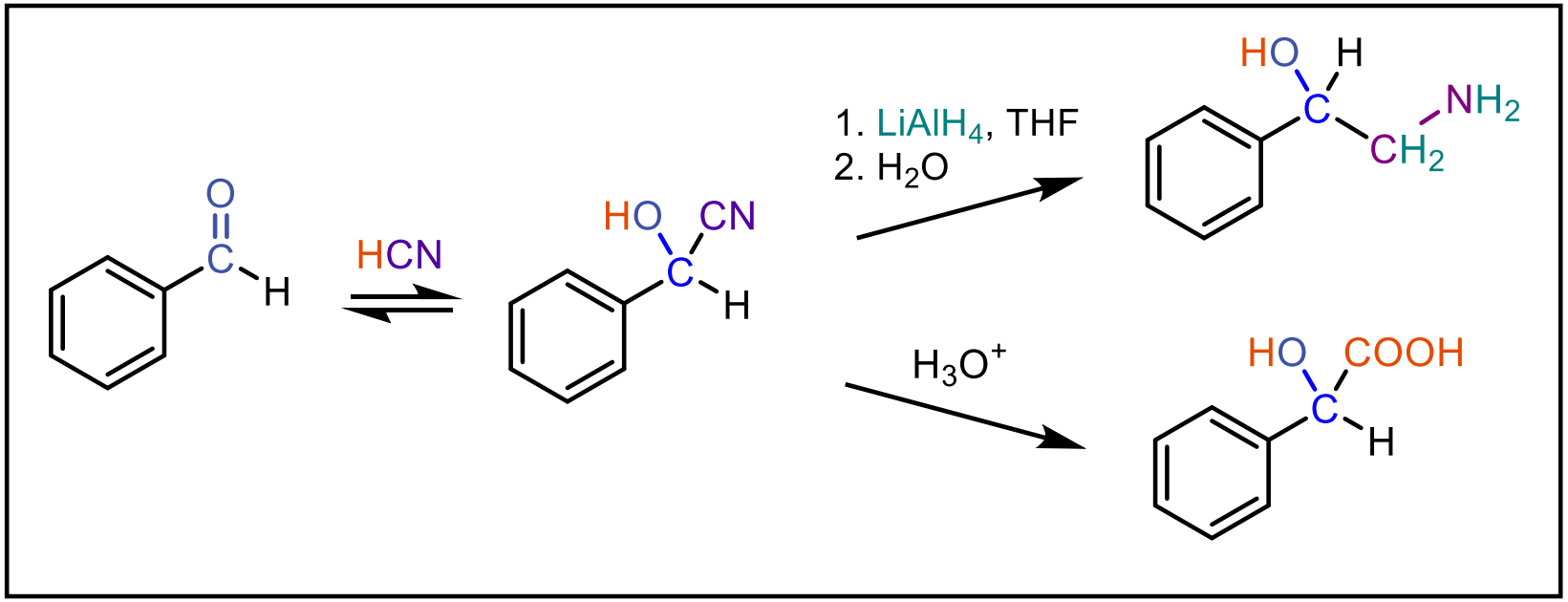

O
C
H
+ H2O
HO
OH
0.1%
99.9%

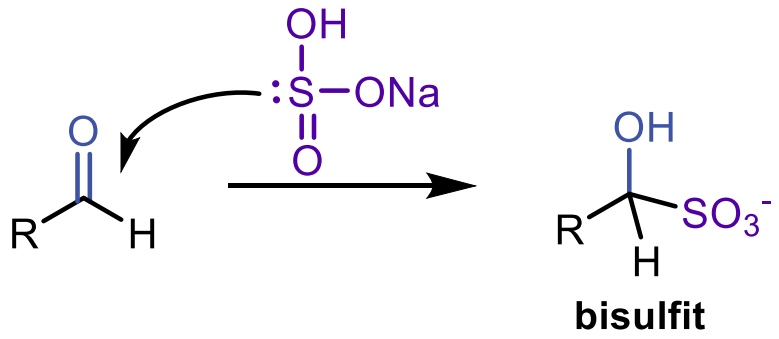

O
C
Cl
H
+ H2O
HO
OH


O
C
R
+ OH-
-O
OH
H+
HO
OH

Adice kyanovodíku - kyanhydriny





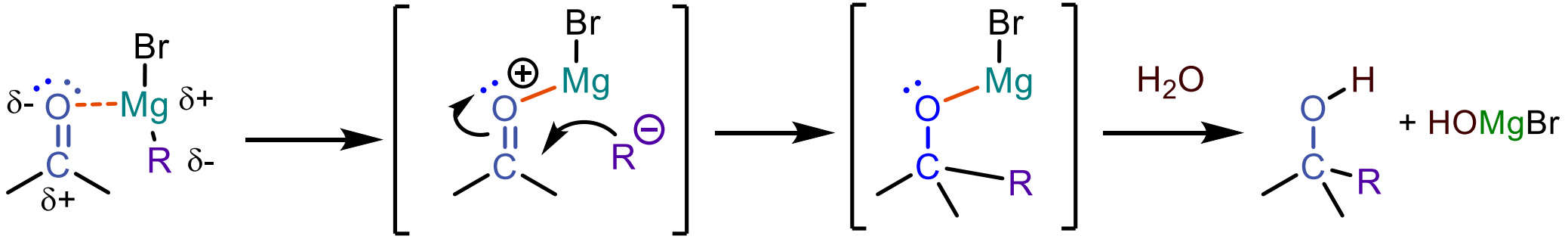


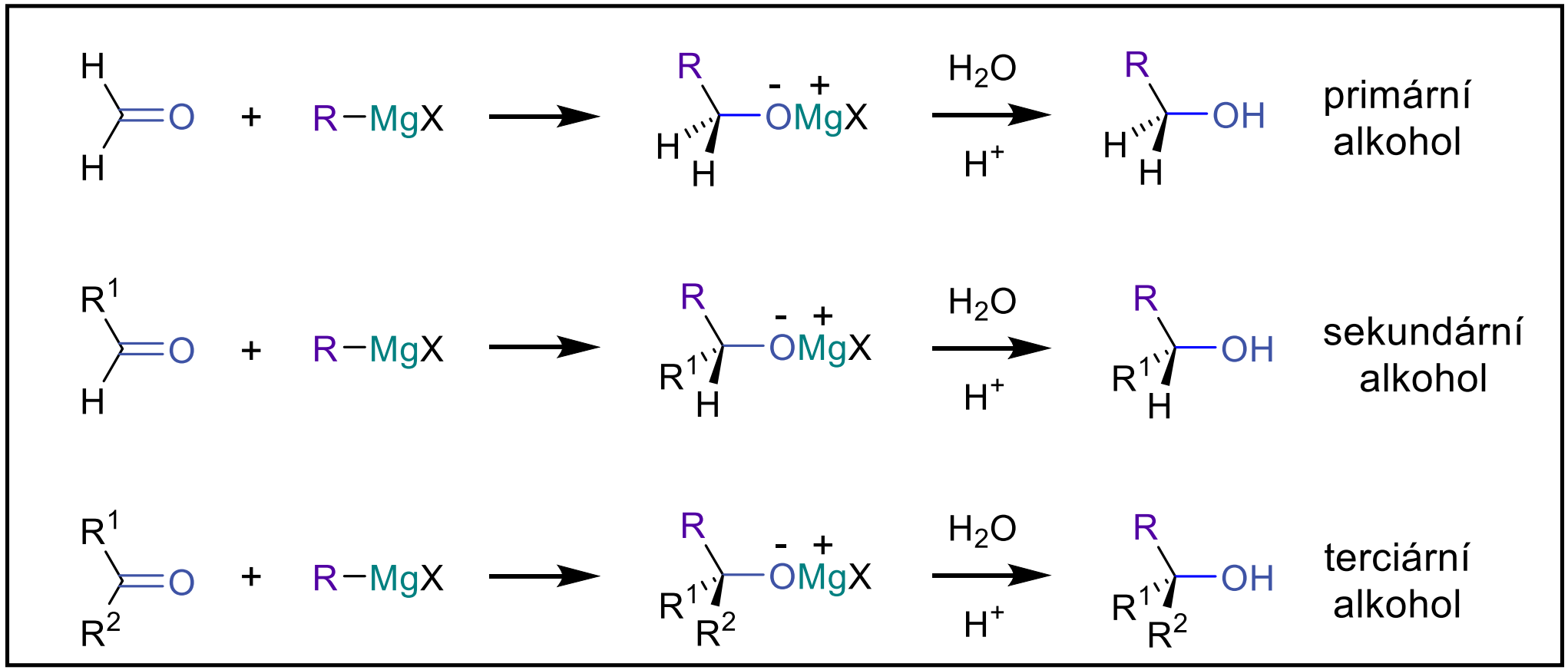
bisulfit

adice hydrogensiřičitanu sodného

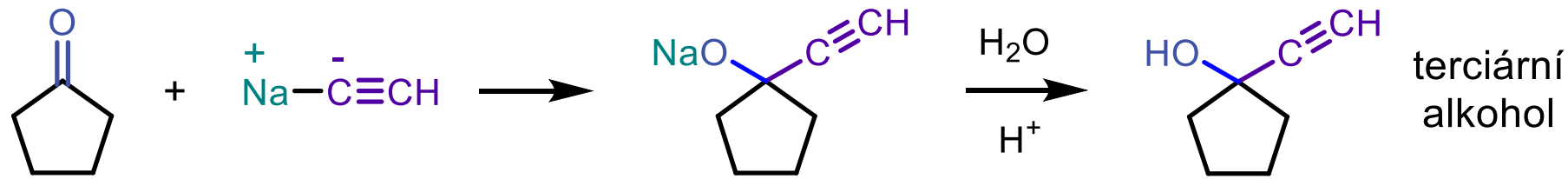
vznik bisulfitů

Adice Grignardových činidel

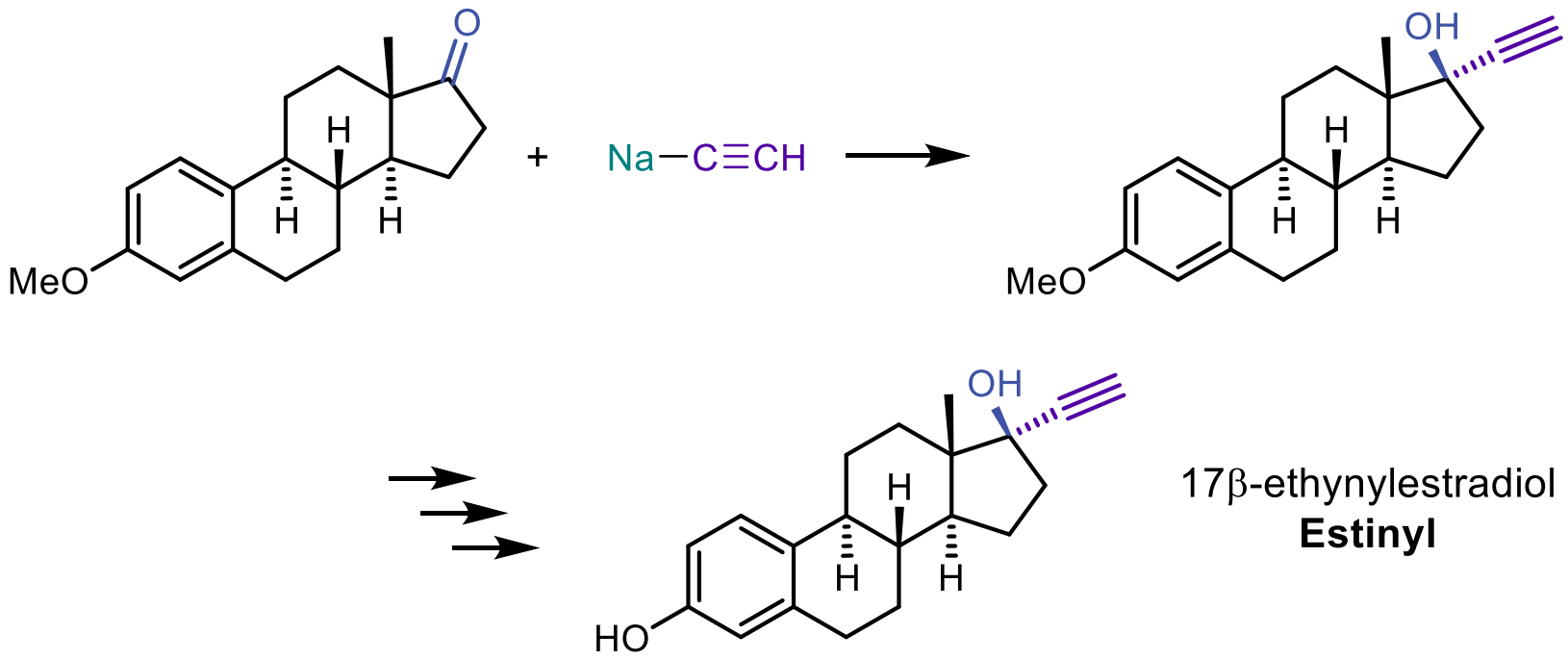




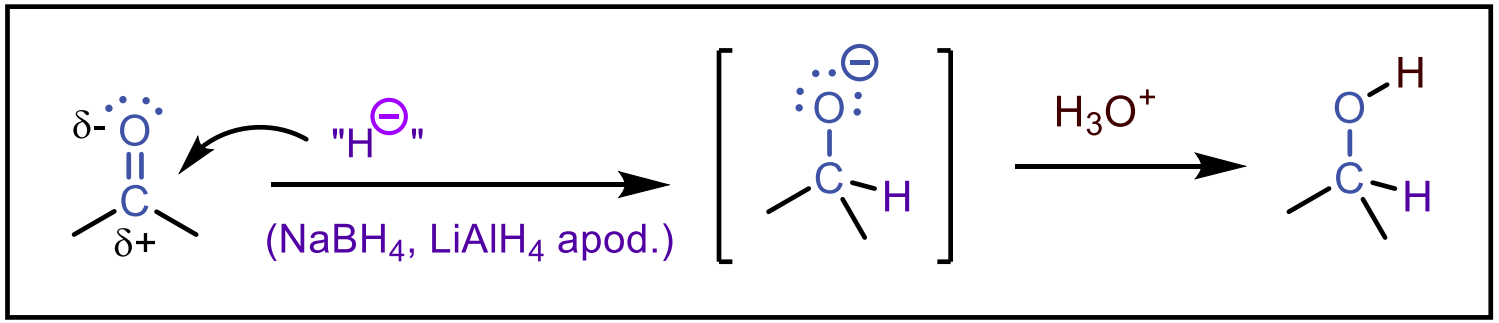
Reakce karbonylových sloučenin s acetylidy vede k tvorbě propargylových alkoholů.

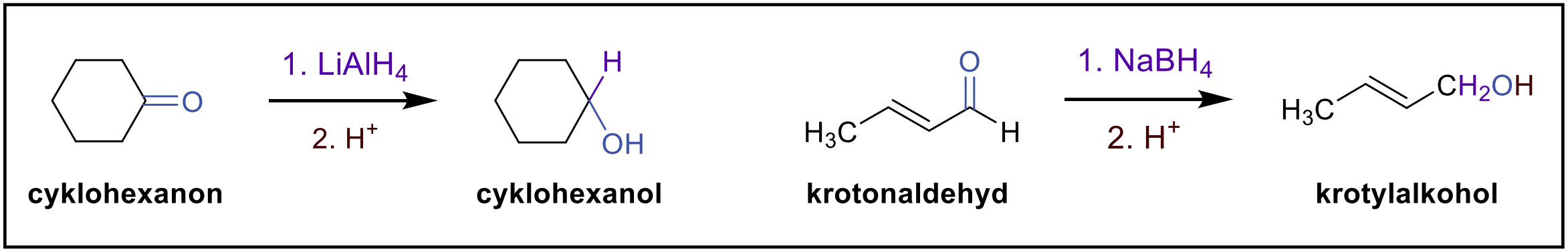


Tato reakce byla využita i k přípravě jednoho z prvních syntetických derivátů estrogenů – ethynylestradiolu (Estinyl). (Inhoff, Schering AG, 1938)



Adice „hydridového aniontu“ - redukce

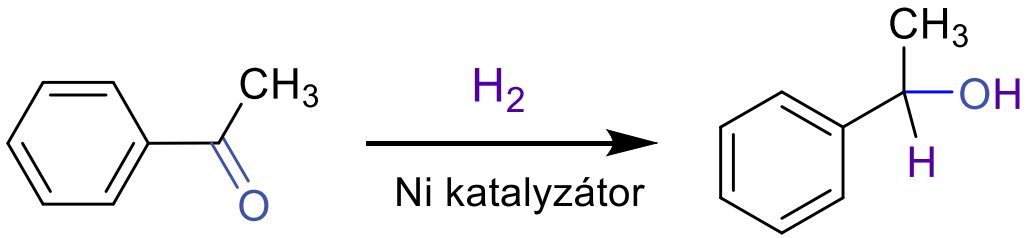




cyklohexanon **cyklohexanol** **krotonaldehyd** **krotylalkohol**

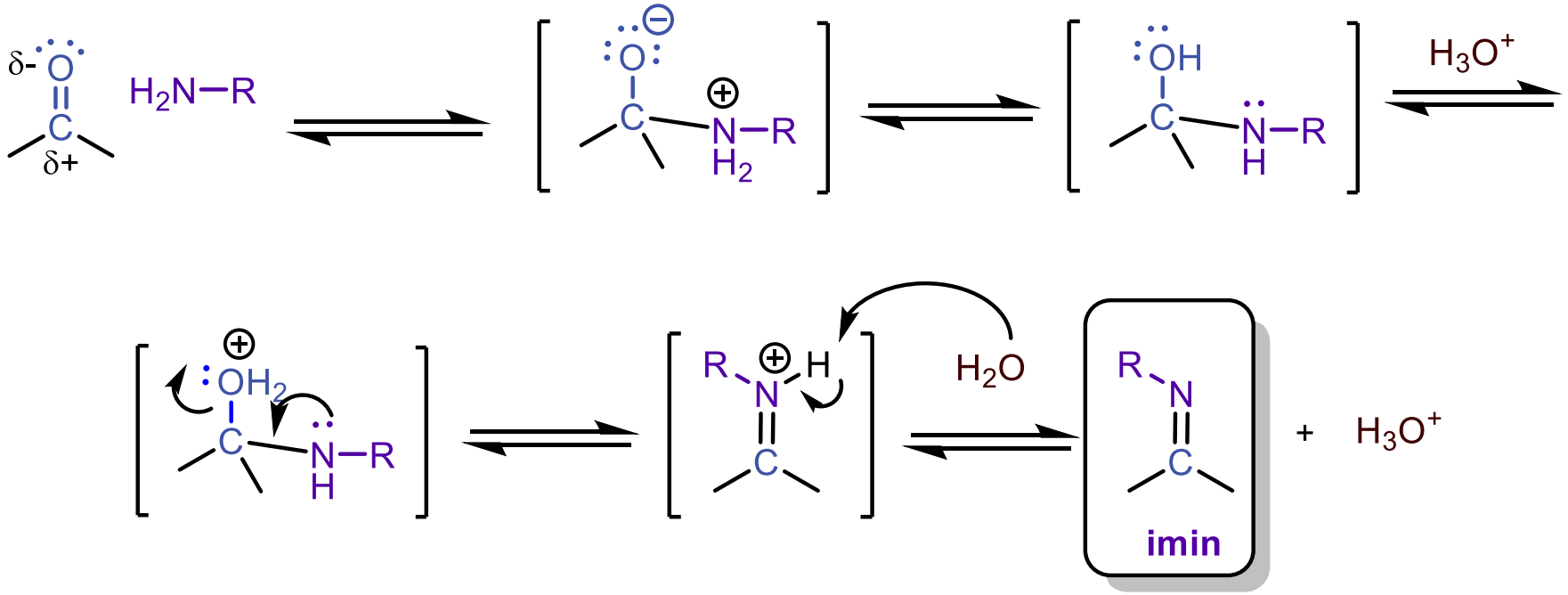
adice vodíku

katalytická hydrogenace

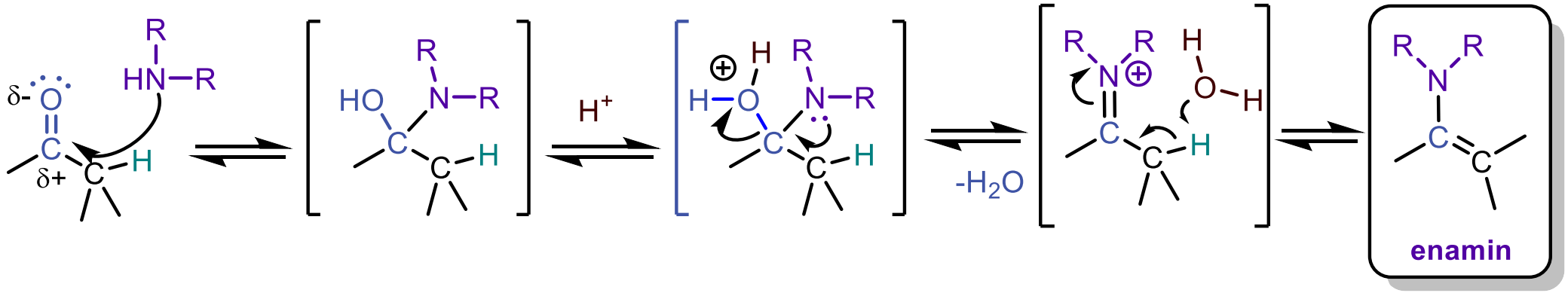


benzofenon **1-fenylethanol**

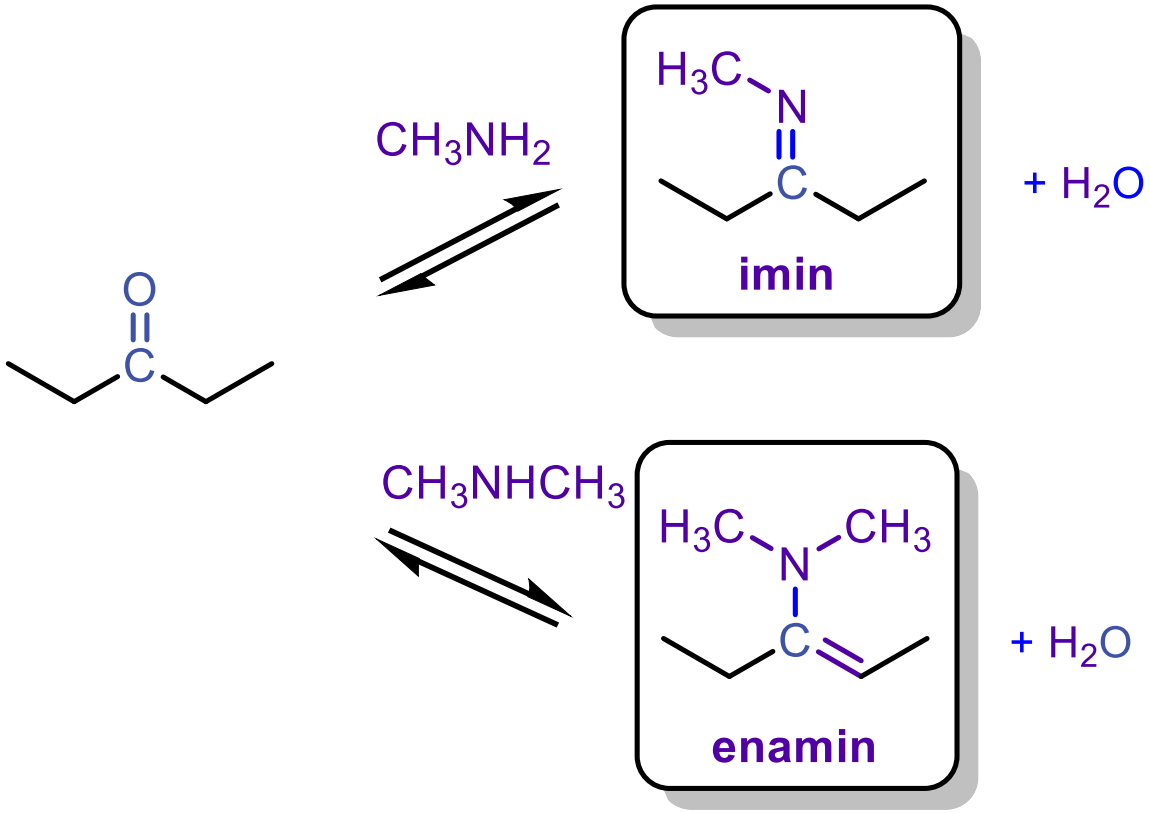
Adice primárních aminů – iminy (Schiffovy báze)



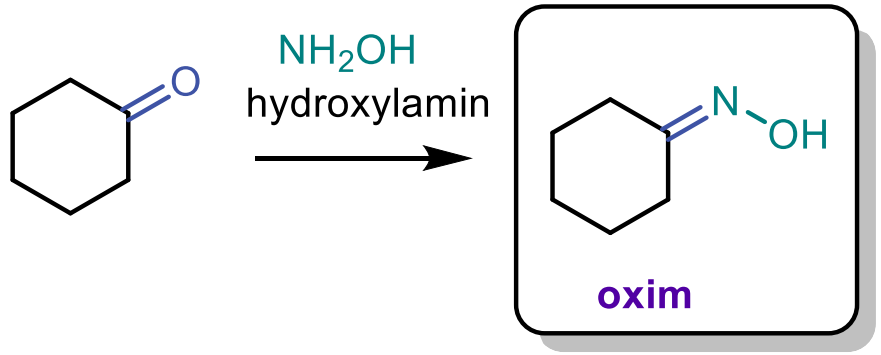
Adice sekundárních aminů – enaminy

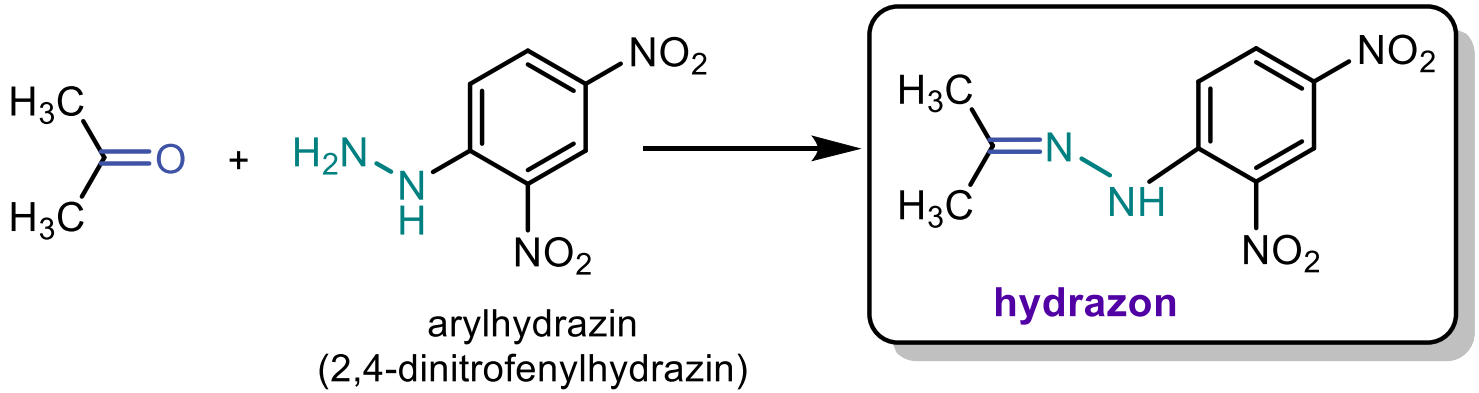


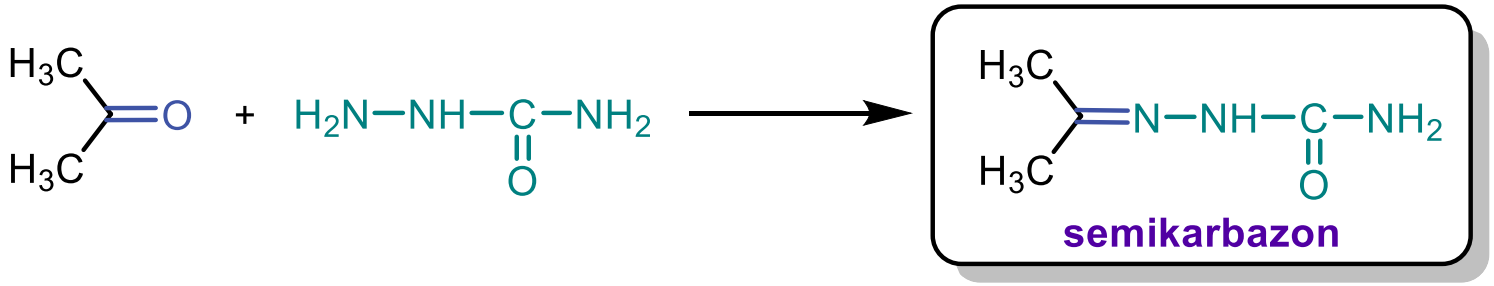
Adice aminů – tvorba iminů nebo enaminů



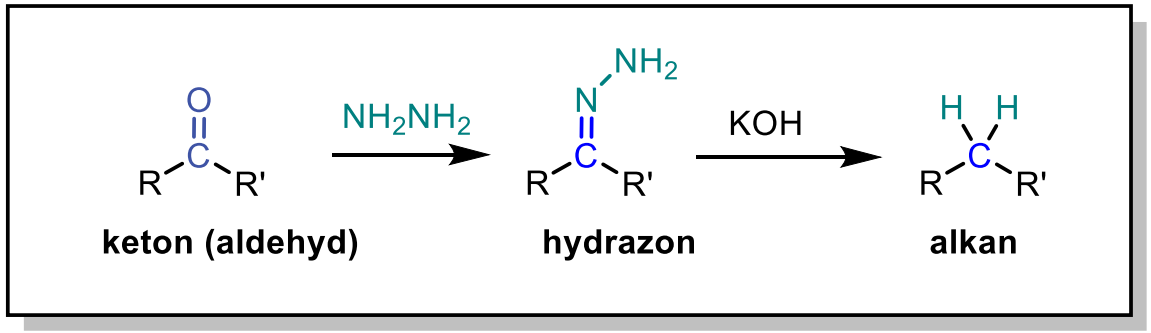
Oximy, hydrazony a příbuzné deriváty

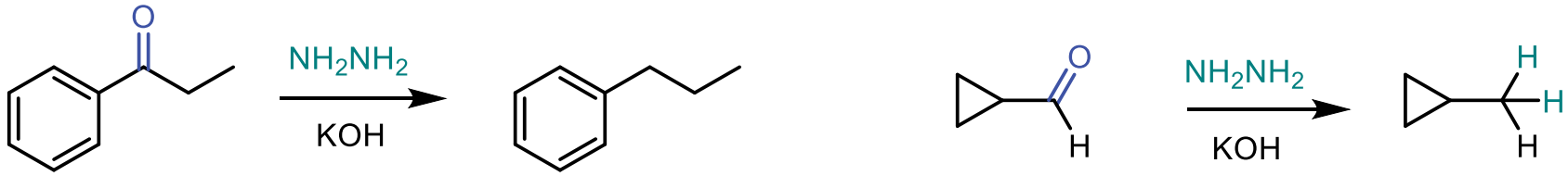


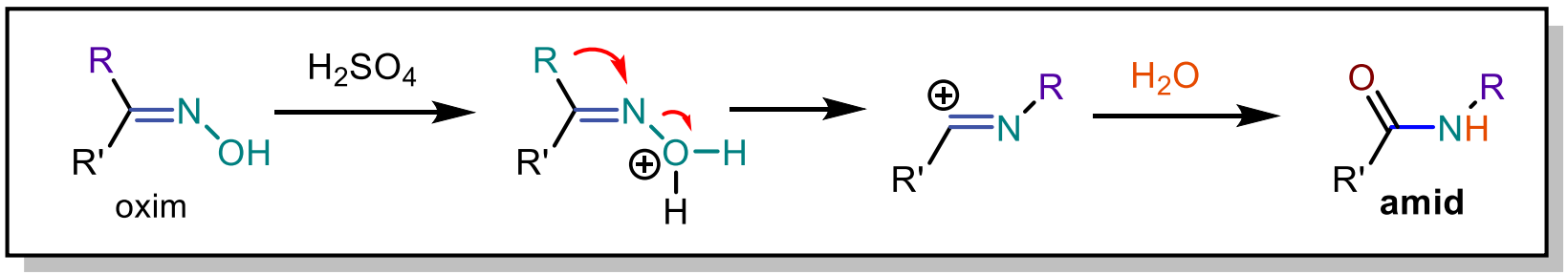


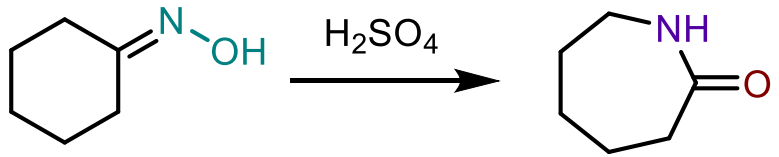


Wolff-Kižněrova redukce – transformace ketonů na alkany

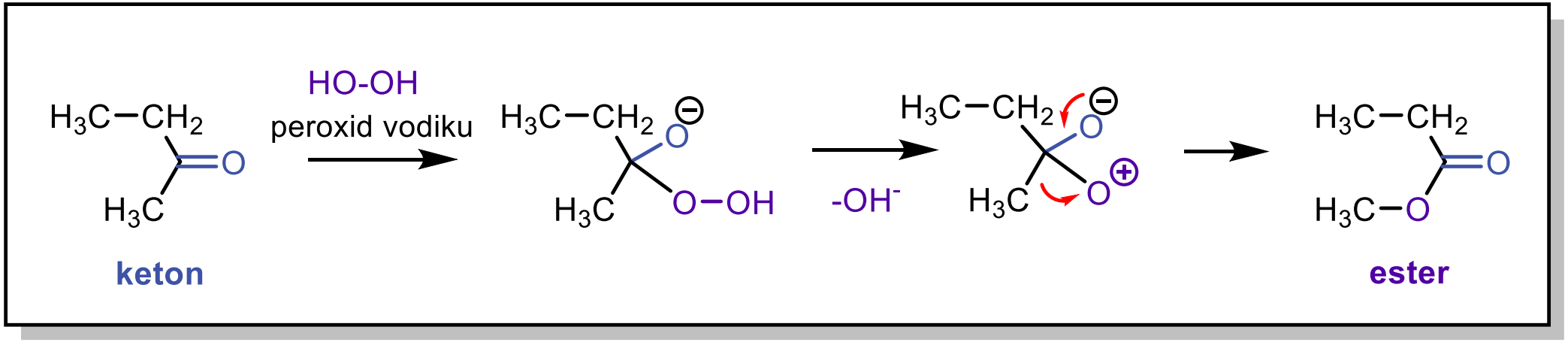


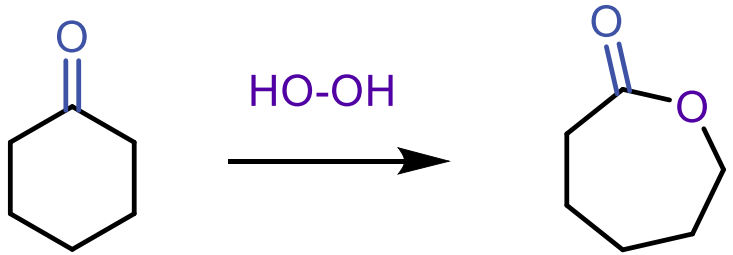






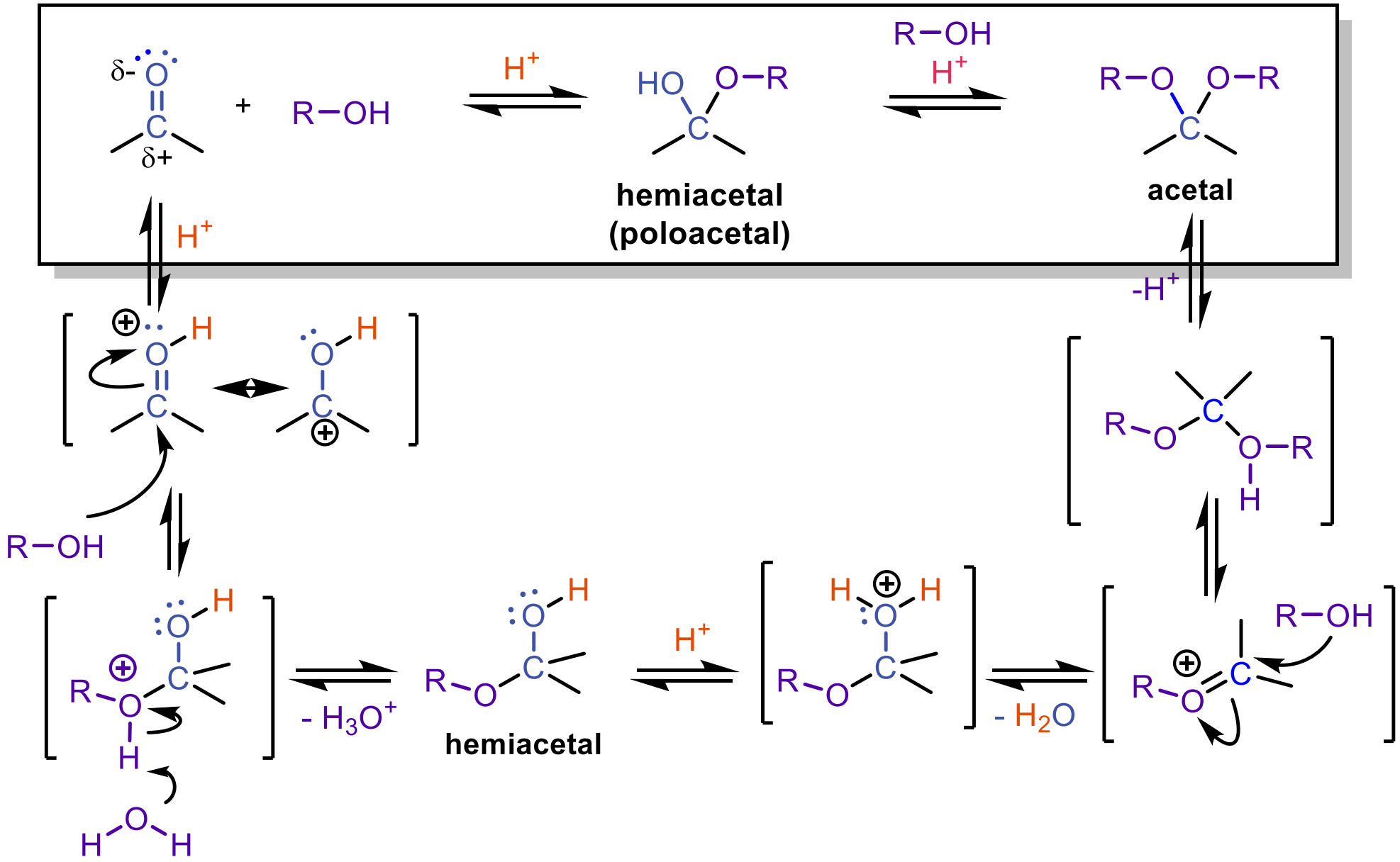
Baeyer-Villigerova reakce



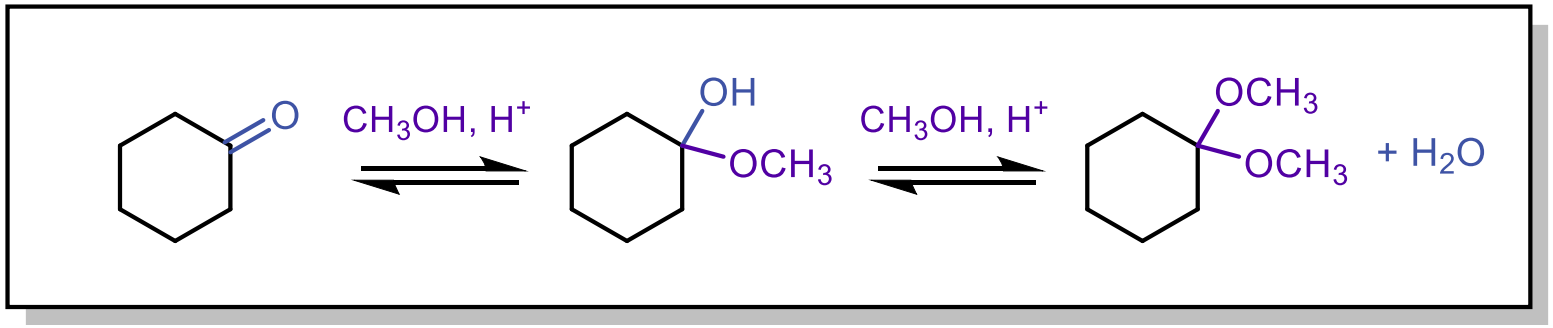


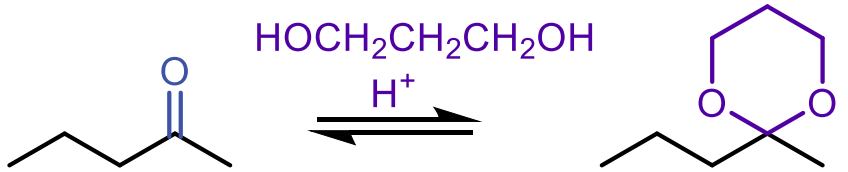
hlavně pro symetrické ketony

Adice alkoholů – acetaly a hemiacetaly

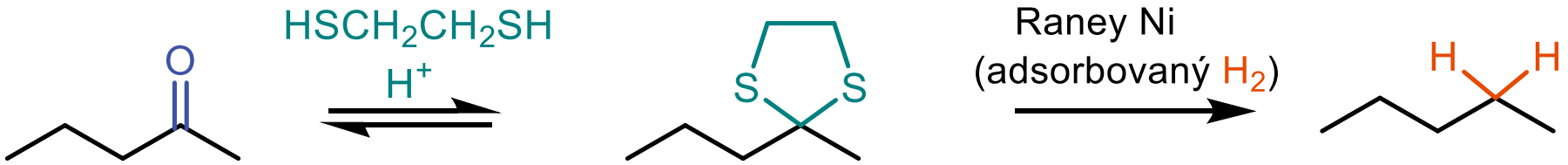


Adice alkoholů – acetaly a hemiacetaly



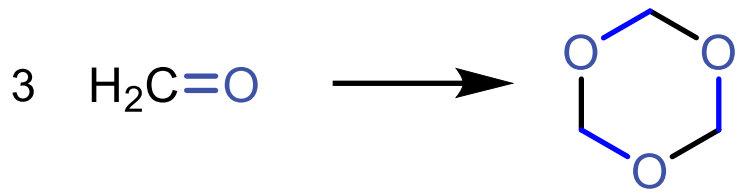


Adice dithiolů – thioacetaly a katalytická redukce na alkany



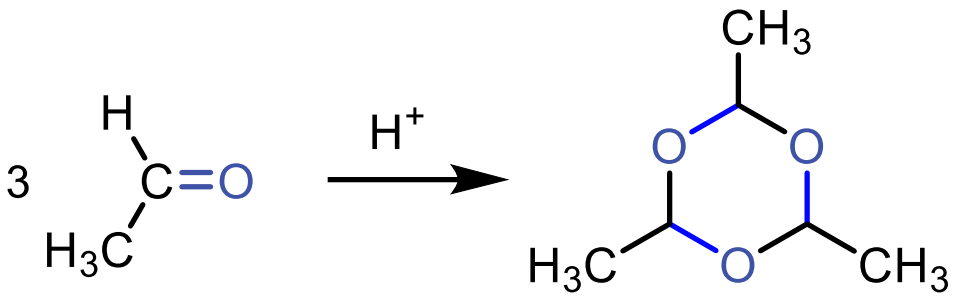
thioacetal

Oligomery a polymery aldehydů

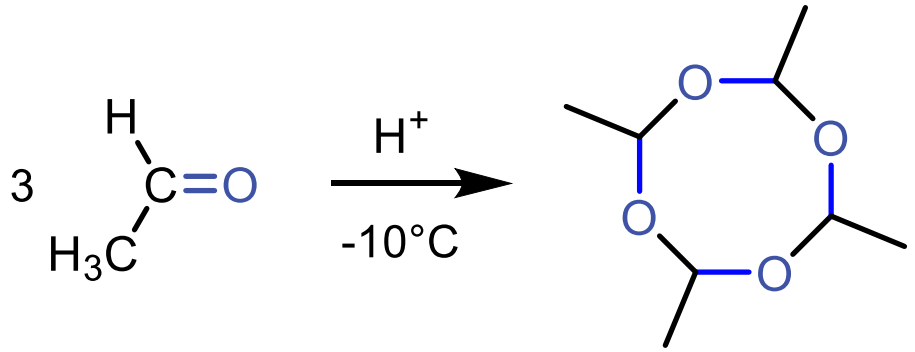


trioxan - krystalický

paraformaldehyd



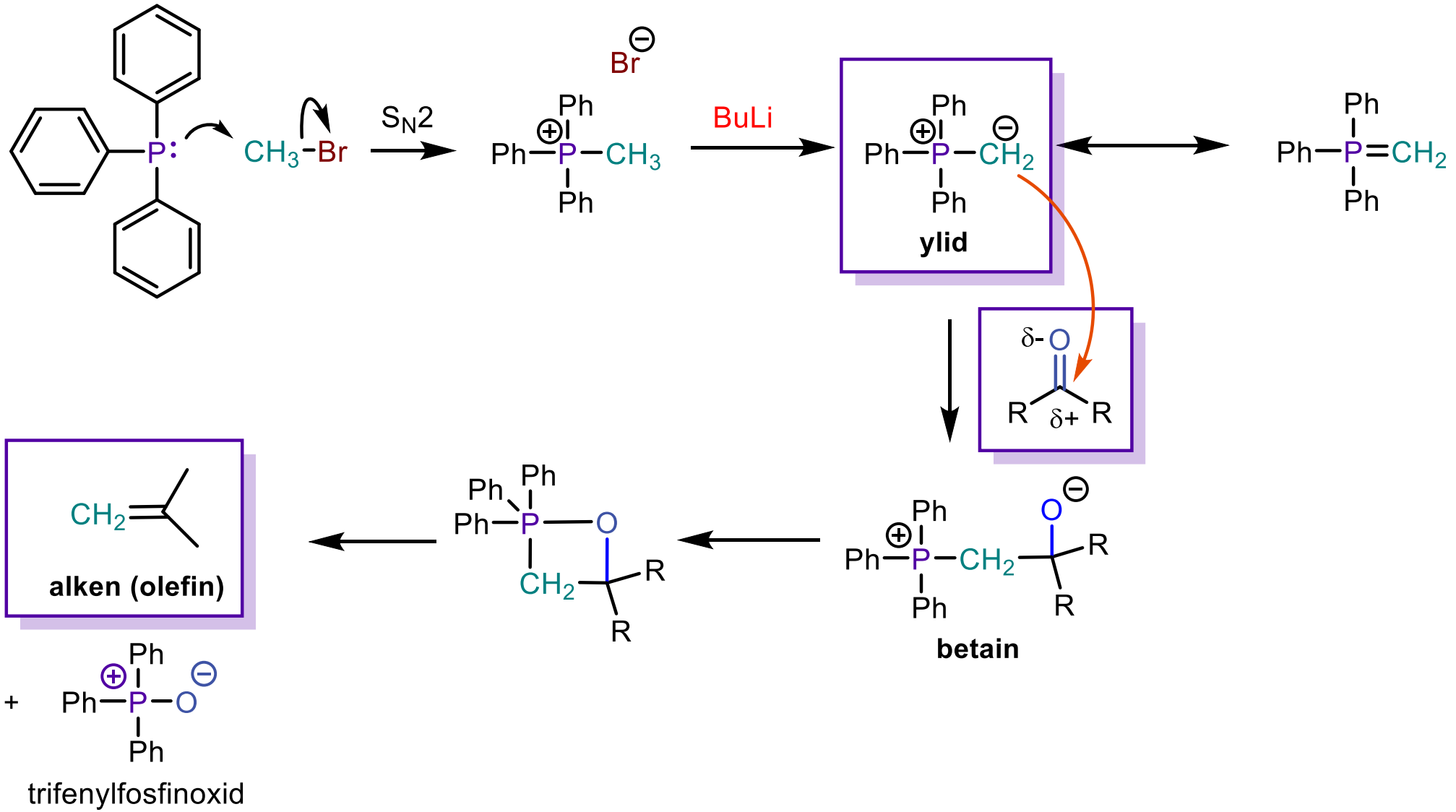
paraldehyd



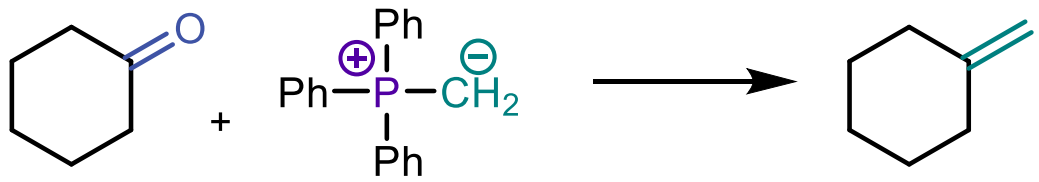
metaldehyd

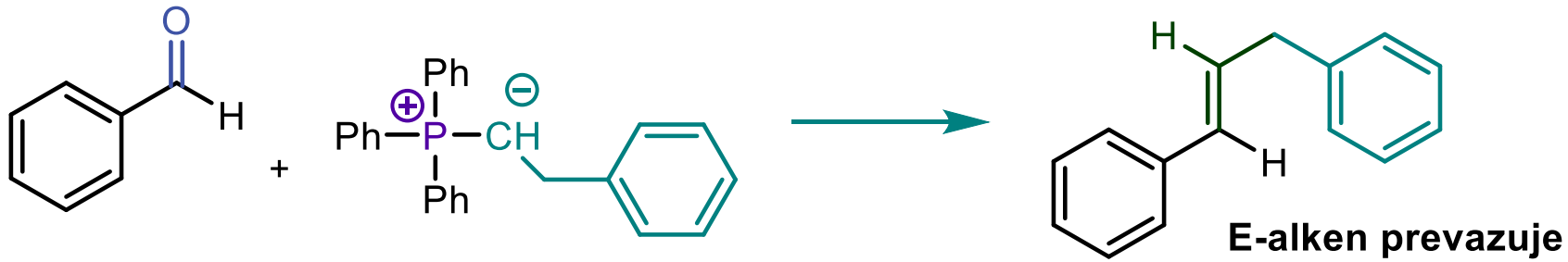
"tuhý líh"

Adice fosforových ylidů – Wittigova reakce



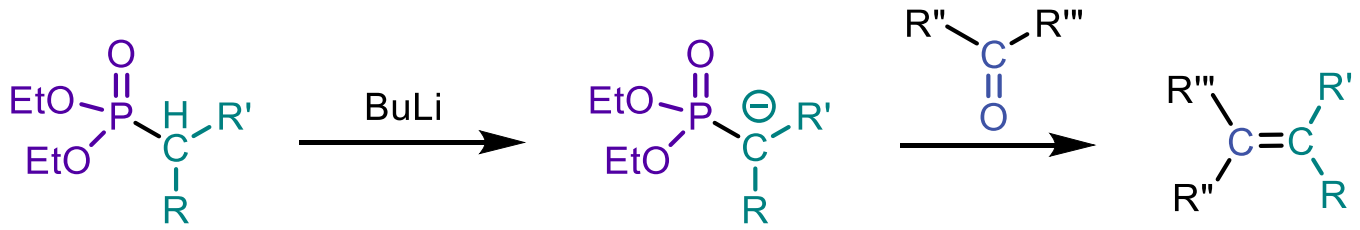
Adice fosforových ylidů – Wittigova reakce



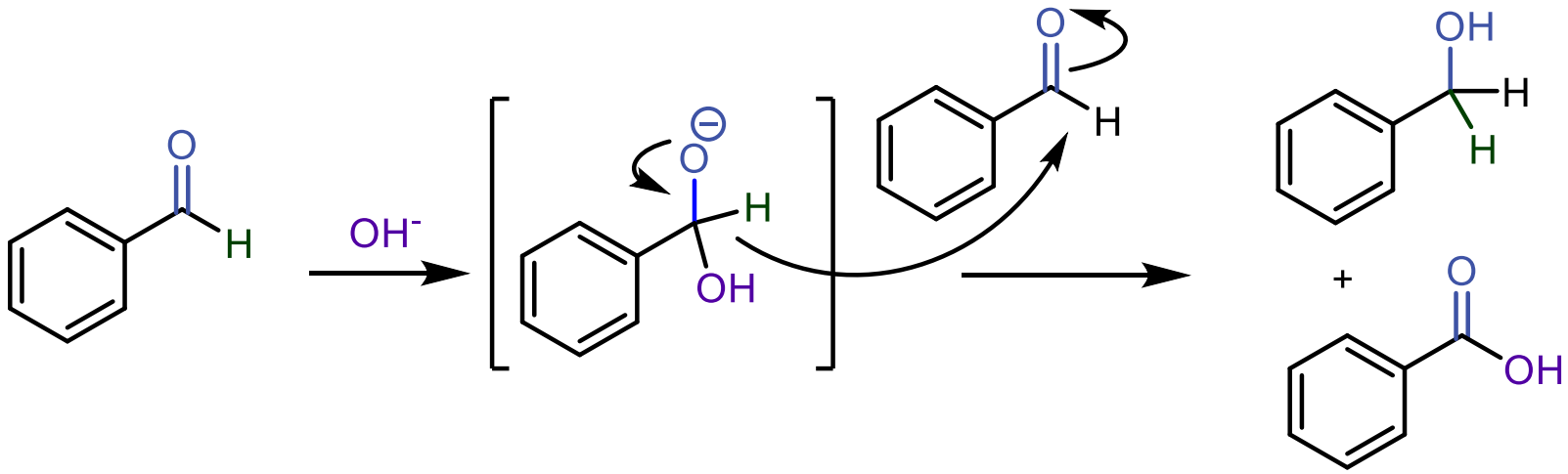


E-alken prevazuje

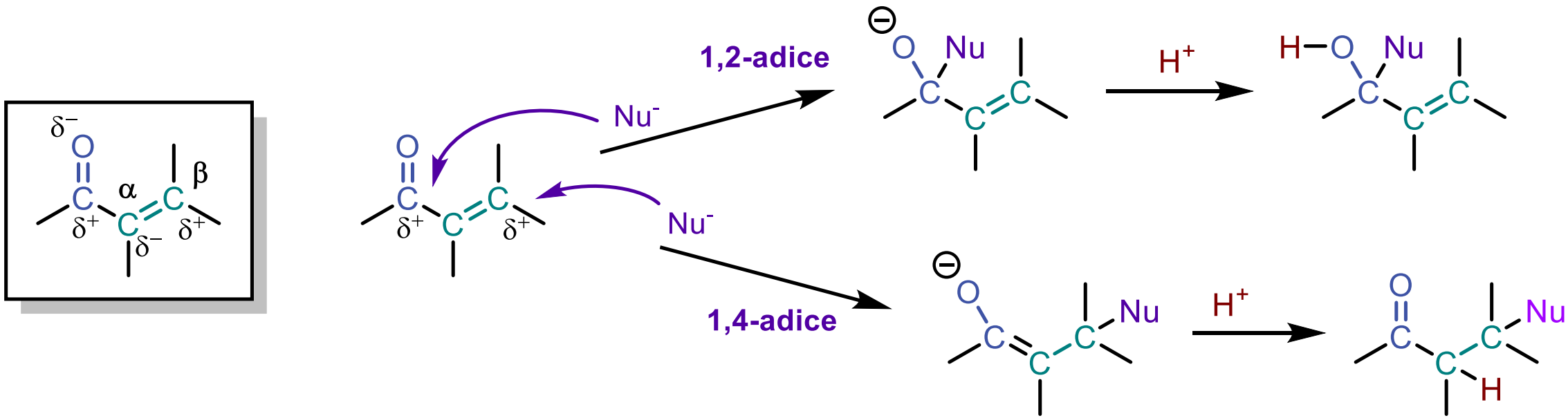
Horner-Emmonsova (Horner-Wittigova, Wadsworth-Emonsova) reakce



Canizzarova reakce – disproporcionace (neenolizovatelných) aldehydů



α,β-Nenasycené aldehydy a ketony - konjugované adice



Adice aminů probíhají obvykle 1,4-adicí

Adice Gilmanových kuprátů probíhají výhradně 1,4-adicí