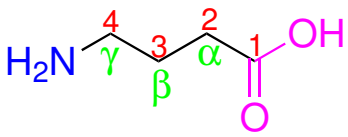
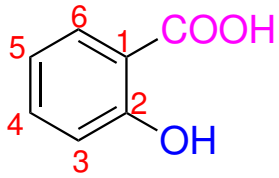
Karboxylové kyseliny a jejich deriváty

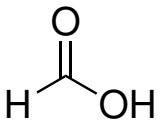


4-aminobutanová kyselina
γ-aminomáselná kyselin



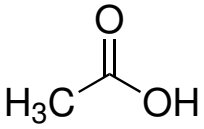
2-hydroxybenzenkarboxylová kyselina
o-hydroxybenzoová kyselina
kyselina salicylová

Triviální názvy karboxylových kyselin a solí (esterů):



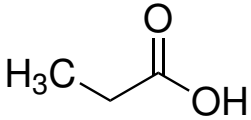
mravenčí

formiát



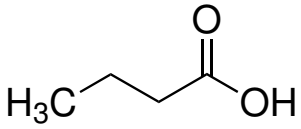
octová

acetát



propionová

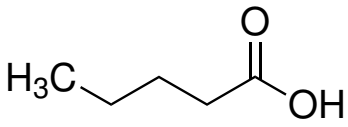
propionát



máselná

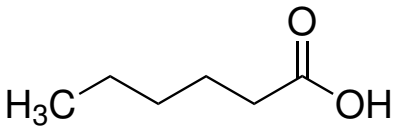
butyrát

Karboxylové kyseliny a jejich deriváty



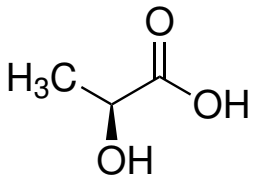
valerová

valerát



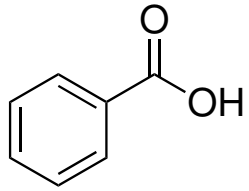
kapronová

kapronát



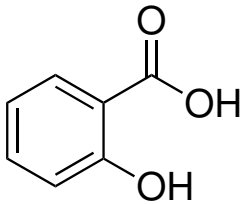
mléčná

laktát



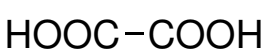
benzoová

benzoát



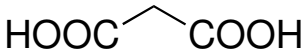
salicylová

salicylát



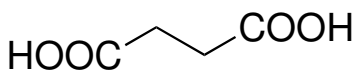
šťavelová

oxalát



malonová

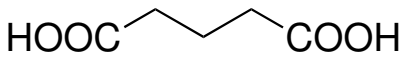
malonát



jantarová

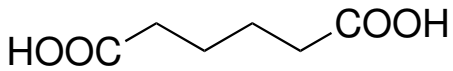
sukcinát

Karboxylové kyseliny a jejich deriváty



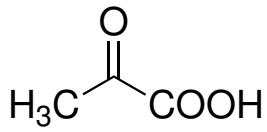
glutarová

glutarát



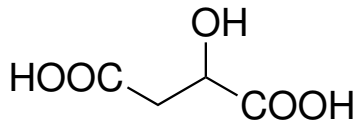
adipová

adipát



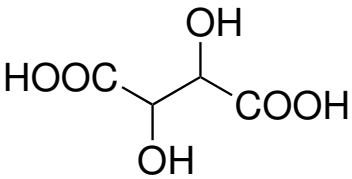
pyrohroznová

pyruvát



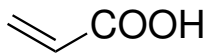
jablečná

malát



hroznová

tartrát



akrylová

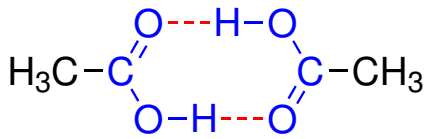
akrylát

Vlastnosti karboxylových kyselin

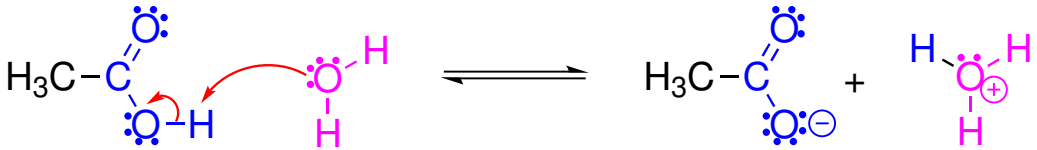
Teploty varu:

	CH_3CH_2OH	$H_3C-C(=O)-OH$
b.v.	78 °C	118 °C

Tvorba dimerů:



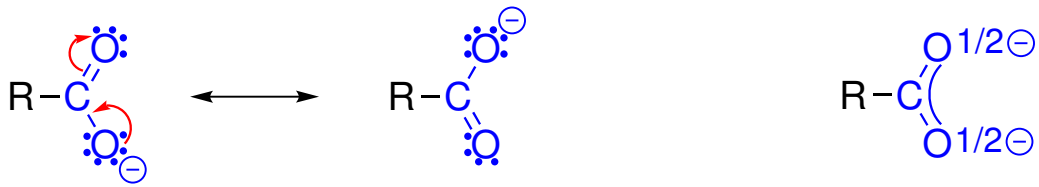
Kyselost:



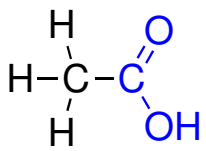
	CH_3CH_2OH	$H_3C-C(=O)-OH$
pK_a	16	4,76

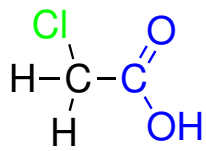
Vlastnosti karboxylových kyselin

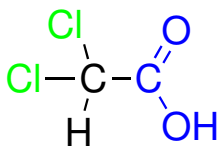
Stabilizace karboxylátového aniontu konjugací:

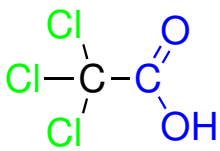


Vliv indukčního efektu na kyselost:

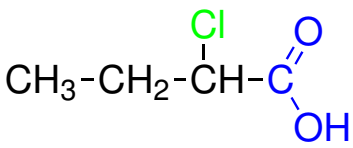


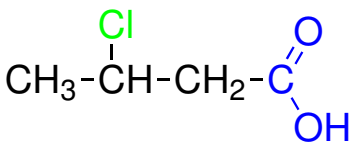


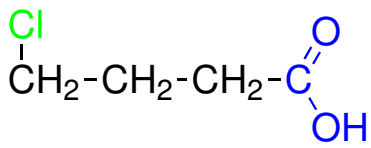


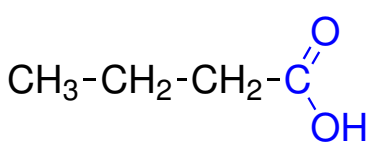


pK_a	4,76	2,9	1,3	0,9





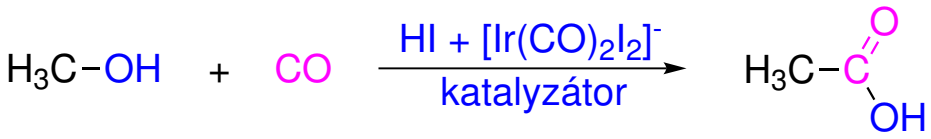




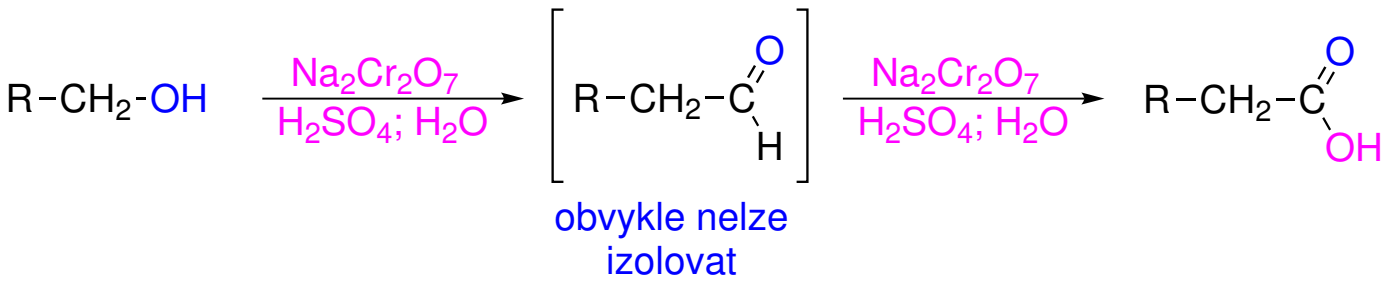
pK_a	2,9	4,1	4,5	4,8

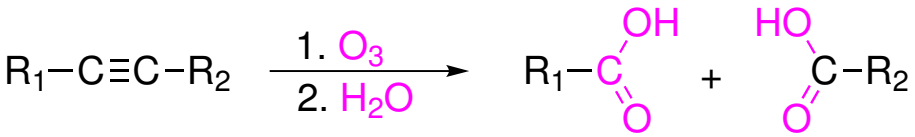
Příprava karboxylových kyselin

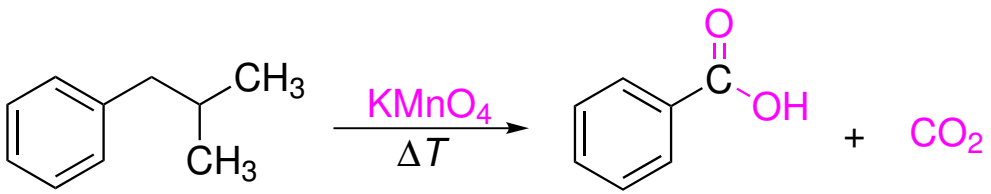
Průmyslová výroba kyseliny octové



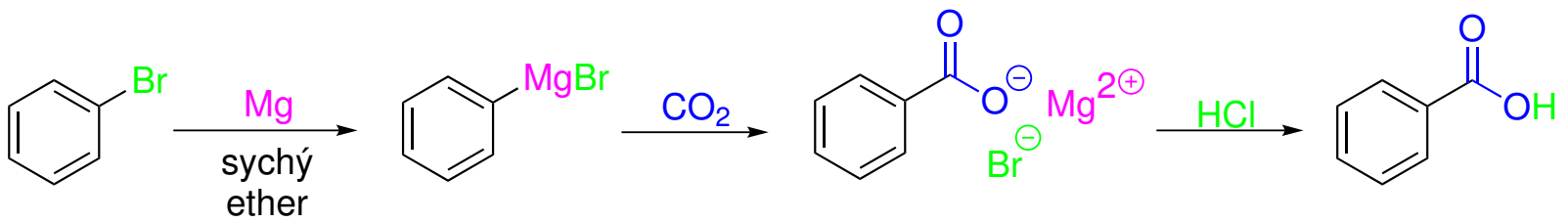
Příprava karboxylových kyselin:

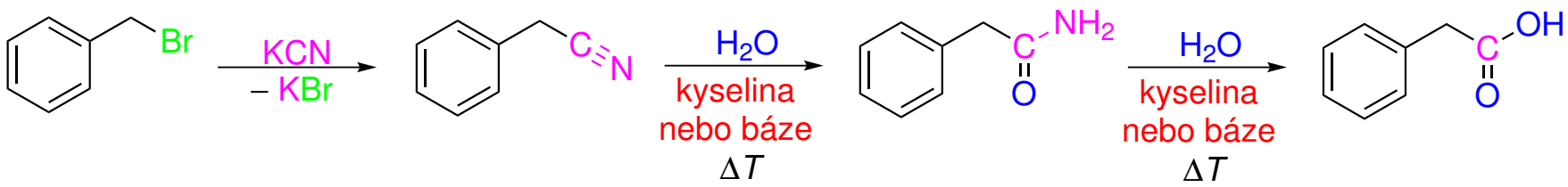




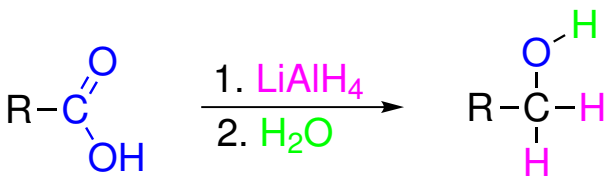


Příprava a reakce karboxylových kyselin



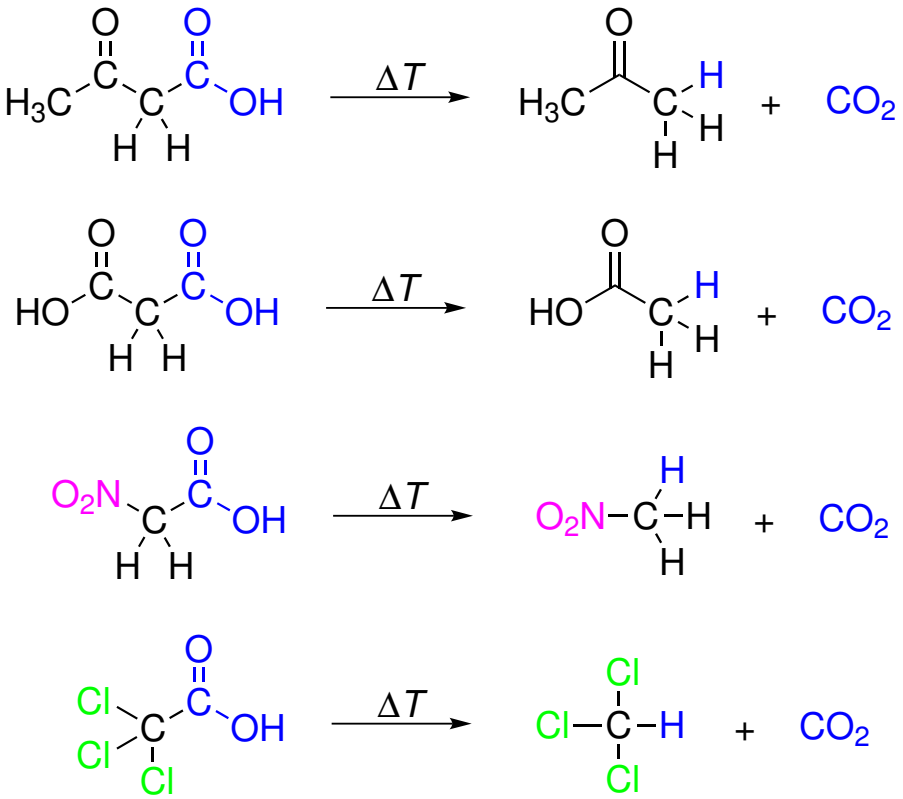


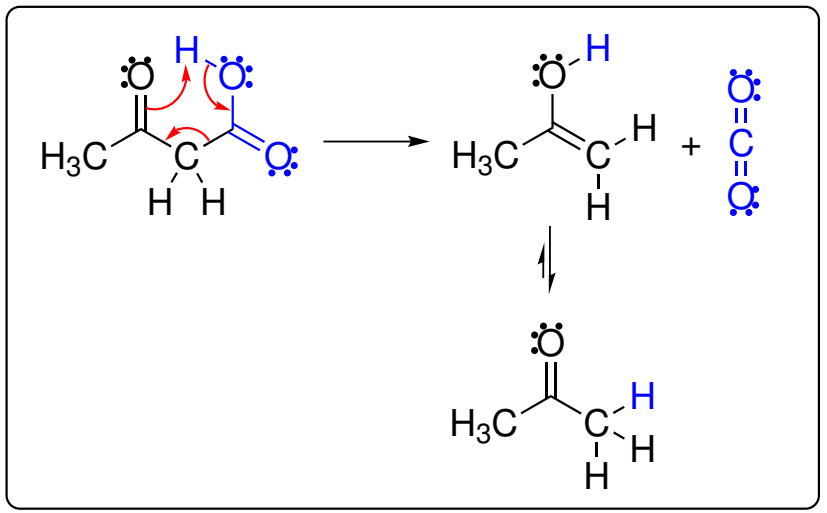
Redukce karboxylových kyselin:



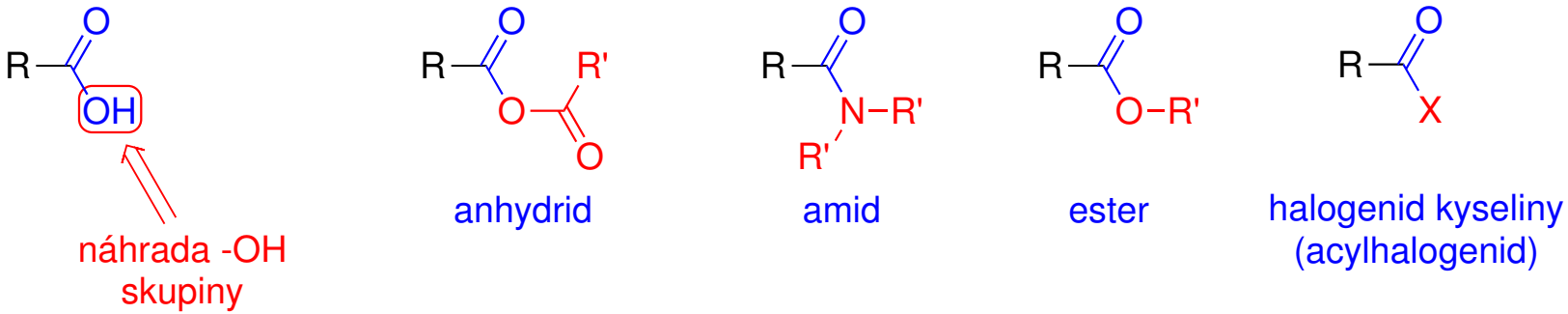
Reakce karboxylových kyselin

Dekarboxylace karboxylových kyselin s elektronakceptorními substituenty na α-atomu uhlíku.

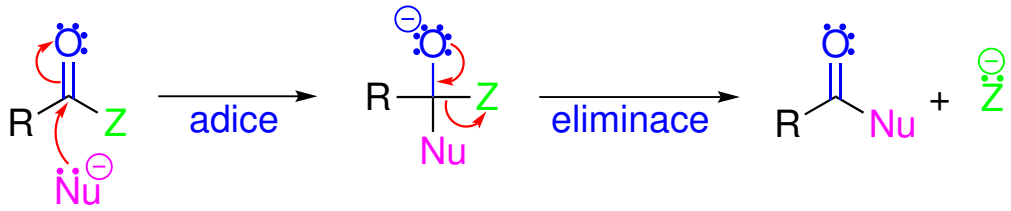




Funkční deriváty karboxylových kyselin

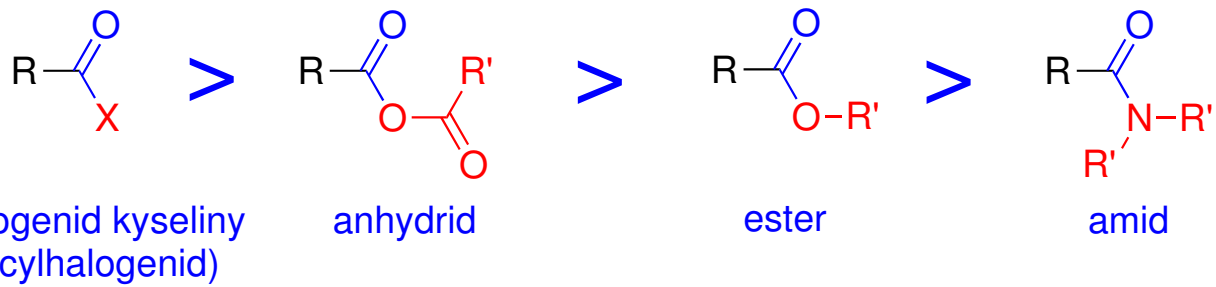


Nukleofilní acylová substituce

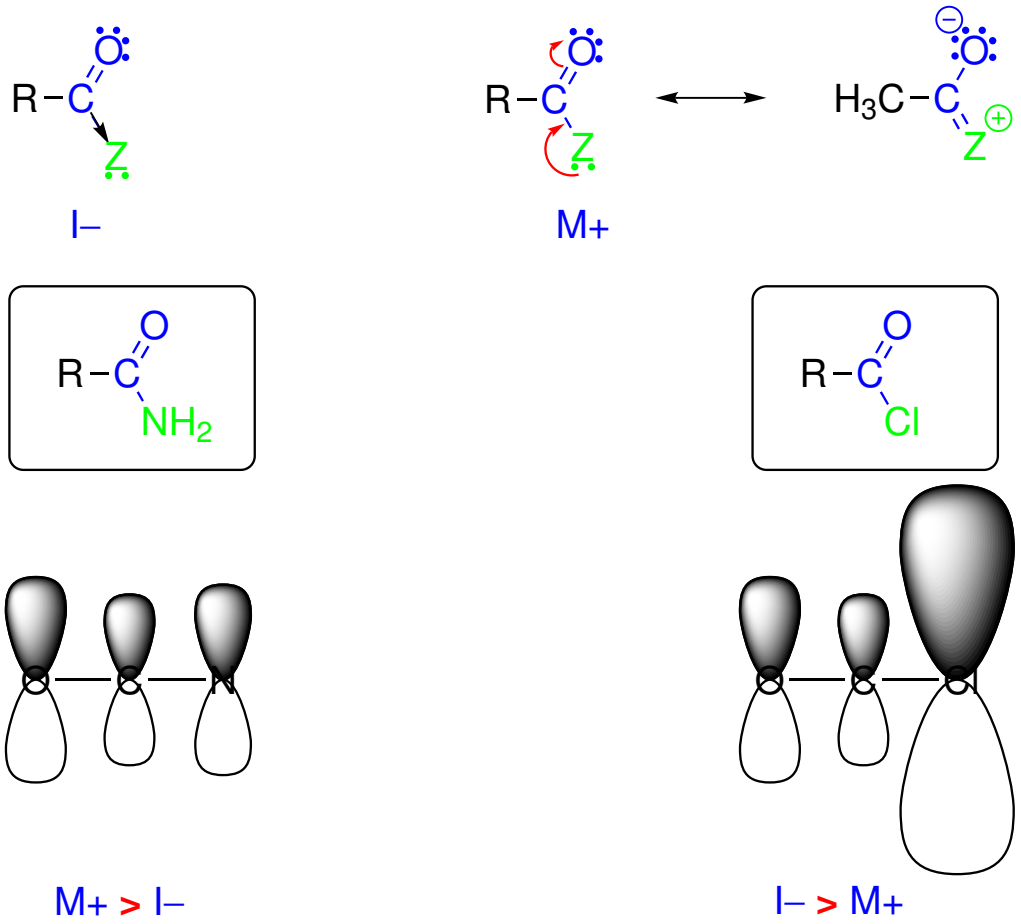


Probíhá adičně-eliminačním mechanismem.

Reaktivita vůči nukleofilům:



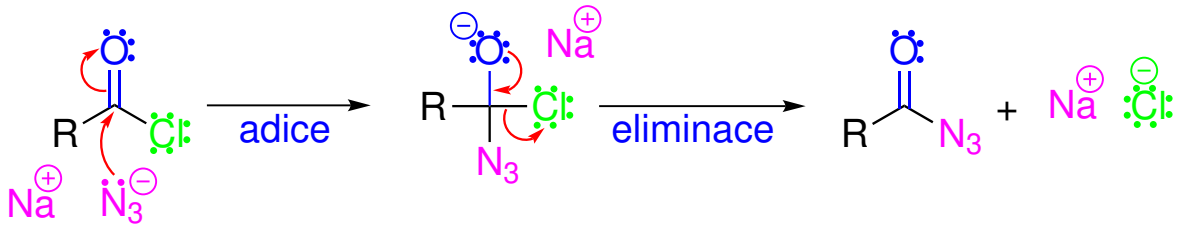
Funkční deriváty karboxylových kyselin



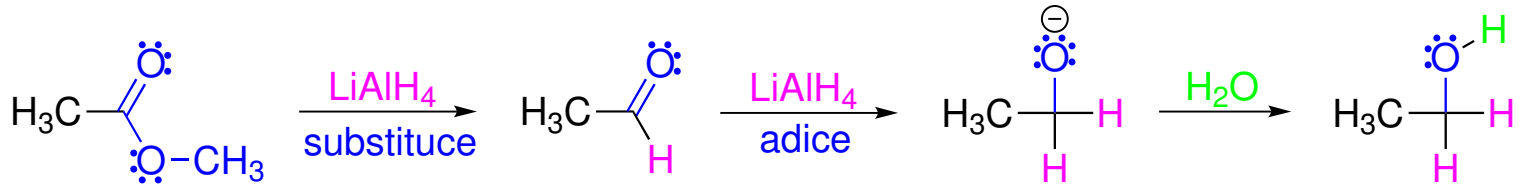
Nukleofilní acylovou substitucí lze převádět funkční deriváty mezi sebou – snadno lze z derivátu reaktivnějšího připravit derivát méně reaktivní.

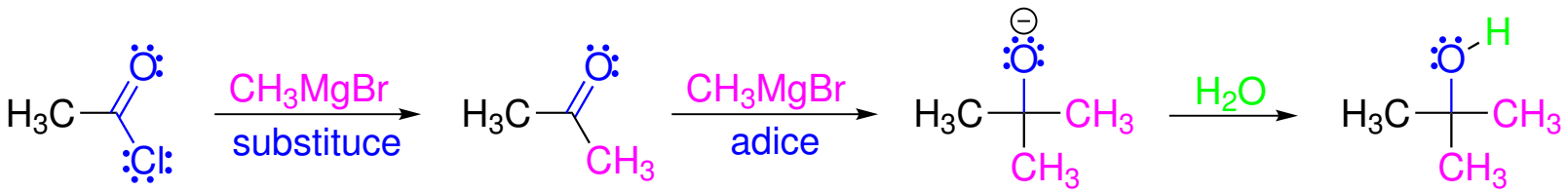
Funkční deriváty karboxylových kyselin

Příprava acylazidů:



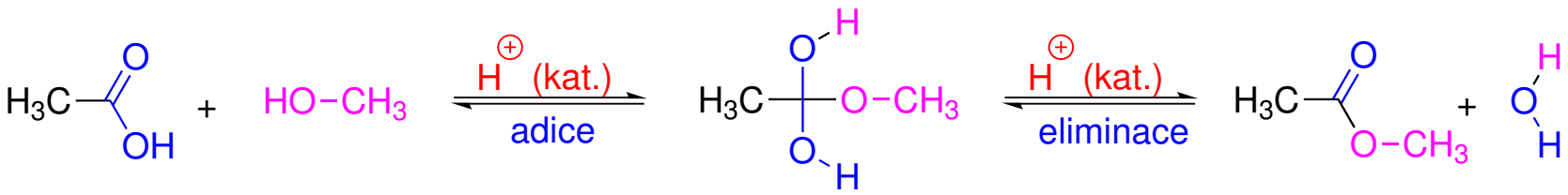
Pokud je nukleofilem organokov nebo komplexní hydrid, může produkt substituce (aldehyd nebo keton) dále reagovat s nukleofilem:



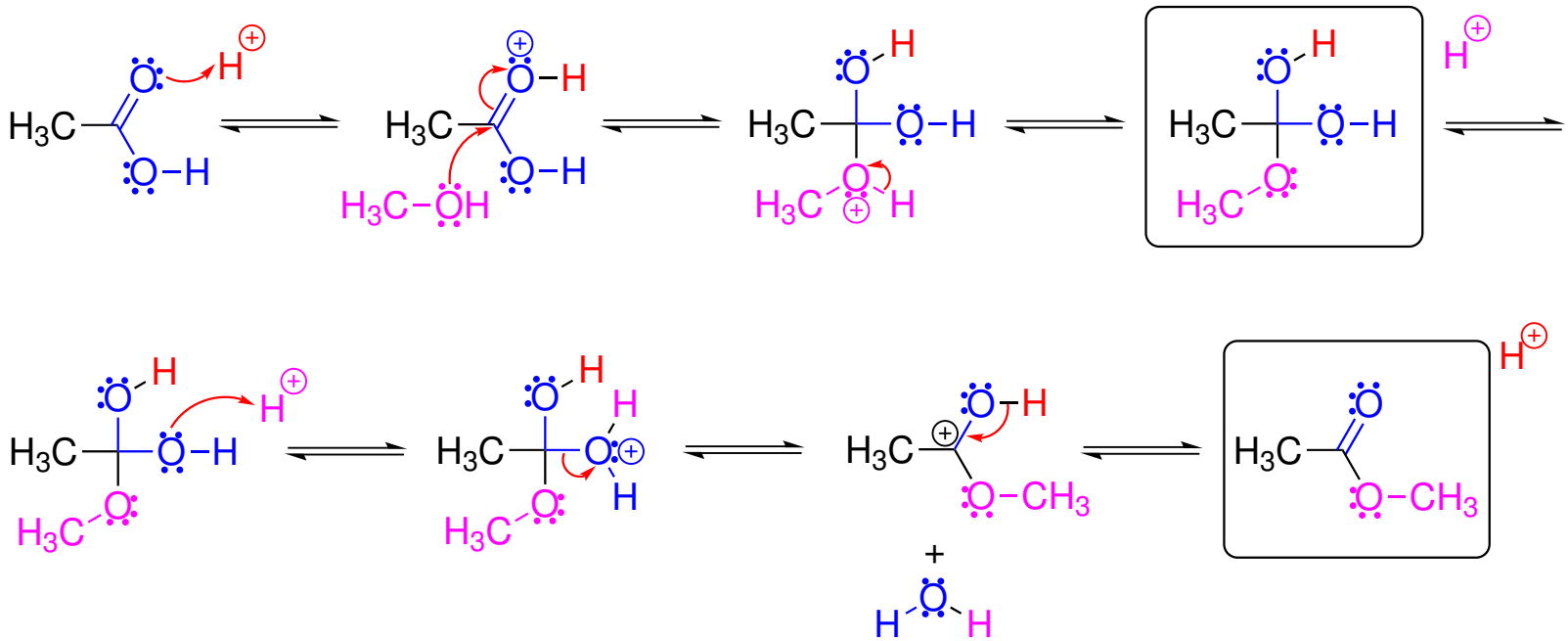


Funkční deriváty karboxylových kyselin

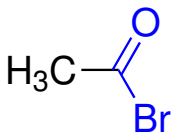
Esterifikace:



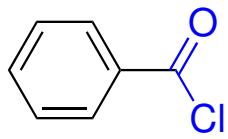
Mechanismus:



Halogenidy karboxylových kyselin

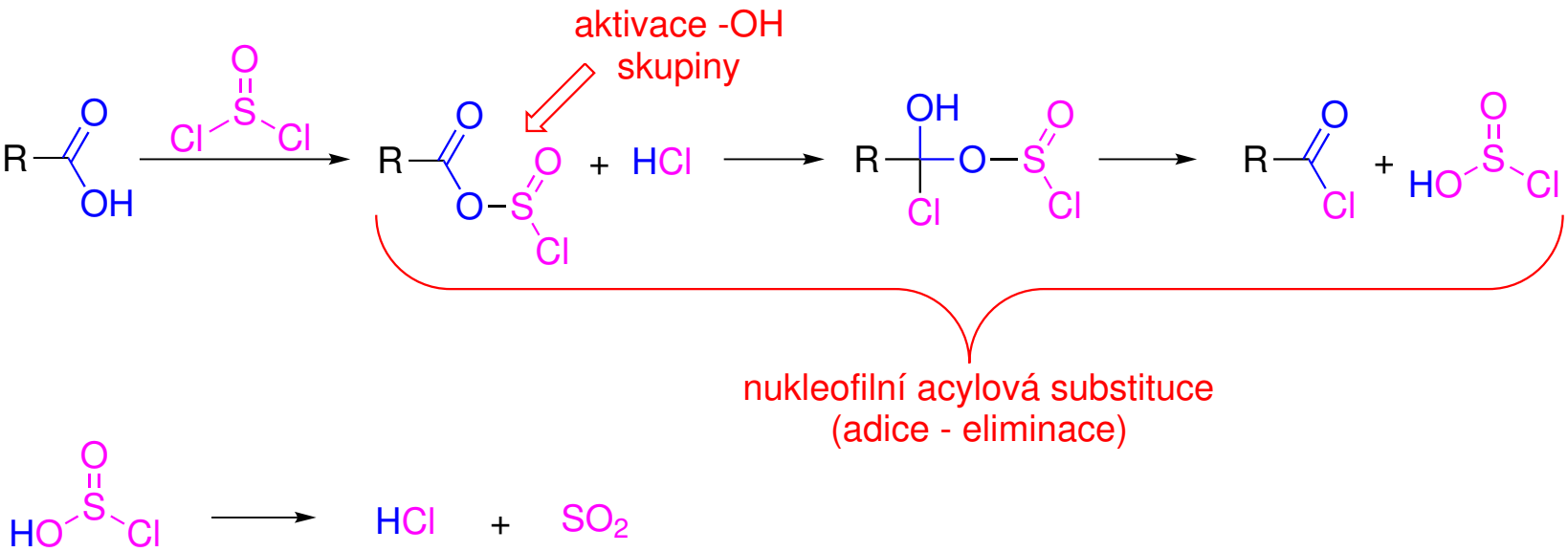


bromid kyseliny octové
acetylbromid



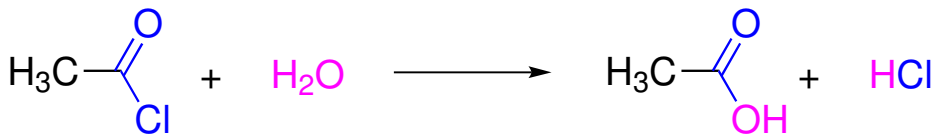
chlorid kyseliny benzoové
benzoylchlorid

Obvykle připravovány reakcí karboxylových kyselin s halogenidy anorganických kyselin.

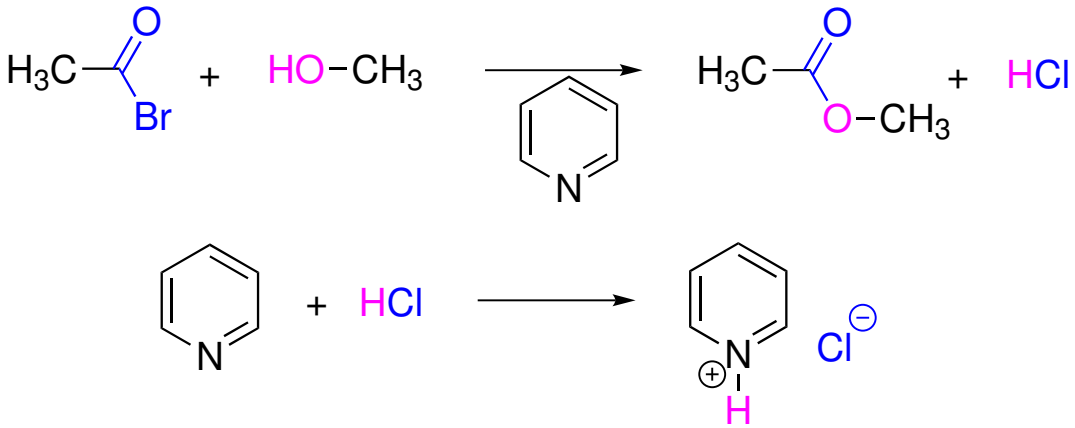


Halogenidy karboxylových kyselin

Hydrolýza halogenidů:

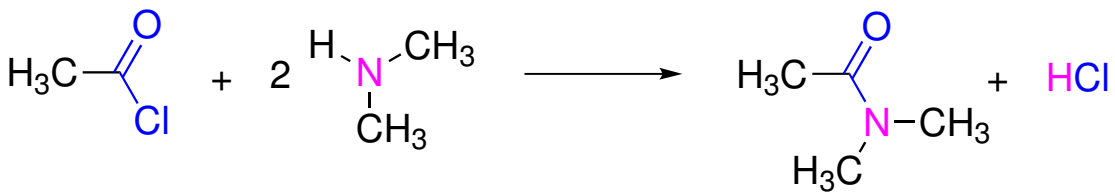


Acylace nukleofilů (alkoholů a aminů):

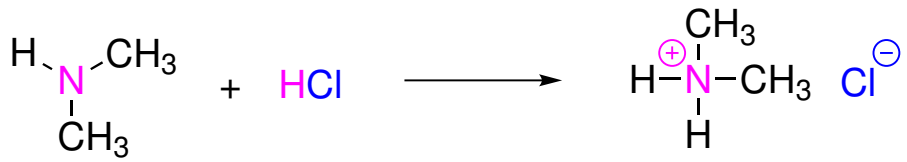


Halogenidy karboxylových kyselin

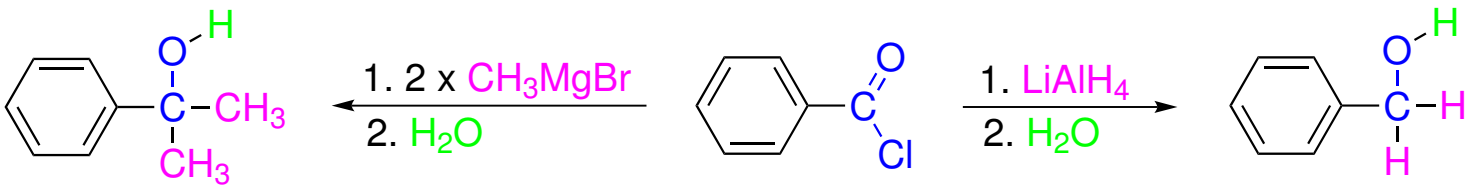
Acylace nukleofilů (alkoholů a aminů):



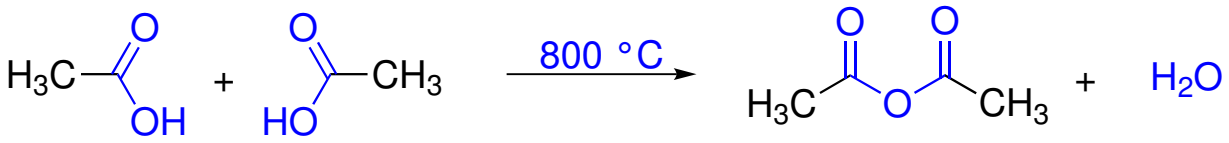
druhý ekvivalent aminu:



Reakce acylhalogenidů s organokovy a $LiAlH_4$:

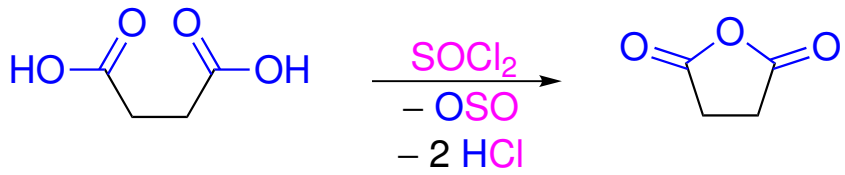


Anhydridy karboxylových kyselin



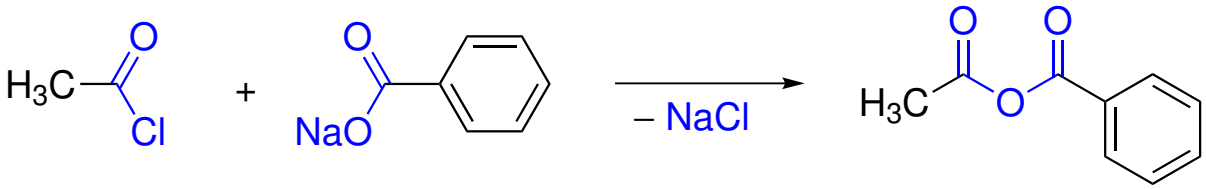
kyselina octová

anhydrid kyseliny octové (acetanhydrid)



kyselina jantarová

anhydrid kyseliny jantarové (sukcinanhydrid)



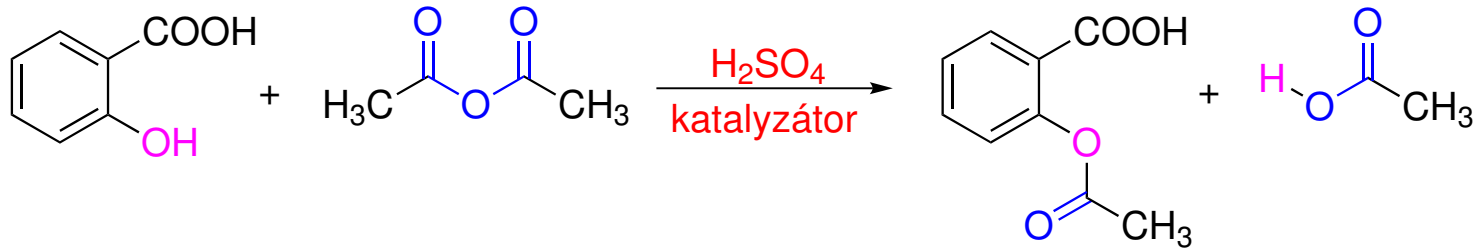
acetylchlorid

natrium-benzoát

smesný anhydrid kyselin octové a benzoové

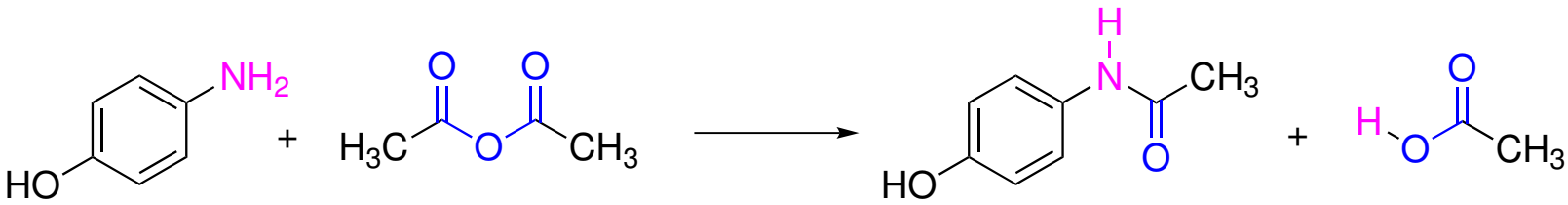
Anhydridy karboxylových kyselin

Acylace nukleofilů (alkoholů a aminů):



kyselina salicylová

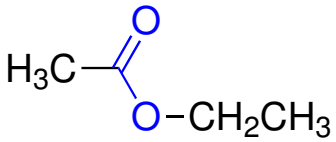
kyselina acetylsalicylová



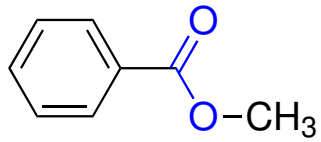
4-aminofenol

N-(4-hydroxyfenyl)acetamid
paracetamol

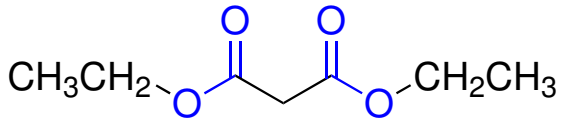
Estery karboxylových kyselin



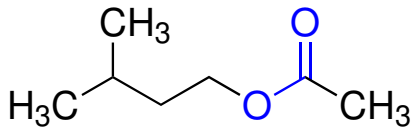
ethylester kyseliny octové
ethyl-acetát



methylester kyseliny benzoové
methyl-benzoát

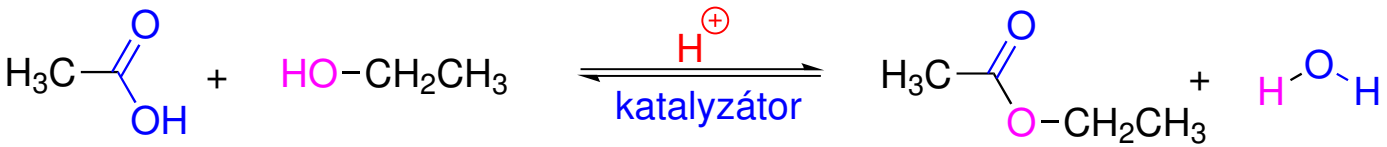


diethylester kyseliny malonové
diethyl-malonát



isopentylester kyseliny octové
isopentyl-acetát
3-methylbutyl-acetát

Fischerova esterifikace:



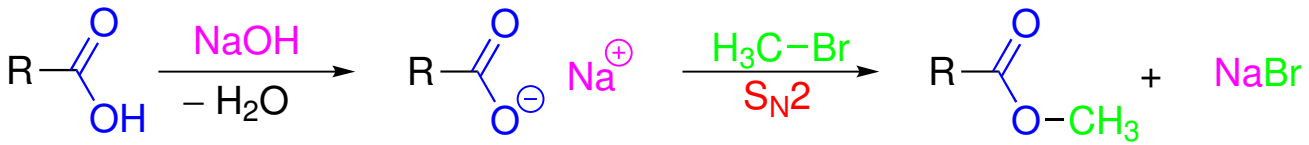
kyselina octová

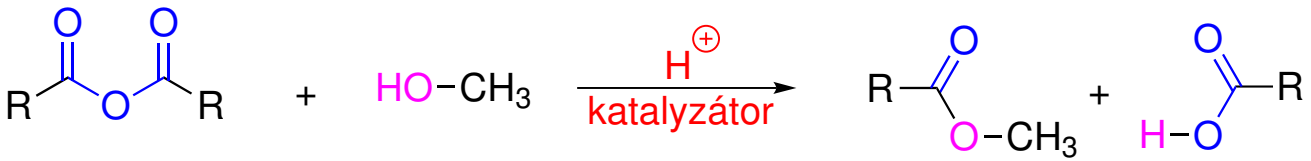
ethanol

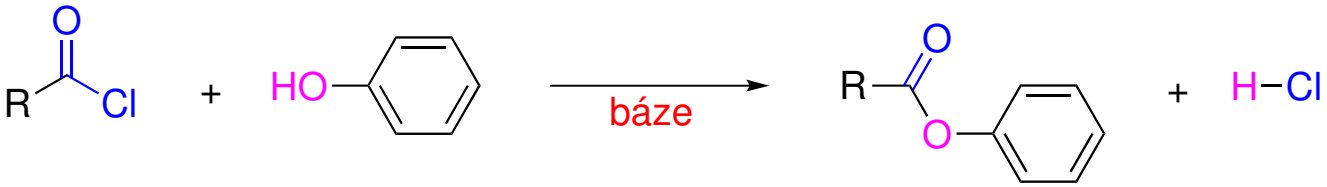
ethyl-acetát

Estery karboxylových kyselin

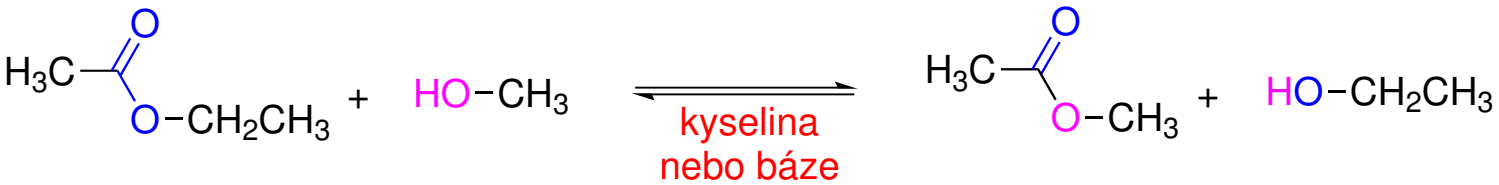
Příprava esterů:





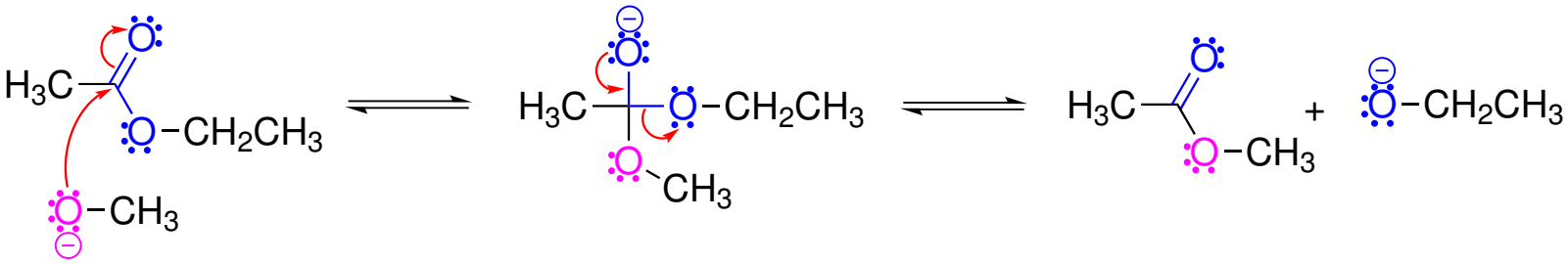


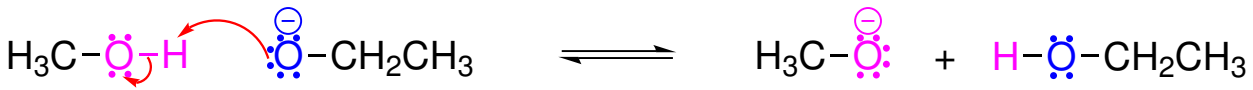
Transesterifikace:



Estery karboxylových kyselin

Mechanismus bazické transesterifikace:

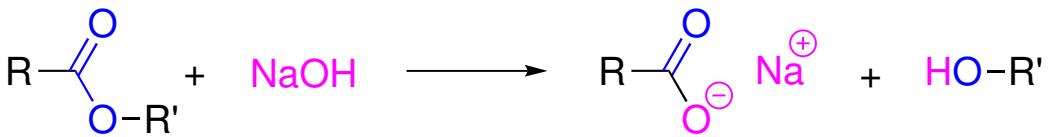




Hydrolýza esterů:

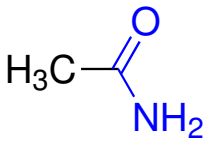
Kysele katalyzovaná hydrolýza – mechanismus je opakem kysele katalyzované esterifikace.

Bazická hydrolýza – saponifikace:

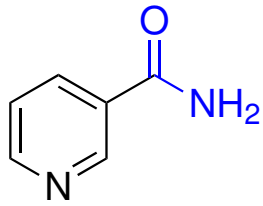


Estery karboxylových kyselin

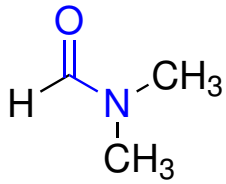
Amidy karboxylových kyselin



amid kyseliny
octové
acetamid
ethanamid

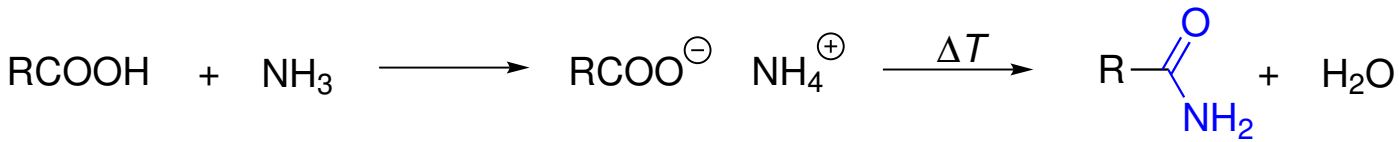


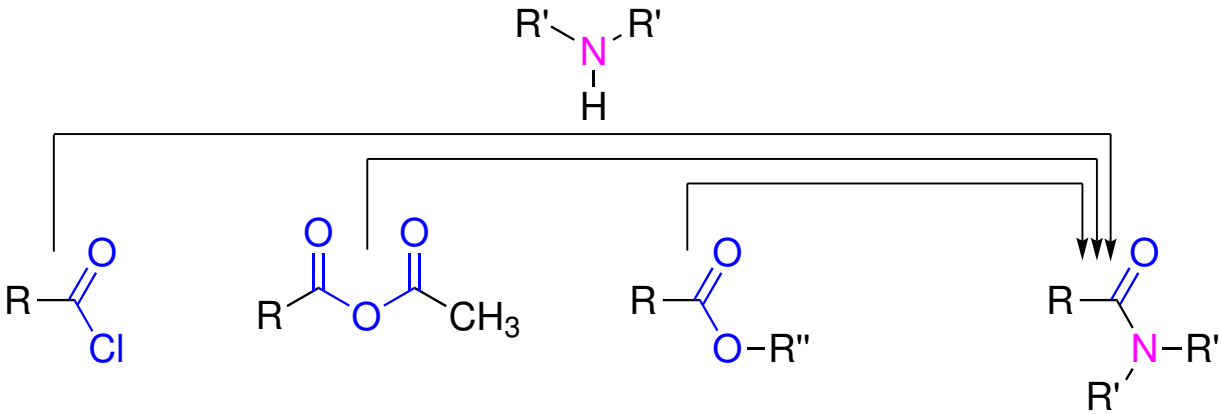
amid kyseliny nikotinové
nikotinamid



N,*N*-dimethylformamid

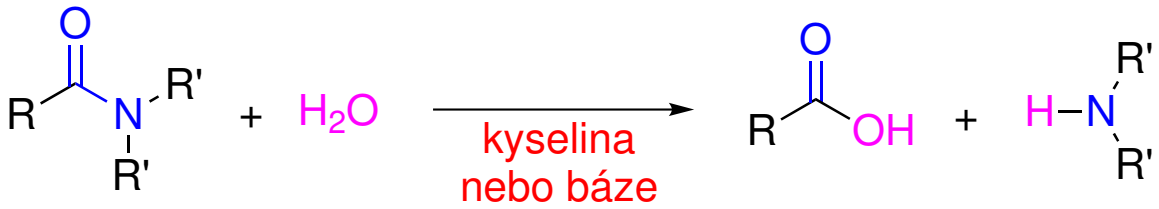
Příprava amidů:



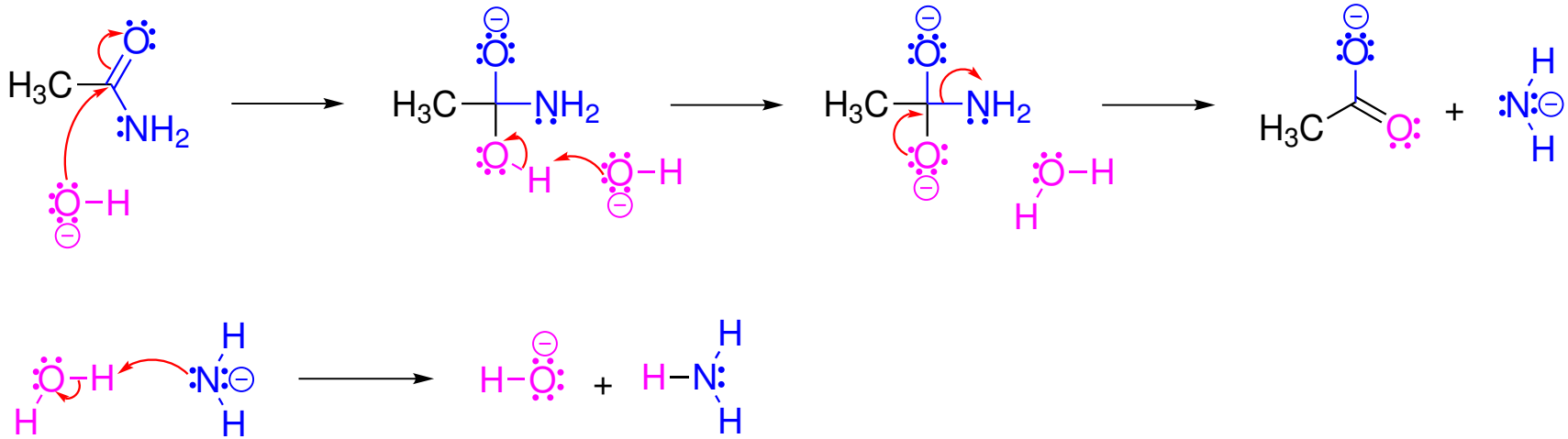


Amidy karboxylových kyselin

Hydrolýza amidů:

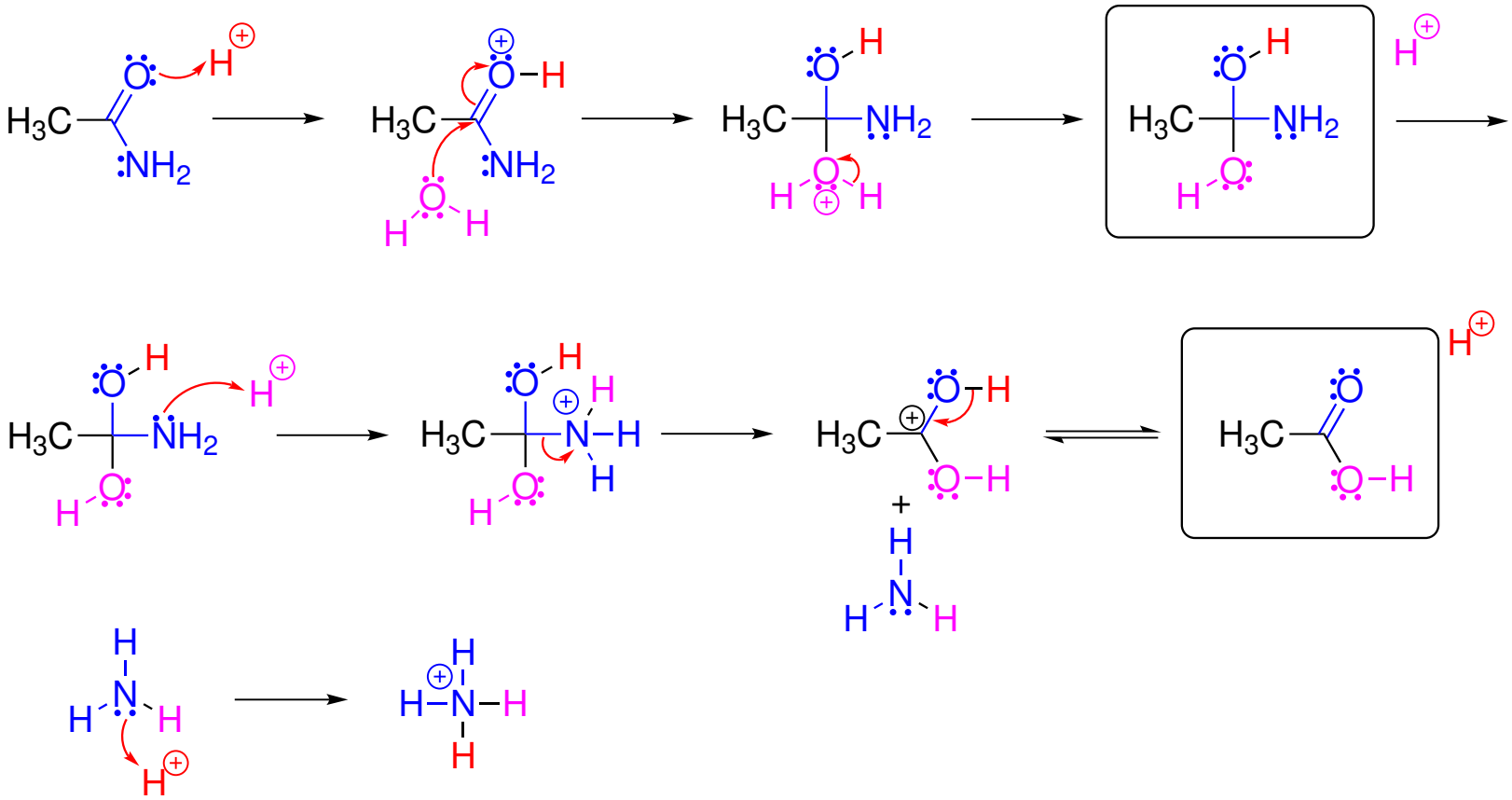


Mechanismus bazické hydrolýzy amidů:

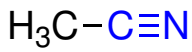


Amidy karboxylových kyselin

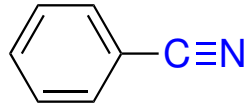
Mechanismus kyselé hydrolýzy amidů:



Nitrily karboxylových kyselin

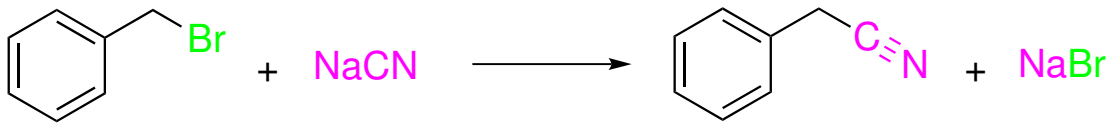


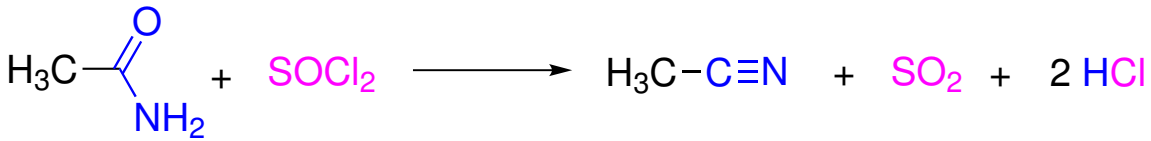
nitril kyseliny octové
acetonitril
ethannitril



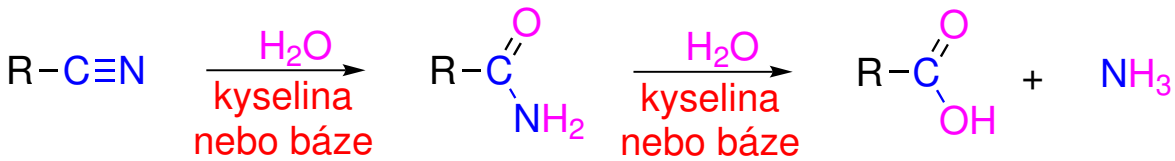
nitril kyseliny benzoové
benzonitril
benzenkarbonitril

Příprava nitrilů:

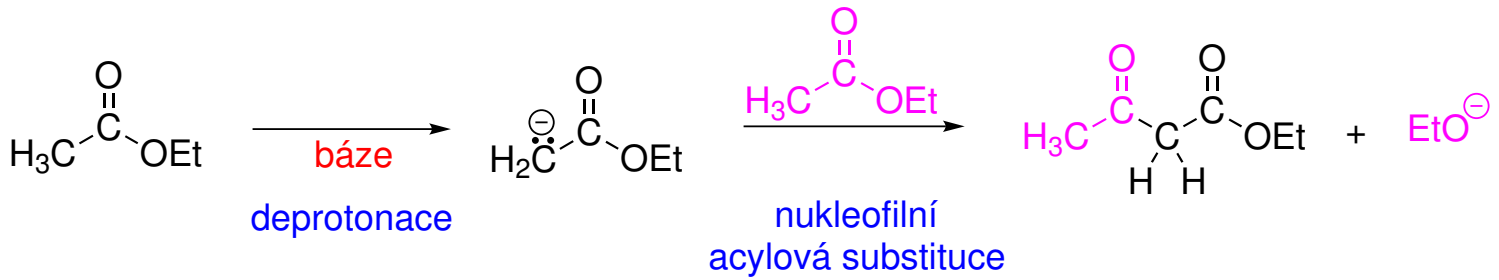




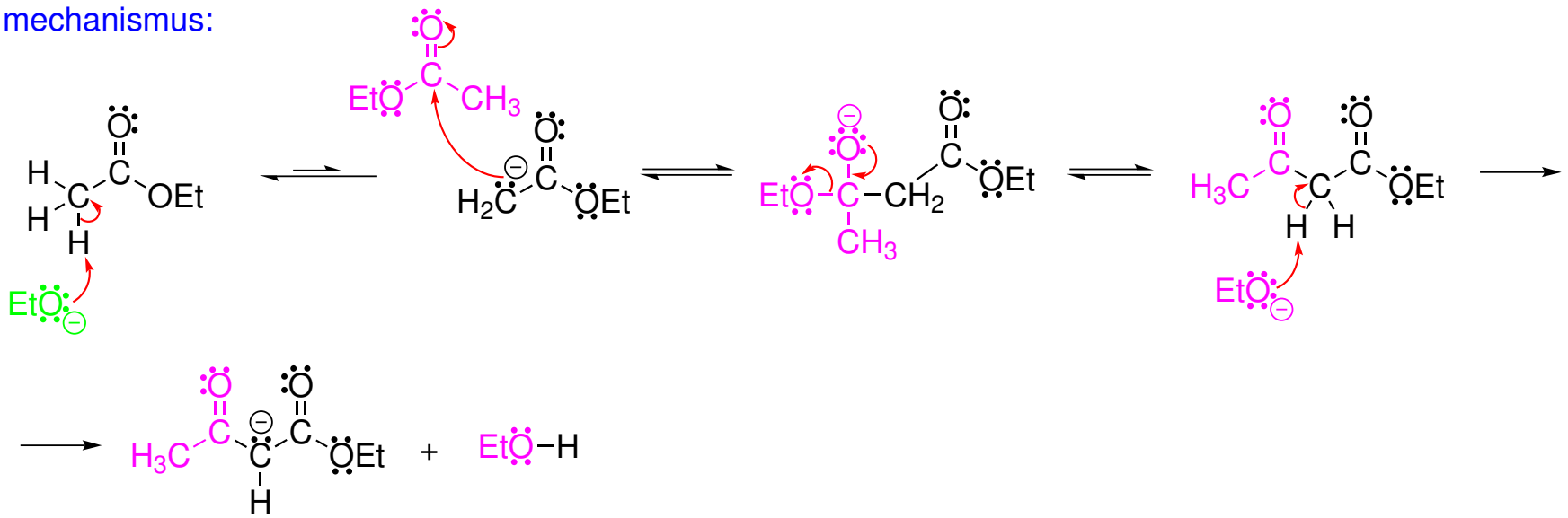
Hydrolýza nitrilů:



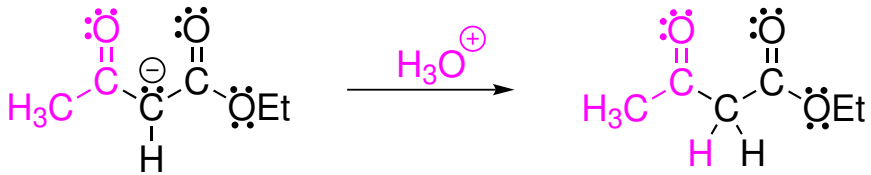
Claisenova reakce



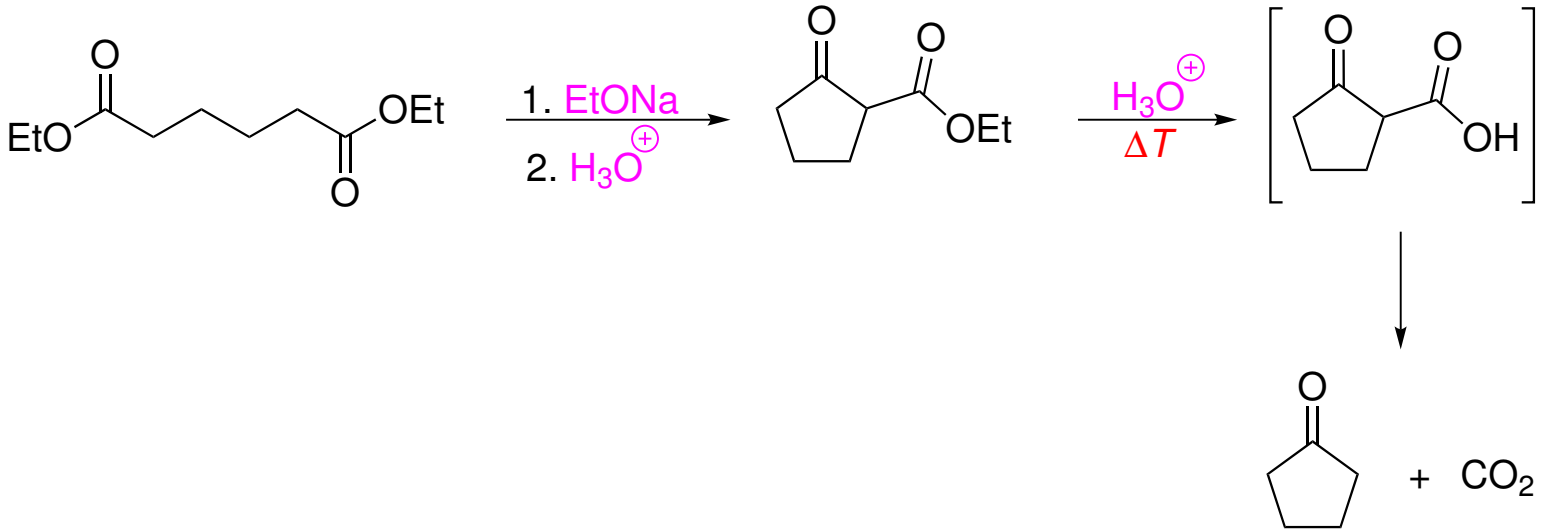
mechanismus:



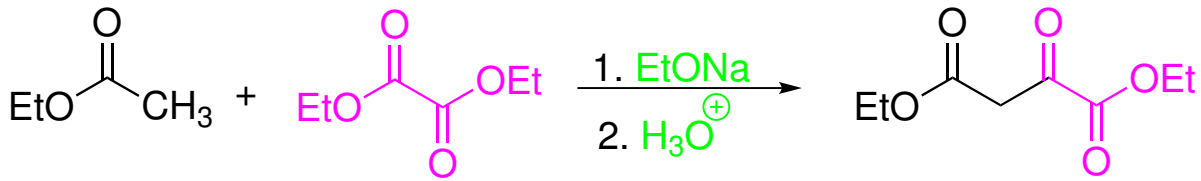
zpracování:

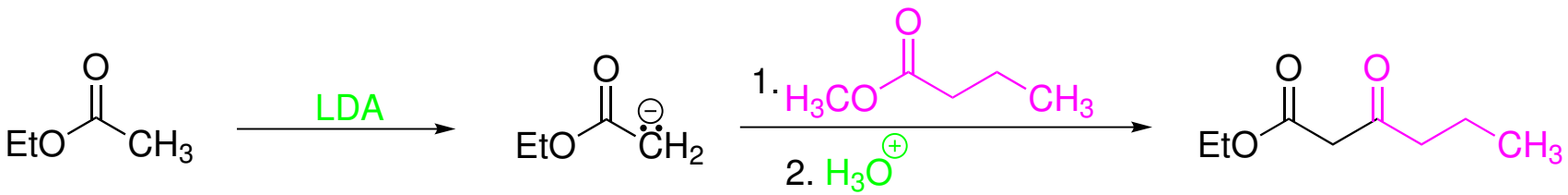


Claisenova reakce

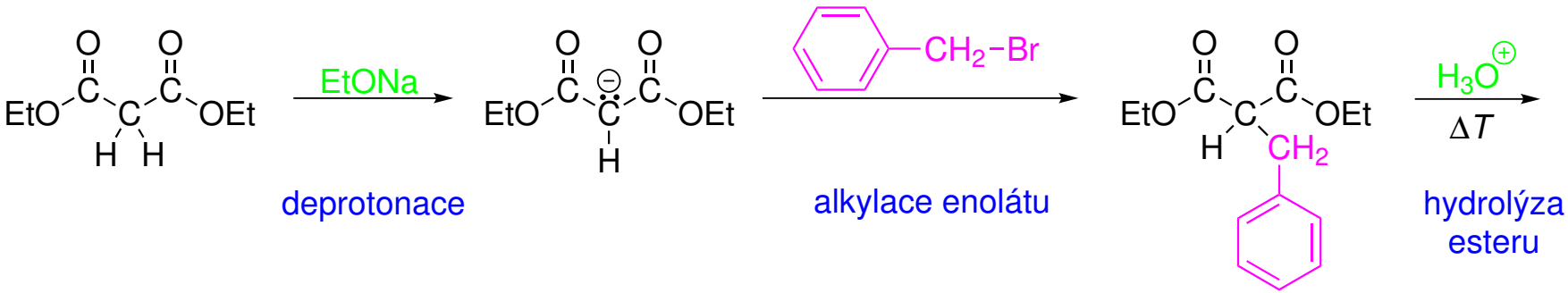


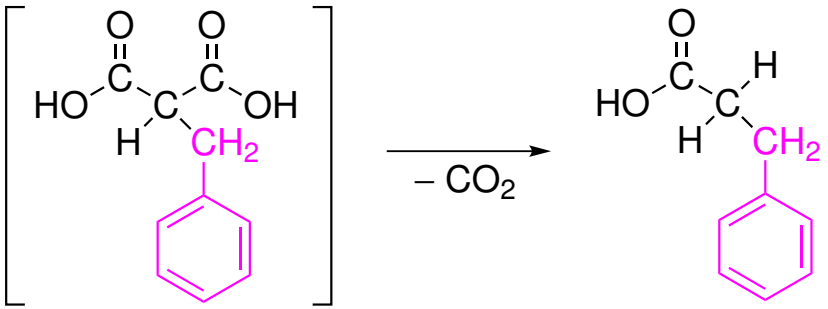
Zkřížená Claisenova reakce:



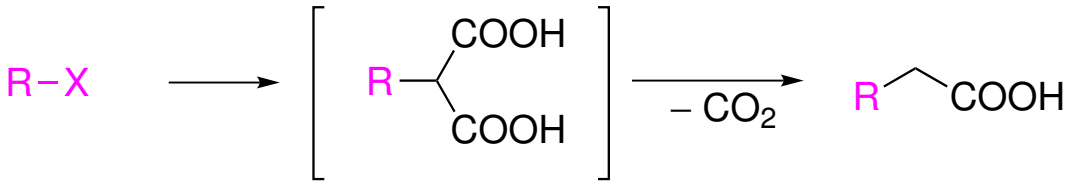


Malonesterové syntézy



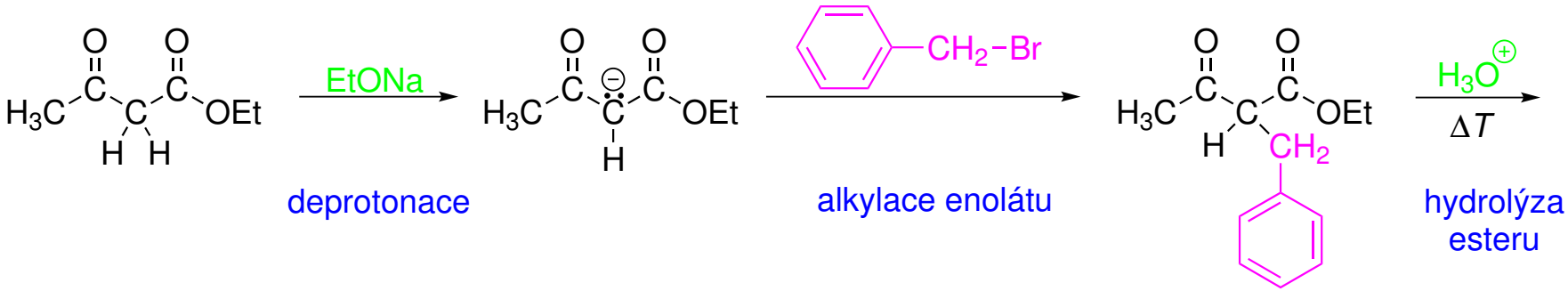


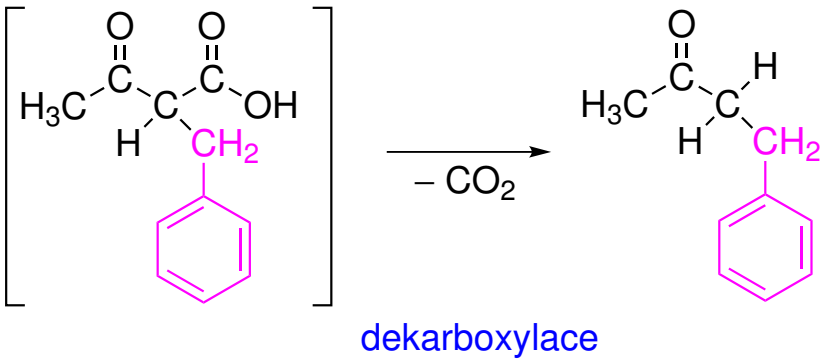
Syntetické použití:



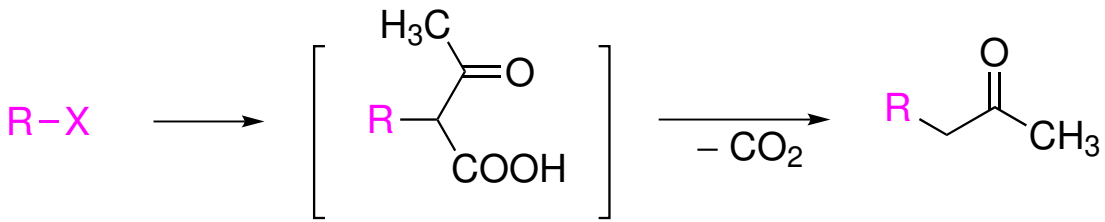
Malonesterové syntézy

Výchozí látkou může být i jiná 1,3-dikarbonylová sloučenina:

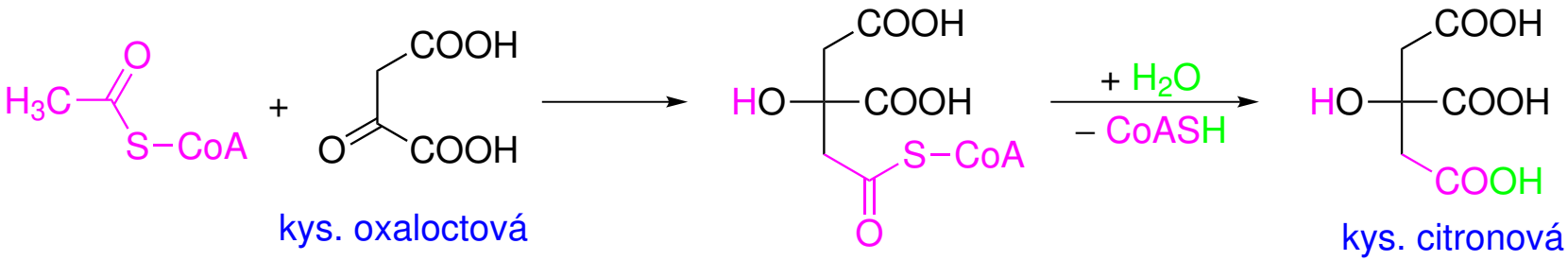




Syntetické použití:

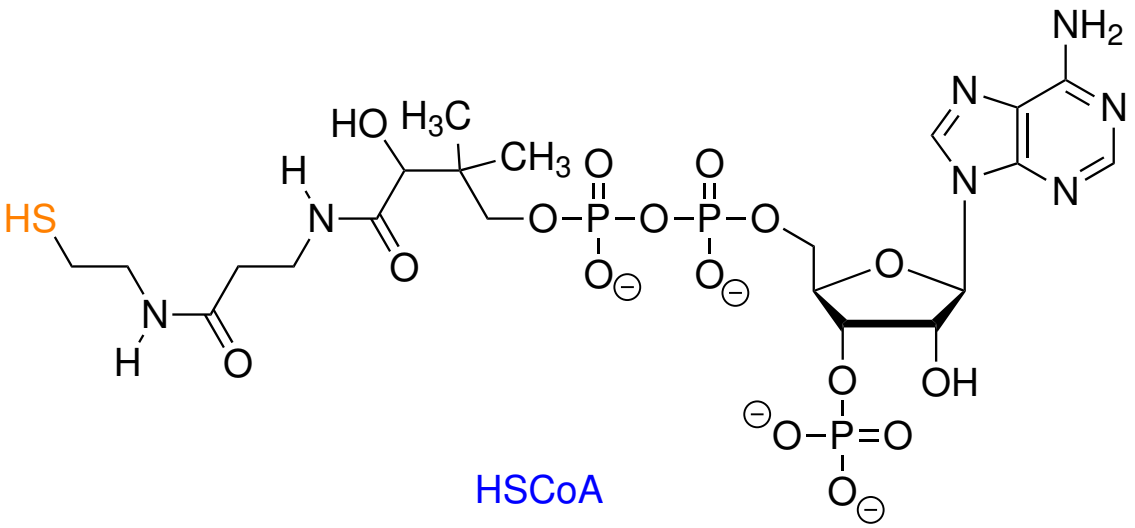


Thioestery



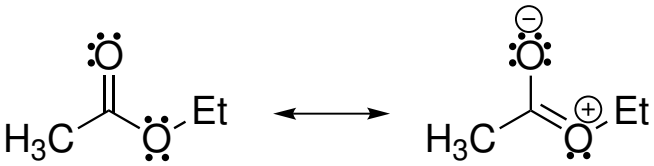
kys. oxaloctová

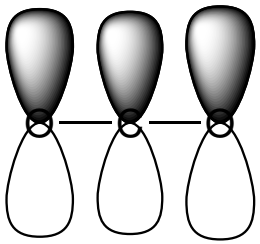
kys. citronová

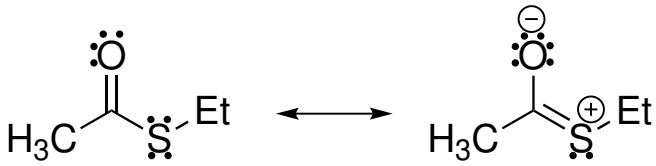


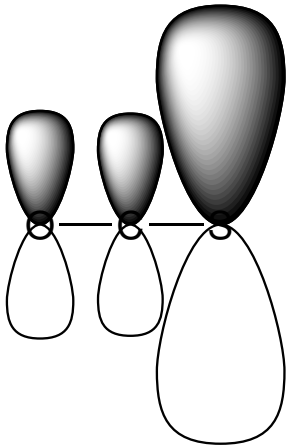
HSCoA

Thioestery

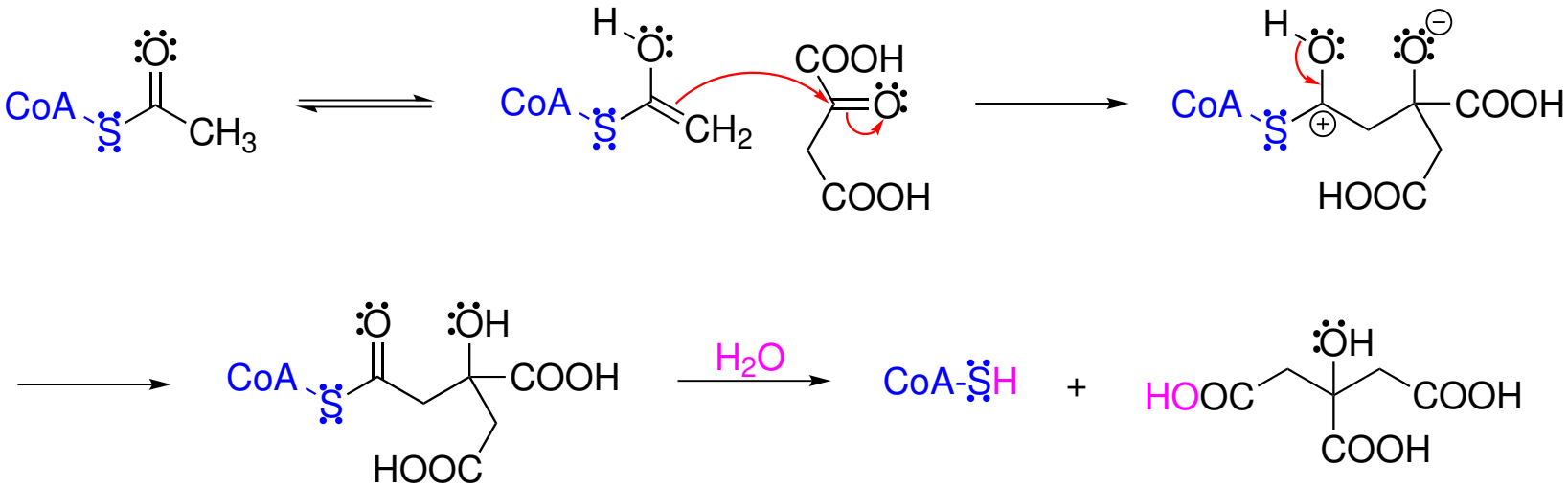




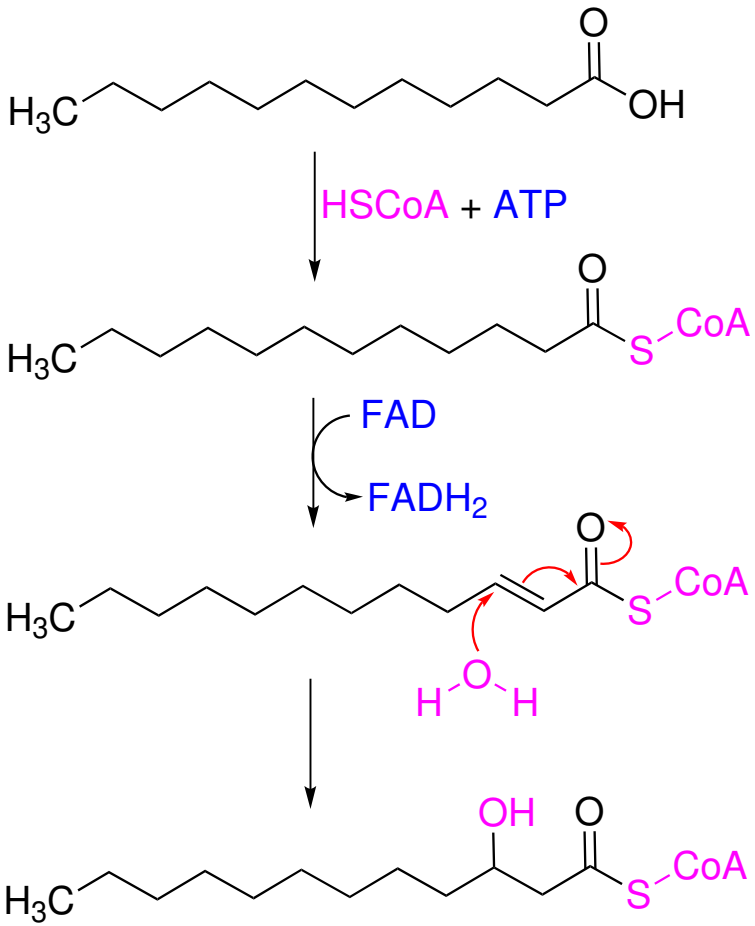




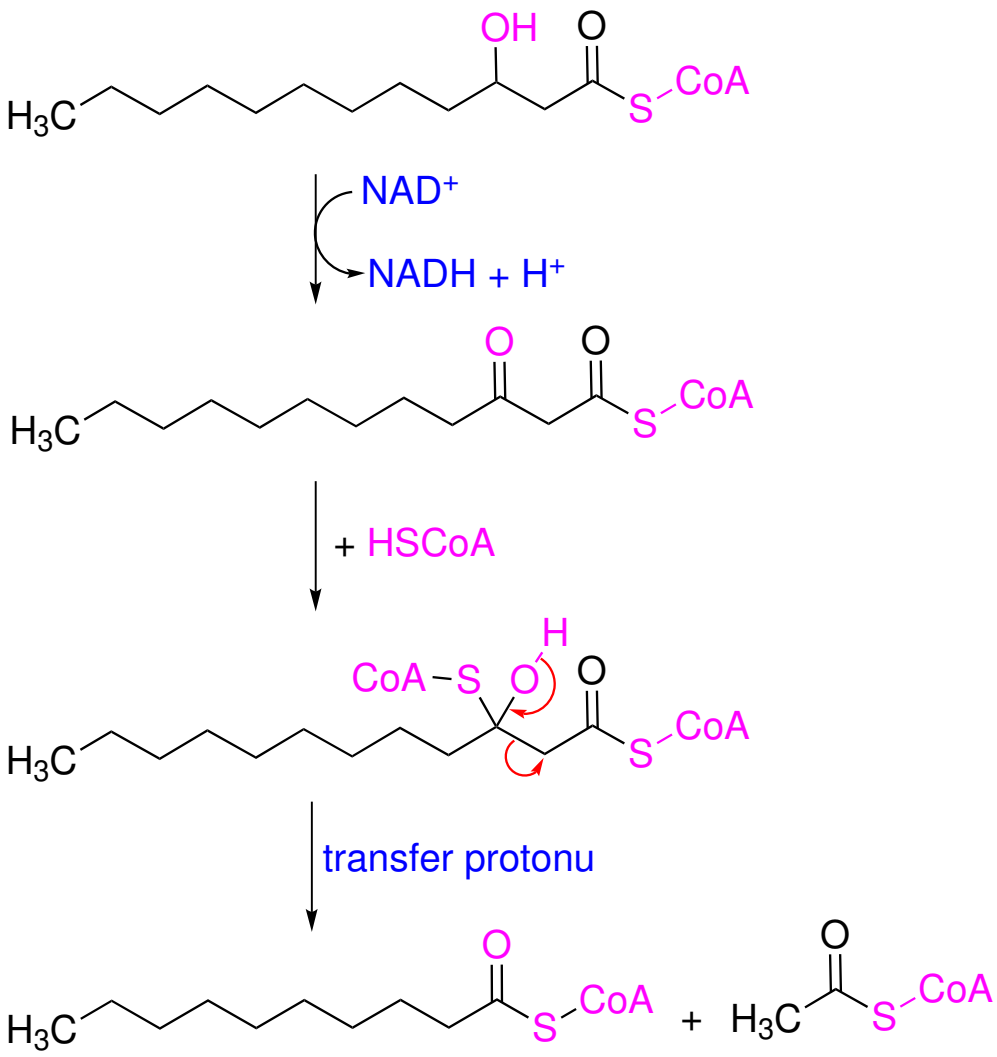
Thioestery



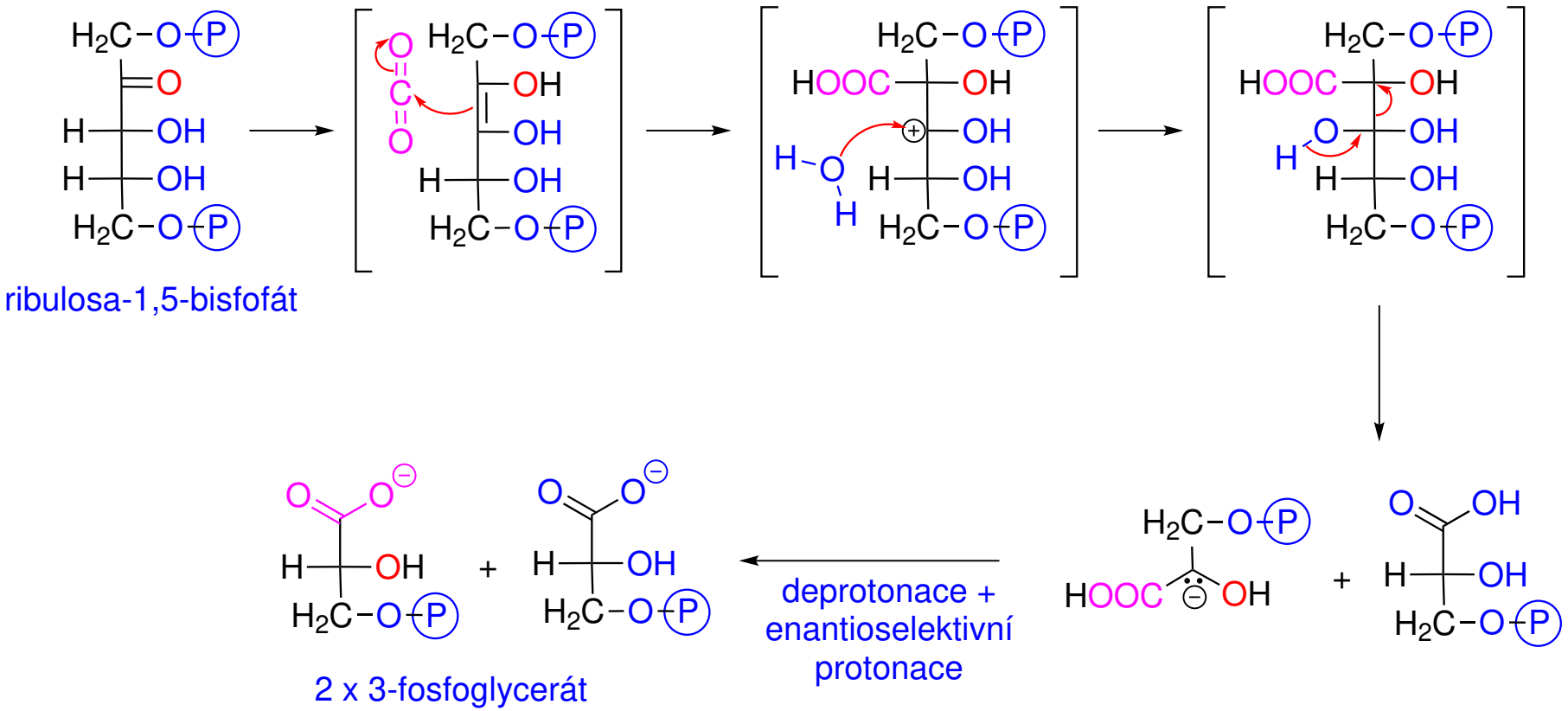
β Oxidace



β Oxidace



Fixace oxidu uhličitého při fotosyntéze



Kyselina uhličitá a její deriváty

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

$$K_{hydr} = \frac{[H_2CO_3]}{[CO_2]} = 2{,}8 \times 10^{-3} \qquad pK_{hydr} = -\log K_{hydr} = 2{,}55$$

Maximální rozpustnost kyseliny uhličité ve vodě je asi 0,034 mol dm^{-3}, nad touto koncentrací se rozkládá na oxid uhličitý a vodu.

Najdeme dvě rozdílné hodnoty pK_{a1} pro disociaci do prvního stupně:

$$K_{a1} = \frac{[H^+] \cdot [HCO_3^-]}{[H_2CO_3]} \qquad pK_{a1} = 3{,}8$$

$$K_{a1,poz} = \frac{[H^+] \cdot [HCO_3^-]}{[CO_2]} = K_{a1} \cdot K_{hydr} \qquad pK_{a1,poz} = 6{,}35$$

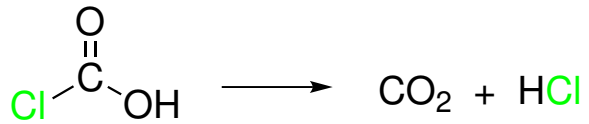
Kyselina uhličitá a její deriváty

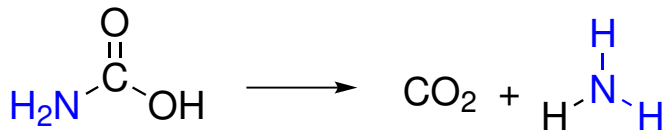
Pro disociaci do druhého stupně:

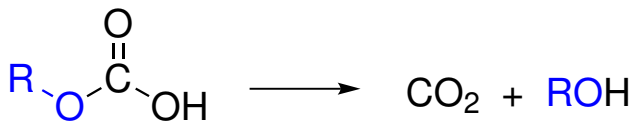
$$K_{a2} = \frac{[H^+] \cdot [CO_3^{2-}]}{[HCO_3^-]} \qquad pK_{a2} = 10{,}2$$

Funkční deriváty kyseliny uhličité

Některé z funkčních derivátů jsou nestálé:



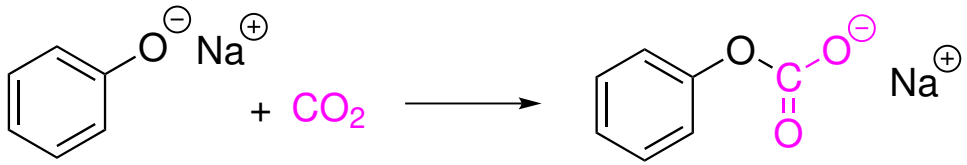




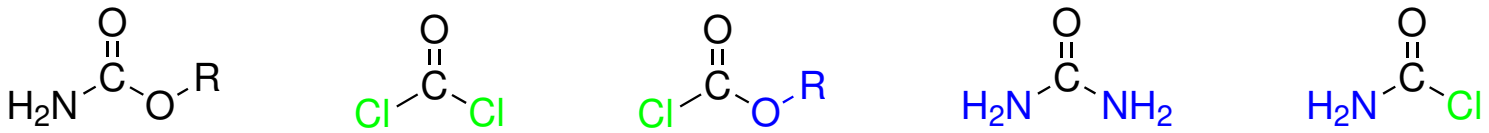
Kyselina uhličitá a její deriváty

Funkční deriváty kyseliny uhličité

Stálé jsou např. soli monoalkyl- nebo monoaryl-karbonátů:

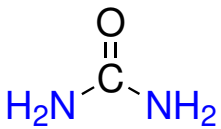


Další stálé deriváty kyseliny uhličité:



Močovina

Diamid kyseliny uhličité.

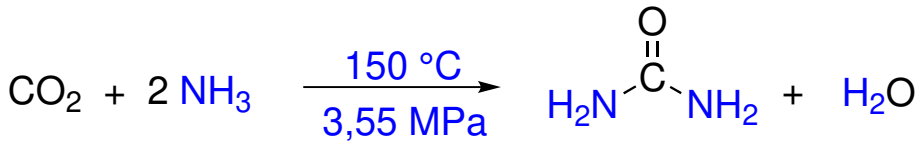


Kyselina uhličitá a její deriváty

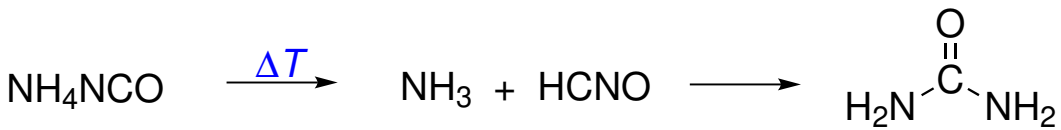
Močovina

Odpadní látka u savců, obojživelníků a některých ryb.

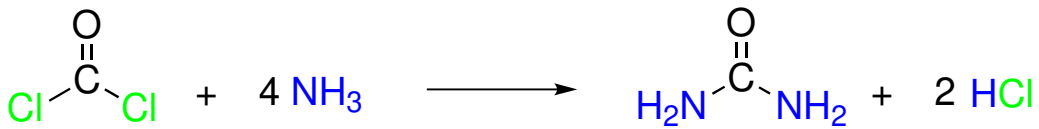
Průmyslová výroba:



Wöhler (1828):



Také:



Močovina

Při zahřívání se močovina rozkládá na kyselinu kyanatou a amoniak: