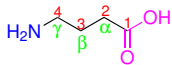


Základy organické chemie

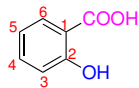
Jaromír Literák



Karboxylové kyseliny a jejich deriváty



4-aminobutanová
kyselina
γ-aminomáselná
kyselin

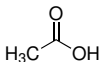


2-hydroxybenzenkarboxylová
kyselina
o-hydroxybenzoová kyselina
kyselina salicylová

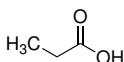
Triviální názvy karboxylových kyselin a solí (esterů):



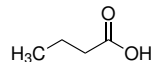
mravenčí
formiát



octová
acetát



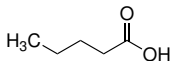
propionová
propionát



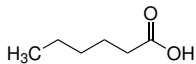
máselná
butyrát



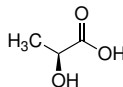
Karboxylové kyseliny a jejich deriváty



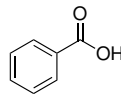
valerová
valerát



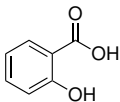
kapronová
kapronát



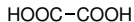
mléčná
laktát



benzoová
benzoát



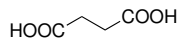
salicylová
salicylát



šťavelová
oxalát



malonová
malonát

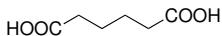


jantarová
sukcinát

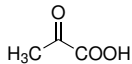
Karboxylové kyseliny a jejich deriváty



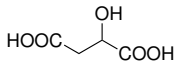
glutarová
glutarát



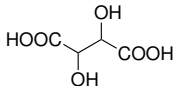
adipová
adipát



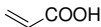
pyrohroznová
pyruvát



jablečná
malát



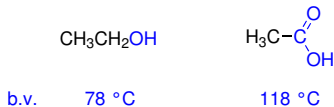
hroznová
tartrát



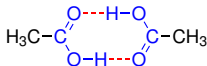
akrylová
akrylát

Vlastnosti karboxylových kyselin

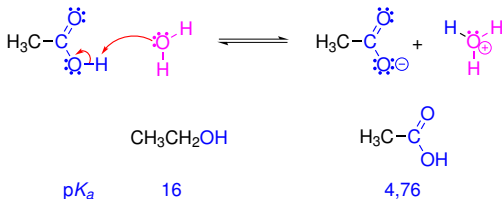
Teploty varu:



Tvorba dimerů:

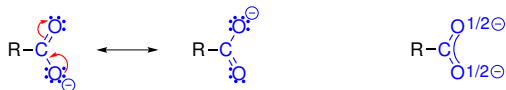


Kyselost:

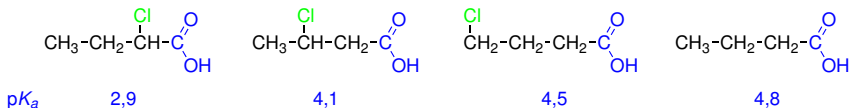
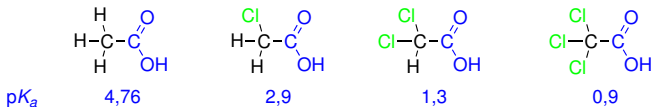


Vlastnosti karboxylových kyselin

Stabilizace karboxylátového aniontu **konjugací**:

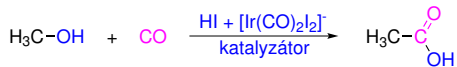


Vliv **indukčního efektu** na kyselost:

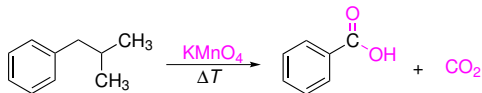
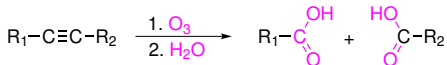


Příprava karboxylových kyselin

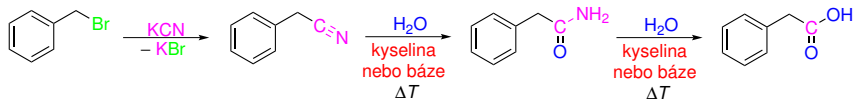
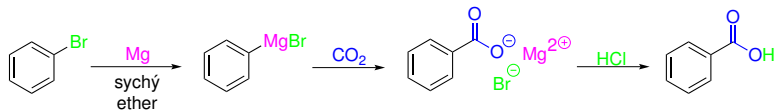
Průmyslová výroba kyseliny octové



Příprava karboxylových kyselin:

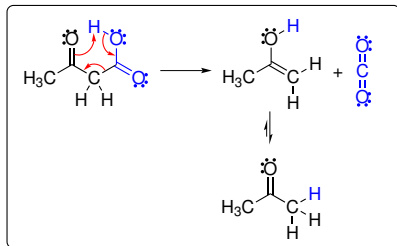
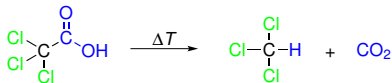
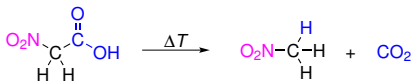
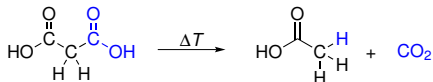
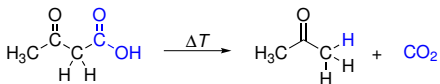


Příprava karboxylových kyselin



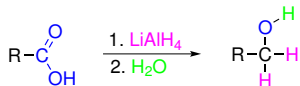
Reakce karboxylových kyselin

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

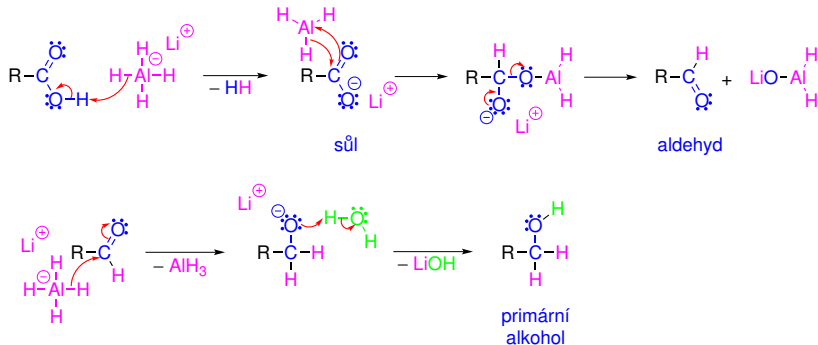


Reakce karboxylových kyselin

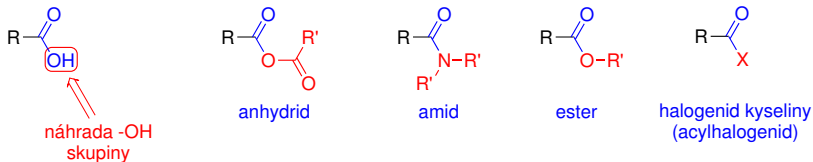
Redukce karboxylových kyselin:



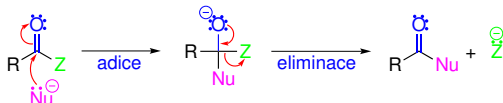
Mechanismus:



Funkční deriváty karboxylových kyselin

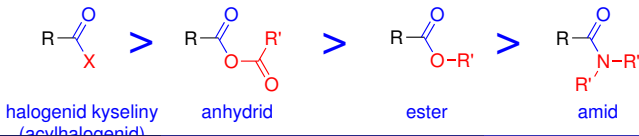


Nukleofilní acylová substituce

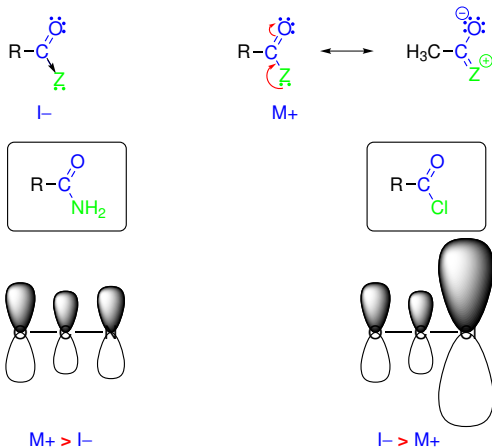


Probíhá adičně-eliminačním mechanismem.

Reaktivita vůči nukleofilům:



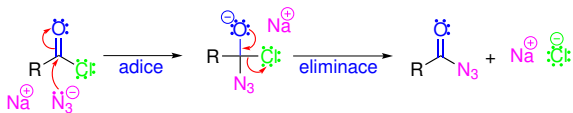
Funkční deriváty karboxylových kyselin



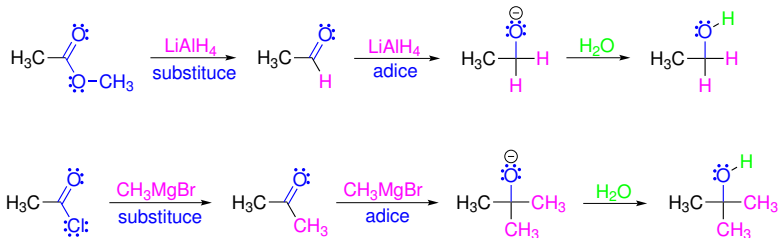
Nukleofilní acylovou substitucí lze **převádět funkční deriváty mezi sebou** – snadno lze z derivátu reaktivnějšího připravit derivát méně reaktivní.

Funkční deriváty karboxylových kyselin

Příprava acylazidů:

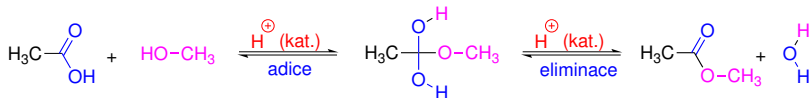


Pokud je nukleofilem **organokov** nebo **komplexní hydrid**, může produkt substituce (aldehyd nebo keton) dále reagovat s nukleofilem:

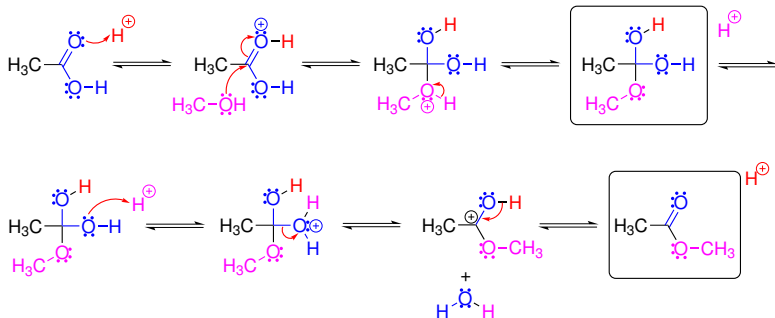


Funkční deriváty karboxylových kyselin

Esterifikace:



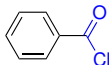
Mechanismus:



Halogenidy karboxylových kyselin

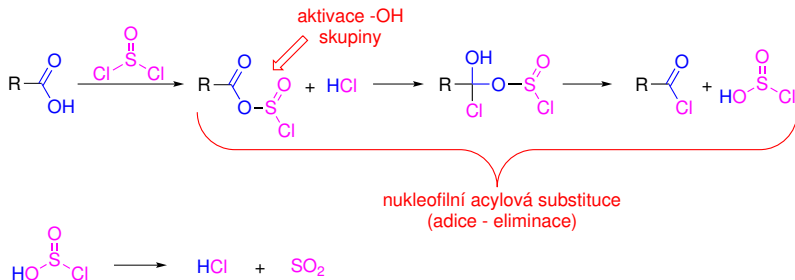


bromid kyseliny octové
acetyl bromid



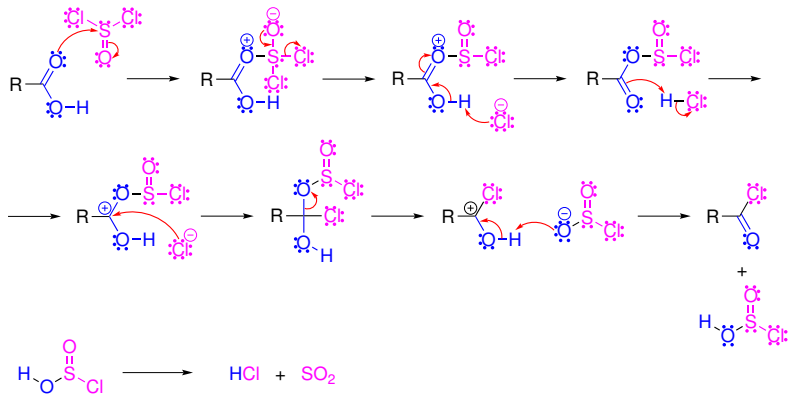
chlorid kyseliny benzoové
benzoylchlorid

Obvykle připravovány reakcí karboxylových kyselin s halogenidy anorganických kyselin.



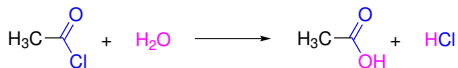
Halogenidy karboxylových kyselin

Mechanismus:

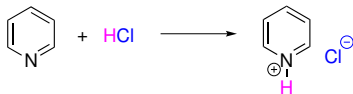
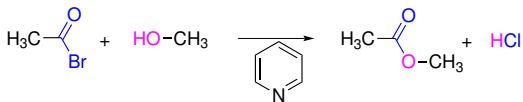


Halogenidy karboxylových kyselin

Hydrolyzá halogenidů:

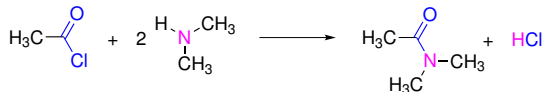


Acylace nukleofilů (alkoholů a aminů):



Halogenidy karboxylových kyselin

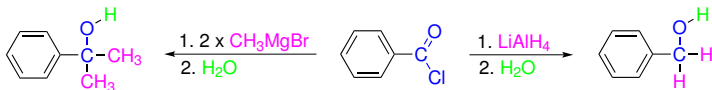
Acylace nukleofilů (alkoholů a aminů):



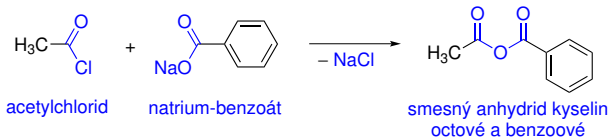
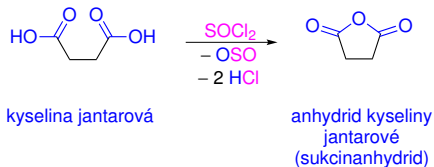
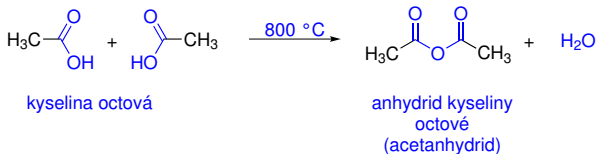
druhý ekvivalent aminu:



Reakce acylhalogenidů s organokovky a LiAlH_4 :

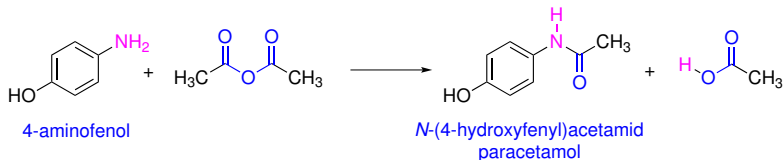
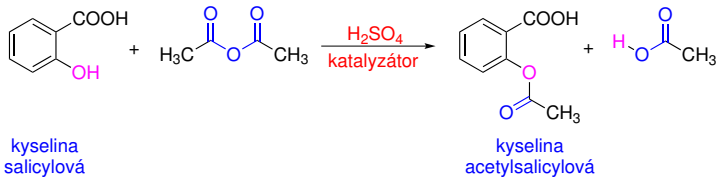


Anhydridy karboxylových kyselin

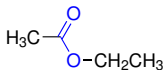


Anhydridy karboxylových kyselin

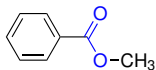
Acylace nukleofilů (alkoholů a aminů):



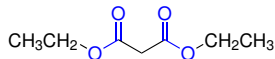
Estery karboxylových kyselin



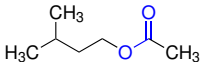
ethylester kyseliny octové
ethyl-acetát



methylester kyseliny benzoové
methyl-benzoát

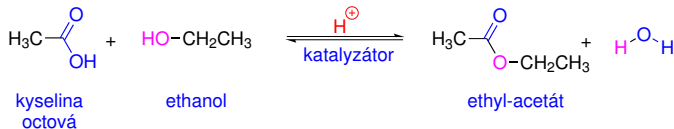


diethylester kyseliny malonové
diethyl-malonát



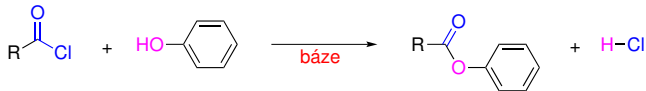
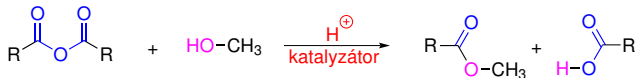
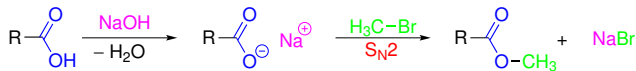
isopentylester kyseliny octové
isopentyl-acetát
3-methylbutyl-acetát

Fischerova esterifikace:

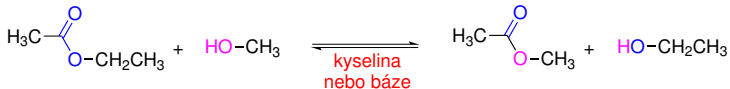


Estery karboxylových kyselin

Příprava esterů:

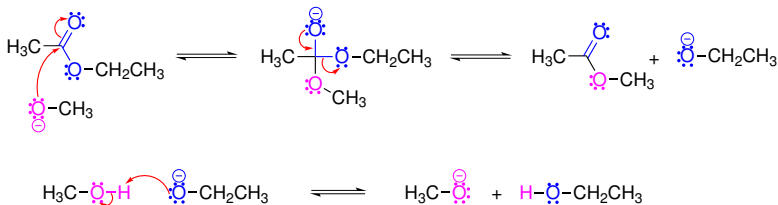


Transesterifikace:



Estery karboxylových kyselin

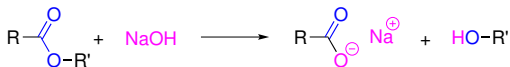
Mechanismus bazické transesterifikace:



Hydrolyza esterů:

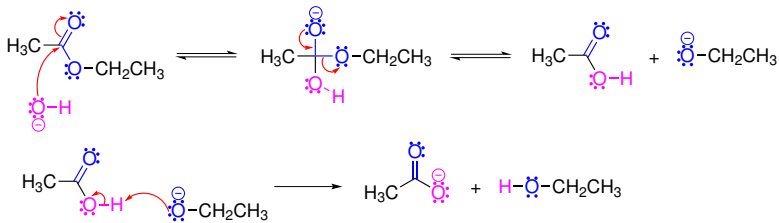
Kysele katalyzovaná hydrolyza – mechanismus je **opakem kysel** katalyzované esterifikace.

Bazická hydrolyza – **saponifikace**:

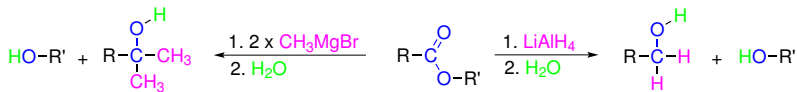


Estery karboxylových kyselin

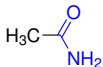
Mechanismus bazické hydrolyzy:



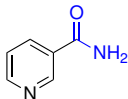
Reakce esterů s organokovky a LiAlH_4 :



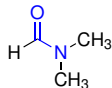
Amidy karboxylových kyselin



amid kyseliny
octové
acetamid
ethanamid

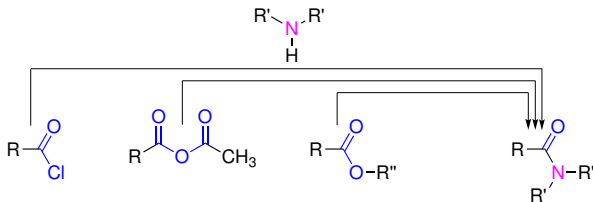
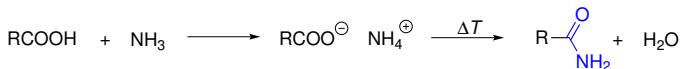


amid kyseliny nikotinové
nikotinamid



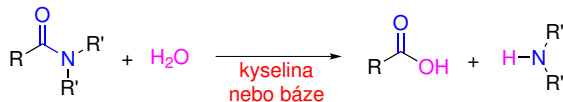
N,N-dimethylformamid

Příprava amidů:

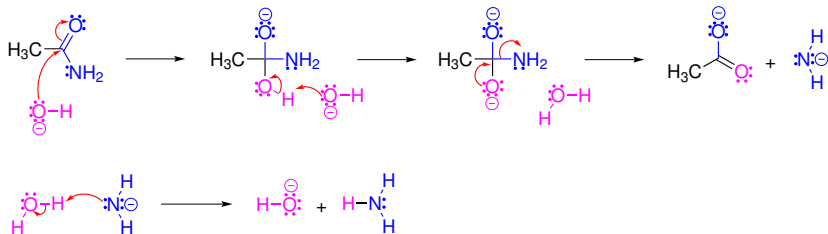


Amidy karboxylových kyselin

Hydrolyza amidů:

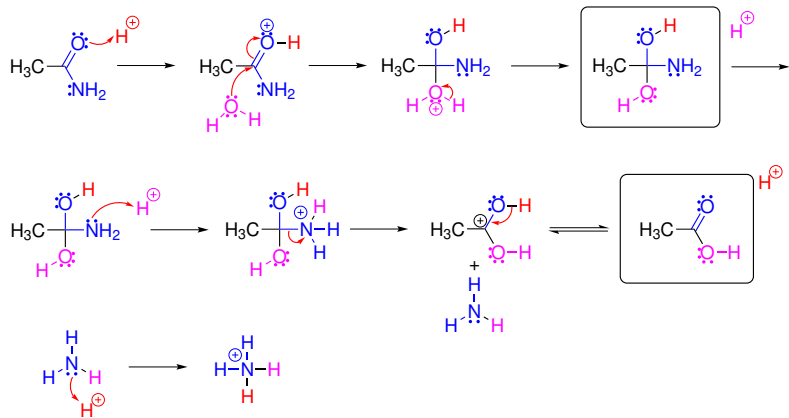


Mechanismus bazické hydrolyzy amidů:



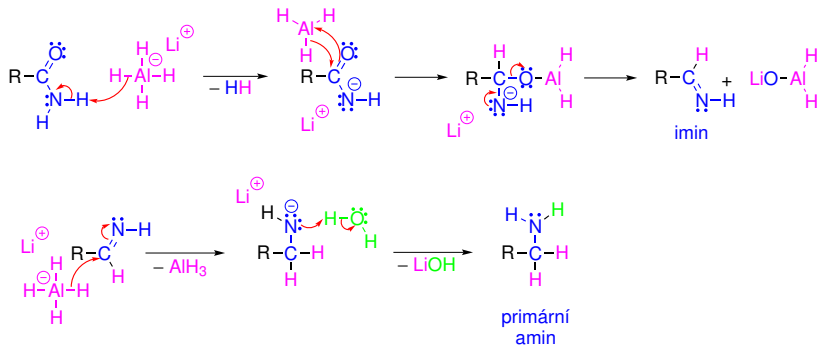
Amidy karboxylových kyselin

Mechanismus kyselého hydrolyzy amidů:



Amidy karboxylových kyselin

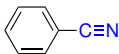
Redukce amidů:



Nitrily karboxylových kyselin

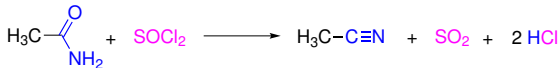
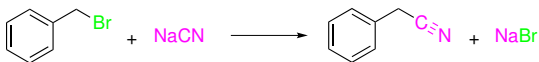


nitril kyseliny octové
acetonitril
ethannitril

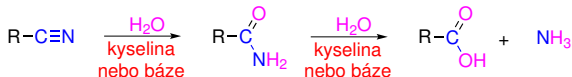


nitril kyseliny benzoové
benzonitril
benzenkarbonitril

Příprava nitrilů:

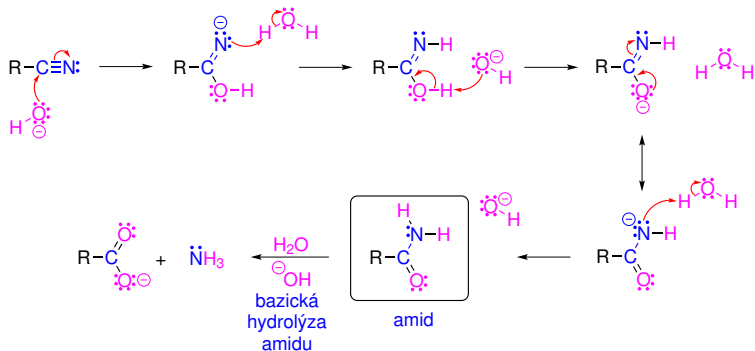


Hydrolyzá nitrilů:



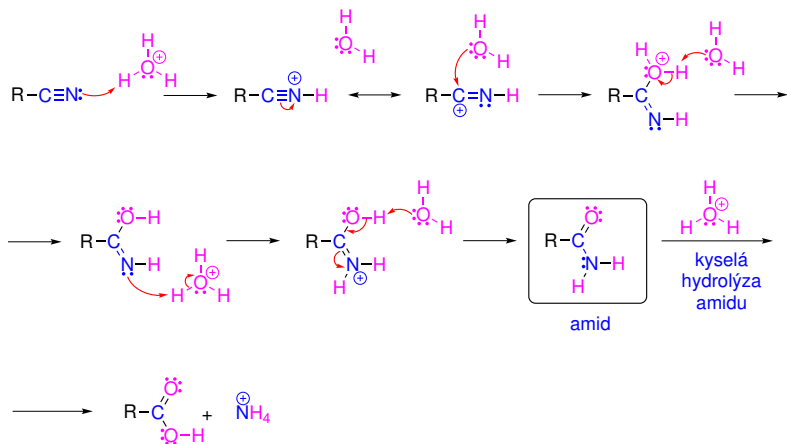
Nitrily karboxylových kyselin

Mechanismus bazické hydrolyzy nitrilů:



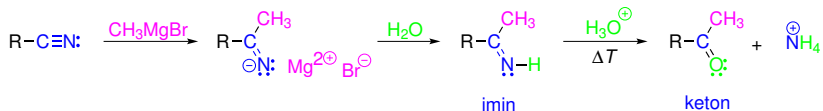
Nitrily karboxylových kyselin

Mechanismus kyselá hydrolyzy nitrilů:

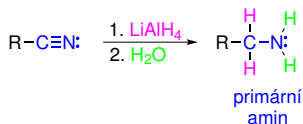


Nitrily karboxylových kyselin

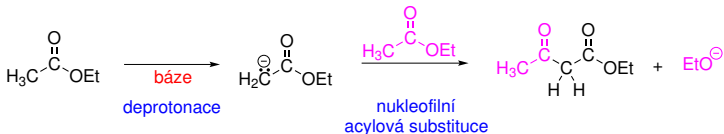
Reakce nitrilů s organokovy – příprava ketonů:



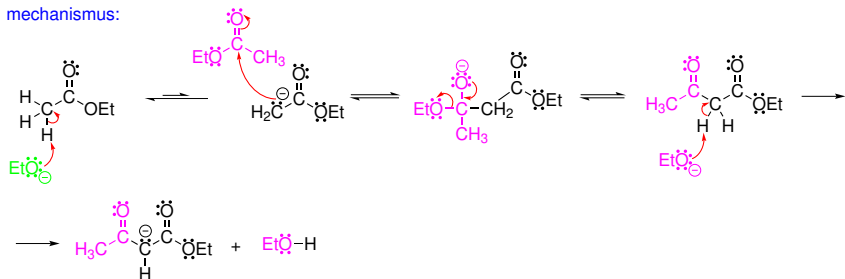
Redukce nitrilů – příprava primárních aminů:



Claisenova reakce



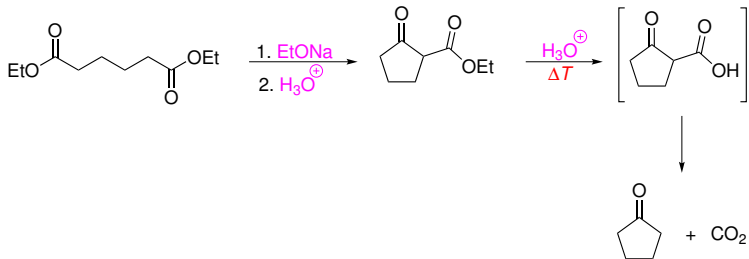
mechanismus:



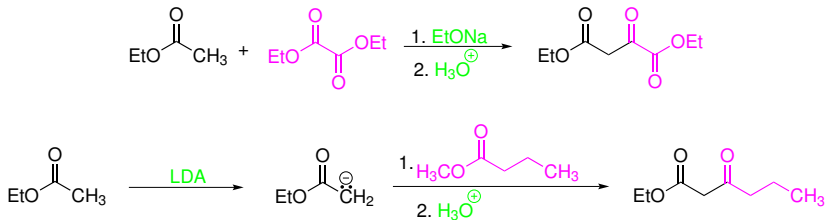
zpracování:



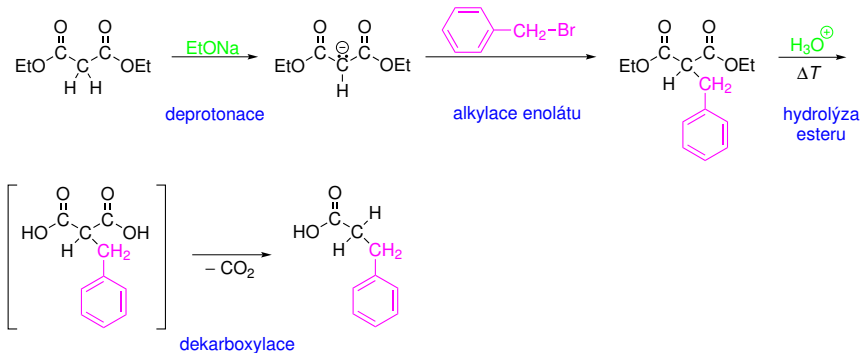
Claisenova reakce



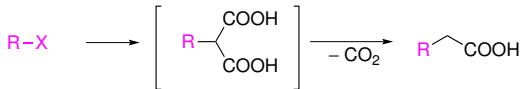
Zkřížená Claisenova reakce:



Malonesterové syntézy

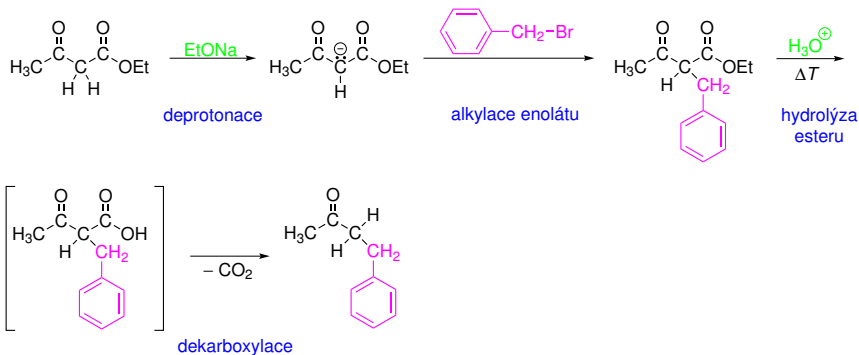


Syntetické použití:

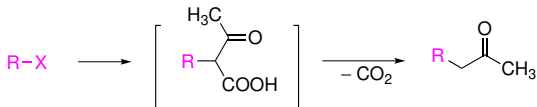


Malonesterové syntézy

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



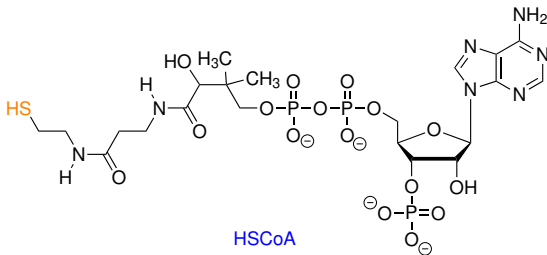
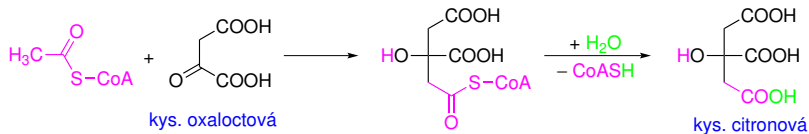
Syntetické použití:



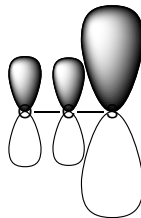
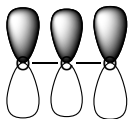
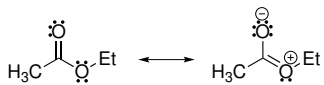
Hellova-Volhardova-Zelinskeho reakce



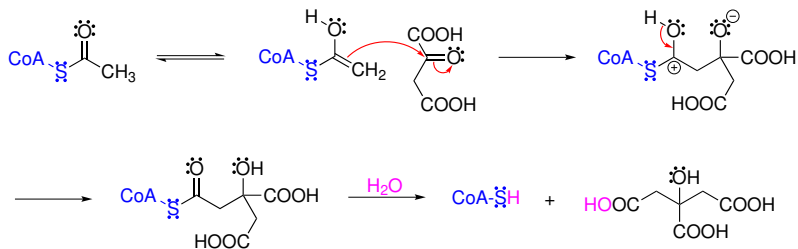
Thioestery

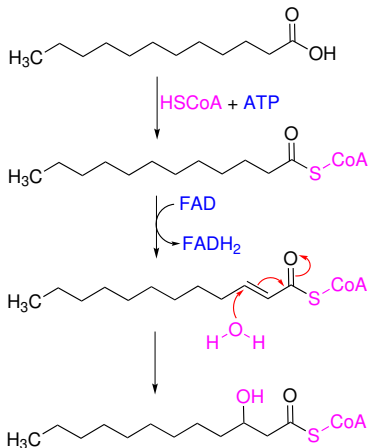


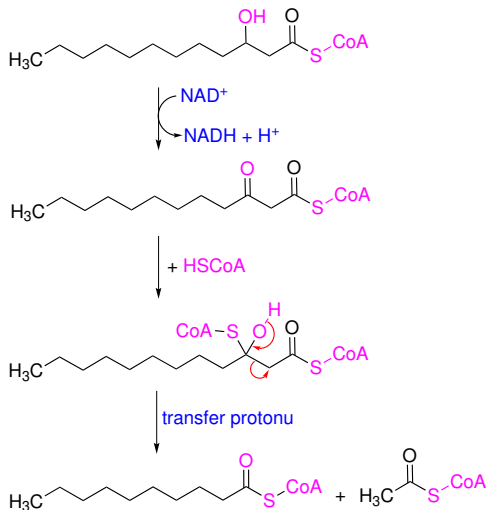
Thioestery



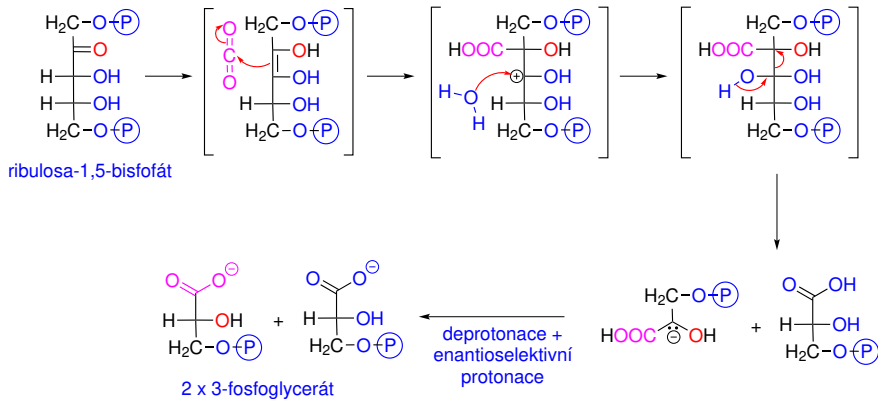
Thioestery







Fixace oxidu uhličitého při fotosyntéze



Kyselina uhličitá a její deriváty



$$K_{hydr} = \frac{[\text{H}_2\text{CO}_3]}{[\text{CO}_2]} = 2,8 \times 10^{-3} \quad \text{p}K_{hydr} = -\log K_{hydr} = 2,55$$

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

Najdeme dvě rozdílné hodnoty $\text{p}K_{a1}$ pro disociaci do prvního stupně:

$$K_{a1} = \frac{[\text{H}^+] \cdot [\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} \quad \text{p}K_{a1} = 3,8$$

$$K_{a1,poz} = \frac{[\text{H}^+] \cdot [\text{HCO}_3^-]}{[\text{CO}_2]} = K_{a1} \cdot K_{hydr} \quad \text{p}K_{a1,poz} = 6,35$$

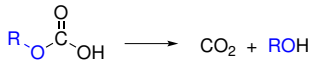
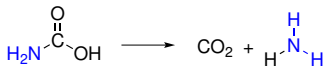
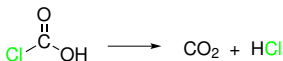
Kyselina uhličitá a její deriváty

Pro disociaci do druhého stupně:

$$K_{a2} = \frac{[\text{H}^+] \cdot [\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \quad pK_{a2} = 10,2$$

Funkční deriváty kyseliny uhličité

Některé z funkčních derivátů jsou **nestálé**:



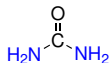
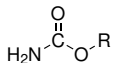
Kyselina uhličitá a její deriváty

Funkční deriváty kyseliny uhličité

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

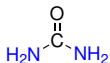


Další stálé deriváty kyseliny uhličité:



Močovina

Diamid kyseliny uhličité.

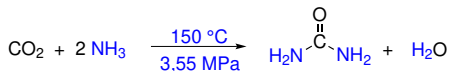


Kyselina uhličitá a její deriváty

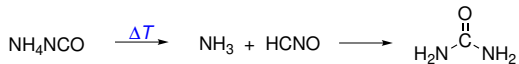
Močovina

Odpadní látka u savců, obojživelníků a některých ryb.

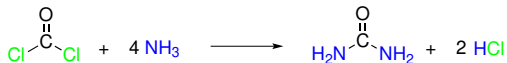
Průmyslová výroba:



Wöhler (1828):



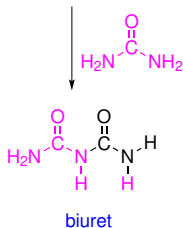
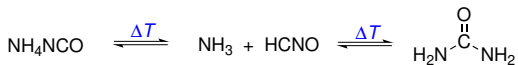
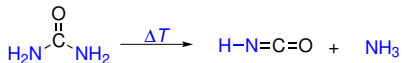
Také:



Kyselina uhličitá a její deriváty

Močovina

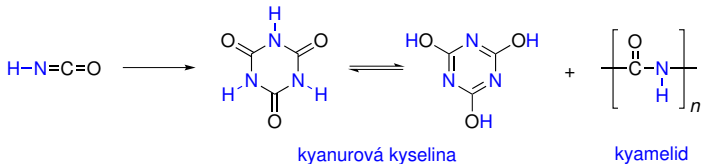
Při zahřívání se močovina rozkládá na kyselinu kyanatou a amoniak:



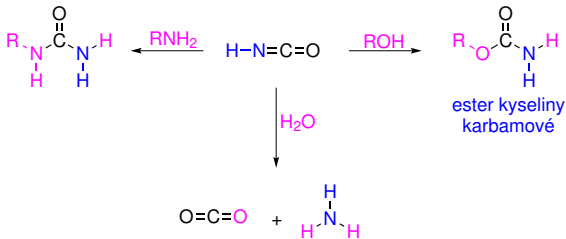
Kyselina uhličitá a její deriváty

Kyselina kyanatá

Kyselina kyanatá je nestálá:



Produkty reakce kyseliny kyanaté s nukleofily:



Příklad č. 1

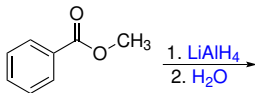
Doplňte produkt/y následující reakce:



Řešení:

Příklad č. 2

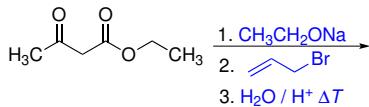
Doplňte produkt/y následující reakce:



Řešení:

Příklad č. 3

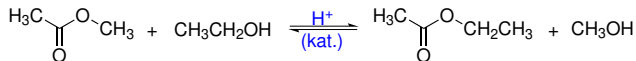
Doplňte produkt/y následující reakce:



Řešení:

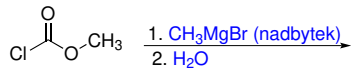
Příklad č. 4

Napište podrobný mechanismus kysele katalyzované transesterifikace methyl-acetátu ethanolem:



Příklad č. 5

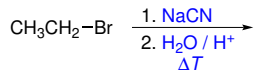
Doplňte produkt/y následující reakce:



Řešení:

Příklad č. 6

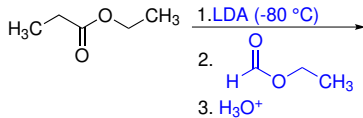
Doplňte produkt/y následující reakce:



Řešení:

Příklad č. 7

Doplňte produkt/y následující reakce:



Řešení: