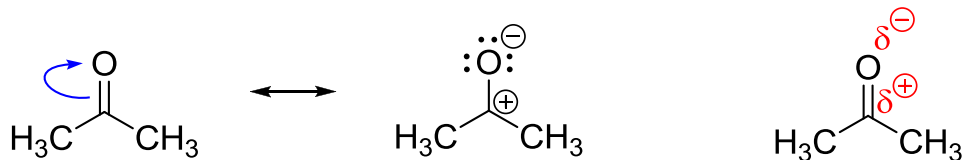
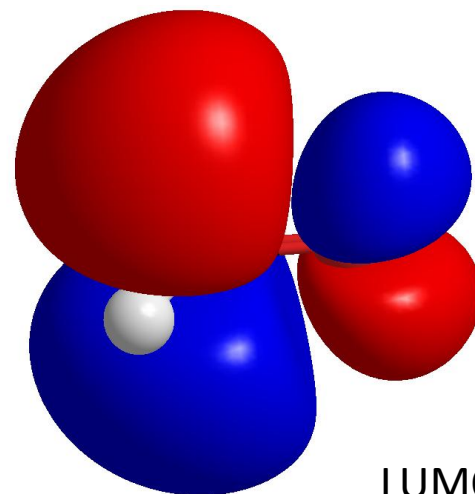
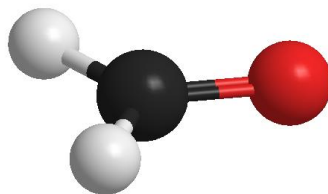
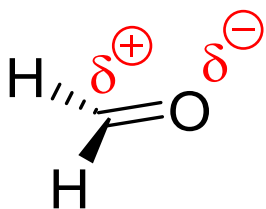
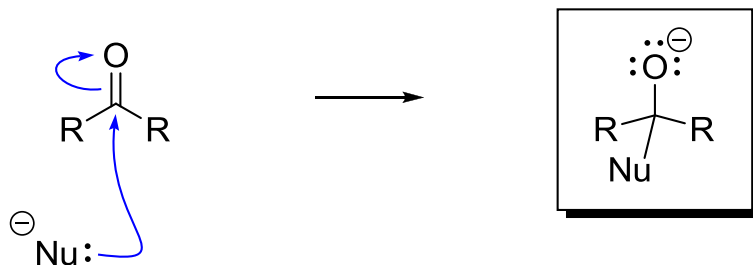


Reaktivita karbonylové skupiny

Karbonylový uhlík je elektrofil...

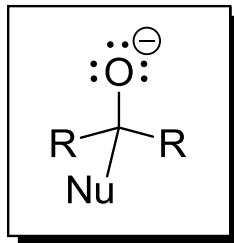


... a je napadán nukleofilem

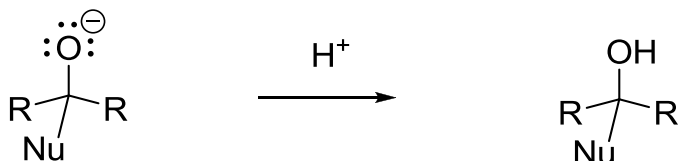


LUMO

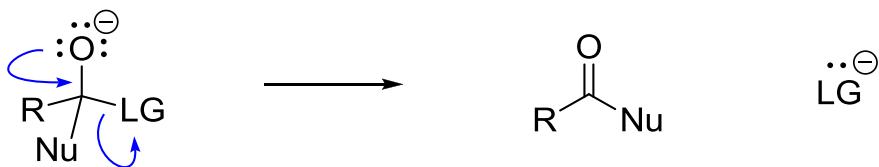
Osud tetraedrického meziprojektu



- není-li **ani jeden** ze tří substituentů (tedy včetně nukleofilu) schopen odstoupit, je možné pouze protonovat alkoxid a vytvořit **alkohol**

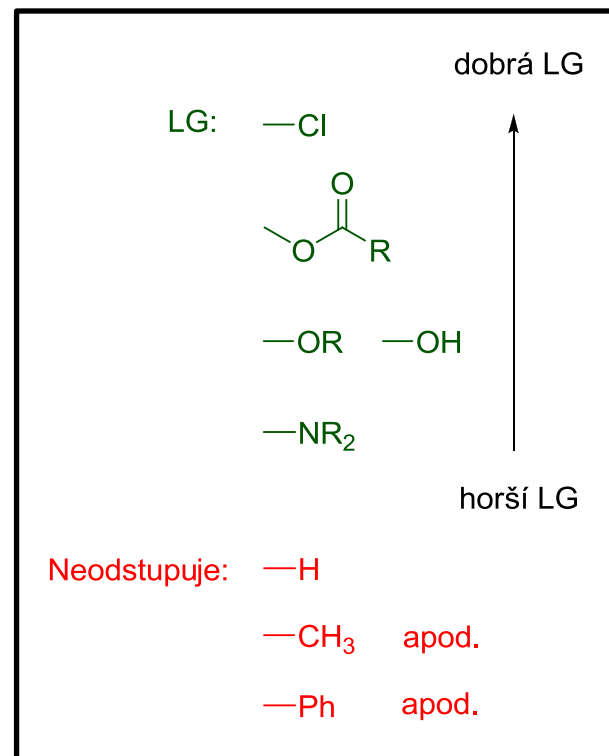


- Je-li **jeden z tří** substituentů odstupující skupina, znovu se vytvoří karbonylová skupina a **odstupující skupina odstoupí**

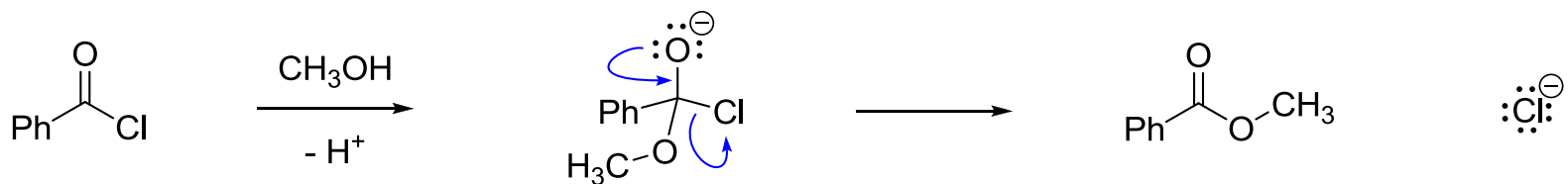
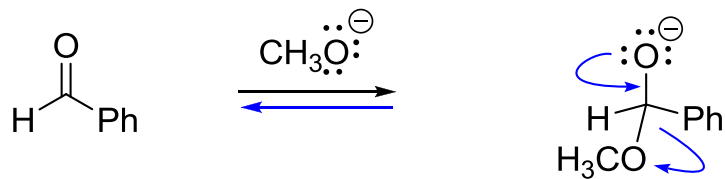
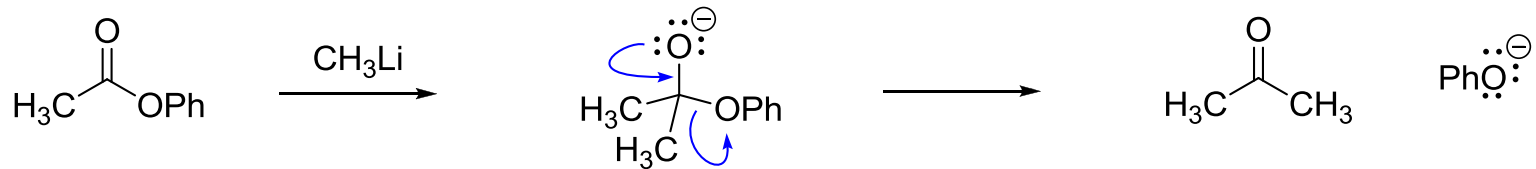
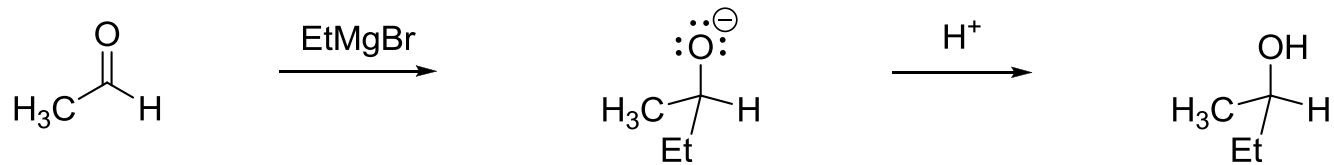


- Je-li **pouze** navázaný **nukleofil** schopen odstoupit, pak je adice **vratná**

- Je-li **více** ze tří substituentů odstupující skupina, znovu se vytvoří karbonylová skupina a odstoupí **nejlepší odstupující skupina**

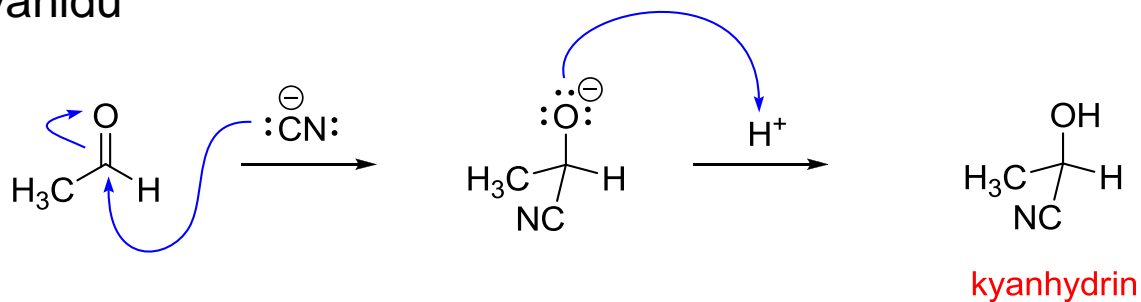


Osud tetraedrického meziprojektu



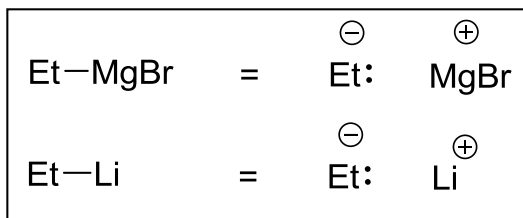
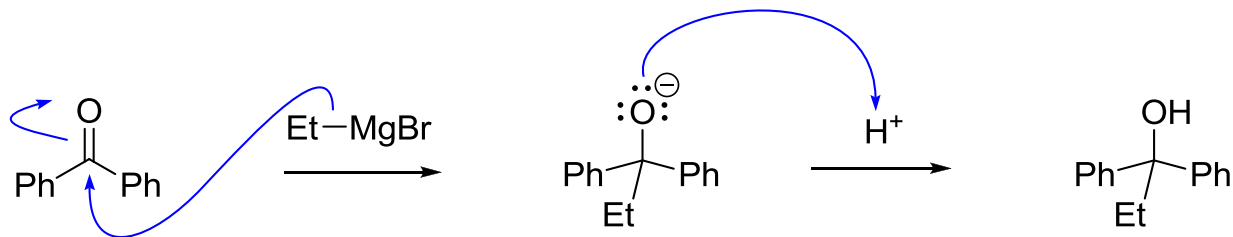
Nukleofilní adice na karbonyl

• Adice kyanidu



Zdroje nukleofilu: HCN, KCN/H⁺, CN⁻/kyselina octová ...

• Adice organokovů

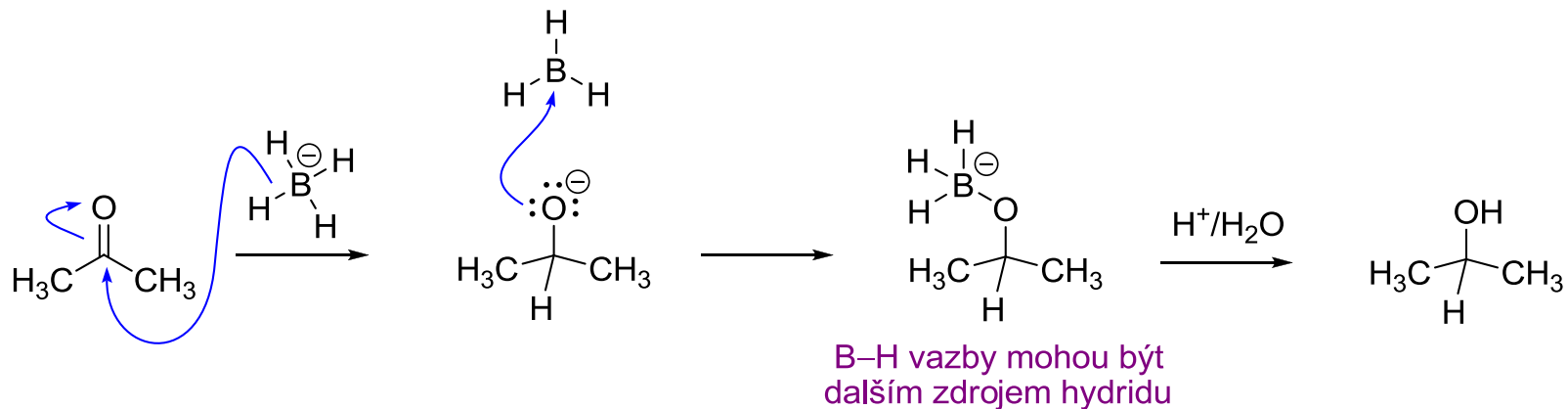


příklady nukleofilů: CH₃Li, PhLi, BuLi,... a jejich hořčnaté analogy

Nukleofilní adice na karbonyl

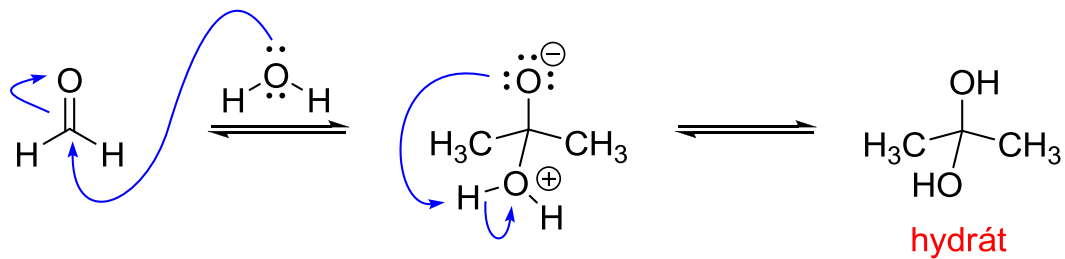
• Adice „hydridu“: redukce

(aldehyd → 1° alkohol; keton → 2° alkohol)

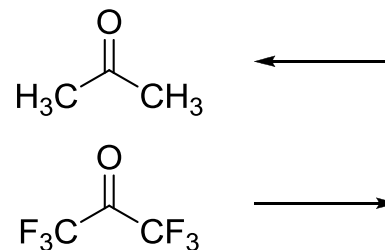


Zdroje nukleofilu: NaBH_4 , LiAlH_4 ,...

• Adice vody

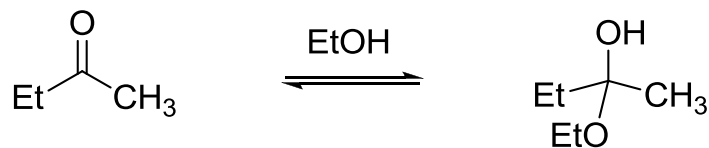


poloha rovnováhy dle reaktivity karbonylu:



Nukleofilní adice na karbonyl

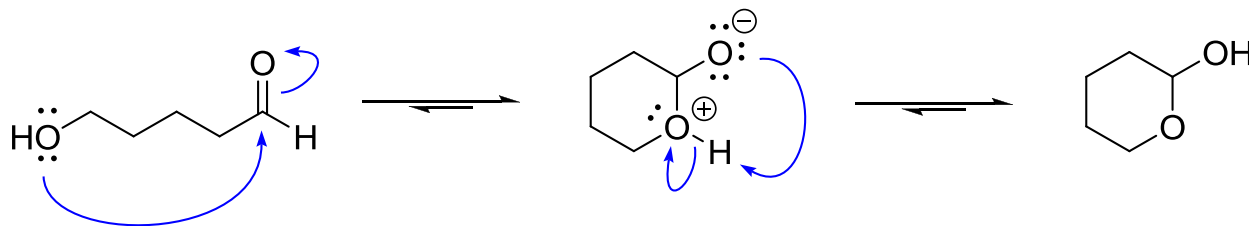
- Adice alkoholu bez katalýzy



hemiacetal

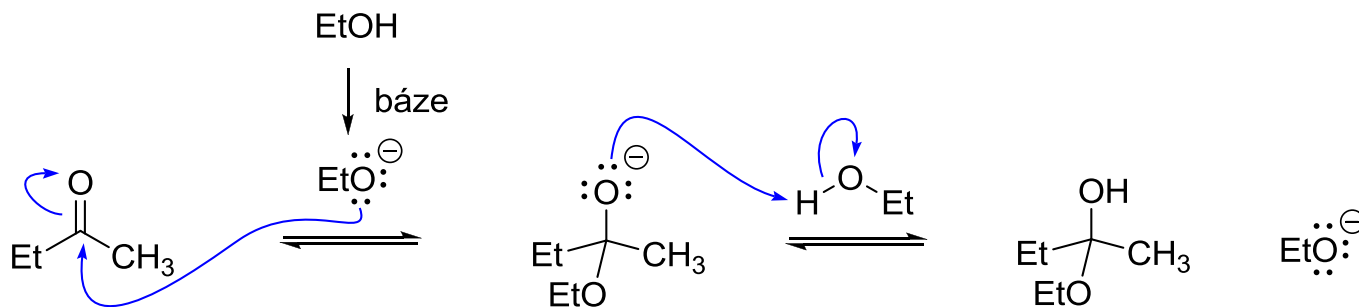
mechanismus a poloha rovnováhy analogicky jako u tvorby hydrátu

cyklické hemiacetaly bývají stabilní:



- Adice alkoholu s bazickou katalýzou

(lepší nukleofil)

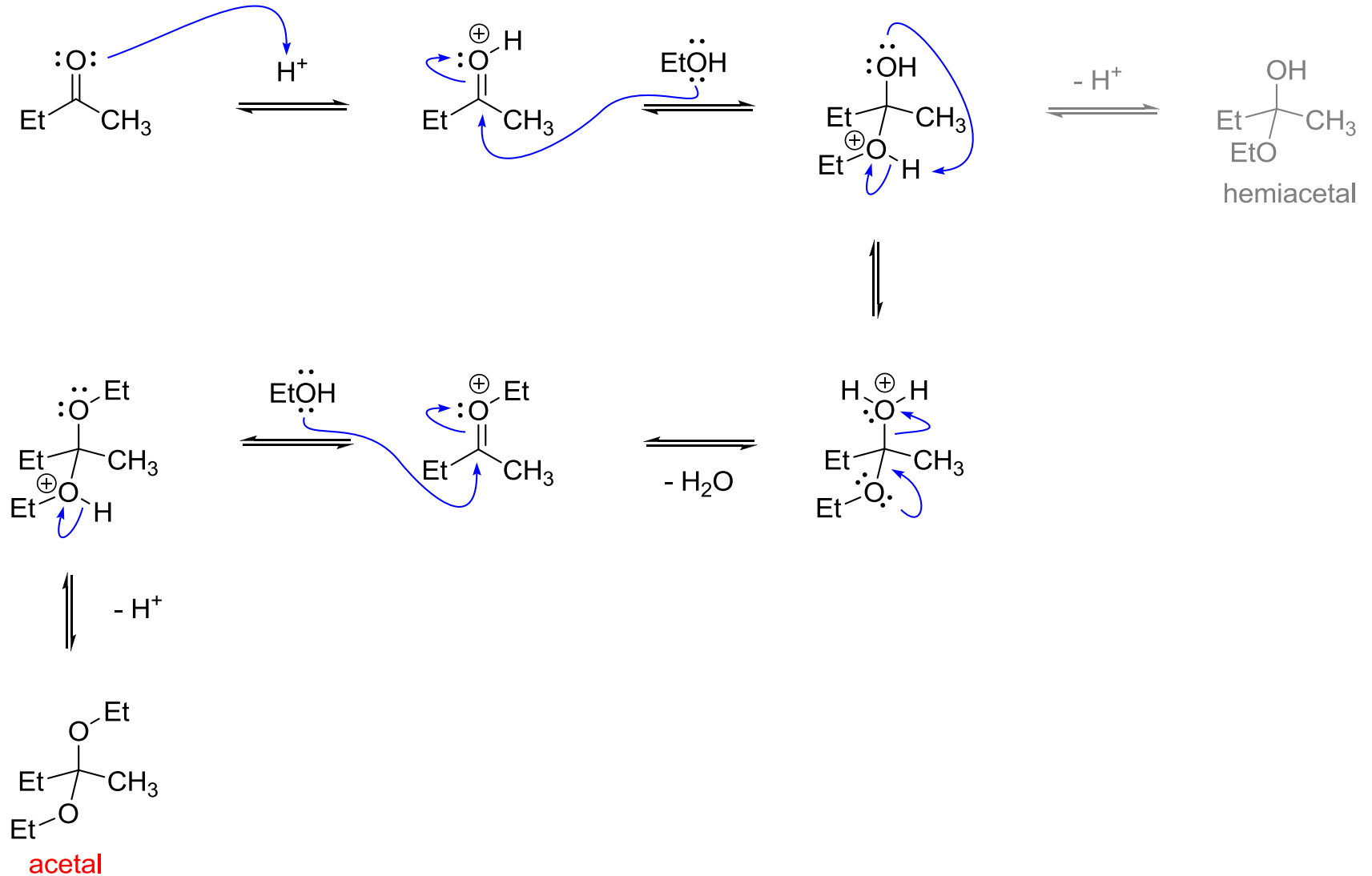


hemiacetal

Nukleofilní adice na karbonyl s následným odstoupením karbonylového kyslíku

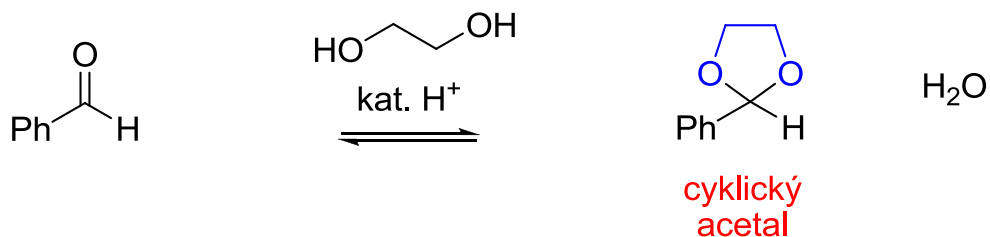
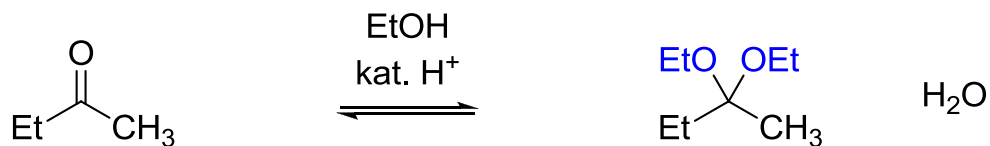
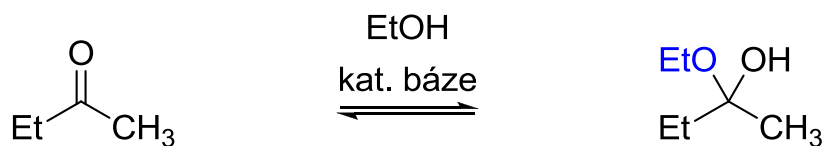
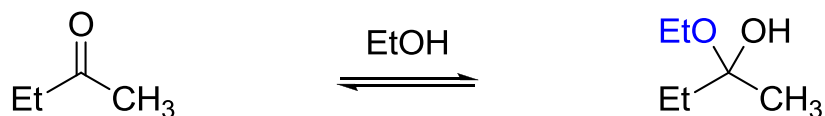
- Adice alkoholu s kyselou katalýzou

(lepší elektrofil)



Nukleofilní adice na karbonyl s následným odstoupením karbonylového kyslíku

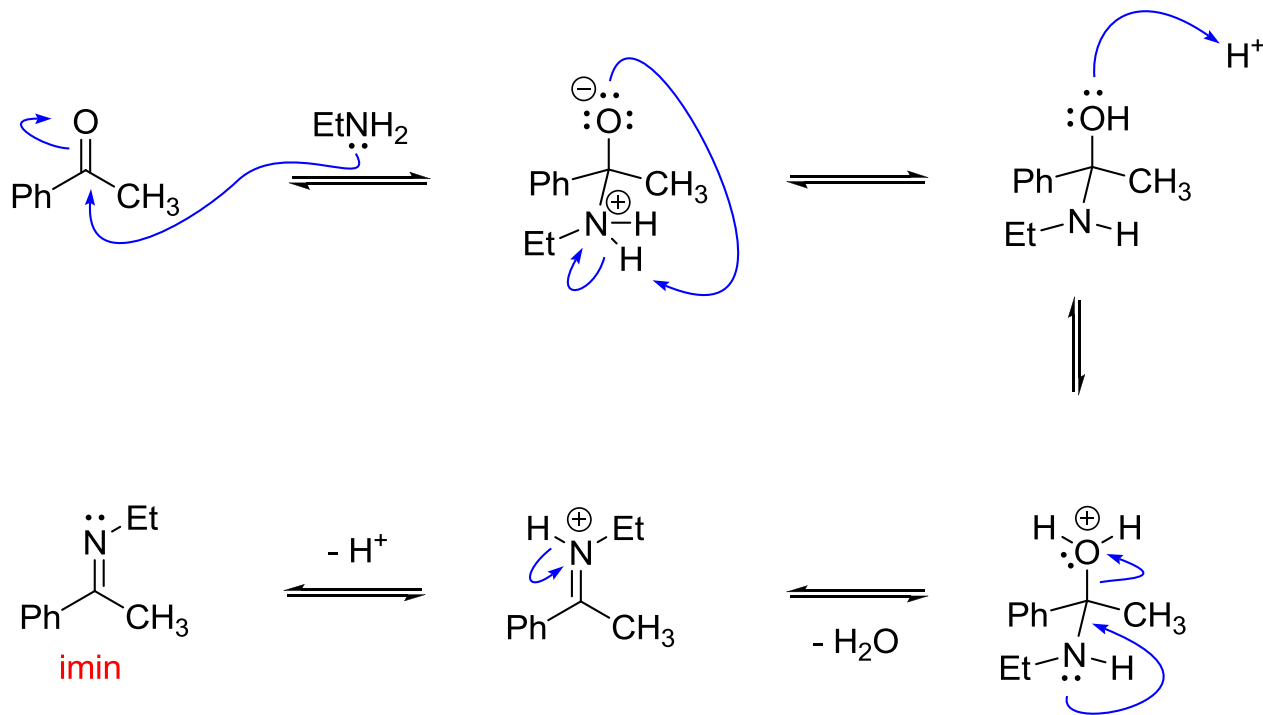
- Adice alkoholu - shrnutí



Nukleofilní adice na karbonyl s následným odstoupením karbonylového kyslíku

• Adice 1° aminu

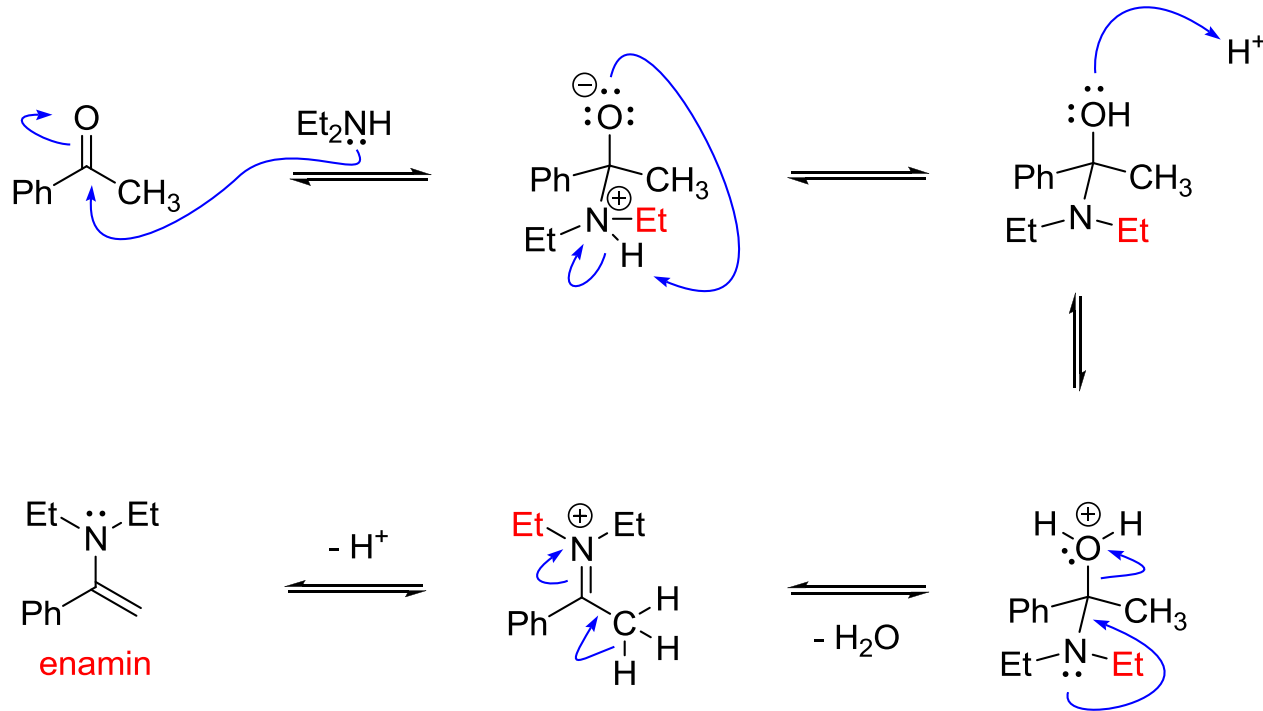
pH = 4-6



Nukleofilní adice na karbonyl s následným odstoupením karbonylového kyslíku

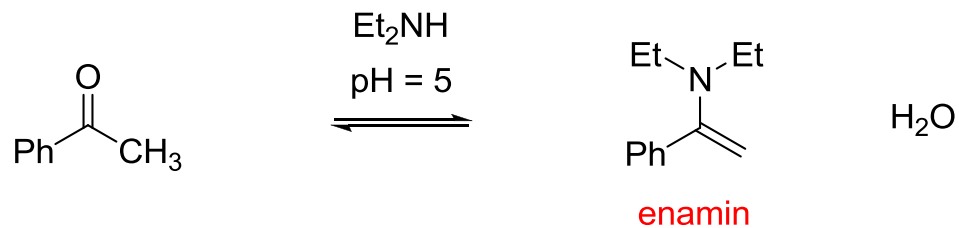
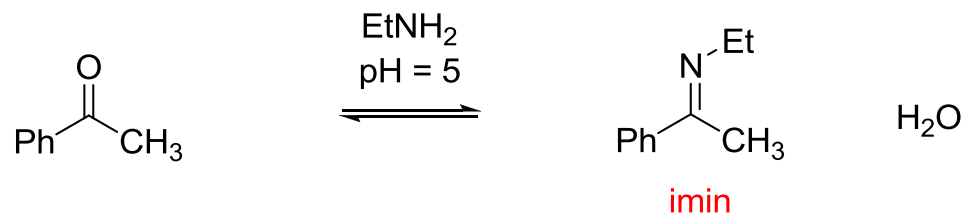
• Adice 2° aminu

pH = 4-6



Nukleofilní adice na karbonyl s následným odstoupením karbonylového kyslíku

- Adice aminů - shrnutí

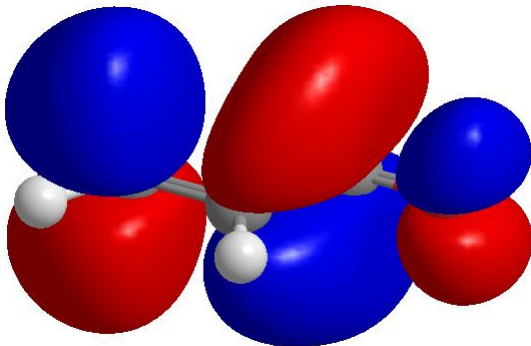


1,4-Adice a 1,2-adice

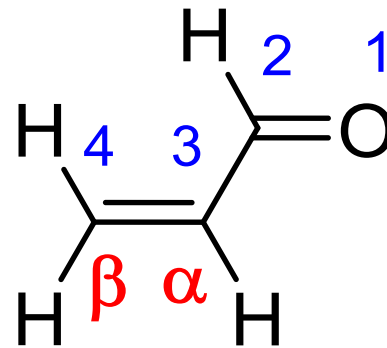
1,4-ADICE (KONJUGOVANÁ ADICE)

1,2-ADICE

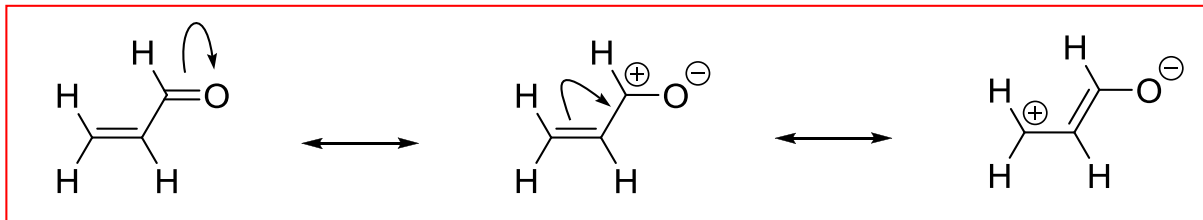
α,β -NENASYCENÁ KARBONYLOVÁ SLOUČENINA



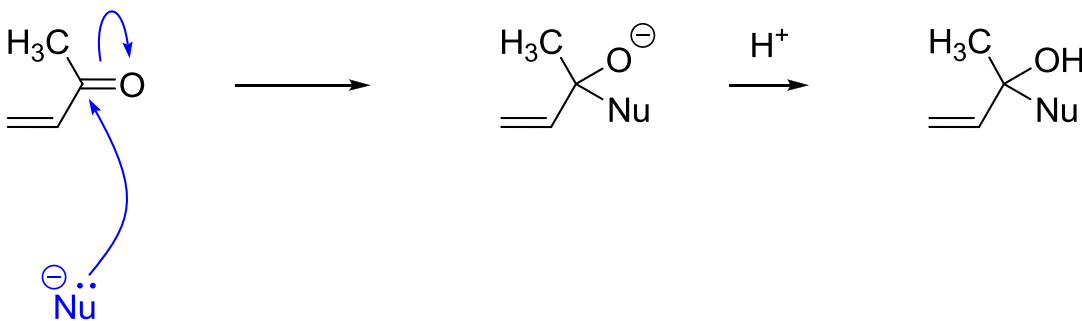
LUMO



1,4-Adice a 1,2-adice

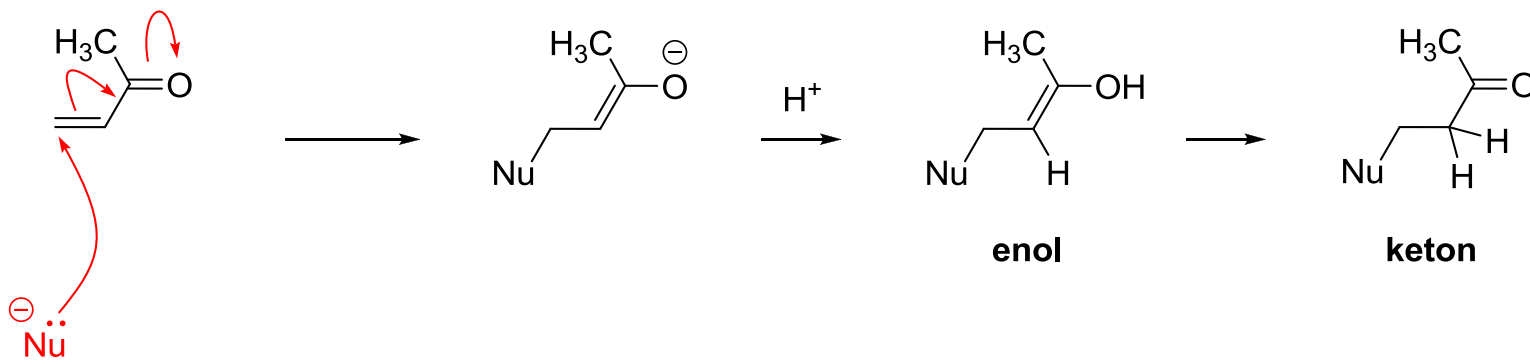


1,2-ADICE

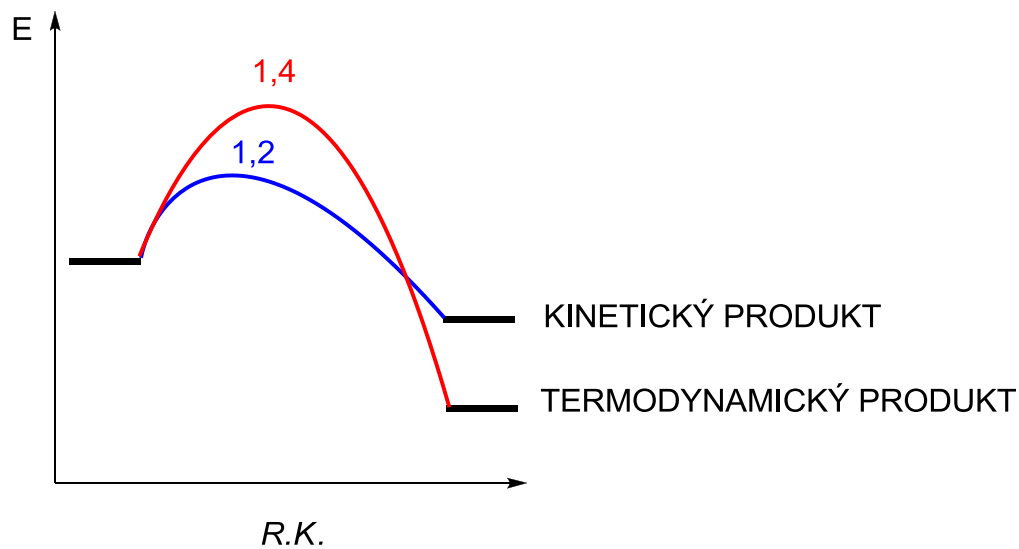
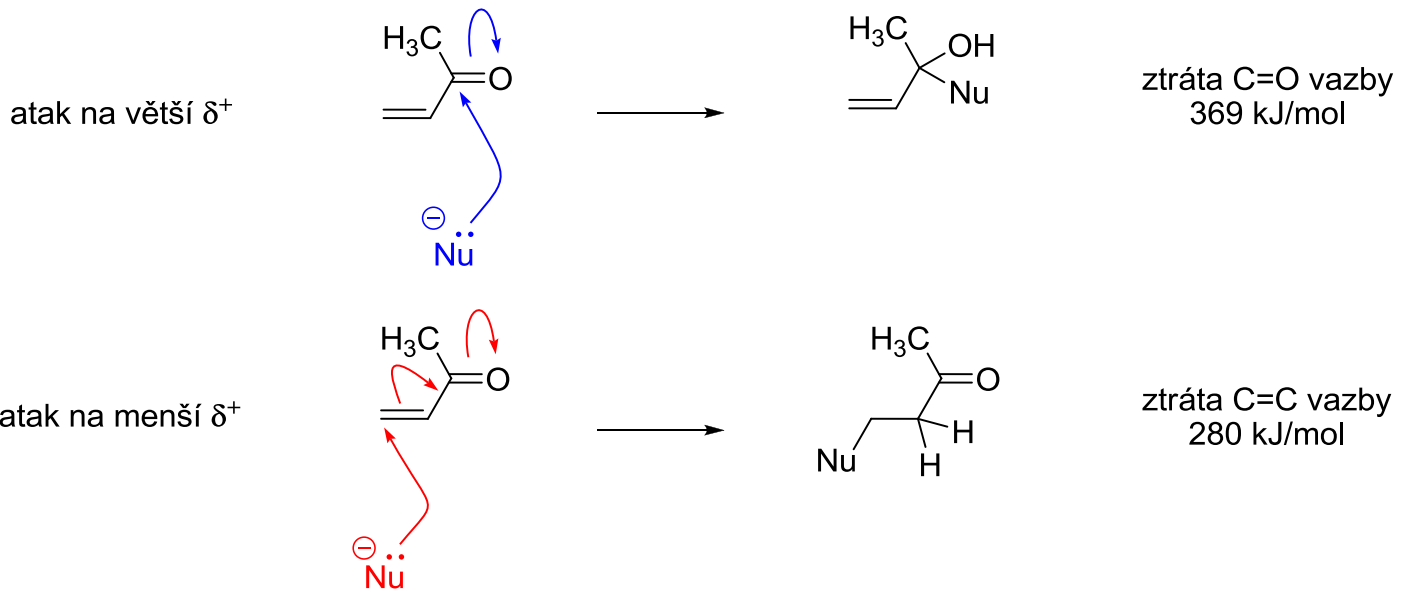


rozdíly v IČ spektru

1,4-ADICE

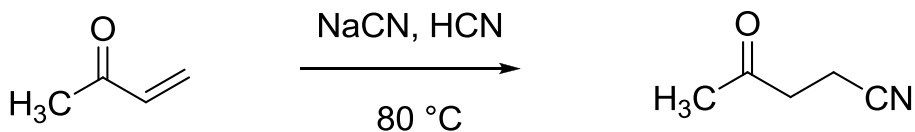
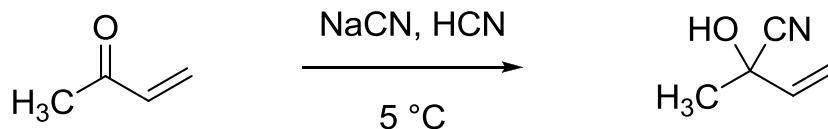


1,4-Adice a 1,2-adice



1,4-Adice a 1,2-adice

REAKČNÍ PODMÍNKY:



nižší teplota, kratší reakční čas

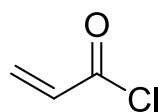
1,2-adice

vyšší teplota, delší reakční čas

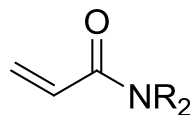
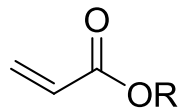
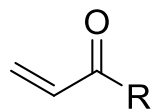
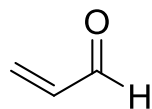
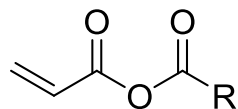
1,4-adice

1,4-Adice a 1,2-adice

ELEKTROFIL:

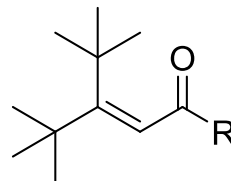


spíše 1,2

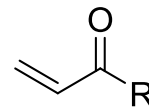
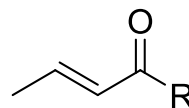
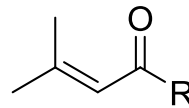


reaktivita C=O

spíše 1,4



pouze 1,2



bránění β -uhlíku

1,2 nebo 1,4

1,4-Adice a 1,2-adice

NUKLEOFIL:

1,2 TVRDÉ

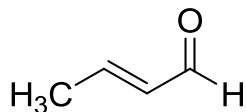
RLi
RMgBr
NH₃
ROH
RO⁻
LiAlH₄

CN⁻
N₃⁻

1,4 MĚKKÉ

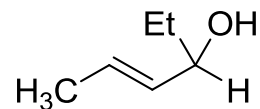
R₂CuLi
RSH
RS⁻
enoláty

1,4-Adice a 1,2-adice

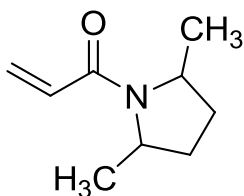


1. EtMgBr, -78 °C

2. H₂O

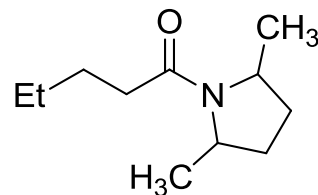


velmi reaktivní karbonyl
lehce bráněná β-pozice
nízká teplota
Grignardovo činidlo

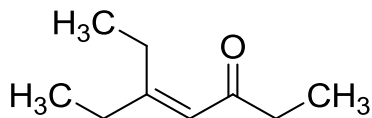


1. EtMgBr, 0 °C

2. H₂O

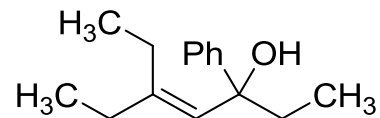


nereaktivní karbonyl
přístupná β-pozice
teplota
Grignardovo činidlo
bráněný karbonyl



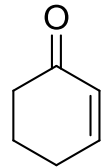
1. PhLi, -78 °C

2. H₂O

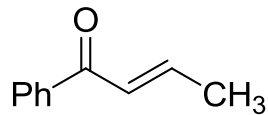
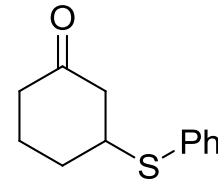


karbonyl
nepřístupná β-pozice
nízká teplota
organolithné činidlo

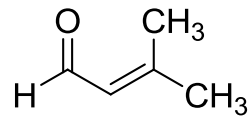
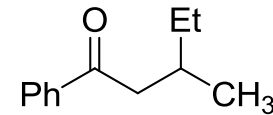
1,4-Adice a 1,2-adice



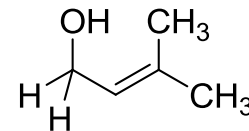
1. PhSNa, 60 °C
2. H₃O⁺



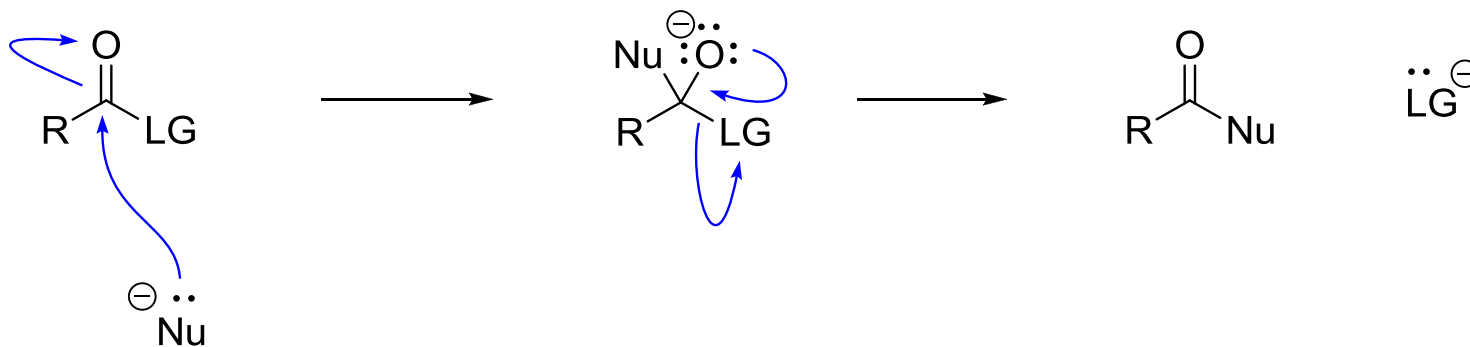
1. Et₂CuLi
2. H₃O⁺



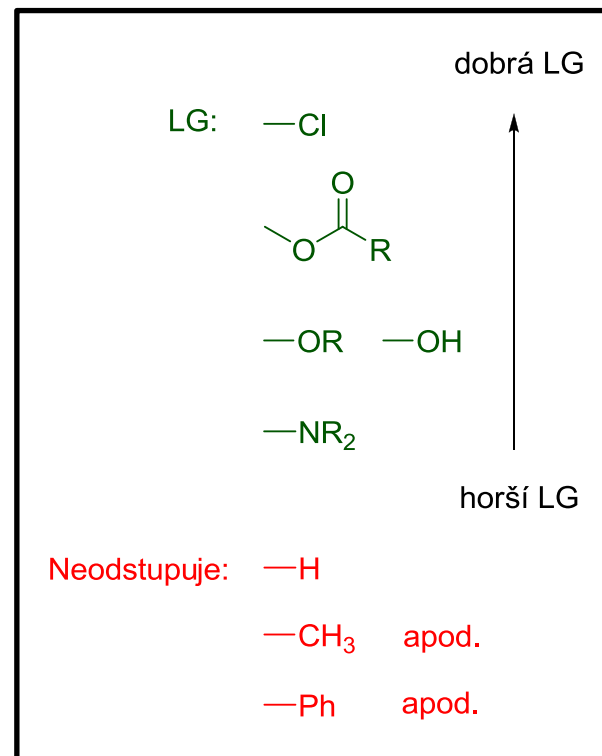
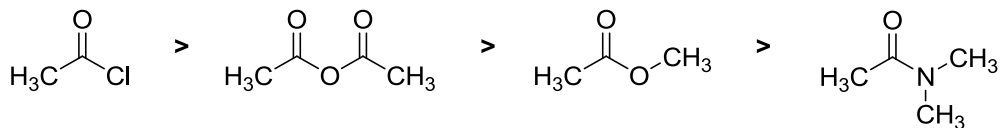
1. LiAlH₄
2. H₃O⁺



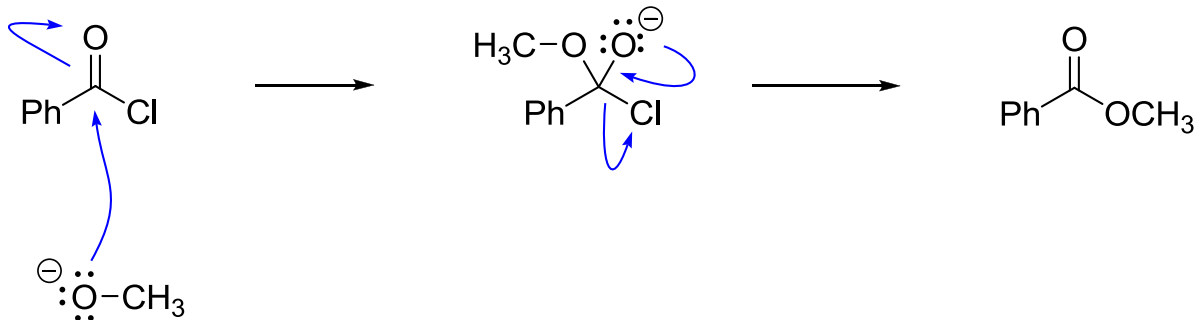
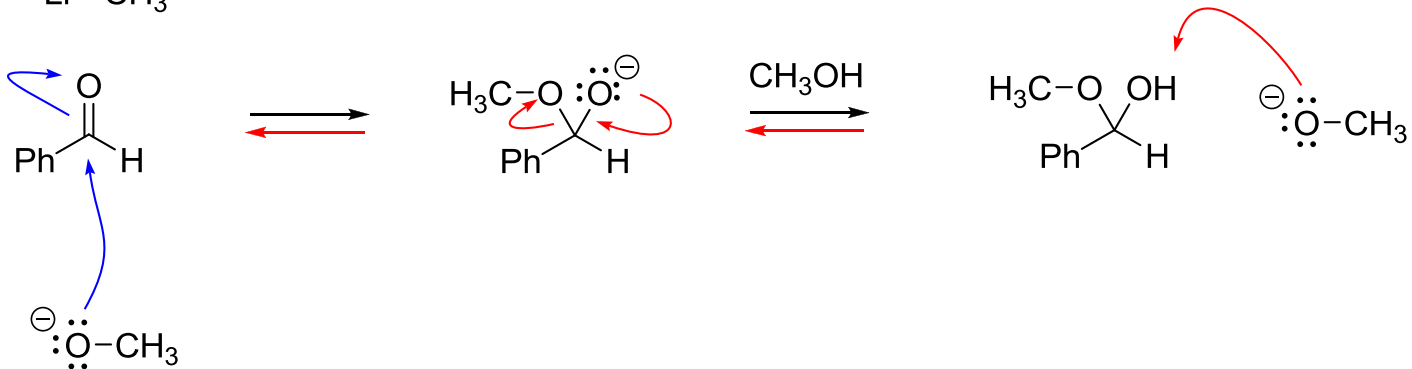
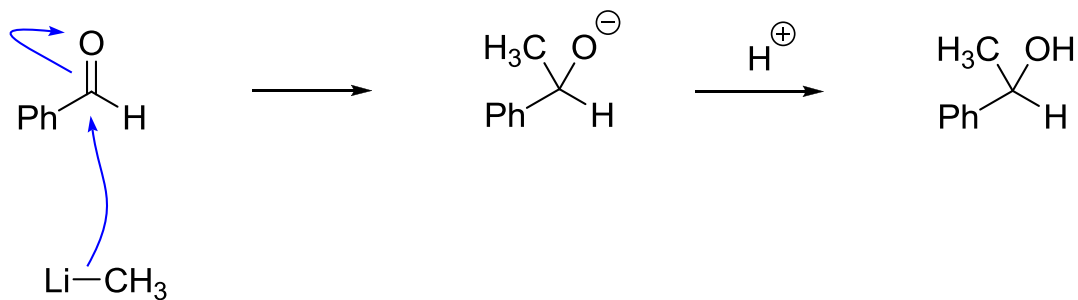
Nukleofilní substituce na karbonylové skupině



Reaktivita vůči nukleofilu:

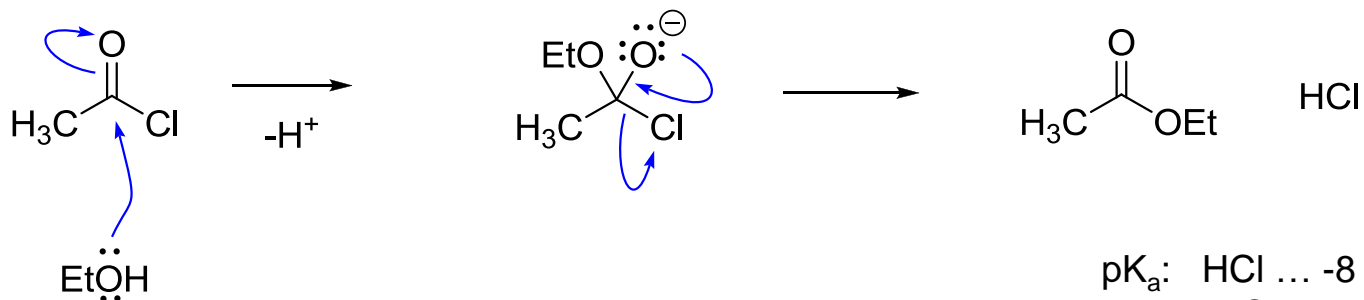


Nukleofilní substituce na karbonylové skupině

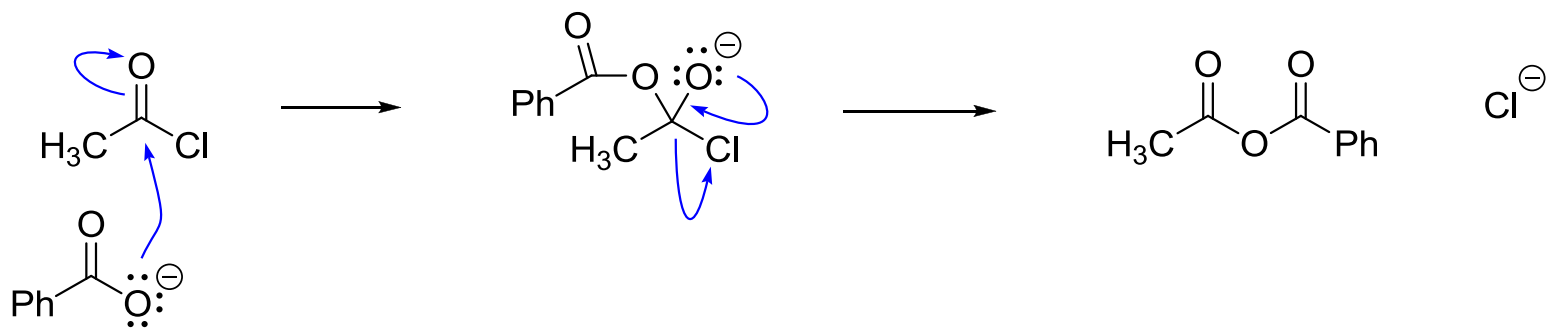


Nukleofilní substituce na karbonylové skupině

méně reaktivní deriváty karboxylových kyselin lze připravit z více reaktivních



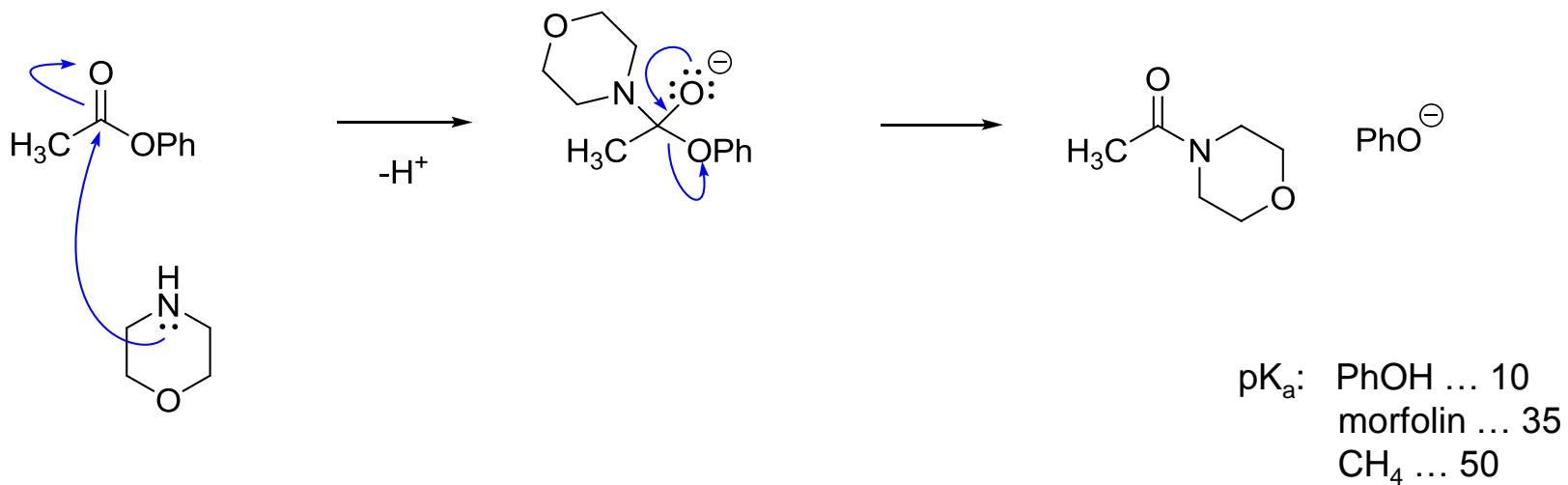
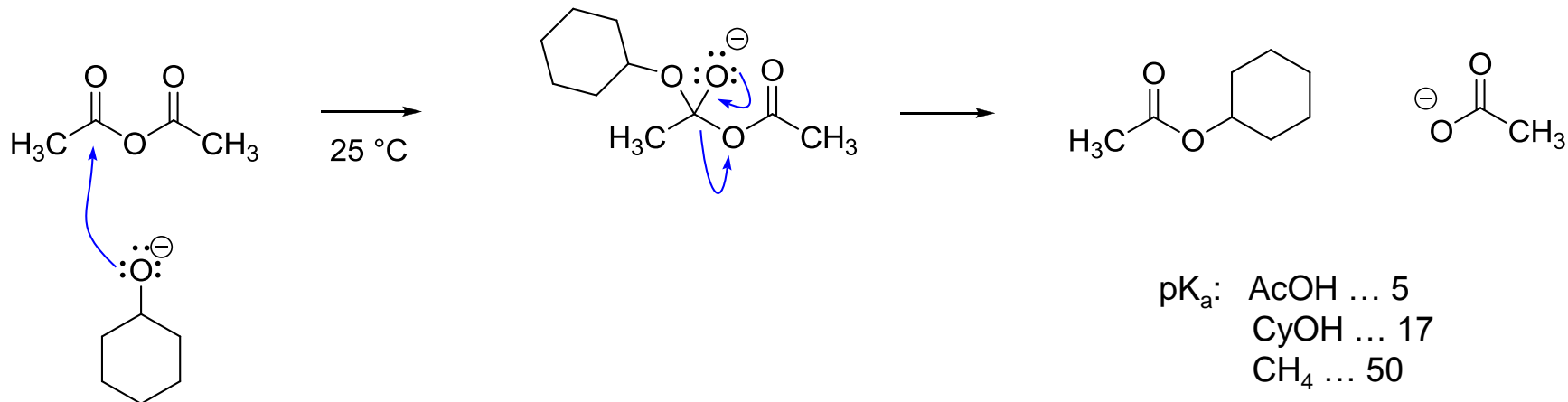
pK_a: HCl ... -8
EtOH ... 16
CH₄ ... 50



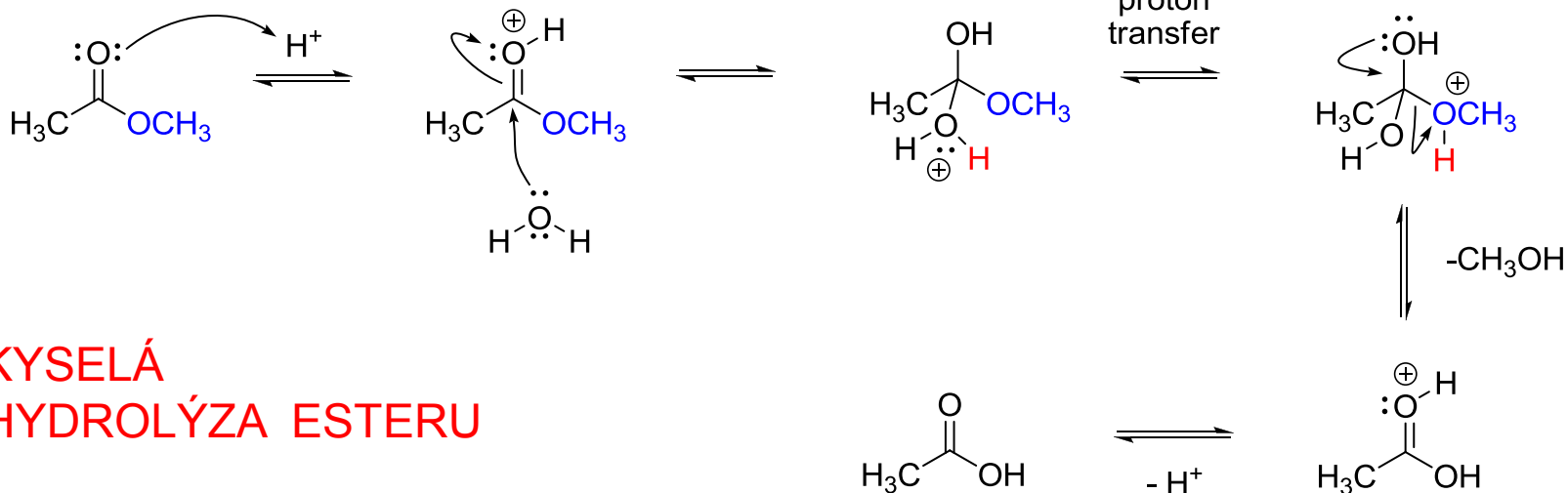
pK_a: HCl ... -8
PhCOOH ... 4
CH₄ ... 50

Nukleofilní substituce na karbonylové skupině

méně reaktivní deriváty karboxylových kyselin lze připravit z více reaktivních

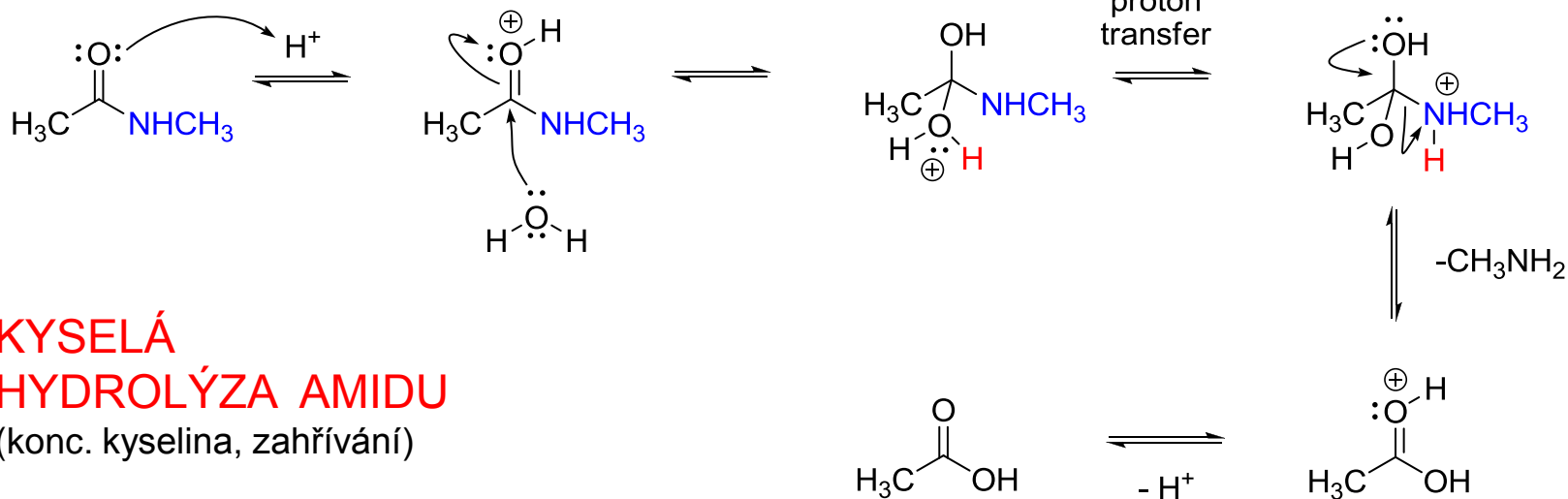


Nukleofilní substituce na karbonylové skupině



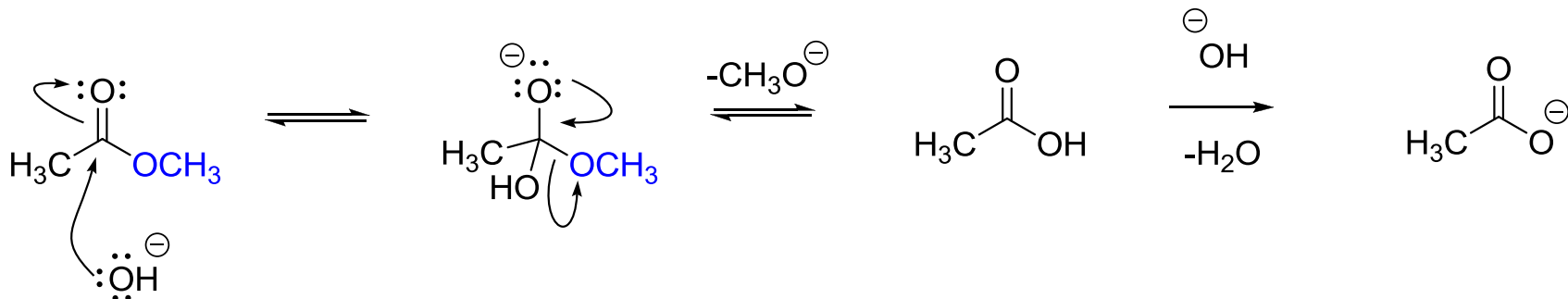
KYSELÁ HYDROLÝZA ESTERU

vratné reakce



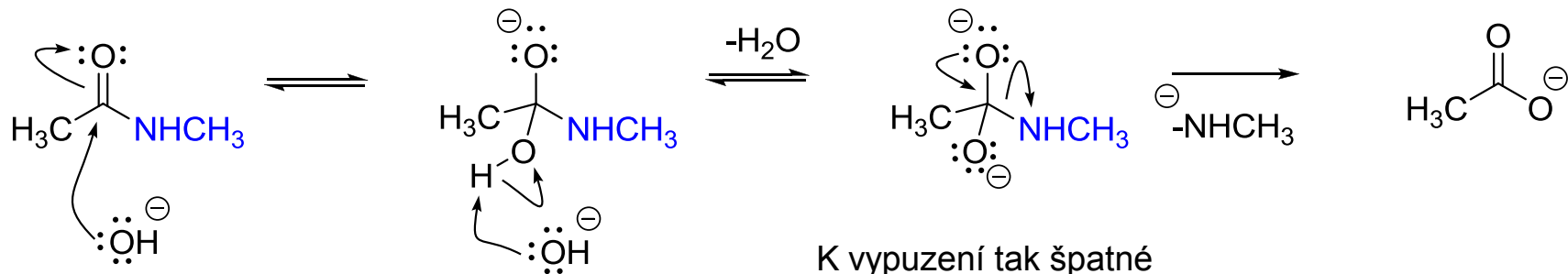
KYSELÁ HYDROLÝZA AMIDU (konc. kyselina, zahřívání)

Nukleofilní substituce na karbonylové skupině



BAZICKÁ HYDROLÝZA ESTERU

nevratné reakce



K vypuzení tak špatné
odstupující skupiny
je nutná tvorba dianiontu.

BAZICKÁ HYDROLÝZA AMIDU

(konc. hydroxid, zahřívání)