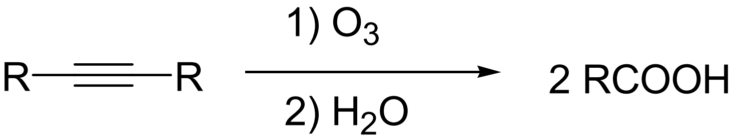
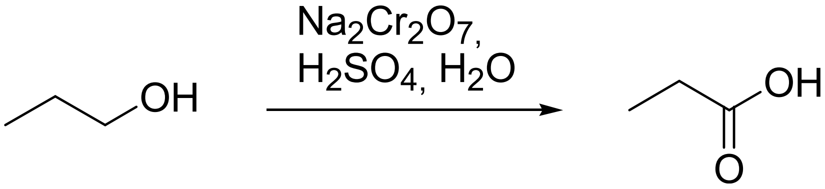
KARBOXYLOVÉ KYSELINY A JEJICH FUNKČNÍ DERIVÁTY

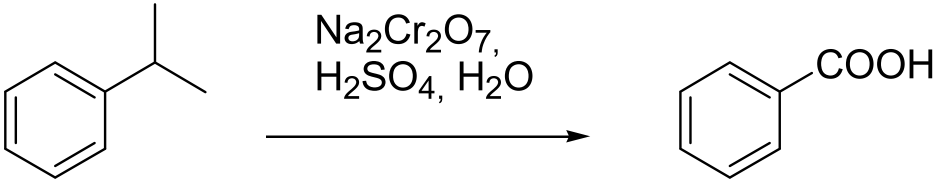
1) Oxidativní štěpení alkynů



2) Oxidace primárních alkoholů

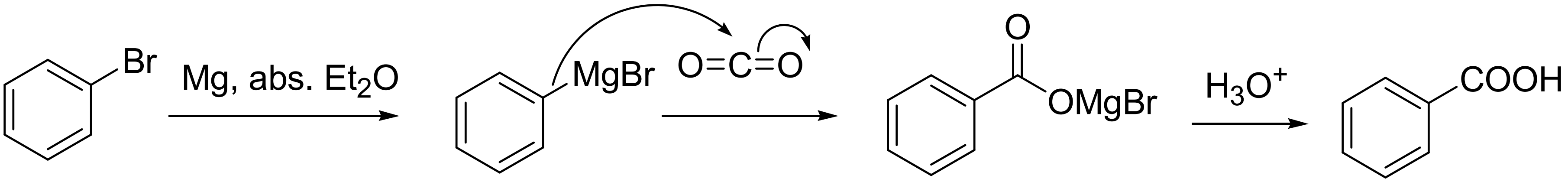


3) Oxidace alkylbenzenů

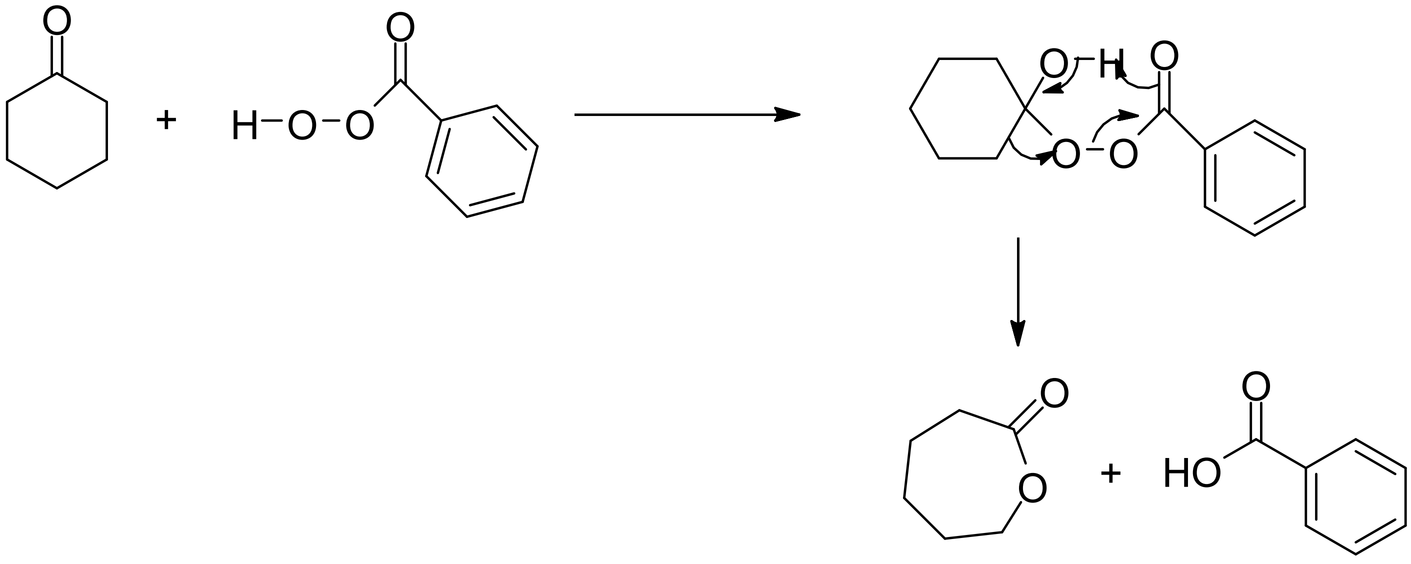


4) Hydrolýza nitrilů

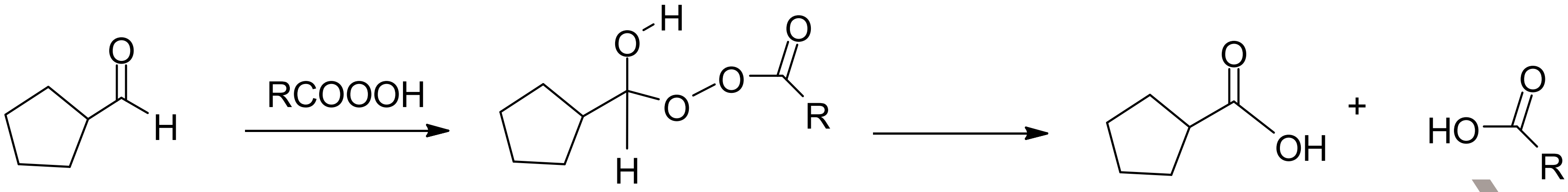
5) Grignardova činidla a oxid uhličitý



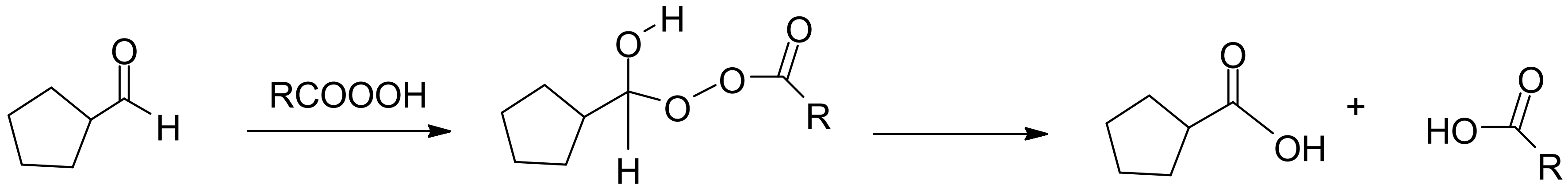
6) Baeyer-Villigerova oxidace aldehydů



methyl < primární < fenyl = sekundární < terciární < H



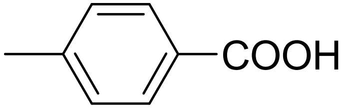
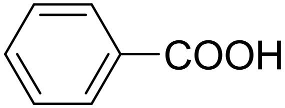
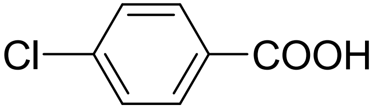
6) Baeyer-Villigerova oxidace aldehydů



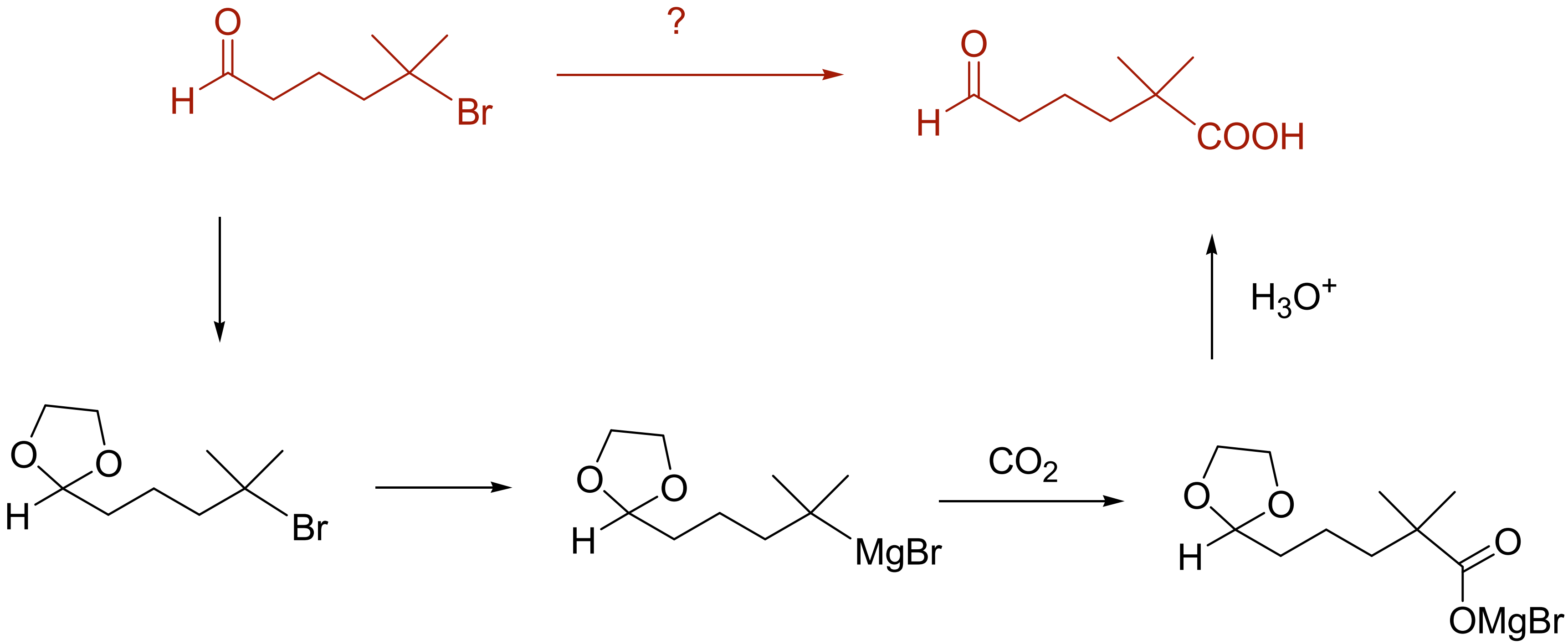
Kyselost karboxylových kyselin

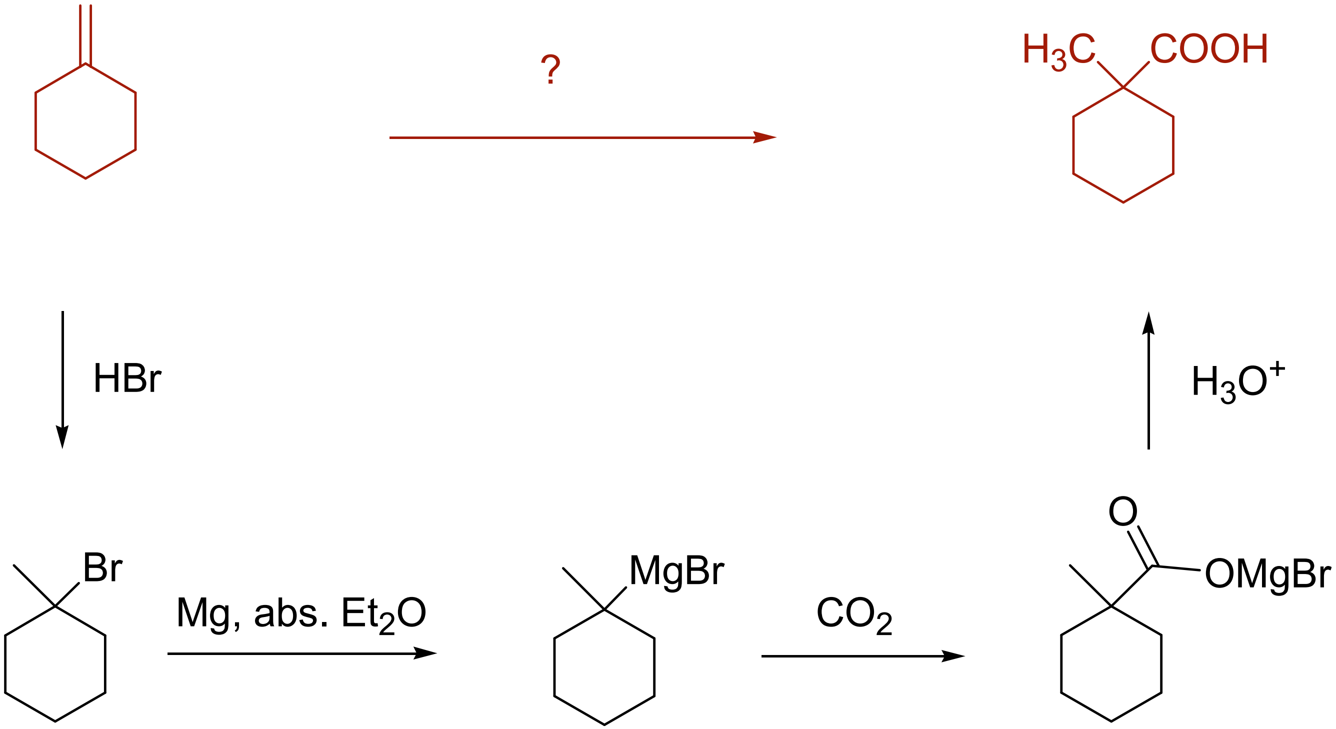
	CH_3COOH	Cl_3CCOOH	PhCOOH	
p*K*a	4,8	0,6	4,2	1,9

	F_3CCOOH	Cl_3CCOOH
p*K*a	0,23	0,63

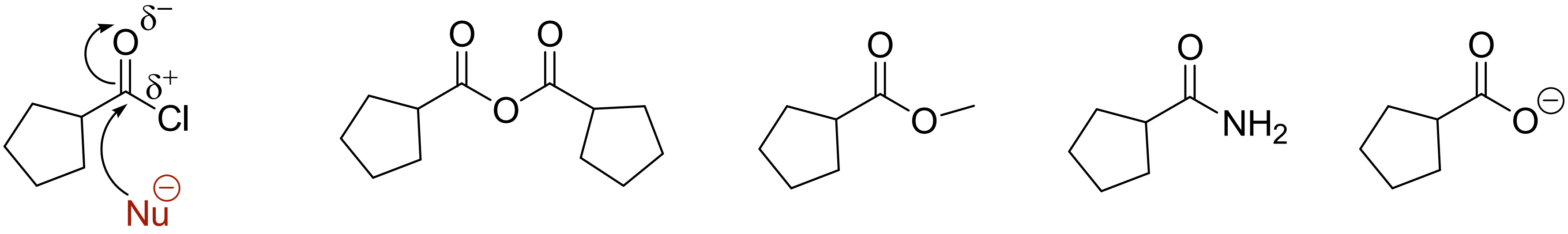
			
p*K*a	4,36	4,20	3,98

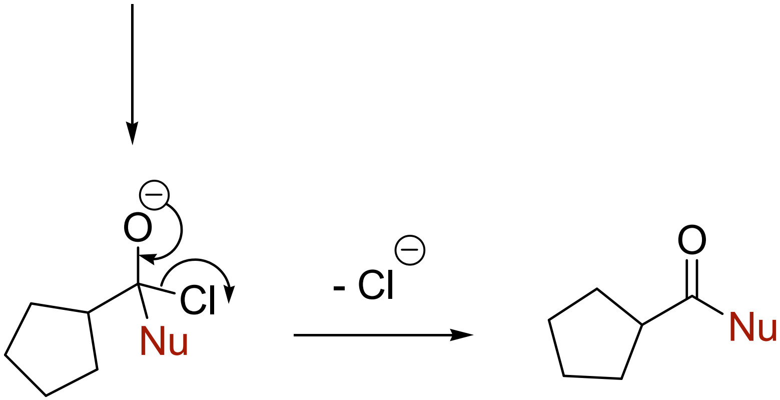
$$\underset{4,8}{CH_3COOH} + NaOH \longrightarrow CH_3COONa + \underset{15,7}{H_2O}$$


?
O
H
Br
COOH
O
O
MgBr
CO_2
H_3O^+
OMgBr

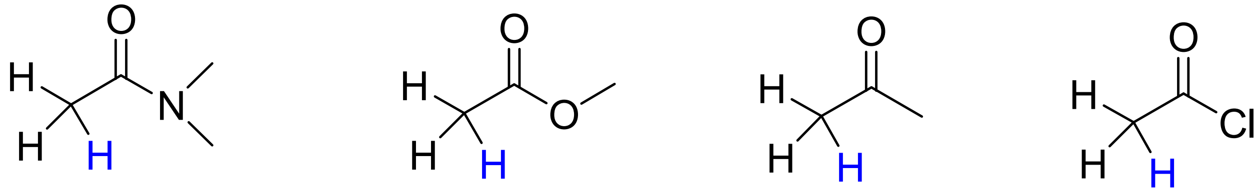

?
H_3C
COOH
HBr
H_3O^+
O
Br
Mg, abs. Et_2O
MgBr
CO_2
OMgBr

Funkční deriváty karboxylových kyselin

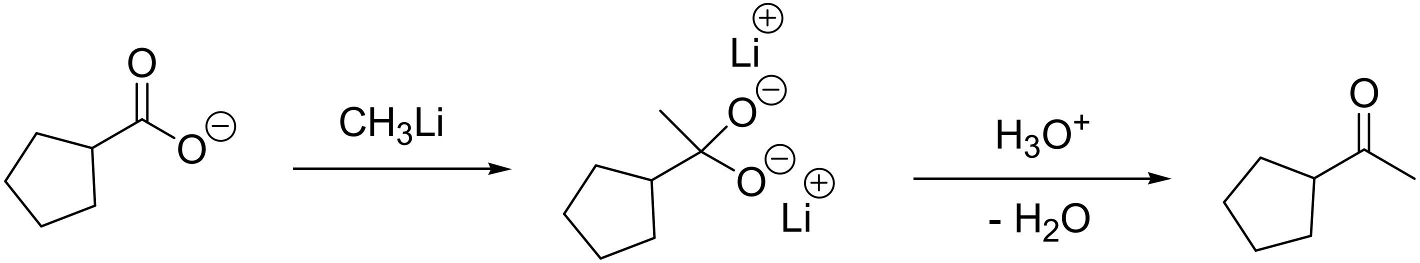




Odstupující skupina	**pK_{AH}**
$R^{\ominus}$	50
$^{\ominus}NH_2$	35
$RO^{\ominus}$	16
$RCOO^{\ominus}$	5
$Cl^{\ominus}$	-7



pK_a	30	25	20	16

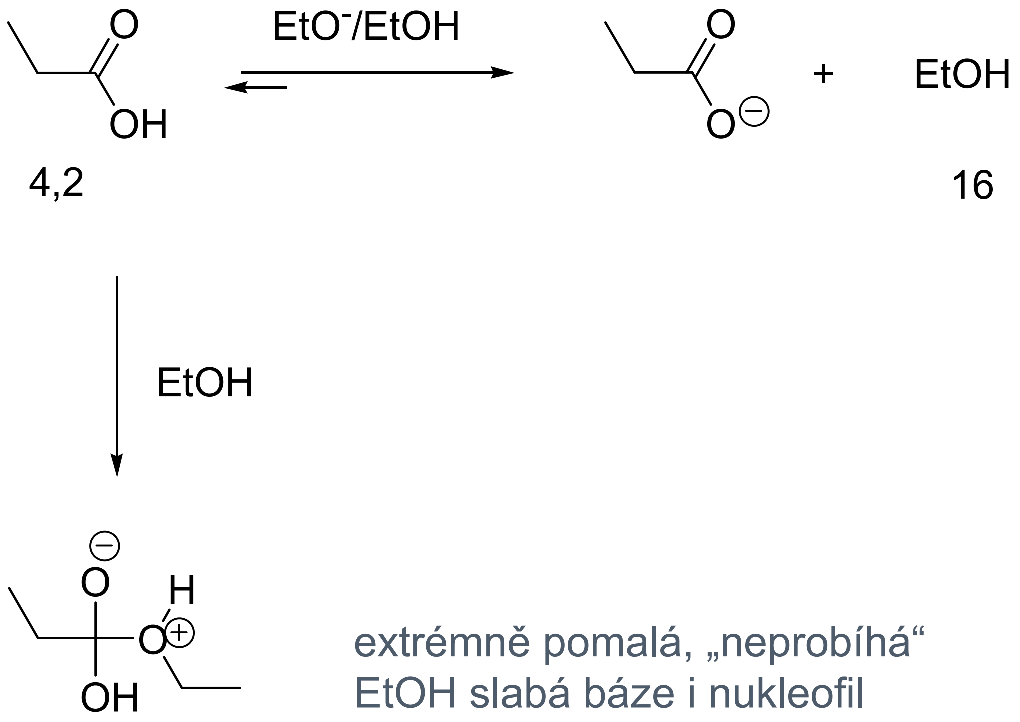


pouze velmi silné nukleofily se adují na karboxylátový anion !!

ESTERY KARBOXYLOVÝCH KYSELIN - příprava

1) Esterifikace a transesterifikace
2) Alkylace karboxylátového iontu
3) Reakce s diazomethanem (methylestery)
4) Z chloridů kyselin

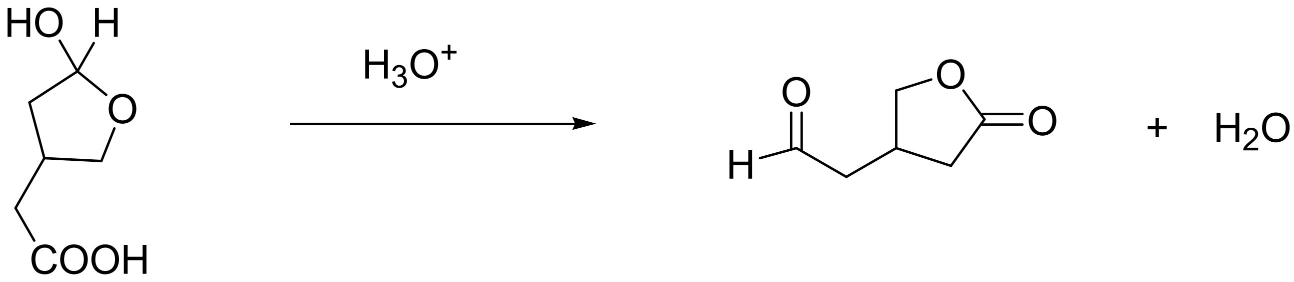
Estery karboxylových kyselin

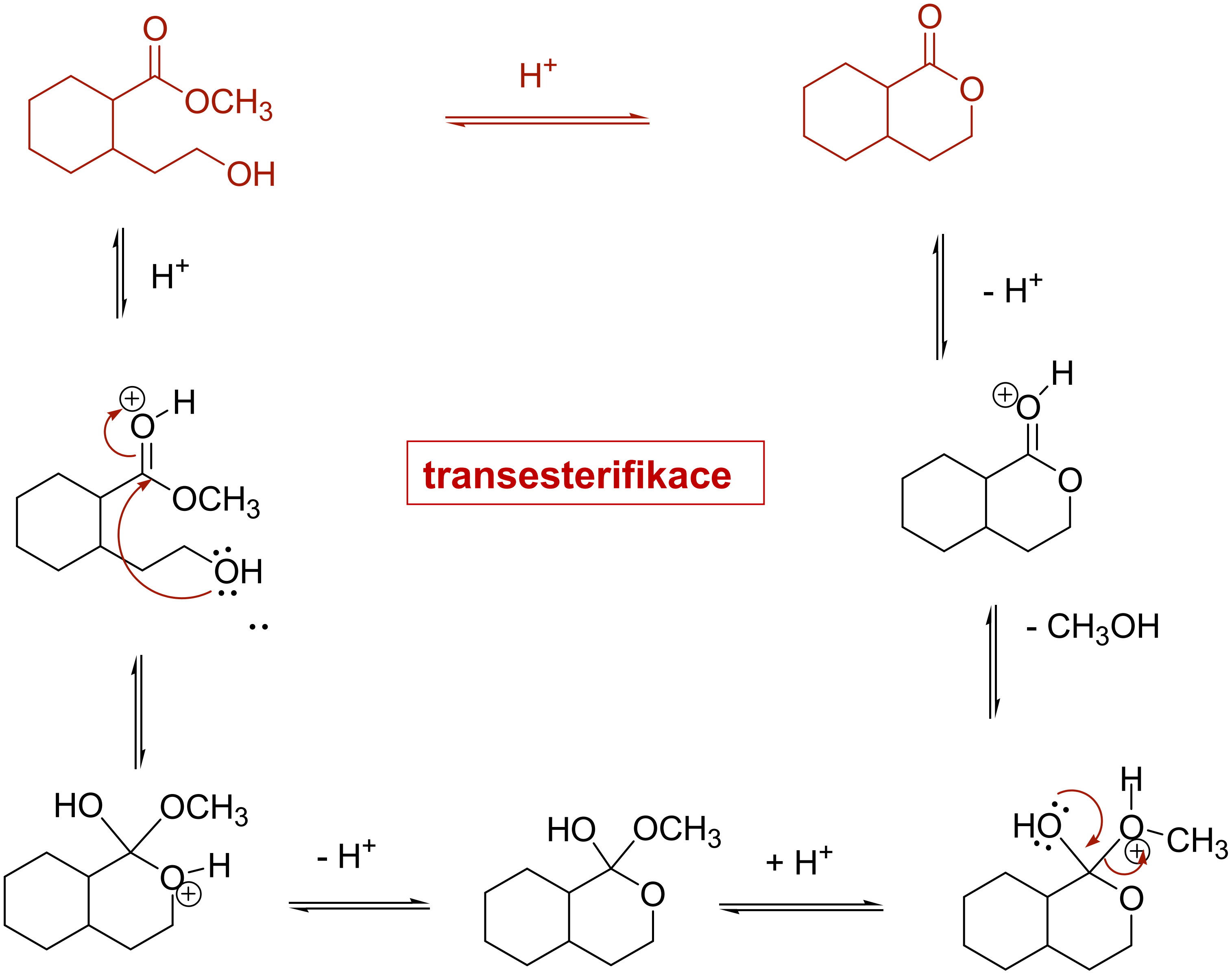


extrémně pomalá, „neprobíhá“
EtOH slabá báze i nukleofil

Esterifikace je kysele katalyzovaná, rovnovážná reakce

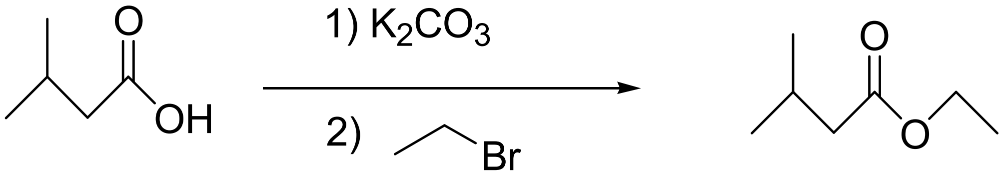
Vysvětlete

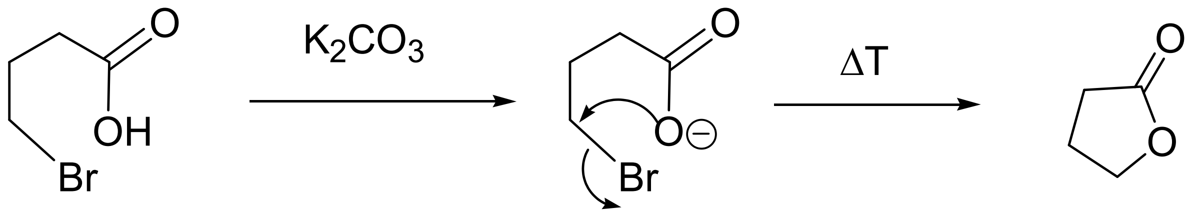




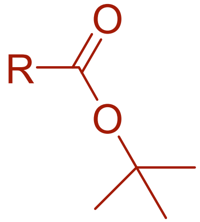
transesterifikace

Alkylace karboxylátového iontu

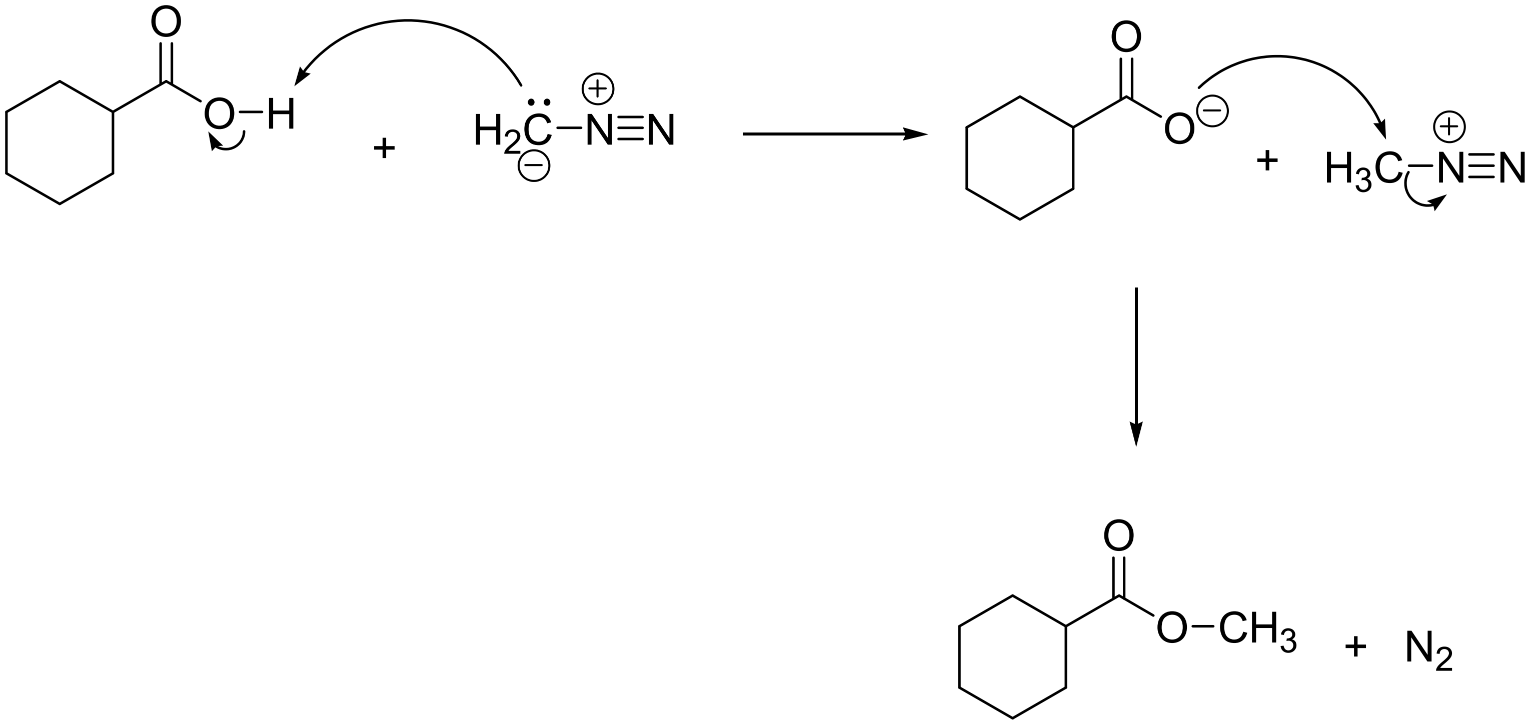




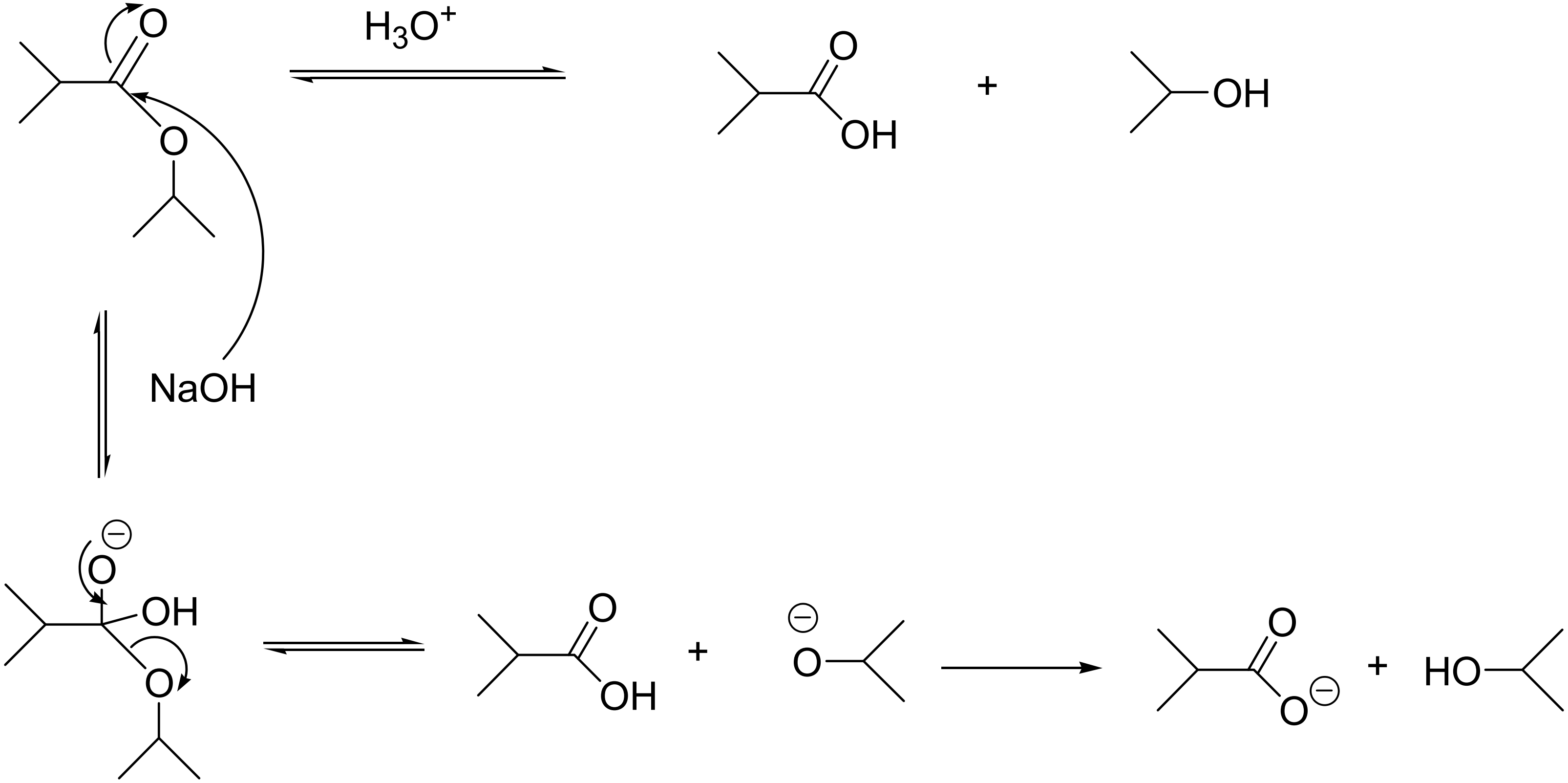
POZOR přes S_N2 nelze

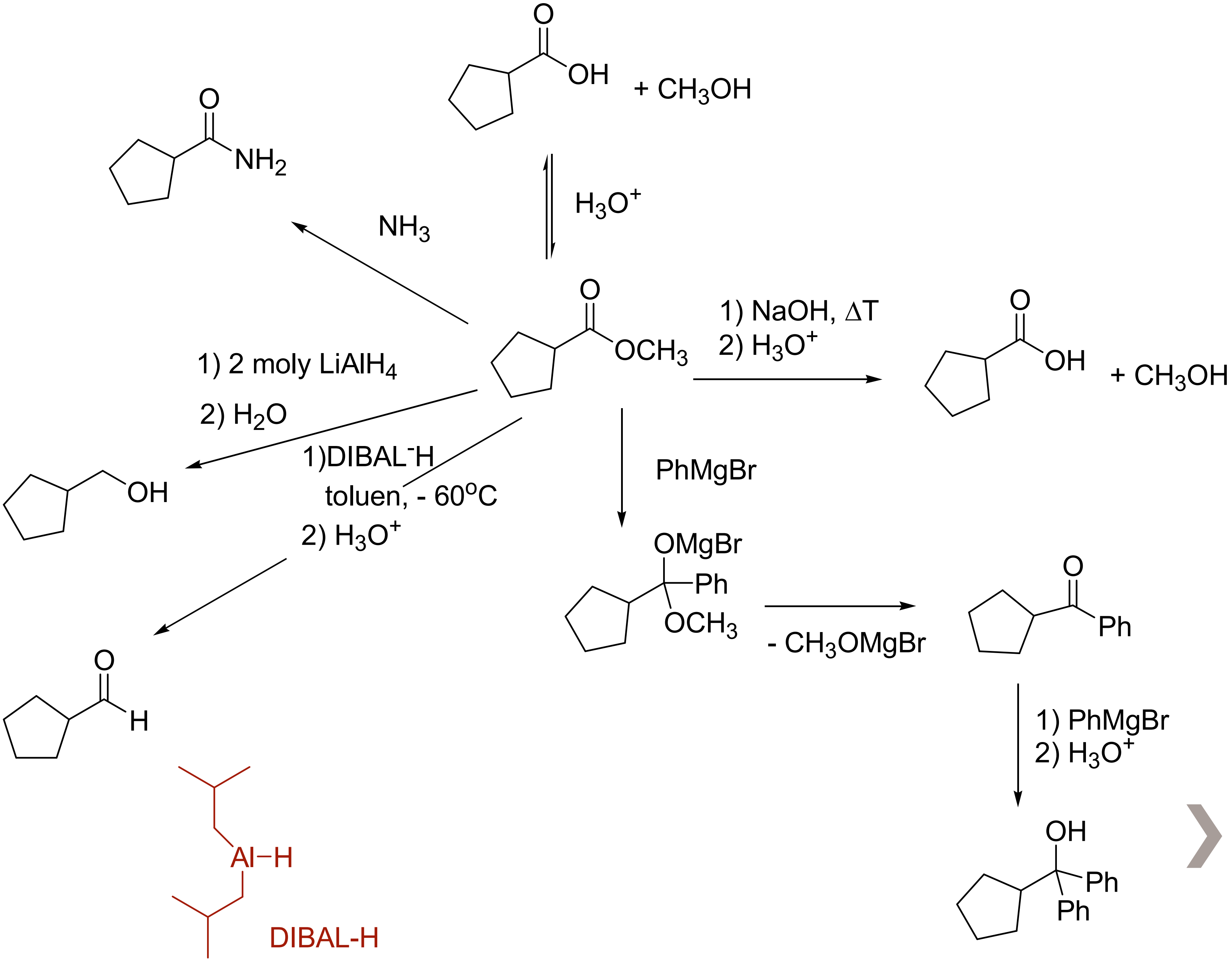


Reakcí s diazomethanem

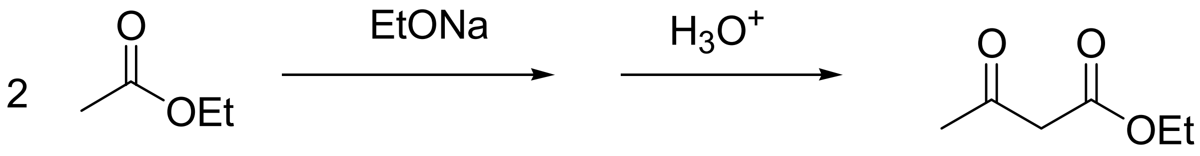


Zmýdelnění



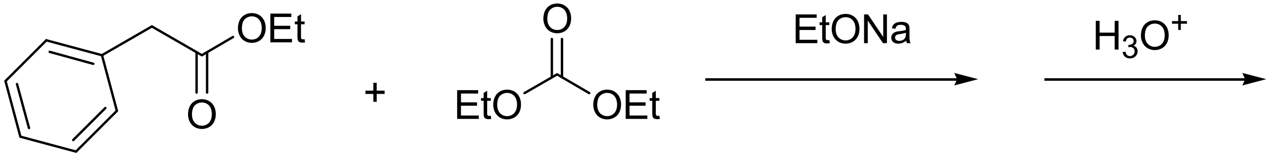

O
OH
+ CH_3OH
O
NH_2
H_3O^+
NH_3
O
OCH_3
1) NaOH, ΔT
2) H_3O^+
O
OH
+ CH_3OH
1) 2 moly $LiAlH_4$
2) H_2O
OH
1)DIBAL⁻H
toluen, - 60°C
2) H_3O^+
PhMgBr
OMgBr
Ph
OCH_3
- CH_3OMgBr
O
Ph
O
H
1) PhMgBr
2) H_3O^+
Al–H
DIBAL-H
OH
Ph
Ph

Claisenova kondenzace

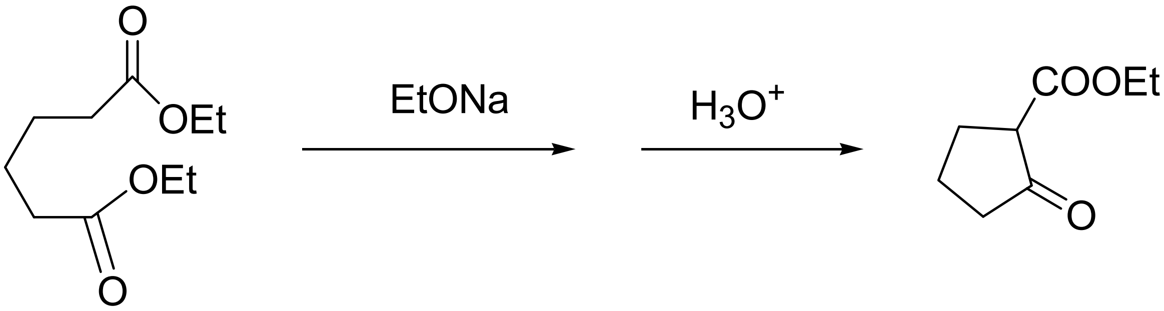


zkřížená Claisenova kondenzace

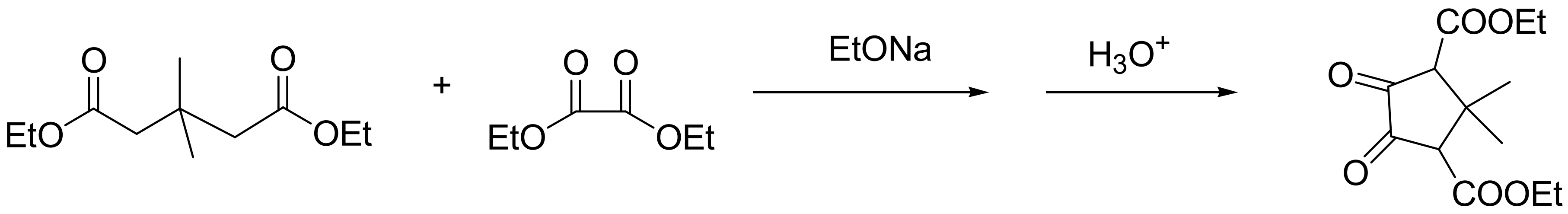
zkřížená Claisenova kondenzace



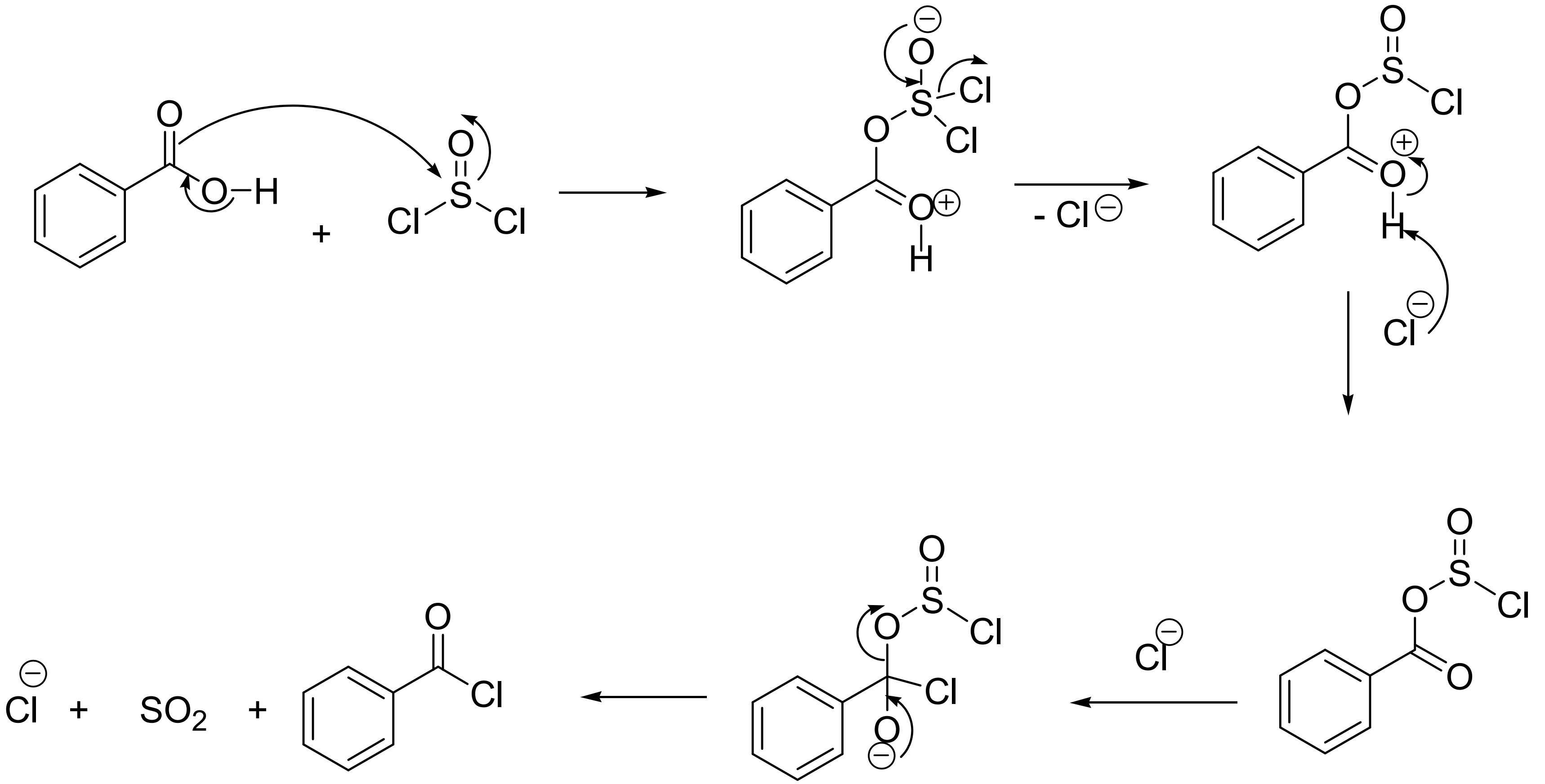
Dieckmannova kondenzace



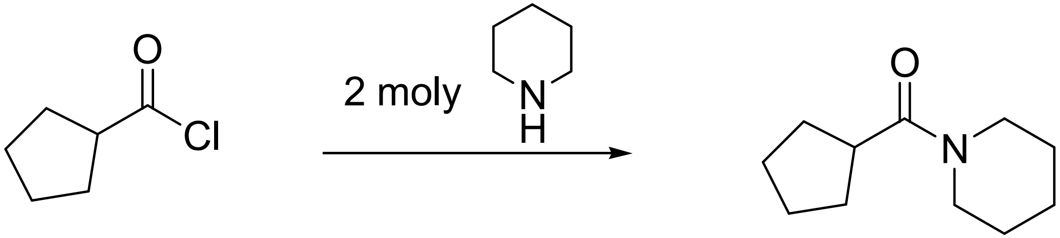
Navrhněte mechanismus reakce

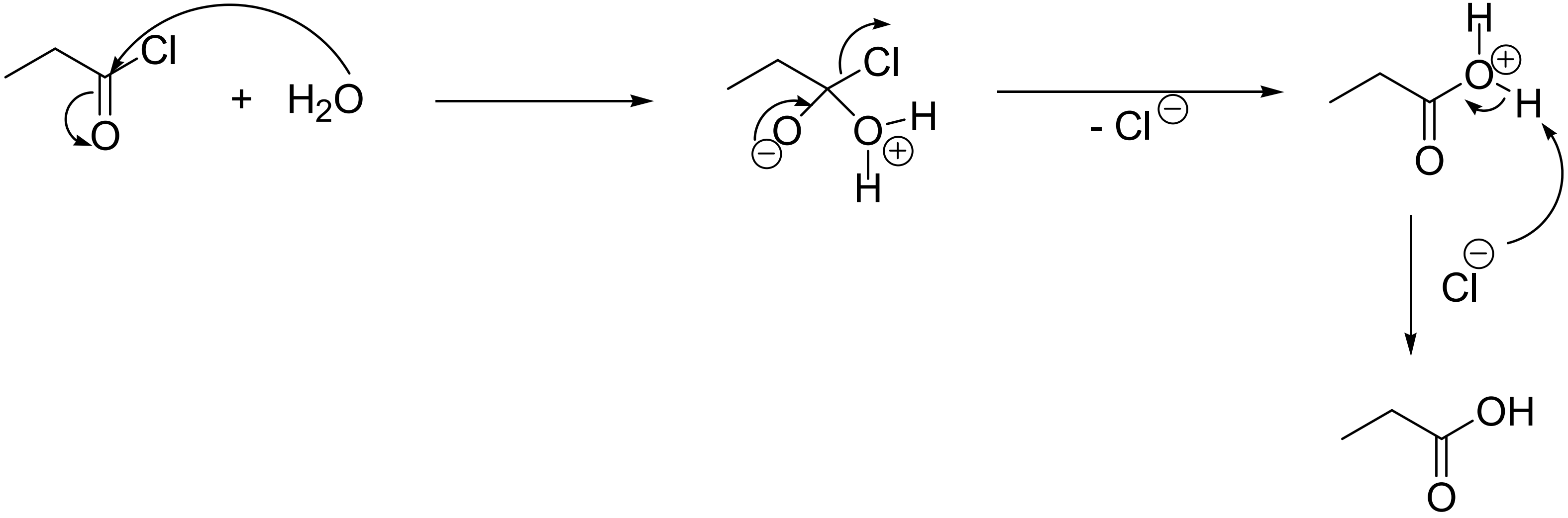


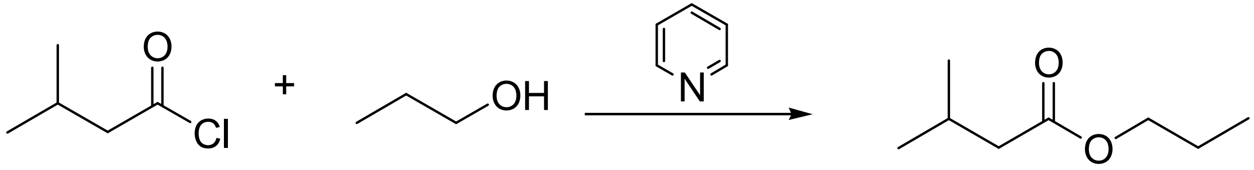
CHLORIDY KARBOXYLOVÝCH KYSELIN - příprava

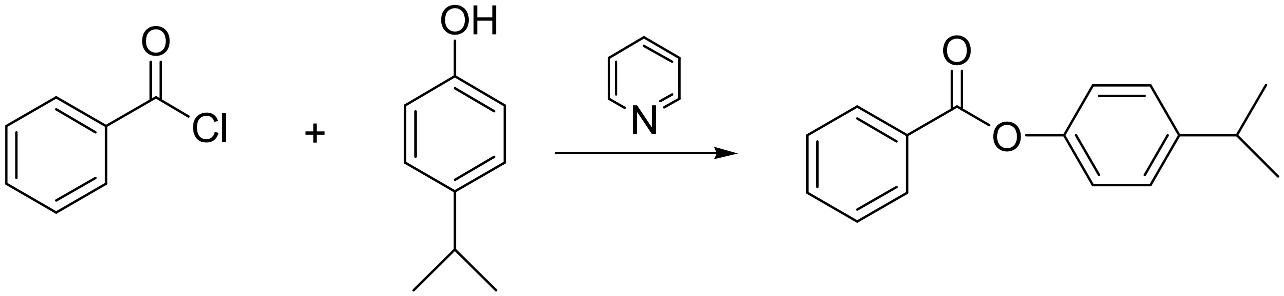


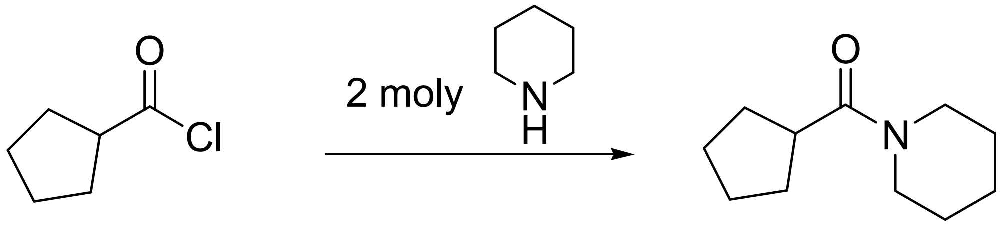
Chloridy kyselin vznik a hydrolýza

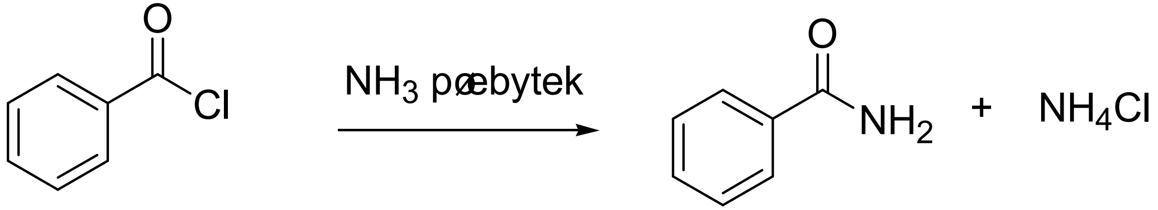


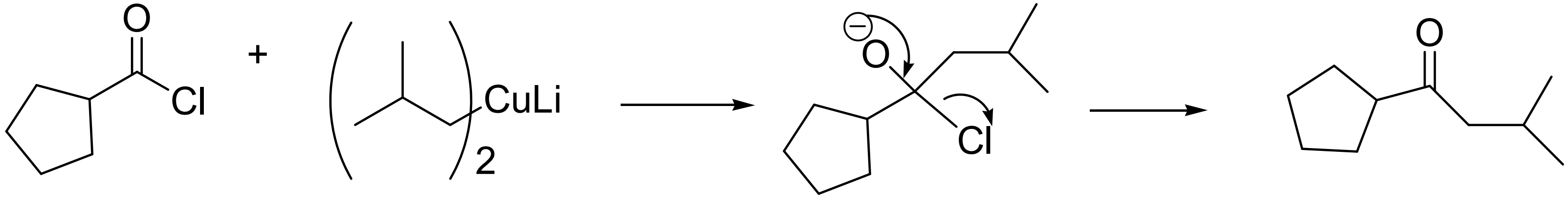



O
Cl
+
OH
N
O
O

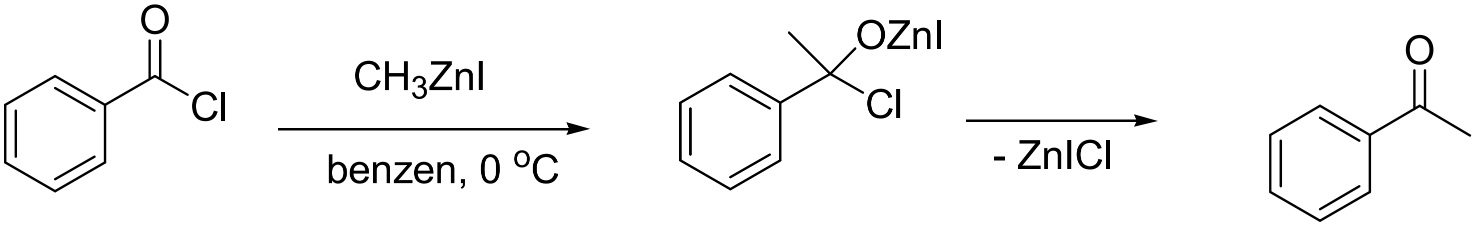

O
Cl
+
OH
N
O
O

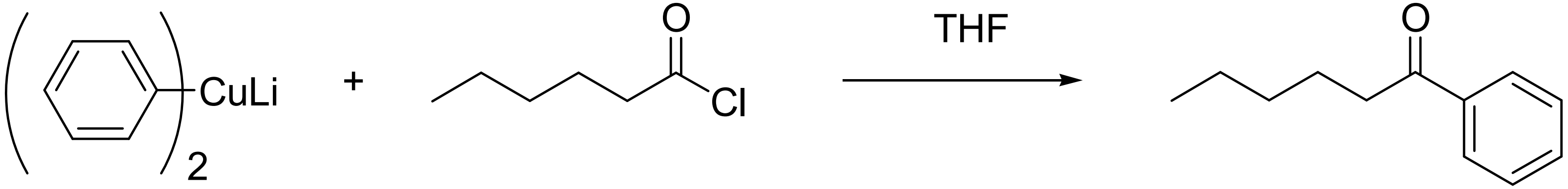

O
Cl
2 moly
N
H
O
N


O
Cl
NH3 pøebytek
O
NH2
+
NH4Cl

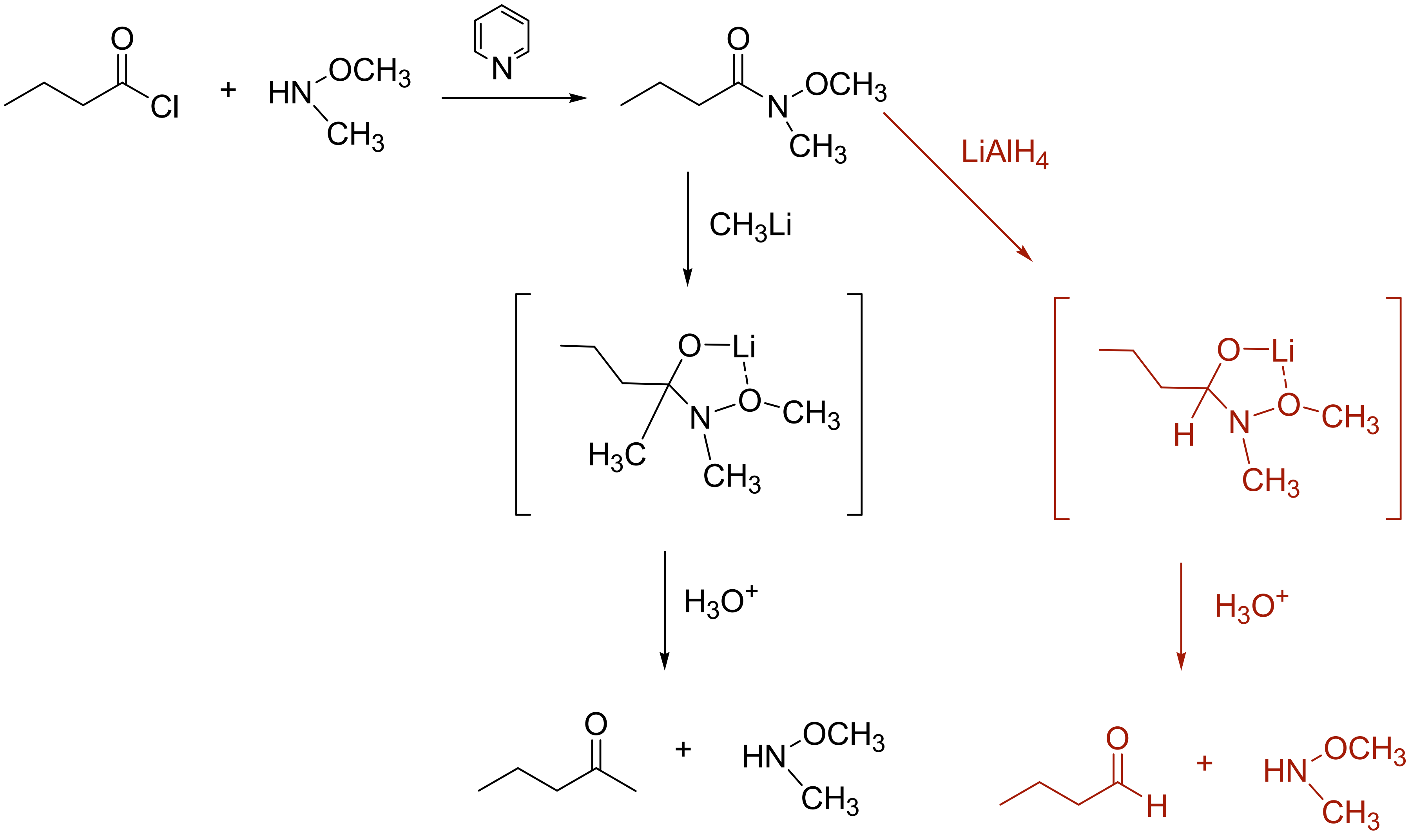


Gilmanovo činidlo

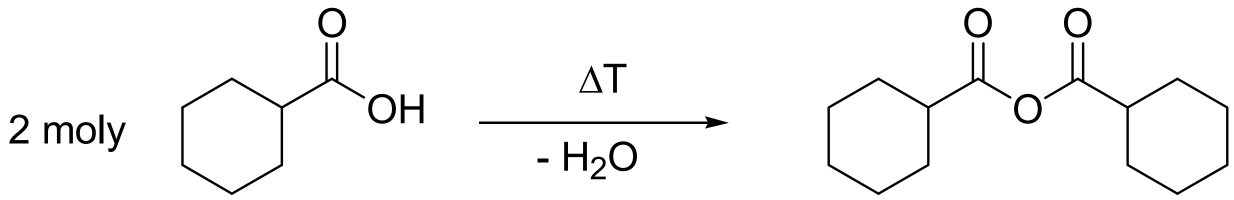


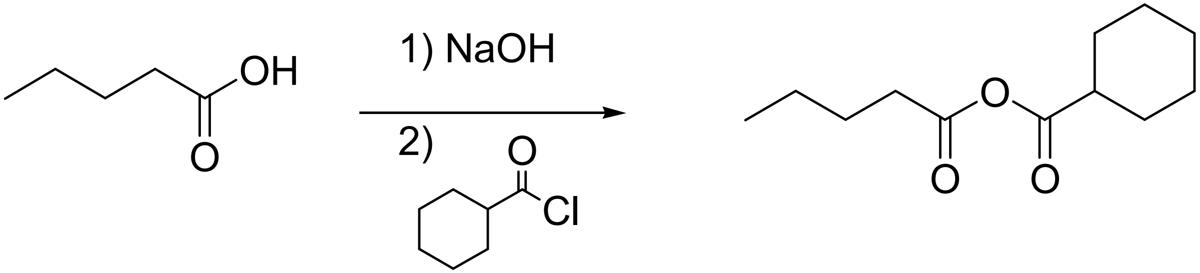


Weinrebův amid



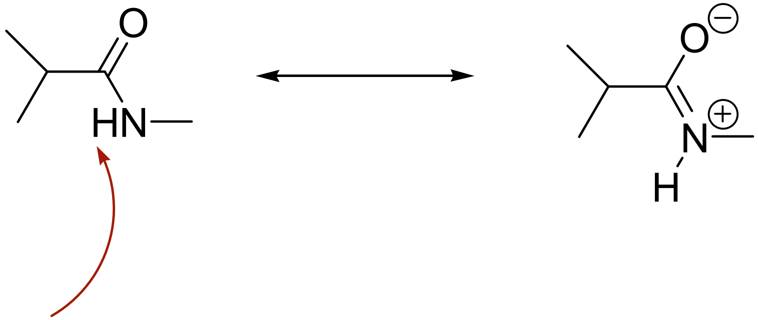
ANHYDRIDY KARBOXYLOVÝCH KYSELIN



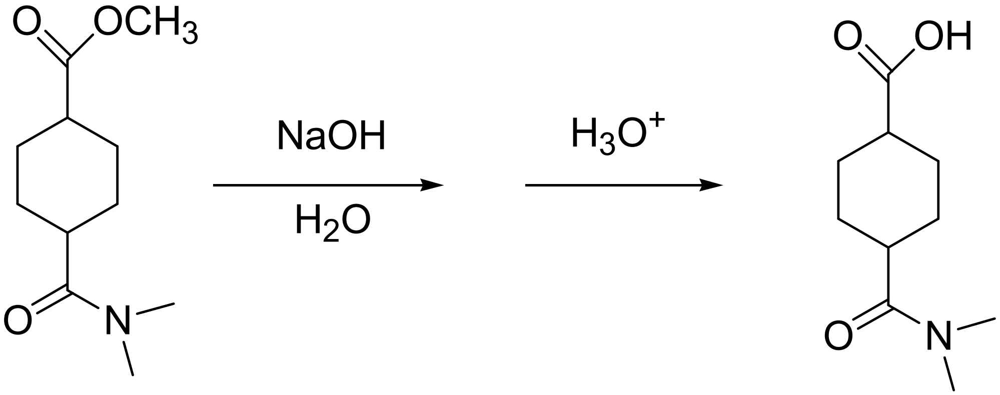


Reaktivita jako u chloridů karboxylových kyselin

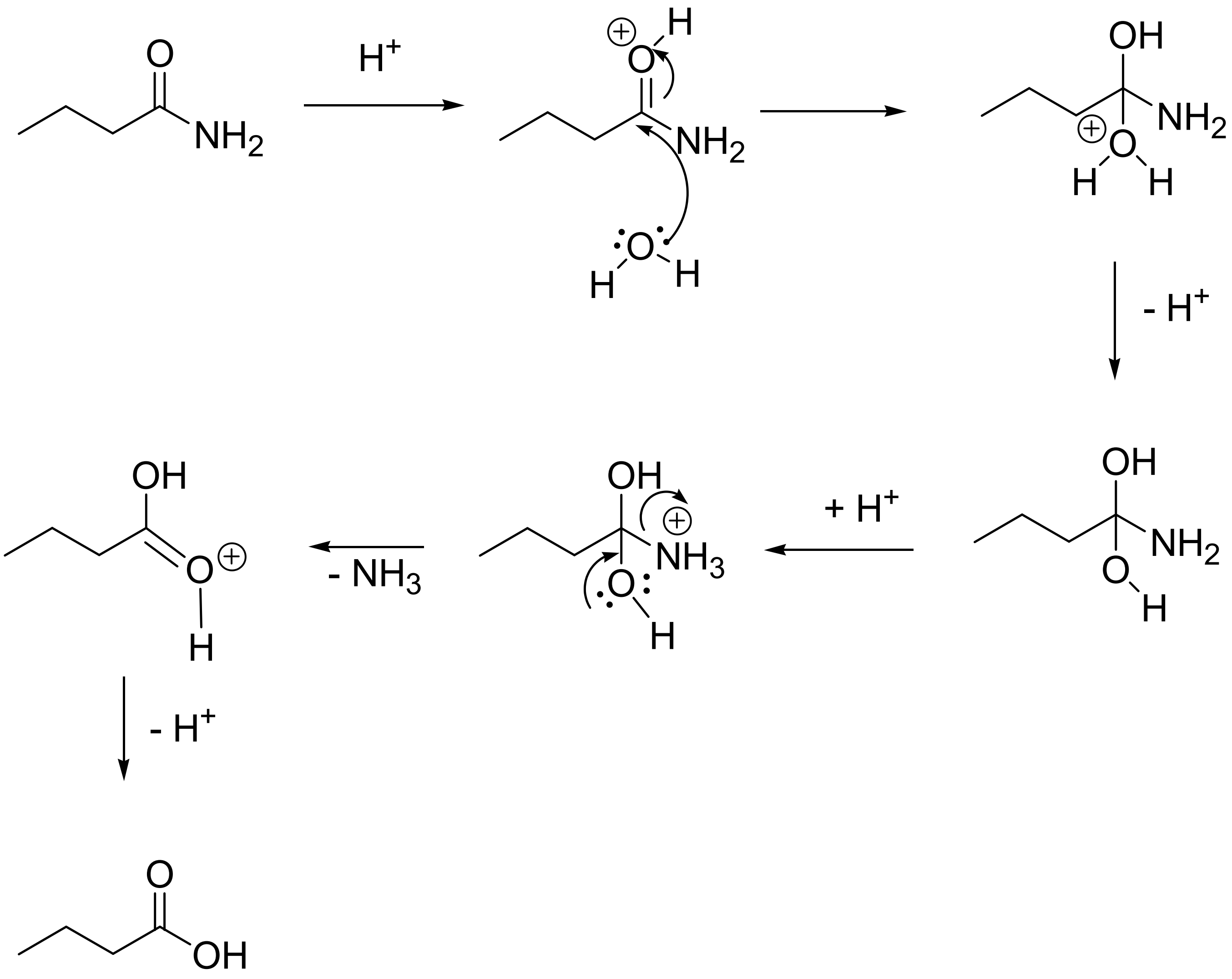
AMIDY KARBOXYLOVÝCH KYSELIN



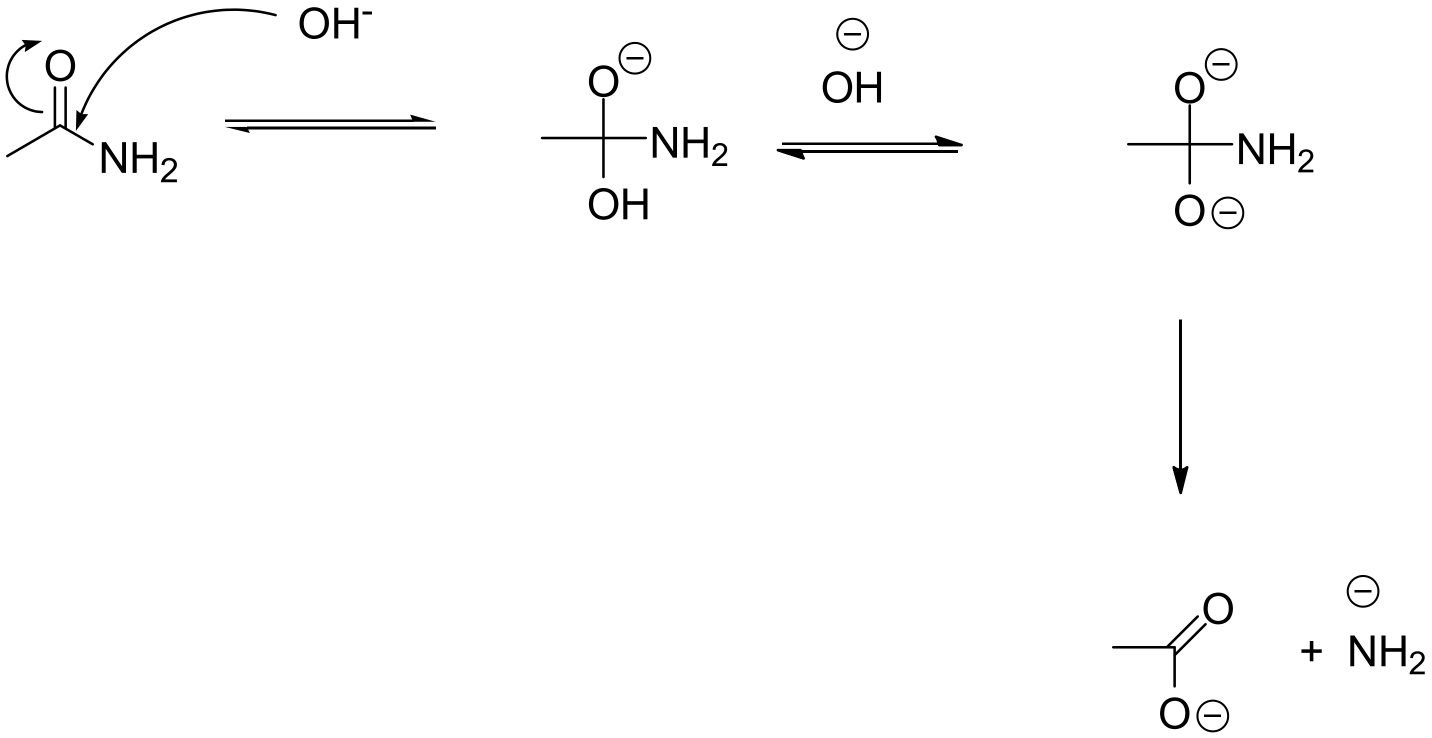
kyselé vodíky
pK_a pøibližnì 13



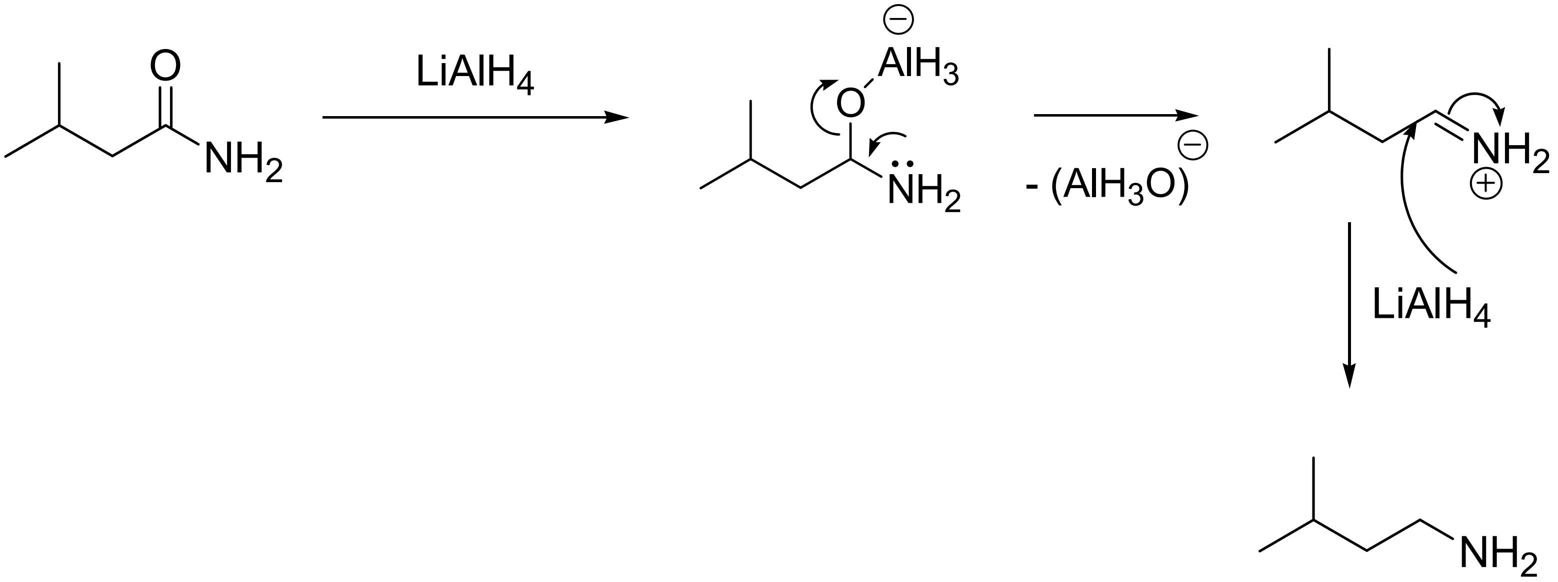
Kyselá hydrolýza amidů



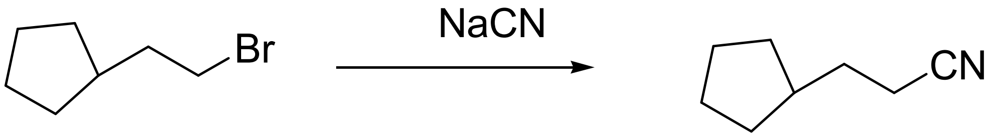
Bazická hydrolýza amidů

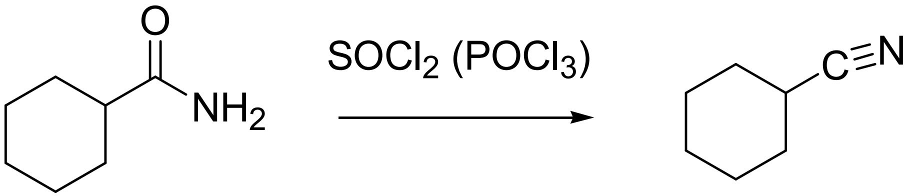


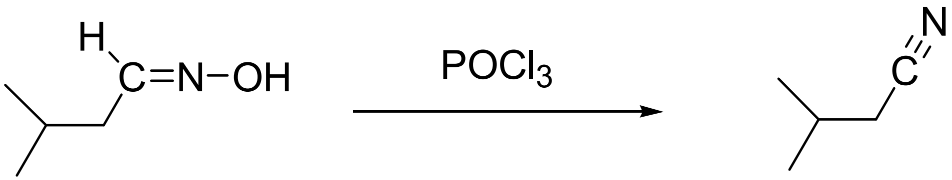
Redukce amidů



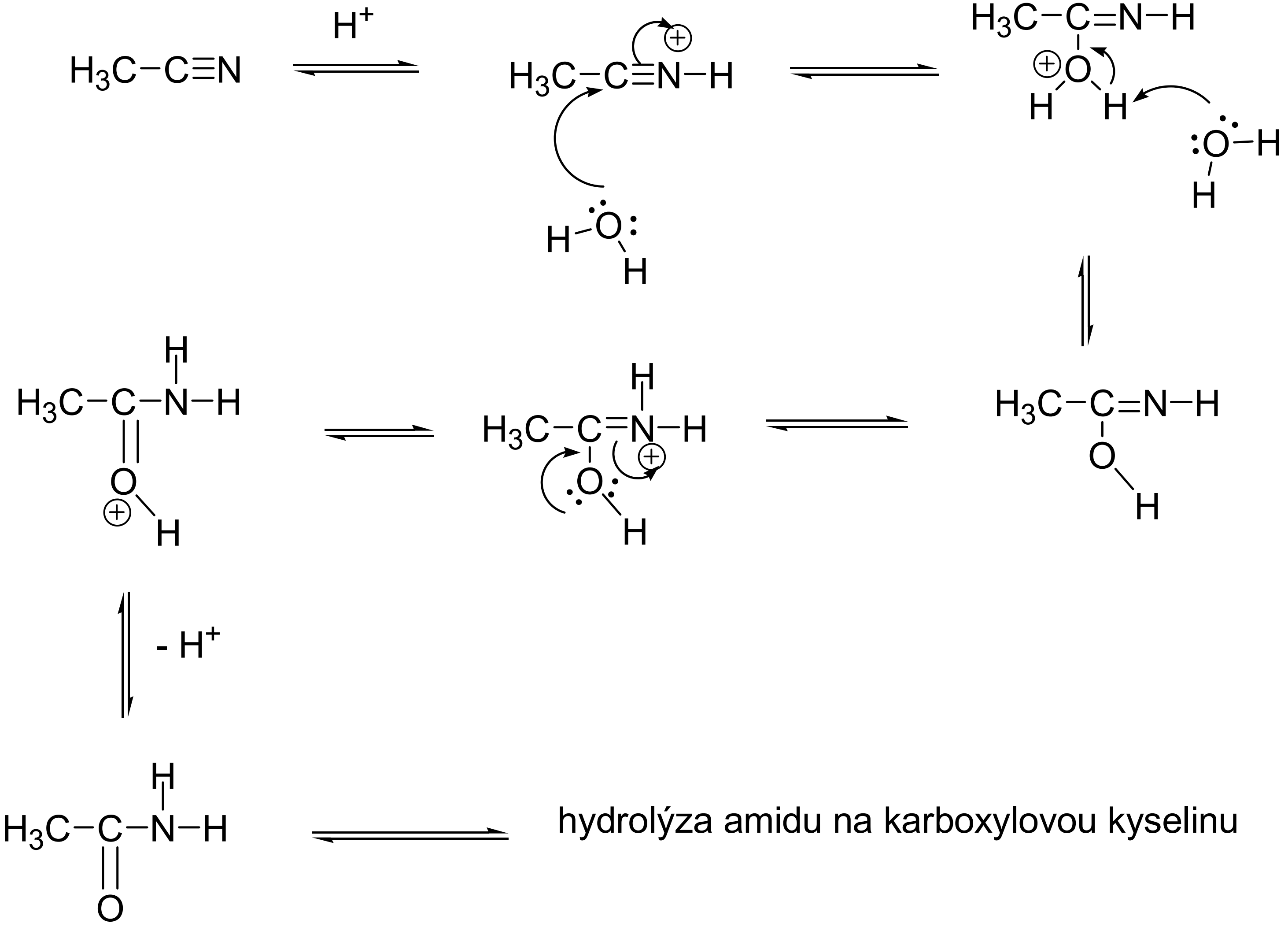
NITRILY KARBOXYLOVÝCH KYSELIN





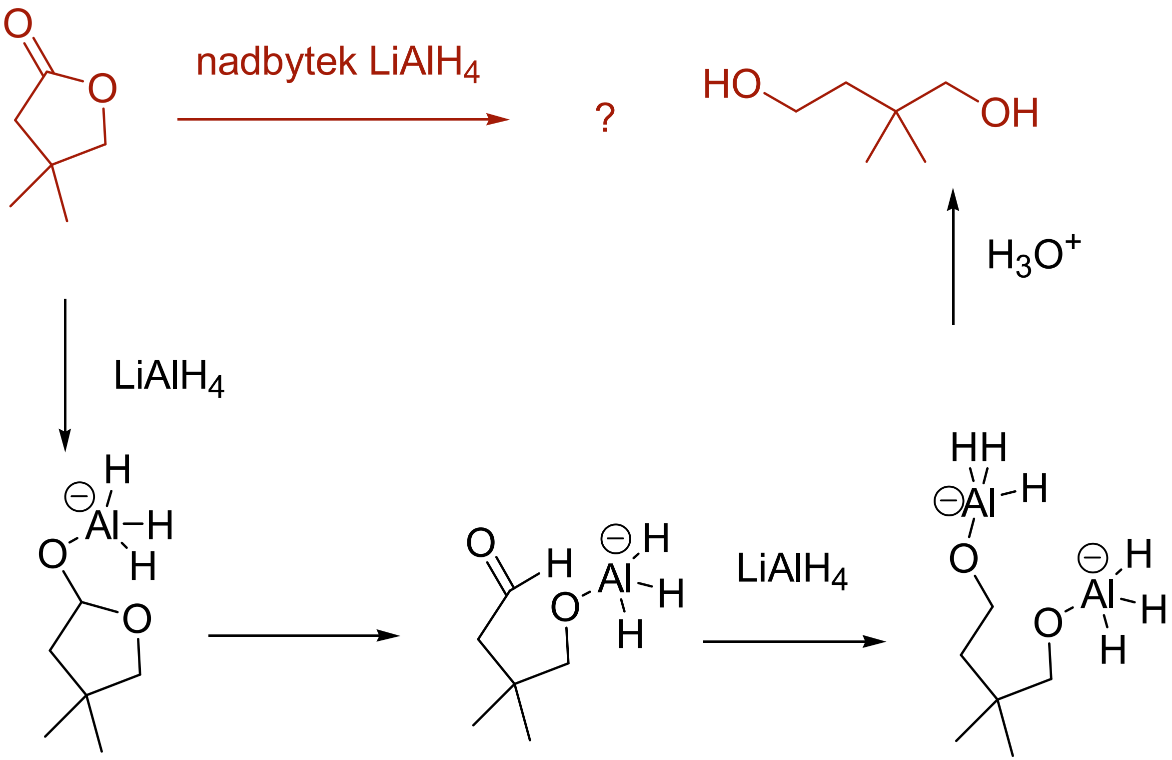


Hydrolýza nitrilů



hydrolýza amidu na karboxylovou kyselinu

LAKTONY A LAKTAMY



Doplňte produkty reakcí