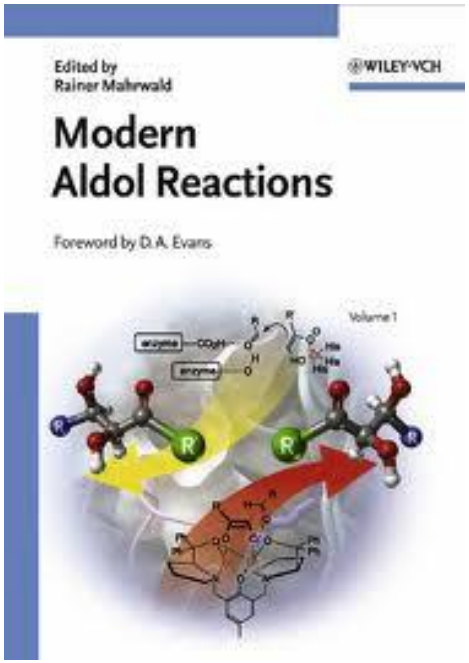
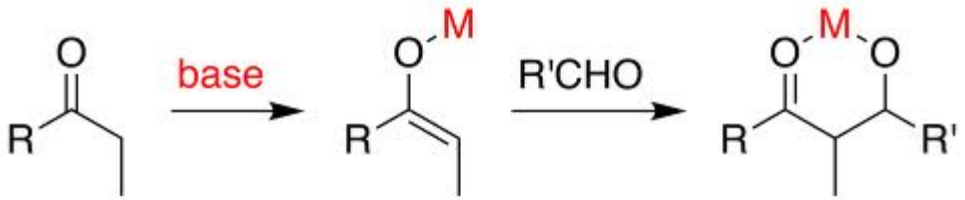
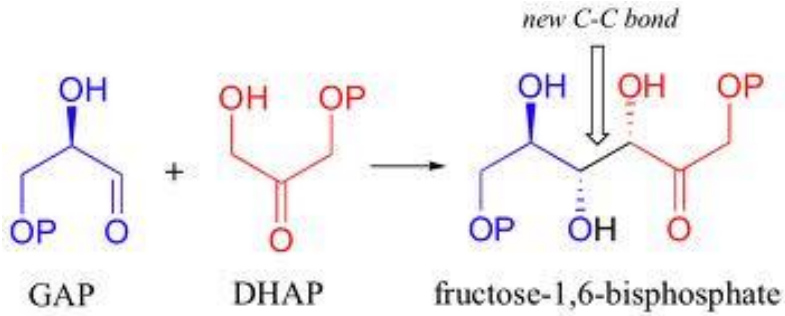
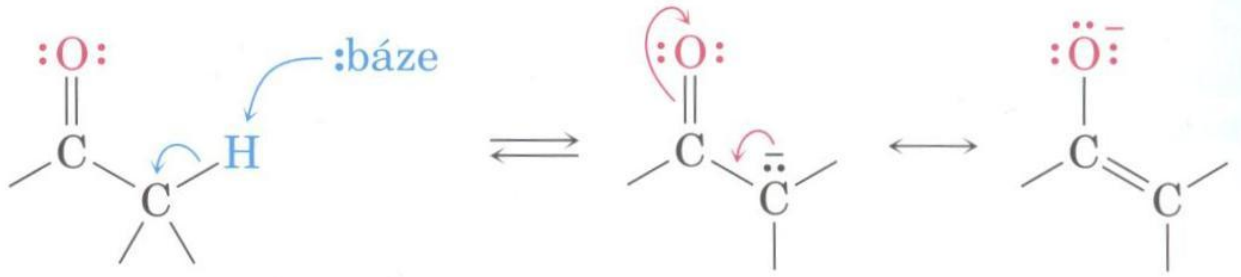
Aldolizace a Michaelovy adice

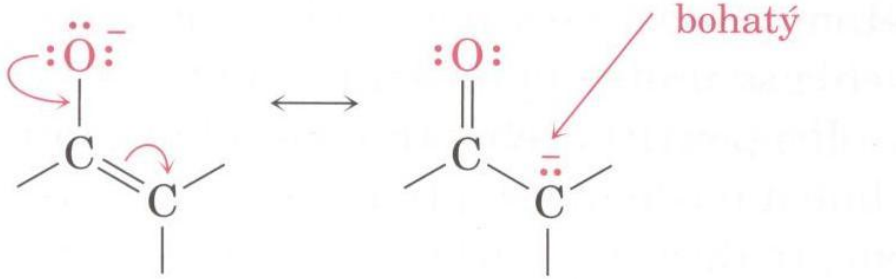




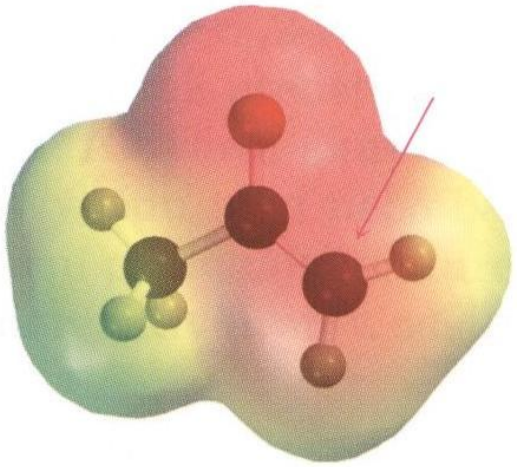




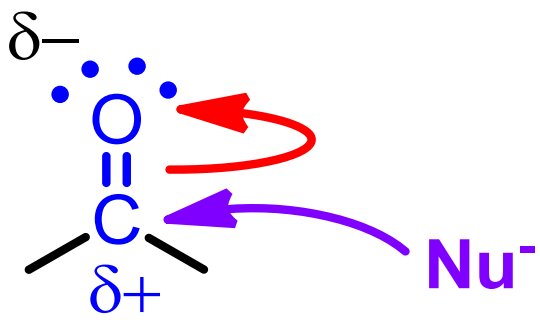
karbonylová sloučenina **enolátový ion**



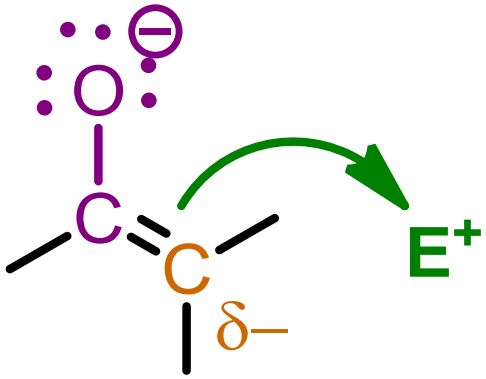
enolátový ion



Reaktivita karbonylové skupiny a enolátového aniontu

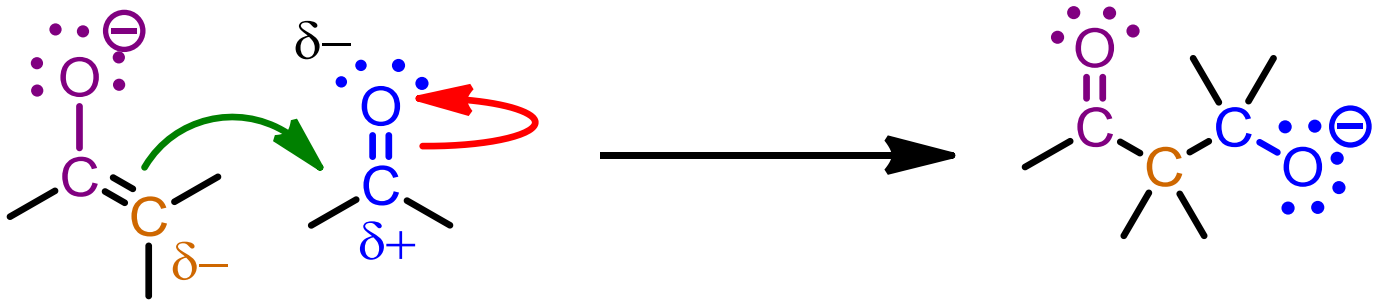


Elektrofilní uhlík karbonylové skupiny je atakován nukleofily

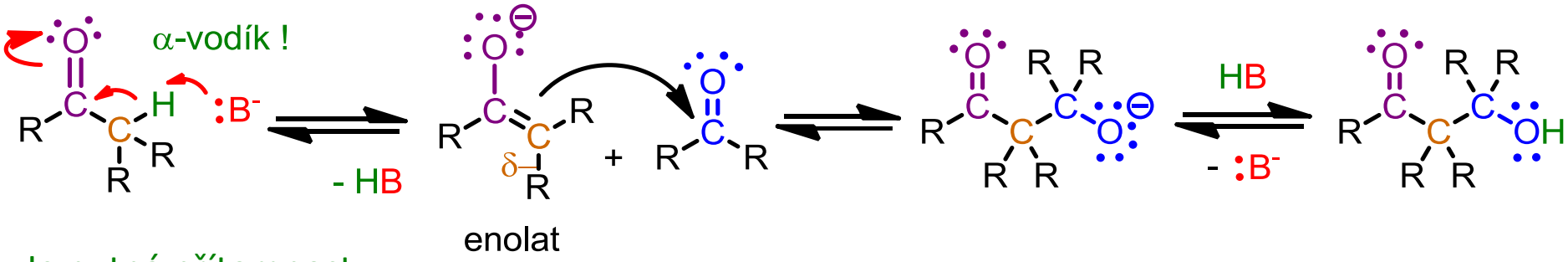


Nukleofilní enolátový ion atakuje elektrofily

Aldolizace



Mechanismus aldolizace

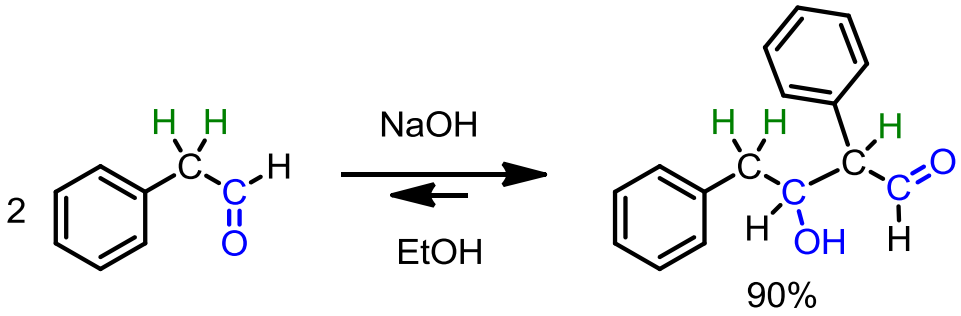


Je nutná přítomnost α-vodíku u jednoho reaktantu

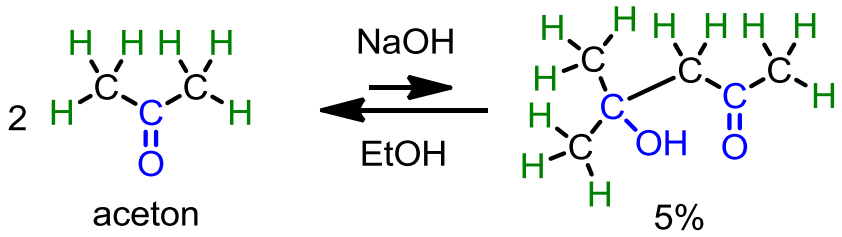
Báze stačí v katalytickém množství

Aldolizace je vratná reakce a rovnováha závisí na typu karbonylové sloučeniny, bázi, rozpouštědle a teplotě

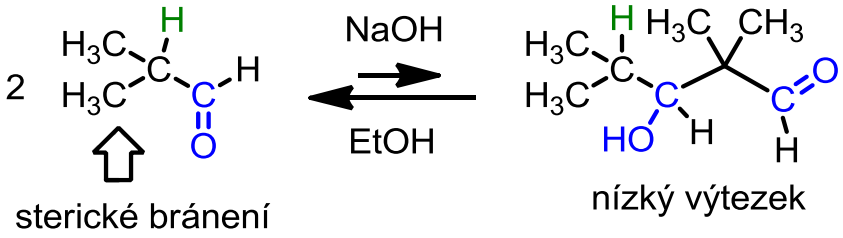
Aldehydy reagují ochotně a rovnováha posunuta k produktům

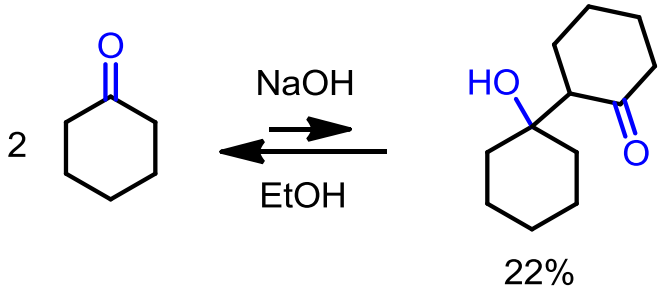


U ketonů obvykle rovnováha ve prospěch reaktantů

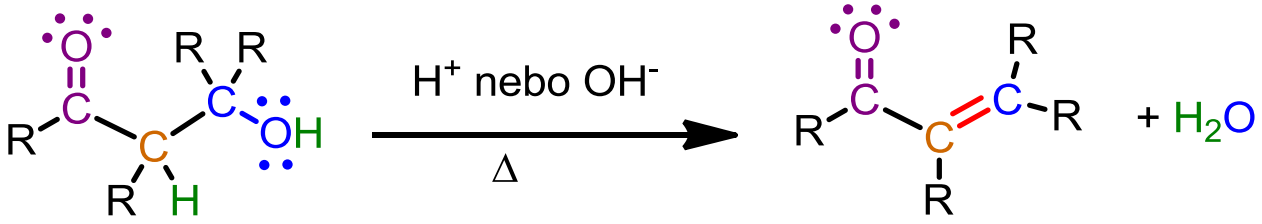


Pokud nejsou stericky bráněné substitucí v α- poloze



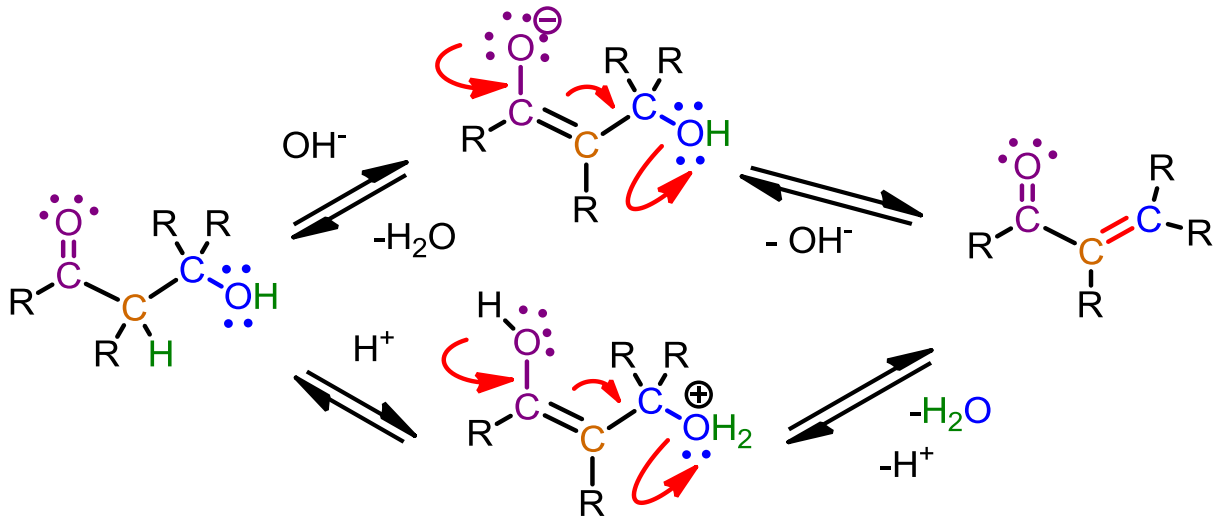


Dehydratace β-hydroxyaldehydů/ketonů – aldolová kondenzace

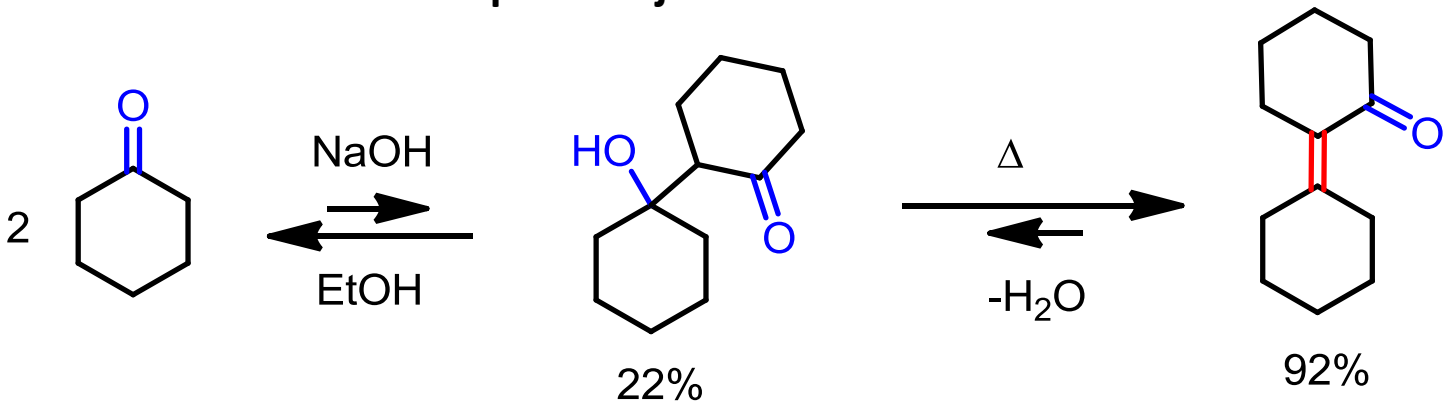


β-hydroxyaldehyd
nebo β-hydroxyketon

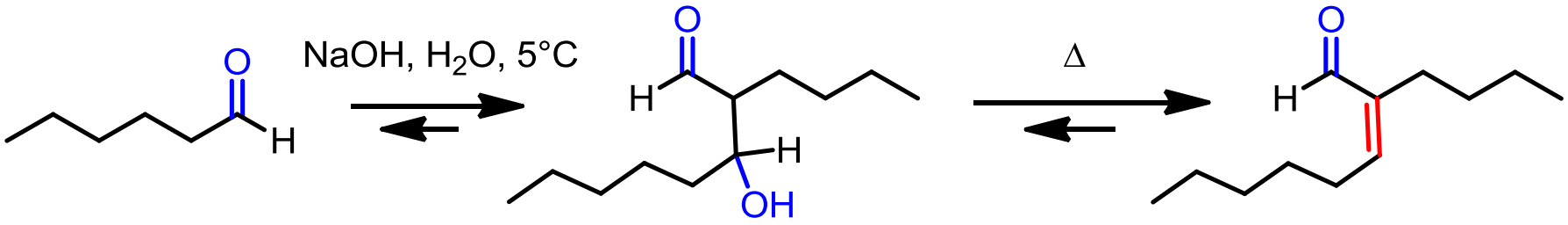
konjugovaný enon



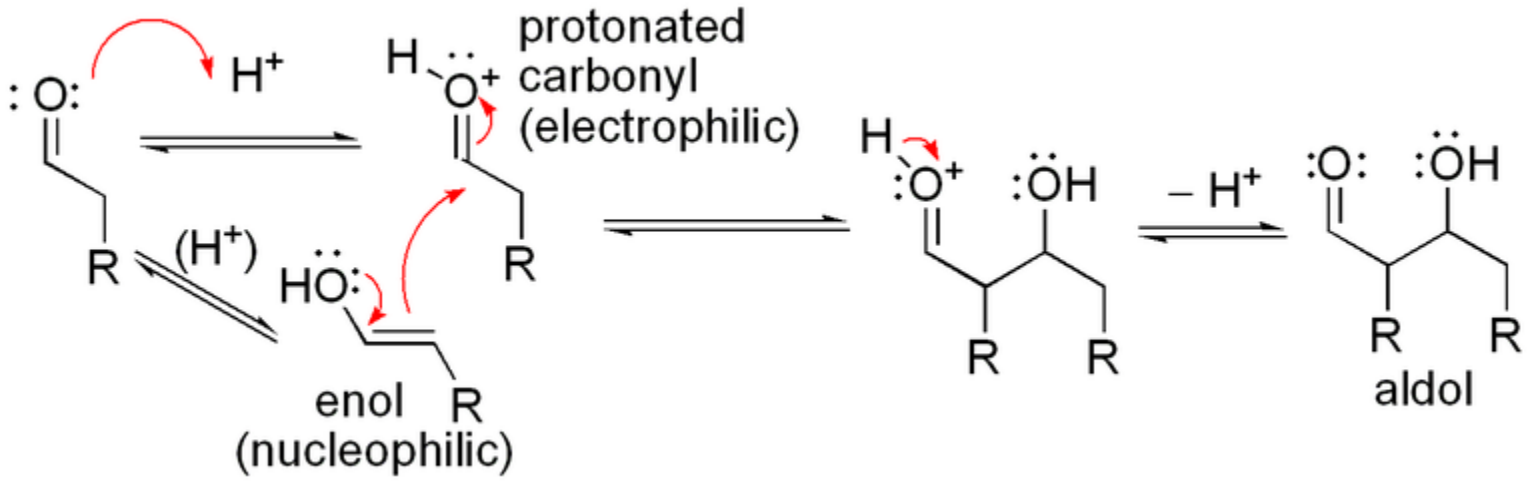
Dehydratace (a odstraňování vody z reakční směsi) posouvá rovnováhu i u reakcí, kde samotná aldolizace probíhá jen málo



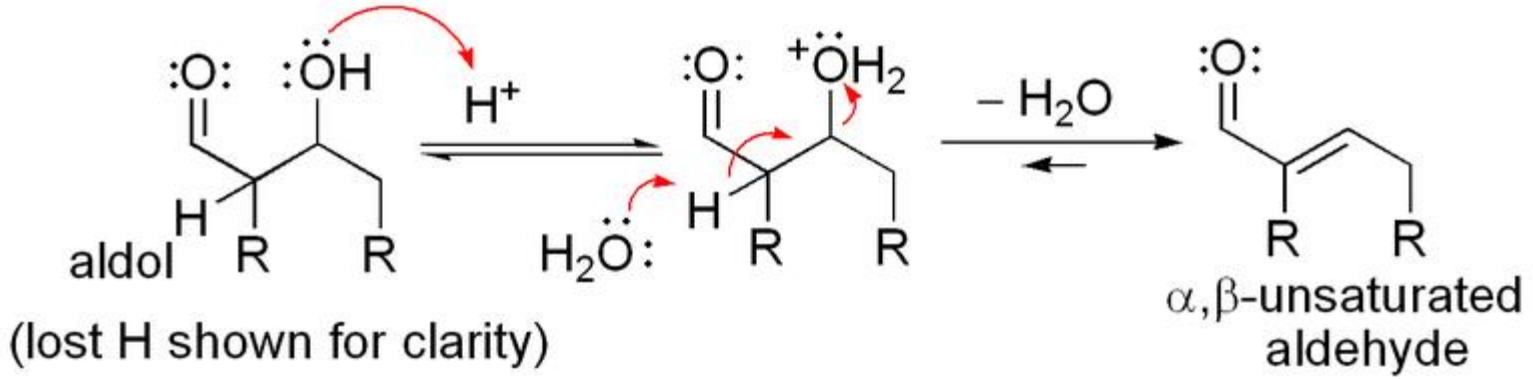
U reakcí aldehydů lze zastavit reakci ve stadiu aldolu pouze za nízké teploty – při zahřívání dochází k dehydrataci (aldolová kondenzace)



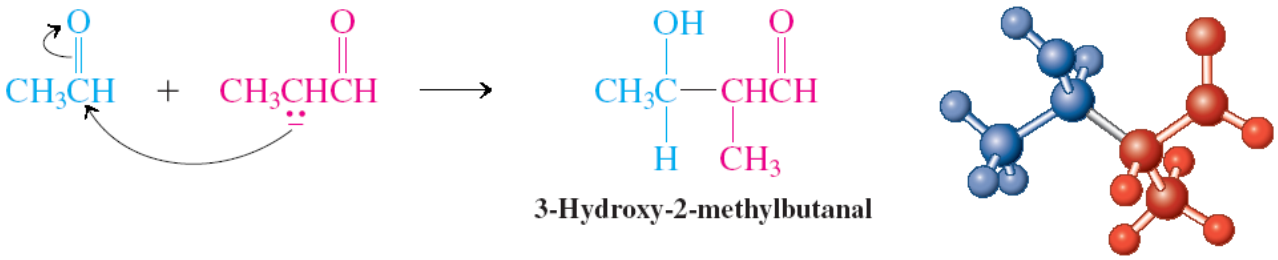
Kysele katalyzovaná aldolizace



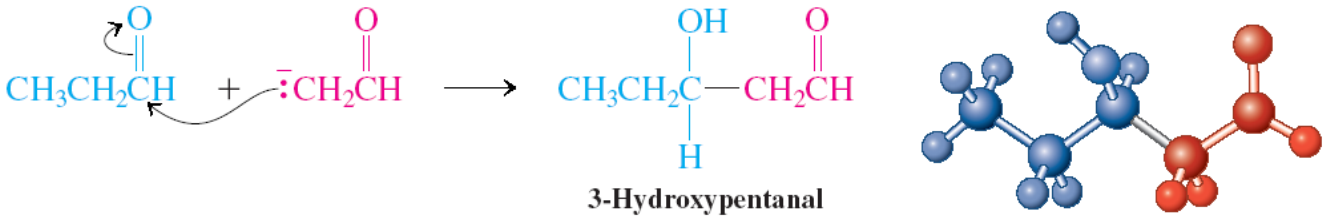
Kysele katalyzovaná dehydratace



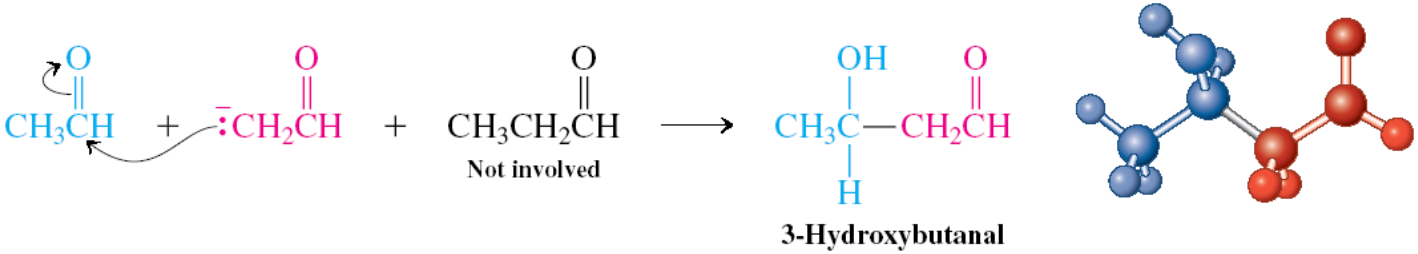
Neselektivní smíšená aldolizace acetaldehydu a propanalu (všechny tyto reakce probíhají paralelně a výsledkem je směs produktů)



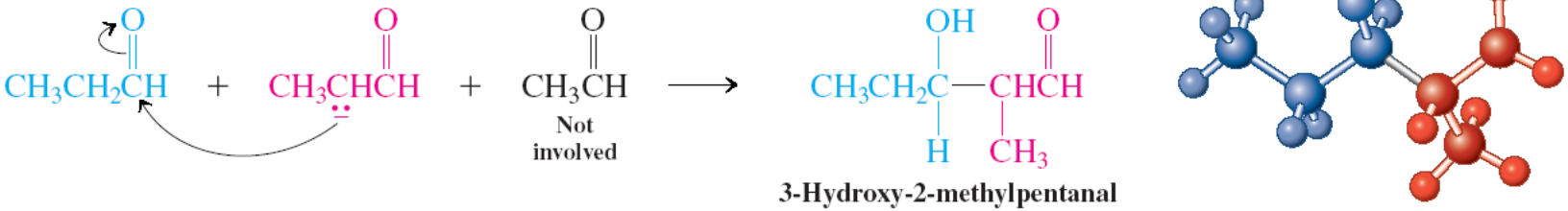
3-Hydroxy-2-methylbutanal



3-Hydroxypentanal



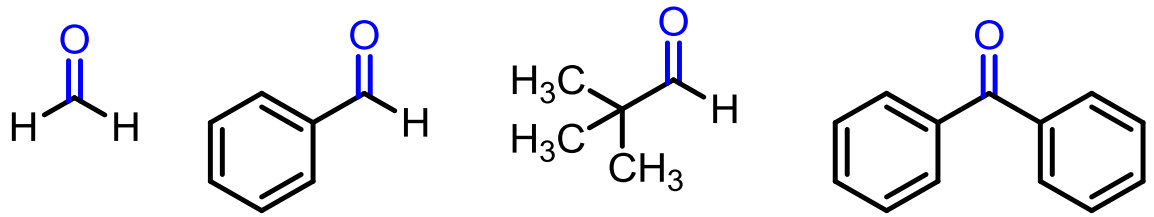
3-Hydroxybutanal

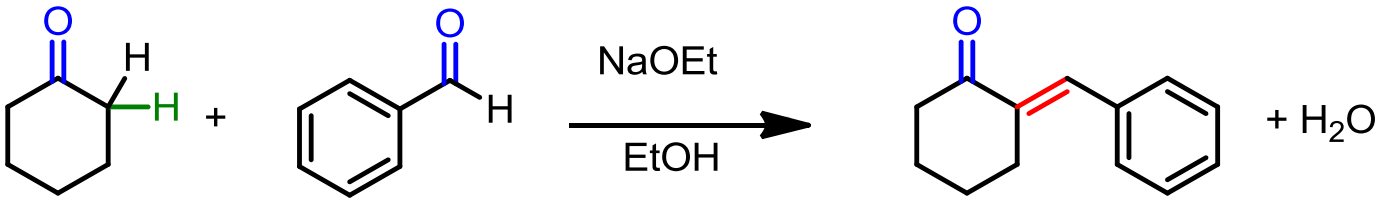


3-Hydroxy-2-methylpentanal

Selektivní smíšená aldolizace (aldolová kondenzace)

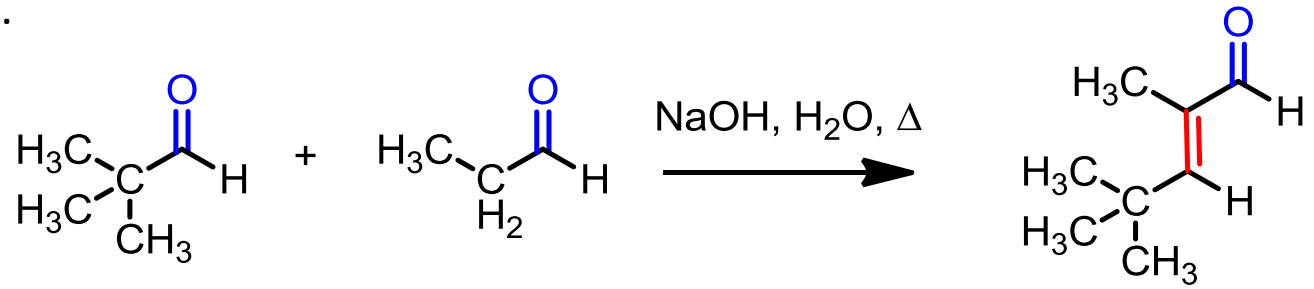
- jeden z reaktantů nemá β-vodíky (není enolizovatelný)





enolizovatelný neenolizovatelný

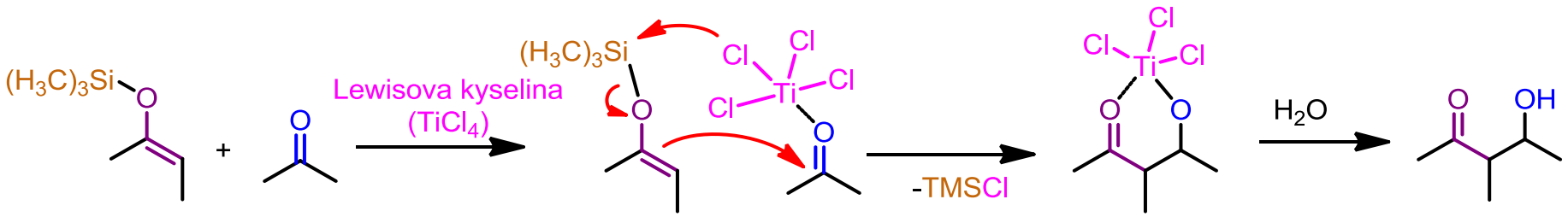
V případě aldehydů je nutno enolizovatelný aldehyd přidávat pomalu, aby se zamezilo samoaldolizaci (vzniká jen malé množství enolátu, který ihned zreaguje s přebytkem druhého reaktantu).

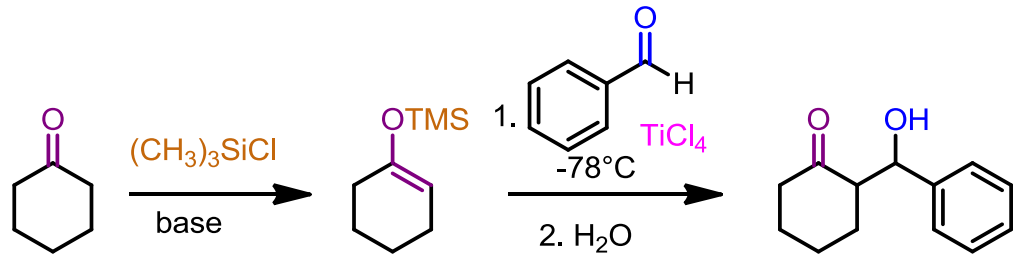


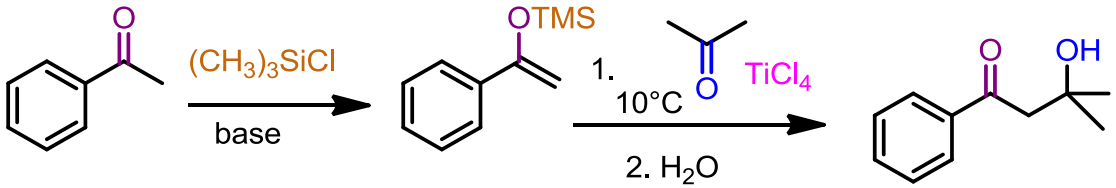
neenolizovatelný enolizovatelný

Selektivní smíšená aldolizace (aldolová kondenzace)

- reakce ketonu/aldehydu se silylenoletherem (Mukayamova reakce)

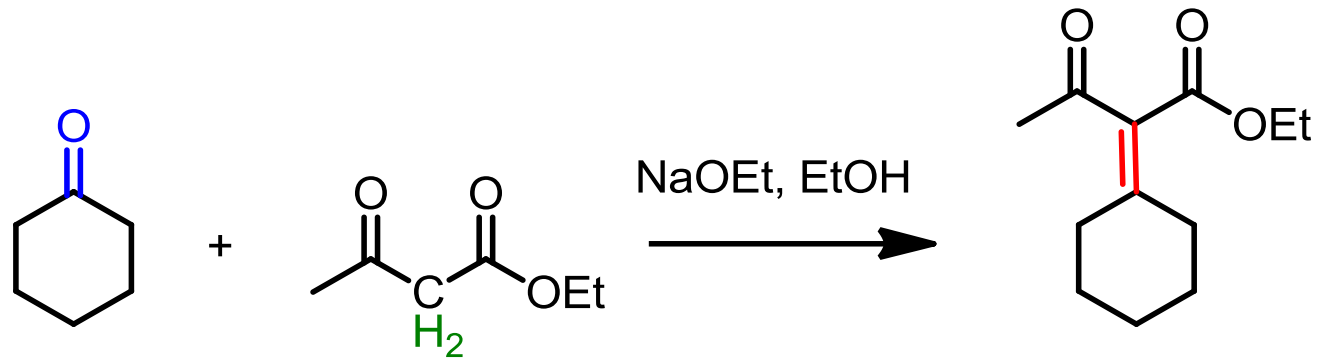




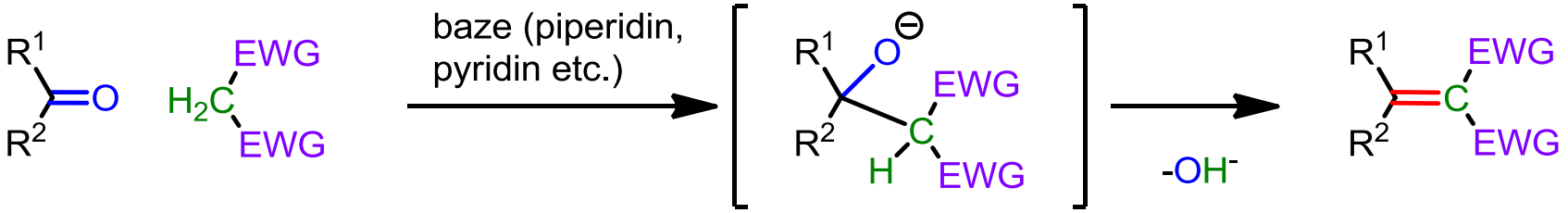


Selektivní smíšená aldolizace (aldolová kondenzace)

- jeden z enolizovatelných reaktantů je výrazně kyselejší než druhý

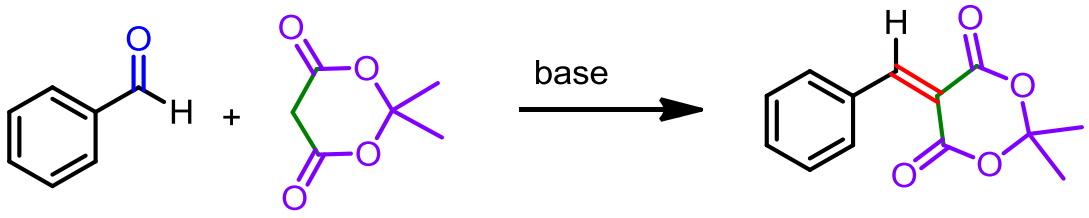


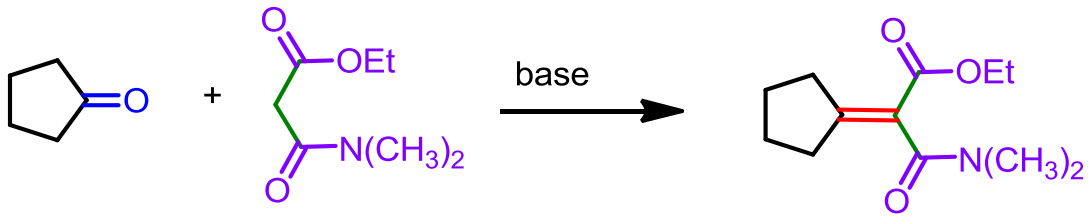
Knoevenagelova kondenzace

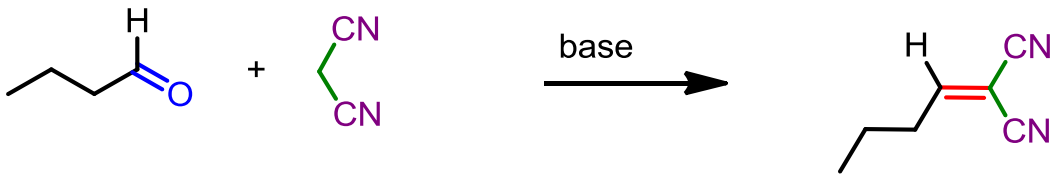


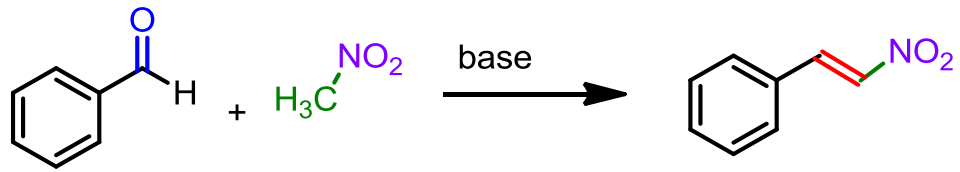
EWG = elektronakceptorní
skupina: COOR, COR, CN, NO_2

Knoevenagelova kondenzace

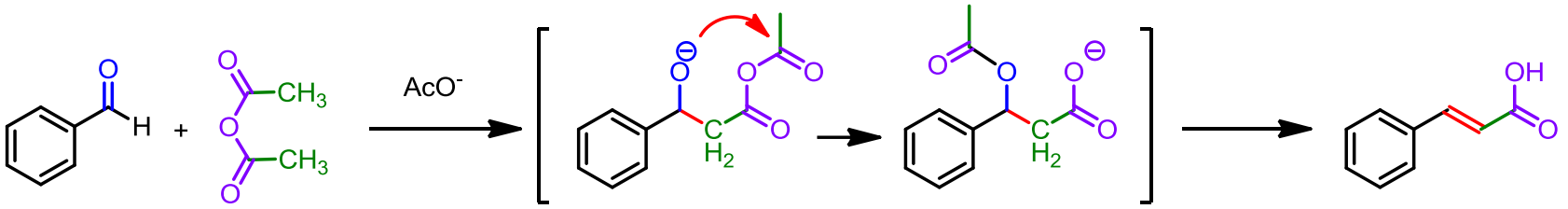






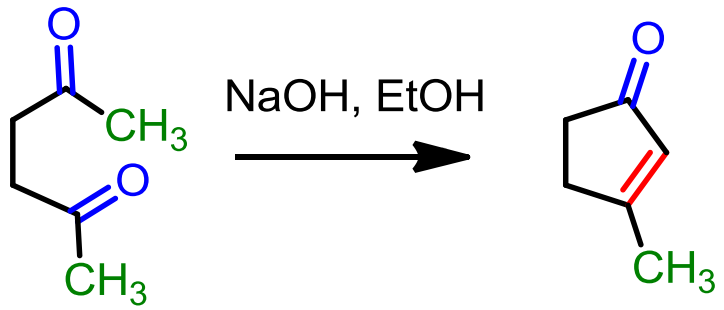


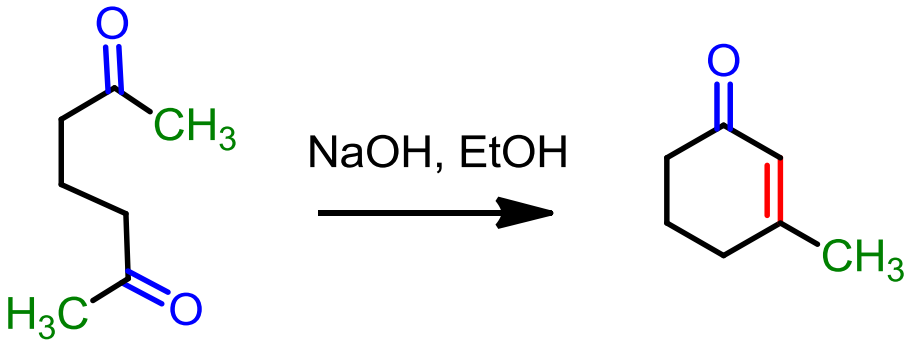
Perkinova reakce

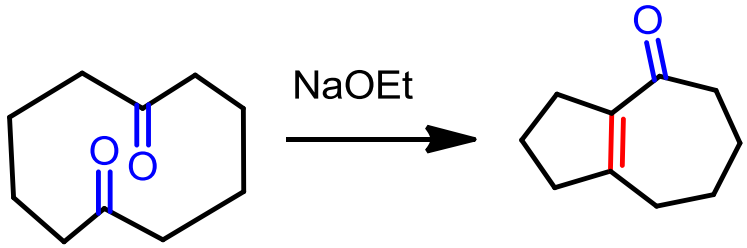


skořicová kyselina

Intramolekulární aldolová kondenzace

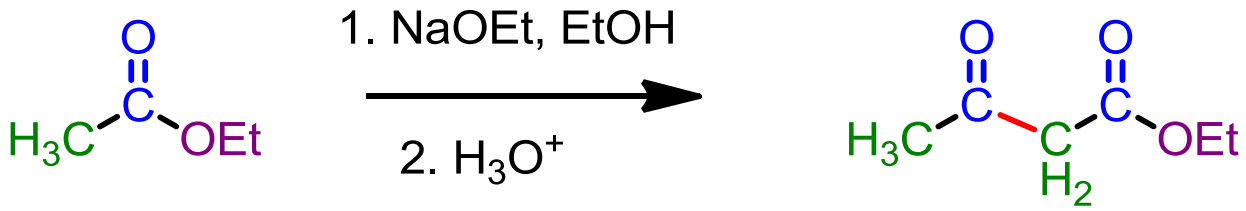


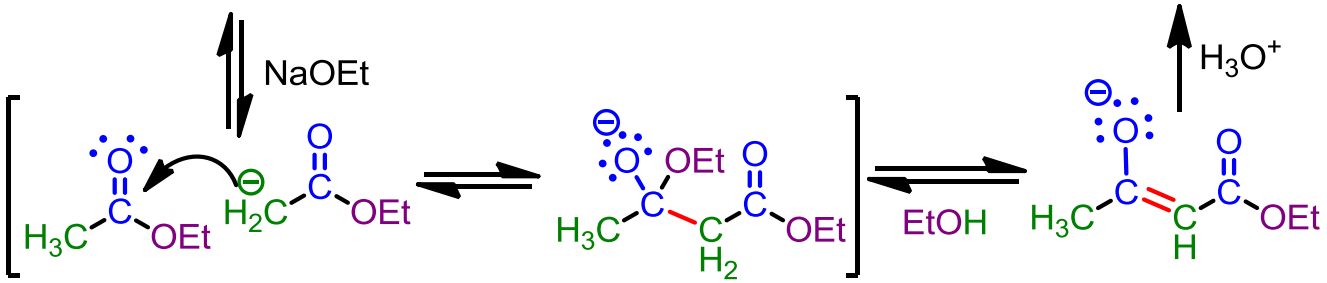


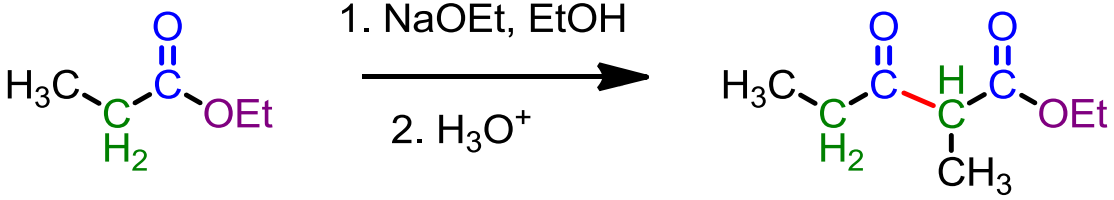


cyklohexan-1,6-dion

Claisenova kondenzace

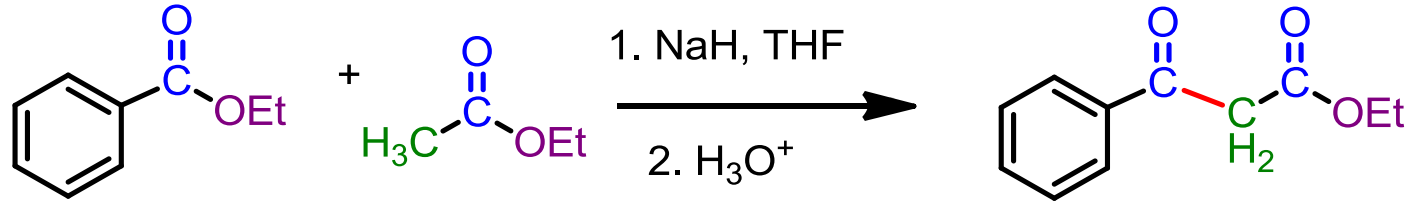


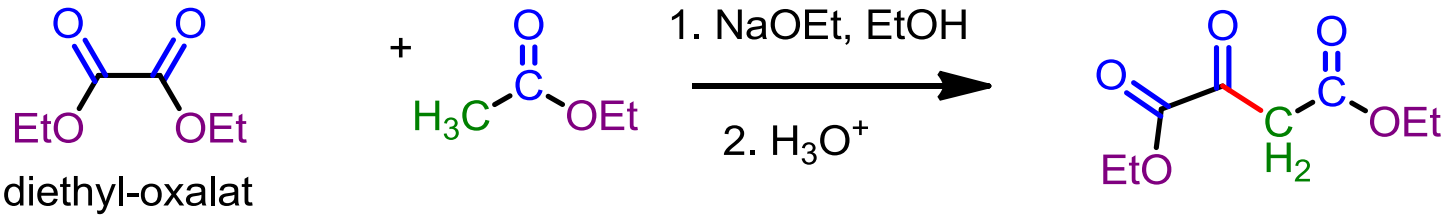




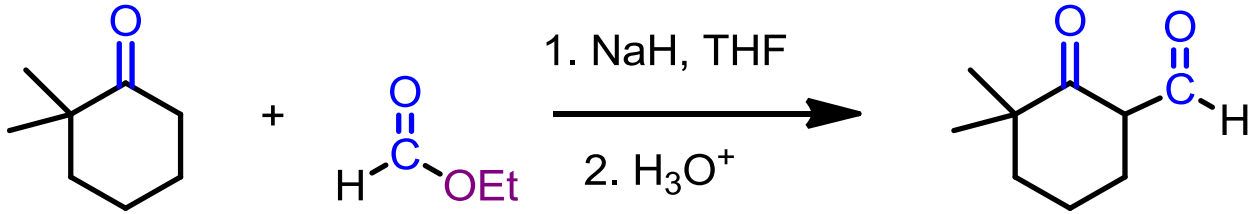
Smíšená Claisenova kondenzace

Selektivně probíhá Claisenova kondenzace, kdy jeden ester nemá α-vodíky

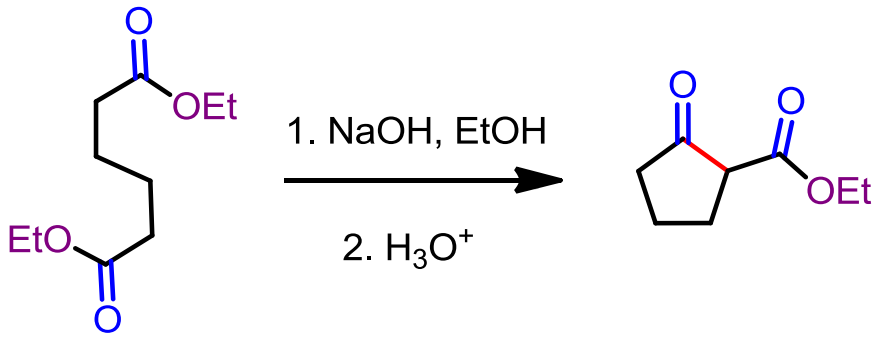


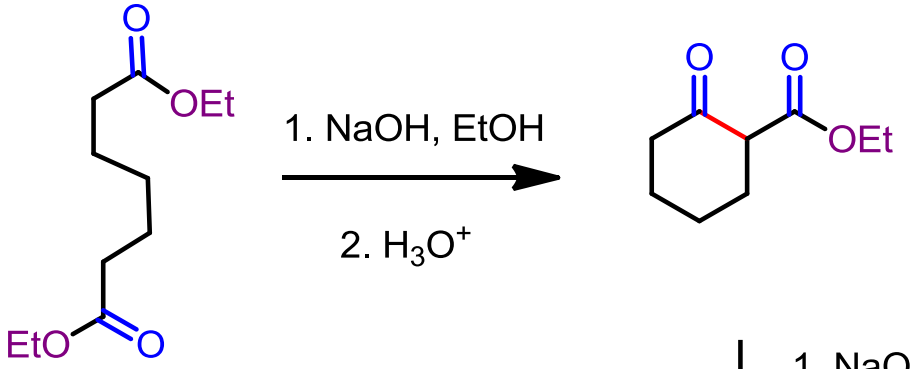


Podobně reagují i ketony s estery

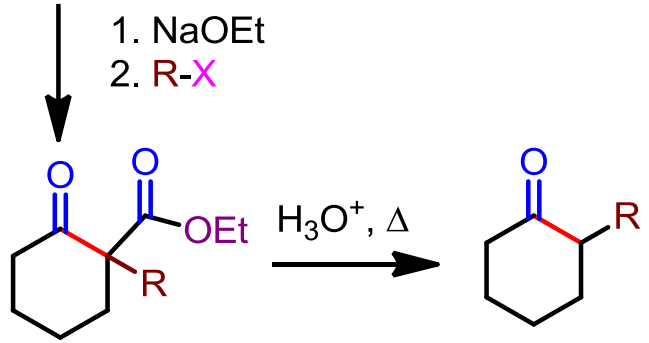


Intramolekulární Claisenova kondenzace – Dieckmannova reakce

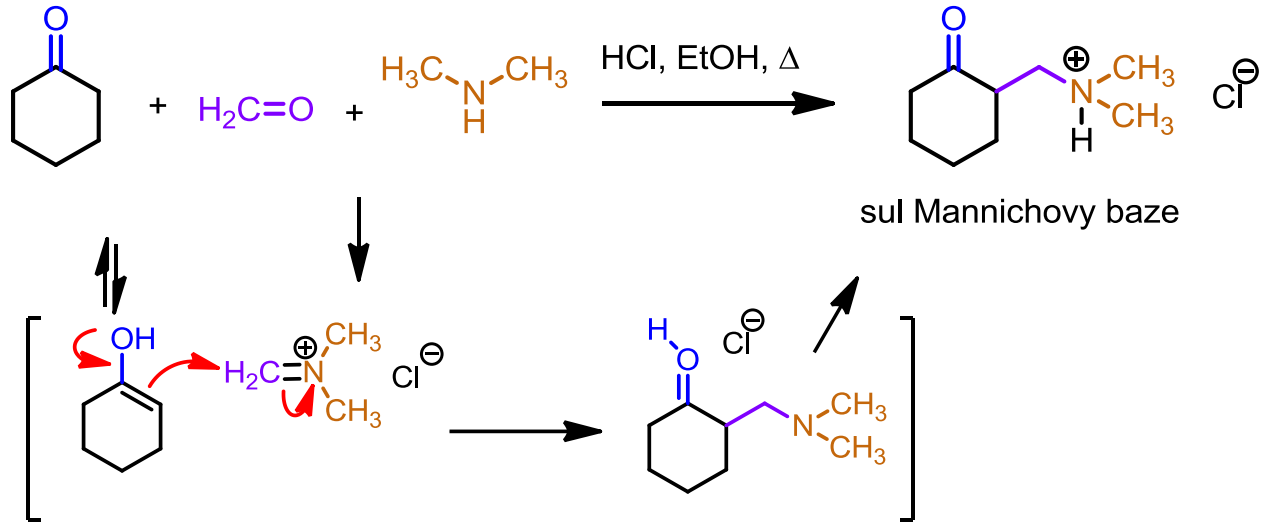


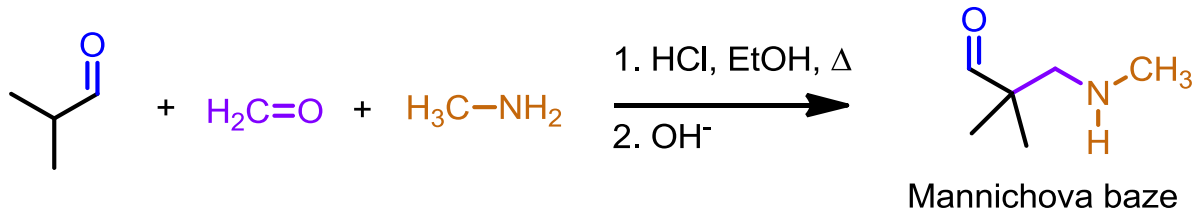


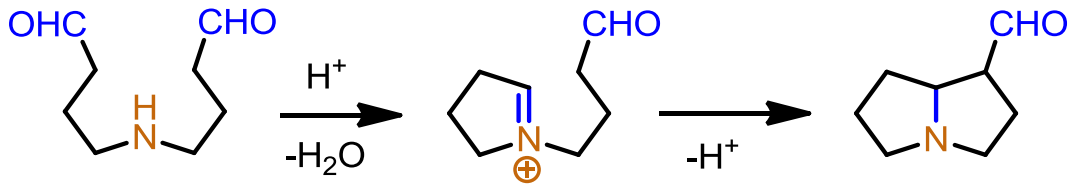
β-ketoestery jsou užitečné intermediáty pro alkylace a dekarboxylace



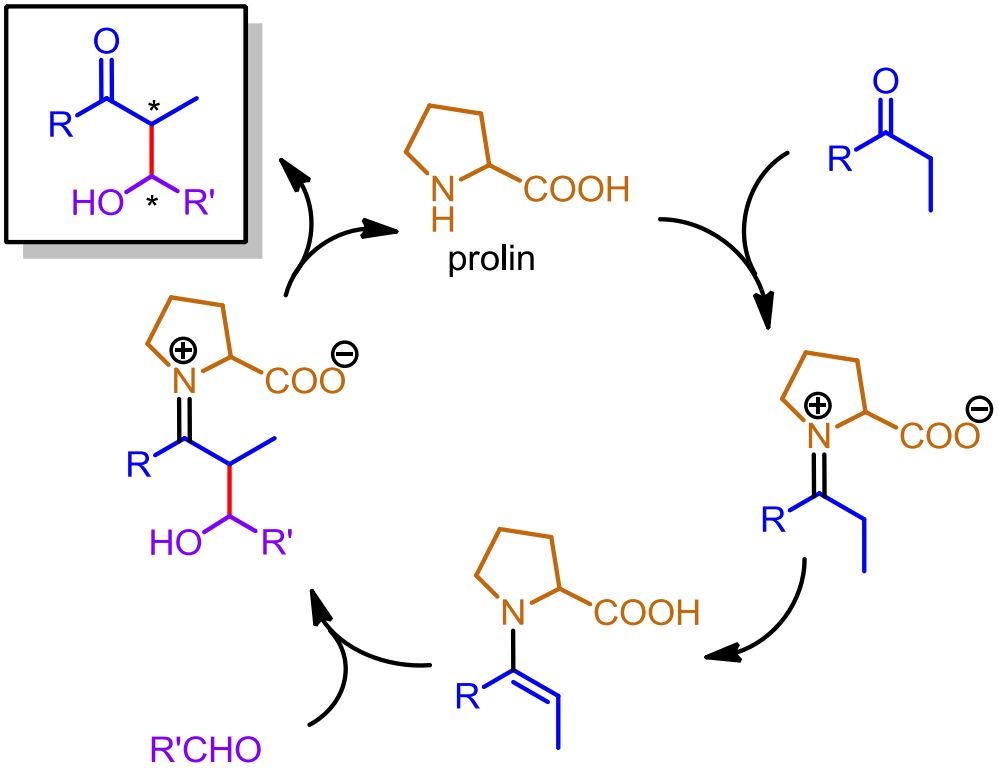
Mannichova reakce



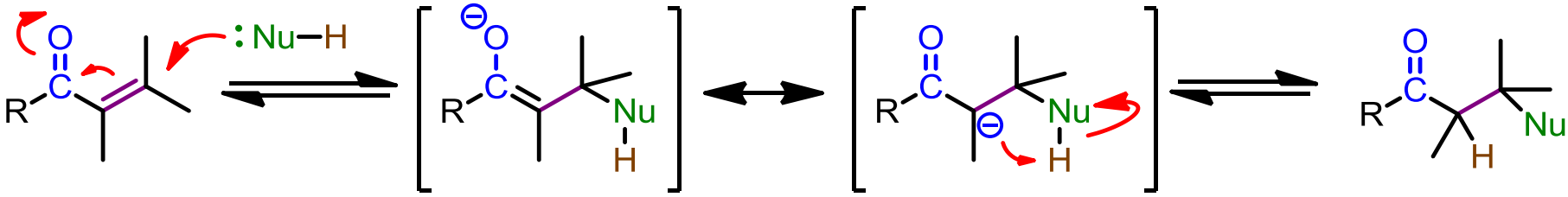




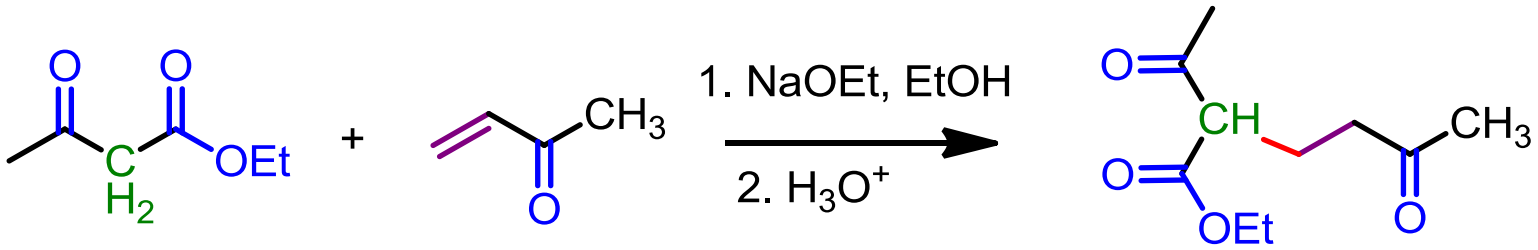
Aldolizace - organokatalýza

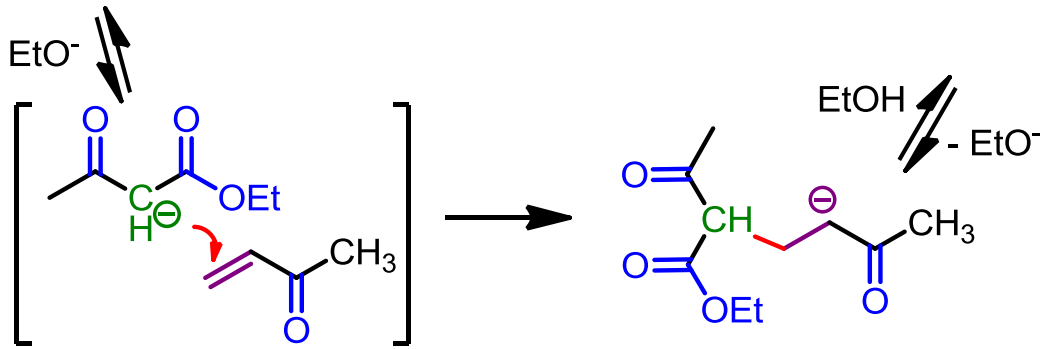


Konjugovaná adice na α,β–nenasycené karbonylové sloučeniny

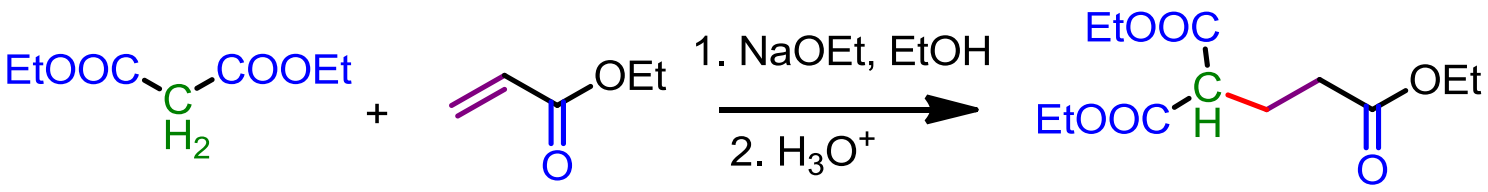


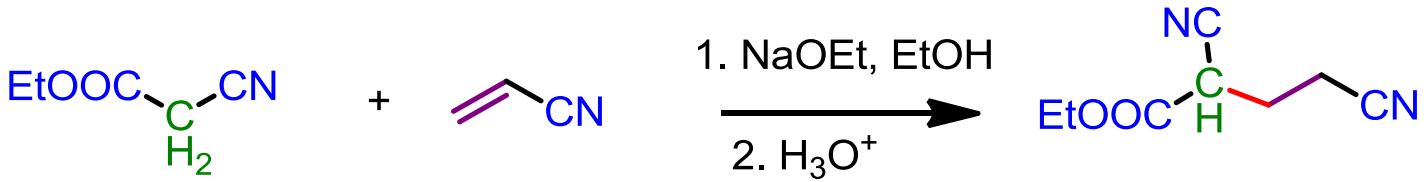
Michaelova adice - konjugovaná adice enolátů na α,β–nenasycené karbonylové sloučeniny

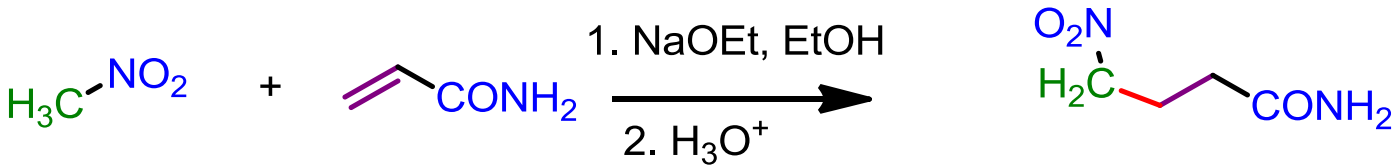




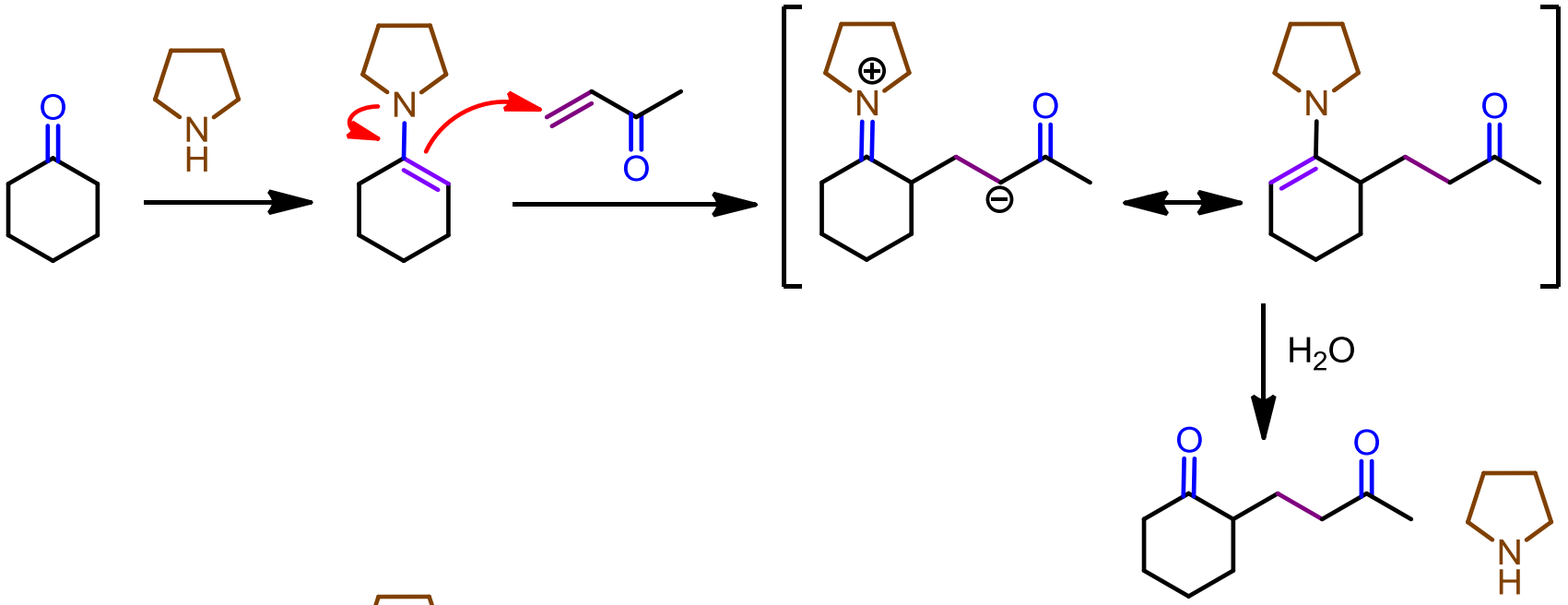
Michaelova adice – další příklady

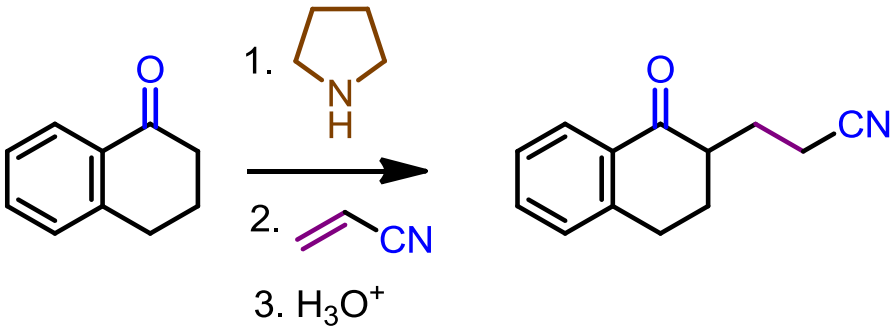






Storkova reakce - Michaelova adice enaminů





Robinsonova anelace - Michaelova adice + aldolová kondenzace