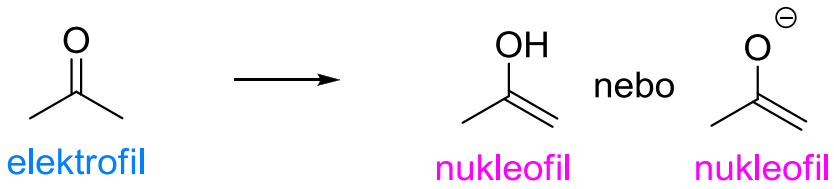
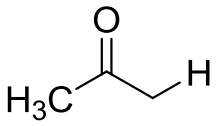
4. Enoly a enoláty

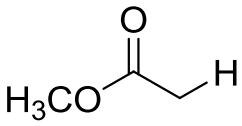


- Tvorba enolátů deprotonací karbonylových sloučenin



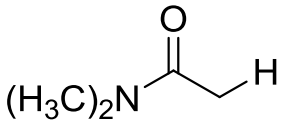
keton

pKa ~ 20



ester

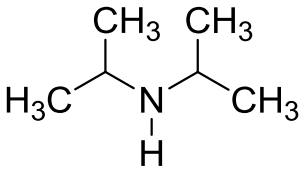
pKa ~ 25



amid

pKa ~ 30

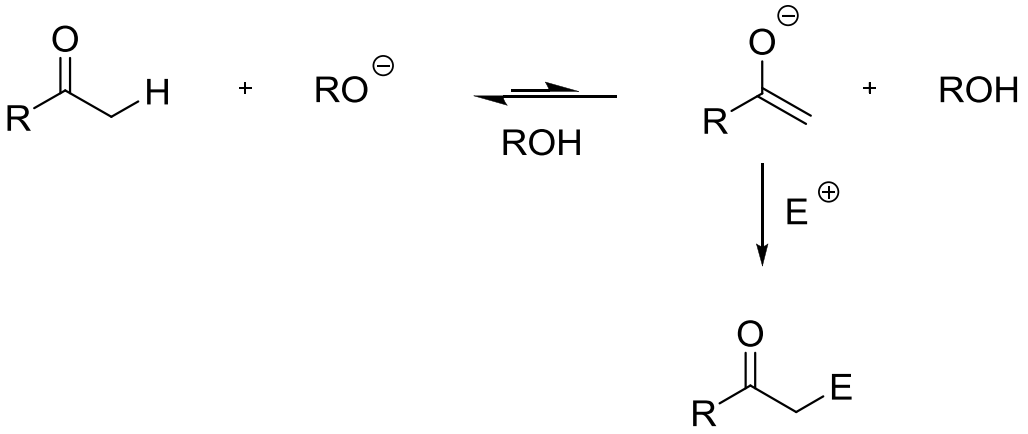
HOH	pKa ~ 16
CH_3OH	pKa ~ 16
*t*BuOH	pKa ~ 19



pKa ~ 36

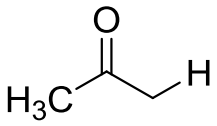
- Reversibilní tvorba enolátu

Deprotonace pomocí NaOH nebo $NaOCH_3$ vede k rovnovážné směsi ve které výchozí karbonylová sloučenina převažuje.



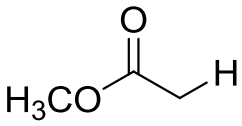
Množství enolátu vytvořené za těchto podmínek je typicky relativně mále. Následující reakce enolátu ovšem umožní postupnou přeměnu výchozí karbonylové sloučeniny (Le Châtelierův princip).

- Tvorba enolátů deprotonací karbonylových sloučenin



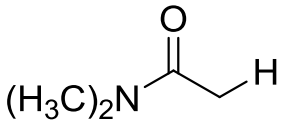
keton

pKa ~ 20



ester

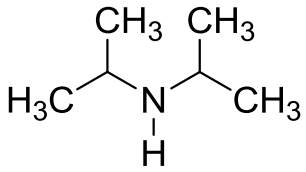
pKa ~ 25



amid

pKa ~ 30

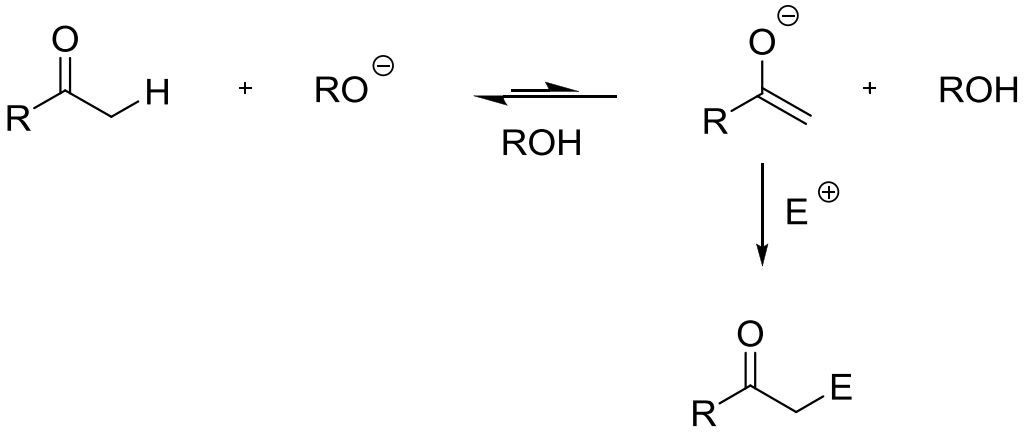
HOH	pKa ~ 16
CH_3OH	pKa ~ 16
*t*BuOH	pKa ~ 19



pKa ~ 36

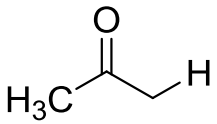
- Reversibilní tvorba enolátu

Deprotonace pomocí NaOH nebo $NaOCH_3$ vede k rovnovážné směsi ve které výchozí karbonylová sloučenina převažuje.



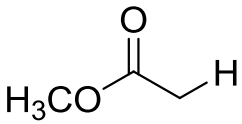
I zdánlivě malá koncentrace enolu/enolátu může udělat spoustu chemie !

- Tvorba enolátů deprotonací karbonylových sloučenin



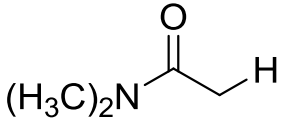
keton

pKa ~ 20



ester

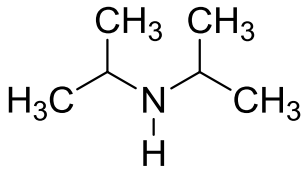
pKa ~ 25



amid

pKa ~ 30

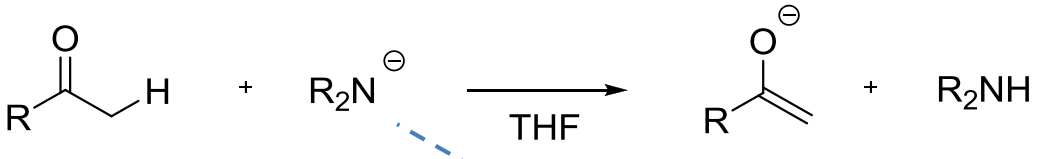
HOH	pKa ~ 16
CH_3OH	pKa ~ 16
*t*BuOH	pKa ~ 19



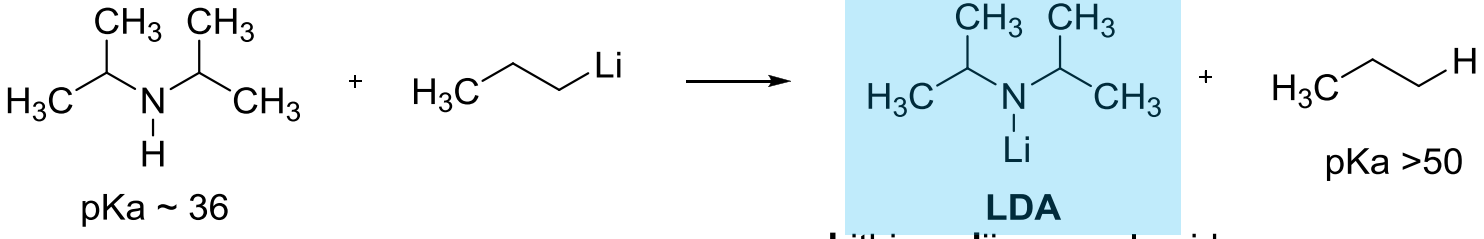
pKa ~ 36

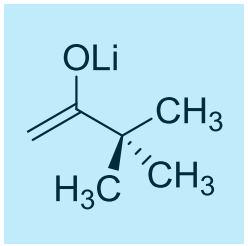
- Ireversibilní tvorba enolátu

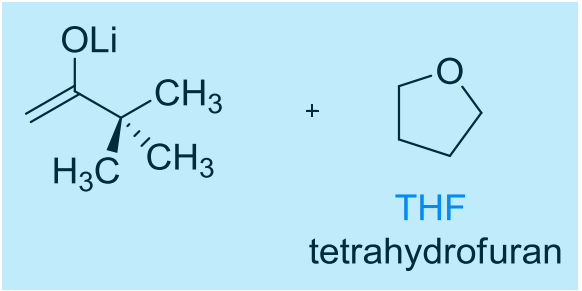
Deprotonace pomocí silné báze v aprotickém rozpouštědle umožňuje kompletní přeměnu karbonylové sloučeniny na enolát (“nevratná” deprotonace).

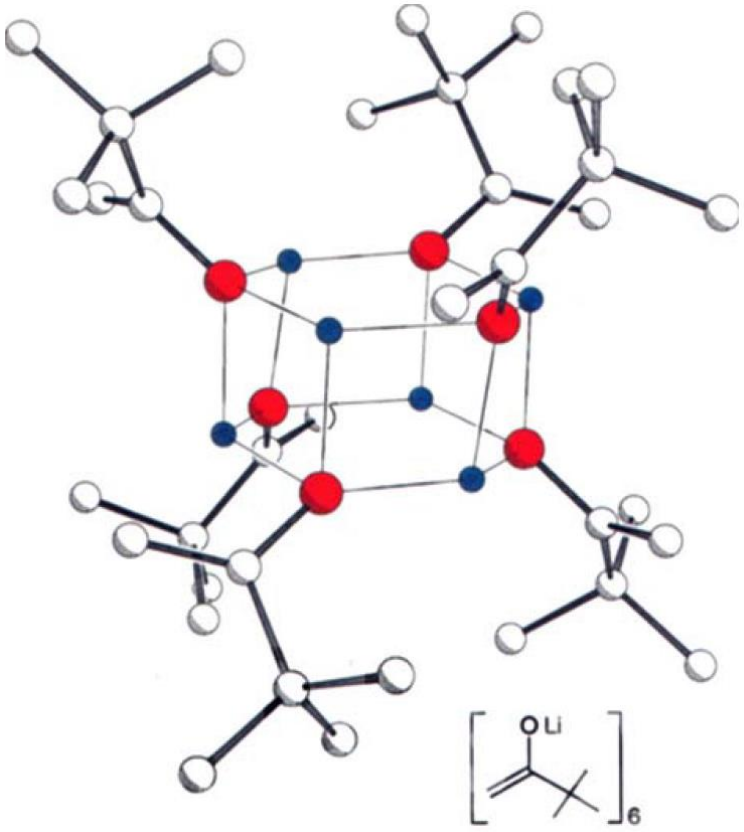


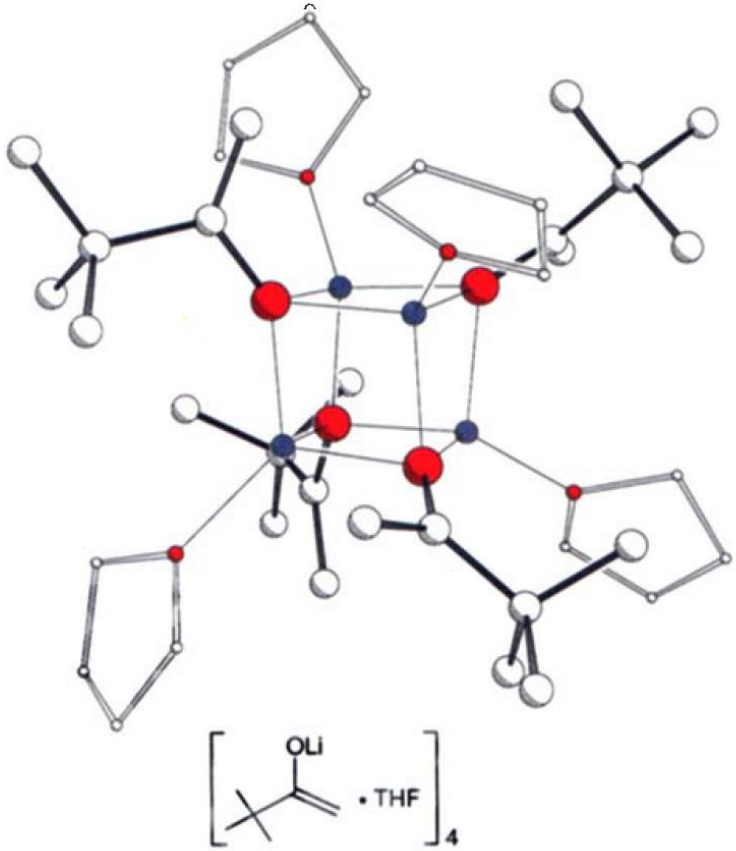
LDA je běžně používaná silná báze:



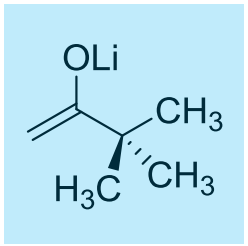


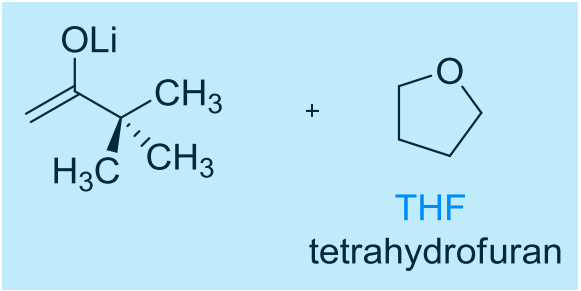


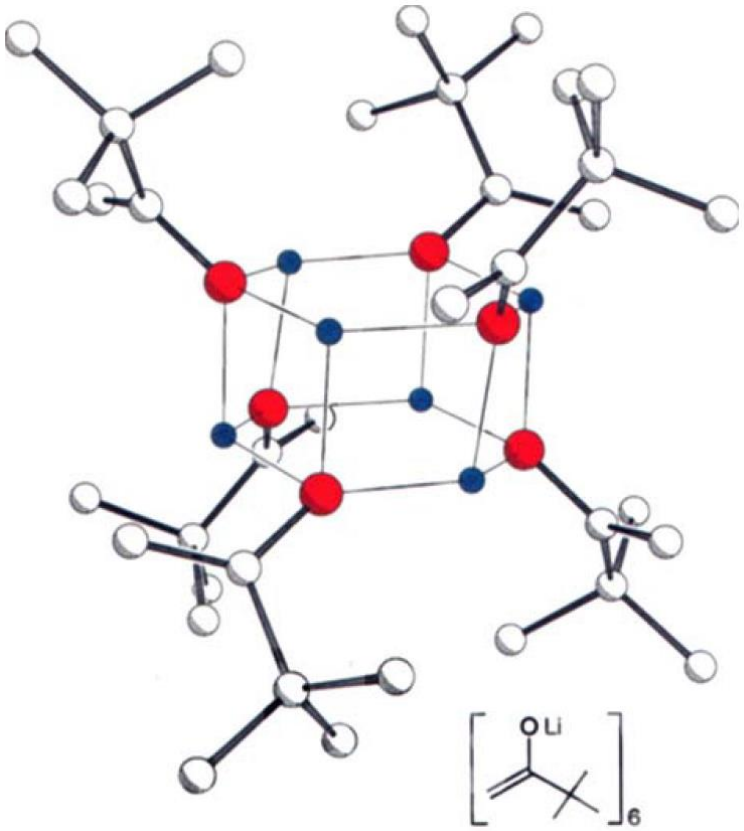


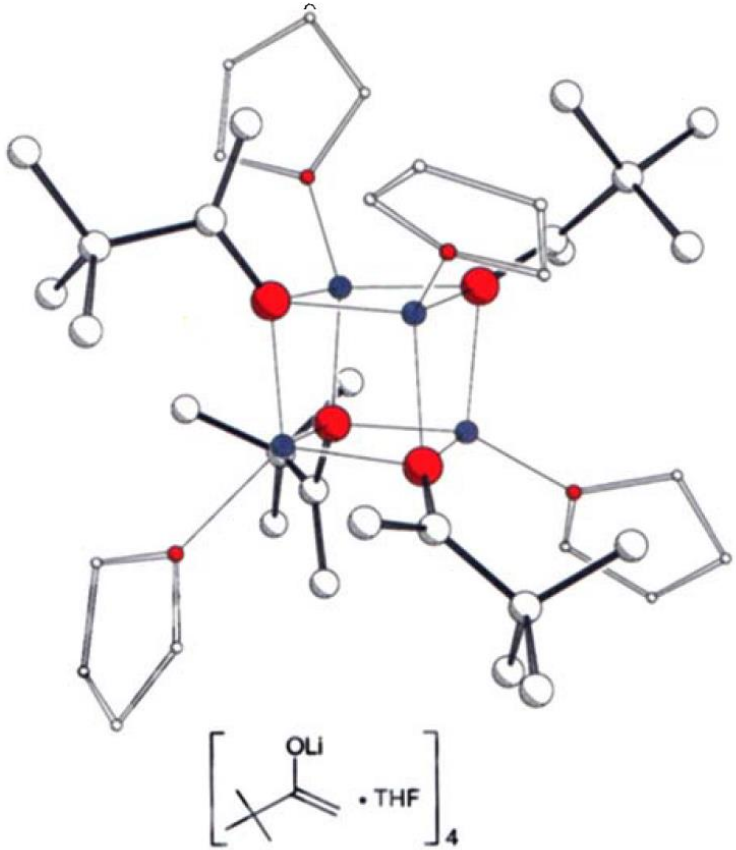


Seebach, D. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1624.



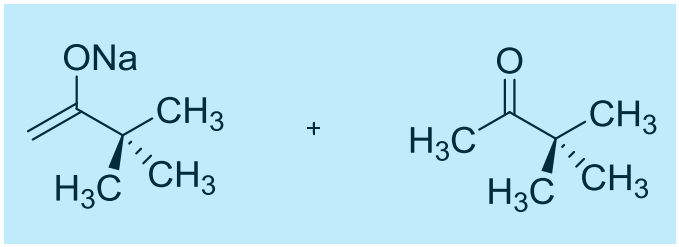


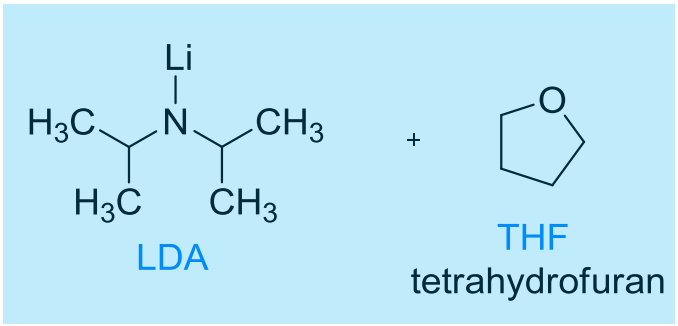


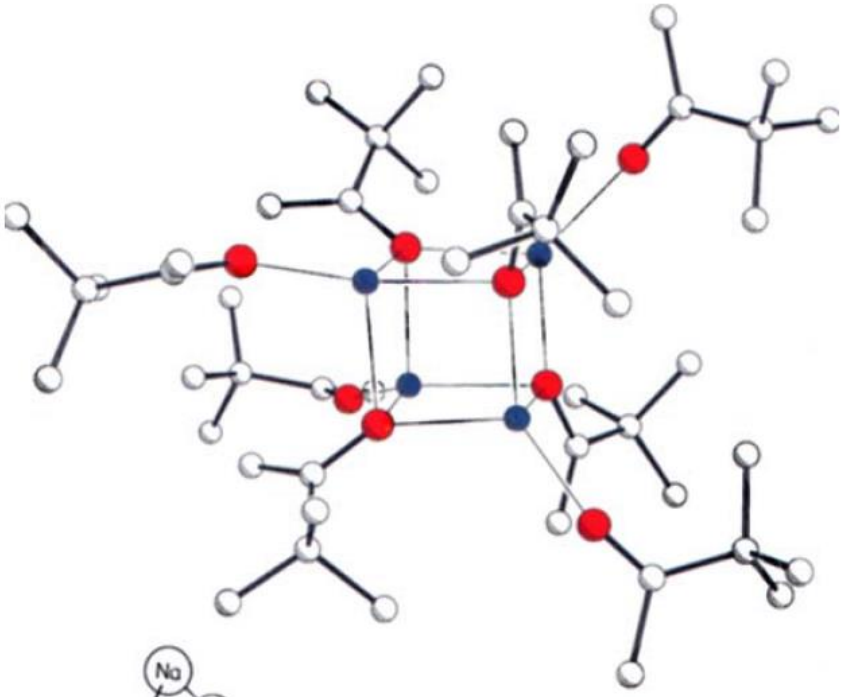


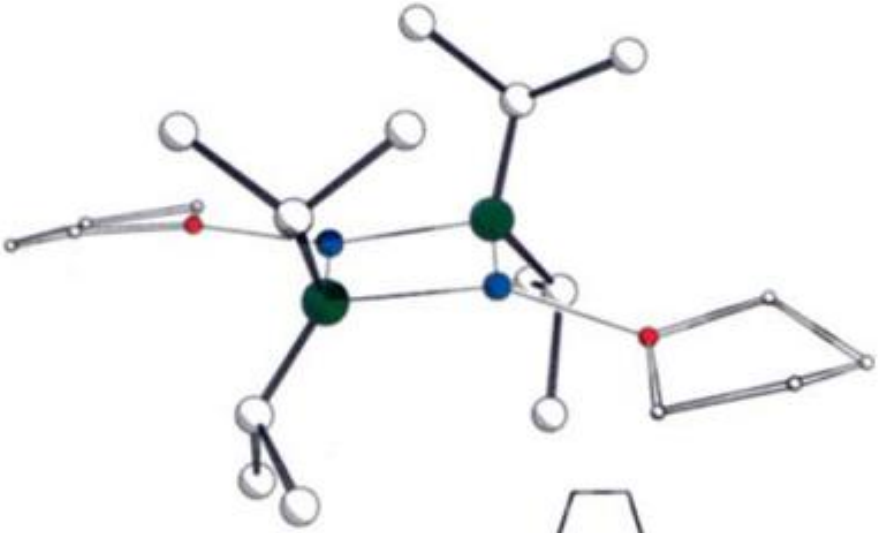
Seebach, D. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1624.

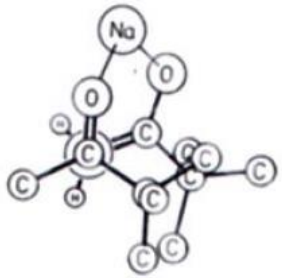
Struktura enolátů

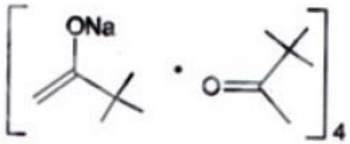


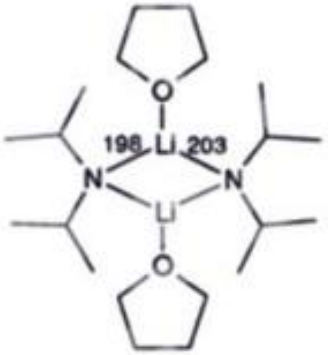












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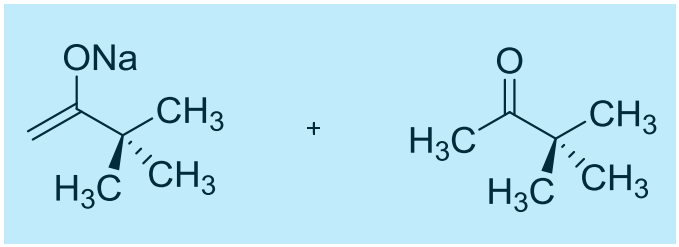
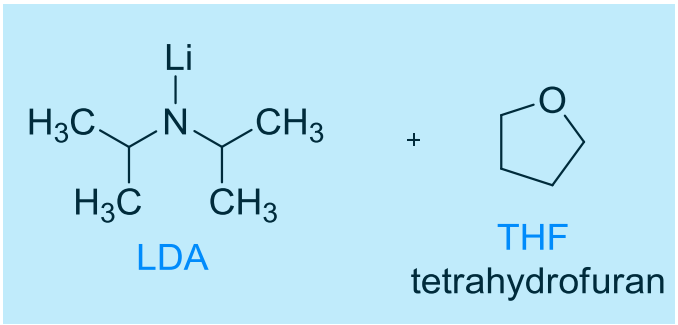
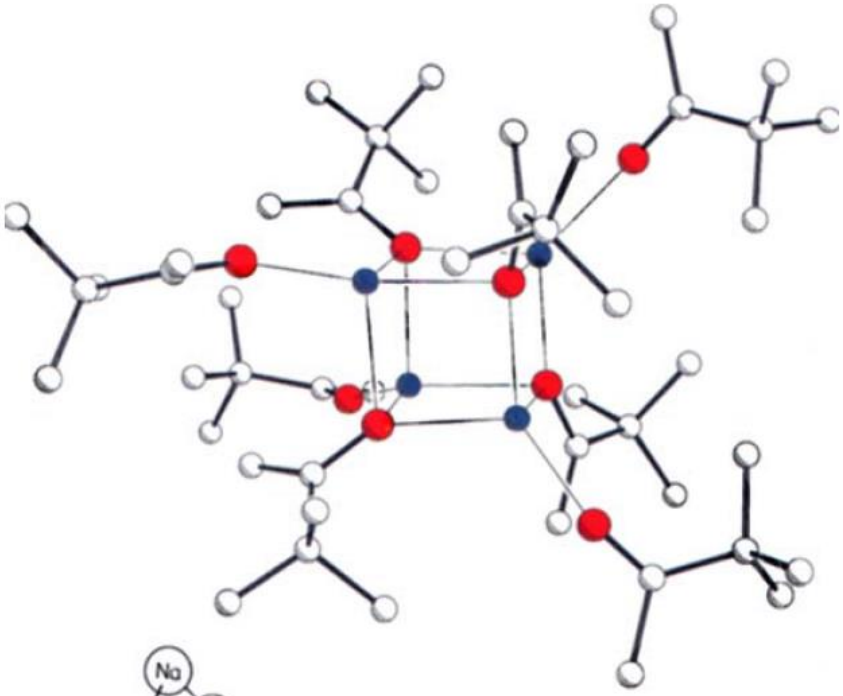
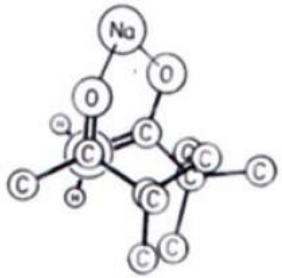
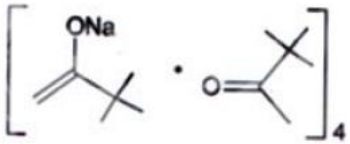
Struktura enolátů

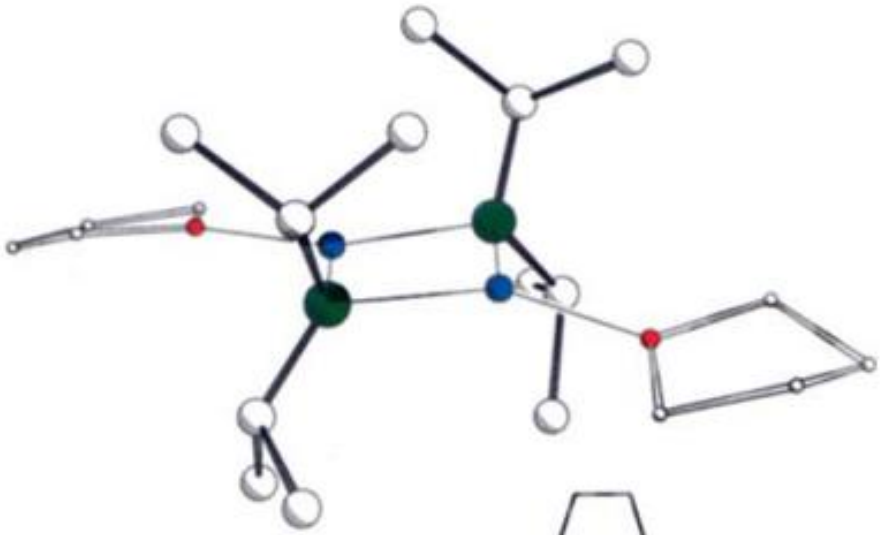


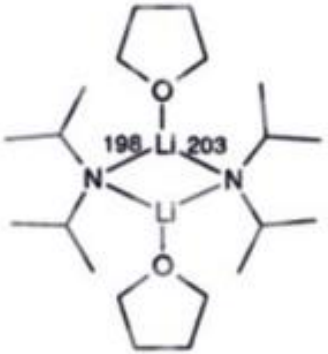








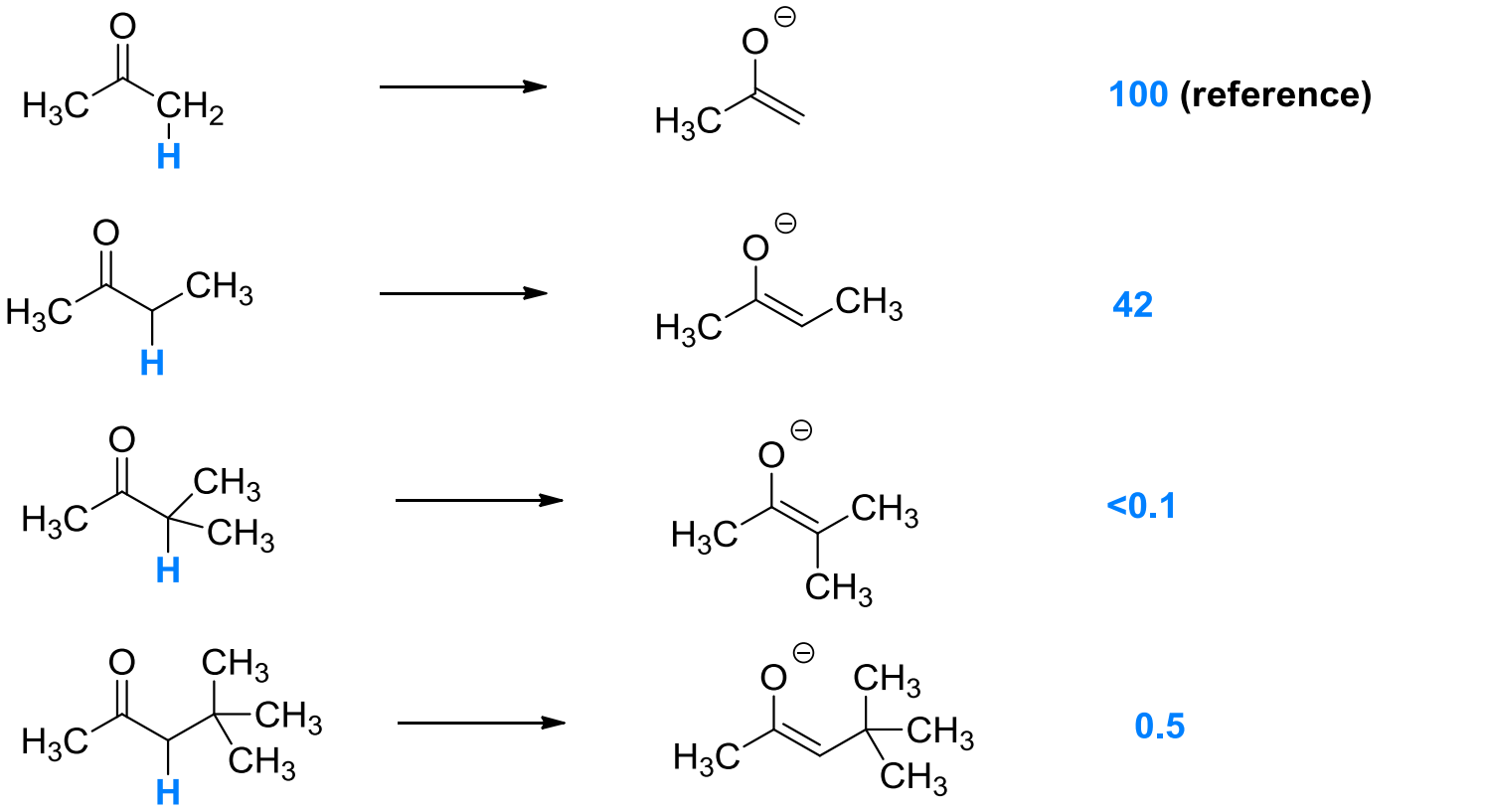




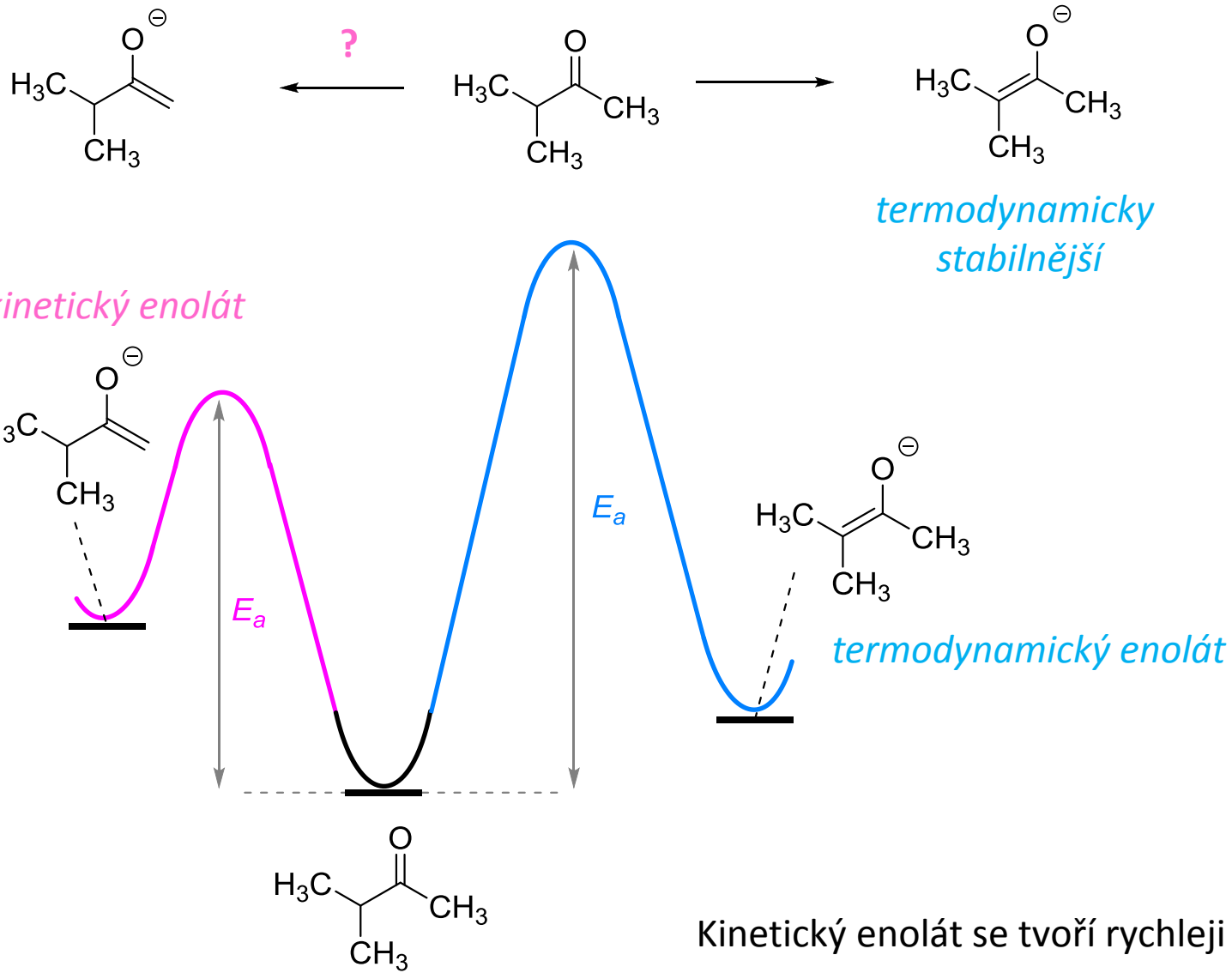
Seebach, D. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1624.

- Rychlost deprotonace je citlivá na sterické efekty

rel. rychlost (Na_2CO_3, D_2O)

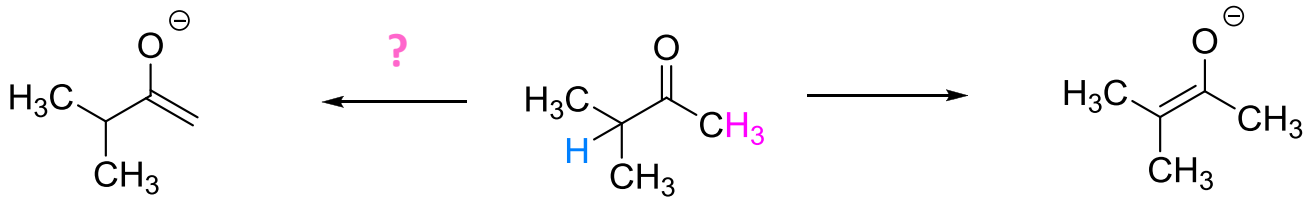


- Regioselektivita enolizace : tvorba kinetického enolátu

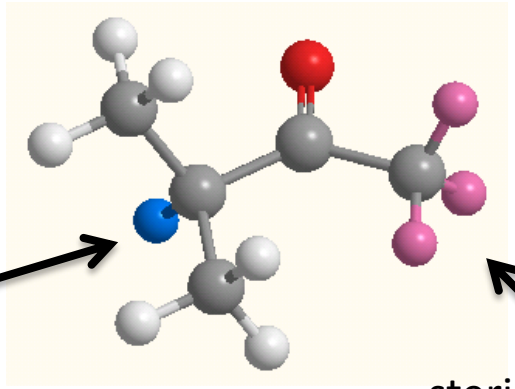


Příprava enolátů

- Regioselektivita enolizace : tvorba kinetického enolátu



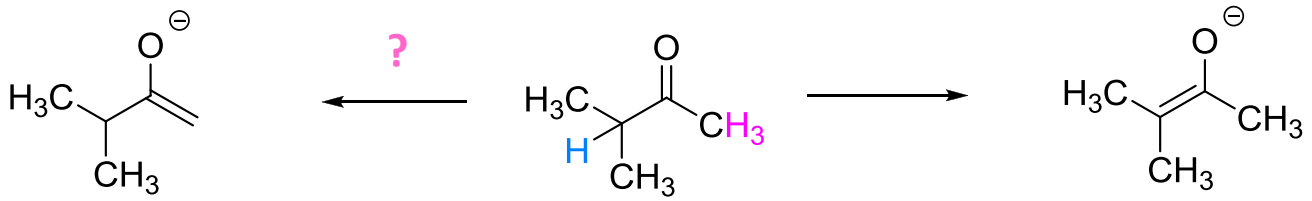
termodynamicky stabilnější



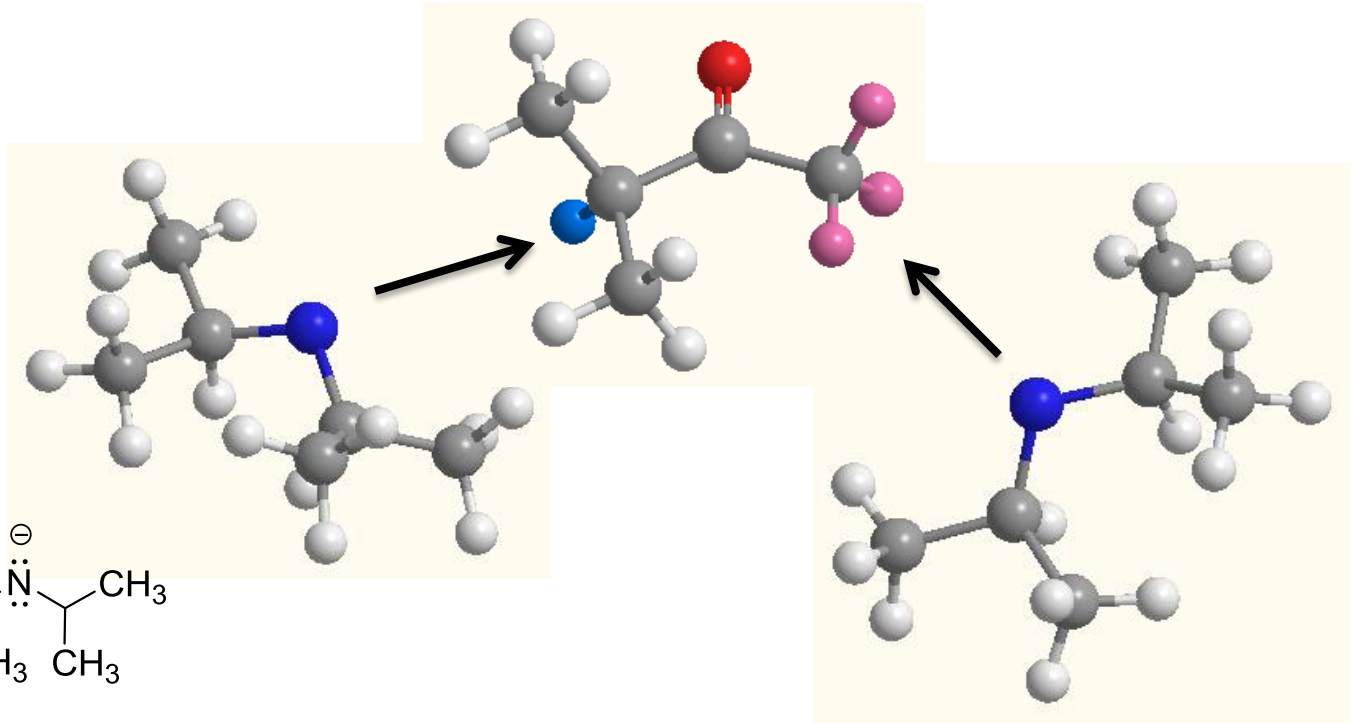
méně dostupný vodík
(sterický bráněné)

stericky dostupnější vodíky
(+ statistický argument)

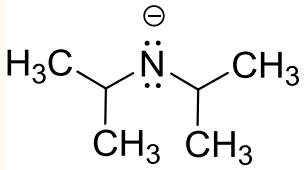
- Regioselektivita enolizace : tvorba kinetického enolátu



termodynamicky stabilnější

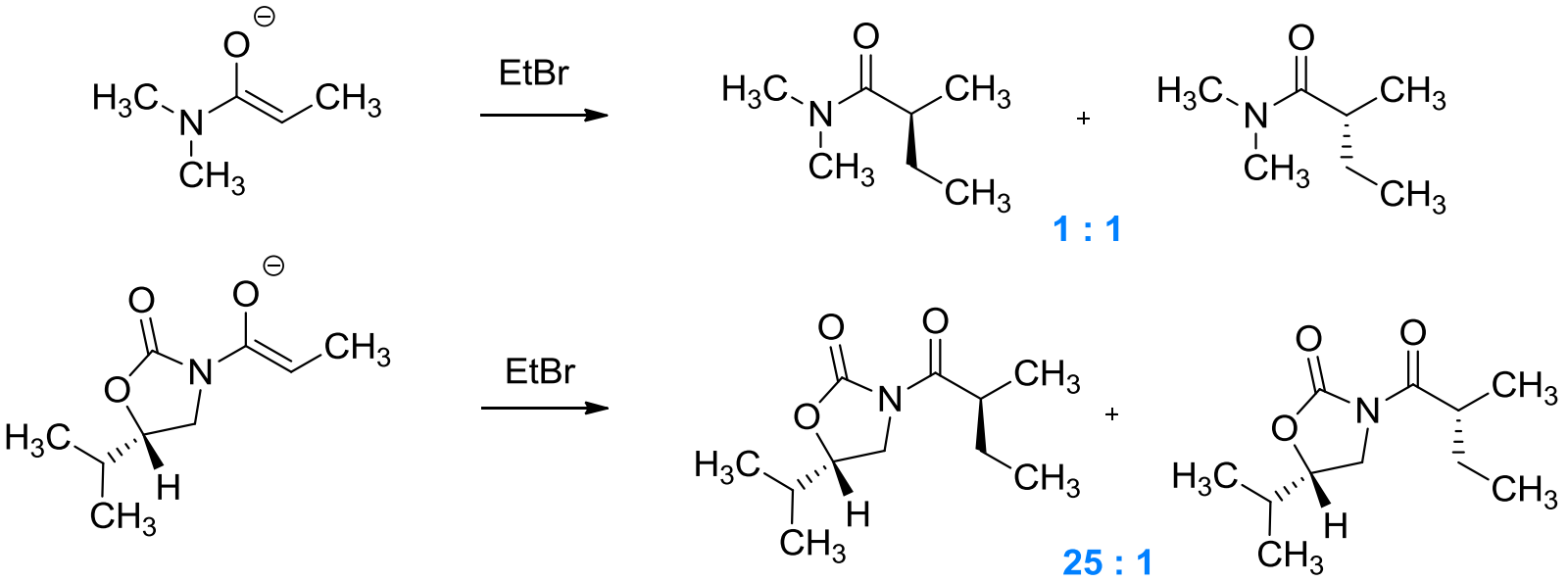


LDA
Lithium **d**iisopropyl**a**mid

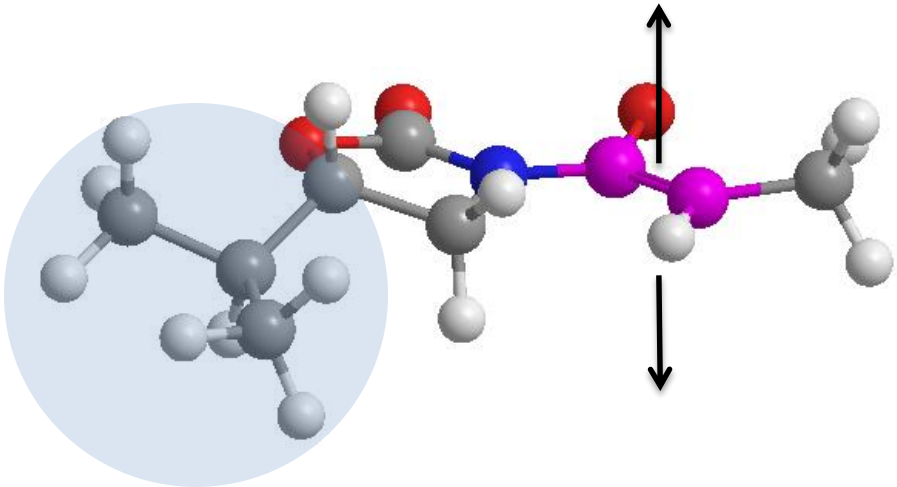


LDA
Lithium **d**iisopropyl**a**mid

- Stereoselektivní alkylace

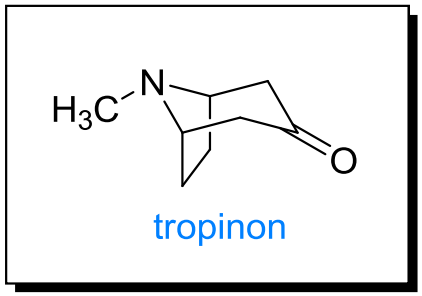


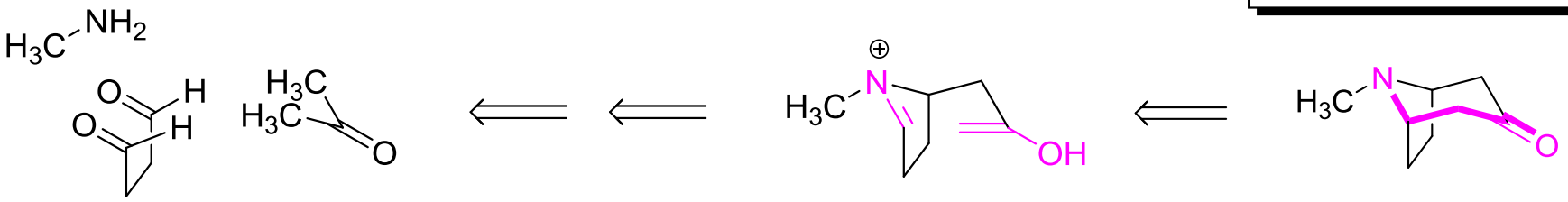
anti vůči objemnému isopropyl substituentu



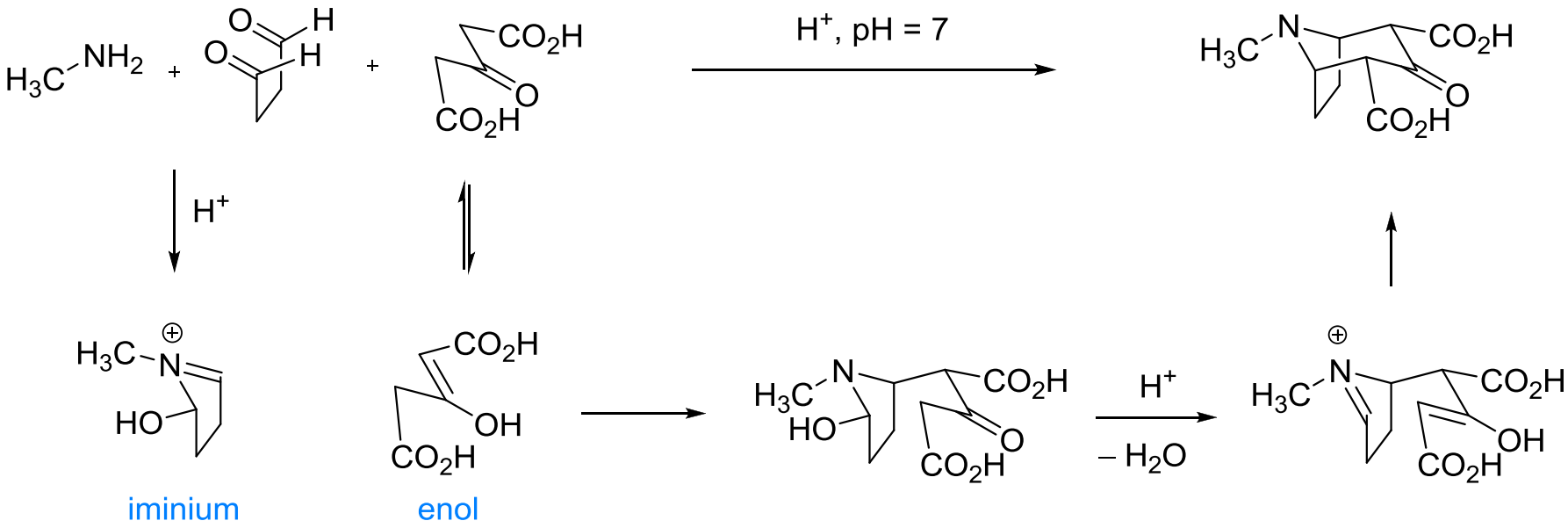
Přítomné stereocentrum ovlivňuje tvorbu nového stereocentra: diastereoselektivita

- Mannichova reakce je často používána v (bio)syntéze alkaloidů

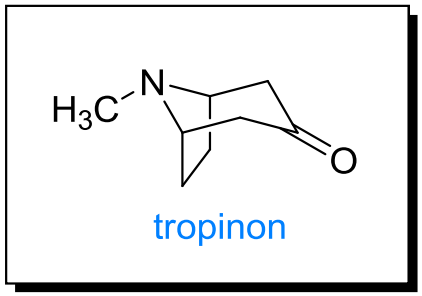


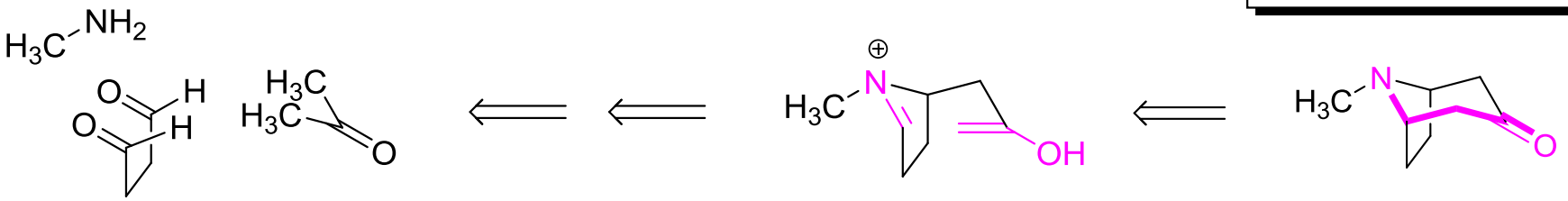


Biomimetická syntéza tropinonu v laboratoři (1917 (!), **Robert Robinson**, Nobel prize)



- Mannichova reakce je často používána v (bio)syntéze alkaloidů





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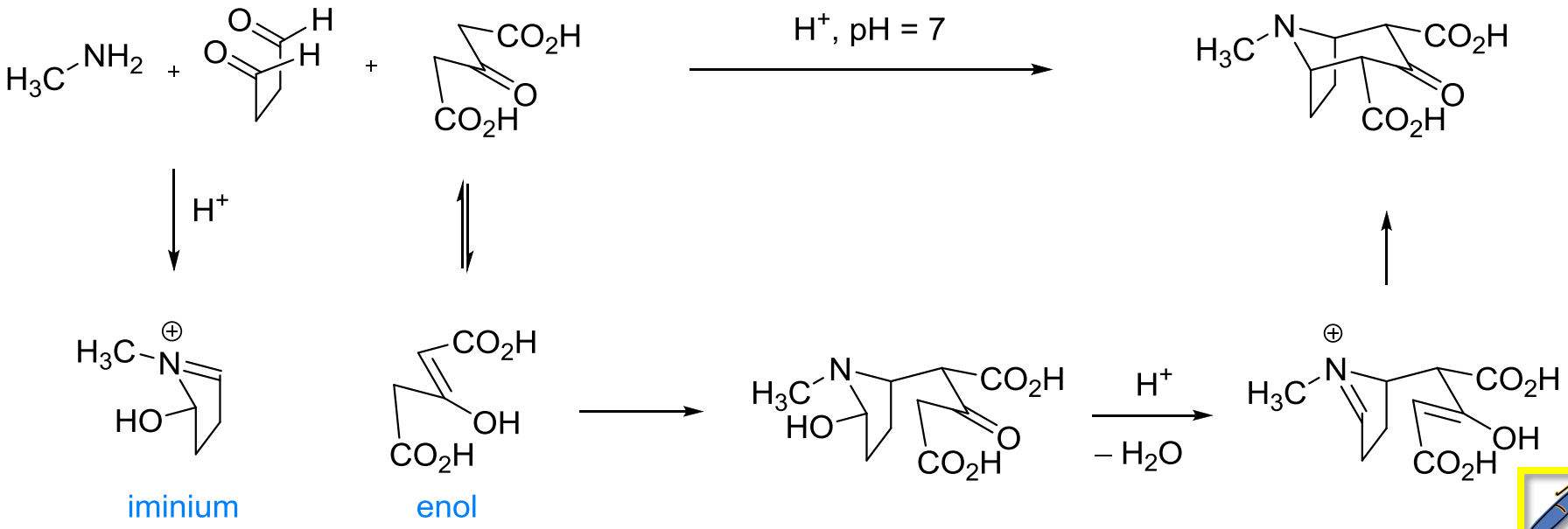
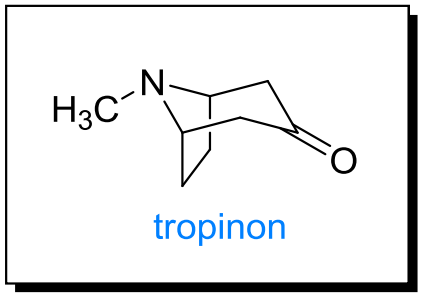
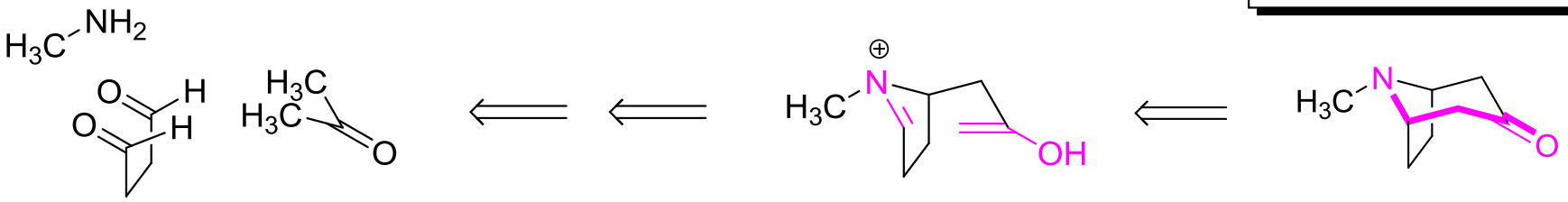
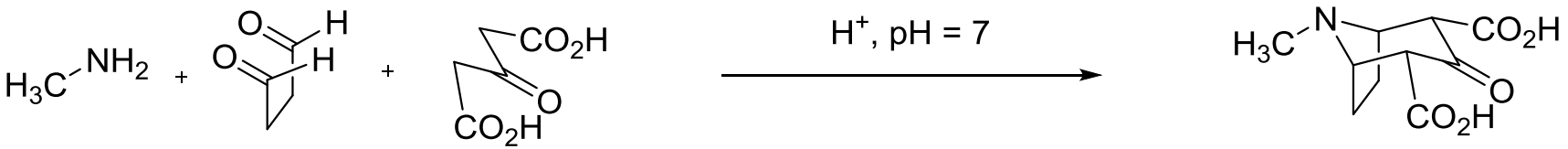


- Mannichova reakce je často používána v (bio)syntéze alkaloidů

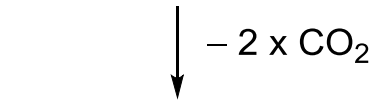


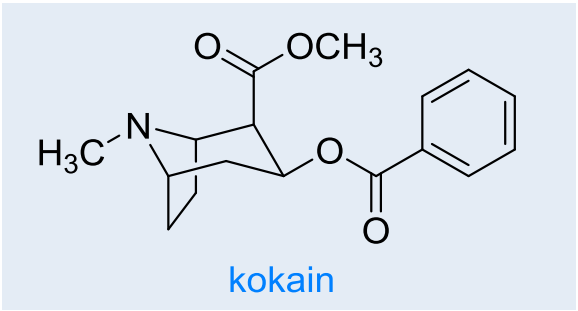


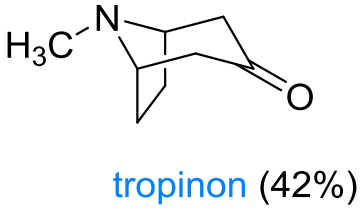
Biomimetická syntéza tropinonu v laboratoři (1917 (!), **Robert Robinson**, Nobel prize)

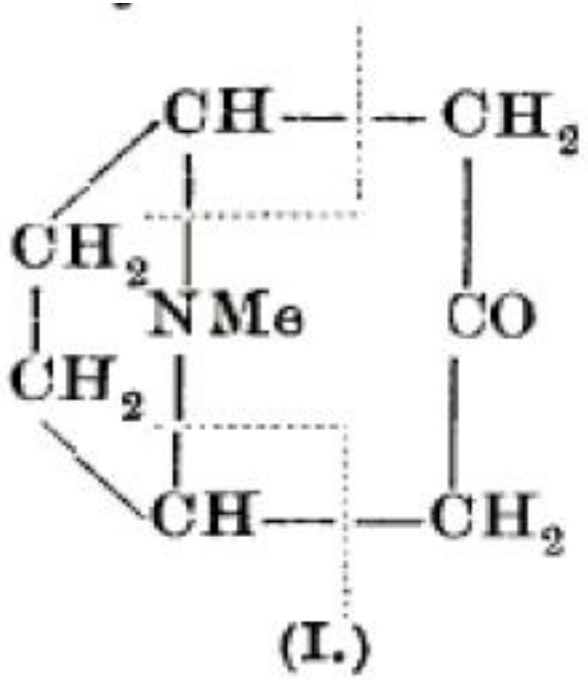


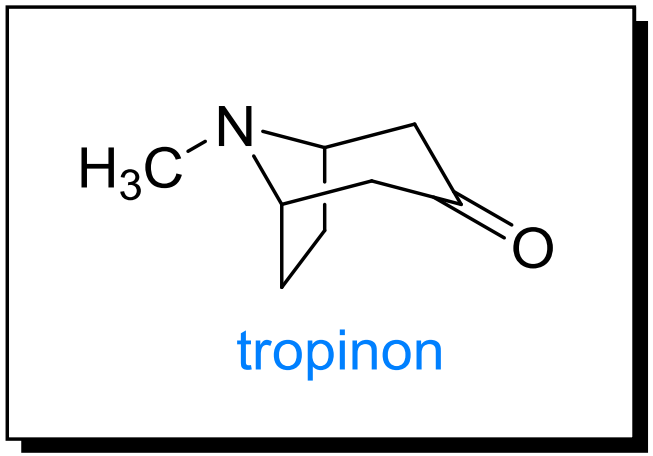
Syntéza tropinonu je skvělý problém na procvičení formálních mechanismů ...





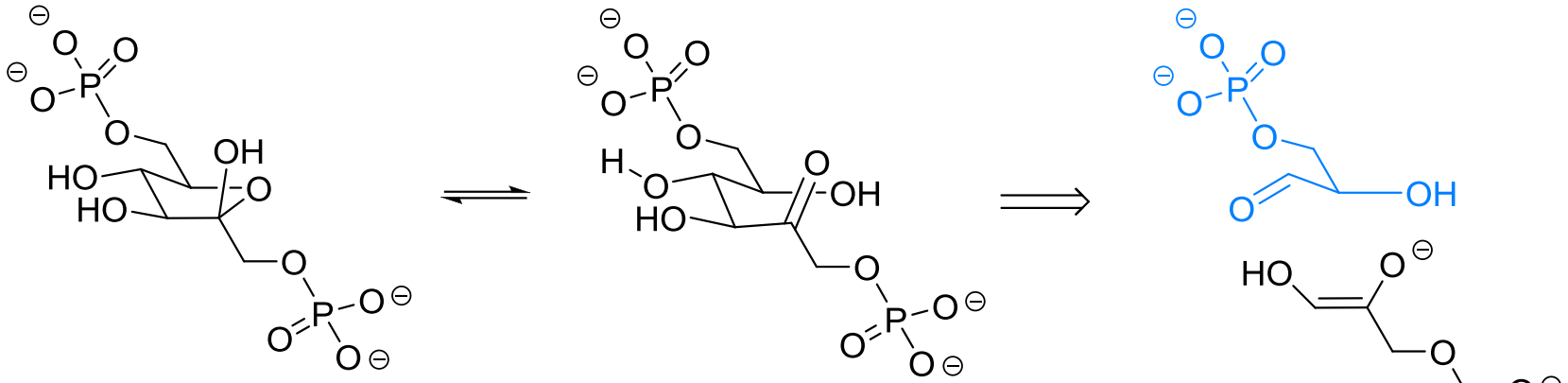



CH
CH2
CH2
NMe
CO
CH2
CH
CH2
(I.)


H3C
N
O
tropinon

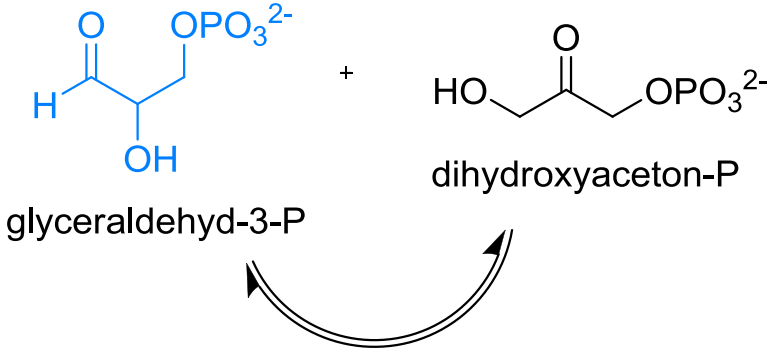
Aldolová reakce v biosyntéze cukrů

- Biosyntéza cukrů



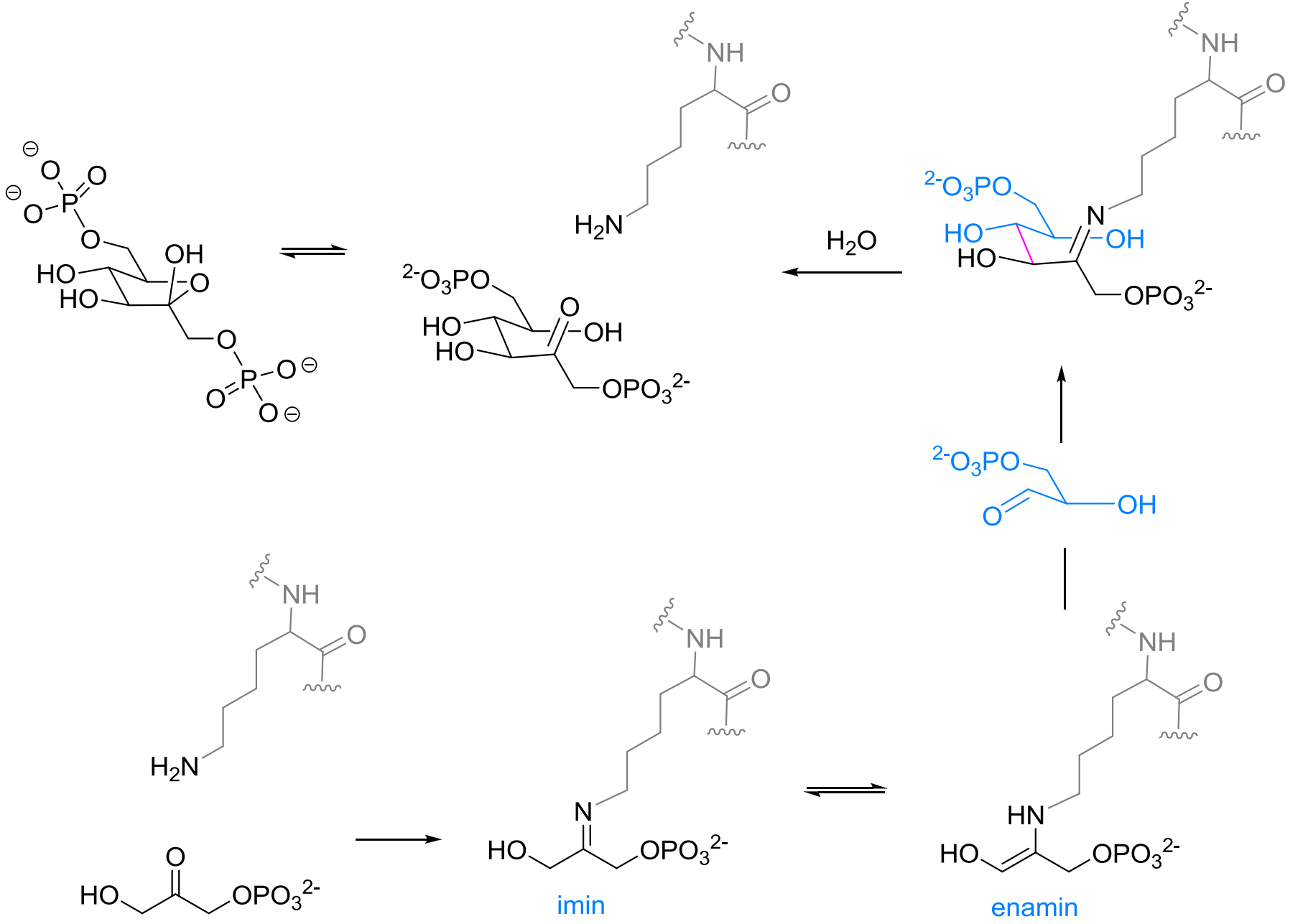
Fruktosa-1,6-P_2

Q: jak rozpoznat strukturní element aldolové reakce?

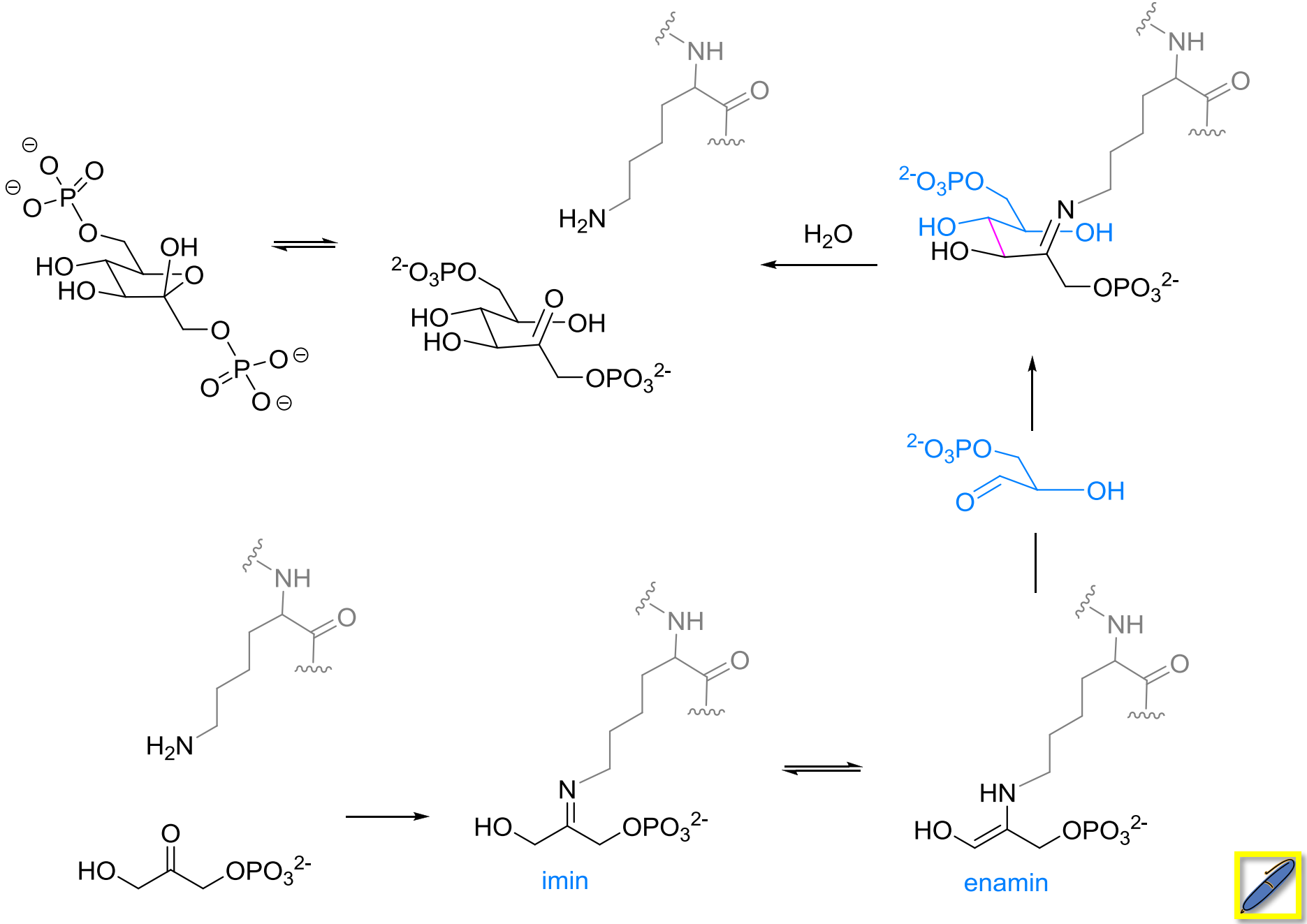


Q: mechanismus izomerace?

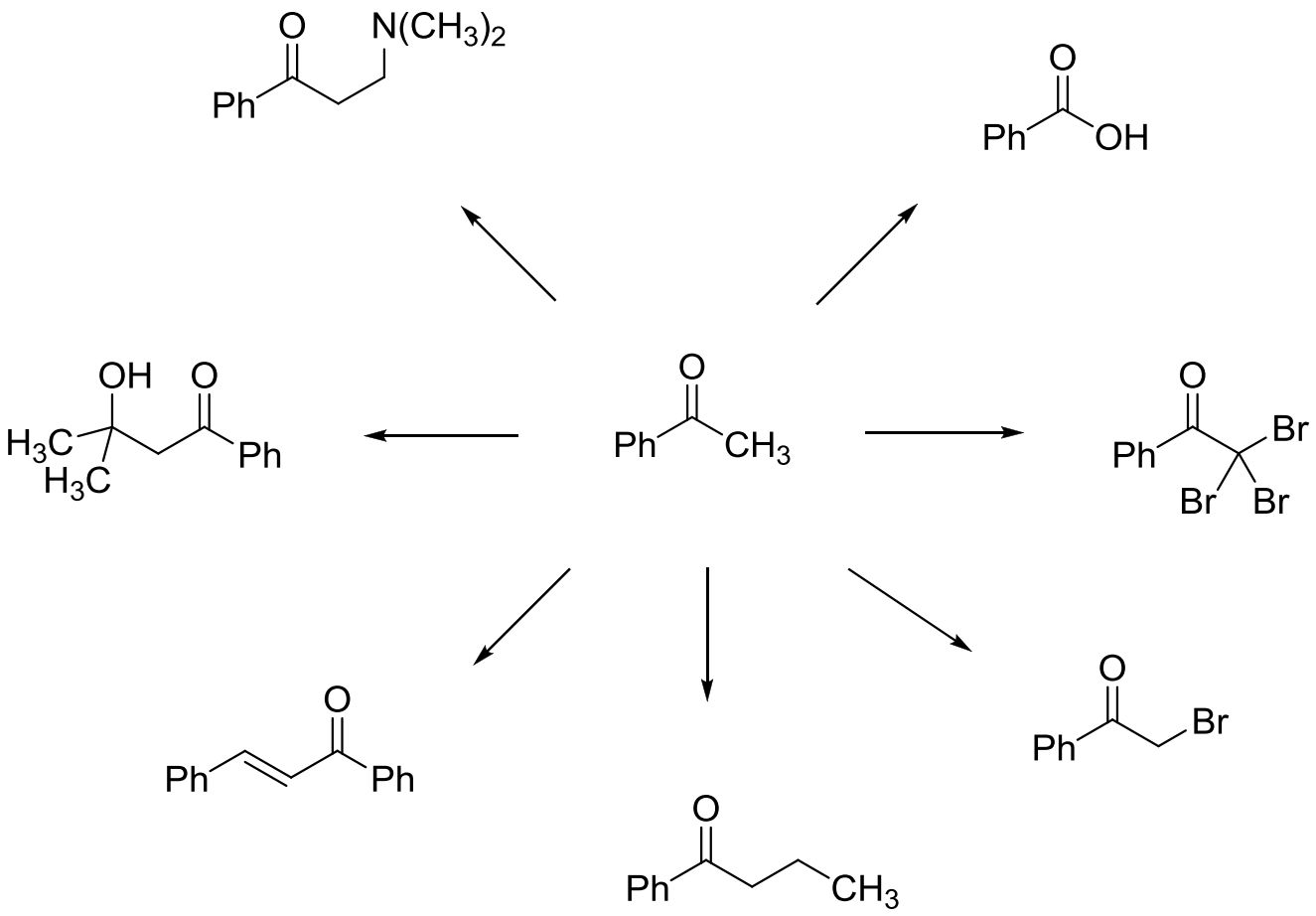
Aldolová reakce v biosyntéze cukrů



Aldolová reakce v biosyntéze cukrů



Transformace enolů a enolátů



Transformace enolů a enolátů