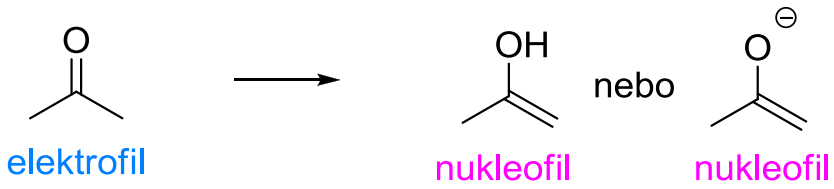
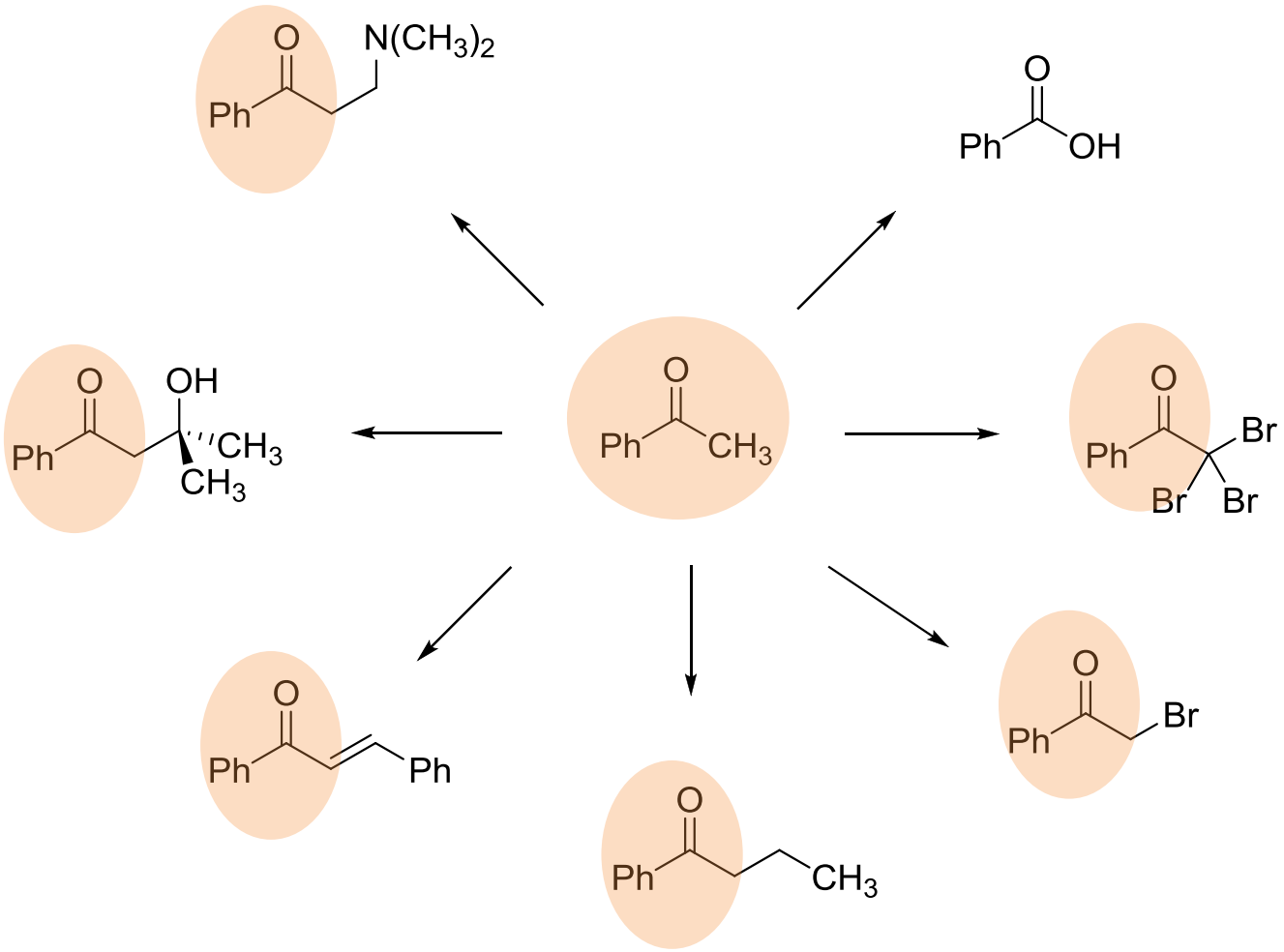
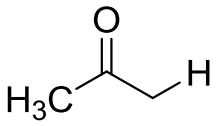
4. Enoly a enoláty



Transformace enolů a enolátů

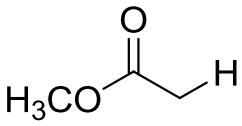


- Tvorba enolátů deprotonací karbonylových sloučenin



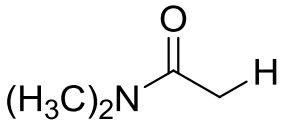
keton

pKa ~ 20



ester

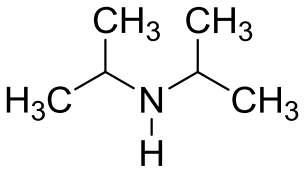
pKa ~ 25



amid

pKa ~ 30

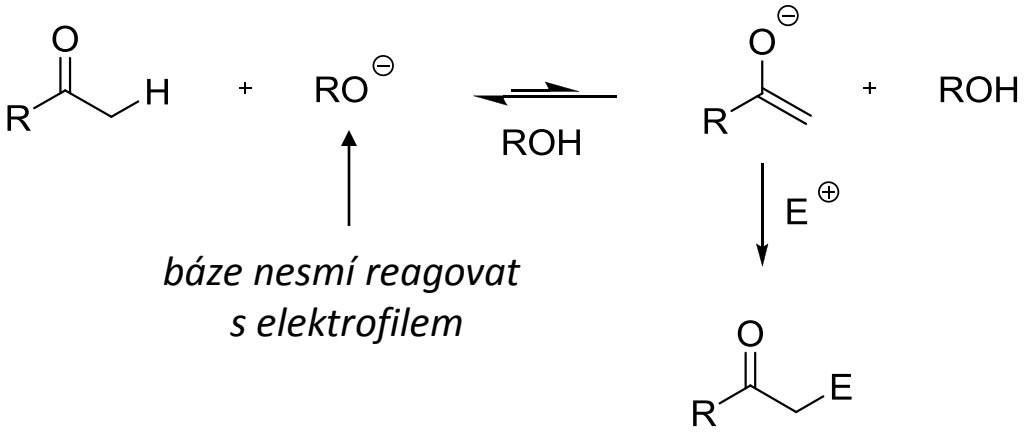
HOH	pKa ~ 16
CH_3OH	pKa ~ 16
*t*BuOH	pKa ~ 19



pKa ~ 36

- Reversibilní tvorba enolátu

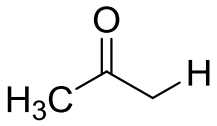
Deprotonace pomocí NaOH nebo $NaOCH_3$ vede k rovnovážné směsi ve které výchozí karbonylová sloučenina převažuje.



báze nesmí reagovat s elektrofilem

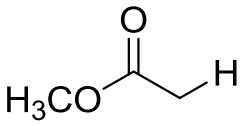
Množství enolátu vytvořené za těchto podmínek je typicky relativně mále. Následující reakce enolátu ovšem umožní postupnou přeměnu výchozí karbonylové sloučeniny (Le Châtelierův princip).

- Tvorba enolátů deprotonací karbonylových sloučenin



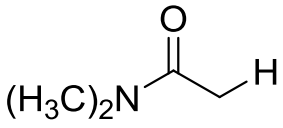
keton

pKa ~ 20



ester

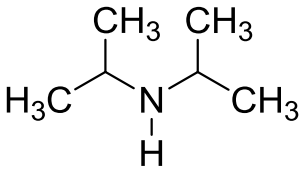
pKa ~ 25



amid

pKa ~ 30

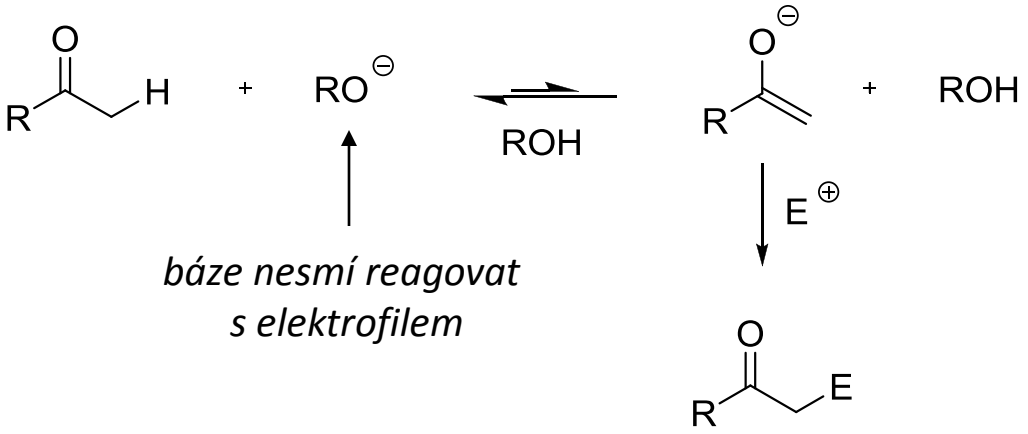
HOH	pKa ~ 16
CH_3OH	pKa ~ 16
*t*BuOH	pKa ~ 19



pKa ~ 36

- Reversibilní tvorba enolátu

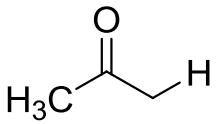
Deprotonace pomocí NaOH nebo $NaOCH_3$ vede k rovnovážné směsi ve které výchozí karbonylová sloučenina převažuje.



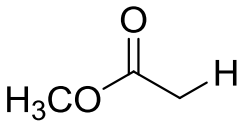
báze nesmí reagovat s elektrofilem

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

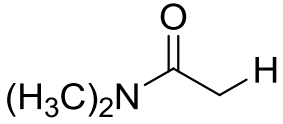
- Tvorba enolátů deprotonací karbonylových sloučenin


keton

pKa ~ 20

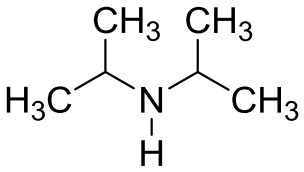

ester

pKa ~ 25


amid

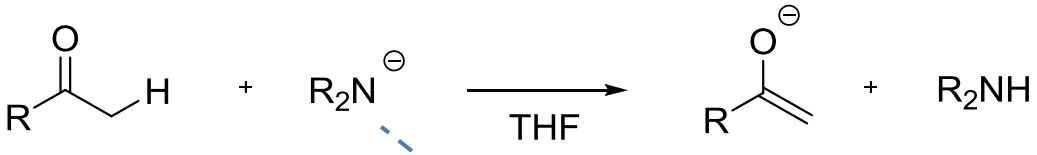
pKa ~ 30

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

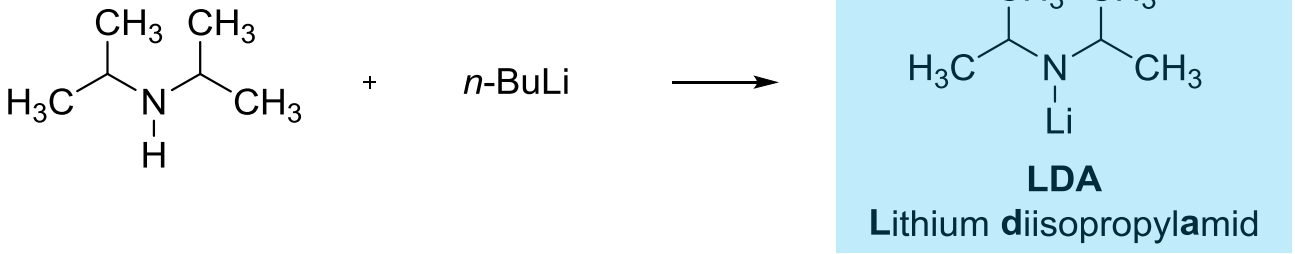

pKa ~ 36

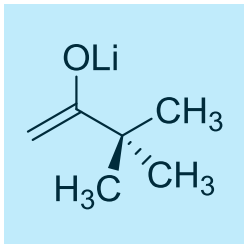
- Ireversibilní tvorba enolátu

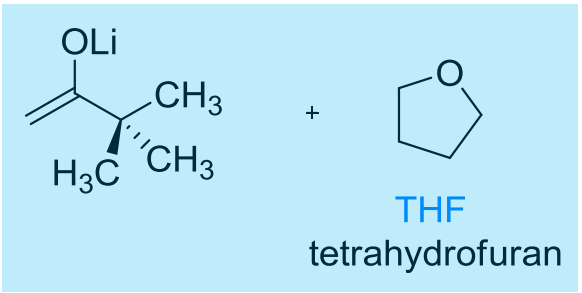
Deprotonace pomocí silné báze v aprotickém rozpouštědle umožňuje kompletní přeměnu karbonylové sloučeniny na enolát (“nevratná” deprotonace).

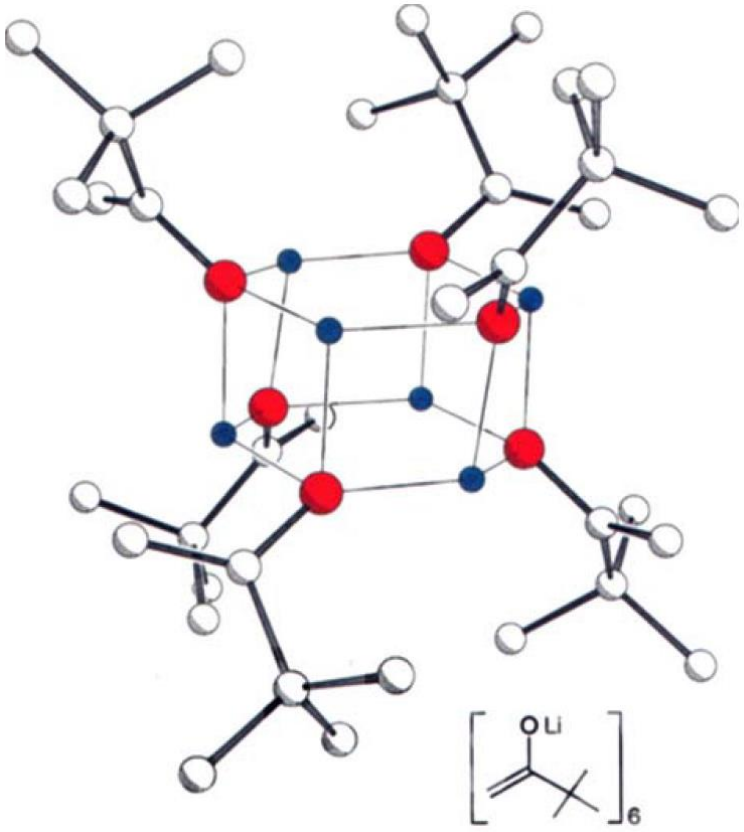


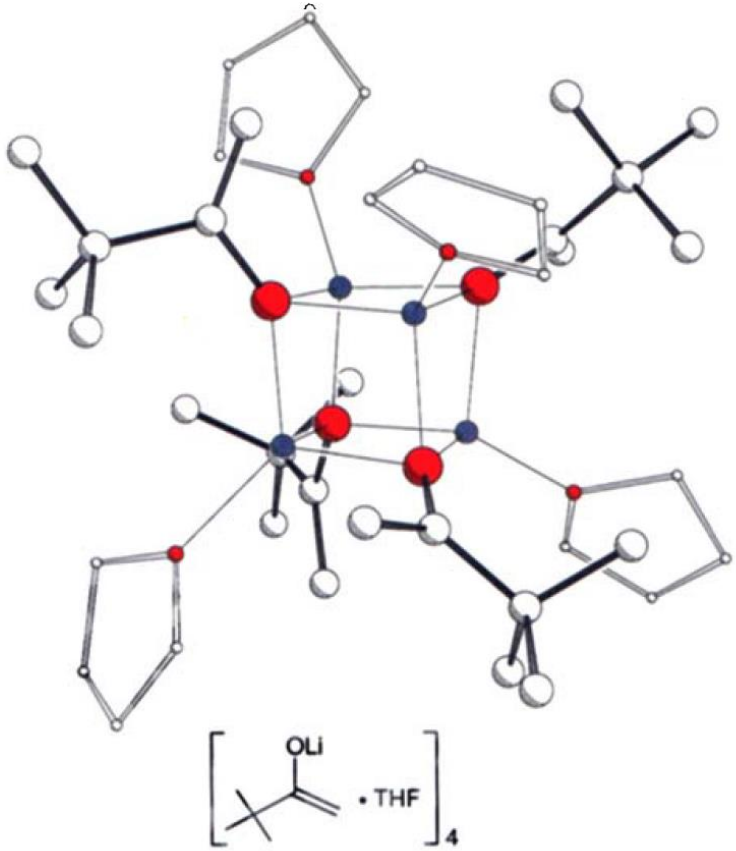
LDA je běžně používaná silná báze:





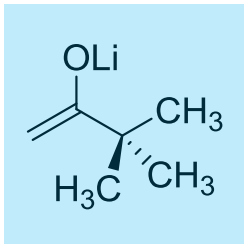


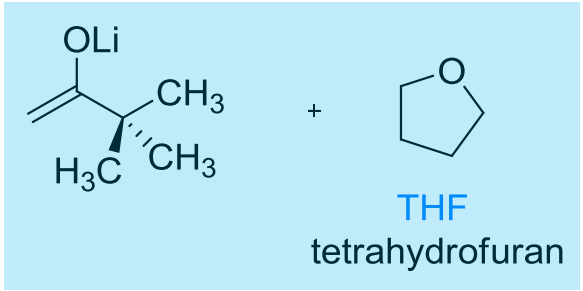


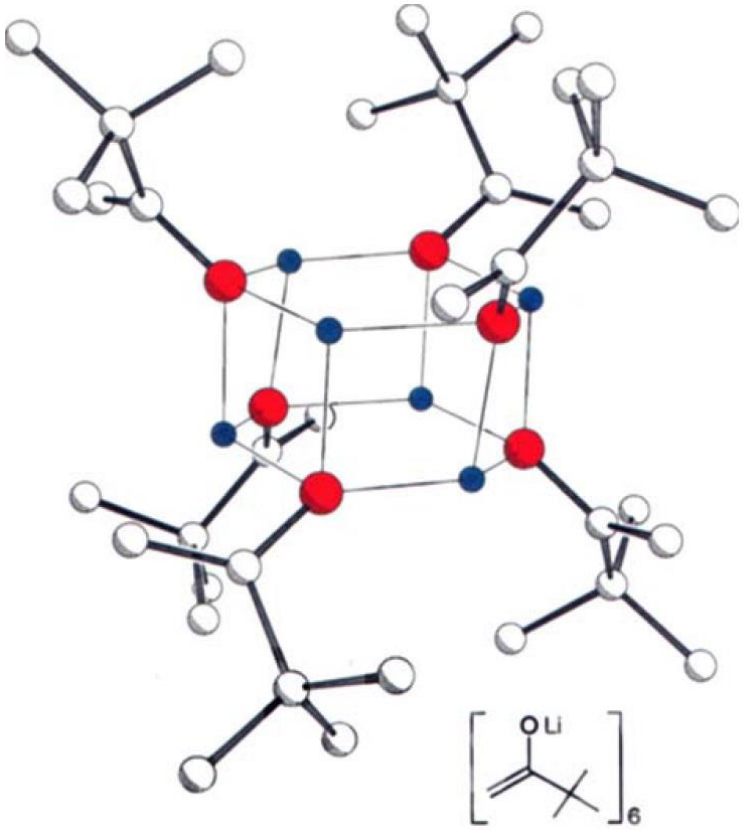


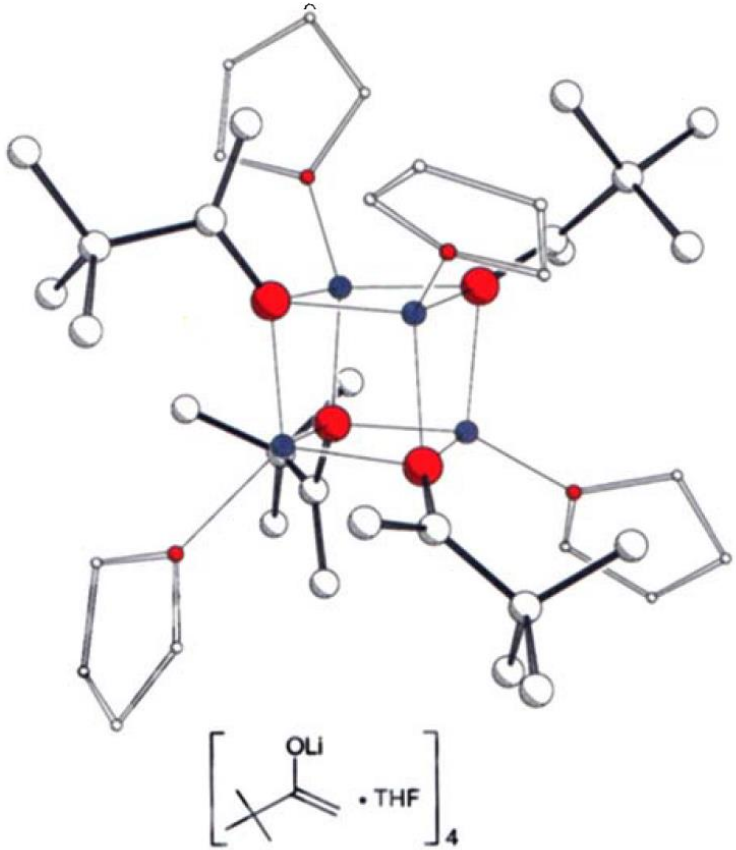
Seebach, D. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1624.

Struktura enolátů









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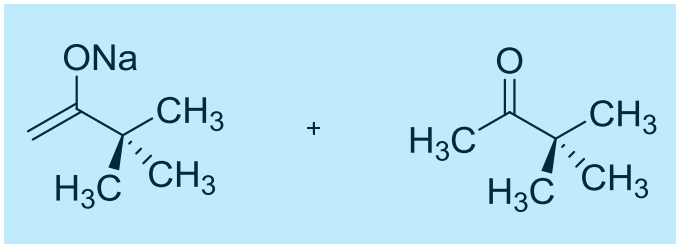
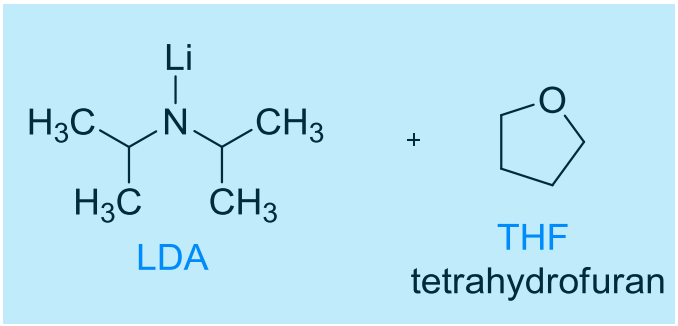
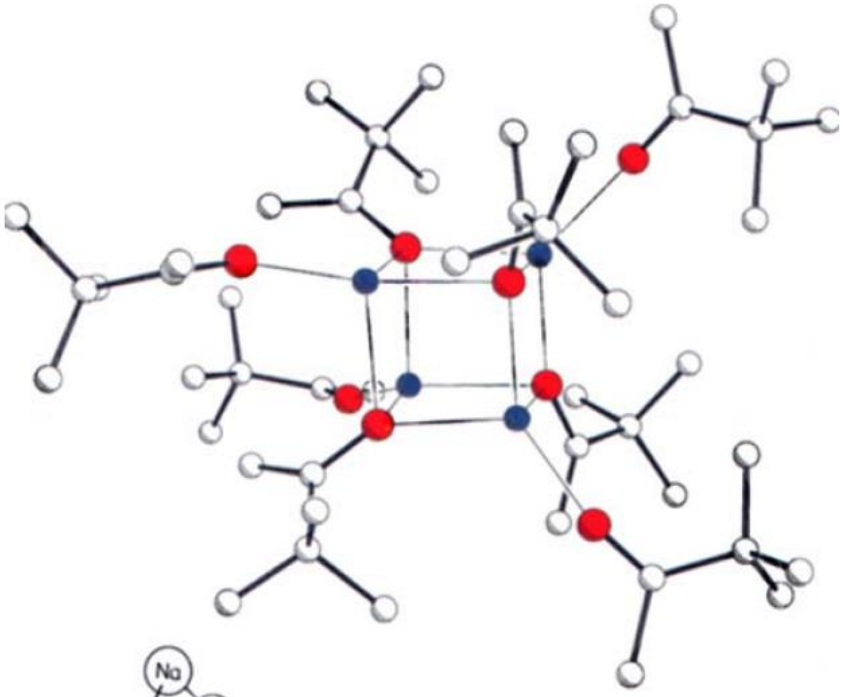
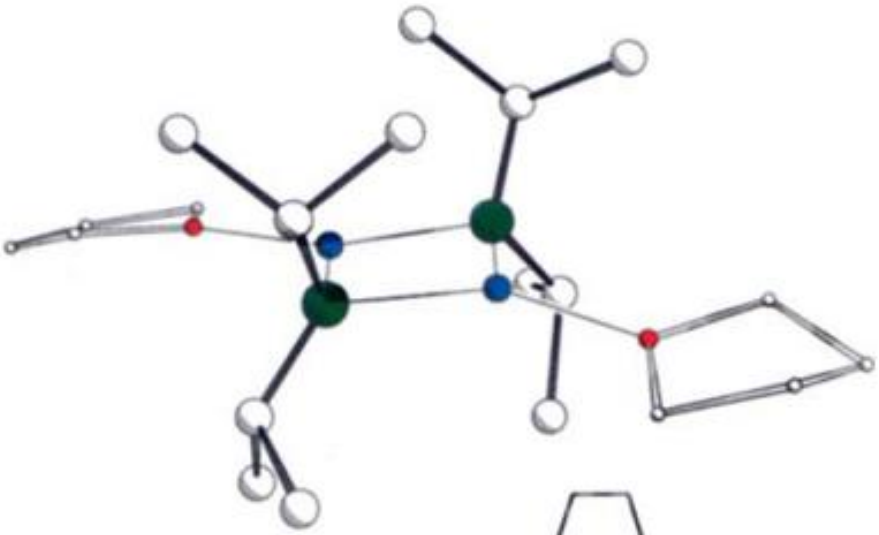
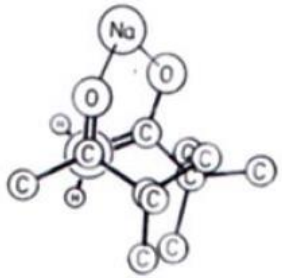
Struktura enolátů

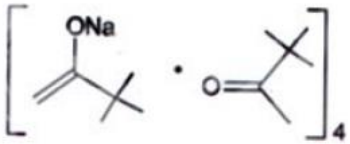


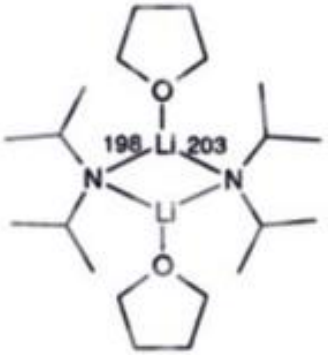












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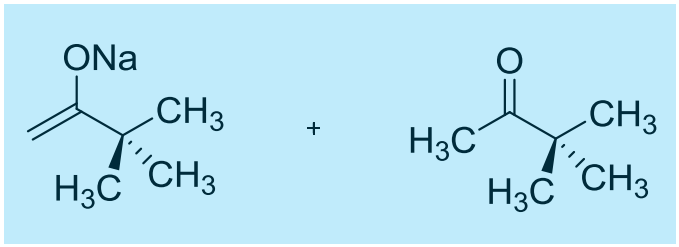
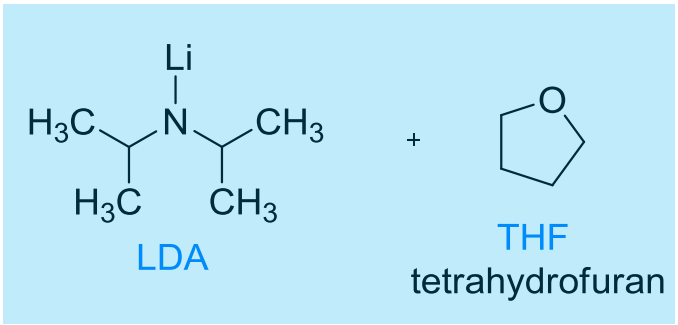
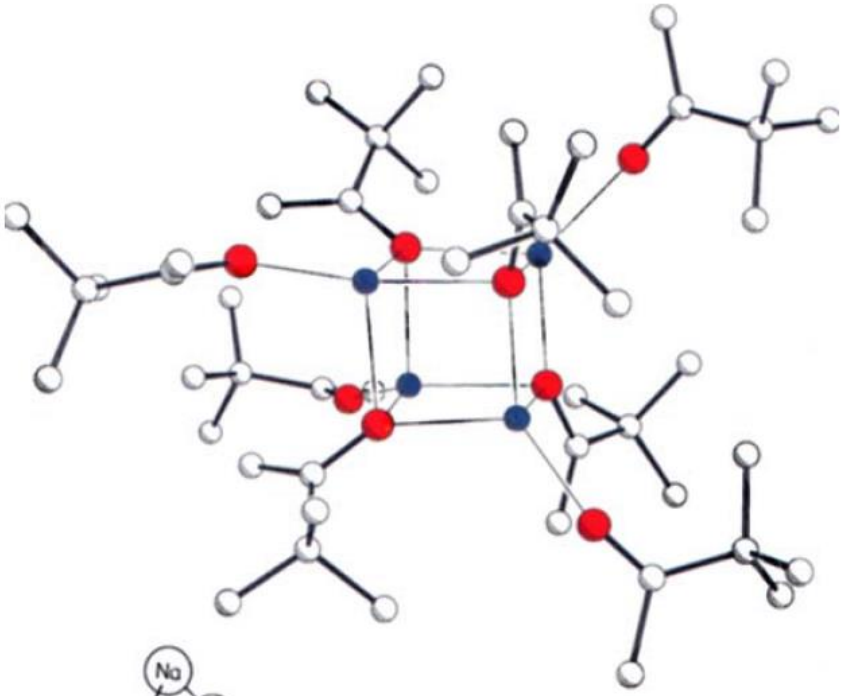
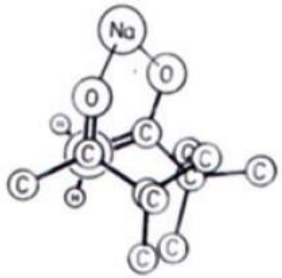
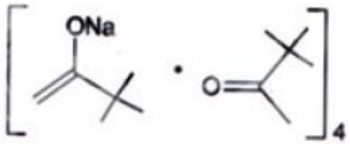
Struktura enolátů

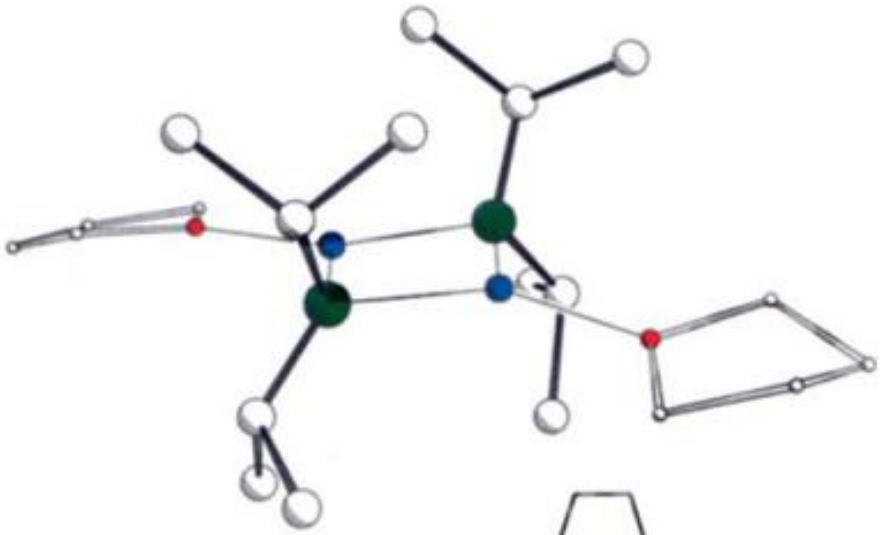


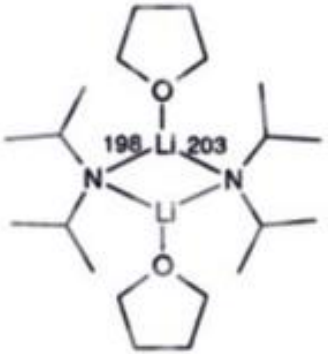






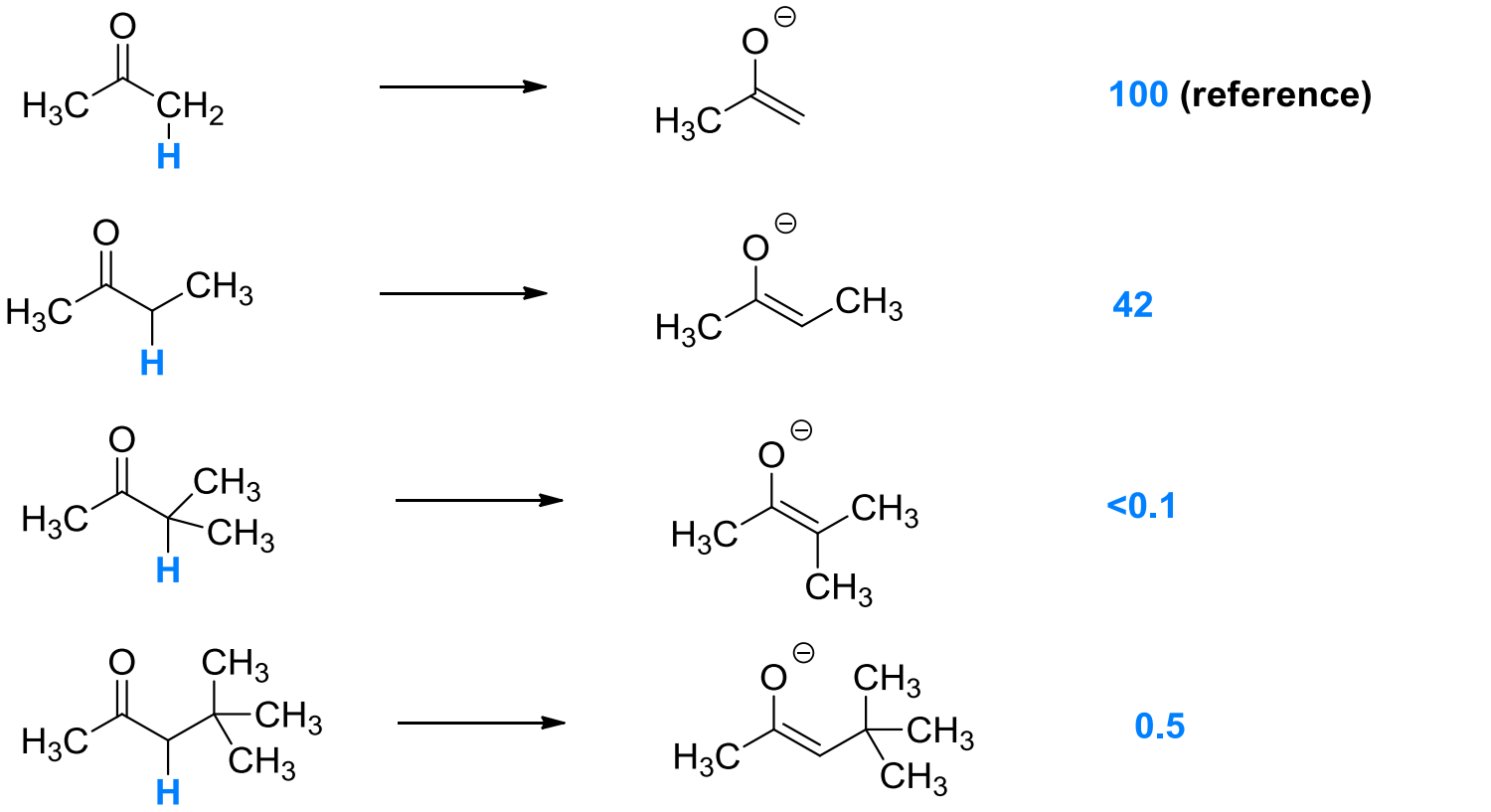




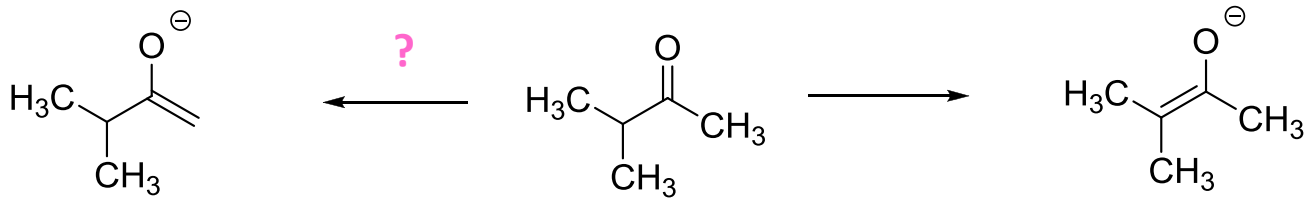


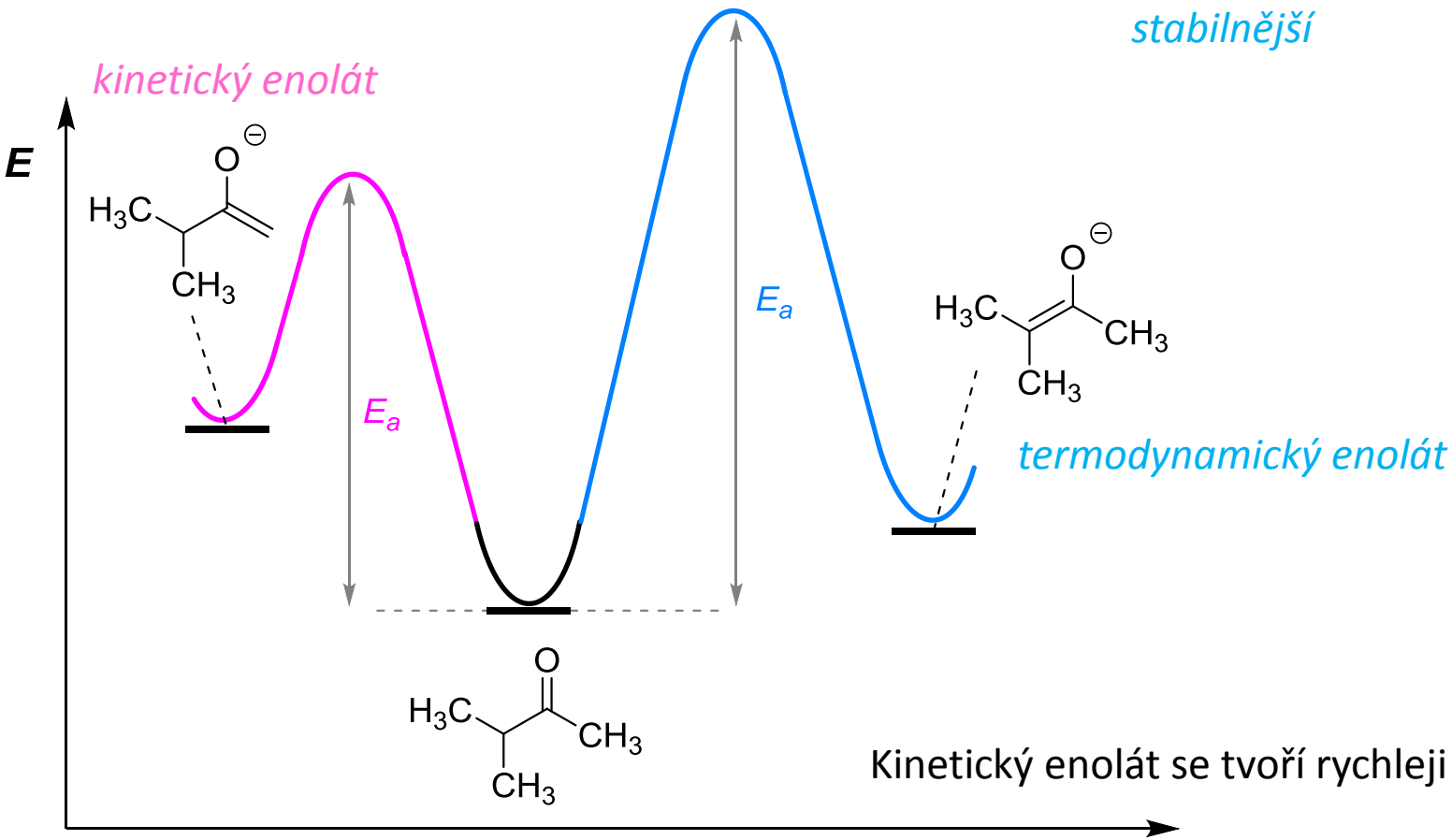
Seebach, D. *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1624.

- Rychlost deprotonace je citlivá na sterické efekty



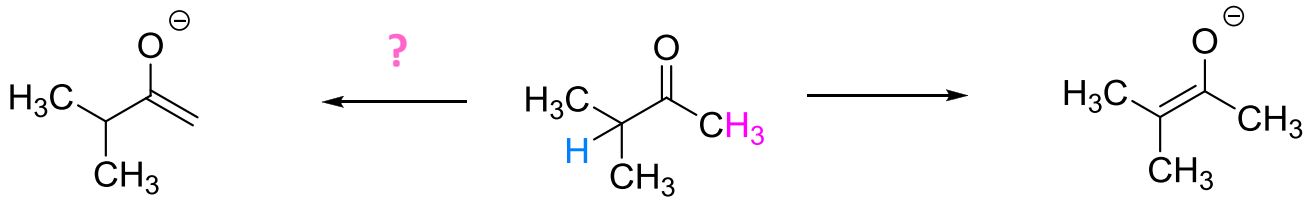
- Regioselektivita enolizace : tvorba kinetického enolátu



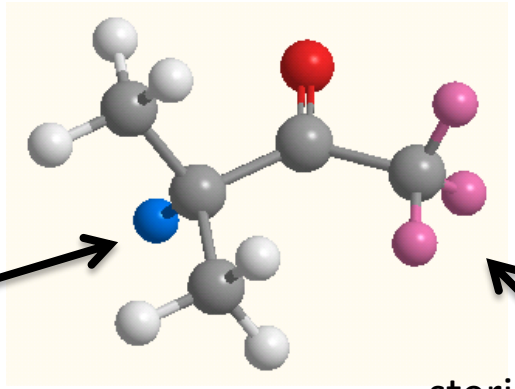


Příprava enolátů

- Regioselektivita enolizace : tvorba kinetického enolátu



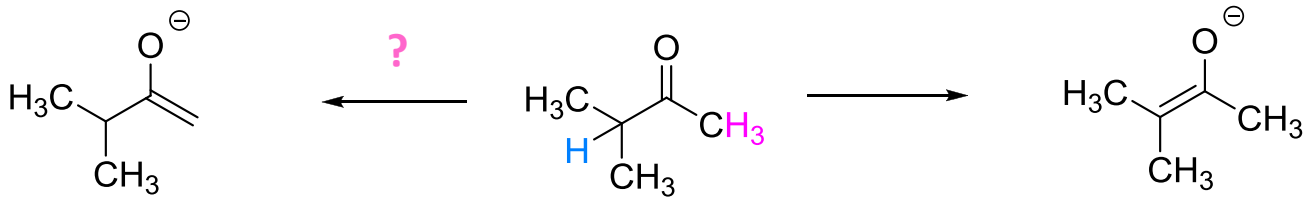
termodynamicky stabilnější

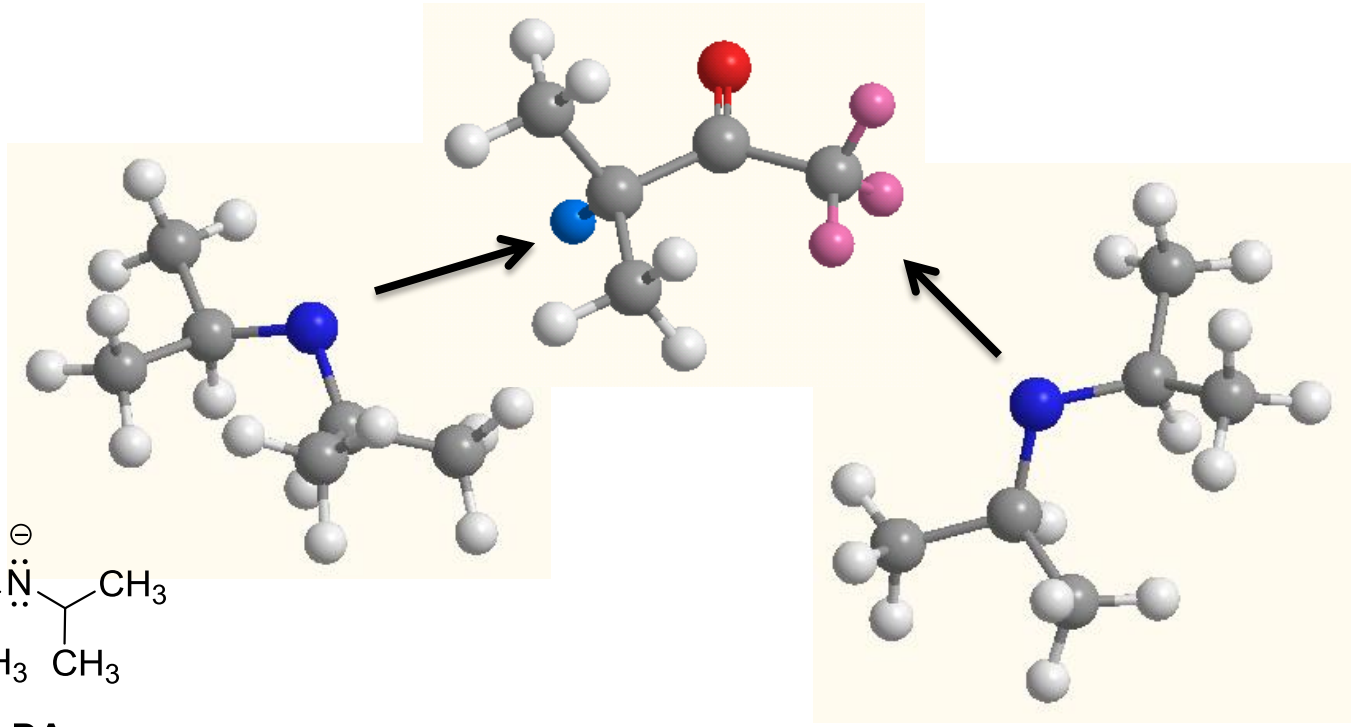


méně dostupný vodík
(sterický bráněné)

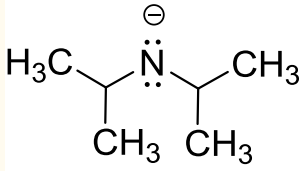
stericky dostupnější vodíky
(+ statistický argument)

- Regioselektivita enolizace : tvorba kinetického enolátu



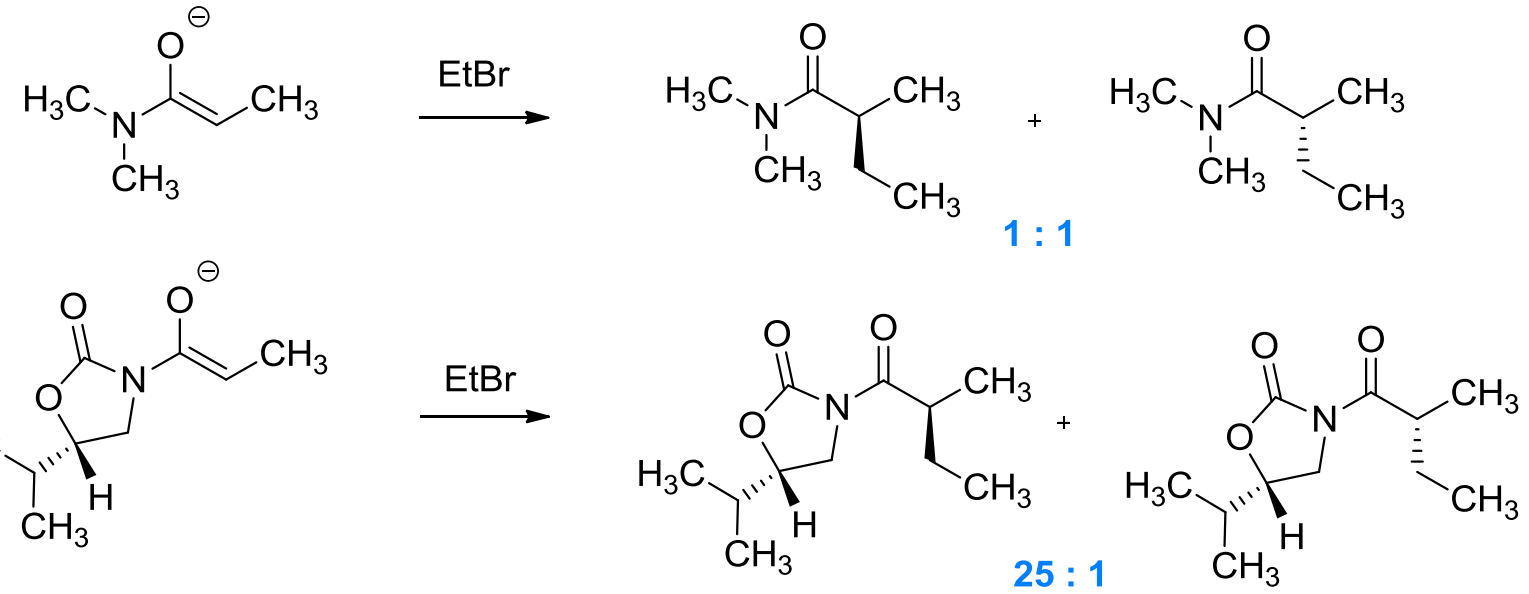


LDA
Lithium **d**iisopropyl**a**mid

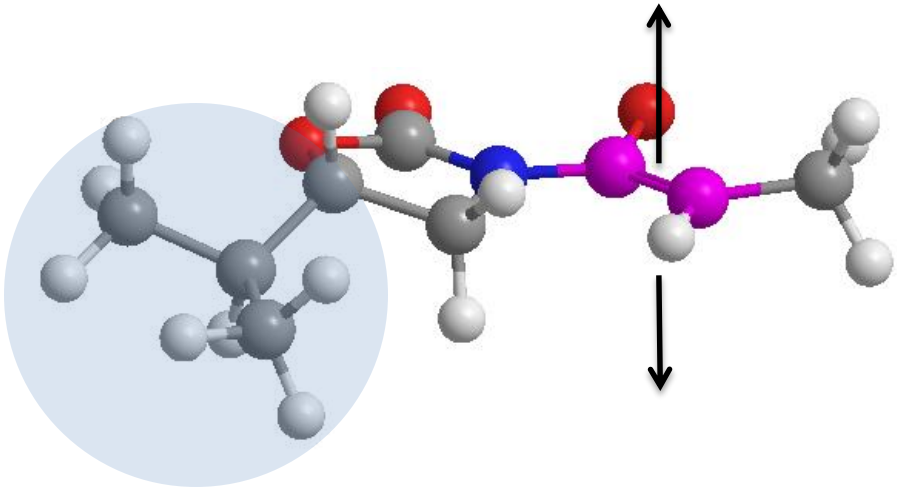


LDA
Lithium **d**iisopropyl**a**mid

- Stereoselektivní alkylace



anti vůči objemnému isopropyl substituentu



Přítomné stereocentrum ovlivňuje tvorbu nového stereocentra: diastereoselektivita