

Typy reakcí

- Adice
- Eliminace
- Substituce
- Přesmyky

Zákonitosti reaktivity

Salemova-Klopmanova rovnice

$$\Delta E = \underbrace{-q_r q_s \frac{\Gamma}{\varepsilon} + \Delta \text{solv.}}_{\text{charge/charge interactions}} + \underbrace{\sum_{\substack{m \\ \text{occ}}} \sum_{\substack{n \\ \text{unocc}}} \left[\frac{2(c_r^m)^2 (c_s^n)^2 \beta^2}{E_m^* - E_n^*} \right]}_{\text{FMO/FMO interactions}}$$

ΔE = energy change on interaction of species Γ with species S

q = total initial charges

Γ = Coulomb repulsion term

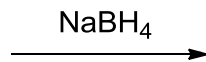
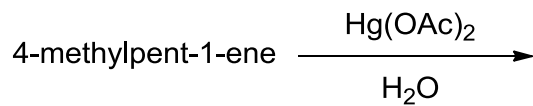
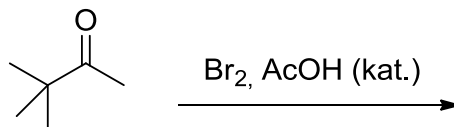
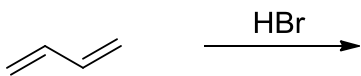
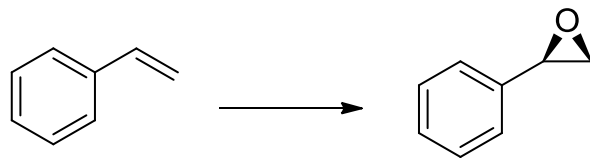
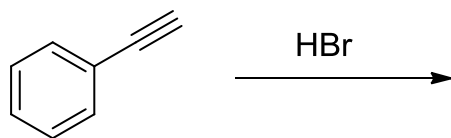
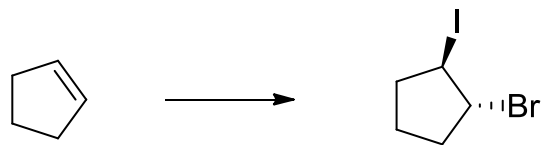
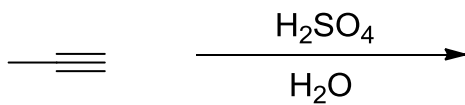
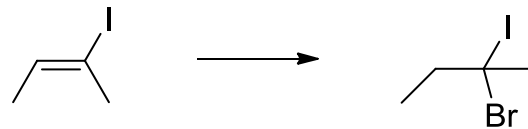
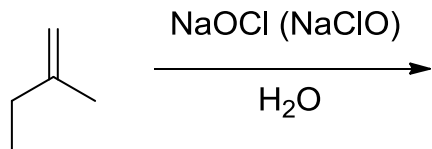
ε = local dielectric constant

$\Delta \text{solv.}$ = solvation and desolvation

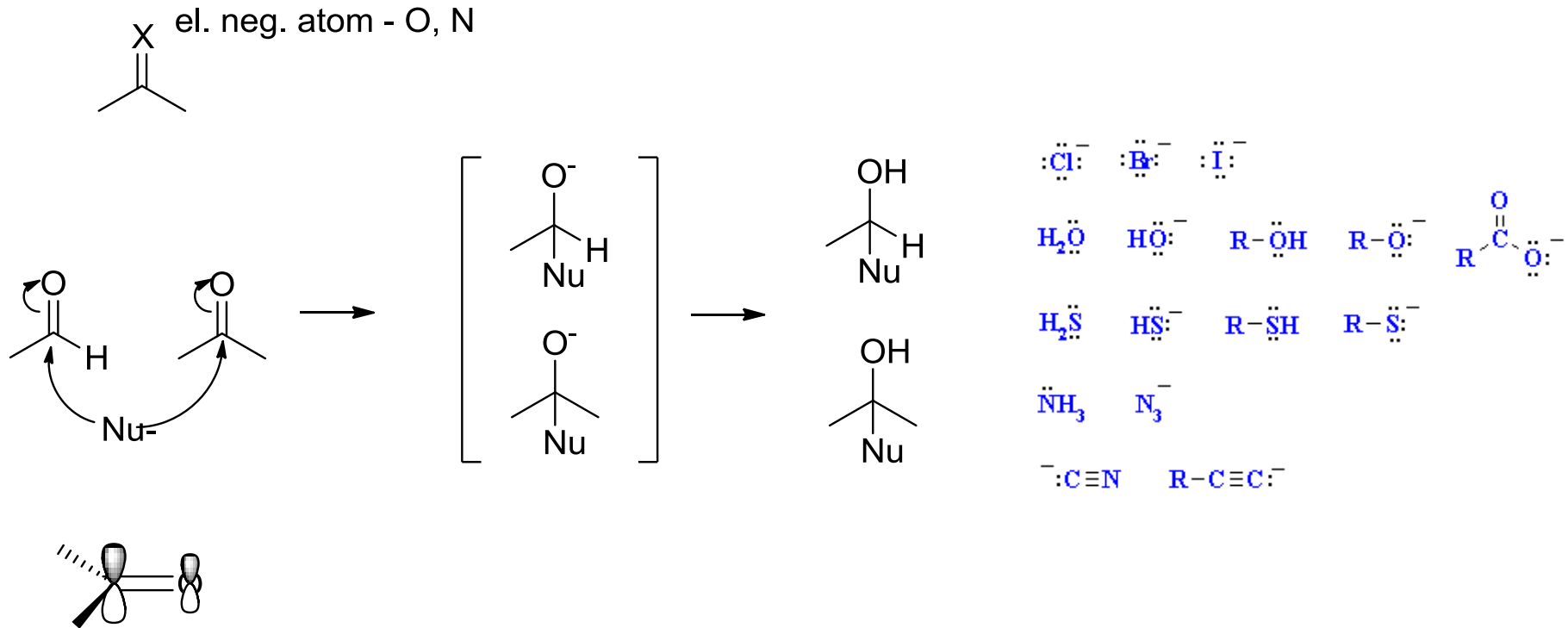
c_r = coefficient of orbital Γ

β = resonance integral

E_m = energy of occupied frontier molecular orbital m

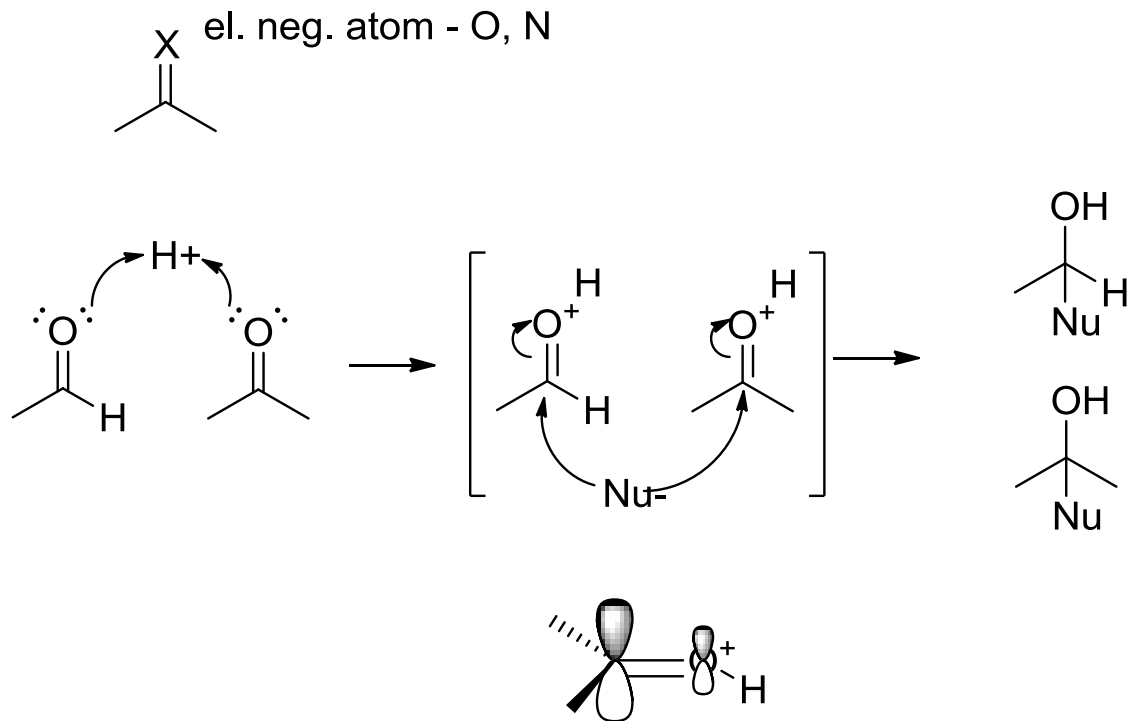


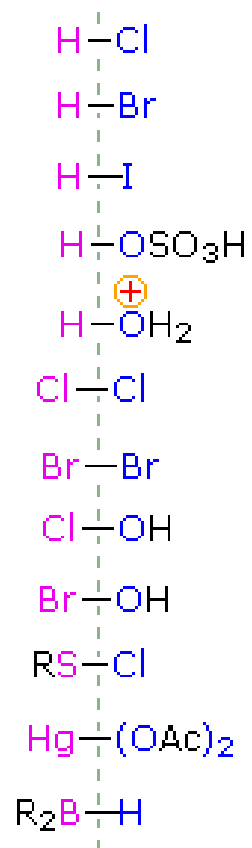
Adice na polarizovanou vazbu



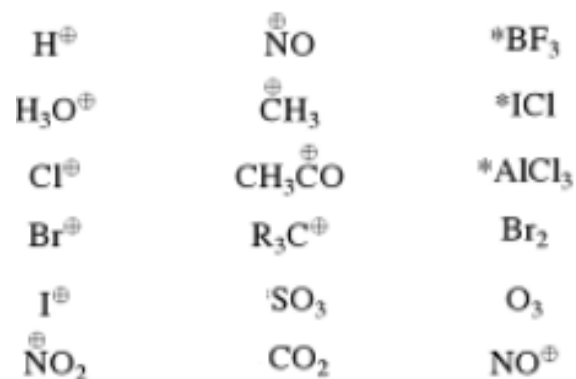
Adice na polarizovanou vazbu

- Kyselá katalýza:

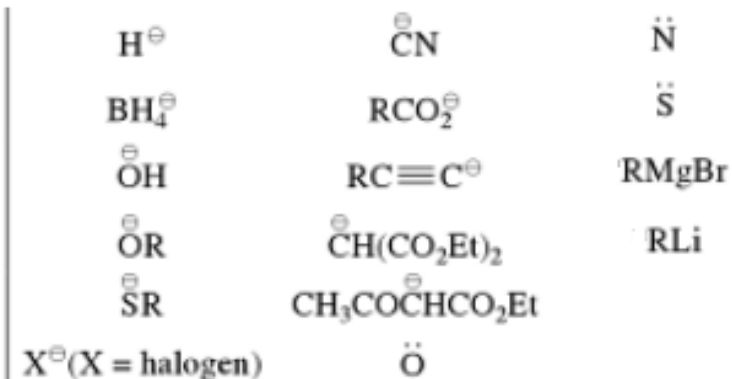


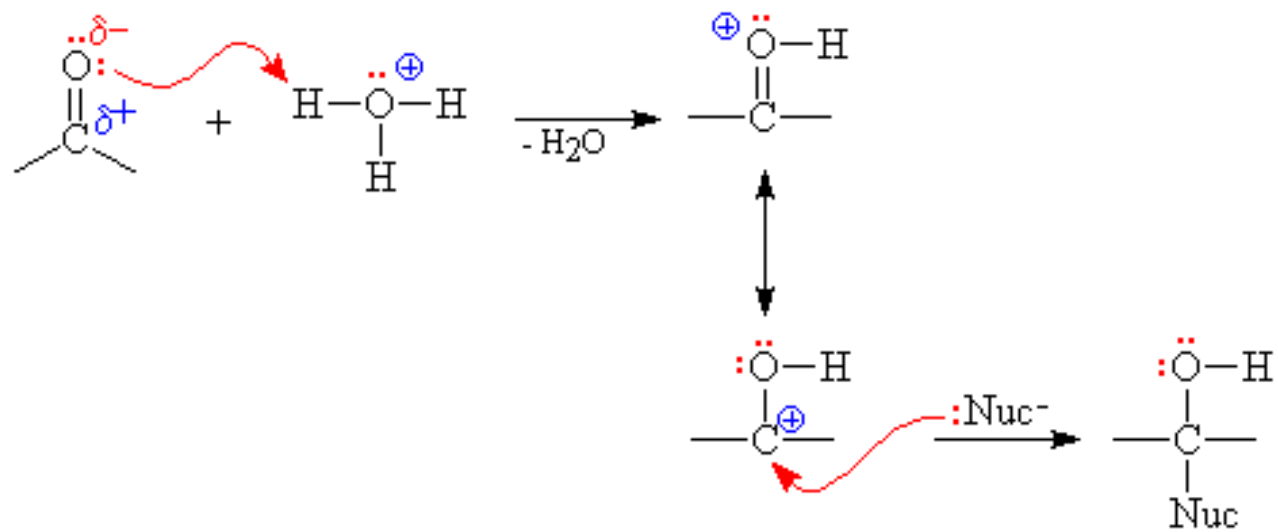
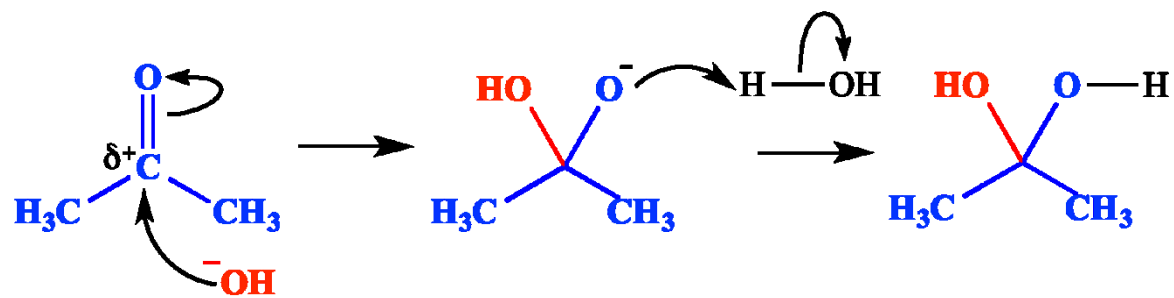


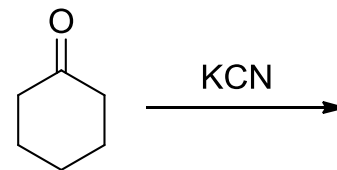
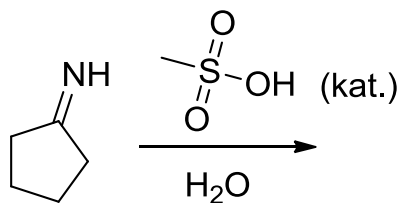
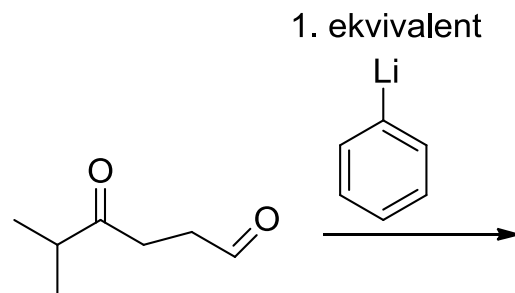
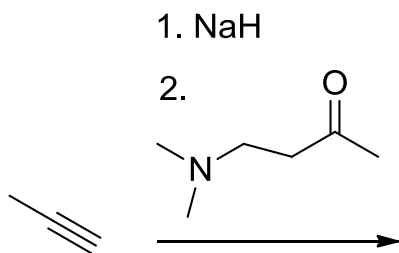
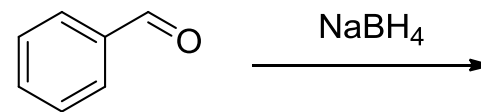
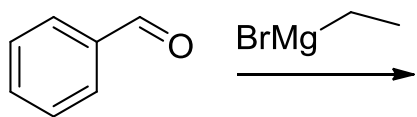
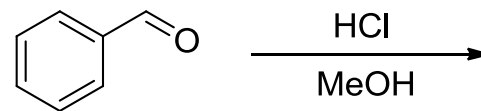
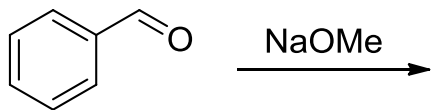
Electrophiles



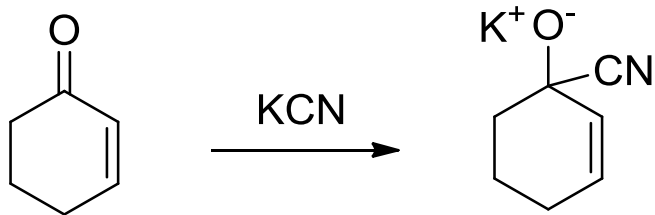
Nucleophiles





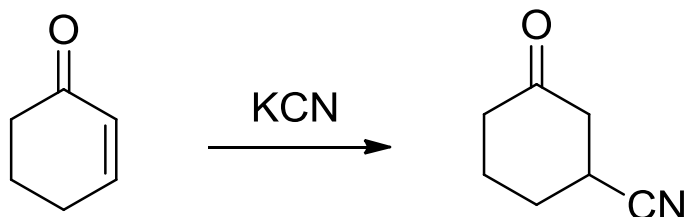


| Tvrdé | Měkké |
|--|-------------------------------------|
| F^- , OH^- , RO^- , SO_4^{2-} , Cl^- , N_3^- , CN^- | I^- , RS^- , RSe^- , S^{2-} |
| H_2O , ROH , ROR' , $RCOR'$, RNH_2 , $RR'NH$, NH_3 , $RMgBr$, RLi | RSH , RSR' , R_3P |
| | alkeny, aromáty ; |



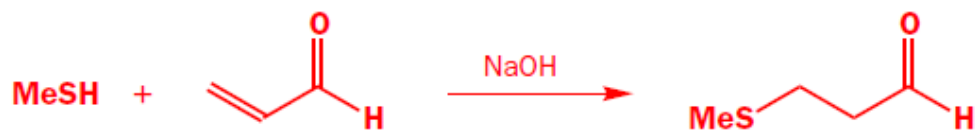
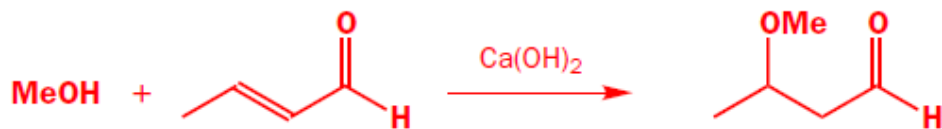
Adice na karbonyl

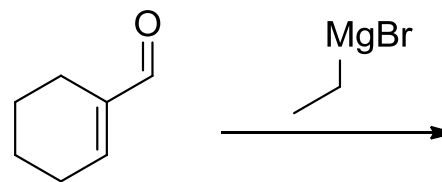
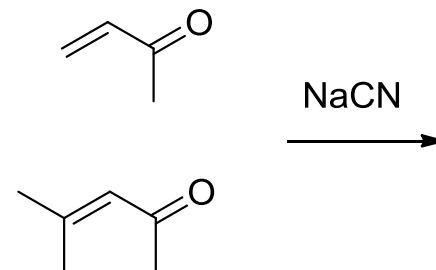
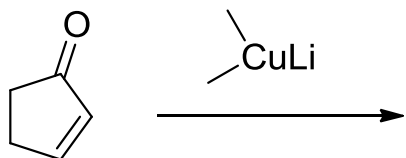
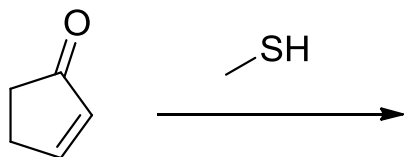
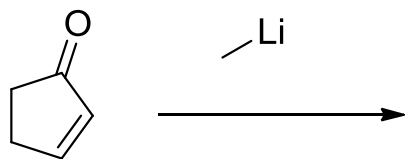
- kinetická kontrola, nižší teplota, kratší rekační doba
- reaktivní karbonyl, chlorid, aldehyd
- stericky bráněný β -uhlík
- tvrdé nukleofily



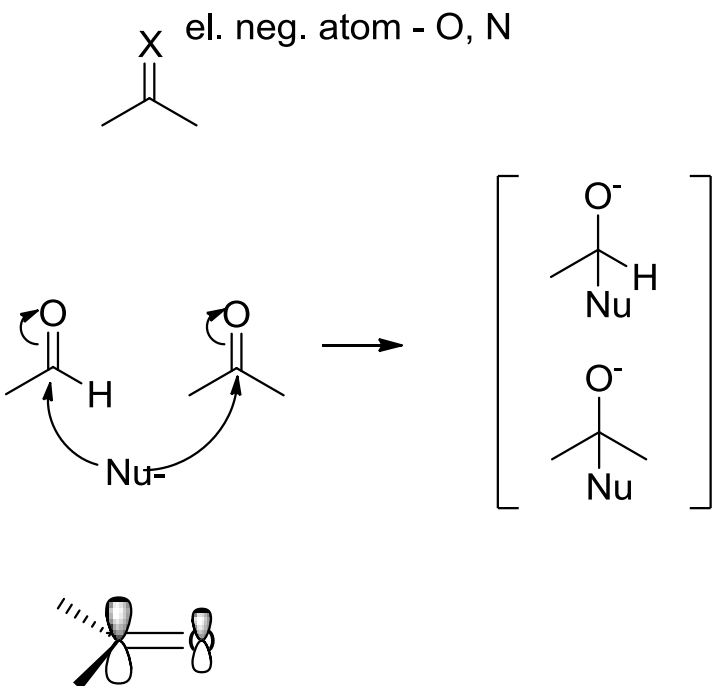
Konjugovaná adice

- termodynamická kontrola, vyšší teplota, delší reakční doba
- málo reaktivní karbonyl $C=O$
- stericky přístupný β -uhlík
- měkké nukleofily

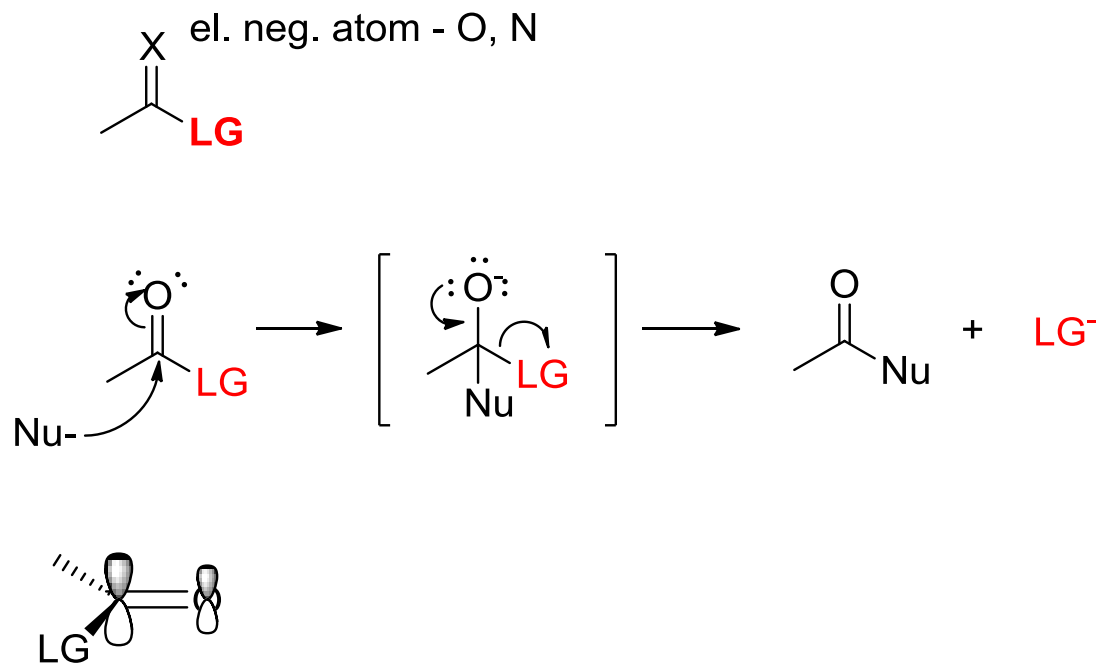




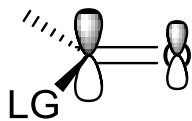
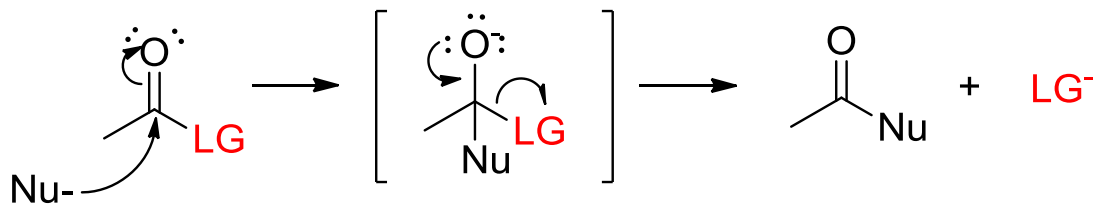
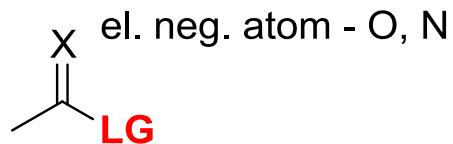
Adice na polarizovanou vazbu



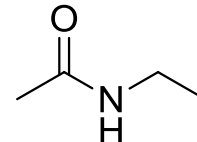
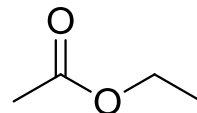
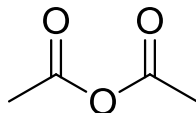
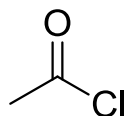
Nukleofilní sub. na karbonylu



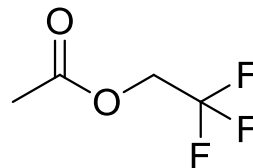
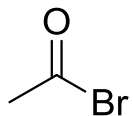
Nukleofilní sub. na karbonylu

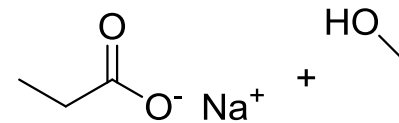
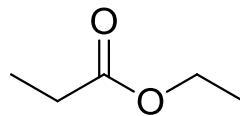
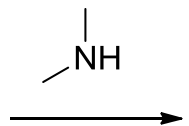
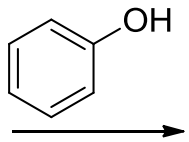
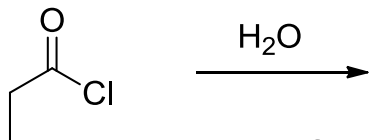


Nejreaktivnější



Nejméně reaktivní





H^+ (kat.)

