

Typy reakcí

- Adice
- Eliminace
- Substituce
- Přesmyky

Zákonitosti reaktivity

Salemova-Klopmanova rovnice

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

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

q = total initial charges

Γ = Coulomb repulsion term

ϵ = local dielectric constant

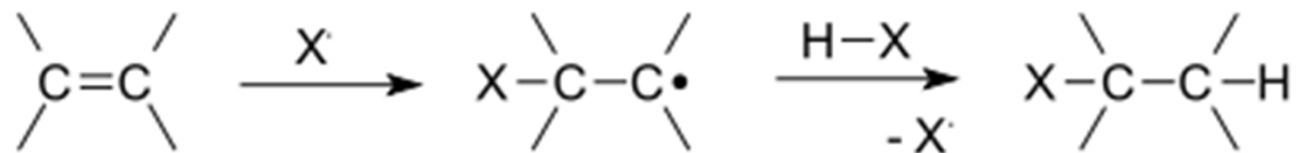
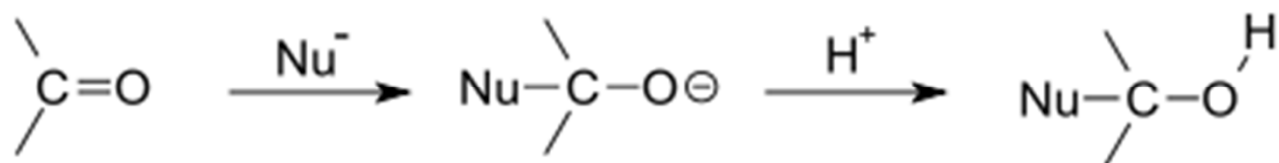
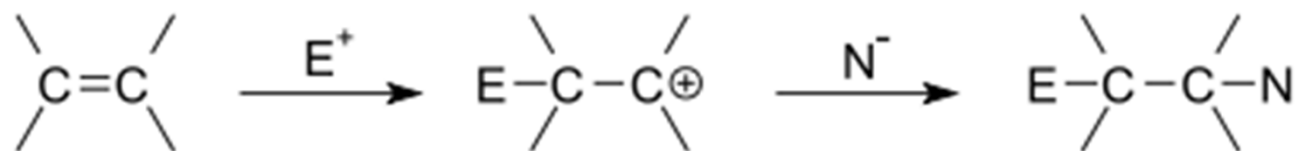
$\Delta \text{solv.}$ = solvation and desolvation

c_r = coefficient of orbital Γ

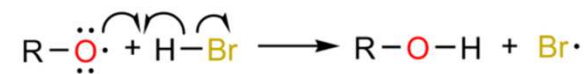
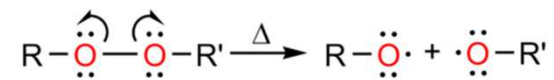
β = resonance integral

E_m = energy of occupied frontier molecular orbital m

Adiční reakce



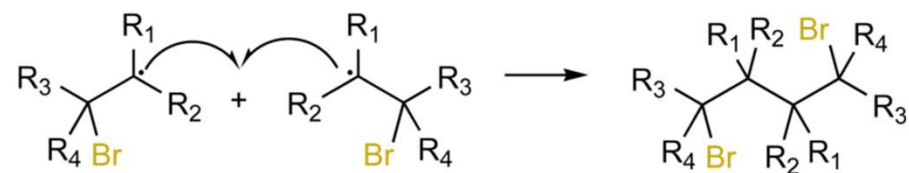
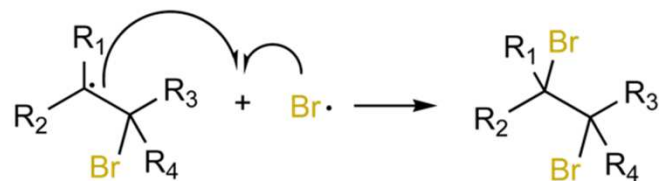
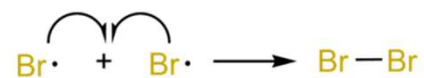
Initiation



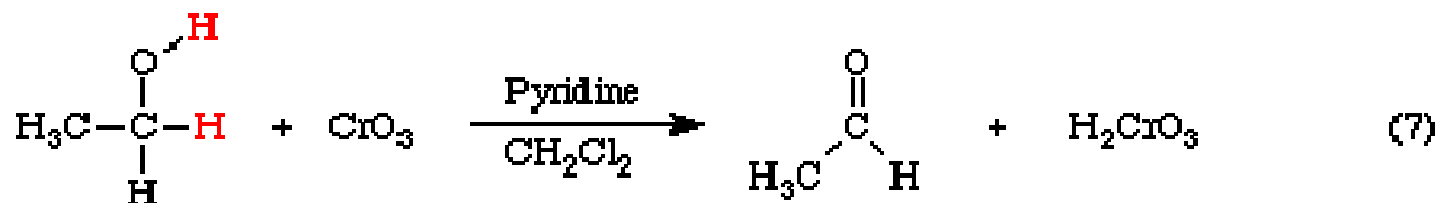
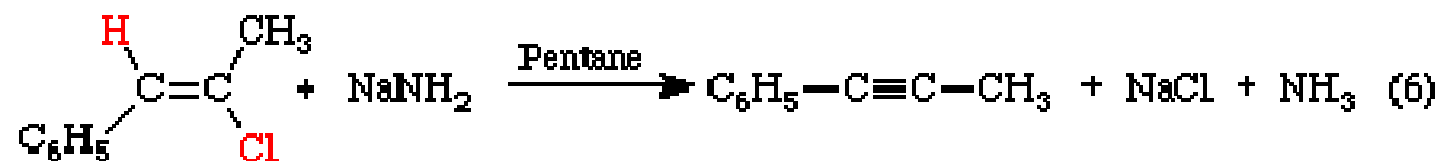
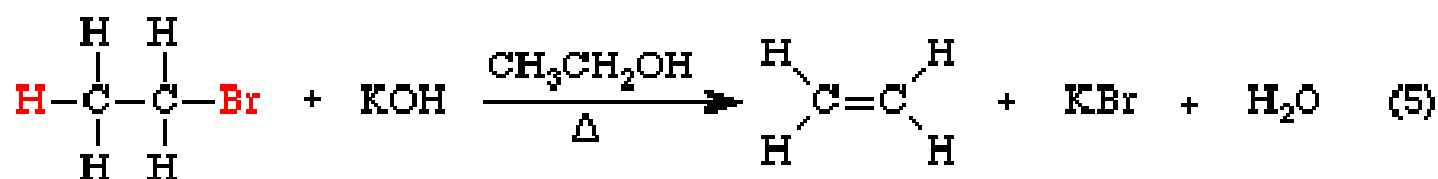
Propagation



Termination

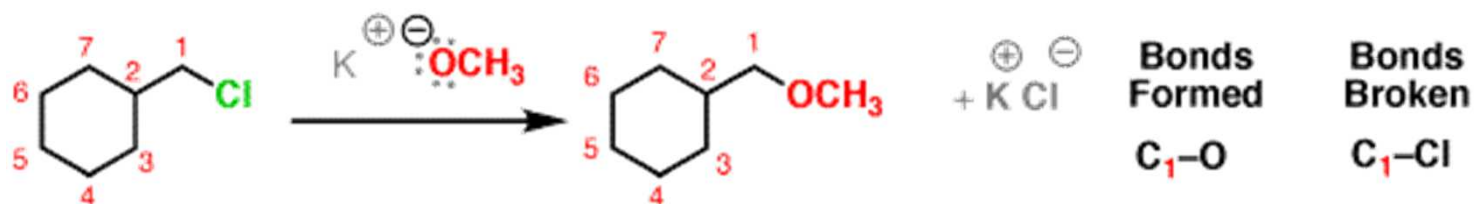


Eliminace

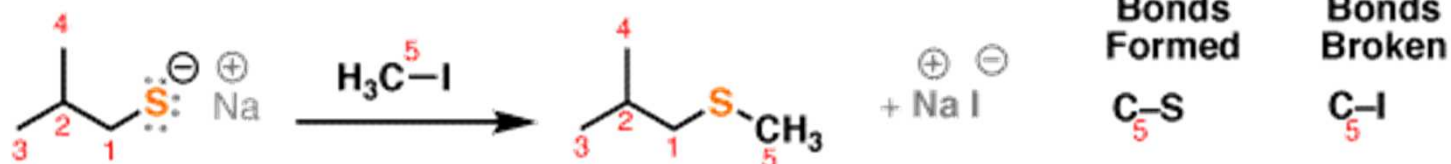


Substitution

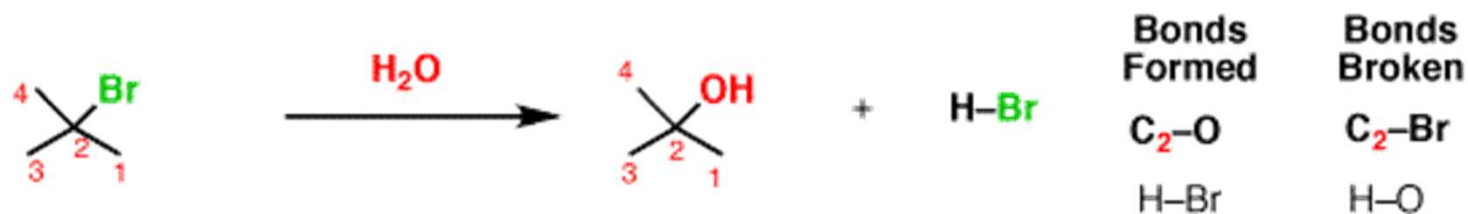
Examples of substitution reactions



numbering is not IUPAC

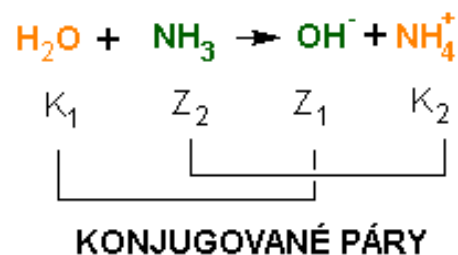


numbering is not IUPAC



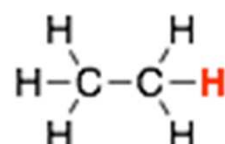
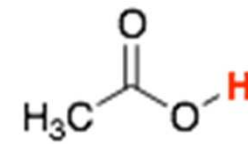
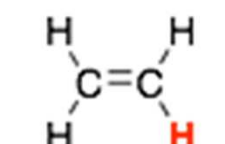
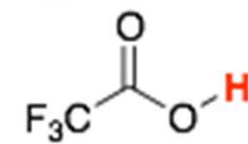
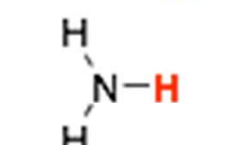
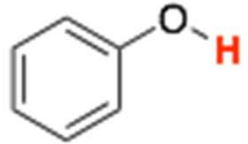
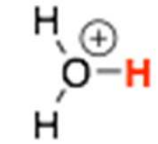
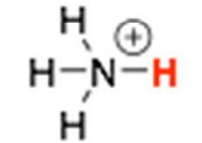
note here than an acid-base reaction also occurs!

Acido-bazické reakce

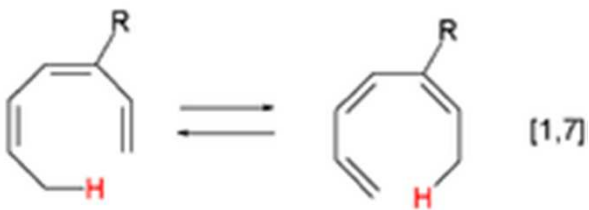
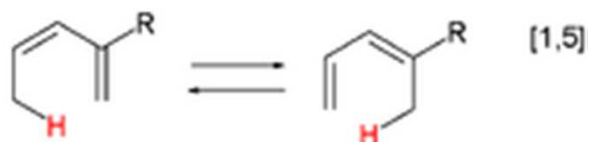
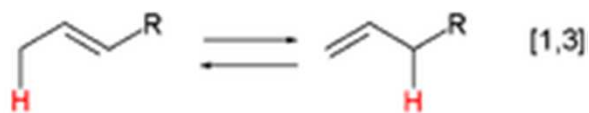
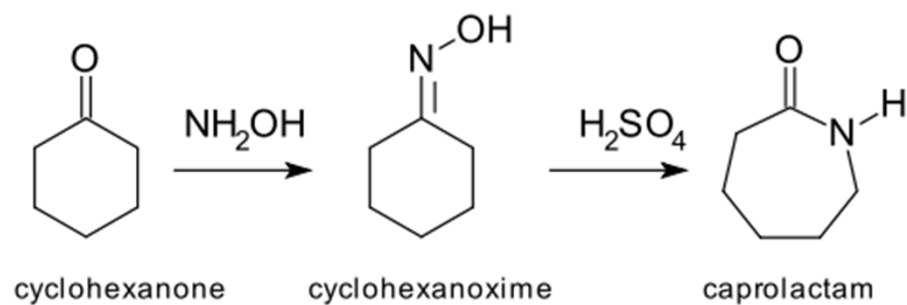


Acid-Base Reaction	Conjugate Acids	Conjugate Bases	K_a	pK_a
$\text{HBr} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^{(+)} + \text{Br}^{(-)}$	HBr $\text{H}_3\text{O}^{(+)}$	$\text{Br}^{(-)}$ H_2O	10^5	-5
$\text{CH}_3\text{CO}_2\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^{(+)} + \text{CH}_3\text{CO}_2^{(-)}$	$\text{CH}_3\text{CO}_2\text{H}$ $\text{H}_3\text{O}^{(+)}$	$\text{CH}_3\text{CO}_2^{(-)}$ H_2O	$1.77 \cdot 10^{-5}$	4.75
$\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^{(+)} + \text{C}_2\text{H}_5\text{O}^{(-)}$	$\text{C}_2\text{H}_5\text{OH}$ $\text{H}_3\text{O}^{(+)}$	$\text{C}_2\text{H}_5\text{O}^{(-)}$ H_2O	10^{-16}	16
$\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^{(+)} + \text{NH}_2^{(-)}$	NH_3 $\text{H}_3\text{O}^{(+)}$	$\text{NH}_2^{(-)}$ H_2O	10^{-34}	34

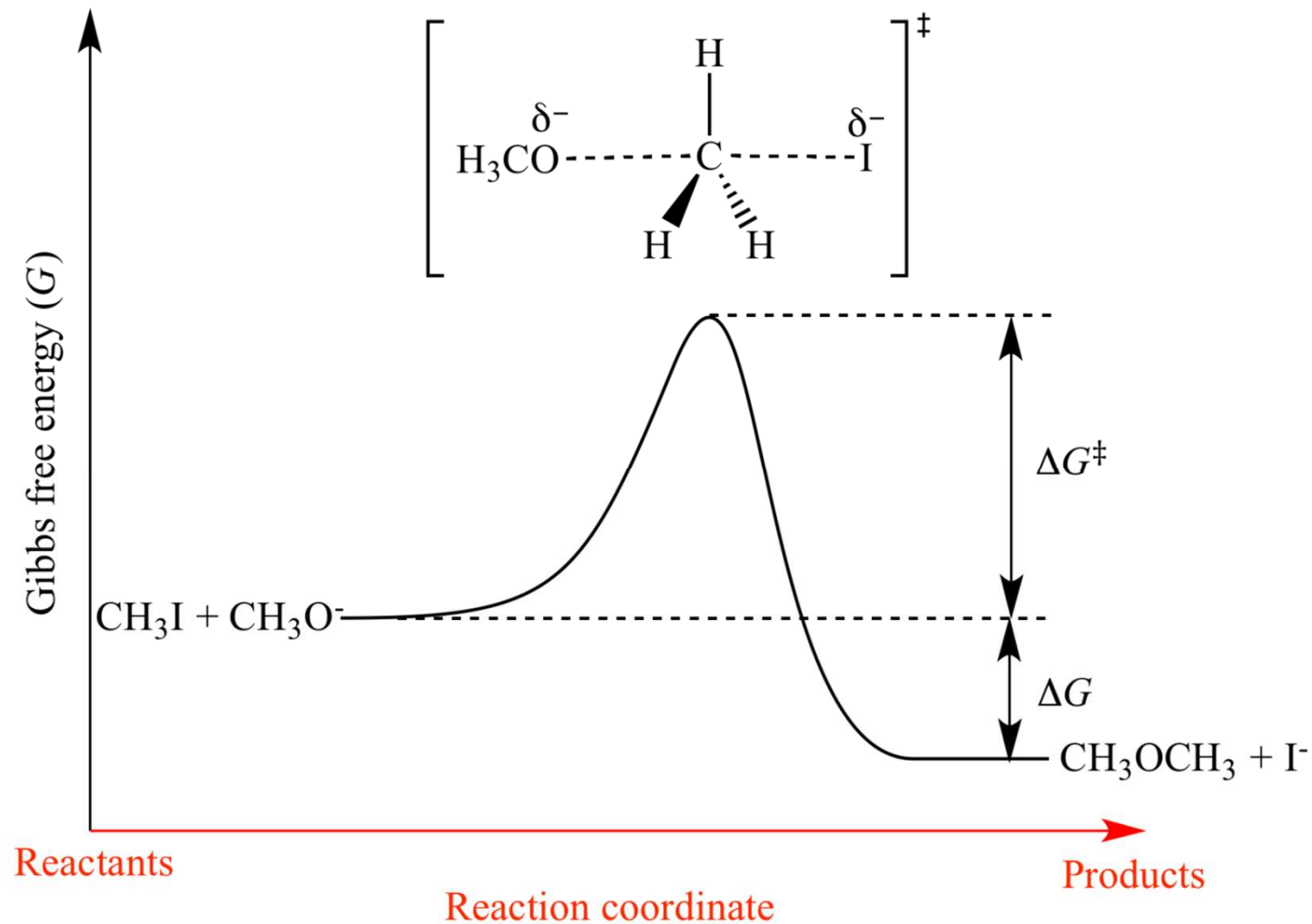
pKa tabulka

acid	pKa (class)	acid	pKa (class)	acid	pKa (class)
	50 (SP3 carbon)	$\text{CH}_3\text{CH}_2\text{-O-H}$	16 (alcohol)		4.8 (carboxylic acid)
	44 (SP2 carbon)	H-O-H	15.7 (conj acid of NaOH)		0.2 (carboxylic acid with electroneg groups)
	38 (amine)		10 (phenol)		-2 (positive oxygen)
H-H	35 (conj acid of H^+)		9.2 (positive nitrogen)	Cl-H	-7 (H-X)
$\text{H-C}\equiv\text{C-H}$	25 (SP carbon)	H-S-H	7 (thiol)	H_2SO_4	-9 (strong acid)

Přesmyky



Kinetika/termodinamika

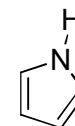
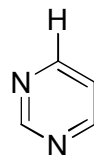
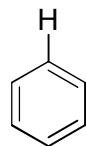
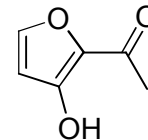
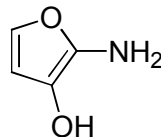
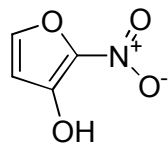
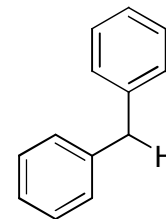
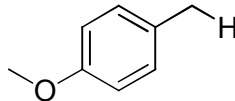
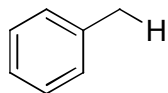
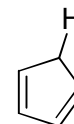
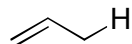
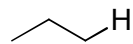


$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

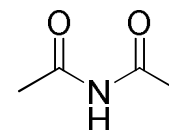
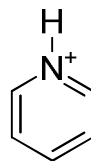
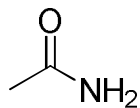
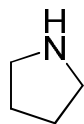
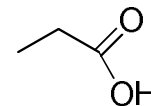
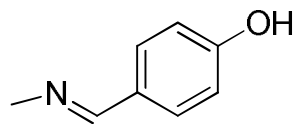
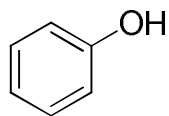
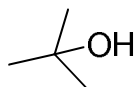
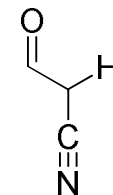
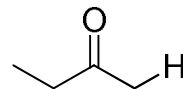
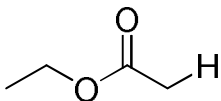
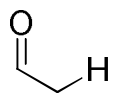
$$\Delta G_i = -RT \ln K$$

$$k = Ae^{\frac{-E_a}{RT}}$$

Seřadte trojice dle kyselosti

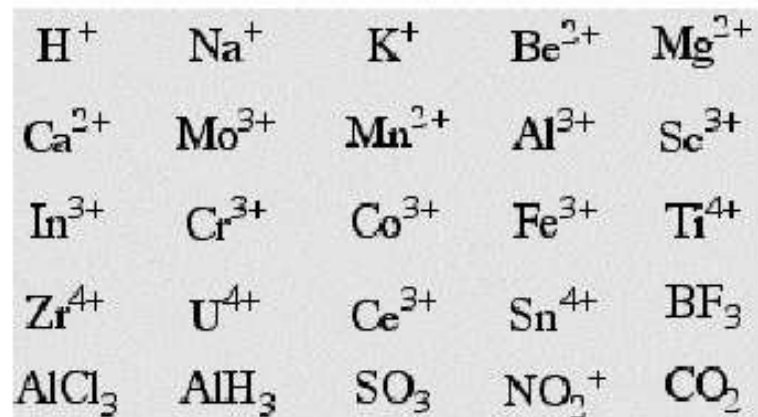


Seřadte čtveřice dle kyselosti

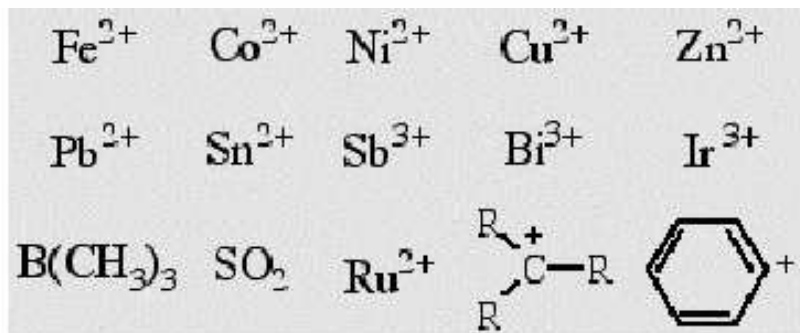


Pearson's HSAB Species

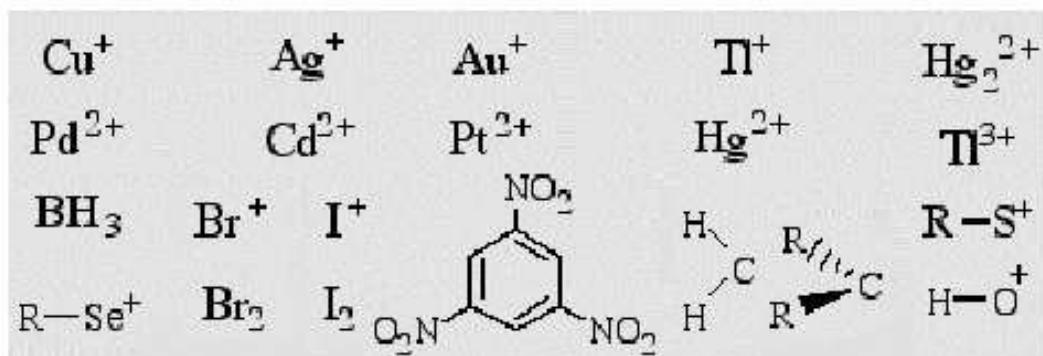
Pearson's Hard Lewis Acids:



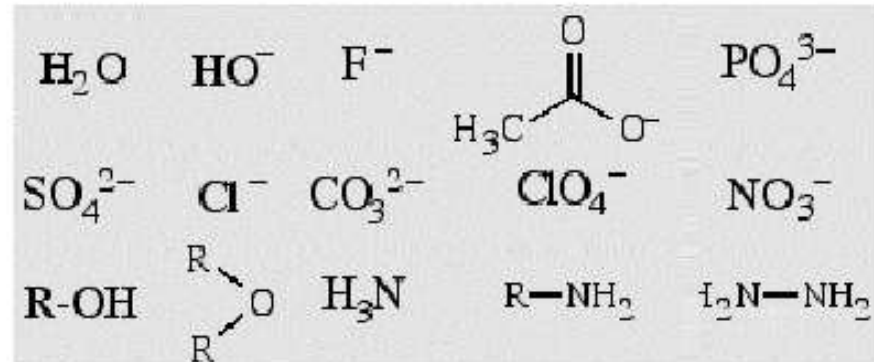
Pearson's Borderline Lewis Acids:



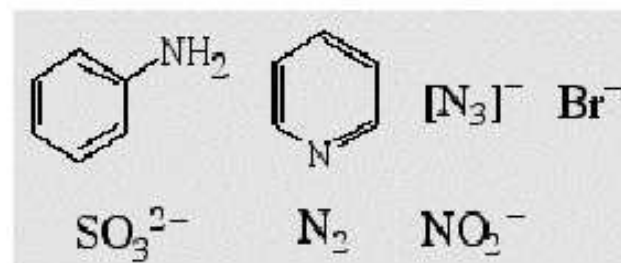
Pearson's Soft Lewis Acids:



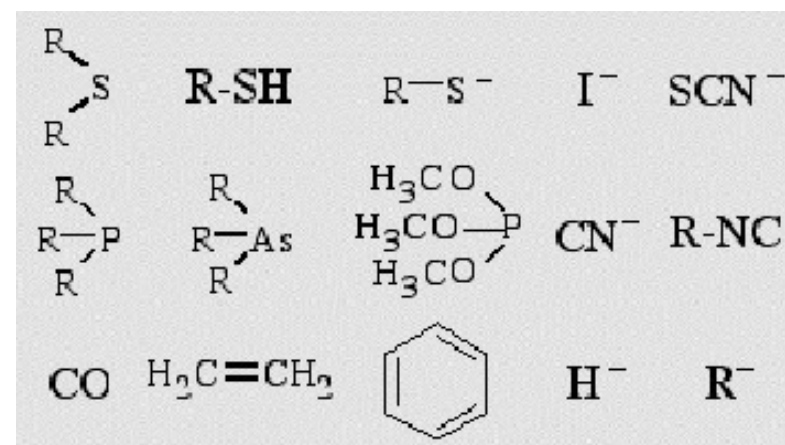
Pearson's Hard Lewis Bases:



Pearson's Borderline Lewis Bases:



Pearson's Soft Lewis Bases:



H^+ , Li^+ , Na^+ , K^+
 Be^{2+} , Mg^{2+} , Ca^{2+} , Sr^{2+} , Sn^{2+}
 Al^{3+} , Se^{3+} , Ga^{3+} , In^{3+} , La^{3+}
 Cr^{3+} , Co^{3+} , Fe^{3+} , As^{3+} , Ir^{3+}
 Si^{4+} , Ti^{4+} , Zr^{4+} , Th^{4+} , Pu^{4+} , VO^{2+}
 UO_2^{2+} , $(CH_3)_2Sn^{2+}$
 $BeMe_2$, BF_3 , BCl_3 , $B(OR)_3$
 $Al(CH_3)_3$, $Ga(CH_3)_3$, $In(CH_3)_3$
 RPO_2^+ , $ROPO_2^+$
 RSO_2^+ , $ROSO_2^+$, SO_3
 I^{7+} , I^{5+} , Cl^{7+}
 R_3C^+ , RCO^+ , CO_2 , NC^+

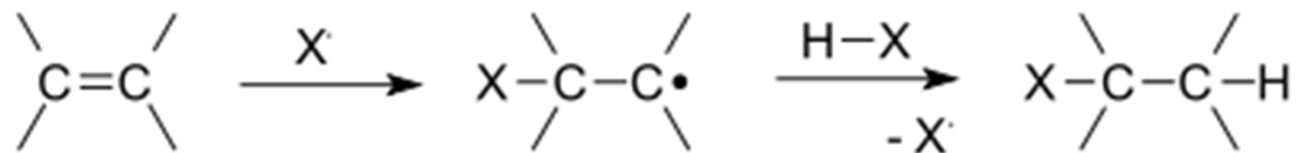
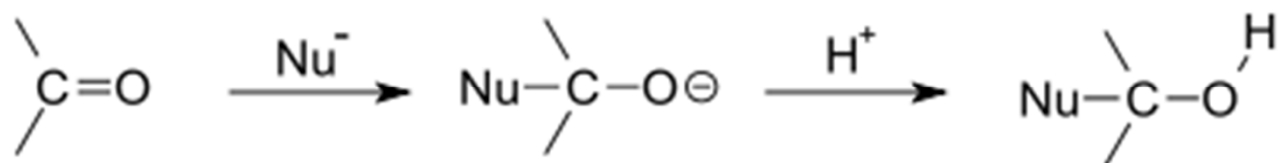
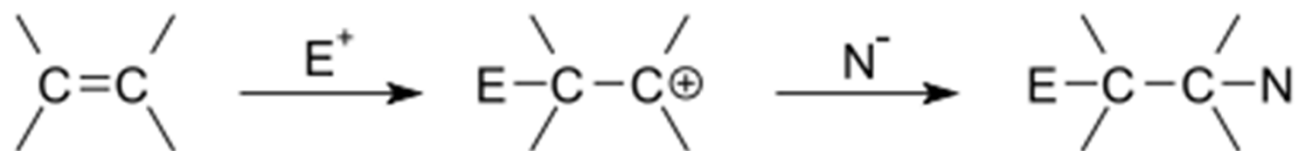
Cu^+ , Ag^+ , Au^+ , Tl^+ , Hg^+ , Cs^+
 Pd^{2+} , Cd^{2+} , Pt^{2+} , Hg^{2+}
 CH_3Hg^+
 Tl^{3+} , $Tl(CH_3)_3$, RH_3
 RS^+ , RSe^+ , RTe^+
 I^+ , Br^+ , HO^+ , RO^+
 I_2 , Br_2 , INC , etc.
Trinitrobenzene, etc.
Chloranil, quinones, etc.
Tetracyanoethylene, etc.
 O , Cl , Br , I , R_3C
 M^0 (metal atoms)
Bulk metals

HX (hydrogen-bonding molecules)

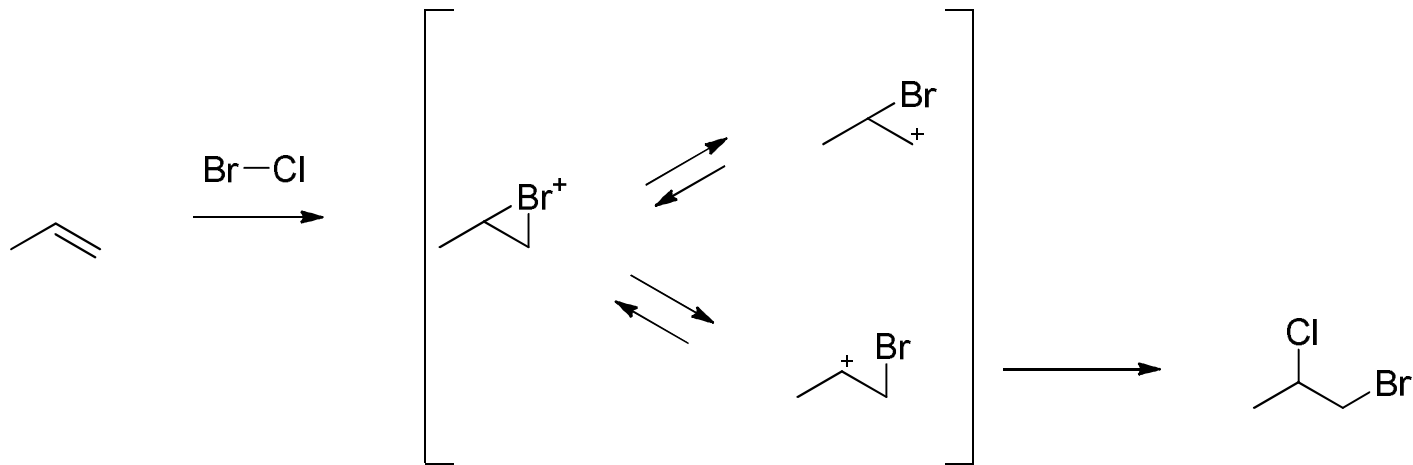
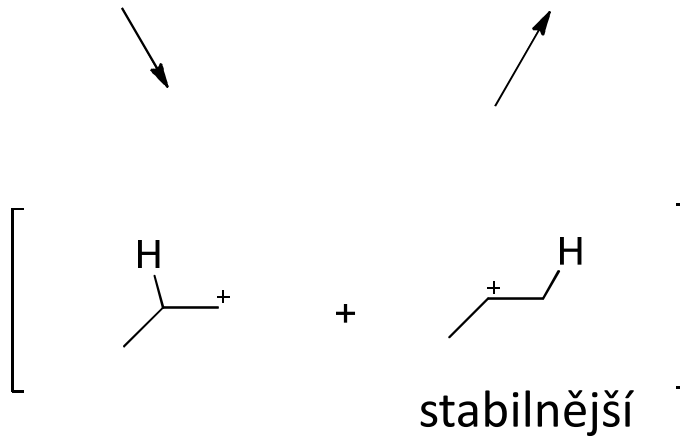
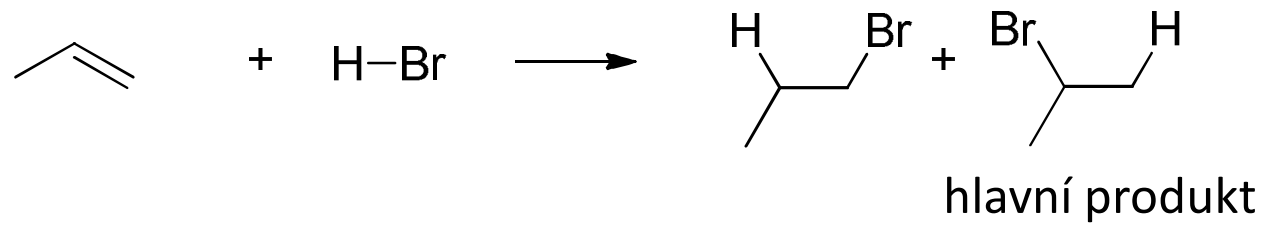
Borderline

Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Pb^{2+}
 $B(CH_3)_3$, SO_2 , NO^+

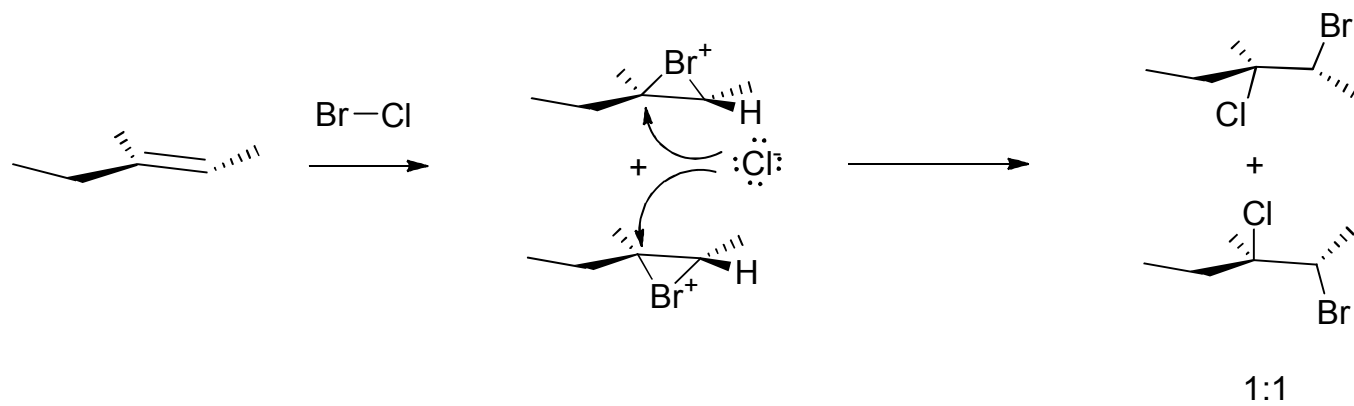
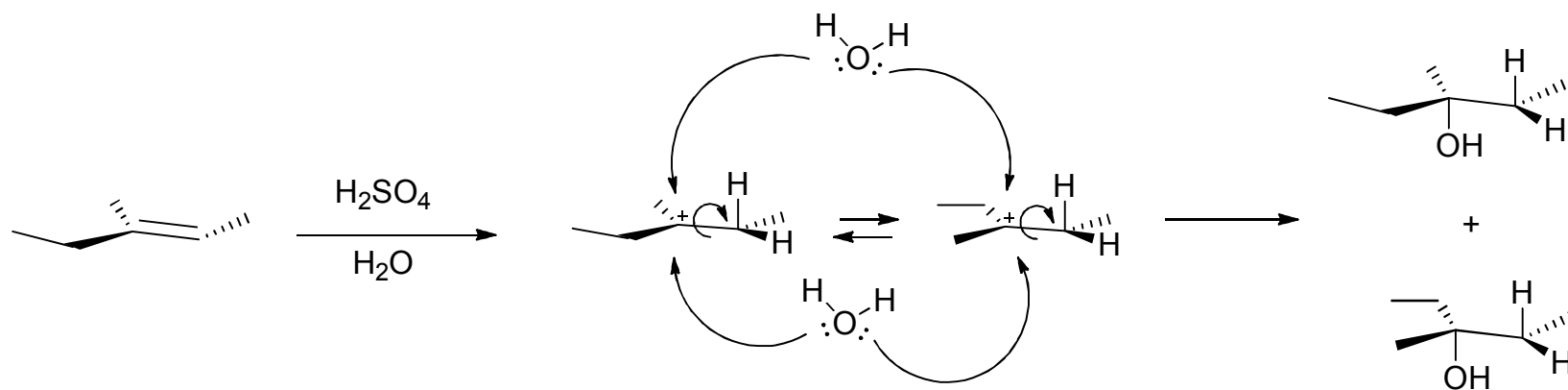
Adice



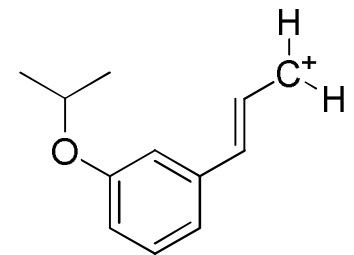
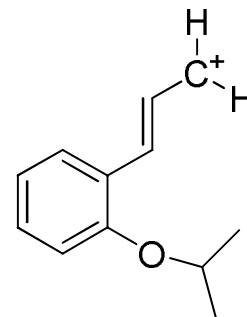
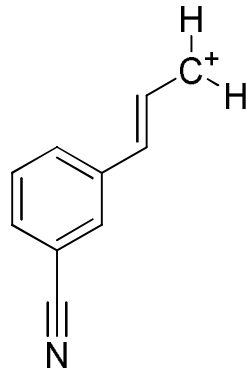
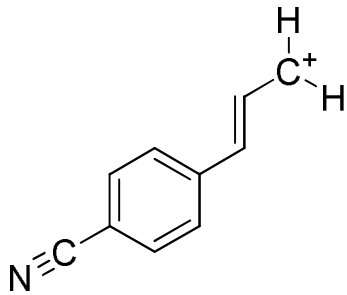
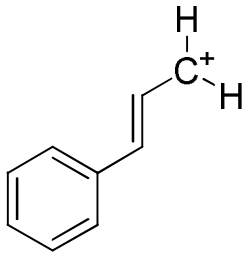
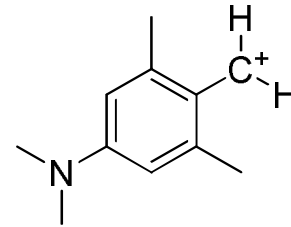
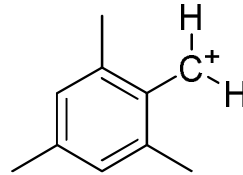
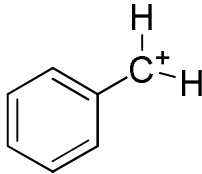
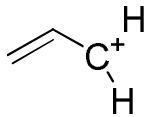
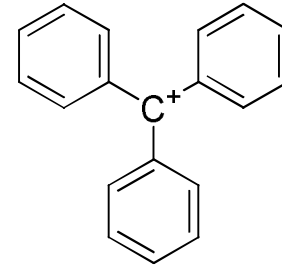
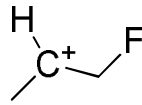
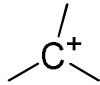
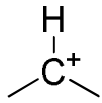
Adice

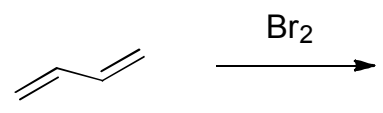
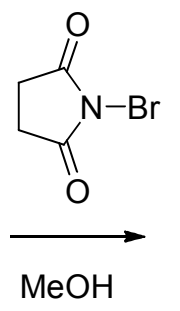
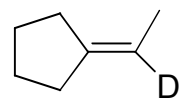
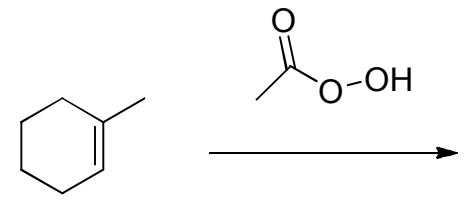
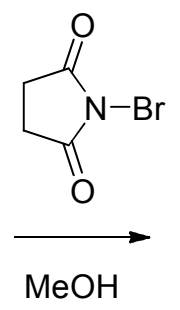
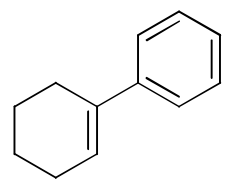
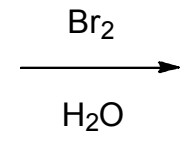
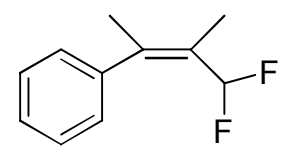
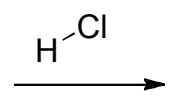
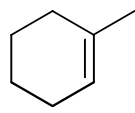


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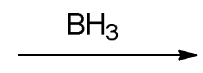


Seřadte dle stability

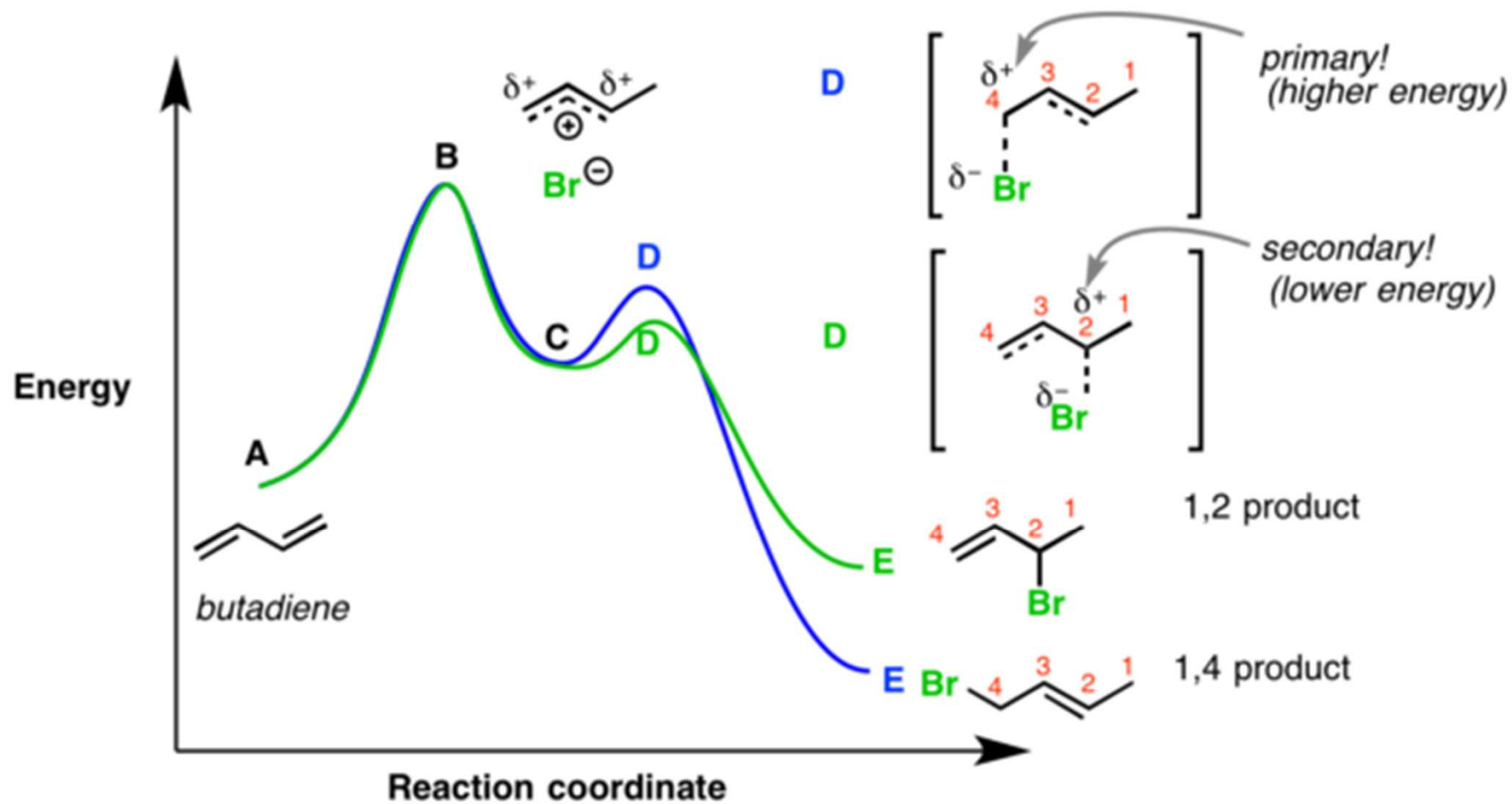


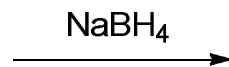
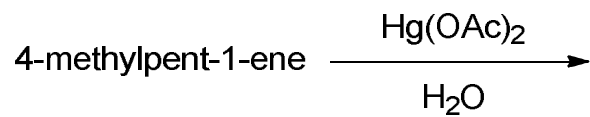
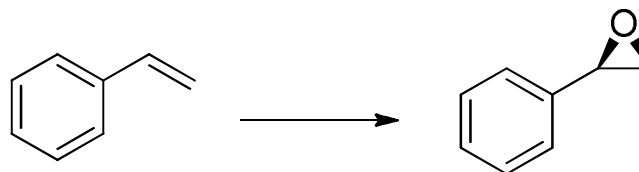
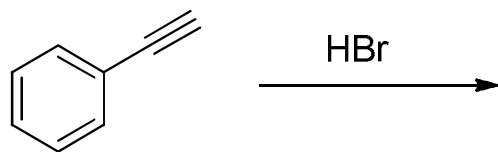
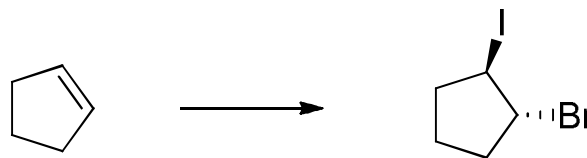
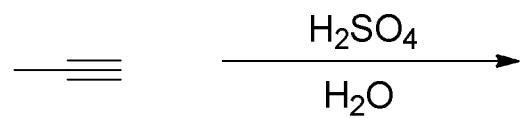
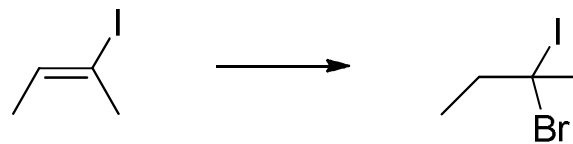
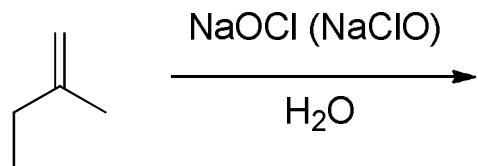


4-methoxy-2-methylbut-1-ene

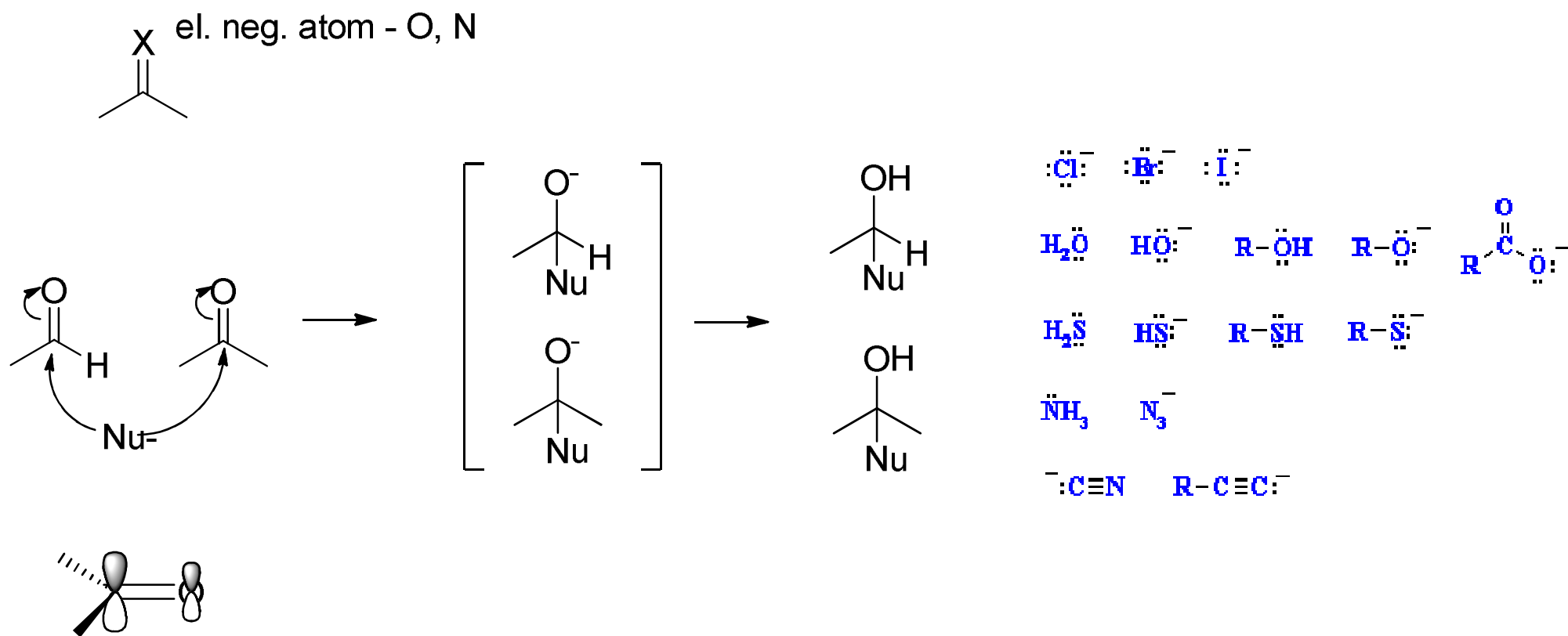


Energy Diagram for 1,2- versus 1,4- additions to butadiene



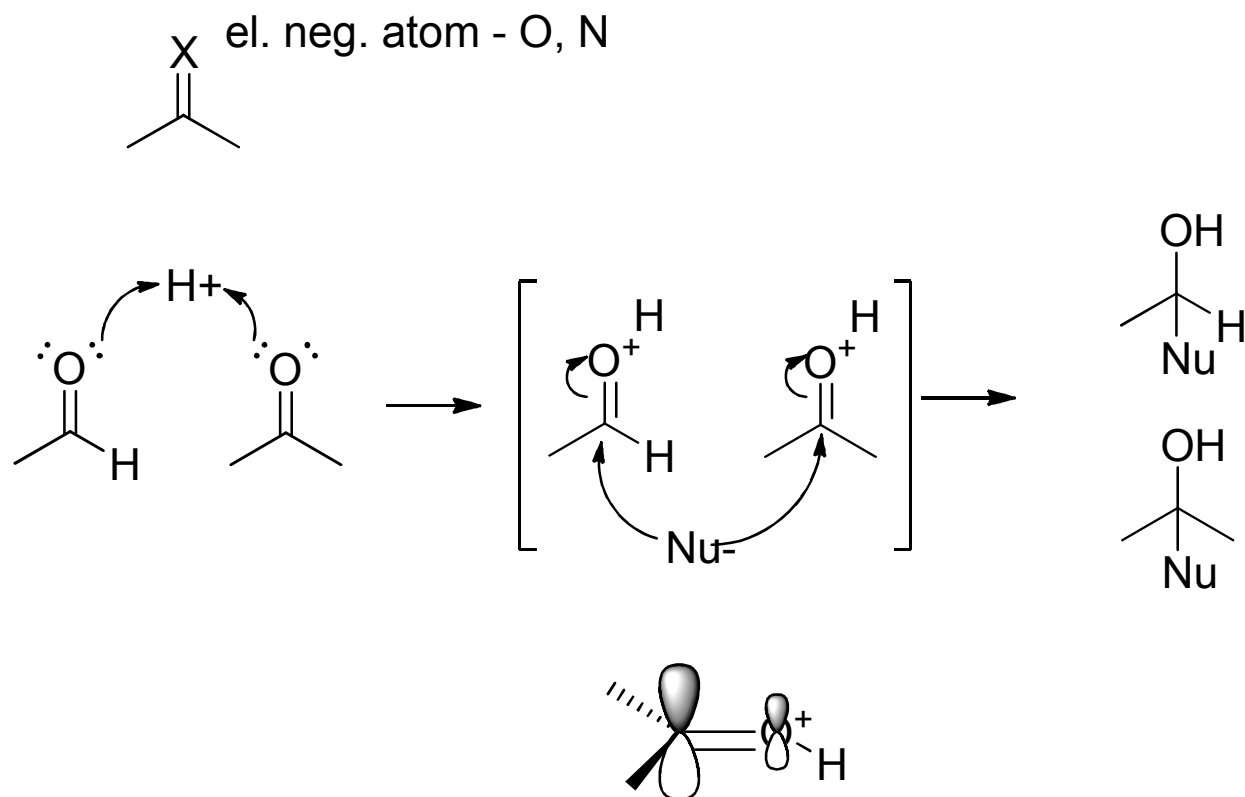


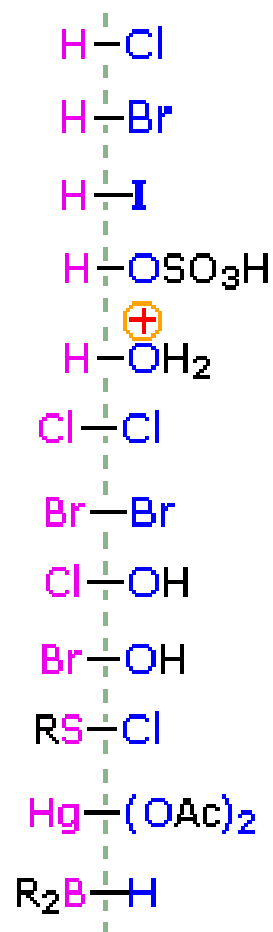
Adice na polarizovanou vazbu



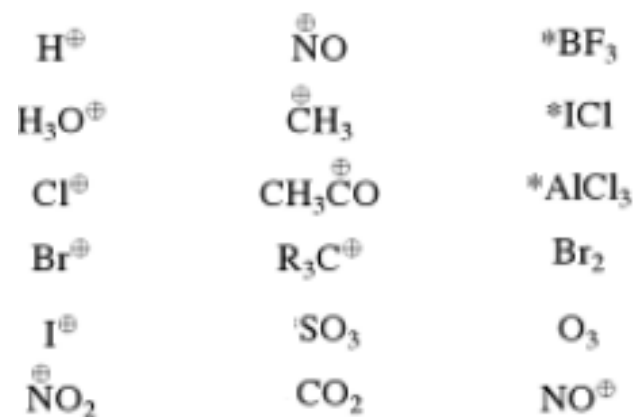
Adice na polarizovanou vazbu

- Kyselá katalýza:

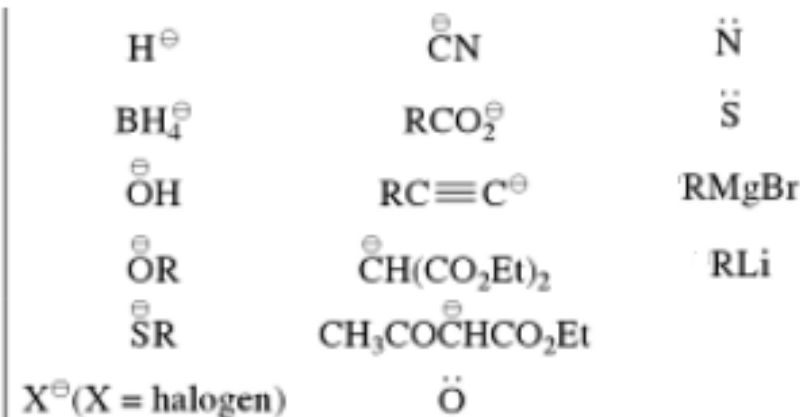


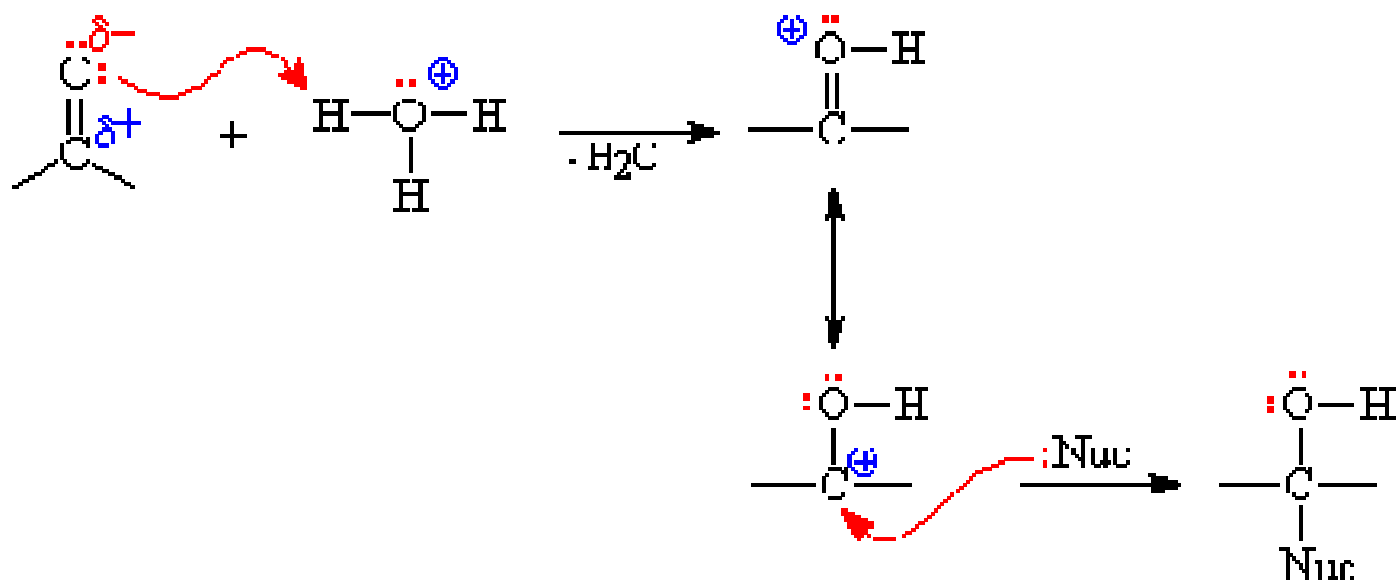
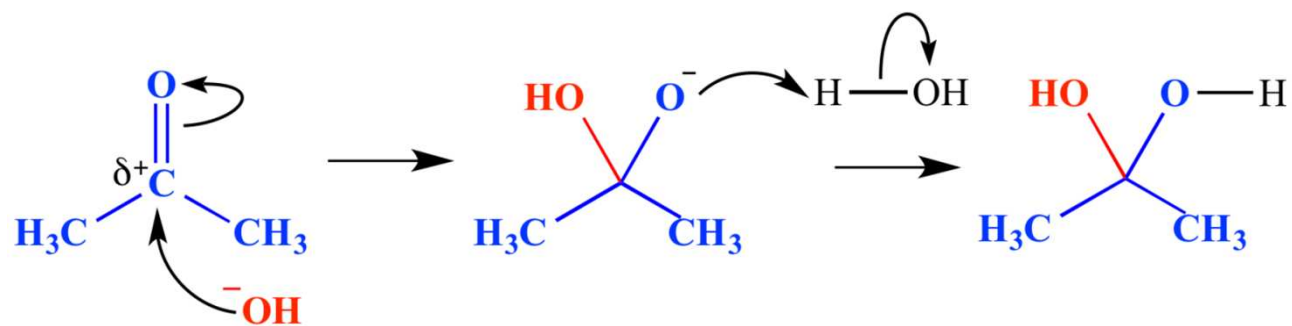


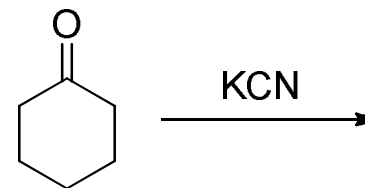
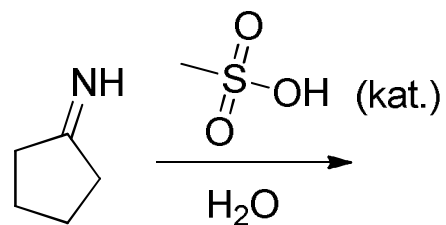
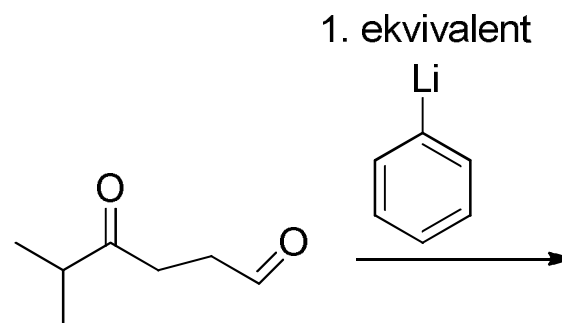
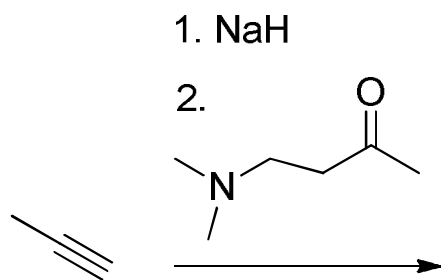
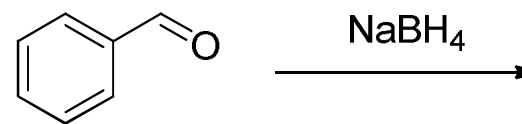
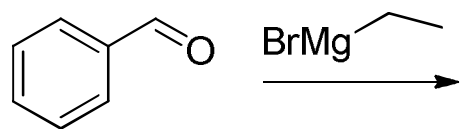
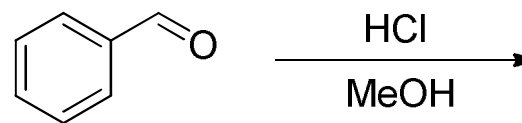
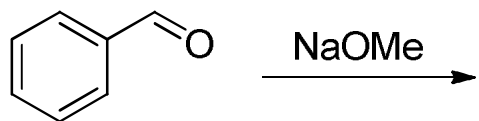
Electrophiles



Nucleophiles







Tvrdé

F^- , OH^- , RO^- , SO_4^{2-} , Cl^- , N_3^- , CN^-

H_2O , ROH , ROR' , $RCOR'$, RNH_2 , $RR'NH$,

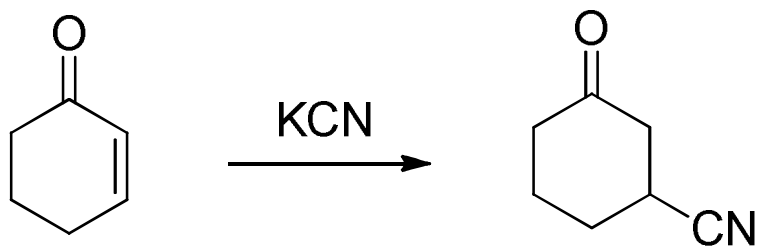
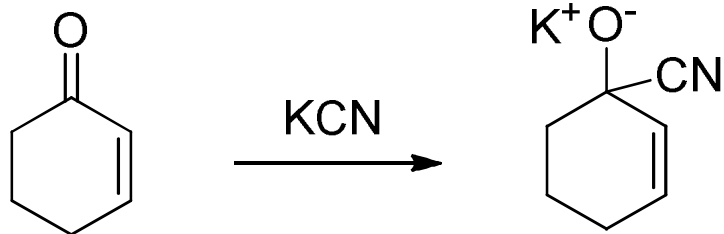
NH_3 , $RMgBr$, RLi Br^-

Měkké

I^- , RS^- , RSe^- , S^{2-}

RSH , RSR' , R_3P

alkeny, aromáty ;

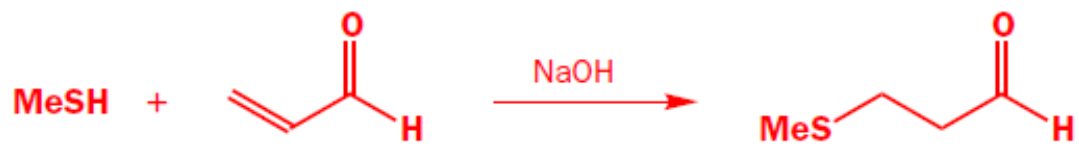
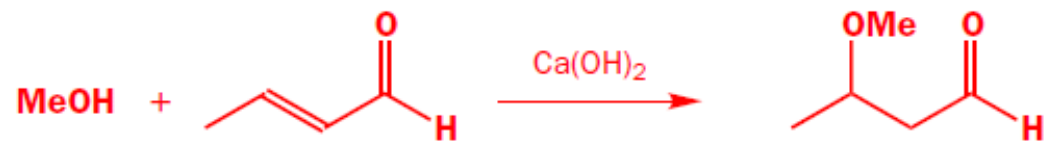
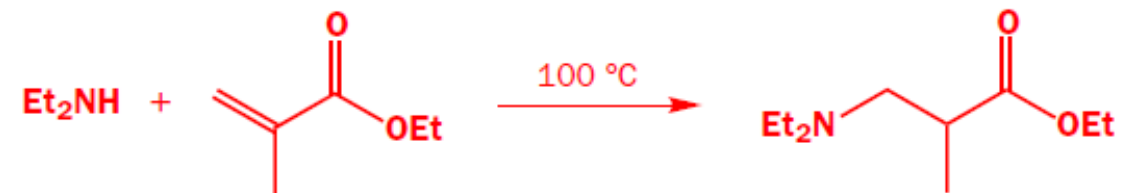


Adice na karbonyl

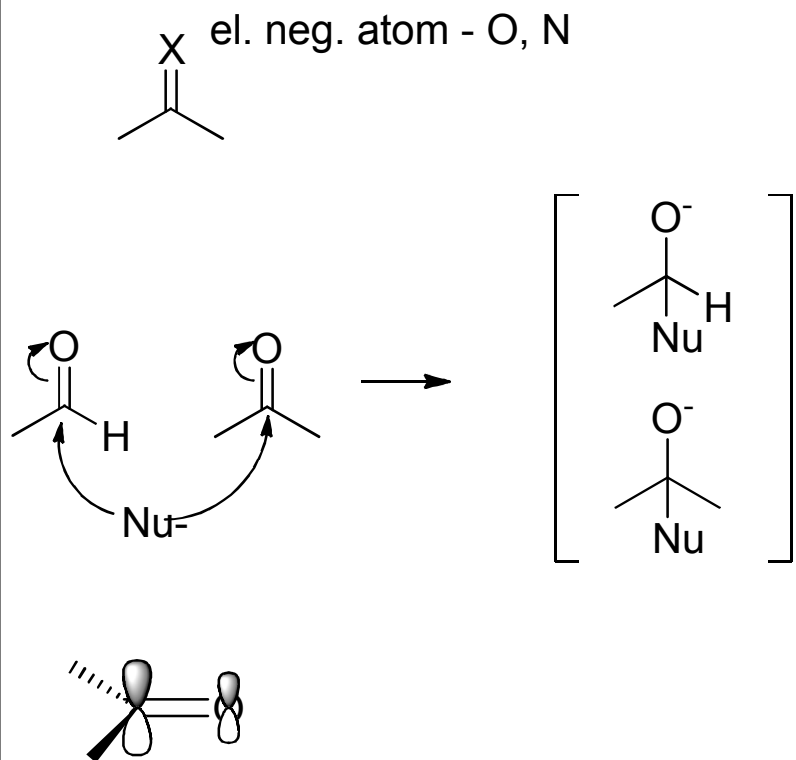
- kinetická kontrola, nižší teplota, kratší rekační doba
- reaktivní karbonyl, chlorid, aldehyd
- stericky bráněný β -uhlík
- tvrdé nukleofily

Konjugovaná adice

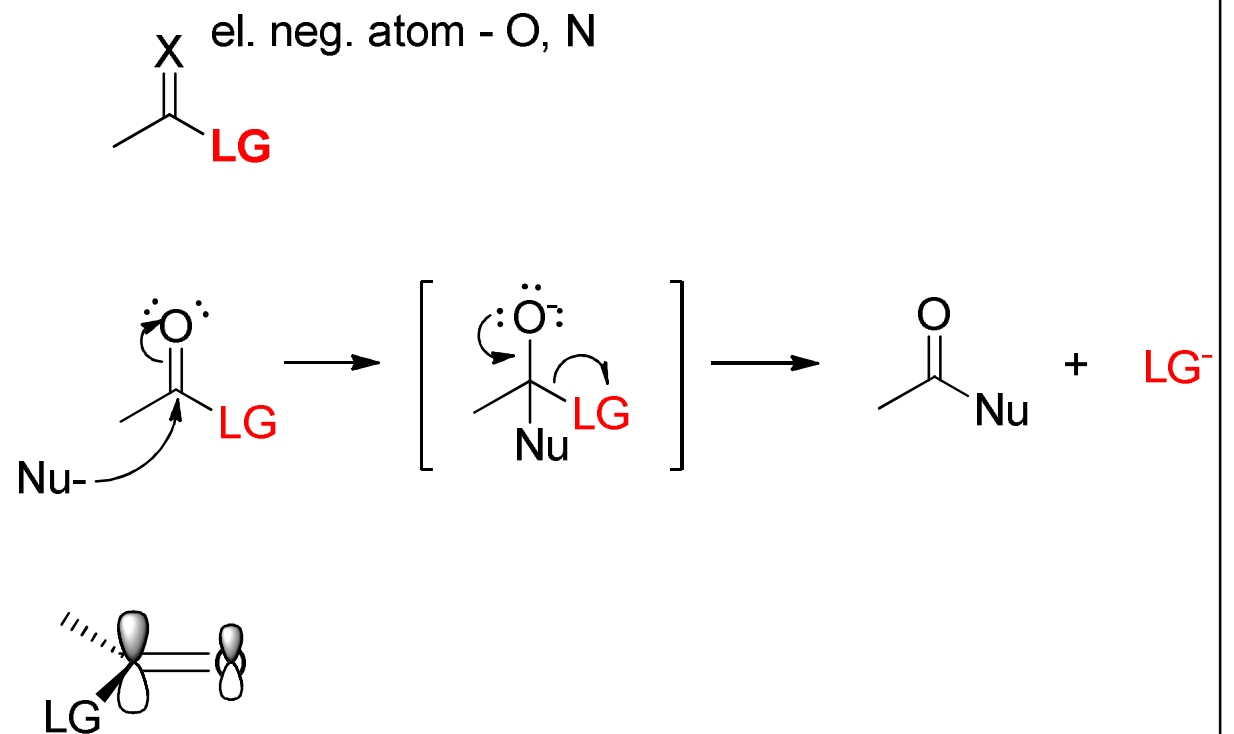
- termodynamická kontrola, vyšší teplota, delší reakční doba
- málo reaktivní karbonyl C=O
- stericky přístupný β -uhlík
- měkké nukleofily



Adice na polarizovanou vazbu



Nukleofilní sub. na karbonylu



Nukleofilní sub. na karbonylu

