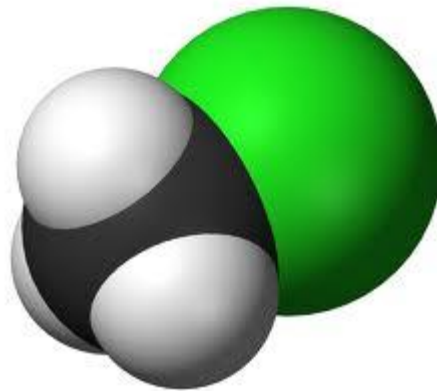
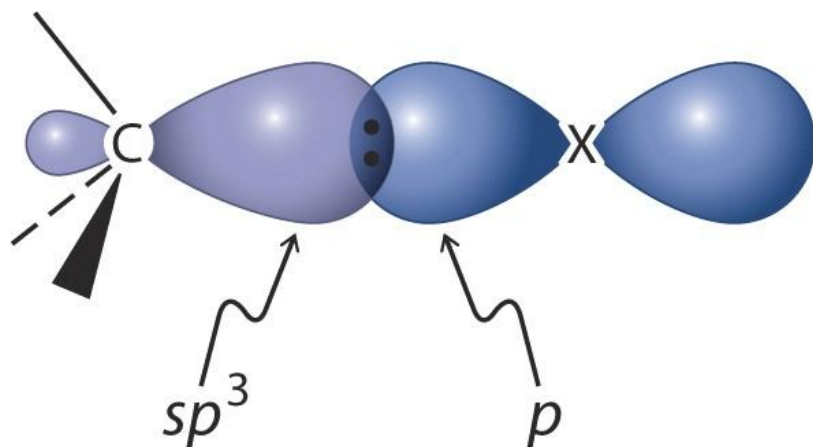


Halogenderiváty

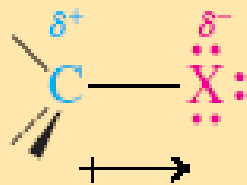




C-X Bond Lengths and Bond Strengths in CH_3X

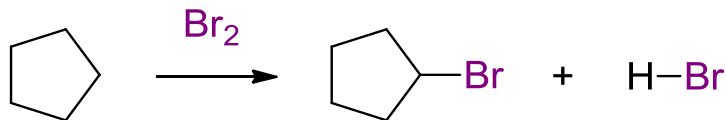
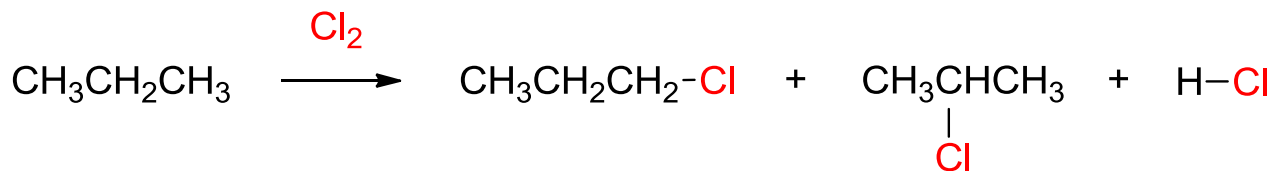
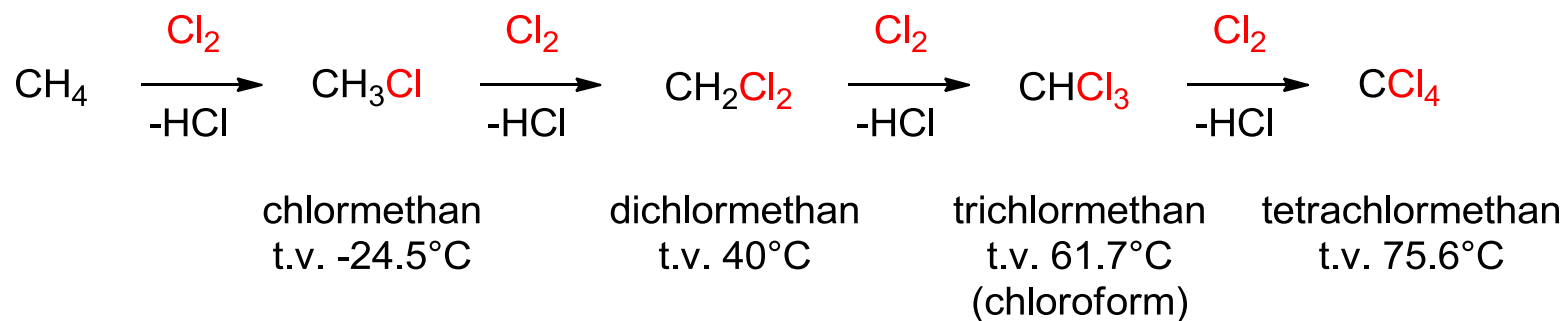
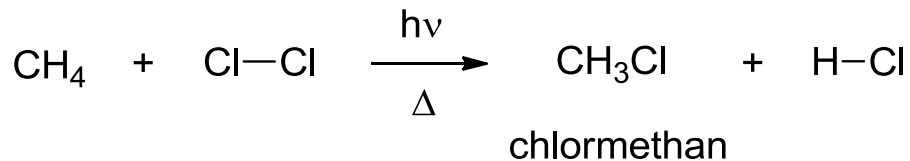
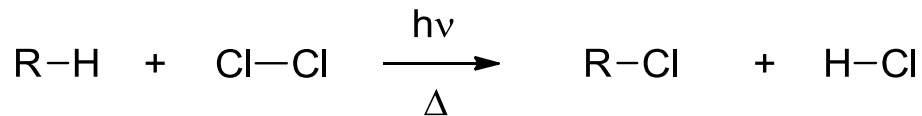
Halo-methane	Bond length (Å)	Bond strength (kcal mol ⁻¹)
CH_3F	1.385	110
CH_3Cl	1.784	85
CH_3Br	1.929	70
CH_3I	2.139	57

The Polar Character of the C-X Bond



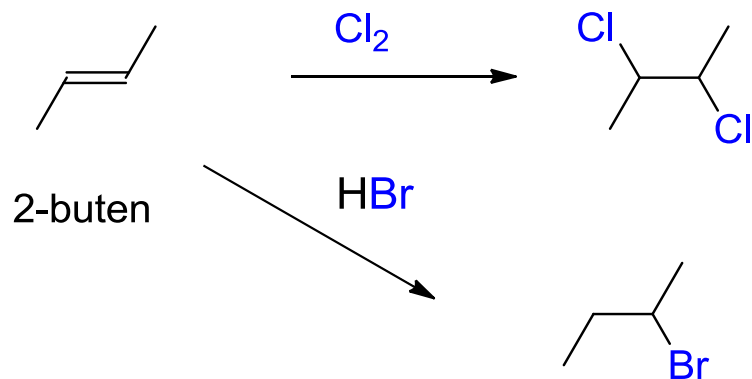
Příprava halogenderivátů

Halogenace alkanů

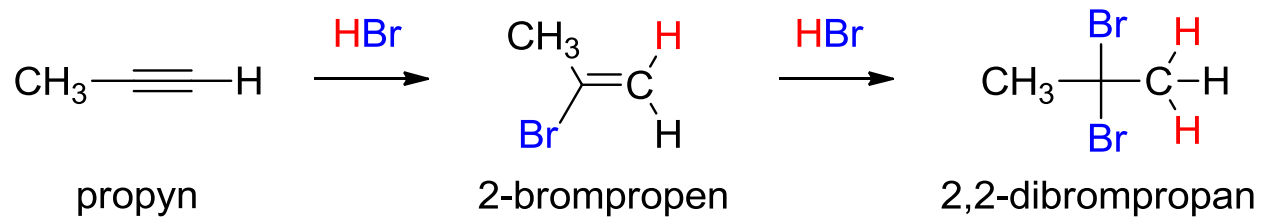
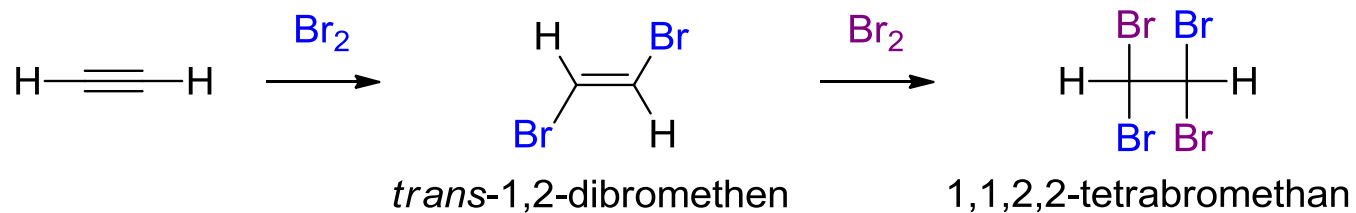


Příprava halogenderivátů

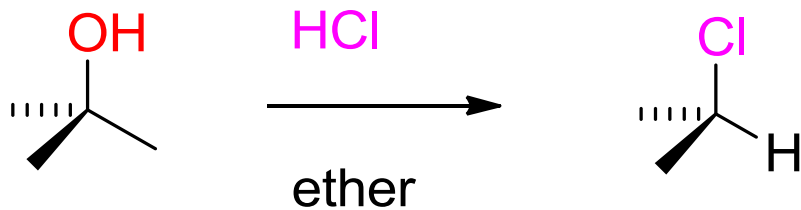
Adice na alkeny



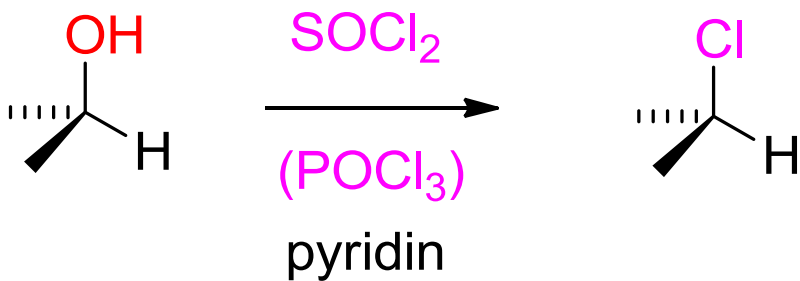
Adice na alkyny



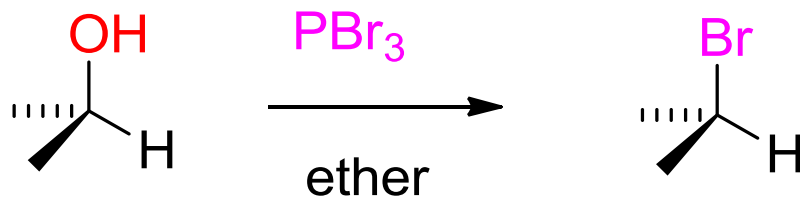
Příprava halogenderivátů z alkoholů



terciární > sekundární > primární

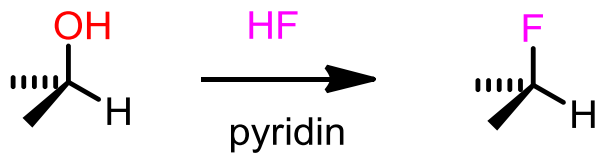


sekundární, primární

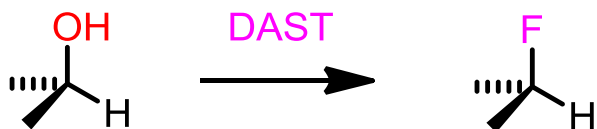


sekundární, primární

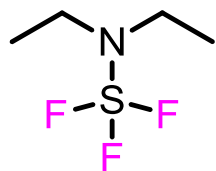
Příprava fluorderivátů z alkoholů



sekundární, primární



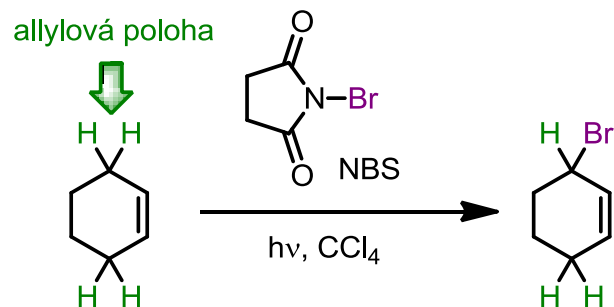
sekundární, primární



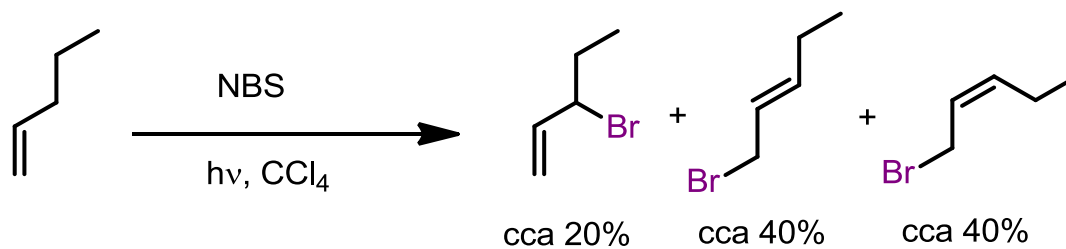
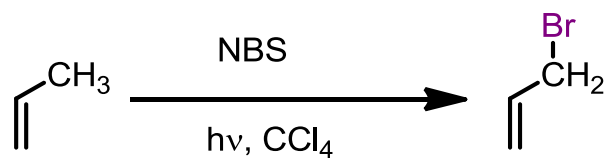
DAST = diethylaminosulfur trifluoride



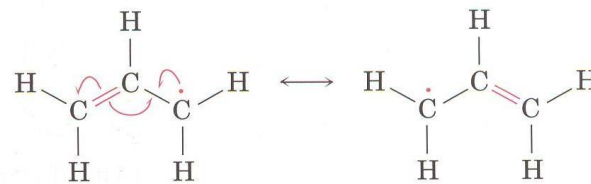
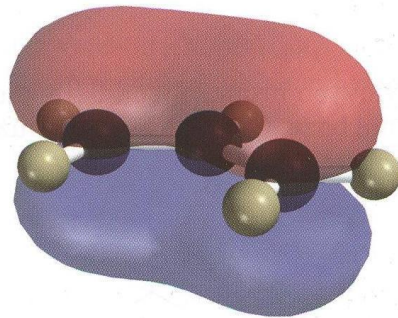
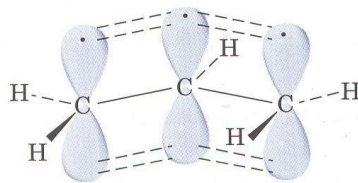
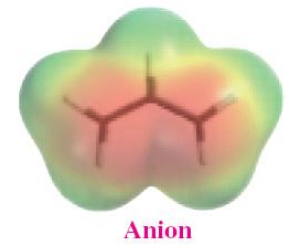
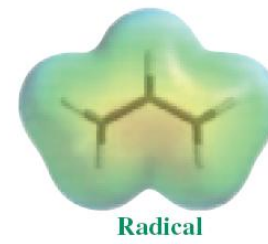
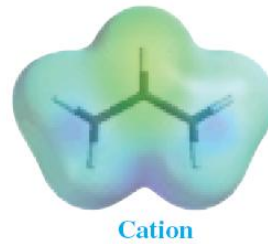
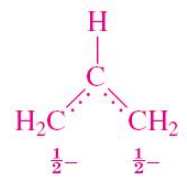
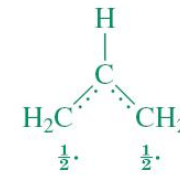
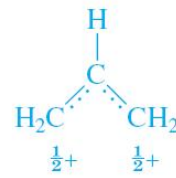
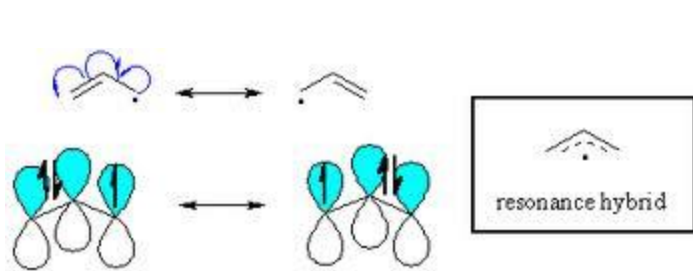
Bromace v allylové poloze

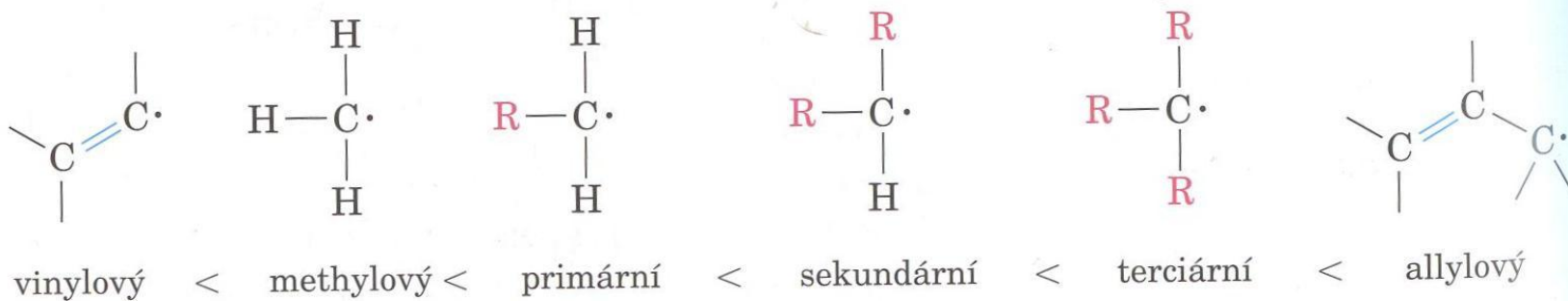


NBS = *N*-bromosukcinimid



Allylové substituce - struktury allylových radikálů, aniontů a kationtů

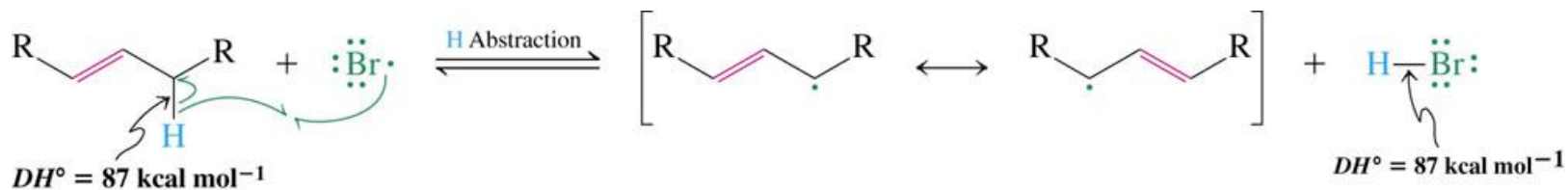
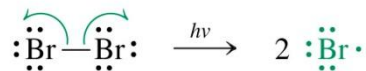




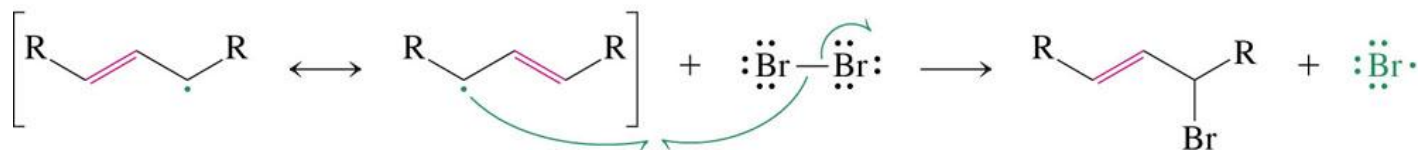
méně stabilní  stabilnější

Mechanism of Allylic Bromination

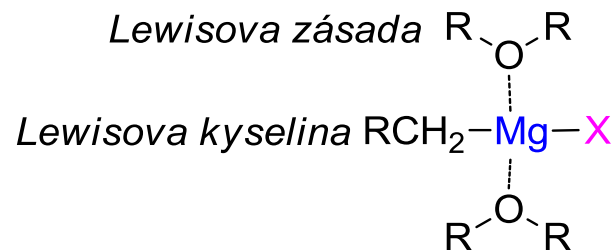
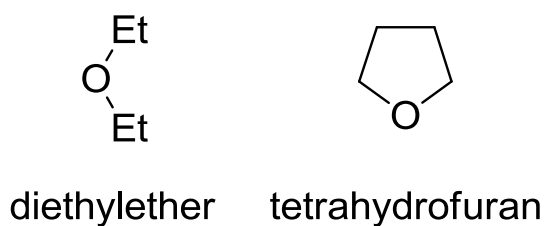
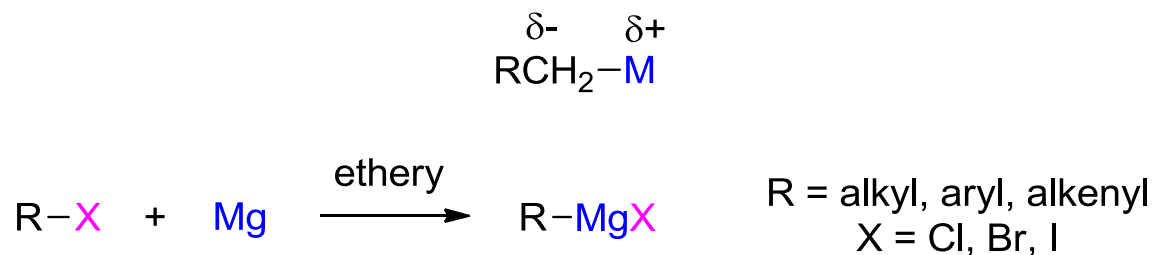
Initiation step



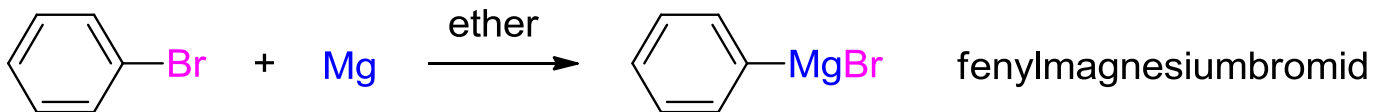
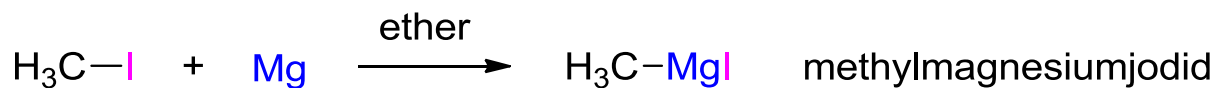
Allylic Radical

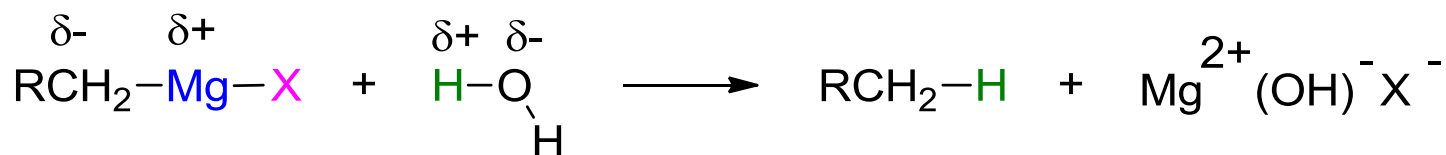
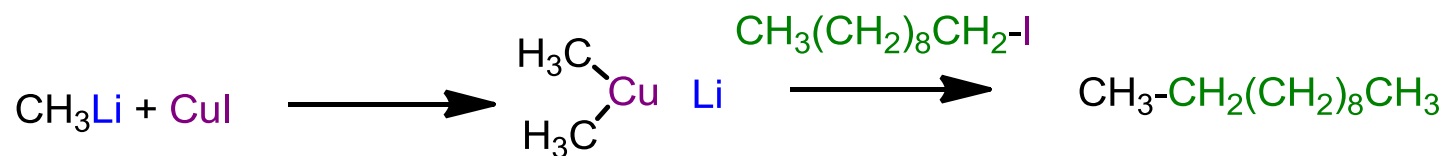
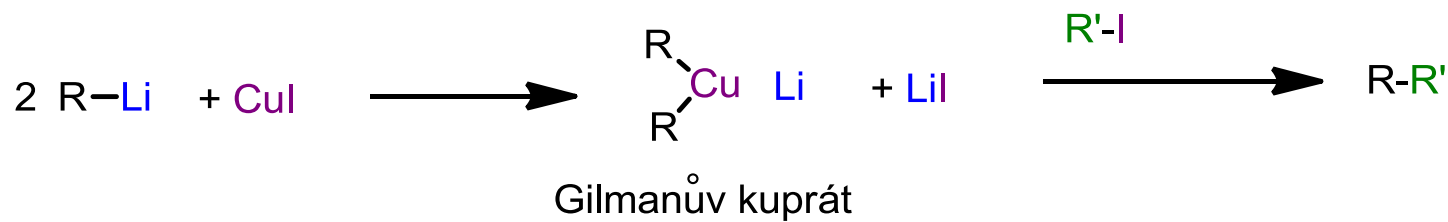
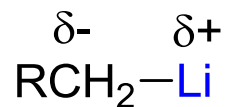
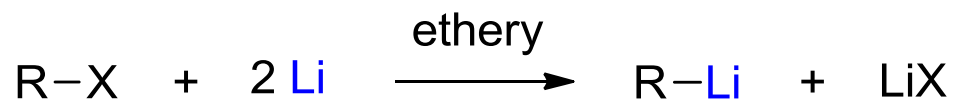


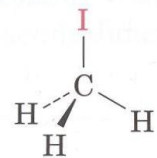
Reakce alkylhalogenidů s kovy



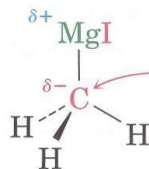
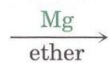
Grignardova činidla





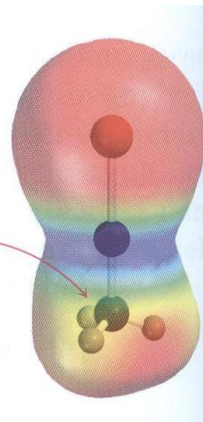


jodmethan



methylmagnesiumjodid

bazický a nukleofilní
charakter

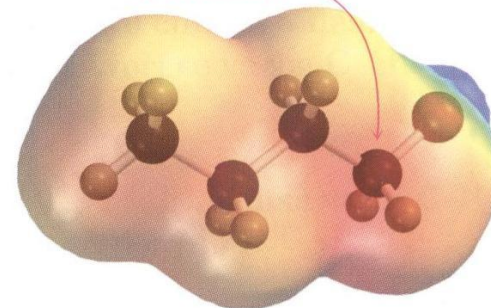


1-brombutan



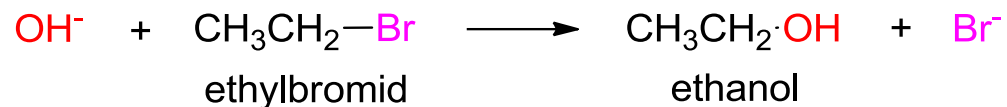
butyllithium

bazický
a nukleofilní



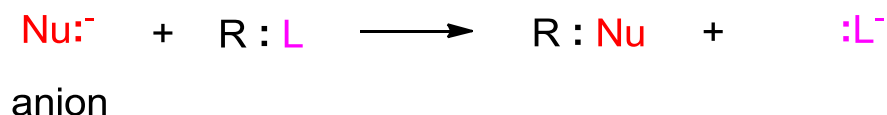
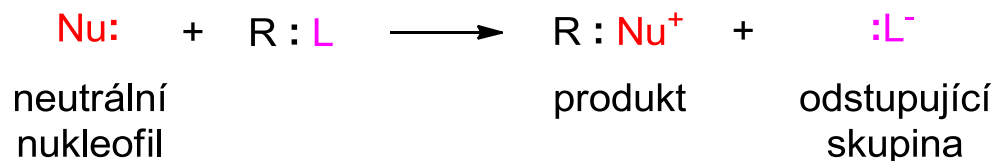
Nukleofilní substituce

Charakteristických reakcí alkyhalogenidů jsou nukleofilní substituční reakce.



Definice nukleofilu:

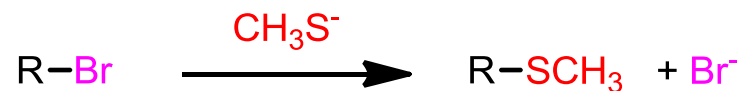
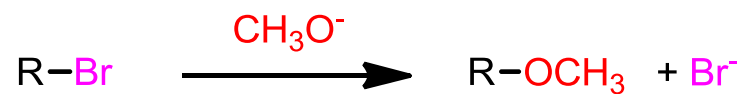
nukleofil je částice (činidlo), které poskytuje elektronový pár na tvorbu nové vazby.



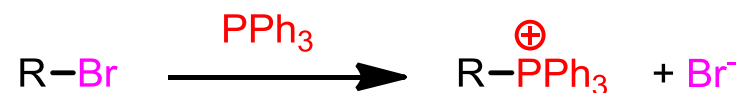
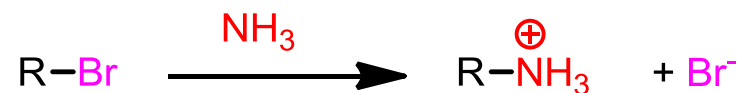
Principiálně jsou reakce uvedené v rovnicích vratné (reversibilní), neboť odstupující skupina je také nukleofilní částicí nesoucí nesdílený elektronový pár, který může být použit na vytvoření nové kovalentní vazby. Nicméně existuje řada způsobů a jak donutit reakci, aby běžela žádaným směrem:

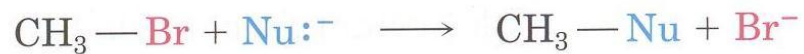
- a) Nu: je silnějším nukleofilem než odstupující skupina :L-,
- b) dále je možné posunout rovnováhu použitím nadbytku jednoho činidla, nebo
- c) odstraňovat jeden z produktů z reakční směsi.


Aniontový nukleofil

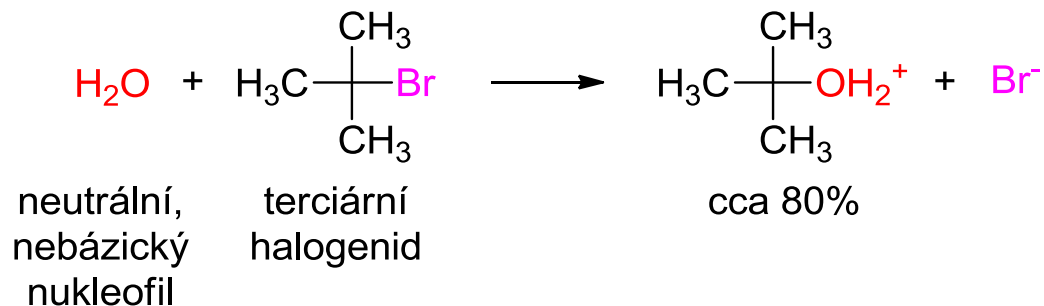
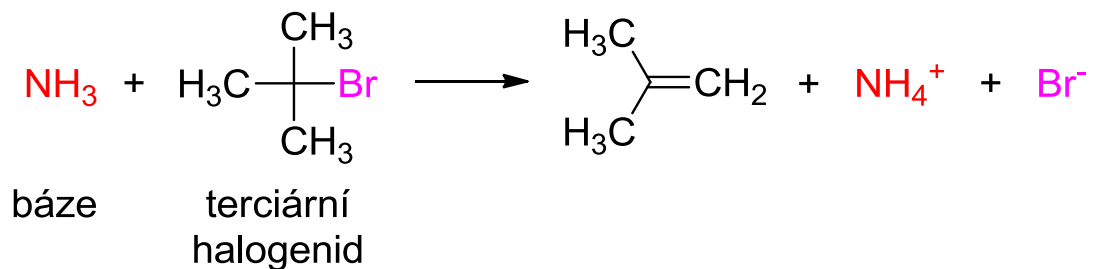
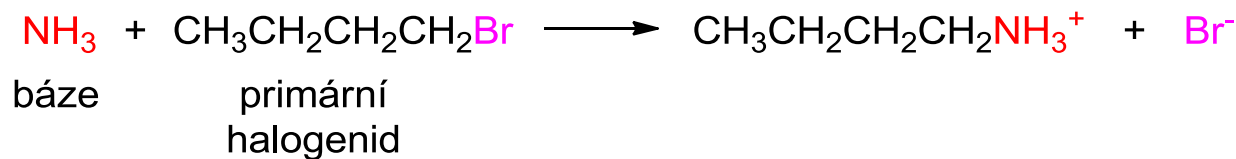
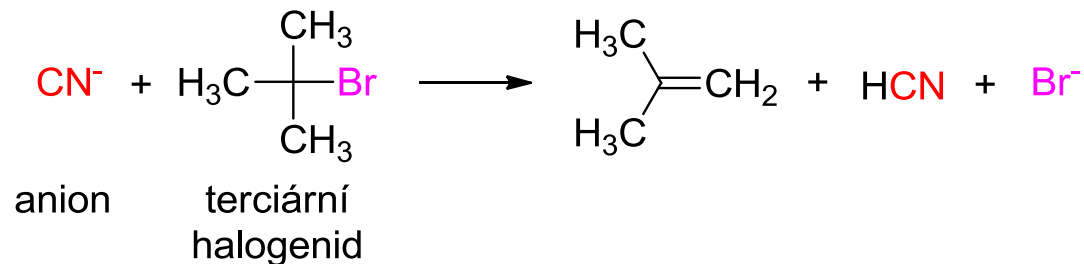
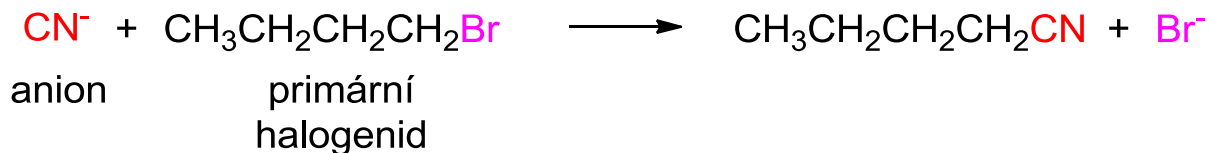


Neutrální nukleofil



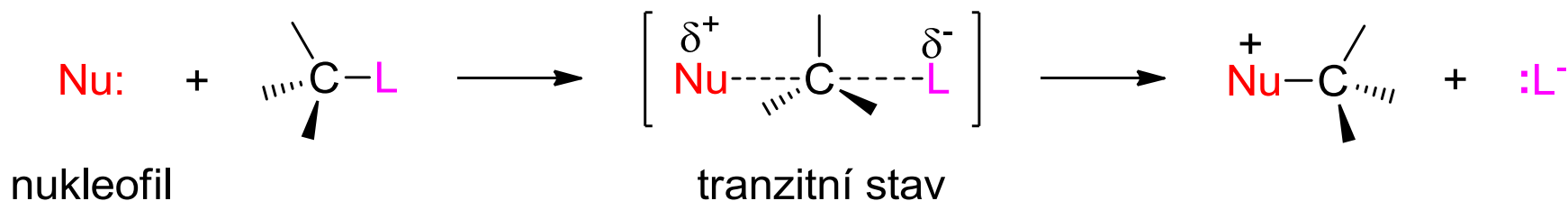


	$\text{Nu} = \text{H}_2\text{O}$	CH_3COO^-	NH_3	Cl^-	OH^-	CH_3O^-	I^-	CN^-	HS^-
relativní reaktivita	1	500	700	1 000	16 000	25 000	100 000	125 000	125 000
		méně reaktivní						reaktivnější	



Mechanismus nukleofilní substituce

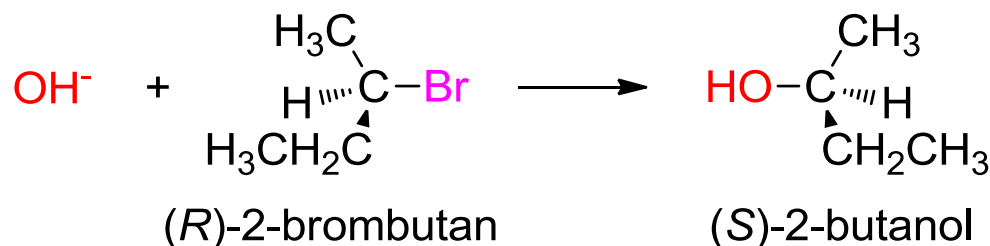
S_N2 mechanismus



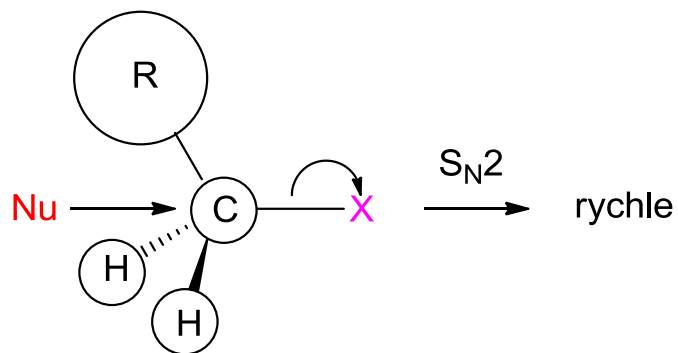
S_N2 mechanismus má několik charakteristických průvodních jevů:

1. **Jelikož se reakce účastní nukleofil a substrát závisí reakční rychlost na koncentraci obou reaktantů.**

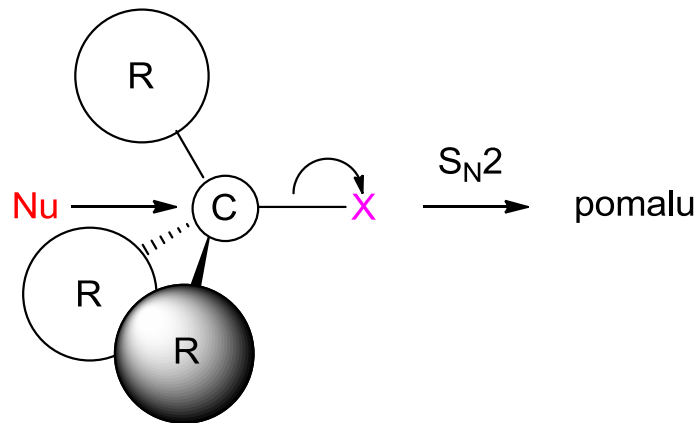
S_N2 substituce probíhá s inverzí konfigurace.



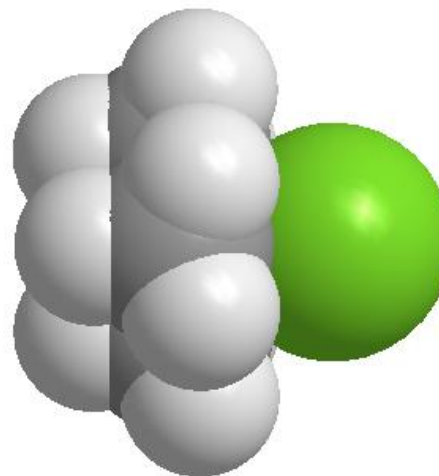
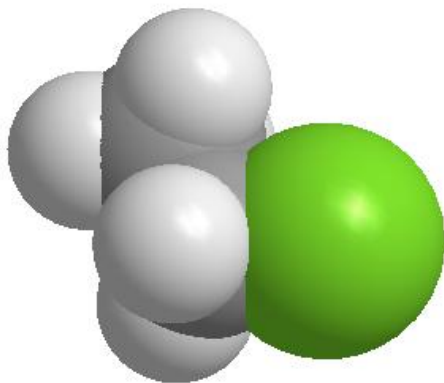
Nukleofilní substituce probíhá nejrychleji pokud je alkylová skupina substrátu methyl nebo primární alkyl a nejpomaleji v případě terciárních alkylů.

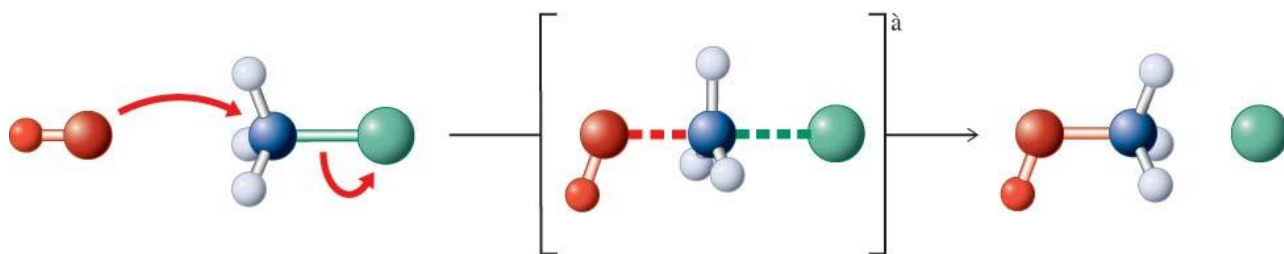
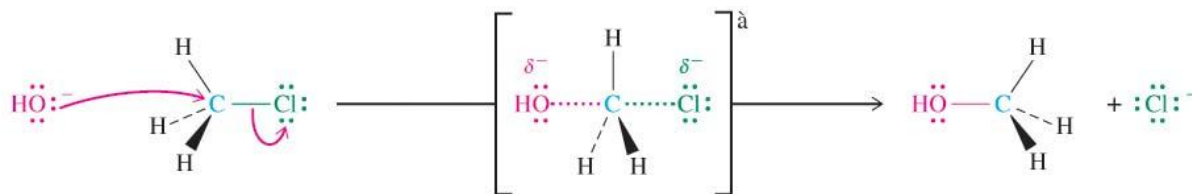


primární alkylhalogenid (odvrácená strana není bráněná)

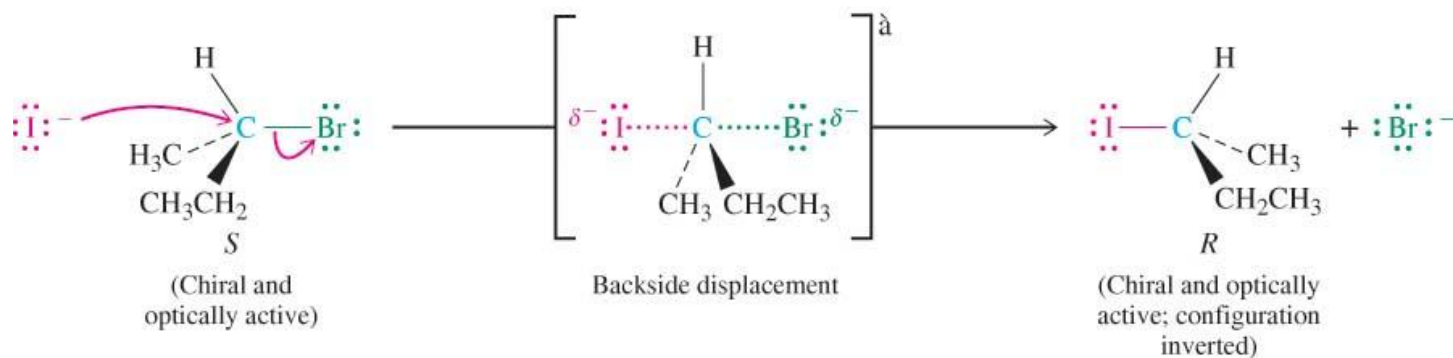


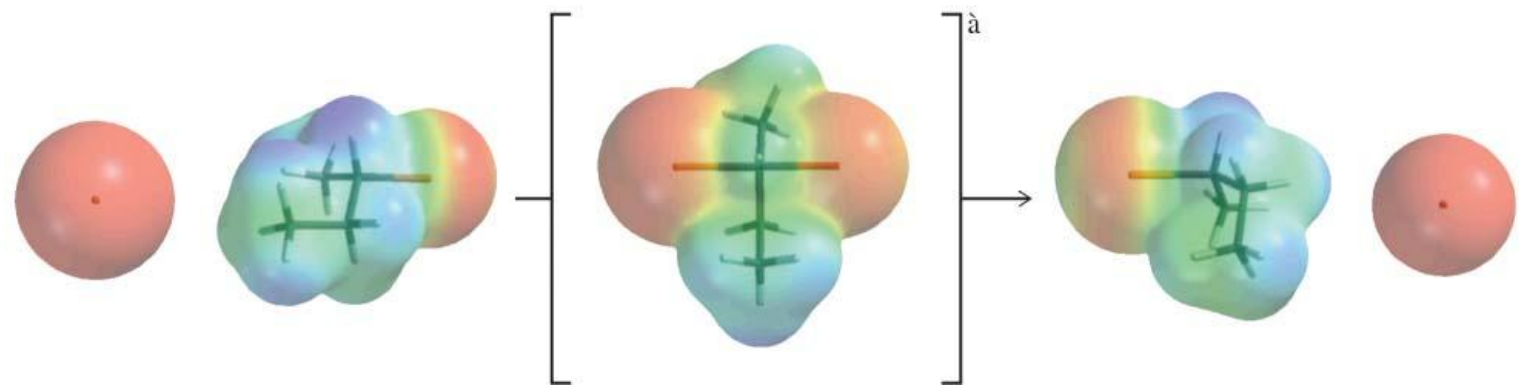
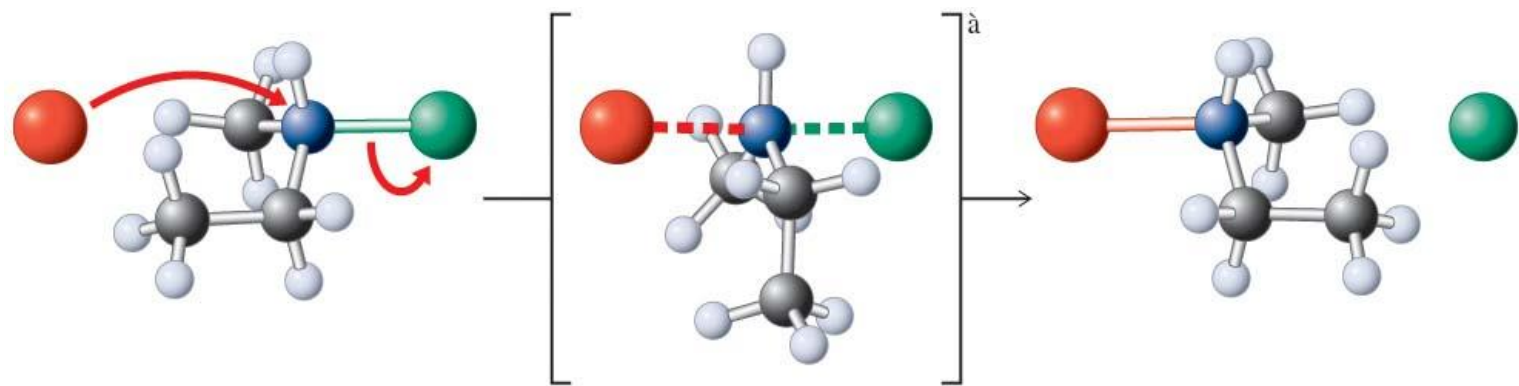
terciární alkylhalogenid (odvrácená strana je bráněná)

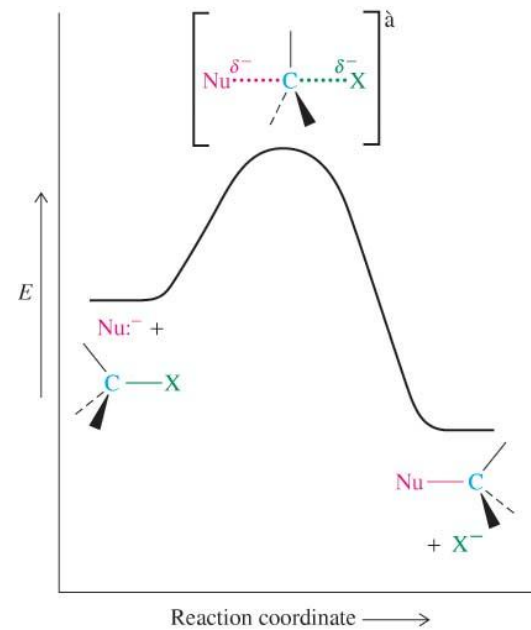
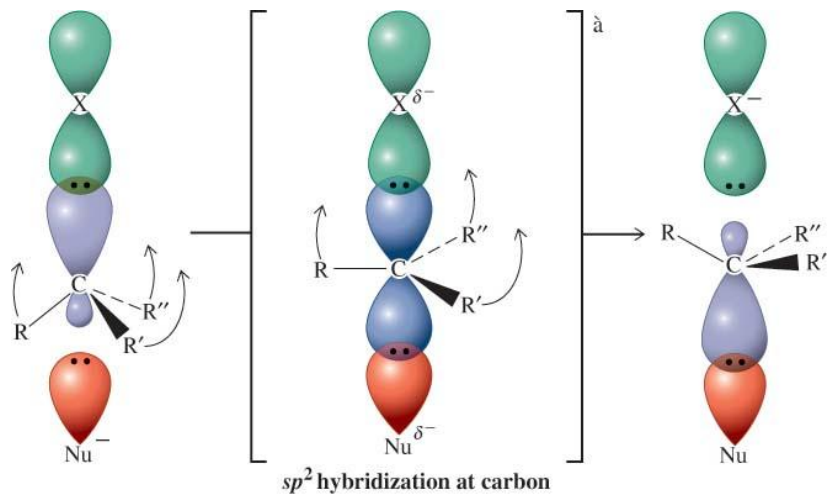




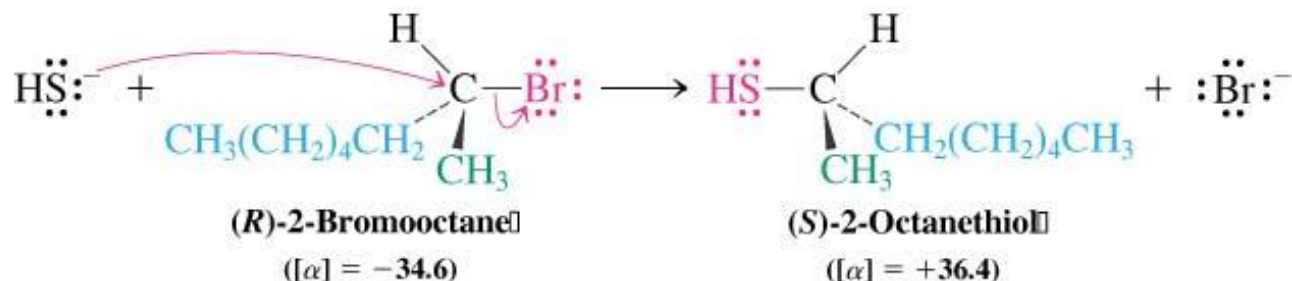
Stereochemistry of the Backside Displacement Mechanism for $\text{S}_{\text{N}}2$ Reactions







Inversion of Configuration of an Optically Pure Compound by S_N2 Reaction



Using Double Inversion to Give Net Retention of Configuration

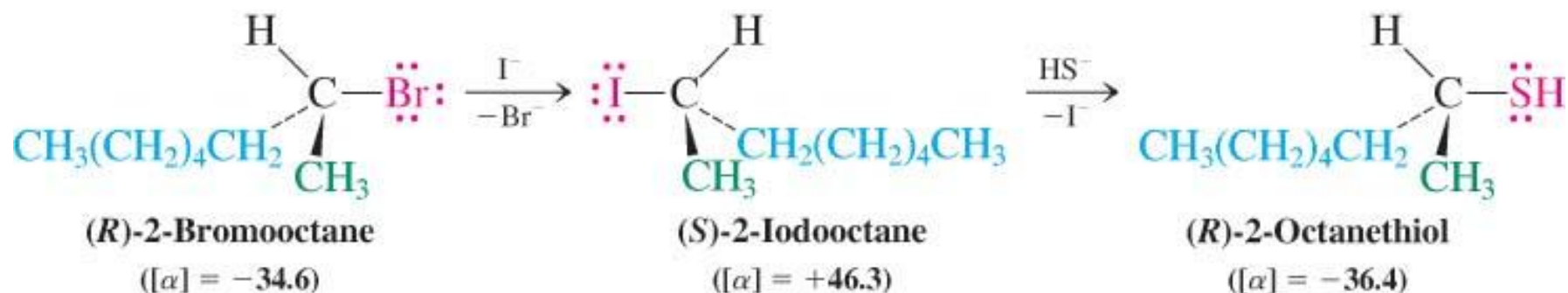
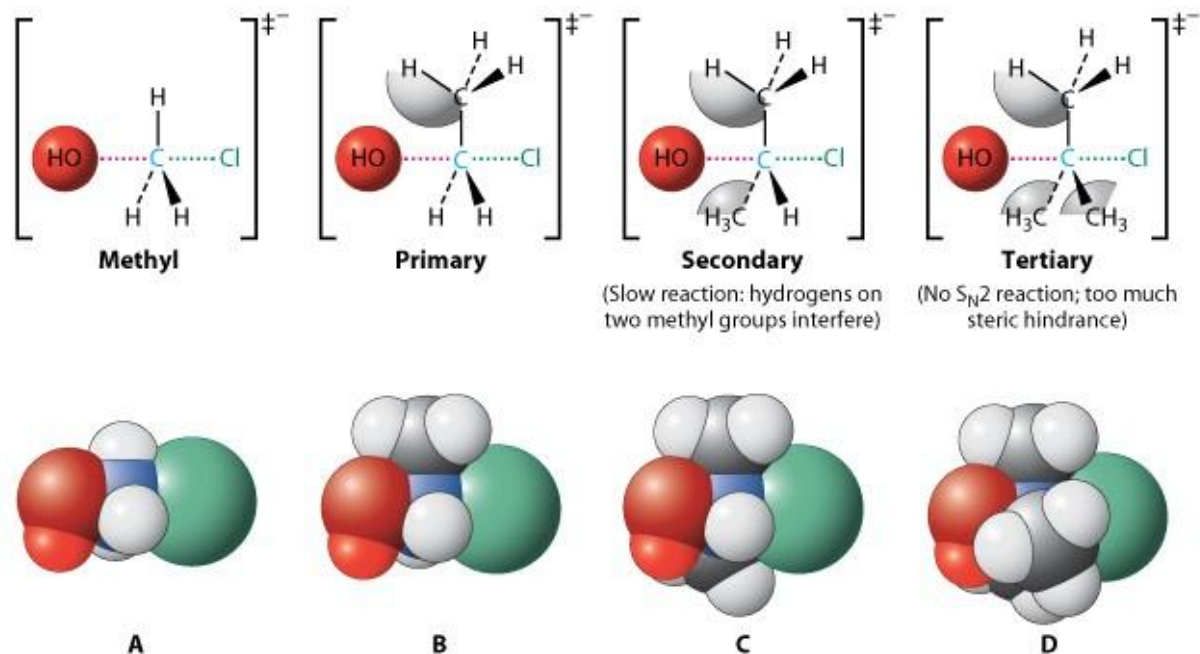


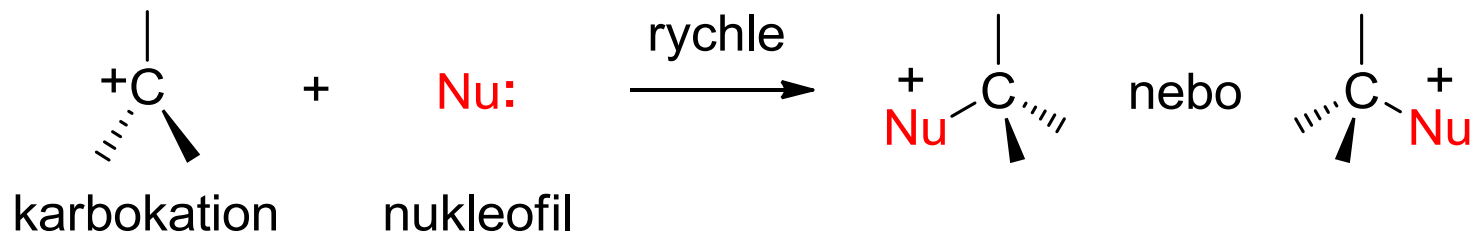
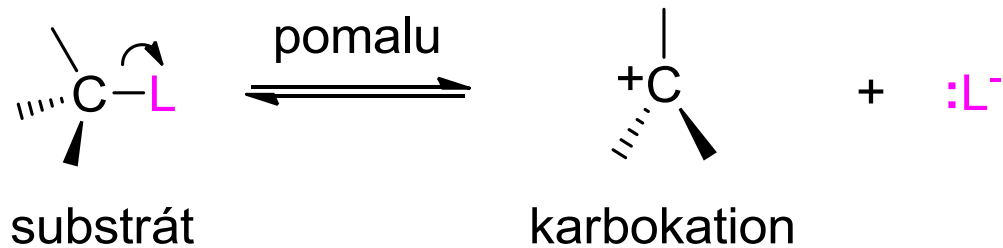
TABLE 6-8

Relative Rates of S_N2
Reaction of Branched
Bromoalkanes with Iodide

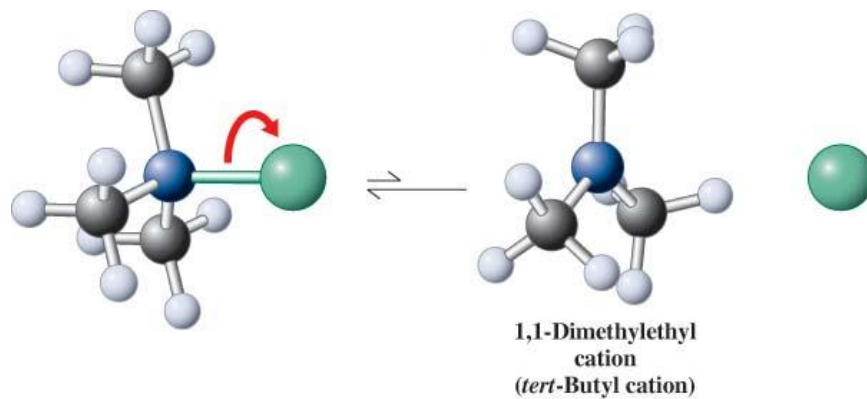
Bromoalkane	Rate
CH_3Br	145
$\text{CH}_3\text{CH}_2\text{Br}$	1
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CHBr} \end{array}$	0.0078
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3\text{CBr} \\ \\ \text{CH}_3 \end{array}$	Negligible

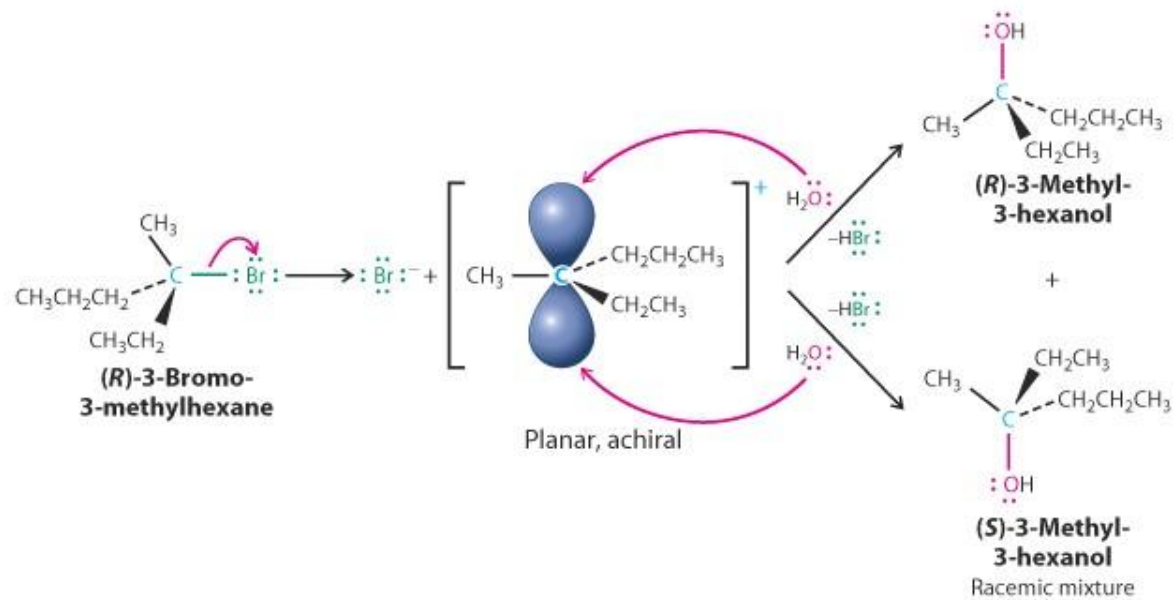


S_N1 mechanismus



Dissociation of Halide to Form a Carbocation

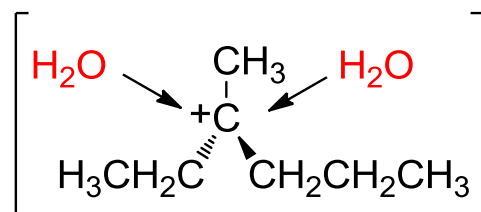
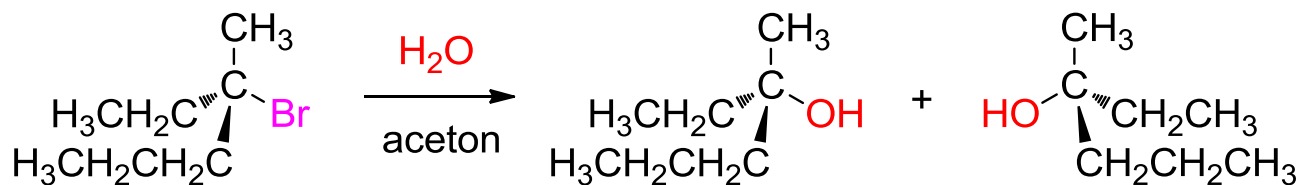




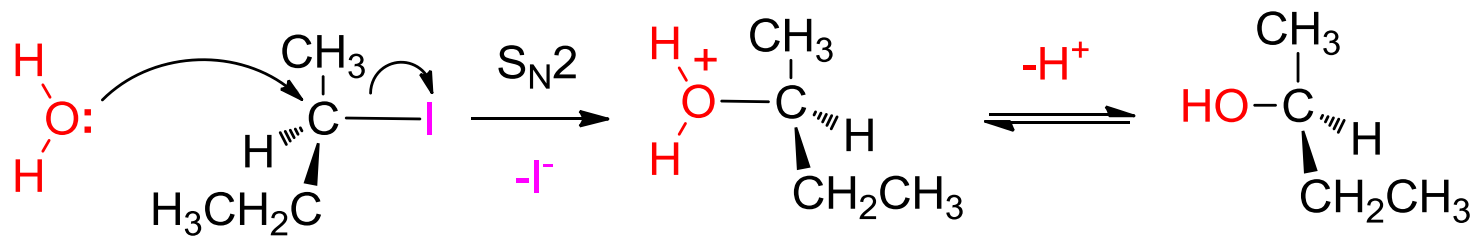
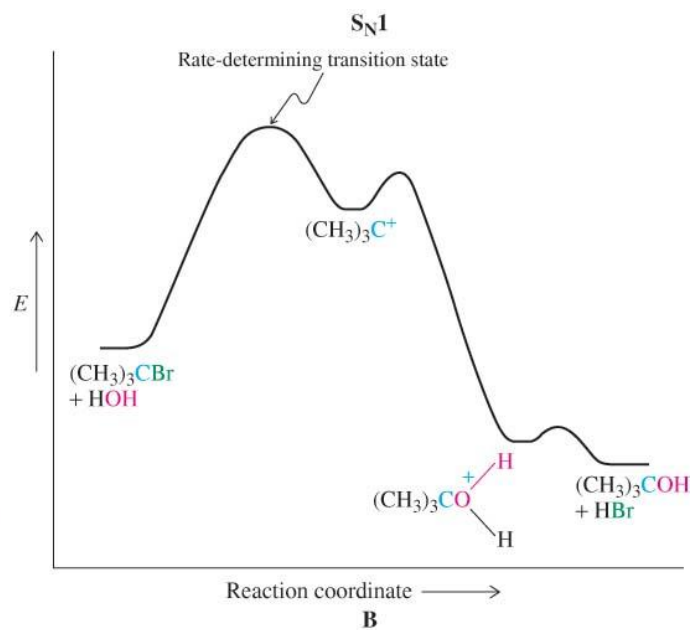
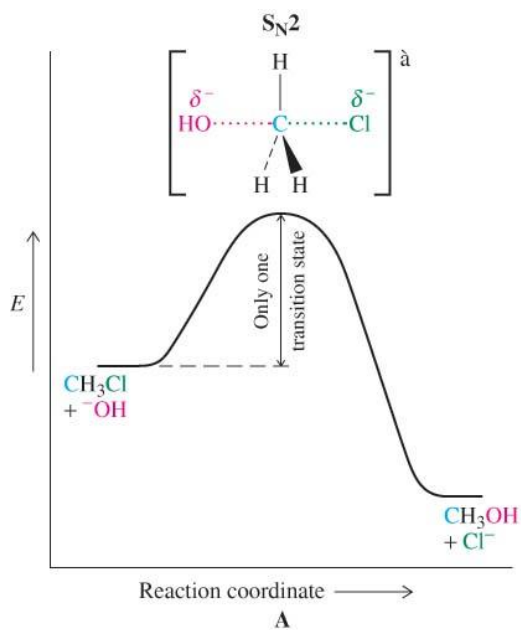
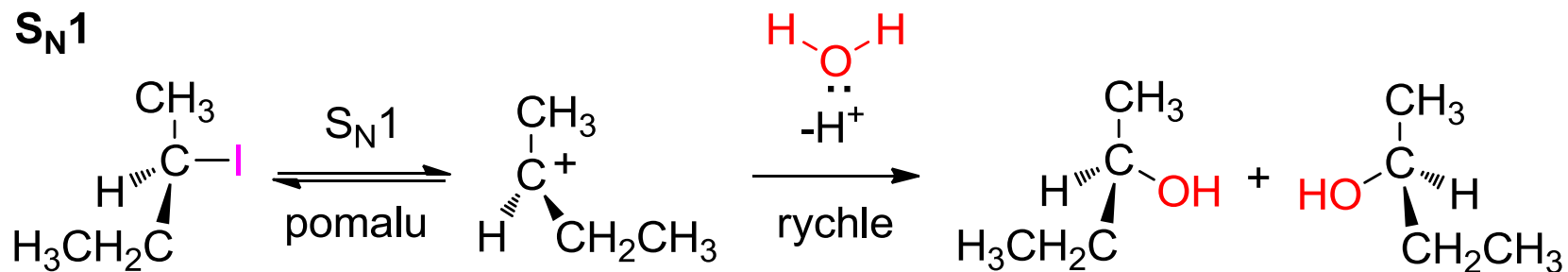
Stejně jako S_N2 mechanismus má i S_N1 mechanismus několik charakteristických průvodních jevů:

1. **Rychlost reakce nezávisí na koncentraci nukleofilu.**

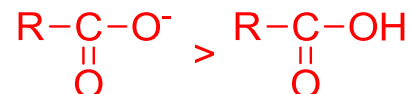
2. **Jestliže na atomu uhlíku nesoucí odstupující skupinu je centrum chiralita, S_N1 substituce probíhá se ztrátou optické aktivity, tj. racemizací.**



3. **Reakce je nejrychlejší v případě, že alkylová skupina substrátu je terciární a nejpomalejší, když je primární.**

S_N2**S_N1**

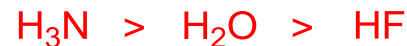
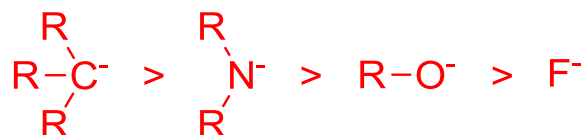
1. Záporně nabité ionty jsou více nukleofilní, neboli lepší donory elektronů než odpovídající neutrální molekuly.



2. Nukleofilita prvků stoupá s klesajícím místem ve skupině periodické tabulky.



3. Nukleofilita prvků ve stejné řadě periodické tabulky klesá se stoupající elektronegativitou (tj. drží pevněji svoje elektrony)



Srovnání S_N1 a S_N2 mechanismus

S_N2 substituce

S_N1 substituce

Struktura halogenidu

primární
sekundární
terciární

běžná
občas
vzácná

vzácná*
občas
běžná

Stereochemie

inverze

racemizace

Nukleofil

reakční rychlost závisí na koncentraci nukleofilu, mechanismus je upřednostňován pokud je nukleofil anion

reakční rychlost nezávisí na koncentraci nukleofilu, mechanismus je pravděpodobnější s neutrálními nukleofily

Rozpouštědlo

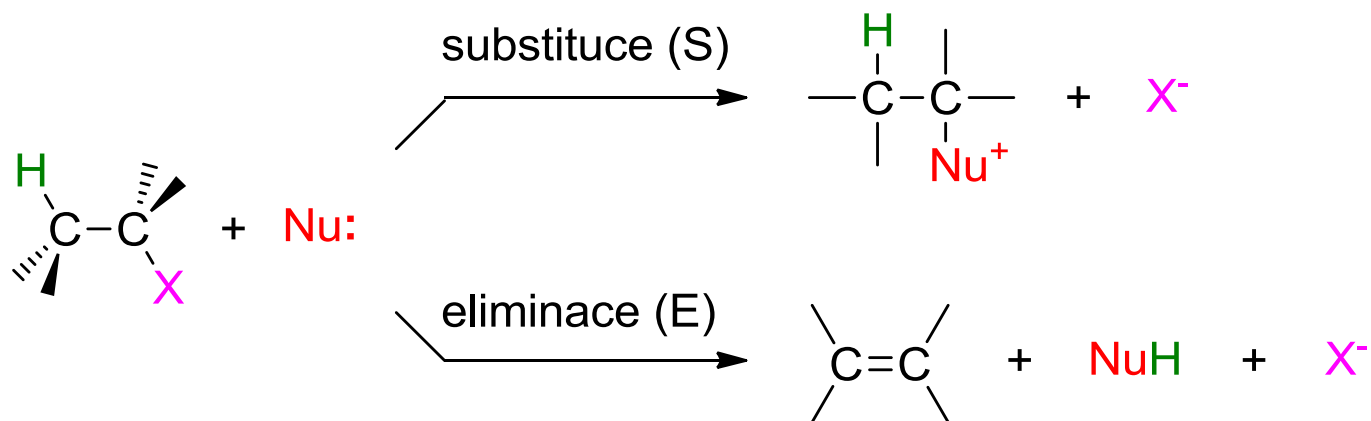
reakční rychlost je málo ovlivněná polaritou rozpouštědla (protická zpomalují)

Vzhledem k tomu, že meziprodukty jsou ionty, reakční rychlost závisí na polaritě rozpouštědla (polární protická urychlují)

* allylové a benzylové substráty tvoří výjimku

Eliminační reakce. E2 a E1 mechanismus

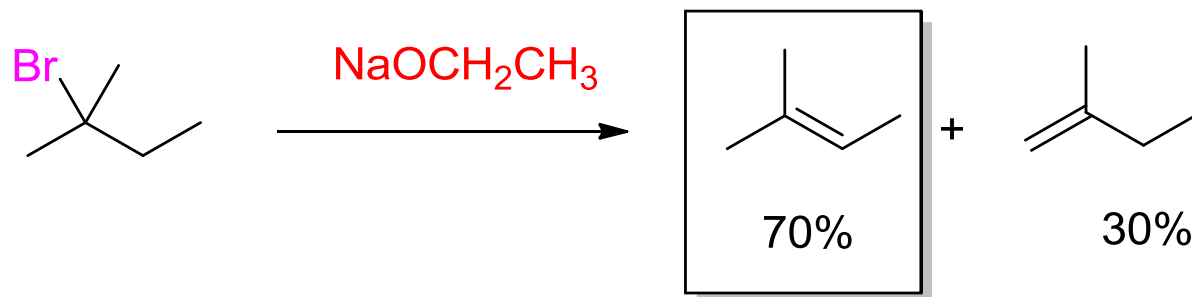
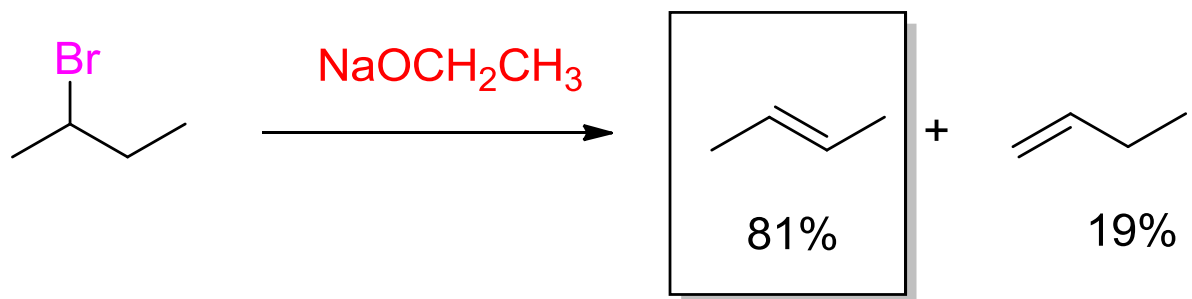
Pokud molekula alkylhalogenidu, ve které je v těsném sousedství C-X skupiny (X = halogen) atom uhlíku nesoucí atom vodíku (C-H skupina), při reakci s nukleofilem mohou nastat dvě vzájemně si konkurující reakce: substituce a eliminace





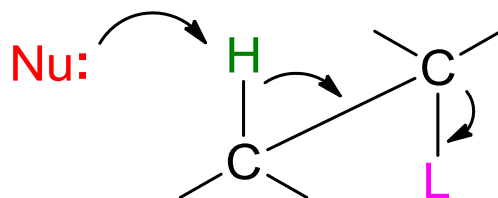
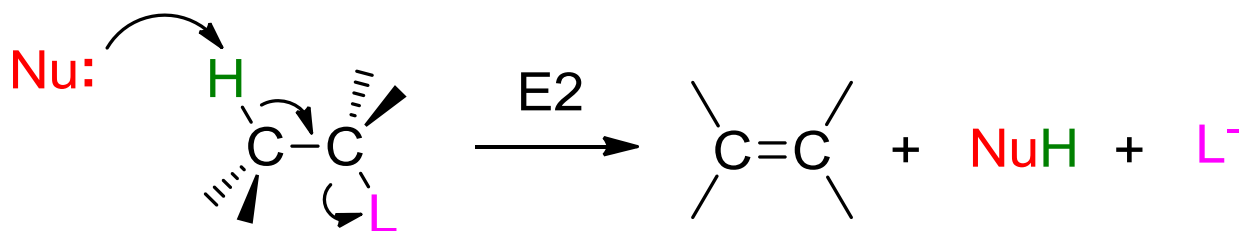
Zajcevovo pravidlo

při eliminaci jako produkt převládá
více substituovaný alken

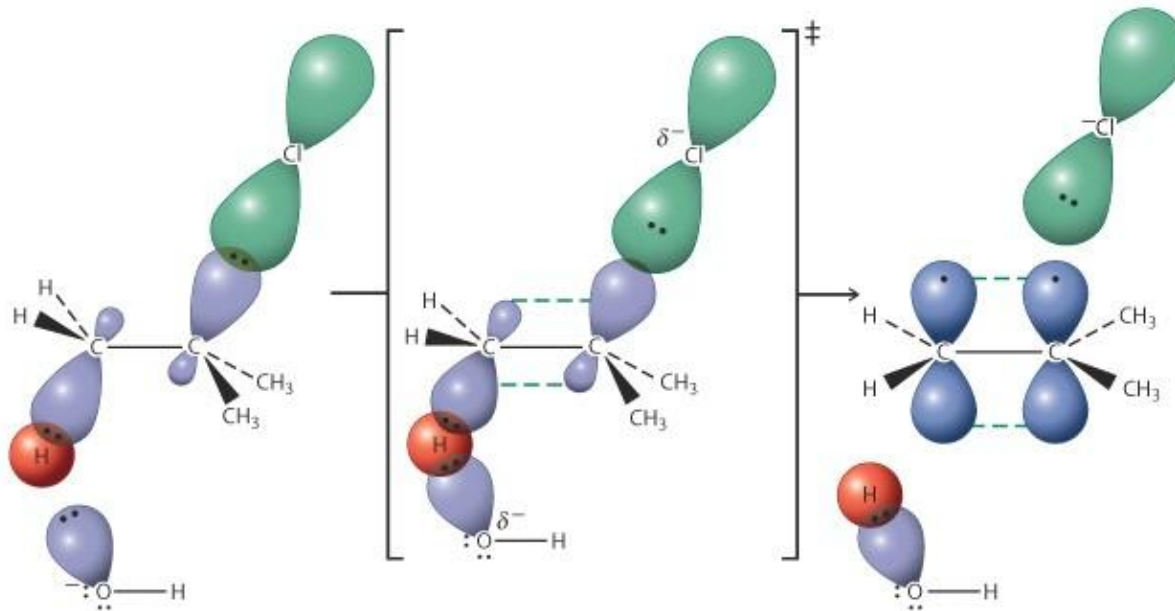


E2 mechanism.

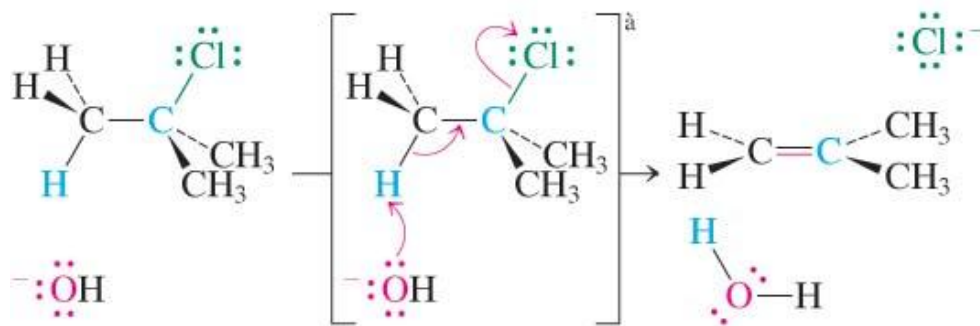
Stejně jako v případě S_N2 substituce se u E2 eliminace jedná o jednokrokový proces.

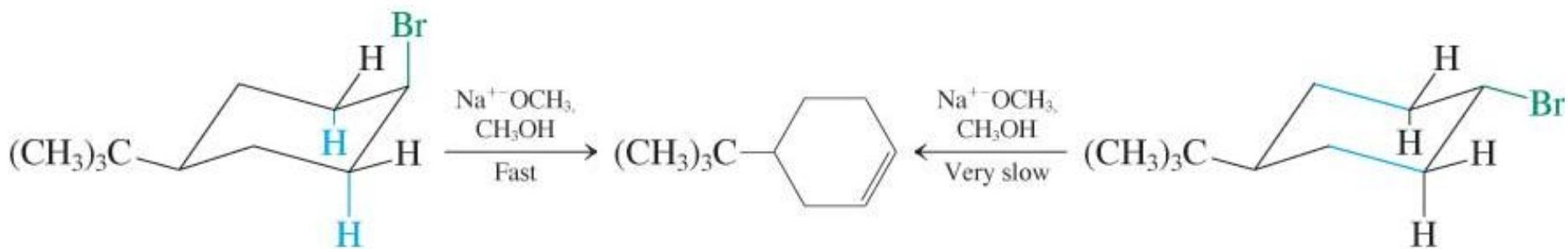
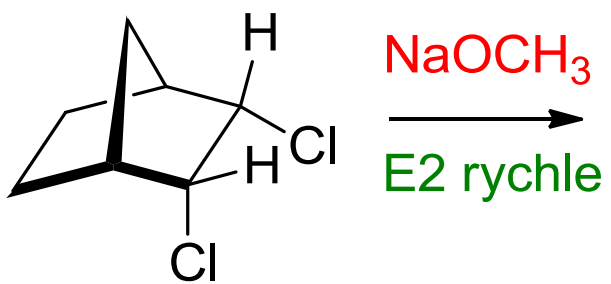
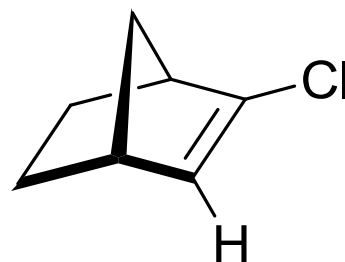
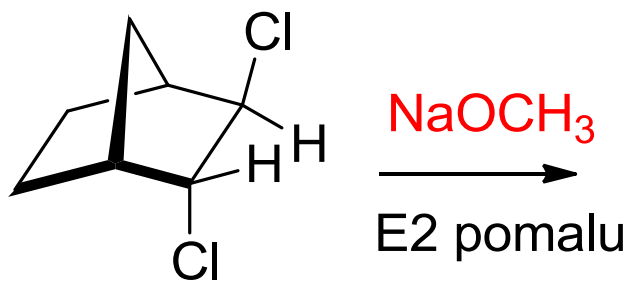


E2 reakce probíhá v jednom kroku.



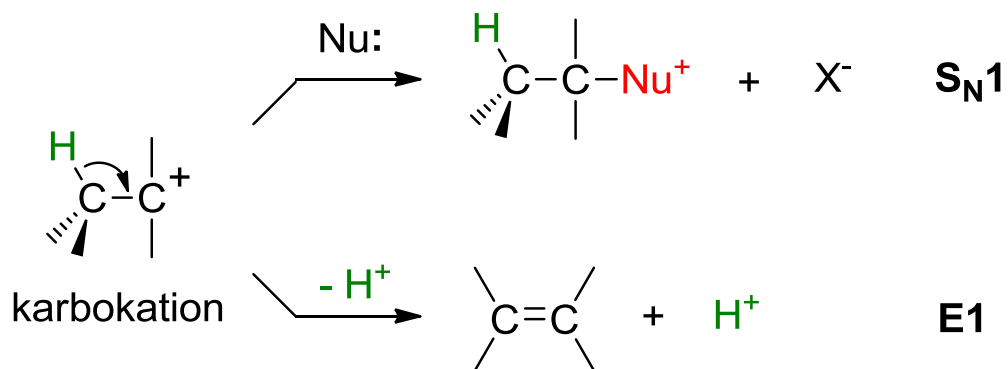
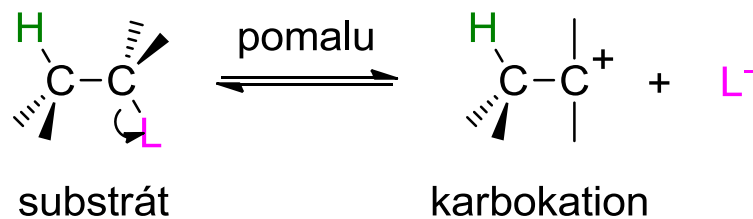
The E2 Reaction Mechanism



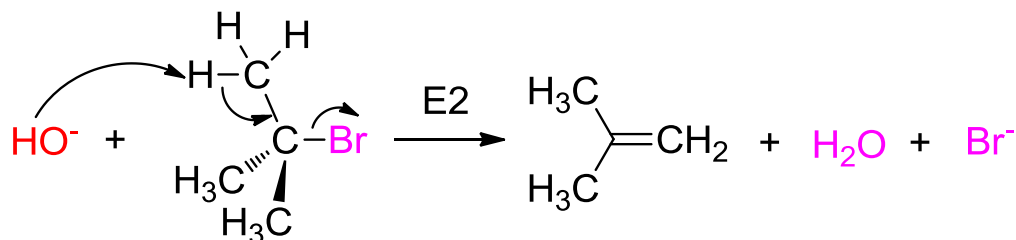
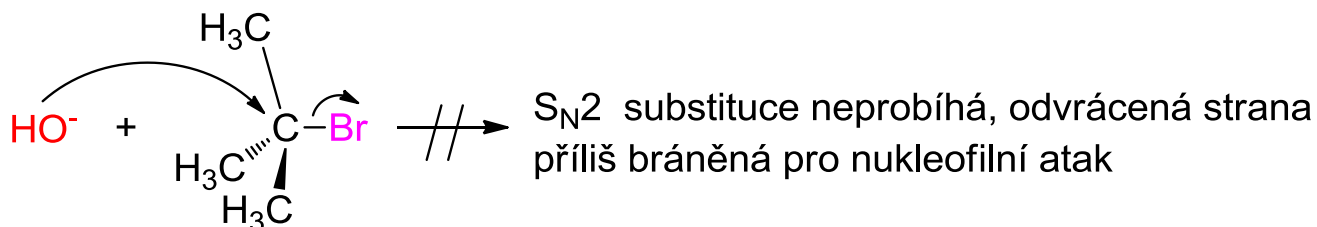
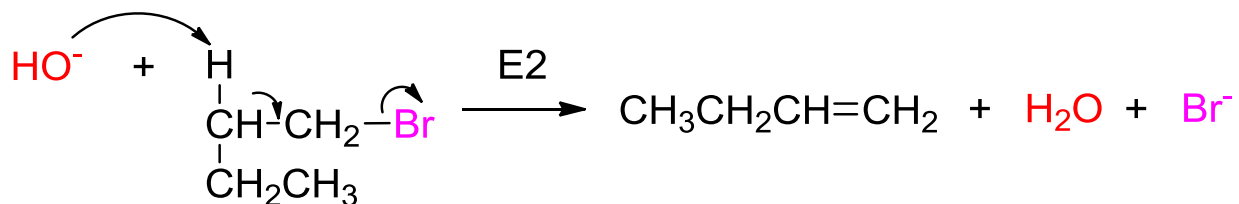
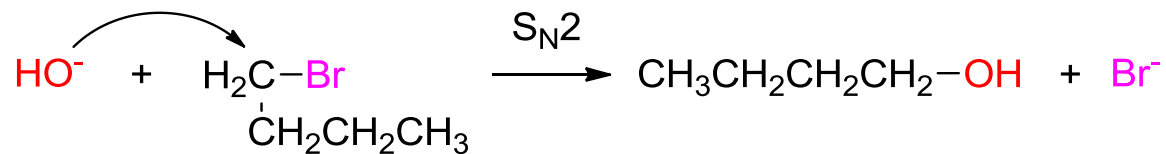


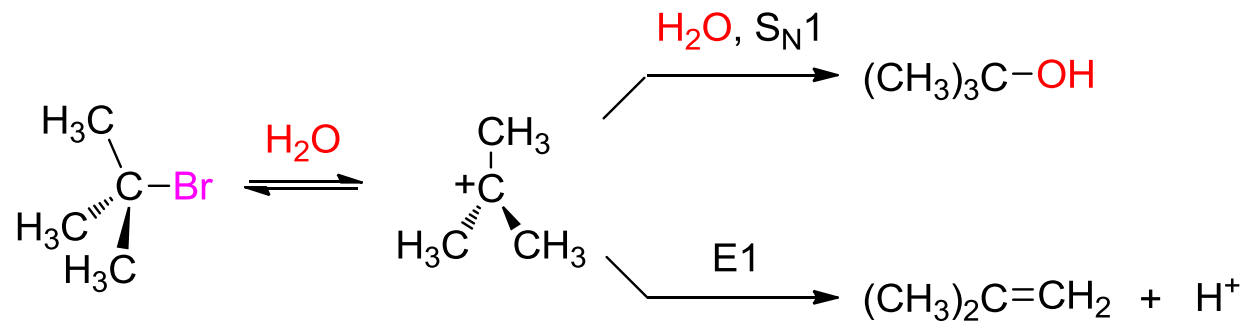
E1 mechanism.

První krok tohoto mechanismu je stejný jako v případě S_N1 substituce, tj. pomalá a rychlost určující ionizace substrátu na karbokation.



Srovnání substituce a eliminace





primární $R-CH_2-X$ \Longrightarrow S_N2

sekundární $\begin{array}{c} R' \\ | \\ R-CH-X \end{array}$ \Longrightarrow S_N2 s nebazickými nukleofily
E2 se silnými bázemi

terciární $\begin{array}{c} R' \\ | \\ R-C-X \\ | \\ R'' \end{array}$ \Longrightarrow obvykle E2
 S_N1 nebo E1 s nebazickými nukleofily