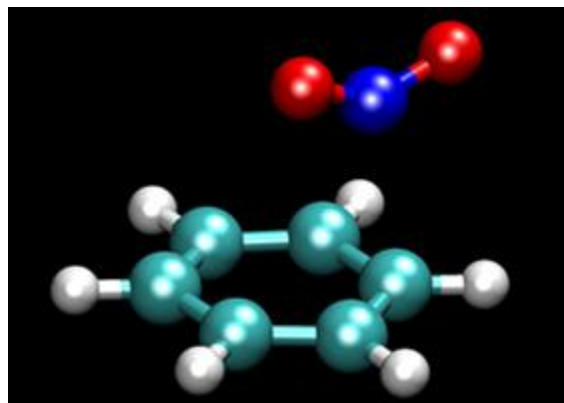
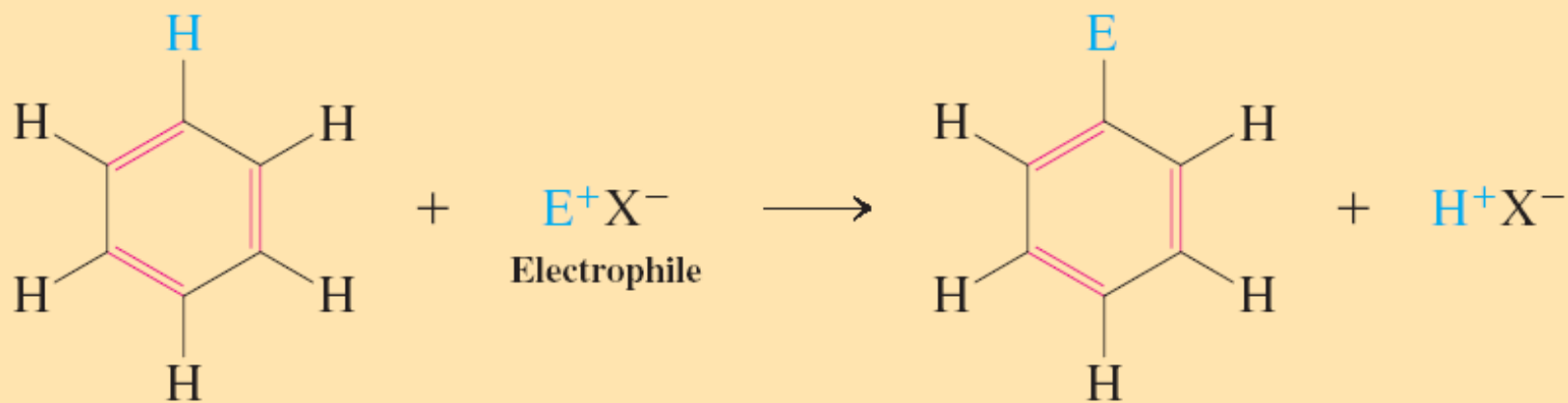


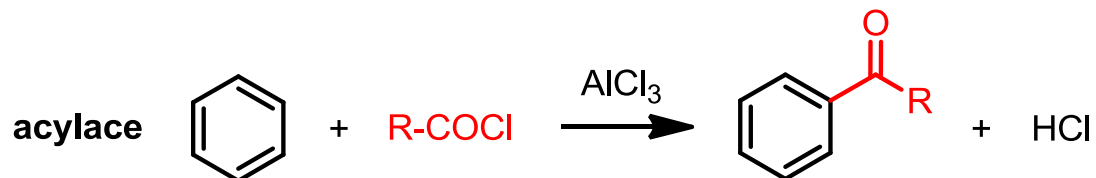
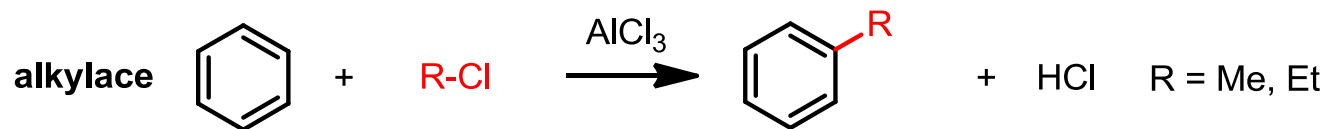
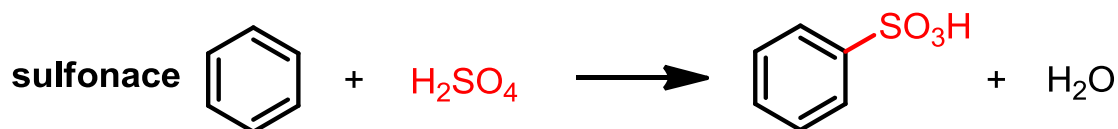
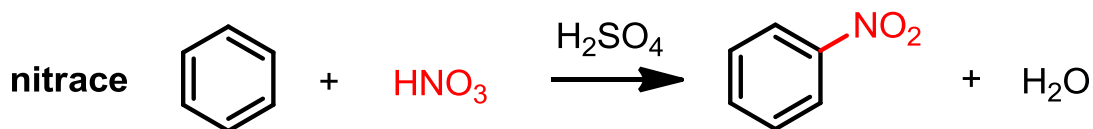
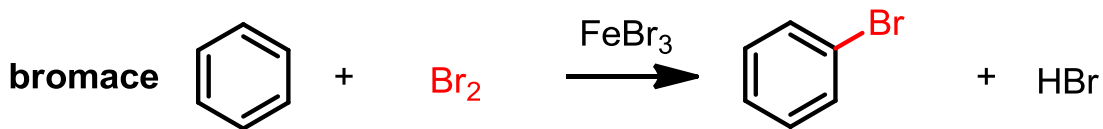
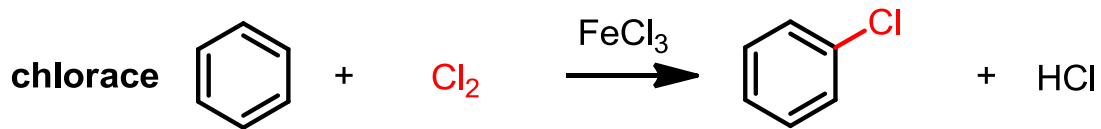
# Elektrofilní aromatické substituce



## Electrophilic Aromatic Substitution

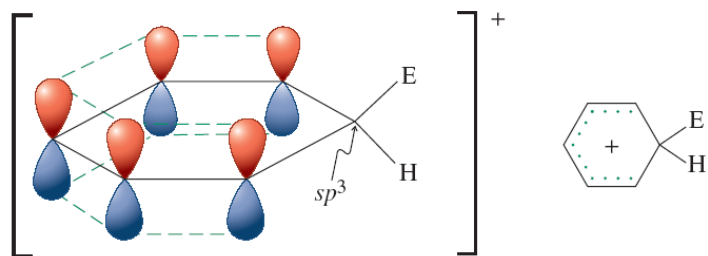
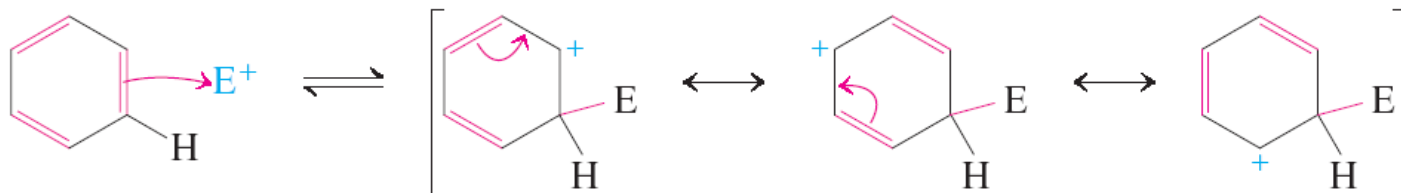


**Elektrofilní  
aromatická  
substituce**

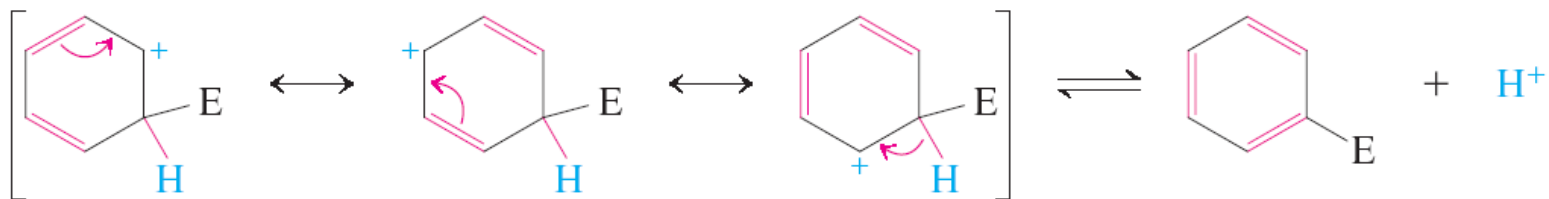


# Mechanismus elektrofilní aromatické substituce

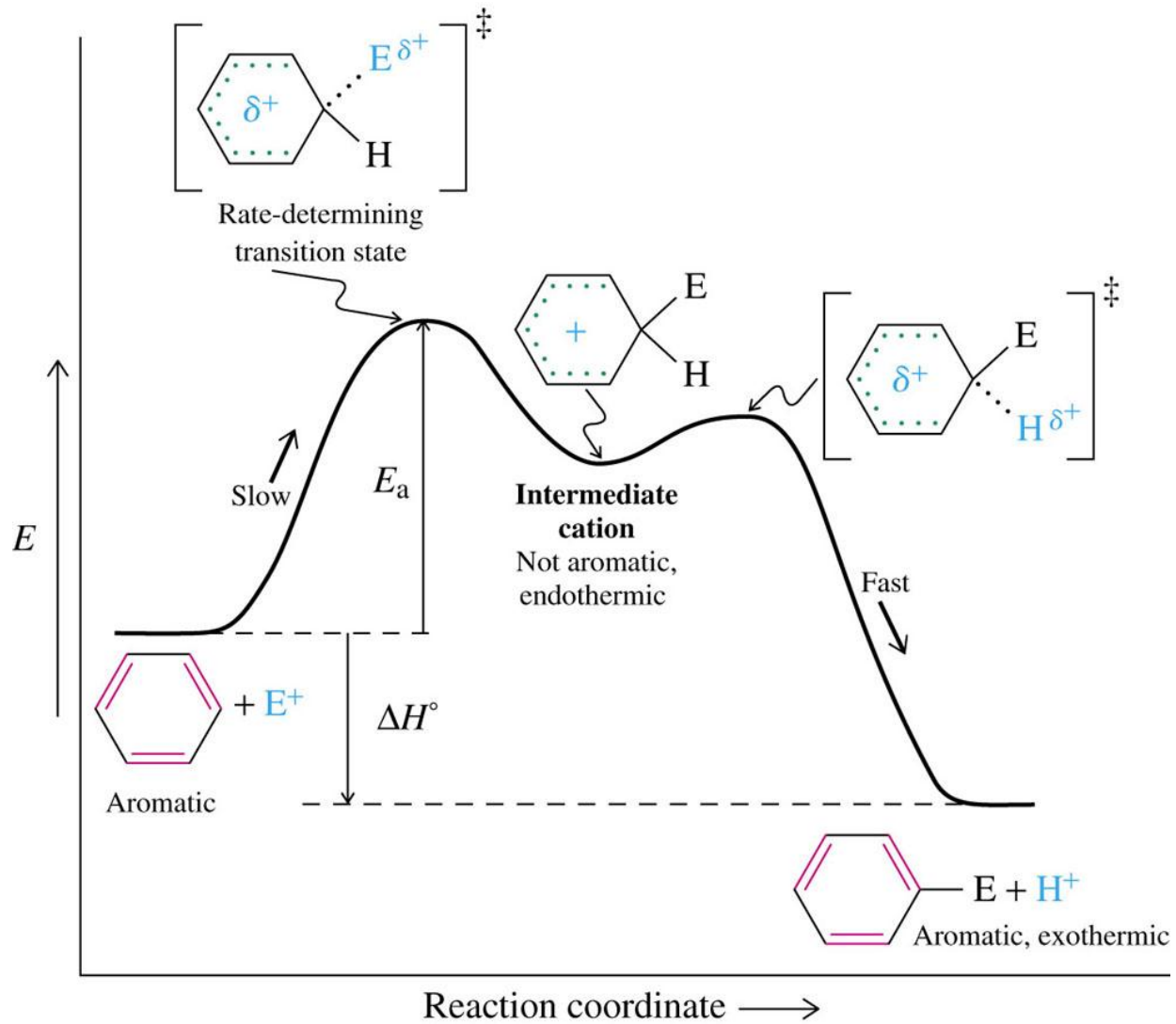
## Krok 1. Elektrofilní atak



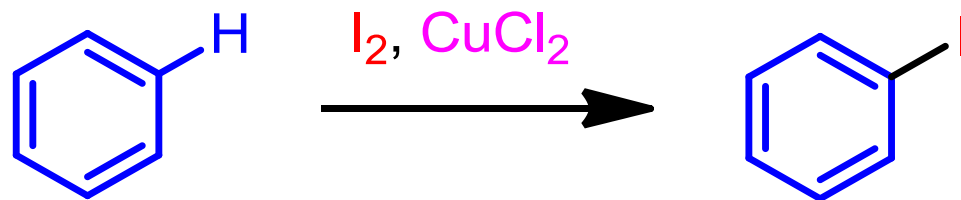
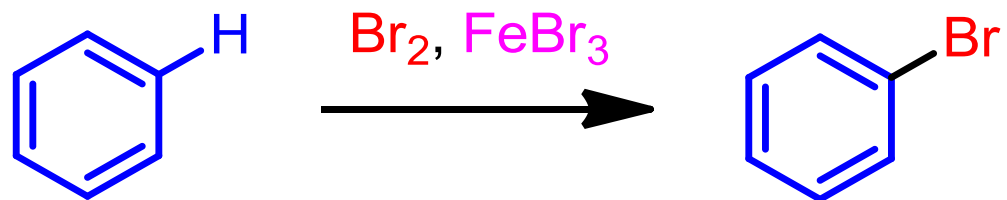
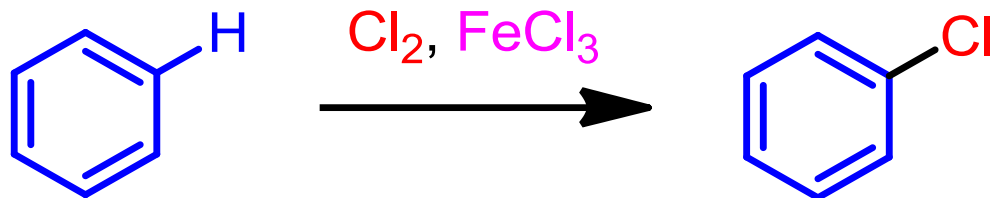
## Krok 2. Ztráta protonu



# Elektrofilní substituce - mechanismus

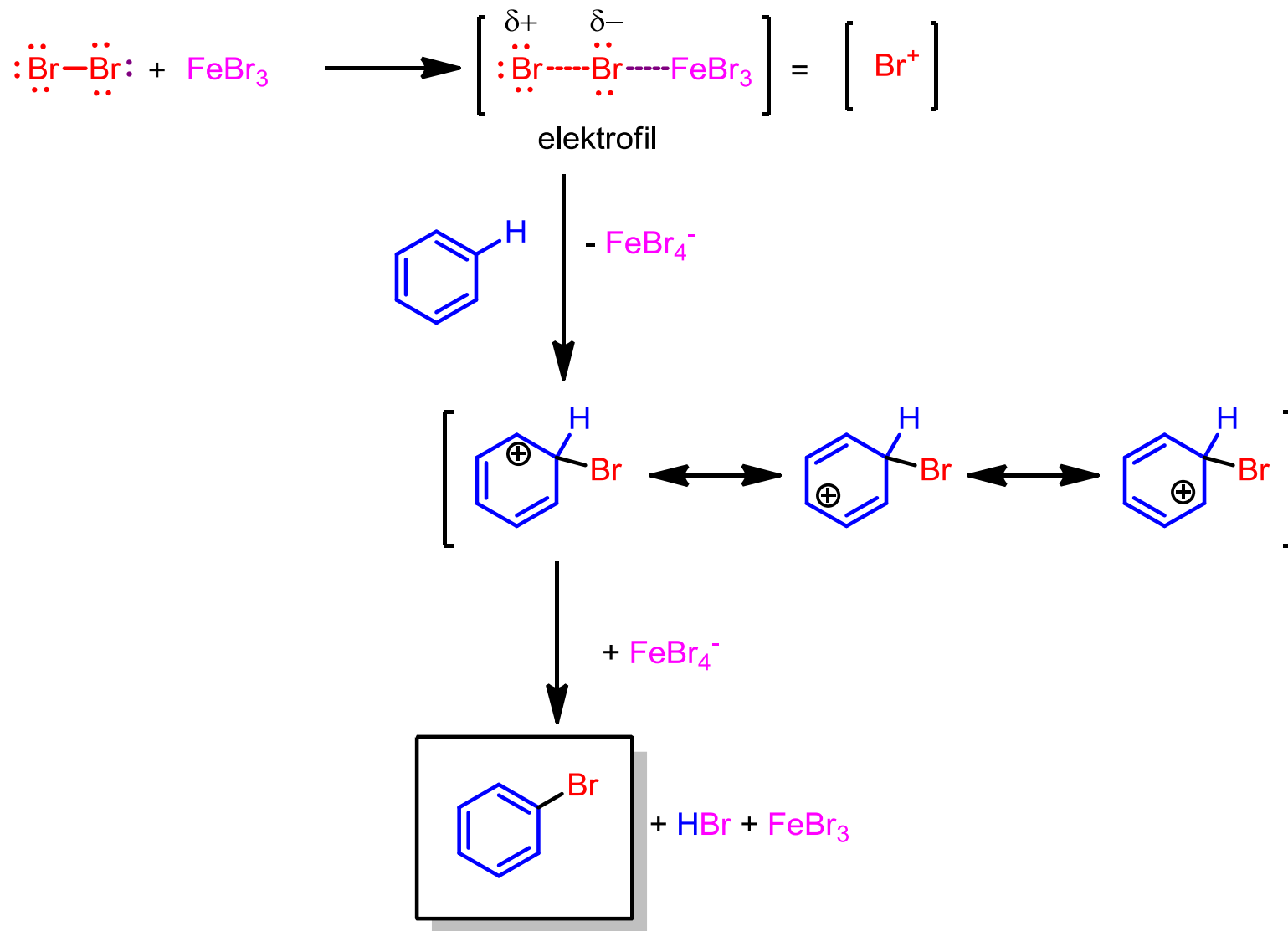


## Elektrofilní halogenace

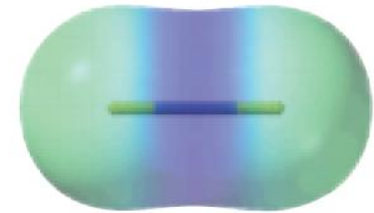
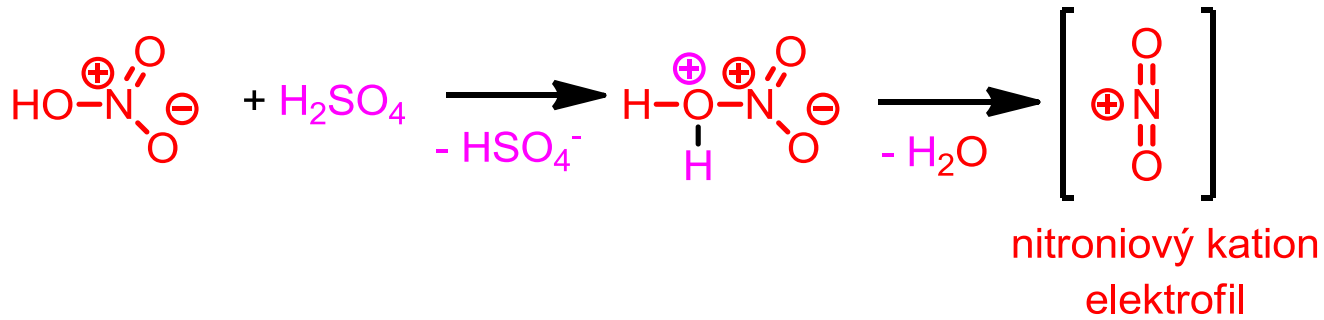
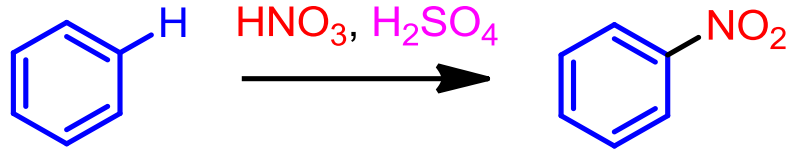


# Elektrofilní halogenace - mechanismus

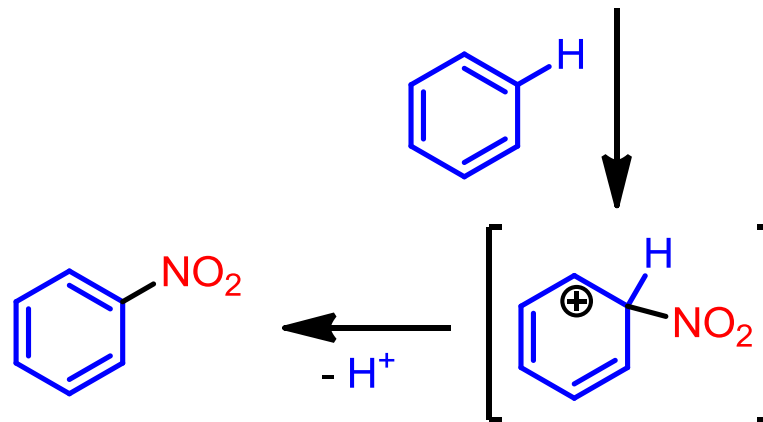
Aktivace Lewisovou kyselinou ( $\text{FeCl}_3$ ,  $\text{FeBr}_3$ ,  $\text{SnCl}_4$ ,  $\text{ZnCl}_2$  atd.)



# Elektrofilní nitrace

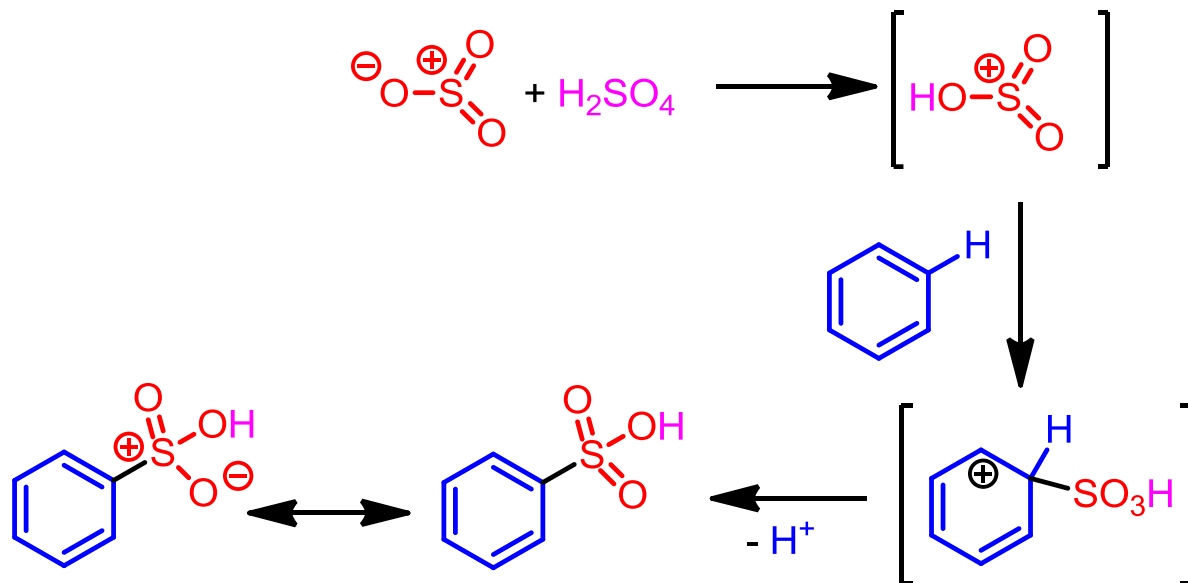
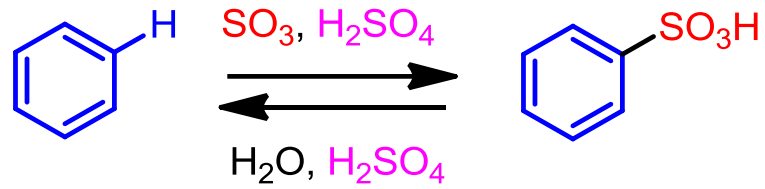


Nitronium ion

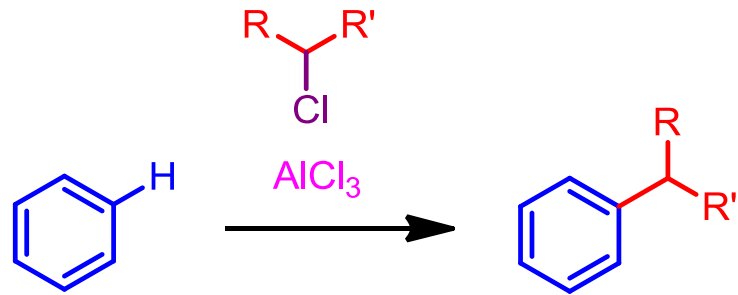




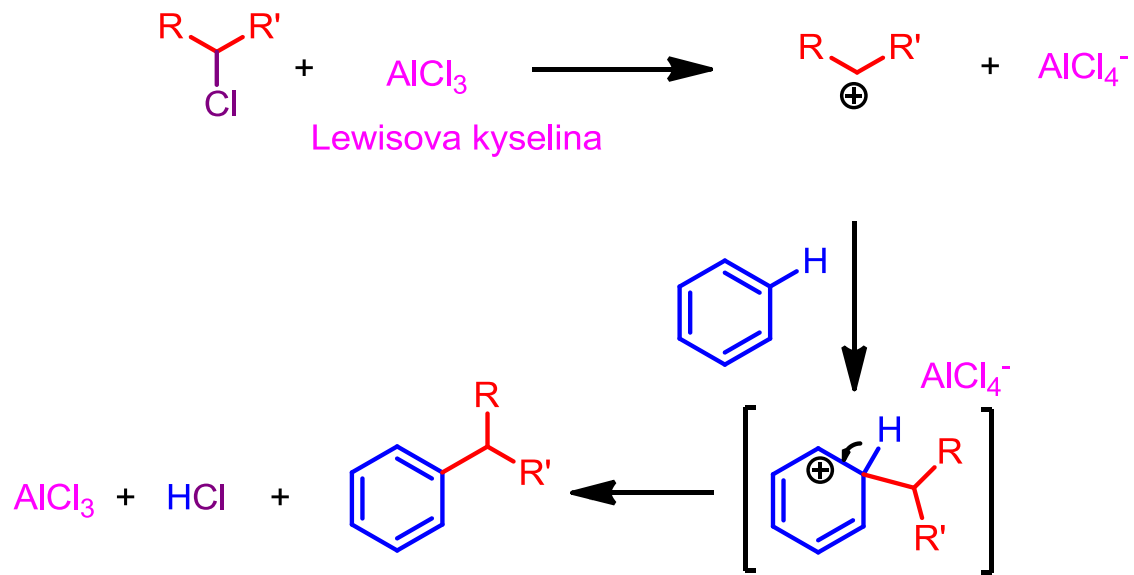
## Elektrofilní sulfonace



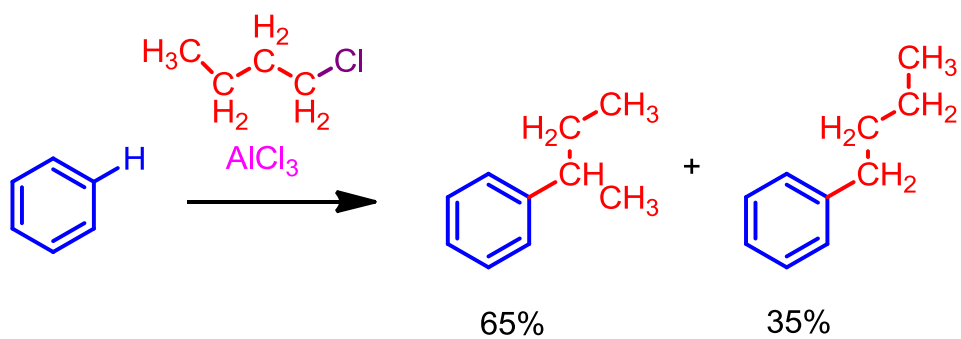
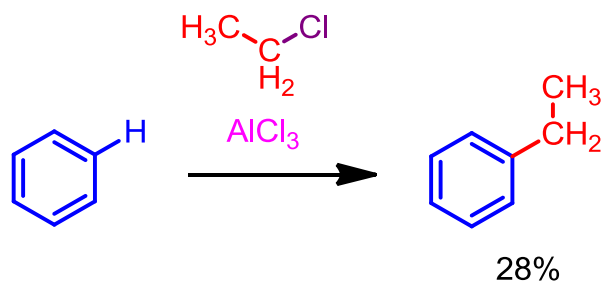
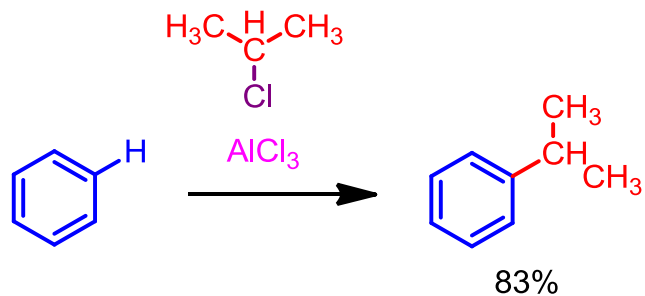
# Elektrofilní alkylace (Friedel-Craftsova alkylace)



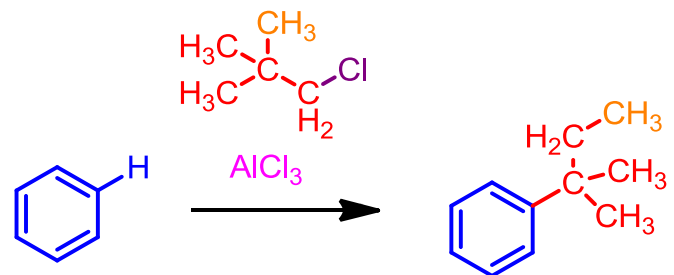
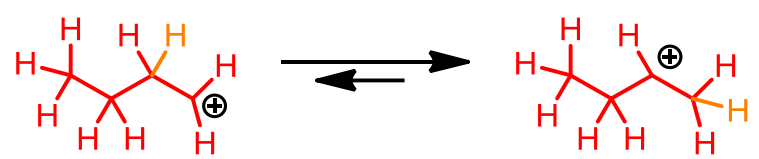
R, R' = H nebo alkyl



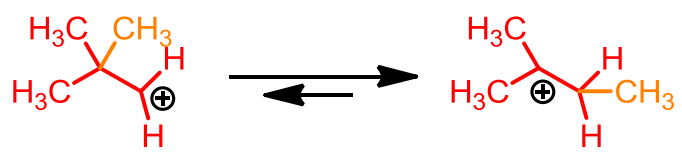
# Elektrofilní alkylace (Friedel-Craftsova alkylace)



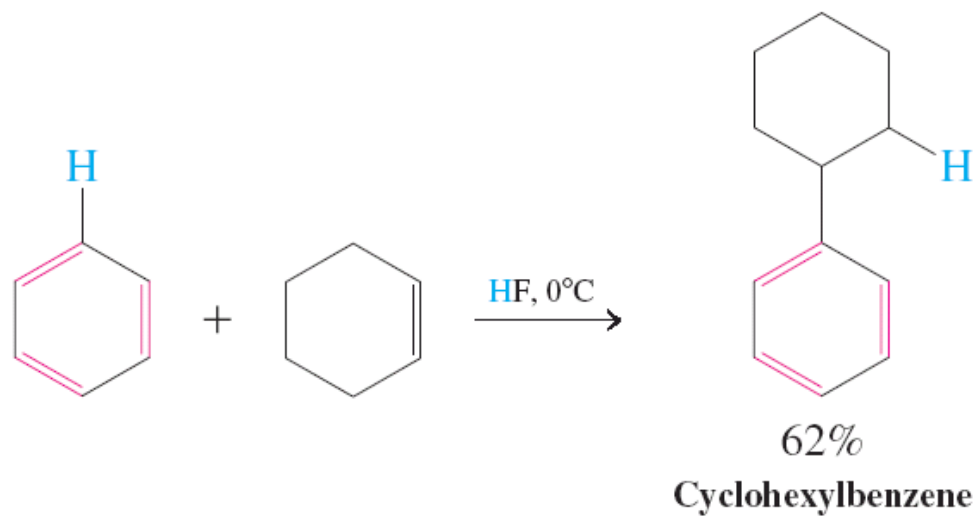
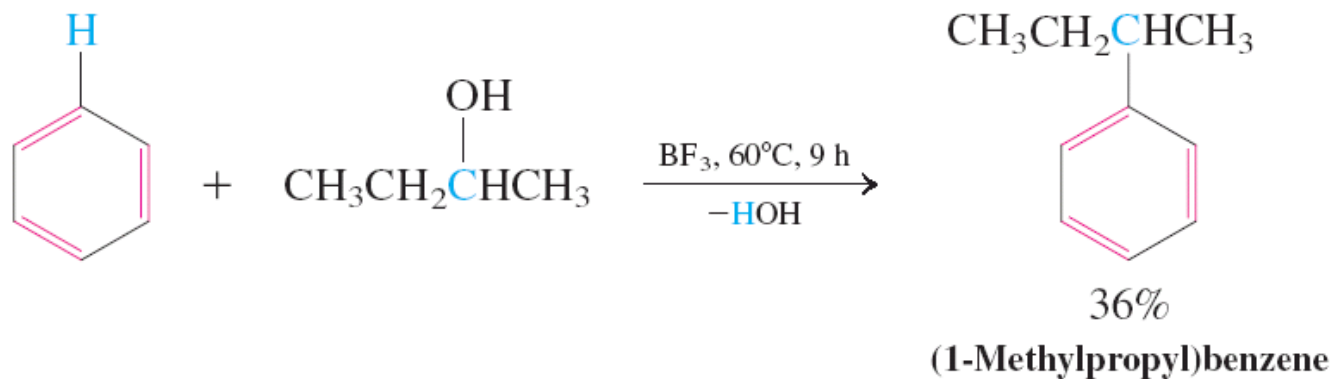
Přesmyk přesunem protonu



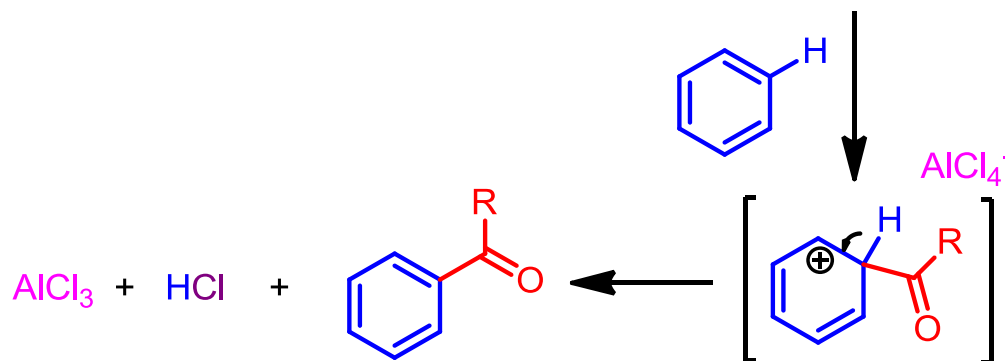
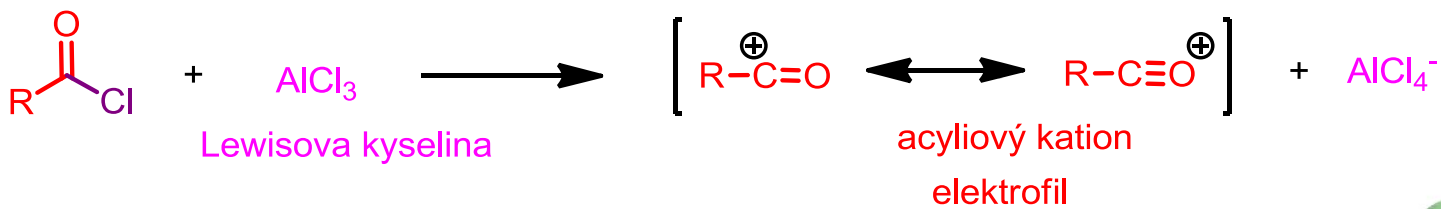
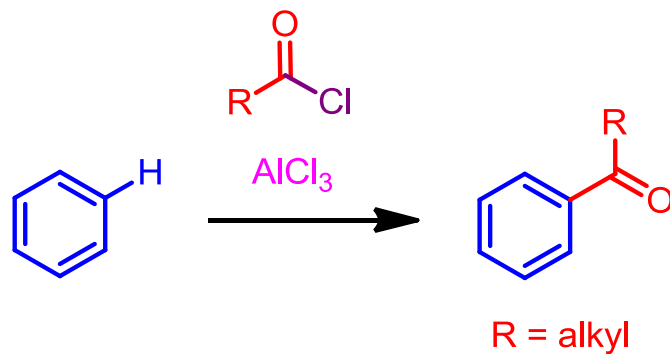
Přesmyk přesunem alkyly



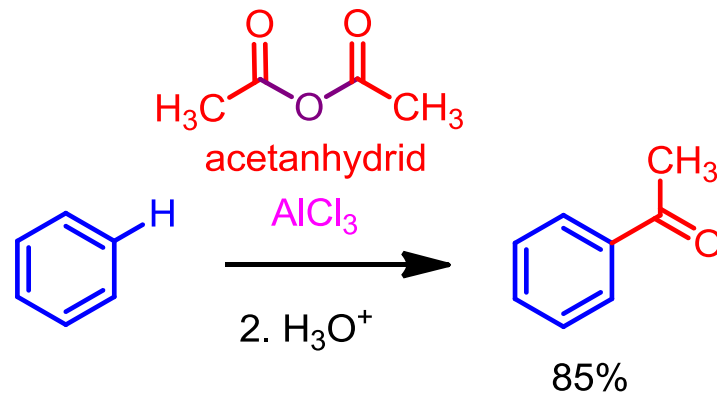
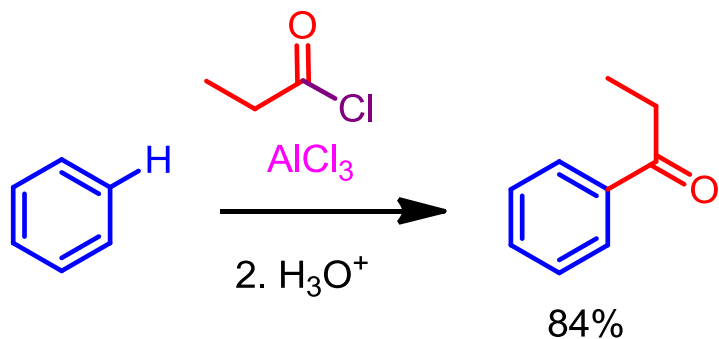
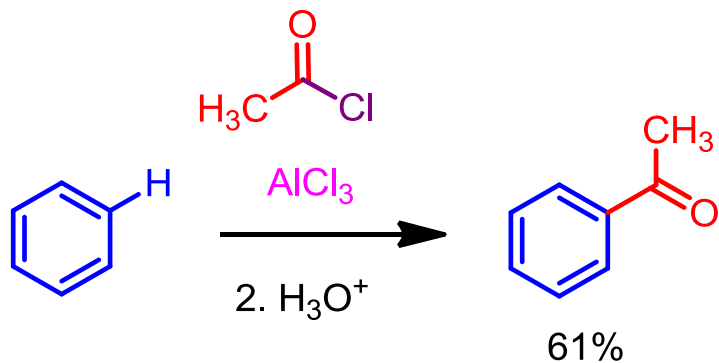
## Friedel-Crafts Alkylations Using Other Carbocation Precursors



# Elektrofilní acylace (Friedel-Craftsova acylace)



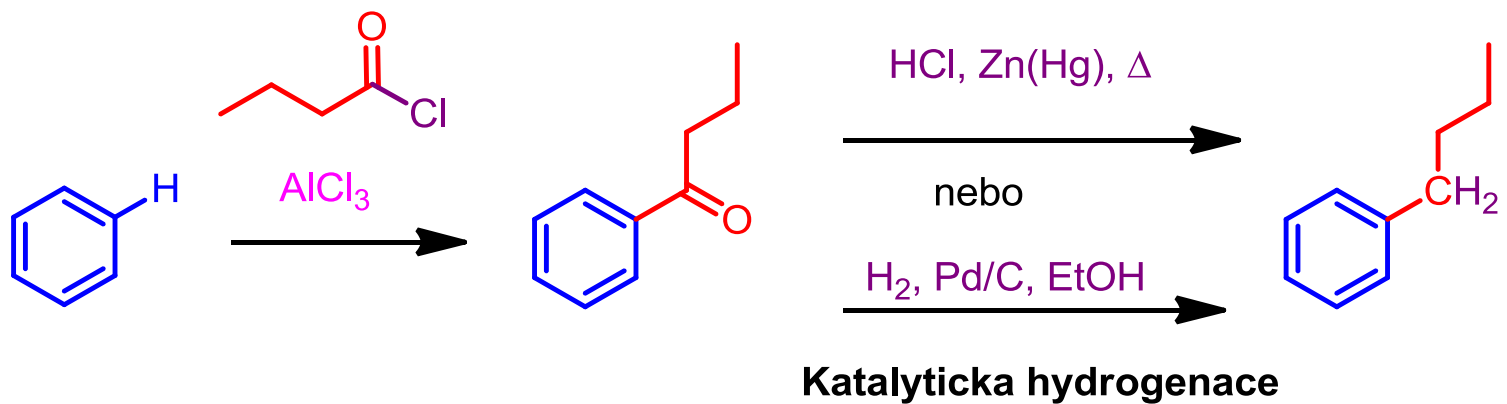
## Elektrofilní acylace (Friedel-Craftsova acylace)



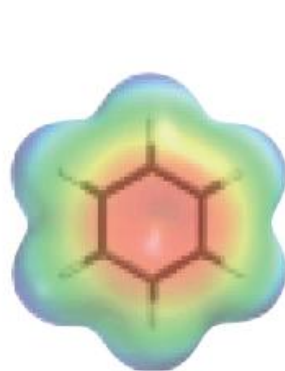
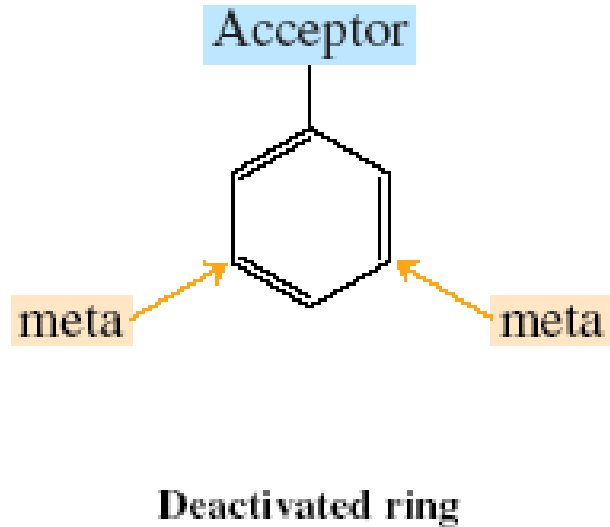
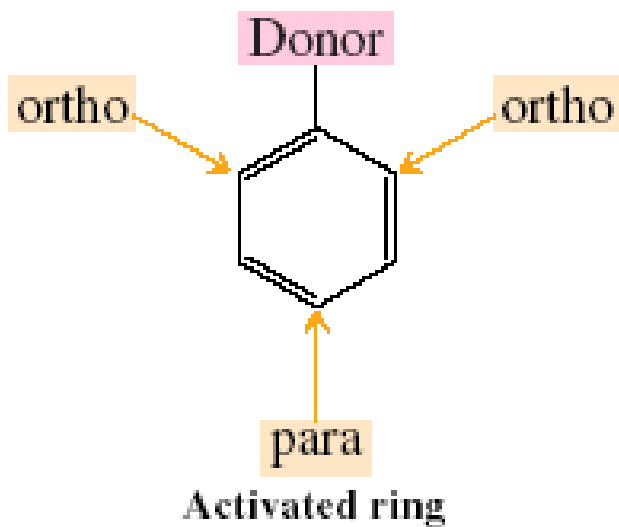
### Příprava acyl chloridů



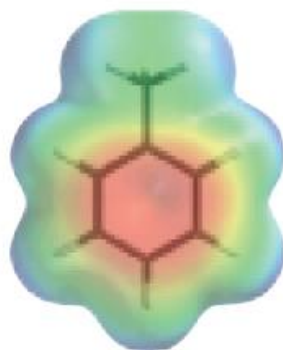
## Příprava alkylbenzenů – acylace + redukce



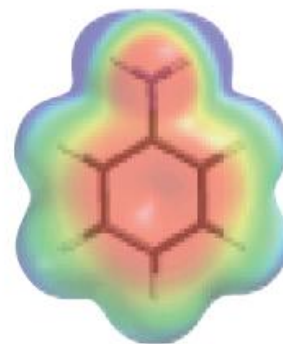
# Elektrofilní substituce derivátů benzenu



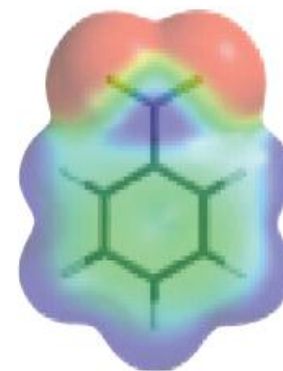
Benzene



Methylbenzene  
(Toluene)



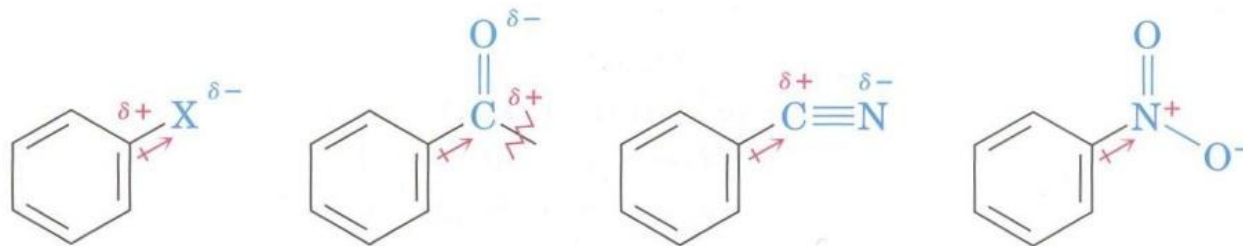
Benzenamine  
(Aniline)



Nitrobenzene

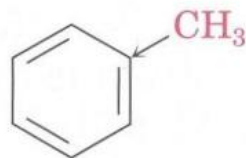


# Induktivní efekt



(X = F, Cl, Br, I)

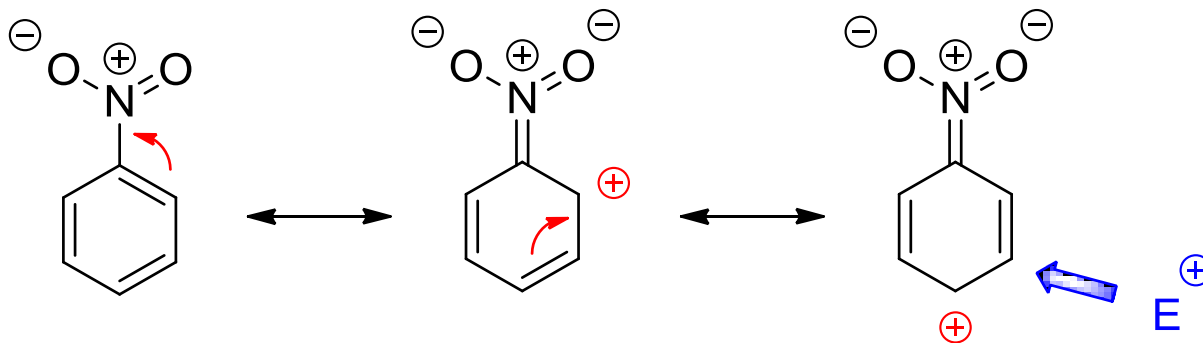
skupiny připojené k aromatickým kruhům mají v důsledku polaritavy svých vazeb elektronakceptorní indukivní efekt ( $-I$ -efekt)



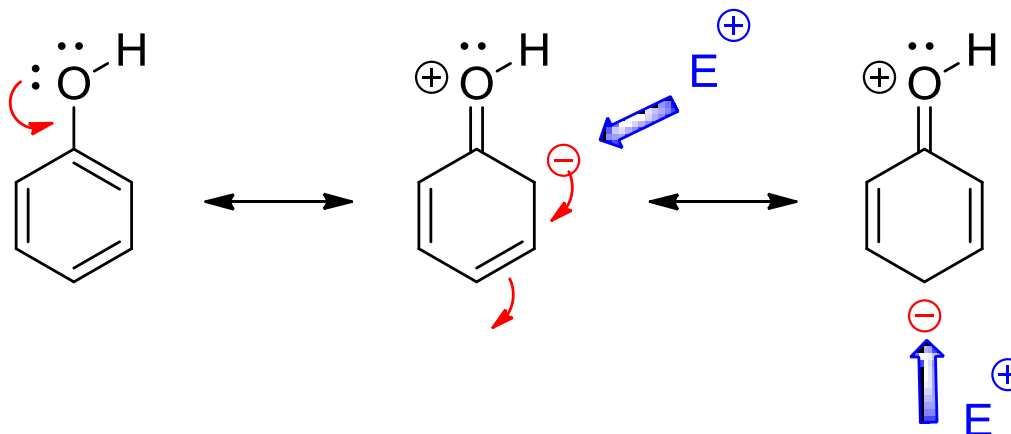
**alkylová skupina; elektrondonorová indukivní skupina**

# Rezonanční (mezomerní) efekt

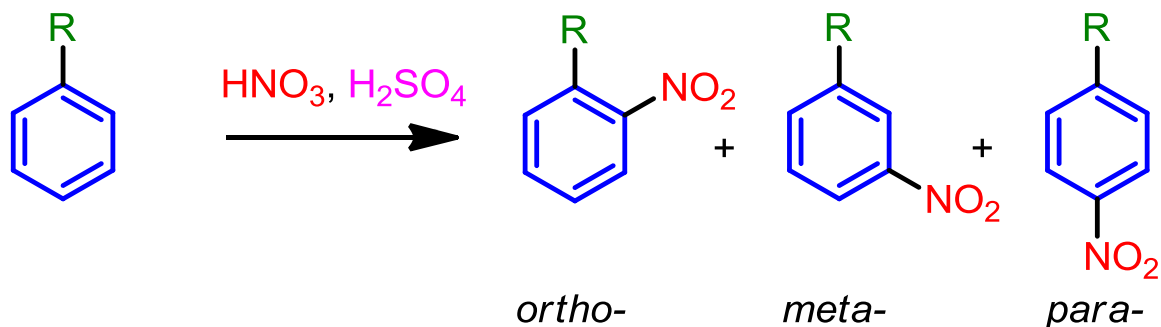
## Elektron-akceptorní skupiny



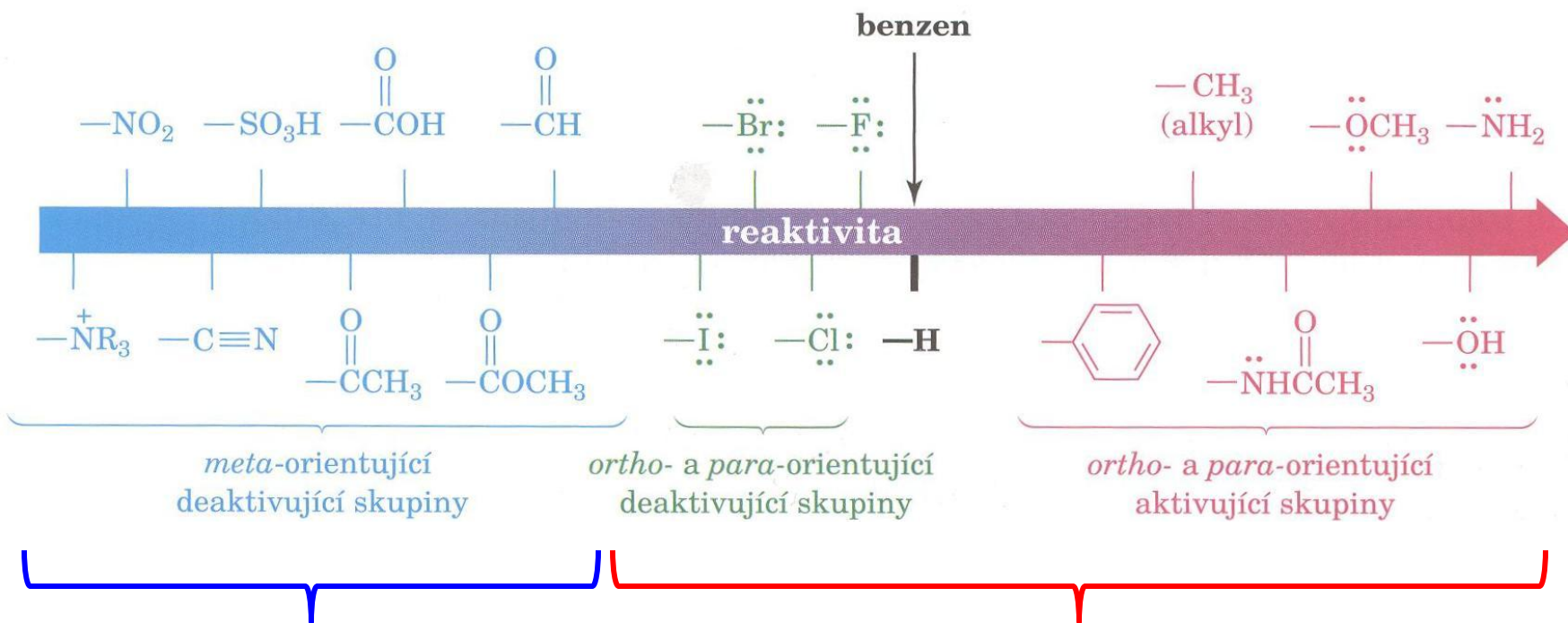
## Elektron-donorní skupiny



# Porovnání rychlosti a direktivního efektu nitrace derivátů benzenu



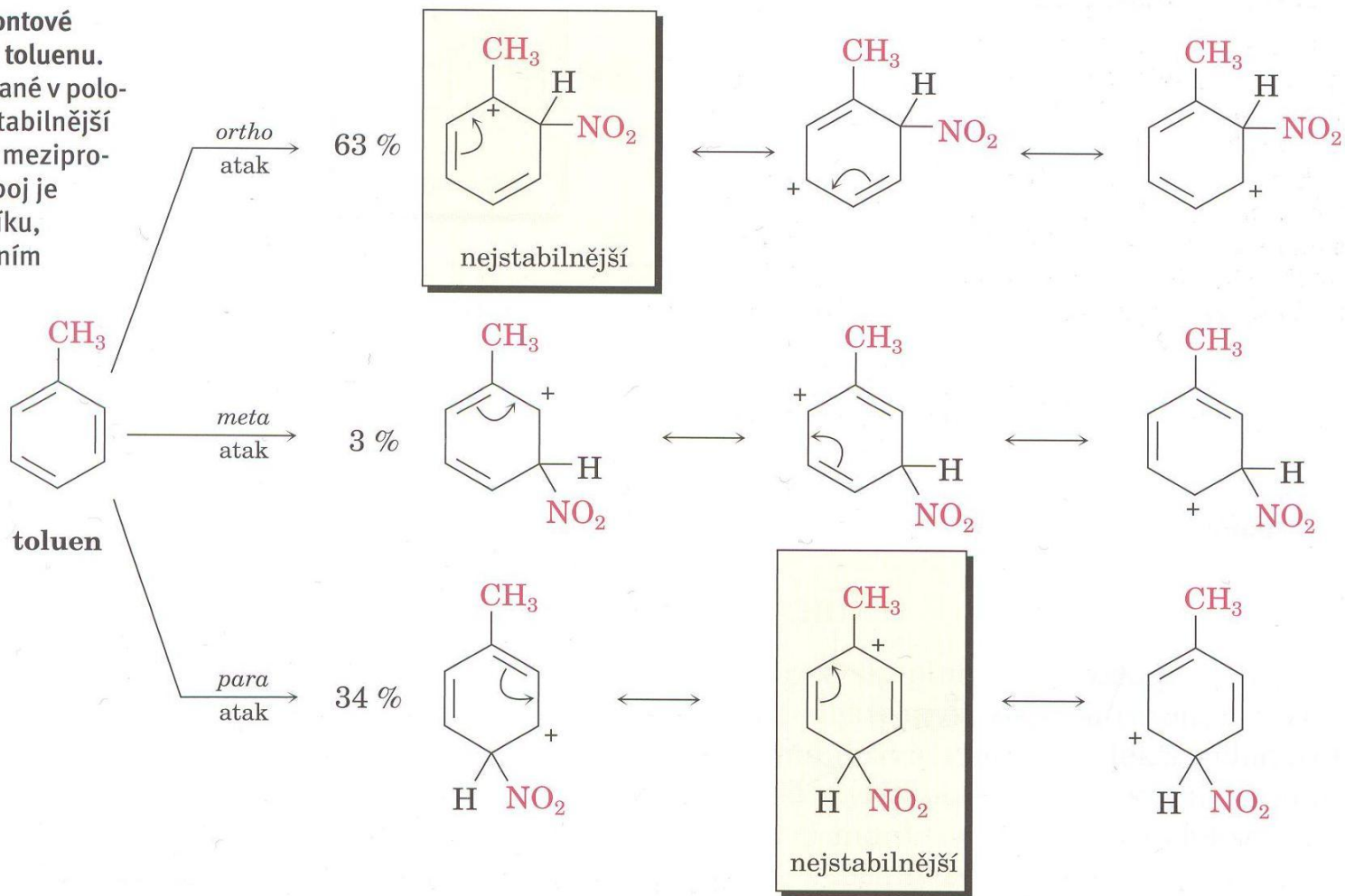
R	Relativní rychlost	Procenta izomeru		
		Ortho	Meta	Para
Ortho, para directors	NH(C <sub>6</sub> H <sub>5</sub> )	$8.4 \times 10^5$	<0.1	29
	OH	1000	<2	58
	CH <sub>3</sub>	25	4	38
	C <sub>6</sub> H <sub>5</sub>	8	<0.6	70
	H	1		
Special: Ortho, para directors	I	0.18	<0.2	59
	Cl	0.033	<0.2	69
	CO <sub>2</sub> CH <sub>2</sub> CH <sub>3</sub>	0.0037	72	4
Meta directors	CF <sub>3</sub>	$2.6 \times 10^{-5}$	91	3
	NO <sub>2</sub>	$6 \times 10^{-8}$	93	2
	N(CH <sub>3</sub> ) <sub>3</sub>	$1.2 \times 10^{-8}$	89	11



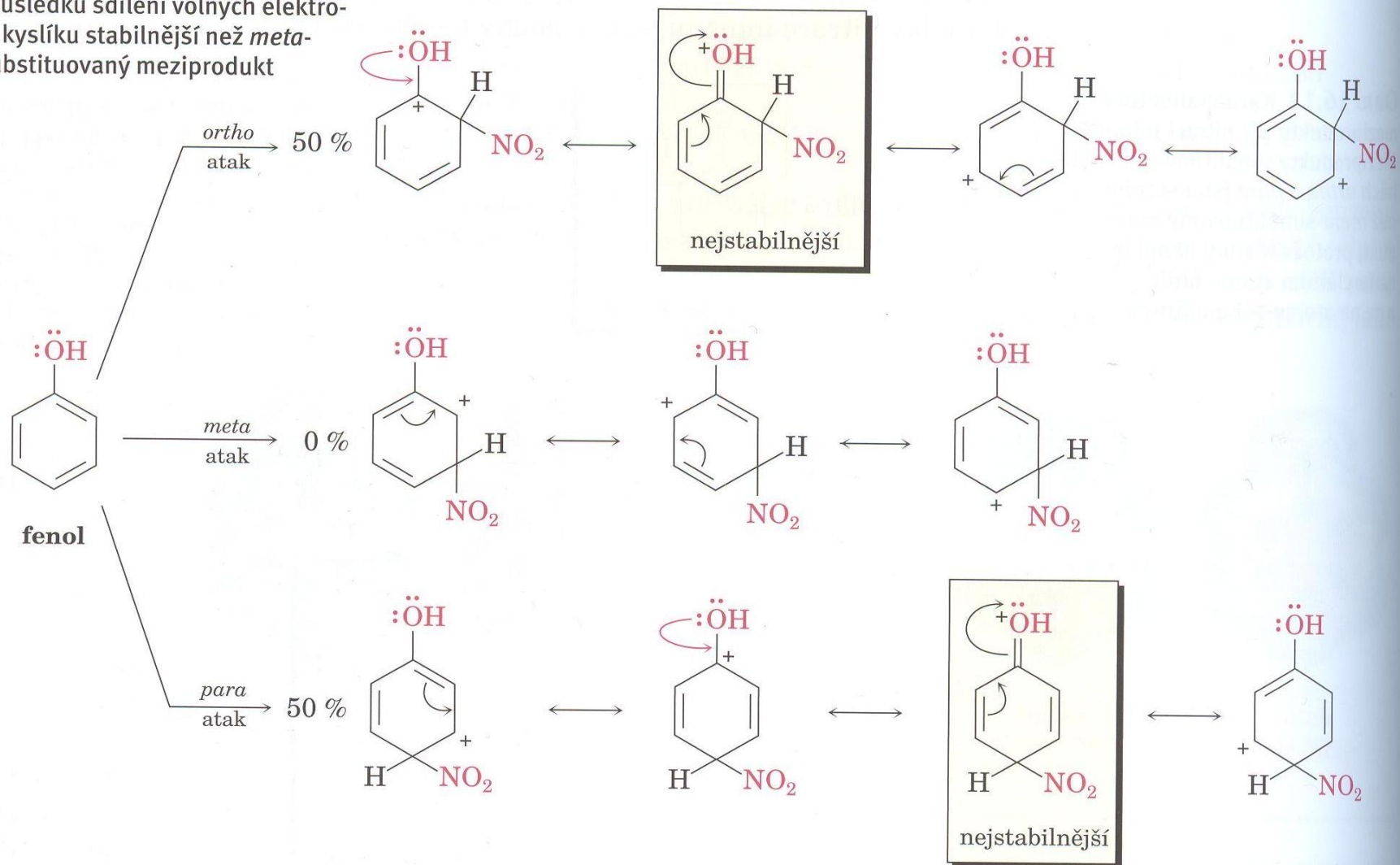
**Substituenty II. třídy**

**Substituenty I. třídy**

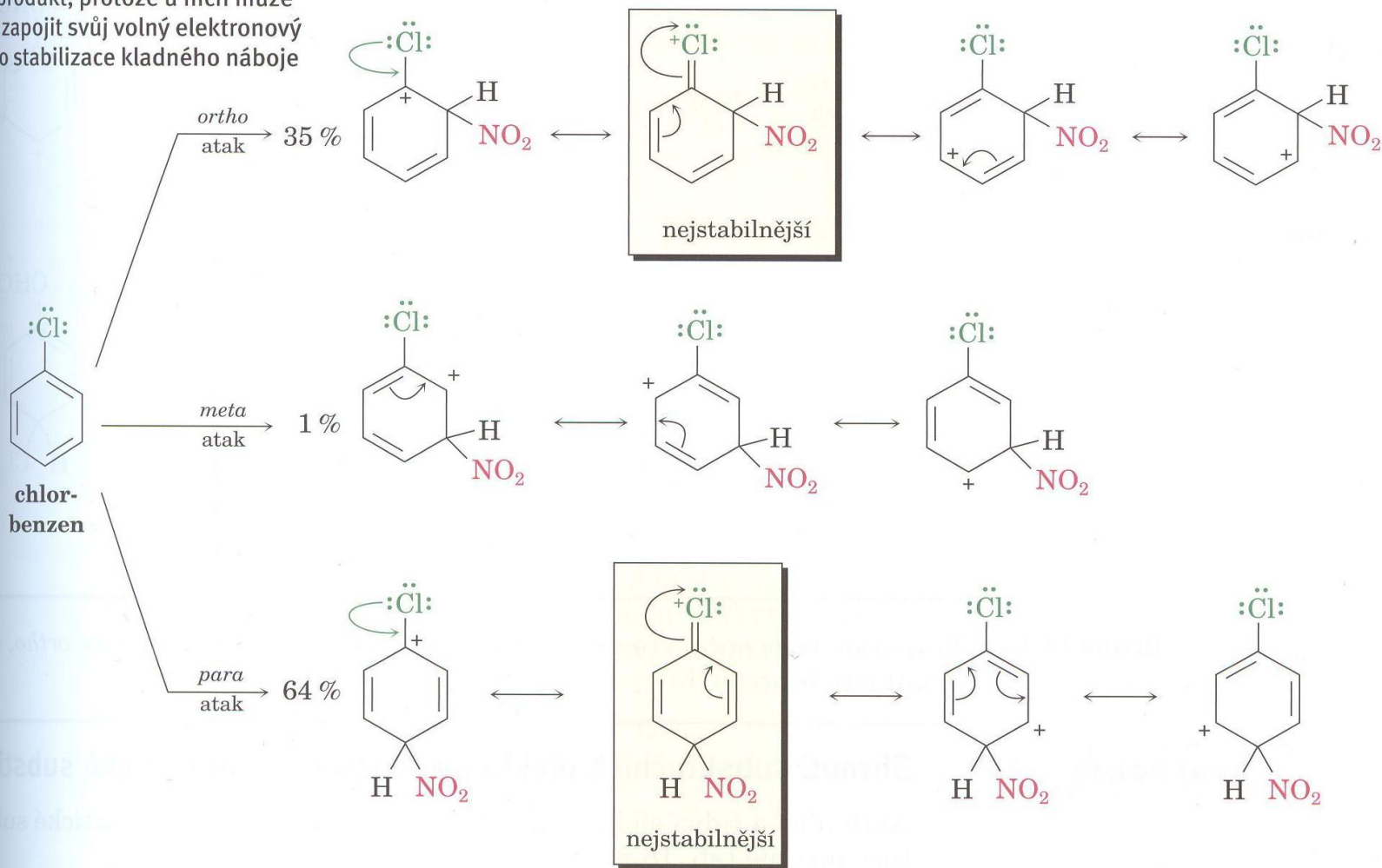
**OBR. 16.12** Karbokationtové meziprodukty při nitraci toluenu. Meziprodukty substituované v polohách *ortho* a *para* jsou stabilnější než *meta*-substituovaný meziprodukt, protože kladný náboj je na terciárním atomu uhlíku, a ne na atomu sekundárním



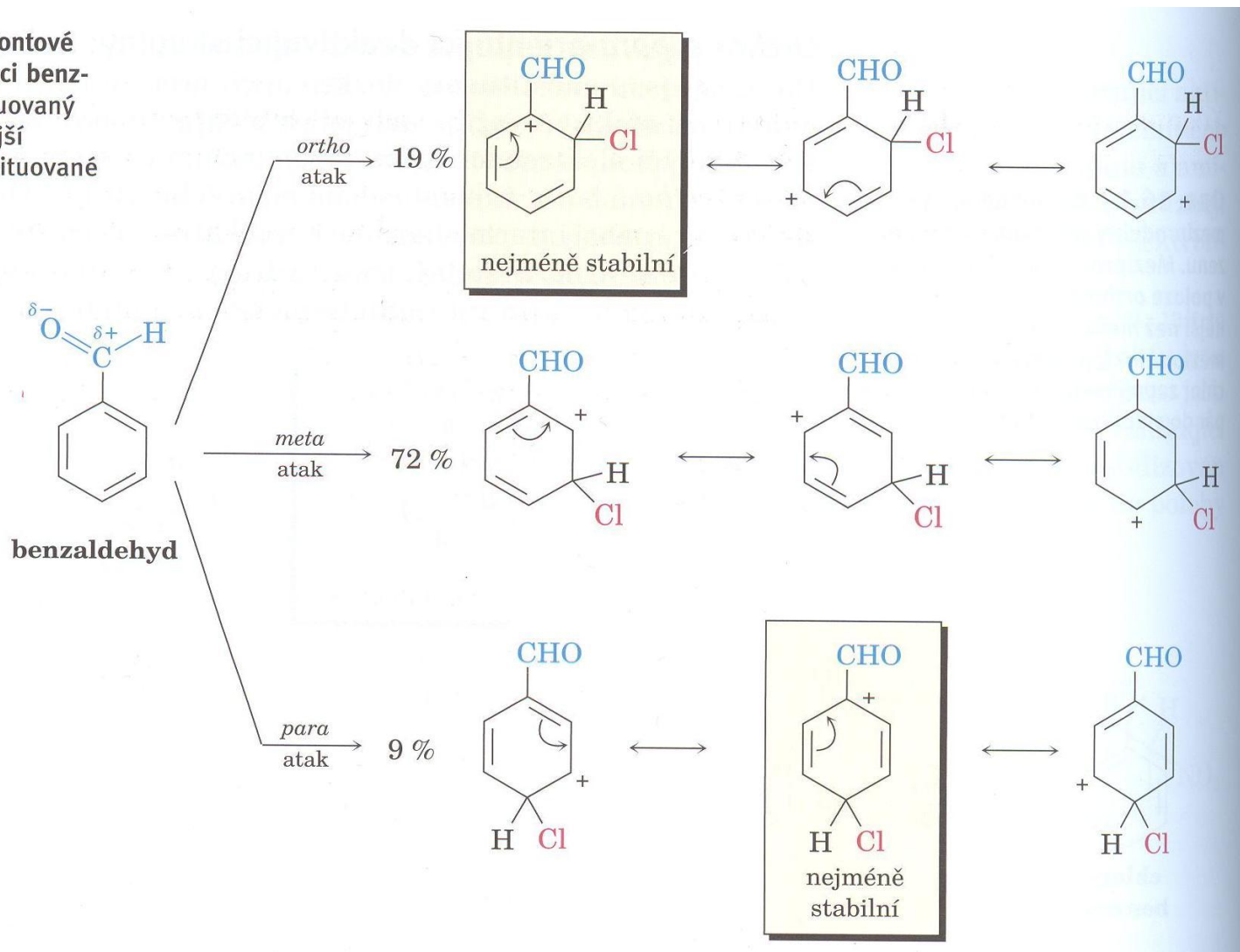
**OBR. 16.13** Karbokationové meziprodukty při nitraci fenolu. Meziprodukty substituované v polohách *ortho* a *para* jsou v důsledku sdílení volných elektronů kyslíku stabilnější než *meta*-substituovaný meziprodukt



**OBR. 16.14** Karbokationové meziprodukty při nitraci chlorbenzenu. Meziprodukty substituované v poloze *ortho* a *para* jsou stabilnější než *meta*-substituovaný meziprodukt, protože u nich může chlor zapojit svůj volný elektronový pár do stabilizace kladného náboje



**OBR. 16.15** Karbokationtové meziprodukty při chloraci benzaldehydu. *meta*-Substituovaný meziprodukt je stabilnější než meziprodukty substituované v poloze *ortho* a *para*

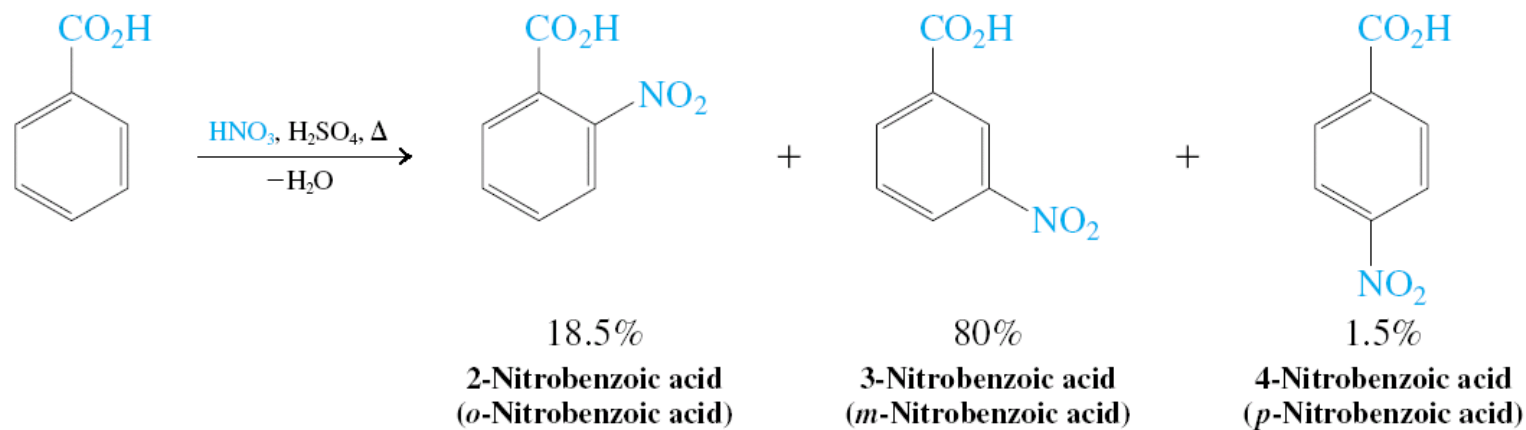




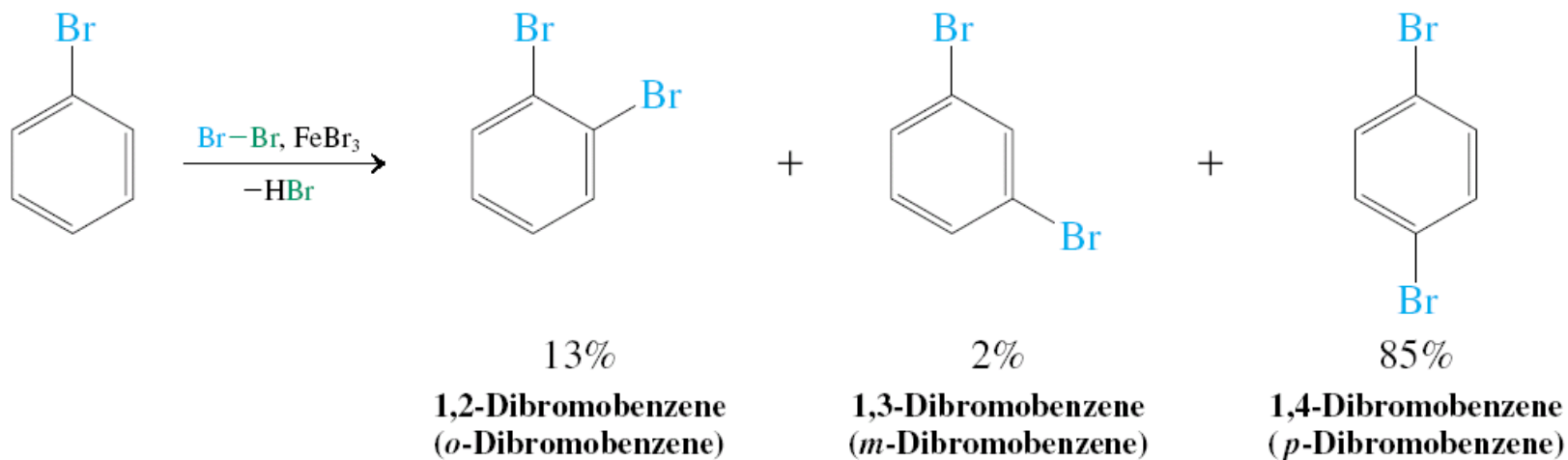
**TABULKA 16.2 Substituční efekty při elektrofilní aromatické substituci**

Substituent	Reaktivita	Orientace	Induktivní efekt	Rezonanční (mezomerní) efekt
$-\text{CH}_3$	aktivující	<i>ortho, para</i>	slabý; elektrondonorní	žádný
$-\ddot{\text{O}}\text{H},$ $-\ddot{\text{N}}\text{H}_2$	aktivující	<i>ortho, para</i>	slabý; elektronakceptorní	silný; elektrondonorní
$-\ddot{\text{F}}:, -\ddot{\text{Cl}}:,$ $-\ddot{\text{Br}}:, -\ddot{\text{I}}:$	deaktivující	<i>ortho, para</i>	silný; elektronakceptorní	slabý; elektrondonorní
$-\overset{+}{\text{N}}(\text{CH}_3)_3$	deaktivující	<i>meta</i>	silný; elektronakceptorní	žádný
$-\text{NO}_2, -\text{CN},$ $-\text{CHO}, -\text{COOCH}_3,$ $-\text{COCH}_3, -\text{COOH}$	deaktivující	<i>meta</i>	silný; elektronakceptorní	silný; elektronakceptorní

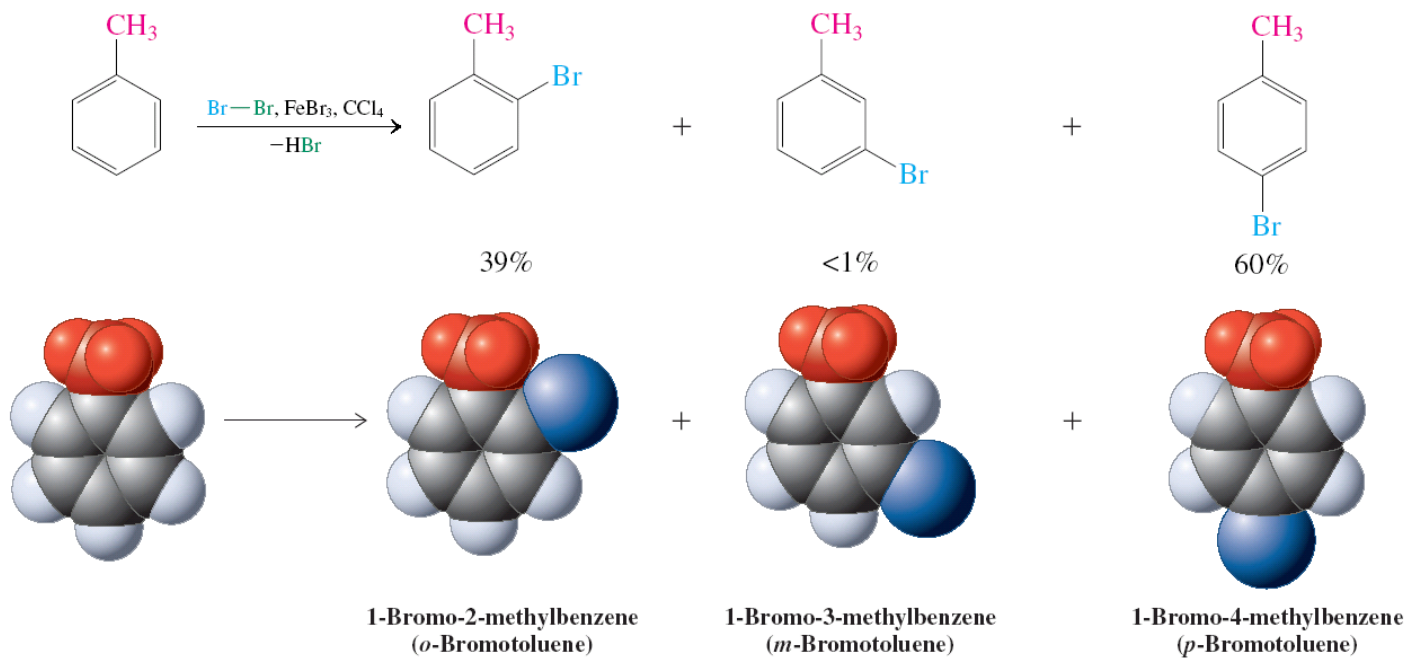
### Electrophilic Meta-Nitration of Benzoic Acid



**Electrophilic Bromination of Bromobenzene Results  
in *ortho*- and *para*-Dibromobenzene**

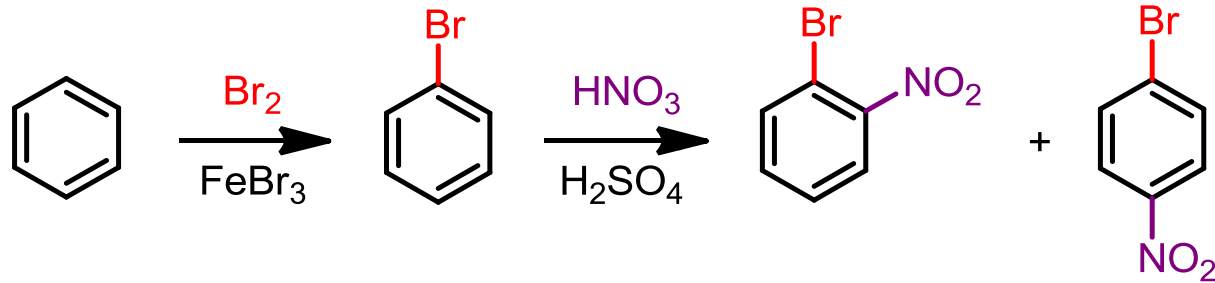


**Electrophilic Bromination of Methylbenzene (Toluene)  
Gives Ortho and Para Substitution**

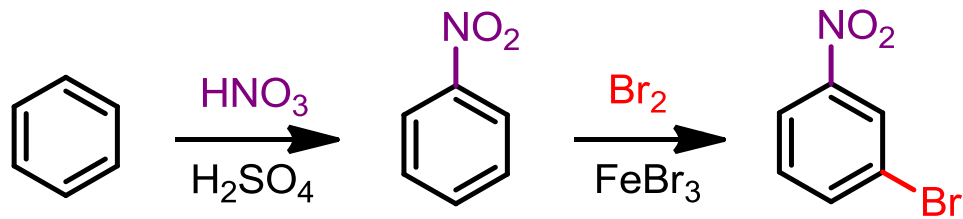


# Význam direktivních efektů v syntéze

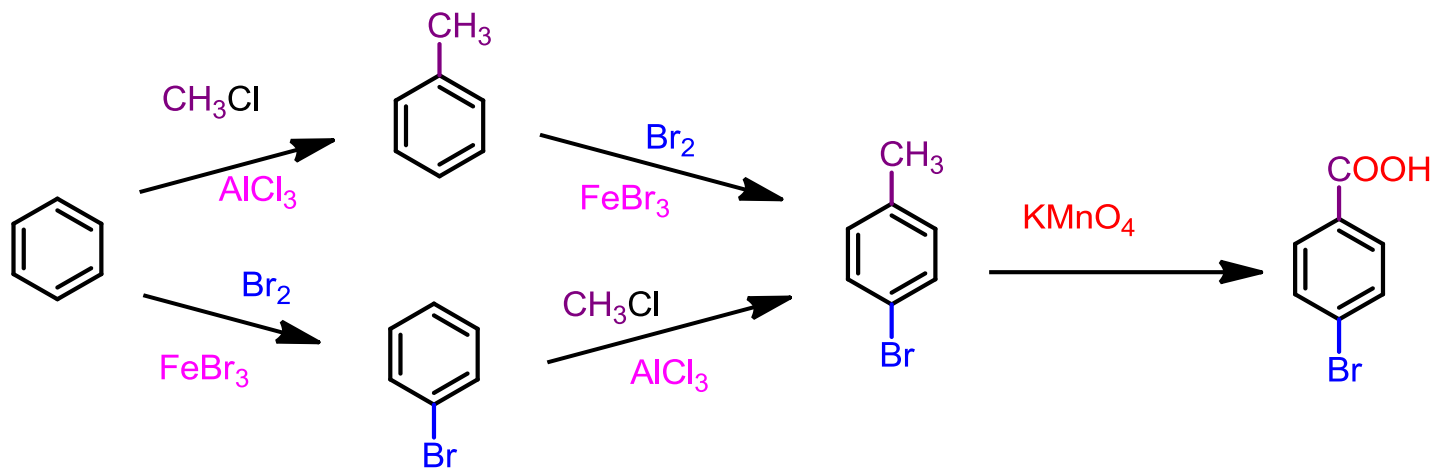
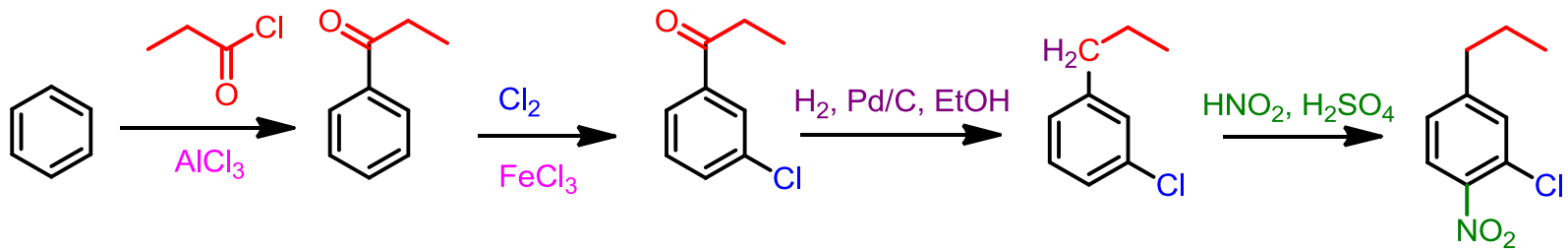
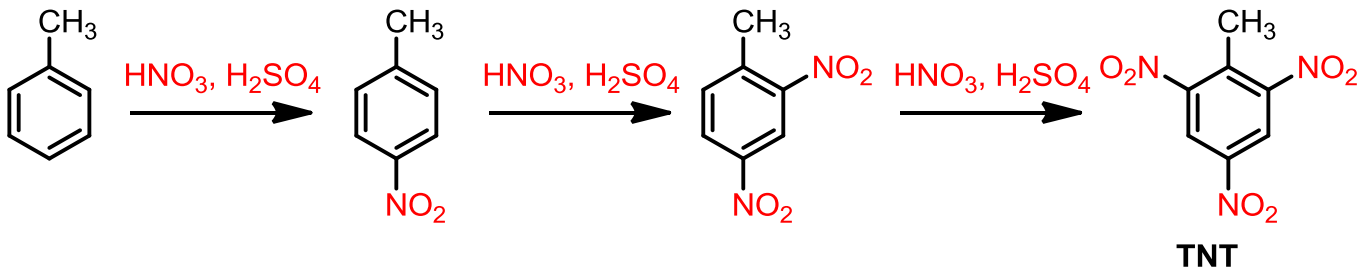
## Příprava 1-brom-2-nitro- a 1-brom-4-nitrobenzenu



## Příprava 1-brom-3-nitrobenzenu

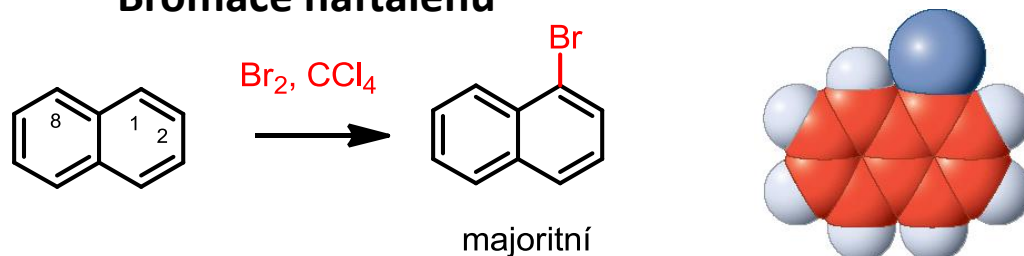


# Význam direktivních efektů v syntéze

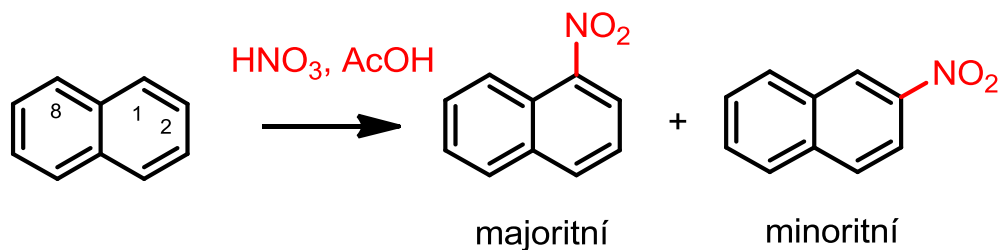


# Elektrofilní substituce naftalenu

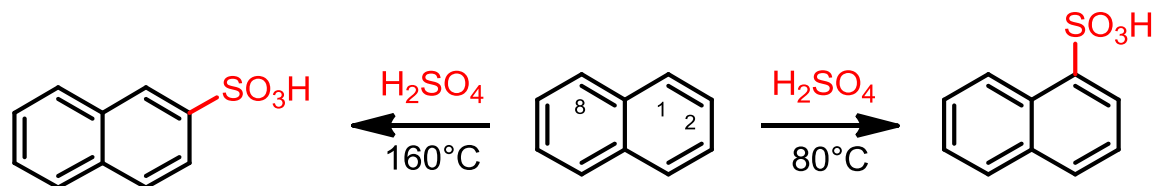
## Bromace naftalenu



## Nitrace naftalenu

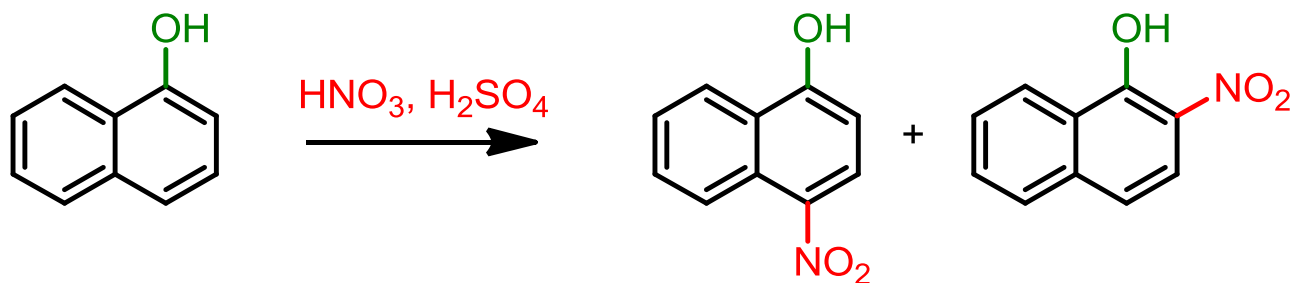


Sulfonace naftalenu je závislá na reakční teplotě (vratná reakce)



# Elektrofilní substituce naftalenu – direktivní efekty

## Elektron-donorní substituent



## Elektron-akceptorní substituent

