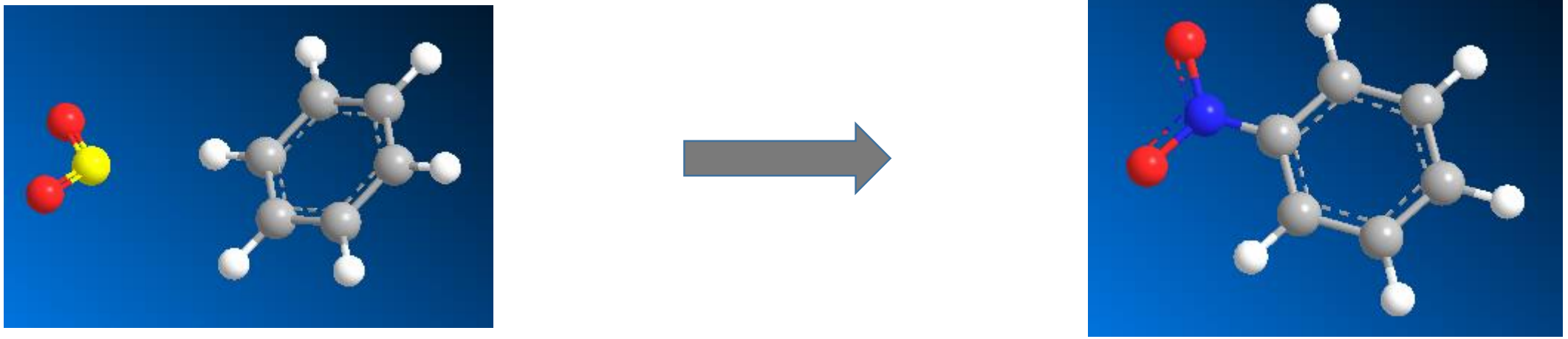
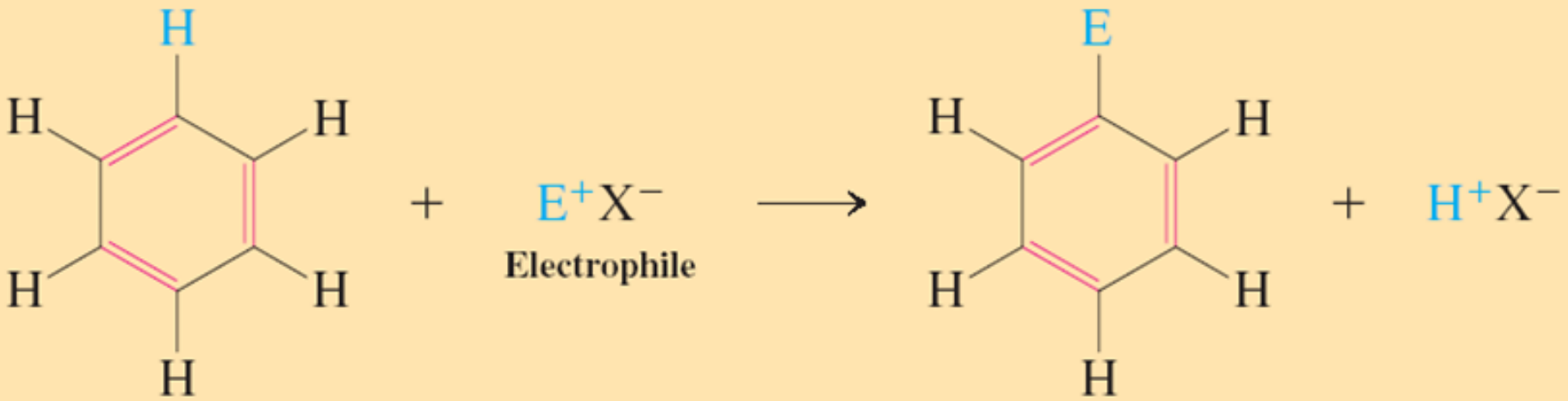
Elekrofilní Aromatická Substituce

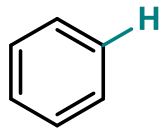
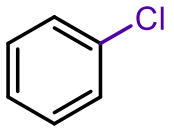
S_EAr

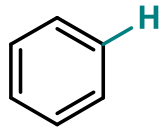
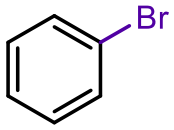


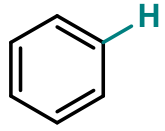
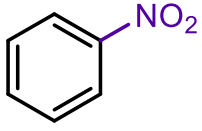
Electrophilic Aromatic Substitution

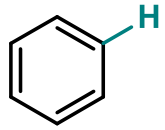
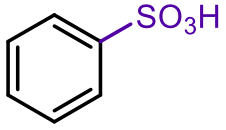


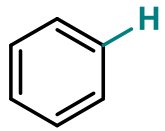
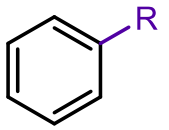
S_EAr

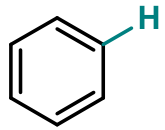
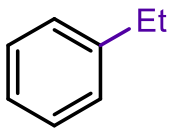
chlorace  + Cl_2 $\xrightarrow{FeCl_3}$  + HCl

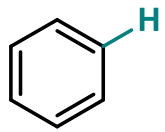
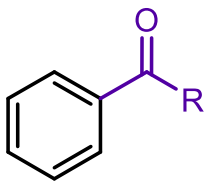
bromace  + Br_2 $\xrightarrow{FeBr_3}$  + HBr

nitrace  + HNO_3 $\xrightarrow{H_2SO_4}$  + H_2O

sulfonace  + H_2SO_4 $\longrightarrow$  + H_2O

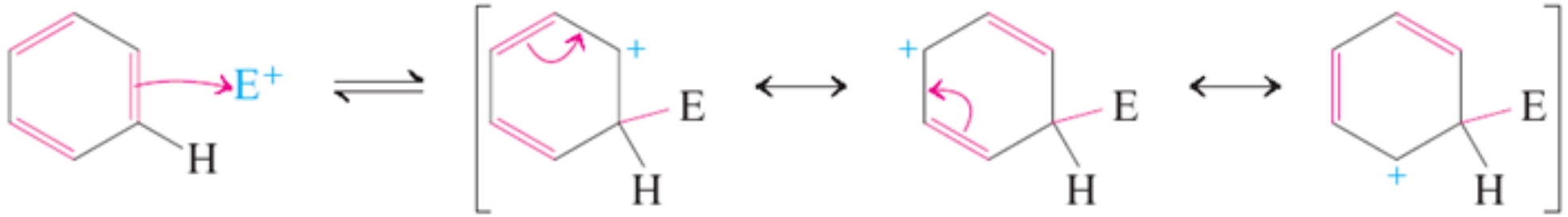
alkylace  + R-Cl $\xrightarrow{AlCl_3}$  + HCl R = Me, Et

alkylace  +  $\xrightarrow{H_2SO_4}$ 

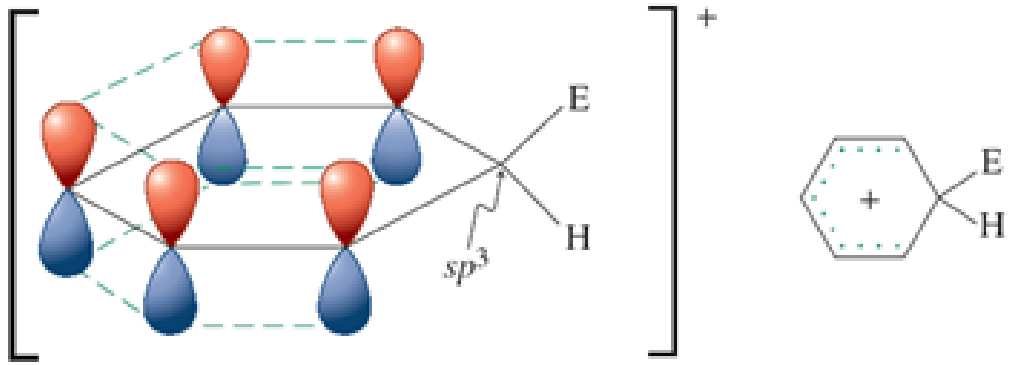
acylace  + R-COCl $\xrightarrow{AlCl_3}$  + HCl

Mechanismus S_EAr:

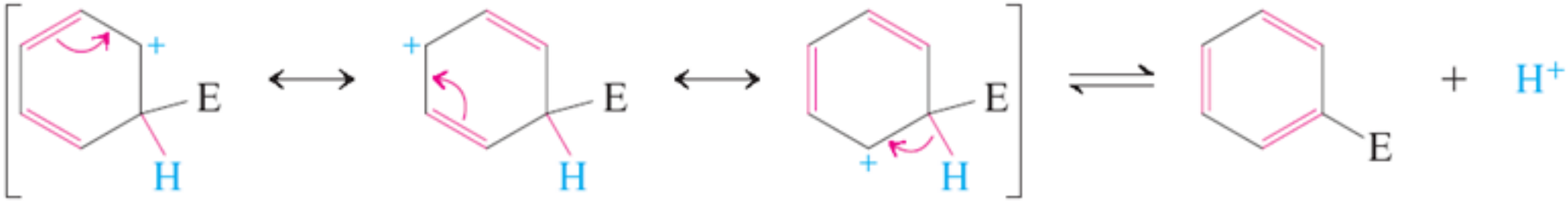
1.



Atak elektrofilu

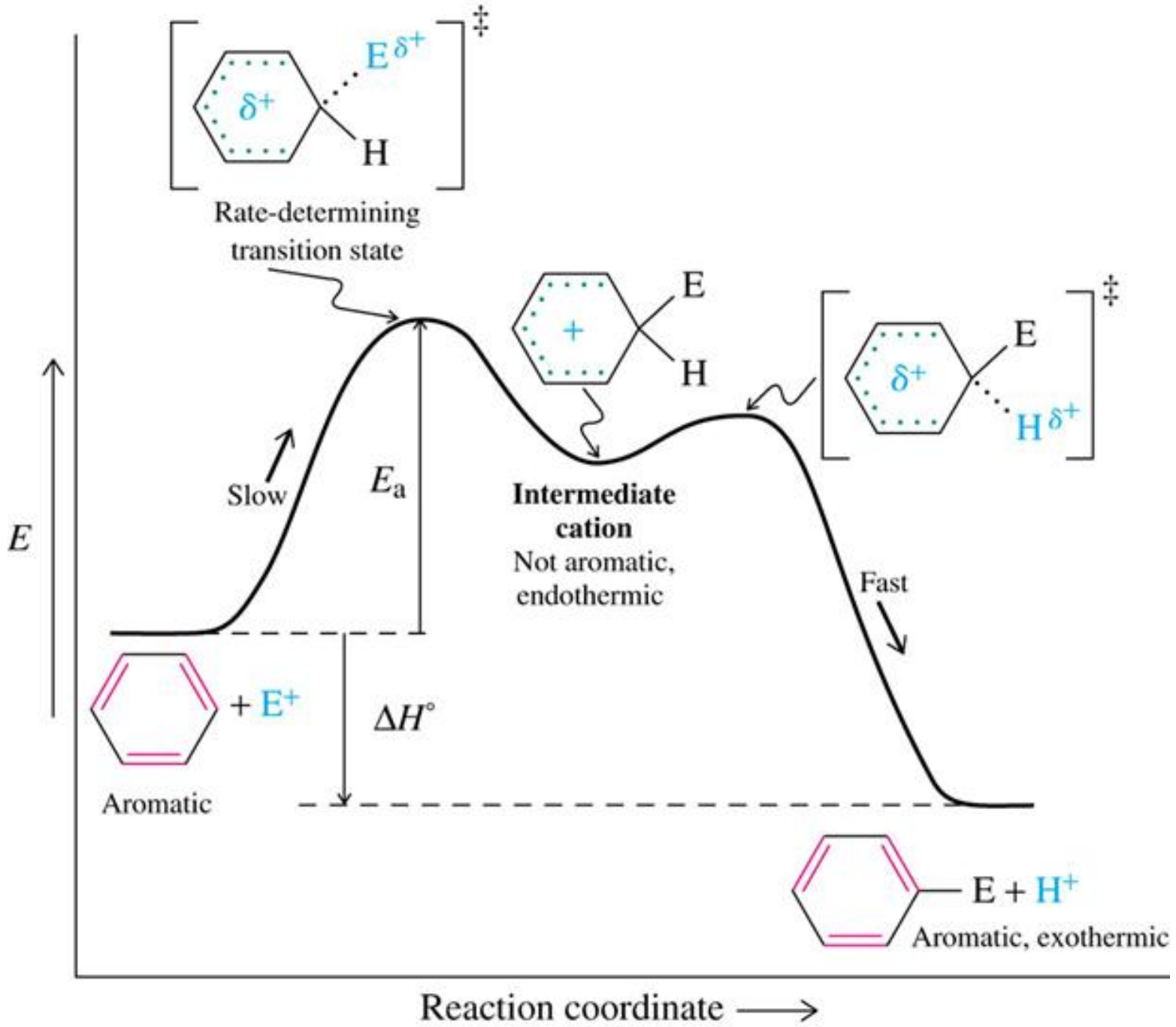


2.

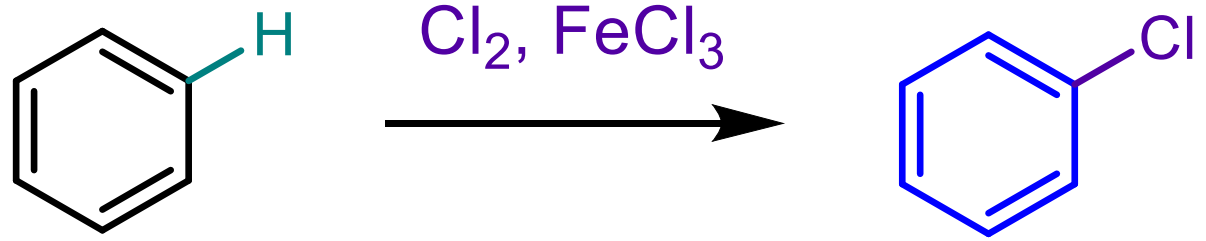


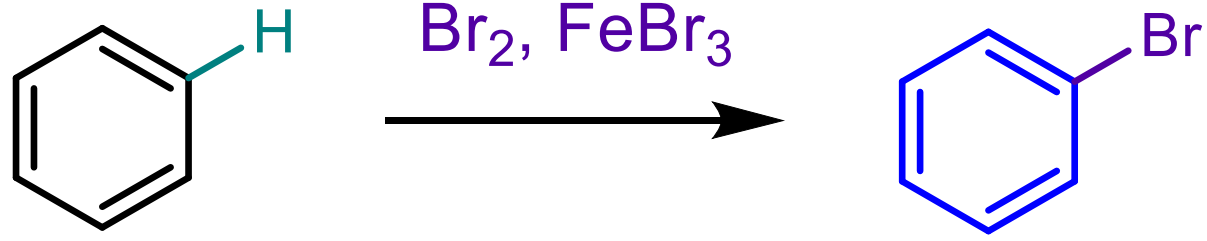
Ztráta protonu

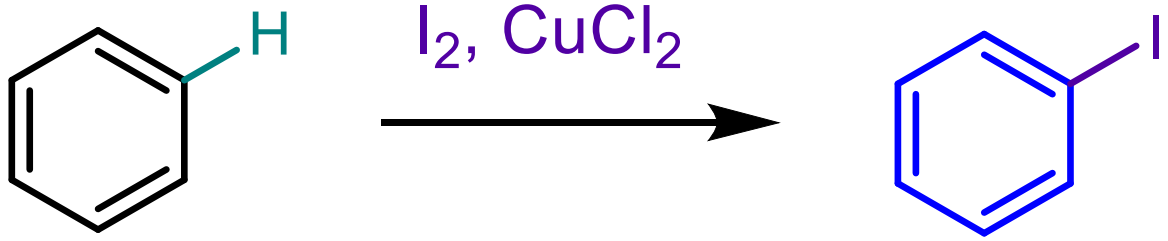
Mechanismus



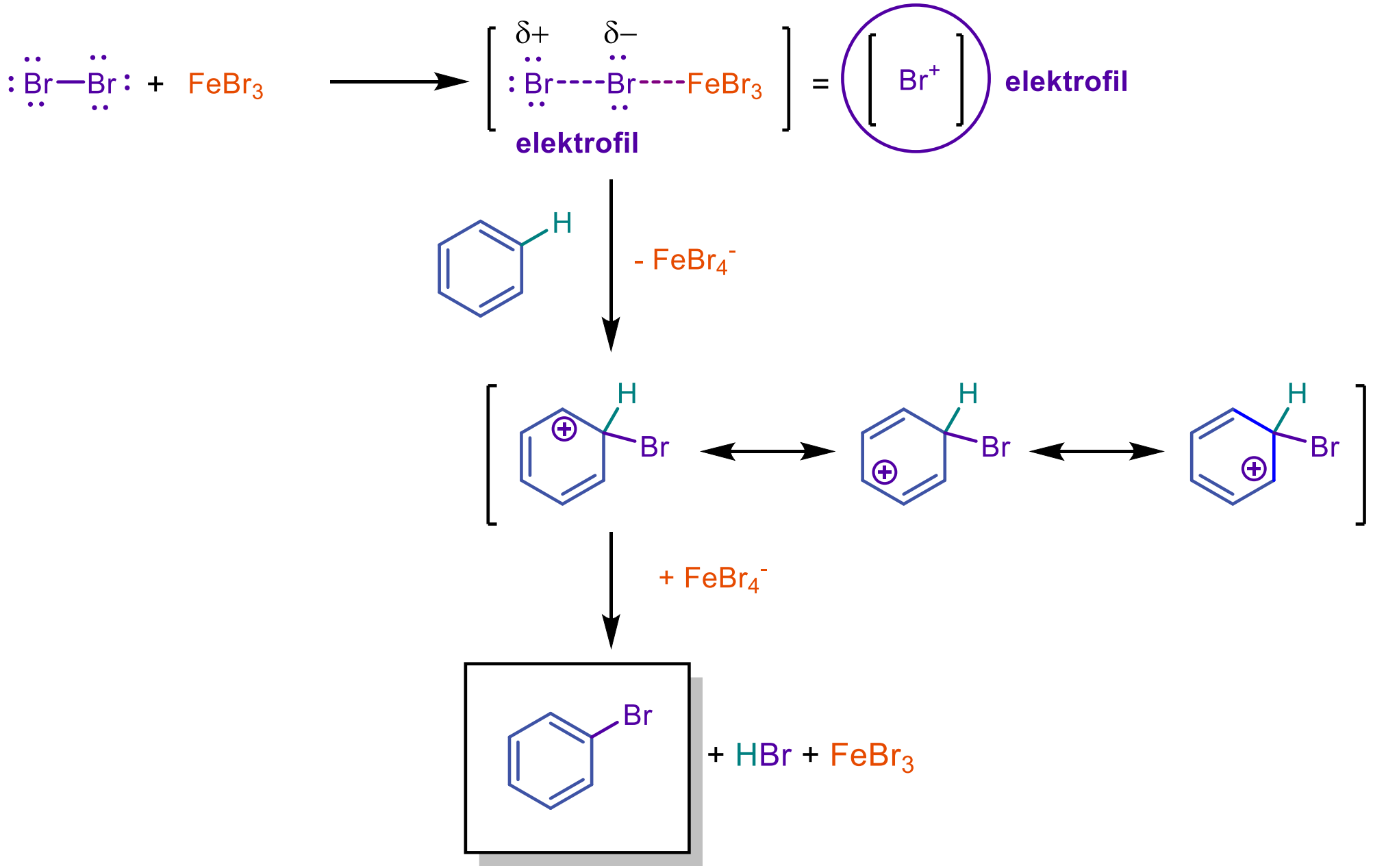
Elekrofilní halogenace



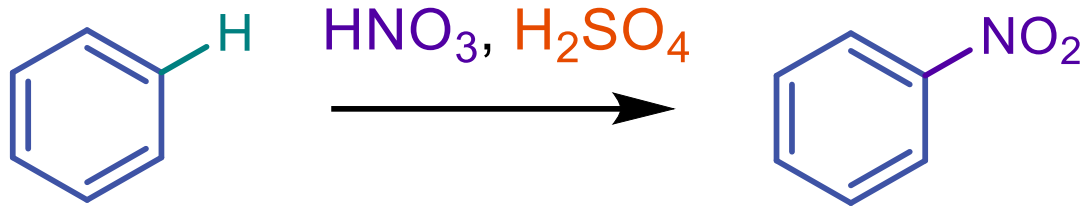


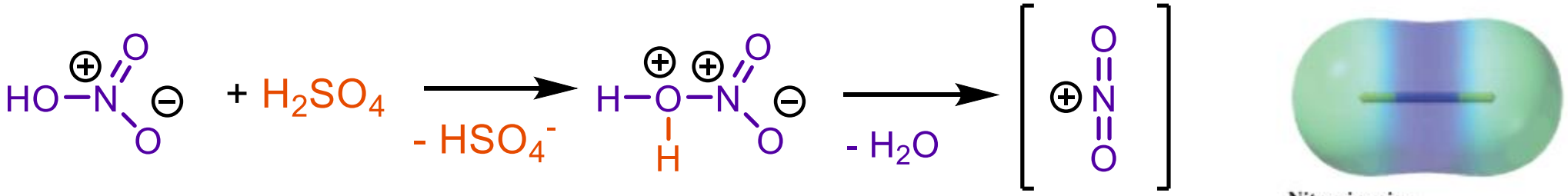


Elektrofilní halogenace - mechanismus



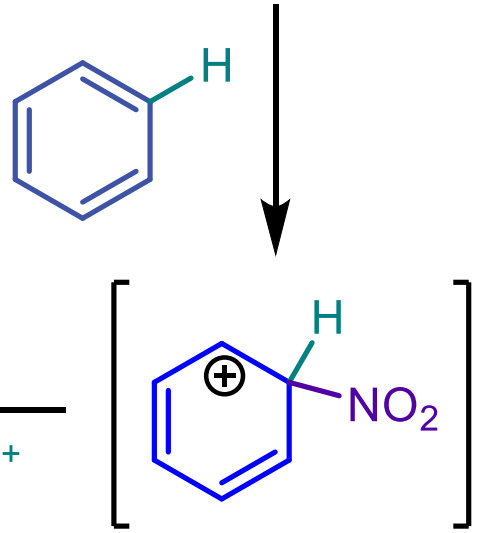
Elektrofilní nitrace



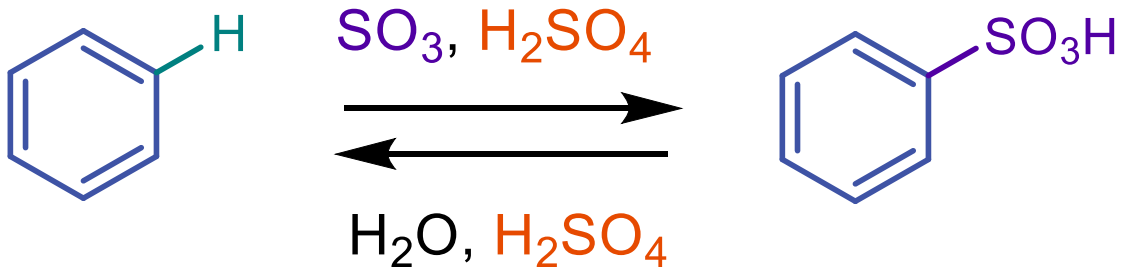


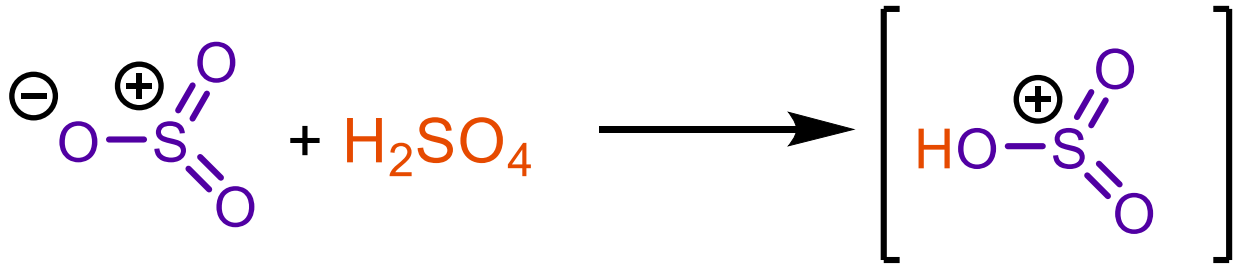
nitroniový kation

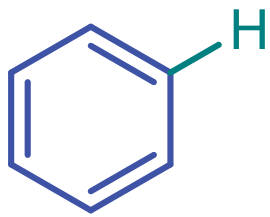
elektrofil

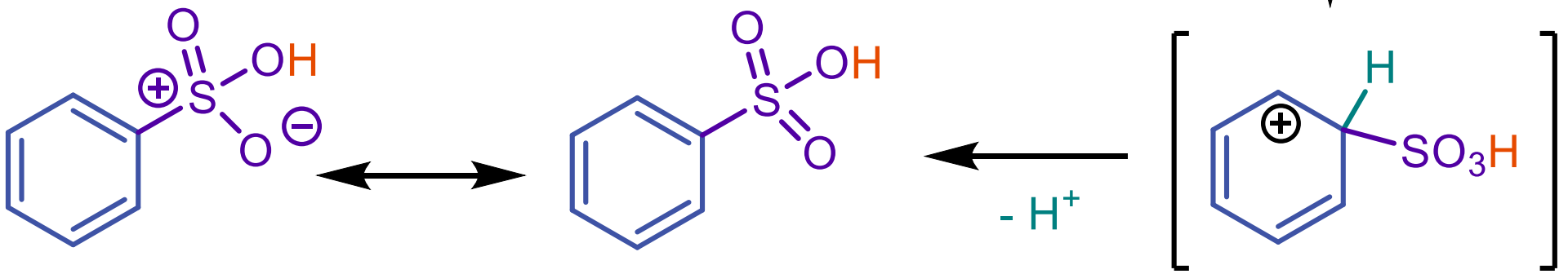


Elektrofilní sulfonace

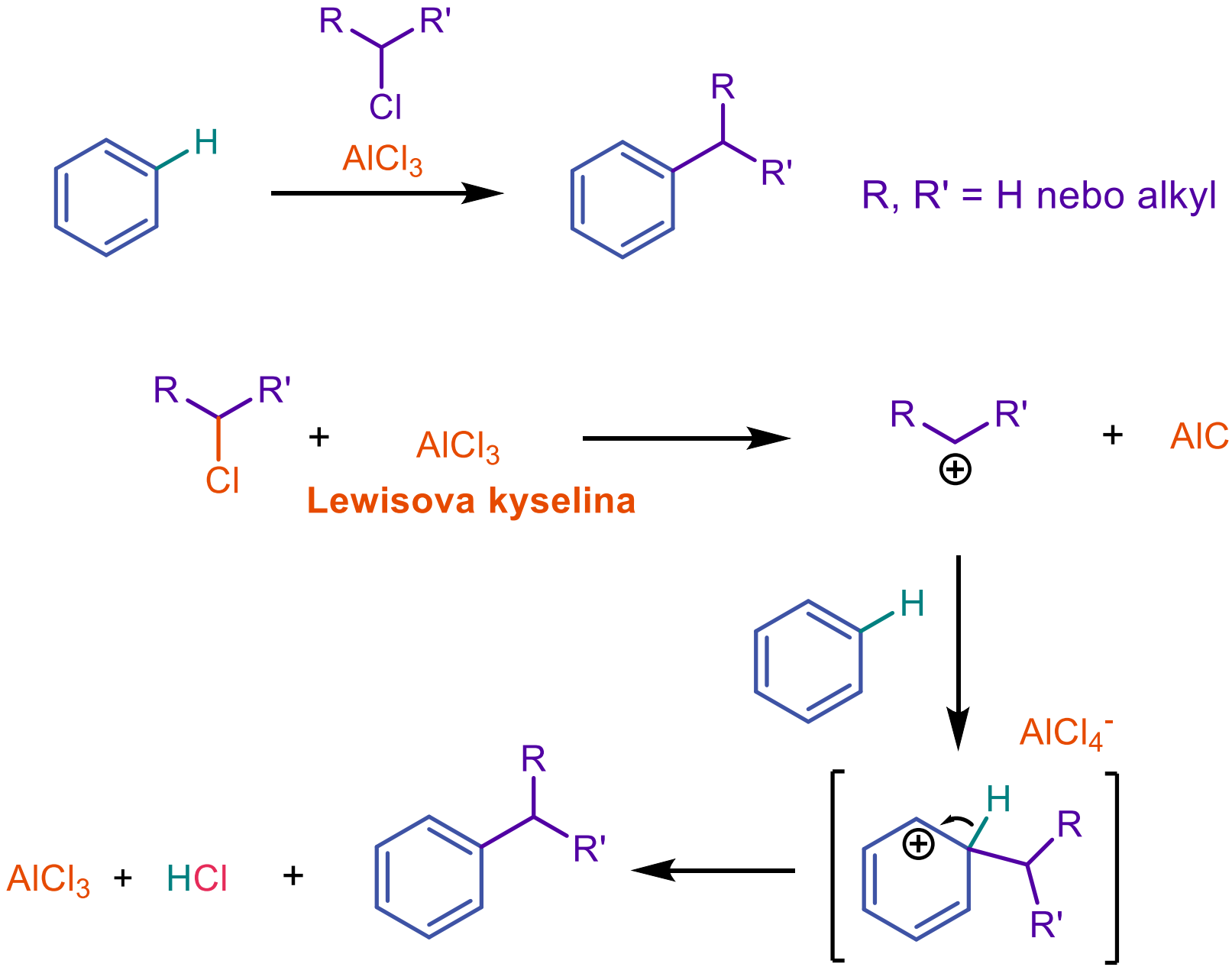




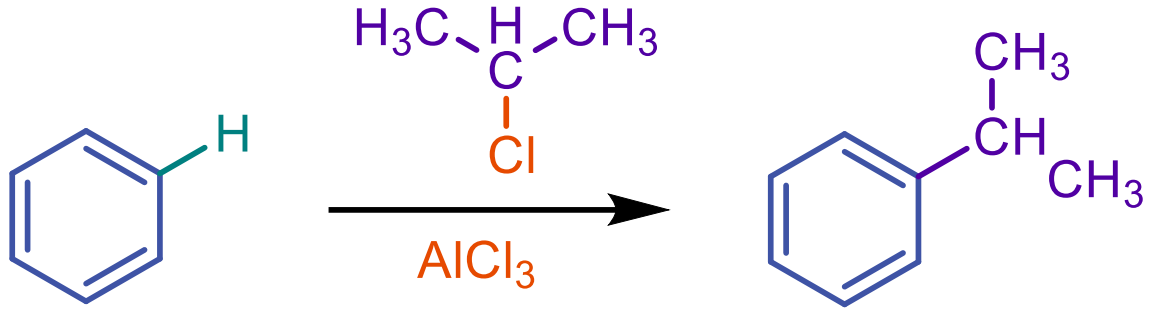




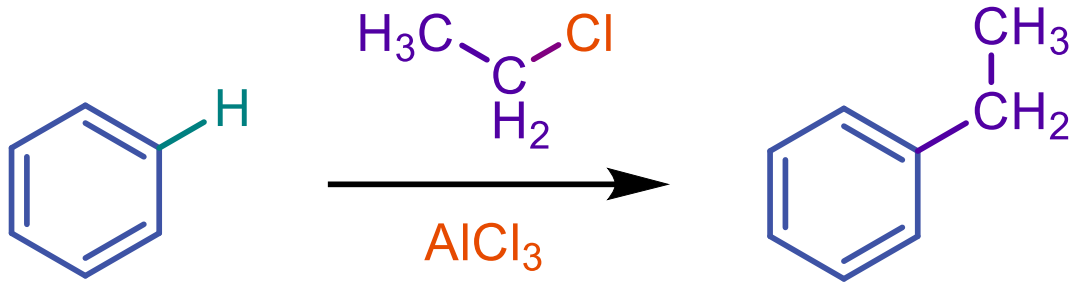
Elektrofilní alkylace (Friedel-Craftsova alkylace)



Elektrofilní alkylace (Friedel-Craftsova alkylace)

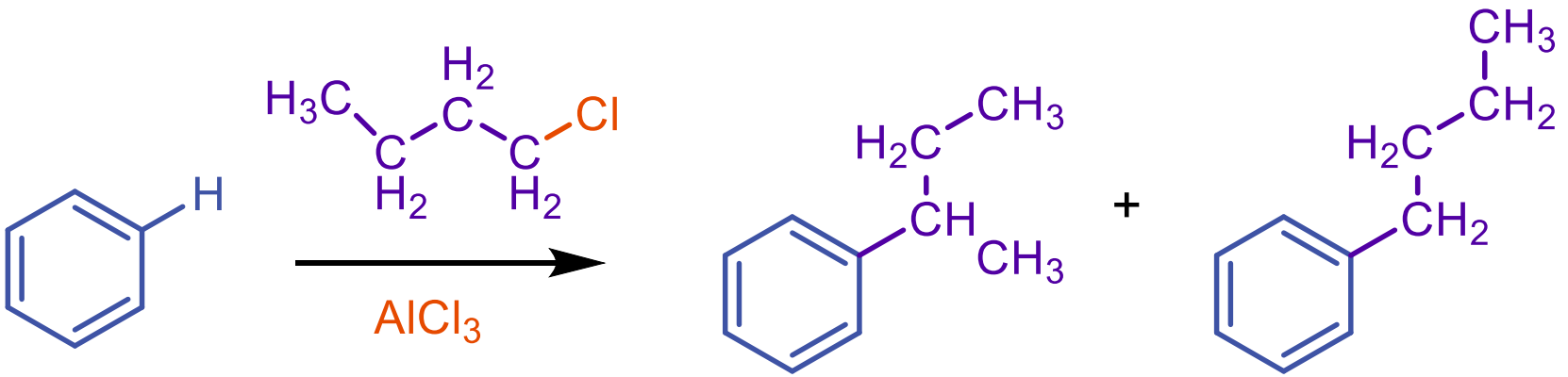


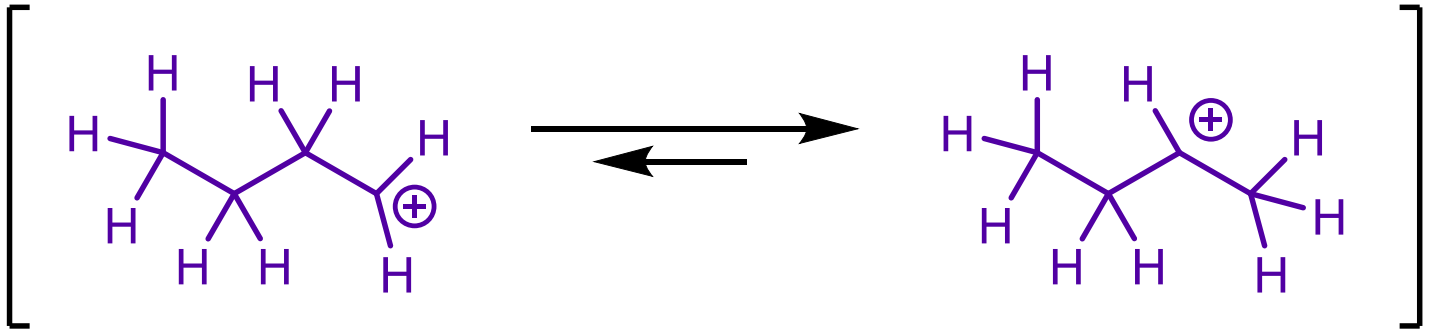
83%



28%

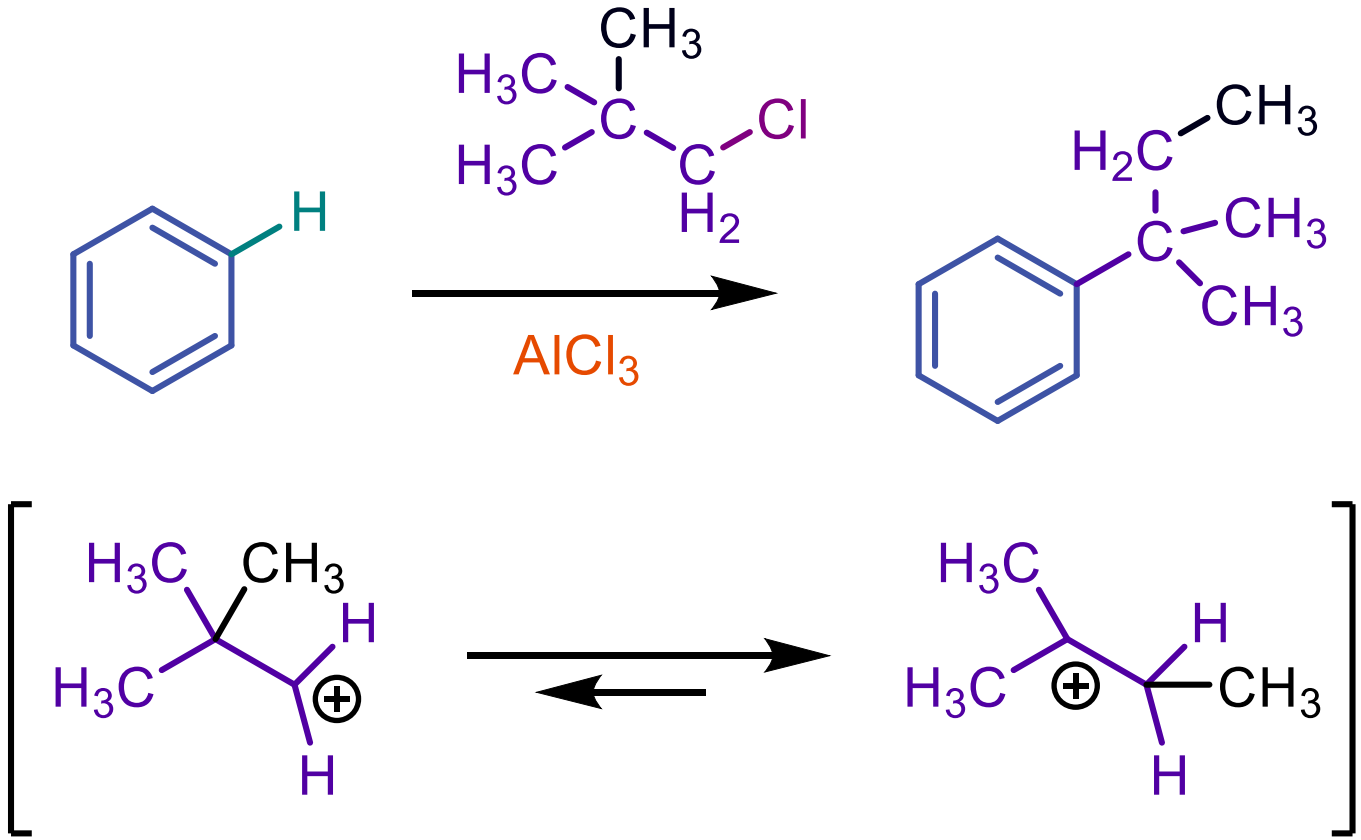
Elektrofilní alkylace (Friedel-Craftsova alkylace)





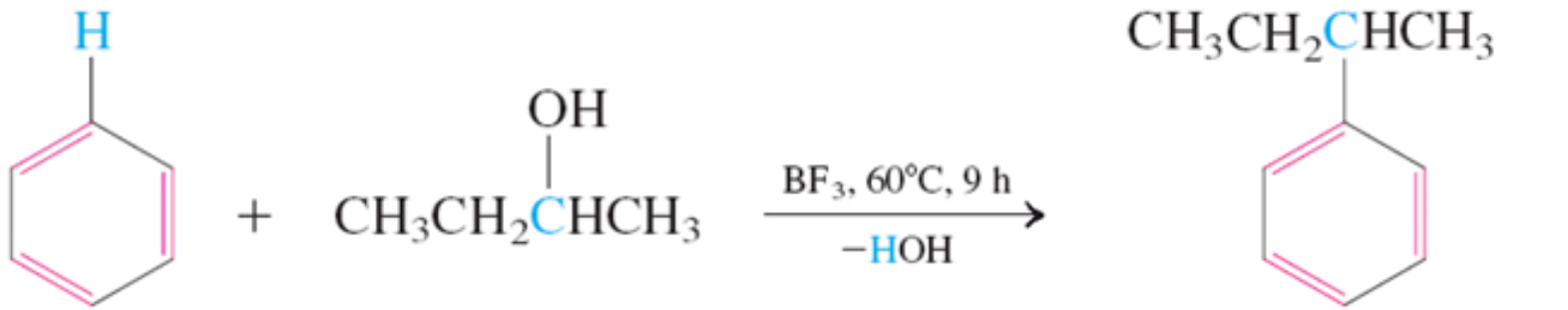
Přesmyk přesunem protonu

Elektrofilní alkylace (Friedel-Craftsova alkylace)



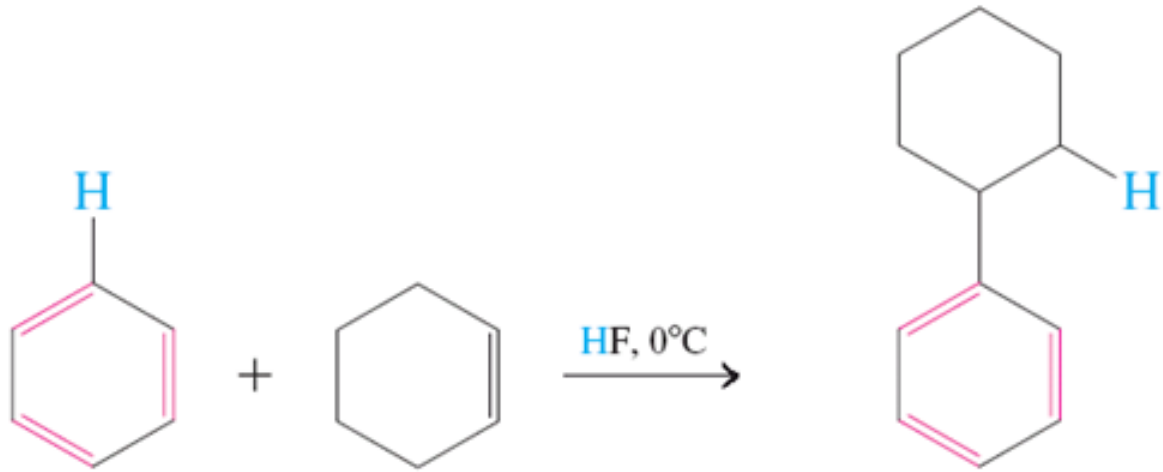
Přesmyk přesunem alkylu

Friedel-Crafts Alkylations Using Other Carbocation Precursors



36%

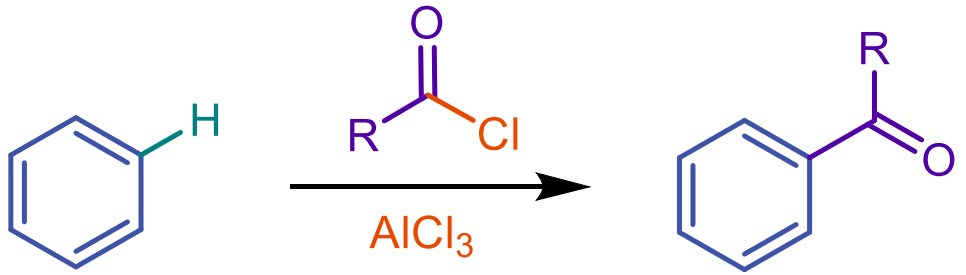
(1-Methylpropyl)benzene



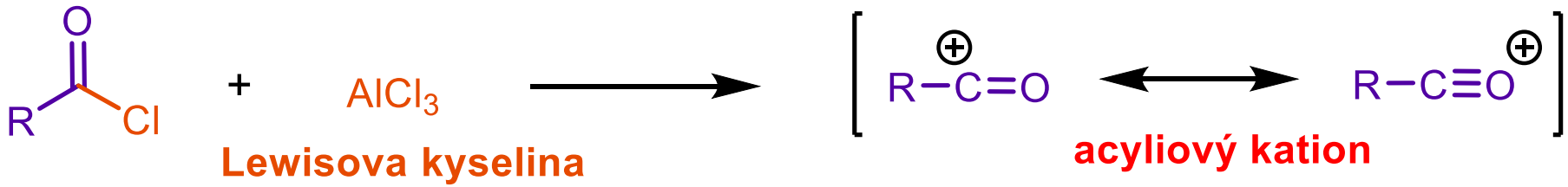
62%

Cyclohexylbenzene

Elektrofilní acylace (Friedel-Craftsova acylace)



R = alkyl

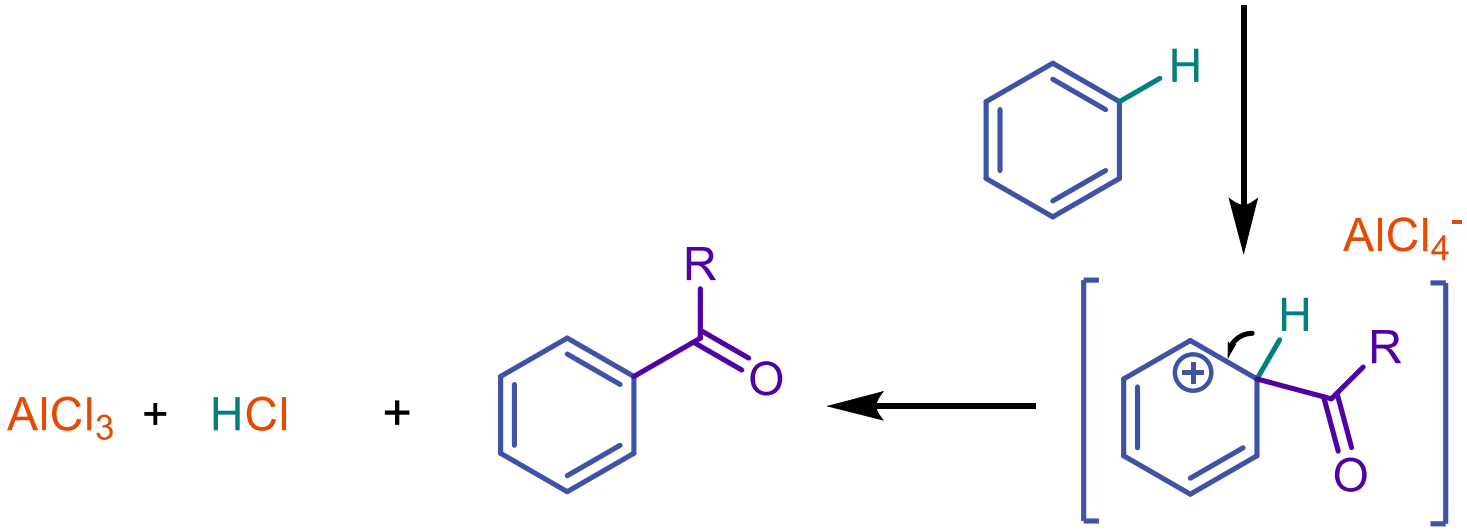


Lewisova kyselina

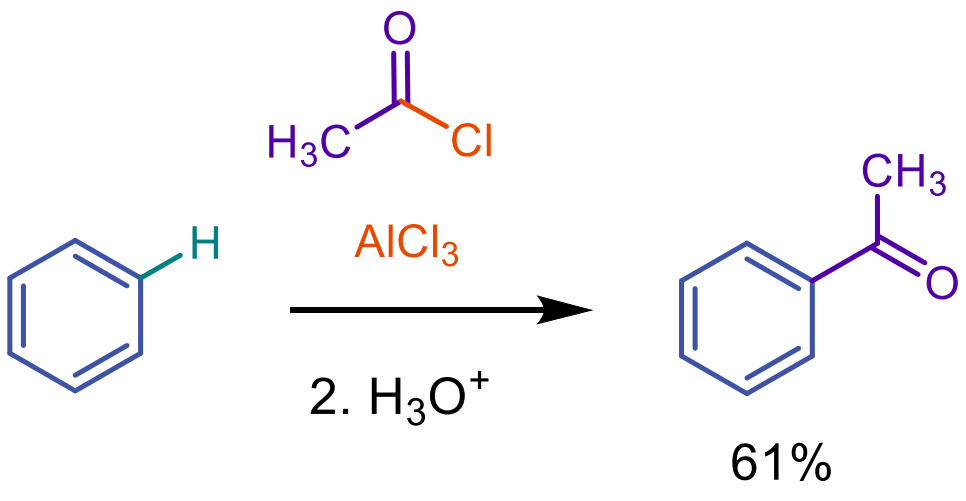
acyliový kation

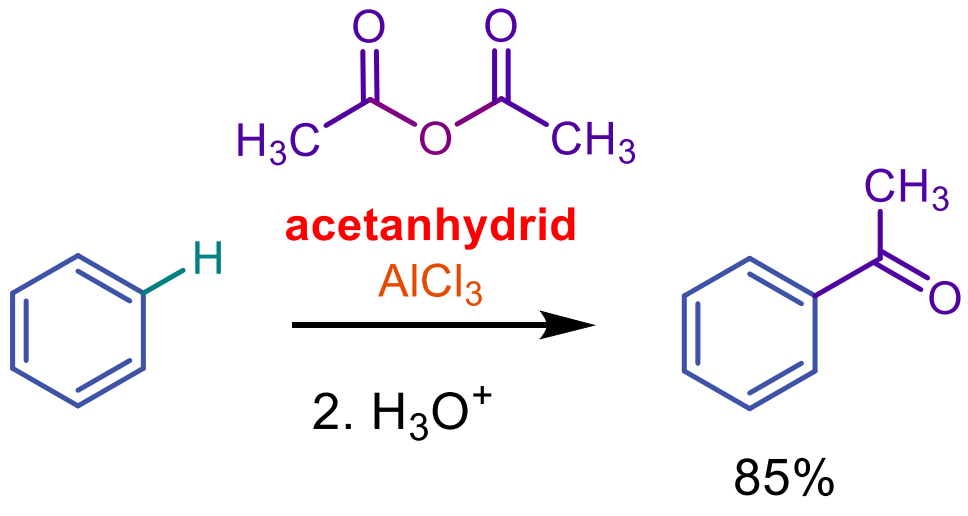
elektrofil

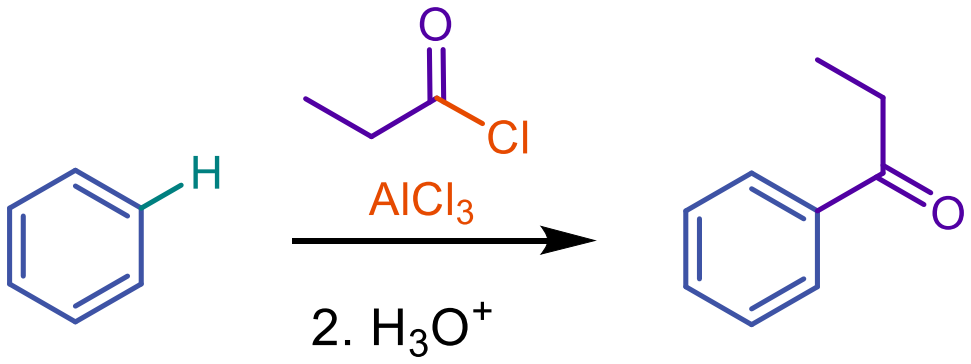
Acetyl cation



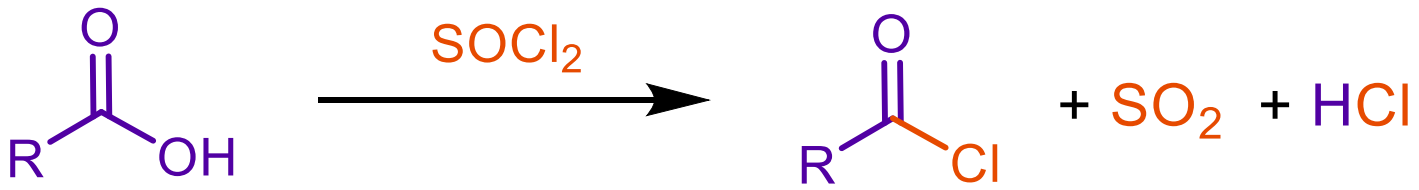
Elektrofilní acylace (Friedel-Craftsova acylace)



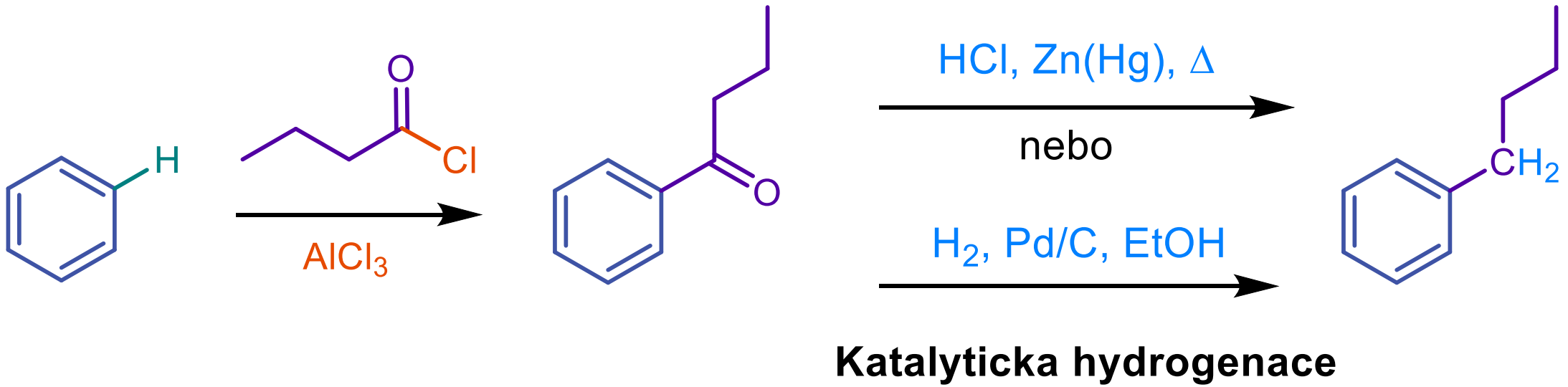




Příprava acyl chloridů



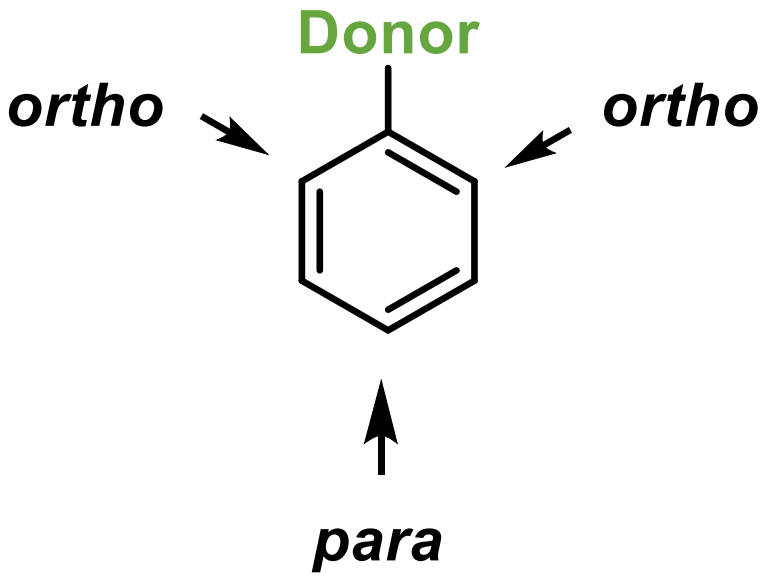
Příprava alkylaromátů (benzenů) — acylace + redukce

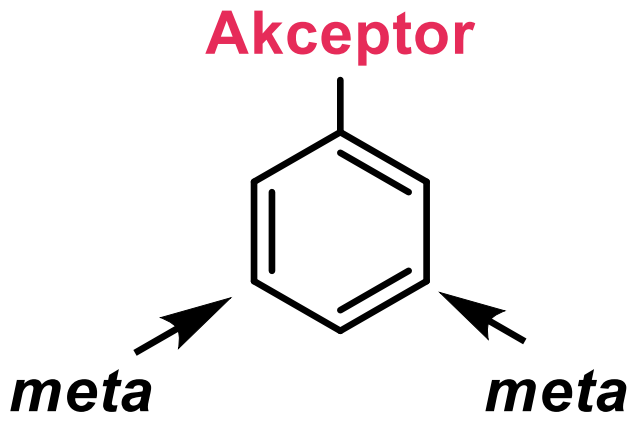


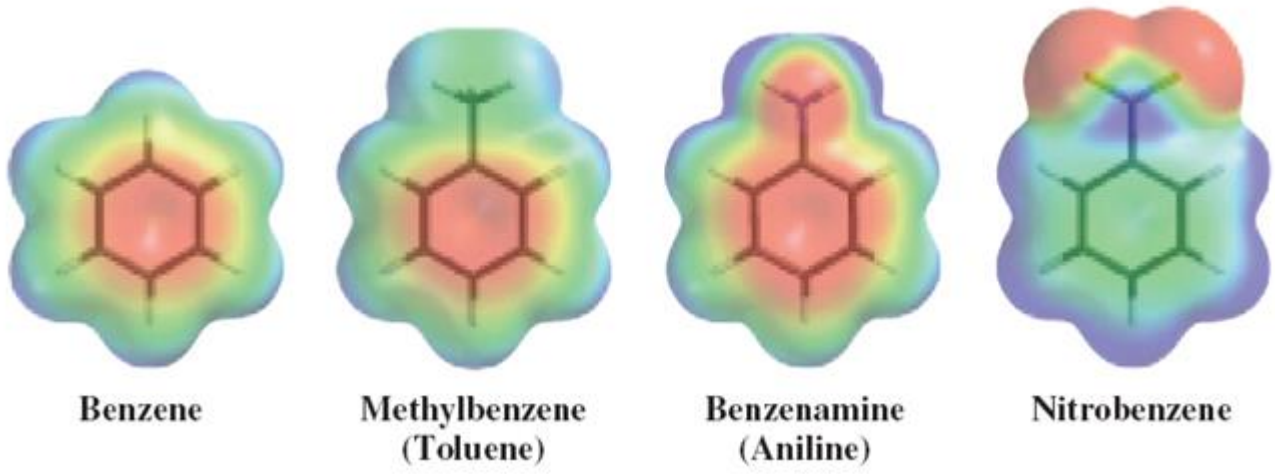
Clemmensenova redukce

Katalyticka hydrogenace

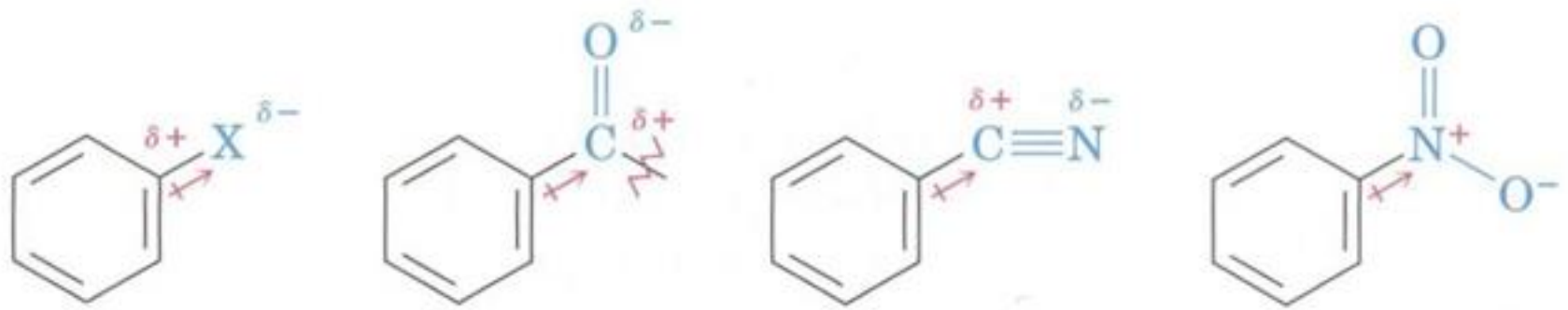
Elektrofilní substituce derivátů benzenu





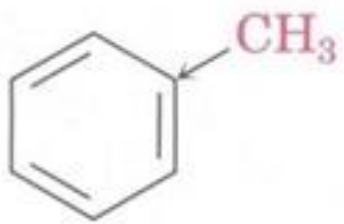


Induktivní efekt



(X = F, Cl, Br, I)

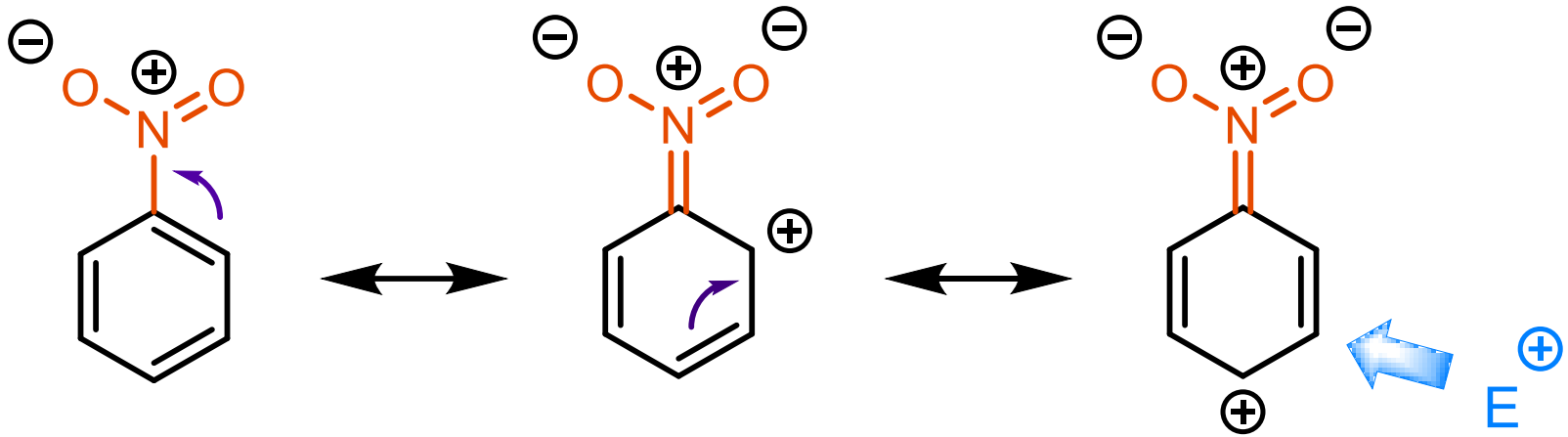
skupiny připojené k aromatickým kruhům mají v důsledku polarity svých vazeb elektronakceptorní induktivní efekt (–*I*-efekt)



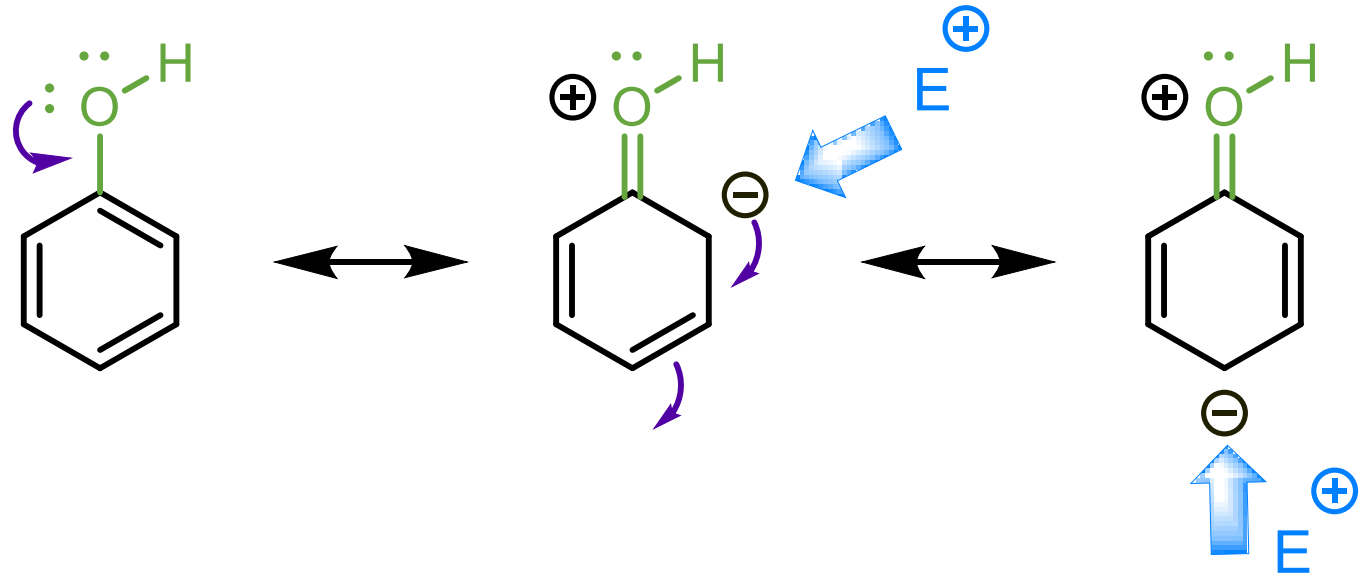
alkylová skupina; elektrondonorová induktivní skupina

Rezonanční (mezomerní) efekt

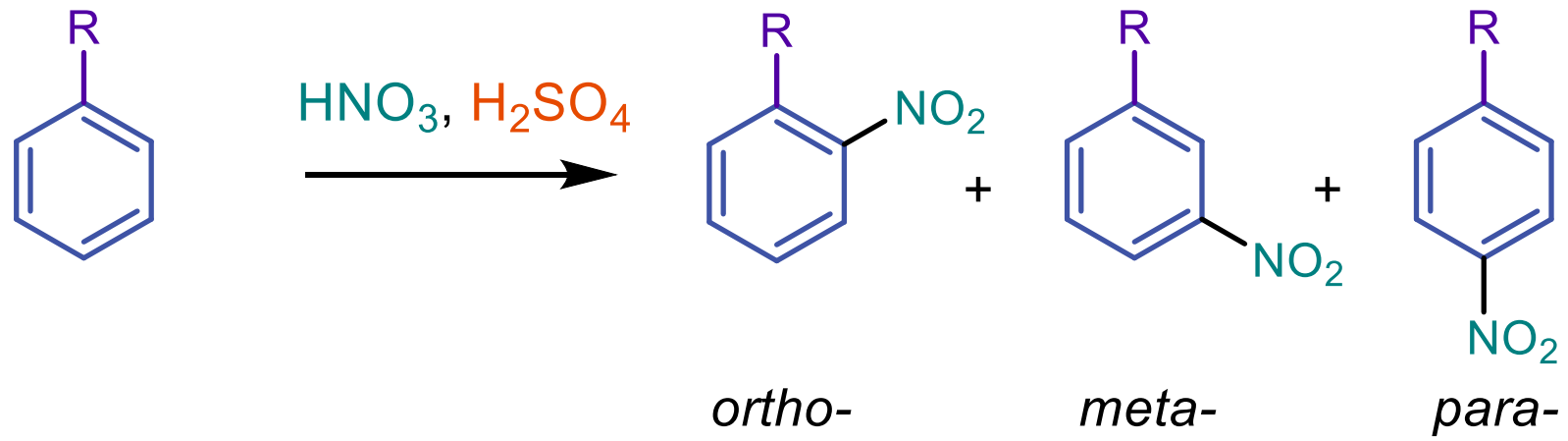
Elektron-akceptorní skupiny



Elektron-donorní skupiny



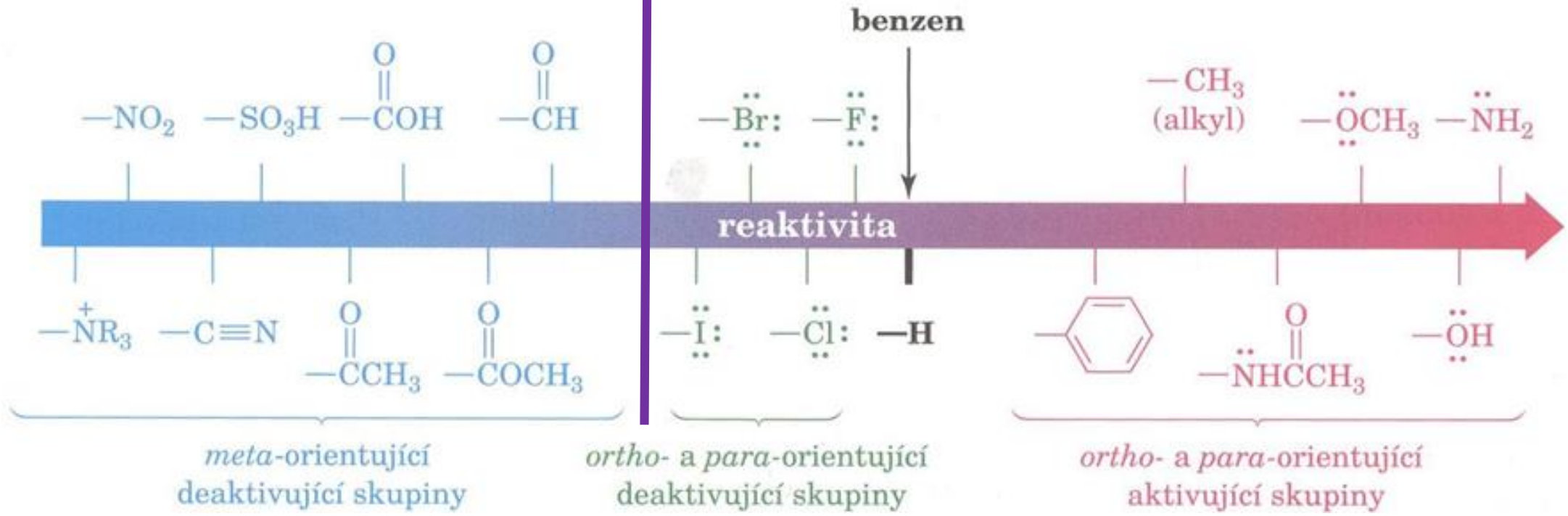
Porovnání rychlosti a direktivního efektu nitrace derivátů benzenu

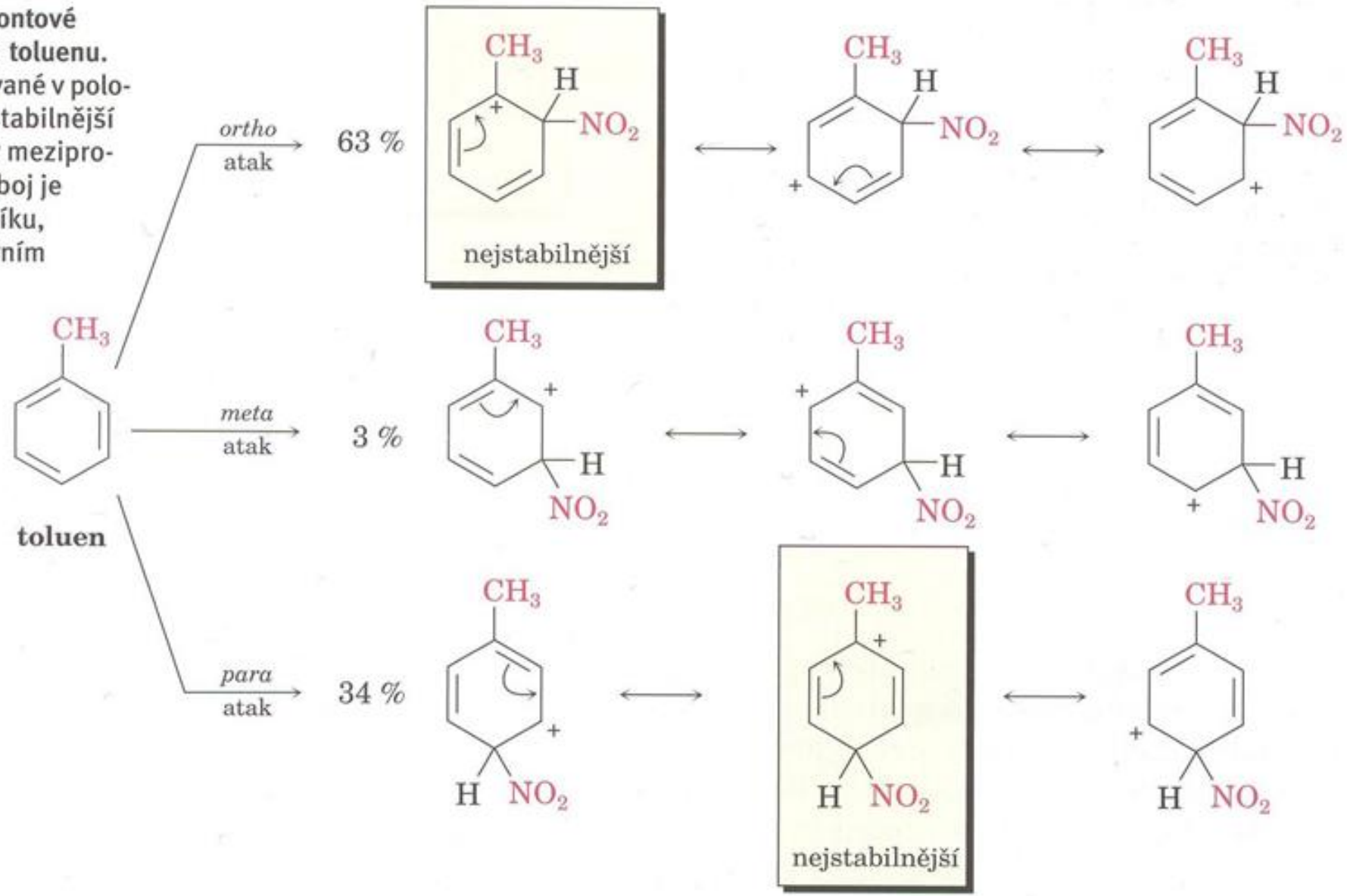


	R		Relative rate		Percentage of isomer		
					Ortho	Meta	Para
Ortho, para directors	$NH(C_6H_5)$	Increasing activation	8.4×10^5	Increasing rate of nitration	71	<0.1	29
	OH		1000		40	<2	58
	CH_3		25		58	4	38
	C_6H_5		8		30	<0.6	70
	H		1				
Special: Ortho, para directors	I	Increasing deactivation	0.18		41	<0.2	59
	Cl		0.033		31	<0.2	69
Meta directors	$CO_2CH_2CH_3$		0.0037		24	72	4
	CF_3		2.6×10^{-5}		6	91	3
	NO_2		6×10^{-8}		5	93	2
	$\overset{+}{N}(CH_3)_3$		1.2×10^{-8}		0	89	11

***meta* — orientující (substituenty II. třídy)**

***ortho*, *para* — orientující (substituenty I. třídy)**

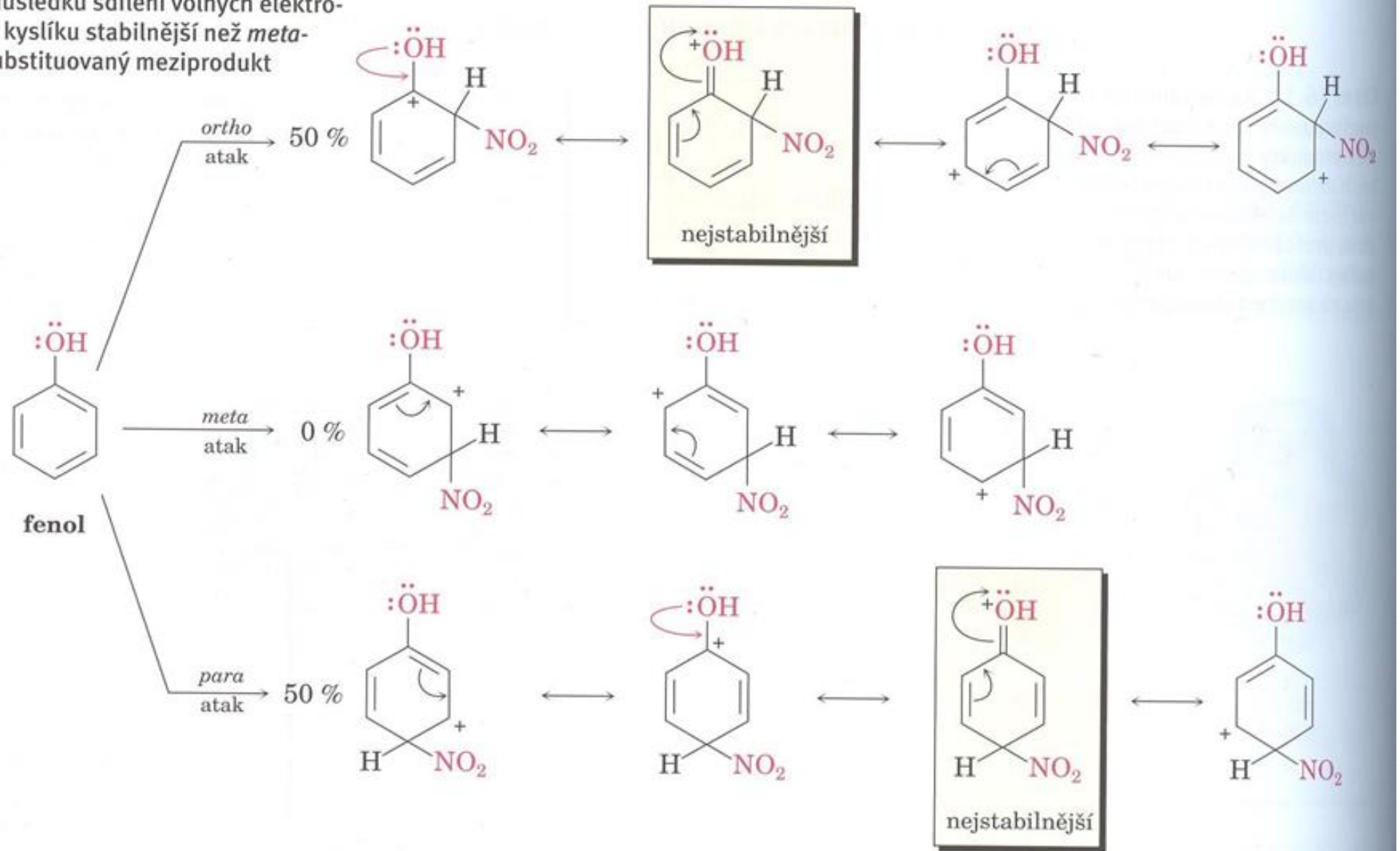




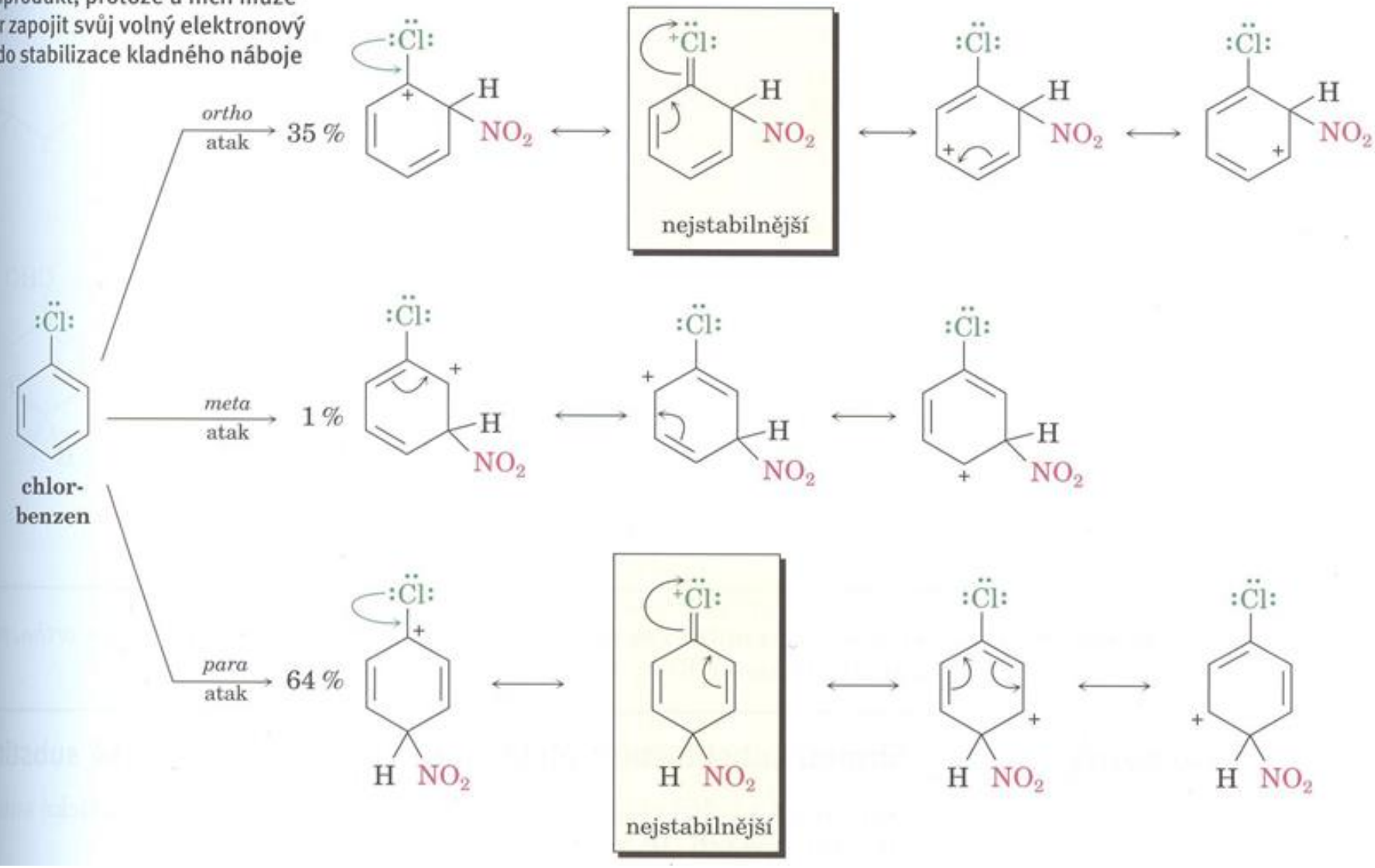
Obr. 16.12 Karbokationtové meziprodukty při nitraci toluenu. Meziprodukty substituované v polohách *ortho* a *para* jsou stabilnější než *meta*-substituovaný meziprodukt, protože kladný náboj je na terciárním atomu uhlíku, a ne na atomu sekundárním

volným elektronovým párem atomu kyslíku. Meziprodukt nitrace do polohy *meta* takovou stabilizaci nemá.

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

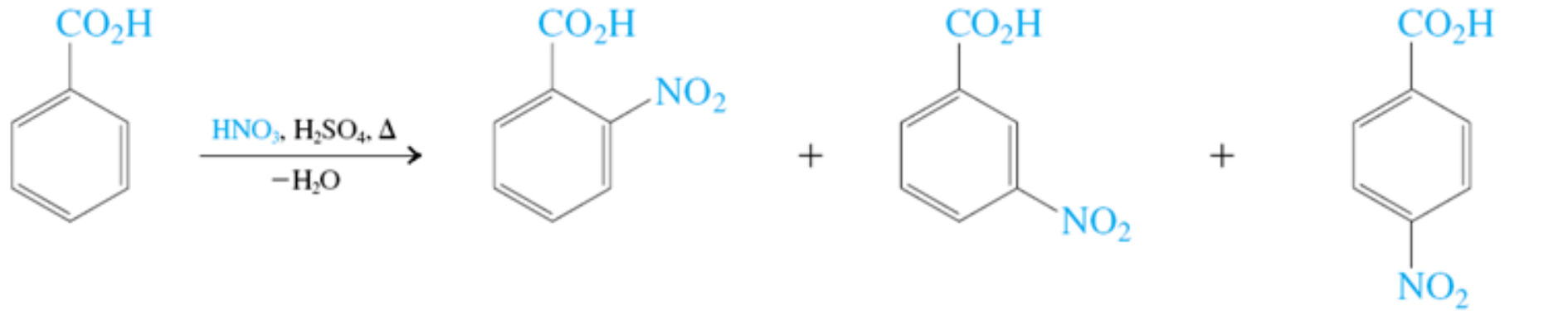


tem. Slabým elektrondonorním rezonančním efektem jsou ovlivněny pouze polohy *ortho* a *para*, nikoliv poloha *meta* (obr. 16.14). Halogeny tak stabilizují kladný náboj intermediárního karbokationtu elektrofilních substitucí do polohy *ortho* a *para* stejně jako hydroxy- a aminoskupina. Meziprodukt reakce do polohy *meta* tuto stabilizaci nemá, a proto vzniká pomaleji.



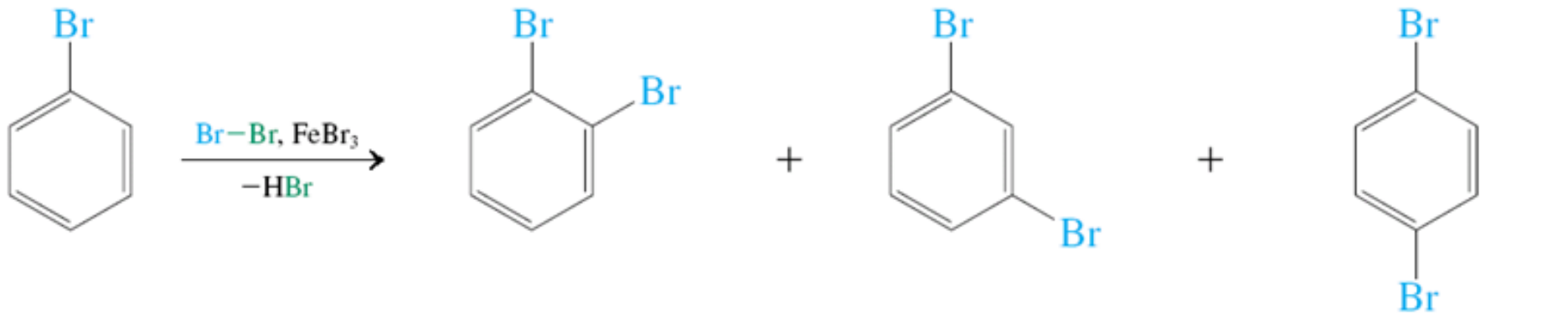
Obr. 16.14 Karbokationtové meziprodukty při nitraci chlorbenzenu. Meziprodukty substituované v poloze *ortho* a *para* jsou stabilnější než *meta*-substituovaný meziprodukt, protože u nich může chlor zapojit svůj volný elektronový pár do stabilizace kladného náboje

Electrophilic Meta-Nitration of Benzoic Acid



18.5%	80%	1.5%
2-Nitrobenzoic acid (*o*-Nitrobenzoic acid)	**3-Nitrobenzoic acid (*m*-Nitrobenzoic acid)**	**4-Nitrobenzoic acid (*p*-Nitrobenzoic acid)**

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

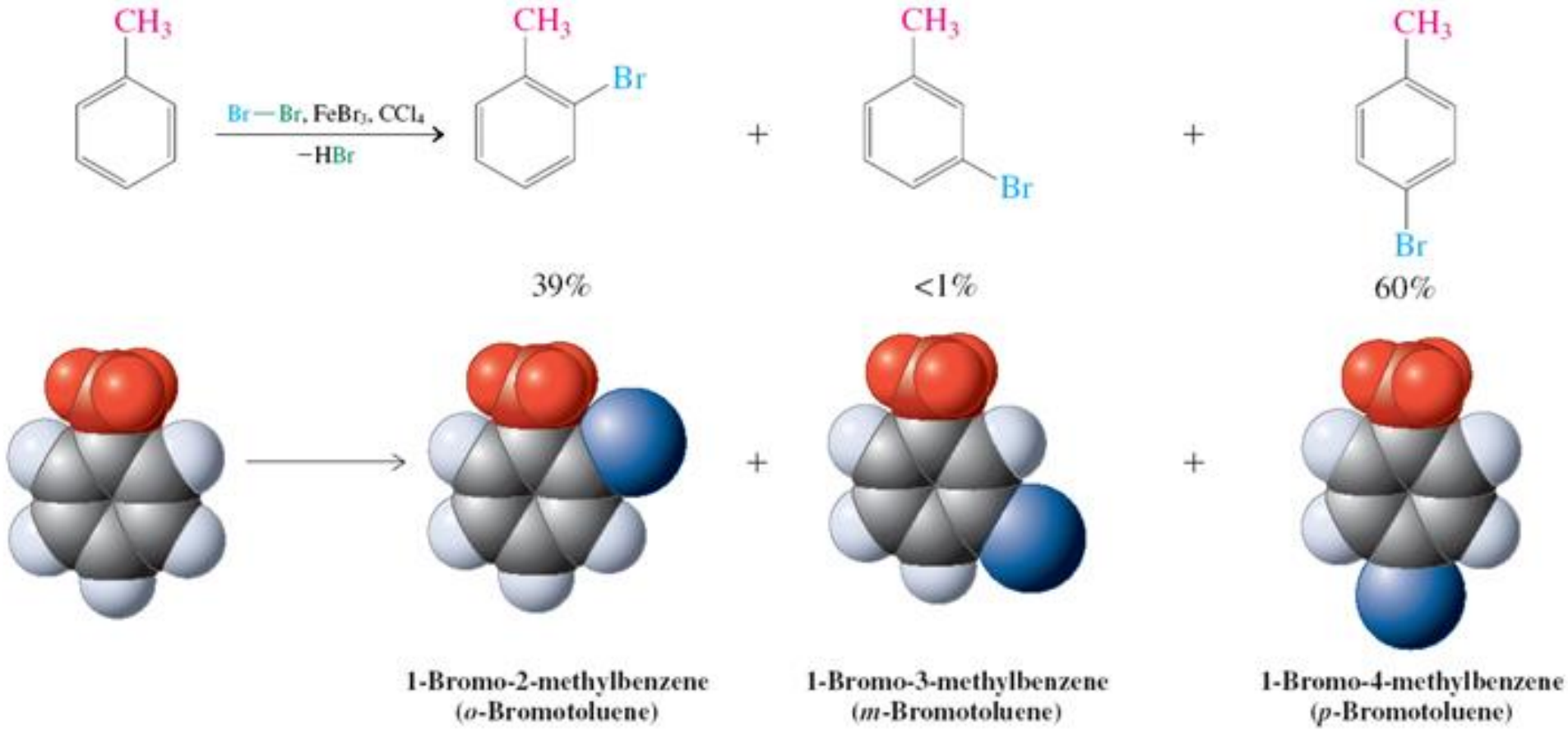


13%
1,2-Dibromobenzene (*o*-Dibromobenzene)

2%
1,3-Dibromobenzene (*m*-Dibromobenzene)

85%
1,4-Dibromobenzene (*p*-Dibromobenzene)

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

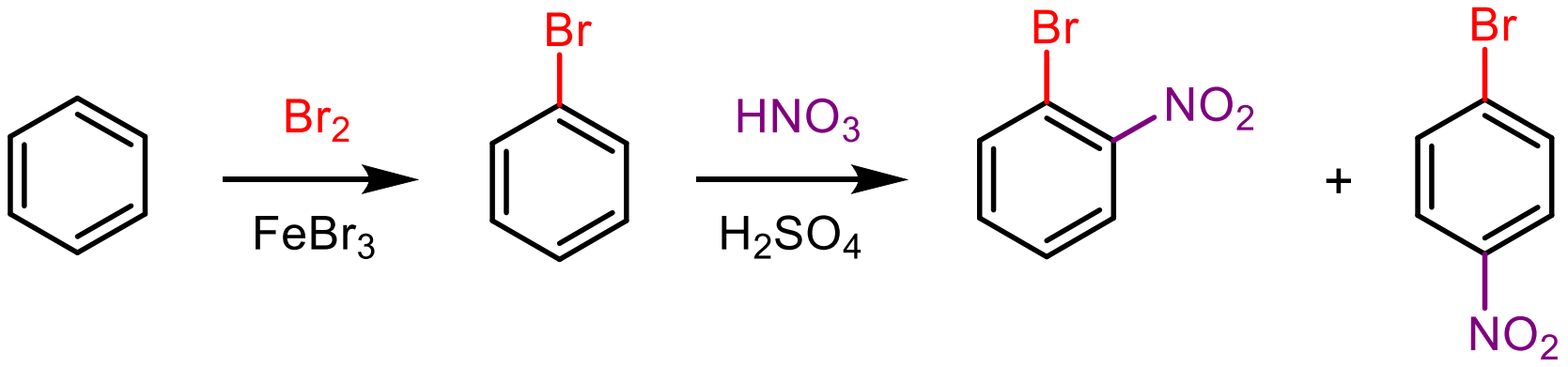


1-Bromo-2-methylbenzene (*o*-Bromotoluene)

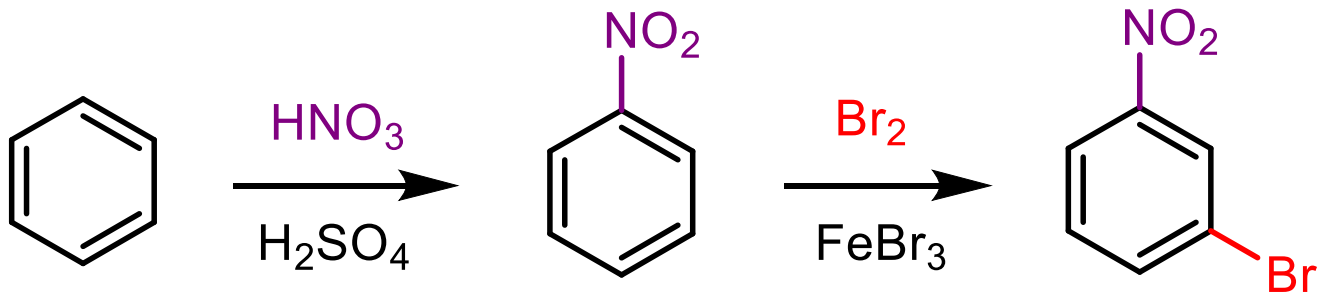
1-Bromo-3-methylbenzene (*m*-Bromotoluene)

1-Bromo-4-methylbenzene (*p*-Bromotoluene)

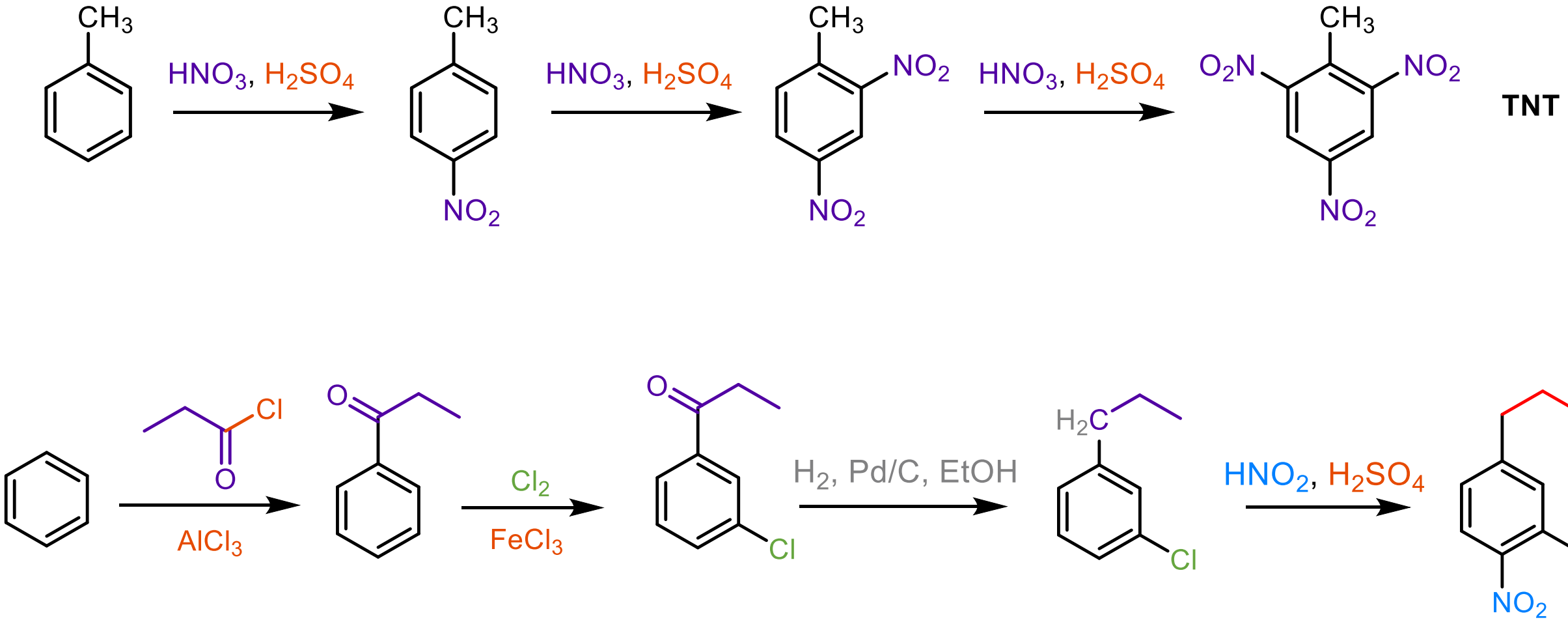
Význam direktivních efektů v syntéze

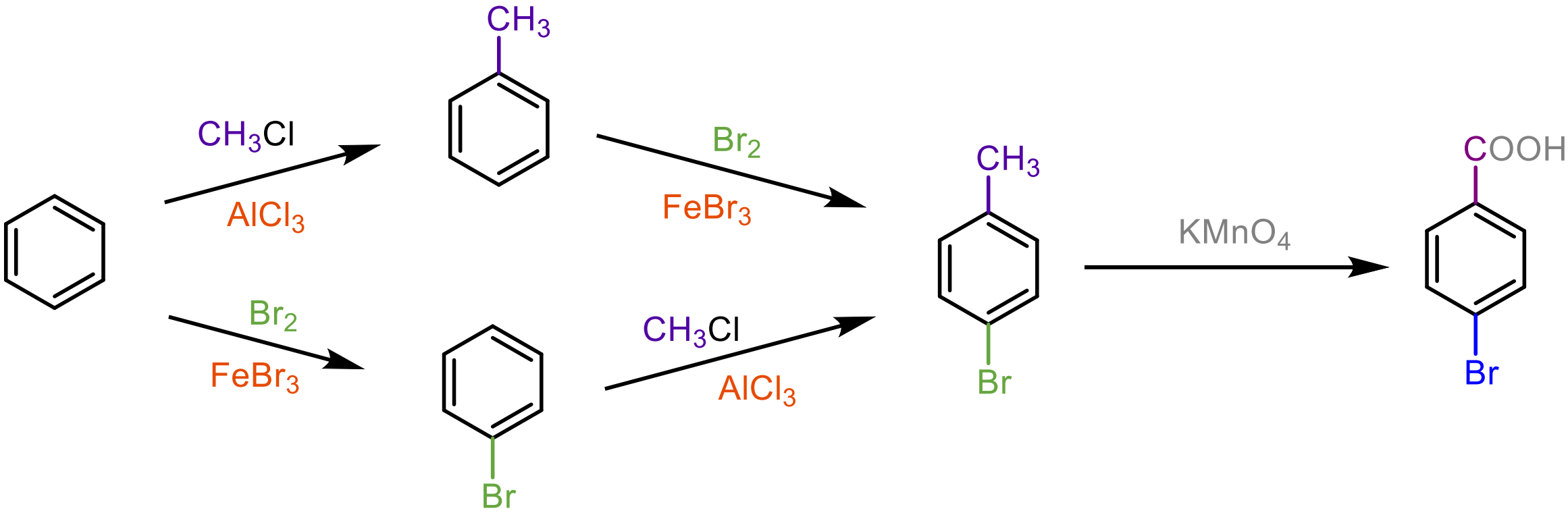


1-brom-2-nitro- a
1-brom-4-nitrobenzen



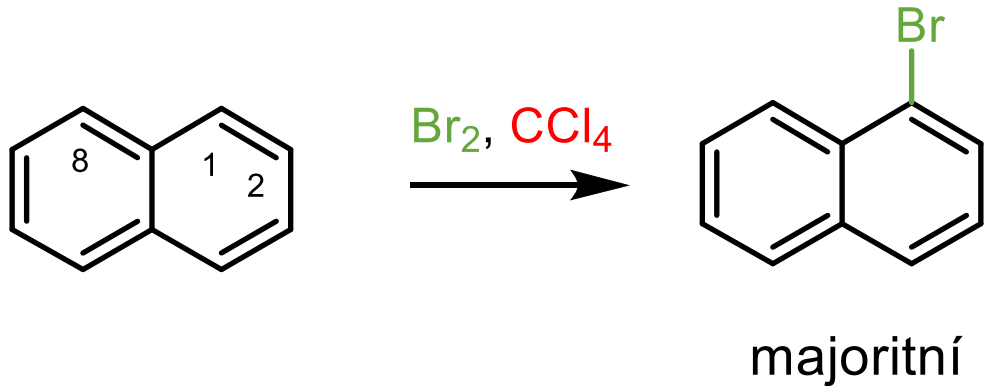
1-brom-3-nitrobenzen


CH3
HNO3, H2SO4
NO2
HNO3, H2SO4
NO2
HNO3, H2SO4
O2N
NO2
NO2
TNT
Cl
O
AlCl3
Cl2
FeCl3
H2, Pd/C, EtOH
H2C
HNO2, H2SO4


CH3Cl
AlCl3
CH3
Br2
FeBr3
CH3
Br
Br2
FeBr3
CH3Cl
AlCl3
CH3
Br
KMnO4
COOH
Br

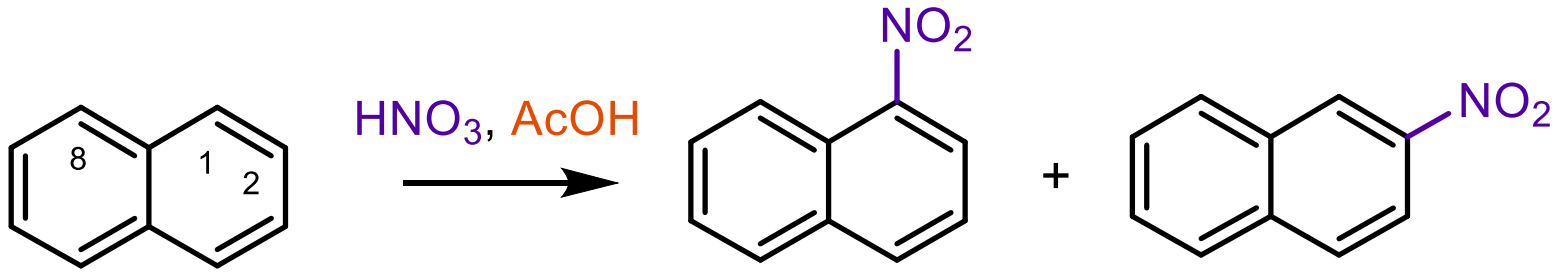
Elektrofilní substituce naftalenu

Bromace



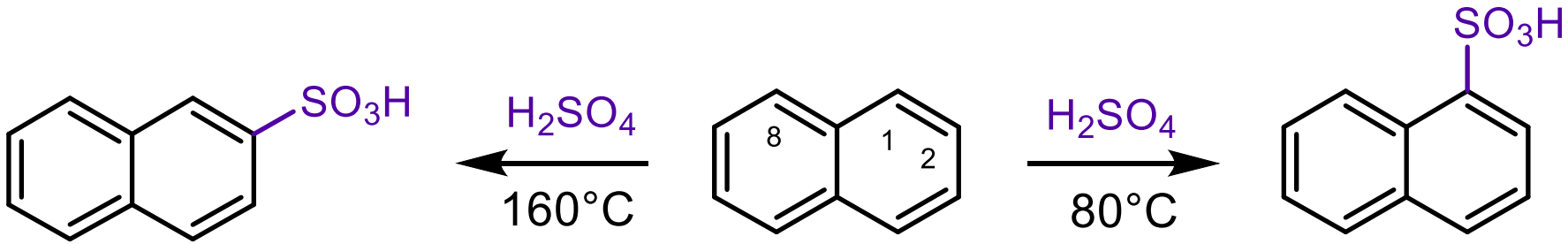
majoritní

Nitrace



majoritní minoritní

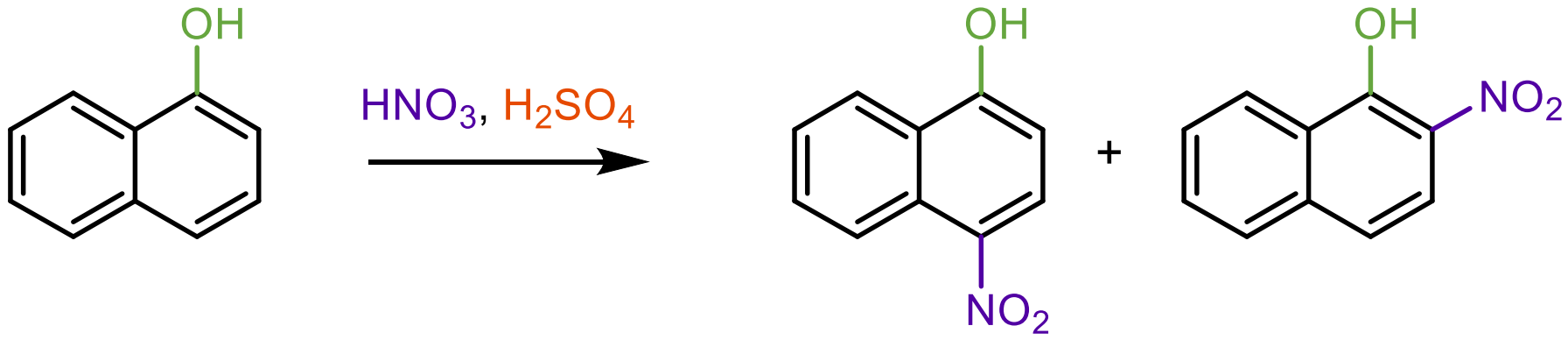
Sulfonace



vratná reakce, závisí na teplotě

Elektrofilní substituce naftalenu – direktivní efekty

Elekrondonorní Skupina (EDG)



Elekronakceptorní Skupina (EWG)