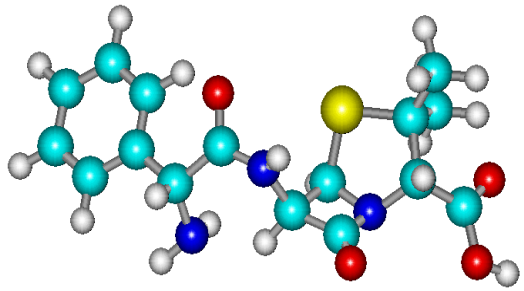
Financováno Evropskou unií
NextGenerationEU
Národní plán obnovy
MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

Chemie organických látek



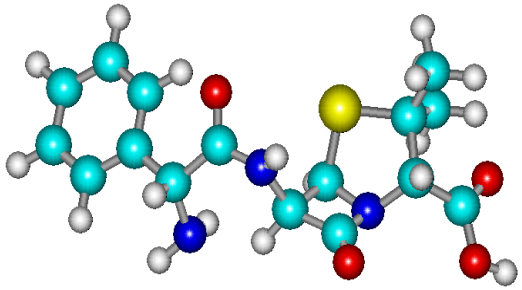



doc. Ing. Pavel Bobáľ, CSc.

MUNI PHARM
Ústav chemických léčiv

Chemie organických látek

6. Chemie benzenu a aromatických sloučenin



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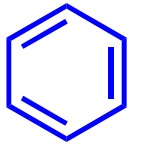
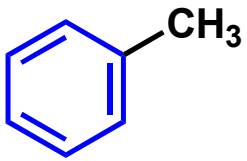
Ústav chemických léčiv

Benzen a aromaticita

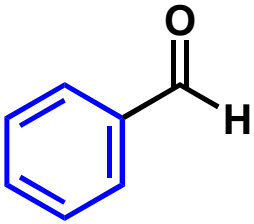
Aromatické látky – rozdílné než vonné látky



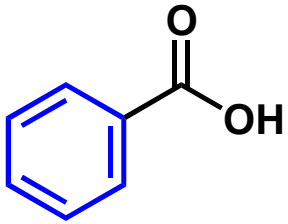
benzen



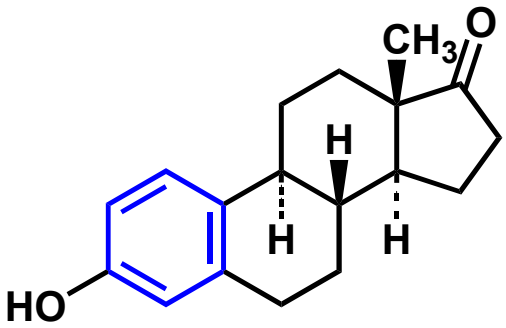
toluen



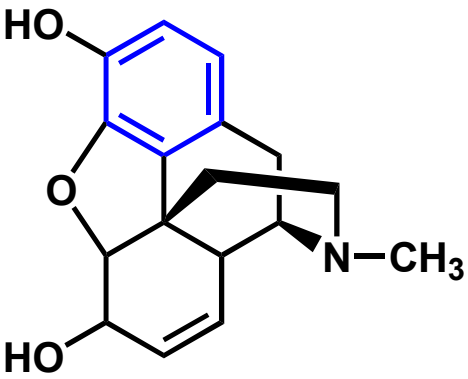
benzaldehyd



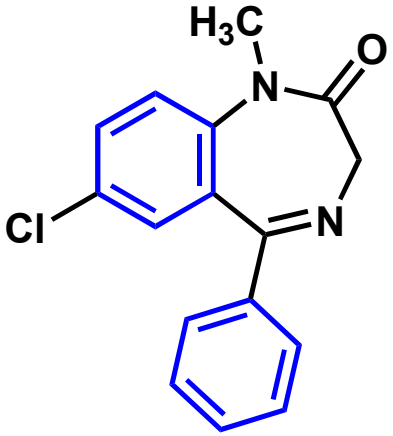
kyselina benzoová



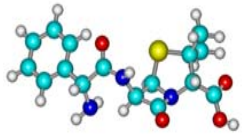
estron



morfin



diazepam



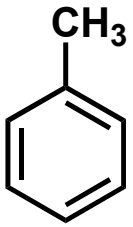
Zdroje aromatických uhlovodíků

Uhlí – základní zdroj – zahřívání na 1 000 °C za nepřístupu vzduchu – tepelné štěpení makromolekul v uhlí – destiluje **dehet**,

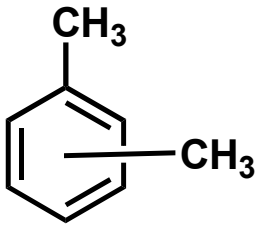
- frakční destilace dehtu – směs aromatických sloučenin (benzen, toluen, xyleny, naftalen, …),

Ropa – alifatické látky x **Uhlí** – aromatické látky

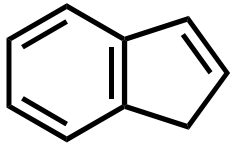
benzen



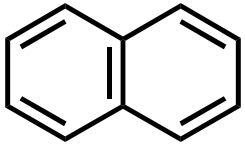
toluen



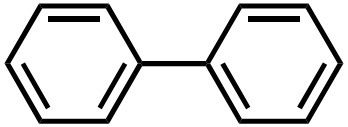
xylen



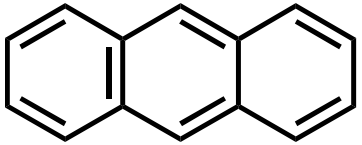
inden



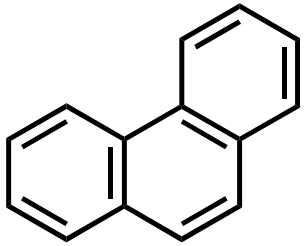
naftalen



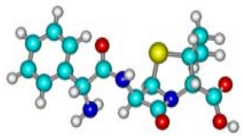
bifenyl



anthracen

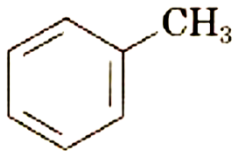
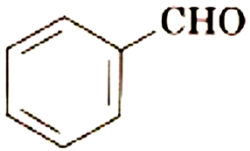
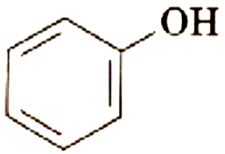
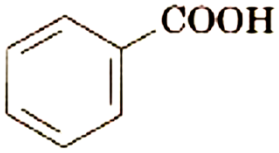
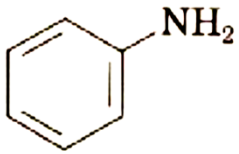
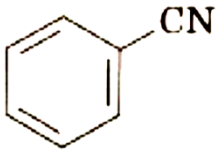
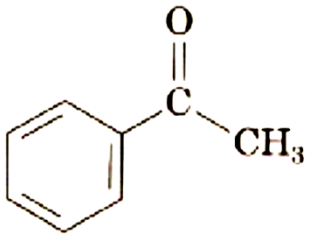
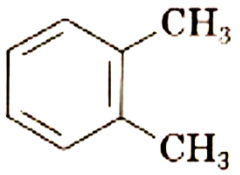
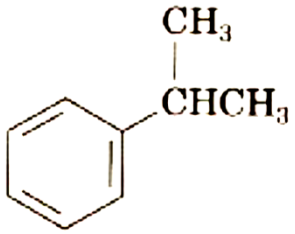
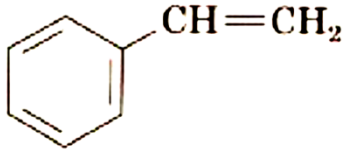


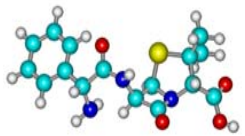
fenanthren



Názvosloví aromatických sloučenin

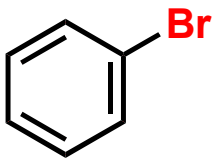
Triviální názvy některých aromatických sloučenin

Vzorec	Název	Vzorec	Název
	toluen (t. v. 111 °C)		benzaldehyd (t. v. 178 °C)
	fenol (t. t . 43 °C)		benzoová kyselina (t. t. 122 °C)
	anilin (t. v. 184 °C)		benzonitril (t. v. 191 °C)
	acetofenon (t. t. 21 °C)		*ortho*-xylen (t. v. 144 °C)
	kumen (t. v. 152 °C)		styren (t. v. 145 °C)



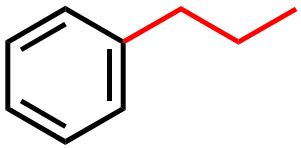
Názvosloví aromatických sloučenin

Monosubstituované deriváty benzenu

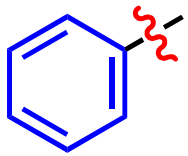


brombenzen

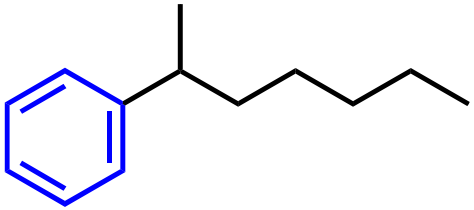
nitrobenzen



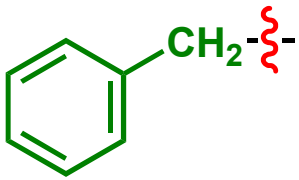
propylbenzen



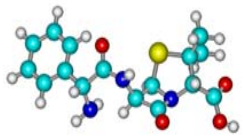
fenylová skupina



2-fenylheptan

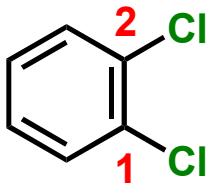


benzylová skupina

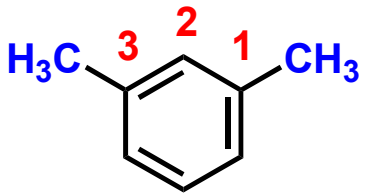


Názvosloví aromatických sloučenin

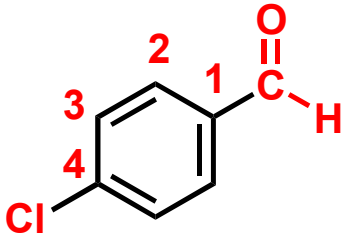
Disubstituované benzeny – ***ortho-, meta-, para-***



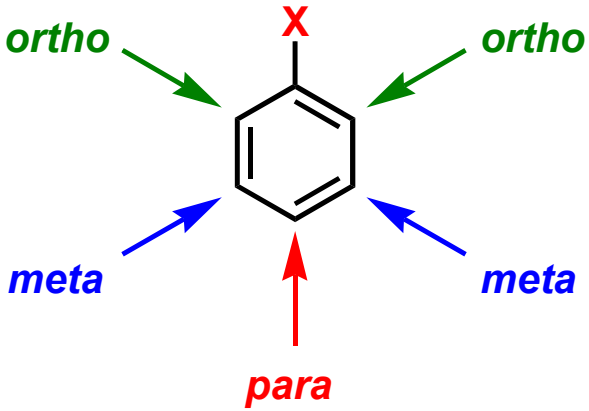
***ortho*-dichlorbenzen**
***o*-dichlorbenzen**

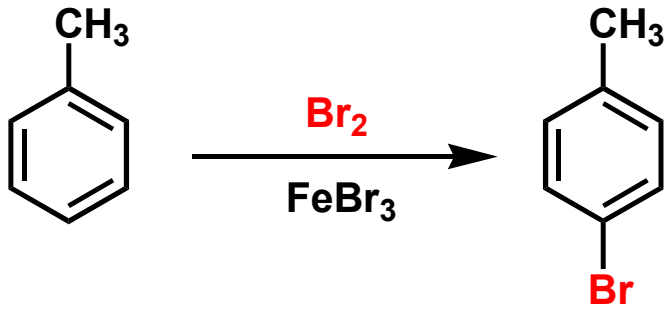


***meta*-xylen**
***m*-xylen**



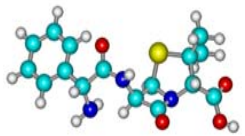
***para*-chlorbenzaldehyd**
***p*-chlorbenzaldehyd**





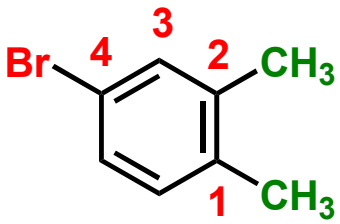
toluen

***p*-brom**toluen

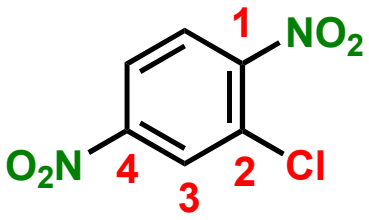


Názvosloví aromatických sloučenin

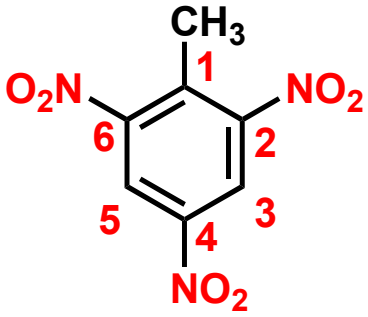
Více než dva substituenty – lokanty nejnižší čísla
– substituenty podle abecedy



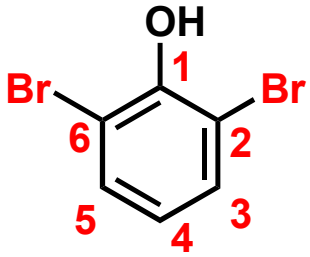
4-brom-1,2-dimethylbenzen



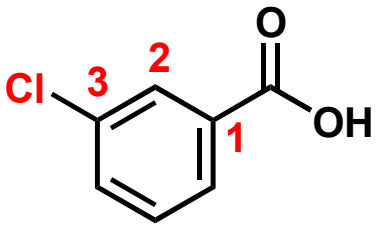
2-chlor-1,4-dinitrobenzen



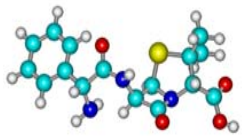
2,4,6-trinitrotoluen (TNT)



2,6-dibromfenol

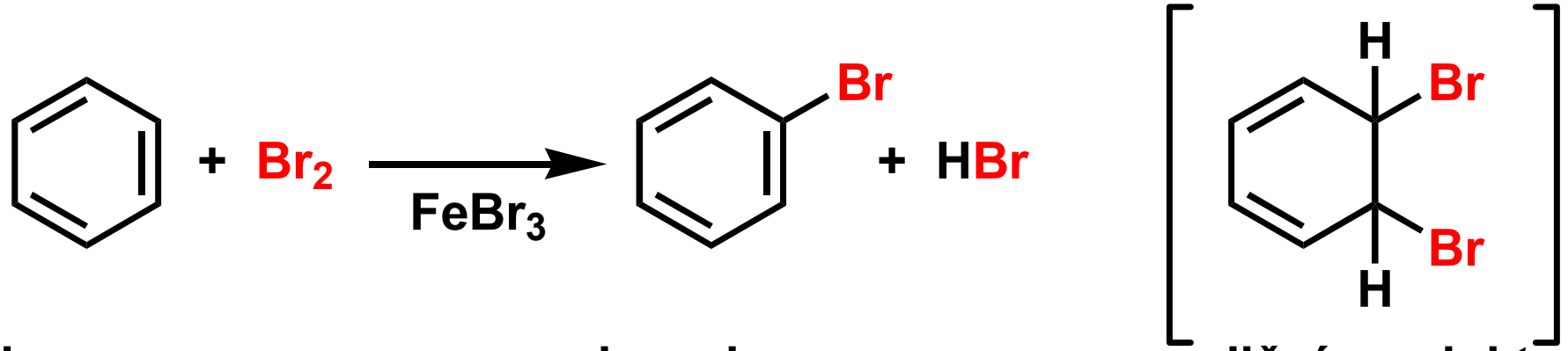


***m*-chlorbenzoová kyselina**



Struktura a stabilita benzenu

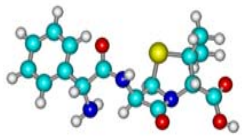
Benzen – „nenasycená“ sloučenina – nemá charakter alkenů,
– nedává adiční produkty,
– dává substituční produkty



benzen

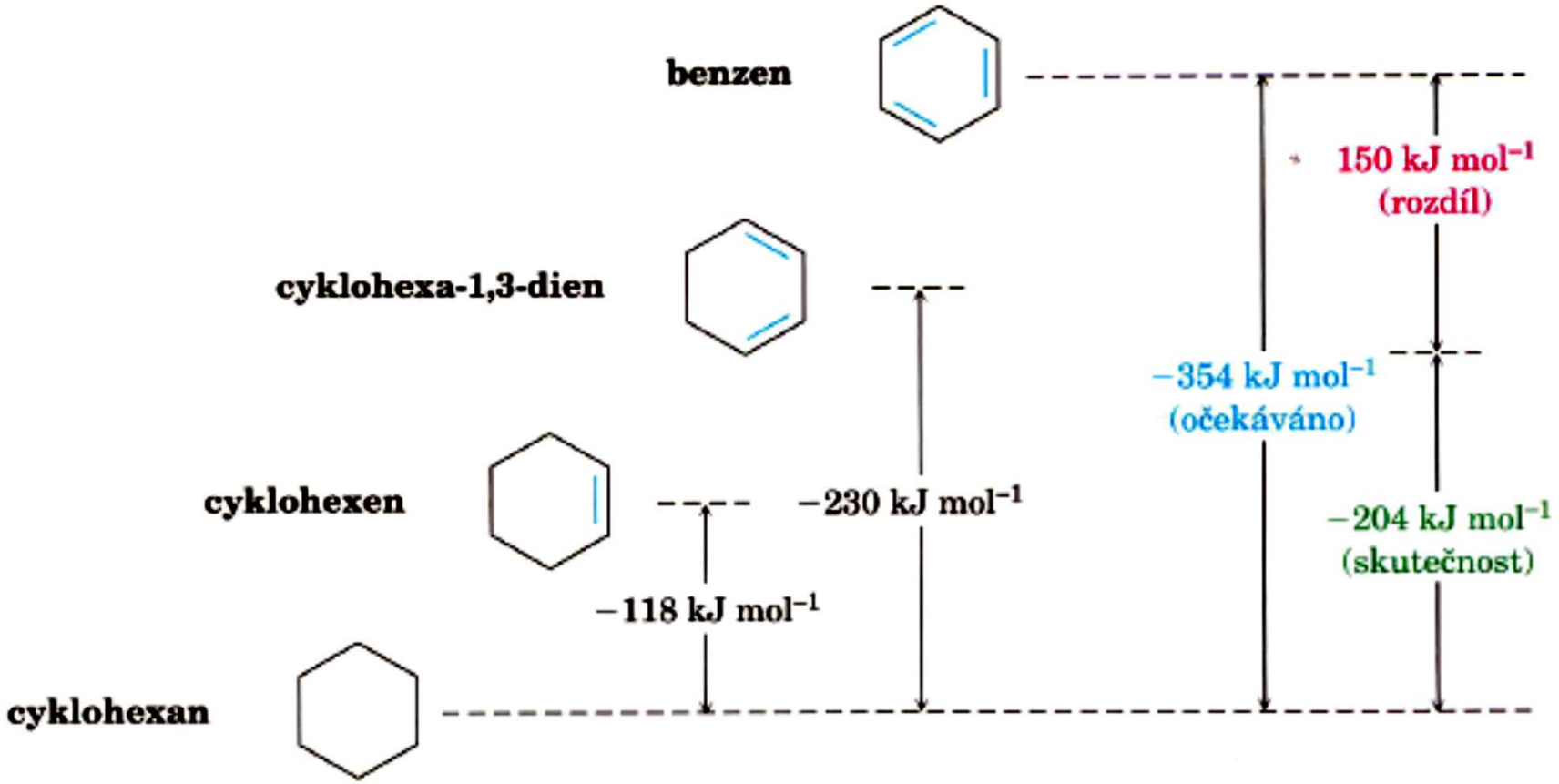
brombenzen (substituční produkt)

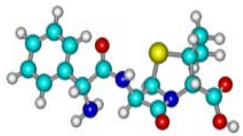
adiční produkt (nevzniká)



Struktura a stabilita benzenu

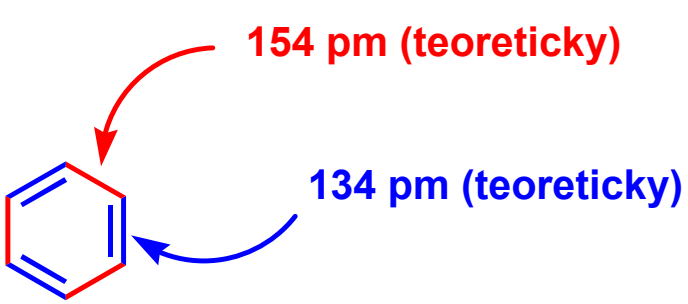
Porovnání hydrogenačních tepel:

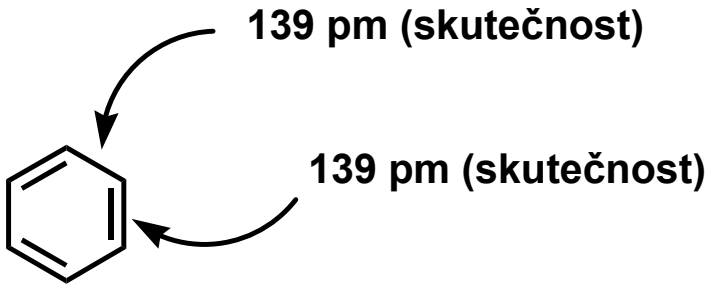




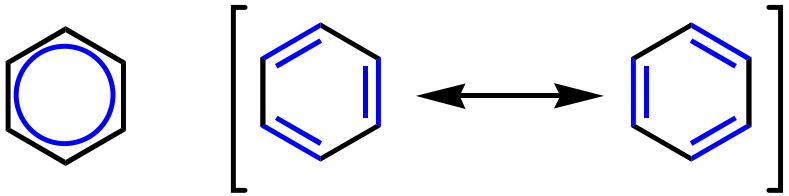
Struktura a stabilita benzenu

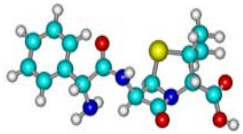
Délky vazeb:





Rezonanční struktury:



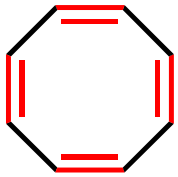


Hückelovo pravidlo – 4n+2

Aromatická molekula

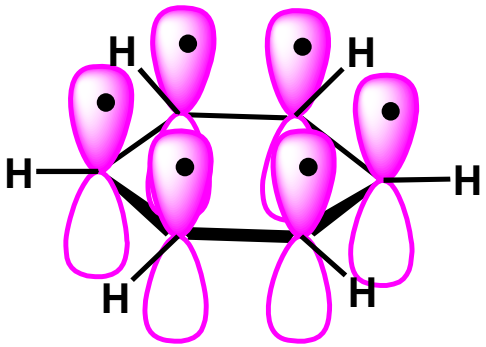
- cyklická konjugovaná,
- planární,
- Hückelovo pravidlo – *4n+2* elektronů *π,*

cyklobutadien

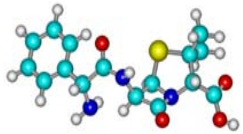


- antiaromatické

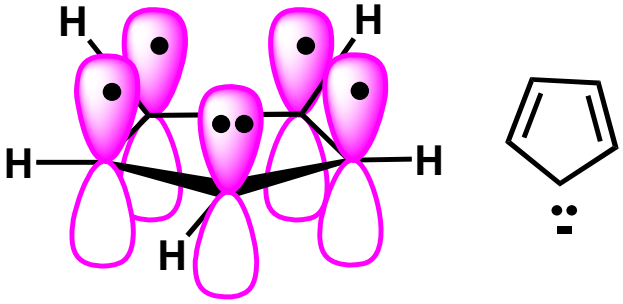
cyklooktatetraen



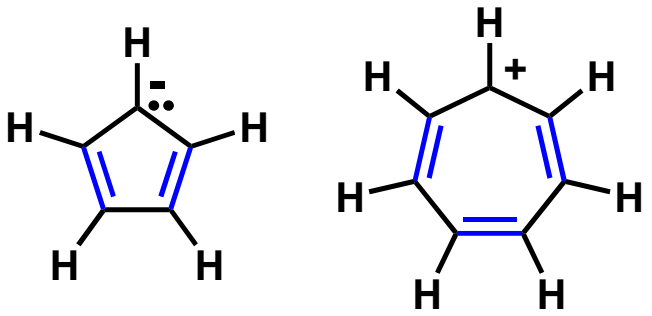
benzen



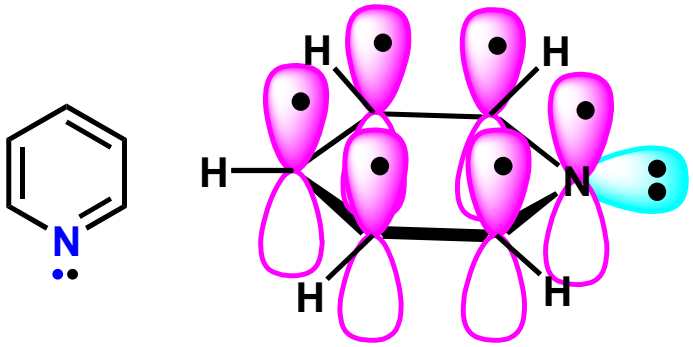
Aromatické látky



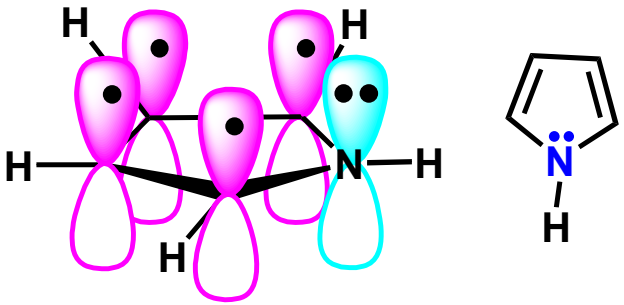
cyklopentadienylový anion



cykloheptatrienylový kation

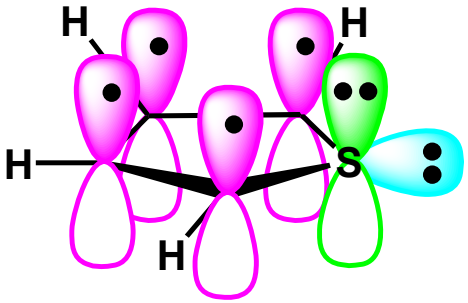


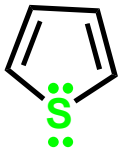
pyridin



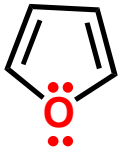
pyrrol

Aromatické látky

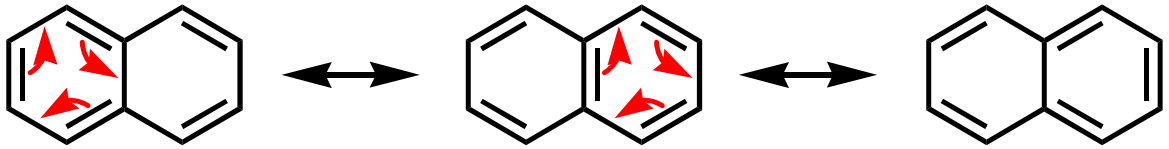




thiofen

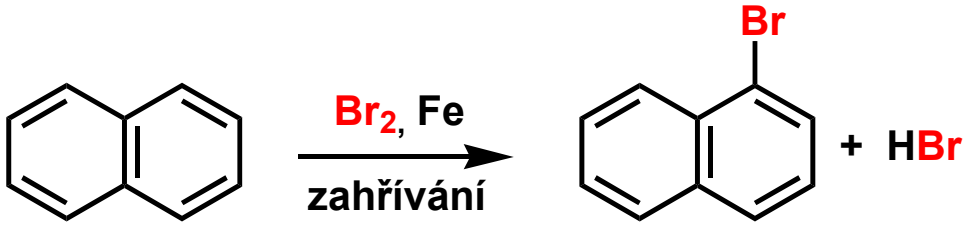


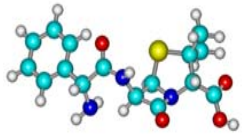
furan



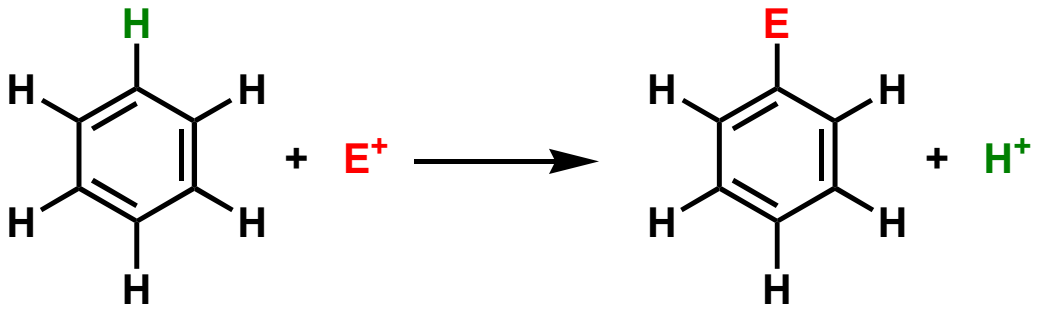
naftalen

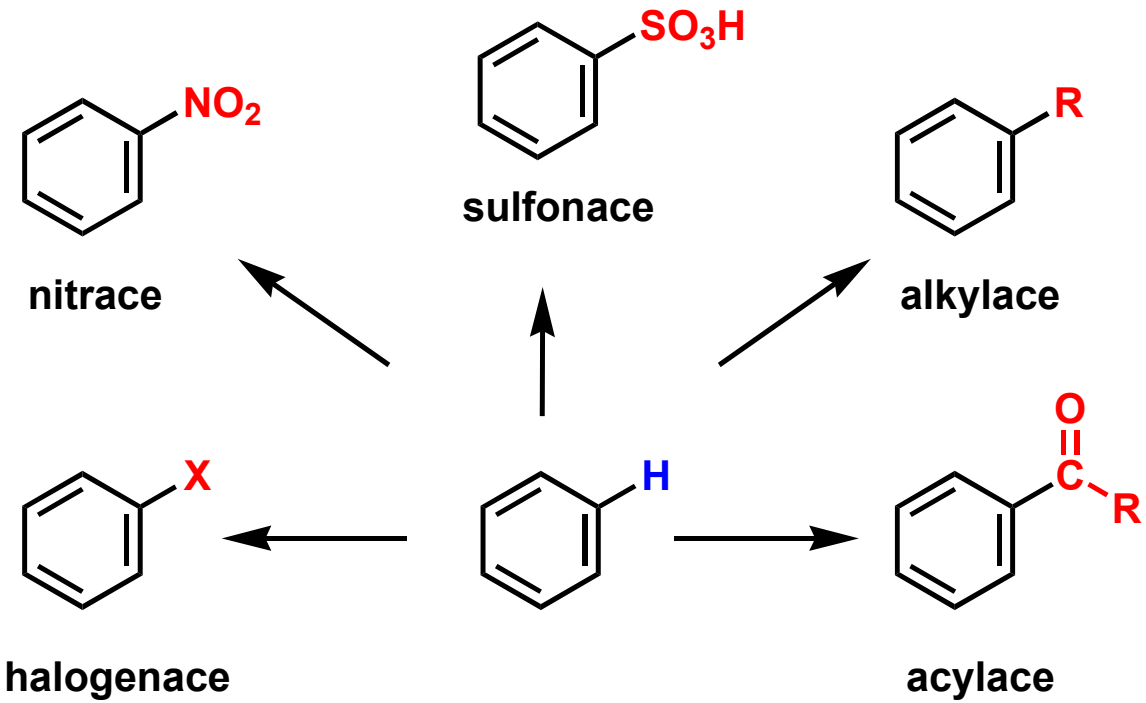
- substituce – ne adice

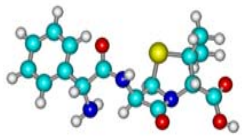




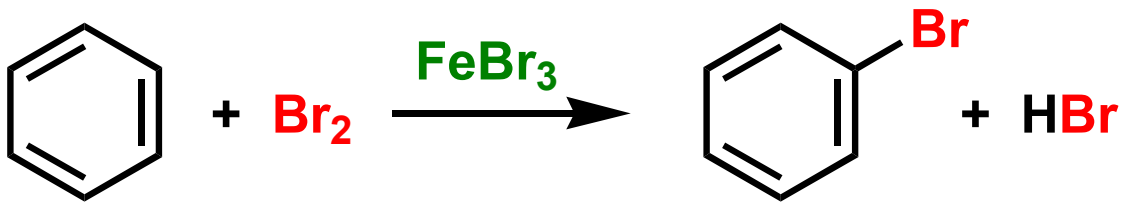
Chemie benzenu: elektrofilní aromatická substituce

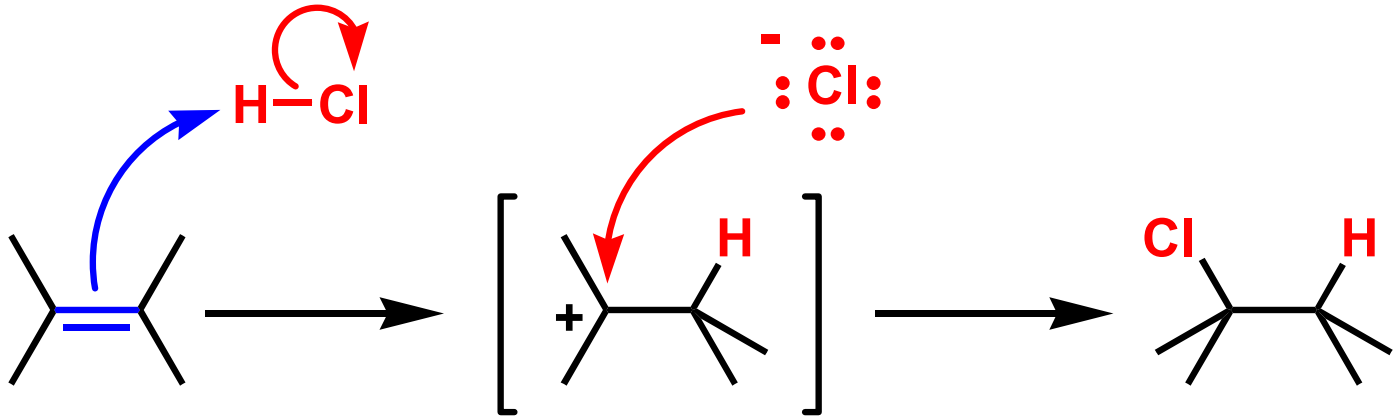


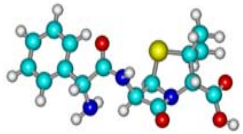




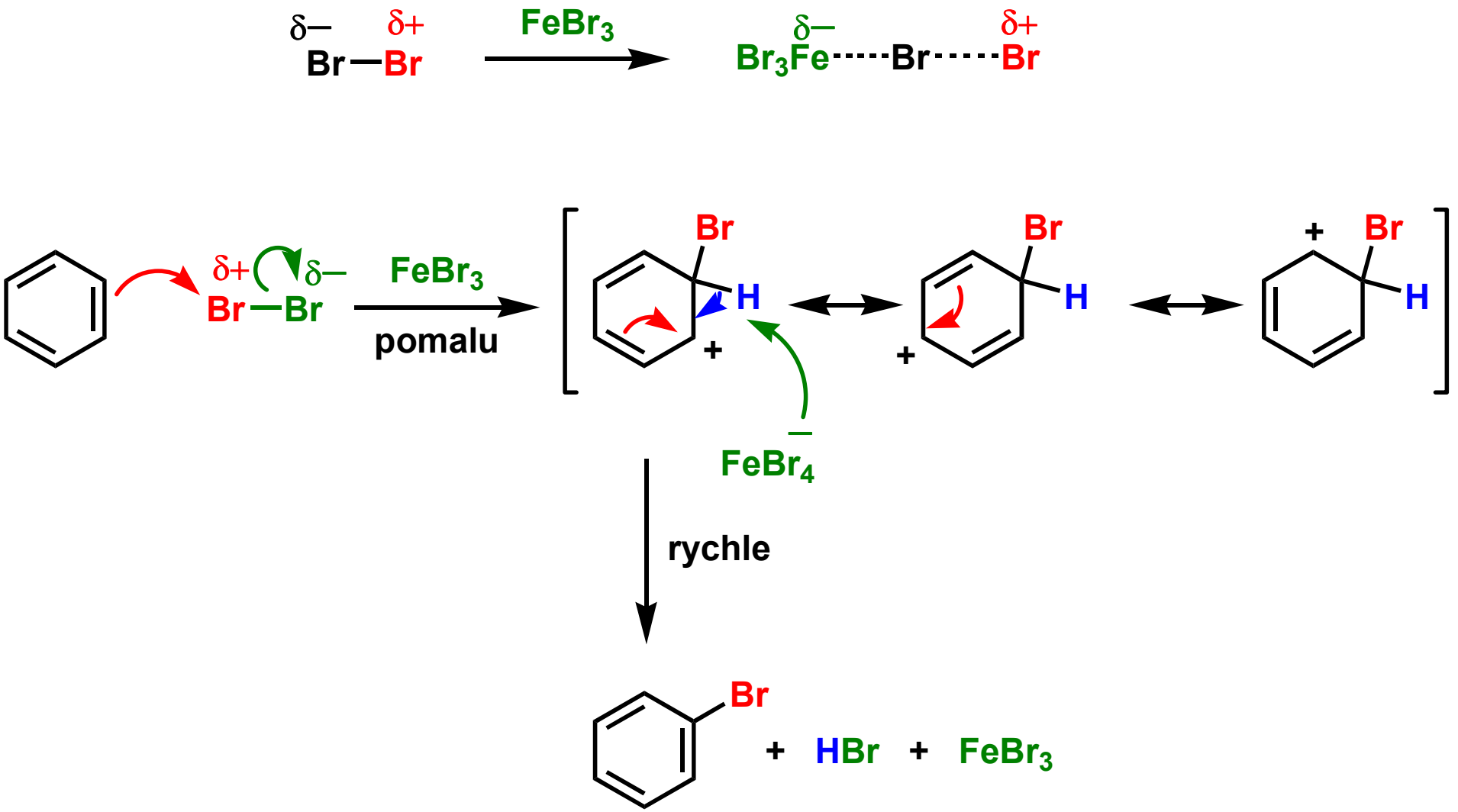
Chemie benzenu: elektrofilní aromatická substituce
Bromace

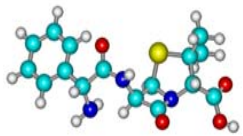






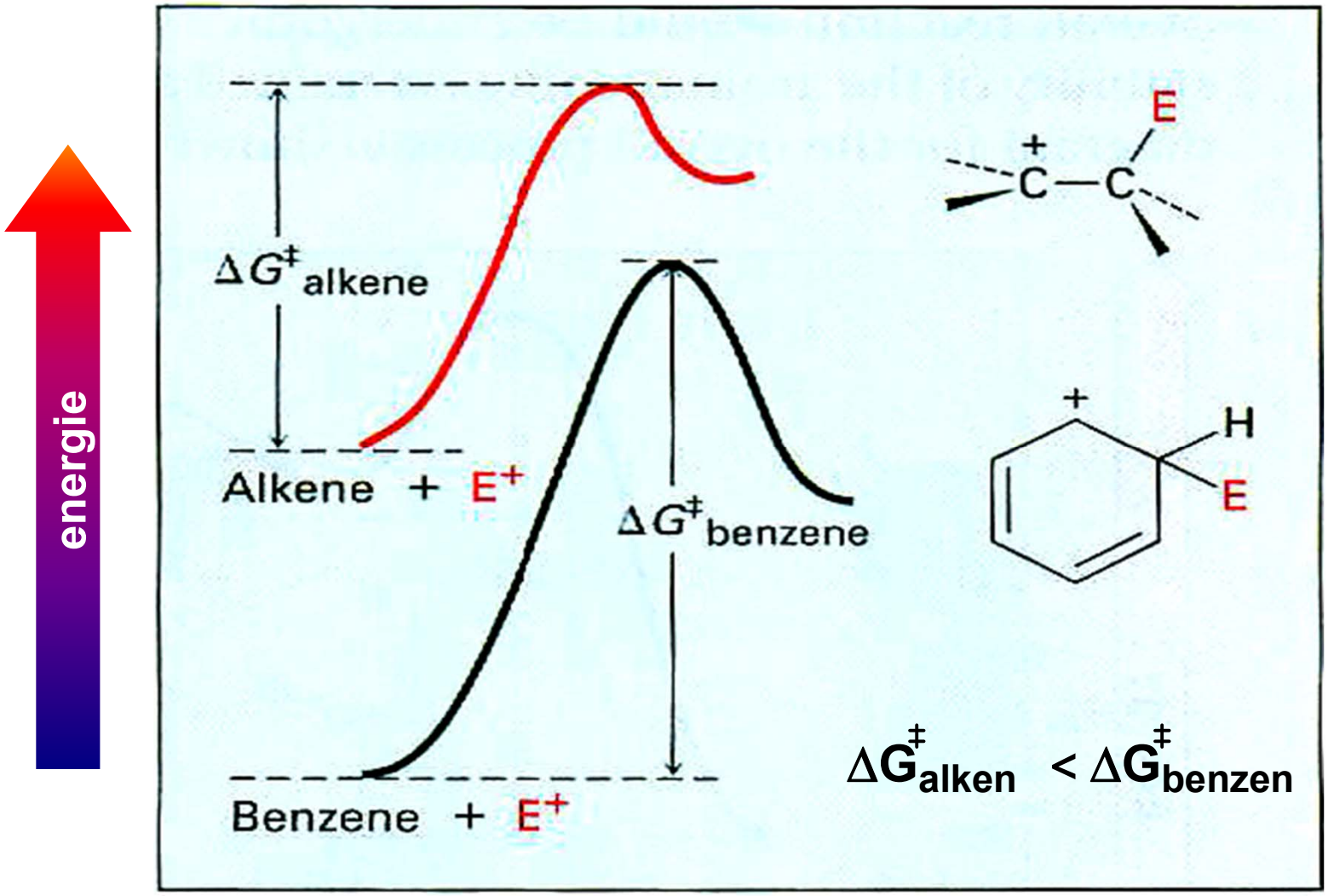
Chemie benzenu: elektrofilní aromatická substituce
Bromace



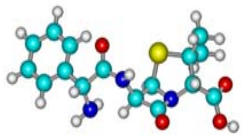


Chemie benzenu: elektrofilní aromatická substituce

Porovnání reakce elektrofilu s alkenem a benzenem

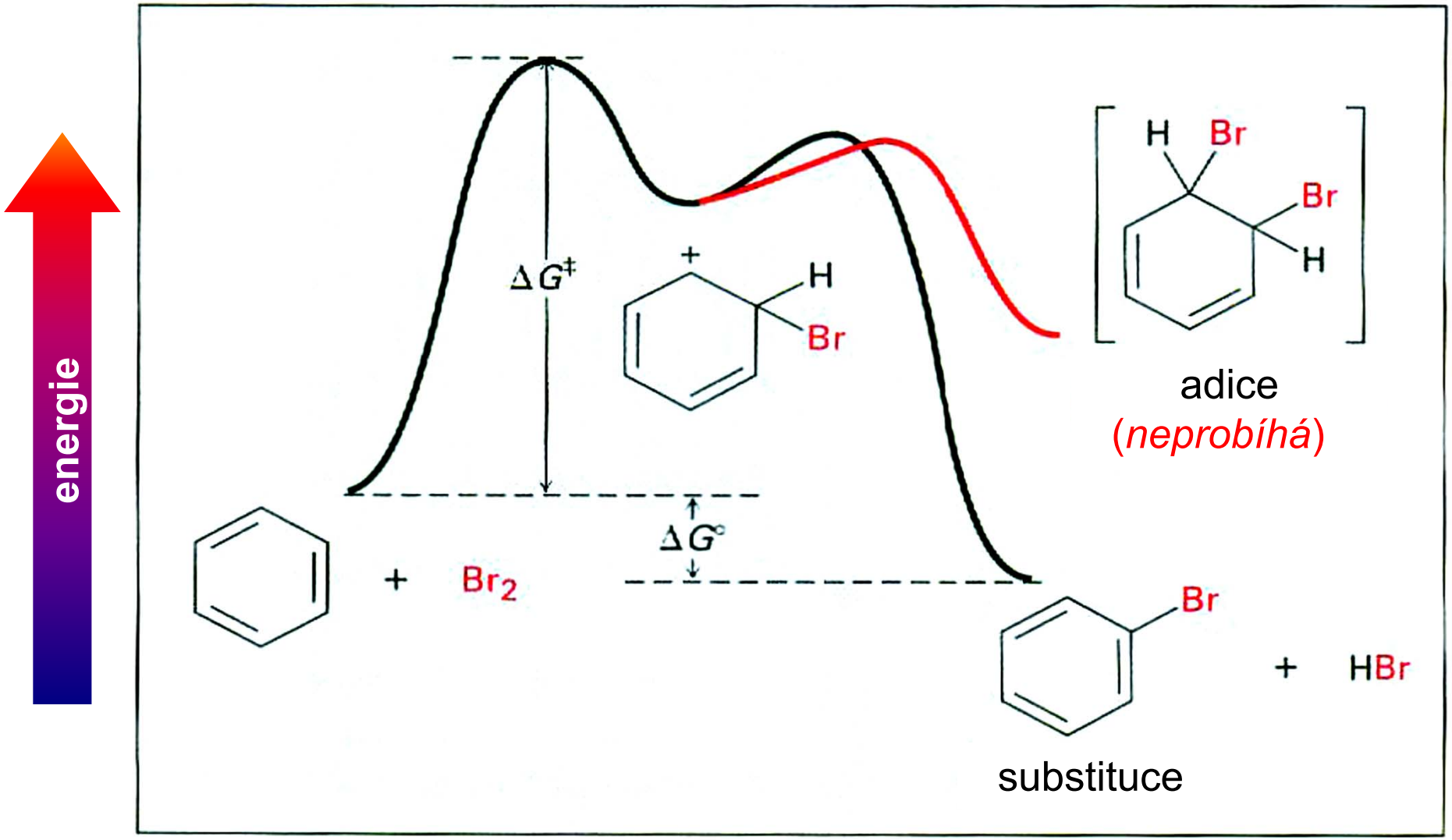


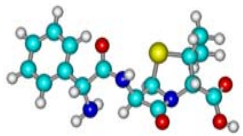
reakční koordináta →



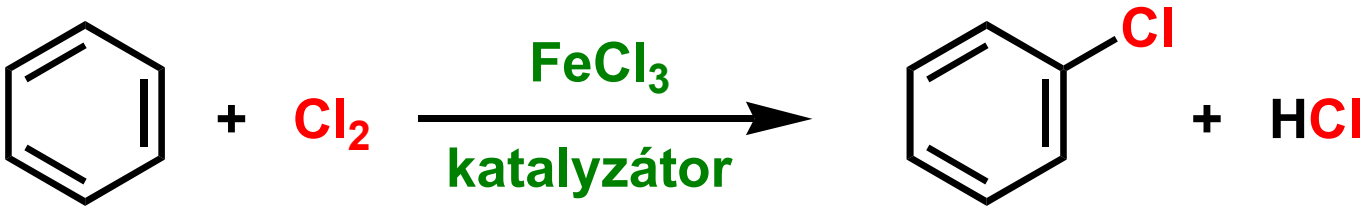
Chemie benzenu: elektrofilní aromatická substituce

Energetický diagram elektrofilní bromace benzenu

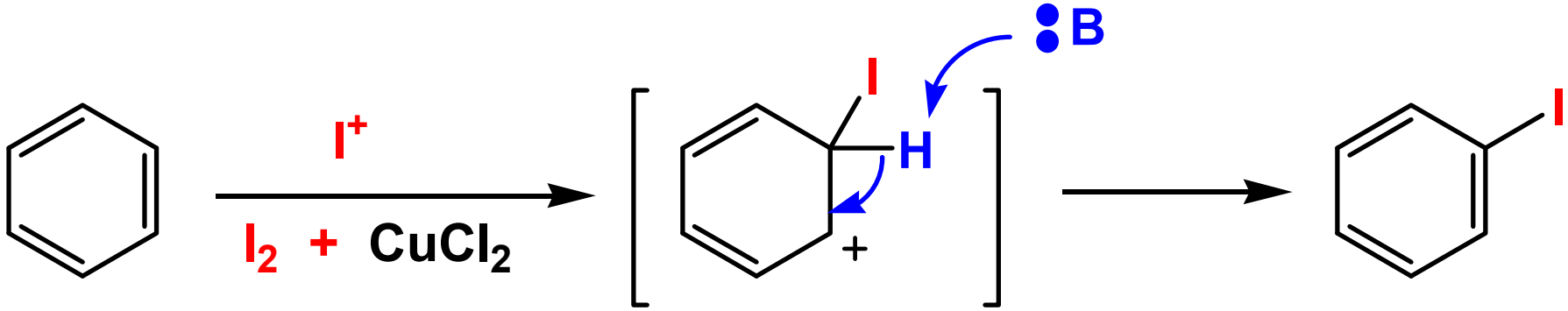


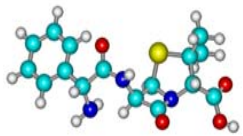


Chemie benzenu: elektrofilní aromatická substituce
Chlorace a jodace



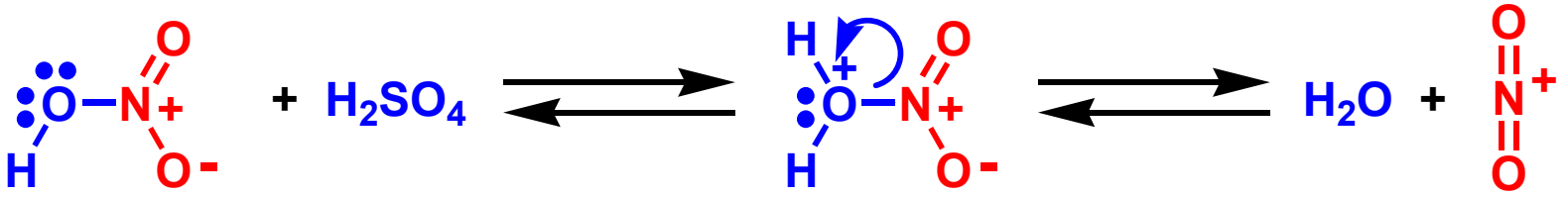
$$I_2 + 2\,Cu^{2+} \longrightarrow 2\,I^{+} + 2\,Cu^{+}$$



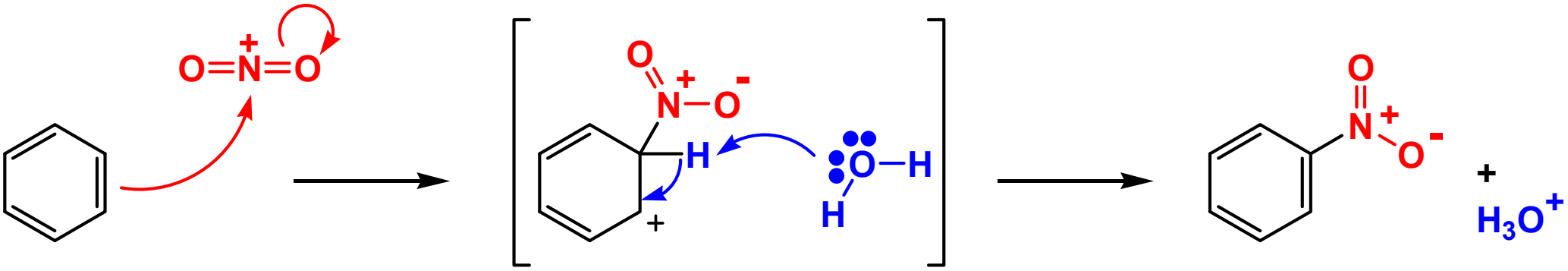


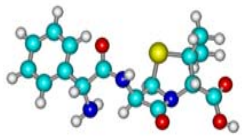
Chemie benzenu: elektrofilní aromatická substituce
Nitrace

- elektrofilem je NO_2^+



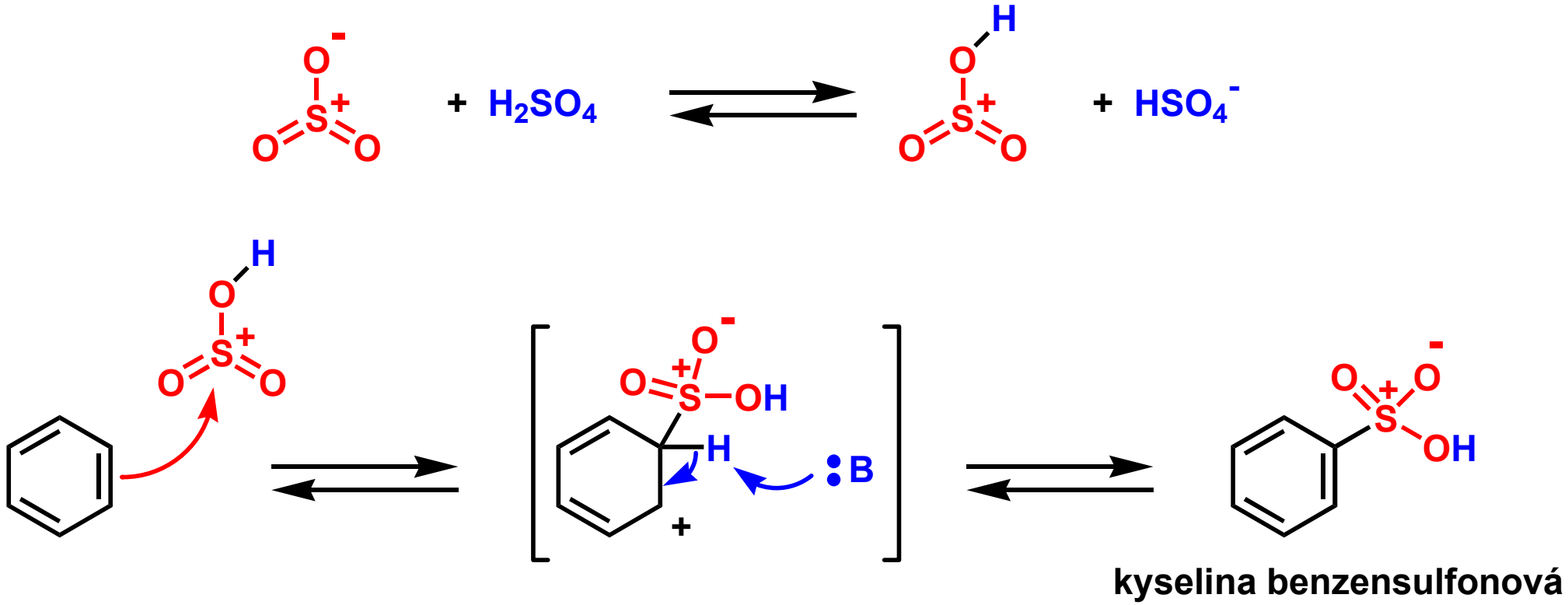
nitroniový ion



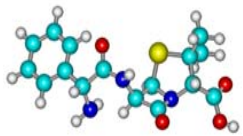


Chemie benzenu: elektrofilní aromatická substituce
Sulfonace

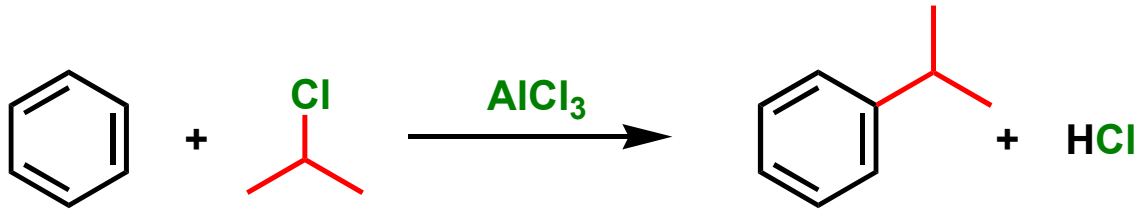
- elektrofilem je HSO_3^+, nebo SO_3,
- oleum nebo koncentrovaná kyselina sírová



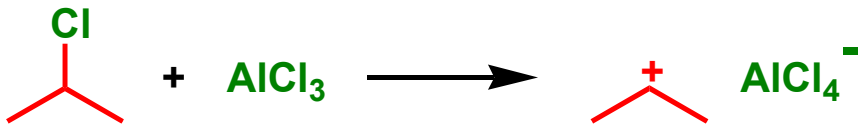
kyselina benzensulfonová

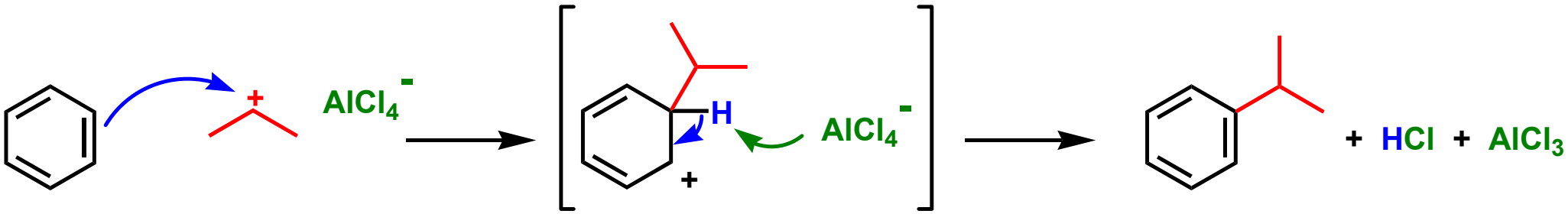


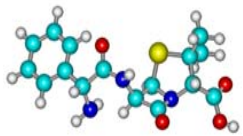
Chemie benzenu: elektrofilní aromatická substituce
Alkylace – Friedelova – Craftsova reakce



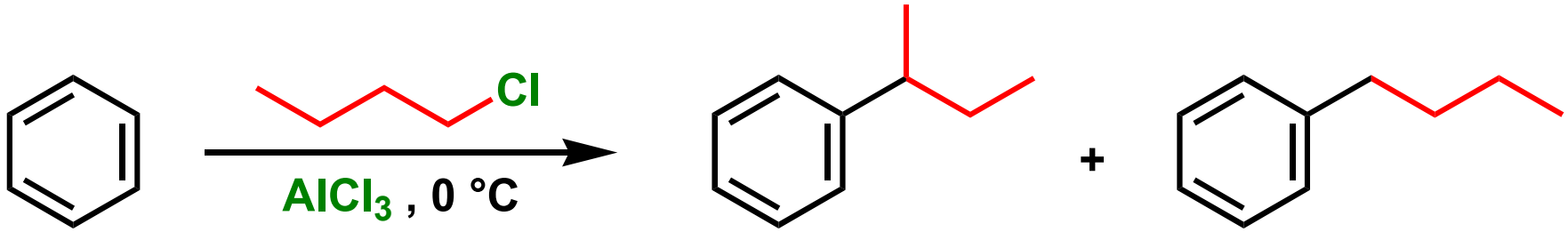
kumen
85 %





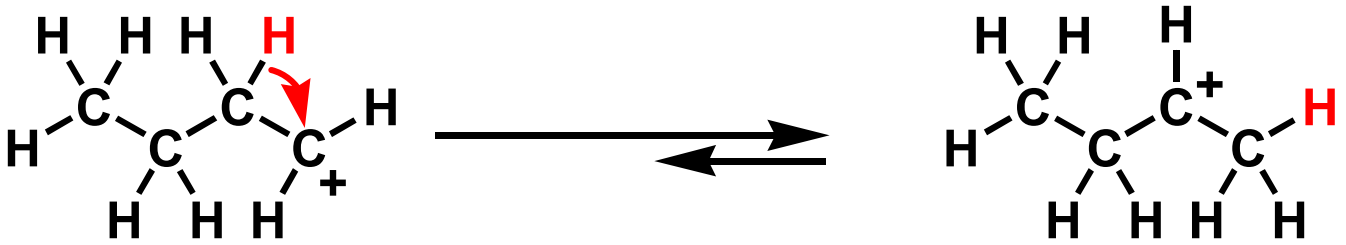


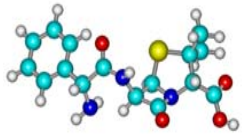
Chemie benzenu: elektrofilní aromatická substituce
Alkylace – Friedelova – Craftsova reakce



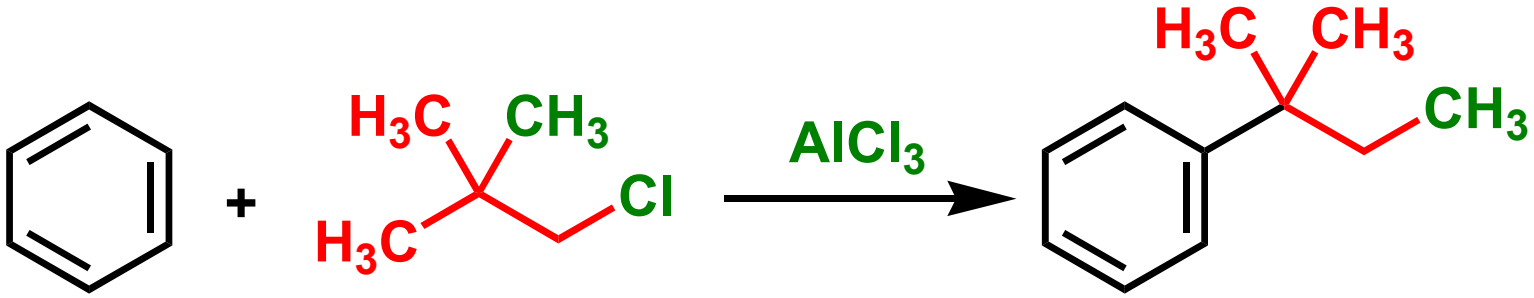
***sek*-butylbenzen**
(65 %)

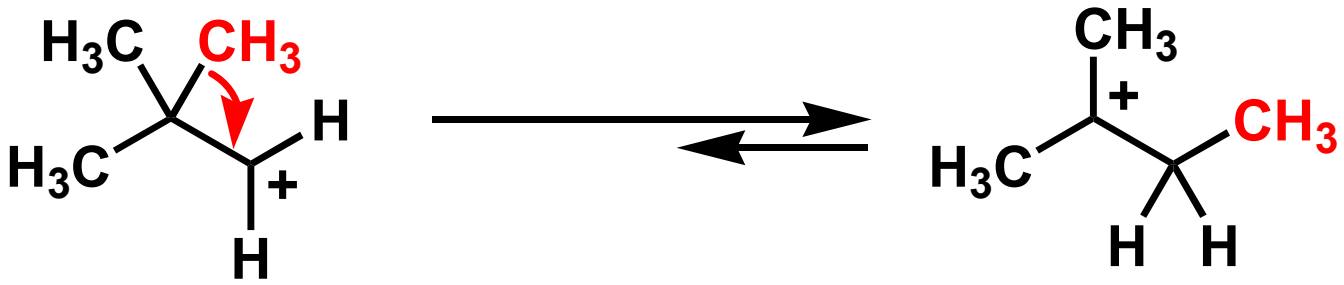
butylbenzen
(35 %)

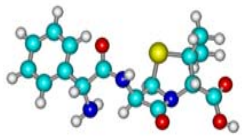




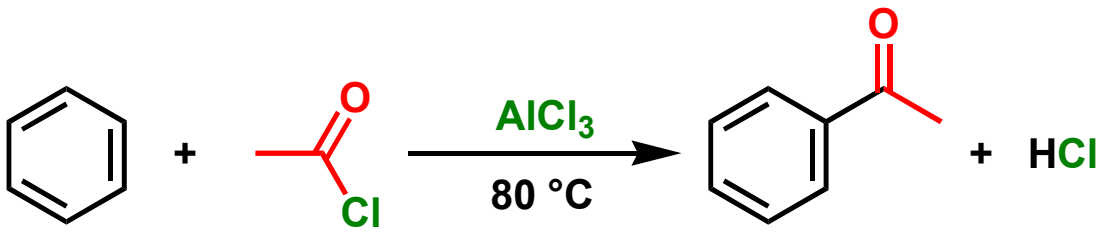
Chemie benzenu: elektrofilní aromatická substituce
Alkylace – Friedelova – Craftsova reakce





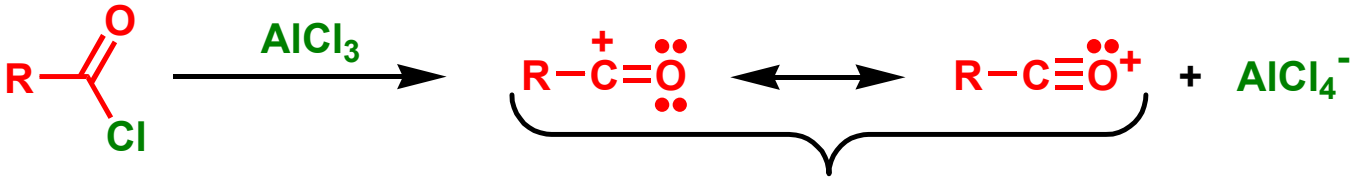


Chemie benzenu: elektrofilní aromatická substituce
Acylace – Friedelova – Craftsova acylace

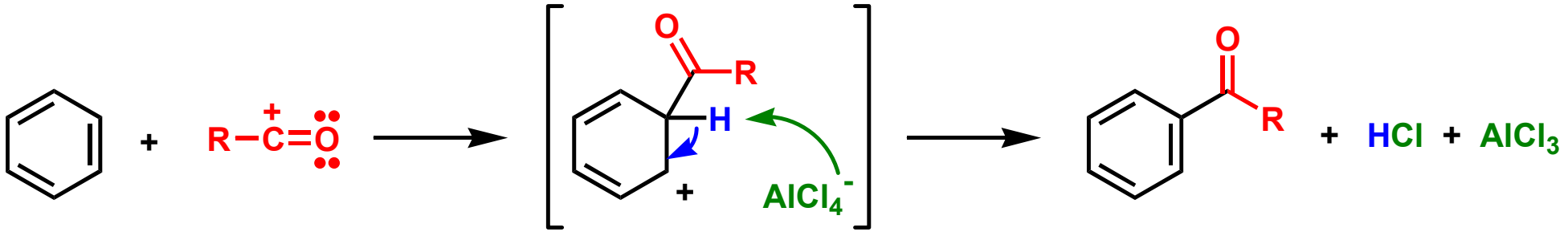


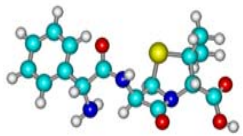
acetylchlorid

acetofenon
(95 %)



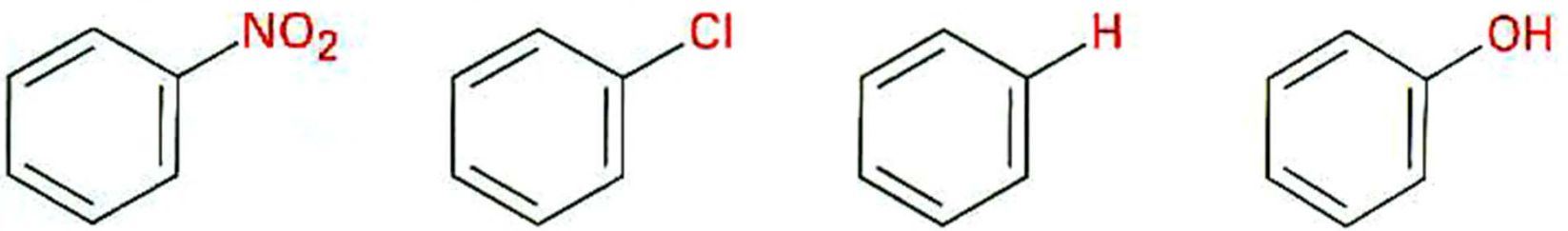
acyliový ion



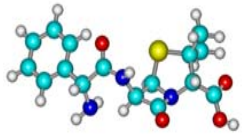


Chemie benzenu: elektrofilní aromatická substituce
Substituční efekty

- substituenty ovlivňují reaktivitu aromatického kruhu

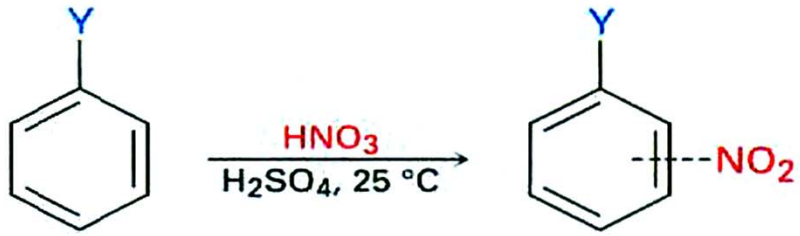


relativní rychlost nitrace	6×10^{-8}	0.033	1	1000



Chemie benzenu: elektrofilní aromatická substituce
Substituční efekty

- substituenty ovlivňují regioselektivitu reakce

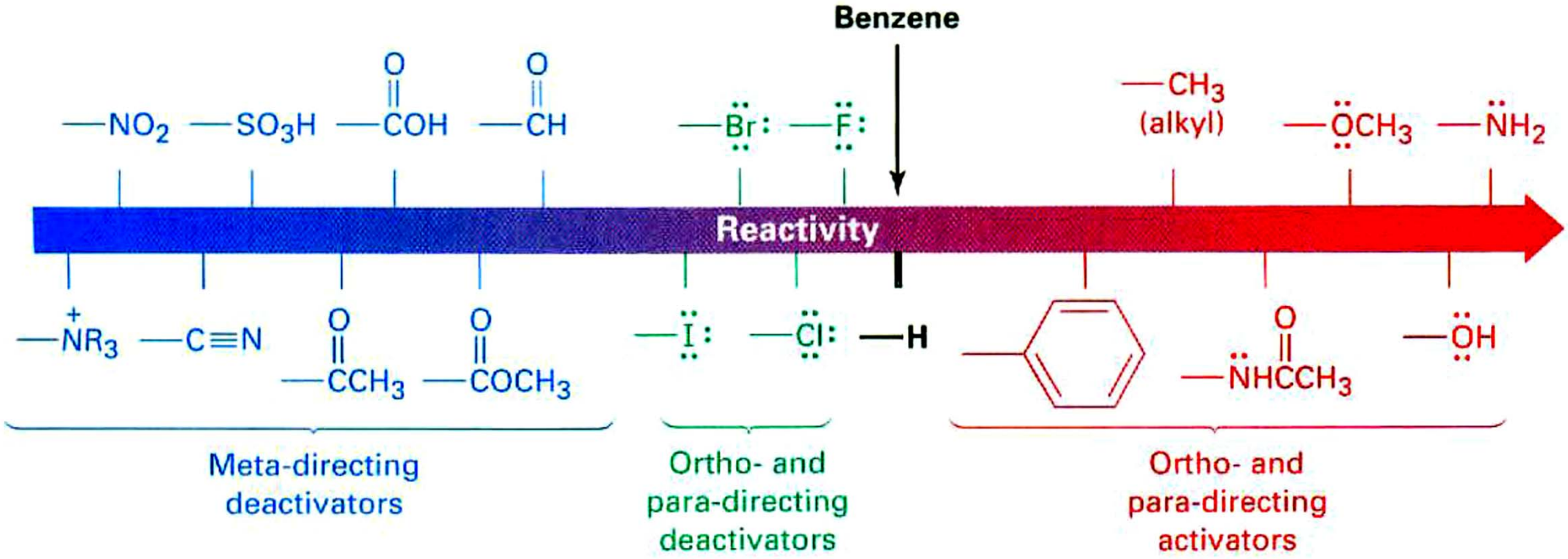


	Product (%)		
	Ortho	Meta	Para
Meta-directing deactivators			
$-\overset{+}{N}(CH_3)_3$	2	87	11
$-NO_2$	7	91	2
$-CO_2H$	22	76	2
$-CN$	17	81	2
$-CO_2CH_3$	28	66	6
$-COCH_3$	26	72	2
$-CHO$	19	72	9

	Product (%)		
	Ortho	Meta	Para
Ortho- and para-directing deactivators			
$-F$	13	1	86
$-Cl$	35	1	64
$-Br$	43	1	56
$-I$	45	1	54
Ortho- and para-directing activators			
$-CH_3$	63	3	34
$-OH$	50	0	50
$-NHCOCH_3$	19	2	79

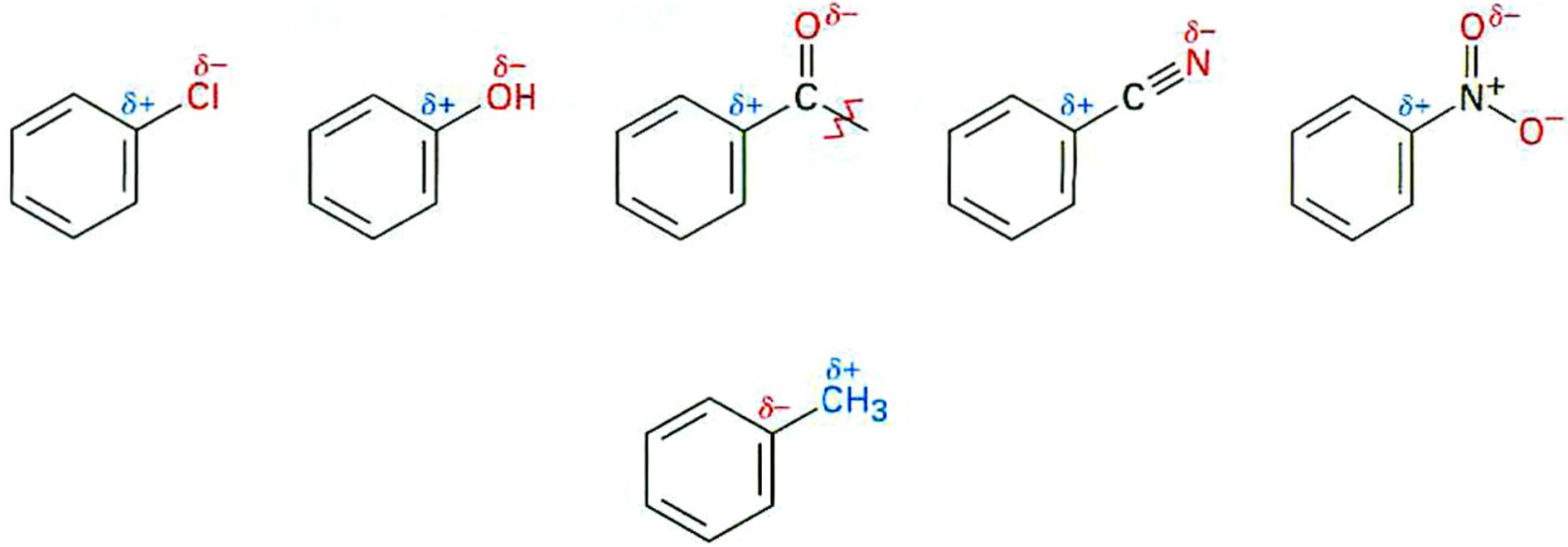
Chemie benzenu: elektrofilní aromatická substituce
Substituční efekty

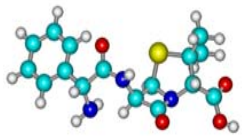
- *ortho-* a *para-* orientující aktivující skupiny,
- *ortho-* a *para-* orientující deaktivující skupiny,
- *meta-* orientující deaktivující skupiny,



Chemie benzenu: elektrofilní aromatická substituce
Substituční efekty

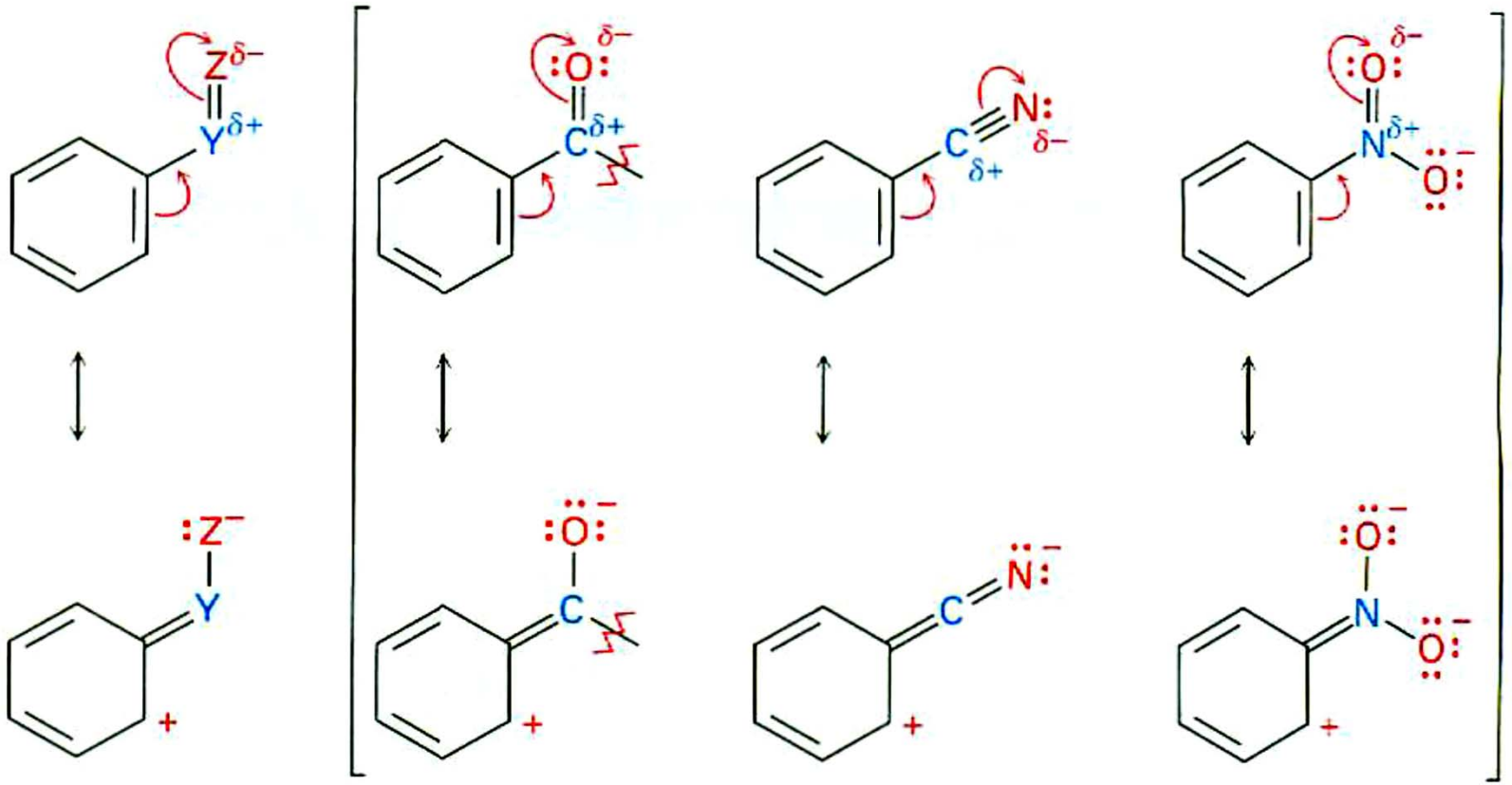
- reaktivita a orientace při elektrofilní aromatické substituci je řízena souhrou **induktivního a rezonančního (mezomerního) efektu**,
- **induktivní efekt**

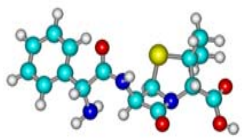




Chemie benzenu: elektrofilní aromatická substituce
Substituční efekty

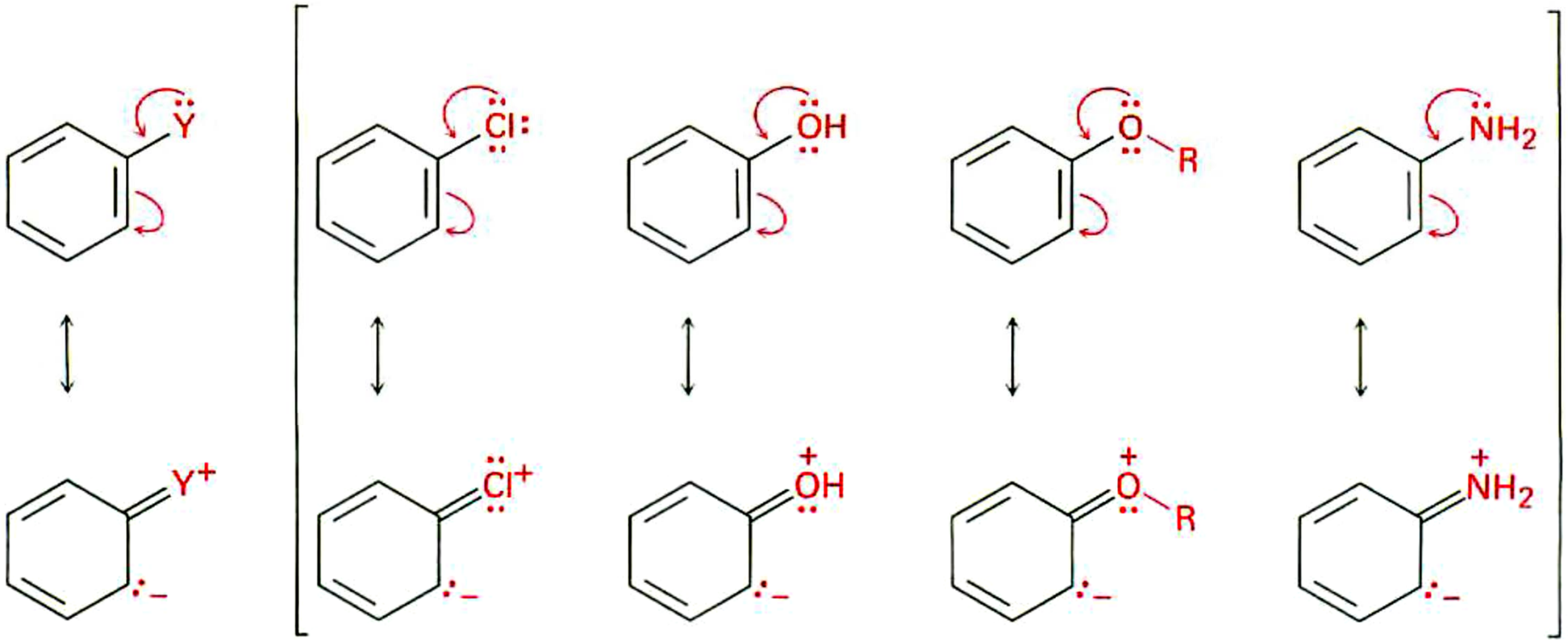
- **rezonanční (mezomerní) efekt** – způsoben donorním nebo akceptroním posunem elektronové hustoty po π–vazbách v důsledku překryvu p-orbitalu substituentu s π–orbitalem aromatického kruhu,
- odtahování elektronů: **–*M*- efekt (elektronakceptory)**

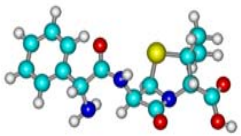




Chemie benzenu: elektrofilní aromatická substituce
Substituční efekty

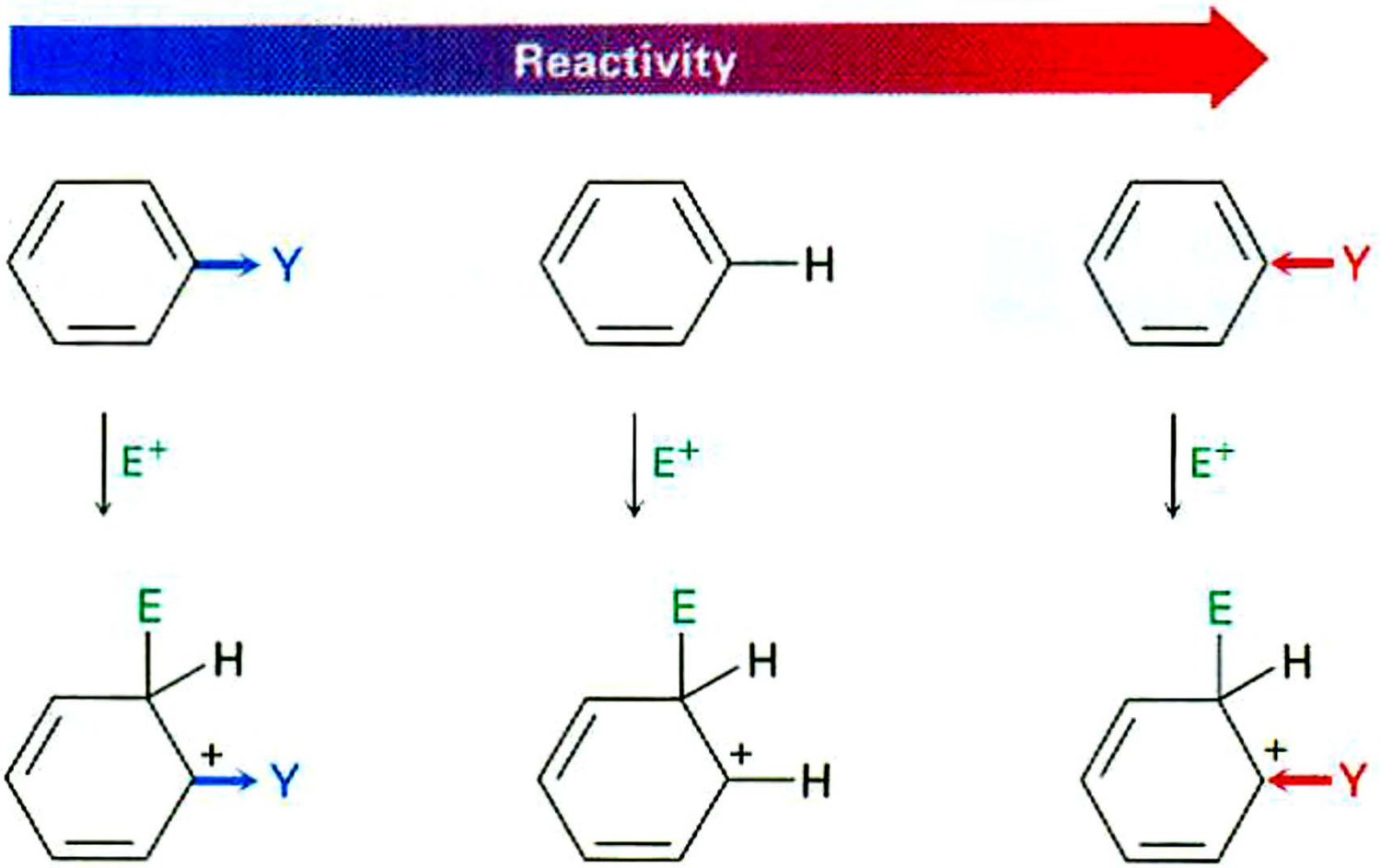
- **rezonanční (mezomerní) efekt** – způsoben donorním nebo akceptroním posunem elektronové hustoty po π–vazbách v důsledku překryvu p-orbitalu substituentu s π–orbitalem aromatického kruhu,
- poskytování elektronů: **+*M*- efekt (elektrondonory)**

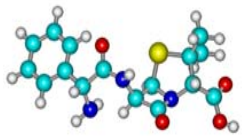




Chemie benzenu: elektrofilní aromatická substituce
Substituční efekty

- aktivace a deaktivace aromatických kruhů



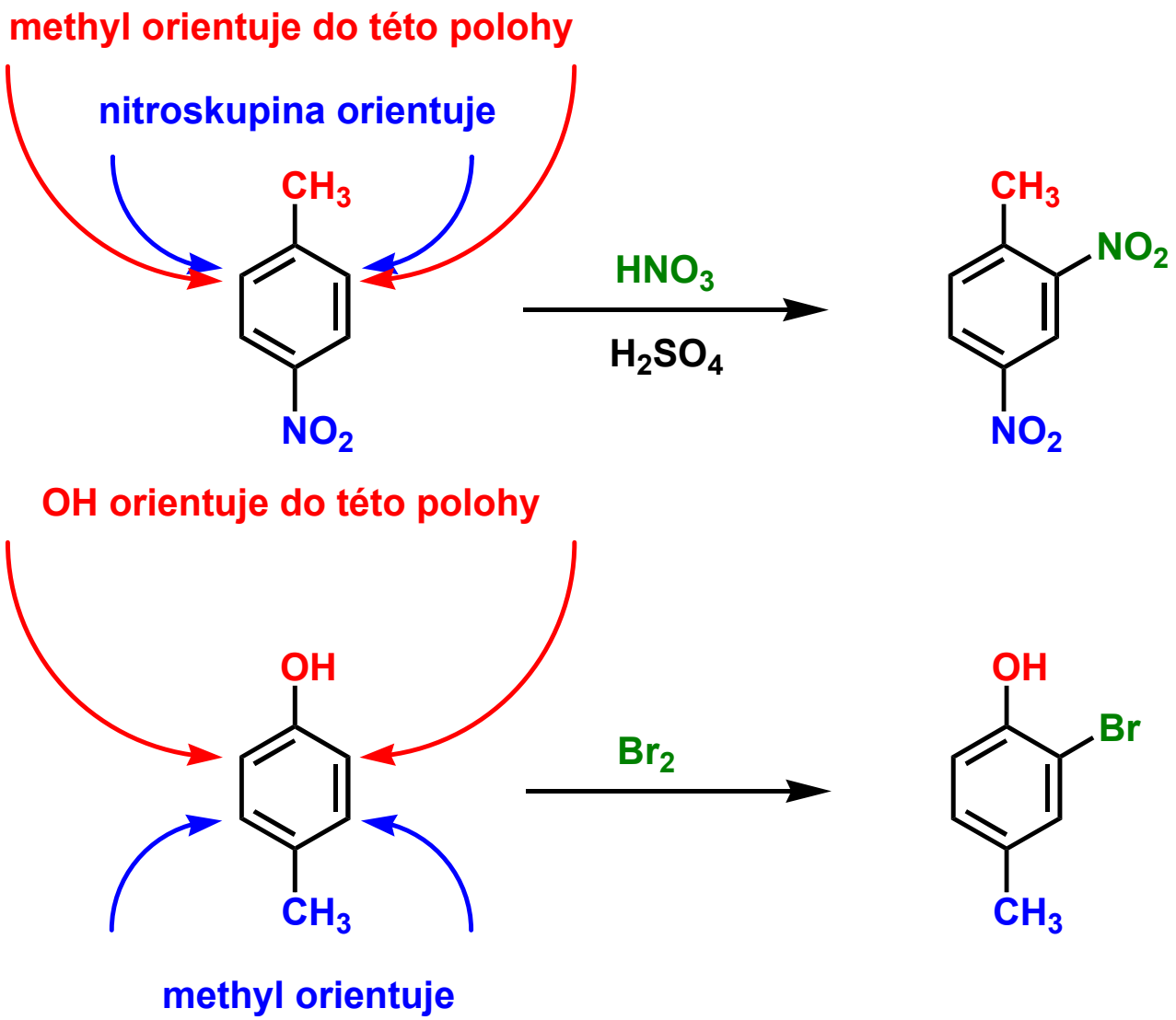


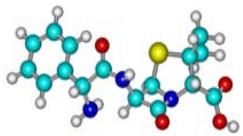
Chemie benzenu: elektrofilní aromatická substituce
Souhrn substitučních efektů

Substituční efekty při elektrofilní aromatické substituci

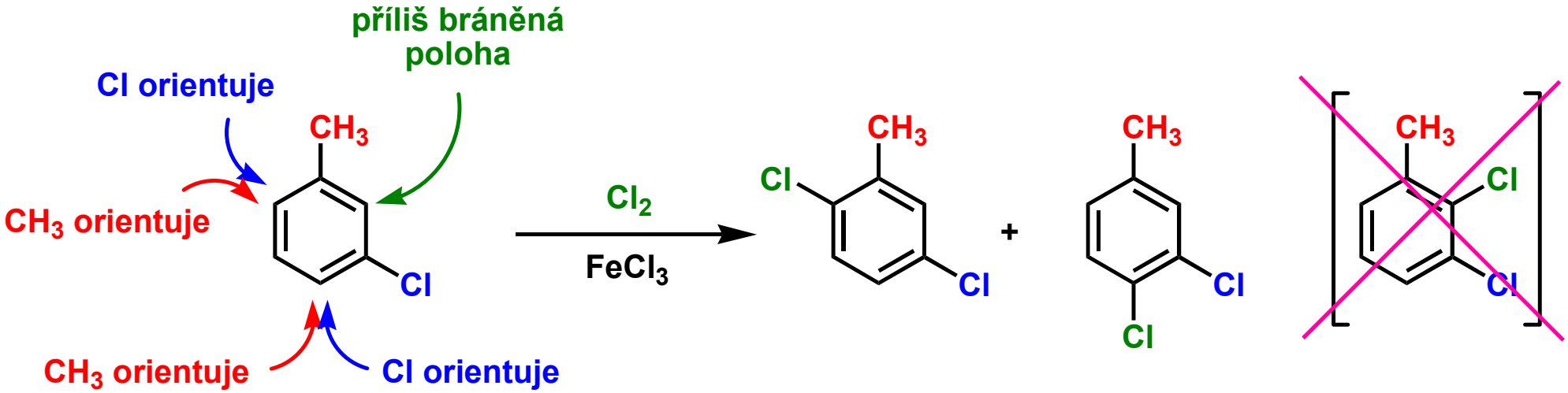
Substituent	Reactivity	Orienting effect	Inductive effect	Resonance effect
$-CH_3$	Activating	Ortho, para	Weak donating	—
$-OH$, $-NH_2$	Activating	Ortho, para	Weak withdrawing	Strong donating
$-F$, $-Cl$ $-Br$, $-I$	Deactivating	Ortho, para	Strong withdrawing	Weak donating
$-NO_2$, $-CN$, $-CHO$, $-CO_2R$ $-COR$, $-CO_2H$	Deactivating	Meta	Strong withdrawing	Strong withdrawing

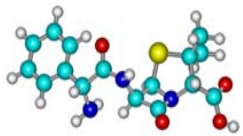
Chemie benzenu: elektrofilní aromatická substituce
Aditivita efektů



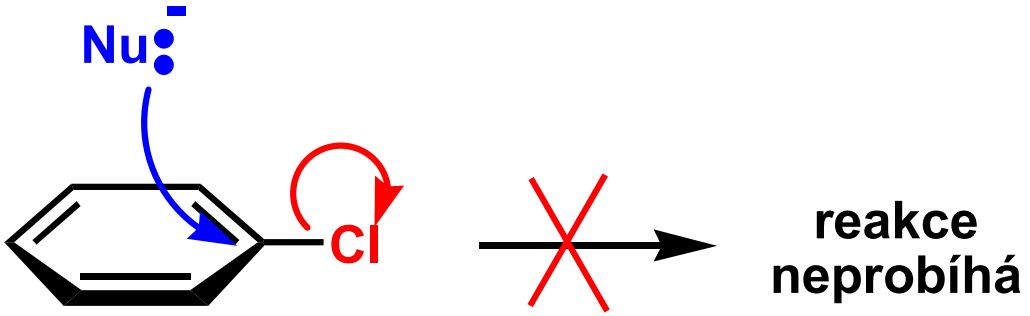


Chemie benzenu: elektrofilní aromatická substituce
Aditivita efektů



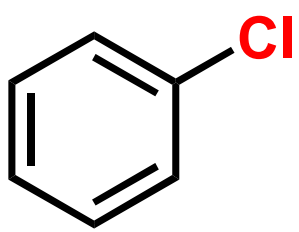


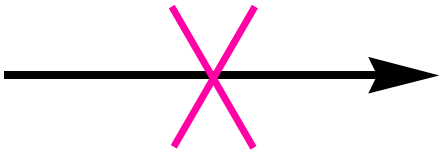
Chemie benzenu: nukleofilní aromatická substituce

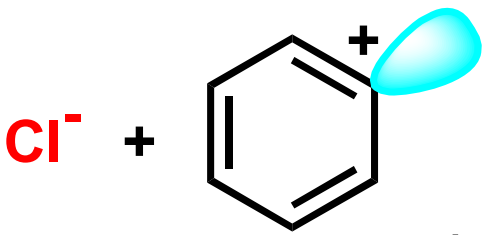


reakce neprobíhá

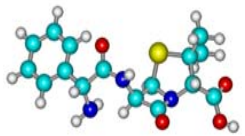
arylhalogenid



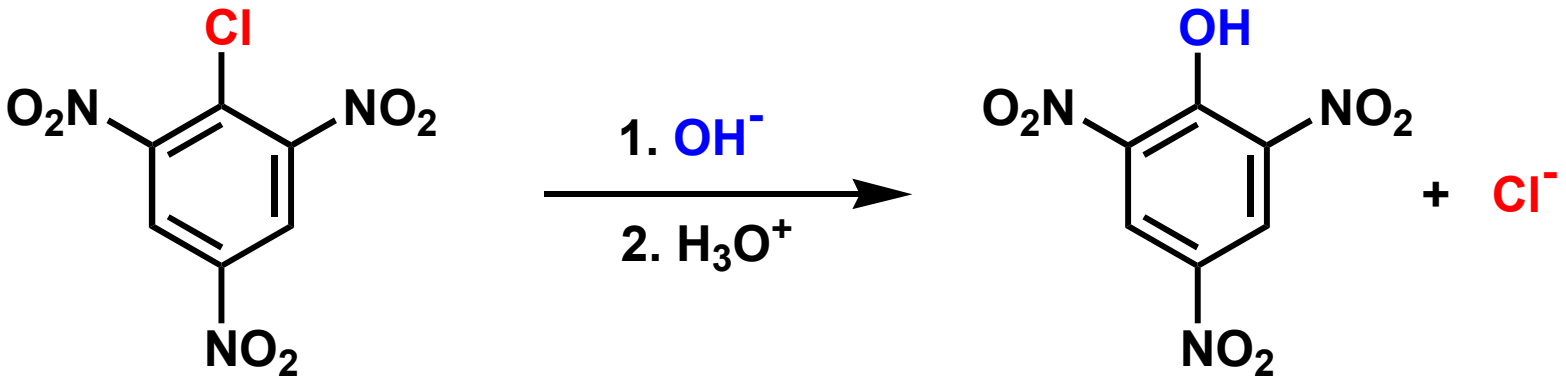




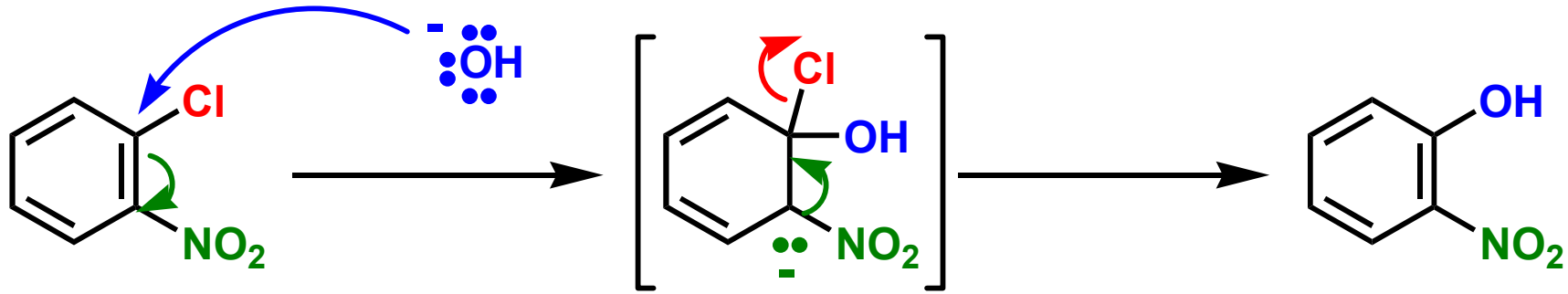
orbital sp^2
(nestabilní kation)



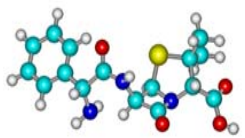
Chemie benzenu: nukleofilní aromatická substituce



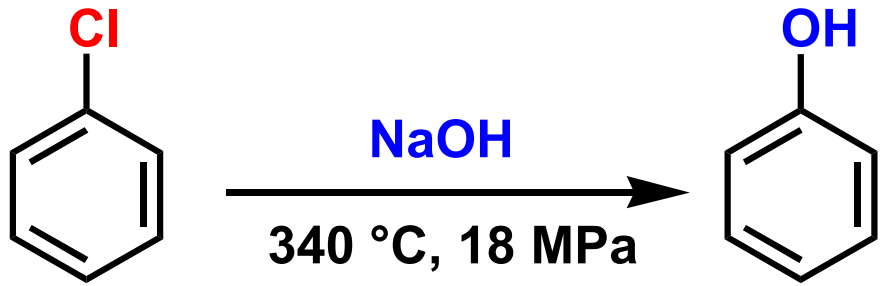
- mechanizmus **adičně – eliminační**: vznik **Meisenheimerova aduktu**



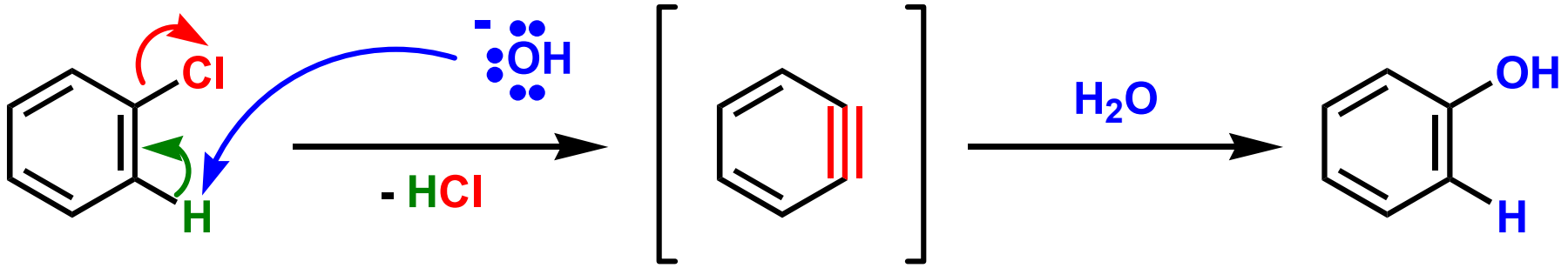
- stabilizace **karbanionu** nitroskupinou (v ***ortho-*** a ***para-*** poloze)
- k stabilizaci v ***meta-*** poloze nedochází!



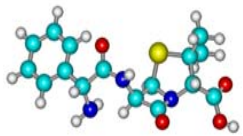
Chemie benzenu: nukleofilní aromatická substituce



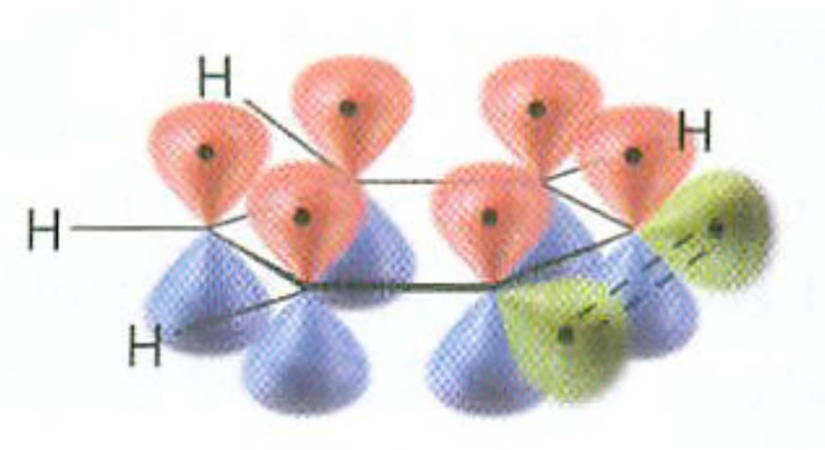
- mechanizmus **eliminačně – adiční**: vznik **benzynu (1,2-dehydrobenzenu)**



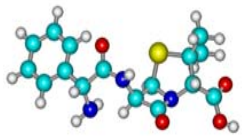
benzyn



Chemie benzenu: nukleofilní aromatická substituce



benzyn

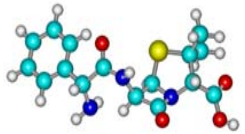


Chemie benzenu: nukleofilní aromatická substituce

Nukleofilní aromatická substituce – pouze substrát se silně elektronakceptorní skupinou (nejlépe více) a pouze:

- mechanizmem **adičně – eliminačním**: vznik **Meisenheimerova aduktu**

- mechanizmem **eliminačně – adičním**: vznik **benzynu (1,2-dehydrobenzenu)**



Chemie benzenu: oxidace postranních řetězců alkylbenzenů

Samostudium: str. 555 – 557

Chemie benzenu: redukce aromatických sloučenin

Samostudium: str. 558 – 559