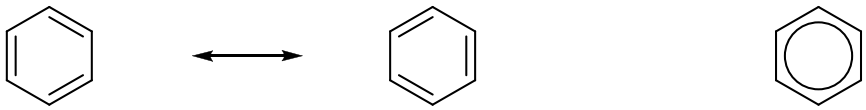
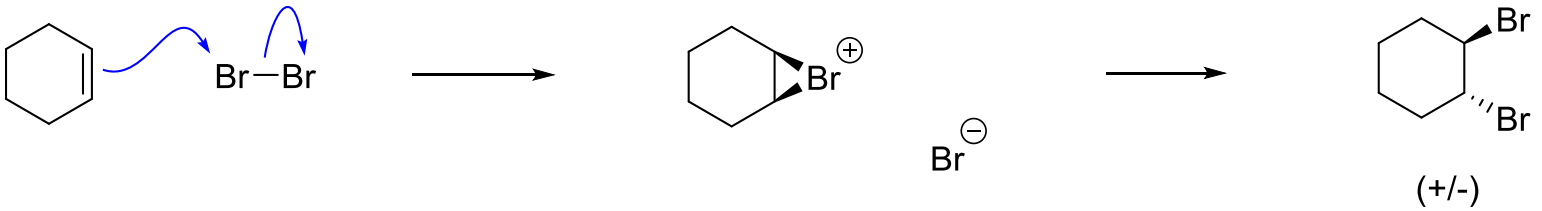
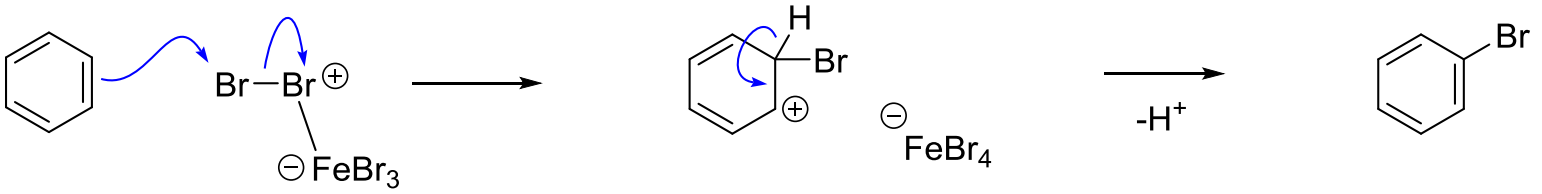
ELEKTROFILNÍ AROMATICKÁ SUBSTITUCE



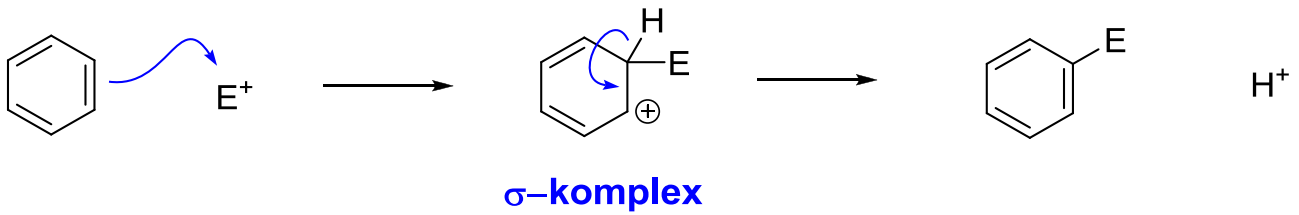
Elektrofilní adice A_E

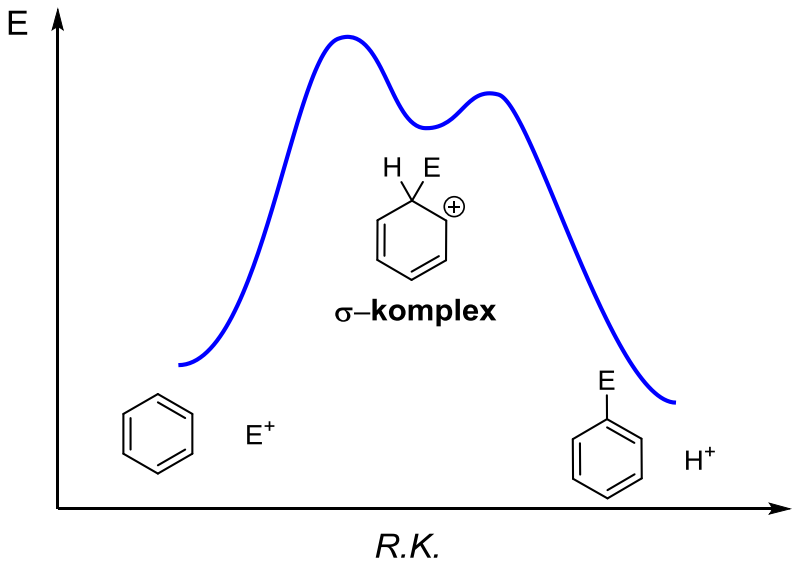


Elektrofilní aromatická substituce S_EAr



MECHANISMUS S_EAr

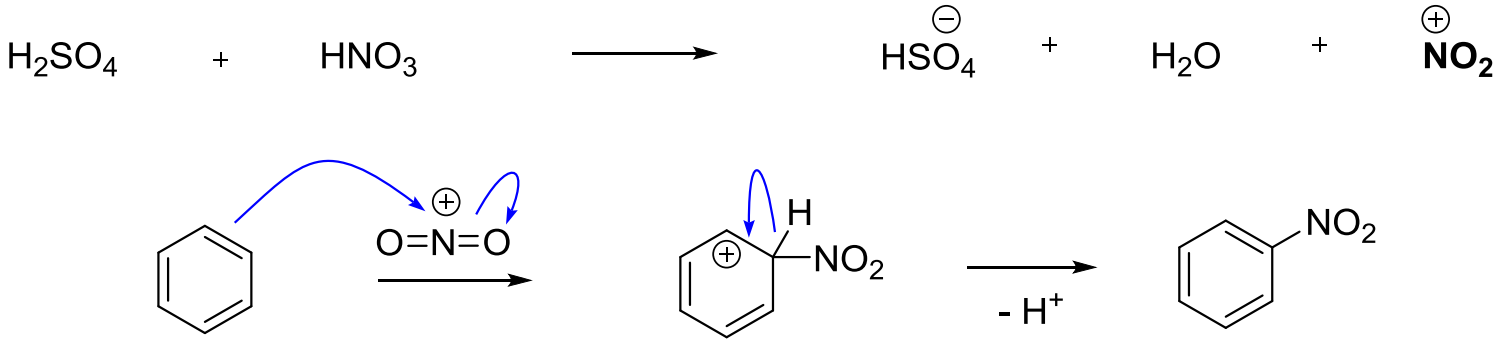




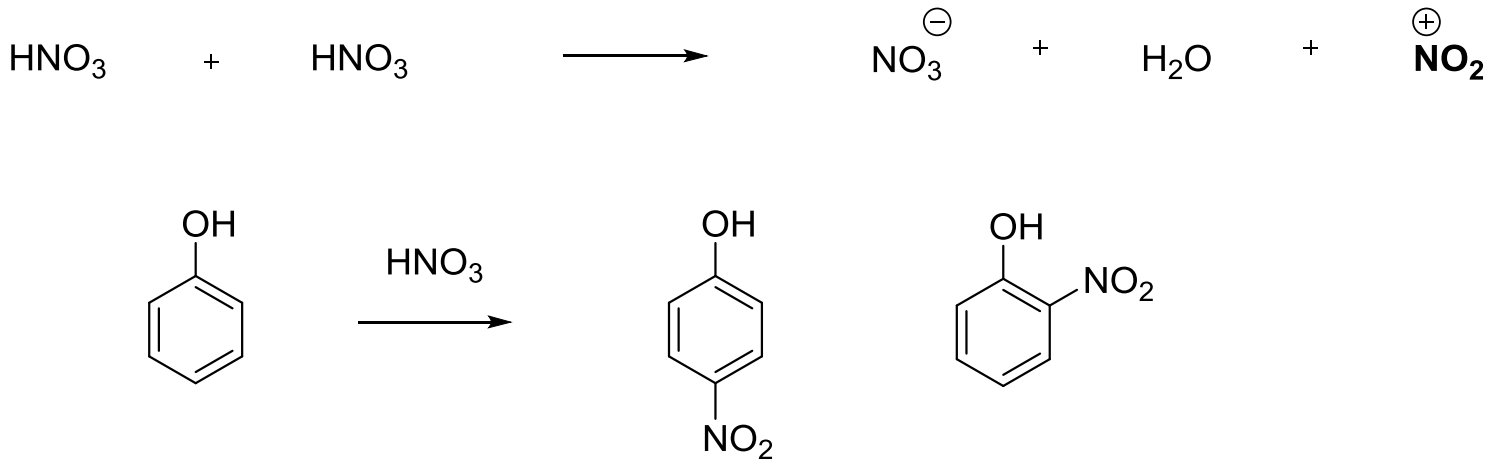
ELEKTROFILY

Nitrace (NO_2^+)

nitrační směs

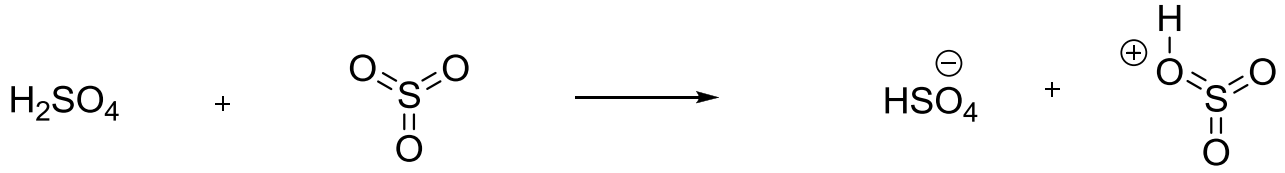


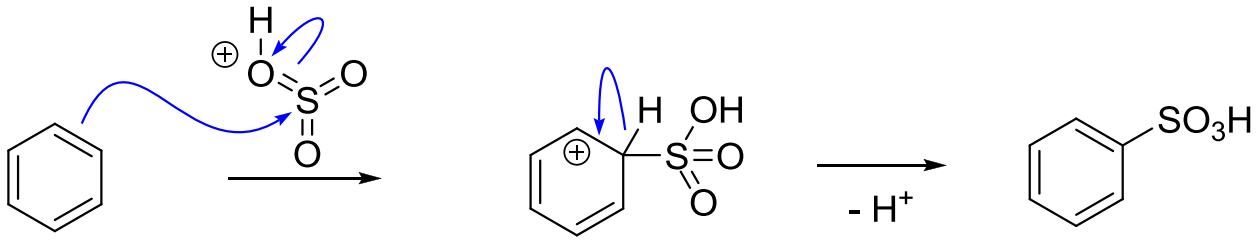
k nitraci aktivovaných aromátů stačí samotná HNO_3

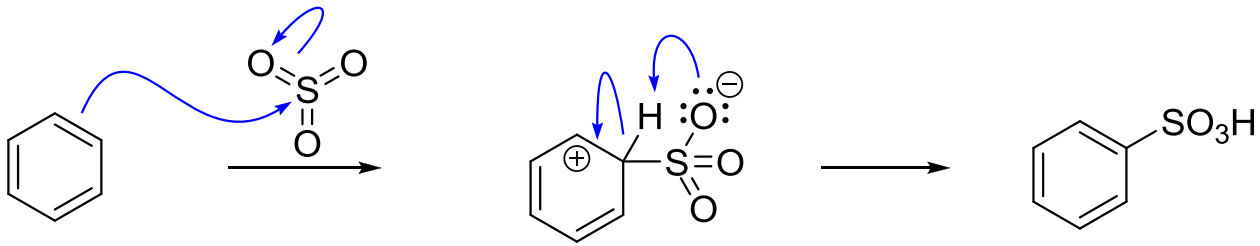


ELEKTROFILY

Sulfonace (SO_3H^+ nebo SO_3)

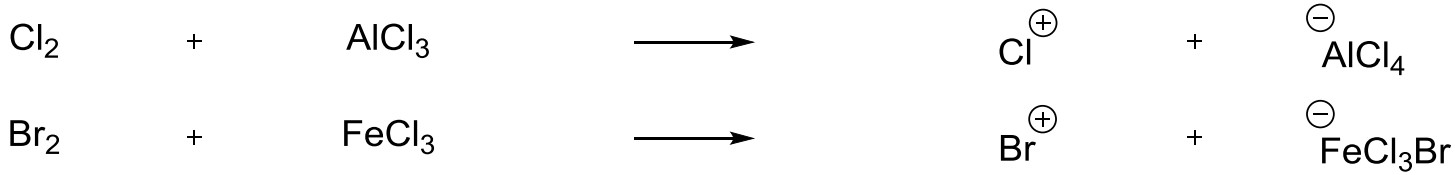


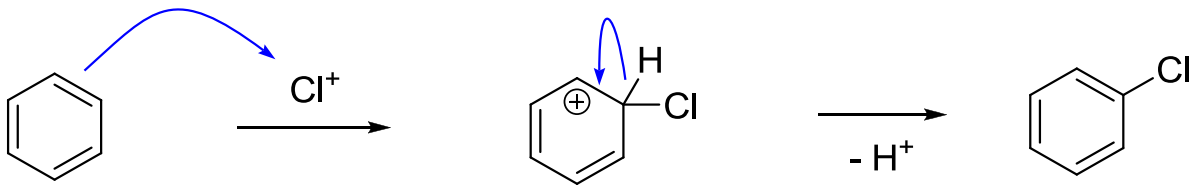




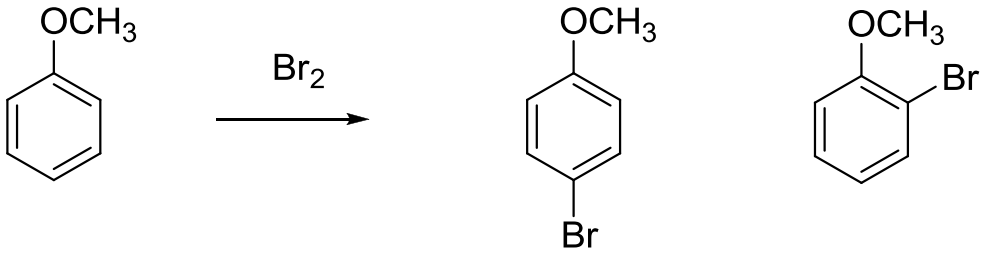
ELEKTROFILY

Halogenace (X^+)



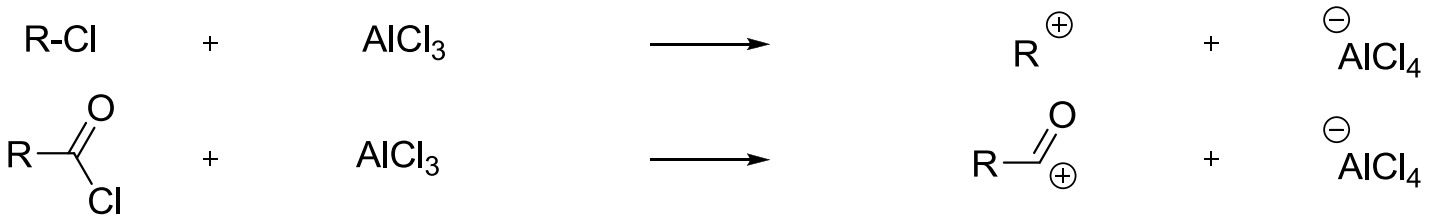


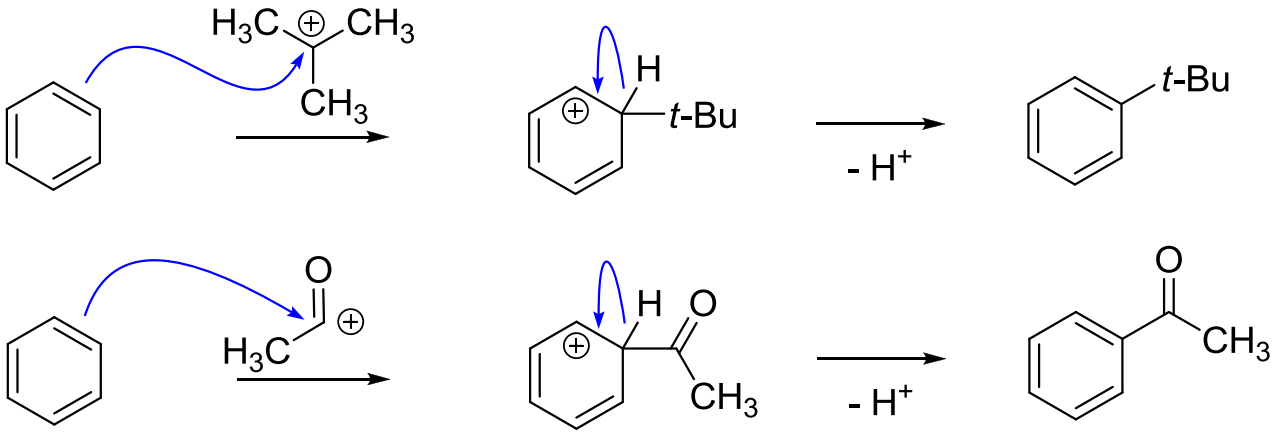
k halogenaci aktivovaných aromátů stačí X_2



ELEKTROFILY

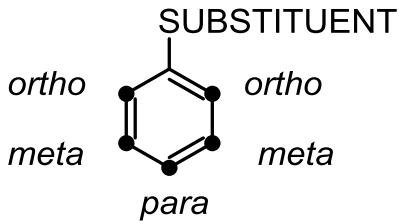
Friedelova-Craftsova alkylace a acylace (R^+ a $R-C\equiv O^+$)



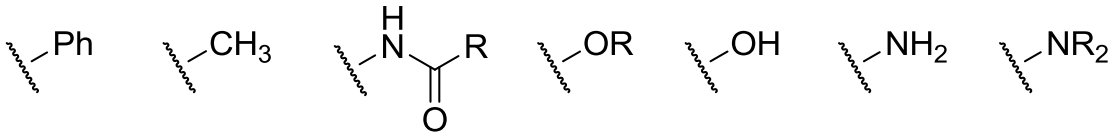


další generace karbokationtu:

REGIOSELEKTIVITA S_EAr U SUBSTITUOVANÝCH BENZENŮ



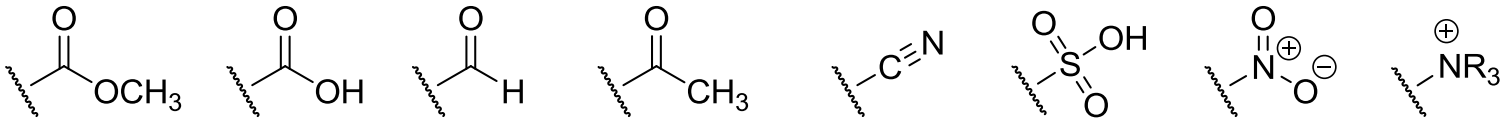
Aktivující: zvyšují rychlost S_EAr ve srovnání s benzenem
***ortho, para*-orientující**



slabě aktivující — silně aktivující

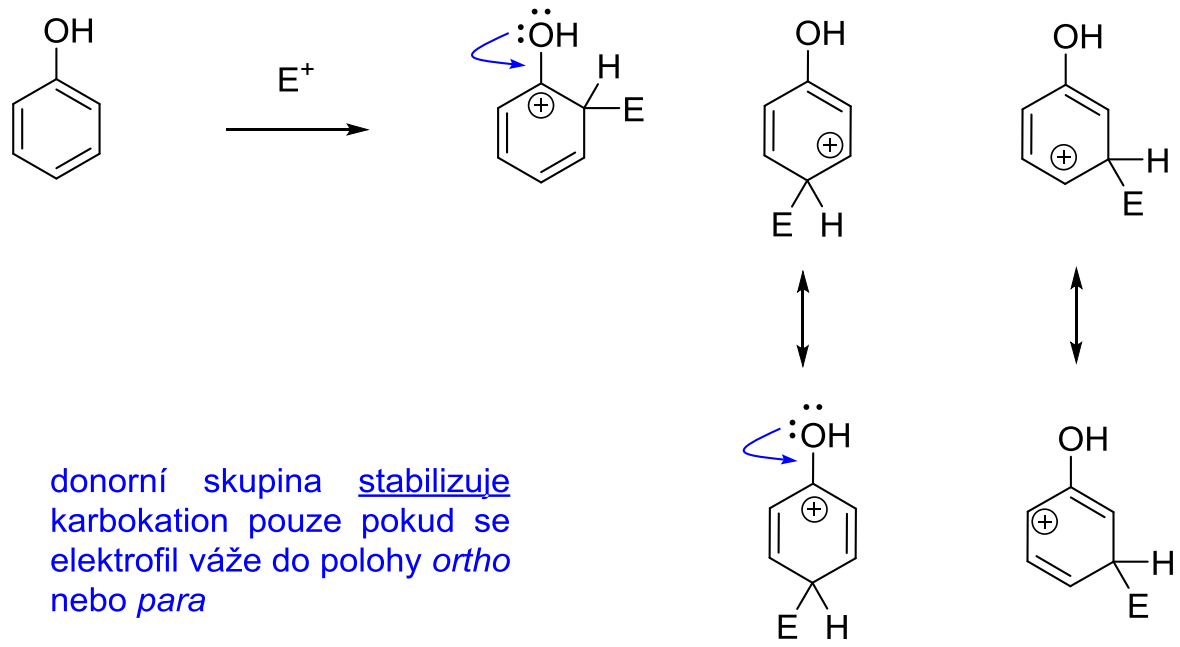
Deaktivující: snižují rychlost S_EAr ve srovnání s benzenem
***ortho, para*-orientující**

Deaktivující: snižují rychlost S_EAr ve srovnání s benzenem
***meta*-orientující**



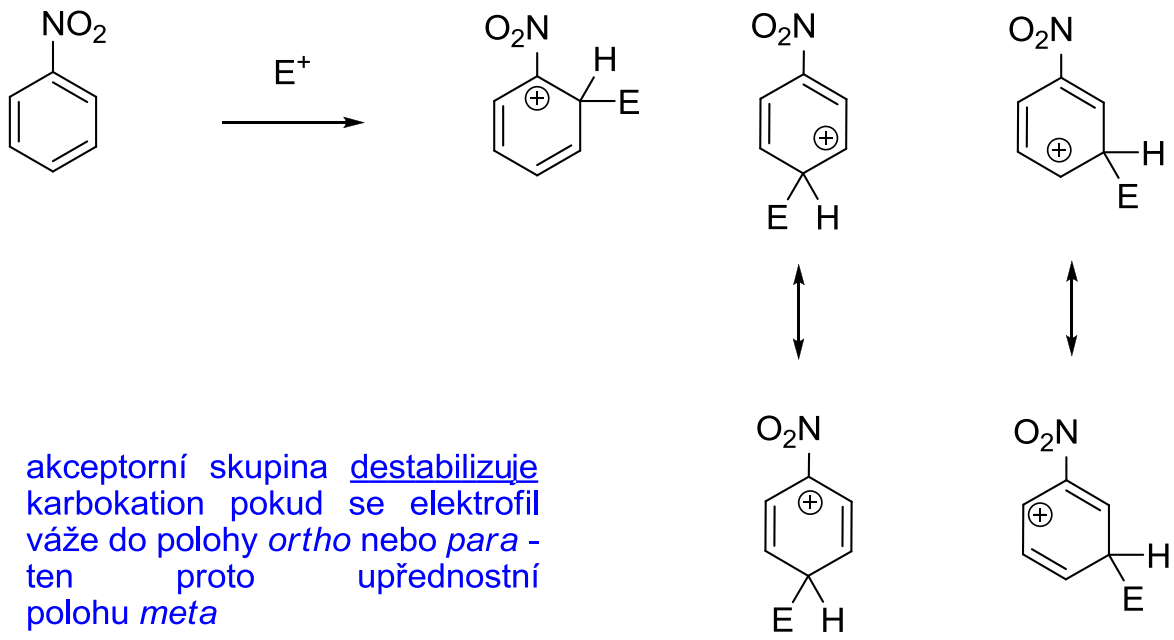
silně deaktivující

REGIOSELEKTIVITA S_EAr U SUBSTITUOVANÝCH BENZENŮ
DONORNÍ SKUPINY



donorní skupina stabilizuje karbokation pouze pokud se elektrofil váže do polohy *ortho* nebo *para*

REGIOSELEKTIVITA S_EAr U SUBSTITUOVANÝCH BENZENŮ
AKCEOPTORNÍ SKUPINY

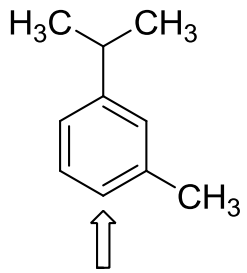


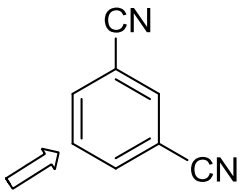
akceptorní skupina destabilizuje karbokation pokud se elektrofil váže do polohy *ortho* nebo *para* - ten proto upřednostní polohu *meta*

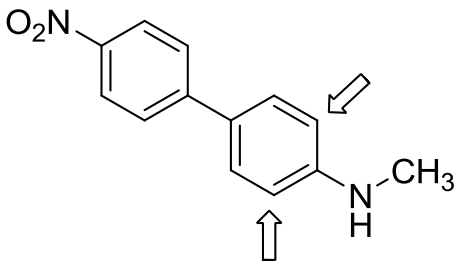
REGIOSELEKTIVITA S_EAr U SUBSTITUOVANÝCH BENZENŮ
VÍCE SUBSTITUENTŮ

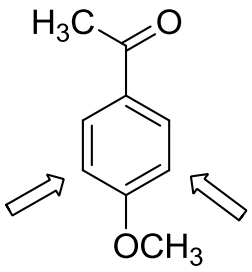
Kam bude útočit elektrofil?

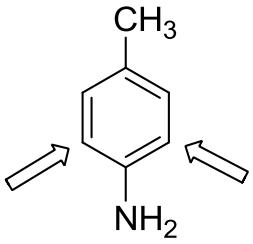
efekt donoru je výraznější

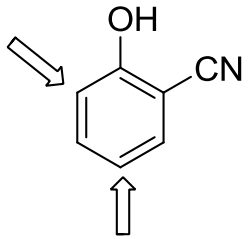


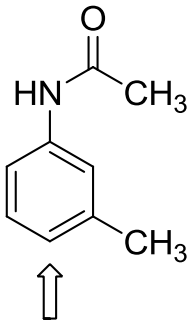




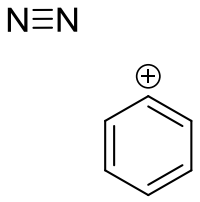


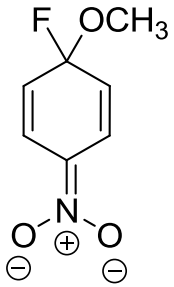


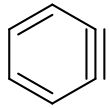




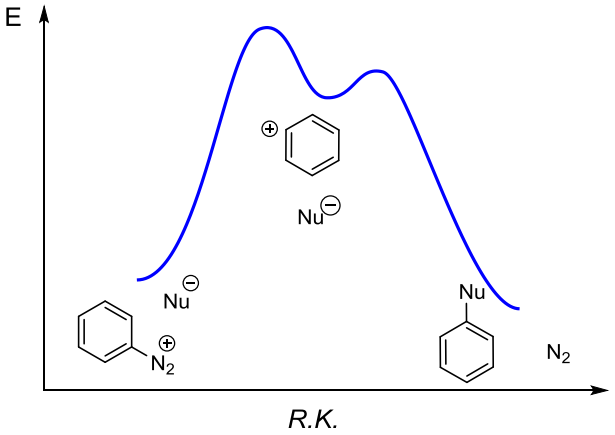
NUKLEOFILNÍ AROMATICKÁ SUBSTITUCE







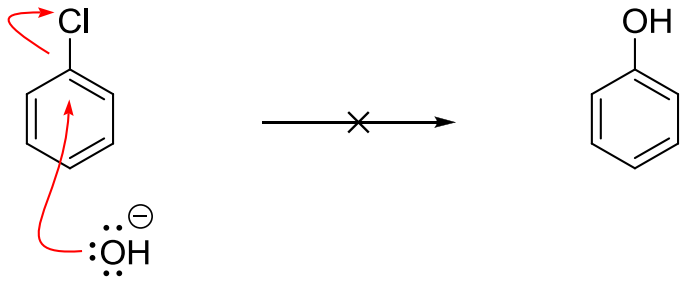
S_N1Ar

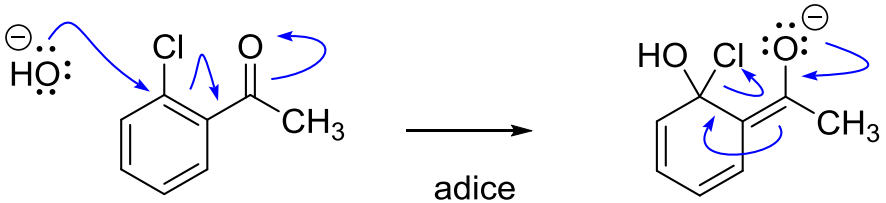


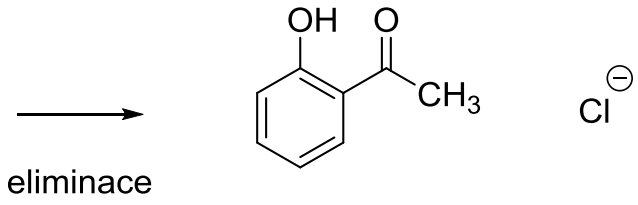
Sandmeyerova reakce (radikálový mechanismus): zdrojem nukleofilu jsou meďné (Cu^{+I})soli.

Na podobu produktů to nemá vliv: s CuBr zavádíme bromid, s CuCN zavádíme kyanid,…

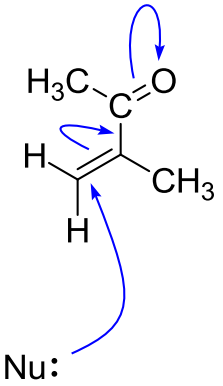
S_N2Ar
Mechanismus Adičně-Eliminační



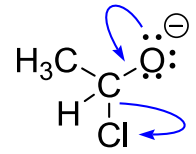




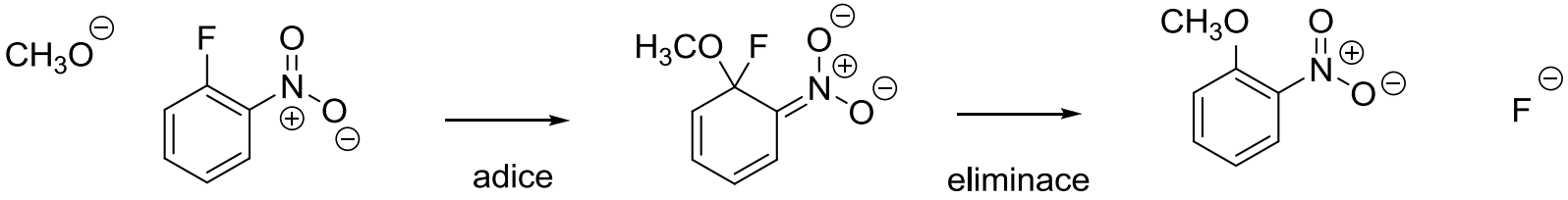
α,β–NENASYCENÝ KARBONYL
1,4-adice



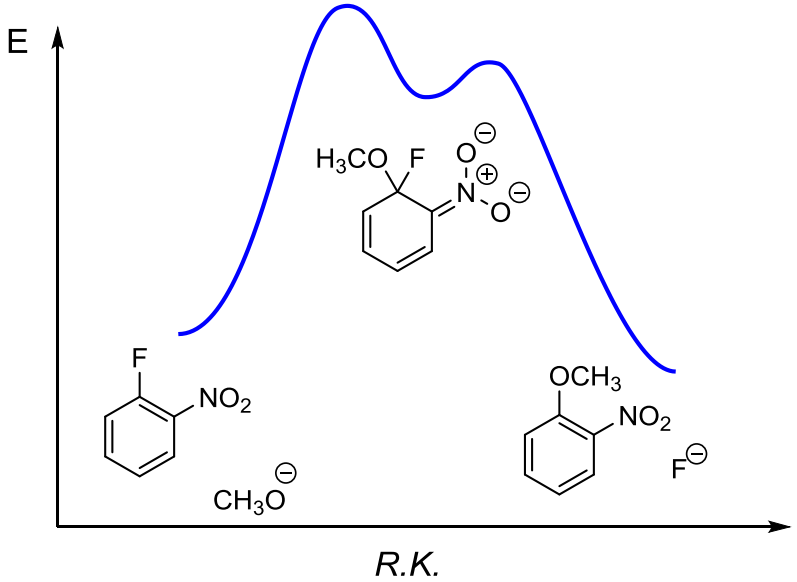
chlorid kyseliny
nukleofilní substituce na karbonylu



S_N2Ar
Mechanismus Adičně-Eliminační

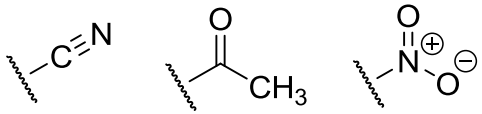


Meisenheimerův komplex



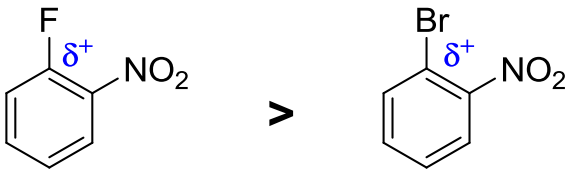
S_N2Ar
Mechanismus Adičně-Eliminační

• vyžaduje přítomnost akceptorních skupin v *ortho* nebo *para* poloze (vůči odstupující skupině), nejlépe v obou
• vyžaduje přítomnost odstupující skupiny



nejlepší

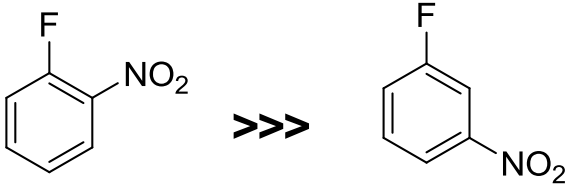
Větší rychlost?



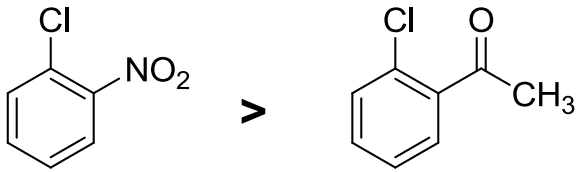
větší δ^+

odstoupení LG není rychlost určující krok

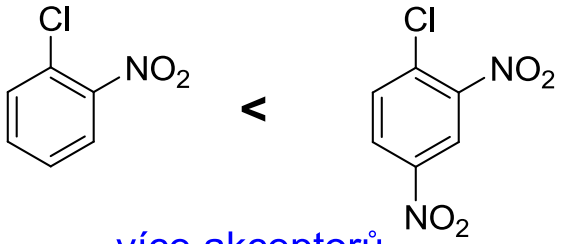
==> kvalita LG nehraje roli



ortho vs. *meta*

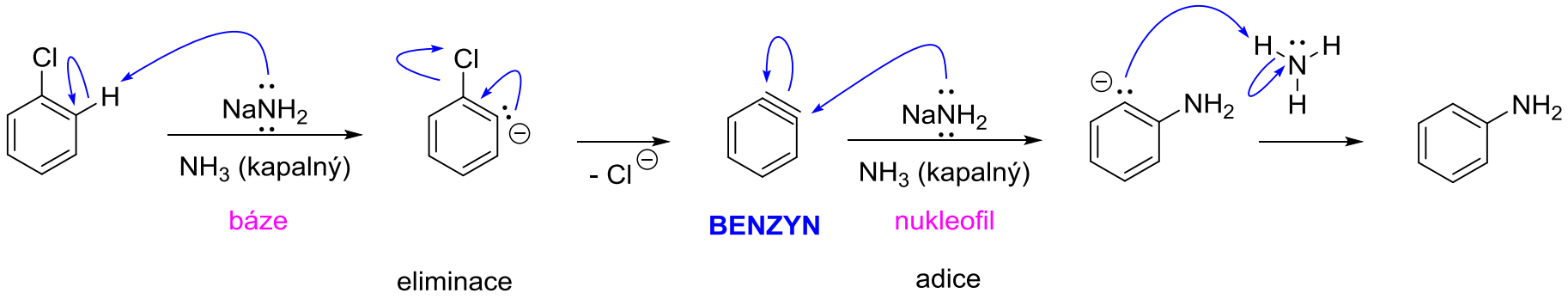


lepší akceptor

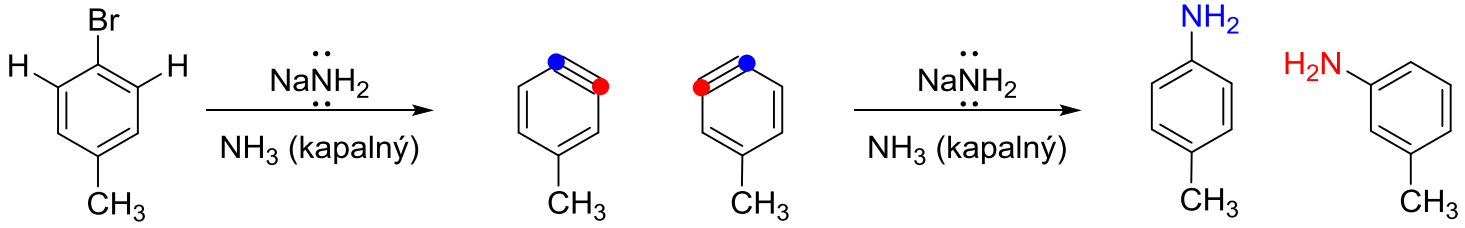


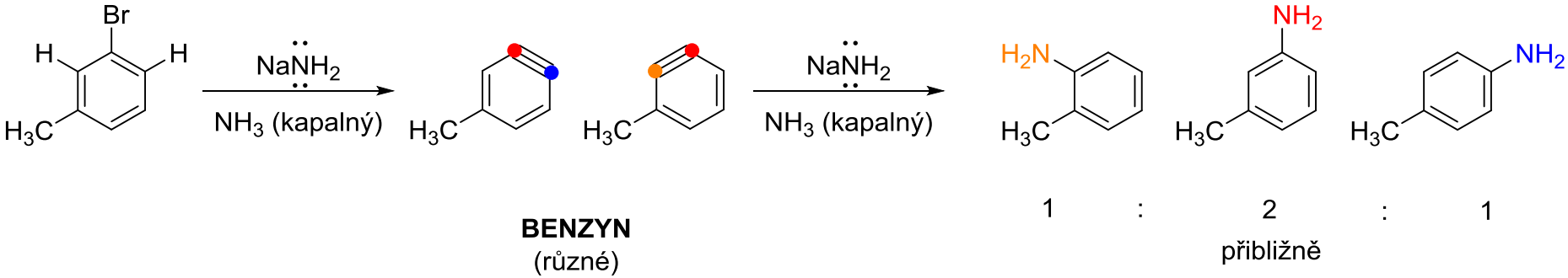
více akceptorů

Benzynový mechanismus
Mechanismus Eliminačně-Adiční



Regioselektivita reakce:





Benzynový mechanismus
Mechanismus Eliminačně-Adiční

Regioselektivita reakce, akceptorní skupina: