TÁMOP-4.1.1.F-14/1/KONV-2015-0006
SZTE TTIK, KTCS, 1a) Duális és moduláris képzésfejlesztés a mesterképzéshez

Nukleofil szubsztitúciós reakciók 4. Aromás nukleofil szubsztitúció

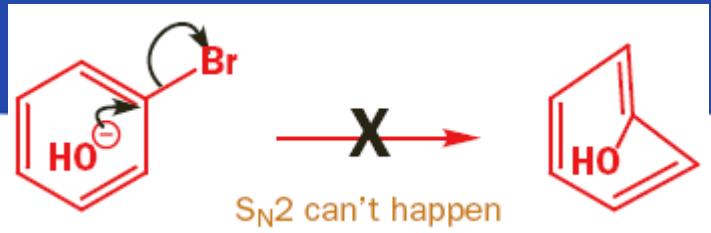
Pálinkó István, egyetemi tanár

SZÉCHENYI 2020
MAGYARORSZÁG KORMÁNYA
Európai Unió
Európai Szociális Alap
BEFEKTETÉS A JÖVŐBE

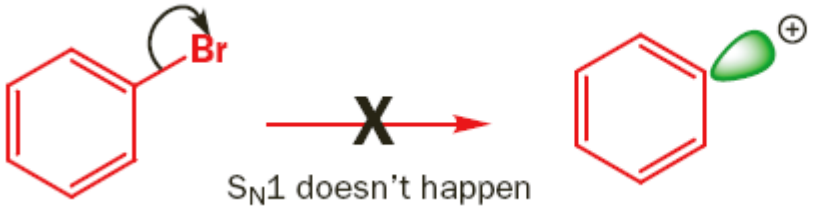
reaction does happen

mechanizmus

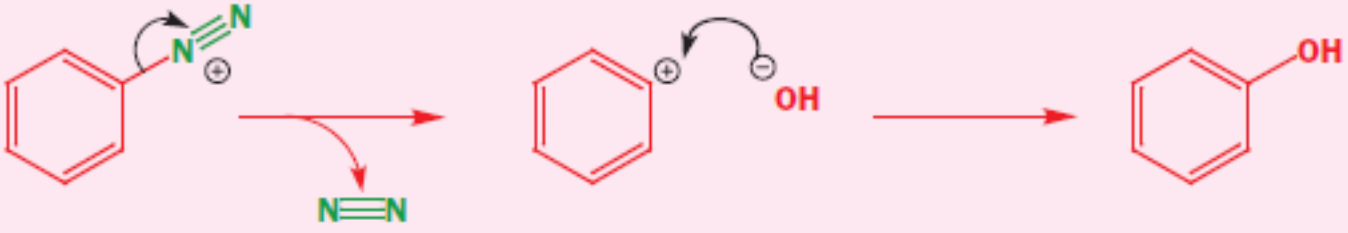
reaction doesn't happen



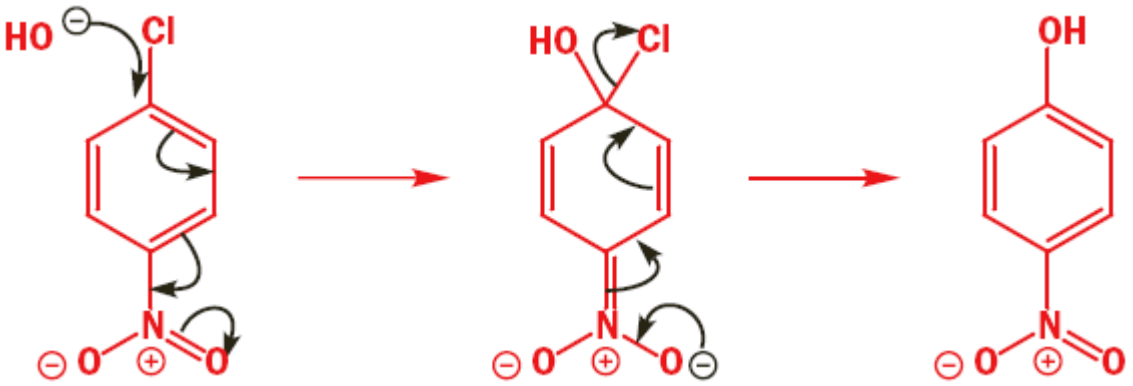
S_N2 at sp^2 C does *not* occur.

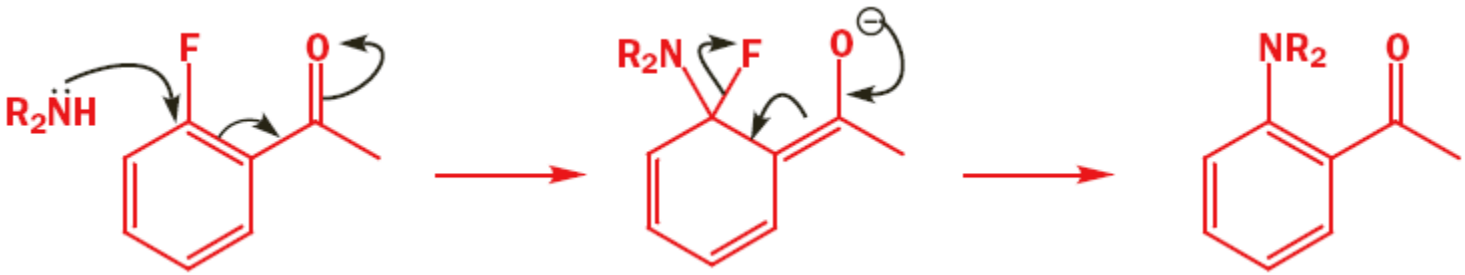


In fact, the mechanism *can* occur, but only with the best leaving group—a molecule of gaseous nitrogen—as we shall see later.



addíciós-eliminációs mechanizmus



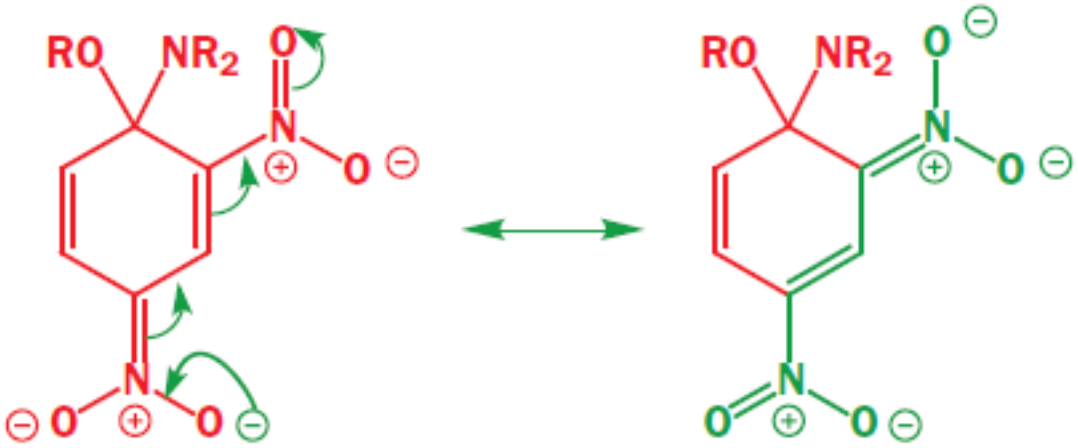


If you try and do the same reaction with a *meta* anion-stabilizing group, it doesn't work. You can't draw the arrows to push the electrons through on to the oxygen atom. Try it yourself.

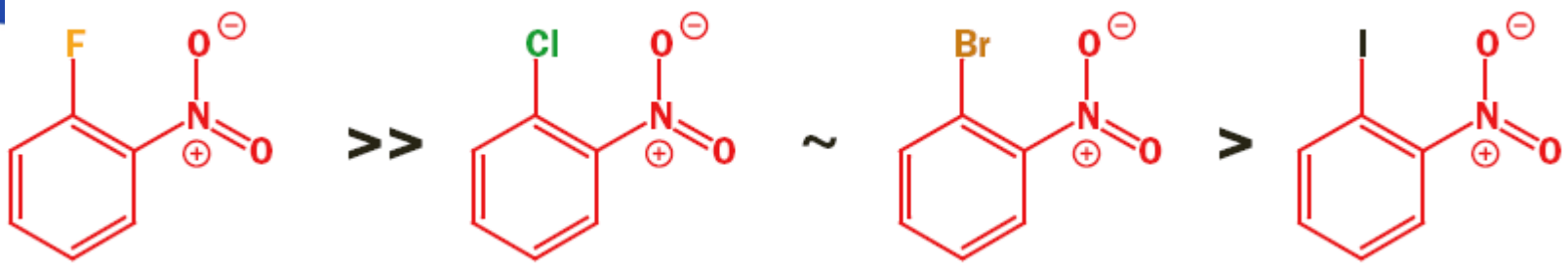
A typical nucleophilic aromatic substitution has:

- an oxygen, nitrogen, or cyanide nucleophile
- a halide for a leaving group
- a carbonyl, nitro, or cyanide group *ortho* or *para* to the leaving group

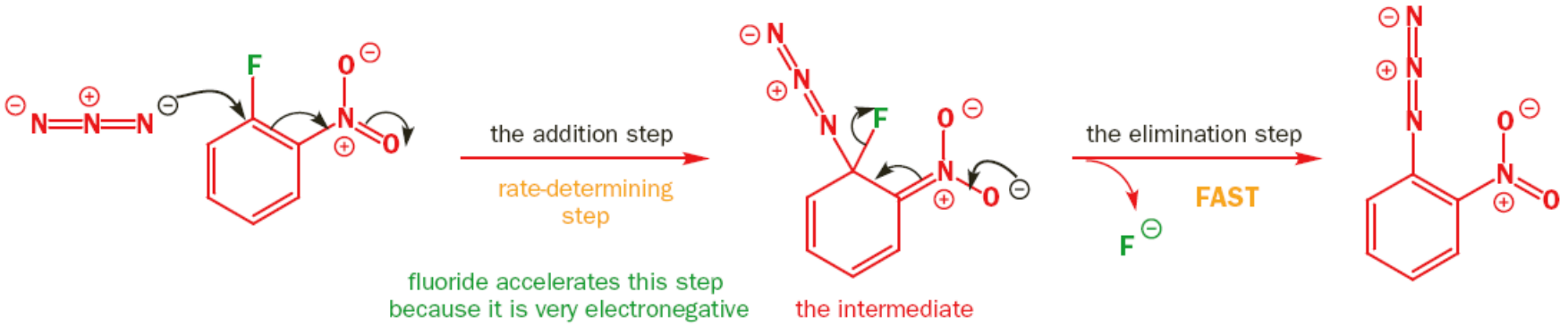
delocalization of the negative charge in the intermediate



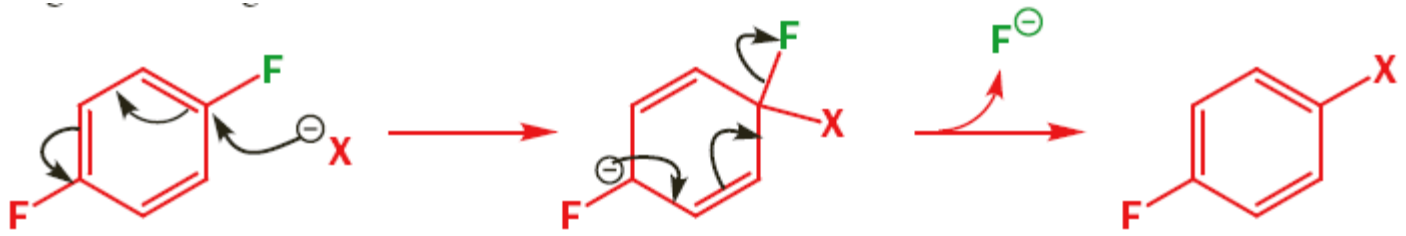
reactivity of 2-halo-1-nitrobenzenes in nucleophilic aromatic substitution



ez megdöbbentő, hiszen nukleofil szubsztitúciós reakciókban, a halogénsorban a fluorid ion a legrosszabb távozó csoport



Fluoride does, in fact, slow down the second step (relative to Cl^-, say), but it accelerates the first step simply by its enormous inductive effect. It is the most electronegative element of all and it stabilizes the anionic intermediate, assisting the acceptance of electrons by the benzene ring.

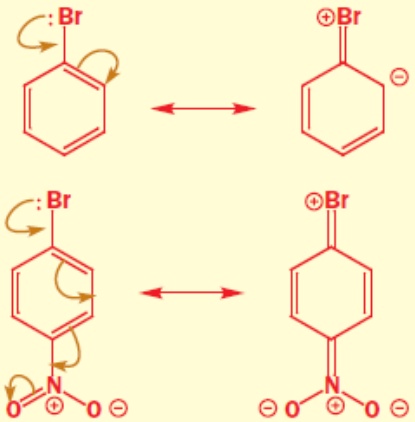


delocalized negative charge
stabilized by two fluorines on ring

Intellectual health warning!

Some textbooks tell you that nucleophilic aromatic substitution doesn't happen with ordinary aryl halides because of conjugation between the lone pairs of the halide and the aromatic system.

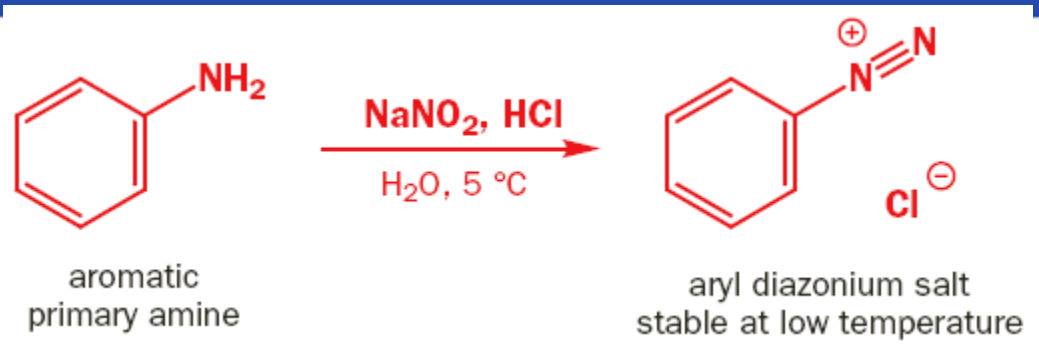
This is supposed to stop the reaction by making the C–Br bond stronger. This is nonsense. The reaction doesn't happen on simple aryl halides because there is no available mechanism. It is easy to show that the false textbook reason is wrong. The conjugation in this nitro compound is much better than in bromobenzene, so it should be even less reactive.

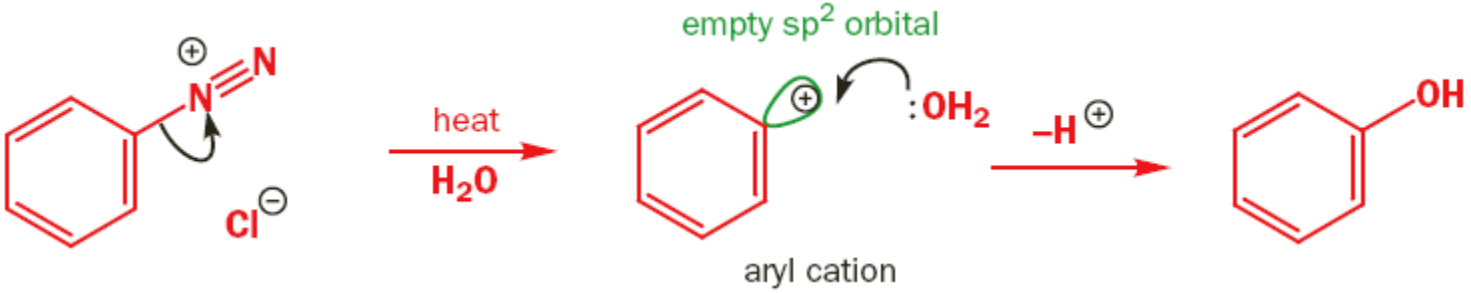


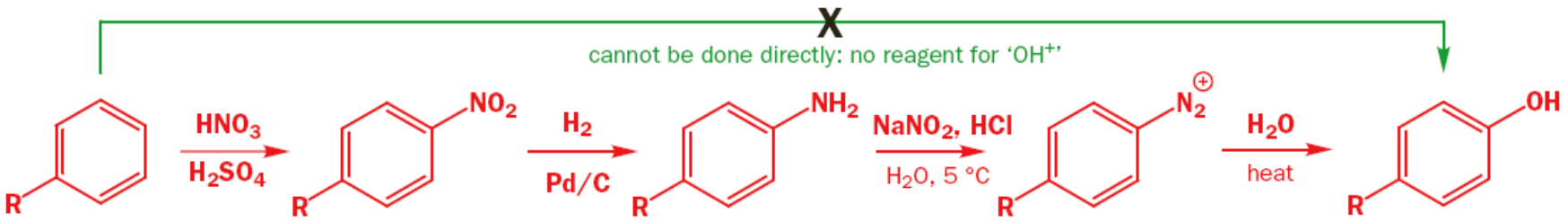
In fact, as you now know, this compound is much *more* reactive towards nucleophiles. The false textbook reason would also suggest that fluoride would work really badly because this same conjugation is stronger with fluoride than with the other halogens as its p orbitals are the right size ($2sp^2$) to conjugate with carbon p orbitals. Again, you already know the opposite to be true.

The strength of the bond to the leaving group does not affect the efficiency of nucleophilic aromatic substitution because that bond is not broken in the rate-determining step. Understand the mechanism and it all becomes clear.

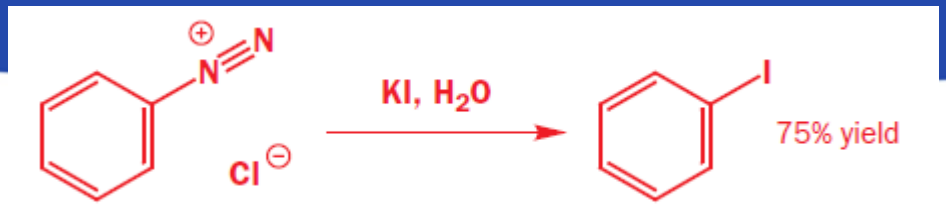
S_N1 mechanizmus

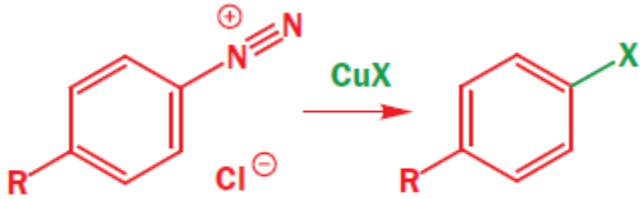


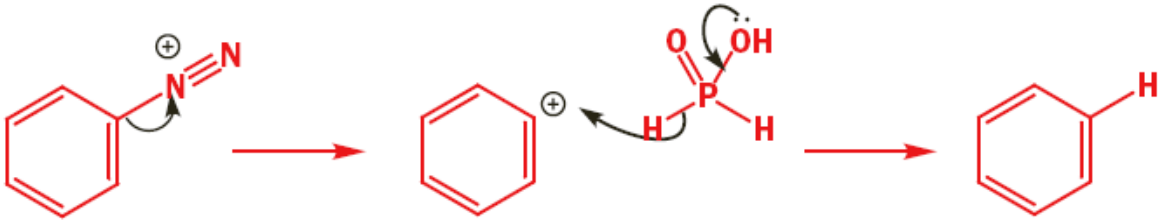



X
cannot be done directly: no reagent for 'OH+'
R
HNO3
H2SO4
NO2
H2
Pd/C
NH2
NaNO2, HCl
H2O, 5 °C
N2
H2O
heat
OH

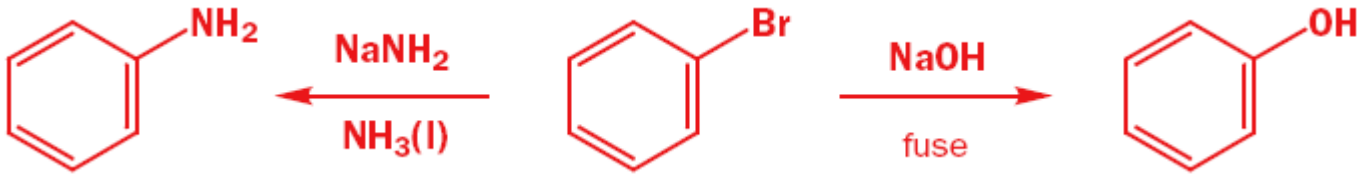
változatok erre a témára – Sandmayer-típusú reakciók



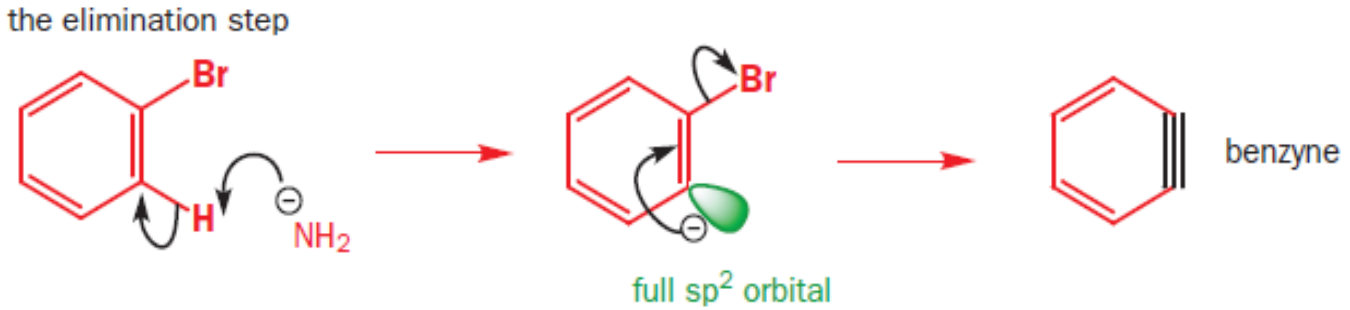


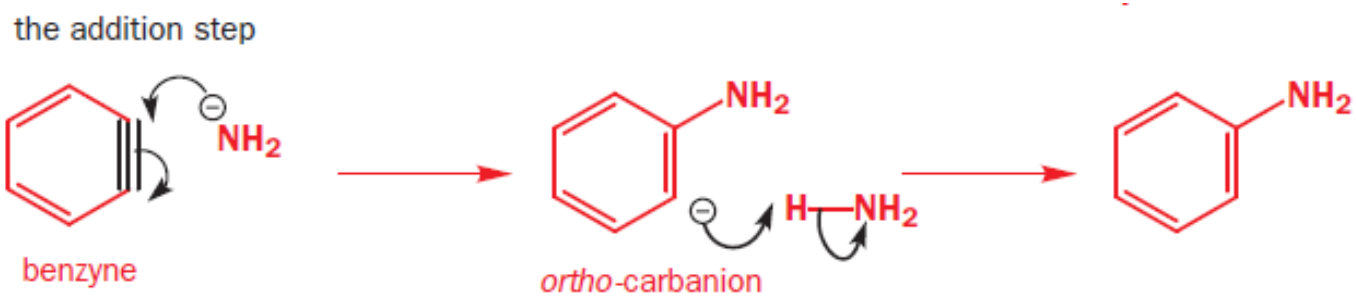


eliminációs-addíciós mechanizmus

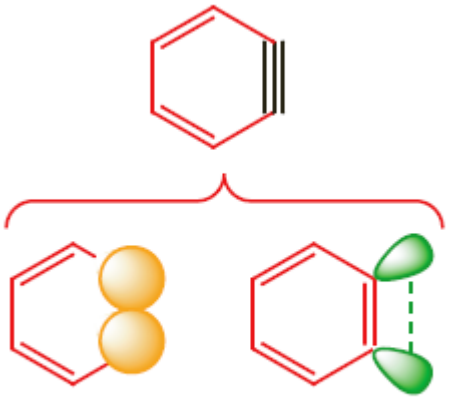


mechanizmus





the π orbitals of benzyne

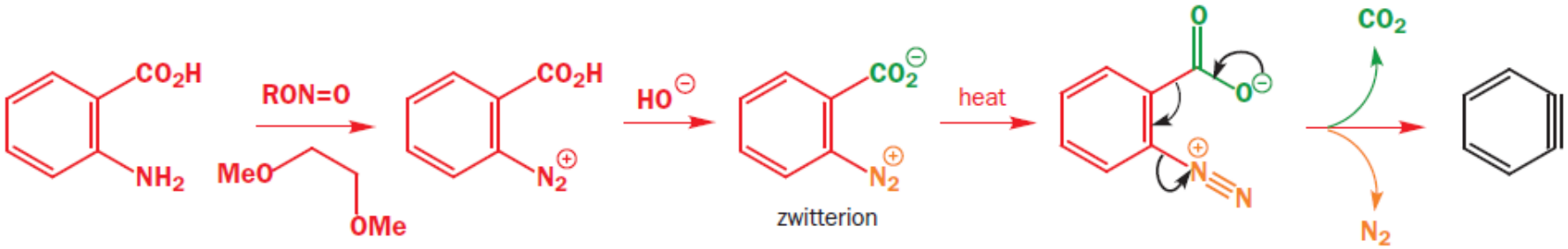


normal π bond
two p orbitals
inside the ring

abnormal π bond
two sp^2 orbitals
outside the ring

benz-in, nem baromság, ilyen állat pedig van

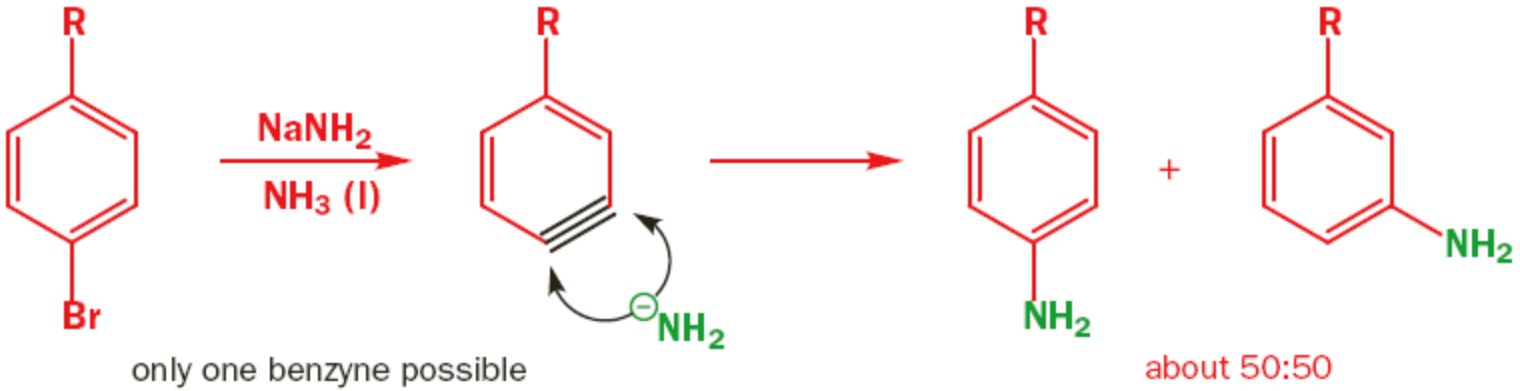
bizonyíték a létezésre



benzyne, *m/e* 76

benzyne dimer, *m/e* 152

bizonyíték arra, hogy a reakció intermedierje



KÖSZÖNÖM A FIGYELMET!

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