

LEC (7)

CHEM 30C

(1)
Nov 4th

(1) DIRECTING-EFFECT SUMMARY

(2) NUCLEOPHILIC AROMATIC SUBSTITUTION

(i) - BENZYNE

(ii) - ADDITION/ELIMINATION

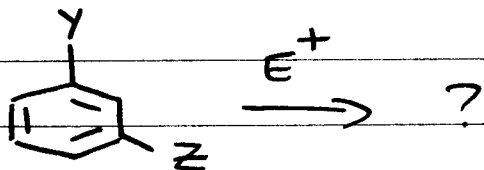
READ: 23.1-23.2 (4th) 20.1-20.2 (3rd)

PROBLEMS: 22.28, 23.43-23.48 (4th)

21.28, 22.42-22.47 (3rd)

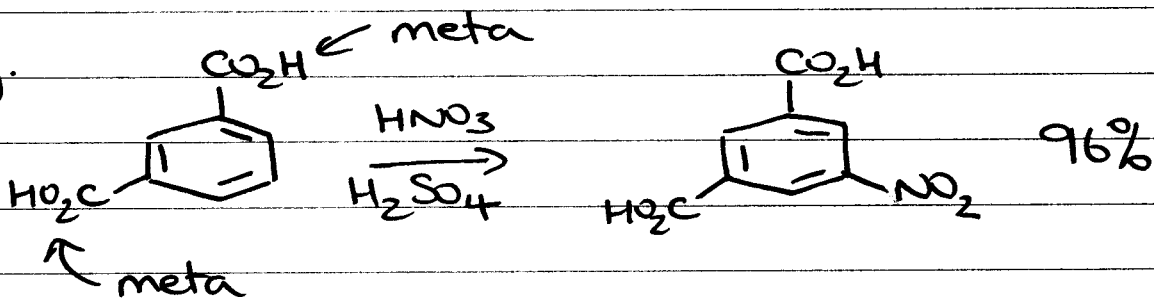
(1) DIRECTING EFFECT SUMMARY

> 1 DIRECTING GROUP

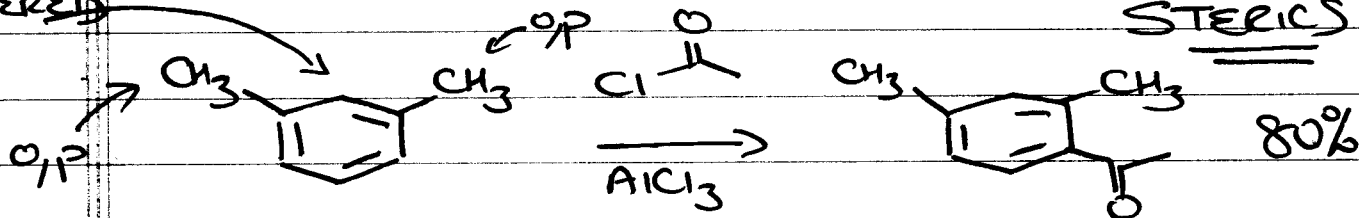


+ Y/Z same directing pref

e.g.

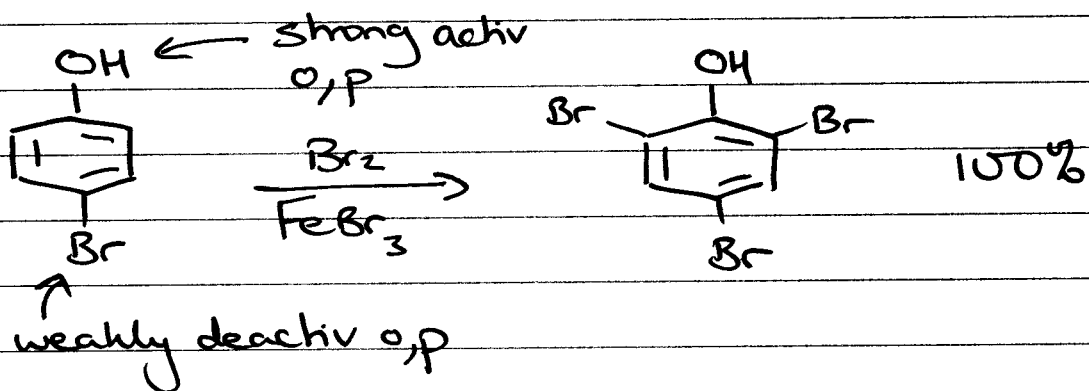


TOO
HINDERED

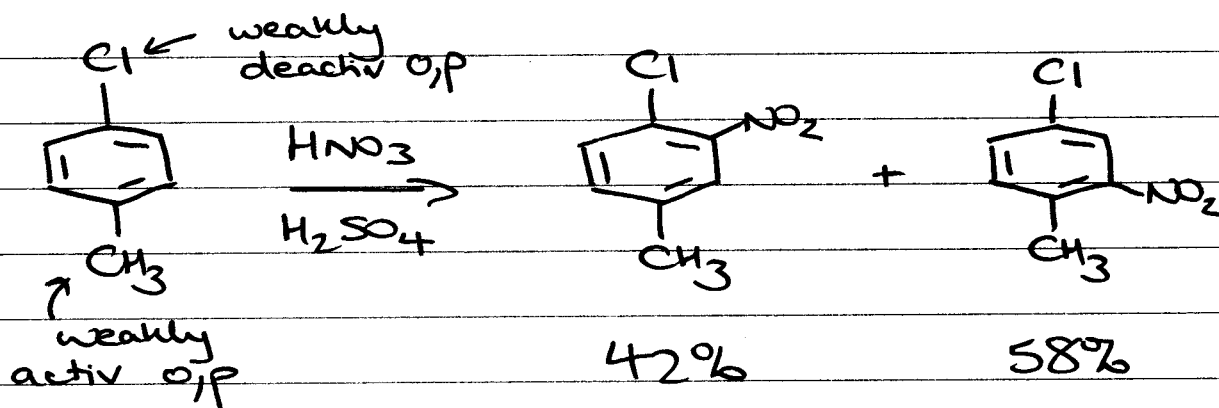


- Y/Z different directing pref

Y > Z, then Y will dominate

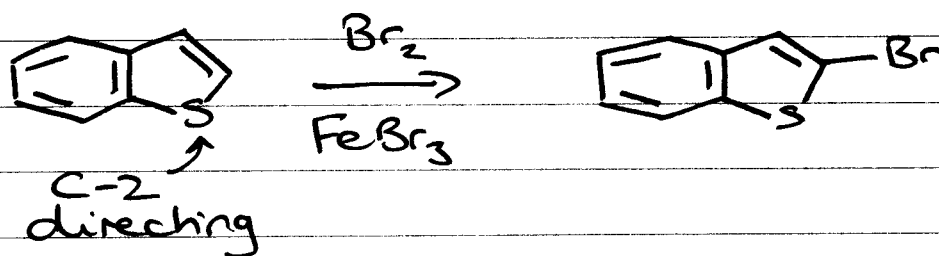


- Y ≈ Z, mixture of products

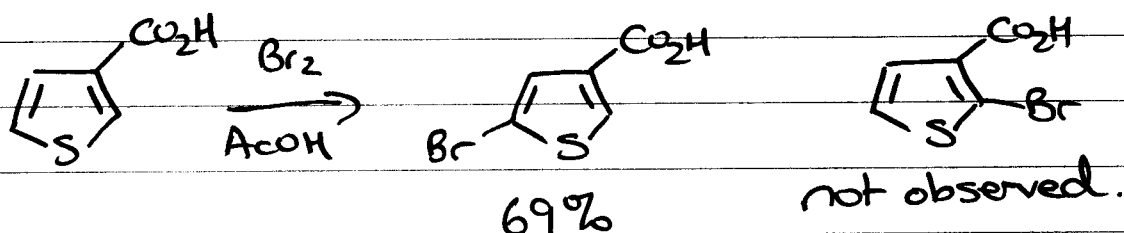
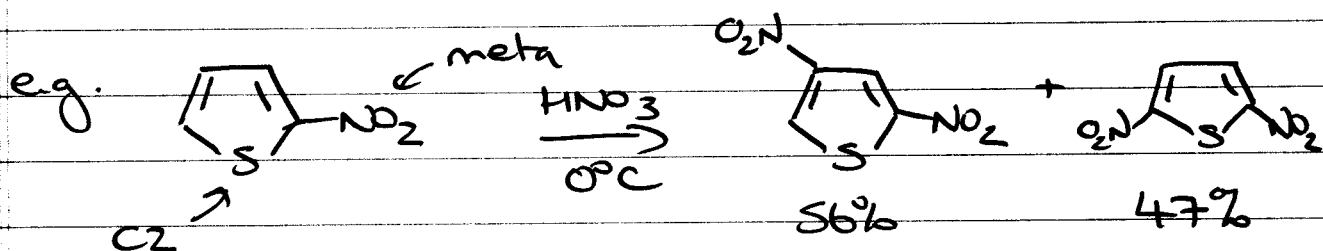


- Two DIFFERENT RINGS

Substitution occurs on more active ring
(pyrrole > furan > thiophene > benzene)

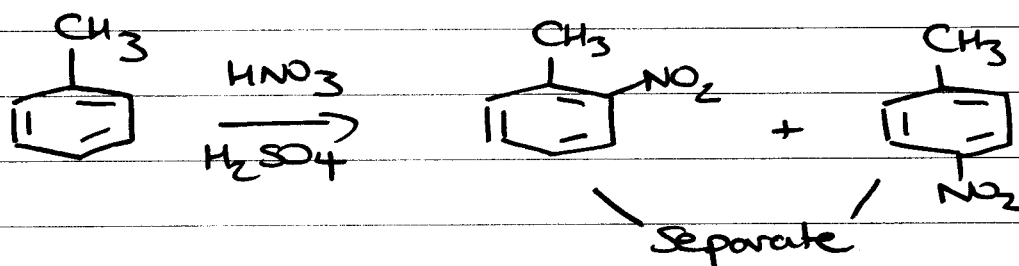


- Heterocycles, heteroatom as well as groups are directing



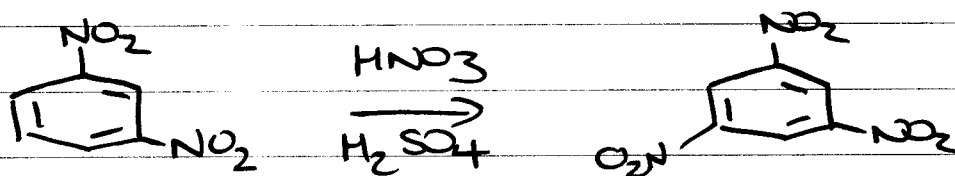
- OTHER ASSUMPTIONS YOU CAN MAKE FOR SYNTHESIS PROBLEMS

(i) SEPARATE ISOMERS

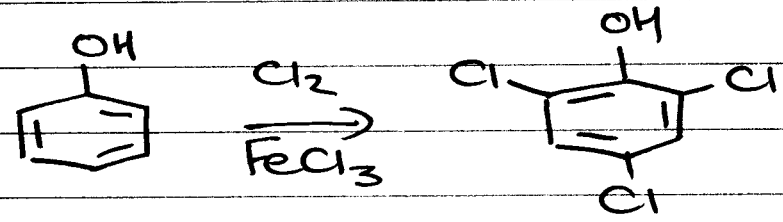


(ii) MULTIPLE SUBSTITUTION

(even if deactivating, reaction can be forced under vigorous conditions)

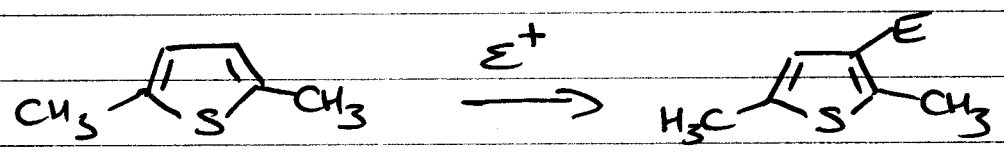


- especially when you have a strong activating group on ring:

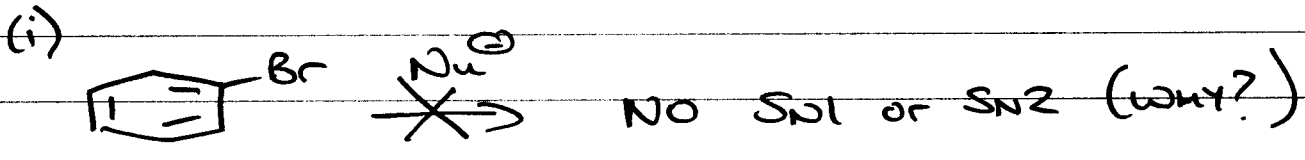


(iii) HETEROCYCLES

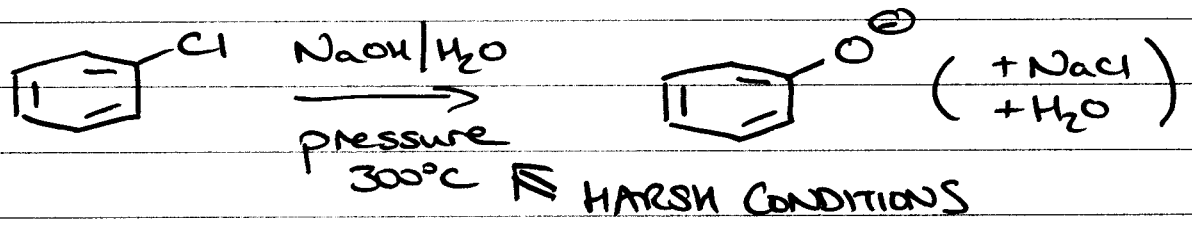
if position 2 is taken, will go to position 3



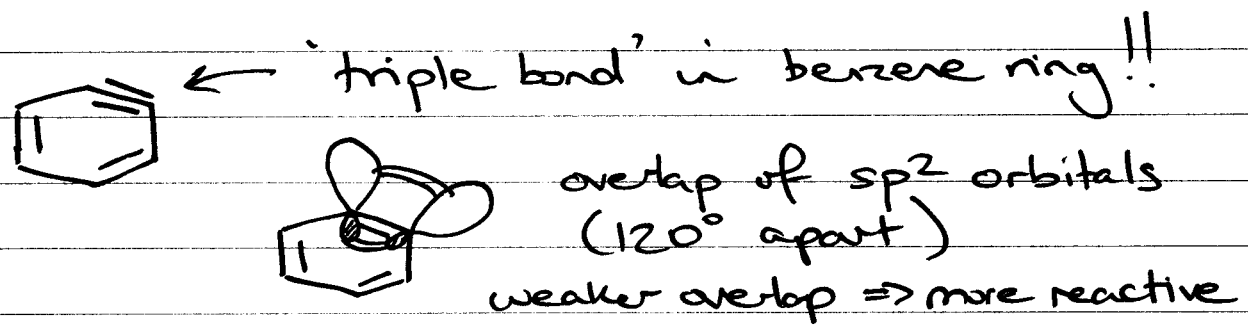
② NUCLEOPHILIC AROMATIC SUBSTITUTION



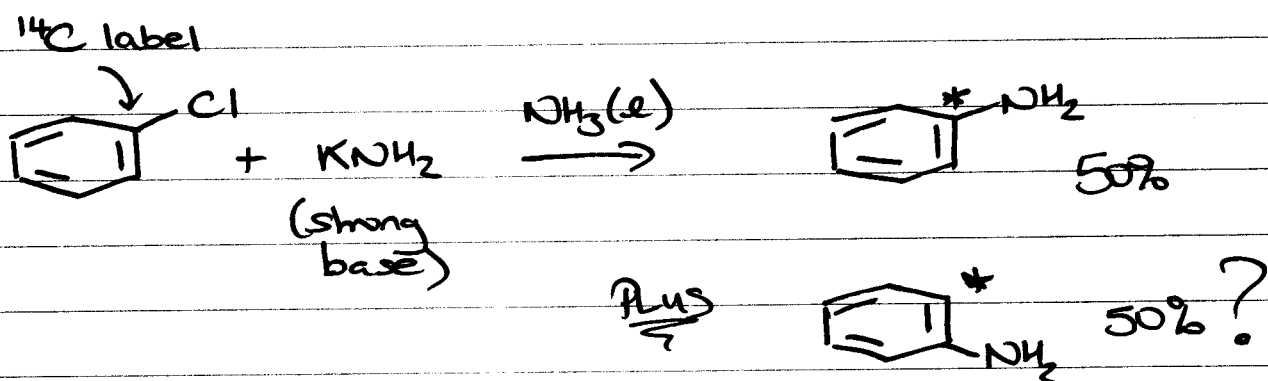
BUT



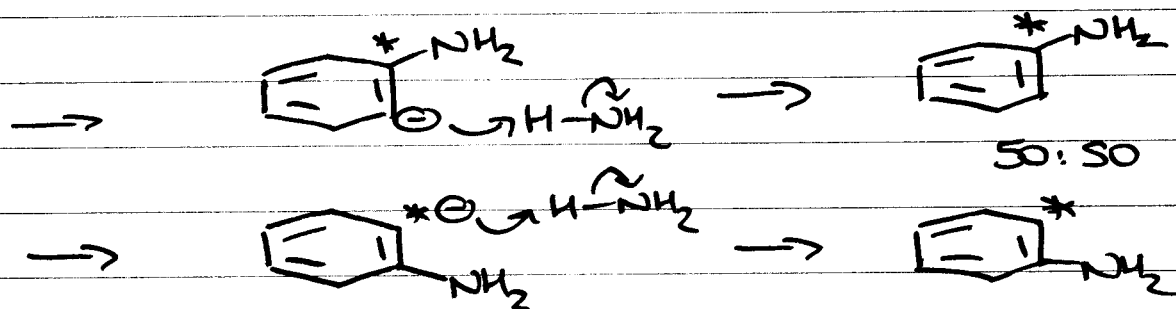
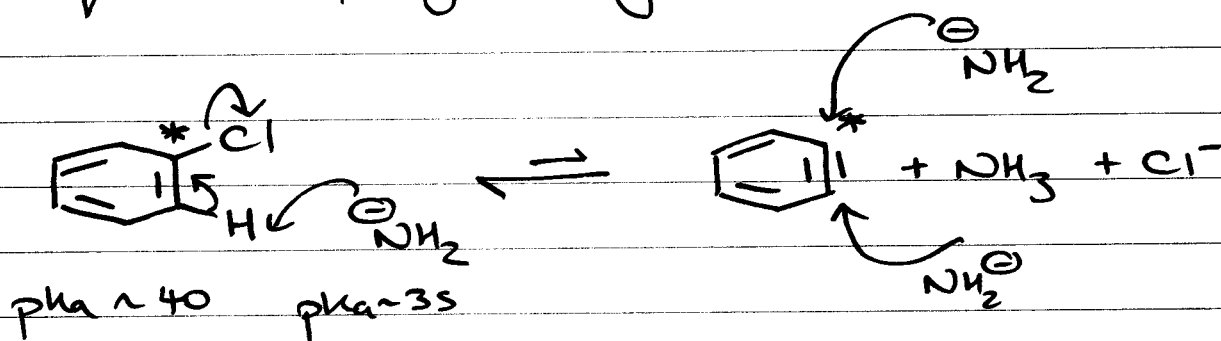
GOES via BENZYNE



PROOF OF BENZYNE intermediate:



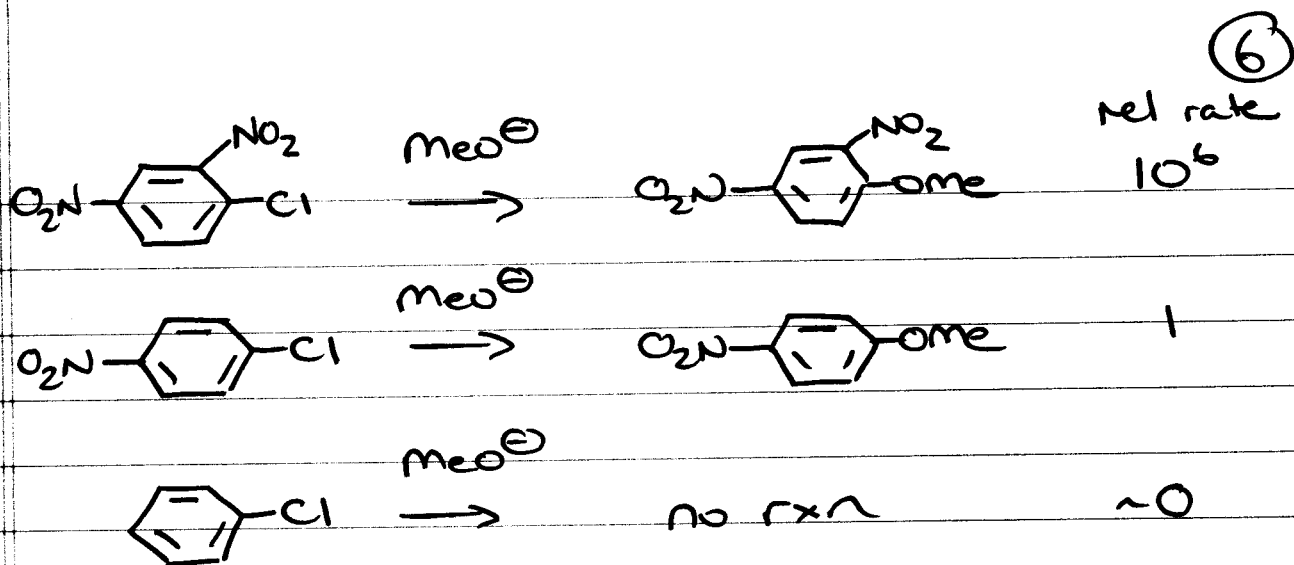
At some point, C1 & C2 must become equivalent, e.g. benzyne



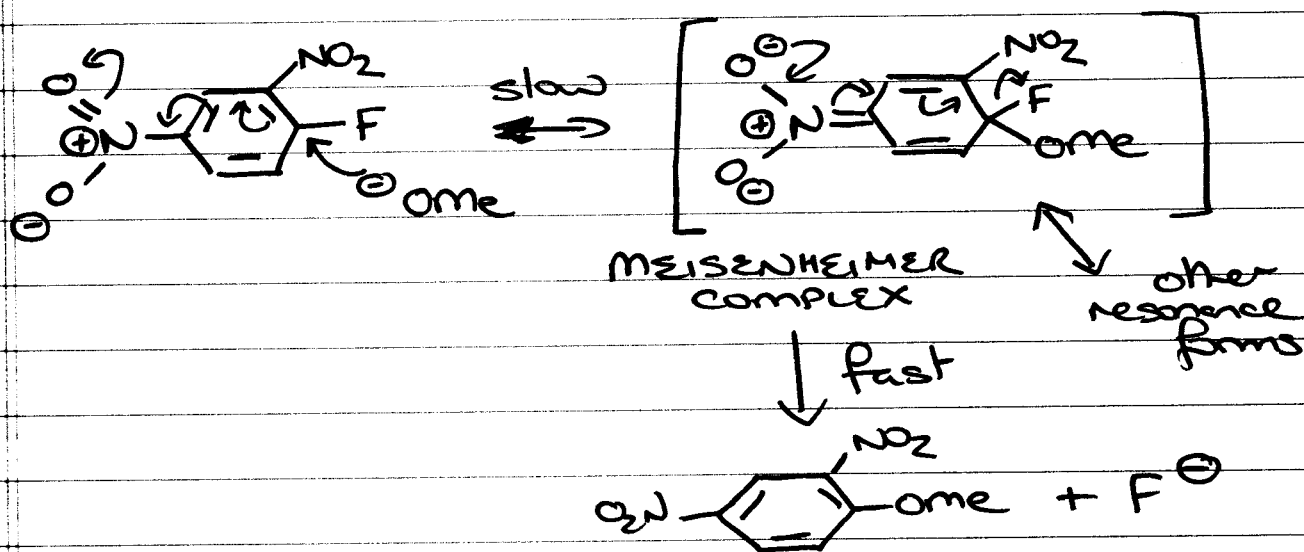
(ELIMINATION / ADDITION PROCESS)

(ii) ADDITION/ELIMINATION

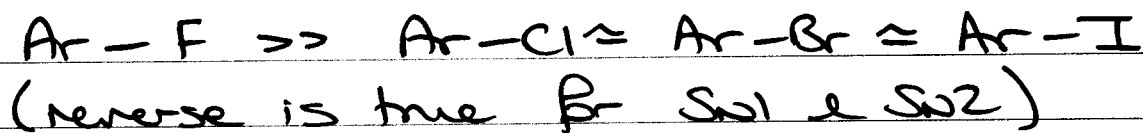
- ARYL HALIDE w/ one or more EWG o,p to halogen undergo Nu substitution under mild conditions



ADDITION complex stabilized by Resonance



Note: order of reactivity



F helps stabilize Meisenheimer complex through the INDUCTIVE EFFECT, and F more EN than $\text{Cl} > \text{Br} > \text{I}$

(7)

Note: loss of halide is not rate-limiting, so C-X bond strength or basicity of halide does not matter.

Differences from S_N2

- frontside attack (no inversion)
- halogen effect reversed
- has an intermediate (Meisenheimer)