

Chapter 23

Aryl Halides

23.1

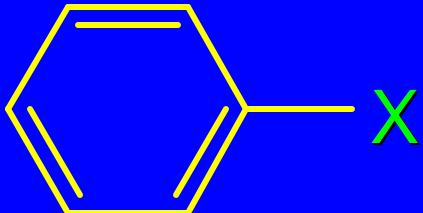
Bonding in Aryl Halides

Aryl Halides

Aryl halides are halides in which the halogen is attached directly to an aromatic ring.

Carbon-halogen bonds in aryl halides are shorter and stronger than carbon-halogen bonds in alkyl halides.

*Table 23.1: C—H and C—Cl Bond
Dissociation Energies of Selected Compounds*

		Bond Energy: kJ/mol (kcal/mol)	
		X = H	X = Cl
$\text{CH}_3\text{CH}_2\text{X}$	sp^3	410 (98)	339 (81)
$\text{H}_2\text{C}=\text{CHX}$	sp^2	452 (108)	368 (88)
	sp^2	469 (112)	406 (97)

Aryl Halides

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Carbon-halogen bonds in aryl halides are shorter and stronger than carbon-halogen bonds in alkyl halides.

Because the carbon-halogen bond is stronger, aryl halides react more slowly than alkyl halides when carbon-halogen bond breaking is rate determining.

23.2

Sources of Aryl Halides

Preparation of Aryl Halides

Halogenation of arenes (Section 12.5)

The Sandmeyer reaction (Section 22.18)

The Schiemann reaction (Section 22.18)

Reaction of aryl diazonium salts with iodide ion
(Section 22.18)

23.3

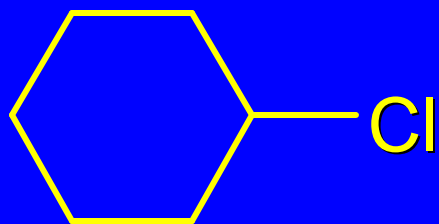
Physical Properties of Aryl Halides

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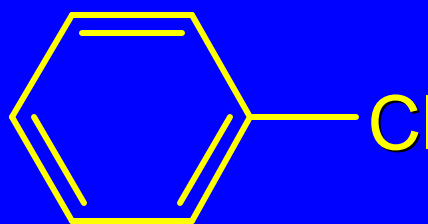
resemble alkyl halides

all are essentially insoluble in water

less polar than alkyl halides



μ 2.2 D



μ 1.7 D

23.4

Reactions of Aryl Halides:
A Review and a Preview

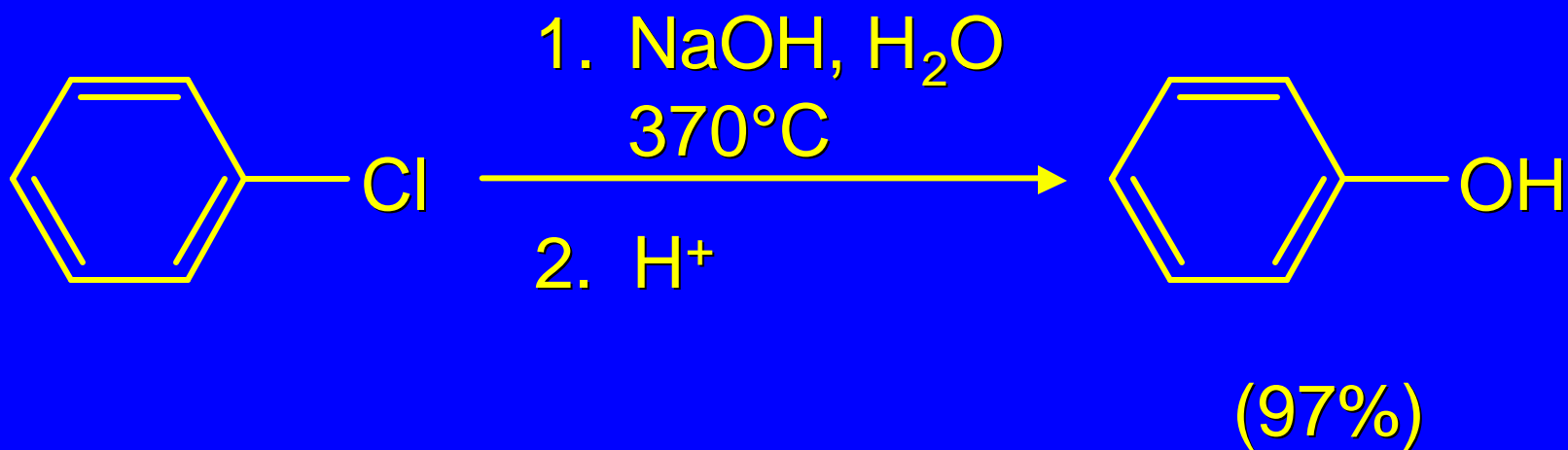
Preparation of Aryl Halides

Electrophilic Aromatic Substitution (Section 12.14)

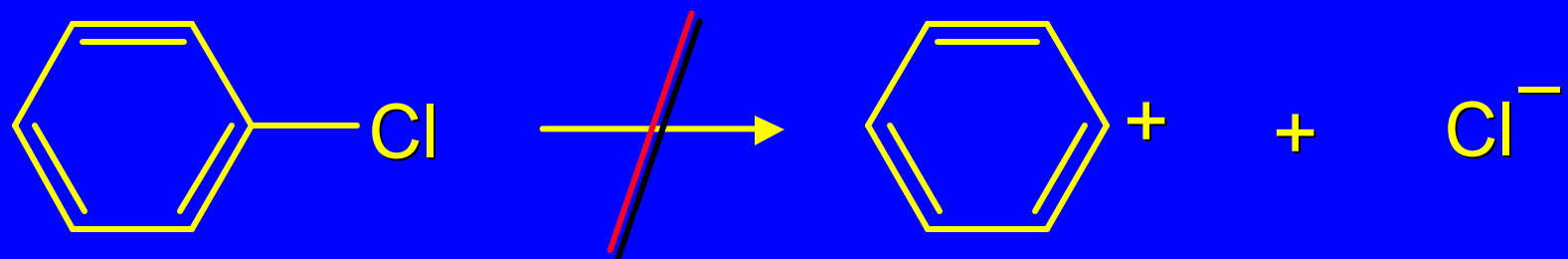
Formation of aryl Grignard reagents (Section 14.4)

We have not yet seen any nucleophilic substitution reactions of aryl halides. Nucleophilic substitution on chlorobenzene occurs so slowly that forcing conditions are required.

Example



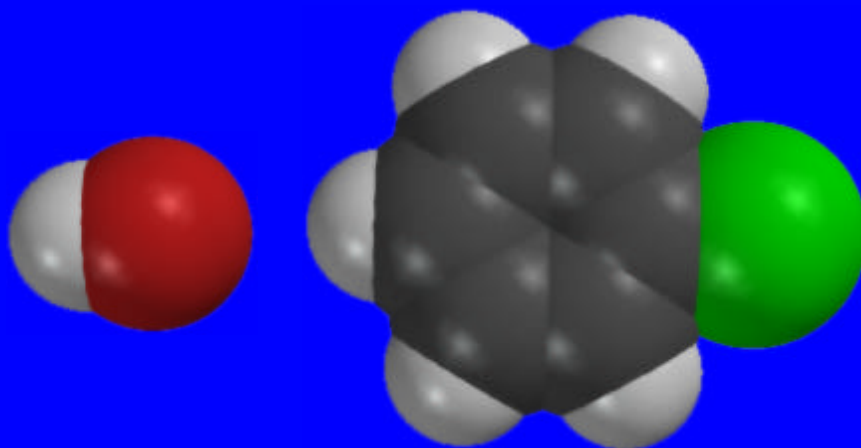
Reasons for Low Reactivity



S_N1 not reasonable because:

- 1) C—Cl bond is strong; therefore, ionization to a carbocation is a high-energy process
- 2) aryl cations are less stable than alkyl cations

Reasons for Low Reactivity



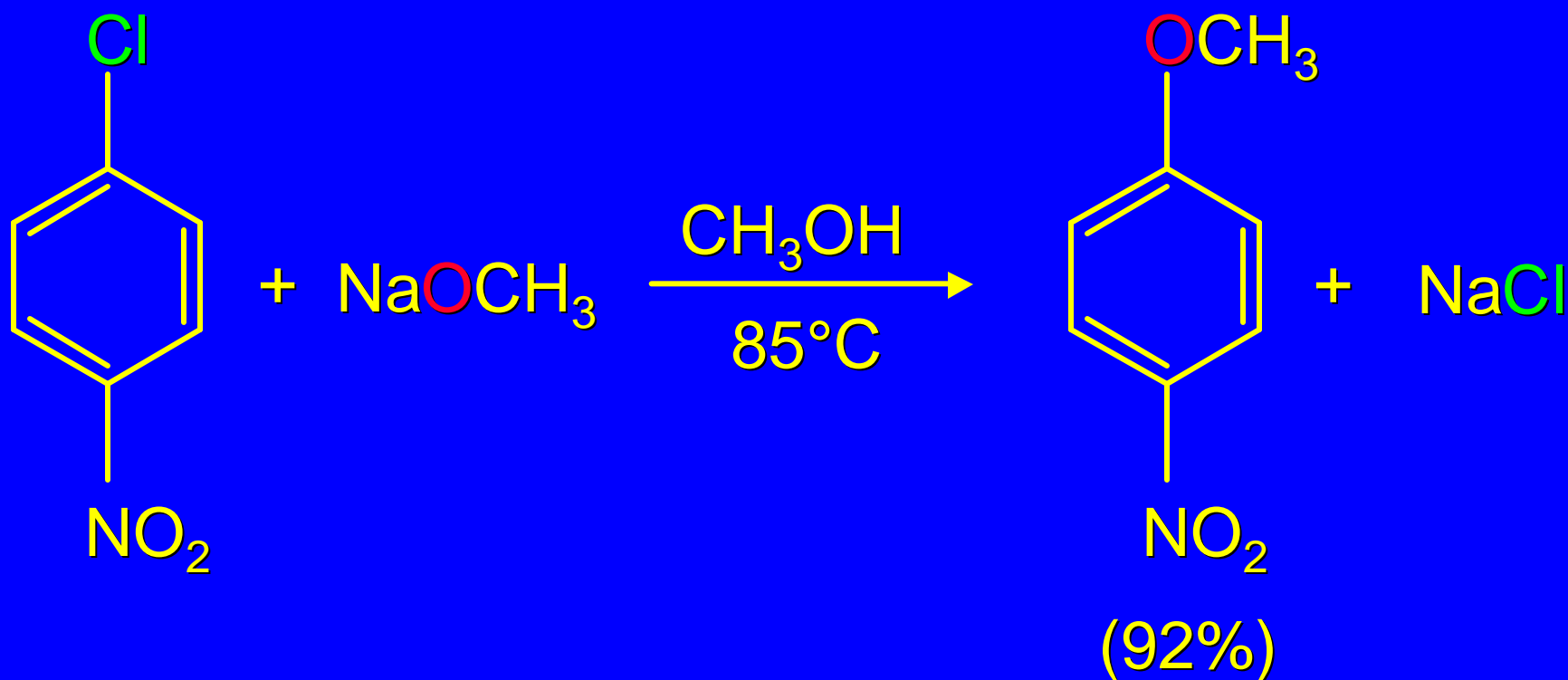
S_N2 not reasonable because ring blocks attack of nucleophile from side opposite bond to leaving group

23.5

Nucleophilic Substitution in
Nitro-Substituted Aryl Halides

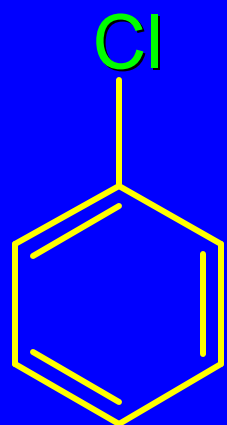
But...

nitro-substituted aryl halides do undergo nucleophilic aromatic substitution readily

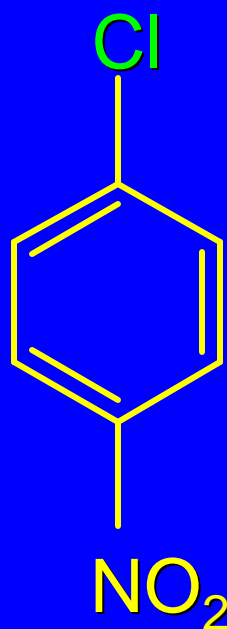


Effect of nitro group is cumulative

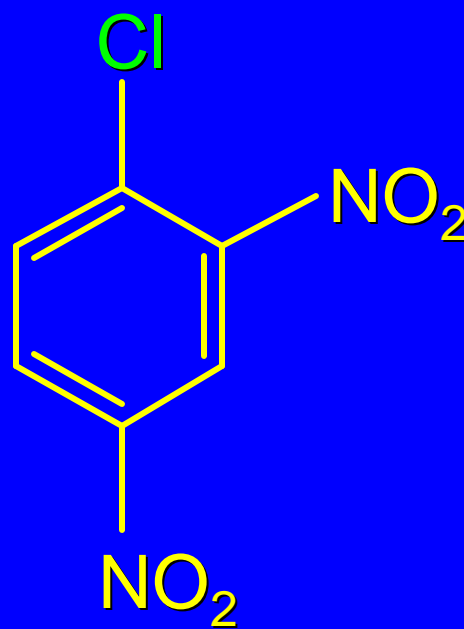
especially when nitro group is ortho and/or para to leaving group



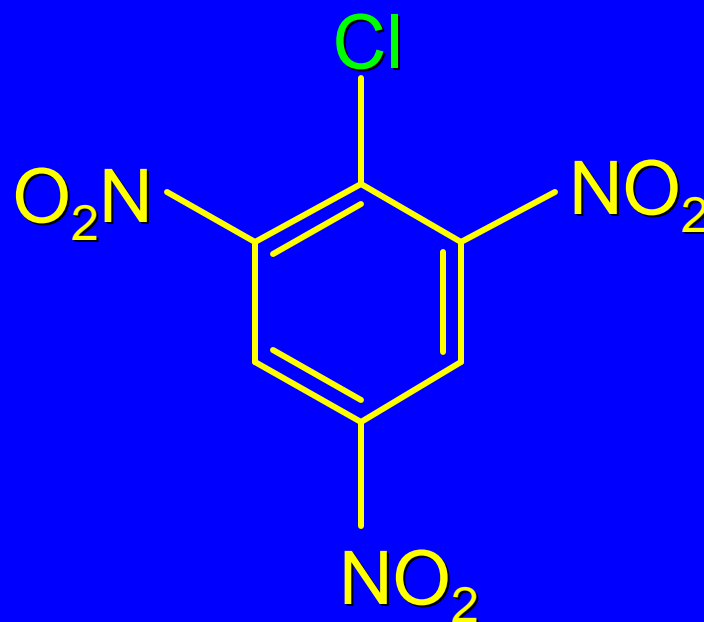
1.0



7×10^{10}



2.4×10^{15}



too fast to measure

Kinetics

follows second-order rate law:

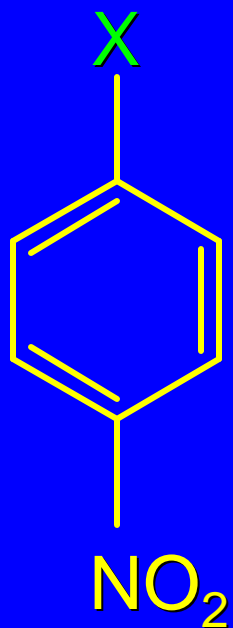
$$\text{rate} = k[\text{aryl halide}][\text{nucleophile}]$$

inference:

both the aryl halide and the nucleophile are involved in rate-determining step

Effect of leaving group

unusual order: $F > Cl > Br > I$



X	Relative Rate*
F	312
Cl	1.0
Br	0.8
I	0.4

*NaOCH₃, CH₃OH, 50°C

General Conclusions About Mechanism

bimolecular rate-determining step in which nucleophile attacks aryl halide

rate-determining step precedes carbon-halogen bond cleavage

rate-determining transition state is stabilized by electron-withdrawing groups (such as NO_2)

23.6
The Addition-Elimination Mechanism
of
Nucleophilic Aromatic Substitution

Addition-Elimination Mechanism

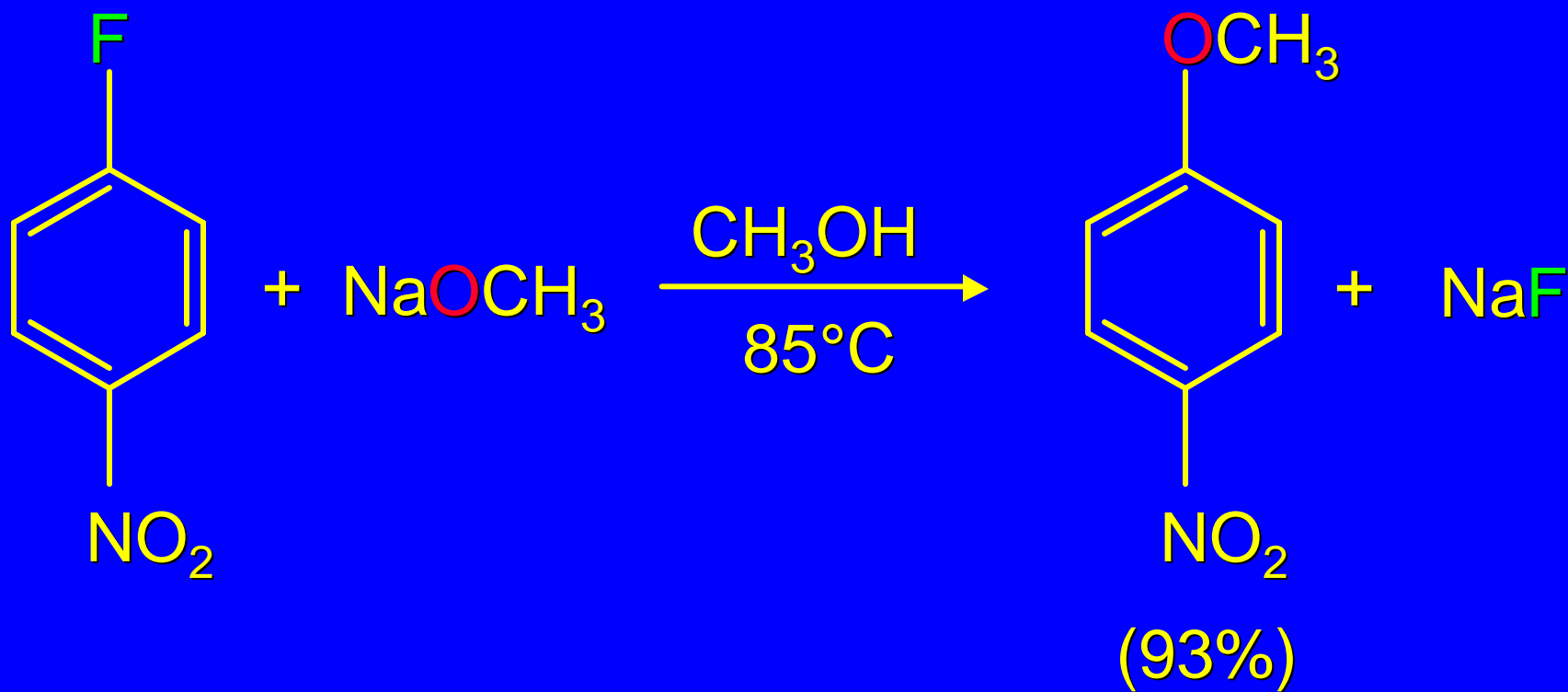
Two step mechanism:

Step 1) nucleophile attacks aryl halide and bonds to the carbon that bears the halogen
(slow: aromaticity of ring lost in this step)

Step 2) intermediate formed in first step loses halide

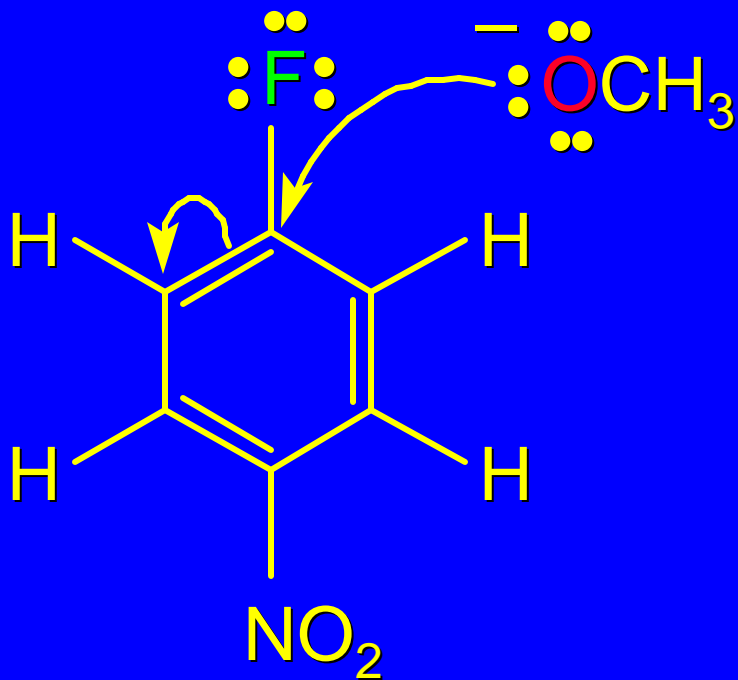
(fast: aromaticity of ring restored in this step)

Reaction



Mechanism

Step 1

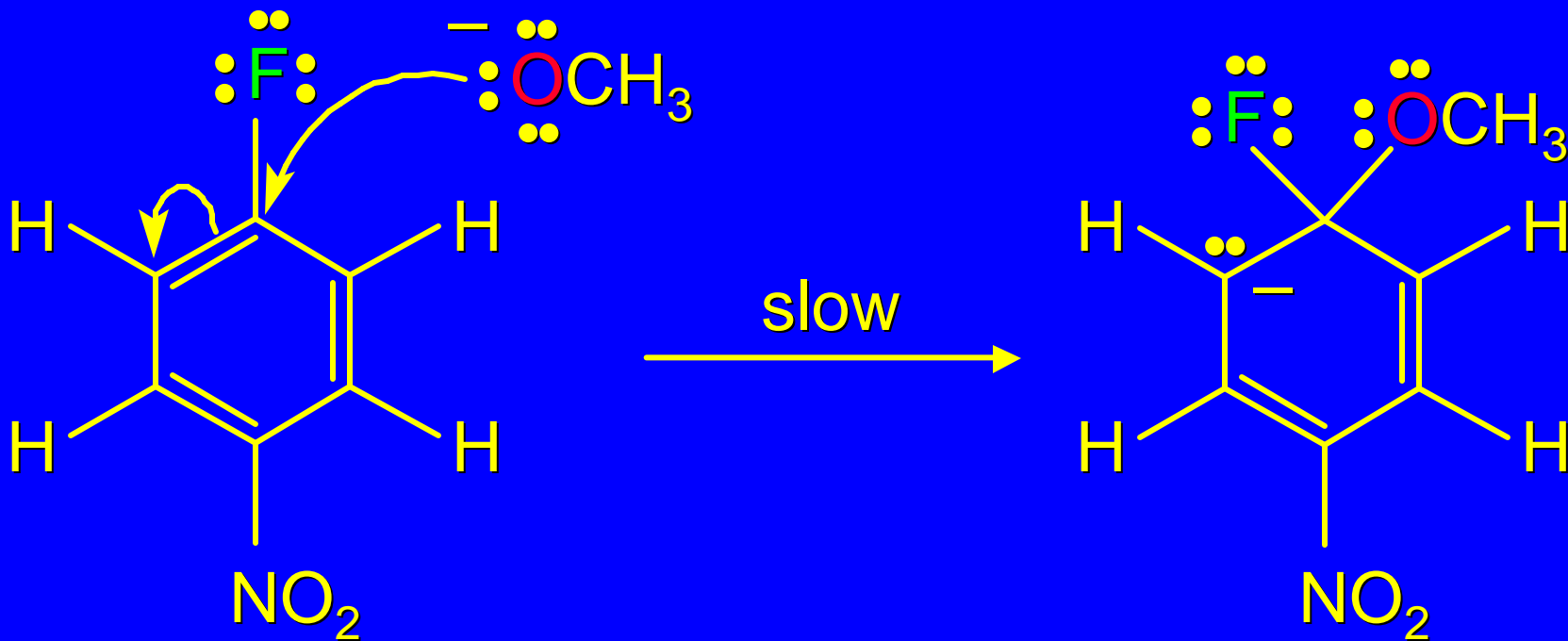


bimolecular

consistent with second-order kinetics; first order in aryl halide, first order in nucleophile

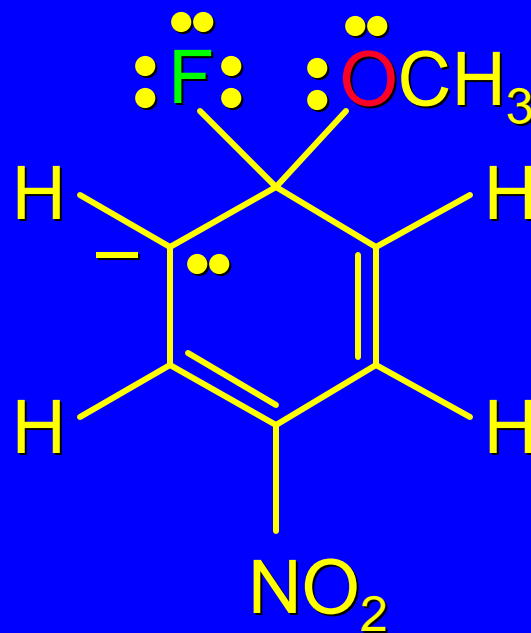
Mechanism

Step 1

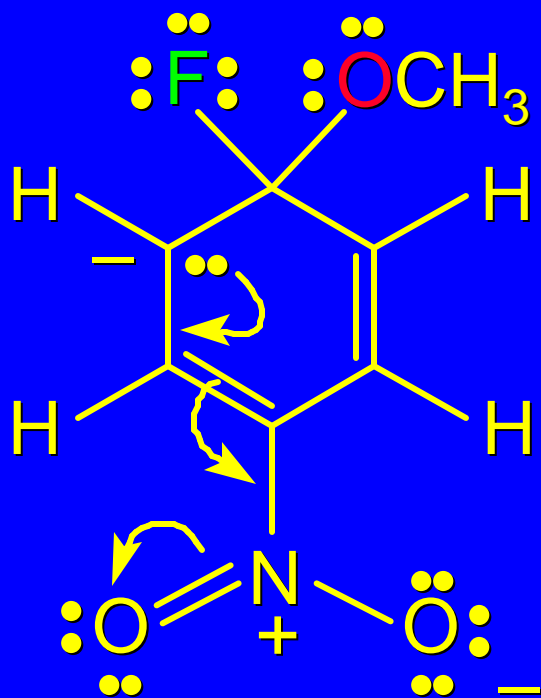


Mechanism

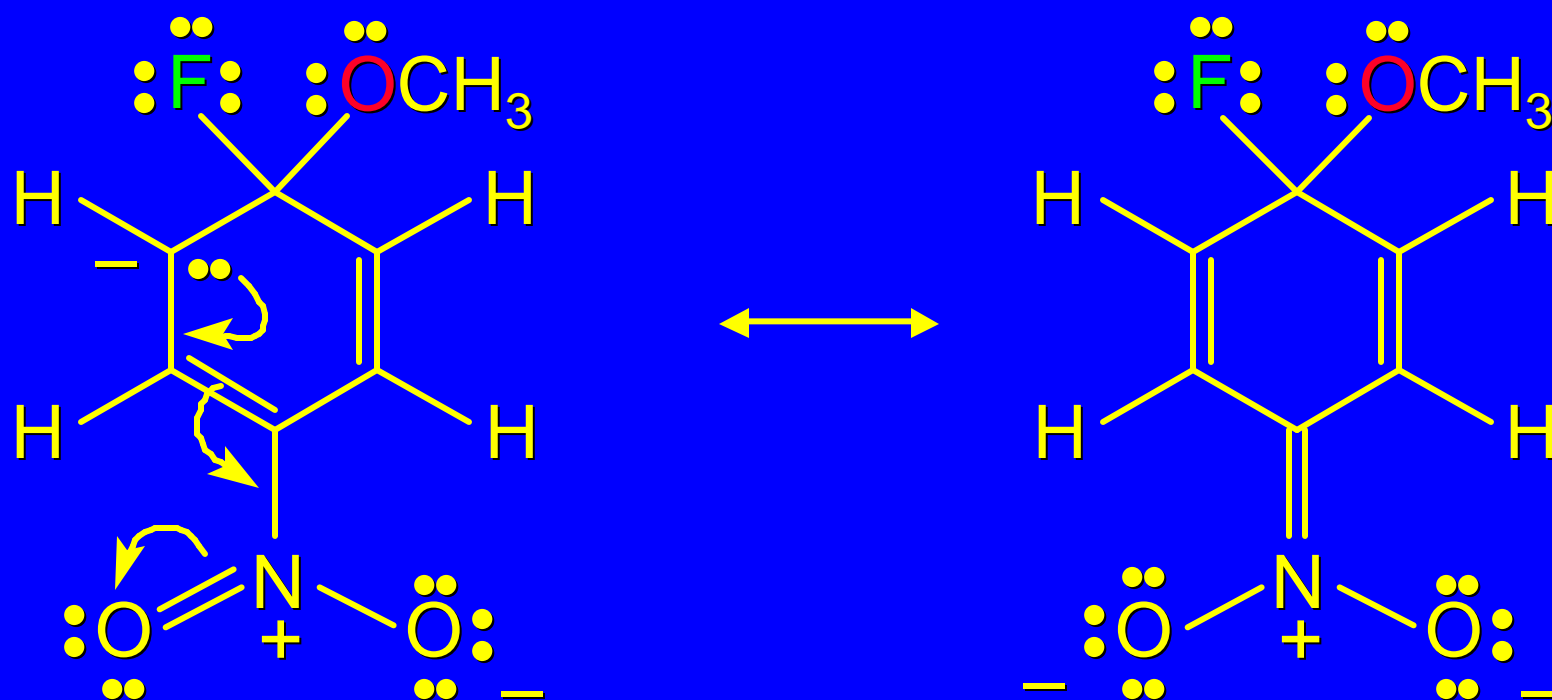
intermediate is
negatively charged
formed faster when
ring bears electron-
withdrawing groups
such as NO_2



Stabilization of Rate-Determining Intermediate by Nitro Group

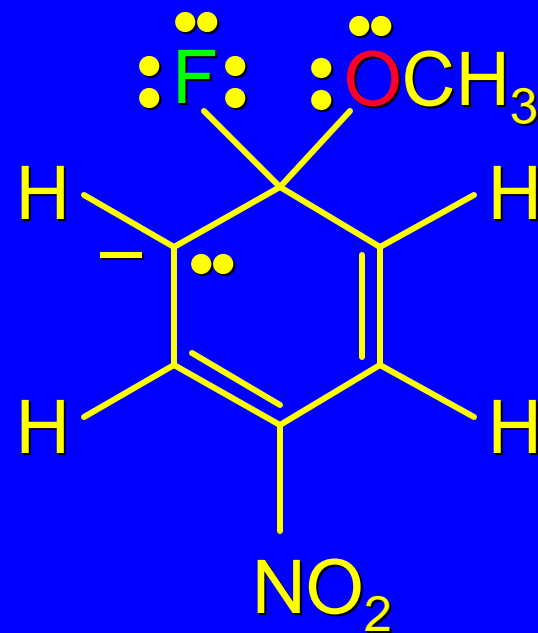


Stabilization of Rate-Determining Intermediate by Nitro Group



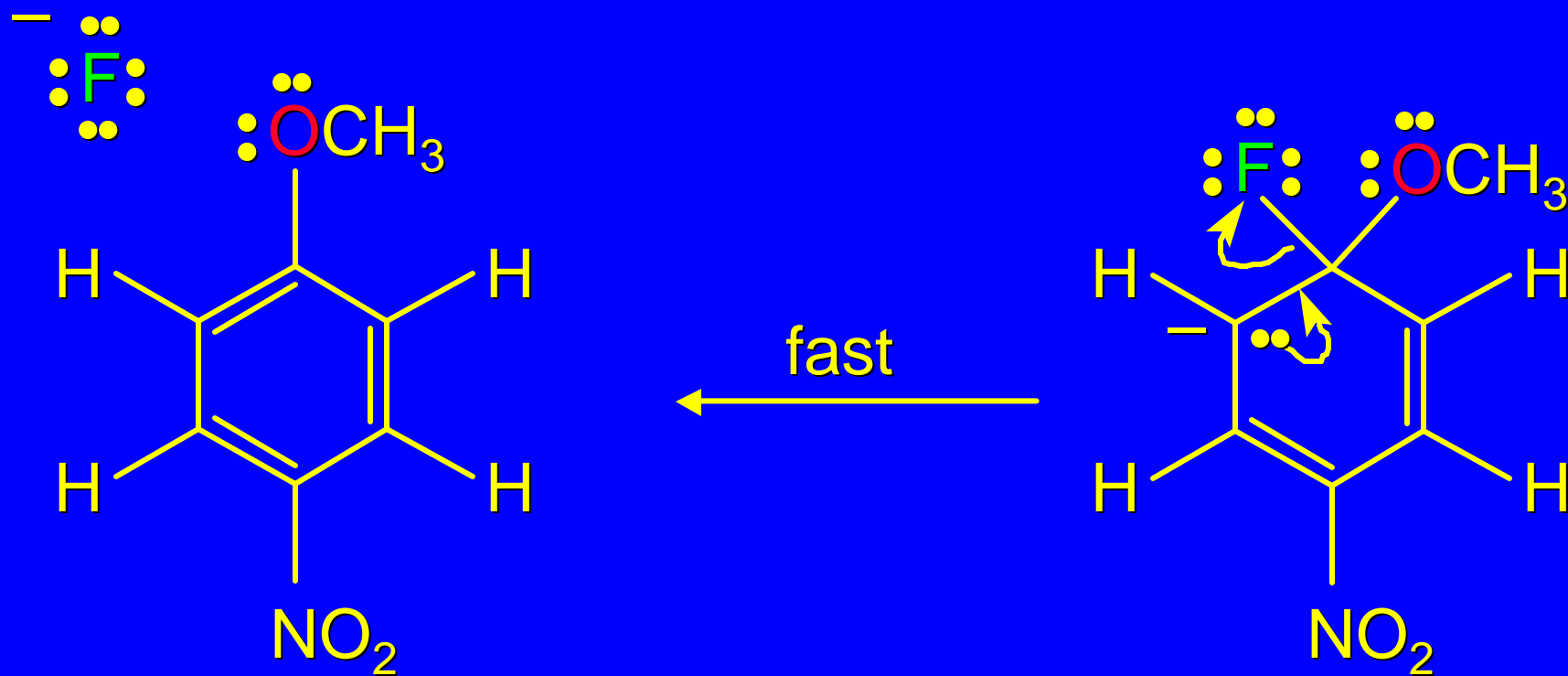
Mechanism

Step 2



Mechanism

Step 2



Leaving Group Effects

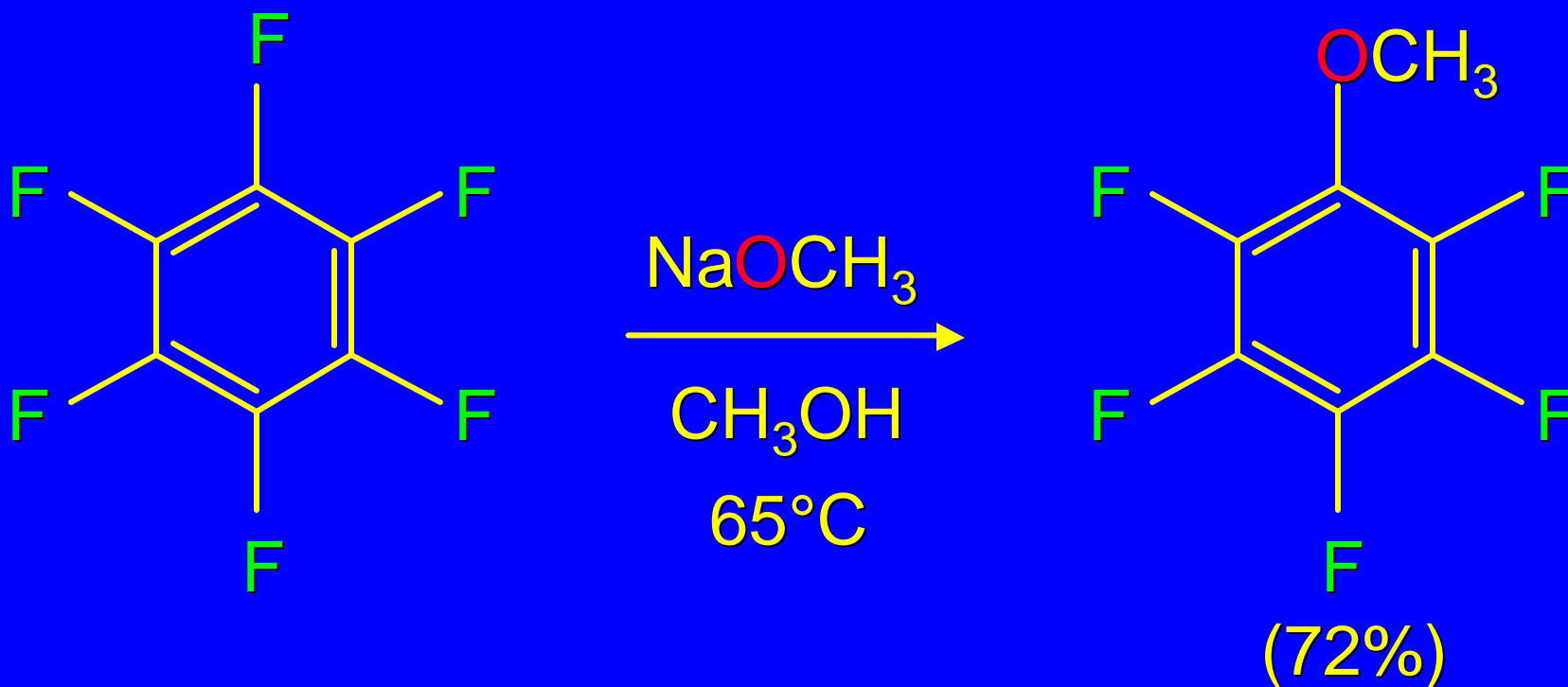
F > Cl > Br > I is unusual, but consistent with mechanism

carbon-halogen bond breaking does not occur until after the rate-determining step

electronegative F stabilizes negatively charged intermediate

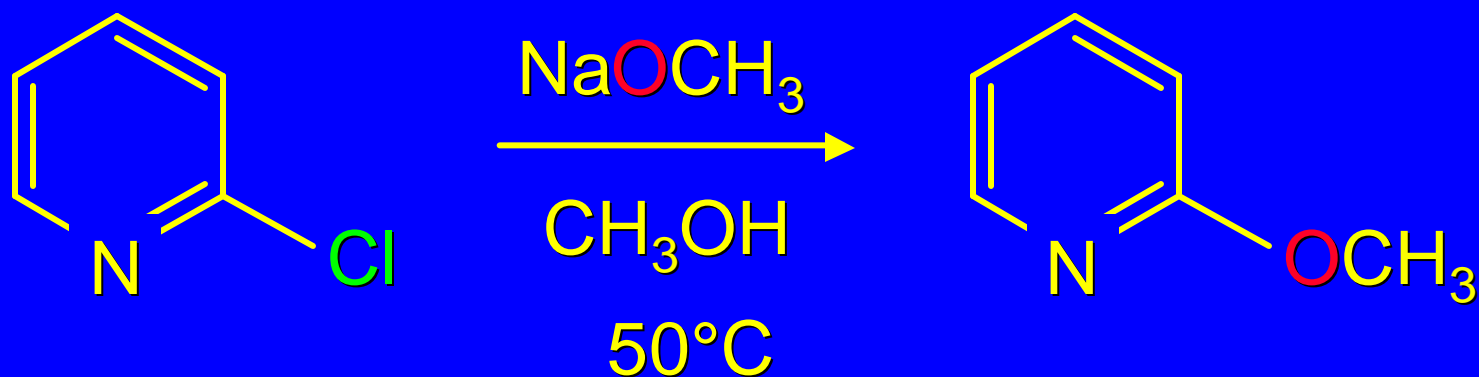
23.7
Related Nucleophilic Aromatic
Substitution Reactions

Example: Hexafluorobenzene



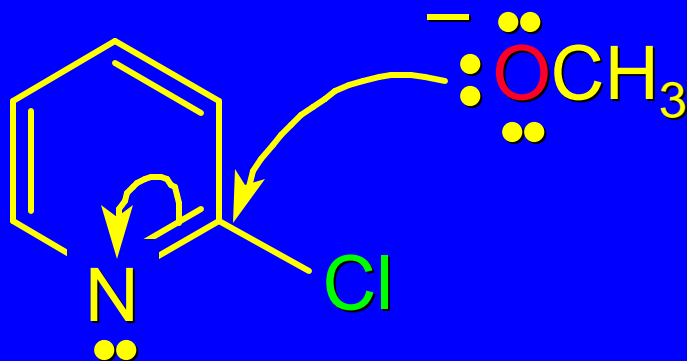
Six fluorine substituents stabilize negatively charged intermediate formed in rate-determining step and increase rate of nucleophilic aromatic substitution.

Example: 2-Chloropyridine



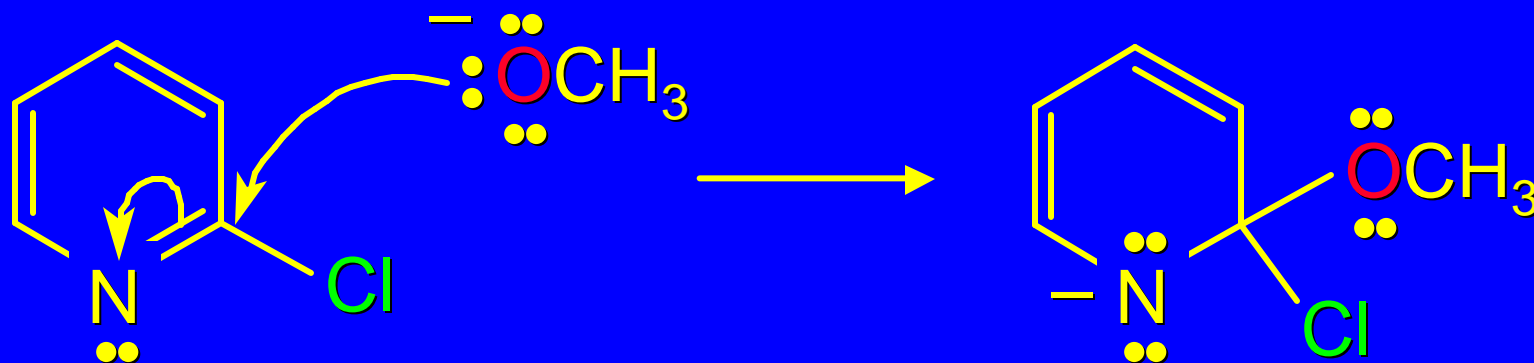
2-Chloropyridine reacts 230,000,000 times faster than chlorobenzene under these conditions.

Example: 2-Chloropyridine



Nitrogen is more electronegative than carbon, stabilizes the anionic intermediate, and increases the rate at which it is formed.

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