CONCEPT: S_NAr ADDITION-ELIMINATION MECHANISM

Unlike EAS, where addition is initiated by the presence of a strong electrophile, addition-elimination can also be initiated by a *strong nucleophile* in the presence of a *good aryl leaving group*.

- Reaction has similarities to S_N² but it is not
- Known as Addition-Elimination Nucleophilic Aromatic Substitution, S_NAr or ipso-substitution.

An early method of preparing phenol called the **Dow Process** used chlorobenzene, NaOH and high heat to force S_NAr.

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CONCEPT: THE MEISENHEIMER COMPLEX

The **Dow Process**, a typical S_NAr reaction, requires tons of heat and pressure to proceed forward.

- This is due to the instability of the anionic sigma-complex
- Withdrawing groups or Heteroatoms to the Ortho or Para positions (WHOP) stabilize the intermediate
 - ☐ A classical trinitrobenzene *Meisenheimer Complex* can proceed in *room temperature*

EXAMPLE: Use resonance structures to determine which of the following ipso-substitutions is more favored.

$$H_2N$$
 CI
 K^+ -OCH₂CH₃
 350° C

EXAMPLE: Which of the following compounds will most readily undergo nucleophilic aromatic substitution in the addition-elimination pathway?

$$\bigcap_{N}^{CI}$$
 \bigcap_{N}^{N} $\bigcap_{$

<u>PRACTICE:</u> Provide the structure and name of the intermediate formed from the reaction of 1-bromo-2,4,6-trinitrobenzene with one equivalent of sodium methoxide.

<u>PRACTICE:</u> Provide the major organic product for the following reaction.

 $\underline{\mathsf{PRACTICE:}}\ \mathsf{Provide}\ \mathsf{the}\ \mathsf{major}\ \mathsf{organic}\ \mathsf{product}\ \mathsf{for}\ \mathsf{the}\ \mathsf{following}\ \mathsf{reaction}.$

<u>PRACTICE:</u> Which of the following compounds is most likely to undergo nucleophilic aromatic substitution via the addition-elimination Pathway?

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