

## ORGANIC CHEMISTRY 2 LECTURE GUIDE 2019

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## Lesson IV.16. Nucleophilic Aromatic Substitution

### *The S<sub>N</sub>Ar reaction*

We have seen that electrophiles can do EAS reactions of Arenes. Now we will briefly explore how aromatic compounds react with **Nucleophiles** instead of electrophiles. Arenes may react with nucleophiles via:

**A** S<sub>N</sub>Ar

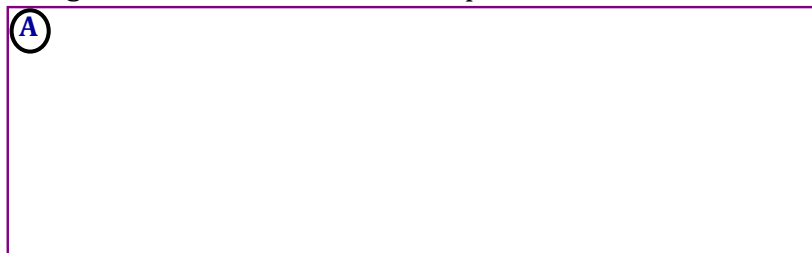
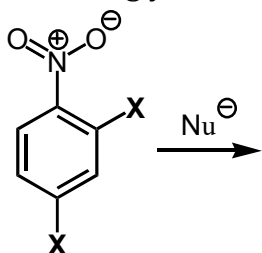
There are some structural requirements for a S<sub>N</sub>Ar reaction to work:

**B**

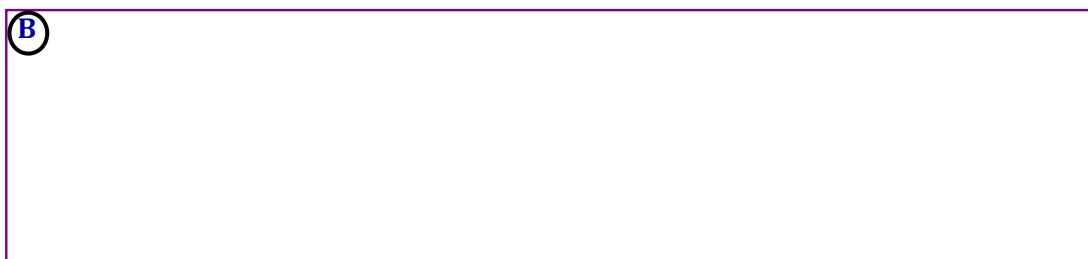
Notes

**Lesson IV.16. Nucleophilic Aromatic Substitution***The S<sub>N</sub>Ar reaction*

The net S<sub>N</sub>Ar reaction is replacement of the substituent that is *ortho*- or *para*- to the strongly withdrawing substituent with the nucleophile:



The S<sub>N</sub>Ar reaction involves a two-step mechanism:



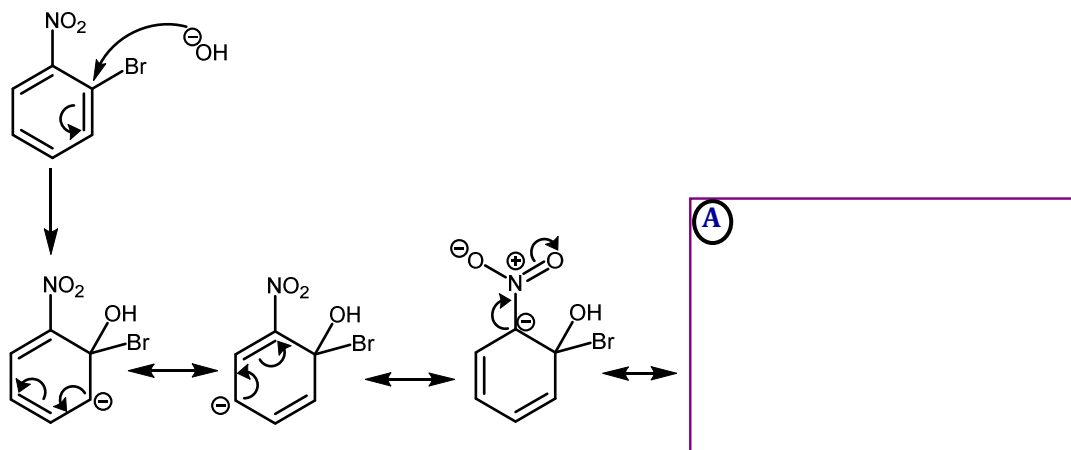
Notes

## Lesson IV.16. Nucleophilic Aromatic Substitution

### The $S_NAr$ reaction

Now that we know the mechanism of the  $S_NAr$  reaction, we can rationalize the requirement for the leaving group to be *o*- or *p*- to the EWG. Let us consider the nucleophilic addition step:

*ortho*- nucleophilic addition



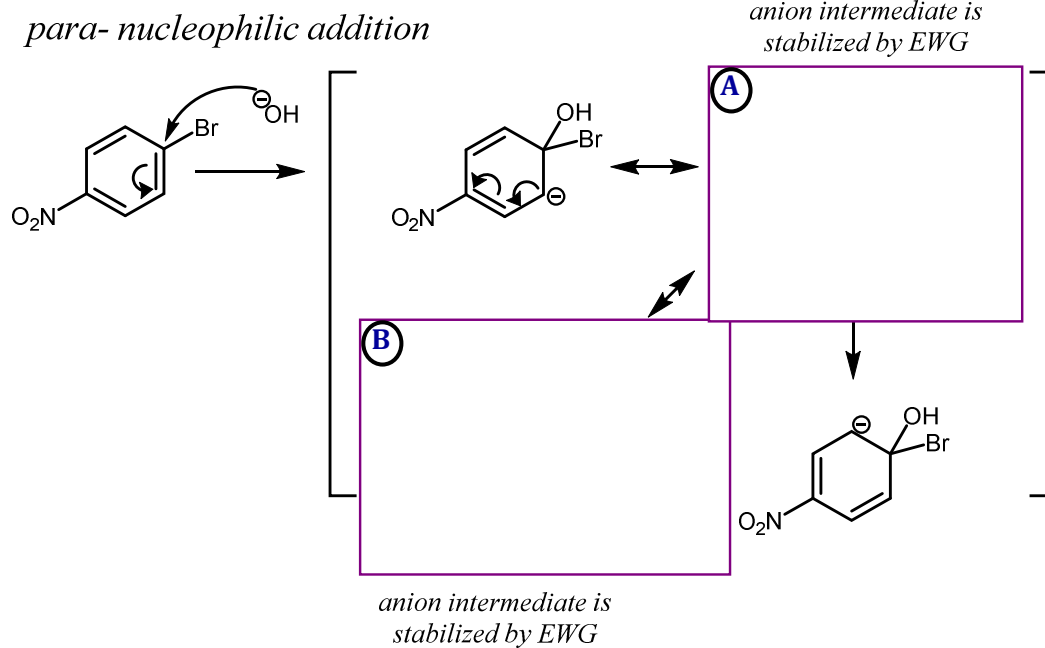
*anion intermediate is stabilized by EWG*

Notes

## Lesson IV.16. Nucleophilic Aromatic Substitution

### The $S_NAr$ reaction

Consider nucleophilic addition to the site *p*- to the EWG:



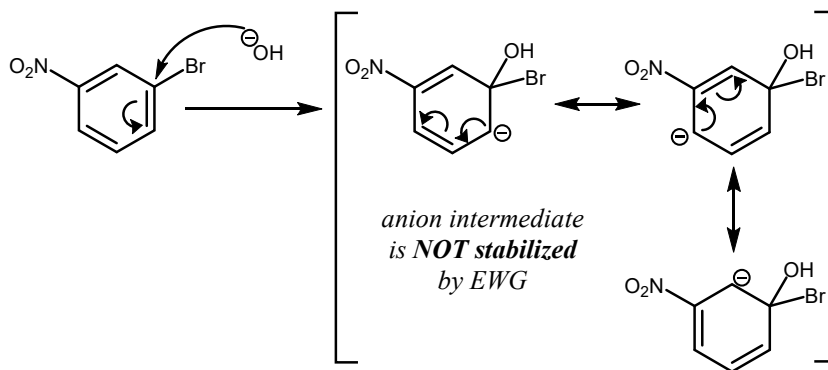
Notes

## Lesson IV.16. Nucleophilic Aromatic Substitution

### The $S_NAr$ reaction

Consider nucleophilic addition to the site *m*- to the EWG:

*meta*- nucleophilic addition



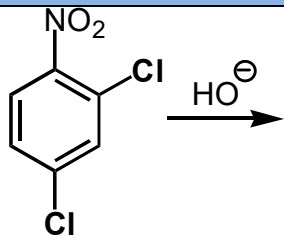
The relative stabilities of the anionic intermediates reveal:

Ⓐ

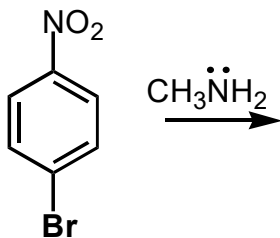
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## Lesson IV.16. Nucleophilic Aromatic Substitution

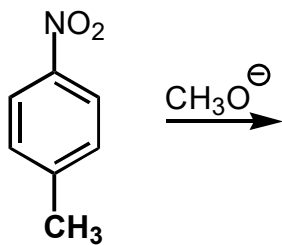
*S<sub>N</sub>Ar reaction practice*



(A)



(B)



(C)

Notes