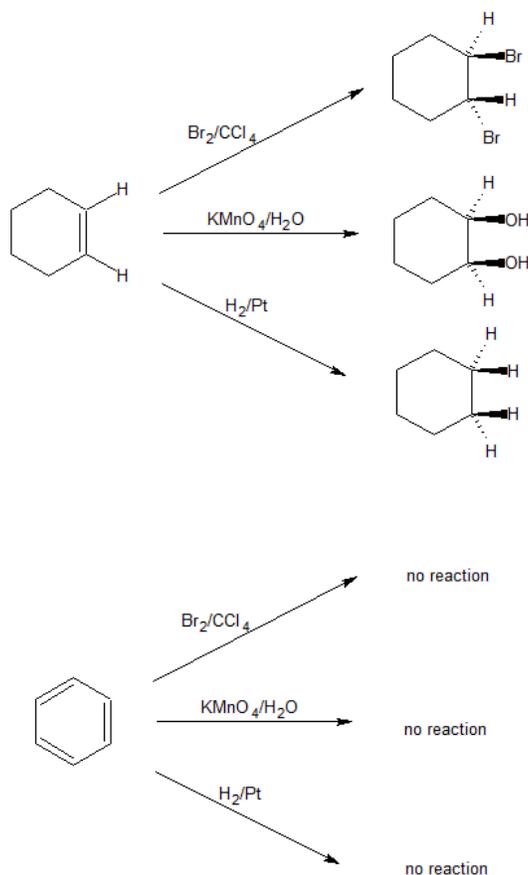


18.1: ELECTROPHILIC AROMATIC SUBSTITUTION (EAS)

BENZENE AND ELECTROPHILIC AROMATIC SUBSTITUTION REACTIONS

While it took chemists many years to determine the structure of benzene and its derivatives, chemists recognized this class of compounds by their distinct aromas and low reactivity compared to isolated alkenes.



With the stability created by the conjugated pi electron system, the lack of chemical reactivity is not surprising. However, over time chemists found ways to catalyze reactions of benzene and its derivatives. With its strong electronic character, benzene is inherently electrophilic. The majority of the reactions for benzene are Electrophilic Aromatic Substitution reactions. One of the benzene hydrogen atoms can be substituted for a different group with electrophilic properties followed by restoration of the stable aromatic ring.

EXAMPLES OF ELECTROPHILIC AROMATIC SUBSTITUTION (EAS)

Many substitution reactions of benzene have been observed, the five most useful are listed below (chlorination and bromination are the most common halogenation reactions). Since the reagents and conditions employed in these reactions are electrophilic, these reactions are commonly referred to as **Electrophilic Aromatic Substitution**. The catalysts and co-reagents serve to generate the strong electrophilic species needed to effect the initial step of the substitution. The specific electrophile believed to function in each type of reaction is listed in the right hand column.

Reaction Type	Typical Equation	Electrophile E ⁽⁺⁾
Halogenation:	$C_6H_6 + Cl_2 \xrightarrow[\text{FeCl}_3 \text{ catalyst}]{\text{heat}}$	$C_6H_5Cl + HCl$ Chlorobenzene Cl ⁽⁺⁾ or Br ⁽⁺⁾
Nitration:	$C_6H_6 + HNO_3 \xrightarrow[\text{H}_2\text{SO}_4 \text{ catalyst}]{\text{heat}}$	$C_6H_5NO_2 + H_2O$ Nitrobenzene NO ₂ ⁽⁺⁾
Sulfonation:	$C_6H_6 + H_2SO_4 + SO_3 \xrightarrow{\text{heat}}$	$C_6H_5SO_3H + H_2O$ Benzenesulfonic acid SO ₃ H ⁽⁺⁾
Alkylation: Friedel-Crafts	$C_6H_6 + R-Cl \xrightarrow[AlCl_3 \text{ catalyst}]{\text{heat}}$	$C_6H_5-R + HCl$ An Arene R ⁽⁺⁾
Acylation: Friedel-Crafts	$C_6H_6 + RCOCl \xrightarrow[AlCl_3 \text{ catalyst}]{\text{heat}}$	$C_6H_5COR + HCl$ An Aryl Ketone RCO ⁽⁺⁾

GENERAL MECHANISM

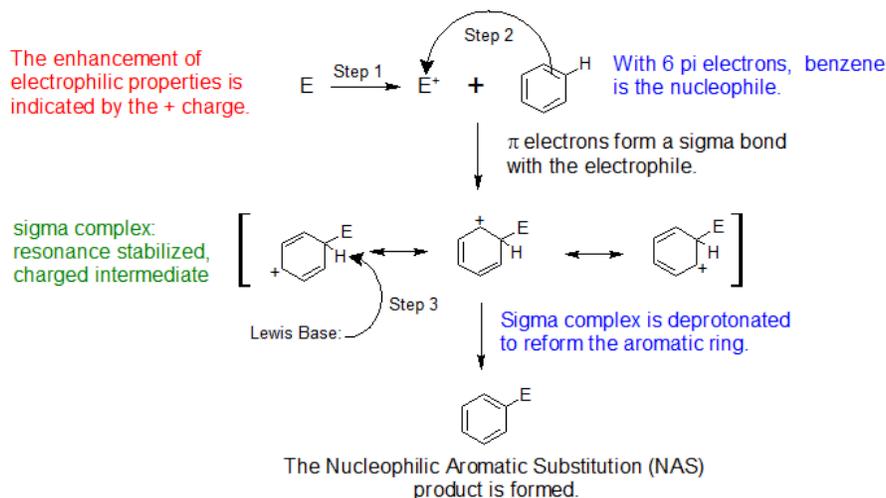
Electrophilic Aromatic Substitution (EAS) reactions include the same three mechanistic steps. Step 1 is needed to create a strong enough Electrophile to create reactivity with the pi electrons of benzene. Because the sigma complex is resonance stabilized, carbocation rearrangement is not a consideration for this intermediate.

Step 1: Formation of a Strong Electrophile

Step 2: Benzene pi electrons form a sigma bond with the Strong Electrophile to create the "sigma complex", a resonance stabilized, charged intermediate

Step 3: Deprotonation of the sigma complex to reform the aromatic ring

The generic mechanism shared by all EAS reactions is shown below.



ACTIVATING AND DEACTIVATION GROUPS

As we study the EAS reactions, we will learn that some substituents increase the reactivity of the benzene ring for EAS reactions and are called "activating groups". Other substituents decrease the reactivity of the benzene ring for EAS reactions and are called "deactivating groups". These groups can be recognized by their effects on the stability of the sigma complex.

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