

Electrophiles for Electrophilic Aromatic Substitution (EAS)

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Klein	EAS Reaction	Conditions	Electrophile (E ⁺)	Mech. to make E ⁺ (first steps in EAS)
18.2	halogenation -X	Br ₂ /FeBr ₃ Cl ₂ /FeCl ₃	$\text{Br}-\overset{\oplus}{\text{Br}}-\overset{\ominus}{\text{FeBr}}_3 \approx \text{Br}^{\oplus}$ $\text{Cl}-\overset{\oplus}{\text{Cl}}-\overset{\ominus}{\text{FeCl}}_3 \approx \text{Cl}^{\oplus}$	great LG $\left\{ \begin{array}{c} \text{Br} \\ \delta^- \\ \text{Br}-\text{Fe}-\text{Br} \cdots \text{Br} \\ \\ \text{Br} \end{array} \right.$
18.4	nitration -NO ₂	HNO ₃ , H ₂ SO ₄	$\text{O}=\overset{\oplus}{\text{N}}=\text{O}$ (nitronium ion)	great LG $\left\{ \begin{array}{c} \text{O} \\ \text{H} \oplus \text{O} \cdots \text{N} \cdots \text{O}^- \\ \text{H} \end{array} \right.$ loss of water LG to make NO ₂ ⁺
18.3	sulfonation* -SO ₃ H	SO ₃ , H ₂ SO ₄	$\text{O}=\text{S}=\text{O} \longleftrightarrow \text{O}=\overset{\oplus}{\text{S}}-\text{O}^-$	N/A (SO ₃ is Electrophile) <i>*reaction is reversible (heat removes -SO₃H group)</i>
18.5	Friedel-Crafts alkylation -R	ROH/HA or ROH/BF ₃ or RX/FeX ₃ or + HA (HF)	R^{\oplus} (carbocation - may rearrange, if unstable)	$\text{R}-\overset{\oplus}{\text{O}}\text{H}_2 \quad \text{R}-\overset{\oplus}{\text{O}}(\text{H})-\text{BF}_3 \quad \text{R}-\overset{\delta+}{\text{X}}-\overset{\delta-}{\text{FeX}}_3$ loss of leaving group (LG) to make carbocation protonate pi bond to make carbocation
18.6	Friedel-Crafts acylation	$\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{Cl} + \text{AlCl}_3$ or $\text{R}-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{R} + \text{AlCl}_3$	$\text{R}-\overset{\oplus}{\text{C}}=\text{O} \longleftrightarrow \text{R}-\text{C}\equiv\overset{\oplus}{\text{O}}$ (acylium ion)	great LG