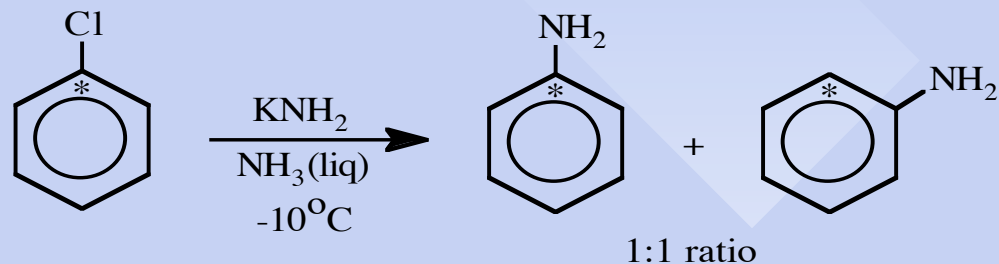
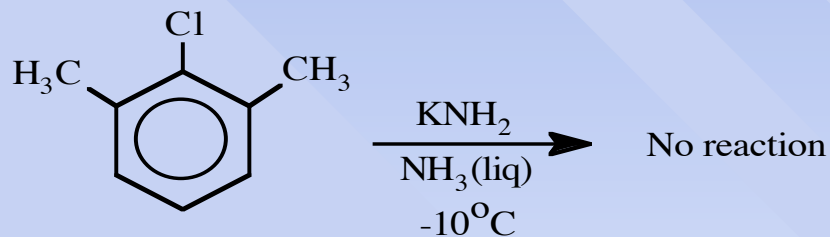
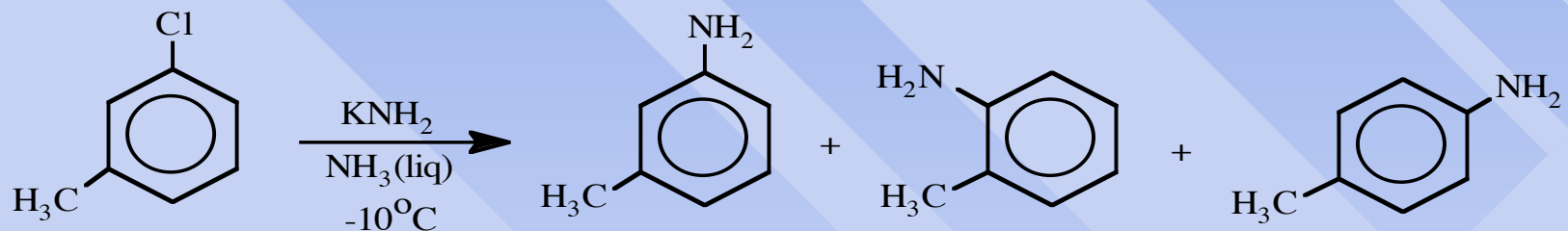
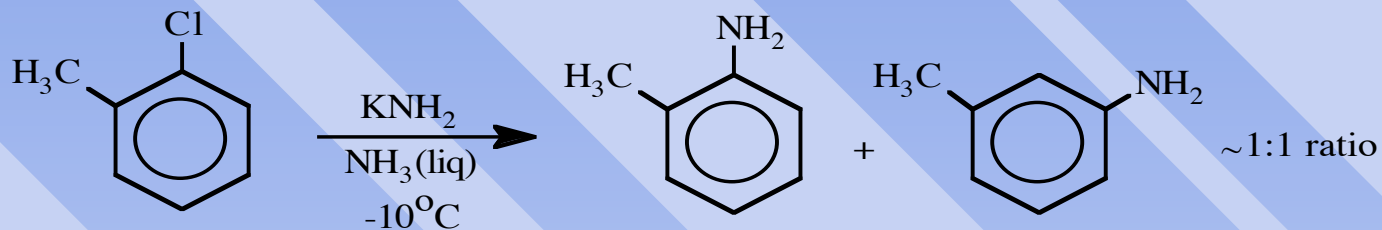
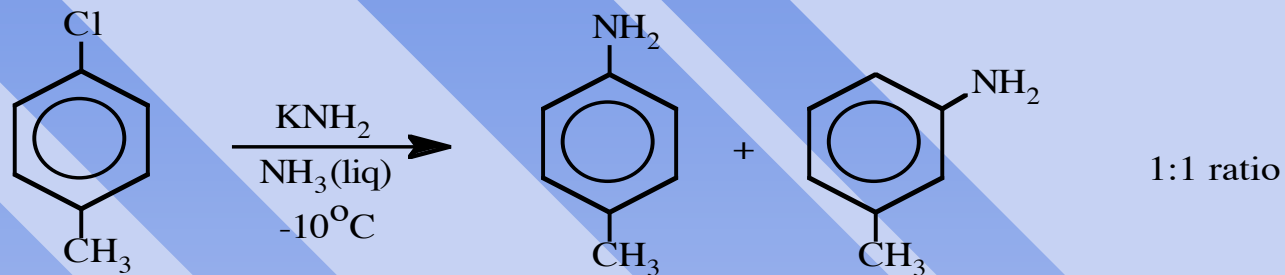
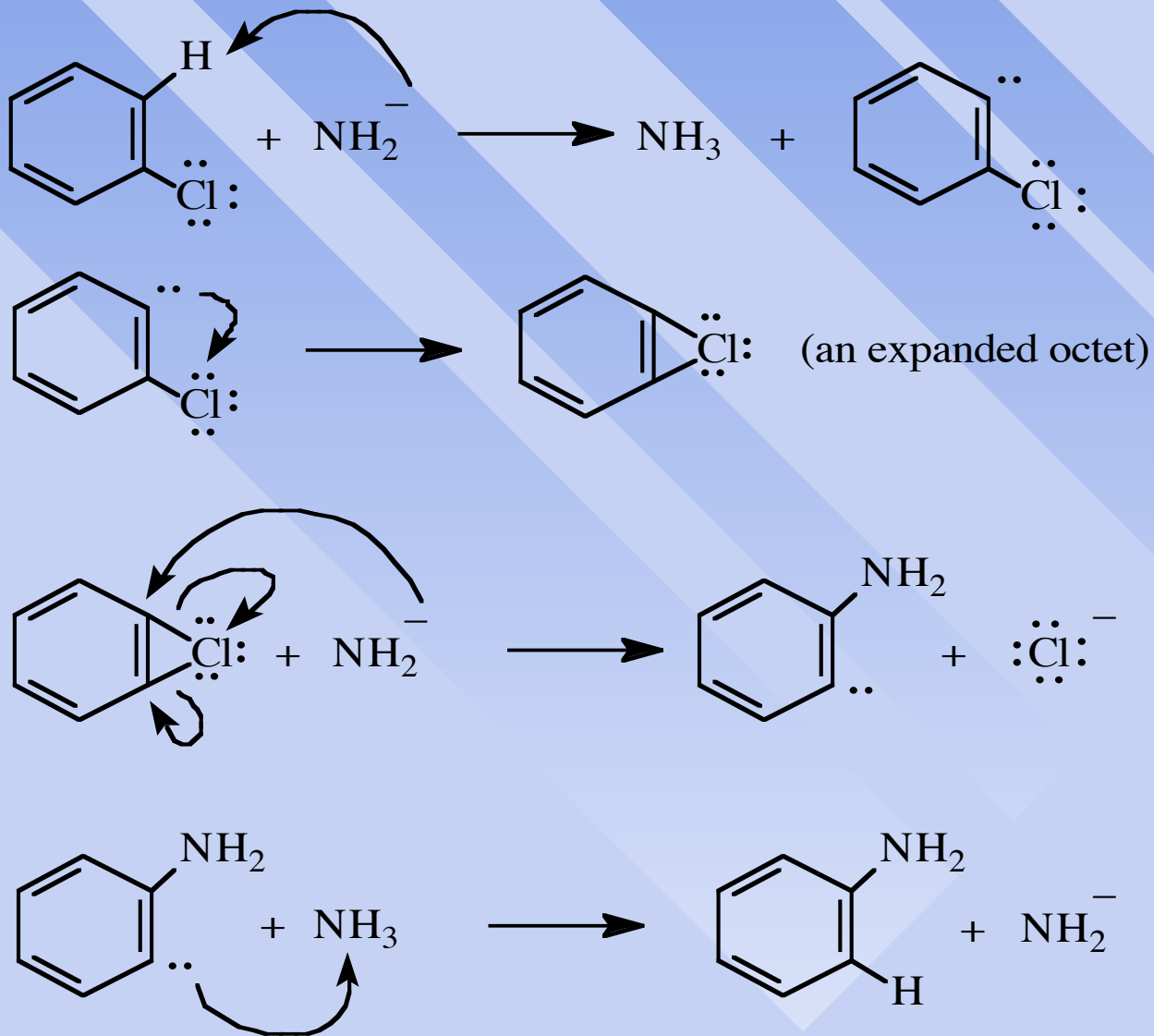


Observations related to Benzyne intermediacy



Possible explanation to account for experimental observations



Facts that preclude an expanded octet chlorine intermediate

- **The substitution reaction proceeds with fluorine instead of chlorine. Whereas an expanded octet is not possible for fluorine, an expanded octet intermediate is not likely**
- **Mass spectral evidence indicates that chlorine is not present, and that the mass of the actual intermediate is independent of its origin.**

Elimination Pathways to Benzyne

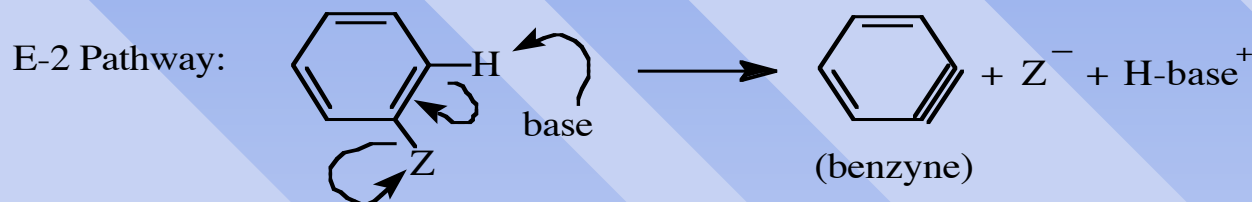
- + A one-step concerted reaction (E-2)
- + A two step reaction that proceeds via a carbanion (E₁CB)

BENZYNE FORMATION VIA ELIMINATION

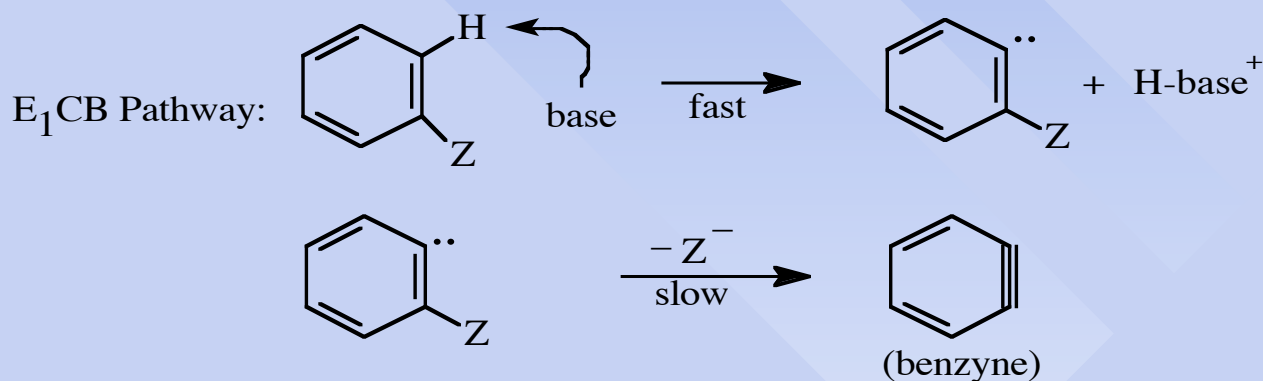
Experimental Observations:

1. When $Z = \text{I, Br, or Cl}$ (below), $k_{\text{H}} / k_{\text{D}} = 5-6$; not valid for $Z = \text{F}$.
2. The rate of reaction depends on the nature of the leaving group: $k_{\text{I}} > k_{\text{Br}} > k_{\text{Cl}} \gg k_{\text{F}}$

Plausible Explanation:



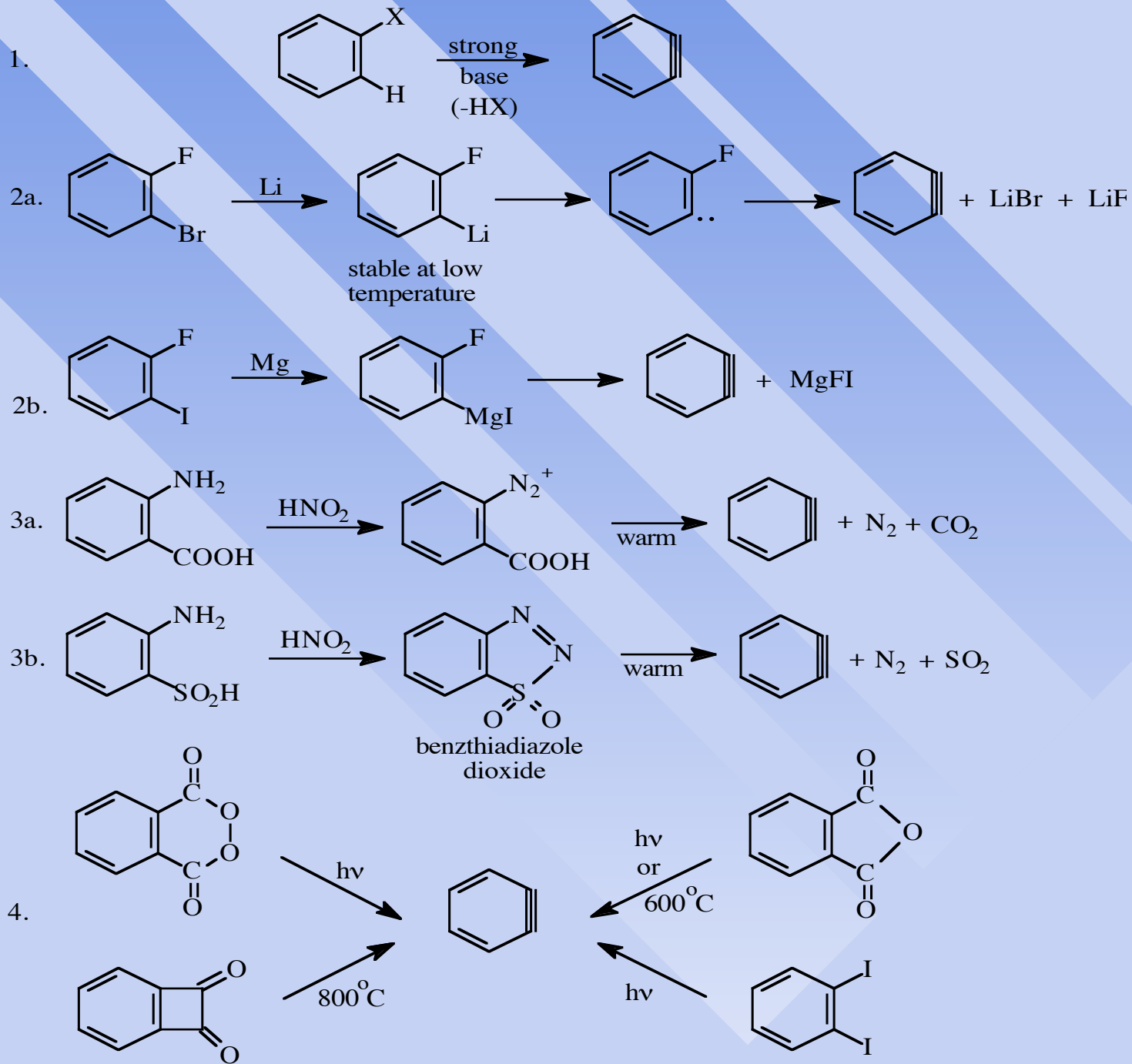
When $Z = \text{I, Br, or Cl}$ but not F, loss of the leaving group and hydrogen abstraction can occur in concerted fashion. C-H bond cleavage occurs in the rds consistent with the observation of a primary kinetic isotope effect.



When $Z = \text{F}$, the greater acidity of the ortho hydrogens and the greater strength of a C-F bond relative to C-I, C-Br, and C-Cl favor carbanion formation.

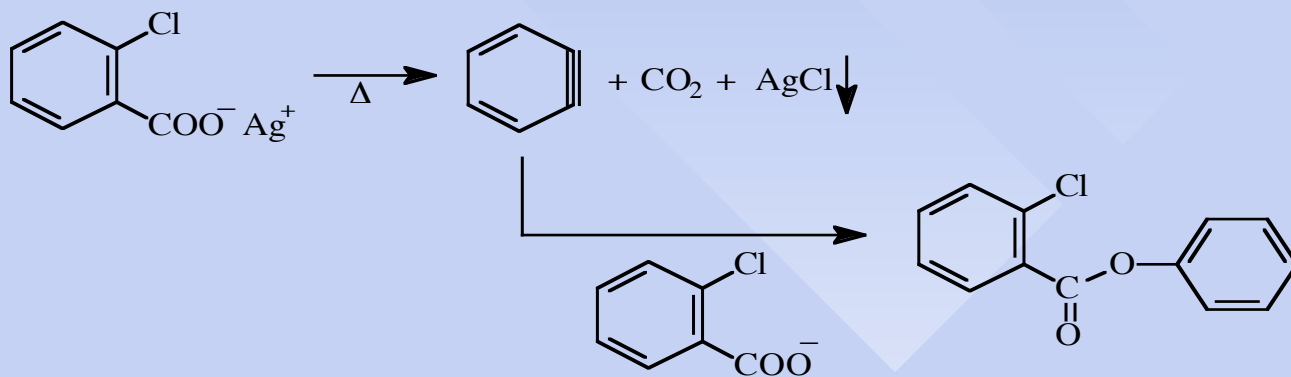
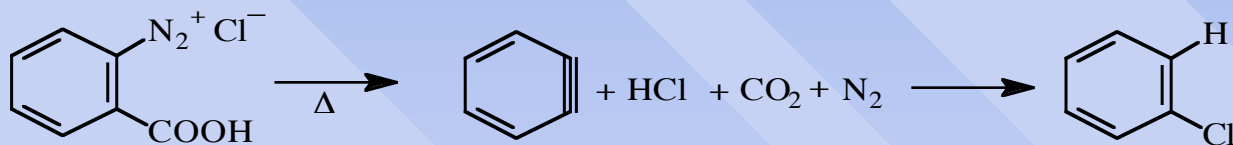
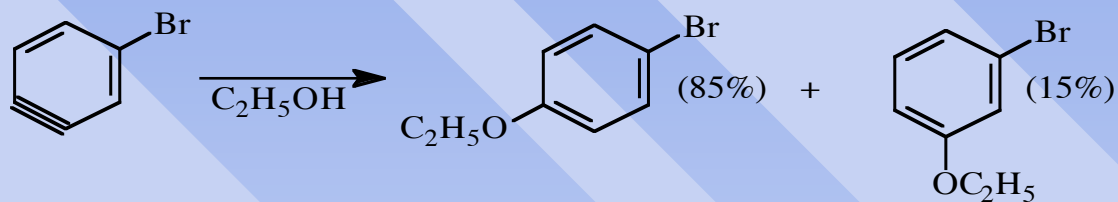
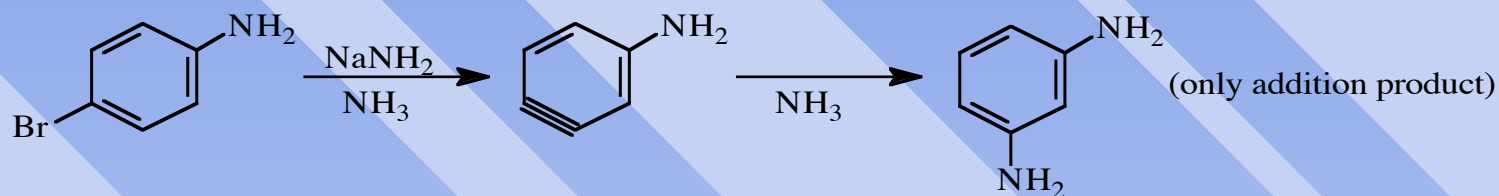
METHODS OF GENERATING BENZYNES

- 1. Dehydrohalogenation**
- 2. Elimination from organolithium or organomagnesium precursors**
- 3. Loss of neutral leaving groups**
- 4. Photolytic and/or Pyrolytic methods**



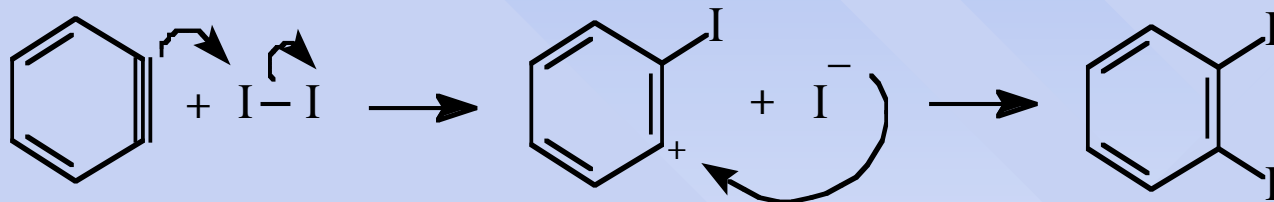
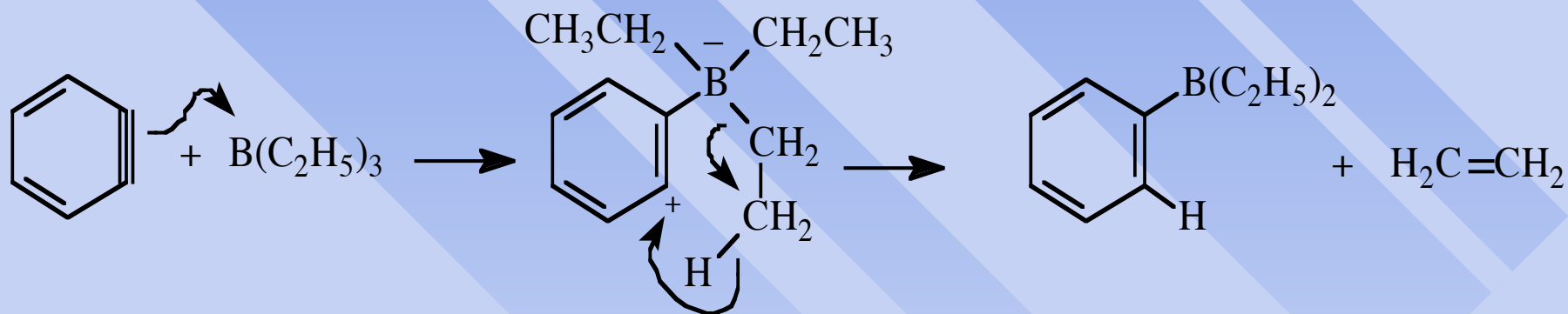
Typical Benzyne Reactions

Nucleophilic addition reactions



Typical Benzyne Reactions

Electrophilic addition reactions



Typical Benzyne Reactions

Cycloaddition reactions

