

UNIT - I Free Radical Reactions Coupling of Alkynes

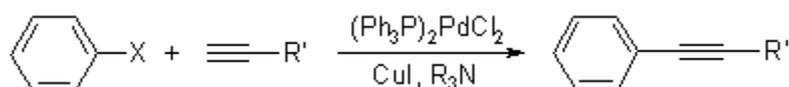
In organic chemistry, the **coupling of alkynes** refers to a broad class of reactions where terminal or internal alkynes are joined to form larger molecules, typically mediated by transition metal catalysts. These reactions are essential for synthesizing complex structures like **1,3-enynes**, **1,3-diynes**, and **conjugated polymers**. Coupling of alkynes involves forming carbon-carbon bonds from terminal alkynes, primarily producing symmetric conjugated diynes via oxidative methods (Glaser/Hay) or unsymmetrical 1,3-enynes via palladium-catalyzed cross-coupling (Sonogashira). These reactions are essential for building complex molecular frameworks in organic synthesis, including macrocycles and natural products.

1. Oxidative Homocoupling (Glaser-type)

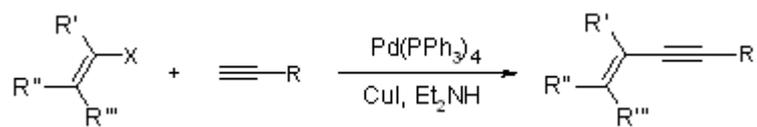
These reactions join two terminal alkynes to form a symmetrical 1,3-diyne

- **Hay Coupling:** A more efficient variant using a catalytic -TMEDA complex, allowing for better solubility and milder conditions.
- **Eglinton Reaction:** Uses stoichiometric amounts of copper(II) salts (e.g., cupric acetate) to effect the coupling.
- **2. Metal-Catalyzed Dimerization to 1,3-Enynes**
- Instead of diynes, transition metals (Pd, Rh, Ru) can catalyze the coupling of alkynes to form **conjugated enynes**
- **Palladium Catalysis:** Particularly the /TDMPP system, which is highly effective for "head-to-tail" coupling, producing specific regioisomers used in natural product synthesis.
- **Rhodium and Ruthenium:** These metals often provide high **stereoselectivity**, allowing for the selective synthesis of *cis*- or *trans*-isomers depending on the ligands used.
- **3. Cross-Coupling Reactions**
- These involve joining an alkyne with a different organic fragment (aryl, vinyl, or another alkyne).
- **Sonogashira Coupling:** The most famous cross-coupling involving alkynes. It joins a terminal alkyne with an aryl or vinyl halide using a **palladium catalyst** and a **copper(I) co-catalyst**.

Sonogashira Coupling



This coupling of terminal alkynes with aryl or vinyl halides is performed with a palladium catalyst, a copper(I) cocatalyst, and an amine base. Typically, the reaction requires anhydrous and anaerobic conditions, but newer procedures have been developed where these restrictions are not important.



Mechanism of the Sonogashira Coupling

