**WITTIG REACTION**

**WITTIG REACTION** - A carbon-carbon double bond forming reaction

Phosphorous-Carbon Ylide (molecule with adjacent positive and negative charges)

\[
\begin{align*}
R \text{C=O} & + \text{Ph}_3\text{P}=\text{CHR} \rightarrow \text{R'C=C'R} + \text{Ph}_3\text{P}=\text{O} \\
\text{PhC=CH} & + \text{H}_2\text{C}=\text{PPh}_3 \rightarrow \text{PhC=CH} + \text{O}=\text{PPh}_3 \\
\text{H=CH} & + \text{Ph}_3\text{P}=\text{C} \rightarrow \text{H}_2\text{C}=\text{C} + \text{O}=\text{PPh}_3 \\
\text{PhC=O} & + \text{Ph}_3\text{P}=\text{C} \rightarrow \text{PhC=CH} + \text{O}=\text{PPh}_3
\end{align*}
\]
**Preparation of Wittig Reagent from Alkyl Halides**

Wittig Reaction

PREPARATION OF WITTIG REAGENT: formation of Ph₃P=CH-Ph from PhCH₂Cl
An S₂N2 reaction

Triphenylphosphine + Benzyl chloride = Benzyltriphenylphosphonium chloride
**WITTIG REACTION**

Benzyltriphenylphosphonium chloride + trans-Cinnamaldehyde yields 1,4-diphenyl-1,3-butadiene (E,E and E,Z) + Triphenylphosphine oxide (E,E) isomer is the major product.

**Trans-cinnamaldehyde**

**1,4-Diphenyl-1,3-butadiene**

**Triphenylphosphine oxide**
**Mechanism of Wittig Reaction**

**Step 1:** Ylide formation: benzyltriphenylphosphonium chloride + NaOH = phosphonium ylide

*Ylide*: a neutral dipolar molecule with opposite charges on adjacent atoms. Ylides function as carbon nucleophiles (resonance forms for ylides to illustrate stability)

\[
\text{Ph}_3\text{P} = \text{CHR} + \text{H} - \text{C} - \text{R}' \rightarrow \text{Ph}_3\text{P} = \theta \text{CHR}
\]

**Step 2:** Nucleophilic attack by ylide carbon on carbonyl carbon on trans-cinnamaldehyde-Betaine formation (arrow-pushing illustration)

*Betaine*: a neutral dipolar molecule with opposite charges on non-adjacent atoms

**Step 3:** Oxophosphetane formation (P-O bond formation)(arrow- pushing illustration)

*Oxophosphetane*: 4-membered ring with phosphorous and oxygen atoms adjacent

**Step 4:** Breakdown of oxophosphetane (arrow-pushing illustration)
**WITTIG REACTION**

**PROCEDURE:**
1. To a 50 mL flask containing 20 mL of dichloromethane add 3.0 g of benzyltriphenylphosphonium chloride and 1.0 mL of trans-cinnamaldehyde.
2. Add 5 mL of freshly prepared 50% NaOH (2.5 g of NaOH in 5% mL H₂O) a magnetic stir-bar, wrap with parafilm and stir the mixture on a stir plate for 30 min.
3. Transfer the mixture to a separatory funnel using 20 mL of dichloromethane and 20 mL of H₂O. Shake, allow the layers to separate and retain the dichloromethane (bottom) layer. Discard the water layer.
4. Dry the dichloromethane layer with anhydrous MgSO₄, filter and evaporate on a hot plate to an oil.
5. Add 35 mL of 50% ethanol, mix and break up large masses with a stir rod.
6. Collect the precipitate on a filter and wash with 10 mL of 50% ethanol.
7. Recrystallize the product from 10 mL 95% ethanol.
8. Take a melting point, calculate a percent yield and obtain an IR spectrum. Look for an absence of a carbonyl stretch at about 1700 cm⁻¹.