Ylide’s - Sulfur, Phosphorous, Nitrogen

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What is Ylide?

✓ A compound having an uncharged molecule containing a negatively charged carbon atom directly bonded to a positively charged atom of sulphur, phosphorus, nitrogen or another element.

OR

✓ A ylide or ylid is a neutral dipolar molecule containing a formally negatively charged atom (usually a carbanion) directly attached to a heteroatom (usually nitrogen, phosphorus or sulphur), with a formal positive charge and in which both atoms have full octets of electrons.

Types of Ylide’s

1. Sulfur Ylide
2. Phosphorous Ylide
3. Nitrogen Ylide
✓ **Sulfur ylide:** Dimethylsulphonium methylide and dimethylsulfoxonium methylide (Corey-Chaykovsky reagent) are two important types of sulfur ylides.

✓ **Preparation:**

Sulfur ylides are prepared by deprotonation of the corresponding sulfonium salts, which can be prepared from the reaction of either dimethylsulphide or dimethylsulphoxide with methyl iodide.
✓ **Synthesis of Epoxides Vs Cyclopropanation**

Stabilized ylide forms cyclopropane ring (thermodynamically favored product) whereas unstable ylide provided the epoxide (kinetically favored product), when reacted with alpha, beta unsaturated ketones. But gives same product with simple ketones (without conjugated double bond).
**Phosphorous Ylide**

Methods of preparation:

1. Reaction of Alkyl halide with Triphenyl phosphine

   $$\text{PPh}_3 + R'\text{CH}_2\text{X} \xrightarrow{\text{Heat}} \text{Ph}_3\text{P}^-\text{CH}_2R'\text{X}^-$$

   $$X = \text{I, Br, Cl} \quad \text{Phosphonium salt}$$

   $$\text{Ph}_3\text{P}^-\text{CH}_2R'\text{X}^- \xrightarrow{\text{Base}} \text{PPh}_3\text{CH}_2R' \leftarrow \text{Ph}_3\text{P}^-\text{CH}_2R'$$

   Ylide     Ylene

2. Addition of a carbanion to a vinyl phosphonium salt

   $$\text{Ph}_3\text{P}^-\text{CH} \equiv \text{C}_2\text{H} + \text{R'}\text{Li} \xrightarrow{\text{Vinyl phosphonium}} \text{Ph}_3\text{P}^-\text{CH} \equiv \text{C}_2\text{H} \leftarrow \text{Ph}_3\text{P}^-\text{CH} \equiv \text{C}_2\text{H}$$

   Phosphonium Ylide
3. Addition of carbene to phosphene

\[
: \text{PPh}_3 + \text{CX}_2 \rightarrow \text{PPh}_3 \xrightarrow{X} \xrightarrow{X} \\
\text{Example:} \\
\text{Ph}_3\text{P} + \text{CBr}_4 \rightarrow \text{PPh}_3 \xrightarrow{\text{Br}} \xrightarrow{\text{Br}} + \text{Br}_2
\]

Triphenyl phosphine reacts with carbon tetrahalide to form dihalo ylide.
✓ Unstabilized ylides have either H or alkyl groups connected to the C atom.

✓ Alkyl groups donate electrons through the inductive effect, electron donating groups destabilize charge separation, so the reactions of such unstabilized ylides occur through the ylide form.

✓ Unstabilised ylide give Z selectivity in the reaction.

✓ e.g.

$$\text{Ph}_3\text{P} + \text{Br} \text{OMe} \xrightarrow{\text{Heat}} \text{Ph}_3\text{P} \text{OMe} \xrightarrow{\text{NaH or KOTBu}} \text{Ph}_3\text{P} \xrightarrow{\text{THF reflux}}$$
Phosphorous stabilised ylide

✓ Stabilized ylides have electron withdrawing groups connected to the C atom.
✓ Electron withdrawing groups stabilize negative charge through resonance.
✓ Stabilized ylide give E selectivity in the reaction.
✓ e.g. Preparation and reaction of Phosphorous stabilized ylide

\[
\text{Ph}_3\text{P} + \text{BrCH}_2\text{O} \xrightarrow{\text{Heat}} \text{Ph}_3\text{P}^+\text{CH}_2\text{O}^- + \text{Br}^- \quad \text{Ph}_3\text{P} + \text{BrCH}_2\text{O} \xrightarrow{\text{Na}_2\text{CO}_3, \text{H}_2\text{O}} \text{Ph}_3\text{P}^+\text{CH}_2\text{O}^- \quad \text{Ph}_3\text{P} + \text{Ph}_2\text{C}^+\text{CH}_2\text{O}^- \xrightarrow{\text{DCM, RT}} \text{Major} + \text{Minor}
\]

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Horner-Wadsworth-Emmons reaction

- Horner-Wadsworth-Emmons is one of the variations of the stabilized ylide which gives the E selective alkene.
- Preparation of the alkyl phosphonate - The Arbuzov reaction

\[
\begin{align*}
R-X + P(OEt)_3 \xrightarrow{\text{Heat}} & \quad R\text{-}\text{Et}X + \text{EtX} \\
X = \text{Cl, Br, I} \quad \text{Triethyl phosphite} & \quad X = \text{Cl, Br, I}
\end{align*}
\]

Mechanism

Triethyl phosphite

X = Cl, Br, I
Horner-wadsworth-Emmons reaction

Phosphonoacetate + Base → E-Alkene + Water Soluble

**Base:** NaOEt, NaHMDS, KO-t-Bu, NaH etc.

**Example:**

Phosphonoacetate + Base (NaH) → E-Alkene + Water Soluble
**Nitrogen Ylide**

✓ **Nitrogen ylide**: The nitrogen ylide are formed as intermediates in Sommelet rearrangement. This method is used for the conversion of the tetraalkylammonium halides into tertiary aromatic amines.

![Chemical diagram](image-url)

- **NaNH₂** + **liq NH₃** → **H₃C⁺N⁺CH₂**
- **H₃C⁺N⁺CH₂** → **H₃C⁺N⁺CH₃**

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