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Wittig Reaction

This reaction is named after its discover, the German chemist Georg wittig. This is an extremely useful reaction for the synthesis of alkenes by the interaction of aldehydes or ketones with triphenyl-phosphine ylide (wittig reagent).

e.g. - Benzophenone gives 1,1-diphenylethylene by treatment with triphenylphosphine-methylene.

$$(C_6H_5)_2C=O + H_2C=P(C_6H_5)_3 \longrightarrow (C_6H_5)_2C=CH_2 + (C_6H_5)_3P=O$$

1,1-diphenylethylene

Triphenylphosphine-oxide

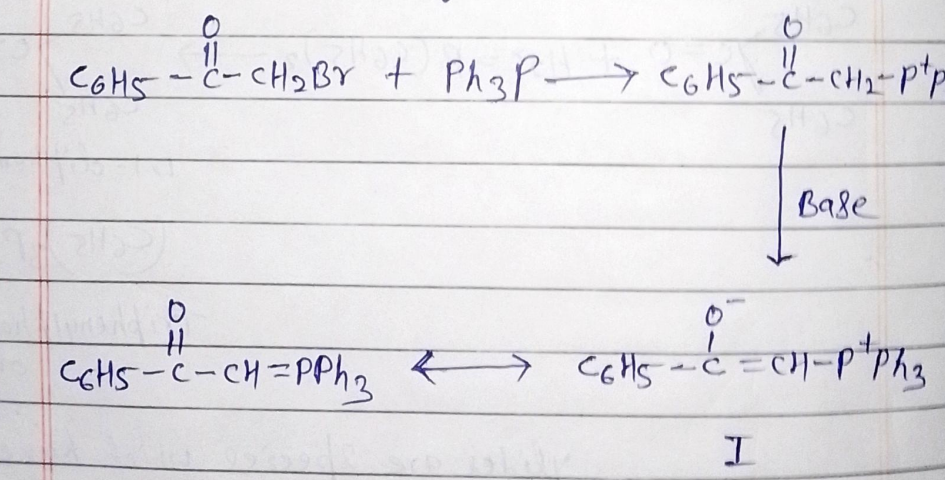
ylides are species which have charges of opposite sign an adjacent atom in their ground state, which are prepared by treatment of strong base (C_6H_5Li) on phosphonium salt (Triphenyl-Phosphine and alkyl halide)

$$(C_6H_5)_3P \xrightarrow{CH_3Br} (C_6H_5)_3^{+}CH_3Br^{-}$$

$$(C_6H_5)_3^{+}CH_3Br^{-} \xrightarrow[C_6H_5ONa]{C_6H_5Li \text{ or}} (C_6H_5)_3P{=}CH_2 + LiBr + C_6H_6$$

The carbonyl compound is then added directly to the ethereal solution to accomplish wittig reaction.

Reactivities of the wittig reagents vary according to their structures. usually, they are highly reactive, unstable reagents which are strongly nucleophilic and consequently react readily with a carbonyl group. However, the presence of electron-withdrawing substituent in the alkylidene portion of the ylide decreases its nucleophilic character and hence such reagents do not react readily with the carbonyl compounds.



The ylide I is a stable solid and does not react with cyclohexanone. Its usual stability is believed to be due to resonance.

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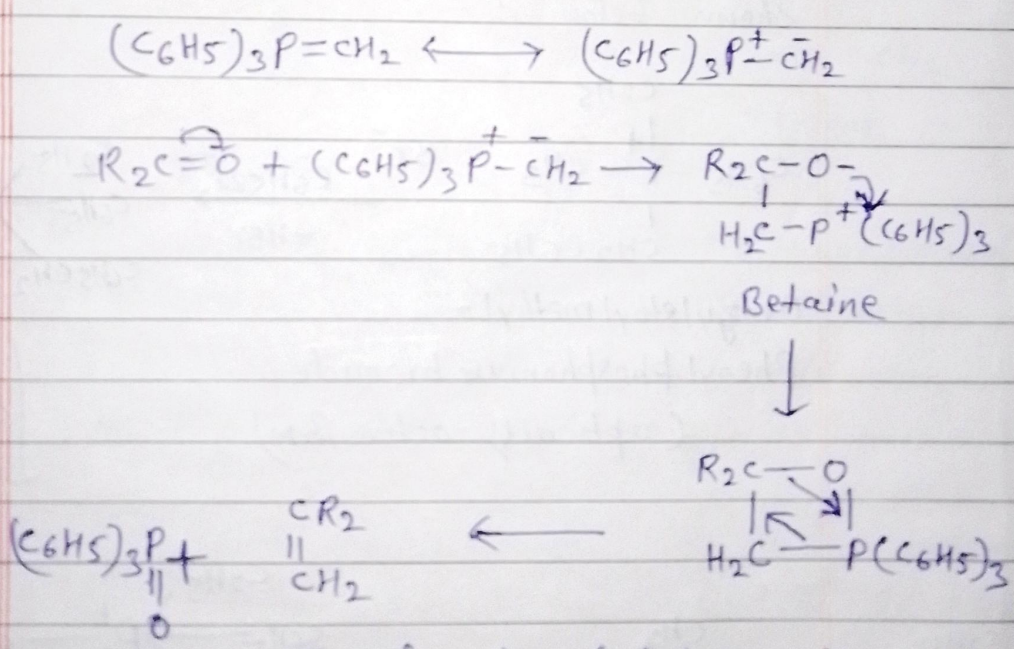
Mechanism :- The triphenyl phosphine ylide which is a resonance hybrid of a methylene and an ylide, attacks on the carbonyl compound and forms a new carbon - carbon bond between the electronegative carbon atom of the phosphorane and the electronegative carbon atom of the carbonyl group. The dipolar transition state (betaine) then collapse by intermolecular attack of the negatively charged oxygen on the positively charged Phosphorous atom via a four centre transition state.



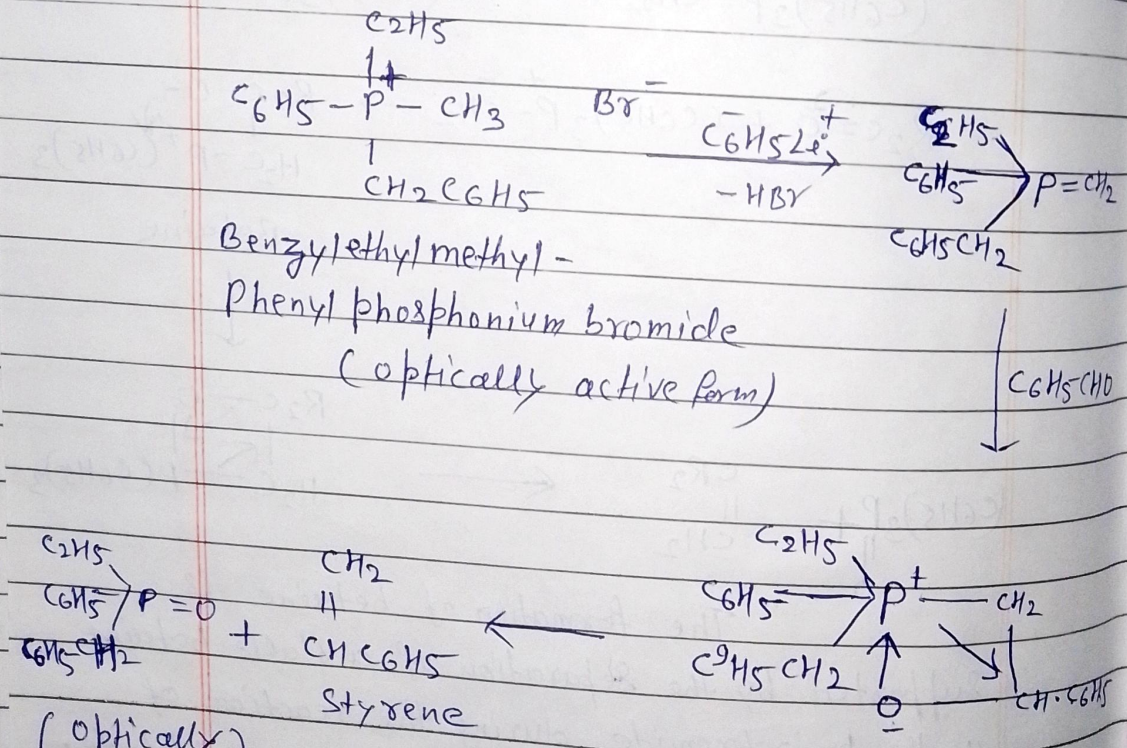
The formation of betaine is supported by the separation of a stable betaine as the hydrobromide during the reaction of methylene triphenylphosphorane with Benzaldehyde.

$$(C_6H_5)_3\overset{+}{P}-\overset{-}{C}H_2 + C_6H_5CHO \longrightarrow (C_6H_5)_3\overset{+}{P}CH_2\underset{}{\overset{O^-}{\overset{|}{C}H}}C_6H_5$$

$$\downarrow HBr$$

$$\left[(C_6H_5)_3\overset{+}{P}CH_2\overset{OH}{\overset{|}{C}H}\cdot C_6H_5\right]Br^-$$

This type of mechanism is further supported by the fact that the wittig reaction of an optically active phosphonium salt proceeds with complete reaction of stereochemical configuration as shown below :-



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Applications :-

(i) **Preparation of olefins :-** This reaction provides a method for the preparation of olefins where the position of the double bond is definite.

a. $C_6H_5(CH_3)C=O \xrightarrow{CH_2=P(C_6H_5)_3} C_6H_5(CH_3)C=CH_2$

Acetophenone → α-methyl Styrene

b. $C_6H_5 \cdot CH=O \xrightarrow{CH_2=P(C_6H_5)_3} C_6H_5 \cdot CH=CH_2$

Styrene

(ii) **Synthesis of natural products :-** various natural products such as squalene, β-carotene, vit. A_1, vit. D_3, corticoids etc. can be synthesised by this reaction.

(iii) **Preparation of carbodi-imides :-** It is an important reagent used during the synthesis of polypeptides and nucleic acids, can be prepared from isocyanates in the following manner.

$$RN=C=O + R'_3P=O \longrightarrow RN=PR'_3 + CO_2$$

$$RN=C=O + RN=PR'_3 \longrightarrow RN=C=NR + R'_3P=O$$

carbodi-imide

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where R may be alkyl, alicyclic or aromatic group. e.g. - In dicyclohexyl carbodi-imide, $R = C_6H_{11}$ (cyclohexyl).