

(1)

Date _____
Page _____

Class - P.G. Sem II

Subject - Chemistry

Paper - C-C-VIII

Unit - 1

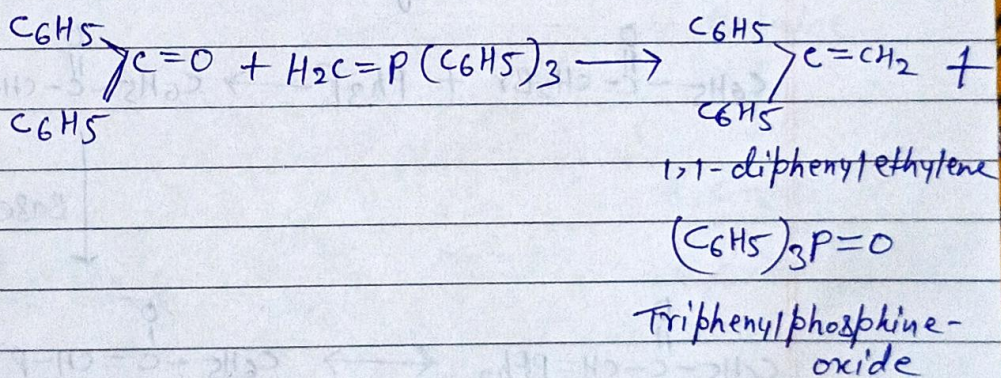
Dr. Rashmi Sonka

Dept. of Chemistry, H.D.J.C. Ara

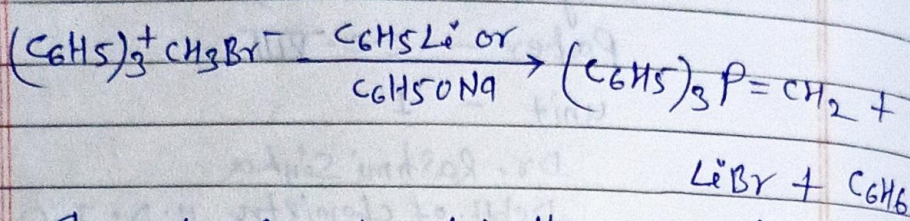
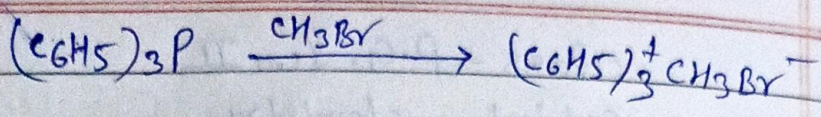
Wittig Reaction

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 triphenylphosphine ylide (Wittig reagent).

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

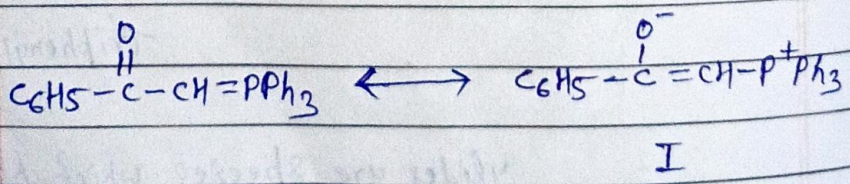
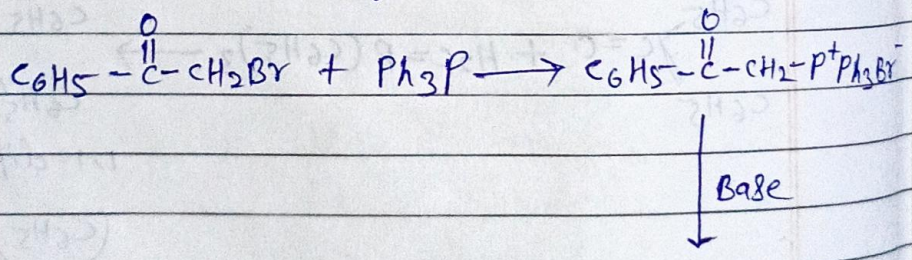


ylides are species which have charges of opposite sign on adjacent atom in their ground state, which are prepared by treatment of strong base ($\text{C}_6\text{H}_5\text{Li}$) on phosphonium salt (Triphenylphosphine and alkyl halide)



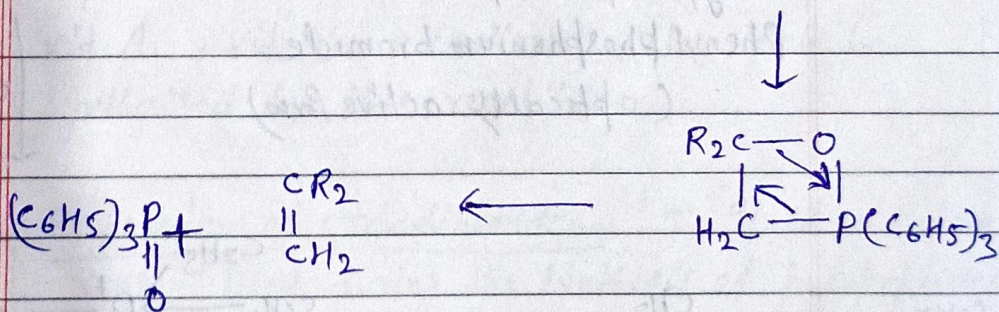
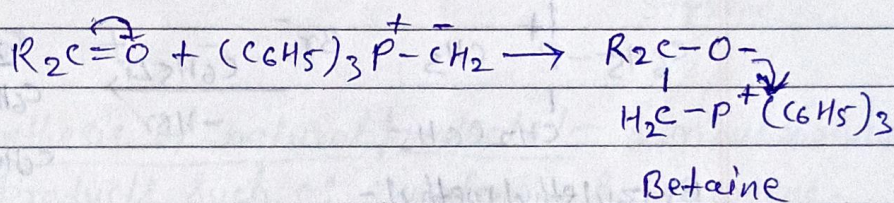
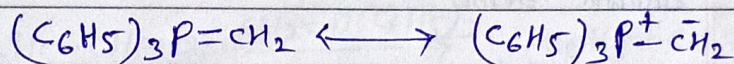
The carbonyl compound is then added directly to the ethereal solution to accomplish Wittig reaction.

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 compound.

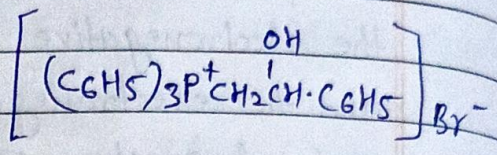
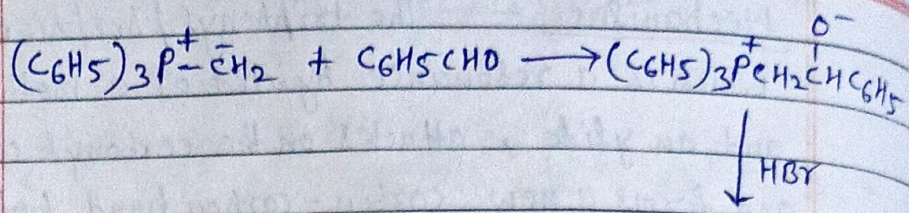


The ylide I is a stable solid and does not react with cyclohexanone. Its usual stability is believed to be due to resonance.

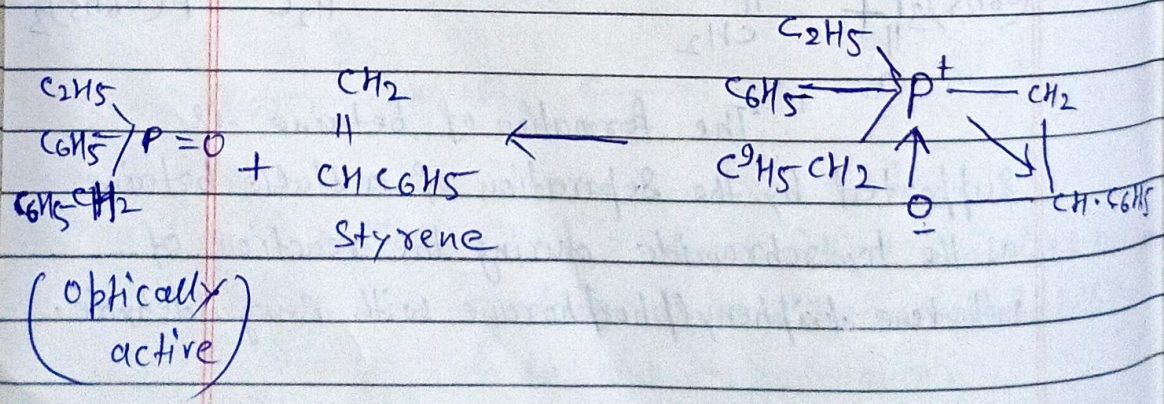
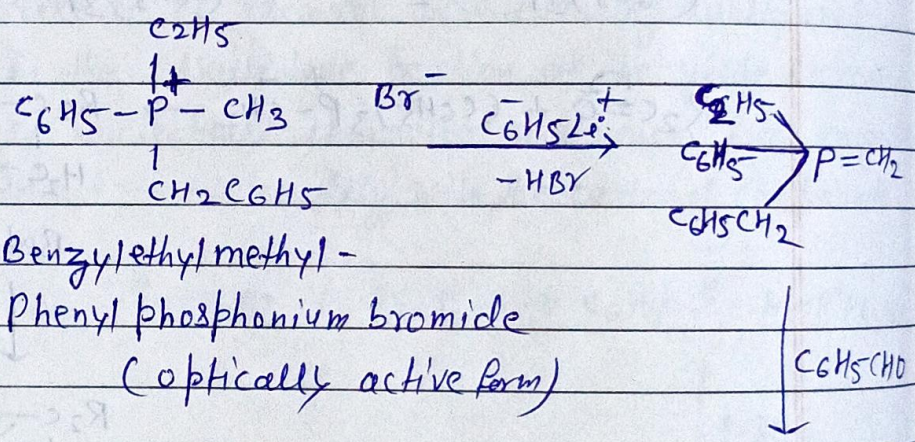
Mechanism 1 — The triphenyl phosphine ylide which is a resonance hybrid of a methylene and an ylide, attacks on the carbonyl compound and forms a new carbon-carbon bond between the electronegative carbon atom of the phosphorane and the electronegative carbon atom of the carbonyl group. The dipolar transition state (betaine) then collapses by intermolecular attack of the negatively charged oxygen on the positively charged phosphorus 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.

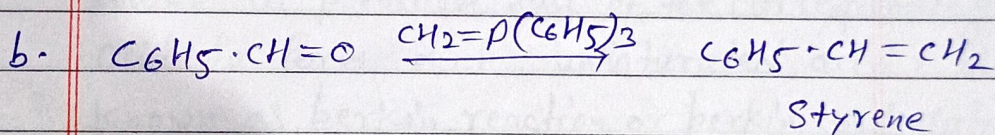
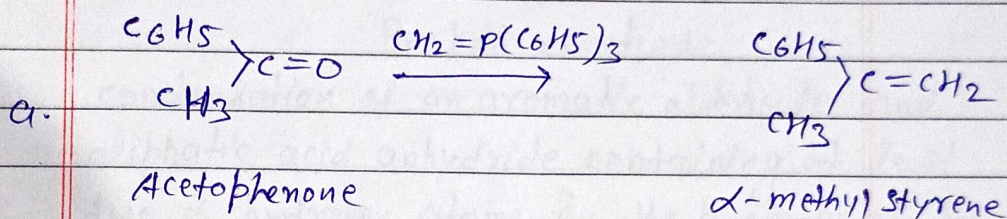


This type of mechanism is further supported by the fact that the Wittig reaction of an optically active phosphonium salt proceeds with complete retention of stereochemical configuration as shown below :-



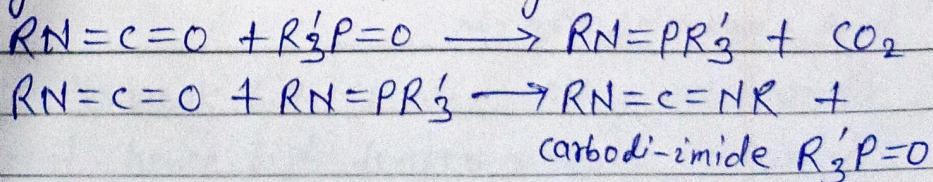
Applications!-

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



- (ii) Synthesis of natural products! — various natural products such as squalene, β-carotene, vit. A₁, vit. D₃, 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.



6

Date _____

Page _____

where R may be alkyl, alicyclic or aromatic group. e.g. - in dicyclohexyl carbodi-imide,
~~the~~ ~~the~~ ~~the~~ R = C₆H₁₁ (cyclohexyl).