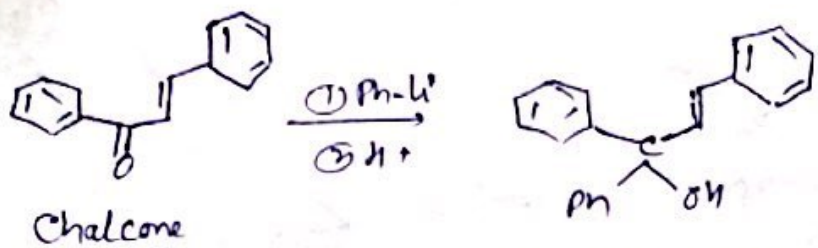
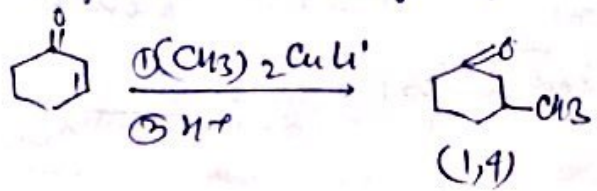


It has been observed that Grignard reagents react with α, β unsaturated compounds to give 1,2 or 1,4 addition products depending upon the structure of the carbonyl compounds. It is due to steric hindrance, organolithium reagents give exclusively the 1,2 addition products.

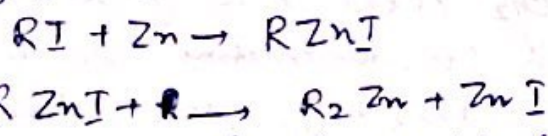


Exclusive formation of 1,4 addition product - can be achieved by the use of lithium dialkyl cuprates. A characteristic of the reaction is that only one of the R groups of R_2CuLi adds to the substrate, the other is wasted.



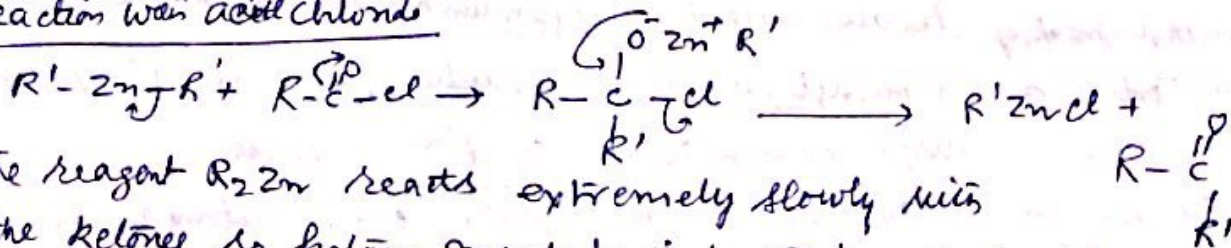
Organozinc Compounds.

They were first organic compounds to be prepared in the laboratory. Organozinc compounds are far less reactive and are not used commonly for organic synthesis.



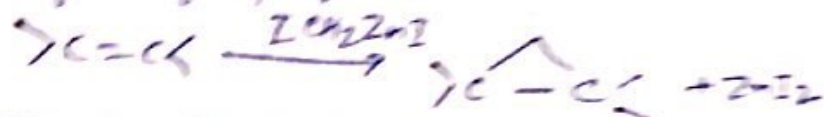
They are non polar, low boiling liquids. They do not react with CO_2 and react slowly with ketones, esters and cyanides.

Reaction with acid chlorides

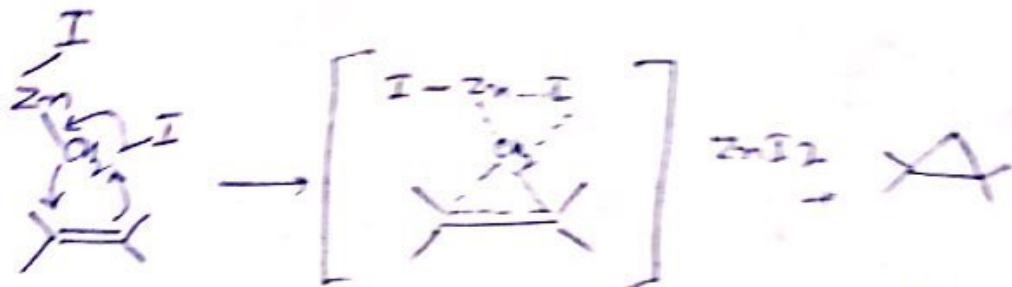


The reagent R_2Zn reacts extremely slowly with the ketones. So ketones must be isolated from the reaction mixture. Organozinc compounds are obtained as intermediates in the well known Reformatsky reaction, This reaction is used for the prepn of β -hydroxy acids.

34 A very useful organic compound. While reacts with alkenes to give cyclopropane derivatives.



The reaction takes place via a concerted manner, involving a cyclic transition state.



This reaction is known as Simmons-Smith Reaction and the organozinc compound, iodomethyl zinc iodide, is known as Simmons-Smith Reagent.

Wittig Reaction V.IMP

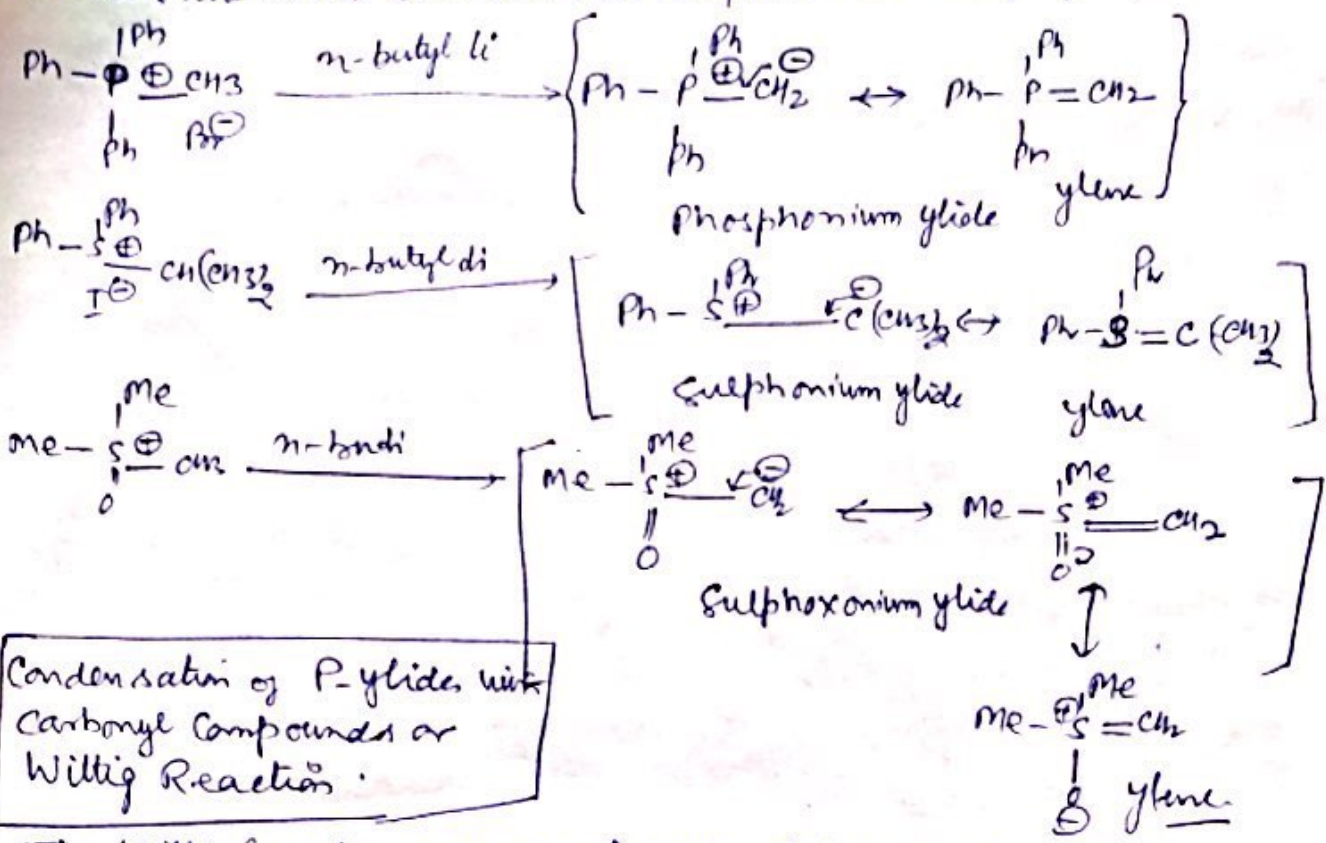
It is possible to remove a proton from the methyl group of alkylmethyl ammonium iodide ($R_3N^+CH_3I^-$) with a strong base, whereby a betaine is produced with the structure $R_3N^+CH_2^-$. betaine in which the positive and negative charges are localized adjacent atoms as in $R_3N^+CH_2^-$ is called an ylide. The 'yl' refers to the covalent bond in the structure $R_3N^+CH_2^-$ while 'e' refers to the presence of ionic bond in the same structure. ylide $R_3N^+CH_2^-$ is called ammonium ylide or an N-ylide.

With strong base it is also possible to remove a proton from methyl group of trialkyl methyl phosphonium halide, trimethyl sulphoni-iodide or trimethyl sulphoxonium iodide, forming phosphonium or sulphoxonium ylides or Por S-ylides.

The N-atom is the centre of the N-ylide. P and S atoms in the ylide of the Por S-ylides may exceed their valency electron octet. They share a fifth electron pair. Thus Resonance forms exist in which the hetero atom exceeds its valency electrons. These are called ylidene resonance forms.

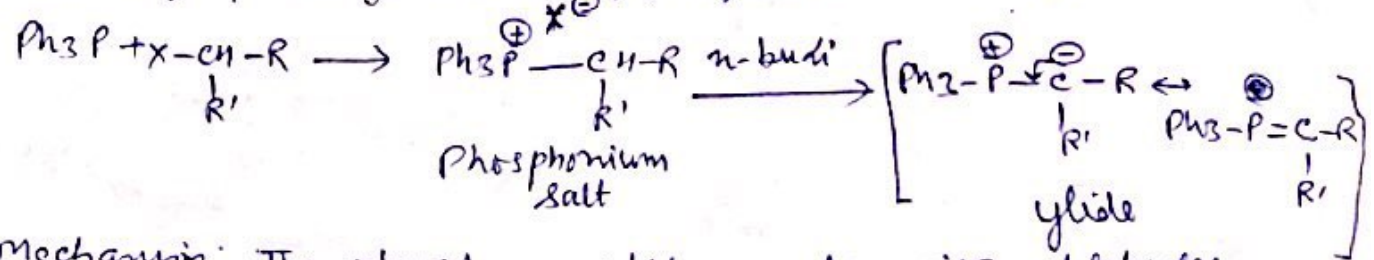
Wittig Reaction (contd.)

The 'ene' part of the designation 'ylone' refers to the double bond between the hetero atom and the deprotonated alkyl group.

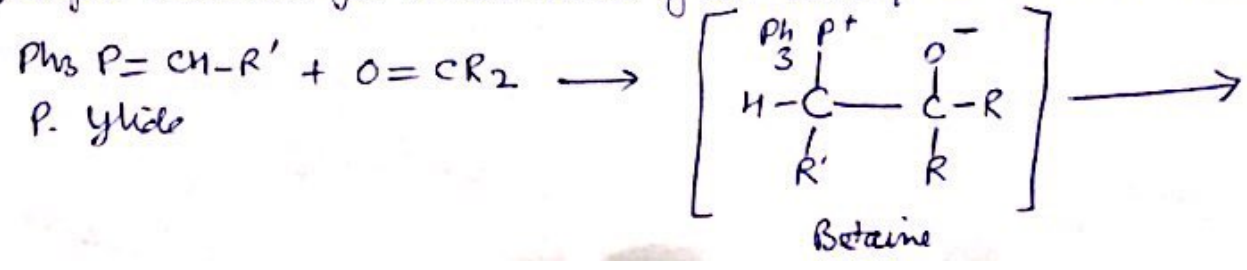


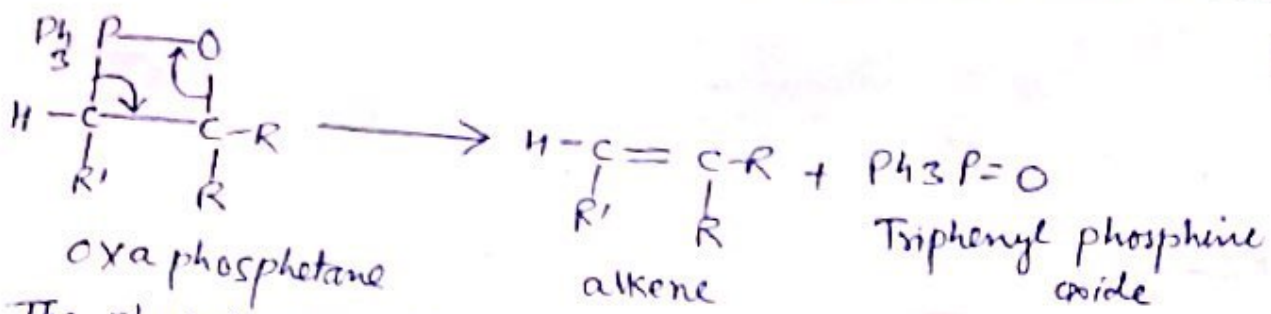
Condensation of P-ylides with Carbonyl Compounds or Wittig Reaction.

The Wittig Reaction is a C,C forming olefin synthesis for phosphonium ylides and Carbonyl Compounds. In the Wittig Reaction an aldehyde or a ketone is treated with a phosphorous ylide (phosphorane) to give an olefine. The phosphorous ylides are prepared by treatment of phosphonium salt with a base and phosphonium salts are prepared by interaction of phosphine and an alkyl halide



Mechanism: The phosphorous ylide reacts with aldehydes or ketones to form an intermediate betaine, which eliminates tri phenyl phosphine oxide to give an olefine. This is very useful reaction for introduction of an exocyclic double bond.

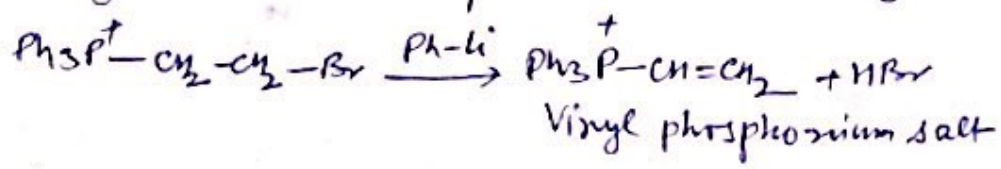




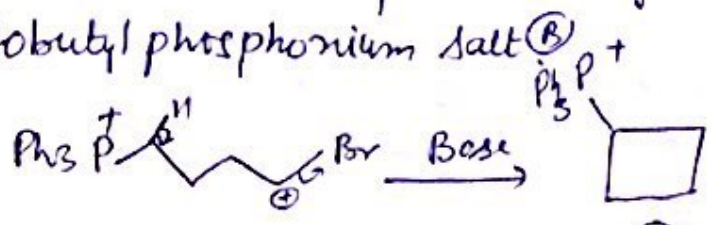
The phosphonium salt contains acidic hydrogen, which can be removed by a moderately strong base (e.g. phenyl lithium or NaH.) to give phosphorus ylide known as Wittig reagent. Phosphorus ylides because of negative charge on carbon atom are strong nucleophiles and add to carbon-oxygen double bond of aldehydes or ketones to form betaine which collapses to a four membered ring called oxaphosphetane.

It has been postulated that either of the intermediates i.e. betaine or ^{oxe}phosphetane may decompose to give the product, the alkene. This reaction is extremely useful for preparing alkenes from aldehydes or ketones.

If the phosphonium salt contains a leaving group such as Br, OMe or PhSP⁺ in the β-position, treatment with base gives elimination product and not the ylide.



Another side reaction of phosphonium salt bearing a hetero atom is intramolecular displacement of hetero atom to form triphenyl cyclobutyl phosphonium salt.



Some other applications include - (1) Inclusion of Exocyclic methylene gp (2) Prep of α,β unsaturated esters and (3) Synthesis of Diene etc.