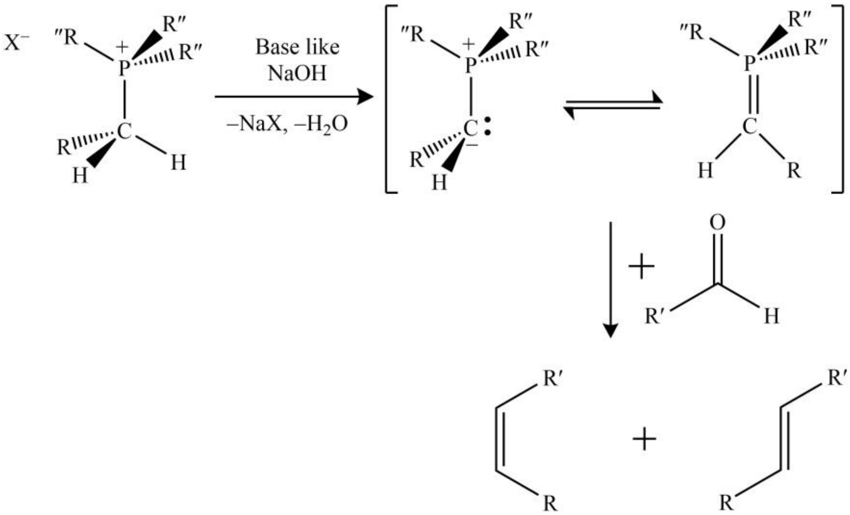
❖ Wittig Reaction

The Wittig olefination (or Wittig reaction) may simply be defined as a chemical transformation where a ketone or aldehyde reacts with a triphenyl phosphonium ylide (Wittig reagent).

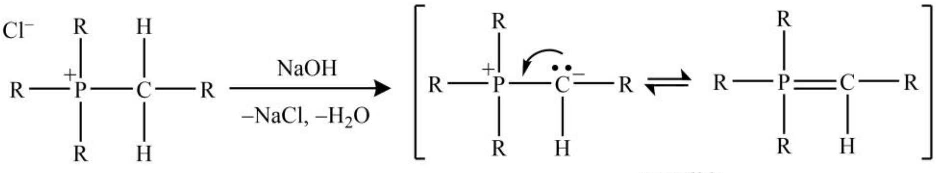
The conversion of aldehydes and ketones to alkenes is one of the most common uses of Wittig reactions. Usually, the Wittig reaction is employed to add a methylene group using $Ph_3P=CH_2$ (methylenetriphenylphosphorane or Wittig reagent). The importance of Wittig reaction can be imagined by the fact that George Wittig, who invented this reaction, was awarded the Nobel prize in 1979 for the same work.



With help of Wittig reagent, a camphor-like ketone, which has a very much sterically hindered carbon, can also be transformed into its methylene derivative. Now before we proceed further to study different aspects of Wittig reaction, we need to first know what a Wittig reagent actually is and how does it behave around different kinds of substrates.

➢ *The Wittig Reagent (An Organophosphorus Ylide)*

The Wittig reagent is a ylide, and a ylide may be defined as a compound with opposite charges on adjacent atoms both of which have complete octets. These ylides are obtained as the zwitterionic conjugate bases of the cationic part of phosphonium salts.



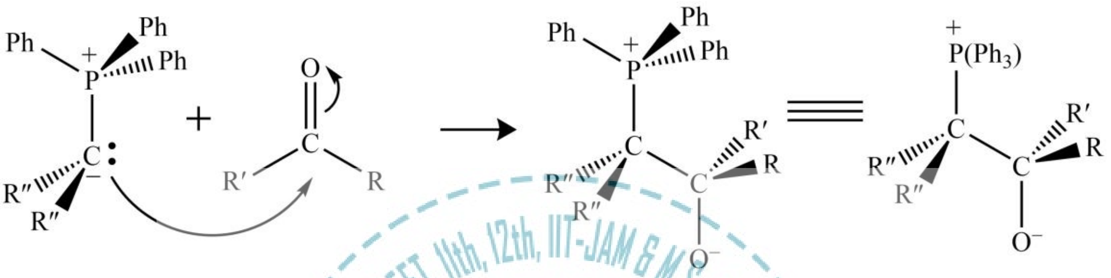
An Ylide

Since these ylides are stabilized by $p\pi$-$d\pi$ bonding, the carbanions adjacent to the phosphonium centers also get stability benefits from the same. It is also obvious that the phosphorus's ability to hold more than eight valence electrons permits for a resonance structure with double-bonded; and therefore, enhances the stability.

➢ ***Mechanism of Wittig Reaction***

The NMR studies have confirmed the formation of two intermediates after the generation of the first carbon-carbon bond during the Wittig reaction, the betaine (a dipolar species) and oxaphosphatane (a four-membered heterocyclic structure). The final product will be obtained by the cleavage of oxaphosphatane to alkene and phosphine oxide which is irreversible and exothermic in nature. Precisely, the mechanism can primarily be divided into three steps as given below.

1. Nucleophilic attack on the carbonyl:

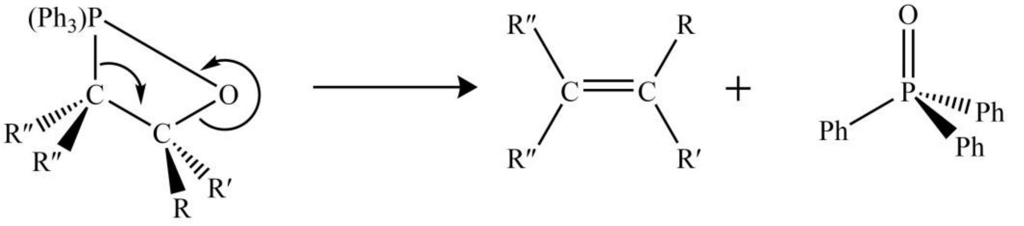


Betain

2. Formation of four-membered ring:

Oxaphosphatane

3. Generation of the alkene:

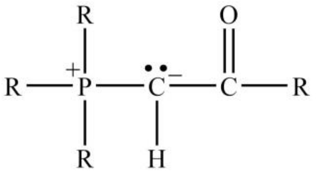


Oxaphosphatane

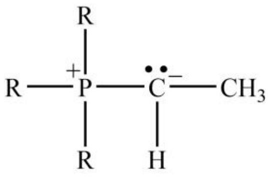
A major benefit of the alkene synthesis via Wittig's route is that, unlike alcohol dehydration, the site of the double bond is fixed absolutely.

➢ *Stereochemistry of Wittig Reaction*

In the case of aldehydes, the geometry around double bonds can easily be predicted by analyzing the ylide’s nature. With unstable ylides (R_3 = alkyl), (Z)-alkenes are formed with reasonable to very high selectivity. With stable ylides (R_3 = ester or ketone), (E)-alkenes are formed with a very high magnitude of selectivity. The selectivity ratio (E/Z) is usually very poor with semi-stabilized ylides (R_3 = aryl).



will give E-alkene

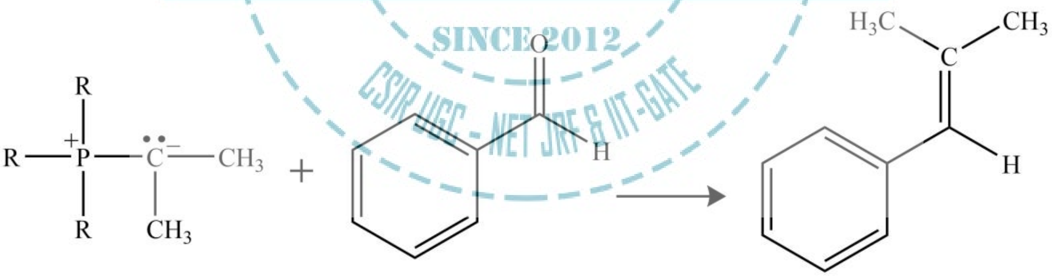


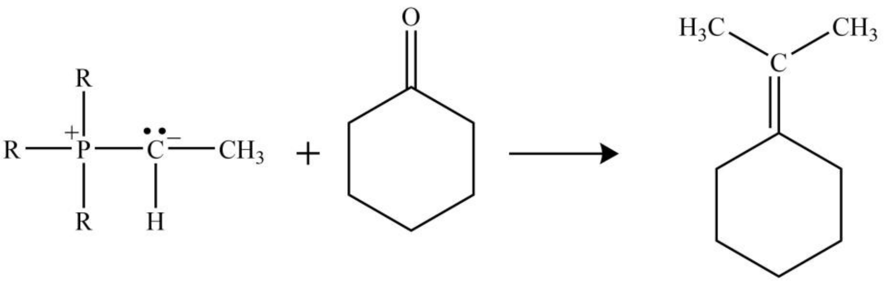
will give Z-alkene

If we want to get (E)-alkene but from a destabilized ylide, the Schlosser modification of the Wittig reaction can be employed. Otherwise, the (E)-alkene selectively can also be obtained via Julia olefination and its different variants. Since the (E)-enoate (α, β-unsaturated ester) are prepared via Horner-Wadsworth-Emmons reaction, the same can be used as a substitute for the Wittig reaction. On a final note, the Still-Gennari modification of the Horner-Wadsworth-Emmons reaction can be used to get (Z)-enoate.

➢ *Examples of Wittig Reaction*

Some of the most common examples of organic chemical transformation via Wittig reagent are given below.



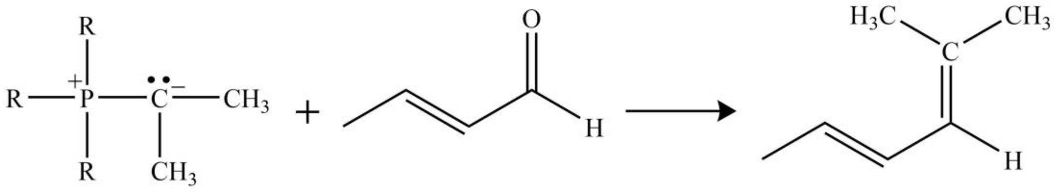


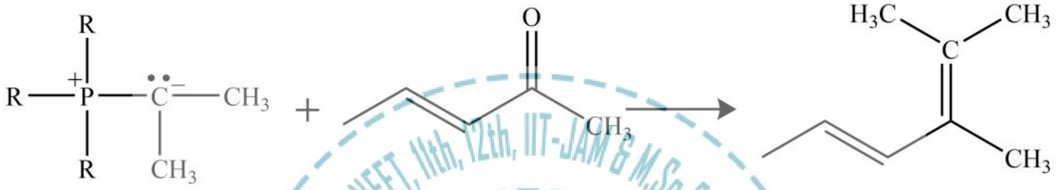
It has been observed that the Wittig reagents usually tolerate carbonyl compounds with numerous types of functional groups like OH, OR, epoxide, aromatic nitro, and ester groups.

- ***Applications of Wittig Reaction***

Some of the most common applications of organic chemical transformation via Wittig reagent are given below.

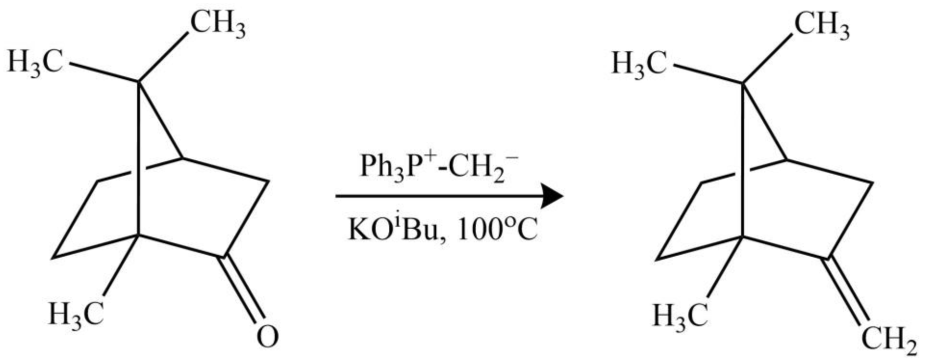
1. The conversion of aldehydes and ketones to alkenes is one of the most common uses of Wittig reactions.





2. The Schlosser modification Wittig reaction can be used to get allylic alcohols by the reaction of the betaine ylide with a secondary aldehyde.

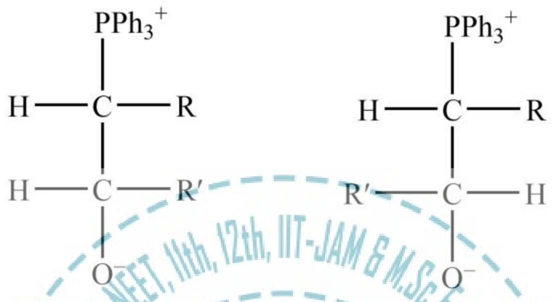
3. Even a sterically hindered ketone such as camphor can be converted to its methylene derivative.



➢ *Limitations of the Wittig reaction*

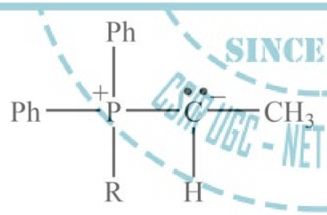
Some of the most common limitations of organic chemical transformation via Wittig reagent are given below.

1. The Wittig reaction proceeds mainly via the erythro betaine intermediate that gives rise to the Z-alkene, which is problematic if the E-isomer is the desired product. This limitation can be overcome by converting the erythro betaine into threo betaine using phenyllithium at low temperature which can afford to yield the E-alkene (Schlosser modification).

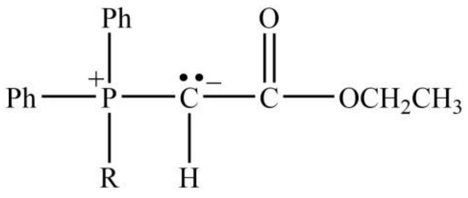


erythro betain (gives Z-alkene) threo betain (gives E-alkene)

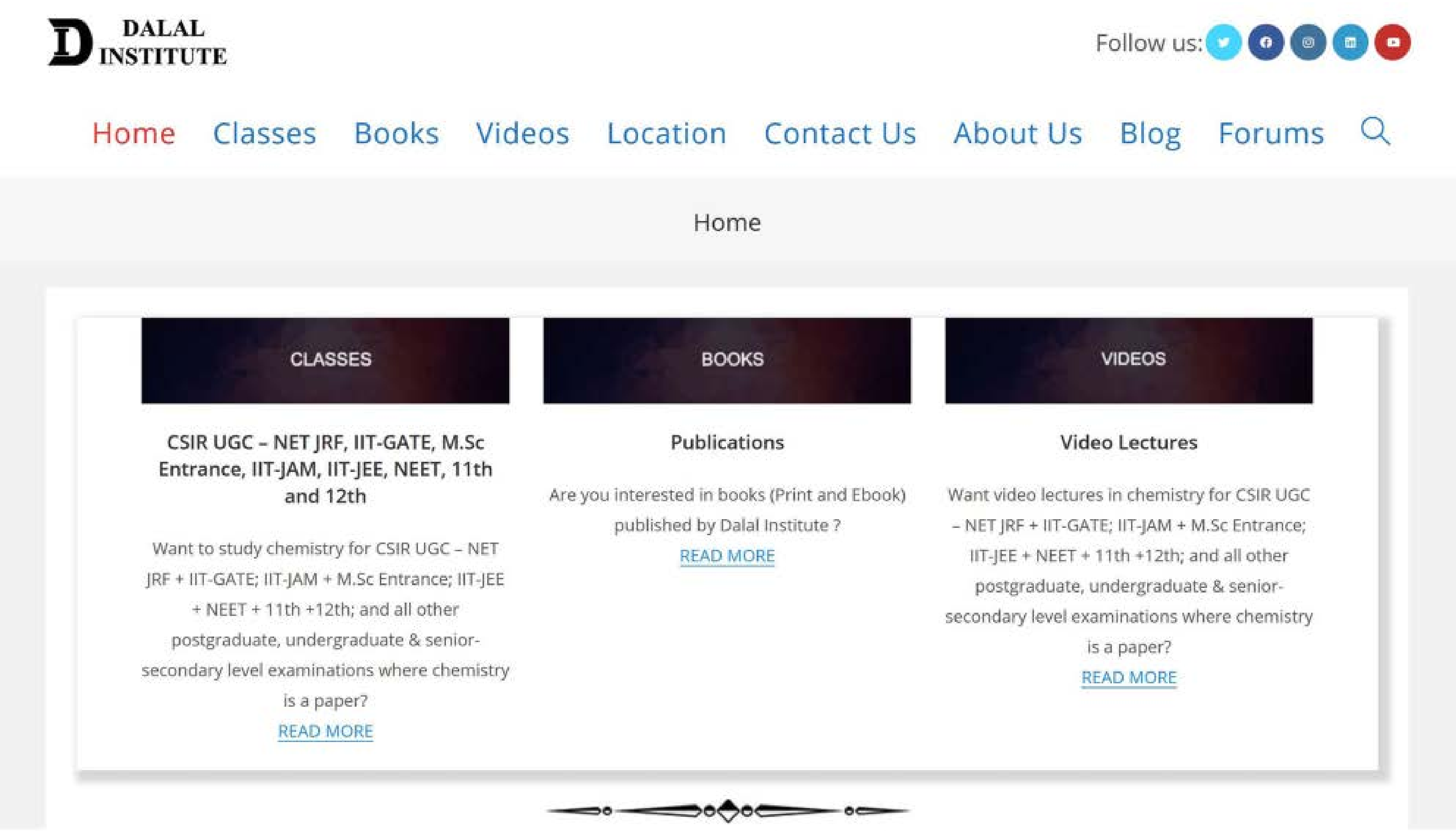
2. The yield given by conventional Wittig reaction is very low when a sterically hindered ketone is used, and the rate of transformation was also found to be very small. This is especially true for stabilized ylides. This limitation can be overcome by using a phosphonate ester (Horner-Wadsworth-Emmons reaction).



Non-stablized ylide



Stablized ylide



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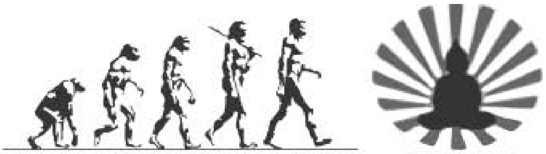

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