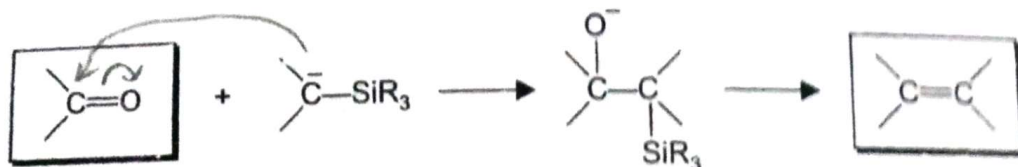


## SCHEME 7.35

## (B) Peterson Reaction—Synthesis of Alkenes (silyl Wittig reaction)

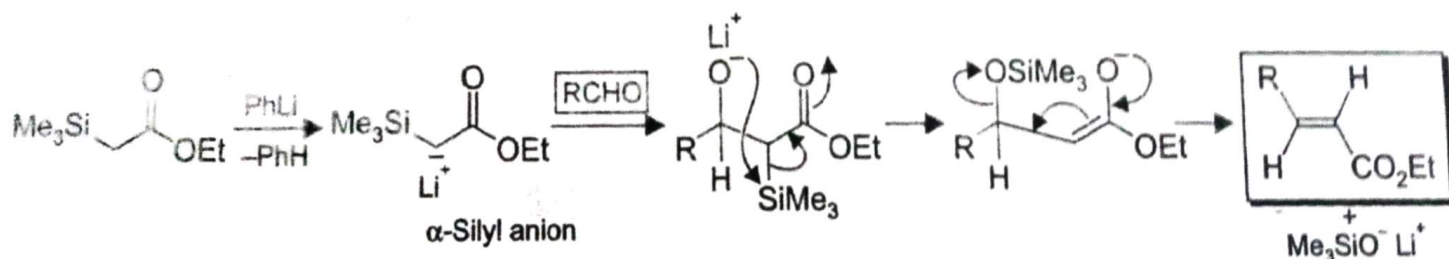
The Peterson silicon based alkene synthesis may be viewed as silicon version of Wittig reaction (Scheme 7.35a). Although the use of silicon stabilized carbanions is less common than those derived from phosphorus or sulphur, there are several significant advantages in steric terms.



The Peterson synthesis—use of silicon stabilized carbanions

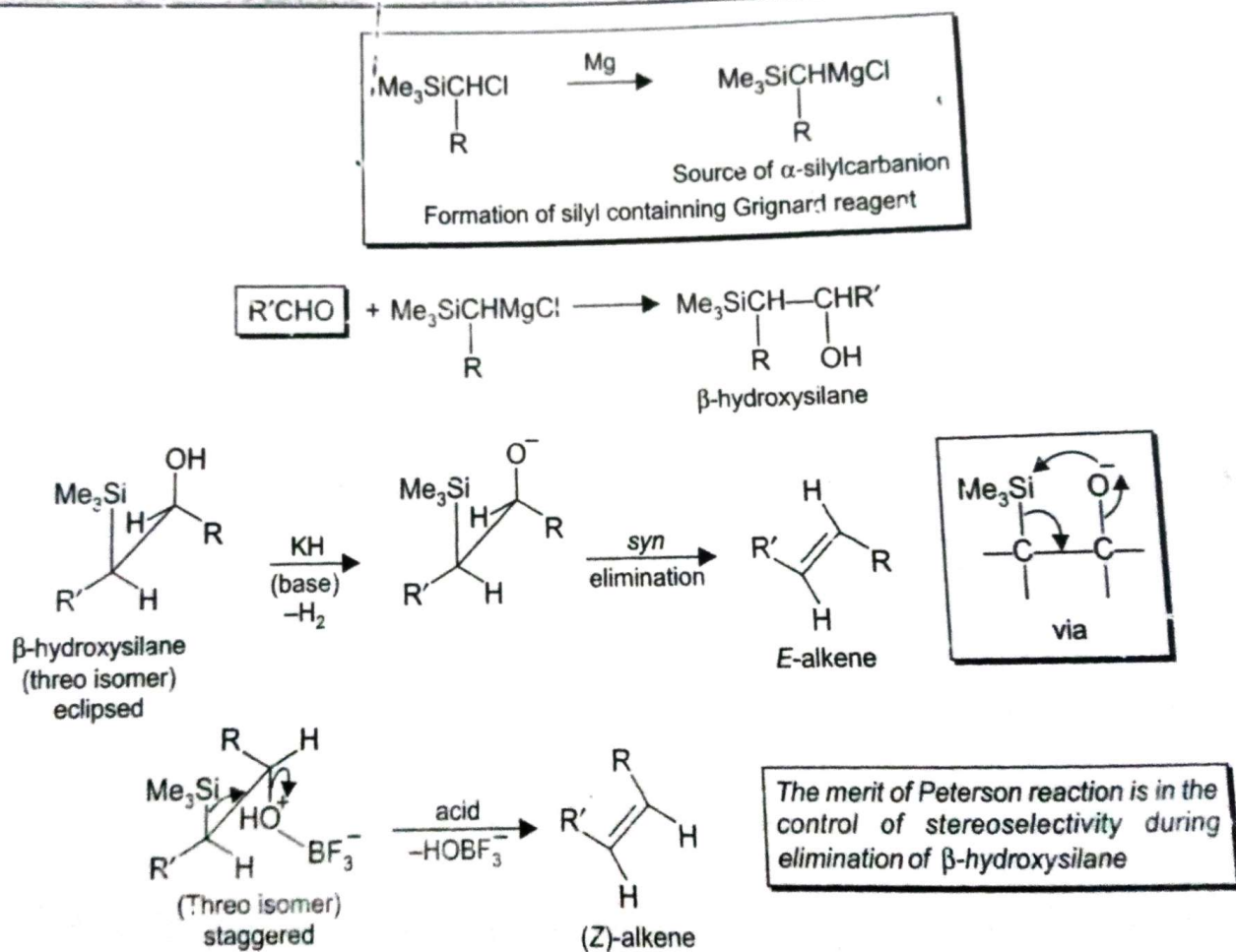
## SCHEME 7.35a

The reaction can be carried out in two ways. In the first method the reactant e.g., ethyl  $\alpha$ -trimethylsilylacetate has a CH group which is adjacent to both a silicon containing moiety (which is normally  $\text{SiMe}_3$ ) and a  $-M$  group displays a base induced reaction with an aldehyde or ketone to yield the alkene directly (Scheme 7.35b). The driving force for the reaction is the formation of strong silicon-oxygen bond, which converts the oxygen atom in to a much better silyloxy leaving group. In this case the more stable olefin isomer is formed because equilibration occurs in the enolate intermediate.



## SCHEME 7.35b

In the second alternative when the group of  $-M$  type is absent in the reactant, one generates a C-metal bond adjacent to the  $\text{SiMe}_3$  group. The reagent is therefore, trimethylsilylmethyl Grignard which adds to the carbonyl group of the reactant to form a  $\beta$ -hydroxysilane after hydrolysis. In this case the second step is needed to convert  $\beta$ -hydroxysilane into alkene (since the product alkene is not conjugated). These  $\beta$ -hydroxysilanes can be formed as diastereomers as *threo*, *erythro* form. These are separated and either of the diastereomers undergoes elimination of the trialkylsilyl group and the hydroxyl group to yield the alkene. The elimination is carried out under basic ( $\text{KH}$ ) or acidic ( $\text{H}^+$  or  $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ) conditions. Either diastereomer displays over 90% stereoselectivity and can give *E* or *Z* alkene, the elimination being *syn* under basic conditions and *anti* under acidic conditions (Scheme 7.35c).



SCHEME 7.35c