Course Code: MSCH6002

**Course Name: Reagents and Heterocyclic Chemistry** 

# Peterson olefination Reaction

GALGOTIAS UNIVERSITY

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### TOPICS COVERED

- ➤ Peterson Olefination Reaction
- > Mechanism in presence of Acid
- ➤ Mechanism in presence of Base
- > Reactions related to topic
- ➤ More examples

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## What is Peterson Olefination

The Peterson olefination (also called the Peterson reaction) is the chemical reaction of  $\alpha$ -silyl carbanions with ketones (or aldehydes) to form a  $\beta$ -hydroxysilane which eliminates to form alkenes.

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### **Mechanism of Peterson Olefination**

One attractive feature of the Peterson olefination is that it can be used to prepare either cis- or trans-alkenes from the same  $\beta$ -hydroxysilane. Treatment of the  $\beta$ -hydroxysilane with acid will yield one alkene, while treatment of the same  $\beta$ -hydroxysilane with base will yield the alkene of opposite stereochemistry.

In the first step of the Peterson Olefination, addition of the silylcarbanion to a carbonyl compound and subsequent aqueous work up leads to diastereomeric adducts.

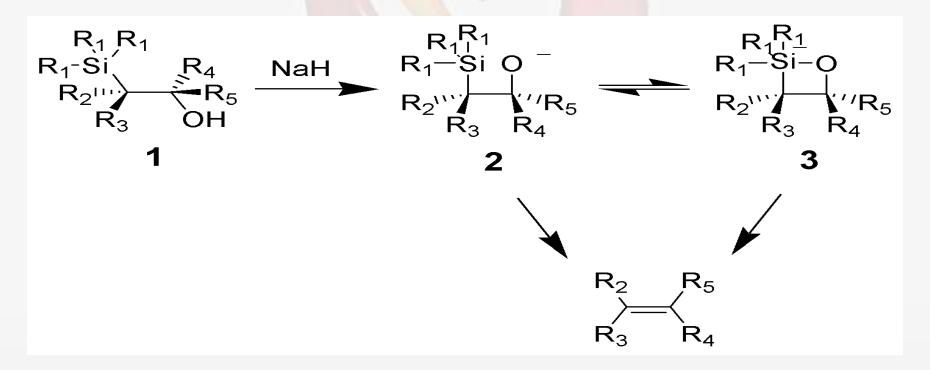
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#### **Basic elimination**

The action of base upon a  $\beta$ -hydroxysilane (1) results in a concerted *syn* elimination of (2) or (3) to form the desired alkene. The penta-coordinate silicate intermediate (3) is postulated, but no proof exists to date.



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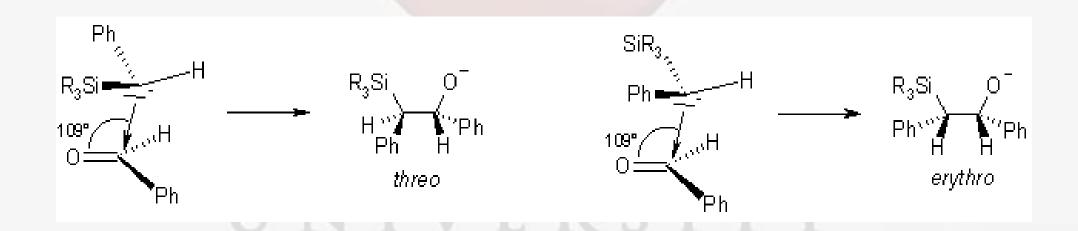
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#### **Acidic elimination**

The treatment of the  $\beta$ -hydroxysilane (1) with acid results in protonation and an *anti* elimination to form the desired alkene.

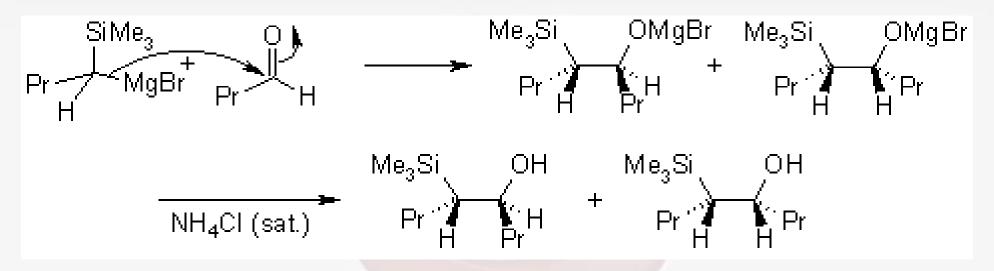
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Some of these reactions are stereoselective and may be rationalized with simple models: The reaction of benzaldehyde and a silylcarbanion gives the *threo*-product if the silyl group is small. This implies that in the transition state, the two sterically demanding groups are *anti*. As the silyl group becomes more sterically demanding than trimethylsilyl, the selectivity shifts towards the *erythro*-isomer.

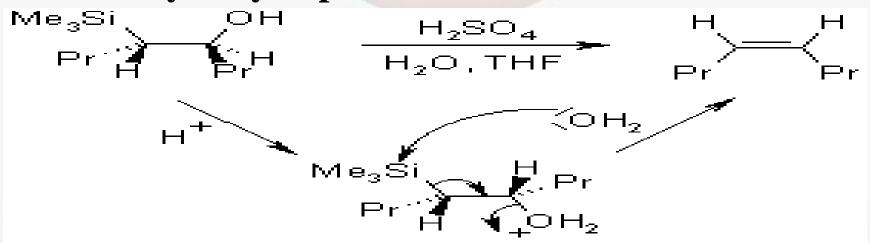


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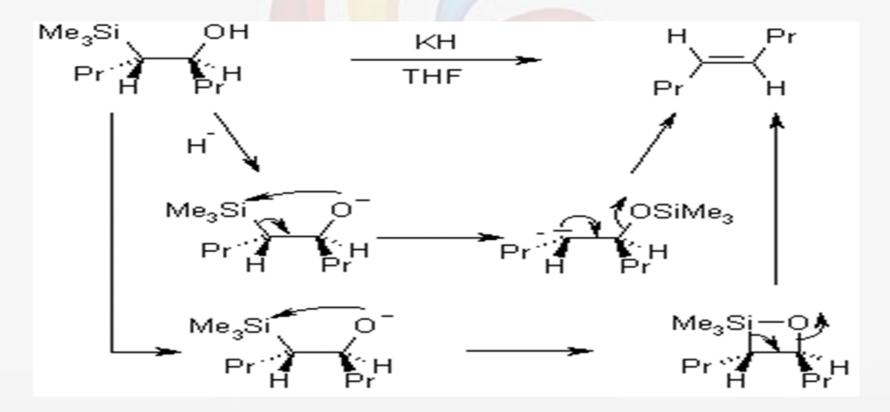
### Acidic hydrolysis proceeds via an anti-elimination



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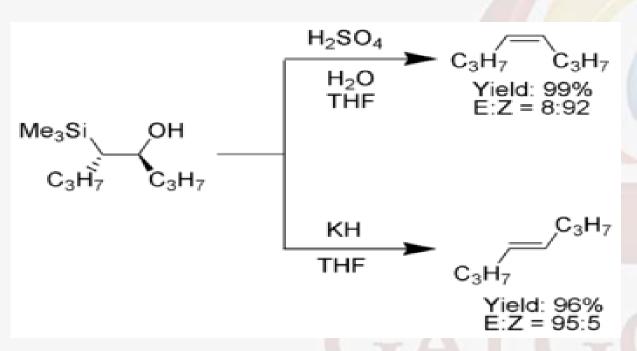
In contrast, the base-catalyzed elimination may proceed via a 1,3-shift of the silyl group after deprotonation, or with the formation of a pentacoordinate 1,2-oxasiletanide that subsequently undergoes cycloreversion:

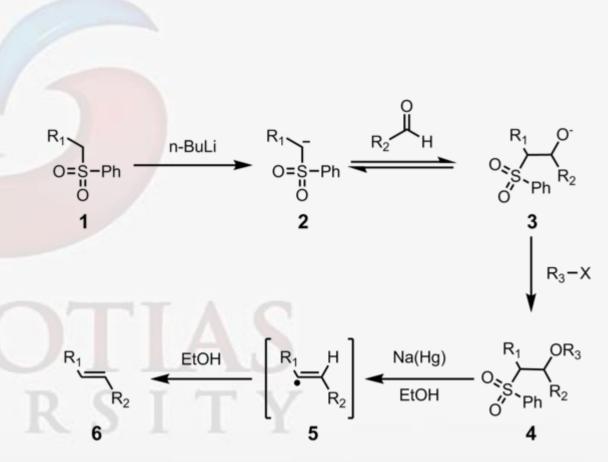


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### **Examples**





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## **Examples**

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### References

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