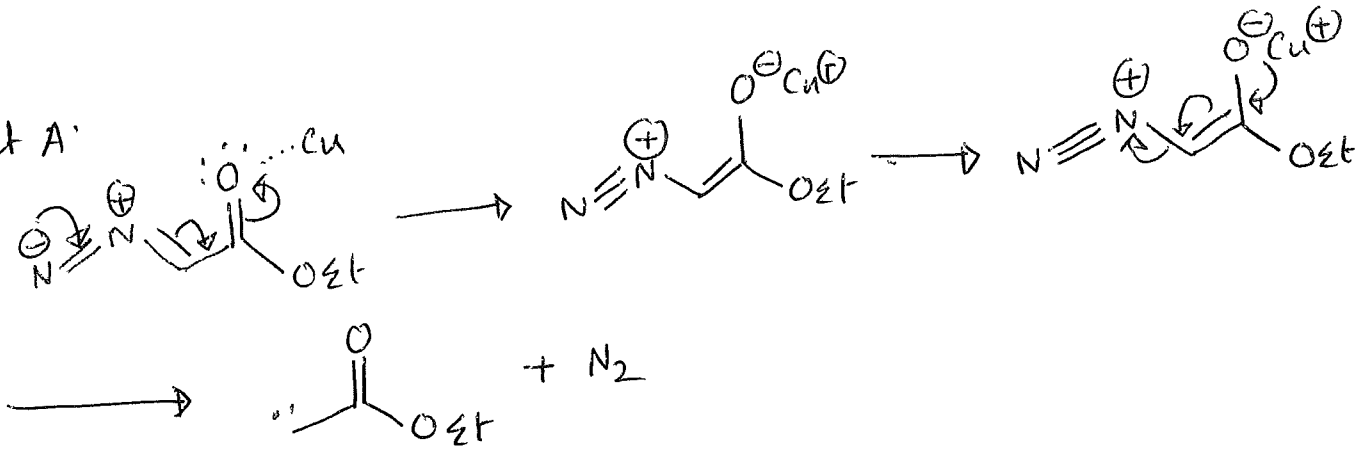
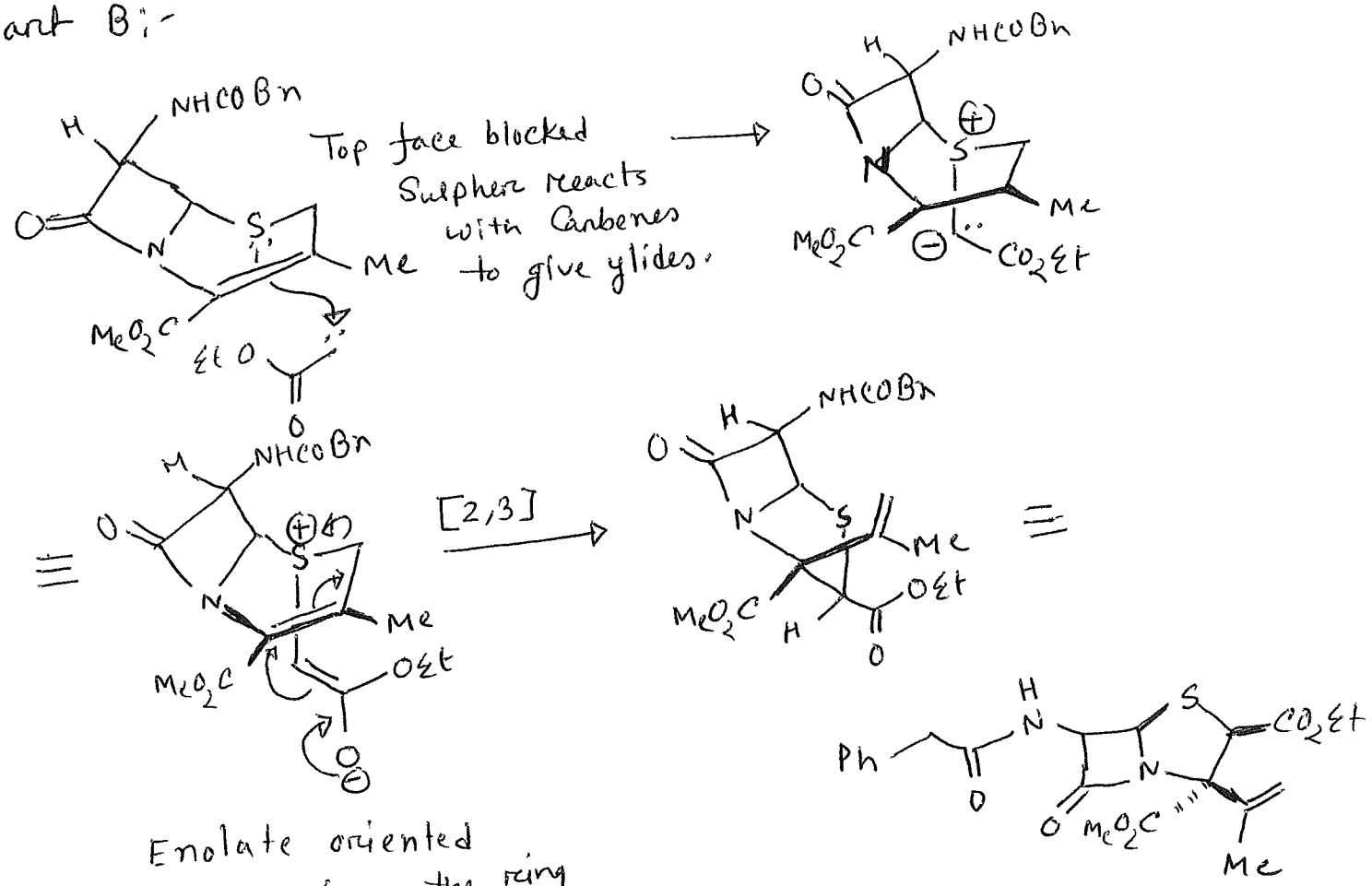
Reaction Mechanism Practice 3
Dr. Peter Andreana Group

Problem No. 1 :-

Part A:

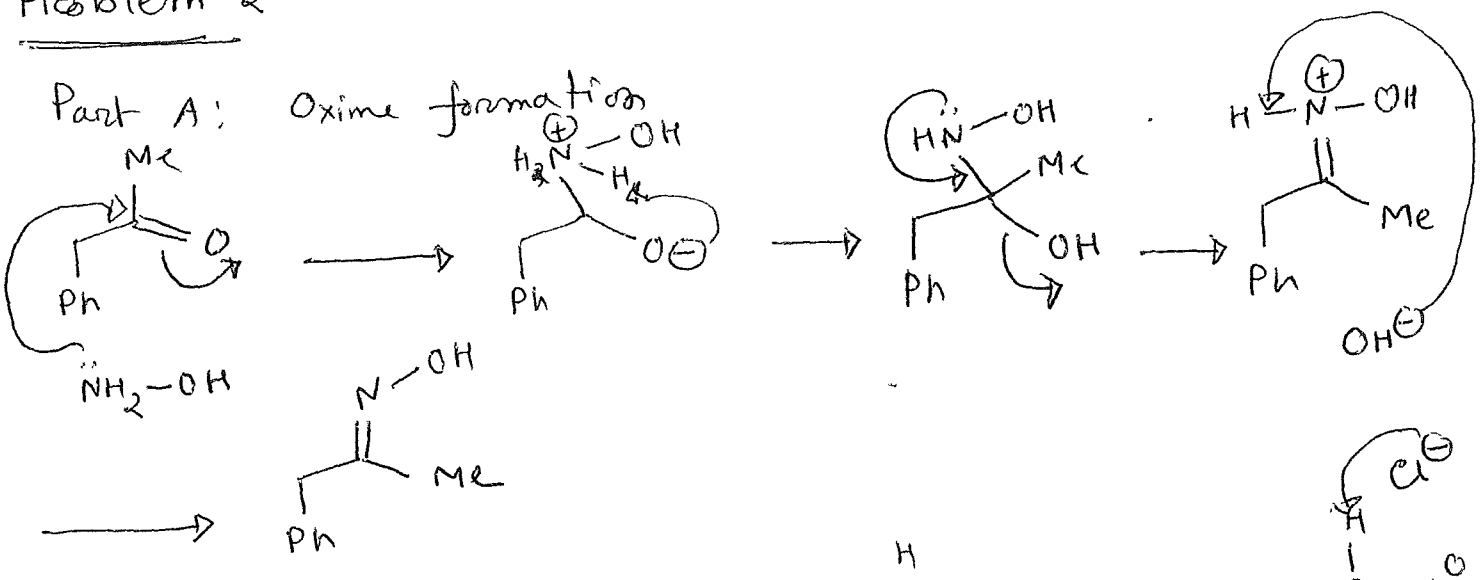


Part B:-

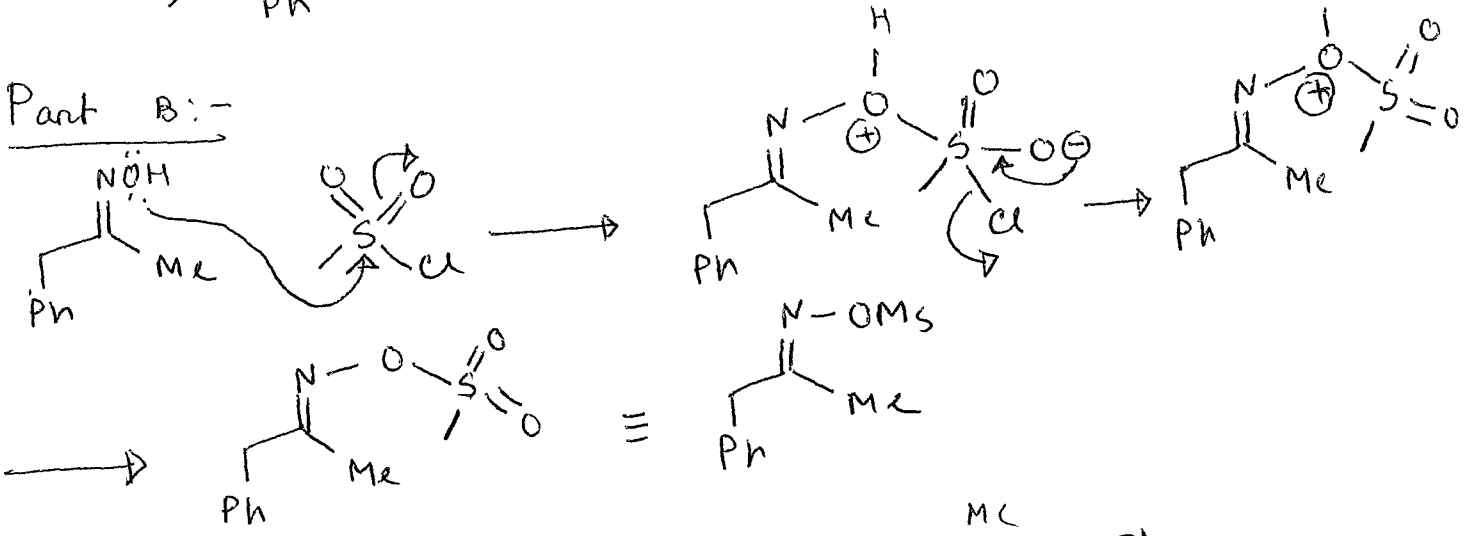


Problem 2:

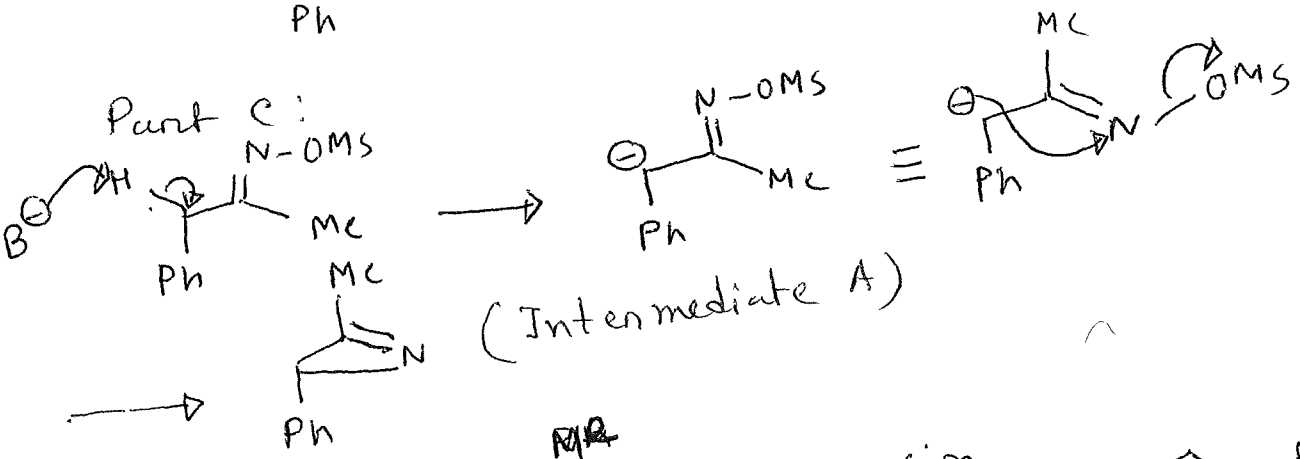
Part A: Oxime formation



Part B:-

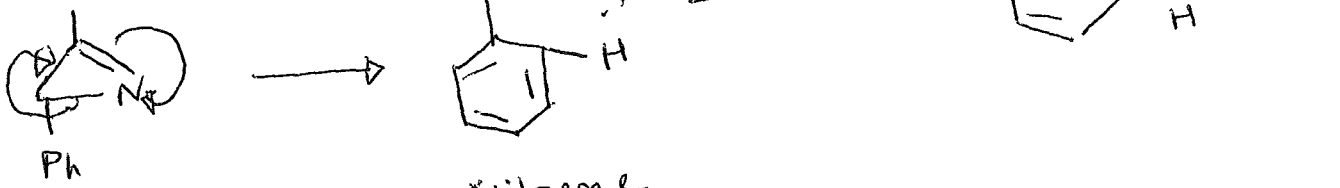


Part C:



(Intermediate A)

Part D

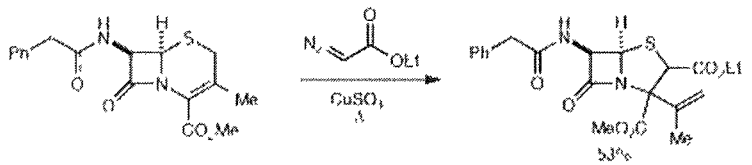


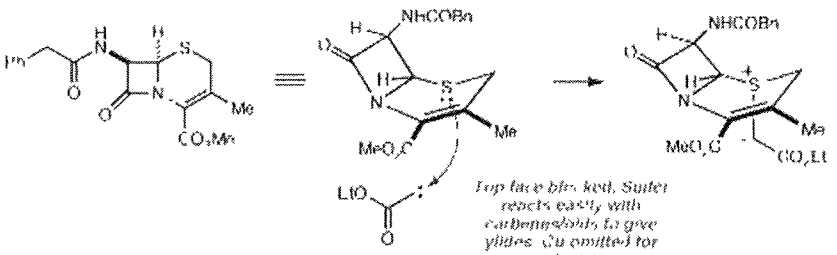
Nitrene

(A)

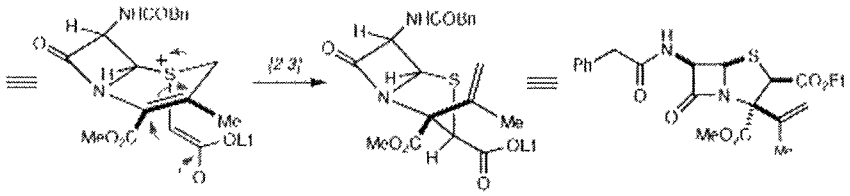
Problem 1

Provide a mechanism for the following transformation and predict the stereochemistry of the product (Yashimoto M. *Tetrahedron Lett* **1972**, 2923)





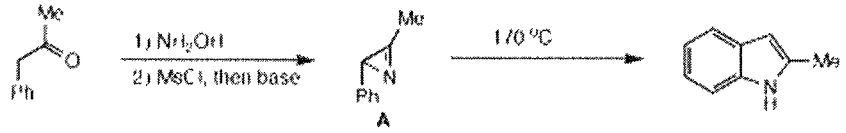
Top face blocked. Sulfur reacts easily with carbenoids to give ylides. Cu omitted for clarity



Enolate created away from ring

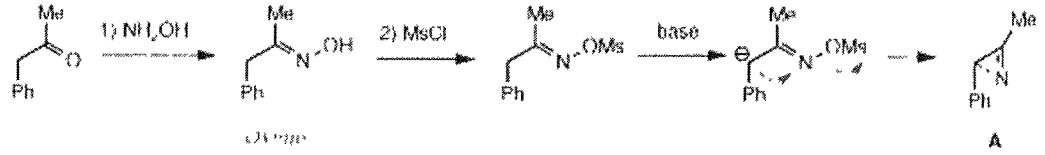
Problem 2

Taber recently reported the synthesis of substituted indoles utilizing the Neber reaction. The reaction shown below is a representative example of the reaction sequence (*JACS* **2006**, *128*, 1058)



A

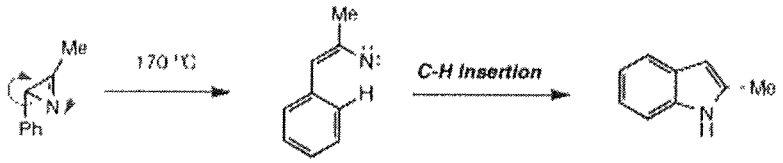
Part A. In the space provided show a reasonable mechanism for the conversion of the ketone into the intermediate azirine **A**



Oxime

A

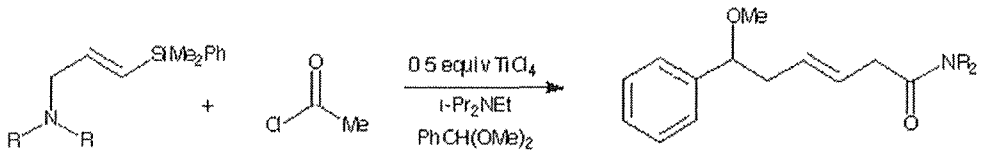
Part B. In the space provided show a reasonable mechanism for the conversion of the intermediate azirine to the corresponding indole product.



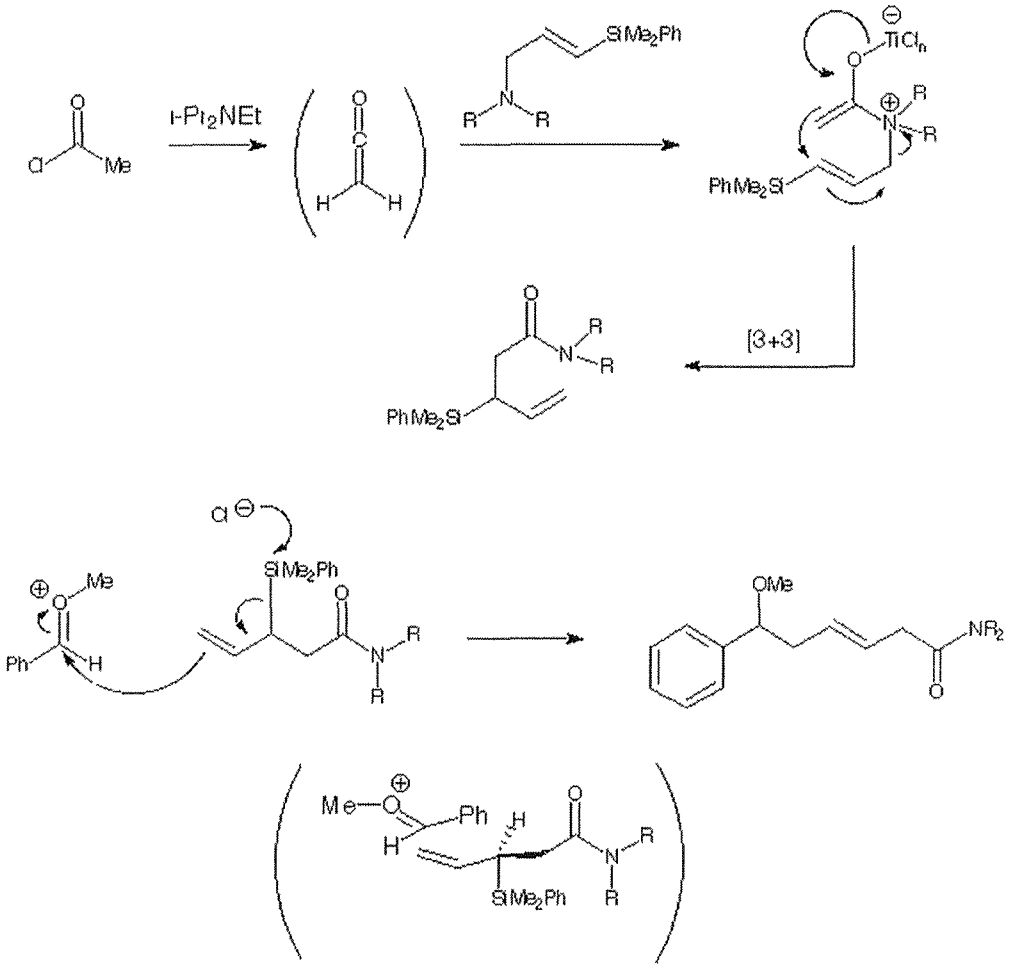
Nitrene

Problem 4

In the Panel lecture he described the transformation illustrated below. This transformation is an extrapolation of the recent publication of MacMillan and co-workers (*JACS*, **1999**, *121*, 9726).



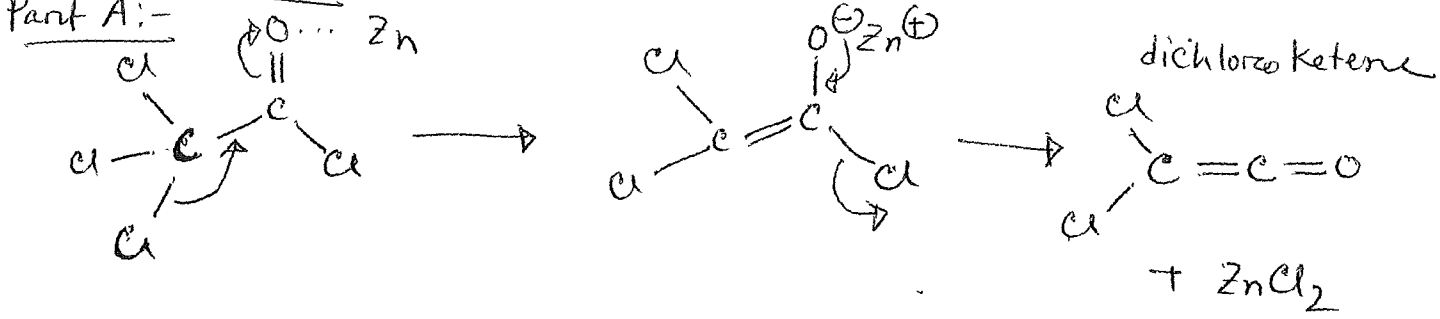
Provide a detailed mechanism for the illustrated transformation. Use three-dimensional representations, where relevant, to illustrate the stereochemical aspects of the individual steps.



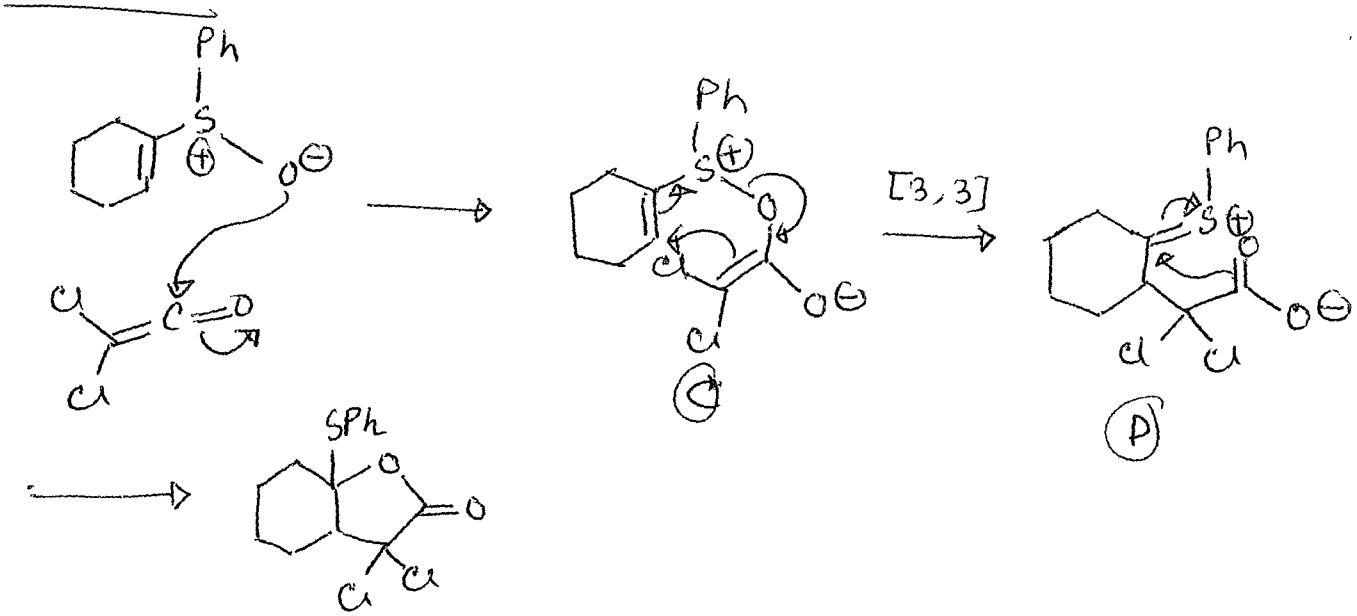
Alignment of crotylsilane necessary for *trans* olefin geometry

Problem - 3 :-

Part A :-



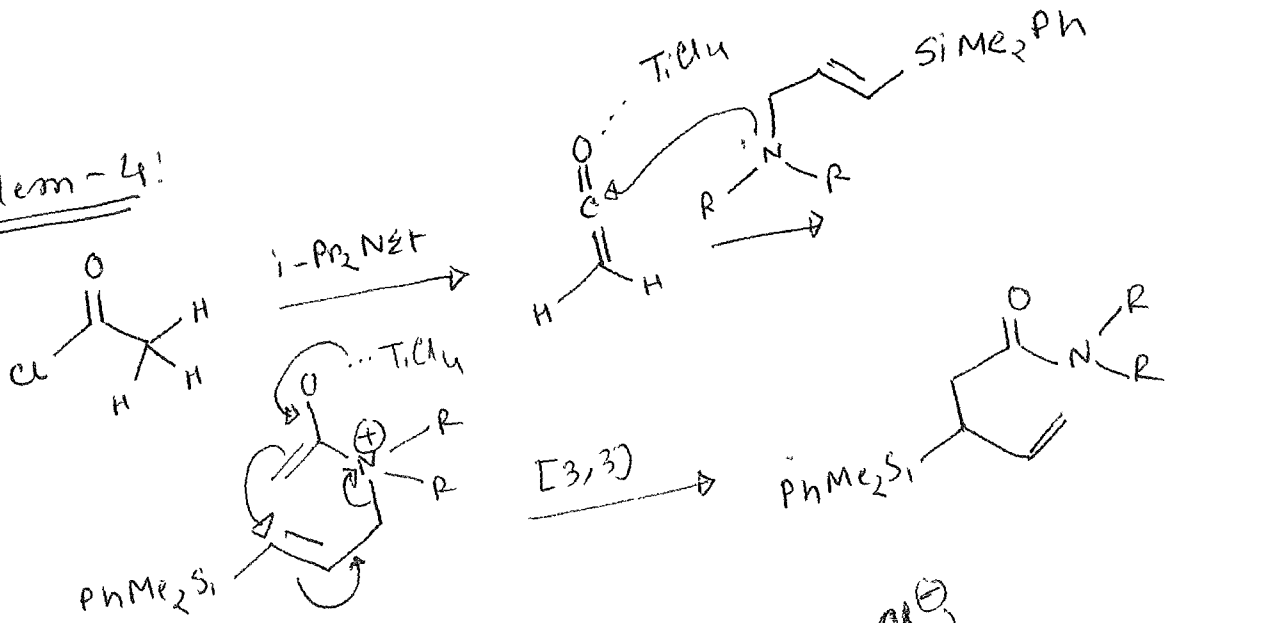
Part B :-



Zinc and an α-chloroacetyl chloride is a recipe for making a ketene, in this case dichloroketene. This very electrophilic intermediate is attacked by the oxygen atom of the sulfoxide to give the Zwitterion C. Then it undergo [3,3]-sigmatropic rearrangement.

Problem - 4:

Part A:



Part B: