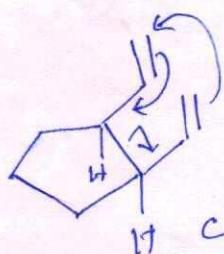
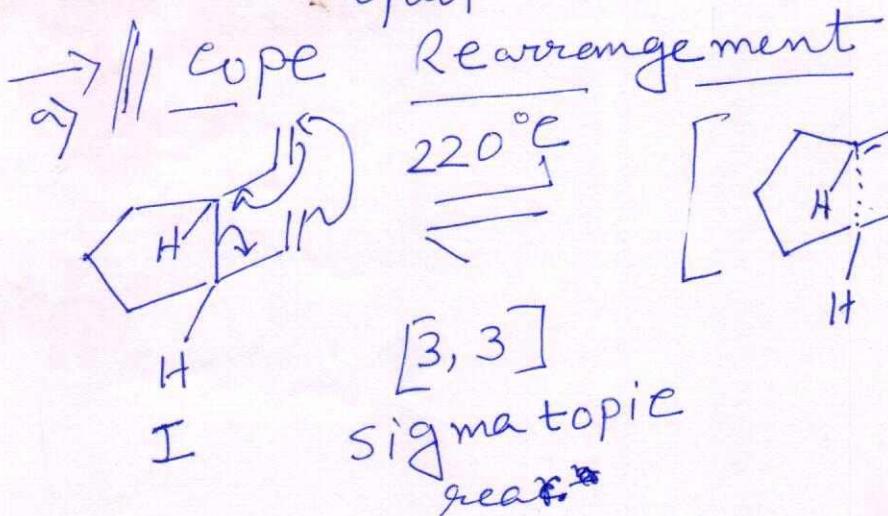


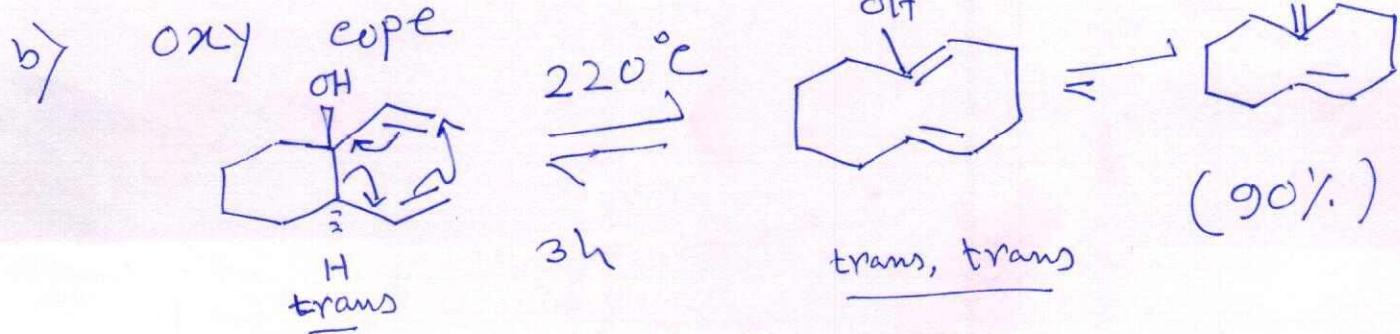
1976 \Rightarrow Isolated by Persons et al.
Sex pheromone
200 μg from 7500 female cockroaches
Stereochemistry was not known before synthesis
1979 \Rightarrow Total synthesis by Still et al.



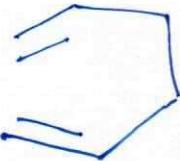
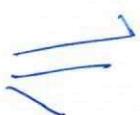
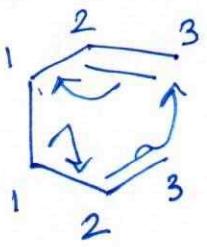
cis-1,2-divinyl cyclopentane



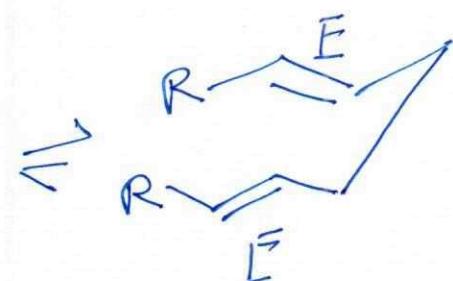
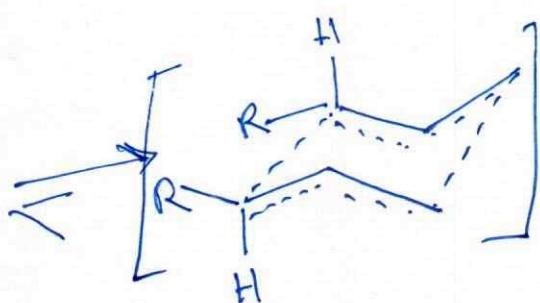
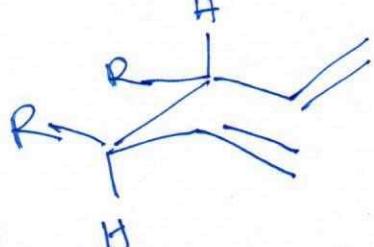
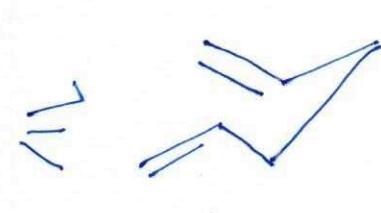
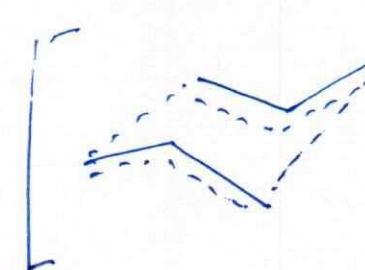
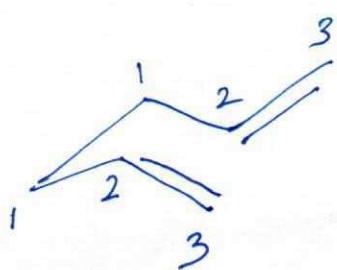
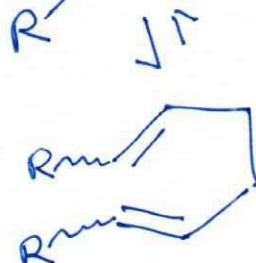
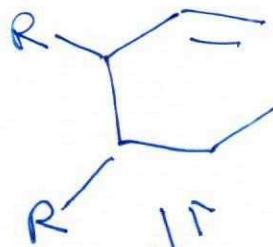
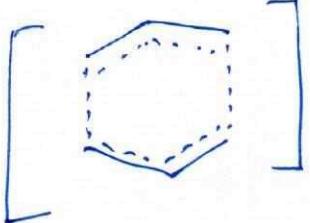
JACS, 1979, 101, 2493



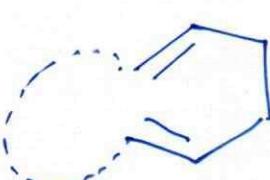
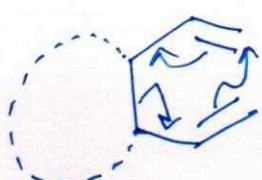
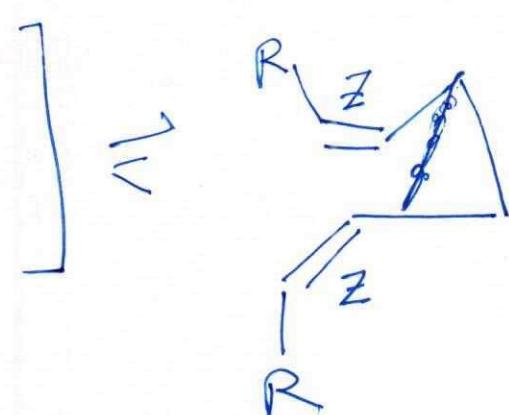
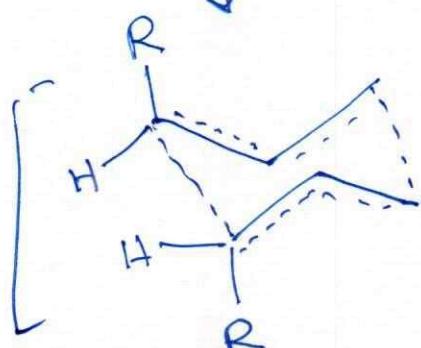
(1a)



via

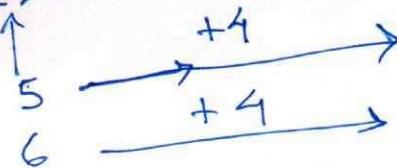
Equatorial

FLIP

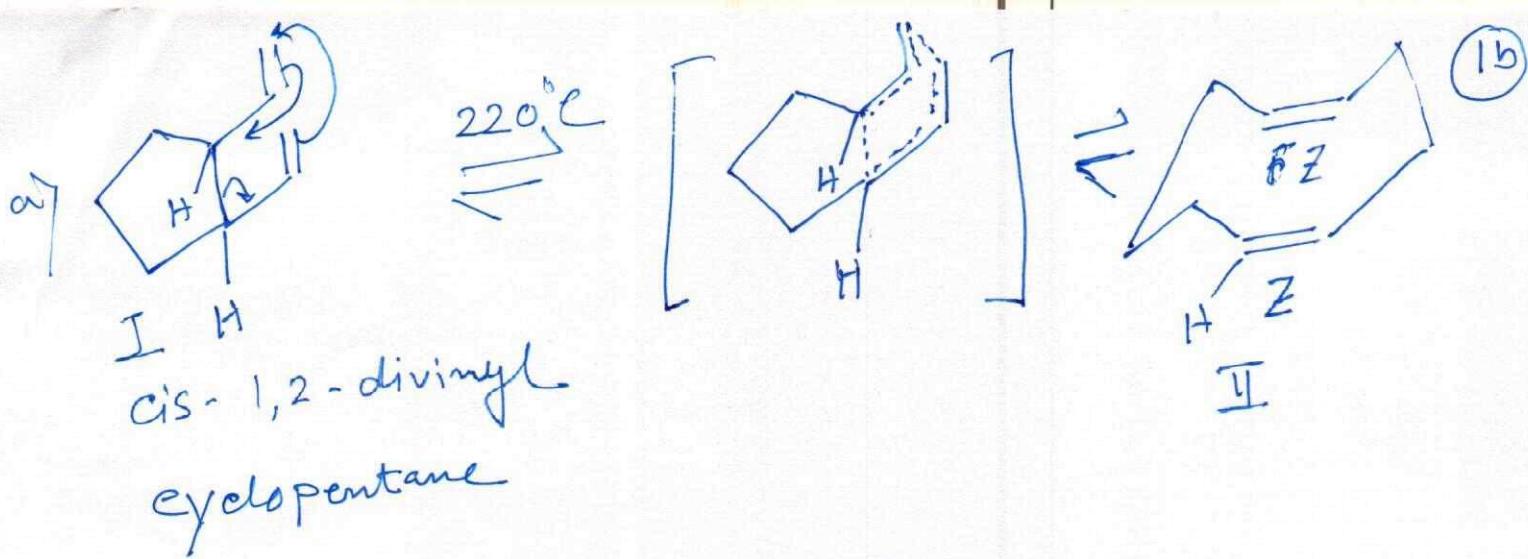


Macrocycle

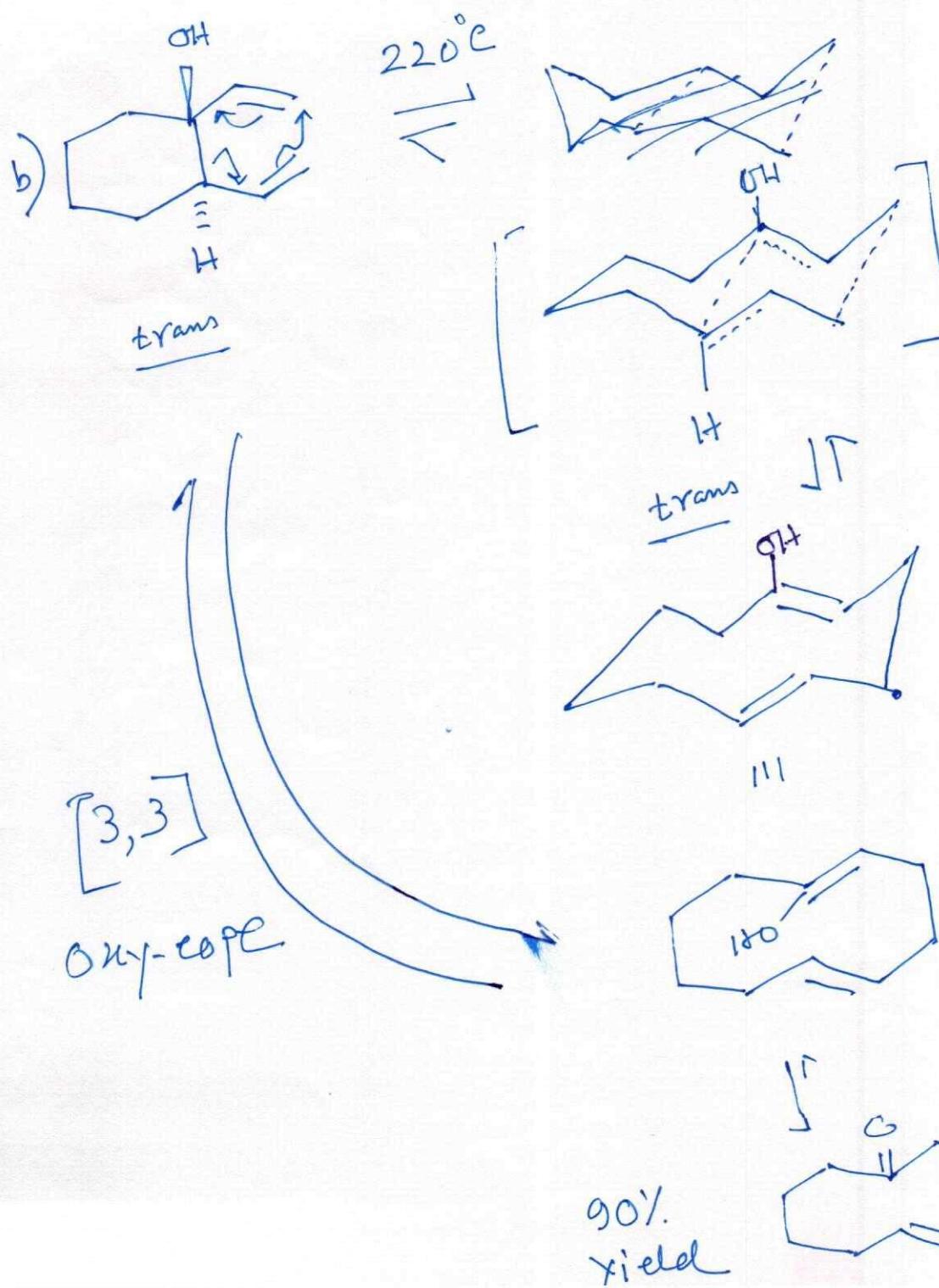
9 membered ring



10

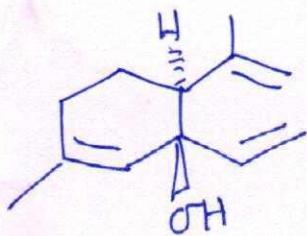


$$I : II = 95 : 5$$

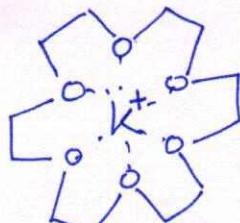
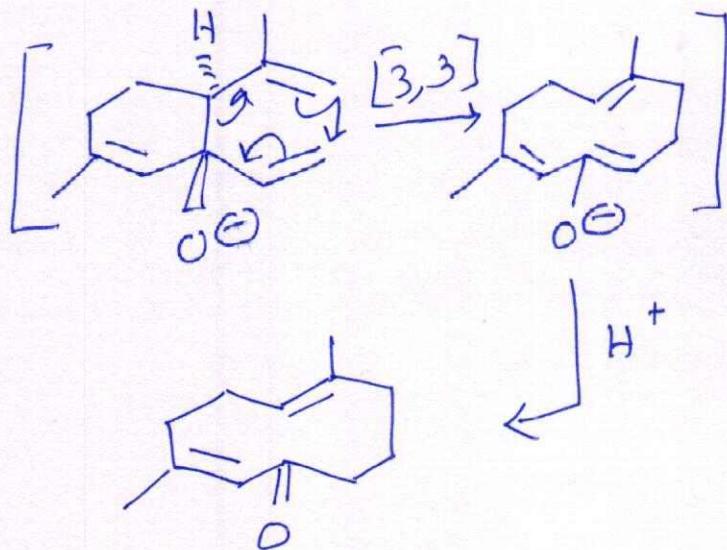


②

c) anionic oxy-cope

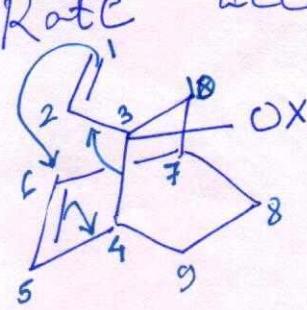


KH, THF
18-crown-6
18 h, 25 °C

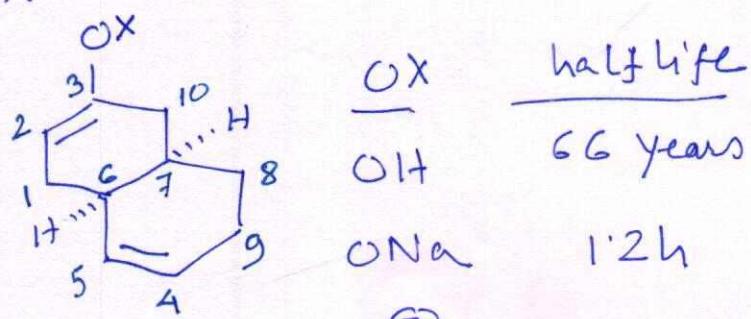


naked anion

Rate acceleration in anionic oxy-cope is dramatic!

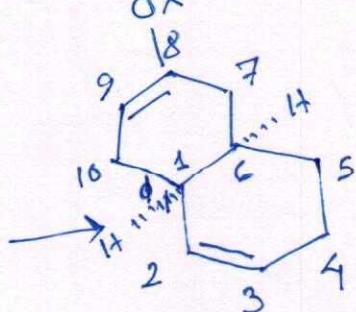
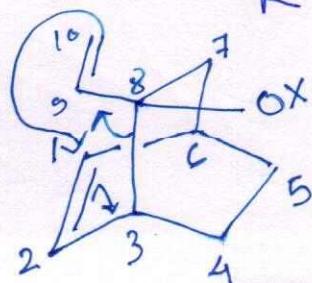
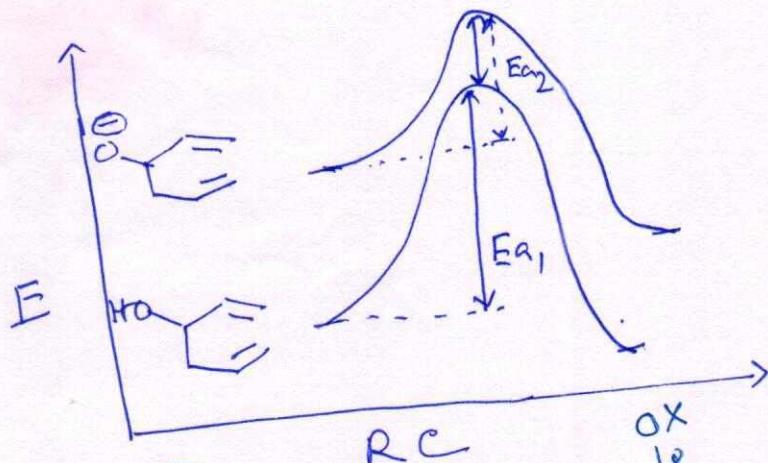


66 °C
THF



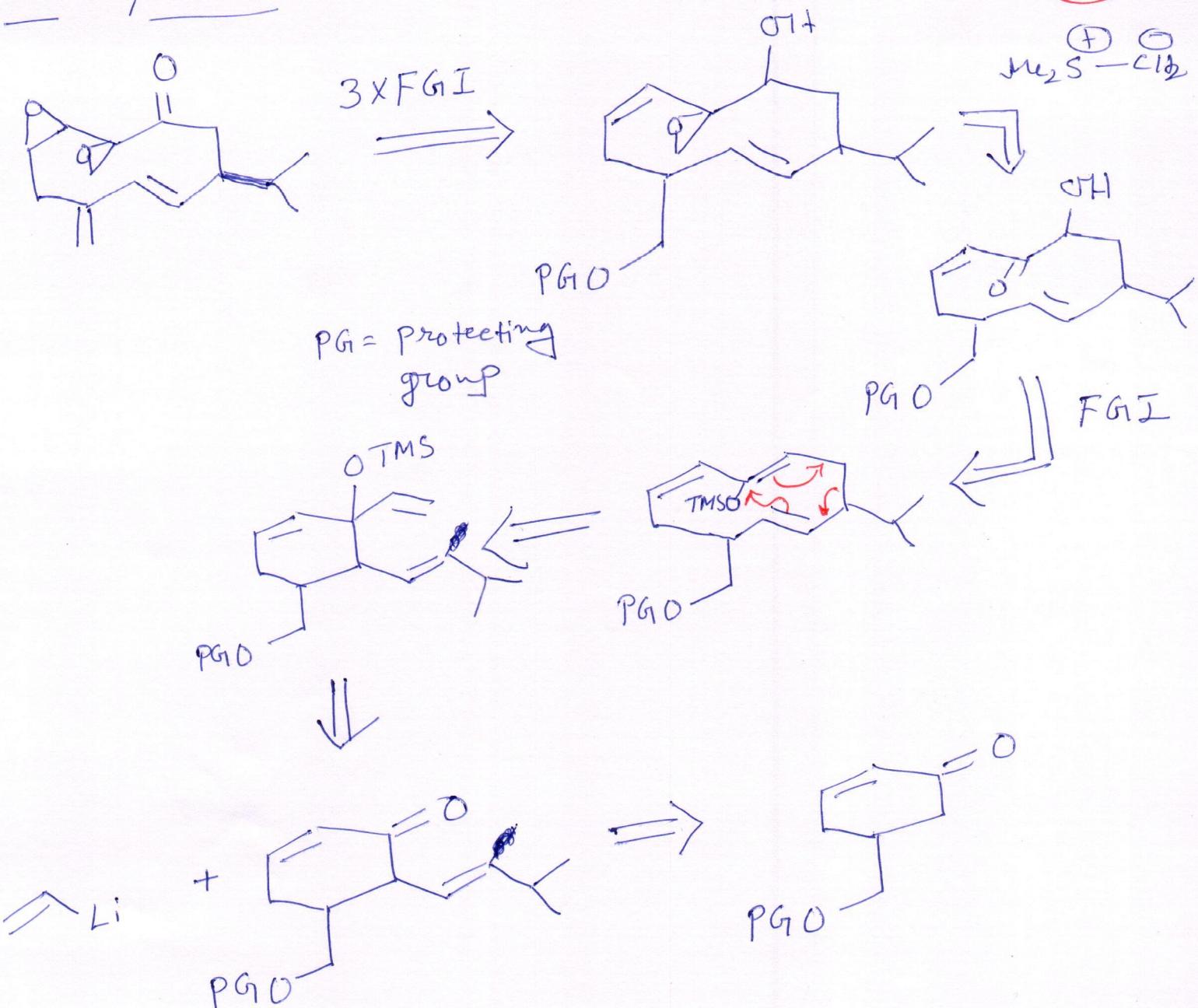
$\Rightarrow 10^{12} - 10^{17}$ rate acceleration

$E_{\alpha_1} > E_{\alpha_2}$



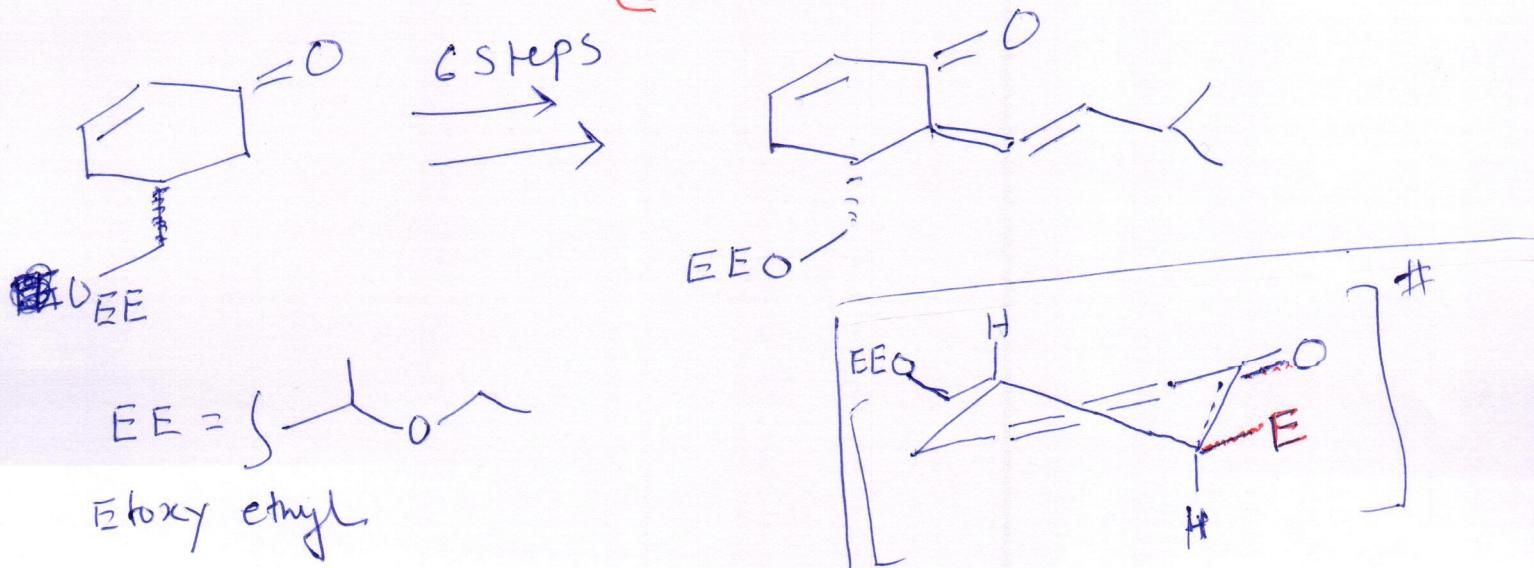
Retrosynthesis:

(3a)

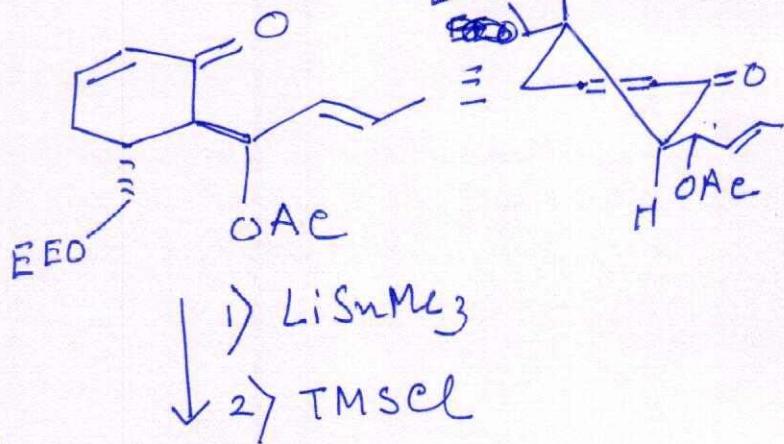
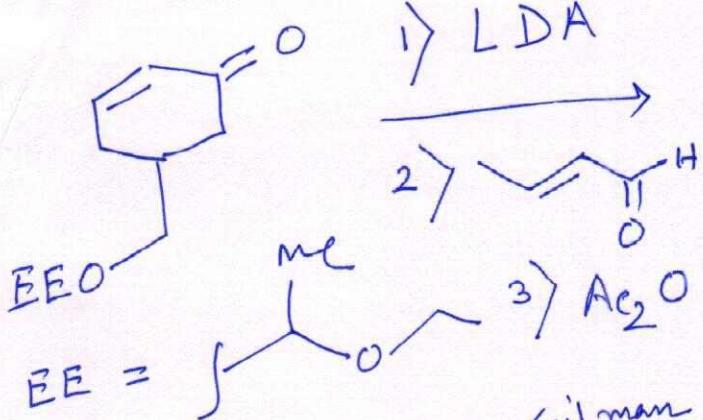


Forward Synthesis:

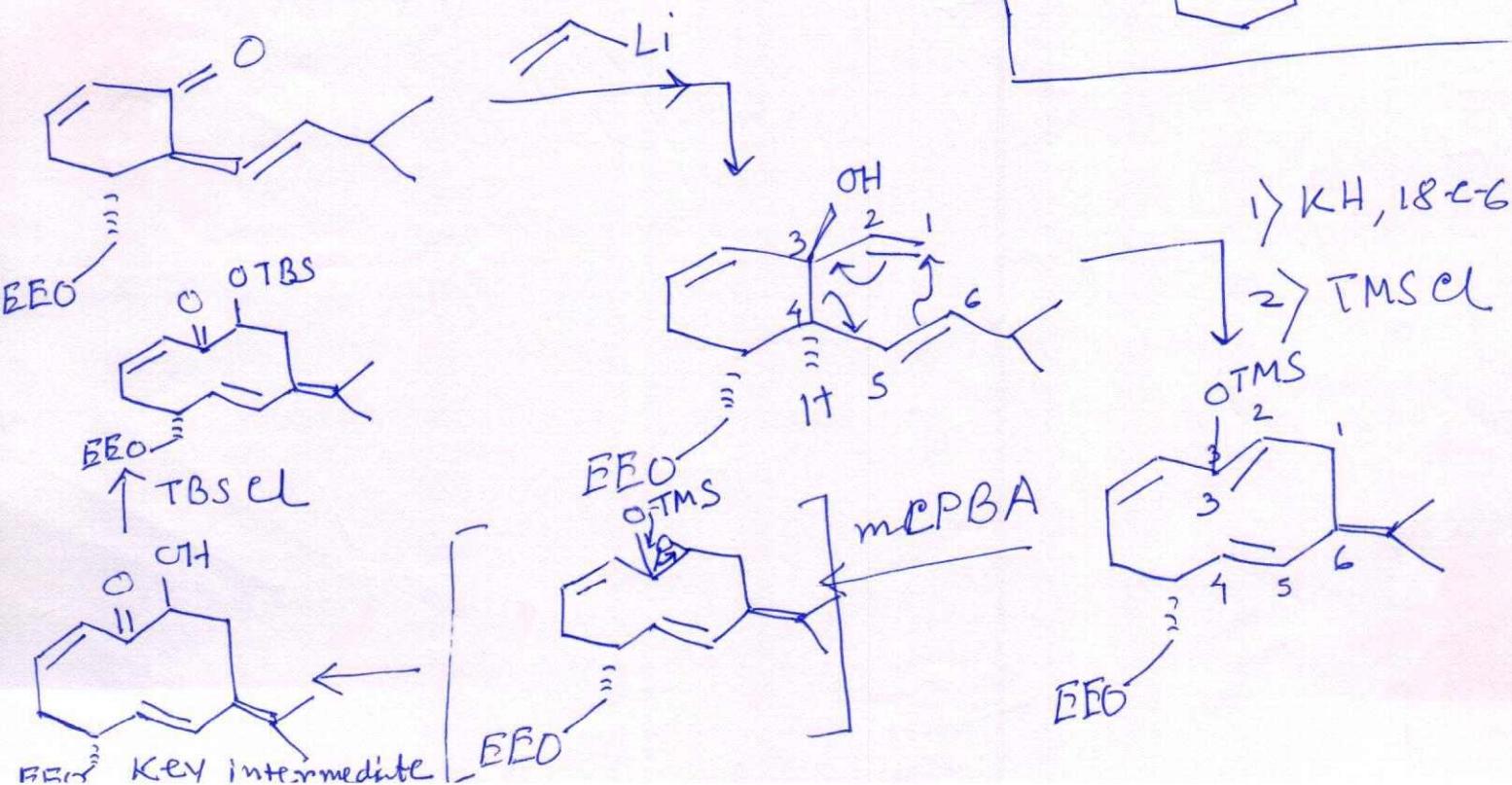
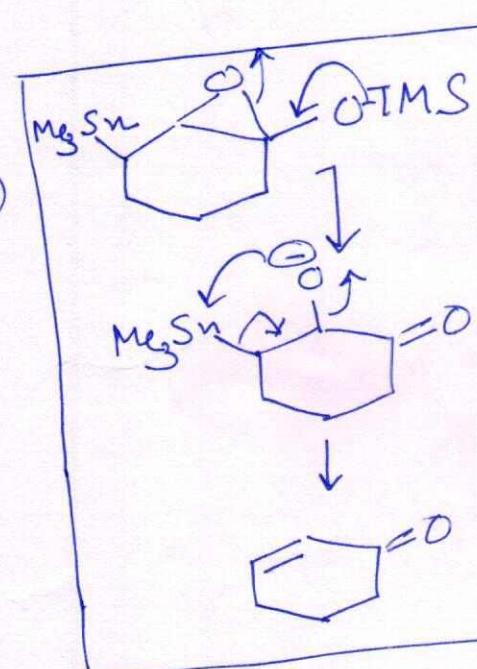
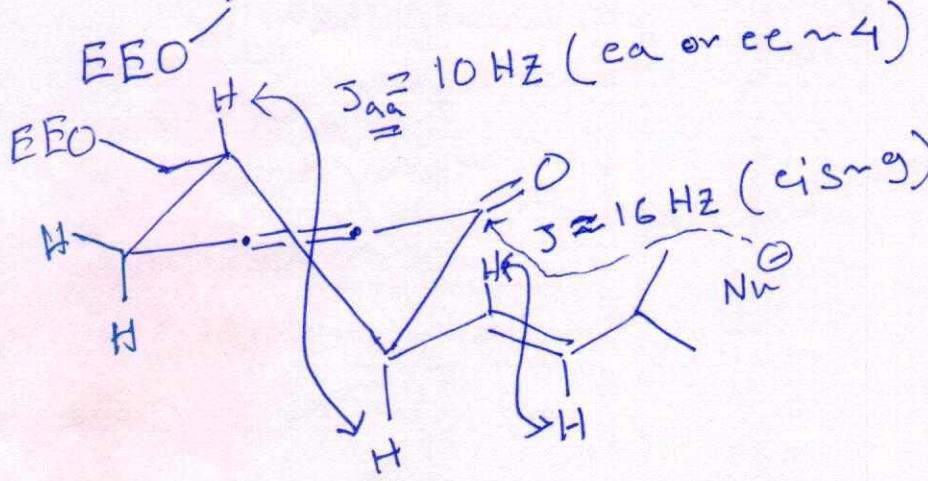
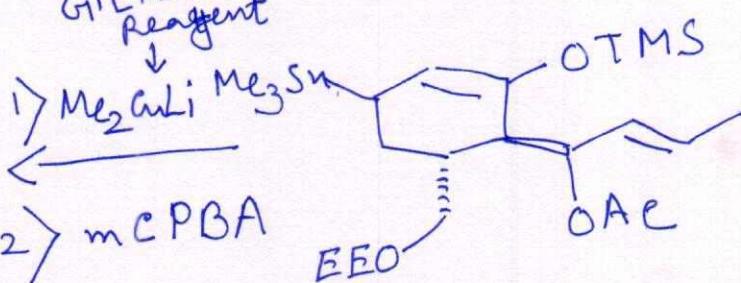
(see page 3 for details)

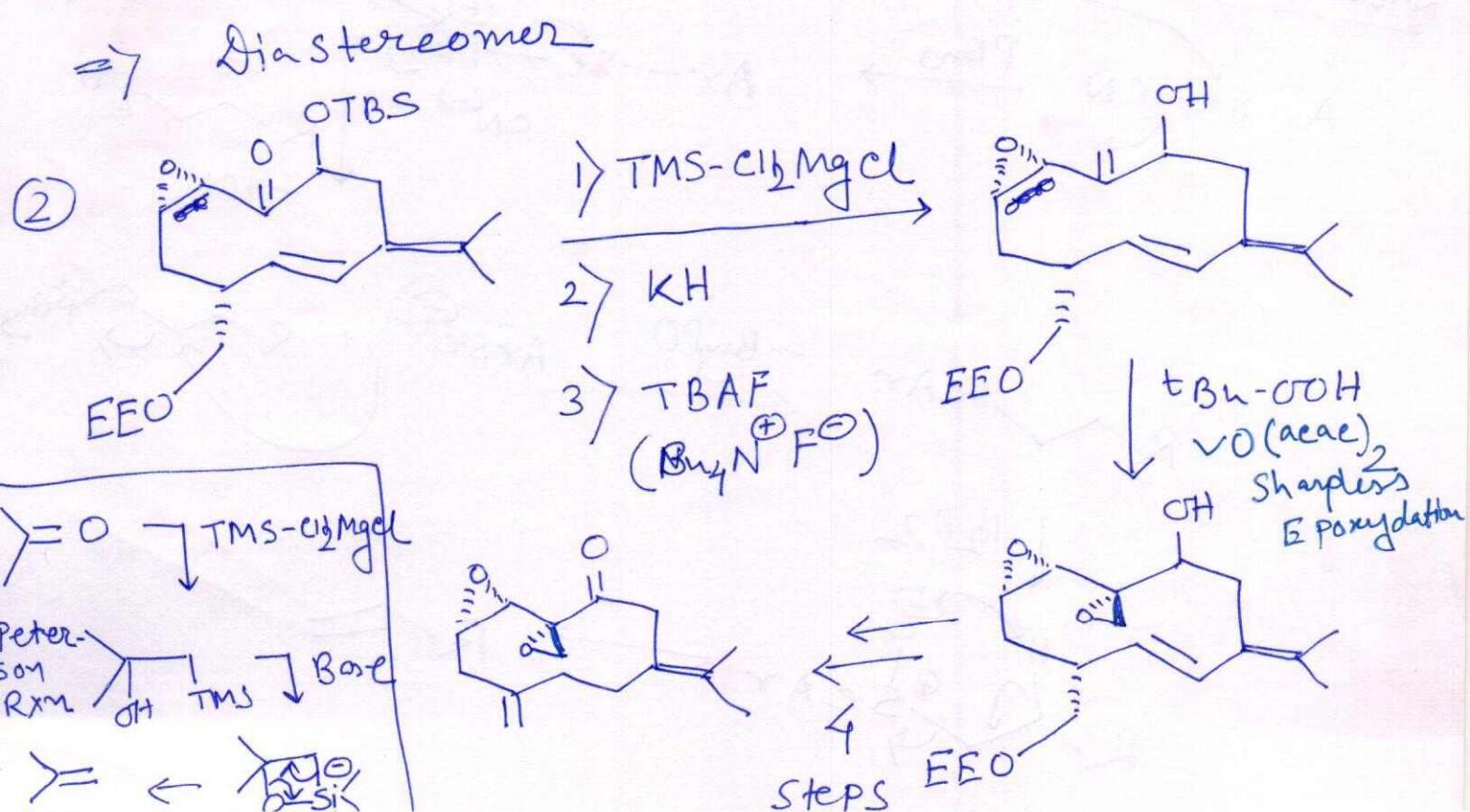
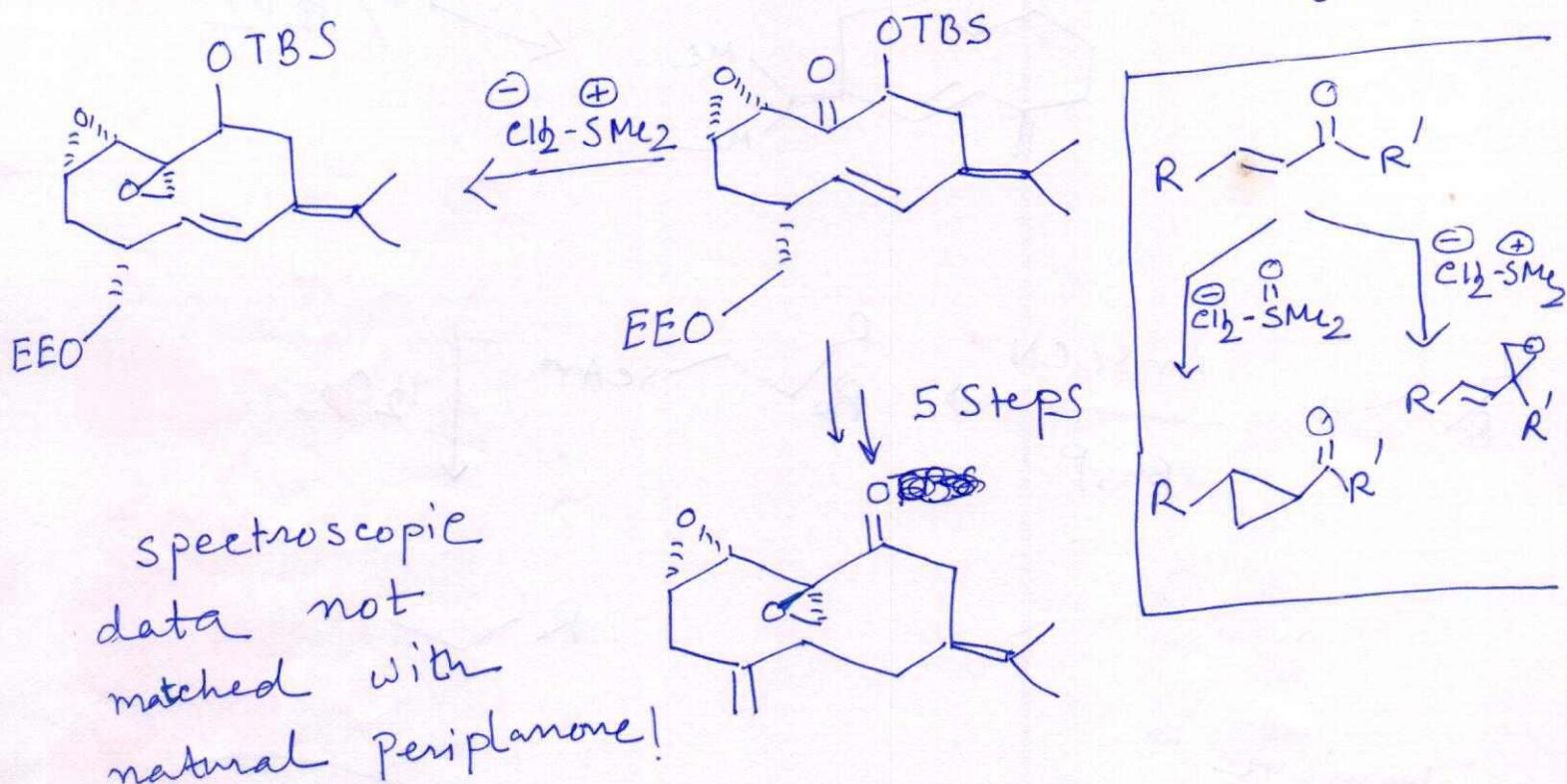
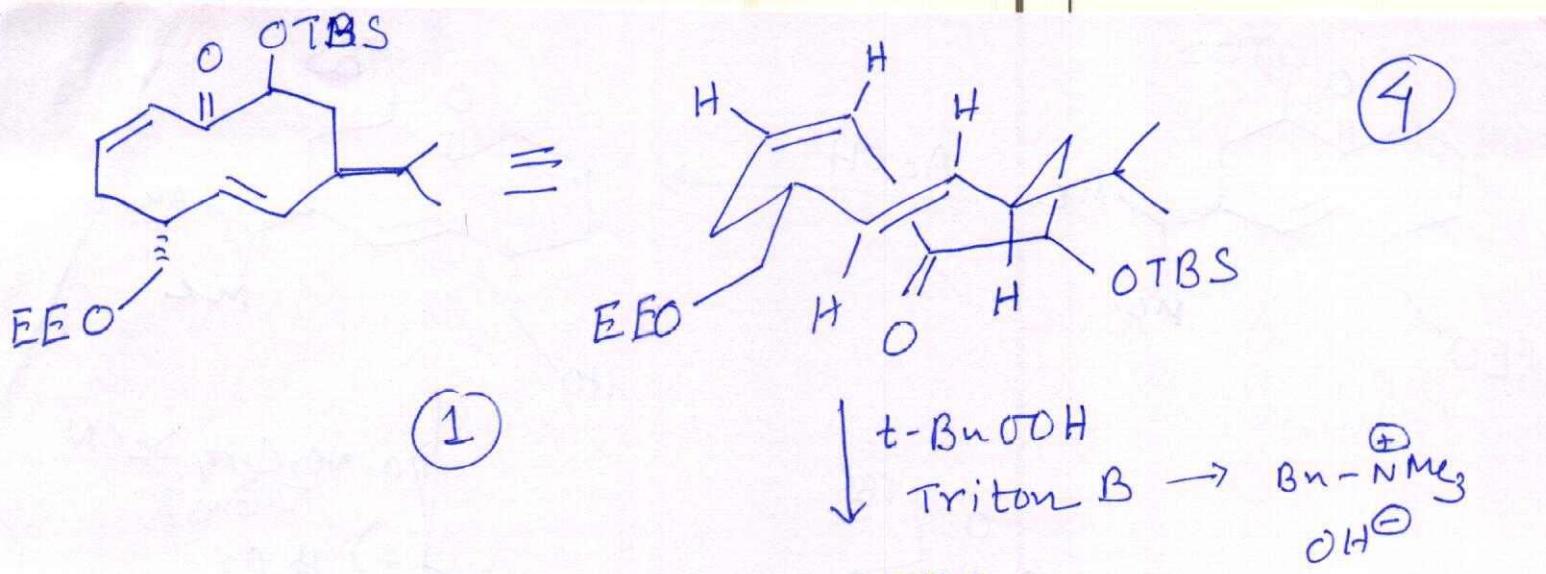


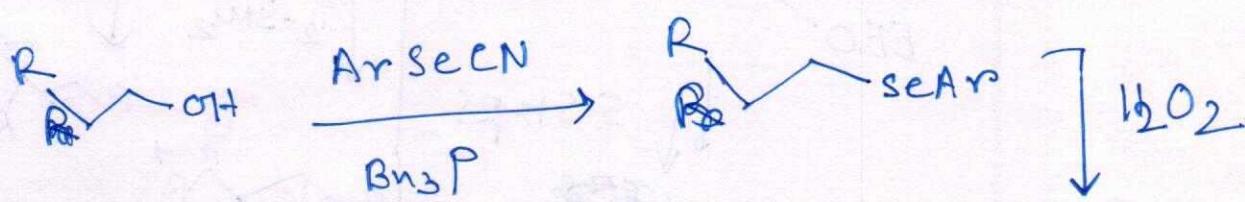
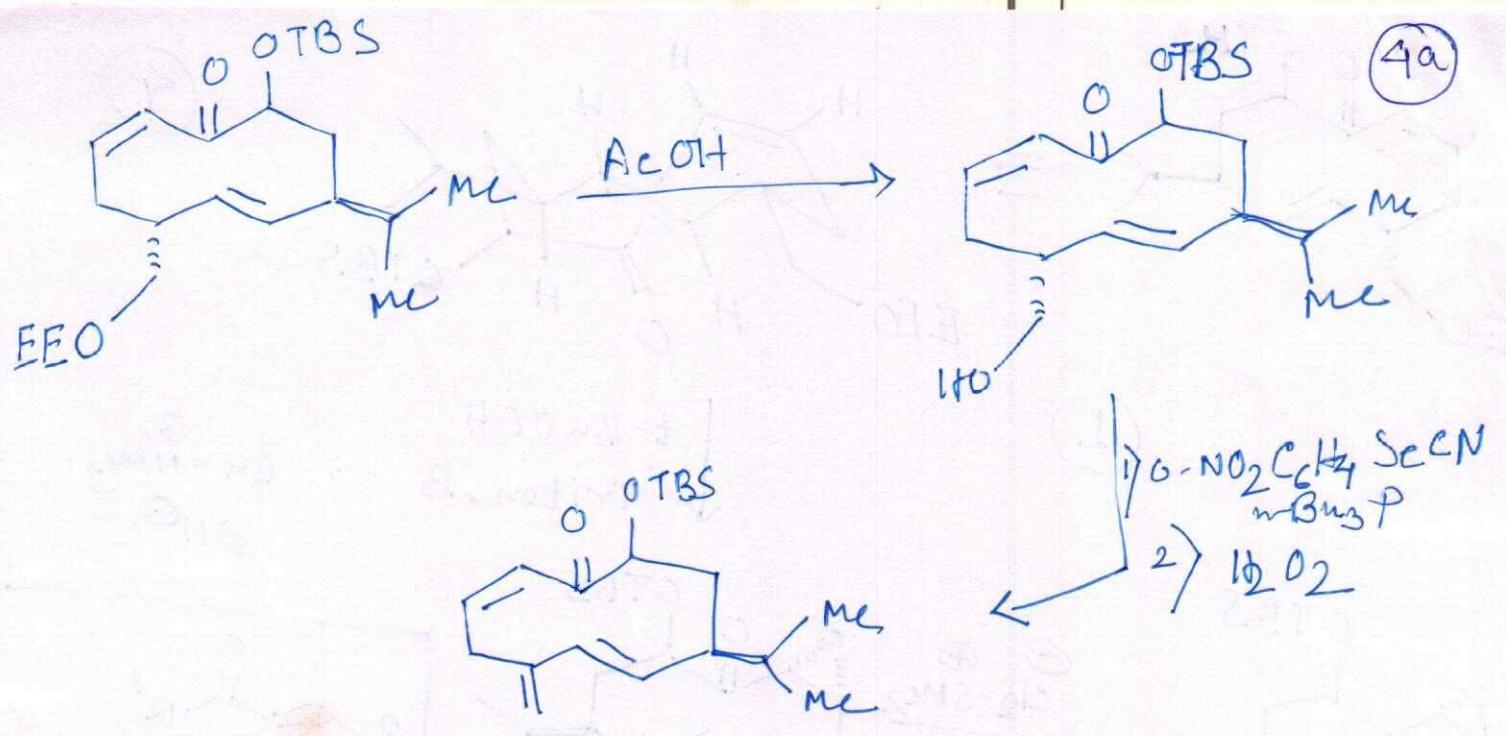
Synthesis



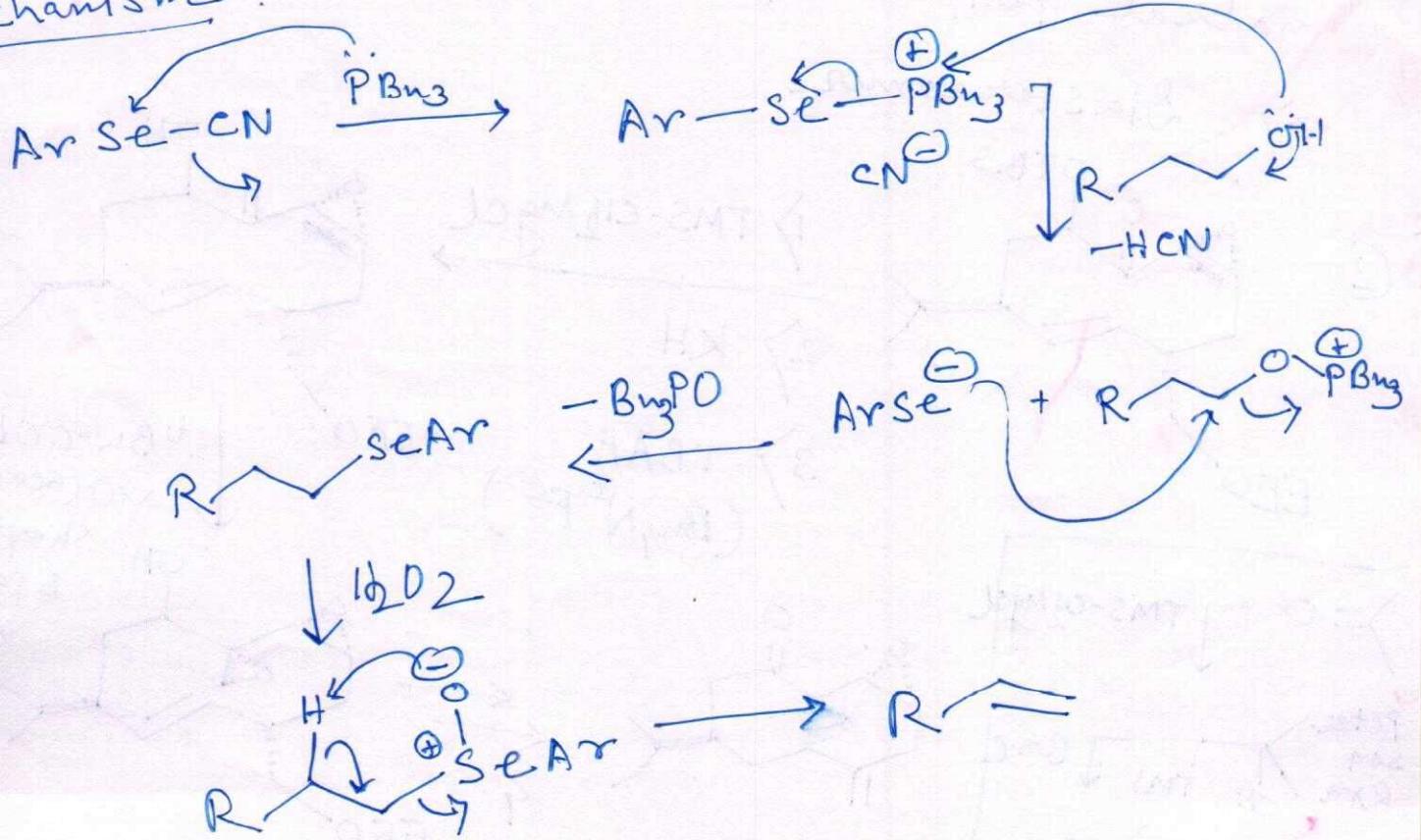
Gilman Reagent





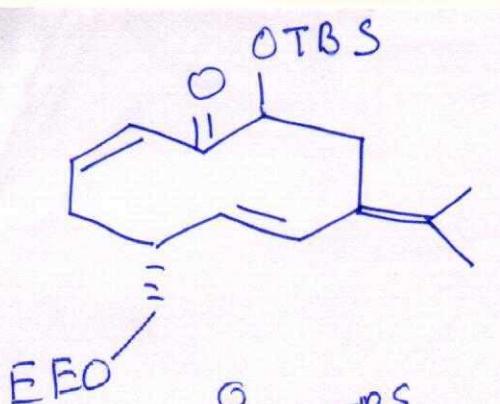


Mechanism:

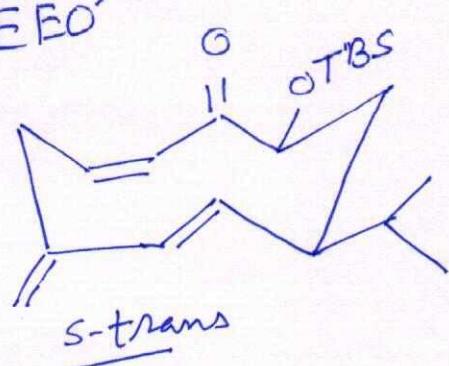
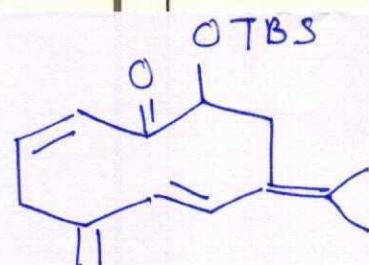


5

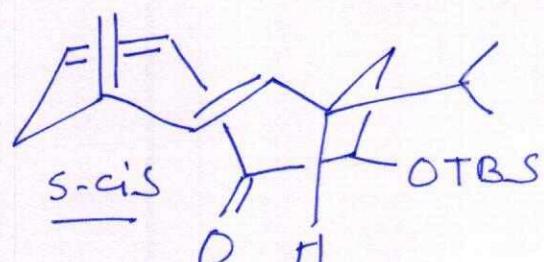
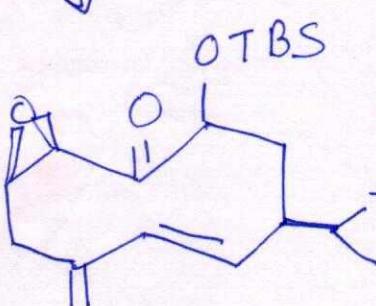
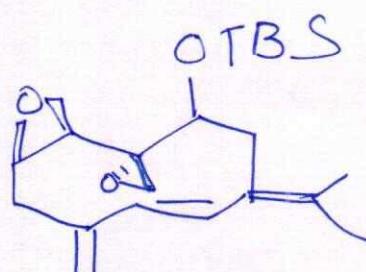
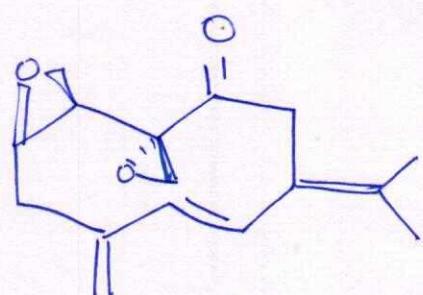
3>



3 steps



↔


 $t\text{Bu}-\text{OOH}$
 KH

 $\text{CH}_2^-\text{SMe}_2^+$

 $\downarrow 1> \text{TBAF}$
 $\downarrow 2> \text{CrO}_3, \text{Py}$

 (\pm) -Periplanone B