

①

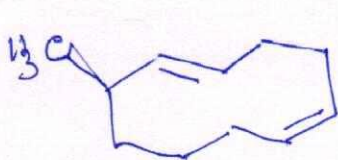
Macrocyclic Stereocontrol (macrocycle ≥ 9 membered ring) ①



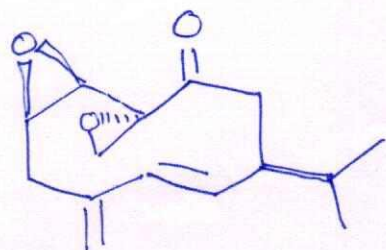
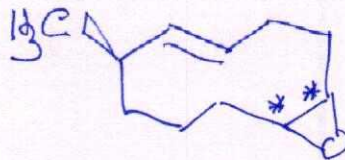
Epoxidation



Which Subs.
will deliver
higher selecti-
vity in epoxidation



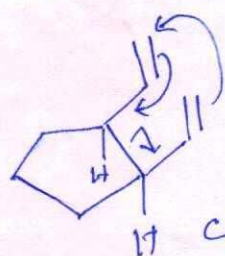
"



periplanone B

1976 \Rightarrow Isolated by Persoons et al.
Sex pheromone
200 μ g from 7500 female
cockroaches

Stereochemistry was not known before
1979 \Rightarrow Total synthesis by
Still et al.

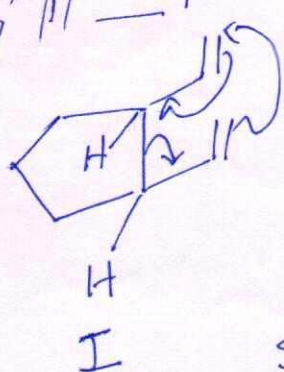


cis-1,2-divinyl
cyclopentane

JACS, 1979, 101, 2493

cope

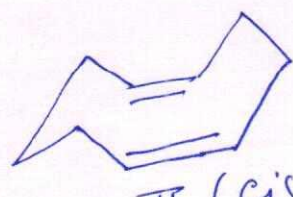
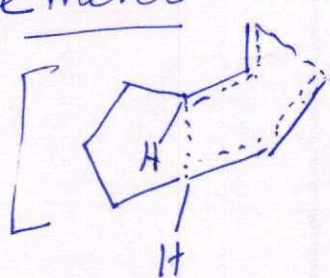
Rearrangement



220°C

[3,3]

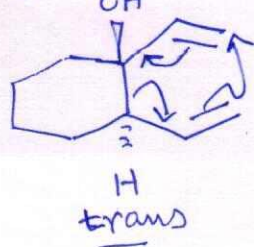
sigmatopic
rearrangement



II (cis,cis)
9 membered
ring

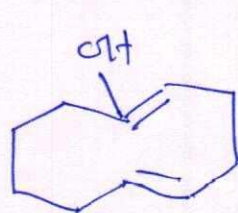
I : II = 95 : 5

b) oxy cope

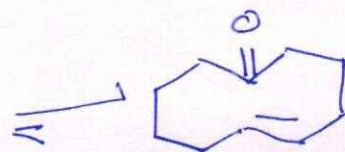


220°C

3h

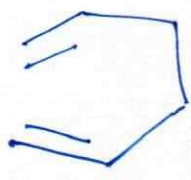
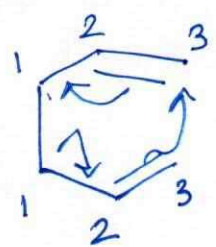


trans, trans

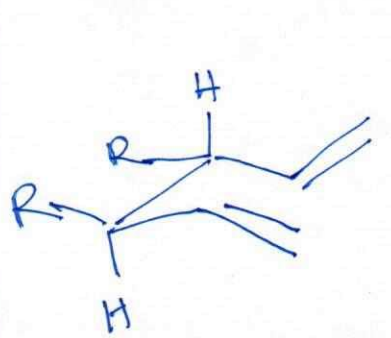
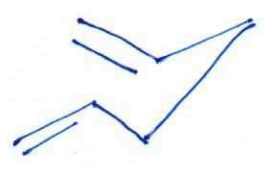
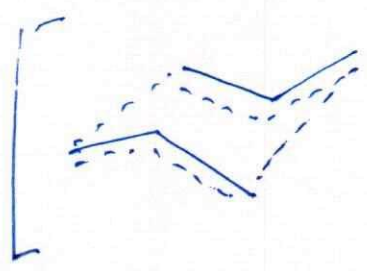
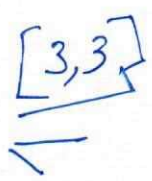
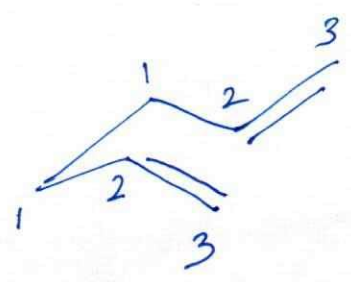
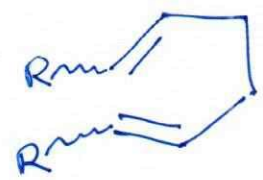
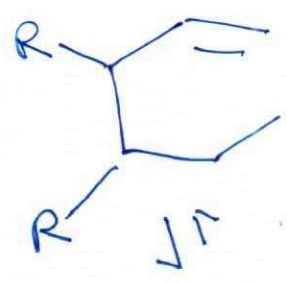
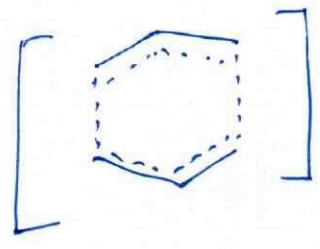


(90%)

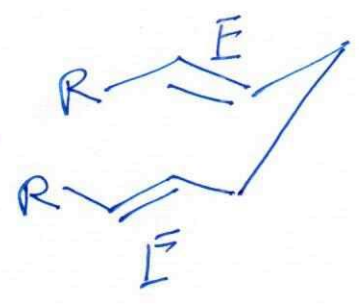
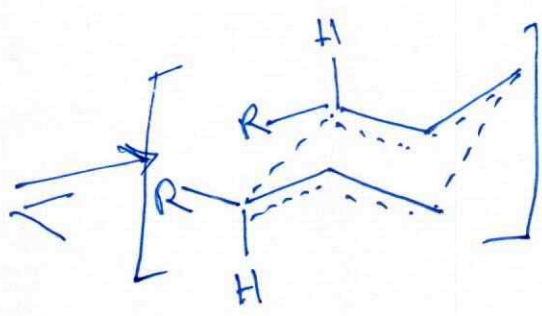
1a



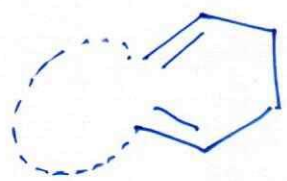
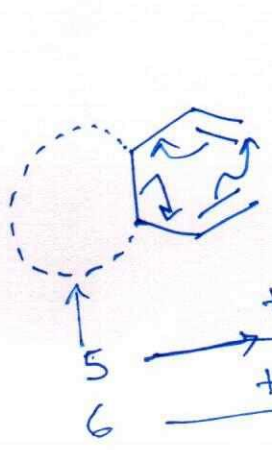
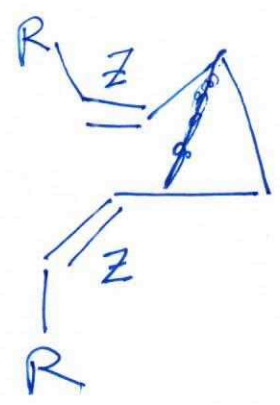
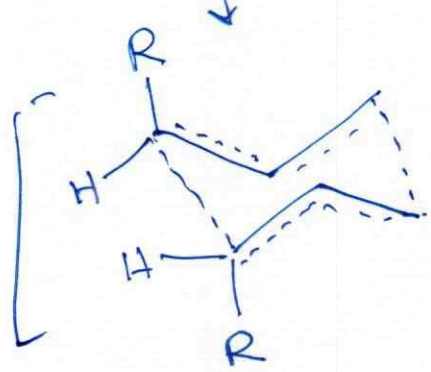
via



Equatorial



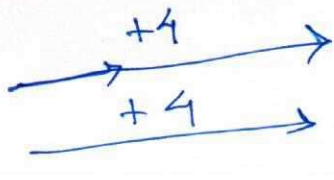
FLIP

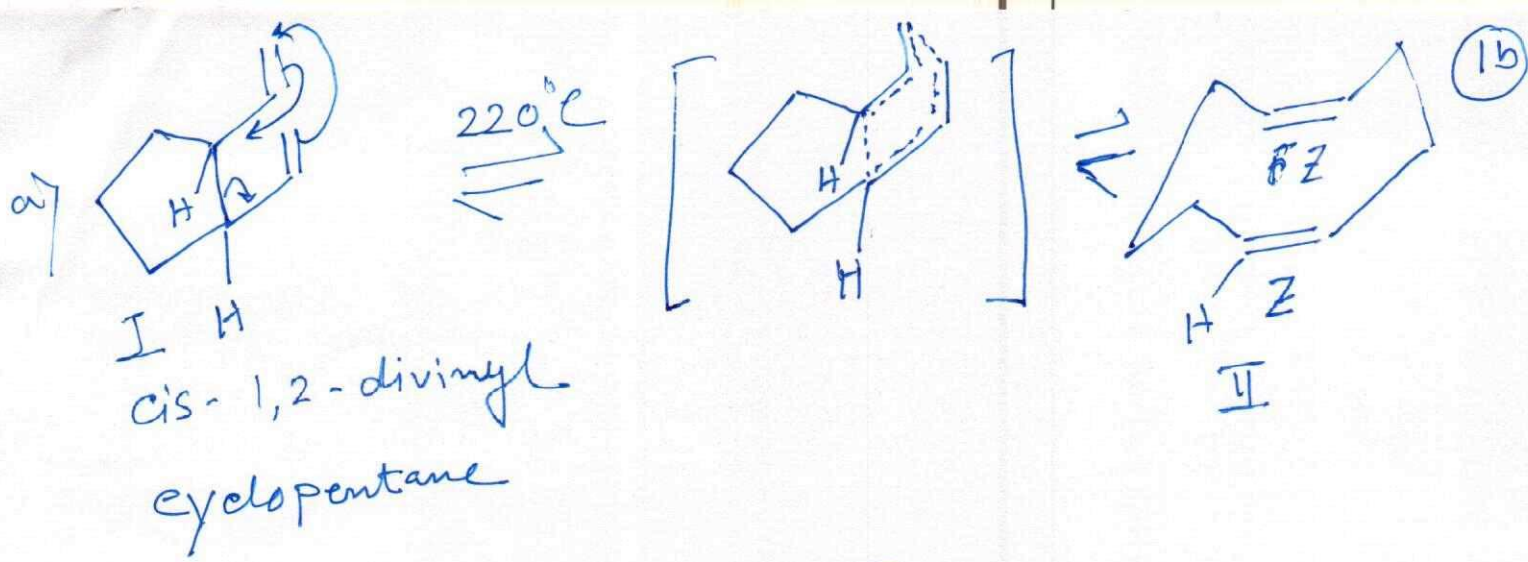


Macrocycle

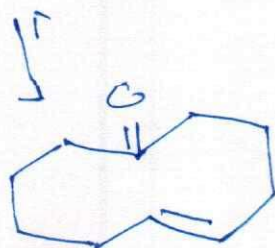
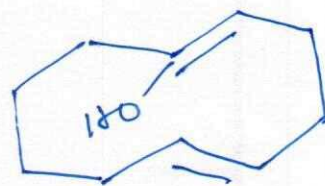
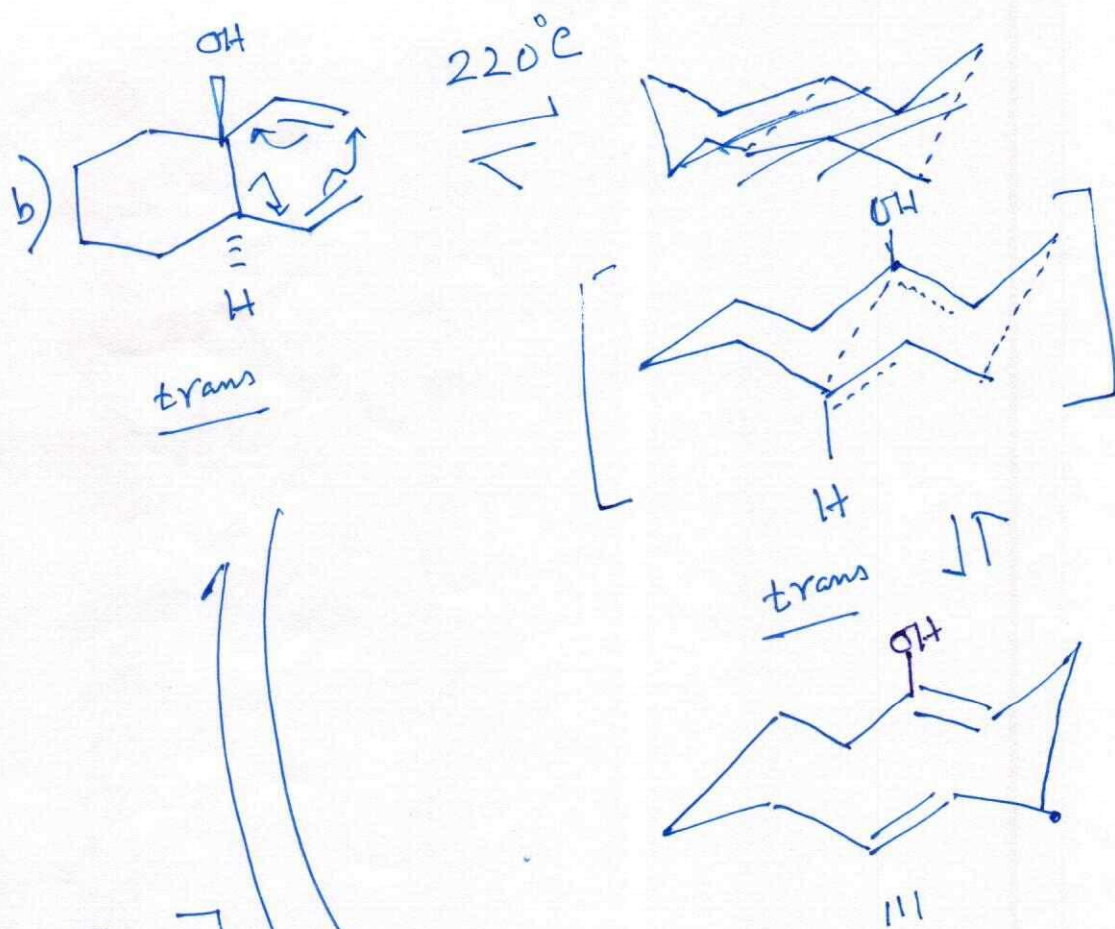
9 membered ring

10 " "





I : II = 95 : 5



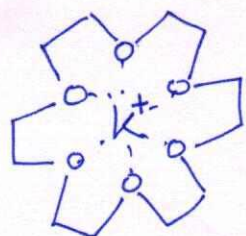
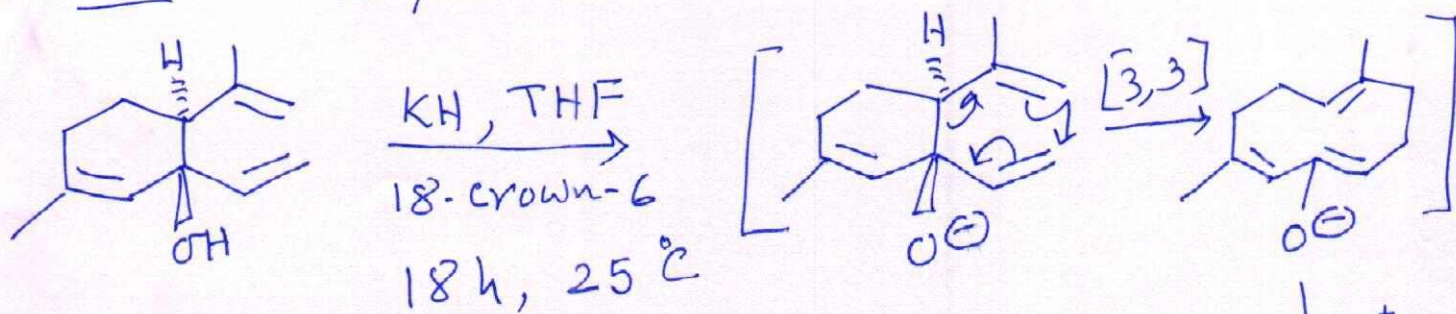
90%
yield

[3,3]

oxy-cope

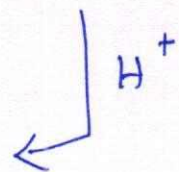
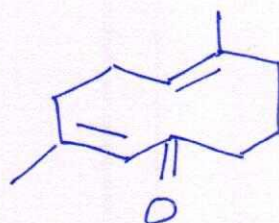
c) Anionic oxy cope

(2)

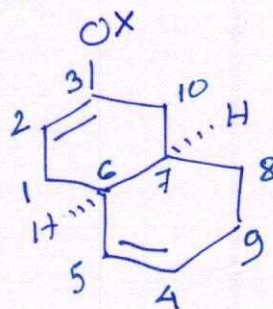
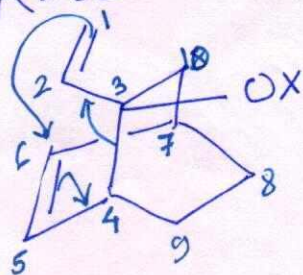


18-c-6

naked
anion



Rate acceleration in ^{anionic} oxy cope is dramatic!



OX

half life

OH

66 years

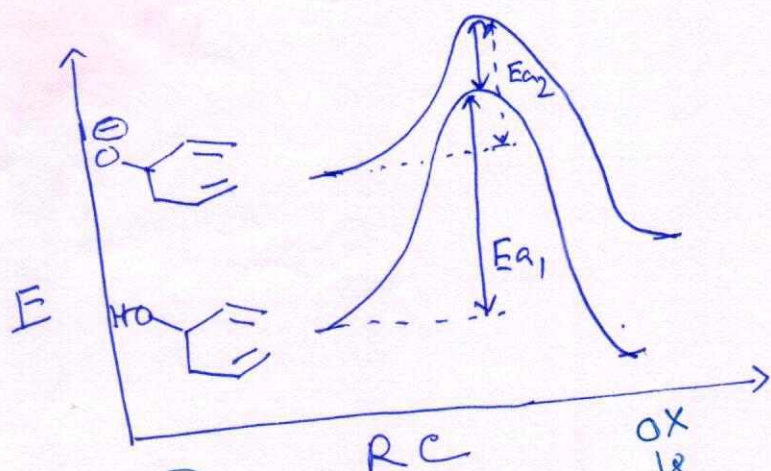
ONa

1.2h

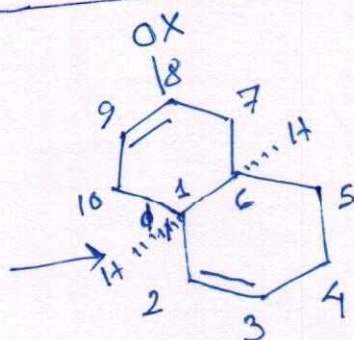
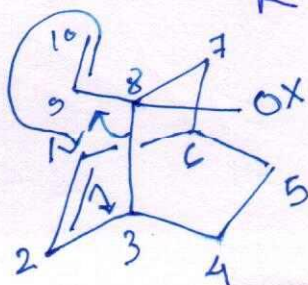
O⁻

7 sec

⇒ 10¹² - 10¹⁷ rate acceleration

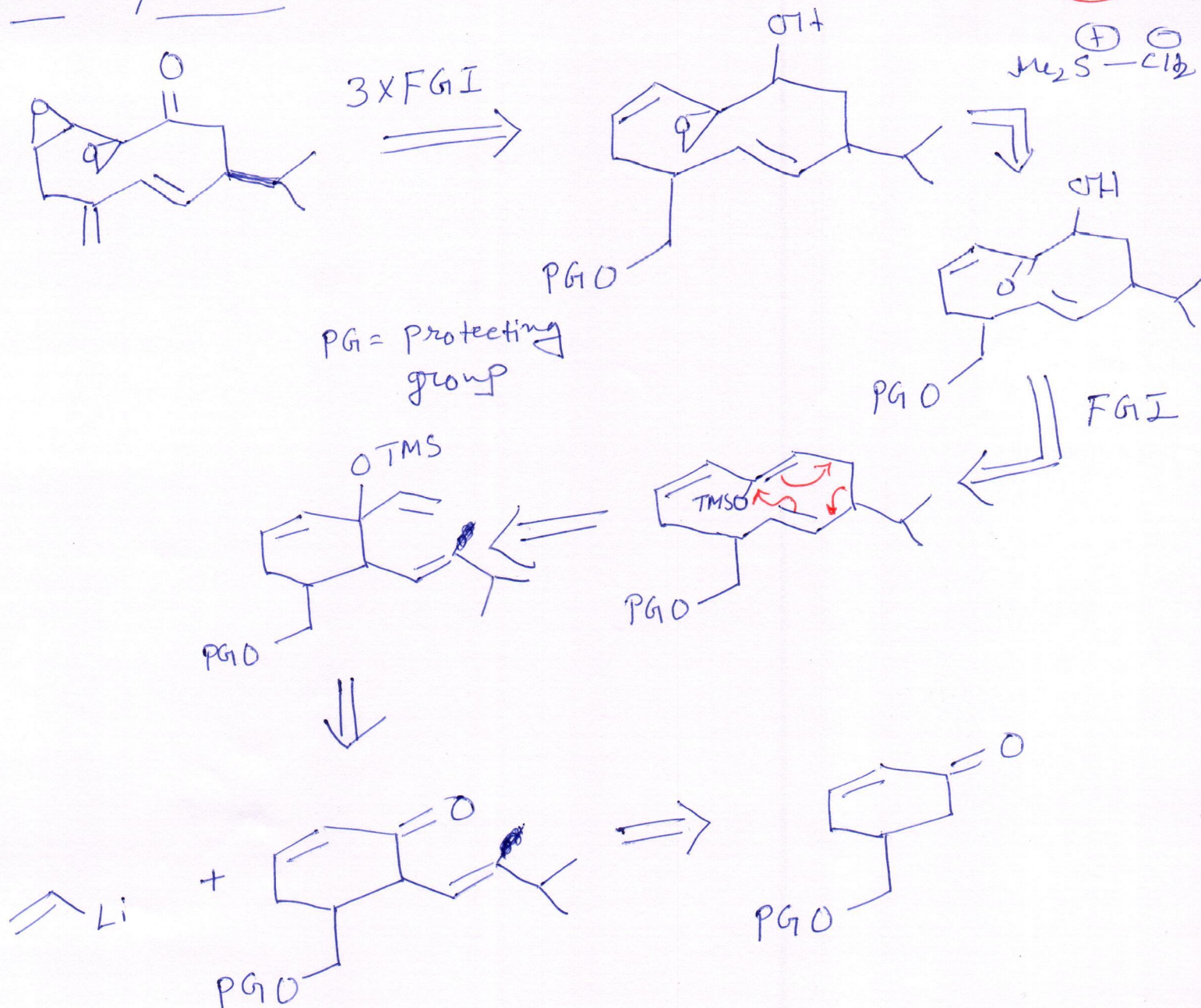


$$E_{a1} > E_{a2}$$



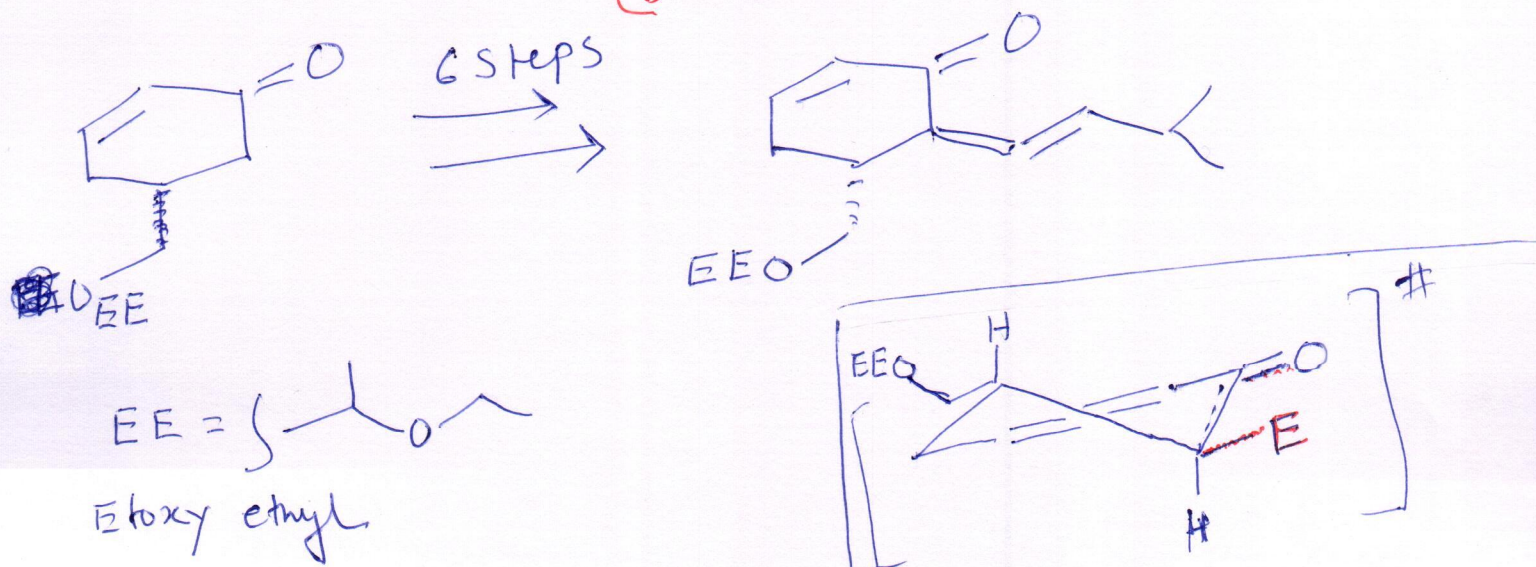
RetroSynthesis:

(3a)

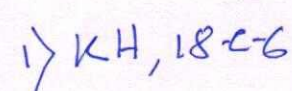
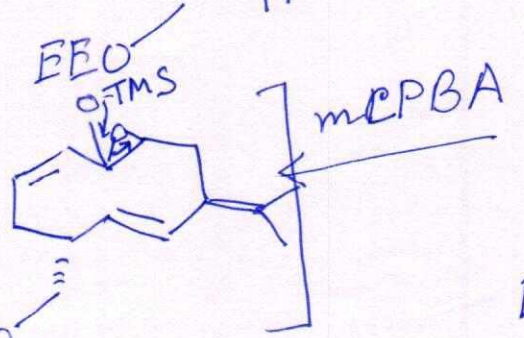
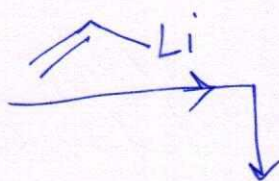
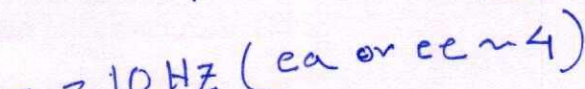
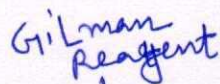
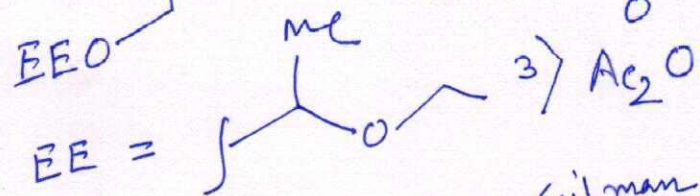


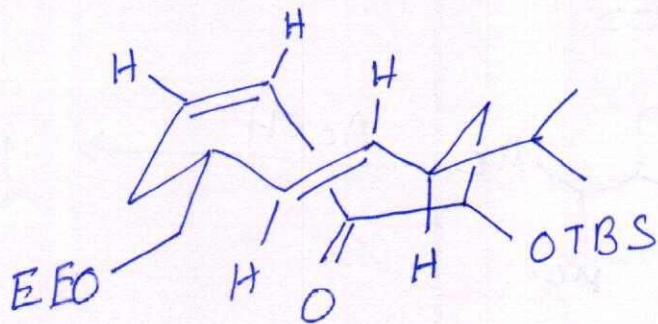
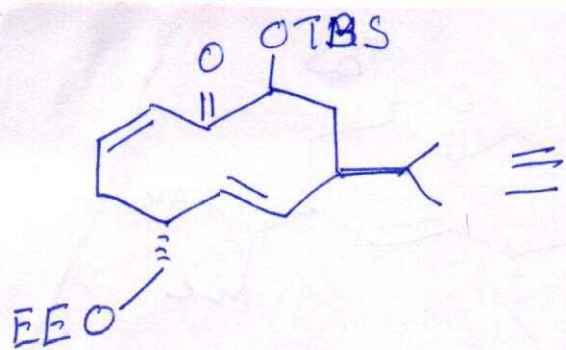
Forward Synthesis:

(see page 3 for details)



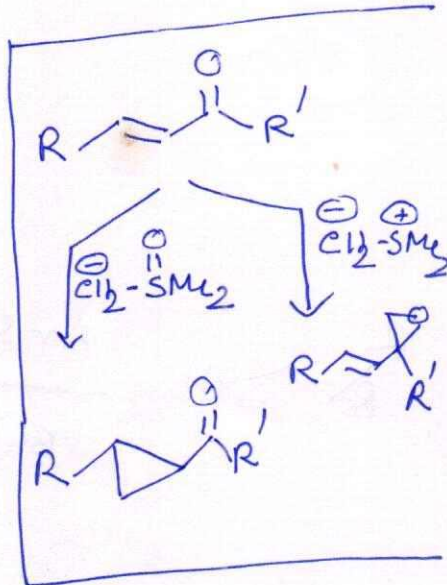
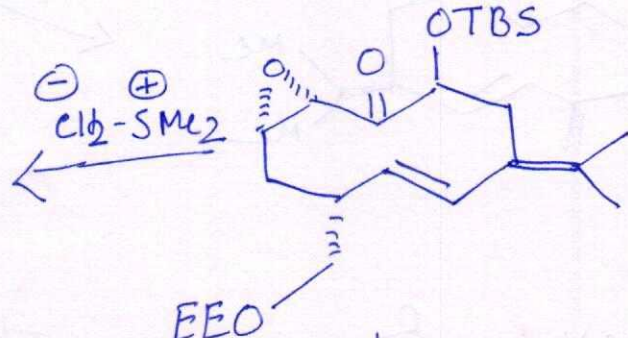
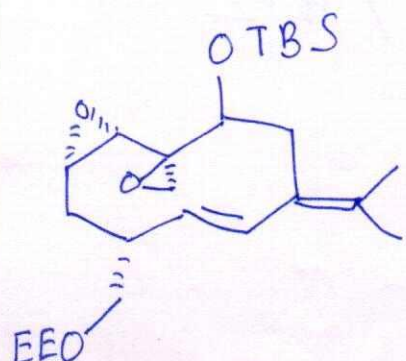
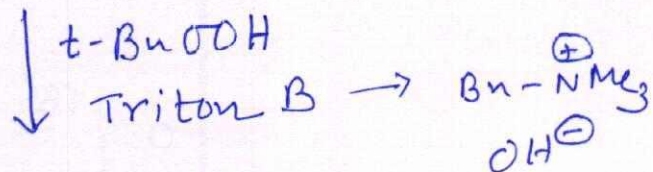
③





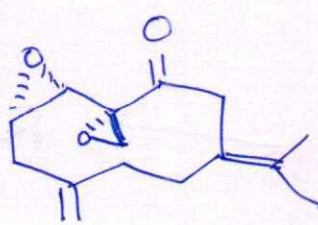
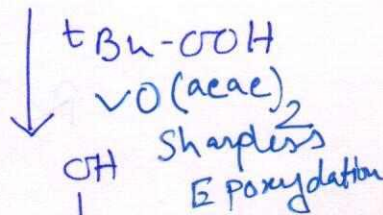
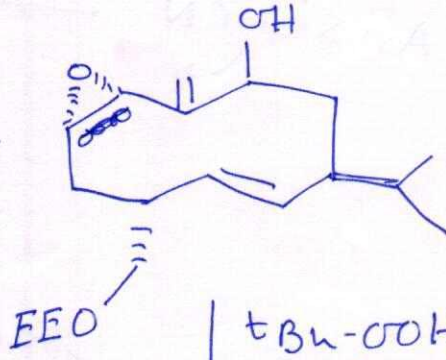
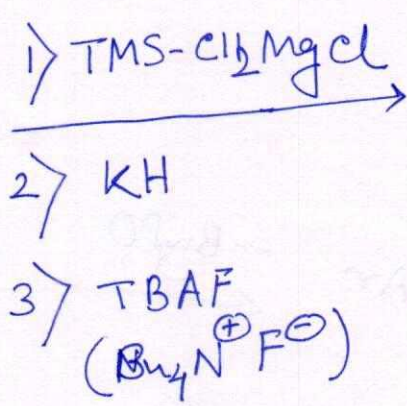
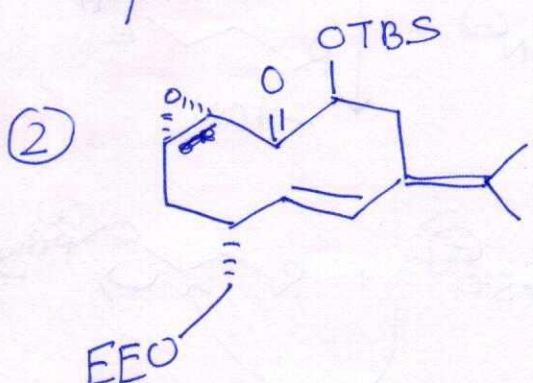
(4)

(1)

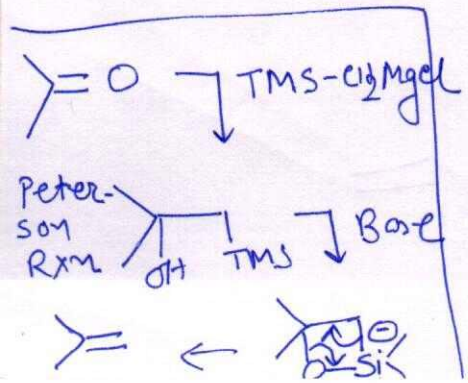
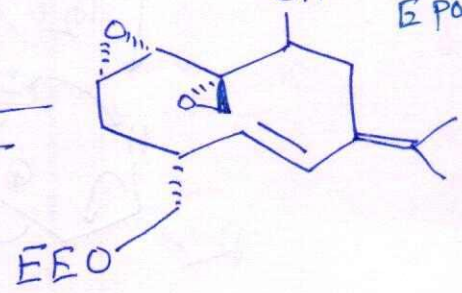


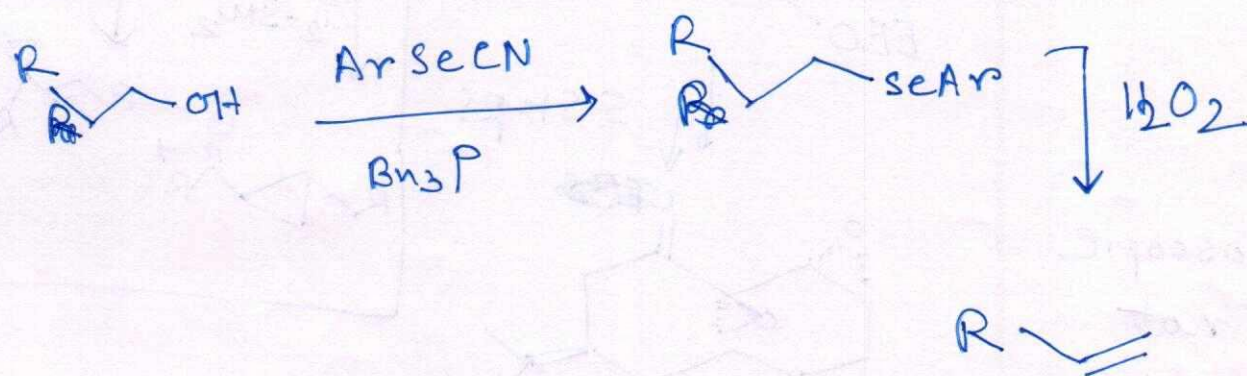
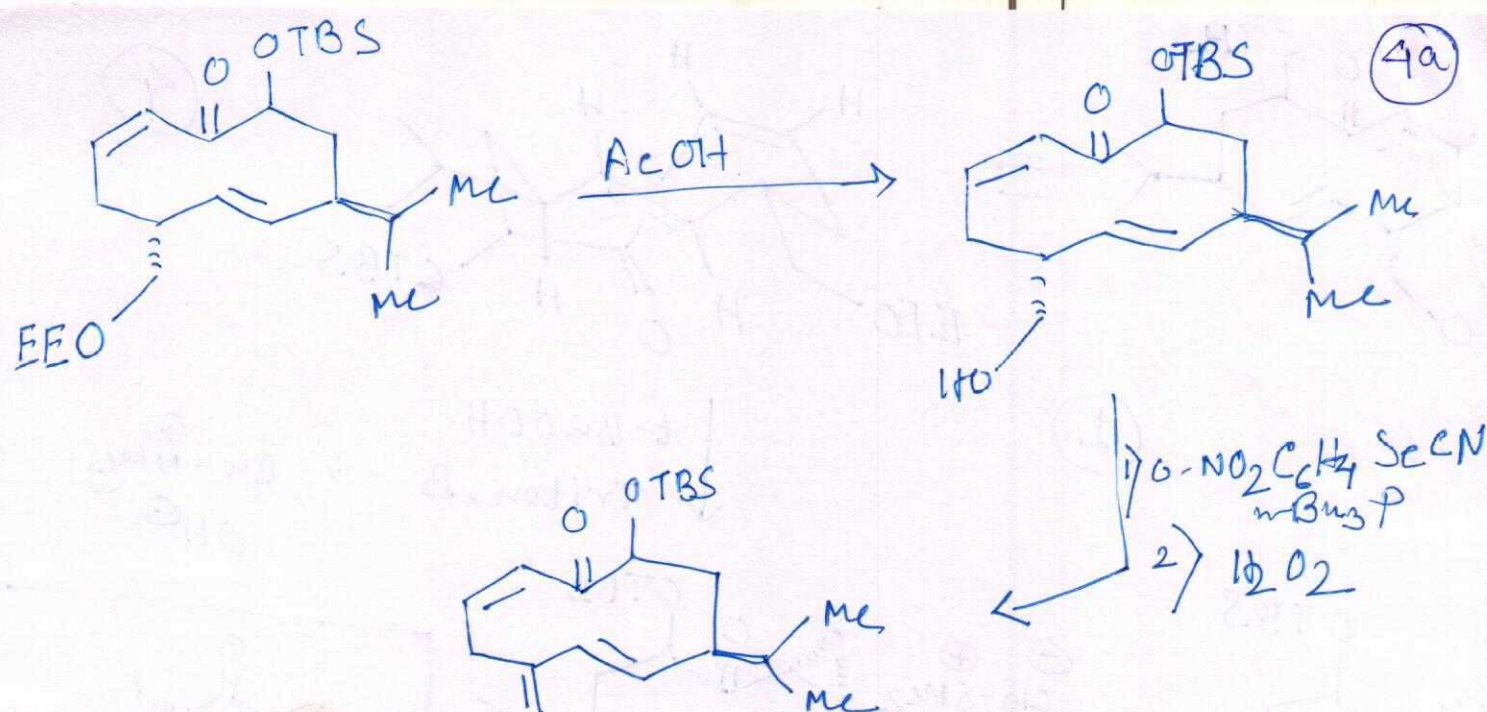
spectroscopic data not matched with natural Periplanone!

\Rightarrow Diastereomer

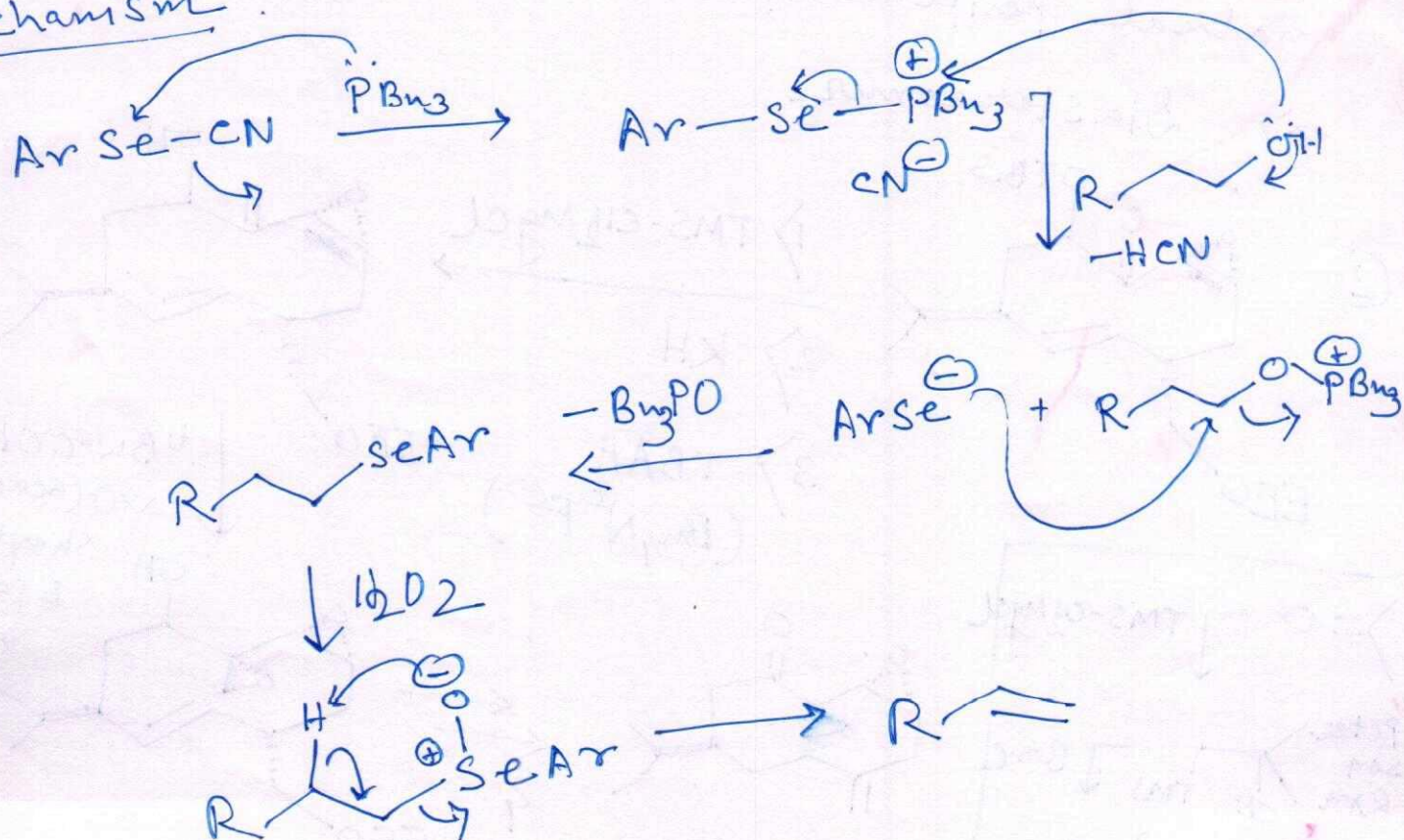


4 steps



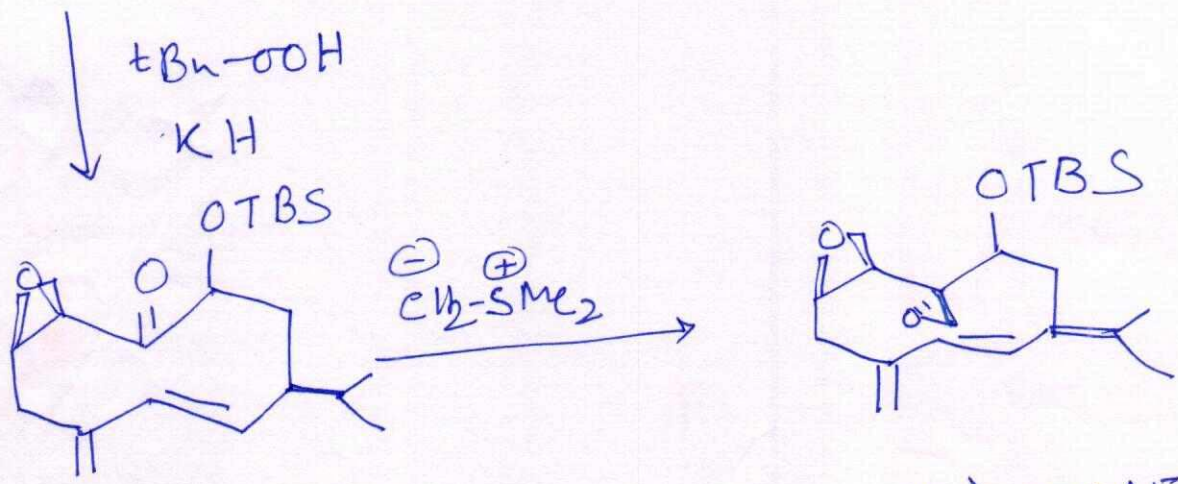
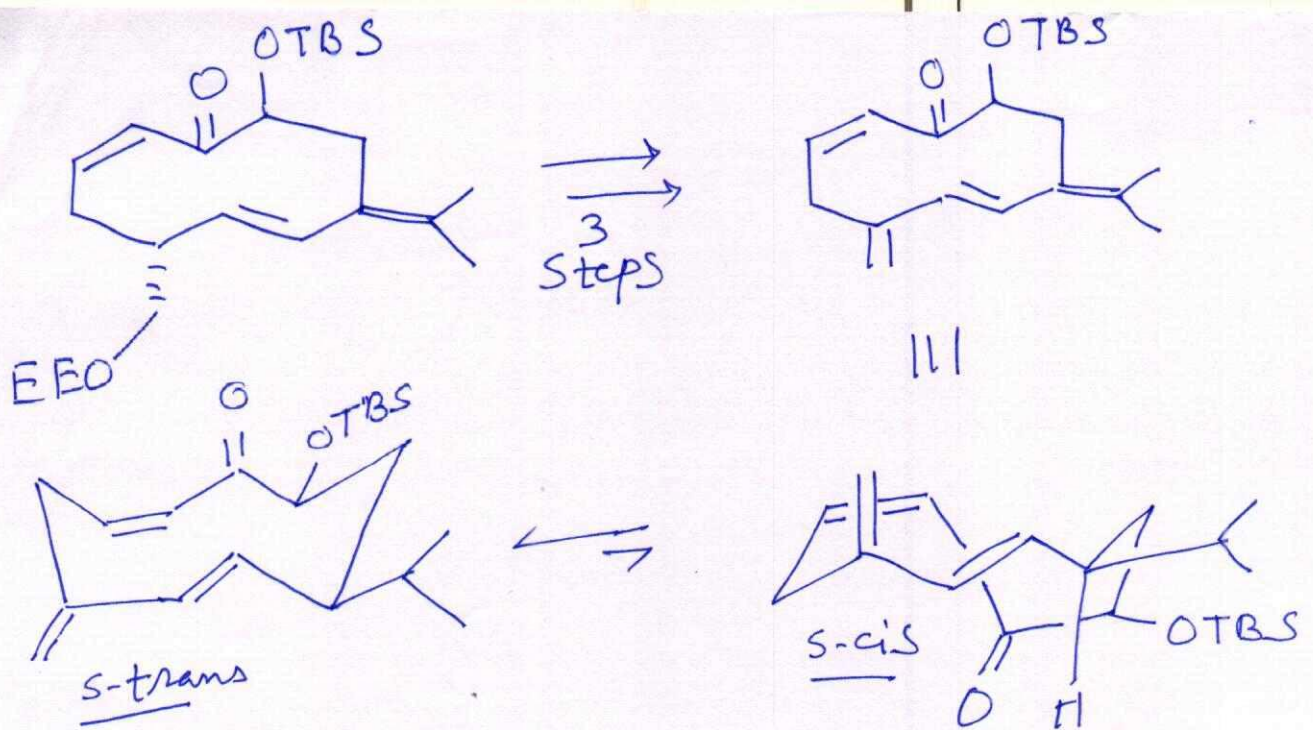


Mechanism:

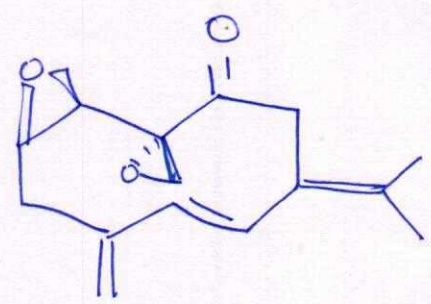


5

3



1) TBAF
2) CrO_3, Py



(\pm)-Periplanone B